# Synthesis of Cyclopropenium-Appended Organocatalysts and Applications

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## *Abstract*

Enclosed within this dissertation is the development and application of multiple cyclopropenium-containing compounds formally belonging to two closely-related classes of organocatalysts, namely thioureas and squaramides. The former catalyst, coined as a thiourea-cyclopropenium, is deployed in pyranylation reactions of alcohols and phenols, as well as Friedel–Crafts alkylation, while the latter—a squaramide-cyclopropenium catalyst—targets oxime ether bond formation. Accompanying these innovative synthetic methodologies are comprehensive experimental and computational mechanistic studies that work in synergy to delineate numerous key features, all of which provide valuable information with respect to understanding the multifaceted nature of catalysis. Experimental and spectral data are provided for all new compounds.

## *Acknowledgements*

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A very special thanks is owed to my parents, Emir and Tanya Smajlagic. It is because of their unconditional love and support that allowed me to successfully complete my Doctoral studies. Not only did they provide emotional and mental support, but they

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# Table of Contents

## *List of Tables*

## *List of Schemes*

## *List of Figures*

## *List of abbreviations*

| | |
|---|---|
| AEXB | anti-electrostatic halogen bond |
| BHB | three-centered hydrogen bond |
| BINOL | 1,1'-bi-2-napthol |
| CsF | caesium fluoride |
| DCM | dichloromethane |
| DEPT | distortionless enhancement by polarization transfer |
| DFT | density functional theory |
| DHP | 3,4-dihydro-*2H*-pyran |
| DMSO | dimethyl sulfoxide |
| dr | diastereomer ratio |
| er | enantiomer ratio |
| ESP | electrostatic potential surface |
| H-bond | hydrogen bond |
| H-bonding | hydrogen bonding |
| HOMO | highest occupied molecular orbital |
| KF | potassium fluoride |
| KIE | kinetic isotope effect |
| LUMO | lowest unoccupied molecular orbital |
| MCCS | Monte Carlo conformational searches |
| MeCN | acetonitrile |
| MTP | 2-methoxytetrahydropyran |
| NBO | natural bond order |

| | |
|---|---|
| NCI | non-covalent interaction |
| NMR | nuclear magnetic resonance |
| NOESY | nuclear Overhauser enhancement spectroscopy |
| SOMO | singularly-occupied molecular orbital |
| THF | tetrahydrofuran |
| TLC | thin layer chromatography |
| TOF | turnover frequency |
| RPKA | reaction progress kinetic analysis |
| VTNA | variable time normalization analysis |
| vtNMR | variable temperature nuclear magnetic resonance |
| XB | halogen bond |

## *1.0 Introduction*

The field of catalysis has significantly contributed to the development of innovative technologies enabling the sustainable production of bulk and fine chemicals.[1] The prospect of developing an efficient catalyst comes with mechanistic understanding. After a well-devised catalyst is realized, various empirical methods, and/or physical organic parameters, are routinely employed for gaining insight and probing the mechanistic underpinnings of catalysis. Moreover, classical kinetics, Reaction Progress Kinetic Analysis (RPKA)[2] and Variable Time Normalization Analysis (VTNA)[3] serve as indispensable kinetic techniques to provide a better understanding of the catalyzed reaction pathway(s), which is of use in both industrial and academic settings. This spans from metal- to metal-free-catalyzed, i.e., organocatalyzed, approaches.[4]

Organocatalyzed processes offering broad chemical scope, chemo-, regio-, and/or stereoselectivity, and rapid reaction rates, is a major theme of modern-day catalysis.[5] The impetus supporting this burgeoning field being the attractive non-metal feature,[5d] functional group tolerance,[6] and eco-friendliness.[5d] In this context, thiourea organocatalysis has gained widespread popularity and with it broad utility,[5e,7] such as in host–guest (catalyst–substrate) applications involving attractive interactions facilitating chemical transformations. This includes uses in anion-binding catalysis,[8] H-bond donor/Brønsted acid catalysis,[5e,9] charge-enhanced catalysis,[10] and multifunctional catalysis.[11] Alternatively, squaramides have appeared in the literature as superior counterparts to thioureas, wherein their aromatic nature plays an influential role in promoting organic reactions.[12]

As synthetic organic chemistry evolves over time so do the approaches taken to reach the target compounds. Despite the utility and common use of conventional neutral catalysts to accelerate reactions, the expectations of catalyst performance continues to increase,[5a] e.g., turnover frequency (TOF), reaction rates, catalyst stability etc. In spite of this, as a putative solution, many efforts have been focused towards pursuing charged catalysts as, arguably, superior alternatives to access desired reactivity.[8c,10,13] In particular, non-benzenoid systems, such as aromatic aminocyclopropenium ions, have attracted attention from both experimental- and theoretical chemists owing to its remarkable properties, including high cation stability, low oxidation potential and an atypical reactivity profile.[14] Below follows generic examples of non-benzenoid structures (**1**–**3**) that have been found to promote organic reactions (Figure 1).

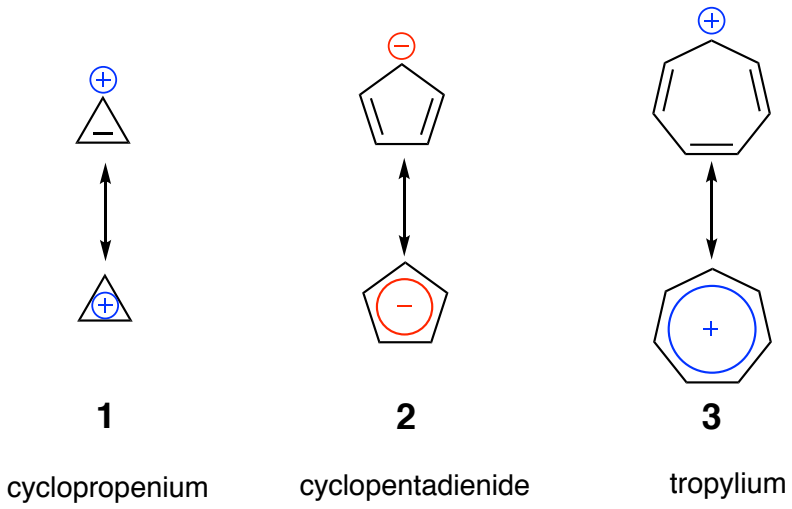



***Figure 1.*** *Non-benzenoid aromatic ions.*

The focal point of this thesis will be placed upon the innovative discoveries centered around cyclopropenium-appended (**1**) molecules as organocatalysts targeting various applications. The discussion will begin with the discovery of the thiourea-

cyclopropenium organocatalyst, where it was found to efficiently catalyze the pyranylation of phenols, primary, secondary and tertiary alcohols under operationally simple and mild reaction conditions (Figure 2).[15] Accompanying this synthetic work is a comprehensive mechanistic investigation[16] revealing several salient features that govern the mechanism at hand, ultimately leading to the proposal of a most probable reaction pathway.

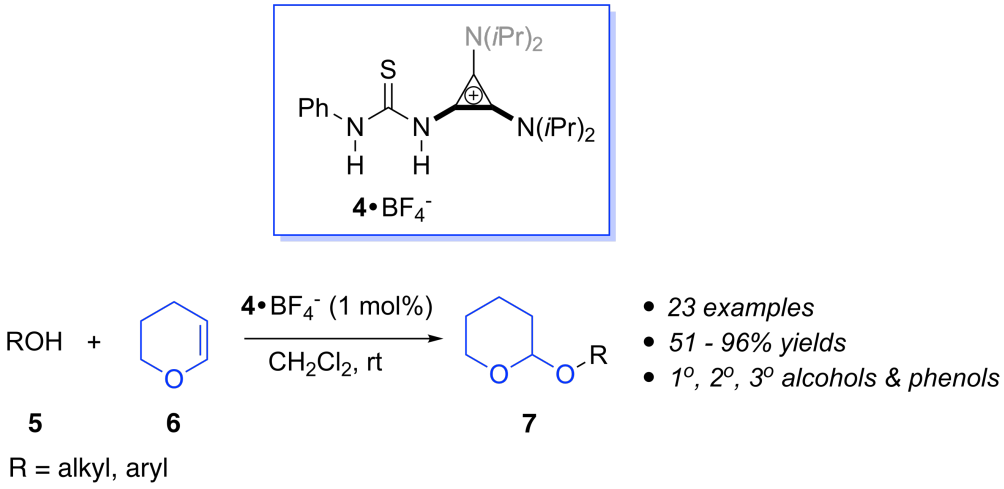



***Figure 2.*** *General conditions for the pyranylation of alcohols and phenols using thiourea catalyst* ***4***$\cdot BF_4^-$.

Next, the synthetic utility and multifunctional nature of catalyst **4**$\cdot BF_4^-$ will be underscored by presenting a novel Friedel–Crafts alkylation method[17] (Figure 3). This section leads to an interesting discussion since the reactivity taking place at the catalyst's active site was found to shift from one end of the substrate activation continuum to the other—a true dichotomy!

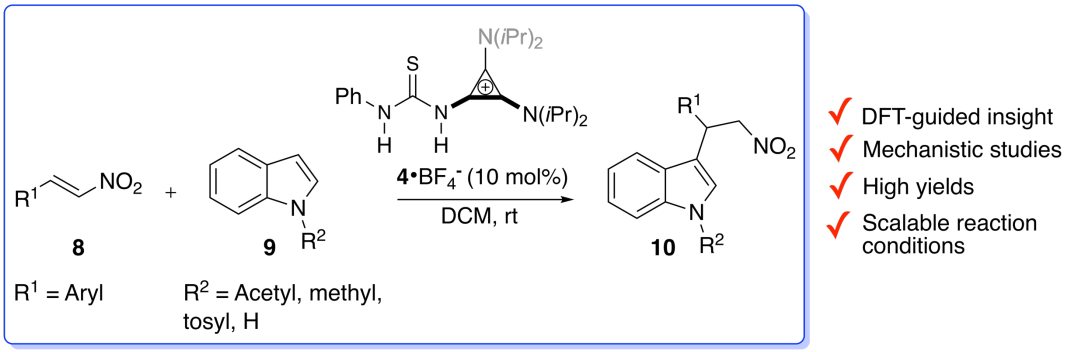



***Figure 3.*** *General conditions for Friedel–Crafts alkylation using thiourea catalyst* ***4***·$BF_4^-$.

As a final component to conclude the results and discussion section, a second-generation catalyst bearing a cyclopropenium component, namely a squaramide-cyclopropenium organocatalyst (**11**·$BF_4^-$), will be discussed in detail. This congener was found to be superior relative to other (thio)urea and squaramide organocatalysts for the formation of a novel bond between an oxime and DHP, and, in doing so, adds to the portfolio of oxime ether bond types (Figure 4).

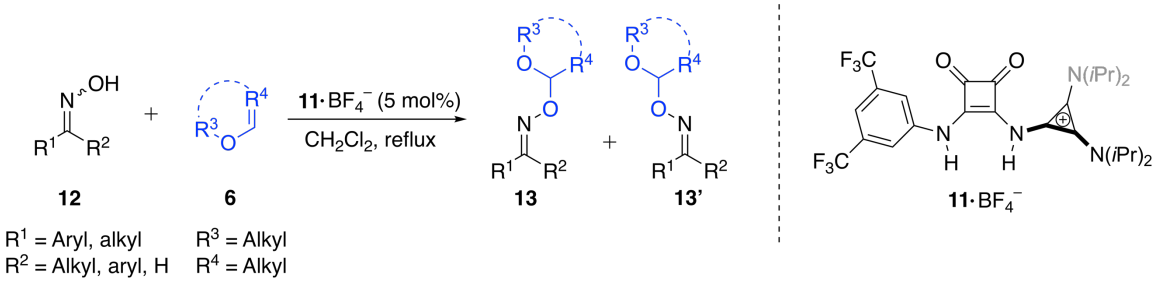



***Figure 4.*** *General conditions for oxime ether formation using thiourea catalyst* ***11***·$BF_4^-$.

The next section will cover the historical aspect, as well as provide pertinent background information for each of the above-mentioned undertakings.

## *2.0 Historical*

The coming sub-sections will address various aspects of catalysis, with the overarching objective being to become more familiar with the content presented in the results and discussion section of this dissertation. As such, the sub-sections to be discussed are as follows: 1) the emergence of organocatalysis, 2) thiourea and squaramide organocatalysis and 3) evolution of cyclopropeniums and congeners.

## *2.1 The emergence of organocatalysis*

Catalysis, as we know today, appears to have emerged as a relatively new discipline of chemistry given the recent coined terminology by chemists', with a pertinent example being "organocatalysis."[18] However, the term "catalysis" was introduced some centuries ago, when Jöns Jacob Berzelius used this word to rationalize certain chemical phenomena, such as wine and beer fermentation, and the breakdown of starch to common sugars in the presence of acid.[19] Though this was not the *true* inception of catalysis, Berzelius was among the first to bring this concept to fruition, as supported by his remarkable documented observation(s). Being a man of science, he sought to provide an explanation for these phenomena in which he elegantly stated the following:

*"I will therefore call it the 'catalytic force' and I will call 'catalysis' the decomposition of bodies by this force, in the same way that we call by 'analysis' the decomposition of bodies by chemical affinity."*

In contemporary times, emphasis is still placed on catalysis for enabling large-scale manufacturing, fine chemical production, pharmaceutical synthesis, renewable energies, and countless other important processes.[1]

Although some organic catalysts employed nowadays in industry are rather complex, the first reported example of an organic catalyst was among the simplest of structures—an aldehyde consisting of a two-carbon chain length, namely acetaldehyde. In 1860, Justus von Liebig used aqueous acetaldehyde as an organic catalyst to assist in the conversion of cyanogen (**14**) to oxamide (**15**)[20] (Figure 5). Therein, this aldehyde served the role of a catalyst to facilitate a clean reaction scenario—owing to its ability to form a hemiacetal—where only hydrolysis of nitriles was observed. In fact, it is hypothesized that this type of reactivity was prevalent during the prebiotic period[21]—preceding the advent of life on Earth.

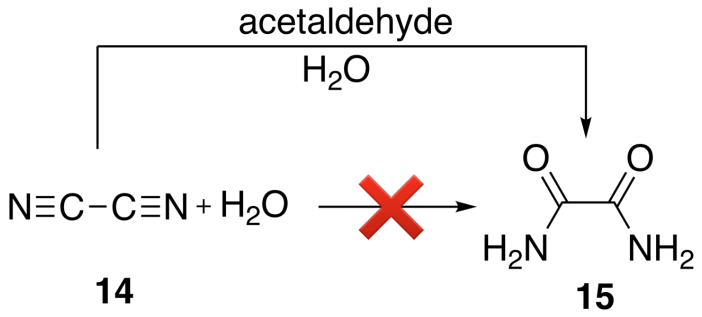


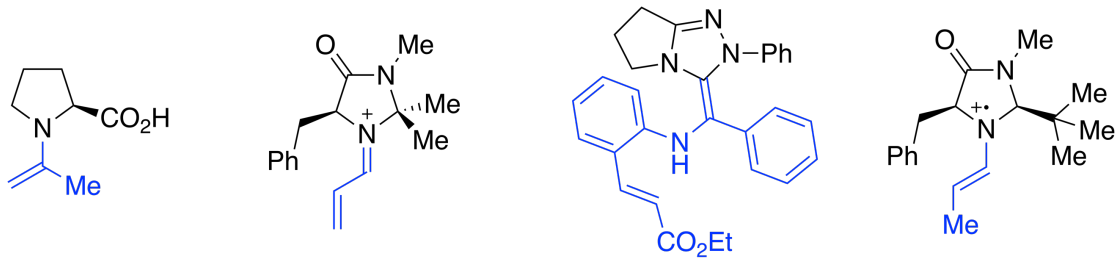

***Figure 5.*** *First organic catalyzed reaction.*

This seminal report by von Liebig enticed the chemical community during the twentieth century to further explore metal-free-catalyzed transformations. This led to an explosive era, during which chemists were moving on different fronts conducting investigatory studies revealing the function of various classes of organic catalysts, including cinchona alkaloids,[22] amino acids,[23] onium salts,[24] and others. It was not until the mid-twentieth century that Wolfgang Langenbeck made parallels between the catalytic action of enzymes and organic small-molecules.[25] With the number of reports using organic

small-molecules as catalysts steadily increasing, Langenbeck coined the term "organic catalysis" to describe this area of chemistry, and classified the different modes of organic catalysis as being either covalent or non-covalent .[26] Although many chemists helped pioneer this field of "organic catalysis," MacMillan truly revitalized the field upon introducing the term "organocatalysis" in the year 2000.[27] Since then, organocatalysis remains a vital pillar of catalysis. Henceforth, the term "organocatalysis" will be used throughout this dissertation.

### *2.1.1 Covalent catalysis*

Organocatalytic methodologies typically fall under two main types of substrate activation modes, namely covalent- and non-covalent organocatalysis. Since the work presented within this dissertation will be centered around non-covalent organocatalysis, its covalent counterpart will only briefly be touched upon. As the name implies, covalent organocatalysis involves a catalyst–substrate interaction through formation of covalent bonds. Efforts towards the establishment of covalent organocatalysis have led to four main classes, including (i) enamine, (ii) iminium ion, (iii) *N*-heterocyclic carbene and (iv) SOMO[28] (Figure 6).




**16** **17** **18** **19**

(i) (ii) (iii) (iv)

***Figure 6.*** *Four classifications of covalent organocatalysis.*

The structures above represent reactive intermediates consisting of a representative catalyst (black) and substrate (blue), from which then the desired reactivity can be channeled.

### *2.1.2 Non-covalent catalysis*

Within the last two decades, arguably, there has been a paradigm shift in the way that catalytic systems are being designed. This transition from covalent- to non-covalent catalysis was indisputably influenced by the knowledge acquired from the advancements in enzymatic catalysis. In fact, small-molecule organic catalysts that exploit non-covalent interactions, such as H-bonding,[29] electrostatic interactions,[30] $\pi$-$\pi$,[31] cation-$\pi$,[32] hydrophobic[33] and *Van der Waals* forces[34] are sometimes referred to as "artificial enzymes."[35] These attractive non-covalent interactions, in conjunction with steric directing effects, are crucial for lowering the activation barrier of reactions and enabling stereocontrol, respectively.[36] However, since these interactions are generally weaker and less dependent on distance and direction than covalent interactions, it is of the utmost importance to judiciously design an organocatalyst that has multiple sites tailored to engaging in non-covalent interactions. Having covered some rudimentary aspects that contribute to transition state stabilization, the next section of this dissertation will delve into more specific types of non-covalent interactions, namely H-bond catalysis and Brønsted acid catalysis.

### *2.1.3 Hydrogen bond catalysis*

The hydrogen bond, in and of itself, is a remarkable topic of discussion. Not only is there a rich and fascinating history associated with this subject, but the fine details are a contentious subject marred in ambiguity. It is generally accepted that the discovery of the

hydrogen bond took place in 1920,[37] where Latimer and Rodebush were the first to describe this phenomenon in the context of water; however, the first reported instance actually dates back to 1912.[38] Though this "hydrogen bond" terminology was not used throughout the manuscript, their findings involving the states of various amines in aqueous solutions suggested that there are apparent attractive intermolecular forces that "join the molecules together" when an alkyl group was switched out for a hydrogen atom.

Since then, H-bonding has been shown to be omnipresent. Moreover, this concept plays a key role in sustaining life, as supported by its active presence in biomolecules, such as proteins, carbohydrates and nucleic acids, as well as other inorganic molecules, e.g., $H_2O$ that serve a plethora of purposes. In fact, enzymes exert many of their prominent catalytic functions through the help of H-bonding, which takes place in aqueous media; in essence, an ocean-wide H-bond network.

The forces that constitute a formal hydrogen bond have been and continue to be a topic of investigation. A significant contribution to H-bond stability, however, has been ascribed to Coulombic forces (electrostatic interactions). The polarity of a hydrogen bond donor (D–H), wherein D is an electronegative atom, e.g., O or N creates a partial positive charge on the proton allowing for an attractive electrostatic interaction with an in-coming acceptor (Lewis base (A)). Working in concert, or being alternative driving forces for H-bond formation, are polarization and charge transfer. The latter involving a process, in which $n \rightarrow \sigma^*$ transfer of electron density from the non-bonding orbitals of a Lewis base (A) to an antibonding orbital of the D–H hydrogen atom. Collectively, these two forces contribute to the "covalency" of the newly formed H-bond.[39]

The percentage of covalency in hydrogen bonding affects the magnitude of bond directionality. Bond directionality arises from efficient atomic orbital overlap and the spatial arrangement of atoms with respect to neighbouring bonds. As such, covalent bonds are highly directional, whereas ionic bonds are nondirectional.[40] According to this concept, hydrogen bonds can be classified based on their strength, i.e., weak vs. strong H-bonds spanning from ~ 0.2–40 kcal $mol^{-1}$.[41] The stronger the H-bond, the more covalent, and, thus, directional they are.[42] Most notably, hydrogen bonds can also be classified based on other facets or phenomena, such as cooperative hydrogen bonding[43] and types of hydrogen bond engagement for electrophilic substrate activation.

As mentioned above, there is plenty of room for discussion centered around the hydrogen bond and its intricacies. However, I would like to shed light on one final aspect of hydrogen bonding, namely a few major types of hydrogen bonds that are frequently encountered for electrophilic substrate activation (Figure 7). Until 1939, the hydrogen atom was thought to participate in only one covalent bond and one H-bond. It was that year that Albrecht and Corey were the first to propose the notion that a hydrogen atom can engage in a three-centered hydrogen bond (BHB), otherwise known as a bifurcated hydrogen bond.[44] The term "bifurcated H-bond" has since evolved from its original definition involving one hydrogen atom and two acceptors, and extends to two hydrogen atoms and one acceptor—though BHB remains confined to its original configuration.[45] A close relative to the bifurcated hydrogen bond is the dual or two-point hydrogen bond (two hydrogen atoms and two acceptors).

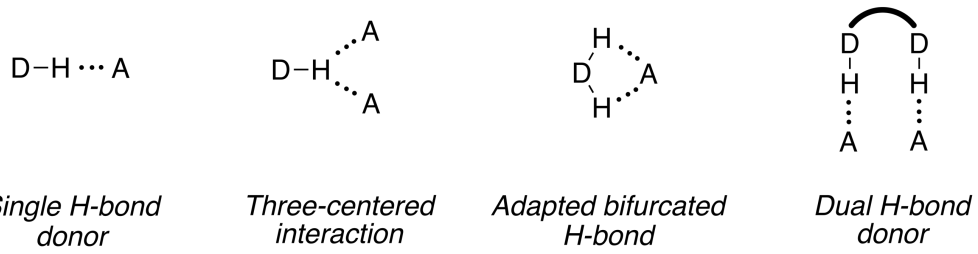



***Figure 7.*** *General representation of commonly encountered hydrogen bonds.*

The electrophilic activation of a molecule by the simultaneous donation of two hydrogen bonds is a common theme in enzymatic catalysis and organocatalysis. In fact, these strategies were found to exhibit increased strength and directionality relative to single H-bond donors.[46] These small-molecule H-bond donor organic catalysts activate substrates through LUMO-lowering mechanisms. A classic example depicting this mode of activation is *via* thiourea catalysis that parallels enzymatic pockets inherent to serine proteases, wherein amide carbonyls are susceptible towards serine nucleophilic attack (Figure 8).

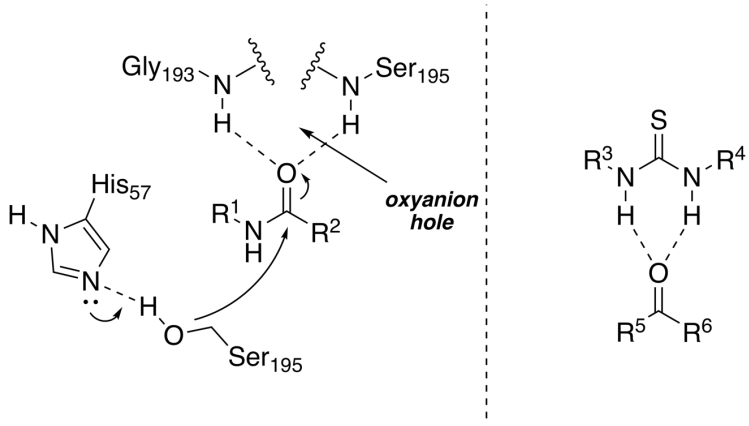



***Figure 8.*** *Electrophilic activation mode comparison between enzymatic catalysis and organocatalysis.*

The dual H-bond mode of activation, as seen in the mock serine protease example (left-hand side) and organocatalytic example (right-hand side) proceed through a so-called "oxyanion hole." Therein, the incipient negative charge of the tetrahedral intermediate is stabilized by the two adjacent, partially positive hydrogen atoms.[28] An abundance of reports[5e,28,46] exist that disclose various catalysts operating through this mechanism; however, the focus of this dissertation will be placed mostly on (thio)urea and squaramide organocatalysts. Prior to covering the relevant aspects surrounding these catalysts, a brief discussion of Brønsted acids will be presented.

### *2.1.4 Brønsted acid catalysis*

Our discussion of Brønsted acids begins with what is todays common commodity; vinegar, otherwise known as acetic acid. The correlation between sour taste and acidity was attributed to this acid, and remains a common descriptor in the context of acids. It is rather interesting that acetic acid has even deeper roots than mineral acids (sulfuric, hydrochloric and nitric)! Nevertheless, the discovery of mineral acids and oxygen kept chemists busy during the eighteenth century. It was during this time that a direct correlation between a hydrogen atom and acidity was made.[47] This concept was further developed by Arrhenius, who recognized that acids dissociate in aqueous solutions generating a high concentration of $H^+$ ions, whereas alkaline solutions are comprised of an excess of $OH^-$ ions. In 1923 Johannes Nicolaus Brønsted and Thomas Martin Lowry advanced a theory, namely the Brønsted-Lowry theory, extending beyond aqueous solutions—a Brønsted-Lowry acid donates a proton, while a Brønsted-Lowry base accepts a proton.[48]

Differentiating between H-bond catalysis and Brønsted acid catalysis is not a simple task.[49] Usually, to some extent, a pre-equilibrium, wherein H-bonding precedes the

transfer of a proton takes place.[28] A key distinctive feature, however, is the presence of an ion pair in Brønsted acid catalysis, as opposed to sole H-bonding interactions. (Figure 9). From a mechanistic standpoint, Brønsted acid catalysis can be further categorized as either specific acid catalysis or general acid catalysis. The former involves reversible proton transfer in the presence of a "specific acid," meaning a protonated solvent, e.g., hydronium prior to the rate-limiting step. In contrast, general acid catalysis refers to a process, where proton transfer of a "general acid," any acid that will impact the rate of the reaction, is involved in the rate-determining step.[50]

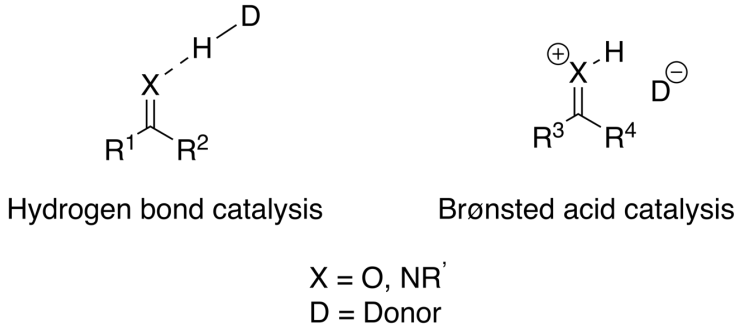
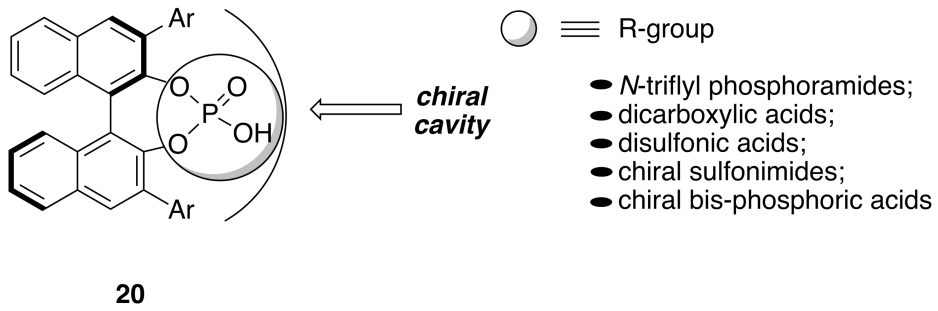



***Figure 9.*** *Representative depiction of intermediates involved in hydrogen bond catalysis vs. Brønsted acid catalysis.*

Irrespective of the mechanism, Brønsted acid catalysis has obtained a revered status in organic synthesis owing to its contribution to the efficient formation of carbon–carbon and carbon–oxygen bonds.[51] What is more, this realm of non-covalent catalysis has shown tremendous promise in terms of advancing total synthesis[52] by adding to the synthetic chemists' toolbox. The archetypal Brønsted acid that triggered a renaissance in the field of Brønsted acid organocatalysis was BINOL-derived phosphoric acid (**20**), as independently brought to fruition by Akiyama[53] and Terada[54] in 2004 (Figure 10). This pioneering work

led to the development of other axially chiral, BINOL-derived Brønsted acids, where stereoinduction hinges upon a catalyst–substrate interaction within the chiral cavity.[55]




**20**

***Figure 10.*** *First reported BINOL-derived Brønsted acid (**20**) with other developments highlighted.*

One of the key factors that quantifies the strength of a Brønsted acid is p$K_a$, which is a term that refers to the willingness of a Brønsted acid to donate a proton and stabilize its conjugate base. However, strictly relying on the p$K_a$ of the catalyst at hand will only provide a modicum of mechanistic information. Moreover, employing other empirical methods and/or physical organic parameters are imperative for gaining insight and probing the mechanistic underpinnings of catalysis. In particular, kinetic studies,[3,4] nucleophilicity and electrophilicity parameters,[56] and colorimetric assays[57] are often used to provide insight into reaction profiles. With respect to the latter, Kozlowski introduced pyrazinone sensor **21** to determine the effectiveness of H-bonding catalysts (Figure 11). In theory, a better understanding of secondary catalyst–substrate interactions, such as sterics and H-bonding directionality could be assessed.

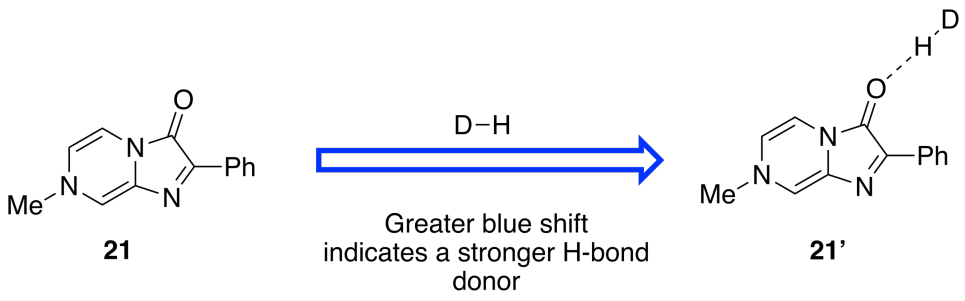



***Figure 11.*** *Representative H-bonding interaction with a colorimetric sensor for assessing H-bond strength.*

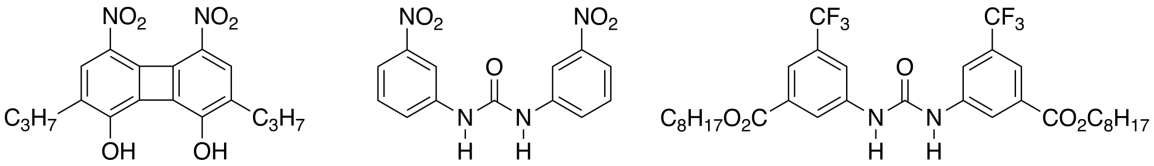
Likewise, modern-day computational tools offer a powerful means for acquiring mechanistic understanding and, as such, continue to gain popularity. This is evidenced by numerous reports in drug design,[58] method development, and material applications.[59] Further to this point, key in advancing chemical discovery has been the use of DFT computational calculations as an effective and versatile resource for examining reactivity, e.g., H-bond orchestrated catalyst–substrate interactions and catalysis.[60]

With a variety of methods available to assess catalyst performance and reactivity, it is becoming less difficult to hone particular catalytic features. For instance, there has been a direct correlation between charge and acidity leading to higher catalytic performance. This has been observed in electrostatically enhanced thioureas,[10] as well as other well-established cationic H-bond donors, including amidinium,[61] ammonium,[62] guanidinium,[63] pyridinium,[64] and quinolinium ions.[65] Furthermore, Lambert has demonstrated that aromaticity is a pivotal acidifying element in the field of Brønsted acid catalysis.[66]

Having a deeper understanding of non-covalent H-bond- and Brønsted acid catalysis, the following section will shift focus to two distinct, yet related, popular classes of organocatalysts, namely (thio)ureas and squaramides.

### *2.1.5 Thiourea and squaramide organocatalysis*

In search of new Brønsted acid catalysts, chemists' stumbled upon neutral small-molecule organic thioureas and squaramides that paradoxically fit more of the description of being H-bonding catalysts, rather than Brønsted acids.[51] Preceding their discovery, several research groups made significant contributions in the chemistry community that set the stage for future developments (Figure 12). In 1990, Kelly and co-workers were the first group to advance biphenylene diols (**22**) as capable molecular recognition and substrate activation agents *via* bifurcated H-bonding targeting a Diels–Alder reaction.[67] The same year, Etter and co-workers discovered that electron-deficient diaryl ureas (**23**) have a predilection for forming co-crystals with various carbonyl-containing compounds.[68] It was from these precedent works that Curran and Kuo, for the first time, employed a novel electron-deficient (trifluoromethyl group), yet soluble (octyl ester) urea (**24**) for the radical-mediated allylation of α-(phenylseleno)-sulfoxides,[69] as well as the Claisen rearrangement.[70]

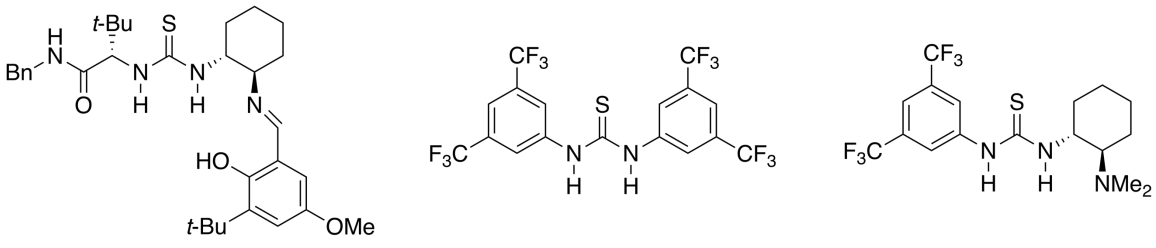



**22** **23** **24**

***Figure 12.*** *Evolution of H-bonding catalysts.*

A truly ground-breaking report was put forth in 1998 by Jacobsen and Sigman.[71] They were the first to demonstrate that chiral (thio)ureas (**25**) function as competent catalysts to induce stereoselectivity (Figure 13). This inspired others, such as Schreiner and

Takemoto, who eventually became key players, to further add to the field of thiourea catalysis; a strong impetus being the enhanced differences in acidities, i.e., p$K_a$ thiourea = 21.0; p$K_a$ urea = 26.9.[72] Schreiner demonstrated that the strategic positioning of two trifluoromethyl groups in the 3,5-positions on the aromatic rings of a thiourea (**26**) proved to be the most effective in terms of catalytic activity.[9f,73] In fact, thanks to the joint effort of four trifluoromethyl groups, the experimental p$K_a$ of thiourea **26** was determined to be 8.5 in DMSO.[74] This catalyst is the most acidic neutral thiourea to date. Takemoto, however, was interested in pursuing a different avenue; one in which he is highly recognized for his efforts. Of course, he decided to incorporate the 3,5-bistrifluoromethyl aryl moiety as a design element, as a result of Schreiner's seminal work. Moreover, he and his group were the first to introduce the concept of bifunctionality into thiourea catalysis (**27**) in 2003.[75] These types of catalysts are comprised of three components: (1) a domain with an amine or phosphine group that functions as either a base or nucleophile, (2) a thiourea hydrogen bond domain for further substrate activation and (3) a chiral skeleton that establishes a chiral environment.[76]




**25** **26** **27**

***Figure 13.*** *Landmark thiourea catalysts reported by Jacobsen,[71] Schreiner[9f] and Takemoto.[75]*

Although (thio)urea catalysts continue to be used, and their reactivity further fine-tuned, e.g., replacement of four $CF_3$ groups with two charged centers led to a 400 fold increase in reactivity,[10b] the use of squaramides (derived from squaric acids) as alternatives

has attracted considerable attention. In 2010, Rawal and co-workers left a sizable footprint in the organocatalysis community by disclosing a report, wherein enantioselective Michael addition reactions enabled by a chiral squaramide catalyst (**28**) were not only possible, but highly efficient,[77] and since, has been recognized as a prominent figure in the context of squaramide catalysis (Figure 14). This report clearly piqued interest, as attested to by various groups across the globe rushing to develop efficient methods for accessing this class of catalyst, as well as deploying them in search of novel bond disconnections.[78] Rawal, again, demonstrated his efforts by providing facile access to a wide-range of thiosquaramides and squaramides from common intermediate **29** in 2018.[79]

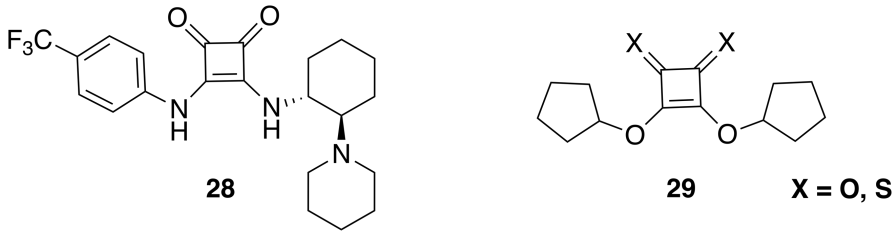



***Figure 14.*** *Rawal's first reported chiral squaramide catalyst (left-hand side) and squarate ester ((thio)squaramide catalyst precursor (right-hand side)).*

The squaramido functionality offers five main differences relative to (thio)urea motifs that, ultimately, impact reactivity. A few of these differences are highlighted in Figure 15. The first difference stems from binding capability. It is well-established that (thio)ureas engage in tight anion-binding; however, the same cannot be said regarding cations.[30] In contrast, the squaramido functionality can simultaneously bind an anion and cation—a process formally referred to as ditopic binding. A theoretical study from 2002 suggested that the squaramido functionality becomes more aromatic upon complexation to

a cation.[80] What is more, squaramides harbour more bifunctional character with respect to different H-bonding patterns owing to their structure, which features two H-bond donors (N–H) and two H-bond acceptors (C=O).[78b] Another difference that sets squaramides apart from (thio)ureas is rigidity. Although electron delocalization, which restricts the rotation of the C–N bond occurs in both (thio)ureas and squaramides, the latter are more rigid due to the additional delocalization throughout the cyclobutenedione system. As a result, the carbonyl and amine groups become coplanar.[81] Two additional structural differences between thioureas and squaramides are the distances between the two N–H groups, as well as geometry. The former was investigated by both Takemoto[82] and Rawal,[83] where they ascertained bond distances of ~ 2.13 Å and ~ 2.72 for generic thiourea and squaramide N–H groups, respectively. Furthermore, the squaramide N–H groups are tilted slightly inward by ~ 6° because of the square geometric structure.[83] The final major difference arises from p$K_a$. The above-mentioned structural and physical differences have a direct influence on the p$K_a$ of squaramides. In 2014, Li and Cheng determined the experimental p$K_a$ values of various squaramide catalysts in DMSO and compared these values to their thiourea counterparts.[84] It was found that the analogous squaramide structures were more acidic up to 2 p$K_a$ units. This result alone helps support the notion that squaramides are stronger H-bond donors, when compared to thioureas. One way to further augment the p$K_a$ of thioureas and squaramides is through the introduction of charge.

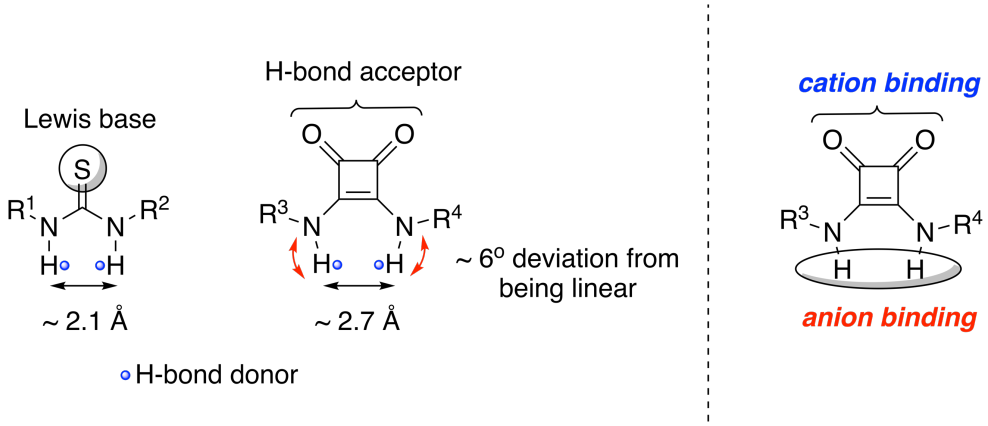



***Figure 15.*** *Outlined differences comparing thioureas and squaramides (left-hand side), and depiction of ditopic binding as an inherent property of squaramides (right-hand side).*

This brings us to the last topic of discussion with respect to the introduction. This final section will encompass a brief overview and history of cyclopropeniums—the smallest member of the Hückel aromatic systems. Hopefully, this will help evoke an appreciation for these non-benzenoid carbocycles, and further, *deepen* the understanding of how they can be used to promote catalysis.

## *2.2 Evolution of cyclopropeniums and congeners*

Organic chemists have been, and continue to be, enticed by the notion of exploring the depth and breadth of molecular structure and function ever since the advent of organic synthesis in 1828, when Wöhler synthesized urea.[85] There is definitely something alluring about the ability to successfully make molecules, especially if these molecules are non-existent in Nature. A particular area of interest that has captivated the chemical community for centuries is that of highly strained molecules. In fact, Adolf von Baeyer sparked this surge of interest in 1885 after he announced his presumption that three- and four-membered

rings were not as pervasive as other structures in Nature due to the possibility of having deformed carbon–carbon bond angles, thus, contributing to their instability.[86] The race among chemists to directly correlate reactivity with strain and stability then began in the early 1900s.

Special attention was paid to Dem'yanov and Doyarenko, as they were the first to report the synthesis of cyclopropene in 1922 *via* thermal decomposition (~ 300 $^{o}$C) of trimethylcyclopropylammonium hydroxide.[87] However, because obtaining this type of molecule was considered to be an arduous task at the time, it wasn't until the 1950's that truly sparked chemists' curiosities in terms of investigating these strained systems. The reasoning was two-fold: (1) accessing these unsaturated carbocycles became easier over time, thanks to advancements in carbene chemistry,[88] and (2) in 1952, Roberts and co-workers revealed that the cyclopropenyl cation abides to Hückel's 4n+2π-rule, where n = 0.[89] As such, exploratory studies centered around cyclopropene and the cyclopropenium ion then began.

With respect to cyclopropene, Baeyer was correct to assume that three-membered rings suffered from severe strain owing to bond deviations. The increased reactivity of such systems is attributed to three main factors that ultimately perturb the σ- and π-orbital framework: (1) angle strain, (2) twisting and (3) pyramidalization (Figure 16). The first point arises from the presence of one or more trigonal centers leading to deviations from ideal bond-angles of 120$^{o}$, whereas the latter two distort the alkene π-bond forcing the p-orbitals out of co-planarity, which consequently increases reactivity. Further to this point, as a result of this weaker π-bond, the HOMO energy of the molecule is increased allowing for a more facile interaction with its reaction partner. Another well-known concept that has

been put forth is strain-release-driven reactivity, wherein favourable $sp^2 \rightarrow sp^3$ rehybridization takes place.[90]

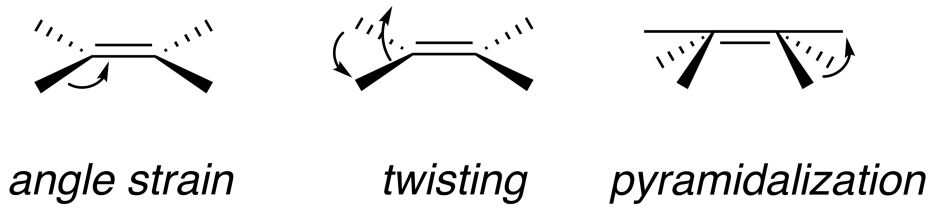


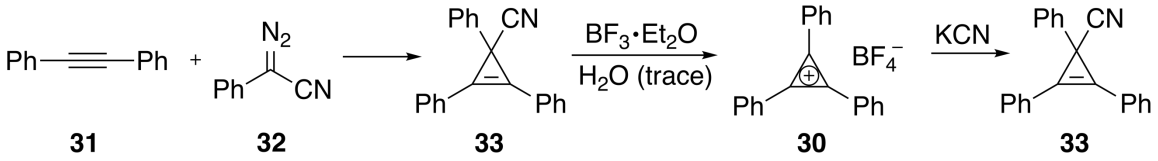

***Figure 16.*** *Factors contributing to cyclopropene instability.*

### *2.2.1 Aminocyclopropeniums: synthesis and stability*

The chemical community was well aware of the intricacies centered around the instability of cyclopropene, and, thus, it was uncertain whether the energetic penalty of high ring strain could be superseded by aromatic stability. However, a landmark disclosure by Breslow in 1957 cleared up any ambiguity associated with this theoretical curiosity by providing experimental verification of the first isolated cyclopropenium ion, namely *s*-triphenylcyclopropenyl cation[91] **30** (Scheme 1). This synthesis commenced with a reaction between diphenyl acetylene (**31**) and phenyldiazoacetonitrile (**32**) to furnish 1,2,3-triphenylcyclopropenyl cyanide (**33**). This intermediate was determined to be soluble in non-polar solvents and did not precipitate in the presence of ethanolic silver nitrate, meaning it is not ionic. Further treatment with a solution of boron trifluoride etherate with trace amounts of water (contains fluoroboric-, hydroxyfluoroboric- and boric acids) resulted in formation of *s*-triphenylcyclopropenyl cation **30** as a white crystalline solid. This compound was confirmed by elemental analysis, and further characterized after conversion to its picrate salt. Notably, a characteristic feature inherent to picrate salts is a bright yellow colour, which was observed for the cyclopropenium compound at hand.

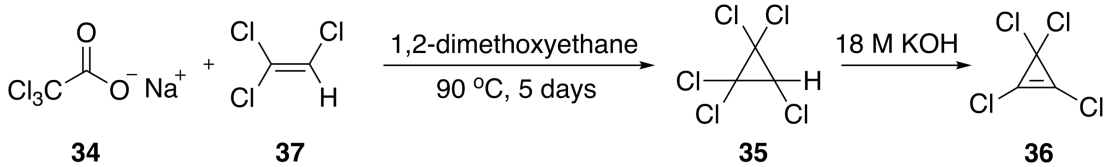
Further evidence was seen by regenerating compound **33** upon reaction of compound **30** with potassium cyanide.

***Scheme 1.*** *First reported synthesis and isolation of the s-triphenylcyclopropenyl cation.*



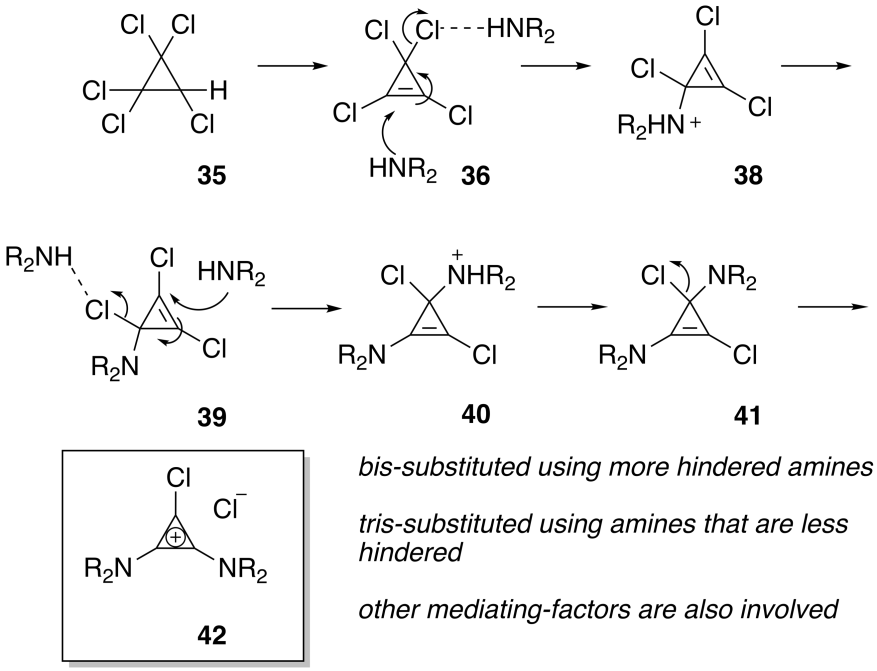

As mentioned above, the other primary impetus responsible for the burgeoning interest in cyclopropene chemistry was advancements of new carbene-based synthetic methods. To this end, Wagner indirectly laid the groundwork for the ability to access cyclopropenimine compounds after disclosing a new approach to the synthesis of dichlorocarbene ($:CCl_2$) in 1959.[92] This reactive intermediate was formed *via* thermal decarboxylation of sodium trichloroaceteate (**34**) in 1,2-dimethoxyethane. Tobey and West quickly moved on this finding,[93] and exploited Wagner's method for the synthesis of pentachlorocyclopropane (**35**) and its congener tetrachlorocyclopropene (**36**) (Scheme 2). Compound **35** is accessed by reacting sodium trichloroaceteate (**34**) with trichloroethylene (**37**) in the presence of 1,2-dimethoxyethane at 90 °C for 5 days. Tetrachlorocyclopropene (**36**) can be obtained by subsequent dehydrohalogenation under extremely basic conditions. The Dudding laboratory employs Tobey and West's method to this day.

***Scheme 2****. Synthesis of pentachlorocyclopropane and tetrachlorocyclopropene.*



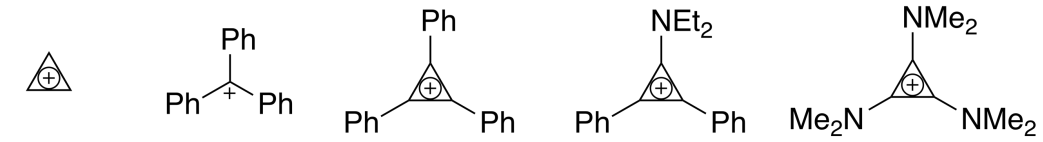
The preparation of aminocyclopropenium compounds begins with either tetrachlorocyclopropene[94] or pentachlorocyclopropane.[95] Yoshida proposed a mechanistic rationale from tetrachlorocyclopropene[94] that involves a series of $S_N2$' steps terminating with an ionization step. The point where ionization actually takes place is a controversial topic, and cannot be easily pinpointed owing to this being a rapid process.[14] Nonetheless, the mechanism for this process is provided in Scheme 3. Utilizing pentachlorocyclopropane as starting material *in lieu* of tetrachlorocyclopropene renders a similar mechanism, with the exception that tetrachlorocyclopropene is generated *in situ* by base-induced elimination.[93] This was demonstrated by Taylor and co-workers in 1994.[95] It is customary to employ at least 6 equivalents of amine in order to obtain a higher yield of the desired aminocyclopropenium product.

***Scheme 3.*** *Presumed mechanism for accessing bis- or tris-substituted aminocyclopropenium compounds.*



Preceding the advent of tetrachlorocyclopropene, Breslow and co-workers showcased the thermodynamic stability of several cyclopropenium compounds with disparate aryl and alkyl substituents.[96] They managed to gauge their stability based on p$K_{R+}$, which is an empirical parameter corresponding to 50% conversion of a cation to its carbinol at a particular pH. From their findings, they noticed that there is a greater degree of carbocation stabilization in the presence of alkyl substituents, rather than aryl substituents. This prompted Yoshida to install alkylamino substituents (see the above scheme), as it was postulated that they would confer further stabilization.[97] In fact, the first advanced cyclopropenium of this kind was a tris-substituted (dialkylamino)cyclopropenium (**43**)—a sub-class of one of the most stable carbocations to date.[14] This stability is attributed to conjugative effects; thus, compensating for the energetic penalty of its incomplete octet. To put this into perspective, a range of carbocations with their corresponding measured p$K_{R+}$ values is offered in Scheme 4.[96]

***Scheme 4.*** *Reported p$K_{R+}$ values for various carbocations.*



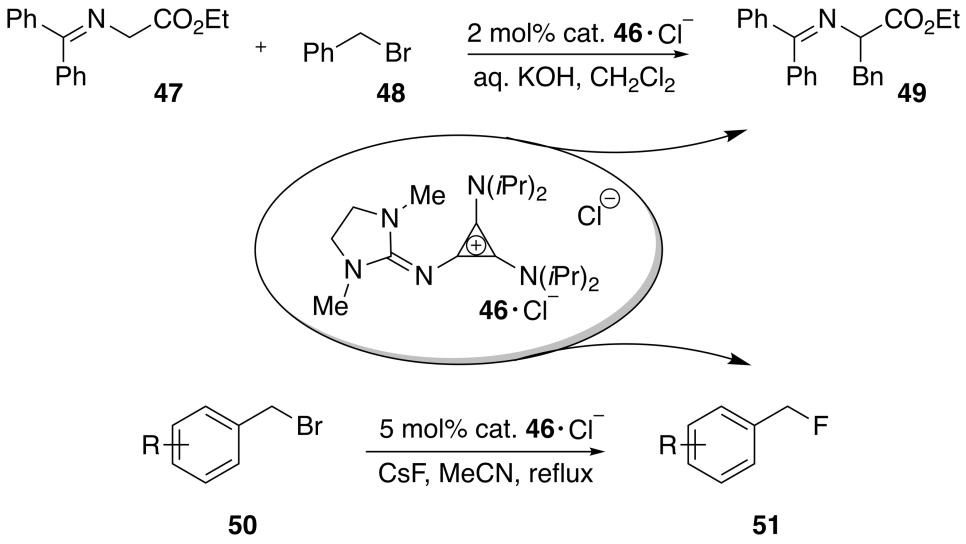

**1** (-7.4) **44** (-6.6) **30** (3.1) **45** (>10) **43** (13)

### *2.2.2 Applications of cyclopropenium-appended molecules as catalysts*

The incorporation of aminoalkyl substituents extends even further than simply imparting stabilization, in that, an enhanced dispersion of positive charge is manifested when compared to other onium salts, including ammonium, phosphonium and guanidinium

systems.[98] Paradoxically, this leads to an electron-excessive carbenium salt, as observed by Weiss and co-workers,[99] ultimately creating a repulsive interaction in the presence of an electron-rich counteranion. This interaction was coined as "ion pair strain," wherein a favourable electrostatic interaction was superseded by repulsion between the HOMO of the counteranion and the HOMO of the aminocyclopropenium ion (donor–donor ion pair strain). This phenomenon renders a "naked" ion, which has obvious implications in catalysis. In fact, Dudding and co-workers[100] observed ion pair strain with the help of X-ray analysis and DFT calculations for a novel, hybrid cyclopropenium/guanidine system (**46**·$Cl^-$) (Scheme 5). They then used this as leverage to promote two phase-transfer-catalyzed processes, namely benzylation and benzylic fluorination.

***Scheme 5.*** *A cyclopropenium-based phase-transfer catalyst exhibiting ion pair strain applied in benzylation and fluorination.*



Shortly thereafter, Dudding and co-workers advanced a protonated dicationic variant that functioned as a strong Brønsted acid.[101] To the best of my knowledge, this is the first instance of a cyclopropenium-based compound functioning as a Brønsted acid catalyst, where a proton is fully transferred and not just engaged in a H-bonding interaction. This reported catalyst (**52**·2$BF_4^-$) exhibited two striking features: (1) a computed p$K_a$ of 0.9 in MeCN, thus, falling in the realm of being classified as a superacid (sulfuric acid has a p$K_a$ of 7.2 in MeCN)[102] and (2) donor–donor ion pair strain with the two tetrafluoroborate counteranions residing at relatively distant points from the cyclopropenium-appended molecule, as opposed to engaging in electrostatic interactions or H-bonding with the hydrogen-containing nitrogen atom. An X-ray crystal structure of **52**·2$BF_4^-$ is offered in Figure 17 A. In addition to these remarkable features, they further demonstrated the synthetic utility of this catalyst by pursuing two different hydroamination routes (Figure 17 B). The first involves various phenylacetylenes with electron-poor anilines as reaction partners in the presence of a gold precatalyst complex (**53**), whereas the second solely relied on catalyst **52**·2$BF_4^-$ to induce hydroamination of alkenes.

The disclosure described above functions as a direct antithesis to the original premise that cyclopropenimine compounds were *strong Brønsted bases*.[14] In fact, theoretical studies revealing their strong basic character have been steadily gaining traction since 1999.[103] This basicity arises from the presence of a latent cyclopropenium ion.[104] The ability to aromatize, or rearomatize, serves as the driving force for chemical reactions,[105] making this class of non-benzenoid aromatic ions ideal candidates for promoting catalysis. This is, no doubt, a common theme to both Brønsted base- and Brønsted acid catalysis, wherein initiating reactivity of the former hinges upon accepting a proton to generate

aromaticity, and the latter on facile proton transfer owing to charge-enhanced acidity. Nevertheless, both strategies are, to some extent, based on aromatic cation activation involving shuttling between charged and neutral states.

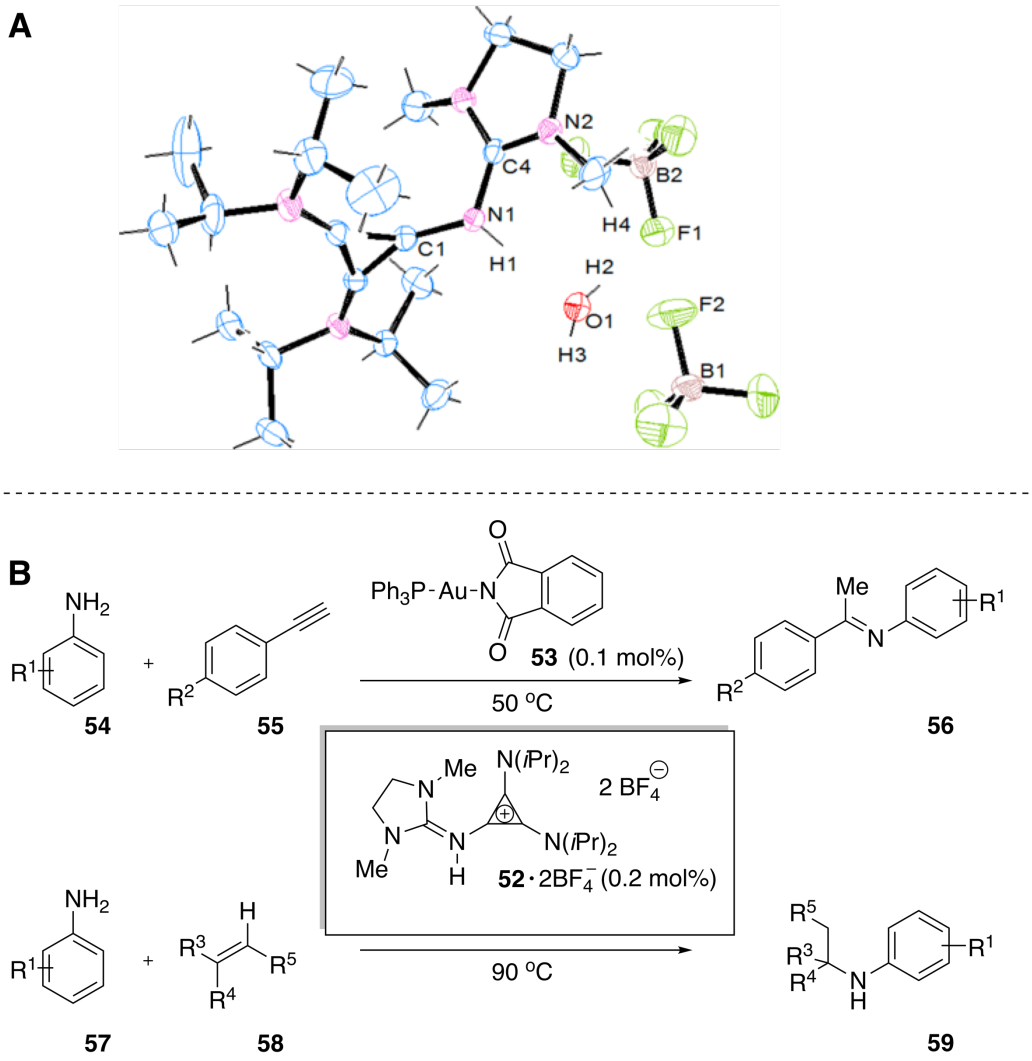
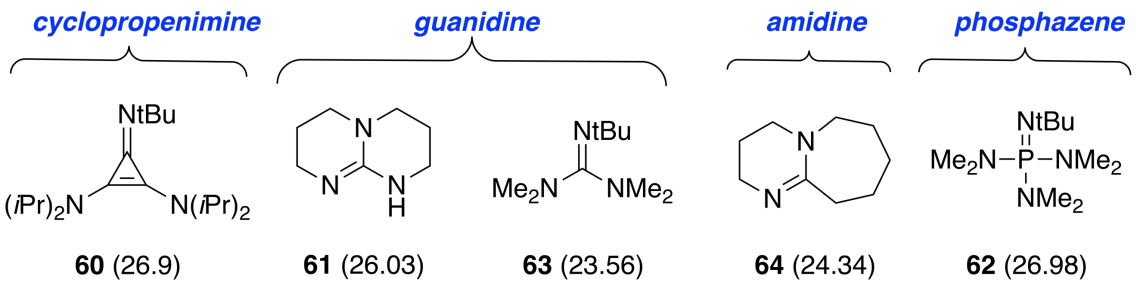



***Figure 17.*** *(A) X-ray structure of* ***54***$\cdot 2BF_4^-$*.*[102] *(B) Hydroamination mediated by a cyclopropenium-based strong Brønsted acid.*

Although it was well-accepted, early on, that cyclopropenimines feature strong basic character, it wasn't until 2012 that Lambert and co-workers demonstrated their utility in catalysis as strong, chiral organic Brønsted bases.[104] The impetus for this pursuit was manifold. Aside from numerous theoretical studies supporting their strong basicity,[103] Lambert and co-workers were the first to experimentally measure the acidity of the conjugate acid ($pK_{BH+}$) of cyclopropenimine **60** in MeCN.[104] They found that cyclopropenimine **60** (26.9) had a comparable $pK_{BH+}$ to guanidine **61** (26.03) and phosphazene base **62** (26.98), thus, fitting the description of being classified as a so-called "superbase" (Scheme 6). A superbase is a chemical entity comprised of at least two bases[106] leading to a synergistic relationship, and, thus, an enhancement in basicity relative to the independent bases. Moreover, cyclopropenimine superbases come with two, key inherent advantages, including ease of synthesis and aromatic resonance stabilization upon protonation, whereas amidines and guanidines have limited basicity owing to their framework,[104] and phosphazenes suffer from complicated preparative routes.[107]

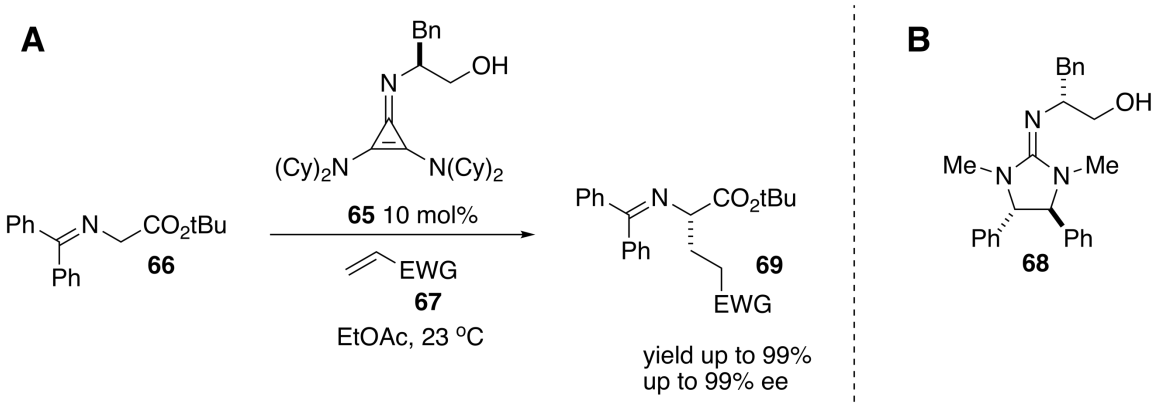
***Scheme 6.*** *A range of reported strong organic bases. Their corresponding $pK_{BH+}$ values are in parentheses.*




With these characteristic basic traits in mind, Lambert and co-workers were prompted to deploy cyclopropenimine **65** as a catalyst for a Michael reaction between *tert*-butyl glycinate benzophenone imine (**66**) and a range of Michael acceptors (**67**) (Scheme

7 A).[104] They gauged the reactivity of this catalyst against a similar chiral guanidine catalyst (**68**), and found that catalyst **65**, using a catalyst loading of 10 mol%, outperformed catalyst **68** at 20 mol% employing neat conditions and in the presence of solvent (Scheme 7 B).

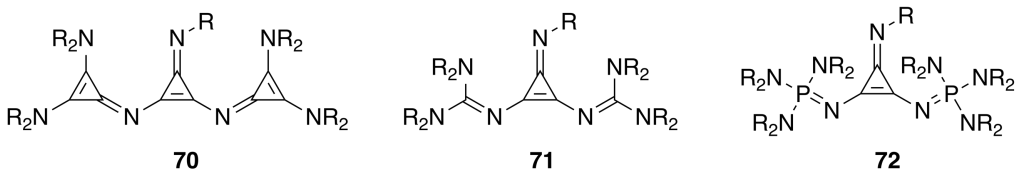
***Scheme 7.*** *(A) Cyclopropenimine-catalyzed Michael addition. (B) Chiral guanidine catalyst.*



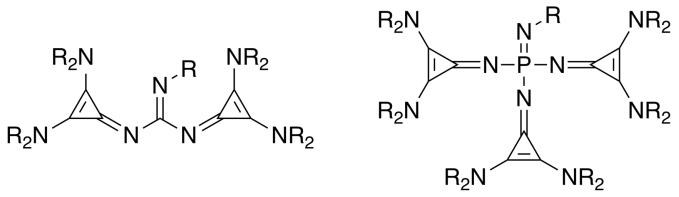

By analogy, the combination of multiple superbases renders a "higher-order superbase." In 2015, Nacsa and Lambert developed six new classes of higher-order superbases, with five that incorporate cyclopropenimine functionality.[108] A generic skeleton showcasing these five classes (**70**–**74**) is depicted in Scheme 8. They were able to fine-tune the basicity of these superbases by modulating either the core and/or substituents. Each class was comprised of either a cyclopropenimine-, guanidine- or phosphazene core. Notably, they were able to observe remarkable p$K_{BH+}$ values in MeCN, spanning from high twenties-to-mid forties. (29–42.1). A striking observation of this work, however, is that superbases with a cyclopropenimine core proved to be less efficient in terms of imparting stronger basicity to the imino group (cyclopropenimine < guanidine < phosphazene). This trend was ascribed to the incipient cyclopropenyl cation being the least stabilized relative to the other cations.[109]

***Scheme 8.*** *Five new classes of higher-order cyclopropenimine superbases.*

cyclopropenimine core:

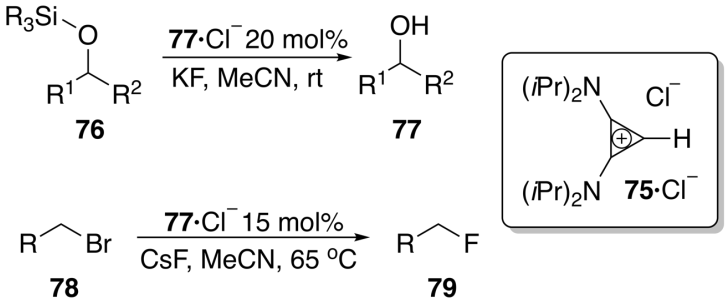



cyclopropenimine substituents:




Since then, the cationic nature of cyclopropenium compounds has been leveraged to tap into other non-covalent interactions, such as H-bonding and its close relative halogen bonding. For instance, Dudding and co-workers published two back-to-back phase-transfer-catalyzed methodologies employing a bis(dialkylamino)cyclopropenium catalyst (**75**·$Cl^-$) (Scheme 9).[110] It was posited that this would be an efficient phase-transfer catalyst due to three main factors: (1) presence of lipophilic alkyl groups, (2) a π-polarizable aromatic cation and (3) an acidic C–H moiety allowing for H-bonding interactions. With this in mind, they first exploited this catalyst's features for the *O*-silyl ether deprotection of various alcohols using solid KF as a mild fluoride source,[110b] followed by benzylic fluorination using more reactive CsF.[110a] A common theme among these reports was cyclopropenium-mediated fluoride shuttling from the solid phase to the organic phase *via* H-bonding.

***Scheme 9.*** *O-Silyl ether deprotection (top) and benzylic fluorination (bottom) mediated by a phase-transfer cyclopropenium catalyst.*




Another recent addition contributing to H-bond catalysis was a report by the Guo and Li research groups, where they developed a new type of tris(monoalkylamino)cyclopropenium (**80**·$Cl^-$) that exhibited ion pair strain.[111] Cyclopropenium **80**·$Cl^-$ was deployed in ring-opening polymerization of lactones operating through cooperative organocatalysis (Figure 18). This reactivity hinged upon a weakly coordinating cation to function as a strong H-bond donor and its corresponding "naked" anion as a strong H-bond acceptor. Supporting this mechanistic hypothesis was a large distance (>4 Å) between the cyclopropenium core and chloride counteranion, thus, revealing a "loose" interaction, as observed *via* X-ray analysis of the single-crystal. Furthermore, using a fluoride counteranion *in lieu* of a chloride proved to be inefficient, presumably due to the formation of a "tight" ion pair. Likewise, no reactivity was observed when the monoalkylamino groups were substituted out for dialkylamino groups, owing to loss of the H-bond donor domain.

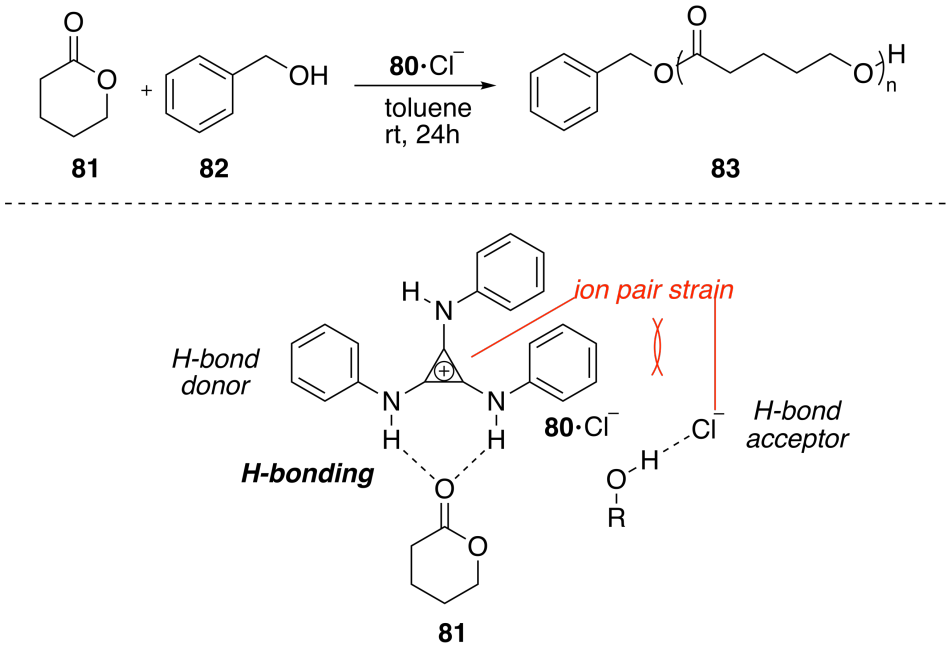



***Figure 18.*** *Ring-opening polymerization using benzyl alcohol as the initiator (top). Cooperative mode of substrate activation (bottom).*

### *2.2.3 The first example of a cyclopropenium compound exhibiting XB donor character*

In 2020, Huber and Weiss entered uncharted territory after disclosing a report, in which an unconventional type of halogen bonding—a non-covalent interaction between a an electrophilic region on a halogen atom and a Lewis base—was observed using cyclopropenium-containing compounds.[112] The forces that govern halogen bonding have been under great scrutiny[113] since its first reported occurrence in 1814, when Colin described a reaction between ammonia and iodine.[114] Moreover, two generally accepted bonding contributions have been primarily attributed to charge transfer and/or electrostatic effects. The former theory was proposed as early as 1950 by Mulliken, and describes a n→σ*-type orbital interaction,[115] whereas the latter arises from a rationale centered around the σ-hole theory formulated by Politzer and co-workers in 1994.[116] The σ-hole theory is

quite complex and consists of numerous mediating factors,[113] but, in essence, the σ-hole is a positively charged region on a halogen atom that lies *trans* to the σ-bond, and arises from anisotropy of electron density.[117] The ability to fine-tune the strength of the incipient halogen bond (XB) (by increasing the size of the σ-hole) traditionally involves neutral[118] or cationic[119] XB donors. Anionic XB donors can also engage in halogen bonding, though pinpointing this interaction on electrostatic reasoning is counterintuitive.

Halogen bonding involving anionic XB donors has been formally coined as "anti-electrostatic" XBs (AEXBs).[112] Huber and Weiss were the first to demonstrate such an AEXB interaction between an anionic XB donor, namely an anionic iodocyclopropenium (**84**·$TDA^+$), and a structurally different anion (Figure 19). Through the help of computational calculations, they realized that no positive electrostatic potential could be found on compound **84**, albeit a slightly less negative electrostatic potential was seen in the elongation of the C–I bond. Further calculations in the presence of halides (X = Cl and I) revealed that halogen bonding was taking place. They came to this conclusion as a result of the I···I and I···Cl bond distances being shorter than the sum of the van der Waals radii.[120] To corroborate their computational findings, a co-crystal of **84** in the presence iodine was grown with the speculation that iodine would induce favourable polarization of the XB donor. They further base their argument in favour of n→σ*-type orbital interactions, as opposed to the σ-hole theory. This case-in-point anionic XB donor has implications in catalysis, especially anion-binding catalysis.[8]

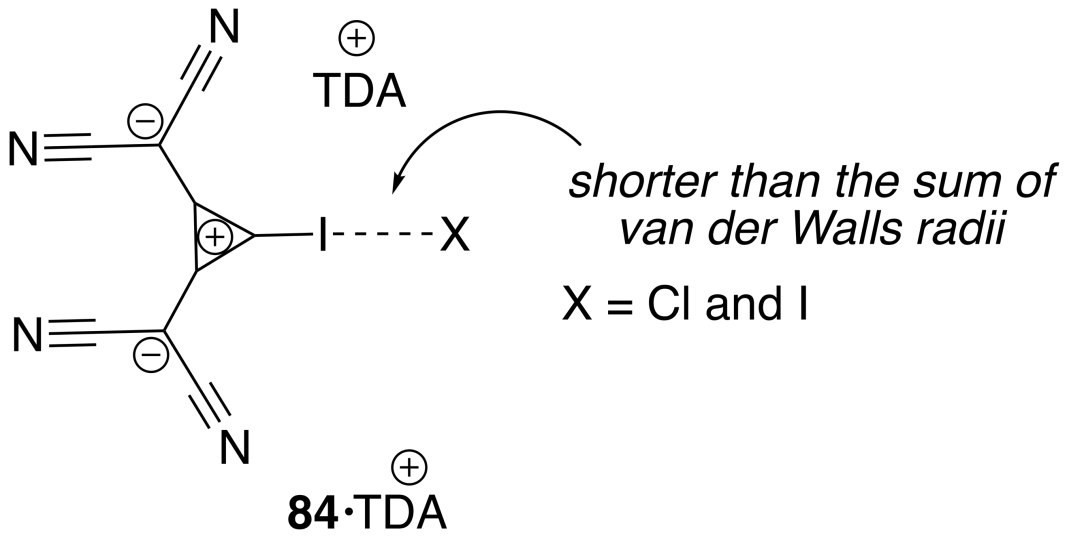



***Figure 19.*** *An anionic iodocyclopropenium halogen bonding interaction.*

### *3.0 Disclaimer*

Select publications have been included in this thesis that highlight some of my primary work throughout my 5-year duration in the Doctoral program at Brock University, which are listed in chronological order. Aspects of this thesis that were not performed by the candidate, Ivor Smajlagic, will be clarified below.

(1) Adapted with permission from Smajlagic, I.; Durán, R.; Pilkington, M.; Dudding, T. Cyclopropenium Enhanced Thiourea Catalysis. *J. Org. Chem.* **2018**, *83*, 13973–13980. Copyright 2018 American Chemical Society. The candidate performed all of the experimental- and synthetic work. Dr. Melanie Pilkington performed X-ray diffraction studies on a single-crystal of **4**·$BF_4^-$, wherein the crystal was grown by the candidate. Rocio Durán determined the computed p$K_a$ of thiourea **4**. Dr. Travis Dudding performed the remainder of the computations. Razvan Simionescu helped with the set-up and analysis of NMR experiments. The writing of the manuscript was initiated by the candidate from which then a rigorous revision process took place between the candidate and supervisor, Dr. Travis Dudding, ultimately leading to publication.

(2) No permission was required from Elsevier. Smajlagic, I.; Carlson, B.; Rosano, N.; Foy, H.; Dudding, T. Charge-Enhanced Thiourea Catalysts as Hydrogen Bond Donors for Friedel–Crafts Alkylations. *Tetrahedron* **2019**, *75*, 130757–130763. The candidate performed the majority of experiments (~70%), including synthetic work and chemical kinetics. Brenden Carlson contributed his efforts to this work by helping establish the substrate scope. Nicholas Rosano synthesized all trans-β-nitrostyrene analogs, which

were used as starting material. Hayden Foy completed all computations. The writing of the manuscript was initiated by the candidate from which then a rigorous revision process took place between the candidate and supervisor, Dr. Travis Dudding, ultimately leading to publication.

(3) Adapted with permission from Smajlagic, I.; Guest, M.; Durán, R.; Herrera, B.; Dudding, T. Mechanistic Insight toward Understanding the Role of Charge in Thiourea Organocatalysis. *J. Org. Chem.* **2020**, *85*, 585–593. Copyright 2020 American Chemical Society. The candidate performed all of the experimental- and synthetic work. Matt Guest performed most computations (~80%) with assistance from Dr. Travis Dudding and Rocio Durán. Razvan Simionescu helped with the set-up and analysis of NMR experiments. The writing of the manuscript was initiated by the candidate from which then a rigorous revision process took place between the candidate and supervisor, Dr. Travis Dudding, ultimately leading to publication.

The last section of the Results and Discussion entitled "*Second-Generation Squaramide-Cyclopropenium as a Brønsted Acid Organocatalyst*" is not yet published. The contributions to the work that was chosen to be highlighted by the candidate follows below. The candidate performed majority of the experiments (~95%). Brandon White and Oyindamola Azeez assisted in the purification and characterization of products. Computational modeling was performed by the candidate. Dr. Melanie Pilkington performed X-ray diffraction studies on a single-crystal of **11**·$BF_4^-$, wherein the crystal was grown by the candidate.

## *4.0 Results and Discussion*

### *4.1 Introduction*

Having become more familiar with the content relating to the anticipated chemistry, *vide infra*, the next section of this dissertation will now be discussed. In a specific sense, these sub-sections are compartmentalized by varying modes of catalytic reactivity; however, aspects such as synthesis and other domains/techniques will also be discussed. In this way, it places emphasis on how molecular structure affects chemical reactivity; the intellectual basis of organic chemistry. The sub-sections are listed as follows:

1) Thiourea-cyclopropenium as a Brønsted acid organocatalyst
2) Thiourea-cyclopropenium as a hydrogen bond donor organocatalyst
3) Second-generation squaramide-cyclopropenium as a Brønsted acid organocatalyst

### *4.2 Thiourea-cyclopropenium as a Brønsted acid organocatalyst*

As an in-coming graduate student in the Dudding laboratory (2016), there were frequent talks centered around achieving the arduous synthesis of a thiourea-cyclopropenium molecule, as envisioned by Dr. Dudding. Being overzealous, yet a novice in the field of synthesis, I volunteered to take on this task and assist in pioneering this idea by bringing it to fruition. In theory, combining the two components—thiourea and cyclopropenium—would lead to a charge-enhanced catalyst that is presumably more efficient in catalyzing reactions than neutral, achiral, state-of-the-art thiourea organocatalysts. Given this basis, as well as the established interest in developing novel cyclopropenium systems in the Dudding group, cyclopropenium-augmented thiourea **4** was explored (Figure 20A). Motivating this enterprise was the premise that **4** would exhibit both cationic H-bond donor (*domain A*) and electrostatically-enhanced character due to the

presence of the cyclopropenium ring (*domain B*), in addition to a Lewis basic sulfur atom that could serve as a H-bond acceptor (*domain C*). A view supported by the computed NBO charges and the ESP of envisioned **4** (*Z*,*Z*-conformer), with positively charged N–H hydrogens and cyclopropenium ring carbon atoms (Figure 20B). Exploring this concept further, the first thiourea-cyclopropenium and its application as a Brønsted acid catalyst (**4**·$BF_4^-$) for the synthetically important pyranylation of alcohols and phenols was investigated (Figure 20C).

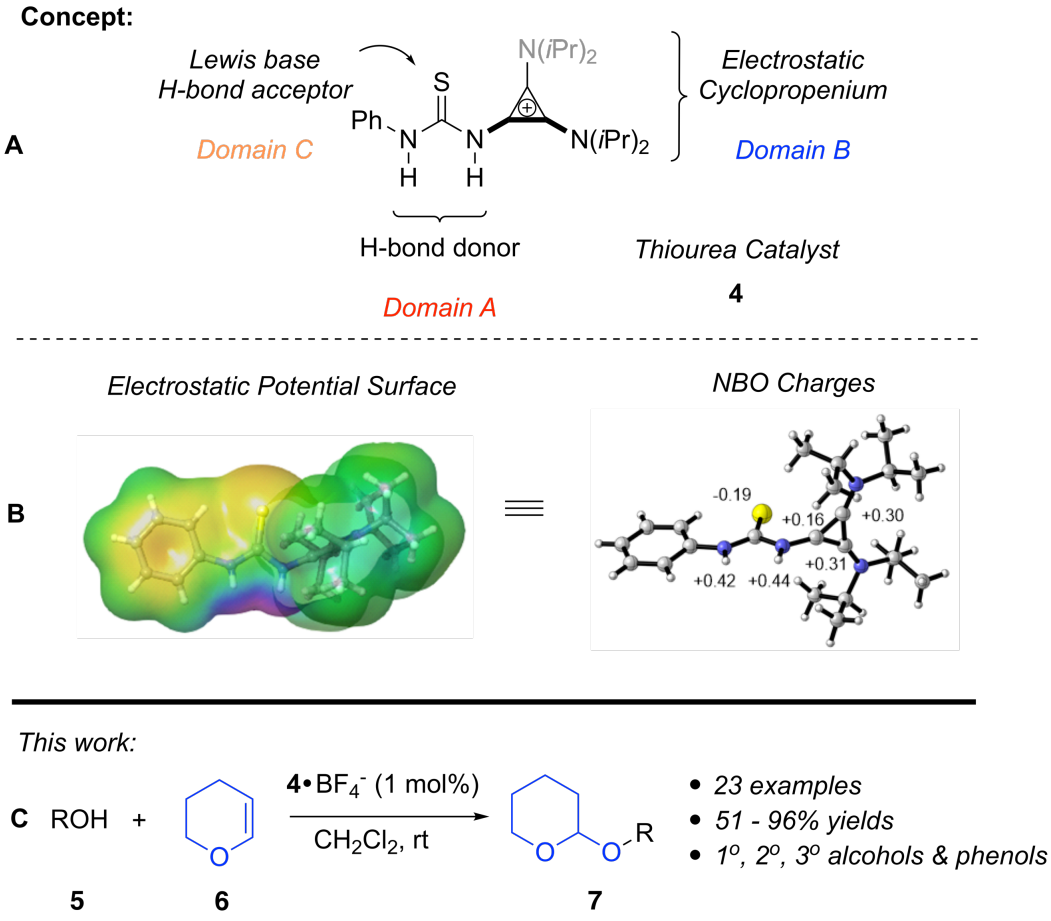



***Figure 20.*** *(**A**) Cyclopropenium as a new charged domain for (thio)urea catalysts. (**B**) ESP with isodensity value 0.0001 au (left-hand side) and computed NBO charges of select atoms of thiourea **4** at the B3LYP/6-31G+(d,p) level of theory (right-hand side). (**C**) General conditions for the pyranylation of alcohols and phenols using thiourea catalyst **4**·$BF_4^-$.*

### *4.2.1 Exploratory studies centered around structure determination, optimizations and substrate scope*

At the outset of this experimental investigation, the synthesis of this envisioned thiourea was pursued, ultimately leading to a short preparative route involving the treatment of phenyl isothiocyanate with 2,3-bis(diisopropylamino)cyclopropenimine in DCM affording **4**·$BF_4^-$ in 44% isolated yield. Subsequent X-ray diffraction studies on a single-crystal of **4**·$BF_4^-$ revealed several interesting features, *viz*., a *Z*,*Z*-conformation and short intermolecular contacts between the thiourea N–H hydrogen atoms and $BF_4^-$ counterion, such that, N(4)-H(4)···F(1) = 2.312 Å and N(3)-H(3)···F(2) = 2.003 Å (Figure 21a). Furthermore, the phenyl and thiourea groups were co-planar ($\theta_{C(16)\text{-}N(4)\text{-}C(17)\text{-}C(22)}$ = 174.4(4)°), consistent with extended π-conjugation, while in contrast the orthogonal ($\theta_{C(16)\text{-}N(3)\text{-}C(3)\text{-}C(1)}$ = 87.7(5)°) alignment of the cyclopropenium ring and the thiourea functionality was indicative of poor π-conjugation (see Appendix A for details). Supporting this bonding scenario was a slight lengthening (~0.03 Å) of the N(3)–C(16) bond distance when compared to the N(4)–C(16) distance of 1.352(4) Å. Meanwhile, the computed acidity of the N(3)–H(3) group (p$K_a$ = 5.42 in DMSO) was considerably greater than the N(4)–H(4) group (p$K_a$ = 11.7 in DMSO), presumably as a result of the electrostatically-enhanced H-bond donor capacity conferred by the adjacent positively charged cyclopropenium moiety (Figure 21b).

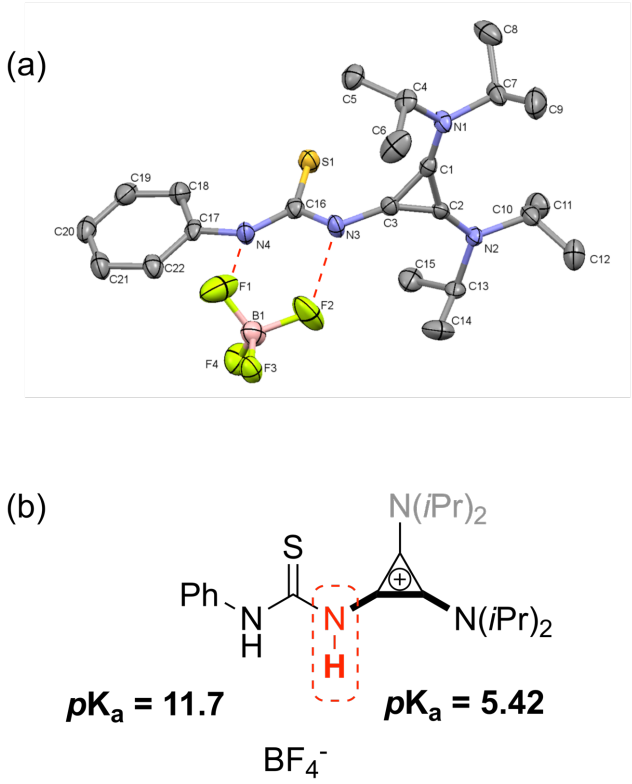
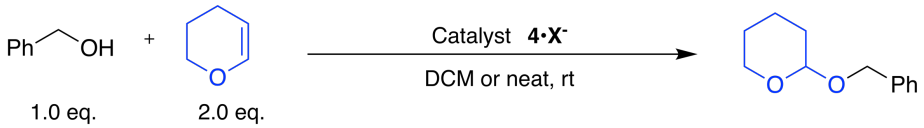



***Figure 21.*** *(a) Thermal ellipsoid plot of the molecular structure of* ***4***$\cdot BF_4^-$ *with appropriate labelling scheme. Thermal ellipsoids are plotted at 50%. Only selected H-atoms are shown. Short N-H···F contacts are shown as red dashed lines. (b) Two-dimensional representation of* ***4***$\cdot BF_4^-$ *highlighting the computed* $pK_a$ *values in DMSO.*

Having insight into the structural and physical properties of thiourea **4**$\cdot BF_4^-$, we next explored its use as a catalyst for the pyranylation of alcohols (**5**) with DHP (**6**). The results are summarized in Table 1. Initial efforts to facilitate the pyranylation of alcohols consisted of using benzyl alcohol (**5a**) and **6** as substrates in dilute conditions (0.5 M in alcohol and 1.0 M in DHP), which led to poor conversion rates even after 12 hours (entries 1 and 2). A phenomenon presumably arising from the lack of interactions between the substrates and the catalyst, which speaks to the molecularity of the reaction. To circumvent this issue, we subjected the substrates of interest and catalyst to different reaction conditions that were more optimal involving low catalyst loading (1 mol%) and more concentrated reaction

conditions (1.0 M in alcohol and 2.0 M in DHP) affording full conversion of **7a** in 3 h (entry 3). Furthermore, these conditions were then applied using reported electrostatically enhanced thiourea, 1-methyl-3-(3-phenylthioureido)pyridinium iodide[10b] (1 mol%), which resulted in no conversion after 6 hours. Next, the use of solvent-free conditions and a 1:2 reagent stoichiometry provided a similar reaction outcome, though a slightly longer reaction time was required (entry 5). Notably, there was a three-fold rate acceleration in comparison to Schreiner's reported thiourea for the pyranylation of **5a** under the same solvent-free reaction conditions.[9e]

***Table 1.*** *Optimization of reaction conditions.*




1.0 eq. 2.0 eq.

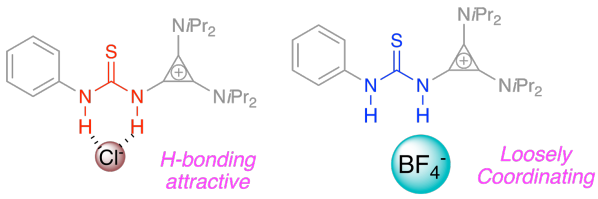
**5a** **6** **7a**

| entry | catalyst | loading (mol%) | conversion[d] (1 h) | conversion[d] (6 h) | conversion[d] (12 h) |
|---|---|---|---|---|---|
| 1 | **4**·$BF_4^-$ [a] | 1 | 3% | 6% | 11% |
| 2 | **4**·$BF_4^-$ [a] | 10 | 13% | 20% | 28% |
| 3 | **4**·$BF_4^-$ [b] | 1 | 35% | 100% | 100% |
| 4 | **4**·$BF_4^-$ [b] | 10 | 24% | 100% | 100% |
| 5 | **4**·$BF_4^-$ [c] | 1 | 28% | 100% | 100% |
| 6 | **4**·$BF_4^-$ [c] | 10 | 30% | 100% | 100% |
| 7 | **4**·$Cl^-$ [b] | 1 | 0% | 0% | 0% |
| 8 | **4**·$Cl^-$ [b] | 10 | 28% | 50% | 100% |

Reactions were performed at room temperature using the following conditions: [a]0.5 mmol **5a**, 1.0 mmol **6** and 1.0 mL DCM. [b]0.5 mmol **5a**, 1.0 mmol **6** and 0.5 mL DCM. [c]1.0 mmol **5a**, 2.0 mmol **6** under neat conditions. [d]Conversion was determined *via* $^1$H NMR spectroscopic analysis of the crude reaction mixtures. This involved monitoring the disappearance of the signal at 6.37 ppm for **6** and appearance of the signal at 4.51 ppm for the THP protected product (**7a**).

Also apparent from the optimization studies was the observation of catalyst inhibition in the presence of a chloride counterion (entries 7 and 8) attributed to tight anion-binding in solution,[8] as supported by a downfield shift of the N–H hydrogen atoms of thiourea **4**·$Cl^-$ vs **4**·$BF_4^-$ ($^1$H NMR ($CDCl_3$) $\Delta\delta$N(4)–H = 2.59 ppm and $\Delta\delta$N(3)–H = 2.84 ppm), see Table 2. This data is consistent with the literature, in that, a strong thiourea-chloride complex is formed (thiourea **4**·$Cl^-$), and, thus, reduced reactivity is observed. On the other hand, tetrafluoroborate, being a weaker coordinating counteranion, was found to exhibit enhanced reactivity, albeit still possessing H-bond acceptor character, yet to a lesser extent.

***Table 2.*** *$^1$H NMR data comparing N–H chemical shifts for thiourea catalysts **4**·$BF_4^-$ & **4**·$Cl^-$ in $CDCl_3$.*



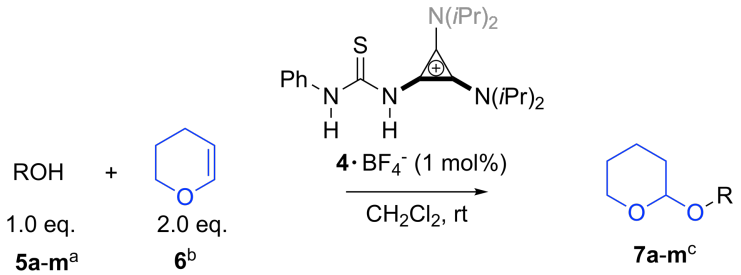

| Thiourea Catalysts | $\delta$N(4)–H (ppm) | $\delta$N(3)–H (ppm) | $\Delta\delta$N(4)–H (ppm) | $\Delta\delta$N(3)–H (ppm) |
|---|---|---|---|---|
| **4**·Cl– | 12.1 | 11.8 | | |
| | | | 2.59 | 2.84 |
| **4**·$BF_4$– | 9.51 | 8.96 | | |

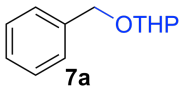
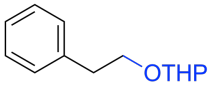
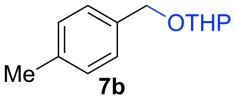
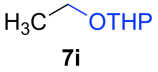
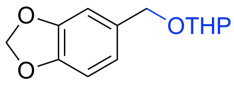
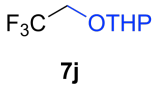
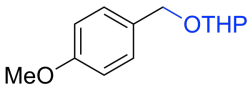
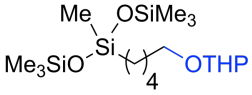
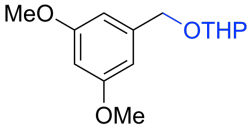
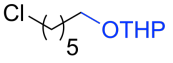
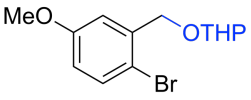
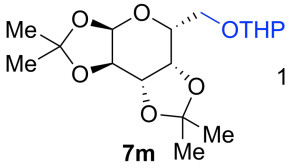
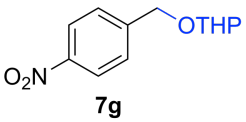
[a] A significant downfield shift is observed for both N(4)–H and N(3)–H atoms of thiourea **4**·$Cl^-$, respectively. It can be inferred that the protons are being deshielded by the chloride counteranion.

