AN ABSTRACT OF THE DISSERTATION OF

Daniel McCauley-Walden for the degree of Doctor of Philosophy in Chemistry presented on June 4, 2018.

Title: Computational Rationalizations of Mechanism and Stereocontrol in Small-Molecule Lewis Base Organocatalysis.

Abstract approved:

Paul Ha-Yeon Cheong

My work has focused on investigating synthetic organic reactions using applied computational methods. Non-covalent interactions are critical to catalysis, mechanism, and stereoselectivity, with the most prominent interaction for isothioureas being the S···O contact between the catalyst sulfur atom and the oxygen of the acyl group.

A comprehensive joint experimental and computational investigation into the isothiourea-catalyzed transformation of allylic ammonium ester salt substrates into α-amino acid derivatives. Kinetic isotope effects (KIEs) and description of the potential energy surface allowed accurate corroboration of computed secondary KIEs with experiment. The turnover-limiting and stereodeterming transition state is a [2,3]-sigmatropic rearrangement of an allylic ammonium ylide. Stereoselectivity is afforded through rigidification of the catalyst-substrate complex through a S···O non-covalent interaction. In such an arrangement, rearrangement takes place *endo*, *anti* to the catalyst stereodirecting group, allowing a stabilizing π-cation between the substrate and planar positively-charged catalyst to select for the major TS.

Isothiourea-catalyzed annulations of benzoxazoles and benzothiazoles were discovered to proceed to lactone or lactam products on the basis of the benzothiazole's ability to engage in a second S···O interaction in addition the substrate-catalyst S···O

interaction already present in both lactonization and lactamization TSs. In the absence of the second S···O, a C–H···O between the substrate and the catalyst oxygen atom favors lactonization. Computed TSs and truncated model systems discovered and detailed the interplay between the two non-bonding interactions (S···O and C–H···O), which ultimately leads to chemodivergence when using thiazole or oxazole derived substrates. Interactions between S and O atoms have previously been elements of enantiocontrol, but have never been evoked as central to chemoselectivity.

A study on the scope and origins of stereocontrol in the kinetic resolution of tertiary oxindole alcohols illustrates the importance of the substrate amide C=O moiety interacting with the isothiourea catalyst (C=O···isothiouronium) as imparting high selectivity. Partial charge calculations of the acylated catalyst point to a positive charge on the central isothiourea carbon (isothiouronium) Computed TSs allowed the development of a stereocontrol model in which stabilization of the isothiouronium with the substrate amide C=O leads to faster acylation of the (*S*)-alcohol. Hammett parameters and amide C=O stretching frequencies of the substrate showed good correlation with the *s* factor, in agreement with theoretical predictions.

Regiodivergent and catalyst-selective *O*- to *C*- or *N*-carboxyl transfer is disclosed, with DMAP catalysis favoring *N*-carboxylation and NHC catalysis leading to selective *C*-carboxylation. Computations unveiled the mechanism and source of regiodivergence from the mechanistically shared enolate intermediate. Computed TSs for the *N*- and *C*-carboxylation pathways for both DMAP and NHC catalysts showed that greater spatial overlap in the ion pair consisting of the overall negatively-charged enolate species and the positively-charged acylated catalyst leads to regiodivergence for each catalyst.

A theoretical and experimental project studying the formation mechanism and reactivity of highly unstable aza-*ortho*-quinone methide (aoQM) intermediates in synthesis and asymmetric *N*-heterocyclic carbene (NHC) catalysis. Compared to their oxygen analogs (*ortho*-quinone methides), aoQMs were found to be >10 kcal/mol more unstable. A byproduct of aoQM formation in the presence of cesium carbonate base is cesium chloride, with a computed equilibrium in favor of cesium chloride of ~30 kcal/mol. A nucleophilic substitution pathway which bypasses aoQM formation was considered, but

was found as consistently higher in energy than the aoQM pathway once the cesium carbonate equilibrium is considered. With the aoQM-mediated mechanism established, a stereocontrol model was developed for the NHC-catalyzed asymmetric synthesis of dihydroquinolones.

Computational Rationalizations of Mechanism and Stereocontrol in Small-Molecule Lewis Base Organocatalysis

by
Daniel McCauley-Walden

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APPROVED:

Major Professor, representing Chemistry

Chair of the Department of Chemistry

Dean of the Graduate School

I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

Daniel McCauley-Walden, Author

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CONTRIBUTIONS OF AUTHORS

Chapter 2. Thomas H. West, and James E. Taylor conducted the synthesis and experiments for this project. Alexander C. Brueckner and Ryne C. Johnston also contributed to computations. Paul H.-Y. Cheong, Guy C. Lloyd-Jones, and Andrew D. Smith contributed in part to the preparation and review of the manuscript.

Chapter 3. Emily R. T. Robinson, Charlene Fallan, and Mark D. Greenhalgh conducted the synthesis and experiments for this project. Paul H.-Y. Cheong and Andrew D. Smith contributed in part to the preparation and review of the manuscript.

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Chapter 6. Ashley A. Jaworski and M. Todd Hovey conducted the synthesis and experiments for this project. Ryne C. Johnston and Hannah V. Baker also contributed to computations. Matthew P. Meyer, Paul H.-Y. Cheong and Karl A. Scheidt contributed in part to the preparation and review of the manuscript.

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Dedicated to
Annette,
my parents,
family and friends,
teachers.

Chapter 1.

Introduction

1.1 The Tandem of Theory and Experiment

Advances in affordable computing technologies and new quantum-mechanical theories have expanded the reach of quantum mechanics from simplified models with many structural approximations and truncations to large, realistic systems with considerable conformational flexibility and structural complexity. Theory remains a powerful tool in the chemist's arsenal, and demonstrations of its power in the generation of chemical hypotheses that govern selectivities, reactivities, and mechanisms abound in the literature.[1] The increasingly complex and multifunctional nature of contemporary organocatalytic transformations complicate the generation of hypotheses, as List[2] observed nearly a decade ago, "Often there is little knowledge of a given reaction mechanism and the exact mode of activation is unknown." The research summarized in the following chapters applied state-of-the-art electronic structure methods to real-world catalytic reactions. Thereotical mechanistic analyses and transition state (TS) models help explain and predict selectivity in contemporary synthetic transformations through experimental collaboration[3] or in important classes of reactions that have gone unstudied by theory because of their complexity.

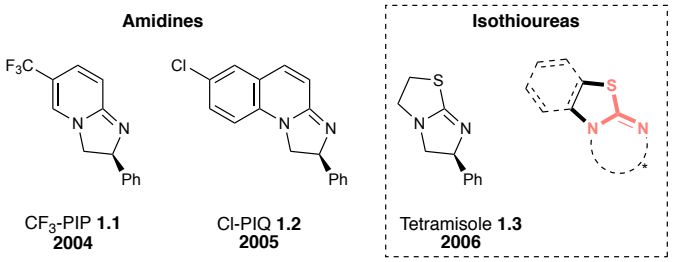
1.2 Enantioselective Organocatalysis

1.2.1 The advent of Lewis base catalysis

The work of Birman's laboratory has been pivotal in the rise of small-molecule Lewis base catalysis over the last two decades. Initial investigations of chiral amidines CF_3-PIP **1.1** in 2004[4] and Cl-PIQ **1.2** in 2005[5] were shown as competent acyl transfer catalysts, culminating in the synthesis and application of the isothiourea-based tetramisole **1.3** in 2006 (Scheme 1.1).[6] Birman's work was an influential contribution to the burgeoning subfield of enantioselective acyl transfer which had already been greatly influenced by the

groups of Vedejs[7] (chiral DMAP and phosphines), Spivey,[8] Yamada,[9] Fu[10] (chiral DMAP), Oriyama,[11] Jündig[12] (chiral diamines), and Miller[13] (peptide catalysis). Corey's discolosure of the guanidinium-catayzed Strecker reaction also provides a vital contribution to the field.[14] Carbon-reactive *N*-heterocyclic carbenes (NHCs) represent a prominent class of Lewis-base catalysts in organic synthesis and methodology.[15] NHCs have significant advantages over isothoureas, exemplified by their ubiquitous application. The reactivity and selectivity of an NHC can be tuned and optimized through structural modifications and catalyst screening. NHCs are also capable of acyl anion equivalent intermediates (Umpolung reactivity), in addition to traditional acyl/enolate methodologies.

Scheme 1.1 Timeline of Birman's catalysts from amidines to isothioureas.



1.2.2 Catalytic activation

At the heart of organocatalysis is covalent catalysis, where the substrate is recognized and bound as an activated catalyst–substrate complex, profoundly altering the substrate frontier molecular orbitals to unlock or lower previously inaccessible reactivities. Additional types of catalysis might fall under the term "non-covalent catalysis" although such a term is usually reserved for activation through urea/thiourea dual hydrogen bond catalysis[16] or even *Cinchona*-based phase transfer catalysis.[17] Lewis base catalysts impart reactivity on both nucleophilic and electrophilic reactive intermediates. Catalyst electron donation facilitates HOMO activation to generate a nucleophilic complex. Conversely, LUMO-activating catalysts increase the electrophilicity of the substrate by functioning as an electron-withdrawing group. Moreover, many catalysts can demonstrate both types of activation (i.e., bifunctional).[16] Proline and its derivatives provide a wealth of clear

examples highlighting bifunctional activation, with covalent complexes formed with the amine group and secondary activation through hydrogen-bond donating side chains.[18]

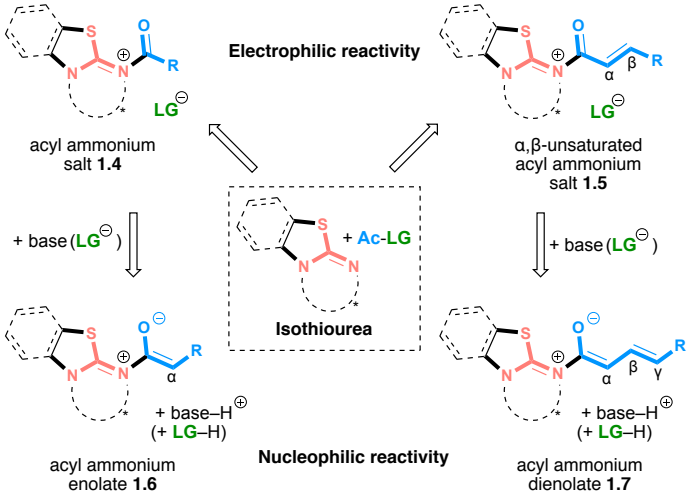
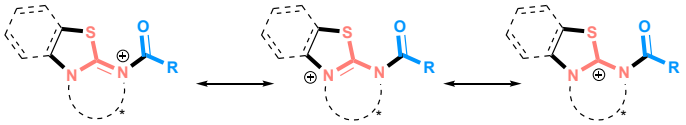


Figure 1.2 Reactive intermediates derived from isothiourea-based catalysts.

Isothiourea-derived catalysts can access a number of acyl reactive intermediates with both electrophilic and nucleophilic capabilities (Figure 1.2). On reaction with a select acylating agent (acyl halides or anhydrides, Figure 1.2, blue), the covalent isothiourea-acyl complex is formed, usually as a salt complex with the leaving group (denoted as green "LG", Figure 1.2). While the Lewis structure of this species is typically drawn such that one of the catalyst nitrogen atoms bears a formal positive charge, partial charge calculations suggest a resonance structure resembling a partial positive charge on the central isothiourea carbon atom (i.e. carbocationic character, see Scheme 1.3 and Figure 4.8). Acyl ammonium **1.4** can react with nucleophiles directly at the carbonyl moeity, or extended electrophiles such as α,β-unsaturated acyl ammoniums **1.5** can undergo conjugate addition at the β-carbon. These intermediates can also undergo deprotonation to yield nucleophilic enolate species **1.6** and **1.7**, typically as a result of secondary or tertiary amine bases added to the reaction mixture (commonly diisopropylamine or Hunig's base), or from the anionic leaving group as a result of catalyst acylation. Enolate-ammonium species can also be reached directly by reacting the catalyst with ketenes.

Scheme 1.3 Acylated isothiourea catalyst resonance structures.



1.3 Substrate-Catalyst Complex Rigidificaition

While forming a covalent bond between the catalyst and substrate is crucial for Lewis base activation, non-covalent interactions (NCIs) are among the most common secondary interactions imparting catalysis and stereoselectivity within the field of organocatalysis.[19] For reactions operating under kinetic control, NCIs help stabilize a single TS over additional competing TSs, leading to stereodiscrimination. The vast majority of these stereodetermining TSs involve bond formation between prochiral groups. As a result, effective selectivity is influenced by two primary principles (Figure 1.4, top): (1) a chiral center or chiral element (e.g. axial chirality, C_2 symmetry) in close proximity to the forming bond, and (2) rigidification of the catalyst-substrate complex. A high degree of enantioselectivity is displayed when both conditions are met. NCIs are commonly employed components of catalyst structure for restricting torsional rotation, which in turn increases selectivity.

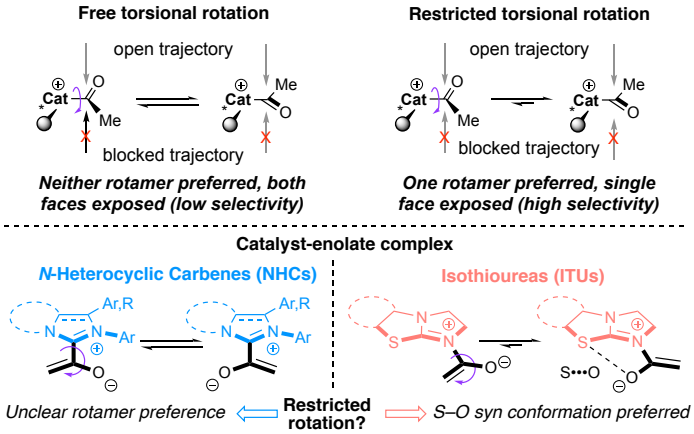


Figure 1.4 (Top) Facial selectivity is decreased in a freely-rotating catalyst-acyl complex. (Bottom) Predicting the more stable NHC-acyl conformation (if a preference exists) is not straightforward. Conversely, acylated isothioureas prefer the rotamer displaying an S···O interaction.

1.3.2 The S···O interaction

Despite the plurality of NHC classes currently displayed in the literature, very few explicitly address the problem of rigidification of the NHC-acyl reactive intermediate, leaving hypothesis-driven catalyst design as a significant challenge (Figure 1.4, bottom left). While high selectivities are routinely achieved using this method, without some degree of structural consistency, developing a stereocontrol model to rationalize selectivity requires novel analysis for each new disclosure of NHC synthetic methodologies. There remains to be a cohesive NHC stereocontrol model complete with predictive power. Lewis base catalysts based on the isothiourea core exhibit a less routinely exploited NCI in catalysis – the S–O "close contact" (S···O).[20] In a choice between two torsional conformations, the acylated catalyst exhibits upwards of 4 kcal/mol preference for the acyl oxygen atom placed *syn* to the sulfur atom (Figure 1.4, bottom right).[21] In this conformation, the catalyst-acyl complex is planar and effectively rigid, with the S–O distance around 20% below the sum of the van der Waals radii.[22] Stereocontrol models built around this catalyst family are greatly simplified by the energetic stability of the S–O *syn* conformation.

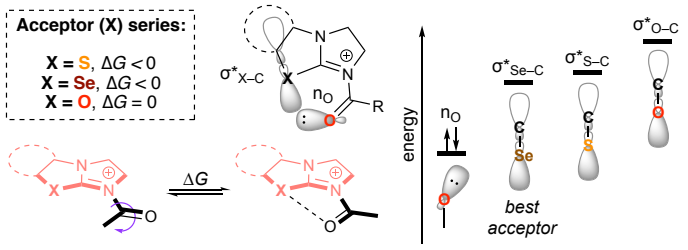
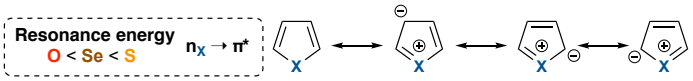


Figure 1.5 Delocalization of oxygen lone-pair (n_O) density into the C–X antibonding orbital ($\sigma^*_{X–C}$) of the catalyst chalcogen–carbon bond (X–C) is the primary origin of chalcogen···O non-covalent interactions in isothiourea catalysts.

The S···O interaction itself is a subset of NCIs collectively termed *chalcogen bonding*[23] which is generally considered the oxygen, sulfur, and selenium analogue to *halogen bonding*.[24] The most important contributor to the relative strength of chalcogen bonding in isothioureas, and therefore the stability of the chalcogen···O *syn* conformation realtive to

the *anti* conformation, is the identity of the chalcogen itself. When varying the X atom in the acceptor series, the rotameric ΔG of the *syn* rotamer with respect to acceptor atom increases in magnitude (from smallest to largest ΔG) X = O, X = S, X = Se, with the conformational preference associated with oxygen being much less than sulfur and selenium (Figure 1.5). This ordering is rationalized based on the orbital interactions that contribute to favoring a single rotamer. The primary orbital interaction that contributes to stabilization of the *syn* conformer over the *anti* is delocalization of the donor oxygen lone pair into the anti-bonding orbital of the X–C bond ($n_O \rightarrow \sigma^*_{X–C}$).[21] Figure 1.5 presents a qualitative understanding of the trends of this orbital interaction in terms of a molecular orbital description. The Se–C bond corresponds to the the lowest energy σ* acceptor orbital of the series, with $\sigma^*_{O–C}$ being the highest in energy.[25] The Se–C bond has the largest discrepancy in atomic size leading to poor orbital overlap when mixing the carbon and selenium atomic orbitals. Polarizability also plays a significant role in relative acceptor ability, with a trend of increasing polarizability going down the chalcogen group (O to S to Se).[26] Since the $\sigma^*_{Se–C}$ is closest in energy to the oxygen lone pair, within the presented chalcogen series, lone pair delocalization into the $\sigma^*_{Se–C}$ and $\sigma^*_{S–C}$ occurs with greater stabilization of the electron pair (n_O) than $\sigma^*_{O–C}$.

Scheme 1.6 Resonance stabilization trends of furan, thiophene, and selenophene.



Rationales based on electrostatic attraction and dipole-dipole minimization have also been proposed as a contributor to the stability of X···O interactions.[20f] Hyperconjugation of the X-atom lone pair with the adjacent π* orbital is thought to yield a partial positive charge charge for X = S and Se (Scheme 1.6). For a furan-based cycle (X = O), the magnitiude of the hyperconjugative effect is diminished relative to thio- and selenophenes as shown by the increasing order of heterocyclic resonance energies (O < Se < S).[27] Higher electronegativity and decreased lone pair conjugation leads to a negative partial charge on the furan oxygen atom. Even with the positive charge on S and Se in place, a recent experimental and computational study by Cockroft found that the strength of

chalcogen···O interactions have surprisingly little dependence on solvent polarity, suggesting that electrostatic attraction has minimal effect on stabilizing S–O and Se–O non-bonding interactions.[20c] These results suggest the orbital interaction, with possible σ-hole character,[28] is the dominant origin of the S···O non-covalent interaction.

1.4 Chalcogen Bonding in NHCs

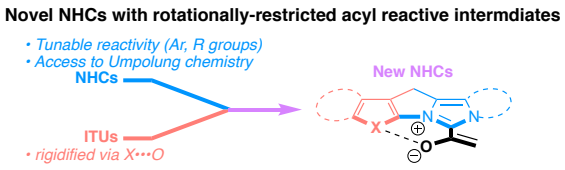


Figure 1.7 The proposed new catalyst structure combines NHC tunable reactivity and Umpolung chemistry with chalcogen•••O interactions seen in isothioureas.

From the perspective of experimental methodology and synthesis, understanding the interactions that control NHC catalysis and selectivity can be an arduous and convoluted process, often leading to time consuming and resource draining experiments (e.g. catalyst screening). It is therefore postulated that a chiral NHC catalyst that takes advantage of S···O (and/or Se···O) interactions akin to those seen in isothioureas will experience the same high degree of acyl intermediate rigidification (Figure 1.7). NHC stereocontrol models with this interaction in place are greatly simplified, leading to *testable, hypothesis-driven* rational design. Each component of the catalyst is capable of being put in context with respect to its effect on the conformational free energy, leading to a complete understanding of each structural feature's contribution or hindrance to stereoselectivity. While my initial research probing the rational design of an NHC family capable of chalcogen···O interactions is not present in this disseration, I plan to pursure a significant portion of my future research efforts to this endeavor.

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Chapter 2.

Catalytic Enantioselective [2,3]-Rearrangements of Allylic Ammonium Ylides: A Mechanistic and Computational Study

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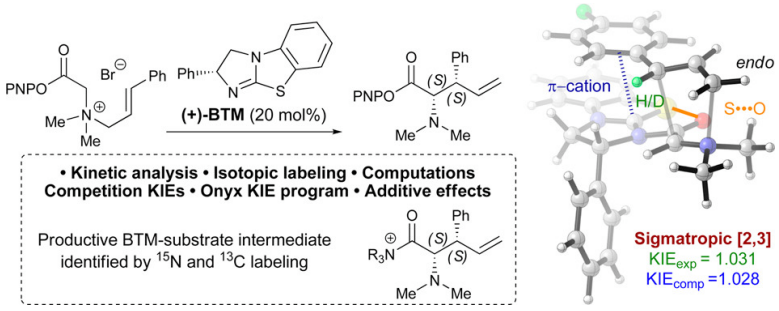
2.1 Abstract

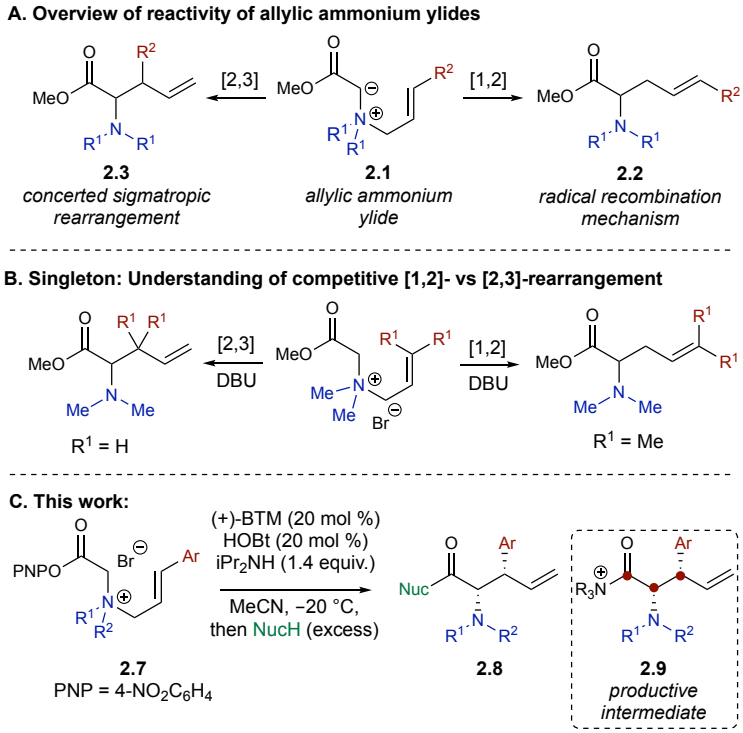
A mechanistic study of the isothiourea-catalyzed enantioselective [2,3]-rearrangement of allylic ammonium ylides is described. Reaction kinetic analyses using ^{19}F NMR and density functional theory computations have elucidated a reaction profile and allowed identification of the catalyst resting state and turnover-rate limiting step. A catalytically relevant catalyst–substrate adduct has been observed, and its constitution elucidated unambiguously by ^{13}C and ^{15}N isotopic labeling. Isotopic entrainment has shown the observed catalyst–substrate adduct to be a genuine intermediate on the productive cycle toward catalysis. The influence of HOBt as an additive upon the reaction, catalyst resting state, and turnover-rate limiting step has been examined. Crossover experiments have probed the reversibility of each of the proposed steps of the catalytic cycle. Computations were also used to elucidate the origins of stereocontrol, with a 1,5-S···O interaction and the catalyst stereodirecting group providing transition structure rigidification and enantioselectivity, while preference for cation–π interactions over C–H···π is responsible for diastereoselectivity.



2.2 Introduction

The [2,3]-rearrangement of allylic ammonium ylides **2.1** is a direct and elegant method toward the synthesis of α-amino acid derivatives containing multiple stereocenters.[29] The mechanism of this process, and that of the competitive [1,2]-Stevens rearrangement, has been much discussed and disputed within the literature. A concerted thermally allowed sigmatropic process is thought to be operative in the [2,3]-rearrangement leading to **2.3**, while a radical mechanism involving bond cleavage and recombination is usually favored for [1,2]-rearrangement and yield of **2.2** (Scheme 2.1a).[30]

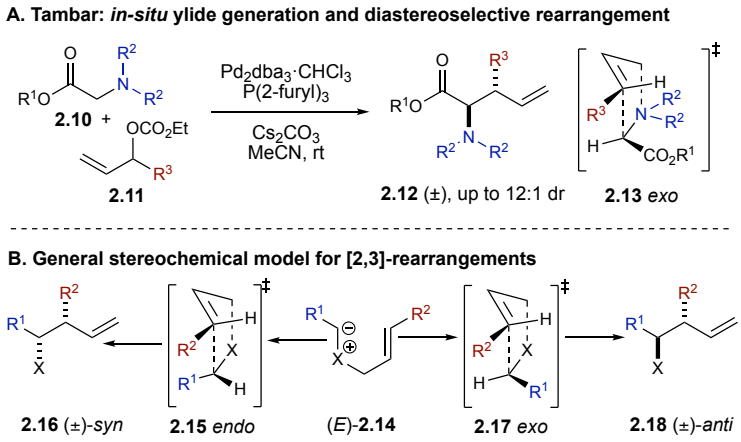
Scheme 2.1 Rearrangements of allylic ammonium ylides.



To date, few mechanistic analyses of [2,3]-rearrangements of allylic ammonium ylides have been conducted, although Jacobsen and co-workers have recently reported a detailed mechanistic investigation into the related thiourea-catalyzed [2,3]-Wittig rearrangement.[31] The experimental and computational work of Singleton and co-workers thoroughly probed the competitive [2,3]- and [1,2]-rearrangements of allylic ammonium ylides promoted by

DBU (Scheme 2.1b). Through ^{13}C kinetic isotope effects, crossover experiments, and computation, these studies demonstrate that the origin of competitive [1,2]- and [2,3]-rearrangement is the common loose transition state leading to dynamic bond cleavage.[32] The development of both catalytic and stereoselective variants of the [2,3]-rearrangement of allylic ammonium ylides has been a significant synthetic challenge. Tambar and co-workers have reported a tandem ammonium salt formation and diastereoselective [2,3]-rearrangement process, exploiting Pd-catalyzed allylic substitution to form the reactive ammonium salt *in situ*, giving (±)-*anti*-α-amino acid derivatives **2.12** with excellent diastereocontrol via proposed transition state **2.13** (Scheme 2.2a).[33] The observed diastereoselectivity of this [2,3]-rearrangement process, and indeed most [2,3]-rearrangements, can be rationalized through the *exo*- or *endo*-transition states **2.15** and **2.17** initially described by Houk and Marshall for the related [2,3]-Wittig rearrangement (Scheme 2.2b).[34]

Scheme 2.2 Stereochemical models for [2,3]-rearrangements.



Prior to our studies within this area, only limited methods capable of imparting enantiocontrol in the [2,3]-rearrangement of allylic ammonium ylides had been developed. Sweeney first demonstrated a chiral auxiliary approach to allow access to enantiomerically enriched α-amino acid derivatives,[35] while the use of a superstoichiometric chiral Lewis acid promoter was subsequently reported by Somfai.[36] Catalytic enantioselective variants were unknown until 2014, when our laboratory reported an isothiourea-catalyzed[37] [2,3]-

rearrangement of allylic quaternary ammonium salts **2.19** to give *syn*-α-amino acid derivatives **2.21** with excellent levels of diastereo- and enantiocontrol (Figure 2.3).[38] Treatment of quaternary ammonium salts **2.19** bearing an activated *p*-nitrophenol ester, either isolated or generated *in situ*, with catalytic (+)-benzotetramisole ((+)-BTM) **2.20**, cocatalytic hydroxybenzotriazole (HOBt), and *i*Pr_2NH), gave stereoselective [2,3]-rearrangement into *syn*-α-amino acid derivatives with excellent levels of stereocontrol. This process can be performed in the absence of HOBt; however, its addition provides a subtle enhancement in both diastereo- and enantioselectivity. We tentatively proposed a Lewis base catalytic cycle, initiated by nucleophilic addition of (+)-BTM **2.20** into the activated ester substrate to form an acyl ammonium intermediate prior to the formation of ammonium ylide **2.22**. However, alternative mechanistic pathways using either Lewis or Brønsted base catalysis proceeding via different intermediates can be envisaged (Figure 2.3, bottom). For example, assuming Lewis base catalysis is operative, the reaction could proceed through initial formation of a ketene intermediate **2.23** en route to acyl ammonium ylide **2.22**. Furthermore, the origin of the observed diastereo- and enantiocontrol in the rearrangement process is currently unknown. Herein we report experimental and computational investigations into the mechanism and origins of stereocontrol in the isothiourea-catalyzed [2,3]-rearrangement of allylic ammonium ylides (Scheme 2.1, bottom). *In situ* NMR analysis has allowed a reaction profile to be elucidated, while isotopic-labeling studies have unambiguously identified a genuine productive catalytic intermediate **2.9** (Scheme 2.1c). Kinetic analysis has given insight into the overall process, and crossover studies have provided information about the reversibility of each step. Kinetic isotope effects have also been used to probe the stereodetermining [2,3]-rearrangement step of the process. Computational reaction coordinate modeling provides deeper insight into the catalytic cycle, and transition state modeling reveals the origins of stereochemical control.

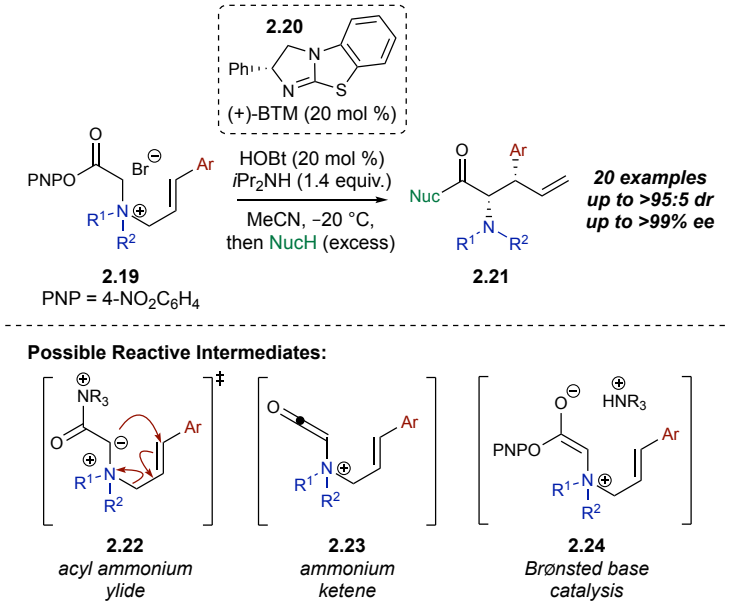


Figure 2.3 Catalytic enantioselective [2,3]-rearrangement.

2.2 Computational Studies

2.2.1 Computational Methods

We computed all intermediates, transition structures (TSs), and possible salt complexes involved in the catalytic cycle shown in Figure 2.4. Exhaustive searches were performed to locate all pertinent conformations. Geometries and thermodynamic corrections were computed at the M06-2X[39]/6-31G(d)[40] level of theory as implemented in Gaussian 09.[41] Vibrational frequencies and thermal corrections to the Gibbs free energy were calculated at −20 °C and 1 atm to match the experimental conditions. Further energy refinements were completed using M06-2X/6-311++G(2df,p).[42] Implicit solvation corrections were applied using the polarized continuum model (PCM)[43] with UFF radii[44] for acetonitrile in both the geometry optimizations and the single-point energy refinements. The hybrid meta-GGA functional M06-2X is generally more robust than B3LYP at accounting for dispersion and nonbonding interactions routinely found in organocatalytic reactions.[45] Kinetic isotope effects were calculated using the theory of Bigeleisen and Mayer[46] along with the rigid-rotor harmonic oscillator approach ($\Delta H \Delta S$).[47] Quantum mechanical tunneling effects were

also calculated for both methods using the one-dimensional parabolic approximation.[48] The calculation of the KIE was automated by use of the Onyx isotope effect program.[49]

2.2.2 Computed Catalytic Cycle

The catalytic cycle and the computed reaction coordinate are summarized in Figure 2.4. Direct acylation begins with BTM attack on allylic ammonium activated substrate (**TS-II**, $\Delta G^{\ddagger}$ = 14.8 kcal/mol) to form tetrahedral intermediate **III**. Release of $PNPO^{-}$ (**TS-IV**, $\Delta G^{\ddagger}$ = 12.0 kcal/mol) gives dication **V**. Indirect acylation through formation of the ammonium ketene III′ was ruled an unlikely reactive intermediate based on its unfavorable thermodynamics ($\Delta G^{\ddagger}$ = 22.0 kcal/mol). The endergonicity of dication **V** ($\Delta G^{\ddagger}$ = 3.3 kcal/mol) confirms the observed reversibility of catalyst acylation. Dication **V** is in equilibrium with ylide **VII** (ΔG = 1.6 kcal/mol) through deprotonation of the α-proton of **V** by $PNPO^{-}$ ($\Delta G^{\ddagger}$ = 11.4 kcal/mol), also in agreement with the experimentally observed reversibility of the deprotonation step.[50,51] NBO analyses reveal significant enolate character of ylide intermediate **VII**. Intermediate **VII** subsequently undergoes stereoselective and turnover-rate limiting [2,3]-rearrangement (**TS-VIII-(2*S*,3*S*)-Major**, $\Delta G^{\ddagger}$ = 17.3 kcal/mol) to yield enantio- and diastereoenriched acyl ammonium product-catalyst complex **IX**. Catalyst turnover is found to be stepwise, begins with $PNPO^{-}$ attack (**TS-X**) and ends with catalyst and product release (**TS-XII**). The barrier for $PNPO^{-}$ attack as calculated from intermediate **IX** ($\Delta G^{\ddagger}$ = 16.9 kcal/mol) indicates that, in the absence of HOBt, this step is highly competitive with rearrangement as turnover-rate limiting.

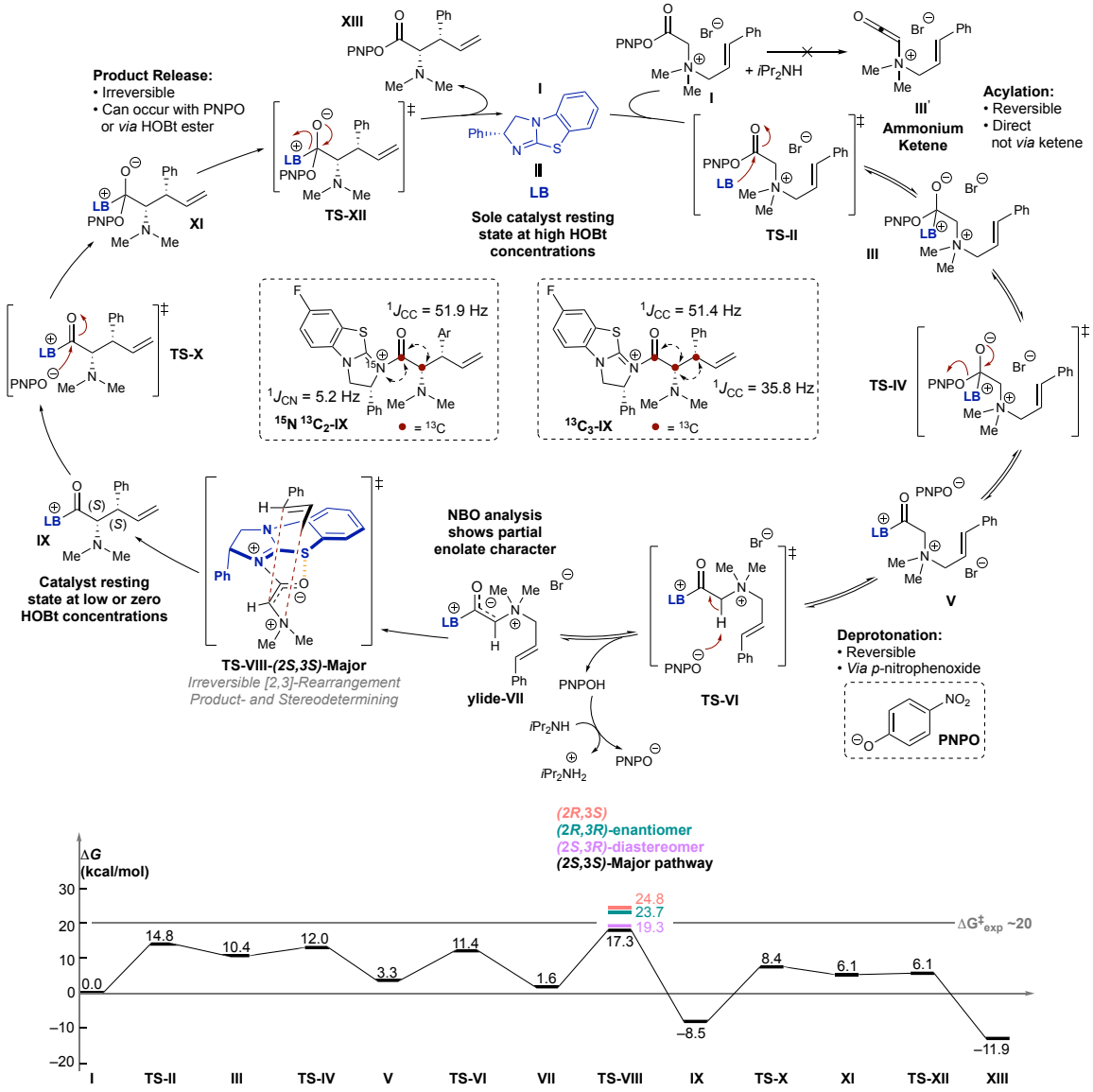


Figure 2.4 Proposed catalytic cycle and computed reaction coordinate.

2.3 Effect of Counterions on the Theoretical KIE

The presence of counterions posed a challenge to the accuracy of DFT and significantly increased the complexity of the conformational search and the number of relevant structures to consider.[52] Almost all species present in the catalytic cycle prior to catalyst turnover bear a positive charge, with intermediate **V** being dicationic. Species indicated to include a counterion in Figure 2.4 were optimized with the explicit ion shown. Given the charged nature of the species present, the identification of the structures that compose the

free energy span[53] resulted from considering all possible counterion coordination combinations for all conformations of each charged species in the catalytic cycle. This exhaustive process led to the identification of acyl substrate **I** and **TS-VIII** as the two states contributing to the free energy span. Computed barriers show the rearrangement step as the first irreversible step of the mechanism, thereby allowing kinetic isotopic fractionation to occur. The computed KIE then depends on the vibrational frequencies of **I** and **TS-VIII**, and could then be utilized to corroborate the computed thermodynamics and barriers of this free energy span.[54]

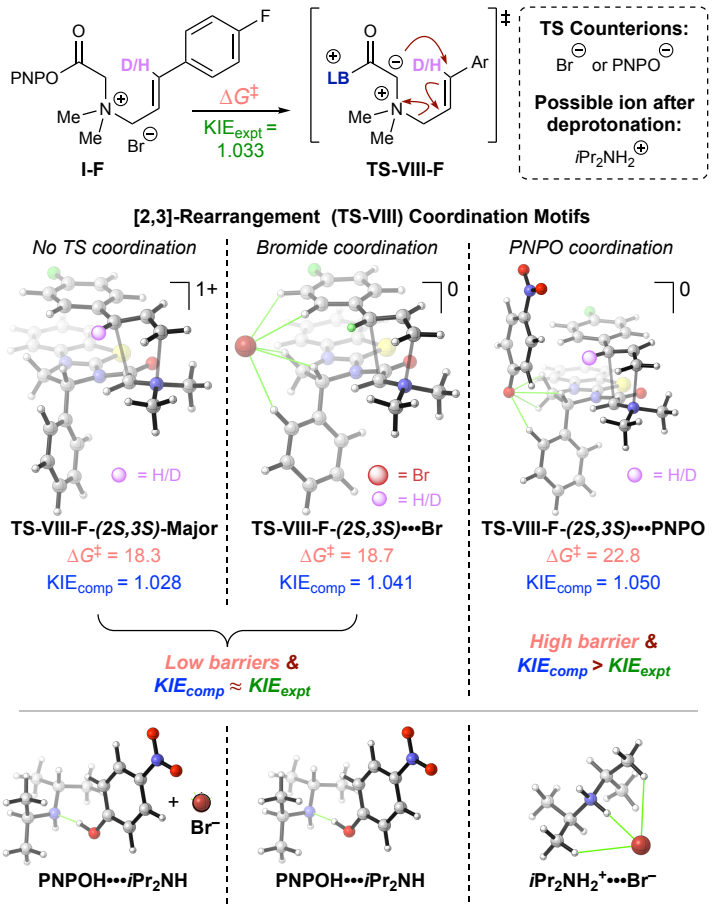


Figure 2.5 Computed TSs, ions, complexes, and KIEs involving the 4-fluoro substituted substrate **I-F**. The computed KIE depends on the coordination state of substrate **I-F** and **TS-VIII-F**. The violet highlighted atom is the isotopic proton (H/D). All energies in kcal/mol. Shaded gray lines represent forming/breaking bonds. Green lines represent C−H electrostatic interactions and hydrogen bonds.

In a multistep reaction with highly charged and zwitterionic species, leveraging KIE prescribes a means to identify not only the structures that compose the free energy span but also which ions coordinate, the specific binding site of the counterion,[55] and the conformation.[56] We sought to identify the coordination state of **TS-VIII** by leveraging both the KIE and computed barriers for **TS-VIII-F**, i.e. bearing the 4-fluoro substituent used for KIE determination (Figure 2.5). Coordination to **TS-VIII-F**, formation of byproduct salt complexes, and conformations all affect the barrier in going from **I-F** to **TS-VIII-F**. Two possible counterions, $PNPO^-$ and Br^-, were considered as TS counterions, while $i Pr_2NH_2^+$ was evaluated as a component of the possible remaining complexes (Figure 2.5). No coordination to the TS (Figure 2.5, left) leaves H-bond complex PNPOH···$i Pr_2NH$ as the lowest-energy remaining complex, giving an overall $\Delta G^‡$ = 18.3 kcal/mol. Bromide ion binding to the TS (**TS-VIII-F-(2*S*,3*S*)···Br**, Figure 2.5, middle) also leaves complex PNPOH···$i Pr_2NH$ ($\Delta G^‡$ = 18.7 kcal/mol). $PNPO^-$ binding and the complexation of $i Pr_2NH_2^+$ and Br^- gives an even higher barrier (**TS-VIII-F-(2*S*,3*S*)···PNPO**, $\Delta G^‡$ = 22.8 kcal/mol). With no counterion coordination to the TS (**TS-VIII-F-(2*S*,3*S*)-Major**), the KIE_{comp} of 1.028 matches well with experiment (KIE_{exp} = 1.031). Bromide complexation, which is 0.4 kcal/mol higher, also matches fairly closely, giving a KIE_{comp} of 1.041.[57] $PNPO^-$ complexation leads to an erroneously large magnitude of rate difference between k_H/k_D, yielding a KIE_{comp} of 1.050.

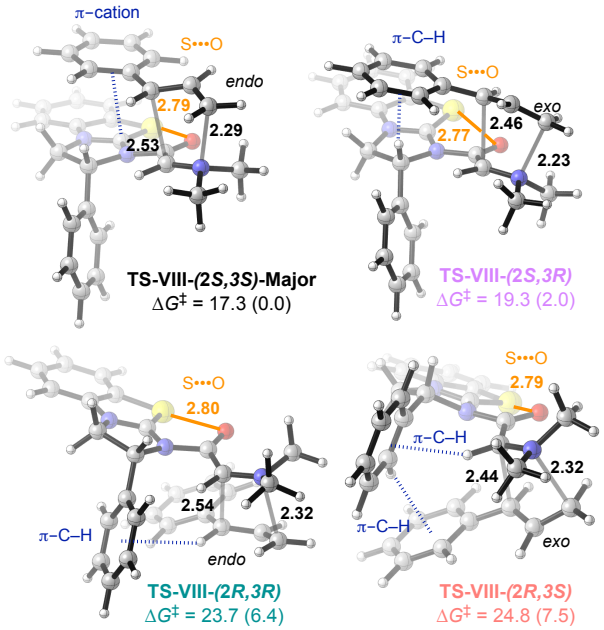


Figure 2.6 Stereodetermining [2,3]-rearrangement TSs. All energies in kcal/mol, and distances in Å. Shaded gray lines represent forming/breaking bonds. Solid orange lines represent nonbonding S···O interactions. Dashed blue lines represent aromatic interactions.

2.4 Stereocontrol Model

The computed diastereomeric [2,3]-rearrangement TSs are shown in Figure 2.6. All TSs feature concerted C−C bond formation and ammonium N−C bond cleavage. The four main elements that control the stereochemical outcome of the reaction are disclosed in the following sections (Figure 2.7).

2.4.1 E vs. Z configuration of the ylide/enolate

NBO analysis indicates that both ylide **VII** and **TS-VIII-(2*S*,3*S*)-Major** have significant enolate character.[58] Ylide **VII** displays a C−O bond order of 1.39 and a C−C bond order of 1.52 (Figure 2.7, bottom left inset), while **TS-VIII-(2*S*,3*S*)-Major** displays a C−O bond order of 1.54 and a C−C bond order of 1.21. The computed bond order of 1.52 for ylide **VII** suggests partial C−C double bond character leading to distinct isomeric *E* and *Z* enolate configurations prior to rearrangement with the configurations set in place by the

deprotonation step. The *Z*-configuration is heavily favored over the *E*, as shown in the model system **Z/*E*-model-VII** where the *Z* is favored by >16 kcal/mol. All stable [2,3]-rearrangement transition structures feature the *Z*-enolate.

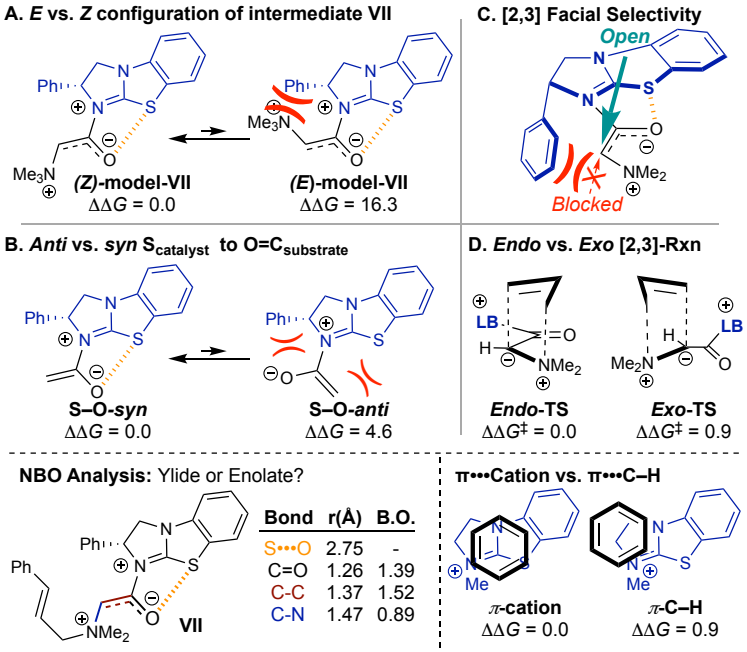


Figure 2.7 Computed model systems (all energies in kcal/mol and distances in Å). (a) Preference for *Z* over *E* enolate. Enolate-like character indicated by bond orders (B. O.) estimated from the Wiberg bond indices (bottom left inset). (a) Effect of S···O interaction on acylated catalyst conformation. (a) With the acylated catalyst conformation held rigid (S···O), the BTM stereodirecting Ph sterically biases the open enolate face. (a) *Endo* rearrangement is favored. In the major TS, this preference is reinforced by a π–cation interaction (bottom right inset).

2.4.2 Anti vs. syn $S_{catalyst}$ to $O_{substrate}$

In all the lowest energy conformations of the **ylide-VII** and rearrangement **TS-VIII**, the S–O relationship is *syn*. The *syn* distances (~2.7–2.8 Å) are significantly below the sum of the van der Waals radii (3.4 Å), indicating close-contact S···O interactions (Figures 2.6 and 2.7, orange lines).[20] Computed model systems show >4 kcal/mol preference for the conformation which contains the 1,5-S···O interaction (**S–O-*anti/syn***, Figure 2.7b). All [2,3]-rearrangement TSs that do not bear the S···O interaction are higher by >6 kcal/mol. The conformational bias toward the S–O *syn* arrangement is proposed to result from n_O to

σ^*_{C-S} delocalization coupled with electrostatic attraction of the partially positive sulfur atom and partially negative oxygen atom.[21]

2.4.3 Facial selectivity of rearrangement

The S···O interaction significantly rigidifies the **ylide-VII** structure, leaving conformational freedom only to the substrate cinnamyl group. With rearrangement possible from either face of the catalyst isothiourea plane, the facial selectivity is controlled by the catalyst Ph stereodirecting group (Figure 2.7c). The most favorable [2,3]-TSs favor approach opposite to this group (**TS-VIII-(2*S*,3*S*)-Major** and **TS-VIII-(2*S*,3*R*)**, Figure 2.6). Approach on the same side as the stereodirecting Ph is disfavored by >6 kcal/mol (**TS-VIII- (2*R*,3*R*)** and **TS-VIII-(2*R*,3*S*)**).

2.4.4 Endo vs. exo-[2,3]-TS

Rearrangement can occur either *endo* or *exo* with respect to the substrate C=O (Figure 2.7). In the simple allyl model TS, the *endo*/*exo* preference is ~1 kcal/mol. This preference is ~2 kcal/mol between **TS-VIII-(2*S*,3*S*)-Major** and **TS-VIII-(2*S*,3*R*)**, and additional interactions contribute to the diastereoselectivity. In the major TS there is a π−cation interaction,[59] which is favored over the π-C−H interaction found in the minor.[60] Truncated fully optimized model systems probing the difference in energy between these interactions in the context of cationic BTM reveal a ~1 kcal/mol preference for **π-cation** over **π-C−H** (Figure 2.7, bottom right inset). These two factors contribute to the computed 2 kcal/mol preference for **TS-VIII-(2*S*,3*S*)-Major** over **TS-VIII-(2*S*,3*R*)**, in good agreement with the experimental selectivity of 1.5 kcal/mol.

2.5 Conclusions

The experimental and computational investigation reported herein has provided mechanistic and stereochemical insight into the enantioselective isothiourea-catalyzed

[2,3]-rearrangement of allylic ammonium ylides. Analysis by *in situ* ^{19}F NMR has allowed reaction profiles to be established and has identified an intermediate species.

Isotopic labeling of catalyst (^{15}N) and substrate (^{13}C) has confirmed the constitution of the catalytic intermediate as **IX** by ^{13}C NMR. Isotopic entrainment has shown **IX** to be an irreversibly generated intermediate that is productive toward catalysis. A series of crossover experiments have provided detailed information regarding the reversibility of each individual step of the catalytic cycle. The turnover-rate limiting step of the process varies between product release and [2,3]-rearrangement, depending on substrate conversion. The effect of excess HOBt upon the reaction is to accelerate product release, thus generating a greater proportion of the free BTM catalyst. This may then result in more effective interception of the background racemic reaction, and thus greater diversion onto the enantioselective pathway. Computational analysis has provided finer detail for the fundamental steps in the catalytic cycle as well as the key interactions that control the stereochemical outcome of the process. The insight gained into this process will have implications in a wider context, especially in the use of activated esters in Lewis base catalysis, which is currently under investigation in our laboratories.

2.6 Acknowledgment

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Chapter 3.

Non-Bonding 1,5-S···O Interactions Govern Chemo- and Enantioselectivity in Isothiourea-Catalyzed Annulations of Benzazoles

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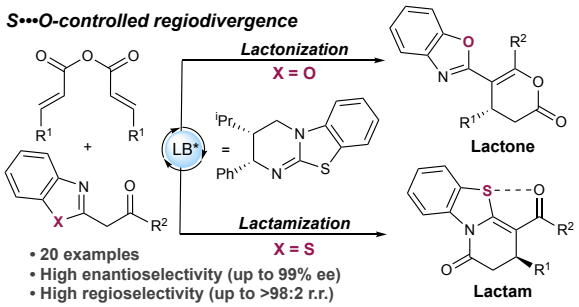
3.1 Abstract

Isothiourea-catalyzed annulations between 2-acyl benzazoles and α,β-unsaturated acyl ammonium intermediates are selectively tuned to form either lactam or lactone heterocycles in good yields (up to 95%) and high ee (up to 99%) using benzothiazole or benzoxazole derivatives, respectively. Computation gives insight into the significant role of two 1,5-S···O interactions in controlling the structural preorganization and chemoselectivity observed within the lactam synthesis with benzothiazoles as nucleophiles. When using benzazoles the absence of a second stabilizing non-bonding 1,5-S···O interaction leads to a dominant C–H···O interaction in determining structural preorganization and lactone formation.



3.2 Introduction

Nitrogen-containing heterocycles are of wide-spread importance in pharmaceutical, agrochemical and material science industries.[61] In particular, benzazoles have found broad-reaching applications as bioactive compounds in medicinal chemistry, with a range of therapeutic treatments exploiting their anti-bacterial, anti-fungal, anti-parasitic and anti-cancer properties.[62] In addition, they are key components of useful ligands[63] as well as organic semiconductors and dyes.[64] The prevalence of the benzazole motif in these applications has led the synthetic community to develop numerous methodologies for the use of benzazole containing nucleophiles for the rapid synthesis of complex heterocycles.[65]

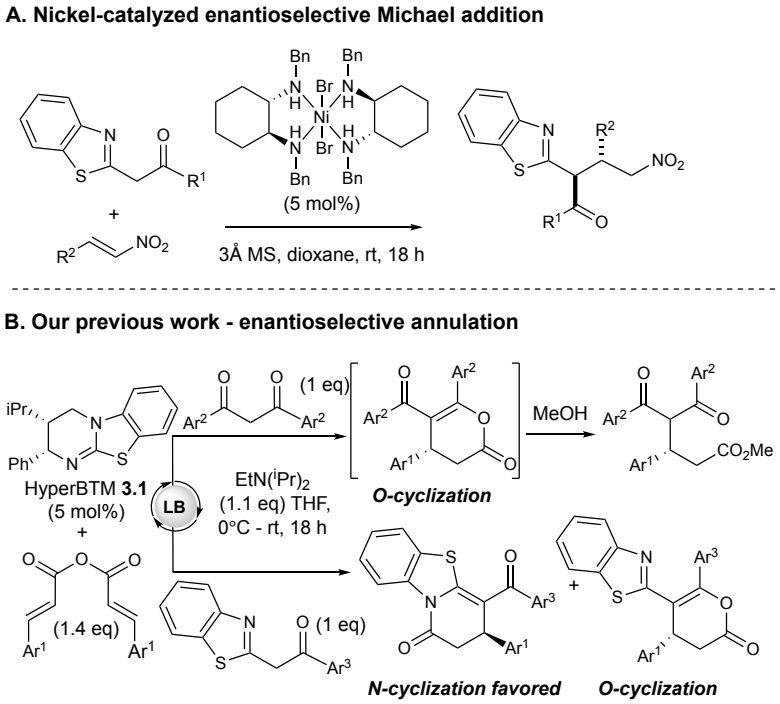


Figure 3.1 Previous work using benzazoles in enantioselective catalysis. (a) Nickel-catalyzed Michael addition to nitroalkenes; (b) isothiourea-catalyzed enantioselective annulation with α,β-unsaturated acyl ammonium intermediates.

Despite this interest, catalytic enantioselective functionalization of benzazole derivatives has received limited attention, with only a small number of enantioselective protocols developed to date.[66] As a representative example of such an approach, Lam has shown that benzazoles undergo catalytic enantioselective nickel-catalyzed Michael-additions to

nitroalkenes, giving the desired products in high yields, moderate to excellent dr and good to excellent enantioselectivity (Figure 3.1a).[67] As part of our ongoing research employing isothioureas[68] in catalysis,[69] we recently developed an enantioselective annulation process utilizing α,β-unsaturated acyl ammonium intermediates.[70,71] In this annulation process, reaction of this intermediate with symmetrical 1,3-dicarbonyl nucleophiles generates functionalized esters in high ee after ring-opening through a postulated Michael addition-lactonization/ring-opening process (17 examples, up to 96% ee). Notably, preliminary results using unsymmetrical 2-phenacylbenzothiazole as a nucleophile gave functionalized lactams preferentially (~85:15 lactam:lactone), resulting from preferential *N*- rather than *O*-cyclization, through a Michael addition-lactamization process in up to 86% ee in three isolated examples (Figure 3.1b).

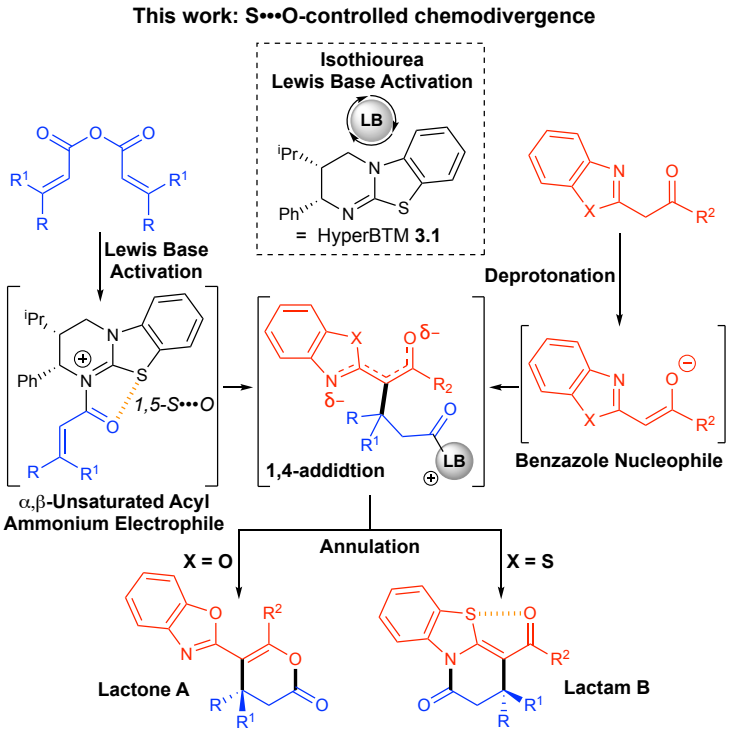


Figure 3.2 Chemo- and enantioselective isothiourea-catalyzed annulation of acylbenzazoles with α,β-unsaturated acyl ammonium intermediates.

This manuscript builds upon the intriguing chemoselectivity observed in the preferential formation of lactams in this latter process, and subsequently explores the effect of changing both carbonyl substitution and the heteroatom within a series of acylbenzazole nucleophiles. As a

result, we have developed a highly chemoselective method to access either lactam **A** or lactone **B** heterocyclic products in excellent enantioselectivity through use of acylbenzothiazole or acylbenzoxazole derivatives respectively (Figure 3.2). Furthermore, through computations, the role that non-bonding 1,5-S···O interactions and C–H···O interactions play in governing the unusual regioselectivity of these processes is highlighted. The importance of non-bonding S···O interactions has been widely recognized in structural and medicinal chemistry in the solid state (commonly ascribed to a stabilizing n_O to σ^* interaction),[21] and has been used as a key controlling element to rationalize enantioselective isothiourea-catalyzed reactions.[20] The focus of ongoing work within our research groups will be the demonstration of alternative examples of how non-bonding S···O interactions can facilitate selectivity in catalysis could lead to its broader utilization, akin to the current widespread use of hydrogen bonding and other non-bonding interactions in synthesis.[72] To the best of our knowledge, S···O interactions have not been invoked to describe the origins of chemoselectivity in a catalytic reaction.

3.3 Probing the Effects of Acyl and Benzazole Substituents

Initial investigations sequentially probed substituent effects on the chemo- and enantioselectivity of this annulation process, with variation of heterocycle (benzothiazole vs. benzoxazole) tested (Figure 3.3). Consistent with our previous studies, using homoanhydride **3.2** as α,β-unsaturated acyl ammonium precursors with isothiourea HyperBTM **3.1** (5 mol%) in bench-grade THF, 2-phenacylbenzothiazole **3.3** gave preferentially lactam product **3.5** (88:12 lactam **3.5**:lactone **3.6**), with **3.5** isolated in 86% yield and 83% ee that was recrystallized to give **3.5** in 68% yield and 97% ee. A small amount of the lactone constitutional isomer **3.6** was also isolated (9% yield, 86% ee). The potential for isomerization of lactone to the lactam was investigated under a range of conditions. Treatment of the minor lactone product **3.6** with base and HyperBTM **3.1**, or to the reaction conditions, led to no interconversion of lactone to lactam, consistent with the observed product ratios arising from kinetic control. While using 2-phenacylbenzothiazole leads to preferential formation of lactam **3.5**, remarkably, 2-phenacylbenzoxazole **3.4** afforded exclusively lactone product (>95:5 **3.6**:**3.5**) with the lactone **3.6** isolated in 95% yield and 98% ee. The seemingly trivial substrate change from

benzothiazole to benzoxazole in this system promotes a change in chemoselectivity in the annulation process to selectively facilitate lactone (*O*-cyclization) rather than lactam (*N*-cyclization) product formation.

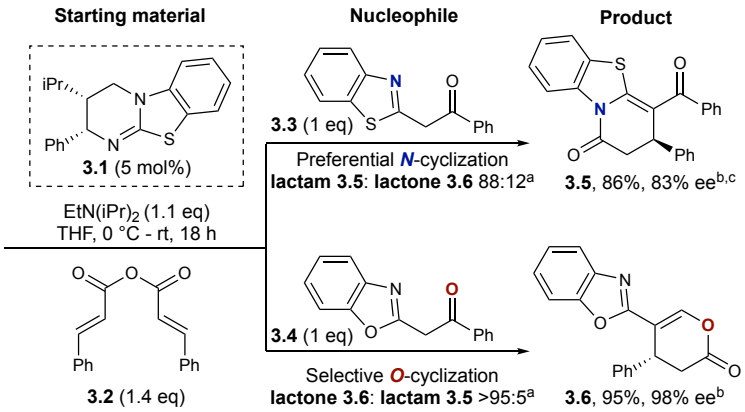


Figure 3.3 Probing the effects of acyl and benzazole substituents on annulation chemo- and enantioselectivity. [a]Ratio of constitutional isomers arising from either *N*- or *O*-cyclization calculated from ^{1}H NMR spectra of crude reaction product. [b]ee values obtained *via* chiral HPLC. [c]Following a single recrystallization ee could be enhanced to 97%.

3.4 Computational Studies

Computations were undertaken to provide insight into the observed chemoselectivity when using the benzoxazole and benzothiazole nucleophiles (X = O or S, respectively). For this purpose, we have specifically computed the intermediates and transition structures involved in the formation of products **3.5** (lactam) and **3.6** (lactone) using 2-phenacylbenzothiazole **3.3** and 2-phenacylbenzoxazole **3.4**.

3.4.1 Computational methods

All energy refinements and geometries were computed in solution using the implicit polarizable continuum model (PCM) with tetrahydrofuran as solvent (M06-2X[39]/6-31+G(d,p)[42]/PCM(THF)//M06-2X/6-31G(d)[40]/PCM[43](THF)) using the UFF radii[44] for THF as implemented in Gaussian 09.[41] The M06-2X DFT method has been successfully used to rationalize mechanisms and selectivities of synthetic reactions by us and others.[73]

Given the zwitterionic nature of many of the intermediates in the reaction, we also took into account the ability of M06-2X to accurately evaluate dispersion-heavy and ionic systems relative to the less computationally expensive B3LYP method.[74]

3.4.2 Mechanism and catalytic cycle

The catalytic cycle is shown in Figure 3.4. Stepwise *N*-acylation of HyperBTM leads to the α,β-unsaturated acyl ammonium intermediate. Stereodetermining 1,4-addition of the anionic benzazole nucleophile and proton transfer leads to the pre-cyclization intermediate, which can either lactamize or lactonize. Restoration of the carbonyl π-bond from the tetrahedral intermediate releases the product and regenerates HyperBTM **3.1**.

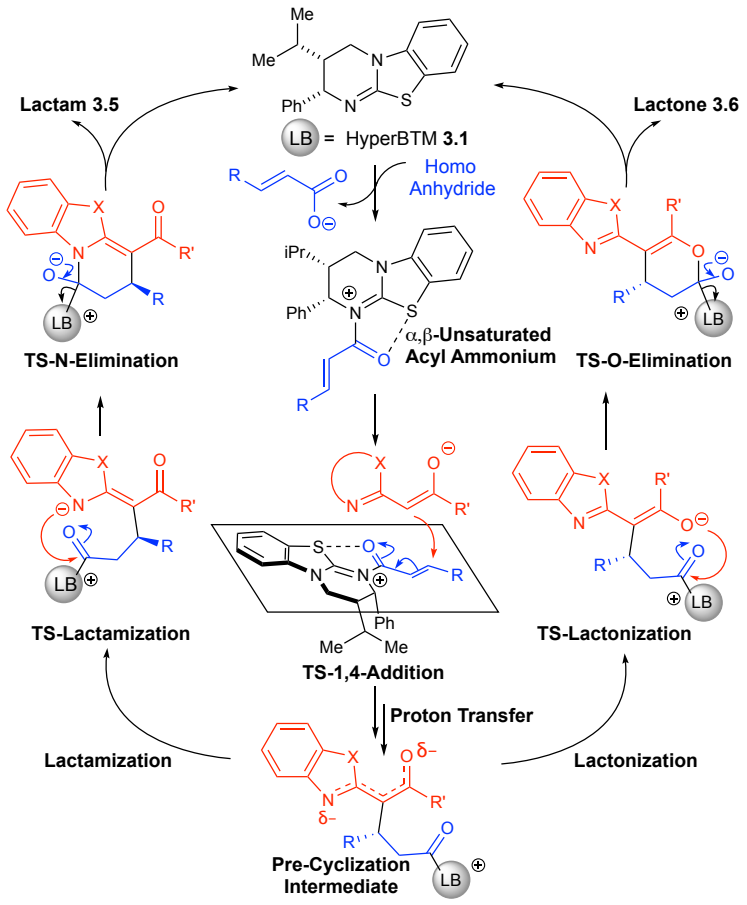
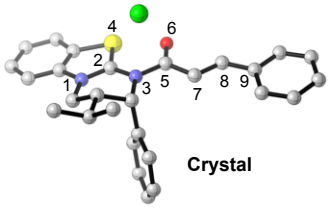


Figure 3.4 Catalytic cycle of the isothiourea-catalyzed annulations between 2-acyl benzazoles and homoanhydrides to form the lactam (left) or the lactone (right) using benzothiazole (X = S) or benzoxazole (X = O) derivatives, respectively.

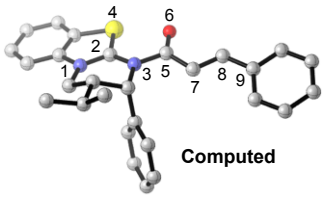
3.4.3 S···O interaction

Considering this mechanistic scheme, within all key reactive intermediates and transition states where S- and O-atoms contain 1,5-connectivity (such as from the carbonyl C=O and isothiourea S within the acylammonium intermediate, or 2-phenacylbenzothiazole carbonyl-O and benzothiazole-S), these atoms are co-planar. The internuclear distances (within the range of 2.53–2.70 Å) are significantly less than the sum of the van der Waals radii (3.4 Å).[22] These observations are consistent with an attractive force between the S- and O-atoms and in line with previous computations by Tantillo and Romo[21a] as well as by Houk and Birman.[20e] Unique to this system, however, is how this interaction dominates the structural preorganization of all key reactive intermediates and transition states of this annulation process.

Table 3.5 Computed vs. crystal structure of the α,β-unsaturated acyl ammonium intermediate.



Crystal



Computed

Entry	Geometric Parameter	Computed [a]	Crystal
1	4–6 [b]	2.57	2.48
2	2–4	1.74	1.74
3	1–2	1.33	1.33
4	2–3	1.35	1.36
5	3–5	1.43	1.41
6	5–7	1.47	1.47
7	7–8	1.35	1.33
8	8–9	1.46	1.46
9	4–2–1 [c]	113	114
10	4–2–3	125	125
11	2–3–5	119	118
12	3–5–6	119	118
13	6–5–7	124	122
14	2–3–5–6	11	6

[a]M06-2X/6-31G(d)/PCM(THF) geometry optimization. [b]Distances given in Å. [c]Angles and dihedrals in degrees.

3.4.4 S···O interaction in the enantiocontrol of 1,4-addition

All stable conformations of the α,β-unsaturated acyl ammonium intermediate exhibit coplanarity of the 1,5-O and S atoms. This is corroborated by the crystal structure of this intermediate which show the S–O being coplanar at a distance of 2.48 Å (Table 3.5). This crystal structure was used as a benchmark for the computational method, with theory able to reproduce interatomic distances of the isothiourea core (Table 3.5, entries 2–4) and the extended electrophilic π-system (entries 5–8). Of note is the shorter S–O distance in the crystal structure vs. the computed structure (entry 1). Angles (entries 9–13) and the dihedral between the catalyst and the acyl group (entry 14) were also in good agreement with experiment. In addition, both anionic nucleophiles prefer the planar arrangement (Figure 3.6), with the 1,5-S–O *syn* conformation favored by ~7 kcal/mol in the case of benzothiazole. Taken together, these factors rigidify and planarize both the electrophilic α,β-unsaturated acyl ammonium intermediate and the incoming nucleophile, dramatically simplifying the stereochemical model. Independent of the nucleophile identity, 1,4-addition occurs *anti* to the catalyst stereodirecting groups on the less hindered face (**TS-1,4-Addition**, Figure 3.4). The computed enantioselectivities of 99% in both cases are in reasonable agreement with experiments (83% and 98% ee for **3.5** and **3.6**, respectively, Figure 3.3).

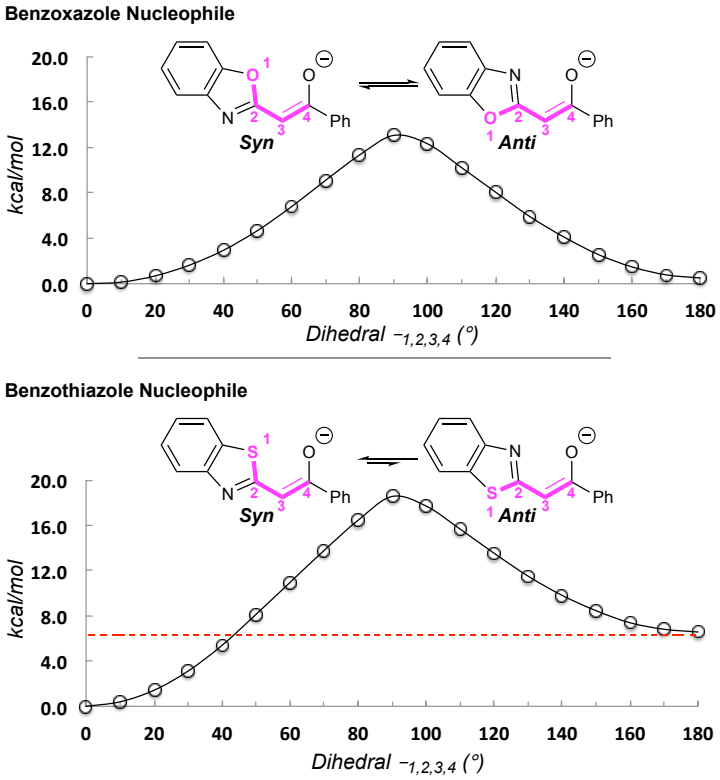


Figure 3.6 Conformational preferences of anionic benzoxazole and benzothiazole nucleophiles.

3.4.5 Lactamization vs. lactonization

The interplay between S···O and C–H···O interactions[75] (between the anionic nucleophile atoms and C–H α-to the positively-charged nitrogen of the acylated HyperBTM) governs cyclization chemoselectivity. Figure 3.7 shows computed model complexes analogous to the pre-cyclization intermediate, featuring truncated simplified structures of both HyperBTM catalyst and benzazole nucleophiles. In the oxazole model system, the conformation with one S···O and one C–H···O interaction is favored by 2.5 kcal/mol over the conformation featuring the unfavorable O···O. However, in the thiazole model, the conformation featuring two S···O interactions, rather than one S···O and one C–H···O, is preferred by 3.7 kcal/mol.

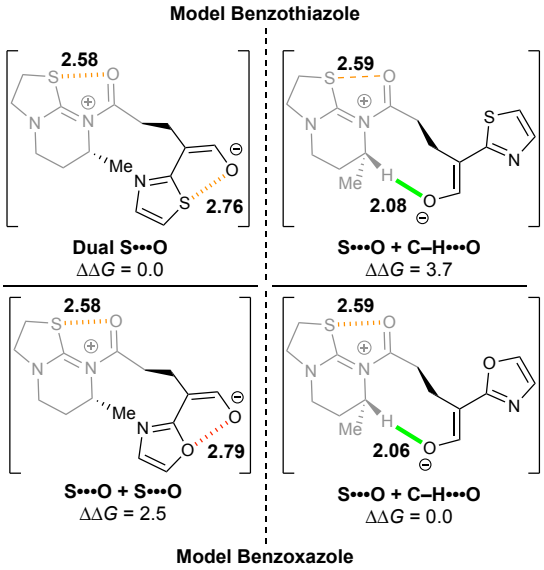


Figure 3.7 Model systems probing the relative energetic values (kcal/mol) between S···O and C–H···O nonbonding interactions.

These preferences carry over to the cyclization transition structures (Figure 3.8). In the benzoxazole case, both annulations occur *via* a boat-like six-membered transition structure *anti* to the catalyst stereodirecting groups (phenyl and isopropyl) to minimize steric occlusion. The **Favored-Lactonization-(X=O)-TS** is preferred over the **Disfavored-Lactamization-(X=O)-TS** ($\Delta G^{\ddagger}$ = 11.1 and 14.3 kcal/mol, respectively) due to a stabilizing C–H···O involving the *ortho* C–H of the catalyst and the incoming oxygen atom. In the latter, a β-C–H is involved in a repulsive interaction with the incoming benzoxazole. The computed selectivity of 99:1 matches well with the experimental selectivity of 98:2 seen with lactone **5B**.

The benzothiazole lactone closure occurs exactly as the benzoxazole case through the **Disfavored-Lactonization-(X=S)-TS** ($\Delta G^{\ddagger}$ = 11.7 kcal/mol). The **Favored-Lactamization-(X=S)-TS** has a lower barrier ($\Delta G^{\ddagger}$ = 10.6 kcal/mol), and the computed selectivity of 88:12 matches experiments. Interestingly, lactamization occurs on the same face as the catalyst stereodirecting groups, previously thought to be disfavored due to the steric occlusion.

Two key stabilizing interactions are present in benzothiazole lactamization that are not found in lactonization: (1) π-stacking of the catalyst phenyl and the fused benzene of the benzothiazole ring,[76] and (2) a second 1,5-S···O interaction within the former

benzothiazole nucleophile. The switch in chemoselectivity in favor of lactam formation using the benzothiazole is attributed to the penalty of breaking the 1,5-S···O present within the benzothiazole nucleophile for the lactonization process to proceed.

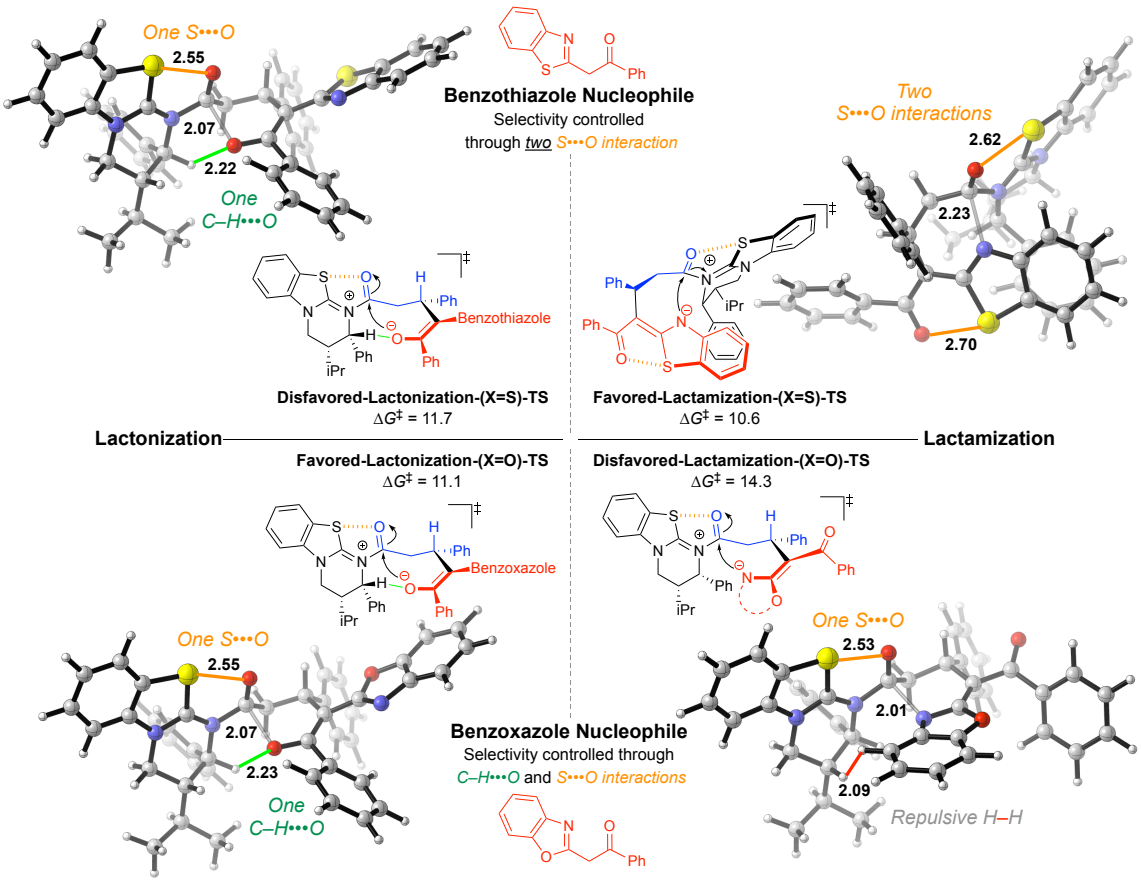


Figure 3.8 Computed chemoselectivity determining cyclization transition structures for benzoxazole and thiazole nucleophiles. All transition structures are stepwise (tetrahedral intermediate formation followed by HBTM release) except for **Favored-Lactamization-(X=S)-TS**. Forming bonds shown in grey. S···O interactions shown in orange, C–H···O highlighted in green, and van der Waals repulsion shown in red. Aromatic interaction shaded in purple. Relative energy values given in kcal/mol.

3.5 Conclusions

To conclude, we have demonstrated the scope and limitations of the organocatalytic enantioselective functionalization of a range of benzazole nucleophiles using the isothiourea HyperBTM **3.**1 and α,β-unsaturated homoanhydrides as α,β-unsaturated acyl ammonium precursors. The chemoselectivity observed during the cyclization is influenced

by the nature of the benzazole and the carbonyl employed within the acylbenzazole, with benzothiazole preferentially using the ring-nitrogen to extrude the catalyst, whereas the benzoxazole moiety prefers to cyclize through the β-carbonyl substituent. Computations elucidated the importance of non-covalent 1,5-S···O interactions in determining the chemoselectivity within these processes. Specifically, the use of benzothiazole nucleophiles allows two stabilizing 1,5-S···O interactions in the preferred lactamization transition structure, while benzoxazole contains one stabilizing 1,5-S···O and one C–H···O interaction in the lactonization transition structure. Future research within our laboratories is aimed at harnessing the collaboration between theory and experiments towards the development of isothiourea Lewis base catalysts in new enantioselective transformations.

3.6 Acknowledgments

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Chapter 4.

C=O···Isothiouronium Interaction Dictates Enantiodiscrimination in Acylative Kinetic Resolution of Tertiary Alcohols

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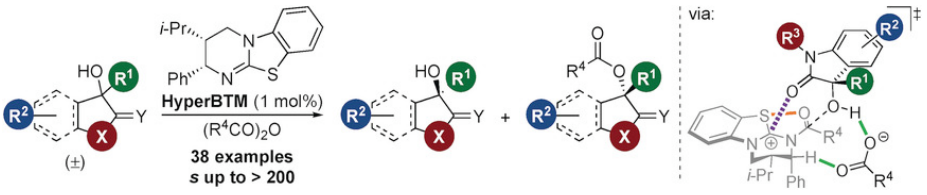
4.1 Abstract

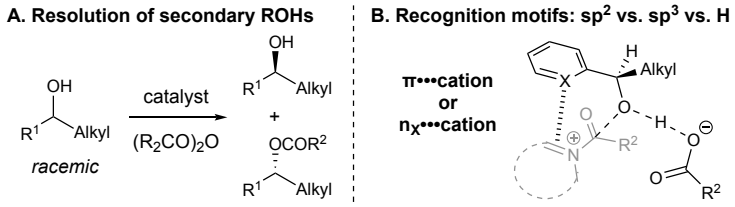
A combination of experimental and computational studies has identified a C=O···isothiouronium interaction as key to efficient enantiodiscrimination in the kinetic resolution of tertiary heterocyclic alcohols bearing up to three potential recognition motifs at the stereogenic carbinol center. This discrimination was exloited in the isothiourea-catalyzed acylative kinetic resolution of tertiary heterocyclic alcohols (38 examples, *s* factors up to > 200). The reaction proceeds at low catalyst loadings (generally 1 mol%) with either isobutyric or acetic anhydride as the acylating agent under mild conditions.



4.2 Introduction

The catalytic kinetic resolution (KR) of racemates offers an effective approach to the separation of enantiomers,[77] with an enormous range of processes and catalysts developed for applications in academia and industry.[78] Among the most popular methods is the acylative KR of alcohols[79] as this approach allows simple separation of the enantiomerically enriched alcohol and ester products. Within this area, the use of small-molecule Lewis base catalysts is well developed for the catalytic acylative KR of secondary alcohols (Scheme 4.1a). In such processes, enantiodiscrimination is dictated by the relative ability of the two non-hydrogen substituents at the stereogenic carbinol center to stabilize the catalytic cationic acyl transfer intermediate. Therefore, a common prerequisite for the selective KR of an alcohol substrate is the presence of one electron-rich sp^2-hybridized substituent (e.g., aryl, carbonyl), which acts as a cation recognition motif,[80] and one non-stabilizing sp^3-hybridized alkyl substituent (Scheme 4.1b).

Scheme 4.1 Lewis base catalyzed acylative kinetic resolution of secondary alcohols.

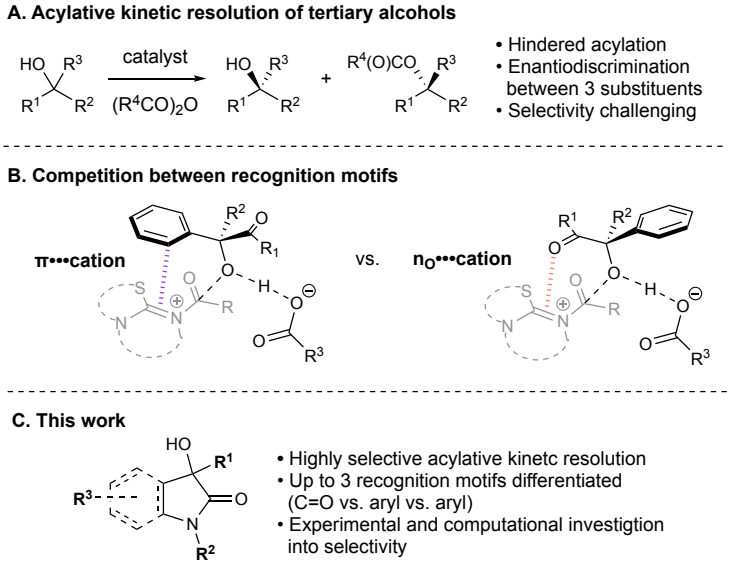


Lewis basic isothiourea catalysts, first developed for acyl transfer reactions by Birman[81] and Okamoto,[82] have emerged as exceptional catalysts for the acylative KR of secondary alcohols[83] and the KR or desymmetrization of diols,[84] amongst other applications.[85] The high selectivity factors (*s*) obtained for the KR of secondary alcohols have been attributed to the presence of an effective recognition motif on the racemic alcohol, allowing one antipode to react preferentially with a chiral acyl isothiouronium intermediate. Established recognition motifs in isothiourea-catalyzed KR include aryl,[81, 83a-83c,83h,83i] heteroaryl,[83e] alkenyl,[83a,83h] alkynyl,[83a,83h] C=O,[83d,83f] and P=O[83g] substituents. Consequently, high selectivity is only commonly observed for stereogenic carbinols

bearing one of these motifs in combination with an alkyl substituent and a hydrogen atom. An unmet challenge within acylative KR is the ability to resolve alcohols bearing multiple recognition motifs, with the relative strengths of the different interactions only poorly understood. For example, the KR of ethyl mandelate, which contains two recognition motifs (a π-system and a carbonyl group), is ineffective ($s < 2$).[83c]

In this context, this work investigates such cases through the isothiourea-catalyzed acylative KR of tertiary alcohols (Scheme 4.2a). The efficient KR ($s > 20$) of tertiary alcohols is particularly challenging as 1) they are difficult to acylate owing to their hindered nature, and 2) the catalyst must distinguish between three substituents at the reactive carbinol center. The presence of multiple recognition motifs (e.g., aryl and carbonyl groups) provides an additional challenge as the acylation of both substrate enantiomers may be promoted by different carbinol substituents, resulting in poor selectivity (Scheme 4.2b).

Scheme 4.2 Challenges faced in the kinetic resolution of tertiary alcohols.



For the KR of tertiary alcohols, the situation is further complicated if three recognition motifs are present, with potential for competition between six stabilized transition states for acylation (three for each substrate enantiomer). As such, only two non-enzymatic

acylative KRs of tertiary alcohols have been reported to date, using either a pentapeptide catalyst or through oxidative NHC catalysis.[86] In both cases, high catalyst loadings (10 mol %) were required. Herein, the isothiourea-catalyzed acylative KR of tertiary 3-hydroxyoxindole and 3-hydroxypyrrolidin-2-one derivatives,[87] in which either two or three of the carbinol substituents can potentially act as recognition motifs, is investigated (Scheme 4.2c). The key structural features of catalyst–substrate recognition that allow effective enantiodiscrimination are explored both experimentally and computationally.

4.3 Results and Discussion

Optimization studies focused on the KR of 3-allyl-3-hydroxyoxindole (**4.1**), which bears two potential recognition motifs at the tertiary carbinol center, namely an aryl π-system and a carbonyl group. A highly efficient KR process was identified (s > 100) using isothiourea catalyst HyperBTM (**4.2**; 1 mol %) and isobutyric anhydride in $CHCl_3$ at 0 °C (Figure 4.3). The use of less sterically hindered anhydrides provided lower s values while alternative isothiourea catalysts, namely tetramisole **4.3** and benzotetramisole **4.4**, were ineffective in terms of both conversion and selectivity (s < 2). Industrially preferable solvents (EtOAc, *i*-PrOAc, $(MeO)_2CO$, toluene) also provided synthetically useful levels of selectivity (s = 34–41),[88] albeit lower than those obtained in $CHCl_3$.

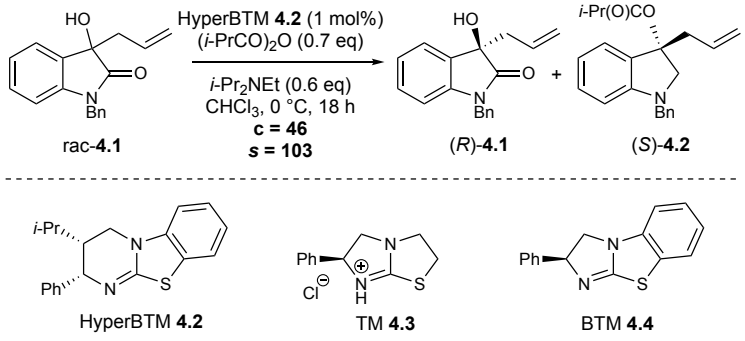
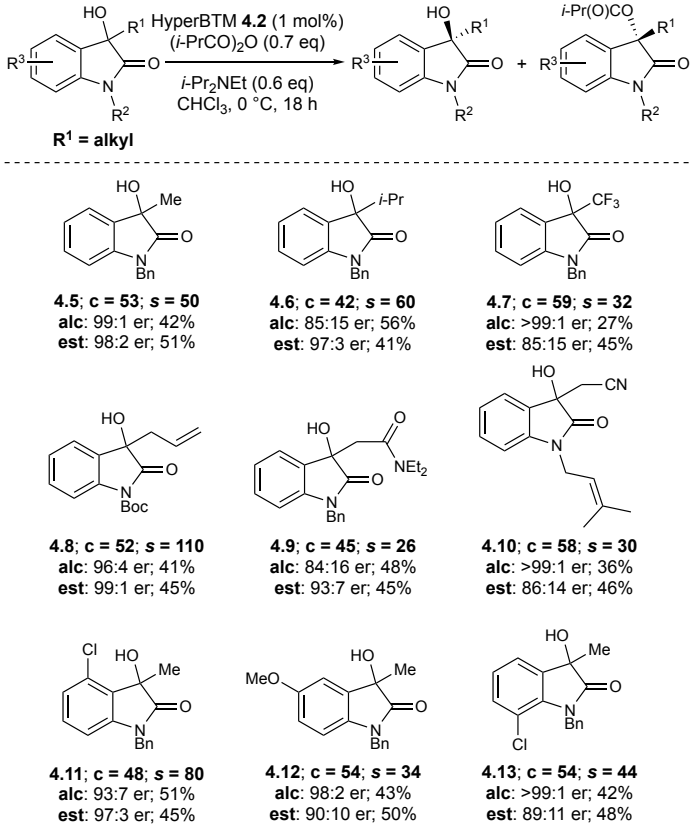


Figure 4.3 Optimized kinetic resolution conditions. Conversion (**c**) determined by HPLC analysis on a chiral stationary phase; s factors calculated using equation given in reference 77a.

The scope and limitations of the KR process were first evaluated for a range of 3-alkyl-substituted 3-hydroxyoxindole derivatives through variation of the 3-alkyl, nitrogen, and benzenoid ring substituents (Table 4.4). Simple alkyl chains, including an α-branched *i*-Pr and a CF_3 group, were well tolerated (alcohols **4.5–4.7**; s = 32–110), as were a range of *N* substituents, including benzyl, allyl, and *tert*-butoxycarbonyl (Boc) groups (alcohols **4.8–4.10**; s = 26–110). Alcohols **4.9** and **4.10**, bearing Lewis basic amide and nitrile substituents, which could potentially act as competitive recognition motifs, were also resolved with good selectivity (s = 26 and 30). Nitrile-containing 3-hydroxyoxindole derivatives, including **4.10**, are intermediates in the synthesis of bioactive pyrrolidinoindoline alkaloid natural products, such as CPC-1 and flustraminol B.[89] For the KR of this substrate, improved selectivity factors were obtained in the presence of isobutyric acid and without *i*-Pr_2NEt as a surrogate base. This effect can be attributed to suppression of a non-selective base-promoted background acylation, identified by control studies. Substitution around the benzenoid ring in every position with both electron-donating and -withdrawing groups was also tolerated but substitution in the 4-position led to reduced reactivity, presumably owing to increased steric hindrance. For the KR of **4.11**, a higher catalyst loading of 10 mol % was therefore required. A current limitation of this method is that exceptionally sterically hindered 3-*tert*-butyl-substituted derivatives are unreactive.

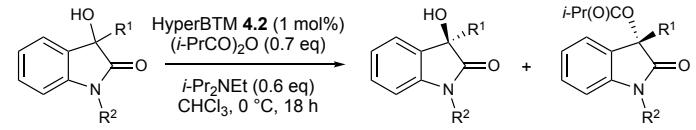
Table 4.4 Substrate scope with respect to 3-alkyl-3-hydroxyindole derivatives (sp^2 vs. sp^2 vs. sp^3).

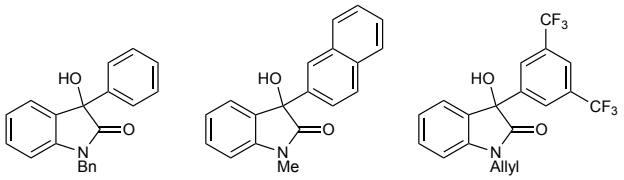


The developed method was next challenged in the KR of 3-aryl-substituted 3-hydroxyoxindole derivatives, in which all three carbinol substituents could act as competitive recognition motifs (two aryl π-systems and a carbonyl group; Table 4.5). Notably, these derivatives were resolved with excellent selectivity (*s* up to >200), indicating exceptional enantiodiscrimination by the isothiourea catalyst. The resolution of oxindole derivatives **4.14–4.17**, bearing phenyl, 2-naphthyl, and aryl groups with both electron-withdrawing and -donating substituents at the 3-position, proceeded with excellent selectivity (*s* = 60–200).[90] The resolution of 4-*N*,*N*-dimethylaminophenyl-substituted alcohol **4.18** enabled the isolation of highly enantiomerically enriched (*R*)-**4.18** (97:3 e.r.) at 49 % conversion; however, the isobutyric ester was obtained as a racemate (52:48 e.r.). This phenomenon was attributed to racemization of the ester by reversible ionization promoted by the presence of the electron-donating NMe_2 group. Various heteroaromatic

substituents were successfully incorporated, including furyl, benzoxazolyl, and Brønsted and Lewis basic 2- and 3-pyridyl groups (**4.29**–**4.22**, *s* = 15–70). The method was equally applicable to the KR of the 3-alkenyl-substituted 3-hydroxyoxindole derivatives **4.23**–**4.25**, in which the catalyst was again capable of differentiating between three potential recognition motifs at the carbinol stereocenter. Excellent *s* values were obtained in each case (*s* = 50–80); however, incorporation of an alkyne substituent at the tertiary alcohol center (sp^2 vs. sp^2 vs. sp) resulted in very low selectivity (*s* = 2).

Table 4.5 Substrate scope with respect to 3-aryl- and 3-alkenyl-3-hydroxyindole derivatives (sp^2 vs. sp^2 vs. sp^2).

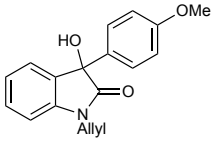




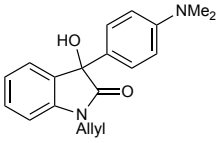
4.14; **c = 53**; ***s* = 120**
alc: >99:1 er; 41%
est: 95:5 er; 48%

4.15; **c = 51**; ***s* = 180**
alc: 99:1 er; 43%
est: 98:2 er; 32%

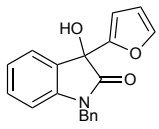
4.16; **c = 51**; ***s* = 60**
alc: 96:4 er; 43%
est: 95:5 er; 45%



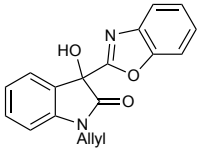
4.17; **c = 49**; ***s* = 200**
alc: 97:3 er; 50%
est: 98:2 er; 48%



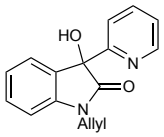
4.18; **c = 49**; ***s* > 200**
alc: 97:3 er; 47%
est: 52:48 er; 21%



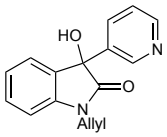
4.19; **c = 46**; ***s* = 70**
alc: 90:10 er; 45%
est: 97:3 er; 27%



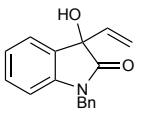
4.20; **c = 51**; ***s* = 15**
alc: 89:11 er; 43%
est: 87:13 er; 37%



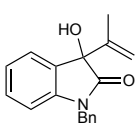
4.21; **c = 42**; ***s* = 60**
alc: 86:14 er; 50%
est: 96:4 er; 39%



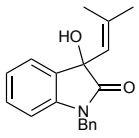
4.22; **c = 52**; ***s* = 70**
alc: 98:2 er; 42%
est: 94:6 er; 44%



4.23; **c = 53**; ***s* = 50**
alc: >99:1 er; 36%
est: 91:9 er; 48%



4.24; **c = 40**; ***s* = 80**
alc: 83:17 er; 60%
est: 98:2 er; 33%



4.25; **c = 44**; ***s* = 60**
alc: 87:13 er; 51%
est: 97:3 er; 40%

4.3.1 Computational methods

Computational studies on the KR of 3-methyl- and 3-phenyl-3-hydroxyoxindole derivatives **4.5** and **4.14** were used to further elucidate the mechanism and origin of enantiodiscrimination of this KR process. Geometry optimizations and single point energy refinements were completed using the Gaussian 09 computational package.[41] All pertinent points on the potential energy surfaces (ground state and/or transition state) were located with geometry optimizations using M06-2X[39]/6-31G(d)[40] with implicit solvent modelled with the polarized continuum model[43] (PCM) using the dielectric constant (ε = 4.7113) and universal force field[44] (UFF) radii of chloroform. Minima were confirmed with vibrational frequency computations, with ground state minima having zero imaginary vibrational frequencies and transition state minima having one imaginary frequency corresponding to the vibrational mode of the forming/breaking bond. Frequencies were computed at 1 atm and 273.15 K (0 °C) in order to match experimental reaction conditions as close as possible. Higher level single point energy refinements were computed with M06-2X/6-311++G(2df,p)[42] also in PCM (chloroform). Final corrected energies were the sum of the single point energy refinement and the Gibbs thermal correction factor of the respective optimized structure. All reported computed thermodynamics and barriers are derived from differences in the final corrected energies.

4.3.2 Brief mechanism and catalytic cycle

The computed intermediates and transition state structures relevant to alcohol **4.5** acylation are shown in Figure 4.6. Starting material **I** and ternary complex **II** are in equilibrium, with **(*S*)-II** (ΔG = 2.6 kcal/mol) and **(*R*)-II** (ΔG = 4.0 kcal/mol) rapidly exchanging between the two diastereomeric forms. Ternary complexes **II** are favored over binary complex **ion-pair** + **4.5** (ΔG = 13.6 kcal/mol), and significantly lower in energy than all three components infinitely separated (**S···O-*syn*** + **isobutyrate** + **4.5**, ΔG = 22.4 kcal/mol). These results suggest minimal formation of the acylated catalyst in the absence of alcohol. The inherent entropic penalty of bringing together these three components in a rigid complex is greatly

outweighed by stabilizing interactions between the alcohol group and the isobutyrate anion (through hydrogen bonding) and either the amide moiety or benzenoid ring of the alcohol substrate with the catalyst isothiouronium (through a C=O···isothiouronium interaction (Figures 4.8) for **(*S*)-II** and a π···isothiouronium interaction for **(*R*)-II**). These interactions persist throughout alcohol acylation and catalyst turnover (Figure 4.6, **II→TS-V**, Figure 4.7).

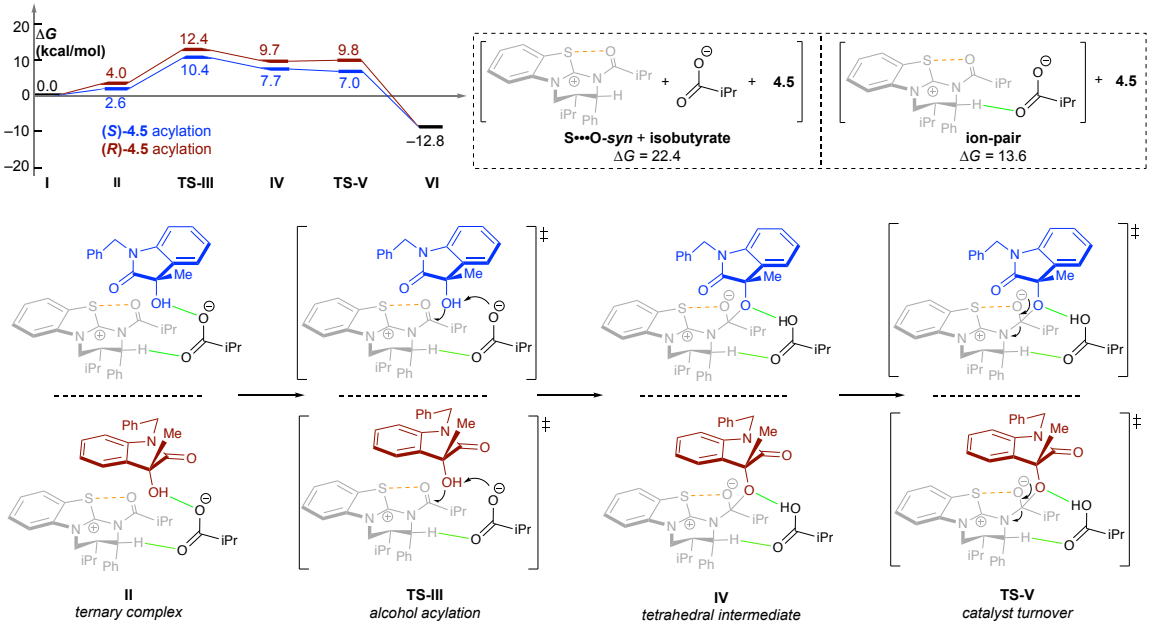


Figure 4.6 Computed reaction coordinate and structures for the acylation of alcohol **4.5** using isobutyric anhydride and HyperBTM **4.2** catalyst in the presence of *i*-Pr_2NEt base at 0 °C. Acylation of the fast reacting (*S*)-alcohol shown in blue. Acylation of the slow reacting (*R*)-alcohol shown in brown. The starting material (**I**, ΔG = 0.0) is composed of substrate **4.5**, catalyst **4.2**, isobutyric anhydride, and *i*-Pr_2NEt. The ΔG of ester product **VI** (ΔG = –12.8) also incorporates an infinitely separated ammonium···isobutyrate salt complex as a by-product.

The stereochemistry-determining acylation transition states and general mechanism in Figure 4.6 and Figure 4.7 were calculated following the established Lewis base promoted acylative pathway described by Zipse, Spivey, and co-workers.[91] Chelation by isobutyrate is critical; The isobutyrate counterion simultaneously deprotonates the alcohol and engages in a non-classical hydrogen bond to the catalyst $^{+}$NC–H group (green lines, Figure 4.6).[92] The lowest-energy diastereomeric transition state structures (TSs) for the acylation of the *S*

enantiomer (**(*S*)-TS-III**) and the *R* enantiomer (**(*R*)-TS-III**) of alcohol **4.5** (R^1 = Me) are shown in Figure 4.7. The predicted $\Delta\Delta G^{\ddagger}$ value of 2.0 kcal/mol for the KR of **4.5** is in good agreement with the experimental *s* value of 50 ($\Delta\Delta G^{\ddagger}$ = 2.1 kcal/mol).

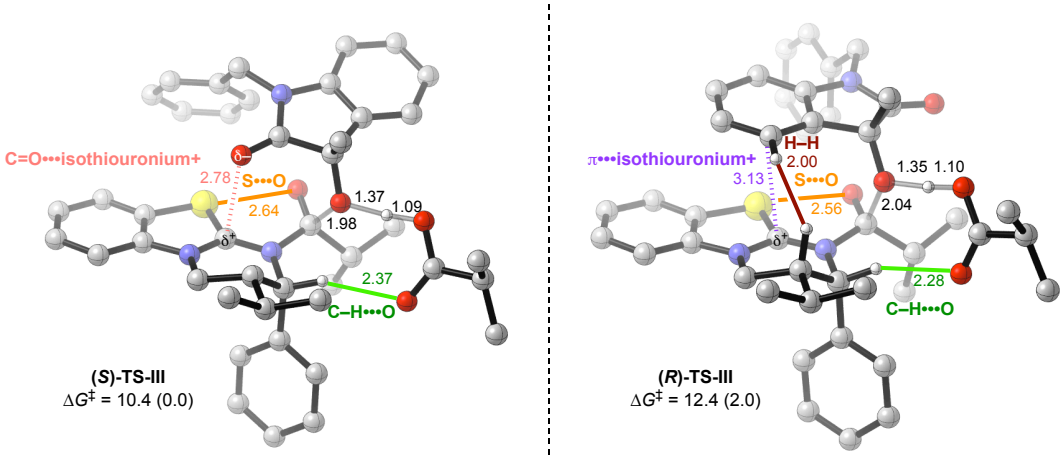


Figure 4.7 Computed stereodetermining transition states for the acylation of alcohol substrate **4.6** (R^1 = Me). Forming and breaking bonds shown in grey, non-bonding C–H···O and S···O interactions[20,21] shown in green and orange, respectively. Barrier from starting material **I** shown with the relative energy of the structures in parentheses. The critical interactions that impart selectivity are a C=O···isothiouronium found in **(*S*)-TS-III** interaction (pink) and a π···isothiouronium (purple) seen in **(*R*)-TS-III**.

4.3.3 Isothiouronium interaction

The diastereomeric TSs for the acylation of both enantiomers of the alcohol share the S···O interaction and the two-point isobutyrate binding. Furthermore, the acylated HyperBTM catalyst displays partial carbocationic character at the central carbon of the isothiourea, and this moiety is denoted as an "isothiouronium" when the catalyst is acylated and overall positively charged. The high selectivity of this resolution is then a result of effective discrimination between the three carbinol center substituents in terms of their ability to stabilize the partial carbocation character within the heavily preorganized acylated HyperBTM. In **(*S*)-TS-III**, the substrate carbonyl group is in close proximity to the isothiouronium carbon atom. In contrast, the critical stabilizing interaction in the disfavored **(*R*)-TS-III** is a π···isothiouronium interaction involving the substrate benzenoid ring. It is hypothesized that the comparative stabilizing ability of the amide C–O and the

benzenoid aromatic ring ultimately leads to selectivity given that all other components of **(*S*)-TS-III** and **(*R*)-TS-III** are geometrically equivalent.

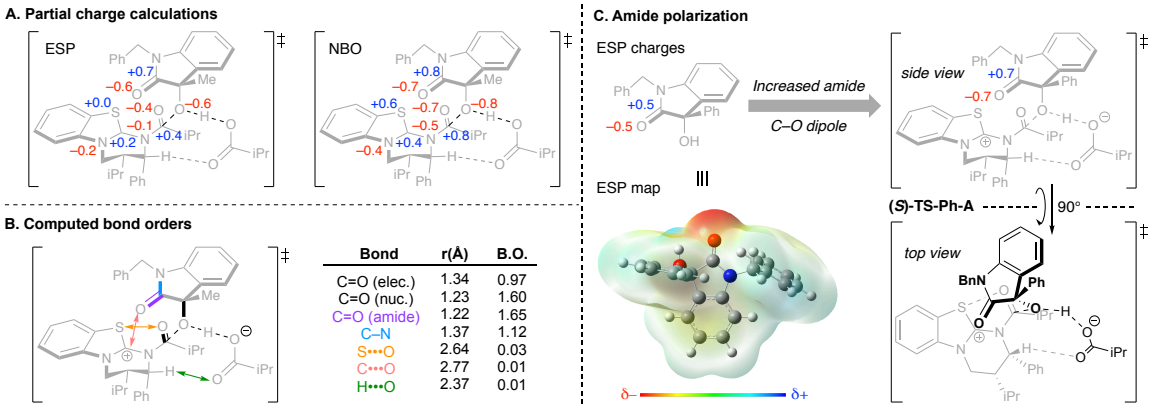


Figure 4.8 Charge and bonding analysis of **(*S*)-TS-III** and **(*S*)-TS-Ph-A**. (a) Pertinent computed partial electrostatic potential (ESP) and natural bond order (NBO) partial charges for **(*S*)-TS-III**. Values rounded to one decimal place for clarity. (b) Computed interatomic distances (Å) and Wiberg bond indices as a measure of bonding order (B. O.) for **(*S*)-TS-III**. Bond orders rounded to two decimal places for clarity. (c) Computed ESP partial charge calculations of the amide C–O bond in substrate **4.14** and **(*S*)-TS-Ph-A**. The ESP mapped on total electron density for **4.14** is also shown.

Both electrostatic potential (ESP) and natural bond order[93] (NBO) partial charge calculations give the central isothiourea carbon a small positive charge (Figure 4.8a, +0.2 and +0.4, respectively). The ESP partial charges show each nitrogen bearing a partial negative charge, and the S atom as neutral. NBO gives slightly different charges, showing a significant partial positive on the sulfur atom (+0.6) and maintaining partial negative charges on the nitrogen atoms. Taken together, the ESP and NBO partial charges are in qualitative agreement. Any interaction between the amide dipole of the alcohol substrate and the isothiouronium is considered primarily as an electrostatic attraction on the basis of the computed partial charges in combination with the computed Wiberg bond indices[94] (Figure 4.8b), which indicates very little bonding character between the amide O atom and the isothiouronium C atom (0.01). For comparison, the C–O bond of the alcohol has a bond index of 0.97, and the C–O bond of the electrophilic acyl group has a bond index of 1.60. Furthermore, computed ESP maps and partial charges of substrate **4.14** (Figure 4.8c, R^1 = Ph) also show an increase in magnitude of the amide O atom negative charge in going from

substrate to the acylation TS (–0.5 in substrate **4.14** vs. –0.7 in **(*S*)-TS-Ph-A**), suggesting polarization of the oxygen atom when in vicinity to the isothiouronium positive charge. Computed partial charges of the amide C atom suggest not only polarization of the O atom, but also the entire amide C=O moiety (C = +0.5 in **4.14** vs. C = +0.7 in **(*S*)-TS-Ph-A**), indicating that close contact with the positively charged catalyst increases the magnitude of the amide dipole.

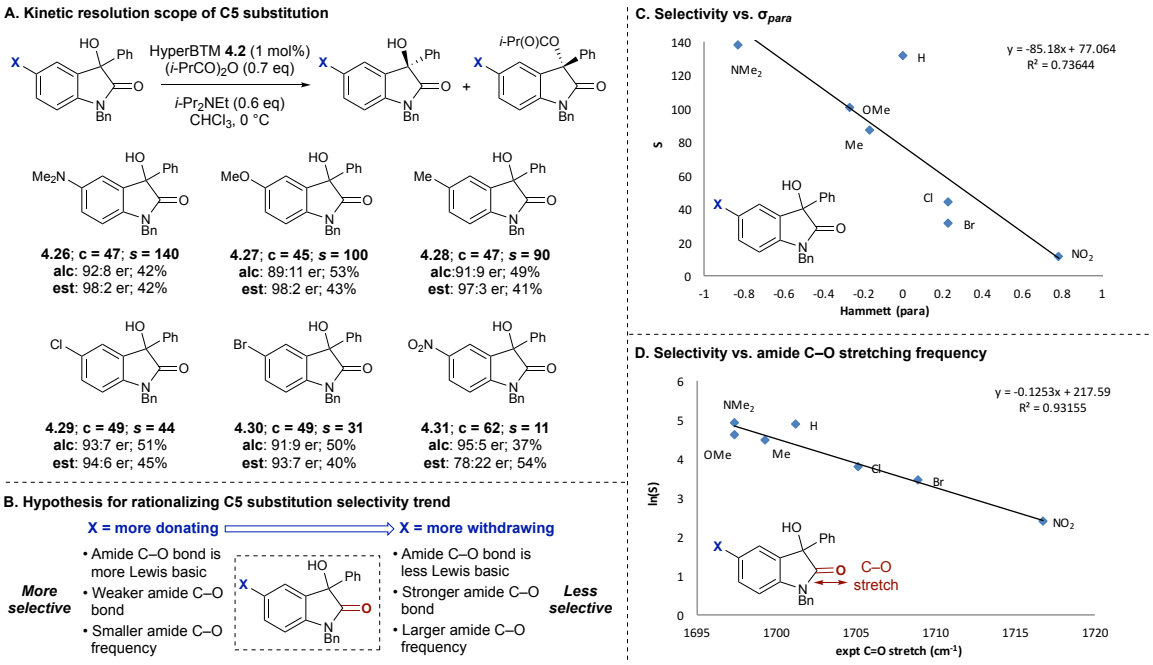


Figure 4.9 (a) Effect of the C5 substituent on selectivity. (b) Proposed rationalization for the observed increased selectivity using electron-donating functional groups in the C5 position. **(**c) Plot of selectivity (*s*) versus Hammett *para*-σ constants[95] for 5-substituted analogues **4.26-4.31** and **4.14** (X = H)**.** (d) For substrates, **4.14**, **4.26-4.31** the natural logarithm of the *s* factor as a function of the experimental amide C–O stretching mode yields a linear correlation. Overall, selectivity shows a higher correlation with the C–O stretching mode ($R^2 = 0.93$) compared to *para*-Hammett values ($R^2 = 0.74$).

The nature of the C=O···isothiouronium interaction suggests that modulation of the electron density of the amide O atom should affect the strength of the interaction. The computed alcohol acylation TSs reveal the presence of this interaction only in the most stable acylation TS of the *(S)*-alcohol, implicating this interaction as crucial for stereodiscrimination. To investigate this hypothesis, a series of 3-phenyl-3-hydroxylindole derivatives **4.26-4.31** was prepared with electronically differentiated substituents at the 5-

position (Figure 4.9a). Groups which donate electron density (NMe_2, OMe, Me) all gave excellent selectivity, while Cl, Br, and NO_2 led to lower selectivity ($s < 45$).

Substitution of the substrate benzenoid ring in the 5-position has a direct effect on the electron density of the amide O atom due to *para* conjugation between the 5-substituent and the amide nitrogen. Additionally, the computed TSs for acylation of both the *(S)*- and *(R)*-alcohol show this position as having minimal steric contact with the catalyst and carboxylate counterion, suggesting that any trend in selectivity displayed by substitution at the 5-position is likely an electronic effect (Figure 4.9b). Substitution of the benzenoid ring in the 5-position with an electron-donating group increases conjugation of the amide nitrogen lone pair into the amide C–O, thus weakening the C–O bond (resulting in lower C–O stretching frequency) and increasing electron density on oxygen (which in turn should enhance the C=O···isothiouronium interaction). We therefore proposed that selectivity should correlate well with both Hammett values and the magnitude of substrate amide C–O IR stretch frequency.[96] Hammett analysis of the 5-substituted alcohols **4.14**, **4.26-4.31**, bearing both electron-donating and electron-withdrawing groups, showed moderate correlation between the *s* factor and σ_{para} ($R^2 = 0.74$, Figure 4.9c). The experimental C–O stretching frequencies show good exponential correlation found between *s* factor and C–O stretching frequency ($R^2 = 0.93$, Figure 4.9d). This trend in selectivity is consistent with the ability of the amide of the fast-reacting enantiomer to engage in a TS-stabilizing C=O···isothiouronium interaction.

4.3.4 Conformational analysis

The formation of complex **II** is fundamental to the selectivity of the kinetic resolution. Once this complex forms, the conformation of the core oxindole alcohol structure is essentially "locked in" as the reaction proceeds through acylation (**TS-III**) and catalyst turnover (**TS-V**). Because of the rigidity of **II**, any critical non-bonding interactions identified in **II** are conserved throughout the forward direction of the reaction until the complex is broken apart with turnover allowing the start of a new catalytic cycle. The convenient result is that a thorough and comprehensive conformational search of any of

the species **II**, **TS-III**, **IV** or **TS-V** provides accurate information on the conformational space of all four structures.

We began by probing the low-energy conformations of **(*S*)-TS-III** ($\Delta G^{\ddagger}$ = 10.4 kcal/mol), with the twelve lowest energy conformers shown in Figure 4.10. All other conformers are greater than 7 kcal/mol higher in energy than **(*S*)-TS-III**, with the exception of **(*S*)-TS-III-A** that lies only 0.5 kcal/mol higher in energy ($\Delta G^{\ddagger}$ = 10.9 kcal/mol), and is acquired by rotating the amide NBn group in **(*S*)-TS-III** such that it points away from the catalyst. The lowest energy TS in which acylation occurs to the *re*-face of the acyl group is **(*S*)-TS-III-B**, which is prohibitively disfavored ($\Delta G^{\ddagger}$ = 18.3 kcal/mol). **(*S*)-TS-III-C**, **(*S*)-TS-III-F**, and **(*S*)-TS-III-G** all proceed with alcohol attack on the *re*-face, and represent small conformational changes such as rotation of the isobutyrate *i*-Pr and amide NBn groups relative to **(*S*)-TS-III-B**. The remainder of the conformers show alcohol attack on the *si*-face, but do not contain the C=O···isothiouronium interaction. In **(*S*)-TS-III-D** and **(*S*)-TS-III-H**, the amide group points toward the equatorial HyperBTM *i*-Pr group, effectively replacing the amide-isothiouronium interaction with multiple non-bonding C–H···O interactions. We gain information on the mode of isobutyrate anion binding through structures such as **(*S*)-TS-III-I**, where the isobutyrate carboxylate moiety acts as the donor when interacting with the catalyst isothiouronium, displacing the amide away from the catalyst entirely. The isobutyrate-catalyst interaction seen in **(*S*)-TS-III-I** appears to be much weaker (C–O distance = 2.89 Å) than the C=O-catalyst interaction found in **(*S*)-TS-III** (C–O distance = 2.77 Å).

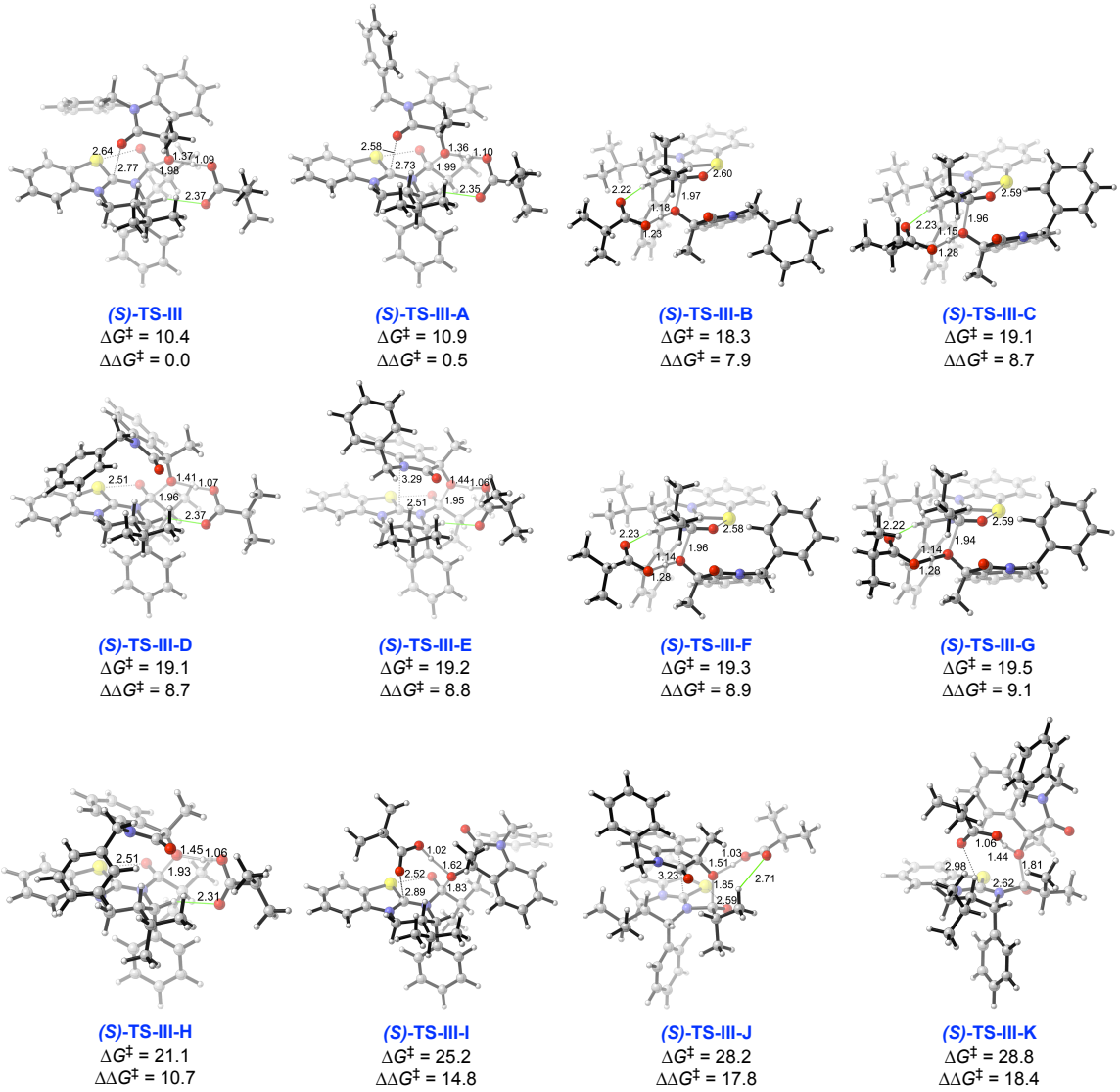


Figure 4.10 The twelve lowest energy computed TS for acylation of the fast reacting *(S)*-alcohol.

The conclusions of probing the conformational space of acylation TSs involving the (*S*)-enantiomer of the alcohol can be applied to that of the TSs involving the (*R*)-enantiomer (Figure 4.11). The critical interaction in **(*R*)-TS-III** ($\Delta G^{\ddagger}$ = 12.4 kcal/mol) is a cation-π between the benzenoid ring and the planar isothiouronium catalyst. All conformations which disrupt this interaction are disfavored. Figure 4.11 shows the four lowest energy conformations for TSs for the acylation of the (*R*)-enantiomer of the alcohol. As seen with the acylation of the (*S*)-enantiomer, the next highest energy conformer is **(*R*)-TS-III-A**

($\Delta G^{\ddagger}$ = 14.7 kcal/mol), a result of rotation of the amide NBn moiety from its lower energy conformation in **(*R*)-TS-III**. In **(*R*)-TS-III-C** ($\Delta G^{\ddagger}$ = 31.9 kcal/mol) acylation takes places on the *re*-face of the acyl group, yet the attack remains *anti* to the catalyst stereodirecting groups. This is achieved as the acyl group rotates away from the catalyst S atom, thus breaking the S···O nonbonding interaction between the catalyst and the acyl group. Such a conformation also has the result of displacing the isobutyrate outside the catalyst, where it can engage in a weak S···O interaction (S–O distance = 2.79 Å) while simultaneously deprotonating the alcohol.

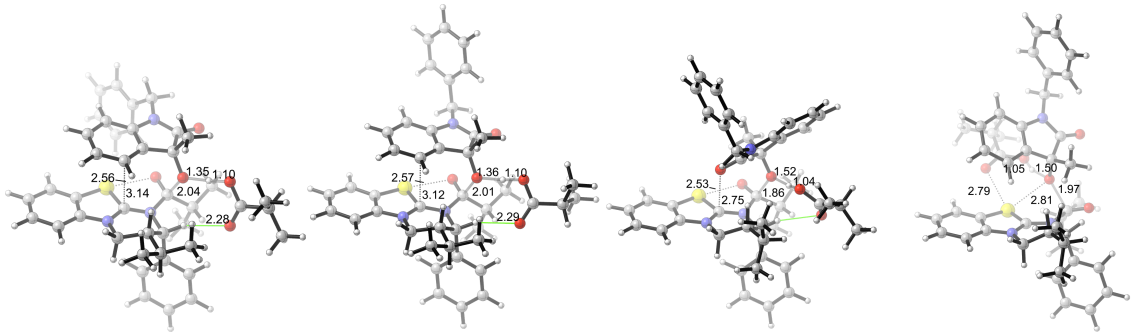


Figure 4.11 The twelve lowest energy computed TS for the acylation of the slow reacting *(R)*-alcohol.

Perhaps the most enlightening conformers are **(*S*)-TS-III-E** ($\Delta G^{\ddagger}$ = 19.2 kcal/mol) and **(*R*)-TS-III-B** ($\Delta G^{\ddagger}$ = 21.7 kcal/mol). These structures represent acylation TSs with the "opposite" critical interaction. **(*S*)-TS-III-E** sees the benzenoid ring engage in the same cation-π interaction as **(*R*)-TS-III** and **(*R*)-TS-III-B** contains the same C=O···isothiouronium interaction found in **(*S*)-TS-III**. Of particular interest is **(*R*)-TS-III-B**, which is over 9 kcal/mol higher in energy than **(*R*)-TS-III** even though the conformer contains a closer C=O···isothiouronium interaction (C–O distance = 2.53 Å) than **(*S*)-TS-III**. Analysis of these structures helps to elucidate the complex origins of selectivity in this reaction. While **(*R*)-TS-III-B** and **(*S*)-TS-III** share a similar C=O···isothiouronium interaction, the configuration of the alcohol stereocenter in **(*R*)-TS-III-B** places the bulky NBn group on the opposite side of the catalyst. The isobutyrate anion now rests below the oxindole ring structure rather than to the side as seen in **(*S*)-TS-III**. To accommodate the

location of the isobutyrate ion, the catalyst *i*-Pr is rotated to avoid disfavored steric interactions with the isobutyrate anion. This torsion results in slight distortion within the catalyst due to steric repulsion between the catalyst Ph and a methyl group of the catalyst *i*-Pr, which now reside within proximity to each other. These structures suggest that **(*S*)-TS-III** is the structure that best balances favorable steric and electronic requirements. It exhibits the C=O···isothiouronium interaction, but not at the cost of incurring additional energetic penalties through catalyst distortion and disruption of favorable non-bonding interactions.

4.3.5 Discrimination among three carbinol π-systems

Alcohol **4.14** (R^1 = Ph) provides an ideal theoretical case study of the how the different groups composing the tertiary alcohol interact with the catalyst in the alcohol acylation TS. Since all three functional groups bound to the tertiary carbon bear π systems, all three groups could potentially serve as stabilizing donors when in close proximity to the planar catalyst isothiouronium moiety. With the S···O interaction and isobutyrate two-point binding in place, the difference in energy ($\Delta\Delta G^{\ddagger}$) between the acylation TSs for the (*S*)- and (*R*)- enantiomers of the alcohol is a direct result of the catalyst discriminating between the three groups as a function of their ability to stabilize the catalyst positive charge (Figure 4.12). The three possible donors are: (A) amide C=O (B) benzenoid ring carbon (C) R^1 = Ph ring. For acylation of the (*S*)-enantiomer of the alcohol, the lowest energy conformer is **(*S*)-TS-Ph-A** (Figure 4.13, $\Delta G^{\ddagger}$ = 10.9 kcal/mol) which displays the C=O···isothiouronium interaction, consistent with the acylation TS for the (*S*)-enantiomer of alcohol **4.5** (R^1 = Me). The next lowest energy conformer **(*S*)-TS-Ph-B** ($\Delta G^{\ddagger}$ = 19.5 kcal/mol) contains the benzenoid π-cation interaction, followed by the conformer with a π-cation interaction between the carbinol Ph and the catalyst (**(*S*)-TS-Ph-C**, $\Delta G^{\ddagger}$ = 22.8 kcal/mol).

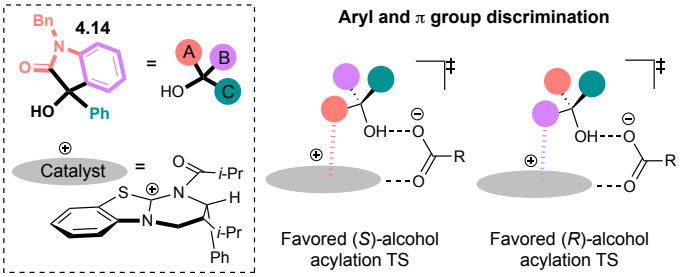


Figure 4.12 The three groups of the tertiary alcohol are discriminated based on their ability to stabilize the positively-charged acylated catalyst.

The lowest energy TS for the acylation of the (*R*)-enantiomer of the alcohol is **(*R*)-TS-Ph-B** ($\Delta G^{\ddagger}$ = 14.4 kcal/mol). This TS contains the same stabilizing benzenoid π-cation interaction observed for the acylation of the (*R*)-enantiomer of the alcohol when R^1 = Me, R^3 = Bn. The next lowest energy TS is **(*R*)-TS-Ph-C** ($\Delta G^{\ddagger}$ = 17.8 kcal/mol), which contains a stabilizing π-cation interaction between the R^1 = Ph and the catalyst. **(*S*)-TS-Ph-C** and **(*R*)-TS-Ph-C** differ in energy by 5 kcal/mol in favor of **(*R*)-TS-Ph-C**. In **(*S*)-TS-Ph-C**, the amide carbonyl group points to the transferring carbonyl, away from possible C-H···O interactions found between the amide carbonyl and the catalyst in **(*R*)-TS-Ph-C**.

The lowest energy TSs found for the acylation of the (*S*)- and (*R*)-enantiomers of the alcohol (R^1 = Ph, R^3 = Bn) are consistent with the lowest energy TSs found when R^1 = Me, R^3 = Bn. For both alcohols, the TS for the acylation of the (*S*)-enantiomer involves a stabilizing C=O···isothiouronium interaction, and the TS for the acylation of the (*R*)-enantiomer involves a stabilizing π···isothiouronium interaction. For the acylation of the alcohol where R^1 = Ph, R^3 = Bn, the computed selectivity of 3.5 kcal/mol between **(*S*)-TS-Ph-A** and **(*R*)-TS-Ph-B** slightly overestimates the experimental selectivity of 2.6 kcal/mol, but is in good agreement with the experimental trend of R^1 = Ph showing higher selectivity than R^1 = Me.

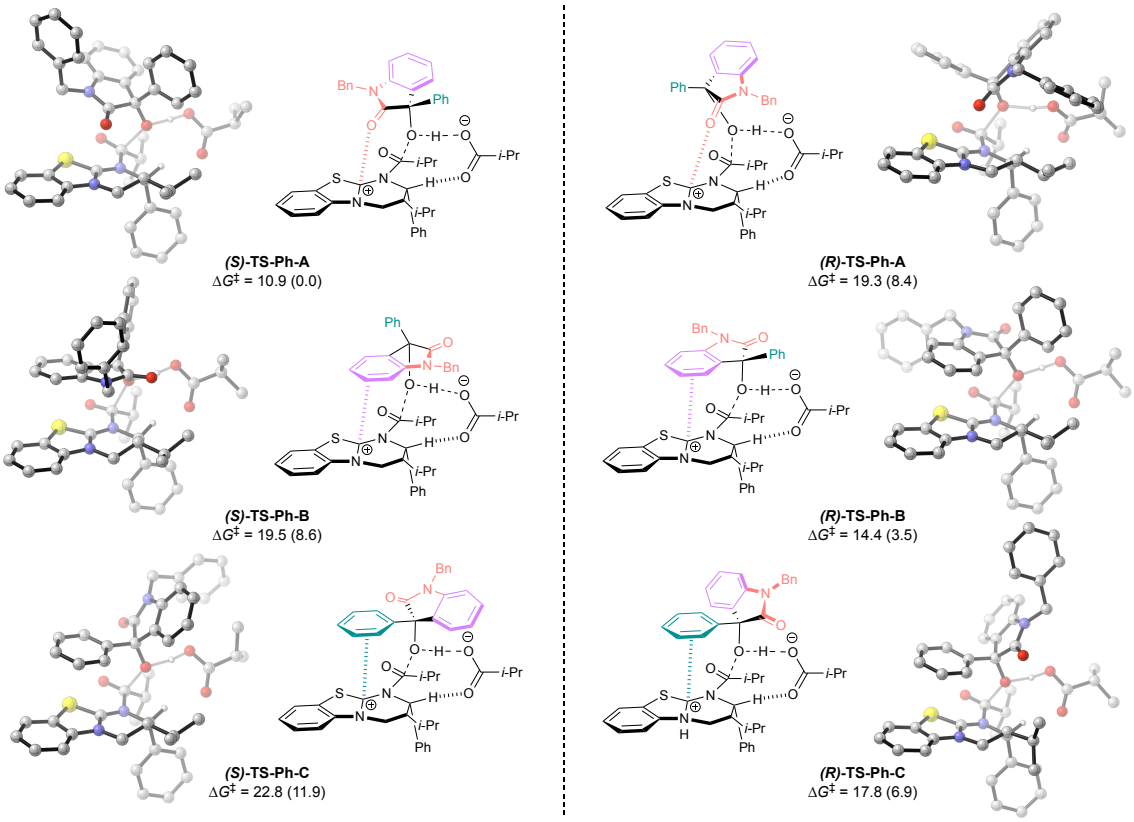


Figure 4.13 Computed acylation transition states for alcohol **4.14**. Acylation of the fast-reacting **(*S*)-4.14** shown on the left, and TSs for the slow-reacting **(*R*)-4.14** on the right.

4.3.6 Alternate acylation mechanisms

Four alternative mechanisms to Lewis base catalysis were considered as plausible pathways for the acylation reaction (Figure 4.14), all of which are eliminated as viable mechanisms on the basis of their unreasonably high computed barriers. A stepwise mechanism was initially envisioned, with alcohol deprotonation occurring prior to alkoxide attack on the acylated HyperBTM (**(*S*)-TS-alkoxide-attack** ($\Delta G^{\ddagger}$ = 30.1 kcal/mol)). Without the carboxylate chelation, the barrier is computed as far above the estimated 21 kcal/mol barrier at 0 °C, highlighting the role of the two-point binding motif of the isobutyrate has in catalysis. We next postulated HyperBTM acting as a Brønsted base, and not a Lewis base catalyst. In such a TS, HyperBTM deprotonates the alcohol concomitant to acylation (**(*S*)-TS-HBTM-base-catalysis** ($\Delta G^{\ddagger}$ = 24.3 kcal/mol)). In a similar fashion, Brønsted base catalysis with *i*-Pr_2NEt was also considered, yielding a very disfavored TS

(**TS-amine-base-catalysis** ($\Delta G^{\ddagger}$ = 36.6 kcal/mol)). Finally, the uncatalyzed acylation (**TS-uncatalyzed** ($\Delta G^{\ddagger}$ = 30.1 kcal/mol)) is computed as 6.5 kcal/mol lower than **TS-amine-base-catalysis**. This is likely due to **TS-uncatalyzed** being concerted – acylation takes place simultaneously to isobutyrate release and carboxylate deprotonation of the alcohol substrate. In light of the high computed barriers of all alternative acylation mechanisms, HyperBTM acylation prior to acyl transfer remains the favored pathway.

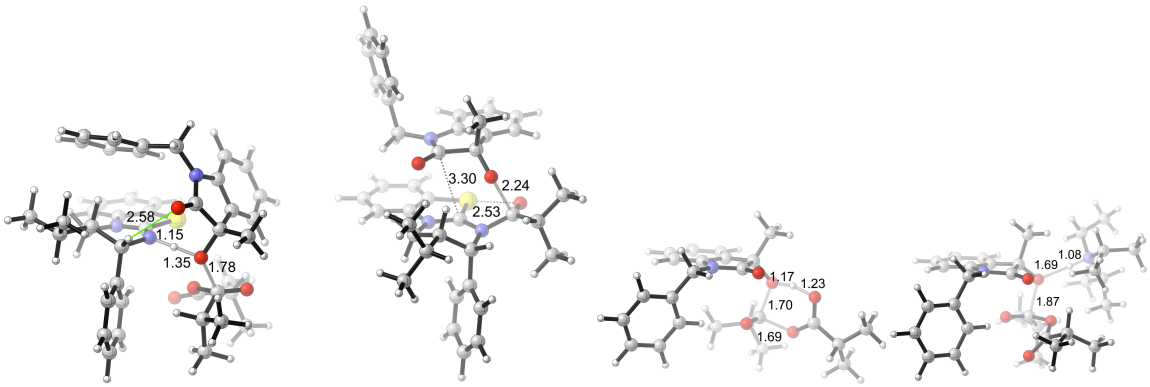


Figure 4.14 Additional mechanisms for acylation of alcohol **4.5.**

4.4 Conclusion

In conclusion, a C=O···isothiouronium interaction has been identified as the key recognition motif that leads to efficient enantiodiscrimination in the KR of a number of heterocyclic tertiary alcohols. By exploiting this interaction, a combination of isothiourea catalyst HyperBTM **4.2** (generally 1 mol %) and either isobutyric or acetic anhydride enables the KR of a range of heterocyclic tertiary alcohols with excellent selectivity (38 examples, *s* factors up to >200). Significantly, the substrate scope includes tertiary alcohol substrates that contain up to three recognition motifs at the stereogenic tertiary carbinol center. The interactions identified as a requirement for selectivity in this KR process should be readily applicable to other enantioselective transformations, and work is currently underway to exploit these in alternative catalytic processes.

4.5 Acknowledgements

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Chapter 5.

Catalyst Selective and Regiodivergent *O*- to *C*- or *N*-Carboxyl Transfer of Pyrazolyl Carbonates: Synthetic and Computational Studies

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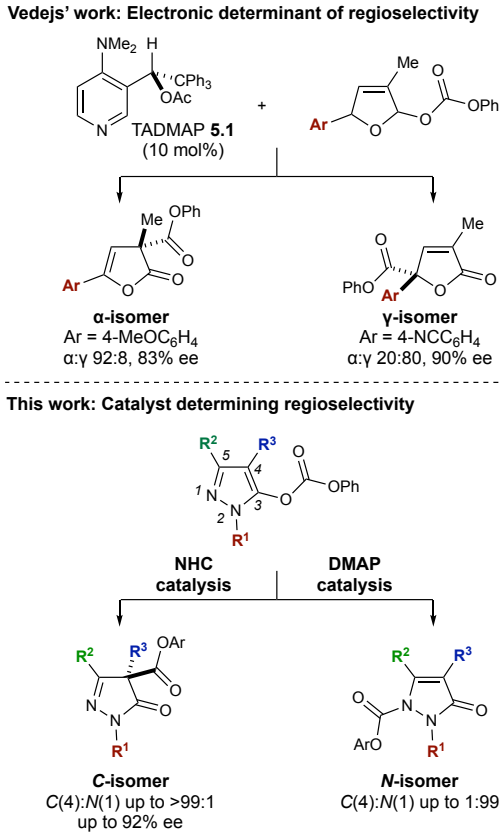
5.1 Abstract

The regiodivergent *O*- to *C*- or *N*-carboxyl transfer of pyrazolyl carbonates is described, with DMAP giving preferential *N*-carboxylation and triazolinylidenes promoting selective *C*-carboxylation (both with up to > 99:1 regioselectivity). An enantioselective *O*- to *C*-carboxyl variant using NHC catalysis is demonstrated (up to 92% ee), while mechanistic and DFT studies outline the pathways operative in this system and provide insight into the reasons for the observed selectivity.

5.2 Introduction

The organocatalyzed rearrangement of oxazolyl carbonates to the corresponding 4- or 2-carboxyazlactones was first described by Steglich and Höfle over forty years ago.[97] This reaction process has since attracted considerable attention thanks to its potential to generate synthetically useful α,α-disubstituted α-amino acid derivatives and is often regarded as a benchmark for the evaluation of Lewis base-catalyzed reaction processes. Initially promoted by the achiral Lewis bases 4-dimethylaminopyridine (DMAP) or 4-pyrrolidinopyridine (PPY), the groups of Fu,[98] Vedejs,[99] Richards[100]and Gotor[101] have shown that chiral DMAP or PPY derivatives can induce high enantiocontrol in this reaction process.[102] Alternative chiral Lewis base catalysts that have been applied to this enantioselective rearrangement include chiral phosphines by Vedejs, asymmetric imidazoles by Zhang,[103] and a variety of isothioureas by Gröger (acyl transfer),[104] Smith[105] and Okamoto.[106] A dual-catalytic approach that utilizes DMAP and a chiral thiourea has been demonstrated by Seidel,[107] while an ammonium betaine catalyst for this process has been utilized by Ooi.[108] Within this area we have previously shown that *N*-heterocyclic carbenes (NHCs) are versatile catalysts for the racemic Steglich rearrangement of oxazolyl carbonates.[109] Achiral triazolinylidenes promote this rearrangement process with low catalyst loadings and offer access to sterically hindered products, although chiral NHCs resulted in only modest enantiocontrol.

Scheme 5.1 Lewis base promoted regiodivergent and enantioselective *O*- to *C*- or *N*-carboxyl transfer of pyrazolyl carbonates.



The potential of this strategy to access stereodefined products with a quaternary stereogenic center has seen this process extended to incorporate the asymmetric rearrangement of furanyl, indolyl and benzofuranyl carbonates,[110] alongside applications in total synthesis.[111] Notably, Vedejs *et al.* have investigated the regio- and enantioselective *O*- to *C*-carboxyl transfer of 5-arylfuranyl carbonates using TADMAP **5.1**,[112] with the regioselectivity dependent upon the electronic nature of the 5-aryl substituent (Scheme 5.1). Electron-donating aryl substituents favor α-functionalization (α:γ up to 92:8), while an electron-withdrawing substituent favors γ-functionalization (α:γ up to 20:80). Building upon these precedents, we considered alternative molecular scaffolds upon which to investigate *catalyst selective* regio- and enantioselective *O*-to *C*-carboxyl transfer processes.[113] While originally exploited in the dyeing and photographic industries, pyrazolinones and their derivatives have displayed a wide range of medicinal and

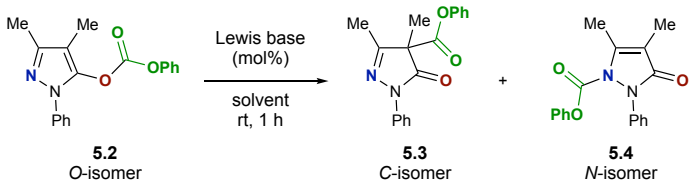
pharmacological activities such as analgesic[114] and antipyretic properties,[115] anti-inflammatory,[116] anti-tumor,[117] anti-microbial,[118] anti-retroviral[119] as well as anti-ischemic effects[120] and neuroprotective properties.[121] These diverse applications have encouraged recent interest in novel synthetic methods to access enantioenriched pyrazolinones[122] and served as inspiration for our studies concerning the regio- and enantioselective *O*- to *C*-carboxyl transfer of pyrazolyl carbonates. Notably, triazolinylidene NHCs promote the rearrangement to generate *C*(4)-α,α-disubstituted pyrazolinones with high regioselectivity (up to >99:1 C:N) and in up to 92% ee, while catalytic DMAP gives *N*(1)-carboxyl pyrazolinones with high regioselectivity (up to 1:99 *C*:*N*). A mechanistic rationale for this observed selectivity is provided by computational studies on a representative model system.

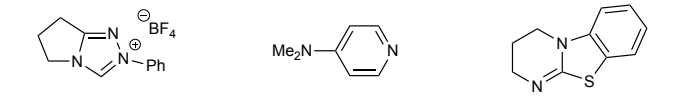
5.3 Model Studies: Catalyst Selective *O*- to *C*- or *N*-Carboxyl Transfer

Initial studies screened a range of Lewis base catalysts for their ability to promote the regioselective *O*- to *C*- or *N*-carboxyl transfer of a model *N*(2)-phenyl substituted pyrazolyl carbonate **2** that was readily prepared from commercially available materials (Table 5.2). In all cases, generation of the parent pyrazolinone as a side-product amounted to typically ~5% of the crude reaction product mixture, so only a ratio of *C*- to *N*-regioisomeric products is given unless stated. Treatment of **5.2** with an NHC catalyst (generated *in situ* by deprotonation of the triazolium salt **5.5** with KHMDS) in THF gave the *C*-regioisomer **5.3** with high selectivity (>99:1 *C*:*N*), isolated in 44% yield (entry 1). Further optimization showed that this NHC-promoted transformation could be performed using lower catalyst loadings in toluene (entries 2–4) while still giving **5.3** with excellent regioselectivity (>99:1 *C*:*N*). Remarkably, the use of DMAP in CH_2Cl_2 favored *N*-carboxylation with high regioselectivity (7:93 *C*:*N*), giving **5.4** in 56% yield (entry 5). The regiochemistry of this carboxyl transfer was confirmed by X-ray crystal structure analysis of *N*-carboxylate **4**. Rearrangement with isothiourea DHPB also favored the *N*-carboxyl regioisomer but with lower reactivity compared to DMAP (entry 6). Further investigation of the DMAP-promoted reaction showed that THF and toluene proved poor solvents for this process, giving only ~25% conversion to product with modest *C*:*N* ratios (entries 7 and

8). These results indicate that catalyst promoted regiodivergent selectivity is observed in this process under either NHC or DMAP catalysis.

Table 5.2 Model studies for Lewis base catalyst selective carboxyl transfer.





5.5 DMAP DHPB

Entry	Lewis base (mol %)	Solvent	Conversion[a]	*C*:*N*
1	Precat **5.5** (20)[b]	THF	>95	>99:1[c]
2	Precat **5.5** (10)	Toluene	>95	99:1
3	Precat **5.5** (5)	Toluene	>95	>99:1
4	Precat **5.5** (2)	Toluene	>95	99:1
5	**DMAP** (20)	CH_2Cl_2	73	7:93
6	**DHPB** (20)	CH_2Cl_2	66	9:91
7	**DMAP** (20)	Toluene	25	18:82
8	**DMAP** (20)	THF	25	23:77

[a]Reaction conversion and *C*:*N* product ratio established by ^{1}H NMR spectroscopic analysis of crude reaction mixture; [b]NHC generated by deprotonation with KHMDS; [c]17% parent pyrazolinone generated.

5.4 Mechanistic Investigations

With this rearrangement reaction producing two regioisomeric products, the possibility of product interconversion due to the reversibility of the C–C and C–N bond-forming processes was investigated on model *N*(2)-Me substrates **5.6** and **5.8** (Figure 5.3). First, *N*-carboxylate **5.6** (1:99 *C*:*N*) was resubmitted to both DMAP and NHC catalysis (Figure 5.3a). With DMAP, exclusively starting material was returned after overnight reaction, while treatment with an achiral NHC precatalyst **5.5** gave the *C*-regioisomer **5.8** (99 : 1 C : N). Furthermore, treatment of *N*-carboxylate **5.6** with the chiral NHC derived from precatalyst **5.7** gave 10% conversion to *C*-carboxylate **5.8** in 84% ee. However, while treatment of enantioenriched *C*-carboxylate **5.8** (87% ee) with either DMAP or chiral NHC **5.7** returned **5.8** exclusively (87% ee), treatment with the achiral NHC derived

from **5.5** gave *C*-carboxyl **5.8** in racemic form.[123] Treatment of (±)-*C*-carboxylate **5.8** with chiral NHC **5.7** also returned (±)-**5.8**.

These results, combined with a crossover experiment upon a mixture of *N*-carboxylate products,[124] indicate that *O*- to *C*- or *N*-carboxyl transfer reactions with DMAP are *irreversible* in this model system, with *N*-carboxylation kinetically preferred; *N*- to *C*-carboxyl transfer is disfavored with DMAP. With the achiral NHC derived from precatalyst **5.5**, *O*- to *C*- or *N*-carboxyl transfer reactions are *reversible*, with the *C*-isomer thermodynamically preferred, while *N*- to *C*-carboxyl transfer is also favored. However, with the chiral NHC, *O*- to *C*-carboxyl transfer is *irreversible* with high enantiocontrol, while *N*- to *C*-carboxyl transfer is also allowed with good enantiocontrol.

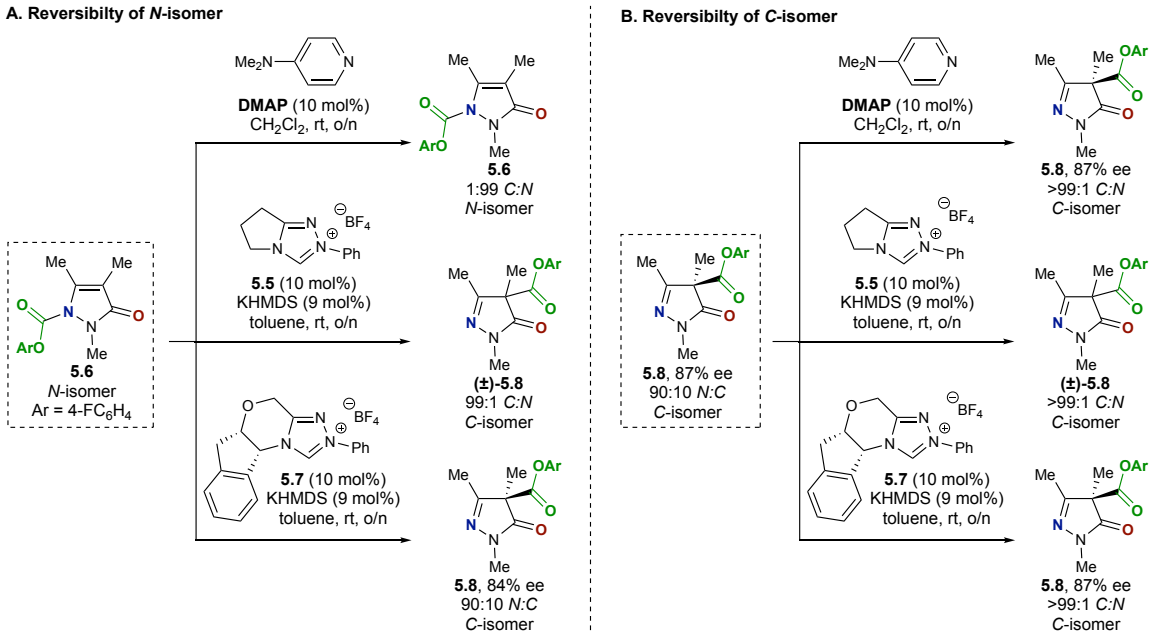


Figure 5.3 Probing the reversibility of rearrangement. (a) Re-treatment of *N*-carboxyl **5.6** with DMAP and NHCs derived from **5.5** and **5.7**. (b) Re-treatment of *C*-carboxyl **5.8** with DMAP and NHCs derived from **5.5** and **5.7**.

5.5 Computational Insight

5.5.1 Computational methods

Computations were next performed on a simplified model substrate to elucidate the mechanism and origins of the observed regioselectivity. We employed M06-2X[39]/6-31+G(d,p)[42]/PCM[43]//M06-2X/6-31G(d)[40]/PCM in toluene for NHC catalysis and dichloromethane for DMAP catalysis, as implemented in Gaussian09.[41] Manual, exhaustive conformational searches were performed to ensure all relevant intermediates and transition state structures (TSs) were located. Intrinsic reaction coordinate (IRC) computations were performed on all TSs to verify reaction pathways.

5.5.2 General mechanism and catalytic cycle

C- and *N*-carboxylations share the same general mechanism shown in Figure 5.4. Initial *O*-carboxylate attack by catalyst (**TS-II**) and subsequent tetrahedral intermediate collapse (**TS-IV**) leads to common intermediates, enolate **5.9** and carboxylated catalyst (**CO_2Me-Cat**). Regiodivergence occurs by recapture of carboxyl group by enolate **5.9** at either *C*(4)- or *N*(1)- (**TS-VI**). The dissociation of the catalyst from the resulting tetrahedral intermediate (**TS-VIII**) releases the final products (**IX**).

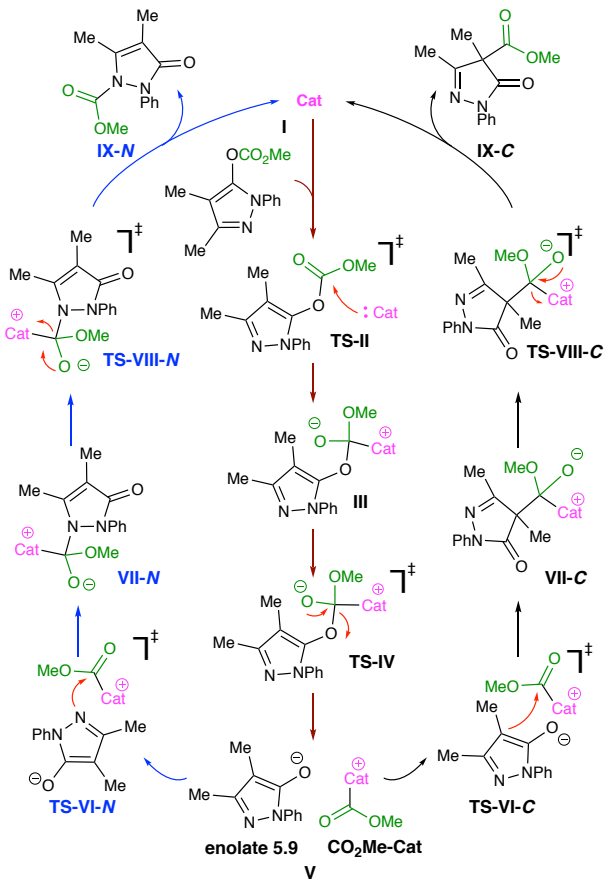


Figure 5.4 Detailed proposed mechanism for *C*- and *N*-carboxylation.

5.5.3 DMAP catalysis

The DMAP-mediated carboxyl transfer preferentially results in *N*-carboxylation. Shown in Figure 5.4, initial *O*-carboxylate attack (**TS-II**) by DMAP affords tetrahedral intermediate **III**, collapse of which (**TS-IV**, 20.4 kcal/mol) affords ion pair intermediate **V** (**CO_2Me-DMAP** and enolate **5.9**). The *C*- vs. *N*-regiocontrol is established when the substrate enolate **5.9** attacks the carboxylated DMAP either via *C*(4)- or *N*(1). Consistent with the experimental results, the *N*-carboxylation process is favored computationally by ~5 kcal/mol (**DMAP-TS-VI-*N***, $\Delta G^{\ddagger}$ = 21.9 kcal/mol vs. **DMAP-TS-VI-*C***, $\Delta G^{\ddagger}$ = 26.6 kcal/mol). Interestingly, the *N*-carboxylation is stepwise addition of enolate and extrusion of catalyst, whereas the *C*-carboxylation process (black, Figure 5.5) proceeds via a concerted, asynchronous carboxylation.[125] This difference in

concerted/stepwise behavior reflects the lack of electrostatic stabilizing effects in **DMAP-TS-VI-*C*** vs. **DMAP-TS-VI-*N***. In **DMAP-TS-VI-*N***, there is a substantial spatial overlap between the positively charged carboxylated DMAP and the attacking enolate **5.9**, as the enolate oxygen and π-bond is in closer proximity to the carboxylated DMAP. This is in contrast to **DMAP-TS-VI-*C***, where there is a relatively poor spatial overlap, with only the enolate oxygen in proximity to the positively charged DMAP ring.

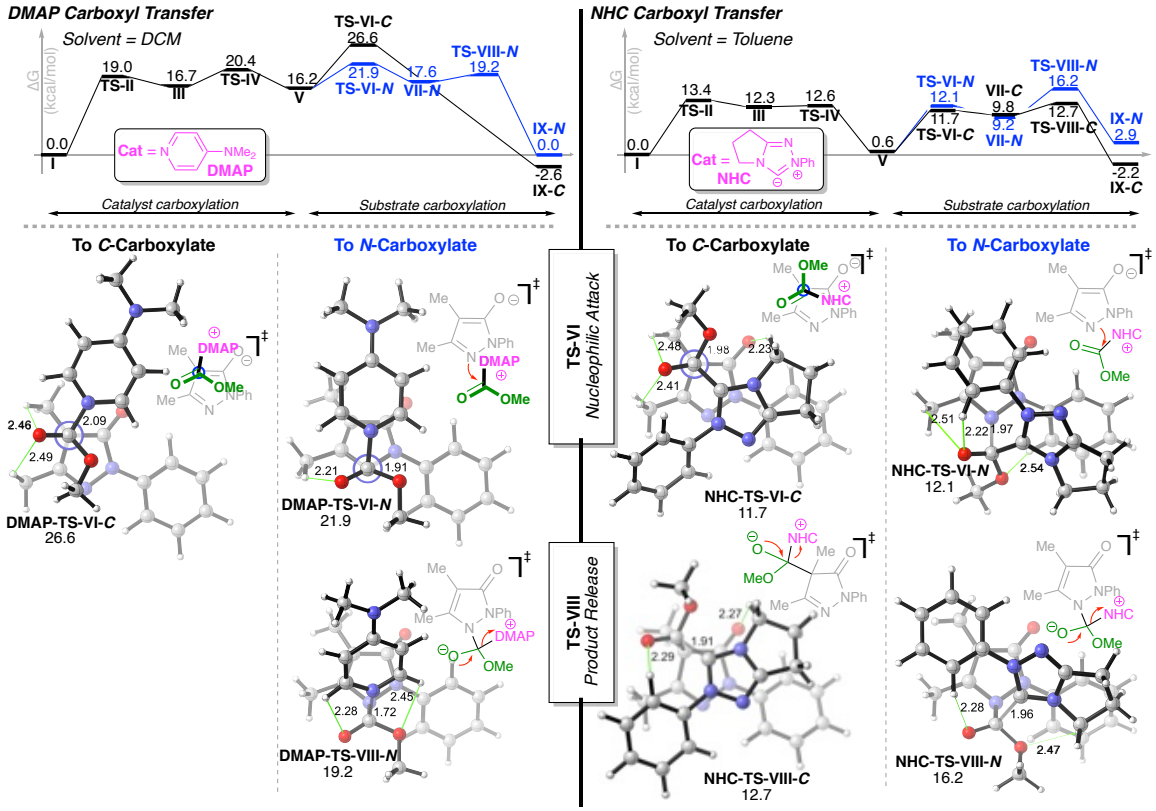


Figure 5.5 Reaction coordinate diagrams (top) and regioisomeric TSs (bottom) for DMAP-catalyzed (left) and NHC-catalyzed (right) carboxyl transfer from *O*-carboxylate (**I**) to *C*-carboxylate (black) and *N*-carboxylate (blue) products (**IX**).

5.5.4 NHC catalysis

NHC catalysis leads preferentially to *C*-carboxypyrazolinone product. NHC attack of the *O*-carboxylate substrate (**TS-II**, 13.4 kcal/mol) and subsequent collapse (**TS-IV**, 12.6 kcal/mol) of the tetrahedral intermediate (**III**, 12.3 kcal/mol) leads to ion pair intermediates **V** (**CO_2Me–NHC** and enolate **5.9**). The NHC favors the *C*-carboxylation

pathway by 3.5 kcal/mol (>99:1 *C*:*N*, **NHC-TS-VIII-*C*** and **NHC-TS-VIII-*N***), in agreement with experiments. This selectivity arises due to the large relative instability of **NHC-TS-VIII-*N***, where the close proximity of the enolate oxygen and the relatively negatively charged areas of the carboxylated NHC results in a destabilizing repulsive interaction. This is in contrast to **NHC-TS-VIII-*C***, where this repulsive interaction is replaced by stabilizing C–H···O hydrogen bonds between the NHC and the enolate **5.9**. The computed reaction coordinates corroborate the experimentally observed reversibility of the NHC-catalyzed process. NHC addition to the *N*-carboxylated product (**NHC-TS-VIII-*N***) is energetically accessible, with a reverse barrier of 13.3 kcal/mol (from **NHC-IX-*N***). The forward process leading to the *C*-carboxylation is favored by 2.6 kcal/mol over the forward process for the *N*-carboxylation (Figure 5.5), resulting in exclusive production of *C*-carboxylated product upon retreatment of *N*-carboxylated product with achiral NHC (as observed by experiment in Figure 5.3a).

5.5.5 Structural comparison of enolate π vs. σ reactivity

The remarkable switch in regioselectivity observed between DMAP and NHC catalysis in this system is a result of the markedly different reactivity patterns of the intermediate carboxylated DMAP or NHC and their interaction with the pyrazoline enolate as illustrated in Figure 5.5. This is most striking in **DMAP-TS-VI-*N***, where favored nucleophilic attack from the substrate does not originate from the *N*(1)-lone pair of the substrate enolate in the σ-plane, but rather the π-system of the extended enolate. This is in contrast to the analogous (disfavored) **NHC-TS-VI-*N***, where nucleophilic attack is predicted to occur from the *N*(1)-lone pair of the substrate enolate in the σ-plane. As yet, the exact origins of this π vs. σ reactivity are unknown. Our working hypothesis is that the relatively sterically unencumbered conjugated DMAP promotes π-π electrostatic interactions,[126] allowing the π-system of the extended enolate to be an energetically more competent nucleophile compared with the σ-*N*(1)-lone pair.

5.6 Conclusion

In conclusion, the regiodivergent *O*- to *C*- or *N*-carboxyl transfer of pyrazolyl carbonates has been investigated, with DMAP giving preferential *N*-carboxylation and triazolinylidenes promoting selective *C*-carboxylation (both with up to 99:1 regioselectivity). An enantioselective *O*- to *C*-carboxyl variant using NHC catalysis is demonstrated (up to 92% ee), while mechanistic and DFT studies outline the pathways operative in this system and delineate insight into the structural reasons for the observed selectivity. Current investigations from within our groups are focused upon the demonstration of further Lewis base-mediated organocatalytic transformations and developing further computational insight into these transformations.

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Chapter 6.

Formation of Aza-*ortho*-quinone Methides Under Room Temperature Conditions: Cs_2CO_3 Effect

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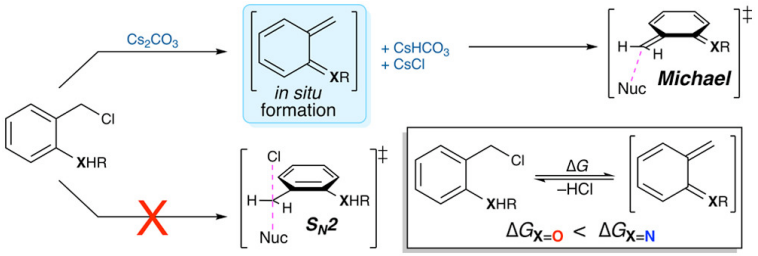
6.1 Abstract

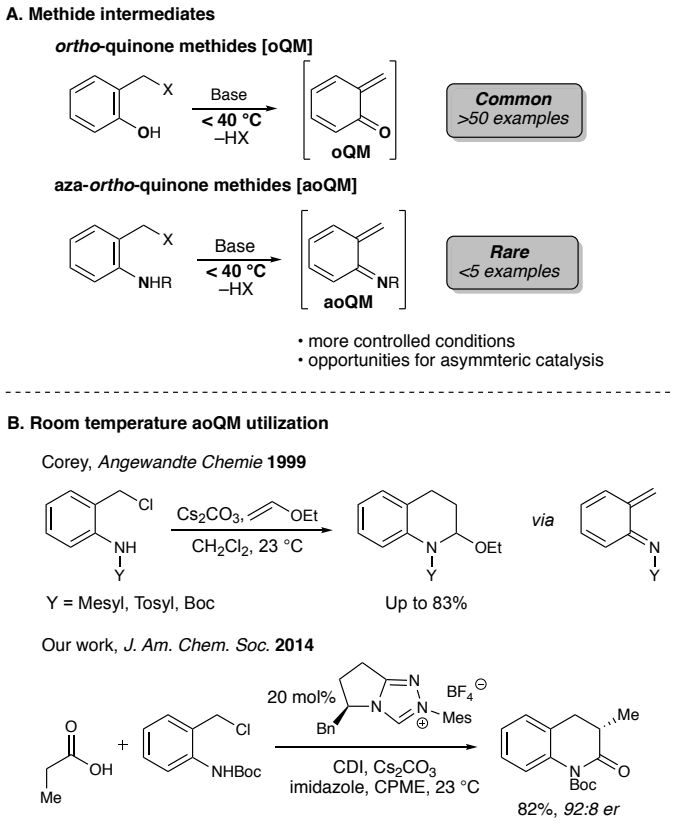
Since the first report of a facile, room temperature process to access aza-*ortho*-quinone methides (aoQMs) by Corey in 1999, this chemistry has remained dormant until our report of an enantioselective catalytic example in 2014. We report a theoretical and experimental study of the key to success behind these successful examples to enable broader exploitation of this useful intermediate. We have discovered that transformations involving the aoQM are remarkably facile with barriers 30 kcal/mol), precluding their formation under mild conditions. The use of Cs_2CO_3 as base is critical. It provides a thermodynamically and kinetically favorable means to form aoQMs, independent of the salt solubility and base strength. The exothermic formation of salt byproducts provides a driving force (average ΔG = −30.8 kcal/mol) compensating for the majority of the inherent unfavorable thermodynamics of aoQM formation.



6.1 Introduction

Quinone methides, particularly ortho-quinone methides (oQMs), are highly reactive and useful intermediates[127] with numerous examples in synthetic methodologies,[128] total syntheses,[129] and natural product chemistry.[130] A multitude of reports disclose oQM use under mild conditions.[131] In contrast, reports of *in situ* generation of aza-*ortho*-quinone methides (aoQMs) as reactive intermediates under mild conditions are demonstrably rare (Scheme 6.1a).[132] E.J. Corey first reported the use of aoQMs as useful reactive intermediates in 1999,[133] and for more than a decade, this chemistry remained underexplored until our report in 2014 (Scheme 6.1b).[134] While there are examples of aoQMs being formed as a result of pyrolysis, photolysis, with nonremovable stabilizing groups,[135] or from even more reactive precursors,[136] the difficulty of its generation under mild conditions have likely limited aoQMs as general electrophiles in catalysis and synthesis.

Scheme 6.1 Summary of oQM chemistry and recent aoQM chemistry.



In this report, we studied three reactions that can proceed through aoQM intermediacy using experiments and theory.[137] We have identified the enabling factor behind successful cases of aoQM-mediated reactions under mild conditions. Herein, we describe the thermodynamic and kinetic effect Cs_2CO_3 has in accessing the reactive aoQM intermediate in synthesis and asymmetric catalysis. Our results highlight and refine the cesium effect[138] that has been at the forefront of many organic reactions that take place under basic conditions. While this current study focuses on the use of ortho substituted benzyl chloride precursors as substrates, we will continue to leverage our newfound understanding to develop novel substrates for aoQM-mediated reactions.

6.2 Results and Discussion

6.2.1 Computational details

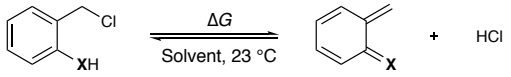
Geometry optimizations were performed with the M06-2X method[39] with SDD+ECP[139] for Cs and 6-31G(d)[40] basis sets for all other atoms. Solvation was modeled implicitly using PCM[43] with the solvent employed in the experiments. Explicit THF solvation was also considered (Figure 6.3b). All geometry optimizations, vibrational frequency analyses, and PCM solvation corrections were completed using Gaussian 09.[41] Energy refinements were computed at M06-2X/def2-QZVPP[140] using the ORCA computational package[141] with PCM solvation corrections at M06-2X/6-311++G(2df,p)[42] and SDD+ECP using Gaussian 09.

Reliable energetics involving partially heterogeneous, strongly ionic acid/base reactions in which constituent reactants, intermediates, or products can potentially dimerize/oligomerize are theoretically challenging at present, and these results should be taken as a model process that assumes homogeneity, precluding nucleation/oligomerization and other experimental anomalies. Regardless, the key discovery here is that the Cs_2CO_3 is critical in effecting aoQM formation under mild conditions.

6.2.2 Inherent stability of aoQM vs. oQM

The discrepancy between the proliferation of oQM over aoQM mediated reactions was first investigated. We evaluated the effect of the heteroatom on the quinone equilibria. The computed equilibria in dichloromethane, diethyl ether, and tetrahydrofuran between the ortho substituted benzyl chloride precursor and their corresponding methides are shown in Table 6.2. The oQM is more stable than the aoQM by ~10 kcal/mol, corresponding to ~10^7-fold ease of forming the oQM at room temperature. The stability differences are attributed to the relative π-bond strengths between carbon and the heteroatoms. The stronger, more polarized C=O π-bond in the oQM derivatives helps mitigate the energetic penalty of losing aromaticity. The C=O π-bond is stronger than C=N π-bond by 10−15 kcal/mol, matching the stability differences between oQM and aoQM.[142]

Table 6.2 Computed *ortho*-quinone and aza-*ortho*-quinone methide equilibria



X	Δ*G* (DCM)	Δ*G* (DEE)	Δ*G* (THF)
O	19.6	19.9	19.7
NH	29.1	29.3	29.1
NBoc	32.9	33.4	33.0

6.2.3 Cesium carbonate equilibrium facilitates aoQM production

Any reaction which generates methides must overcome the resonance energy of benzene.[143] Under harsh conditions, much of this energy will come from light or heat. Under milder reaction conditions, the harnessing of chemical energy will play a much larger role. We postulated that the basic conditions used to generate these reactive intermediates may be responsible in mitigating the unfavorable thermodynamics. Specifically, we considered the thermodynamic effect of converting Cs_2CO_3 and HCl to $CsHCO_3$ and CsCl. Computations utilizing implicit solvation showed that this reaction is highly exergonic in three different polar aprotic solvents (ΔG_{avg} = −30.8 kcal/mol, blue arrows, Figure 6.3a). The equilibrium of cesium carbonate and HCl with cesium

bicarbonate and cesium chloride was also investigated with explicit THF solvation included directly in the geometry optimizations.[144] The equilibrium remains highly exergonic (ΔG = −43 kcal/mol), and in line with the conclusions granted using implicit solvation methods. By coupling this highly favored equilibrium with the unstable aoQM formation process, aoQMs were now shown to be in equilibrium with the *ortho*-amino benzyl chloride precursors under ambient conditions (ΔG aoQM 1.7−3.2 kcal/mol, Figure 6.3a).

We wondered if other more moderate bases, such as imidazole, behave similarly. Computations suggested that the complexation of an imidazole to the *in situ* generated HCl puts the NBoc-protected aoQM at ~25 kcal/mol (ΔG_{avg} = 25.9 kcal/mol, Figure 6.3a, green arrows). The thermodynamic stabilization afforded by the formation of an imidazole-HCl complex is ~8 kcal/mol, which would predict little aoQM formation at room temperature from thermodynamics alone.[145]

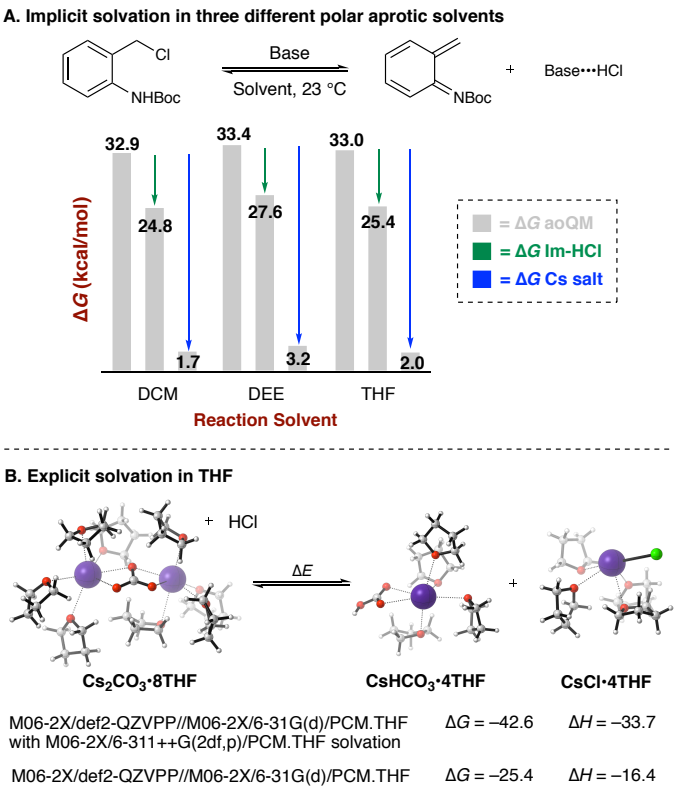


Figure 6.3 Effect of *in situ* salt formation on aoQM thermodynamics with imidazole and cesium carbonate as base.

6.2.4 Mechanism of aoQM formation

Three pathways for aoQM formation can be envisioned (Figure 6.4), beginning with fast deprotonation of the labile amine proton by cesium carbonate (**Deprotonation-TS**, $\Delta G^{\ddagger}$ = 3.6 kcal/mol). All computed mechanisms originate from the postdeprotonation cesium complex (ΔG = 0.4 kcal/mol). Two modes of intramolecular S_N2 attack[146] followed by electrocyclic ring opening were considered (magenta and blue pathways). While the barrier of **6-exotet-TS** ($\Delta G^{\ddagger}$ = 24.6 kcal/mol) lies close to the estimated experimental barrier, the intermediate that follows presents a significant thermodynamic sink (ΔG = −18.1 kcal/mol). The stability of this intermediate hinders **Oxazine-opening-TS** from occurring, even if electrocyclic ring opening gives a reasonable barrier from starting material ($\Delta G^{\ddagger}$ = 21.4 kcal/mol). The computed barrier to **Oxazine-opening-TS** of 39.5 kcal/mol (relative to the benzoxazine intermediate) is consistent with computed and experimental barriers of retro-Diels−Alder reactions of 1,2-benzoxazines to form oQMs.[147] A similar trend is observed for **6-exotet-TS**, although both the initial ring closure ($\Delta G^{\ddagger}$ = 33.7 kcal/mol) and **Azitidine-opening-TS** ($\Delta G^{\ddagger}$ = 38.8 kcal/mol) are highly disfavored regardless of the thermodynamics of the fused ring intermediate. Ultimately, simple elimination of the chloride leaving group is computed as the favored pathway (**Elimination-TS**, $\Delta G^{\ddagger}$ = 12.1 kcal/mol).

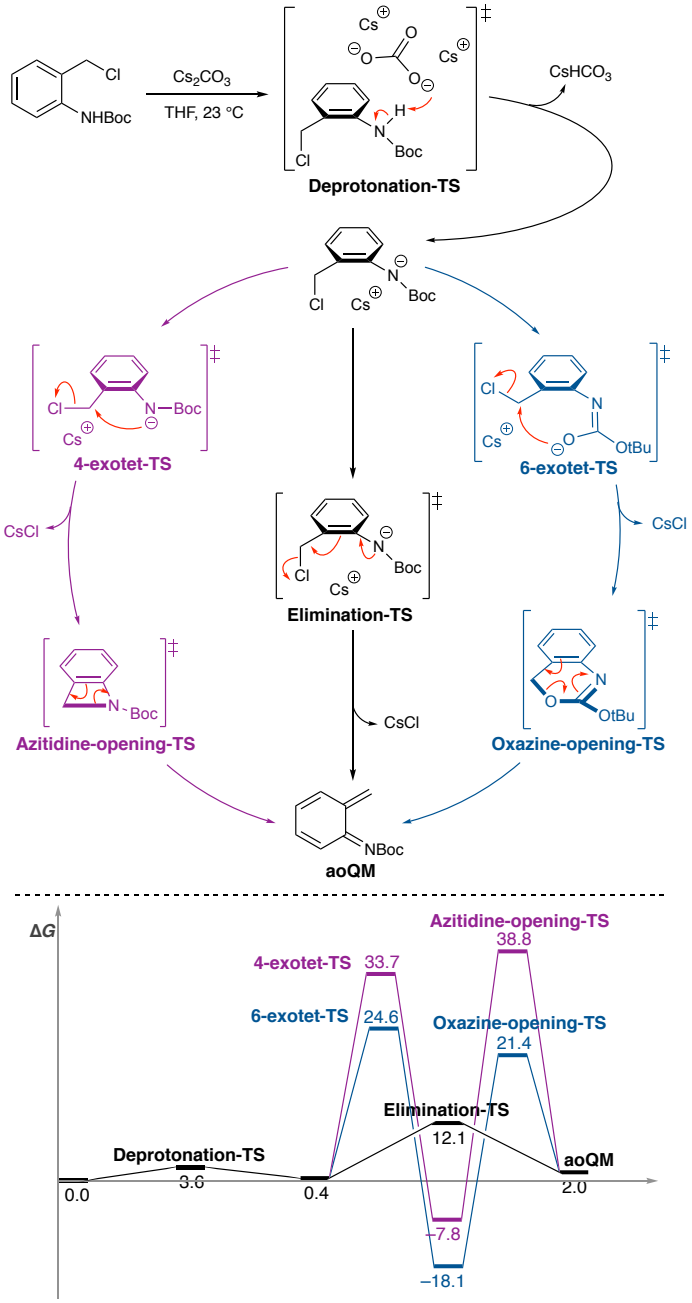


Figure 6.4 Computed mechanisms of aoQM formation in THF solvation. Stepwise deprotonation followed by chloride elimination is the favored mechanism (black) over intramolecular S_N2 and ring-opening (blue and magenta).

Elimination of the chloride leaving group results in loss of aromaticity, typically seen as a formidable hurdle in most room temperature reactions. Complexation of the cesium cation with the departing leaving group and the partially anionic nitrogen atom (Figure 6.5,

Elimination-TS) is hypothesized to offset this penalty to the point of facile aoQM formation under ambient conditions. Considering that the equilibrium between the *ortho* substituted benzyl chloride precursor and cesium bicarbonate slightly favors the starting material by 0.4 kcal/mol, it is proposed that the main driving force is the formation of the ionic Cs−Cl bond itself. This effect is apparent is the highly exergonic formation of the fused azitidine ($\Delta G = -7.8$ kcal/mol) and oxazine ring ($\Delta G = -18.1$ kcal/mol) intermediates (Figure 6.4, bottom), where aromaticity is intact and ring formation is concomitant with CsCl salt formation.

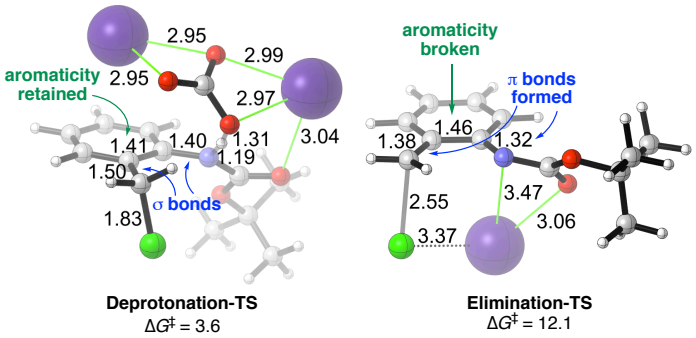


Figure 6.5 Computed TSs of the stepwise deprotonation/elimination mechanism for aoQM formation.

6.2.5 Applications to dihydroquinolone synthesis

Corey's dihydroquinolone reaction was hypothesized to occur via a concerted or stepwise Diels−Alder to an aoQM generated *in situ*. From our previous computations, we can already predict that the cesium carbonate in solution will render the aoQM accessible under room temperature conditions. What is unknown is whether an alternative mechanism competes with the subsequent cycloaddition step. One such possible mechanism is direct nucleophilic substitution, in which the vinyl ether may directly add to the aoQM precursor via S_N2-like transition state followed by loss of HCl and cyclization to furnish the observed dihydroquinolone product (**Corey-SN2-TS**, Figure 6.6, top panel). The developing negative charge of the departing chloride is stabilized by the vicinal N−H (2.41 Å). Even with the anionic Cl leaving group stabilized through hydrogen bonding, the S_N2 barrier is considerably high (37.3 kcal/mol). The most favorable pathway is formation of the aoQM

(ΔG = 2.0 kcal/mol) followed by concerted [4+2] (**Corey-Diels−Alder-TS**, $\Delta G^{\ddagger}$ = 17.8 kcal/mol). In the absence of cesium carbonate, no reaction is expected to occur given the high energy of the S_N2 ($\Delta G^{\ddagger}$ = 37.3 kcal/mol) and [4+2] ($\Delta G^{\ddagger}$ = 48.8 kcal/mol) pathways, both which lie far below the estimated barrier of 24 kcal/mol.

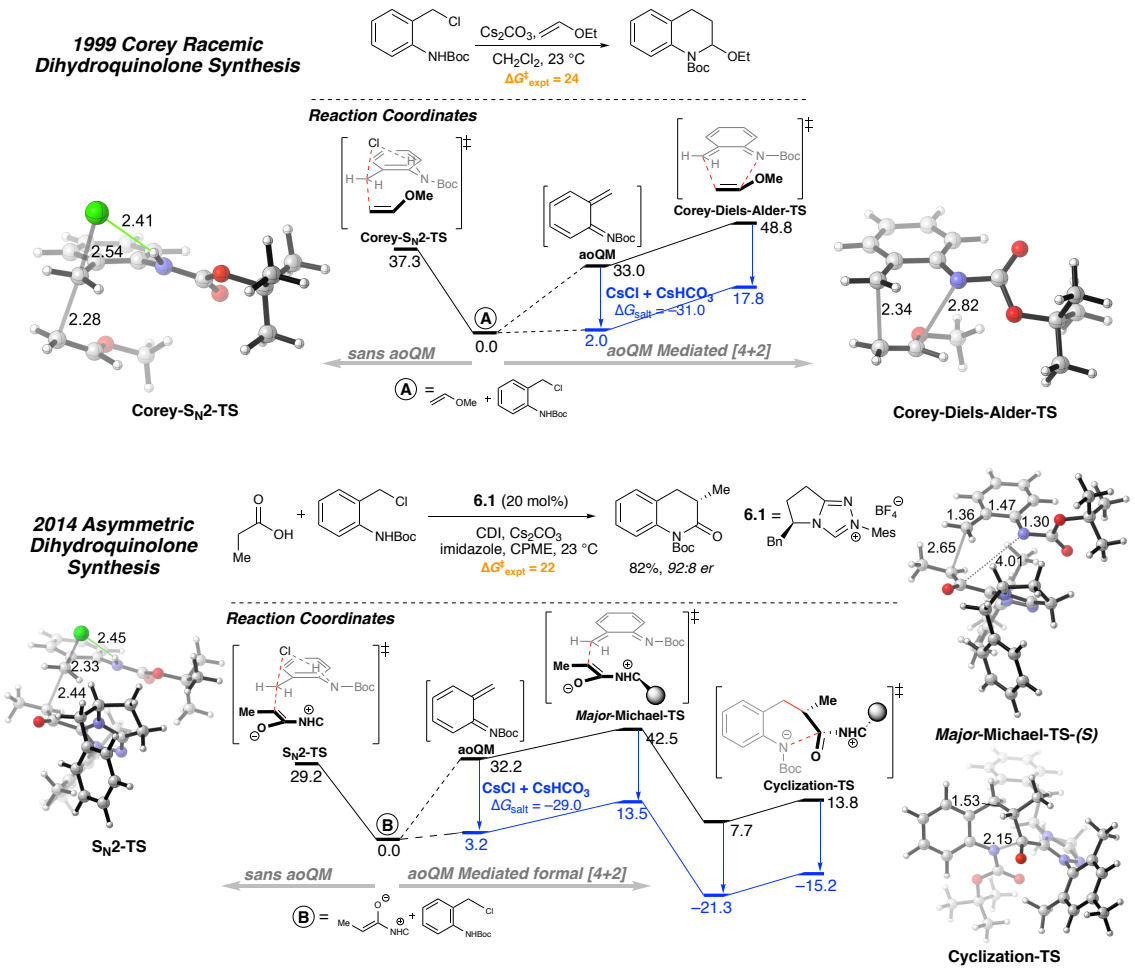


Figure 6.6 Corey's dihydroquinolone synthesis from vinyl ethers (top); NHC-**6.1**-catalyzed dihydroquinolone synthesis from propanoic acid (bottom). Bidirectional reaction coordinate diagrams shown. To the right, two energetics for the aoQM-mediated reaction: parent reaction without formation of any salt byproducts (black) and with C_2CO_3 (CsCl + $CsHCO_3$, blue). To the left, energetics for the non-aoQM mediated S_N2 process.

Analysis of the NHC-catalyzed asymmetric dihydroquinolone synthesis reveals similar energetic trends (Figure 6.6, bottom panel). While the nucleophilic substitution pathway is lower in energy than the Corey example (**SN2-TS**, $\Delta G^{\ddagger}$ = 29.2 kcal/ mol), it still lies above the estimated room temperature barrier, and significantly below the **Major-Michael-TS-**

(*S*) ($\Delta G^{\ddagger}$ = 13.5 kcal/mol) as mediated by aoQM formation. Dihydroquinolone formation is stepwise, beginning with Michael addition and followed by cyclization (**Cyclization-TS**, $\Delta G^{\ddagger}$ = −15.2 kcal/mol). Release of the NHC from the resultant tetrahedral intermediate leads to product and begins a new catalytic cycle.

6.2.6 Computed enantioselectivity model

Unlike the achiral Corey example, stereoselectivity is critical in the NHC-catalyzed reaction. Our goal is to develop a stereocontrol model that assumes an aoQM mediated stereodetermining C−C bond formations step. Agreement of the computed enantioselectivity with experiment provides additional evidence for aoQM intermediacy. In both the major and minor stereodeterming Michael TSs (Figure 6.7), the developing negative charge on the nitrogen of the aoQM in the transition state is mitigated by the proximity to the positively charged heterocycle of the NHC catalyst. Conjugative stabilization of the developing negative charge on the nitrogen by the BOC group is not realized in these transition states, the π/π* system of the BOC group is orthogonal to the conjugated π system of the aoQM (∠C=N/ C=O = ~95°) responsible for charge delocalization resulting from nucleophilic attack of the aoQM in the transition state. Moreover, the nitrogen is bent significantly (~120°), indicating that charge delocalization of the in-plane lone pair is also not present.

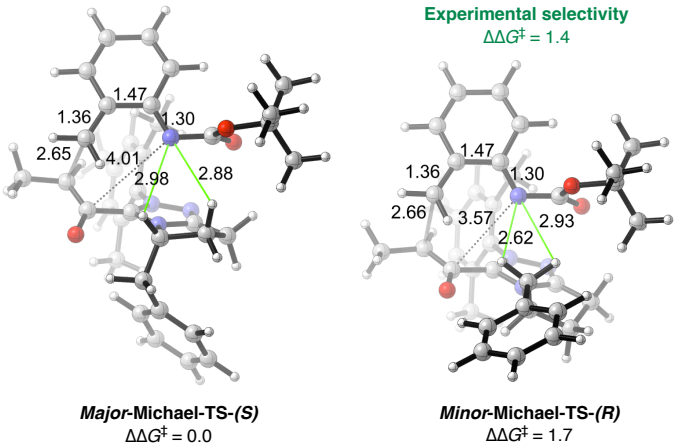


Figure 6.7 Enantiodetermining transition structures of NHC **6.1**-catalyzed dihydroquinolone synthesis from propanoic acid (Figure 6.6, bottom panel). Green lines represent stabilizing C–H···N interactions.

Enantiocontrol arises from differential stabilization of the developing negative charge at the nitrogen of the aoQM in the Michael step. Both transition structures experience proximity of the aoQM nitrogen to the cationic nitrogen atoms of the NHC catalyst. The major transition structure (**Major-Michael-TS-(*S*)**) experiences greater stabilization of the anionic aoQM nitrogen via a $^{+}$NCH···N^{-} interaction[148] (Figure 4, green lines). In the minor transition structure (**Minor-Michael-TS-(*R*)**), the chiral benzyl group replaces this interaction with a significantly weaker $^{+}$NCCH$_2$···N^{-} interaction.[149] The computed enantioselectivity of 1.7 kcal/mol agrees well with the experimental value of 1.4 kcal/mol.

6.2.7 Experimental evidence for aoQM formation

With all computations thus far suggesting aoQM intermediacy, a model experiment was devised to test these findings. We performed the NHC **6.2**-catalyzed addition of benzaldehyde to *ortho*-amino benzyl chloride (Figure 6.8). This model reaction was chosen so that the reaction could be performed in a sufficiently large scale to provide details of the rate-determining step by measuring the ^{13}C isotope effects (IEs) at natural abundance by observing fractionation in the recovered starting materials.[150] The computed energetics were consistent with the previous reactions (Figure 6.6). There was a large preference for the ***rac*-Stetter-TS** (Right, blue pathway) over the ***rac*-SN2-TS** (Left, black pathway) by ~20 kcal/mol.

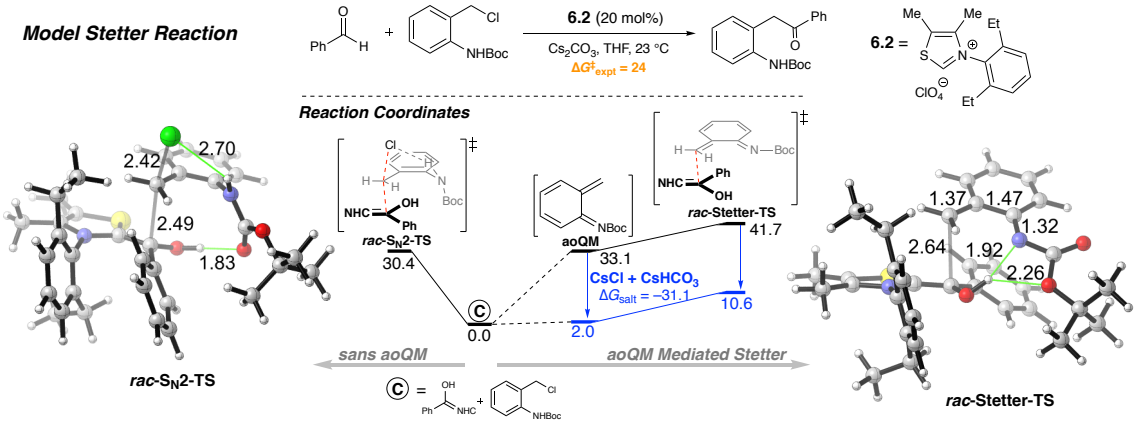


Figure 6.8 NHC **6.2**-catalyzed Stetter-type reaction of benzaldehyde. Bidirectional reaction coordinate diagrams shown. To the right, two energetics for the aoQM-mediated reaction: parent reaction without formation of any salt byproducts (black) and with C_2CO_3 ($CsCl + CsHCO_3$, blue). To the left, energetics for the non-aoQM mediated S_N2 process.

In comparing the experimental and computed[151,152] isotope effects, ***rac*-SN2-TS** and ***rac*-Stetter-TS** both showed significant KIE deviations only at C1, but the latter was in better agreement with experiments (7.3% vs. 2.7% error at C1, Figure 6.9). Computed equilibrium isotope effects for the formation of the aoQM intermediate were more consistent with experimental values, and suggested this step may be rate determining. While equilibrium isotope effects are not rigorous substitutes for comparison with experimental KIE measurements, they offer a valid approximation, considering that the transition state immediately prior to aoQM formation is product-like in geometry.

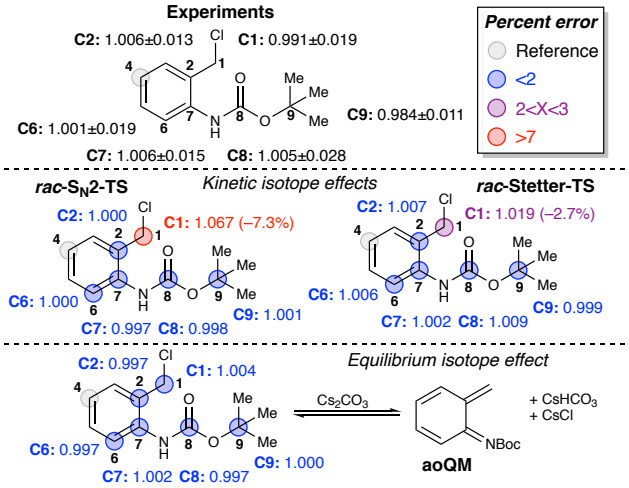


Figure 6.9 Natural abundance isotope effects (IE) results. Experiments (top, average of triplicate runs with standard deviations), computed kinetic IE for S_N2 and Stetter (middle), and equilibrium IE (bottom).

Furthermore, the *N*-methylated precursor, which cannot form the aoQM, did not provide any α-aryl ketone product after 48 h, instead yielding exclusively the benzoin adduct (Figure 6.10, top). This suggested that the preclusion of the aoQM dramatically slowed down the Stetter process. We anticipated that methylation of the substrate might also affect the barrier of the nucleophilic addition step. The computed barrier of 30.3 kcal/mol (**Me-*rac*-SN2-TS**, Figure 6.10, bottom) is essentially identical to ***rac*-SN2-TS** ($\Delta G^{\ddagger}$ = 30.4 kcal/mol), indicating that methylation likely shuts down **Deprotonation-TS** (Figures 6.4 and 6.5) without targeting the S_N2 pathway.

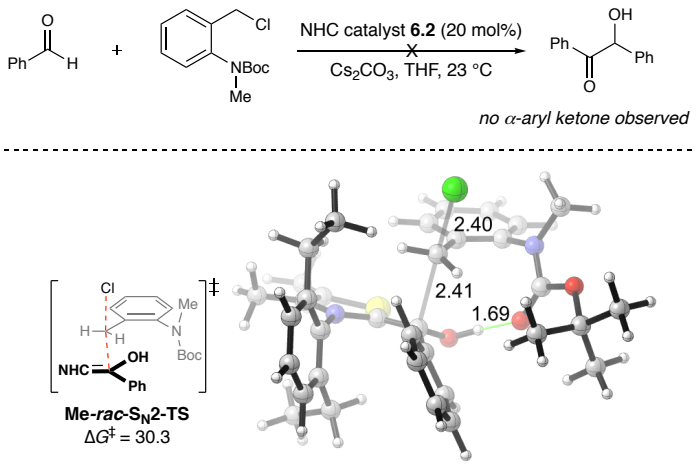
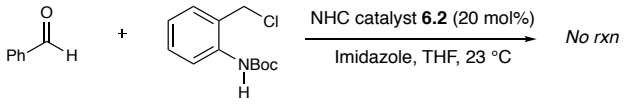


Figure 6.10 Effect of substrate *N*-methylation on the NHC-catalyzed Stetter reaction.

Analysis of the formation of imidazole-HCl indicated that while exergonic, the ~8 kcal/mol stabilization provided was not enough to drive aoQM formation (Figure 6.3a). As an experimental test, the model Stetter reaction was run with imidazole as base in place of Cs_2CO_3. As predicted by theory, there was no reaction with imidazole base (Scheme 6.11). These computations and experiments, in combination with the isotope effect data, provided evidence supporting aoQM intermediacy for low temperature aoQM mediated processes utilizing cesium carbonate base.

Scheme 6.11 Effect of imidazole base on the NHC-catalyzed Stetter reaction.



6.3 Conclusions

To summarize, we have combined theory and experiments toward the understanding of the synthetic accessibility of aza-*ortho*-quinone methides, an underutilized reactive synthetic intermediate with significant potential. Specifically, we have discovered what enables the formation of aoQMs as viable reaction intermediates in synthesis under room temperature conditions. The loss of aromaticity over the course of the methide formation is balanced by the exergonic formation of metal chloride and metal bicarbonate salts (>30 kcal/mol), an independent effect from salt solubility and strength of the base. This energetic trade off is distinctly different from the parent oQMs, where the relative strength of the C=O π bond is enough to render this species accessible even in the absence of this thermodynamic and kinetic Cs_2CO_3 effect. The impact of salt formation in organocatalysis, especially in rendering high energy reactive intermediates thermodynamically accessible, is currently not well understood. We illustrate a thorough and enabling understanding that allows the community to leverage the utility and unique reactivity of aoQMs in asymmetric catalysis and chemical synthesis. These discoveries will enable a broader discovery and development platform integrating mild aoQM generation and its use in catalytic reactions, as oQM has for decades.

6.4 Experimental Section

6.4.1 KIE experimental parameters

Data was collected from a total of three Stetter reactions taken to 90.0, 88.8, and 89.7% completion, respectively.[153] The unreacted benzyl chloride from the model Stetter reaction with catalyst **6.2** and benzaldehyde was recovered and analyzed by quantitative ^{13}C NMR spectroscopy. All samples were prepared identically as described: 60 mg of recovered

starting material was dissolved in 0.5 mL of $CDCl_3$ and then filtered through a 3 mm plug of Celite directly into a 5 mm high-precision NMR tube. Each NMR tube was filled to a constant sample height of 5 cm. Spectra were acquired on a Bruker Avance III 500 MHz spectrometer using proton-decoupled pulses with 80 s delays between pulses. 65536 data points were collected, which were then zero-filled to 256k before Fourier transformation. A zeroth order baseline correction was applied to all spectra, and integrations were measured using a ± 0.5 ppm region centered on each peak. The starting benzyl chloride used in all reactions and reference measurements came from the same synthetic batch. T1 values were measured for each sample using the inversion−recovery method to ensure the absence of any paramagnetic impurities.

6.4.2 General procedure for NHC-catalyzed addition of benzaldehyde to aoQMs

tert-Butyl (2-(chloromethyl)phenyl)- carbamate (1.209 g, 5 mmol), 3-(2,6-diethylphenyl)-4,5-dimethylthiazol-3-ium perchlorate **6.2** (0.346 g, 1.00 mmol), 2-methoxynaphthalene (NMR internal standard, 0.395 g, 2.500 mmol), and freshly dried and powdered cesium carbonate (1.955 g, 6.00 mmol) were combined in an oven-dried 250 mL round-bottom flask fitted with a magnetic stirbar under argon. The reaction flask was evacuated under reduced pressure for 15 min, then backfilled with argon 3 times. THF (50 mL) was added and the mixture was stirred for 30 s, until all soluble materials went into solution. A 100 μL aliquot was taken for NMR analysis (T0). Benzaldehyde (0.612 mL, 6.00 mmol) was added to the flask via syringe, and the reaction vessel was sealed and stirred vigorously under static argon. 100 μL aliquots were taken periodically to monitor consumption of the starting material. When an NMR aliquot indicated high (~90%) conversion (12−16h), the entire reaction mixture was filtered through a 1 cm pad of Celite and a final aliquot of the filtrate was taken to determine the percent conversion of benzyl chloride at the end time point (Tf). The filtered reaction mixture was concentrated under reduced pressure, and the residue was applied to a 2-in. pad of silica gel. Elution with 4:1 hexanes:ethyl acetate (until all remaining starting material had been collected, ~ 200 mL, TLC monitoring) followed by concentration of the eluent provided the crude recovered starting material. The

recovered benzyl chloride was further purified by elution on a 50 g SNAP biotage column, (gradient 2−15% hexanes:ethyl acetate, 14 column volumes). The pure fractions of recovered benzyl chloride were collected, concentrated, dried under reduced pressure and then analyzed by quantitative ^{13}C NMR spectroscopy.

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Chapter 7.

Conclusion

The widespread application of organocatalysis in synthetic organic methodology and total synthesis has been in large part due to Lewis base catalysts. Catalysts based on the thiourea core (isothioureas) and *N*-heterocyclic carbenes (NHCs) compose a large portion of the field. My reasearch has studied the mechanisms in great detail of both types of catalysts, allowing comprehensive sterecontrol models to be built, and enchanced understanding of subtle details such as by-product salt effects.

Stereocontrol in a chemical reaction, whether a peptide or a small-molecule catalyst, relies on preorgonaization of the catalyst-substrate complex. Forming a C–C bond between two prochiral funcitonal groups in one stereochemical orientation at a faster rate than all other possiblilies is necessitated by a chiral element of the catalyst and promoted by catalyst-substrate rigidity. Isothiourea catalysts are able to utilize S–O non-covalent interaction, thereby favoring one rotamer of the acylated catalyst over the other: The structural consequence is a planar, inflexible complex fostering high degrees of stereoselectivity in kinetic resolutions, Steglich rearrangments, and sigmatropic rearrangements. While NHCs can't take advantage of chalcogen bonding, Breslow-type reactive intermediates can be accessed through *Umpolung*-type chemistry.

Applied theory excels at informing, understanding, and prediciting experiment. As such, the complexity and speed of computational analysis expected in modern chemistry has gone hand in hand with the intracacies of today's synthesis and methodology. Much like how computers and the relative processing power seem primitive in the mide to late 20th century, theoretical capabilities of the future will truly be unrecognizable.

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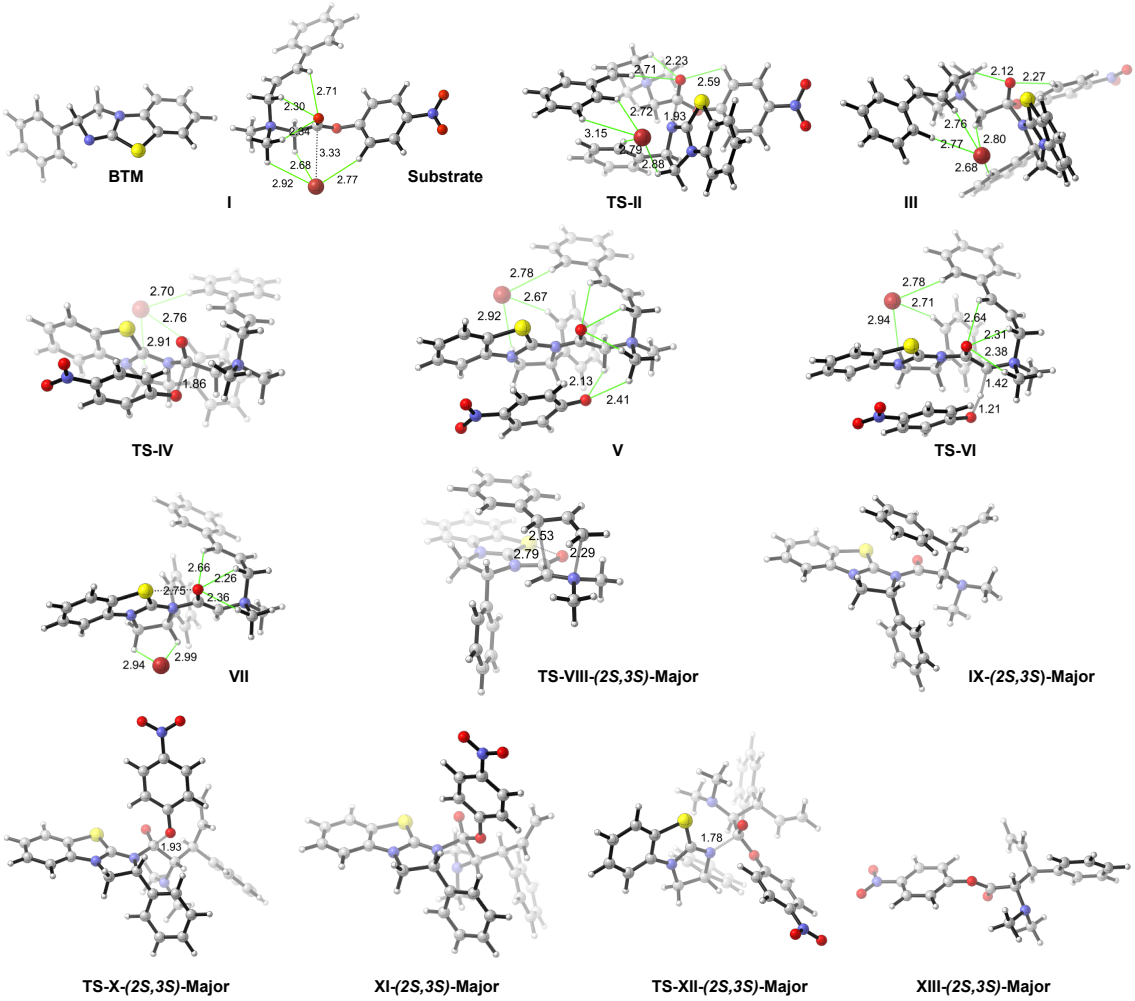
Appendix I:

Computational Data for Chapter 2

Catalytic Enantioselective [2,3]-Rearrangements of Allylic Ammonium Ylides: A Mechanistic and Computational Study

Structures from reaction coordinate - Lowest energy *(2S,3S)*-Major pathway

Optimized structures of the lowest energy (2*S*,3*S*) pathway.



I BTM

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

# M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
SCRF=(PCM,SOLVENT=acetonitrile) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C15H12N2S C1[X(C15H12N2S)] #Atoms= 30
Charge = 0 Multiplicity = 1

SCF Energy= -1086.20408765 Predicted Change= -1.193935D-08

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?

```
 Force      0.00001 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00121 ||  0.00180   [ YES ]      0.00121 ||  0.00180   [ YES ]
---------------------------------------------------------------------
     Atomic              Coordinates (Angstroms)
      Type               X           Y           Z
---------------------------------------------------------------------
      C         4.752939    -0.842780     0.710759
      C         4.208039     0.434650     0.556319
      C         2.894269     0.545840     0.131249
      C         2.127469    -0.597900    -0.153871
      C         2.667759    -1.869480     0.003579
      C         3.988019    -1.976890     0.441609
      S         1.958889     2.038090    -0.123771
      C         0.536029     1.071840    -0.518791
      N         0.862139    -0.268980    -0.606881
      N        -0.680981     1.407530    -0.698271
      C        -1.380481     0.141050    -1.020841
      C        -2.714301     0.005499    -0.325211
      C        -0.392321    -1.010530    -0.636561
      C        -2.910181     0.535379     0.951829
      C        -4.124921     0.357839     1.608969
      C        -5.154411    -0.356771     0.997839
      C        -4.964211    -0.889161    -0.275621
      C        -3.750121    -0.705191    -0.933881
      H         5.778469    -0.947120     1.048159
      H         4.796259     1.319880     0.775379
      H         2.071669    -2.749450    -0.215541
      H         4.423209    -2.962410     0.571499
      H        -1.544551     0.114320    -2.106171
      H        -0.376611    -1.814500    -1.374351
      H        -0.613321    -1.425600     0.355329
      H        -2.106911     1.096880     1.420559
      H        -4.269061     0.780079     2.598989
      H        -6.102011    -0.494261     1.509509
      H        -5.763081    -1.441931    -0.760531
      H        -3.605821    -1.115551    -1.930701
---------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 253.150 Kelvin      Pressure= 1.00000 Atm
=====================================================
 SCF Energy=     -1086.20408765   Predicted Change= -1.193935D-08
 Zero-point correction (ZPE)=            -1085.9650      0.23900
 Internal Energy (U)=                    -1085.9551      0.24897
 Enthalpy (H)=                           -1085.9543      0.24977
 Gibbs Free Energy (G)=                  -1085.9990      0.20502
---------------------------------------------------------------------
 Frequencies --     22.6451              35.0649              72.9117

=====================================================
 #m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
 SCRF=(PCM,SOLVENT=acetonitrile)
---------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C15H12N2S   C1[X(C15H12N2S)]  #Atoms= 30
 Charge = 0       Multiplicity = 1
---------------------------------------------------------------------------
```

SCF Energy= -1086.45470662
==========

I Substrate

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=acetonitrile) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C19H21BrN2O4 C1[X(C19H21BrN2O4)] #Atoms= 47
Charge = 0 Multiplicity = 1

SCF Energy= -3718.28765247 Predicted Change= -2.209613D-08
==========
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00399	0.00180	[NO]	0.00399	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.398822	-1.048723	0.082722
O	-0.119385	-1.010362	1.251363
C	-1.592579	-1.720600	-0.556604
N	-2.596690	-2.235262	0.425074
C	-3.067292	-1.146012	1.399201
C	-3.355251	0.154525	0.721008
C	-2.567095	1.222914	0.901671
C	-2.735423	2.555500	0.302286
C	-2.036719	-3.382003	1.218493
C	-3.768509	-2.734111	-0.365909
O	0.304861	-0.443113	-0.891697
C	1.499920	0.168949	-0.528752
C	1.555540	1.555731	-0.580424
C	2.755009	2.187898	-0.278345
C	3.847027	1.400970	0.066795
N	5.113328	2.065917	0.389508
O	5.147994	3.283475	0.338929
O	6.064705	1.367002	0.692572
C	3.791660	0.011965	0.119477
C	2.593451	-0.618572	-0.185419
C	-1.724060	3.505510	0.495620
C	-1.816480	4.772757	-0.073307
C	-2.930002	5.110163	-0.838495
C	-3.949562	4.175913	-1.028537
C	-3.855248	2.910402	-0.463770
H	-2.090022	-1.008701	-1.217080
H	-2.274366	-1.036874	2.137127
H	-3.952497	-1.568691	1.881461
H	-4.239150	0.208852	0.089721
H	-1.694486	1.115432	1.547686

H	-2.817425	-3.723569	1.898755
H	-1.163653	-3.032552	1.764349
H	-1.738883	-4.169041	0.526188
H	-4.495409	-3.156813	0.326893
H	-3.417636	-3.499339	-1.058321
H	-4.208019	-1.903237	-0.917199
H	-1.209645	-2.567267	-1.134452
H	0.671055	2.121105	-0.853512
H	2.847475	3.266147	-0.306297
H	4.672546	-0.555874	0.391210
H	2.483536	-1.700708	-0.173232
H	-0.856649	3.242640	1.096331
H	-1.022182	5.495523	0.083564
H	-3.008605	6.097559	-1.282396
H	-4.822529	4.437681	-1.618014
H	-4.660853	2.198696	-0.615730
Br	0.992062	-3.975733	-0.624135

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -3718.28765247 Predicted Change= -2.209613D-08

Zero-point correction (ZPE)=	-3717.9043	0.38327
Internal Energy (U)=	-3717.8857	0.40193
Enthalpy (H)=	-3717.8849	0.40274
Gibbs Free Energy (G)=	-3717.9514	0.33622

Frequencies -- 13.8063 22.8512 28.4002

==========
#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=acetonitrile)

Pointgroup= C1 Stoichiometry= C19H21BrN2O4 C1[X(C19H21BrN2O4)] #Atoms= 47
Charge = 0 Multiplicity = 1

SCF Energy= -3721.06884042
==========

TS-II

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)
iop(1/8=18) freq=noraman temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C34H33BrN4O4S C1[X(C34H33BrN4O4S)] #Atoms= 77
Charge = 0 Multiplicity = 1

SCF Energy= -4804.50070304 Predicted Change= -2.001208D-09
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?

Force	0.00000 ||	0.00045 [YES]	0.00000 ||	0.00030 [YES]
Displ	0.00119 ||	0.00180 [YES]	0.00119 ||	0.00180 [YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.065238	-2.054268	-0.190248
N	0.046984	-0.308360	0.639798
C	-1.280827	-2.517050	0.370473
N	-1.861317	-3.689116	-0.375400
C	-3.017010	-4.196217	0.432108
C	-0.850862	-4.781709	-0.534311
O	0.269796	-1.853116	-1.383708
C	-0.221469	-0.000965	2.069212
C	-1.701919	-0.089488	2.362200
C	0.415684	1.403488	2.282863
C	0.947679	0.534597	0.236227
C	2.198078	2.429021	0.679030
C	2.573398	2.174703	-0.648126
S	1.767595	0.729850	-1.290733
C	2.695940	3.528250	1.366892
C	3.580023	4.371466	0.697051
C	3.962135	4.117935	-0.621533
C	3.461681	3.010405	-1.307343
C	-2.606509	0.650792	1.593414
C	-3.976517	0.465399	1.758374
C	-4.452540	-0.446737	2.702221
C	-3.554225	-1.164867	3.488045
C	-2.181740	-0.987999	3.314754
N	1.345722	1.447432	1.156484
C	-2.353979	-3.277365	-1.771450
C	-3.432025	-2.243143	-1.718251
C	-3.140864	-0.941513	-1.844695
C	-4.075310	0.187183	-1.743592
C	-5.469118	0.034724	-1.722450
C	-6.290890	1.140327	-1.538411
C	-5.736183	2.411698	-1.365332
C	-4.352809	2.571597	-1.391166
C	-3.531467	1.467087	-1.594358
H	-1.164461	-2.823243	1.411711
H	-2.008036	-1.709558	0.307869
H	-2.633204	-4.617784	1.361126
H	-3.537626	-4.961670	-0.144624
H	-3.685003	-3.362235	0.650246
H	-0.429241	-5.016260	0.443326
H	-0.070282	-4.433768	-1.210129
H	-1.352562	-5.654048	-0.953143
H	0.309155	-0.745655	2.679985
H	0.932319	1.488632	3.239744
H	-0.316069	2.210268	2.157358
H	2.398090	3.720944	2.392302
H	3.977781	5.239109	1.213328
H	4.652432	4.787986	-1.122715
H	3.750382	2.813862	-2.334775
H	-2.230389	1.363674	0.859638

H	-4.671161	1.027132	1.138091
H	-5.521138	-0.595443	2.825352
H	-3.919498	-1.872015	4.226455
H	-1.480204	-1.569758	3.908647
H	-2.693876	-4.207945	-2.232767
H	-1.469303	-2.908486	-2.289020
H	-4.451516	-2.584207	-1.555098
H	-2.092200	-0.666380	-1.982252
H	-5.914270	-0.947590	-1.852888
H	-7.368981	1.012396	-1.525594
H	-6.384825	3.268897	-1.211120
H	-3.890276	3.542338	-1.238255
H	-2.453350	1.610791	-1.587919
C	2.954612	-2.775978	-0.859381
C	2.365135	-2.333015	0.325071
O	1.060150	-2.636757	0.628072
C	3.084676	-1.586816	1.258370
C	4.406649	-1.253619	1.000870
C	4.974927	-1.687782	-0.191174
N	6.369055	-1.339470	-0.471767
O	6.972732	-0.680815	0.358263
O	6.855368	-1.726718	-1.520909
C	4.276808	-2.448459	-1.122562
H	4.765974	-2.771305	-2.033165
H	2.375449	-3.358318	-1.564480
H	2.598995	-1.268109	2.174969
H	4.989462	-0.668321	1.700925
Br	-0.865142	3.460406	-0.375305

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -4804.50070304 Predicted Change= -2.001208D-09
Zero-point correction (ZPE)= -4803.8773 0.62331
Internal Energy (U)= -4803.8487 0.65196
Enthalpy (H)= -4803.8479 0.65277
Gibbs Free Energy (G)= -4803.9353 0.56531

Frequencies -- -177.3072 12.4302 18.6553

==========
#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=acetonitrile)

Pointgroup= C1 Stoichiometry= C34H33BrN4O4S C1[X(C34H33BrN4O4S)] #Atoms= 77
Charge = 0 Multiplicity = 1

SCF Energy= -4807.52538148
==========

III

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)

SCRF=(PCM,SOLVENT=acetonitrile) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C34H33BrN4O4S C1[X(C34H33BrN4O4S)] #Atoms= 77
Charge = 0 Multiplicity = 1

SCF Energy= -4804.51618390 Predicted Change= -8.811517D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00114	0.00180	[YES]	0.00114	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.148039	5.867966	-0.531453
C	-0.653464	5.868418	0.775473
C	-0.018657	4.748469	1.305669
C	0.094089	3.628278	0.492410
C	-0.408521	3.615683	-0.814912
C	-1.028427	4.740330	-1.342219
N	0.708496	2.418563	0.799967
C	0.562616	1.475101	-0.138855
S	-0.142042	2.049113	-1.606120
C	1.054215	1.789900	2.076264
C	1.603995	0.420510	1.599116
C	1.340110	-0.733530	2.536237
N	0.976967	0.290970	0.250408
C	0.866534	-0.920727	-0.678326
O	0.731133	-0.556452	-1.892075
C	-0.256990	-1.802485	-0.061945
N	-0.845813	-2.803527	-1.025085
C	-1.744708	-2.131851	-2.066442
C	-2.965381	-1.498491	-1.479160
C	-4.185193	-1.992267	-1.727548
C	-5.468909	-1.450239	-1.253219
C	-1.652390	-3.775598	-0.223498
C	0.229699	-3.555527	-1.748220
O	2.089244	-1.692479	-0.346661
C	3.305560	-1.224359	-0.685425
C	0.065135	-0.976414	3.057232
C	-0.143001	-2.062803	3.902711
C	0.914203	-2.907627	4.238931
C	2.185309	-2.666499	3.722709
C	2.394916	-1.582799	2.873420
C	3.549220	-0.041874	-1.405019
C	4.858078	0.350674	-1.645523
C	5.908750	-0.433106	-1.182662
N	7.276278	-0.010744	-1.442231
O	7.453446	1.035576	-2.047736
O	8.185164	-0.722302	-1.041206
C	5.687445	-1.615390	-0.479557
C	4.385009	-2.004661	-0.233107

C	-5.549404	-0.454776	-0.267454
C	-6.788571	0.025307	0.140231
C	-7.964109	-0.477115	-0.420297
C	-7.894222	-1.472143	-1.392012
C	-6.654744	-1.955856	-1.801132
H	-1.635038	6.754600	-0.922863
H	-0.760817	6.756292	1.389591
H	0.372445	4.742816	2.317515
H	-1.418164	4.737923	-2.354705
H	0.136069	1.686105	2.664478
H	1.804073	2.365158	2.618842
H	2.686125	0.501622	1.433882
H	0.131255	-2.374874	0.782542
H	-2.015956	-2.928002	-2.765149
H	-1.093841	-1.406412	-2.555029
H	-2.828469	-0.595980	-0.881555
H	-4.264997	-2.878687	-2.359382
H	-2.192787	-4.429090	-0.910394
H	-2.357162	-3.223555	0.397058
H	-0.972155	-4.357899	0.398156
H	0.745736	-2.858092	-2.405173
H	-0.242956	-4.358802	-2.314119
H	0.921754	-3.963143	-1.011366
H	-1.070025	-1.155279	0.285115
H	-0.772778	-0.347031	2.760968
H	-1.136265	-2.251109	4.298739
H	0.746514	-3.751919	4.900657
H	3.013134	-3.320250	3.978665
H	3.384207	-1.397095	2.461209
H	2.722979	0.536205	-1.795304
H	5.068834	1.259185	-2.196578
H	6.526795	-2.206840	-0.135113
H	4.167834	-2.914346	0.316520
H	-4.644832	-0.061796	0.193083
H	-6.839489	0.794489	0.905366
H	-8.928156	-0.098357	-0.094924
H	-8.803034	-1.873635	-1.829598
H	-6.599789	-2.733887	-2.558689
Br	-2.369792	1.143352	1.210599

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -4804.51618390 Predicted Change= -8.811517D-09

Zero-point correction (ZPE)=	-4803.8907	0.62543
Internal Energy (U)=	-4803.8621	0.65403
Enthalpy (H)=	-4803.8613	0.65484
Gibbs Free Energy (G)=	-4803.9489	0.56722

Frequencies -- 11.5736 16.3056 17.4579

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=acetonitrile)

Pointgroup= C1 Stoichiometry= C34H33BrN4O4S C1[X(C34H33BrN4O4S)] #Atoms= 77
Charge = 0 Multiplicity = 1

SCF Energy= -4807.53429683
==========

TS-IV

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)
iop(1/8=18) freq=noraman temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C34H33BrN4O4S C1[X(C34H33BrN4O4S)] #Atoms= 77
Charge = 0 Multiplicity = 1

SCF Energy= -4804.50548792 Predicted Change= -6.969207D-10
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00165	0.00180	[YES]	0.00165	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.183127	1.690026	-0.104851
N	0.002083	0.410534	0.569941
C	1.428440	2.422831	0.405185
N	1.859485	3.573092	-0.458209
C	2.983678	4.252514	0.263103
C	0.750777	4.559803	-0.665103
O	-0.171381	1.713094	-1.290307
C	0.278945	0.137666	2.012586
C	1.760325	0.093824	2.306625
C	-0.452872	-1.213068	2.244926
C	-0.986424	-0.397695	0.164442
C	-2.343049	-2.156254	0.705449
C	-2.753277	-1.889332	-0.606447
S	-1.845241	-0.546799	-1.313839
C	-2.915482	-3.175932	1.457016
C	-3.919919	-3.926498	0.856843
C	-4.342136	-3.660235	-0.450712
C	-3.765082	-2.636730	-1.196934
C	2.600978	-0.713921	1.533881
C	3.978110	-0.669614	1.732205
C	4.518072	0.162913	2.713780
C	3.678142	0.946093	3.502615
C	2.300046	0.915774	3.294892
N	-1.360381	-1.260156	1.100972
C	2.359095	3.111488	-1.836231
C	3.447008	2.089444	-1.748418

C	3.163302	0.785154	-1.862787
C	4.093815	-0.344785	-1.743452
C	5.486527	-0.197677	-1.676381
C	6.298317	-1.309788	-1.486327
C	5.734562	-2.581938	-1.352584
C	4.351912	-2.735737	-1.422345
C	3.541202	-1.624812	-1.631550
H	1.248496	2.820742	1.404266
H	2.272022	1.731688	0.437762
H	2.596933	4.678177	1.188798
H	3.379229	5.040248	-0.378553
H	3.757262	3.516463	0.483625
H	0.332064	4.820769	0.306042
H	-0.009186	4.087644	-1.282797
H	1.172644	5.434354	-1.161176
H	-0.198357	0.939975	2.585904
H	-0.999615	-1.232481	3.188226
H	0.228306	-2.067151	2.165172
H	-2.584532	-3.374765	2.470695
H	-4.386203	-4.730964	1.415420
H	-5.130153	-4.260202	-0.892775
H	-4.089303	-2.432591	-2.211770
H	2.173575	-1.373171	0.777974
H	4.627818	-1.280369	1.109983
H	5.592736	0.200480	2.863596
H	4.094195	1.592344	4.269044
H	1.645571	1.548685	3.889466
H	2.689472	4.028478	-2.330368
H	1.480389	2.714793	-2.340599
H	4.463210	2.437572	-1.578862
H	2.117821	0.506072	-2.014540
H	5.938712	0.785096	-1.775487
H	7.375925	-1.186608	-1.437848
H	6.375144	-3.444306	-1.193983
H	3.887077	-3.710148	-1.303510
H	2.462447	-1.759646	-1.657415
C	-2.798385	2.893352	-0.594801
C	-2.229658	2.402959	0.605089
O	-0.989059	2.683621	0.935113
C	-3.017090	1.546408	1.414718
C	-4.274425	1.136064	1.012491
C	-4.774734	1.600745	-0.204999
N	-6.078190	1.148161	-0.647843
O	-6.682219	0.343210	0.048736
O	-6.518757	1.584970	-1.702924
C	-4.057392	2.494178	-1.001439
H	-4.487647	2.849699	-1.930113
H	-2.215395	3.573750	-1.204152
H	-2.602737	1.194692	2.355720
H	-4.867185	0.458417	1.615689
Br	0.664993	-3.345795	-0.415254

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -4804.50548792 Predicted Change= -6.969207D-10
Zero-point correction (ZPE)= -4803.8813 0.62416
Internal Energy (U)= -4803.8528 0.65267
Enthalpy (H)= -4803.8520 0.65347
Gibbs Free Energy (G)= -4803.9381 0.56734

Frequencies -- -212.0957 16.0960 25.3782

==========
#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=acetonitrile)

Pointgroup= C1 Stoichiometry= C34H33BrN4O4S C1[X(C34H33BrN4O4S)] #Atoms= 77
Charge = 0 Multiplicity = 1

SCF Energy= -4807.53193794
==========

V

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=acetonitrile) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C34H33BrN4O4S C1[X(C34H33BrN4O4S)] #Atoms= 77
Charge = 0 Multiplicity = 1

SCF Energy= -4804.51587791 Predicted Change= -1.642916D-08
==========
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00184	0.00180	[NO]	0.00184	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.726876	1.439298	-0.855386
N	0.031956	0.602129	0.002290
C	1.739465	2.336233	-0.178160
N	2.452551	3.255870	-1.116286
C	3.394540	4.064082	-0.273206
C	1.490186	4.194303	-1.791175
O	0.520161	1.388126	-2.052011
C	-0.002954	0.645409	1.503446
C	1.352953	0.412911	2.123960
C	-1.074440	-0.428497	1.830429
C	-1.019541	-0.128849	-0.450918
C	-2.798562	-1.416718	0.132679
C	-2.853066	-1.489768	-1.264637
S	-1.549184	-0.566074	-2.014687
C	-3.732575	-2.055945	0.939918

C	-4.730035	-2.781874	0.302527
C	-4.789383	-2.864578	-1.094407
C	-3.856283	-2.217410	-1.895915
C	2.149522	-0.661635	1.720010
C	3.437867	-0.796687	2.230948
C	3.924377	0.123883	3.159331
C	3.120354	1.181394	3.580474
C	1.838299	1.331177	3.056474
N	-1.742975	-0.608200	0.538965
C	3.258240	2.495271	-2.182618
C	4.052042	1.367258	-1.603861
C	3.635462	0.100150	-1.733009
C	4.269256	-1.096458	-1.161798
C	5.609655	-1.131752	-0.754937
C	6.128630	-2.274076	-0.155395
C	5.315731	-3.390332	0.056273
C	3.981160	-3.361199	-0.344557
C	3.468260	-2.227217	-0.966245
H	1.205974	2.951644	0.552938
H	2.491075	1.724070	0.323362
H	2.808862	4.654252	0.431712
H	3.967529	4.718379	-0.929362
H	4.058516	3.387431	0.264642
H	0.819558	4.598486	-1.032295
H	0.915661	3.634546	-2.525040
H	2.072702	4.977999	-2.274947
H	-0.370203	1.638761	1.775194
H	-1.775626	-0.080480	2.589568
H	-0.625270	-1.390972	2.097994
H	-3.683180	-1.977725	2.020649
H	-5.478742	-3.290547	0.899978
H	-5.581910	-3.437877	-1.562944
H	-3.907063	-2.278638	-2.977468
H	1.759909	-1.391569	1.011262
H	4.061317	-1.620838	1.893601
H	4.929995	0.017734	3.554351
H	3.495148	1.898533	4.303663
H	1.220642	2.173825	3.358203
H	3.884046	3.257903	-2.652644
H	2.529415	2.131440	-2.903950
H	4.960703	1.605842	-1.055085
H	2.705758	-0.084015	-2.274265
H	6.251035	-0.270601	-0.921217
H	7.170650	-2.295777	0.148588
H	5.725268	-4.276510	0.531535
H	3.322600	-4.206804	-0.168234
H	2.416908	-2.212447	-1.246095
C	-2.625536	2.582545	-0.849958
C	-1.966269	2.983346	0.366893
O	-0.833588	3.553839	0.367828
C	-2.651484	2.636846	1.589943
C	-3.804618	1.888447	1.596004
C	-4.366440	1.466493	0.380323
N	-5.503318	0.606021	0.385551
O	-6.001152	0.285277	1.465777

O	-5.944073	0.198382	-0.688347
C	-3.779434	1.834946	-0.840714
H	-2.149786	2.849123	-1.790298
H	-2.207264	2.967911	2.525528
H	-4.285179	1.606035	2.526631
H	-4.237282	1.501310	-1.766135
Br	0.133238	-3.239569	-0.027156

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -4804.51587791 Predicted Change= -1.642916D-08
Zero-point correction (ZPE)= -4803.8916 0.62421
Internal Energy (U)= -4803.8624 0.65343
Enthalpy (H)= -4803.8616 0.65423
Gibbs Free Energy (G)= -4803.9482 0.56762

Frequencies -- 22.0048 28.1715 38.5020

==========
#m062x/6-311++G(2df,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN)

Pointgroup= C1 Stoichiometry= C34H33BrN4O4S C1[X(C34H33BrN4O4S)] #Atoms= 77
Charge = 0 Multiplicity = 1

SCF Energy= -4807.54607763
==========

TS-VI

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
# M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
SCRF=(PCM,SOLVENT=acetonitrile)
opt=(maxcycle=250,calcfc,ts,noeigentest,gdiis) iop(1/8=18) freq=noraman
temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C34H33BrN4O4S C1[X(C34H33BrN4O4S)] #Atoms= 77
Charge = 0 Multiplicity = 1

SCF Energy= -4804.49953004 Predicted Change= -2.455645D-09
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00045	0.00180	[YES]	0.00045	0.00180	[YES]

Atomic Coordinates (Angstroms)

Type	X	Y	Z
C	0.496048	1.441301	-0.782390
N	-0.001451	0.455580	0.105620
C	1.209858	2.521761	-0.126880

N	1.964527	3.425972	-1.045800
C	2.847007	4.277672	-0.189320
C	1.016287	4.320241	-1.783610
O	0.189259	1.350870	-1.966640
C	0.143999	0.410540	1.600780
C	1.564639	0.214721	2.069180
C	-0.820450	-0.742270	1.985520
C	-1.077070	-0.276830	-0.249340
C	-2.759070	-1.632791	0.475130
C	-3.029960	-1.569232	-0.897190
S	-1.849050	-0.571241	-1.748830
C	-3.562899	-2.354572	1.351470
C	-4.662669	-3.006923	0.811600
C	-4.951099	-2.935483	-0.557970
C	-4.140179	-2.217662	-1.428830
C	2.333560	-0.854628	1.609430
C	3.653250	-0.987387	2.033890
C	4.202189	-0.064537	2.923460
C	3.430039	0.996602	3.392670
C	2.113519	1.138492	2.961910
N	-1.651120	-0.857961	0.787990
C	2.822538	2.690192	-2.082890
C	3.660168	1.593883	-1.508190
C	3.378979	0.310072	-1.765840
C	4.154390	-0.860677	-1.328830
C	5.509600	-0.783856	-0.981910
C	6.187571	-1.917016	-0.544800
C	5.521561	-3.139876	-0.442370
C	4.172371	-3.223337	-0.784610
C	3.499621	-2.094498	-1.241110
H	0.195597	3.203020	0.598470
H	1.884228	2.169312	0.650820
H	2.224076	4.773372	0.555940
H	3.345606	5.012162	-0.822210
H	3.579547	3.639143	0.304600
H	0.451986	4.894361	-1.047820
H	0.353327	3.693621	-2.378600
H	1.592756	4.986351	-2.427140
H	-0.233081	1.360480	1.991080
H	-1.422410	-0.497411	2.861260
H	-0.295550	-1.694960	2.113300
H	-3.336539	-2.395842	2.411380
H	-5.313628	-3.577973	1.464700
H	-5.822979	-3.449103	-0.948310
H	-4.365799	-2.159492	-2.487910
H	1.897140	-1.580828	0.923860
H	4.254980	-1.809477	1.655680
H	5.232509	-0.170676	3.249300
H	3.852248	1.717483	4.085540
H	1.512118	1.978961	3.302200
H	3.432137	3.467342	-2.553310
H	2.121648	2.291622	-2.814850
H	4.528808	1.864953	-0.911230
H	2.480149	0.085382	-2.341940
H	6.039549	0.160414	-1.072800

H	7.240110	-1.849075	-0.287100
H	6.054552	-4.021236	-0.098450
H	3.631852	-4.161067	-0.692680
H	2.438821	-2.168298	-1.471300
C	-2.241282	2.984759	-0.397170
C	-1.821472	2.986989	0.954150
O	-0.698613	3.566280	1.329830
C	-2.614952	2.287359	1.899360
C	-3.723622	1.562518	1.504610
C	-4.071732	1.537708	0.152010
N	-5.189681	0.726057	-0.282630
O	-5.824491	0.109727	0.561540
O	-5.442461	0.682747	-1.480570
C	-3.352182	2.264498	-0.796270
H	-1.672073	3.550839	-1.127050
H	-2.313782	2.313169	2.942500
H	-4.307671	0.993668	2.219430
H	-3.659732	2.241988	-1.835080
Br	0.223071	-3.340380	-0.272980

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -4804.49953004 Predicted Change= -2.455645D-09
Zero-point correction (ZPE)= -4803.8799 0.61953
Internal Energy (U)= -4803.8515 0.64800
Enthalpy (H)= -4803.8507 0.64880
Gibbs Free Energy (G)= -4803.9349 0.56458

Frequencies -- -1180.4115 25.5937 34.9476

==========

#m062x/6-311++G(2df,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN)

Pointgroup= C1 Stoichiometry= C34H33BrN4O4S C1[X(C34H33BrN4O4S)] #Atoms= 77
Charge = 0 Multiplicity = 1

SCF Energy= -4807.53018140

==========

VII

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

# M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
SCRF=(PCM,SOLVENT=acetonitrile) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C28H28BrN3OS C1[X(C28H28BrN3OS)] #Atoms= 62
Charge = 0 Multiplicity = 1

SCF Energy= -4292.70509363 Predicted Change= -1.963305D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00003	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00204	0.00180	[NO]	0.00204	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-5.316685	-3.034080	0.082918
C	-4.238964	-2.478194	0.764758
C	-3.362569	-1.680501	0.037977
C	-3.546900	-1.442054	-1.330016
C	-4.621664	-2.006252	-2.005865
C	-5.505361	-2.805117	-1.283865
N	-2.220320	-1.040058	0.499210
C	-1.600597	-0.289961	-0.407578
S	-2.296912	-0.362010	-1.979073
C	-1.714695	-0.769834	1.843601
C	-0.538182	0.219629	1.563977
C	0.797727	-0.288934	2.055911
N	-0.577973	0.385341	0.092078
C	0.092539	1.402233	-0.683562
O	-0.213844	1.424528	-1.904441
C	0.975564	2.181953	0.011206
N	1.767271	3.179166	-0.723620
C	0.873678	4.244064	-1.288356
C	2.728810	3.810503	0.226473
C	2.550135	2.567173	-1.898994
C	3.440783	1.438789	-1.495215
C	3.030700	0.170618	-1.619789
C	3.784658	-1.045858	-1.279945
C	3.232806	-2.288774	-1.614795
C	3.894494	-3.473918	-1.304491
C	5.124107	-3.432340	-0.650663
C	5.683356	-2.199636	-0.308928
C	5.020344	-1.018132	-0.618185
C	1.493053	-1.274862	1.353158
C	2.702680	-1.761098	1.840437
C	3.223401	-1.265508	3.035568
C	2.533135	-0.281379	3.739213
C	1.323520	0.207634	3.248696
H	1.272873	2.020889	1.033523
H	-6.020488	-3.657021	0.624439
H	-4.083276	-2.654663	1.823701
H	-4.771365	-1.824069	-3.064855
H	-6.352535	-3.253474	-1.791363
H	-1.375034	-1.692671	2.317873
H	-2.504678	-0.288954	2.423830
H	-0.777205	1.194223	2.002274
H	1.481045	4.957664	-1.848749
H	0.370568	4.734426	-0.456148
H	0.149914	3.751608	-1.936123
H	3.383327	3.035130	0.624618
H	2.159213	4.268215	1.035481
H	3.307227	4.564775	-0.308072

H	3.108637	3.396957	-2.340425
H	1.779205	2.227458	-2.590111
H	4.432079	1.681816	-1.119603
H	2.031198	0.002601	-2.025836
H	2.272342	-2.322440	-2.123889
H	3.450008	-4.427350	-1.572870
H	5.643884	-4.353116	-0.405053
H	6.637948	-2.160931	0.206857
H	5.461181	-0.068920	-0.328145
H	1.098007	-1.651444	0.411733
H	3.242881	-2.519309	1.279863
H	4.169127	-1.642333	3.412848
H	2.937103	0.112117	4.666734
H	0.787756	0.982736	3.791151
Br	-3.427762	2.053539	0.914328

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -4292.70509363 Predicted Change= -1.963305D-08
Zero-point correction (ZPE)= -4292.1927 0.51238
Internal Energy (U)= -4292.1701 0.53496
Enthalpy (H)= -4292.1693 0.53576
Gibbs Free Energy (G)= -4292.2431 0.46193

Frequencies -- 11.4696 21.2217 28.3522

==========
#m062x/6-311++G(2df,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN)

Pointgroup= C1 Stoichiometry= C28H28BrN3OS C1[X(C28H28BrN3OS)] #Atoms= 62
Charge = 0 Multiplicity = 1

SCF Energy= -4295.56143761
==========

TS-VIII-(2S,3S)-Major

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)
iop(1/8=18) freq=noraman temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C28H28N3OS(1+) C1[X(C28H28N3OS)] #Atoms= 61
Charge = 1 Multiplicity = 1

SCF Energy= -1720.71656134 Predicted Change= -2.596565D-10
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00069	0.00180	[YES]	0.00069	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	5.479846	1.208733	0.192579
C	4.196529	1.387652	0.695907
C	3.146605	0.830249	-0.025279
C	3.359371	0.117811	-1.212201
C	4.646493	-0.059688	-1.706981
C	5.702688	0.496455	-0.991688
N	1.790289	0.865379	0.284364
C	1.008992	0.211288	-0.565945
S	1.841453	-0.491274	-1.893986
C	1.022411	1.480589	1.368310
C	-0.450646	1.163766	0.955826
C	-1.258880	2.399370	0.625880
N	-0.282559	0.285764	-0.234066
C	-1.261979	-0.521645	-0.895676
O	-0.855492	-1.188379	-1.849927
C	-2.564200	-0.444448	-0.329201
H	-2.747091	0.247758	0.479967
N	-3.671212	-1.035346	-0.854455
C	-4.945786	-0.414640	-0.476274
C	-3.659353	-1.527198	-2.239139
C	-3.831129	-3.037572	0.238962
C	-2.470945	-3.196721	0.357010
C	-1.741803	-2.315935	1.156963
C	-0.286932	-2.330632	1.309968
C	0.564228	-2.918341	0.358662
C	1.946557	-2.879612	0.522718
C	2.512762	-2.243534	1.626494
C	1.679987	-1.665734	2.586515
C	0.299069	-1.709189	2.428454
C	-0.957678	3.149563	-0.513623
C	-1.678898	4.303627	-0.798722
C	-2.704398	4.715175	0.052617
C	-3.005872	3.969909	1.189123
C	-2.283904	2.812119	1.475680
H	6.322193	1.630131	0.730277
H	4.014905	1.935092	1.614549
H	4.820831	-0.612112	-2.623830
H	6.714832	0.373567	-1.360985
H	1.211642	2.555286	1.397623
H	1.295760	1.022500	2.320946
H	-0.939620	0.585754	1.744741
H	-4.918671	-0.142011	0.580080
H	-5.751190	-1.132499	-0.639811
H	-5.127269	0.482327	-1.078872
H	-3.536183	-0.690098	-2.935730
H	-4.615144	-2.018765	-2.425165
H	-2.843950	-2.232538	-2.372880
H	-4.419398	-3.652165	-0.436315
H	-4.383371	-2.501194	1.005897
H	-1.951709	-3.858552	-0.332687
H	-2.288569	-1.791095	1.939743

H	0.145240	-3.382288	-0.528286
H	2.587312	-3.331931	-0.228648
H	3.591523	-2.204131	1.742242
H	2.108783	-1.185308	3.461390
H	-0.344814	-1.268539	3.187316
H	-0.163866	2.830786	-1.185915
H	-1.442158	4.881126	-1.686401
H	-3.268291	5.614509	-0.173182
H	-3.804953	4.284542	1.852538
H	-2.520526	2.228179	2.362047

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1720.71656134 Predicted Change= -2.596565D-10
Zero-point correction (ZPE)= -1720.2082 0.50829
Internal Energy (U)= -1720.1876 0.52895
Enthalpy (H)= -1720.1868 0.52976
Gibbs Free Energy (G)= -1720.2546 0.46188

Frequencies -- -183.3728 15.2444 24.2295

==========

#m062x/6-311++G(2df,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN)

Pointgroup= C1 Stoichiometry= C28H28N3OS(1+) C1[X(C28H28N3OS)] #Atoms= 61
Charge = 1 Multiplicity = 1

SCF Energy= -1721.16802424

==========

IX

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062X/6-31G(d) scf=(direct,tight,maxcycle=300,xqc)
SCRF=(PCM,SOLVENT=CH3CN) opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman
temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C28H28N3OS(1+) C1[X(C28H28N3OS)] #Atoms= 61
Charge = 1 Multiplicity = 1

SCF Energy= -1720.76239806 Predicted Change= -1.058544D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00020	0.00180	[YES]	0.00020	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.025464	-0.368432	-0.941671

C	-2.390915	-0.523046	-0.286768
H	-2.439735	0.125452	0.606161
C	-2.473325	-2.008347	0.213914
H	-3.313328	-2.053635	0.916066
C	-1.204346	-2.328223	0.997127
C	-2.742430	-2.964630	-0.920626
H	-2.126554	-2.860603	-1.811376
C	-3.679201	-3.906842	-0.861286
H	-3.843656	-4.598590	-1.681371
H	-4.315765	-4.019652	0.014182
N	-3.431866	-0.181504	-1.239794
C	-3.287721	1.202315	-1.691035
H	-4.068314	1.416325	-2.425277
H	-2.319301	1.345373	-2.179680
H	-3.373978	1.930115	-0.864954
C	-4.756284	-0.368626	-0.654996
H	-4.886628	0.210252	0.276728
H	-4.939291	-1.424886	-0.449206
H	-5.505115	-0.030918	-1.375414
N	-0.017838	0.242339	-0.178441
O	-0.729157	-0.834008	-2.020771
C	-1.109742	-1.940786	2.337269
H	-1.981100	-1.517790	2.834296
C	0.089641	-2.073489	3.036378
H	0.145260	-1.761889	4.074991
C	1.212278	-2.603088	2.402261
H	2.149397	-2.700375	2.941195
C	1.118365	-3.025478	1.076371
H	1.982288	-3.456883	0.579214
C	-0.082452	-2.895125	0.381638
H	-0.136624	-3.217551	-0.654717
C	1.279153	0.126169	-0.527848
N	2.086765	0.688496	0.353395
C	1.354204	1.264904	1.485196
H	1.614923	2.317545	1.606294
H	1.596407	0.707104	2.392445
C	-0.135110	1.074790	1.060563
C	-0.883476	2.354058	0.771236
H	-0.652006	0.492512	1.824241
C	3.441915	0.547189	0.067012
C	3.616739	-0.161662	-1.127996
S	2.066210	-0.621501	-1.849495
C	4.520513	1.014100	0.811644
H	4.367376	1.558679	1.736924
C	5.790821	0.747619	0.319430
H	6.656201	1.093576	0.873762
C	5.975106	0.041220	-0.876869
H	6.980694	-0.148753	-1.235510
C	4.893291	-0.422446	-1.616250
H	5.037990	-0.968279	-2.541900
C	-0.536574	3.140631	-0.330340
H	0.283200	2.844880	-0.982313
C	-1.252761	4.298953	-0.611011
H	-0.985838	4.902024	-1.472566
C	-2.313694	4.680354	0.210782

H	-2.875033	5.581699	-0.013230
C	-2.652859	3.904986	1.316709
H	-3.478041	4.198369	1.957294
C	-1.940116	2.739877	1.595174
H	-2.212316	2.124994	2.449636

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -1720.76239806 Predicted Change= -1.058544D-09
Zero-point correction (ZPE)= -1720.2519 0.51048
Internal Energy (U)= -1720.2310 0.53134
Enthalpy (H)= -1720.2302 0.53214
Gibbs Free Energy (G)= -1720.2982 0.46417

Frequencies -- 18.0953 30.0661 44.1898

==========
#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=acetonitrile)

Pointgroup= C1 Stoichiometry= C28H28N3OS(1+) C1[X(C28H28N3OS)] #Atoms= 61
Charge = 1 Multiplicity = 1

SCF Energy= -1721.21148249
==========

TS-X

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
# M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
SCRF=(PCM,SOLVENT=acetonitrile)
opt=(maxcycle=250,calcfc,ts,noeigentest,gdiis) iop(1/8=18) freq=noraman
temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C34H32N4O4S C1[X(C34H32N4O4S)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -2232.07093010 Predicted Change= -1.405956D-10
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00016	0.00180	[YES]	0.00016	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.221427	-0.016720	-0.586677
C	1.745395	-0.186967	-0.492731
C	2.446373	0.956418	-1.278051
C	3.956219	0.804022	-1.192044
C	2.070414	2.342640	-0.815132

C	1.537180	3.272274	-1.601982
N	2.049203	-1.536807	-0.957029
C	3.275649	-2.134228	-0.454080
C	1.891627	-1.770632	-2.381832
N	-0.563612	-1.059856	0.115496
O	-0.314467	0.417089	-1.601891
C	4.605380	0.824988	0.047409
C	5.985277	0.667825	0.131086
C	6.742366	0.495469	-1.027468
C	6.109336	0.494188	-2.267827
C	4.726320	0.652388	-2.346257
C	-1.710854	-1.473207	-0.396250
N	-2.434745	-2.210096	0.448517
C	-1.732979	-2.392687	1.717743
C	-0.537911	-1.406473	1.572301
C	0.767555	-1.969087	2.084369
C	-3.596037	-2.755458	-0.089510
C	-3.765029	-2.342963	-1.416794
S	-2.453527	-1.267638	-1.942853
C	-4.511625	-3.592578	0.537855
C	-5.612564	-4.007427	-0.204727
C	-5.791559	-3.594810	-1.529021
C	-4.870491	-2.755041	-2.150149
C	1.553536	-1.187540	2.932517
C	2.730440	-1.701239	3.475658
C	3.120956	-3.005344	3.180342
C	2.344928	-3.785752	2.323466
C	1.178433	-3.266602	1.771204
O	0.141790	1.224682	0.891664
C	-0.665129	2.233230	0.805636
C	-0.302847	3.475564	1.406196
C	-1.137967	4.568791	1.367062
C	-2.369848	4.465413	0.708942
N	-3.244622	5.603488	0.660206
O	-4.319171	5.497243	0.075488
O	-2.887454	6.644397	1.205006
C	-2.763999	3.267838	0.105928
C	-1.930668	2.169301	0.154065
H	2.033496	-0.137673	0.559026
H	2.144571	0.864745	-2.327740
H	2.293624	2.575512	0.225274
H	1.308253	4.267122	-1.231235
H	1.291383	3.060424	-2.640091
H	3.182533	-3.226369	-0.499385
H	3.423596	-1.850383	0.591837
H	4.170633	-1.841611	-1.026107
H	0.958630	-1.328152	-2.740184
H	1.854503	-2.850729	-2.561204
H	2.724125	-1.361655	-2.980669
H	4.025324	0.945876	0.960569
H	6.471701	0.677672	1.102102
H	7.818732	0.368946	-0.962583
H	6.690268	0.369832	-3.177009
H	4.235653	0.649922	-3.317094
H	-1.415727	-3.433725	1.814712

H	-2.377016	-2.129635	2.557542
H	-0.753410	-0.474057	2.096190
H	-4.366081	-3.907198	1.565719
H	-6.343780	-4.663393	0.255126
H	-6.659848	-3.932272	-2.084324
H	-5.008362	-2.435260	-3.177367
H	1.241368	-0.170194	3.155685
H	3.334488	-1.085638	4.134742
H	4.031137	-3.411694	3.610292
H	2.653502	-4.796948	2.077122
H	0.594223	-3.874650	1.084663
H	0.657816	3.532640	1.908573
H	-0.856359	5.507251	1.830587
H	-3.728106	3.213776	-0.386677
H	-2.239415	1.241785	-0.312398

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -2232.07093010 Predicted Change= -1.405956D-10
Zero-point correction (ZPE)= -2231.4641 0.60680
Internal Energy (U)= -2231.4369 0.63394
Enthalpy (H)= -2231.4361 0.63475
Gibbs Free Energy (G)= -2231.5196 0.55129

Frequencies -- -130.1490 14.2368 17.6410

==========
#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=acetonitrile)

Pointgroup= C1 Stoichiometry= C34H32N4O4S C1[X(C34H32N4O4S)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -2232.70588267
==========

XI

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN) opt=(verytight,maxcycle=250,gdiis) iop(1/8=18)
freq=noraman temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C34H32N4O4S C1[X(C34H32N4O4S)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -2232.07663849 Predicted Change= -1.323685D-11
==========
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00000	[YES]	0.00000	0.00000	[YES]
Displ	0.00016	0.00000	[NO]	0.00016	0.00000	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.179257	0.229922	-0.676235
C	1.680473	-0.124917	-0.488219
C	2.578961	0.846701	-1.303520
C	4.048487	0.511175	-1.092843
C	2.386462	2.309583	-0.975085
C	2.155566	3.257428	-1.879596
N	1.854467	-1.540400	-0.818914
C	2.897371	-2.255651	-0.099677
C	1.906117	-1.870160	-2.236113
N	-0.642983	-0.709046	0.294455
O	-0.299344	0.187027	-1.845143
C	4.611476	0.527803	0.188651
C	5.954335	0.216848	0.379985
C	6.762017	-0.107759	-0.709953
C	6.217138	-0.107555	-1.991509
C	4.871459	0.204987	-2.177955
C	-1.369243	-1.686519	-0.168336
N	-2.109545	-2.305522	0.766879
C	-1.841415	-1.738862	2.088760
C	-0.960472	-0.500177	1.733875
C	0.279606	-0.334740	2.580700
C	-2.837812	-3.398313	0.312878
C	-2.660928	-3.572808	-1.067164
S	-1.579809	-2.339317	-1.758022
C	-3.656711	-4.242909	1.052815
C	-4.302065	-5.273988	0.374371
C	-4.134002	-5.451743	-1.001096
C	-3.311738	-4.599727	-1.737275
C	0.621408	0.932219	3.054691
C	1.797933	1.121708	3.775173
C	2.640857	0.040981	4.028944
C	2.301807	-1.228050	3.561601
C	1.126826	-1.413958	2.837686
O	0.038922	1.514971	0.073616
C	-1.025340	2.303601	-0.108092
C	-0.880722	3.625952	0.353016
C	-1.935331	4.515838	0.287880
C	-3.144857	4.081099	-0.252168
N	-4.260186	5.008384	-0.324972
O	-5.308576	4.617327	-0.817888
O	-4.101548	6.139498	0.111457
C	-3.310956	2.781757	-0.721675
C	-2.254818	1.886639	-0.653135
H	1.918403	-0.013224	0.575614
H	2.336077	0.708924	-2.363785
H	2.497635	2.579483	0.075917
H	2.068824	4.303002	-1.599162
H	2.037116	3.017814	-2.933984
H	2.655952	-3.326409	-0.095391
H	2.947678	-1.909605	0.935578
H	3.896907	-2.138526	-0.549663

H	1.137659	-1.314619	-2.773184
H	1.711239	-2.942707	-2.354297
H	2.892923	-1.660515	-2.685310
H	3.991022	0.769029	1.050349
H	6.371909	0.226331	1.382634
H	7.808788	-0.353632	-0.559676
H	6.837958	-0.351768	-2.848446
H	4.450193	0.204693	-3.180756
H	-1.313186	-2.468616	2.708415
H	-2.770005	-1.450705	2.583233
H	-1.562709	0.412355	1.802794
H	-3.785754	-4.098299	2.120197
H	-4.945999	-5.948287	0.928840
H	-4.647594	-6.262197	-1.506585
H	-3.180497	-4.737160	-2.805480
H	-0.029555	1.775792	2.839657
H	2.056672	2.112028	4.136521
H	3.559517	0.186520	4.588807
H	2.956582	-2.072759	3.753068
H	0.888185	-2.401398	2.448040
H	0.079802	3.924525	0.759586
H	-1.835511	5.534126	0.643102
H	-4.265636	2.478575	-1.134455
H	-2.362425	0.883381	-1.040612

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2232.07663849 Predicted Change= -1.323685D-11
Zero-point correction (ZPE)= -2231.4687 0.60789
Internal Energy (U)= -2231.4414 0.63520
Enthalpy (H)= -2231.4406 0.63601
Gibbs Free Energy (G)= -2231.5252 0.55134

Frequencies -- 9.6354 14.2098 19.0556

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=acetonitrile)

Pointgroup= C1 Stoichiometry= C34H32N4O4S C1[X(C34H32N4O4S)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -2232.70967192

==========

TS-XII

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

# M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
SCRF=(PCM,SOLVENT=acetonitrile)
opt=(maxcycle=250,calcfc,ts,noeigentest,gdiis) iop(1/8=18) freq=noraman
temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C34H32N4O4S C1[X(C34H32N4O4S)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -2232.07524636 Predicted Change= -3.351094D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00057	0.00180	[YES]	0.00057	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.110338	-0.455161	-0.879225
C	-1.611994	-0.187245	-0.654079
C	-2.492580	-1.283906	-1.322965
C	-3.951472	-1.056148	-0.950650
C	-2.121663	-2.702027	-0.958923
C	-1.840947	-3.650099	-1.848858
N	-1.902078	1.173331	-1.098787
C	-2.923048	1.893991	-0.356439
C	-2.078836	1.361206	-2.529710
N	0.621838	0.727514	0.224249
O	0.401607	-0.339489	-2.000184
C	-4.347916	-1.048948	0.391785
C	-5.676737	-0.828895	0.740601
C	-6.636029	-0.619866	-0.250233
C	-6.255956	-0.645270	-1.589777
C	-4.923123	-0.866136	-1.934792
C	1.051536	1.879590	-0.169616
N	1.698867	2.603287	0.774421
C	1.771228	1.848316	2.022921
C	0.991109	0.541050	1.650603
C	-0.240169	0.272292	2.487790
C	2.197617	3.824546	0.350937
C	1.900485	4.045188	-1.003382
S	0.991225	2.688067	-1.709451
C	2.902093	4.762313	1.096832
C	3.307118	5.931265	0.455673
C	3.014863	6.155475	-0.891006
C	2.306151	5.211596	-1.634964
C	-0.518389	-1.025121	2.918103
C	-1.694435	-1.301267	3.612947
C	-2.602522	-0.278358	3.881128
C	-2.329160	1.020990	3.454651
C	-1.153053	1.293420	2.760500
O	0.204097	-1.621070	-0.075884
C	1.390658	-2.243373	-0.196824
C	1.423500	-3.566668	0.272909
C	2.605533	-4.284053	0.266899
C	3.756743	-3.667522	-0.217546
N	5.006537	-4.412806	-0.227622
O	6.008147	-3.856480	-0.652193
O	4.997059	-5.561361	0.189609

C	3.746682	-2.358853	-0.689226
C	2.561906	-1.638243	-0.682843
H	-1.783131	-0.223330	0.426508
H	-2.388634	-1.184074	-2.409956
H	-2.130680	-2.940323	0.105161
H	-1.614699	-4.667914	-1.545342
H	-1.822772	-3.437416	-2.915409
H	-2.770354	2.970988	-0.502314
H	-2.834378	1.674940	0.710692
H	-3.950613	1.651960	-0.674910
H	-1.301402	0.821508	-3.071431
H	-1.981555	2.429497	-2.755904
H	-3.071490	1.034838	-2.886349
H	-3.610101	-1.202855	1.177509
H	-5.963485	-0.817973	1.788314
H	-7.672460	-0.442812	0.020389
H	-6.996658	-0.492317	-2.369029
H	-4.630933	-0.884433	-2.982382
H	1.295796	2.399757	2.837940
H	2.812064	1.645780	2.285094
H	1.660226	-0.322901	1.715323
H	3.125744	4.581808	2.143009
H	3.859284	6.677812	1.016708
H	3.341009	7.073039	-1.368619
H	2.078825	5.384491	-2.681757
H	0.183745	-1.824335	2.694158
H	-1.901353	-2.314520	3.943386
H	-3.520360	-0.492249	4.420184
H	-3.034550	1.821274	3.656676
H	-0.957344	2.305787	2.410805
H	0.501407	-4.006678	0.637665
H	2.646651	-5.304853	0.626190
H	4.663950	-1.913999	-1.055248
H	2.532100	-0.626120	-1.061785

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-2232.07524636	Predicted Change= -3.351094D-09
Zero-point correction (ZPE)=	-2231.4683	0.60693
Internal Energy (U)=	-2231.4410	0.63417
Enthalpy (H)=	-2231.4402	0.63497
Gibbs Free Energy (G)=	-2231.5257	0.54950

Frequencies -- -160.5532 3.7197 14.7184

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=acetonitrile)

Pointgroup= C1 Stoichiometry= C34H32N4O4S C1[X(C34H32N4O4S)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -2232.70783354

==========

XIII

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

# M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
SCRF=(PCM,SOLVENT=acetonitrile) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C19H20N2O4 C1[X(C19H20N2O4)] #Atoms= 45
Charge = 0 Multiplicity = 1

SCF Energy= -1145.87254909 Predicted Change= -3.228679D-09

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00233	0.00180	[NO]	0.00233	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.034080	0.256620	0.290090
C	1.469520	0.501220	-0.172340
C	2.305660	-0.732600	0.230030
C	3.785460	-0.533290	-0.032090
C	1.771750	-1.934310	-0.516640
C	1.046459	-2.898490	0.044950
N	1.992920	1.762650	0.332860
C	2.150320	1.841490	1.779660
C	1.238960	2.901910	-0.173460
O	-0.300330	-0.022660	1.411650
C	4.248550	-0.128850	-1.288370
C	5.611090	0.019469	-1.527850
C	6.533330	-0.236991	-0.513400
C	6.082500	-0.643571	0.739260
C	4.716300	-0.791651	0.975100
O	-0.852110	0.455981	-0.727550
C	-2.197210	0.249991	-0.478560
C	-3.062550	1.311141	-0.720050
C	-4.427430	1.124341	-0.545130
C	-4.876260	-0.122489	-0.128120
N	-6.314800	-0.323108	0.061730
O	-6.693900	-1.417928	0.441280
O	-7.058250	0.615082	-0.169780
C	-4.017400	-1.189499	0.113910
C	-2.655640	-0.999759	-0.066890
H	1.448980	0.578940	-1.265250
H	2.151810	-0.908520	1.300690
H	1.994970	-1.969060	-1.583560
H	0.670349	-3.736640	-0.533730
H	0.810179	-2.882820	1.106760
H	2.786290	1.027890	2.137050
H	1.194130	1.810870	2.324850

H	2.650270	2.785330	2.015530
H	0.220540	2.972100	0.249120
H	1.155950	2.835630	-1.262270
H	1.771001	3.823040	0.080110
H	3.540340	0.077230	-2.087840
H	5.954540	0.337989	-2.507400
H	7.596300	-0.119481	-0.700180
H	6.792600	-0.846391	1.535290
H	4.367710	-1.114730	1.953470
H	-2.661450	2.264961	-1.043590
H	-5.134260	1.924831	-0.723090
H	-4.415111	-2.144259	0.433940
H	-1.950180	-1.805599	0.102610

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-1145.87254909	Predicted Change= -3.228679D-09
Zero-point correction (ZPE)=	-1145.5061	0.36641
Internal Energy (U)=	-1145.4888	0.38374
Enthalpy (H)=	-1145.4880	0.38454
Gibbs Free Energy (G)=	-1145.5508	0.32171

Frequencies -- 14.0785 20.6738 28.8973

==========

#m062x/6-311++G(2df,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN)

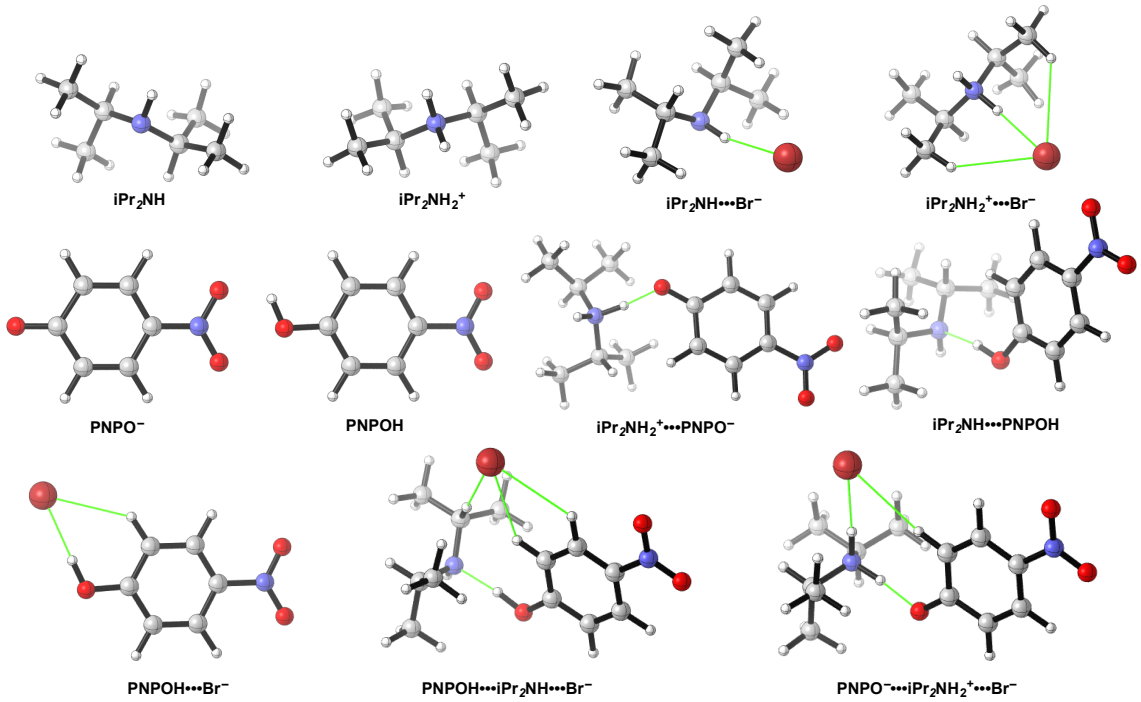
Pointgroup= C1 Stoichiometry= C19H20N2O4 C1[X(C19H20N2O4)] #Atoms= 45
Charge = 0 Multiplicity = 1

SCF Energy= -1146.25902910

==========

Salt and Complexes

Optimized ions and salt complexes.