With the optimal conditions identified, **4**·$BF_4^-$ was applied to the reaction of various alkyl- and aryl-substituted primary alcohols (Table 3). For example, functionalized benzyl alcohols (**5a–g**) provided high yields in short reaction times, e.g., *p*-methyl substituted **5b** provided a 93% yield of product **7b** in 4 h. Likewise, methylene acetal protected substrate

**5c** afforded the pyranyl product **7c** in 90% yield after 3 h, while the electron-rich *p*-methoxy and 3,5-dimethoxy substituted benzyl alcohols (**5d** and **5e**) provided products **7d** and **7e** in high yields after slightly longer reaction times. Furthermore, compound **5f** with an inductively withdrawing *m*-methoxy group and sterically demanding *o*-bromo substituent afforded the pyranyl product **7f** in 85% yield. Benzyl alcohol substrate **5g** bearing an electron deficient *p*-nitro group afforded product **7g** in 92% yield after 5.5 h. The reaction of 3-phenyl-1-propanol (**5h**), furnished product **7h** in 70% yield after 48 h. In the case of the latter, the attenuated reactivity compared to benzyl alcohols may be ascribed to the loss of non-covalent interactions that include π-π-(aryl-aryl) stacking phenomena that subsequently impart transition state stabilization, though this does not rule out other possible modes of action that may account for this observed reactivity. Similarly, ethanol (**5i**), and electron-poor trifluoroethanol (**5j**) reacted sluggishly, albeit in high isolated yields. Conversely, primary alcohols bearing extended functionalized aliphatic side chains (**5k** and **5l**) afforded the desired products (entries **7k** and **7l**) in good to excellent yields. Extending our catalytic methodology to sugar analogues, we reacted substrate **5m** that furnished the pyranyl product **7m** in 96% yield after 1.5 h.

***Table 3.*** *Pyranylation of primary alcohols.*

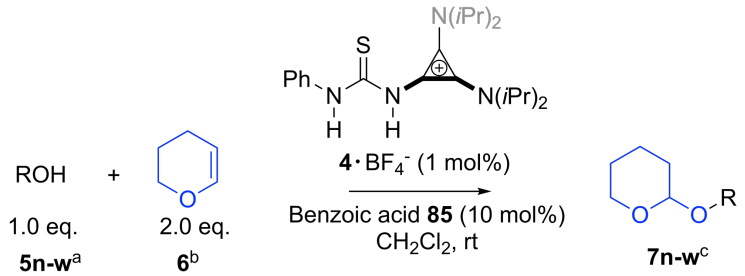


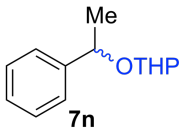
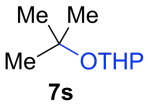
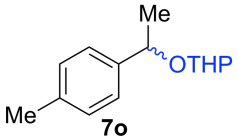
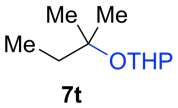
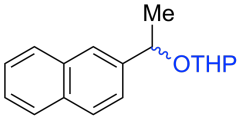
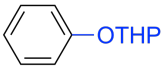
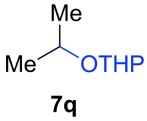
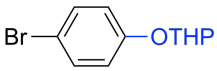
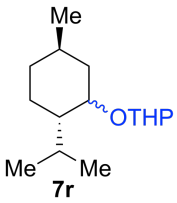
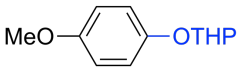

| Entry | Product | Time (h) | Yield (%) | Entry | Product | Time (h) | Yield (%) |
|---|---|---|---|---|---|---|---|
| 1 |  **7a** | 1.5 | 95 | 8 |  **7h** | 48 | 70 |
| 2 |  **7b** | 4 | 93 | 9 |  **7i** | 29 | 93 |
| 3 |  **7c** | 3 | 90 | 10 |  **7j** | 52 | 80 |
| 4 |  **7d** | 10.5 | 91 | 11 |  **7k** | 24 | 82 |
| 5 |  **7e** | 8 | 88 | 12 |  **7l** | 0.7 | 94 |
| 6 |  **7f** | 9 | 85 | 13 |  **7m** | 1.5 | 96 |
| 7 |  **7g** | 5.5 | 92 | | | | |

[a] 5.0 mmol of respective alcohols. [b] 10.0 mmol DHP. [c] The reaction was performed in 5.0 mL DCM at room temperature under an inert atmosphere. The yields provided are reported as isolated yields after flash chromatography. There was no conversion witnessed in the absence of **4**·$BF_4^-$.

The reaction of secondary alcohols was then probed using α-methyl benzyl alcohol (**5n**) as the substrate together with **6** under our optimized conditions (*vide supra*), which raised immediate concerns as product **7n** was produced in a low yield after 24 h. Nevertheless, the addition of benzoic acid (**85**) as a co-catalyst (10 mol%) remedied this lack of reactivity, as conferred by a 93% yield of the sterically congested pyranyl product **7n** after 5.5 h (Table 4). Employing these modified conditions, α-methyl benzyl/napthyl alcohols were also reacted with **6** to afford products **7o** and **7p** in good to excellent yields. The use of sterically hindered aliphatic substrates such as *iso*-propanol and menthol likewise afforded products **7q** and **7r** in high yields. The extension of our methodology to the reactions of tertiary alcohols also resulted in good yields of the desired products > 80%. Finally, the reactivity of phenols was explored using substrates **5u–w** all of which gave the desired pyranyl products (entries, **7u–w**) in moderate to excellent yields.

***Table 4.*** *Pyranylation of higher-substituted alcohols and phenols.*




| Entry | Product | Time (h) | Yield (%) | Entry | Product | Time (h) | Yield (%) |
|---|---|---|---|---|---|---|---|
| 1[d] |  **7n** | 5.5 | 93 | 6 |  **7s** | 84 | 88 |
| 2[d] |  **7o** | 20 | 94 | 7 |  **7t** | 65 | 84 |
| 3[d] |  **7p** | 80 | 70 | 8 |  **7u** | 80 | 73 |
| 4 |  **7q** | 96 | 94 | 9 |  **7v** | 7 | 92 |
| 5[d] |  **7r** | 46 | 96 | 10 |  **7w** | 94 | 51 |

[a] 5.0 mmol of respective alcohols or phenols (ROH). [b] 10.0 mmol DHP. [c] The reaction was performed in 5.0 mL DCM at room temperature under an inert atmosphere. The yields provided are reported as isolated yields after flash chromatography. There was no conversion witnessed in the absence of **4**·$BF_4^-$ with or without benzoic acid. [d] The diastereomeric ratio (d.r.) of compounds **7n–p** and **7r** is 1:1.

### *4.2.2 Mechanistic studies*

Initial efforts to probe the mechanism of these reactions will now be discussed. A solution of catalyst **4**·$BF_4^-$ (1 equiv) was monitored by $^1$H NMR as aliquots of benzyl alcohol (1–10 equiv) were added. This experiment resulted in a pronounced downfield shift of the alcohol O–H signal that was attributed to the presence of a H-bonding interaction between the thiocarbonyl sulfur atom and the alcohol that, based on DFT calculations, was computed be a favorable process ($\Delta E_{int}$ = -21.5 kcal/mol) linked to $S_{LP} \rightarrow \sigma_{(O\text{-}H)}^*$ donor-acceptor interactions ($E_{NBO}$ = 4.94 kcal/mol). The conspicuous lack of a change in the thiourea N–H signal, though unexpected, suggests the presence of weak or non-existent interactions between the alcohol oxygen atom and the thiourea N–H hydrogens. Further, kinetic studies revealed a first-order dependency with respect to both alcohol and DHP (see appendix A for details). Lastly, additional $^1$H NMR titration experiments were performed to better understand the role of the co-catalyst (**85**) in the reactions of phenols, secondary and tertiary alcohols. Upon titration of **85** (1–2 equiv), it was observed that the thiourea N–H signals were participating in rapid proton exchange events with benzoic acid on the NMR timescale, thus, providing evidence for the formation of a thiourea-benzoic acid complex, as further supported by variable temperature NMR studies (see Appendix A for details). This is consistent with previous reports of Brønsted acids enhancing the catalytic activity of thioureas through a concept formally referred to as cooperative catalysis.[121]

From the above findings, a putative catalytic cycle is put forth for the thiourea-mediated pyranylation of primary alcohols (Figure 22). A pre-equilibrium establishing metastable catalyst–substrate H-bond complex **5**·**4** (step I) initiates the cycle. A subsequent reaction with DHP (**6**), *via* proton transfer transition state **TS1** (step II), then provides oxocarbenium

intermediate **6i** and **5·4-H**, corresponding to a tight or loose ion pair (solvent-separated vs. solvent-shared). Addition of alcohol then results in the formation of transient oxonium species **6i'** by transition state **TSII** (step III). Deprotonation of the latter by *in situ* derived thiourea conjugate base **4-H** then provides the pyranyl product **7** concomitant with regeneration of catalyst **4** (step IV).

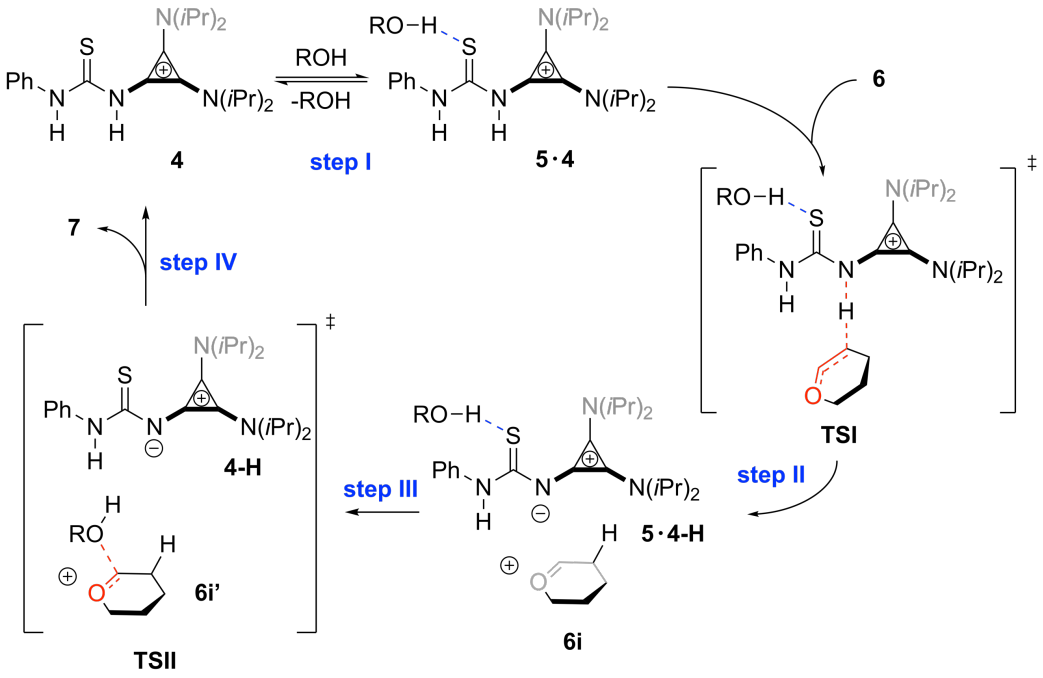



***Figure 22.*** *Mechanistic proposal for the thiourea-catalyzed (**4**) pyranylation of primary alcohols.*

This proposed cycle, however, does not take conformational dynamics into consideration and was constructed based on preliminary mechanistic information. Moreover, recent efforts in the literature investigating the putative role of thiourea *Z,Z-*, *E,Z-, Z,E-* and *E,E*-orientations, and their correlated conformational dynamics highlights the importance of these underappreciated, yet catalytically active conformers[9d,h,122] (Figure 23A). In this respect, thiourea *Z,Z*-orientations have historically been widely invoked in

transition state models; however, contemporary examples in the literature suggest other thiourea rotamers are likely vital for reactivity (Figure 23B). Critical in this sense are environmental stimuli, e.g., solvent stabilization rigidifying catalyst conformation, and with it, influencing transition state organization.[7a,b,122,123,124,125,126]

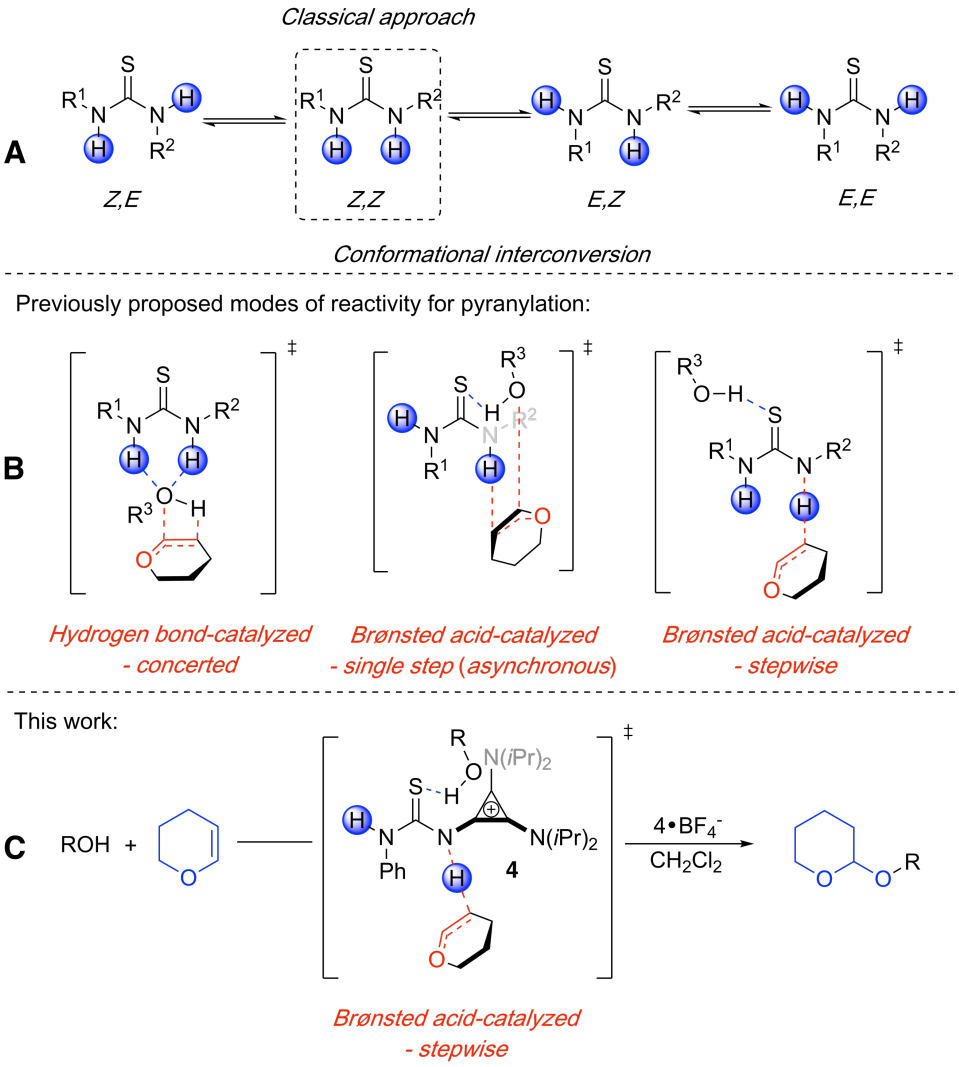



***Figure 23.*** *(**A**) General depiction of thiourea conformers. (**B**) Previous reported modes of reactivity for pyranylation reactions using thioureas. (**C**) Computational investigation of pyranylations using thiourea **4**·$BF_4^-$.*

In light of these developments, it was obvious that further investigatory studies were imperative in order to get a better understanding of the mechanistic picture (Figure 23C). This uncertainty, along with the well-established dynamic nature of biomimetic thiourea catalysts, e.g., Schreiner's thiourea, as demonstrated by Schreiner,[9d] Pápai and Varga,[9h] and Baldauf,[122b] provided a strong impetus to delineate the operative role of thiourea **4**·$BF_4^-$ in pyranylations and other transformations. Further, it was anticipated the knowledge acquired from this undertaking would offer insights into hydrogen bond catalysis, Brønsted acid catalysis, charge-enhanced catalysis, multifunctional catalysis, and conformational dynamics broadly applicable in organocatalysis.

To commence this experimental investigation, the rotamer distribution of **4**·$BF_4^-$ was explored by 1D NOESY and vtNMR (600 MHz, $CD_2Cl_2$) analysis (Figure 24). Irradiation of the adjacent cyclopropenium ring N(3)–H hydrogen atom (green) gave rise to NOE signals correlating to both the N(4)–H (blue) and *ortho*-aryl C(22)–H (grey) hydrogens with the latter signal being weaker in intensity. A similar trend emerged upon irradiation of the N(4)–H hydrogen, though a stronger correlation to the *ortho*-aryl C(22)–H (grey) hydrogen was observed. In contrast, correlation between the N(3)–H hydrogen and the hydrogens of the *N*-diisopropyl methyl groups was not observed, thus, suggesting a distal spatial relationship between the groups (Figure 24A). Evident from these NOE findings is a preferred solution-phase *Z,Z*-orientation of **4**·$BF_4^-$ that is consistent with the reported crystal structure, *vide supra*.

Prompted by these results, it was anticipated that VT analysis would reveal the presence of other rotamers of **4**·$BF_4^-$ at lower temperatures (Figure 24B). Initially, a well-resolved methine signal at 4.08–4.12 ppm, indicative of rapid conformer exchange at 295.1 K, was

observed that upon cooling to 230.4 K resulted in a broad signal at ~4.09 ppm, telling of restricted rotation about the C(3)–N(3) bond. Further cooling of the sample to 203.2 K led to splitting of this poorly resolved methine signal to a doublet (4.36–4.60 ppm) and a singlet at 3.74 ppm, supporting the presence of two or possibly more distinct rotamers. Consistent with this was the extrapolated activation barrier ($\Delta G^{\ddagger}$) of 10.2 kcal/mol and rate constant $k_c$ = 974.1 $s^{-1}$ for this exchange process at coalescence (230.4 K). The non-equivalency of these methine signals was attributed to anisotropic shielding by the π-polarizable cyclopropenium ring and π-electron system of the thiocarbonyl. Likewise, a 1D NOESY experiment conducted at 193.0 K revealed the presence of a *Z,Z*-orientation. Confirming this orientation was the observed N(3)–H and N(4)–H correlation that resulted in a strong NOE signal ascribed to interactions with the tetrafluoroborate counterion, hence rigidifying this conformation.[8] Irrespective, all of these conformers would be accessible experimentally, as further supported by the computed 12.5 kcal/mol rotational barrier for conversion of conformer *E,Z*-**4** to *Z,Z*-**4** (see Appendix A). In attempting to freeze out additional rotamers, the sample was cooled to 182.1 K; however, no further signal separation was observed with respect to the *ortho*-aryl hydrogen atoms, thus, confirming C(17)–N(4) bond rotation was a low barrier process.

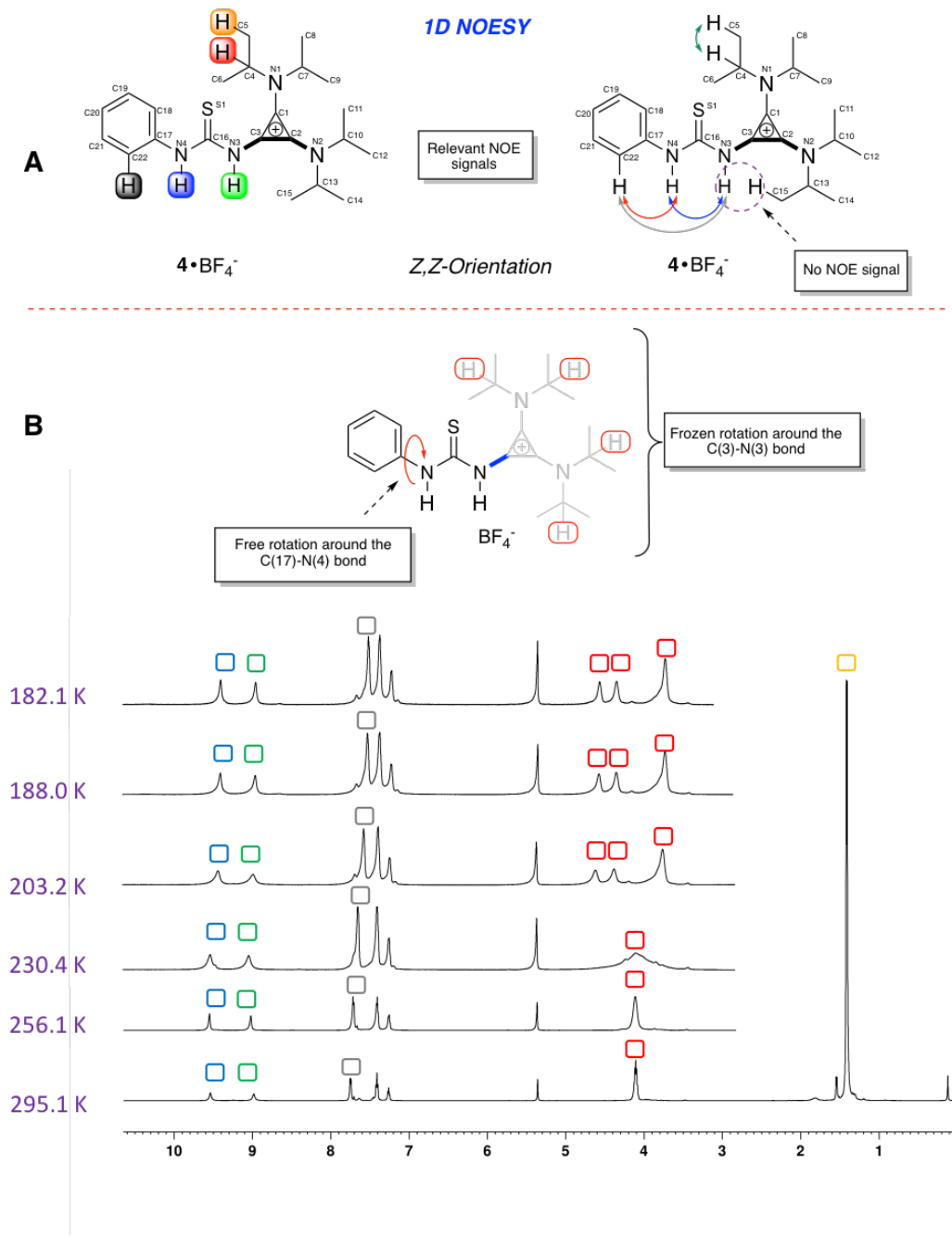


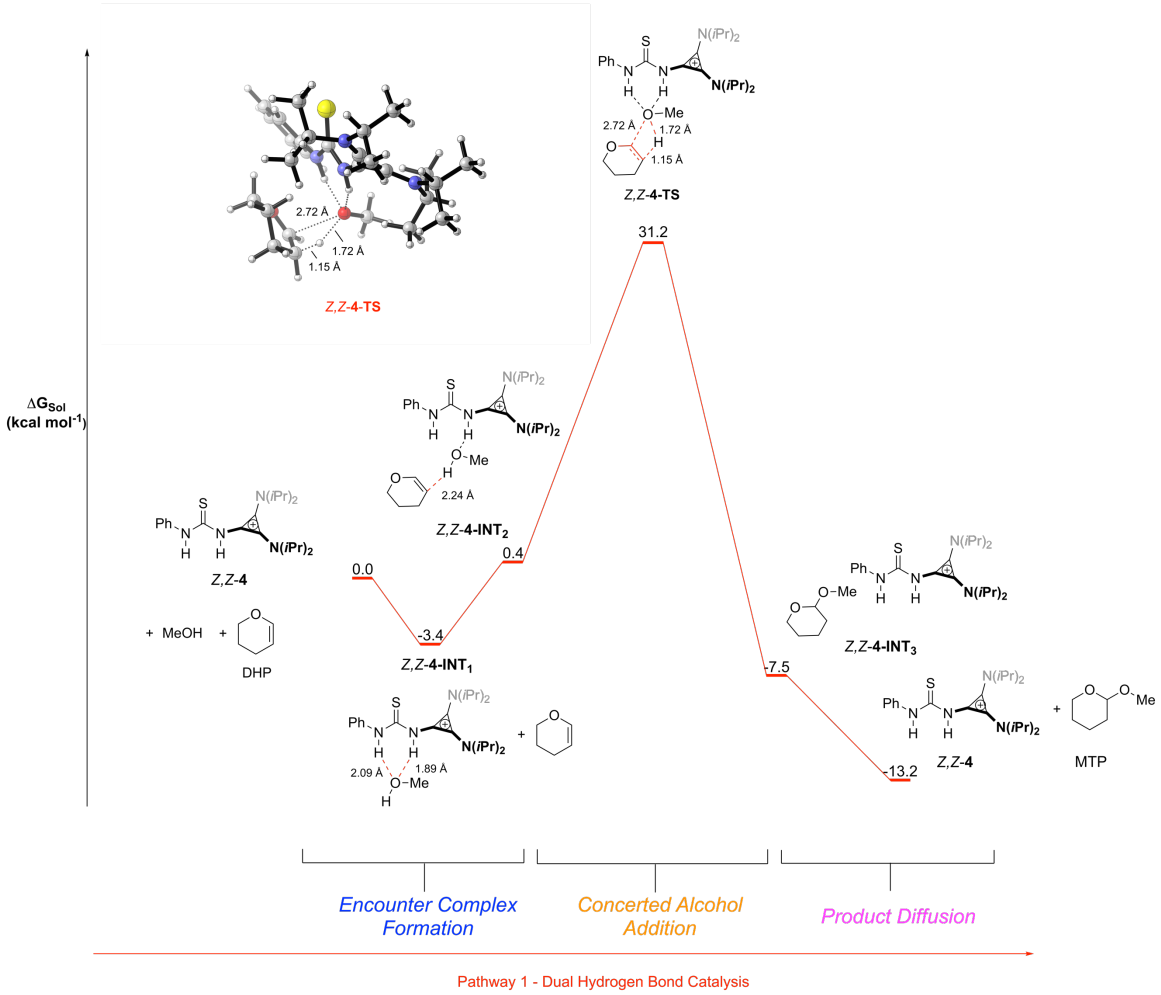

***Figure 24.*** *A) Correlations between hydrogen atoms for* ***4***$\cdot BF_4^-$ *based on 1D NOESY experiments with atoms labelled.* ***B****) Variable temperature* $^1H$ *NMR spectra with select thiourea* ***4***$\cdot BF_4^-$ *conformers frozen.*

Having insight into the conformational dynamics of thiourea catalyst **4**·$BF_4^-$, the mechanism(s) involving pyranylation of alcohols using DFT were explored. Emerging from these efforts were mechanistic pathways centered around either rate-determining (1) alcohol addition by thiourea bifurcated *dual hydrogen bond activation* (Pathway 1, Scheme 10) or (2) alcohol addition by *Brønsted acid catalysis* (Pathway 2, Scheme 11).

Pathway 1 (*dual hydrogen bond activation*) proceeds from thiourea **4** in the *Z,Z*-rotamer geometry (as observed by NMR), wherein a bifurcated H-bond complex *Z,Z*-**4-INT$_1$** displaying N–H···O hydrogen bond distances of 2.09 Å and 1.89 Å occurs (Scheme 10). Encounter complex *Z,Z*-**4-INT$_2$** then emerges, wherein the alcohol hydrogen atom resides directly atop the alkene of DHP at a distance of 2.31 Å. Inherent to this intermediate, and certainly linked to the cyclopropenium charge, was a large degree of charge polarization across the N(3)–H···O–H hydrogen bond subassembly (NBO charges N = -0.671 e, H = 0.459 e, O = -0.795 e, H = 0.510 e) setting the stage for proton transfer to the β-carbon of the vinyl ether of DHP. Rate-determining alcohol addition involving C–O bond formation, coupled with proton transfer, follows by transition state *Z,Z*-**4-TS** having a sizable Gibbs free energy activation barrier of 30.8 kcal/mol with respect to *Z,Z*-**4-INT$_2$**. In terms of both the energetic span model and TOF, *Z,Z*-**4-INT$_1$** corresponds to the TOF-determining intermediate, while the TOF-determining transition state was *Z,Z*-**4-TS**, thus, resulting in an overall energy span of 34.6 kcal mol$^{-1}$ (TON = 7.2x10$^{-11}$, TOF = 2.7x10$^{-13}$ s$^{-1}$).[127] The defining metrics of first-order saddle point *Z,Z*-**4-TS** entailed an elongated C···O bond-making distance of 2.72 Å, as well as C···H and O···H proton transfer distances of 1.15 Å and 1.72 Å. Intermediate complex *Z,Z*-**4-INT$_3$** then forms, where after separation of the

pyranylated product (MTP), an overall exergonic process, thiourea *Z,Z*-**4** is liberated making it available for another reaction cycle.

***Scheme 10***. *Pathway 1: dual hydrogen bond activation catalyzed by charged thiourea conformer Z,Z-**4**.*

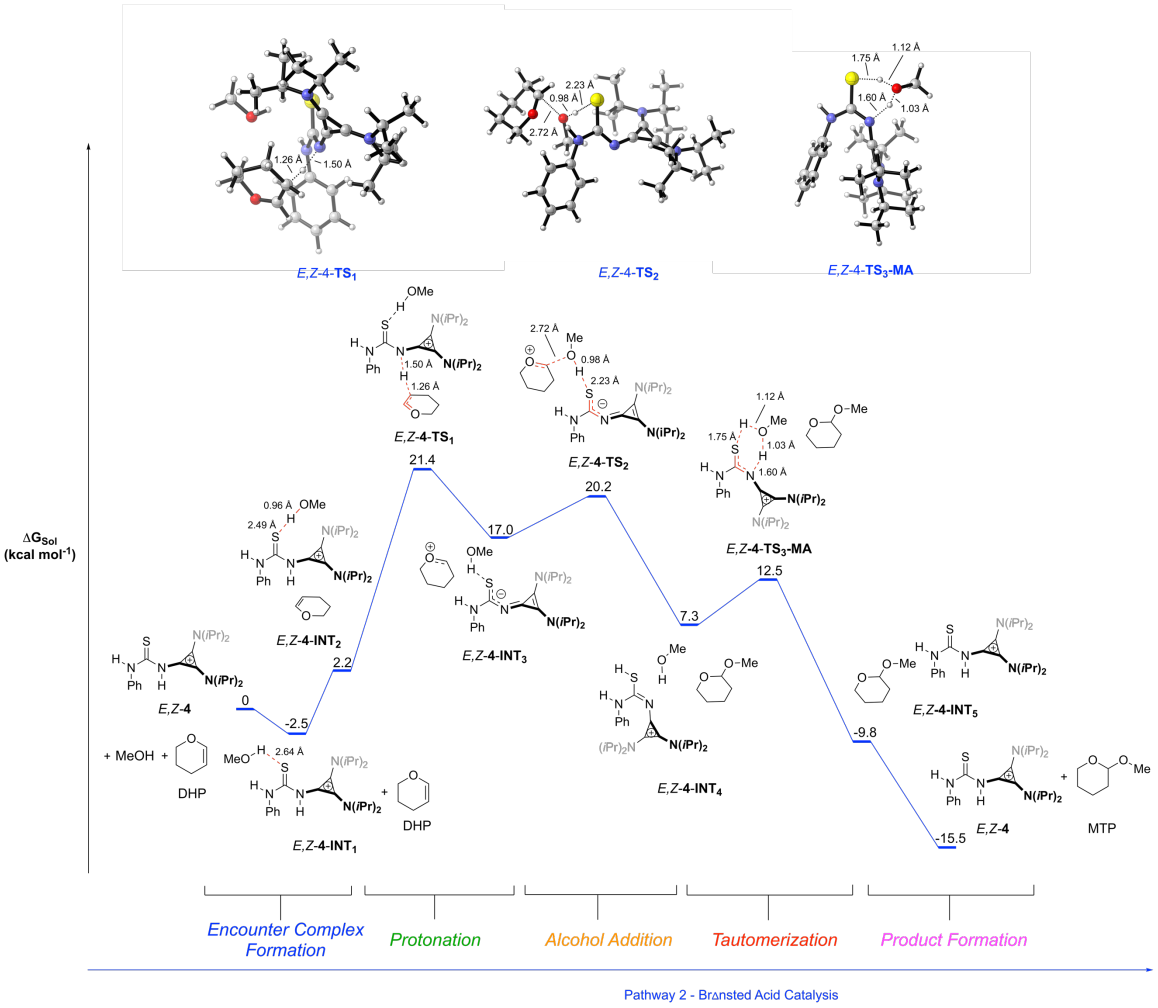



Alternatively, pathway 2 (*Brønsted acid catalysis*) initiates from *E,Z*-rotamer catalyst conformation *E,Z*-**4** that, in the presence of methanol, forms H-bond complex *E,Z*-**4-INT$_1$** featuring a S···H–O hydrogen bond measuring 2.64 Å (Scheme 11). Next, complex *E,Z*-**4-INT$_2$** follows in which the cyclopropenium N–H hydrogen is primed for protonation of the vinyl ether alkene of DHP, while the alcohol acts as a bridging element bringing the catalyst and DHP in close proximity. Proton transfer transition state *E,Z*-**4-TS$_1$** then ensues

with a Gibbs free energy activation barrier of 21.4 kcal/mol with respect to the starting material.

Similarly, in terms of the energy span model, *E*,*Z*-**4-TS$_1$** was the TOF-determining transition state and *E*,*Z*-**4-INT$_1$** was the TOF-determining intermediate leading to an energy span of 23.9 kcal mol$^{-1}$ for this cycle (TON = 8.3x10$^{-4}$, TOF = 1.7x10$^{-5}$ s$^{-1}$ ).[127] The defining features of this structure are proton transfer distances of 1.50 Å and 1.26 Å with the alcohol component residing 4.52 Å from the vinyl ether α-carbon atom. Alternatively, protonation by the anilino nitrogen hydrogen N(4)–H was disfavored by 4.5 kcal/mol relative to transition state *E*,*Z*-**4-TS$_1$**, thus, making this protonation process unlikely and further highlighting the significance of the cyclopropenium charge. Oxonium-thiourea anion ion pair *E*,*Z*-**4-INT$_3$** follows on the reaction pathway, residing 4.4 kcal/mol below transition state *E*,*Z*-**4-TS$_1$**. Next, alcohol addition *via* *E*,*Z*-**4-TS$_2$**, displaying a C···O bond forming distance of 2.72 Å, followed by proton transfer provides ion pair *E*,*Z*-**4-INT$_4$**. Thiol-to-nitrogen methanol-assisted proton tautomerization by 6-membered cyclic transition state *E*,*Z*-**4-TS$_4$-MA** with a barrier of 12.5 kcal/mol then furnishes complex *E*,*Z*-**4-INT$_5$**. The key metrics of this transition state structure being S···H and N···H distances of 1.75 Å and 1.60 Å, as well as corresponding O··H distances of 1.12 Å and 1.03 Å, respectively. Finally, this energetically favored pathway finishes with separation of the pyranylated product MTP and liberation of catalyst *E*,*Z*-**4** for another catalytic cycle. From these findings, based on the energetic span model, pathway 2 is energetically favored among the proposed mechanisms. It is important to note that exploration of pathway 2 *via* cyclopropenium nitrogen protonation was performed for all conformations of thiourea **4**; however, only a mechanism involving the *E,Z*-conformer was found to exist.

***Scheme 11***. *Pathway 2: Brønsted acid catalysis by charged thiourea conformer E,Z-**4**.*




To corroborate these computed findings, putative catalyst–substrate interactions were probed using $^{1}$H NMR by sequentially adding DHP to thiourea catalyst **4**·$BF_4^-$ that resulted in no spectroscopic changes, and, by inference, the lack of any interaction (Figure 25). Conversely, the sulfur of the catalyst engages in H-bonding with alcohols, as mentioned above. This evidence suggests that thiourea catalyst **4**·$BF_4^-$ plays a key bifunctional role[11] in these reactions by initially forming a more reactive metastable alcohol–catalyst complex (function 1) primed for proton transfer to DHP (function 2).

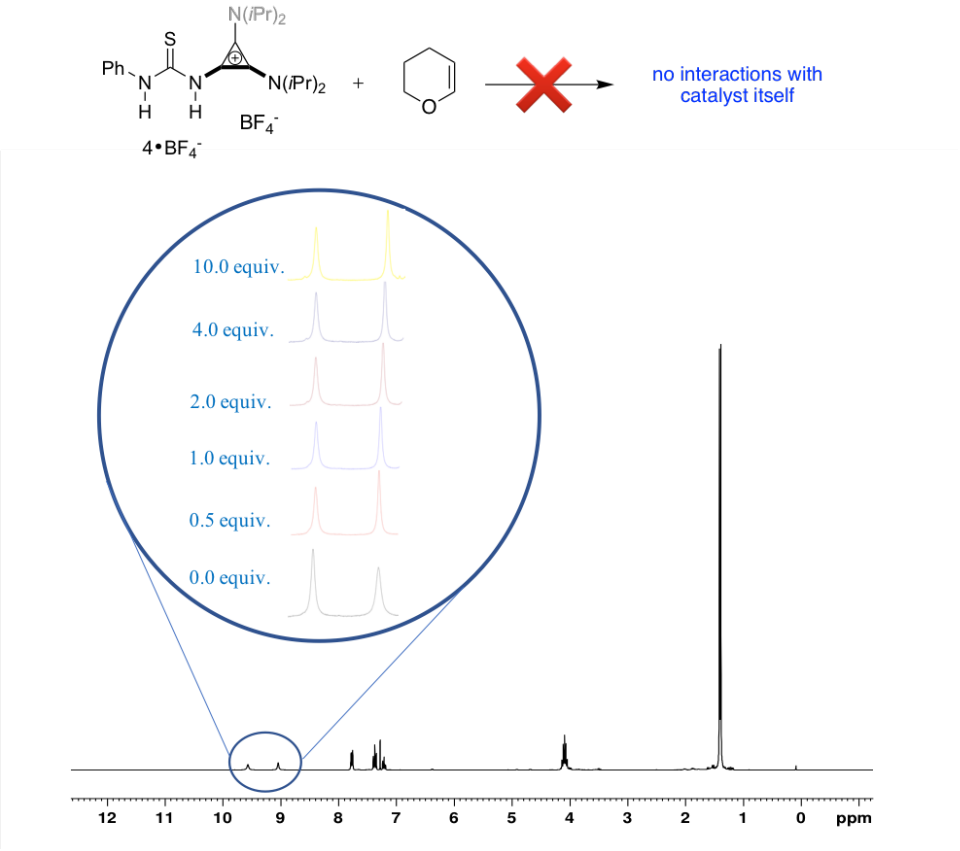
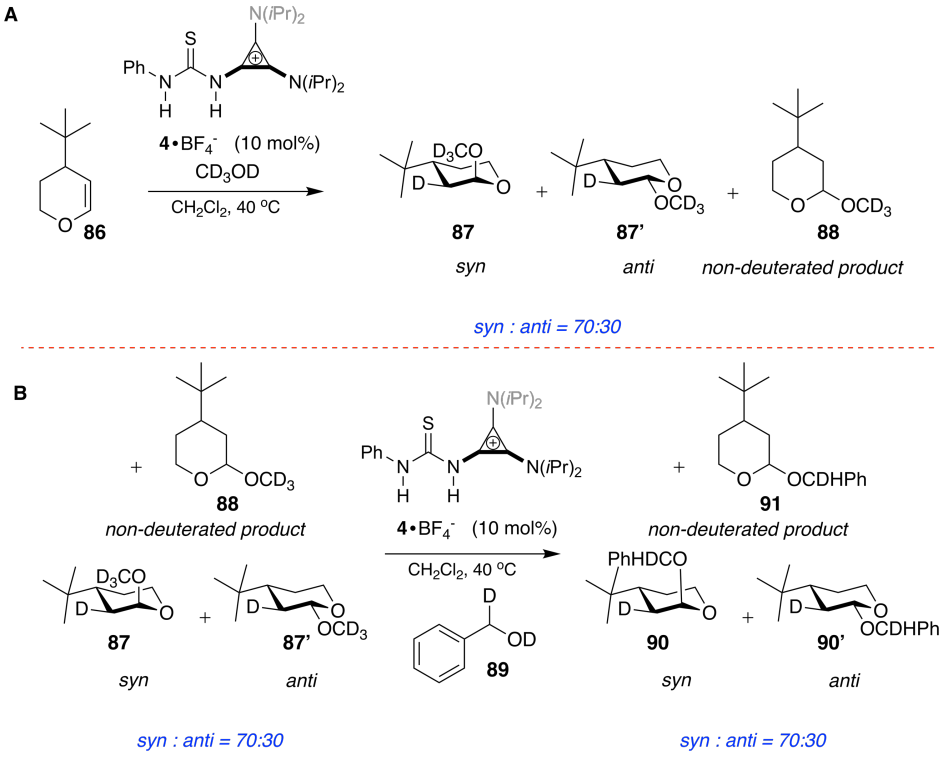



***Figure 25.*** *$^{1}$H NMR spectra depicting no interactions between thiourea **4**·$BF_4^-$ and DHP.*

Next, the *anti*/*syn*-stereochemistry of alcohol addition to the alkene of DHP was investigated by reacting conformationally locked analogue 4-(*tert*-butyl)-3,4-dihydro-*2H*-pyran in methanol-$d_4$ in the presence of thiourea catalyst **4**·$BF_4^-$. Monitoring this reaction by $^{1}$H NMR over a duration of 48 hours revealed the formation of a diastereomeric mixture of pyranylated products with a kinetically-controlled preference for *syn* product formation (*syn* : *anti* ratio of 70:30), consistent with a Brønsted acid mode of catalysis (Scheme 12A). In contrast, a concerted H-bond-mediated reaction mechanism for alcohol addition proceeding through a pivotal intermediate displaying a ridged host–guest (catalyst–substrate) interaction allowing for nucleophilic attack from only one face would give rise to a single stereoisomer, thus, opposing the likelihood of a concerted reaction mechanism under the employed conditions.

Subsequently, a series of control experiments using ethanol and benzyl alcohol were performed, wherein alkoxide exchange was observed (see Appendix A). Intrigued by the ability of thiourea catalyst **4**·$BF_4^-$ to induce alkoxide exchange, the reaction conditions were subjected to phenyl (*O*,1-$^2H_2$) methanol (**89**) to distinguish between alkoxide exchange and epimerization (Scheme 12B). From this experiment was observed a *syn* : *anti* product ratio of 70:30 mirroring that seen with methanol-$d_4$, which was ascribed to analogous mechanisms of alcohol addition. Based on this outcome, epimerization can be ruled out in favour of a catalyst-controlled stereoselective kinetic reaction scenario.

***Scheme 12.*** *Mechanistic investigation of alcohol addition using deuterium-labeled alcohols: (A) Investigating the stereochemistry of addition using methanol-$d_4$ and 4-(tert- Butyl)-3,4-dihydro-2H-pyran. (B) Investigating the stereochemistry of addition using phenyl (O,1-$^2H_2$) methanol and a mixture of syn and anti product isomers (methyl adduct).*



To gain further insight into the putative Brønsted acid-mediated mechanism, $^{13}C$ KIE studies were pursued using Jacobsen's DEPT method[128] analyzing the product at low conversion at natural abundance (Figure 26). More specifically, the DEPT-55 method was employed under pseudo-first-order conditions measuring KIEs at 2% product conversion. From this study, substantial inverse kinetic isotope effects were observed at the $\alpha$- and $\beta$-carbons with values of 0.892, and 0.898, respectively taking into account a 1.5% uncertainty in NMR integrations, thus, resulting in an uncertainty of 0.003[129] in the KIEs. These KIE findings are telling of two key features: (1) the observed large and inverse KIEs suggest that a multistep reaction involving a pre-equilibrium prior to the rate-determining step is plausible,[130] and (2) the observed similar KIEs at the $\beta$- and $\alpha$-carbons are indicative of $sp^2 \rightarrow sp^3$ rehybridization and negligible rehybridization, respectively at the rate-determining step. Though, this does not rule out other possible conclusions that can be drawn from these trends. Taken together, the experimental and computational findings support that thiourea-catalyzed (**4**) pyranylations is a stepwise Brønsted acid mechanism.

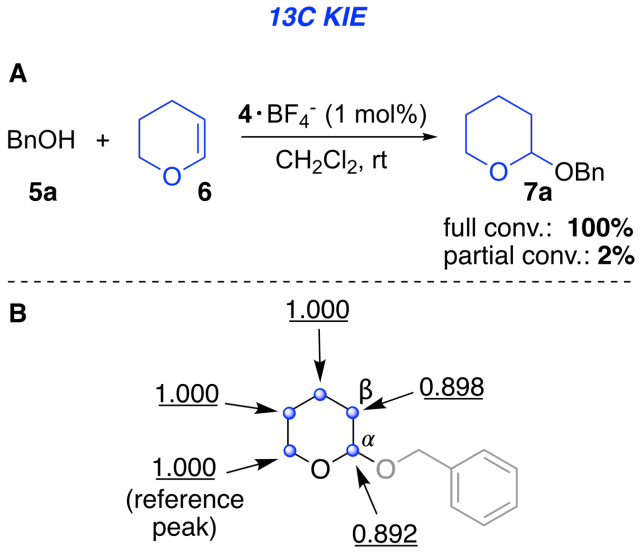



***Figure 26.*** *(A) $^{13}C$ kinetic isotope effect. (B) $^{13}C$ isotopic composition of THP protected alcohol from a reaction taken to 2% product conversion.*

### *4.2.3 2-Deoxyglycosylation*

Having established charge-enhanced thiourea catalyst **4**·$BF_4^-$-induced diastereoselection, the use of 3,4,6-tri-*O*-benzyl-D-galactal (**92**) as a bio-relevant 2-deoxysugar glycosyl donor equivalent[131] was investigated. In exploring this further application of catalyst **4**·$BF_4^-$, **92** was reacted at reflux to afford 2-deoxygalactosylated product **93** in 84% yield with exclusive α-facial selectivity (Figure 27, top). Inspired by this result, the origin of this selectivity was sought by performing molecular mechanics searches.

Thus, utilizing the optimized structure of *E,Z*-**4**-$\mathbf{TS_I}$ as a template, *O*-benzyl functionality was appended and α- vs. β-stereofacial alcohol addition considered, resulting in two representative transition state models (Figure 27, bottom). These models were then imported into the program MacroModel.[132] The internal coordinates of the atoms of the catalyst, alcohol and vinyl ether were frozen, and MCCS with the OPLS3 force field[133] performed to generate an array of conformers for α- and β-stereofacial alcohol addition.

Visible from the superposition of the conformers for α-stereofacial alcohol addition was an open cavity allowing for more accessible alcohol addition (Figure 27, bottom left-hand side**)**, whereas alcohol addition to the more sterically shielded *β*-face was impeded by the presence of bulky benzyl groups steering the catalyst away from the site of reactivity (Figure 27, bottom right-hand side). While granted, these simple molecular mechanics models offer a preliminary basis for understanding α- vs. β-stereofacial alcohol addition a more thorough mechanistic investigation is required to unravel the fine details with respect to this transformation.

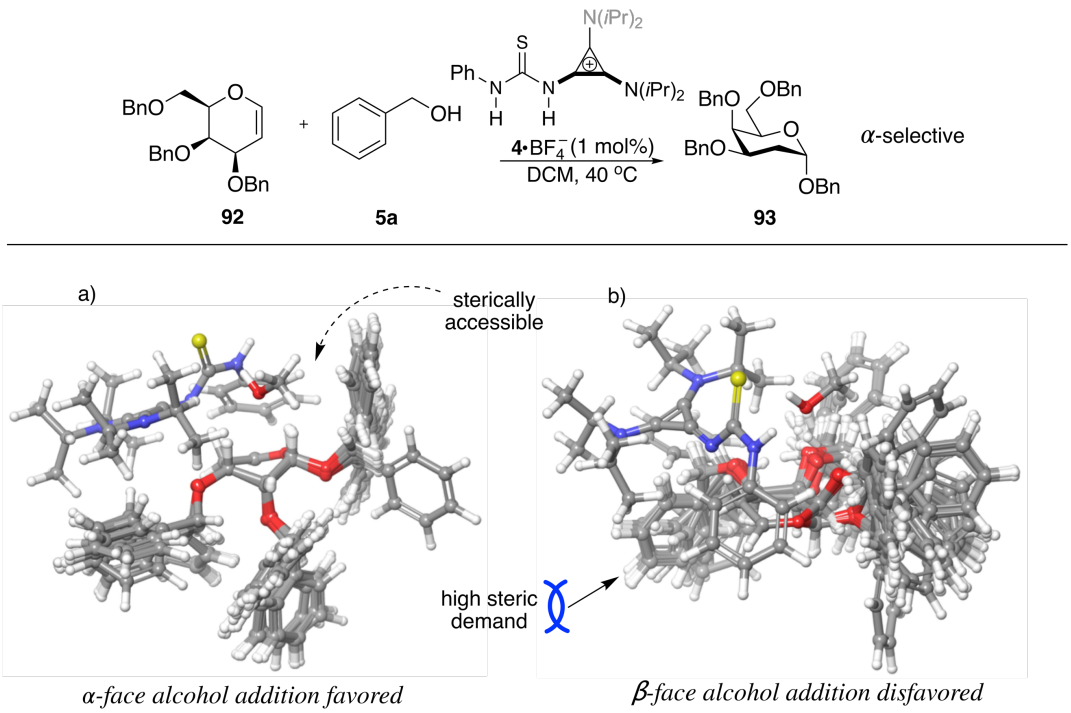



***Figure 27.*** *2-Deoxygalactosylation of 3,4,6-tri-O-benzyl-D-galactal facilitated by thiourea* ***4***$\cdot BF_4^-$ *(top). Comparison of α- vs β-stereofacial alcohol addition (bottom) (Superposition of conformers within 10 kJ/mol of the global minima).*

To conclude this section, experimental and computational studies of a cationic thiourea (**4**) for the successful pyranylation of various alcohols and phenols, and glycosylation of a 2-deoxy sugar were presented. Arising from these studies was the importance of conformational dynamics, which is especially relevant in molecules with many degrees of freedom, wherein structural- and catalytic features are interdependent.[134] Further, a distinct feature of the Brønsted acid catalytic reactivity examined was "charge-enhanced acidity,"[135] which is a timely concept gaining traction in the last decade for rational design of small-molecule-based organocatalysts.[10,100,101,103b,110] The basis of this appeal stems from enhanced substrate activation relative to neutral catalysts, much like that found in more complex enzymatic counterparts. Further, the analysis discussed above demonstrates

judiciously designed organocatalysts having a charged moiety provide a general tool for improving catalytic reactivity. These works were published in 2018[15] and 2020.[16]

### *4.3 Thiourea-cyclopropenium as a hydrogen bond donor organocatalyst*

#### *4.3.1 Optimizations and establishment of synthetic utility*

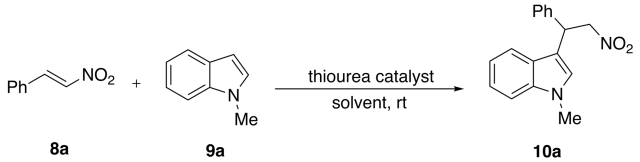
Having established thiourea **4** as an efficient catalyst in pyranylation, the next section of this dissertation will delve into the details regarding its potential as a multifunctional catalyst targeting Friedel–Crafts alkylation. Notably, these heterocyclic indole products are prevalent motifs in Nature, such as in natural products, offering broad-spectrum bioactivity, e.g., antibacterial, antifungal, and anti-inflammatory properties.[136]

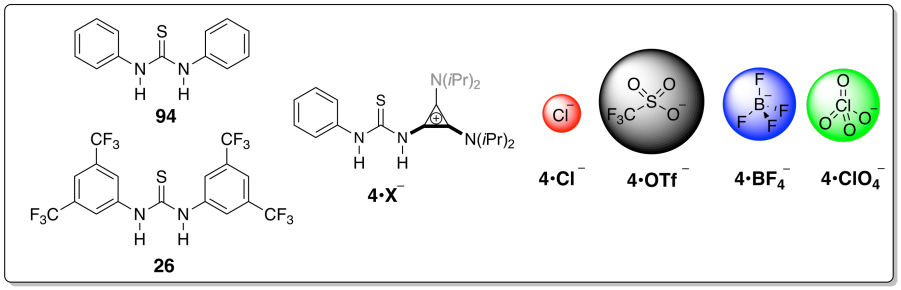
The majority of reported organocatalyzed approaches for this transformation, however, are limited by one, or more, of the following: (1) poor substrate scope, (2) use of costly reagents and/or expensive catalyst(s) often prepared by multi-step synthetic routes, (3) lack of scalability and (4) high catalyst loadings. From these precedents, it was postulated that thiourea catalyst **4** would serve as a viable H-bond donor organocatalyst for Friedel–Crafts alkylation reactions, as supported by the studies below.

Initial efforts involved the experimental use of thiourea **4** as a H-bond catalyst for Friedel–Crafts alkylation (Table 5). In this vein, an initial control reaction performed in the absence of catalyst led to essentially no conversion after 44 hours (entry 1), while sluggish reactivity was observed using neutral thiourea catalysts **94** and **26** (entries 2 and 3, respectively). Based on these results, and with the aim of improving reactivity, the use of various charged thiourea catalyst salts of **4** were investigated. The logic for doing this being possible tight anion-binding, i.e., very short intermolecular N–H···counteranion contacts as a possible source of attenuated reactivity.[8] Corroborating this hypothesis, thiourea **4** with

an inexpensive and weakly coordinating tetrafluoroborate counteranion provided superior results relative to **4**·$ClO_4^-$, **4**·$Cl^-$, and **4**·$CF_3SO_3^-$ (entries 4–7). Next, various solvents were screened using thiourea **4**·$BF_4^-$ (entries 7–12) resulting in DCM as the solvent of choice affording an optimal conversion of 96% (entry 7). This finding comes as no surprise given solvents with expected H-bond acceptor character are prone to disrupt catalyst–substrate interactions. Lastly, reducing the catalyst loadings to 5 mol%, and even as low as 1 mol% attenuated conversion (entries 13 and 14).

***Table 5***. *Optimization of reaction conditions.*[a]



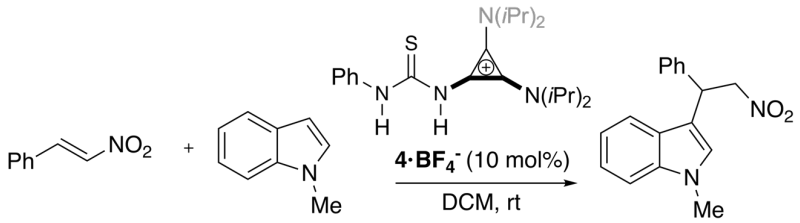




| entry | solvent | catalyst | catalyst load (mol%) | conversion[b] |
|---|---|---|---|---|
| 1 | $CH_2Cl_2$ | - | - | <5% |
| 2 | $CH_2Cl_2$ | **94** | 10 | <5% |
| 3 | $CH_2Cl_2$ | **26** | 10 | 34% |
| 4 | $CH_2Cl_2$ | **4**•$ClO_4^-$ | 10 | 82% |
| 5 | $CH_2Cl_2$ | **4**•$Cl^-$ | 10 | 10% |
| 6 | $CH_2Cl_2$ | **4**•$CF_3SO_3^-$ | 10 | 46% |
| 7 | $CH_2Cl_2$ | **4**•$BF_4^-$ | 10 | 96% |
| 8 | $C_6H_5CH_3$ | **4**•$BF_4^-$ | 10 | 64% |
| 9 | THF | **4**•$BF_4^-$ | 10 | 36% |
| 10 | $CHCl_3$ | **4**•$BF_4^-$ | 10 | 90% |
| 11 | $CH_3CH_2CN$ | **4**•$BF_4^-$ | 10 | 29% |
| 12 | MeCN | **4**•$BF_4^-$ | 10 | 58% |
| 13 | $CH_2Cl_2$ | **4**•$BF_4^-$ | 5 | 50% |
| 14 | $CH_2Cl_2$ | **4**•$BF_4^-$ | 1 | 18% |

[a]Reactions were performed at room temperature using the following conditions: 0.5 mmol **8a**, 1.5 mmol **9a,** 0.05 mmol catalyst, and 0.5 mL solvent for 44 h. [b]Conversion was determined *via* $^1$H NMR spectroscopic analysis of the crude reaction mixtures. This involved monitoring the disappearance of the signal at 8.00 ppm for (**8a**) and appearance of the signal at 5.21 ppm for the FC alkylated product (**10a**).

With optimized reaction conditions in hand, the scope of this reaction with respect to indole was investigated (Figure 28). Unprotected indole **9b** reacted with *trans*-$\beta$-nitrostyrene to afford product **10b** in very good yield, while *N*-protected indoles[137] **9c** and **9d** resulted in no conversion, presumably owing to reduced indole nucleophilicity imparted by the electron withdrawing *N*-tosyl and *N*-acetyl groups. Next, the scope of this reaction with respect to the nitroalkene component was explored. Non-functionalized 2-furyl and 2-napthyl nitroalkenes (**8b** and **8c**) reacted to afford products **10e** and **10f** in good-to-excellent yields, while electron-rich alkoxy- and alkyl nitroalkenes (**8d–g**) provided variable yields. For instance, *trans*-4-methyl-$\beta$-nitrostyrene (**8d**) reacted smoothly to afford product **10g** in excellent yield, whereas alkoxy substituted *trans*-$\beta$-nitrostyrenes (**8e**–**g**) all led to poor conversions (**10h–j**). Further, halogenated *trans*-$\beta$-nitrostyrenes (**8h–l**) provided products **10k–o** in good-to-excellent yields. The high yields of fluorinated products **10k** and electron-poor **10o** is notable given the importance of organofluorine compounds in pharmaceuticals,[138] agrochemicals,[139] and material science[140] industries.

***Scheme 13.*** *Gram-scale reaction catalyzed by thiourea* ***4***$\cdot BF_4^-$.




**8a** (6.7 mmol, 1.0 g) **9a** (20 mmol, 2.6 g) **10a** (1.8 g , 97%)

Following establishment of the scope, the practicality of this reaction was demonstrated by the gram-scale preparation of Friedel–Crafts alkylation product **10a** in excellent yield (97%, 1.8 g), Scheme 13.

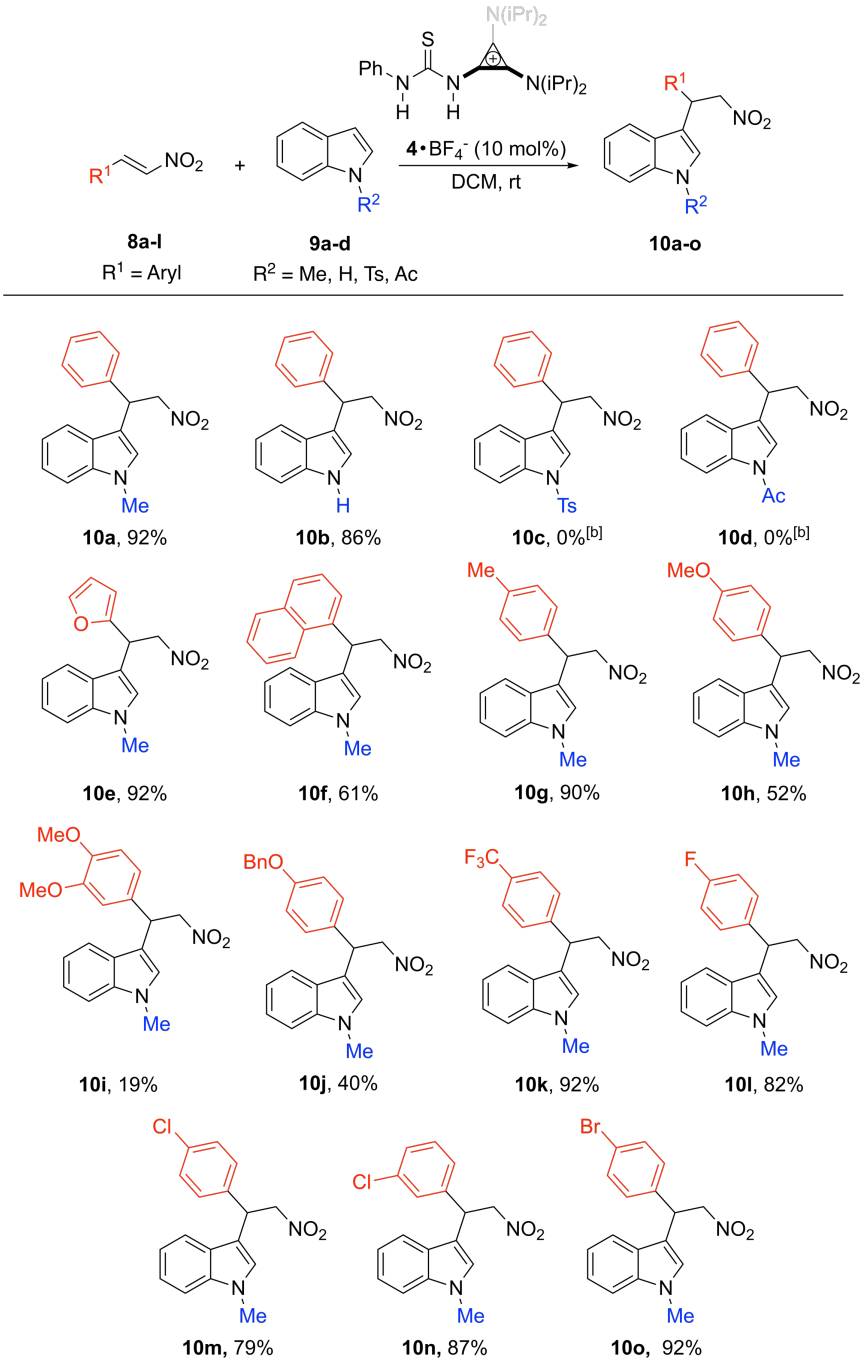
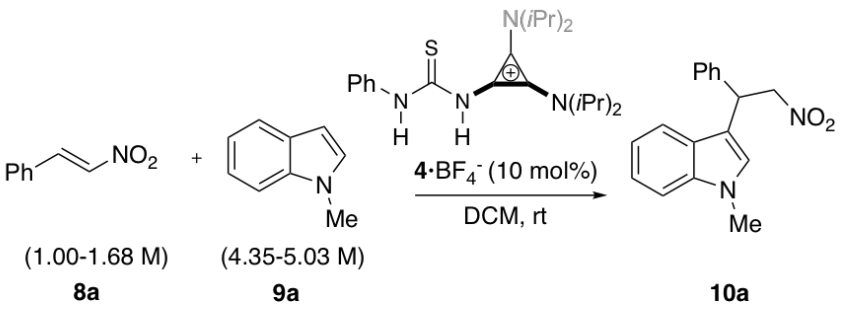



***Figure 28***. *Employment of thiourea 4·$BF_4^-$ for Friedel–Crafts alkylation[a].*

[a]Reactions were performed at room temperature using the following conditions: 0.5 mmol of respective nitroalkene, 1.5 mmol of respective indole, 0.05 mmol **4**·$BF_4^-$, and 0.5 mL DCM for 44 h. The yields of isolated products are reported after flash chromatography. [b]No reaction occurred using these *N*-functionalized indoles.

### *4.3.2 Mechanistic studies*

Finally, to probe the underlying mechanism of this Friedel–Crafts reactivity, and thereby determine the reaction order and stability of catalyst **4**·$BF_4^-$, binding studies in conjunction with VTNA were performed. Addition of increasing equivalents of substrate *trans*-$\beta$-nitrostyrene (**8a**) to catalyst **4**·$BF_4^-$ in $CDCl_3$ resulted in a slight downfield shift of the N–H hydrogen atom ($^1$H NMR, $\Delta\delta = 0.04$ ppm), thus, consistent with a LUMO-lowering mode of substrate activation, as opposed to a Brønsted acid mode of reactivity, see Appendix B. Next, the robustness of the catalyst was probed by VTNA (Figure 29).




| entry | [**8a**] (M) | [**9a**] (M) | [**10a**] (M) | [**4**•$BF_4^-$] (M) | [reduction] |
|---|---|---|---|---|---|
| Expt 1: standard conditions | 1.68 | 5.03 | 0.00 | 0.168 | 0.680 |
| Expt 2: reduced concentration | 1.00 | 4.35 | 0.00 | 0.168 | 0.680 |

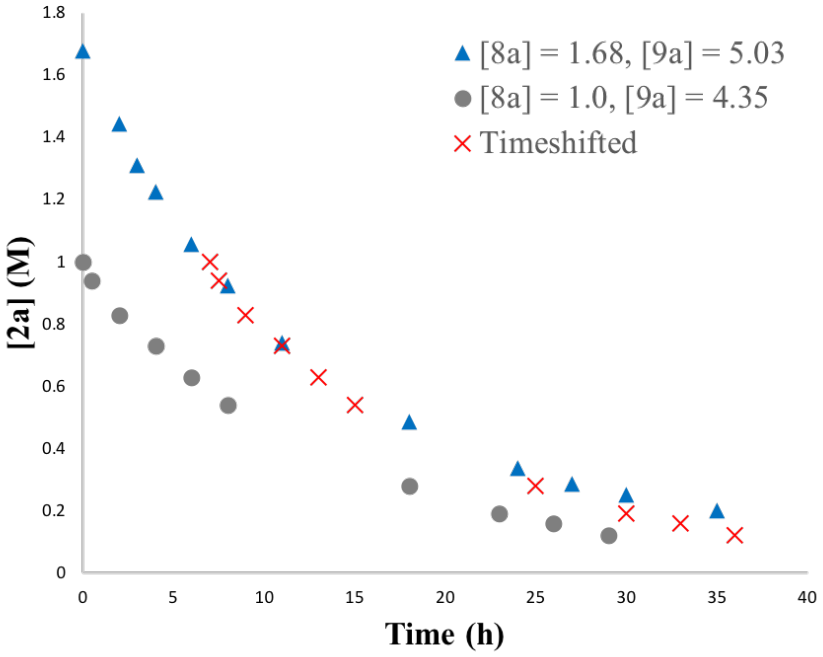



***Figure 29***. *Plot of time (h) vs. concentration (M) for two independent starting concentrations of trans-β-nitrostyrene performed under synthetically relevant conditions for the determination of thiourea* ***4***·$BF_4^-$ *robustness.*

Overlay of the two curves, as seen in Figure 29, is telling of steady-state catalyst concentration with catalytic turnover affected by neither catalyst deactivation nor product

inhibition (see Appendix B for further details). Further analysis revealed a 0.8-order dependency in catalyst indicative of a high proportion of the catalyst persisting as monomeric species in solution, much unlike that of previous thiourea-catalyzed[10b,c] processes (Figure 30). This divergence, presumably arises from key structural differences, i.e., the bulky cyclopropenium diisopropylamine substituents abating formation of dimeric or higher-order aggregate complexes. Collectively, these kinetic results shed light on and speak to the value of incorporating cyclopropenium building blocks as core components to H-bond organocatalysts, such as thiourea catalysts.

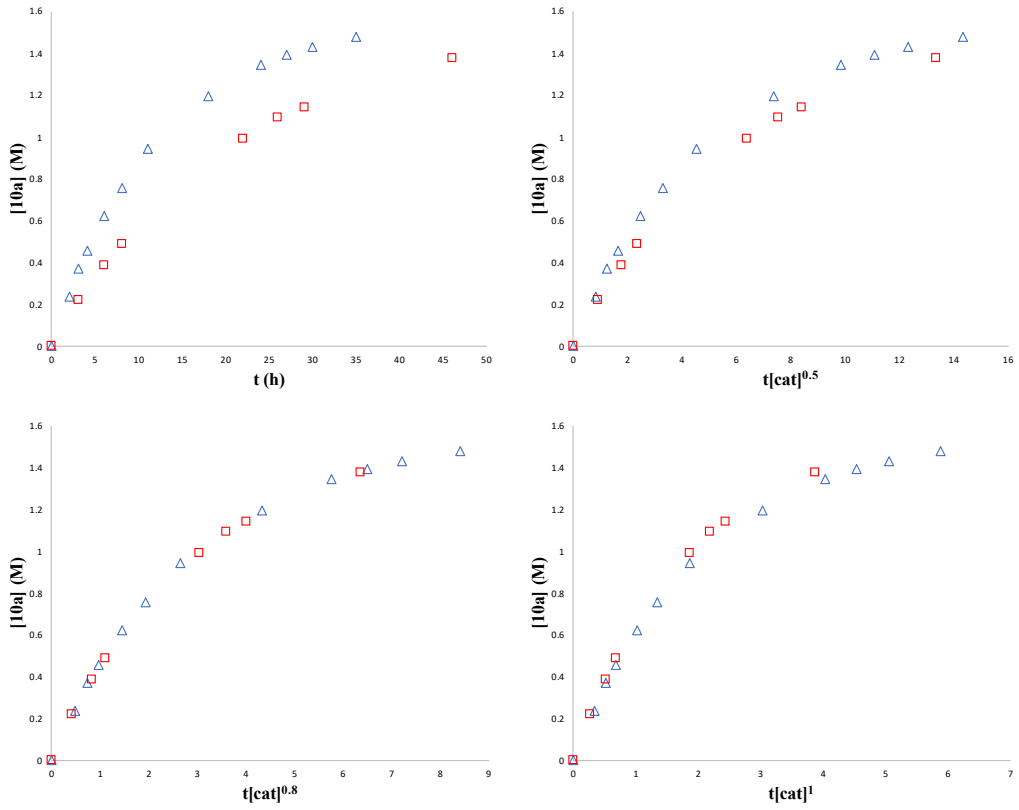



***Figure 30.***. *Plot of time (h) vs. concentration (M) for two independent starting concentrations of thiourea* ***4***·$BF_4^-$ *(blue triangle - 0.168 M; red square - 0.084 M) performed under synthetically relevant conditions (top left). Plots of normalized time scale ($t[cat]_o^{\gamma}$) vs. concentration (M) for the determination of the order in catalyst (top right and bottom).*

On the basis of the above findings, the tentative DFT-supported catalytic cycle depicted in Figure 31 is offered. The cycle initiates in formation of complex **4**·**8a**, which subsequently reacts by rate-determining indole addition transition state **TS1** with a Gibbs free activation energy ($\Delta G^{\neq}$) of 20.5 kcal/mol relative to the separate starting reagents and catalyst. Salient features of this transition state include a C···C bond-forming distance of 2.05 Å associated with a synclinal orientation of the styrene and indole substrates as defined by dihedral angle $\theta_{C(1)\text{-}C(2)\text{-}C(3)\text{-}C(4)}$ measuring -52.1°. Further was a slightly skewed double H-bond manifold with N–H···O distances of 1.84 Å and 1.75 Å linked to a *Z*,*Z*-thiourea conformation. Though less obvious, was stabilizing charge-polarized π–π stacking between the indole ring and the nitroalkene, clearly visible from the green isosurfaces in the NCI plot of Figure 31. From **TS1**, zwitterionic nitronate-azocarbenium intermediate **4**·**10a'** ensues that, following a series of proton transfer events, leads to exergonic product (**10a**) formation and catalyst turnover.

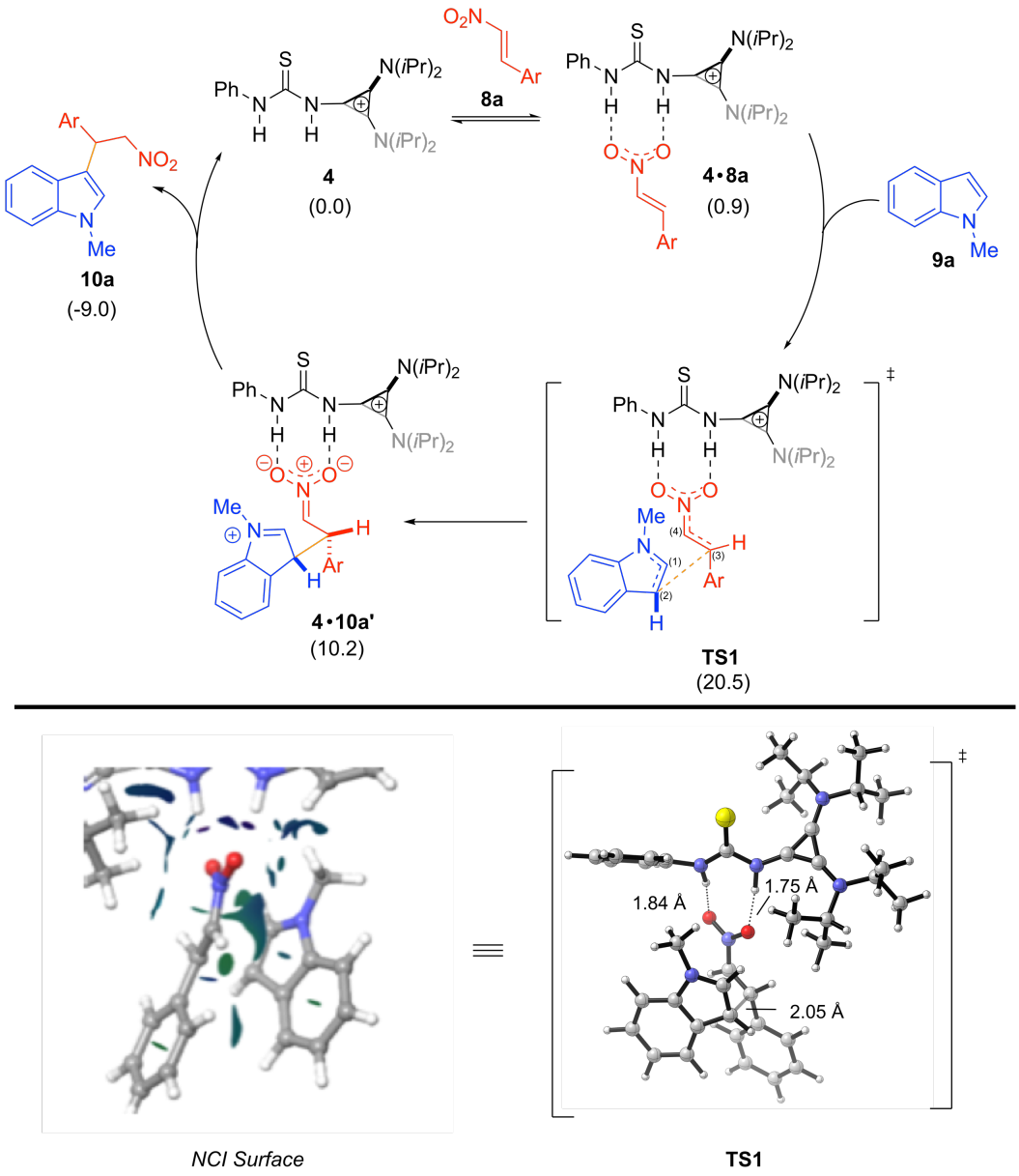



***Figure 31.*** *Mechanistic proposal for thiourea-catalyzed (**4**) Friedel–Crafts alkylation. Reported relative Gibbs free energies in kcal/mol are enclosed in parentheses.*

In closing, a charge-enhanced, thiourea-catalyzed Friedel–Crafts alkylation method was discussed as a second application for catalyst **4**. Inherent to the mechanism of these Friedel–Crafts alkylations is a steady-state concentration of a monomeric charged thiourea catalyst, much at odds with existing state-of-the-art reactivity patterns accessible using

thiourea catalysts. Additionally, DFT calculations and $^{1}H$ NMR binding studies revealed a dual hydrogen bond-mediated LUMO-lowering mode of substrate activation is pivotal to this reactivity, and, thus, the above work helps support the multifunctional- and dynamic nature of catalyst **4**. This work was published in 2019.[17]

### *4.4 Second-generation squaramide-cyclopropenium as a Brønsted acid organocatalyst*

#### *4.4.1 Optimization studies and demonstration of reaction practicality*

Although the work discussed hitherto showcased catalyst **4** as a robust alternative leading to enhanced reaction rates relative to commonly used thioureas, Professor Dudding and I yearned to further contribute to the field of strong Brønsted acid catalysts that are augmented by a cyclopropenium cation. Naturally, the latter aim of my thesis work turned towards pursuing squaramides as potentially more reactive counterparts.

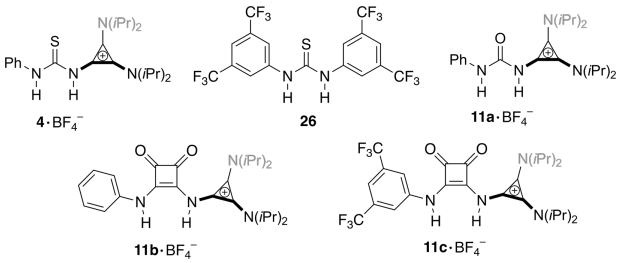
In keeping a common theme with respect to the work reported above, oximes were employed *in lieu* of alcohols for the formation of oxime ether linkages using vinyl ethers as reaction partners. We sought to access this class of compounds by enabling an activation principle that would proceed through a key oxocarbenium intermediate. The logic at the core for this enterprise being rooted in the heavy surge of interest for the development of novel oxime ether bonds and its subsequent application as putative precursors in photochemical reactions through, for instance, nitrogen-centered radicals.[141]

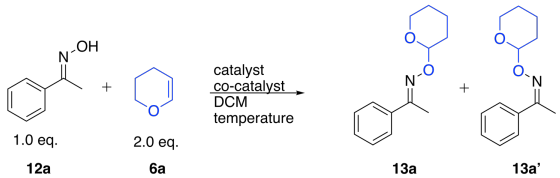
To commence this experimental investigation, a range of (thio)urea- and squaramide organocatalysts were screened in the presence of acetophenone oxime (**12a**) and DHP (**6a**) as model substrates in DCM. The results are presented in Table 6. A rather interesting finding was that the use of highly acidic, neutral- and charged (thio)urea catalysts (10 mol%) led to sluggish reactivity, albeit the use of thiourea **4**·$BF_4^-$ resulted in a marginal

improvement in product formation with a dr ratio of 1:2.7 of *Z* and *E* stereoisomers. These low-yielding trends were consistent at room temperature, at reflux conditions and in the presence of benzoic acid as a supposed co-catalyst. The seemingly facile thiourea-catalyzed synthetic protocol involving an alcohol and a vinyl ether proved to be ineffective when the alcohol was switched out for an oxime. This phenomena speaks to weak, or an absence of, attractive non-covalent interactions required for substrate activation,[7a] presumably arising from less than ideal H-bonding, i.e., deviations in geometry (H-bond spacing and H-bond angle)[78b] and/or p$K_a$.[84]

In contrast, this reaction was promoted by squaramide **11b**·$BF_4^-$ (5 mol%), whose constituents parallel that of thiourea **4**·$BF_4^-$, functioning as a superior H-bond donor. At room temperature, a conversion of 35% was achieved with a poor dr ratio of 1:1.5 after 48 hours. The addition of benzoic acid appeared to slightly attenuate reactivity by possibly engaging in non-productive H-bonds with the catalyst, and, thus, tying up the squaramide N–H moiety—though maintaining the same selectivity. However, under reflux conditions, a conversion of 86% was reached hand-in-hand with an excellent dr ratio of 1:19 after 9 hours. The application of squaramide **11c**·$BF_4^-$ (5 mol%) was strongly responsive even at room temperature yielding the product in 90% conversion after 30 hours with an appreciable 1:3 diastereoselectivity. A similar event was observed in the presence of benzoic acid, however. Optimal conditions were realized once the reactants and catalyst **11c**·$BF_4^-$ were subjected to reflux, resulting in 90% conversion after only 3 hours and a 1:19 diastereomeric mixture. The identity and structure of squaramide **11c**·$BF_4^-$ was confirmed by single-crystal X-ray diffraction analysis, see Appendix C.

***Table 6.*** *Effect of the change in reaction variables for the formation of an oxime ether linkage.*[a]




| | | | | |
|---|---|---|---|---|
| | ***Room temperature (rt)*** | | | |
| entry | catalyst (mol%) | time (h) | conv (%)[e] | dr (Z/E)[b] |
| 1 | **4**·$BF_4^-$ (10) | 48 | <5 | nd[d] |
| 2 | **26** (10) | 48 | nr[c] | - |
| 3 | **11a**·$BF_4^-$ (10) | 48 | <5 | nd[d] |
| 4 | **11b**·$BF_4^-$ (5) | 48 | 35 | 1:1.5 |
| 5 | **11c**·$BF_4^-$ (5) | 30 | 90 | 1:3 |
| | ***Benzoic acid co-catalyst (10 mol%) (rt)*** | | | |
| entry | catalyst (mol%) | time (h) | conv (%)[e] | dr (Z/E)[b] |
| 6 | **4**·$BF_4^-$ (10) | 48 | <5 | nd[d] |
| 7 | **26** (10) | 48 | nr[c] | - |
| 8 | **11a**·$BF_4^-$ (10) | 48 | <5 | nd[d] |
| 9 | **11b**·$BF_4^-$ (5) | 48 | 33 | 1:1.5 |
| 10 | **11c**·$BF_4^-$ (5) | 30 | 84 | 1:3 |
| | ***Reflux*** | | | |
| entry | catalyst (mol%) | time (h) | conv (%)[e] | dr (Z/E)[b] |
| 11 | **4**·$BF_4^-$ (10) | 20 | 15 | 1:1.6 |
| 12 | **26** (10) | 20 | <5 | nd[d] |
| 13 | **11a**·$BF_4^-$ (10) | 20 | 12 | 1:2.6 |
| 14 | **11b**·$BF_4^-$ (5) | 9 | 86 | 1:19 |
| 15 | **11c**·$BF_4^-$ (5) | 3 | 90 | 1:19 |

[a]Reaction conditions: oxime (0.52 mmol), vinyl ether (1.03 mmol) and squaramide **11c**·$BF_4^-$ (5 mol%) in 0.5 mL DCM stirred for the indicated time. [b]*Z*/*E* ratios were assigned with the help of using 1D NOESY NMR. [c]nr: no reaction. [d]nd: not determined. [e]Conversion involved monitoring the disappearance of the signal at ~ 7.65 ppm for **12a** and appearance of the signal at ~ 7.71 ppm for product **13a**.

We then sought to test the generality of this squaramide-catalyzed oxime ether-forming protocol (Table 7). A panoply of oximes as substrates were found to be excellent reaction partners in the presence of DHP, resulting in moderate-to-excellent yields. Electron-poor ketoximes **12b** and **12c** reacted to afford the products in moderate-to-good yields with excellent selectivity (**13b**; 76% yield, 1:19 dr and **13c**; 61%, 1:19 dr). In sharp contrast, phenyl-substituted aldoxime **12d**, and electron-rich aldoximes **12e** and **12f**, furnished the products in good-to-excellent yields, albeit in ~ 1:1 diastereomeric mixtures (**13d**; 97% yield, 1:1 dr, **13e**; 92% yield, 1:1 dr, **13f**; 76%, 1:1.2 dr). Electron-rich aldoximes **12g** and **12h** having a sterically demanding bromine substituent at the *ortho* position were well-tolerated solely providing the *E* stereoisomer (**13g**; 70% yield, *E* and **13h**; 79% yield, *E*). Substrates **12i–k**, with diverse positioning of the phenyl substituents—biphenyl, benzyl and $–CH_2Ph$—all performed well in this reaction, and provided variable yields (**13i** to **13k**; 48–74% yield, 1:1 to 1:>19 dr). Extending this method to other types of (hetero)aromatic aldoximes (**12l–o**) manifested in moderate-to-good yields (**13l** to **13o**; 48–80% yield, 2:1 dr and 1:1.2 to 1:6 dr). These findings showcase that other systems, such as α,β-unsaturated oximes, as well as structurally diverse aromatic-based substrates, are tolerant of this protocol. A striking observation, however, was that benzyl protected indole product **13m** was enriched in the *Z* stereoisomer (2:1 dr). This can be rationalized by invoking that a more stable transition state benefitting from π–π and/or cation–π interactions between the substrates and catalyst takes place to provide a higher proportion of the less stable *Z* stereoisomer.

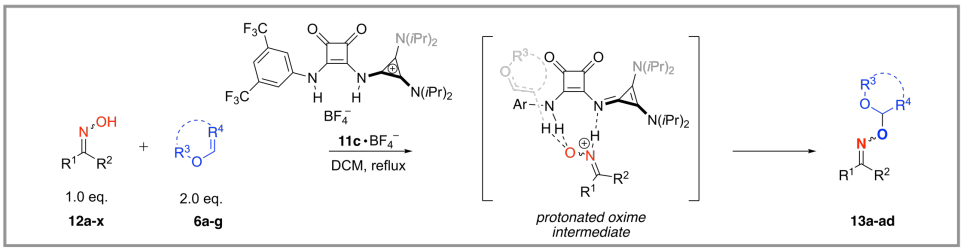
Additionally, a range of cyclic aliphatic substrates were surveyed (**12p–v**). Non-functionalized simple frameworks, such as cyclopentanone- and cycloheptanone oxime,

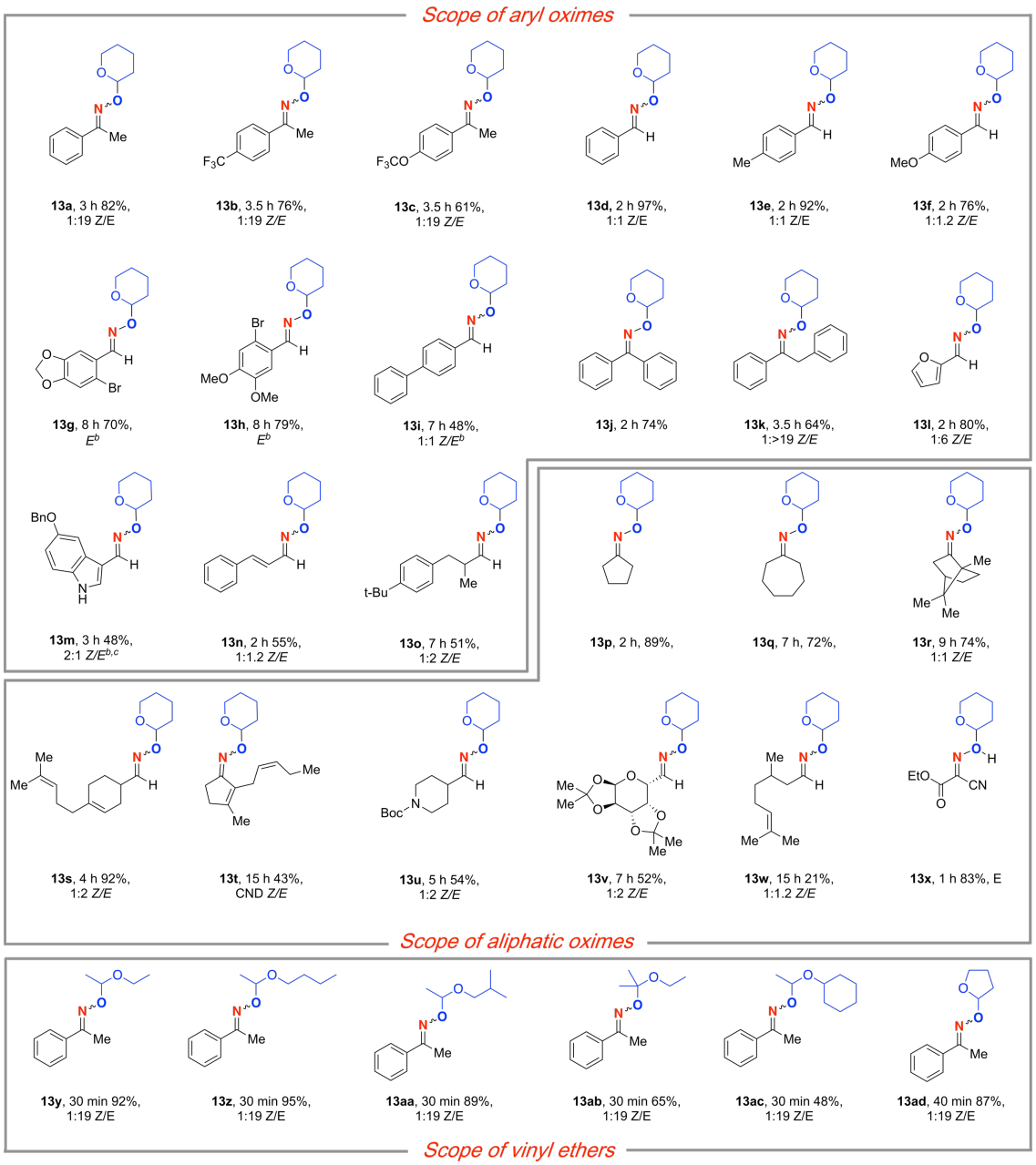
reacted smoothly to afford products **13p** and **13q** in good-to-very good yields (89% and 72%, respectively), as did more complex substrates **12r** and **12s** (**13r**; 74% yield, 1:1 dr and **13s**; 92% yield, 1:2 dr). Employing more sterically encumbered oximes (**12t–v**), however, attenuated reactivity (**13t** to **13v**; 43–54% yield, 1:2 dr). Nonetheless, a salient strength of this protocol is preservation of the acid-labile protecting groups. Furthermore, open-chain aliphatic oxime **12w** reacted sluggishly to provide product **13w** (21% yield, 1:1.2 dr), whereas synthetically relevant OxymaPure[142] **12x** furnished product **13x** in a very good yield as a single geometric isomer (83%, *E*). To further demonstrate the feasibility of this protocol, disparate vinyl ether substrates were examined in the presence of oxime **12a** that led to moderate-to-excellent yields, as well as excellent selectivity in a short duration of ~30 minutes (**13y** to **13ad**; 48–95% yield, 1:19 dr).

### *4.4.2 Mechanistic studies*

Having insight into the substrate scope, we yearned to grasp a firm understanding of the underlying catalytic mechanism. As such, a rigorous mechanistic analysis delving into the details of this process was undertaken. These set of studies were initiated with VTNA—a contemporary research technique reported by Burés[3,4] that utilizes concentration-against-time reaction profiles allowing one to extrapolate valuable kinetic information using the naked-eye (Figure 32A). Upon visual inspection, the conspicuous overlay of the two curves indicated that neither catalyst deactivation nor product inhibition persisted (Figure 32A, top-most). Further exploratory studies involved employing the normalized time scale method as a means to elucidate the order in catalyst, which revealed

***Table 7.*** *Scope of oxime ether formation*[a]




[a]Reaction conditions: oxime (0.52 mmol), vinyl ether (1.03 mmol) and squaramide **11c**·$BF_4^-$ (5 mol%) in 0.5 mL DCM stirred for the indicated time. *Z*/*E* ratios were assigned with the help of using 1D NOESY NMR.

The yields provided are reported as isolated yields after flash chromatography. [b]An additional 0.5 mL of THF was added for solubility. [c]This product was further recrystallized from hexanes/chloroform.

that the reaction has a 0.8-order dependency on catalyst **11c**·$BF_4^-$.

At first sight, this finding suggests that a majority of the catalyst is present as a monomeric species. However, given the steric complexity of catalyst **11c**, as well as the presence of a $BF_4^-$ counterion, the possibility of other mediating-factors contributing to this order in catalyst cannot be rule out. Delineating the order of the starting material components was then carried out. The 0.8-order relationship in [oxime] points to a pre-equilibrium event between the catalyst and oxime. Meanwhile, a 1.2-order dependency in [vinyl ether] was observed.

To corroborate these findings that were arrived at using VTNA, $^1$H NMR spectroscopy was exploited to hone in on each specific interaction by conducting titration experiments (Figure 32B). The first study was comprised of gradually increasing the concentration of catalyst **11c**·$BF_4^-$, as we were curious whether catalyst dimerization was in fact responsible for the assigned order in catalyst (Figure 32B, left-hand side). Upon inspection of these $^1$H NMR spectra, an upfield shift was observed with respect to the nitrogen-bound hydrogen atom proximal to the cyclopropenium moiety. Therefore, this observation negates the idea of catalyst dimerization at higher concentrations, and instead, the 0.8-order in catalyst can be argued from the perspective of $BF_4^-$-induced shielding of the proton nucleus. A plausible rationale supporting this hypothesis is centered around concentration effects. With a higher concentration of the $BF_4^-$ counterion, there is a higher degree of N–H···F–$BF_3^-$ interactions, where the electronegative fluorine atom(s),

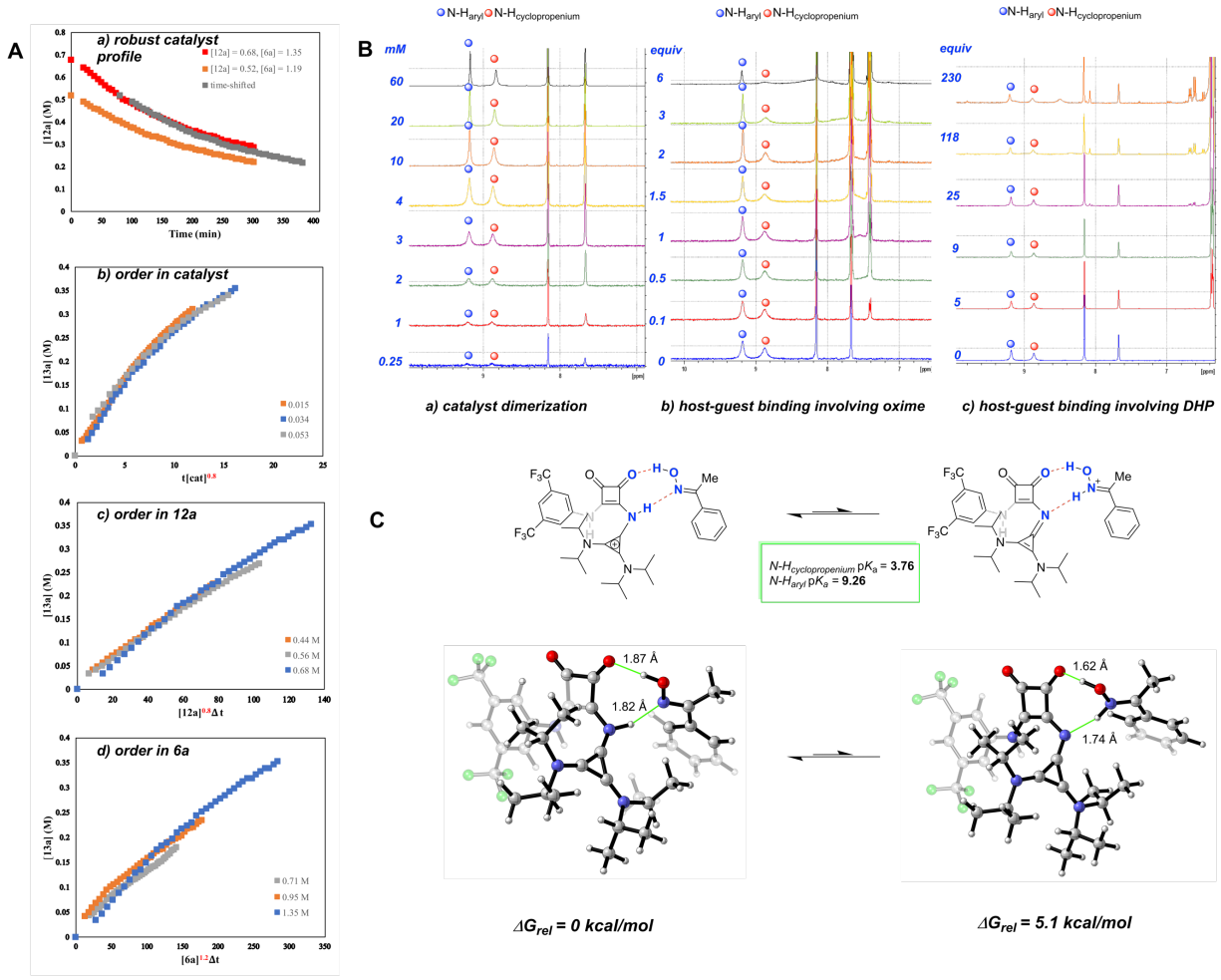



***Figure 32.*** *(a) VTNA plots depicting a robust catalyst profile, as well as the order in catalyst and substrates. (b)* $^1$*H NMR spectra illustrating the absence of catalyst dimerization, rapid proton exchange involving catalyst* ***11c*** *and oxime, and an apparent lack of catalyst–substrate interactions in the presence of DHP. (c) 2D, and 3D images calculated at the IEFPCM$_{(DCM)}$ωB97X-D/6-311++G(d,p)/def2-TZV//ωB97X-D/6-31G(d)/def2-TZV level of theory showing a pre-equilibrium between catalyst* ***11c*** *and oxime, with the N–H$_{(aryl/cyclopropenium)}$ p$K_a$'s and H-bond distances highlighted.*

presumably impart a build-up of electron density within the cyclopropenium/N–H moiety hemisphere. The nature of this shielding arises from a concept formally referred to as donor–donor ion pair strain.[99] Moreover, this electron excessive carbenium exhibits interionic repulsion with the $BF_4^-$ counterion that, in turn, generates repulsion in the

electric field,[143] which is accompanied by electron redistribution.[144] This proposed interaction comes as no surprise when dealing with alkylamino cyclopropenium compounds.[100,101,111] As a consequence, paradoxically, a higher concentration of catalyst renders a less efficient catalytic species owing to catalyst–counterion non-covalent interactions. Next, turning to host–guest binding studies, rapid proton exchange events were observed between the oxime and the acidic nitrogen-bound hydrogen atom proximal to the cyclopropenium cation. This was seen from the apparent broadening of the singlet with increasing equivalents of oxime, and is thus in line with the 0.8-order dependency on [oxime] (Figure 32B, middle). This pre-equilibrium exchange process is further supported by the computed low relative Gibbs free energy, where a putative binding mode is depicted in Figure 32C. Lastly, even after the addition of 230 equivalents of DHP, no significant catalyst–substrate interaction could be pinpointed. This is tell-tale of a mechanism that involves a trimeric complex, namely one that allows the vinyl ether component to interact with a catalyst–oxime adduct, and not solely the catalyst (Figure 32B, right-hand side).