Br-

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=acetonitrile) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= OH Stoichiometry= Br(1-) OH[O(Br)] #Atoms= 1
Charge = -1 Multiplicity = 1

SCF Energy= -2571.94190755 Predicted Change= 0.000000D+00

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00000	0.00180	[YES]	0.00000	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
Br	0.000000	0.000000	0.000000

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2571.94190755 Predicted Change= 0.000000D+00
Zero-point correction (ZPE)= -2571.9419 0.00000
Internal Energy (U)= -2571.9407 0.00120
Enthalpy (H)= -2571.9399 0.00200
Gibbs Free Energy (G)= -2571.9553 -0.01340

==========
#m062x/6-311++G(2df,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN)

Pointgroup= OH Stoichiometry= Br(1-) OH[O(Br)] #Atoms= 1
Charge = -1 Multiplicity = 1

SCF Energy= -2574.35485311
==========

iPr$_2$NH

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
# M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
SCRF=(PCM,SOLVENT=acetonitrile) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C6H15N C1[X(C6H15N)] #Atoms= 22
Charge = 0 Multiplicity = 1

SCF Energy= -292.269046065 Predicted Change= -3.958437D-08
==========
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00004	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00199	0.00180	[NO]	0.00199	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-0.013890	-0.666509	-0.082732
C	1.220069	0.109032	-0.260172
C	2.364370	-0.874077	-0.487732
C	1.546679	1.059072	0.896348
C	-1.222321	0.093901	0.253348
C	-2.369040	-0.896350	0.430608
C	-1.545741	1.096531	-0.850302
H	1.098489	0.704512	-1.174302
H	3.293240	-0.346347	-0.722382
H	2.128110	-1.555348	-1.309752
H	2.537210	-1.472507	0.415638
H	1.626019	0.497792	1.835718
H	2.501489	1.565393	0.721018
H	0.779079	1.828482	1.024368
H	-1.105341	0.651911	1.198678
H	-3.288020	-0.378240	0.720828

H	-2.549550	-1.432420	-0.507062
H	-2.136130	-1.633710	1.206798
H	-2.510241	1.574960	-0.655202
H	-1.601091	0.580631	-1.815582
H	-0.791031	1.885481	-0.925542
H	0.150900	-1.333679	0.673288

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -292.269046065 Predicted Change= -3.958437D-08

Zero-point correction (ZPE)=	-292.0608	0.20822
Internal Energy (U)=	-292.0538	0.21516
Enthalpy (H)=	-292.0530	0.21596
Gibbs Free Energy (G)=	-292.0875	0.18147

Frequencies -- 88.0981 108.0666 186.4900

==========

#m062x/6-311++G(2df,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN)

Pointgroup= C1 Stoichiometry= C6H15N C1[X(C6H15N)] #Atoms= 22
Charge = 0 Multiplicity = 1

SCF Energy= -292.368750385

==========

$iPr_2NH_2^+$

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=acetonitrile) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C6H16N(1+) C1[X(C6H16N)] #Atoms= 23
Charge = 1 Multiplicity = 1

SCF Energy= -292.729112296 Predicted Change= -4.303755D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00261	0.00180	[NO]	0.00261	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-0.000003	0.650046	-0.000139
C	-1.274114	-0.130711	0.260379
C	-1.533599	-1.100734	-0.880318
C	-2.404982	0.870096	0.449045
C	1.274156	-0.130742	-0.260392

C	1.533542	-1.100775	0.880322
C	2.405004	0.870109	-0.448888
H	-0.162473	1.273857	-0.801044
H	0.162465	1.274167	0.800524
H	-1.094955	-0.668753	1.193829
H	-2.495333	-1.588245	-0.705671
H	-0.772520	-1.881313	-0.949403
H	-1.591827	-0.573196	-1.838267
H	-2.186637	1.583768	1.248279
H	-2.602410	1.419774	-0.476913
H	-3.312704	0.327144	0.720441
H	1.095155	-0.668831	-1.193841
H	0.772235	-1.881110	0.949598
H	2.495077	-1.588613	0.705482
H	1.592174	-0.573229	1.838247
H	2.186761	1.583695	-1.248226
H	3.312841	0.327224	-0.720033
H	2.602141	1.419878	0.477076

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -292.729112296 Predicted Change= -4.303755D-08

Zero-point correction (ZPE)=	-292.5053	0.22376
Internal Energy (U)=	-292.4983	0.23080
Enthalpy (H)=	-292.4975	0.23160
Gibbs Free Energy (G)=	-292.5321	0.19691

Frequencies -- 90.2579 112.2002 173.8561

==========

#m062x/6-311++G(2df,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN)

Pointgroup= C1 Stoichiometry= C6H16N(1+) C1[X(C6H16N)] #Atoms= 23
Charge = 1 Multiplicity = 1

SCF Energy= -292.824447343

==========

$iPr_2NH_2^+ \bullet\bullet\bullet Br^-$

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

# M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
SCRF=(PCM,SOLVENT=acetonitrile) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C6H16BrN C1[X(C6H16BrN)] #Atoms= 24
Charge = 0 Multiplicity = 1

SCF Energy= -2864.70196049 Predicted Change= -2.228987D-08

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00004	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00076	0.00180	[YES]	0.00076	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	0.942349	0.086431	-0.590599
C	1.506021	-1.058178	0.206871
C	3.017341	-0.945996	0.319101
C	1.050293	-2.347569	-0.462209
C	1.234497	1.494291	-0.132569
C	0.428305	2.427660	-1.027199
C	0.864617	1.650111	1.336131
H	1.031661	-0.976419	1.188681
H	3.479481	-0.927075	-0.673969
H	3.397262	-1.820605	0.852701
H	3.330379	-0.055345	0.869971
H	1.489273	-2.446738	-1.460879
H	-0.040587	-2.368901	-0.541609
H	1.374444	-3.200528	0.138431
H	-0.641974	2.238828	-0.890669
H	0.680856	2.290810	-2.083059
H	0.641664	3.464430	-0.757679
H	2.305527	1.652103	-0.284929
H	-0.172553	1.336289	1.494211
H	0.960465	2.703331	1.610791
H	1.518558	1.071822	1.993821
H	-0.105771	-0.031431	-0.570929
H	1.240489	-0.011209	-1.567929
Br	-2.162630	-0.309894	0.096471

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -2864.70196049 Predicted Change= -2.228987D-08

Zero-point correction (ZPE)=	-2864.4779	0.22399
Internal Energy (U)=	-2864.4693	0.23259
Enthalpy (H)=	-2864.4685	0.23340
Gibbs Free Energy (G)=	-2864.5083	0.19356

Frequencies -- 61.4392 86.0946 97.0418

#m062x/6-311++G(2df,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN)

Pointgroup= C1 Stoichiometry= C6H16BrN C1[X(C6H16BrN)] #Atoms= 24
Charge = 0 Multiplicity = 1

SCF Energy= -2867.19650969

$iPr_2NH_2^+$•••$PNPO^-$

```
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
 ======================================================
 #M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=acetonitrile) opt=(maxcycle=250,gdiis) iop(1/8=18)
 freq=noraman temp=253.15
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
 ---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C12H20N2O3   C1[X(C12H20N2O3)]  #Atoms= 37
 Charge = 0         Multiplicity = 1
 ---------------------------------------------------------------------
 SCF Energy= -804.056031032       Predicted Change= -3.856173D-08
 ======================================================
 Optimization completed.          {Found       1       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00001 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00714 ||  0.00180   [ NO ]       0.00714 ||  0.00180   [ NO ]
 ---------------------------------------------------------------------
      Atomic              Coordinates (Angstroms)
       Type              X           Y           Z
 ---------------------------------------------------------------------
      N       -2.780121    0.186586   -0.537309
      C       -2.484522    1.573803   -0.034658
      C       -1.859085    1.516376    1.350054
      C       -3.720858    2.460428   -0.095482
      C       -3.765725   -0.639941    0.257619
      C       -3.036955   -1.616269    1.174066
      C       -4.682470   -1.366177   -0.718065
      H       -2.582111    1.180216    2.099866
      H       -1.527973    2.519402    1.630494
      H       -0.990735    0.850391    1.365764
      H       -4.474937    2.163125    0.638693
      H       -4.174267    2.446898   -1.091442
      H       -3.428251    3.489202    0.129286
      H       -1.745870    1.958397   -0.744436
      H       -3.136569    0.282838   -1.492657
      H       -4.356386    0.059347    0.855435
      H       -2.366244   -1.106686    1.869234
      H       -2.443430   -2.321060    0.587433
      H       -3.780505   -2.167486    1.755727
      H       -4.100986   -2.029205   -1.367659
      H       -5.243474   -0.661976   -1.340401
      H       -5.399021   -1.976165   -0.163071
      C        1.591644   -1.772204   -0.008838
      C        0.587840   -0.857160   -0.464669
      O       -0.623820   -1.245184   -0.624155
      C        1.018982    0.482572   -0.728791
      C        2.325203    0.873559   -0.540128
      C        3.268045   -0.055375   -0.081867
      N        4.624015    0.352713    0.117386
      O        4.935703    1.516098   -0.132088
      O        5.435819   -0.472362    0.532940
      C        2.895804   -1.382365    0.180620
      H        1.285046   -2.793979    0.191660
      H       -1.823379   -0.363709   -0.622309
      H        0.290467    1.196170   -1.103106
```

```
     H        2.638632      1.891037     -0.744436
     H        3.643724     -2.083752      0.532635
---------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 253.150 Kelvin       Pressure= 1.00000 Atm
=====================================================
 SCF Energy=     -804.056031032   Predicted Change= -3.856173D-08
 Zero-point correction (ZPE)=            -803.7365       0.31948
 Internal Energy (U)=                    -803.7227       0.33329
 Enthalpy (H)=                           -803.7219       0.33409
 Gibbs Free Energy (G)=                  -803.7752       0.28081
---------------------------------------------------------------------
 Frequencies --     18.5414              23.9927              41.7875

=====================================================
 #m062x/6-311++G(2df,p) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=CH3CN)
---------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C12H20N2O3   C1[X(C12H20N2O3)]  #Atoms= 37
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -804.340932519
=====================================================
```

$iPr_2NH_2^+$•••$PNPO^-$•••Br^-

```
---------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
=============================================
 # M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
 SCRF=(PCM,SOLVENT=acetonitrile) opt=(maxcycle=250,gdiis) iop(1/8=18)
 freq=noraman temp=253.15
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C12H20BrN2O3(1-)   C1[X(C12H20BrN2O3)]  #Atoms= 38
 Charge = -1        Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -3376.03132515       Predicted Change= -1.217424D-09
=============================================
 Optimization completed.          {Found       2       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00000 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00062 ||  0.00180   [ YES ]      0.00062 ||  0.00180   [ YES ]
---------------------------------------------------------------------
     Atomic             Coordinates (Angstroms)
      Type              X           Y           Z
---------------------------------------------------------------------
     N        2.153854     -0.718559      0.057494
     C        2.866750     -1.205339     -1.160910
     C        1.980652     -0.851231     -2.350356
     C        3.130210     -2.699907     -1.052057
     C        2.800181     -0.890267      1.393212
     C        4.161342     -0.208532      1.417007
     C        1.836653     -0.300386      2.418202
     H        1.987612      0.304356     -0.068237
     H        1.189638     -1.210521      0.089486
```

H	3.808178	-0.650812	-1.227971
H	1.789264	0.226630	-2.371221
H	1.024471	-1.380365	-2.272858
H	2.470043	-1.142582	-3.283003
H	2.191897	-3.229543	-0.854168
H	3.844212	-2.936089	-0.257940
H	3.543497	-3.066481	-1.995134
H	4.052361	0.837218	1.106892
H	4.880843	-0.701005	0.756390
H	4.564932	-0.233570	2.432550
H	2.902301	-1.967169	1.559886
H	2.235863	-0.432321	3.426833
H	0.862661	-0.796119	2.356065
H	1.701167	0.769883	2.225463
Br	1.821622	2.514201	-0.287864
C	-3.669697	-1.519373	0.146129
C	-2.458067	-2.165580	0.180339
C	-1.214405	-1.452593	0.111778
O	-0.098636	-2.079430	0.151673
C	-1.302677	-0.022891	0.001045
C	-2.517614	0.620324	-0.032609
C	-3.706892	-0.120278	0.039658
N	-4.963654	0.553367	0.004871
O	-4.978754	1.781569	-0.080658
O	-5.997819	-0.112847	0.060921
H	-4.601206	-2.071374	0.201126
H	-2.410215	-3.246983	0.263895
H	-0.390541	0.568004	-0.057652
H	-2.572086	1.700141	-0.115819

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -3376.03132515 Predicted Change= -1.217424D-09
Zero-point correction (ZPE)= -3375.7108 0.32044
Internal Energy (U)= -3375.6951 0.33614
Enthalpy (H)= -3375.6943 0.33694
Gibbs Free Energy (G)= -3375.7536 0.27768

Frequencies -- 9.6734 27.1851 38.6272

==========

#m062x/6-311++G(2df,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN)

Pointgroup= C1 Stoichiometry= C12H20BrN2O3(1-) C1[X(C12H20BrN2O3)] #Atoms= 38
Charge = -1 Multiplicity = 1

SCF Energy= -3378.71392060

==========

$iPr_2NH{\bullet\bullet\bullet}Br^-$

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062X/6-31G(d) scf=(direct,tight,maxcycle=300,xqc)
SCRF=(PCM,SOLVENT=CH3CN) opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman
temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C6H15BrN(1-) C1[X(C6H15BrN)] #Atoms= 23
Charge = -1 Multiplicity = 1

SCF Energy= -2864.22355380 Predicted Change= -2.465689D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00055	0.00180	[YES]	0.00055	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-1.103786	0.070018	-0.640031
C	-1.331008	1.434719	-0.146636
C	-0.958017	1.645693	1.326305
C	-0.522479	2.377788	-1.034901
C	-1.640213	-1.012760	0.186823
C	-1.169743	-2.334299	-0.413209
C	-3.163029	-0.944202	0.247148
H	-1.038865	2.703641	1.598752
H	-1.609272	1.078013	1.999057
H	0.075585	1.316520	1.487585
H	-2.397643	1.667189	-0.275480
H	-0.702050	3.424439	-0.770688
H	-0.781691	2.230223	-2.087750
H	0.546788	2.165449	-0.911428
H	-0.086881	-0.058792	-0.654335
H	-1.252997	-0.964584	1.220571
H	-1.518342	-3.183146	0.183860
H	-1.552472	-2.443280	-1.434058
H	-0.074695	-2.358951	-0.446906
H	-3.510529	-0.036962	0.752310
H	-3.565473	-1.805091	0.790528
H	-3.575386	-0.948671	-0.768486
Br	2.327924	-0.293650	0.080100

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2864.22355380 Predicted Change= -2.465689D-09
Zero-point correction (ZPE)= -2864.0144 0.20905
Internal Energy (U)= -2864.0058 0.21775
Enthalpy (H)= -2864.0050 0.21855
Gibbs Free Energy (G)= -2864.0453 0.17819

Frequencies -- 58.9298 73.4400 91.3848

==========

#M062X/6-311++G(2df,p) scf=(maxcycle=300,direct,tight) density=current

SCRF=(PCM,SOLVENT=CH3CN)

Pointgroup= C1 Stoichiometry= C6H15BrN(1-) C1[X(C6H15BrN)] #Atoms= 23
Charge = -1 Multiplicity = 1

SCF Energy= -2866.72701368
==========

$iPr_2NH•••PNPOH•••Br^-$

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
# M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
SCRF=(PCM,SOLVENT=acetonitrile) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C12H20BrN2O3(1-) C1[X(C12H20BrN2O3)] #Atoms= 38
Charge = -1 Multiplicity = 1

SCF Energy= -3376.02239353 Predicted Change= -2.468484D-08
==========
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00233	0.00180	[NO]	0.00233	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	2.673684	-1.179291	0.309567
C	2.683686	0.098609	1.054710
C	4.082691	0.693816	1.213031
C	2.038303	-0.138924	2.416413
C	3.110354	-1.129102	-1.102803
C	3.350345	-2.560484	-1.572144
C	2.049451	-0.450883	-1.964541
H	3.291523	-1.826169	0.807068
H	2.065252	0.812704	0.500356
H	4.544830	0.924626	0.249127
H	4.738055	-0.000171	1.753945
H	4.029559	1.625460	1.784824
H	2.641414	-0.833392	3.014262
H	1.033846	-0.561270	2.311499
H	1.959695	0.801939	2.968848
H	2.430747	-3.146608	-1.465455
H	4.140340	-3.045471	-0.988814
H	3.648476	-2.572457	-2.624106
H	4.052572	-0.569835	-1.189722
H	1.801969	0.560398	-1.623113
H	1.129237	-1.047594	-1.958506
H	2.403775	-0.384642	-2.997938
C	-3.160482	-1.932878	0.211350
C	-1.950232	-2.590648	0.316035
C	-0.739796	-1.870799	0.275338

O	0.397503	-2.554324	0.381739
C	-0.776347	-0.471469	0.126022
C	-1.985455	0.190281	0.017036
C	-3.168424	-0.544735	0.061449
N	-4.436879	0.144853	-0.052620
O	-4.428509	1.361126	-0.186202
O	-5.465918	-0.517517	-0.010884
H	-4.097069	-2.476296	0.243296
H	-1.909918	-3.668309	0.432331
H	1.231684	-1.947553	0.355790
H	0.137081	0.113791	0.084018
H	-1.991389	1.267961	-0.105941
Br	0.509472	2.889799	-0.318258

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -3376.02239353 Predicted Change= -2.468484D-08
Zero-point correction (ZPE)= -3375.7025 0.31983
Internal Energy (U)= -3375.6869 0.33547
Enthalpy (H)= -3375.6861 0.33628
Gibbs Free Energy (G)= -3375.7442 0.27812

Frequencies -- 24.7403 37.8003 41.9719

==========
#m062x/6-311++G(2df,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN)

Pointgroup= C1 Stoichiometry= C12H20BrN2O3(1-) C1[X(C12H20BrN2O3)] #Atoms= 38
Charge = -1 Multiplicity = 1

SCF Energy= -3378.70895061
==========

iPr$_2$NH•••PNPOH.log

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
# M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
SCRF=(PCM,SOLVENT=acetonitrile) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C12H20N2O3 C1[X(C12H20N2O3)] #Atoms= 37
Charge = 0 Multiplicity = 1

SCF Energy= -804.065886930 Predicted Change= -7.419587D-10
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00062	0.00180	[YES]	0.00062	0.00180	[YES]

Atomic Coordinates (Angstroms)

Type	X	Y	Z
N	-2.834050	-0.086239	-0.330210
C	-2.816380	1.390271	-0.259810
C	-4.178450	2.000731	0.067470
C	-2.277080	1.911631	-1.588180
C	-3.313520	-0.813769	0.865520
C	-3.429140	-2.291279	0.504010
C	-2.346870	-0.610669	2.026500
H	-3.441380	-0.341389	-1.113490
H	-2.113810	1.667331	0.535050
H	-4.524570	1.721291	1.066350
H	-4.927600	1.673031	-0.663190
H	-4.119020	3.092391	0.028350
H	-1.304530	1.464771	-1.819540
H	-2.162610	2.998271	-1.557100
H	-2.968500	1.666331	-2.402860
H	-4.128970	-2.441399	-0.324940
H	-3.792370	-2.863289	1.362110
H	-2.451970	-2.687519	0.208370
H	-4.307740	-0.449919	1.160400
H	-2.674520	-1.196909	2.889480
H	-2.287240	0.436091	2.339220
H	-1.342740	-0.948999	1.743940
C	2.971570	-1.129490	-0.716670
C	1.717440	-1.574280	-1.085470
C	0.564370	-0.857080	-0.710710
O	-0.615420	-1.330370	-1.099150
C	0.703690	0.320580	0.048970
C	1.959060	0.770370	0.418310
C	3.081890	0.042480	0.032630
N	4.396670	0.514860	0.419550
O	4.474390	1.552820	1.062320
O	5.371400	-0.145050	0.086830
H	3.864350	-1.673840	-0.999490
H	1.596020	-2.480730	-1.668360
H	-1.411720	-0.764589	-0.771190
H	-0.179620	0.876100	0.346070
H	2.077760	1.676460	1.000070

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -804.065886930 Predicted Change= -7.419587D-10
Zero-point correction (ZPE)= -803.7470 0.31886
Internal Energy (U)= -803.7331 0.33272
Enthalpy (H)= -803.7323 0.33353
Gibbs Free Energy (G)= -803.7856 0.28021

Frequencies -- 22.4149 28.4238 35.6880

==========

#m062x/6-311++G(2df,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN)

Pointgroup= C1 Stoichiometry= C12H20N2O3 C1[X(C12H20N2O3)] #Atoms= 37
Charge = 0 Multiplicity = 1

SCF Energy= -804.349225481
==========

PNPOH•••Br⁻

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=acetonitrile) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C6H5BrNO3(1-) C1[X(C6H5BrNO3)] #Atoms= 16
Charge = -1 Multiplicity = 1

SCF Energy= -3083.73440348 Predicted Change= -3.084019D-07
==========
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00005	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00384	0.00180	[NO]	0.00384	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.290602	1.342248	0.000253
C	1.030726	1.909648	0.000153
C	-0.113895	1.093201	-0.000182
O	-1.304187	1.701770	-0.000028
C	0.023104	-0.306533	-0.000323
C	1.284836	-0.874790	-0.000288
C	2.405671	-0.047371	0.000004
N	3.726717	-0.646319	0.000055
O	4.699896	0.094703	0.000009
O	3.810751	-1.866572	0.000123
H	3.182688	1.956355	0.000408
H	0.902321	2.986420	0.000247
H	-2.042513	1.034692	-0.002907
H	-0.869495	-0.924174	-0.000475
H	1.411210	-1.950687	-0.000412
Br	-3.652834	-0.477600	0.000121

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -3083.73440348 Predicted Change= -3.084019D-07
Zero-point correction (ZPE)= -3083.6244 0.10996
Internal Energy (U)= -3083.6169 0.11747
Enthalpy (H)= -3083.6161 0.11827
Gibbs Free Energy (G)= -3083.6555 0.07881

Frequencies -- 45.3894 64.0337 71.4132

```
=============================================================
 #m062x/6-311++G(2df,p) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=CH3CN)
------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C6H5BrNO3(1-)   C1[X(C6H5BrNO3)]  #Atoms= 16
 Charge = -1        Multiplicity = 1
------------------------------------------------------------------------
 SCF Energy= -3086.32666790
=============================================================
```

PNPOH

```
------------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
=============================================================
 #M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=acetonitrile) opt=(maxcycle=250,gdiis) iop(1/8=18)
 freq=noraman temp=253.15
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C6H5NO3   C1[X(C6H5NO3)]  #Atoms= 15
 Charge = 0         Multiplicity = 1
------------------------------------------------------------------------
 SCF Energy= -511.770747969       Predicted Change= -1.121550D-07
=============================================================
 Optimization completed.           {Found       2       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00013 ||  0.00045   [ YES ]      0.00003 ||  0.00030   [ YES ]
 Displ      0.00067 ||  0.00180   [ YES ]      0.00067 ||  0.00180   [ YES ]
------------------------------------------------------------------------
     Atomic              Coordinates (Angstroms)
      Type              X             Y          Z
------------------------------------------------------------------------
      C       -2.068711       0.015161       0.000009
      O       -3.414308       0.087993      -0.000037
      C       -1.366606       1.227831       0.000023
      C        0.016254       1.222580       0.000040
      C        0.685932       0.000715       0.000040
      N        2.141290      -0.007519       0.000057
      O        2.712450      -1.087380      -0.000026
      O        2.724132       1.066047      -0.000081
      C        0.005008      -1.212274       0.000029
      C       -1.380179      -1.204087       0.000000
      H       -3.799919      -0.802412      -0.000138
      H       -1.923966       2.157691       0.000013
      H        0.579754       2.147334       0.000046
      H        0.557999      -2.143384       0.000024
      H       -1.931281      -2.139433      -0.000028
------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 253.150 Kelvin       Pressure= 1.00000 Atm
=============================================================
 SCF Energy=     -511.770747969   Predicted Change= -1.121550D-07
 Zero-point correction (ZPE)=              -511.6615       0.10923
 Internal Energy (U)=                      -511.6557       0.11504
```

Enthalpy (H)= -511.6549 0.11584
Gibbs Free Energy (G)= -511.6884 0.08226

Frequencies -- 64.1266 116.3954 238.3685

==========
#m062x/6-311++G(2df,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN)

Pointgroup= C1 Stoichiometry= C6H5NO3 C1[X(C6H5NO3)] #Atoms= 15
Charge = 0 Multiplicity = 1

SCF Energy= -511.959317788
==========

PNPO$^-$

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=acetonitrile) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C6H4NO3(1-) C1[X(C6H4NO3)] #Atoms= 14
Charge = -1 Multiplicity = 1

SCF Energy= -511.298853998 Predicted Change= -7.208171D-07
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00044	0.00045	[YES]	0.00007	0.00030	[YES]
Displ	0.00104	0.00180	[YES]	0.00104	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.197218	0.000005	-0.000279
O	-3.448935	-0.000003	0.000434
C	-1.415496	1.225722	-0.000048
C	-0.047287	1.222033	-0.000200
C	0.658308	-0.000006	-0.000343
N	2.068760	0.000000	-0.000197
O	2.674717	-1.079574	0.000287
O	2.674708	1.079577	0.000297
C	-0.047292	-1.222036	-0.000189
C	-1.415488	-1.225717	-0.000050
H	-1.964918	2.163058	0.000181
H	0.515739	2.149181	-0.000241
H	0.515711	-2.149198	-0.000225
H	-1.964936	-2.163040	0.000173

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm
==========

SCF Energy= -511.20297 Predicted Change= -7.208171D-07
Zero-point correction (ZPE)= -511.6615 0.095881
Internal Energy (U)= -511.19729 0.101556
Enthalpy (H)= -511.19649 0.102358
Gibbs Free Energy (G)= -511.22981 0.069036

Frequencies -- 80.4392 101.9551 241.7296

==========
#m062x/6-311++G(2df,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN)

Pointgroup= C1 Stoichiometry= C6H4NO3(1-) C1[X(C6H4NO3)] #Atoms= 14
Charge = -1 Multiplicity = 1

SCF Energy= -511.495911108
==========

Ketene

III'

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN) opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman
temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C13H16NO(1+) C1[X(C13H16NO)] #Atoms= 31
Charge = 1 Multiplicity = 1

SCF Energy= -634.476817330 Predicted Change= -2.548699D-07
==========
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00004	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.02359	0.00180	[NO]	0.02359	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.471803	0.853915	-0.866160
N	-2.869630	-0.199925	0.069254
C	-2.932509	0.323084	1.476186
H	-3.678684	1.115576	1.509576
H	-1.954523	0.715331	1.754828
H	-3.206816	-0.501180	2.134946
C	-1.909417	-1.405186	-0.002663
C	-0.527104	-1.053944	0.428627
H	-0.331220	-1.010486	1.497086
C	0.448836	-0.837502	-0.464948
C	1.839510	-0.468055	-0.168942
H	0.212056	-0.950880	-1.523953
H	-1.940160	-1.729004	-1.044484

H	-2.361859	-2.170095	0.633764
C	-4.239427	-0.672940	-0.326944
H	-4.555211	-1.431829	0.388023
H	-4.181701	-1.095293	-1.329915
H	-4.915757	0.180444	-0.307691
H	-2.981234	0.928254	-1.816313
C	-1.433730	1.637949	-0.620248
O	-0.557826	2.370027	-0.429838
C	2.242021	-0.003669	1.091573
H	1.511151	0.118802	1.885357
C	3.571315	0.323063	1.327984
H	3.871556	0.684096	2.306527
C	4.517887	0.196412	0.310080
H	5.555437	0.453627	0.498852
C	4.126830	-0.251211	-0.949543
H	4.857237	-0.345977	-1.746632
C	2.794726	-0.575205	-1.187598
H	2.486931	-0.922389	-2.170476

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-634.476817330	Predicted Change= -2.548699D-07
Zero-point correction (ZPE)=	-634.2090	0.26777
Internal Energy (U)=	-634.1982	0.27854
Enthalpy (H)=	-634.1974	0.27935
Gibbs Free Energy (G)=	-634.2434	0.23337

Frequencies -- 24.3487 33.5800 43.7697

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=acetonitrile)

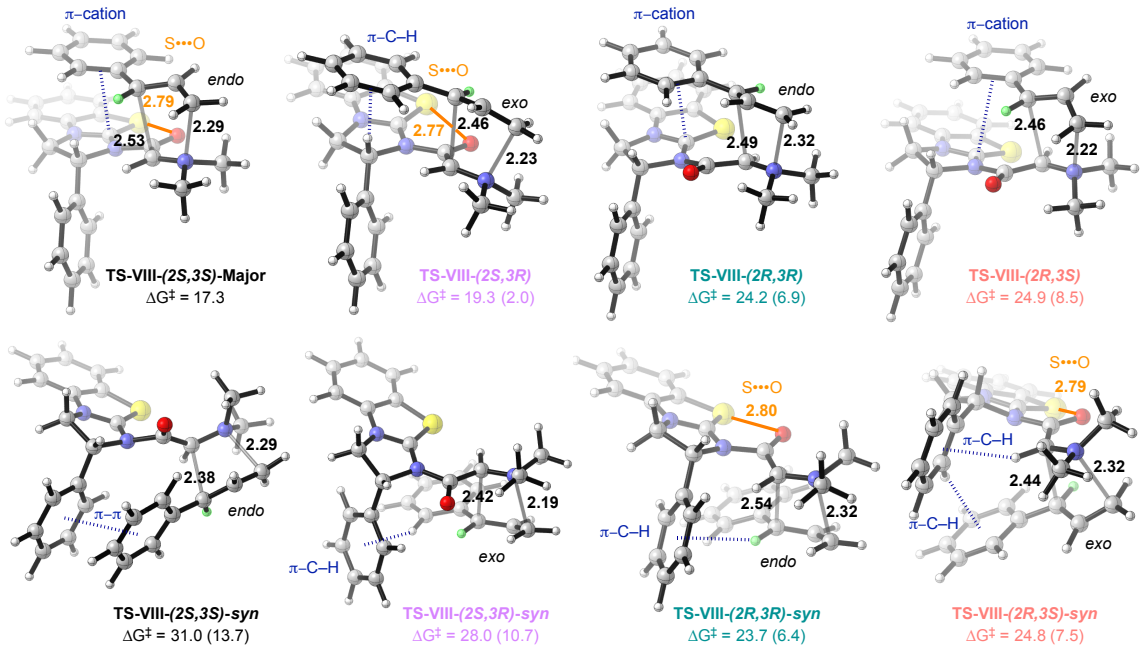
Pointgroup= C1 Stoichiometry= C13H16NO(1+) C1[X(C13H16NO)] #Atoms= 31
Charge = 1 Multiplicity = 1

SCF Energy= -634.682398499

==========

Stereodetermining [2,3]-rearrangement transitions structures

Diastereomeric transition structures (TSs) that determine the stereochemistry of the forming C–C bond during [2,3]-sigmatropic rearrangement.



TS-VIII-(2*S*,3*R*)-Major

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)
iop(1/8=18) freq=noraman temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C28H28N3OS(1+) C1[X(C28H28N3OS)] #Atoms= 61
Charge = 1 Multiplicity = 1

SCF Energy= -1720.71656134 Predicted Change= -2.596565D-10

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00069	0.00180	[YES]	0.00069	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	5.479846	1.208733	0.192579
C	4.196529	1.387652	0.695907
C	3.146605	0.830249	-0.025279
C	3.359371	0.117811	-1.212201
C	4.646493	-0.059688	-1.706981

C	5.702688	0.496455	-0.991688
N	1.790289	0.865379	0.284364
C	1.008992	0.211288	-0.565945
S	1.841453	-0.491274	-1.893986
C	1.022411	1.480589	1.368310
C	-0.450646	1.163766	0.955826
C	-1.258880	2.399370	0.625880
N	-0.282559	0.285764	-0.234066
C	-1.261979	-0.521645	-0.895676
O	-0.855492	-1.188379	-1.849927
C	-2.564200	-0.444448	-0.329201
H	-2.747091	0.247758	0.479967
N	-3.671212	-1.035346	-0.854455
C	-4.945786	-0.414640	-0.476274
C	-3.659353	-1.527198	-2.239139
C	-3.831129	-3.037572	0.238962
C	-2.470945	-3.196721	0.357010
C	-1.741803	-2.315935	1.156963
C	-0.286932	-2.330632	1.309968
C	0.564228	-2.918341	0.358662
C	1.946557	-2.879612	0.522718
C	2.512762	-2.243534	1.626494
C	1.679987	-1.665734	2.586515
C	0.299069	-1.709189	2.428454
C	-0.957678	3.149563	-0.513623
C	-1.678898	4.303627	-0.798722
C	-2.704398	4.715175	0.052617
C	-3.005872	3.969909	1.189123
C	-2.283904	2.812119	1.475680
H	6.322193	1.630131	0.730277
H	4.014905	1.935092	1.614549
H	4.820831	-0.612112	-2.623830
H	6.714832	0.373567	-1.360985
H	1.211642	2.555286	1.397623
H	1.295760	1.022500	2.320946
H	-0.939620	0.585754	1.744741
H	-4.918671	-0.142011	0.580080
H	-5.751190	-1.132499	-0.639811
H	-5.127269	0.482327	-1.078872
H	-3.536183	-0.690098	-2.935730
H	-4.615144	-2.018765	-2.425165
H	-2.843950	-2.232538	-2.372880
H	-4.419398	-3.652165	-0.436315
H	-4.383371	-2.501194	1.005897
H	-1.951709	-3.858552	-0.332687
H	-2.288569	-1.791095	1.939743
H	0.145240	-3.382288	-0.528286
H	2.587312	-3.331931	-0.228648
H	3.591523	-2.204131	1.742242
H	2.108783	-1.185308	3.461390
H	-0.344814	-1.268539	3.187316
H	-0.163866	2.830786	-1.185915
H	-1.442158	4.881126	-1.686401
H	-3.268291	5.614509	-0.173182
H	-3.804953	4.284542	1.852538

H -2.520526 2.228179 2.362047

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1720.71656134 Predicted Change= -2.596565D-10
Zero-point correction (ZPE)= -1720.2082 0.50829
Internal Energy (U)= -1720.1876 0.52895
Enthalpy (H)= -1720.1868 0.52976
Gibbs Free Energy (G)= -1720.2546 0.46188

Frequencies -- -183.3728 15.2444 24.2295

==========

#m062x/6-311++G(2df,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN)

Pointgroup= C1 Stoichiometry= C28H28N3OS(1+) C1[X(C28H28N3OS)] #Atoms= 61
Charge = 1 Multiplicity = 1

SCF Energy= -1721.16802424

==========

TS-VIII-(2*S*,3*R*)

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)
iop(1/8=18) freq=noraman temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C28H28N3OS(1+) C1[X(C28H28N3OS)] #Atoms= 61
Charge = 1 Multiplicity = 1

SCF Energy= -1720.71257160 Predicted Change= -1.365755D-07

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.04547	0.00180	[NO]	0.04547	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	5.846187	0.724501	0.206012
C	4.553985	1.083225	0.571604
C	3.507879	0.498946	-0.134348
C	3.735229	-0.414294	-1.171548
C	5.030554	-0.768787	-1.531050
C	6.082282	-0.187890	-0.829181
N	2.141650	0.688196	0.056725
C	1.364124	-0.003634	-0.766963
S	2.216251	-0.986174	-1.888739

C	1.357329	1.572414	0.921697
C	-0.105462	1.120241	0.621792
C	-1.044435	2.267490	0.335277
N	0.063617	0.202760	-0.544784
C	-0.929543	-0.526251	-1.281713
O	-0.520010	-1.162491	-2.257903
C	-2.233347	-0.472040	-0.730320
N	-3.355810	-0.943742	-1.358164
C	-3.460431	-3.101307	-0.824337
C	-4.599748	-0.451341	-0.752757
C	-3.416182	-0.979884	-2.826125
C	-1.957666	2.656378	1.314419
C	-2.818749	3.726754	1.080958
C	-2.773244	4.403387	-0.135192
C	-1.862682	4.012409	-1.116873
C	-0.997071	2.948996	-0.882470
C	-2.884684	-2.939807	0.420517
C	-1.561887	-2.513919	0.471094
C	-0.849611	-2.026286	1.654551
C	0.554397	-2.012028	1.650222
C	1.269099	-1.434656	2.696369
C	0.589668	-0.869113	3.775168
C	-0.806689	-0.898791	3.804739
C	-1.520325	-1.467637	2.755574
H	-2.396460	0.083463	0.182816
H	6.685497	1.162185	0.735288
H	4.362794	1.788765	1.372903
H	5.214161	-1.476986	-2.331746
H	7.101912	-0.448621	-1.090620
H	1.534484	2.612585	0.635766
H	1.620754	1.418615	1.969040
H	-0.480149	0.530298	1.463395
H	-4.516558	-3.328131	-0.940082
H	-3.519114	-2.871359	1.301556
H	-0.928716	-2.778010	-0.375290
H	-2.829249	-3.306205	-1.685696
H	-4.704687	0.626379	-0.924224
H	-4.578133	-0.650830	0.320775
H	-5.444698	-0.977131	-1.199143
H	-2.499604	-1.410429	-3.221126
H	-3.546316	0.035169	-3.218666
H	-4.272720	-1.591886	-3.114730
H	-1.999292	2.114835	2.256975
H	-3.528251	4.025115	1.846097
H	-3.448981	5.232057	-0.321511
H	-1.828745	4.535168	-2.067388
H	-0.293502	2.639342	-1.651824
H	1.085492	-2.460317	0.812463
H	2.355206	-1.425175	2.667991
H	1.141692	-0.409052	4.588560
H	-1.340109	-0.459496	4.642056
H	-2.606702	-1.444578	2.770276

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

```
=============================================
 SCF Energy=     -1720.71257160   Predicted Change= -1.365755D-07
 Zero-point correction (ZPE)=          -1720.2044      0.50811
 Internal Energy (U)=                  -1720.1836      0.52890
 Enthalpy (H)=                         -1720.1828      0.52970
 Gibbs Free Energy (G)=                -1720.2521      0.46043
 ---------------------------------------------------------------------
 Frequencies --   -232.8911             5.8446            23.4731

=============================================
 #m062x/6-311++G(2df,p) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=CH3CN)
 ---------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C28H28N3OS(1+)   C1[X(C28H28N3OS)]  #Atoms= 61
 Charge = 1         Multiplicity = 1
 ---------------------------------------------------------------------------
 SCF Energy= -1721.16341099
=============================================
```

TS-VIII-(2R,3R)

```
 ---------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
=============================================
 #m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=CH3CN) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)
 iop(1/8=18) freq=noraman temp=253.15
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
 ---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C28H28N3OS(1+)   C1[X(C28H28N3OS)]  #Atoms= 61
 Charge = 1         Multiplicity = 1
 ---------------------------------------------------------------------
 SCF Energy= -1720.70584159       Predicted Change= -8.277241D-09
=============================================
 Optimization completed.          {Found       2       times}
 Item      Max Val.   Criteria   Pass?     RMS Val.   Criteria   Pass?
 Force      0.00001 ||  0.00045   [ YES ]     0.00000 ||  0.00030   [ YES ]
 Displ      0.00170 ||  0.00180   [ YES ]     0.00170 ||  0.00180   [ YES ]
 ---------------------------------------------------------------------
     Atomic             Coordinates (Angstroms)
      Type              X           Y           Z
 ---------------------------------------------------------------------
      C         5.255299      1.115323     -0.604450
      C         4.044478      1.519133     -0.055500
      C         2.898289      0.859842     -0.486860
      C         2.955389     -0.165398     -1.437100
      C         4.168290     -0.567757     -1.983420
      C         5.317839      0.087524     -1.553380
      N         1.592839      1.063601     -0.058560
      C         0.686659      0.244810     -0.585740
      S         1.347630     -0.818039     -1.774540
      C         1.003098      1.983380      0.915000
      C        -0.503142      1.604859      0.861090
      C        -1.407563      2.718359      0.387750
      N        -0.537961      0.452229     -0.094560
```

C	-1.709160	-0.393322	-0.077200
C	-1.768790	-1.423182	-1.062960
N	-2.883559	-2.176092	-1.285780
C	-2.899189	-2.868652	-2.578420
C	-4.213309	-1.695173	-0.882210
C	-2.700818	-3.959062	0.181370
C	-1.891098	-3.271972	1.050490
C	-0.627769	-2.852331	0.624190
C	0.331881	-2.120040	1.455990
O	-2.526581	-0.140982	0.800120
C	-2.527453	3.070488	1.138590
C	-3.360224	4.102567	0.711540
C	-3.080784	4.778417	-0.473530
C	-1.966474	4.421828	-1.233180
C	-1.131933	3.395689	-0.802560
C	1.706791	-2.216099	1.176630
C	2.644710	-1.499938	1.912640
C	2.227680	-0.673579	2.956390
C	0.868370	-0.582820	3.260730
C	-0.071380	-1.295150	2.520600
H	-1.020030	-1.473111	-1.840080
H	-1.915938	-3.302132	-2.771010
H	-3.156859	-2.172583	-3.384900
H	-3.639128	-3.669763	-2.542290
H	-4.481400	-0.801754	-1.458870
H	-4.218580	-1.460233	0.177380
H	-4.930029	-2.490064	-1.092800
H	-2.267627	-4.498072	-0.656770
H	-3.726828	-4.208483	0.435690
H	-2.309099	-2.870692	1.971130
H	-0.193948	-3.381811	-0.224050
H	6.168968	1.605834	-0.287160
H	3.987238	2.310263	0.684340
H	4.217450	-1.365487	-2.716150
H	6.278080	-0.207596	-1.961590
H	1.178217	3.014900	0.602630
H	1.443938	1.809971	1.898040
H	-0.843372	1.231349	1.826950
H	-2.748702	2.529558	2.054220
H	-4.228494	4.375027	1.302930
H	-3.730165	5.581527	-0.807490
H	-1.747444	4.944068	-2.158960
H	-0.264003	3.121539	-1.400060
H	2.036441	-2.862259	0.366780
H	3.700151	-1.584338	1.669360
H	2.955139	-0.109018	3.531660
H	0.536979	0.054190	4.076070
H	-1.127760	-1.188961	2.750140

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1720.70584159 Predicted Change= -8.277241D-09
Zero-point correction (ZPE)= -1720.1977 0.50811
Internal Energy (U)= -1720.1771 0.52873

```
 Enthalpy (H)=                          -1720.1763       0.52953
 Gibbs Free Energy (G)=                 -1720.2431       0.46269
---------------------------------------------------------------------
 Frequencies --   -199.6368             28.5073             33.2866

=============================================
 #m062x/6-311++G(2df,p) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=CH3CN)
---------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C28H28N3OS(1+)   C1[X(C28H28N3OS)]  #Atoms= 61
 Charge = 1         Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -1721.15790768
=============================================
```

TS-VIII-(2*R*,3*S*)

```
---------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
=============================================
 #m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=CH3CN) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)
 iop(1/8=18) freq=noraman temp=253.15
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C28H28N3OS(1+)   C1[X(C28H28N3OS)]  #Atoms= 61
 Charge = 1         Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -1720.70305839       Predicted Change= -7.149331D-09
=============================================
 Optimization completed.          {Found       2       times}
 Item      Max Val.   Criteria   Pass?      RMS Val.   Criteria   Pass?
 Force      0.00003 ||  0.00045   [ YES ]     0.00000 ||  0.00030   [ YES ]
 Displ      0.00156 ||  0.00180   [ YES ]     0.00156 ||  0.00180   [ YES ]
---------------------------------------------------------------------
     Atomic             Coordinates (Angstroms)
      Type              X           Y           Z
---------------------------------------------------------------------
      C       -4.860805     2.141843     0.262400
      C       -3.600664     2.278649    -0.309250
      C       -2.581366     1.481627     0.199440
      C       -2.808009     0.581257     1.245300
      C       -4.067619     0.446541     1.814890
      C       -5.092027     1.240943     1.308420
      N       -1.261057     1.413174    -0.230590
      C       -0.511879     0.491392     0.372680
      S       -1.344791    -0.326636     1.641760
      C       -0.550945     2.038772    -1.345330
      C        0.904824     1.552608    -1.112870
      C        1.825816     2.624486    -0.574320
      N        0.727061     0.440009    -0.128060
      C        1.820229    -0.485384     0.056300
      C        1.547976    -1.649003     0.823240
      N        2.524244    -2.539336     1.192950
      C        2.063581    -3.514184     2.188850
      C        3.893455    -2.074309     1.460620
```

C	2.791581	-3.842426	-0.581870
C	1.449560	-3.861373	-0.906670
C	0.860083	-2.666392	-1.307150
C	-0.578626	-2.397498	-1.377660
O	2.853369	-0.204486	-0.546410
C	2.995407	2.938983	-1.263190
C	3.835550	3.946451	-0.795790
C	3.513081	4.637602	0.369560
C	2.347451	4.320765	1.066280
C	1.504728	3.318737	0.594680
C	-1.043693	-1.322147	-2.151670
C	-2.389222	-0.963104	-2.146540
C	-3.298874	-1.675491	-1.367150
C	-2.855837	-2.765792	-0.615780
C	-1.512678	-3.121526	-0.618140
H	0.559565	-1.840621	1.213440
H	1.136330	-3.972822	1.839400
H	1.888703	-3.020194	3.151410
H	2.823379	-4.287626	2.307970
H	3.927826	-1.555629	2.425480
H	4.215997	-1.403680	0.669100
H	4.544933	-2.949481	1.497960
H	3.290288	-4.714288	-0.167730
H	3.436302	-3.074308	-1.002900
H	0.831578	-4.695221	-0.580090
H	1.497635	-1.954373	-1.829520
H	-5.679563	2.745225	-0.113820
H	-3.415473	2.971539	-1.122910
H	-4.246431	-0.258299	2.619040
H	-6.086557	1.153956	1.731570
H	-0.633572	3.125032	-1.289560
H	-0.973356	1.679993	-2.288090
H	1.328453	1.125627	-2.022600
H	3.251566	2.385913	-2.162410
H	4.743640	4.186929	-1.339280
H	4.169003	5.420570	0.736800
H	2.093162	4.855595	1.975720
H	0.595948	3.080959	1.144840
H	-0.337082	-0.770339	-2.769630
H	-2.729260	-0.125653	-2.750380
H	-4.344193	-1.382699	-1.344350
H	-3.558958	-3.327541	-0.008510
H	-1.178370	-3.945587	0.006360

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1720.70305839 Predicted Change= -7.149331D-09

Zero-point correction (ZPE)=	-1720.1948	0.50821
Internal Energy (U)=	-1720.1742	0.52882
Enthalpy (H)=	-1720.1734	0.52962
Gibbs Free Energy (G)=	-1720.2406	0.46239

Frequencies -- -228.2772 23.0838 31.5932

```
=============================================
 #m062x/6-311++G(2df,p) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=CH3CN)
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C28H28N3OS(1+)   C1[X(C28H28N3OS)]  #Atoms= 61
 Charge = 1         Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -1721.15498616
=============================================
```

TS-VIII-(2*S*,3*S*)-*syn*

```
---------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
=============================================
 #m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=CH3CN) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)
 iop(1/8=18) freq=noraman temp=253.15
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C28H28N3OS(1+)   C1[X(C28H28N3OS)]  #Atoms= 61
 Charge = 1         Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -1720.69339959       Predicted Change= -1.106786D-10
=============================================
 Optimization completed.          {Found       2       times}
 Item      Max Val.   Criteria   Pass?     RMS Val.   Criteria   Pass?
 Force      0.00000 ||  0.00045   [ YES ]     0.00000 ||  0.00030   [ YES ]
 Displ      0.00025 ||  0.00180   [ YES ]     0.00025 ||  0.00180   [ YES ]
---------------------------------------------------------------------
     Atomic             Coordinates (Angstroms)
      Type              X           Y           Z
---------------------------------------------------------------------
      C         0.546034    1.302563    0.786575
      O         1.060958    1.341500    1.888755
      C         0.575344    2.241049   -0.292485
      N         0.699196    3.596675   -0.129200
      C         0.008707    4.412747   -1.129580
      C         0.628340    4.150083    1.225523
      N        -0.252207    0.114018    0.460580
      C        -1.550059    0.213235    0.132916
      N        -2.287454   -0.779124    0.619968
      C        -1.506162   -1.579425    1.573754
      C        -0.062238   -1.190401    1.149817
      C         0.496713   -2.246632    0.215374
      S        -2.454397    1.383778   -0.747495
      C        -3.928050    0.461130   -0.405077
      C        -3.651081   -0.683015    0.351989
      C        -5.227122    0.763274   -0.795051
      C        -6.237932   -0.108347   -0.402623
      C        -5.956909   -1.249260    0.358597
      C        -4.658540   -1.556671    0.746898
      C         1.072073   -3.385289    0.781513
      C         1.473947   -4.445723   -0.025039
      C         1.301947   -4.375497   -1.405927
      C         0.735119   -3.237865   -1.975032
```

C	0.330783	-2.177061	-1.167559
H	0.200327	1.908673	-1.253611
H	0.159232	3.979553	-2.120301
H	0.429180	5.420326	-1.115582
H	-1.065925	4.465785	-0.915147
H	-0.369276	3.990569	1.654437
H	0.829550	5.220548	1.165482
H	1.374336	3.669410	1.855469
H	-1.693550	-2.643852	1.436595
H	-1.769073	-1.270869	2.588976
H	0.586175	-1.027988	2.012645
H	-5.445239	1.648029	-1.382496
H	-7.261025	0.103458	-0.692911
H	-6.766394	-1.908755	0.651309
H	-4.432189	-2.440151	1.333603
H	1.208768	-3.440616	1.859242
H	1.926863	-5.323552	0.425408
H	1.614539	-5.202173	-2.036374
H	0.606148	-3.172589	-3.051047
H	-0.094003	-1.287469	-1.625125
C	2.900034	4.007440	-0.604470
C	3.293527	2.784070	-0.126271
C	2.831482	1.620205	-0.753454
C	3.213879	0.270921	-0.318231
C	3.553353	-0.017431	1.015032
C	4.003579	-1.284617	1.370825
C	4.130078	-2.283594	0.406497
C	3.781331	-2.015686	-0.915724
C	3.316659	-0.755255	-1.269787
H	3.143787	4.928779	-0.082864
H	2.572877	4.112379	-1.635417
H	3.760704	2.714464	0.853297
H	2.548213	1.703782	-1.801647
H	3.459501	0.753629	1.771662
H	4.263169	-1.491485	2.404966
H	4.484283	-3.271079	0.687098
H	3.860768	-2.793579	-1.668717
H	3.045207	-0.548340	-2.302527

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1720.69339959 Predicted Change= -1.106786D-10

Zero-point correction (ZPE)=	-1720.1857	0.50769
Internal Energy (U)=	-1720.1651	0.52826
Enthalpy (H)=	-1720.1643	0.52906
Gibbs Free Energy (G)=	-1720.2320	0.46137

Frequencies -- -220.1662 12.4081 24.8991

==========

#m062x/6-311++G(2df,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN)

Pointgroup= C1 Stoichiometry= C28H28N3OS(1+) C1[X(C28H28N3OS)] #Atoms= 61

Charge = 1 Multiplicity = 1

SCF Energy= -1721.14564693

==========

TS-VIII-(2*S*,3*R*)-*syn*

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)
iop(1/8=18) freq=noraman temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C28H28N3OS(1+) C1[X(C28H28N3OS)] #Atoms= 61
Charge = 1 Multiplicity = 1

SCF Energy= -1720.70159382 Predicted Change= -2.417687D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00086	0.00180	[YES]	0.00086	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.623950	-0.060102	-1.420751
N	0.227160	0.283689	-1.304481
O	2.334240	0.780747	-1.969451
C	2.041128	-1.293653	-0.855111
N	3.287048	-1.826194	-1.106851
C	3.404797	-3.214144	-0.644991
C	3.936388	-1.623375	-2.410991
C	-0.847351	-0.412890	-0.907011
N	-1.984200	0.142681	-1.331671
C	-1.710979	1.254691	-2.249361
C	-0.256699	1.590919	-1.873181
C	-0.111678	2.684289	-0.832551
S	-1.102442	-1.824650	0.042209
C	-2.843482	-1.665448	-0.211791
C	-3.145411	-0.534928	-0.978961
C	-3.849893	-2.499777	0.261319
C	-5.162972	-2.171246	-0.058671
C	-5.460411	-1.040776	-0.830301
C	-4.457641	-0.203357	-1.302551
C	1.111463	3.351248	-0.716661
C	1.301364	4.303608	0.281809
C	0.269514	4.603059	1.169719
C	-0.954797	3.949170	1.052679
C	-1.144328	2.992050	0.057999
H	1.337658	-1.947702	-0.360531
H	2.780556	-3.873303	-1.258891
H	3.083577	-3.272584	0.396919
H	4.447456	-3.526945	-0.716031

H	3.890409	-0.573745	-2.686521
H	3.439188	-2.232064	-3.174961
H	4.977708	-1.939036	-2.319821
H	-1.809869	0.898231	-3.277501
H	-2.393928	2.086001	-2.077391
H	0.349991	1.807839	-2.750401
H	-3.616634	-3.375967	0.855869
H	-5.968413	-2.804515	0.296289
H	-6.493831	-0.811785	-1.065951
H	-4.682860	0.672004	-1.901841
H	1.915903	3.106067	-1.402651
H	2.255824	4.813957	0.363469
H	0.417315	5.346569	1.946359
H	-1.765036	4.178421	1.737799
H	-2.102598	2.482221	0.003279
C	4.622889	-0.786625	0.283229
C	3.728579	-0.811714	1.335609
C	2.543680	-0.095743	1.192109
C	1.347069	-0.251072	2.025429
C	0.410230	0.791799	2.064279
C	-0.781720	0.657870	2.770009
C	-1.051711	-0.521560	3.462229
C	-0.117832	-1.559621	3.449729
C	1.066478	-1.431062	2.733469
H	5.515058	-1.406886	0.276799
H	3.809068	-1.592934	2.088499
H	2.583620	0.823187	0.607219
H	4.621810	0.058975	-0.401031
H	0.634761	1.719459	1.544299
H	-1.495579	1.476931	2.778549
H	-1.982581	-0.632739	4.009629
H	-0.323293	-2.479851	3.988109
H	1.766058	-2.262273	2.701309

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1720.70159382 Predicted Change= -2.417687D-09
Zero-point correction (ZPE)= -1720.1931 0.50843
Internal Energy (U)= -1720.1727 0.52886
Enthalpy (H)= -1720.1719 0.52966
Gibbs Free Energy (G)= -1720.2378 0.46370

Frequencies -- -255.7371 31.8841 36.2440

==========

#m062x/6-311++G(2df,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN)

Pointgroup= C1 Stoichiometry= C28H28N3OS(1+) C1[X(C28H28N3OS)] #Atoms= 61
Charge = 1 Multiplicity = 1

SCF Energy= -1721.15285895

==========

TS-VIII-(2*R*,3*R*)-syn

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)
iop(1/8=18) freq=noraman temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C28H28N3OS(1+) C1[X(C28H28N3OS)] #Atoms= 61
Charge = 1 Multiplicity = 1

SCF Energy= -1720.70704448 Predicted Change= -4.962353D-09

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00220	0.00180	[NO]	0.00220	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.018027	-0.684762	-1.249917
N	0.032890	0.334870	-0.963978
C	2.347961	-0.185790	-1.256891
N	3.457647	-0.833834	-1.692964
C	4.483669	-0.005489	-2.332283
C	3.331489	-2.174309	-2.266078
O	0.585094	-1.820176	-1.444251
C	0.158671	1.823056	-1.115939
C	0.892142	2.474179	0.036074
C	-1.327044	2.289146	-1.219339
C	-1.256487	0.010453	-0.835572
C	-3.416665	0.779623	-0.755140
C	-3.606744	-0.597513	-0.588167
S	-2.074456	-1.484104	-0.634746
C	-4.485012	1.670004	-0.779419
C	-5.760474	1.138435	-0.627490
C	-5.958975	-0.236577	-0.454876
C	-4.885692	-1.121429	-0.435096
C	2.095136	3.146075	-0.181453
C	2.767573	3.745849	0.881949
C	2.232862	3.685437	2.165834
C	1.018816	3.034150	2.384556
C	0.349246	2.435223	1.321995
H	2.500364	0.860635	-1.037209
H	4.575084	0.940541	-1.795453
H	4.217310	0.195953	-3.376080
H	5.438563	-0.532961	-2.294973
H	2.810610	-2.130468	-3.229241
H	2.765613	-2.806662	-1.584507
H	4.334519	-2.578724	-2.408685
H	0.682753	2.015817	-2.055057
H	-1.597272	2.610274	-2.227500
H	-1.551380	3.082541	-0.505146

H	-4.324159	2.734242	-0.913189
H	-6.616116	1.804436	-0.642254
H	-6.965429	-0.622405	-0.336147
H	-5.040018	-2.187137	-0.305353
H	2.508884	3.204822	-1.185971
H	3.705319	4.261789	0.703661
H	2.754586	4.152669	2.994779
H	0.592278	2.994316	3.382095
H	-0.599908	1.931317	1.496683
C	4.548104	-1.285525	0.299145
C	3.409317	-1.782682	0.876701
C	2.313271	-0.958493	1.162873
C	1.040253	-1.501038	1.638068
C	0.205539	-0.724956	2.460568
C	-0.985231	-1.236613	2.964339
C	-1.367820	-2.543404	2.660850
C	-0.554272	-3.326230	1.842459
C	0.625714	-2.807695	1.320955
H	4.757575	-0.218957	0.324387
H	5.376076	-1.933557	0.026188
H	3.281614	-2.861615	0.930000
H	2.495444	0.096453	1.367200
H	0.525079	0.275207	2.735811
H	-1.607003	-0.620701	3.607153
H	-2.293514	-2.947845	3.058609
H	-0.849856	-4.341037	1.593457
H	1.229144	-3.417361	0.656621
N	-2.061375	1.069068	-0.883369

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1720.70704448 Predicted Change= -4.962353D-09
Zero-point correction (ZPE)= -1720.1987 0.50826
Internal Energy (U)= -1720.1781 0.52893
Enthalpy (H)= -1720.1773 0.52973
Gibbs Free Energy (G)= -1720.2443 0.46265

Frequencies -- -191.0932 25.8324 31.5746

==========

#m062x/6-311++G(2df,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN)

Pointgroup= C1 Stoichiometry= C28H28N3OS(1+) C1[X(C28H28N3OS)] #Atoms= 61
Charge = 1 Multiplicity = 1

SCF Energy= -1721.15858559

==========

TS-VIII-(2*R*,3*S*)-*syn*

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current

SCRF=(PCM,SOLVENT=CH3CN) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)
iop(1/8=18) freq=noraman temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C28H28N3OS(1+) C1[X(C28H28N3OS)] #Atoms= 61
Charge = 1 Multiplicity = 1

SCF Energy= -1720.70521686 Predicted Change= -4.355132D-09

==========

Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00349	0.00180	[NO]	0.00349	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.641094	-1.559758	-0.634315
N	-0.284151	-0.473847	-0.847640
C	2.006022	-1.179430	-0.517547
N	3.034702	-2.075371	-0.568132
C	4.350260	-1.442741	-0.679468
C	2.917383	-3.314092	-1.343606
O	0.149108	-2.678967	-0.467500
C	-1.587901	-0.664665	-0.602628
N	-2.338204	0.363054	-0.982666
C	-1.506703	1.443488	-1.519272
C	-0.185999	0.692919	-1.805100
C	1.051621	1.540069	-1.695900
S	-2.470595	-1.943454	0.132095
C	-3.935806	-0.952255	0.008647
C	-3.682128	0.267191	-0.630847
C	-5.219868	-1.275164	0.433257
C	-6.230560	-0.344637	0.212598
C	-5.966720	0.875666	-0.420969
C	-4.687671	1.201349	-0.855486
C	1.314447	2.303366	-0.557107
C	2.501638	3.024643	-0.465971
C	3.423320	2.995258	-1.511819
C	3.156798	2.243790	-2.654289
C	1.973101	1.516381	-2.743978
H	2.267864	-0.132216	-0.526184
H	4.442953	-0.673025	0.090375
H	4.473543	-0.984488	-1.668685
H	5.123718	-2.196701	-0.526634
H	3.036458	-3.101346	-2.413012
H	1.946519	-3.770196	-1.165513
H	3.708901	-3.994557	-1.022987
H	-1.395715	2.224768	-0.761352
H	-1.939478	1.860096	-2.428436
H	-0.235191	0.254738	-2.807484
H	-5.424910	-2.220008	0.924344
H	-7.239558	-0.571431	0.538895
H	-6.773516	1.583102	-0.577588
H	-4.475318	2.144037	-1.347656

H	0.614165	2.311583	0.275240
H	2.707955	3.604102	0.428389
H	4.348781	3.557255	-1.435292
H	3.870170	2.217881	-3.471610
H	1.768064	0.915673	-3.626025
C	3.123929	-2.898311	1.596744
C	2.805974	-1.678164	2.136361
C	1.542549	-1.131750	1.879068
C	1.123077	0.223118	2.245247
C	-0.247403	0.524003	2.317590
C	-0.688657	1.800046	2.654774
C	0.236440	2.803695	2.941064
C	1.601623	2.518796	2.879620
C	2.041432	1.249338	2.522520
H	4.122498	-3.317974	1.677853
H	2.335438	-3.575632	1.278216
H	3.598267	-1.051864	2.540471
H	0.733984	-1.840054	1.709494
H	-0.973466	-0.265763	2.135861
H	-1.753513	2.006500	2.705240
H	-0.102081	3.798755	3.211549
H	2.328041	3.295862	3.098934
H	3.107902	1.058147	2.444019

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-1720.70521686	Predicted Change= -4.355132D-09
Zero-point correction (ZPE)=	-1720.1970	0.50819
Internal Energy (U)=	-1720.1763	0.52890
Enthalpy (H)=	-1720.1755	0.52970
Gibbs Free Energy (G)=	-1720.2432	0.46193

Frequencies -- -197.5044 13.9911 21.6152

==========

#m062x/6-311++G(2df,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN)

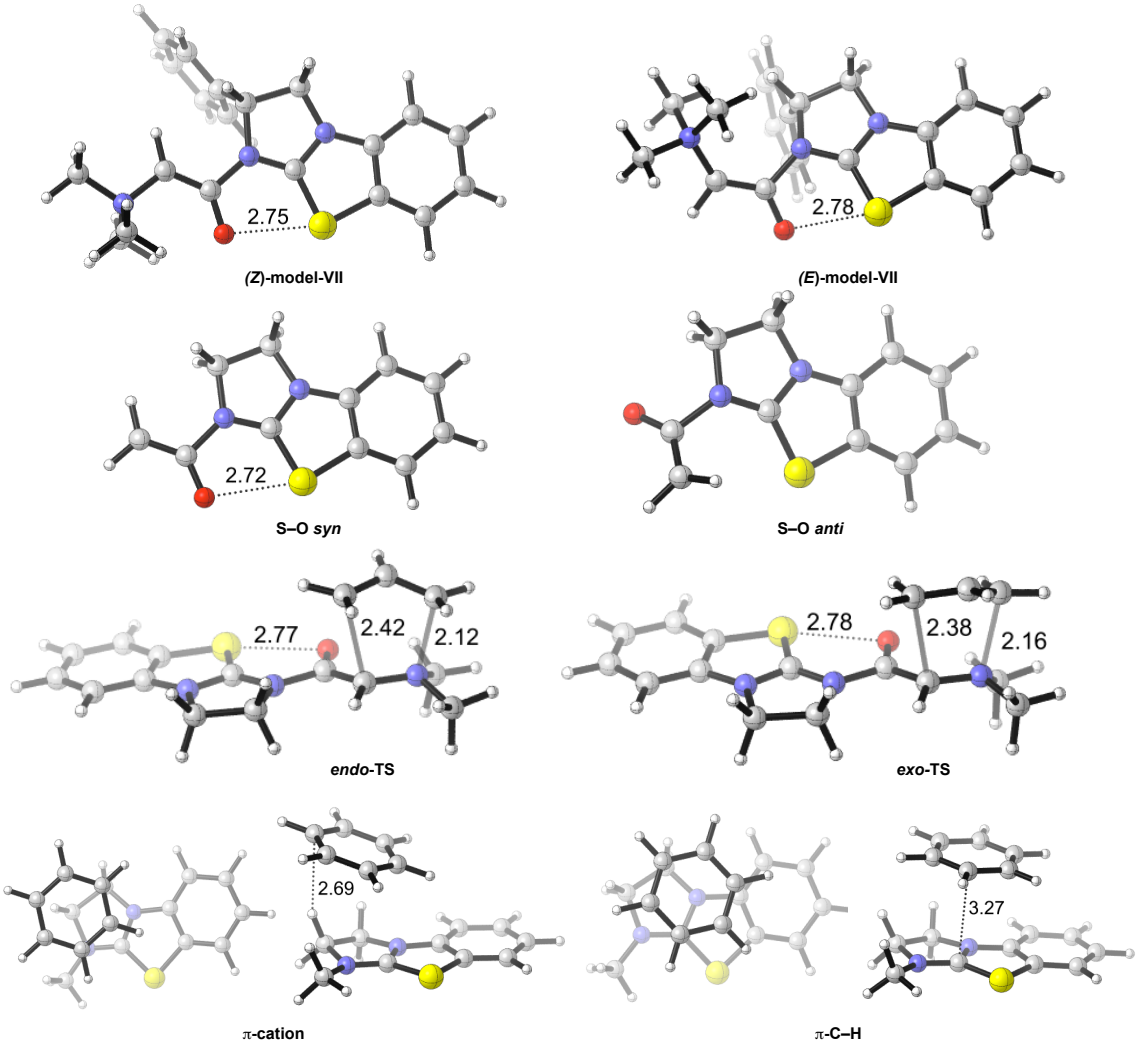
Pointgroup= C1 Stoichiometry= C28H28N3OS(1+) C1[X(C28H28N3OS)] #Atoms= 61
Charge = 1 Multiplicity = 1

SCF Energy= -1721.15620480

==========

Model systems

Truncated model systems computed to give atomistic insight into the interactions responsible for enantio- and diastereoselectivity.



(*Z*)-model-VII

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062X/6-31G(d) scf=(direct,tight,maxcycle=300,xqc)
SCRF=(PCM,SOLVENT=CH3CN) opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman
temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C20H22N3OS(1+) C1[X(C20H22N3OS)] #Atoms= 47
Charge = 1 Multiplicity = 1

SCF Energy= -1412.41571249 Predicted Change= -4.818707D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00314	0.00180	[NO]	0.00314	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-3.492683	-0.906688	0.336744
C	-4.783616	-1.295360	0.673707
C	-5.833559	-0.448470	0.327606
C	-5.598106	0.757600	-0.340481
C	-4.309070	1.154359	-0.680354
C	-3.266640	0.303774	-0.330493
N	-1.906756	0.484852	-0.565300
C	-1.125959	-0.500272	-0.125049
S	-1.978102	-1.785165	0.642836
C	-1.128553	1.526832	-1.237475
C	0.339821	1.013219	-1.060632
C	1.205834	1.969044	-0.269931
N	0.158165	-0.287980	-0.370085
C	1.162523	-1.288069	-0.057887
C	2.431302	-0.986728	-0.469960
N	3.513047	-1.947182	-0.184985
C	4.790477	-1.394594	-0.726915
C	3.243579	-3.270891	-0.842130
C	3.667119	-2.157759	1.294626
O	0.721558	-2.302244	0.537581
C	1.028757	2.115624	1.107603
C	1.804080	3.028214	1.815355
C	2.756301	3.801465	1.151055
C	2.931927	3.658654	-0.222425
C	2.157902	2.741933	-0.932066
H	-4.967260	-2.231340	1.190312
H	-6.849278	-0.731677	0.581041
H	-6.434131	1.397876	-0.599954
H	-4.118664	2.088384	-1.197923
H	-1.282078	2.489410	-0.745819
H	-1.422754	1.594377	-2.286239
H	0.792014	0.819805	-2.037456
H	4.986217	-0.439829	-0.238339
H	4.674567	-1.252155	-1.801444
H	5.593956	-2.101682	-0.519982
H	3.181381	-3.101889	-1.916489
H	2.295911	-3.641207	-0.455170
H	4.060452	-3.954404	-0.604509
H	2.716474	-2.530548	1.671772
H	3.908942	-1.194970	1.743450
H	4.468512	-2.878044	1.467206
H	2.740894	-0.065986	-0.935399
H	0.292063	1.509495	1.630571
H	1.666895	3.135251	2.886714
H	3.361276	4.511303	1.706224
H	3.674188	4.254834	-0.743462
H	2.297783	2.624440	-2.003934

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -1412.41571249 Predicted Change= -4.818707D-08
Zero-point correction (ZPE)= -1412.0203 0.39536
Internal Energy (U)= -1412.0042 0.41150
Enthalpy (H)= -1412.0034 0.41230
Gibbs Free Energy (G)= -1412.0613 0.35431

Frequencies -- 24.4091 33.0447 38.1690

==========
#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=acetonitrile)

Pointgroup= C1 Stoichiometry= C20H22N3OS(1+) C1[X(C20H22N3OS)] #Atoms= 47
Charge = 1 Multiplicity = 1

SCF Energy= -1412.77355677
==========

(*E*)-model-VII

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#m062X/6-31G(d) scf=(direct,tight,maxcycle=300,xqc)
SCRF=(PCM,SOLVENT=CH3CN) opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman
temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C20H22N3OS(1+) C1[X(C20H22N3OS)] #Atoms= 47
Charge = 1 Multiplicity = 1

SCF Energy= -1412.38896566 Predicted Change= -1.942848D-08
==========
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00187	0.00180	[NO]	0.00187	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.250858	-1.196804	-1.040462
N	-0.399714	-0.622140	0.025119
C	-2.533334	-1.618108	-0.791602
N	-3.240959	-1.904551	0.474017
C	-2.347536	-2.463024	1.542272
C	-4.251630	-2.978236	0.170632
C	-4.006346	-0.711526	0.976932
O	-0.685403	-1.245004	-2.155398
C	-0.717154	0.508760	0.943430
C	-1.243115	1.724146	0.206590

C	0.646350	0.759122	1.652691
C	0.924119	-0.612285	-0.169552
C	2.963673	0.098245	0.609031
C	3.350813	-0.746841	-0.437973
S	1.947135	-1.414354	-1.293603
C	3.895726	0.755843	1.403957
C	5.239582	0.546424	1.115945
C	5.635473	-0.290514	0.066482
C	4.696396	-0.944323	-0.725701
C	-1.948730	2.680727	0.942033
C	-2.400433	3.844541	0.328083
C	-2.152897	4.057019	-1.027129
C	-1.456521	3.101779	-1.762807
C	-0.999109	1.935658	-1.151343
N	1.574992	0.154432	0.699538
H	-3.093934	-1.928152	-1.660424
H	-1.602983	-1.731077	1.837974
H	-1.851772	-3.341554	1.131415
H	-2.963476	-2.730626	2.400954
H	-3.716185	-3.855286	-0.190123
H	-4.929767	-2.605929	-0.596223
H	-4.800922	-3.206417	1.084317
H	-4.733581	-0.441741	0.211821
H	-3.324356	0.121921	1.124030
H	-4.508536	-0.969693	1.910788
H	-1.437002	0.197690	1.699981
H	0.717009	0.238903	2.611308
H	0.851704	1.822458	1.782678
H	3.582072	1.402656	2.216032
H	5.992896	1.042546	1.718077
H	6.691251	-0.434748	-0.134978
H	5.003633	-1.591191	-1.540230
H	-2.143924	2.515108	1.999638
H	-2.949491	4.581179	0.905760
H	-2.508336	4.962388	-1.508864
H	-1.269549	3.259821	-2.820188
H	-0.482731	1.183642	-1.742679

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1412.38896566 Predicted Change= -1.942848D-08
Zero-point correction (ZPE)= -1411.9937 0.39521
Internal Energy (U)= -1411.9777 0.41124
Enthalpy (H)= -1411.9769 0.41204
Gibbs Free Energy (G)= -1412.0344 0.35455

Frequencies -- 19.7892 28.5749 46.9980

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=acetonitrile)

Pointgroup= C1 Stoichiometry= C20H22N3OS(1+) C1[X(C20H22N3OS)] #Atoms= 47
Charge = 1 Multiplicity = 1

SCF Energy= -1412.74775393
==========

S–O-*syn*

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN) opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman
temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C11H10N2OS C1[X(C11H10N2OS)] #Atoms= 25
Charge = 0 Multiplicity = 1

SCF Energy= -1007.79930686 Predicted Change= -1.053965D-08
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00005	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00038	0.00180	[YES]	0.00038	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-0.164370	0.966319	-0.000081
C	0.721080	-0.039081	0.000059
S	0.001370	-1.608141	0.000059
C	0.513221	2.266259	0.000049
C	2.009410	1.841079	0.000049
N	1.967980	0.366819	0.000189
C	-1.496910	0.573489	-0.000151
C	-2.623000	1.388509	-0.000261
C	-1.599850	-0.824591	-0.000111
C	-3.867860	0.765109	-0.000331
C	-2.845340	-1.437771	-0.000181
C	-3.980110	-0.627761	-0.000291
C	3.101810	-0.582642	0.000269
C	4.330190	0.002098	0.000279
O	2.717190	-1.783892	0.000299
H	4.465940	1.074908	0.000159
H	5.207680	-0.630932	0.000459
H	0.237431	2.832269	0.891519
H	2.538991	2.187768	0.889349
H	0.237481	2.832439	-0.891331
H	2.538941	2.187588	-0.889351
H	-2.528129	2.469209	-0.000291
H	-4.764420	1.375620	-0.000411
H	-2.932450	-2.519161	-0.000151
H	-4.962030	-1.088470	-0.000351

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm
==========

```
 SCF Energy=     -1007.79930686   Predicted Change= -1.053965D-08
 Zero-point correction (ZPE)=            -1007.6041      0.19520
 Internal Energy (U)=                    -1007.5949      0.20433
 Enthalpy (H)=                           -1007.5941      0.20513
 Gibbs Free Energy (G)=                  -1007.6357      0.16351
---------------------------------------------------------------------
 Frequencies --     45.7193              65.0590              91.3141

=============================================
 #m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
 SCRF=(PCM,SOLVENT=acetonitrile)
---------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C11H10N2OS   C1[X(C11H10N2OS)]  #Atoms= 25
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -1008.04242598
=============================================
```

S–O-*anti*

```
---------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
=============================================
 #M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=CH3CN) opt=(maxcycle=250) freq=noraman temp=253.15
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C11H10N2OS   C1[X(C11H10N2OS)]  #Atoms= 25
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -1007.79174483       Predicted Change= -3.173448D-09
=============================================
 Optimization completed.          {Found       2       times}
 Item      Max Val.   Criteria   Pass?      RMS Val.   Criteria   Pass?
 Force      0.00000 ||  0.00045   [ YES ]     0.00000 ||  0.00030   [ YES ]
 Displ      0.00043 ||  0.00180   [ YES ]     0.00043 ||  0.00180   [ YES ]
---------------------------------------------------------------------
     Atomic             Coordinates (Angstroms)
      Type              X           Y           Z
---------------------------------------------------------------------
      N       -0.178560     0.956931    -0.122039
      C        0.719720    -0.039529    -0.135399
      S        0.006550    -1.613089    -0.022159
      C        0.495889     2.254131    -0.241569
      C        1.977329     1.843301    -0.043799
      N        1.962330     0.373881    -0.197989
      C       -1.504590     0.554810    -0.034709
      C       -2.638471     1.358830    -0.013959
      C       -1.597460    -0.841760     0.043581
      C       -3.874480     0.726820     0.088651
      C       -2.832450    -1.466290     0.146621
      C       -3.972970    -0.664930     0.168681
      C        3.192650    -0.449198     0.098341
      C        3.167490    -1.672928    -0.507529
      O        3.993710     0.135172     0.853241
      H        2.446820    -1.910068    -1.279779
```

H	3.968821	-2.373848	-0.311379
H	0.140249	2.942511	0.526071
H	2.352299	2.077991	0.953881
H	0.305549	2.675881	-1.231259
H	2.635539	2.290522	-0.788409
H	-2.554851	2.438570	-0.076219
H	-4.775831	1.329899	0.105851
H	-2.906939	-2.546720	0.207881
H	-4.948470	-1.131911	0.248761

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -1007.79174483 Predicted Change= -3.173448D-09
Zero-point correction (ZPE)= -1007.5969 0.19478
Internal Energy (U)= -1007.5878 0.20388
Enthalpy (H)= -1007.5870 0.20468
Gibbs Free Energy (G)= -1007.6283 0.16337

Frequencies -- 53.5599 82.5762 110.9036

==========
#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=acetonitrile)

Pointgroup= C1 Stoichiometry= C11H10N2OS C1[X(C11H10N2OS)] #Atoms= 25
Charge = 0 Multiplicity = 1

SCF Energy= -1008.03503119
==========

***Endo*-TS**

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)
iop(1/8=18) freq=noraman temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C16H20N3OS(1+) C1[X(C16H20N3OS)] #Atoms= 41
Charge = 1 Multiplicity = 1

SCF Energy= -1258.77756890 Predicted Change= -2.190672D-08
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00004	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00165	0.00180	[YES]	0.00165	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	5.542060	0.464771	0.183550
C	4.367899	1.206311	0.119250

C	3.175270	0.501850	-0.002010
C	3.146390	-0.897300	-0.058470
C	4.324490	-1.631959	0.007510
C	5.522100	-0.933699	0.128950
N	1.885849	1.018990	-0.082530
C	0.926820	0.107160	-0.201950
S	1.490870	-1.516400	-0.214740
C	1.345339	2.383180	-0.094340
C	-0.183121	2.120740	-0.176400
N	-0.286280	0.647580	-0.289590
C	-1.464970	-0.168690	-0.377460
O	-1.273780	-1.386880	-0.407580
C	-2.676740	0.562990	-0.405660
N	-3.914480	-0.017400	-0.580370
C	-4.937231	0.919560	-1.072050
C	-3.995870	-1.320900	-1.266840
H	-2.652771	1.642880	-0.428400
H	6.490179	0.982681	0.278370
H	4.374399	2.290061	0.161050
H	4.309590	-2.715549	-0.035380
H	6.454210	-1.485449	0.181440
H	1.724419	2.920790	-0.964760
H	1.633309	2.906350	0.818020
H	-0.705431	2.450880	0.724200
H	-0.628711	2.591100	-1.053470
H	-4.877681	1.850130	-0.505210
H	-5.922450	0.473580	-0.925990
H	-4.782441	1.126230	-2.135780
H	-3.606760	-1.230400	-2.286370
H	-5.046410	-1.613290	-1.300770
H	-3.416950	-2.059600	-0.719920
C	-4.637110	-0.522640	1.353040
C	-3.395610	-0.715220	1.952370
C	-2.547950	0.368850	2.007360
H	-1.509880	0.265800	2.314950
H	-2.954431	1.376650	2.030420
H	-5.302360	-1.357570	1.147990
H	-5.120550	0.447550	1.442560
H	-2.989150	-1.719600	2.039830

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-1258.77756890	Predicted Change=	-2.190672D-08
Zero-point correction (ZPE)=		-1258.4331	0.34441
Internal Energy (U)=		-1258.4189	0.35864
Enthalpy (H)=		-1258.4181	0.35944
Gibbs Free Energy (G)=		-1258.4710	0.30647

Frequencies -- -287.3031 24.6504 41.8663

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=acetonitrile)

Pointgroup= C1 Stoichiometry= C16H20N3OS(1+) C1[X(C16H20N3OS)] #Atoms= 41
Charge = 1 Multiplicity = 1

SCF Energy= -1259.09046948
==========

***Exo*-TS**

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)
iop(1/8=18) freq=noraman temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C16H20N3OS(1+) C1[X(C16H20N3OS)] #Atoms= 41
Charge = 1 Multiplicity = 1

SCF Energy= -1258.77654623 Predicted Change= -6.226723D-09
==========
Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00273	0.00180	[NO]	0.00273	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	5.555024	0.496552	0.191357
C	4.378085	1.222628	0.053460
C	3.191114	0.502170	-0.023800
C	3.171087	-0.897062	0.032829
C	4.352490	-1.616433	0.171432
C	5.543943	-0.902210	0.249912
N	1.899495	1.002136	-0.160557
C	0.949127	0.077570	-0.212035
S	1.521837	-1.537211	-0.094302
C	1.351734	2.358344	-0.284248
C	-0.174241	2.082401	-0.362792
N	-0.269546	0.603637	-0.348442
C	-1.436648	-0.217524	-0.395354
O	-1.247185	-1.435761	-0.349779
C	-2.662817	0.495533	-0.400200
N	-3.878548	-0.125232	-0.605776
C	-4.955208	0.836225	-0.872845
C	-3.962880	-1.306622	-1.478140
H	-2.652537	1.574847	-0.460951
H	6.498892	1.026873	0.254887
H	4.377906	2.306224	0.007621
H	4.344141	-2.699945	0.216385
H	6.478911	-1.440734	0.358346
H	1.739728	2.828739	-1.188942
H	1.626402	2.950538	0.589096
H	-0.707703	2.487416	0.499374
H	-0.611167	2.470693	-1.283167

H	-4.799275	1.323620	-1.841791
H	-4.963203	1.587599	-0.080761
H	-5.910252	0.308994	-0.878796
H	-3.181673	-2.014638	-1.215271
H	-3.855616	-1.006778	-2.526595
H	-4.943810	-1.763720	-1.331917
C	-4.451255	-0.901251	1.326888
C	-3.947351	0.173943	2.041136
C	-2.581535	0.390727	1.972498
H	-2.139892	1.314393	2.338730
H	-1.909897	-0.460587	1.902381
H	-5.519963	-1.065842	1.214431
H	-4.610462	0.987031	2.326953
H	-3.816260	-1.766991	1.149892

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1258.77654623 Predicted Change= -6.226723D-09
Zero-point correction (ZPE)= -1258.4324 0.34408
Internal Energy (U)= -1258.4180 0.35848
Enthalpy (H)= -1258.4172 0.35928
Gibbs Free Energy (G)= -1258.4707 0.30579

Frequencies -- -308.2890 25.2898 31.4368

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=acetonitrile)

Pointgroup= C1 Stoichiometry= C16H20N3OS(1+) C1[X(C16H20N3OS)] #Atoms= 41
Charge = 1 Multiplicity = 1

SCF Energy= -1259.08898277

==========

π-cation

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN) opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman
temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C16H17N2S(1+) C1[X(C16H17N2S)] #Atoms= 36
Charge = 1 Multiplicity = 1

SCF Energy= -1127.14298165 Predicted Change= -5.288038D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00945	0.00180	[NO]	0.00945	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-3.881746	-0.186678	-0.188066
C	-3.519801	0.412128	1.022392
C	-2.218737	0.328664	1.509252
C	-1.293730	-0.374798	0.748094
C	-1.655801	-0.988034	-0.457705
C	-2.951667	-0.895636	-0.945626
N	0.061146	-0.547823	1.004865
C	0.715579	-1.271453	0.094695
S	-0.274151	-1.807531	-1.215399
C	0.921286	-0.241081	2.153560
C	2.298828	-0.744191	1.650949
N	1.979089	-1.467018	0.402882
C	2.999887	-2.070579	-0.433027
H	-4.901303	-0.101299	-0.547174
H	-4.263817	0.957136	1.593120
H	-1.925904	0.802455	2.440265
H	-3.231465	-1.361765	-1.884125
H	0.568346	-0.790349	3.028939
H	0.914237	0.830580	2.354803
H	2.775916	-1.426929	2.355631
H	2.980278	0.080205	1.423173
H	2.525402	-2.647564	-1.228087
H	3.609699	-2.739207	0.176828
H	3.632583	-1.293387	-0.872305
C	-0.437282	2.359033	-0.724030
C	0.367944	2.816265	0.318735
C	1.733206	2.529588	0.322165
C	2.292213	1.780168	-0.714335
C	1.485401	1.319249	-1.754164
C	0.120984	1.610987	-1.759221
H	-1.502143	2.574421	-0.723644
H	-0.067911	3.395282	1.127859
H	2.362894	2.891353	1.130603
H	3.357992	1.566885	-0.717037
H	1.919098	0.733977	-2.560542
H	-0.508525	1.250807	-2.568146

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1127.14298165 Predicted Change= -5.288038D-08

Zero-point correction (ZPE)=	-1126.8415	0.30145
Internal Energy (U)=	-1126.8286	0.31437
Enthalpy (H)=	-1126.8278	0.31517
Gibbs Free Energy (G)=	-1126.8788	0.26415

Frequencies -- 33.1105 44.0957 47.3734

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=acetonitrile)

Pointgroup= C1 Stoichiometry= C16H17N2S(1+) C1[X(C16H17N2S)] #Atoms= 36
Charge = 1 Multiplicity = 1

SCF Energy= -1127.40597819
==========

π-C–H

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN) opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman
temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C16H17N2S(1+) C1[X(C16H17N2S)] #Atoms= 36
Charge = 1 Multiplicity = 1

SCF Energy= -1127.14180316 Predicted Change= -9.402377D-09
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00055	0.00180	[YES]	0.00055	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	4.129640	-0.868892	-0.593671
C	3.651019	-1.610152	0.490469
C	2.441599	-1.297372	1.103919
C	1.725970	-0.219022	0.596979
C	2.201840	0.523568	-0.492601
C	3.408770	0.209798	-1.100951
N	0.501470	0.272159	1.032949
C	0.037940	1.318349	0.345449
S	1.077621	1.827769	-0.935181
C	-0.407580	-0.080091	2.129289
C	-1.636500	0.801840	1.798539
N	-1.131539	1.739509	0.772859
C	-1.982799	2.740730	0.157749
H	5.075670	-1.135473	-1.051621
H	4.231049	-2.446953	0.864189
H	2.065749	-1.867182	1.946999
H	3.776760	0.784788	-1.943441
H	0.056350	0.179349	3.083279
H	-0.642020	-1.145021	2.102539
H	-1.996610	1.359180	2.664079
H	-2.456160	0.220050	1.363299
H	-1.415689	3.291280	-0.594271
H	-2.333129	3.435680	0.922769
H	-2.838959	2.251750	-0.316901
C	-2.078040	-0.328860	-1.693461

C	-1.041910	-1.175141	-1.297871
C	-1.290011	-2.207991	-0.393711
C	-2.576721	-2.398980	0.110659
C	-3.615171	-1.558730	-0.291371
C	-3.365610	-0.522450	-1.191801
H	-1.884400	0.473320	-2.400971
H	-0.040910	-1.036571	-1.701111
H	-0.481061	-2.865321	-0.085971
H	-2.770171	-3.203790	0.813329
H	-4.617441	-1.710129	0.097509
H	-4.175090	0.129441	-1.507201

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1127.14180316 Predicted Change= -9.402377D-09
Zero-point correction (ZPE)= -1126.8398 0.30200
Internal Energy (U)= -1126.8271 0.31464
Enthalpy (H)= -1126.8263 0.31544
Gibbs Free Energy (G)= -1126.8764 0.26534

Frequencies -- 29.6507 43.4256 55.8366

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=acetonitrile)

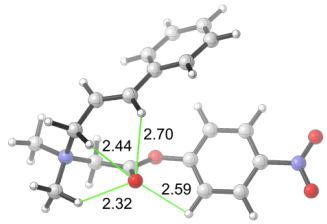
Pointgroup= C1 Stoichiometry= C16H17N2S(1+) C1[X(C16H17N2S)] #Atoms= 36
Charge = 1 Multiplicity = 1

SCF Energy= -1127.40455245

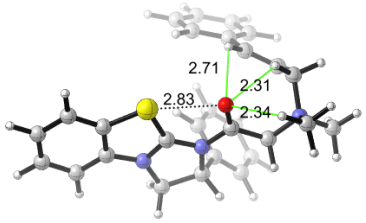
==========

Additional coordination motifs of the [2,3] TS

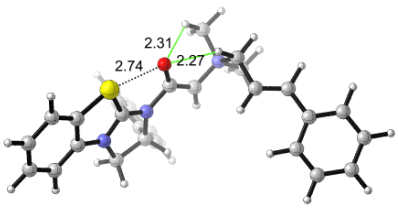
Alternative counterion identities and coordination for key intermediates and TSs along the reaction coordinate.



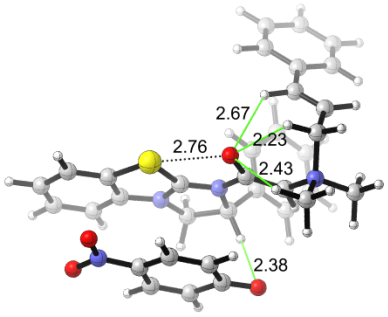
Substrate I (no coordination)



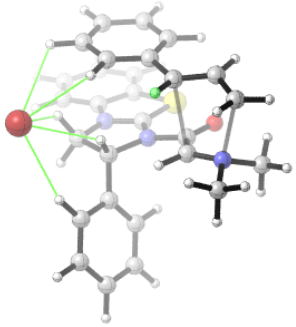
V (no coordination)



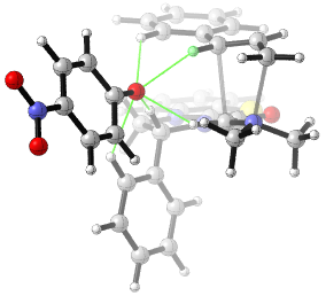
VII (no coordination)



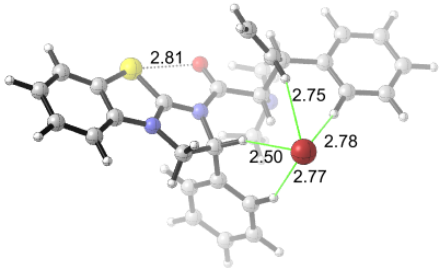
VII•••PNPO⁻



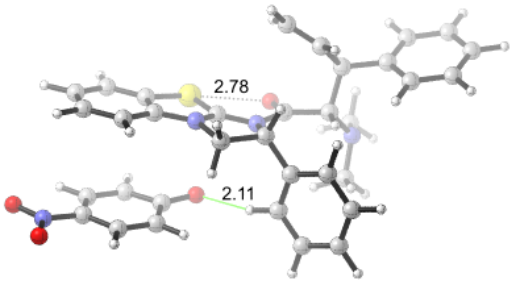
TS-VIII-*(2S,3S)*•••Br⁻



TS-VIII-*(2S,3S)*•••PNPO⁻



IX•••Br⁻



IX•••PNPO⁻

TS-VIII-F-(2*S*,3*S*)•••Br

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

# M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
SCRF=(PCM,SOLVENT=acetonitrile)
opt=(maxcycle=250,calcfc,ts,noeigentest,gdiis) iop(1/8=18) freq=noraman
temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C28H28BrN3OS C1[X(C28H28BrN3OS)] #Atoms= 62
Charge = 0 Multiplicity = 1

SCF Energy= -4292.68085731 Predicted Change= -9.972808D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00089	0.00180	[YES]	0.00089	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	5.526490	0.800238	-0.943610
C	4.224970	1.211139	-0.680830
C	3.210889	0.278509	-0.871230
C	3.477559	-1.024571	-1.310920
C	4.782749	-1.428301	-1.569800
C	5.802739	-0.499882	-1.382850
N	1.847819	0.456410	-0.665450
C	1.108339	-0.622790	-0.885670
S	1.995208	-1.987250	-1.442050
C	1.035870	1.590580	-0.214150
C	-0.413600	1.027191	-0.337430
C	-1.245840	1.731111	-1.390330
N	-0.190511	-0.404969	-0.667940
C	-1.135431	-1.476199	-0.714460
O	-0.689122	-2.577269	-1.053610
C	-2.455021	-1.114468	-0.336200
N	-3.535432	-1.941348	-0.452930
C	-4.829651	-1.249647	-0.454210
C	-3.493722	-3.065998	-1.399760
C	-1.304800	1.274661	-2.707720
C	-2.055380	1.969472	-3.653520
C	-2.745769	3.123232	-3.289010
C	-2.681849	3.582782	-1.974610
C	-1.935419	2.890042	-1.024750
H	-2.669661	-0.088318	-0.071630
H	6.340700	1.502728	-0.803090
H	4.001520	2.215119	-0.336410
H	4.998618	-2.436122	-1.907930
H	6.828309	-0.792142	-1.580300
H	1.196520	2.449420	-0.868990
H	1.266950	1.854700	0.819850
H	-0.892660	1.109971	0.642570
H	-4.834221	-0.487017	0.326620
H	-5.619022	-1.975027	-0.250180
H	-5.009701	-0.777577	-1.426650
H	-3.404642	-2.688868	-2.425470
H	-4.425742	-3.623487	-1.296960
H	-2.646062	-3.705988	-1.172760
H	-0.772961	0.372391	-2.998900
H	-2.101570	1.606072	-4.675360
H	-3.332179	3.661792	-4.026950
H	-3.219349	4.480772	-1.685850
H	-1.866749	3.243512	0.002640
C	-3.633392	-3.087978	1.487920
C	-2.278942	-3.029588	1.735340
C	-1.689802	-1.790299	1.968240
C	-0.262241	-1.538259	2.158850
C	0.730438	-2.478270	1.835790

C	2.078498	-2.162470	1.985870
C	2.466929	-0.902430	2.442380
C	1.489409	0.038850	2.769640
C	0.143509	-0.279239	2.632930
H	-4.118233	-4.016887	1.201140
H	-4.286482	-2.303617	1.861300
H	-1.659322	-3.893089	1.505510
H	-2.346611	-0.981298	2.285950
H	0.451458	-3.452529	1.446980
H	2.832598	-2.900241	1.726080
H	3.520639	-0.658931	2.541490
H	1.758550	1.031860	3.119780
H	-0.599171	0.478411	2.873010
Br	-0.461719	3.251811	2.455000

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -4292.68085731 Predicted Change= -9.972808D-09
Zero-point correction (ZPE)= -4292.1719 0.50891
Internal Energy (U)= -4292.1494 0.53136
Enthalpy (H)= -4292.1486 0.53216
Gibbs Free Energy (G)= -4292.2209 0.45993

Frequencies -- -192.2721 22.1130 28.9728

==========
#m062x/6-311++G(2df,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=CH3CN)

Pointgroup= C1 Stoichiometry= C28H28BrN3OS C1[X(C28H28BrN3OS)] #Atoms= 62
Charge = 0 Multiplicity = 1

SCF Energy= -4295.53197786
==========

TS-VIII-F-(2*S*,3*S*)•••PNPO

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
# M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
SCRF=(PCM,SOLVENT=acetonitrile)
opt=(verytight,maxcycle=250,calcfc,ts,noeigentest,gdiis) iop(1/8=18)
freq=noraman temp=253.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C34H32N4O4S C1[X(C34H32N4O4S)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -2232.03941843 Predicted Change= -3.821412D-12
==========
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00000	[YES]	0.00000	0.00000	[YES]

Displ 0.00013 || 0.00000 [NO] 0.00013 || 0.00000 [NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-6.173043	2.205242	-2.032523
C	-4.795561	2.200540	-1.842192
C	-4.287434	1.335919	-0.879043
C	-5.119975	0.499031	-0.123995
C	-6.495650	0.507912	-0.322326
C	-7.012074	1.372092	-1.284145
N	-2.955829	1.148586	-0.524271
C	-2.753036	0.222150	0.407854
S	-4.193401	-0.498529	1.012918
C	-1.697276	1.755207	-0.965715
C	-0.652826	1.090330	-0.012387
C	-0.014110	2.072506	0.946193
N	-1.467636	0.078154	0.713210
C	-1.015220	-0.976312	1.573573
O	-1.904995	-1.650514	2.108985
C	0.392500	-1.086823	1.651635
N	1.037709	-1.950215	2.493508
C	2.457304	-1.625535	2.682911
C	0.380541	-2.378936	3.737021
C	-0.727490	2.595656	2.026828
C	-0.129258	3.526436	2.870930
C	1.182396	3.940610	2.638948
C	1.893500	3.421367	1.560003
C	1.296542	2.488048	0.714211
H	1.026098	-0.459432	1.035460
H	-6.601239	2.868194	-2.776425
H	-4.138166	2.840140	-2.421219
H	-7.145831	-0.138364	0.257356
H	-8.082780	1.396944	-1.454418
H	-1.737203	2.837959	-0.831249
H	-1.519326	1.512257	-2.014649
H	0.124595	0.575464	-0.585592
H	2.901698	-1.398633	1.710983
H	2.964590	-2.484845	3.125589
H	2.563974	-0.757534	3.343846
H	0.239762	-1.517371	4.400485
H	1.026222	-3.110750	4.224915
H	-0.584119	-2.822259	3.505428
H	-1.747294	2.268986	2.219839
H	-0.685479	3.926661	3.712889
H	1.647592	4.663392	3.302012
H	2.918139	3.732140	1.378208
H	1.847292	2.054248	-0.115388
C	1.183308	-3.878705	1.420225
C	0.082801	-3.700907	0.600704
C	0.105021	-2.656297	-0.311905
C	-0.996553	-2.255924	-1.186538
C	-2.318886	-2.687040	-0.994627
C	-3.336061	-2.251934	-1.840200
C	-3.057938	-1.376643	-2.889876

C	-1.746038	-0.943967	-3.094582
C	-0.728147	-1.372331	-2.248642
H	1.178597	-4.611727	2.222466
H	2.163120	-3.561772	1.073709
H	-0.850277	-4.203657	0.843790
H	1.068395	-2.212414	-0.561299
H	-2.559714	-3.343313	-0.163868
H	-4.355588	-2.586277	-1.668955
H	-3.855637	-1.035444	-3.542799
H	-1.518310	-0.269119	-3.915261
H	0.293399	-1.019690	-2.381186
C	5.536179	0.784199	-0.045330
C	6.191129	0.394232	-1.225994
N	7.588118	0.612765	-1.363726
O	8.150721	0.253276	-2.400825
O	8.202438	1.157316	-0.442916
C	5.471519	-0.212252	-2.271593
C	4.122334	-0.422773	-2.141434
C	3.399792	-0.042398	-0.952418
O	2.152604	-0.236990	-0.830999
C	4.186333	0.573578	0.089639
H	6.112338	1.248432	0.747469
H	6.000711	-0.504741	-3.171801
H	3.556998	-0.890098	-2.942710
H	3.671455	0.871683	0.999415

Statistical Thermodynamic Analysis
Temperature= 253.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2232.03941843 Predicted Change= -3.821412D-12
Zero-point correction (ZPE)= -2231.4341 0.60530
Internal Energy (U)= -2231.4061 0.63327
Enthalpy (H)= -2231.4053 0.63407
Gibbs Free Energy (G)= -2231.4935 0.54589

Frequencies -- -217.1963 1.9364 9.0726

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=acetonitrile)

Pointgroup= C1 Stoichiometry= C34H32N4O4S C1[X(C34H32N4O4S)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -2232.67900556

==========

Derivation of lowest energy (2*S*,3*S*) reaction coordinate

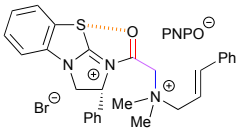
Computational protocol for obtaining the lowest energy pathway of the direct acylation mechanism. Activated PNPO ester ammonium substrate. For each ground state and transition state, the explicit coordination of the structure and the remaining possible complexes was included in calculating the $\Delta G/\Delta G^{\ddagger}$ of each state. The difference between direct complexation and infinite separation is given by "•••" and "+", respectively. Barriers highlighted in blue are the lowest computed barriers and thermodynamics for each state.

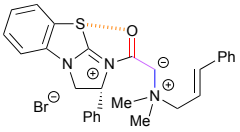
Coordination motifs and complexes	ΔG (kcal/mol)
Substrate I	
Substrate **I**+ + Br- ---> [Substrate **I**•••Br-]	–6.4 (0.0 for reaction coord.)
TS-II	
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **TS-II-Re** + iPr_2NH	14.8
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **TS-II-Si** + iPr_2NH	15.9
III	
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **III** + iPr_2NH (*Re* BTM attack pathway)	10.4
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **III** + iPr_2NH (*Si* BTM attack pathway)	11.5
TS-IV	
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **TS-IV** + iPr_2NH (*Re* BTM attack pathway)	12.0
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **TS-IV** + iPr_2NH (*Si* BTM attack pathway)	16.9
Dication V	
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> Dication **V**++ + PNPO- + Br- + iPr_2NH	10.8
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> [Dication **V**++•••PNPO-•••Br-] + iPr_2NH	3.3
Deprotonation TS-VI	
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **TS-VI•••Br** + iPr_2NH (PNPO- as base, forming *Z* configuration)	11.4
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **TS-VI•••PNPO-•••Br** (iPr_2NH as base, forming *Z* config.)	22.5
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **TS-VI•••Br** + PNPO- (iPr_2NH as base, forming *Z* config.)	21.4
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **TS-VI** + Br- + PNPO- (iPr_2NH as base, forming *Z* config.)	26.1
Ylide/(Z)-Enolate VII	
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> Ylide **VII**+ + PNPO- + iPr_2NH_2+ + Br-	10.9
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> Ylide **VII**+ + PNPO- + Br- + [iPr_2NH_2+•••Br-]	6.4
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> Ylide **VII**+ + [PNPO-••• iPr_2NH_2+] + Br-	7.4
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> Ylide **VII**+ + [PNPO-•••iPr_2NH_2+•••Br-]	2.4
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> Ylide **VII**+ + [PNPOH•••iPr_2NH•••Br-]	5.8
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> Ylide **VII**+ + [PNPOH•••iPr_2NH] + Br-	1.8
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> Ylide **VII**+ + PNPOH + iPr_2NH + Br-	4.7
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> Ylide **VII**+ + PNPOH + iPr_2NH•••Br-	8.9
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> Ylide **VII**+ + PNPOH•••Br- + iPr_2NH	3.1
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> [Ylide **VII**+•••Br-] + PNPO- + iPr_2NH_2+	10.7
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> [Ylide **VII**+•••Br-] + [PNPO-•••iPr_2NH_2+]	7.1
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> [Ylide **VII**+•••Br-] + [PNPOH•••iPr_2NH]	1.6
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> [Ylide **VII**+•••Br-] + PNPOH + iPr_2NH	4.5
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> [Ylide **VII**+•••PNPO-] + iPr_2NH_2+ + Br-	11.1
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> [Ylide **VII**+•••PNPO-] + [iPr_2NH_2+•••Br-]	6.6

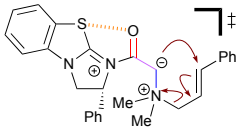
TS-VIII-(2S,3S)	
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **TS-VIII**+ + PNPO- + iPr_2NH_2+ + Br-	26.5
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **TS-VIII**+ + PNPO- + Br- + [iPr_2NH_2+•••Br-]	22.0
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **TS-VIII**+ + [PNPO-••• iPr_2NH_2+] + Br-	22.9
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **TS-VIII**+ + [PNPO-•••iPr_2NH_2+•••Br-]	18.0
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **TS-VIII**+ + [PNPOH•••iPr_2NH•••Br-]	21.4
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **TS-VIII**+ + [PNPOH•••iPr_2NH] + Br-	17.3
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **TS-VIII**+ + PNPOH + iPr_2NH + Br-	24.5
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **TS-VIII**+ + PNPOH + iPr_2NH•••Br-	20.2
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **TS-VIII**+ + PNPOH•••Br- + iPr_2NH	18.7
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> [**TS-VIII**+•••Br-] + PNPO- + iPr_2NH_2+	28.0
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> [**TS-VIII**+•••Br-] + [PNPO-•••iPr_2NH_2+]	24.4
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> [**TS-VIII**+•••Br-] + [PNPOH•••iPr_2NH]	18.8
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> [**TS-VIII**+•••Br-] + PNPOH + iPr_2NH	21.7
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> [**TS-VIII**+•••PNPO-] + iPr_2NH_2+ + Br-	26.4
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> [**TS-VIII**+•••PNPO-] + [iPr_2NH_2+•••Br-]	21.9
Acyl ammonium IX-(2S,3S)	
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **IX**+ + PNPO- + iPr_2NH_2+ + Br-	0.6
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **IX**+ + PNPO- + Br- + [iPr_2NH_2+•••Br-]	–3.8
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **IX**+ + [PNPO-••• iPr_2NH_2+] + Br-	–2.9
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **IX**+ + [PNPO-•••iPr_2NH_2+•••Br-]	–7.9
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **IX**+ + [PNPOH•••iPr_2NH•••Br-]	–4.5
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **IX**+ + [PNPOH•••iPr_2NH] + Br-	–8.5
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **IX**+ + PNPOH + iPr_2NH + Br-	–1.4
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **IX**+ + PNPOH + iPr_2NH•••Br-	–5.6
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **IX**+ + PNPOH•••Br- + iPr_2NH	–7.2
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> [**IX**+•••Br-] + PNPO- + iPr_2NH_2+	1.7
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> [**IX**+•••Br-] + [PNPO-•••iPr_2NH_2+]	–1.9
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> [**IX**+•••Br-] + [PNPOH•••iPr_2NH]	–7.5
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> [**IX**+•••Br-] + PNPOH + iPr_2NH	–4.6
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> [**IX**+•••PNPO-] + iPr_2NH_2+ + Br-	1.5
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> [**IX**+•••PNPO-] + [iPr_2NH_2+•••Br-]	–3.0
TS-X-(2S,3S)	
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **TS-X** + [iPr_2NH_2+•••Br-] (*Re* PNPO attack pathway)	9.7
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **TS-X** + [iPr_2NH_2+•••Br-] (*Si* PNPO attack pathway)	8.4
XI-(2S,3S)	
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **XI** + [iPr_2NH_2+•••Br-] (*Re* PNPO attack pathway)	6.5
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **XI** + [iPr_2NH_2+•••Br-] (*Si* PNPO attack pathway)	6.1
TS-XII-(2S,3S)	
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **TS-XII** + [iPr_2NH_2+•••Br-] (*Re* PNPO attack pathway)	6.7
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **TS-XII** + [iPr_2NH_2+•••Br-] (*Si* PNPO attack pathway)	6.1
PNPO product XIII-(2S,3S)	
[Substrate **I**+•••Br-] + iPr_2NH + BTM ---> **XIII** + [iPr_2NH_2+•••Br-]	–11.9

Wiberg Bond Indices and Interatomic Distances of Key Intermediates and TSs

Select computed interatomic distances and estimations of the bond order using Wiberg bond index (NAO basis) for species **V**, **VII**, and **TS-VIII-(2*S*,3*S*)-Major**.

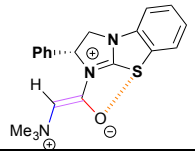


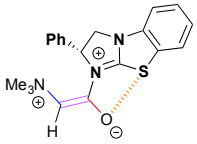


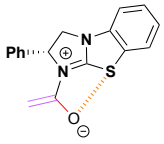


	V		**VII**		**TS-VIII-(2*S*,3*S*)-Major**	
	r (Å)	B. O.	r (Å)	B. O.	r (Å)	B. O.
S•••O	2.85	-	2.75	-	2.79	-
C=O	1.22	1.70	1.26	1.39	1.23	1.54
C–C	1.51	0.98	1.37	1.52	1.42	1.21
C–N	1.49	0.90	1.47	0.89	1.36	1.20

Select computed interatomic distances and estimations of the bond order using Wiberg bond index (NAO basis) for the enolate-ylide model systems.

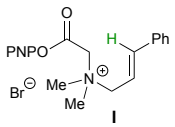






	(*Z*)-model-VII		**(*E*)-model-VII**		**S–O *syn***	
	r (Å)	B. O.	r (Å)	B. O.	r (Å)	B. O.
S•••O	2.75	-	2.78	-	2.72	-
C=O	1.27	1.40	1.25	1.42	1.26	1.37
C–C	1.38	1.52	1.37	1.55	1.36	1.62
C–N	1.47	0.89	1.49	0.89	-	-

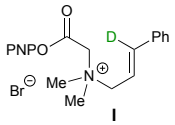
Tabulated Frequencies for Computed KIE



I

Unlabeled

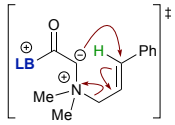
13.8084	418.2296	956.7049	1322.0381	1753.3809
22.8518	424.3460	962.7419	1322.3644	1887.1315
28.4108	428.9910	979.7369	1346.3600	3127.4408
37.0352	456.3788	1005.2979	1351.1528	3131.0681
45.5990	491.5636	1011.7319	1359.1013	3135.1534
52.9490	508.7162	1017.9199	1373.8525	3139.8602
61.6467	522.1508	1019.6045	1379.2155	3182.5665
61.8138	544.4252	1027.4253	1385.7162	3200.1906
67.9607	552.4014	1032.7190	1422.0280	3211.6693
69.0918	586.0581	1035.1069	1445.7855	3213.4891
91.4947	629.8181	1042.7065	1458.0783	3221.3480
118.5503	634.8387	1043.5658	1462.6024	3225.4255
127.3674	641.0444	1060.6499	1482.5212	3226.7133
147.1792	662.7559	1073.9586	1483.5893	3229.3004
192.4429	700.6359	1115.5844	1487.1474	3232.6682
199.8603	712.3201	1127.0871	1500.7906	3233.4732
214.3364	756.4769	1133.5995	1509.4488	3239.2844
240.8519	770.1341	1154.7897	1509.8969	3243.2745
250.7467	792.1082	1157.3993	1517.7909	3253.5590
268.9275	798.8132	1186.0353	1525.4988	3256.6414
286.8454	838.6949	1190.4913	1535.2380	3258.2911
305.3652	849.8425	1194.0373	1554.8273	3279.8298
313.8861	872.3977	1218.4282	1561.0925	3290.3315
345.6061	881.7603	1227.4753	1674.1324	
373.7393	896.1841	1245.3264	1683.0898	
393.6594	903.0011	1258.4428	1692.2357	
405.8199	913.0946	1270.8911	1697.7887	
414.3722	920.9524	1279.3411	1735.5888	



I

Labeled

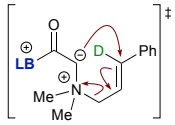
13.8056	417.7361	920.0631	1280.6535	1736.5526
22.8488	422.9001	950.7912	1322.3536	1887.0644
28.3890	428.9630	963.8016	1327.0491	2352.5379
36.9669	454.8273	974.7468	1350.3434	3127.4408
45.5239	484.3092	1000.6807	1353.8956	3131.0682
52.9108	507.9660	1005.3285	1366.7381	3135.1537
61.2775	521.7365	1011.8416	1373.8631	3139.8625
61.6498	543.3484	1018.3170	1379.2396	3200.1896
67.9100	550.5898	1023.0198	1420.3005	3211.6692
69.0657	585.0027	1035.0241	1445.7291	3213.3697
90.6481	627.4823	1038.6482	1457.9584	3221.3085
117.8184	630.9186	1038.8409	1462.4961	3225.4085
125.7299	640.9423	1043.9984	1482.5186	3226.7131
146.8964	662.6083	1063.9509	1483.5807	3229.2646
192.2106	700.6280	1078.6924	1486.9624	3232.6625
199.7418	711.6605	1120.1645	1500.7710	3233.4705
214.0981	748.2862	1128.9709	1507.5946	3239.2841
240.3999	756.4998	1133.6083	1509.8086	3243.2716
248.2407	791.2465	1155.6642	1517.1503	3253.5558
254.2927	796.8153	1157.3992	1525.1255	3256.6414
285.2750	818.4998	1189.6342	1534.9312	3258.2896
305.1605	831.0384	1191.8165	1554.8238	3279.8297
312.6984	849.9209	1199.8859	1560.0138	3290.3315
345.4906	872.3266	1219.7928	1673.6422	
371.3310	882.1333	1229.6884	1683.0894	
393.5170	899.8807	1249.3562	1692.2328	
402.7499	907.8665	1270.2077	1697.5831	
414.2723	912.4471	1277.5112	1735.5875	



TS-VIII-*(2S,3S)*-Major

Unlabeled

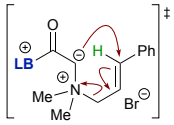
-183.3694	437.4142	950.2943	1253.2004	1687.8361
15.2433	460.3437	970.7977	1277.7639	1688.9648
24.2287	464.4958	982.4359	1293.3115	1693.9770
31.9140	487.4705	993.8889	1306.1865	1704.5083
41.8391	520.7977	1002.0707	1316.9336	1722.1557
45.6029	535.8068	1005.5856	1326.4064	3086.3206
66.9460	540.9297	1008.8889	1336.2619	3087.1579
83.3933	546.7746	1014.8599	1339.0562	3138.1880
88.3247	589.7901	1019.2903	1346.3272	3148.9099
90.3505	593.0331	1021.0621	1368.2100	3173.2105
114.3789	613.5360	1026.8361	1369.5759	3179.9270
123.2580	624.1579	1029.2463	1373.2940	3185.3791
141.1091	627.2991	1032.6985	1381.4984	3194.3318
157.2279	631.5063	1042.7690	1399.8387	3195.9250
175.6018	644.0114	1060.2202	1415.6821	3199.6631
192.2604	695.7898	1062.5839	1428.8001	3200.7410
198.8865	711.7400	1069.9573	1461.1036	3200.9759
203.3753	717.1230	1071.0830	1475.9674	3204.4687
215.3539	718.2316	1076.9511	1476.2886	3214.7272
223.6967	727.5243	1082.6631	1492.8895	3217.3681
235.4887	734.3897	1119.8255	1505.1340	3219.1962
246.8049	745.6930	1121.0947	1510.5656	3229.6183
255.3334	760.5610	1130.0833	1512.8459	3230.9269
269.1073	770.8670	1132.2525	1518.4353	3234.4355
277.7040	789.2526	1146.5252	1523.1632	3237.1699
292.7873	791.5262	1169.6149	1526.9436	3239.5738
319.2713	799.9007	1179.5483	1528.3026	3239.7999
323.9932	839.0322	1182.5280	1537.4963	3239.9780
356.5047	849.1134	1189.9400	1539.1491	3243.3034
366.6313	871.2971	1195.3306	1561.6326	3251.4647
378.4220	876.9171	1200.7294	1564.9945	3251.9031
394.5227	881.1835	1210.1622	1575.3340	3278.2590
413.3429	895.1482	1217.3362	1619.2455	3280.9140
429.3863	919.7427	1228.9153	1633.0456	
430.2072	939.0703	1233.5563	1666.2426	
433.5437	948.3402	1237.5574	1676.8081	



TS-VIII-*(2S,3S)*-Major

Labeled

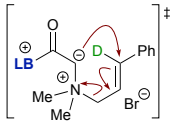
-183.2785	437.1039	947.7881	1237.7929	1687.7582
15.1902	458.8933	950.2761	1253.1788	1688.9647
24.2189	464.0004	970.7977	1289.5480	1693.9755
31.9011	484.4839	979.1212	1301.2698	1704.5082
41.8046	520.7943	993.9208	1306.1919	1721.9367
45.5443	526.8645	1002.0605	1316.9197	2357.2680
66.9116	540.9036	1007.1304	1336.2319	3086.3208
83.0822	546.5670	1012.2485	1337.0038	3087.1584
88.3134	589.7576	1017.5430	1346.3225	3138.1880
90.3479	593.0169	1019.6037	1366.2760	3148.9165
114.3328	612.1290	1021.0629	1369.5736	3173.2104
123.2363	616.7555	1027.3078	1369.8842	3179.9275
141.0696	627.2236	1029.2438	1373.2945	3185.7059
156.7098	631.4343	1032.7295	1399.8332	3195.7120
175.4376	643.8589	1059.8383	1415.6648	3199.2274
191.8859	688.6401	1062.5788	1428.7411	3199.6651
198.7450	710.1800	1063.6636	1461.0990	3200.9750
203.3714	712.9222	1069.9561	1475.8746	3204.4651
215.2807	717.8857	1076.9061	1476.2817	3214.7177
223.0946	718.2684	1082.6426	1492.5349	3217.3680
235.4772	727.5245	1089.6777	1505.1175	3219.1959
246.7804	734.7422	1119.6333	1510.4957	3229.6183
255.2963	746.5169	1122.4826	1512.7362	3230.9269
268.9407	770.8642	1130.0850	1518.4133	3234.4341
277.6495	776.1818	1132.2423	1521.1034	3237.1699
292.7833	789.4713	1146.5003	1523.6903	3239.5738
315.1228	799.7407	1169.6157	1528.2544	3239.7962
323.6053	803.6310	1179.7073	1528.4161	3239.9777
352.4930	824.5861	1182.5721	1539.1276	3243.3034
365.4813	839.1838	1189.9363	1558.6783	3251.4647
373.2790	871.2971	1195.3303	1564.9944	3251.9031
392.9513	877.6124	1200.5764	1574.8044	3278.2557
413.3335	881.1864	1210.8964	1616.7406	3280.8946
422.3698	894.8604	1217.3587	1627.4396	
429.6218	921.6705	1229.6465	1663.2023	
430.2068	938.9735	1237.1803	1676.8050	



TS-VIII•••Br

Unlabeled

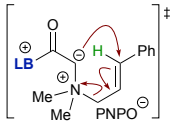
-192.2720	432.1679	962.0362	1255.8994	1689.4265
22.1130	433.7433	964.8998	1277.4637	1691.3408
28.9727	441.0234	966.9878	1290.1721	1701.3543
32.7285	456.2404	985.1095	1299.8943	1714.6222
36.1877	461.2045	999.7433	1304.0978	3083.2907
44.9209	490.3421	1000.7740	1326.5543	3086.9666
53.9981	519.9857	1011.6398	1334.1423	3141.7418
69.2263	540.6807	1014.8150	1341.0572	3153.8061
72.3068	544.9886	1015.1517	1342.1769	3171.4141
78.9023	550.5118	1019.0493	1365.9112	3173.3326
84.2167	592.6089	1019.2254	1367.3252	3176.5129
92.9629	593.8355	1031.6035	1371.1345	3183.5424
107.2190	615.7858	1041.1019	1378.2060	3198.8997
118.9808	624.6824	1043.0892	1402.2278	3201.5428
134.3550	627.9587	1048.9805	1411.3112	3204.4450
154.4624	629.8575	1061.6354	1424.8175	3210.1714
159.3551	644.5505	1064.7195	1455.0303	3211.5097
179.2950	701.6321	1066.9320	1473.5197	3211.7409
190.4421	713.1443	1071.0178	1474.0458	3213.8449
197.6369	722.6602	1077.1308	1490.6642	3217.2384
206.6653	725.1650	1077.9687	1503.0539	3219.1431
216.0279	728.9308	1115.6869	1510.4438	3226.6625
219.8430	731.9283	1119.3072	1511.7705	3230.0802
237.4389	748.7248	1127.3379	1517.6572	3231.7155
253.3795	758.4100	1132.8885	1521.6647	3232.4721
262.1444	767.7208	1143.6314	1527.5018	3236.9121
271.0078	783.1713	1167.9486	1530.0710	3238.0316
279.8145	795.9671	1175.7415	1537.5055	3244.1457
291.0042	802.8659	1184.0084	1540.0445	3250.2116
327.5012	838.9740	1186.1754	1559.8113	3252.0390
331.7664	849.3217	1186.4874	1561.5727	3267.2388
366.1458	876.0652	1199.8254	1569.5234	3283.5689
367.6345	889.8901	1207.8072	1618.9630	
381.2723	893.1883	1214.6920	1629.7026	
398.1690	897.7191	1219.7754	1666.4514	
417.7927	917.4210	1232.4667	1676.0163	
428.9782	937.8586	1235.3154	1683.1336	



TS-VIII•••Br

Labeled

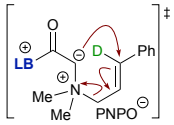
-192.1927	428.9690	937.8495	1238.6999	1689.3542
22.0957	433.5813	961.8666	1255.8872	1691.3389
28.9423	440.9530	964.8984	1287.7739	1701.3538
32.6337	456.1875	966.9878	1296.6429	1714.3732
36.1807	459.8908	977.4663	1300.9984	2348.7027
44.8973	487.9615	1000.5724	1304.1037	3083.2913
53.9082	519.9822	1009.2246	1334.1401	3086.9667
69.2108	536.9856	1012.9422	1339.5176	3141.7418
72.2859	541.2084	1015.1148	1341.0560	3153.8067
78.8768	548.3113	1017.9154	1365.7300	3171.4149
83.9749	592.5835	1019.1190	1366.3666	3173.3350
92.9419	593.8113	1019.6547	1367.5546	3176.8040
107.2142	614.5217	1031.6378	1371.1346	3198.8997
118.9472	618.0286	1043.0634	1402.2235	3201.5376
134.2992	627.3249	1044.8443	1411.2257	3204.4200
154.2823	629.7025	1061.5938	1424.7688	3210.1690
158.9273	644.3334	1063.5678	1455.0219	3211.5095
179.1817	691.5006	1064.9694	1473.4708	3211.7407
190.2005	709.8718	1066.9307	1474.0339	3213.5174
197.5053	718.8373	1077.1114	1490.4915	3217.2345
206.4619	722.9097	1077.9605	1503.0350	3219.1431
215.8652	725.7687	1087.6873	1510.4141	3226.6513
219.3263	728.9885	1115.5027	1511.7407	3230.0802
237.4297	732.0353	1121.5164	1517.4627	3231.7155
253.3285	748.6506	1127.3353	1521.6369	3232.4696
262.1389	767.7199	1132.8742	1523.6396	3236.9121
270.7319	774.3989	1143.6170	1527.6331	3238.0316
279.8063	783.1899	1167.9486	1531.6006	3244.1457
290.9881	802.8333	1175.7183	1539.9349	3250.2116
325.8118	808.9894	1184.0088	1557.4905	3252.0390
329.5187	824.8213	1186.1929	1561.5724	3267.2342
359.1273	839.0417	1186.5515	1568.7456	3283.5379
366.6555	876.0651	1199.7885	1615.2472	
378.1541	889.9025	1207.5034	1624.0561	
394.4851	895.0201	1214.7142	1663.4946	
417.7925	896.4498	1219.7625	1676.0130	
421.8710	919.7179	1235.0632	1683.1318	



TS-VIII•••PNPO

Unlabeled

-217.1941	425.8604	879.3778	1212.6487	1622.6382
1.9741	432.8182	881.8107	1218.9325	1634.6069
9.0764	433.2271	886.5757	1229.0749	1652.9857
21.4418	433.7864	896.8269	1240.1584	1666.4279
26.0374	437.2298	926.4051	1243.3213	1676.8496
29.0546	456.3348	938.9363	1252.4488	1679.0923
32.0809	461.7541	949.2732	1277.5179	1683.1663
42.8495	464.4040	953.6108	1287.9031	1690.0321
44.2011	493.8242	974.4678	1292.4914	1692.0881
56.8420	494.5577	995.0751	1306.2447	1697.5885
63.6586	518.8997	996.3594	1326.7828	1709.5082
73.1189	538.2521	997.7448	1328.2907	3080.2212
79.1266	541.3577	999.0960	1345.0520	3083.3825
85.4188	548.4024	1001.8553	1346.0193	3136.7100
88.3402	556.3583	1002.3145	1348.5062	3156.1000
99.2649	587.5043	1005.4765	1350.2450	3165.8371
100.5762	592.3777	1007.9272	1360.4916	3173.0148
107.7925	616.1417	1015.8524	1367.6395	3177.4921
116.8089	625.2967	1019.1046	1368.7540	3195.7561
133.8958	626.7670	1021.6686	1379.9740	3196.2541
138.4245	628.8525	1030.1956	1387.6683	3196.4632
158.3145	638.1160	1031.2507	1402.5067	3197.9959
177.8052	643.4570	1033.6794	1416.3711	3200.9273
189.2256	658.5831	1056.6799	1426.7405	3203.8681
193.5073	696.2733	1060.3255	1447.5472	3208.5411
206.3323	711.2679	1062.5803	1453.4408	3209.9058
216.5925	712.7401	1067.5305	1475.1045	3214.4700
224.4554	720.4332	1069.0036	1479.8330	3216.3835
235.7666	725.1361	1074.2570	1494.2340	3219.5663
246.6017	728.6157	1077.2673	1504.9562	3222.7166
254.7800	732.8584	1116.0161	1510.5977	3228.3321
267.2887	755.5223	1116.3076	1512.5586	3233.0299
271.0997	774.5150	1120.8992	1520.0900	3235.3340
278.7776	786.4874	1124.2367	1522.7080	3236.5201
283.1490	789.7635	1131.7363	1530.2783	3240.6348
292.0566	794.2531	1142.8097	1534.3507	3242.6074
322.3027	795.6010	1144.8077	1536.1709	3244.1883
333.1085	813.8418	1170.2125	1541.2126	3251.1268
362.2448	822.8917	1176.0710	1545.2829	3251.8633
368.9155	837.8001	1180.6812	1553.2815	3252.5355
377.5731	840.6393	1186.2626	1561.3773	3256.0675
380.6433	858.4536	1189.7017	1578.5145	3264.4945
401.3833	867.6433	1201.8733	1582.4543	3267.4955
417.6221	871.7083	1205.3231	1613.8429	



TS-VIII•••PNPO

Labeled

-217.1589	424.5775	872.0374	1205.3043	1615.6079
2.0521	426.0053	879.3789	1212.6298	1630.7236
9.0670	432.8188	881.7806	1218.9323	1652.9852
21.4418	433.2336	886.5758	1229.1330	1662.5156
26.0078	433.8545	896.3090	1242.7025	1676.8320
29.0215	456.3309	921.8585	1243.8239	1679.0083
32.0750	461.6777	938.6475	1252.3638	1683.1628
42.8448	464.0962	948.2890	1287.2183	1689.8690
44.1443	492.2541	953.6044	1287.9059	1692.0846
56.8308	494.3739	974.4677	1296.9537	1697.5857
63.6319	518.8941	978.1559	1306.2480	1709.1135
73.0744	529.9084	995.0895	1326.9456	2362.3370
79.1144	541.0807	996.6816	1341.0559	3080.2223
85.3464	548.2391	999.1515	1345.9205	3083.3828
88.1058	556.3564	1002.0332	1348.4629	3136.7100
99.2476	587.4947	1005.4262	1350.2446	3156.1002
100.5639	592.3634	1007.2606	1360.4896	3165.8386
107.7537	615.7862	1014.1777	1365.6175	3173.0176
116.7809	619.0862	1018.8837	1367.7863	3177.5986
133.8714	626.3566	1021.6684	1368.8340	3195.9594
138.4003	628.2764	1028.1369	1386.2922	3196.4146
157.7047	638.1123	1030.0561	1402.4579	3197.3482
177.5563	643.1218	1032.2075	1416.3267	3200.9273
188.9191	658.5793	1033.8939	1426.7078	3201.2248
193.3776	692.7009	1059.8181	1447.5141	3208.4413
206.3212	710.3506	1062.5620	1453.4200	3209.9056
216.5216	712.7295	1064.3696	1475.0192	3214.4671
224.2997	720.3478	1067.5463	1479.8137	3216.3834
235.6580	725.1356	1068.9676	1494.2162	3219.5641
246.5812	728.5587	1077.0696	1504.9389	3222.7166
254.7130	732.2748	1090.6004	1510.5974	3228.3277
267.2537	738.1063	1115.8159	1512.5491	3233.0299
270.6268	755.2714	1118.0027	1520.0893	3235.3310
278.7379	774.5203	1120.8904	1522.4357	3236.5200
283.0521	786.4895	1124.2352	1526.7424	3240.6347
292.0450	789.7817	1131.7141	1530.4884	3242.6074
322.2450	794.8529	1142.7752	1535.6667	3244.1883
329.2880	804.6417	1144.6463	1537.1624	3251.1268
355.7468	814.5953	1170.2125	1545.2749	3251.8633
368.1293	822.8617	1176.0709	1553.2805	3252.5354
374.0336	836.9427	1180.6857	1560.8567	3256.0675
380.3579	840.5139	1186.3318	1576.8158	3264.4166
398.5438	847.1586	1189.7023	1582.4419	3267.4810
417.6205	867.6469	1201.8513	1612.7742	

Appendix II:

Computational Data for Chapter 3

Non-Bonding 1,5-S···O Interactions Govern Chemo- and Enantioselectivity in Isothiourea-Catalyzed Annulations of Benzazoles

Full Computed Reaction Coordinate

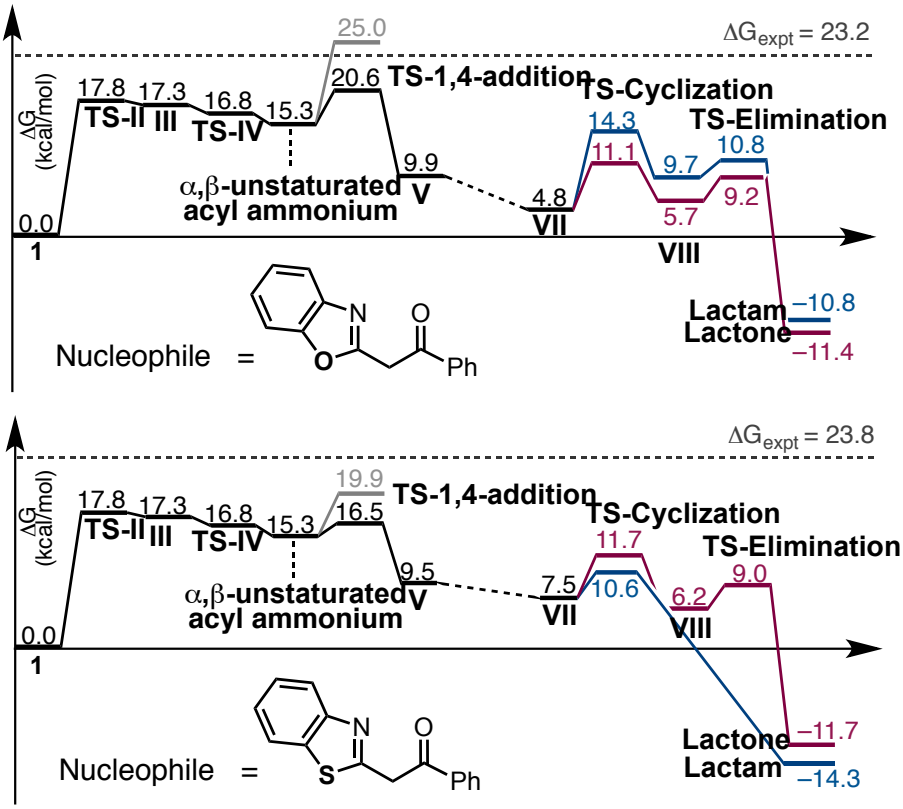


Figure A1.8 Reaction coordinates for acylation of the catalyst, cyclization, and turnover for benzoxazole (top) and benzothiazole (bottom) nucleophiles.