As a concluding study to provide further insight into the working mechanistic proposal, a computational assessment at the IEFPCM$_{(DCM)}$ωB97X-D/6-311++G(d,p)/def2-TZV//ωB97X-D/6-31G(d)/def2-TZV level of theory taking a look at the three-dimensional reaction landscape of **12a**, **6a** and **11c** is put forth. Preceding this investigation, the p$K_a$ of catalyst **11c** was computed in DMSO, abiding to the method of Xue and Ji,[145] providing a p$K_a$ of 3.76. Notably, this obtained value is 1.77 p$K$ units less acidic than sulfuric acid (p$K_a$($H_2SO_4$)$_{DMSO}$ = 1.99),[146] which is just outside the realm of quantifying catalyst **11c** as being a superacid.

With this in mind, a thorough investigation into the conformational space of this flexible catalyst[147] was undertaken. From these exploratory studies, a myriad of proton transfer first-order saddle points were located, ultimately revealing the structure depicted in Figure 33 (**TS1**) as being the most energetically favourable process, having a Gibbs free energy activation barrier ($\Delta G^{\ddagger}$) of 5.5 kcal $mol^{-1}$ relative to the starting material components. This is in agreement with the NMR binding studies and 0.8-order in [oxime]. This transition state (**TS1**) was found to adopt a bowl-shaped structure, which is leveraged on the formation of a rigid H-bond network, thus enabling facile proton transfer to the nitrogen atom of the oxime functional group. Defining features of this transition state include a N···H bond-breaking distance of 1.32 Å and a N···H bond-forming distance of 1.24 Å. In bolstering this proposed binding mode, it is well-established that squaramides have exceptional H-bond acceptor properties owing to the increase in aromaticity upon binding.[12]

Following this event, delicate structural reorganization takes place, where a unique two-point binding-like mode emerges priming the charged oxime for yet another proton transfer event to DHP, with an O···H bond-breaking distance of 1.29 Å and a C···H bond-forming distance of 1.34 Å, as well as a barrier of 11.9 kcal $mol^{-1}$ (**TS2**, Figure 33). Further contributing to the stabilization of this transition state was a favourable cation–π interaction between the incipient oxocarbenium intermediate and the electron-deficient aryl moiety. No doubt, the more labile oxygen-bound proton, as a result of charge-enhanced acidity, also played a role in making this an unencumbered process. Unfortunately, a Hammet correlation to corroborate this key mechanistic step could not be determined, however, owing to low solubility of *para*-substituted electron-poor oximes in $CD_2Cl_2$ and $CDCl_3$.

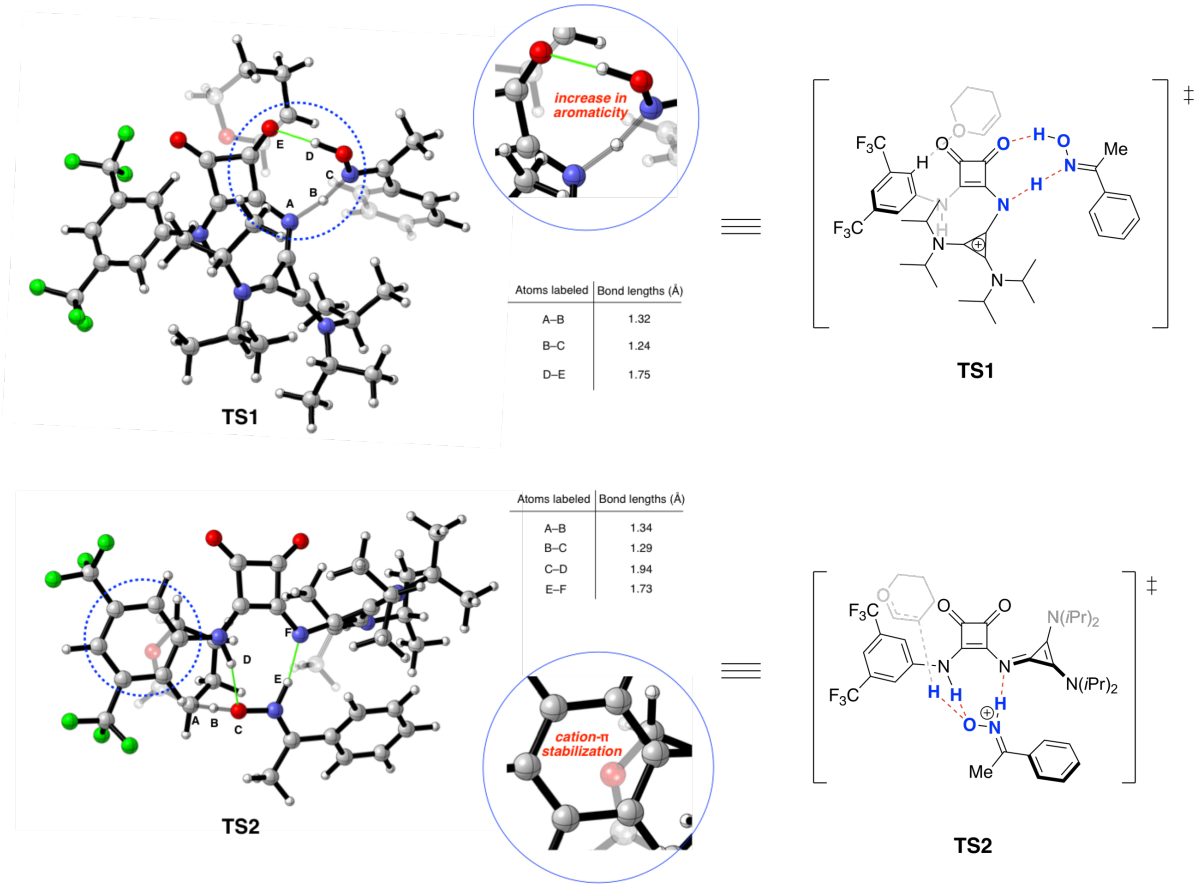



***Figure 33.*** *(a) Calculated potential energy profile for the* ***11c***·$BF_4^-$*-catalyzed formation of oxime ethers. (b) Calculated geometries of transition state structures, with key stabilizing interactions highlighted.*

Further computational analysis revealed that oxime addition to DHP was a barrierless process. With respect to the last step, which involves furnishing the product and regenerating the catalyst, it is actively being pursued, and, thus, was not included as a part of the discussion herein.

To recap, this latter work involved the development and application of a novel squaramide-cyclopropenium as a catalyst enabling the formation of an oxime ether linkage. Salient features of this catalyst, including geometry, formation of a favourable H-bond network and low p$K_a$ collectively played indispensable roles in lowering the kinetic barriers

through transition state stabilization—that the other examined catalysts lacked. The practicality of this method was established through the presentation of a wide-range of substrates. Finally, a Brønsted acid mode of reactivity was found to exist, as supported by NMR studies and computational modelling.

### *5.0 Summary and future directions*

The body of work presented throughout this dissertation provides a compelling basis for the development and future use of cyclopropenium frameworks as charged constructs for enabling catalysis, seeing potential in the pharmaceutical and material science industries. The story began by disclosing a novel thiourea-cyclopropenium (**4**) that was found to exhibit enhanced reactivity relative to achiral, neutral state-of-the-art thiourea catalysts (**26**) and a select charged thiourea catalyst (1-methyl-3-(3-phenylthioureido)pyridinium iodide) for the pyranylation of primary, secondary and tertiary alcohols, and phenols. Furthermore, the multifunctional character of this catalyst was demonstrated by showcasing its successful use in another application, namely Friedel–Crafts alkylation. These works encompass a manifold of theoretical and experimental studies that go hand-in-hand to unravel the fine details with respect to each mechanism. Notably, the former mechanism was found to operate through a Brønsted acid mode of reactivity, whereas in the latter case, a shift in the mechanism to two-point H-bonding was observed.

We then segued into a similar, yet chemically distinct class of organocatalysts, that being, squaramides. Therein, a squaramide-cyclopropenium organocatalyst (**11c**) was deployed to catalyze the formation of a novel oxime ether bond linkage using oximes and vinyl ethers as reaction partners. Accompanying this synthetic protocol was a

comprehensive mechanistic investigation, revealing the order in catalyst and substrates, as well as a putative host–guest binding interaction that was corroborated by DFT studies collectively pointing to a Brønsted acid mode of reactivity. A notable feature of this work was that squaramide **11c** vastly outperformed catalyst **26**, as well as various charged cyclopropenium-bearing (thio)urea and squaramide catalysts.

Since the work reported in this dissertation adds to the library of (thio)urea and squaramide catalysts, and therefore is in its infancy with respect to this type of catalyst design, it is my view that the direction regarding (thio)urea and squaramide catalysts—bearing a cyclopropenium motif—is, in a sense, limitless. What I mean by this is that there is a tremendous amount of free-play. It is hoped that since the groundwork is laid out, the future generation of students can extend it to numerous areas. Below are listed three contemporary "hot topic" research areas that can be classified as being distinct, but, of course, can also overlay to some extent.

(1) An obvious point of departure would be to synthesize a chiral variant (squaramide or (thio)urea) to target an application that is underdeveloped (low er or dr), or to pursue a novel bond disconnection—though the latter may be an arduous task. An example of a chiral squaramide variant is provided in Figure 34A. An aminoindanol chiral appendage was chosen for the following reasons: rigidity, possession of two stereogenic centers and the ability to coordinate to metals and/or act as H-bond donors/acceptors.[148]

(2) Taking advantage of the charged moiety, in conjunction with the enhanced H-bond donor capacity, makes these types of catalysts ideal candidates in the context of phase-transfer catalysis. A phase-transfer agent enhances the rate of the reaction by transporting one, or more, reactants across the interface between different phases[149]

(extraction-type mechanism). In this case, the lipophilic cyclopropenium cation can be leveraged to help shuttle anions into the organic phase (Figure 34A, right-hand side).

(3) Fine-tuning the catalyst by introducing an appropriate light-absorbing platform capable of triggering photocatalysis is, no doubt, of topical interest (Figure 34B). This is especially relevant as it can build from the above-mentioned oxime ether formation protocol (demonstrating multifunctional character) by honing in on either light-induced oxime ether N–O scission or accessing diradicals that would reside on the oxime moiety or, conversely, on an alkene distal to the oxime. This type of reactivity is far-reaching, in that, a plethora of reactivities could be accessed, such as cycloadditions, radical additions and radical cascade reactions, among others.[150]

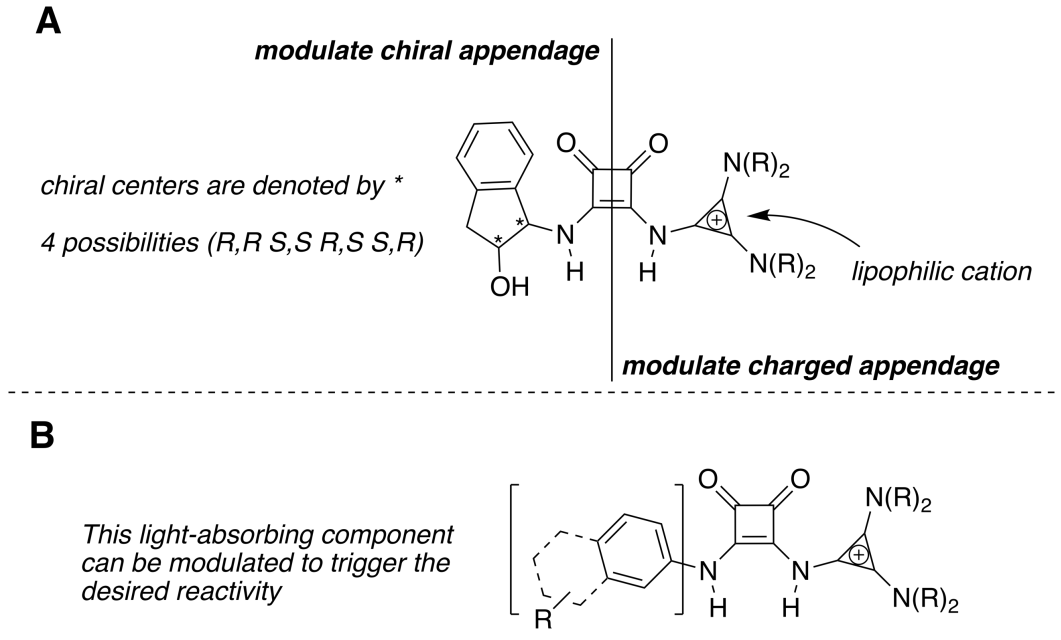



***Figure 34.*** *(a) Plausible rationale for the design of future cyclopropenium-squaramide chiral and/or phase-transfer catalysts. (b) A rudimentary depiction of a cyclopropenium-squaramide compound with a photo-active component necessary for facilitating photocatalysis.*

## *6.0 Experimental section*

### Materials and methods

All materials were obtained from commercially available suppliers and used as received unless otherwise stated. The solvents employed in the reactions were all dried using the following methods: DCM and MeCN were distilled from $CaH_2$, and THF was distilled from sodium/benzophenone. All reactions were conducted in oven-dried round-bottom flasks under an inert atmosphere ($N_2$) and monitored by TLC using silica gel 60 F254 EMD Merck, whilst visualized with a hand-held UV lamp. Flash column chromatography was performed over Silicycle ultrapure silica gel (230-400 mesh). NMR spectra were recorded on a Bruker DPX-300 spectrometer ($^1$H 300 MHz, $^{13}$C 75.5 MHz, $^{19}$F 292.4 MHz, $^{11}$B 96.3 MHz) and Bruker Avance AV I 600 spectrometer ($^1$H 600 MHz) in $CDCl_3$. The observed chemical shifts are reported as $\delta$-values (ppm) relative to tetramethylsilane (TMS). 1D NOESY NMR experiments were used to assist in isomer identification. $^{13}$C NMR KIE experiments were conducted to provide further support for the mechanistic hypothesis. Mass spectra were obtained on an MSI/Kratos concept IS Mass spectrometer. 4-(*tert*-butyl)-3,4-dihydro-*2H*-pyran,[151] phenyl (*O*,1-$^2H_2$) methanol,[152] 1,2:3,4-di-*O*-isopropylidene-$\alpha$-D-galactopyranose,[153] 1-methyl-3-(3-phenylthioureido)pyridinium iodide,[10c] *trans*-$\beta$-nitrostyrene derivatives,[154] catalysts **94**,[155] **26**,[156] and indole derivatives **5a**,[157] **5c**,[158] **5d**,[159] oximes,[160] and **29**[79] were prepared according to literature procedures and the spectra match accordingly.

**Chloro[bis(diisopropylamino)]cyclopropenium (95)·$BF_4^-$**[161]

To a stirred solution of tetrachlorocyclopropene (1.0 g, 5.62 mmol, 1.00 equiv.) in DCM (12.0 mL) at 0 °C was added diisopropylamine (4.0 mL, 28.1 mmol, 5.00 equiv.) dropwise. The solution stirred for 6 h while gradually warming to room temperature. Next, $NaBF_4$ (0.80 g, 7.31 mmol, 1.30 equiv.) was added in one portion and the resulting mixture stirred overnight. The solution was then extracted with water (5x 35.0 mL), dried over $MgSO_4$ and concentrated in vacuo to afford an orange solid. The crude material was then dissolved in DCM (5.0 mL), purified with diethyl ether ((15.0 mL washes) – 3x) and dried under high vacuum to obtain a white powder (1.51g, 76%). $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.41–1.43 (d, $J$ = 6.78 Hz; 24H), 3.81–3.94 (m, 2H), 4.01–4.21 (m, 2H).

**2,3-Bis(diisopropylamino)cyclopropenimine (96)·$BF_4^-$**

Ammonia gas (excess) was vigorously bubbled through a solution of **(95)** (1.51 g**,** 4.21 mmol, 1.00 equiv.) in DCM (16.0 mL) at 0 °C for 1 h. The solution was maintained at a temperature of ~ 0°C for the entire duration. After 15 minutes a white precipitate began to crash out indicating product formation. After completion of the reaction, as observed by TLC, the salt was filtered off and the filtrate collected. The filtrate was then concentrated and washed with diethyl ether to further purify **96** (3x 10.0 mL washed) affording a beige solid (1.36 g, 95%). Mp: 142–144 °C; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.30–1.32 (d, $J$ = 6.78 Hz; 24 H), 3.71–3.84 (m, 4 H), 6.08 (s, 2H); $^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 22.3, 50.8, 113.9, 114.7; $^{19}$F{$^1$H} NMR (292.4 MHz, $CDCl_3$, 25 °C) $\delta$ = -151.7; $^{11}$B{$^1$H} NMR (96.3 MHz, $CDCl_3$, 25 °C) $\delta$ = -1.0; HRMS (FAB-DFS) *m/z*: $[M - BF_4]^+$ Calcd for $C_{15}H_{30}N_3^+$ 252.2434; Found 252.2435.

**2,3-Bis(diisopropylamino)cyclopropenimine (97)**[162]

Compound **96 (**1.36 g, 4.01 mmol, 1.00 equiv.**)** was dissolved in DCM (15.00 mL) and the resulting solution was washed with 3 M NaOH (3 x 80.0 equiv.), dried over $MgSO_4$ and concentrated *in vacuo* affording an off-white solid (0.86 g, 80–85%). $^1$H NMR (300 MHz, $CDCl_3$, 25 $^o$C): $\delta$ = 1.16–1.18 (d, $J$ = 6.60 Hz; 24 H), 3.53–3.67 (m, 4 H).

***N*-(2,3-Bis(diisopropylamino)cyclopropenium)-*N'*-phenyl-thiourea (4)·Cl$^-$**

A solution of phenyl isothiocyanate (0.92 g, 6.82 mmol, 2.0 equiv.) in DCM (3.00 mL) was added dropwise to a solution of **97** (0.86 g**,** 3.41 mmol, 1.0 equiv.) in DCM (6.00 mL) at room temperature. After vigorously stirring for 1 hour, the reaction was extracted with 3 M HCl until disappearance of **97**, as visualized *via* TLC. The combined organic layers were dried over $MgSO_4$ and concentrated. The resulting residue was then washed with diethyl ether (3 x 15.0 mL) to afford a yellow solid (0.71 g, 49%). Mp: 159–161$^o$C; $^1$H NMR (300 MHz, $CDCl_3$, 25 $^o$C): $\delta$ =1.42–1.44 (d, $J$ = 6.63 Hz; 24 H), 4.14–4.18 (m, 4 H), 7.16–7.20 (t, $J$ = 7.32 Hz; 1H), 7.33–7.38 (t, $J$ = 7.62 Hz; 2H), 7.86–7.89 (d, $J$ = 7.92 Hz; 2H), 11.8 (s, 1H), 12.1 (s, 1H); $^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$, 25 $^o$C): $\delta$ = 22.1, 51.6, 107.4, 123.1, 125.0–125.5 (d, $J$ = 32.4 Hz), 128.4, 138.7, 178.8; HRMS (FAB-DFS) *m/z*: [M – Cl]$^+$ Calcd for $C_{22}H_{35}N_4S^+$ 387.2566; Found 387.2570.

***N*-(2,3-Bis(diisopropylamino)cyclopropeniminyl)-*N'*-phenyl-thione (98)**

Thiourea **4**·Cl$^-$ (0.71 g, 1.67 mmol) was dissolved in DCM (10.00 mL) and washed with saturated bicarbonate (1 x 30.0 mL), dried over $MgSO_4$ and solvent evaporated resulting in a chartreuse solid (0.62 g, 96%). Mp: 165–167 $^o$C; $^1$H NMR (300 MHz, $CDCl_3$, 25 $^o$C): $\delta$ = 1.34–1.36 (d, $J$ = 6.60 Hz; 24H), 4.01–4.10 (m, 4H), 6.91–6.95 (t, $J$ = 7.2 Hz; 1H), 7.20–7.25 (t, $J$ = 7.50 Hz; 2H), 7.56–7.59 (d, $J$ = 7.8 Hz; 2H), 7.69 (s, 1H); $^{13}$C{$^1$H}

NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 22.0, 50.4, 119.5, 121.5–121.6 (d, $J$ = 6.27 Hz), 124.0, 128.4, 141.0, 178.5; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{34}N_4S$ 386.2504; Found 386.2495.

*N*-[2,3-Bis(diisopropylamino)cyclopropenium]-*N*'-phenyl-thiourea (4)·$ClO_4^-$.

Thiourea **4**·$Cl^-$ (100 mg, 0.24 mmol) was dissolved in DCM (2.00 mL) and washed with saturated bicarbonate (1 x 6.0 mL). The conjugate base was then acidified with a 3 M solution of 70% $HClO_{4(aq)}$ (1 x 4.0 mL), dried over $MgSO_4$ and concentrated *in vacuo* to afford a viscous green oil. The oil was then triturated with diethyl ether (2 x 5.0 mL) to furnish thiourea **4**·$ClO_4^-$ as a pale-green solid (98 mg, 85%). Mp: 125−127 °C; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.40−1.42 (d, $J$ = 6.8 Hz; 24H), 4.05−4.14 (m, 4H), 7.19−7.24 (t, $J$ = 7.4 Hz; 1H), 7.35−7.40 (t, $J$ = 7.6 Hz; 2H), 7.75−7.78 (d, $J$ = 7.8 Hz; 2H), 9.30 (s, 1H), 9.75 (s, 1H); $^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 21.9, 51.9, 106.2, 123.5, 126.1, 126.4 128.7, 138.2, 178.1.

*N*-[2,3-Bis(diisopropylamino)cyclopropenium]-*N*'-phenyl-thiourea (4)·$CF_3SO_3^-$.

Thiourea **4**·$Cl^-$ (100 mg, 0.24 mmol) was dissolved in DCM (2.00 mL) and washed with saturated bicarbonate (6.0 mL). The conjugate base was then acidified with a 3 M solution of trifluoromethanesulfonic acid (1 x 2.0 mL), dried over $MgSO_4$ and concentrated *in vacuo* to afford a viscous green oil. The oil was then triturated with diethyl ether (2 x 5.0 mL) to furnish thiourea **4**·$CF_3SO_3^-$ as a pale-green solid (96 mg, 76%). Mp: 147−149 °C; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.39−1.41 (d, $J$ = 6.8 Hz; 24H), 4.01−4.15 (m, 4H), 7.17−7.22 (t, $J$ = 7.4 Hz; 1H), 7.34−7.39 (t, $J$ = 7.6 Hz; 2H), 7.77−7.80 (d, $J$ = 7.9 Hz; 2H), 9.84 (s, 1H), 10.1 (s, 1H); $^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 21.9, 51.9,

106.6, 123.4, 125.9, 126.8 128.6, 138.4, 178.3; $^{19}F\{^{1}H\}$ NMR (292.4 MHz, $CDCl_3$, 25 °C) $\delta$ = -78.3.

**_N_-(2,3-Bis(diisopropylamino)cyclopropenium)-_N'_-phenyl-thiourea (4)·$BF_4^-$**

Compound **98** (0.62 g, 1.60 mmol) was dissolved in DCM (10.00 mL) and washed with a 3 M solution of 50% $HBF_{4(aq)}$ (1 x 30.0 mL), dried over $MgSO_4$ and concentrated *in vacuo* to afford a viscous green oil. The oil was then titrated with diethyl ether (1 x 15.0 mL) to furnish thiourea **4**·$BF_4^-$ as a lime-green solid (0.71 g, 93%). Mp: 121–123 °C; $^{1}H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.38–1.40 (d, $J$ = 6.60 Hz; 24H), 4.02–4.15 (m, 4H), 7.18–7.23 (t, $J$ = 7.50 Hz; 1H), 7.34–7.40 (t, $J$ = 7.50 Hz; 2H), 7.75–7.78 (d, $J$ = 8.1 Hz; 2H), 8.96 (s, 1H), 9.51 (s, 1H); $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 21.8, 51.9, 106.1, 123.5, 126.1–126.4 (d, $J$ = 23.2 Hz), 128.6, 138.2, 178.0; $^{19}F\{^{1}H\}$ NMR (292.4 MHz, $CDCl_3$, 25 °C) $\delta$ = -149.2; $^{11}B\{^{1}H\}$ NMR (96.3 MHz, $CDCl_3$, 25 °C) $\delta$ = -0.8.

**Representative procedure for the thiourea-catalyzed pyranylation of primary alcohols.**

To an oven-dried 25.0 mL round-bottom flask charged with thiourea **4**·$BF_4^-$ (24 mg, 1 mol%); primary alcohols (5.0 mmol) and DHP (10.0 mmol) were combined and subsequently diluted in DCM (5.0 mL). The resulting solution was stirred at room temperature under an inert atmosphere. Reaction progress was monitored *via* TLC. After removal of the solvent, the crude material was subjected to flash chromatography using a hexanes/ethyl acetate solvent system to yield the THP-protected alcohol.

**Characterization data of the products (7a–m). NMR data are consistent with the literature.**

**2-(Benzyloxy)tetrahydropyran (7a)**[163]

(0.91 g, 95%), Clear oil. $^{1}$H NMR (300 MHz, $CDCl_3$, 25 $^{o}$C): $\delta$ = 1.53–2.00 (m, 6H), 3.56–3.63 (m, 1H), 3.94–4.02 (m, 1H), 4.53–4.58 (d, $J$ = 12.1 Hz; 1H), 4.75–4.78 (t, $J$ = 3.48 Hz; 1H), 4.83–4.87 (d, $J$ = 12.1 Hz; 1H), 7.29–7.44 (m, 5H).

**2-(4-Methylbenzyloxy)tetrahydropyran (7b)**[164]

(0.92 g, 89%), Clear oil. $^{1}$H NMR (300 MHz, $CDCl_3$, 25 $^{o}$C): $\delta$ = 1.52–1.96 (m, 6H), 2.37 (s, 3H), 3.54–3.61 (m, 1H), 3.92–4.00 (m, 1H), 4.48–4.51 (d, $J$ = 11.8 Hz; 1H), 4.71–4.74 (t, $J$ = 3.51 Hz; 1H), 4.76–4.80 (d, $J$ = 11.8 Hz; 1H), 7.17–7.20 (d, $J$ = 7.89 Hz; 2H), 7.28–7.30 (d, $J$ = 7.95 Hz; 2H).

**5-(Tetrahydro-2H-pyran-2-yloxy)methylbenzo[d][1,3]dioxole (7c)**[165]

(1.06 g, 90%), Clear oil. $^{1}$H NMR (300 MHz, $CDCl_3$, 25 $^{o}$C): $\delta$ = 1.49–1.92 (m, 6H), 3.53–3.60 (m, 1H), 3.88–3.97 (m, 1H), 4.40–4.44 (d, $J$ = 11.7 Hz; 1H), 4.68–4.72 (overlapping signals, 2H), 5.96 (s, 2H), 6.77–6.82 (m, 2H), 6.85–6.90 (m, 1H).

**2-(4-Methoxybenzyloxy)tetrahydropyran (7d)**[166]

(1.01 g, 91%), Clear oil. $^{1}$H NMR (300 MHz, $CDCl_3$, 25 $^{o}$C): $\delta$ = 1.49–1.95 (m, 6H), 3.53–3.60 (m, 1H), 3.83 (s, 3H), 3.91–3.99 (m, 1H), 4.44–4.48 (d, $J$ = 11.6 Hz; 1H), 4.70–4.72 (t, $J$ = 3.54 Hz; 1H), 4.72–4.76 (d, $J$ = 15.8 Hz; 1H), 6.88–6.93 (d, $J$ = 11.6 Hz; 2H), 7.30–7.33 (d, $J$ = 8.64 Hz; 2H).

**2-(3,5-Dimethoxybenzyloxy)tetrahydropyran (7e)**

(1.11 g, 88%), Clear oil. $^{1}$H NMR (300 MHz, $CDCl_3$, 25 $^{o}$C): $\delta$ = 1.53–1.97 (m, 6H), 3.53–3.60 (m, 1H), 3.81 (s, 6H), 3.89–3.98 (m, 1H), 4.46–4.50 (d, $J$ = 12.3 Hz; 1H), 4.71–4.73 (t, $J$ = 3.60 Hz; 1H), 4.73–4.77 (d, $J$ = 15.3 Hz; 1H), 6.40–6.41 (t, $J$ = 2.22 Hz; 1H), 6.55–6.56 (d, $J$ = 2.20 Hz; 2H); $^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$, 25 $^{o}$C): $\delta$ = 19.4, 25.5, 30.6,

55.3, 62.2, 68.7, 97.7, 99.5, 105.5, 140.7, 160.8; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{20}O_4$ 252.1362; Found 252.1358.

**2-(2-Bromo-5-methoxybenzyloxy)tetrahydropyran (7f)**[167]

(1.28 g, 85%), Clear oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 $^o$C): $\delta$ =1.52–2.00 (m, 6H), 3.56–3.63 (m, 1H), 3.82 (s, 3H), 3.91–4.00 (m, 1H), 4.54–4.58 (d, $J$ = 13.5 Hz; 1H), 4.78–4.81 (t, $J$ = 3.45 Hz; 1H), 4.80–4.83 (d, $J$ = 9.10 Hz; 1H), 6.70–6.74 (dd, $J$ = 8.7, 3.09 Hz; 1H), 7.12–7.13 (d, $J$ = 3.09 Hz; 1H), 7.42–7.45 (d, $J$ = 8.7 Hz; 1H).

**2-(4-Nitrobenzyloxy)tetrahydropyran (7g)**[165]

(1.09 g, 92%), Clear oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 $^o$C): $\delta$ = 1.54–1.97 (m, 6H), 3.54–3.61 (m, 1H), 3.86–3.94 (m, 1H), 4.60–4.64 (d, $J$ = 13.5 Hz; 1H), 4.74–4.76 (t, $J$ = 3.45 Hz; 1H), 4.88–4.92 (d, $J$ =13.5 Hz; 1H), 7.53–7.56 (d, $J$ = 8.67 Hz; 2H), 8.20–8.23 (d, $J$ = 8.70 Hz; 2H).

**2-(2-Phenylethoxy)tetrahydropyran (7h)**[168]

(0.72 g, 70%), Clear oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 $^o$C): $\delta$ = 1.47–1.90 (m, 6H), 2.92–2.96 (t, $J$ = 7.26 Hz; 2H), 3.44–3.51 (m, 1H), 3.60–3.68 (dd, $J$ = 16.9, 7.17 Hz; 1H), 3.75–3.82 (m, 1H), 3.94–4.02 (dd, $J$ = 17.0, 7.35 Hz; 1H), 4.61–4.63 (t, $J$ = 2.88 Hz; 1H), 7.19–7.34 (m, 5H).

**2-Ethoxytetrahydropyran (7i)**

(0.60 g, 93%), Clear oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 $^o$C): $\delta$ = 1.20–1.25 (t, $J$ = 7.11 Hz; 3H), 1.47–1.87 (m, 6H), 3.41–3.53 (overlapping signals, 2H), 3.75–3.91 (overlapping signals, 2H), 4.57–4.60 (t, $J$ = 2.76 Hz; 1H); $^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$, 25 $^o$C): $\delta$ = 15.2, 19.8, 25.5, 30.8, 62.4–62.8 (d, $J$ = 31.7 Hz), 98.7; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_7H_{14}O_2$ 130.0994; Found 130.0985.

**2-(2,2,2-Trifluoroethoxy)tetrahydropyran (7j)**[169]

(0.74 g, 80%), Clear oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 $^o$C): $\delta$ = 1.55–1.93 (m, 6H), 3.51–3.61 (m, 1H), 3.80–3.81 (m, 1H), 3.84–3.96 (dq, $J$ = 8.70 Hz; 1H), 3.99–4.10 (dq, $J$ = 12.3 Hz; 1H), 4.76–4.78 (t, $J$ = 3.15 Hz; 1H).

**2-(5-(1,1,1,3,5,5,5-Heptamethyltrisiloxan-3-yl)-pentoxy)tetrahydropyran (7k)**

(1.61 g, 82%), Clear oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 $^o$C): $\delta$ = 0.011 (s, 3H), 0.100 (s, 18H), 0.457–0.509 (m, 2H), 1.35–1.44 (m, 4H), 1.51–1.96 (m, 8H), 3.36–3.44 (m, 1H), 3.48–3.55 (m, 1H), 3.71–3.80 (m, 1H), 3.85–3.95 (m, 1H), 4.58–4.61 (t, $J$ = 4.29 Hz; 1H); $^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$, 25 $^o$C): $\delta$ = -0.303, 1.84, 17.6, 19.7, 23.0, 25.5, 29.5–29.8 (d, $J$ = 18.4 Hz), 30.8, 62.3, 67.6, 98.8; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{40}O_4Si_3$ 392.2234; Found 392.2224.

**6-(Chloro-hexyloxy)tetrahydropyran (7l)**[170]

(1.04 g, 94%), Clear oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 $^o$C): $\delta$ = 1.33–1.65 (m, 10 H), 1.66–1.89 (m, 4H), 3.34–3.41 (m, 1H), 3.45–3.54 (m, 3H), 3.69–3.77 (m, 1H), 3.81–3.89 (m, 1H), 4.55–4.57 (t, $J$ = 2.52 Hz; 1H).

**2,2,7,7-Tetramethyl-5-(((tetrahydro-*2H*-pyran-2-yl)oxy)methyl)tetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran (7m)**[171]

(1.63 g, 96%), Clear oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 $^o$C): $\delta$ = 1.25 (s, 3H), 1.26 (s, 3H), 1.36 (s, 3H), 1.46 (s, 3H), 1.51–1.85 (m, 6H), 3.38–3.45 (m, 1H), 3.52–3.66 (m, 1H), 3.69–3.85 (m, 2H), 3.91–3.97 (m, 1H), 4.16–4.19 (dd, $J$ = 1.53, 7.95 Hz; 1H), 4.20–4.23 (m, 1H), 4.50–4.60 (m, 2H), 5.43–5.47 (t, $J$ = 6.24 Hz; 1H).

**Representative procedure for the thiourea-catalyzed pyranylation of higher-substituted alcohols and phenols.**

To an oven-dried 25.0 mL round-bottom flask charged with thiourea **4**·$BF_4^-$ (24 mg, 1 mol%) and benzoic acid (61.0 mg, 10 mol%); alcohols, or phenols, (5.0 mmol) and DHP (10.0 mmol) were combined and subsequently diluted in DCM (5.0 mL). The resulting solution was stirred at room temperature under an inert atmosphere. Reaction progress was monitored *via* TLC. After removal of the solvent, the crude material was subjected to flash chromatography using a hexanes/ethyl acetate solvent system to yield the THP-protected product.

**Characterization data of the products (7n–w). NMR data are consistent with the literature.**

**2-(1-Phenylethoxy)-tetrahydropyran (7n)**[172]

(0.96 g, 93%), Clear oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 $^o$C): 1:1 diastereomeric mixture $\delta$ = 1.49–1.99 (overlapping signals, 18H), 3.40–3.47 (m, 1H), 3.50–3.57 (m, 1H), 3.71–3.79 (m, 1H), 3.97–4.05 (m, 1H), 4.45–4.48 (t, $J$ = 3.21 Hz; 1H), 4.86–4.91 (m, 1H), 4.92–4.97 (overlapping signals, 2H), 7.26–7.48 (m, 10H).

**2-(4-Methylphenylethoxy)-tetrahydropyran (7o)**

(1.04 g, 94%), Clear oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 $^o$C): 1:1 diastereomeric mixture $\delta$ = 1.45–1.94 (overlapping signals, 18H), 2.38 (s, 6H), 3.38–3.46 (m, 1H), 3.47–3.54 (m, 1H), 3.69–3.77 (m, 1H), 3.95–4.02 (m, 1H), 4.41–4.43 (m, 1H), 4.80–4.85 (m, 1H), 4.86–4.92 (overlapping signals, 2H), 7.16–7.34 (m, 8H).; $^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$, 25 $^o$C): $\delta$ =19.2, 19.9, 21.1, 21.9, 24.3, 25.5 (d, $J$ = 1.81 Hz), 30.9, 61.9, 62.8, 72.9–73.0 (d, $J$

= 11.9 Hz), 96.0–96.1 (d, $J$ = 8.83 Hz), 126.0, 126.4, 128.9, 129.1, 136.5, 137.0, 140.6, 141.5.; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{20}O_2$ 220.1463; Found 220.1457.

**2-(1-Napthalenylethoxy)-tetrahydropyran (7p)**

(0.90 g, 70%), Clear oil. $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): 1:1 diastereomeric mixture $\delta$ = 1.49–2.02 (overlapping signals, 18H), 3.42–3.49 (m, 1H), 3.53–3.60 (m, 1H), 3.74–3.82 (m, 1H), 4.03–4.11 (m, 1H), 4.51–4.54 (t, $J$ = 3.42 Hz; 1H), 5.02–5.04 (m, 1H), 5.07–5.18 (overlapping signals, 2H), 7.49–7.66 (m, 6H), 7.84–7.93 (m, 8H).; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 19.4, 19.9, 22.2, 24.3, 25.6 (d, $J$ = 3.40 Hz), 30.9–40.0 (d, $J$ = 3.85 Hz), 62.1, 62.8, 73.4, 96.1, 96.5, 124.4 (d, $J$ = 1.96 Hz), 124.8, 125.5–125.6 (d, $J$ = 4.53 Hz), 125.8–125.9 (d, $J$ = 8.91 Hz), 126.1, 127.7–127.8 (d, $J$ = 5.06 Hz), 127.9–128.0 (d, $J$ = 6.95 Hz), 128.1, 128.4, 132.8, 133.1, 133.3–133.4 (d, $J$ = 6.57 Hz), 141.1, 142.1.; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{20}O_2$ 256.1463; Found 256.1458.

**2-Isopropoxytetrahydropyran (7q)**[173]

(0.69 g, 96%), Clear oil. $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.05–1.07 (d, $J$ = 6.12 Hz; 3H), 1.15–1.17 (d, $J$ = 6.30 Hz; 3H), 1.44–1.55 (m, 4H), 1.57–1.68 (m, 1H), 1.71–1.83 (m, 1H), 3.38–3.45 (m, 1H), 3.80–3.92 (overlapping signals, 2H), 4.58–4.61 (t, $J$ = 3.75 Hz; 1H).

**2-(2-Isopropyl-5-methylcyclohexyloxy)-tetrahydropyran (7r)**

(1.13 g, 94%), Clear oil. $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): 1:1 diastereomeric mixture $\delta$ = 0.769–1.09 (overlapping signals, 24H), 1.20–1.46 (m, 4H), 1.50–1.90 (overlapping signals, 16H), 2.06–2.20 (m, 3H), 2.32–2.42 (m, 1H), 3.28–3.37 (td, 10.6, 4.38, Hz; 1H), 3.45–3.53 (m, 3H), 3.86–4.02 (m, 2H), 4.59–4.62 (m, 1H), 4.80–4.82 (t, $J$ = 3.51 Hz; 1H).; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 15.6, 16.3, 19.7, 20.3, 21.2 (d, $J$ = 3.55 Hz),

22.2, 22.4, 23.0, 23.3, 25.2, 25.5, 25.6 (d, $J$ = 2.34 Hz), 31.2, 31.3, 31.4, 31.8, 34.4, 34.6, 40.1, 43.6, 48.2, 48.9, 62.4, 63.0, 74.1, 79.9, 94.4, 101.3; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{28}O_2$ 240.2089; Found 240.2085.

**2-*tert*-Butyloxy-tetrahydropyran (7s)**[165]

(0.70 g, 88%), Clear oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 $^o$C): $\delta$ = 1.26 (s, 9H), 1.47–1.53 (m, 4H), 1.63–1.70 (m, 1H), 1.81–1.91 (m, 1H), 3.42–3.50 (m, 1H), 3.94–4.00 (m, 1H), 4.73–4.75 (t, $J$ = 3.18 Hz; 1H).

**2-(1,1-Dimethyl-propoxy)-tetrahydropyran (7t)**[174]

(0.72 g, 84%), Clear oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 $^o$C): $\delta$ = 0.86–0.91 (t, $J$ = 7.44 Hz; 3H), 1.18–1.20 (d, $J$ = 4.38 Hz; 6H), 1.46–1.60 (m, 6H), 1.62–1.68 (m, 1H), 1.81–1.88 (m, 1H), 3.41–3.48 (m, 1H), 3.93–4.00 (m, 1H), 4.71–4.73 (t, $J$= 3.09 Hz; 1H).

**2-Phenoxytetrahydropyran (7u)**[174]

(0.65 g, 73%), Clear oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 $^o$C): $\delta$ = 1.59–1.81 (m, 3H), 1.88–1.93 (m, 2H), 2.01–2.13 (m, 1H), 3.60–3.68 (m, 1H), 3.92–4.00 (m, 1H), 5.45–5.47 (t, $J$ = 3.27 Hz; 1H), 6.99–7.05 (m, 1H) 7.08–7.11 (m, 2H), 7.28–7.35 (m, 2H).

**2-(4-Bromophenoxy)-tetrahydropyran (7v)**[174]

(1.18 g, 92%), Clear oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 $^o$C): $\delta$ = 1.58–1.77 (m, 3H), 1.85–190 (m, 2H), 1.92–2.10 (m, 1H), 3.58–3.65 (m, 1H), 3.85–3.93 (m, 1H), 5.38–5.40 (t, $J$ = 3.18 Hz; 1H), 6.93–6.99 (m, 2H), 7.38–7.40 (m, 2H).

**2-(4-Methoxyphenoxy)-tetrahydropyran (7w)**[174]

(0.53 g, 51%), Clear oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 $^o$C): $\delta$ = 1.58–1.78 (m, 3H), 1.85–1.90 (m, 2H), 1.97–2.10 (m, 1H), 3.58–3.65 (m, 1H), 3.80 (s, 3H), 3.93–4.01 (m, 1H), 5.31–5.33 (t, $J$ = 3.33 Hz; 1H), 6.82–6.88 (m, 2H), 7.00–7.05 (m, 2H).

**Characterization data for the mixture of non-deuterated and deuterated *syn* and *anti* products: (NMR data are consistent with literature).**[9h]

*syn* isomer: $^{1}$H NMR (300 MHz, $CDCl_3$, 25 $^{o}$C) δ = 0.84 (s, 9H), 1.43–1.44 (m, 1H), 1.62 (d, *J* = 3.42 Hz; 1H), 1.66–1.68 (t, *J* = 3.39 Hz; 1H), 1.72–1.76 (d, *J* = 12.4 Hz; 1H), 3.62–3.68 (ddd, *J* = 11.1, 4.9, 1.6 Hz; 1H), 3.69–3.78 (td, 12.1, 2.3 Hz; 1H), 4.76–4.77 (d, *J* = 3.4 Hz; 1H); $^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$, 25 $^{o}$C): *δ* = 26.7, 26.8, 30.7–31.2 (t, *J* = 19.6 Hz), (non-deuterated: 31.3), 31.8, (non-deuterated: 38.7), 38.8, 60.0, 98.6.

*anti* isomer: $^{1}$H NMR (300 MHz, $CDCl_3$, 25 $^{o}$C) δ = 0.86 (s, 9H), 1.03–1.06 (m, 1H), 1.19–1.23 (t, *J* = 6.99 Hz; 1H), 1.25–1.32 (m, 1H), 1.53 (m, 1H), 3.36–3.44 (m, 1H), 4.05–4.12 (m, 1H), 4.21–4.25 (d, *J* = 9.18 Hz; 1H); $^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$, 25 $^{o}$C): *δ* = 26.4, 27.1, 32.0, 32.4-32.9 (t, *J* = 18.5 Hz), (non-deuterated: 32.9), 44.6, 65.6, 103.6.

**2-Methoxytetrahydropyran (99)**.[170]

(0.53 g, 91%), Clear oil. $^{1}$H NMR (300 MHz, $CDCl_3$, 25 $^{o}$C): *δ* = 1.49–1.90 (m, 6H), 3.41 (s, 3H), 3.49–3.56 (m, 1H), 3.83–3.90 (m, 1H), 4.51–4.53 (t, *J* = 2.97 Hz; 1H).

**Characterization data for the mixture of non-deuterated and deuterated *syn* and *anti* products (benzyl adduct):**

*syn* isomer: $^{1}$H NMR (300 MHz, $CDCl_3$, 25 $^{o}$C) δ = 0.87 (s, 9H), 1.47–1.49 (m, 1H), 1.68–1.71 (t, *J* = 3.51 Hz; 1H), 1.73–1.75 (t, *J* = 3.51 Hz; 1H), 1.77–1.83 (m, 1H), 3.68–3.74 (ddd, *J* = 11.0, 4.8, 1.7 Hz; 1H), 3.82–3.90 (td, 12.7, 2.3 Hz; 1H), 4.97–4.98 (d, *J* = 3.5 Hz; 1H), 7.37–7.40 (m, 5H); $^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$, 25 $^{o}$C): *δ* = 21.9, 26.8, 26.9, 30.7–31.2 (t, *J* = 19.8 Hz), (non-deuterated: 31.3), 31.9, (non-deuterated: 38.6), 38.7, 60.3, 96.6, 128.1, 128.3, 128.4, 128.5.

*anti* isomer: $^{1}$H NMR (300 MHz, $CDCl_3$, 25 $^{o}$C) δ = 0.88 (s, 9H), 1.07–1.09 (m, 1H), 1.26–1.29 (overlapping signals; 1H), 1.31–1.36 (m, 1H), 1.58 (m, 1H), 3.40–3.48 (m, 1H), 4.10–4.16 (m, 1H), 4.43–4.46 (m; 1H), 7.28–7.36 (m, 5H); $^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$, 25 $^{o}$C): $\delta$ = 26.5, 27.1, 32.1, 32.6–33.0 (t, $J$ = 20.4 Hz), (non-deuterated: 33.1), 44.7, 65.7, 101.5, 127.0, 127.5, 127.6, 127.8.

**Procedure for the thiourea-catalyzed 2-deoxygalactosylation (NMR data are consistent with literature).**[171]

To an oven-dried 10.0 mL round-bottom flask charged with thiourea **4**·$BF_4^-$ (4.0 mg, 1 mol%) 3,4,6-tri-*O*-benzyl-D-galactal (0.400 mg ,0.960 mmol) (**92**) and benzyl alcohol (87 mg, 0.805 mmol) were combined and subsequently diluted in DCM (1.5 mL). The resulting solution was stirred until near full consumption of **92**, as determined by $^{1}$H NMR spectroscopy analysis (~ 12 hours) at 40 $^{o}$C under an inert atmosphere. Next, the crude material was subjected to flash column chromatography using hexanes:EtOAc (9:1) as a co-solvent system to furnish the title compound **93** as a clear and colourless oil (354 mg, 84%, $\alpha$-anomer). $^{1}$H NMR (300 MHz, $CDCl_3$, 25 $^{o}$C) δ = 2.06–2.11 (dd, $J$ = 12.7, 4.6 Hz; 1H), 2.25–2.35 (m, 1H), 3.58–3.69 (m, 2H), 3.99–4.06 (m, 3H), 4.45–4.73 (m, 7H), 4.96–5.00 (d, $J$ = 11.6 Hz, 1H), 5.12–5.13 (d, $J$ = 3.06 Hz; 1H), 7.28–7.39 (m, 20H).

**Representative procedure for the thiourea-catalyzed Friedel–Crafts alkylation.**

To an oven-dried 5.0 mL round-bottom flask charged with thiourea **4**·$BF_4^-$ (24 mg, 10 mol%); respective indole (1.5 mmol) and nitroalkene (0.5 mmol) were combined and subsequently diluted in DCM (0.5 mL). The resulting solution was stirred for 44 hours at room temperature under an inert atmosphere. Reaction progress was monitored *via* TLC.

After removal of the solvent, the crude material was subjected to flash chromatography using a hexanes/ethyl acetate solvent system to yield the Friedel–Crafts alkylated product.

**Characterization data of the products (10a–o). NMR data are consistent with the literature.**

1-Methyl-3-(2-nitro-1-phenylethyl)-*1H*-indole (10a).[175]

(129 mg, 92%), pink solid. $^1$H NMR (300 MHz, $CDCl_3$, 25 $^o$C): $\delta$ = 3.78 (s, 3H), 4.93−5.00 (dd, $J$ = 12.3, 8.5 Hz; 1H), 5.05−5.12 (dd, $J$ = 12.4, 7.4 Hz; 1H), 5.19−5.24 (t, $J$ = 7.9 Hz; 1H), 6.89 (s, 1H), 7.07−7.13 (t, $J$ = 6.9 Hz; 1H), 7.23−7.39 (m, 7H), 7.47−7.49 (d, $J$ = 7.9 Hz; 1H).

3-(2-Nitro-1-phenylethyl)-*1H*-indole (10b).[175]

(115 mg, 86%), brown solid. $^1$H NMR (300 MHz, $CDCl_3$, 25 $^o$C): $\delta$ = 4.94−5.01 (dd, $J$ = 12.3, 8.4 Hz; 1H), 5.06−5.13 (dd, $J$ = 12.3, 7.6 Hz; 1H), 5.19−5.25 (t, $J$ = 7.9 Hz; 1H), 7.05−7.13 (m, 2H), 7.20−7.39 (m, 7H), 7.46−7.49 (d, $J$ = 7.9; 1H), 8.09 (br, 1H).

3-(1-(Furan-2-yl)-2-nitroethyl)-1-methyl-*1H*-indole (10e).[175]

(124 mg, 92%) yellow oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 $^o$C): δ = 3.78 (s, 3H), 4.91−4.98 (dd, $J$ = 12.5, 7.4 Hz; 1H), 5.05−5.12 (dd, $J$ = 12.5, 8.1 Hz; 1H), 5.27−5.32 (t, $J$ = 7.7 Hz; 1H), 6.22−6.23 (d, $J$ = 3.3 Hz; 1H), 6.36−6.37 (dd, $J$ = 3.1, 1.9 Hz; 1H), 7.03 (s, 1H), 7.16−7.21 (m, 1H), 7.28−7.38 (m, 1H), 7.43−7.44 (d, $J$ = 1.1 Hz; 3H), 7.60−7.62 (d, $J$ = 7.9 Hz; 1H).

1-Methyl-3-(1-(naphthalen-2-yl)-2-nitroethyl)-*1H*-indole (10f).[176]

(101 mg, 61%) yellow oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 $^o$C): δ = 3.5 (s, 3H), 5.11−5.14 (dd, $J$ = 7.4, 1.3 Hz; 2H), 6.07−6.12 (t, $J$ = 7.7 Hz; 1H), 6.86 (s, 1H), 7.07−7.12

(m, 1H), 7.23−7.34 (m, 2H), 7.39−7.60 (m, 5H), 7.80−7.83 (dd, *J* = 6.5, 2.8 Hz; 1H), 7.90−7.93 (m, 1H), 8.27−8.30 (d, *J* = 7.9 Hz; 1H).

1-Methyl-3-(2-nitro-1-p-tolylethyl)-*1H*-indole (10g).[176]

(132 mg, 90%) colourless oil. $^{1}$H NMR (300 MHz, $CDCl_3$, 25 $^{o}$C): δ = 2.34 (s, 3H), 3.77 (s, 3H), 4.90−4.97 (dd, *J* = 12.4, 8.6 Hz; 1H), 5.03−5.10 (dd, *J* = 12.2, 7.3 Hz; 1H), 5.17−5.23 (t, *J* = 7.9 Hz; 1H), 6.88 (s, 1H), 7.08−7.17 (m, 3H), 7.22−7.33 (m, 4H), 7.48−7.50 (d, *J* = 7.9 Hz; 1H).

3-(1-(4-Methoxy)-2-nitroethyl)-1-methyl-*1H*-indole (10h).[176]

(81 mg, 52%) colourless oil. $^{1}$H NMR (300 MHz, $CDCl_3$, 25 $^{o}$C): δ = 3.77 (s, 3H), 3.82 (s, 3H), 4.93−4.97 (dd, *J* = 12.4, 8.6 Hz; 1H), 5.04−5.11 (dd, *J* = 12.3, 7.4 Hz; 1H), 5.17−5.23 (t, *J* = 7.9 Hz; 1H), 6.91−6.93 (d, *J* = 8.7 Hz; 3H), 7.12−7.18 (m, 1H), 7.28−7.37 (m, 4H), 7.51−7.54 (d, *J* = 7.9 Hz; 1H).

3-(1-(3,4-Dimethoxy)-2-nitroethyl)-1-methyl-*1H*-indole (10i).[177]

(32 mg, 19%) yellow oil. $^{1}$H NMR (300 MHz, $CDCl_3$, 25 $^{o}$C): δ = 3.77 (s, 3H), 3.85 (s, 3H), 3.88 (s, 3H), 4.89−4.96 (dd, *J* = 12.2, 8.6 Hz; 1H), 5.03−5.09 (dd, *J* = 12.2, 7.2 Hz; 1H), 5.13−5.18 (t, *J* = 8.0 Hz; 1H), 6.83−6.93 (m, 4H), 7.08−7.13 (m, 1H), 7.23−7.34 (m, 2H), 7.48−7.50 (d, *J* = 7.9 Hz; 1H).

3-(1-(4-Benzyloxy)-2-nitroethyl)-1-methyl-*1H*-indole (10j).

(77 mg, 40%) colorless oil. $^{1}$H NMR (300 MHz, $CDCl_3$, 25 $^{o}$C): δ = 3.77 (s, 3H), 4.88−4.95 (dd, *J* = 12.3, 8.7 Hz; 1H), 5.03−5.09 (dd, *J* = 12.3, 7.8 Hz; 1H), 5.05 (s, 2H), 5.14−5.20 (t, *J* = 7.9 Hz; 1H), 6.88 (s, 1H), 6.95−6.99 (m, 2H), 7.09−7.14 (m, 1H), 7.24−7.45 (m, 10H); $^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$, 25 $^{o}$C): δ = 32.8, 40.9, 70.1, 79.8, 109.5, 113.1, 115.2, 119.1, 119.4, 122.2, 126.3, 126.5, 127.5, 128.0, 128.6, 128.8, 131.7,

136.9, 137.3, 158.2; HRMS (EI-DFS) *m/z*: $[M+H]^+$ Calc'd for $C_{24}H_{22}O_3N_2$ 386.1636; Found 386.1627.

3-(1-(4-Fluorophenyl)-2-nitroethyl)-1-methyl-*1H*-indole (10k).[176]

(137 mg, 92%) yellow oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.78 (s, 3H), 4.89−4.96 (dd, *J* = 12.4, 8.7 Hz; 1H), 5.04−5.10 (dd, *J* = 12.4, 7.2 Hz; 1H), 5.17−5.23 (t, *J* = 7.9 Hz; 1H), 6.88 (s, 1H), 7.01−7.14 (m, 3H), 7.25−7.36 (m, 4H), 7.43−7.46 (d, *J* = 8.0 Hz; 1H).

3-(1-(4-Chlorophenyl)-2-nitroethyl)-1-methyl-*1H*-indole (10l).[176]

(141 mg, 82%) colorless oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.78 (s, 3H), 4.89−4.96 (dd, *J* = 12.5, 8.7 Hz; 1H), 5.03−5.10 (dd, *J* = 12.3, 7.2 Hz; 1H), 5.17−5.22 (t, *J* = 7.8 Hz; 1H), 6.89 (s, 1H), 7.10−7.16 (m, 1H), 7.26−7.36 (m, 6H), 7.44−7.47 (d, *J* = 7.9 Hz; 1H).

3-(1-(3-Chlorophenyl)-2-nitroethyl)-1-methyl-*1H*-indole (10m).[176]

(136 mg, 79%) colorless oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.78 (s, 3H), 4.88−4.95 (dd, *J* = 12.5, 8.6 Hz; 1H), 5.02−5.09 (dd, *J* = 12.6, 7.4 Hz; 1H), 5.16−5.21 (t, *J* = 7.9 Hz; 1H), 6.90 (s, 1H), 7.09−7.14 (m, 1H), 7.24−7.29 (m, 4H), 7.32−7.35 (m, 2H), 7.44−7.47 (d, *J* = 8.0 Hz; 1H).

3-(1-(4-Bromophenyl)-2-nitroethyl)-1-methyl-*1H*-indole (10n).[176]

(156 mg, 87%) colorless oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.79 (s, 3H), 4.90−4.97 (dd, *J* = 12.5, 8.7 Hz; 1H), 5.03−5.09 (dd, *J* = 12.5, 7.2 Hz; 1H), 5.14−5.20 (t, *J* = 7.7 Hz; 1H), 6.87 (s, 1H), 7.08−7.13 (m, 1H), 7.23−7.34 (m, 4H), 7.42−7.44 (d, *J* = 8.0 Hz; 1H), 7.46−7.49 (dd, *J* = 6.6, 1.8 Hz; 2H).

1-Methyl-3-(2-nitro-1-(4-(trifluoromethyl)phenyl)ethyl)-*1H*-indole (10o).[175]

(160 mg, 92%) yellow oil. $^{1}$H NMR (300 MHz, $CDCl_3$, 25 $^{o}$C): δ = 3.79 (s, 3H), 4.95−5.02 (dd, *J* = 12.7, 8.8 Hz; 1H), 5.07−5.13 (dd, *J* = 12.7, 7.2 Hz; 1H), 5.26−5.31 (t, *J* = 7.9 Hz; 1H), 6.89 (s, 1H), 7.01−7.16 (m, 1H), 7.26−7.36 (m, 2H), 7.40−7.52 (m, 3H), 7.61−7.63 (d, *J* = 8.2 Hz; 2H).

**_N_-(2,3-Bis(diisopropylamino)cyclopropenium)-_N'_-phenyl-urea (11a)·$BF_4^-$.**

A solution of phenyl isocyanate (123 mg, 1.0 mmol, 1.0 equiv.) in DCM (1.00 mL) was added dropwise to a 10.0 mL flame-dried round-bottom flask containing a solution of **97** (260 mg**,** 1.0 mmol, 1.0 equiv.) in DCM (3.00 mL). The solution was vigorously stirred for 1 hour at room temperature under an inert atmosphere. Following this event, the solution was washed with 3 M HCl until disappearance of **97**, as visualized *via* TLC. Next, the organic layer was first washed with saturated bicarbonate (1 x 30 mL) followed by a wash using a 3 M solution of 50% $HBF_{4(aq)}$ (1 x 30.0 mL). The organic layer was then dried over $MgSO_4$ and concentrated *in vacuo* to afford a viscous, colorless oil. The oil was then triturated with diethyl ether (1 x 10.0 mL) to furnish urea **11a**·$BF_4^-$ as a white solid (225 mg, 47%). Mp: 171–173 $^{o}$C; $^{1}$H NMR (300 MHz, $CDCl_3$, 25 $^{o}$C): *δ* = 1.38–1.40 (d, *J* = 6.8 Hz; 24H), 4.11–4.24 (m, 4H), 7.06–7.11 (t, *J* = 7.4 Hz; 1H), 7.29–7.34 (overlapping signals; 2H), 7.60–7.63 (d, *J* = 7.8 Hz; 2H), 8.48 (s, 1H), 8.91 (s, 1H); $^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$, 25 $^{o}$C): *δ* = 21.7, 51.0, 106.2, 119.6 (d, *J* = 6.6 Hz), 123.8, 128.8, 137.9, 149.8; $^{19}$F{$^{1}$H} NMR (292.4 MHz, $CDCl_3$, 25 $^{o}$C) *δ* = -148.8; $^{11}$B{$^{1}$H} NMR (96.3 MHz, $CDCl_3$, 25 $^{o}$C) *δ* = -0.8; HRMS (FAB-DFS) *m/z*: $[M - BF_4]^+$ Calcd for $C_{22}H_{35}N_4O^+$ 371.2794; Found 371.2802.

**3-((2,3-Bis(diisopropylamino)cyclopropenimine-4-(cyclopentyloxy)cyclobut-3-ene-1,2-dione (100).**

To a flame-dried 50.0 mL round-bottom flask charged with **97** (3.62 g, 14.4 mmol, 3.0 equiv.) and **29** (1.20 g**,** 4.80 mmol, 1.0 equiv.) was added DCM (15.0 mL). The solution was vigorously stirred for 1 hour at room temperature under an inert atmosphere. Next, the solution was washed with 3 M HCl until disappearance of **97**, as visualized via TLC. The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The resulting residue was then triturated with ice-cold hexane to afford an off-white solid. (1.93 g, 97%). Mp: 171–173 °C; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ =1.39–1.41 (d, $J$ = 6.0 Hz; 24 H), 1.59–1.72 (m, 2H), 1.84–1.97 (m, 2H), 2.02–2.08 (m, 4H), 3.82–3.95 (m, 4H), 5.74–5.79 (m, 1H); $^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 21.9, 23.7, 33.7, 50.7, 85.0, 123.0, 178.2, 182.5, 185.7, 197.0; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{37}O_3N_3$ 415.2835; Found 415.2826.

**3-((2,3-Bis(diisopropylamino)cyclopropenium-4-(phenylamino)cyclobut-3-ene-1,2-dione (11b)·$BF_4^-$.**

To a flame-dried 25.0 mL round-bottom flask charged with **100** (300 mg, 0.722 mmol, 1.0 equiv) was added DCM (4.0 mL). Aniline (0.65 mL, 7.12 mmol, 10 equiv) was then slowly added to the solution. Next, the flask was equipped with a reflux condenser and heated in an oil bath to reflux, whilst stirred under an inert atmosphere for 7 days. The resulting solution was washed with 3 M HCl (2 x 50 mL), and the aqueous layer extracted with DCM (3 x 5 mL). Then, the combined organic fractions were washed with saturated bicarbonate (1 x 20 mL) followed by 3 M $HBF_4$ (1 x 20.0 mL), dried over $MgSO_4$ and concentrated down to a dark yellow residue. The residue was then subjected to vacuum

filtration, where it was washed multiple times with ethyl acetate until a light yellow powder was obtained. (136 mg, 37%). Mp: 213–215 °C; $^{1}$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ =1.41–1.43 (d, $J$ = 6.9 Hz; 24 H), 3.90–3.99 (m, 4H), 7.14–7.19 (t, $J$ = 7.4 Hz; 1H), 7.36–7.41 (t, $J$ = 8.4 Hz; 2H), 7.61–7.64 (d, $J$ = 7.8 Hz; 2H), 8.88 (s, 1H), 9.02 (s, 1H); $^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 21.7, 52.2, 104.3, 119.9, 124.6, 124.9, 129.2, 137.4, 161.7, 169.4, 182.8, 184.0; $^{19}$F{$^{1}$H} NMR (292.4 MHz, $CDCl_3$, 25 °C) $\delta$ = -147.4; $^{11}$B{$^{1}$H} NMR (96.3 MHz, $CDCl_3$, 25 °C) $\delta$ = -0.8; HRMS (FAB-DFS) *m/z*: $[M - BF_4]^+$ Calcd for $C_{25}H_{35}O_2N_4^+$ 423.2744; Found 423.2749.

**3-((2,3-Bis(diisopropylamino)cyclopropenium-4-((3,5-bis(trifluoromethyl)phenyl)amino)cyclobut-3-ene-1,2-dione (11c)·$BF_4^-$.**

To a flame-dried 50.0 mL round-bottom flask charged with **100** (1.3 g, 3.13 mmol, 1.0 equiv) was added DCM (15.0 mL). 3,5-Bis(trifluoromethyl)aniline (2.70 mL, 17.3 mmol, 5.5 equiv) was then slowly added to the solution. Next, the flask was equipped with a reflux condenser and heated in an oil bath to reflux, whilst stirred under an inert atmosphere for 7 days. The resulting black solution was washed with 3 M HCl (2 x 200 mL), and the aqueous layer extracted with DCM (3 x 10 mL). Then, the combined organic fractions were washed with saturated bicarbonate (1 x 50 mL) followed by 3 M $HBF_4$ (1 x 50.0 mL), dried over $MgSO_4$ and concentrated down to a dark red residue. The residue was then subjected to vacuum filtration, wherein it was washed multiple times with ethyl acetate until an off-white powder was obtained. (1.02 g, 50%). Mp: 230–232 °C; $^{1}$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.41–1.43 (d, $J$ = 6.8 Hz; 24 H), 3.87–3.99 (m, 4H), 7.63 (s, 1H), 8.14 (s, 2H), 9.01 (s, 1H), 9.28 (s, 1H); $^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 21.6, 52.3, 103.6, 117.6, 119.7, 121.2, 124.8, 125.4, 132.5, 132.9, 139.2, 163.1, 168.6, 183.1,

183.3; $^{19}F\{^{1}H\}$ NMR (292.4 MHz, $CDCl_3$, 25 °C) $\delta$ = -146.5, -63.1; $^{11}B\{^{1}H\}$ NMR (96.3 MHz, $CDCl_3$, 25 °C) $\delta$ = -0.8; HRMS (FAB-DFS) *m/z*: $[M - BF_4]^+$ Calcd for $C_{27}H_{33}O_2N_4F_6^+$ 559.2491; Found 559.2512.

**Characterization data of oxime products (101–103).**

**(*Z/E*)-3-Methyl-2-((Z)-pent-2-en-1-yl)cyclopent-2-enone oxime (101).**

(0.97 g, 89%), yellow-brown oil. $^{1}H$ NMR (300 MHz, $CDCl_3$, 25 °C) $\delta$ = 1.00 (m, 3H, *major* and *minor*), 1.89 (s, 3H, *major* and *minor*), 2.08–2.20 (m, 2H, *major* and *minor*), 2.41–2.45 (m, 2H, *major* and *minor*), 2.66–2.70 (m, 2H, *major* and *minor*), 2.97–2.99 (m, 2H, *major* and *minor*), 5.31–5.40 (m, 2H, *major* and *minor*), 8.52 (s, 1H); $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 14.2, 15.3, 21.6, 22.6, 24.5, 34.3, 125.1, 125.6, 132.0, 133.0, 151.6, 168.2; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{17}NO$ 179.1310; Found 179.1301.

**(*Z/E*)-3-(4-(*tert*-Butyl)phenyl)-2-methylpropanal oxime (102).**

(0.98 g, 92%), yellow oil. $^{1}H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.07–1.12 (t, *J* = 9.2 Hz; 3H, *major* and *minor*), 1.34, (s, 9H, *major* and *minor*), 2.58–2.87 (m, 3H, *major* and *minor*), 6.62–6.64 (d, *J* = 7.4 Hz; 1H, *minor*), 7.11–7.16 (t, *J* = 9.2 Hz; 2H, *major* and *minor*), 7.32–7.35 (d, *J* = 8.2 Hz, 2H, *major* and *minor*), 7.42–7.44 (d, *J* = 5.9 Hz; 1H, *major*); $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 16.8, 17.3, 31.1, 31.4, 34.4, 36.1, 39.6, 40.4, 125.2–125.3 (d, *J* = 4.5 Hz), 128.7–128.8 (d, *J* = 6.8 Hz), 136.0, 149.1, 155.9, 156.7; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{21}NO$ 219.1623; Found 219.1615.

**(*Z/E*)-4-(4-Methylpent-3-en-1-yl)cyclohex-3-enecarbaldehyde oxime (103).**

(0.58 g, 54%), clear oil. $^{1}$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.62 (s, 3H, *major* and *minor*), 1.70 (s, 3H, *major* and *minor*), 1.83–2.23 (m, 10H, *major* and *minor*), 2.42–2.54 (m, 1H, *major*), 3.18–3.27 (m, 1H, *minor*), 5.09–5.13 (m, 1H, *major* and *minor*), 5.41 (m, 1H, *major* and *minor*), 6.64–6.66 (d, $J$ = 7.2 Hz; 1H, *minor*), 7.41–7.43 (d, $J$ = 6.2 Hz; 1H, *major*), 8.78 (s, 1H, *major* and *minor*); $^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 17.7, 23.8, 24.2, 25.2, 25.6, 25.7, 26.4, 26.6, 26.9, 27.3, 28.2, 28.8, 29.8, 30.2 31.1, 31.8 34.5, 35.0, 37.7 (d, $J$ = 8.4 Hz), 118.8, 120.6 (d, $J$ = 5.6 Hz), 124.2, 131.5, 135.8, 137.7, 155.4, 156.2; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{21}NO$ 207.1623; Found 207.1617.

**Representative procedure for squaramide-catalyzed oxime ether formation.**

To an oven-dried 5.0 mL round-bottom flask charged with vinyl ether (1.03 mmol) was added DCM (0.5 mL). The respective oxime (0.52 mmol) and catalyst **11c**·$BF_4^-$ (17 mg, 5 mol %) were then added to the solution. Next, the flask was equipped with a reflux condenser and heated in an oil bath to reflux, whilst stirred under an inert atmosphere. Reaction progress was monitored via TLC. After removal of the solvent, the crude material was subjected to flash chromatography using a hexanes/ethyl acetate solvent system to furnish the respective oxime ether product.

**Characterization data of oxime ether products (13a–ad).**

**(Z/*E*)-Acetophenone *O*-tetrahydro-2*H*-pyran-2-yl oxime (13a).**

(179 mg, 82%, 1:3 *Z*/*E*), clear oil.$^{1}$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ =1.53–1.95 (m, 6H, *E* and *Z*); 2.33 (s, 3H, *E* and *Z*), 3.50–3.57 (m, 1H, *Z*), 3.63–3.70 (m, 1H, *E*), 3.86–3.91 (m, 1H, *Z*), 3.93–4.00 (m, 1H, *E*), 4.97–5.00 (m, 1H, *Z*), 5.43–5.45 (m, 1H, *E*), 7.36–

7.38 (m, 3H, *E* and *Z*), 7.68–7.72 (m, 2H, *E* and *Z*), $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 13.0, 19.8–20.1 (d, $J$ = 22.6 Hz), 25.3–25.4 (d, $J$ = 7.6 Hz), 29.1, 30.7, 63.1, 94.6, 101.1, 126.3, 129.2, 136.5, 156.3; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{17}NO_2$ 219.1259; Found 219.1252.

**(*E*)-Acetophenone *O*-tetrahydro-2*H*-pyran-2-yl oxime (13a).**

(179 mg, 82%, 1:19 *Z*/*E*), clear oil. $^{1}H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.62–1.93 (m, 6H), 2.34 (s, 3H), 3.63–3.71 (m, 1H), 3.93–4.01 (m, 1H), 5.43–5.45 (m, 1H), 7.36–7.38 (m, 3H), 7.68–7.72 (m, 2H); $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 13.0, 20.1, 25.3, 29.2, 63.2, 101.1, 126.4, 128.3, 129.2, 136.5, 156.3.

**(*E*)-1-(4-(Trifluoromethyl)phenyl)ethenone *O*-tetrahydro-2*H*-pyran-2-yl oxime (13b).**

(113 mg, 76%, 1:19 *Z*/*E*), clear oil. $^{1}H$ NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.64–1.92 (m, 6H), 2.34 (s, 3H), 3.65–3.71 (m, 1H), 3.92–3.99 (m, 1H), 5.42–5.44 (m, 1H), 7.61–7.64 (d, $J$ = 8.2 Hz; 2H), 7.80–7.83 (d, $J$ = 8.1 Hz; 2H); $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C) δ = 12.8, 19.9, 25.2, 29.0, 63.1, 101.3, 125.2, 125.8, 126.6, 139.8, 154.9; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{16}F_3NO_2$ 287.1133; Found 287.1129.

**(*E*)-1-(4-(Trifluoromethoxy)phenyl)ethenone *O*-tetrahydro-2*H*-pyran-2-yl oxime (13c)**

(96 mg, 61%, 1:19 *Z*/*E*), yellow oil. $^{1}H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.62–1.92 (m, 6H), 2.32 (s, 3H), 3.64–3.70 (m, 1H), 3.92–3.99 (m, 1H), 5.41–5.44 (m, 1H), 7.20–7.23 (d, $J$ = 8.2 Hz; 2H), 7.72–7.75 (d, $J$ = 8.9 Hz; 2H); $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 12.9, 20.0, 25.2, 29.0, 63.1, 101.2, 118.7, 120.6, 122.1, 127.8, 135.1, 149.9, 155.0; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{16}F_3NO_3$ 303.1082; Found 303.1078.

**(*E*)-Benzaldehyde *O*-tetrahydro-*2H*-pyran-2-yl oxime (13d).**

(52 mg, 98%, 1:1 *Z*/*E*), clear oil. $^{1}$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.58–1.93 (m, 6H), 3.62–3.70 (m, 1H), 3.94–4.01 (m, 1H), 5.40–5.42 (m, 1H), 7.37–7.39 (m, 3H), 7.63–7.66 (m, 2H) 8.21 (s, 1H); $^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$, 25 °C) δ = 19.8, 25.2, 28.9, 62.9, 101.0, 127.4, 128.6, 130.0, 132.0, 150.4; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{15}NO_2$ 205.1103; Found 205.1095.

**(*Z*)-Benzaldehyde *O*-tetrahydro-*2H*-pyran-2-yl oxime (13d').**

(51 mg, 96%), clear oil. $^{1}$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.60–1.91 (m, 6H), 3.65–3.72 (m, 1H), 3.89–3.97 (m, 1H), 5.42–5.44 (m, 1H), 7.43–7.47 (overlapping signals, 4H), 7.93–7.96 (m, 2H); $^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$, 25 °C) δ = 19.7, 25.2, 28.7, 62.6, 101.4, 127.4, 128.5, 130.2, 130.6, 131.0, 147.4.

**(*E*)-4-Methylbenzaldehyde *O*-tetrahydro-2*H*-pyran-2-yl oxime (13e).**

(55 mg, 96%, 1:1 *Z*/*E*), clear oil. $^{1}$H NMR (300 MHz, $CDCl_3$, 25 °C): *δ* = 1.59–1.93 (m, 6H), 2.38 (s, 3H), 3.63–3.70 (m, 1H), 3.94–4.02 (m, 1H), 5.38–5.40 (m, 1H), 7.17–7.20 (d, *J* = 8.0 Hz, 2H), 7.52–7.55 (d, *J* = 8.1 Hz; 2H), 8.19 (s, 1H); $^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$, 25 °C): *δ* = 19.9, 21.5, 25.2, 29.0, 63.0, 101.0, 127.3, 129.3, 140.3, 150.5; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{17}NO_2$ 219.1259; Found 219.1252.

**(*Z*)-4-Methylbenzaldehyde *O*-tetrahydro-2*H*-pyran-2-yl oxime (13e').**

(50 mg, 88%), clear oil. $^{1}$H NMR (300 MHz, CDCl3, 25 °C): *δ* = 1.57–1.91 (m, 6H), 2.41 (s, 3H), 3.64–3.71 (m, 1H), 3.89–3.97 (m, 1H), 5.41–5.43 (m, 1H), 7.24–7.28 (d, *J* = 8.1 Hz; 2H), 7.41 (s, 1H), 7.83–7.86 (d, *J* = 8.2 Hz; 2H); $^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$, 25 °C): *δ* = 19.7, 21.5, 25.2, 28.7, 62.6, 63.4, 98.5, 101.3, 98.5, 101.3, 128.0, 129.2, 131.1, 140.6, 147.4.

**(*E*)-4-Methoxybenzaldehyde *O*-tetrahydro-2*H*-pyran-2-yl oxime (13f).**

(58 mg, 95%, 1:1.2 *Z*/*E*), clear oil. $^{1}$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.57–1.93 (m, 6H) 3.62–3.69 (m, 1H), 3.84 (s, 3H), 4.01–4.02 (m, 1H), 5.36–5.39 (m, 1H), 6.88–6.92 (d, *J* = 8.8 Hz; 2H), 7.57–7.61 (d, *J* = 8.8 Hz; 2H), 8.17 (s, 1H); $^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$, 25 °C) δ = 19.9, 25.2, 29.0, 55.3, 63.0, 100.9, 114.1, 124.6, 128.9, 150.1, 161.1; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{17}NO_3$ 235.1208; Found 235.1205.

**(*Z*)-4-Methoxybenzaldehyde *O*-tetrahydro-2*H*-pyran-2-yl oxime (13f').**

(35 mg, 57%), clear oil. $^{1}$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.61–1.95 (m, 6H), 3.65–3.72 (m, 1H), 3.87 (s, 3H), 3.89–3.97 (m, 1H), 5.40–5.42 (m, 1H,), 6.94–6.97 (d, *J* = 8.9 Hz; 2H) 7.37 (s, 1H), 7.91–7.94 (d, *J* = 8.9 Hz; 2H); $^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$, 25 °C) δ = 19.8, 25.2, 28.8, 55.3, 62.7, 101.3, 113.8, 123.7, 133.0, 147.0, 160.8.

**(*E*)-6-Bromobenzo[d][1,3]dioxole-5-carabaldehyde *O*-tetrahydro-2*H*-pyran-2-yl oxime (13g).**

(119 mg, 70%, *E*), white solid. Mp: 92–94 °C; $^{1}$H NMR (600 MHz, $CDCl_3$, 25 °C): *δ* = 1.63–1.94 (m, 6H), 3.63–3.70 (m, 1H), 3.94–4.02 (m, 1H), 5.37–5.40 (m, 1H), 6.02 (s, 2H), 6.71 (s, 1H), 7.45 (s, 1H), 8.52 (s, 1H); $^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$, 25 °C): *δ* = 19.6, 25.2, 28.8, 62.9, 101.1,102.1, 108.8, 112.6, 116.0, 124.8, 147.6, 149.5, 150.0; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{14}BrNO_4$ 327.0106; Found 327.0104.

**(*E*)-2-Bromo-4,5-dimethoxybenzalehyde *O*-tetrahydro-*2H*-pyran-2-yl oxime (13h).**

(140 mg, 79%, *E*), white solid. Mp: = 150–152 °C; $^{1}$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.60–1.93 (m, 6H) 3.64–3.71 (m, 1H), 3.91 (s, 3H) 3.93 (s, 3H) 3.96–4.03 (m, 1H) 5.41–5.44 (m, 1H) 7.01 (s, 1H), 7.45 (s, 1H), 8.52 (s, 1H*);* $^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$, 25

°C) δ = 19.6, 25.2, 28.9, 56.1, 62.8, 101.0, 109.2, 115.1, 115.4, 123.5 148.5, 149.6, 151.2; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{18}BrNO_4$ 343.0419; Found 343.0415.

**(*E*)-[1,1'-Biphenyl]-4-carbaldehyde *O*-tetrahydro-2*H*-pyran-2-yl oxime (13i).** (70 mg, 96%, 1:1 *Z*/*E*), yellow solid. Mp: 76–78 °C; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.60–1.96 (m, 6H), 3.67–3.73 (m, 1H), 3.97–4.05 (m, 1H), 5.43–5.45 (m, 1H), 7.36–7.42 (m, 1H), 7.45–7.50 (m, 2H), 7.62–7.65 (d, $J$ = 8.1 Hz; 4H), 7.72–7.75 (d, $J$ = 8.3 Hz; 2H), 8.27 (s, 1H); $^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 19.8, 25.2, 28.9, 63.0, 101.1, 127.1, 127.3, 127.7–127.9 (d, $J$ = 9.6 Hz), 128.9, 130.9, 140.4, 142.8, 150.1; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{19}NO_2$ 281.1416; Found 281.1405.

**Benzophenone *O*-tetrahydro-2*H*-pyran-2-yl oxime (13j).** (108 mg, 74%), white solid. Mp: 64–66 °C; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.53–1.81 (m, 6H), 3.66–3.72 (m, 1H), 3.86–3.93 (m, 1H), 5.48–5.51 (t, $J$ = 3.7 Hz; 1H), 7.34–7.39 (m, 3H), 7.45–7.46 (m, 5H), 7.55–7.58 (dd, $J$ = 6.1, 1.9 Hz; 2H); $^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 19.5, 25.3, 28.8, 62.7, 101.1, 127.9, 128.1–128.3 (d, $J$ = 9.8 Hz), 128.8, 129.3–129.4 (d, $J$ = 7.6 Hz), 130.1, 132.4, 133.5, 136.4; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{19}NO_2$ 281.1416; Found 281.1410.

**(*E*)-1,2-Diphenylethanone *O*-tetrahydro-2*H*-pyran-2-yl oxime (13k).**

(98 mg, 64%, 1:>19 *Z*/*E*), clear oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.48–1.91 (m, 6H), 3.61–3.68 (m, 1H), 3.77–3.85 (m, 1H), 4.15–4.20 (d, $J$ = 14.5 Hz; 1H), 4.32–4.36 (d, $J$ = 14.5 Hz; 1H), 5.52–5.55 (t, $J$ = 3.0 Hz; 1H), 7.20–7.24 (m, 1H), 7.29–7.31 (d, $J$ = 4.4 Hz; 4H), 7.35–7.38 (m, 3H), 7.73–7.76 (m, 2H); $^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$, 25 °C) δ = 19.5, 25.3, 29.0, 33.2, 62.6, 100.9, 126. 3, 126.9, 128.4, 128.6 (d, $J$ = 1.4 Hz), 129.3,

135.6, 137.0, 157.6; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{21}NO_2$ 295.1572; Found 295.1565.

**(*Z/E*)-Furan-2-carbaldehyde *O*-tetrahydro-*2H*-pyran-2-yl oxime (13l).**

(81 mg, 80%, 1:6 *Z*/*E*), brown oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.56–1.95 (m, 6H, *E* and *Z*), 3.64–3.71 (m, 1H, *E* and *Z*), 3.87–3.95 (m, 1H, *E* and *Z*), 5.36–5.39 (m, 1H, *Z*), 5.44–5.46 (m, 1H, *E*), 6.45–6.47 (m, 1H, *Z*), 6.54–6.56 (m, 1H, *E*), 6.67–6.68 (d, *J* = 3.4 Hz; 1H, *Z*), 7.27–7.29 (d, *J* = 3.4 Hz; 1H, *E*), 7.48–7.49 (d, *J* = 1.2 Hz; 1H, *E* and *Z*), 7.56 (s, 1H, *E*), 8.08 (s, 1H, *Z*); $^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$, 25 °C) δ = 19.7, 19.8, 25.1, 28.6, 28.8, 62.5, 63.1, 101.2, 111.6, 112.2, 113.1, 117.9, 137.5, 140.5, 143.5, 144.3, 145.2; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{13}NO_3$ 195.0895; Found 195.0892.

**(*Z*)-6-(Benzyloxy)-*1H*-indole-3-carbaldehyde *O*-tetrahydro-*2H*-pyran-2-yl oxime (13m').**

(87 mg, 73%, 2:1 *Z*/*E*), white solid. Mp: 180–182 °C; flash chromatography (hexanes:EtOAc/DCM = 80:16:4) followed by recrystallization (hexanes/chloroform); $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.60–1.94 (m, 6H), 3.66–3.72 (m, 1H), 4.00–4.01 (m, 1H) 5.15 (s, 2H), 5.44–5.46 (m, 1H), 6.97–7.01 (d *J* = 2.4, 8.8 Hz; 1H), 7.26–7.29 (m, 1H), 7.34–7.43 (m, 4H), 7.50–7.53 (d *J* = 7.1 Hz; 2H) 7.77–7.78 (d, *J* = 2.3 Hz; 1H), 8.32 (s, 1H), 8.41 (s, 1H); $^{13}$C{$^1$H} NMR (75.5 MHz, $d_6$-DMSO, 25 °C) δ = 20.0, 25.4, 29.3, 62.2, 70.2, 100.5, 105.8 108.5, 112.6, 113.1, 125.1, 128.1 (d, *J* = 5.4 Hz), 130.7, 132.4, 138.1, 146.9, 153.7; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{22}N_2O_3$ 350.1630; Found 350.1625.

**(1(*Z*/*E*),2*E*)-Cinnamaldehyde *O*-tetrahydro-2*H*-pyran-2-yl oxime (13n).**

(66 mg, 55%, 1:1.2 *Z*/*E*), clear yellow oil. $^{1}$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.56–1.92 (m, 6H, *E* and *Z*), 3.63–3.70 (m, 1H, *E* and *Z*), 3.93–4.01 (m, 1H, *E* and *Z*), 4.96–4.99 (m, 1H, *Z*) 5.30–5.32 (m, 1H, *E*), 6.81–6.99 (m, 1H, *E* and *Z*), 7.31–7.40 (overlapping signals, *E* and *Z*), 7.44–7.47 (dd, *J* = 6.7, 1.1 Hz; 2H, *E* and *Z*), 7.99–8.03 (d, *J* = 9.2 Hz; 1H, *E*); $^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 19.8, 25.1, 25.5, 28.8, 30.7, 63.1, 94.7, 100.9, 122.1, 127.0, 128.8 (d, *J* = 6.8 Hz), 135.9, 139.2, 152.2; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{17}NO_2$ 231.1259; Found 231.1256.

**(*E*)-3-(4-(*tert*-Butyl)-phenyl)-2-methylpropanal *O*-tetrahydro-2*H*-pyran-2-yl oxime (13o).**

(80 mg, 77%, 1:2 *Z*/*E*), clear oil. $^{1}$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.08–1.11 (d, *J* = 6.7 Hz; 3H), 1.34 (s, 9H), 1.59–1.85 (m, 6H), 2.55–2.64 (m, 1H), 2.70–2.91 (m, 2H), 3.57–3.67 (m, 1H), 3.85–3.99 (m, 1H), 5.21–5.25 (m, 1H), 7.11–7.14 (d, *J* = 8.0 Hz; 2H), 7.31–7.34 (m, 2H), 7.44–7.47 (dd, *J* = 5.4, 1.5 Hz; 1H); $^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$, 25 °C) δ = 17.4 (d, *J* = 7.6 Hz), 19.9, 20.1, 25.2, 28.9 (d, *J* = 5.5 Hz), 31.4, 34.4, 36.0 (d, *J* = 2.8 Hz), 40.3, 40.4, 62.9, 63.2, 100.3, 100.6, 125.2, 128.9 136.0 (d, *J* = 2.4 Hz), 149.0, 156.6; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{29}NO_2$ 303.2198; Found 303.2191.

**Cyclopentanone *O*-tetrahydro-*2H*-pyran-2-yl oxime (13p).**

(85 mg, 89%), clear oil. $^{1}$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.54–1.85 (m, 10H), 2.36–2.50 (m, 4H), 3.56–3.64 (m, 1H), 3.90–3.97 (m, 1H), 5.16–5.19 (m, 1H,); $^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$, 25 °C) δ = 20.3, 24.6, 25.1, 25.2, 27.8, 29.1, 31.1, 63.5, 100.7, 168.3; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{17}NO_2$ 183.1259; Found 183.1252.

**Cycloheptanone *O*-tetrahydro-*2H*-pyran-2-yl oxime (13q).**

(79 mg, 72%), clear oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.52–1.84 (m, 14H), 2.40–2.44 (m, 2H), 2.59–2.63 (m, 2H), 3.58–3.65 (m, 1H), 3.88–3.95 (m 1H), 5.18–5.20 (m, 1H); $^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$, 25 °C) δ = 20.3, 24.6, 25.3, 27.6, 29.2 (d, *J* = 6.5 Hz), 30.4 (d, *J* = 4.6 Hz*)*, 33.8, 63.3, 100.5, 165.5; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{21}NO_2$ 211.1572; Found 211.1565.

**(*Z/E*)-1,6,6-Trimethylbicyclo[3.1.1]heptan-3-one *O*-tetrahydro-*2H*-pyran-2-yl oxime (13r).**

(97 mg, 74%, 1:1 *Z*/*E*), clear oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.802 (s, 3H, *E* and *Z*), 0.907 (s, 3H, *E* and *Z*), 1.04, (s, 3H, *E* and *Z*), 1.18–1.29 (m, 1H, *E* and *Z*), 1.49–1.90 (overlapping signals, 10H, *E* and *Z*), 2.04 (s, 1H, *Z*), 2.11 (s, 1H, *E*), 2.51–2.60 (m, 1H, *E* and *Z*), 3.56–3.63 (m, 1H, *E* and *Z*), 3.82–3.97 (m, 1H, *E* and *Z*), 5.17–5.20 (m, 1H, *E*), 5.23–5.26 (m, 1H, *Z*); $^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$, 25 °C) δ = 11.1, 11.2, 18.5, 18.5, 19.5, 19.6, 19.9*,* 20.4, 25.3, 25.4, 27.2, 27.3, 29.3, 29.4, 32.7, 32.8, 33.8, 33.9, 43.6, 43.7, 48.0, 48.3, 51.8, 51.9, 62.6*,* 63.5, 100.0, 100.8, 170.8, 171.0; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{25}NO_2$ 251.1885; Found 251.1883.

**(*E*)-4-(4-Methylpent-3-en-1-yl)cyclohex-3-enecarbaldehyde *O*-tetrahydro-2*H*-pyran-2-yl oxime (13s).**

(94 mg, 95%, 1:2 *Z*/*E*), clear oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): *δ* = 1.60 (overlapping signals, 5H) 1.69 (s, 3H), 1.80–2.23 (overlapping signals, 14H), 2.50–2.60 (m, 1H), 3.59–3.65 (m, 1H), 3.91–3.97 (m, 1H), 5.06–5.11 (m, 1H), 5.19–5.21 (m, 1H), 5.38–5.43 (m, 1H), 7.43–7.47 (dd, *J* = 7.3, 3.5 Hz; 1H); $^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$, 25 °C): *δ* = 17.7, 20.1, 25.2, 25.7, 26.3, 26.8 (d, *J* = 5.6 Hz), 27.1 (d, *J* = 3.3 Hz), 28.9, 34.4 (d, *J* = 4.3

Hz), 34.9, 37.6, 63.3, 100.6, 118.5, 120.5 (d, $J$ = 3.4 Hz), 124.2, 131.4, 135.8, 137.6, 156.3 (d, $J$ = 3.1 Hz); HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{29}NO_2$ 291.2198; Found 291.2190.

**(*Z*)-4-(4-Methylpent-3-en-1-yl)cyclohex-3-enecarbaldehyde *O*-tetrahydro-2*H*-pyran-2-yl oxime (13s').**

(45 mg, 86%,), clear oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.62 (overlapping signals, 5H), 1.70 (s, 3H), 1.77–2.23 (overlapping signals, 14H), 3.14–3.24 (m, 1H), 3.63–3.68 (m, 1H), 3.88–3.97 (m, 1H), 5.09–5.13 (m, 1H), 5.24–5.28 (m, 1H), 5.41–5.45 (m, 1H), 6.68–6.71 (d, $J$ = 7.1 Hz; 1H); $^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 17.7, 19.9 (d, $J$ = 6.4 Hz), 25.2, 25.7, 26.4, 27.0 (d, $J$ = 2.2 Hz), 28.4, 28.8, 30.7 (d, $J$ = 2.1 Hz), 37.7, 62.9, 63.2, 100.7, 118.8, 120.6, 124.2, 131.5, 137.7, 156.9 (d, $J$ = 4.8 Hz).

**(*Z/E*)-3-Methyl-2-((*Z*)-pent-2-en-1-yl)cyclopent-2-enone *O*-tetrahydro-*2H*-pyran-2-yl oxime (13t).**

(59 mg, 43%, C.N.D.) clear oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.963–1.01 (t, $J$ = 7.5 Hz; 3H), 1.57–1.86 (m, 6H), 1.87 (s, 3H), 2.15–2.19 (m, 2H), 2.37–2.41 (m, 2H), 2.65–2.69 (m, 2H), 2.90–3.10 (qd, $J$ = 14.7, 4.6 Hz; 2H), 3.57–3.64 (m, 1H), 3.91–3.98 (m, 1H), 5.24–5.26 (m, 1H), 5.35–5.38 (t, $J$ = 4.8 Hz, 2H); $^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$, 25 °C) δ = 14.2 15.4, 20.2, 20.5, 22.5, 25.1, 25.4, 29.4, 34.3, 63.2, 101.0, 125.9, 133.3, 151.4, 168.7; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{25}NO_2$ 263.1885; Found 263.1881. Note: the *Z*/*E* isomer configuration could not be determined (C.N.D.) for this compound.

**(*Z/E*)-*tert*-Buty-l,4-((((tetrahydro-*2H*-pyran-2-yl)oxy)imino)methyl)piperidine-1-carboxylate (13u).**

(87 mg, 54% 1:2 *Z*/*E*), clear oil. $^{1}$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.44 (s, 9H, *E* and *Z*), 1.51–1.84 (overlapping signals, 10H, *E* and *Z*), 2.39–2.50 (m, 1H, *E*), 2.73–2.81 (m, 2H, *E* and *Z*), 3.02–3.10 (m, 1H, *Z*), 3.56–3.63 (m, 1H, *E* and *Z*), 3.88–3.95 (m, 1H, *E* and *Z*), 4.05–4.09 (m, 2H, *E* and *Z*), 5.17–5.19 (m, 1H, *E*), 5.21–5.22 (m, 1H, *Z*) 6.59–6.61 (d, *J* = 6.9 Hz; 1H, *Z*), 7.37–7.39 (d, *J* = 6.5 Hz; 1H, *E*); $^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$, 25 °C) δ = 20.0, 25.1, 28.4, 28.9, 29.2, 29.3, 36.9, 63.3, 79.5, 100.7, 154.8, 155.2; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{29}N_2O_4$ 313.2127; Found 313.2119.

**(Z/*E*)-2,2,7,7-Tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*4',5'-*d*]pyran-5-carbaldehyde *O*-tetrahydro-2*H*-pyran-2-yl oxime (13v).**

(97 mg, 79%, 1:2, *Z*/*E*), yellow oil. $^{1}$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.33–1.36 (t, *J* = 4.4 Hz; 6H, *E* and *Z*), 1.49 (s, 3H, *E* and *Z*), 1.56 (s, 3H, *E* and *Z*), 1.59–1.83 (m, 6H, *E* and *Z*), 3.60–3.70 (m, 1H, *E* and *Z*), 3.79–3.95 (m, 1H, *E* and *Z*), 4.29–4.40 (m, 1H, *E* and *Z*), 4.50–4.68 (overlapping signals, 2H, *E* and *Z*), 5.00–5.05 (td, *J* = 5.2, 1.9 Hz; 1H, *E*), 5.27–5.31 (m, 1H, *E)* 5.38–5.41 (t, *J* = 2.9 Hz; 1H, *Z*), 5.55–5.59 (m, 1H, *E* and *Z*), 6.87–6.91 (m, 1H, *E*), 7.51–7.56 (m, 1H, *Z*); $^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$, 25 °C) δ = 19.0, 19.3, 19.5, 19.7, 19.9, 24.3 (d, *J* = 5.0 Hz), 24.5, 24.8, 25.0 (d, *J* = 2.0 Hz), 25.1, 25.9, 26.0 (d, *J* = 3.9 Hz), 26.1, 28.4, 28.6 (d, *J* = 4.7 Hz), 62.1, 62.3, 62.9, 63.5, 63.9, 66.5 (d, *J* = 3.2 Hz), 70.1, 70.2, 70.3, 70.6 (d, *J* = 4.4 Hz), 71.4, 71.5, 72.9, 73.6, 96.1, 96.2 (d, *J* = 2.8 Hz), 100.2, 100.3, 100.7, 101.0, 108.9, 109.6, 109.7; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{27}NO_7$ 357.1788; Found 357.1780.

**(*E*)-3,7-Dimethloct-6-enal *O*-tetrahydro-2*H*-pyran-2-yl oxime (13w).**

(28 mg, 39%, 1:1.2 *Z*/*E*), clear oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 0.923–0.952 (dd, $J$ = 4.6, 2.1 Hz; 3H), 1.17–1.44 (m, 4H), 1.59 (s, 3H), 1.67 (s, 3H), 1.76–2.29 (overlapping signals, 9H), 3.56–3.64 (m, 1H), 3.89–3.96 (m, 1H), 5.05–5.10 (m, 1H), 5.19–5.22 (m, 1H), 7.47–7.52 (t, $J$ = 6.5 Hz; 1H); $^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 17.6, 19.4 (d, $J$ = 6.6 Hz), 20.0 (d, $J$ = 1.7 Hz), 25.2, 25.4 (d, $J$ = 2.4 Hz), 25.7, 28.9, 31.0 (d, $J$ = 6.6 Hz), 36.4 (d, $J$ = 2.1 Hz), 36.6, 36.8, 63.1 (d, $J$ = 4.2 Hz), 100.5 (d, $J$ = 3.5 Hz), 124.3, 131.5, 152.2 (d, $J$ = 2.1 Hz); HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{28}NO_2$ 254.2120; Found 254.2000.

**(*E*)-Ethyl-2-cyano-2-(((tetrahydro-*2H*-pyran-2-yl)oxy)imino)acetate (13x).**

(98 mg, 83%, *E*), clear oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.39–1.44 (t, $J$ = 7.1 Hz; 3H) 1.64–2.02 (m, 6H), 3.72–3.79 (m, 1H), 3.82–3.90 (td, $J$ = 10.5, 2.9 Hz; 1H), 4.40–4.48 (dq, $J$ = 7.1, 1.8 Hz; 2H), 5.70–5.71 (m, 1H); $^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$, 25 °C) δ = 14.0, 18.1, 24.6, 27.9, 62.6, 63.6, 104.7, 107.6, 157.8; HRMS (CI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{15}N_2O_4$ 227.1032; Found 227.1027.

**(*E*)-Acetophenone *O*-(1-ethoxyethyl) oxime (13y).**

(99 mg, 92%, 1:19 *Z*/*E*), clear oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.24–1.29 (t, $J$ = 7.1 Hz, 3H), 1.51–1.53 (d, $J$ = 5.4 Hz; 3H), 2.30 (s, 3H), 3.65–3.75 (m, 1H), 3.90–4.00 (m, 1H), 5.43–5.49 (q, $J$ = 5.4 Hz; 1H), 7.38–7.41 (m, 3H), 7.68–7.71 (m, 2H); $^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 12.9, 15.4, 20.4, 64.2, 103.8, 126.1, 128.4, 129.1, 136.7, 154.4; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{17}NO_2$ 207.1259; Found 207.1252.

**(*E*)-Acetophenone *O*-(1-butoxyethyl) oxime (13z).**

(116 mg, 95%, 1:19 *Z*/*E*), clear oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 0.95–0.97 (m, 3H), 1.36–1.46 (m, 2H), 1.50–1.52 (d, $J$ = 5.5 Hz; 3H), 1.60–1.66 (m, 2H), 2.30 (s, 3H), 3.60–3.67 (m, 1H), 3.86–3.93 (m, 1H), 5.42–5.47 (q, $J$ = 5.4 Hz; 1H), 7.38–7.40 (m, 3H), 7.68–7.71 (m, 2H); $^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 12.8, 13.9, 19.3, 20.3, 32.0, 68.5, 104.0, 126.1, 128.3, 129.0, 136.8, 154.4; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{21}NO_2$ 235.1572; Found 235.1564.

**(*E*)-Acetophenone *O*-(1-isobutoxyethyl) oxime (13aa).**

(109 mg, 89%, 1:19 *Z*/*E*), clear oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 0.929–0.964 (q, $J$ = 3.5 Hz; 6H), 1.50–1.52 (d, $J$ = 5.4 Hz; 3H), 1.83–1.97 (m, 1H) 2.30 (s, 3H), 3.37–3.42 (m, 1H), 3.63–3.68 (m, 1H), 5.40–5.45 (q, $J$ = 5.4 Hz; 1H), 7.38–7.41 (m, 3H), 7.68–7.71 (m, 2H); $^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 12.9, 19.4 (d, $J$ = 6.8 Hz), 20.2, 28.7, 75.6, 104.1, 126.1, 128.4, 129.0, 136.8, 154.4; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{21}NO_2$ 235.1572; Found 235.1566.

**(*E*)-Acetophenone *O*-(2-ethoxypropan-2-yl) oxime (13ab).**

(75 mg, 65%, 1:19 *Z*/*E*), clear oil. $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.19–1.23 (t, $J$ = 7.1 Hz; 3H), 1.61 (s, 6H), 2.28 (s, 3H), 3.58–3.65 (q, $J$ = 7.1 Hz; 2H), 7.38–7.40 (m, 3H), 7.73–7.76 (m, 2H); $^{13}$C{$^1$H} NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 12.5, 15.7, 24.7, 57.0, 103.7, 126.2, 128.3, 128.9, 137.1, 154.1; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{19}NO_2$ 221.1416; Found 221.1408.

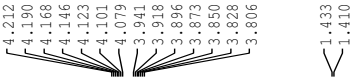
**(*E*)-Acetophenone *O*-(1-(cyclohexyloxy)ethyl) oxime (13ac).**

(65 mg, 48%, 1:19 *Z*/*E*), clear oil. $^{1}$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.19–1.42 (m, 5H), 1.49–1.50 (d, $J$ = 5.4 Hz; 3H), 1.53–1.58 (m, 1H), 1.74–1.79 (m, 2H), 1.91–2.00 (m, 2H), 2.28 (s, 3H), 3.78–3.87 (m, 1H), 5.53–5.59 (q, $J$ = 5.4 Hz; 1H), 7.37–7.41 (m, 3H), 7.67–7.70 (m, 2H); $^{13}$C{1H} NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta$ = 12.9, 20.9, 24.2, 24.4, 25.7, 32.4, 32.5, 33.6, 76.3, 102.0, 126.0, 128.4, 129.0, 136.8, 154.3; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{23}NO_2$ 261.1729; Found 261.1725.

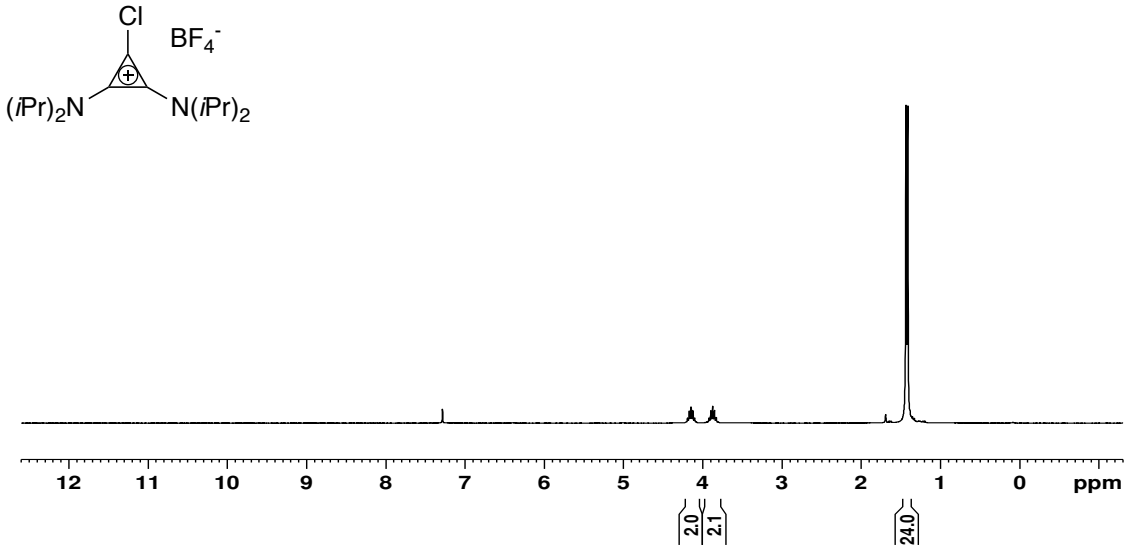
**(*E*)-Acetophenone *O*-tetrahydrofuran-2-yl oxime (13ad).**

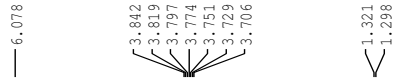
(92 mg, 87%, 1:19 *Z*/*E*), clear oil. $^{1}$H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.89–2.17 (m, 4H), 2.26 (s, 3H), 3.96–4.09 (overlapping signals, 2H), 5.93–5.95 (t, $J$ = 3.5 Hz; 1H), 7.36–7.38 (m, 3H), 7.69–7.72 (m, 2H); $^{13}$C{$^{1}$H} NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta$ =12.9, 24.0, 30.9, 67.9, 106.5, 126.2, 128.3, 129.1, 136.5, 155.8; HRMS (EI-DFS) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{15}NO_2$ 205.1103; Found 205.1099.

## *7.0 Spectra*

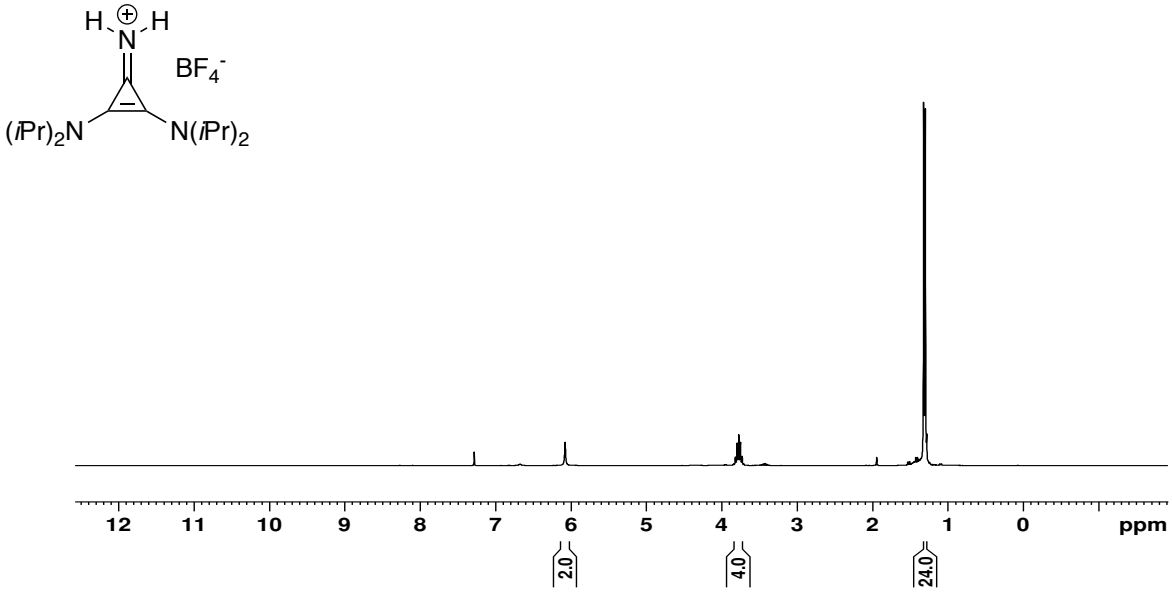


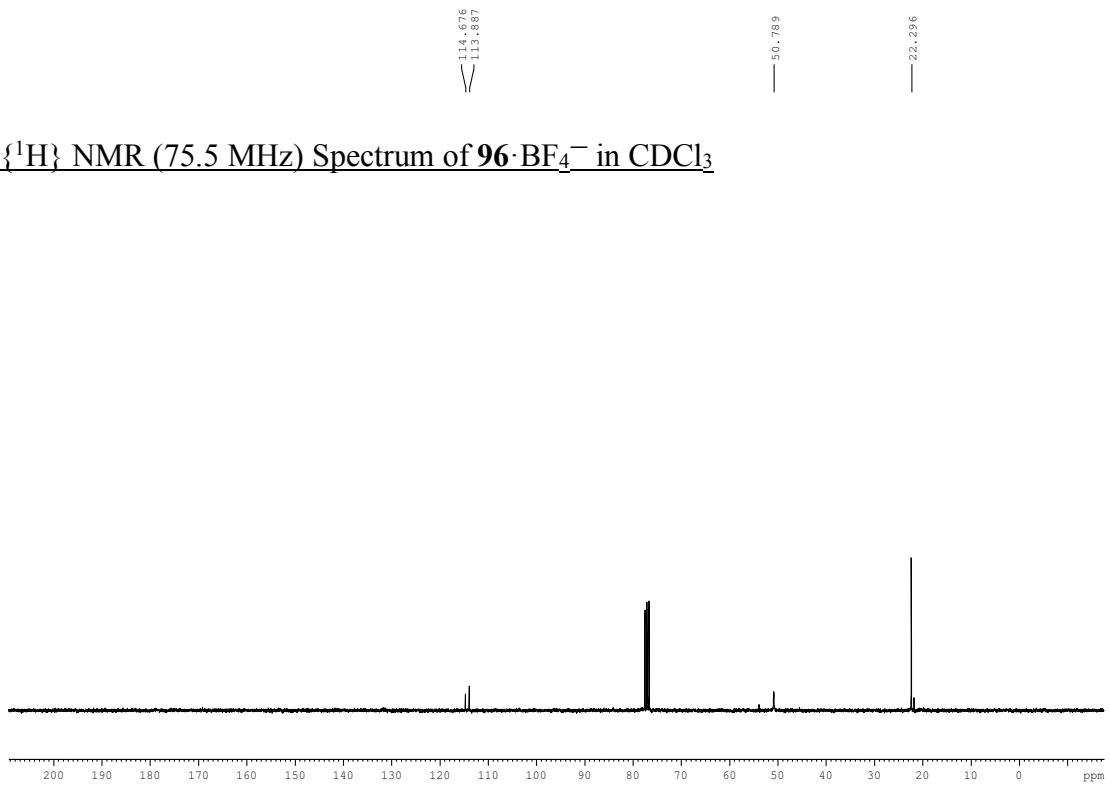

$^1$H NMR (300 MHz) Spectrum of **95**·$BF_4^-$ in $CDCl_3$



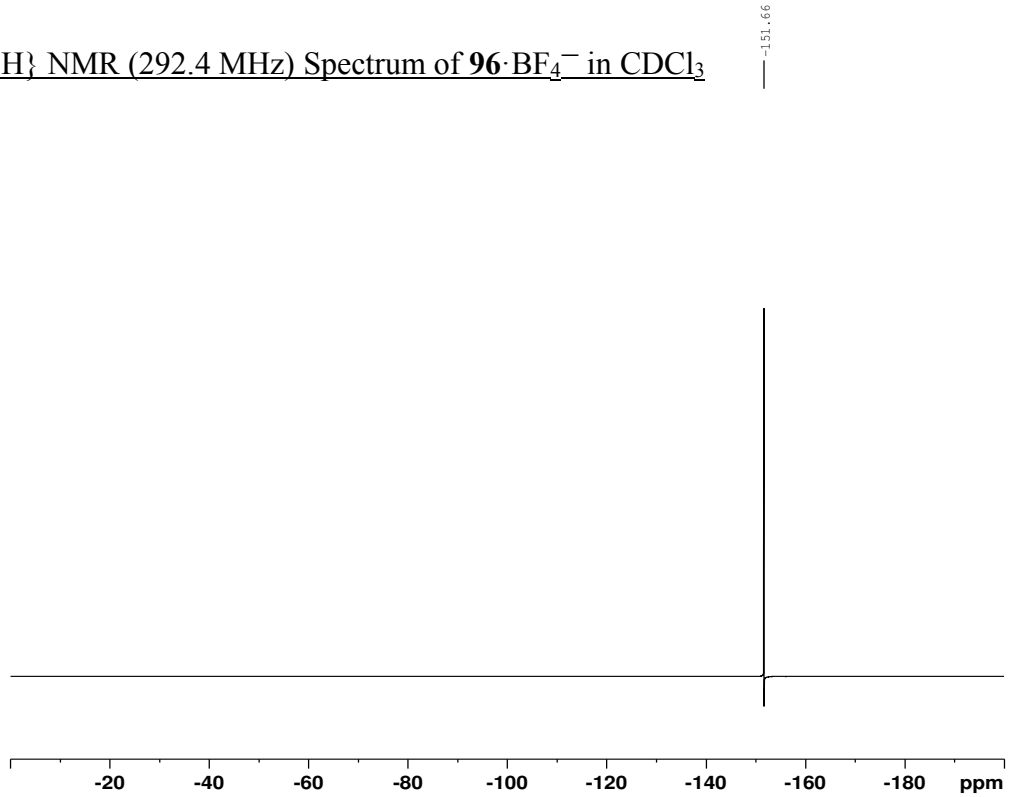




$^1$H NMR (300 MHz) Spectrum of **96**·$BF_4^-$ in $CDCl_3$



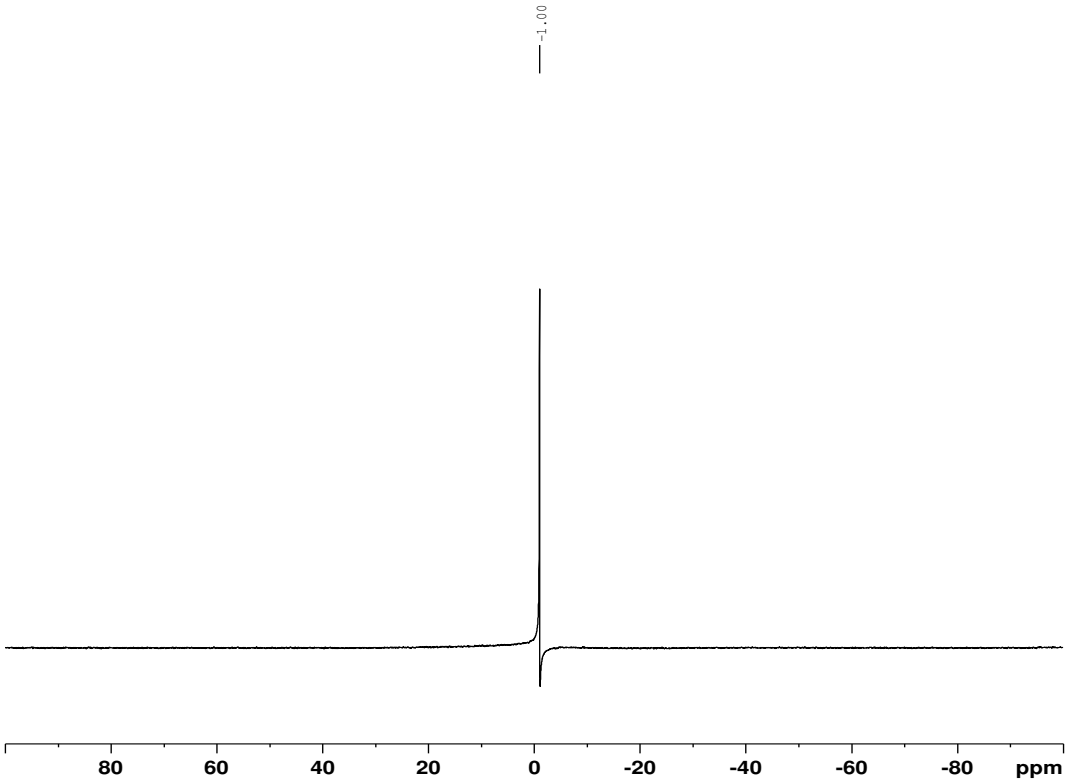



$^{13}C\{^{1}H\}$ NMR (75.5 MHz) Spectrum of **96**·$BF_4^-$ in $CDCl_3$

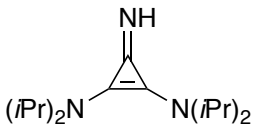



$^{19}F\{^{1}H\}$ NMR (292.4 MHz) Spectrum of **96**·$BF_4^-$ in $CDCl_3$

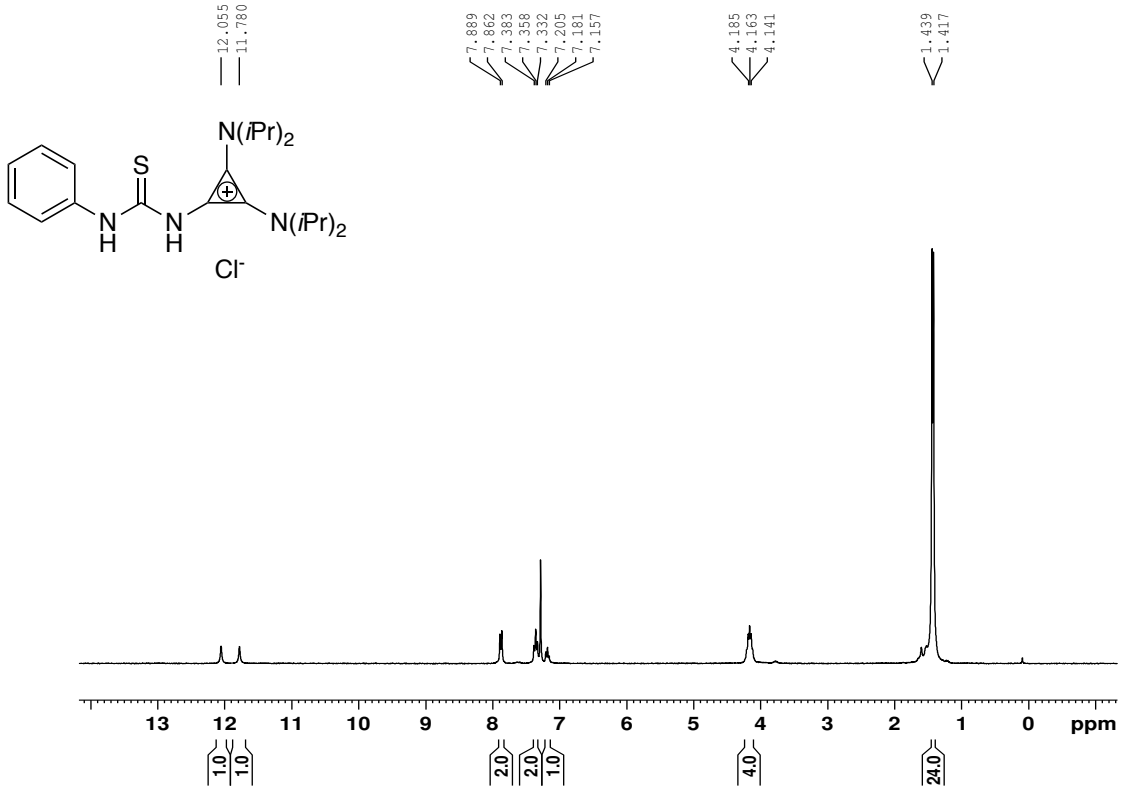
$^{11}B\{^{1}H\}$ NMR (96.3 MHz) Spectrum of **96**·$BF_4^-$ in $CDCl_3$



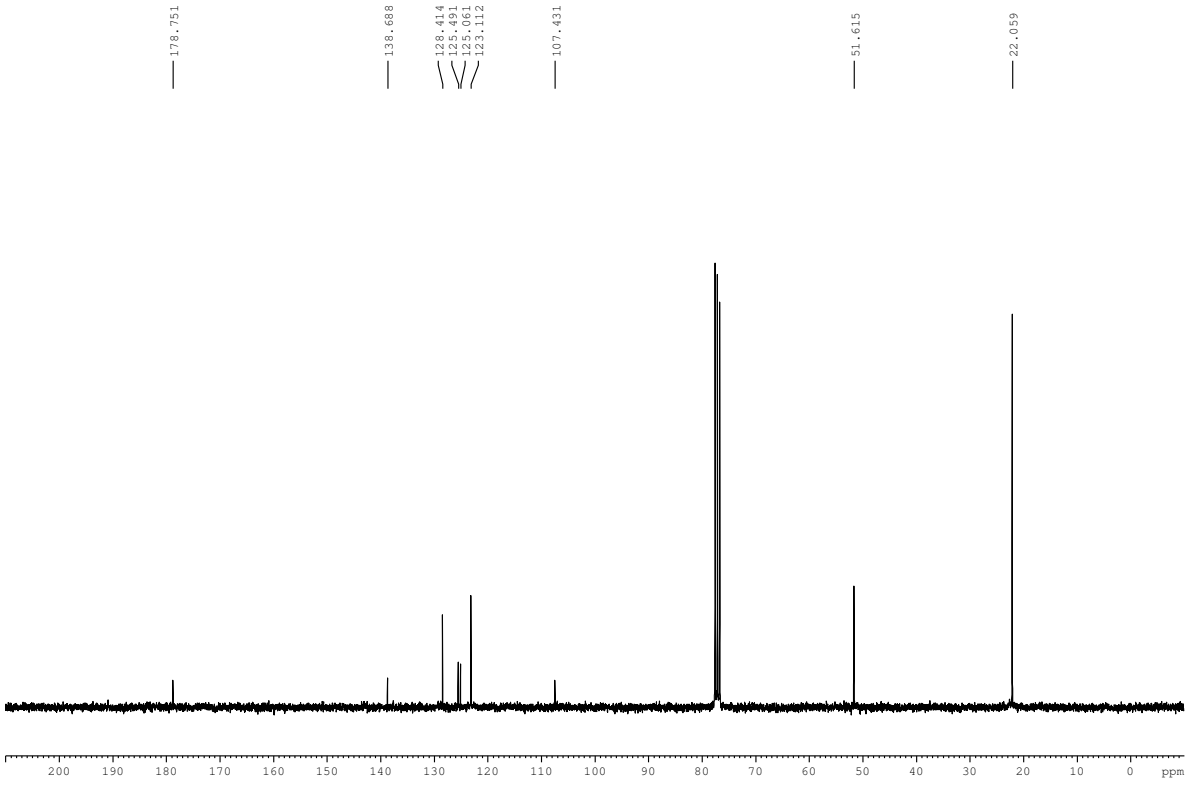

$^{1}H$ NMR (300 MHz) Spectrum of **97** in $CDCl_3$



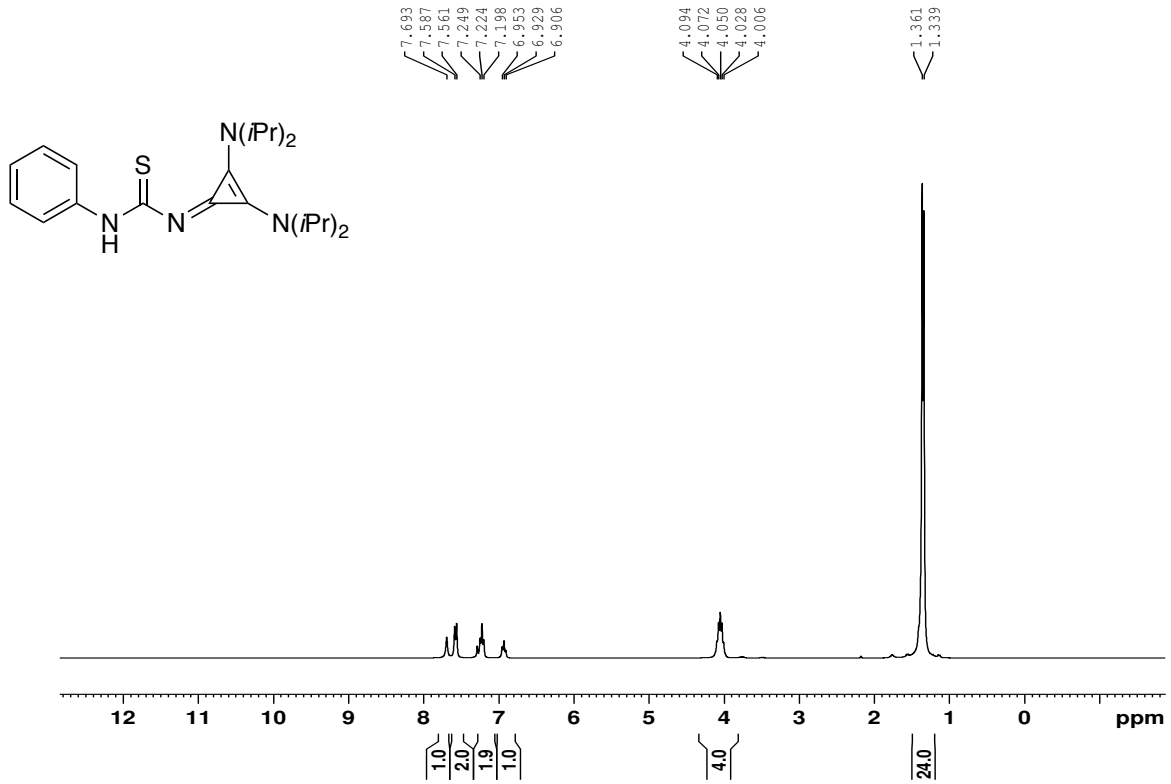
$^{1}$H NMR (300 MHz) Spectrum of **4**·Cl$^{-}$ in $CDCl_3$



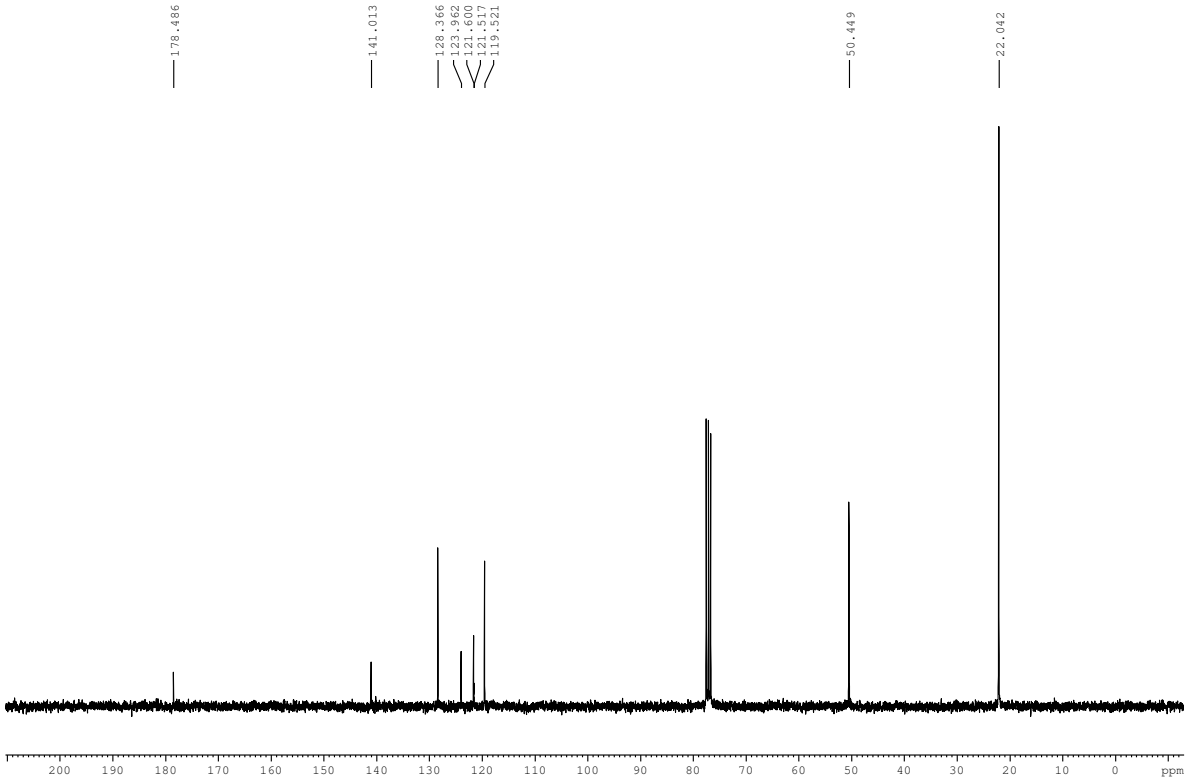

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **4**·Cl$^{-}$ in $CDCl_3$



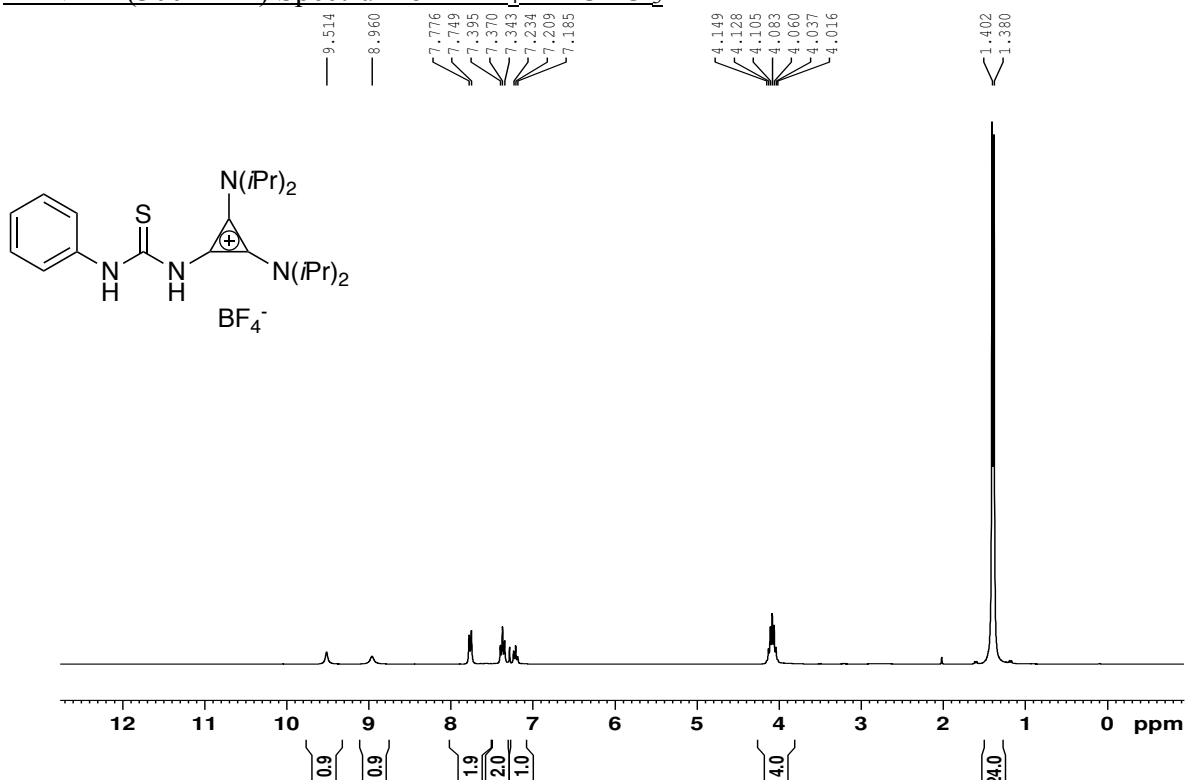
$^{1}$H NMR (300 MHz) Spectrum of **98** in $CDCl_3$



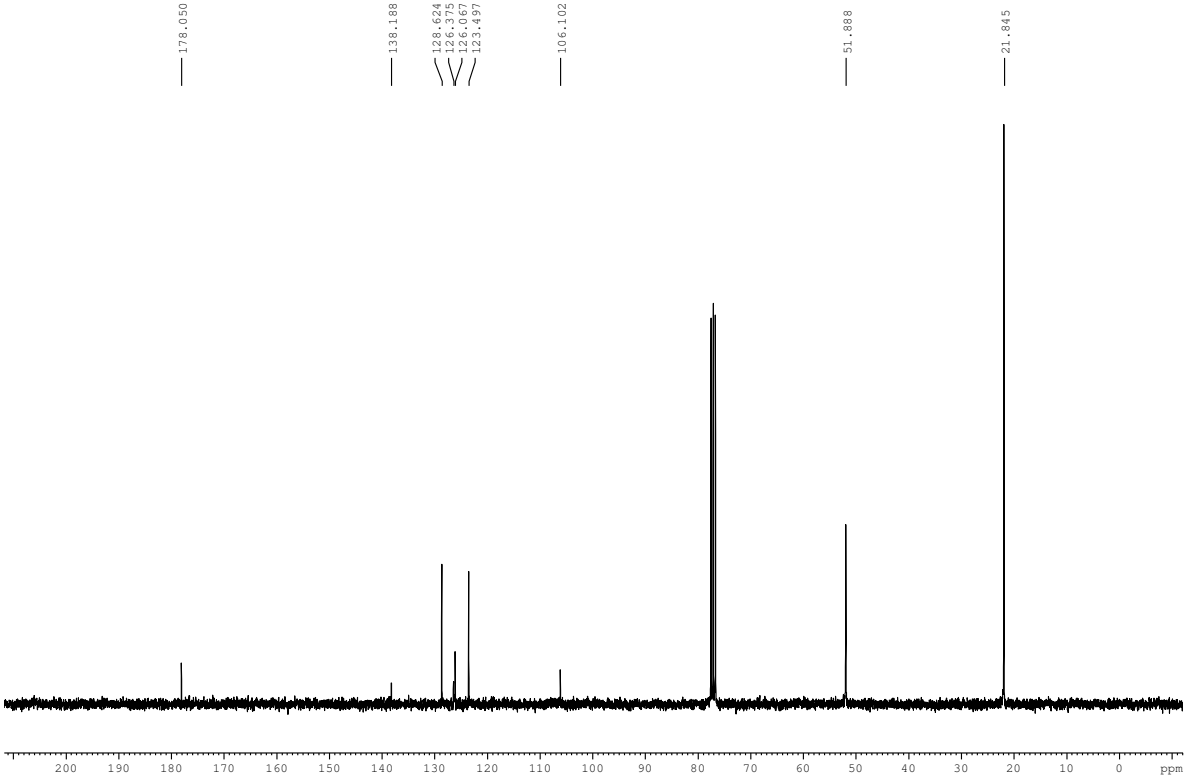

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **98** in $CDCl_3$



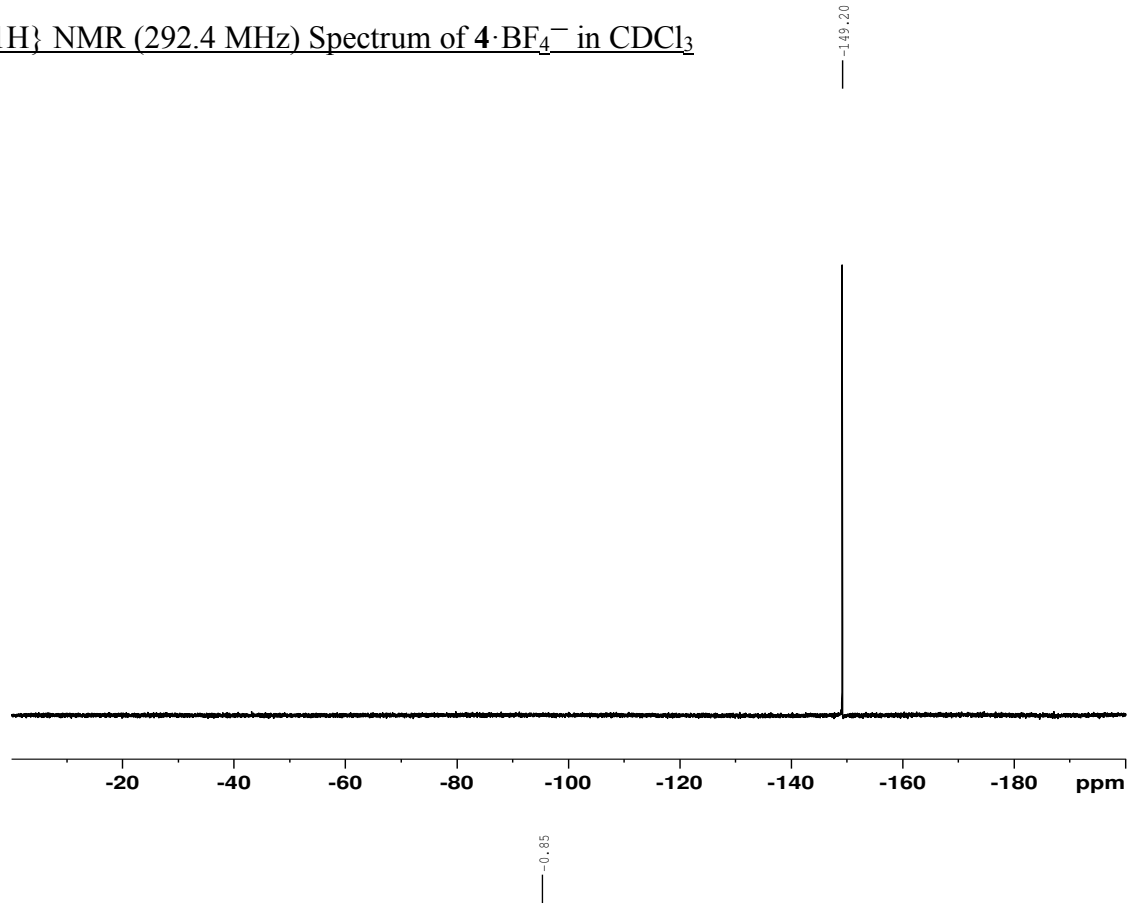
$^{1}$H NMR (300 MHz) Spectrum of **4**·$BF_4^-$ in $CDCl_3$



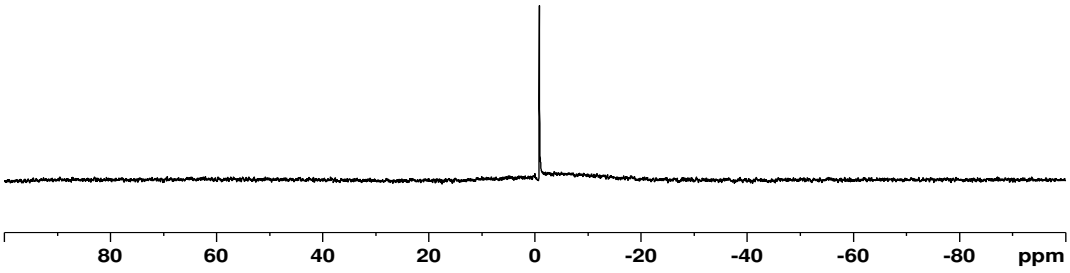

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **4**·$BF_4^-$ in $CDCl_3$



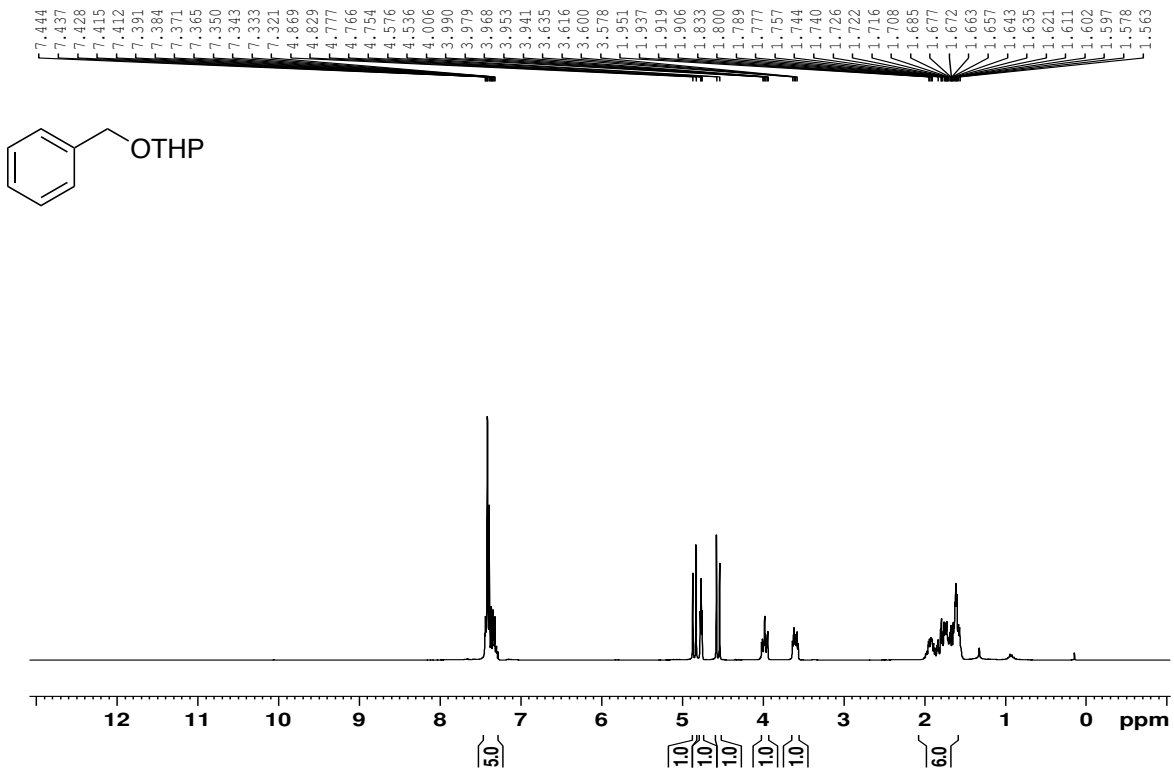
$^{19}F\{1H\}$ NMR (292.4 MHz) Spectrum of **4**·$BF_4^-$ in $CDCl_3$



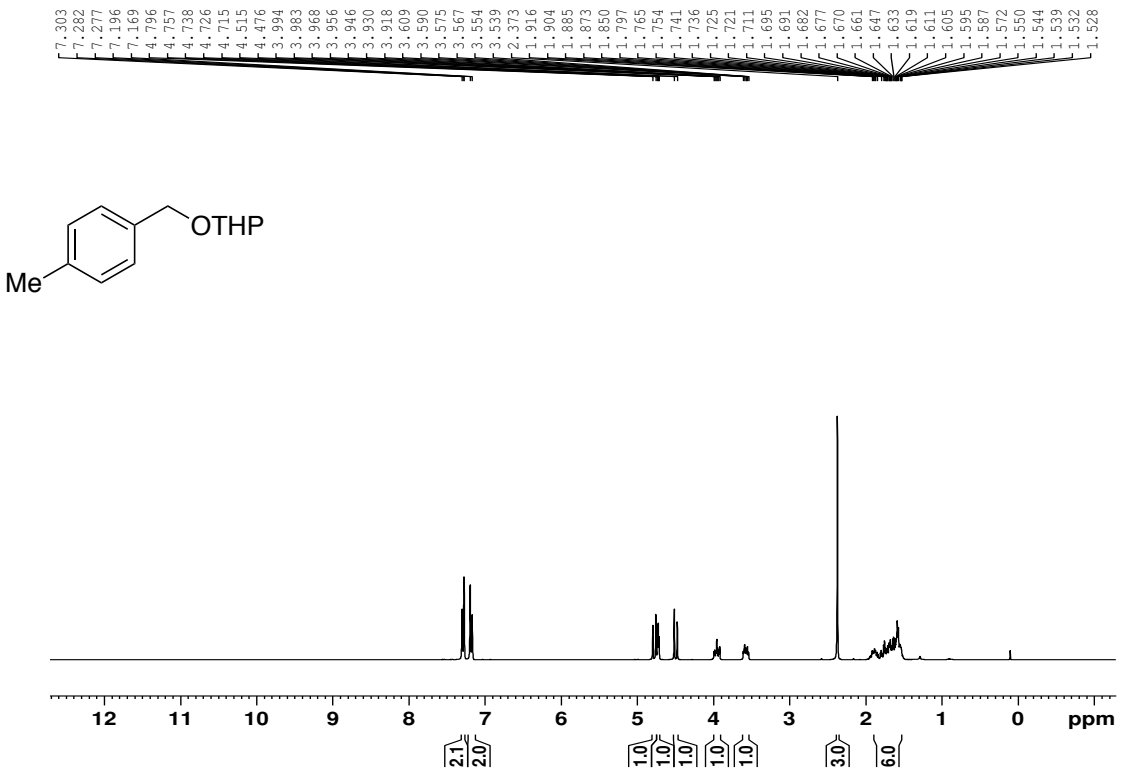

$^{11}B\{^1H\}$ NMR (96.3 MHz) Spectrum of **4**·$BF_4^-$ in $CDCl_3$



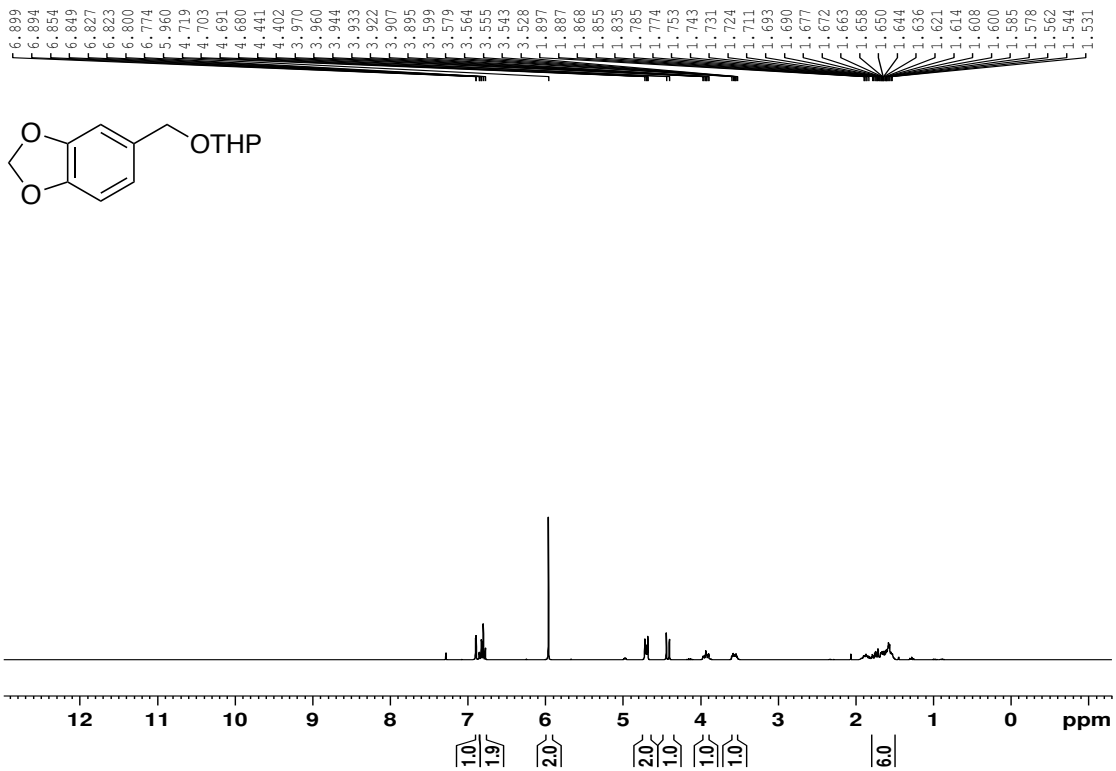
$^1$H NMR (300 MHz) Spectrum of **7a** in $CDCl_3$



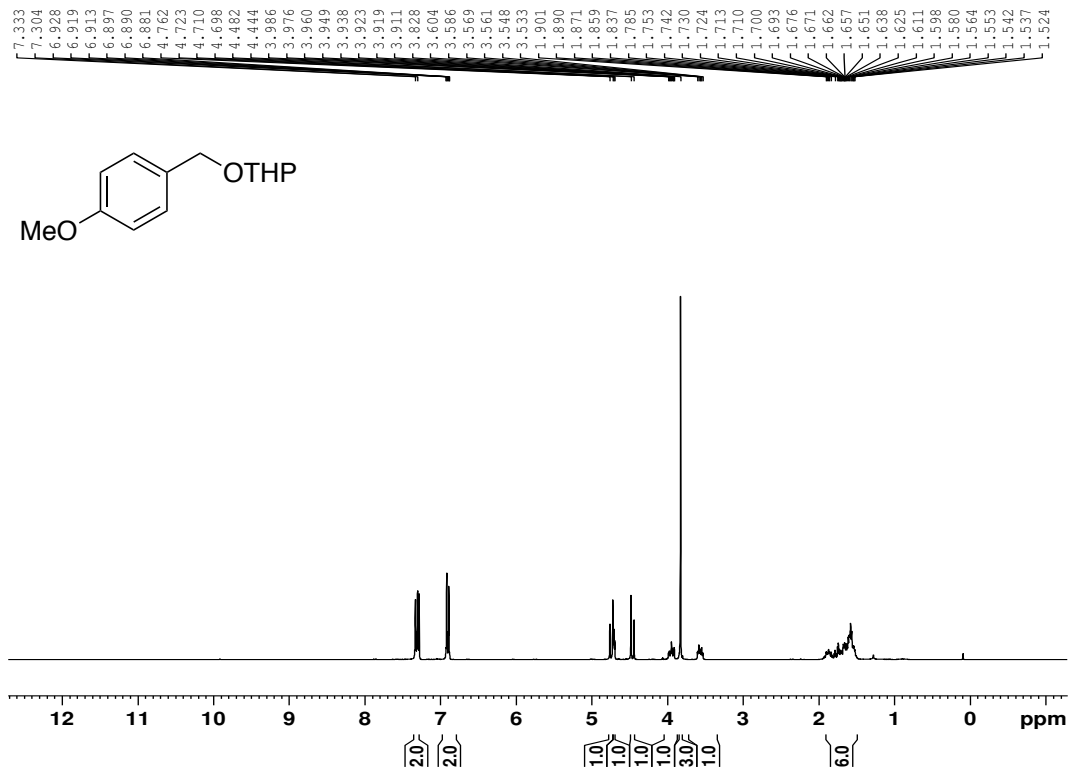

$^1$H NMR (300 MHz) Spectrum of **7b** in $CDCl_3$



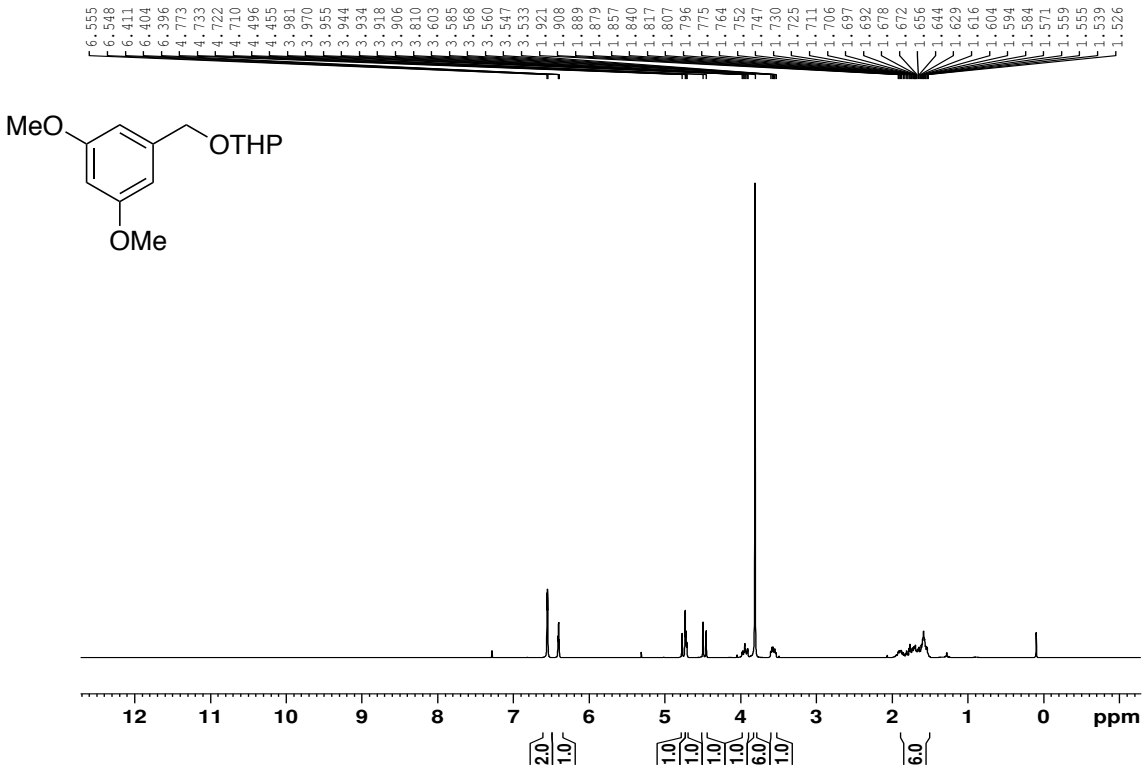
$^1$H NMR (300 MHz) Spectrum of **7c** in $CDCl_3$



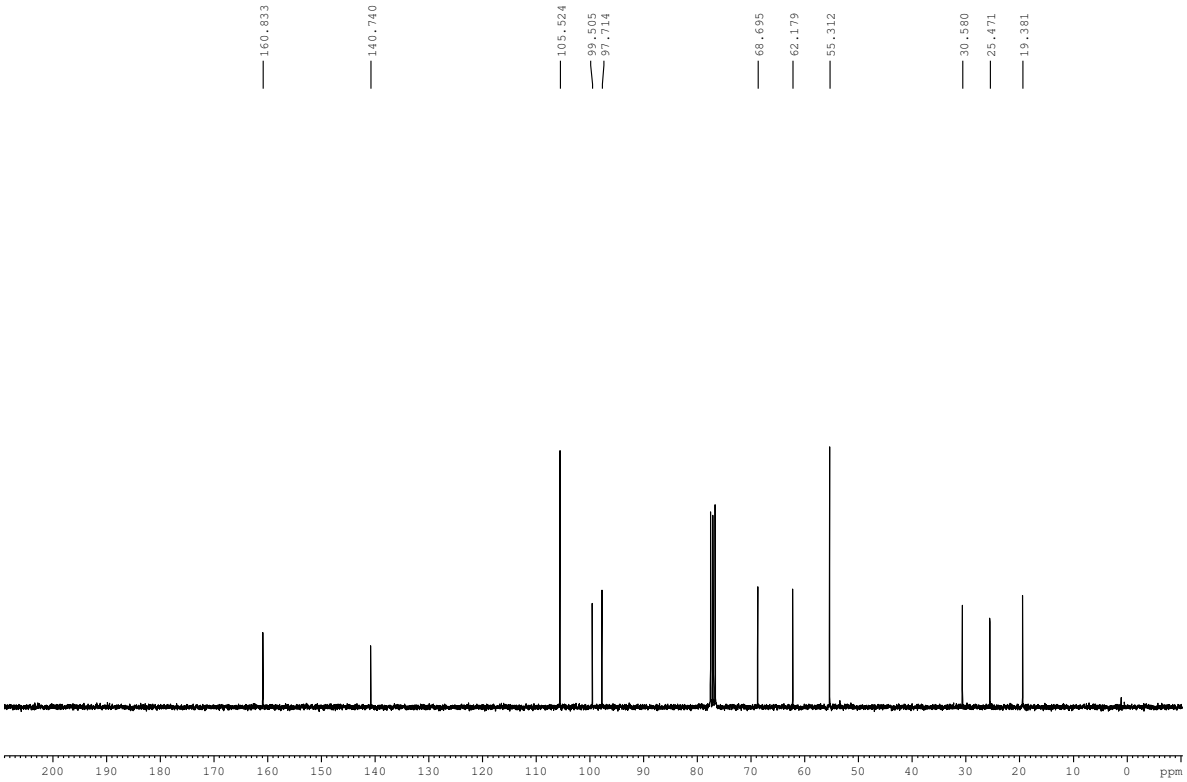

$^1$H NMR (300 MHz) Spectrum of **7d** in $CDCl_3$



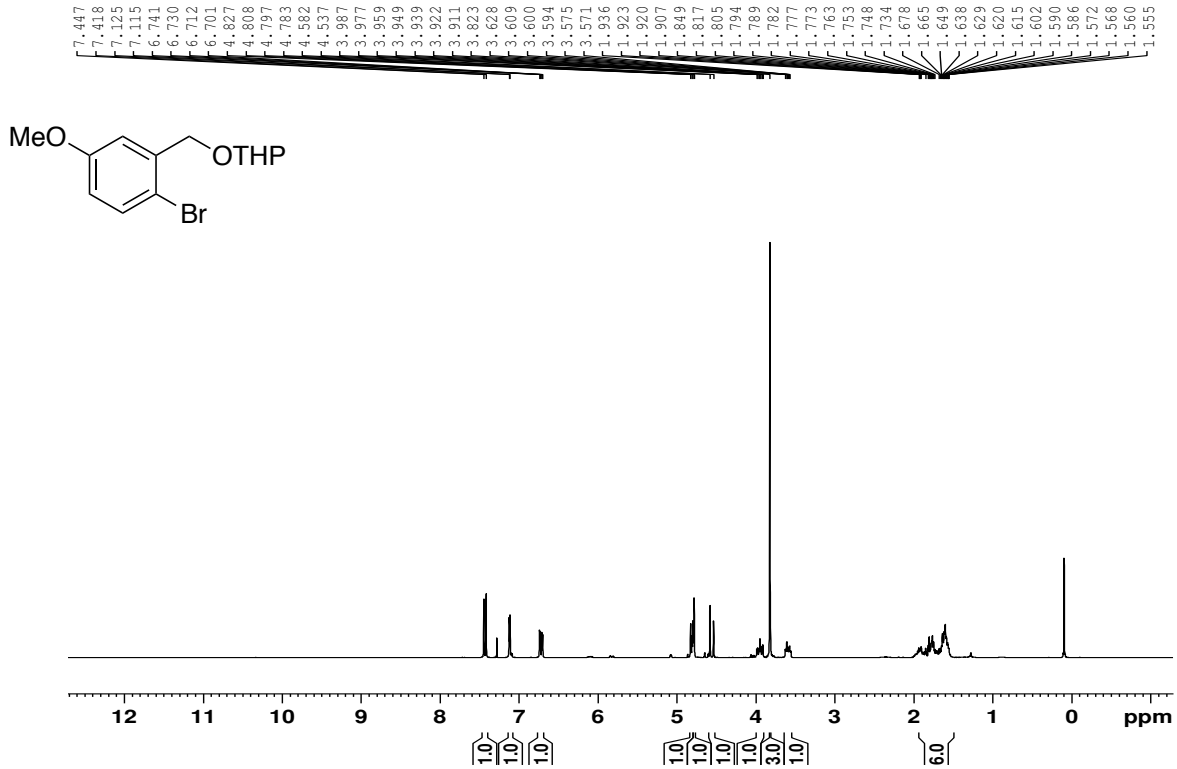
$^{1}$H NMR (300 MHz) Spectrum of **7e** in $CDCl_3$



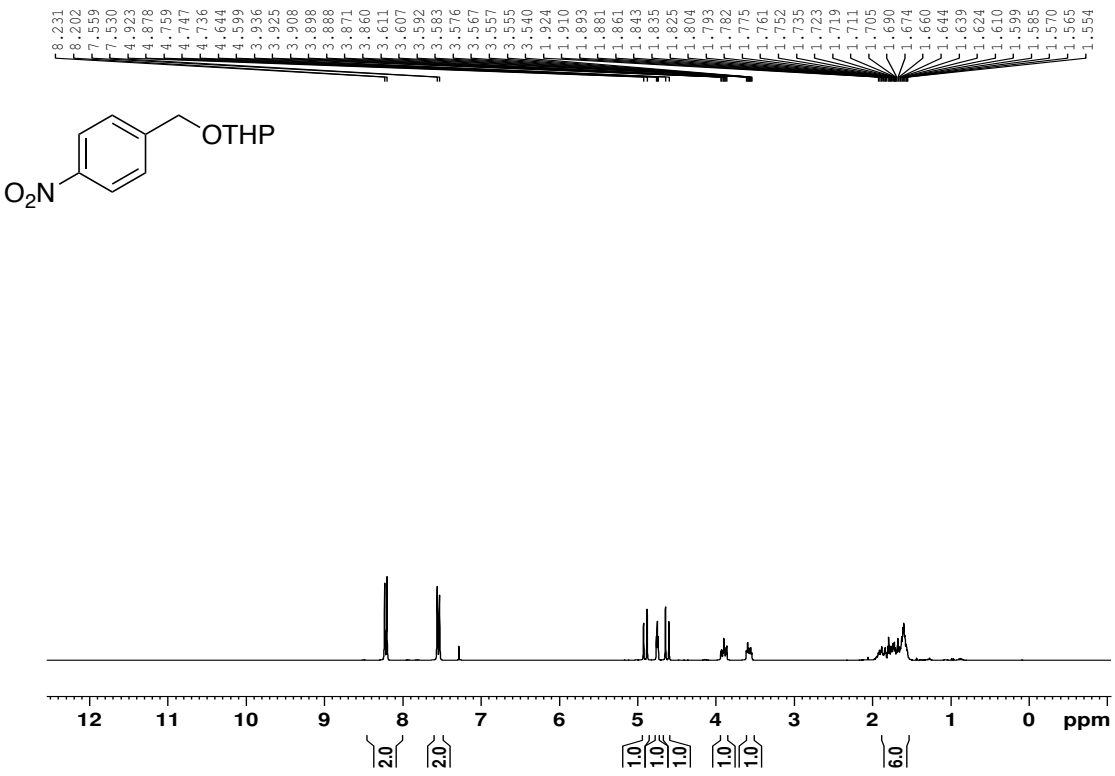

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **7e** in $CDCl_3$



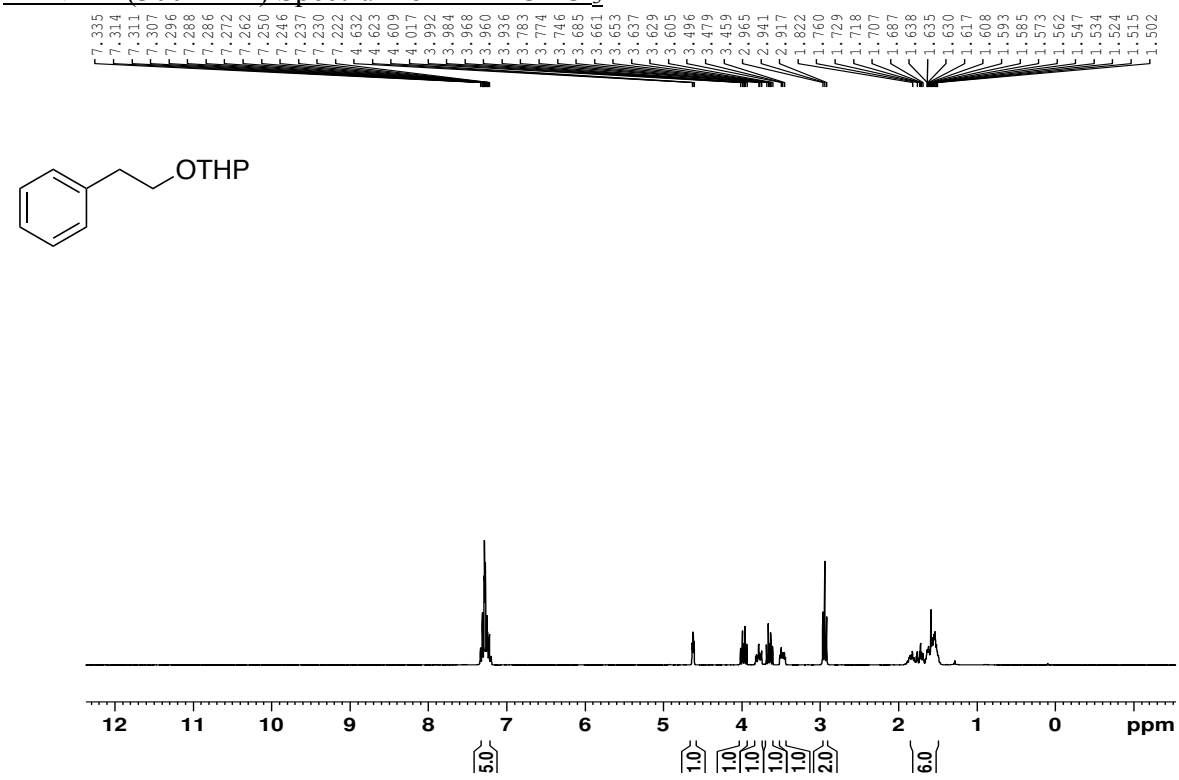
$^1$H NMR (300 MHz) Spectrum of **7f** in $CDCl_3$



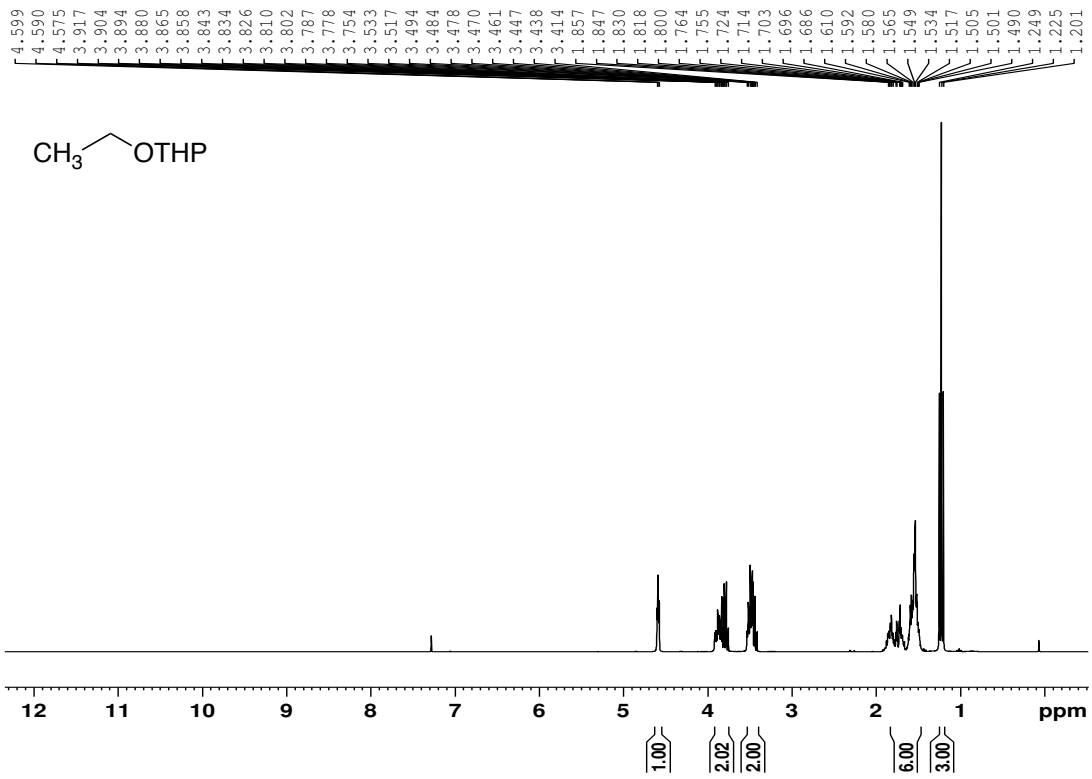

$^1$H NMR (300 MHz) Spectrum of **7g** in $CDCl_3$



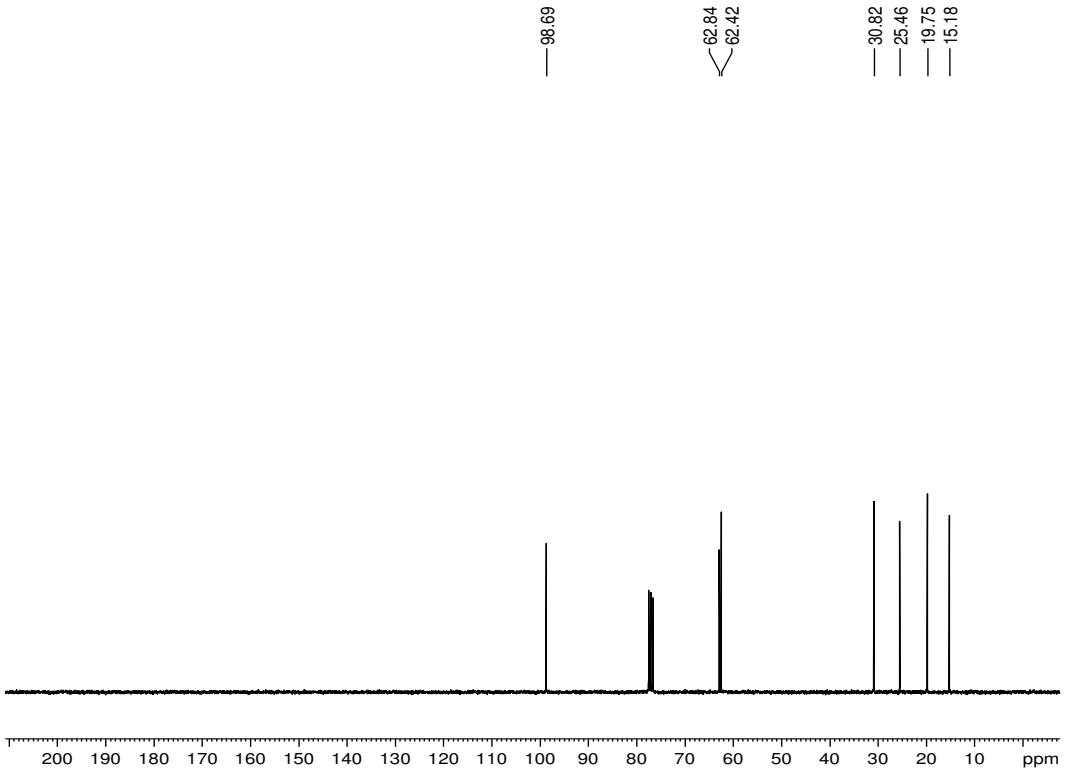
$^1$H NMR (300 MHz) Spectrum of **7h** in $CDCl_3$



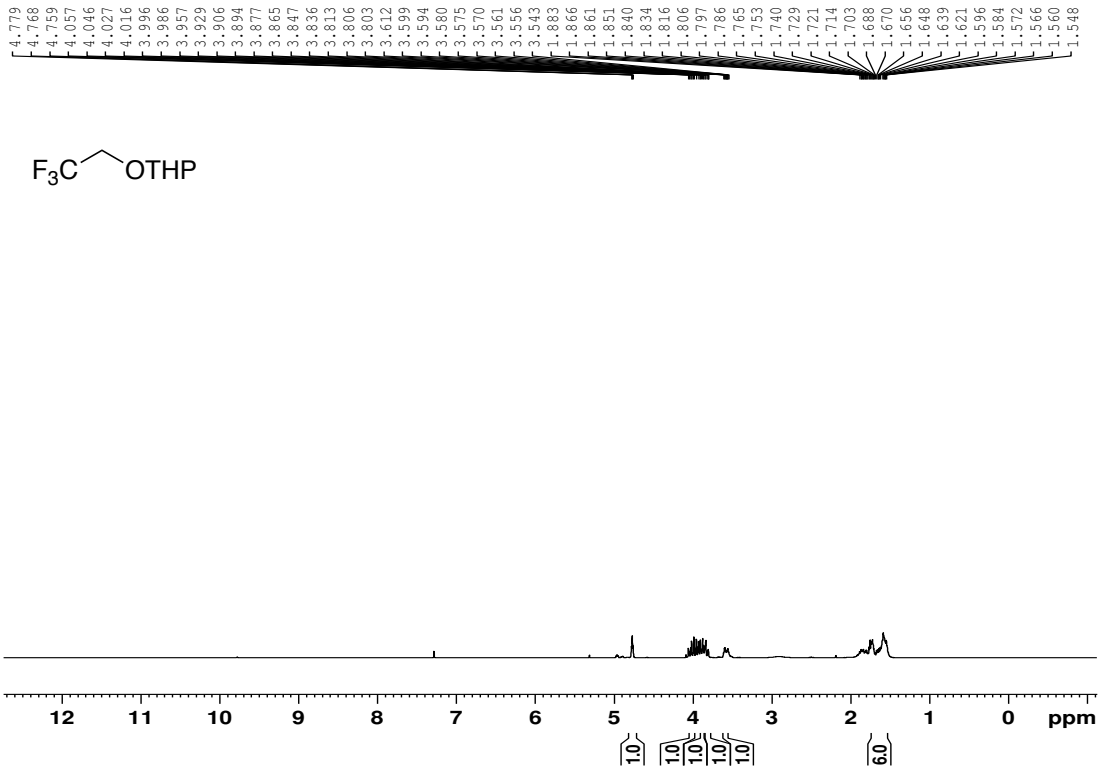

$^1$H NMR (300 MHz) Spectrum of **7i** in $CDCl_3$



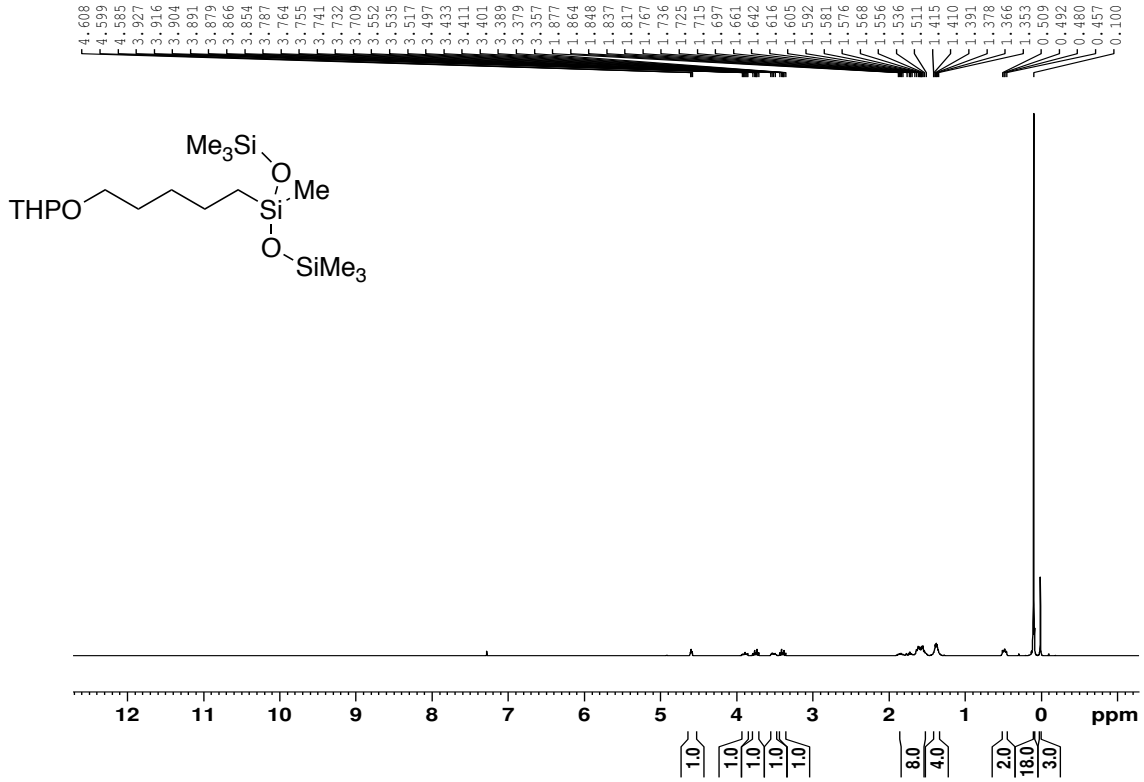
$^{13}C\{^{1}H\}$ NMR (75.5 MHz) Spectrum of **7i** in $CDCl_3$



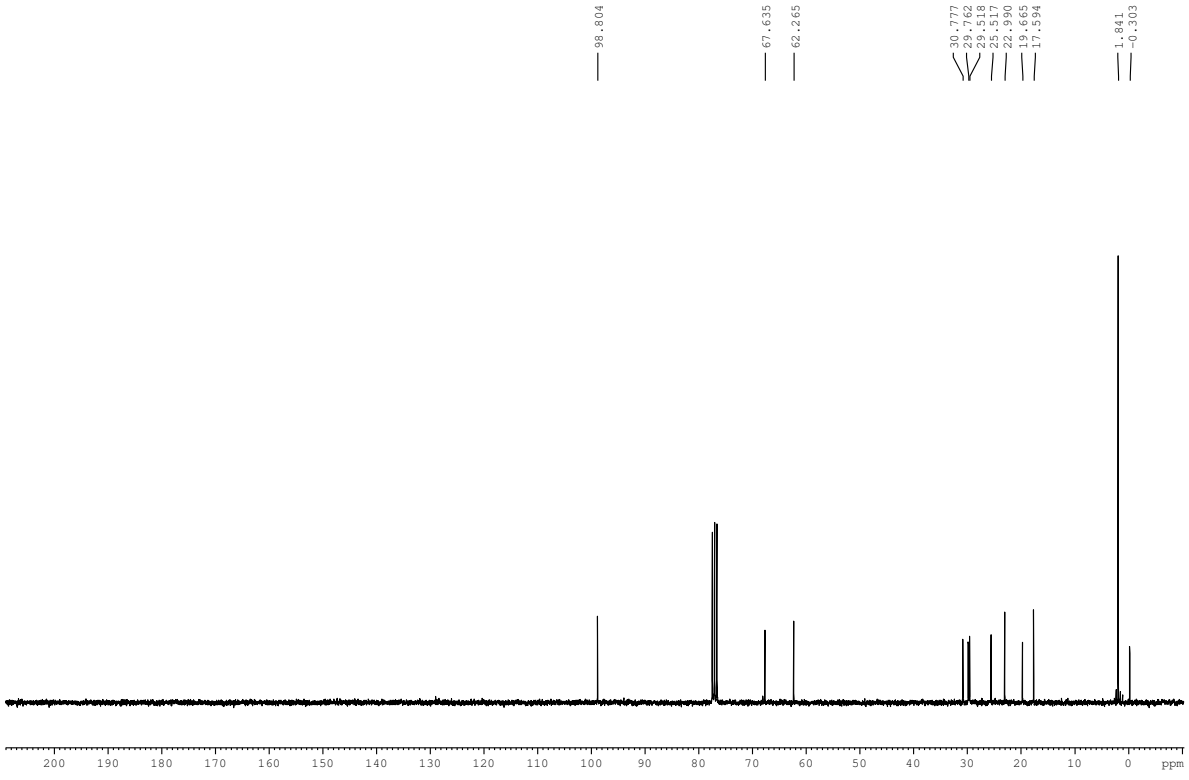

$^{1}H$ NMR (300 MHz) Spectrum of **7j** in $CDCl_3$



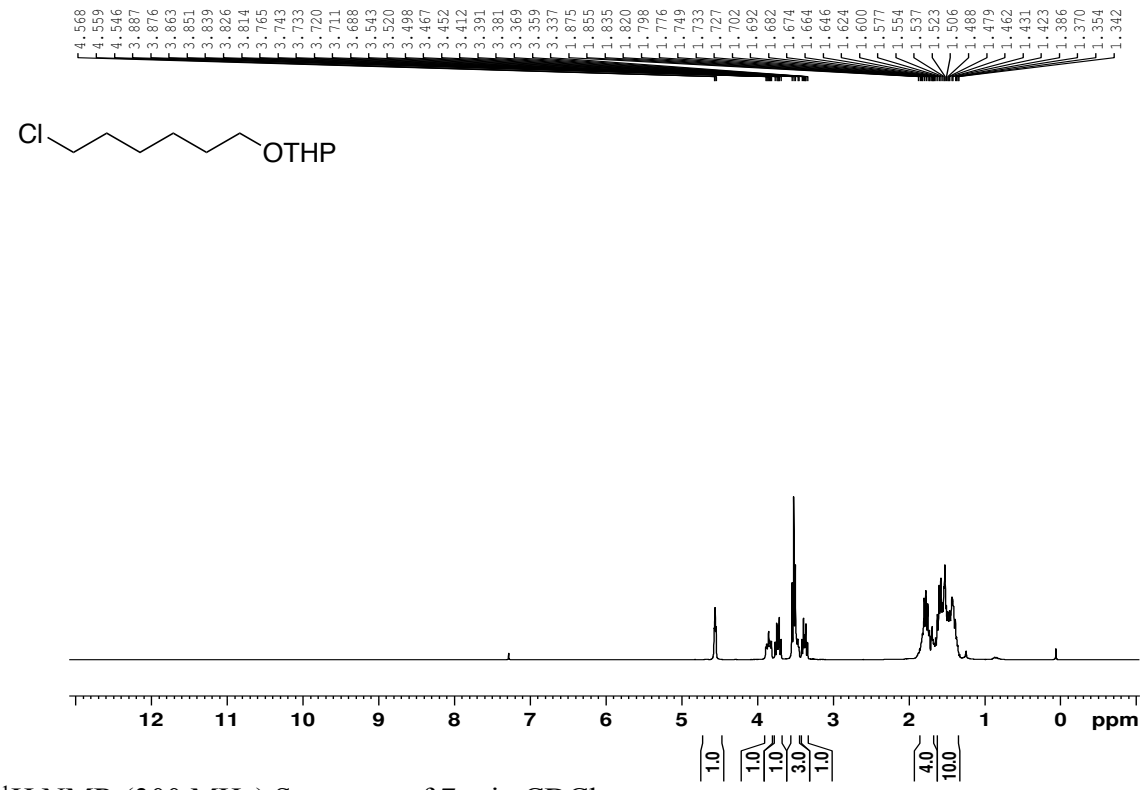
$^{1}$H NMR (300 MHz) Spectrum of **7k** in $CDCl_3$



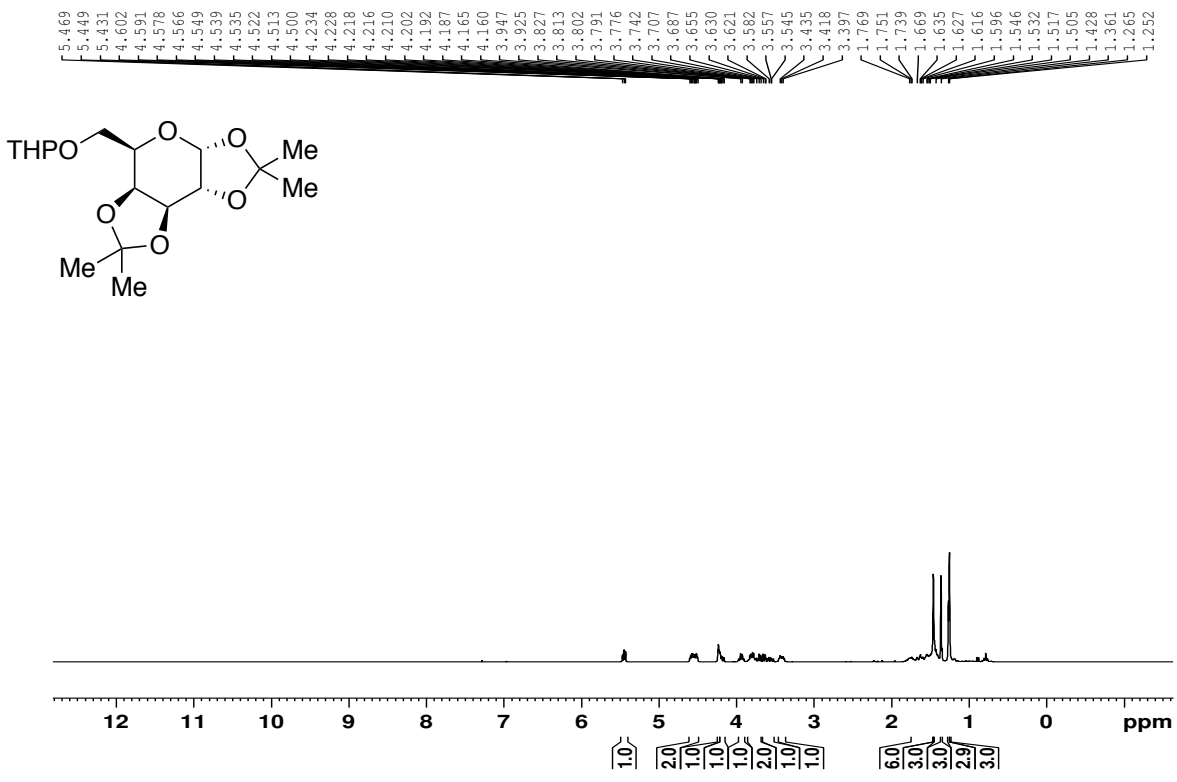

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **7k** in $CDCl_3$



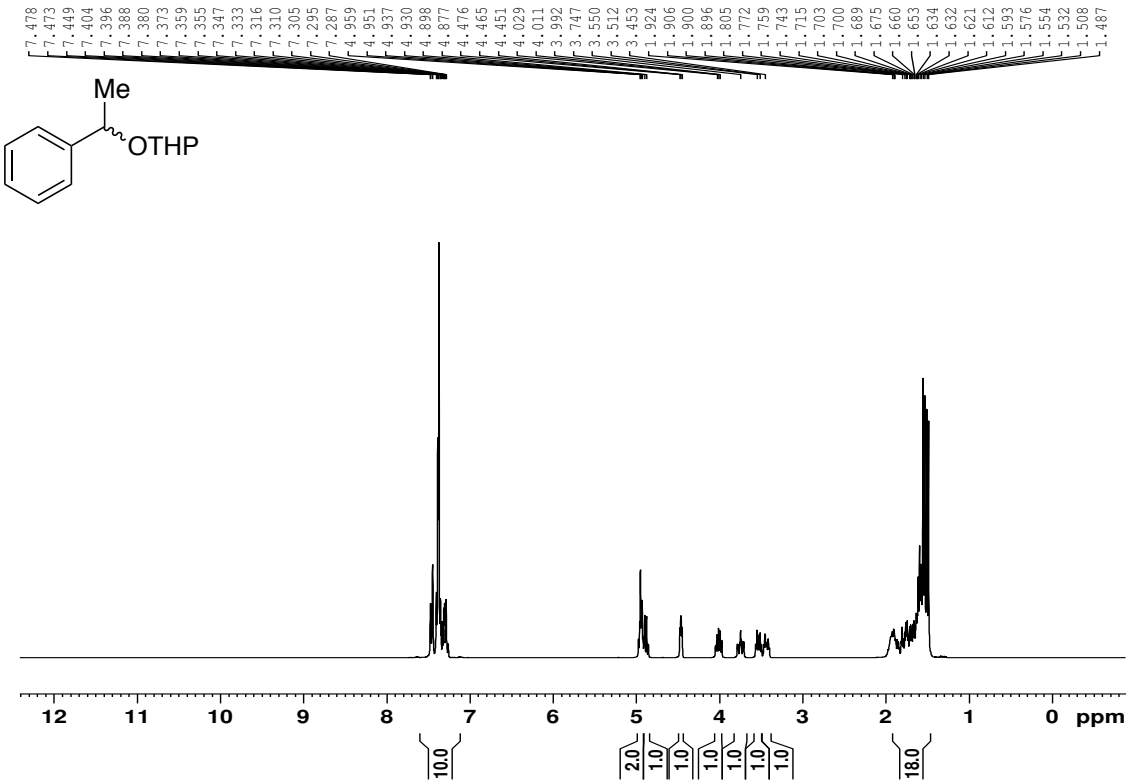
$^1$H NMR (300 MHz) Spectrum of **7l** in $CDCl_3$



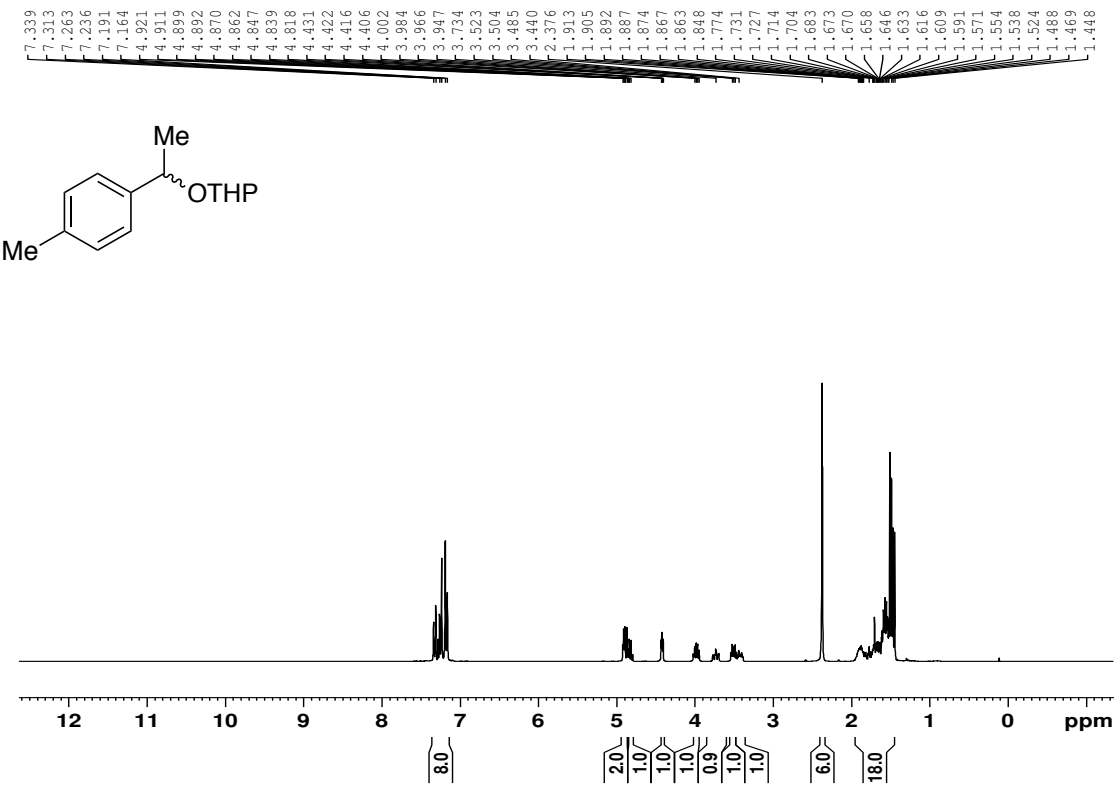

$^1$H NMR (300 MHz) Spectrum of **7m** in $CDCl_3$



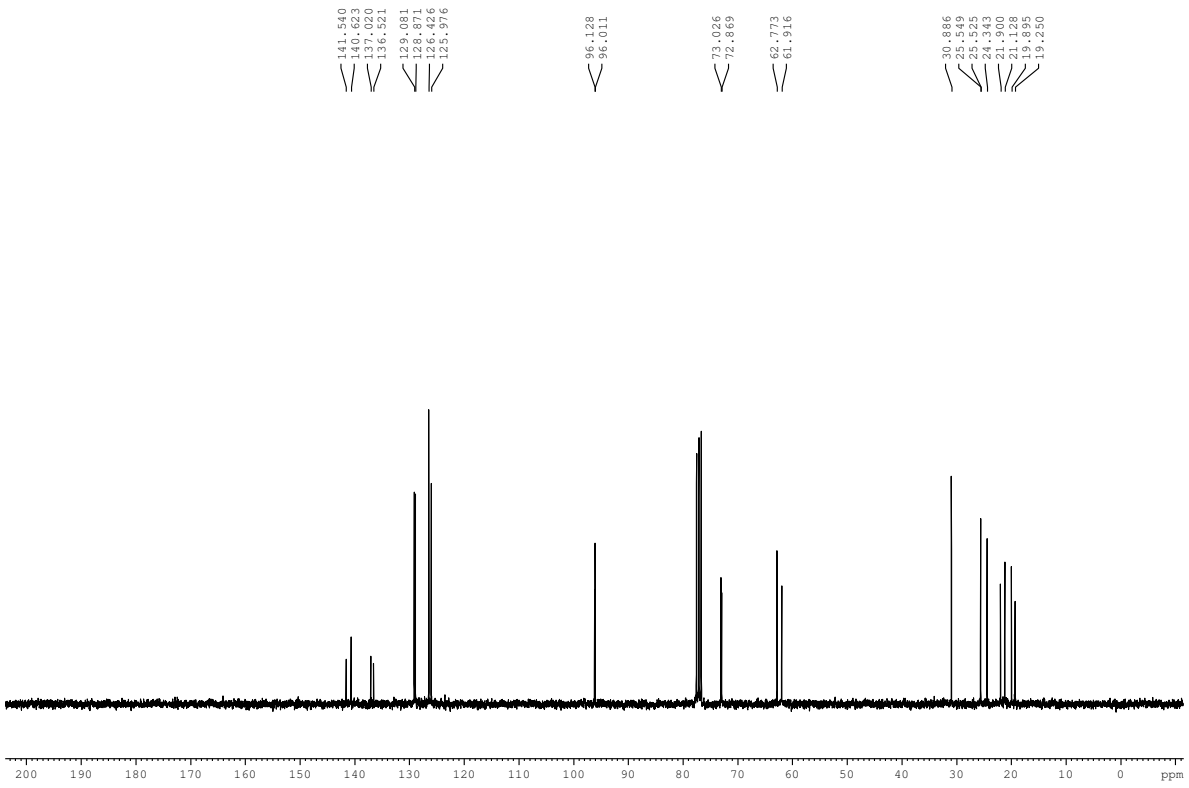
$^1$H NMR (300 MHz) Spectrum of **7n** in $CDCl_3$