HyperBTM 3.1

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C19H20N2S C1[X(C19H20N2S)] #Atoms= 42
Charge = 0 Multiplicity = 1

SCF Energy= -1243.38807245 Predicted Change= -3.780822D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00101	0.00180	[YES]	0.00101	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-4.267420	0.777623	1.763328
H	-4.684114	1.285391	2.627153

C	-2.912754	0.937488	1.470282
H	-2.278106	1.553704	2.098307
C	-2.393224	0.279698	0.359486
C	-3.216158	-0.534538	-0.433990
C	-4.561425	-0.690580	-0.138925
H	-5.191996	-1.319702	-0.758905
C	-5.086194	-0.024034	0.970244
H	-6.137209	-0.136761	1.213712
N	-1.079739	0.321747	-0.090745
C	-0.804409	-0.457605	-1.199410
S	-2.300558	-1.260125	-1.754835
C	-0.045848	1.170346	0.485639
H	0.351326	0.714204	1.403846
H	-0.512145	2.122687	0.753275
C	1.066640	1.396643	-0.540502
C	2.246292	2.178181	0.064661
C	3.241229	2.603820	-1.018707
H	2.752334	3.264235	-1.745136
H	3.660221	1.756559	-1.567170
H	4.075753	3.154365	-0.573555
H	2.761835	1.517410	0.775054
C	1.774395	3.421066	0.827066
H	1.158582	4.060698	0.182599
H	2.635818	4.009927	1.156437
H	1.190070	3.168491	1.716731
H	0.638407	2.005826	-1.350865
C	1.465749	0.044231	-1.190441
C	2.205648	-0.880832	-0.232987
H	2.145325	0.262760	-2.020410
N	0.310836	-0.639398	-1.780956
C	1.523195	-1.676383	0.693223
H	0.436374	-1.677091	0.713878
C	2.219574	-2.488734	1.584790
H	1.670389	-3.099287	2.295272
C	3.611903	-2.526877	1.560180
H	4.154372	-3.163346	2.252487
C	4.302157	-1.750730	0.632764
H	5.386857	-1.782168	0.593867
C	3.601866	-0.939270	-0.256699
H	4.149870	-0.349419	-0.987322

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1243.38807245 Predicted Change= -3.780822D-09

Zero-point correction (ZPE)=	-1243.0335	0.35456
Internal Energy (U)=	-1243.0150	0.37305
Enthalpy (H)=	-1243.0140	0.37399
Gibbs Free Energy (G)=	-1243.0803	0.30768

Frequencies -- 31.5000 37.6909 62.6480

==========

#M062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C19H20N2S C1[X(C19H20N2S)] #Atoms= 42
Charge = 0 Multiplicity = 1

SCF Energy= -1243.43328732
==========

Cinnamic anhydride 3.2

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011
==========
#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C18H14O3 C1[X(C18H14O3)] #Atoms= 35
Charge = 0 Multiplicity = 1

SCF Energy= -919.635362424 Predicted Change= -1.533633D-09
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00109	0.00180	[YES]	0.00109	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	0.269734	1.060641	-0.253978
C	-0.951475	1.446848	0.262854
C	-1.978729	0.445247	-0.065337
H	-1.668669	-0.404667	-0.662696
C	-3.233985	0.635940	0.367431
H	-3.422680	1.537466	0.949744
C	-4.391736	-0.230579	0.135417
O	-1.099514	2.444158	0.916855
C	1.266422	1.997513	-0.460555
C	2.613193	1.415077	-0.392881
H	3.401058	2.122779	-0.628012
C	2.851797	0.136409	-0.063622
H	1.998959	-0.504506	0.150779
C	4.166623	-0.505228	0.034384
O	1.029833	3.147255	-0.718678
C	-5.642562	0.189604	0.606536
H	-5.720568	1.139071	1.129559
C	-6.776991	-0.590447	0.409011
H	-7.738781	-0.249131	0.778073
C	-6.673791	-1.806624	-0.261192
H	-7.556335	-2.419202	-0.417434
C	-5.432179	-2.238703	-0.731880
H	-5.348986	-3.187958	-1.251628
C	-4.300523	-1.459171	-0.536723
H	-3.340897	-1.809433	-0.904485
C	4.221080	-1.878432	0.307200
H	3.293769	-2.429144	0.442178
C	5.442204	-2.538002	0.403140

H	5.466917	-3.602386	0.613676
C	6.628263	-1.829340	0.230747
H	7.583568	-2.339163	0.307312
C	6.587626	-0.459639	-0.036499
H	7.511189	0.095407	-0.166925
C	5.369188	0.197906	-0.134144
H	5.354475	1.264136	-0.337054

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -919.635362424 Predicted Change= -1.533633D-09

Zero-point correction (ZPE)=	-919.3592	0.27614
Internal Energy (U)=	-919.3410	0.29429
Enthalpy (H)=	-919.3401	0.29523
Gibbs Free Energy (G)=	-919.4107	0.22457

Frequencies -- 8.7854 13.5528 33.4022

==========

#M062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C18H14O3 C1[X(C18H14O3)] #Atoms= 35
Charge = 0 Multiplicity = 1

SCF Energy= -919.681633796

==========

Benzothiazole 3.3

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C15H11NOS C1[X(C15H11NOS)] #Atoms= 29
Charge = 0 Multiplicity = 1

SCF Energy= -1106.08031711 Predicted Change= -7.035219D-10

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00065	0.00180	[YES]	0.00065	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-3.172204	1.382292	0.967016
H	-3.024349	1.964193	1.870931
C	-4.243198	1.609461	0.118637
H	-4.960297	2.389038	0.354564
C	-4.414989	0.844380	-1.046456
H	-5.261705	1.042107	-1.695934

C	-3.520167	-0.161311	-1.383610
H	-3.655063	-0.750495	-2.284591
C	-2.441849	-0.389492	-0.527300
C	-2.259290	0.371935	0.643352
S	-1.156770	-1.560607	-0.655131
C	-0.496046	-0.936055	0.855029
C	0.761017	-1.529702	1.421621
C	1.910767	-1.472732	0.415024
C	2.540802	-0.154592	0.109491
O	2.277115	-2.493992	-0.132633
H	0.605019	-2.584770	1.661718
H	1.003826	-0.986489	2.338371
N	-1.143954	0.036196	1.399381
C	2.103580	1.037874	0.696015
H	1.270281	1.041151	1.392068
C	2.727380	2.239459	0.371442
H	2.383832	3.164187	0.823674
C	3.787195	2.254648	-0.532227
H	4.272481	3.193390	-0.781427
C	4.226679	1.066824	-1.118717
H	5.053254	1.080220	-1.821963
C	3.604274	-0.132349	-0.800253
H	3.928079	-1.068093	-1.244311

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1106.08031711 Predicted Change= -7.035219D-10
Zero-point correction (ZPE)= -1105.8558 0.22448
Internal Energy (U)= -1105.8417 0.23860
Enthalpy (H)= -1105.8407 0.23954
Gibbs Free Energy (G)= -1105.8996 0.18066

Frequencies -- 18.2847 25.8674 47.4198

==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C15H11NOS C1[X(C15H11NOS)] #Atoms= 29
Charge = 0 Multiplicity = 1

SCF Energy= -1106.11556028

==========

Benzoxazole 3.4

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C15H11NO2 C1[X(C15H11NO2)] #Atoms= 29
Charge = 0 Multiplicity = 1

SCF Energy= -783.115706156 Predicted Change= -6.173327D-10

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00128	0.00180	[YES]	0.00128	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	3.331916	-1.188450	-0.910631
H	3.402428	-1.746894	-1.837718
C	4.245108	-1.361462	0.123280
H	5.053595	-2.075358	0.004976
C	4.148386	-0.634646	1.322312
H	4.884174	-0.800331	2.102297
C	3.133554	0.294276	1.536914
H	3.048482	0.860714	2.456943
C	2.236272	0.446705	0.492261
C	2.310660	-0.260928	-0.708123
O	1.148776	1.272896	0.409622
C	0.628323	1.024167	-0.825724
C	-0.592151	1.798257	-1.187973
C	-1.717230	1.604054	-0.166430
C	-2.341314	0.255136	-0.026741
O	-2.080769	2.545912	0.507177
H	-0.908606	1.486994	-2.186413
H	-0.362179	2.866616	-1.202566
N	1.252186	0.141335	-1.527942
C	-3.314637	0.084912	0.965152
H	-3.569249	0.931428	1.594382
C	-3.936645	-1.145013	1.130590
H	-4.690190	-1.273729	1.900824
C	-3.591479	-2.214910	0.303326
H	-4.076729	-3.177614	0.431547
C	-2.624929	-2.051783	-0.686279
H	-2.356925	-2.884505	-1.328258
C	-1.998049	-0.819855	-0.853775
H	-1.240862	-0.709893	-1.623760

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-783.115706156	Predicted Change= -6.173327D-10
Zero-point correction (ZPE)=	-782.8871	0.22858
Internal Energy (U)=	-782.8736	0.24204
Enthalpy (H)=	-782.8727	0.24299
Gibbs Free Energy (G)=	-782.9298	0.18581

Frequencies -- 16.7098 31.9724 59.8107

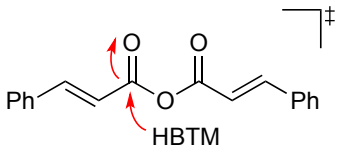
#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C15H11NO2 C1[X(C15H11NO2)] #Atoms= 29

Charge = 0 Multiplicity = 1

SCF Energy= -783.152457418

==========



TS-II

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C37H34N2O3S C1[X(C37H34N2O3S)] #Atoms= 77
Charge = 0 Multiplicity = 1

SCF Energy= -2163.02240715 Predicted Change= -3.756551D-09

==========

Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.01256	0.00180	[NO]	0.01256	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.931469	5.979914	-0.017960
H	2.120910	6.896501	0.530688
C	1.178514	4.972837	0.582452
H	0.775295	5.099706	1.581312
C	0.951699	3.807111	-0.142085
C	1.451468	3.654522	-1.437697
C	2.198678	4.661679	-2.033460
H	2.586100	4.541202	-3.039903
C	2.439263	5.828089	-1.309143
H	3.022782	6.624660	-1.758164
N	0.241013	2.683271	0.284524
C	0.155835	1.677411	-0.631662
S	0.963560	2.114628	-2.146214
C	-0.273053	2.531763	1.644645
H	-1.216390	3.085640	1.743935
H	0.462025	2.978961	2.317720
C	-0.461091	1.052775	1.975369
C	-1.145427	0.855903	3.339244
C	-1.136407	-0.620258	3.745297
H	-0.106635	-0.993132	3.799328
H	-1.684483	-1.255221	3.044748
H	-1.593683	-0.745885	4.731330

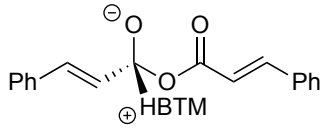
H	-2.187922	1.191444	3.248521
C	-0.467999	1.686386	4.434378
H	-0.577741	2.762737	4.271974
H	0.602874	1.454650	4.489142
H	-0.910056	1.456601	5.408442
H	0.535630	0.590635	2.021252
C	-1.188311	0.342069	0.812060
C	-2.647551	0.735537	0.639444
H	-1.141011	-0.730050	1.002963
N	-0.435203	0.547775	-0.426744
C	-0.383687	-0.661076	-1.753526
O	1.034876	-1.070492	-1.621203
C	1.587771	-1.500357	-0.484415
C	3.028871	-1.785100	-0.683864
H	3.425335	-1.610891	-1.678366
C	3.767561	-2.232624	0.339503
C	5.199092	-2.553492	0.321858
H	3.256699	-2.377767	1.290984
O	1.004545	-1.636602	0.576325
C	-1.308725	-1.740323	-1.256260
H	-0.917261	-2.471358	-0.556436
C	-2.583865	-1.733006	-1.650591
C	-3.626068	-2.677925	-1.220540
H	-2.901697	-0.926261	-2.310632
O	-0.586278	-0.072522	-2.817086
C	-3.028024	1.925295	0.010845
H	-2.277649	2.591304	-0.407186
C	-4.373550	2.261575	-0.117881
H	-4.649717	3.187379	-0.613288
C	-5.360592	1.410214	0.373573
H	-6.409075	1.671260	0.267862
C	-4.993259	0.213718	0.984615
H	-5.752385	-0.473247	1.346421
C	-3.647367	-0.119967	1.110228
H	-3.371072	-1.074777	1.552129
C	6.008183	-2.353855	-0.806833
H	5.581273	-1.943284	-1.716747
C	7.359267	-2.671564	-0.770542
H	7.973480	-2.509384	-1.650890
C	7.928416	-3.194617	0.391944
H	8.985282	-3.441393	0.416001
C	7.136866	-3.396553	1.519283
H	7.571801	-3.802112	2.427293
C	5.783184	-3.076437	1.482675
H	5.164349	-3.233260	2.362564
C	-3.326047	-3.916234	-0.636093
H	-2.290129	-4.226279	-0.532201
C	-4.342908	-4.759908	-0.204626
H	-4.094619	-5.717533	0.243021
C	-5.678379	-4.384086	-0.352428
H	-6.470781	-5.045822	-0.016400
C	-5.989596	-3.160298	-0.940363
H	-7.026360	-2.861485	-1.062527
C	-4.970398	-2.317653	-1.374359
H	-5.210940	-1.356754	-1.822721

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -2163.02240715 Predicted Change= -3.756551D-09
Zero-point correction (ZPE)= -2162.3904 0.63197
Internal Energy (U)= -2162.3533 0.66902
Enthalpy (H)= -2162.3524 0.66996
Gibbs Free Energy (G)= -2162.4645 0.55783

Frequencies -- -181.5675 5.7549 11.0832
==========
#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C37H34N2O3S C1[X(C37H34N2O3S)] #Atoms= 77
Charge = 0 Multiplicity = 1

SCF Energy= -2163.11220778
==========



III

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011
==========
#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C37H34N2O3S C1[X(C37H34N2O3S)] #Atoms= 77
Charge = 0 Multiplicity = 1

SCF Energy= -2163.02339797 Predicted Change= -1.762699D-08
==========
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00697	0.00180	[NO]	0.00697	0.00180	[YES]

Atomic Coordinates (Angstroms)

Type	X	Y	Z
C	1.075572	6.307405	-0.122621
H	1.173931	7.241231	0.420639
C	0.535520	5.199558	0.525137
H	0.207673	5.262790	1.556992
C	0.423977	4.016382	-0.198707
C	0.826990	3.939276	-1.531836
C	1.361723	5.049022	-2.174828

H	1.673962	4.990104	-3.212539
C	1.487519	6.234881	-1.455613
H	1.906488	7.111099	-1.938647
N	-0.069564	2.792766	0.268490
C	-0.078734	1.803394	-0.654405
S	0.505550	2.346758	-2.222020
C	-0.466435	2.581483	1.661458
H	-1.458987	3.022430	1.822752
H	0.254578	3.117614	2.282664
C	-0.454736	1.094375	1.997583
C	-1.046847	0.824062	3.391545
C	-0.863351	-0.643489	3.787041
H	0.198981	-0.913805	3.768783
H	-1.393388	-1.329300	3.121346
H	-1.240481	-0.811990	4.800111
H	-2.122060	1.048642	3.354039
C	-0.405714	1.721849	4.454888
H	-0.635174	2.780766	4.303409
H	0.684750	1.603094	4.455324
H	-0.772251	1.447551	5.448420
H	0.590358	0.755077	1.996093
C	-1.145478	0.289276	0.878428
C	-2.649494	0.482708	0.769886
H	-0.938932	-0.761745	1.070790
N	-0.481008	0.586106	-0.399363
C	-0.358335	-0.485164	-1.571829
O	1.149741	-0.833122	-1.507000
C	1.758924	-1.236448	-0.405229
C	3.201874	-1.495822	-0.650005
H	3.562679	-1.317367	-1.657548
C	3.980572	-1.935142	0.346140
C	5.414224	-2.243406	0.279179
H	3.502982	-2.086554	1.313708
O	1.226853	-1.385040	0.686585
C	-1.120391	-1.725468	-1.146040
H	-0.656719	-2.396489	-0.428271
C	-2.347713	-1.929388	-1.626527
C	-3.236243	-3.048017	-1.272427
H	-2.753039	-1.179174	-2.304742
O	-0.603372	0.037447	-2.683140
C	-3.218664	1.625831	0.199986
H	-2.589321	2.411528	-0.210787
C	-4.602467	1.764787	0.119365
H	-5.026046	2.657807	-0.329643
C	-5.438277	0.759657	0.600010
H	-6.516327	0.866833	0.530065
C	-4.881562	-0.390131	1.154962
H	-5.521476	-1.192881	1.508499
C	-3.498429	-0.525566	1.234477
H	-3.072953	-1.443408	1.632955
C	6.179929	-2.044299	-0.879241
H	5.716469	-1.641589	-1.774727
C	7.533622	-2.353517	-0.892262
H	8.112950	-2.192209	-1.796096
C	8.149143	-2.867634	0.250289

H	9.207552	-3.108533	0.236418
C	7.401131	-3.068695	1.407033
H	7.871890	-3.468008	2.299929
C	6.044805	-2.757119	1.419518
H	5.460512	-2.914309	2.322635
C	-2.755288	-4.250206	-0.735468
H	-1.685513	-4.392576	-0.610588
C	-3.632395	-5.269573	-0.383277
H	-3.243073	-6.197261	0.025194
C	-5.006517	-5.108654	-0.563278
H	-5.689079	-5.907517	-0.290093
C	-5.496397	-3.921706	-1.103400
H	-6.564057	-3.789004	-1.250686
C	-4.616790	-2.903481	-1.459353
H	-4.999054	-1.973491	-1.872997

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2163.02339797 Predicted Change= -1.762699D-08

Zero-point correction (ZPE)=	-2162.3902	0.63310
Internal Energy (U)=	-2162.3528	0.67057
Enthalpy (H)=	-2162.3518	0.67151
Gibbs Free Energy (G)=	-2162.4639	0.55947

Frequencies -- 10.1889 18.2994 20.9709

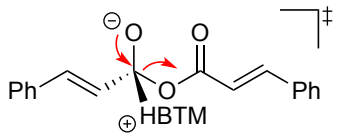
==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C37H34N2O3S C1[X(C37H34N2O3S)] #Atoms= 77
Charge = 0 Multiplicity = 1

SCF Energy= -2163.11451983

==========



TS-IV

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C37H34N2O3S C1[X(C37H34N2O3S)] #Atoms= 77
Charge = 0 Multiplicity = 1

SCF Energy= -2163.02090696 Predicted Change= -1.891779D-09

```
=============================================================================
 Optimization completed on the basis of negligible forces.          {Found       2       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00000 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00301 ||  0.00180   [ NO ]       0.00301 ||  0.00180   [ YES ]
-----------------------------------------------------------------------------
     Atomic              Coordinates (Angstroms)
      Type              X           Y           Z
-----------------------------------------------------------------------------
      C         1.513782    6.226192   -0.040213
      H         1.749577    7.109817    0.542864
      C         0.943754    5.127684    0.594884
      H         0.726446    5.148593    1.657042
      C         0.656690    4.009417   -0.183010
      C         0.919771    3.988676   -1.551754
      C         1.486513    5.090388   -2.183320
      H         1.689984    5.075009   -3.248916
      C         1.784831    6.209349   -1.411852
      H         2.230512    7.078686   -1.882991
      N         0.095756    2.804113    0.258917
      C        -0.094607    1.893052   -0.714313
      S         0.397256    2.476672   -2.287946
      C        -0.189673    2.541577    1.672091
      H        -1.122009    3.050130    1.949156
      H         0.628846    2.981867    2.244779
      C        -0.266062    1.041665    1.923502
      C        -0.735515    0.728416    3.354786
      C        -0.643743   -0.773660    3.636177
      H         0.370762   -1.136884    3.436517
      H        -1.333057   -1.357366    3.020711
      H        -0.884269   -0.978473    4.683560
      H        -1.784714    1.043497    3.446279
      C         0.091279    1.497249    4.390226
      H        -0.195862    1.193047    5.400880
      H        -0.053124    2.579727    4.321819
      H         1.160101    1.284588    4.266199
      H         0.740085    0.621056    1.791002
      C        -1.126506    0.350229    0.852304
      C        -2.620918    0.612391    0.913001
      H        -0.936368   -0.715678    0.960305
      N        -0.600657    0.696014   -0.484546
      C        -0.736878   -0.256356   -1.625415
      O         1.087829   -0.841985   -1.623951
      C         1.660491   -1.296450   -0.568803
      C         3.117081   -1.611898   -0.760949
      H         3.522299   -1.414234   -1.749352
      C         3.851195   -2.108212    0.240394
      C         5.278490   -2.459829    0.211242
      H         3.337224   -2.271351    1.187228
      O         1.123086   -1.482611    0.536178
      C        -1.395746   -1.541017   -1.232064
      H        -0.869246   -2.191499   -0.541257
      C        -2.626572   -1.792359   -1.685079
      C        -3.446821   -2.956425   -1.316110
      H        -3.098041   -1.052265   -2.330907
```

O	-0.877198	0.251416	-2.730945
C	-3.474617	-0.419654	1.311643
H	-3.058780	-1.397022	1.545590
C	-4.852110	-0.226133	1.367462
H	-5.498048	-1.045594	1.667292
C	-5.396055	1.007327	1.017403
H	-6.469953	1.161346	1.054099
C	-4.556298	2.037966	0.601060
H	-4.973500	2.996135	0.307116
C	-3.178766	1.840479	0.544464
H	-2.546883	2.647326	0.180711
C	6.085933	-2.277173	-0.921400
H	5.659476	-1.861129	-1.829202
C	7.431441	-2.621062	-0.895174
H	8.041423	-2.471714	-1.781054
C	8.000396	-3.155012	0.262177
H	9.052504	-3.422269	0.278917
C	7.211178	-3.342256	1.393581
H	7.643520	-3.756989	2.299019
C	5.863212	-2.996484	1.365536
H	5.247778	-3.142782	2.249857
C	-4.840408	-2.862255	-1.417736
H	-5.282604	-1.941549	-1.790184
C	-5.655885	-3.922529	-1.033015
H	-6.734817	-3.831189	-1.113707
C	-5.086912	-5.098591	-0.549643
H	-5.719423	-5.930035	-0.254489
C	-3.699234	-5.207869	-0.454899
H	-3.250915	-6.126732	-0.089450
C	-2.885269	-4.147097	-0.835046
H	-1.805110	-4.246682	-0.775960

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2163.02090696 Predicted Change= -1.891779D-09
Zero-point correction (ZPE)= -2162.3885 0.63233
Internal Energy (U)= -2162.3511 0.66972
Enthalpy (H)= -2162.3502 0.67066
Gibbs Free Energy (G)= -2162.4634 0.55749

Frequencies -- -114.8179 7.5217 16.2836

Favored-Lactonization-(X=O)-TS

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)
iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.13243384 Predicted Change= -5.035723D-09

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00126	0.00180	[YES]	0.00126	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	4.052756	-0.838226	-0.399409
C	2.798714	-0.797481	-0.877352
N	1.884654	0.043053	-0.396124
C	0.523573	0.008070	-0.922693
C	-0.299090	1.261840	-0.778163
H	-0.123983	1.767026	0.170791
H	0.003145	1.953843	-1.576131
O	0.280659	-0.829213	-1.774089
C	2.209732	0.925558	0.744575
H	1.283656	0.975699	1.316677
C	2.611495	2.308335	0.264978
C	3.250943	0.226012	1.641077
H	2.785571	-0.715571	1.967387
C	3.612743	1.041401	2.895338
C	2.404643	1.173475	3.827026
H	2.673714	1.758536	4.710990
H	2.073979	0.184128	4.163481
H	1.550259	1.665209	3.354814
H	3.925371	2.043383	2.573104
C	4.774896	0.402261	3.663362
H	5.714700	0.432866	3.104067
H	4.551295	-0.643398	3.907139
H	4.938191	0.936405	4.603676
C	4.475956	-0.125680	0.810568
H	5.130055	-0.806722	1.357550
H	5.049012	0.765203	0.526162
C	4.908718	-1.699686	-1.099276
C	4.245138	-2.365580	-2.126719
S	2.548294	-1.906212	-2.203284
C	6.263526	-1.906422	-0.852798
H	6.783893	-1.374702	-0.064040
C	6.932406	-2.814793	-1.664947
H	7.988583	-2.995024	-1.496807
C	6.268984	-3.494703	-2.692487
H	6.815516	-4.198490	-3.310753
C	4.917054	-3.277238	-2.934967
H	4.399360	-3.799801	-3.732392
C	2.168873	3.431549	0.968912
H	1.511809	3.305750	1.826234
C	2.549118	4.711577	0.576094
H	2.194246	5.572952	1.133043
C	3.371361	4.885111	-0.534609
H	3.665008	5.882619	-0.845466
C	3.803778	3.773196	-1.252750
H	4.433083	3.899622	-2.128139

C	3.423982	2.492734	-0.857039
H	3.753217	1.639069	-1.445103
C	-1.796528	0.940829	-0.939537
H	-1.951319	0.660804	-1.989288
C	-2.549034	2.246609	-0.702194
C	-2.279853	-0.198055	-0.051278
C	-3.601844	-0.678101	-0.343963
C	-1.445232	-0.824121	0.873718
C	-1.957741	-1.718474	1.966133
O	-0.172952	-0.658949	0.904838
C	-2.869319	3.082829	-1.773116
H	-2.627161	2.765613	-2.785470
C	-3.503007	4.305229	-1.560461
H	-3.752065	4.938722	-2.406929
C	-3.822874	4.710621	-0.266330
H	-4.320022	5.661155	-0.098039
C	-3.503519	3.884297	0.809866
H	-3.751675	4.189871	1.822356
C	-2.871021	2.663003	0.591376
H	-2.632041	2.011207	1.428983
O	-4.311794	0.097152	-1.248816
C	-5.494703	-0.553464	-1.427596
C	-5.460441	-1.701111	-0.628000
N	-4.244642	-1.755676	0.033577
C	-6.560676	-0.200562	-2.233809
H	-6.546603	0.699129	-2.839034
C	-7.652784	-1.071467	-2.217495
H	-8.520825	-0.844627	-2.828119
C	-7.647512	-2.229040	-1.426651
H	-8.515749	-2.880812	-1.441204
C	-6.558310	-2.563014	-0.622989
H	-6.556415	-3.460121	-0.012521
C	-3.064643	-1.368089	2.743069
H	-3.627524	-0.473695	2.490999
C	-3.443693	-2.155457	3.824572
H	-4.301726	-1.870691	4.426232
C	-2.723662	-3.308939	4.136924
H	-3.023103	-3.926341	4.978696
C	-1.613922	-3.660517	3.371338
H	-1.046666	-4.554444	3.613500
C	-1.224622	-2.858338	2.301625
H	-0.345779	-3.106160	1.714306

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2448.13243384 Predicted Change= -5.035723D-09
Zero-point correction (ZPE)= -2447.4195 0.71289
Internal Energy (U)= -2447.3792 0.75322
Enthalpy (H)= -2447.3782 0.75416
Gibbs Free Energy (G)= -2447.4954 0.63699

Frequencies -- -107.7350 11.6842 19.6170

==========

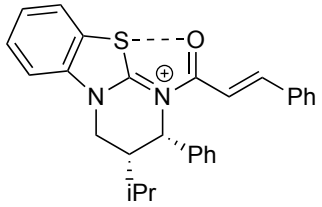
#M062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current

SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.23239713

==========



α,β−unsaturated acyl ammonium

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C28H27N2OS(1+) C1[X(C28H27N2OS)] #Atoms= 59
Charge = 1 Multiplicity = 1

SCF Energy= -1665.46191819 Predicted Change= -5.735051D-09

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00214	0.00180	[NO]	0.00214	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-6.166109	-0.920994	0.419624
H	-7.144371	-0.465355	0.525261
C	-5.070035	-0.112771	0.151680
H	-5.179375	0.961613	0.057122
C	-3.829886	-0.737145	0.028525
C	-3.688202	-2.114071	0.177532
C	-4.791205	-2.922617	0.442857
H	-4.681852	-3.995769	0.556081
C	-6.030902	-2.308467	0.561386
H	-6.906261	-2.912776	0.772243
N	-2.601382	-0.116358	-0.238168
C	-1.561635	-0.952255	-0.262441
S	-2.018554	-2.610282	-0.021174
C	-2.500269	1.321300	-0.523463
H	-2.528658	1.875394	0.422294
H	-3.378081	1.580696	-1.115867
C	-1.226226	1.588092	-1.307664
C	-1.025966	3.087930	-1.601625

C	0.121228	3.301208	-2.593738
H	-0.114190	2.826914	-3.553453
H	1.076853	2.896761	-2.247672
H	0.265875	4.369867	-2.773953
H	-0.784306	3.594532	-0.658580
C	-2.304078	3.717086	-2.166861
H	-3.115033	3.749773	-1.433679
H	-2.653550	3.165526	-3.047774
H	-2.102961	4.746602	-2.475199
H	-1.312806	1.065480	-2.271322
C	-0.035247	0.949650	-0.563884
C	0.295301	1.587081	0.774498
H	0.828833	1.020042	-1.226876
N	-0.291660	-0.507653	-0.414108
C	0.785043	-1.443088	-0.360148
C	2.140427	-0.895382	-0.244394
H	2.280088	0.147134	0.008579
C	3.181997	-1.732271	-0.405246
C	4.597643	-1.392284	-0.284009
H	2.957882	-2.768688	-0.654102
O	0.525256	-2.630704	-0.391770
C	-0.314877	1.172612	1.960969
H	-1.021123	0.345696	1.964825
C	-0.008382	1.798964	3.166858
H	-0.488681	1.464737	4.080752
C	0.915280	2.839826	3.201363
H	1.155712	3.323525	4.142482
C	1.537819	3.250035	2.024725
H	2.267649	4.053012	2.043447
C	1.231437	2.624849	0.819677
H	1.728588	2.946307	-0.092554
C	5.042639	-0.123629	0.121940
H	4.327635	0.655999	0.368650
C	6.400385	0.142689	0.222486
H	6.735302	1.124561	0.540667
C	7.335136	-0.849816	-0.080303
H	8.396396	-0.636778	0.000365
C	6.906404	-2.112485	-0.481410
H	7.630034	-2.886919	-0.713882
C	5.545627	-2.381363	-0.580248
H	5.206427	-3.365765	-0.891097

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1665.46191819 Predicted Change= -5.735051D-09
Zero-point correction (ZPE)= -1664.9675 0.49436
Internal Energy (U)= -1664.9404 0.52149
Enthalpy (H)= -1664.9394 0.52244
Gibbs Free Energy (G)= -1665.0263 0.43556

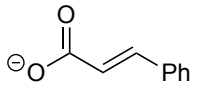
Frequencies -- 16.3996 27.3485 33.0210

==========

#M062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C28H27N2OS(1+) C1[X(C28H27N2OS)] #Atoms= 59
Charge = 1 Multiplicity = 1

SCF Energy= -1665.52071455
==========



Cinnamyl acetate

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011
==========
#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C9H7O2(1-) C1[X(C9H7O2)] #Atoms= 18
Charge = -1 Multiplicity = 1

SCF Energy= -497.527506487 Predicted Change= -4.152790D-11
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00024	0.00180	[YES]	0.00024	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.697650	1.258769	0.000101
H	1.296468	2.269386	0.000186
C	0.806587	0.177077	-0.000073
C	-0.641120	0.445848	-0.000127
H	-0.935582	1.495199	-0.000427
C	-1.638108	-0.444147	0.000201
H	-1.450670	-1.517507	0.000585
C	-3.109538	-0.029431	0.000039
O	-3.353799	1.200870	-0.000260
O	-3.925158	-0.982734	0.000214
C	1.345877	-1.118872	-0.000213
H	0.680504	-1.977095	-0.000415
C	2.720868	-1.319957	-0.000133
H	3.115310	-2.332018	-0.000248
C	3.594379	-0.231403	0.000067
H	4.668207	-0.391885	0.000120
C	3.075703	1.060733	0.000177
H	3.743625	1.917120	0.000317

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -497.527506487 Predicted Change= -4.152790D-11

Zero-point correction (ZPE)= -497.3898 0.13767
Internal Energy (U)= -497.3806 0.14687
Enthalpy (H)= -497.3796 0.14781
Gibbs Free Energy (G)= -497.4261 0.10135

Frequencies -- 24.6044 84.1683 108.3655

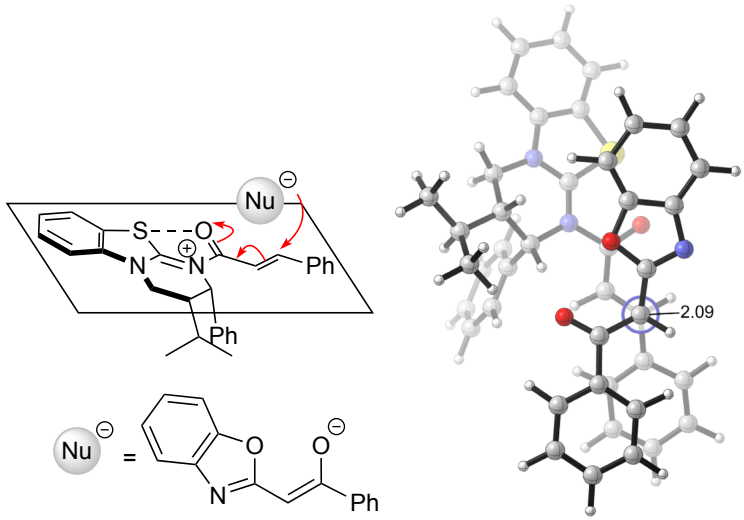
==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C9H7O2(1-) C1[X(C9H7O2)] #Atoms= 18
Charge = -1 Multiplicity = 1

SCF Energy= -497.574409223

==========



TS-1,4-addition-benzoxazole-Major

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)
iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.11606298 Predicted Change= -6.701876D-10

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00038	0.00180	[YES]	0.00038	0.00180	[YES]

Atomic Coordinates (Angstroms)

Type	X	Y	Z
N	3.506622	0.828395	-0.059146
C	2.579804	0.071366	-0.673227
N	1.277740	0.311591	-0.561127
C	0.315892	-0.585670	-1.217376
C	-1.010604	-0.130033	-1.280732
H	-1.244644	0.890872	-1.022567
C	-2.037729	-1.080896	-1.410284
C	-3.415499	-0.707550	-1.819015
H	-1.723815	-2.066000	-1.753679
O	0.782151	-1.654596	-1.628358
C	0.781481	1.384440	0.333193
H	-0.132313	0.972613	0.770404
C	0.451325	2.638247	-0.453502
C	1.785615	1.608999	1.481399
H	1.828214	0.663447	2.040411
C	1.336906	2.706669	2.464182
C	0.079309	2.271984	3.222213
H	0.308477	1.408378	3.858492
H	-0.745729	1.979968	2.568122
H	-0.265874	3.083126	3.870558
H	1.111366	3.610396	1.883197
C	2.441013	3.050210	3.469184
H	2.783742	2.149863	3.993974
H	2.054630	3.745604	4.219901
H	3.306832	3.525863	2.998802
C	3.172506	1.872737	0.914163
H	3.926595	1.816986	1.701435
H	3.237968	2.856399	0.432732
C	4.828707	0.487251	-0.373708
C	4.888106	-0.597591	-1.246312
S	3.283603	-1.200233	-1.643075
C	5.983108	1.119337	0.081198
H	5.937302	1.977919	0.741875
C	7.205300	0.620139	-0.355873
H	8.120429	1.094793	-0.018499
C	7.272333	-0.475439	-1.222892
H	8.238360	-0.844698	-1.549670
C	6.113515	-1.096517	-1.676687
H	6.159798	-1.945826	-2.350324
C	-4.277225	-1.700094	-2.301036
H	-3.909834	-2.720264	-2.390524
C	-5.587990	-1.398728	-2.655745
H	-6.240490	-2.181835	-3.030302
C	-6.062014	-0.094342	-2.526999
H	-7.087053	0.143542	-2.794843
C	-5.213658	0.902390	-2.049093
H	-5.577766	1.919612	-1.939724
C	-3.900203	0.600346	-1.703522
H	-3.255016	1.387337	-1.322128
C	-0.725305	3.333524	-0.157465
H	-1.403787	2.933470	0.594228
C	-1.041793	4.507510	-0.835782
H	-1.959399	5.036722	-0.598430

C	-0.189537	4.993400	-1.825623
H	-0.437780	5.905335	-2.359261
C	0.973618	4.294965	-2.140144
H	1.633282	4.658006	-2.921990
C	1.290499	3.121617	-1.459475
H	2.187917	2.572186	-1.736258
C	1.466881	-4.816953	0.612501
H	1.151991	-5.771578	0.204081
C	2.782126	-4.588997	1.006061
H	3.514195	-5.383713	0.901791
C	3.187084	-3.356830	1.542066
H	4.220233	-3.219807	1.845295
C	2.288161	-2.301493	1.694105
H	2.594845	-1.352611	2.121376
C	0.989926	-2.544119	1.276606
C	0.557275	-3.767951	0.755375
O	-0.083627	-1.701866	1.287965
C	-1.113913	-2.447591	0.763547
C	-2.392894	-1.834570	0.508477
H	-3.144170	-2.584160	0.291724
C	-2.807554	-0.610070	1.156470
C	-4.278666	-0.314816	1.289922
O	-1.995820	0.258757	1.503625
N	-0.789978	-3.673559	0.451312
C	-5.289229	-1.233861	0.990801
H	-5.048936	-2.242145	0.672112
C	-6.628275	-0.865978	1.089027
H	-7.402150	-1.587473	0.844599
C	-6.975538	0.419268	1.496934
H	-8.021094	0.703451	1.570676
C	-5.974976	1.337124	1.815799
H	-6.239089	2.339445	2.139845
C	-4.639507	0.970286	1.711923
H	-3.847491	1.674854	1.944719

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2448.11606298 Predicted Change= -6.701876D-10
Zero-point correction (ZPE)= -2447.4053 0.71071
Internal Energy (U)= -2447.3647 0.75133
Enthalpy (H)= -2447.3637 0.75227
Gibbs Free Energy (G)= -2447.4785 0.63753

Frequencies -- -374.7227 18.2373 26.3049

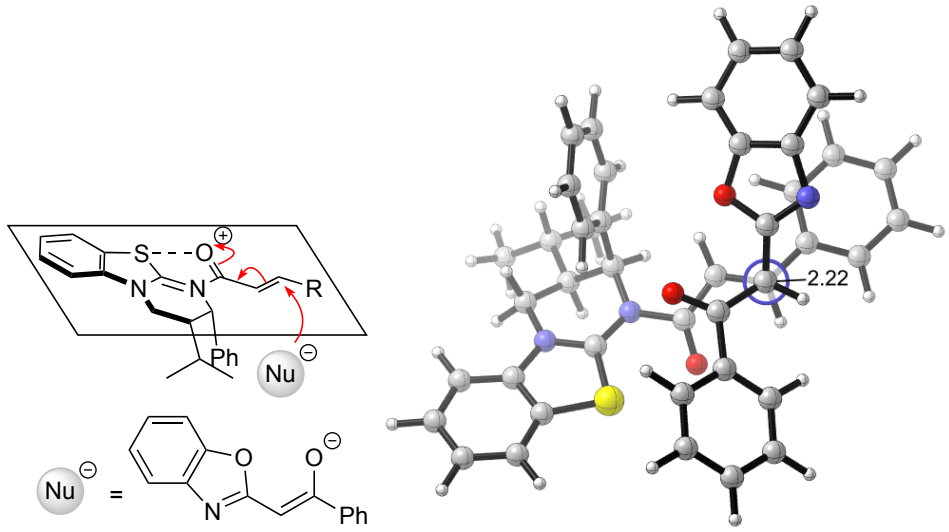
==========

#M062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.21766814

==========



TS-1,4-addition-benzoxazole-*minor*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.10290370 Predicted Change= -4.794267D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00167 ||	0.00180	[YES]	0.00167 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	2.627562	0.807984	-0.385039
C	1.538694	1.206893	0.290287
N	0.822539	0.384908	1.039393
C	-0.442071	0.882507	1.645572
C	-1.562857	0.036955	1.546625
H	-2.422850	0.411485	2.093755
C	-1.759282	-1.002169	0.612922
C	-2.915250	-1.920884	0.790669
H	-0.881923	-1.511384	0.216313
O	-0.374868	1.995350	2.160594
C	1.359437	-0.950704	1.355855
H	0.495197	-1.555814	1.624380
C	2.273762	-0.921821	2.570843
C	2.003609	-1.517823	0.072323

H	1.224517	-1.487766	-0.701323
C	2.478847	-2.973814	0.213298
C	1.268844	-3.907436	0.314592
H	1.592533	-4.945001	0.439149
H	0.672420	-3.846421	-0.606900
H	0.615209	-3.664236	1.159293
H	3.075806	-3.056363	1.131305
C	3.355130	-3.406868	-0.965735
H	2.825251	-3.258398	-1.914226
H	3.595677	-4.470569	-0.878947
H	4.301488	-2.858919	-1.005570
C	3.108855	-0.576891	-0.389714
H	3.395790	-0.810128	-1.417276
H	3.998687	-0.641923	0.249690
C	3.217484	1.811940	-1.162790
C	2.534435	3.023224	-1.052556
S	1.199807	2.902941	0.082324
C	4.345602	1.688097	-1.968200
H	4.886231	0.751110	-2.042758
C	4.763623	2.812608	-2.672451
H	5.638820	2.742502	-3.309308
C	4.077383	4.026422	-2.571286
H	4.421834	4.888492	-3.132147
C	2.956620	4.145714	-1.755696
H	2.424305	5.087083	-1.670549
C	-2.744410	-3.295063	0.585504
H	-1.769966	-3.671501	0.281698
C	-3.804288	-4.180501	0.766143
H	-3.650795	-5.243868	0.608683
C	-5.054442	-3.701524	1.148556
H	-5.882864	-4.389129	1.288022
C	-5.236365	-2.332931	1.348768
H	-6.210387	-1.952032	1.640575
C	-4.177351	-1.448851	1.174506
H	-4.333746	-0.382618	1.305653
C	2.223886	-2.000256	3.458846
H	1.511183	-2.803561	3.286403
C	3.066100	-2.053092	4.565599
H	3.010110	-2.897437	5.245342
C	3.966178	-1.017663	4.804815
H	4.619801	-1.051154	5.670600
C	4.013364	0.068290	3.934585
H	4.702202	0.886187	4.120757
C	3.171490	0.118309	2.825821
H	3.214422	0.988742	2.176714
C	-3.369143	5.139802	0.846858
H	-3.136524	6.119057	1.252797
C	-4.710287	4.733418	0.758148
H	-5.488681	5.411177	1.094791
C	-5.063792	3.484959	0.255588
H	-6.099755	3.168748	0.191038
C	-4.031046	2.643256	-0.161996
C	-2.704844	3.076386	-0.069416
C	-2.328408	4.311214	0.430164
H	-1.288172	4.605996	0.503341

N	-4.045076	1.358330	-0.690943
C	-2.785657	1.076217	-0.894064
C	-2.259412	-0.202818	-1.287659
H	-3.047986	-0.869512	-1.613317
C	-0.965993	-0.344306	-1.924943
C	-0.661062	-1.661720	-2.600026
O	-0.066014	0.499795	-1.865123
O	-1.915708	2.072999	-0.548246
C	0.555011	-1.764127	-3.286903
H	1.198577	-0.889883	-3.321125
C	0.925375	-2.953488	-3.903517
H	1.867229	-3.015258	-4.441061
C	0.090306	-4.068518	-3.826329
H	0.380970	-5.000940	-4.300612
C	-1.120484	-3.978908	-3.143714
H	-1.776452	-4.841833	-3.081320
C	-1.499373	-2.780366	-2.541291
H	-2.446815	-2.737711	-2.014332

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2448.10290370 Predicted Change= -4.794267D-09
Zero-point correction (ZPE)= -2447.3929 0.70995
Internal Energy (U)= -2447.3519 0.75093
Enthalpy (H)= -2447.3510 0.75188
Gibbs Free Energy (G)= -2447.4673 0.63556

Frequencies -- -372.2761 20.3856 26.1715

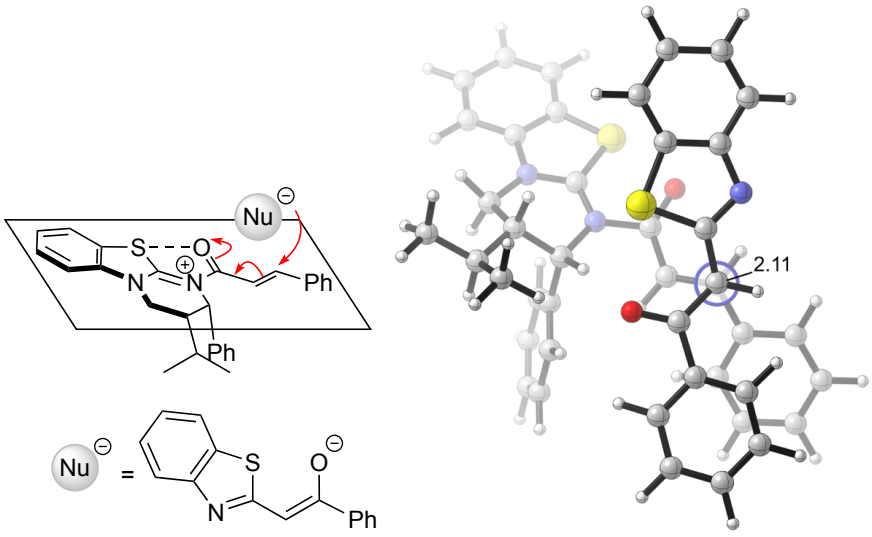
==========

#M062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.20539636

==========



TS-1,4-addition-benzothiazole-*Major*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011
==========
#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C43H37N3O2S2 C1[X(C43H37N3O2S2)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2771.08369558 Predicted Change= -9.067552D-09
==========
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00605	0.00180	[NO]	0.00605	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-3.623812	-1.025350	-0.147010
C	-2.683225	-0.283839	-0.758586
N	-1.392598	-0.397517	-0.476126
C	-0.413827	0.479223	-1.150348
C	0.907282	0.005426	-1.142508
C	1.961590	0.885474	-1.433767
C	3.267934	0.413275	-1.958052
O	-0.878440	1.498775	-1.668218
C	-0.947175	-1.298327	0.611565
C	-0.494883	-2.644918	0.079697
C	-2.054176	-1.374293	1.681641
C	-1.651037	-2.225794	2.898444
C	-0.511763	-1.551714	3.670038
C	-2.834916	-2.460849	3.841617

C	-3.348533	-1.848358	1.035274
C	-4.911332	-0.871378	-0.676435
C	-4.938801	0.061302	-1.711516
S	-3.349629	0.770748	-1.983885
C	-6.060533	-1.544803	-0.272167
C	-7.247187	-1.247725	-0.933674
C	-7.283444	-0.306702	-1.967504
C	-6.129087	0.359986	-2.366102
C	4.156912	1.344001	-2.509910
C	5.399776	0.948410	-2.992472
C	5.777243	-0.391753	-2.926917
C	4.899485	-1.328631	-2.384830
C	3.653162	-0.931705	-1.910647
C	0.670439	-3.206144	0.611153
C	1.123082	-4.446563	0.170692
C	0.417685	-5.135854	-0.814221
C	-0.734417	-4.575182	-1.360191
C	-1.187619	-3.333648	-0.917954
H	1.114342	-0.995355	-0.793635
H	1.660653	1.864773	-1.806002
H	-0.082767	-0.793691	1.050460
H	-2.218276	-0.343344	2.031934
H	-0.861790	-0.602811	4.095120
H	0.363463	-1.329909	3.052482
H	-0.190274	-2.189732	4.498921
H	-1.307898	-3.202533	2.532767
H	-3.281766	-1.508112	4.151479
H	-2.493993	-2.977094	4.743773
H	-3.617444	-3.076838	3.388076
H	-4.192713	-1.710875	1.713651
H	-3.298192	-2.904517	0.742969
H	-6.032505	-2.283186	0.521674
H	-8.157106	-1.760748	-0.641552
H	-8.221769	-0.093963	-2.468102
H	-6.153756	1.090278	-3.168066
H	3.865216	2.391545	-2.552085
H	6.074084	1.685224	-3.418672
H	6.748794	-0.705037	-3.296983
H	5.186347	-2.374681	-2.330136
H	2.979779	-1.675745	-1.493884
H	1.232672	-2.644612	1.354902
H	2.032910	-4.867679	0.587423
H	0.772156	-6.099920	-1.164872
H	-1.278107	-5.099045	-2.140024
H	-2.072648	-2.896464	-1.375498
C	-0.486339	5.511222	0.145877
C	-1.748443	5.899851	0.564814
C	-2.530414	5.060015	1.375193
C	-2.056381	3.818057	1.776239
C	-0.785757	3.424572	1.352474
C	0.007686	4.259140	0.538808
S	0.076946	1.947099	1.679582
C	1.420031	2.557023	0.686503
C	2.583076	1.756474	0.384464
C	2.863577	0.548034	1.115433

C	4.246196	-0.033577	1.078876
O	1.956066	-0.091448	1.677524
N	1.238306	3.747353	0.184993
C	5.374330	0.690295	0.679873
C	6.621385	0.075445	0.623784
C	6.757087	-1.268028	0.966396
C	5.640382	-1.993312	1.380598
C	4.396760	-1.377114	1.439755
H	0.126379	6.150429	-0.481936
H	-2.140610	6.865824	0.261781
H	-3.516615	5.384545	1.691864
H	-2.660675	3.169049	2.403148
H	3.407605	2.346500	0.001070
H	5.291046	1.737433	0.409126
H	7.488447	0.647293	0.307393
H	7.730500	-1.746820	0.915046
H	5.741356	-3.039544	1.653711
H	3.516914	-1.928269	1.755641

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2771.08369558 Predicted Change= -9.067552D-09
Zero-point correction (ZPE)= -2770.3771 0.70657
Internal Energy (U)= -2770.3354 0.74819
Enthalpy (H)= -2770.3345 0.74914
Gibbs Free Energy (G)= -2770.4539 0.62977

Frequencies -- -359.2090 7.8688 18.5685

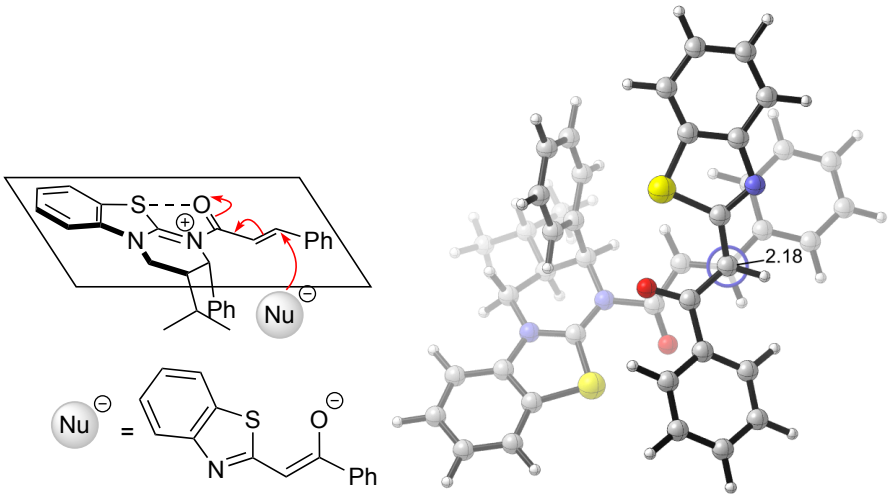
==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C43H37N3O2S2 C1[X(C43H37N3O2S2)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2771.18475399

==========



TS-1,4-addition-benzothiazole-*minor*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C43H37N3O2S2 C1[X(C43H37N3O2S2)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2771.08208225 Predicted Change= -1.100400D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00042	0.00180	[YES]	0.00042	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-3.782828	-0.872142	0.240065
C	-2.823854	-0.001742	0.598856
N	-1.636491	-0.399469	1.050049
C	-0.635370	0.610551	1.389383
C	0.703655	0.186380	1.476678
C	1.669276	1.185205	1.650855
C	3.063537	0.887644	2.040168
O	-1.067240	1.753682	1.565587
C	-1.323566	-1.840707	1.113297
C	-0.667619	-2.336397	-0.165000
C	-2.609978	-2.604309	1.498439
C	-2.389849	-4.114578	1.700782
C	-1.472695	-4.379715	2.898041
C	-3.719246	-4.847095	1.913989
C	-3.686830	-2.317522	0.461523

C	-4.913175	-0.276579	-0.332945
C	-4.800919	1.111591	-0.369299
S	-3.280306	1.660358	0.328014
C	-6.036558	-0.932009	-0.830081
C	-7.056120	-0.147796	-1.357802
C	-6.955478	1.247403	-1.388047
C	-5.826947	1.891947	-0.892790
C	3.834362	1.895792	2.630286
C	5.156029	1.665044	2.995902
C	5.734441	0.417605	2.766603
C	4.979361	-0.593292	2.174422
C	3.655513	-0.361975	1.816516
C	0.342383	-3.298055	-0.080061
C	0.921119	-3.824783	-1.231779
C	0.493059	-3.394111	-2.485984
C	-0.496044	-2.418018	-2.578096
C	-1.066476	-1.884802	-1.425552
H	0.987843	-0.826384	1.230575
H	1.289478	2.137040	2.017153
H	-0.619657	-1.939408	1.941541
H	-2.948189	-2.182527	2.456039
H	-1.323304	-5.455646	3.026107
H	-1.926290	-3.991257	3.817361
H	-0.484834	-3.922881	2.794853
H	-1.918947	-4.516146	0.794161
H	-4.282554	-4.398144	2.741145
H	-3.529787	-5.893805	2.167948
H	-4.351295	-4.837872	1.021293
H	-4.664414	-2.645066	0.820031
H	-3.474454	-2.813775	-0.493676
H	-6.112789	-2.013696	-0.816963
H	-7.942543	-0.630298	-1.755159
H	-7.765712	1.835303	-1.805664
H	-5.743516	2.973521	-0.916663
H	3.387226	2.873190	2.798780
H	5.735712	2.459355	3.456547
H	6.768139	0.235285	3.044478
H	5.426140	-1.564154	1.981215
H	3.087086	-1.154979	1.336123
H	0.686618	-3.635235	0.894989
H	1.706798	-4.569372	-1.145832
H	0.937258	-3.806385	-3.387086
H	-0.816062	-2.056063	-3.549967
H	-1.801892	-1.091041	-1.522615
C	5.556890	-2.544168	-2.429015
C	6.498948	-1.592281	-2.007207
C	6.095035	-0.370145	-1.491903
C	4.724587	-0.089323	-1.391174
C	3.786674	-1.057684	-1.808400
C	4.195250	-2.283896	-2.334754
N	4.189579	1.077619	-0.889381
C	2.882448	1.037790	-0.898166
C	2.064964	2.066827	-0.308696
C	0.700890	2.250972	-0.733631
C	0.053908	3.593470	-0.536140

O	0.040564	1.320012	-1.221205
S	2.171632	-0.451006	-1.551906
C	-1.082985	3.892953	-1.292015
C	-1.725973	5.118756	-1.151444
C	-1.243904	6.059939	-0.242488
C	-0.113270	5.767846	0.518453
C	0.535163	4.545827	0.367747
H	5.895328	-3.494445	-2.830374
H	7.558177	-1.818174	-2.085913
H	6.813432	0.372074	-1.157488
H	3.464304	-3.018689	-2.659530
H	2.642909	2.941388	-0.027159
H	-1.450020	3.146472	-1.989222
H	-2.603033	5.343230	-1.751809
H	-1.744668	7.016649	-0.128350
H	0.264845	6.493324	1.232402
H	1.409213	4.332006	0.975967

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2771.08208225 Predicted Change= -1.100400D-09

Zero-point correction (ZPE)=	-2770.3746	0.70745
Internal Energy (U)=	-2770.3334	0.74858
Enthalpy (H)=	-2770.3325	0.74953
Gibbs Free Energy (G)=	-2770.4481	0.63393

Frequencies -- -305.9726 18.7695 25.6698

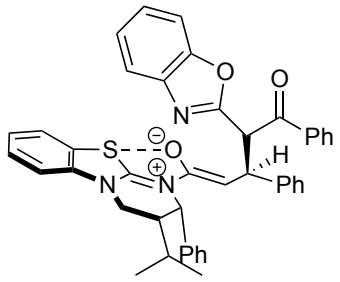
==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C43H37N3O2S2 C1[X(C43H37N3O2S2)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2771.18271562

==========



V-oxazole

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman

#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.12857881 Predicted Change= -1.498141D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00282	0.00180	[NO]	0.00282	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-7.377018	-1.999748	-1.286691
C	-6.927178	-2.804614	-2.337119
C	-5.575692	-2.854300	-2.667847
C	-4.685383	-2.085554	-1.926532
C	-5.143282	-1.278241	-0.887390
C	-6.491202	-1.224099	-0.544860
S	-2.938593	-1.943186	-2.145282
C	-2.874668	-0.847964	-0.776272
N	-4.096793	-0.580149	-0.271917
N	-1.764974	-0.363568	-0.251930
C	-0.447817	-0.717070	-0.871732
C	0.651549	-0.498358	-0.095618
C	2.015675	-0.674408	-0.691499
C	2.731378	-1.969394	-0.336397
C	2.916990	0.533826	-0.255386
C	4.232580	0.539196	-1.040739
C	5.501777	0.085207	-0.390843
O	4.225201	0.892907	-2.204855
C	2.163628	1.805671	-0.457906
O	-0.548073	-1.175672	-2.036646
C	-1.830776	0.529555	0.919304
C	-1.634927	-0.239440	2.214914
C	-3.135561	1.352842	0.861606
C	-3.271136	2.363066	2.014923
C	-2.182500	3.435574	1.924034
C	-4.647031	3.037239	2.007634
C	-4.325893	0.406737	0.783698
C	-0.840128	0.311059	3.224097
C	-0.660870	-0.357002	4.432067
C	-1.271575	-1.591196	4.643498
C	-2.054155	-2.153929	3.638285
C	-2.233075	-1.483848	2.430415
C	3.624160	-2.550835	-1.240361
C	4.359597	-3.681512	-0.891981
C	4.209462	-4.248185	0.371439
C	3.309725	-3.685407	1.276037
C	2.573119	-2.557703	0.921469
O	1.643585	2.043112	-1.691887
C	0.949403	3.208927	-1.551944
C	1.103938	3.630137	-0.229980

N	1.892152	2.693047	0.442807
C	0.212631	3.897566	-2.502334
C	-0.387188	5.073879	-2.060117
C	-0.241056	5.525083	-0.737123
C	0.505402	4.815367	0.197688
C	6.691526	0.275752	-1.103636
C	7.903606	-0.148832	-0.575893
C	7.936148	-0.784437	0.665601
C	6.755572	-0.986551	1.376456
C	5.541964	-0.546572	0.856047
H	-8.433019	-1.978217	-1.039519
H	-7.636774	-3.400289	-2.901249
H	-5.223241	-3.479065	-3.482186
H	-6.841755	-0.608975	0.276741
H	0.577978	-0.170638	0.932527
H	1.923754	-0.620277	-1.782981
H	3.097573	0.471229	0.820446
H	-0.992087	1.217726	0.786057
H	-3.101303	1.920685	-0.079763
H	-1.169636	3.025307	1.971192
H	-2.285913	4.152939	2.743813
H	-2.267257	3.986286	0.979538
H	-3.160427	1.819728	2.962762
H	-4.680477	3.825950	2.764826
H	-5.457504	2.336834	2.229421
H	-4.847485	3.499402	1.033257
H	-5.230609	0.953474	0.511483
H	-4.498906	-0.108492	1.737235
H	-0.339609	1.261702	3.054539
H	-0.035429	0.082789	5.202622
H	-1.128990	-2.116270	5.582652
H	-2.520829	-3.122391	3.788365
H	-2.825099	-1.952345	1.647607
H	3.752752	-2.101699	-2.223376
H	5.050707	-4.117589	-1.607218
H	4.783017	-5.127920	0.647197
H	3.178009	-4.129331	2.258646
H	1.860898	-2.128259	1.622386
H	0.112168	3.538646	-3.520031
H	-0.980215	5.658479	-2.755929
H	-0.724573	6.450454	-0.440306
H	0.617305	5.160538	1.220429
H	6.642711	0.759978	-2.073422
H	8.822833	0.009328	-1.131068
H	8.881657	-1.125418	1.076329
H	6.777038	-1.490442	2.337567
H	4.631487	-0.735853	1.414252

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2448.12857881 Predicted Change= -1.498141D-08

Zero-point correction (ZPE)=	-2447.4161	0.71240
Internal Energy (U)=	-2447.3747	0.75379
Enthalpy (H)=	-2447.3738	0.75474

Gibbs Free Energy (G)= -2447.4943 0.63423

Frequencies -- 9.2967 15.4895 17.9875

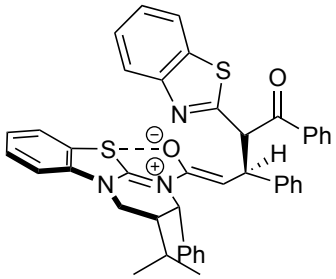
==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.23149702

==========



V-thiazole

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C43H37N3O2S2 C1[X(C43H37N3O2S2)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2771.09811887 Predicted Change= -2.395198D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00275	0.00180	[NO]	0.00275	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	5.831415	2.180043	-3.183055
H	6.832328	2.594693	-3.237457
C	4.907337	2.467144	-4.191673
H	5.197705	3.098022	-5.024855
C	3.614514	1.954544	-4.137453
H	2.891344	2.177509	-4.915484
C	3.269196	1.146242	-3.059765
C	4.198350	0.855533	-2.063947
C	5.491181	1.371272	-2.102534
H	6.209808	1.164002	-1.317230

S	1.707496	0.389326	-2.741750
C	2.357656	-0.298171	-1.264019
N	3.655704	0.023072	-1.076661
N	1.675450	-1.037836	-0.405750
C	0.207383	-1.219685	-0.597778
C	-0.496586	-1.697512	0.462764
H	-0.016761	-1.954991	1.393934
C	-2.007372	-1.747390	0.460436
H	-2.332965	-1.776074	1.505248
C	-2.586163	-2.978587	-0.225413
C	-2.633107	-0.454117	-0.125115
H	-2.471703	-0.445429	-1.205641
C	-4.132233	-0.371576	0.188672
C	-4.977782	0.608756	-0.569028
O	-4.625309	-1.064059	1.055722
C	-1.995282	0.776642	0.474792
O	-0.199955	-0.831393	-1.734462
C	2.333647	-1.537259	0.815979
H	1.864573	-2.504241	1.006830
C	2.068471	-0.616472	1.997871
C	3.827177	-1.795991	0.525744
H	3.865576	-2.523335	-0.298548
C	4.588630	-2.399036	1.720711
C	4.090942	-3.814193	2.029235
H	4.611526	-4.214636	2.903945
H	4.295339	-4.479622	1.182351
H	3.018073	-3.859874	2.235342
H	4.413313	-1.760100	2.595405
C	6.098290	-2.443890	1.460741
H	6.598621	-2.985072	2.268833
H	6.544746	-1.446478	1.411389
H	6.317387	-2.966850	0.521778
C	4.460315	-0.508012	0.024770
H	5.456105	-0.700000	-0.377728
H	4.537429	0.244987	0.819259
C	1.949916	0.766626	1.846289
H	2.023180	1.222420	0.860915
C	1.691532	1.578759	2.948642
H	1.577213	2.649887	2.810421
C	1.552005	1.018711	4.215676
H	1.335021	1.653459	5.069398
C	1.671058	-0.359538	4.376698
H	1.550919	-0.808790	5.357579
C	1.922342	-1.169797	3.273498
H	1.985824	-2.247615	3.404119
C	-3.417227	-3.857926	0.471413
H	-3.667542	-3.639110	1.506032
C	-3.934366	-4.996177	-0.144998
H	-4.575772	-5.669365	0.416838
C	-3.633971	-5.265087	-1.477796
H	-4.039386	-6.148386	-1.962566
C	-2.808453	-4.390752	-2.184414
H	-2.567779	-4.594844	-3.224186
C	-2.285024	-3.259428	-1.564006
H	-1.626972	-2.583634	-2.105567

S	-0.901908	1.806836	-0.455575
C	-0.803645	2.872808	0.915942
C	-1.565783	2.341411	1.974771
N	-2.241176	1.166229	1.680877
C	-0.089326	4.064109	1.062099
H	0.492190	4.471556	0.241075
C	-0.149699	4.717456	2.286039
H	0.389123	5.650289	2.419970
C	-0.896752	4.188856	3.351941
H	-0.922065	4.717424	4.299581
C	-1.605694	3.006826	3.205640
H	-2.189117	2.587433	4.018964
C	-4.484360	1.384005	-1.622682
H	-3.447892	1.302350	-1.933281
C	-5.322490	2.275218	-2.287735
H	-4.932429	2.873609	-3.104904
C	-6.656203	2.396871	-1.906143
H	-7.308034	3.091746	-2.427024
C	-7.154811	1.625707	-0.855555
H	-8.194131	1.719563	-0.556623
C	-6.319277	0.737368	-0.191915
H	-6.686449	0.128425	0.627713

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2771.09811887 Predicted Change= -2.395198D-08
Zero-point correction (ZPE)= -2770.3889 0.70917
Internal Energy (U)= -2770.3471 0.75095
Enthalpy (H)= -2770.3462 0.75189
Gibbs Free Energy (G)= -2770.4664 0.63166

Frequencies -- 11.7033 17.9618 22.0346

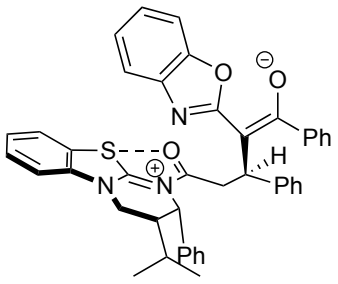
==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C43H37N3O2S2 C1[X(C43H37N3O2S2)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2771.19780624

==========



VII-oxazole

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.14332650 Predicted Change= -6.806262D-09
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00122	0.00180	[YES]	0.00122	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-2.572354	1.318220	-0.265028
C	-1.662001	0.716796	-1.034196
N	-1.286892	-0.565770	-0.835346
C	-0.210649	-1.089657	-1.617511
C	0.539466	-2.317761	-1.167544
H	0.581861	-2.999390	-2.022205
H	0.098378	-2.833422	-0.320755
C	1.981537	-1.845603	-0.823909
C	1.994547	-0.664676	0.136759
C	3.028598	0.282089	-0.101406
C	1.082885	-0.588613	1.208786
C	0.678430	0.736818	1.821301
O	0.418801	-1.579554	1.626931
H	2.394430	-1.467008	-1.763914
C	2.841458	-3.025385	-0.406027
O	0.137890	-0.468400	-2.597964
C	-2.095329	-1.420601	0.080795
H	-1.398408	-2.150715	0.481824
C	-3.195872	-2.121701	-0.691954
C	-2.531904	-0.584916	1.292594
H	-1.598568	-0.293465	1.784177
C	-3.359598	-1.387945	2.310913
C	-2.553052	-2.575964	2.843167
H	-1.576844	-2.237446	3.206675
H	-2.374148	-3.334983	2.076665
H	-3.090444	-3.060553	3.663703
H	-4.264620	-1.760947	1.809899
C	-3.783642	-0.491642	3.479408
H	-4.478811	0.296463	3.173888
H	-2.905020	-0.017321	3.934527
H	-4.283033	-1.087079	4.248969
C	-3.253271	0.683367	0.869405
H	-3.232491	1.410399	1.684626
H	-4.296285	0.498716	0.582609
C	-2.784278	2.667544	-0.575261

C	-1.990644	3.083469	-1.640756
S	-1.019962	1.765430	-2.265488
C	-3.649770	3.546444	0.074190
H	-4.275022	3.223902	0.898679
C	-3.683298	4.859321	-0.376153
H	-4.345451	5.567279	0.110202
C	-2.880317	5.284946	-1.442793
H	-2.926640	6.317838	-1.770018
C	-2.026001	4.401775	-2.089453
H	-1.403205	4.724503	-2.916718
C	-3.287841	-3.513569	-0.620755
H	-2.555992	-4.071381	-0.042222
C	-4.295786	-4.197317	-1.297250
H	-4.350684	-5.279198	-1.229774
C	-5.219337	-3.494862	-2.065470
H	-6.003736	-4.024470	-2.596574
C	-5.124837	-2.107680	-2.160055
H	-5.831636	-1.552684	-2.768696
C	-4.120709	-1.425913	-1.479183
H	-4.057490	-0.346218	-1.589479
C	3.898596	-3.442780	-1.217264
H	4.102473	-2.906875	-2.141202
C	4.696804	-4.526028	-0.850042
H	5.518326	-4.833603	-1.490666
C	4.441549	-5.208963	0.335639
H	5.059417	-6.054419	0.623436
C	3.390093	-4.796141	1.154661
H	3.190503	-5.320392	2.085141
C	2.598005	-3.711602	0.789855
H	1.787899	-3.368581	1.428291
C	0.502133	1.881655	1.037606
H	0.845995	1.874693	0.006403
C	-0.127941	3.011679	1.554543
H	-0.277898	3.884394	0.923484
C	-0.572806	3.017805	2.876463
H	-1.066788	3.895988	3.281737
C	-0.374951	1.891847	3.676235
H	-0.709486	1.893959	4.709805
C	0.234321	0.756821	3.146640
H	0.341320	-0.144202	3.743959
O	3.314730	1.219840	0.874331
C	4.359409	1.943477	0.379719
C	4.689017	1.401452	-0.868588
N	3.829349	0.350829	-1.145296
C	5.007925	3.017006	0.957323
H	4.716184	3.405067	1.927131
C	6.059342	3.567008	0.217564
H	6.608910	4.410938	0.622217
C	6.413515	3.047235	-1.033510
H	7.234737	3.502079	-1.579378
C	5.739859	1.962154	-1.595891
H	6.017651	1.564872	-2.566918

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

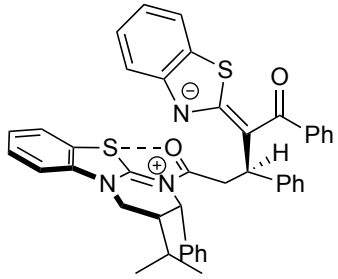
SCF Energy= -2448.14332650 Predicted Change= -6.806262D-09
Zero-point correction (ZPE)= -2447.4292 0.71404
Internal Energy (U)= -2447.3886 0.75469
Enthalpy (H)= -2447.3876 0.75563
Gibbs Free Energy (G)= -2447.5050 0.63823

Frequencies -- 8.6466 18.4369 20.4383

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.24360280



VII-thiazole

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C43H37N3O2S2 C1[X(C43H37N3O2S2)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2771.10599663 Predicted Change= -1.705358D-08

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00003	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00159	0.00180	[YES]	0.00159	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-2.787630	1.294757	-0.304358
C	-1.834938	0.733401	-1.052642
N	-1.413182	-0.533851	-0.847376
C	-0.304431	-1.016535	-1.609952
C	0.457959	-2.240586	-1.169571

H	0.531590	-2.897419	-2.041667
H	0.002635	-2.788312	-0.351480
C	1.886368	-1.760328	-0.785679
C	1.882489	-0.594305	0.199254
C	2.972445	0.313603	0.037149
C	0.934769	-0.559138	1.243341
C	0.494920	0.738704	1.886341
O	0.268297	-1.565080	1.615015
H	2.314417	-1.362158	-1.709279
C	2.750997	-2.937829	-0.371731
O	0.053056	-0.367851	-2.569452
C	-2.211904	-1.421061	0.046123
H	-1.499790	-2.128934	0.459152
C	-3.270238	-2.153958	-0.755587
C	-2.703073	-0.606673	1.251977
H	-1.792178	-0.277672	1.764137
C	-3.519054	-1.445719	2.250650
C	-2.676586	-2.598739	2.802999
H	-1.730111	-2.218237	3.201250
H	-2.435535	-3.342586	2.038646
H	-3.218614	-3.113571	3.601739
H	-4.394313	-1.856295	1.726738
C	-4.010642	-0.569303	3.407561
H	-4.731175	0.187933	3.083423
H	-3.165128	-0.057668	3.884574
H	-4.503163	-1.186229	4.164521
C	-3.468874	0.629602	0.812615
H	-3.502245	1.356648	1.627206
H	-4.495127	0.398753	0.499171
C	-3.051291	2.633679	-0.620351
C	-2.251482	3.084350	-1.666973
S	-1.207549	1.810939	-2.266569
C	-3.970374	3.473082	0.007515
H	-4.600944	3.122529	0.816324
C	-4.051241	4.783243	-0.444772
H	-4.755494	5.461319	0.024710
C	-3.242558	5.243903	-1.492320
H	-3.326717	6.273686	-1.821737
C	-2.334471	4.399856	-2.117457
H	-1.706619	4.750624	-2.929369
C	-3.324753	-3.547845	-0.683703
H	-2.595941	-4.083712	-0.081175
C	-4.290549	-4.261448	-1.390019
H	-4.315826	-5.344372	-1.322174
C	-5.209262	-3.587164	-2.188586
H	-5.960497	-4.140057	-2.743444
C	-5.152292	-2.197965	-2.282907
H	-5.855473	-1.664633	-2.914696
C	-4.190185	-1.486431	-1.572657
H	-4.155801	-0.405491	-1.683694
C	3.859032	-3.297601	-1.142379
H	4.098567	-2.714053	-2.027725
C	4.662235	-4.377966	-0.777959
H	5.522660	-4.641312	-1.386471
C	4.363046	-5.115270	0.364410

H	4.985107	-5.958610	0.649439
C	3.261951	-4.759248	1.143818
H	3.027071	-5.325694	2.040687
C	2.464194	-3.677908	0.781714
H	1.616445	-3.379500	1.392629
C	0.233460	1.871939	1.109353
H	0.550491	1.879413	0.069214
C	-0.439687	2.966673	1.648490
H	-0.657263	3.831031	1.025912
C	-0.838373	2.946831	2.984571
H	-1.364302	3.796891	3.409081
C	-0.554443	1.833084	3.776890
H	-0.854699	1.818978	4.820668
C	0.094638	0.731535	3.226143
H	0.271089	-0.161864	3.818207
S	3.417893	1.560137	1.267401
C	4.815335	1.982644	0.306551
C	4.847011	1.163428	-0.841939
N	3.825832	0.249342	-0.960565
C	5.781506	2.957337	0.537599
H	5.740673	3.583122	1.423949
C	6.809098	3.106543	-0.391284
H	7.576349	3.856185	-0.225610
C	6.857423	2.297480	-1.533458
H	7.663797	2.428228	-2.248866
C	5.886850	1.331372	-1.765797
H	5.914438	0.701909	-2.649777

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2771.10599663 Predicted Change= -1.705358D-08
Zero-point correction (ZPE)= -2770.3948 0.71117
Internal Energy (U)= -2770.3535 0.75242
Enthalpy (H)= -2770.3526 0.75336
Gibbs Free Energy (G)= -2770.4709 0.63508

Frequencies -- 12.9939 14.6221 27.0676

==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C43H37N3O2S2 C1[X(C43H37N3O2S2)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2771.20441792

==========

Disfavored-Lactamization-(X=O)-TS

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest)

freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.12448628 Predicted Change= -9.033427D-09
==========

Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.01384	0.00180	[NO]	0.01384	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	3.772491	-0.328835	-0.150724
C	2.589181	-0.346402	-0.787701
N	1.511136	0.255587	-0.295704
C	0.235380	0.192891	-1.048362
C	-0.715372	1.344411	-0.786366
O	0.279029	-0.369762	-2.134793
C	1.575896	0.986362	0.988353
C	1.784588	2.472575	0.748464
C	2.637333	0.344477	1.906234
C	2.769861	1.049536	3.269578
C	1.484312	0.900336	4.088074
C	3.946516	0.487836	4.074174
C	3.968689	0.268575	1.173519
C	4.810961	-0.970572	-0.841431
C	4.365022	-1.530304	-2.035760
S	2.651062	-1.228262	-2.295915
C	6.142006	-1.068039	-0.444034
C	7.012596	-1.759145	-1.279312
C	6.568527	-2.332656	-2.475490
C	5.239285	-2.221744	-2.868278
C	2.684931	2.935528	-0.215117
C	2.887589	4.301756	-0.395793
C	2.188358	5.221786	0.380605
C	1.277527	4.769367	1.332549
C	1.074962	3.403937	1.510662
C	-2.135330	1.070111	-1.305039
C	-2.921956	2.356957	-1.090001
C	-2.798176	-0.141270	-0.669072
C	-4.168472	-0.364122	-1.068733
C	-5.086463	-1.261410	-0.277544
O	-4.658524	0.231955	-2.036973
C	-2.018620	-1.106243	-0.046643
C	-3.499110	2.650737	0.147160
C	-4.146769	3.864883	0.361685
C	-4.222003	4.808883	-0.660907
C	-3.646134	4.526553	-1.897733
C	-3.000377	3.310071	-2.106481
O	-2.524143	-2.354627	0.245778
C	-1.460271	-3.113145	0.650775

C	-0.313915	-2.308423	0.614264
N	-0.704150	-1.031831	0.242176
C	-1.466698	-4.439073	1.021636
C	-0.224177	-4.996193	1.352531
C	0.939937	-4.229704	1.298070
C	0.917291	-2.879424	0.931455
C	-5.048500	-1.315645	1.117679
C	-5.976128	-2.080628	1.818075
C	-6.944973	-2.807949	1.127697
C	-6.992415	-2.753585	-0.264519
C	-6.076060	-1.970954	-0.960568
H	-0.769428	1.605505	0.270630
H	-0.303040	2.212921	-1.317675
H	0.602784	0.812158	1.452996
H	2.303815	-0.683681	2.101279
H	1.281581	-0.158391	4.287633
H	0.605995	1.318730	3.590073
H	1.589830	1.409673	5.050140
H	2.955913	2.115782	3.087420
H	3.951840	0.923946	5.077106
H	4.913899	0.712541	3.615821
H	3.859516	-0.600209	4.183025
H	4.661248	-0.382017	1.709552
H	4.429318	1.257501	1.059176
H	6.495910	-0.616048	0.475812
H	8.055452	-1.849394	-0.995254
H	7.268820	-2.867147	-3.108112
H	4.890917	-2.659224	-3.797932
H	3.223324	2.235771	-0.850216
H	3.587776	4.645368	-1.150540
H	2.343065	6.286226	0.235995
H	0.713357	5.478348	1.929983
H	0.345145	3.061195	2.239990
H	-2.067429	0.905667	-2.389380
H	-3.448730	1.908176	0.940872
H	-4.596034	4.073061	1.328670
H	-4.728658	5.755125	-0.496529
H	-3.704749	5.252460	-2.703751
H	-2.555377	3.091127	-3.074914
H	-2.383952	-5.016961	1.039301
H	-0.169588	-6.039802	1.643826
H	1.891698	-4.690661	1.543439
H	1.841099	-2.313456	0.883962
H	-4.288315	-0.750957	1.651010
H	-5.945287	-2.109509	2.903261
H	-7.665044	-3.409849	1.674261
H	-7.749154	-3.314035	-0.805493
H	-6.114708	-1.898352	-2.043276

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2448.12448628 Predicted Change= -9.033427D-09
Zero-point correction (ZPE)= -2447.4128 0.71158
Internal Energy (U)= -2447.3724 0.75204

Enthalpy (H)= -2447.3715 0.75298
Gibbs Free Energy (G)= -2447.4892 0.63522

Frequencies -- -138.4921 4.8783 17.7797
==========
#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.22560001
==========

Disfavored-Lactonization-(X=S)-TS

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011
==========
#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)
iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C43H37N3O2S2 C1[X(C43H37N3O2S2)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2771.09554176 Predicted Change= -1.272284D-08
==========
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00204	0.00180	[NO]	0.00204	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	4.074300	-1.024251	-0.331106
C	2.839139	-0.899864	-0.843806
N	1.995443	0.045774	-0.434420
C	0.636476	0.079602	-0.965785
C	-0.108433	1.386253	-0.876725
H	0.115962	1.931159	0.038682
H	0.214677	2.015284	-1.717332
O	0.335433	-0.779481	-1.775372
C	2.376387	0.957337	0.665577
H	1.448015	1.122602	1.210977
C	2.915371	2.267062	0.120861
C	3.325564	0.215233	1.626477
H	2.765711	-0.661729	1.982817
C	3.727027	1.058035	2.850463
C	2.511586	1.342688	3.737191
H	2.808645	1.942381	4.602207
H	2.082774	0.404134	4.106639
H	1.718914	1.886183	3.216766
H	4.136477	2.011063	2.490244

C	4.807221	0.356929	3.681444
H	4.488063	-0.654603	3.960337
H	4.989106	0.915631	4.603877
H	5.761617	0.283410	3.151560
C	4.533114	-0.287844	0.851732
H	5.109918	-0.993732	1.451663
H	5.191064	0.531917	0.537367
C	4.862549	-1.999923	-0.956198
C	4.164882	-2.662327	-1.962989
S	2.520001	-2.057446	-2.112993
C	6.185518	-2.314688	-0.657149
H	6.732247	-1.785804	0.115352
C	6.787194	-3.327233	-1.394923
H	7.817471	-3.592808	-1.184360
C	6.088814	-4.003773	-2.401380
H	6.581790	-4.791594	-2.960400
C	4.769498	-3.678291	-2.696947
H	4.225814	-4.198751	-3.478228
C	3.757665	2.307961	-0.993961
H	4.009793	1.394472	-1.527404
C	4.267582	3.520419	-1.452066
H	4.917261	3.534777	-2.321363
C	3.937024	4.708026	-0.804498
H	4.331244	5.652955	-1.164520
C	3.086143	4.678563	0.297968
H	2.809988	5.600305	0.800077
C	2.575861	3.465992	0.753451
H	1.899734	3.454151	1.604913
C	-1.630103	1.153086	-0.993168
H	-1.828036	0.886363	-2.040466
C	-2.288410	2.507078	-0.737334
C	-2.167031	0.038285	-0.104814
C	-3.495644	-0.440265	-0.397687
C	-1.363479	-0.588500	0.846988
C	-1.914580	-1.455555	1.944102
O	-0.089053	-0.444122	0.902443
C	-2.590574	2.923017	0.561722
H	-2.406908	2.239224	1.387782
C	-3.139855	4.180858	0.795188
H	-3.376599	4.486560	1.810208
C	-3.394275	5.042732	-0.270567
H	-3.829954	6.020971	-0.090966
C	-3.092558	4.638594	-1.569366
H	-3.292083	5.301559	-2.406203
C	-2.541552	3.379594	-1.797879
H	-2.315508	3.061189	-2.813734
S	-4.672115	0.646040	-1.233966
C	-5.837642	-0.647611	-1.221763
C	-5.272320	-1.773033	-0.585437
N	-3.967709	-1.634922	-0.167585
C	-7.137877	-0.668033	-1.723187
H	-7.559520	0.204436	-2.212815
C	-7.885504	-1.830953	-1.574197
H	-8.902096	-1.866185	-1.953066
C	-7.338369	-2.955736	-0.940012

H	-7.938604	-3.854548	-0.835000
C	-6.041418	-2.937120	-0.447886
H	-5.607215	-3.802938	0.042080
C	-1.185276	-2.582990	2.325793
H	-0.282055	-2.828962	1.776184
C	-1.609508	-3.376035	3.388724
H	-1.042960	-4.260630	3.664825
C	-2.754326	-3.028826	4.102189
H	-3.082718	-3.639402	4.938129
C	-3.472035	-1.886255	3.745254
H	-4.356656	-1.603091	4.308044
C	-3.055816	-1.106291	2.671745
H	-3.614996	-0.218043	2.388809

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2771.09554176 Predicted Change= -1.272284D-08
Zero-point correction (ZPE)= -2770.3865 0.70897
Internal Energy (U)= -2770.3455 0.74998
Enthalpy (H)= -2770.3446 0.75093
Gibbs Free Energy (G)= -2770.4636 0.63190

Frequencies -- -116.2652 12.0058 17.8171

==========

#M062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C43H37N3O2S2 C1[X(C43H37N3O2S2)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2771.19453032

==========

Favored-Lactamization-(X=S)-TS

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C43H37N3O2S2 C1[X(C43H37N3O2S2)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2771.09894699 Predicted Change= -7.886391D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00147	0.00180	[YES]	0.00147	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z

N	3.439401	-0.200867	-1.301812
C	2.494968	0.694232	-0.977469
N	1.239225	0.326889	-0.716260
C	0.167113	1.331735	-0.824088
C	-1.053806	0.866445	-1.604821
O	0.495080	2.495688	-0.729143
C	0.958492	-1.115858	-0.564327
C	1.333109	-1.675636	0.799009
C	1.660485	-1.841160	-1.735568
C	1.304714	-3.332224	-1.859813
C	-0.175026	-3.505277	-2.215387
C	2.167447	-4.025786	-2.918963
C	3.160865	-1.617240	-1.587952
C	4.716376	0.350412	-1.470172
C	4.711641	1.733692	-1.300476
S	3.103275	2.326886	-0.907782
C	5.883904	-0.340846	-1.782987
C	7.049699	0.401630	-1.928242
C	7.049387	1.791762	-1.767251
C	5.879251	2.474497	-1.453852
C	2.439556	-1.261014	1.548379
C	2.749953	-1.886581	2.751736
C	1.965838	-2.937961	3.222506
C	0.856183	-3.347589	2.491883
C	0.540802	-2.713390	1.293414
C	-2.450765	0.877494	-0.926988
C	-2.871412	2.309814	-0.576898
C	-2.604133	-0.135002	0.186453
C	-1.676104	-0.035467	1.242805
C	-3.635303	-1.110865	0.270031
C	-4.745172	-1.160358	-0.753096
O	-3.681788	-1.971624	1.176994
C	-3.192432	2.710912	0.721228
C	-3.607826	4.015662	0.984630
C	-3.718064	4.942905	-0.047320
C	-3.417248	4.551550	-1.350709
C	-3.000947	3.249232	-1.607407
S	-1.795055	-0.908651	2.791779
C	-0.371135	-0.050557	3.350924
C	0.089347	0.821381	2.343763
N	-0.651461	0.800491	1.186338
C	0.301212	-0.161634	4.563862
C	1.433831	0.621326	4.774487
C	1.886259	1.502168	3.783541
C	1.221887	1.613798	2.568427
C	-5.445244	-0.024973	-1.171936
C	-6.516643	-0.142655	-2.055681
C	-6.893926	-1.394911	-2.535035
C	-6.208240	-2.533662	-2.112177
C	-5.151607	-2.415762	-1.215765
H	-1.075630	1.565711	-2.447085
H	-0.891044	-0.123963	-2.035601
H	-0.122096	-1.219283	-0.659303
H	1.332116	-1.340900	-2.659099

H	-0.386076	-3.048052	-3.189602
H	-0.852469	-3.056710	-1.481708
H	-0.424998	-4.567938	-2.282903
H	1.498445	-3.812361	-0.892305
H	3.224710	-4.060325	-2.639566
H	2.082095	-3.515989	-3.886346
H	1.832170	-5.057901	-3.054975
H	3.685041	-1.854646	-2.515981
H	3.578946	-2.223467	-0.775344
H	5.888040	-1.418504	-1.902975
H	7.974910	-0.110227	-2.169408
H	7.973971	2.345941	-1.886433
H	5.875231	3.551782	-1.327750
H	3.051922	-0.423250	1.227795
H	3.600746	-1.539286	3.329493
H	2.209828	-3.421297	4.163601
H	0.217693	-4.144322	2.860375
H	-0.352262	-3.012887	0.749025
H	-3.111753	0.562390	-1.742047
H	-3.125486	1.994175	1.533191
H	-3.848216	4.304323	2.003742
H	-4.042908	5.958325	0.158861
H	-3.513875	5.259045	-2.169162
H	-2.784889	2.954682	-2.632731
H	-0.049658	-0.845306	5.331707
H	1.966917	0.549594	5.717588
H	2.766210	2.110970	3.971090
H	1.553567	2.300550	1.794056
H	-5.164445	0.953186	-0.787784
H	-7.060536	0.745200	-2.364310
H	-7.724743	-1.485165	-3.228456
H	-6.505708	-3.513243	-2.474794
H	-4.627490	-3.296152	-0.855653

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2771.09894699 Predicted Change= -7.886391D-09
Zero-point correction (ZPE)= -2770.3903 0.70860
Internal Energy (U)= -2770.3496 0.74928
Enthalpy (H)= -2770.3487 0.75022
Gibbs Free Energy (G)= -2770.4648 0.63406

Frequencies -- -75.4058 11.9587 16.3033

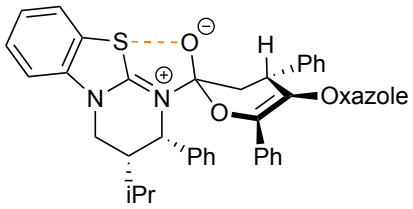
==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C43H37N3O2S2 C1[X(C43H37N3O2S2)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2771.19836373

==========



VII-oxazole-favored

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.13904796 Predicted Change= -5.266725D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00155	0.00180	[YES]	0.00155	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	4.174167	-0.503131	-0.414099
C	2.906244	-0.527409	-0.878476
N	1.905291	0.009387	-0.220100
C	0.459879	-0.161416	-0.751993
C	-0.295338	1.162256	-0.619377
H	-0.239488	1.573866	0.394026
H	0.131464	1.894444	-1.311761
O	0.431499	-0.730068	-1.882987
C	2.136941	0.665498	1.075495
H	1.214385	0.505293	1.637672
C	2.370344	2.159200	0.911356
C	3.275038	-0.070685	1.816325
H	2.945254	-1.114756	1.920505
C	3.556753	0.485352	3.223909
C	2.360796	0.258739	4.152441
H	2.566563	0.677774	5.141720
H	2.172286	-0.814352	4.273475
H	1.439205	0.718713	3.785911
H	3.737742	1.564733	3.133846
C	4.803043	-0.157048	3.842428
H	5.720416	0.110731	3.310238
H	4.714185	-1.250222	3.848849
H	4.918444	0.174982	4.878269
C	4.520217	-0.062968	0.938959
H	5.261195	-0.768818	1.319670
H	4.975413	0.934768	0.893573

C	5.124534	-1.039105	-1.292841
C	4.534094	-1.525362	-2.456861
S	2.780627	-1.304559	-2.450291
C	6.499034	-1.107064	-1.087298
H	6.955769	-0.711660	-0.186532
C	7.272996	-1.691677	-2.085766
H	8.347521	-1.756766	-1.951774
C	6.688106	-2.190647	-3.252705
H	7.311718	-2.642676	-4.016632
C	5.311725	-2.111708	-3.449017
H	4.854983	-2.497477	-4.354807
C	1.826662	3.042712	1.848324
H	1.212429	2.656328	2.658320
C	2.049251	4.413029	1.748599
H	1.615825	5.084135	2.483408
C	2.814618	4.920862	0.701600
H	2.985256	5.989476	0.617873
C	3.347705	4.050724	-0.245913
H	3.933621	4.437861	-1.073730
C	3.124733	2.679300	-0.143677
H	3.531368	2.020687	-0.907122
C	-1.758754	0.880208	-0.974773
H	-1.794665	0.632050	-2.042996
C	-2.595484	2.125178	-0.740942
C	-2.258768	-0.318621	-0.180934
C	-3.696229	-0.553970	-0.264617
C	-1.399652	-1.166475	0.443000
C	-1.740483	-2.392197	1.214302
O	-0.062254	-1.029244	0.374887
C	-2.925846	2.966054	-1.804824
H	-2.613891	2.696893	-2.811429
C	-3.651876	4.135460	-1.589998
H	-3.903146	4.776296	-2.430048
C	-4.061709	4.477098	-0.303143
H	-4.631462	5.385728	-0.133688
C	-3.740036	3.641908	0.765475
H	-4.059320	3.897943	1.771478
C	-3.011955	2.475789	0.546547
H	-2.768186	1.820375	1.380401
O	-4.246732	-0.195061	-1.475556
C	-5.577903	-0.448210	-1.344251
C	-5.779440	-0.957000	-0.060185
N	-4.554178	-0.994393	0.601922
C	-6.592546	-0.260624	-2.268429
H	-6.401620	0.138726	-3.257936
C	-7.870083	-0.617664	-1.841775
H	-8.706925	-0.495036	-2.521737
C	-8.100216	-1.131660	-0.555006
H	-9.112866	-1.395843	-0.267383
C	-7.063355	-1.309512	0.355490
H	-7.236925	-1.707507	1.349676
C	-2.596701	-2.385265	2.316524
H	-3.086659	-1.463817	2.606271
C	-2.819454	-3.559680	3.032421
H	-3.481037	-3.546608	3.893159

C	-2.194988	-4.744411	2.651133
H	-2.376212	-5.658584	3.208563
C	-1.330531	-4.753470	1.556285
H	-0.838112	-5.673690	1.256994
C	-1.093365	-3.579530	0.851470
H	-0.409627	-3.565036	0.007831

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2448.13904796 Predicted Change= -5.266725D-09

Zero-point correction (ZPE)=	-2447.4261	0.71287
Internal Energy (U)=	-2447.3855	0.75353
Enthalpy (H)=	-2447.3845	0.75448
Gibbs Free Energy (G)=	-2447.5038	0.63521

Frequencies -- 8.9015 13.0897 21.0731

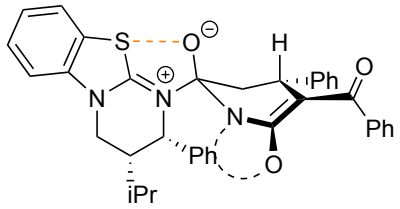
==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.23916785

==========



VII-oxazole-disfavored

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.13199510 Predicted Change= -3.045435D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00129 ||	0.00180	[YES]	0.00129 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z

N	3.771633	-0.078233	-0.005113
C	2.671589	-0.016610	-0.790772
N	1.452120	0.037949	-0.308620
C	0.199515	0.005173	-1.333214
C	-0.613531	1.270652	-1.026668
O	0.600768	-0.187176	-2.520236
C	1.243366	0.092400	1.149270
C	1.144573	1.511999	1.678397
C	2.333015	-0.753543	1.840076
C	2.154205	-0.895522	3.369942
C	2.627400	-2.281365	3.819712
C	2.856768	0.184548	4.201119
C	3.703061	-0.219155	1.449903
C	4.989100	-0.031028	-0.696077
C	4.798728	0.013606	-2.074849
S	3.085704	-0.003413	-2.505146
C	6.262112	-0.024455	-0.134297
C	7.350098	0.014283	-1.001782
C	7.168239	0.047030	-2.386830
C	5.888975	0.046860	-2.937003
C	0.183742	1.802765	2.650668
C	0.099377	3.075590	3.207443
C	0.972221	4.077864	2.789630
C	1.917849	3.802472	1.804702
C	2.000999	2.528055	1.248043
C	-2.046987	1.195196	-1.577757
C	-2.739350	2.501630	-1.230188
C	-2.756742	-0.023551	-1.008920
C	-4.206690	-0.103178	-1.145706
C	-5.025989	-0.977175	-0.237057
O	-4.791116	0.586457	-1.979668
C	-1.975325	-1.099204	-0.692070
C	-3.173707	2.755027	0.073675
C	-3.738845	3.981020	0.410894
C	-3.874201	4.978501	-0.554002
C	-3.441032	4.736684	-1.855156
C	-2.877200	3.506433	-2.187609
O	-2.438863	-2.340679	-0.364698
C	-1.354819	-3.188914	-0.322628
C	-0.198873	-2.464934	-0.614307
N	-0.606064	-1.142448	-0.753716
C	-1.359487	-4.538846	-0.054146
C	-0.116282	-5.182874	-0.105846
C	1.046012	-4.481763	-0.425203
C	1.029855	-3.106833	-0.689855
C	-4.665869	-1.209251	1.092403
C	-5.499518	-1.948994	1.925897
C	-6.694506	-2.470128	1.432017
C	-7.062085	-2.236844	0.107266
C	-6.236402	-1.481734	-0.718757
H	-0.678974	1.449747	0.050462
H	-0.074173	2.109464	-1.477189
H	0.284207	-0.405605	1.325150
H	2.235503	-1.755654	1.401505

H	3.693727	-2.418792	3.603526
H	2.073514	-3.076342	3.310675
H	2.490286	-2.404443	4.898318
H	1.076606	-0.830285	3.572082
H	3.946214	0.077150	4.141022
H	2.578318	0.071799	5.253132
H	2.594230	1.199821	3.890907
H	4.488821	-0.918363	1.750355
H	3.908028	0.754099	1.908828
H	6.407690	-0.039987	0.940307
H	8.353898	0.021438	-0.590579
H	8.031874	0.075549	-3.042446
H	5.743418	0.075074	-4.012046
H	-0.508659	1.026085	2.968756
H	-0.653958	3.285165	3.960382
H	0.905543	5.072591	3.218557
H	2.589353	4.582649	1.460250
H	2.730283	2.339097	0.463845
H	-1.995614	1.114878	-2.672359
H	-3.073204	1.976045	0.827509
H	-4.075633	4.158773	1.428227
H	-4.317422	5.934948	-0.293497
H	-3.546634	5.504703	-2.615849
H	-2.543858	3.319499	-3.205846
H	-2.278493	-5.066785	0.172522
H	-0.063867	-6.247882	0.092356
H	1.990034	-5.013833	-0.480881
H	1.934201	-2.579517	-0.970632
H	-3.734996	-0.797855	1.473634
H	-5.219820	-2.117573	2.961406
H	-7.341361	-3.053312	2.080645
H	-7.994868	-2.637674	-0.277422
H	-6.515734	-1.271073	-1.746481

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2448.13199510 Predicted Change= -3.045435D-09
Zero-point correction (ZPE)= -2447.4191 0.71280
Internal Energy (U)= -2447.3784 0.75354
Enthalpy (H)= -2447.3775 0.75449
Gibbs Free Energy (G)= -2447.4950 0.63696

Frequencies -- 10.2160 14.2392 25.5468

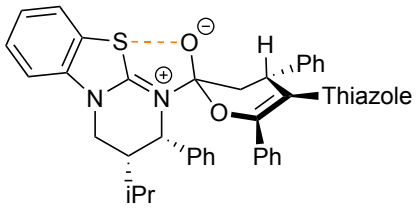
==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.23442163

==========



VIII-thiazole-disfavored

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

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#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C43H37N3O2S2 C1[X(C43H37N3O2S2)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2771.10239863 Predicted Change= -4.638835D-09

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00705	0.00180	[NO]	0.00705	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-4.316757	0.554031	-0.348926
C	-3.057680	0.545472	-0.838252
N	-2.046487	0.044543	-0.168391
C	-0.609052	0.165257	-0.742440
C	0.099871	-1.185256	-0.615133
H	0.063652	-1.582219	0.405324
H	-0.376608	-1.907849	-1.284990
O	-0.598932	0.710262	-1.886952
C	-2.259846	-0.543576	1.162548
H	-1.322751	-0.370870	1.696064
C	-2.519891	-2.040089	1.081374
C	-3.373895	0.247073	1.884212
H	-3.033296	1.292123	1.918797
C	-3.629029	-0.216870	3.329557
C	-2.410390	0.059437	4.214409
H	-1.502784	-0.438684	3.863040
H	-2.599777	-0.283447	5.235770
H	-2.205845	1.135787	4.251954
H	-3.820318	-1.297960	3.313999
C	-4.856252	0.475057	3.932420
H	-4.758947	1.565645	3.867049
H	-4.951404	0.211273	4.989751
H	-5.787075	0.182197	3.438097
C	-4.637516	0.197718	1.034756
H	-5.367008	0.929556	1.387678
H	-5.098641	-0.798075	1.057919

C	-5.284144	1.029128	-1.243880
C	-4.715997	1.435722	-2.448900
S	-2.962117	1.220403	-2.458773
C	-6.655201	1.107625	-1.019971
H	-7.095572	0.773096	-0.086926
C	-7.448258	1.620372	-2.042753
H	-8.520630	1.691201	-1.895067
C	-6.885551	2.039678	-3.251154
H	-7.524156	2.436147	-4.033245
C	-5.512361	1.951372	-3.465023
H	-5.071921	2.275564	-4.402582
C	-1.999705	-2.877438	2.072579
H	-1.385725	-2.455430	2.864783
C	-2.245513	-4.247204	2.049799
H	-1.829755	-4.881882	2.826061
C	-3.011301	-4.801538	1.026780
H	-3.200380	-5.870047	1.003723
C	-3.520896	-3.978646	0.026152
H	-4.106520	-4.403238	-0.783301
C	-3.274804	-2.607485	0.051468
H	-3.663488	-1.987951	-0.752758
C	1.559194	-0.958642	-1.022242
H	1.551821	-0.686816	-2.087951
C	2.347805	-2.244435	-0.862938
C	2.129384	0.208490	-0.229787
C	3.584732	0.392861	-0.331498
C	1.319513	1.106385	0.382850
C	1.741909	2.344723	1.091248
O	-0.029070	1.030516	0.345581
C	2.867134	-2.626732	0.377093
H	2.759108	-1.956006	1.226700
C	3.531539	-3.841744	0.523044
H	3.933035	-4.124023	1.491956
C	3.684957	-4.692536	-0.570177
H	4.204101	-5.639395	-0.456492
C	3.173403	-4.318533	-1.810681
H	3.292920	-4.972555	-2.669474
C	2.511350	-3.101164	-1.953128
H	2.115638	-2.807378	-2.923007
S	4.281146	0.525984	-1.963943
C	5.863763	0.625609	-1.249109
C	5.741190	0.554632	0.152164
N	4.447241	0.409272	0.630706
C	7.110540	0.757257	-1.863118
H	7.198284	0.812025	-2.943177
C	8.235500	0.817743	-1.051902
H	9.215079	0.921646	-1.507575
C	8.125036	0.746682	0.345954
H	9.021538	0.793904	0.955760
C	6.886975	0.615173	0.954177
H	6.784297	0.557852	2.033034
C	2.686858	2.356222	2.119640
H	3.164514	1.430085	2.414900
C	3.011836	3.553493	2.754971
H	3.743846	3.552985	3.557128

C	2.398285	4.742996	2.372125
H	2.656561	5.673570	2.868623
C	1.443741	4.734194	1.354916
H	0.958156	5.657694	1.054234
C	1.108612	3.540302	0.727874
H	0.356565	3.515397	-0.055230

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2771.10239863 Predicted Change= -4.638835D-09

Zero-point correction (ZPE)=	-2770.3931	0.70927
Internal Energy (U)=	-2770.3518	0.75056
Enthalpy (H)=	-2770.3508	0.75150
Gibbs Free Energy (G)=	-2770.4723	0.63006

Frequencies -- 6.0288 9.8316 18.6432

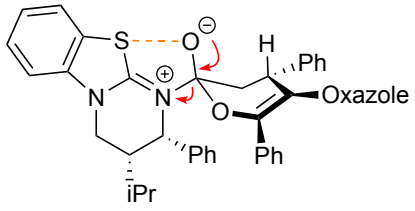
==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C43H37N3O2S2 C1[X(C43H37N3O2S2)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2771.20145237

==========



TS-Elimination-oxazole-favored

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)
iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.13609113 Predicted Change= -1.774365D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00135 ||	0.00180	[YES]	0.00135 ||	0.00180	[YES]

Atomic	Coordinates (Angstroms)

Type	X	Y	Z
N	-4.385021	-0.276331	-0.263759
C	-3.178907	-0.495470	-0.858134
N	-2.130180	0.240319	-0.704515
C	-0.569224	-0.373484	-1.401991
C	-0.069577	-1.290355	-0.300603
H	-0.205787	-0.830406	0.679964
H	-0.624476	-2.231913	-0.333833
O	-0.767067	-0.789211	-2.545064
C	-2.187387	1.446350	0.131624
H	-1.576206	2.183372	-0.393813
C	-1.519696	1.178829	1.471014
C	-3.626945	2.005475	0.199005
H	-3.865823	2.347451	-0.818664
C	-3.755273	3.211097	1.147768
C	-2.856425	4.365478	0.698209
H	-2.994091	5.229270	1.355358
H	-3.111583	4.674409	-0.322582
H	-1.795546	4.103391	0.717913
H	-3.433743	2.885752	2.146872
C	-5.204705	3.698122	1.244215
H	-5.865255	2.959829	1.708583
H	-5.601331	3.935324	0.249311
H	-5.254605	4.607831	1.849672
C	-4.635293	0.911737	0.546740
H	-5.647337	1.251652	0.313909
H	-4.600702	0.654056	1.613225
C	-5.349657	-1.255423	-0.513471
C	-4.876946	-2.256731	-1.365193
S	-3.217005	-1.948439	-1.874901
C	-6.641602	-1.301832	-0.000052
H	-7.005418	-0.535898	0.676236
C	-7.454972	-2.370866	-0.372150
H	-8.465652	-2.425706	0.018308
C	-6.988964	-3.367663	-1.230248
H	-7.638435	-4.191094	-1.506932
C	-5.690676	-3.318518	-1.735609
H	-5.321764	-4.090762	-2.402727
C	-0.396287	1.923177	1.836815
H	-0.025906	2.696504	1.167065
C	0.276949	1.661282	3.029161
H	1.152052	2.247508	3.293824
C	-0.163207	0.640126	3.867330
H	0.364621	0.425658	4.791501
C	-1.275129	-0.119304	3.504330
H	-1.611260	-0.930940	4.142020
C	-1.946826	0.147105	2.314526
H	-2.776517	-0.492306	2.021213
C	1.428112	-1.537809	-0.522074
H	1.564066	-2.132415	-1.434546
C	1.971052	-2.325435	0.657589
C	2.121000	-0.191743	-0.679128
C	3.578062	-0.223310	-0.582398
C	1.421041	0.927232	-0.988922

C	1.938050	2.314460	-1.108394
O	0.100209	0.915269	-1.285449
C	2.266681	-3.683070	0.539712
H	2.152275	-4.171448	-0.425167
C	2.708463	-4.411068	1.643195
H	2.936276	-5.467509	1.536118
C	2.860586	-3.785297	2.878312
H	3.205533	-4.351419	3.738234
C	2.569907	-2.427269	3.003608
H	2.686701	-1.930952	3.962773
C	2.129135	-1.703604	1.900009
H	1.901780	-0.642866	1.997076
O	4.131274	-1.380159	-1.082841
C	5.471740	-1.237925	-0.890618
C	5.675261	0.003589	-0.286040
N	4.437287	0.614757	-0.095189
C	6.491760	-2.118194	-1.211959
H	6.298051	-3.075831	-1.681357
C	7.778390	-1.690351	-0.892065
H	8.621270	-2.334505	-1.120630
C	8.011123	-0.446488	-0.282100
H	9.031306	-0.157110	-0.050972
C	6.968340	0.419367	0.031379
H	7.144476	1.380898	0.501653
C	2.613840	2.937029	-0.056216
H	2.819519	2.376806	0.848909
C	3.018462	4.264092	-0.177177
H	3.539394	4.744965	0.644886
C	2.754590	4.973052	-1.346759
H	3.076981	6.005702	-1.440170
C	2.067903	4.359079	-2.393927
H	1.854181	4.910542	-3.304179
C	1.647225	3.039730	-2.269192
H	1.095269	2.557586	-3.070286

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2448.13609113 Predicted Change= -1.774365D-09
Zero-point correction (ZPE)= -2447.4236 0.71246
Internal Energy (U)= -2447.3834 0.75268
Enthalpy (H)= -2447.3824 0.75363
Gibbs Free Energy (G)= -2447.4992 0.63687

Frequencies -- -113.0459 11.7940 20.1080

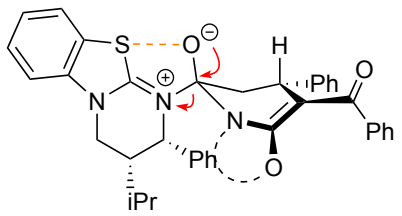
==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.23518934

==========



TS-Elimination-oxazole-disfavored

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.13233794 Predicted Change= -4.223498D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00145	0.00180	[YES]	0.00145	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	3.756185	-0.014229	0.146123
C	2.720835	0.174985	-0.711567
N	1.467218	0.052210	-0.370555
C	0.267253	0.206706	-1.581877
C	-0.528815	1.436714	-1.132134
O	0.819859	0.178794	-2.710168
C	1.122932	-0.278812	1.019849
C	0.831904	0.948596	1.863401
C	2.212737	-1.201096	1.604983
C	1.898072	-1.728731	3.024006
C	2.451966	-3.147760	3.183885
C	2.406080	-0.840178	4.165276
C	3.565241	-0.509260	1.509406
C	5.018725	0.278361	-0.381917
C	4.945119	0.657752	-1.721058
S	3.286555	0.636353	-2.322613
C	6.235403	0.223300	0.290853
C	7.386533	0.548252	-0.422811
C	7.320850	0.918487	-1.768022
C	6.096959	0.975270	-2.430577
C	-0.270357	0.929028	2.722015
C	-0.545096	2.013412	3.551123
C	0.278990	3.136050	3.523595
C	1.367315	3.172924	2.654044
C	1.639821	2.088086	1.824049

C	-1.998382	1.426809	-1.597969
C	-2.640021	2.693758	-1.058347
C	-2.689713	0.159878	-1.114973
C	-4.147707	0.113480	-1.119117
C	-4.893974	-0.871117	-0.263101
O	-4.793361	0.909443	-1.798273
C	-1.906315	-0.955244	-1.023909
C	-2.917617	2.820237	0.305793
C	-3.424727	4.008467	0.822069
C	-3.661490	5.093149	-0.021833
C	-3.386975	4.976313	-1.381936
C	-2.877735	3.783993	-1.893936
O	-2.342774	-2.229337	-0.800525
C	-1.260587	-3.071831	-0.946425
C	-0.135806	-2.315428	-1.269489
N	-0.555480	-0.992500	-1.250582
C	-1.233076	-4.440822	-0.803946
C	0.007733	-5.057051	-1.016394
C	1.137607	-4.314109	-1.361484
C	1.090316	-2.921675	-1.500096
C	-4.416170	-1.288658	0.981199
C	-5.181501	-2.135110	1.778036
C	-6.425822	-2.577360	1.331130
C	-6.909976	-2.159793	0.091934
C	-6.151867	-1.299148	-0.694448
H	-0.536275	1.515492	-0.042264
H	-0.006979	2.311101	-1.531946
H	0.203476	-0.870508	0.967664
H	2.241177	-2.066432	0.928549
H	3.541669	-3.157614	3.060981
H	2.021424	-3.828295	2.442361
H	2.228087	-3.540099	4.180525
H	0.803946	-1.787921	3.104426
H	3.501276	-0.854859	4.215726
H	2.032825	-1.224306	5.119290
H	2.080054	0.199483	4.070009
H	4.372971	-1.215932	1.722412
H	3.646685	0.331302	2.207477
H	6.289458	-0.055524	1.337660
H	8.347151	0.512981	0.080033
H	8.230242	1.167505	-2.304209
H	6.041444	1.264130	-3.475219
H	-0.921773	0.057797	2.736730
H	-1.407223	1.984317	4.210206
H	0.065568	3.984949	4.165292
H	2.002124	4.052489	2.614688
H	2.476576	2.143896	1.131314
H	-2.027039	1.467343	-2.696065
H	-2.734138	1.974221	0.966624
H	-3.634100	4.088836	1.885016
H	-4.058434	6.021188	0.378261
H	-3.571408	5.813563	-2.048856
H	-2.666160	3.695757	-2.956959
H	-2.123629	-5.002351	-0.546944
H	0.084262	-6.134747	-0.920585

H	2.077468	-4.826967	-1.537332
H	1.956646	-2.342801	-1.800604
H	-3.447116	-0.938069	1.326899
H	-4.809838	-2.448484	2.748832
H	-7.020481	-3.241772	1.950852
H	-7.880237	-2.500473	-0.256141
H	-6.521806	-0.945342	-1.651747

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2448.13233794 Predicted Change= -4.223498D-09

Zero-point correction (ZPE)=	-2447.4200	0.71228
Internal Energy (U)=	-2447.3799	0.75237
Enthalpy (H)=	-2447.3790	0.75331
Gibbs Free Energy (G)=	-2447.4939	0.63838

Frequencies -- -32.9649 11.9014 16.3197

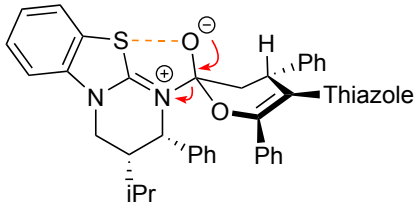
==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.23415504

==========



TS-Elimination-thiazole-disfavored

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

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#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C43H37N3O2S2 C1[X(C43H37N3O2S2)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2771.09926087 Predicted Change= -2.671274D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00156	0.00180	[YES]	0.00156	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-4.530550	-0.177794	-0.334962
C	-3.315531	-0.411088	-0.902724
N	-2.249736	0.285958	-0.689816
C	-0.705450	-0.343275	-1.349511
C	-0.279105	-1.337396	-0.282070
H	-0.438166	-0.919501	0.713600
H	-0.869530	-2.252545	-0.380206
O	-0.862243	-0.693282	-2.523531
C	-2.295036	1.479957	0.165276
H	-1.674245	2.217078	-0.348127
C	-1.628908	1.191560	1.501043
C	-3.725589	2.062050	0.234304
H	-3.942741	2.446866	-0.773001
C	-3.842355	3.236072	1.223828
C	-2.911020	4.384489	0.828463
H	-1.856713	4.097484	0.856893
H	-3.040678	5.227912	1.513082
H	-3.142309	4.734234	-0.184894
H	-3.543281	2.868965	2.215285
C	-5.281843	3.752117	1.316508
H	-5.657151	4.035956	0.325562
H	-5.321104	4.639454	1.955114
H	-5.966036	3.012424	1.742725
C	-4.764486	0.979605	0.522975
H	-5.763965	1.354742	0.290195
H	-4.754009	0.675963	1.577423
C	-5.515888	-1.116923	-0.650546
C	-5.047837	-2.097402	-1.528712
S	-3.365905	-1.818187	-1.980487
C	-6.822273	-1.145875	-0.173549
H	-7.183050	-0.397502	0.523726
C	-7.654758	-2.174777	-0.610240
H	-8.677102	-2.215103	-0.249540
C	-7.193411	-3.150155	-1.495197
H	-7.858532	-3.942028	-1.822346
C	-5.880623	-3.119693	-1.962883
H	-5.515248	-3.876124	-2.649752
C	-0.472635	1.893372	1.848207
H	-0.071502	2.633086	1.158455
C	0.192433	1.627915	3.043796
H	1.093800	2.180189	3.292320
C	-0.289979	0.645014	3.904688
H	0.229178	0.429419	4.833626
C	-1.430741	-0.077857	3.557003
H	-1.798126	-0.862205	4.211453
C	-2.093504	0.191602	2.362292
H	-2.949186	-0.418506	2.082197
C	1.215535	-1.649470	-0.452461
H	1.355406	-2.239191	-1.368822
C	1.668966	-2.484676	0.731604
C	1.977337	-0.339731	-0.596119
C	3.451611	-0.398879	-0.595326

C	1.333711	0.822072	-0.856693
C	1.953647	2.170588	-0.860724
O	0.010065	0.908497	-1.127833
C	1.659076	-1.933903	2.017050
H	1.391395	-0.886132	2.144567
C	2.001916	-2.704507	3.120421
H	1.989518	-2.261908	4.112674
C	2.363897	-4.042879	2.954630
H	2.633280	-4.646335	3.816208
C	2.379820	-4.597356	1.679062
H	2.661958	-5.636797	1.539303
C	2.032400	-3.819491	0.573169
H	2.043568	-4.256643	-0.422594
S	4.317285	0.040710	-2.082186
C	5.814215	-0.356281	-1.295225
C	5.539649	-0.809416	0.011334
N	4.200987	-0.822658	0.368987
C	7.123074	-0.281900	-1.777296
H	7.328070	0.068736	-2.783465
C	8.153422	-0.671258	-0.933419
H	9.178123	-0.624148	-1.288189
C	7.891189	-1.125996	0.369509
H	8.717593	-1.423956	1.006735
C	6.593586	-1.197142	0.848634
H	6.372737	-1.545980	1.852237
C	2.924053	2.521699	0.085218
H	3.238611	1.791602	0.825829
C	3.470128	3.801152	0.085414
H	4.221318	4.065006	0.823507
C	3.045369	4.744370	-0.849160
H	3.471417	5.743004	-0.846188
C	2.064296	4.406115	-1.779355
H	1.725178	5.139415	-2.504581
C	1.514276	3.128306	-1.781238
H	0.746148	2.858063	-2.498698

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2771.09926087 Predicted Change= -2.671274D-09
Zero-point correction (ZPE)= -2770.3909 0.70831
Internal Energy (U)= -2770.3499 0.74927
Enthalpy (H)= -2770.3490 0.75022
Gibbs Free Energy (G)= -2770.4684 0.63079

Frequencies -- -97.9503 9.1840 12.4138

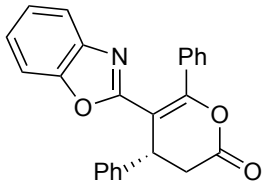
==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C43H37N3O2S2 C1[X(C43H37N3O2S2)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2771.19777085

==========



Benzoxazole-derived lactone

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011
==========
#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C24H17NO3 C1[X(C24H17NO3)] #Atoms= 45
Charge = 0 Multiplicity = 1

SCF Energy= -1204.75433108 Predicted Change= -1.306763D-09
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00054	0.00180	[YES]	0.00054	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.589575	0.773368	-1.829101
H	-2.102299	1.138813	-2.741921
H	-3.590082	0.420501	-2.081052
C	-2.722687	1.943822	-0.897109
O	-3.718578	2.567497	-0.661771
O	-1.554008	2.345353	-0.301517
C	-0.397212	1.588829	-0.362925
C	0.774063	2.409898	0.004130
C	-0.442133	0.285279	-0.700415
C	0.673452	-0.641678	-0.553653
C	-1.729673	-0.330554	-1.198557
C	-2.481848	-1.078049	-0.107959
H	-1.471205	-1.047186	-1.983867
C	0.662704	3.352854	1.031382
H	-0.276951	3.454213	1.564794
C	1.752130	4.149855	1.367427
H	1.661848	4.873025	2.171598
C	2.952084	4.022581	0.670982
H	3.800244	4.648172	0.930903
C	3.060143	3.098804	-0.367837
H	3.987698	3.010264	-0.924293
C	1.975526	2.297156	-0.703133
H	2.052420	1.591847	-1.525767
C	-2.595355	-0.556351	1.183457
H	-2.091454	0.373062	1.440017

C	-3.338031	-1.225175	2.153093
H	-3.418065	-0.808050	3.152204
C	-3.971368	-2.426807	1.844300
H	-4.545648	-2.950413	2.602208
C	-3.859122	-2.955926	0.560309
H	-4.344414	-3.895299	0.313506
C	-3.118777	-2.283518	-0.408646
H	-3.029233	-2.699039	-1.409486
N	0.801674	-1.767950	-1.183286
C	1.972382	-2.319574	-0.669157
C	2.490296	-1.446757	0.289900
O	1.644517	-0.378115	0.367723
C	2.638971	-3.510765	-0.959523
H	2.251428	-4.200488	-1.701354
C	3.812177	-3.768240	-0.259980
H	4.359462	-4.683902	-0.458646
C	4.310765	-2.871669	0.701389
H	5.230002	-3.113756	1.224518
C	3.655963	-1.679868	1.000950
H	4.029831	-0.979078	1.738221

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1204.75433108 Predicted Change= -1.306763D-09
Zero-point correction (ZPE)= -1204.3978 0.35646
Internal Energy (U)= -1204.3767 0.37756
Enthalpy (H)= -1204.3758 0.37851
Gibbs Free Energy (G)= -1204.4504 0.30389

Frequencies -- 24.2780 29.4332 31.5152

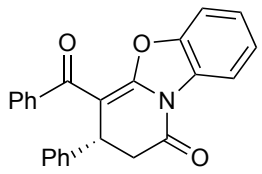
==========

#M062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C24H17NO3 C1[X(C24H17NO3)] #Atoms= 45
Charge = 0 Multiplicity = 1

SCF Energy= -1204.80942288

==========



Benzoxazole-derived lactam

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C24H17NO3 C1[X(C24H17NO3)] #Atoms= 45
Charge = 0 Multiplicity = 1

SCF Energy= -1204.75411750 Predicted Change= -2.869599D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00153	0.00180	[YES]	0.00153	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.082643	-2.029825	-1.920840
H	-1.139171	-1.560841	-2.911989
H	-1.324483	-3.087739	-2.041793
C	-2.181494	-1.392733	-1.102130
O	-3.311724	-1.813595	-0.990093
N	-1.805267	-0.188731	-0.506147
C	-0.517812	0.353133	-0.605770
C	0.557056	-0.347297	-1.025964
C	1.901643	0.210436	-1.236679
C	2.375910	1.383537	-0.436922
C	0.321492	-1.817211	-1.351268
C	0.626545	-2.664874	-0.119842
H	1.042262	-2.078419	-2.131948
C	1.954269	-2.745446	0.321153
H	2.732911	-2.239853	-0.245046
C	2.285123	-3.467038	1.461683
H	3.320870	-3.520341	1.783393
C	1.291334	-4.125256	2.187447
H	1.547886	-4.690593	3.077887
C	-0.028130	-4.056962	1.756026
H	-0.810548	-4.569410	2.307528
C	-0.358952	-3.333288	0.608532
H	-1.398192	-3.311218	0.292402
O	2.664802	-0.315130	-2.040624
C	-2.660890	0.798548	0.018244
C	-1.864932	1.926962	0.176445
O	-0.570967	1.653491	-0.222967
C	-4.007023	0.816316	0.341847
H	-4.625381	-0.062342	0.216151
C	-4.512442	2.024489	0.835717
H	-5.561776	2.081649	1.104358
C	-3.703380	3.149762	0.992890
H	-4.131716	4.067390	1.381274
C	-2.343852	3.123456	0.660313
H	-1.698763	3.987000	0.771355
C	2.062427	1.510143	0.918316
H	1.413350	0.777226	1.390321
C	2.598626	2.556624	1.661618
H	2.364817	2.645651	2.717821
C	3.436815	3.487284	1.049552
H	3.847366	4.309438	1.627988

C	3.757037	3.359765	-0.301920
H	4.415117	4.081616	-0.775437
C	3.241304	2.299955	-1.039318
H	3.497250	2.170898	-2.086539

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1204.75411750 Predicted Change= -2.869599D-09
Zero-point correction (ZPE)= -1204.3979 0.35619
Internal Energy (U)= -1204.3768 0.37730
Enthalpy (H)= -1204.3758 0.37824
Gibbs Free Energy (G)= -1204.4499 0.30417

Frequencies -- 19.2803 23.3982 40.1930

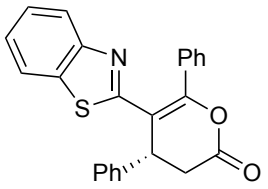
==========

#M062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C24H17NO3 C1[X(C24H17NO3)] #Atoms= 45
Charge = 0 Multiplicity = 1

SCF Energy= -1204.80886451

==========



Benzothiazole-derived lactone

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C24H17NO2S C1[X(C24H17NO2S)] #Atoms= 45
Charge = 0 Multiplicity = 1

SCF Energy= -1527.71868312 Predicted Change= -6.264164D-09

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00327	0.00180	[NO]	0.00327	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.777661	-0.181369	-1.839703

H	-2.470788	0.323607	-2.764317
H	-3.561583	-0.901944	-2.075950
C	-3.359370	0.867942	-0.934722
O	-4.521396	1.058531	-0.709747
O	-2.442547	1.709628	-0.361177
C	-1.084098	1.448040	-0.406277
C	-0.306115	2.653015	-0.055540
C	-0.611325	0.224938	-0.708274
C	0.778576	-0.203401	-0.498402
C	-1.555140	-0.849783	-1.195689
C	-1.956795	-1.824736	-0.098789
H	-1.032111	-1.413664	-1.974035
C	-0.695599	3.449529	1.026261
H	-1.570441	3.174160	1.606992
C	0.044410	4.579733	1.358449
H	-0.252185	5.187725	2.207006
C	1.162999	4.929896	0.603666
H	1.737287	5.813528	0.863659
C	1.538627	4.152206	-0.490683
H	2.399353	4.431897	-1.089391
C	0.805960	3.018278	-0.821685
H	1.088538	2.411690	-1.677539
C	-2.124909	-1.416113	1.225827
H	-1.912167	-0.386995	1.507193
C	-2.549876	-2.321399	2.196514
H	-2.673968	-1.989621	3.222781
C	-2.809155	-3.645760	1.853258
H	-3.137422	-4.351267	2.610248
C	-2.641927	-4.061828	0.533729
H	-2.836877	-5.094053	0.259113
C	-2.218691	-3.155748	-0.433808
H	-2.086445	-3.482666	-1.462661
N	1.328331	-1.132145	-1.214755
C	2.586590	-1.456722	-0.737702
C	2.991641	-0.749883	0.411795
S	1.732885	0.353001	0.883855
C	3.444424	-2.406451	-1.307818
H	3.127340	-2.948554	-2.192672
C	4.679693	-2.627743	-0.721747
H	5.355218	-3.360305	-1.151278
C	5.073109	-1.914346	0.423024
H	6.046340	-2.104098	0.864218
C	4.238472	-0.968445	1.000399
H	4.543948	-0.416820	1.883137

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

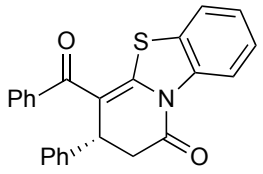
==========

SCF Energy= -1527.71868312 Predicted Change= -6.264164D-09

Zero-point correction (ZPE)=	-1527.3655	0.35311
Internal Energy (U)=	-1527.3438	0.37488
Enthalpy (H)=	-1527.3428	0.37582
Gibbs Free Energy (G)=	-1527.4200	0.29859

Frequencies -- 9.2935 20.4105 32.8593

```
=============================================================================
 #M062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=THF)
-----------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C24H17NO2S   C1[X(C24H17NO2S)]  #Atoms= 45
 Charge = 0         Multiplicity = 1
-----------------------------------------------------------------------------
 SCF Energy= -1527.77296732
=============================================================================
```



Benzothiazole-derived lactam

```
-----------------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevC.01 23-Sep-2011
=============================================================================
 #M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
-----------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C24H17NO2S   C1[X(C24H17NO2S)]  #Atoms= 45
 Charge = 0         Multiplicity = 1
-----------------------------------------------------------------------------
 SCF Energy= -1527.72434948       Predicted Change= -5.666021D-10
=============================================================================
 Optimization completed.          {Found       2       times}
 Item     Max Val.   Criteria   Pass?     RMS Val.   Criteria   Pass?
 Force     0.00000 ||  0.00045   [ YES ]     0.00000 ||  0.00030   [ YES ]
 Displ     0.00053 ||  0.00180   [ YES ]     0.00053 ||  0.00180   [ YES ]
-----------------------------------------------------------------------------
    Atomic             Coordinates (Angstroms)
     Type              X           Y           Z
-----------------------------------------------------------------------------
      C       -0.205047    1.259479    2.030452
      H       -0.348877    0.632773    2.921347
      H        0.110973    2.250332    2.360489
      C       -1.570174    1.404703    1.409830
      O       -2.302954    2.346114    1.611881
      N       -1.982775    0.309592    0.629726
      C       -1.086049   -0.702338    0.256545
      C        0.256175   -0.645128    0.493875
      C        1.103986   -1.691575   -0.066479
      C        2.594252   -1.583723    0.096071
      C        0.842399    0.601220    1.125694
      C        1.409201    1.550983    0.080839
      H        1.670595    0.319328    1.778277
      C        2.726707    1.998085    0.192629
      H        3.342605    1.641085    1.015497
      C        3.261802    2.878133   -0.746183
      H        4.290393    3.211831   -0.648342
```

C	2.480228	3.322526	-1.809035
H	2.893801	4.008649	-2.541615
C	1.165635	2.875220	-1.933697
H	0.552663	3.209582	-2.765082
C	0.636411	1.991129	-0.998208
H	-0.383579	1.632790	-1.121475
O	0.638168	-2.631691	-0.710630
C	-3.317918	0.093499	0.206341
C	-3.445703	-1.126162	-0.461002
S	-1.913423	-1.983868	-0.612698
C	-4.430687	0.912542	0.396318
H	-4.339264	1.860781	0.903501
C	-5.659427	0.473258	-0.093194
H	-6.531775	1.102980	0.048001
C	-5.786386	-0.746612	-0.756978
H	-6.754023	-1.066280	-1.128881
C	-4.672590	-1.559075	-0.947229
H	-4.754773	-2.510459	-1.462893
C	3.384029	-1.525805	-1.053934
H	2.905361	-1.543549	-2.028764
C	4.767942	-1.429980	-0.945882
H	5.376843	-1.369339	-1.842467
C	5.370613	-1.419776	0.310857
H	6.450744	-1.349952	0.394725
C	4.587521	-1.510143	1.460212
H	5.055415	-1.523523	2.439682
C	3.201095	-1.584576	1.354182
H	2.591298	-1.662986	2.250925

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1527.72434948 Predicted Change= -5.666021D-10
Zero-point correction (ZPE)= -1527.3714 0.35290
Internal Energy (U)= -1527.3496 0.37465
Enthalpy (H)= -1527.3487 0.37559
Gibbs Free Energy (G)= -1527.4245 0.29976

Frequencies -- 15.1501 28.5051 32.9279

==========

#M062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

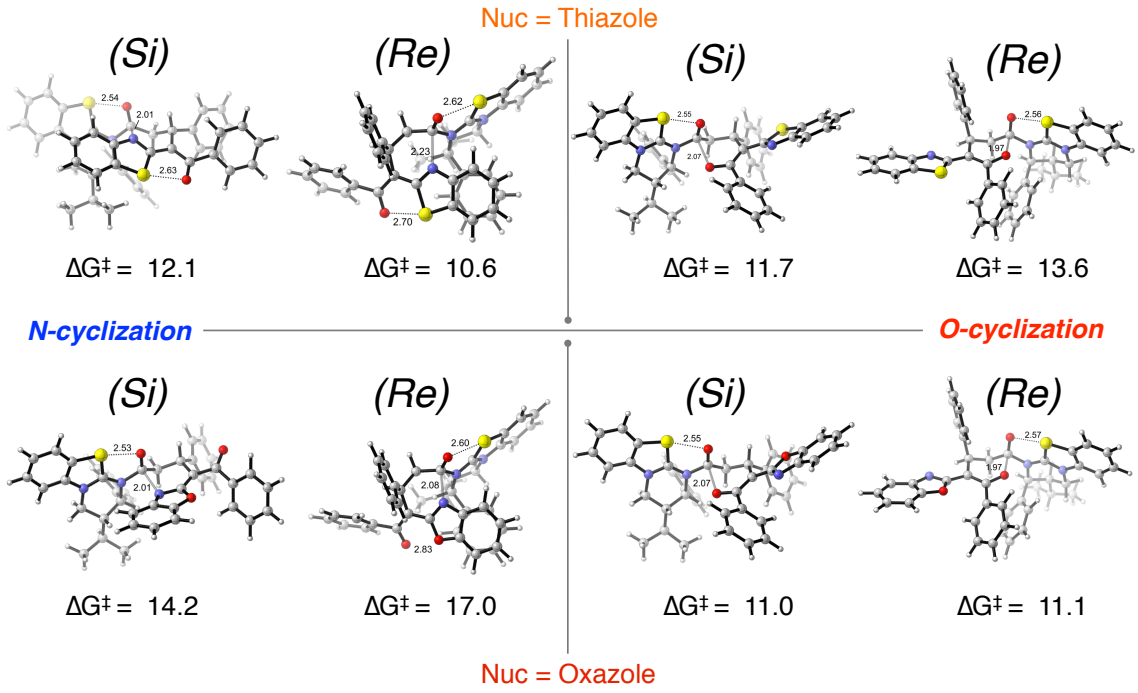
Pointgroup= C1 Stoichiometry= C24H17NO2S C1[X(C24H17NO2S)] #Atoms= 45
Charge = 0 Multiplicity = 1

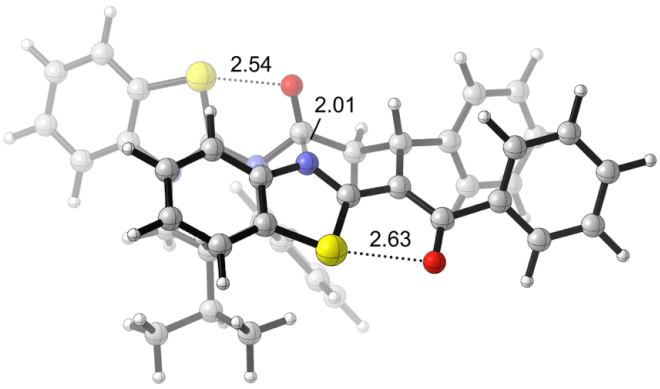
SCF Energy= -1527.77826500

==========

Annulation Facial Selectivity

Eight diastereomeric ring-closure (annulation) transition states.