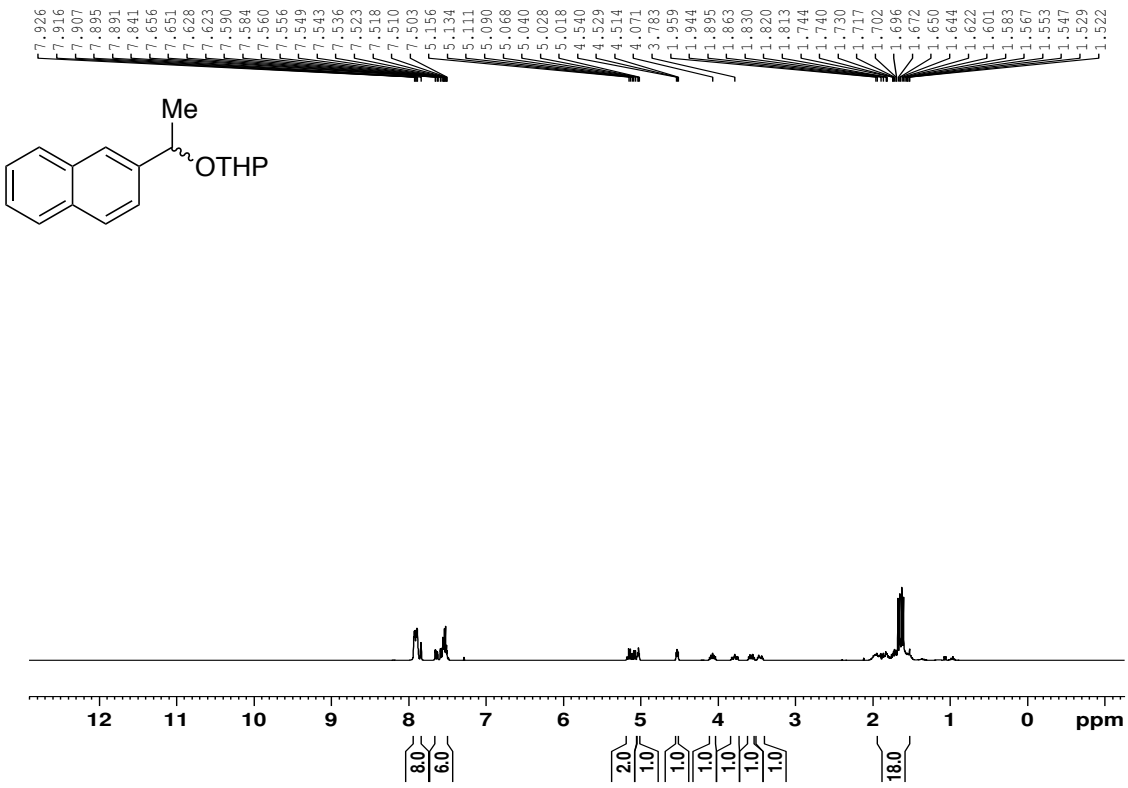

$^1$H NMR (300 MHz) Spectrum of **7o** in $CDCl_3$



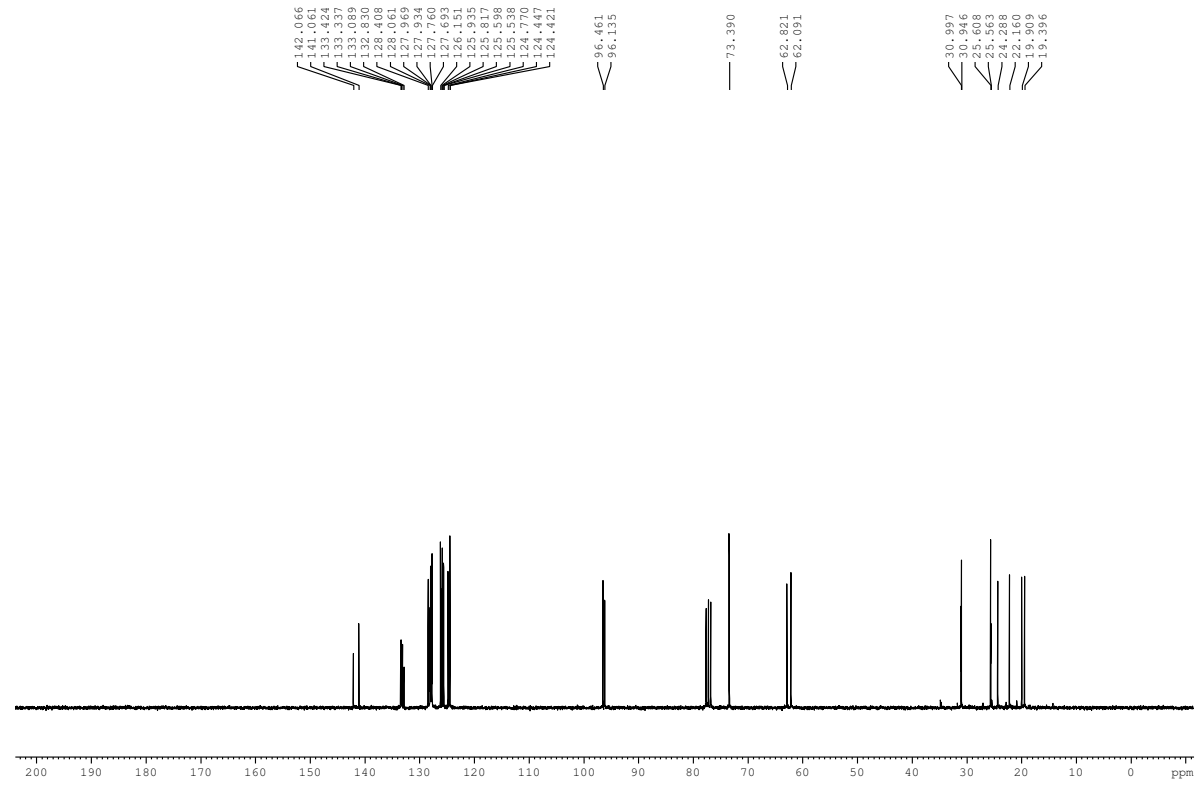
$^{13}C\{^{1}H\}$ NMR (75.5 MHz) Spectrum of **7o** in $CDCl_3$



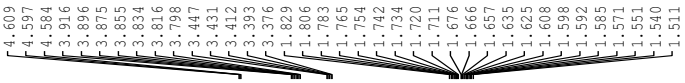

$^{1}H$ NMR (300 MHz) Spectrum of **7p** in $CDCl_3$

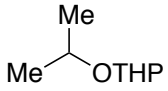


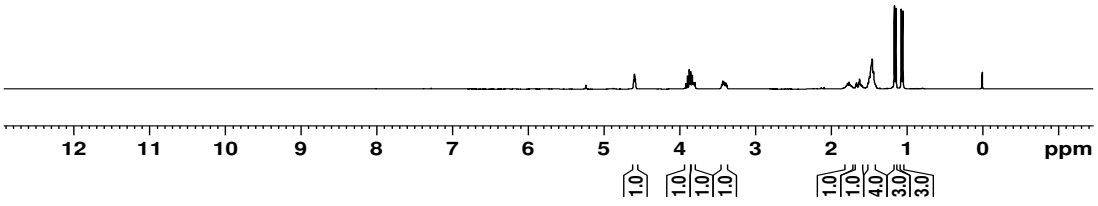
$^{13}C\{^{1}H\}$ NMR (75.5 MHz) Spectrum of **7p** in $CDCl_3$



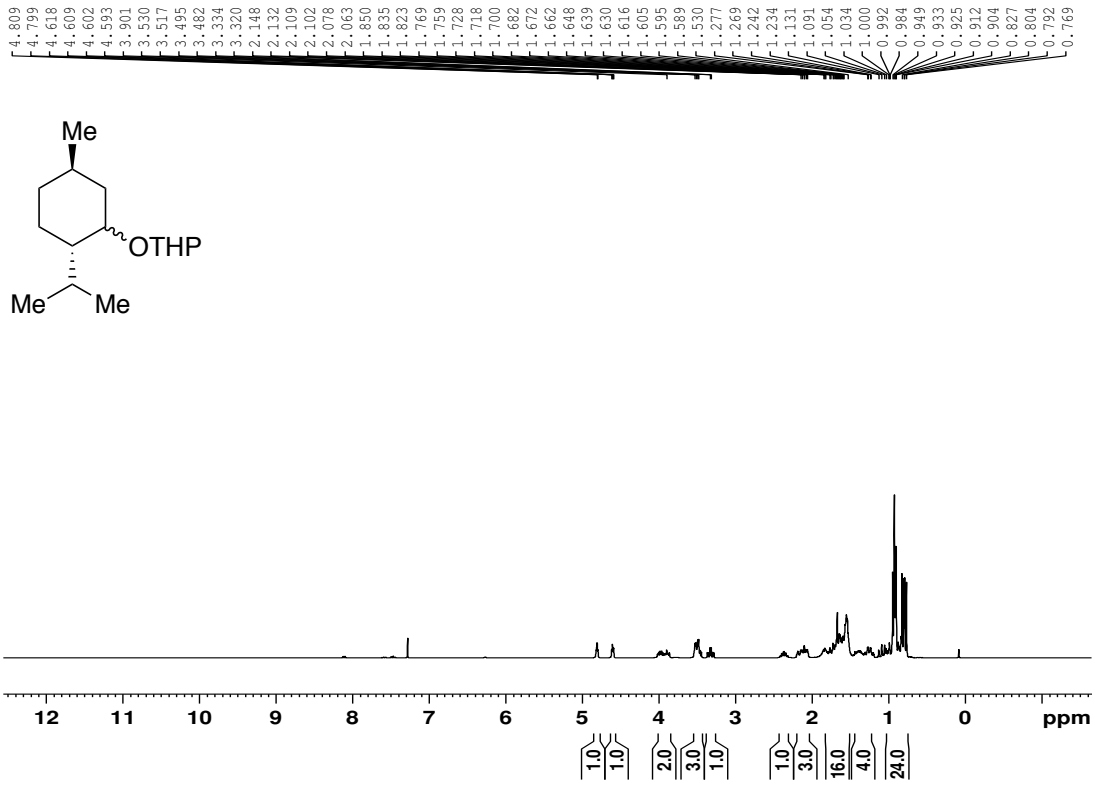

$^{1}H$ NMR (300 MHz) Spectrum of **7q** in $CDCl_3$



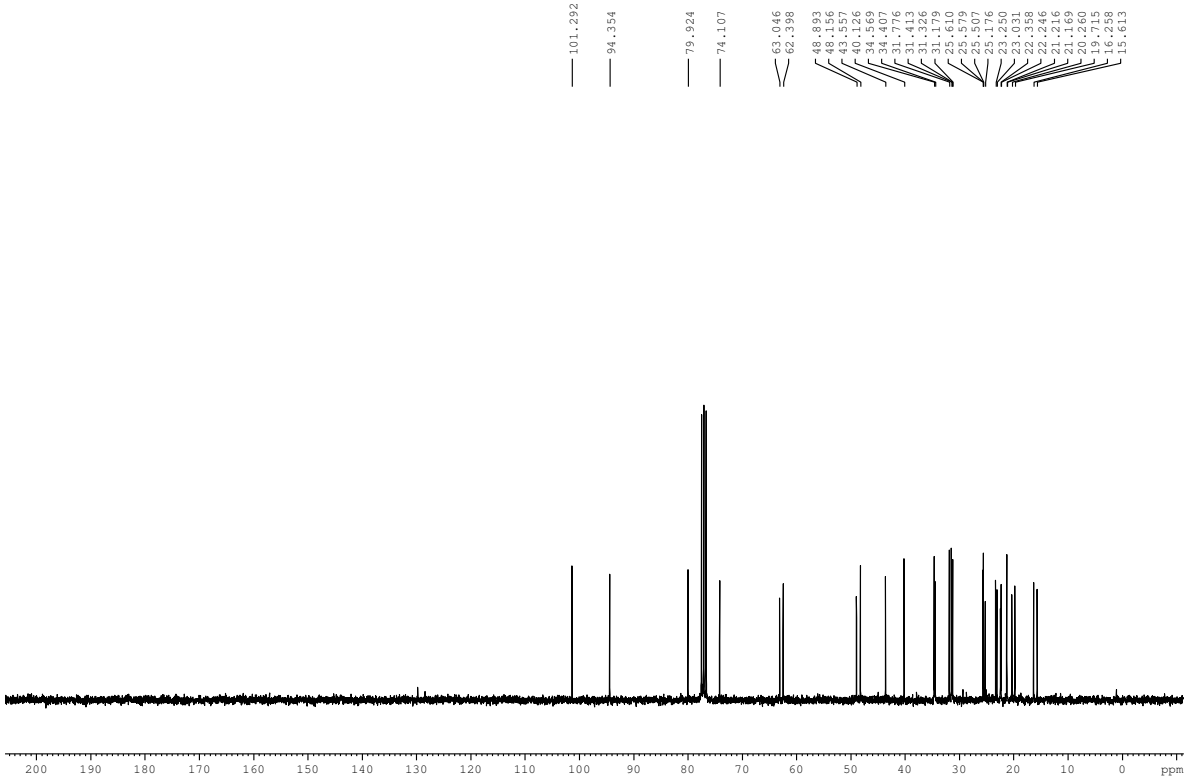



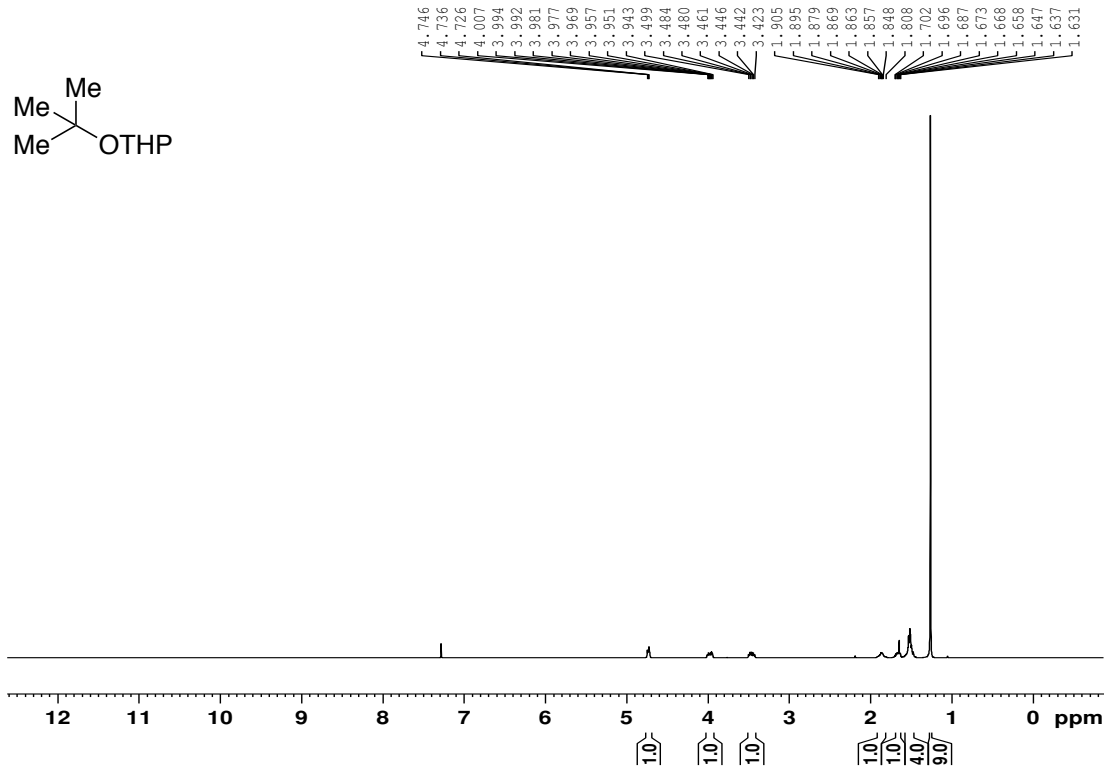
$^{1}$H NMR (300 MHz) Spectrum of **7r** in $CDCl_3$



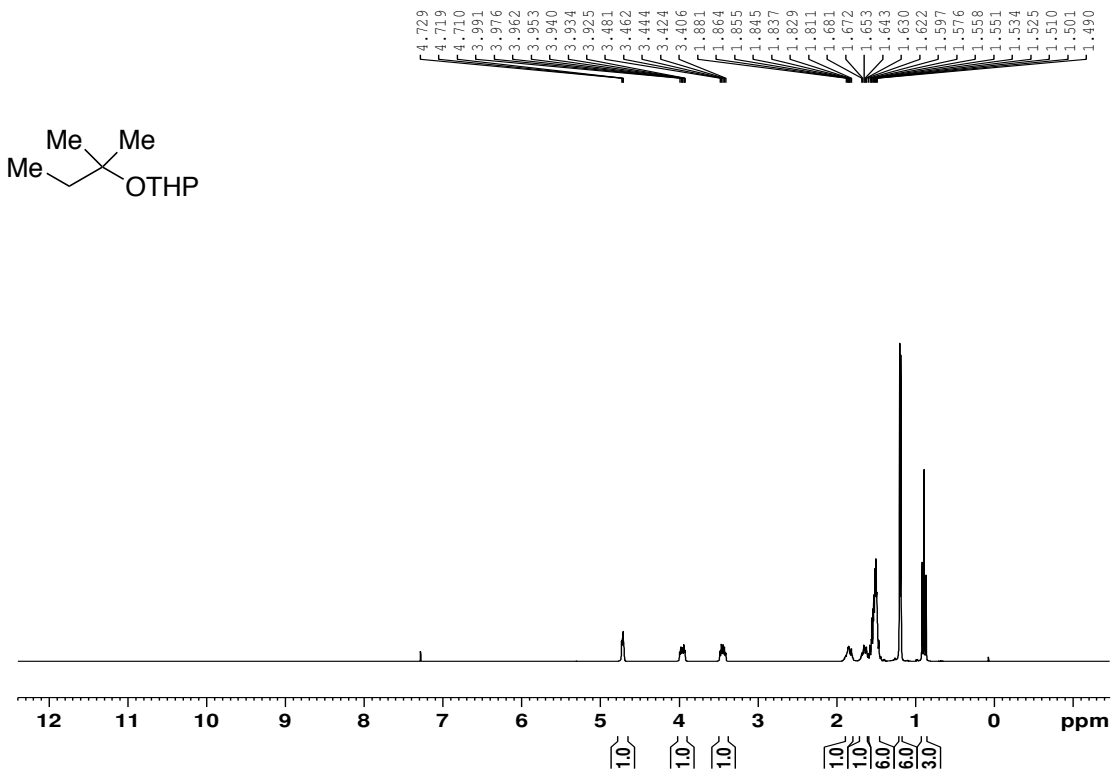

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **7r** in $CDCl_3$



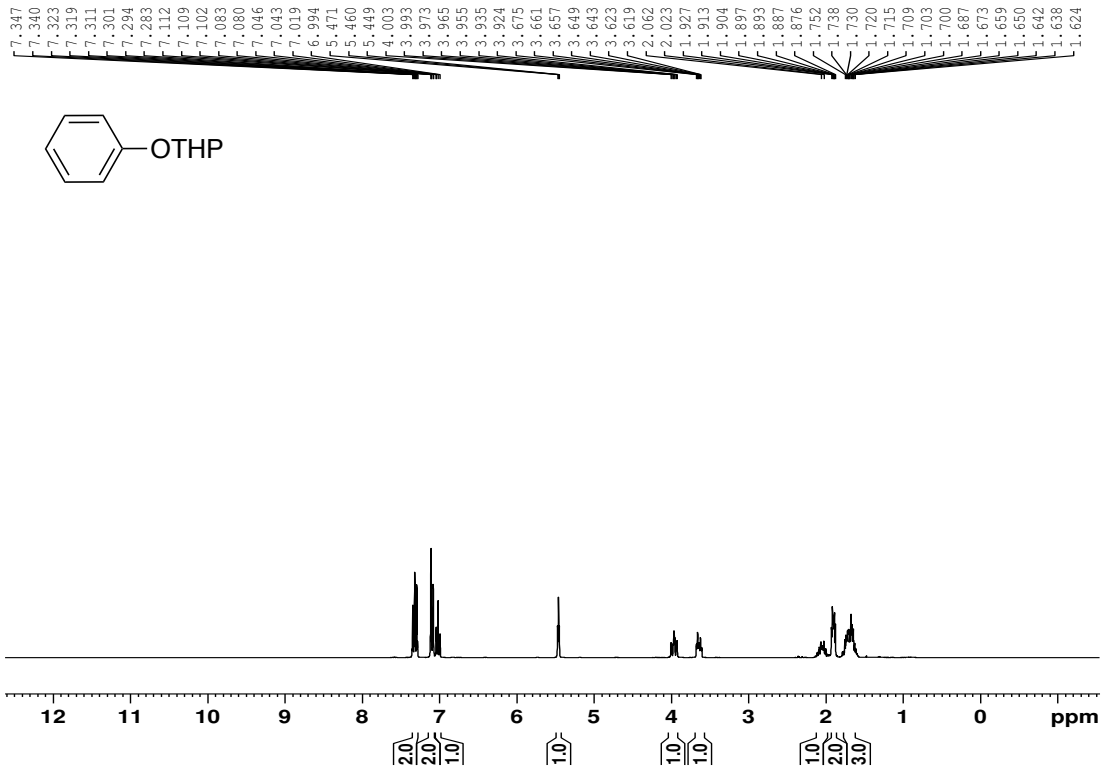
$^1$H NMR (300 MHz) Spectrum of **7s** in $CDCl_3$



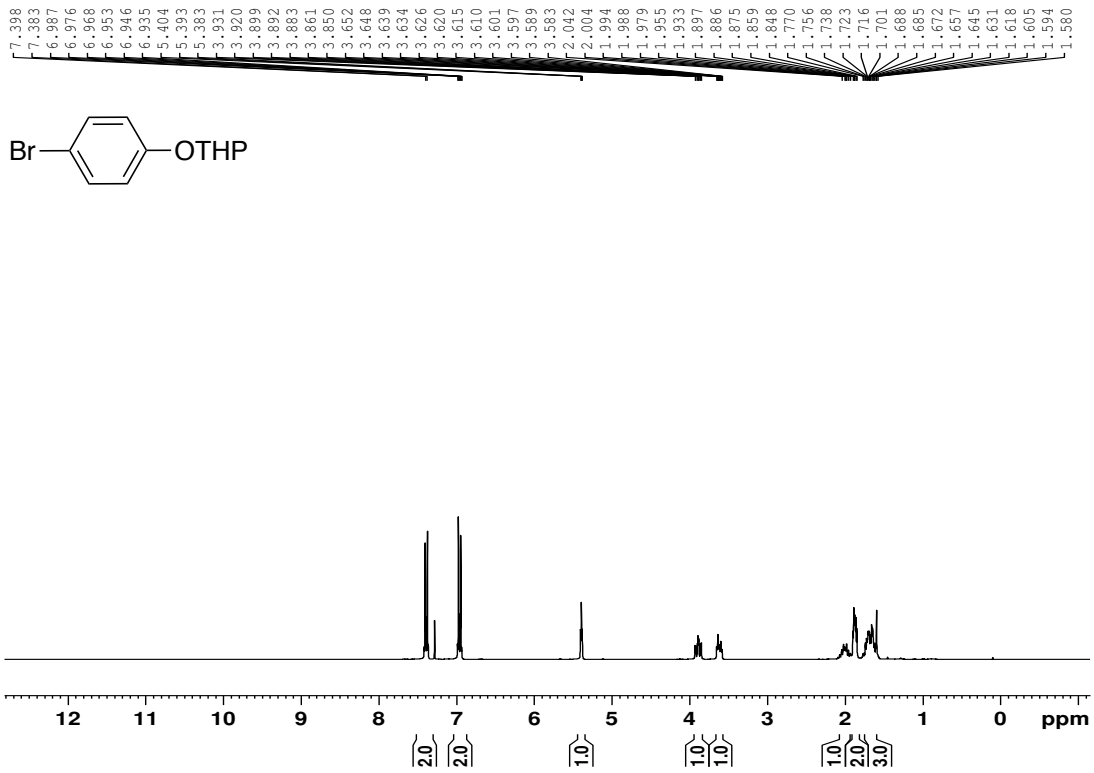

$^1$H NMR (300 MHz) Spectrum of **7t** in $CDCl_3$



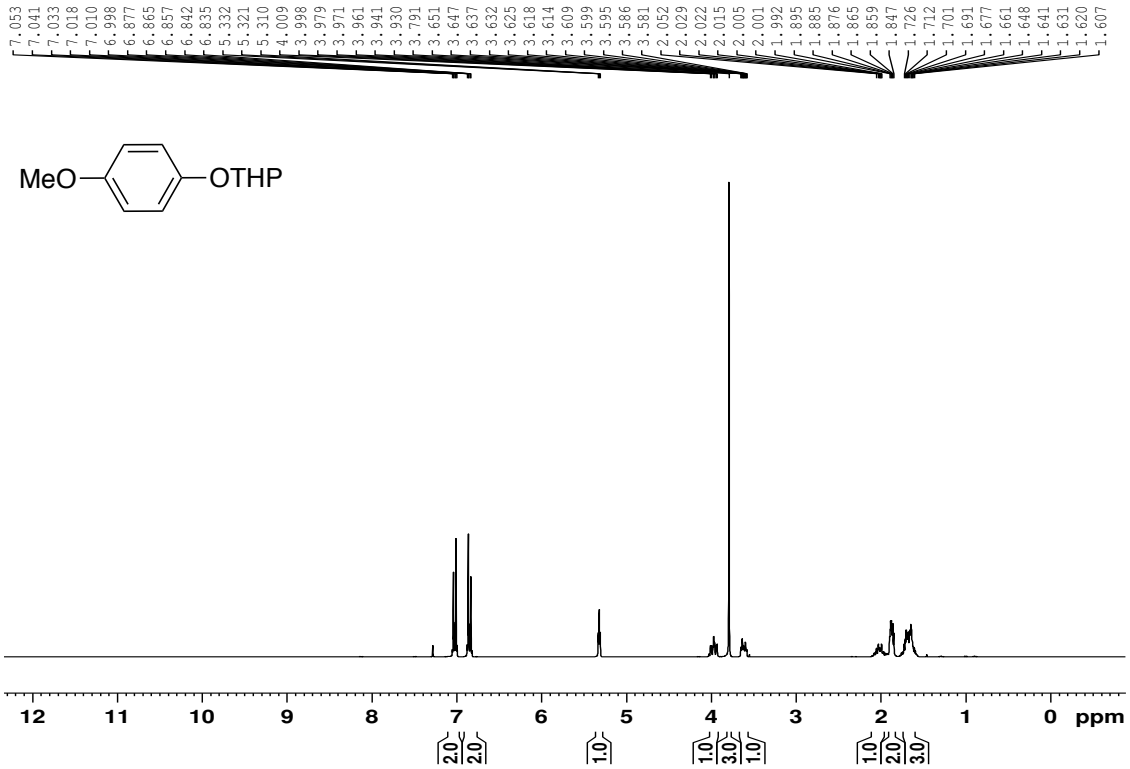
$^1$H NMR (300 MHz) Spectrum of **7u** in $CDCl_3$



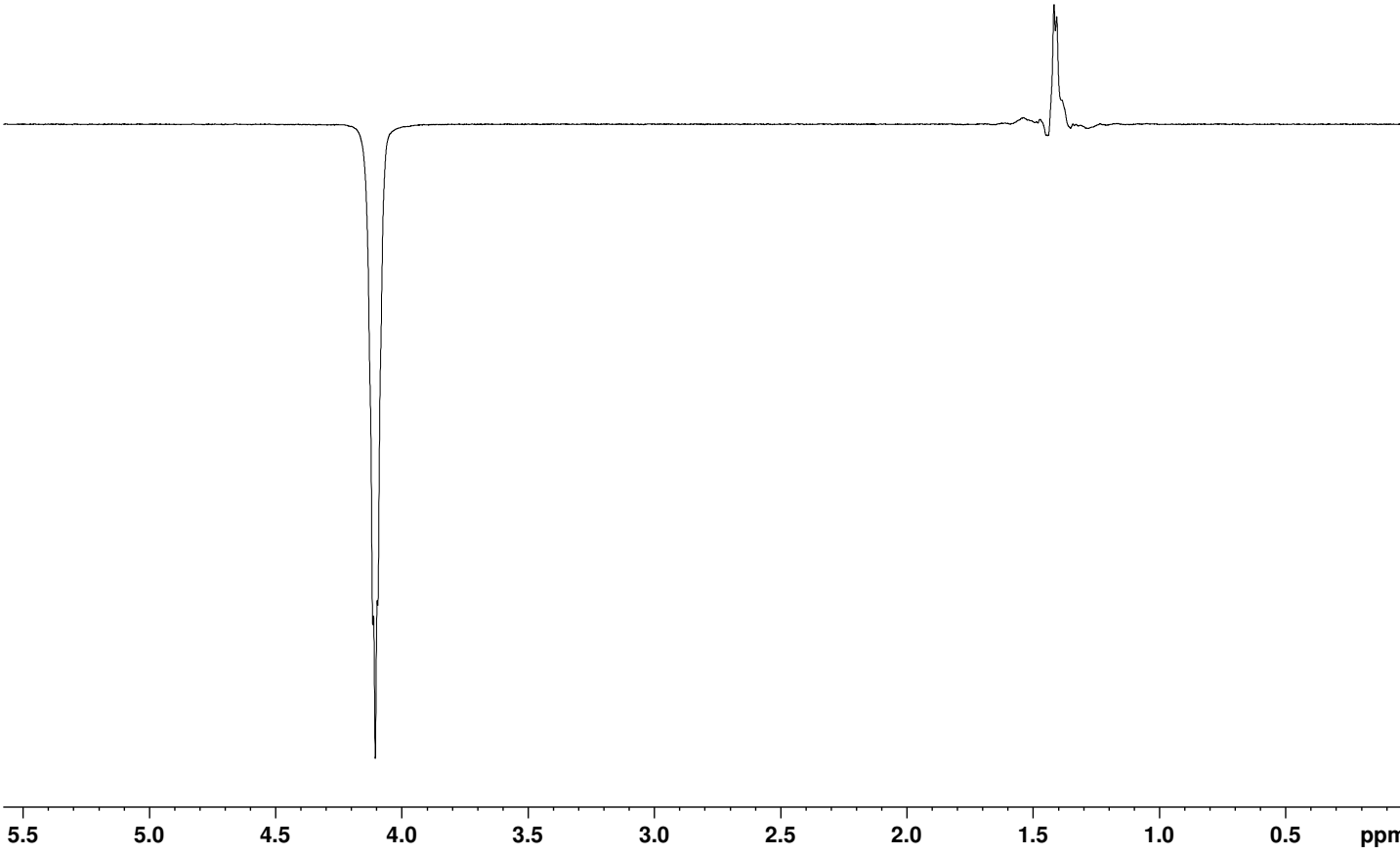

$^1$H NMR (300 MHz) Spectrum of **7v** in $CDCl_3$



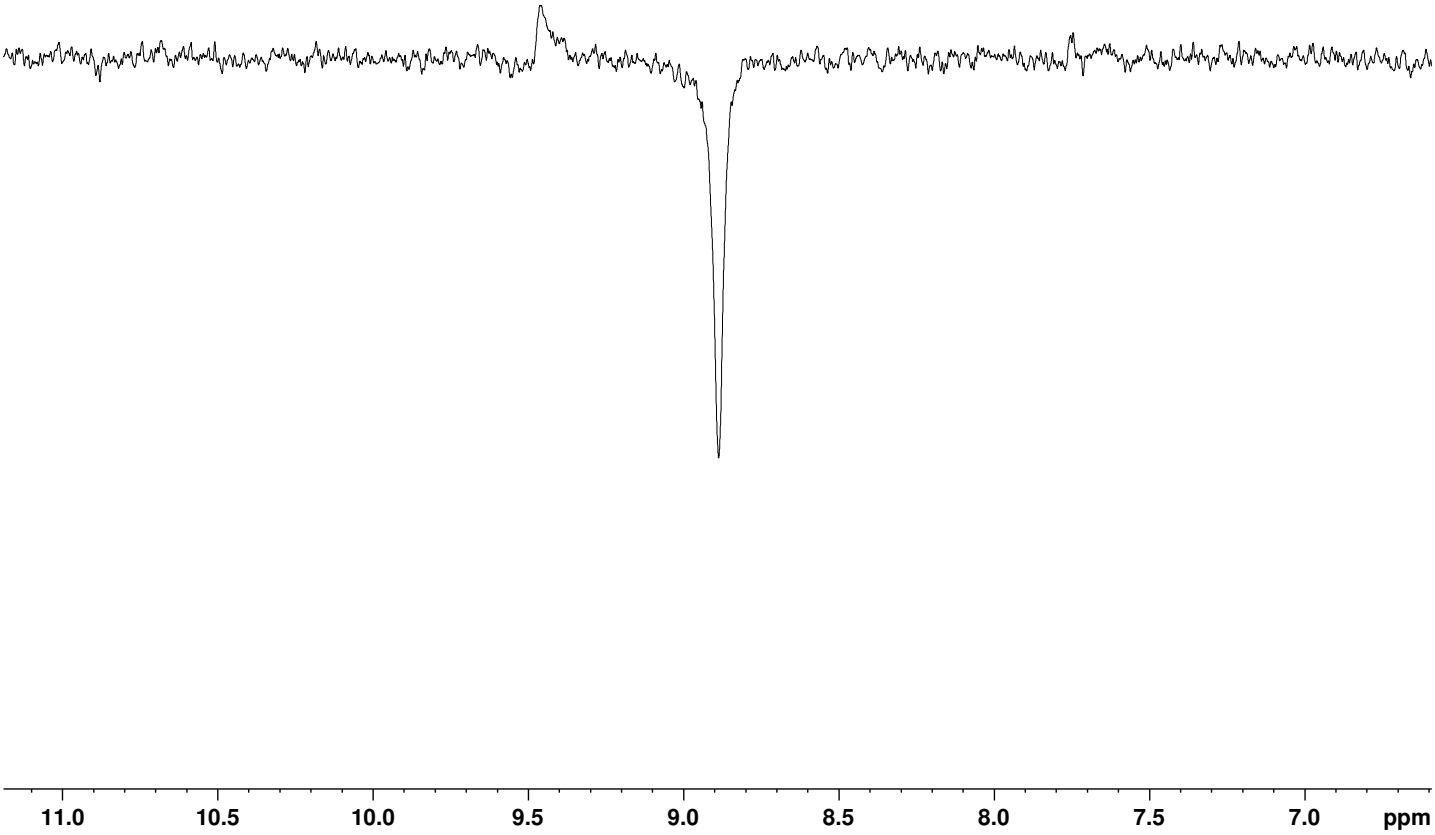
$^{1}$H NMR (300 MHz) Spectrum of **7w** in $CDCl_3$



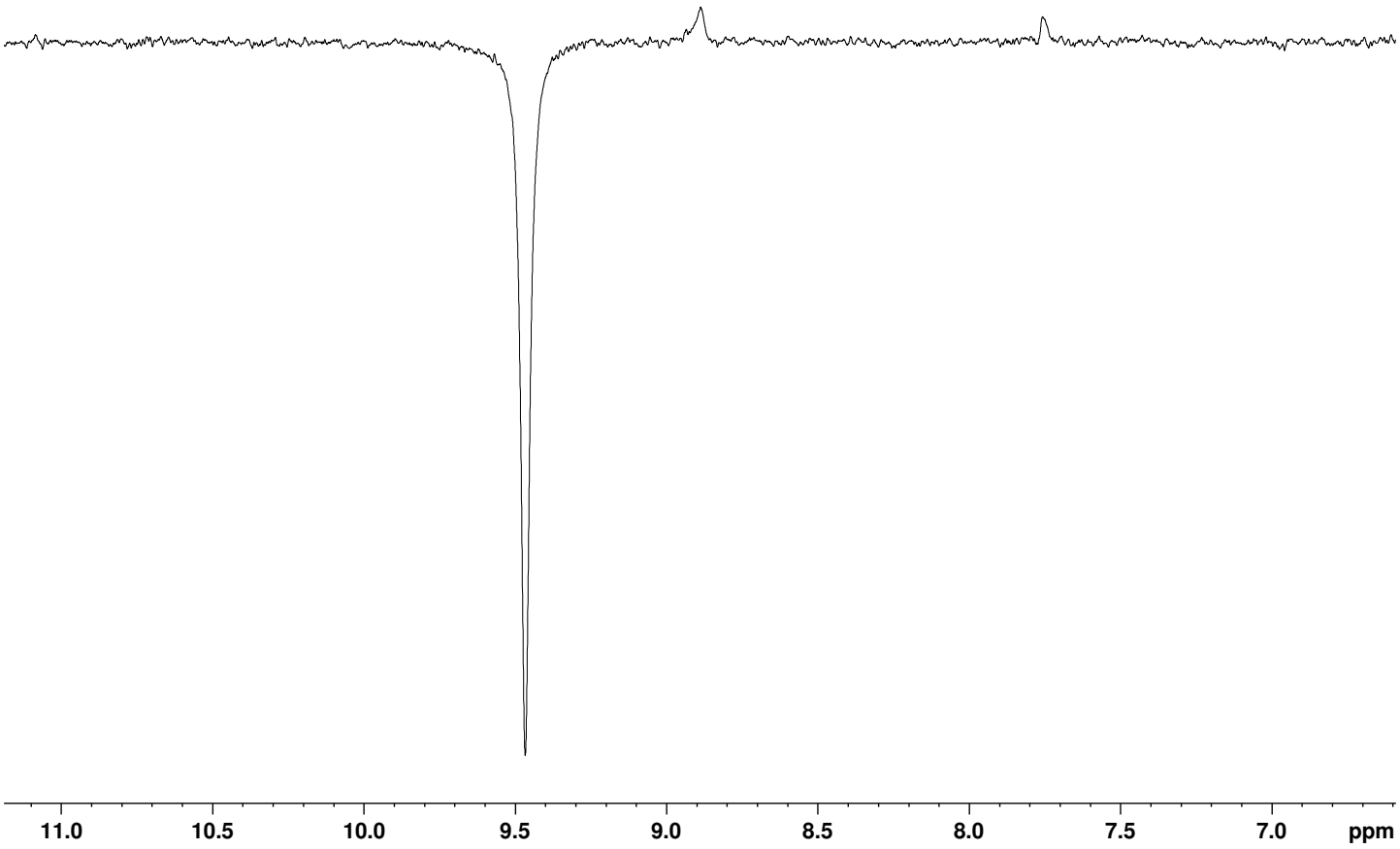
1D NOESY NMR Spectrum of Thiourea **4**·$BF_4^-$ with Irradiation at the Methine Signal (600 MHz, $CD_2Cl_2$, 297.8 K)



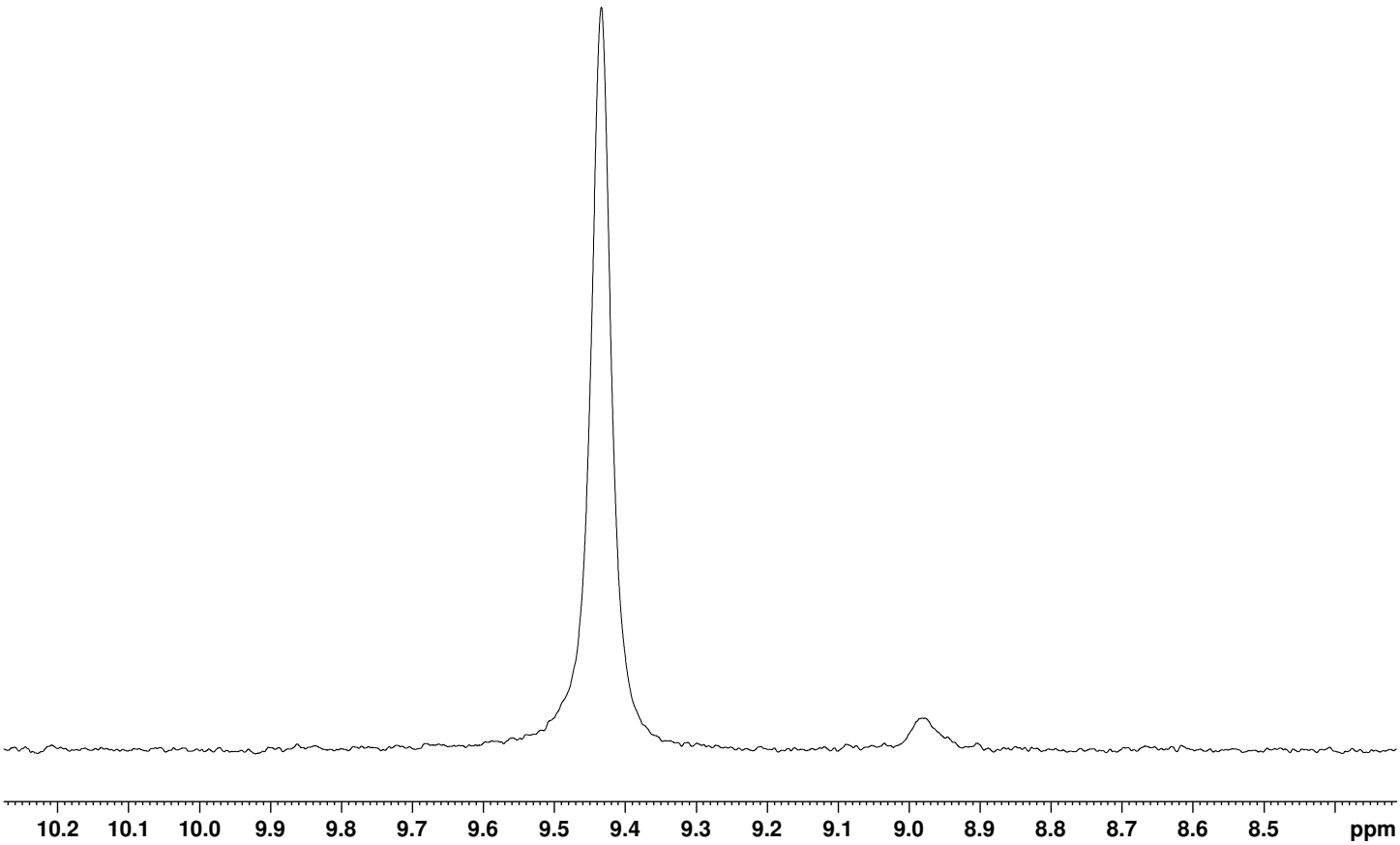
1D NOESY NMR Spectrum of Thiourea **4**·$BF_4^-$ with Irradiation at the N(3)–H Signal (600 MHz, $CD_2Cl_2$, 297.8 K)



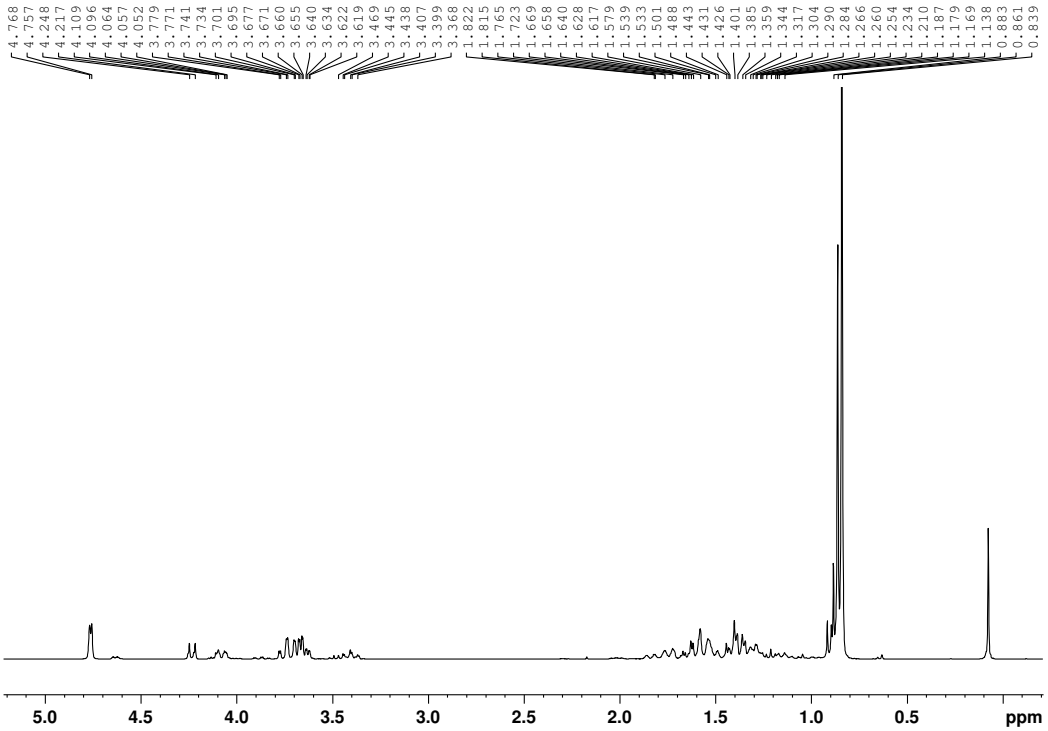
1D NOESY NMR Spectrum of Thiourea **4**·$BF_4^-$ with Irradiation at the N(4)–H Signal (600 MHz, $CD_2Cl_2$, 297.8 K)



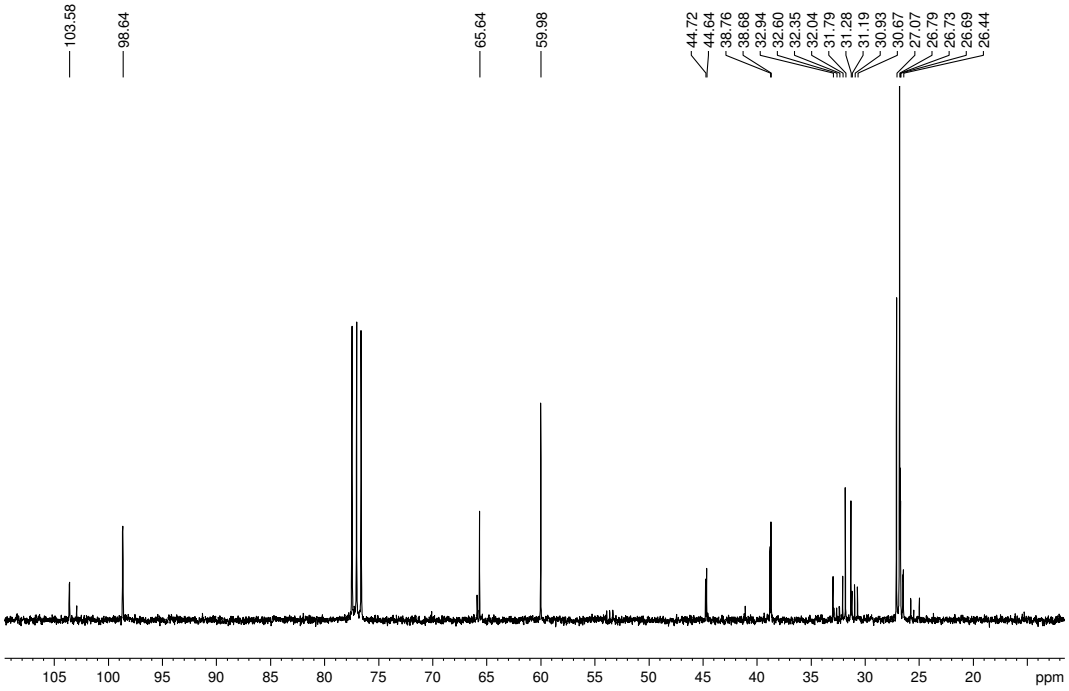
1D NOESY NMR Spectrum of Thiourea **4**·$BF_4^-$ with Irradiation at the N(4)–H Signal (600 MHz, $CD_2Cl_2$, 193.0 K)



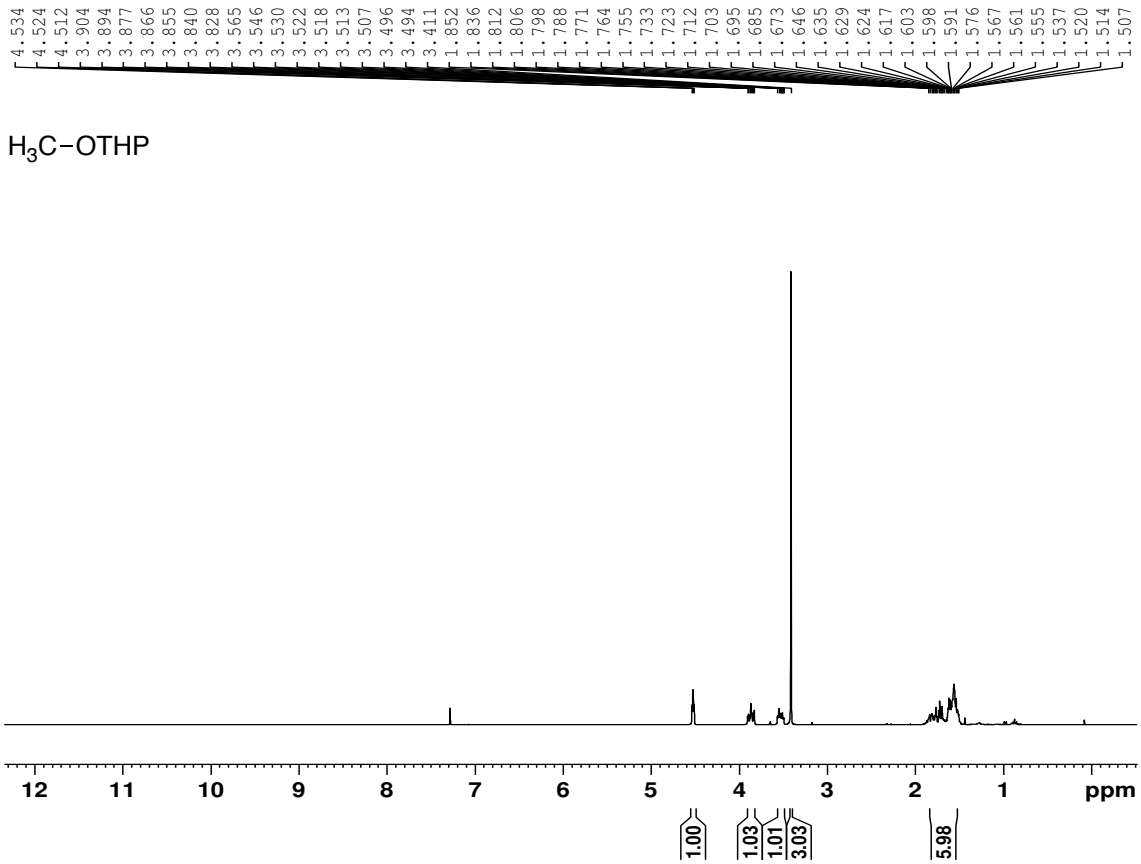
$^{1}$H NMR (300 MHz) Spectrum of Deuterated Mixture - *syn* and *anti* Product Isomers (**87**, **87'**, **88**) in $CDCl_3$



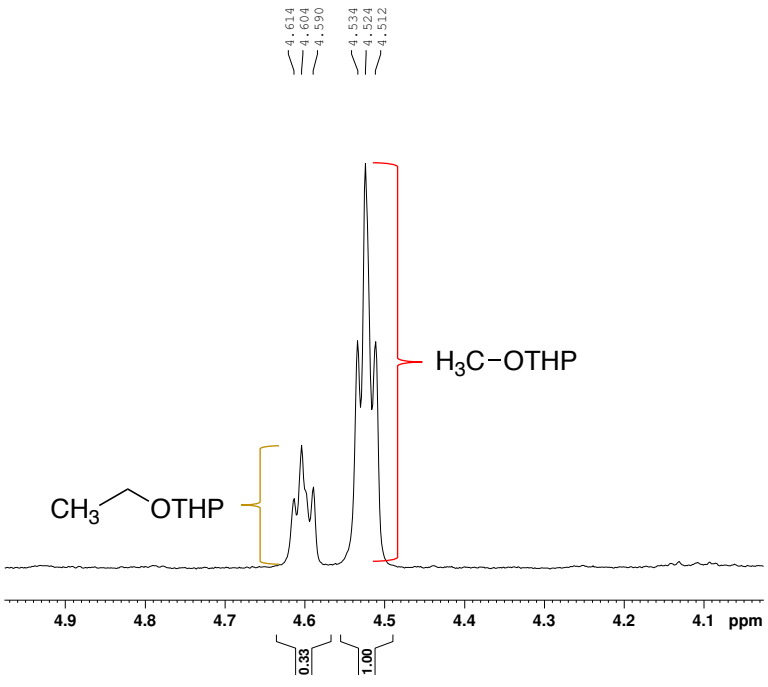

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of a Deuterated Mixture - *syn* and *anti* Product Isomers (**87**, **87'**, **88**) in $CDCl_3$



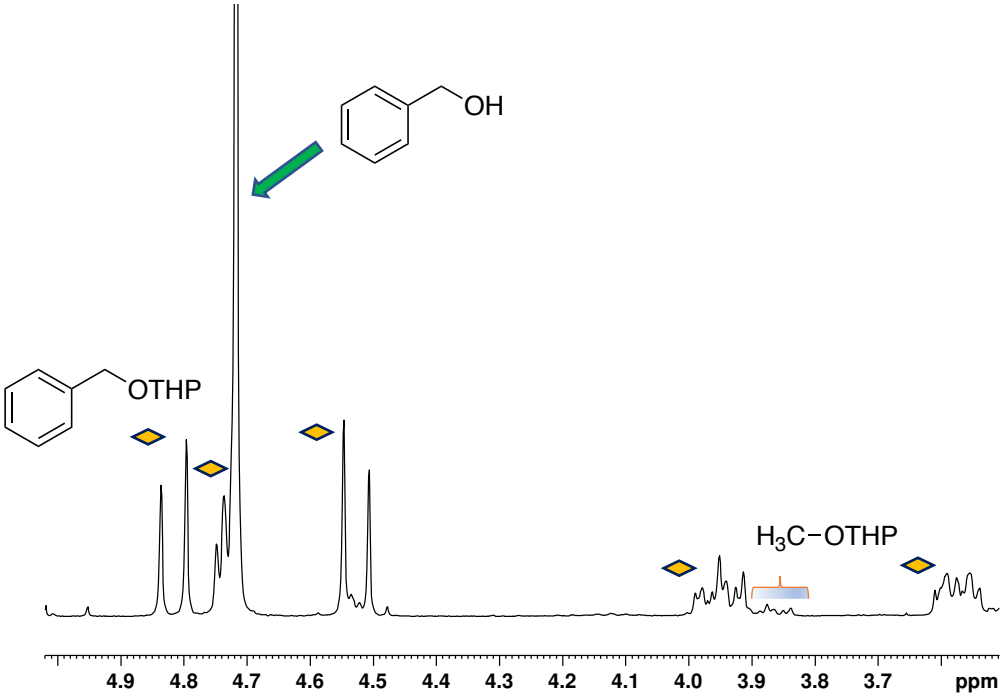
$^1$H NMR (300 MHz) Spectrum of **99** in $CDCl_3$



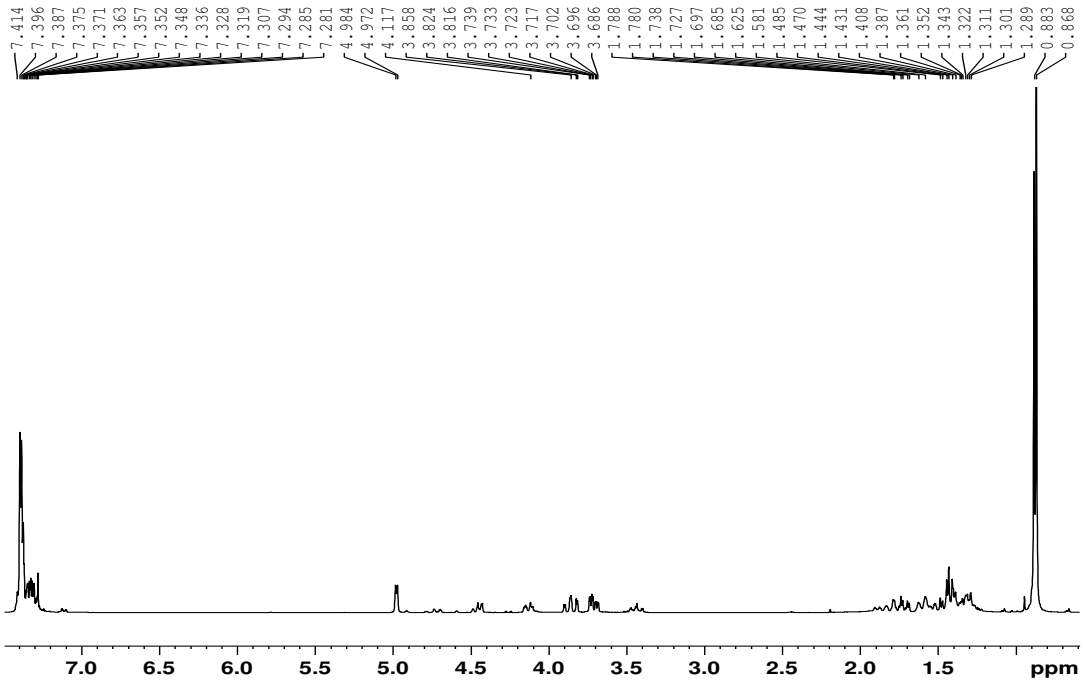

$^1$H NMR Spectrum of **99** and **7i** (3:1)



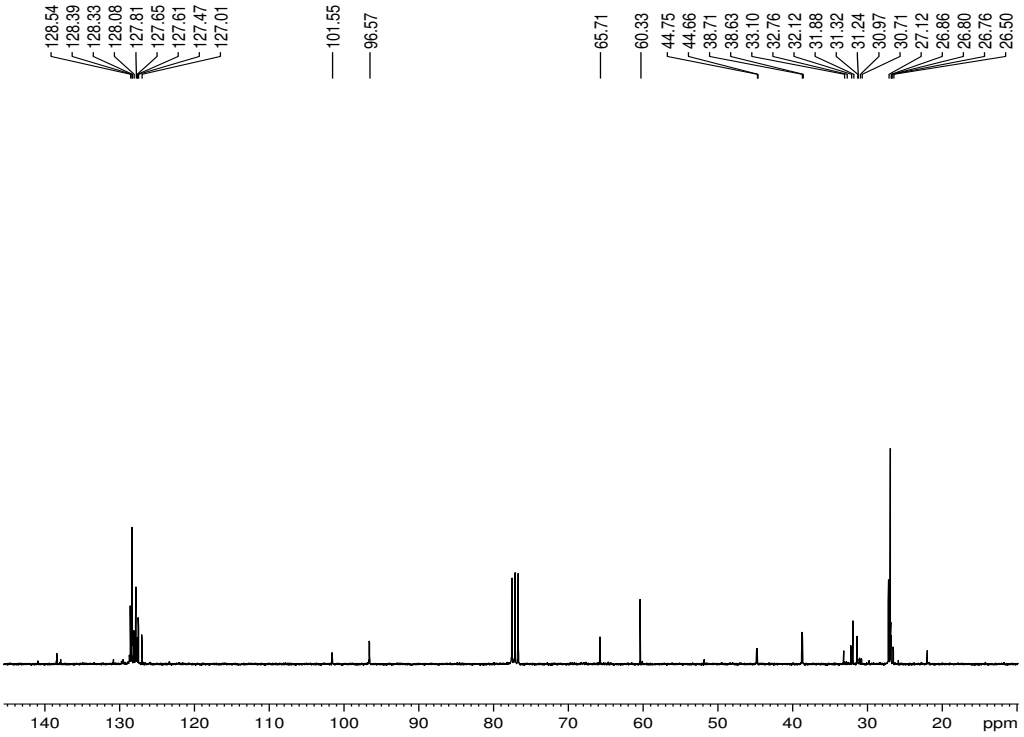
$^{1}$H NMR (300 MHz) Spectrum of **99** (Minor), **5a**, and **7a** (Major) in $CDCl_3$



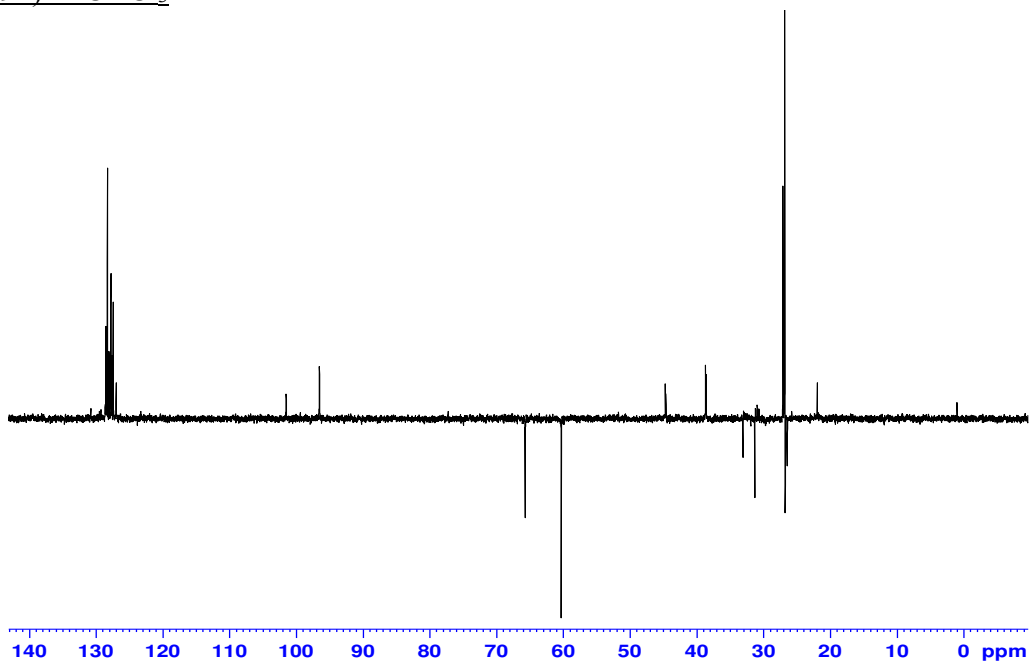

$^{1}$H NMR (300 MHz) Spectrum of Deuterated Mixture - *syn* and *anti* Product Isomers (**90**, **90'**, **91**) in $CDCl_3$



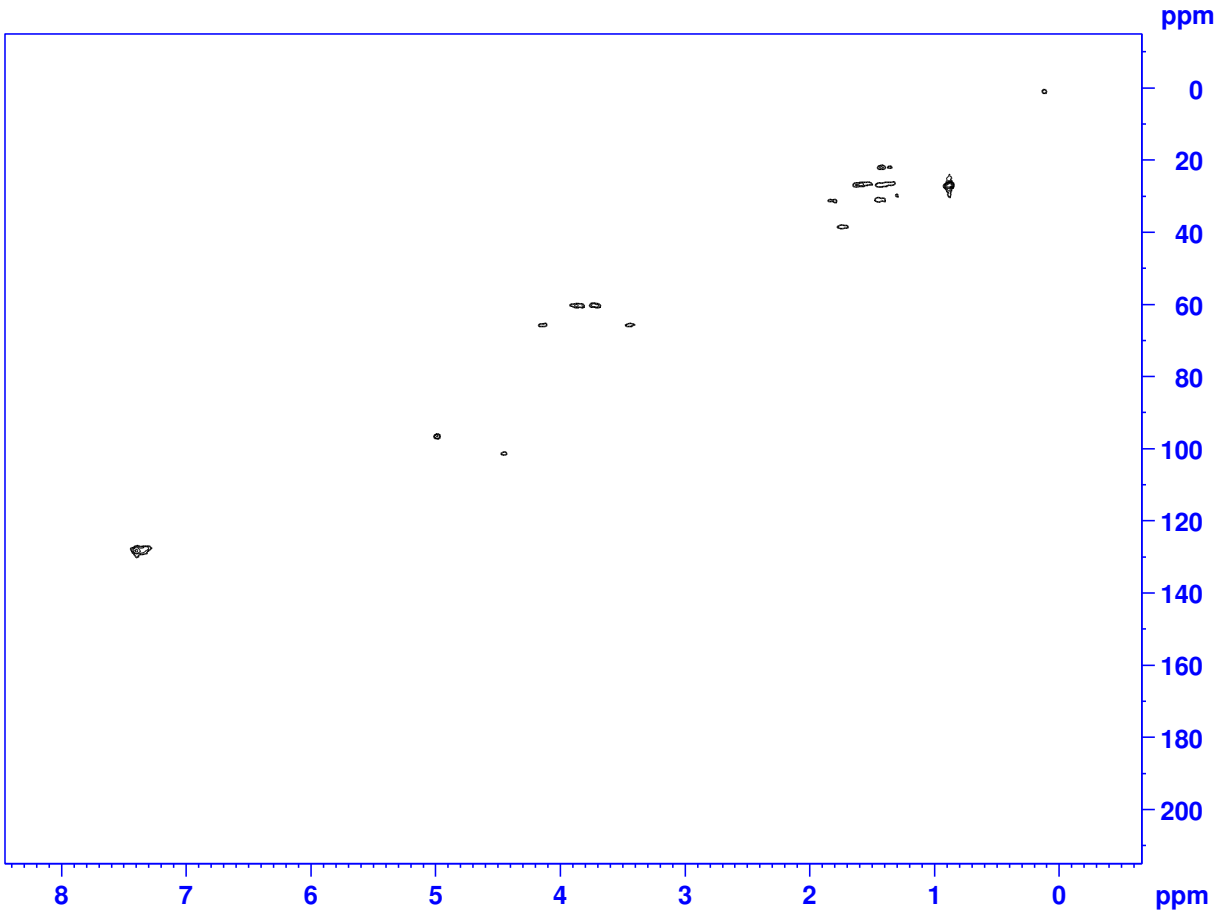
$^{13}C\{^{1}H\}$ NMR (75.5 MHz) Spectrum of Deuterated Mixture - *syn* and *anti* Product Isomers (**90**, **90'**, **91**) in $CDCl_3$



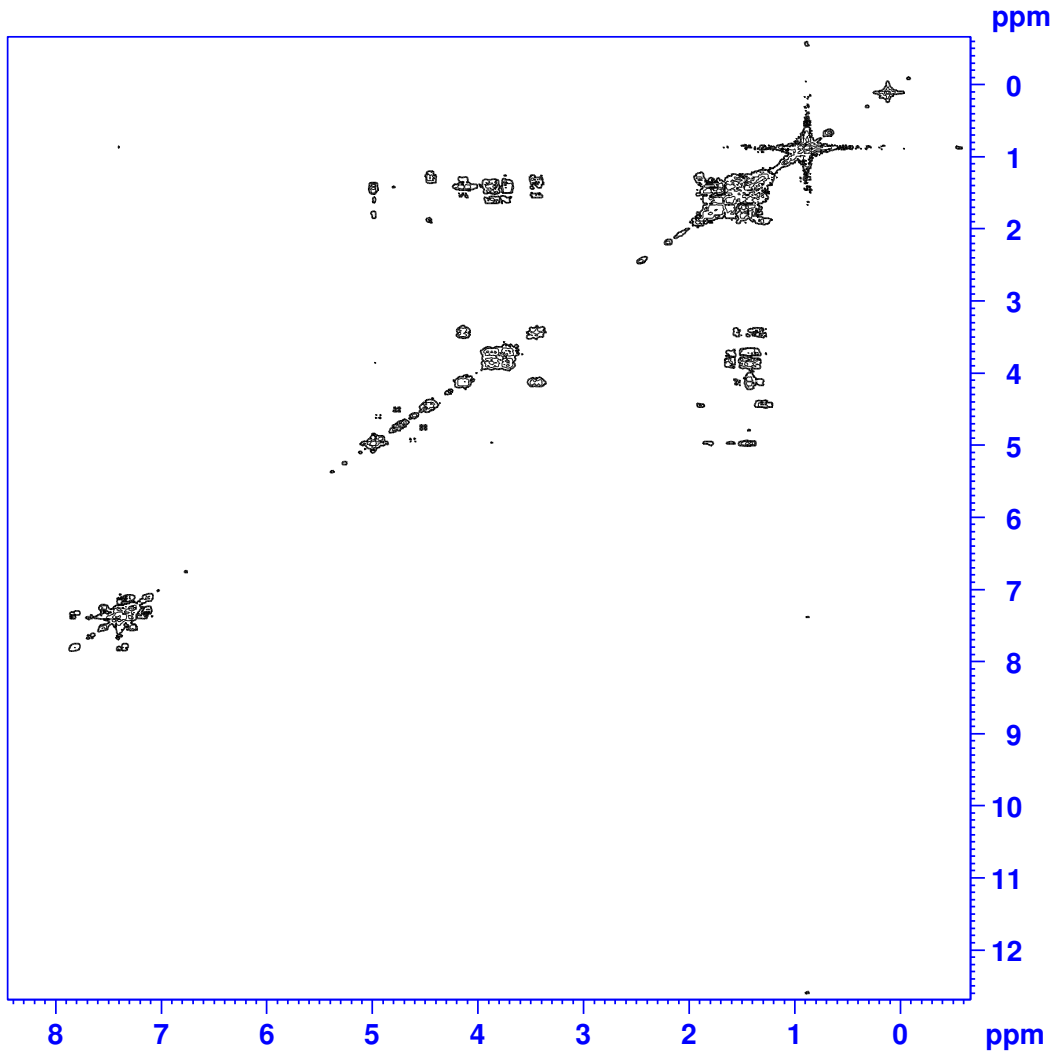

DEPT-135 NMR Spectrum of Deuterated Mixture - *syn* and *anti* Product Isomers (**90**, **90'**, **91**) in $CDCl_3$



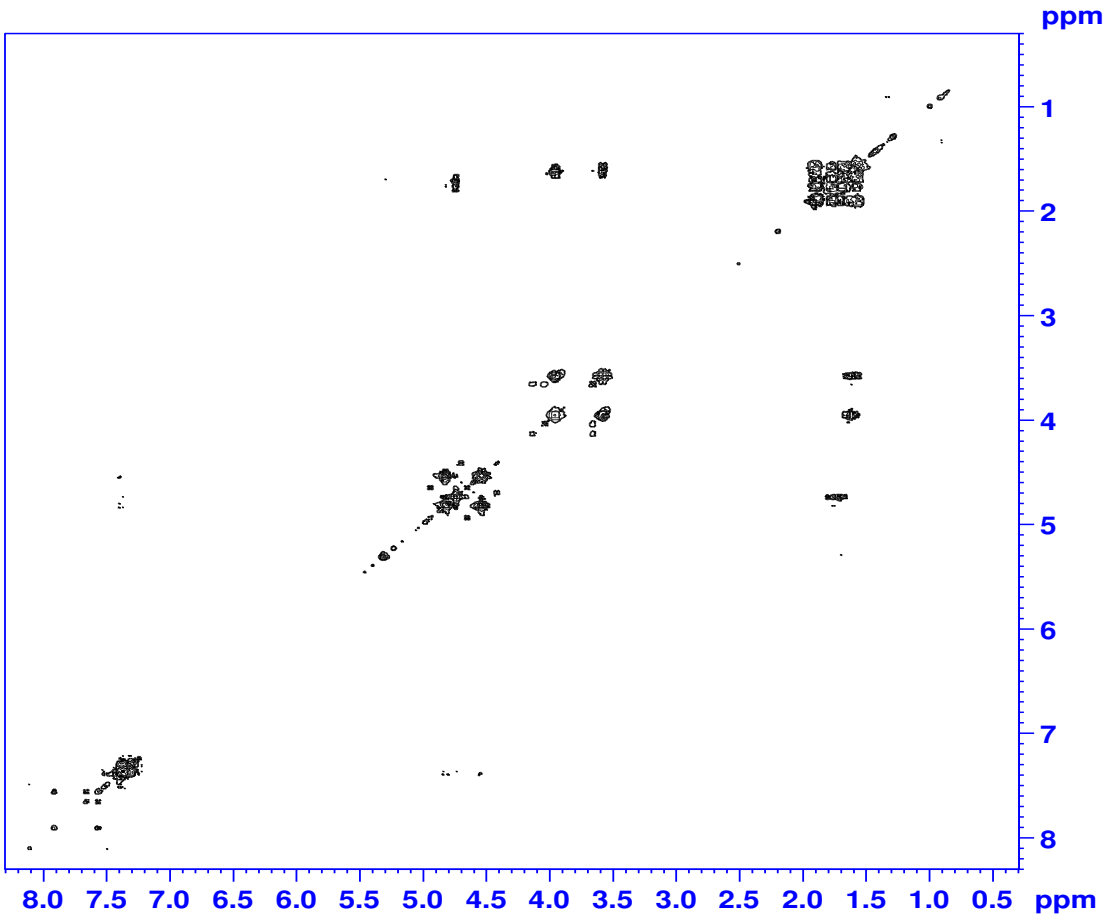
2D HSQC NMR Spectrum of Deuterated Mixture - *syn* and *anti* Product Isomers (**90**, **90'**, **91**) in $CDCl_3$



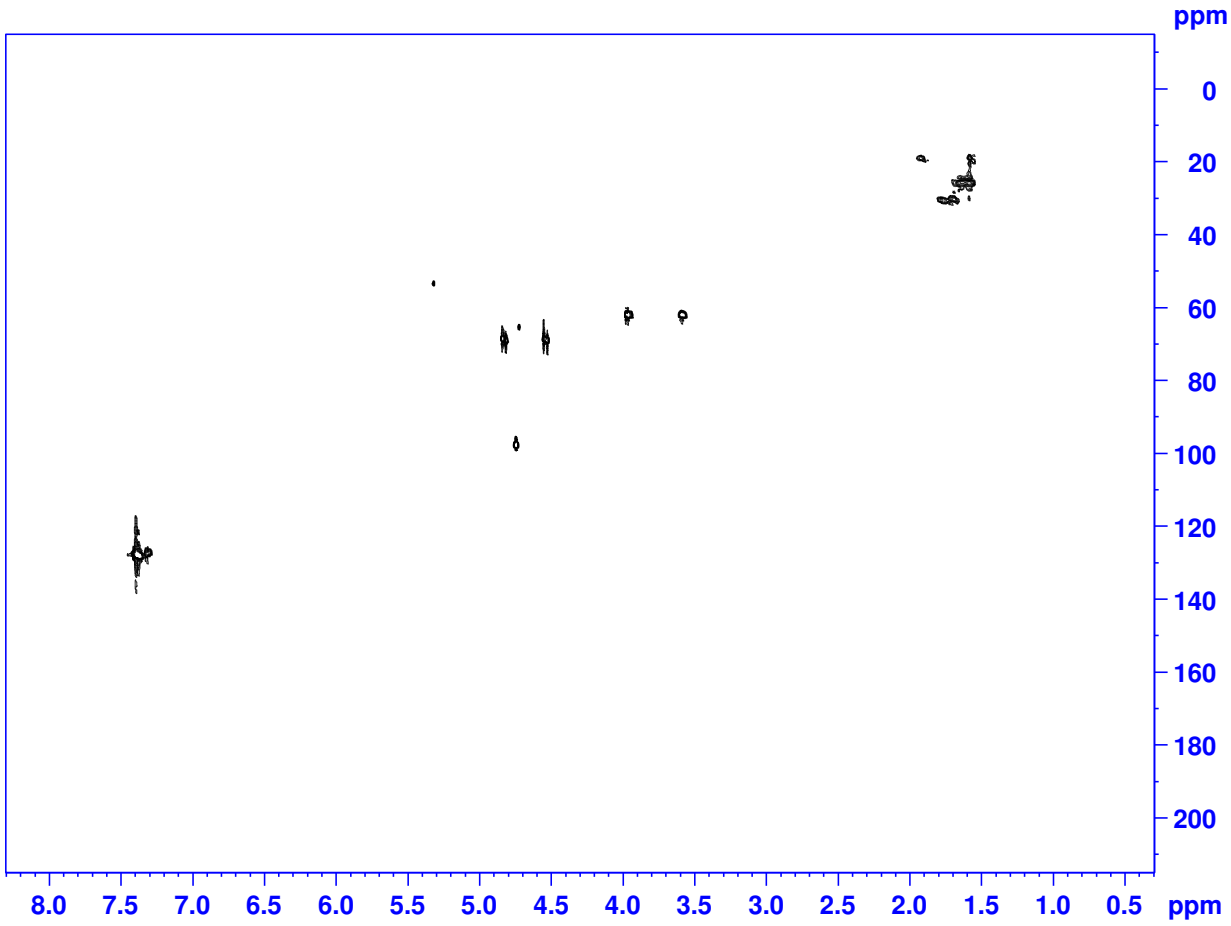
2D COSY NMR Spectrum of Deuterated Mixture - *syn* and *anti* Product Isomers (**90**, **90'**, **91**) in $CDCl_3$



2D COSY NMR Spectrum of **7a** in $CDCl_3$



2D HSQC NMR Spectrum **7a** in $CDCl_3$



DEPT-55 NMR Spectrum of **7a** (100% conversion to product) in $CDCl_3$

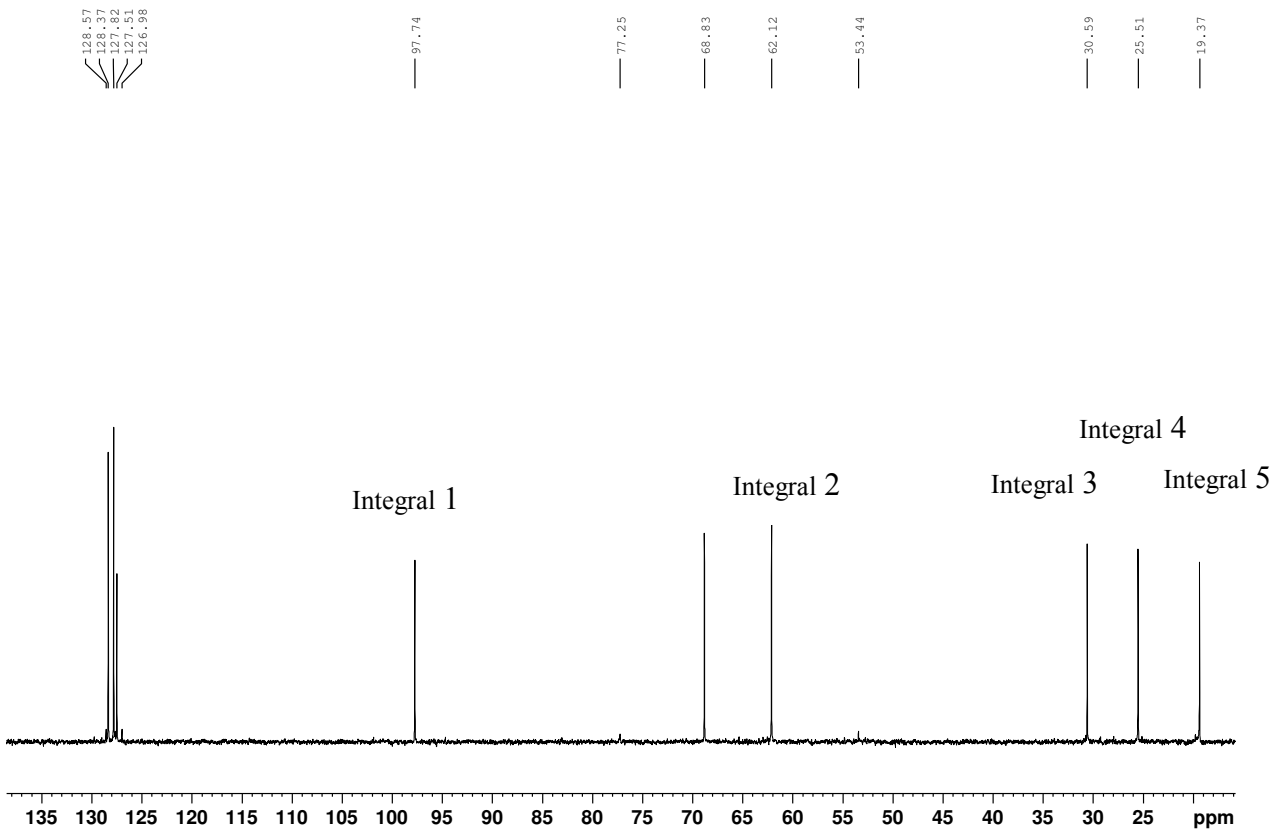



***Table 8.*** *Integration values denoted for the peaks of interest at 100% conversion.*

| Object | Integral [abs] | Integral [rel] | Peaks | Range (F1) from | Range (F1) to | (F1) [ppm] |
|---|---|---|---|---|---|---|
| Integral 1 | 413486340.5 | 0.7528 | 1 | 97.892 | 97.591 | 97.7418 |
| Integral 2 | 549266376.3 | 1 | 1 | 62.316 | 61.931 | 62.1233 |
| Integral 3 | 439738826.3 | 0.8006 | 1 | 30.74 | 30.45 | 30.5949 |
| Integral 4 | 461883042.8 | 0.8409 | 1 | 25.868 | 25.272 | 25.5701 |
| Integral 5 | 481648078.3 | 0.8769 | 1 | 19.68 | 19.09 | 19.3847 |

DEPT-55 NMR Spectrum of **7a** (2% conversion to product) in $CDCl_3$

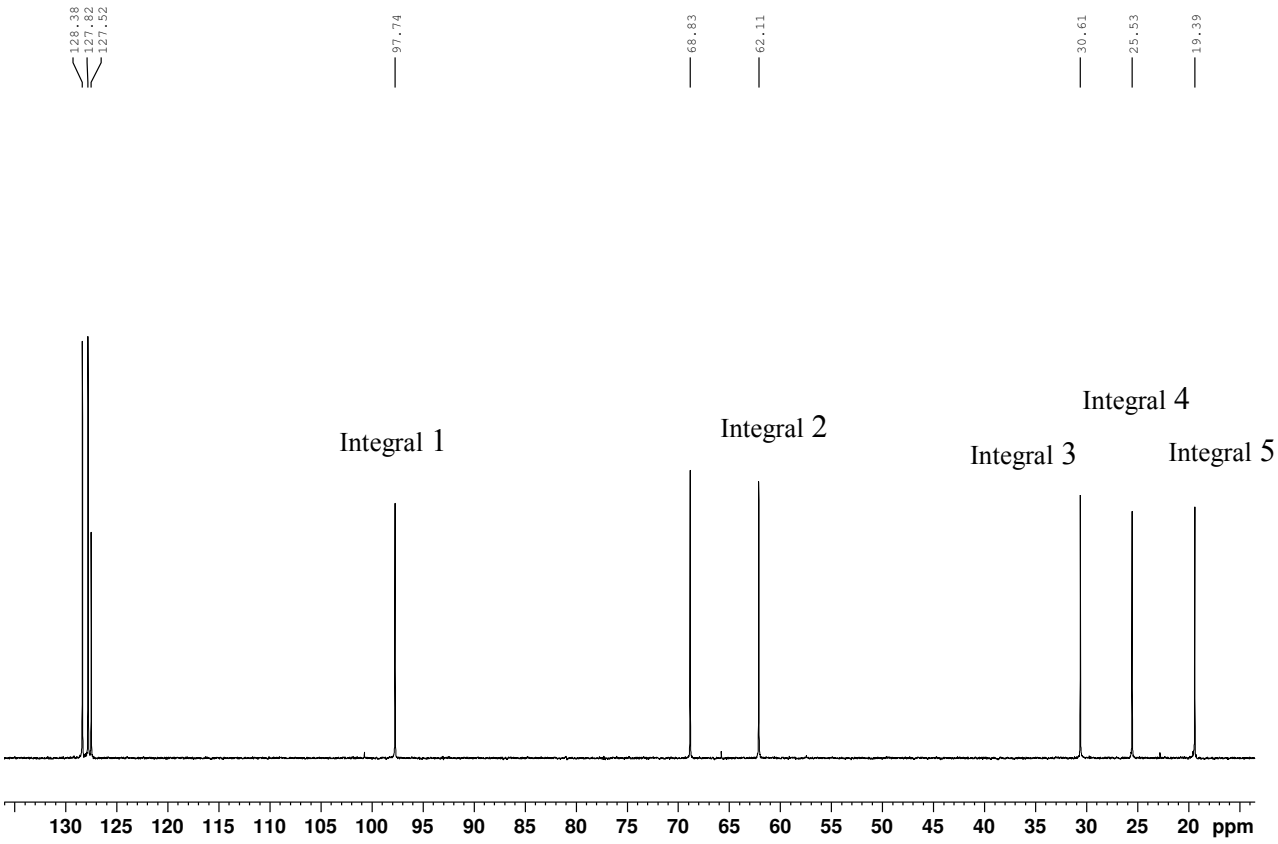
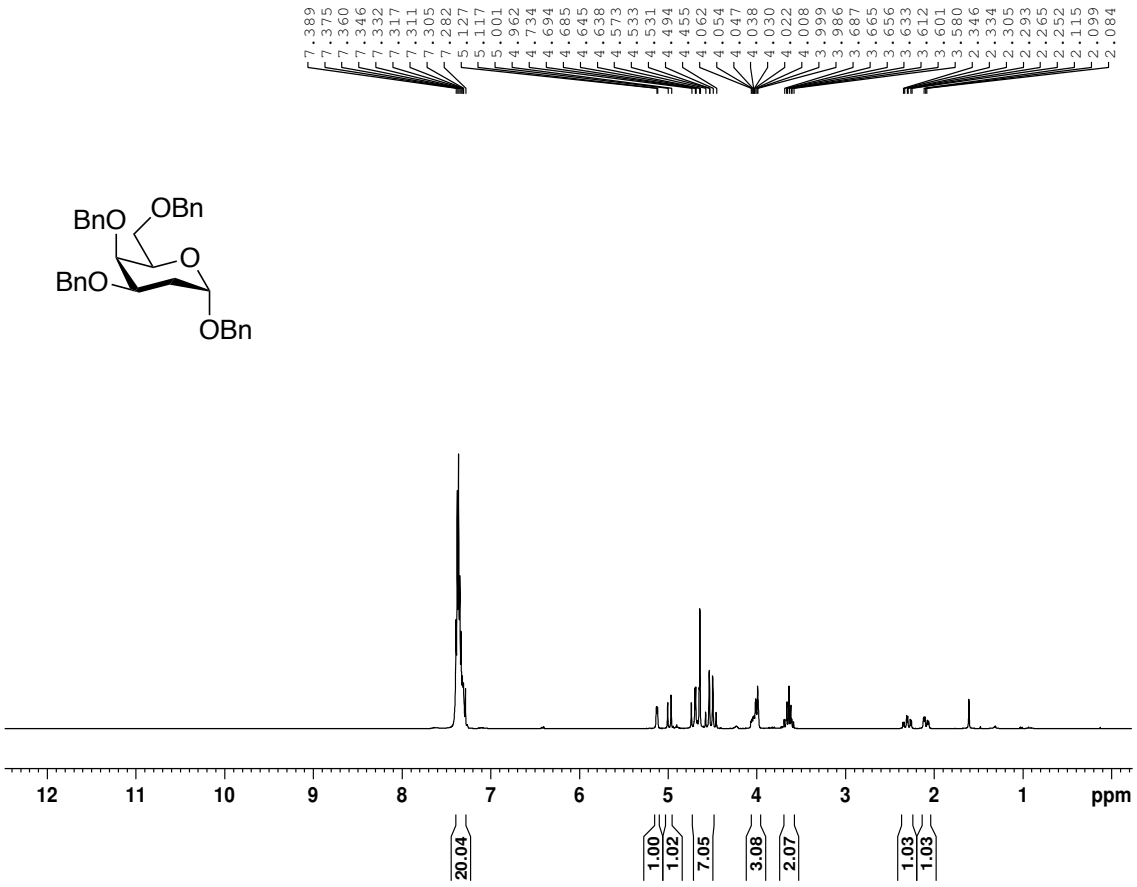


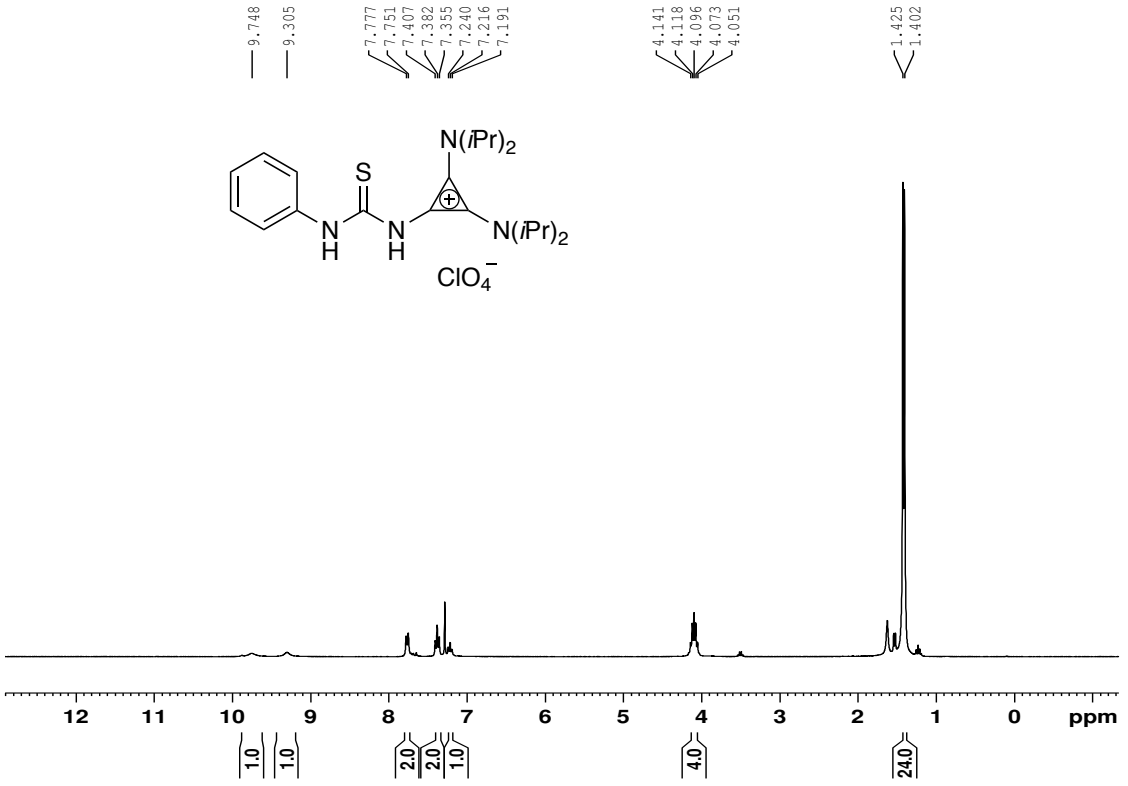

***Table 9.*** *Integration values denoted for the peaks of interest at 2% conversion.*

| Object | Integral [abs] | Integral [rel] | Peaks | Range (F1) from | Range (F1) to | (F1) [ppm] |
|---|---|---|---|---|---|---|
| Integral 1 | 1450629516 | 0.8404 | 1 | 97.733 | 97.226 | 97.7556 |
| Integral 2 | 1726021660 | 1 | 1 | 62.503 | 61.709 | 62.1059 |
| Integral 3 | 1539357156 | 0.8919 | 1 | 30.954 | 30.16 | 30.5569 |
| Integral 4 | 1452714348 | 0.8417 | 1 | 25.815 | 25.213 | 25.5137 |
| Integral 5 | 1504962524 | 0.8719 | 1 | 19.74 | 19.07 | 19.405 |

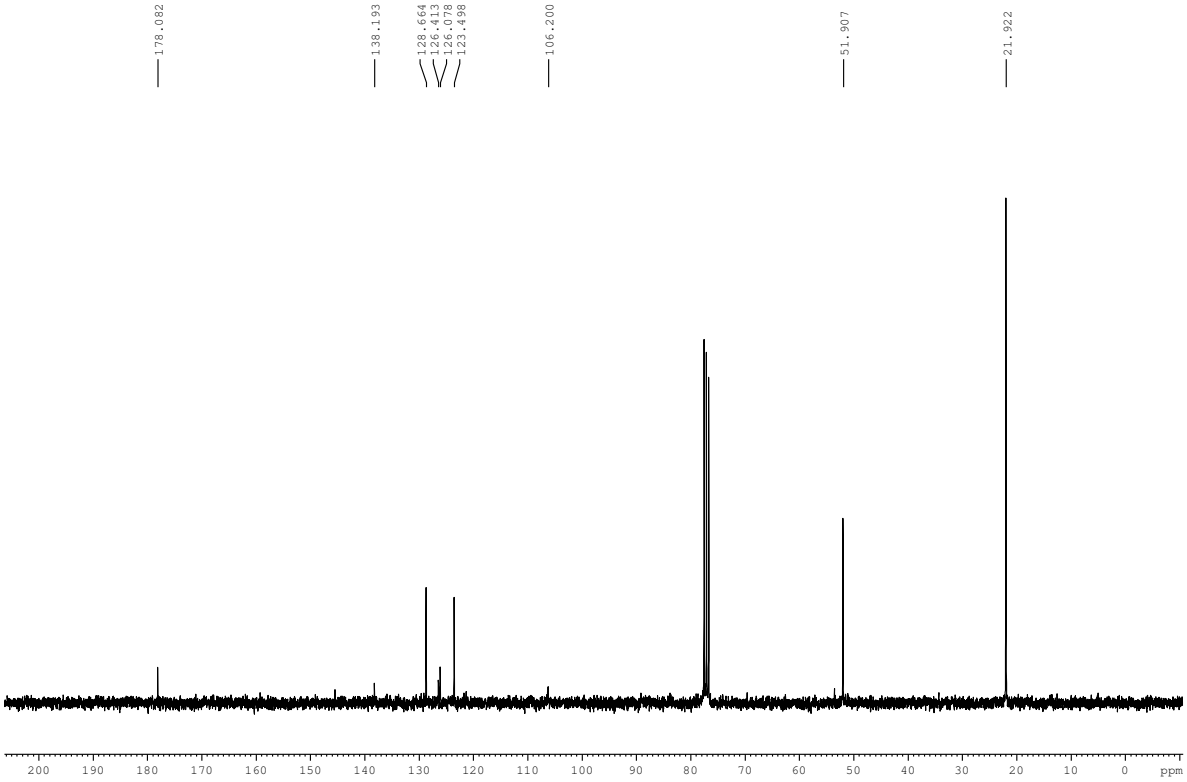
$^1$H NMR (300 MHz) Spectrum of **93** in $CDCl_3$



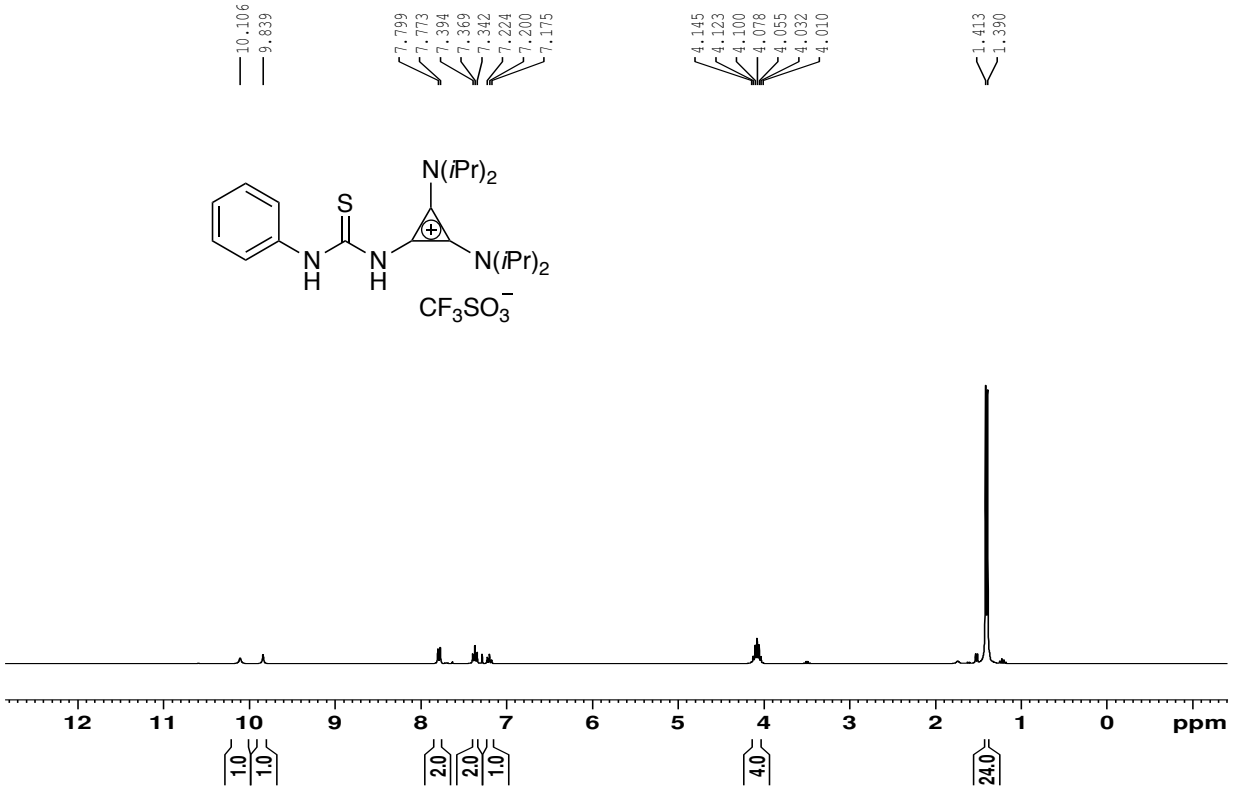

$^1$H NMR (300 MHz) Spectrum of **4**·$ClO_4^-$ in $CDCl_3$



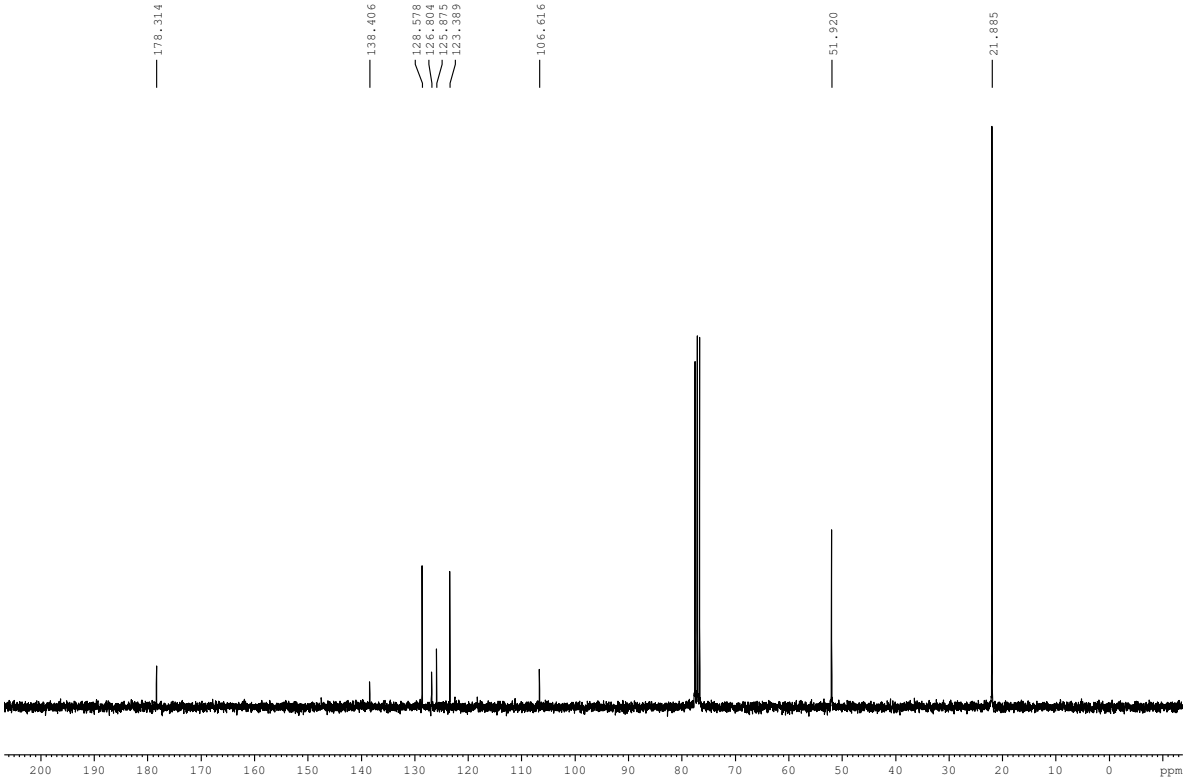
$^{13}C\{^{1}H\}$ NMR (75.5 MHz) Spectrum of **4**·$ClO_4^-$ in $CDCl_3$



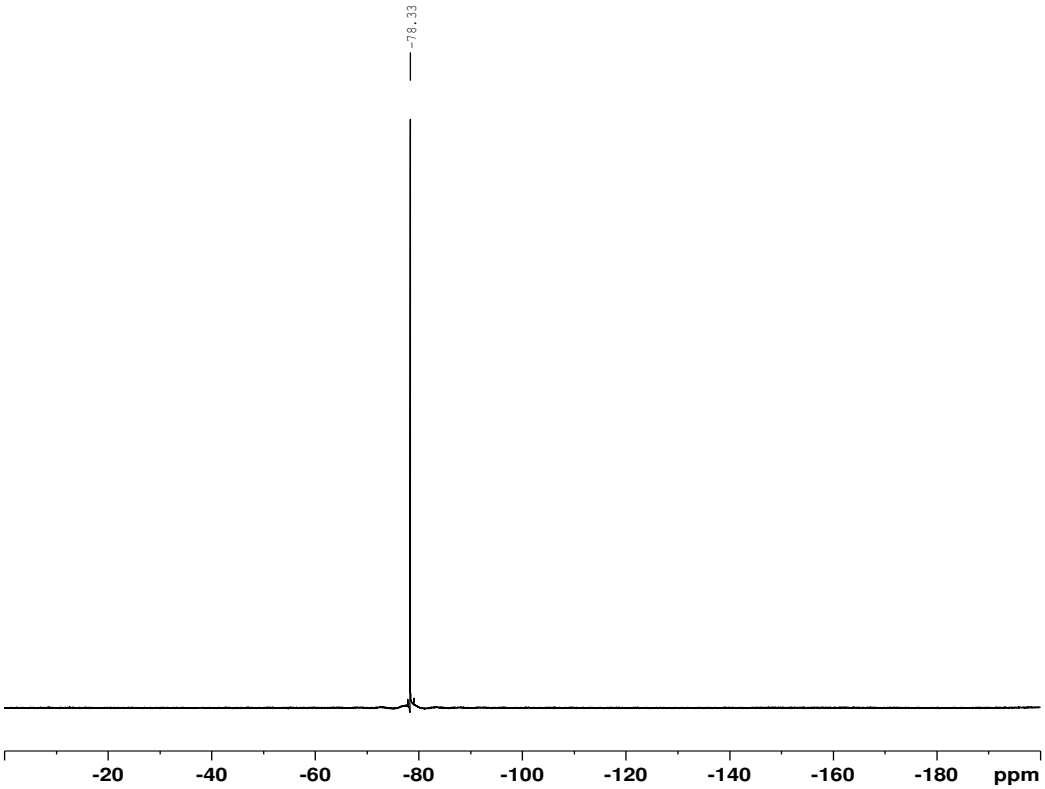

$^{1}H$ NMR (300 MHz) Spectrum of **4**·$CF_3SO_3^-$ in $CDCl_3$



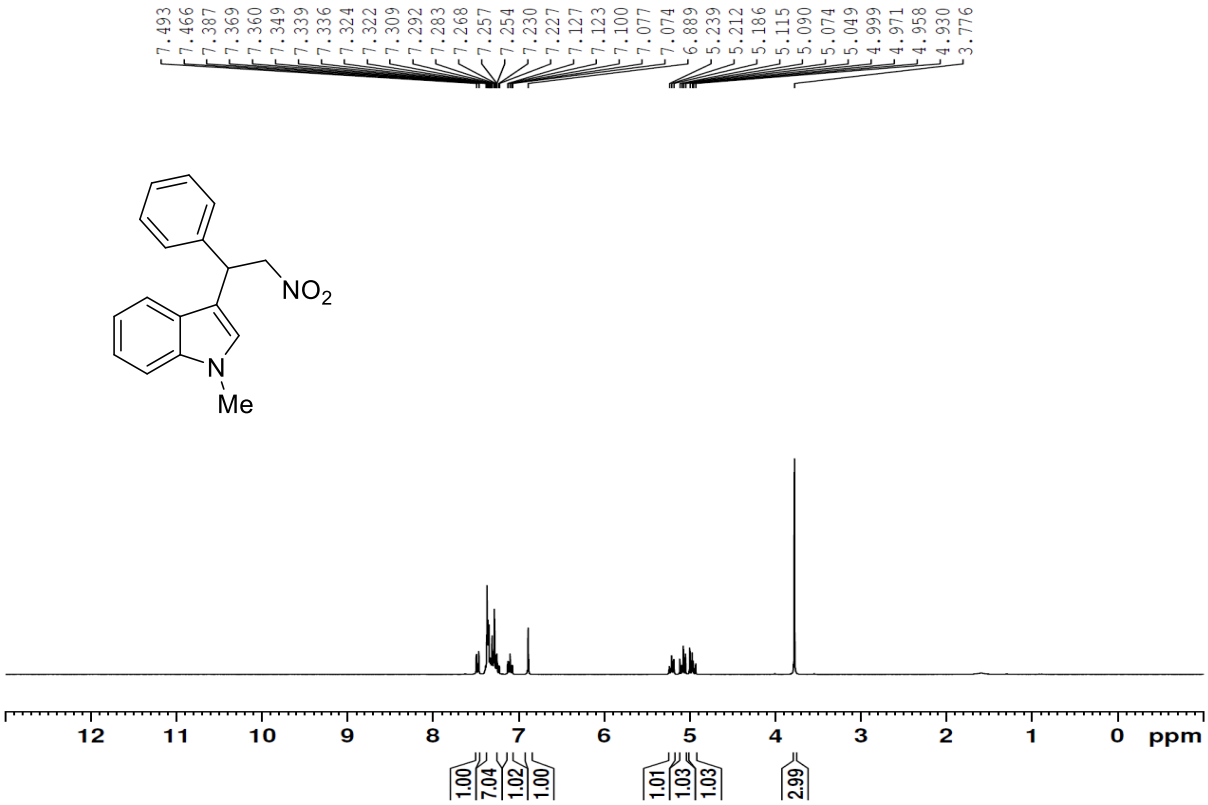
$^{13}C\{^{1}H\}$ NMR (75.5 MHz) Spectrum of **4**·$CF_3SO_3^-$ in $CDCl_3$



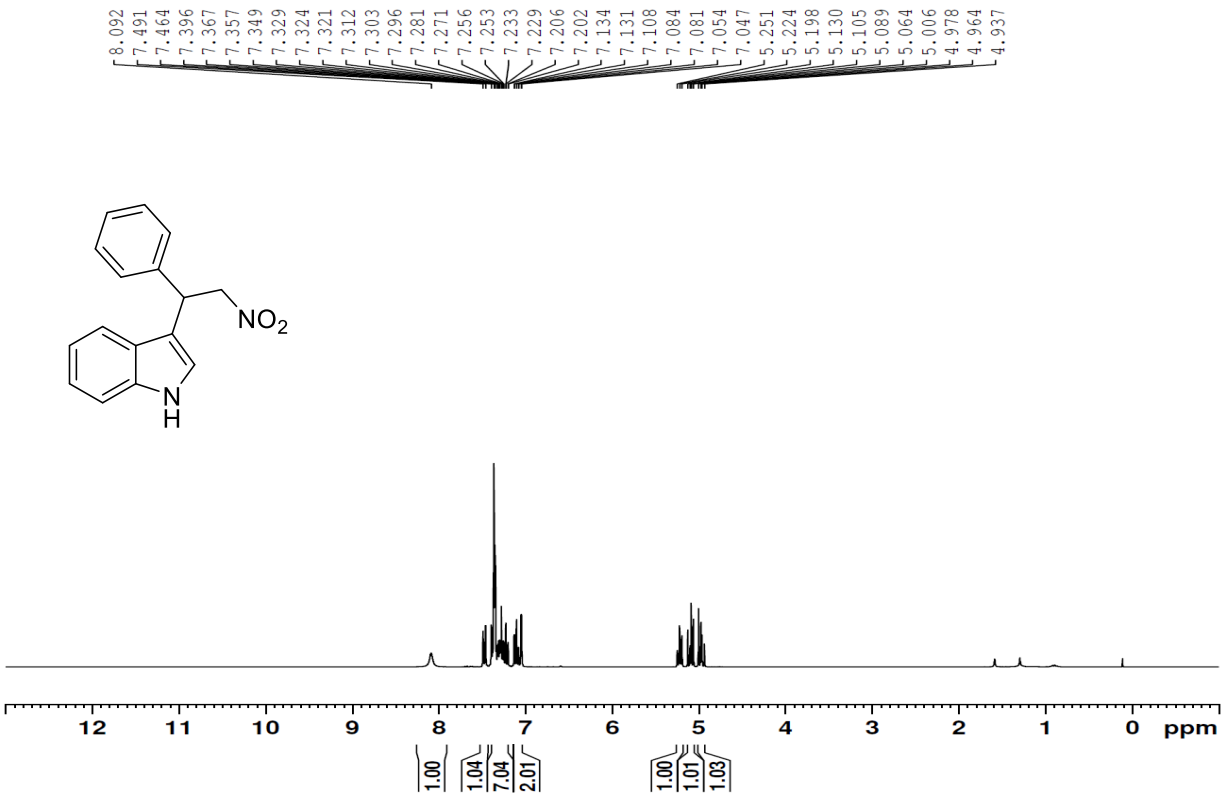

$^{19}F\{^{1}H\}$ NMR (292.4 MHz) Spectrum of **4**·$CF_3SO_3^-$ in $CDCl_3$



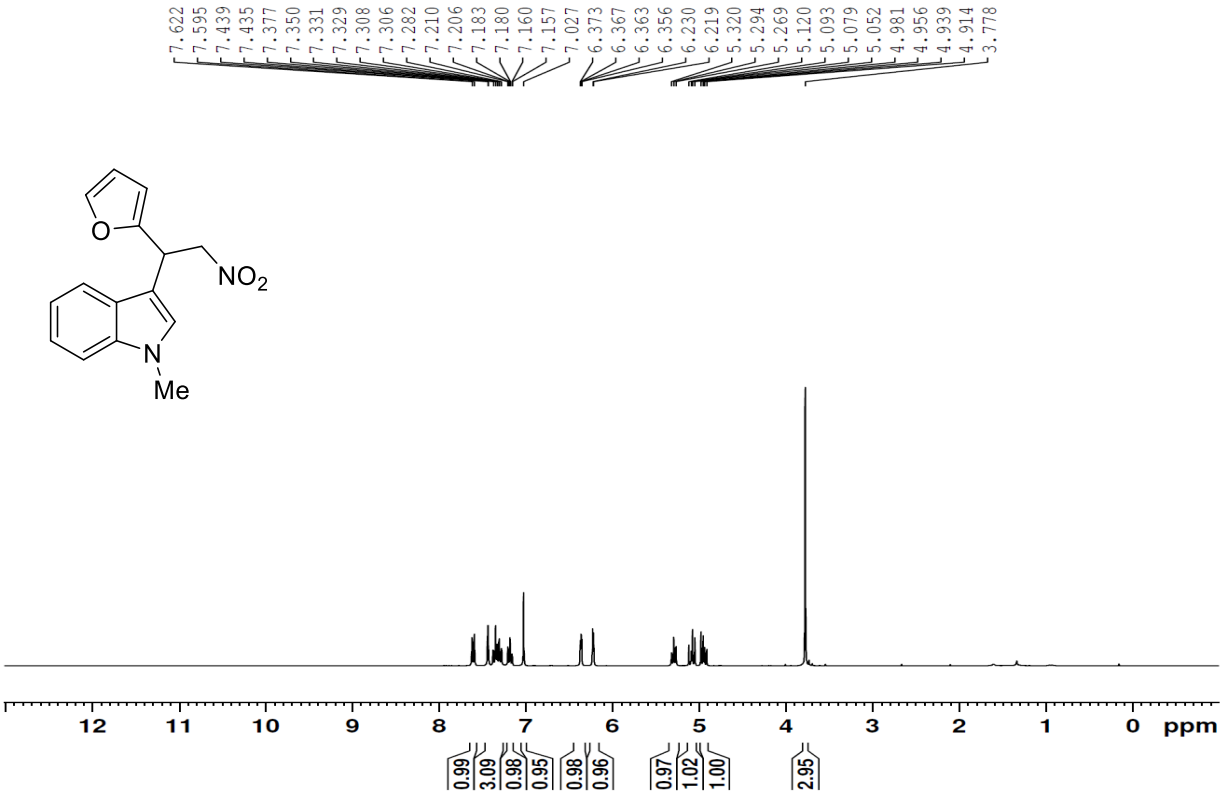
$^1$H NMR (300 MHz) Spectrum of **10a** in $CDCl_3$



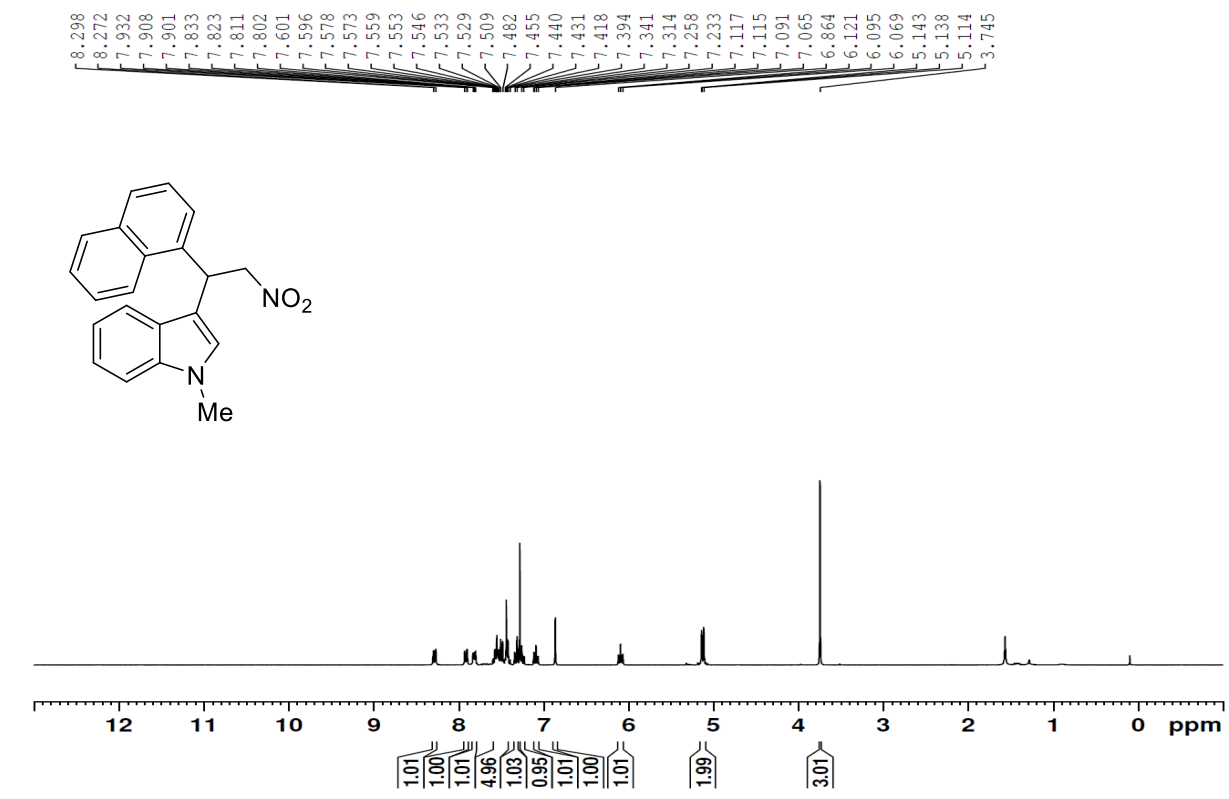

$^1$H NMR (300 MHz) Spectrum of **10b** in $CDCl_3$



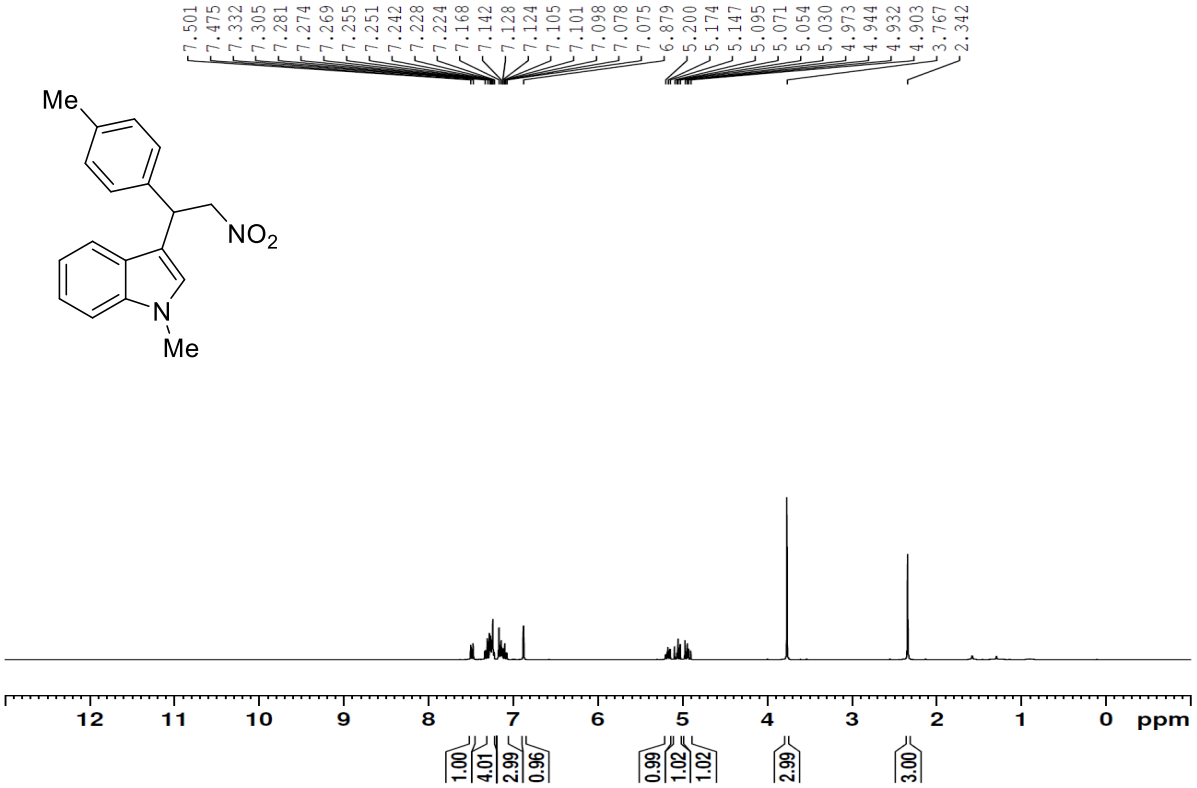
$^1$H NMR (300 MHz) Spectrum of **10e** in $CDCl_3$



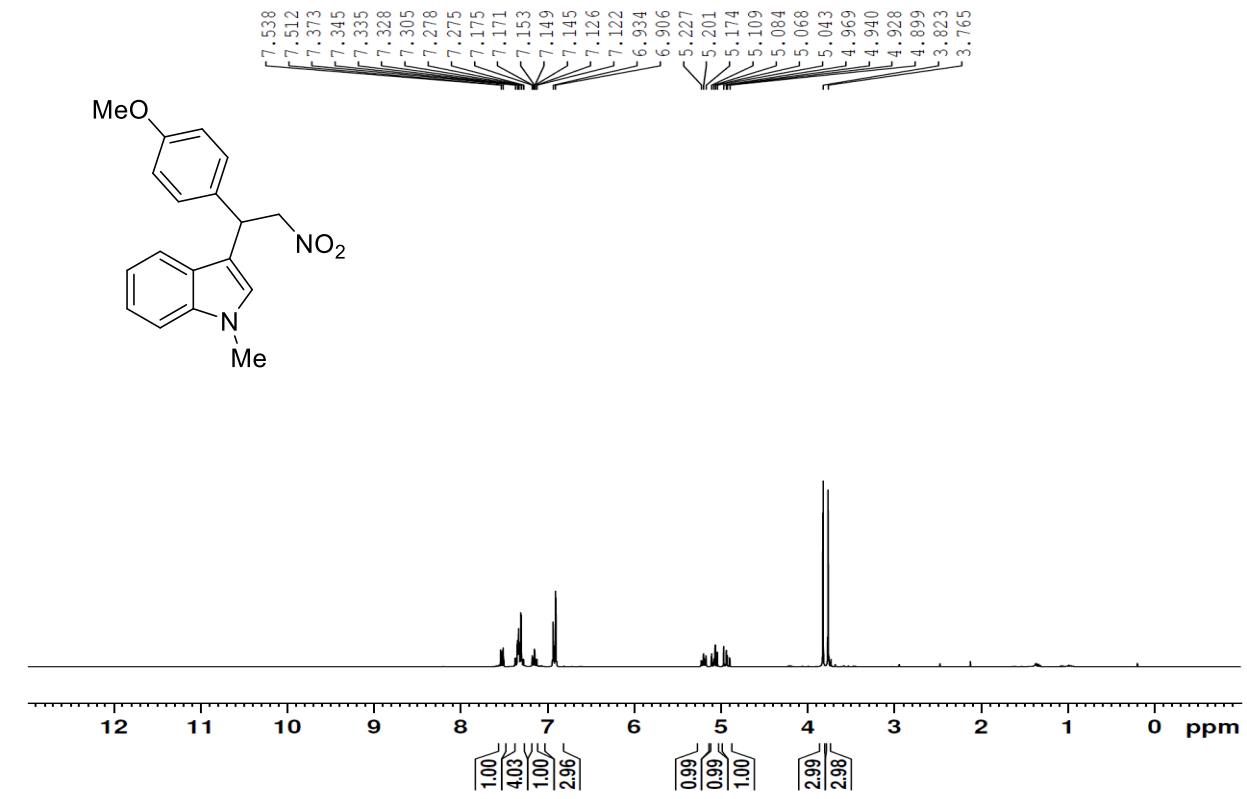

$^1$H NMR (300 MHz) Spectrum of **10f** in $CDCl_3$



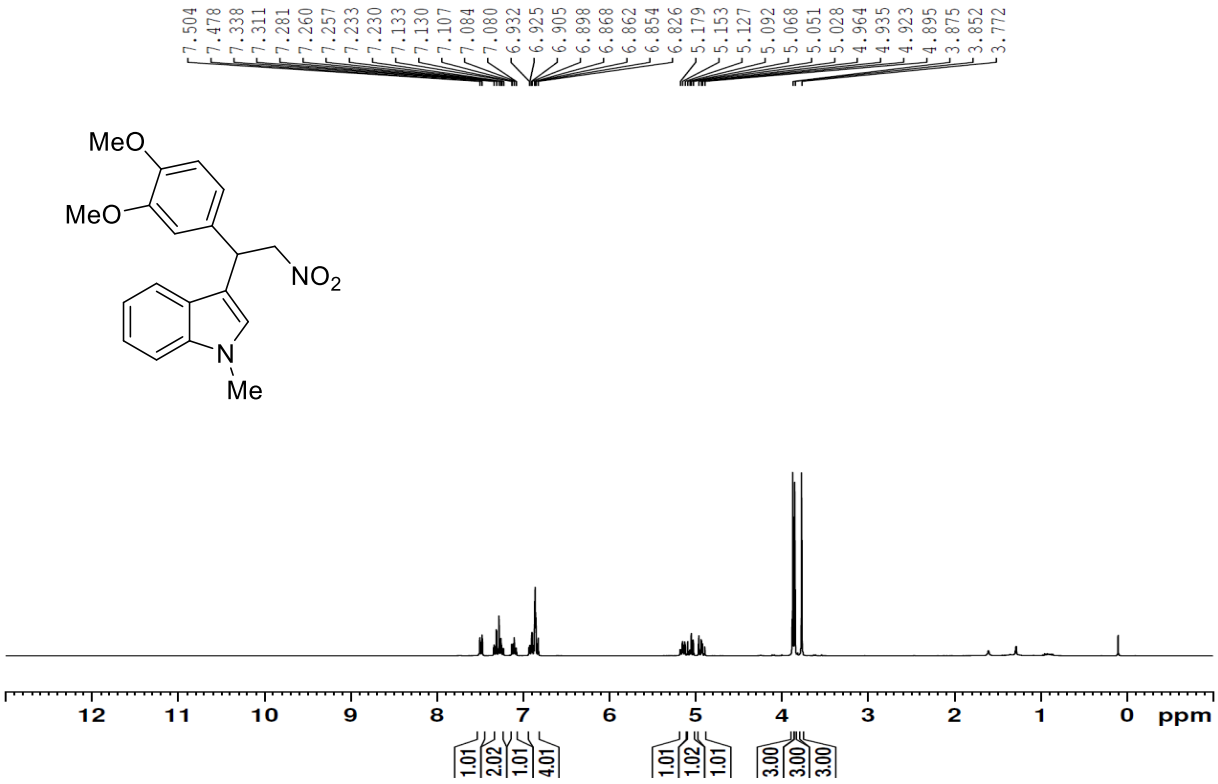
$^1$H NMR (300 MHz) Spectrum of **10g** in $CDCl_3$



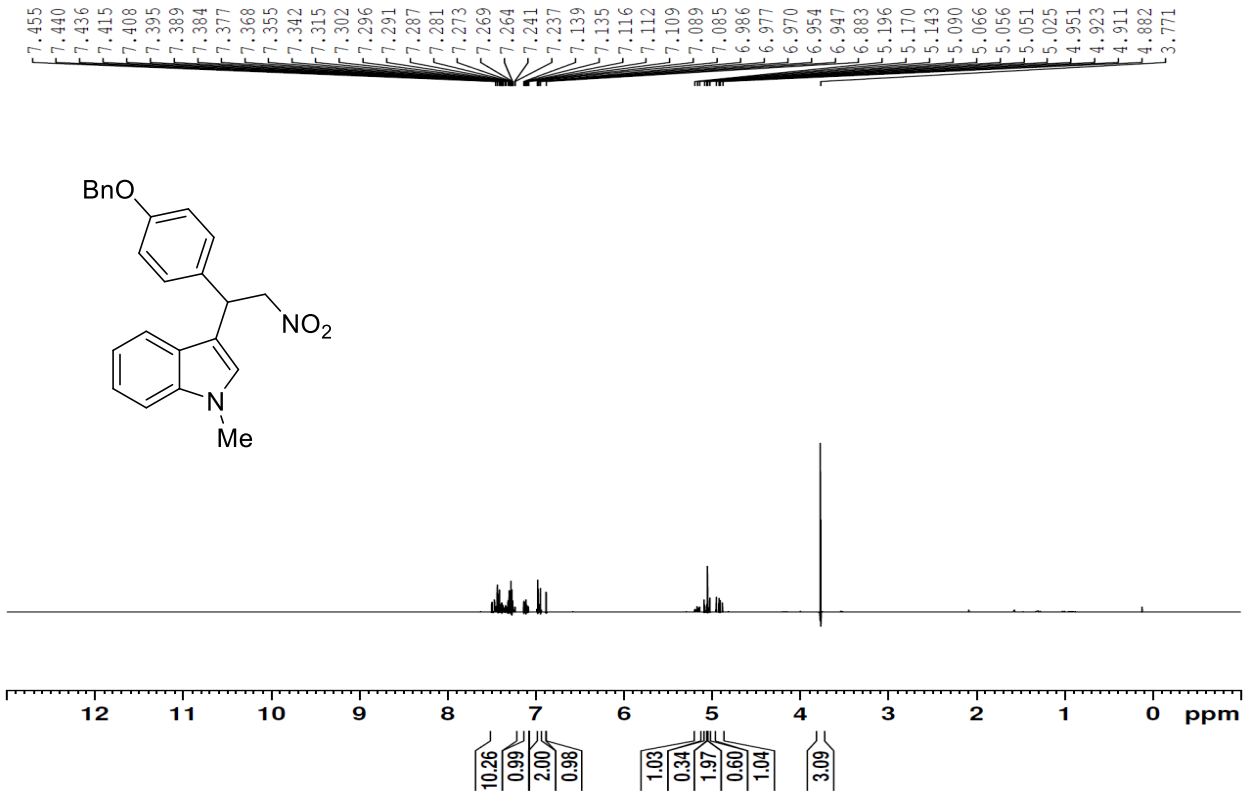

$^1$H NMR (300 MHz) Spectrum of **10h** in $CDCl_3$



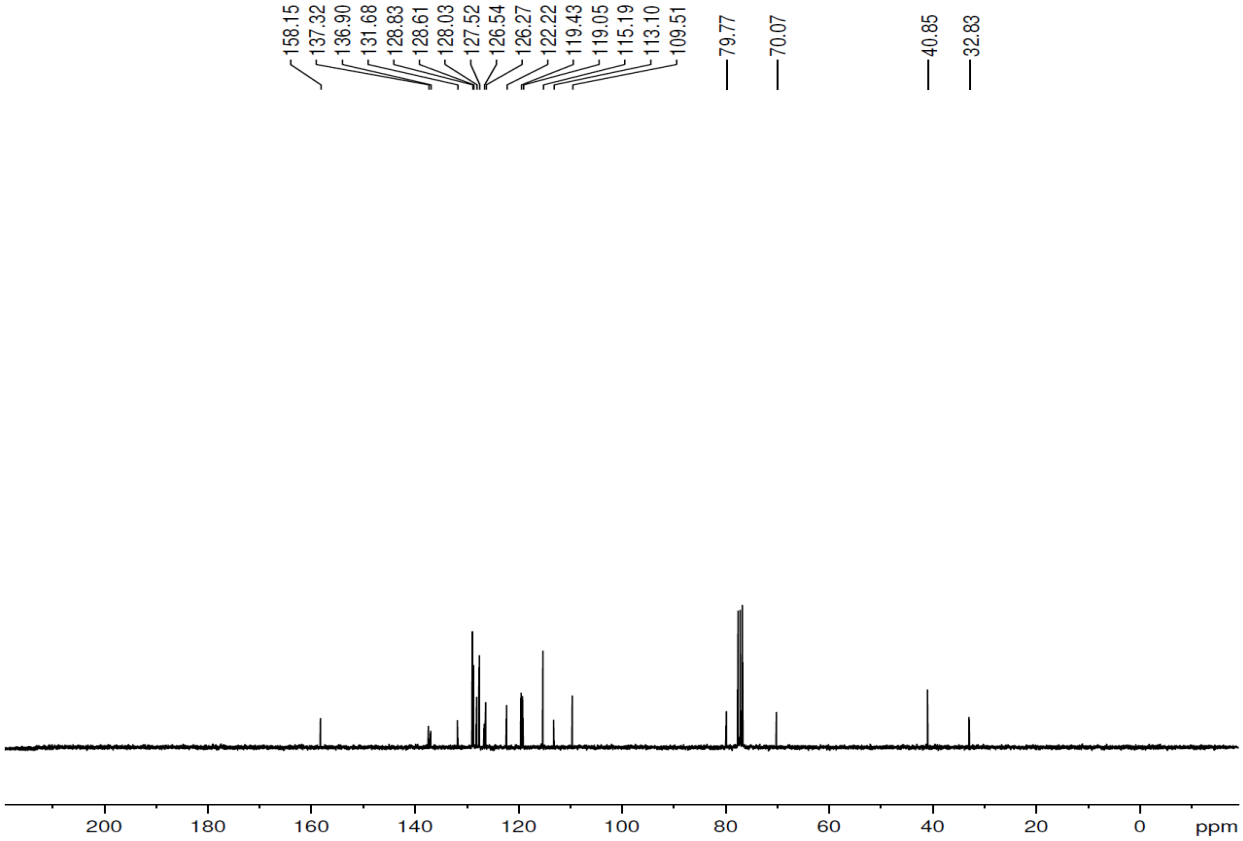
[1]H NMR (300 MHz) Spectrum of **10i** in $CDCl_3$



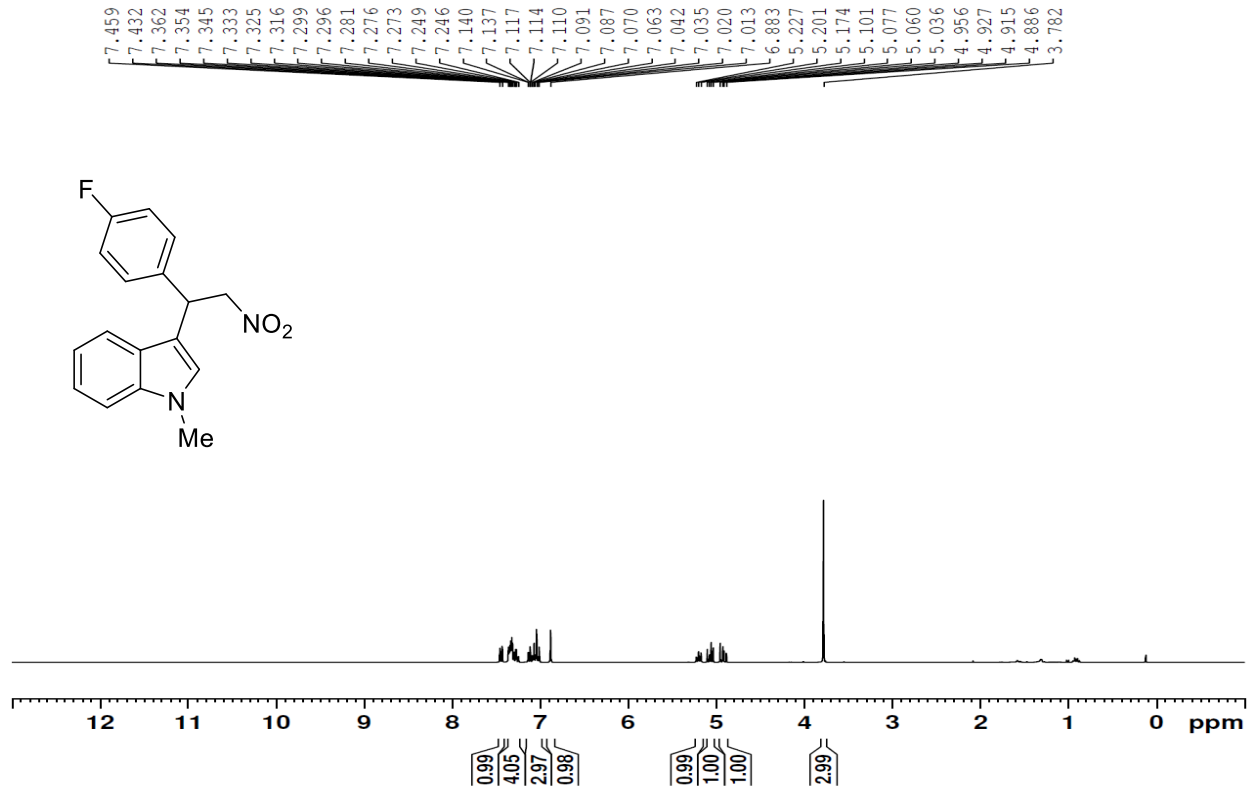

[1]H NMR (300 MHz) Spectrum of **10j** in $CDCl_3$



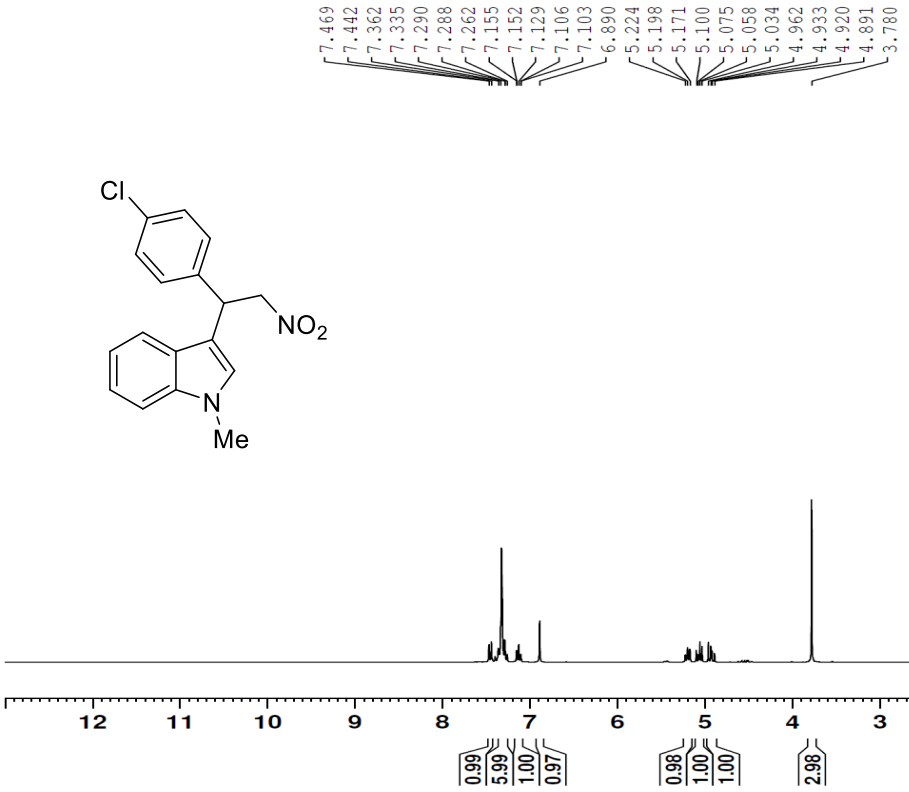
$^{13}C\{^{1}H\}$ NMR (75.5 MHz) Spectrum of **10j** in $CDCl_3$



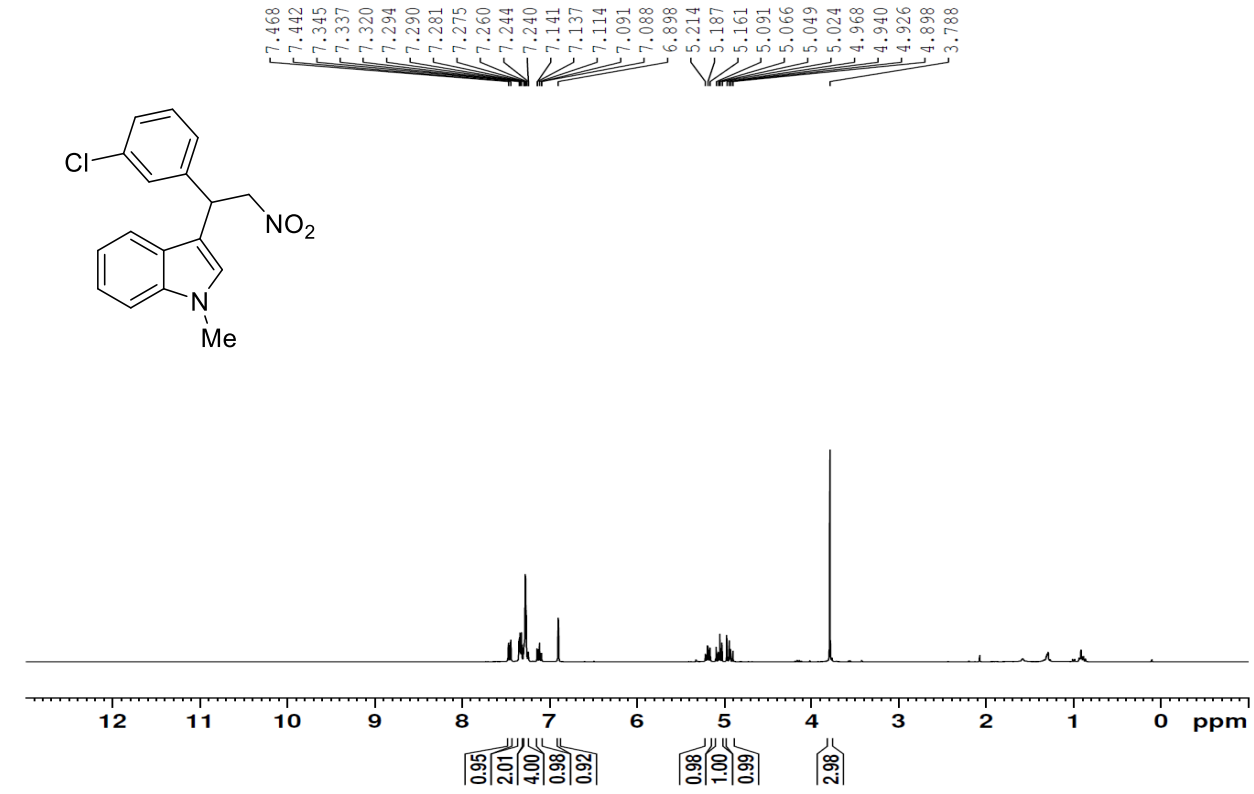

$^{1}H$ NMR (300 MHz) Spectrum of **10k** in $CDCl_3$



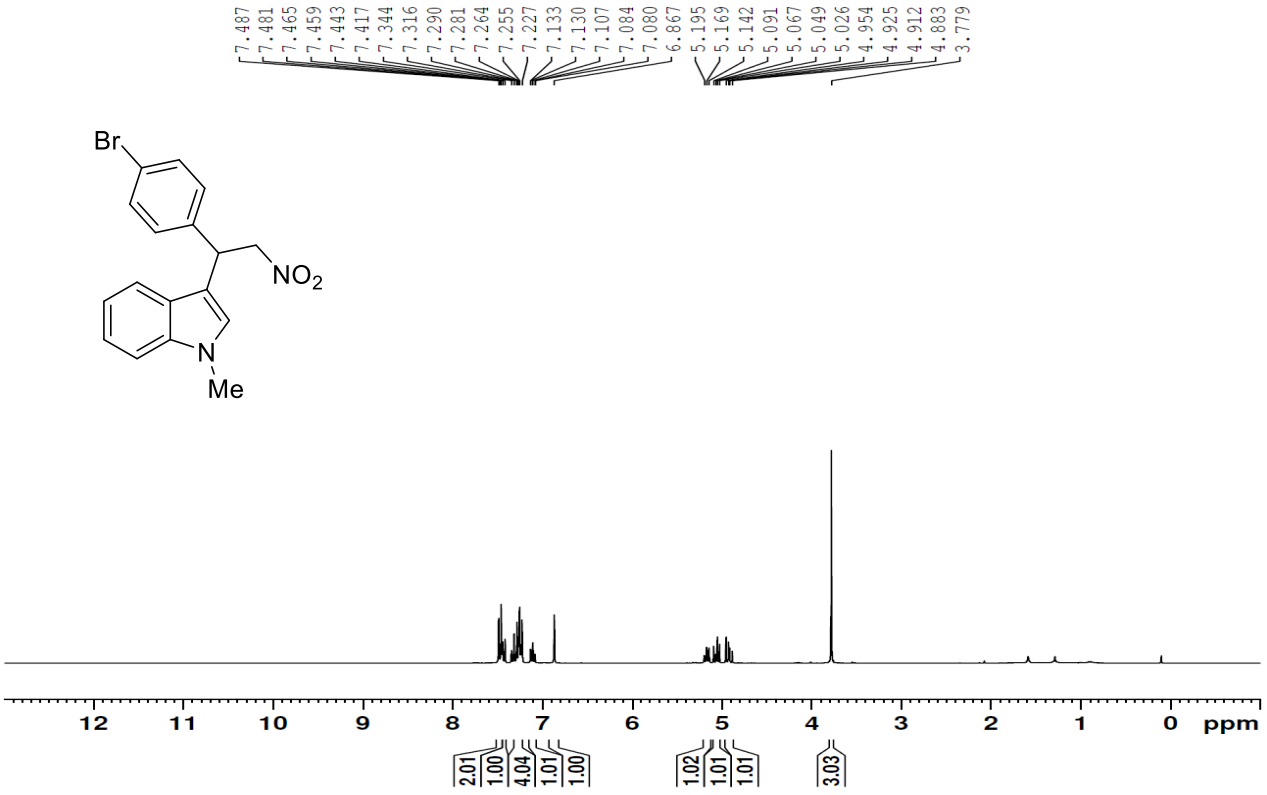
$^1$H NMR (300 MHz) Spectrum of **10l** in $CDCl_3$



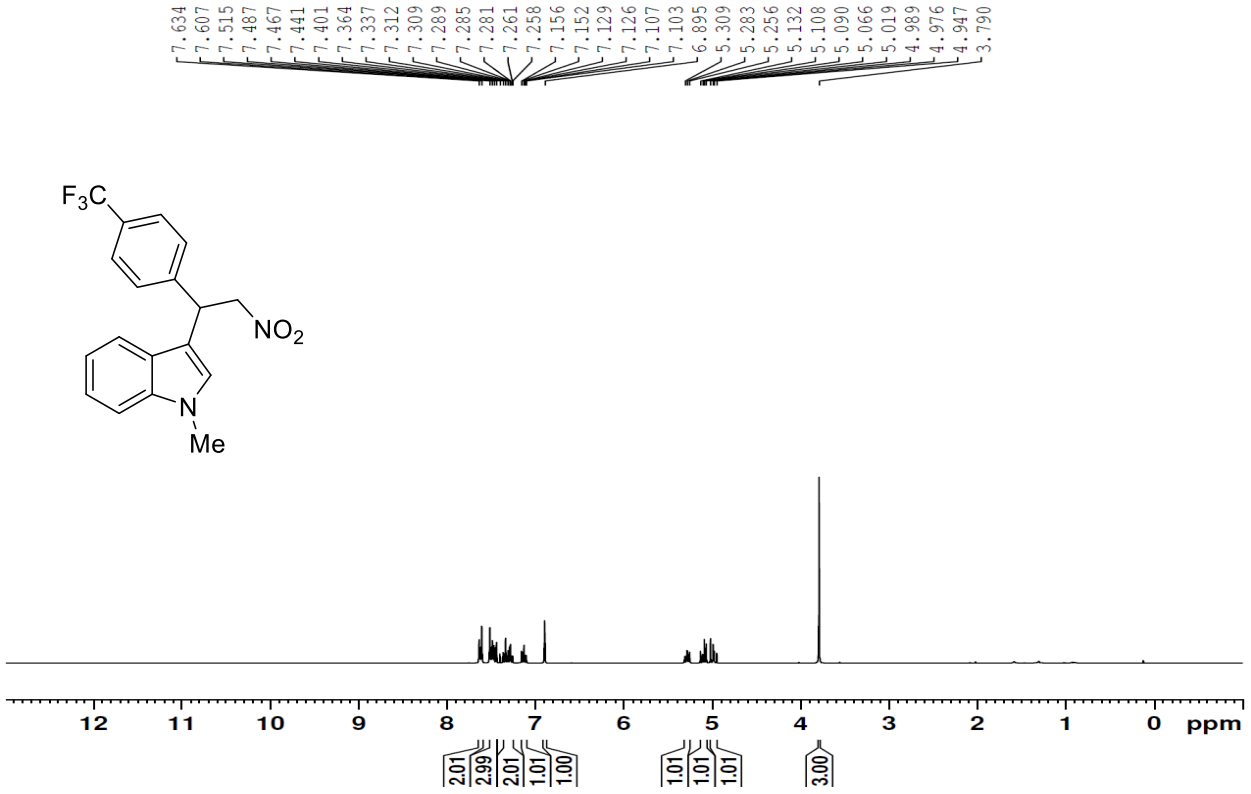

$^1$H NMR (300 MHz) Spectrum of **10m** in $CDCl_3$



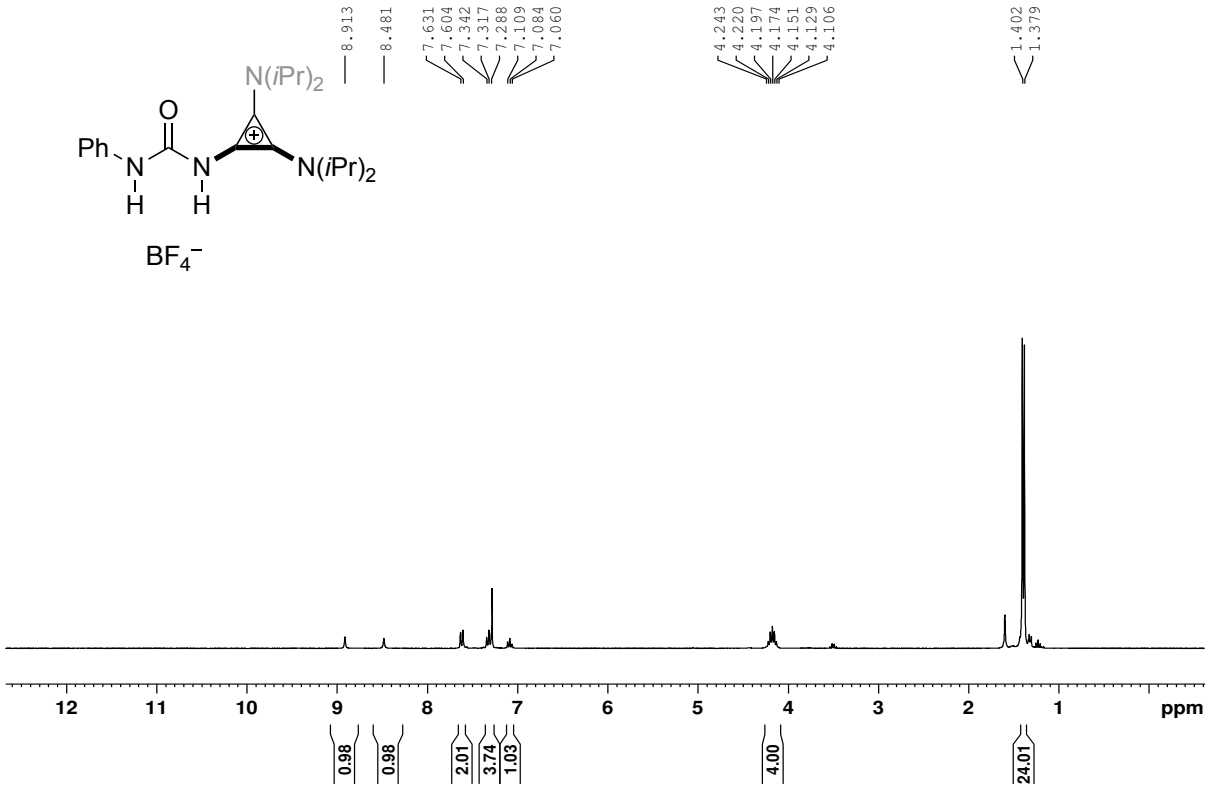
$^1$H NMR (300 MHz) Spectrum of **10n** in $CDCl_3$



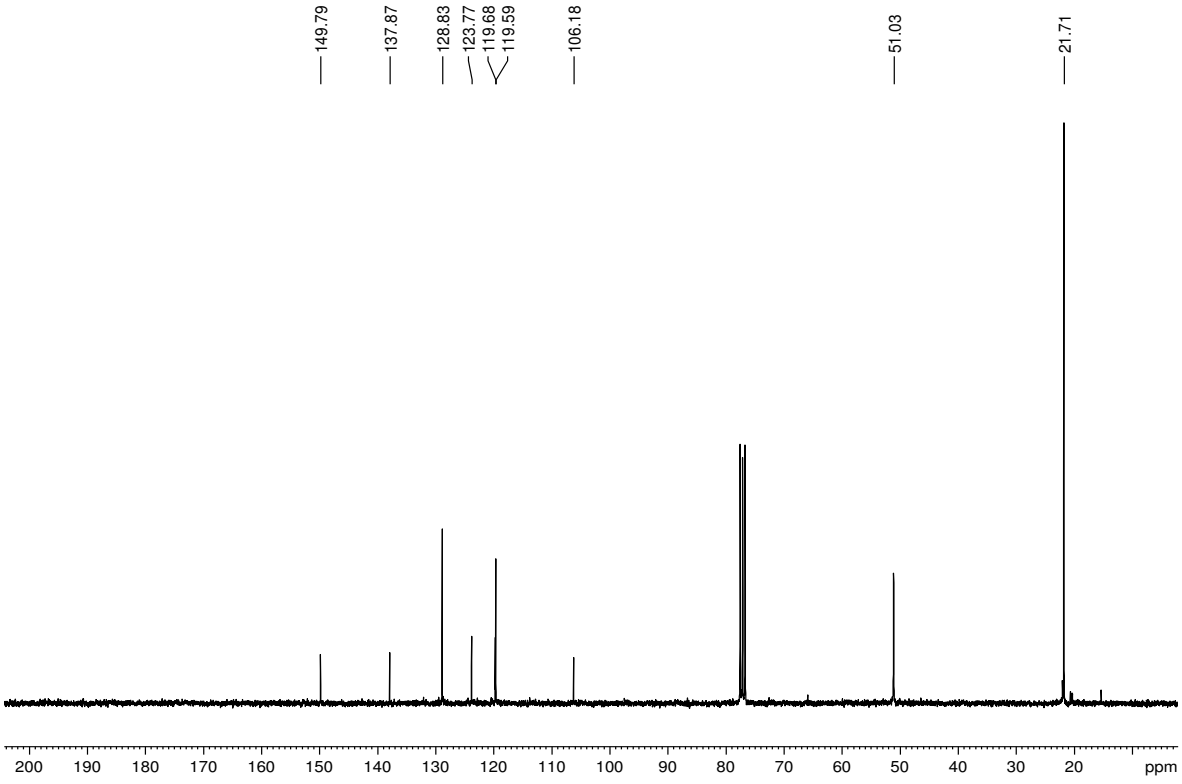

$^1$H NMR (300 MHz) Spectrum of **10o** in $CDCl_3$



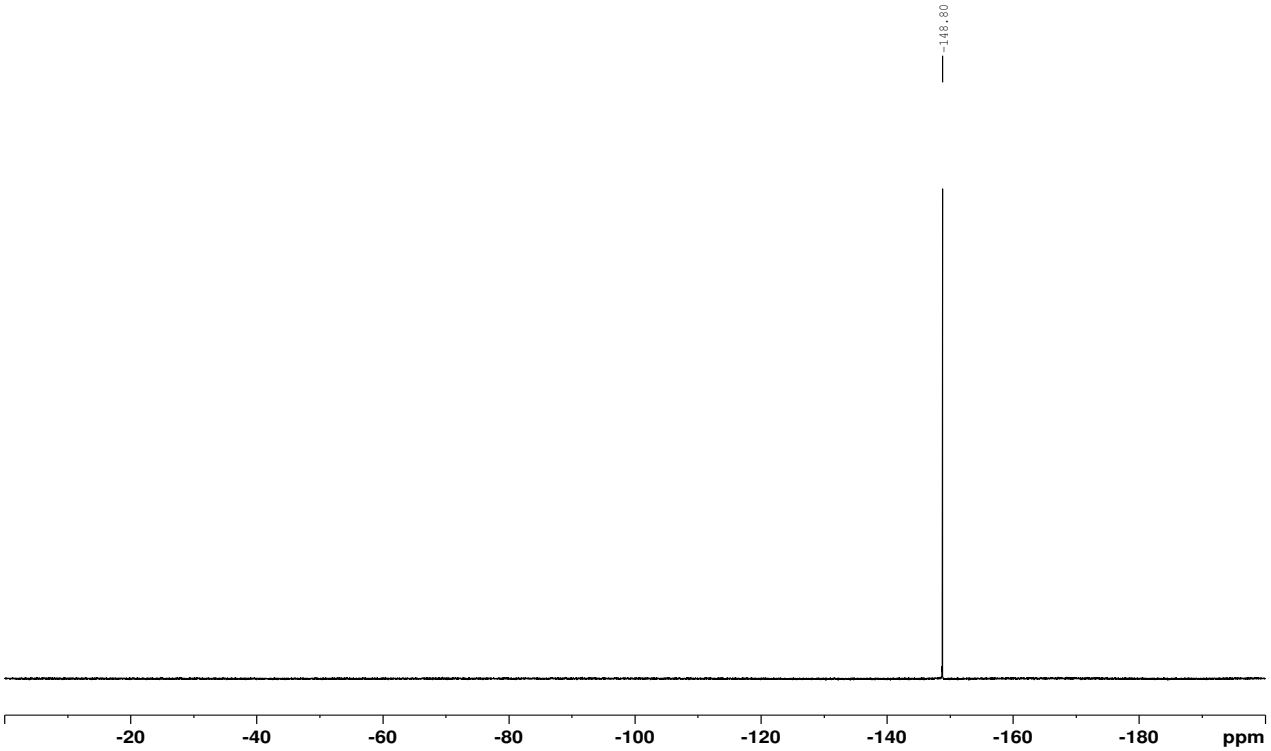
$^{1}$H NMR (300 MHz) Spectrum of **11a**·$BF_4^-$ in $CDCl_3$



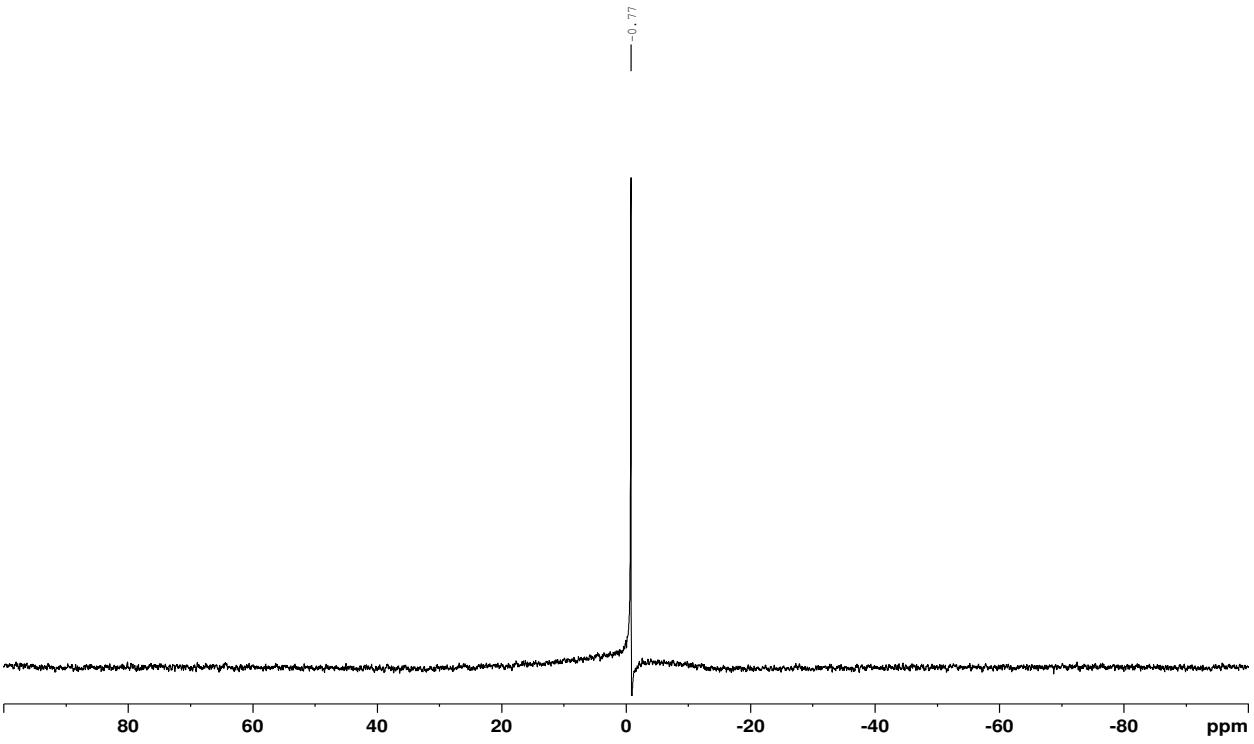

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **11a**·$BF_4^-$ in $CDCl_3$



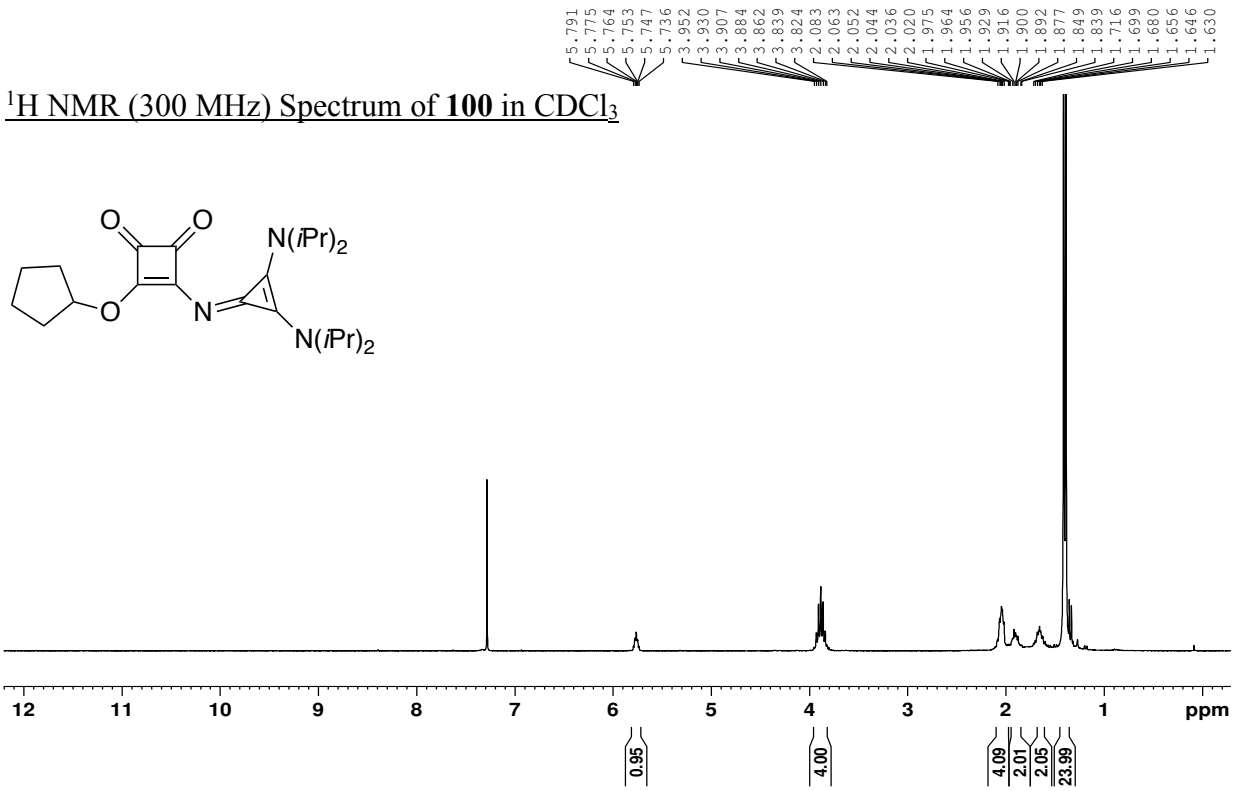
$^{19}F\{^{1}H\}$ NMR (292.4 MHz) Spectrum of **11a**·$BF_4^-$ in $CDCl_3$



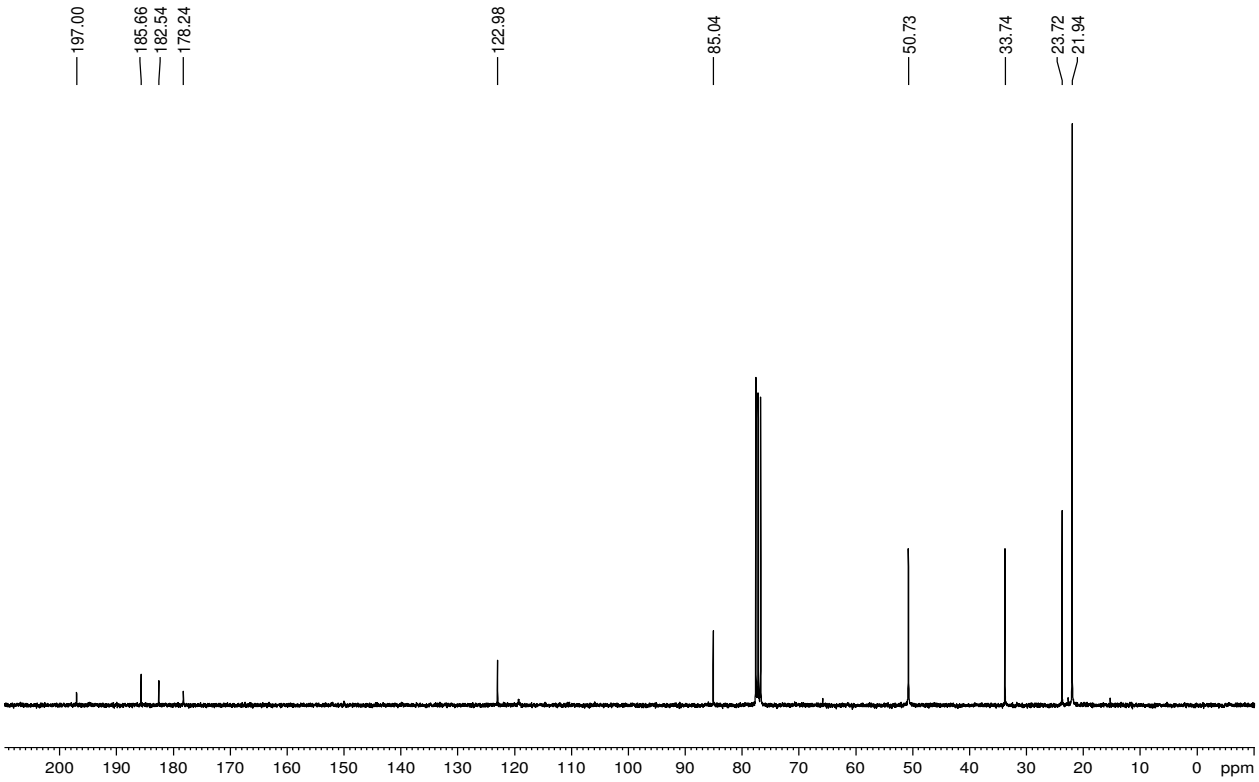

$^{11}B\{^{1}H\}$ NMR (96.3 MHz) Spectrum of **11a**·$BF_4^-$ in $CDCl_3$



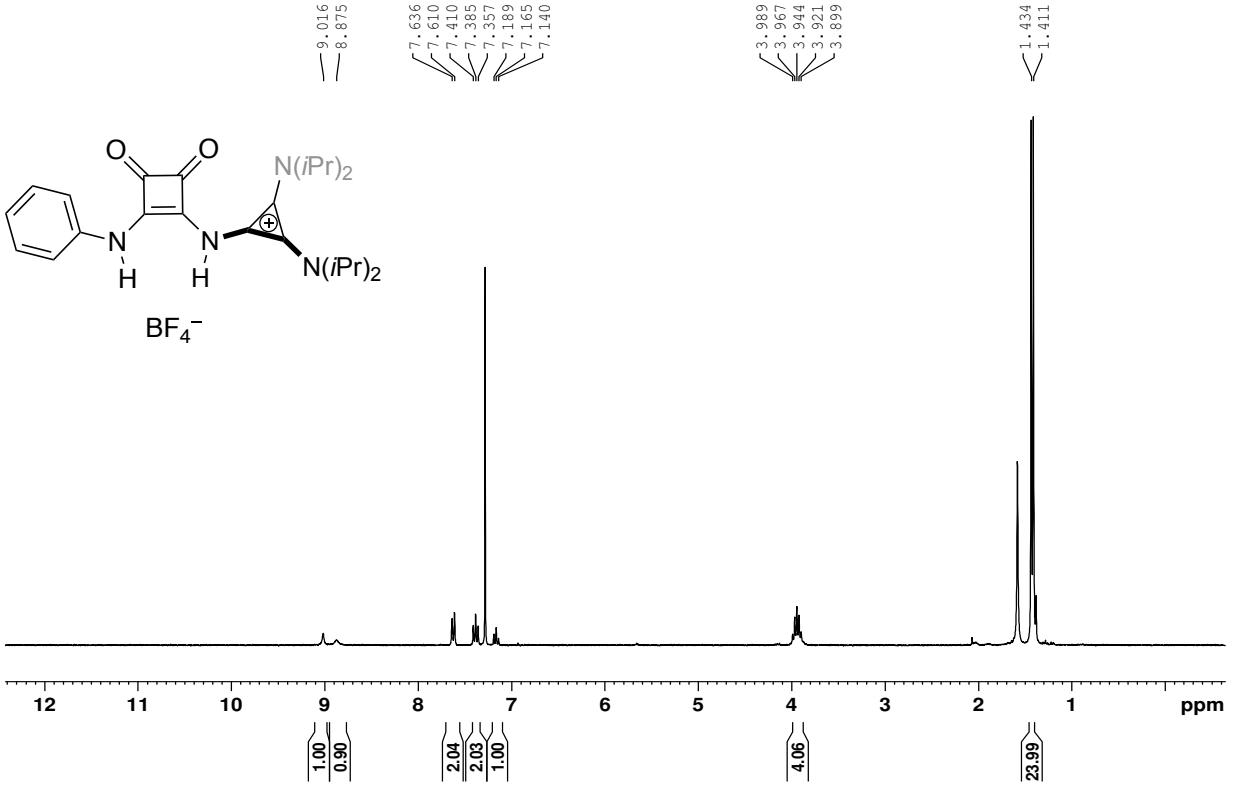
$^{1}$H NMR (300 MHz) Spectrum of **100** in $CDCl_3$



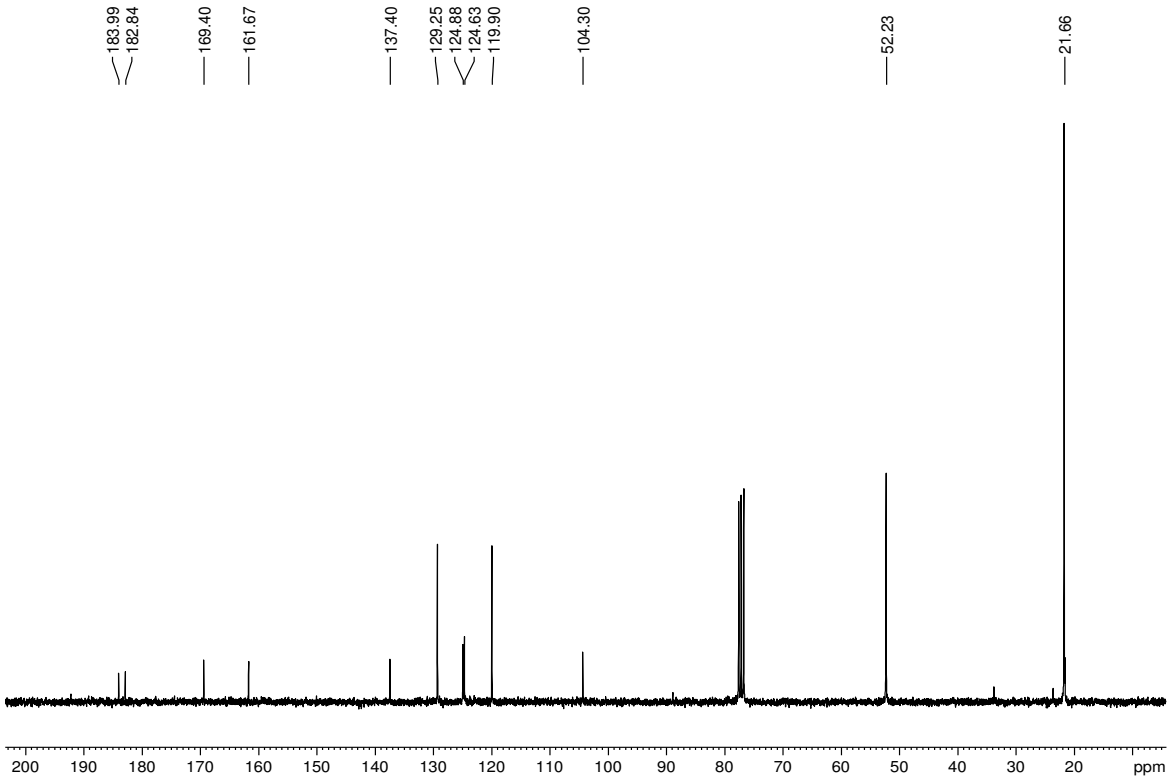

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **100** in $CDCl_3$



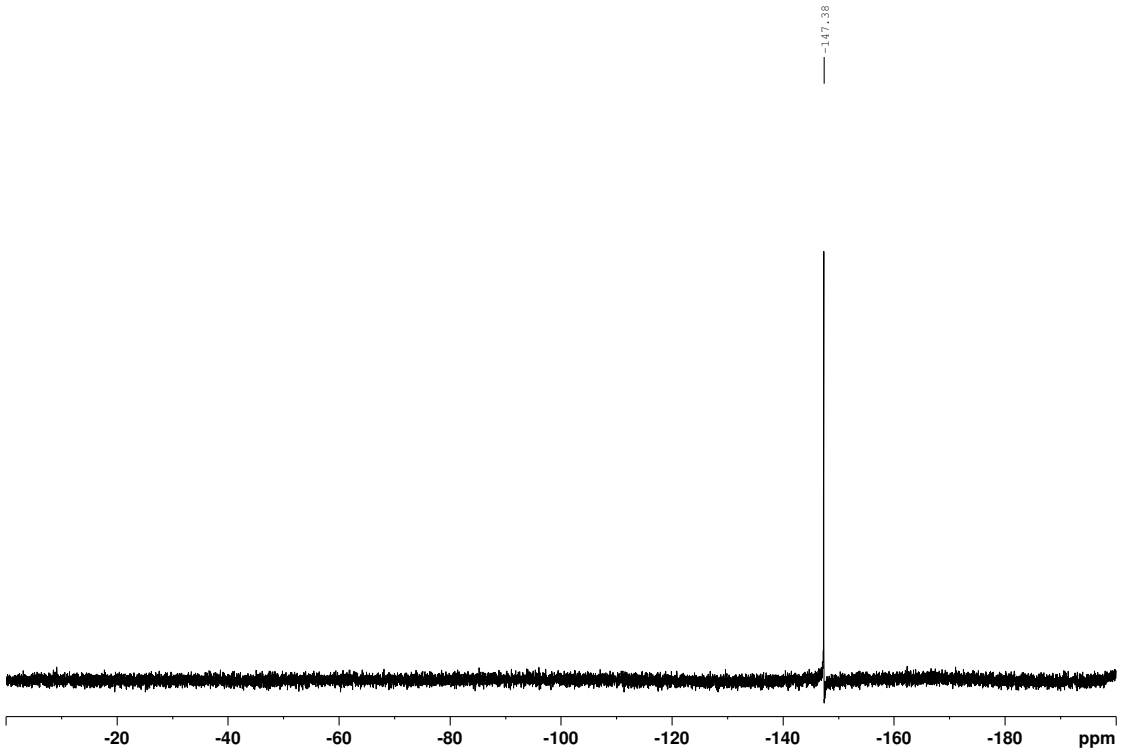
$^{1}$H NMR (300 MHz) Spectrum of **11b**·$BF_4^-$ in $CDCl_3$



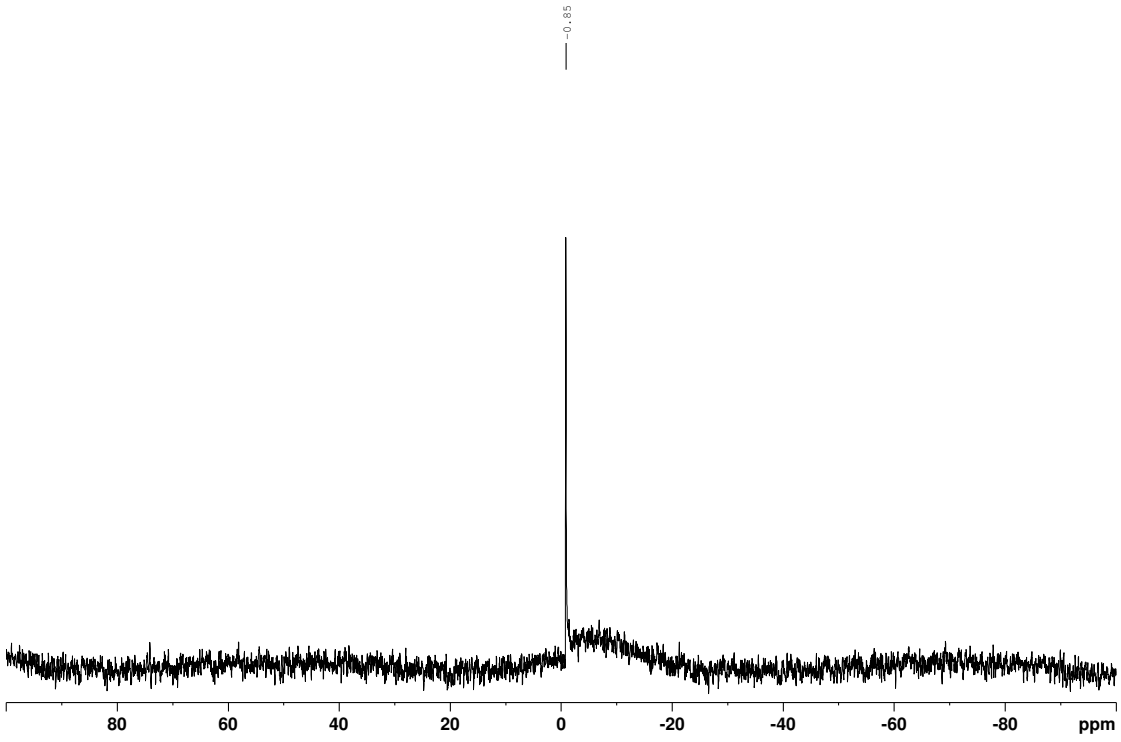

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **11b**·$BF_4^-$ in $CDCl_3$



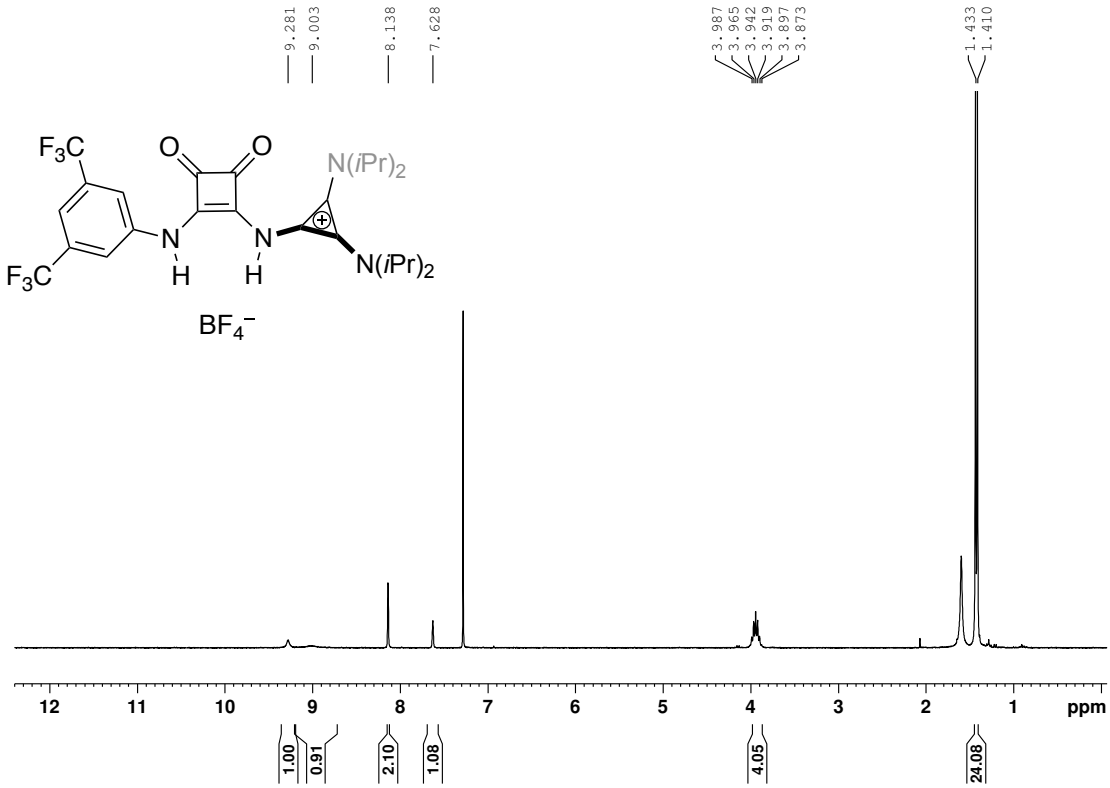
$^{19}F\{^{1}H\}$ NMR (292.4 MHz) Spectrum of **11b**·$BF_4^-$ in $CDCl_3$



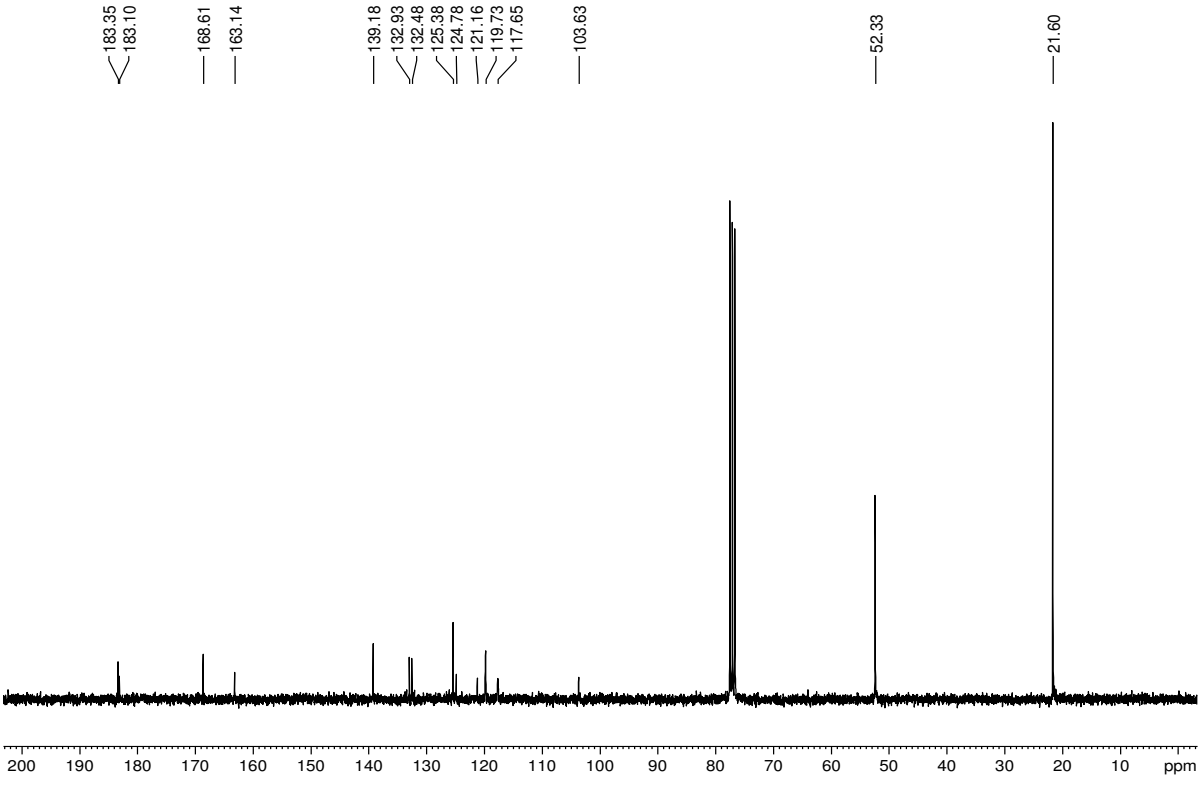

$^{11}B\{^{1}H\}$ NMR (96.3 MHz) Spectrum of **11b**·$BF_4^-$ in $CDCl_3$



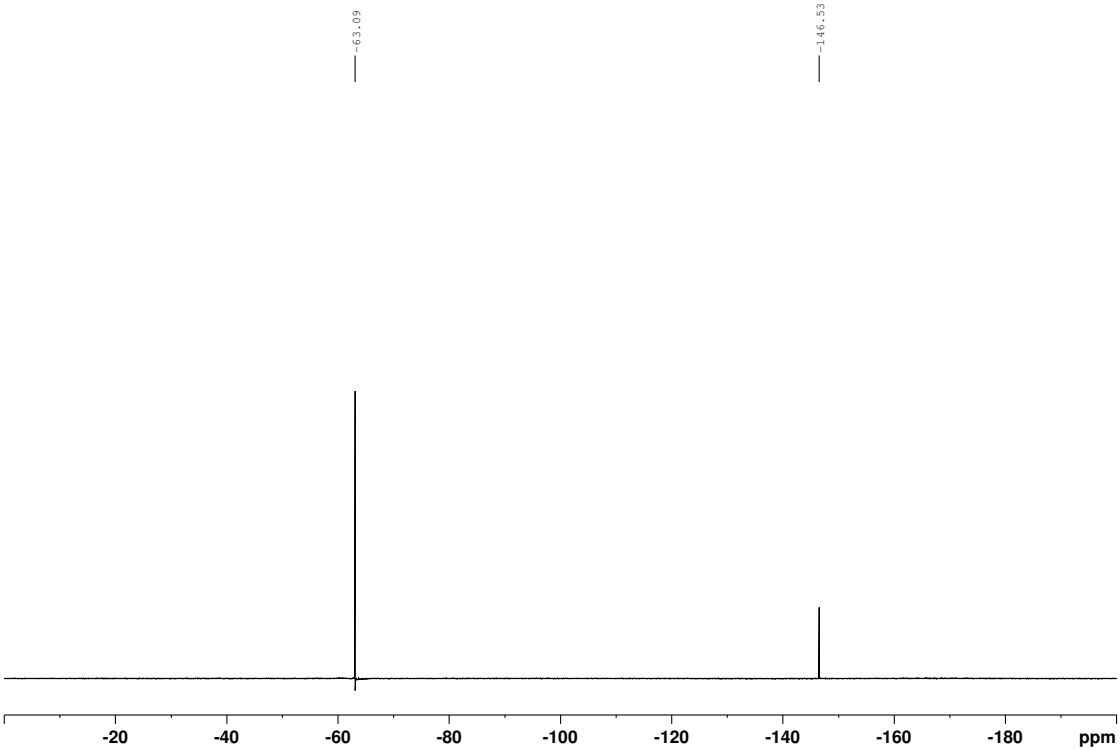
$^{1}$H NMR (300 MHz) Spectrum of **11c**·$BF_4^-$ in $CDCl_3$



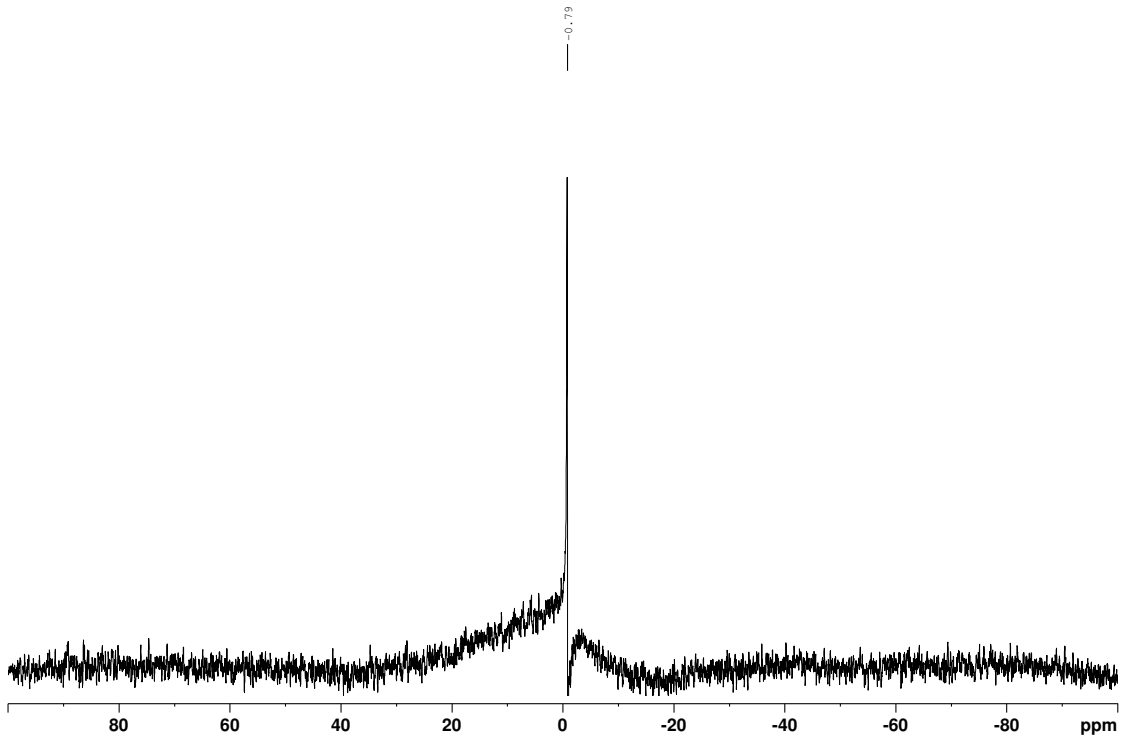

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **11c**·$BF_4^-$ in $CDCl_3$



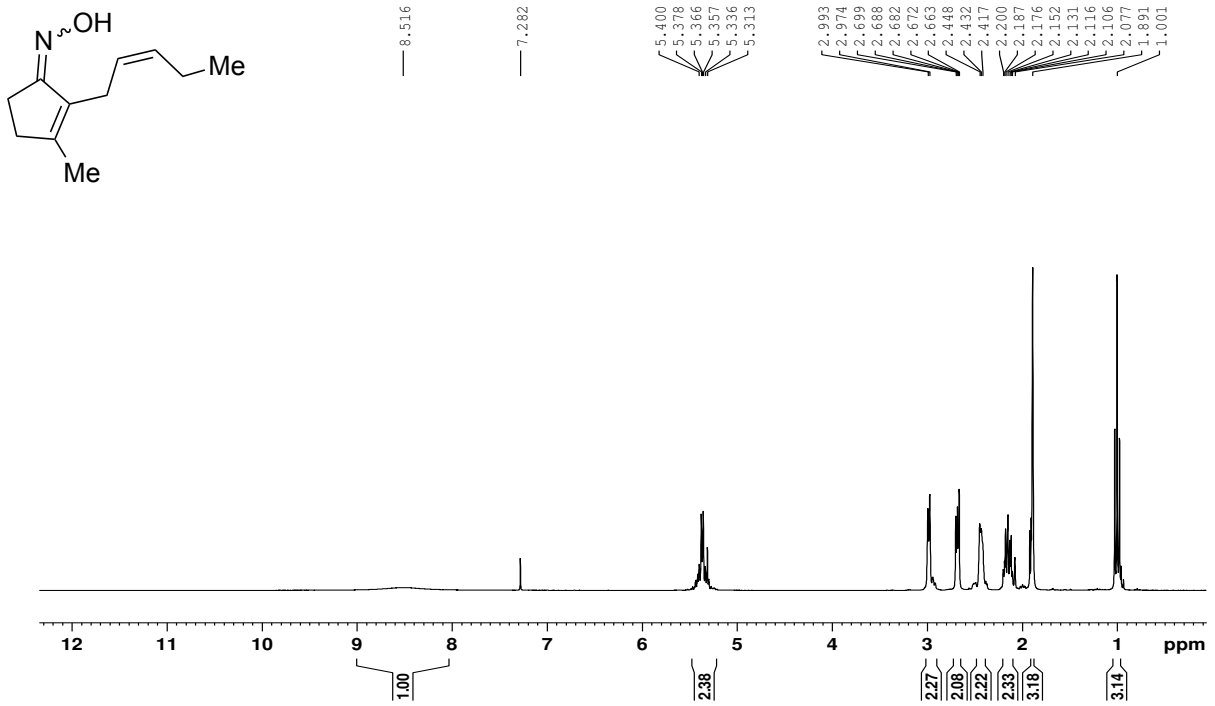
$^{19}F\{^{1}H\}$ NMR (292.4 MHz) Spectrum of **11c**·$BF_4^-$ in $CDCl_3$