Thiazole-*N*-*si*-cyclization-TS

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)
iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C43H37N3O2S2 C1[X(C43H37N3O2S2)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2771.10098022 Predicted Change= -8.792690D-09

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00137	0.00180	[YES]	0.00137	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-3.748571	-0.549885	-0.023574
C	-2.644009	-0.778056	-0.753038
N	-1.424062	-0.497364	-0.304507
C	-0.249171	-0.699797	-1.204663
C	0.999476	-1.183726	-0.493699
H	0.973869	-1.008946	0.582542
H	0.986430	-2.268304	-0.647790
O	-0.516222	-1.060929	-2.345822
C	-1.259316	0.037666	1.067536
H	-0.363950	0.662634	1.025517
C	-1.038155	-1.077047	2.078149
C	-2.453091	0.959570	1.406469
H	-2.451160	1.767641	0.661821
C	-2.357760	1.603522	2.802620
C	-1.154972	2.544377	2.897758
H	-1.261193	3.362353	2.175619
H	-0.201100	2.050631	2.694993
H	-1.095519	2.978824	3.900084
H	-2.245637	0.801637	3.544487
C	-3.631522	2.391187	3.129342
H	-3.837338	3.129211	2.343800
H	-3.503450	2.931834	4.071410
H	-4.509869	1.748419	3.239323
C	-3.750103	0.180917	1.246350
H	-4.602288	0.862454	1.211318
H	-3.902056	-0.532271	2.066698
C	-4.933602	-1.030595	-0.596869
C	-4.707504	-1.611691	-1.841721
S	-3.005941	-1.544509	-2.286148
C	-6.208664	-0.973483	-0.040606
H	-6.381586	-0.535091	0.935840
C	-7.256867	-1.510938	-0.779598
H	-8.260704	-1.482026	-0.369880
C	-7.037532	-2.087216	-2.035188
H	-7.872967	-2.499621	-2.590546
C	-5.759466	-2.141978	-2.581309
H	-5.585360	-2.590133	-3.553857
C	-1.770362	-2.266850	2.047541
H	-2.496506	-2.451588	1.259884
C	-1.566767	-3.247601	3.016045
H	-2.143218	-4.166392	2.977241
C	-0.624222	-3.054900	4.022425
H	-0.465095	-3.821166	4.774236
C	0.123458	-1.879908	4.050080
H	0.873996	-1.727166	4.818951

C	-0.080260	-0.901204	3.081645
H	0.523680	0.003000	3.095837
C	2.326375	-0.602282	-1.055356
H	2.219835	-0.587923	-2.150737
C	3.403239	-1.607805	-0.692175
C	2.524109	0.812686	-0.518624
C	1.389420	1.620422	-0.610432
C	3.711018	1.416280	0.025206
C	5.088177	0.895526	-0.284865
O	3.659973	2.455417	0.711397
C	3.805886	-1.780257	0.634975
H	3.378869	-1.145400	1.409391
C	4.771140	-2.724904	0.967354
H	5.086877	-2.833037	2.000938
C	5.337759	-3.526265	-0.023381
H	6.096218	-4.259386	0.234458
C	4.921114	-3.382812	-1.343813
H	5.351666	-4.006022	-2.122224
C	3.957710	-2.431301	-1.671802
H	3.645215	-2.310887	-2.706774
S	1.235266	3.251919	0.095668
C	-0.378041	3.375278	-0.591740
C	-0.689607	2.205489	-1.308079
N	0.288017	1.234879	-1.273273
C	-1.298152	4.413267	-0.476599
H	-1.054153	5.309178	0.087059
C	-2.539894	4.279771	-1.097152
H	-3.270931	5.077099	-1.010489
C	-2.836978	3.138352	-1.852008
H	-3.795119	3.063197	-2.357485
C	-1.916850	2.102798	-1.975421
H	-2.124607	1.228760	-2.585614
C	5.440264	0.445019	-1.557251
H	4.686416	0.405186	-2.339801
C	6.747955	0.048952	-1.825820
H	7.014185	-0.297953	-2.819892
C	7.711872	0.096283	-0.821215
H	8.729664	-0.220698	-1.028810
C	7.369762	0.561505	0.448499
H	8.120774	0.609125	1.231624
C	6.067509	0.973244	0.708386
H	5.788949	1.355978	1.685660

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2771.10098022 Predicted Change= -8.792690D-09

Zero-point correction (ZPE)=	-2770.3914	0.70952
Internal Energy (U)=	-2770.3512	0.74968
Enthalpy (H)=	-2770.3503	0.75062
Gibbs Free Energy (G)=	-2770.4630	0.63796

Frequencies -- -128.6508 22.9958 26.9458

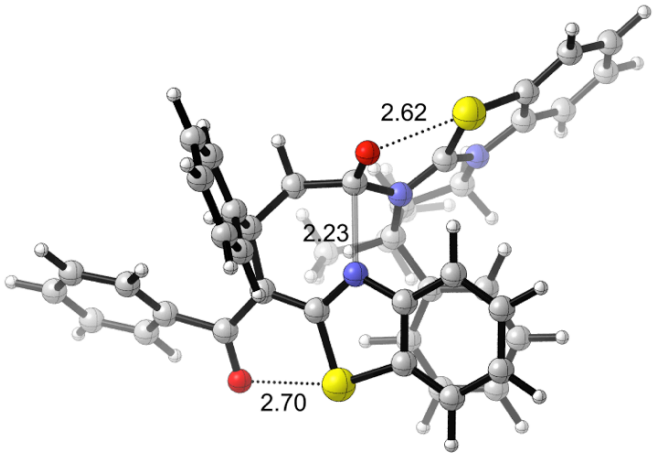
==========

#M062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current

SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C43H37N3O2S2 C1[X(C43H37N3O2S2)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2771.19995224
==========



Thiazole-*N*-*re*-cyclization-TS

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011
==========
#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C43H37N3O2S2 C1[X(C43H37N3O2S2)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2771.09894699 Predicted Change= -7.886391D-09
==========
==
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00147	0.00180	[YES]	0.00147	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	3.439401	-0.200867	-1.301812
C	2.494968	0.694232	-0.977469
N	1.239225	0.326889	-0.716260
C	0.167113	1.331735	-0.824088
C	-1.053806	0.866445	-1.604821
O	0.495080	2.495688	-0.729143
C	0.958492	-1.115858	-0.564327

C	1.333109	-1.675636	0.799009
C	1.660485	-1.841160	-1.735568
C	1.304714	-3.332224	-1.859813
C	-0.175026	-3.505277	-2.215387
C	2.167447	-4.025786	-2.918963
C	3.160865	-1.617240	-1.587952
C	4.716376	0.350412	-1.470172
C	4.711641	1.733692	-1.300476
S	3.103275	2.326886	-0.907782
C	5.883904	-0.340846	-1.782987
C	7.049699	0.401630	-1.928242
C	7.049387	1.791762	-1.767251
C	5.879251	2.474497	-1.453852
C	2.439556	-1.261014	1.548379
C	2.749953	-1.886581	2.751736
C	1.965838	-2.937961	3.222506
C	0.856183	-3.347589	2.491883
C	0.540802	-2.713390	1.293414
C	-2.450765	0.877494	-0.926988
C	-2.871412	2.309814	-0.576898
C	-2.604133	-0.135002	0.186453
C	-1.676104	-0.035467	1.242805
C	-3.635303	-1.110865	0.270031
C	-4.745172	-1.160358	-0.753096
O	-3.681788	-1.971624	1.176994
C	-3.192432	2.710912	0.721228
C	-3.607826	4.015662	0.984630
C	-3.718064	4.942905	-0.047320
C	-3.417248	4.551550	-1.350709
C	-3.000947	3.249232	-1.607407
S	-1.795055	-0.908651	2.791779
C	-0.371135	-0.050557	3.350924
C	0.089347	0.821381	2.343763
N	-0.651461	0.800491	1.186338
C	0.301212	-0.161634	4.563862
C	1.433831	0.621326	4.774487
C	1.886259	1.502168	3.783541
C	1.221887	1.613798	2.568427
C	-5.445244	-0.024973	-1.171936
C	-6.516643	-0.142655	-2.055681
C	-6.893926	-1.394911	-2.535035
C	-6.208240	-2.533662	-2.112177
C	-5.151607	-2.415762	-1.215765
H	-1.075630	1.565711	-2.447085
H	-0.891044	-0.123963	-2.035601
H	-0.122096	-1.219283	-0.659303
H	1.332116	-1.340900	-2.659099
H	-0.386076	-3.048052	-3.189602
H	-0.852469	-3.056710	-1.481708
H	-0.424998	-4.567938	-2.282903
H	1.498445	-3.812361	-0.892305
H	3.224710	-4.060325	-2.639566
H	2.082095	-3.515989	-3.886346
H	1.832170	-5.057901	-3.054975
H	3.685041	-1.854646	-2.515981

H	3.578946	-2.223467	-0.775344
H	5.888040	-1.418504	-1.902975
H	7.974910	-0.110227	-2.169408
H	7.973971	2.345941	-1.886433
H	5.875231	3.551782	-1.327750
H	3.051922	-0.423250	1.227795
H	3.600746	-1.539286	3.329493
H	2.209828	-3.421297	4.163601
H	0.217693	-4.144322	2.860375
H	-0.352262	-3.012887	0.749025
H	-3.111753	0.562390	-1.742047
H	-3.125486	1.994175	1.533191
H	-3.848216	4.304323	2.003742
H	-4.042908	5.958325	0.158861
H	-3.513875	5.259045	-2.169162
H	-2.784889	2.954682	-2.632731
H	-0.049658	-0.845306	5.331707
H	1.966917	0.549594	5.717588
H	2.766210	2.110970	3.971090
H	1.553567	2.300550	1.794056
H	-5.164445	0.953186	-0.787784
H	-7.060536	0.745200	-2.364310
H	-7.724743	-1.485165	-3.228456
H	-6.505708	-3.513243	-2.474794
H	-4.627490	-3.296152	-0.855653

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2771.09894699 Predicted Change= -7.886391D-09

Zero-point correction (ZPE)=	-2770.3903	0.70860
Internal Energy (U)=	-2770.3496	0.74928
Enthalpy (H)=	-2770.3487	0.75022
Gibbs Free Energy (G)=	-2770.4648	0.63406

Frequencies -- -75.4058 11.9587 16.3033

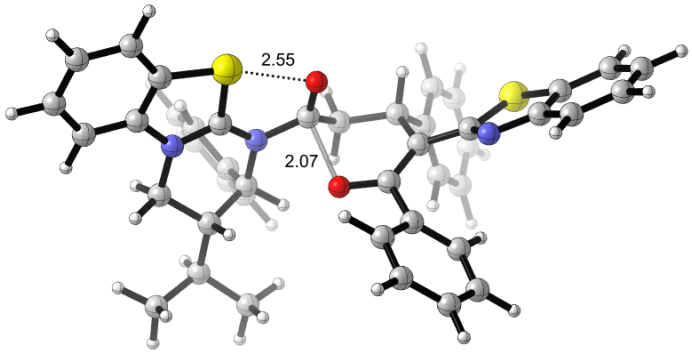
==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C43H37N3O2S2 C1[X(C43H37N3O2S2)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2771.19836373

==========



Thiazole-*O*-*si*-cyclization-TS

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011
==========
#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)
iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C43H37N3O2S2 C1[X(C43H37N3O2S2)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2771.09554176 Predicted Change= -1.272284D-08
==========
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00204	0.00180	[NO]	0.00204	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	4.074300	-1.024251	-0.331106
C	2.839139	-0.899864	-0.843806
N	1.995443	0.045774	-0.434420
C	0.636476	0.079602	-0.965785
C	-0.108433	1.386253	-0.876725
H	0.115962	1.931159	0.038682
H	0.214677	2.015284	-1.717332
O	0.335433	-0.779481	-1.775372
C	2.376387	0.957337	0.665577
H	1.448015	1.122602	1.210977
C	2.915371	2.267062	0.120861
C	3.325564	0.215233	1.626477
H	2.765711	-0.661729	1.982817
C	3.727027	1.058035	2.850463
C	2.511586	1.342688	3.737191
H	2.808645	1.942381	4.602207
H	2.082774	0.404134	4.106639
H	1.718914	1.886183	3.216766
H	4.136477	2.011063	2.490244
C	4.807221	0.356929	3.681444

H	4.488063	-0.654603	3.960337
H	4.989106	0.915631	4.603877
H	5.761617	0.283410	3.151560
C	4.533114	-0.287844	0.851732
H	5.109918	-0.993732	1.451663
H	5.191064	0.531917	0.537367
C	4.862549	-1.999923	-0.956198
C	4.164882	-2.662327	-1.962989
S	2.520001	-2.057446	-2.112993
C	6.185518	-2.314688	-0.657149
H	6.732247	-1.785804	0.115352
C	6.787194	-3.327233	-1.394923
H	7.817471	-3.592808	-1.184360
C	6.088814	-4.003773	-2.401380
H	6.581790	-4.791594	-2.960400
C	4.769498	-3.678291	-2.696947
H	4.225814	-4.198751	-3.478228
C	3.757665	2.307961	-0.993961
H	4.009793	1.394472	-1.527404
C	4.267582	3.520419	-1.452066
H	4.917261	3.534777	-2.321363
C	3.937024	4.708026	-0.804498
H	4.331244	5.652955	-1.164520
C	3.086143	4.678563	0.297968
H	2.809988	5.600305	0.800077
C	2.575861	3.465992	0.753451
H	1.899734	3.454151	1.604913
C	-1.630103	1.153086	-0.993168
H	-1.828036	0.886363	-2.040466
C	-2.288410	2.507078	-0.737334
C	-2.167031	0.038285	-0.104814
C	-3.495644	-0.440265	-0.397687
C	-1.363479	-0.588500	0.846988
C	-1.914580	-1.455555	1.944102
O	-0.089053	-0.444122	0.902443
C	-2.590574	2.923017	0.561722
H	-2.406908	2.239224	1.387782
C	-3.139855	4.180858	0.795188
H	-3.376599	4.486560	1.810208
C	-3.394275	5.042732	-0.270567
H	-3.829954	6.020971	-0.090966
C	-3.092558	4.638594	-1.569366
H	-3.292083	5.301559	-2.406203
C	-2.541552	3.379594	-1.797879
H	-2.315508	3.061189	-2.813734
S	-4.672115	0.646040	-1.233966
C	-5.837642	-0.647611	-1.221763
C	-5.272320	-1.773033	-0.585437
N	-3.967709	-1.634922	-0.167585
C	-7.137877	-0.668033	-1.723187
H	-7.559520	0.204436	-2.212815
C	-7.885504	-1.830953	-1.574197
H	-8.902096	-1.866185	-1.953066
C	-7.338369	-2.955736	-0.940012
H	-7.938604	-3.854548	-0.835000

C	-6.041418	-2.937120	-0.447886
H	-5.607215	-3.802938	0.042080
C	-1.185276	-2.582990	2.325793
H	-0.282055	-2.828962	1.776184
C	-1.609508	-3.376035	3.388724
H	-1.042960	-4.260630	3.664825
C	-2.754326	-3.028826	4.102189
H	-3.082718	-3.639402	4.938129
C	-3.472035	-1.886255	3.745254
H	-4.356656	-1.603091	4.308044
C	-3.055816	-1.106291	2.671745
H	-3.614996	-0.218043	2.388809

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2771.09554176 Predicted Change= -1.272284D-08
Zero-point correction (ZPE)= -2770.3865 0.70897
Internal Energy (U)= -2770.3455 0.74998
Enthalpy (H)= -2770.3446 0.75093
Gibbs Free Energy (G)= -2770.4636 0.63190

Frequencies -- -116.2652 12.0058 17.8171

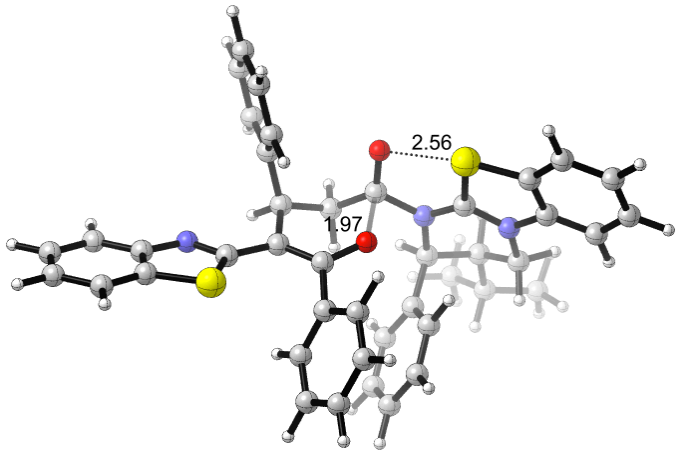
==========

#M062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C43H37N3O2S2 C1[X(C43H37N3O2S2)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2771.19453032

==========



Thiazole-*O*-*re*-cyclization-TS

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current

SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C43H37N3O2S2 C1[X(C43H37N3O2S2)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2771.09517293 Predicted Change= -6.643546D-11

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00035	0.00180	[YES]	0.00035	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-4.094409	0.507724	-0.236259
C	-2.892005	1.100848	-0.138715
N	-2.034820	0.829848	0.838657
C	-0.688120	1.458725	0.755201
C	0.304928	1.034589	1.811310
H	0.163770	1.698885	2.673542
H	0.130483	0.004951	2.130478
O	-0.657012	2.544253	0.200238
C	-2.364187	-0.221403	1.823392
H	-1.860649	0.075047	2.745311
C	-1.869226	-1.598354	1.409922
C	-3.884716	-0.166150	2.099984
H	-4.102152	0.854364	2.447160
C	-4.343554	-1.146578	3.195707
C	-3.743930	-0.772656	4.553836
H	-4.064284	0.233785	4.848082
H	-2.650937	-0.791821	4.560207
H	-4.087236	-1.472249	5.321240
H	-3.999260	-2.151934	2.920484
C	-5.871439	-1.179106	3.309762
H	-6.167227	-1.796251	4.162786
H	-6.348227	-1.601519	2.420600
H	-6.272614	-0.171156	3.471127
C	-4.639926	-0.378193	0.794940
H	-5.692321	-0.112087	0.912048
H	-4.573337	-1.417482	0.449753
C	-4.809153	0.838163	-1.395024
C	-4.117691	1.756200	-2.182249
S	-2.584548	2.212929	-1.450904
C	-6.051001	0.339352	-1.779716
H	-6.580082	-0.390609	-1.177085
C	-6.585958	0.800615	-2.977859
H	-7.550084	0.426209	-3.304501
C	-5.901663	1.730863	-3.767050
H	-6.341337	2.074346	-4.697197
C	-4.659362	2.219576	-3.376543
H	-4.122755	2.938888	-3.986297
C	-1.328195	-2.439256	2.385075

H	-1.209776	-2.076328	3.403571
C	-0.933151	-3.737697	2.067775
H	-0.512994	-4.376192	2.838576
C	-1.065320	-4.203545	0.763569
H	-0.743230	-5.207899	0.506081
C	-1.582094	-3.363851	-0.221067
H	-1.640062	-3.703923	-1.250956
C	-1.980086	-2.070216	0.097962
H	-2.325926	-1.414042	-0.695066
C	1.768964	1.117295	1.331202
H	2.364417	0.855724	2.214025
C	2.204458	2.527670	0.946388
C	2.070207	0.063855	0.284067
C	3.471818	-0.238756	0.135580
C	1.044424	-0.416819	-0.514921
C	1.157703	-1.667072	-1.334604
O	-0.125791	0.117340	-0.566609
C	2.393069	2.905620	-0.383385
H	2.216543	2.173355	-1.166865
C	2.795826	4.198411	-0.706110
H	2.937979	4.474267	-1.747267
C	3.018020	5.137168	0.299986
H	3.334274	6.145185	0.048375
C	2.836977	4.769670	1.631436
H	3.015083	5.490221	2.424661
C	2.437493	3.473209	1.947618
H	2.310507	3.187664	2.990711
S	4.178185	-0.939073	-1.362570
C	5.771985	-0.710671	-0.692088
C	5.656062	-0.126396	0.585983
N	4.369487	0.129846	1.011793
C	7.011653	-1.036314	-1.237052
H	7.087210	-1.490723	-2.220064
C	8.153769	-0.756287	-0.493460
H	9.130417	-0.992999	-0.903859
C	8.054469	-0.170128	0.775919
H	8.957890	0.041502	1.339673
C	6.817312	0.144897	1.320833
H	6.727909	0.598337	2.303055
C	0.586362	-1.702030	-2.609476
H	0.142172	-0.795424	-3.009650
C	0.583781	-2.881080	-3.348621
H	0.151852	-2.896286	-4.345003
C	1.129198	-4.045155	-2.805977
H	1.120748	-4.967713	-3.378917
C	1.676411	-4.023322	-1.524525
H	2.084074	-4.931800	-1.090896
C	1.691551	-2.839202	-0.793219
H	2.097619	-2.819578	0.214562

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2771.09517293 Predicted Change= -6.643546D-11
Zero-point correction (ZPE)= -2770.3866 0.70847

Internal Energy (U)= -2770.3460 0.74913
Enthalpy (H)= -2770.3450 0.75008
Gibbs Free Energy (G)= -2770.4617 0.63346

Frequencies -- -134.0813 14.8830 20.3018

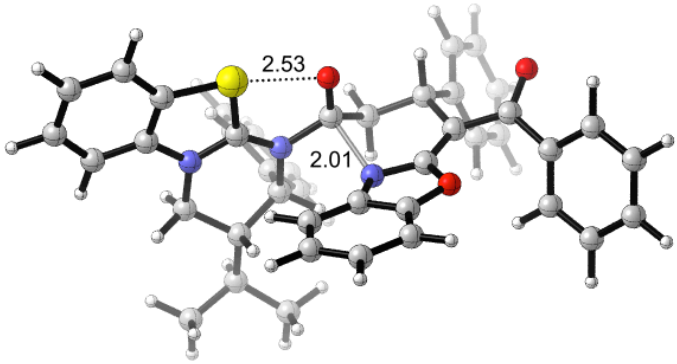
==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C43H37N3O2S2 C1[X(C43H37N3O2S2)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2771.19297595

==========



Oxazole-*N*-*si*-cyclization-TS

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.12448628 Predicted Change= -9.033427D-09

==========

Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.01384	0.00180	[NO]	0.01384	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	3.772491	-0.328835	-0.150724
C	2.589181	-0.346402	-0.787701
N	1.511136	0.255587	-0.295704
C	0.235380	0.192891	-1.048362
C	-0.715372	1.344411	-0.786366

O	0.279029	-0.369762	-2.134793
C	1.575896	0.986362	0.988353
C	1.784588	2.472575	0.748464
C	2.637333	0.344477	1.906234
C	2.769861	1.049536	3.269578
C	1.484312	0.900336	4.088074
C	3.946516	0.487836	4.074174
C	3.968689	0.268575	1.173519
C	4.810961	-0.970572	-0.841431
C	4.365022	-1.530304	-2.035760
S	2.651062	-1.228262	-2.295915
C	6.142006	-1.068039	-0.444034
C	7.012596	-1.759145	-1.279312
C	6.568527	-2.332656	-2.475490
C	5.239285	-2.221744	-2.868278
C	2.684931	2.935528	-0.215117
C	2.887589	4.301756	-0.395793
C	2.188358	5.221786	0.380605
C	1.277527	4.769367	1.332549
C	1.074962	3.403937	1.510662
C	-2.135330	1.070111	-1.305039
C	-2.921956	2.356957	-1.090001
C	-2.798176	-0.141270	-0.669072
C	-4.168472	-0.364122	-1.068733
C	-5.086463	-1.261410	-0.277544
O	-4.658524	0.231955	-2.036973
C	-2.018620	-1.106243	-0.046643
C	-3.499110	2.650737	0.147160
C	-4.146769	3.864883	0.361685
C	-4.222003	4.808883	-0.660907
C	-3.646134	4.526553	-1.897733
C	-3.000377	3.310071	-2.106481
O	-2.524143	-2.354627	0.245778
C	-1.460271	-3.113145	0.650775
C	-0.313915	-2.308423	0.614264
N	-0.704150	-1.031831	0.242176
C	-1.466698	-4.439073	1.021636
C	-0.224177	-4.996193	1.352531
C	0.939937	-4.229704	1.298070
C	0.917291	-2.879424	0.931455
C	-5.048500	-1.315645	1.117679
C	-5.976128	-2.080628	1.818075
C	-6.944973	-2.807949	1.127697
C	-6.992415	-2.753585	-0.264519
C	-6.076060	-1.970954	-0.960568
H	-0.769428	1.605505	0.270630
H	-0.303040	2.212921	-1.317675
H	0.602784	0.812158	1.452996
H	2.303815	-0.683681	2.101279
H	1.281581	-0.158391	4.287633
H	0.605995	1.318730	3.590073
H	1.589830	1.409673	5.050140
H	2.955913	2.115782	3.087420
H	3.951840	0.923946	5.077106
H	4.913899	0.712541	3.615821

H	3.859516	-0.600209	4.183025
H	4.661248	-0.382017	1.709552
H	4.429318	1.257501	1.059176
H	6.495910	-0.616048	0.475812
H	8.055452	-1.849394	-0.995254
H	7.268820	-2.867147	-3.108112
H	4.890917	-2.659224	-3.797932
H	3.223324	2.235771	-0.850216
H	3.587776	4.645368	-1.150540
H	2.343065	6.286226	0.235995
H	0.713357	5.478348	1.929983
H	0.345145	3.061195	2.239990
H	-2.067429	0.905667	-2.389380
H	-3.448730	1.908176	0.940872
H	-4.596034	4.073061	1.328670
H	-4.728658	5.755125	-0.496529
H	-3.704749	5.252460	-2.703751
H	-2.555377	3.091127	-3.074914
H	-2.383952	-5.016961	1.039301
H	-0.169588	-6.039802	1.643826
H	1.891698	-4.690661	1.543439
H	1.841099	-2.313456	0.883962
H	-4.288315	-0.750957	1.651010
H	-5.945287	-2.109509	2.903261
H	-7.665044	-3.409849	1.674261
H	-7.749154	-3.314035	-0.805493
H	-6.114708	-1.898352	-2.043276

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2448.12448628 Predicted Change= -9.033427D-09

Zero-point correction (ZPE)=	-2447.4128	0.71158
Internal Energy (U)=	-2447.3724	0.75204
Enthalpy (H)=	-2447.3715	0.75298
Gibbs Free Energy (G)=	-2447.4892	0.63522

Frequencies -- -138.4921 4.8783 17.7797

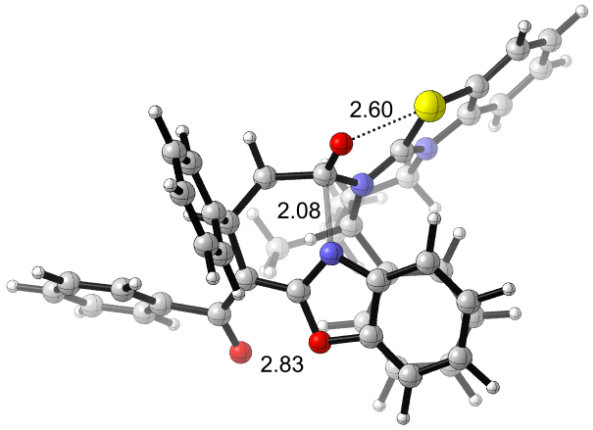
==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.22560001

==========



Oxazole-*N*-*re*-cyclization-TS

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011
==========
#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.12651398 Predicted Change= -6.734049D-09
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00174	0.00180	[YES]	0.00174	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-3.347510	0.666871	-1.100170
C	-2.457810	-0.339839	-1.112200
N	-1.192300	-0.162750	-0.748040
C	-0.167980	-1.158510	-1.167890
C	1.064480	-0.506921	-1.800630
O	-0.591531	-2.246910	-1.514180
C	-0.821579	1.120150	-0.118110
C	-1.152249	1.182770	1.365000
C	-1.474739	2.248060	-0.944060
C	-1.021838	3.659190	-0.533570
C	0.483612	3.833080	-0.764340
C	-1.789778	4.732141	-1.312080
C	-2.986819	2.074141	-0.867860
C	-4.653420	0.281512	-1.430630
C	-4.732780	-1.074808	-1.741080
S	-3.164221	-1.861749	-1.598040
C	-5.776119	1.104042	-1.472600

C	-6.984550	0.523953	-1.841660
C	-7.068840	-0.835167	-2.161350
C	-5.942031	-1.649748	-2.117550
C	-2.297350	0.610011	1.929010
C	-2.575730	0.771511	3.283190
C	-1.715539	1.508821	4.092910
C	-0.559489	2.056830	3.545930
C	-0.274879	1.888900	2.192790
C	2.452960	-0.615691	-1.108550
C	3.004319	-2.044992	-1.192700
C	2.477540	0.012119	0.270220
C	1.554310	-0.568341	1.155670
C	3.220461	1.176368	0.631220
C	4.361051	1.623738	-0.254180
O	2.978371	1.881618	1.630830
C	3.433209	-2.757812	-0.071260
C	3.966428	-4.040342	-0.195370
C	4.090948	-4.633542	-1.447900
C	3.685818	-3.926892	-2.578650
C	3.151479	-2.648852	-2.447630
O	1.575010	-0.411911	2.515080
C	0.542590	-1.183890	2.985080
C	-0.066621	-1.808900	1.890980
N	0.603149	-1.401390	0.753260
C	0.116999	-1.344600	4.287370
C	-0.983121	-2.187940	4.474010
C	-1.608181	-2.821080	3.393310
C	-1.161671	-2.646910	2.082520
C	5.276940	0.725737	-0.810800
C	6.351421	1.191707	-1.565060
C	6.514771	2.559317	-1.777390
C	5.610322	3.461647	-1.217350
C	4.548771	2.994728	-0.449050
H	1.116120	-0.988211	-2.781050
H	0.866250	0.552179	-1.989170
H	0.261521	1.197070	-0.208620
H	-1.168679	2.089930	-1.989430
H	0.731322	3.656859	-1.818610
H	1.095741	3.159469	-0.155550
H	0.784602	4.855649	-0.517510
H	-1.233498	3.790010	0.535690
H	-2.857158	4.738711	-1.071530
H	-1.681098	4.579941	-2.392840
H	-1.395077	5.723660	-1.072740
H	-3.486959	2.656381	-1.644420
H	-3.375199	2.375891	0.112700
H	-5.716189	2.157192	-1.221030
H	-7.876109	1.140353	-1.878840
H	-8.024311	-1.262267	-2.446100
H	-6.002531	-2.704268	-2.364720
H	-2.972900	0.004521	1.330990
H	-3.461710	0.307861	3.705660
H	-1.932559	1.631481	5.149800
H	0.139551	2.600300	4.174330
H	0.671111	2.256879	1.799520

H	3.094280	-0.009442	-1.756670
H	3.359259	-2.302542	0.911260
H	4.285918	-4.574852	0.694560
H	4.507218	-5.631642	-1.544880
H	3.791698	-4.368312	-3.565350
H	2.857609	-2.106591	-3.343700
H	0.603560	-0.836000	5.112300
H	-1.359431	-2.351470	5.478800
H	-2.459802	-3.467879	3.582020
H	-1.639961	-3.138779	1.241500
H	5.153030	-0.341563	-0.638330
H	7.063330	0.486687	-1.983750
H	7.348821	2.921267	-2.371280
H	5.739232	4.528497	-1.374870
H	3.850482	3.685328	0.015180

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2448.12651398 Predicted Change= -6.734049D-09
Zero-point correction (ZPE)= -2447.4135 0.71291
Internal Energy (U)= -2447.3737 0.75273
Enthalpy (H)= -2447.3728 0.75367
Gibbs Free Energy (G)= -2447.4856 0.64088

Frequencies -- -111.3969 17.1657 23.9791

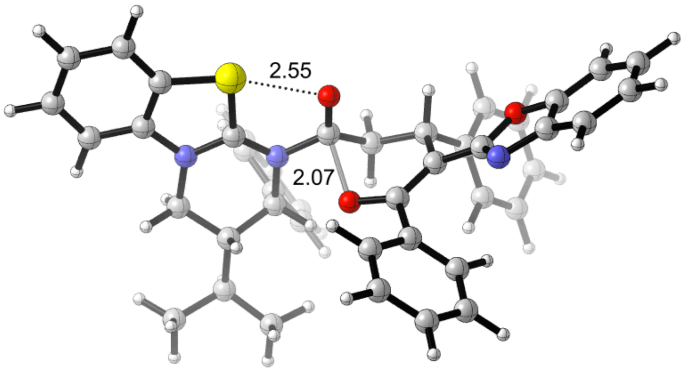
==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.22673263

==========



Oxazole-*O*-*si*-cyclization-TS

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

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#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current

SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)
iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.13243384 Predicted Change= -5.035723D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00126	0.00180	[YES]	0.00126	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	4.052756	-0.838226	-0.399409
C	2.798714	-0.797481	-0.877352
N	1.884654	0.043053	-0.396124
C	0.523573	0.008070	-0.922693
C	-0.299090	1.261840	-0.778163
H	-0.123983	1.767026	0.170791
H	0.003145	1.953843	-1.576131
O	0.280659	-0.829213	-1.774089
C	2.209732	0.925558	0.744575
H	1.283656	0.975699	1.316677
C	2.611495	2.308335	0.264978
C	3.250943	0.226012	1.641077
H	2.785571	-0.715571	1.967387
C	3.612743	1.041401	2.895338
C	2.404643	1.173475	3.827026
H	2.673714	1.758536	4.710990
H	2.073979	0.184128	4.163481
H	1.550259	1.665209	3.354814
H	3.925371	2.043383	2.573104
C	4.774896	0.402261	3.663362
H	5.714700	0.432866	3.104067
H	4.551295	-0.643398	3.907139
H	4.938191	0.936405	4.603676
C	4.475956	-0.125680	0.810568
H	5.130055	-0.806722	1.357550
H	5.049012	0.765203	0.526162
C	4.908718	-1.699686	-1.099276
C	4.245138	-2.365580	-2.126719
S	2.548294	-1.906212	-2.203284
C	6.263526	-1.906422	-0.852798
H	6.783893	-1.374702	-0.064040
C	6.932406	-2.814793	-1.664947
H	7.988583	-2.995024	-1.496807
C	6.268984	-3.494703	-2.692487
H	6.815516	-4.198490	-3.310753
C	4.917054	-3.277238	-2.934967
H	4.399360	-3.799801	-3.732392
C	2.168873	3.431549	0.968912

H	1.511809	3.305750	1.826234
C	2.549118	4.711577	0.576094
H	2.194246	5.572952	1.133043
C	3.371361	4.885111	-0.534609
H	3.665008	5.882619	-0.845466
C	3.803778	3.773196	-1.252750
H	4.433083	3.899622	-2.128139
C	3.423982	2.492734	-0.857039
H	3.753217	1.639069	-1.445103
C	-1.796528	0.940829	-0.939537
H	-1.951319	0.660804	-1.989288
C	-2.549034	2.246609	-0.702194
C	-2.279853	-0.198055	-0.051278
C	-3.601844	-0.678101	-0.343963
C	-1.445232	-0.824121	0.873718
C	-1.957741	-1.718474	1.966133
O	-0.172952	-0.658949	0.904838
C	-2.869319	3.082829	-1.773116
H	-2.627161	2.765613	-2.785470
C	-3.503007	4.305229	-1.560461
H	-3.752065	4.938722	-2.406929
C	-3.822874	4.710621	-0.266330
H	-4.320022	5.661155	-0.098039
C	-3.503519	3.884297	0.809866
H	-3.751675	4.189871	1.822356
C	-2.871021	2.663003	0.591376
H	-2.632041	2.011207	1.428983
O	-4.311794	0.097152	-1.248816
C	-5.494703	-0.553464	-1.427596
C	-5.460441	-1.701111	-0.628000
N	-4.244642	-1.755676	0.033577
C	-6.560676	-0.200562	-2.233809
H	-6.546603	0.699129	-2.839034
C	-7.652784	-1.071467	-2.217495
H	-8.520825	-0.844627	-2.828119
C	-7.647512	-2.229040	-1.426651
H	-8.515749	-2.880812	-1.441204
C	-6.558310	-2.563014	-0.622989
H	-6.556415	-3.460121	-0.012521
C	-3.064643	-1.368089	2.743069
H	-3.627524	-0.473695	2.490999
C	-3.443693	-2.155457	3.824572
H	-4.301726	-1.870691	4.426232
C	-2.723662	-3.308939	4.136924
H	-3.023103	-3.926341	4.978696
C	-1.613922	-3.660517	3.371338
H	-1.046666	-4.554444	3.613500
C	-1.224622	-2.858338	2.301625
H	-0.345779	-3.106160	1.714306

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2448.13243384 Predicted Change= -5.035723D-09
Zero-point correction (ZPE)= -2447.4195 0.71289

Internal Energy (U)= -2447.3792 0.75322
Enthalpy (H)= -2447.3782 0.75416
Gibbs Free Energy (G)= -2447.4954 0.63699

Frequencies -- -107.7350 11.6842 19.6170

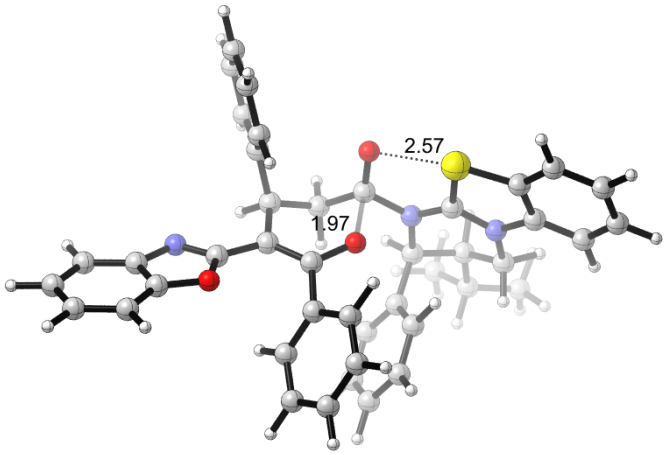
==========

#M062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.23239713

==========



Oxazole-*O*-*re*-cyclization-TS

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

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#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)
iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.13205596 Predicted Change= -6.026860D-10

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00119	0.00180	[YES]	0.00119	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-3.971463	0.363666	-0.290541
C	-2.802136	1.019910	-0.196139
N	-1.941961	0.816634	0.794783
C	-0.625654	1.506326	0.707051
C	0.372011	1.148724	1.783433
O	-0.636363	2.579997	0.129267
C	-2.228860	-0.219133	1.810083
C	-1.639909	-1.574915	1.456203
C	-3.753920	-0.247741	2.061507
C	-4.170927	-1.230614	3.171827
C	-3.613161	-0.793989	4.529234
C	-5.696036	-1.348714	3.266619
C	-4.476751	-0.531775	0.752197
C	-4.696440	0.639305	-1.457147
C	-4.048219	1.577876	-2.256835
S	-2.543624	2.123060	-1.526136
C	-5.910361	0.072837	-1.837151
C	-6.463314	0.487518	-3.043912
C	-5.822303	1.436736	-3.846732
C	-4.606981	1.992431	-3.461189
C	-1.031812	-2.328781	2.462811
C	-0.535755	-3.603717	2.197948
C	-0.634786	-4.133961	0.915318
C	-1.221144	-3.381174	-0.099956
C	-1.717418	-2.109564	0.166283
C	1.836035	1.286192	1.319382
C	2.219116	2.713676	0.939055
C	2.184069	0.234516	0.289221
C	3.582243	-0.068699	0.201020
C	1.198336	-0.310752	-0.519855
C	1.376113	-1.574072	-1.310524
O	0.006644	0.169744	-0.592510
C	2.326652	3.682268	1.940507
C	2.679833	4.993937	1.635606
C	2.939507	5.356335	0.315267
C	2.843930	4.395968	-0.689469
C	2.487021	3.086192	-0.377968
O	4.077280	-0.678610	-0.931849
C	5.422392	-0.770453	-0.726987
C	5.695488	-0.185165	0.513934
N	4.504128	0.250831	1.075733
C	6.384654	-1.323718	-1.551084
C	7.697533	-1.267375	-1.077452
C	8.001399	-0.684963	0.160875
C	7.011323	-0.136865	0.974646
C	0.726413	-1.696232	-2.541155
C	0.766887	-2.895155	-3.247364
C	1.436940	-3.995743	-2.714442
C	2.068459	-3.887679	-1.475953
C	2.038255	-2.683648	-0.779648
H	0.188717	1.822859	2.629729

H	0.239989	0.119631	2.122180
H	-1.763504	0.140192	2.729897
H	-4.036768	0.765207	2.382733
H	-2.521125	-0.751936	4.549652
H	-3.927563	-1.494747	5.307902
H	-3.993314	0.199168	4.796065
H	-3.764734	-2.219682	2.922855
H	-5.968609	-1.963404	4.129081
H	-6.135711	-1.816590	2.381059
H	-6.155939	-0.361984	3.400096
H	-5.544318	-0.326197	0.850985
H	-4.343893	-1.572350	0.431006
H	-6.404422	-0.672663	-1.223850
H	-7.407361	0.061822	-3.366585
H	-6.275365	1.742831	-4.783518
H	-4.104357	2.726427	-4.082157
H	-0.935254	-1.914459	3.463995
H	-0.061790	-4.171939	2.992178
H	-0.233197	-5.119087	0.698208
H	-1.256830	-3.769088	-1.113724
H	-2.116709	-1.515937	-0.651267
H	2.429962	1.052028	2.212347
H	2.138541	3.402627	2.975916
H	2.761921	5.731188	2.429257
H	3.219690	6.377211	0.073035
H	3.048635	4.666933	-1.721413
H	2.408479	2.337953	-1.161894
H	6.131936	-1.771547	-2.505806
H	8.496992	-1.683108	-1.682329
H	9.034810	-0.661730	0.492931
H	7.247451	0.312490	1.933751
H	0.181983	-0.841276	-2.930863
H	0.270342	-2.974578	-4.210195
H	1.461457	-4.935072	-3.259123
H	2.575108	-4.746945	-1.046114
H	2.504983	-2.607083	0.198685

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2448.13205596 Predicted Change= -6.026860D-10
Zero-point correction (ZPE)= -2447.4207 0.71131
Internal Energy (U)= -2447.3804 0.75156
Enthalpy (H)= -2447.3795 0.75250
Gibbs Free Energy (G)= -2447.4961 0.63595

Frequencies -- -133.8467 11.0549 16.1845

==========

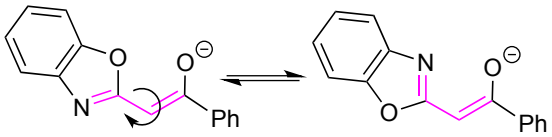
#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C43H37N3O3S C1[X(C43H37N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2448.23128315

==========

Anionic nucleophile dihedral rotation geometries and energies



Anionic Benzoxazole

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

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#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,modredundant,gdiis) iop(1/8=18)
Modredundant Input: D 13 8 9 10 S 18 10.000

Pointgroup= C1 Stoichiometry= C15H10NO2(1-) C1[X(C15H10NO2)] #Atoms= 28
Charge = -1 Multiplicity = 1

Optimization completed. {Found 19 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00125	0.00180	[YES]	0.00125	0.00180	[YES]

Dihedral = 0

SCF = -782.6216
XYZ =
28
000-oxazole-Ph.com

C	5.38346300	-0.48949700	-0.06830700
C	4.31539700	-1.37683100	-0.21348000
C	3.01985300	-0.86114200	-0.13640900
C	2.84760600	0.51448700	0.08161600
C	3.88736900	1.41048000	0.22884900
C	5.18013200	0.87787500	0.14941500
N	1.78264200	-1.46189900	-0.23824000
C	0.91005000	-0.47577700	-0.08622600
C	-0.49185000	-0.58288800	-0.10499100
C	-1.40001900	0.48647600	0.03602200
C	-2.87817200	0.12770400	0.02450500
O	-1.11515600	1.69815900	0.14333900
O	1.50637300	0.75859600	0.11222400
C	-3.37845200	-1.13339700	0.36457300
C	-4.74882000	-1.38425700	0.34683200
C	-5.64190200	-0.37757300	-0.01480600
C	-5.15477400	0.88614700	-0.34630100
C	-3.78611700	1.13438500	-0.31690700
H	6.39932700	-0.86995800	-0.12569100
H	4.47989900	-2.43656200	-0.38217400
H	3.70785400	2.46720300	0.39625000
H	6.03481500	1.53825300	0.25723000
H	-0.85535000	-1.58777500	-0.27184400
H	-2.69650200	-1.92106000	0.67054800
H	-5.12004800	-2.36703700	0.62354700
H	-6.70989400	-0.57469900	-0.03108100

H	-5.84410400	1.67855700	-0.62476400
H	-3.38681600	2.11517700	-0.55515000

Dihedral = 10
SCF = -782.62138
XYZ =
28
010-oxazole-Ph.com

C	5.38210300	-0.48161200	-0.12051800
C	4.31336100	-1.36138000	-0.30215800
C	3.01817400	-0.85498800	-0.17293800
C	2.84768400	0.50447300	0.13071000
C	3.88803600	1.39322800	0.31332400
C	5.18023600	0.86982000	0.18174300
N	1.77990300	-1.45065100	-0.29413700
C	0.90876700	-0.47749000	-0.06955200
C	-0.49307300	-0.58842400	-0.04113900
C	-1.39964600	0.49062500	0.02026100
C	-2.87782500	0.13227300	0.02063800
O	-1.11343400	1.70631400	0.05130200
O	1.50711200	0.74195100	0.20102200
C	-3.37810900	-1.10973700	0.42543400
C	-4.74768400	-1.36448400	0.41210700
C	-5.64012400	-0.38034000	-0.00875700
C	-5.15316000	0.86515600	-0.40360600
C	-3.78510500	1.11763400	-0.37946000
H	6.39744200	-0.85545600	-0.21693200
H	4.47723300	-2.40844600	-0.53746000
H	3.70906000	2.43761500	0.54601300
H	6.03539200	1.52461200	0.31661300
H	-0.85872900	-1.59359200	-0.20224800
H	-2.69577700	-1.87741500	0.77765900
H	-5.11894200	-2.33181200	0.73861700
H	-6.70761400	-0.58043700	-0.02175800
H	-5.84236400	1.63977000	-0.72857000
H	-3.38625400	2.08506200	-0.66810600

Dihedral = 20
SCF = -782.6205
XYZ =
28
020-oxazole-Ph.com

C	5.37705900	-0.48392600	-0.19442000
C	4.30045800	-1.34943500	-0.39650600
C	3.01119100	-0.84686100	-0.20794700
C	2.85407600	0.49444700	0.17294000
C	3.90227400	1.36995200	0.37449300
C	5.18826400	0.85022900	0.18377700
N	1.76689400	-1.43118600	-0.33092500
C	0.90642200	-0.47030800	-0.03058300
C	-0.49435300	-0.58364100	0.05953100
C	-1.40103100	0.49745800	0.04011800
C	-2.87849000	0.13766600	0.02881100
O	-1.11572200	1.71348200	0.01145700
O	1.51732600	0.72958000	0.29496100

C	-3.38664300	-1.08028400	0.49291100
C	-4.75489500	-1.33973200	0.45979500
C	-5.63779300	-0.38430400	-0.04068900
C	-5.14312000	0.83789000	-0.49456300
C	-3.77660300	1.09597000	-0.45011400
H	6.38819600	-0.85539100	-0.33423600
H	4.45379300	-2.38299900	-0.69119500
H	3.73376200	2.40108000	0.66661600
H	6.04940900	1.49395700	0.33324500
H	-0.86140500	-1.58958000	-0.09568900
H	-2.71077600	-1.82372000	0.90455400
H	-5.13311300	-2.28787500	0.83145300
H	-6.70423200	-0.58831300	-0.06979400
H	-5.82570100	1.58965900	-0.88110800
H	-3.37192500	2.04626100	-0.78404500

Dihedral = 30
SCF = -782.619
XYZ =
28
030-oxazole-Ph.com

C	5.37129000	-0.47270500	-0.25744900
C	4.28912800	-1.32099100	-0.49789800
C	3.00580500	-0.83226300	-0.24564100
C	2.85818700	0.47833300	0.23263200
C	3.91239800	1.33702400	0.47369100
C	5.19237900	0.83120700	0.21935100
N	1.75686900	-1.40436600	-0.38937100
C	0.90471400	-0.46707100	-0.00901700
C	-0.49566500	-0.58421600	0.11844400
C	-1.39986700	0.49485100	0.01738800
C	-2.87789100	0.13888900	0.01876800
O	-1.11028300	1.70604600	-0.08963700
O	1.52516500	0.70365300	0.39783300
C	-3.39142300	-1.04496800	0.55856200
C	-4.76045300	-1.30177200	0.53712100
C	-5.63842500	-0.37763600	-0.02694500
C	-5.13805200	0.81067500	-0.55786600
C	-3.77076800	1.06654000	-0.52552300
H	6.37877900	-0.83262100	-0.44556100
H	4.43328600	-2.33001600	-0.87135600
H	3.75312000	2.34458200	0.84279200
H	6.05799400	1.46149700	0.39759800
H	-0.86221700	-1.59246400	-0.02670200
H	-2.71845800	-1.76187900	1.01935400
H	-5.14356300	-2.22326900	0.96645700
H	-6.70552800	-0.57940400	-0.04581500
H	-5.81704200	1.53880600	-0.99301300
H	-3.36165500	1.99236700	-0.91745500

Dihedral = 40
SCF = -782.616915
XYZ =
28
040-oxazole-Ph.com

C	5.35703800	-0.47077200	-0.33597800
C	4.26306400	-1.29581400	-0.60128700
C	2.99089200	-0.81710800	-0.28332900
C	2.86471500	0.46036500	0.28203900
C	3.93127300	1.29669500	0.54870200
C	5.19972000	0.80094900	0.22862400
N	1.73290600	-1.37116800	-0.43175400
C	0.89880600	-0.45730600	0.02996500
C	-0.49893400	-0.57413500	0.21222300
C	-1.39729600	0.49908200	0.02903900
C	-2.87547400	0.14680300	0.02482600
O	-1.09894200	1.70084200	-0.14630400
O	1.53922900	0.67931300	0.49980500
C	-3.40095300	-0.99722800	0.63402600
C	-4.76896600	-1.25748300	0.59812200
C	-5.63329700	-0.37730800	-0.05073400
C	-5.12083200	0.77162200	-0.65180800
C	-3.75478800	1.03215700	-0.60414500
H	6.35670900	-0.82259800	-0.57398400
H	4.39052600	-2.27973300	-1.04173700
H	3.78892700	2.27951700	0.98519000
H	6.07452800	1.41307100	0.42437400
H	-0.86836500	-1.58402300	0.08137400
H	-2.73790400	-1.67804400	1.15981000
H	-5.16218500	-2.14716300	1.08204500
H	-6.69952500	-0.58231200	-0.08136800
H	-5.78906000	1.46576400	-1.15415900
H	-3.33610500	1.92933300	-1.04898000

Dihedral = 50

SCF = -782.61415

XYZ =

28

050-oxazole-Ph.com

C	5.34781000	-0.47943600	-0.39924400
C	4.23627900	-1.27024500	-0.69259800
C	2.97915200	-0.79457400	-0.31646600
C	2.88336500	0.44374800	0.33356700
C	3.96842100	1.24722100	0.62885300
C	5.22131200	0.75524000	0.24986000
N	1.70840600	-1.31858000	-0.47657500
C	0.89783400	-0.42742800	0.05825900
C	-0.49986400	-0.54297700	0.27949400
C	-1.40268400	0.50781200	0.01054800
C	-2.87962500	0.14978000	0.01791700
O	-1.10874400	1.69722100	-0.24307400
O	1.56720100	0.66369700	0.59603700
C	-3.40398000	-0.96468700	0.68060800
C	-4.77105500	-1.23079400	0.65254200
C	-5.63597800	-0.38615000	-0.04131200
C	-5.12467400	0.73344900	-0.69624800
C	-3.75942800	0.99987700	-0.65723200
H	6.33670200	-0.82842400	-0.68182500
H	4.33908700	-2.22571600	-1.19745400
H	3.85017100	2.20274300	1.12841600

H	6.10939100	1.34129600	0.46452200
H	-0.86368700	-1.55842900	0.17121800
H	-2.74100000	-1.61599100	1.24260000
H	-5.16316700	-2.09679300	1.17864900
H	-6.70152100	-0.59560500	-0.06512200
H	-5.79267500	1.39977400	-1.23528200
H	-3.34111100	1.87484600	-1.14469000

Dihedral = 60
SCF = -782.6108
XYZ =
28
060-oxazole-Ph.com

C	5.33398600	-0.48715400	-0.46445100
C	4.20289300	-1.23808300	-0.78426100
C	2.96330500	-0.76630400	-0.35016000
C	2.90046100	0.42790900	0.37982000
C	4.00656600	1.19324400	0.70183600
C	5.24147200	0.70578800	0.26468900
N	1.67937700	-1.25934200	-0.51606000
C	0.89559400	-0.39686700	0.09247300
C	-0.50075600	-0.51405800	0.35823400
C	-1.40462400	0.50647100	0.00016400
C	-2.88190300	0.15019700	0.01457000
O	-1.10613600	1.67701100	-0.32969900
O	1.59487900	0.64661600	0.68809800
C	-3.41189800	-0.93509200	0.71991300
C	-4.77892900	-1.20150900	0.69327200
C	-5.63870000	-0.38594100	-0.04090600
C	-5.12194000	0.70491100	-0.73849400
C	-3.75654900	0.97130300	-0.70196600
H	6.31062200	-0.83307400	-0.78978600
H	4.27596600	-2.16001400	-1.35270300
H	3.91763400	2.11562100	1.26555800
H	6.14398400	1.26229200	0.49699600
H	-0.85555300	-1.53678500	0.28772900
H	-2.75372000	-1.56295600	1.31325800
H	-5.17530200	-2.04464300	1.25236000
H	-6.70426700	-0.59551900	-0.06305700
H	-5.78526900	1.34868500	-1.30970600
H	-3.33354600	1.82386700	-1.22380300

Dihedral = 70
SCF = -782.6071
XYZ =
28
070-oxazole-Ph.com

C	5.32750100	-0.44251300	-0.52024900
C	4.18636500	-1.13663900	-0.91954900
C	2.95685900	-0.71094200	-0.41543200
C	2.91154600	0.38302100	0.45708300
C	4.02953900	1.09094200	0.86279600
C	5.25363400	0.64986600	0.35538400
N	1.66393800	-1.16824700	-0.62649700
C	0.89602800	-0.38341300	0.08893400

C	-0.50688400	-0.50801800	0.35870500
C	-1.40409300	0.48987400	-0.06030600
C	-2.88382000	0.14751200	-0.00665400
O	-1.09822700	1.63515900	-0.47213900
O	1.61204800	0.57232000	0.80277100
C	-3.40943100	-0.88865200	0.77228500
C	-4.77811200	-1.14648300	0.78479400
C	-5.64539200	-0.36947800	0.01811400
C	-5.13322200	0.67240300	-0.75379100
C	-3.76522700	0.92937000	-0.75773600
H	6.29770700	-0.75372200	-0.89578600
H	4.24420100	-1.98071100	-1.59956600
H	3.95586900	1.93588000	1.53877200
H	6.16436200	1.16454800	0.64522000
H	-0.85714900	-1.53482400	0.33442400
H	-2.74438000	-1.48343600	1.39148400
H	-5.16998500	-1.95056000	1.40160100
H	-6.71274600	-0.57085600	0.02799100
H	-5.80215800	1.28640600	-1.35067200
H	-3.34558600	1.74408300	-1.33931100

Dihedral = 80
SCF = -782.60355
XYZ =
28
080-oxazole-Ph.com

C	5.30826200	-0.35600600	-0.62413100
C	4.15250800	-0.96710700	-1.10537100
C	2.94090700	-0.62787800	-0.50243700
C	2.92575000	0.29817500	0.54591300
C	4.06052200	0.92247700	1.03734200
C	5.26520800	0.57108100	0.42796800
N	1.63630400	-1.03436500	-0.75553100
C	0.89507800	-0.38268100	0.10010700
C	-0.51444700	-0.52357900	0.37560500
C	-1.39920700	0.47166100	-0.05786600
C	-2.88260000	0.14696700	-0.00521100
O	-1.07751700	1.61114300	-0.48305500
O	1.63740300	0.43135800	0.95020300
C	-3.42305800	-0.86926200	0.78973800
C	-4.79404800	-1.11450300	0.79831600
C	-5.64932300	-0.34458100	0.01105200
C	-5.12257700	0.67810400	-0.77657000
C	-3.75222400	0.92288900	-0.77594700
H	6.26623900	-0.59951800	-1.07366300
H	4.18586300	-1.68106700	-1.92226400
H	4.01074000	1.63930100	1.84969200
H	6.18795600	1.02458700	0.77631200
H	-0.86283000	-1.55147900	0.37813200
H	-2.76653300	-1.45729700	1.42444000
H	-5.19751000	-1.90239000	1.42846400
H	-6.71856100	-0.53597600	0.01770900
H	-5.78210900	1.28680000	-1.38923600
H	-3.32096900	1.72306200	-1.36909600

Dihedral = 90
SCF = -782.6008
XYZ =
28
090-oxazole-Ph.com

C	5.28997100	0.52605900	-0.53495400
C	4.11670000	0.80339900	-1.23087000
C	2.92461300	0.28972200	-0.71894700
C	2.94211500	-0.47162500	0.45341900
C	4.09745700	-0.75742900	1.16522400
C	5.28136100	-0.24059100	0.64150800
N	1.60969100	0.39069200	-1.16203200
C	0.89679400	-0.27290900	-0.29831000
C	-0.52303300	-0.57480700	-0.31151400
C	-1.39468600	0.27130900	0.36779200
C	-2.88214300	0.07024000	0.12840000
O	-1.06126200	1.19296700	1.16337400
O	1.66489000	-0.84616600	0.71242700
C	-3.43652800	-1.11895900	-0.35753200
C	-4.80981500	-1.23748900	-0.55795900
C	-5.65544000	-0.16608700	-0.27299500
C	-5.11558300	1.01962400	0.22312100
C	-3.74299800	1.12982600	0.42734500
H	6.23459100	0.91090800	-0.90682800
H	4.12029600	1.39889800	-2.13814500
H	4.07775100	-1.35044100	2.07285400
H	6.21757700	-0.43591900	1.15508400
H	-0.87133900	-1.15465600	-1.15911300
H	-2.78845400	-1.96691200	-0.56003800
H	-5.22208500	-2.17127700	-0.93049500
H	-6.72653500	-0.25818700	-0.42907000
H	-5.76726200	1.85797200	0.45470400
H	-3.30411700	2.03866500	0.82649400

Dihedral = 100
SCF = -782.602
XYZ =
28
100-oxazole-Ph.com

C	5.29724300	0.51106600	0.10803100
C	4.21435100	1.19461500	-0.44030200
C	2.97015000	0.56463300	-0.41527700
C	2.85193400	-0.71123400	0.14605100
C	3.91487700	-1.41313100	0.69076400
C	5.15168200	-0.76881900	0.66445900
N	1.72487800	0.96084700	-0.88950600
C	0.91368200	-0.01941400	-0.60634800
C	-0.51440600	-0.12850800	-0.77253700
C	-1.38631000	0.57030000	0.06795200
C	-2.85070100	0.14670500	0.03849600
O	-1.10101400	1.53927800	0.81739900
O	1.54938900	-1.07878900	0.04814400
C	-3.29465200	-1.13694900	-0.29617500
C	-4.65220700	-1.45144700	-0.28204200
C	-5.59350600	-0.48495200	0.06570900

C	-5.16319200	0.79543700	0.41147400
C	-3.80534100	1.09992600	0.40624400
H	6.27805500	0.97693900	0.10574600
H	4.32679300	2.18356000	-0.87290800
H	3.78754600	-2.40154700	1.11857700
H	6.01879300	-1.26781400	1.08587100
H	-0.85442600	-1.05367300	-1.22511700
H	-2.57505300	-1.91058100	-0.54679100
H	-4.97415300	-2.45747300	-0.53684800
H	-6.65183600	-0.72955200	0.07489400
H	-5.88844400	1.55555800	0.68977700
H	-3.45005200	2.08539300	0.69000400

Dihedral = 110
SCF = -782.60535
XYZ =
28
110-oxazole-Ph.com

C	5.27607300	0.52639500	0.21415900
C	4.18566000	1.23749400	-0.28457500
C	2.95358900	0.58564100	-0.33854200
C	2.85713600	-0.74074100	0.09893100
C	3.92615900	-1.46939600	0.59049700
C	5.15125900	-0.80162700	0.64537300
N	1.70961000	1.00075800	-0.79435200
C	0.91502700	-0.02206800	-0.61857800
C	-0.50064800	-0.14474700	-0.79784600
C	-1.39568600	0.62525000	-0.03809900
C	-2.84780100	0.15745800	0.00526300
O	-1.13304300	1.68063700	0.58618400
O	1.56323400	-1.12475600	-0.05210900
C	-3.27257800	-1.14874500	-0.26124000
C	-4.62001600	-1.49416900	-0.17900100
C	-5.57116800	-0.53795000	0.17018400
C	-5.16036300	0.76509400	0.44682000
C	-3.81241400	1.10158000	0.37116700
H	6.24645900	1.01049900	0.27114500
H	4.28368700	2.26474900	-0.62094900
H	3.81357600	-2.49652400	0.92035100
H	6.02248600	-1.32183500	1.03121000
H	-0.82113000	-1.12851600	-1.12185500
H	-2.54872100	-1.91742000	-0.51292800
H	-4.92603900	-2.51669400	-0.38248200
H	-6.62159300	-0.80753400	0.23244200
H	-5.89258100	1.51849500	0.72499100
H	-3.47032100	2.10561600	0.59885900

Dihedral = 120
SCF = -782.6088
XYZ =
28
120-oxazole-Ph.com

C	5.27891500	0.54257300	0.24785300
C	4.16669300	1.27590200	-0.16579900
C	2.94538400	0.60879000	-0.26367200

C	2.88176500	-0.75510100	0.05000700
C	3.97144700	-1.50488200	0.45410400
C	5.18651500	-0.82161900	0.55321900
N	1.68905900	1.04095500	-0.66112500
C	0.91460800	-0.01171400	-0.56825900
C	-0.49257100	-0.15684600	-0.74173300
C	-1.41631700	0.65276000	-0.05624000
C	-2.85849200	0.15789600	0.00228100
O	-1.18638300	1.75615300	0.48883200
O	1.59204900	-1.14976400	-0.11673800
C	-3.25104100	-1.17511300	-0.15925300
C	-4.59267200	-1.54108800	-0.07106300
C	-5.56901900	-0.57895300	0.17866100
C	-5.19019800	0.75153100	0.35052800
C	-3.84813100	1.10916800	0.27075700
H	6.24088700	1.03890200	0.33528900
H	4.24064400	2.33215700	-0.40451300
H	3.88320900	-2.56094600	0.68554000
H	6.07330200	-1.35964700	0.87349100
H	-0.79906400	-1.15893400	-1.01809400
H	-2.50671700	-1.94600900	-0.33128200
H	-4.87482300	-2.58340800	-0.19124200
H	-6.61481300	-0.86506500	0.24483000
H	-5.94292200	1.50967000	0.54905600
H	-3.52976500	2.13566300	0.41972100

Dihedral = 130
SCF = -782.6122
XYZ =
28
130-oxazole-Ph.com

C	5.27983300	0.58176900	0.24615300
C	4.14041100	1.30684900	-0.10599800
C	2.93339000	0.61553800	-0.21418100
C	2.91182100	-0.76454600	0.03004900
C	4.02743600	-1.50527900	0.37261500
C	5.22843600	-0.79742500	0.48253900
N	1.65945300	1.03655500	-0.55976800
C	0.91287500	-0.04178700	-0.50459100
C	-0.48564800	-0.22123600	-0.66223300
C	-1.42813000	0.64683400	-0.07765000
C	-2.87015600	0.15375500	-0.00135300
O	-1.20688600	1.79493400	0.36632000
O	1.62863500	-1.18468400	-0.13151000
C	-3.26235200	-1.18494600	-0.11024900
C	-4.60462500	-1.54658800	-0.01781300
C	-5.58253200	-0.57480900	0.18470600
C	-5.20449600	0.76146300	0.30398300
C	-3.86184200	1.11566500	0.21774800
H	6.23064000	1.09834000	0.33932000
H	4.18361000	2.37550200	-0.29067000
H	3.96992000	-2.57371600	0.55100100
H	6.13453900	-1.32855600	0.75664500
H	-0.77835000	-1.24184800	-0.87447700
H	-2.51909800	-1.96347300	-0.24749300

H	-4.88633000	-2.59282600	-0.09824200
H	-6.62889000	-0.85792500	0.25450800
H	-5.95832000	1.52710600	0.46561700
H	-3.54440700	2.14797400	0.32134800

Dihedral = 140
SCF = -782.61506
XYZ =
28
140-oxazole-Ph.com

C	5.29648500	0.60457700	0.19502400
C	4.12957600	1.33245400	-0.04417100
C	2.92988700	0.62826600	-0.15195300
C	2.94444100	-0.76800700	-0.02174900
C	4.08636200	-1.51054100	0.20938600
C	5.27997900	-0.78941600	0.32205800
N	1.63433000	1.05139600	-0.39593600
C	0.90833800	-0.04510900	-0.39224200
C	-0.48610500	-0.24824200	-0.51367800
C	-1.44473200	0.64062700	0.01191100
C	-2.88661600	0.15066400	0.03549600
O	-1.24025100	1.79957000	0.43297700
O	1.66212900	-1.20073900	-0.15938900
C	-3.26271500	-1.19609500	0.07348800
C	-4.60744900	-1.56045100	0.09684500
C	-5.60028400	-0.58312100	0.07865600
C	-5.23754100	0.76288800	0.05195800
C	-3.89326900	1.12111000	0.04055300
H	6.24174100	1.13177200	0.28598700
H	4.14662000	2.41312500	-0.14326200
H	4.05462400	-2.59073100	0.30449800
H	6.20682600	-1.32137800	0.51242500
H	-0.77839400	-1.26568300	-0.74053200
H	-2.50272200	-1.97077400	0.10975600
H	-4.87997900	-2.61149000	0.13509100
H	-6.64833300	-0.86825800	0.09223000
H	-6.00472600	1.53248500	0.04194400
H	-3.58913200	2.16286700	0.03521000

Dihedral = 150
SCF = -782.6175
XYZ =
28
150-oxazole-Ph.com

C	5.30168000	0.60853500	0.22014600
C	4.12240900	1.33881900	0.06072600
C	2.92766100	0.63124900	-0.07616200
C	2.95893600	-0.77092700	-0.04873500
C	4.11252000	-1.51501600	0.10214100
C	5.30220700	-0.79066600	0.24136400
N	1.62513500	1.05804100	-0.26302600
C	0.90887800	-0.04503600	-0.33138600
C	-0.47876700	-0.26472200	-0.45679600
C	-1.45903800	0.65821300	-0.03757300
C	-2.89574900	0.15406400	0.01455900

O	-1.27215800	1.85403900	0.27088300
O	1.67811300	-1.20670000	-0.19507000
C	-3.25642800	-1.19345200	0.12094800
C	-4.59651800	-1.57173200	0.16934200
C	-5.60087300	-0.60764700	0.11229300
C	-5.25369300	0.73938700	0.01908600
C	-3.91393600	1.11186300	-0.02125800
H	6.24344300	1.13848500	0.32988700
H	4.12650200	2.42403400	0.04250700
H	4.09391400	-2.59961000	0.11457000
H	6.23873300	-1.32463100	0.36805100
H	-0.75990100	-1.29145300	-0.64997600
H	-2.48836700	-1.95738100	0.19199300
H	-4.85601300	-2.62294900	0.25883700
H	-6.64539100	-0.90368900	0.14735200
H	-6.02972200	1.49898800	-0.02097000
H	-3.62251400	2.15560900	-0.07974600

Dihedral = 160
SCF = -782.61925
XYZ =
28
160-oxazole-Ph.com

C	5.31281300	0.62906500	0.15944300
C	4.11743900	1.34767300	0.08845900
C	2.92685800	0.62919700	-0.02759900
C	2.97896000	-0.77239300	-0.07034700
C	4.14773800	-1.50458500	-0.00467000
C	5.33328600	-0.76918600	0.11492800
N	1.61165200	1.04458200	-0.12744100
C	0.90766100	-0.06648800	-0.21774500
C	-0.47679000	-0.30683200	-0.30621400
C	-1.46635500	0.64490300	0.01575600
C	-2.90709900	0.15275700	0.02955800
O	-1.28220300	1.85436800	0.26508000
O	1.69895800	-1.22081900	-0.18194500
C	-3.28021300	-1.18315600	0.21086000
C	-4.62307600	-1.55439900	0.21604100
C	-5.61747400	-0.59441300	0.03807300
C	-5.25818200	0.74205200	-0.13086100
C	-3.91613000	1.10846200	-0.12609100
H	6.25129900	1.16827600	0.25116400
H	4.10648900	2.43242800	0.12237300
H	4.14395500	-2.58882100	-0.04161300
H	6.28131300	-1.29459600	0.17461800
H	-0.75461000	-1.33594800	-0.48956800
H	-2.51984000	-1.94083000	0.37304800
H	-4.89306800	-2.59593100	0.36654800
H	-6.66411800	-0.88492700	0.03908800
H	-6.02643200	1.49857600	-0.26468700
H	-3.61720800	2.14537100	-0.24149900

Dihedral = 170
SCF = -782.62036
XYZ =

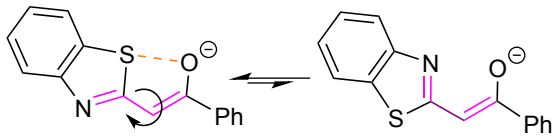
28
170-oxazole-Ph.com

C	5.31605100	0.63607100	0.14824700
C	4.11252600	1.34464400	0.16880700
C	2.92469200	0.62361600	0.04023700
C	2.98806300	-0.77120100	-0.10315200
C	4.16449100	-1.49316300	-0.12762500
C	5.34738900	-0.75500900	0.00348500
N	1.60343600	1.03070900	0.01680800
C	0.90677400	-0.08003100	-0.13159000
C	-0.47488900	-0.33205100	-0.20295100
C	-1.47070400	0.64103300	0.02446000
C	-2.91223800	0.15403500	0.02654000
O	-1.28803200	1.86335100	0.19782700
O	1.70923100	-1.22477700	-0.20690700
C	-3.29306900	-1.16341700	0.30193800
C	-4.63646700	-1.53306500	0.29749000
C	-5.62254100	-0.58995500	0.01501300
C	-5.25533500	0.72900800	-0.24946300
C	-3.91326200	1.09485800	-0.23406000
H	6.25234400	1.17791800	0.24667600
H	4.09368200	2.42408500	0.28041900
H	4.16883600	-2.57206100	-0.24163100
H	6.30122800	-1.27310900	-0.00798200
H	-0.75063100	-1.36268200	-0.38042800
H	-2.53795700	-1.90450300	0.54615100
H	-4.91338300	-2.55917600	0.52265600
H	-6.66964300	-0.87874800	0.00935400
H	-6.01809400	1.47281500	-0.46302400
H	-3.60891100	2.11966600	-0.42145400

Dihedral = 180
SCF = -782.6208
XYZ =
28
180-oxazole-Ph.com

C	5.32140700	0.63677000	0.05740200
C	4.11875900	1.33761500	0.17328200
C	2.92784200	0.61551200	0.08435500
C	2.98797100	-0.77218000	-0.11732000
C	4.16331900	-1.48656900	-0.23482900
C	5.34941100	-0.74750900	-0.14221100
N	1.60608900	1.01501300	0.15696400
C	0.90589200	-0.09313900	0.00382000
C	-0.47632900	-0.35037900	-0.01599800
C	-1.47335400	0.64021600	0.10852600
C	-2.91522100	0.15937500	0.05199800
O	-1.29154900	1.86879400	0.22955100
O	1.70692100	-1.22834000	-0.16869100
C	-3.32081500	-1.13474800	0.39413400
C	-4.66271700	-1.50276400	0.32308300
C	-5.62145300	-0.58191200	-0.09491100
C	-5.22954200	0.71434400	-0.42785800
C	-3.88992700	1.07994000	-0.34413800
H	6.25983600	1.17986200	0.12366300

H	4.10281500	2.41181200	0.32753800
H	4.16445000	-2.56025500	-0.39049400
H	6.30306600	-1.25886400	-0.22819600
H	-0.75482500	-1.38112800	-0.18928500
H	-2.58725000	-1.85565800	0.74267000
H	-4.96081800	-2.50966400	0.60146000
H	-6.66707600	-0.87010000	-0.15346500
H	-5.97089200	1.44000100	-0.75119700
H	-3.56635600	2.08782900	-0.58432600



Anionic Benzothiazole

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,modredundant,gdiis) iop(1/8=18)
Modredundant Input: D 13 8 9 10 S 18 10.000

Pointgroup= C1 Stoichiometry= C15H10NOS(1-) C1[X(C15H10NOS)] #Atoms= 28
Charge = -1 Multiplicity = 1

==========

Optimization completed. {Found 19 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00054 ||	0.00180	[YES]	0.00054 ||	0.00180	[YES]

Dihedral = 0

SCF = -1105.59447
XYZ =
28
000-thiazole-Ph.com

C	-5.33313800	0.95875500	-0.12292900
C	-4.10394000	1.60043600	-0.19804100
C	-2.92234600	0.84815400	-0.10695800
C	-3.01770400	-0.55269400	0.05997300
C	-4.25089900	-1.19398300	0.13460500
C	-5.41257200	-0.43026900	0.04265900
N	-1.65049300	1.36416500	-0.16388100
C	-0.73418700	0.42020500	-0.04639300
C	0.65726500	0.63825600	-0.05504100
C	1.59496200	-0.40204500	0.04984800
C	3.06546100	-0.04623300	0.02231400
O	1.29903900	-1.61957500	0.14436300
S	-1.40930900	-1.23882400	0.14182000
C	3.56075000	1.22413900	0.33482200
C	4.92893200	1.48196200	0.29780800
C	5.82407500	0.47338400	-0.05419400

C	5.34140900	-0.79874500	-0.35826900
C	3.97464600	-1.05447300	-0.31167800
H	-6.24671800	1.54271500	-0.19160200
H	-4.03638000	2.67695700	-0.32480200
H	-4.30741300	-2.27143500	0.26343600
H	-6.38214100	-0.91532300	0.10148600
H	0.96909800	1.66556300	-0.19498800
H	2.87781000	2.01398900	0.63245300
H	5.29740400	2.47191300	0.55135300
H	6.89064700	0.67612600	-0.08465600
H	6.03254900	-1.59209300	-0.62908700
H	3.57894700	-2.04087500	-0.53160700

Dihedral = 10
SCF = -1105.59383
XYZ =
28
010-thiazole-Ph.com

C	-5.32640600	0.96457800	-0.20238800
C	-4.09297300	1.59857000	-0.27377900
C	-2.91705400	0.84632200	-0.12744800
C	-3.02299000	-0.54645100	0.09168800
C	-4.26000700	-1.18106500	0.15790900
C	-5.41586300	-0.41701200	0.01220700
N	-1.64190700	1.35480800	-0.17785700
C	-0.73199900	0.41155400	-0.01408700
C	0.65812000	0.63095400	0.04668600
C	1.59756900	-0.41391800	0.05845800
C	3.06660200	-0.05219700	0.02140900
O	1.30595300	-1.63519900	0.08777700
S	-1.41912400	-1.23542900	0.22506200
C	3.56506000	1.19915300	0.39926100
C	4.93123600	1.46451600	0.34856100
C	5.82126500	0.48278300	-0.08374800
C	5.33566400	-0.77084700	-0.45290900
C	3.97104700	-1.03509000	-0.39151700
H	-6.23574600	1.54860300	-0.31387600
H	-4.01811500	2.66914500	-0.44010500
H	-4.32387600	-2.25309200	0.32304200
H	-6.38861900	-0.89611900	0.06687700
H	0.97039700	1.66060200	-0.07569600
H	2.88619600	1.96638600	0.75872100
H	5.30222000	2.43856300	0.65447600
H	6.88630800	0.69149100	-0.12549500
H	6.02308900	-1.54310400	-0.78678700
H	3.57421600	-2.00875800	-0.66116700

Dihedral = 20
SCF = -1105.5922
XYZ =
28
020-thiazole-Ph.com

C	-5.31130100	0.97967800	-0.28982100

C	-4.07066200	1.60098500	-0.34659100
C	-2.90619300	0.84455900	-0.14286100
C	-3.03095400	-0.53940200	0.11834000
C	-4.27469400	-1.16250600	0.16536600
C	-5.41902000	-0.39381700	-0.03539100
N	-1.62524600	1.34052900	-0.17656300
C	-0.72816600	0.39503700	0.03329800
C	0.65870600	0.61063900	0.16711400
C	1.60077400	-0.43003500	0.07975600
C	3.06726300	-0.05918000	0.02495200
O	1.31409600	-1.65188900	0.04184600
S	-1.43692100	-1.23608800	0.30988200
C	3.57239000	1.16954200	0.46397600
C	4.93553300	1.44445700	0.38988900
C	5.81565700	0.49526600	-0.12766900
C	5.32358400	-0.73585700	-0.55881200
C	3.96223700	-1.01039200	-0.47400600
H	-6.21176300	1.56696700	-0.44678100
H	-3.98151600	2.66482400	-0.54586200
H	-4.35263800	-2.22856700	0.36007200
H	-6.39713400	-0.86315900	0.00659000
H	0.97008300	1.64364900	0.07004100
H	2.90098400	1.91005500	0.88772800
H	5.31241200	2.40000300	0.74317900
H	6.87834600	0.71145800	-0.18776900
H	6.00408600	-1.48255000	-0.95838900
H	3.56091000	-1.96770300	-0.79098900

Dihedral = 30

SCF = -1105.5895

XYZ =

28

030-thiazole-Ph.com

C	-5.29226700	0.99871400	-0.36195000
C	-4.04325700	1.60374300	-0.41264000
C	-2.89250800	0.84118300	-0.16098500
C	-3.03935900	-0.53222000	0.14157800
C	-4.29085400	-1.14042400	0.17867700
C	-5.42141600	-0.36497900	-0.06789700
N	-1.60456800	1.32157200	-0.18364100
C	-0.72311300	0.37369600	0.07059300
C	0.65825700	0.58133600	0.27676500
C	1.60298100	-0.44563600	0.08951200
C	3.06712700	-0.06525100	0.02716500
O	1.31941100	-1.66301400	-0.02532300
S	-1.45801200	-1.23896500	0.38494900
C	3.57899100	1.13816700	0.52468800
C	4.93945200	1.42205500	0.43529100
C	5.80985600	0.50799700	-0.15658400
C	5.31115300	-0.69813900	-0.64667100
C	3.95290100	-0.98229500	-0.54634200
H	-6.18205300	1.59103800	-0.55594600
H	-3.93719600	2.65966800	-0.64344200
H	-4.38535800	-2.19914400	0.40344700

H	-6.40575900	-0.82152300	-0.03098000
H	0.96906300	1.61773800	0.21176700
H	2.91545800	1.85138700	1.00423400
H	5.32201100	2.35790200	0.83253600
H	6.87023400	0.73172300	-0.22899200
H	5.98421400	-1.41854400	-1.10321800
H	3.54660000	-1.92137800	-0.90772300

Dihedral = 40
SCF = -1105.585875
XYZ =
28
040-thiazole-Ph.com

C	-5.26938200	1.02857100	-0.43462400
C	-4.00800300	1.60777800	-0.48241500
C	-2.87785400	0.83450200	-0.17731400
C	-3.05787200	-0.52244900	0.17736000
C	-4.32113100	-1.10640600	0.20963400
C	-5.43061900	-0.31977500	-0.09037000
N	-1.57902100	1.28799200	-0.19844000
C	-0.72016100	0.33522100	0.10227600
C	0.66006100	0.52692700	0.35045600
C	1.61069500	-0.47154600	0.05798000
C	3.07160100	-0.07185800	0.01113600
O	1.34014300	-1.67779300	-0.15528800
S	-1.49661600	-1.24519400	0.48005800
C	3.57793300	1.09664400	0.59022700
C	4.93612200	1.39577500	0.51461900
C	5.80976300	0.53231300	-0.14433000
C	5.31647800	-0.63910000	-0.71692700
C	3.96065500	-0.93892400	-0.63060800
H	-6.14316000	1.62908600	-0.67087400
H	-3.87601200	2.65104600	-0.75359200
H	-4.44088000	-2.15349000	0.47287700
H	-6.42411500	-0.75626000	-0.05687200
H	0.96708600	1.56691500	0.32221700
H	2.91266100	1.76880100	1.12378600
H	5.31453100	2.30411000	0.97490600
H	6.86830400	0.76802600	-0.20486500
H	5.99164400	-1.32092400	-1.22667200
H	3.55808000	-1.85385300	-1.05305100

Dihedral = 50
SCF = -1105.5815
XYZ =
28
050-thiazole-Ph.com

C	-5.23429600	1.08520100	-0.49943800
C	-3.95461300	1.62280800	-0.54486400
C	-2.85525000	0.82483200	-0.19547400
C	-3.08365800	-0.51301700	0.20136500
C	-4.36517100	-1.05674100	0.23028400
C	-5.44308900	-0.24547900	-0.11437700
N	-1.54131100	1.23599000	-0.21106800
C	-0.71649700	0.27082500	0.13414900

C	0.66485200	0.43671600	0.41819000
C	1.62442800	-0.51896000	0.02338400
C	3.07867700	-0.08791300	0.00008100
O	1.37522900	-1.70559600	-0.29545900
S	-1.55339700	-1.26325200	0.57088800
C	3.56966400	1.03301000	0.67801600
C	4.92086800	1.36518200	0.61675900
C	5.80369000	0.58358200	-0.12692600
C	5.32633400	-0.54105000	-0.79811900
C	3.97760200	-0.87508800	-0.72522900
H	-6.08525900	1.70441000	-0.76802900
H	-3.78454000	2.65206700	-0.84648500
H	-4.52271200	-2.08991600	0.52600400
H	-6.45037500	-0.64926400	-0.08367500
H	0.96696800	1.47923000	0.43583000
H	2.89819000	1.64048100	1.27719000
H	5.28627300	2.23494900	1.15556000
H	6.85659600	0.84571300	-0.17644400
H	6.00750700	-1.15983300	-1.37572700
H	3.58780100	-1.75641000	-1.22409600

Dihedral = 60
SCF = -1105.577
XYZ =
28
060-thiazole-Ph.com

C	-5.20004500	1.11665100	-0.56873200
C	-3.90626900	1.61800600	-0.62225000
C	-2.83463800	0.81089400	-0.21494300
C	-3.10214600	-0.49861500	0.24570600
C	-4.39859400	-1.00682100	0.28466100
C	-5.44860600	-0.18656000	-0.11815300
N	-1.50852700	1.18606800	-0.23807500
C	-0.71281400	0.22121700	0.16000800
C	0.67667900	0.35819200	0.44745800
C	1.63039900	-0.54918100	-0.05992500
C	3.08182900	-0.10804300	-0.02960400
O	1.38785300	-1.68851200	-0.52337600
S	-1.59679900	-1.25738000	0.68552700
C	3.56823700	0.87863500	0.83481600
C	4.91445700	1.23495300	0.82148600
C	5.79572900	0.61213000	-0.06081400
C	5.32298200	-0.37941800	-0.91953700
C	3.97898600	-0.74025200	-0.89432400
H	-6.03091700	1.74228700	-0.88144000
H	-3.70429600	2.62501300	-0.97466000
H	-4.58748900	-2.01843900	0.63156400
H	-6.46661100	-0.56194400	-0.08174800
H	0.98318800	1.39670300	0.53368200
H	2.89248900	1.35499700	1.53908500
H	5.27828400	1.99631700	1.50570000
H	6.84508400	0.89246800	-0.07350300
H	6.00494600	-0.87328700	-1.60635000
H	3.59385900	-1.52114500	-1.54234900

Dihedral = 70
SCF = -1105.5725
XYZ =
28
070-thiazole-Ph.com

C	-5.18078800	1.11195000	-0.62005500
C	-3.88215700	1.60057900	-0.66304700
C	-2.82721500	0.79644900	-0.21109800
C	-3.11314600	-0.49620400	0.28339500
C	-4.41564700	-0.99165500	0.31409300
C	-5.44882500	-0.17544800	-0.13510000
N	-1.49472700	1.15791000	-0.22803100
C	-0.71537500	0.20126000	0.20631300
C	0.68470300	0.31298100	0.49461500
C	1.62343800	-0.51110500	-0.15440100
C	3.08217600	-0.09830900	-0.06200600
O	1.36710300	-1.56040900	-0.79343800
S	-1.62254600	-1.24460600	0.78176100
C	3.58148500	0.76961300	0.91498300
C	4.93396900	1.10030500	0.94914700
C	5.81018800	0.56825900	0.00401500
C	5.32493600	-0.30619600	-0.96732800
C	3.97406800	-0.64018500	-0.99144500
H	-5.99994700	1.73405400	-0.96838400
H	-3.66393500	2.59421400	-1.04242700
H	-4.62034500	-1.99051700	0.68756500
H	-6.47065400	-0.54117100	-0.10849000
H	0.99008900	1.33383900	0.70764800
H	2.91021000	1.17178500	1.66793600
H	5.30658200	1.77071000	1.71860400
H	6.86459100	0.82812100	0.02945500
H	6.00299600	-0.72988500	-1.70311500
H	3.57653700	-1.33330900	-1.72572500

Dihedral = 80
SCF = -1105.56825
XYZ =
28
080-thiazole-Ph.com

C	-5.13463100	1.23209100	-0.51091200
C	-3.82244700	1.68242900	-0.48544200
C	-2.80030700	0.80186200	-0.10839800
C	-3.12890700	-0.52712200	0.24106000
C	-4.44672700	-0.98272000	0.20396700
C	-5.44680700	-0.09160300	-0.16849000
N	-1.45610100	1.12379000	-0.06878600
C	-0.71294700	0.10884000	0.27399600
C	0.69701200	0.13756000	0.57876100
C	1.62077500	-0.47300600	-0.28386700
C	3.08022500	-0.09686500	-0.09680600
O	1.35604100	-1.30175500	-1.19118800
S	-1.66797700	-1.36086600	0.68260000
C	3.59727600	0.41974100	1.09618500
C	4.94759200	0.74186700	1.20711700

C	5.80431100	0.55397700	0.12331000
C	5.30131300	0.03071800	-1.06710200
C	3.95270400	-0.29833700	-1.16950500
H	-5.93034900	1.91109700	-0.80228700
H	-3.56814300	2.70335200	-0.75320800
H	-4.68713200	-2.00856500	0.46611500
H	-6.47931000	-0.42624400	-0.19427900
H	1.00823400	1.05951900	1.06287000
H	2.93913100	0.54904100	1.95061100
H	5.33409200	1.13414600	2.14372300
H	6.85728000	0.80685300	0.20873700
H	5.96406400	-0.12366900	-1.91438600
H	3.54352800	-0.72076400	-2.08172500

Dihedral = 90

SCF = -1105.5649

XYZ =

28

090-thiazole-Ph.com

C	-5.12787500	1.28121000	0.27727200
C	-3.81625600	1.62729100	0.56459500
C	-2.80046800	0.68170700	0.37516000
C	-3.12956900	-0.60461000	-0.10454500
C	-4.44989500	-0.94993900	-0.39970800
C	-5.44345900	0.00050700	-0.20145100
N	-1.45458100	0.91279000	0.61360900
C	-0.71923500	-0.11909300	0.33398900
C	0.71087200	-0.27981800	0.54955300
C	1.59904900	-0.02347500	-0.49278500
C	3.07642300	0.02997400	-0.13925100
O	1.29388600	0.17376200	-1.70170100
S	-1.67151000	-1.54346700	-0.21236700
C	3.62682400	-0.56153700	1.00312300
C	4.99105600	-0.46866400	1.26813200
C	5.83111700	0.21756100	0.39209300
C	5.29582300	0.79936400	-0.75605300
C	3.93271700	0.69688800	-1.01913500
H	-5.91990700	2.00952400	0.42179400
H	-3.55688200	2.61552300	0.93163300
H	-4.69492100	-1.93979500	-0.77192600
H	-6.47624300	-0.25216100	-0.42130000
H	1.03914500	-0.17080500	1.57819200
H	2.98451500	-1.11954100	1.67844900
H	5.40192200	-0.93929700	2.15722500
H	6.89497700	0.29093300	0.59916400
H	5.94392600	1.33099600	-1.44785600
H	3.49587100	1.12626500	-1.91508900

Dihedral = 100

SCF = -1105.56625

XYZ =

28

100-thiazole-Ph.com

C	-5.14141600	1.10885000	0.13530000

C	-3.87741700	1.45644600	0.59054500
C	-2.81331700	0.56283000	0.41629900
C	-3.05030600	-0.67593000	-0.22071500
C	-4.32331400	-1.03007200	-0.66729900
C	-5.36478000	-0.12617000	-0.48992900
N	-1.51869900	0.78469800	0.85161300
C	-0.72625800	-0.21061900	0.58993700
C	0.70248800	-0.27517500	0.76749800
C	1.53259800	0.50016600	-0.05207100
C	3.02588500	0.19062300	-0.02492500
O	1.16957800	1.45196600	-0.78747000
S	-1.55011900	-1.55008700	-0.31327100
C	3.58293300	-1.01470000	0.41717500
C	4.96211000	-1.21205500	0.40885900
C	5.81403100	-0.20549600	-0.04193500
C	5.27178300	0.99607500	-0.49485300
C	3.89288000	1.18399900	-0.49190100
H	-5.96764400	1.80123600	0.26527300
H	-3.69330800	2.40869300	1.07835400
H	-4.49520900	-1.98668600	-1.15095500
H	-6.35998500	-0.38106100	-0.84112100
H	1.08763800	-1.19610800	1.19125800
H	2.94008500	-1.82115300	0.75576200
H	5.37168600	-2.15816500	0.75202100
H	6.88928200	-0.35933500	-0.04560800
H	5.92622700	1.78637600	-0.85278500
H	3.44999000	2.10635000	-0.85330400

Dihedral = 110

SCF = -1105.5695

XYZ =

28

110-thiazole-Ph.com

C	-5.15426200	1.10060800	0.01854600
C	-3.88390400	1.50429300	0.40708600
C	-2.81647500	0.60111800	0.32154400
C	-3.06115900	-0.70525800	-0.16087000
C	-4.33874400	-1.11442900	-0.53821200
C	-5.38324700	-0.19955200	-0.45150400
N	-1.51869800	0.87423900	0.70992600
C	-0.72672700	-0.14875400	0.55848900
C	0.69351900	-0.21111700	0.73677500
C	1.56046200	0.59908100	-0.01748200
C	3.03630000	0.21419100	-0.01818400
O	1.25140000	1.62392400	-0.66858700
S	-1.55932400	-1.58415400	-0.17954700
C	3.52273900	-1.07119500	0.24368100
C	4.89001300	-1.33856400	0.21388500
C	5.79855500	-0.32339700	-0.07801800
C	5.32620200	0.95930500	-0.35188900
C	3.95923300	1.21800000	-0.32969100
H	-5.98191900	1.80076300	0.08185000
H	-3.69833900	2.50781100	0.77761200
H	-4.51302900	-2.12253400	-0.90192300
H	-6.38295000	-0.49790200	-0.75176700

H	1.07125900	-1.16253600	1.09601800
H	2.83175800	-1.88248100	0.45032500
H	5.24584900	-2.34580300	0.41241400
H	6.86433300	-0.53201900	-0.09872700
H	6.02559900	1.75768900	-0.58503000
H	3.57128200	2.20642200	-0.55374400

Dihedral = 120
SCF = -1105.5729
XYZ =
28
120-thiazole-Ph.com

C	-5.14180900	1.11214700	-0.10050100
C	-3.86534800	1.53684800	0.24506800
C	-2.80692000	0.61887300	0.24381900
C	-3.06857500	-0.72392100	-0.11716600
C	-4.35092800	-1.15282800	-0.44970100
C	-5.38717400	-0.22326700	-0.44443000
N	-1.50782700	0.91280600	0.60369000
C	-0.72487900	-0.12987800	0.54422800
C	0.68625400	-0.20090300	0.72776500
C	1.57772100	0.66361000	0.05979300
C	3.03951600	0.23179500	0.00405200
O	1.29957900	1.75907300	-0.47572900
S	-1.57447500	-1.61865100	-0.06362800
C	3.48024000	-1.09028400	0.12690800
C	4.83556200	-1.40318800	0.04481200
C	5.77720800	-0.39744900	-0.16202500
C	5.35051100	0.92284600	-0.29723200
C	3.99514100	1.22825200	-0.22234200
H	-5.96151900	1.82456500	-0.10186100
H	-3.66735000	2.56928100	0.51657900
H	-4.53783700	-2.18897400	-0.71538800
H	-6.39131800	-0.53818400	-0.71097800
H	1.05867200	-1.17533500	1.02359800
H	2.76249800	-1.89286500	0.26282600
H	5.15563000	-2.43751300	0.13482400
H	6.83380100	-0.64152400	-0.22468300
H	6.07682900	1.71358700	-0.46407800
H	3.64124700	2.24723300	-0.34107200

Dihedral = 130
SCF = -1105.57613
XYZ =
28
130-thiazole-Ph.com

C	-5.13904500	1.14659500	-0.10942600
C	-3.84450100	1.56739800	0.16834000
C	-2.80153400	0.63169500	0.19176600
C	-3.10065200	-0.72629200	-0.07301500
C	-4.39933000	-1.14990200	-0.33960900
C	-5.41933500	-0.20195100	-0.36166800
N	-1.48654100	0.92403600	0.48398100
C	-0.72286900	-0.13749400	0.45849200
C	0.68500700	-0.23839000	0.61221100

C	1.59714400	0.66400800	0.02317300
C	3.05707200	0.22784200	-0.01484700
O	1.34008300	1.79120200	-0.45057800
S	-1.62234200	-1.64834100	-0.00710200
C	3.48479700	-1.10385500	0.00280500
C	4.84109700	-1.41947200	-0.04871100
C	5.79549800	-0.40695600	-0.11708900
C	5.38163000	0.92414200	-0.14694000
C	4.02568400	1.23308900	-0.10517400
H	-5.94542300	1.87393200	-0.13038200
H	-3.62052800	2.61084800	0.36801100
H	-4.61208400	-2.19665900	-0.53507500
H	-6.43666400	-0.51315800	-0.57796300
H	1.05090900	-1.22306300	0.87973900
H	2.75658200	-1.90840500	0.03246000
H	5.15212600	-2.46042300	-0.04254900
H	6.85272800	-0.65327400	-0.15475900
H	6.11802300	1.72090800	-0.20739300
H	3.68294600	2.26215400	-0.14354300

Dihedral = 140

SCF = -1105.578835

XYZ =

28

140-thiazole-Ph.com

C	-5.12576900	1.17859500	-0.14103600
C	-3.81706400	1.58980500	0.08027800
C	-2.79029900	0.63734000	0.13834800
C	-3.12225600	-0.72805700	-0.03542800
C	-4.43385700	-1.14110500	-0.24623800
C	-5.43756600	-0.17634300	-0.30294900
N	-1.46412500	0.92216600	0.37604400
C	-0.71922400	-0.15524700	0.39126300
C	0.68381000	-0.28092700	0.52188300
C	1.60806400	0.66513500	0.02321900
C	3.06681300	0.22786700	-0.02186200
O	1.35878100	1.82558500	-0.36323100
S	-1.65989900	-1.67579200	0.05380000
C	3.48842100	-1.10361800	-0.10059000
C	4.84433900	-1.42159200	-0.14438900
C	5.80355300	-0.41189800	-0.10883800
C	5.39558400	0.91977800	-0.04407600
C	4.04013100	1.23196000	-0.01076300
H	-5.91820200	1.91996500	-0.18937200
H	-3.56966400	2.63914000	0.20912500
H	-4.66995500	-2.19354200	-0.37258300
H	-6.46532800	-0.48024900	-0.47594300
H	1.04652500	-1.27528000	0.75341800
H	2.75566400	-1.90284400	-0.15420400
H	5.15159000	-2.46139600	-0.21311200
H	6.86050000	-0.66041300	-0.13917300
H	6.13611800	1.71470500	-0.02161500
H	3.70167900	2.26257200	0.02326400

Dihedral = 150

SCF = -1105.5810
XYZ =
28
150-thiazole-Ph.com

C	-5.12727900	1.19010300	-0.16995400
C	-3.80811900	1.59977700	-0.01722500
C	-2.78802900	0.64211900	0.07188900
C	-3.13952500	-0.72806600	-0.00221900
C	-4.46015300	-1.13871800	-0.14754700
C	-5.45713700	-0.16845200	-0.23397900
N	-1.45334500	0.92761200	0.24836200
C	-0.71882900	-0.15753100	0.31516200
C	0.67978200	-0.30413100	0.43471300
C	1.62231800	0.67080700	0.03279500
C	3.07857800	0.22744300	-0.01690300
O	1.38817300	1.85931500	-0.26352200
S	-1.68519000	-1.68631300	0.11205600
C	3.49232400	-1.09742600	-0.18995300
C	4.84675000	-1.42132400	-0.23707400
C	5.81158700	-0.42410100	-0.11026000
C	5.41129500	0.90182300	0.05009600
C	4.05772300	1.22078300	0.08640900
H	-5.91362000	1.93617600	-0.24050900
H	-3.54730600	2.65243300	0.03582800
H	-4.70995300	-2.19445100	-0.19767600
H	-6.49265000	-0.47177500	-0.35310000
H	1.03468100	-1.30692000	0.63926800
H	2.75434400	-1.88351800	-0.31613600
H	5.14865500	-2.45490700	-0.38134800
H	6.86730800	-0.67734200	-0.14393300
H	6.15666600	1.68664600	0.14507200
H	3.72521700	2.24822000	0.19358600

Dihedral = 160
SCF = -1105.5827
XYZ =
28
160-thiazole-Ph.com

C	-5.12854700	1.20881700	-0.14089600
C	-3.79949100	1.60714500	-0.05976700
C	-2.78713100	0.64110000	0.03031700
C	-3.15775900	-0.72628300	0.03407300
C	-4.48746100	-1.12526400	-0.04203200
C	-5.47634500	-0.14662900	-0.13179600
N	-1.44288500	0.91672500	0.12862300
C	-0.71753300	-0.17523100	0.20509800
C	0.67980700	-0.34079900	0.27929100
C	1.63060400	0.66047200	-0.02926900
C	3.08981700	0.22618200	-0.03729600
O	1.40183600	1.86189600	-0.27138100
S	-1.71147700	-1.69875400	0.13632600
C	3.51850600	-1.08299200	-0.27952400
C	4.87525300	-1.40058100	-0.27879700
C	5.82690500	-0.41327900	-0.03190300
C	5.41200500	0.89788400	0.19834700

C	4.05679600	1.21185400	0.18484400
H	-5.90828600	1.96162000	-0.21355800
H	-3.52451200	2.65753300	-0.06558000
H	-4.75138200	-2.17874400	-0.03598300
H	-6.51917100	-0.44134100	-0.19636500
H	1.03273200	-1.34721100	0.46775400
H	2.79144800	-1.85985300	-0.49561300
H	5.18941300	-2.42124900	-0.47830700
H	6.88420600	-0.66201600	-0.02741000
H	6.14762200	1.67555100	0.38444100
H	3.71451700	2.22915100	0.34594600

Dihedral = 170
SCF = -1105.58361
XYZ =
28
170-thiazole-Ph.com

C	-5.12035100	1.22591900	-0.15235300
C	-3.78487100	1.61088300	-0.12977600
C	-2.78051600	0.63794800	-0.02208500
C	-3.16736100	-0.72259200	0.05956700
C	-4.50282100	-1.10814700	0.04042100
C	-5.48334200	-0.12257800	-0.06719700
N	-1.43094600	0.90090100	0.01689400
C	-0.71670400	-0.19706700	0.12436900
C	0.67763500	-0.37980800	0.17407500
C	1.63177700	0.64634100	-0.02440700
C	3.09410300	0.22291300	-0.03203500
O	1.39769800	1.86135600	-0.17139200
S	-1.73063300	-1.70830400	0.17262000
C	3.53581400	-1.07008900	-0.33150600
C	4.89483100	-1.37765900	-0.32838200
C	5.83581900	-0.39632900	-0.02399000
C	5.40790400	0.89921000	0.26382600
C	4.05047000	1.20319000	0.25036900
H	-5.89307800	1.98447200	-0.23892800
H	-3.49873400	2.65626200	-0.19537600
H	-4.77805000	-2.15671800	0.10624500
H	-6.53090800	-0.40681400	-0.08583100
H	1.02631800	-1.39219200	0.33468600
H	2.81824200	-1.84119100	-0.59478900
H	5.21908600	-2.38559400	-0.57148400
H	6.89492500	-0.63721600	-0.01917500
H	6.13510000	1.67299000	0.49426900
H	3.69793900	2.20889100	0.45594600

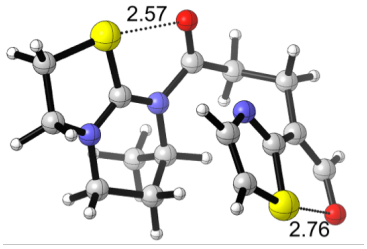
Dihedral = 180
SCF = -1105.584
XYZ =
28
180-thiazole-Ph.com

C	-5.12183900	1.22436700	-0.11809900
C	-3.78567600	1.60322100	-0.17698600
C	-2.78004000	0.63135300	-0.07038300

C	-3.16741300	-0.72117600	0.09723000
C	-4.50325000	-1.10092200	0.15604300
C	-5.48488800	-0.11659700	0.04708800
N	-1.42944800	0.88740600	-0.11636900
C	-0.71496200	-0.20936700	0.00640200
C	0.67918200	-0.39748500	0.00965900
C	1.63262500	0.64316100	-0.09717800
C	3.09541000	0.22731500	-0.05472200
O	1.39640400	1.86249900	-0.19341600
S	-1.73011200	-1.70773000	0.19793600
C	3.56016400	-1.03741300	-0.42980400
C	4.91843700	-1.34265700	-0.37238700
C	5.83399200	-0.38786000	0.06568200
C	5.38272000	0.87978000	0.43166000
C	4.02696300	1.18334200	0.36120300
H	-5.89540600	1.98213400	-0.20429000
H	-3.50018600	2.64278400	-0.30665500
H	-4.77770700	-2.14388300	0.28448400
H	-6.53307500	-0.39585100	0.08994900
H	1.03063900	-1.41060700	0.16057000
H	2.86095900	-1.78389500	-0.79459500
H	5.26299400	-2.32669700	-0.67734400
H	6.89232900	-0.62728100	0.11404900
H	6.09020500	1.63173100	0.77024300
H	3.65739700	2.16904100	0.62608600

S•••O vs. O•••O vs. C–H•••O Interaction Model Systems

Model Benzothiazole



Dual S•••O

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C15H19N3O2S2 C1[X(C15H19N3O2S2)] #Atoms= 41
Charge = 0 Multiplicity = 1

SCF Energy= -1693.67041650 Predicted Change= -5.280747D-10
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00039	0.00180	[YES]	0.00039	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.978031	0.247640	0.095412
S	2.984794	0.613395	-1.293715
C	4.280184	-0.512840	-0.656393
C	3.562474	-1.496256	0.249505
N	2.421202	-0.768570	0.817259
C	1.689368	-1.379630	1.930811
C	0.232427	-0.975778	1.838445
C	0.105530	0.528861	1.641795
C	0.594509	1.345606	2.833649
N	0.862793	0.925349	0.420889
C	0.357863	1.928946	-0.463212
C	-0.901926	2.666915	-0.091383
C	-2.151650	2.119137	-0.840760
C	-2.706808	0.808488	-0.363466
C	-2.045087	-0.390434	-0.743927
C	-3.883910	0.762660	0.398716
O	-4.461047	-0.258497	0.831997
O	0.962047	2.185003	-1.478897
N	-0.917454	-0.433961	-1.439318
C	-0.501060	-1.727766	-1.637450

C	-1.281634	-2.707241	-1.109859
S	-2.650954	-1.999857	-0.301675
H	5.015894	0.078384	-0.108784
H	4.761439	-1.007130	-1.499412
H	4.200034	-1.845894	1.063664
H	3.174446	-2.360495	-0.302799
H	2.158849	-1.071254	2.870290
H	1.804946	-2.462224	1.832738
H	-0.294738	-1.262046	2.751285
H	-0.234573	-1.493201	0.995674
H	0.454033	2.416072	2.660217
H	1.659221	1.175454	3.022362
H	0.032750	1.063206	3.728090
H	-0.943318	0.737252	1.426677
H	-1.086939	2.698555	0.982895
H	-1.889494	2.074280	-1.905266
H	-2.924624	2.888235	-0.730677
H	-4.326719	1.760006	0.621792
H	-0.718418	3.690239	-0.430913
H	0.412570	-1.900146	-2.199295
H	-1.140440	-3.777525	-1.160215

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1693.67041650 Predicted Change= -5.280747D-10
Zero-point correction (ZPE)= -1693.3342 0.33612
Internal Energy (U)= -1693.3143 0.35611
Enthalpy (H)= -1693.3133 0.35705
Gibbs Free Energy (G)= -1693.3825 0.28789

Frequencies -- 25.5290 51.6458 74.4340

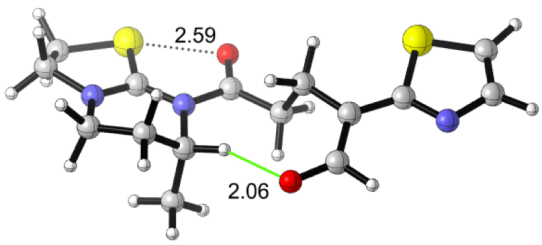
==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C15H19N3O2S2 C1[X(C15H19N3O2S2)] #Atoms= 41
Charge = 0 Multiplicity = 1

SCF Energy= -1693.72116434

==========



C–H•••O + S•••O

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

```
=====================================================================
 #m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C15H19N3O2S2   C1[X(C15H19N3O2S2)]  #Atoms= 41
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -1693.66057232       Predicted Change= -6.594856D-09
=====================================================================
 Optimization completed.          {Found       2       times}
 Item      Max Val.   Criteria   Pass?      RMS Val.   Criteria   Pass?
 Force      0.00001 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00136 ||  0.00180   [ YES ]      0.00136 ||  0.00180   [ YES ]
---------------------------------------------------------------------
     Atomic              Coordinates (Angstroms)
      Type              X           Y           Z
---------------------------------------------------------------------
      C       -2.908395    -0.424276    -0.013861
      S       -3.423515    -2.087746     0.180780
      C       -5.168721    -1.574389    -0.031454
      C       -5.125663    -0.270003    -0.808326
      N       -3.861789     0.382066    -0.444134
      C       -3.671848     1.786178    -0.828921
      C       -2.189602     2.085158    -0.938363
      C       -1.439468     1.502485     0.252108
      C       -1.860349     2.089778     1.595383
      N       -1.664610     0.025930     0.258447
      C       -0.633543    -0.891227     0.630745
      C        0.723043    -0.314608     0.901432
      C        1.481884    -0.068408    -0.433395
      C        2.725241     0.739862    -0.211101
      C        4.024899     0.157152    -0.188456
      C        2.543628     2.098383     0.073257
      O        1.430039     2.680230     0.149644
      O       -0.869842    -2.079033     0.631963
      S        4.230296    -1.606283    -0.386895
      C        5.951357    -1.408690    -0.228965
      C        6.231760    -0.093983    -0.044374
      N        5.175617     0.780848    -0.019198
      H       -5.612274    -1.442753     0.956481
      H       -5.700996    -2.356597    -0.571215
      H       -5.953199     0.391371    -0.544442
      H       -5.124854    -0.431579    -1.892264
      H       -4.169436     2.413740    -0.082842
      H       -4.181459     1.926777    -1.786065
      H       -2.030903     3.165140    -0.970334
      H       -1.786925     1.658216    -1.862184
      H       -1.255603     1.669888     2.403942
      H       -2.912874     1.888895     1.821368
      H       -1.705026     3.171908     1.580311
      H       -0.373512     1.686663     0.098616
      H        0.671328     0.625826     1.453678
      H        0.819935     0.477356    -1.119910
      H        1.684171    -1.038131    -0.902287
```

H	3.463990	2.685157	0.250056
H	1.262719	-1.051523	1.499392
H	6.629038	-2.247163	-0.286505
H	7.235913	0.299338	0.079145

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1693.66057232 Predicted Change= -6.594856D-09

Zero-point correction (ZPE)=	-1693.3249	0.33558
Internal Energy (U)=	-1693.3044	0.35611
Enthalpy (H)=	-1693.3035	0.35706
Gibbs Free Energy (G)=	-1693.3758	0.28476

Frequencies -- 23.5339 34.2560 44.1627

==========

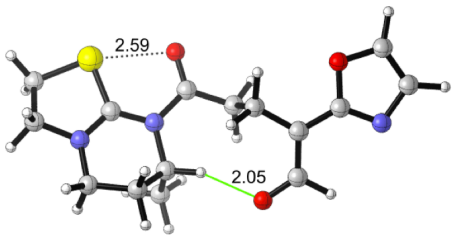
#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C15H19N3O2S2 C1[X(C15H19N3O2S2)] #Atoms= 41
Charge = 0 Multiplicity = 1

SCF Energy= -1693.71218317

==========

Model Benzoxazole



C–H•••O + S•••O

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C15H19N3O3S C1[X(C15H19N3O3S)] #Atoms= 41
Charge = 0 Multiplicity = 1

SCF Energy= -1370.69489759 Predicted Change= -1.090137D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00299	0.00180	[NO]	0.00299	0.00180	[YES]

Atomic Coordinates (Angstroms)

Type	X	Y	Z
C	-2.694427	-0.399751	-0.024057
S	-3.283950	-2.038827	0.172746
C	-5.004071	-1.447141	-0.039997
C	-4.902404	-0.148633	-0.820373
N	-3.610450	0.447307	-0.458073
C	-3.355494	1.839823	-0.848835
C	-1.860647	2.073098	-0.949587
C	-1.143697	1.460439	0.246173
C	-1.545788	2.068009	1.586062
N	-1.433351	-0.004651	0.251451
C	-0.443847	-0.966151	0.626831
C	0.933068	-0.446852	0.906498
C	1.710043	-0.225125	-0.423403
C	2.969552	0.553899	-0.188044
C	4.252954	-0.072312	-0.221493
C	2.840934	1.900677	0.141528
O	1.750121	2.526023	0.251043
O	-0.732209	-2.142744	0.624071
O	4.294607	-1.418622	-0.459944
C	5.626196	-1.755739	-0.439172
C	6.320740	-0.626765	-0.192726
N	5.452224	0.444682	-0.054911
H	-5.440910	-1.293360	0.947757
H	-5.571623	-2.205552	-0.577836
H	-5.699542	0.549989	-0.558909
H	-4.909149	-0.313599	-1.903755
H	-3.829247	2.493152	-0.109427
H	-3.852611	1.997625	-1.809895
H	-1.654795	3.145053	-0.982523
H	-1.471413	1.627166	-1.870166
H	-0.972363	1.614833	2.399462
H	-2.609838	1.925390	1.802288
H	-1.329940	3.139739	1.573636
H	-0.068953	1.599220	0.103816
H	0.915681	0.492511	1.462883
H	1.064362	0.330916	-1.118339
H	1.906940	-1.199686	-0.877995
H	3.786303	2.447246	0.324873
H	1.439523	-1.208293	1.502113
H	5.871368	-2.790246	-0.613526
H	7.391628	-0.504348	-0.105450

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-1370.69489759	Predicted Change= -1.090137D-08
Zero-point correction (ZPE)=	-1370.3558	0.33907
Internal Energy (U)=	-1370.3357	0.35915
Enthalpy (H)=	-1370.3347	0.36010
Gibbs Free Energy (G)=	-1370.4064	0.28846

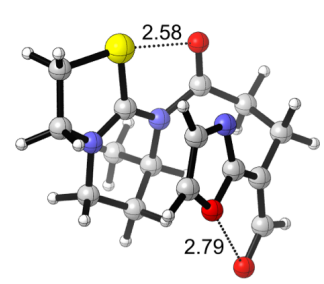
Frequencies -- 18.3608 30.2943 49.2790

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C15H19N3O3S C1[X(C15H19N3O3S)] #Atoms= 41
Charge = 0 Multiplicity = 1

SCF Energy= -1370.74913825

==========



S•••O + O•••O

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C15H19N3O3S C1[X(C15H19N3O3S)] #Atoms= 41
Charge = 0 Multiplicity = 1

SCF Energy= -1370.69724354 Predicted Change= -1.756837D-08

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00006	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00137	0.00180	[YES]	0.00137	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.387279	-0.479784	0.106625
S	-2.523547	-0.502097	-1.225938
C	-3.724821	0.467055	-0.239149
C	-2.921547	1.146640	0.857881
N	-1.754890	0.293392	1.109842
C	-0.987008	0.528669	2.336960
C	0.426270	-0.007326	2.202280
C	0.439314	-1.340054	1.464285
C	-0.219112	-2.481248	2.235260
N	-0.244098	-1.196729	0.147067
C	0.235208	-1.807639	-1.054966
C	1.689824	-2.176444	-1.142776
C	2.532744	-0.925588	-1.543302
C	2.469817	0.239335	-0.591810
C	1.435721	1.197649	-0.804708

C	3.373886	0.306134	0.480823
O	3.427299	1.118132	1.426773
O	-0.516222	-1.931655	-1.994588
N	0.485600	1.157194	-1.722357
C	-0.294262	2.275110	-1.477294
C	0.201550	2.955781	-0.421620
O	1.315797	2.284894	0.015481
H	-4.469523	-0.218330	0.167747
H	-4.212902	1.190299	-0.891769
H	-3.492729	1.248725	1.783017
H	-2.548241	2.129286	0.547453
H	-1.537303	0.061212	3.160758
H	-0.978539	1.609817	2.505125
H	0.847218	-0.158168	3.199712
H	1.069894	0.706545	1.684815
H	-0.145855	-3.419406	1.678235
H	-1.279669	-2.277459	2.417880
H	0.278728	-2.609738	3.200111
H	1.478424	-1.573055	1.250793
H	2.080301	-2.615219	-0.223436
H	2.209646	-0.623696	-2.544994
H	3.566471	-1.279918	-1.629623
H	4.125687	-0.521871	0.453309
H	1.753446	-2.931760	-1.929748
H	-1.158754	2.511320	-2.083333
H	-0.052657	3.867253	0.094833

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1370.69724354 Predicted Change= -1.756837D-08
Zero-point correction (ZPE)= -1370.3575 0.33973
Internal Energy (U)= -1370.3380 0.35919
Enthalpy (H)= -1370.3371 0.36013
Gibbs Free Energy (G)= -1370.4042 0.29303

Frequencies -- 53.7049 65.1210 74.1677

==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF)

Pointgroup= C1 Stoichiometry= C15H19N3O3S C1[X(C15H19N3O3S)] #Atoms= 41
Charge = 0 Multiplicity = 1

SCF Energy= -1370.74968136

==========

Appendix III:

Computational Data for Chapter 4

A C=O···Isothiouronium Interaction Dictates Enantiodiscrimination in Acylative Kinetic Resolutions of Tertiary Heterocyclic Alcohols

Partial Computed Reaction Coordinate

HyperBTM 4.2

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062X/6-31G(d) scf=(direct,tight,maxcycle=300,xqc)
SCRF=(PCM,SOLVENT=Chloroform) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman temp=273.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C19H20N2S C1[X(C19H20N2S)] #Atoms= 42
Charge = 0 Multiplicity = 1

SCF Energy= -1243.38685782 Predicted Change= -1.152064D-08

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00067	0.00180	[YES]	0.00067	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	4.560840	-0.686071	0.138946
C	3.215636	-0.531234	0.434436
C	2.391433	0.279459	-0.361468
C	2.909733	0.934310	-1.474455
C	4.264468	0.775533	-1.767666
C	5.084470	-0.022375	-0.972425
S	2.302152	-1.254085	1.757924
C	0.804488	-0.455427	1.201259
N	1.078316	0.321053	0.089211
N	-0.309973	-0.636330	1.783510
C	-1.465514	0.044066	1.191879
C	-2.204184	-0.882765	0.235240
C	-1.067772	1.395800	0.539214
C	-2.248044	2.176894	-0.065255
C	-1.777060	3.417355	-0.832190
C	-3.239729	2.606684	1.019508
C	0.043221	1.166977	-0.488076
C	-3.600652	-0.935191	0.252024
C	-4.299904	-1.746821	-0.637858
C	-3.608314	-2.529333	-1.558766
C	-2.215866	-2.497547	-1.576060
C	-1.520515	-1.684992	-0.684023
H	5.192472	-1.312481	0.760646
H	2.273867	1.547544	-2.104211
H	4.680107	1.281102	-2.633301
H	6.135558	-0.134461	-1.215902
H	-2.145483	0.263051	2.021404
H	-0.637854	2.005994	1.347985
H	-2.766207	1.514772	-0.772403

H	-1.159286	4.058455	-0.191012
H	-2.638613	4.006167	-1.161283
H	-1.195042	3.161976	-1.722599
H	-2.748896	3.270069	1.741911
H	-3.656583	1.761461	1.572689
H	-4.075907	3.155260	0.575004
H	0.508435	2.118842	-0.759751
H	-0.355976	0.707659	-1.403965
H	-4.149658	-0.340222	0.977772
H	-5.384912	-1.773579	-0.604296
H	-4.149985	-3.166219	-2.251330
H	-1.665632	-3.113782	-2.280819
H	-0.433657	-1.691219	-0.697959

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm
==========
==
SCF Energy= -1243.38685782 Predicted Change= -1.152064D-08
Zero-point correction (ZPE)= -1243.0322 0.35458
Internal Energy (U)= -1243.0166 0.37023
Enthalpy (H)= -1243.0157 0.37109
Gibbs Free Energy (G)= -1243.0736 0.31317

Frequencies -- 31.8938 38.4344 63.0270
==========
==
#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=chloroform)

Pointgroup= C1 Stoichiometry= C19H20N2S C1[X(C19H20N2S)] #Atoms= 42
Charge = 0 Multiplicity = 1

SCF Energy= -1243.68539429
==========
==

Isobutyric anhydride 4.2

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
==
#m062X/6-31G(d) scf=(direct,tight,maxcycle=300,xqc)
SCRF=(PCM,SOLVENT=Chloroform) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman temp=273.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C8H14O3 C1[X(C8H14O3)] #Atoms= 25
Charge = 0 Multiplicity = 1

SCF Energy= -538.747750239 Predicted Change= -1.156179D-08
==========
==
Optimization completed. {Found 1 times}
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?

```
 Force      0.00002 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00215 ||  0.00180   [ NO ]       0.00215 ||  0.00180   [ YES ]
---------------------------------------------------------------------------
     Atomic             Coordinates (Angstroms)
      Type              X           Y           Z
---------------------------------------------------------------------------
      C       -1.958834   -0.454038    0.354335
      C       -1.197854    0.728895   -0.206379
      O        0.152433    0.840655    0.132532
      C        0.986162   -0.215520   -0.098736
      C        2.353410    0.027544    0.496159
      C        2.986561    1.267332   -0.153494
      C        3.226121   -1.211458    0.337242
      O        0.642038   -1.178051   -0.735197
      O       -1.693132    1.624691   -0.824396
      C       -2.608411   -1.226443   -0.796584
      C       -3.015343    0.086885    1.327328
      H        2.190374    0.242855    1.559749
      H        3.132294    1.103492   -1.226046
      H        3.964266    1.454989    0.297852
      H        2.362351    2.152826   -0.017312
      H        4.201522   -1.040186    0.799953
      H        3.379754   -1.435840   -0.722259
      H        2.766834   -2.086025    0.804313
      H       -1.267164   -1.107157    0.890705
      H       -1.849878   -1.628841   -1.471681
      H       -3.273333   -0.566446   -1.361723
      H       -3.199375   -2.054932   -0.396372
      H       -3.703002    0.755161    0.801509
      H       -2.558409    0.638479    2.154030
      H       -3.587821   -0.745931    1.744530
---------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 273.150 Kelvin       Pressure= 1.00000 Atm
===========================================================================
==
 SCF Energy=     -538.747750239   Predicted Change= -1.156179D-08
 Zero-point correction (ZPE)=              -538.5319       0.21576
 Internal Energy (U)=                      -538.5206       0.22706
 Enthalpy (H)=                             -538.5198       0.22792
 Gibbs Free Energy (G)=                    -538.5681       0.17961
---------------------------------------------------------------------------
 Frequencies --     18.5733              45.9062              66.8938
===========================================================================
==
 #m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
 SCRF=(PCM,SOLVENT=chloroform)
---------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C8H14O3   C1[X(C8H14O3)]  #Atoms= 25
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -538.936020957
===========================================================================
==
```

Alcohol 4.5

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062x/6-31G(d) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman temp=273.15
SCRF=(PCM,SOLVENT=chloroform)
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C16H15NO2 C1[X(C16H15NO2)] #Atoms= 34
Charge = 0 Multiplicity = 1

SCF Energy= -823.619963590 Predicted Change= -5.965886D-10

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00059	0.00180	[YES]	0.00059	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.149532	1.891976	-0.805786
C	-0.807485	3.051733	-0.383053
C	-2.020966	2.991229	0.298194
C	-2.615615	1.754551	0.576081
C	-1.974335	0.602291	0.163340
C	-0.756645	0.679747	-0.519807
C	-2.360418	-0.847551	0.301112
C	-3.644633	-1.217266	-0.432678
O	-2.421076	-1.214377	1.667705
C	-1.153422	-1.563506	-0.341208
O	-0.993010	-2.769157	-0.363593
N	-0.296244	-0.614524	-0.832022
C	1.001512	-0.916709	-1.396989
C	2.147615	-0.502376	-0.494391
C	2.024777	-0.565663	0.894615
C	3.096417	-0.214778	1.710936
C	4.300639	0.201653	1.146619
C	4.426746	0.270329	-0.238682
C	3.352157	-0.076209	-1.054433
H	0.804764	1.941302	-1.320437
H	-0.355497	4.017418	-0.587136
H	-2.505396	3.907431	0.619189
H	-3.558355	1.698435	1.113094
H	-3.786292	-2.302407	-0.397532
H	-3.604369	-0.903747	-1.479839
H	-4.492452	-0.727710	0.053921
H	-2.437146	-2.186539	1.689222
H	1.094746	-0.430688	-2.374872
H	1.009072	-1.999195	-1.559677
H	1.083886	-0.881609	1.339632
H	2.989240	-0.264810	2.790159

```
     H        5.135184      0.477239      1.783770
     H        5.359046      0.602234     -0.685489
     H        3.449084     -0.014124     -2.135958
---------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 273.150 Kelvin       Pressure= 1.00000 Atm
=====================================================================
==
 SCF Energy=     -823.619963590   Predicted Change= -5.965886D-10
 Zero-point correction (ZPE)=            -823.3403       0.27965
 Internal Energy (U)=                    -823.3269       0.29301
 Enthalpy (H)=                           -823.3260       0.29387
 Gibbs Free Energy (G)=                  -823.3795       0.24040
---------------------------------------------------------------------
 Frequencies --     27.9544              34.1424              40.8616
=====================================================================
==
 #m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
 SCRF=(PCM,SOLVENT=chloroform)
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C16H15NO2   C1[X(C16H15NO2)]  #Atoms= 34
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -823.894712971
=====================================================================
==
```

***i*-Pr$_2$NEt**

```
---------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
=====================================================================
==
 #m062x/6-31G(d) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
 opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman temp=273.15
 SCRF=(PCM,SOLVENT=chloroform)
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C8H19N   C1[X(C8H19N)]  #Atoms= 28
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -370.843647001       Predicted Change= -6.924063D-08
=====================================================================
==
 Optimization completed.          {Found       1       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00003 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00340 ||  0.00180   [ NO ]       0.00340 ||  0.00180   [ YES ]
---------------------------------------------------------------------
     Atomic              Coordinates (Angstroms)
      Type              X             Y          Z
---------------------------------------------------------------------
     N         0.001895      0.271764      0.212118
     C        -0.313505      1.452675     -0.583387
     C         0.265402      2.730816      0.017940
     C        -1.032518     -0.772786      0.201475
```

C	-2.118531	-0.428006	1.221706
C	-1.664964	-1.071764	-1.167397
C	1.384327	-0.194951	0.054967
C	1.648987	-1.071173	-1.177377
C	1.870433	-0.887775	1.328521
H	0.012096	1.349695	-1.634703
H	1.358468	2.711467	0.057594
H	-0.107415	2.860748	1.037823
H	-0.027687	3.600941	-0.577819
H	-1.402369	1.559798	-0.612588
H	-2.619884	0.509309	0.952871
H	-1.678596	-0.304174	2.214764
H	-2.881224	-1.212755	1.265276
H	-0.544147	-1.692781	0.543230
H	-2.284270	-0.236287	-1.510749
H	-2.314691	-1.949890	-1.091669
H	-0.911408	-1.271527	-1.933125
H	1.988016	0.712983	-0.060054
H	2.721488	-1.268953	-1.275119
H	1.312231	-0.583383	-2.098116
H	1.139851	-2.037975	-1.092921
H	1.709691	-0.240096	2.194656
H	2.937594	-1.120621	1.253816
H	1.341203	-1.831068	1.503321

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -370.843647001 Predicted Change= -6.924063D-08
Zero-point correction (ZPE)= -370.5784 0.26519
Internal Energy (U)= -370.5681 0.27545
Enthalpy (H)= -370.5673 0.27631
Gibbs Free Energy (G)= -370.6110 0.23257

Frequencies -- 58.6672 78.3433 119.4143

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=chloroform)

Pointgroup= C1 Stoichiometry= C8H19N C1[X(C8H19N)] #Atoms= 28
Charge = 0 Multiplicity = 1

SCF Energy= -370.963655935

==========

Ion-pair

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062x/6-31G(d) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman temp=273.15

SCRF=(PCM,SOLVENT=chloroform)
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C27H34N2O3S C1[X(C27H34N2O3S)] #Atoms= 67
Charge = 0 Multiplicity = 1

SCF Energy= -1782.13882633 Predicted Change= -5.572920D-09
==========
==
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00122	0.00180	[YES]	0.00122	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-4.308466	-1.898657	-1.172065
C	-3.015558	-1.458167	-0.899442
C	-2.527333	-1.443636	0.404669
C	-3.304582	-1.877165	1.477698
C	-4.592738	-2.315196	1.200861
C	-5.092284	-2.324244	-0.107489
S	-1.813842	-0.890549	-2.042240
C	-0.702835	-0.625666	-0.733106
N	-1.212917	-0.963379	0.457813
N	0.555173	-0.168937	-0.868039
C	1.397680	0.084661	0.331415
C	2.377389	-1.057974	0.529158
C	0.498528	0.364001	1.550811
C	1.298341	0.662146	2.832614
C	0.365234	0.783511	4.042136
C	2.088634	1.965341	2.672005
C	-0.502399	-0.762842	1.725798
C	3.685975	-0.788962	0.939668
C	4.587036	-1.825612	1.165545
C	4.192954	-3.148109	0.976355
C	2.896092	-3.426259	0.553136
C	1.995685	-2.387461	0.328218
C	-1.886562	3.327886	0.131385
C	-0.582554	2.826328	-0.544092
O	-0.729107	2.216454	-1.630608
C	1.044456	0.100496	-2.179440
C	2.443855	0.658284	-2.344642
C	2.362463	2.189274	-2.456997
C	3.068582	0.040375	-3.597160
O	0.345658	-0.171052	-3.129426
O	0.502184	3.033691	0.065300
C	-1.630524	4.130448	1.400462
C	-2.804903	2.133035	0.405742
H	-4.689099	-1.905683	-2.187887
H	-2.921466	-1.885461	2.491670
H	-5.220242	-2.656905	2.016825
H	-6.103357	-2.669970	-0.293406
H	1.909138	1.025817	0.123105

H	-0.054694	1.276776	1.302135
H	1.994983	-0.166490	3.020069
H	-0.428695	1.515922	3.847880
H	0.927744	1.125722	4.915459
H	-0.103046	-0.168758	4.310075
H	2.854501	1.903466	1.894086
H	2.590960	2.218481	3.610645
H	1.415735	2.780464	2.386724
H	-0.033711	-1.706711	2.031198
H	-1.258992	-0.489152	2.462826
H	4.007420	0.240713	1.073514
H	5.600614	-1.597539	1.479920
H	4.896634	-3.956528	1.147166
H	2.583519	-4.452769	0.389253
H	0.993853	-2.622985	-0.024514
H	3.060600	0.387712	-1.485022
H	3.371488	2.582756	-2.615610
H	1.910920	2.639225	-1.568293
H	1.739215	2.457502	-3.315186
H	2.475379	0.289213	-4.480189
H	3.132714	-1.049119	-3.519359
H	4.078048	0.438655	-3.729600
H	-2.389002	3.965558	-0.608573
H	-0.961350	4.972572	1.206941
H	-1.147601	3.501629	2.158144
H	-2.567255	4.514520	1.820980
H	-3.784819	2.454008	0.776159
H	-2.368482	1.478772	1.175241
H	-2.948851	1.545822	-0.506527

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1782.13882633 Predicted Change= -5.572920D-09
Zero-point correction (ZPE)= -1781.5650 0.57376
Internal Energy (U)= -1781.5376 0.60120
Enthalpy (H)= -1781.5367 0.60206
Gibbs Free Energy (G)= -1781.6198 0.51900

Frequencies -- 23.7996 36.7040 38.6329

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=chloroform)

Pointgroup= C1 Stoichiometry= C27H34N2O3S C1[X(C27H34N2O3S)] #Atoms= 67
Charge = 0 Multiplicity = 1

SCF Energy= -1782.62594579

==========

isobutyrate

```
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
 ============================================================================
 ==
 #m062x/6-31G(d) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
 opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman temp=273.15
 SCRF=(PCM,SOLVENT=chloroform)
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
 ----------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C4H7O2(1-)   C1[X(C4H7O2)]  #Atoms= 13
 Charge = -1        Multiplicity = 1
 ----------------------------------------------------------------------------
 SCF Energy= -307.072424537       Predicted Change= -5.077290D-09
 ============================================================================
 ==
 Optimization completed on the basis of negligible forces.           {Found       2       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00000 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00279 ||  0.00180   [ NO ]       0.00279 ||  0.00180   [ YES ]
 ----------------------------------------------------------------------------
      Atomic              Coordinates (Angstroms)
       Type              X              Y         Z
 ----------------------------------------------------------------------------
      C       -0.907085      -0.089599      -0.047310
      C        0.601183       0.116634      -0.392959
      C        1.134764       1.337312       0.358249
      C        1.450649      -1.119507      -0.123798
      O       -1.247010      -1.215887       0.386068
      O       -1.640015       0.911894      -0.239302
      H        1.114236       1.156122       1.440654
      H        2.170196       1.569644       0.079896
      H        0.505397       2.205517       0.150461
      H        0.639574       0.347966      -1.468275
      H        2.499692      -0.951659      -0.399705
      H        1.413372      -1.382413       0.938843
      H        1.076658      -1.982271      -0.681091
 ----------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 273.150 Kelvin       Pressure= 1.00000 Atm
 ============================================================================
 ==
 SCF Energy=     -307.072424537   Predicted Change= -5.077290D-09
 Zero-point correction (ZPE)=              -306.9652       0.10715
 Internal Energy (U)=                      -306.9594       0.11293
 Enthalpy (H)=                             -306.9586       0.11380
 Gibbs Free Energy (G)=                    -306.9930       0.07938
 ----------------------------------------------------------------------------
 Frequencies --     31.9452              240.0506              250.4646
 ============================================================================
 ==
 #m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
 SCRF=(PCM,SOLVENT=chloroform)
 ----------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C4H7O2(1-)   C1[X(C4H7O2)]  #Atoms= 13
 Charge = -1        Multiplicity = 1
 ----------------------------------------------------------------------------
```

SCF Energy= -307.202901863

==========

==

(*S*)-II

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

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==

#m062X/6-31G(d) scf=(direct,tight,maxcycle=300,xqc)
SCRF=(PCM,SOLVENT=Chloroform) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman temp=273.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C43H49N3O5S C1[X(C43H49N3O5S)] #Atoms= 101
Charge = 0 Multiplicity = 1

SCF Energy= -2605.80485258 Predicted Change= -8.341083D-08

==========

==

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00456	0.00180	[NO]	0.00456	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.747100	4.625810	-0.677790
C	1.684570	3.735640	-0.552030
C	0.752090	3.876720	0.472610
C	0.834690	4.920670	1.390970
C	1.892540	5.811650	1.258690
C	2.839790	5.666890	0.238450
S	1.334930	2.329810	-1.541240
C	-0.075270	2.002110	-0.567350
N	-0.226460	2.877110	0.430440
N	-0.968810	1.032180	-0.810070
C	-0.683640	0.059710	-1.823380
C	-1.828370	-0.764570	-2.357680
C	-2.377270	0.006040	-3.572590
C	-1.342469	-2.160460	-2.736140
O	0.422370	0.052880	-2.319050
C	-2.160840	0.883830	0.073120
C	-3.361540	1.591990	-0.519730
C	-1.763090	1.307390	1.497930
C	-2.901420	1.128100	2.518000
C	-2.509240	1.691220	3.888160
C	-3.276420	-0.349890	2.659480
C	-1.227640	2.729410	1.493180
C	-4.577390	0.903990	-0.580550
C	-5.709800	1.525819	-1.102750
C	-5.638150	2.832949	-1.578170
C	-4.424710	3.516600	-1.539170
C	-3.292650	2.899140	-1.013980

H	-2.617040	-0.881400	-1.616370
H	-3.224720	-0.543100	-3.992020
H	-1.607810	0.102990	-4.345570
H	-2.725630	1.007150	-3.295950
H	-0.483679	-2.109730	-3.412040
H	-1.060619	-2.714980	-1.837640
H	-2.153929	-2.698170	-3.235300
H	3.478740	4.509350	-1.470130
H	0.098720	5.041240	2.177890
H	1.981740	6.633240	1.961030
H	3.656690	6.375850	0.159320
H	-2.360940	-0.187190	0.118690
H	-0.932300	0.643760	1.771980
H	-3.778290	1.683970	2.156210
H	-2.379400	2.777930	3.878220
H	-1.574620	1.236650	4.239770
H	-3.287710	1.463840	4.622220
H	-4.034000	-0.470370	3.440890
H	-2.395660	-0.939180	2.945710
H	-3.666620	-0.784280	1.735610
H	-0.710040	2.947510	2.429200
H	-2.020680	3.472800	1.342350
H	-4.616960	-0.132410	-0.248780
H	-6.647550	0.980599	-1.149770
H	-6.520180	3.313069	-1.990630
H	-4.355760	4.529290	-1.924300
H	-2.347970	3.439020	-1.019010
C	2.648711	-2.152850	-0.653780
C	3.505781	-2.805040	-1.525630
C	3.138931	-4.092710	-1.934750
C	1.965281	-4.691890	-1.482880
C	1.120191	-4.017690	-0.592170
C	1.475691	-2.746110	-0.182960
C	0.782850	-1.787630	0.761540
C	0.783381	-2.292420	2.207350
O	-0.505120	-1.414290	0.364450
C	1.692850	-0.542830	0.667040
O	1.503590	0.531350	1.218390
N	2.769670	-0.854130	-0.118690
C	3.864620	0.049320	-0.395540
C	5.188840	-0.446490	0.150790
C	6.360210	-0.278610	-0.587140
C	7.585600	-0.699810	-0.074280
C	7.645970	-1.300150	1.180430
C	6.477200	-1.476100	1.919670
C	5.255450	-1.051180	1.407100
H	4.423881	-2.343100	-1.874980
H	3.786801	-4.631630	-2.619490
H	1.705421	-5.689220	-1.822990
H	0.191511	-4.459610	-0.237280
H	1.784341	-2.596050	2.530760
H	0.108071	-3.150750	2.276670
H	0.419970	-1.494160	2.862480
H	-1.100539	-2.245600	0.430110
H	3.936460	0.210220	-1.478380

H	3.589200	1.002920	0.067800
H	6.312070	0.181030	-1.571900
H	8.490750	-0.566250	-0.658990
H	8.598270	-1.635670	1.579240
H	6.518061	-1.947590	2.896920
H	4.342920	-1.192910	1.981450
C	-3.139089	-3.203420	0.418220
C	-4.186539	-4.221980	0.894910
C	-4.022369	-4.426380	2.404690
C	-5.606399	-3.800911	0.537820
O	-3.524989	-2.129080	-0.091520
O	-1.925129	-3.527750	0.615470
H	-4.222559	-3.488400	2.937720
H	-4.723279	-5.180530	2.777880
H	-3.003479	-4.741320	2.640770
H	-3.946529	-5.171100	0.397240
H	-6.329239	-4.559151	0.858150
H	-5.854819	-2.855551	1.031840
H	-5.714749	-3.646221	-0.538850

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2605.80485258 Predicted Change= -8.341083D-08
Zero-point correction (ZPE)= -2604.9508 0.85403
Internal Energy (U)= -2604.9084 0.89642
Enthalpy (H)= -2604.9075 0.89728
Gibbs Free Energy (G)= -2605.0257 0.77908

Frequencies -- 13.4724 20.0858 21.3026

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=chloroform)

Pointgroup= C1 Stoichiometry= C43H49N3O5S C1[X(C43H49N3O5S)] #Atoms= 101
Charge = 0 Multiplicity = 1

SCF Energy= -2606.55781598

==========

(*R*)-II

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062X/6-31G(d) scf=(direct,tight,maxcycle=300,xqc)
SCRF=(PCM,SOLVENT=Chloroform) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman temp=273.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C43H49N3O5S C1[X(C43H49N3O5S)] #Atoms= 101
Charge = 0 Multiplicity = 1

SCF Energy= -2605.80214727 Predicted Change= -4.494311D-08
==========
==
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.01497	0.00180	[NO]	0.01497	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-3.668209	3.549912	-0.189580
C	-2.438749	2.917661	-0.026790
C	-1.289889	3.429131	-0.623610
C	-1.320519	4.597141	-1.382700
C	-2.548269	5.228641	-1.538140
C	-3.709909	4.711402	-0.951280
S	-2.109700	1.419081	0.819650
C	-0.426250	1.556501	0.394250
N	-0.172099	2.625690	-0.371030
N	0.548680	0.730560	0.807240
C	0.196570	-0.425790	1.567650
C	1.283639	-1.200610	2.269780
C	1.335100	-0.663610	3.711770
C	0.971439	-2.695200	2.226530
O	-0.982150	-0.653579	1.743080
C	1.955740	0.940110	0.359900
C	2.741520	1.675810	1.426280
C	1.945190	1.598210	-1.030250
C	3.353310	1.846069	-1.602810
C	3.281271	2.613509	-2.927710
C	4.093680	0.523789	-1.816580
C	1.122001	2.875080	-1.012660
C	3.995510	1.183819	1.800290
C	4.745950	1.847369	2.769380
C	4.250031	2.997689	3.377990
C	2.992561	3.481019	3.022440
C	2.241661	2.822130	2.052990
H	2.251699	-1.057930	1.794660
H	2.117899	-1.193620	4.261140
H	0.378460	-0.831510	4.217200
H	1.565960	0.406960	3.740500
H	-0.011821	-2.906210	2.658470
H	1.731469	-3.230390	2.803360
H	0.988809	-3.061700	1.197450
H	-4.566349	3.141872	0.262160
H	-0.421439	5.005441	-1.830500
H	-2.602528	6.140291	-2.123190
H	-4.655699	5.223532	-1.091150
H	2.375630	-0.059480	0.223710
H	1.437630	0.871910	-1.678190
H	3.914511	2.456329	-0.881210
H	2.910131	3.636299	-2.808810
H	2.631930	2.091810	-3.642470

H	4.277951	2.680809	-3.372510
H	5.050560	0.707109	-2.316320
H	3.501710	-0.148411	-2.452100
H	4.291500	-0.009801	-0.884490
H	0.897771	3.201150	-2.030810
H	1.635751	3.688990	-0.486580
H	4.357410	0.259589	1.352690
H	5.715780	1.454619	3.059150
H	4.833521	3.508839	4.137440
H	2.591251	4.367110	3.504440
H	1.248851	3.196160	1.810610
C	-2.654341	-1.276519	-1.510580
C	-3.787820	-0.509358	-1.744300
C	-3.617630	0.706302	-2.414280
C	-2.360460	1.126921	-2.842800
C	-1.234050	0.326041	-2.612310
C	-1.383761	-0.871879	-1.935770
C	-0.376921	-1.947429	-1.590120
C	0.112339	-2.681150	-2.844700
O	0.692509	-1.448410	-0.842750
C	-1.257071	-2.942509	-0.785320
O	-0.881941	-3.958599	-0.237300
N	-2.567041	-2.511819	-0.852980
C	-3.697001	-3.281498	-0.372310
C	-4.500111	-2.574238	0.699200
C	-3.851121	-1.959018	1.770980
C	-4.588741	-1.312038	2.758230
C	-5.981601	-1.281598	2.689040
C	-6.633071	-1.900378	1.625140
C	-5.892821	-2.540928	0.632470
H	-4.767590	-0.832418	-1.408100
H	-4.484270	1.333862	-2.600570
H	-2.255340	2.077531	-3.357560
H	-0.257330	0.635050	-2.978320
H	-0.728541	-3.041269	-3.445310
H	0.710809	-1.990160	-3.446490
H	0.739239	-3.525210	-2.546090
H	1.491579	-2.092430	-0.898120
H	-4.346811	-3.533278	-1.219920
H	-3.271302	-4.213099	0.013790
H	-2.766551	-1.974929	1.821420
H	-4.073230	-0.831908	3.585070
H	-6.555050	-0.776998	3.460730
H	-7.716911	-1.880147	1.562280
H	-6.402001	-3.015278	-0.203630
C	3.729399	-2.624431	-0.435010
C	5.047859	-3.321291	-0.813140
C	6.208199	-2.898342	0.078680
C	5.346999	-3.052481	-2.291510
O	3.744889	-1.746621	0.457550
O	2.712629	-2.989570	-1.098380
H	5.990759	-3.093361	1.131940
H	7.123249	-3.435232	-0.194590
H	6.394349	-1.823952	-0.025690
H	4.868738	-4.398441	-0.697770

```
      H        4.498849     -3.349931     -2.912110
      H        6.237069     -3.600602     -2.618450
      H        5.532959     -1.983401     -2.454040
---------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 273.150 Kelvin       Pressure= 1.00000 Atm
=====================================================================
==
 SCF Energy=     -2605.80214727   Predicted Change= -4.494311D-08
 Zero-point correction (ZPE)=            -2604.9479      0.85421
 Internal Energy (U)=                    -2604.9057      0.89640
 Enthalpy (H)=                           -2604.9048      0.89726
 Gibbs Free Energy (G)=                  -2605.0225      0.77956
---------------------------------------------------------------------
 Frequencies --      5.4242              12.4009              24.3854
=====================================================================
==
 #m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
 SCRF=(PCM,SOLVENT=chloroform)
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C43H49N3O5S   C1[X(C43H49N3O5S)]  #Atoms= 101
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -2606.55617477
=====================================================================
==
```

***(S)*-TS-III**

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---------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
=====================================================================
==
 #m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=Chloroform)
 opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
 temp=273.15
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C43H49N3O5S   C1[X(C43H49N3O5S)]  #Atoms= 101
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -2605.79447233       Predicted Change= -1.919005D-09
=====================================================================
==
 Optimization completed.          {Found       2       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00001 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00088 ||  0.00180   [ YES ]      0.00088 ||  0.00180   [ YES ]
---------------------------------------------------------------------
     Atomic              Coordinates (Angstroms)
      Type              X             Y          Z
---------------------------------------------------------------------
      C        4.757952     -2.481598     -0.016820
      C        3.404782     -2.160559     -0.027780
      C        2.507332     -2.891739     -0.805260
```

C	2.927372	-3.967649	-1.582070
C	4.280563	-4.289568	-1.562330
C	5.186362	-3.557398	-0.788750
S	2.601751	-0.845279	0.815340
C	1.070481	-1.374050	0.161160
N	1.200732	-2.408810	-0.685860
N	-0.116779	-0.899390	0.512660
C	-0.216870	0.421610	1.176350
C	-1.311320	0.490269	2.229450
C	-0.803959	-0.309041	3.438920
C	-1.585080	1.941449	2.608150
O	0.827720	1.053620	1.280460
C	-1.336199	-1.578201	0.023780
C	-1.765408	-2.711131	0.941590
C	-1.088569	-1.978001	-1.443460
C	-2.323468	-2.569911	-2.142150
C	-1.980658	-3.041911	-3.559030
C	-3.459849	-1.545162	-2.199630
C	0.103872	-2.921230	-1.511420
C	-3.124428	-2.835962	1.247350
C	-3.577938	-3.872652	2.059960
C	-2.678517	-4.793722	2.589840
C	-1.320427	-4.666871	2.307480
C	-0.867068	-3.635011	1.489730
H	-2.232510	0.038969	1.852740
H	-1.560389	-0.307311	4.229150
H	0.111170	0.145320	3.833830
H	-0.589939	-1.351071	3.178300
H	-0.647771	2.455379	2.843330
H	-2.070571	2.472089	1.787280
H	-2.238530	1.980279	3.485300
H	5.453531	-1.906098	0.584620
H	2.225153	-4.539379	-2.178900
H	4.633453	-5.124868	-2.157720
H	6.236312	-3.830157	-0.787950
H	-2.112909	-0.814771	0.024330
H	-0.806599	-1.042841	-1.947380
H	-2.661858	-3.440002	-1.561470
H	-1.277308	-3.880261	-3.563210
H	-1.540948	-2.223051	-4.141940
H	-2.886358	-3.372652	-4.075890
H	-4.300929	-1.945952	-2.774630
H	-3.120089	-0.625182	-2.692930
H	-3.830749	-1.267892	-1.210010
H	0.487772	-2.990260	-2.532140
H	-0.158708	-3.929240	-1.163480
H	-3.823658	-2.093932	0.871780
H	-4.636308	-3.950143	2.289760
H	-3.029817	-5.597822	3.229070
H	-0.607687	-5.369881	2.727630
H	0.200282	-3.546670	1.304430
C	1.123619	3.716530	-0.615960
C	1.661338	4.924321	-0.197010
C	0.779318	5.873020	0.333750
C	-0.584862	5.613799	0.434460

C	-1.106222	4.387979	-0.000480
C	-0.243651	3.440290	-0.518000
C	-0.516481	2.070759	-1.113550
C	-1.188101	2.219119	-2.492690
O	-1.249850	1.191529	-0.331790
C	0.922460	1.576420	-1.408120
O	1.237380	0.493880	-1.876370
N	1.790499	2.615621	-1.179890
C	3.210949	2.521111	-1.436020
C	4.030169	2.041642	-0.253260
C	3.667639	2.341741	1.061600
C	4.438570	1.880102	2.125020
C	5.581590	1.118012	1.889070
C	5.950470	0.820423	0.578260
C	5.173920	1.276662	-0.484990
H	2.726928	5.124961	-0.259160
H	1.172887	6.825420	0.675680
H	-1.247813	6.365349	0.851030
H	-2.171162	4.176869	0.065340
H	-0.621261	2.894289	-3.142330
H	-2.198531	2.616299	-2.362250
H	-1.244430	1.233009	-2.964560
H	3.334900	1.824531	-2.270200
H	3.559199	3.504661	-1.773650
H	2.755209	2.894181	1.261330
H	4.139059	2.109142	3.143340
H	6.181110	0.759643	2.720530
H	6.841040	0.229973	0.380930
H	5.452540	1.024052	-1.505530
C	-4.451350	1.224428	0.118740
C	-5.877490	1.697027	-0.119260
C	-6.118270	1.789917	-1.632180
C	-6.886880	0.778056	0.556820
O	-4.194820	0.135998	0.623310
O	-3.542641	2.069198	-0.296490
H	-2.538510	1.639228	-0.250190
H	-6.004090	0.803077	-2.095800
H	-7.134251	2.142506	-1.833430
H	-5.409561	2.475707	-2.102000
H	-5.947771	2.707897	0.301310
H	-7.903140	1.154566	0.406800
H	-6.824209	-0.229374	0.133950
H	-6.697840	0.700216	1.630570

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

==

SCF Energy= -2605.79447233 Predicted Change= -1.919005D-09
Zero-point correction (ZPE)= -2604.9435 0.85096
Internal Energy (U)= -2604.9018 0.89261
Enthalpy (H)= -2604.9009 0.89347
Gibbs Free Energy (G)= -2605.0161 0.77833

Frequencies -- -207.0884 14.8649 18.6602

```
================================================================================
==
 #m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
 SCRF=(PCM,SOLVENT=chloroform)
--------------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C43H49N3O5S   C1[X(C43H49N3O5S)]  #Atoms= 101
 Charge = 0         Multiplicity = 1
--------------------------------------------------------------------------------
 SCF Energy= -2606.54465096
================================================================================
==
```

***(S)*-IV**

```
--------------------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
================================================================================
==
 #m062x/6-31G(d) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
 opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman temp=273.15
 SCRF=(PCM,SOLVENT=chloroform)
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
--------------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C43H49N3O5S   C1[X(C43H49N3O5S)]  #Atoms= 101
 Charge = 0         Multiplicity = 1
--------------------------------------------------------------------------------
 SCF Energy= -2605.80442289       Predicted Change= -1.188235D-10
================================================================================
==
 Optimization completed.          {Found       2       times}
 Item      Max Val.   Criteria   Pass?      RMS Val.   Criteria   Pass?
 Force      0.00000 ||  0.00045   [ YES ]     0.00000 ||  0.00030   [ YES ]
 Displ      0.00137 ||  0.00180   [ YES ]     0.00137 ||  0.00180   [ YES ]
--------------------------------------------------------------------------------
     Atomic             Coordinates (Angstroms)
      Type              X           Y           Z
--------------------------------------------------------------------------------
      C       -3.893328      3.623984      0.277666
      C       -2.649147      3.012643      0.184137
      C       -1.625088      3.598913     -0.559568
      C       -1.805817      4.815759     -1.209722
      C       -3.051254      5.430105     -1.103265
      C       -4.084675      4.842744     -0.369810
      S       -2.151945      1.469984      0.877730
      C       -0.542681      1.700119      0.204024
      N       -0.461276      2.824997     -0.544387
      N        0.485089      0.927419      0.436053
      C        0.251469     -0.552202      1.007276
      C        1.190227     -0.712425      2.219490
      C        0.764380      0.262862      3.315134
      C        1.090225     -2.147875      2.738665
      O       -0.985725     -0.765951      1.184573
      C        1.806315      1.314395     -0.082901
      C        2.567355      2.210517      0.884067
      C        1.616037      1.928587     -1.488398
      C        2.934845      2.271976     -2.200239
```

C	2.686163	3.035242	-3.505484
C	3.740059	1.004324	-2.498488
C	0.699689	3.142700	-1.376552
C	3.932111	1.978657	1.081603
C	4.679438	2.801017	1.922313
C	4.072584	3.863519	2.586164
C	2.710495	4.094282	2.408512
C	1.964799	3.275382	1.564208
H	2.223848	-0.501603	1.909651
H	1.388607	0.133759	4.204717
H	-0.277621	0.067171	3.588660
H	0.847517	1.304566	2.992289
H	0.044273	-2.383838	2.957687
H	1.457981	-2.879611	2.015988
H	1.674506	-2.258263	3.657735
H	-4.694490	3.161334	0.845524
H	-1.002869	5.275848	-1.775844
H	-3.215760	6.381168	-1.598638
H	-5.046955	5.338901	-0.300615
H	2.363102	0.380968	-0.190209
H	1.081968	1.165913	-2.073248
H	3.524791	2.915939	-1.533530
H	2.243861	4.021365	-3.335582
H	2.016626	2.467495	-4.163404
H	3.629974	3.186163	-4.038071
H	4.680486	1.262640	-2.995675
H	3.174119	0.351297	-3.174855
H	3.981467	0.428968	-1.600635
H	0.316975	3.426825	-2.360233
H	1.228360	4.003734	-0.945412
H	4.404380	1.132426	0.591314
H	5.737174	2.601801	2.065961
H	4.654009	4.501215	3.244864
H	2.221955	4.911072	2.930912
H	0.899349	3.464098	1.459810
C	-2.085917	-3.106789	-0.700175
C	-2.964436	-4.133675	-0.390509
C	-2.422651	-5.294275	0.173216
C	-1.055825	-5.416925	0.409270
C	-0.184525	-4.371635	0.077170
C	-0.711712	-3.217748	-0.469491
C	-0.031208	-1.976550	-0.994646
C	0.769928	-2.266352	-2.265780
O	0.862381	-1.348815	-0.091897
C	-1.237200	-1.101051	-1.411005
O	-1.179122	0.008212	-1.913292
N	-2.373781	-1.858032	-1.274068
C	-3.691744	-1.383856	-1.629159
C	-4.656705	-1.296518	-0.461855
C	-4.211259	-1.249550	0.860514
C	-5.134597	-1.135078	1.899489
C	-6.499805	-1.068799	1.630171
C	-6.945475	-1.124453	0.310895
C	-6.026628	-1.243734	-0.727808
H	-4.031251	-4.037437	-0.564811

H	-3.086826	-6.113419	0.431387
H	-0.663265	-6.329001	0.846848
H	0.886730	-4.465798	0.240267
H	0.133387	-2.744858	-3.015637
H	1.605882	-2.933917	-2.039114
H	1.152739	-1.324056	-2.669124
H	-3.537721	-0.394083	-2.071987
H	-4.113030	-2.033150	-2.407514
H	-3.145203	-1.298788	1.072973
H	-4.780971	-1.100775	2.925857
H	-7.214097	-0.980930	2.443301
H	-8.008016	-1.081653	0.090703
H	-6.375965	-1.293863	-1.756986
C	4.159844	-2.320684	0.109619
C	5.349269	-3.249794	-0.008823
C	5.323346	-3.924653	-1.387879
C	6.651823	-2.498286	0.233935
O	4.233913	-1.111320	0.213114
O	2.996387	-2.966875	0.066716
H	2.255189	-2.298535	0.092233
H	5.414877	-3.174175	-2.180623
H	6.164094	-4.617873	-1.478648
H	4.394914	-4.479699	-1.540110
H	5.212491	-4.025327	0.754770
H	7.498352	-3.188510	0.181511
H	6.790109	-1.722443	-0.524834
H	6.655828	-2.014420	1.213922

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2605.80442289 Predicted Change= -1.188235D-10
Zero-point correction (ZPE)= -2604.9494 0.85498
Internal Energy (U)= -2604.9076 0.89678
Enthalpy (H)= -2604.9067 0.89764
Gibbs Free Energy (G)= -2605.0237 0.78065

Frequencies -- 7.7618 15.1900 16.2826

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=chloroform)

Pointgroup= C1 Stoichiometry= C43H49N3O5S C1[X(C43H49N3O5S)] #Atoms= 101
Charge = 0 Multiplicity = 1

SCF Energy= -2606.55126031

==========

***(R)*-IV**

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