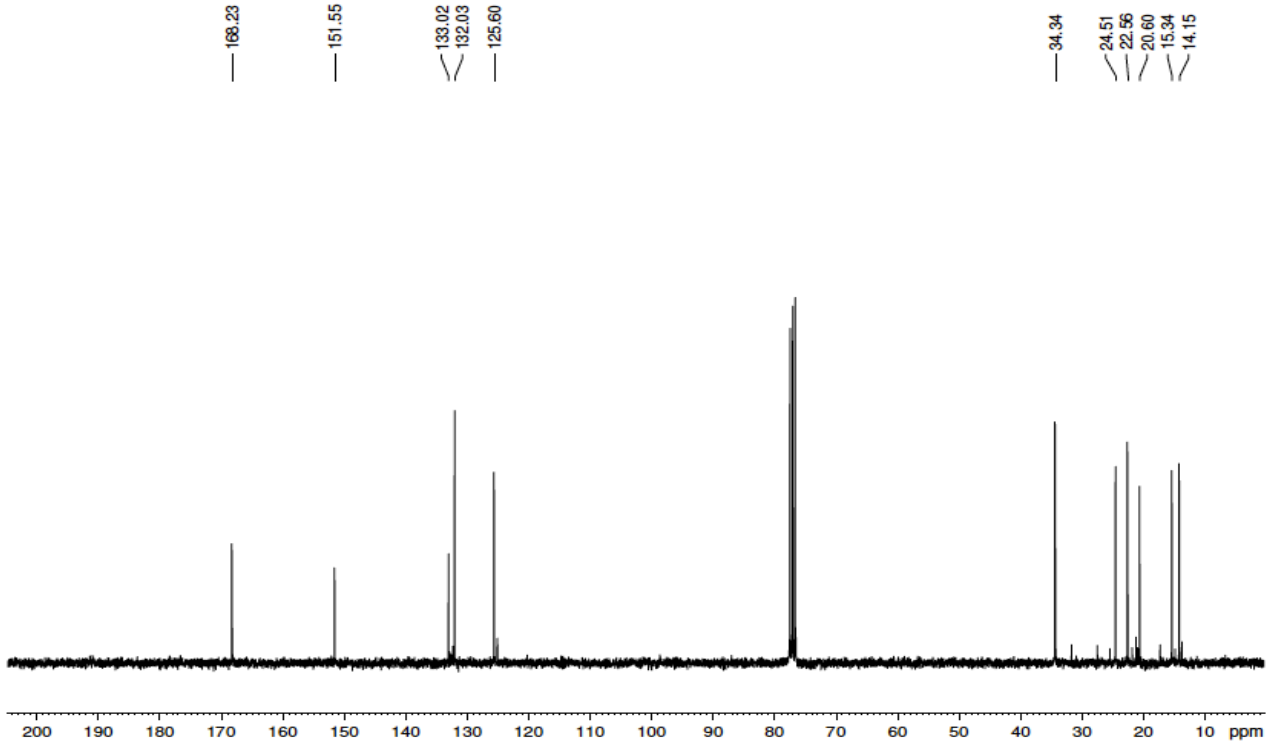

$^{11}B\{^{1}H\}$ NMR (96.3 MHz) Spectrum of **11c**·$BF_4^-$ in $CDCl_3$



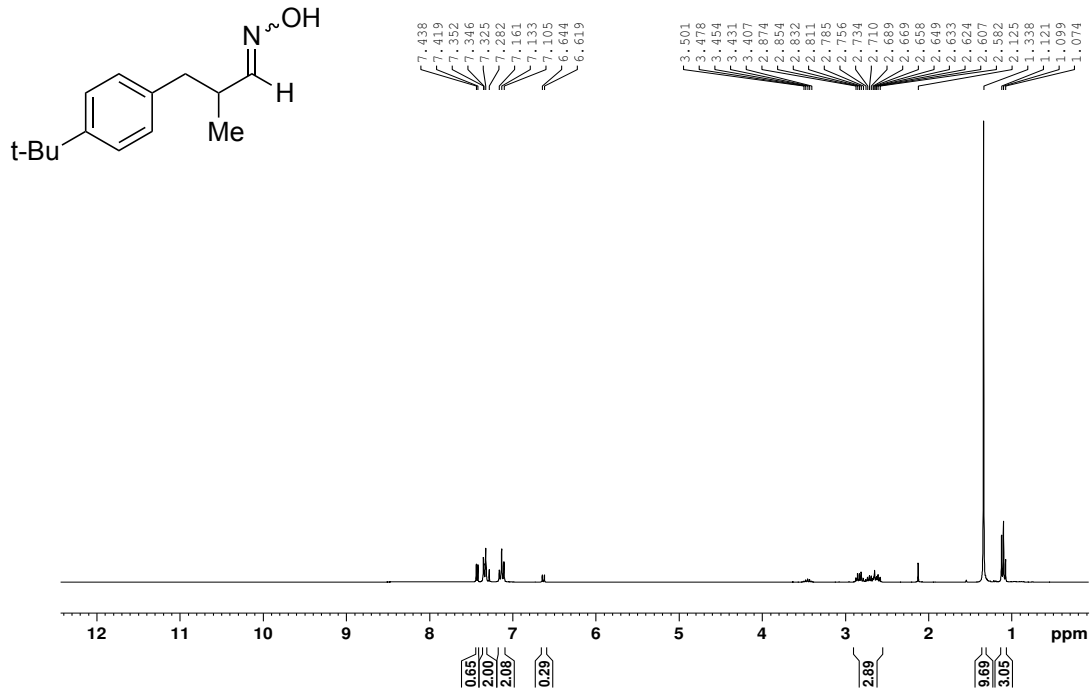
$^{1}$H NMR (300 MHz) Spectrum of **101** in $CDCl_3$



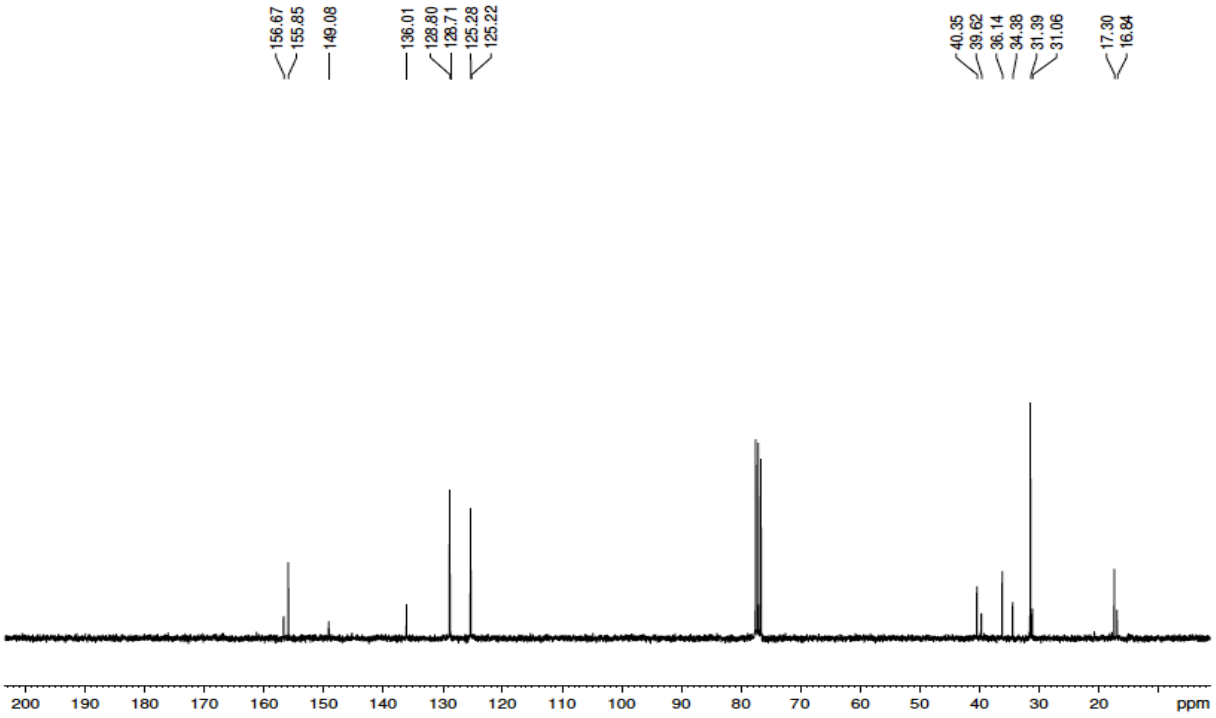

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **101** in $CDCl_3$



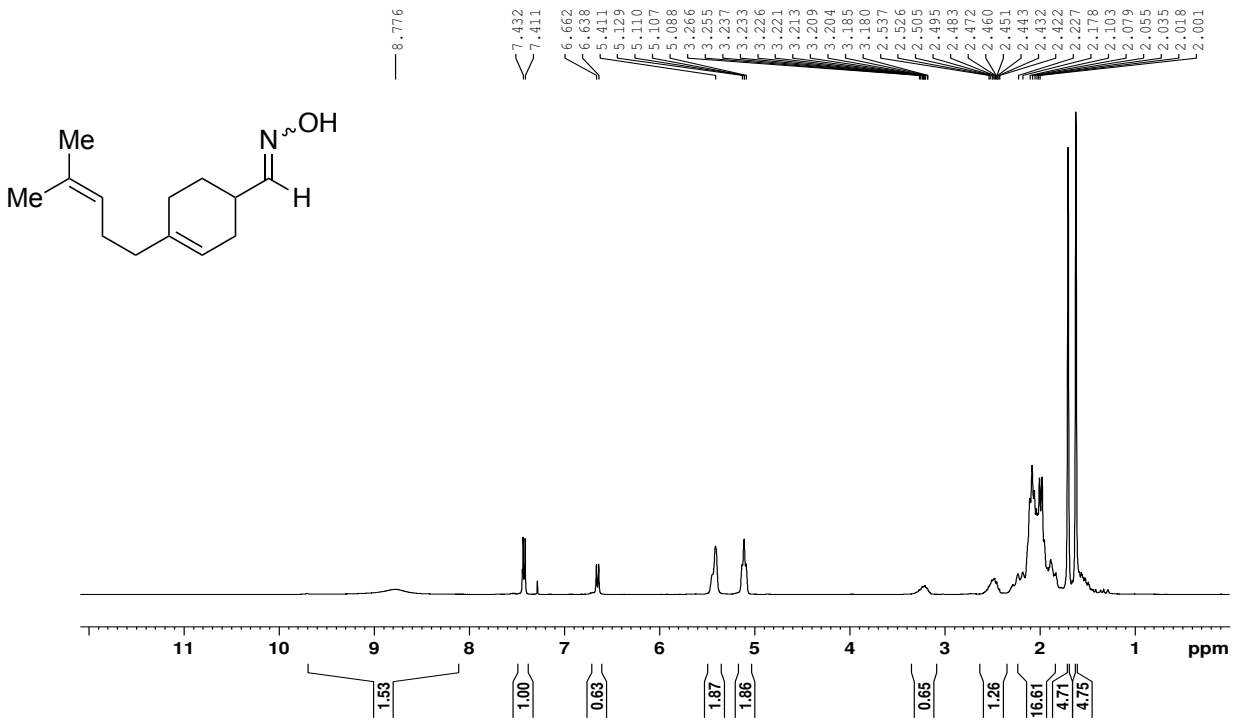
$^{1}$H NMR (300 MHz) Spectrum of **102** in $CDCl_3$



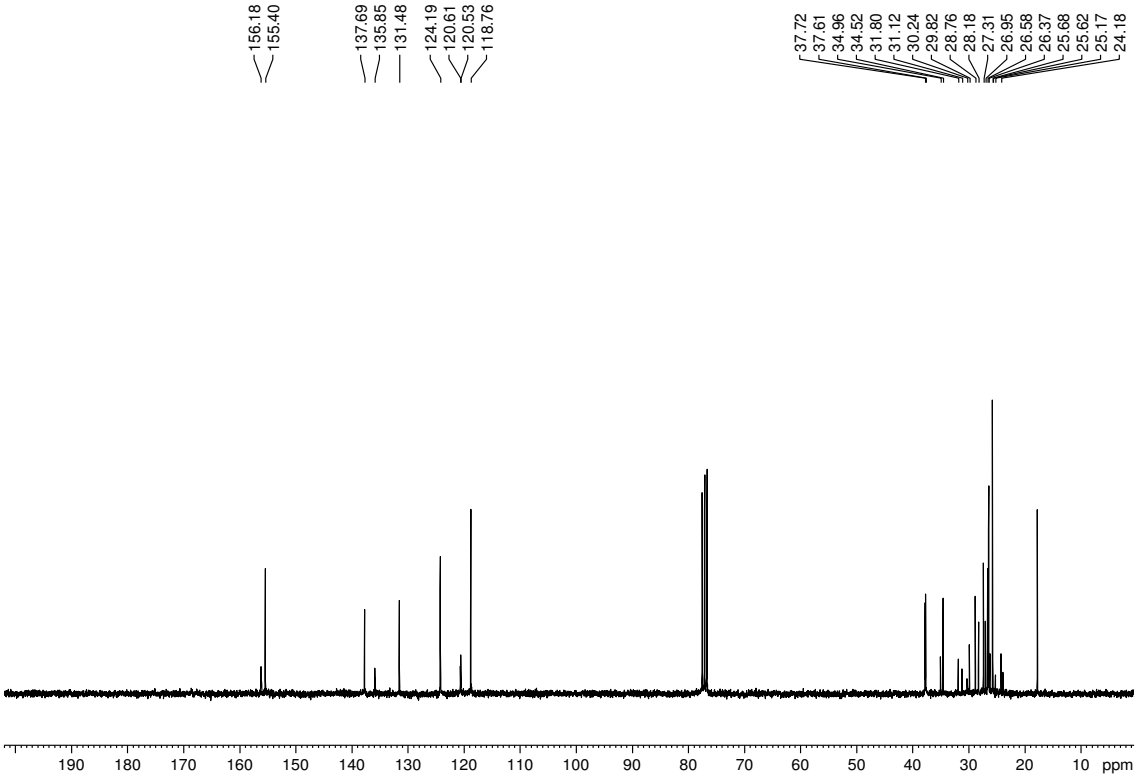

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **102** in $CDCl_3$



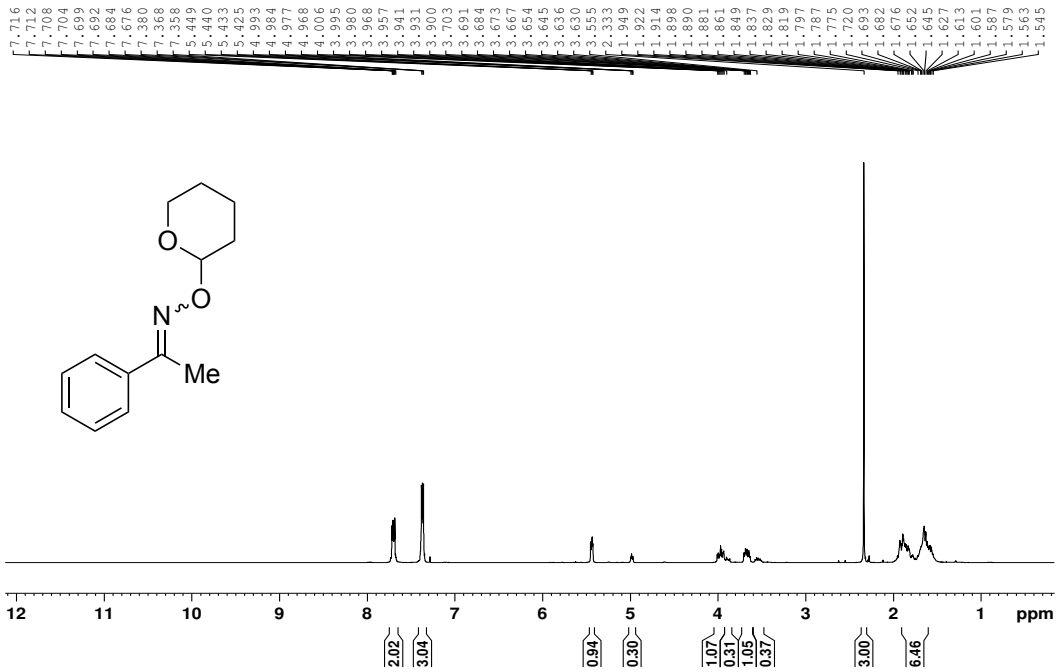
$^{1}$H NMR (300 MHz) Spectrum of **103** in $CDCl_3$



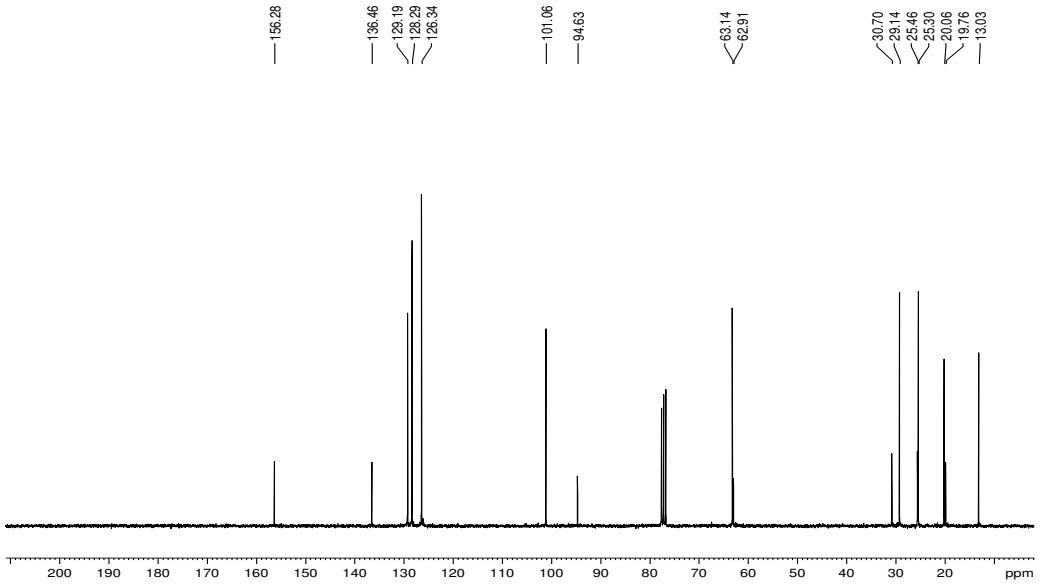

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **103** in $CDCl_3$



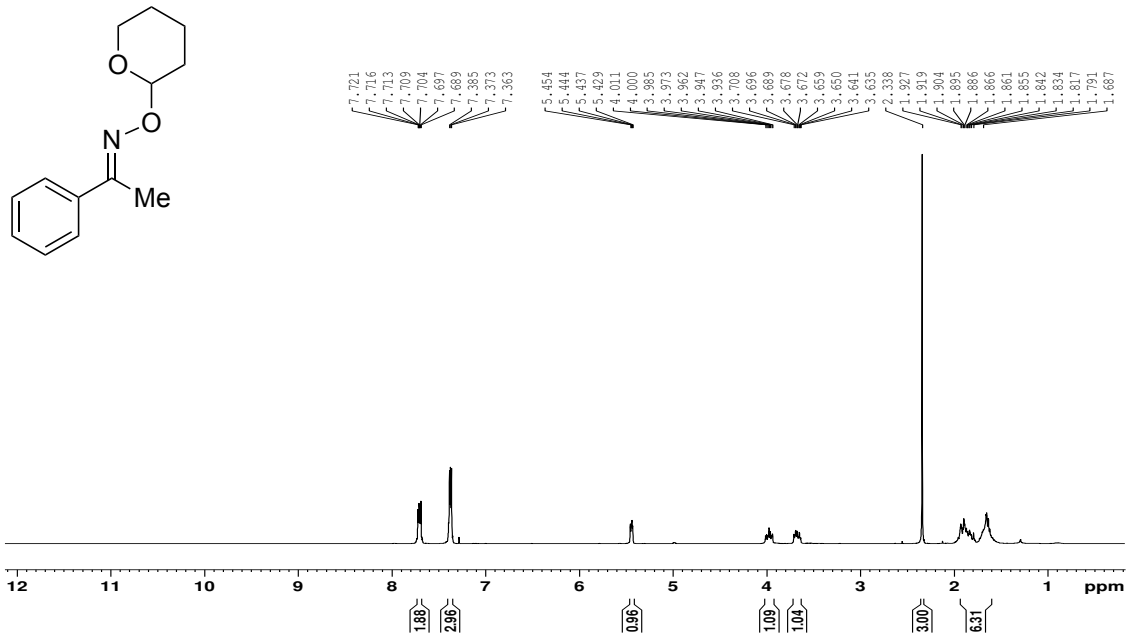
$^{1}$H NMR (300 MHz) Spectrum of a 1:3 *Z*/*E* mixture of **13a** in $CDCl_3$



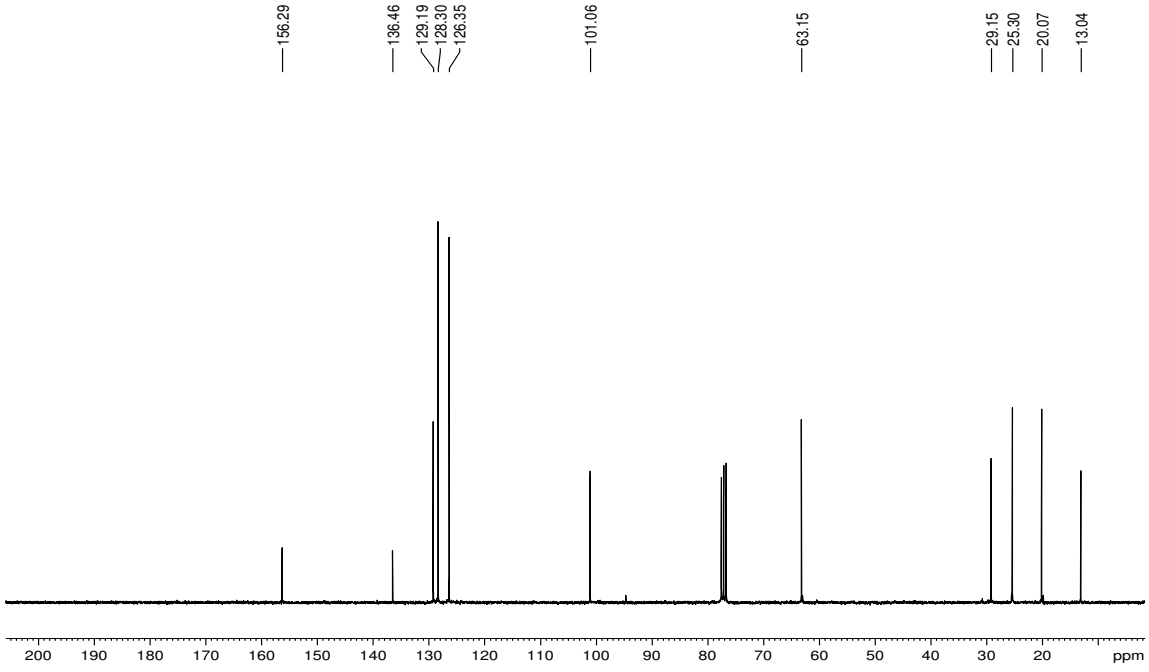

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of a 1:3 *Z*/*E* mixture of **13a** in $CDCl_3$



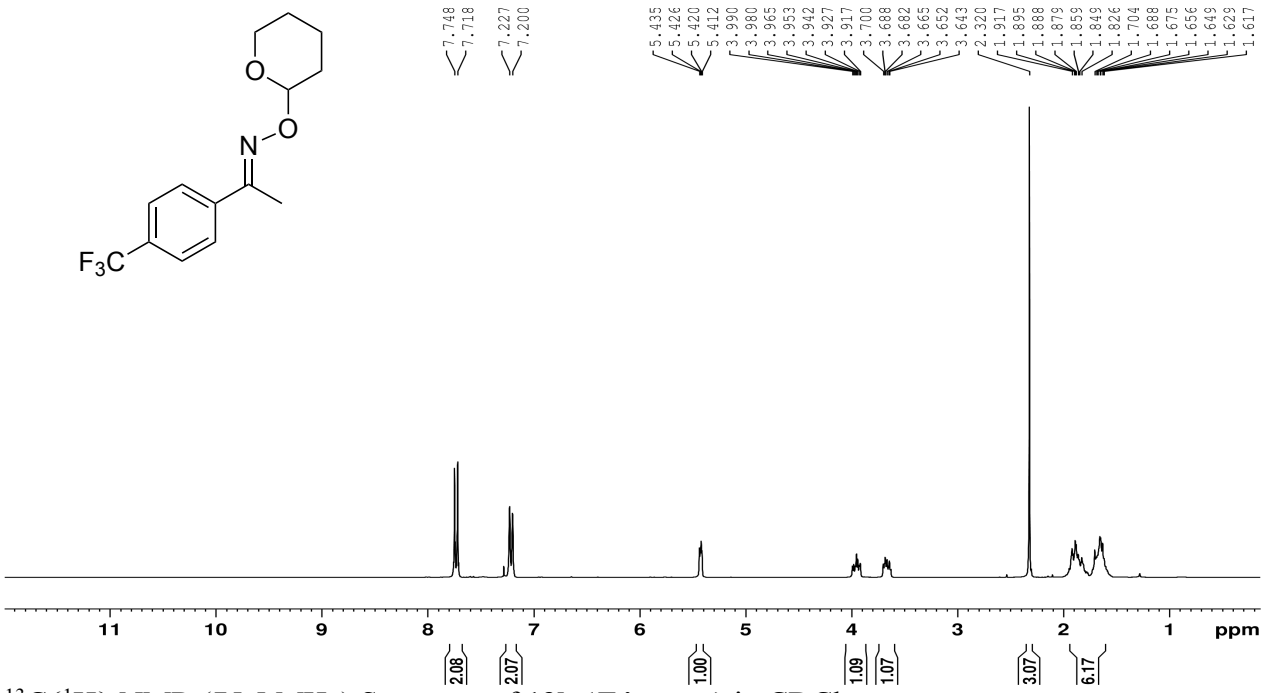
$^{1}$H NMR (300 MHz) Spectrum of **13a (*E* isomer)** in $CDCl_3$



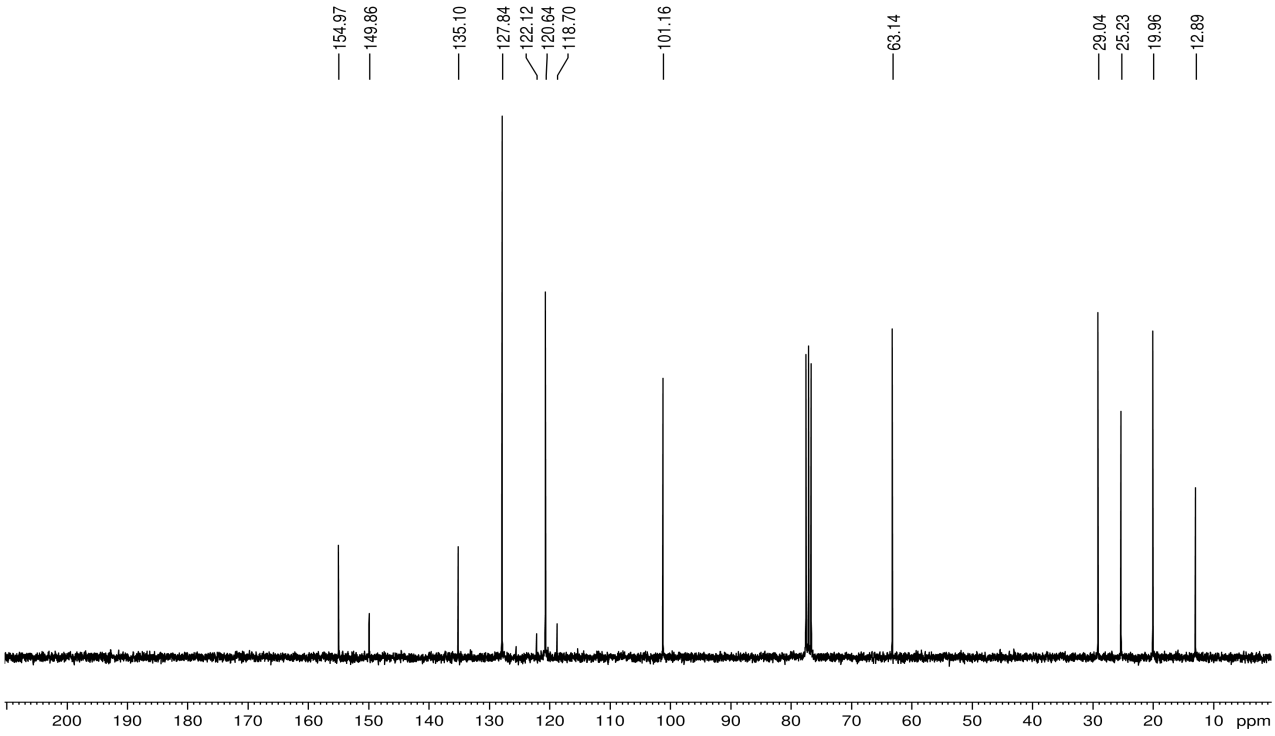

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **13a (*E* isomer)** in $CDCl_3$



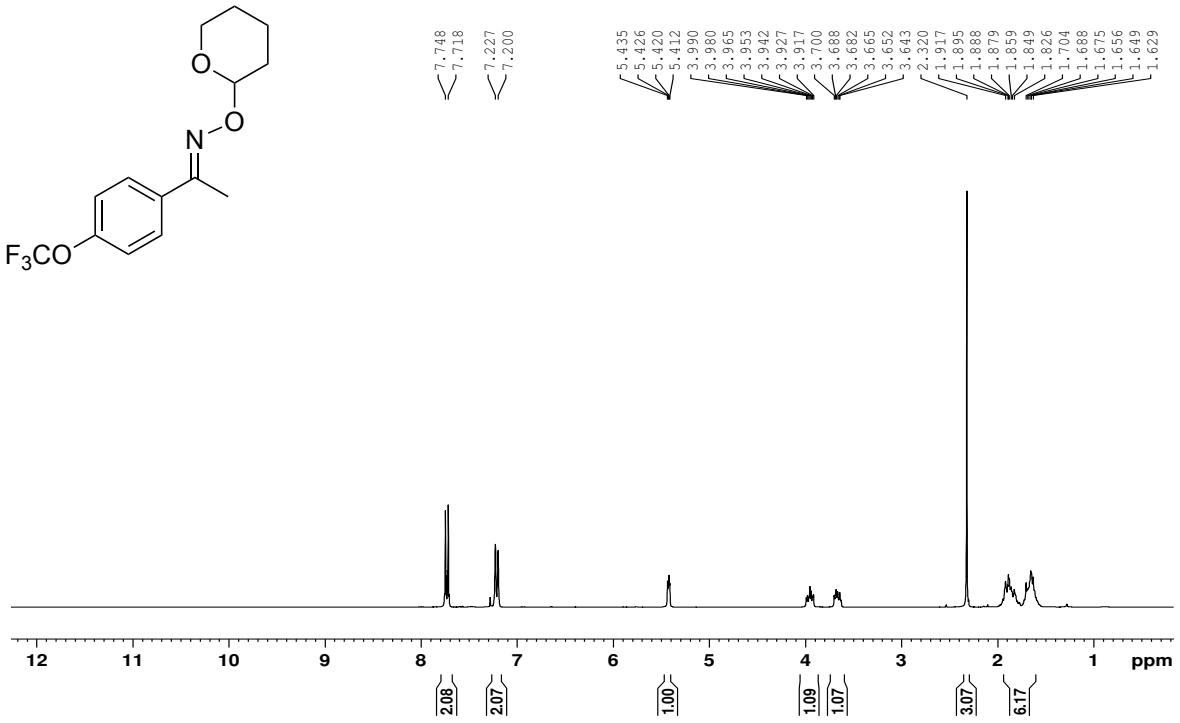
$^{1}$H NMR (300 MHz) Spectrum of **13b (*E* isomer)** in $CDCl_3$



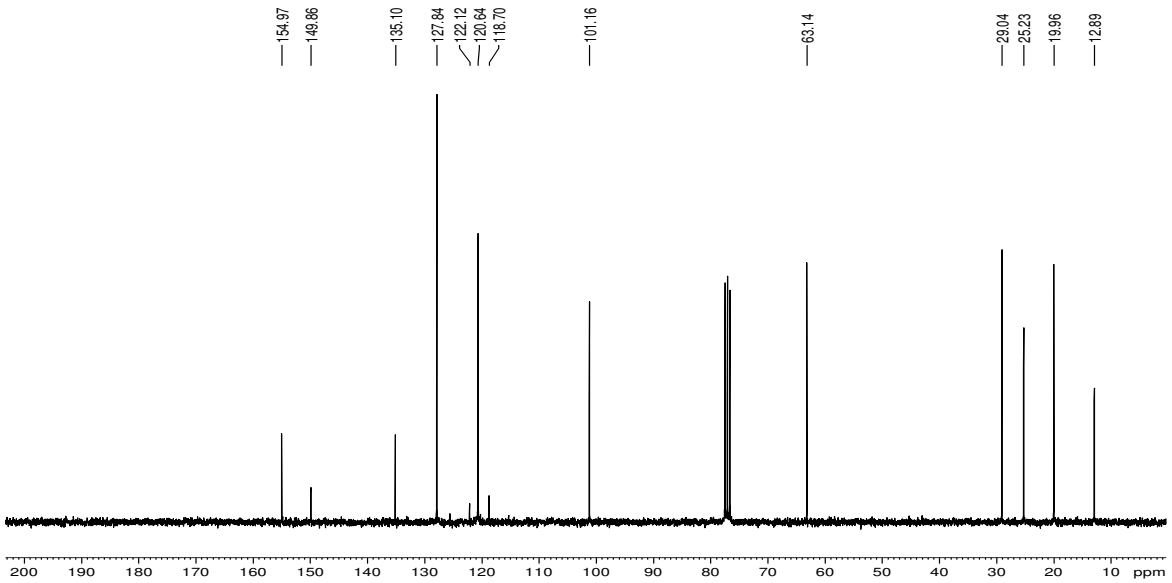

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **13b (*E* isomer)** in $CDCl_3$



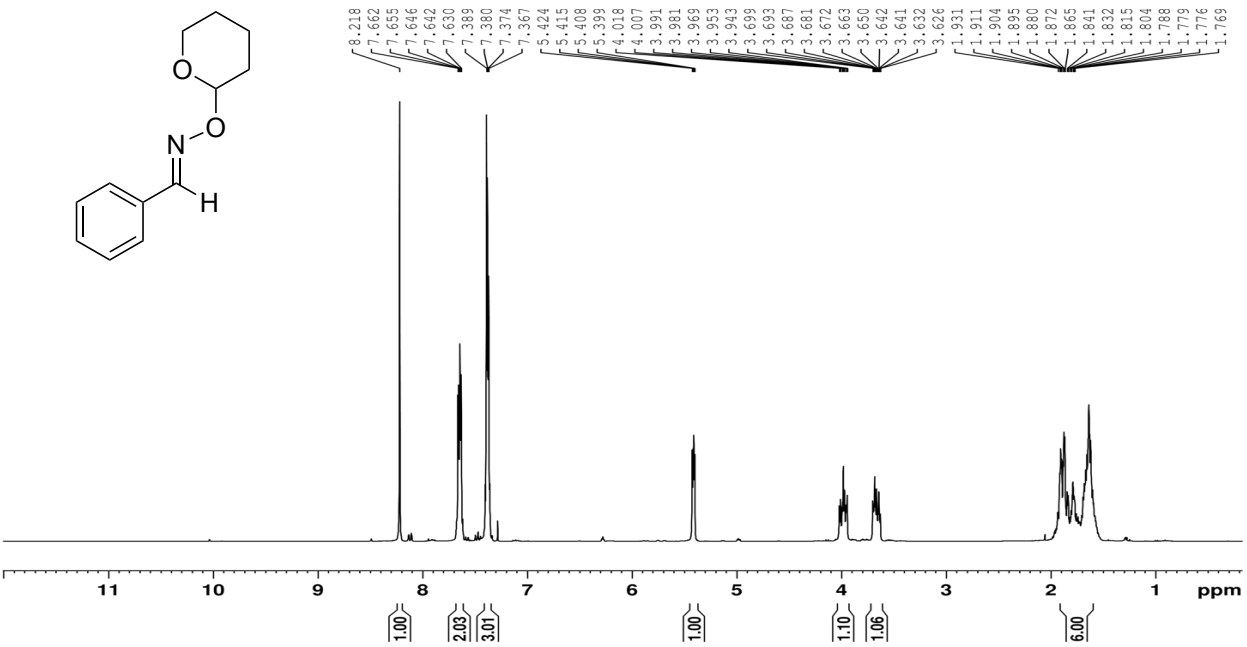
$^{1}$H NMR (300 MHz) Spectrum of **13c (*E* isomer)** in $CDCl_3$



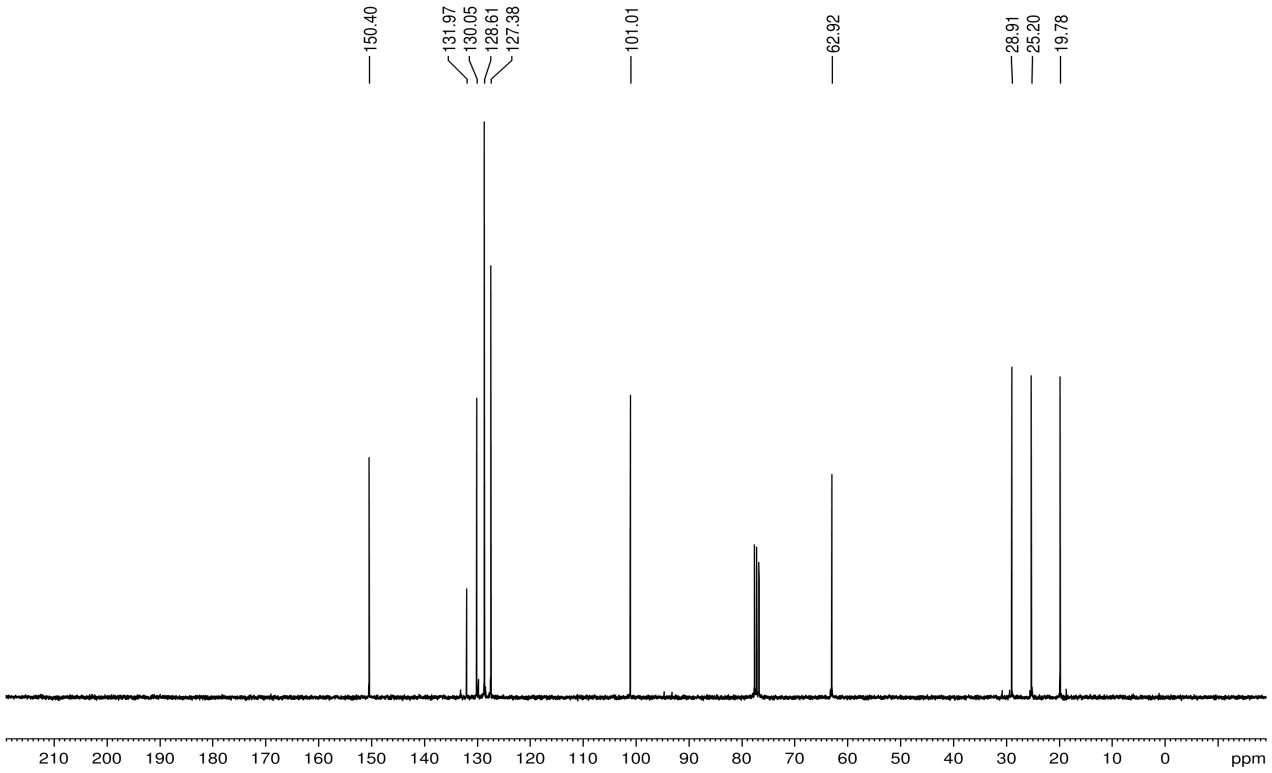

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **13c (*E* isomer)** in $CDCl_3$



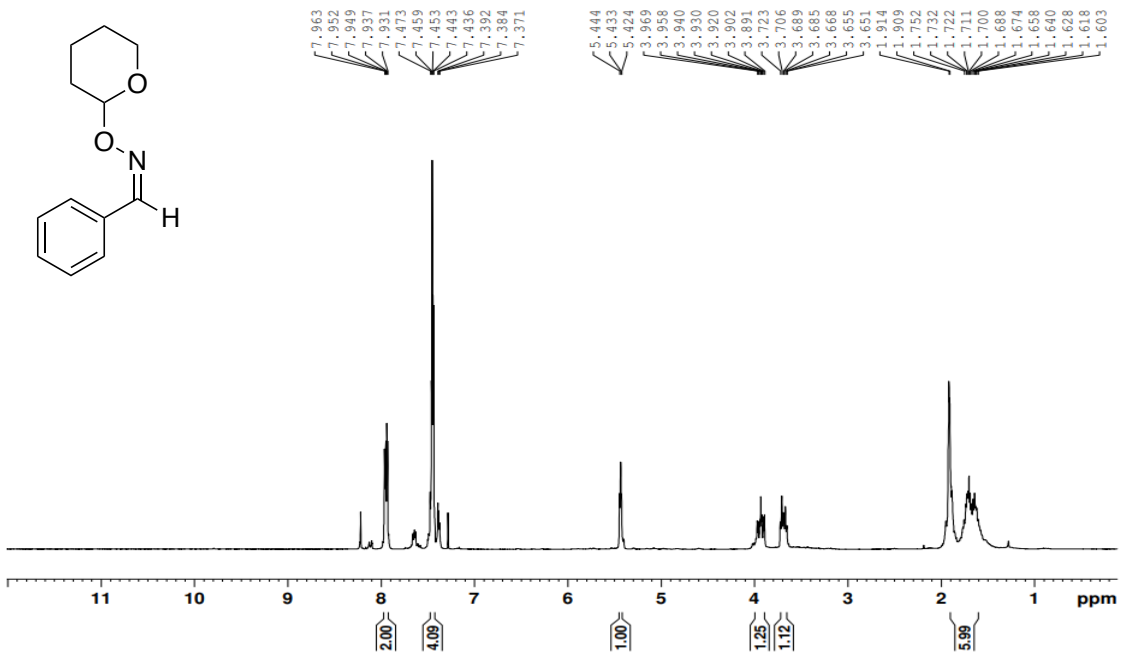
$^{1}$H NMR (300 MHz) Spectrum of **13d (*E* isomer)** in $CDCl_3$



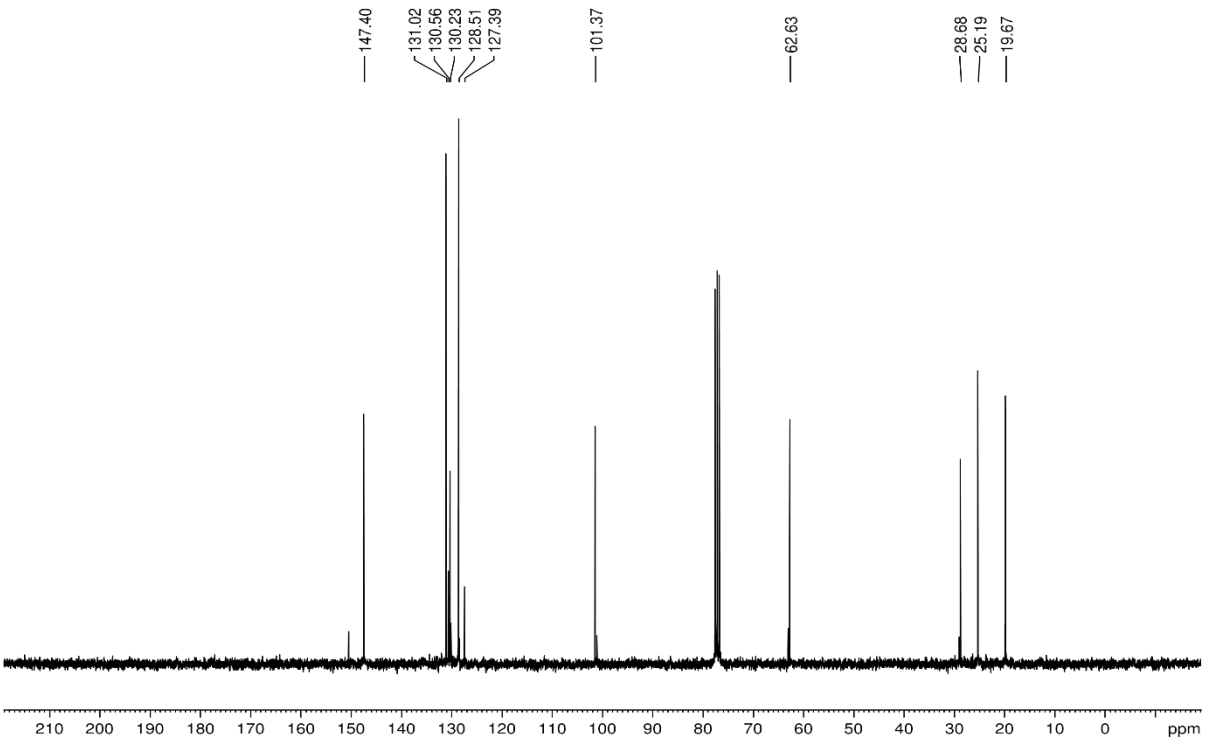

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **13d (*E* isomer)** in $CDCl_3$



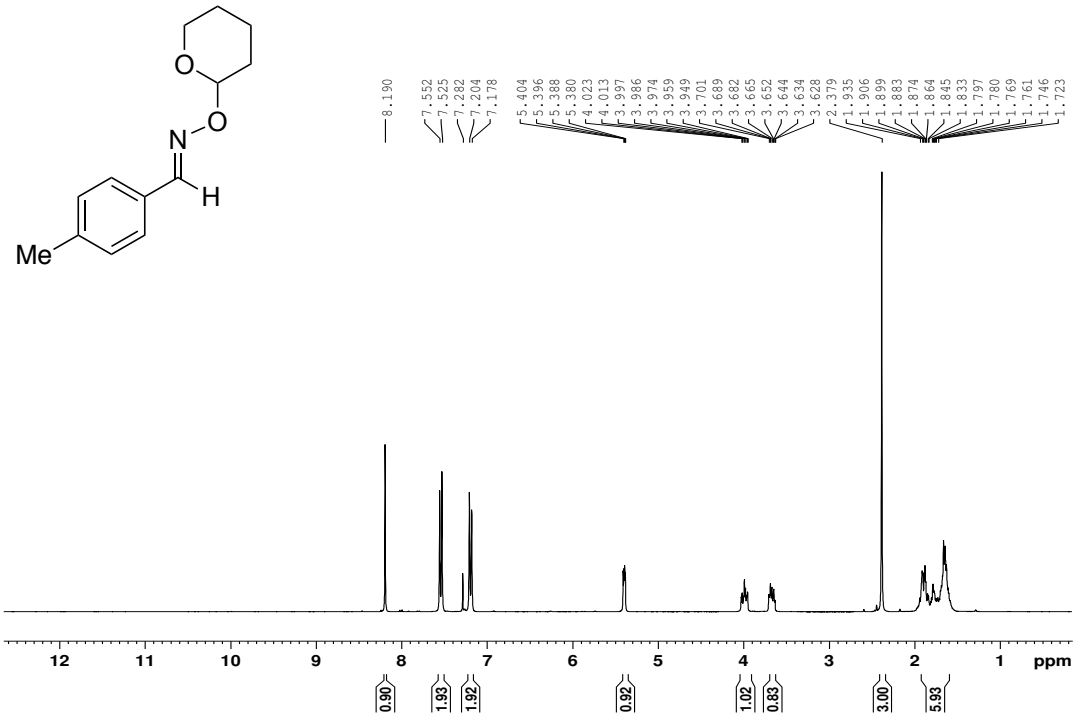
$^{1}$H NMR (300 MHz) Spectrum of **13d (*Z* isomer)** in $CDCl_3$



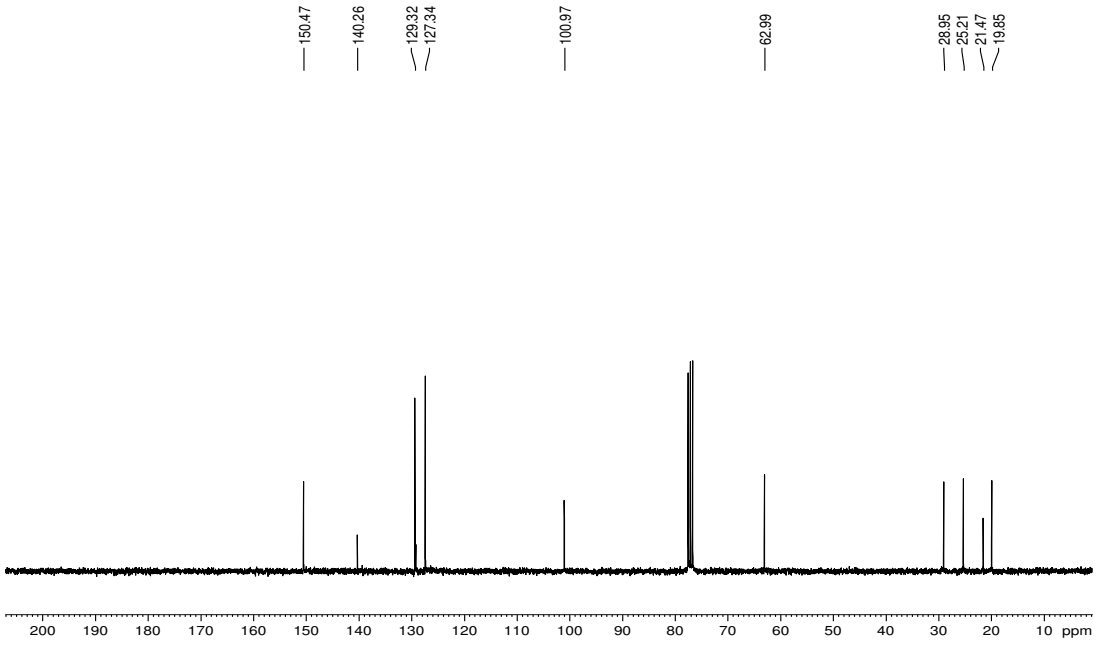

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **13d (*Z* isomer)** in $CDCl_3$



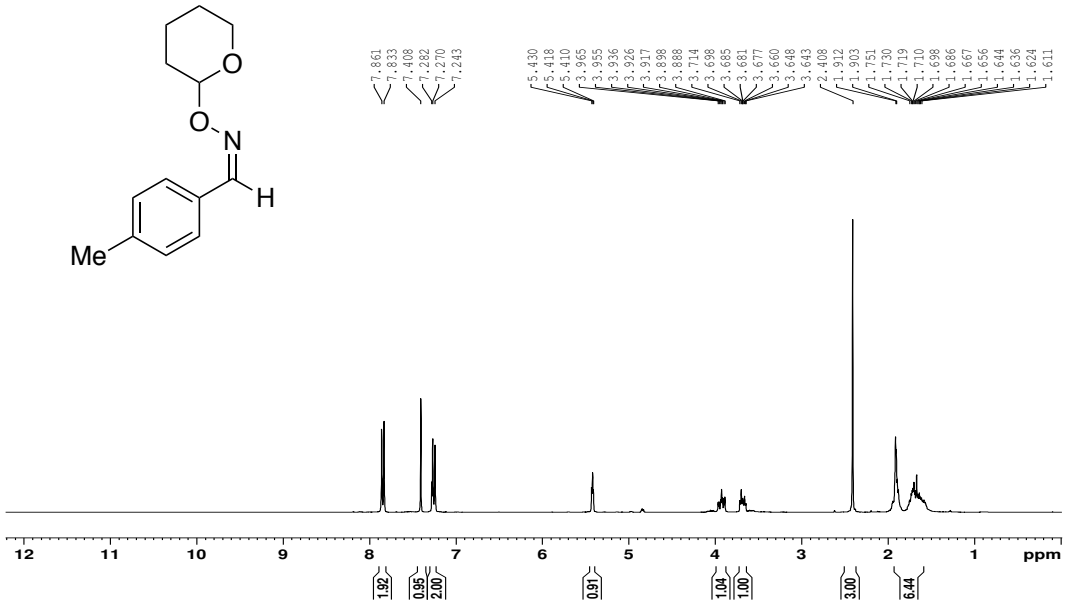
$^{1}$H NMR (300 MHz) Spectrum of **13e (*E* isomer)** in $CDCl_3$



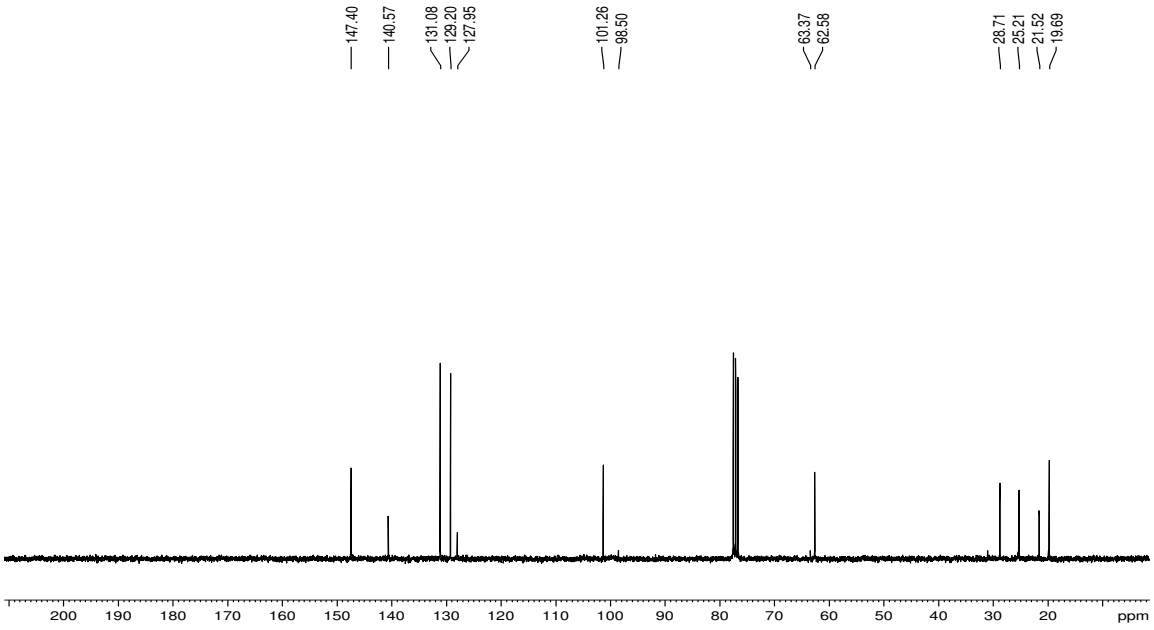

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **13e (*E* isomer)** in $CDCl_3$



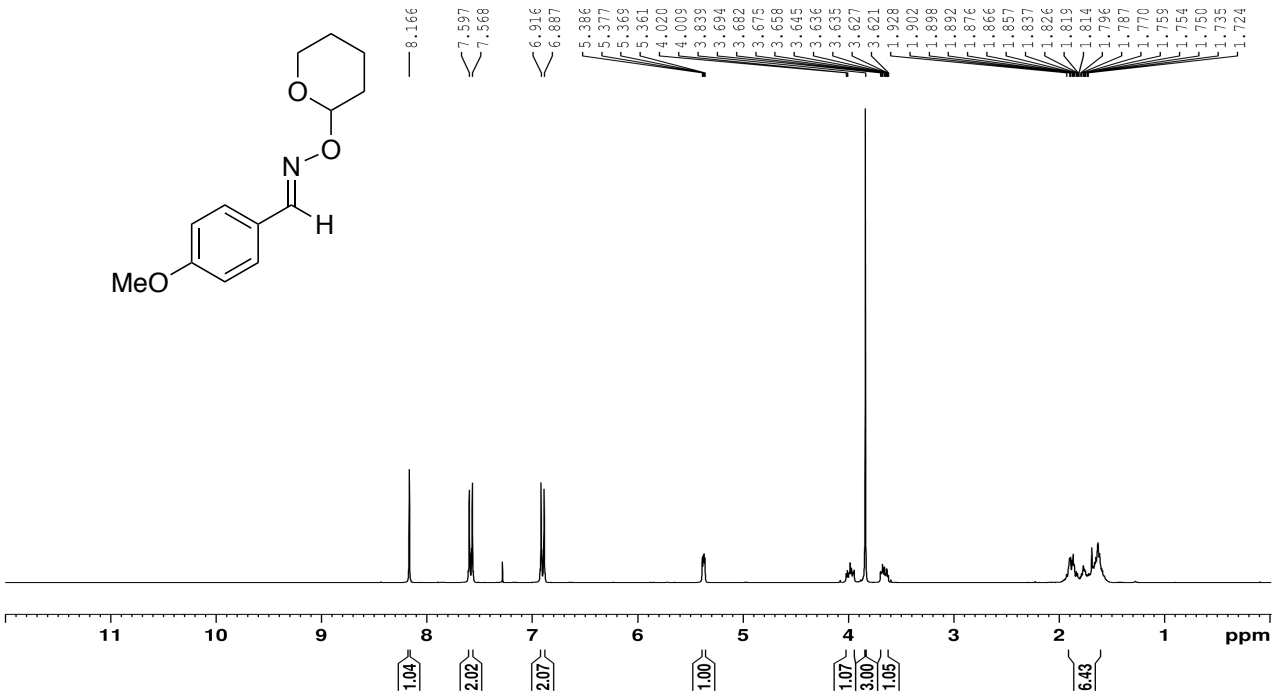
$^{1}$H NMR (300 MHz) Spectrum of **13e (*Z* isomer)** in $CDCl_3$



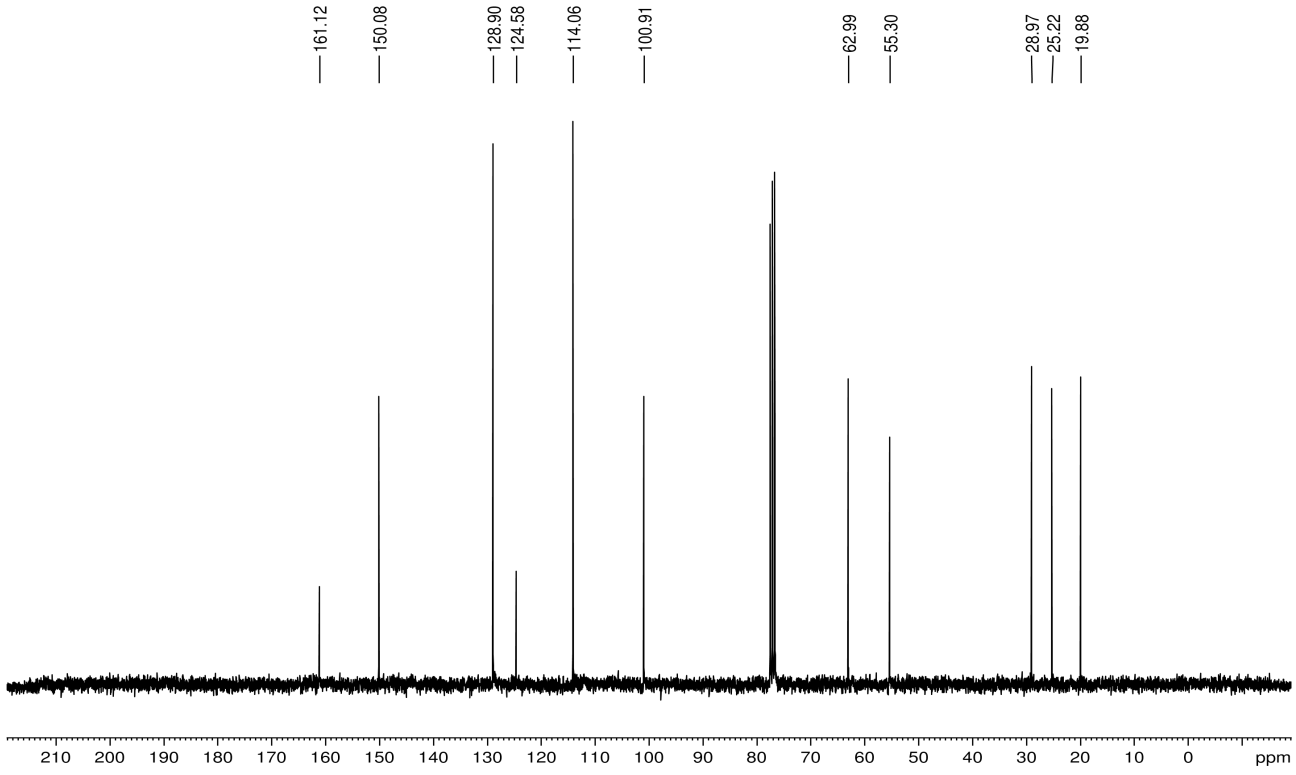

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **13e (*Z* isomer)** in $CDCl_3$



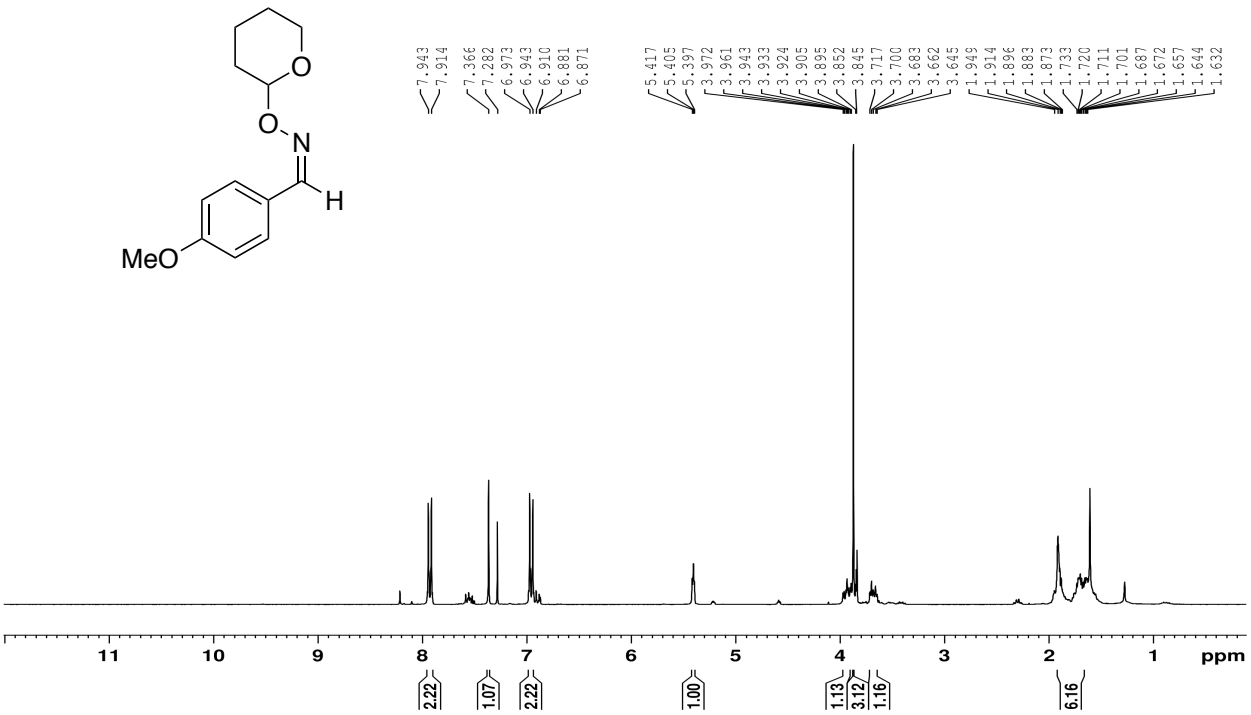
$^{1}$H NMR (300 MHz) Spectrum of **13f (*E* isomer)** in $CDCl_3$



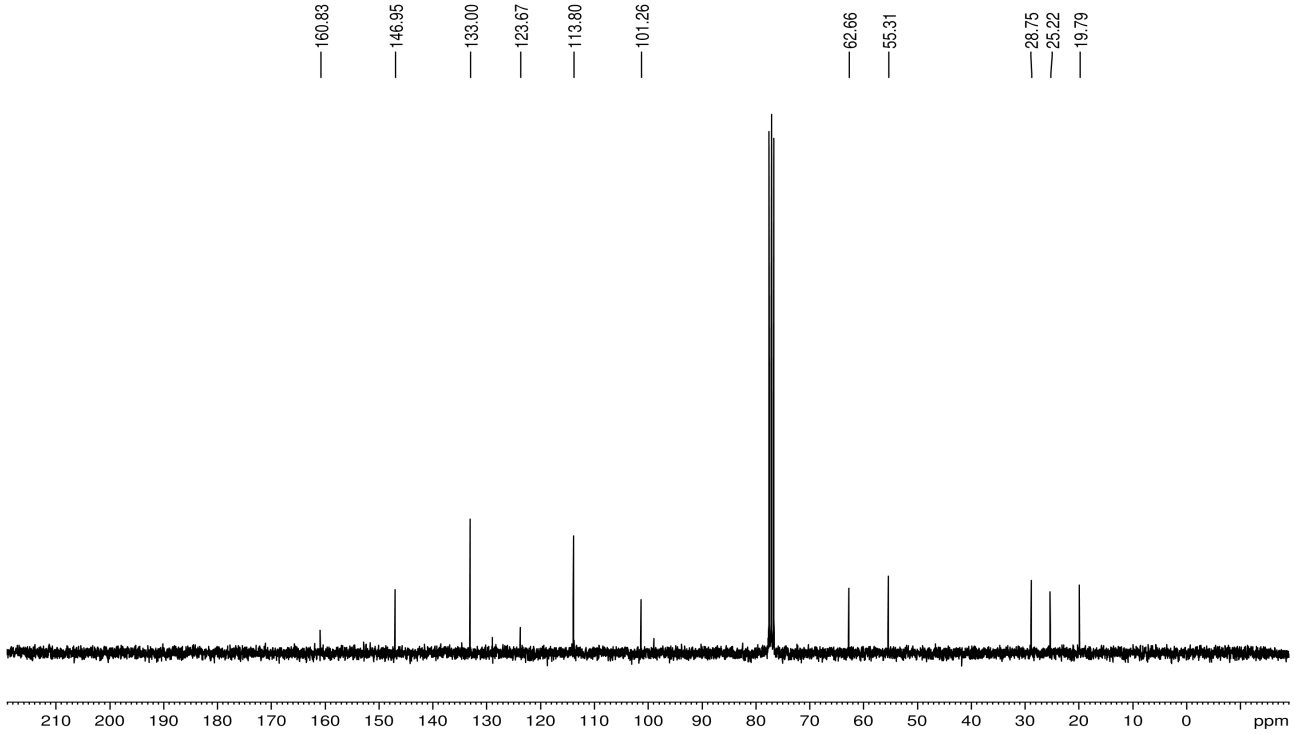

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **13f (*E* isomer)** in $CDCl_3$



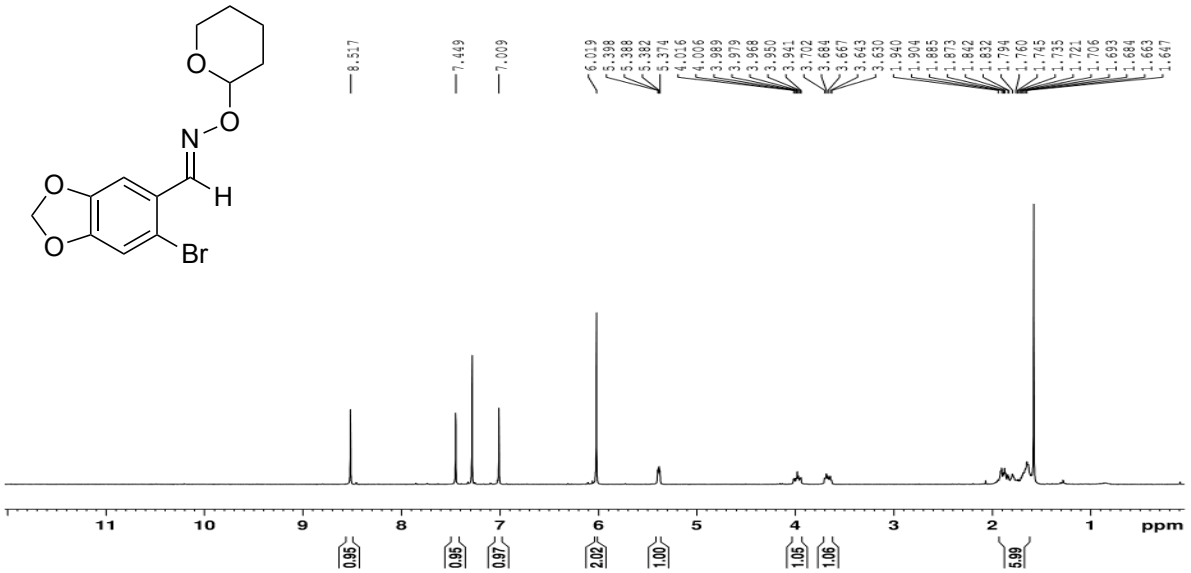
$^{1}$H NMR (300 MHz) Spectrum of **13f (*Z* isomer)** in $CDCl_3$



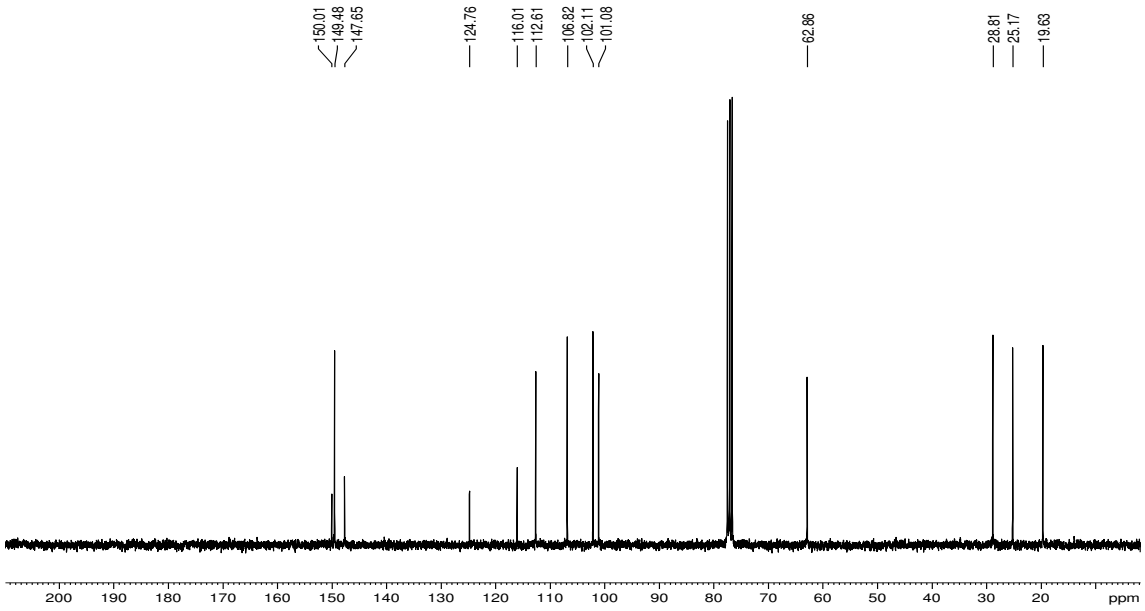

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **13f (*Z* isomer)** in $CDCl_3$



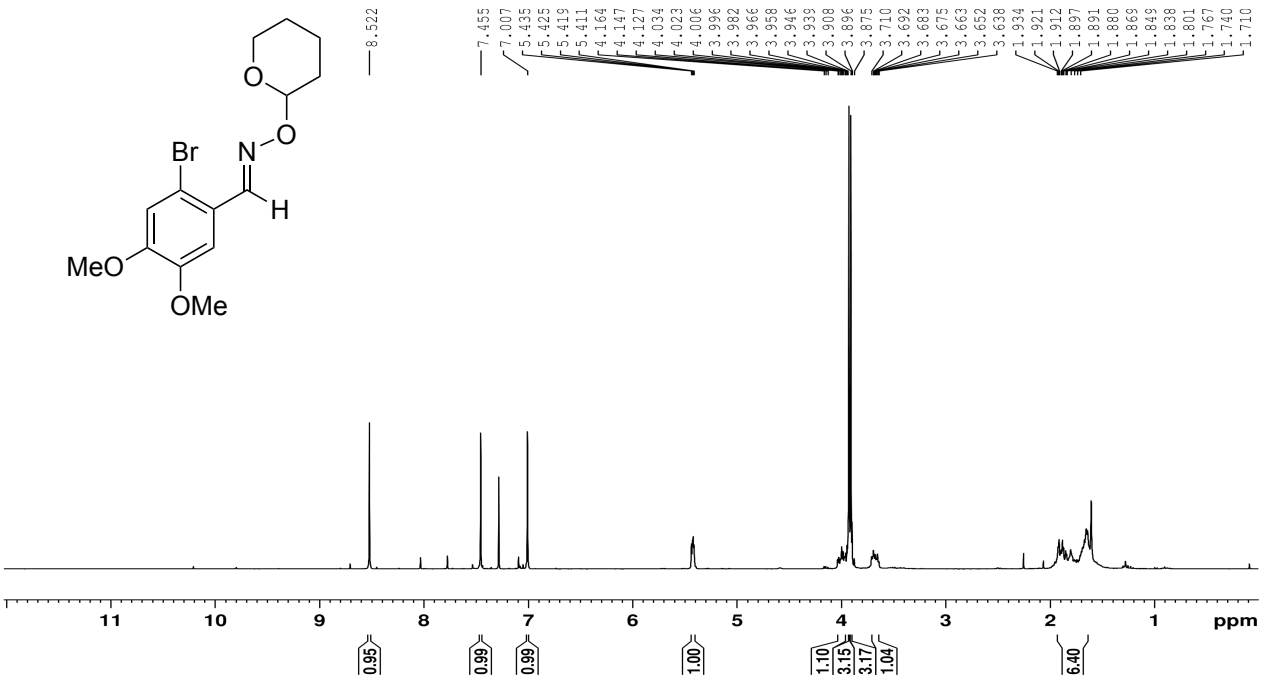
$^{1}$H NMR (300 MHz) Spectrum of **13g (*E* isomer)** in $CDCl_3$



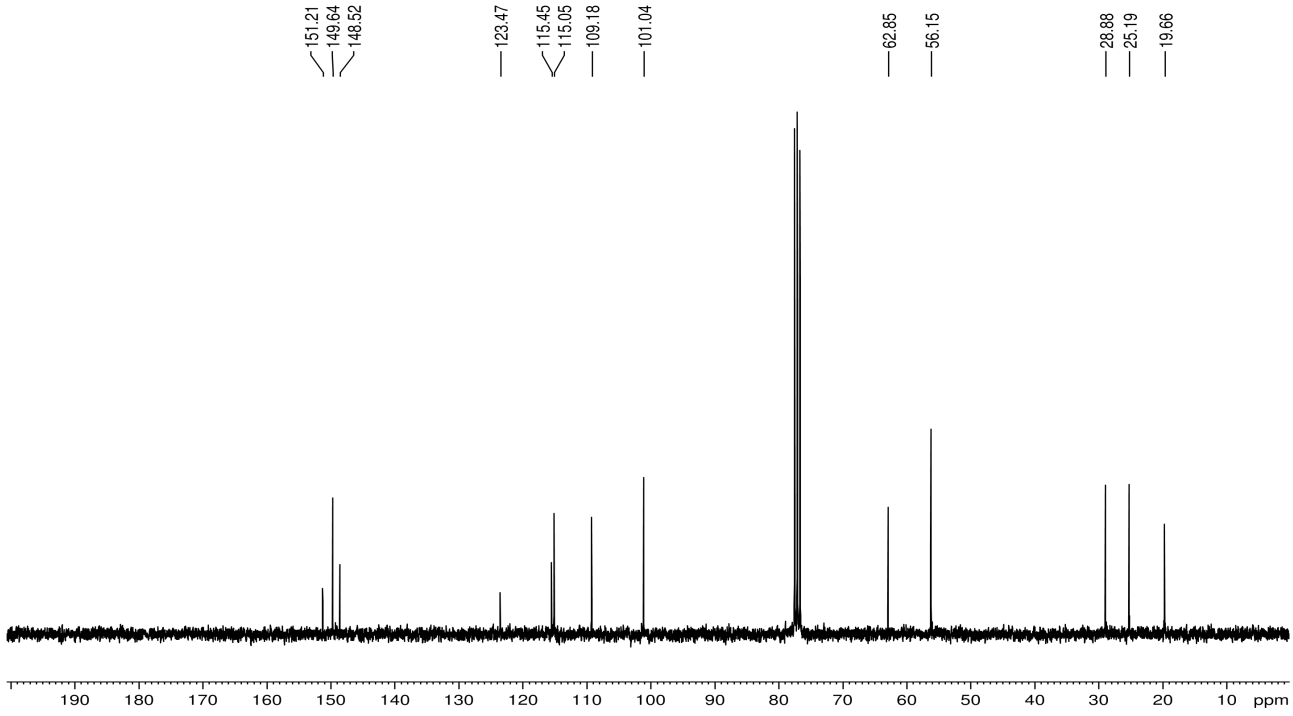

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **13g (*E* isomer)** in $CDCl_3$



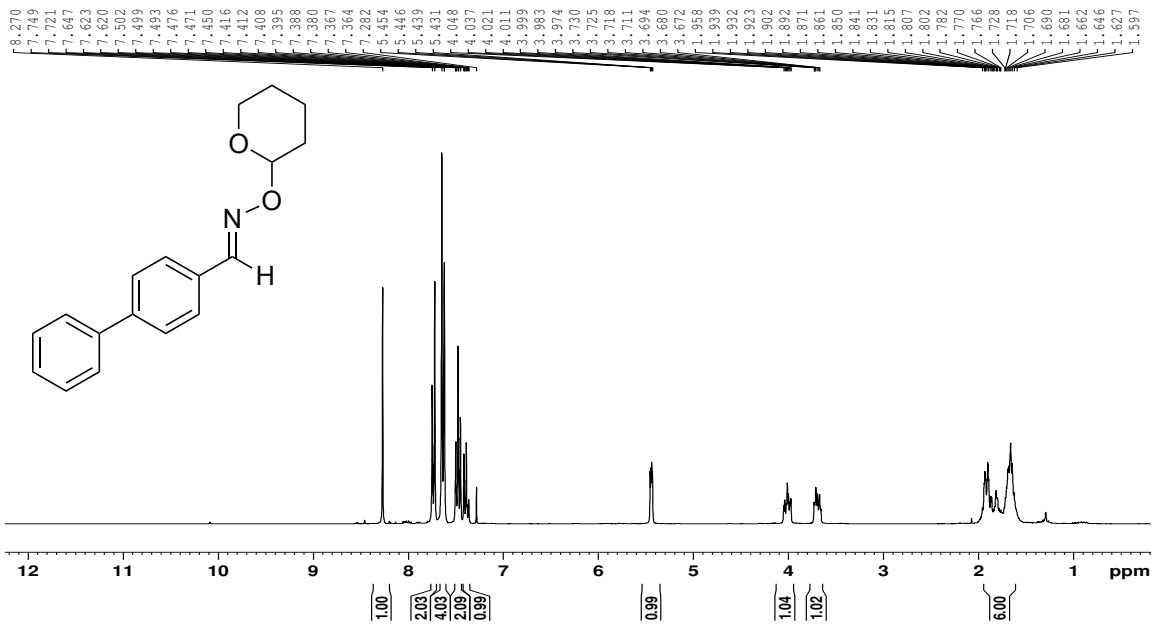
$^{1}$H NMR (300 MHz) Spectrum of **13h (*E* isomer)** in $CDCl_3$



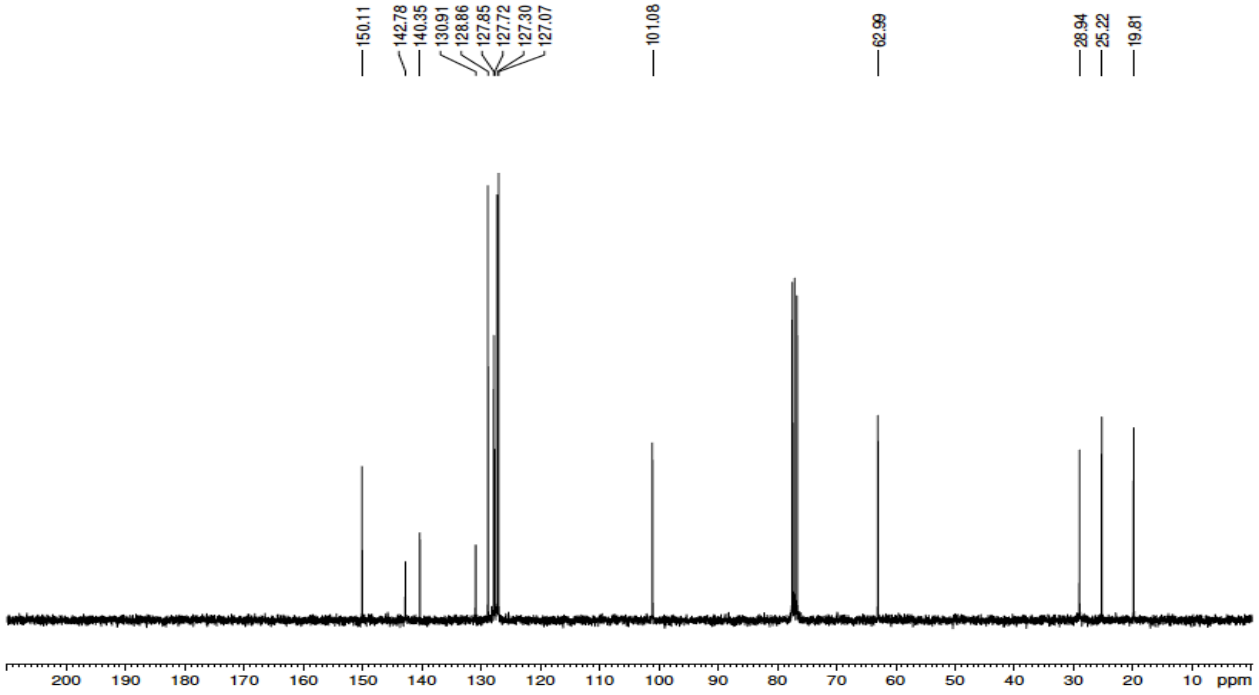

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **13h (*E* isomer)** in $CDCl_3$



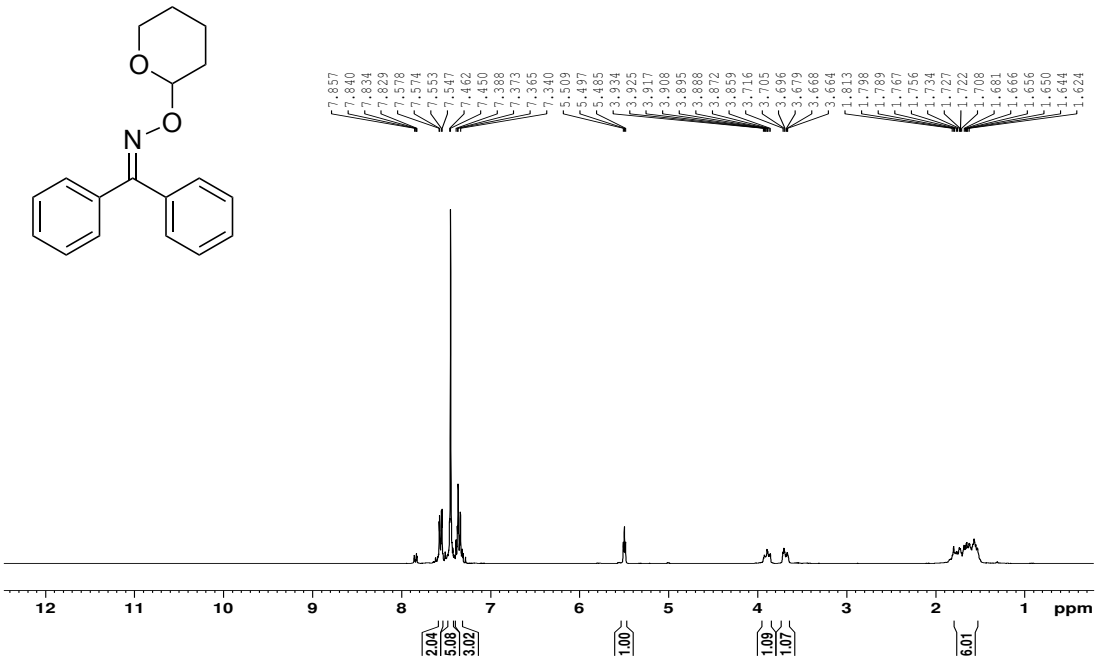
$^{1}$H NMR (300 MHz) Spectrum of **13i (*E* isomer)** in $CDCl_3$



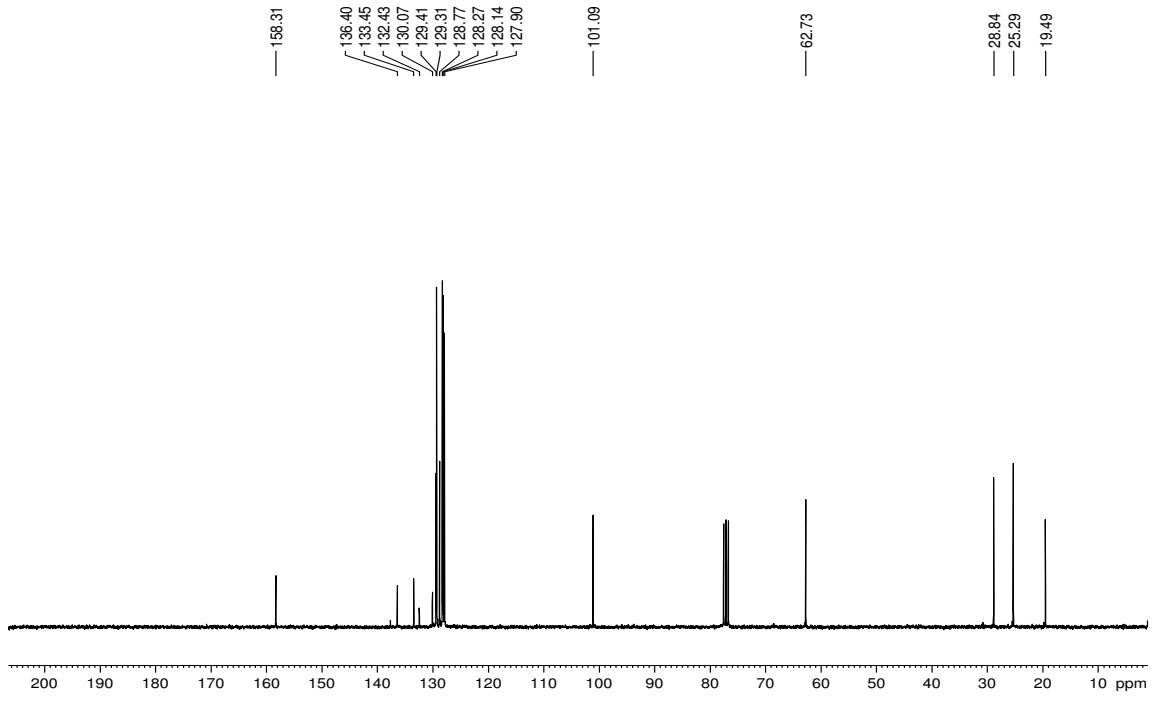

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **13i (*E* isomer)** in $CDCl_3$



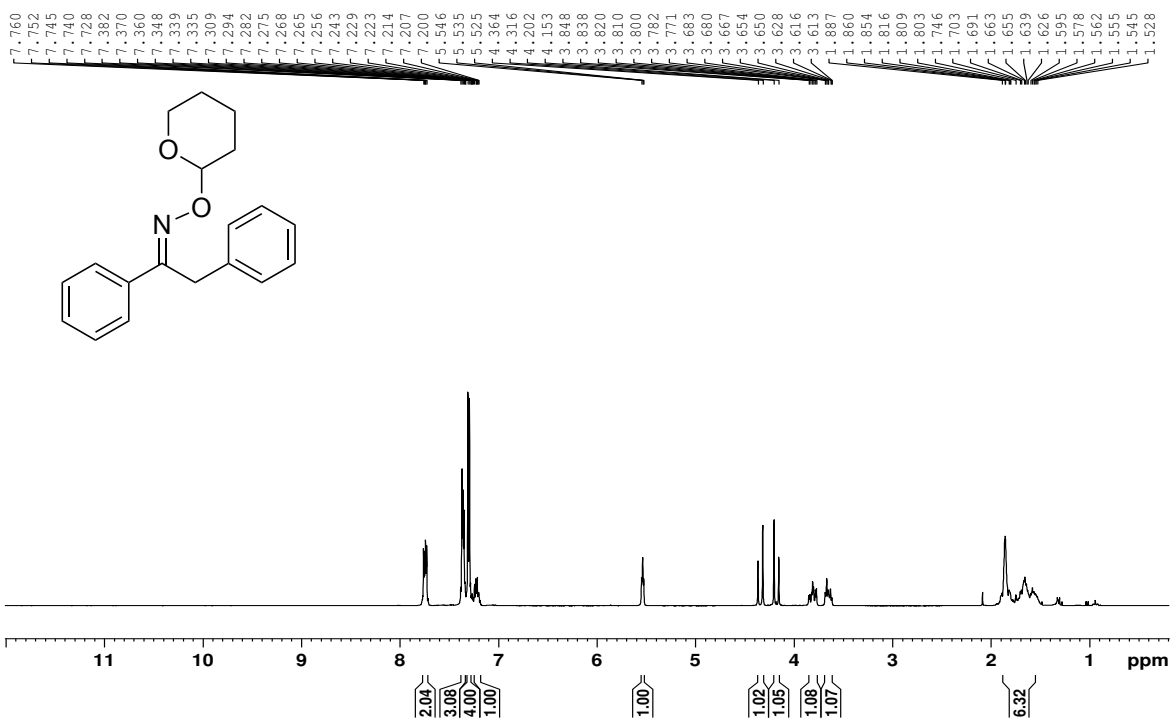
$^{1}$H NMR (300 MHz) Spectrum of **13j** in $CDCl_3$



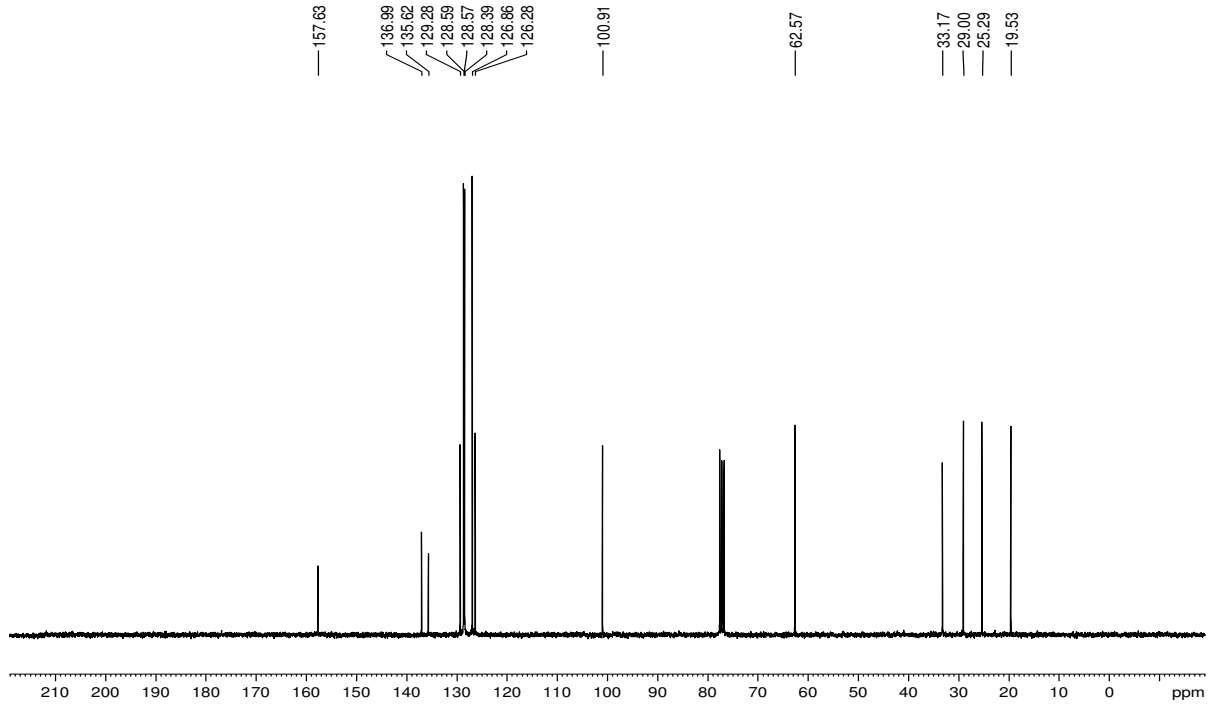

$^{13}$C{$^{1}$H} (75.5 MHz) NMR Spectrum of **13j** in $CDCl_3$



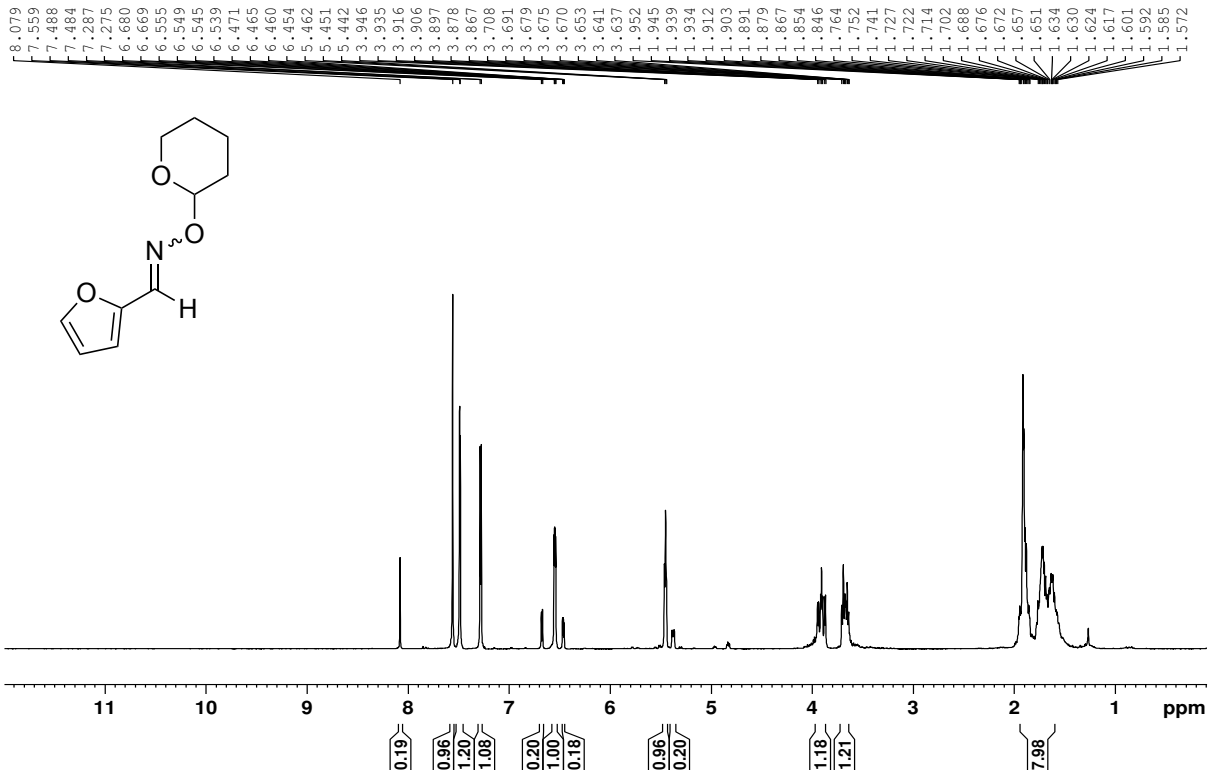
$^{1}$H NMR (300 MHz) Spectrum of **13k (*E* isomer)** in $CDCl_3$