```
================================================================================
==
 #m062x/6-31G(d) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
 opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman temp=273.15
 SCRF=(PCM,SOLVENT=chloroform)
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
--------------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C43H49N3O5S   C1[X(C43H49N3O5S)]  #Atoms= 101
 Charge = 0         Multiplicity = 1
--------------------------------------------------------------------------------
 SCF Energy= -2605.80326150       Predicted Change= -1.249006D-08
================================================================================
==
 Optimization completed.          {Found       2       times}
 Item      Max Val.   Criteria   Pass?     RMS Val.   Criteria   Pass?
 Force      0.00001 ||  0.00045   [ YES ]     0.00000 ||  0.00030   [ YES ]
 Displ      0.00137 ||  0.00180   [ YES ]     0.00137 ||  0.00180   [ YES ]
--------------------------------------------------------------------------------
     Atomic             Coordinates (Angstroms)
      Type              X           Y           Z
--------------------------------------------------------------------------------
      C       -3.795056       3.312715      -0.110153
      C       -2.529953       2.742495      -0.035310
      C       -1.427863       3.390263      -0.591561
      C       -1.550178       4.629166      -1.213520
      C       -2.818834       5.200433      -1.277010
      C       -3.930041       4.550781      -0.734351
      S       -2.098167       1.182652       0.657689
      C       -0.421331       1.457122       0.197605
      N       -0.257267       2.637576      -0.449703
      N        0.572967       0.650549       0.463413
      C        0.265106      -0.873868       0.899762
      C        1.237513      -1.227941       2.040177
      C        0.857755      -0.427869       3.285445
      C        1.134498      -2.725323       2.334691
      O       -0.973052      -1.014712       1.132574
      C        1.954839       1.070385       0.172922
      C        2.580988       1.790791       1.359106
      C        1.990487       1.890059      -1.133854
      C        3.398342       2.375119      -1.523638
      C        3.352673       3.275226      -2.763079
      C        4.334866       1.192605      -1.782272
      C        1.007831       3.054705      -1.051323
      C        3.838241       1.386202       1.814965
      C        4.449573       2.038002       2.884543
      C        3.810561       3.100834       3.515954
      C        2.550818       3.503284       3.077149
      C        1.940307       2.853333       2.008237
      H        2.267083      -0.995502       1.745852
      H        1.568120      -0.626761       4.094175
      H       -0.142942      -0.722278       3.616640
      H        0.853331       0.649693       3.097776
      H        0.097537      -2.983055       2.569237
      H        1.765338      -2.980526       3.192370
      H        1.438447      -3.337983       1.483319
```

H	-4.655785	2.801355	0.309850
H	-0.688742	5.137862	-1.632985
H	-2.940714	6.166148	-1.756112
H	-4.909059	5.013781	-0.798860
H	2.510806	0.145283	0.000168
H	1.645830	1.209820	-1.922960
H	3.796105	2.962907	-0.684797
H	2.815443	4.211073	-2.582658
H	2.868904	2.757219	-3.600444
H	4.368347	3.536259	-3.074326
H	5.320383	1.553721	-2.092169
H	3.939251	0.564201	-2.591025
H	4.470074	0.557803	-0.903652
H	0.776738	3.426675	-2.053345
H	1.428418	3.883464	-0.465959
H	4.326989	0.536851	1.346387
H	5.423329	1.704316	3.229910
H	4.284133	3.605747	4.352144
H	2.036000	4.320290	3.573235
H	0.942337	3.162678	1.708069
C	-2.537291	-1.471137	-1.519481
C	-3.629366	-0.746440	-1.976107
C	-3.374812	0.429616	-2.688718
C	-2.073030	0.842937	-2.960002
C	-0.986901	0.078545	-2.513891
C	-1.221820	-1.060380	-1.768291
C	-0.276493	-2.080736	-1.171209
C	0.422410	-2.892030	-2.262495
O	0.742349	-1.590684	-0.313446
C	-1.258361	-3.035310	-0.443500
O	-0.954393	-4.015966	0.202993
N	-2.540253	-2.661285	-0.786893
C	-3.727755	-3.357810	-0.341059
C	-4.598616	-2.534271	0.586997
C	-4.021008	-1.712961	1.558104
C	-4.834586	-0.976043	2.415980
C	-6.223383	-1.054054	2.316199
C	-6.799858	-1.872579	1.348213
C	-5.988091	-2.605968	0.484749
H	-4.644717	-1.066247	-1.764540
H	-4.211420	1.028609	-3.035985
H	-1.898898	1.757303	-3.519156
H	0.029513	0.378951	-2.751246
H	-0.312774	-3.256798	-2.985043
H	1.148856	-2.261442	-2.784122
H	0.936827	-3.747272	-1.816992
H	2.235165	-2.503449	-0.372573
H	-4.310960	-3.675156	-1.214444
H	-3.366111	-4.259133	0.164518
H	-2.937439	-1.638613	1.624902
H	-4.378969	-0.335851	3.166449
H	-6.852711	-0.476087	2.986418
H	-7.880312	-1.936086	1.258703
H	-6.438934	-3.237768	-0.277709
C	4.143992	-2.540459	-0.219028

C	5.351136	-3.377413	-0.586896
C	6.622311	-2.783744	0.007021
C	5.431512	-3.489130	-2.116393
O	4.202915	-1.452182	0.322280
O	2.998384	-3.106872	-0.580031
H	6.553348	-2.701385	1.094623
H	7.482326	-3.411346	-0.242373
H	6.796173	-1.781169	-0.395589
H	5.172885	-4.379178	-0.177418
H	4.524597	-3.936323	-2.529344
H	6.287917	-4.107004	-2.399860
H	5.566067	-2.497525	-2.562838

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2605.80326150 Predicted Change= -1.249006D-08

Zero-point correction (ZPE)=	-2604.9475	0.85576
Internal Energy (U)=	-2604.9060	0.89721
Enthalpy (H)=	-2604.9051	0.89808
Gibbs Free Energy (G)=	-2605.0196	0.78358

Frequencies -- 12.1578 24.0984 27.5389

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=chloroform)

Pointgroup= C1 Stoichiometry= C43H49N3O5S C1[X(C43H49N3O5S)] #Atoms= 101
Charge = 0 Multiplicity = 1

SCF Energy= -2606.55112559

==========

***(S)*-TS-V**

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
geom=allcheck guess=read SCRF=(PCM,SOLVENT=Chloroform)
freq=(readfc,noraman) temp=273.15

Pointgroup= C1 Stoichiometry= C43H49N3O5S C1[X(C43H49N3O5S)] #Atoms= 101
Charge = 0 Multiplicity = 1

==========

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-3.946889	3.553005	0.284283
C	-2.679979	2.989426	0.212534

C	-1.672849	3.591176	-0.546315
C	-1.902772	4.781020	-1.229983
C	-3.173125	5.348295	-1.147628
C	-4.185761	4.743144	-0.401738
S	-2.125357	1.495830	0.960308
C	-0.516511	1.743770	0.263518
N	-0.482630	2.866635	-0.509588
N	0.502642	0.985735	0.493003
C	0.239246	-0.717618	1.083003
C	1.210349	-0.787349	2.263136
C	0.772190	0.183030	3.355804
C	1.201366	-2.223486	2.800330
O	-0.979383	-0.885311	1.247224
C	1.802145	1.352919	-0.075022
C	2.601764	2.225836	0.883339
C	1.593320	1.989159	-1.470664
C	2.901980	2.343934	-2.196568
C	2.640451	3.136710	-3.481899
C	3.699231	1.081225	-2.535012
C	0.674385	3.200850	-1.336236
C	3.972030	1.992062	1.036699
C	4.742522	2.798434	1.872183
C	4.153392	3.846375	2.574556
C	2.786308	4.078215	2.441089
C	2.017232	3.274111	1.603364
H	2.218402	-0.529340	1.910666
H	1.431682	0.097414	4.224567
H	-0.249417	-0.053450	3.670199
H	0.797320	1.218680	3.006851
H	0.181158	-2.505102	3.079875
H	1.563243	-2.947067	2.065690
H	1.838276	-2.296669	3.686944
H	-4.730789	3.074267	0.862658
H	-1.116692	5.256717	-1.806593
H	-3.372631	6.275821	-1.673903
H	-5.168088	5.200568	-0.352728
H	2.345227	0.412900	-0.206382
H	1.051971	1.235231	-2.059871
H	3.504158	2.971383	-1.525206
H	2.216460	4.125898	-3.284980
H	1.950589	2.592706	-4.138854
H	3.576198	3.284850	-4.029372
H	4.642189	1.348038	-3.022789
H	3.129600	0.454899	-3.233247
H	3.935511	0.474967	-1.656343
H	0.292279	3.497745	-2.316287
H	1.204998	4.056782	-0.896572
H	4.430274	1.157218	0.514247
H	5.804320	2.598776	1.980932
H	4.752117	4.472013	3.229286
H	2.313167	4.883910	2.994086
H	0.948644	3.460825	1.529970
C	-2.100093	-3.101570	-0.723971
C	-2.987521	-4.125397	-0.431255
C	-2.455703	-5.299158	0.115235

C	-1.090528	-5.437350	0.352903
C	-0.209522	-4.394478	0.038655
C	-0.727177	-3.230186	-0.494124
C	-0.036291	-1.982628	-0.985055
C	0.795926	-2.232754	-2.241912
O	0.844262	-1.385836	-0.040588
C	-1.233189	-1.088344	-1.394634
O	-1.163680	0.028651	-1.873382
N	-2.375903	-1.839719	-1.273855
C	-3.688615	-1.351827	-1.633631
C	-4.662095	-1.273462	-0.472785
C	-4.223309	-1.224804	0.851520
C	-5.150733	-1.114277	1.887009
C	-6.514977	-1.053976	1.611839
C	-6.954701	-1.111548	0.290454
C	-6.031084	-1.226571	-0.744808
H	-4.053224	-4.017578	-0.604584
H	-3.127466	-6.116235	0.359293
H	-0.707219	-6.358496	0.779085
H	0.860379	-4.498394	0.204978
H	0.173638	-2.675015	-3.024653
H	1.618403	-2.918059	-2.020115
H	1.198861	-1.280131	-2.598800
H	-3.524167	-0.356992	-2.060662
H	-4.106842	-1.987257	-2.424584
H	-3.158795	-1.270144	1.068171
H	-4.801359	-1.078394	2.914664
H	-7.232907	-0.969525	2.421963
H	-8.016328	-1.073252	0.065665
H	-6.375810	-1.277749	-1.775334
C	4.196305	-2.313734	0.059235
C	5.399648	-3.222713	-0.070907
C	5.334245	-3.960322	-1.416294
C	6.692624	-2.432108	0.085129
O	4.245913	-1.102310	0.134015
O	3.042076	-2.983933	0.065524
H	2.298359	-2.327356	0.105754
H	5.368054	-3.245253	-2.245264
H	6.191722	-4.631736	-1.512953
H	4.418524	-4.549344	-1.502371
H	5.312613	-3.965736	0.731575
H	7.552836	-3.104239	0.024361
H	6.779393	-1.684781	-0.709105
H	6.725210	-1.908458	1.043612

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

==

SCF Energy= mination of G		
Zero-point correction (ZPE)=	-2604.9496	0.85353
Internal Energy (U)=	-2604.9078	0.89532
Enthalpy (H)=	-2604.9069	0.89618
Gibbs Free Energy (G)=	-2605.0249	0.77822

```
 Frequencies --   -178.5325               6.9215              12.1243
=======================================================================================
==
 #M062X/6-311++G(2df,p) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=Chloroform)
---------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C43H49N3O5S   C1[X(C43H49N3O5S)]  #Atoms= 101
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -2606.55007765
=======================================================================================
==
```

***(R)*-TS-V**

```
---------------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
=======================================================================================
==
 #m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
 temp=273.15 SCRF=(PCM,SOLVENT=chloroform)
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C43H49N3O5S   C1[X(C43H49N3O5S)]  #Atoms= 101
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -2605.80256942       Predicted Change=  1.138155D-08
=======================================================================================
==
 Optimization completed.           {Found       2       times}
 Item      Max Val.   Criteria   Pass?      RMS Val.    Criteria   Pass?
 Force      0.00002 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00125 ||  0.00180   [ YES ]      0.00125 ||  0.00180   [ YES ]
---------------------------------------------------------------------------
     Atomic              Coordinates (Angstroms)
      Type              X             Y          Z
---------------------------------------------------------------------------
      C       -3.817139       3.248351      -0.138160
      C       -2.540509       2.708631      -0.052520
      C       -1.448289       3.371251      -0.615110
      C       -1.600789       4.597331      -1.255150
      C       -2.882789       5.138841      -1.331790
      C       -3.980249       4.473641      -0.782640
      S       -2.077819       1.175531       0.673670
      C       -0.394439       1.466220       0.206490
      N       -0.262409       2.651390      -0.457250
      N        0.592760       0.674200       0.478460
      C        0.252010      -1.020840       0.945030
      C        1.273280      -1.289180       2.052700
      C        0.891690      -0.495790       3.299170
      C        1.269880      -2.791950       2.354860
      O       -0.966350      -1.107289       1.191040
      C        1.963821       1.095220       0.169110
      C        2.597021       1.798710       1.362620
      C        1.996431       1.934810      -1.127650
```

C	3.402861	2.430220	-1.509320
C	3.358151	3.351790	-2.732850
C	4.342711	1.254429	-1.787950
C	1.004031	3.092260	-1.034620
C	3.858661	1.397930	1.809690
C	4.466951	2.038669	2.887940
C	3.820701	3.086690	3.536720
C	2.556311	3.484720	3.107040
C	1.948441	2.844590	2.030790
H	2.273810	-1.000290	1.713930
H	1.650970	-0.625590	4.076590
H	-0.068940	-0.851770	3.683960
H	0.801490	0.573370	3.086520
H	0.259550	-3.115850	2.623000
H	1.941860	-3.003610	3.192540
H	1.587390	-3.388390	1.495820
H	-4.666019	2.722941	0.288900
H	-0.750349	5.120451	-1.679570
H	-3.023988	6.094341	-1.826020
H	-4.969589	4.912681	-0.856180
H	2.523190	0.173800	-0.018560
H	1.654561	1.266070	-1.928520
H	3.799331	3.004080	-0.660270
H	2.820451	4.283950	-2.535800
H	2.874381	2.848690	-3.579330
H	4.373841	3.618589	-3.039550
H	5.331351	1.622709	-2.079200
H	3.955050	0.647080	-2.616390
H	4.469770	0.597489	-0.924140
H	0.785101	3.480280	-2.033410
H	1.413431	3.914010	-0.430910
H	4.354100	0.560639	1.326850
H	5.444441	1.708359	3.226140
H	4.292331	3.583379	4.378960
H	2.036181	4.290370	3.616140
H	0.947301	3.149230	1.735680
C	-2.555410	-1.503809	-1.496930
C	-3.628420	-0.759339	-1.967390
C	-3.342040	0.408491	-2.681180
C	-2.029540	0.797241	-2.939600
C	-0.963650	0.013401	-2.481700
C	-1.231700	-1.119679	-1.738860
C	-0.312130	-2.152170	-1.130900
C	0.388350	-2.986800	-2.200680
O	0.708800	-1.665630	-0.266930
C	-1.313010	-3.080039	-0.394410
O	-1.024511	-4.049819	0.274740
N	-2.584890	-2.688369	-0.752120
C	-3.788940	-3.352209	-0.297470
C	-4.655500	-2.482299	0.591590
C	-4.075200	-1.662669	1.562220
C	-4.882670	-0.874399	2.379230
C	-6.269930	-0.899988	2.238510
C	-6.849910	-1.717988	1.272310
C	-6.043110	-2.502538	0.449690

H	-4.652410	-1.056319	-1.765130
H	-4.162919	1.022861	-3.038920
H	-1.833059	1.707911	-3.497320
H	0.062830	0.292150	-2.701550
H	-0.345150	-3.362270	-2.919160
H	1.120850	-2.371740	-2.731970
H	0.895279	-3.834930	-1.732910
H	2.286000	-2.496990	-0.416140
H	-4.367570	-3.688539	-1.166610
H	-3.447601	-4.241909	0.241490
H	-2.992680	-1.629979	1.660510
H	-4.423890	-0.235809	3.129040
H	-6.895280	-0.282918	2.876740
H	-7.928870	-1.741248	1.151740
H	-6.496240	-3.132868	-0.312580
C	4.191810	-2.505421	-0.270170
C	5.411570	-3.311911	-0.662350
C	6.674230	-2.706331	-0.062160
C	5.488020	-3.397901	-2.193480
O	4.228840	-1.441811	0.317950
O	3.054050	-3.072870	-0.661930
H	6.605900	-2.640891	1.026550
H	7.543420	-3.316561	-0.322340
H	6.831800	-1.695451	-0.450580
H	5.253139	-4.323491	-0.268630
H	4.587859	-3.854381	-2.610840
H	6.353869	-3.996811	-2.488630
H	5.604590	-2.397641	-2.625200

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2605.80256942 Predicted Change= 1.138155D-08
Zero-point correction (ZPE)= -2604.9476 0.85492
Internal Energy (U)= -2604.9064 0.89607
Enthalpy (H)= -2604.9056 0.89693
Gibbs Free Energy (G)= -2605.0192 0.78328

Frequencies -- -165.5347 17.4189 25.1755

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=chloroform)

Pointgroup= C1 Stoichiometry= C43H49N3O5S C1[X(C43H49N3O5S)] #Atoms= 101
Charge = 0 Multiplicity = 1

SCF Energy= -2606.55062248

==========

ammonium•••isobutyrate

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

```
=============================================================================
==
 #m062x/6-31G(d) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
 opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman temp=273.15
 SCRF=(PCM,SOLVENT=chloroform)
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
-----------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C12H27NO2   C1[X(C12H27NO2)]  #Atoms= 42
 Charge = 0         Multiplicity = 1
-----------------------------------------------------------------------------
 SCF Energy= -678.441412696       Predicted Change= -5.710190D-09
=============================================================================
==
 Optimization completed.          {Found       2       times}
 Item      Max Val.   Criteria   Pass?     RMS Val.   Criteria   Pass?
 Force      0.00001 ||  0.00045   [ YES ]     0.00000 ||  0.00030   [ YES ]
 Displ      0.00053 ||  0.00180   [ YES ]     0.00053 ||  0.00180   [ YES ]
-----------------------------------------------------------------------------
     Atomic             Coordinates (Angstroms)
      Type              X           Y           Z
-----------------------------------------------------------------------------
      N       -1.248428    0.015281   -0.128700
      C       -1.299154   -0.757427   -1.407243
      C       -0.702034   -2.153006   -1.284537
      C       -2.124067   -0.501730    0.989323
      C       -3.418482   -1.157113    0.514295
      C       -1.324384   -1.415626    1.917066
      C       -1.400702    1.496184   -0.384612
      C       -0.906751    2.297210    0.816839
      C       -2.812911    1.890254   -0.796026
      H       -2.328082   -0.789761   -1.773869
      H       -0.587717   -2.573086   -2.287230
      H       -1.329616   -2.836794   -0.708577
      H        0.284956   -2.102321   -0.816068
      H       -0.690756   -0.179699   -2.104396
      H       -4.034985   -1.365813    1.393242
      H       -3.238466   -2.108421    0.006445
      H       -3.994934   -0.510119   -0.151598
      H       -2.399855    0.383997    1.566835
      H       -0.420604   -0.916588    2.274168
      H       -1.025449   -2.341008    1.417867
      H       -1.946444   -1.679255    2.777226
      H       -0.701991    1.677327   -1.204864
      H       -1.611543    2.277161    1.654209
      H       -0.790254    3.341638    0.514461
      H        0.063237    1.924273    1.157192
      H       -2.816561    2.950124   -1.065669
      H       -3.524161    1.757466    0.026033
      H       -3.166133    1.325544   -1.663708
      C        1.915208    0.252514   -0.412190
      C        3.429287    0.172686   -0.206419
      C        3.854989   -1.294890   -0.113122
      C        3.835276    0.936944    1.054593
      O        1.454853    0.710073   -1.469160
      O        1.207421   -0.194209    0.565822
```

```
      H        3.571806     -1.849248     -1.014145
      H        3.369707     -1.768287      0.745950
      H        4.939849     -1.378263      0.011513
      H        3.349979      0.493613      1.929098
      H        3.537695      1.989270      0.996557
      H        4.919914      0.897385      1.200541
      H        3.892802      0.633612     -1.084724
      H       -0.159230     -0.082622      0.203325
---------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 273.150 Kelvin       Pressure= 1.00000 Atm
=====================================================================
==
 SCF Energy=     -678.441412696   Predicted Change= -5.710190D-09
 Zero-point correction (ZPE)=            -678.0532       0.38813
 Internal Energy (U)=                    -678.0363       0.40501
 Enthalpy (H)=                           -678.0355       0.40588
 Gibbs Free Energy (G)=                  -678.0951       0.34624
---------------------------------------------------------------------
 Frequencies --     26.4592              36.1674              58.9967
=====================================================================
==
 #m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
 SCRF=(PCM,SOLVENT=chloroform)
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C12H27NO2   C1[X(C12H27NO2)]  #Atoms= 42
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -678.674489121
=====================================================================
==
```

4.5-ester

```
---------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
=====================================================================
==
 #m062x/6-31G(d) gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
 opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman temp=273.15
 SCRF=(PCM,SOLVENT=chloroform)
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C20H21NO3   C1[X(C20H21NO3)]  #Atoms= 45
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -1054.81583092       Predicted Change= -8.835096D-09
=====================================================================
==
 Optimization completed.          {Found       1       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00000 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.01207 ||  0.00180   [ NO ]       0.01207 ||  0.00180   [ NO ]
---------------------------------------------------------------------
      Atomic             Coordinates (Angstroms)
       Type              X           Y           Z
```

C	-3.053840	-0.221330	-0.315621
C	-4.540070	-0.501620	-0.332791
C	-5.097580	-0.339480	-1.741351
C	-4.781820	-1.913610	0.222629
O	-2.342680	-0.090560	-1.282301
H	-5.006220	0.222150	0.346609
H	-4.918090	0.666430	-2.129171
H	-6.174960	-0.525870	-1.739071
H	-4.623360	-1.052610	-2.421721
H	-4.287420	-2.659520	-0.408471
H	-4.395360	-2.011500	1.239399
H	-5.853600	-2.129390	0.231399
C	0.474040	1.056660	-0.193781
C	1.245439	2.078050	-0.724241
C	0.876839	3.390700	-0.408671
C	-0.216371	3.662560	0.410029
C	-0.972521	2.615000	0.950299
C	-0.619230	1.317070	0.639149
C	-1.174640	-0.001300	1.110949
C	-0.896150	-0.267100	2.585349
O	-2.583040	-0.168200	0.950009
C	-0.373820	-1.020530	0.264409
O	-0.551780	-2.220460	0.245039
N	0.618410	-0.326780	-0.379751
C	1.602340	-0.946670	-1.244521
C	3.001570	-0.875800	-0.669501
C	3.236960	-1.309529	0.637299
C	4.519360	-1.265029	1.173109
C	5.581220	-0.785259	0.405899
C	5.353130	-0.352429	-0.896721
C	4.065830	-0.396809	-1.431121
H	0.172790	-0.161990	2.789339
H	-1.214090	-1.282720	2.834909
H	-1.445820	0.451700	3.198559
H	2.103250	1.870590	-1.355541
H	1.460409	4.212030	-0.812931
H	-0.479381	4.690750	0.635109
H	-1.823901	2.816930	1.594789
H	1.282730	-1.986740	-1.361301
H	1.565130	-0.468590	-2.230181
H	2.407670	-1.686700	1.232229
H	4.692870	-1.606029	2.189239
H	6.582070	-0.748019	0.824849
H	6.174770	0.024391	-1.498131
H	3.887550	-0.055339	-2.448481

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1054.81583092 Predicted Change= -8.835096D-09
Zero-point correction (ZPE)= -1054.4408 0.37497
Internal Energy (U)= -1054.4221 0.39368
Enthalpy (H)= -1054.4212 0.39454

```
 Gibbs Free Energy (G)=                -1054.4893        0.32645
---------------------------------------------------------------------------
 Frequencies --      8.1209               12.1562               21.8857
===========================================================================
==
 #m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
 SCRF=(PCM,SOLVENT=chloroform)
---------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C20H21NO3   C1[X(C20H21NO3)]  #Atoms= 45
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -1055.16045427
===========================================================================
==
```

Structures from the conformational analysis

***(S)*-TS-III-A**

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
==
#m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Chloroform)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
temp=273.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C43H49N3O5S C1[X(C43H49N3O5S)] #Atoms= 101
Charge = 0 Multiplicity = 1

SCF Energy= -2605.79277352 Predicted Change= -4.064703D-09
==========
==
Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00665	0.00180	[NO]	0.00665	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.523336	4.698896	-0.986203
C	1.526809	3.758114	-0.747660
C	0.619258	3.935511	0.295119
C	0.661032	5.060352	1.113333
C	1.653226	6.002910	0.865609
C	2.575421	5.825260	-0.170008
S	1.244604	2.239376	-1.590200
C	-0.127703	1.924980	-0.545546
N	-0.290415	2.877218	0.386035
N	-0.976968	0.918151	-0.681849
C	-0.606853	-0.236370	-1.533116
C	-1.783930	-0.876386	-2.251309
C	-2.199329	0.088210	-3.372766
C	-1.376939	-2.226868	-2.831003
O	0.514714	-0.198958	-2.022702
C	-2.167593	0.843917	0.195850
C	-3.360690	1.560640	-0.411036
C	-1.757399	1.333735	1.597999
C	-2.878738	1.211251	2.642913
C	-2.469885	1.848522	3.974955
C	-3.250816	-0.256377	2.868292
C	-1.231707	2.758419	1.503212
C	-4.602318	0.918752	-0.393395
C	-5.732929	1.549453	-0.909117
C	-5.636623	2.825012	-1.458498
C	-4.399790	3.464801	-1.497399
C	-3.270598	2.837745	-0.977537
H	-2.618073	-1.018720	-1.559619

H	-3.063566	-0.318474	-3.906074
H	-1.378236	0.209722	-4.087340
H	-2.474819	1.074894	-2.987305
H	-0.478483	-2.120456	-3.446832
H	-1.169137	-2.948575	-2.039446
H	-2.186201	-2.617896	-3.455695
H	3.238421	4.558648	-1.790033
H	-0.057796	5.201495	1.912980
H	1.707514	6.889473	1.488160
H	3.341245	6.573761	-0.342303
H	-2.395808	-0.218598	0.277625
H	-0.918782	0.688989	1.893161
H	-3.761351	1.745818	2.263469
H	-2.339210	2.932688	3.900369
H	-1.530679	1.414906	4.340069
H	-3.239277	1.664745	4.730584
H	-4.007741	-0.337627	3.655017
H	-2.368356	-0.824604	3.189321
H	-3.644270	-0.738927	1.970370
H	-0.676012	3.025413	2.405009
H	-2.044623	3.482439	1.360379
H	-4.671668	-0.091809	0.000909
H	-6.688924	1.034902	-0.890930
H	-6.516585	3.313533	-1.865464
H	-4.309217	4.452661	-1.938633
H	-2.312399	3.346987	-1.045130
C	2.762017	-2.047047	-0.749774
C	3.729210	-2.638353	-1.546320
C	3.429145	-3.891369	-2.093224
C	2.213024	-4.519750	-1.837393
C	1.256017	-3.905657	-1.017922
C	1.535666	-2.662504	-0.484698
C	0.728980	-1.780962	0.451420
C	0.682675	-2.391049	1.863831
O	-0.557388	-1.464924	0.037105
C	1.647051	-0.535390	0.559296
O	1.412651	0.484480	1.191170
N	2.819066	-0.801547	-0.099080
C	3.910468	0.138044	-0.219565
C	5.193643	-0.357778	0.415806
C	6.419588	-0.129776	-0.209102
C	7.606577	-0.554581	0.384279
C	7.575025	-1.218439	1.607692
C	6.351938	-1.454275	2.234484
C	5.168352	-1.025880	1.641276
H	4.683976	-2.156658	-1.733168
H	4.164594	-4.380732	-2.724652
H	2.008482	-5.493053	-2.272169
H	0.305624	-4.390001	-0.804352
H	1.687994	-2.630252	2.227575
H	0.086337	-3.307275	1.845538
H	0.217159	-1.669772	2.542725
H	-1.356689	-2.555607	0.154054
H	4.077909	0.362840	-1.280722
H	3.566371	1.057101	0.267215

H	6.445114	0.380749	-1.169233
H	8.554459	-0.374046	-0.113633
H	8.497973	-1.556259	2.068907
H	6.320204	-1.975568	3.186474
H	4.213095	-1.212752	2.126494
C	-3.209613	-3.243892	0.380185
C	-4.032056	-4.444343	0.823940
C	-3.691634	-4.753212	2.288626
C	-5.523180	-4.198742	0.632418
O	-3.718578	-2.153659	0.136713
O	-1.924540	-3.479021	0.322743
H	-3.962212	-3.904596	2.927588
H	-4.252017	-5.627812	2.632154
H	-2.624050	-4.950411	2.411090
H	-3.707247	-5.293604	0.210569
H	-6.095612	-5.081327	0.933048
H	-5.848174	-3.350069	1.241697
H	-5.758391	-3.969556	-0.410262

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2605.79277352 Predicted Change= -4.064703D-09

Zero-point correction (ZPE)=	-2604.9407	0.85198
Internal Energy (U)=	-2604.8992	0.89354
Enthalpy (H)=	-2604.8983	0.89441
Gibbs Free Energy (G)=	-2605.0150	0.77767

Frequencies -- -211.7632 8.8420 16.6747

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=chloroform)

Pointgroup= C1 Stoichiometry= C43H49N3O5S C1[X(C43H49N3O5S)] #Atoms= 101
Charge = 0 Multiplicity = 1

SCF Energy= -2606.54325898

==========

***(S)*-TS-III-B**

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Chloroform)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
temp=273.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C43H49N3O5S C1[X(C43H49N3O5S)] #Atoms= 101
Charge = 0 Multiplicity = 1

SCF Energy= -2605.77834415 Predicted Change= -5.914557D-10
==========
==
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00065	0.00180	[YES]	0.00065	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.715298	5.433374	-0.716702
C	-0.043912	4.215024	-0.700536
C	1.319798	4.161628	-0.414174
C	2.052189	5.311100	-0.129981
C	1.374096	6.524959	-0.139605
C	0.006908	6.587078	-0.428399
S	-0.699842	2.614431	-1.020251
C	0.880092	1.924384	-0.746850
N	1.813145	2.853337	-0.468870
N	1.167090	0.630861	-0.757318
C	0.291882	-0.287092	-1.545221
C	1.062883	-1.162272	-2.526170
C	0.156343	-2.243235	-3.104939
C	1.562150	-0.235155	-3.645635
O	-0.823242	0.142501	-1.805349
C	2.420171	0.196054	-0.092420
C	2.281081	0.130527	1.424777
C	3.569977	1.093415	-0.591822
C	4.936809	0.736093	0.018336
C	6.030770	1.667184	-0.514038
C	5.305204	-0.720527	-0.263284
C	3.248950	2.571024	-0.354641
C	2.125734	1.249331	2.254166
C	2.046245	1.105508	3.637949
C	2.106265	-0.158344	4.219123
C	2.249461	-1.278822	3.403928
C	2.340657	-1.132839	2.021818
H	1.910128	-1.640648	-2.029989
H	0.709342	-2.809621	-3.861208
H	-0.721343	-1.791287	-3.576689
H	-0.190223	-2.927252	-2.330452
H	2.218270	0.559756	-3.276432
H	0.711216	0.234039	-4.150696
H	2.122270	-0.816279	-4.383469
H	-1.775264	5.479310	-0.943796
H	3.113157	5.264558	0.090775
H	1.918476	7.436828	0.080598
H	-0.499331	7.546357	-0.428859
H	2.596230	-0.825340	-0.434144
H	3.636942	0.929856	-1.675853
H	4.860152	0.875388	1.105932
H	5.865043	2.714222	-0.240512
H	6.090551	1.605011	-1.607478

H	7.003844	1.373847	-0.109584
H	6.306353	-0.933221	0.124363
H	4.607409	-1.431399	0.185658
H	5.314397	-0.912003	-1.343578
H	3.755231	3.201152	-1.091569
H	3.577863	2.887095	0.642340
H	2.020950	2.248087	1.846687
H	1.922388	1.987337	4.259549
H	2.036944	-0.268807	5.296918
H	2.291812	-2.271976	3.841573
H	2.450629	-2.005051	1.383525
C	-2.824251	2.037708	1.957970
C	-3.451063	1.292110	0.951214
C	-2.820331	0.129831	0.532155
C	-1.608758	-0.295990	1.088275
C	-1.021092	0.425839	2.105380
C	-1.627882	1.615516	2.532056
N	-3.243518	-0.784709	-0.439374
C	-4.379974	-0.592517	-1.309220
C	-5.706228	-0.708042	-0.585556
C	-2.321410	-1.795975	-0.605207
O	-2.426596	-2.713860	-1.393397
C	-1.200245	-1.608669	0.457009
O	0.089204	-1.598106	-0.093011
C	-1.325441	-2.761486	1.461959
C	-6.758460	0.153513	-0.894286
C	-7.988623	0.027466	-0.251229
C	-8.173334	-0.961063	0.711841
C	-7.123336	-1.822180	1.028243
C	-5.897171	-1.695668	0.383014
H	-3.292020	2.955314	2.303046
H	-4.399539	1.606135	0.526023
H	-0.110644	0.063992	2.570536
H	-1.167555	2.199732	3.323562
H	-4.294347	-1.362752	-2.082688
H	-4.298354	0.386351	-1.799176
H	0.540522	-2.686865	-0.211900
H	-1.186288	-3.715868	0.948693
H	-2.308880	-2.745315	1.942615
H	-0.551217	-2.647027	2.227542
H	-6.613612	0.929460	-1.642564
H	-8.799844	0.705388	-0.499063
H	-9.129712	-1.059041	1.216247
H	-7.260374	-2.593289	1.780236
H	-5.075258	-2.363199	0.630879
O	3.006428	-3.002578	-0.625692
C	2.235115	-3.948868	-0.415852
C	2.782182	-5.363292	-0.243311
C	4.128837	-5.538425	-0.933925
C	2.885251	-5.630597	1.264970
O	0.960837	-3.843793	-0.253958
H	4.511646	-6.552558	-0.781361
H	4.852701	-4.825700	-0.529046
H	4.050199	-5.357544	-2.010059
H	3.592987	-4.928616	1.721909

```
      H        3.244020     -6.646933      1.455393
      H        1.912912     -5.506039      1.749898
      H        2.043168     -6.051866     -0.667214
---------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 273.150 Kelvin       Pressure= 1.00000 Atm
=====================================================================
==
 SCF Energy=     -2605.77834415   Predicted Change= -5.914557D-10
 Zero-point correction (ZPE)=            -2604.9286      0.84972
 Internal Energy (U)=                    -2604.8870      0.89133
 Enthalpy (H)=                           -2604.8861      0.89220
 Gibbs Free Energy (G)=                  -2605.0016      0.77667
---------------------------------------------------------------------
 Frequencies --   -666.7690              14.7253              19.3787
=====================================================================
==
 #m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
 SCRF=(PCM,SOLVENT=chloroform)
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C43H49N3O5S   C1[X(C43H49N3O5S)]  #Atoms= 101
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -2606.53041163
=====================================================================
==
```

***(S)*-TS-III-C**

```
---------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
=====================================================================
==
 #m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=Chloroform)
 opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
 temp=273.15
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C43H49N3O5S   C1[X(C43H49N3O5S)]  #Atoms= 101
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -2605.78148136       Predicted Change= -1.835885D-09
=====================================================================
==
 Optimization completed.          {Found       2       times}
 Item      Max Val.   Criteria   Pass?      RMS Val.   Criteria   Pass?
 Force      0.00001 ||  0.00045   [ YES ]     0.00000 ||  0.00030   [ YES ]
 Displ      0.00060 ||  0.00180   [ YES ]     0.00060 ||  0.00180   [ YES ]
---------------------------------------------------------------------
     Atomic             Coordinates (Angstroms)
      Type              X           Y           Z
---------------------------------------------------------------------
      C       -3.865082      3.492657     -0.636011
      C       -2.597341      2.919588     -0.645881
      C       -1.456592      3.721199     -0.679091
```

C	-1.541113	5.110769	-0.693861
C	-2.810403	5.678248	-0.674591
C	-3.959253	4.880367	-0.645831
S	-2.186540	1.209068	-0.636041
C	-0.492521	1.629309	-0.670411
N	-0.283651	2.957480	-0.711521
N	0.515140	0.767650	-0.622961
C	0.281841	-0.621830	-1.099531
C	1.283011	-1.091900	-2.148131
C	1.124792	-2.587700	-2.404501
C	0.977501	-0.305000	-3.432581
O	-0.889839	-0.973651	-1.132271
C	1.851110	1.283211	-0.235671
C	1.984770	1.479721	1.270369
C	2.145409	2.542581	-1.073481
C	3.518558	3.169172	-0.772071
C	3.747458	4.417162	-1.630011
C	4.646139	2.161453	-0.998331
C	1.032558	3.580310	-0.903121
C	1.289329	2.448770	2.005969
C	1.499759	2.590131	3.376129
C	2.397619	1.758231	4.039339
C	3.083480	0.781632	3.320429
C	2.881110	0.647481	1.948489
H	2.305831	-0.890799	-1.821051
H	1.812512	-2.890019	-3.201261
H	1.341212	-3.172059	-1.510221
H	0.101962	-2.812220	-2.721941
H	-0.042369	-0.520300	-3.768551
H	1.670321	-0.606649	-4.223001
H	1.070350	0.777450	-3.299211
H	-4.754291	2.871217	-0.616871
H	-0.651303	5.730249	-0.719401
H	-2.907154	6.758518	-0.683481
H	-4.937773	5.348197	-0.630531
H	2.560980	0.501671	-0.512051
H	2.151899	2.219951	-2.123221
H	3.520878	3.468182	0.285589
H	3.017537	5.207592	-1.428211
H	3.693108	4.166332	-2.696451
H	4.740887	4.831423	-1.435181
H	5.615649	2.644203	-0.841441
H	4.584540	1.295943	-0.334251
H	4.621829	1.783623	-2.028101
H	0.956928	4.213910	-1.791221
H	1.230068	4.229390	-0.041861
H	0.539489	3.081320	1.545629
H	0.947068	3.346480	3.925249
H	2.556459	1.866241	5.107879
H	3.779410	0.119412	3.826819
H	3.408301	-0.118038	1.384629
C	-3.098650	0.169148	2.906109
C	-3.300399	-0.989472	2.146179
C	-2.174969	-1.632962	1.650839
C	-0.883329	-1.155001	1.899669

C	-0.695760	-0.035421	2.682769
C	-1.817990	0.644569	3.175149
N	-2.108458	-2.808072	0.891219
C	-3.243197	-3.629442	0.526639
C	-4.276208	-2.904923	-0.312611
C	-0.803398	-3.114311	0.563259
O	-0.453777	-4.076391	-0.090011
C	0.127082	-2.102200	1.295619
O	1.074031	-1.475040	0.471619
C	0.857762	-2.892060	2.390919
C	-3.879448	-2.036133	-1.331161
C	-4.836219	-1.382403	-2.103591
C	-6.194929	-1.593464	-1.871291
C	-6.593498	-2.462114	-0.858581
C	-5.636328	-3.111024	-0.080301
H	-3.962540	0.696957	3.299719
H	-4.298959	-1.364743	1.946389
H	0.308330	0.293260	2.926769
H	-1.683630	1.535839	3.781309
H	-3.716167	-4.019653	1.437069
H	-2.823867	-4.478712	-0.022601
H	2.032722	-2.092519	0.348209
H	1.507322	-2.205969	2.943639
H	1.464823	-3.677219	1.933479
H	0.140363	-3.342340	3.083509
H	-2.820188	-1.865022	-1.501641
H	-4.517699	-0.706073	-2.892081
H	-6.938949	-1.082445	-2.474981
H	-7.649118	-2.630575	-0.667581
H	-5.949727	-3.779444	0.718669
O	4.169431	-1.040378	-0.554531
C	4.100012	-2.245458	-0.267181
C	5.285292	-3.174787	-0.533911
C	4.865053	-4.228337	-1.565351
C	6.521412	-2.406206	-0.982541
O	3.070282	-2.826688	0.237679
H	3.978453	-4.768758	-1.226091
H	5.673604	-4.945737	-1.737961
H	4.629483	-3.748537	-2.522891
H	6.814221	-1.657266	-0.241841
H	6.319602	-1.879756	-1.920491
H	7.362392	-3.089156	-1.140971
H	5.490993	-3.692037	0.412149

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2605.78148136 Predicted Change= -1.835885D-09
Zero-point correction (ZPE)= -2604.9307 0.85068
Internal Energy (U)= -2604.8895 0.89191
Enthalpy (H)= -2604.8887 0.89277
Gibbs Free Energy (G)= -2605.0014 0.78007

Frequencies -- -395.5042 17.1398 22.5801

```
=============================================================================
==
 #m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
 SCRF=(PCM,SOLVENT=chloroform)
-----------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C43H49N3O5S   C1[X(C43H49N3O5S)]  #Atoms= 101
 Charge = 0         Multiplicity = 1
-----------------------------------------------------------------------
 SCF Energy= -2606.53252154
=============================================================================
==
```

***(S)*-TS-III-D**

```
-----------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
=============================================================================
==
 #m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=Chloroform)
 opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
 temp=273.15
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
-----------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C43H49N3O5S   C1[X(C43H49N3O5S)]  #Atoms= 101
 Charge = 0         Multiplicity = 1
-----------------------------------------------------------------------
 SCF Energy= -2605.78353956       Predicted Change= -7.914087D-10
=============================================================================
==
 Optimization completed on the basis of negligible forces.          {Found       2       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00000 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00189 ||  0.00180   [ NO ]       0.00189 ||  0.00180   [ YES ]
-----------------------------------------------------------------------
     Atomic              Coordinates (Angstroms)
      Type              X             Y          Z
-----------------------------------------------------------------------
      C       -4.831860     -0.771749     -2.247023
      C       -3.540899     -0.789137     -1.727869
      C       -3.203135     -1.668724     -0.703706
      C       -4.117660     -2.587665     -0.196956
      C       -5.402937     -2.576316     -0.726628
      C       -5.760934     -1.672912     -1.733544
      S       -2.162277      0.196852     -2.210422
      C       -1.159729     -0.654927     -1.048673
      N       -1.875297     -1.511384     -0.295888
      N        0.155880     -0.540945     -0.929919
      C        0.884348      0.393490     -1.837511
      C        2.234187     -0.097868     -2.348006
      C        1.975628     -1.179164     -3.407982
      C        2.975841      1.068096     -3.004566
      O        0.166830      1.084023     -2.545856
      C        0.869276     -1.369079      0.076661
      C        1.316288     -2.709919     -0.490195
      C       -0.039229     -1.522394      1.318923
```

C	0.623661	-2.305446	2.466267
C	-0.360714	-2.520560	3.621070
C	1.861670	-1.573231	2.988892
C	-1.357940	-2.162301	0.910256
C	0.469941	-3.531637	-1.246034
C	0.905548	-4.771359	-1.706568
C	2.194230	-5.213207	-1.416165
C	3.044753	-4.400604	-0.672671
C	2.611582	-3.156664	-0.216547
H	2.825937	-0.507819	-1.522600
H	2.929923	-1.549282	-3.794777
H	1.411587	-0.746162	-4.240967
H	1.417005	-2.032317	-3.018598
H	3.953678	0.729010	-3.360447
H	3.121842	1.893277	-2.307936
H	2.401300	1.430891	-3.862338
H	-5.102902	-0.081628	-3.039368
H	-3.840234	-3.280411	0.590647
H	-6.137328	-3.280579	-0.350298
H	-6.771199	-1.680273	-2.128508
H	1.741870	-0.773219	0.356675
H	-0.249720	-0.508703	1.683157
H	0.924117	-3.289226	2.078850
H	-0.756425	-1.557774	3.967165
H	0.149266	-2.997650	4.463324
H	-1.207215	-3.158432	3.346940
H	2.294536	-2.126076	3.829197
H	1.582730	-0.572549	3.335576
H	2.638258	-1.450846	2.229946
H	-2.115713	-2.013243	1.684898
H	-1.248061	-3.237660	0.719722
H	-0.529261	-3.199141	-1.516341
H	0.237412	-5.388145	-2.299838
H	2.534719	-6.178882	-1.776745
H	4.056578	-4.727679	-0.452640
H	3.290195	-2.512715	0.334156
C	-1.176708	3.414839	0.061908
C	-2.264811	4.128912	-0.421615
C	-2.140100	4.716534	-1.684694
C	-0.965895	4.594542	-2.424412
C	0.120495	3.879110	-1.910734
C	0.006293	3.280034	-0.671234
C	1.034684	2.540422	0.174992
C	2.062195	3.567107	0.698964
O	1.681493	1.456378	-0.389894
C	0.186628	2.155049	1.409487
O	0.544844	1.494770	2.370844
N	-1.044790	2.749687	1.295770
C	-2.003735	2.731310	2.382734
C	-2.876860	1.496694	2.403513
C	-2.769460	0.578856	3.447165
C	-3.616714	-0.528722	3.506554
C	-4.572175	-0.726192	2.513479
C	-4.667401	0.175658	1.452078
C	-3.821461	1.277289	1.395504

H	-3.180054	4.237083	0.152835
H	-2.976658	5.277906	-2.089955
H	-0.894737	5.056810	-3.403788
H	1.037140	3.768454	-2.483499
H	2.683559	3.905290	-0.135835
H	1.561638	4.432677	1.144573
H	2.701030	3.091488	1.448428
H	3.081418	1.460083	-0.190732
H	-1.432307	2.791538	3.313539
H	-2.617022	3.634812	2.304796
H	-2.023306	0.739283	4.221388
H	-3.529353	-1.232596	4.329473
H	-5.236767	-1.584328	2.555557
H	-5.399880	0.014383	0.665248
H	-3.898917	1.978455	0.567139
C	4.693410	0.494482	0.421239
C	6.180824	0.653999	0.697555
C	6.387257	1.766347	1.733883
C	6.803542	-0.662586	1.143715
O	4.082588	-0.539841	0.659834
O	4.140672	1.569347	-0.080979
H	7.454859	1.917037	1.919823
H	5.954623	2.708221	1.388816
H	5.912981	1.494598	2.683546
H	6.634334	0.981063	-0.247037
H	7.878482	-0.538703	1.305936
H	6.650793	-1.446894	0.397739
H	6.348160	-1.000418	2.079565

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2605.78353956 Predicted Change= -7.914087D-10
Zero-point correction (ZPE)= -2604.9303 0.85323
Internal Energy (U)= -2604.8893 0.89423
Enthalpy (H)= -2604.8884 0.89510
Gibbs Free Energy (G)= -2605.0014 0.78206

Frequencies -- -166.1122 11.0491 21.7166

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=chloroform)

Pointgroup= C1 Stoichiometry= C43H49N3O5S C1[X(C43H49N3O5S)] #Atoms= 101
Charge = 0 Multiplicity = 1

SCF Energy= -2606.53459417

==========

***(S)*-TS-III-E**

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

```
=============================================================================
==
 #m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=Chloroform)
 opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
 temp=273.15
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
-----------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C43H49N3O5S   C1[X(C43H49N3O5S)]  #Atoms= 101
 Charge = 0         Multiplicity = 1
-----------------------------------------------------------------------------
 SCF Energy= -2605.78474882       Predicted Change= -5.830953D-09
=============================================================================
==
 Optimization completed.           {Found       2       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00001 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00132 ||  0.00180   [ YES ]      0.00132 ||  0.00180   [ YES ]
-----------------------------------------------------------------------------
      Atomic              Coordinates (Angstroms)
       Type              X           Y           Z
-----------------------------------------------------------------------------
      C         3.509458    -3.962762     0.694885
      C         2.350673    -3.230641     0.458789
      C         2.007429    -2.838719    -0.832786
      C         2.788569    -3.192896    -1.930961
      C         3.940432    -3.935069    -1.691013
      C         4.301311    -4.313544    -0.393903
      S         1.200116    -2.640665     1.645138
      C         0.282251    -1.874792     0.367507
      N         0.834454    -2.073385    -0.847782
      N        -0.847824    -1.201037     0.536280
      C        -1.317933    -0.911447     1.934299
      C        -2.829992    -0.823095     2.112712
      C        -3.359301    -2.262085     2.216812
      C        -3.168070    -0.069145     3.399750
      O        -0.616991    -1.377516     2.821657
      C        -1.637950    -0.766095    -0.644601
      C        -2.683846    -1.812253    -0.998986
      C        -0.704352    -0.430089    -1.828864
      C        -1.466068    -0.033582    -3.109204
      C        -0.506136     0.138564    -4.291606
      C        -2.242213     1.267679    -2.892500
      C         0.261530    -1.572846    -2.096846
      C        -4.010010    -1.419368    -1.193459
      C        -4.980645    -2.358683    -1.537043
      C        -4.639947    -3.699919    -1.688598
      C        -3.320816    -4.100965    -1.488937
      C        -2.350791    -3.163651    -1.145687
      H        -3.290497    -0.308263     1.268023
      H        -4.452500    -2.248088     2.262680
      H        -2.978368    -2.727378     3.131695
      H        -3.067270    -2.884143     1.366842
      H        -2.619529    -0.505135     4.240513
      H        -4.239815    -0.161579     3.602363
```

H	-2.912092	0.987733	3.326910
H	3.784299	-4.251948	1.704214
H	2.512237	-2.909120	-2.940384
H	4.566324	-4.222723	-2.528932
H	5.207705	-4.887353	-0.232993
H	-2.130096	0.160173	-0.336040
H	-0.117875	0.441975	-1.530395
H	-2.170652	-0.839443	-3.355385
H	-0.034496	-0.800955	-4.596346
H	0.285991	0.858859	-4.049455
H	-1.049458	0.525198	-5.158768
H	-2.748908	1.561025	-3.817809
H	-1.549677	2.067917	-2.605368
H	-2.994927	1.188734	-2.104001
H	1.094395	-1.221619	-2.710468
H	-0.224018	-2.405149	-2.622848
H	-4.282754	-0.377990	-1.045188
H	-6.009062	-2.039430	-1.676368
H	-5.398450	-4.431300	-1.950207
H	-3.046425	-5.146542	-1.589785
H	-1.336766	-3.508446	-0.955488
C	2.278441	0.640444	1.061254
C	3.503430	-0.005467	1.154239
C	3.862540	-0.515701	2.405579
C	3.022843	-0.375753	3.508661
C	1.789208	0.273991	3.385005
C	1.411207	0.770114	2.151046
C	0.205866	1.604247	1.733561
O	-1.049350	1.014830	1.836898
C	0.229224	2.945167	2.486187
C	0.537521	1.892784	0.250155
O	-0.137153	2.546845	-0.526186
N	1.721135	1.264997	-0.071077
C	2.385550	1.390505	-1.350704
C	3.592192	2.305694	-1.302337
C	4.809995	1.908814	-1.851235
C	5.910497	2.764064	-1.821664
C	5.798243	4.022215	-1.237148
C	4.581850	4.423536	-0.684713
C	3.484395	3.569772	-0.717534
H	-2.064166	1.999115	1.570214
H	-0.001660	2.757803	3.539080
H	-0.524233	3.615802	2.065813
H	1.214182	3.419978	2.418430
H	4.168908	-0.092150	0.300561
H	4.817057	-1.022239	2.514854
H	3.327072	-0.776508	4.470486
H	1.121197	0.366108	4.236116
H	2.683463	0.394116	-1.704217
H	1.633435	1.789190	-2.040845
H	4.900290	0.922824	-2.302127
H	6.855469	2.442781	-2.249063
H	6.655026	4.688214	-1.209653
H	4.488121	5.404439	-0.228913
H	2.533640	3.884749	-0.292554

C	-3.609393	2.630902	0.515243
C	-4.317462	3.898237	0.069720
C	-5.591348	3.580361	-0.703058
C	-3.331414	4.715770	-0.777541
O	-3.845017	1.537198	0.014126
O	-2.710617	2.834477	1.444034
H	-6.284521	2.985383	-0.101943
H	-6.095183	4.504376	-1.002212
H	-5.353130	3.007169	-1.604272
H	-4.553916	4.469591	0.974730
H	-2.425160	4.949784	-0.213765
H	-3.796965	5.650597	-1.103973
H	-3.041236	4.148043	-1.668978

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm
==========
==
SCF Energy= -2605.78474882 Predicted Change= -5.830953D-09
Zero-point correction (ZPE)= -2604.9319 0.85280
Internal Energy (U)= -2604.8909 0.89378
Enthalpy (H)= -2604.8901 0.89464
Gibbs Free Energy (G)= -2605.0018 0.78294

Frequencies -- -180.9936 21.0810 22.2630
==========
==
#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=chloroform)

Pointgroup= C1 Stoichiometry= C43H49N3O5S C1[X(C43H49N3O5S)] #Atoms= 101
Charge = 0 Multiplicity = 1

SCF Energy= -2606.53529736
==========
==

***(S)*-TS-III-F**

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
==
#m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Chloroform)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
temp=273.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C43H49N3O5S C1[X(C43H49N3O5S)] #Atoms= 101
Charge = 0 Multiplicity = 1

SCF Energy= -2605.78101030 Predicted Change= -1.564872D-09
==========
==
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00033	0.00180	[YES]	0.00033	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-3.885171	3.550589	-0.273450
C	-2.625531	2.970989	-0.387040
C	-1.479171	3.764400	-0.419910
C	-1.549521	5.152260	-0.332140
C	-2.810532	5.725639	-0.209220
C	-3.965021	4.936039	-0.179800
S	-2.235330	1.261610	-0.519480
C	-0.540090	1.668980	-0.603760
N	-0.318061	2.995260	-0.564350
N	0.459310	0.799080	-0.665820
C	0.185190	-0.555490	-1.216260
C	1.121690	-0.963189	-2.346900
C	0.943901	-2.441029	-2.683140
C	0.744590	-0.098860	-3.560950
O	-0.989540	-0.897490	-1.203410
C	1.820370	1.279561	-0.321010
C	2.036920	1.376971	1.185110
C	2.081839	2.586781	-1.093650
C	3.475069	3.185321	-0.828100
C	3.664809	4.490761	-1.606570
C	4.580630	2.193202	-1.189650
C	0.990569	3.619211	-0.798910
C	2.945170	0.481131	1.759020
C	3.217770	0.514071	3.124790
C	2.593070	1.453021	3.942190
C	1.688659	2.352151	3.382740
C	1.407859	2.312021	2.018390
H	2.162590	-0.783959	-2.067490
H	-0.094739	-2.646610	-2.959830
H	1.587561	-2.695469	-3.531310
H	1.203701	-3.077959	-1.837520
H	-0.293650	-0.294140	-3.849790
H	1.389620	-0.350569	-4.407230
H	0.847290	0.973720	-3.367050
H	-4.778571	2.935289	-0.254270
H	-0.655902	5.766300	-0.358100
H	-2.896042	6.804469	-0.136070
H	-4.936461	5.408409	-0.081860
H	2.504260	0.511011	-0.685270
H	2.029519	2.329221	-2.159950
H	3.539779	3.408651	0.246210
H	4.674009	4.881192	-1.447000
H	2.960419	5.270711	-1.299790
H	3.538299	4.320201	-2.682640
H	4.541980	1.274772	-0.598690
H	4.505520	1.904942	-2.245750
H	5.560839	2.655782	-1.038250
H	0.866719	4.304040	-1.642690

H	1.246159	4.215811	0.084210
H	3.428080	-0.251959	1.118370
H	3.920800	-0.197229	3.547900
H	2.805260	1.481821	5.006490
H	1.185589	3.082241	4.009620
H	0.659939	2.998280	1.638410
C	-2.987390	-0.015011	2.993630
C	-3.229500	-1.128011	2.178760
C	-2.131859	-1.738910	1.589200
C	-0.828599	-1.273240	1.797250
C	-0.599280	-0.200440	2.633290
C	-1.694020	0.446980	3.222420
N	-2.106709	-2.867020	0.759080
C	-3.260829	-3.666731	0.408990
C	-4.324059	-2.902811	-0.354310
C	-0.821529	-3.149580	0.343870
O	-0.506959	-4.068690	-0.384730
C	0.147031	-2.183470	1.087280
O	1.053711	-1.510879	0.253650
C	0.927341	-3.034809	2.098760
C	-5.674579	-3.119261	-0.079160
C	-6.659989	-2.438012	-0.791920
C	-6.299179	-1.526872	-1.781150
C	-4.950049	-1.304441	-2.054850
C	-3.965129	-1.989721	-1.347670
H	-3.828810	0.487009	3.462250
H	-4.237659	-1.492681	2.009780
H	0.416410	0.116700	2.842560
H	-1.527040	1.301090	3.872250
H	-3.696559	-4.092461	1.322010
H	-2.871189	-4.494391	-0.192700
H	1.990631	-2.125699	0.040700
H	0.241341	-3.528080	2.793970
H	1.598941	-2.379559	2.662180
H	1.515481	-3.787919	1.568890
H	-5.958079	-3.822352	0.701110
H	-7.707829	-2.615512	-0.568900
H	-7.065250	-0.991582	-2.334060
H	-4.660960	-0.594581	-2.825050
H	-2.913199	-1.809411	-1.550580
O	4.082990	-1.039789	-0.919750
C	4.049661	-2.244999	-0.624700
C	5.293801	-3.118588	-0.799170
C	6.416461	-2.374908	-1.511550
C	5.736881	-3.635828	0.574340
O	3.029611	-2.858739	-0.140840
H	6.087351	-1.999568	-2.484100
H	7.278361	-3.032928	-1.662850
H	6.737091	-1.513278	-0.917780
H	4.923211	-4.174298	1.065130
H	6.033941	-2.798598	1.217170
H	6.596441	-4.306488	0.476860
H	4.980271	-3.981888	-1.400040

Statistical Thermodynamic Analysis

```
 Temperature= 273.150 Kelvin       Pressure= 1.00000 Atm
=====================================================================================
==
 SCF Energy=     -2605.78101030   Predicted Change= -1.564872D-09
 Zero-point correction (ZPE)=            -2604.9294      0.85151
 Internal Energy (U)=                    -2604.8883      0.89262
 Enthalpy (H)=                           -2604.8875      0.89349
 Gibbs Free Energy (G)=                  -2605.0011      0.77990
-------------------------------------------------------------------------------
 Frequencies --   -312.4590               9.1768              16.1932
=====================================================================================
==
 #m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
 SCRF=(PCM,SOLVENT=chloroform)
-------------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C43H49N3O5S   C1[X(C43H49N3O5S)]  #Atoms= 101
 Charge = 0         Multiplicity = 1
-------------------------------------------------------------------------------
 SCF Energy= -2606.53209081
=====================================================================================
==
```

***(S)*-TS-III-G**

```
-------------------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
=====================================================================================
==
 #m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=Chloroform)
 opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
 temp=273.15
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
-------------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C43H49N3O5S   C1[X(C43H49N3O5S)]  #Atoms= 101
 Charge = 0         Multiplicity = 1
-------------------------------------------------------------------------------
 SCF Energy= -2605.78083015       Predicted Change= -1.606591D-09
=====================================================================================
==
 Optimization completed on the basis of negligible forces.          {Found       2       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00000 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00304 ||  0.00180   [ NO ]       0.00304 ||  0.00180   [ YES ]
-------------------------------------------------------------------------------
     Atomic              Coordinates (Angstroms)
      Type              X             Y          Z
-------------------------------------------------------------------------------
      C       -3.992848       3.384511      -0.561394
      C       -2.704400       2.860696      -0.597960
      C       -1.596371       3.706421      -0.638342
      C       -1.734540       5.091793      -0.635352
      C       -3.024212       5.609730      -0.589443
      C       -4.140622       4.767718      -0.552501
      S       -2.226780       1.167333      -0.612695
      C       -0.550262       1.654245      -0.663480
```

N	-0.395041	2.989997	-0.695175
N	0.491605	0.834141	-0.635794
C	0.309236	-0.563118	-1.117664
C	1.309431	-0.977773	-2.191143
C	1.208252	-2.475525	-2.465438
C	0.949276	-0.188363	-3.459598
O	-0.847128	-0.964429	-1.133662
C	1.811364	1.401011	-0.262716
C	1.956265	1.589426	1.243504
C	2.043514	2.678903	-1.093103
C	3.391853	3.359222	-0.799636
C	3.560600	4.623921	-1.647299
C	4.558241	2.403037	-1.048402
C	0.891161	3.667689	-0.901337
C	1.237760	2.529218	1.995010
C	1.457366	2.664449	3.364360
C	2.387782	1.855444	4.010795
C	3.097780	0.908487	3.275852
C	2.886118	0.780511	1.904635
H	2.329057	-0.738134	-1.879905
H	1.906258	-2.740668	-3.266458
H	1.446823	-3.063279	-1.578813
H	0.194541	-2.734838	-2.786154
H	1.638301	-0.453181	-4.266383
H	1.002271	0.895140	-3.314288
H	-0.067585	-0.439562	-3.779488
H	-4.857045	2.729134	-0.535307
H	-0.869963	5.745798	-0.666888
H	-3.162509	6.685471	-0.583177
H	-5.136120	5.196810	-0.515365
H	2.548638	0.650818	-0.555419
H	2.052189	2.365687	-2.145584
H	3.393088	3.647767	0.260837
H	2.801568	5.382743	-1.431241
H	3.505858	4.380905	-2.715540
H	4.538377	5.076398	-1.458337
H	5.507880	2.925067	-0.895620
H	4.541115	1.528170	-0.394229
H	4.539371	2.036466	-2.082448
H	0.775875	4.303567	-1.783736
H	1.074588	4.318854	-0.038634
H	0.464995	3.143419	1.547657
H	0.886314	3.397356	3.926375
H	2.553536	1.958389	5.078783
H	3.820174	0.264715	3.768800
H	3.433467	0.038951	1.327695
C	-3.046830	0.031818	2.945476
C	-3.202674	-1.131679	2.182169
C	-2.054961	-1.713666	1.663036
C	-0.784997	-1.170990	1.890646
C	-0.641082	-0.046749	2.676245
C	-1.787596	0.571682	3.193288
N	-1.942600	-2.880053	0.895708
C	-3.041874	-3.753326	0.543273
C	-4.115103	-3.078628	-0.287017

C	-0.630408	-3.116789	0.540738
O	-0.245209	-4.054796	-0.127297
C	0.260751	-2.062990	1.262825
O	1.161381	-1.386391	0.424410
C	1.051579	-2.817976	2.340654
C	-5.461806	-3.348634	-0.041863
C	-6.455801	-2.749560	-0.813796
C	-6.108131	-1.867468	-1.833564
C	-4.763117	-1.592143	-2.078350
C	-3.769276	-2.195382	-1.311757
H	-3.929224	0.511769	3.358646
H	-4.183970	-1.557472	1.998663
H	0.348487	0.333543	2.903252
H	-1.688633	1.465692	3.802108
H	-3.487019	-4.162530	1.459322
H	-2.589704	-4.583966	-0.008399
H	2.139075	-1.962125	0.276987
H	1.665005	-2.099268	2.893250
H	1.700052	-3.559620	1.867734
H	0.370893	-3.317589	3.036489
H	-5.735690	-4.028309	0.762115
H	-7.500461	-2.967280	-0.612451
H	-6.880884	-1.395315	-2.432830
H	-4.484383	-0.905071	-2.872581
H	-2.721253	-1.973689	-1.492963
O	4.217744	-0.816222	-0.643697
C	4.191923	-2.032933	-0.395533
C	5.380788	-2.900841	-0.802629
C	5.604542	-4.076183	0.143345
C	5.121695	-3.385332	-2.235345
O	3.202235	-2.659322	0.131138
H	5.780473	-3.736757	1.168870
H	6.470284	-4.666196	-0.175442
H	4.723758	-4.723812	0.150278
H	4.225172	-4.014460	-2.260769
H	5.967000	-3.975187	-2.604269
H	4.967748	-2.538524	-2.911673
H	6.258561	-2.245758	-0.807788

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2605.78083015 Predicted Change= -1.606591D-09
Zero-point correction (ZPE)= -2604.9294 0.85140
Internal Energy (U)= -2604.8883 0.89248
Enthalpy (H)= -2604.8874 0.89334
Gibbs Free Energy (G)= -2605.0004 0.78041

Frequencies -- -363.9816 15.9291 16.5761

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=chloroform)

Pointgroup= C1 Stoichiometry= C43H49N3O5S C1[X(C43H49N3O5S)] #Atoms= 101
Charge = 0 Multiplicity = 1

SCF Energy= -2606.53222351
==========

***(S)*-TS-III-H**

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Chloroform)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
temp=273.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C43H49N3O5S C1[X(C43H49N3O5S)] #Atoms= 101
Charge = 0 Multiplicity = 1

SCF Energy= -2605.78380512 Predicted Change= -9.735211D-10
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00166	0.00180	[YES]	0.00166	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	4.864260	0.352875	-2.113857
C	3.526029	0.435776	-1.740908
C	3.122128	1.312015	-0.737077
C	4.024813	2.167923	-0.111783
C	5.359195	2.090559	-0.495628
C	5.777892	1.188029	-1.479339
S	2.171407	-0.474325	-2.390510
C	1.092230	0.360128	-1.291387
N	1.749550	1.216732	-0.483408
N	-0.227018	0.221109	-1.262745
C	-0.870512	-0.823895	-2.117467
C	-2.287770	-0.512664	-2.588703
C	-2.164043	0.418309	-3.804408
C	-2.999550	-1.802199	-2.998335
O	-0.104025	-1.438249	-2.848309
C	-1.047702	1.093660	-0.384126
C	-1.525732	2.314618	-1.153180
C	-0.254662	1.405443	0.899452
C	-0.996290	2.230379	1.975481
C	-2.319918	1.560986	2.351915
C	-1.194970	3.726116	1.699789
C	1.101907	2.003285	0.569656
C	-0.641122	3.144429	-1.850763

C	-1.107046	4.271318	-2.522900
C	-2.465667	4.579026	-2.515400
C	-3.355514	3.744631	-1.844033
C	-2.889889	2.617632	-1.170580
H	-2.865560	-0.031019	-1.798600
H	-1.565178	1.308876	-3.593245
H	-3.158392	0.749255	-4.118927
H	-1.696228	-0.121513	-4.634091
H	-3.229298	-2.422389	-2.131206
H	-2.365731	-2.377562	-3.680378
H	-3.931582	-1.555810	-3.516981
H	5.182178	-0.340316	-2.886077
H	3.699939	2.866582	0.651400
H	6.084219	2.745896	-0.024129
H	6.825328	1.144385	-1.758222
H	-1.908237	0.484156	-0.096201
H	-0.062755	0.431251	1.366210
H	-0.339506	2.164283	2.852110
H	-2.179638	0.486245	2.517691
H	-3.072937	1.680841	1.566282
H	-2.719121	2.007154	3.269250
H	-1.905800	3.911775	0.891218
H	-0.258989	4.238754	1.455081
H	-1.592169	4.196775	2.605508
H	1.748813	1.966497	1.452830
H	1.032313	3.041495	0.228136
H	0.418063	2.904556	-1.906349
H	-0.407600	4.903531	-3.061314
H	-2.828256	5.456227	-3.042432
H	-4.418657	3.965279	-1.849838
H	-3.586812	1.956080	-0.663296
C	1.813767	-2.609017	0.407031
C	3.163649	-2.826996	0.164562
C	3.508690	-3.479947	-1.022216
C	2.531710	-3.903332	-1.921029
C	1.179159	-3.666987	-1.657068
C	0.823306	-2.997086	-0.500451
C	-0.548096	-2.713893	0.100669
C	-1.214824	-4.057347	0.456598
O	-1.428694	-1.925627	-0.628411
C	-0.153068	-2.049954	1.443375
O	-0.911223	-1.639548	2.305672
N	1.220425	-2.029272	1.547230
C	1.890799	-1.809700	2.819235
C	2.313668	-0.384498	3.104097
C	3.556749	0.098733	2.688956
C	3.978125	1.375495	3.055729
C	3.153327	2.189671	3.830342
C	1.900793	1.723826	4.227295
C	1.483675	0.444654	3.863550
H	3.928934	-2.518735	0.869898
H	4.557058	-3.665156	-1.236955
H	2.822698	-4.416047	-2.832367
H	0.412741	-3.976832	-2.360437
H	-1.491396	-4.558824	-0.475786

H	-2.114036	-3.876117	1.050168
H	-0.533909	-4.704632	1.019293
H	-2.740619	-1.961909	-0.011136
H	1.193976	-2.135667	3.597461
H	2.762123	-2.471545	2.848953
H	4.214216	-0.531868	2.094869
H	4.954982	1.729706	2.740070
H	3.486670	3.179139	4.127772
H	1.251936	2.352420	4.830327
H	0.508939	0.073559	4.173277
C	-4.374746	-1.072429	0.668940
C	-5.512139	-1.265920	1.657068
C	-6.564303	-0.173513	1.515649
C	-4.911338	-1.290038	3.070416
O	-4.152811	-0.000536	0.120206
O	-3.645036	-2.148043	0.506067
H	-6.991600	-0.156883	0.509169
H	-7.373889	-0.330368	2.234695
H	-6.115903	0.806311	1.705182
H	-5.951092	-2.249055	1.451701
H	-4.470067	-0.315318	3.307889
H	-5.690496	-1.498869	3.809612
H	-4.130409	-2.049973	3.155754

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2605.78380512 Predicted Change= -9.735211D-10
Zero-point correction (ZPE)= -2604.9304 0.85332
Internal Energy (U)= -2604.8895 0.89420
Enthalpy (H)= -2604.8887 0.89507
Gibbs Free Energy (G)= -2604.9990 0.78476

Frequencies -- -177.1038 25.4658 32.9797

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=chloroform)

Pointgroup= C1 Stoichiometry= C43H49N3O5S C1[X(C43H49N3O5S)] #Atoms= 101
Charge = 0 Multiplicity = 1

SCF Energy= -2606.53408411

==========

***(S)*-TS-III-I**

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Chloroform)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman

temp=273.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C43H49N3O5S C1[X(C43H49N3O5S)] #Atoms= 101
Charge = 0 Multiplicity = 1

SCF Energy= -2605.77357958 Predicted Change= -4.518524D-09
==========
==
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00113	0.00180	[YES]	0.00113	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	4.851660	-2.588870	-2.205210
C	3.972490	-1.649440	-1.678020
C	4.429690	-0.644340	-0.829670
C	5.774650	-0.541000	-0.485860
C	6.651980	-1.482590	-1.016200
C	6.198710	-2.493740	-1.868630
S	2.223360	-1.594580	-1.862460
C	2.177670	-0.156740	-0.857270
N	3.392540	0.187990	-0.397250
N	1.097540	0.561100	-0.613400
C	-0.261880	-0.025290	-0.946080
C	-1.249060	1.031230	-1.440490
C	-0.731080	1.586730	-2.776240
C	-2.603710	0.371310	-1.683530
O	-0.221220	-1.120540	-1.506440
C	1.203750	1.792450	0.199430
C	1.399380	3.030750	-0.655700
C	2.262490	1.584460	1.298040
C	2.475520	2.812740	2.199680
C	3.550430	2.531140	3.255460
C	1.177890	3.236970	2.888810
C	3.590650	1.139480	0.695760
C	2.455300	3.159420	-1.565390
C	2.589900	4.312700	-2.333340
C	1.674260	5.355650	-2.203230
C	0.615600	5.233770	-1.308340
C	0.480460	4.076970	-0.544960
H	-1.354010	1.841470	-0.712920
H	-0.633170	0.766810	-3.495300
H	0.236050	2.085980	-2.687910
H	-1.450060	2.309150	-3.175400
H	-3.370270	1.127100	-1.881670
H	-2.932460	-0.228620	-0.837670
H	-2.540090	-0.300400	-2.544410
H	4.492460	-3.379290	-2.856720
H	6.129480	0.244430	0.172630
H	7.705060	-1.426180	-0.761820
H	6.902510	-3.215000	-2.269920

H	0.238210	1.857280	0.700160
H	1.883710	0.751180	1.901500
H	2.819100	3.644740	1.568090
H	4.537160	2.363620	2.813880
H	3.286330	1.646180	3.846640
H	3.638610	3.380190	3.939560
H	0.454740	3.650020	2.180860
H	1.376680	4.011450	3.635640
H	0.713460	2.386100	3.402460
H	4.176940	0.612780	1.452680
H	4.171430	1.992660	0.321540
H	3.160800	2.345250	-1.707620
H	3.409110	4.393570	-3.041060
H	1.779970	6.252660	-2.805320
H	-0.113980	6.031610	-1.210990
H	-0.369910	3.973650	0.126610
C	-3.973220	0.421340	1.394320
C	-5.042040	1.304630	1.361430
C	-4.763150	2.664870	1.533890
C	-3.462210	3.114580	1.742820
C	-2.400300	2.201590	1.777210
C	-2.655220	0.858710	1.577010
C	-1.731540	-0.345260	1.600820
C	-1.309900	-0.631620	3.056480
O	-0.569300	-0.284910	0.837830
C	-2.712770	-1.488780	1.219960
O	-2.437860	-2.651480	1.005670
N	-3.995010	-0.972360	1.245460
C	-5.181850	-1.768930	0.989370
C	-5.671970	-1.656790	-0.438450
C	-6.918950	-1.110610	-0.735820
C	-7.349620	-1.008200	-2.058360
C	-6.530670	-1.452420	-3.092090
C	-5.282930	-2.004740	-2.800540
C	-4.857380	-2.109740	-1.480700
H	-6.057590	0.959820	1.196530
H	-5.581030	3.378300	1.506110
H	-3.271200	4.173290	1.886330
H	-1.386660	2.542180	1.971600
H	-0.636350	0.166190	3.384310
H	-2.173790	-0.669120	3.727870
H	-0.783130	-1.589470	3.093700
H	0.234900	-1.677470	0.992670
H	-4.901670	-2.801510	1.216660
H	-5.964710	-1.463850	1.692380
H	-7.562400	-0.768530	0.072040
H	-8.322950	-0.579710	-2.277650
H	-6.862710	-1.371760	-4.122680
H	-4.641590	-2.356440	-3.603170
H	-3.885640	-2.540270	-1.247070
C	1.899740	-2.510210	1.563800
C	2.568810	-3.849070	1.837310
C	3.713110	-4.029170	0.831010
C	1.610020	-5.034320	1.821890
O	2.510220	-1.459740	1.705480

```
      O       0.654700    -2.594930     1.150510
      H       4.378050    -3.159990     0.832470
      H       3.311830    -4.151870    -0.181440
      H       4.296240    -4.922020     1.075950
      H       3.012960    -3.745100     2.835160
      H       1.163850    -5.155060     0.830860
      H       0.796640    -4.901690     2.539760
      H       2.149340    -5.953000     2.073200
---------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 273.150 Kelvin       Pressure= 1.00000 Atm
=====================================================================
==
 SCF Energy=     -2605.77357958   Predicted Change= -4.518524D-09
 Zero-point correction (ZPE)=            -2604.9202      0.85330
 Internal Energy (U)=                    -2604.8790      0.89452
 Enthalpy (H)=                           -2604.8781      0.89539
 Gibbs Free Energy (G)=                  -2604.9920      0.78153
---------------------------------------------------------------------
 Frequencies --   -135.7257              15.1894              21.2386
=====================================================================
==
 #m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
 SCRF=(PCM,SOLVENT=chloroform)
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C43H49N3O5S   C1[X(C43H49N3O5S)]  #Atoms= 101
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -2606.52436604
=====================================================================
==
```

***(S)*-TS-III-J**

```
---------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
=====================================================================
==
 #m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=Chloroform)
 opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
 temp=273.15
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C43H49N3O5S   C1[X(C43H49N3O5S)]  #Atoms= 101
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -2605.76549461       Predicted Change= -3.105248D-09
=====================================================================
==
 Optimization completed.           {Found       2       times}
 Item      Max Val.   Criteria   Pass?      RMS Val.    Criteria   Pass?
 Force      0.00000 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00177 ||  0.00180   [ YES ]      0.00177 ||  0.00180   [ YES ]
---------------------------------------------------------------------
     Atomic              Coordinates (Angstroms)
```

Type	X	Y	Z
C	-2.084957	2.170353	3.979931
C	-2.015298	1.471863	2.778971
C	-2.197870	0.090303	2.751561
C	-2.477811	-0.632107	3.907591
C	-2.551740	0.071524	5.104781
C	-2.352578	1.455583	5.143731
S	-1.709227	2.116672	1.171361
C	-1.721449	0.490732	0.534461
N	-2.024661	-0.429537	1.464661
N	-1.501340	0.176662	-0.734789
C	-1.025038	1.304041	-1.640379
C	-0.677189	0.893291	-3.067379
C	-1.968759	0.779483	-3.890819
C	0.219323	1.965249	-3.687979
O	-1.537066	2.393002	-1.402159
C	-1.972642	-1.138747	-1.203239
C	-3.479142	-1.133535	-1.466369
C	-1.517703	-2.199528	-0.173129
C	-1.809115	-3.660218	-0.557839
C	-1.379577	-4.611598	0.565521
C	-1.087586	-4.051859	-1.850159
C	-2.106633	-1.865447	1.191981
C	-4.025723	-2.113944	-2.304419
C	-5.392423	-2.160822	-2.557179
C	-6.242642	-1.219501	-1.981149
C	-5.708400	-0.225072	-1.169469
C	-4.337630	-0.177054	-0.919209
H	-0.129630	-0.052790	-3.063649
H	-2.646050	-0.007246	-3.549099
H	-1.717149	0.574122	-4.935699
H	-2.511287	1.729053	-3.848209
H	1.151763	2.068128	-3.134259
H	-0.293016	2.932600	-3.671299
H	0.433383	1.701849	-4.728629
H	-1.933905	3.244583	4.005241
H	-2.628062	-1.705806	3.880631
H	-2.765301	-0.466056	6.022421
H	-2.411407	1.980803	6.091021
H	-1.447952	-1.334248	-2.139819
H	-0.429303	-2.093170	-0.105509
H	-2.891165	-3.775806	-0.700269
H	-0.334606	-4.430030	0.849131
H	-1.461148	-5.649988	0.231981
H	-1.996607	-4.506167	1.462551
H	-0.002616	-3.975990	-1.718899
H	-1.354065	-3.426248	-2.706329
H	-1.320007	-5.087908	-2.113489
H	-1.541893	-2.369428	1.980701
H	-3.160673	-2.167156	1.254941
H	-3.375284	-2.839245	-2.784529
H	-5.789684	-2.926762	-3.215769
H	-7.309182	-1.250679	-2.179659
H	-6.355129	0.531239	-0.735979

H	-3.951829	0.642946	-0.322389
C	1.454450	0.067868	0.949131
C	1.172541	0.705788	2.142531
C	1.056540	-0.060362	3.310071
C	1.261868	-1.437552	3.270271
C	1.590617	-2.089853	2.074581
C	1.675908	-1.311283	0.929161
N	1.918028	-1.728293	-0.391789
C	2.400226	-3.044004	-0.766159
C	3.858815	-3.233146	-0.408549
C	1.838279	-0.668653	-1.275199
O	2.006879	-0.763973	-2.477089
C	1.641741	0.631187	-0.449739
O	0.660712	1.497089	-0.896369
C	3.012842	1.337635	-0.526649
C	4.267744	-4.238437	0.464301
C	5.616984	-4.387579	0.784971
C	6.562115	-3.527080	0.234961
C	6.157496	-2.517659	-0.639599
C	4.812767	-2.372297	-0.960559
H	0.817024	2.936739	-0.456599
H	2.252525	-3.122944	-1.847569
H	1.782714	-3.809273	-0.280279
H	1.032543	1.783908	2.160741
H	0.800531	0.421459	4.249341
H	1.179197	-2.019482	4.183371
H	1.783515	-3.158423	2.055951
H	3.179933	1.670415	-1.553869
H	3.823711	0.671174	-0.210719
H	2.995773	2.210885	0.132001
H	3.529563	-4.912055	0.894091
H	5.926752	-5.173939	1.466501
H	7.612405	-3.641061	0.484911
H	6.892177	-1.846320	-1.073349
H	4.491858	-1.594017	-1.650409
C	1.697997	4.625577	-0.834049
C	1.922929	6.020127	-0.266049
C	2.695930	6.891766	-1.247179
C	2.639639	5.909876	1.085721
O	2.183966	4.243577	-1.882499
O	0.939686	3.878488	-0.048059
H	2.180930	6.960007	-2.208689
H	2.820902	7.900986	-0.843199
H	3.687260	6.466744	-1.431039
H	0.927420	6.447698	-0.090599
H	2.063078	5.303097	1.787491
H	2.788030	6.903216	1.519931
H	3.624888	5.447084	0.957341

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2605.76549461 Predicted Change= -3.105248D-09
Zero-point correction (ZPE)= -2604.9123 0.85309

```
 Internal Energy (U)=                  -2604.8710      0.89442
 Enthalpy (H)=                         -2604.8702      0.89528
 Gibbs Free Energy (G)=                -2604.9854      0.78001
 ---------------------------------------------------------------------
 Frequencies --   -151.5947              9.2071             20.3613
 =====================================================================
 ==
 #m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
 SCRF=(PCM,SOLVENT=chloroform)
 ---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C43H49N3O5S   C1[X(C43H49N3O5S)]  #Atoms= 101
 Charge = 0         Multiplicity = 1
 ---------------------------------------------------------------------
 SCF Energy= -2606.51803675
 =====================================================================
 ==
```

***(S)*-TS-III-K**

```
 ---------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
 =====================================================================
 ==
 #m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=Chloroform)
 opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
 temp=273.15
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
 ---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C43H49N3O5S   C1[X(C43H49N3O5S)]  #Atoms= 101
 Charge = 0         Multiplicity = 1
 ---------------------------------------------------------------------
 SCF Energy= -2605.76904665       Predicted Change= -2.164602D-09
 =====================================================================
 ==
 Optimization completed.          {Found       2       times}
 Item      Max Val.   Criteria   Pass?     RMS Val.   Criteria   Pass?
 Force      0.00001 ||  0.00045   [ YES ]     0.00000 ||  0.00030   [ YES ]
 Displ      0.00047 ||  0.00180   [ YES ]     0.00047 ||  0.00180   [ YES ]
 ---------------------------------------------------------------------
      Atomic              Coordinates (Angstroms)
       Type              X           Y           Z
 ---------------------------------------------------------------------
       C       -2.360250      4.332000     -1.659400
       C       -2.333140      3.011900     -1.224000
       C       -2.758810      2.674610      0.059790
       C       -3.233770      3.641200      0.941120
       C       -3.257870      4.961480      0.502730
       C       -2.824660      5.306410     -0.780570
       S       -1.848311      1.586590     -2.132060
       C       -2.114421      0.602570     -0.711510
       N       -2.638301      1.304940      0.306110
       N       -1.877261     -0.695610     -0.654240
       C       -1.148261     -1.328110     -1.850810
       C       -0.906181     -2.828180     -1.632370
       C       -0.511711     -3.467580     -2.962320
```

C	0.104159	-3.211661	-0.543420
O	-1.510991	-0.887550	-2.939240
C	-2.428011	-1.459590	0.480430
C	-3.844371	-1.940640	0.225370
C	-2.241711	-0.628230	1.764150
C	-2.662541	-1.376390	3.050830
C	-4.131831	-1.203650	3.453230
C	-1.753211	-0.962820	4.211570
C	-2.911141	0.730760	1.622930
C	-4.181061	-3.244080	0.601320
C	-5.488451	-3.706170	0.477580
C	-6.475851	-2.870230	-0.037520
C	-6.144041	-1.578270	-0.440180
C	-4.836641	-1.116490	-0.313170
H	-1.900241	-3.220160	-1.366580
H	-1.250651	-3.254830	-3.736850
H	-0.430911	-4.552040	-2.834760
H	0.464629	-3.090921	-3.279140
H	-0.096851	-4.232641	-0.199850
H	0.097849	-2.548321	0.325970
H	1.113509	-3.179671	-0.956850
H	-2.028130	4.593050	-2.659100
H	-3.573500	3.379170	1.936960
H	-3.619910	5.733550	1.173290
H	-2.851540	6.343300	-1.098000
H	-1.803461	-2.340580	0.603920
H	-1.161031	-0.452670	1.816060
H	-2.491071	-2.444980	2.861260
H	-4.369391	-1.894360	4.267860
H	-4.824711	-1.402930	2.630400
H	-4.319971	-0.189360	3.824550
H	-0.706741	-1.201240	3.997330
H	-2.040811	-1.477930	5.133370
H	-1.823831	0.116170	4.397420
H	-2.514181	1.424830	2.369320
H	-3.998751	0.665080	1.738490
H	-3.410691	-3.902260	0.998090
H	-5.732601	-4.720840	0.776230
H	-7.495901	-3.227489	-0.137010
H	-6.903931	-0.925790	-0.858680
H	-4.599431	-0.109250	-0.645440
C	3.497969	0.726009	-1.281530
C	4.370529	1.660139	-0.743960
C	3.887620	2.961559	-0.568480
C	2.584300	3.298709	-0.923210
C	1.724010	2.335419	-1.466680
C	2.186259	1.045299	-1.647780
C	1.496319	-0.200451	-2.195170
C	1.145809	-0.036001	-3.675630
O	0.420929	-0.573391	-1.373530
C	2.651479	-1.240811	-2.098700
O	2.622239	-2.400021	-2.472620
N	3.750049	-0.629791	-1.543480
C	5.013489	-1.294531	-1.318490
C	5.444659	-1.306931	0.135610

C	4.515169	-1.233981	1.174820
C	4.948309	-1.268891	2.499360
C	6.304419	-1.379501	2.798450
C	7.233629	-1.450172	1.763100
C	6.803689	-1.408081	0.439470
H	5.382879	1.391089	-0.459860
H	4.544390	3.716359	-0.146360
H	2.228250	4.313129	-0.773090
H	0.703350	2.595419	-1.727840
H	2.044869	0.258789	-4.226960
H	0.761839	-0.972511	-4.083390
H	0.383379	0.735899	-3.796770
H	0.777569	-0.404561	0.008350
H	5.790449	-0.816091	-1.928630
H	4.880939	-2.314851	-1.692750
H	3.454309	-1.129271	0.953210
H	4.220289	-1.207391	3.303000
H	6.635889	-1.404461	3.832060
H	8.293769	-1.530252	1.984150
H	7.531279	-1.453602	-0.367980
C	1.004809	0.947459	1.414290
C	2.024069	1.392229	2.448410
C	1.846450	2.861899	2.803770
C	1.912219	0.487789	3.682550
O	0.043279	1.619899	1.078940
O	1.251619	-0.264521	0.941930
H	1.944110	3.491839	1.915580
H	2.598180	3.169669	3.537220
H	0.853260	3.033469	3.230670
H	3.008779	1.230089	1.988700
H	0.951219	0.649279	4.184850
H	2.709239	0.715739	4.397050
H	1.980419	-0.568191	3.404910

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2605.76904665 Predicted Change= -2.164602D-09
Zero-point correction (ZPE)= -2604.9157 0.85333
Internal Energy (U)= -2604.8749 0.89412
Enthalpy (H)= -2604.8740 0.89499
Gibbs Free Energy (G)= -2604.9860 0.78303

Frequencies -- -179.5828 14.8443 25.0801

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=chloroform)

Pointgroup= C1 Stoichiometry= C43H49N3O5S C1[X(C43H49N3O5S)] #Atoms= 101
Charge = 0 Multiplicity = 1

SCF Energy= -2606.52006152

==========
==

***(R)*-TS-III-A**

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
==
#m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Chloroform)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
temp=273.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C43H49N3O5S C1[X(C43H49N3O5S)] #Atoms= 101
Charge = 0 Multiplicity = 1

SCF Energy= -2605.78859771 Predicted Change= -4.925898D-10
==========
==
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00054	0.00180	[YES]	0.00054	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.877239	5.231198	-0.871965
C	0.177125	4.045668	-0.675962
C	-0.851944	3.975188	0.260479
C	-1.231319	5.085030	1.010542
C	-0.535046	6.271365	0.804197
C	0.508328	6.345173	-0.124064
S	0.468462	2.487595	-1.432051
C	-0.839248	1.797248	-0.499307
N	-1.397688	2.688973	0.339710
N	-1.292116	0.557917	-0.618231
C	-0.481741	-0.445562	-1.351101
C	-1.292768	-1.538840	-2.028099
C	-1.938595	-0.904874	-3.271699
C	-0.388069	-2.696273	-2.439714
O	0.573369	-0.045060	-1.825421
C	-2.486372	0.124570	0.145993
C	-3.757692	0.308194	-0.663307
C	-2.496927	0.827555	1.516290
C	-3.705715	0.451252	2.393076
C	-3.737511	1.283128	3.680469
C	-3.686740	-1.036202	2.747757
C	-2.403944	2.337434	1.342755
C	-4.648322	-0.764121	-0.761698
C	-5.839108	-0.629980	-1.472984
C	-6.149648	0.572802	-2.101070
C	-5.258982	1.641465	-2.021779
C	-4.070947	1.510481	-1.307454

H	-2.070297	-1.913683	-1.359884
H	-2.574089	-1.643103	-3.769875
H	-1.159499	-0.589203	-3.973527
H	-2.558967	-0.037311	-3.027249
H	-0.978679	-3.438841	-2.986610
H	0.076709	-3.171681	-1.575644
H	0.410761	-2.334923	-3.094139
H	1.689357	5.283376	-1.589827
H	-2.041826	5.030669	1.729144
H	-0.809357	7.151630	1.375465
H	1.036865	7.281863	-0.264828
H	-2.332669	-0.938597	0.337917
H	-1.588796	0.476360	2.022614
H	-4.617818	0.667913	1.820161
H	-2.792068	1.183957	4.228157
H	-4.539569	0.928314	4.334112
H	-3.916129	2.346518	3.493863
H	-2.775656	-1.279386	3.308981
H	-3.713910	-1.685777	1.870730
H	-4.545490	-1.280535	3.380790
H	-2.091377	2.809572	2.278005
H	-3.369762	2.764703	1.043169
H	-4.388348	-1.714204	-0.301086
H	-6.519451	-1.473124	-1.544356
H	-7.075096	0.675122	-2.659339
H	-5.484558	2.578182	-2.522129
H	-3.376876	2.347724	-1.285166
C	2.862351	0.517477	0.244279
C	3.516336	1.739672	0.305202
C	2.960212	2.731841	1.120132
C	1.807115	2.491056	1.862307
C	1.182466	1.237023	1.805349
C	1.698038	0.256565	0.978538
C	1.277953	-1.187691	0.745011
C	1.605039	-2.019770	1.999907
O	-0.043470	-1.391373	0.372797
C	2.303009	-1.625643	-0.337200
O	2.368214	-2.713144	-0.876009
N	3.213549	-0.605518	-0.508947
C	4.322220	-0.669580	-1.434970
C	5.657731	-0.785827	-0.730504
C	5.842405	-1.778226	0.236344
C	7.064081	-1.907237	0.887616
C	8.116150	-1.044256	0.578638
C	7.938848	-0.054932	-0.383946
C	6.711860	0.073024	-1.034765
H	4.429962	1.919110	-0.253259
H	3.442393	3.703349	1.177797
H	1.398241	3.273276	2.495381
H	0.304065	1.036830	2.413056
H	0.922395	-1.728492	2.804311
H	1.468840	-3.081609	1.779422
H	2.635597	-1.847448	2.328225
H	-0.416887	-2.692128	0.549383
H	4.137306	-1.550495	-2.057712

H	4.303443	0.214949	-2.082684
H	5.020118	-2.451702	0.469642
H	7.198634	-2.681959	1.636328
H	9.069879	-1.144449	1.087664
H	8.752879	0.621297	-0.627007
H	6.573161	0.847354	-1.786157
C	-1.915328	-4.020834	0.597545
C	-2.242155	-5.502348	0.690921
C	-1.578625	-6.151218	1.905540
C	-1.794919	-6.180457	-0.610020
O	-2.787840	-3.178541	0.394733
O	-0.644760	-3.751639	0.708353
H	-1.886009	-5.666543	2.837385
H	-1.851686	-7.209512	1.964501
H	-0.490677	-6.077451	1.824380
H	-3.331144	-5.570280	0.777168
H	-2.272603	-5.720296	-1.480732
H	-2.057962	-7.242661	-0.594649
H	-0.710094	-6.092970	-0.726087

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2605.78859771 Predicted Change= -4.925898D-10
Zero-point correction (ZPE)= -2604.9359 0.85262
Internal Energy (U)= -2604.8948 0.89372
Enthalpy (H)= -2604.8940 0.89459
Gibbs Free Energy (G)= -2605.0076 0.78098

Frequencies -- -200.8277 18.3452 20.9461

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=chloroform)

Pointgroup= C1 Stoichiometry= C43H49N3O5S C1[X(C43H49N3O5S)] #Atoms= 101
Charge = 0 Multiplicity = 1

SCF Energy= -2606.54047085

==========

***(R)*-TS-III-B**

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Chloroform)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
temp=273.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C43H49N3O5S C1[X(C43H49N3O5S)] #Atoms= 101

Charge = 0 Multiplicity = 1

SCF Energy= -2605.78051149 Predicted Change= -2.007579D-09

==========

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Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00212	0.00180	[NO]	0.00212	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.917074	5.651422	0.842617
C	1.138067	4.289542	0.667214
C	1.263198	3.751750	-0.612041
C	1.190406	4.552142	-1.748609
C	0.974306	5.914380	-1.567755
C	0.837584	6.459559	-0.287656
S	1.264439	3.046451	1.906676
C	1.513358	1.842698	0.658475
N	1.466477	2.368532	-0.578949
N	1.784704	0.566006	0.877065
C	1.491492	-0.017766	2.229129
C	2.347320	-1.236285	2.571933
C	3.758067	-0.726101	2.891768
C	1.745612	-1.950358	3.779123
O	1.240877	0.815775	3.098923
C	2.066637	-0.323001	-0.266708
C	3.546322	-0.420859	-0.573938
C	1.182863	0.104126	-1.447850
C	1.250186	-0.841828	-2.666397
C	2.336257	-0.500651	-3.692034
C	-0.124430	-0.883794	-3.339466
C	1.462953	1.557369	-1.798905
C	4.088298	-1.685200	-0.819258
C	5.429013	-1.821687	-1.172257
C	6.243678	-0.696765	-1.272766
C	5.715613	0.564913	-1.005119
C	4.374829	0.702807	-0.656112
H	2.385071	-1.941118	1.739327
H	4.198443	-0.177168	2.053004
H	4.415270	-1.569307	3.124946
H	3.724319	-0.060385	3.760315
H	1.614330	-1.243715	4.604712
H	0.773256	-2.375758	3.522803
H	2.411622	-2.753775	4.109049
H	0.810447	6.071855	1.837305
H	1.303866	4.132300	-2.742070
H	0.913985	6.560329	-2.437150
H	0.669114	7.524821	-0.171275
H	1.725044	-1.310706	0.033515
H	0.160938	0.055303	-1.055468
H	1.461276	-1.847650	-2.273544
H	2.394294	-1.295587	-4.441799

H	3.325792	-0.393586	-3.237947
H	2.098454	0.428692	-4.223437
H	-0.876161	-1.270145	-2.642806
H	-0.111558	-1.526156	-4.226098
H	-0.431496	0.119216	-3.661996
H	0.679046	1.955901	-2.450540
H	2.430254	1.679939	-2.298404
H	3.452988	-2.563173	-0.717837
H	5.839305	-2.809558	-1.358215
H	7.289427	-0.802196	-1.544365
H	6.349227	1.444627	-1.062179
H	3.984259	1.692470	-0.429955
C	-3.075797	-1.371909	0.498310
C	-4.044535	-2.258960	0.060215
C	-4.239894	-3.417627	0.820724
C	-3.493218	-3.661113	1.970428
C	-2.525610	-2.740789	2.396524
C	-2.327375	-1.591762	1.657013
C	-1.326211	-0.459288	1.835337
C	-1.579053	0.306484	3.135904
O	-0.021879	-0.952606	1.678240
C	-1.696512	0.451959	0.632199
O	-1.207485	1.537264	0.355379
N	-2.662962	-0.173754	-0.112232
C	-3.225380	0.369264	-1.331030
C	-4.613004	0.941327	-1.129188
C	-5.669971	0.566630	-1.956542
C	-6.939851	1.112487	-1.771381
C	-7.158727	2.034535	-0.752223
C	-6.104523	2.411454	0.080304
C	-4.838341	1.868261	-0.108013
H	-1.033977	1.249762	3.140625
H	-1.241036	-0.297810	3.982665
H	-2.651930	0.500222	3.240793
H	-0.102130	-1.975415	0.554827
H	-4.633839	-2.063599	-0.830501
H	-4.990687	-4.135647	0.504894
H	-3.663914	-4.568947	2.540205
H	-1.934405	-2.930180	3.288923
H	-2.529394	1.147875	-1.661027
H	-3.243028	-0.416824	-2.095135
H	-5.500805	-0.158443	-2.749686
H	-7.757333	0.811660	-2.419485
H	-8.147053	2.458802	-0.604562
H	-6.270082	3.132577	0.874834
H	-4.012397	2.166075	0.534449
C	0.535135	-3.616531	-0.284441
C	0.100871	-4.767226	-1.180140
C	-0.719863	-4.296953	-2.380803
C	1.310518	-5.597613	-1.600043
O	1.581964	-3.629684	0.345933
O	-0.327244	-2.619858	-0.230603
H	-1.596063	-3.725885	-2.065173
H	-0.112100	-3.662606	-3.035735
H	-1.052876	-5.160386	-2.964614

```
      H       -0.550403     -5.382160     -0.541675
      H        0.991726     -6.474523     -2.170505
      H        1.880947     -5.928433     -0.730449
      H        1.977365     -5.001658     -2.233818
---------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 273.150 Kelvin       Pressure= 1.00000 Atm
=====================================================================
==
 SCF Energy=     -2605.78051149   Predicted Change= -2.007579D-09
 Zero-point correction (ZPE)=             -2604.9265      0.85392
 Internal Energy (U)=                     -2604.8855      0.89501
 Enthalpy (H)=                            -2604.8846      0.89587
 Gibbs Free Energy (G)=                   -2604.9987      0.78175
---------------------------------------------------------------------
 Frequencies --   -161.2304              15.7185              17.6990
=====================================================================
==
 #m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
 SCRF=(PCM,SOLVENT=chloroform)
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C43H49N3O5S   C1[X(C43H49N3O5S)]  #Atoms= 101
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -2606.53017855
=====================================================================
==
```

***(R)*-TS-III-C**

```
---------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
=====================================================================
==
 #m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=Chloroform)
 opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
 temp=273.15
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C43H49N3O5S   C1[X(C43H49N3O5S)]  #Atoms= 101
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -2605.75991197       Predicted Change= -5.434274D-09
=====================================================================
==
 Optimization completed.           {Found       2       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00001 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00100 ||  0.00180   [ YES ]      0.00100 ||  0.00180   [ YES ]
---------------------------------------------------------------------
     Atomic              Coordinates (Angstroms)
      Type              X             Y          Z
---------------------------------------------------------------------
      C        0.760901      4.270470     -0.885850
      C        1.330971      3.024860     -0.645160
```

C	2.258471	2.467449	-1.525990
C	2.678181	3.163509	-2.657790
C	2.122261	4.417489	-2.888470
C	1.170251	4.962910	-2.019700
S	0.977090	1.939950	0.672470
C	2.053410	0.752679	0.013050
N	2.645300	1.179699	-1.129840
N	2.235940	-0.460831	0.516330
C	1.521470	-1.055710	1.735870
C	1.486930	-0.199200	2.999520
C	0.705330	-0.971290	4.060500
C	2.922950	0.095179	3.443320
O	1.613599	-2.263080	1.802410
C	3.144700	-1.405901	-0.166240
C	4.507230	-1.423631	0.493980
C	3.158770	-1.126351	-1.677040
C	4.029830	-2.123841	-2.476880
C	5.497930	-1.710051	-2.630760
C	3.412019	-2.365771	-3.857200
C	3.514260	0.328139	-1.943930
C	5.197280	-0.243541	0.788270
C	6.477870	-0.290321	1.331250
C	7.081140	-1.519442	1.592270
C	6.391829	-2.699101	1.322660
C	5.109249	-2.649361	0.781740
H	0.967570	0.742150	2.819400
H	1.242930	-1.880450	4.343220
H	-0.273460	-1.255620	3.665840
H	0.572810	-0.349370	4.950790
H	3.506600	-0.830181	3.505320
H	2.914330	0.564139	4.431850
H	3.434140	0.773539	2.752370
H	0.009531	4.664740	-0.211050
H	3.413701	2.749319	-3.338320
H	2.431651	4.977439	-3.764520
H	0.743081	5.936850	-2.233080
H	2.681349	-2.382861	-0.020070
H	2.118420	-1.258711	-2.006900
H	4.003779	-3.074451	-1.927390
H	5.977540	-1.481041	-1.674940
H	5.592520	-0.834671	-3.284500
H	6.056369	-2.524971	-3.100860
H	4.017929	-3.072581	-4.432030
H	3.358400	-1.433261	-4.431950
H	2.399249	-2.771871	-3.775130
H	3.335980	0.580669	-2.992540
H	4.559030	0.550099	-1.703640
H	4.730280	0.723429	0.610910
H	7.002470	0.633148	1.555540
H	8.079780	-1.556762	2.016040
H	6.848419	-3.659682	1.539910
H	4.566639	-3.570211	0.582950
C	-3.051570	-0.100689	-0.622910
C	-3.816240	0.754411	-1.404030
C	-3.142320	1.549441	-2.338690

C	-1.760880	1.470950	-2.491730
C	-1.015400	0.590610	-1.697620
C	-1.660510	-0.182770	-0.751970
C	-1.112370	-1.141460	0.297360
C	-0.475141	-2.381770	-0.334280
O	-0.301240	-0.498940	1.226170
C	-2.425000	-1.597780	0.998530
O	-2.515691	-2.385979	1.918940
N	-3.488410	-0.965399	0.391260
C	-4.866700	-1.147179	0.788340
C	-5.669330	-1.915349	-0.241270
C	-6.892950	-1.434069	-0.703270
C	-7.629960	-2.157768	-1.640080
C	-7.143351	-3.368868	-2.123180
C	-5.918021	-3.854879	-1.665660
C	-5.185881	-3.131709	-0.730590
H	-4.896670	0.799491	-1.303030
H	-3.714690	2.232611	-2.959100
H	-1.258630	2.094950	-3.224640
H	0.063660	0.520090	-1.827360
H	0.444160	-2.102420	-0.859670
H	-1.163181	-2.831150	-1.058250
H	-0.230971	-3.107760	0.442750
H	-1.166720	0.603100	1.761420
H	-4.832420	-1.689919	1.738190
H	-5.328360	-0.169579	0.973620
H	-7.272310	-0.485838	-0.328640
H	-8.580410	-1.771328	-1.995340
H	-7.713741	-3.932718	-2.854900
H	-5.534841	-4.799929	-2.038430
H	-4.231761	-3.509519	-0.369300
C	-2.342870	2.242610	1.564560
C	-3.766039	2.648801	1.919380
C	-4.198989	3.877321	1.130700
C	-3.888339	2.860481	3.432980
O	-1.634579	2.916640	0.834230
O	-1.988990	1.115900	2.155930
H	-5.243199	4.120941	1.349120
H	-3.580239	4.739751	1.397250
H	-4.091439	3.709431	0.055760
H	-4.394700	1.791541	1.643070
H	-4.920629	3.108211	3.697670
H	-3.249419	3.690911	3.753650
H	-3.590800	1.963451	3.979960

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2605.75991197 Predicted Change= -5.434274D-09
Zero-point correction (ZPE)= -2604.9069 0.85291
Internal Energy (U)= -2604.8657 0.89412
Enthalpy (H)= -2604.8649 0.89498
Gibbs Free Energy (G)= -2604.9782 0.78161

```
 Frequencies --   -168.8537               19.4828               21.4462
================================================================================
==
 #m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
 SCRF=(PCM,SOLVENT=chloroform)
--------------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C43H49N3O5S   C1[X(C43H49N3O5S)]  #Atoms= 101
 Charge = 0          Multiplicity = 1
--------------------------------------------------------------------------------
 SCF Energy= -2606.51364913
================================================================================
==
```

Acylation transition states with three aromatic carbinol substituents

***(S)*-TS-Ph-A**

```
---------------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
===========================================================================
==
 #m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=Chloroform)
 opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
 temp=273.15
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C48H51N3O5S   C1[X(C48H51N3O5S)]  #Atoms= 108
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -2797.45665083       Predicted Change= -1.641324D-09
===========================================================================
==
 Optimization completed on the basis of negligible forces.           {Found       2       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00000 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00270 ||  0.00180   [ NO ]       0.00270 ||  0.00180   [ YES ]
---------------------------------------------------------------------------
     Atomic              Coordinates (Angstroms)
      Type              X             Y         Z
---------------------------------------------------------------------------
      C         1.741916      5.317337     -0.971914
      C         0.876729      4.256058     -0.730006
      C         0.095096      4.221001      0.422847
      C         0.138103      5.251019      1.358410
      C         1.000183      6.314269      1.110004
      C         1.794545      6.349159     -0.040215
      S         0.642069      2.816292     -1.710999
      C        -0.551593      2.238743     -0.562524
      N        -0.692963      3.065833      0.484483
      N        -1.288972      1.148347     -0.712879
      C        -0.926966      0.181691     -1.777926
      C        -2.100170     -0.546191     -2.415984
      C        -2.879259      0.469530     -3.266733
      C        -1.572431     -1.664940     -3.311971
      O         0.086740      0.443163     -2.411756
      C        -2.325518      0.808728      0.295552
      C        -3.682648      1.364865     -0.094118
      C        -1.834378      1.249139      1.691809
      C        -2.852653      0.960991      2.812591
      C        -2.424857      1.598390      4.139747
      C        -3.048855     -0.541220      3.023696
      C        -1.473276      2.729180      1.676308
      C        -3.868201      2.698201     -0.476638
      C        -5.134924      3.168991     -0.811146
      C        -6.233958      2.313432     -0.765914
      C        -6.056314      0.983715     -0.393775
      C        -4.788009      0.510367     -0.063036
      H        -2.751423     -0.963599     -1.641561
```

H	-3.299488	1.284819	-2.672764
H	-3.704666	-0.037928	-3.774946
H	-2.219322	0.896933	-4.029485
H	-0.965972	-1.242781	-4.118532
H	-0.955314	-2.369172	-2.753616
H	-2.412815	-2.208952	-3.754388
H	2.356295	5.338539	-1.865991
H	-0.479979	5.231096	2.249156
H	1.053867	7.128627	1.824575
H	2.459786	7.188838	-0.210354
H	-2.373002	-0.281600	0.295077
H	-0.912912	0.680611	1.876515
H	-3.812879	1.405142	2.515318
H	-1.415581	1.271810	4.418812
H	-3.107430	1.289615	4.937223
H	-2.435301	2.692184	4.107988
H	-2.123508	-0.983142	3.413159
H	-3.317780	-1.076420	2.108767
H	-3.837416	-0.714415	3.763111
H	-0.846128	2.973782	2.536471
H	-2.368707	3.363600	1.703457
H	-3.019899	3.375027	-0.549326
H	-5.261384	4.203895	-1.114087
H	-7.220958	2.680375	-1.030013
H	-6.905325	0.307280	-0.371122
H	-4.641869	-0.535384	0.197658
C	2.785618	-1.167851	-1.527397
C	3.769060	-1.489005	-2.449071
C	3.617714	-2.688585	-3.154237
C	2.529830	-3.528052	-2.929080
C	1.559672	-3.191519	-1.975898
C	1.693598	-2.003803	-1.283354
C	0.843526	-1.407821	-0.172278
C	1.030014	-2.190776	1.140872
O	-0.496326	-1.244695	-0.460821
C	1.581186	-0.052557	0.071518
O	1.271720	0.813363	0.875594
N	2.702909	-0.026910	-0.710270
C	3.709775	1.011651	-0.634163
C	4.944408	0.540534	0.105865
C	6.212632	0.637045	-0.462509
C	7.335053	0.192286	0.235975
C	7.192422	-0.356654	1.506920
C	5.924395	-0.456271	2.080965
C	4.807406	-0.007343	1.385261
C	2.291175	-2.645653	1.538040
C	2.451978	-3.300818	2.755440
C	1.352865	-3.517935	3.585440
C	0.095295	-3.069433	3.190537
C	-0.064887	-2.402303	1.976497
H	-1.122856	-2.482210	-0.578460
H	4.626609	-0.844261	-2.614515
H	4.369601	-2.968195	-3.886084
H	2.440113	-4.454430	-3.487335
H	0.717369	-3.849282	-1.773294

H	3.962840	1.342130	-1.647862
H	3.237983	1.849711	-0.111230
H	6.325196	1.061116	-1.457965
H	8.318688	0.270892	-0.217004
H	8.065021	-0.706793	2.049833
H	5.806658	-0.883120	3.072549
H	3.817965	-0.081192	1.832658
H	3.153241	-2.491921	0.891669
H	3.437316	-3.648002	3.052752
H	1.477435	-4.034989	4.532099
H	-0.768999	-3.239518	3.827507
H	-1.041783	-2.046574	1.663547
C	-2.752058	-3.451225	-0.084868
C	-3.343000	-4.828178	0.155533
C	-3.106097	-5.771979	-1.021831
C	-2.716643	-5.377916	1.444878
O	-3.336546	-2.423093	0.245550
O	-1.553791	-3.469334	-0.609856
H	-3.527143	-5.370830	-1.948750
H	-2.034306	-5.925580	-1.173950
H	-3.571597	-6.742873	-0.826172
H	-4.416039	-4.680494	0.312567
H	-1.633213	-5.478228	1.322954
H	-2.906364	-4.709107	2.290668
H	-3.133929	-6.361589	1.680944

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2797.45665083 Predicted Change= -1.641324D-09
Zero-point correction (ZPE)= -2796.5504 0.90617
Internal Energy (U)= -2796.5065 0.95013
Enthalpy (H)= -2796.5056 0.95100
Gibbs Free Energy (G)= -2796.6273 0.82930

Frequencies -- -146.2009 9.5511 12.1649

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=chloroform)

Pointgroup= C1 Stoichiometry= C48H51N3O5S C1[X(C48H51N3O5S)] #Atoms= 108
Charge = 0 Multiplicity = 1

SCF Energy= -2798.26370286

==========

***(S)*-TS-Ph-B**

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current

SCRF=(PCM,SOLVENT=Chloroform)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
temp=273.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C48H51N3O5S C1[X(C48H51N3O5S)] #Atoms= 108
Charge = 0 Multiplicity = 1

SCF Energy= -2797.44632762 Predicted Change= -5.411496D-10

==========

==

Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00226	0.00180	[NO]	0.00226	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.267138	-4.860897	-1.581365
C	-1.320185	-3.932916	-1.160243
C	-0.986111	-3.818867	0.186866
C	-1.558618	-4.647052	1.150009
C	-2.497046	-5.580697	0.722532
C	-2.851670	-5.685975	-0.626196
S	-0.463847	-2.760196	-2.144802
C	0.323414	-2.139269	-0.711963
N	-0.052787	-2.797152	0.404193
N	1.217597	-1.159489	-0.695549
C	1.476056	-0.391680	-1.960440
C	2.892677	0.156744	-2.108145
C	3.759975	-0.997922	-2.632867
C	2.922147	1.311402	-3.110460
O	0.860524	-0.787377	-2.940905
C	1.958096	-0.845370	0.552951
C	3.277497	-1.600030	0.598133
C	1.073380	-1.112273	1.789807
C	1.803251	-0.868433	3.126072
C	0.940905	-1.303293	4.316490
C	2.172907	0.608461	3.281135
C	0.478415	-2.510289	1.736345
C	3.348537	-2.976711	0.357319
C	4.566508	-3.647271	0.429553
C	5.730855	-2.949878	0.744611
C	5.669141	-1.578969	0.978799
C	4.451018	-0.906390	0.903800
H	3.275154	0.515430	-1.151526
H	4.809532	-0.689691	-2.654482
H	3.449889	-1.255983	-3.650550
H	3.686107	-1.895938	-2.013683
H	2.329096	1.056125	-3.994335
H	2.529710	2.231294	-2.676033
H	3.954411	1.490966	-3.428186
H	-2.538958	-4.936491	-2.629410
H	-1.282979	-4.576720	2.196417

H	-2.957819	-6.237933	1.452189
H	-3.589049	-6.419944	-0.933344
H	2.147229	0.230607	0.509692
H	0.250406	-0.395942	1.741042
H	2.719971	-1.472843	3.131895
H	0.768387	-2.383701	4.343324
H	-0.033883	-0.799089	4.297586
H	1.435251	-1.028770	5.252850
H	2.830686	0.968570	2.486296
H	2.676210	0.769593	4.240026
H	1.264966	1.222500	3.257827
H	-0.356769	-2.588249	2.435622
H	1.216810	-3.279838	1.997186
H	2.459180	-3.535818	0.074047
H	4.605418	-4.713864	0.230917
H	6.681246	-3.471905	0.797318
H	6.573565	-1.025298	1.211635
H	4.408325	0.168672	1.057055
C	-2.331544	-0.176543	-0.676211
C	-3.348790	-1.086346	-0.929152
C	-3.662435	-1.340437	-2.267938
C	-2.983523	-0.697946	-3.302023
C	-1.960463	0.213177	-3.019896
C	-1.623085	0.456087	-1.701677
C	-0.643080	1.460551	-1.091565
C	-1.112020	2.858218	-1.515090
O	0.706888	1.281972	-1.348201
C	-0.915558	1.255640	0.424567
O	-0.361199	1.830485	1.344328
N	-1.858687	0.263775	0.575089
C	-2.407018	-0.141847	1.856321
C	-3.712425	0.554342	2.176581
C	-3.717404	1.942774	2.346071
C	-4.904037	2.611442	2.626116
C	-6.096501	1.897015	2.748090
C	-6.095096	0.514523	2.590038
C	-4.904673	-0.154117	2.304230
C	-0.457826	3.505917	-2.561912
C	-0.912655	4.742012	-3.016111
C	-2.022426	5.342302	-2.426246
C	-2.680985	4.695620	-1.381817
C	-2.230916	3.457459	-0.933085
H	1.446427	2.461483	-0.794681
H	-3.894017	-1.570912	-0.125377
H	-4.455909	-2.045202	-2.498593
H	-3.250957	-0.906182	-4.333132
H	-1.422747	0.716084	-3.818244
H	-2.536266	-1.231342	1.854817
H	-1.653101	0.116964	2.607490
H	-2.780425	2.490428	2.264047
H	-4.898932	3.689219	2.756975
H	-7.022782	2.418631	2.968004
H	-7.020027	-0.045922	2.685606
H	-4.905051	-1.235282	2.183892
H	0.410212	3.032023	-3.009832

H	-0.395477	5.239129	-3.831627
H	-2.373307	6.307846	-2.777688
H	-3.548028	5.154468	-0.915804
H	-2.763964	2.953975	-0.128117
C	2.826635	3.176394	0.388395
C	3.211934	4.432421	1.149190
C	4.517505	4.241682	1.909991
C	2.053976	4.805588	2.085486
O	3.382278	2.098361	0.559680
O	1.831108	3.364603	-0.443293
H	5.334756	3.966060	1.238227
H	4.790917	5.164043	2.431065
H	4.411151	3.443898	2.651807
H	3.321226	5.229712	0.403869
H	1.126177	4.943856	1.525650
H	1.893893	4.011030	2.823266
H	2.286405	5.729018	2.624263

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2797.44632762 Predicted Change= -5.411496D-10

Zero-point correction (ZPE)=	-2796.5391	0.90719
Internal Energy (U)=	-2796.4953	0.95094
Enthalpy (H)=	-2796.4945	0.95180
Gibbs Free Energy (G)=	-2796.6138	0.83247

Frequencies -- -147.6910 7.7669 22.6433

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=chloroform)

Pointgroup= C1 Stoichiometry= C48H51N3O5S C1[X(C48H51N3O5S)] #Atoms= 108
Charge = 0 Multiplicity = 1

SCF Energy= -2798.25322995

==========

***(S)*-TS-Ph-C**

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Chloroform)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
temp=273.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C48H51N3O5S C1[X(C48H51N3O5S)] #Atoms= 108
Charge = 0 Multiplicity = 1

SCF Energy= -2797.44281026 Predicted Change= -1.042117D-10

==

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00030	0.00180	[YES]	0.00030	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	5.678167	-2.806428	-1.114266
C	4.723705	-1.824145	-0.869449
C	4.845611	-0.979648	0.231520
C	5.928943	-1.065336	1.101381
C	6.886111	-2.041781	0.845601
C	6.762161	-2.905481	-0.246840
S	3.245294	-1.510203	-1.766902
C	2.851201	-0.220905	-0.650670
N	3.767292	-0.093659	0.330095
N	1.806491	0.582341	-0.751592
C	0.705647	0.214795	-1.709324
C	-0.036738	1.419615	-2.278334
C	0.901689	2.092406	-3.291725
C	-1.312818	0.967197	-2.983192
O	0.916329	-0.778433	-2.390581
C	1.617878	1.690140	0.216011
C	2.202704	2.989290	-0.307368
C	2.160598	1.266271	1.594989
C	2.026437	2.352981	2.678006
C	2.672673	1.905239	3.993741
C	0.562629	2.716543	2.929678
C	3.604108	0.797696	1.477319
C	1.409085	4.139407	-0.287632
C	1.917809	5.355360	-0.740320
C	3.220281	5.433561	-1.225254
C	4.012262	4.287343	-1.263561
C	3.506655	3.073077	-0.807396
H	-0.296232	2.125704	-1.483997
H	0.428327	2.994243	-3.691563
H	1.097458	1.406182	-4.122241
H	1.859057	2.382387	-2.849840
H	-2.029989	0.537148	-2.284078
H	-1.776590	1.826270	-3.479280
H	-1.075807	0.208474	-3.733567
H	5.577908	-3.476874	-1.961803
H	6.030501	-0.392817	1.946288
H	7.741006	-2.130209	1.507453
H	7.519699	-3.661639	-0.422766
H	0.537133	1.800282	0.320201
H	1.548794	0.406049	1.895146
H	2.555513	3.247579	2.320980
H	2.248581	0.949434	4.327609
H	2.478625	2.645714	4.775016
H	3.758145	1.790218	3.917130

H	0.003657	1.838496	3.277775
H	0.053049	3.093225	2.041400
H	0.497582	3.481712	3.709617
H	3.890246	0.223905	2.362110
H	4.292355	1.646973	1.376622
H	0.380177	4.068938	0.058136
H	1.288803	6.240100	-0.724857
H	3.614085	6.379286	-1.584365
H	5.023334	4.336028	-1.655949
H	4.128558	2.183499	-0.877440
C	-2.892664	-2.005799	1.222258
C	-3.810871	-2.094572	2.257728
C	-3.427756	-1.597202	3.507206
C	-2.177410	-1.014706	3.694672
C	-1.268269	-0.940633	2.632394
C	-1.615296	-1.467271	1.402133
C	-0.871118	-1.462925	0.065578
C	0.300991	-2.462698	0.082890
O	-0.490680	-0.160372	-0.254918
C	-1.996322	-1.980049	-0.887216
O	-1.965695	-2.036645	-2.101402
N	-3.073487	-2.362604	-0.120132
C	-4.329393	-2.812009	-0.692229
C	-5.339003	-1.694070	-0.848942
C	-5.080448	-0.653812	-1.747149
C	-6.008884	0.366823	-1.922676
C	-7.196609	0.370209	-1.189472
C	-7.454441	-0.656954	-0.286852
C	-6.529062	-1.687676	-0.123040
C	0.430908	-3.496624	-0.845937
C	1.494086	-4.396820	-0.767658
C	2.456311	-4.271664	0.228923
C	2.345647	-3.236118	1.155463
C	1.273247	-2.352332	1.084056
H	-1.699792	0.605299	-0.144181
H	-4.801110	-2.509650	2.103722
H	-4.127832	-1.650847	4.335389
H	-1.908135	-0.608191	4.664355
H	-0.307177	-0.456529	2.777648
H	-4.079780	-3.238468	-1.667804
H	-4.731869	-3.612772	-0.062799
H	-4.151447	-0.660395	-2.312118
H	-5.809168	1.160001	-2.637394
H	-7.917985	1.170478	-1.324826
H	-8.375788	-0.661565	0.287538
H	-6.740793	-2.499288	0.569852
H	-0.288561	-3.590540	-1.651204
H	1.570834	-5.194978	-1.500285
H	3.288358	-4.967561	0.283000
H	3.089424	-3.121750	1.939847
H	1.180888	-1.578826	1.838449
C	-2.613712	2.220023	0.471786
C	-3.946741	2.770962	0.948273
C	-4.636375	3.448999	-0.243048
C	-4.830070	1.688782	1.566201

O	-1.591697	2.898919	0.466840
O	-2.671449	0.987906	0.032116
H	-4.840756	2.710419	-1.024348
H	-5.588559	3.888383	0.070291
H	-4.008406	4.239973	-0.663369
H	-3.704667	3.536197	1.693837
H	-4.317527	1.177783	2.388039
H	-5.754024	2.131986	1.952364
H	-5.092611	0.935867	0.816106

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2797.44281026 Predicted Change= -1.042117D-10
Zero-point correction (ZPE)= -2796.5350 0.90778
Internal Energy (U)= -2796.4916 0.95111
Enthalpy (H)= -2796.4908 0.95198
Gibbs Free Energy (G)= -2796.6072 0.83559

Frequencies -- -132.1844 23.0601 24.1135

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=chloroform)

Pointgroup= C1 Stoichiometry= C48H51N3O5S C1[X(C48H51N3O5S)] #Atoms= 108
Charge = 0 Multiplicity = 1

SCF Energy= -2798.25103256

==========

***(R)*-TS-Ph-A**

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Chloroform)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
temp=273.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C48H51N3O5S C1[X(C48H51N3O5S)] #Atoms= 108
Charge = 0 Multiplicity = 1

SCF Energy= -2797.44667313 Predicted Change= -5.887786D-10

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00038	0.00180	[YES]	0.00038	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-5.472218	1.225322	1.988540
C	-4.378891	0.645707	1.354927
C	-3.751100	-0.470616	1.901934
C	-4.197931	-1.047834	3.087619
C	-5.294916	-0.465800	3.716525
C	-5.925953	0.658084	3.175635
S	-3.604530	1.164454	-0.138129
C	-2.473050	-0.166259	0.005286
N	-2.675111	-0.897380	1.115791
N	-1.539965	-0.466423	-0.879913
C	-1.259214	0.515313	-1.989199
C	-0.760353	-0.145659	-3.275858
C	-1.981278	-0.767927	-3.966975
C	-0.117514	0.893463	-4.190491
O	-2.069068	1.439437	-2.057628
C	-0.719277	-1.685637	-0.704600
C	-1.336328	-2.866926	-1.435870
C	-0.446898	-1.932374	0.793374
C	0.323694	-3.235967	1.076403
C	0.562521	-3.399918	2.582373
C	1.664205	-3.267272	0.342875
C	-1.745162	-1.917780	1.594932
C	-2.651148	-3.281806	-1.195615
C	-3.188007	-4.365760	-1.883988
C	-2.419644	-5.049752	-2.823969
C	-1.115719	-4.635103	-3.079237
C	-0.578999	-3.548142	-2.392232
H	-0.016096	-0.913602	-3.060843
H	-2.526694	-1.455708	-3.313600
H	-1.663187	-1.326925	-4.852483
H	-2.668577	0.024029	-4.281101
H	0.109211	0.440583	-5.160973
H	-0.809396	1.726869	-4.351161
H	0.807423	1.277718	-3.755805
H	-5.957851	2.098297	1.564314
H	-3.714330	-1.923428	3.507025
H	-5.663580	-0.895802	4.641797
H	-6.779039	1.094052	3.684546
H	0.242907	-1.461710	-1.167511
H	0.171144	-1.091676	1.132783
H	-0.292484	-4.076137	0.725027
H	1.070197	-2.516719	2.991244
H	1.202533	-4.267485	2.770296
H	-0.367583	-3.552526	3.138788
H	2.227560	-4.164178	0.620685
H	2.257436	-2.392036	0.624644
H	1.549417	-3.269478	-0.744705
H	-1.533275	-1.681874	2.641188
H	-2.243930	-2.895068	1.552710
H	-3.281179	-2.742377	-0.493029
H	-4.211809	-4.670644	-1.690021
H	-2.841308	-5.892923	-3.362317

H	-0.516178	-5.149203	-3.824199
H	0.427352	-3.202084	-2.622085
C	2.499954	2.326529	0.854819
C	3.819131	2.615201	1.165338
C	4.597842	3.205029	0.163706
C	4.065694	3.479596	-1.093786
C	2.728998	3.175887	-1.380992
C	1.947330	2.603728	-0.395803
C	0.493096	2.129492	-0.429897
C	-0.412114	3.336878	-0.674669
O	0.362730	1.090713	-1.363080
C	0.332928	1.595572	1.026098
O	-0.674794	1.137735	1.540068
N	1.535731	1.712456	1.674135
C	1.708576	1.382121	3.070741
C	2.482676	0.105587	3.342656
C	3.219510	-0.554816	2.359062
C	3.945811	-1.702467	2.685551
C	3.934331	-2.204431	3.982393
C	3.188604	-1.552543	4.964498
C	2.472586	-0.404040	4.645100
C	-1.048312	4.015394	0.362945
C	-1.774726	5.180114	0.106367
C	-1.866564	5.677397	-1.187816
C	-1.230681	5.000715	-2.230760
C	-0.510647	3.842278	-1.974418
H	1.565596	0.205235	-1.184771
H	4.237663	2.378161	2.139087
H	5.635788	3.444662	0.373474
H	4.691607	3.931036	-1.856747
H	2.311842	3.389739	-2.361001
H	2.206917	2.227769	3.561969
H	0.702668	1.302796	3.493070
H	3.214898	-0.191792	1.332952
H	4.520224	-2.209924	1.915065
H	4.498178	-3.098838	4.228423
H	3.165183	-1.939029	5.978929
H	1.895042	0.104858	5.413848
H	-1.001053	3.634224	1.378477
H	-2.270013	5.693496	0.925301
H	-2.431730	6.582621	-1.388648
H	-1.304878	5.376107	-3.247200
H	-0.040776	3.296826	-2.786670
C	2.872249	-1.145281	-1.777036
C	4.281175	-1.626967	-1.481096
C	4.701255	-2.724621	-2.448901
C	5.240373	-0.428980	-1.493673
O	2.206091	-1.529084	-2.724994
O	2.446689	-0.262304	-0.893338
H	4.706371	-2.345737	-3.475259
H	5.706349	-3.081130	-2.205566
H	4.010799	-3.571671	-2.409447
H	4.253537	-2.027124	-0.457804
H	6.253401	-0.755723	-1.241074
H	4.923527	0.334171	-0.777187

```
      H        5.269537       0.027098      -2.489587
 ---------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 273.150 Kelvin       Pressure= 1.00000 Atm
 =====================================================================
 ==
 SCF Energy=     -2797.44667313   Predicted Change= -5.887786D-10
 Zero-point correction (ZPE)=            -2796.5403       0.90631
 Internal Energy (U)=                    -2796.4967       0.94993
 Enthalpy (H)=                           -2796.4958       0.95080
 Gibbs Free Energy (G)=                  -2796.6136       0.83301
 ---------------------------------------------------------------------
 Frequencies --   -145.4962              20.5517              25.4097
 =====================================================================
 ==
 #m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
 SCRF=(PCM,SOLVENT=chloroform)
 ---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C48H51N3O5S   C1[X(C48H51N3O5S)]  #Atoms= 108
 Charge = 0         Multiplicity = 1
 ---------------------------------------------------------------------
 SCF Energy= -2798.25406999
 =====================================================================
 ==
```

***(R)*-TS-Ph-B**

```
 ---------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
 =====================================================================
 ==
 #m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=Chloroform)
 opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
 temp=273.15
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
 ---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C48H51N3O5S   C1[X(C48H51N3O5S)]  #Atoms= 108
 Charge = 0         Multiplicity = 1
 ---------------------------------------------------------------------
 SCF Energy= -2797.44620626       Predicted Change= -1.870060D-09
 =====================================================================
 ==
 Optimization completed.          {Found       2       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00001 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00006 ||  0.00180   [ YES ]      0.00006 ||  0.00180   [ YES ]
 ---------------------------------------------------------------------
     Atomic             Coordinates (Angstroms)
      Type              X           Y           Z
 ---------------------------------------------------------------------
      C       -4.039031      -4.570599       0.691950
      C       -3.573811      -3.270539       0.524900
      C       -3.818541      -2.575229      -0.657820
      C       -4.554061      -3.141349      -1.695830
      C       -5.028051      -4.437069      -1.519020
```

C	-4.773241	-5.145669	-0.340430
S	-2.582060	-2.334679	1.631650
C	-2.581320	-1.008539	0.494730
N	-3.227990	-1.306959	-0.648640
N	-2.064690	0.189651	0.726200
C	-1.059770	0.347211	1.811700
C	-0.955120	1.776801	2.339680
C	-2.210680	2.035081	3.186580
C	0.297070	1.956050	3.190680
O	-0.909970	-0.617159	2.554550
C	-2.205580	1.252891	-0.294040
C	-3.417680	2.124191	-0.042690
C	-2.133030	0.614991	-1.686570
C	-2.111750	1.647331	-2.836330
C	-3.491610	2.043601	-3.371770
C	-1.233640	1.124661	-3.977190
C	-3.216310	-0.441009	-1.834340
C	-4.674550	1.595231	0.267180
C	-5.772150	2.436111	0.432360
C	-5.624690	3.814801	0.292000
C	-4.372149	4.348741	-0.000570
C	-3.272290	3.509201	-0.162280
H	-0.919410	2.493301	1.515050
H	-2.226890	1.352441	4.042610
H	-3.134440	1.897841	2.616920
H	-2.195930	3.062001	3.563610
H	0.297360	1.247990	4.025220
H	1.205860	1.803730	2.605530
H	0.312290	2.971110	3.600720
H	-3.832531	-5.119009	1.605330
H	-4.755661	-2.592969	-2.609620
H	-5.604151	-4.902339	-2.311680
H	-5.152551	-6.155629	-0.228060
H	-1.309330	1.865941	-0.222890
H	-1.155010	0.120961	-1.683280
H	-1.628110	2.544931	-2.428220
H	-3.385870	2.871331	-4.079780
H	-4.176970	2.363881	-2.581180
H	-3.957190	1.212201	-3.915260
H	-1.645990	0.197541	-4.395360
H	-0.218130	0.916251	-3.626100
H	-1.177780	1.856121	-4.789650
H	-3.024130	-1.082119	-2.700980
H	-4.210130	0.006951	-1.942380
H	-4.804250	0.523051	0.400340
H	-6.742550	2.013341	0.674270
H	-6.480959	4.469711	0.420700
H	-4.247619	5.423181	-0.096290
H	-2.288370	3.919731	-0.379190
C	3.616410	-0.229980	0.965820
C	4.766520	-0.043540	1.719130
C	4.651160	-0.163920	3.107140
C	3.428880	-0.460270	3.705380
C	2.282600	-0.644250	2.923390
C	2.380670	-0.530490	1.546330

C	1.323300	-0.617830	0.454720
C	0.707690	-2.016600	0.292650
O	0.375810	0.411870	0.502450
C	2.184120	-0.309680	-0.818330
O	1.769420	-0.185090	-1.954830
N	3.488250	-0.139480	-0.429590
C	4.523660	0.347060	-1.312220
C	5.710920	-0.588380	-1.416210
C	5.548970	-1.971380	-1.324160
C	6.647059	-2.817851	-1.452160
C	7.917980	-2.290761	-1.673880
C	8.085820	-0.910941	-1.763010
C	6.987100	-0.065531	-1.630160
C	-0.058960	-2.297870	-0.846520
C	-0.625251	-3.554559	-1.039580
C	-0.434721	-4.562619	-0.095350
C	0.338239	-4.300400	1.030560
C	0.908309	-3.041220	1.218900
H	1.096010	1.617510	0.340610
H	5.719100	0.180730	1.249520
H	5.533470	-0.022910	3.724360
H	3.363070	-0.544630	4.785540
H	1.317480	-0.852660	3.377100
H	4.046270	0.476430	-2.288840
H	4.853170	1.335830	-0.966910
H	4.559080	-2.382780	-1.143600
H	6.509709	-3.892280	-1.375570
H	8.773549	-2.952221	-1.769550
H	9.073330	-0.490261	-1.927010
H	7.121420	1.012149	-1.690560
H	-0.173710	-1.532959	-1.605540
H	-1.215321	-3.750019	-1.931750
H	-0.884261	-5.540699	-0.240560
H	0.503899	-5.077030	1.771560
H	1.513089	-2.863200	2.100400
C	1.204170	3.482520	-0.309740
C	2.164841	4.636910	-0.552590
C	2.883001	4.995270	0.754350
C	1.446371	5.836080	-1.157420
O	0.006400	3.550960	-0.562150
O	1.784660	2.426240	0.204700
H	3.415210	4.131700	1.158770
H	3.600001	5.803510	0.582420
H	2.161401	5.337560	1.504710
H	2.915181	4.258980	-1.259830
H	0.692901	6.218110	-0.461550
H	2.159861	6.638390	-1.367650
H	0.936711	5.567110	-2.085760

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2797.44620626 Predicted Change= -1.870060D-09
Zero-point correction (ZPE)= -2796.5398 0.90637

```
 Internal Energy (U)=                  -2796.4958      0.95031
 Enthalpy (H)=                         -2796.4950      0.95118
 Gibbs Free Energy (G)=                -2796.6159      0.83025
 ---------------------------------------------------------------------------
 Frequencies --   -154.5758              11.2246              17.9999
 ===========================================================================
 ==
 #m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
 SCRF=(PCM,SOLVENT=chloroform)
 ---------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C48H51N3O5S   C1[X(C48H51N3O5S)]  #Atoms= 108
 Charge = 0         Multiplicity = 1
 ---------------------------------------------------------------------------
 SCF Energy= -2798.25376134
 ===========================================================================
 ==
```

***(R)*-TS-Ph-C**

```
 ---------------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
 ===========================================================================
 ==
 #m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=Chloroform)
 opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
 temp=273.15
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
 ---------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C48H51N3O5S   C1[X(C48H51N3O5S)]  #Atoms= 108
 Charge = 0         Multiplicity = 1
 ---------------------------------------------------------------------------
 SCF Energy= -2797.45359522       Predicted Change= -2.435528D-09
 ===========================================================================
 ==
 Optimization completed.          {Found       2       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00001 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00056 ||  0.00180   [ YES ]      0.00056 ||  0.00180   [ YES ]
 ---------------------------------------------------------------------------
      Atomic              Coordinates (Angstroms)
       Type              X             Y         Z
 ---------------------------------------------------------------------------
      C         3.923273      3.622366      0.961489
      C         2.678103      3.089478      0.645059
      C         1.530853      3.526959      1.302649
      C         1.582224      4.523749      2.273419
      C         2.828035      5.061147      2.578959
      C         3.986064      4.615426      1.933439
      S         2.321162      1.795718     -0.486421
      C         0.624572      1.921120     -0.082391
      N         0.390923      2.837370      0.873549
      N        -0.357349      1.242940     -0.665141
      C        -0.015520      0.102060     -1.533261
      C        -1.005510     -0.211229     -2.641721
      C        -0.847709      0.879781     -3.715501
```

C	-0.687332	-1.576099	-3.248791
O	1.176370	-0.137691	-1.660411
C	-1.771899	1.501112	-0.292791
C	-2.405628	2.525162	-1.215141
C	-1.846428	1.865312	1.203509
C	-3.276028	2.170933	1.692469
C	-3.274687	2.722583	3.122539
C	-4.159409	0.923264	1.636099
C	-0.911417	3.027001	1.514259
C	-3.642348	2.232374	-1.795321
C	-4.259897	3.153594	-2.639511
C	-3.646536	4.372414	-2.917151
C	-2.408376	4.666732	-2.349981
C	-1.791786	3.749082	-1.504411
H	-2.027580	-0.211588	-2.255231
H	-1.562689	0.698742	-4.523551
H	0.162951	0.841250	-4.135611
H	-1.024958	1.886641	-3.328551
H	0.321988	-1.571670	-3.672441
H	-1.399022	-1.787309	-4.053151
H	-0.743722	-2.374729	-2.508801
H	4.819803	3.270046	0.461859
H	0.685415	4.874989	2.772169
H	2.898995	5.839297	3.331319
H	4.946125	5.048985	2.192329
H	-2.277050	0.541172	-0.413041
H	-1.487679	0.974872	1.735749
H	-3.699377	2.937184	1.028969
H	-2.803527	3.707113	3.197599
H	-2.752398	2.037273	3.802029
H	-4.302877	2.825344	3.481439
H	-5.183739	1.177505	1.926599
H	-3.789500	0.172724	2.346839
H	-4.189690	0.460234	0.646839
H	-0.723557	3.090171	2.589269
H	-1.337196	3.981591	1.179639
H	-4.103839	1.266424	-1.602491
H	-5.217437	2.911475	-3.090501
H	-4.124435	5.086454	-3.580671
H	-1.916615	5.609052	-2.570951
H	-0.810086	3.985661	-1.099931
C	2.483649	-1.494542	0.923089
C	3.655429	-0.960333	1.442149
C	3.538290	0.071097	2.379489
C	2.290130	0.524728	2.798909
C	1.123150	-0.045691	2.273859
C	1.220449	-1.030451	1.307509
C	0.143018	-1.873430	0.619309
C	-0.558383	-2.695479	1.712729
O	-0.783731	-1.199049	-0.152601
C	1.025857	-2.820231	-0.248671
O	0.622236	-3.674110	-1.011181
N	2.352988	-2.548622	0.008809
C	3.450247	-3.327303	-0.526001
C	4.449028	-2.513964	-1.323081

C	4.019849	-1.485034	-2.163401
C	4.947299	-0.759785	-2.907151
C	6.307029	-1.056406	-2.822581
C	6.737628	-2.082356	-1.985051
C	5.810837	-2.804255	-1.235331
C	0.098396	-3.728600	2.386119
C	-0.536144	-4.414429	3.417149
C	-1.832444	-4.067508	3.796159
C	-2.488703	-3.034728	3.131659
C	-1.855852	-2.354138	2.092739
H	-1.781332	-2.106688	-0.627951
H	4.627559	-1.325024	1.126089
H	4.439020	0.515696	2.792469
H	2.220831	1.313928	3.542009
H	0.149440	0.264550	2.644239
H	3.965186	-3.840434	0.296639
H	2.983856	-4.091853	-1.155941
H	2.961569	-1.244873	-2.216271
H	4.604970	0.041476	-3.555961
H	7.027289	-0.488467	-3.403831
H	7.795028	-2.317667	-1.908811
H	6.149497	-3.598866	-0.574051
H	1.113496	-4.001771	2.103499
H	-0.018015	-5.221940	3.925809
H	-2.327264	-4.602008	4.601339
H	-3.501873	-2.760997	3.414249
H	-2.367342	-1.560578	1.554979
C	-3.707752	-2.192936	-0.985611
C	-4.894073	-3.140765	-0.977251
C	-6.144402	-2.480204	-1.542801
C	-5.099603	-3.596375	0.475349
O	-3.844621	-0.972486	-1.033361
O	-2.556783	-2.799107	-0.873921
H	-5.989872	-2.149834	-2.573951
H	-6.985663	-3.179553	-1.525341
H	-6.409282	-1.602414	-0.946161
H	-4.615554	-4.013926	-1.577561
H	-4.197854	-4.073346	0.868649
H	-5.932584	-4.302904	0.539689
H	-5.334953	-2.732355	1.109069

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2797.45359522 Predicted Change= -2.435528D-09
Zero-point correction (ZPE)= -2796.5470 0.90650
Internal Energy (U)= -2796.5032 0.95031
Enthalpy (H)= -2796.5024 0.95118
Gibbs Free Energy (G)= -2796.6215 0.83208

Frequencies -- -141.5346 16.1858 21.3325

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current

```
 SCRF=(PCM,SOLVENT=chloroform)
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C48H51N3O5S   C1[X(C48H51N3O5S)]  #Atoms= 108
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -2798.26104159
=====================================================================
==
```

Structures from alternative acylation mechanisms

***(S)*-TS-HBTM-base-catalysis**

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
temp=273.15 SCRF=(PCM,SOLVENT=chloroform)
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C43H49N3O5S C1[X(C43H49N3O5S)] #Atoms= 101
Charge = 0 Multiplicity = 1

SCF Energy= -2605.77675610 Predicted Change= -8.472787D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00003	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00077	0.00180	[YES]	0.00077	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.002468	-2.326758	-2.197690
C	1.042055	-3.511488	-2.920345
C	1.941479	-3.609077	-3.980248
C	2.777936	-2.539841	-4.305572
C	2.738282	-1.348553	-3.584699
C	1.841879	-1.256912	-2.525052
N	1.652944	-0.159636	-1.682886
C	0.696852	-0.334487	-0.743679
S	-0.012818	-1.938715	-0.813368
C	2.441051	1.070420	-1.752910
C	2.411472	1.792917	-0.404951
C	3.142130	3.146110	-0.462336
C	3.345711	3.706279	0.948312
C	4.502719	3.032031	-1.156959
C	0.959953	1.899003	0.106378
C	0.067068	2.860284	-0.663224
N	0.357442	0.563475	0.129111
C	-0.618486	2.460675	-1.813698
C	-1.457158	3.352190	-2.478125
C	-1.621437	4.651835	-2.004703
C	-0.943219	5.057024	-0.856992
C	-0.108392	4.164038	-0.190585
H	0.388090	-4.338537	-2.664079
H	1.986516	-4.525733	-4.558147
H	3.468584	-2.630454	-5.137168
H	3.377229	-0.513581	-3.851317
H	2.054809	1.703449	-2.563043
H	3.466317	0.775442	-1.992282
H	3.849352	4.676707	0.904214

H	3.972099	3.023514	1.534976
H	2.407679	3.843893	1.492892
H	2.520858	3.845918	-1.037653
H	4.412022	2.789751	-2.219977
H	5.116045	2.259224	-0.677441
H	5.041157	3.981631	-1.083467
H	2.938021	1.151465	0.314777
H	0.981919	2.213674	1.154943
H	-0.571646	1.433782	-2.165381
H	-2.000178	3.016507	-3.356848
H	-2.284811	5.341161	-2.518509
H	-1.075100	6.062496	-0.469139
H	0.393480	4.477224	0.721678
C	-3.182953	0.571777	0.576160
C	-3.444077	2.078179	0.509433
C	-4.457331	2.355867	-0.603938
C	-3.953536	2.588016	1.851352
O	-2.423560	0.256820	-0.657270
C	-2.781242	-0.523560	-1.684099
O	-2.227470	-0.337277	-2.751075
C	-3.809411	-1.629184	-1.504012
C	-5.216800	-1.066165	-1.743463
C	-3.502818	-2.767861	-2.475035
O	-3.995609	-0.228316	1.022106
H	-5.278471	-0.601512	-2.733912
H	-5.477457	-0.328862	-0.982433
H	-5.949400	-1.878253	-1.701582
H	-3.745412	-1.982523	-0.474768
H	-2.495335	-3.166597	-2.317126
H	-3.567388	-2.421035	-3.509489
H	-4.222488	-3.579595	-2.331210
H	-5.427347	1.905654	-0.364100
H	-4.115733	1.964800	-1.568441
H	-4.602072	3.435409	-0.714275
H	-2.500004	2.569423	0.255169
H	-4.218982	3.647847	1.780564
H	-3.189106	2.471869	2.622134
H	-4.843801	2.027405	2.155419
C	-1.875931	-3.946333	1.592145
C	-2.260198	-2.615763	1.797297
C	-1.327450	-1.709198	2.273849
C	-0.031077	-2.146860	2.582303
C	0.360773	-3.467606	2.415077
C	-0.582038	-4.361685	1.899339
C	-1.449623	-0.231607	2.620636
C	-2.415968	0.019316	3.777988
O	-1.688942	0.642746	1.548636
C	-0.002703	0.083197	3.101569
O	0.420347	1.168846	3.449452
N	0.736892	-1.073909	3.065478
C	2.127341	-1.118186	3.475891
C	3.127361	-0.867784	2.362055
C	4.153621	0.059771	2.548457
C	5.134204	0.242545	1.573000
C	5.089595	-0.493506	0.390740

C	4.055925	-1.407874	0.186720
C	3.084094	-1.595086	1.167651
H	-2.594084	-4.660433	1.201452
H	-3.266950	-2.273893	1.582937
H	1.365631	-3.799052	2.659181
H	-0.296966	-5.398220	1.746057
H	-2.224996	-0.675245	4.602195
H	-3.439740	-0.109981	3.420198
H	-2.277337	1.043061	4.137004
H	-0.624137	0.522712	0.723710
H	2.248678	-0.358378	4.252290
H	2.309994	-2.095449	3.936696
H	4.188877	0.640728	3.466618
H	5.929121	0.964610	1.736533
H	5.854511	-0.355518	-0.367999
H	4.011045	-1.986047	-0.732917
H	2.290189	-2.319678	1.004031

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2605.77675610 Predicted Change= -8.472787D-09
Zero-point correction (ZPE)= -2604.9251 0.85158
Internal Energy (U)= -2604.8843 0.89242
Enthalpy (H)= -2604.8834 0.89329
Gibbs Free Energy (G)= -2604.9941 0.78258

Frequencies -- -351.7289 17.5536 30.5970

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=chloroform)

Pointgroup= C1 Stoichiometry= C43H49N3O5S C1[X(C43H49N3O5S)] #Atoms= 101
Charge = 0 Multiplicity = 1

SCF Energy= -2606.52673307

==========

***(S)*-TS-alkoxide-attack**

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
temp=273.15 SCRF=(PCM,SOLVENT=chloroform)
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C39H41N3O3S C1[X(C39H41N3O3S)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2298.16405410 Predicted Change= -1.282020D-08

==========
==
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00158	0.00180	[YES]	0.00158	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.610280	-1.463970	-3.306070
C	-0.622420	-1.041520	-2.420130
C	-0.113890	-1.906980	-1.452120
C	-0.555690	-3.224620	-1.351450
C	-1.530810	-3.647090	-2.247740
C	-2.053490	-2.779440	-3.214790
S	0.102710	0.550270	-2.304370
C	1.085120	-0.003640	-0.975610
N	0.838590	-1.279460	-0.642990
N	2.017680	0.736070	-0.366020
C	1.799040	2.181160	-0.390470
C	2.657310	3.062970	0.494610
C	4.053610	3.173950	-0.134110
C	1.985150	4.426790	0.612600
O	1.202740	2.624390	-1.352000
C	2.891270	0.086870	0.637210
C	4.152300	-0.472090	0.008340
C	2.061610	-0.925360	1.441820
C	2.819460	-1.572390	2.622100
C	3.594600	-2.849980	2.277930
C	1.838510	-1.852760	3.764920
C	1.451840	-1.955210	0.507130
C	4.144170	-1.190310	-1.190420
C	5.315540	-1.765400	-1.677730
C	6.510980	-1.625260	-0.976810
C	6.533050	-0.893670	0.208310
C	5.361990	-0.317600	0.691900
H	2.708950	2.637860	1.496890
H	3.978060	3.625180	-1.129000
H	4.548730	2.203050	-0.240210
H	4.689640	3.813940	0.484300
H	1.856250	4.885190	-0.371760
H	1.007270	4.290650	1.078570
H	2.597730	5.088570	1.232360
H	-2.015170	-0.783180	-4.047860
H	-0.154930	-3.898220	-0.602020
H	-1.892320	-4.668250	-2.192290
H	-2.813750	-3.136580	-3.901250
H	3.177970	0.866830	1.338970
H	1.241200	-0.321320	1.845140
H	3.543140	-0.826900	2.980610
H	2.907440	-3.678230	2.067190
H	4.205620	-3.149810	3.134890
H	4.258900	-2.728060	1.416860
H	1.064270	-2.560600	3.447060

H	1.334400	-0.937440	4.086910
H	2.359590	-2.288030	4.623840
H	0.650550	-2.493740	1.019940
H	2.188290	-2.667930	0.118940
H	3.225550	-1.301890	-1.761370
H	5.292740	-2.321810	-2.609520
H	7.422720	-2.073680	-1.358560
H	7.463110	-0.764520	0.752960
H	5.383780	0.259360	1.613840
C	-2.521890	1.192600	-0.412400
C	-3.363250	1.408830	-1.492970
C	-3.339080	2.681440	-2.076990
C	-2.501140	3.680390	-1.587560
C	-1.669390	3.433880	-0.486580
C	-1.686200	2.187280	0.105900
C	-0.905430	1.644970	1.307300
C	-1.593660	2.171480	2.596910
O	0.428610	1.860280	1.346350
C	-1.342950	0.140160	1.251790
O	-0.968950	-0.773230	1.977090
N	-2.299130	-0.014550	0.273460
C	-3.061920	-1.229990	0.081920
C	-4.455830	-1.126140	0.663280
C	-4.617220	-0.774230	2.006700
C	-5.888940	-0.676820	2.560120
C	-7.014810	-0.931170	1.775840
C	-6.860620	-1.283530	0.438600
C	-5.583640	-1.378470	-0.114560
H	-2.676710	1.994330	2.610940
H	-1.409140	3.248270	2.664630
H	-1.135080	1.674330	3.457730
H	-4.013960	0.626770	-1.873940
H	-3.984500	2.887920	-2.925830
H	-2.491980	4.655370	-2.065390
H	-0.998140	4.202270	-0.112670
H	-3.104670	-1.470400	-0.986550
H	-2.493000	-2.019800	0.582630
H	-3.735760	-0.582660	2.615710
H	-6.004550	-0.403530	3.604650
H	-8.007650	-0.852170	2.207980
H	-7.732760	-1.480850	-0.177490
H	-5.462420	-1.651320	-1.160920

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2298.16405410 Predicted Change= -1.282020D-08
Zero-point correction (ZPE)= -2297.4324 0.73155
Internal Energy (U)= -2297.3983 0.76570
Enthalpy (H)= -2297.3974 0.76657
Gibbs Free Energy (G)= -2297.4948 0.66923

Frequencies -- -102.5270 23.0369 24.7496

```
=============================================================================
==
 #m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
 SCRF=(PCM,SOLVENT=chloroform)
-----------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C39H41N3O3S   C1[X(C39H41N3O3S)]  #Atoms= 87
 Charge = 0         Multiplicity = 1
-----------------------------------------------------------------------
 SCF Energy= -2298.80696559
=============================================================================
==
```

TS-uncatalyzed

```
-----------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
=============================================================================
==
 #m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
 temp=273.15 SCRF=(PCM,SOLVENT=chloroform)
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
-----------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C24H29NO5   C1[X(C24H29NO5)]  #Atoms= 59
 Charge = 0         Multiplicity = 1
-----------------------------------------------------------------------
 SCF Energy= -1362.34648211       Predicted Change= -7.834185D-10
=============================================================================
==
 Optimization completed on the basis of negligible forces.          {Found       2       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00000 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00204 ||  0.00180   [ NO ]       0.00204 ||  0.00180   [ YES ]
-----------------------------------------------------------------------
     Atomic             Coordinates (Angstroms)
      Type              X           Y           Z
-----------------------------------------------------------------------
      C         1.866150    1.346553   -0.546226
      C         3.068214    1.675834    0.065296
      C         3.065571    2.765734    0.941988
      C         1.909038    3.503528    1.188526
      C         0.711055    3.166117    0.550191
      C         0.700288    2.081415   -0.306621
      C        -0.411640    1.499103   -1.132017
      C        -0.897155    2.435329   -2.236252
      O        -1.551770    1.141196   -0.353960
      C         0.273875    0.277867   -1.804106
      O        -0.251320   -0.488881   -2.581441
      N         1.602676    0.302221   -1.446363
      C         2.583643   -0.644469   -1.936458
      C         3.263132   -1.434525   -0.835300
      C         2.574905   -1.785519    0.327711
      C         3.214695   -2.524730    1.319575
      C         4.540664   -2.922365    1.159286
      C         5.229100   -2.573523   -0.000255
      C         4.593193   -1.826994   -0.989869
```

H	-2.358115	0.614940	-1.016889
H	3.971121	1.102753	-0.116210
H	3.990210	3.038995	1.440893
H	1.939899	4.343797	1.873925
H	-0.197394	3.735293	0.730196
H	-1.375034	3.311462	-1.790754
H	-0.053422	2.761964	-2.850171
H	-1.612670	1.908314	-2.874872
H	2.034748	-1.308057	-2.612585
H	3.337067	-0.112448	-2.530483
H	1.540272	-1.476484	0.455145
H	2.672662	-2.789900	2.222679
H	5.036715	-3.496373	1.936018
H	6.264177	-2.874052	-0.132179
H	5.136437	-1.545502	-1.889190
C	-1.309643	-0.062992	0.820832
C	-1.176317	0.665662	2.162188
C	-2.167318	0.160563	3.217432
C	0.256000	0.466924	2.671649
O	-2.933400	-0.547456	0.785136
C	-3.599143	-0.691068	-0.298942
C	-4.789162	-1.624045	-0.254428
C	-5.512703	-1.524838	1.091056
C	-5.723776	-1.392854	-1.438407
O	-3.296673	-0.098297	-1.367957
O	-0.596093	-0.942254	0.421842
H	-3.198757	0.408867	2.965350
H	-1.919829	0.619787	4.179156
H	-2.092664	-0.925899	3.328843
H	-1.365480	1.726616	1.977743
H	0.415855	-0.586475	2.924434
H	0.406439	1.065910	3.574573
H	1.011119	0.754988	1.936918
H	-4.832095	-1.717741	1.922567
H	-6.326576	-2.253903	1.125930
H	-5.944710	-0.527078	1.221866
H	-4.347224	-2.627809	-0.335262
H	-6.535972	-2.124384	-1.415014
H	-5.194009	-1.486362	-2.388187
H	-6.163448	-0.391466	-1.389976

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1362.34648211 Predicted Change= -7.834185D-10
Zero-point correction (ZPE)= -1361.8537 0.49273
Internal Energy (U)= -1361.8290 0.51745
Enthalpy (H)= -1361.8281 0.51832
Gibbs Free Energy (G)= -1361.9076 0.43884

Frequencies -- -788.1053 13.0921 20.5374

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current

SCRF=(PCM,SOLVENT=chloroform)

Pointgroup= C1 Stoichiometry= C24H29NO5 C1[X(C24H29NO5)] #Atoms= 59
Charge = 0 Multiplicity = 1

SCF Energy= -1362.80138510
==========
==

TS-amine-base-catalysis

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
==
#m062x/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
temp=273.15 SCRF=(PCM,SOLVENT=chloroform)
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C32H48N2O5 C1[X(C32H48N2O5)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -1733.21982997 Predicted Change= -2.586625D-10
==========
==
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00031	0.00180	[YES]	0.00031	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.035726	-2.191098	-0.579530
C	-3.094358	-3.034887	-0.285820
C	-2.822765	-4.158199	0.505618
C	-1.537760	-4.417288	0.971823
C	-0.482445	-3.548509	0.657065
C	-0.739454	-2.429376	-0.106943
C	0.195450	-1.368596	-0.667354
C	0.925493	-1.995714	-1.870415
O	1.097491	-0.786088	0.209129
C	-0.827650	-0.393485	-1.322547
O	-0.586049	0.677152	-1.854992
N	-2.050806	-1.024321	-1.353876
C	-3.215197	-0.486848	-2.022377
C	-4.244167	0.119031	-1.089800
C	-3.836339	0.893326	-0.001297
C	-4.788183	1.503443	0.810973
C	-6.148438	1.344202	0.548473
C	-6.556765	0.564075	-0.530767
C	-5.605484	-0.047391	-1.345508
H	2.680554	-0.509723	-0.319719
H	-4.099413	-2.822678	-0.638276
H	-3.633988	-4.834121	0.758951

H	-1.351260	-5.294993	1.582854
H	0.525553	-3.749785	1.011829
H	1.563120	-2.812590	-1.522706
H	0.211694	-2.407313	-2.591408
H	1.526205	-1.234212	-2.382331
H	-2.835060	0.277355	-2.708289
H	-3.673176	-1.280367	-2.625613
H	-2.778595	0.997393	0.227434
H	-4.459194	2.104755	1.653452
H	-6.887650	1.820108	1.186226
H	-7.614276	0.426324	-0.736650
H	-5.923566	-0.657169	-2.188765
C	0.106002	0.297011	1.371806
C	0.869603	0.094515	2.671123
C	0.360417	1.136468	3.673592
C	0.666809	-1.322418	3.190237
O	0.556772	1.533182	0.729498
C	-0.315809	2.548340	0.582608
C	0.145166	3.517644	-0.491016
C	-1.024737	4.368394	-0.970736
C	1.283685	4.377944	0.072345
O	-1.303420	2.714253	1.259876
O	-1.066046	-0.019188	1.254886
H	0.858677	1.007583	4.639674
H	-0.718243	1.021553	3.817357
H	0.545518	2.155621	3.321022
H	1.930915	0.275896	2.489437
H	1.065309	-2.051542	2.480976
H	-0.401596	-1.526517	3.310788
H	1.162648	-1.454239	4.157785
H	-0.695777	5.059651	-1.752744
H	-1.442877	4.948755	-0.143332
H	-1.819751	3.735077	-1.375275
H	0.524388	2.908218	-1.316522
H	0.922007	4.989239	0.906693
H	1.669725	5.050603	-0.699824
H	2.110421	3.760078	0.437560
N	3.727805	-0.462095	-0.563732
C	4.099438	-1.890640	-0.870758
C	5.582411	-2.173241	-1.047067
C	3.854207	0.426187	-1.801219
C	5.226726	1.072774	-1.963479
C	2.724434	1.451109	-1.860501
C	4.413014	0.049949	0.689066
C	3.872727	1.425652	1.078236
C	4.221875	-0.970001	1.813833
H	3.671543	-2.494497	-0.068933
H	5.979404	-1.723574	-1.959028
H	5.705323	-3.255611	-1.137680
H	6.185118	-1.843947	-0.197136
H	3.565369	-2.148976	-1.783928
H	6.051611	0.360889	-1.903945
H	5.256480	1.534799	-2.954182
H	5.397094	1.864415	-1.230716
H	1.756784	1.020841	-1.579688

H	2.653479	1.819380	-2.888662
H	2.919027	2.308962	-1.212944
H	3.710987	-0.275087	-2.629521
H	2.781668	1.459982	1.014891
H	4.277972	2.222989	0.452797
H	4.167997	1.638574	2.109044
H	4.496546	-0.507241	2.764543
H	4.848011	-1.855867	1.683673
H	3.175337	-1.285242	1.873857
H	5.475865	0.132435	0.445078

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1733.21982997 Predicted Change= -2.586625D-10
Zero-point correction (ZPE)= -1732.4518 0.76797
Internal Energy (U)= -1732.4172 0.80254
Enthalpy (H)= -1732.4164 0.80340
Gibbs Free Energy (G)= -1732.5134 0.70642

Frequencies -- -174.7215 19.6436 33.8253

==========

#m062x/6-311++G(2df,p) scf=(direct,tight,maxcycle=300) density=current
SCRF=(PCM,SOLVENT=chloroform)

Pointgroup= C1 Stoichiometry= C32H48N2O5 C1[X(C32H48N2O5)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -1733.78983681

==========

Appendix IV:

Computational Data for Chapter 5

Catalyst Selective and Regiodivergent *O*- to *C*- or *N*-Carboxyl Transfer of Pyrazolyl Carbonates: Synthetic and Computational Studies

DMAP-I

Supporting Information: 000-DMAP.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C7H10N2 C1[X(C7H10N2)] #Atoms= 19
Charge = 0 Multiplicity = 1

SCF Energy= -382.089704878 Predicted Change= -8.417504D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00104	0.00180	[YES]	0.00104	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.564001	-1.197520	-0.000102
H	0.082178	-2.167226	-0.000147
C	-0.185755	-0.000019	-0.000197
N	-1.548348	-0.000006	-0.000512
C	-2.269626	-1.258822	0.000218
H	-3.339821	-1.055518	-0.000317
H	-2.033126	-1.855457	0.889582
H	-2.032554	-1.856696	-0.888145
C	-2.269561	1.258844	0.000159
H	-2.032354	1.856709	-0.888173
H	-2.033122	1.855460	0.889554
H	-3.339768	1.055600	-0.000500
C	0.563974	1.197494	-0.000068
H	0.082123	2.167189	-0.000077
C	1.947705	1.130264	0.000071
H	2.518638	2.057254	0.000152
N	2.665249	0.000010	0.000122
C	1.947732	-1.130260	0.000035
H	2.518686	-2.057237	0.000095

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -382.089704878 Predicted Change= -8.417504D-09
Zero-point correction (ZPE)= -381.9252 0.16442
Internal Energy (U)= -381.9168 0.17286
Enthalpy (H)= -381.9158 0.17381
Gibbs Free Energy (G)= -381.9587 0.13096

Frequencies -- 64.2746 98.1133 164.9872

==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current

SCRF=(PCM,SOLVENT=Dichloromethane)

Pointgroup= C1 Stoichiometry= C7H10N2 C1[X(C7H10N2)] #Atoms= 19
Charge = 0 Multiplicity = 1

SCF Energy= -382.112788667
==========

Model Pyrcarbonate I

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011
==========
#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C13H14N2O3 C1[X(C13H14N2O3)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -838.651864305 Predicted Change= -3.891676D-09
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00165	0.00180	[YES]	0.00165	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.708515	-1.025075	0.074074
C	-4.031226	-1.667999	0.339165
H	-3.892067	-2.726147	0.569088
H	-4.690959	-1.582777	-0.530560
H	-4.537354	-1.188913	1.183518
C	-3.460714	1.455564	-0.364882
H	-4.205189	1.241884	-1.138625
H	-2.955571	2.387817	-0.629615
H	-3.998127	1.615370	0.575374
O	-0.327530	1.457494	-0.728611
C	0.761615	-1.257544	-0.185374
C	-2.473439	0.340758	-0.239997
C	-1.114151	0.390838	-0.392074
N	-0.597744	-0.853231	-0.192026
N	-1.584869	-1.727061	0.110195
C	1.166999	-2.238374	0.719285
H	0.437955	-2.665111	1.398336
C	2.495843	-2.646872	0.731302
H	2.812121	-3.411582	1.433701
C	3.420277	-2.072135	-0.139822
H	4.458024	-2.388691	-0.120298
C	3.004022	-1.094389	-1.039539
H	3.713176	-0.652743	-1.732306
C	1.672299	-0.689470	-1.078027
H	1.341643	0.045277	-1.803994
C	0.484338	1.933902	0.256624

O	0.495176	1.548344	1.393031
O	1.239320	2.872850	-0.282914
C	2.172102	3.480287	0.623317
H	2.703672	4.224285	0.034666
H	2.860575	2.726031	1.007278
H	1.637963	3.950892	1.449899

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -838.651864305 Predicted Change= -3.891676D-09
Zero-point correction (ZPE)= -838.3932 0.25861
Internal Energy (U)= -838.3762 0.27556
Enthalpy (H)= -838.3753 0.27651
Gibbs Free Energy (G)= -838.4393 0.21255

Frequencies -- 29.0399 48.0758 63.9209

==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)

Pointgroup= C1 Stoichiometry= C13H14N2O3 C1[X(C13H14N2O3)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -838.691348233

==========

DMAP-TS-II

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)
opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C20H24N4O3 C1[X(C20H24N4O3)] #Atoms= 51
Charge = 0 Multiplicity = 1

SCF Energy= -1220.73614558 Predicted Change= -4.023409D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00164	0.00180	[YES]	0.00164	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	4.358957	-0.717899	-0.678065
C	5.790269	-1.129616	-0.808253
H	6.438680	-0.252560	-0.754776
H	5.968165	-1.637762	-1.761865
H	6.073409	-1.823913	-0.010122

C	3.222163	-1.567467	-0.708078
C	3.170163	-3.053343	-0.866145
H	3.647228	-3.562317	-0.021509
H	3.688911	-3.371920	-1.776821
H	2.132413	-3.390703	-0.913891
C	2.168857	-0.696842	-0.562787
O	0.832402	-0.930010	-0.524128
C	0.392417	-1.507069	0.698818
O	0.680524	-0.620438	1.686030
C	0.368694	-1.103069	2.987748
H	0.630656	-0.301456	3.677123
H	0.942639	-2.004511	3.211839
H	-0.701166	-1.325901	3.058800
O	0.351078	-2.712602	0.841527
N	2.672079	0.569316	-0.461044
C	1.978337	1.788085	-0.266152
N	4.024755	0.556179	-0.530227
C	0.721834	1.991747	-0.838754
H	0.266613	1.211772	-1.437815
C	0.063579	3.200636	-0.627539
H	-0.917276	3.352593	-1.068610
C	0.657795	4.209505	0.126723
H	0.143091	5.152221	0.281872
C	1.922656	4.002702	0.675554
H	2.396801	4.783939	1.261490
C	2.584006	2.794004	0.488145
H	3.564586	2.616309	0.914566
N	-1.464213	-0.966244	0.393449
C	-1.897547	0.289233	0.536470
H	-1.160436	1.004322	0.893138
C	-3.192689	0.670845	0.253715
H	-3.478235	1.705309	0.393982
C	-4.118109	-0.298915	-0.209431
N	-5.399813	0.025578	-0.509368
C	-5.852430	1.399076	-0.366540
H	-5.764594	1.741351	0.671000
H	-6.899553	1.459169	-0.659341
H	-5.275286	2.075825	-1.007084
C	-6.314550	-0.999123	-0.984266
H	-6.446189	-1.791185	-0.238263
H	-5.954314	-1.452374	-1.914895
H	-7.285473	-0.545166	-1.176628
C	-3.634943	-1.624885	-0.339896
H	-4.275423	-2.428668	-0.678177
C	-2.318562	-1.898275	-0.029363
H	-1.902343	-2.899757	-0.112548

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1220.73614558 Predicted Change= -4.023409D-09
Zero-point correction (ZPE)= -1220.3122 0.42384
Internal Energy (U)= -1220.2863 0.44983
Enthalpy (H)= -1220.2853 0.45078
Gibbs Free Energy (G)= -1220.3708 0.36530

Frequencies -- -129.9967 12.0116 22.3105
==========
#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)

Pointgroup= C1 Stoichiometry= C20H24N4O3 C1[X(C20H24N4O3)] #Atoms= 51
Charge = 0 Multiplicity = 1

SCF Energy= -1220.79564184
==========

DMAP-III

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011
==========
#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C20H24N4O3 C1[X(C20H24N4O3)] #Atoms= 51
Charge = 0 Multiplicity = 1

SCF Energy= -1220.73932849 Predicted Change= -4.025534D-08
==========
Optimization completed. {Found 1 times}
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?
Force 0.00003 || 0.00045 [YES] 0.00000 || 0.00030 [YES]
Displ 0.00502 || 0.00180 [NO] 0.00502 || 0.00180 [YES]

Atomic Coordinates (Angstroms)
Type X Y Z

C 4.174164 -1.170739 -0.591624
C 5.522346 -1.814240 -0.657305
H 6.303458 -1.061802 -0.528894
H 5.674564 -2.313506 -1.620255
H 5.634833 -2.572885 0.124365
C 2.915708 -1.818062 -0.692683
C 2.635086 -3.274194 -0.878989
H 2.936641 -3.856523 -0.001546
H 3.175849 -3.674729 -1.743938
H 1.564338 -3.430364 -1.020418
C 2.009047 -0.788234 -0.584707
O 0.661469 -0.791589 -0.604037
C 0.067767 -1.273051 0.660484
O 0.479569 -0.302389 1.588011
C 0.208428 -0.675180 2.927194
H 0.573525 0.139353 3.554008
H 0.717363 -1.607221 3.182801
H -0.870164 -0.802278 3.089336
O 0.164053 -2.478602 0.928942
N 2.716639 0.375477 -0.437343
C 2.224722 1.690116 -0.271753
N 4.051145 0.140097 -0.437458

C 1.075291 2.107458 -0.945680
H 0.558281 1.418405 -1.603562
C 0.612186 3.408566 -0.768310
H -0.283185 3.729112 -1.292981
C 1.298969 4.299462 0.053840
H 0.936970 5.314506 0.181879
C 2.458627 3.879619 0.703031
H 3.005130 4.566806 1.341632
C 2.921862 2.577036 0.549167
H 3.819025 2.234497 1.052329
N -1.461047 -0.852362 0.340224
C -1.821474 0.436247 0.212741
H -1.024436 1.160217 0.343170
C -3.116029 0.800130 -0.054736
H -3.349884 1.852349 -0.143737
C -4.115829 -0.201145 -0.204110
N -5.399736 0.114034 -0.461050
C -5.798069 1.509040 -0.588875
H -5.593928 2.062384 0.333991
H -6.867416 1.554084 -0.786974
H -5.271981 1.995635 -1.417040
C -6.391477 -0.942088 -0.610796
H -6.464225 -1.544741 0.300758
H -6.142056 -1.599247 -1.450756
H -7.362563 -0.489659 -0.802565
C -3.690794 -1.549221 -0.063533
H -4.384753 -2.372776 -0.159892
C -2.373167 -1.824102 0.206550
H -1.979304 -2.826201 0.334908

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1220.73932849 Predicted Change= -4.025534D-08
Zero-point correction (ZPE)= -1220.3147 0.42455
Internal Energy (U)= -1220.2885 0.45073
Enthalpy (H)= -1220.2876 0.45168
Gibbs Free Energy (G)= -1220.3727 0.36656

Frequencies -- 12.5417 27.3553 36.8048

==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)

Pointgroup= C1 Stoichiometry= C20H24N4O3 C1[X(C20H24N4O3)] #Atoms= 51
Charge = 0 Multiplicity = 1

SCF Energy= -1220.80064994

==========

DMAP-TS-IV

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current

SCRF=(PCM,SOLVENT=Dichloromethane)
opt=(maxcycle=250,ts,calcfc,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C20H24N4O3 C1[X(C20H24N4O3)] #Atoms= 51
Charge = 0 Multiplicity = 1

SCF Energy= -1220.73294594 Predicted Change= -2.310756D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00297	0.00180	[NO]	0.00297	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	3.901032	-1.341876	-0.688778
C	5.206610	-2.073910	-0.683387
H	6.027642	-1.379559	-0.489748
H	5.387489	-2.567263	-1.644804
H	5.218985	-2.853253	0.086714
C	2.615961	-1.899597	-0.870648
C	2.226295	-3.330187	-1.059633
H	2.523526	-3.955632	-0.209123
H	2.673039	-3.770754	-1.959890
H	1.137904	-3.394568	-1.147817
C	1.736574	-0.819627	-0.801023
O	0.445862	-0.774357	-0.797989
C	-0.089655	-1.138967	1.104260
O	0.488625	-0.064811	1.664333
C	1.713319	-0.334994	2.355753
H	2.161563	0.641117	2.538623
H	2.376337	-0.948001	1.743177
H	1.499146	-0.843957	3.299038
O	0.188238	-2.292890	1.339437
N	2.542948	0.301063	-0.600576
C	2.137209	1.628883	-0.390792
N	3.867960	-0.027046	-0.516038
C	0.941548	2.110535	-0.938943
H	0.327423	1.444274	-1.532292
C	0.558778	3.428622	-0.707330
H	-0.371645	3.792406	-1.135135
C	1.359918	4.284431	0.047416
H	1.056750	5.312259	0.219747
C	2.559355	3.805200	0.570503
H	3.198082	4.460174	1.155922
C	2.949272	2.486627	0.359433
H	3.879453	2.103607	0.762841
N	-1.478468	-0.779077	0.745857
C	-1.816879	0.494871	0.439103
H	-1.021150	1.224328	0.521853
C	-3.083785	0.814388	0.044137
H	-3.302635	1.847989	-0.185652
C	-4.078111	-0.201114	-0.069634

N	-5.329746	0.078917	-0.454129
C	-5.706141	1.450032	-0.782095
H	-5.563330	2.110053	0.079276
H	-6.757370	1.468544	-1.061904
H	-5.115073	1.825918	-1.623310
C	-6.318661	-0.988715	-0.561335
H	-6.468275	-1.478449	0.405942
H	-6.007806	-1.736710	-1.297485
H	-7.265541	-0.559693	-0.882388
C	-3.668773	-1.529448	0.241754
H	-4.353123	-2.363405	0.174123
C	-2.382853	-1.774795	0.631306
H	-2.008133	-2.762125	0.869825

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1220.73294594 Predicted Change= -2.310756D-08
Zero-point correction (ZPE)= -1220.3086 0.42431
Internal Energy (U)= -1220.2827 0.45019
Enthalpy (H)= -1220.2818 0.45114
Gibbs Free Energy (G)= -1220.3656 0.36729

Frequencies -- -213.4219 18.1866 25.5297

==========

#m062X/6-31+G(d,p) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Dichloromethane)

Pointgroup= C1 Stoichiometry= C20H24N4O3 C1[X(C20H24N4O3)] #Atoms= 51
Charge = 0 Multiplicity = 1

SCF Energy= -1220.79546757

==========

Appendix V:

Computational Data for Chapter 6

Formation of Aza-*ortho*-quinone Methides Under Room Temperature Conditions: Cs_2CO_3 Effect

Methide equilibria and salts

o-OH-benzyl-chloride-DCM.log

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#M062X/6-31G* scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=dichloromethane) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C7H7ClO C1[X(C7H7ClO)] #Atoms= 16
Charge = 0 Multiplicity = 1

SCF Energy= -806.201810017 Predicted Change= -2.968479D-08

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00158	0.00180	[YES]	0.00158	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.265823	-1.236182	-0.171059
H	2.950527	-2.067267	-0.300624
C	2.711113	0.076812	-0.319568
H	3.749484	0.275370	-0.566531
C	1.831655	1.142011	-0.163884
H	2.156675	2.169608	-0.289041
C	0.495920	0.900376	0.153486
C	0.038239	-0.414274	0.332264
C	-1.367858	-0.675691	0.764608
H	-1.650481	-0.088989	1.640307
H	-1.536502	-1.731901	0.967400
Cl	-2.583533	-0.211380	-0.521318
C	0.933338	-1.470346	0.149952
H	0.573857	-2.487915	0.278698
O	-0.316132	1.982166	0.310562
H	-1.243819	1.730980	0.172913

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-806.201810017	Predicted Change= -2.968479D-08
Zero-point correction (ZPE)=	-806.0762	0.12553
Internal Energy (U)=	-806.0683	0.13345
Enthalpy (H)=	-806.0674	0.13439
Gibbs Free Energy (G)=	-806.1095	0.09229

Frequencies -- 76.2789 119.9011 208.4257

M06-2X/6-311++G(2df,p)/PCM(DCM):
-806.3596788
M06-2X/6-311++G(2df,p):

-806.354205
M06-2X/def2-QZVPP:
-806.4144814

o-OH-benzyl-chloride-DEE.log

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#M062X/6-31G* scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=DiethylEther) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C7H7ClO C1[X(C7H7ClO)] #Atoms= 16
Charge = 0 Multiplicity = 1

SCF Energy= -806.200674404 Predicted Change= -4.277773D-08
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00005	0.00045	[YES]	0.00001	0.00030	[YES]
Displ	0.00168	0.00180	[YES]	0.00168	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.268933	-1.233335	-0.171870
H	2.955326	-2.062911	-0.302222
C	2.712230	0.080644	-0.316551
H	3.750824	0.281161	-0.561066
C	1.830879	1.144016	-0.160930
H	2.153341	2.172630	-0.283634
C	0.495003	0.899454	0.152716
C	0.039621	-0.416207	0.328803
C	-1.366014	-0.678908	0.761665
H	-1.645356	-0.095032	1.640481
H	-1.534133	-1.735892	0.961577
Cl	-2.585407	-0.210282	-0.517770
C	0.936452	-1.470463	0.146106
H	0.578455	-2.489010	0.271887
O	-0.320595	1.978211	0.310804
H	-1.244408	1.726954	0.148993

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -806.200674404 Predicted Change= -4.277773D-08
Zero-point correction (ZPE)= -806.0749 0.12567
Internal Energy (U)= -806.0671 0.13354
Enthalpy (H)= -806.0661 0.13449
Gibbs Free Energy (G)= -806.1081 0.09252

Frequencies -- 80.3827 120.9283 210.5129

M06-2X/6-311++G(2df,p)/PCM(DEE):

-806.3585378
M06-2X/6-311++G(2df,p):
-806.3542609
M06-2X/def2-QZVPP:
-806.4145308

o-OH-benzyl-chloride-THF.log

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C7H7ClO C1[X(C7H7ClO)] #Atoms= 16
Charge = 0 Multiplicity = 1

SCF Energy= -806.201585375 Predicted Change= -5.295379D-08
==========
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00001	0.00030	[YES]
Displ	0.00187	0.00180	[NO]	0.00187	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.266485	-1.235575	-0.171403
H	2.951525	-2.066349	-0.301216
C	2.711365	0.077646	-0.318794
H	3.749772	0.276705	-0.565194
C	1.831538	1.142427	-0.162872
H	2.156059	2.170237	-0.287392
C	0.495762	0.900130	0.153529
C	0.038521	-0.414731	0.331469
C	-1.367449	-0.676666	0.763906
H	-1.649519	-0.091019	1.640534
H	-1.535874	-1.733129	0.965676
Cl	-2.584046	-0.210957	-0.520443
C	0.934003	-1.470374	0.148880
H	0.574838	-2.488166	0.276865
O	-0.316920	1.981407	0.310010
H	-1.244023	1.729596	0.169892

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -806.201585375 Predicted Change= -5.295379D-08
Zero-point correction (ZPE)= -806.0760 0.12555
Internal Energy (U)= -806.0681 0.13346
Enthalpy (H)= -806.0671 0.13441
Gibbs Free Energy (G)= -806.1092 0.09233

Frequencies -- 76.9958 120.0611 208.6648

M06-2X/6-311++G(2df,p)/PCM(THF):
-806.3594537
M06-2X/6-311++G(2df,p):
-806.354216
M06-2X/def2-QZVPP:
-806.4144922

o-NH2-benzyl-chloride-DCM.log

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#M062X/6-31G* scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=dichloromethane) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C7H8ClN C1[X(C7H8ClN)] #Atoms= 17
Charge = 0 Multiplicity = 1

SCF Energy= -786.343506099 Predicted Change= -3.453422D-08
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00005	0.00045	[YES]	0.00001	0.00030	[YES]
Displ	0.00146	0.00180	[YES]	0.00146	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.207846	-1.313833	-0.148566
H	2.852816	-2.178131	-0.264521
C	2.703297	-0.025261	-0.344355
H	3.743909	0.122391	-0.617785
C	1.875540	1.081517	-0.203237
H	2.266973	2.082066	-0.367594
C	0.527944	0.925668	0.146509
N	-0.295283	2.033569	0.343622
H	-1.253702	1.908387	0.035133
C	0.029603	-0.374111	0.367416
C	-1.381285	-0.564711	0.811610
H	-1.667434	0.144242	1.590437
H	-1.567481	-1.582210	1.151438
Cl	-2.580633	-0.275970	-0.545118
C	0.872086	-1.473547	0.203583
H	0.467254	-2.469091	0.368624
H	0.085215	2.894515	-0.031834

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -786.343506099 Predicted Change= -3.453422D-08
Zero-point correction (ZPE)= -786.2050 0.13841
Internal Energy (U)= -786.1970 0.14647
Enthalpy (H)= -786.1960 0.14741
Gibbs Free Energy (G)= -786.2383 0.10515

---Frequencies -- 85.4643
109.6780 201.9272

M06-2X/6-311++G(2df,p)/PCM(DCM):
-786.4909602
M06-2X/6-311++G(2df,p):
-786.4846914
M06-2X/def2-QZVPP:
-786.5422949

o-NH2-benzyl-chloride-DEE.log

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#M062X/6-31G* scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=DiethylEther) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C7H8ClN C1[X(C7H8ClN)] #Atoms= 17
Charge = 0 Multiplicity = 1

SCF Energy= -786.342167844 Predicted Change= -1.169385D-07
==========
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00007	0.00045	[YES]	0.00001	0.00030	[YES]
Displ	0.00309	0.00180	[NO]	0.00309	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.212176	-1.309658	-0.150209
H	2.859490	-2.172017	-0.267292
C	2.704769	-0.019702	-0.341687
H	3.745595	0.131173	-0.612517
C	1.873931	1.084405	-0.199776
H	2.263177	2.086374	-0.360964
C	0.526344	0.924257	0.146493
N	-0.301779	2.028784	0.342690
H	-1.257850	1.899644	0.028602
C	0.031063	-0.376776	0.364293
C	-1.379334	-0.570478	0.808581
H	-1.663010	0.133702	1.592771
H	-1.564016	-1.590102	1.143194
Cl	-2.582041	-0.274342	-0.542241
C	0.876423	-1.473412	0.199294
H	0.473774	-2.470370	0.361220
H	0.077758	2.892112	-0.027697

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -786.342167844 Predicted Change= -1.169385D-07
Zero-point correction (ZPE)= -786.2036 0.13847

```
 Internal Energy (U)=                    -786.1956       0.14652
 Enthalpy (H)=                           -786.1947       0.14746
 Gibbs Free Energy (G)=                  -786.2369       0.10526
---------------------------------------------------------------------------
Frequencies --     87.5885             111.4020          203.1151

M06-2X/6-311++G(2df,p)/PCM(DEE):
-786.4896509
M06-2X/6-311++G(2df,p):
-786.4847387
M06-2X/def2-QZVPP:
-786.5423484
```

o-NH2-benzyl-chloride-THF.log

```
---------------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
===========================================================
 #m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C7H8ClN   C1[X(C7H8ClN)]  #Atoms= 17
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -786.343242243       Predicted Change= -1.887580D-08
===========================================================
 Optimization completed.           {Found       2       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00002 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00149 ||  0.00180   [ YES ]      0.00149 ||  0.00180   [ YES ]
---------------------------------------------------------------------------
      Atomic              Coordinates (Angstroms)
       Type             X           Y           Z
---------------------------------------------------------------------------
      C         2.208944    -1.312640    -0.149104
      H         2.854565    -2.176387    -0.265471
      C         2.703518    -0.023650    -0.343839
      H         3.744110     0.124917    -0.616840
      C         1.874922     1.082370    -0.202324
      H         2.265651     2.083314    -0.365978
      C         0.527378     0.925286     0.146755
      N        -0.297116     2.032267     0.343533
      H        -1.255122     1.905841     0.034287
      C         0.029991    -0.374844     0.366915
      C        -1.380754    -0.566405     0.811015
      H        -1.666647     0.141231     1.591156
      H        -1.566631    -1.584483     1.149331
      Cl       -2.580675    -0.275540    -0.544629
      C         0.873263    -1.473511     0.202580
      H         0.469095    -2.469444     0.366897
      H         0.082710     2.893680    -0.031414
---------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin       Pressure= 1.00000 Atm
===========================================================
```

SCF Energy= -786.343242243 Predicted Change= -1.887580D-08
Zero-point correction (ZPE)= -786.2048 0.13842
Internal Energy (U)= -786.1967 0.14648
Enthalpy (H)= -786.1958 0.14743
Gibbs Free Energy (G)= -786.2380 0.10518
---Frequencies -- 86.0592
110.1054 202.1895

M06-2X/6-311++G(2df,p)/PCM(THF):
-786.4907024
M06-2X/6-311++G(2df,p):
-786.4847028
M06-2X/def2-QZVPP:
-786.5423082

o-NHBoc-benzyl-chloride-DCM.log

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

#M062X/6-31G* scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=dichloromethane) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

Pointgroup= C1 Stoichiometry= C12H16ClNO2 C1[X(C12H16ClNO2)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -1132.03760920 Predicted Change= -6.206381D-08

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00003	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00793	0.00180	[NO]	0.00793	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.489028	0.189055	0.375347
C	-2.344919	1.599042	0.851635
C	-1.365305	-0.558737	-0.023835
N	-0.115851	0.085530	-0.053043
C	1.113429	-0.515309	0.059453
O	2.058580	0.428085	-0.065910
C	3.473439	0.075630	0.013009
O	1.301742	-1.699688	0.250229
C	-1.521688	-1.893900	-0.406085
C	-2.785189	-2.475473	-0.391297
C	-3.905878	-1.739368	-0.015969
C	-3.748232	-0.409659	0.358727
C	4.164659	1.420029	-0.180593
C	3.836896	-0.882348	-1.116894
C	3.796473	-0.497716	1.389046
H	-3.261621	1.957594	1.316628
H	-1.512208	1.719727	1.546124
H	5.249238	1.287454	-0.141168

H	3.867934	2.118358	0.607314
H	3.898553	1.850466	-1.150277
H	4.921505	-1.026199	-1.130755
H	3.534357	-0.457718	-2.079248
H	3.354270	-1.851380	-0.984168
H	4.880608	-0.611577	1.484783
H	3.326745	-1.470883	1.533954
H	3.453366	0.187616	2.170406
H	-0.098302	1.085823	-0.211181
H	-0.655106	-2.465455	-0.709213
H	-2.890992	-3.513867	-0.689852
H	-4.890451	-2.194755	-0.013558
H	-4.611234	0.178315	0.659260
Cl	-1.999190	2.759595	-0.516916

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1132.03760920	Predicted Change= -6.206381D-08	
Zero-point correction (ZPE)=	-1131.7700	0.26754
Internal Energy (U)=	-1131.7538	0.28376
Enthalpy (H)=	-1131.7529	0.28470
Gibbs Free Energy (G)=	-1131.8149	0.22266

Frequencies -- 22.7879 44.9845 54.3851

M06-2X/6-311++G(2df,p)/PCM(DCM):
-1132.299532
M06-2X/6-311++G(2df,p):
-1132.29256
M06-2X/def2-QZVPP:
-1132.401215

o-NHBoc-benzyl-chloride-DEE.log

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#M062X/6-31G* scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=DiethylEther) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C12H16ClNO2 C1[X(C12H16ClNO2)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -1132.03618626 Predicted Change= -3.457163D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00003	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00473	0.00180	[NO]	0.00473	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z

C	-2.492018	0.190578	0.371391
C	-2.348296	1.600501	0.847934
C	-1.366627	-0.559535	-0.018283
N	-0.117159	0.084772	-0.040427
C	1.112616	-0.517153	0.064457
O	2.057097	0.428763	-0.057005
C	3.471187	0.074591	0.011065
O	1.302803	-1.701843	0.246516
C	-1.521656	-1.896061	-0.395988
C	-2.786012	-2.475450	-0.388018
C	-3.908550	-1.736741	-0.023982
C	-3.751761	-0.406327	0.347686
C	4.162619	1.419695	-0.177440
C	3.827668	-0.876327	-1.127225
C	3.802164	-0.508909	1.381070
H	-3.267993	1.960505	1.306165
H	-1.521565	1.717346	1.550437
H	5.247420	1.286315	-0.146368
H	3.871646	2.112646	0.617308
H	3.890005	1.857591	-1.141943
H	4.912185	-1.020400	-1.148928
H	3.519238	-0.445493	-2.084967
H	3.345443	-1.845939	-0.997565
H	4.886694	-0.625860	1.469191
H	3.330942	-1.481847	1.522446
H	3.465764	0.171830	2.169358
H	-0.099496	1.084057	-0.204772
H	-0.653292	-2.469998	-0.689077
H	-2.890937	-3.515012	-0.682858
H	-4.893719	-2.190867	-0.027611
H	-4.616074	0.183864	0.640226
Cl	-1.987844	2.762313	-0.514126

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1132.03618626 Predicted Change= -3.457163D-08
Zero-point correction (ZPE)= -1131.7685 0.26767
Internal Energy (U)= -1131.7523 0.28387
Enthalpy (H)= -1131.7513 0.28481
Gibbs Free Energy (G)= -1131.8133 0.22288

---Frequencies -- 23.8460 44.9380 55.4251

M06-2X/6-311++G(2df,p)/PCM(DEE):
-1132.298033
M06-2X/6-311++G(2df,p):
-1132.29262
M06-2X/def2-QZVPP:
-1132.401283

o-NHBoc-benzyl-chloride-THF.log

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C12H16ClNO2 C1[X(C12H16ClNO2)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -1132.03732717 Predicted Change= -4.931142D-09

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00210	0.00180	[NO]	0.00210	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.489452	0.189309	-0.374394
C	2.345241	1.599226	-0.850838
C	1.365565	-0.558916	0.023375
N	0.116112	0.085323	0.051940
C	-1.113250	-0.515691	-0.059957
O	-2.058303	0.428079	0.065207
C	-3.473021	0.075407	-0.012827
O	-1.301829	-1.700048	-0.249568
C	1.521788	-1.894399	0.404492
C	2.785406	-2.475608	0.390399
C	3.906329	-1.738984	0.016899
C	3.748749	-0.409110	-0.357000
C	-4.164280	1.419833	0.180475
C	-3.835910	-0.882128	1.117672
C	-3.796744	-0.498737	-1.388399
H	3.262356	1.957950	-1.314973
H	1.513437	1.718990	-1.546637
H	-5.248903	1.287281	0.141679
H	-3.867960	2.117853	-0.607853
H	-3.897643	1.850814	1.149767
H	-4.920520	-1.026057	1.132208
H	-3.532885	-0.457089	2.079696
H	-3.353266	-1.851149	0.985044
H	-4.880917	-0.612968	-1.483501
H	-3.326751	-1.471796	-1.533089
H	-3.454316	0.186314	-2.170309
H	0.098552	1.085376	0.211551
H	0.654912	-2.466424	0.705843
H	2.891112	-3.514289	0.688006
H	4.891012	-2.194151	0.015205
H	4.611925	0.179299	-0.656243
Cl	1.997187	2.760430	0.516207

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1132.03732717 Predicted Change= -4.931142D-09
Zero-point correction (ZPE)= -1131.7697 0.26756

```
 Internal Energy (U)=                  -1131.7535      0.28378
 Enthalpy (H)=                         -1131.7525      0.28472
 Gibbs Free Energy (G)=                -1131.8146      0.22270
---------------------------------------------------------------------------
Frequencies --     22.9789              44.9773            54.6419

M06-2X/6-311++G(2df,p)/PCM(THF):
-1132.299234
M06-2X/6-311++G(2df,p):
-1132.292573
M06-2X/def2-QZVPP:
-1132.401231
```

oQM-DCM.log

```
---------------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
===========================================================
 #M062X/6-31G* scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=dichloromethane) opt=(maxcycle=250,gdiis) iop(1/8=18)
 freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C7H6O   C1[X(C7H6O)]  #Atoms= 14
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -345.386057243       Predicted Change= -8.179175D-09
===========================================================
 Optimization completed.          {Found       2       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00002 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00017 ||  0.00180   [ YES ]      0.00017 ||  0.00180   [ YES ]
---------------------------------------------------------------------------
     Atomic              Coordinates (Angstroms)
      Type             X             Y          Z
---------------------------------------------------------------------------
      C         0.546872      1.467428      0.000061
      H         0.452213      2.550038      0.000081
      C        -0.679889      0.677709      0.000021
      C        -1.897948      1.243741     -0.000019
      H        -2.023877      2.322371     -0.000029
      H        -2.787009      0.621332     -0.000049
      C        -0.583120     -0.823861      0.000051
      C         0.774099     -1.385142     -0.000029
      H         0.856228     -2.467142     -0.000089
      C         1.857980     -0.581843      0.000001
      H         2.852189     -1.020764     -0.000019
      C         1.753761      0.870627      0.000061
      H         2.665412      1.458216      0.000081
      O        -1.580711     -1.534500     -0.000109
---------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin       Pressure= 1.00000 Atm
===========================================================
 SCF Energy=     -345.386057243    Predicted Change= -8.179175D-09
 Zero-point correction (ZPE)=              -345.2755       0.11049
```

```
 Internal Energy (U)=                  -345.2691       0.11690
 Enthalpy (H)=                         -345.2682       0.11784
 Gibbs Free Energy (G)=                -345.3061       0.07989
---------------------------------------------------------------------------
Frequencies --     89.0601             231.7269          346.1727

M06-2X/6-311++G(2df,p)/PCM(DCM):
-345.5022523
M06-2X/6-311++G(2df,p):
-345.4953984
M06-2X/def2-QZVPP:
-345.5450883
```

oQM-DEE.log

```
---------------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
===========================================================
 #M062X/6-31G* scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=DiethylEther) opt=(maxcycle=250,gdiis) iop(1/8=18)
 freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C7H6O   C1[X(C7H6O)]  #Atoms= 14
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -345.384859399       Predicted Change= -1.240726D-08
===========================================================
 Optimization completed.          {Found       2       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00008 ||  0.00045   [ YES ]      0.00001 ||  0.00030   [ YES ]
 Displ      0.00016 ||  0.00180   [ YES ]      0.00016 ||  0.00180   [ YES ]
---------------------------------------------------------------------------
     Atomic              Coordinates (Angstroms)
      Type              X             Y          Z
---------------------------------------------------------------------------
      C         0.545689       1.467958       0.000046
      H         0.450963       2.550649       0.000091
      C        -0.680727       0.677865      -0.000009
      C        -1.899477       1.241706       0.000013
      H        -2.027373       2.320195       0.000073
      H        -2.786760       0.616789      -0.000040
      C        -0.582821      -0.824326      -0.000118
      C         0.775861      -1.384704      -0.000031
      H         0.857568      -2.466692      -0.000031
      C         1.858656      -0.580798       0.000024
      H         2.853455      -1.018539       0.000059
      C         1.752705       0.871885       0.000053
      H         2.663788       1.460498       0.000102
      O        -1.578869      -1.535051      -0.000015
---------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin       Pressure= 1.00000 Atm
===========================================================
 SCF Energy=     -345.384859399   Predicted Change= -1.240726D-08
 Zero-point correction (ZPE)=                -345.2743       0.11051
```

```
 Internal Energy (U)=                 -345.2679       0.11691
 Enthalpy (H)=                        -345.2669       0.11786
 Gibbs Free Energy (G)=               -345.3049       0.07990
---------------------------------------------------------------------------Frequencies --     89.4767
231.6310         346.0581

M06-2X/6-311++G(2df,p)/PCM(DEE):
-345.5008722
M06-2X/6-311++G(2df,p):
-345.4954457
M06-2X/def2-QZVPP:
-345.5451383
```

oQM-THF.log

```
---------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
=====================================================
 #m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C7H6O   C1[X(C7H6O)]  #Atoms= 14
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -345.385823189       Predicted Change= -1.254504D-07
=====================================================
 Optimization completed.           {Found       2       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00029 ||  0.00045   [ YES ]      0.00004 ||  0.00030   [ YES ]
 Displ      0.00060 ||  0.00180   [ YES ]      0.00060 ||  0.00180   [ YES ]
---------------------------------------------------------------------
     Atomic              Coordinates (Angstroms)
      Type              X             Y         Z
---------------------------------------------------------------------
      C         0.546872      1.467428      0.000061
      H         0.452213      2.550038      0.000081
      C        -0.679889      0.677709      0.000021
      C        -1.897948      1.243741     -0.000019
      H        -2.023877      2.322371     -0.000029
      H        -2.787009      0.621332     -0.000049
      C        -0.583120     -0.823861      0.000051
      C         0.774099     -1.385142     -0.000029
      H         0.856228     -2.467142     -0.000089
      C         1.857980     -0.581843      0.000001
      H         2.852189     -1.020764     -0.000019
      C         1.753761      0.870627      0.000061
      H         2.665412      1.458216      0.000081
      O        -1.580711     -1.534500     -0.000109
---------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin       Pressure= 1.00000 Atm
=====================================================
 SCF Energy=     -345.385823189   Predicted Change= -1.254504D-07
 Zero-point correction (ZPE)=              -345.2753       0.11050
 Internal Energy (U)=                      -345.2689       0.11690
```

Enthalpy (H)= -345.2679 0.11785
Gibbs Free Energy (G)= -345.3059 0.07989
---Frequencies -- 89.2822 232.0333 346.1444

M06-2X/6-311++G(2df,p)/PCM(THF):
-345.5019788
M06-2X/6-311++G(2df,p):
-345.4953984
M06-2X/def2-QZVPP:
-345.5450883

aoQM-NH-DCM.log

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
#m062X/6-31G(d) scf=(direct,tight,maxcycle=300,xqc)
SCRF=(PCM,SOLVENT=dichloromethane) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman temp=298.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
Pointgroup= C1 Stoichiometry= C7H7N C1[X(C7H7N)] #Atoms= 15
Charge = 0 Multiplicity = 1
SCF Energy= -325.507617023 Predicted Change= -1.116071D-07
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00016	0.00045	[YES]	0.00003	0.00030	[YES]
Displ	0.00499	0.00180	[NO]	0.00499	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.605530	-1.447760	-0.001281
H	0.552058	-2.533270	-0.002261
C	-0.659310	-0.713979	-0.000001
C	-1.834700	-1.364008	0.001659
H	-1.873481	-2.449258	0.001649
H	-2.771000	-0.816527	0.003129
C	-0.610288	0.785151	-0.000081
N	-1.704668	1.455782	-0.001731
C	0.728332	1.394220	0.001309
H	0.780343	2.480200	0.002479
C	1.845622	0.644629	0.000759
H	2.820002	1.124958	0.001529
C	1.790870	-0.812211	-0.000911
H	2.721090	-1.370472	-0.001661
H	-1.492667	2.457642	-0.001451

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
SCF Energy= -325.507617023 Predicted Change= -1.116071D-07
Zero-point correction (ZPE)= -325.3849 0.12266

```
 Internal Energy (U)=                  -325.3783       0.12929
 Enthalpy (H)=                         -325.3773       0.13023
 Gibbs Free Energy (G)=                -325.4164       0.09113
---------------------------------------------------------------------------
Frequencies --     29.8665             226.8308          367.6240

M06-2X/6-311++G(2df,p)/PCM(DCM):
-325.6161402
M06-2X/6-311++G(2df,p):
-325.6103658
M06-2X/def2-QZVPP:
-325.6580453
```

aoQM-NH-DEE.log

```
---------------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
===========================================================
 #m062X/6-31G(d) scf=(direct,tight,maxcycle=300,xqc)
 SCRF=(PCM,SOLVENT=diethylether) opt=(maxcycle=250,gdiis) iop(1/8=18)
 freq=noraman temp=298.15
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C7H7N   C1[X(C7H7N)]  #Atoms= 15
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -325.506434349       Predicted Change= -1.214183D-07
===========================================================
 Optimization completed.          {Found       1       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00019 ||  0.00045   [ YES ]      0.00003 ||  0.00030   [ YES ]
 Displ      0.00505 ||  0.00180   [ NO ]       0.00505 ||  0.00180   [ NO ]
---------------------------------------------------------------------------
     Atomic             Coordinates (Angstroms)
      Type              X           Y           Z
---------------------------------------------------------------------------
      C         0.605827    -1.447412    -0.001215
      H         0.552582    -2.532952    -0.002106
      C        -0.659002    -0.713994    -0.000025
      C        -1.834732    -1.363039     0.001618
      H        -1.874480    -2.448296     0.001686
      H        -2.770173    -0.814078     0.002986
      C        -0.610284     0.784842    -0.000250
      N        -1.705150     1.454041    -0.001582
      C         0.728377     1.394094     0.001242
      H         0.780180     2.480139     0.002422
      C         1.845714     0.644907     0.000725
      H         2.820067     1.125393     0.001503
      C         1.791044    -0.811852    -0.000878
      H         2.721308    -1.370074    -0.001571
      H        -1.495100     2.456304    -0.001152
---------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin       Pressure= 1.00000 Atm
===========================================================
 SCF Energy=     -325.506434349   Predicted Change= -1.214183D-07
```

```
 Zero-point correction (ZPE)=              -325.3837       0.12264
 Internal Energy (U)=                      -325.3771       0.12927
 Enthalpy (H)=                             -325.3762       0.13021
 Gibbs Free Energy (G)=                    -325.4152       0.09116
---------------------------------------------------------------------------
Frequencies --     31.6333               226.4739          368.6633

M06-2X/6-311++G(2df,p)/PCM(DEE):
-325.6148946
M06-2X/6-311++G(2df,p):
-325.6103824
M06-2X/def2-QZVPP:
-325.6580636
```

aoQM-NH-THF.log

```
---------------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
===========================================================
 #m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C7H7N   C1[X(C7H7N)]  #Atoms= 15
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -325.507382940       Predicted Change= -4.393157D-08
===========================================================
 Optimization completed.           {Found       1       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00009 ||  0.00045   [ YES ]      0.00001 ||  0.00030   [ YES ]
 Displ      0.00500 ||  0.00180   [ NO ]       0.00500 ||  0.00180   [ NO ]
---------------------------------------------------------------------------
     Atomic              Coordinates (Angstroms)
      Type              X             Y          Z
---------------------------------------------------------------------------
      C         0.605533     -1.447757     -0.001283
      H         0.552064     -2.533267     -0.002255
      C        -0.659306     -0.713975     -0.000004
      C        -1.834704     -1.364011      0.001655
      H        -1.873482     -2.449256      0.001650
      H        -2.770999     -0.816533      0.003129
      C        -0.610289      0.785150     -0.000081
      N        -1.704670      1.455778     -0.001729
      C         0.728331      1.394223      0.001312
      H         0.780338      2.480199      0.002475
      C         1.845621      0.644625      0.000756
      H         2.820003      1.124963      0.001528
      C         1.790873     -0.812209     -0.000908
      H         2.721089     -1.370474     -0.001658
      H        -1.492669      2.457644     -0.001446
---------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin       Pressure= 1.00000 Atm
===========================================================
 SCF Energy=     -325.507382940   Predicted Change= -4.393157D-08
```

Zero-point correction (ZPE)= -325.3847 0.12265
Internal Energy (U)= -325.3781 0.12928
Enthalpy (H)= -325.3771 0.13022
Gibbs Free Energy (G)= -325.4162 0.09110
---Frequencies -- 29.5226 226.7498 367.2788

M06-2X/6-311++G(2df,p)/PCM(THF):
-325.6158921
M06-2X/6-311++G(2df,p):
-325.6103658
M06-2X/def2-QZVPP:
-325.6580454

aoQM-NBoc-DCM.log

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
#m062X/6-31G(d) scf=(direct,tight,maxcycle=300,xqc)
SCRF=(PCM,SOLVENT=dichloromethane) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman temp=298.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
Pointgroup= C1 Stoichiometry= C12H15NO2 C1[X(C12H15NO2)] #Atoms= 30
Charge = 0 Multiplicity = 1
SCF Energy= -671.195075288 Predicted Change= -1.643781D-08
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00174	0.00180	[YES]	0.00174	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.780656	0.989877	-0.046389
C	-2.755563	2.332544	0.020784
C	-1.521851	0.196602	0.101967
N	-0.412915	0.834847	0.270165
C	0.769268	0.142945	0.529129
O	1.706582	0.526867	-0.342088
C	3.066005	0.001187	-0.254085
O	0.939143	-0.624862	1.455167
C	-1.648444	-1.257422	0.010366
C	-2.849389	-1.836644	-0.196697
C	-4.074789	-1.066758	-0.333196
C	-4.035967	0.275935	-0.261859
C	3.709171	0.434229	1.059397
C	3.760402	0.668200	-1.435779
C	3.059812	-1.515002	-0.426089
H	-3.668877	2.911524	-0.077330
H	-1.823023	2.864797	0.173550
H	-0.752147	-1.857683	0.115477
H	-2.912405	-2.918936	-0.266181

H	-5.009785	-1.591613	-0.495449
H	-4.938000	0.872664	-0.365263
H	3.225001	-0.043003	1.912040
H	3.641931	1.521175	1.168812
H	4.767110	0.154516	1.051172
H	4.807922	0.356947	-1.475242
H	3.721002	1.756668	-1.335645
H	3.274157	0.384499	-2.373675
H	2.601680	-2.010743	0.430337
H	4.090148	-1.868759	-0.529382
H	2.511899	-1.786170	-1.334304

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-671.195075288	Predicted Change= -1.643781D-08
Zero-point correction (ZPE)=	-670.9436	0.25139
Internal Energy (U)=	-670.9288	0.26622
Enthalpy (H)=	-670.9279	0.26716
Gibbs Free Energy (G)=	-670.9863	0.20869

Frequencies -- 24.1375 42.4763 65.4103

M06-2X/6-311++G(2df,p)/PCM(DCM):
-671.4183278
M06-2X/6-311++G(2df,p):
-671.4100864
M06-2X/def2-QZVPP:
-671.5090817

aoQM-NBoc-DEE.log

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062X/6-31G(d) scf=(direct,tight,maxcycle=300,xqc)
SCRF=(PCM,SOLVENT=diethylether) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman temp=298.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C12H15NO2 C1[X(C12H15NO2)] #Atoms= 30
Charge = 0 Multiplicity = 1

SCF Energy= -671.193451192 Predicted Change= -8.859564D-10

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00029 ||	0.00180	[YES]	0.00029 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.778481	0.992837	-0.042075
C	-2.747011	2.334943	0.028572
C	-1.522294	0.194301	0.103005

N	-0.412311	0.828798	0.272614
C	0.769403	0.132928	0.525518
O	1.708908	0.530554	-0.337903
C	3.067029	0.004567	-0.252091
O	0.936856	-0.649792	1.438719
C	-1.654491	-1.259601	0.006898
C	-2.857312	-1.833342	-0.201800
C	-4.079834	-1.057987	-0.335659
C	-4.036269	0.284077	-0.259189
C	3.705100	0.418354	1.070238
C	3.766148	0.688987	-1.421139
C	3.063335	-1.509206	-0.445859
H	-3.657620	2.918697	-0.067176
H	-1.811195	2.861164	0.181881
H	-0.760556	-1.862935	0.113297
H	-2.924836	-2.915271	-0.273564
H	-5.017053	-1.578605	-0.499258
H	-4.936510	0.884114	-0.359652
H	3.216582	-0.070285	1.913820
H	3.637682	1.503668	1.194554
H	4.763048	0.138258	1.062977
H	4.813810	0.378053	-1.462067
H	3.726285	1.775748	-1.304740
H	3.282509	0.420341	-2.364765
H	2.599339	-2.016942	0.400286
H	4.094545	-1.861269	-0.547103
H	2.522096	-1.767574	-1.361835

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -671.193451192 Predicted Change= -8.859564D-10

Zero-point correction (ZPE)=	-670.9419	0.25148
Internal Energy (U)=	-670.9271	0.26629
Enthalpy (H)=	-670.9262	0.26724
Gibbs Free Energy (G)=	-670.9846	0.20884

Frequencies -- 24.9291 42.4367 66.5471

M06-2X/6-311++G(2df,p)/PCM(DEE):
-671.4165241
M06-2X/6-311++G(2df,p):
-671.4101337
M06-2X/def2-QZVPP:
-671.5091194

aoQM-NBoc-THF.log

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C12H15NO2 C1[X(C12H15NO2)] #Atoms= 30

Charge = 0 Multiplicity = 1

SCF Energy= -671.194752049 Predicted Change= -9.668198D-09

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00228	0.00180	[NO]	0.00228	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.780185	0.990421	-0.045641
C	-2.753886	2.332965	0.022320
C	-1.521909	0.196128	0.102341
N	-0.412801	0.833663	0.270860
C	0.769357	0.141125	0.528763
O	1.706800	0.527190	-0.341547
C	3.066054	0.001783	-0.253900
O	0.938990	-0.629137	1.452633
C	-1.649613	-1.257917	0.010146
C	-2.850862	-1.836095	-0.197492
C	-4.075630	-1.065122	-0.334045
C	-4.035895	0.277452	-0.261811
C	3.708298	0.432142	1.060970
C	3.761011	0.671567	-1.433752
C	3.060766	-1.514106	-0.429133
H	-3.666635	2.912899	-0.075590
H	-1.820752	2.864027	0.175535
H	-0.753844	-1.858780	0.116046
H	-2.914761	-2.918333	-0.267177
H	-5.011017	-1.589150	-0.496817
H	-4.937554	0.874811	-0.364982
H	3.223284	-0.046693	1.912224
H	3.640997	1.518868	1.172448
H	4.766249	0.152369	1.053165
H	4.808732	0.360913	-1.473267
H	3.720912	1.759778	-1.331343
H	3.275401	0.389739	-2.372534
H	2.602375	-2.011842	0.425972
H	4.091331	-1.867180	-0.532702
H	2.513523	-1.783553	-1.338283

Statistical Thermodynamic Analysis

Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-671.194752049	Predicted Change=	-9.668198D-09
Zero-point correction (ZPE)=	-670.9433	0.25141	
Internal Energy (U)=	-670.9285	0.26623	
Enthalpy (H)=	-670.9275	0.26718	
Gibbs Free Energy (G)=	-670.9860	0.20872	

Frequencies -- 24.4274 42.5174 65.5869

M06-2X/6-311++G(2df,p)/PCM(THF):

-671.4179686
M06-2X/6-311++G(2df,p):
-671.4100983
M06-2X/def2-QZVPP:
-671.5090907

HCl-DCM.log

```
---------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
=====================================================
 #M062X/6-31G* scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=dichloromethane) opt=(maxcycle=250,gdiis) iop(1/8=18)
 freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------
 Pointgroup= C*V   Stoichiometry= ClH   C*V[C*(HCl)]  #Atoms= 2
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -460.758671140       Predicted Change= -1.999007D-08
=====================================================
 Optimization completed.           {Found       2       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00011 ||  0.00045   [ YES ]      0.00011 ||  0.00030   [ YES ]
 Displ      0.00017 ||  0.00180   [ YES ]      0.00017 ||  0.00180   [ YES ]
---------------------------------------------------------------------
      Atomic              Coordinates (Angstroms)
       Type              X              Y          Z
---------------------------------------------------------------------
      Cl        0.000000       0.000000       0.071379
      H         0.000000       0.000000      -1.213451
---------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin       Pressure= 1.00000 Atm
=====================================================
 SCF Energy=     -460.758671140   Predicted Change= -1.999007D-08
 Zero-point correction (ZPE)=              -460.7518       0.00679
 Internal Energy (U)=                      -460.7495       0.00915
 Enthalpy (H)=                             -460.7485       0.01010
 Gibbs Free Energy (G)=                    -460.7697      -0.01109
---------------------------------------------------------------------
 Frequencies --   2982.8778
```

M06-2X/6-311++G(2df,p)/PCM(DCM):
-460.8020267
M06-2X/6-311++G(2df,p):
-460.7993584
M06-2X/def2-QZVPP:
-460.8106404

HCl-DEE.log

```
---------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
=====================================================
 #M062X/6-31G* scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=DiethylEther) opt=(maxcycle=250,gdiis) iop(1/8=18)
```

freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C*V Stoichiometry= ClH C*V[C*(HCl)] #Atoms= 2
Charge = 0 Multiplicity = 1

SCF Energy= -460.758033667 Predicted Change= -5.530696D-10
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00001	0.00030	[YES]
Displ	0.00002	0.00180	[YES]	0.00002	0.00180	[YES]

Atomic Coordinates (Angstroms)

Type	X	Y	Z
Cl	0.000000	0.000000	0.071347
H	0.000000	0.000000	-1.212907

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -460.758033667 Predicted Change= -5.530696D-10
Zero-point correction (ZPE)= -460.7512 0.00681
Internal Energy (U)= -460.7488 0.00917
Enthalpy (H)= -460.7479 0.01011
Gibbs Free Energy (G)= -460.7691 -0.01107

Frequencies -- 2990.2900

M06-2X/6-311++G(2df,p)/PCM(DEE):
-460.8015104
M06-2X/6-311++G(2df,p):
-460.7993619
M06-2X/def2-QZVPP:
-460.8106457

HCl-THF.log

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C*V Stoichiometry= ClH C*V[C*(HCl)] #Atoms= 2
Charge = 0 Multiplicity = 1

SCF Energy= -460.758547822 Predicted Change= -3.869208D-08
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00016	0.00045	[YES]	0.00016	0.00030	[YES]
Displ	0.00024	0.00180	[YES]	0.00024	0.00180	[YES]

```
     Atomic              Coordinates (Angstroms)
      Type              X           Y           Z
---------------------------------------------------------------------
      Cl       0.000000      0.000000      0.071379
      H        0.000000      0.000000     -1.213451
---------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin       Pressure= 1.00000 Atm
=====================================================
 SCF Energy=     -460.758547822   Predicted Change= -3.869208D-08
 Zero-point correction (ZPE)=              -460.7517       0.00679
 Internal Energy (U)=                      -460.7493       0.00915
 Enthalpy (H)=                             -460.7484       0.01010
 Gibbs Free Energy (G)=                    -460.7696      -0.01109
---------------------------------------------------------------------
 Frequencies --   2983.1165

M06-2X/6-311++G(2df,p)/PCM(THF):
-460.8019265
M06-2X/6-311++G(2df,p):
-460.7993584
M06-2X/def2-QZVPP:
-460.8106404
```

imidazole-DCM.log

```
---------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
=====================================================
 #M062X/6-31G* scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=dichloromethane) opt=(maxcycle=250,gdiis) iop(1/8=18)
 freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C3H4N2   C1[X(C3H4N2)]  #Atoms= 9
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -226.129306736       Predicted Change= -1.522097D-07
=====================================================
 Optimization completed.           {Found       2       times}
 Item     Max Val.   Criteria   Pass?     RMS Val.   Criteria   Pass?
 Force     0.00016 ||  0.00045   [ YES ]     0.00005 ||  0.00030   [ YES ]
 Displ     0.00064 ||  0.00180   [ YES ]     0.00064 ||  0.00180   [ YES ]
---------------------------------------------------------------------
     Atomic              Coordinates (Angstroms)
      Type              X           Y           Z
---------------------------------------------------------------------
      N       -0.157900     -1.222082      0.000031
      C       -1.140598     -0.258649     -0.000099
      C       -0.587858      0.994405      0.000161
      N        0.768794      0.785526     -0.000149
      C        0.974885     -0.555872      0.000081
      H       -2.189216     -0.521278     -0.000209
      H       -1.016096      1.984192      0.000201
      H        1.483578      1.499502     -0.000089
      H        1.966898     -0.985825      0.000081
```

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -226.129306736 Predicted Change= -1.522097D-07
Zero-point correction (ZPE)= -226.0569 0.07239
Internal Energy (U)= -226.0532 0.07606
Enthalpy (H)= -226.0522 0.07700
Gibbs Free Energy (G)= -226.0831 0.04616

Frequencies -- 580.6298 662.9158 695.5083

M06-2X/6-311++G(2df,p)/PCM(DCM):
-226.2096894
M06-2X/6-311++G(2df,p):
-226.200148
M06-2X/def2-QZVPP:
--226.2329705

imidazole-DEE.log

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#M062X/6-31G* scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=DiethylEther) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C3H4N2 C1[X(C3H4N2)] #Atoms= 9
Charge = 0 Multiplicity = 1

SCF Energy= -226.127395461 Predicted Change= -1.561622D-07
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00007	0.00045	[YES]	0.00003	0.00030	[YES]
Displ	0.00096	0.00180	[YES]	0.00096	0.00180	[YES]

Atomic Coordinates (Angstroms)

Type	X	Y	Z
N	-0.158233	-1.221598	0.000096
C	-1.140148	-0.258420	-0.000250
C	-0.587669	0.994519	0.000329
N	0.769231	0.785736	-0.000302
C	0.974167	-0.556606	0.000183
H	-2.188561	-0.521452	-0.000438
H	-1.016085	1.984171	0.000523
H	1.483988	1.499191	-0.000460
H	1.965574	-0.987835	0.000250

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -226.127395461 Predicted Change= -1.561622D-07

```
 Zero-point correction (ZPE)=              -226.0550       0.07236
 Internal Energy (U)=                      -226.0513       0.07604
 Enthalpy (H)=                             -226.0504       0.07698
 Gibbs Free Energy (G)=                    -226.0812       0.04613
---------------------------------------------------------------------------Frequencies --    573.2638
660.9693        694.2937

M06-2X/6-311++G(2df,p)/PCM(DEE):
-226.2077162
M06-2X/6-311++G(2df,p):
-226.2001738
M06-2X/def2-QZVPP:
-226.2329978
```

imidazole-THF.log

```
---------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
=====================================================
 #M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C3H4N2   C1[X(C3H4N2)]  #Atoms= 9
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -226.128933023       Predicted Change= -9.261718D-08
=====================================================
 Optimization completed.          {Found       2       times}
 Item     Max Val.   Criteria   Pass?     RMS Val.   Criteria   Pass?
 Force     0.00014 ||  0.00045   [ YES ]     0.00003 ||  0.00030   [ YES ]
 Displ     0.00034 ||  0.00180   [ YES ]     0.00034 ||  0.00180   [ YES ]
---------------------------------------------------------------------
     Atomic             Coordinates (Angstroms)
      Type              X           Y           Z
---------------------------------------------------------------------
      N         0.157911    -1.222083    -0.000033
      C         1.140596    -0.258636     0.000099
      C         0.587849     0.994406    -0.000159
      N        -0.768802     0.785524     0.000153
      C        -0.974877    -0.555883    -0.000081
      H         2.189220    -0.521256     0.000206
      H         1.016083     1.984196    -0.000203
      H        -1.483590     1.499492     0.000091
      H        -1.966890    -0.985841    -0.000080
---------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin       Pressure= 1.00000 Atm
=====================================================
 SCF Energy=     -226.128933023   Predicted Change= -9.261718D-08
 Zero-point correction (ZPE)=              -226.0565       0.07238
 Internal Energy (U)=                      -226.0528       0.07605
 Enthalpy (H)=                             -226.0519       0.07700
 Gibbs Free Energy (G)=                    -226.0827       0.04615
---------------------------------------------------------------------
Frequencies --    579.7986             662.6969        695.4304
```

M06-2X/6-311++G(2df,p)/PCM(THF):
-226.2093011
M06-2X/6-311++G(2df,p):
-226.2001481
M06-2X/def2-QZVPP:
-226.2329706

imidazolium-Cl-DCM.log

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#m062X/6-31G(d) scf=(direct,tight,maxcycle=300,xqc)
SCRF=(PCM,SOLVENT=dichloromethane) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman temp=298.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C3H5ClN2 C1[X(C3H5ClN2)] #Atoms= 11
Charge = 0 Multiplicity = 1

SCF Energy= -686.927291223 Predicted Change= -3.418612D-08
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00005	0.00045	[YES]	0.00001	0.00030	[YES]
Displ	0.00117	0.00180	[YES]	0.00117	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-0.170853	0.044326	0.000010
C	-0.996595	1.142656	0.000019
C	-2.277576	0.680873	-0.000142
N	-2.190215	-0.693137	-0.000010
C	-0.905889	-1.056151	-0.000047
H	0.895494	0.053671	0.000057
H	-0.606977	2.147344	0.000068
H	-3.224141	1.195208	-0.000228
H	-2.971752	-1.337540	0.000005
H	-0.534505	-2.068580	-0.000046
Cl	2.826454	-0.003100	0.000069

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -686.927291223 Predicted Change= -3.418612D-08
Zero-point correction (ZPE)= -686.8418 0.08547
Internal Energy (U)= -686.8359 0.09130
Enthalpy (H)= -686.8350 0.09225
Gibbs Free Energy (G)= -686.8732 0.05409

Frequencies -- 60.6574 84.4279 194.7330

M06-2X/6-311++G(2df,p)/PCM(DCM):
-687.0466285

M06-2X/6-311++G(2df,p):
-687.0046563
M06-2X/def2-QZVPP:
-687.0459093

imidazolium-Cl-DEE.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011
==========
#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=diethylether) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C3H5ClN2 C1[X(C3H5ClN2)] #Atoms= 11
Charge = 0 Multiplicity = 1

SCF Energy= -686.919984174 Predicted Change= -3.175183D-08
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00003	0.00045	[YES]	0.00001	0.00030	[YES]
Displ	0.00132	0.00180	[YES]	0.00132	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	0.158423	0.061017	-0.000181
C	1.000369	1.145648	-0.000045
C	2.275469	0.666846	0.000094
N	2.168696	-0.706268	0.000117
C	0.876944	-1.048439	-0.000124
H	-0.922493	0.077952	-0.000106
H	0.624904	2.155801	-0.000131
H	3.229034	1.168278	0.000082
H	2.940333	-1.361679	0.000210
H	0.488277	-2.054596	-0.000142
Cl	-2.798034	-0.003137	0.000058

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -686.919984174 Predicted Change= -3.175183D-08
Zero-point correction (ZPE)= -686.8351 0.08485
Internal Energy (U)= -686.8293 0.09068
Enthalpy (H)= -686.8283 0.09162
Gibbs Free Energy (G)= -686.8665 0.05340

Frequencies -- 49.1156 94.5105 198.4199

M06-2X/6-311++G(2df,p)/PCM(DEE):
-687.0395654
M06-2X/6-311++G(2df,p):
-687.0066202
M06-2X/def2-QZVPP:
-687.0480061

imidazolium-Cl-THF.log

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062X/6-31G(d) scf=(direct,tight,maxcycle=300,xqc) SCRF=(PCM,SOLVENT=THF)
opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman temp=298.15
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C3H5ClN2 C1[X(C3H5ClN2)] #Atoms= 11
Charge = 0 Multiplicity = 1

SCF Energy= -686.925883839 Predicted Change= -6.648709D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00006	0.00045	[YES]	0.00001	0.00030	[YES]
Displ	0.00243	0.00180	[NO]	0.00243	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-0.168438	0.042141	0.000162
C	-0.992054	1.141782	0.000023
C	-2.274082	0.682760	0.000097
N	-2.189537	-0.691502	-0.000204
C	-0.905485	-1.056653	0.000211
H	0.900311	0.050019	0.000274
H	-0.600217	2.145647	0.000013
H	-3.219511	1.199171	0.000089
H	-2.972267	-1.334292	-0.000418
H	-0.535750	-2.069714	0.000313
Cl	2.821352	-0.003096	-0.000115

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -686.925883839 Predicted Change= -6.648709D-08
Zero-point correction (ZPE)= -686.8404 0.08542
Internal Energy (U)= -686.8346 0.09123
Enthalpy (H)= -686.8337 0.09218
Gibbs Free Energy (G)= -686.8717 0.05408

Frequencies -- 61.0644 86.6774 202.0959

M06-2X/6-311++G(2df,p)/PCM(THF):
-687.0452629
M06-2X/6-311++G(2df,p):
-687.0050095
M06-2X/def2-QZVPP:
-687.046282

Supporting Information:
Cs_2CO_3-DCM.log

```
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
 ================================================
 #M062X/gen pseudo=read scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=dichloromethane) opt=(maxcycle=250) freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/ChkBas Freq
 ---------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= CCs2O3   C1[X(CCs2O3)]  #Atoms= 6
 Charge = 0         Multiplicity = 1
 ---------------------------------------------------------------------------
 SCF Energy= -304.017324299       Predicted Change= -1.339858D-07
 ================================================
 Optimization completed.          {Found       1       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00005 ||  0.00045   [ YES ]      0.00001 ||  0.00030   [ YES ]
 Displ      0.00680 ||  0.00180   [ NO ]       0.00680 ||  0.00180   [ NO ]
 ---------------------------------------------------------------------------
     Atomic             Coordinates (Angstroms)
      Type              X           Y           Z
 ---------------------------------------------------------------------------
      C       -0.002795       1.267478       0.025752
      O       -1.121940       1.905032       0.091165
      O        1.112177       1.898957      -0.119699
      O        0.000720      -0.038217       0.105805
      Cs       2.897999      -0.342210      -0.001114
      Cs      -2.896379      -0.343809      -0.012935
 ---------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin       Pressure= 1.00000 Atm
 ================================================
 SCF Energy=     -304.017324299   Predicted Change= -1.339858D-07
 Zero-point correction (ZPE)=             -304.0011       0.01617
 Internal Energy (U)=                     -303.9937       0.02358
 Enthalpy (H)=                            -303.9927       0.02452
 Gibbs Free Energy (G)=                   -304.0388      -0.02153
 ---------------------------------------------------------------------------
Frequencies --     42.1707              65.3284              76.6941

M06-2X/6-311++G(2df,p)/PCM(DCM):
-304.1606948
M06-2X/6-311++G(2df,p):
-304.0814275
M06-2X/def2-QZVPP:
-304.1547436
```

Cs_2CO_3-DEE.log

```
 ---------------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
 ================================================
 #M062X/gen pseudo=read scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=DiethylEther) opt=(maxcycle=250) freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/ChkBas Freq
 ---------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= CCs2O3   C1[X(CCs2O3)]  #Atoms= 6
 Charge = 0         Multiplicity = 1
 ---------------------------------------------------------------------------
```

SCF Energy= -304.003123768 Predicted Change= -9.161081D-08
==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00003	0.00045	[YES]	0.00001	0.00030	[YES]
Displ	0.00246	0.00180	[NO]	0.00246	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.002726	1.248423	0.027078
O	-1.122080	1.882211	0.087772
O	1.112348	1.876390	-0.116198
O	0.000956	-0.062209	0.109741
Cs	2.869633	-0.336137	-0.001617
Cs	-2.868060	-0.337711	-0.013165

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========

SCF Energy=	-304.003123768	Predicted Change= -9.161081D-08
Zero-point correction (ZPE)=	-303.9868	0.01630
Internal Energy (U)=	-303.9795	0.02362
Enthalpy (H)=	-303.9785	0.02456
Gibbs Free Energy (G)=	-304.0241	-0.02099

Frequencies -- 51.1787 70.5328 83.3498

M06-2X/6-311++G(2df,p)/PCM(DEE):
-304.146022
M06-2X/6-311++G(2df,p):
-304.0836279
M06-2X/def2-QZVPP:
-304.1579717

Cs_2CO_3-THF.log

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========

#m062X/gen pseudo=read scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(verytight,maxcycle=250,gdiis) iop(1/8=18)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/ChkBas Freq

---

Pointgroup= C1 Stoichiometry= CCs2O3 C1[X(CCs2O3)] #Atoms= 6
Charge = 0 Multiplicity = 1

SCF Energy= -304.014581256 Predicted Change= -5.201570D-13
==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00000	[YES]	0.00000	0.00000	[YES]
Displ	0.00001	0.00000	[NO]	0.00001	0.00000	[YES]

Atomic	Coordinates (Angstroms)

Type	X	Y	Z
C	-0.002783	1.263434	0.025565
O	-1.121825	1.900285	0.091361
O	1.112239	1.894126	-0.119365
O	0.000612	-0.043379	0.104609
Cs	2.892893	-0.340924	-0.001048
Cs	-2.891284	-0.342509	-0.012883

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -304.014581256	Predicted Change= -5.201570D-13	
Zero-point correction (ZPE)=	-303.9983	0.01620
Internal Energy (U)=	-303.9909	0.02359
Enthalpy (H)=	-303.9900	0.02453
Gibbs Free Energy (G)=	-304.0360	-0.02142

Frequencies -- 43.5556 65.7497 78.8034

M06-2X/6-311++G(2df,p)/PCM(THF):
-304.157853
M06-2X/6-311++G(2df,p):
-304.0818973
M06-2X/def2-QZVPP:
-304.1554092

CsCl-DCM.log

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

#M062X/gen pseudo=read scf=(maxcycle=300,direct,tight) density=current SCRF=(PCM,SOLVENT=dichloromethane) opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/ChkBas Freq

Pointgroup= C*V Stoichiometry= ClCs C*V[C*(ClCs)] #Atoms= 2
Charge = 0 Multiplicity = 1

SCF Energy= -480.371420883 Predicted Change= -4.260572D-11

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00003	0.00180	[YES]	0.00003	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
Cs	0.000000	0.000000	0.781787
Cl	0.000000	0.000000	-2.529310

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -480.371420883 Predicted Change= -4.260572D-11
Zero-point correction (ZPE)= -480.3711 0.00032
Internal Energy (U)= -480.3680 0.00334
Enthalpy (H)= -480.3671 0.00428
Gibbs Free Energy (G)= -480.3967 -0.02535

Frequencies -- 140.8916

M06-2X/6-311++G(2df,p)/PCM(DCM):
-480.417606
M06-2X/6-311++G(2df,p):
-480.359091
M06-2X/def2-QZVPP:
-480.3799925

CsCl-DEE.log

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#M062X/gen pseudo=read scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=DiethylEther) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/ChkBas Freq
---
Pointgroup= C*V Stoichiometry= ClCs C*V[C*(ClCs)] #Atoms= 2
Charge = 0 Multiplicity = 1

SCF Energy= -480.361677718 Predicted Change= -2.102555D-09
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00001	0.00030	[YES]
Displ	0.00021	0.00180	[YES]	0.00021	0.00180	[YES]

Atomic Coordinates (Angstroms)

Type	X	Y	Z
Cs	0.000000	0.000000	0.771616
Cl	0.000000	0.000000	-2.496404

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -480.361677718 Predicted Change= -2.102555D-09
Zero-point correction (ZPE)= -480.3613 0.00033
Internal Energy (U)= -480.3583 0.00334
Enthalpy (H)= -480.3573 0.00428
Gibbs Free Energy (G)= -480.3869 -0.02528

Frequencies -- 147.8309

M06-2X/6-311++G(2df,p)/PCM(DEE):
-480.4078377
M06-2X/6-311++G(2df,p):
-480.359954

M06-2X/def2-QZVPP:
-480.3814094

CsCl-THF.log

```
---------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
=====================================================
 #m062X/gen pseudo=read scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/ChkBas Freq
---------------------------------------------------------------------
 Pointgroup= C*V   Stoichiometry= ClCs   C*V[C*(ClCs)]  #Atoms= 2
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -480.369581871       Predicted Change= -1.844339D-11
=====================================================
 Optimization completed.           {Found       2       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00000 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00002 ||  0.00180   [ YES ]      0.00002 ||  0.00180   [ YES ]
---------------------------------------------------------------------
      Atomic              Coordinates (Angstroms)
       Type              X             Y          Z
---------------------------------------------------------------------
      Cs        0.000000       0.000000       0.779885
      Cl        0.000000       0.000000      -2.523157
---------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin       Pressure= 1.00000 Atm
=====================================================
 SCF Energy=     -480.369581871   Predicted Change= -1.844339D-11
 Zero-point correction (ZPE)=              -480.3692       0.00032
 Internal Energy (U)=                      -480.3662       0.00334
 Enthalpy (H)=                             -480.3652       0.00428
 Gibbs Free Energy (G)=                    -480.3949      -0.02533
---------------------------------------------------------------------
 Frequencies --    143.0673
```

M06-2X/6-311++G(2df,p)/PCM(THF):
-480.4157611
M06-2X/6-311++G(2df,p):
-480.3592636
M06-2X/def2-QZVPP:
-480.3802637

CsHCO3-DCM.log

```
---------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
=====================================================
 #M062X/gen pseudo=read scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=dichloromethane) opt=(maxcycle=250,gdiis) iop(1/8=18)
 freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/ChkBas Freq
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= CHCsO3   C1[X(CHCsO3)]  #Atoms= 6
```

```
 Charge = 0         Multiplicity = 1
--------------------------------------------------------------------------------
 SCF Energy= -284.484896803       Predicted Change= -8.358388D-10
================================================
 Optimization completed.            {Found       2       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00001 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00011 ||  0.00180   [ YES ]      0.00011 ||  0.00180   [ YES ]
--------------------------------------------------------------------------------
      Atomic              Coordinates (Angstroms)
       Type              X           Y           Z
--------------------------------------------------------------------------------
       C         2.067026       0.037110       0.000179
       O         3.455575       0.073514       0.000295
       O         1.548601      -1.104060       0.000188
       O         1.512891       1.152649       0.000071
       H         3.730876      -0.855579       0.000365
       Cs       -1.241265      -0.006253      -0.000107
--------------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin       Pressure= 1.00000 Atm
================================================
 SCF Energy=     -284.484896803   Predicted Change= -8.358388D-10
 Zero-point correction (ZPE)=             -284.4568       0.02805
 Internal Energy (U)=                     -284.4512       0.03362
 Enthalpy (H)=                            -284.4503       0.03456
 Gibbs Free Energy (G)=                   -284.4889      -0.00409
--------------------------------------------------------------------------------
 Frequencies --     54.5996             142.1576         144.6811

M06-2X/6-311++G(2df,p)/PCM(DCM):
-284.6114037
M06-2X/6-311++G(2df,p):
-284.5692616
M06-2X/def2-QZVPP:
-284.6196157
```

$CsHCO_3$-DEE.log

```
--------------------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
================================================
 #M062X/gen pseudo=read scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=DiethylEther) opt=(maxcycle=250,gdiis) iop(1/8=18)
 freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/ChkBas Freq
--------------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= CHCsO3   C1[X(CHCsO3)]  #Atoms= 6
 Charge = 0         Multiplicity = 1
--------------------------------------------------------------------------------
 SCF Energy= -284.477696801       Predicted Change= -7.216705D-09
================================================
 Optimization completed.            {Found       2       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00004 ||  0.00045   [ YES ]      0.00001 ||  0.00030   [ YES ]
 Displ      0.00069 ||  0.00180   [ YES ]      0.00069 ||  0.00180   [ YES ]
```

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.047385	0.038104	-0.000138
O	3.433764	0.075115	0.000404
O	1.529209	-1.104756	-0.000377
O	1.489248	1.151667	-0.000319
H	3.706092	-0.854700	0.000490
Cs	-1.229239	-0.006366	0.000049

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -284.477696801 Predicted Change= -7.216705D-09

Zero-point correction (ZPE)=	-284.4495	0.02813
Internal Energy (U)=	-284.4440	0.03369
Enthalpy (H)=	-284.4430	0.03463
Gibbs Free Energy (G)=	-284.4816	-0.00394

Frequencies -- 57.7592 141.8905 144.3267

M06-2X/6-311++G(2df,p)/PCM(DEE):
-284.6040777
M06-2X/6-311++G(2df,p):
-284.5699771
M06-2X/def2-QZVPP:
-284.6207495

$CsHCO_3$-THF.log

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062X/gen pseudo=read scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/ChkBas Freq

---

Pointgroup= C1 Stoichiometry= CHCsO3 C1[X(CHCsO3)] #Atoms= 6
Charge = 0 Multiplicity = 1

SCF Energy= -284.483526232 Predicted Change= -1.504275D-07

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00015	0.00045	[YES]	0.00005	0.00030	[YES]
Displ	0.00134	0.00180	[YES]	0.00134	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.063498	0.037293	-0.000144
O	3.451800	0.074747	0.000362
O	1.546362	-1.104675	-0.000309
O	1.507877	1.151928	-0.000274
H	3.726899	-0.854289	0.000437

```
      Cs      -1.239204      -0.006281       0.000040
---------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin       Pressure= 1.00000 Atm
=====================================================
 SCF Energy=     -284.483526232   Predicted Change= -1.504275D-07
 Zero-point correction (ZPE)=            -284.4554       0.02807
 Internal Energy (U)=                    -284.4498       0.03363
 Enthalpy (H)=                           -284.4489       0.03458
 Gibbs Free Energy (G)=                  -284.4875      -0.00405
---------------------------------------------------------------------
Frequencies --     55.5167             142.5037          144.4937

M06-2X/6-311++G(2df,p)/PCM(THF):
-284.6100089
M06-2X/6-311++G(2df,p):
-284.5693947
M06-2X/def2-QZVPP:
-284.619817
```

Corey's [4+2] dihydroquinolone synthesis

Corey-vinyl-ether

```
---------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
=====================================================
 #m062X/gen scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=dichloromethane) opt=(maxcycle=250) freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/ChkBas Freq
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C3H6O   C1[X(C3H6O)]  #Atoms= 10
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -193.018983593       Predicted Change= -2.806034D-07
=====================================================
 Optimization completed.           {Found       2       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00021 ||  0.00045   [ YES ]      0.00006 ||  0.00030   [ YES ]
 Displ      0.00145 ||  0.00180   [ YES ]      0.00145 ||  0.00180   [ YES ]
---------------------------------------------------------------------
      Atomic              Coordinates (Angstroms)
      Type              X             Y          Z
---------------------------------------------------------------------
      C         1.432475      0.570139      0.000007
      C         0.737329     -0.568070     -0.000016
      O        -0.607287     -0.718546      0.000037
      C        -1.362185      0.478115     -0.000021
      H         0.974085      1.551436      0.000090
      H         2.513866      0.519440     -0.000039
      H         1.221660     -1.540437     -0.000074
      H        -1.142782      1.075790     -0.892382
      H        -1.142819      1.075824      0.892320
      H        -2.411430      0.185215     -0.000034
---------------------------------------------------------------------
 Statistical Thermodynamic Analysis
```

Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========

SCF Energy= -193.018983593 Predicted Change= -2.806034D-07
Zero-point correction (ZPE)= -192.9321 0.08678
Internal Energy (U)= -192.9275 0.09141
Enthalpy (H)= -192.9266 0.09236
Gibbs Free Energy (G)= -192.9587 0.06019

Frequencies -- 233.4883 301.4620 350.7600

M06-2X/6-311++G(2df,p)/PCM(DCM):
-193.0941726
M06-2X/6-311++G(2df,p):
-193.0912697
M06-2X/def2-QZVPP:
-193.1216714

Corey-Diels-Alder-TS-*endo*

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========

#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=dichloromethane)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---

Pointgroup= C1 Stoichiometry= C15H21NO3 C1[X(C15H21NO3)] #Atoms= 40
Charge = 0 Multiplicity = 1

SCF Energy= -864.220507563 Predicted Change= -2.085830D-09
==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00096	0.00180	[YES]	0.00096	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.467775	-0.082501	-0.942563
C	2.411093	1.003932	-1.787697
C	3.721578	-0.565821	-0.434991
C	3.774503	-1.627819	0.410769
C	2.552604	-2.252628	0.823613
C	1.331740	-1.818875	0.402481
C	1.218269	-0.691770	-0.496844
N	0.097454	-0.099958	-0.863092
C	-1.122646	-0.670656	-0.593278
O	-1.421093	-1.853417	-0.645812
O	-2.011861	0.311430	-0.312720
C	-3.403691	0.000922	-0.033025
C	-3.515007	-0.858720	1.223587
C	-4.060641	-0.657532	-1.243643
C	-4.012360	1.377299	0.215815
H	3.327843	1.460196	-2.150647

H	1.494673	1.223568	-2.319859
H	4.629972	-0.066658	-0.763603
H	4.722037	-2.005516	0.779050
H	2.604755	-3.097960	1.504943
H	0.425232	-2.308524	0.736425
H	-2.999019	-0.370657	2.057378
H	-3.084347	-1.847600	1.065086
H	-4.569432	-0.971153	1.494550
H	-3.653359	-1.653410	-1.419860
H	-3.901518	-0.041956	-2.134864
H	-5.138372	-0.738173	-1.070494
H	-3.909045	2.006344	-0.673265
H	-3.508010	1.869740	1.052984
H	-5.075101	1.280323	0.455295
C	1.906353	2.863818	-0.454815
C	1.018628	2.261017	0.372058
O	1.466554	1.483138	1.358379
C	0.469815	0.936852	2.219577
H	2.954923	2.899139	-0.181709
H	1.548541	3.531638	-1.228003
H	-0.060020	2.314868	0.241495
H	0.937848	0.108905	2.750509
H	-0.379175	0.575523	1.630583
H	0.132525	1.696756	2.930603

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -864.220507563 Predicted Change= -2.085830D-09
Zero-point correction (ZPE)= -863.8804 0.34005
Internal Energy (U)= -863.8608 0.35966
Enthalpy (H)= -863.8598 0.36060
Gibbs Free Energy (G)= -863.9282 0.29224

Frequencies -- -268.8163 30.8714 39.2504

M06-2X/6-311++G(2df,p)/PCM(DCM):
-864.5126106
M06-2X/6-311++G(2df,p):
-864.5027075
M06-2X/def2-QZVPP:
-864.6300776

Corey-S_N2-TS-*endo*

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=dichloromethane)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C15H22ClNO3 C1[X(C15H22ClNO3)] #Atoms= 42
Charge = 0 Multiplicity = 1

SCF Energy= -1325.02631324 Predicted Change= -1.385248D-09

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00051	0.00180	[YES]	0.00051	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.955020	-1.029892	2.196283
O	2.196451	-1.907083	1.241715
C	2.849505	-0.050211	2.488705
C	1.152115	-2.844592	0.942461
H	0.977245	-1.085292	2.678208
H	3.847944	-0.089632	2.067124
H	2.670627	0.585139	3.347094
H	1.486390	-3.389558	0.061450
H	1.021491	-3.530977	1.782889
H	0.218583	-2.323752	0.713705
C	3.329626	0.352845	-0.845214
C	2.077831	0.612463	-0.267087
C	1.987114	1.388522	0.947084
C	0.921688	0.021417	-0.821527
N	-0.310399	0.419211	-0.287236
C	1.042631	-0.866334	-1.893698
C	2.299751	-1.136947	-2.421099
C	3.446495	-0.519018	-1.914096
C	-1.482254	-0.295892	-0.359822
O	-1.559676	-1.466208	-0.683805
O	-2.493605	0.491612	0.015535
C	-3.856369	-0.032343	0.098968
C	-4.322881	-0.501645	-1.275056
C	-4.654604	1.184593	0.550147
C	-3.923119	-1.139346	1.145658
H	4.211246	0.827595	-0.422466
H	2.812029	2.018651	1.252946
H	1.079241	1.451380	1.522231
H	-0.387134	1.411879	-0.054489
H	0.155557	-1.326019	-2.309941
H	2.382603	-1.824917	-3.256822
H	4.418072	-0.723760	-2.350163
H	-3.774347	-1.387058	-1.597797
H	-4.184446	0.296425	-2.010780
H	-5.388921	-0.743297	-1.226728
H	-4.567791	1.990569	-0.183987
H	-4.287089	1.547275	1.514272
H	-5.709454	0.916263	0.654401
H	-3.526826	-0.777941	2.099693
H	-3.357512	-2.016974	0.829728
H	-4.967721	-1.428274	1.295852
Cl	0.880138	3.462324	-0.024328

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

```
=============================================
 SCF Energy=     -1325.02631324   Predicted Change= -1.385248D-09
 Zero-point correction (ZPE)=          -1324.6722       0.35405
 Internal Energy (U)=                  -1324.6500       0.37623
 Enthalpy (H)=                         -1324.6491       0.37718
 Gibbs Free Energy (G)=                -1324.7243       0.30198
---------------------------------------------------------------------------
Frequencies --   -454.1367              31.5868           35.7709
```

M06-2X/6-311++G(2df,p)/PCM(DCM):
-1325.357241
M06-2X/6-311++G(2df,p):
-1325.334348
M06-2X/def2-QZVPP:
-1325.469475

Enantioselective NHC-catalyzed formal [4+2] dihydroquinolone synthesis

Carbene 6.1

```
---------------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevC.01 23-Sep-2011
=============================================
 #M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=diethylether) opt=(maxcycle=250) freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C21H23N3   C1[X(C21H23N3)]  #Atoms= 47
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -977.898822776       Predicted Change= -1.091775D-08
=============================================
 Optimization completed.          {Found       1       times}
 Item      Max Val.   Criteria   Pass?      RMS Val.   Criteria   Pass?
 Force      0.00000 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00605 ||  0.00180   [ NO ]       0.00605 ||  0.00180   [ YES ]
---------------------------------------------------------------------------
     Atomic             Coordinates (Angstroms)
      Type              X           Y           Z
---------------------------------------------------------------------------
      N       -1.211817     1.423387    -0.998879
      C        0.078690     1.486064    -0.904799
      N        0.552148     0.529848    -0.048850
      C       -0.454495    -0.225362     0.477860
      N       -1.506260     0.367188    -0.141787
      C       -2.876837    -0.008632     0.018126
      C       -3.726328     0.841842     0.730305
      C       -3.203498     2.117419     1.336003
      H       -2.291974     1.927370     1.912553
      H       -2.946912     2.844008     0.558845
      H       -3.948597     2.564086     1.998287
      C       -5.061451     0.464284     0.871757
      H       -5.734434     1.111412     1.430403
      C       -5.548573    -0.722869     0.324942
      C       -7.001529    -1.100428     0.464758
      H       -7.567095    -0.809648    -0.427519
```

H	-7.459589	-0.602827	1.323506
H	-7.119576	-2.180529	0.589477
C	-4.665125	-1.547443	-0.373804
H	-5.030175	-2.479505	-0.800339
C	-3.323993	-1.207878	-0.544826
C	-2.379538	-2.102731	-1.303108
H	-2.918563	-2.939306	-1.753412
H	-1.603236	-2.497174	-0.640624
H	-1.870414	-1.548477	-2.098711
C	1.198525	2.314618	-1.450792
H	1.245202	3.273225	-0.923388
H	1.097965	2.519033	-2.517636
C	2.420549	1.420589	-1.115449
H	3.328418	1.993882	-0.922284
H	2.618384	0.749134	-1.958640
C	2.005734	0.565713	0.106464
H	2.245513	1.090074	1.040067
C	2.610613	-0.836446	0.143504
H	2.339298	-1.355955	-0.782962
H	2.152752	-1.386253	0.972662
C	4.110426	-0.775679	0.300668
C	4.955707	-0.914675	-0.802496
H	4.526426	-1.113504	-1.781839
C	6.337568	-0.809741	-0.659147
H	6.980684	-0.923910	-1.526687
C	6.892240	-0.562484	0.593936
H	7.968968	-0.483100	0.708335
C	6.058409	-0.422784	1.702059
H	6.484271	-0.236942	2.683525
C	4.678561	-0.528601	1.554201
H	4.030273	-0.426722	2.422015

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -977.898822776 Predicted Change= -1.091775D-08
Zero-point correction (ZPE)= -977.4971 0.40164
Internal Energy (U)= -977.4756 0.42317
Enthalpy (H)= -977.4746 0.42412
Gibbs Free Energy (G)= -977.5503 0.34843

Frequencies -- 16.4173 24.8668 33.7045

M06-2X/6-311++G(2df,p)/PCM(DEE):
-978.201776
M06-2X/6-311++G(2df,p):
-978.1923642
M06-2X/def2-QZVPP:
-978.3357607

imidazolyl substrate

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current

SCRF=(PCM,SOLVENT=diethylether) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C6H8N2O C1[X(C6H8N2O)] #Atoms= 17
Charge = 0 Multiplicity = 1

SCF Energy= -418.012754266 Predicted Change= -3.527673D-08
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00004	0.00045	[YES]	0.00001	0.00030	[YES]
Displ	0.00064	0.00180	[YES]	0.00064	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.850978	0.395524	-0.000340
N	0.532709	0.095729	-0.000130
O	-1.208619	1.547565	-0.000089
C	-1.785832	-0.791270	-0.000076
H	-1.557066	-1.407222	0.877717
H	-1.557337	-1.407358	-0.877843
C	-3.244243	-0.354374	0.000117
H	-3.468905	0.247855	-0.882859
H	-3.468630	0.248006	0.883061
H	-3.896994	-1.229747	0.000294
C	1.152183	-1.136547	0.000024
H	0.593792	-2.062233	-0.000031
N	2.449262	-1.028529	0.000195
C	2.704061	0.334344	0.000233
H	3.715814	0.713546	0.000392
C	1.544484	1.043818	-0.000019
H	1.316427	2.097252	-0.000108

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -418.012754266 Predicted Change= -3.527673D-08

Zero-point correction (ZPE)=	-417.8733	0.13945
Internal Energy (U)=	-417.8651	0.14764
Enthalpy (H)=	-417.8641	0.14859
Gibbs Free Energy (G)=	-417.9067	0.10603

---Frequencies -- 66.1588
112.0330 157.5208

M06-2X/6-311++G(2df,p)/PCM(DEE):
-418.1550714
M06-2X/6-311++G(2df,p):
-418.1480967
M06-2X/def2-QZVPP:
-418.2090784

CDI

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

```
=============================================
 #M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=diethylether) opt=(maxcycle=250) freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C7H6N4O   C1[X(C7H6N4O)]  #Atoms= 18
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -564.360675073       Predicted Change= -1.042186D-08
=============================================
 Optimization completed.          {Found       2       times}
 Item      Max Val.   Criteria   Pass?      RMS Val.   Criteria   Pass?
 Force      0.00001 ||  0.00045   [ YES ]     0.00000 ||  0.00030   [ YES ]
 Displ      0.00088 ||  0.00180   [ YES ]     0.00088 ||  0.00180   [ YES ]
---------------------------------------------------------------------
     Atomic             Coordinates (Angstroms)
      Type              X           Y           Z
---------------------------------------------------------------------
      N         2.689519    -1.344045     0.448931
      C         3.305366    -0.264404    -0.165058
      C         2.404915     0.714061    -0.442368
      N         1.179913     0.214986    -0.018871
      C         1.431572    -1.034343     0.528082
      C         0.000000     0.972218     0.000000
      N        -1.179913     0.214985     0.018874
      O         0.000000     2.173585    -0.000001
      C        -1.431571    -1.034343    -0.528082
      N        -2.689519    -1.344045    -0.448933
      C        -3.305366    -0.264405     0.165057
      C        -2.404916     0.714060     0.442369
      H         4.366500    -0.265660    -0.366819
      H         2.481997     1.689299    -0.895648
      H         0.653517    -1.623090     0.993700
      H        -0.653517    -1.623090    -0.993699
      H        -4.366501    -0.265660     0.366817
      H        -2.481998     1.689298     0.895650
---------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin       Pressure= 1.00000 Atm
=============================================
 SCF Energy=     -564.360675073   Predicted Change= -1.042186D-08
 Zero-point correction (ZPE)=              -564.2258       0.13482
 Internal Energy (U)=                      -564.2169       0.14368
 Enthalpy (H)=                             -564.2160       0.14462
 Gibbs Free Energy (G)=                    -564.2609       0.09971
---------------------------------------------------------------------Frequencies --    69.8526
89.5898           127.2262

M06-2X/6-311++G(2df,p)/PCM(DEE):
-564.5504492
M06-2X/6-311++G(2df,p):
-564.5420165
M06-2X/def2-QZVPP:
-564.6194221
```

CO_2

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011
==========
#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=diethylether) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C*V Stoichiometry= CO2 C*V[C*(OCO)] #Atoms= 3
Charge = 0 Multiplicity = 1

SCF Energy= -188.510775326 Predicted Change= -9.900863D-08
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00039	0.00045	[YES]	0.00024	0.00030	[YES]
Displ	0.00029	0.00180	[YES]	0.00029	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	0.000000	0.000000	1.162892
C	0.000000	0.000000	-0.000018
O	0.000000	0.000000	-1.162878

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========

SCF Energy=	-188.510775326	Predicted Change= -9.900863D-08
Zero-point correction (ZPE)=	-188.4988	0.01188
Internal Energy (U)=	-188.4962	0.01450
Enthalpy (H)=	-188.4953	0.01545
Gibbs Free Energy (G)=	-188.5202	-0.00946

Frequencies -- 663.8617 663.8617 1421.2394

M06-2X/6-311++G(2df,p)/PCM(DEE):
-188.5871472
M06-2X/6-311++G(2df,p):
-188.5854364
M06-2X/def2-QZVPP:
-188.6117687

Propionic acid

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011
==========
#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=diethylether) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C3H6O2 C1[X(C3H6O2)] #Atoms= 11
Charge = 0 Multiplicity = 1

SCF Energy= -268.281051233 Predicted Change= -9.261738D-08

```
=============================================
 Optimization completed.          {Found       2       times}
 Item      Max Val.   Criteria   Pass?      RMS Val.   Criteria   Pass?
 Force      0.00018 ||  0.00045   [ YES ]     0.00003 ||  0.00030   [ YES ]
 Displ      0.00072 ||  0.00180   [ YES ]     0.00072 ||  0.00180   [ YES ]
---------------------------------------------------------------------------
     Atomic             Coordinates (Angstroms)
      Type              X           Y           Z
---------------------------------------------------------------------------
      C         0.560570      0.099718     -0.000194
      O         1.674361     -0.655276      0.000143
      O         0.595403      1.306935     -0.000102
      C        -0.688026     -0.746060      0.000099
      C        -1.954622      0.097195     -0.000044
      H         2.434392     -0.046481      0.000199
      H        -0.638935     -1.404177      0.874802
      H        -0.639017     -1.404635     -0.874258
      H        -1.991434      0.740004     -0.882717
      H        -1.991344      0.740439      0.882316
      H        -2.839300     -0.543543      0.000159
---------------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin       Pressure= 1.00000 Atm
=============================================
 SCF Energy=     -268.281051233   Predicted Change= -9.261738D-08
 Zero-point correction (ZPE)=              -268.1891       0.09192
 Internal Energy (U)=                      -268.1834       0.09757
 Enthalpy (H)=                             -268.1825       0.09852
 Gibbs Free Energy (G)=                    -268.2180       0.06295
---------------------------------------------------------------------------
Frequencies --    70.8328            225.4685          256.3122

M06-2X/6-311++G(2df,p)/PCM(DEE):
-268.3864231
M06-2X/6-311++G(2df,p):
-268.3814614
M06-2X/def2-QZVPP:
-268.4229488
```

NHC 6.1-enolate

```
---------------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
=============================================
 #m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=diethylether) opt=(maxcycle=250) freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C24H27N3O   C1[X(C24H27N3O)]  #Atoms= 55
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------------
 SCF Energy= -1169.77810783       Predicted Change= -2.057537D-08
=============================================
 Optimization completed.          {Found       1       times}
 Item      Max Val.   Criteria   Pass?      RMS Val.   Criteria   Pass?
 Force      0.00000 ||  0.00045   [ YES ]     0.00000 ||  0.00030   [ YES ]
```

Displ 0.00590 || 0.00180 [NO] 0.00590 || 0.00180 [YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	0.000389	0.483429	-1.756352
C	-1.139703	-0.140181	-1.725908
N	-1.163201	-1.092332	-0.752024
C	0.003451	-1.049490	-0.087122
C	0.270950	-1.933568	1.101370
O	-0.505353	-2.942785	1.161367
C	1.232316	-1.493485	1.972092
C	1.529155	-2.244011	3.233449
N	0.708096	-0.099398	-0.729015
C	2.071645	0.301230	-0.526887
C	3.089162	-0.532463	-0.993248
C	2.774510	-1.853397	-1.641435
C	4.402269	-0.105224	-0.803243
C	4.697039	1.108661	-0.181043
C	6.124900	1.563174	-0.020783
C	3.643163	1.905522	0.271572
C	2.314381	1.519997	0.110287
C	1.175904	2.344878	0.647978
C	-2.450369	-0.062666	-2.436256
C	-3.153008	-1.350471	-1.930910
C	-2.463016	-1.769880	-0.603738
C	-3.166806	-1.308092	0.683052
C	-3.349492	0.187533	0.747263
C	-2.317261	1.003680	1.224474
C	-2.439864	2.390877	1.205142
C	-3.600941	2.983846	0.712674
C	-4.644082	2.181571	0.255490
C	-4.518086	0.794178	0.276631
H	1.792862	-0.590482	1.757225
H	1.396976	-1.619741	4.126787
H	2.561820	-2.616712	3.261391
H	0.856568	-3.102045	3.312527
H	2.012938	-1.744456	-2.420443
H	3.671017	-2.283474	-2.092398
H	2.391859	-2.560948	-0.896999
H	5.214971	-0.738460	-1.151410
H	6.248179	2.168562	0.881106
H	6.432304	2.176069	-0.875273
H	6.807184	0.711398	0.037938
H	3.860066	2.847591	0.769792
H	1.539204	3.298752	1.036050
H	0.678547	1.809749	1.466708
H	0.421706	2.540826	-0.120305
H	-2.334505	-0.036770	-3.520731
H	-2.978297	0.842680	-2.120325
H	-3.022533	-2.147462	-2.666672
H	-4.224452	-1.198434	-1.787341
H	-2.277728	-2.840337	-0.538290
H	-2.558122	-1.673227	1.516183
H	-4.135533	-1.818201	0.722924

H	-1.418675	0.539936	1.631499
H	-1.631147	3.010188	1.582758
H	-3.697306	4.064991	0.697489
H	-5.559290	2.634713	-0.113501
H	-5.340072	0.172368	-0.071301

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -1169.77810783 Predicted Change= -2.057537D-08

Zero-point correction (ZPE)=	-1169.3093	0.46878
Internal Energy (U)=	-1169.2832	0.49481
Enthalpy (H)=	-1169.2823	0.49575
Gibbs Free Energy (G)=	-1169.3663	0.41171

Frequencies -- 20.6344 32.8177 40.9956

M06-2X/6-311++G(2df,p)/PCM(DEE):
-1170.149108
M06-2X/6-311++G(2df,p):
-1170.134985
M06-2X/def2-QZVPP:
-1170.305863

***Major*-Michael-TS-(*S*)**

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=diethylether)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C36H42N4O3 C1[X(C36H42N4O3)] #Atoms= 85
Charge = 0 Multiplicity = 1

SCF Energy= -1840.99304647 Predicted Change= -2.051392D-09
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00107	0.00180	[YES]	0.00107	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	0.742030	0.542968	-1.562649
C	0.111446	1.446224	-0.872145
N	0.318246	1.292480	0.466049
C	1.101268	0.218095	0.640457
C	1.579173	-0.256056	1.985974
O	1.611324	0.653559	2.867569
C	1.820087	-1.606911	2.114893
C	2.341522	-2.181914	3.395230
N	1.356237	-0.217690	-0.601835

C	2.205103	-1.297551	-1.026404
C	1.612059	-2.489968	-1.444538
C	0.127897	-2.714168	-1.336753
C	2.463405	-3.498238	-1.898076
C	3.847947	-3.333332	-1.933299
C	4.739810	-4.427729	-2.460739
C	4.391764	-2.123735	-1.495155
C	3.585807	-1.083618	-1.040234
C	4.168071	0.217240	-0.558689
C	-0.796954	2.592534	-1.155511
C	-1.413620	2.834377	0.245734
C	-0.423794	2.259955	1.297847
C	0.491233	3.312561	1.946556
C	1.459492	3.937668	0.974919
C	1.159513	5.113892	0.282938
C	2.053689	5.638770	-0.649081
C	3.264695	4.995408	-0.893502
C	3.580930	3.830362	-0.196291
C	2.683854	3.305549	0.730394
H	1.728352	-2.254142	1.250054
H	3.416775	-2.397904	3.340604
H	1.842992	-3.125378	3.650297
H	2.186896	-1.470485	4.211627
H	-0.191817	-3.505324	-2.019427
H	-0.124913	-3.037010	-0.317798
H	-0.452283	-1.810630	-1.547867
H	2.029139	-4.439239	-2.228507
H	5.719245	-4.408117	-1.975589
H	4.901921	-4.306994	-3.537614
H	4.293872	-5.412930	-2.302114
H	5.470025	-1.983476	-1.513188
H	5.230261	0.279830	-0.804903
H	4.064068	0.306944	0.530077
H	3.654092	1.071646	-1.011536
H	-1.539663	2.334108	-1.911037
H	-0.215114	3.452175	-1.501503
H	-2.361996	2.297086	0.329881
H	-1.609487	3.892975	0.429728
H	-0.951010	1.704342	2.074145
H	1.035655	2.816183	2.750315
H	-0.166954	4.073147	2.381114
H	0.220603	5.627586	0.479534
H	1.806644	6.553669	-1.179206
H	3.963726	5.405230	-1.615926
H	4.532302	3.334713	-0.368615
H	2.923189	2.403675	1.292200
C	-1.501045	-3.847900	2.140994
C	-1.481886	-2.414280	1.943761
C	-0.744892	-1.622775	2.772936
C	-2.236025	-1.836923	0.816024
N	-2.159482	-0.562104	0.561583
C	-3.031790	-2.771376	0.029153
C	-3.013235	-4.102809	0.282007
C	-2.228695	-4.670226	1.349938
C	-2.884764	-0.069367	-0.514133

O	-2.491570	-0.042573	-1.664711
O	-4.050565	0.452999	-0.095676
C	-5.038327	0.952412	-1.047054
C	-4.489123	2.123613	-1.856673
C	-6.169799	1.420225	-0.139147
C	-5.504122	-0.191325	-1.942794
H	-0.908229	-4.244693	2.961968
H	-0.780322	-0.541357	2.704222
H	-0.248358	-2.041246	3.642284
H	-3.617884	-2.380243	-0.797666
H	-3.605795	-4.767656	-0.340758
H	-2.239182	-5.742390	1.510966
H	-3.727112	1.795575	-2.564124
H	-4.066254	2.882962	-1.190062
H	-5.309371	2.586245	-2.414705
H	-5.822187	2.220015	0.521637
H	-6.530449	0.591489	0.476568
H	-7.000273	1.798836	-0.741672
H	-5.864298	-1.023934	-1.329542
H	-4.694144	-0.540303	-2.586400
H	-6.329559	0.151469	-2.574173

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1840.99304647 Predicted Change= -2.051392D-09
Zero-point correction (ZPE)= -1840.2711 0.72193
Internal Energy (U)= -1840.2298 0.76323
Enthalpy (H)= -1840.2288 0.76417
Gibbs Free Energy (G)= -1840.3456 0.64741

---Frequencies -- -121.5126 20.1592 26.3913

M06-2X/6-311++G(2df,p)/PCM(DEE):
-1841.581594
M06-2X/6-311++G(2df,p):
-1841.568463
M06-2X/def2-QZVPP:
-1841.834813

***Minor*-Michael-TS-(*R*)**

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=diethylether)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C36H42N4O3 C1[X(C36H42N4O3)] #Atoms= 85
Charge = 0 Multiplicity = 1

SCF Energy= -1840.98834328 Predicted Change= -1.038232D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00592	0.00180	[NO]	0.00592	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	1.174113	-0.750807	-2.367598
C	-0.071670	-1.086630	-2.212494
N	-0.324073	-1.505886	-0.942466
C	0.810264	-1.400783	-0.231814
C	0.898943	-1.858135	1.200482
O	-0.161440	-2.416006	1.618590
C	2.053875	-1.589312	1.905493
C	2.259808	-2.181327	3.268074
N	1.714797	-0.953430	-1.120362
C	3.139347	-0.829086	-0.979273
C	3.903775	-2.000102	-1.077081
C	3.241617	-3.340025	-1.254107
C	5.283955	-1.877165	-0.974338
C	5.897684	-0.632660	-0.792089
C	7.399013	-0.533983	-0.706785
C	5.096097	0.501824	-0.709003
C	3.702374	0.432175	-0.799953
C	2.865768	1.673188	-0.648814
C	-1.309857	-1.144333	-3.042169
C	-2.189862	-2.106855	-2.202142
C	-1.702768	-1.987974	-0.733732
C	-2.524288	-1.019959	0.121773
C	-3.797608	-1.680519	0.587273
C	-3.725384	-2.686679	1.557562
C	-4.878364	-3.329067	1.995984
C	-6.121055	-2.974399	1.470120
C	-6.202049	-1.973811	0.505997
C	-5.044244	-1.332064	0.067243
H	2.879337	-1.075408	1.427992
H	2.856694	-1.526403	3.912208
H	2.785681	-3.144723	3.217662
H	1.293449	-2.364657	3.747778
H	2.508978	-3.317657	-2.067674
H	3.983396	-4.109242	-1.478085
H	2.714402	-3.629296	-0.337167
H	5.899064	-2.771900	-1.041086
H	7.714037	0.464924	-0.396159
H	7.857245	-0.745619	-1.678748
H	7.799787	-1.259118	0.007719
H	5.559799	1.475540	-0.567467
H	1.865998	1.560902	-1.076452
H	3.359485	2.524915	-1.124616
H	2.751994	1.913872	0.415702
H	-1.124578	-1.504142	-4.054664
H	-1.734811	-0.137058	-3.099365
H	-2.044823	-3.131260	-2.554383
H	-3.254289	-1.871950	-2.278172
H	-1.638921	-2.950182	-0.228441

H	-2.747889	-0.113713	-0.453505
H	-1.912733	-0.730434	0.978979
H	-2.750745	-2.947874	1.966498
H	-4.809152	-4.104641	2.753078
H	-7.021678	-3.474047	1.813987
H	-7.166302	-1.688793	0.095545
H	-5.112455	-0.544400	-0.680735
C	1.875501	2.525558	3.178637
C	0.927364	1.678342	2.486745
C	0.659154	0.422530	2.939903
C	0.256846	2.197573	1.282615
N	-0.431685	1.386150	0.535750
C	0.469287	3.606440	0.977621
C	1.345297	4.352564	1.693743
C	2.084112	3.810596	2.807932
C	-1.083540	1.888981	-0.578162
O	-0.679442	1.770054	-1.720250
O	-2.260541	2.442801	-0.242228
C	-3.104606	3.092158	-1.238454
C	-3.478656	2.146965	-2.378603
C	-2.397400	4.341659	-1.752175
C	-4.346014	3.458199	-0.433029
H	2.400645	2.096860	4.028741
H	-0.142051	-0.183794	2.529798
H	1.133890	0.066049	3.849034
H	-0.054312	4.036186	0.128387
H	1.505970	5.391819	1.419346
H	2.783935	4.443262	3.342540
H	-3.825675	1.186559	-1.980916
H	-2.638058	1.975929	-3.050913
H	-4.301757	2.590407	-2.947883
H	-1.474030	4.077167	-2.272631
H	-2.164680	5.012994	-0.919253
H	-3.050506	4.874926	-2.449884
H	-4.835575	2.552595	-0.061223
H	-5.051744	4.008317	-1.061798
H	-4.073992	4.082792	0.422170

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-1840.98834328	Predicted Change= -1.038232D-08
Zero-point correction (ZPE)=	-1840.2666	0.72164
Internal Energy (U)=	-1840.2252	0.76306
Enthalpy (H)=	-1840.2243	0.76401
Gibbs Free Energy (G)=	-1840.3423	0.64599

---Frequencies -- -124.0478
20.8533 22.3994

M06-2X/6-311++G(2df,p)/PCM(DEE):
-1841.577578
M06-2X/6-311++G(2df,p):
-1841.564639
M06-2X/def2-QZVPP:
-1841.830838

post-Major-Michael intermediate

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=diethylether) opt=(maxcycle=250,gdiis) iop(1/8=18)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C36H42N4O3 C1[X(C36H42N4O3)] #Atoms= 85
Charge = 0 Multiplicity = 1

SCF Energy= -1841.05945212 Predicted Change= -4.964177D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00004	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00491	0.00180	[NO]	0.00491	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-1.142858	0.131059	-2.046903
C	0.132198	0.394066	-1.929419
N	0.673240	-0.243111	-0.850303
C	-0.311092	-0.891945	-0.241928
C	-0.260463	-1.699238	1.034761
O	0.554683	-2.587597	1.125802
C	-1.214528	-1.262550	2.114813
C	-2.011010	-2.452523	2.649808
N	-1.403955	-0.668602	-0.969580
C	-2.635875	-1.397612	-0.806272
C	-3.759438	-0.742201	-0.296171
C	-3.728585	0.727326	0.008362
C	-4.900140	-1.514769	-0.089171
C	-4.933716	-2.879025	-0.387247
C	-6.193006	-3.678445	-0.177405
C	-3.790238	-3.481125	-0.914901
C	-2.619875	-2.757638	-1.139011
C	-1.396931	-3.416827	-1.727255
C	1.185293	1.148303	-2.670913
C	2.379760	1.091414	-1.678584
C	2.139136	-0.120552	-0.746572
C	2.789764	-1.430183	-1.214882
C	4.289289	-1.358624	-1.061168
C	4.856903	-1.353597	0.216910
C	6.234405	-1.246391	0.378488
C	7.064181	-1.146926	-0.737869
C	6.507964	-1.154390	-2.013992
C	5.127130	-1.257126	-2.172626
H	-1.882933	-0.511848	1.691535
H	-2.686255	-2.855439	1.886773
H	-2.611021	-2.134393	3.507076
H	-1.333340	-3.246978	2.976151

H	-2.897804	1.010315	0.664541
H	-3.594706	1.303450	-0.913166
H	-4.664667	1.041991	0.475610
H	-5.786627	-1.035751	0.319172
H	-6.811029	-3.663279	-1.081778
H	-6.791071	-3.266372	0.639133
H	-5.965392	-4.722782	0.050280
H	-3.807657	-4.539539	-1.163082
H	-0.945023	-2.791646	-2.504675
H	-1.666079	-4.374850	-2.176163
H	-0.631525	-3.611415	-0.967209
H	0.867582	2.172312	-2.866797
H	1.397065	0.650109	-3.622282
H	2.366641	1.997739	-1.073471
H	3.340819	0.999253	-2.188250
H	2.404071	0.094524	0.290723
H	2.519636	-1.614992	-2.262303
H	2.380329	-2.250137	-0.613667
H	4.210025	-1.426894	1.088834
H	6.661319	-1.242113	1.377081
H	8.139424	-1.064903	-0.612073
H	7.147591	-1.080842	-2.888290
H	4.695145	-1.262206	-3.170929
C	2.097967	-0.225381	3.226261
C	0.842955	0.198087	2.783850
C	-0.378616	-0.576793	3.228505
C	0.726339	1.359774	1.969961
N	-0.528592	1.733013	1.531497
C	1.917389	2.098673	1.744410
C	3.150269	1.670885	2.218047
C	3.262340	0.485036	2.944382
C	-0.608653	2.553640	0.477969
O	0.237489	2.818295	-0.394636
O	-1.864700	3.108822	0.399649
C	-2.155966	4.135805	-0.566744
C	-3.631847	4.439264	-0.311948
C	-1.971132	3.661107	-2.010586
C	-1.313529	5.378839	-0.281063
H	-0.056212	-1.356616	3.927897
H	-1.067264	0.088104	3.762326
H	2.153980	-1.132814	3.824699
H	1.853439	3.014784	1.171130
H	4.035082	2.267053	2.008250
H	4.225686	0.134938	3.302804
H	-3.786508	4.704587	0.737927
H	-4.250023	3.565748	-0.542843
H	-3.961242	5.273496	-0.938908
H	-2.491889	4.347370	-2.687704
H	-2.395718	2.660527	-2.141126
H	-0.916429	3.624879	-2.280421
H	-1.478791	5.714537	0.747947
H	-1.601122	6.189036	-0.959530
H	-0.253979	5.158219	-0.419516

Statistical Thermodynamic Analysis

Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========

SCF Energy= -1841.05945212 Predicted Change= -4.964177D-08
Zero-point correction (ZPE)= -1840.3332 0.72622
Internal Energy (U)= -1840.2924 0.76697
Enthalpy (H)= -1840.2915 0.76791
Gibbs Free Energy (G)= -1840.4065 0.65292

Frequencies -- 13.2729 25.5162 34.2574

M06-2X/6-311++G(2df,p)/PCM(DEE):
-1841.642401
M06-2X/6-311++G(2df,p):
-1841.629295
M06-2X/def2-QZVPP:
-1841.895837

***re*-Cyclization**

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========

#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=diethylether)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
---

Pointgroup= C1 Stoichiometry= C36H42N4O3 C1[X(C36H42N4O3)] #Atoms= 85
Charge = 0 Multiplicity = 1

SCF Energy= -1841.04994093 Predicted Change= -1.175088D-09
==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00139	0.00180	[YES]	0.00139	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-1.842402	-1.823483	-1.744037
C	-0.551103	-1.951237	-1.741165
N	0.011304	-1.396924	-0.625730
C	-0.976590	-0.811541	0.069058
C	-1.000611	0.088115	1.316998
O	-2.008035	0.773779	1.431159
C	-0.270693	-0.398816	2.574906
C	-0.642918	-1.862985	2.834874
N	-2.096300	-1.122841	-0.598693
C	-3.481273	-0.903302	-0.254892
C	-4.099665	0.292203	-0.631986
C	-3.331612	1.380499	-1.325680
C	-5.451315	0.425164	-0.329977
C	-6.170643	-0.587259	0.312438
C	-7.627731	-0.389607	0.643181
C	-5.515179	-1.773167	0.634176

C	-4.161955	-1.961435	0.345242
C	-3.487192	-3.281361	0.616069
C	0.489900	-2.420380	-2.701782
C	1.692337	-1.572011	-2.226039
C	1.492716	-1.410054	-0.702489
C	2.064367	-2.601186	0.082279
C	3.573463	-2.631263	0.006526
C	4.334473	-1.607374	0.580415
C	5.723453	-1.624501	0.495877
C	6.372322	-2.666290	-0.165323
C	5.623919	-3.688661	-0.741648
C	4.233252	-3.667906	-0.656785
C	2.107669	1.949923	3.756200
C	1.533391	1.328841	2.651490
C	1.240716	-0.144681	2.639485
C	1.127106	2.086846	1.528936
N	0.536366	1.347887	0.505547
C	1.280350	3.484675	1.590935
C	1.862636	4.087419	2.701567
C	2.291978	3.330095	3.788276
C	0.428311	1.744405	-0.773802
O	-0.216384	1.130231	-1.633247
O	1.152769	2.851871	-1.101108
C	1.106997	3.408042	-2.436056
C	2.041094	4.610902	-2.329728
C	-0.308615	3.867782	-2.776440
C	1.648647	2.417077	-3.465631
H	-0.732069	0.209106	3.360695
H	-0.233405	-2.189723	3.795011
H	-0.251676	-2.534881	2.061608
H	-1.730805	-1.983034	2.872802
H	-2.606562	1.819648	-0.634468
H	-2.756715	0.988448	-2.169749
H	-4.011034	2.157021	-1.685085
H	-5.959513	1.347290	-0.603671
H	-7.749775	0.377083	1.415421
H	-8.080346	-1.313719	1.010723
H	-8.188382	-0.058406	-0.236288
H	-6.066077	-2.579042	1.113331
H	-2.493759	-3.154994	1.056339
H	-3.359422	-3.842242	-0.316455
H	-4.088206	-3.887388	1.297326
H	0.203210	-2.221277	-3.734519
H	0.668076	-3.495231	-2.592640
H	1.639674	-0.584642	-2.691028
H	2.657031	-2.028400	-2.454889
H	1.862593	-0.455585	-0.326400
H	1.650437	-3.530479	-0.327810
H	1.741131	-2.548424	1.126677
H	3.841170	-0.788424	1.100095
H	6.299320	-0.823186	0.948511
H	7.455793	-2.679487	-0.230510
H	6.120791	-4.503958	-1.258458
H	3.651338	-4.468057	-1.108648
H	2.410197	1.339638	4.604570

H	1.734031	-0.624473	1.790597
H	1.631660	-0.615308	3.549110
H	0.946596	4.095178	0.763030
H	1.975323	5.168286	2.715658
H	2.748868	3.805625	4.650448
H	3.047100	4.287131	-2.046646
H	1.675771	5.310303	-1.571364
H	2.096226	5.133133	-3.289568
H	-0.675229	4.550709	-2.002816
H	-0.985200	3.015526	-2.849679
H	-0.301410	4.402895	-3.731806
H	0.943451	1.602673	-3.630197
H	2.601458	2.004474	-3.116351
H	1.826758	2.934840	-4.413953

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

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SCF Energy=	-1841.04994093	Predicted Change= -1.175088D-09
Zero-point correction (ZPE)=	-1840.3238	0.72606
Internal Energy (U)=	-1840.2840	0.76587
Enthalpy (H)=	-1840.2831	0.76682
Gibbs Free Energy (G)=	-1840.3974	0.65250

Frequencies -- -47.1533 15.9383 20.8463

M06-2X/6-311++G(2df,p)/PCM(DEE):
-1841.631365
M06-2X/6-311++G(2df,p):
-1841.617466
M06-2X/def2-QZVPP:
-1841.884852

S_N2-TS

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

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#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=diethylether)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C36H43ClN4O3 C1[X(C36H43ClN4O3)] #Atoms= 87
Charge = 0 Multiplicity = 1

SCF Energy= -2301.80452522 Predicted Change= -4.944270D-09

==========

Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00329	0.00180	[NO]	0.00329	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z

N	-1.337068	0.122657	-1.665452
C	-1.561748	-0.923855	-0.924433
N	-1.337768	-0.661961	0.397108
C	-0.958311	0.619935	0.495833
C	-0.690543	1.363157	1.785445
O	-1.551928	1.174400	2.677429
C	0.522077	2.036293	1.848726
C	0.829906	2.930837	3.009853
N	-0.960066	1.078343	-0.758289
C	-0.641639	2.412135	-1.195126
C	0.577177	2.613858	-1.845012
C	1.546805	1.479779	-2.035928
C	0.866147	3.911801	-2.262168
C	-0.018561	4.968329	-2.039015
C	0.305498	6.357818	-2.523539
C	-1.220071	4.712598	-1.375048
C	-1.560491	3.432910	-0.941838
C	-2.853583	3.160705	-0.219622
C	-2.020491	-2.328699	-1.118953
C	-1.609236	-2.963484	0.233203
C	-1.583129	-1.822873	1.287096
C	-2.868509	-1.652499	2.111975
C	-4.081468	-1.373309	1.262320
C	-4.360667	-0.059261	0.871526
C	-5.428802	0.215446	0.021244
C	-6.235973	-0.821489	-0.443987
C	-5.980109	-2.130637	-0.041385
C	-4.910459	-2.403027	0.809441
H	1.088154	2.161480	0.929522
H	0.391303	2.532634	3.930453
H	0.413794	3.935785	2.859910
H	1.908753	3.046932	3.149051
H	2.472539	1.829214	-2.496638
H	1.807229	1.020549	-1.074440
H	1.127172	0.687609	-2.664427
H	1.811671	4.101698	-2.764198
H	-0.141949	6.535777	-3.507560
H	1.384552	6.502269	-2.618839
H	-0.087203	7.115614	-1.840596
H	-1.913099	5.529817	-1.189891
H	-3.382861	2.313702	-0.669752
H	-3.505719	4.035409	-0.261156
H	-2.677177	2.920136	0.835904
H	-1.549970	-2.803709	-1.980627
H	-3.105189	-2.337590	-1.267046
H	-0.600086	-3.376625	0.142132
H	-2.284593	-3.764759	0.538021
H	-0.735126	-1.937248	1.968851
H	-2.698292	-0.833409	2.815240
H	-2.994542	-2.579686	2.681055
H	-3.736658	0.742970	1.263237
H	-5.640617	1.240765	-0.268852
H	-7.069745	-0.607809	-1.105554
H	-6.617026	-2.940257	-0.384689
H	-4.719439	-3.425439	1.128746

C	3.633401	1.031294	2.856189
C	2.805719	0.207046	2.084713
C	1.455830	-0.111471	2.522429
C	3.288393	-0.304252	0.859625
N	2.488820	-1.271502	0.217588
C	4.531987	0.108307	0.379014
C	5.307517	0.981956	1.136152
C	4.876934	1.427188	2.385744
C	2.601098	-1.663861	-1.092646
O	3.241619	-1.085635	-1.947235
O	1.859960	-2.770014	-1.278762
C	1.852509	-3.427335	-2.582724
C	0.970752	-4.647304	-2.344012
C	3.262795	-3.872319	-2.960549
C	1.238002	-2.501156	-3.628396
H	3.278761	1.365483	3.826692
H	1.076499	0.204651	3.484765
H	0.766354	-0.539527	1.822982
H	2.037318	-1.938540	0.843958
H	4.890150	-0.267255	-0.569979
H	6.275237	1.292572	0.754712
H	5.505917	2.076808	2.984879
H	-0.043240	-4.350241	-2.061022
H	1.386715	-5.265542	-1.543501
H	0.911931	-5.246468	-3.256687
H	3.690868	-4.481177	-2.158145
H	3.912602	-3.017666	-3.149391
H	3.212825	-4.484333	-3.866171
H	1.907785	-1.672595	-3.862375
H	0.289167	-2.092688	-3.262719
H	1.038515	-3.066832	-4.543603
Cl	1.718208	-2.316035	3.243690

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-2301.80452522	Predicted Change= -4.944270D-09
Zero-point correction (ZPE)=	-2301.0673	0.73720
Internal Energy (U)=	-2301.0239	0.78057
Enthalpy (H)=	-2301.0230	0.78151
Gibbs Free Energy (G)=	-2301.1449	0.65958

Frequencies -- -497.0293 17.9307 20.8231

M06-2X/6-311++G(2df,p)/PCM(DEE):
-2302.431143
M06-2X/6-311++G(2df,p):
-2302.4136
M06-2X/def2-QZVPP:
-2302.687628

Model Stetter reaction

Carbene 6.2

```
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
 ======================================================
 #m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
 ---------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C15H19NS   C1[X(C15H19NS)]  #Atoms= 36
 Charge = 0         Multiplicity = 1
 ---------------------------------------------------------------------------
 SCF Energy= -1035.62843815       Predicted Change= -4.240550D-09
 ======================================================
 Optimization completed.          {Found       2       times}
 Item      Max Val.   Criteria   Pass?      RMS Val.   Criteria   Pass?
 Force      0.00001 ||  0.00045   [ YES ]     0.00000 ||  0.00030   [ YES ]
 Displ      0.00169 ||  0.00180   [ YES ]     0.00169 ||  0.00180   [ YES ]
 ---------------------------------------------------------------------------
      Atomic             Coordinates (Angstroms)
       Type              X           Y           Z
 ---------------------------------------------------------------------------
       S        2.746542    -0.130794    -1.327424
       C        1.045007     0.095697    -1.513499
       N        0.557922     0.030527    -0.262136
       C       -0.863058     0.164220    -0.038769
       C        1.429325    -0.197850     0.827713
       C        0.872196    -0.281870     2.213192
       C        2.711344    -0.310414     0.412467
       C        3.951956    -0.550587     1.213377
       C       -1.379134     1.421389     0.279751
       C       -0.501854     2.649485     0.322326
       C       -0.387907     3.300473    -1.061658
       C       -2.755289     1.519809     0.503090
       C       -3.569846     0.398075     0.413892
       C       -3.025085    -0.845720     0.098931
       C       -1.656899    -0.987087    -0.132020
       C       -1.009106    -2.309559    -0.484932
       C       -1.955355    -3.503475    -0.538012
       H        1.667397    -0.483327     2.931975
       H        0.127509    -1.081328     2.289549
       H        0.378868     0.653410     2.498424
       H        4.442716    -1.479161     0.906400
       H        3.722025    -0.625739     2.278558
       H        4.669312     0.264504     1.078874
       H        0.499336     2.390236     0.684678
       H       -0.925565     3.364767     1.035025
       H        0.038600     2.591697    -1.777667
       H        0.249721     4.188357    -1.023634
       H       -1.375421     3.600916    -1.425713
       H       -3.182155     2.488824     0.749463
       H       -4.637018     0.488230     0.592645
       H       -3.675504    -1.711831     0.036143
       H       -0.205908    -2.512002     0.237223
       H       -0.502941    -2.191876    -1.451199
       H       -2.734255    -3.362288    -1.293549
       H       -2.444289    -3.670949     0.426788
       H       -1.400328    -4.408948    -0.795352
```

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -1035.62843815 Predicted Change= -4.240550D-09
Zero-point correction (ZPE)= -1035.3200 0.30835
Internal Energy (U)= -1035.3025 0.32589
Enthalpy (H)= -1035.3016 0.32683
Gibbs Free Energy (G)= -1035.3656 0.26277
---Frequencies -- 43.7582
52.2731 59.5431

M06-2X/6-311++G(2df,p)/PCM(THF):
-1035.865389
M06-2X/6-311++G(2df,p):
-1035.857979
M06-2X/def2-QZVPP:
-1035.968178

benzaldehyde

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C7H6O C1[X(C7H6O)] #Atoms= 14
Charge = 0 Multiplicity = 1

SCF Energy= -345.424978169 Predicted Change= -1.172449D-07
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00011 ||	0.00045	[YES]	0.00003 ||	0.00030	[YES]
Displ	0.00092 ||	0.00180	[YES]	0.00092 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.529800	0.213596	-0.000017
C	-1.987300	0.470815	-0.000036
O	-2.833140	-0.397405	0.000025
C	0.357818	1.290778	-0.000003
C	1.730347	1.058945	0.000004
C	2.208861	-0.249968	0.000011
C	1.321580	-1.329228	0.000002
C	-0.047640	-1.099142	-0.000010
H	-2.275165	1.541013	0.000087
H	-0.029872	2.306945	-0.000004
H	2.424037	1.893373	0.000010
H	3.279143	-0.432592	0.000011
H	1.703419	-2.345149	0.000005
H	-0.759644	-1.919130	-0.000021

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========

SCF Energy= -345.424978169 Predicted Change= -1.172449D-07
Zero-point correction (ZPE)= -345.3136 0.11131
Internal Energy (U)= -345.3073 0.11759
Enthalpy (H)= -345.3064 0.11854
Gibbs Free Energy (G)= -345.3442 0.08076

Frequencies -- 116.2334 220.5485 245.3310

M06-2X/6-311++G(2df,p)/PCM(THF):
-345.5405856
M06-2X/6-311++G(2df,p):
-345.5346959
M06-2X/def2-QZVPP:
-345.5845982

6.2-Breslow intermediate

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---

Pointgroup= C1 Stoichiometry= C22H25NOS C1[X(C22H25NOS)] #Atoms= 50
Charge = 0 Multiplicity = 1

SCF Energy= -1381.08808728 Predicted Change= -2.665414D-09
==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00143	0.00180	[YES]	0.00143	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.515489	0.561055	0.097441
C	-1.223978	-0.592254	-0.021799
O	-0.620999	-1.827472	-0.217500
C	-2.691300	-0.691853	0.003558
S	-1.238600	2.184683	0.210863
C	0.354999	2.959623	0.140482
C	0.421208	4.449599	0.228334
C	1.335676	2.046844	0.080875
C	2.812010	2.290975	0.121066
N	0.881102	0.713357	0.051437
C	1.809763	-0.369993	-0.080966
C	2.124322	-1.131682	1.058669
C	1.436552	-0.811364	2.366202
C	1.916904	-1.616235	3.568454
C	3.045875	-2.168076	0.917280
C	3.639423	-2.431176	-0.316200

C	3.313097	-1.667354	-1.429892
C	2.388559	-0.622506	-1.333788
C	1.972079	0.140864	-2.570594
C	0.666122	-0.405589	-3.163000
C	-3.505957	0.130016	0.797092
C	-4.892054	0.000151	0.770836
C	-5.496164	-0.964046	-0.030956
C	-4.695655	-1.808987	-0.800377
C	-3.312859	-1.679214	-0.780389
H	0.201468	-1.722426	-0.718646
H	-0.020860	4.811424	1.163298
H	-0.124001	4.918725	-0.597617
H	1.455298	4.797067	0.185789
H	3.310097	1.940452	-0.788362
H	3.262248	1.757710	0.965545
H	3.017770	3.355076	0.236933
H	0.358217	-0.964866	2.225936
H	1.553927	0.261990	2.564744
H	1.733827	-2.686529	3.432894
H	1.383301	-1.299077	4.467863
H	2.988063	-1.474265	3.743930
H	3.308577	-2.776959	1.776104
H	4.358512	-3.239522	-0.406817
H	3.771482	-1.879524	-2.392244
H	2.770957	0.060491	-3.314833
H	1.844221	1.205574	-2.349153
H	-0.172803	-0.256144	-2.474140
H	0.755326	-1.476496	-3.373711
H	0.422819	0.106433	-4.098047
H	-3.057466	0.850947	1.473034
H	-5.499915	0.646758	1.396776
H	-6.576804	-1.065567	-0.048296
H	-5.152814	-2.573120	-1.422449
H	-2.692369	-2.339580	-1.376396

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-1381.08808728	Predicted Change= -2.665414D-09
Zero-point correction (ZPE)=	-1380.6653	0.42278
Internal Energy (U)=	-1380.6403	0.44776
Enthalpy (H)=	-1380.6393	0.44870
Gibbs Free Energy (G)=	-1380.7213	0.36672

Frequencies -- 11.7564 29.1515 41.5494

M06-2X/6-311++G(2df,p)/PCM(THF):
-1381.441145
M06-2X/6-311++G(2df,p):
-1381.433246
M06-2X/def2-QZVPP:
-1381.592283

***rac*-Statter-TS**

```
 Using  Gaussian 09:  AM64L-G09RevD.01 24-Apr-2013
 ======================================================
 #m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
 SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest)
 freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
 ---------------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C34H40N2O3S   C1[X(C34H40N2O3S)]  #Atoms= 80
 Charge = 0         Multiplicity = 1
 ---------------------------------------------------------------------------
 SCF Energy= -2052.30550588       Predicted Change= -1.602807D-08
 ======================================================
 Optimization completed.          {Found       1       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00001 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00261 ||  0.00180   [ NO ]       0.00261 ||  0.00180   [ YES ]
 ---------------------------------------------------------------------------
      Atomic             Coordinates (Angstroms)
       Type              X           Y           Z
 ---------------------------------------------------------------------------
      C       -1.503921     -0.869482     -0.628686
      C       -0.201136     -0.423816     -0.685553
      O        0.037682      0.891730     -0.371859
      C        0.911924     -1.158265     -1.310299
      S       -2.033272     -2.462930     -1.177006
      C       -3.715163     -2.100034     -0.782308
      C       -4.747596     -3.151998     -1.029450
      C       -3.835795     -0.857866     -0.286042
      C       -5.098396     -0.163507      0.114857
      N       -2.613864     -0.156973     -0.190391
      C       -2.614986      1.236019      0.181018
      C       -2.508462      2.203981     -0.831261
      C       -2.333031      1.829942     -2.284798
      C       -3.618355      1.325146     -2.951061
      C       -2.562325      3.545937     -0.462334
      C       -2.718620      3.917120      0.870321
      C       -2.820963      2.942492      1.853033
      C       -2.772386      1.581717      1.529734
      C       -2.857418      0.542561      2.630405
      C       -3.936343      0.825153      3.680267
      C        1.089287     -2.545425     -1.210720
      C        2.204107     -3.167833     -1.772804
      C        3.168356     -2.420359     -2.436794
      C        3.010494     -1.034693     -2.534197
      C        1.903597     -0.412752     -1.977166
      H        0.871583      0.898579      0.157454
      H       -4.779456     -3.432768     -2.087374
      H       -5.739758     -2.799645     -0.742043
      H       -4.531705     -4.057589     -0.452571
      H       -5.108673      0.067611      1.184245
      H       -5.960943     -0.790948     -0.109825
      H       -5.206020      0.782106     -0.426475
      H       -1.545418      1.075862     -2.384482
      H       -1.981271      2.718420     -2.819554
      H       -3.456109      1.172670     -4.022103
```

H	-4.429336	2.050881	-2.830201
H	-3.946217	0.370696	-2.527539
H	-2.471583	4.307522	-1.232400
H	-2.753957	4.967853	1.141760
H	-2.931283	3.240170	2.891465
H	-1.884776	0.486961	3.137298
H	-3.023290	-0.446842	2.193229
H	-4.920035	0.958557	3.218789
H	-3.715250	1.728437	4.254803
H	-4.000801	-0.006298	4.387273
H	0.383471	-3.149563	-0.652014
H	2.320952	-4.242558	-1.667306
H	4.038999	-2.903952	-2.868676
H	3.759417	-0.439111	-3.048773
H	1.796527	0.666353	-2.033829
C	1.186390	-1.908780	1.796447
C	-0.012200	-1.252787	1.811491
C	2.427362	-1.172559	1.504532
N	2.289352	0.097810	1.165657
C	3.362531	0.889503	0.821914
O	2.857852	1.984895	0.207147
C	3.720464	3.017971	-0.333348
O	4.554805	0.715392	1.010743
C	3.650509	-1.935261	1.551553
C	3.622220	-3.279338	1.784740
C	2.410449	-4.006509	2.020015
C	1.232612	-3.334083	2.018212
C	2.722917	4.017421	-0.910185
C	4.598010	2.445278	-1.442997
C	4.543714	3.668132	0.775622
H	-0.933727	-1.801123	1.993084
H	-0.067384	-0.170812	1.788118
H	4.585076	-1.426832	1.367152
H	4.561516	-3.826538	1.786366
H	2.449100	-5.075362	2.198395
H	0.290202	-3.846041	2.197556
H	2.078628	4.411718	-0.119001
H	2.091606	3.531161	-1.660455
H	3.253423	4.849784	-1.381233
H	3.971589	1.975394	-2.208670
H	5.299327	1.707270	-1.051849
H	5.162815	3.255818	-1.914219
H	5.281104	2.973987	1.178864
H	3.884408	4.000394	1.583815
H	5.061391	4.544511	0.372958

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-2052.30550588	Predicted Change= -1.602807D-08
Zero-point correction (ZPE)=	-2051.6296	0.67584
Internal Energy (U)=	-2051.5898	0.71563
Enthalpy (H)=	-2051.5889	0.71657
Gibbs Free Energy (G)=	-2051.7020	0.60344

---Frequencies -- -135.0337
15.6305 22.2655

M06-2X/6-311++G(2df,p)/PCM(THF):
-2052.87652
M06-2X/6-311++G(2df,p):
-2052.864379
M06-2X/def2-QZVPP:
-2053.119263

***rac*-S_N2-TS**

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C34H41ClN2O3S C1[X(C34H41ClN2O3S)] #Atoms= 82
Charge = 0 Multiplicity = 1

SCF Energy= -2513.11453480 Predicted Change= -4.326604D-09
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00112	0.00180	[YES]	0.00112	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.463608	0.732677	-0.739349
C	-0.171597	0.213584	-0.822659
O	0.571029	0.885718	-1.766667
C	0.210202	-1.209402	-0.597543
S	-1.805299	2.238620	-1.550924
C	-3.470905	2.214536	-0.988249
C	-4.368991	3.358982	-1.335324
C	-3.729371	1.095760	-0.284357
C	-5.033423	0.667270	0.309376
N	-2.609609	0.243971	-0.158194
C	-2.757156	-1.119109	0.281365
C	-2.878803	-1.392379	1.649837
C	-2.867247	-0.314335	2.714696
C	-1.789035	-0.510536	3.786216
C	-3.019609	-2.730094	2.034111
C	-3.019881	-3.750250	1.093156
C	-2.904129	-3.448735	-0.261207
C	-2.787291	-2.130526	-0.695035
C	-2.750339	-1.833388	-2.177453
C	-4.116701	-1.400003	-2.722535
C	0.156150	-1.862791	0.639299
C	0.429003	-3.224219	0.737036
C	0.774551	-3.955448	-0.396712

C	0.867370	-3.309071	-1.628274
C	0.602718	-1.947649	-1.725423
H	1.533151	0.715079	-1.641358
H	-5.379295	3.190332	-0.958736
H	-4.428623	3.494419	-2.420058
H	-4.000070	4.294610	-0.902843
H	-5.297066	-0.341961	-0.022515
H	-5.826904	1.347490	-0.000432
H	-4.997030	0.660237	1.402866
H	-3.848709	-0.308157	3.206559
H	-2.751672	0.671883	2.253687
H	-1.878136	0.263543	4.553560
H	-0.778501	-0.435884	3.373616
H	-1.886445	-1.483721	4.275713
H	-3.127443	-2.967862	3.088994
H	-3.117889	-4.783239	1.412948
H	-2.911375	-4.246515	-0.999387
H	-2.422495	-2.740463	-2.695707
H	-2.007073	-1.063121	-2.405416
H	-4.427539	-0.439485	-2.299416
H	-4.883674	-2.143831	-2.484705
H	-4.074579	-1.285853	-3.809459
H	-0.142073	-1.324786	1.531873
H	0.358070	-3.711622	1.704657
H	0.978131	-5.019177	-0.320376
H	1.149047	-3.865774	-2.517229
H	0.667409	-1.445052	-2.686162
C	0.967774	2.461185	0.691993
C	0.412696	1.304802	1.340848
C	2.292708	2.402296	0.217032
N	3.099587	1.306461	0.610133
C	3.615828	0.404237	-0.266717
O	4.468132	-0.406948	0.352988
C	5.117378	-1.509434	-0.357218
O	3.316336	0.368996	-1.457119
C	2.815640	3.431245	-0.551639
C	2.035506	4.556499	-0.818813
C	0.752167	4.666011	-0.287565
C	0.218881	3.623773	0.463265
C	5.926817	-2.182732	0.743926
C	6.034344	-0.950884	-1.439437
C	4.065209	-2.459721	-0.912835
H	0.962913	0.380887	1.370735
H	-0.599247	1.322094	1.727029
H	5.264995	-2.554311	1.531461
H	6.635920	-1.475883	1.183986
H	6.484506	-3.025865	0.327065
H	6.748211	-0.245473	-1.003128
H	5.459351	-0.446528	-2.217500
H	6.596539	-1.772716	-1.893356
H	3.530611	-2.014797	-1.752561
H	3.340417	-2.714886	-0.132609
H	4.551161	-3.381396	-1.248399
H	3.202472	1.135134	1.608347
H	3.836217	3.358846	-0.913422

H	2.447467	5.363767	-1.415838
H	0.163714	5.559857	-0.467218
H	-0.780980	3.699863	0.879875
Cl	1.368609	1.586725	3.542916

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2513.11453480 Predicted Change= -4.326604D-09

Zero-point correction (ZPE)=	-2512.4240	0.69049
Internal Energy (U)=	-2512.3822	0.73224
Enthalpy (H)=	-2512.3813	0.73318
Gibbs Free Energy (G)=	-2512.4980	0.61650

Frequencies -- -472.4656 20.6943 28.3442

M06-2X/6-311++G(2df,p)/PCM(THF):
-2513.725666
M06-2X/6-311++G(2df,p):
-2513.705049
M06-2X/def2-QZVPP:
-2513.966198

Methylated S_N2 pathway

methylated-*o*-amino-benzyl-chloride

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C13H18ClNO2 C1[X(C13H18ClNO2)] #Atoms= 35
Charge = 0 Multiplicity = 1

SCF Energy= -1171.32054784 Predicted Change= -2.421741D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00070	0.00180	[YES]	0.00070	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.986966	-1.557222	0.979890
C	3.049258	-1.007983	1.688031
C	3.502310	0.272784	1.374153
C	2.891454	0.990351	0.353154
C	1.824914	0.449423	-0.368972
C	1.205858	1.237200	-1.483936
Cl	0.282802	2.671920	-0.864486
C	1.368983	-0.833201	-0.040561
N	0.320276	-1.452748	-0.787940

C	0.701535	-2.462422	-1.765882
C	-1.005581	-1.181292	-0.570752
O	-1.144878	-0.247197	0.380245
C	-2.472570	0.215048	0.770941
C	-3.280813	-0.940967	1.353016
C	-3.171397	0.872698	-0.414699
C	-2.164664	1.246642	1.849727
O	-1.913855	-1.722369	-1.176921
H	1.617058	-2.551724	1.212275
H	3.521239	-1.575805	2.483455
H	4.331368	0.709257	1.921774
H	3.240415	1.989741	0.105459
H	1.965980	1.651419	-2.146333
H	0.500912	0.643632	-2.063497
H	1.179048	-3.317136	-1.276051
H	1.403238	-2.033847	-2.488122
H	-0.196794	-2.795852	-2.282574
H	-2.719785	-1.422237	2.160443
H	-3.516222	-1.682499	0.588926
H	-4.215031	-0.551864	1.769540
H	-4.100002	1.338720	-0.070632
H	-3.407867	0.139859	-1.187001
H	-2.528860	1.651448	-0.837242
H	-1.624660	0.780568	2.679174
H	-3.097369	1.670905	2.232311
H	-1.549888	2.052193	1.438679

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1171.32054784 Predicted Change= -2.421741D-09

Zero-point correction (ZPE)=	-1171.0251	0.29542
Internal Energy (U)=	-1171.0071	0.31344
Enthalpy (H)=	-1171.0061	0.31438
Gibbs Free Energy (G)=	-1171.0725	0.24796

Frequencies -- 14.8581 48.0079 60.1347

M06-2X/6-311++G(2df,p)/PCM(THF):
-1171.592079
M06-2X/6-311++G(2df,p):
-1171.58468
M06-2X/def2-QZVPP:
-1171.698172

Me-*rac*-S_N2-TS

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)
iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C35H43ClN2O3S C1[X(C35H43ClN2O3S)] #Atoms= 85

Charge = 0 Multiplicity = 1

SCF Energy= -2552.39989062 Predicted Change= -2.865986D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00173	0.00180	[YES]	0.00173	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.569539	0.735960	-0.804152
C	-0.343759	0.083225	-0.983562
O	0.340888	0.660114	-2.036689
C	-0.091390	-1.372803	-0.774269
S	-1.810054	2.240890	-1.646304
C	-3.383961	2.457915	-0.903383
C	-4.164174	3.699255	-1.200170
C	-3.701120	1.405633	-0.122755
C	-4.977578	1.167809	0.618868
N	-2.689891	0.419998	-0.082016
C	-2.965200	-0.894283	0.440647
C	-2.977089	-1.090249	1.827830
C	-2.680349	0.015431	2.820379
C	-1.576459	-0.333524	3.823966
C	-3.278328	-2.372426	2.297710
C	-3.545265	-3.413894	1.419521
C	-3.527639	-3.189256	0.045850
C	-3.247399	-1.926120	-0.471084
C	-3.297918	-1.704021	-1.966196
C	-4.611556	-1.057179	-2.422066
C	0.238038	-2.142262	-1.900826
C	0.452654	-3.511866	-1.790145
C	0.356242	-4.141464	-0.549526
C	0.061537	-3.382836	0.580289
C	-0.148053	-2.011167	0.470336
H	1.302277	0.536074	-1.855399
H	-4.309695	3.820606	-2.278277
H	-3.642209	4.588708	-0.832491
H	-5.147209	3.666165	-0.727368
H	-4.825508	1.177052	1.701976
H	-5.405699	0.197314	0.348190
H	-5.702299	1.943373	0.370891
H	-3.599561	0.236689	3.378181
H	-2.416079	0.936387	2.289669
H	-0.614059	-0.509126	3.334118
H	-1.831574	-1.224225	4.404943
H	-1.432182	0.493526	4.524566
H	-3.304084	-2.550885	3.368935
H	-3.772073	-4.403228	1.805089
H	-3.737020	-4.003656	-0.642540
H	-3.182865	-2.677045	-2.454570
H	-2.454112	-1.092225	-2.299916
H	-4.718388	-0.044293	-2.020446

H	-5.470940	-1.648925	-2.091274
H	-4.643611	-0.986989	-3.513006
H	0.316060	-1.649725	-2.865016
H	0.696124	-4.089457	-2.677079
H	0.522268	-5.210987	-0.463410
H	-0.004351	-3.853373	1.556789
H	-0.372825	-1.441971	1.365551
C	1.214504	2.183141	0.440542
C	0.769856	0.915340	0.983118
C	2.528298	2.381199	-0.043343
N	3.560672	1.420251	0.187959
C	3.593917	0.241259	-0.476565
O	4.653620	-0.488227	-0.127239
C	4.728836	-1.905548	-0.488305
O	2.756864	-0.113859	-1.305529
C	2.892961	3.607924	-0.583578
C	1.984456	4.665383	-0.629601
C	0.706783	4.502155	-0.106421
C	0.331178	3.271595	0.422050
C	6.023956	-2.347535	0.181150
C	4.822836	-2.072516	-2.001783
C	3.529767	-2.636088	0.104217
C	4.605892	1.763658	1.159123
H	-0.176670	0.859240	1.503059
H	1.333906	0.007350	0.838064
H	6.873975	-1.789745	-0.223061
H	6.187378	-3.413470	0.000352
H	5.972592	-2.178008	1.260394
H	5.610117	-1.426274	-2.402695
H	3.876830	-1.829937	-2.486401
H	5.083717	-3.111010	-2.228246
H	3.471791	-2.452509	1.182538
H	3.642826	-3.712766	-0.057857
H	2.598396	-2.312896	-0.365485
H	4.727277	0.948960	1.872918
H	4.279864	2.651980	1.697316
H	5.557802	1.959309	0.657184
H	3.909557	3.737987	-0.942842
H	2.288374	5.617649	-1.052053
H	0.002586	5.327902	-0.107802
H	-0.657968	3.145558	0.854182
Cl	1.852475	1.000566	3.124709

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-2552.39989062	Predicted Change= -2.865986D-09
Zero-point correction (ZPE)=	-2551.6803	0.71958
Internal Energy (U)=	-2551.6371	0.76269
Enthalpy (H)=	-2551.6362	0.76363
Gibbs Free Energy (G)=	-2551.7554	0.64448

Frequencies -- -521.0095 17.5205 32.7702

M06-2X/6-311++G(2df,p)/PCM(THF):

-2553.020573
M06-2X/6-311++G(2df,p):
-2553.00014
M06-2X/def2-QZVPP:
-2553.266897

Mechanism of aoQM formation

Deprotonation-TS

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#M062X/gen pseudo=read scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)
iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/ChkBas Freq

---

Pointgroup= C1 Stoichiometry= C13H16ClCs2NO5 C1[X(C13H16ClCs2NO5)] #Atoms= 38
Charge = 0 Multiplicity = 1

SCF Energy= -1436.08425060 Predicted Change= -4.947679D-09

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00218	0.00180	[NO]	0.00218	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.314162	1.588222	1.044132
O	-1.223760	2.014325	-0.157503
O	-0.169484	1.420229	1.728645
O	-2.407553	1.269320	1.596254
Cs	-3.427174	0.220229	-0.968142
C	-2.159385	-2.720694	0.607376
C	-2.289498	-3.152789	-0.709562
C	-1.373974	-2.702625	-1.662395
C	-0.354928	-1.829748	-1.297570
C	-0.208842	-1.397815	0.030415
N	0.775476	-0.474931	0.407610
C	2.068230	-0.537804	0.039280
O	2.872903	0.372524	0.246685
O	2.405191	-1.702885	-0.558206
C	3.756226	-1.947928	-1.020885
C	4.732429	-1.951101	0.152467
C	4.149612	-0.937863	-2.096084
C	3.654645	-3.345532	-1.624950
C	-1.137383	-1.848477	0.992916
C	-1.011688	-1.451642	2.431586
Cl	0.320692	-2.410928	3.238861
H	4.379239	-2.639664	0.926589
H	4.832466	-0.954510	0.582286
H	5.713781	-2.293092	-0.191398
H	4.250587	0.062483	-1.674433

H	3.392082	-0.921184	-2.887280
H	5.103755	-1.234889	-2.542862
H	2.928264	-3.354541	-2.443622
H	3.331307	-4.063875	-0.866038
H	4.627230	-3.659155	-2.014777
H	-2.858878	-3.070096	1.363104
H	-3.086505	-3.835256	-0.986922
H	-1.456978	-3.027575	-2.695502
H	0.352260	-1.473558	-2.039366
H	-1.918873	-1.689929	2.985623
H	-0.753350	-0.400229	2.558120
H	0.416857	0.460338	1.051722
Cs	1.554094	3.103983	0.000752

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -1436.08425060 Predicted Change= -4.947679D-09
Zero-point correction (ZPE)= -1435.8039 0.28033
Internal Energy (U)= -1435.7792 0.30498
Enthalpy (H)= -1435.7783 0.30592
Gibbs Free Energy (G)= -1435.8649 0.21927

Frequencies -- -459.1921 12.9422 21.7393

M06-2X/6-311++G(2df,p)/PCM(THF):
-1436.484729
M06-2X/6-311++G(2df,p):
-1436.435134
M06-2X/def2-QZVPP:
-1436.60197

post-Deprotonation-TS-Cs-complex

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013
==========
#m062X/gen pseudo=read scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/ChkBas Freq
---
Pointgroup= C1 Stoichiometry= C12H15ClCsNO2 C1[X(C12H15ClCsNO2)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -1151.58382528 Predicted Change= -6.281335D-07
==========
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00021	0.00045	[YES]	0.00001	0.00030	[YES]
Displ	0.00974	0.00180	[NO]	0.00974	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-3.253605	-1.550847	-0.413508
C	-3.437069	-1.170417	-1.738383

C	-2.306939	-0.894065	-2.513715
C	-1.028813	-0.982585	-1.978850
C	-0.816962	-1.352068	-0.626742
N	0.407763	-1.480275	-0.020181
C	1.409766	-0.693426	-0.405553
O	2.590431	-1.126978	0.141933
C	3.796846	-0.352002	0.013911
O	1.378718	0.340972	-1.102536
C	-1.976314	-1.648635	0.141599
C	-1.810006	-2.044690	1.564813
C	4.242884	-0.260112	-1.444857
C	4.813625	-1.164032	0.814255
C	3.633074	1.031486	0.645714
Cs	-0.930802	1.871132	0.046761
H	-2.681251	-2.560481	1.966482
H	-0.895917	-2.611557	1.724763
H	-4.114278	-1.781752	0.211076
H	-4.433154	-1.101916	-2.162738
H	-2.425279	-0.609375	-3.556329
H	-0.165053	-0.752123	-2.591291
H	3.532293	0.323343	-2.029725
H	4.317885	-1.265251	-1.872766
H	5.230136	0.210778	-1.500725
H	4.908644	-2.169947	0.394475
H	4.493889	-1.252256	1.857098
H	5.793922	-0.678713	0.786664
H	3.229440	0.928551	1.659027
H	2.960129	1.651958	0.053385
H	4.608066	1.525285	0.714625
Cl	-1.610106	-0.566501	2.661656

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1151.58382528 Predicted Change= -6.281335D-07
Zero-point correction (ZPE)= -1151.3299 0.25392
Internal Energy (U)= -1151.3114 0.27235
Enthalpy (H)= -1151.3105 0.27330
Gibbs Free Energy (G)= -1151.3803 0.20348

Frequencies -- 17.7903 22.2502 41.2117

M06-2X/6-311++G(2df,p)/PCM(THF):
-1151.860902
M06-2X/6-311++G(2df,p):
-1151.833063
M06-2X/def2-QZVPP:
-1151.948537

Elimination-TS

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#m062X/gen pseudo=read scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)

iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/ChkBas Freq

---

Pointgroup= C1 Stoichiometry= C12H15ClCsNO2 C1[X(C12H15ClCsNO2)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -1151.56614560 Predicted Change= -2.570993D-09

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00260	0.00180	[NO]	0.00260	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.920483	2.315032	0.205077
C	2.833106	2.754543	-1.078210
C	1.590094	2.605084	-1.773054
C	0.495341	2.025623	-1.202230
C	0.534237	1.534118	0.158008
N	-0.473708	0.960208	0.785637
C	-1.554738	0.495141	0.087112
O	-2.683125	0.679192	0.788804
C	-3.952517	0.142176	0.324713
O	-1.515644	-0.102054	-0.988140
C	1.796850	1.714952	0.872036
C	1.922677	1.264425	2.166715
C	-4.346444	0.774751	-1.007588
C	-4.921128	0.573109	1.421049
C	-3.890641	-1.381082	0.244692
Cs	1.109351	-1.675266	-0.825685
H	2.835885	1.442855	2.721900
H	1.048748	0.946789	2.719446
H	3.844782	2.416390	0.768211
H	3.676561	3.221419	-1.573764
H	1.515868	2.971979	-2.793592
H	-0.426331	1.926916	-1.763025
H	-3.679889	0.454558	-1.809078
H	-4.312036	1.865970	-0.926329
H	-5.370978	0.482360	-1.258183
H	-4.935744	1.663325	1.508938
H	-4.619530	0.149361	2.383427
H	-5.931091	0.226189	1.185287
H	-3.535629	-1.790917	1.195780
H	-3.228081	-1.708055	-0.557198
H	-4.894413	-1.774261	0.055521
Cl	2.549398	-1.211827	2.184744

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1151.56614560 Predicted Change= -2.570993D-09
Zero-point correction (ZPE)= -1151.3138 0.25225
Internal Energy (U)= -1151.2954 0.27073

Enthalpy (H)= -1151.2944 0.27167
Gibbs Free Energy (G)= -1151.3649 0.20119
---Frequencies -- -166.7576
14.5514 24.2422

M06-2X/6-311++G(2df,p)/PCM(THF):
-1151.840518
M06-2X/6-311++G(2df,p):
-1151.809625
M06-2X/def2-QZVPP:
-1151.924544

4-exo-tet-TS

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

#M062X/gen pseudo=read scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)
iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/ChkBas Freq

Pointgroup= C1 Stoichiometry= C12H15ClCsNO2 C1[X(C12H15ClCsNO2)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -1151.53604925 Predicted Change= -9.422128D-09

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00168	0.00180	[YES]	0.00168	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.715628	-1.118475	1.982865
C	-1.386221	-0.683913	1.892779
N	-0.039060	1.196863	0.745756
C	-1.431340	2.160135	-0.302836
C	-1.145954	0.433095	1.091574
C	1.199348	0.684546	0.711114
O	2.081823	1.594527	0.237283
C	3.488271	1.274024	0.114942
Cl	-3.179431	3.158886	-1.490329
O	1.523942	-0.464740	1.044346
C	-2.184407	1.074944	0.410556
C	-3.494528	0.650726	0.501479
C	-3.750064	-0.471174	1.305804
C	4.093938	0.990070	1.487403
C	4.080324	2.554982	-0.465942
C	3.701792	0.114287	-0.857145
Cs	0.015127	-2.368530	-0.782019
H	-2.947478	-1.980114	2.603100
H	-0.585165	-1.182257	2.427392
H	3.683704	0.074188	1.913552
H	3.886377	1.824352	2.164958

H	5.179594	0.885133	1.393650
H	3.889559	3.398491	0.203810
H	3.631531	2.774823	-1.439322
H	5.160944	2.445149	-0.594270
H	3.181580	0.318167	-1.799339
H	3.333991	-0.822337	-0.436637
H	4.769955	0.011042	-1.073017
H	-0.961329	1.979762	-1.258853
H	-4.286290	1.162982	-0.032814
H	-4.766583	-0.837815	1.406127
H	-1.257925	3.120726	0.159442

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1151.53604925 Predicted Change= -9.422128D-09
Zero-point correction (ZPE)= -1151.2827 0.25328
Internal Energy (U)= -1151.2646 0.27138
Enthalpy (H)= -1151.2637 0.27232
Gibbs Free Energy (G)= -1151.3324 0.20357

Frequencies -- -564.4191 21.4383 28.3528

M06-2X/6-311++G(2df,p)/PCM(THF):
-1151.81035
M06-2X/6-311++G(2df,p):
-1151.762674
M06-2X/def2-QZVPP:
-1151.875626

6-exo-tet-TS

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#M062X/gen pseudo=read scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)
iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/ChkBas Freq

---

Pointgroup= C1 Stoichiometry= C12H15ClCsNO2 C1[X(C12H15ClCsNO2)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -1151.54785424 Predicted Change= -5.540263D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00925	0.00180	[NO]	0.00925	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.089159	-1.301439	1.728870
C	-0.354988	-0.185122	0.988929
N	-1.548497	-0.286073	0.300381

C	-2.264578	0.823512	0.247186
O	-3.532581	0.770415	-0.226396
C	-4.255364	-0.460057	-0.470918
O	-1.912096	1.986868	0.596595
C	0.455336	0.977092	1.011565
C	0.096983	2.081156	0.094815
Cl	2.073080	2.472656	-0.936463
C	1.577766	1.039607	1.843879
C	1.973843	-0.059310	2.597101
C	1.231457	-1.243743	2.514336
C	-5.641610	0.043694	-0.867970
C	-4.354388	-1.301324	0.799710
C	-3.638411	-1.240338	-1.629992
Cs	2.645180	-0.934867	-0.843065
H	-0.515632	-2.202683	1.690285
H	-5.574847	0.678163	-1.756901
H	-6.080521	0.629338	-0.054774
H	-6.301173	-0.800615	-1.088918
H	-4.754312	-0.693599	1.618132
H	-3.377770	-1.690418	1.088395
H	-5.039773	-2.137649	0.627233
H	-2.663920	-1.639938	-1.350805
H	-3.522299	-0.583737	-2.498807
H	-4.303001	-2.064527	-1.910045
H	0.063402	3.106206	0.430942
H	-0.314377	1.854460	-0.876081
H	2.172005	1.948550	1.848390
H	2.853524	-0.001422	3.229494
H	1.537106	-2.117711	3.082564

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-1151.54785424	Predicted Change= -5.540263D-08
Zero-point correction (ZPE)=	-1151.2947	0.25313
Internal Energy (U)=	-1151.2768	0.27100
Enthalpy (H)=	-1151.2759	0.27194
Gibbs Free Energy (G)=	-1151.3438	0.20402

Frequencies -- -543.7553 17.2352 29.6916

M06-2X/6-311++G(2df,p)/PCM(THF):
-1151.823575
M06-2X/6-311++G(2df,p):
-1151.786537
M06-2X/def2-QZVPP:
-1151.901221

post-4-exo-tet intermediate

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C12H15NO2 C1[X(C12H15NO2)] #Atoms= 30
Charge = 0 Multiplicity = 1

SCF Energy= -671.215456146 Predicted Change= -1.646380D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00061	0.00180	[YES]	0.00061	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-3.909700	-1.190028	0.112095
C	-2.537062	-1.402195	-0.104529
C	-1.799661	-0.239252	-0.178319
N	-0.485720	0.231390	-0.385284
C	0.704291	-0.394418	-0.153742
O	1.693107	0.508066	-0.114066
C	3.074771	0.078252	0.084851
O	0.804398	-1.601444	-0.036167
C	-2.329935	1.043525	-0.039932
C	-0.934543	1.641608	-0.196862
C	-3.674950	1.250314	0.164691
C	-4.463304	0.085955	0.237769
C	3.218483	-0.595126	1.445912
C	3.844585	1.392716	0.050277
C	3.510199	-0.830341	-1.060437
H	-4.565484	-2.052675	0.182518
H	-2.106216	-2.391344	-0.200365
H	2.664718	-1.534257	1.478709
H	2.848984	0.069072	2.233506
H	4.276281	-0.799457	1.637121
H	3.491197	2.062477	0.839682
H	3.711666	1.887471	-0.916167
H	4.910489	1.202788	0.203454
H	3.326734	-0.337997	-2.020537
H	2.973510	-1.779491	-1.036005
H	4.583272	-1.026745	-0.974610
H	-0.754911	2.265583	-1.074298
H	-0.508993	2.100608	0.698336
H	-4.118280	2.234605	0.275223
H	-5.532013	0.180589	0.401636

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-671.215456146	Predicted Change= -1.646380D-09
Zero-point correction (ZPE)=	-670.9618	0.25356
Internal Energy (U)=	-670.9477	0.26770
Enthalpy (H)=	-670.9468	0.26864
Gibbs Free Energy (G)=	-671.0033	0.21214

Frequencies -- 26.8691 53.1477 82.2743

M06-2X/6-311++G(2df,p)/PCM(THF):
-671.4369498
M06-2X/6-311++G(2df,p):
-671.4306417
M06-2X/def2-QZVPP:
-671.5296074

post-6-exo-tet intermediate

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,gdiis) iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C12H15NO2 C1[X(C12H15NO2)] #Atoms= 30
Charge = 0 Multiplicity = 1

SCF Energy= -671.235463079 Predicted Change= -9.573738D-09

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00195	0.00180	[NO]	0.00195	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.058658	-1.646091	0.070421
C	1.371394	-0.433742	0.146989
N	-0.030430	-0.437195	0.273456
C	-0.627872	0.656476	-0.016527
O	-1.938961	0.816498	-0.103188
C	-2.872636	-0.306001	-0.024864
O	-0.044702	1.831140	-0.320980
C	2.085504	0.768203	0.077651
C	1.266052	2.014750	0.239172
C	3.465726	0.759608	-0.080953
C	4.150501	-0.452747	-0.154613
C	3.442959	-1.651832	-0.076377
C	-4.216313	0.372912	-0.264977
C	-2.829503	-0.927823	1.366851
C	-2.583281	-1.320193	-1.126561
H	1.492552	-2.571115	0.121913
H	-4.234757	0.846858	-1.250575
H	-4.397662	1.137221	0.496014
H	-5.018692	-0.368205	-0.216041
H	-2.980010	-0.155342	2.127352
H	-1.876945	-1.427291	1.544914
H	-3.638506	-1.659302	1.455670
H	-1.640496	-1.839234	-0.952185
H	-2.545221	-0.818072	-2.098470
H	-3.393470	-2.055246	-1.151757
H	1.145223	2.277021	1.298864

H	1.695088	2.868983	-0.286109
H	4.006809	1.700872	-0.139743
H	5.229179	-0.460886	-0.272603
H	3.972078	-2.598122	-0.135372

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-671.235463079	Predicted Change= -9.573738D-09
Zero-point correction (ZPE)=	-670.9807	0.25468
Internal Energy (U)=	-670.9671	0.26830
Enthalpy (H)=	-670.9662	0.26925
Gibbs Free Energy (G)=	-671.0209	0.21451

Frequencies -- 45.0987 53.0308 112.2980

M06-2X/6-311++G(2df,p)/PCM(THF):
-671.4559399
M06-2X/6-311++G(2df,p):
-671.4503958
M06-2X/def2-QZVPP:
-671.5492315

Azitidine-opening-TS

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

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#M062X/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)
iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C12H15NO2 C1[X(C12H15NO2)] #Atoms= 30
Charge = 0 Multiplicity = 1

SCF Energy= -671.137066774 Predicted Change= -8.130713D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00150	0.00180	[YES]	0.00150	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	3.607715	-1.064865	0.410754
C	2.270066	-1.340331	0.181986
N	0.078387	-0.013899	-0.007447
C	0.932243	1.831263	-0.741829
C	1.437062	-0.225797	-0.036789
C	-0.733061	-1.043892	-0.482207
O	-2.050855	-0.793946	-0.541571
C	-2.767783	0.216103	0.226965
O	-0.336021	-2.133974	-0.850019
C	2.002312	1.054486	-0.220571

C	3.344165	1.332254	0.087446
C	4.143759	0.246194	0.385297
C	-2.488096	0.035077	1.714765
C	-4.223843	-0.117998	-0.086412
C	-2.448585	1.630081	-0.251435
H	4.274298	-1.887965	0.652271
H	1.873680	-2.344466	0.247480
H	0.769130	2.874911	-0.465769
H	0.417884	1.504744	-1.637438
H	-1.440535	0.241880	1.943221
H	-2.729464	-0.987361	2.021808
H	-3.114781	0.724719	2.288683
H	-4.442066	-1.153472	0.188479
H	-4.421593	0.009368	-1.154944
H	-4.888710	0.544215	0.474992
H	-2.426454	1.660788	-1.345637
H	-1.493289	1.979588	0.139076
H	-3.233044	2.310862	0.093664
H	3.745730	2.338650	0.022805
H	5.199800	0.388736	0.588334

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

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SCF Energy= -671.137066774 Predicted Change= -8.130713D-09
Zero-point correction (ZPE)= -670.8869 0.25009
Internal Energy (U)= -670.8728 0.26417
Enthalpy (H)= -670.8719 0.26512
Gibbs Free Energy (G)= -670.9281 0.20894

Frequencies -- -623.3781 35.8971 49.8225

M06-2X/6-311++G(2df,p)/PCM(THF):
-671.3597239
M06-2X/6-311++G(2df,p):
-671.3488039
M06-2X/def2-QZVPP:
-671.4476554

Oxazine-opening-TS

Using Gaussian 09: AM64L-G09RevD.01 24-Apr-2013

==========

#M062X/gen scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=THF) opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis)
iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/ChkBas Freq

---

Pointgroup= C1 Stoichiometry= C12H15NO2 C1[X(C12H15NO2)] #Atoms= 30
Charge = 0 Multiplicity = 1

SCF Energy= -671.157979886 Predicted Change= -2.332663D-09

==========

Optimization completed. {Found 2 times}
Item Max Val. Criteria Pass? RMS Val. Criteria Pass?

Force	0.00002	0.00045	[YES]	0.00000	0.00030 [YES]
Displ	0.00157	0.00180	[YES]	0.00157	0.00180 [YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.780336	-1.606436	0.390970
C	1.259991	-0.274128	0.391193
N	-0.055928	-0.094729	0.531682
C	-0.670903	0.990717	-0.019071
O	-1.992589	0.876795	-0.224654
C	-2.773465	-0.344488	-0.081406
O	-0.192736	2.075234	-0.392747
C	2.204666	0.787521	0.130434
C	1.830405	2.062897	0.484176
C	3.495990	0.492602	-0.416439
C	3.925184	-0.799506	-0.476479
C	3.059575	-1.846494	-0.032073
C	-4.154083	0.106040	-0.554492
C	-2.842129	-0.781415	1.379152
C	-2.244234	-1.444442	-0.997120
H	1.112659	-2.415796	0.667791
H	-4.107202	0.452807	-1.590909
H	-4.520585	0.925292	0.071050
H	-4.861452	-0.725696	-0.493211
H	-3.154075	0.060936	2.005040
H	-1.876241	-1.147322	1.725692
H	-3.587394	-1.576884	1.481376
H	-1.281312	-1.820137	-0.650687
H	-2.136361	-1.061372	-2.017070
H	-2.962466	-2.270369	-1.016590
H	1.146146	2.232104	1.303778
H	2.389436	2.927923	0.134403
H	4.143093	1.319037	-0.697465
H	4.918857	-1.041058	-0.836221
H	3.422994	-2.869795	-0.062621

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

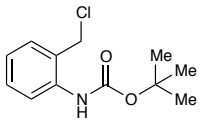
SCF Energy=	-671.157979886	Predicted Change= -2.332663D-09
Zero-point correction (ZPE)=	-670.9074	0.25049
Internal Energy (U)=	-670.8935	0.26440
Enthalpy (H)=	-670.8926	0.26535
Gibbs Free Energy (G)=	-670.9482	0.20968

Frequencies -- -469.8745 28.5910 58.6244

M06-2X/6-311++G(2df,p)/PCM(THF):
-671.3880859
M06-2X/6-311++G(2df,p):
-671.3792955
M06-2X/def2-QZVPP:
-671.4782491

Computed Isotope Effect Information

Unlabeled Tabulated Frequencies



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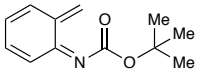
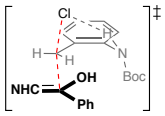
22.9789	461.1390	952.2759	1364.2044	3094.2924
44.9773	465.8814	978.7828	1424.4101	3147.5893
54.6419	478.3514	982.8727	1426.9709	3160.3328
86.9350	516.9531	1014.4923	1447.2935	3163.2991
103.6563	549.4976	1063.7094	1495.7683	3165.2902
114.1999	580.7522	1068.3281	1506.2735	3173.3428
123.3864	620.7152	1093.4441	1509.2483	3209.0709
184.3438	681.4618	1097.2577	1510.5013	3214.4457
212.4599	760.4769	1151.8564	1515.7590	3215.3033
229.3756	765.8670	1187.8396	1522.8297	3220.7041
255.6882	776.0979	1198.5079	1529.5630	3225.9264
266.9812	783.5048	1224.5346	1536.4203	3236.6777
285.0138	792.5981	1240.5574	1548.0754	3292.4901
309.4256	843.2951	1290.5841	1582.2416	3611.0298
321.3463	870.3180	1298.8289	1679.3604	
349.4785	905.1214	1309.0057	1707.4620	
365.8710	931.6262	1317.4512	1836.7565	
416.6659	947.1172	1329.6420	3081.7545	
431.7055	949.5165	1346.2182	3089.0088	



Unlabeled

24.4274	450.5302	950.8103	1366.5607	1802.1436
42.5174	463.3289	972.2053	1415.7079	3084.8932
65.5869	476.3524	978.7254	1422.3836	3087.9131
73.7601	482.1938	1004.1195	1426.3532	3094.9561
114.9492	546.3041	1016.4147	1445.6035	3157.8174
157.5690	589.1698	1019.3062	1453.9127	3165.4829
208.7011	677.7888	1033.9274	1486.2427	3167.6920
213.2824	724.2688	1052.2416	1495.9836	3176.0110
224.9277	744.8674	1067.4846	1509.3707	3195.3730
257.5261	757.3508	1082.3696	1510.8627	3202.3280
267.4381	800.3454	1186.8703	1520.3242	3208.1864
280.5704	818.8361	1192.5173	1528.6819	3215.7882
332.9369	852.3293	1229.2292	1546.0839	3228.2100
367.0574	868.2419	1259.5479	1648.7069	3241.0660
376.9746	879.7689	1297.6824	1674.7786	3250.9046
433.6003	926.6905	1307.0213	1705.8380	3294.5418
439.7764	947.6027	1328.6354	1761.2912	

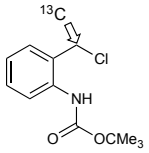


rac-S_N2-TS

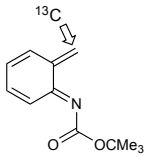
Unlabeled

-472.4656	373.2560	902.5871	1302.4113	1666.7564
20.6943	378.7639	920.4029	1304.5246	1683.4380
28.3442	385.7775	926.6987	1308.9934	1685.2143
33.3520	399.4300	939.9593	1311.4761	1694.6529
40.6913	424.0913	945.3634	1327.7886	1696.2335
44.8368	431.2566	950.1355	1332.4320	1742.2516
48.8134	436.4273	953.9238	1342.1015	1773.1642
58.5371	441.4413	957.3906	1343.8751	3072.6681
63.2950	463.2952	976.4386	1349.5481	3078.9574
68.5942	468.2120	982.3911	1361.3140	3083.2944
70.3455	471.3230	985.7306	1366.2042	3083.7294
76.4272	484.7531	997.8239	1368.0140	3087.9176
86.1811	491.2048	1002.2362	1372.8623	3090.2234
87.7748	513.5778	1004.2545	1388.2528	3092.7024
91.1312	535.5320	1015.8958	1420.4220	3092.9047
98.5470	540.4266	1016.8909	1421.3839	3097.2973
99.5782	544.4000	1020.5959	1423.9114	3137.6138
104.3290	552.8813	1025.5098	1425.4794	3138.1821
110.8292	554.8081	1031.1559	1435.7905	3146.3401
123.5411	563.2344	1034.8844	1443.0977	3156.1854
128.7493	569.9068	1060.6065	1446.1909	3158.9531
132.3476	580.7870	1062.3607	1449.1701	3160.2977
140.9714	583.6060	1066.3150	1491.4236	3163.4268
147.3852	622.5537	1069.3390	1493.0325	3166.0298
153.6192	626.7332	1071.8673	1495.3913	3170.8460
159.2260	632.6346	1078.1790	1496.1085	3171.7624
167.2430	643.8023	1083.6277	1496.8632	3172.5363
181.1096	647.0588	1095.6410	1500.7951	3178.2887
186.7563	677.0050	1099.7555	1508.1993	3182.1912
196.7143	709.2023	1106.7322	1508.6932	3194.1315
218.1583	720.4738	1108.7473	1510.6118	3195.6633
218.9338	740.1579	1116.3035	1514.0826	3203.3665
225.0218	742.5952	1122.4632	1515.6494	3203.4654
234.8802	768.5502	1138.8301	1515.8970	3209.2908
238.1124	775.7094	1154.2197	1520.8818	3214.7455
245.8559	780.8632	1158.6881	1521.3157	3218.7972
254.8917	783.2475	1181.5233	1522.6221	3223.0650
263.9718	788.4242	1181.8986	1524.7721	3227.2200
270.5478	794.8097	1186.4333	1526.1451	3227.2547
280.4325	802.7022	1196.1291	1528.1105	3230.5220
297.8278	806.2972	1211.1477	1531.4283	3235.0107
305.5307	824.8031	1221.8634	1534.1876	3240.0355
315.2102	851.7105	1226.3736	1536.5827	3241.3466
316.4520	853.0586	1256.8013	1543.7466	3245.9011
319.5466	877.6845	1269.8387	1548.7568	3257.0426
341.3062	882.7921	1276.3130	1573.1916	3383.2876
356.6910	889.9130	1294.7609	1593.3526	3481.1793
363.0776	900.2301	1299.1013	1666.0794	3539.6876

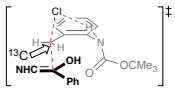
^{13}C Isotopomers Tabulated Frequencies



23.0005	460.8400	952.2724	1363.8816	3094.2865
44.9547	465.8796	978.7841	1424.4107	3140.9539
54.6376	478.1721	982.6905	1426.9718	3160.3060
86.9120	516.7450	1014.4911	1447.2943	3163.2913
103.3078	548.6422	1063.6919	1495.7684	3165.2811
114.0124	575.8787	1068.3288	1501.6932	3173.3644
123.3516	620.5468	1093.2409	1509.2466	3208.4488
183.6674	667.3853	1096.8555	1510.4970	3209.0888
212.4557	758.8368	1151.2938	1514.5642	3214.4750
228.3392	763.4595	1187.8364	1522.5703	3215.3063
255.4311	775.3198	1198.4249	1529.5618	3225.8868
266.7964	782.3172	1224.1825	1536.1085	3236.6616
284.9728	792.1062	1238.6230	1548.0659	3292.4837
308.0622	838.0594	1289.8561	1582.0595	3610.9480
320.8770	868.2806	1298.8251	1679.2212	
349.2464	904.4394	1307.8792	1707.2855	
365.8505	922.7896	1313.4412	1836.7422	
415.7307	947.1164	1327.5974	3081.7601	
431.2322	949.2437	1344.5591	3088.9906	

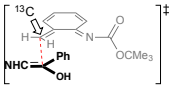


24.3267	448.9233	950.7982	1365.0313	1802.1188
42.3868	463.1535	967.5948	1415.1275	3084.8974
65.3806	475.4839	978.7235	1422.3786	3087.9212
73.2180	481.3388	1000.7833	1426.3477	3094.9501
114.9338	544.8002	1009.7318	1445.6005	3157.8343
157.3336	588.7753	1018.4195	1453.4493	3165.4722
208.2520	677.7394	1033.8925	1485.7830	3167.6979
213.2575	723.8534	1052.0521	1495.9828	3176.0067
223.3689	743.2039	1067.4819	1509.3698	3188.9504
256.7368	757.3474	1082.2100	1510.8648	3202.3535
266.8661	799.7796	1185.3388	1520.3202	3208.2090
280.5686	818.7736	1192.4993	1528.6795	3215.8280
332.8751	851.1682	1229.2303	1546.0838	3228.2602
366.8503	868.0799	1258.3259	1648.6450	3241.0501
375.3547	877.7476	1297.6799	1658.4052	3250.9195
432.6313	926.6656	1306.9995	1701.7583	3280.8650
439.5125	947.5984	1328.5019	1757.4644	



***rac*-S_N2-TS**

-458.6593	378.3718	926.6779	1311.2404	1696.0773
20.6965	381.7079	939.9026	1327.7515	1742.2461
28.3118	399.3413	945.3360	1332.0365	1773.1684
33.3511	424.0589	950.1370	1341.9050	3072.6924
40.6811	431.2018	953.4045	1343.7465	3078.9745
44.8158	436.1796	957.3833	1349.5121	3083.2794
48.8054	440.1196	976.4239	1361.2910	3083.7224
58.5332	463.2188	979.8957	1366.1815	3087.8924
63.2699	467.6578	984.0843	1367.6739	3090.2094
68.5730	471.1973	997.7727	1372.8216	3092.7368
70.2844	484.7257	1002.2261	1388.2332	3092.8814
76.3911	490.6517	1004.1757	1420.3356	3097.2928
86.1648	513.2758	1015.8479	1421.3890	3137.6662
87.7609	535.5114	1016.8706	1423.9031	3138.1672
91.0136	540.3722	1020.3623	1425.4793	3146.3079
98.5338	544.1437	1024.8832	1435.7898	3156.1760
99.5505	552.7720	1030.6734	1443.0024	3158.9472
104.0604	554.7428	1034.8667	1446.1930	3160.3168
110.6969	562.2079	1060.6103	1449.1703	3163.4506
123.5175	568.4876	1062.3547	1484.8341	3165.9822
128.7072	580.4661	1066.3108	1493.0207	3170.8666
132.3146	581.5430	1069.3288	1495.3833	3171.7328
140.7890	622.4354	1071.8424	1496.0967	3172.5864
147.3770	626.7124	1078.1825	1496.8175	3178.2706
153.5974	632.5483	1083.3304	1500.7859	3182.2295
159.2240	643.7854	1095.6370	1508.1988	3194.1702
167.1953	647.0409	1099.7424	1508.6920	3195.6657
181.0653	676.9007	1106.7166	1510.6111	3203.3429
186.7411	709.1746	1108.4642	1514.0706	3203.4997
196.7009	720.4502	1116.2979	1515.5076	3209.3261
218.0561	740.0795	1122.4219	1515.8986	3214.7416
218.9521	742.5895	1138.8092	1519.0696	3218.7583
224.5173	767.7054	1153.5017	1521.2478	3223.0496
234.7796	775.6426	1158.5574	1521.7605	3227.2001
238.0298	780.7928	1181.5179	1524.5769	3227.2609
245.8240	783.2415	1181.8959	1526.1461	3230.5266
254.8801	788.0547	1186.4276	1527.9500	3234.9919
263.6561	794.8018	1196.1245	1531.3082	3239.3014
270.3430	802.2474	1211.1298	1533.8488	3240.1047
280.4091	806.2681	1221.7990	1536.5696	3241.3996
297.8270	824.7907	1226.3027	1543.5864	3257.0473
305.5699	847.9875	1255.3385	1548.6264	3369.4716
315.2040	851.7383	1269.8383	1572.6739	3481.2006
316.3809	876.4657	1276.3007	1593.0430	3539.6096
319.4935	881.9668	1294.7442	1665.8927	
341.2057	889.9042	1299.0670	1666.7459	
356.4841	900.2248	1301.4035	1683.4363	
363.0405	902.5865	1303.0474	1685.2082	
373.1125	919.6026	1308.4437	1694.6488	



rac-Stetter-TS

-132.9445	392.9627	943.1549	1326.4339	1762.4585
15.6282	408.8245	945.4125	1338.7952	1782.4588
22.2451	428.2094	950.2226	1342.3737	3072.1756
28.1370	436.0040	954.8125	1355.1535	3079.6949
36.3560	439.3219	972.5583	1365.6348	3080.8031
45.9853	441.4783	974.6611	1373.8545	3081.3763
48.4313	467.1824	984.9119	1383.0480	3084.1465
52.9765	475.7343	994.9018	1388.8699	3088.6475
57.3632	483.7450	997.8361	1390.4353	3088.9172
65.5338	486.8903	1000.3749	1412.2744	3092.1998
67.0760	497.0450	1006.7443	1421.1830	3096.1421
72.9410	500.0968	1011.4811	1422.3366	3135.3282
82.9776	529.2017	1014.3517	1424.7845	3138.6424
94.1856	535.8874	1034.5579	1434.5202	3143.1185
96.9106	543.7886	1037.1774	1440.6889	3154.8290
110.8687	547.9182	1043.8179	1443.2376	3157.0197
115.2282	565.4779	1045.2062	1445.2076	3157.3558
121.1244	574.6418	1060.4291	1447.5063	3157.5748
126.3032	585.4032	1060.7119	1488.3154	3160.6723
130.8789	602.1273	1065.1312	1493.1704	3162.8934
137.7352	616.2076	1070.4893	1494.7135	3167.3839
143.9036	622.4118	1075.2786	1495.6957	3169.5498
160.8202	629.8905	1077.8403	1496.3574	3173.8498
165.0307	640.0985	1087.7475	1500.6564	3178.7280
182.9194	703.3993	1097.1005	1505.1549	3183.2140
190.8916	712.9926	1103.5740	1506.7220	3201.7455
199.9495	725.2637	1105.6493	1509.1726	3203.7370
210.8408	732.2417	1110.2624	1510.0102	3207.3221
216.0237	750.6158	1123.1143	1511.5648	3207.8196
221.5555	762.6531	1134.6751	1517.5844	3210.8770
233.8498	770.8250	1151.4434	1519.4819	3211.5572
243.8683	776.6214	1171.7442	1521.7912	3213.6907
248.2987	781.9046	1181.9697	1522.0345	3218.0437
260.4909	785.1902	1185.9520	1526.1956	3218.9421
265.5176	791.5723	1192.1256	1529.2769	3228.8453
272.7741	799.0054	1199.6723	1532.2325	3238.2647
279.3206	800.5797	1209.8993	1536.6149	3238.5143
285.9247	820.3458	1213.8735	1541.5629	3239.0178
288.3771	828.4882	1230.9333	1543.3112	3240.4965
290.7874	831.9472	1258.4030	1550.7412	3286.3292
305.2719	836.7908	1270.5344	1598.4109	3293.6245
318.5930	873.8040	1280.4778	1623.5179	3464.6043
329.9873	878.6430	1292.5507	1633.9594	
351.4773	889.4624	1294.4392	1668.6458	
358.4832	893.3117	1295.9928	1683.2581	
362.7755	910.3849	1303.3501	1686.6389	
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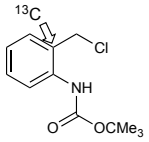

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86.9131	516.9331	1014.4830	1447.2930	3163.2913
103.4673	548.8965	1063.6532	1495.7674	3165.2811
114.0448	576.7994	1068.3288	1504.7321	3173.3644
123.2897	619.7935	1093.0122	1509.2427	3209.0887
184.2656	681.3330	1096.3784	1509.9240	3214.4501
212.4551	755.1880	1149.3528	1510.7641	3215.3061
229.1372	764.7401	1187.8313	1522.1534	3220.7016
255.5715	774.9596	1196.9575	1529.5575	3225.9170
266.9822	781.5855	1219.8616	1530.7563	3236.6571
285.0103	792.3585	1230.9270	1547.7983	3292.4834
308.2686	842.1343	1285.5508	1579.6514	3610.9486
321.0283	869.4998	1298.8248	1668.6529	
349.3355	904.6087	1307.0990	1699.9458	
365.8625	931.0208	1315.5289	1836.6329	
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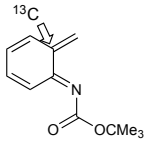
431.0875	949.2824	1343.8421	3088.9906	



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73.7354	544.7168	1019.2453	1482.6849	3176.0067
114.9396	587.8690	1033.9095	1495.9828	3195.3214
157.5147	677.7373	1052.2216	1509.3697	3202.3535
208.1185	723.5420	1067.4823	1510.8648	3208.2090
213.2512	743.6183	1082.3145	1520.3202	3215.8259
224.3588	750.5236	1184.5487	1528.6795	3228.2596
257.3866	800.1293	1192.1852	1546.0823	3241.0479
267.1804	818.5803	1229.2230	1647.5670	3250.9192
280.5682	851.8495	1254.7614	1656.2818	3294.5552
332.9306	866.3518	1297.6785	1701.7335	
367.0138	878.2407	1306.8664	1752.9694	
376.7971	926.6774	1327.0894	1802.0928	
432.7283	947.5984	1353.8500	3084.8974	
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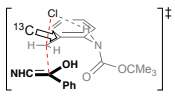

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33.3497	424.0748	950.1384	1341.4015	3072.6927
40.6765	431.1773	953.8387	1342.5394	3078.9746
44.8267	436.3990	957.1762	1349.4689	3083.2795
48.8137	439.5588	976.4370	1358.2799	3083.7224
58.5324	462.6320	981.9397	1361.3197	3087.8924
63.2646	467.4589	985.5602	1366.2840	3090.2095
68.5882	470.9542	997.8098	1372.6518	3092.7370
70.3105	484.1430	1002.2277	1388.2326	3092.8814
76.4148	488.3911	1004.2135	1420.3970	3097.2928
86.1601	513.5345	1015.8896	1421.3889	3137.6665
87.7587	535.4763	1016.8999	1423.9035	3138.1672
91.0793	539.7945	1020.5550	1425.4691	3146.3079
98.5341	542.2453	1025.3950	1435.7890	3156.1760
99.5663	552.6958	1031.0246	1443.0753	3158.9472
104.2259	554.7899	1034.8761	1446.1932	3160.3168
110.7511	562.9127	1060.6106	1449.1735	3163.4506
123.5276	569.1889	1062.3598	1491.0622	3165.9822
128.7150	580.7135	1066.3171	1493.0309	3170.8673
132.3372	582.1212	1069.3282	1495.3870	3171.7328
140.8263	621.8187	1071.8454	1496.1038	3172.5870
147.3842	626.7195	1078.1825	1496.8597	3178.2706
153.6060	632.6308	1083.5681	1500.7859	3182.2295
159.2209	643.7962	1095.6370	1508.1860	3194.1702
167.2359	647.0439	1099.7388	1508.6914	3195.6657
181.0876	676.9714	1106.6923	1510.6000	3203.3429
186.7517	709.1983	1108.4679	1512.8228	3203.4997
196.7093	720.4669	1116.2964	1514.6477	3209.3261
218.1119	733.7500	1122.4413	1515.8979	3214.7418
218.9491	742.5565	1138.8206	1516.4525	3218.7567
224.7371	767.5579	1153.0208	1521.2371	3223.0498
234.7979	772.9399	1158.6059	1521.6807	3227.1962
238.0192	780.4303	1181.5243	1524.5238	3227.2609
245.8315	783.2279	1181.8935	1526.0450	3230.5301
254.8862	788.2396	1186.3023	1527.9775	3234.9844
263.8020	794.8018	1196.1247	1529.1262	3240.0194
270.3837	802.3915	1211.1063	1531.3682	3241.3106
280.4102	806.2502	1221.6555	1536.5526	3245.8634
297.8254	824.7908	1226.1878	1542.5445	3257.0964
305.5547	851.7001	1250.8163	1548.5551	3383.3235
315.1187	852.5499	1269.8389	1569.5260	3481.2047
315.6988	877.2675	1276.3001	1593.1461	3539.6102
319.3250	882.5438	1289.4765	1653.7615	
340.8142	889.9046	1294.7833	1666.7476	
356.6660	900.1483	1299.1591	1683.4365	
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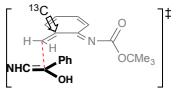

***rac*-Stetter-TS**

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57.3571	474.8527	987.7082	1373.4150	3080.8031
65.5299	482.7056	994.9312	1382.2999	3081.3763
67.0762	486.7530	998.0559	1388.3411	3084.1465
72.9768	497.1141	1000.5189	1390.4352	3088.6475
82.9907	499.8713	1006.7462	1404.9187	3088.9173
94.1919	529.2099	1011.4890	1421.1803	3092.1998
96.8974	535.9269	1014.3615	1422.2530	3096.1421
110.8762	544.9622	1034.5481	1424.7737	3135.3311
115.2338	547.9150	1037.1735	1433.4278	3138.6424
121.1348	565.4796	1043.8185	1437.1545	3143.1185
126.3861	574.6716	1045.7701	1441.7331	3154.8290
131.1080	585.4034	1060.4311	1443.3391	3157.0197
137.7392	601.1911	1060.8110	1447.4879	3157.3558
143.9408	616.2879	1065.1313	1486.7922	3157.5748
160.8251	622.4178	1070.4941	1492.2711	3160.6723
165.0339	629.9024	1075.2787	1493.7351	3162.8934
182.9168	640.1006	1077.8403	1494.7129	3167.3839
190.9568	703.4003	1087.9122	1496.3258	3169.5515
200.7832	713.0423	1097.1022	1500.6134	3173.8499
210.9486	725.3630	1103.5793	1504.5661	3178.7280
216.8585	732.2381	1105.6499	1506.5677	3189.7802
222.0463	750.7497	1110.2618	1508.9382	3201.7455
233.8619	760.2346	1123.1160	1509.9999	3203.7371
243.9228	766.2191	1134.7147	1511.5613	3207.3231
248.3919	776.6093	1151.4469	1517.5833	3207.8280
260.7678	781.9026	1171.4307	1519.4142	3210.8770
265.7628	785.1341	1181.9654	1521.7032	3211.5572
272.7132	791.5725	1185.9526	1521.9854	3213.6907
279.3198	799.0258	1192.1620	1526.1928	3218.0437
285.8675	800.8181	1199.6721	1529.1949	3218.9421
288.3231	820.3421	1209.8271	1532.2316	3228.8454
290.6392	829.1546	1213.8618	1536.6140	3238.2632
305.2682	831.9737	1230.9303	1541.5622	3238.5139
318.6100	837.3045	1256.9994	1543.3104	3239.0178
330.9198	873.8539	1270.5336	1550.6503	3240.4975
351.6642	879.9602	1280.4800	1599.9964	3293.6230
358.7277	888.4834	1292.5363	1623.1375	3299.6963
362.7884	893.3125	1294.3963	1631.6295	3464.6015
367.3110	910.3832	1295.9697	1668.5554	
384.8491	931.3255	1302.7343	1683.2548	
392.9670	940.7598	1306.0655	1686.6389	
408.8059	943.1609	1311.3776	1694.6133	
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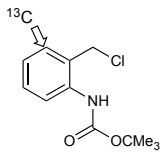

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284.9976	775.8744	1148.8039	1509.2488	3165.2811
308.4180	782.6376	1186.9315	1510.4668	3173.3644
320.5533	792.2941	1197.5856	1513.0903	3209.0887
349.2083	842.4281	1224.3467	1522.4446	3212.8572
365.8600	868.2519	1239.9590	1529.5608	3215.3055
415.2450	902.8002	1289.5520	1531.6652	3220.2705
431.2941	929.2972	1298.8253	1547.7891	3221.4157
459.4414	947.1120	1308.0370	1578.9562	3232.7804
465.8809	948.8164	1317.2583	1676.9113	3292.4818
477.3118	952.2637	1328.7045	1691.4373	3610.9487
516.9239	977.9468	1344.4544	1836.6849	
547.5555	978.8115	1359.5910	3081.7601	
579.3144	1013.9991	1424.4105	3088.9906	
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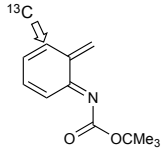

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73.7362	481.8853	1000.4940	1426.3263	3094.9501
114.9365	545.3421	1015.7703	1445.6004	3157.8343
157.4860	584.7337	1017.8807	1453.7951	3165.4722
208.2951	677.7176	1033.5748	1478.4878	3167.6979
213.2629	723.4577	1051.5387	1495.9828	3176.0067
224.4242	742.0304	1067.4805	1509.3697	3195.3988
257.3711	755.1752	1081.9019	1510.8648	3202.3535
266.8472	799.7372	1183.8189	1520.3195	3206.8266
280.5606	815.9248	1192.5040	1528.6795	3208.2091
332.9037	851.9068	1229.2276	1546.0837	3227.7093
367.0301	866.9210	1259.0493	1633.5042	3240.1602
376.6558	877.9820	1297.6798	1674.5619	3250.8702
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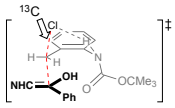

rac-S_N2-TS

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28.3123	399.4145	945.2235	1331.6656	1773.0269
33.3481	424.0755	950.1258	1341.7232	3072.6927
40.6691	431.0631	953.7739	1343.2917	3078.9746
44.8298	436.3785	956.3156	1349.5107	3083.2795
48.8145	441.1186	976.4093	1361.0606	3083.7224
58.5312	462.8235	979.5894	1362.7065	3087.8924
63.2585	467.1280	981.9703	1366.2964	3090.2095
68.5897	470.9831	997.7771	1372.7231	3092.7370
70.3142	484.5752	1002.2260	1388.2386	3092.8814
76.4055	489.7147	1004.1861	1420.4119	3097.2928
86.0620	513.4965	1014.8877	1421.3888	3137.6663
87.6856	535.5234	1016.1101	1423.9031	3138.1672
91.0497	540.2883	1020.3839	1425.4761	3146.3079
98.5215	543.2291	1024.9827	1435.7885	3156.1760
99.5670	552.7579	1030.6734	1443.0746	3158.9472
104.1105	554.7446	1034.8670	1446.1936	3160.3168
110.8035	562.4648	1060.6106	1449.1716	3163.4506
123.5275	568.8728	1062.2251	1489.5667	3165.9822
128.6653	580.7895	1066.1839	1493.0262	3170.8673
132.3119	582.4910	1069.3273	1495.3855	3171.7328
140.8692	619.1781	1071.7656	1496.1008	3172.5870
147.3769	626.7015	1078.1804	1496.8600	3178.2706
153.6124	632.6238	1080.9482	1500.7862	3182.2295
159.1828	643.7904	1095.6367	1508.1930	3194.1702
167.1725	647.0322	1099.7294	1508.6922	3195.6657
180.3264	676.9594	1106.1541	1510.6096	3203.3429
186.7427	709.2016	1107.1701	1513.9682	3203.4997
196.6923	720.4382	1116.3001	1515.5671	3209.3261
218.0561	738.8519	1122.4503	1515.8989	3214.7418
218.9367	742.5712	1138.8188	1519.5839	3215.6171
224.5015	766.2929	1150.7289	1521.2629	3222.8466
234.7854	774.9853	1158.4411	1521.9488	3223.0500
237.9152	780.7246	1181.5234	1524.7043	3227.2605
245.8155	783.2348	1181.8971	1526.0790	3230.5301
254.8817	787.9455	1186.1444	1528.0478	3232.9059
263.6852	794.8025	1196.1247	1530.0888	3240.0140
270.3522	802.2286	1211.1439	1531.4465	3240.4542
280.4090	806.2443	1221.8507	1536.5580	3245.8723
297.8224	824.7925	1226.2070	1542.7518	3257.0965
305.5492	851.4451	1255.4122	1548.6244	3383.3240
315.0213	851.9054	1269.8391	1570.1867	3481.2053
315.5469	876.5342	1276.3048	1593.2286	3539.6106
319.2512	882.1497	1294.7539	1661.0567	
340.4044	889.8866	1299.0741	1666.7430	
356.6732	899.7298	1301.6931	1683.4364	
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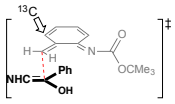

rac-Stetter-TS

-134.7827	392.9771	943.1606	1327.2419	1762.4614
15.6075	408.9136	945.4447	1339.0502	1782.4235
22.2465	428.1801	950.2270	1342.5826	3072.1771
28.1244	436.1728	954.8937	1355.4480	3079.6949
36.3673	440.3531	972.5566	1365.5896	3080.8031
45.9660	442.3508	973.2082	1373.9304	3081.3763
48.4322	466.8801	987.2927	1383.0271	3084.1465
52.9480	475.6425	994.2427	1388.4992	3088.6475
57.2907	483.4117	995.3181	1390.4231	3088.9173
65.5357	486.8836	1000.4977	1406.8775	3092.1998
67.0679	496.9834	1006.7467	1421.1823	3096.1421
72.9295	497.4729	1011.4915	1422.3350	3135.3311
82.9685	529.1992	1014.3623	1424.7837	3138.6424
94.1787	535.9543	1034.4958	1434.5257	3143.1185
96.8300	545.9986	1037.1698	1440.6875	3154.8290
110.8328	548.0114	1043.8136	1443.2351	3157.0197
115.2078	565.4802	1044.7206	1444.9333	3157.3558
121.1322	574.5815	1060.3591	1447.5042	3157.5748
125.9765	585.3529	1060.4346	1484.2776	3160.6723
131.0156	598.5223	1065.1308	1489.6993	3162.8934
137.7356	616.2821	1070.4878	1493.6307	3167.3839
144.1100	622.4168	1075.2786	1494.7200	3169.5516
160.8267	629.9001	1077.8403	1496.3247	3173.8499
165.0333	640.0974	1086.9683	1500.6275	3178.7280
182.9262	703.4022	1097.1020	1505.2992	3189.7849
190.9533	713.0219	1103.5792	1506.7542	3199.3553
200.6220	725.3022	1105.6502	1509.3185	3201.7455
210.9546	732.2343	1110.2626	1510.0202	3203.7371
216.9283	749.4256	1123.1163	1511.5649	3207.3379
222.1193	761.3954	1134.7145	1517.5839	3210.4758
233.8634	770.1310	1151.4490	1519.5608	3210.8790
243.9113	776.3576	1170.6055	1521.8320	3213.6907
248.3739	781.8853	1181.9581	1522.0864	3218.0418
260.7476	785.1668	1185.9452	1526.1972	3218.9421
265.6884	791.5637	1191.3338	1529.3052	3228.8445
272.6946	798.9955	1199.6723	1532.2325	3237.5332
279.2183	800.6317	1210.0495	1536.6151	3238.4491
285.7816	820.3274	1214.0083	1541.5616	3239.0172
288.1253	828.1286	1230.9379	1543.3108	3240.4869
290.0386	831.9662	1258.9874	1550.7276	3293.6226
305.2682	837.0303	1270.5377	1597.1096	3299.6985
318.6117	873.8326	1280.4807	1624.6274	3464.6083
331.0095	879.1986	1292.5591	1642.3749	
351.6537	888.3627	1294.4474	1668.8666	
358.7515	893.3134	1295.9891	1683.2664	
362.7842	910.3863	1303.3673	1686.6387	
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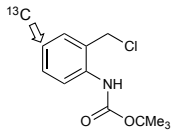

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103.3731	545.5804	1063.6895	1495.7682	3165.2811
114.1268	579.4489	1068.3289	1503.5868	3173.3644
123.3410	617.0016	1085.7836	1509.2485	3208.4667
183.7716	680.6790	1095.8149	1510.4722	3209.0889
212.4503	758.2747	1151.2971	1512.6473	3215.3051
228.8525	765.7976	1186.1499	1522.0288	3220.7028
255.2349	775.9606	1198.3792	1529.5570	3224.1236
266.9734	782.6883	1224.3049	1533.1631	3233.9230
285.0086	791.9087	1239.5763	1547.9831	3292.4819
308.8118	839.9239	1289.8020	1577.6905	3610.9487
321.0796	866.2972	1298.8253	1667.6048	
349.2617	903.9829	1308.7066	1702.4584	
365.8639	931.4067	1317.3362	1836.7346	
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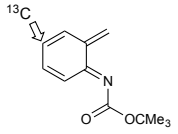

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73.7323	545.9630	1016.1844	1479.2808	3176.0067
114.9364	585.8717	1032.4237	1495.9828	3195.4032
157.2272	676.7840	1052.0900	1509.3697	3202.3535
208.2774	724.2077	1067.4819	1510.8648	3208.2090
213.2586	744.3666	1082.3013	1520.3204	3213.5748
224.5894	755.3623	1186.3334	1528.6795	3226.6078
257.4037	799.4815	1191.9936	1546.0836	3234.6538
267.0560	817.5271	1229.2316	1630.5645	3250.6395
280.5667	849.4538	1259.4348	1673.4612	3294.5564
332.9264	867.0246	1297.6801	1700.4031	
367.0158	875.1861	1307.0186	1755.1298	
376.8631	926.5769	1328.6398	1802.1056	
433.2218	947.5984	1363.6752	3084.8974	
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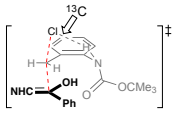

rac-S_N2-TS

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33.3374	424.0877	950.1375	1342.0228	3072.6927
40.6578	431.1786	953.9121	1343.7918	3078.9746
44.8357	436.3887	957.3469	1349.5351	3083.2795
48.7842	440.7935	976.4394	1359.6617	3083.7224
58.5134	463.1460	982.0280	1361.3285	3087.8924
63.2560	467.5359	985.6875	1366.3010	3090.2095
68.5785	471.0902	997.8150	1372.7549	3092.7370
70.1942	484.7307	1002.2275	1388.2374	3092.8814
76.3986	490.9532	1004.2082	1420.4144	3097.2928
85.9365	513.4783	1012.6789	1421.3890	3137.6665
87.5372	535.4827	1016.0812	1423.9036	3138.1672
91.0837	539.6055	1020.5658	1425.4801	3146.3079
98.5154	541.7183	1025.4351	1435.7920	3156.1760
99.5581	552.6781	1031.0951	1443.0836	3158.9472
104.0722	554.7640	1034.8779	1446.1936	3160.3168
110.8152	562.8810	1060.6106	1449.1733	3163.4506
123.5252	569.5719	1062.3619	1489.5026	3165.9822
128.6563	580.8039	1066.3198	1493.0242	3170.8673
132.3010	583.2792	1069.3199	1495.3749	3171.7328
140.9089	618.3197	1071.6871	1496.0953	3172.5870
147.3818	626.7189	1076.1670	1496.8623	3178.2706
153.6090	632.6273	1078.1883	1500.7730	3182.2295
159.1859	643.7952	1095.6370	1508.1991	3194.1702
167.1819	647.0444	1099.7412	1508.6882	3195.6657
180.0991	676.9907	1106.7025	1510.5922	3203.3429
186.7402	709.2007	1108.4598	1512.0673	3203.4997
196.6829	720.4671	1116.3015	1514.8700	3209.3261
218.0355	738.0451	1122.4571	1515.8971	3213.3543
218.9420	742.5722	1138.8226	1516.0565	3214.7419
224.5314	768.3941	1153.5127	1521.2394	3223.0498
234.7888	775.5556	1158.6210	1521.7023	3225.9348
238.0777	780.7775	1181.5142	1524.6720	3227.2605
245.8381	783.2332	1181.8964	1526.1341	3230.5297
254.8857	788.1213	1184.7127	1528.0035	3233.1437
263.8713	794.8014	1196.1247	1531.3546	3239.3222
270.4618	802.1011	1211.1429	1533.4110	3240.0271
280.4128	806.2480	1221.8480	1536.5733	3245.8733
297.8099	824.7809	1226.3487	1543.4872	3257.0966
305.5708	849.2100	1256.3875	1548.7110	3383.3242
315.1904	851.7489	1269.8393	1571.5909	3481.2053
316.2742	874.2102	1276.3065	1593.2363	3539.6106
319.4917	881.5533	1294.7556	1656.3574	
341.0804	889.8958	1299.0888	1666.7403	
356.6798	899.8693	1302.0515	1683.4364	
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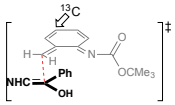

rac-Stetter-TS

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22.2475	428.2236	950.2266	1342.3211	3072.1771
28.1137	436.2224	954.9370	1354.9982	3079.6949
36.3434	440.6700	972.5634	1365.6097	3080.8031
45.9584	441.7705	979.6642	1373.7984	3081.3763
48.4391	467.3306	987.7284	1383.0828	3084.1465
52.9389	475.7038	994.8232	1388.9092	3088.6475
57.1386	483.0900	995.9634	1390.4281	3088.9173
65.5262	486.7510	1000.5105	1412.3672	3092.1998
67.0600	496.7480	1006.7466	1421.1832	3096.1421
72.9382	497.4537	1011.4925	1422.3410	3135.3311
82.9928	529.2016	1014.3645	1424.7846	3138.6424
94.1949	535.9825	1033.6793	1434.4433	3143.1185
96.9159	546.7587	1035.9036	1440.0392	3154.8290
110.8194	548.0371	1037.4243	1442.9841	3157.0197
115.2304	565.4802	1043.8222	1443.4757	3157.3558
121.1261	574.7261	1060.4310	1447.5080	3157.5748
125.9570	585.3904	1060.7868	1488.8185	3160.6723
130.9402	599.1383	1065.1314	1491.2008	3162.8934
137.7278	616.2693	1070.4947	1493.6627	3167.3839
143.5989	622.4152	1075.2789	1494.7197	3169.5516
160.8234	629.8964	1077.8403	1496.3244	3173.8499
165.0330	640.1032	1087.9915	1500.6353	3178.7280
182.9250	703.3895	1097.1024	1505.4388	3189.8357
190.9495	712.9234	1103.5794	1506.8449	3201.7455
200.6902	724.8337	1105.6502	1509.1848	3203.7371
210.9484	732.2476	1110.2629	1510.0202	3206.1973
216.8568	751.2309	1123.1162	1511.5604	3207.3405
222.1781	763.1161	1134.7300	1517.5836	3210.8769
233.8682	769.3901	1151.4507	1519.5784	3211.5311
243.9785	776.6478	1172.2029	1521.8386	3213.6907
248.3815	781.9045	1181.9696	1522.0831	3218.0428
260.5783	784.9672	1185.9541	1526.1978	3218.9421
265.5953	791.5701	1192.3465	1529.3428	3228.7618
272.7543	798.9903	1199.6723	1532.2317	3229.5053
279.3787	800.6471	1210.0518	1536.6147	3238.4436
285.8835	820.3158	1214.0397	1541.5593	3239.0169
288.3784	827.7461	1230.9388	1543.3046	3240.4876
290.7339	831.9257	1259.5033	1550.7737	3293.6215
305.2683	836.6150	1270.5380	1587.0613	3299.6988
318.6121	873.5379	1280.4816	1624.2697	3464.6075
331.0176	875.4196	1292.5942	1641.2191	
351.6363	888.1842	1294.4596	1668.8437	
358.7519	893.3127	1295.9918	1683.2653	
362.7942	910.3856	1303.3529	1686.6387	
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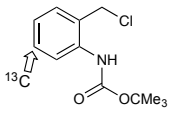

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86.9228	516.9786	1010.2313	1447.2941	3163.2913
103.0421	546.3717	1063.2814	1495.7668	3165.2811
113.9694	576.2784	1068.3281	1502.5609	3173.3644
123.2702	619.1954	1086.2014	1509.2475	3207.8491
184.1813	680.0657	1097.1489	1510.3502	3209.0891
212.4479	760.1679	1151.1516	1511.2049	3215.3054
228.8699	765.6297	1186.2921	1522.1023	3220.6084
254.9035	775.6719	1198.4508	1529.5598	3222.7933
266.9752	781.7014	1224.3170	1534.4662	3236.1309
284.9942	792.0980	1240.2196	1547.9788	3292.3779
309.0180	842.6272	1290.2272	1579.3784	3610.9487
320.7827	864.2796	1298.8255	1664.8443	
349.3810	904.0427	1308.2856	1703.1033	
365.8691	931.1024	1317.4063	1836.7198	
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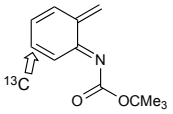

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73.7373	481.7927	1003.2932	1426.3247	3094.9501
114.9222	542.9003	1013.1963	1445.5970	3157.8343
157.0133	587.1719	1016.4672	1452.0410	3165.4722
208.2374	677.6834	1028.1151	1482.1039	3167.6979
213.2658	723.0621	1051.8381	1495.9828	3176.0067
224.6368	744.8035	1067.4814	1509.3697	3195.4033
257.4287	753.9576	1082.1291	1510.8648	3202.3535
267.0701	800.2062	1186.3720	1520.3205	3208.2090
280.5654	818.8115	1192.0218	1528.6792	3215.2853
332.9170	851.8881	1229.2197	1546.0798	3220.3843
367.0378	867.1505	1258.9259	1630.2787	3240.5136
376.9277	873.9763	1297.6800	1674.3352	3249.3986
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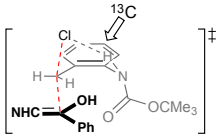

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28.2641	399.4216	945.1550	1331.2048	1773.1284
33.3232	424.0787	950.1176	1341.7877	3072.6927
40.6517	431.2341	953.7527	1343.2626	3078.9746
44.8289	436.4161	956.3386	1349.5269	3083.2795
48.7034	440.8353	976.4124	1360.1004	3083.7224
58.4865	463.1392	979.7731	1361.4846	3087.8924
63.2289	468.1571	984.1405	1366.2960	3090.2095
68.4899	471.3124	997.8030	1372.7232	3092.7370
70.0891	484.6532	1002.2254	1388.2375	3092.8814
76.3985	490.5191	1004.1923	1420.4144	3097.2928
86.1053	513.4428	1014.3664	1421.3887	3137.6665
87.6250	535.4702	1016.1431	1423.9035	3138.1672
91.0989	539.6273	1020.5470	1425.4779	3146.3079
98.5239	541.8495	1025.3607	1435.7895	3156.1760
99.5640	552.6155	1031.0015	1443.0830	3158.9472
104.1528	554.7114	1034.8751	1446.1936	3160.3168
110.7338	561.8089	1060.6107	1449.1732	3163.4506
123.5285	568.1460	1062.2260	1489.6237	3165.9822
128.6891	580.5725	1066.1544	1493.0257	3170.8673
132.3436	581.6114	1069.3229	1495.3826	3171.7328
140.8821	621.6218	1071.7052	1496.0996	3172.5870
147.3743	626.7130	1077.4979	1496.8603	3178.2706
153.6080	632.6231	1078.1958	1500.7792	3182.2295
159.2082	643.7958	1095.6371	1508.1973	3194.1702
167.2099	647.0498	1099.7437	1508.6910	3195.6657
181.0347	676.9869	1106.7094	1510.6029	3203.3429
186.7379	709.1999	1108.4079	1513.2043	3203.4997
196.7017	720.4688	1116.3019	1515.0434	3209.3261
218.0559	739.2694	1122.4543	1515.8984	3212.9097
218.9384	742.5787	1138.8221	1516.6124	3214.7418
224.5073	767.9955	1153.1528	1521.2412	3223.0498
234.7958	773.7818	1158.5398	1521.7140	3225.2370
238.0066	780.4798	1181.5144	1524.6642	3227.2605
245.8245	783.2254	1181.8967	1526.1400	3230.5300
254.8844	788.1748	1184.6143	1528.0199	3234.4893
263.7947	794.8008	1196.1247	1531.3743	3239.1287
270.4282	802.6749	1211.1459	1533.6157	3240.0270
280.4187	806.2688	1221.8584	1536.5739	3245.8746
297.8256	824.7873	1226.2844	1543.4925	3257.0966
305.5644	851.6954	1256.2369	1548.7077	3383.3242
315.1910	852.5266	1269.8393	1571.3604	3481.2053
316.1428	873.1716	1276.3065	1593.2168	3539.6105
319.4281	881.5246	1294.7550	1649.9022	
341.0963	889.8946	1299.1030	1666.7457	
356.6832	900.1614	1302.3289	1683.4366	
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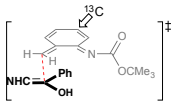
373.2467	920.4074	1308.6060	1693.4218	



rac-Stetter-TS

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22.2480	428.1904	950.2182	1342.5502	3072.1771
28.1260	436.2115	954.9381	1355.3985	3079.6949
36.3030	440.6363	972.5635	1365.6445	3080.8031
45.9658	441.8342	977.3472	1373.9423	3081.3763
48.4373	466.2640	988.3752	1383.0365	3084.1465
52.9733	475.4245	994.9389	1388.7143	3088.6475
57.1424	483.8275	997.8853	1390.4330	3088.9173
65.5105	486.7762	1000.5735	1409.0808	3092.1998
67.0478	497.1018	1006.7466	1421.1822	3096.1421
72.7811	499.4457	1011.4948	1422.3354	3135.3311
82.9578	529.1961	1014.3641	1424.7837	3138.6424
94.1793	535.9502	1028.9142	1434.5221	3143.1185
96.8742	542.2465	1037.0491	1440.6560	3154.8290
110.8780	547.9298	1039.4186	1443.2397	3157.0197
115.1896	565.4793	1043.8246	1444.8001	3157.3558
121.1258	574.7658	1060.4315	1447.5009	3157.5748
126.3068	585.4131	1060.6662	1488.8377	3160.6723
130.9926	601.1746	1065.1310	1492.5666	3162.8934
137.7403	616.2972	1070.4894	1494.4704	3167.3839
144.1115	622.4182	1075.2788	1494.7493	3169.5516
160.8267	629.9060	1077.8403	1496.3308	3173.8499
165.0333	640.0987	1087.6940	1500.6399	3178.7280
182.9241	703.4029	1097.1022	1505.5531	3189.8348
190.9521	713.0413	1103.5793	1506.8656	3200.3090
200.5894	725.3773	1105.6503	1509.6934	3201.7455
210.9397	732.2448	1110.2626	1510.0777	3203.7372
216.8287	751.5832	1123.1162	1511.5705	3207.3323
222.1762	762.2066	1134.7211	1517.5842	3209.2548
233.8555	769.0543	1151.4497	1519.6273	3210.8775
243.9441	776.4249	1172.8944	1521.8770	3213.6907
248.3508	781.8673	1181.9786	1522.2974	3218.0436
260.5385	784.6804	1185.9570	1526.2018	3218.9421
265.6328	791.5760	1190.7518	1529.3637	3228.8454
272.7645	799.0155	1199.6722	1532.2325	3237.8893
279.3196	800.6995	1210.0797	1536.6150	3238.4649
285.8912	820.3453	1214.0188	1541.5626	3239.0174
288.3336	829.3976	1230.9391	1543.2787	3240.4957
290.5880	832.0066	1258.8736	1550.8054	3293.5130
305.2715	837.8726	1270.5365	1584.2216	3299.6988
318.6213	873.4832	1280.4814	1625.3075	3464.6057
330.9445	874.8770	1292.5046	1638.1589	
351.6600	887.7416	1294.4211	1668.6358	
358.7484	893.3134	1295.9786	1683.2553	
362.7842	910.3883	1303.3690	1686.6389	
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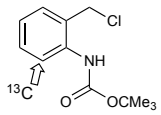

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86.7279	516.9916	1012.9227	1447.2934	3163.2913
103.4107	548.6859	1063.5585	1495.7683	3165.2811
113.9266	579.2545	1068.3287	1505.4391	3173.3644
123.3645	616.7462	1089.5633	1509.2487	3209.0887
183.7508	680.3458	1094.2333	1510.4674	3214.4260
212.4482	759.3506	1148.9067	1512.9442	3215.3061
228.9684	763.2412	1187.4187	1522.3531	3220.7034
254.9995	776.0350	1198.3493	1529.5618	3225.8949
266.9694	783.2969	1223.4752	1532.9433	3236.6560
285.0052	792.3512	1237.6220	1547.7859	3281.8874
308.4469	838.3263	1290.2810	1577.4083	3610.9475
320.7299	869.3182	1298.8254	1675.9231	
349.2073	901.4136	1308.2924	1694.5492	
365.8702	930.8631	1317.2986	1836.6842	
415.8598	947.1014	1326.8773	3081.7601	
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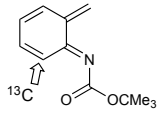

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64.9255	481.9770	1015.5788	1448.1296	3167.6979
73.7470	544.8119	1016.8715	1481.5861	3176.0067
114.9258	584.7543	1031.5563	1495.9828	3195.4032
156.9447	676.5511	1051.9576	1509.3697	3202.3531
208.2488	720.8329	1067.4814	1510.8648	3208.2089
213.2519	742.7507	1082.1203	1520.3172	3215.7996
224.4688	757.3204	1182.7891	1528.6794	3226.6243
257.3425	799.8291	1192.0436	1546.0834	3238.1426
266.8781	818.0148	1229.2240	1633.8966	3244.9315
280.5621	849.6972	1257.5744	1674.7172	3294.5564
332.8898	863.9283	1297.6799	1700.5566	
367.0415	878.4955	1306.9989	1755.0681	
376.8729	926.2359	1328.5092	1801.9370	
433.2550	947.5979	1364.1870	3084.8974	
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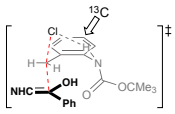

rac-S_N2-TS

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33.3317	424.0734	950.1374	1341.9530	3072.6927
40.6597	431.1430	953.6264	1343.1716	3078.9746
44.8241	436.4195	957.2247	1349.5350	3083.2795
48.7360	440.6843	976.4296	1361.3114	3083.7224
58.5030	462.8811	980.0177	1362.1377	3087.8924
63.2043	467.6651	984.9580	1366.3272	3090.2095
68.5222	471.0275	997.8068	1372.8189	3092.7370
70.2321	484.5610	1002.2289	1388.2390	3092.8814
76.4093	489.8272	1004.2370	1420.4149	3097.2928
86.1290	513.5405	1015.8141	1421.3890	3137.6665
87.7606	535.5176	1016.6619	1423.9036	3138.1672
91.0803	540.3141	1020.5683	1425.4668	3146.3079
98.5345	543.5444	1025.4577	1435.7907	3156.1760
99.5520	552.7732	1031.0730	1443.0817	3158.9472
104.2839	554.7729	1034.8777	1446.1937	3160.3168
110.6801	562.7743	1060.6107	1449.1732	3163.4506
123.5380	569.1976	1062.3516	1490.4161	3165.9822
128.7294	580.7721	1066.3118	1493.0285	3170.8673
132.3455	582.6988	1069.3281	1495.3862	3171.7328
140.8353	618.9473	1071.8380	1496.1021	3172.5870
147.3752	626.7051	1078.1263	1496.8606	3178.2706
153.6087	632.6246	1078.3296	1500.7879	3182.2295
159.1842	643.7915	1095.6367	1508.1918	3194.1702
167.1549	647.0389	1099.7326	1508.6922	3195.6657
180.1152	676.9730	1106.6085	1510.6096	3203.3429
186.7487	709.1997	1107.9238	1513.9950	3203.4997
196.6875	720.4633	1116.3007	1515.5689	3209.3261
218.0406	738.3629	1122.4488	1515.8989	3214.7418
218.9404	742.5690	1138.8212	1519.7383	3216.7495
224.6335	766.6154	1151.3648	1521.2645	3223.0498
234.8137	775.6261	1158.4559	1521.9524	3223.6063
238.0902	780.8073	1181.5229	1524.6597	3227.2605
245.8430	783.2388	1181.8966	1526.0978	3230.5298
254.8869	787.6121	1186.0553	1528.0714	3231.2861
263.9191	794.8025	1196.1247	1530.6082	3239.9870
270.4920	802.1744	1211.1442	1531.4103	3240.1144
280.4186	806.2691	1221.8495	1536.5564	3245.8752
297.8028	824.7846	1226.1865	1542.8281	3257.0966
305.5618	847.9545	1254.1690	1548.5812	3383.3242
315.1211	851.7377	1269.8392	1570.0293	3481.2053
315.8229	876.8995	1276.3061	1593.2472	3539.6097
319.3468	882.1394	1294.7547	1661.8606	
340.5617	889.8651	1299.0995	1666.7301	
356.6478	898.0045	1302.2151	1682.3011	
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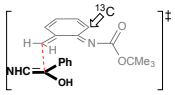
373.2246	920.2489	1308.4808	1685.2090	



rac-Stetter-TS

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28.1466	436.2275	954.9392	1355.2849	3079.6949
36.3369	440.6894	972.5632	1365.5946	3080.8031
45.9790	442.2518	979.1279	1373.8520	3081.3763
48.4281	465.8091	988.4652	1383.1056	3084.1465
52.9965	475.4326	994.9314	1388.5928	3088.6475
57.2959	483.1147	998.0876	1390.4106	3088.9173
65.5042	486.7365	1000.5981	1409.2881	3092.1998
67.0554	497.1311	1006.7469	1421.1821	3096.1421
72.8722	500.0805	1011.4951	1422.3353	3135.3311
82.9722	529.2059	1014.3656	1424.7850	3138.6424
94.1528	535.9610	1031.6060	1434.2980	3143.1185
96.8451	545.5071	1037.1642	1437.4032	3154.8290
110.9002	547.9621	1042.3863	1441.7596	3157.0197
115.1379	565.4802	1043.8222	1443.2832	3157.3558
121.1272	574.5738	1060.4304	1447.5005	3157.5748
125.8285	585.3425	1060.6659	1484.7183	3160.6723
131.0097	598.1531	1065.1310	1491.7444	3162.8934
137.7303	616.2849	1070.4941	1494.0682	3167.3839
143.7642	622.4178	1075.2789	1494.7462	3169.5516
160.8231	629.8988	1077.8403	1496.3278	3173.8499
165.0337	640.1001	1087.4053	1500.6261	3178.7280
182.9248	703.3974	1097.1023	1505.3170	3189.8365
190.9522	712.9812	1103.5788	1506.7432	3201.7455
200.7668	725.0305	1105.6502	1509.4811	3203.7371
210.9357	732.2405	1110.2628	1510.0287	3207.3228
216.7505	749.2931	1123.1162	1511.5679	3207.8148
222.0779	762.6810	1134.7254	1517.5842	3210.8770
233.8540	770.5079	1151.4504	1519.5811	3211.5273
243.9380	776.3479	1172.8370	1521.8441	3213.6907
248.3803	781.8981	1181.9633	1522.1196	3218.0437
260.6011	784.8078	1185.9445	1526.1978	3218.9421
265.7028	791.5667	1189.5308	1529.2994	3228.8455
272.7455	799.0287	1199.6722	1532.2326	3238.2611
279.2685	800.8365	1209.7399	1536.6151	3238.5131
285.8152	820.3359	1213.7781	1541.5619	3239.0178
288.2364	827.2222	1230.9386	1543.3058	3240.4976
290.2732	831.9142	1257.5218	1550.7150	3283.0578
305.2712	836.0323	1270.5333	1597.4946	3299.6983
318.6146	873.8251	1280.4819	1625.5899	3464.6022
330.9234	879.5834	1292.3451	1639.9692	
351.6610	885.5681	1294.3460	1668.5649	
358.7350	893.3133	1295.9689	1683.2507	
362.7770	910.3902	1303.3632	1686.6389	
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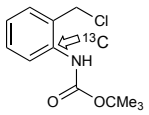

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103.6425	544.2992	1062.7647	1495.7682	3165.2811
114.0928	579.7591	1068.3275	1504.2588	3173.3644
123.3235	618.2547	1091.2804	1509.2486	3209.0887
184.2562	679.8016	1094.3278	1510.4809	3214.4509
212.4529	754.5797	1150.6682	1513.3457	3215.3061
229.2358	765.1606	1187.7666	1522.2823	3220.7035
255.3513	775.7145	1197.7586	1529.5588	3225.9209
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284.9916	791.2888	1237.7722	1547.7720	3292.4652
308.7756	840.6220	1289.2599	1574.8277	3610.9481
320.8121	869.9046	1298.8248	1666.1722	
349.3750	904.2142	1305.5485	1700.9194	
365.8642	931.2223	1316.0473	1836.4329	
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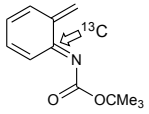

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65.5230	481.3036	1016.3349	1449.5068	3167.6979
73.7023	546.1012	1018.8364	1485.5586	3176.0067
114.9343	587.4539	1033.8791	1495.9827	3195.4016
157.1540	677.6165	1049.5930	1509.3694	3202.3535
207.9893	723.8012	1067.4753	1510.8648	3208.2090
213.2427	742.9402	1080.8176	1520.3019	3215.8286
224.4819	752.1321	1178.5479	1528.6795	3228.2602
257.4526	798.8621	1190.9279	1546.0695	3241.0498
267.4106	814.7591	1229.2268	1641.9580	3250.9120
280.5704	851.4220	1249.6708	1657.4942	3294.5559
332.9267	862.9999	1297.6795	1698.2188	
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376.6544	926.3863	1327.1152	1801.9163	
432.8995	947.5966	1360.7881	3084.8974	
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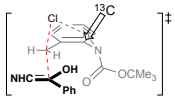
449.5374	972.0170	1422.3785	3094.9501	



rac-S_N2-TS

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28.3364	399.4262	944.9567	1327.8035	1772.7481
33.3460	424.0794	950.1032	1340.5158	3072.6927
40.6730	431.1813	952.9762	1341.9502	3078.9746
44.8271	436.4095	955.9395	1349.5200	3083.2795
48.8067	439.8637	976.4351	1359.9477	3083.7224
58.5300	462.9621	982.1713	1361.4441	3087.8924
63.2416	467.4896	985.3814	1366.2945	3090.2095
68.5902	470.9556	997.8147	1372.6525	3092.7370
70.3302	484.4775	1002.2296	1388.2352	3092.8814
76.4177	488.1609	1004.2423	1420.4053	3097.2928
86.1058	513.3952	1015.8914	1421.3889	3137.6665
87.7311	535.5182	1016.8558	1423.9037	3138.1672
91.1039	540.2439	1020.5903	1425.4723	3146.3079
98.5385	542.9107	1025.4967	1435.7920	3156.1760
99.5502	552.8298	1031.1400	1443.0772	3158.9472
104.3083	554.7553	1034.8796	1446.1933	3160.3168
110.6850	562.9588	1060.6105	1449.1736	3163.4506
123.5406	569.5435	1062.1150	1489.6340	3165.9822
128.7337	580.8104	1066.0887	1493.0255	3170.8673
132.3482	583.0270	1069.3298	1495.3818	3171.7328
140.8169	619.5473	1071.8592	1496.0986	3172.5870
147.3848	626.7206	1078.1826	1496.8570	3178.2706
153.6122	632.6297	1083.4302	1500.7821	3182.2295
159.2174	643.7967	1095.6367	1508.1986	3194.1702
167.2316	647.0489	1099.7250	1508.6918	3195.6657
180.9749	676.9825	1103.9320	1510.6054	3203.3429
186.7516	709.2017	1106.8776	1513.5827	3203.4997
196.7076	720.4715	1116.3006	1515.3890	3209.3261
218.1160	735.4596	1122.4582	1515.8986	3214.7418
218.9481	742.5527	1138.8226	1517.4428	3218.7569
224.8223	768.2295	1152.9960	1521.2467	3223.0498
234.8203	775.3986	1158.5370	1521.7699	3227.1970
238.0018	780.8381	1181.5240	1524.6820	3227.2609
245.8277	783.2404	1181.8970	1526.1287	3230.5301
254.8853	787.7306	1186.4369	1528.0124	3234.9781
263.7619	794.8026	1196.1246	1531.3283	3240.0195
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297.8253	824.7742	1224.6061	1542.8578	3257.0966
305.5543	850.1265	1248.2244	1548.6173	3383.3237
315.1594	851.7469	1269.8390	1565.7880	3481.2035
315.8444	877.1717	1276.3026	1592.8793	3539.6102
319.3460	882.5056	1294.7429	1656.7963	
341.0544	889.9071	1299.1046	1666.7409	
356.6734	900.1213	1301.9182	1683.4358	
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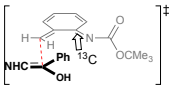

***rac*-Stetter-TS**

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22.2481	428.2028	950.2072	1342.2035	3072.1771
28.1538	436.1454	954.9352	1354.5652	3079.6949
36.3853	440.1470	972.5634	1365.6038	3080.8031
45.9856	441.8515	979.6361	1373.6037	3081.3763
48.4361	466.9152	988.2348	1382.7444	3084.1465
52.9988	476.0308	994.9315	1388.6508	3088.6474
57.3532	484.0899	998.3511	1390.4304	3088.9173
65.5093	486.8990	1000.5917	1411.5794	3092.1998
67.0755	496.3519	1006.7467	1421.1821	3096.1421
73.0365	497.1875	1011.4952	1422.2197	3135.3311
83.0156	529.2080	1014.3653	1424.7772	3138.6424
94.1795	535.9734	1034.5566	1433.3291	3143.1185
96.9341	546.8509	1037.1755	1436.8993	3154.8290
110.8864	548.0378	1043.8162	1441.7665	3157.0197
115.2171	565.4796	1045.1944	1443.3806	3157.3558
121.1316	574.7064	1059.1139	1447.5098	3157.5748
126.3098	585.4010	1060.4319	1483.6511	3160.6723
131.0878	600.4500	1065.1301	1493.1815	3162.8934
137.7369	616.2656	1070.4733	1494.6717	3167.3839
143.7522	622.4157	1075.2756	1495.6437	3169.5516
160.8249	629.8995	1077.8403	1496.3528	3173.8499
165.0339	640.1026	1084.3428	1500.6395	3178.7280
182.9150	703.3966	1097.1021	1502.5899	3189.8346
190.9551	713.0151	1103.5780	1506.4640	3201.7455
200.5022	724.8844	1105.6500	1508.1814	3203.7370
210.9342	732.2434	1110.2627	1509.9877	3207.3231
216.7813	750.0551	1123.1164	1511.5539	3207.8294
222.0479	762.5357	1134.7239	1517.5844	3210.8770
233.8535	762.9253	1151.4509	1519.2561	3211.5590
243.8553	776.6381	1171.5751	1521.1801	3213.6907
248.3255	781.9070	1181.9691	1521.9297	3218.0437
260.7015	785.0292	1185.9490	1526.1835	3218.9421
265.7827	791.5656	1189.8446	1529.0880	3228.8454
272.7487	798.9531	1199.6715	1532.2324	3238.2647
279.3404	800.4843	1208.4892	1536.6149	3238.5143
285.9301	820.2365	1213.2233	1541.5552	3239.0178
288.3837	826.9121	1230.9305	1543.2745	3240.4976
290.9922	831.9460	1248.8548	1550.3297	3293.6154
305.2676	836.4181	1270.5195	1598.9449	3299.6979
318.6106	873.8545	1280.4689	1616.3137	3464.5760
330.9938	879.6407	1289.7230	1640.6510	
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358.7439	893.3137	1295.8767	1683.2537	
362.7838	910.3892	1303.3674	1686.6389	
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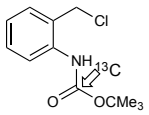

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86.8609	516.9205	1014.4887	1447.2645	3163.2912
103.5550	549.4333	1063.6058	1495.7671	3165.2811
114.0886	580.6313	1068.3275	1506.2574	3173.3638
123.3633	620.4356	1093.0960	1509.2465	3209.0884
184.0299	681.4499	1096.7895	1510.4329	3214.4508
212.4545	750.9578	1151.5649	1512.3518	3215.3050
229.3084	760.2694	1187.8288	1522.5319	3220.7036
255.4973	765.6039	1198.4475	1529.5607	3225.9213
266.9578	782.9917	1220.0763	1532.9820	3236.6691
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309.1465	843.1996	1277.3729	1580.1378	3610.9482
320.6469	869.6786	1298.8196	1679.2506	
349.1490	905.0517	1307.9795	1707.0107	
365.6764	931.4151	1313.9439	1789.8736	
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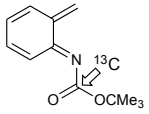

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65.5912	475.8981	978.7226	1422.3772	3087.9210
73.5458	482.1135	1004.1119	1426.2042	3094.9495
114.9325	545.6926	1016.3969	1445.5731	3157.8341
157.5098	588.9779	1019.2766	1453.8606	3165.4721
208.5662	677.3420	1033.9083	1486.2205	3167.6978
213.2740	718.7238	1051.1061	1495.9823	3176.0062
224.9273	741.8249	1067.4775	1509.3692	3195.4033
257.4638	757.3424	1081.0924	1510.8634	3202.3531
267.2812	799.1106	1186.7745	1520.1862	3208.2084
280.5562	818.1900	1192.4697	1528.6730	3215.8294
332.4721	837.7061	1224.4625	1546.0004	3228.2603
366.6485	868.1058	1259.2716	1648.4003	3241.0501
376.3186	876.6418	1293.4674	1674.6370	3250.9193
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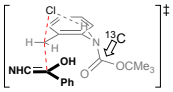

rac-S_N2-TS

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33.3522	424.0869	950.1238	1332.8905	3072.6927
40.6817	431.0589	953.3025	1342.3523	3078.9746
44.8183	436.2079	956.3532	1349.4916	3083.2795
48.8147	440.7552	976.4290	1361.2759	3083.7223
58.5320	463.2354	982.3616	1366.1057	3087.8923
63.2676	467.8164	985.6661	1367.5259	3090.2095
68.5510	471.0894	997.8162	1372.7239	3092.7370
70.3446	484.7453	1002.2298	1388.2324	3092.8808
76.3200	490.9970	1004.2447	1420.3787	3097.2928
86.0289	513.5606	1015.8973	1421.3877	3137.6665
87.7013	535.5300	1016.9019	1423.9034	3138.1672
91.1244	540.4134	1020.5955	1425.4206	3146.3079
98.5330	544.3027	1025.5050	1435.7924	3156.1760
99.5439	552.8783	1031.1466	1443.0821	3158.9470
104.3076	554.8044	1034.8798	1446.1604	3160.3168
110.8235	563.2241	1060.6107	1449.1731	3163.4506
123.5255	569.8852	1062.3207	1491.2993	3165.9821
128.6960	580.6506	1066.2895	1493.0343	3170.8673
132.2783	583.5464	1069.3311	1495.3916	3171.7325
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147.3762	626.7326	1078.1826	1496.8531	3178.2704
153.5993	632.6359	1083.6218	1500.7930	3182.2295
159.2237	643.7962	1095.6371	1508.1729	3194.1699
167.2073	647.0122	1099.7427	1508.6929	3195.6657
180.9585	676.6523	1106.6738	1510.6026	3203.3422
186.7487	709.1547	1107.9864	1514.0607	3203.4997
196.6990	720.4195	1116.3009	1514.9685	3209.3261
218.1236	739.2929	1122.4608	1515.8989	3214.7418
218.9413	742.5804	1138.8214	1520.8663	3218.7583
224.8982	755.7147	1154.1326	1521.3071	3223.0498
234.8348	773.2649	1158.6723	1522.4782	3227.2007
238.0342	780.0807	1181.5217	1523.3385	3227.2609
245.8410	781.3307	1181.8972	1525.3844	3230.5301
254.8870	783.2520	1186.4426	1526.4551	3234.9923
263.8456	794.8016	1196.1246	1528.1131	3240.0195
270.4476	800.7626	1211.1392	1531.4223	3241.3143
280.4215	806.2111	1221.8052	1536.5588	3245.8823
297.8266	824.7879	1224.8161	1542.6591	3257.0966
305.5679	851.7109	1256.5741	1548.7180	3383.3242
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316.1157	877.2294	1276.3004	1592.8898	3539.6102
319.4298	882.5384	1294.7546	1665.8535	
341.1233	889.9060	1298.8100	1666.7428	
356.3724	900.2137	1300.4274	1683.4344	
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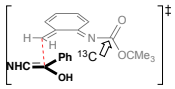

***rac*-Stetter-TS**

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28.1481	436.2292	954.9122	1354.9756	3079.6949
36.3975	440.5035	972.5577	1365.5988	3080.8031
45.9907	441.3213	979.7969	1373.8926	3081.3763
48.4409	466.9523	988.5074	1382.5009	3084.1465
53.0039	476.0215	994.9341	1387.8716	3088.6467
57.3037	484.3816	998.4000	1390.4040	3088.9173
65.4115	486.9505	1000.6070	1411.4819	3092.1998
67.0622	497.1409	1006.7469	1421.1828	3096.1421
73.0409	500.1184	1011.4937	1422.2988	3135.3311
83.0188	529.2103	1014.3667	1424.7840	3138.6424
94.1854	535.9831	1034.5665	1434.4974	3143.1185
96.9337	547.2058	1037.1774	1440.7020	3154.8289
110.9056	548.1259	1043.8172	1443.1931	3157.0197
115.2233	565.4804	1045.7908	1445.3110	3157.3556
121.1145	574.8259	1060.4314	1447.5044	3157.5748
126.3805	585.4296	1060.7372	1488.3937	3160.6723
130.8082	602.1325	1065.1282	1493.1834	3162.8934
137.7405	616.3039	1070.4919	1494.7077	3167.3839
144.1749	622.4180	1075.2782	1496.2685	3169.5516
160.8232	629.9084	1077.8403	1496.6922	3173.8493
165.0339	640.1013	1087.4453	1500.6504	3178.7280
182.9287	703.3927	1097.1020	1505.2408	3189.8364
190.9560	712.9573	1103.5759	1506.7506	3201.7455
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216.8821	749.3687	1123.1142	1511.5659	3207.8300
222.1949	762.5558	1134.6716	1517.5844	3210.8762
233.8750	765.6939	1151.4445	1519.5718	3211.5593
243.9783	772.5806	1169.3353	1521.8643	3213.6907
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260.7355	782.1088	1185.9583	1526.1990	3218.9421
265.9522	791.4910	1191.9115	1529.3445	3228.8454
272.8087	795.6344	1199.6695	1532.2325	3238.2648
279.4040	799.1496	1202.8688	1536.6151	3238.5144
285.9201	820.2652	1212.5987	1541.5631	3239.0178
288.4117	829.2227	1230.9364	1543.2318	3240.4976
290.9145	831.8991	1258.8093	1550.7733	3293.6229
305.2673	834.8071	1270.5376	1603.1423	3299.6988
318.6050	873.8187	1280.0123	1625.5942	3464.6062
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351.3792	889.2986	1293.8553	1668.8514	
358.6288	893.3139	1295.7234	1683.2658	
362.7096	910.3886	1303.3662	1686.6387	
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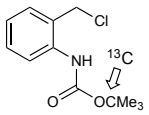

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114.1927	580.2380	1066.9016	1506.2710	3173.3559
123.3314	619.6010	1093.3942	1509.0473	3209.0858
184.3109	681.4567	1097.1427	1509.7697	3214.4510
212.4415	760.4702	1151.8253	1515.5936	3215.3029
228.9554	765.8327	1187.8364	1521.3612	3220.7037
255.6484	776.0978	1198.4831	1528.4453	3225.9213
266.9766	783.4995	1209.0448	1536.3586	3236.6691
285.0084	792.4715	1237.7150	1546.6548	3292.4837
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321.3454	868.1779	1278.8427	1679.3515	
349.3081	905.1022	1295.3787	1707.4628	
365.8061	931.0803	1314.4581	1836.5864	
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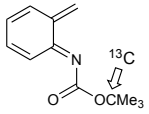

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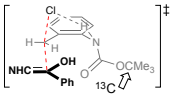
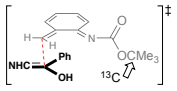
114.8657	588.3828	1033.9092	1495.9728	3195.4033
157.5043	677.7504	1050.7902	1509.0784	3202.3512
208.6578	724.2515	1066.0487	1510.3088	3208.2057
213.2641	744.7053	1082.1057	1518.5912	3215.8294
224.6416	757.3479	1186.8527	1527.5173	3228.2604
257.4687	799.7383	1192.4733	1544.6783	3241.0502
267.4208	818.6104	1210.4314	1648.7050	3250.9195
280.5612	852.1523	1259.4930	1674.7470	3294.5564
332.7545	868.0881	1270.1977	1705.8150	
366.9875	879.0551	1282.1958	1761.2795	
376.6740	922.1311	1324.2825	1801.9584	
431.9863	944.2139	1366.4636	3084.8901	
439.6038	947.2937	1415.6172	3087.9182	
449.6545	972.1915	1420.9446	3094.9470	



rac-S_N2-TS

-472.4690	378.7438	926.6782	1311.1453	1696.2329
20.6567	385.6854	939.9318	1327.5624	1742.2495
28.3413	399.4267	941.9601	1332.3770	1772.9710
33.3267	424.0816	946.7379	1341.9135	3072.6927
40.6821	429.9069	952.9470	1343.3155	3078.9746
44.8028	435.4966	956.2589	1349.5386	3083.2795
48.7896	440.6161	976.3722	1361.3114	3083.7169
58.5357	462.9609	982.3463	1366.1978	3087.8865
63.2779	466.4932	985.6968	1367.9508	3090.2095
68.5747	469.4989	997.8163	1372.8577	3092.7370
70.3400	484.6789	1002.2299	1388.2393	3092.8791
76.3987	490.3916	1004.2454	1419.6586	3097.2928
86.1545	513.5488	1015.8975	1420.4021	3137.6665
87.7425	535.5290	1016.9031	1423.6799	3138.1672
91.1224	540.4129	1020.5959	1423.9207	3146.3079
98.5164	544.3334	1025.5049	1435.7927	3156.1760
99.5370	552.8811	1031.1466	1443.0852	3158.9451
104.2987	554.8073	1034.8798	1446.0067	3160.3168
110.8143	563.2258	1060.6098	1449.1735	3163.4506
123.5227	569.8620	1061.0130	1491.4195	3165.9790
128.7261	580.7876	1064.9221	1492.9550	3170.8673
132.2913	583.4466	1069.3248	1495.3916	3171.7263
140.9627	621.3211	1071.8585	1496.1066	3172.5870
147.3849	626.7301	1078.1826	1496.8624	3178.2642
153.6080	632.6354	1083.6328	1500.7933	3182.2295
159.2216	643.7990	1095.6371	1507.8534	3194.1677
167.2381	647.0518	1099.7439	1508.6842	3195.6657
181.0979	676.9757	1106.7184	1510.4875	3203.3405
186.7516	709.2016	1108.5632	1513.9531	3203.4997
196.7073	720.4722	1116.3022	1514.2138	3209.3261
218.1207	740.1478	1122.4609	1515.8989	3214.7418
218.9335	742.5932	1138.8220	1520.8594	3218.7583
224.9285	768.5089	1154.2107	1521.3092	3223.0498
234.8160	775.7214	1158.6718	1522.6038	3227.2008
238.0767	780.8645	1181.5235	1524.6054	3227.2609
245.8425	783.2417	1181.8968	1524.7853	3230.5301
254.8856	788.3880	1186.4445	1528.1069	3234.9924
263.8456	794.8029	1196.1244	1531.4226	3240.0195
270.4596	802.5519	1208.2612	1534.0112	3241.3144
280.4164	806.2823	1211.2472	1536.5768	3245.8825
297.8272	824.7931	1221.8718	1542.3103	3257.0966
305.5726	851.2626	1255.2618	1548.7474	3383.3243
315.2055	851.8589	1269.8387	1572.9308	3481.2043
316.4321	875.8972	1272.1157	1593.3256	3539.6102
319.5426	882.2074	1276.3034	1666.0815	
341.2106	889.9080	1281.2403	1666.7512	
356.6425	900.1846	1294.7585	1683.4366	
363.0397	902.3213	1302.4621	1685.2087	
373.2441	920.3801	1305.9599	1694.6542	



rac-Stetter-TS

-135.0227	436.1089	988.4713	1412.2973	3138.6424
15.6016	439.3364	994.9395	1419.5987	3143.1185
22.2462	440.8787	998.4208	1420.6169	3154.8265
28.0766	466.4108	1000.6098	1424.7850	3157.0197
36.4018	474.7760	1006.7469	1434.5354	3157.3524
45.9749	483.5047	1011.4934	1440.7216	3157.5748
48.3496	486.8836	1014.3662	1443.0689	3160.6648
52.9984	497.1335	1034.5668	1445.3200	3162.8934
57.3433	500.0489	1037.1775	1447.5123	3167.3839
65.5356	529.2111	1043.8188	1489.3009	3169.5516
67.0863	535.9842	1045.8382	1493.2111	3173.8429
73.0261	546.6132	1059.5461	1494.7140	3178.7280
83.0192	548.0116	1060.4317	1496.2765	3189.8366
94.2064	565.4801	1063.8219	1496.7618	3201.7455
96.9343	574.7005	1070.4786	1500.6568	3203.7348
110.9076	585.4075	1075.2761	1505.4823	3207.3231
115.2350	601.2338	1077.8403	1506.6761	3207.8301
121.0630	616.3032	1087.8428	1509.3946	3210.8742
126.3886	622.4179	1097.1024	1509.6906	3211.5593
131.1498	629.9084	1103.5791	1511.5653	3213.6907
137.7409	640.1042	1105.6501	1517.5844	3218.0437
144.1655	703.4035	1110.2627	1518.5572	3218.9421
160.8272	713.0417	1123.1160	1521.7722	3228.8455
165.0334	725.3704	1134.7145	1522.0251	3238.2648
182.9296	732.2484	1151.4462	1524.9369	3238.5144
190.9524	751.7215	1172.0416	1529.3465	3239.0179
200.7452	763.1700	1181.9771	1532.2326	3240.4976
210.9307	771.0001	1185.9580	1536.6151	3293.6232
216.9063	776.6738	1191.4363	1541.5624	3299.6988
222.1059	781.9104	1199.6719	1541.8223	3464.6099
233.8747	785.2576	1202.8126	1550.7833	
243.9653	791.5760	1212.5365	1603.3895	
248.3975	799.0156	1230.6523	1625.6795	
260.7715	800.5855	1253.6314	1642.6124	
265.9014	820.3436	1266.3291	1668.8663	
272.8007	828.7730	1270.5278	1683.2665	
279.4283	831.9790	1277.9179	1686.6389	
285.9403	837.2250	1280.5040	1694.6651	
288.4346	873.8702	1294.7357	1721.6434	
291.1210	880.2630	1296.3451	1762.4710	
305.2718	889.4712	1303.4664	1782.3036	
318.6200	893.3140	1311.3278	3072.1771	
331.0528	910.3819	1326.3922	3079.6949	
351.5946	931.3255	1339.0550	3080.7959	
358.7231	938.7013	1342.6070	3081.3763	
362.7536	941.2721	1355.4938	3084.1434	
367.2686	942.8441	1365.6434	3088.6441	
384.9019	946.7007	1373.9520	3088.9173	
392.9627	954.9360	1383.1107	3092.1998	
408.9284	972.5436	1388.8726	3096.1421	
428.1999	979.7861	1390.4359	3135.3311	