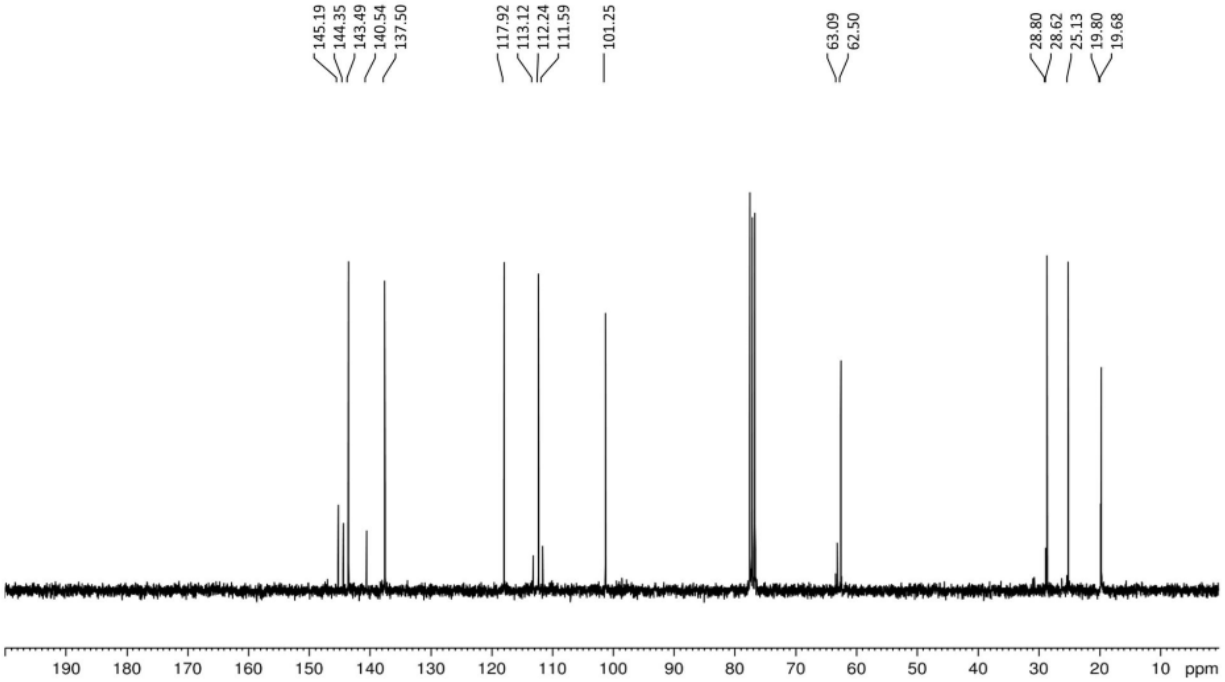

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **13k (*E* isomer)** in $CDCl_3$



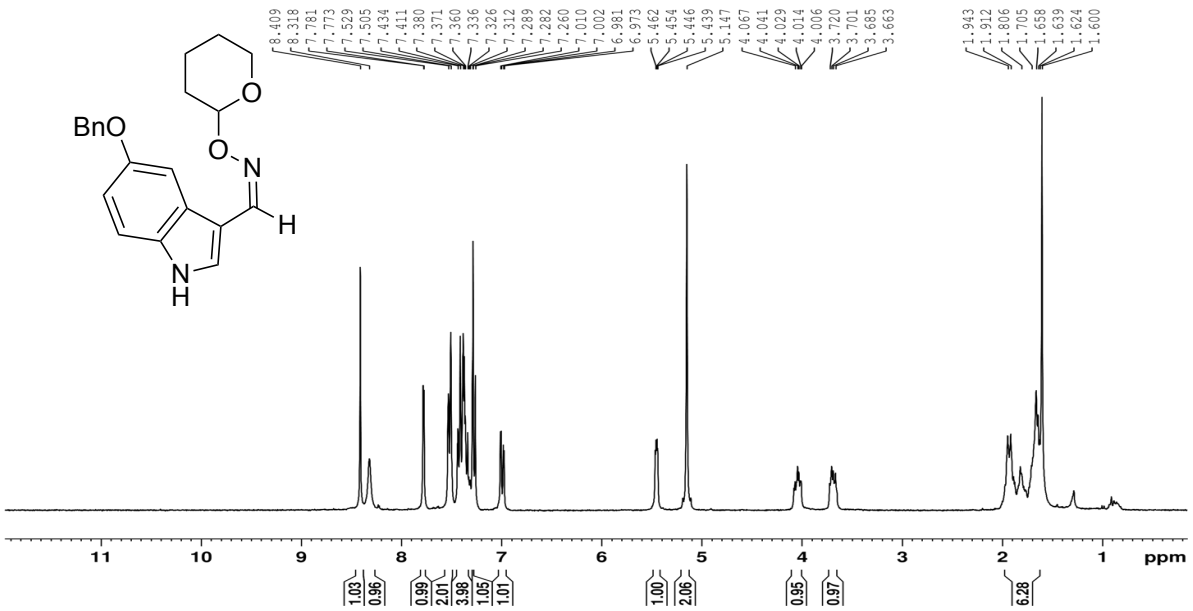
$^{1}$H NMR (300 MHz) Spectrum of a 1:6 *Z*/*E* mixture of **13l** in $CDCl_3$



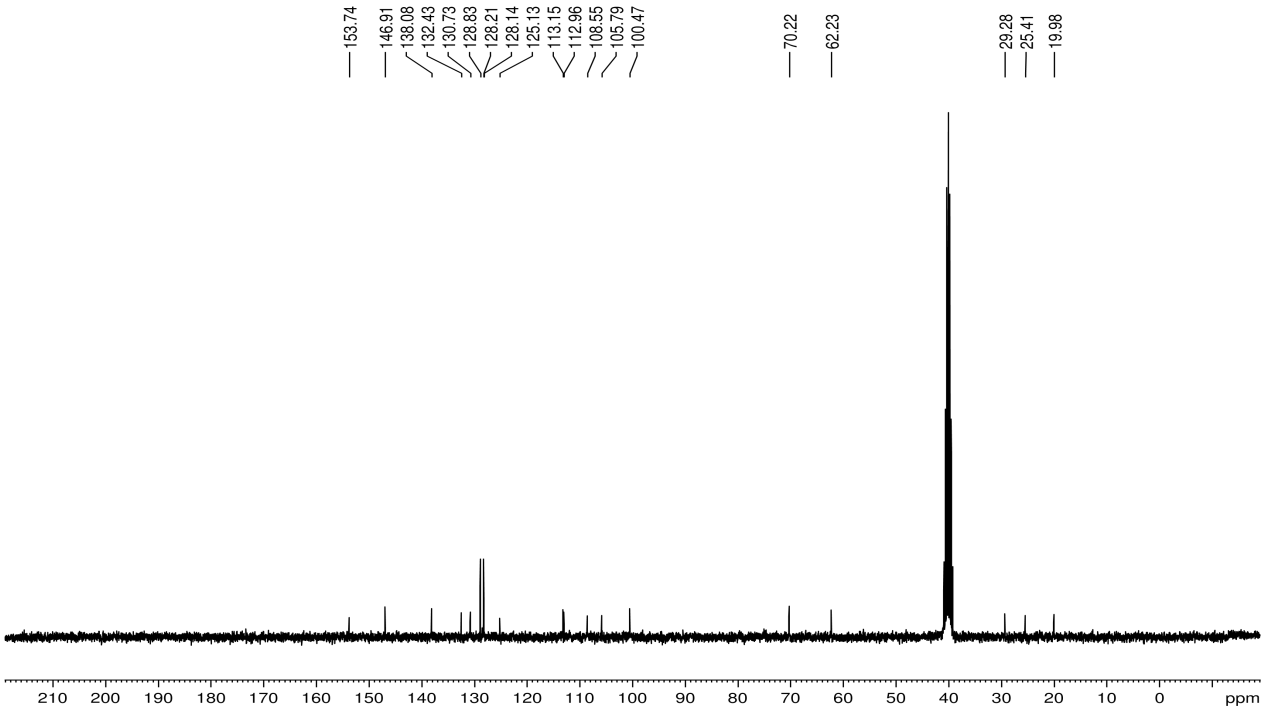

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of a 1:6 *Z*/*E* mixture of **13l** in $CDCl_3$



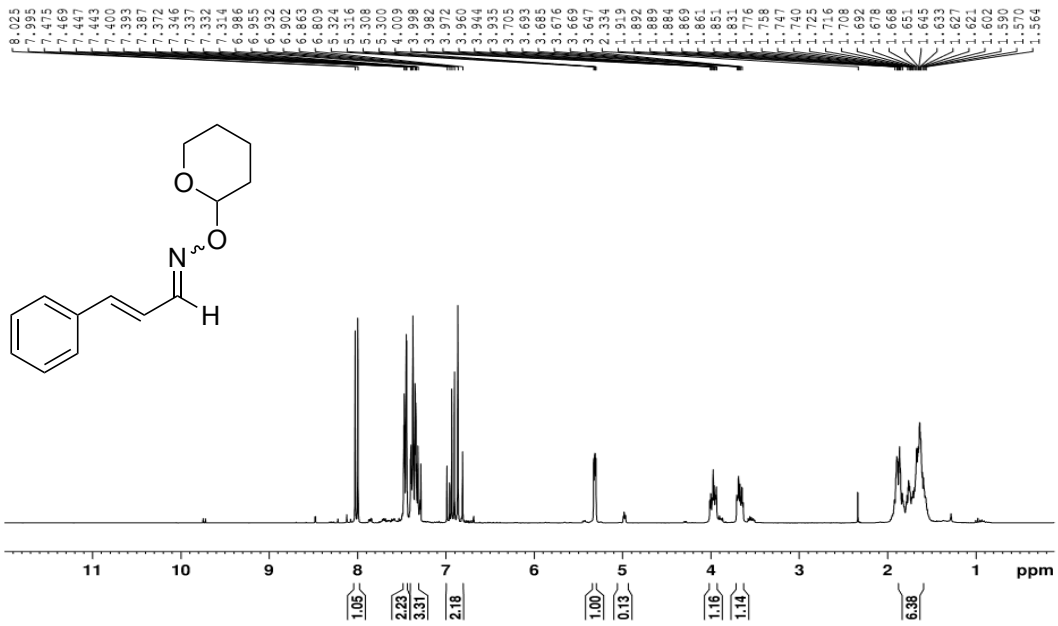
$^{1}$H NMR (300 MHz) Spectrum of **13m (*Z* isomer)** in $CDCl_3$



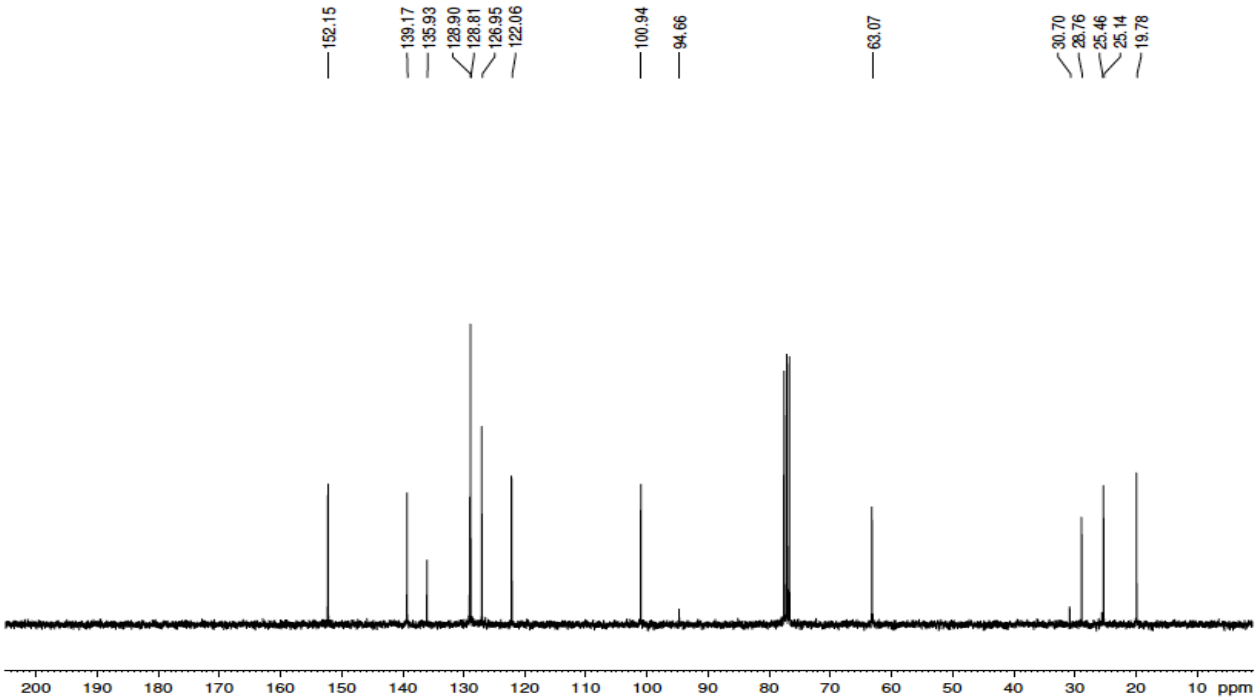

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **13m (*Z* isomer)** in $d_6$-DMSO



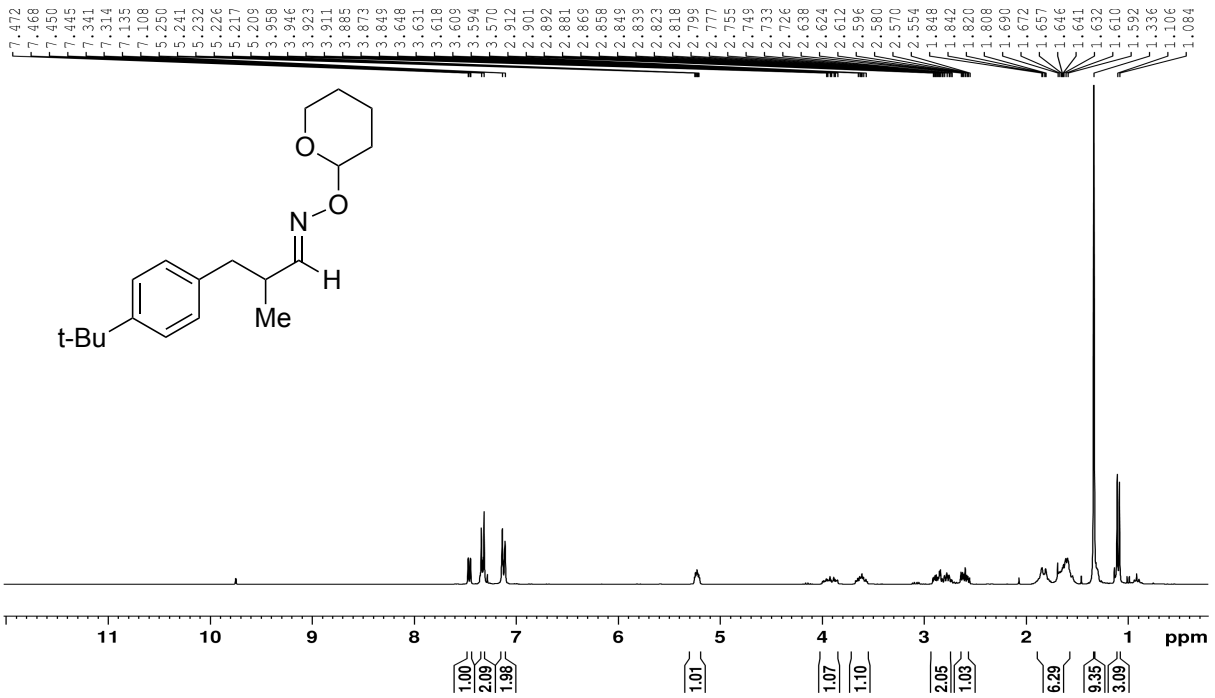
$^{1}$H NMR (300 MHz) Spectrum of a 1:~8 *Z*/*E* mixture of **13n** in $CDCl_3$



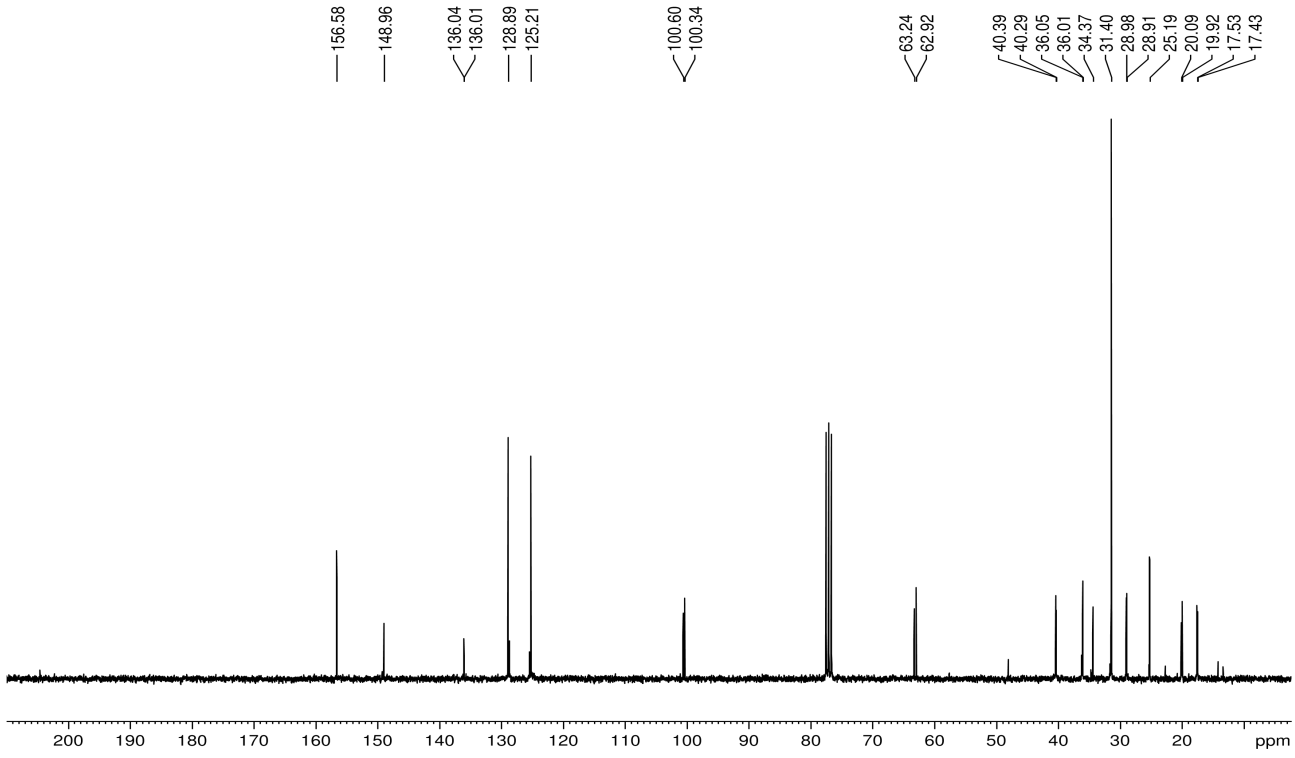

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of a 1:~8 *Z*/*E* mixture of **13n** in $CDCl_3$



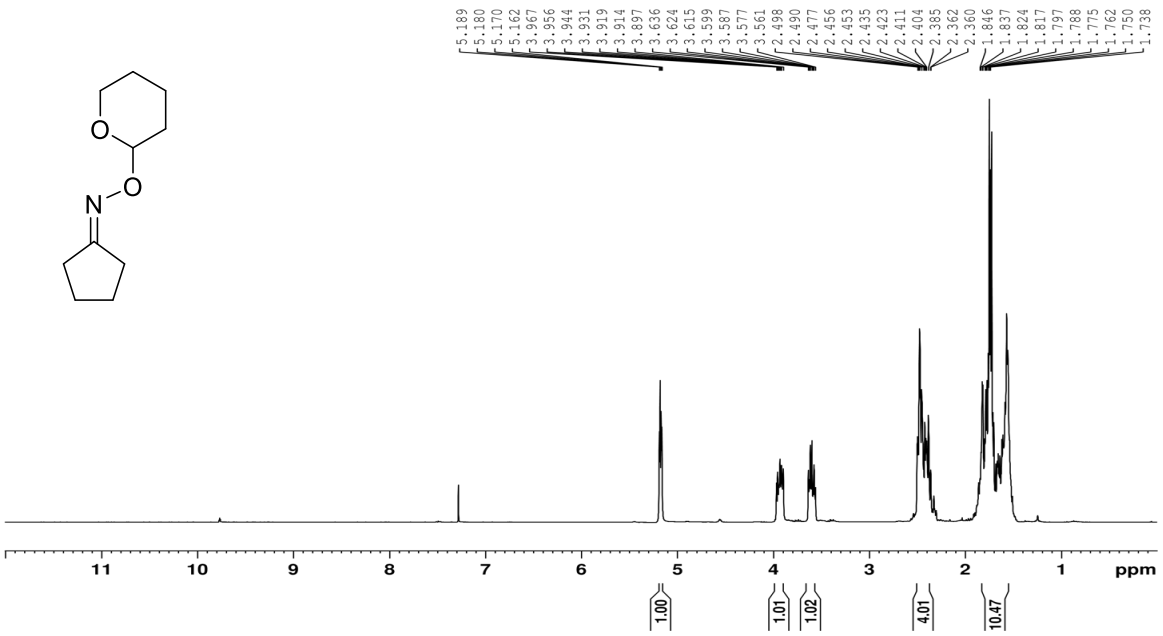
$^{1}$H NMR (300 MHz) Spectrum of **13o (*E* isomer)** in $CDCl_3$



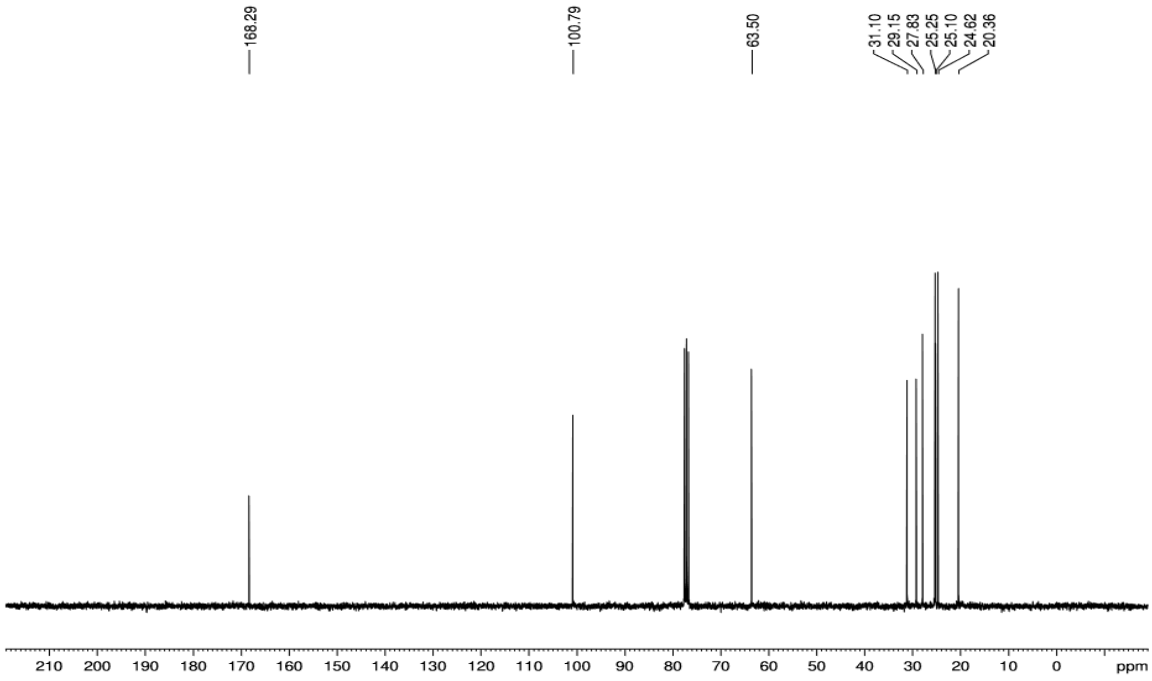

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **13o (*E* isomer)** in $CDCl_3$



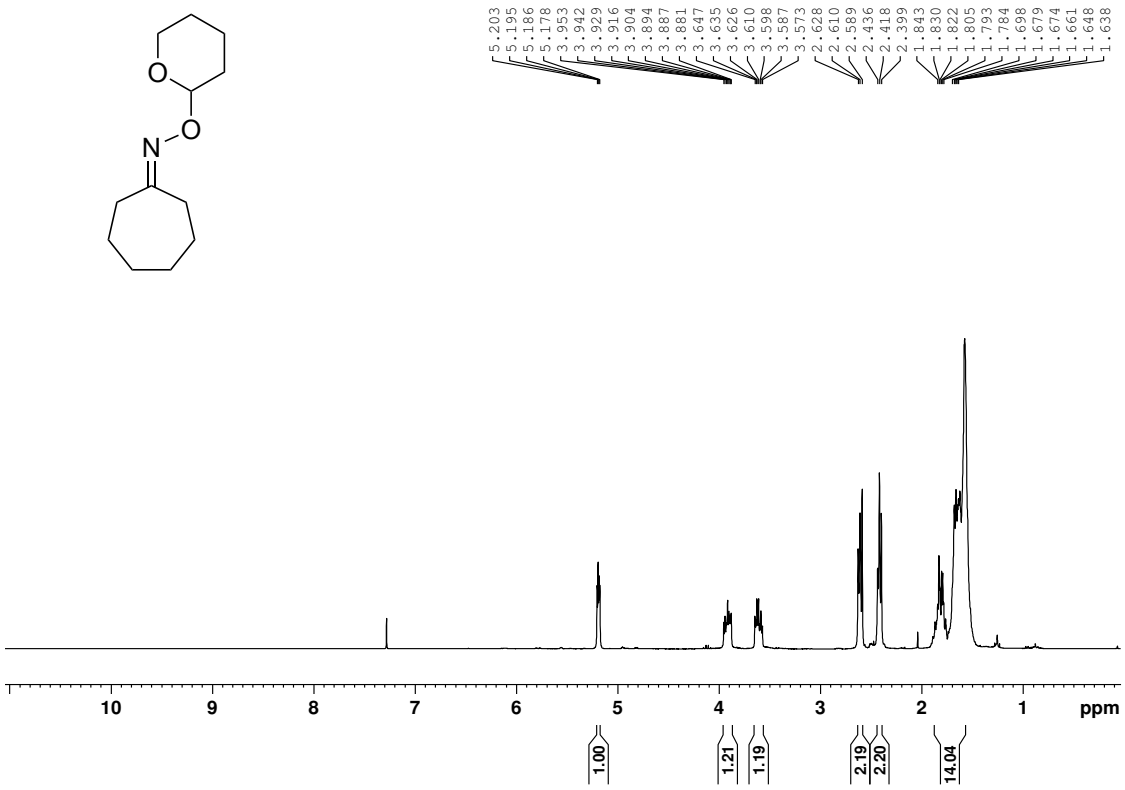
$^{1}$H NMR (300 MHz) Spectrum of **13p** in $CDCl_3$



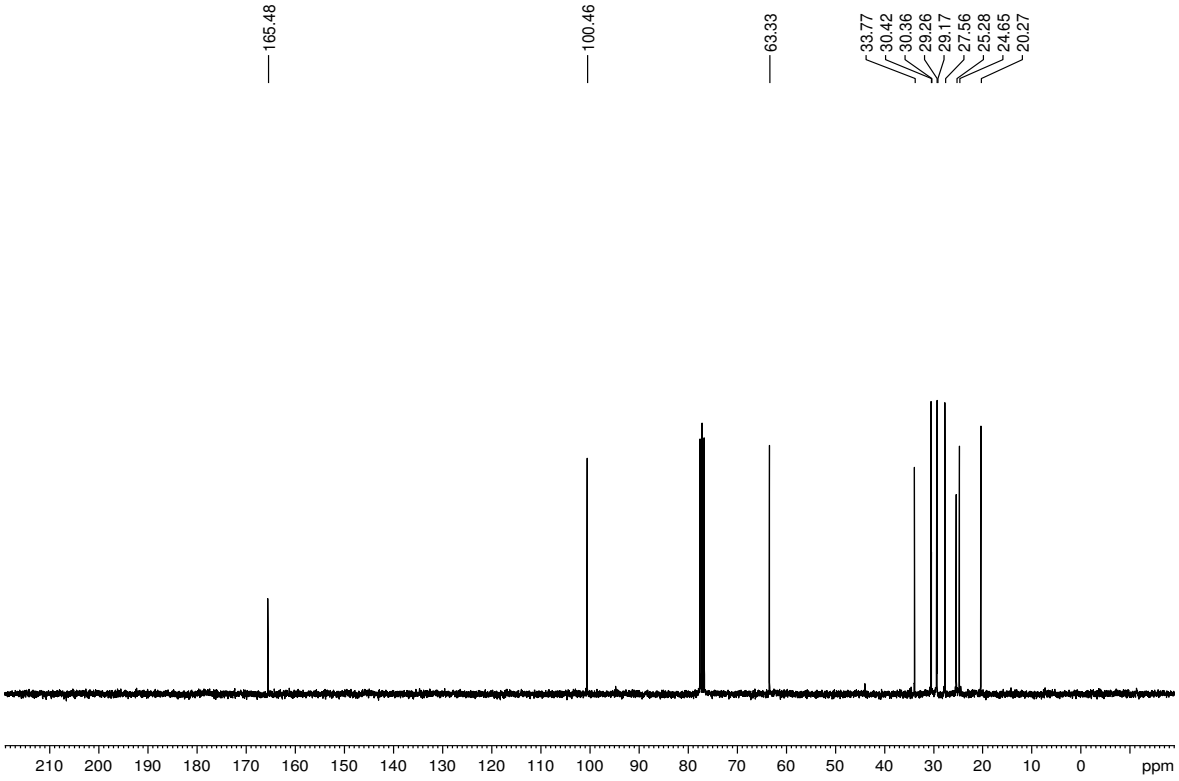

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **13p** in $CDCl_3$



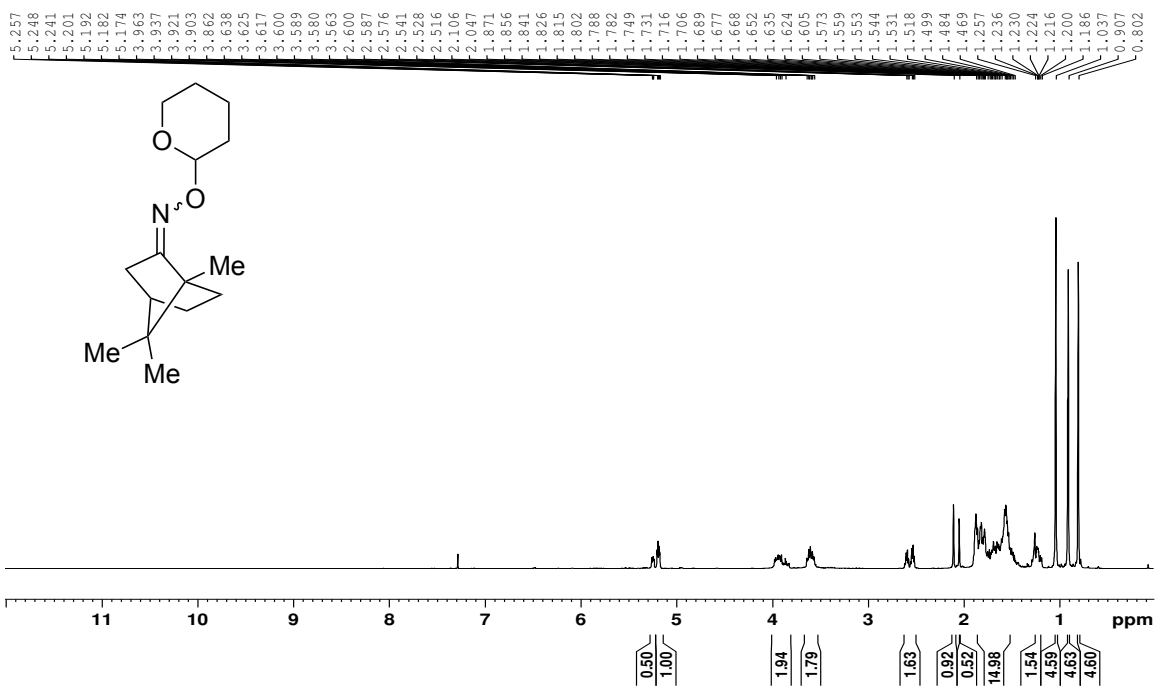
$^{1}$H NMR (300 MHz) Spectrum of **13q** in $CDCl_3$



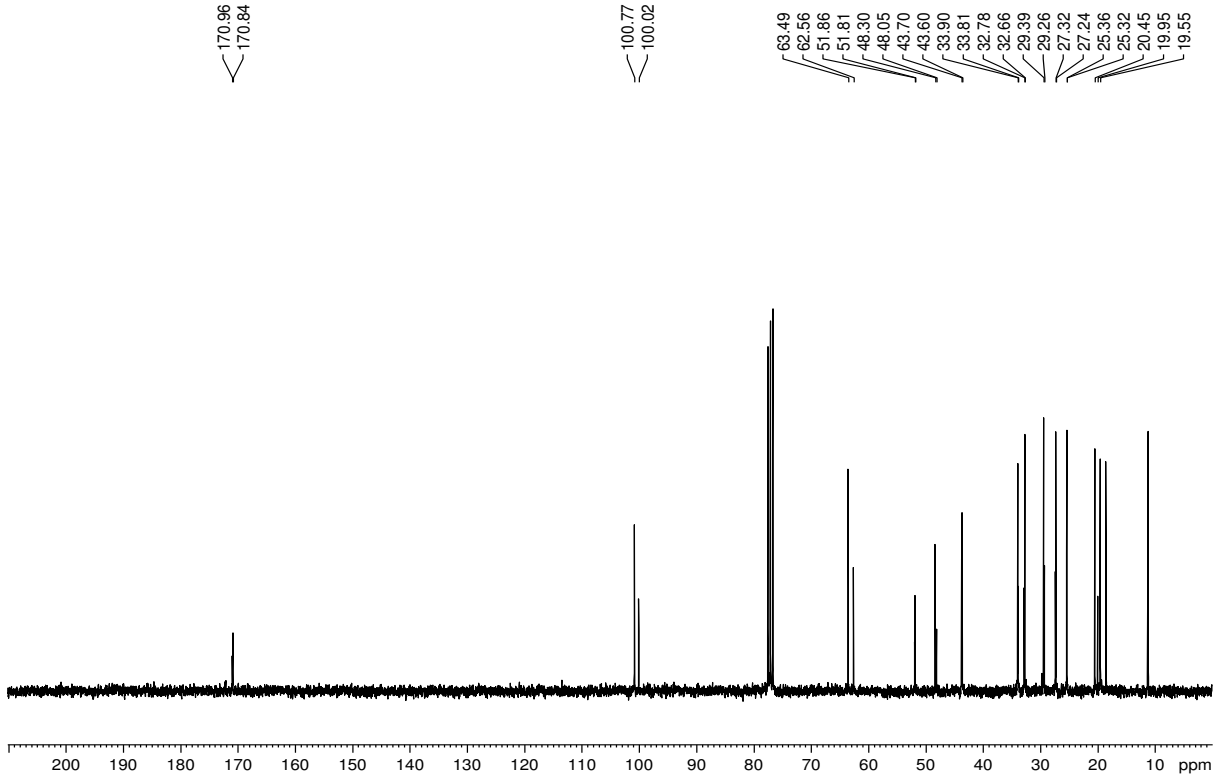

$^{13}$C{$^{1}$H} (75.5 MHz) NMR Spectrum of **13q** in $CDCl_3$



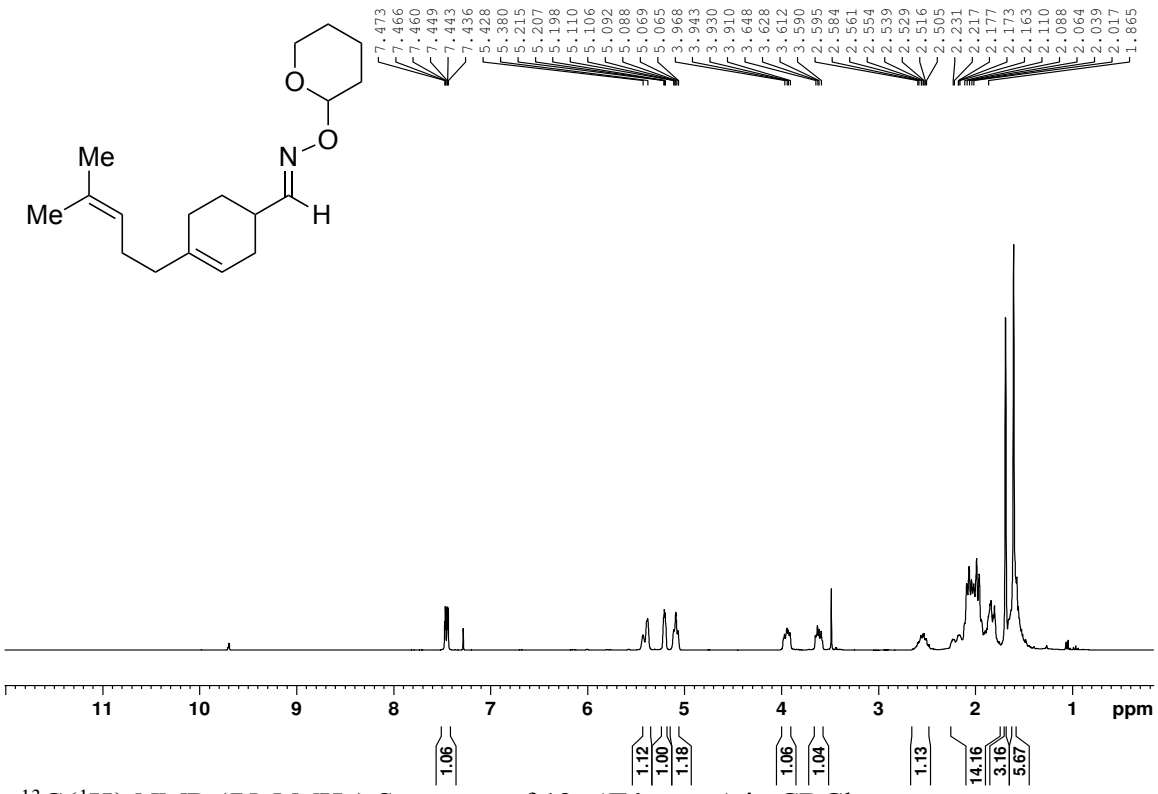
$^{1}$H NMR (300 MHz) Spectrum of a 1:2 *Z*/*E* mixture of **13r** in $CDCl_3$



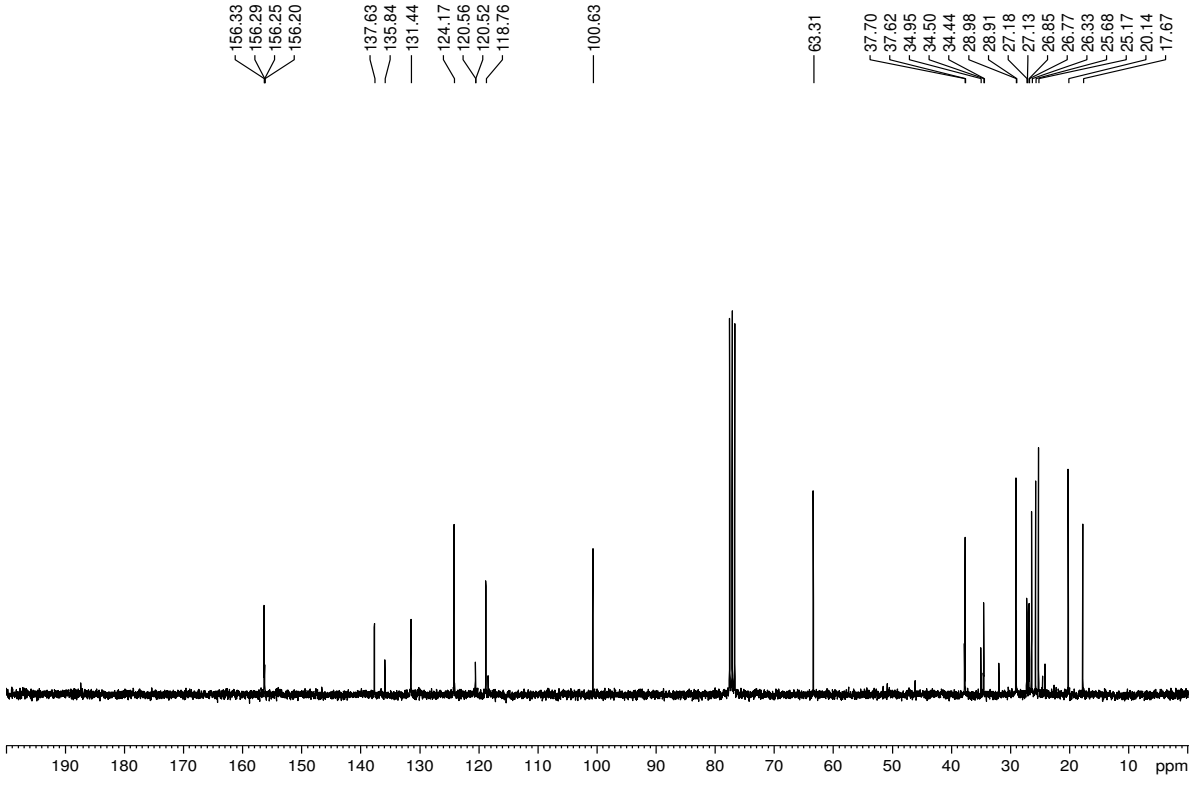

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of a 1:2 *Z*/*E* mixture of **13r** in $CDCl_3$



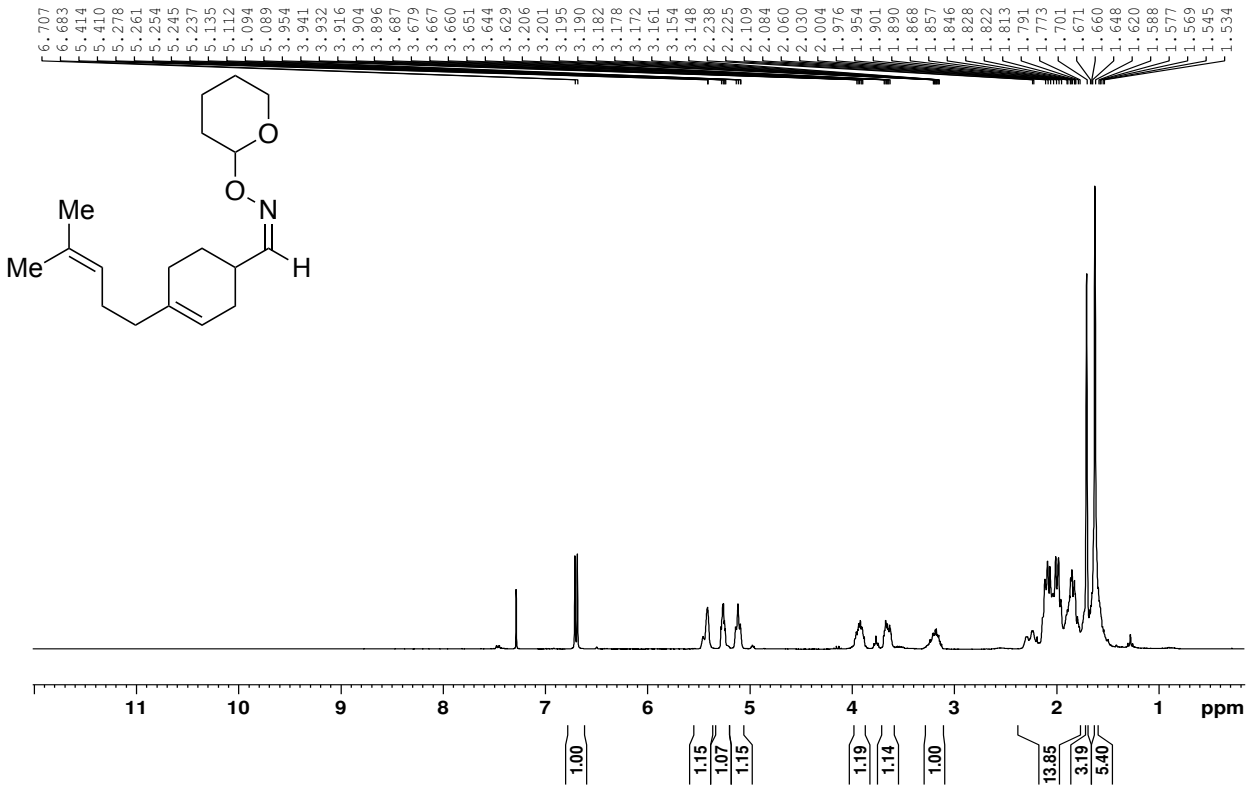
$^{1}$H NMR (300 MHz) Spectrum of **13s (*E* isomer)** in $CDCl_3$



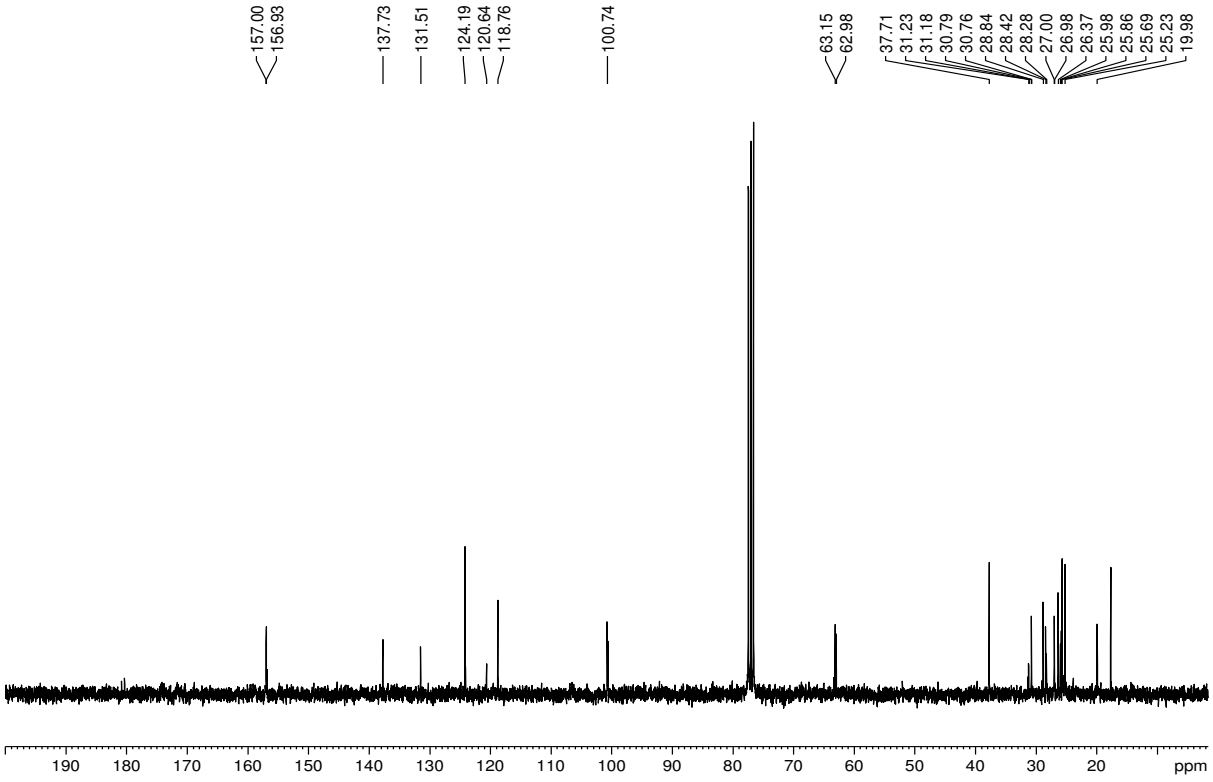

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **13s (*E* isomer)** in $CDCl_3$



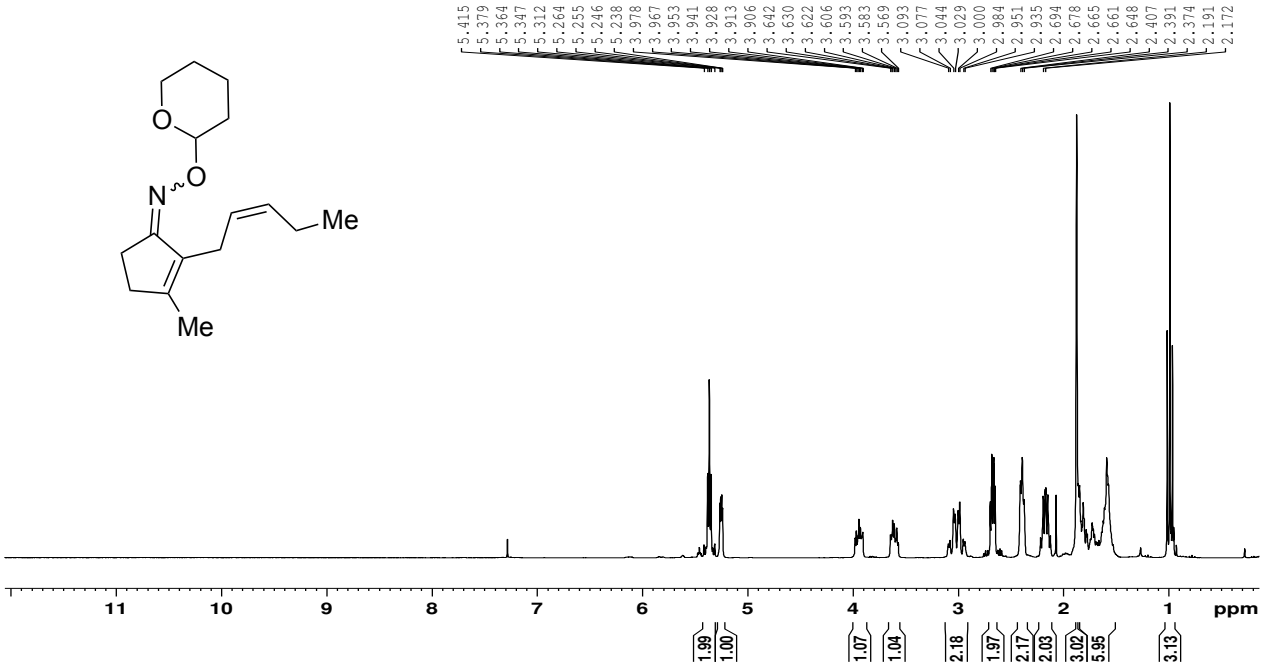
$^{1}$H NMR (300 MHz) Spectrum of **13s (*Z* isomer)** in $CDCl_3$



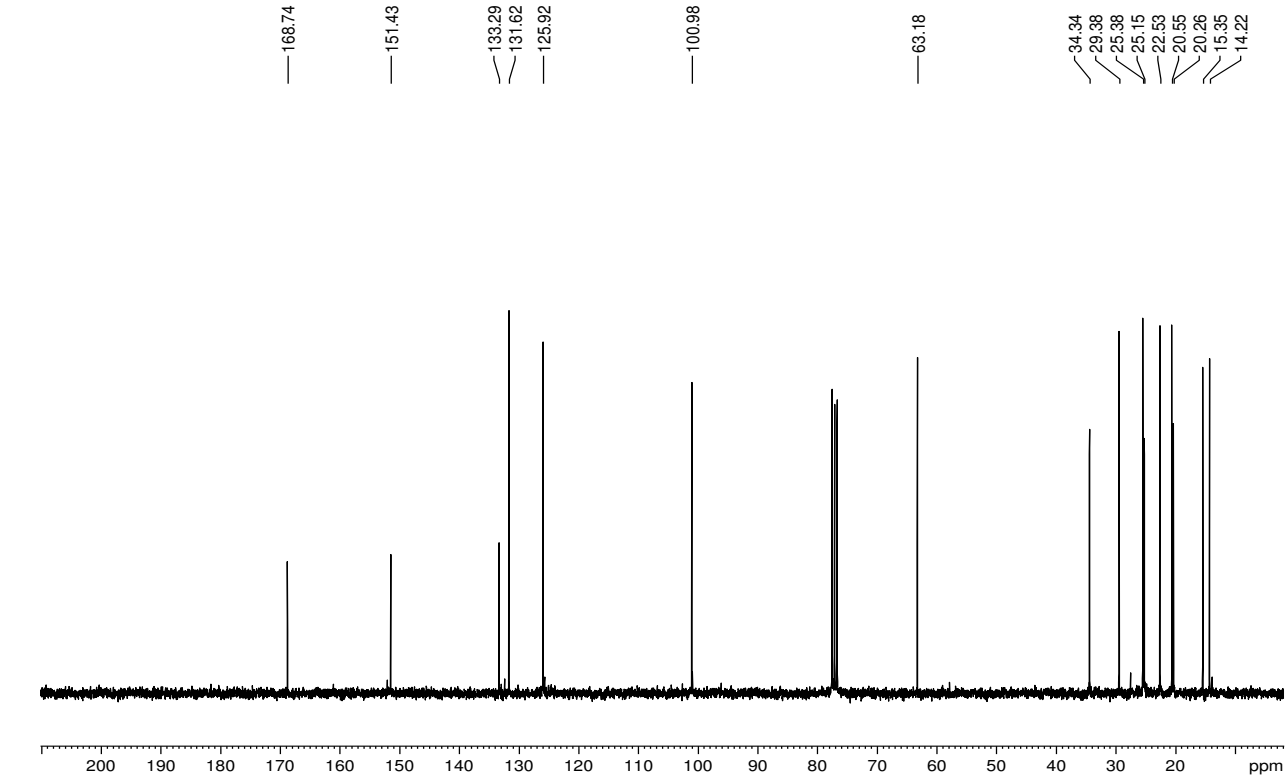

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **13s (*Z* isomer)** in $CDCl_3$



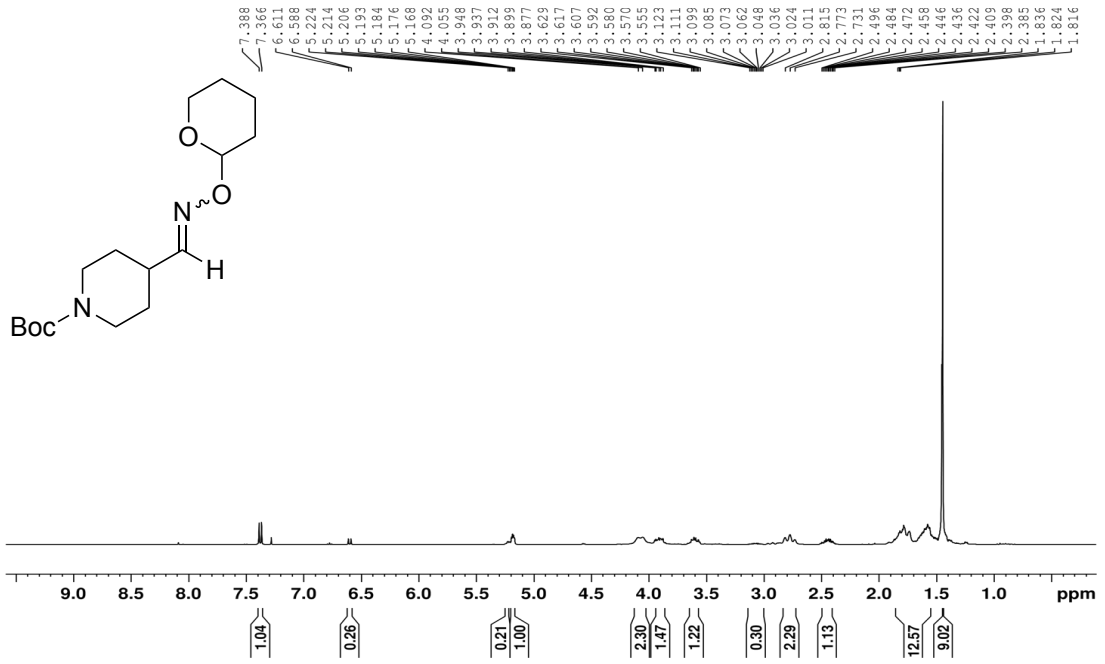
$^{1}$H NMR (300 MHz) Spectrum of **13t (C.N.D.)** in $CDCl_3$



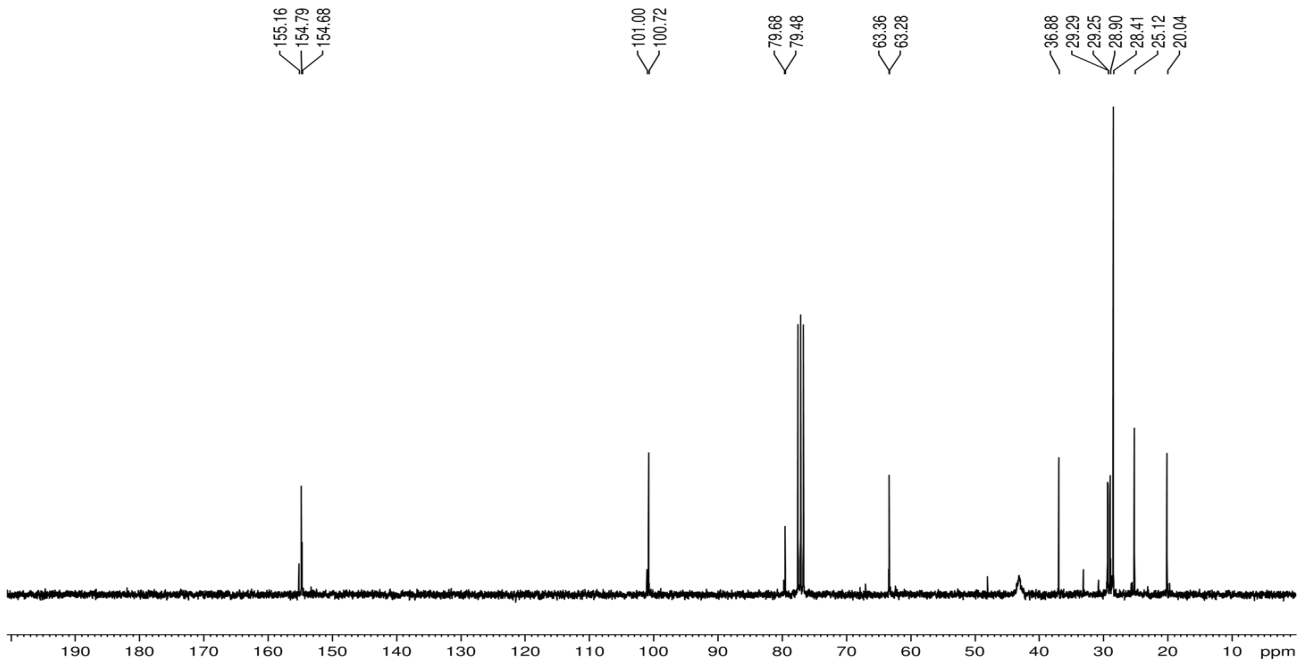

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **13t (C.N.D.)** in $CDCl_3$



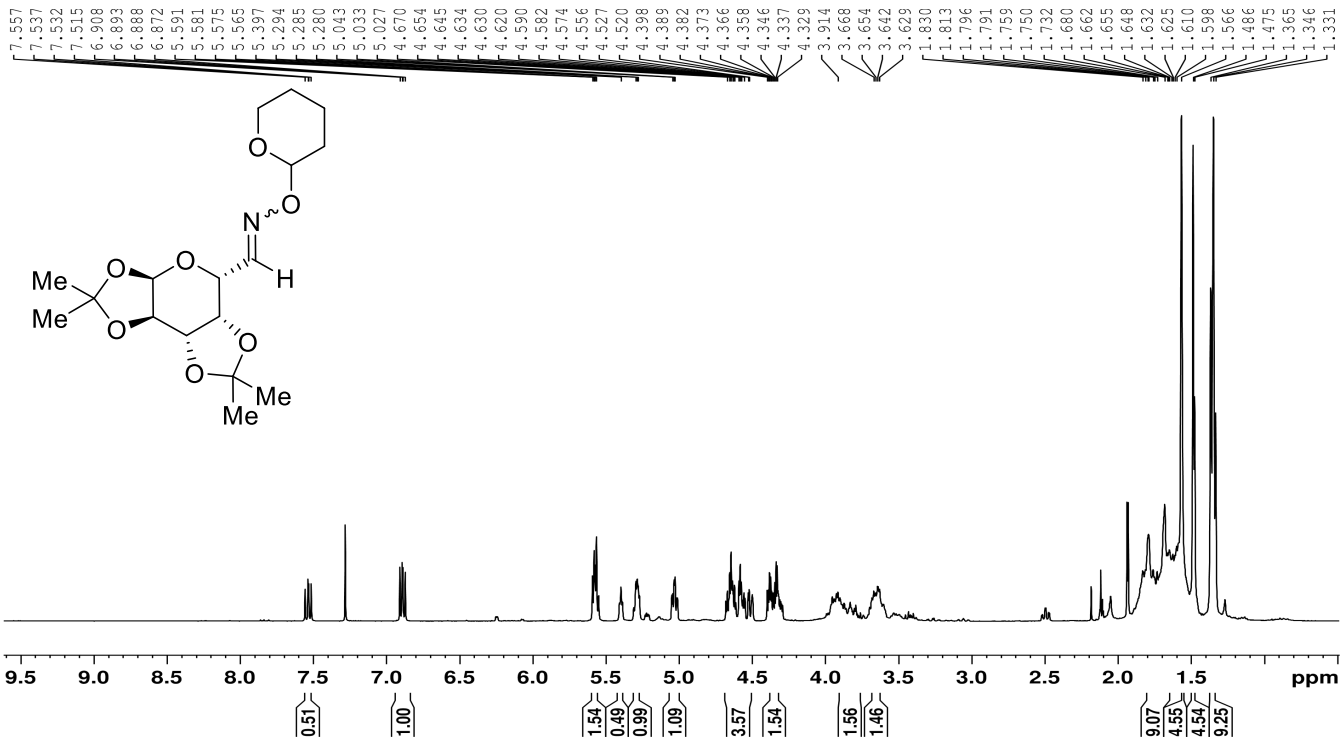
$^{1}$H NMR (300 MHz) Spectrum of a 1:5 *Z*/*E* mixture of **13u** in $CDCl_3$



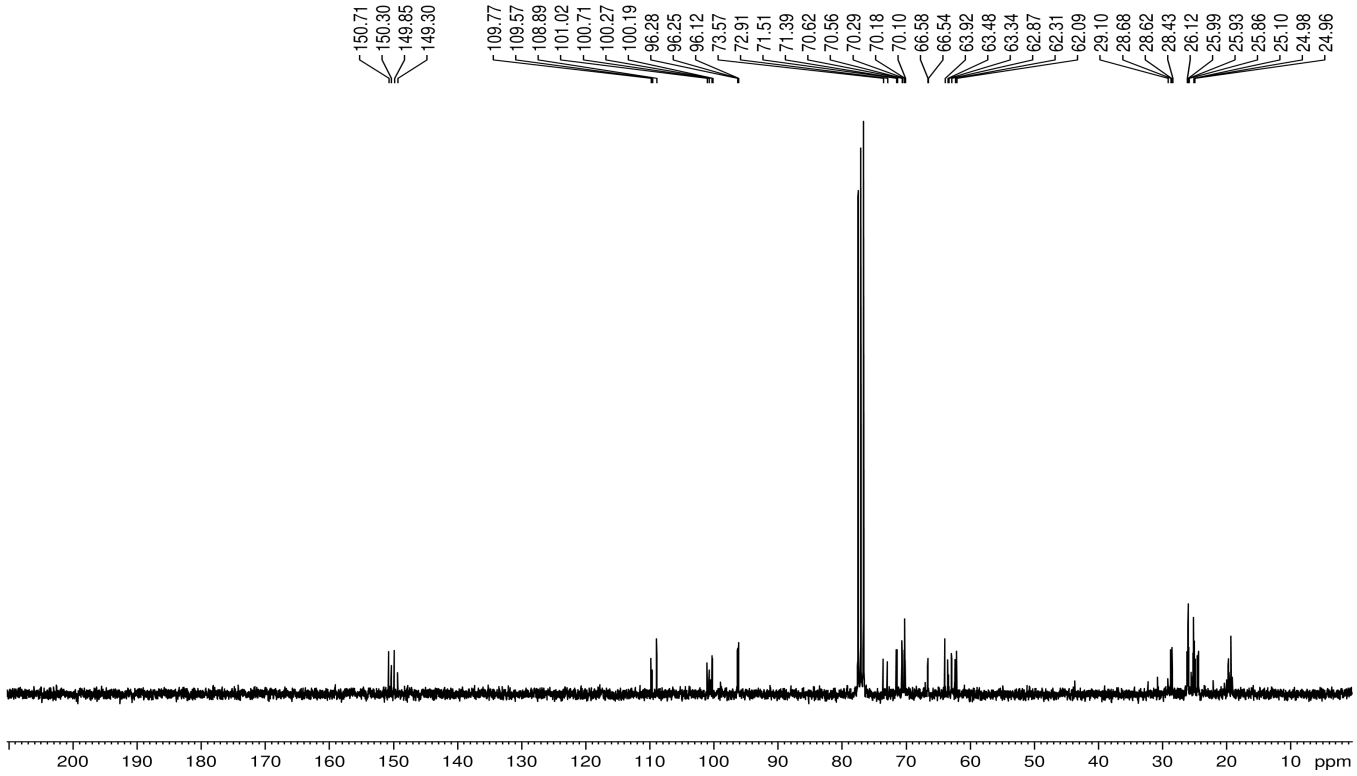

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of a 1:5 *Z*/*E* mixture of **13u** in $CDCl_3$



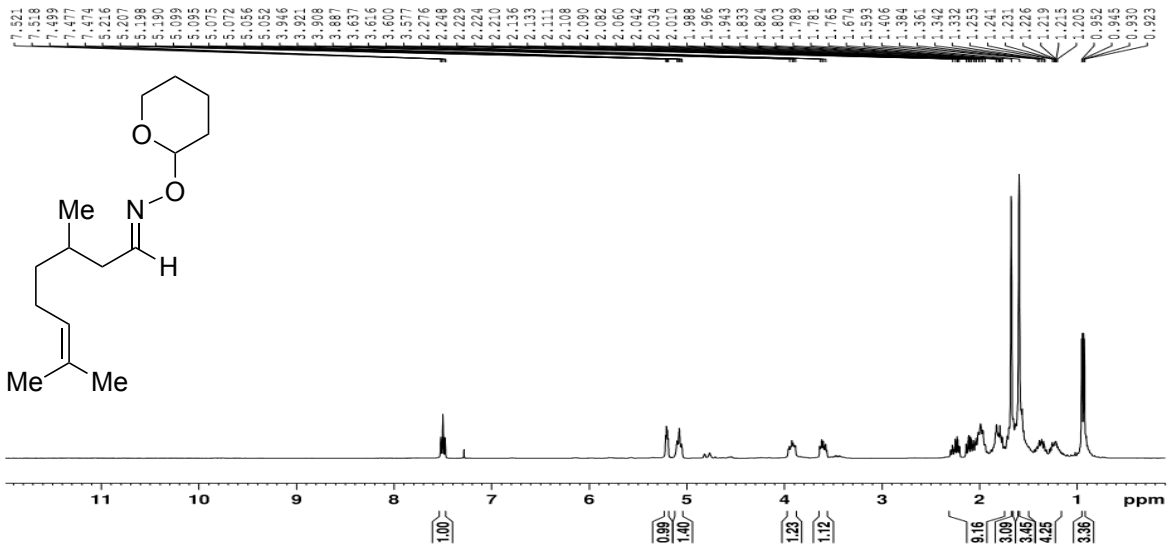
$^{1}$H NMR (300 MHz) Spectrum of a 1:2 *Z*/*E* mixture of **13v** in $CDCl_3$



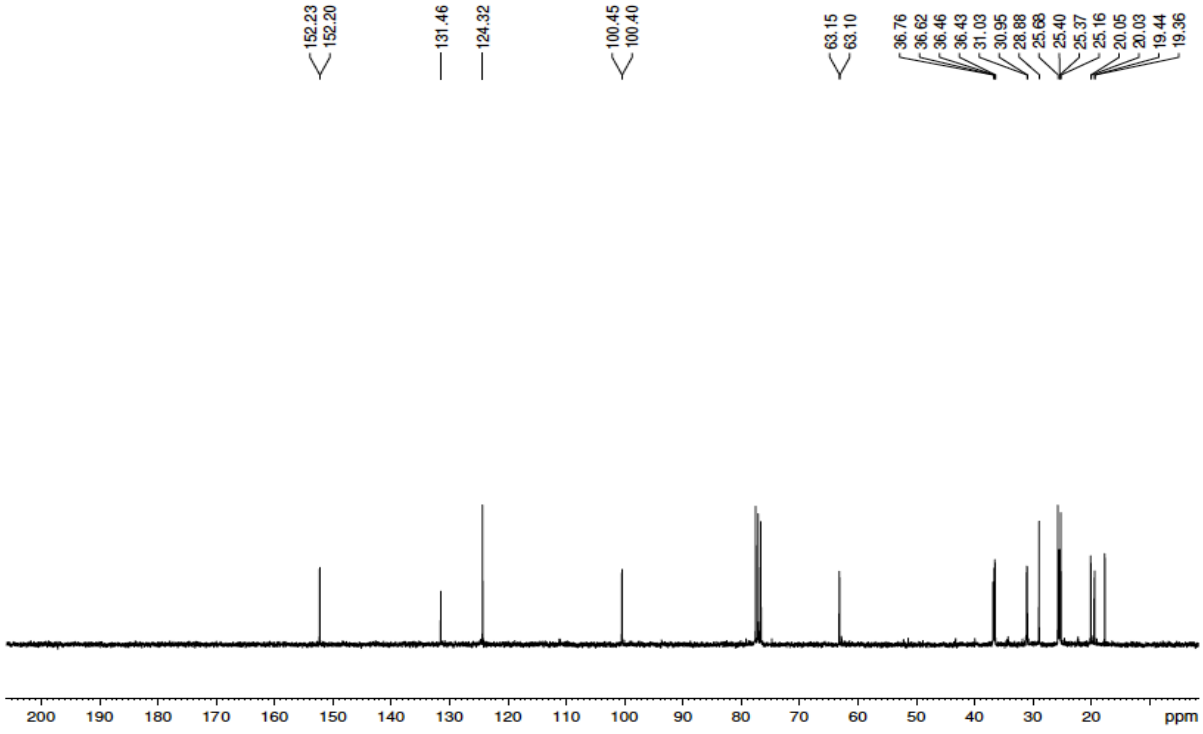

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of a 1:2 *Z*/*E* mixture of **13v** in $CDCl_3$



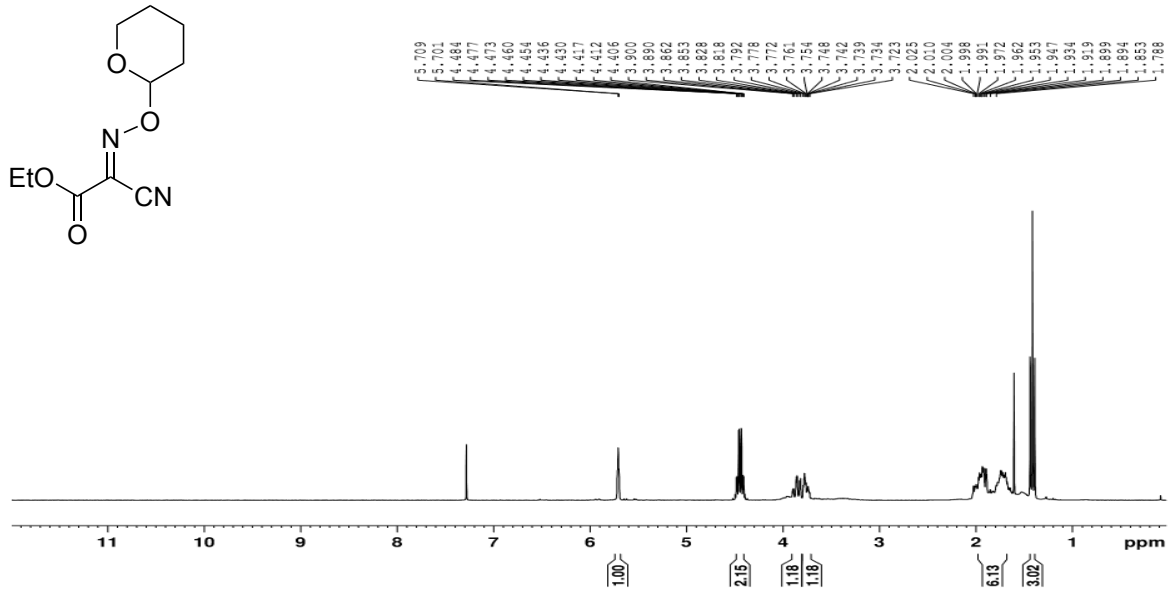
$^{1}$H NMR (300 MHz) Spectrum of **13w (*E* isomer)** in $CDCl_3$



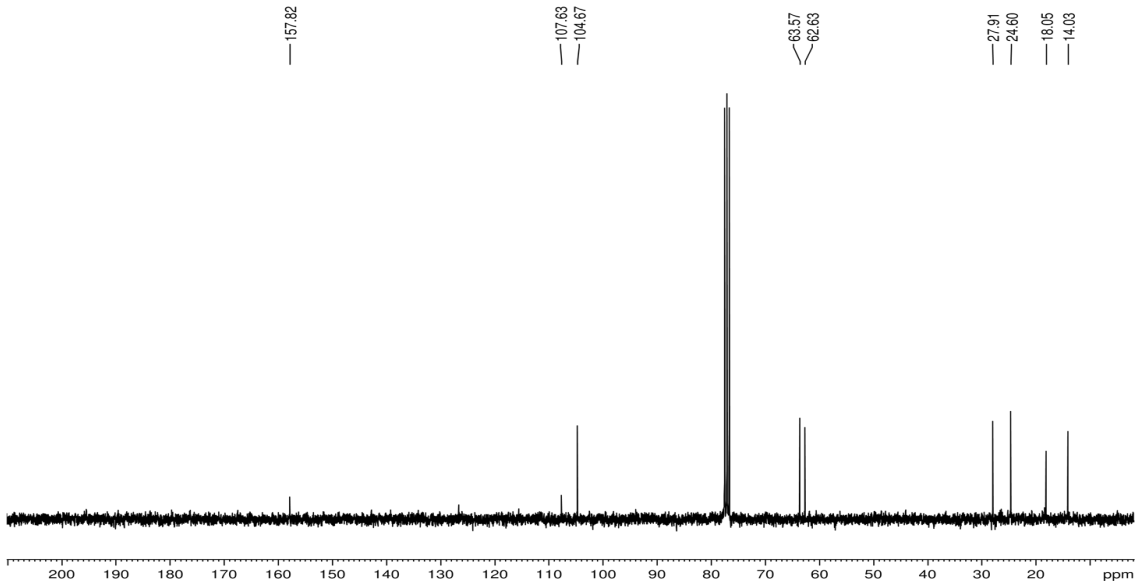

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **13w (*E* isomer)** in $CDCl_3$



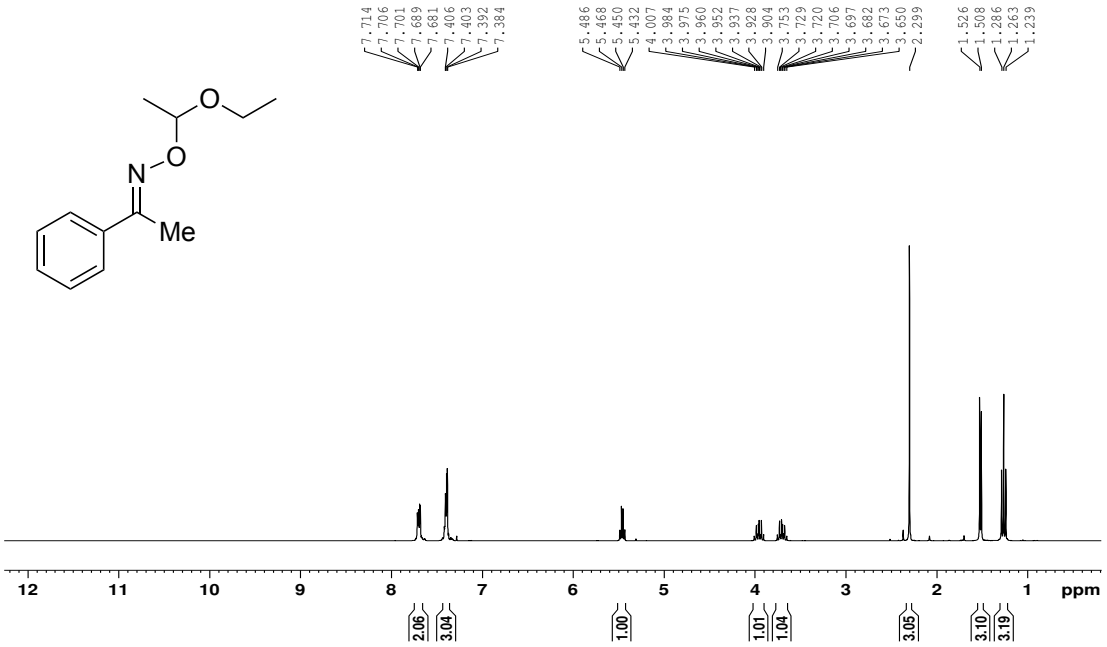
$^{1}$H NMR (300 MHz) Spectrum of **13x (*E* isomer)** in $CDCl_3$



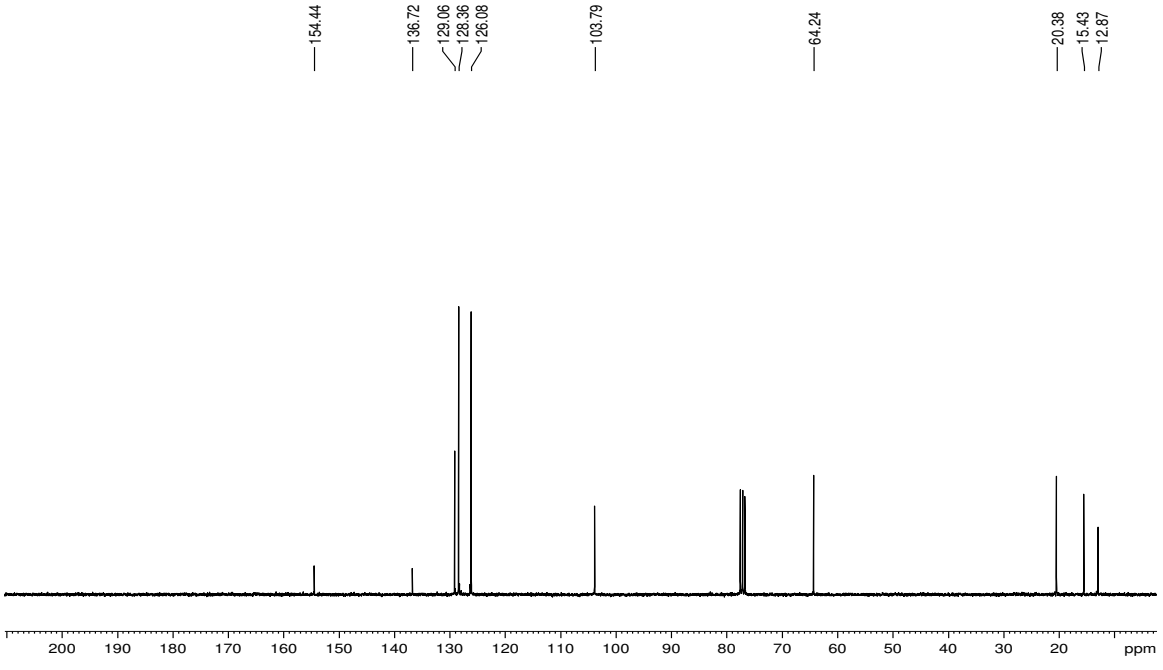

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **13x (*E* isomer)** in $CDCl_3$



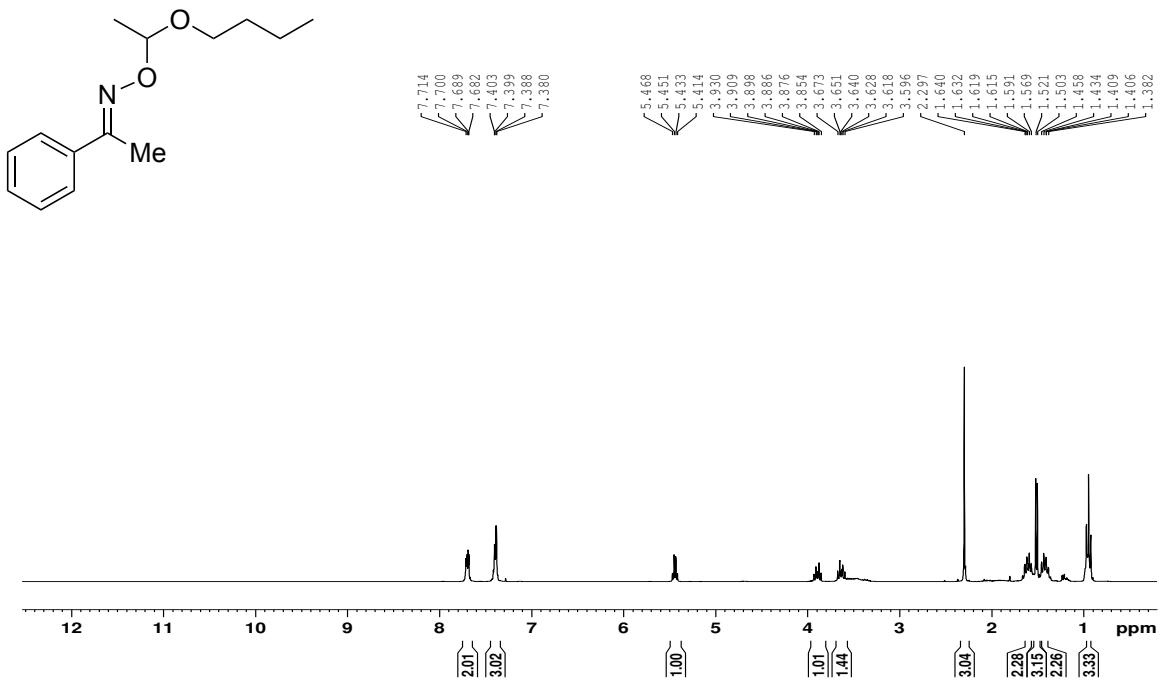
$^{1}$H NMR (300 MHz) Spectrum of **13y (*E* isomer)** in $CDCl_3$



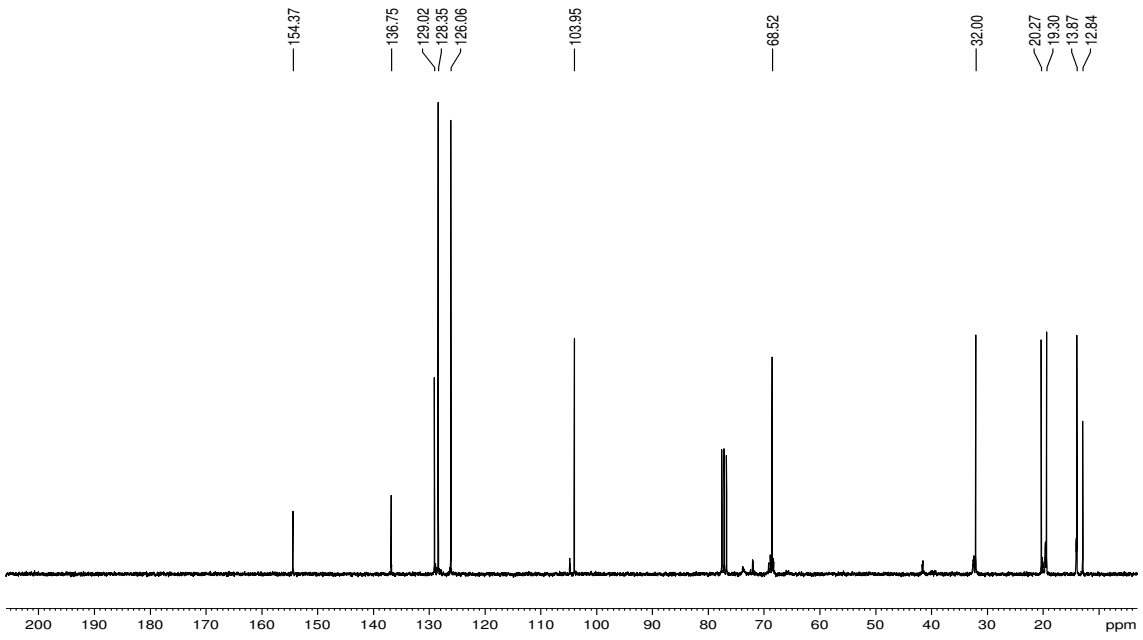

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **13y (*E* isomer)** in $CDCl_3$



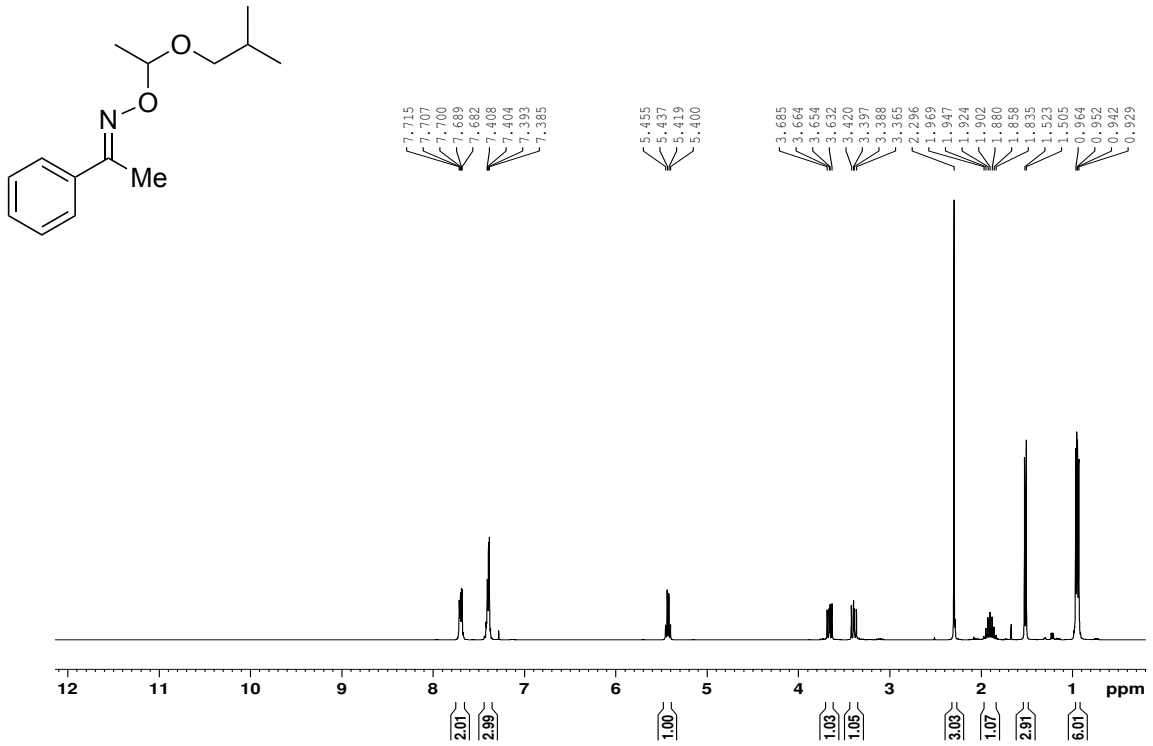
$^{1}$H NMR (300 MHz) Spectrum of **13z (*E* isomer)** in $CDCl_3$



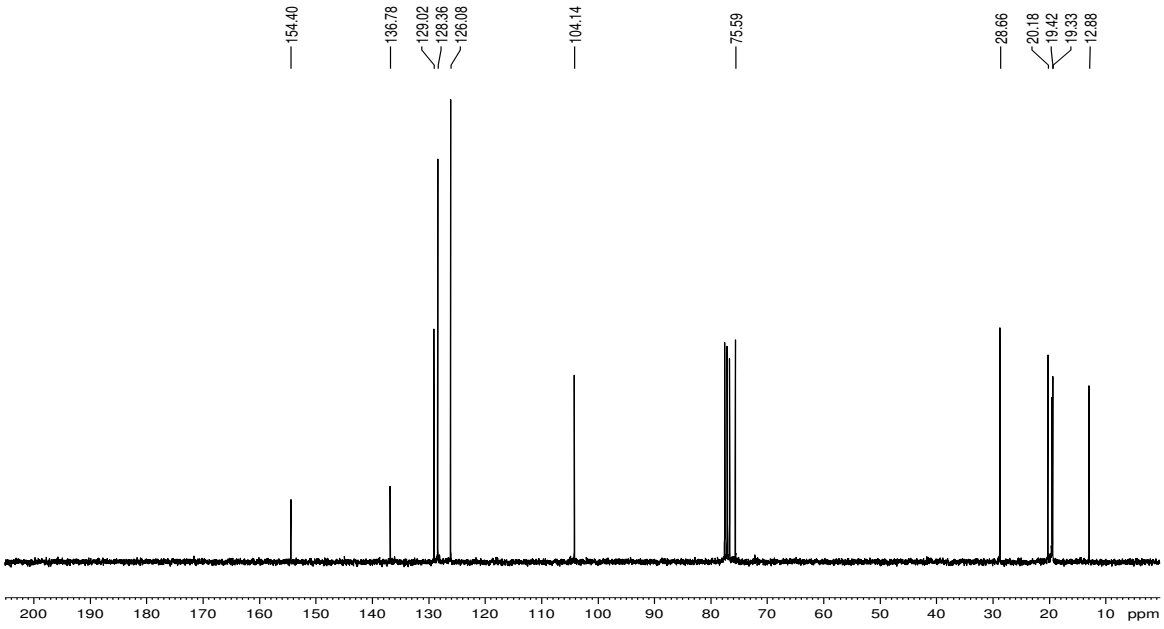

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **13z (*E* isomer)** in $CDCl_3$



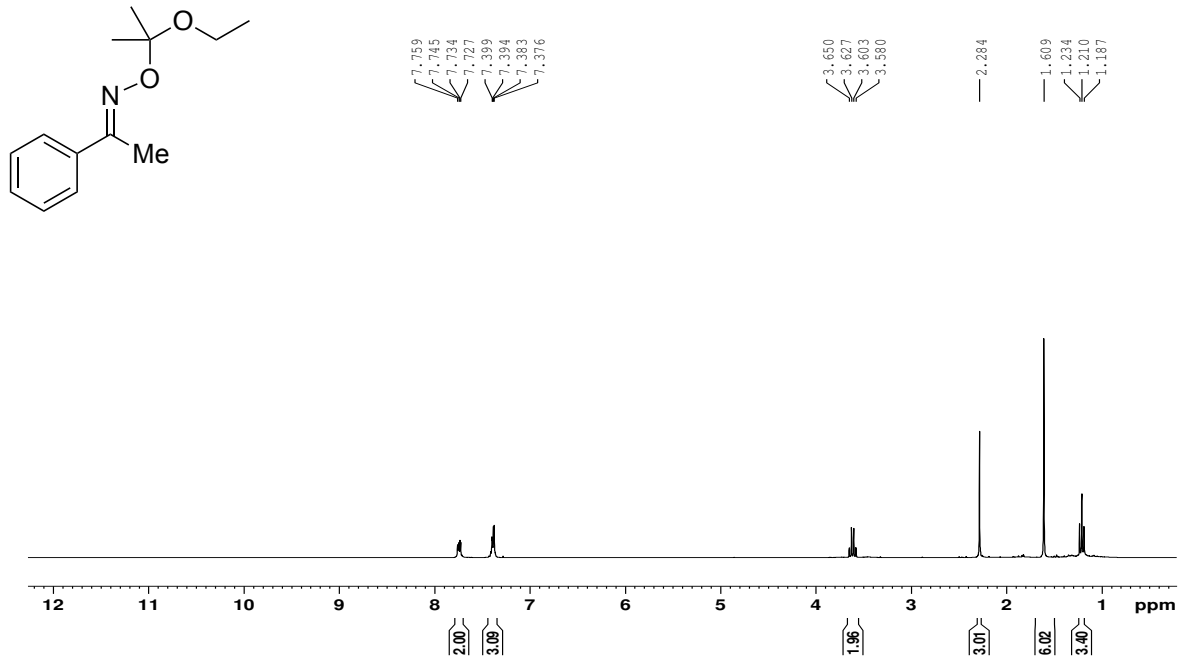
$^{1}$H NMR (300 MHz) Spectrum of **13aa (*E* isomer)** in $CDCl_3$



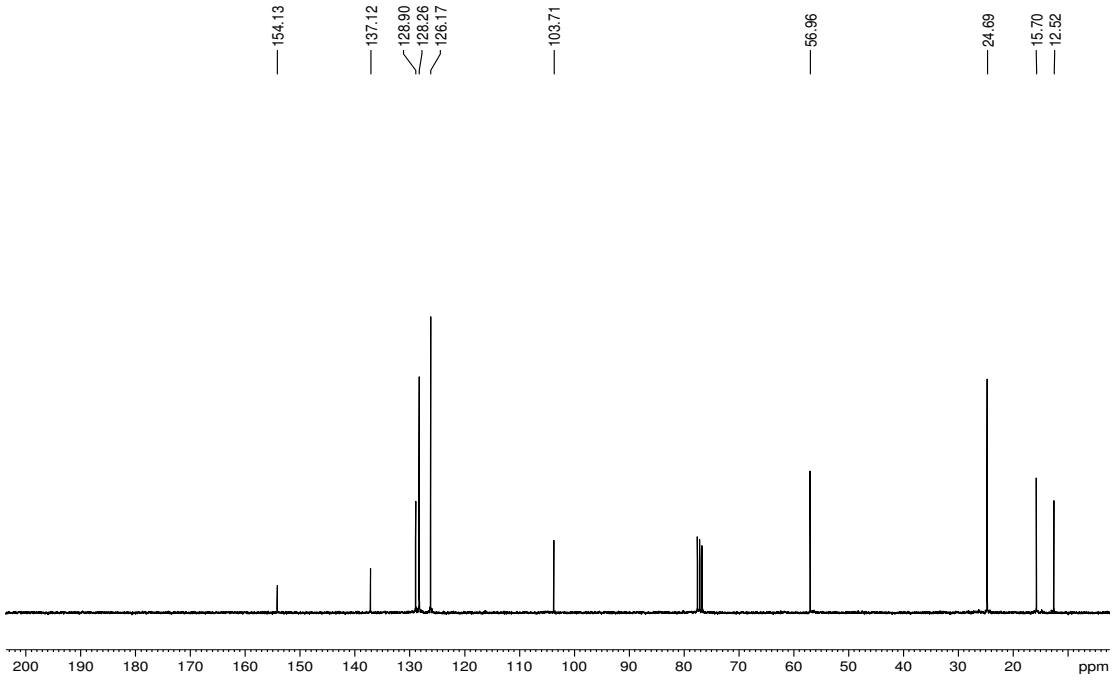

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **13aa (*E* isomer)** in $CDCl_3$



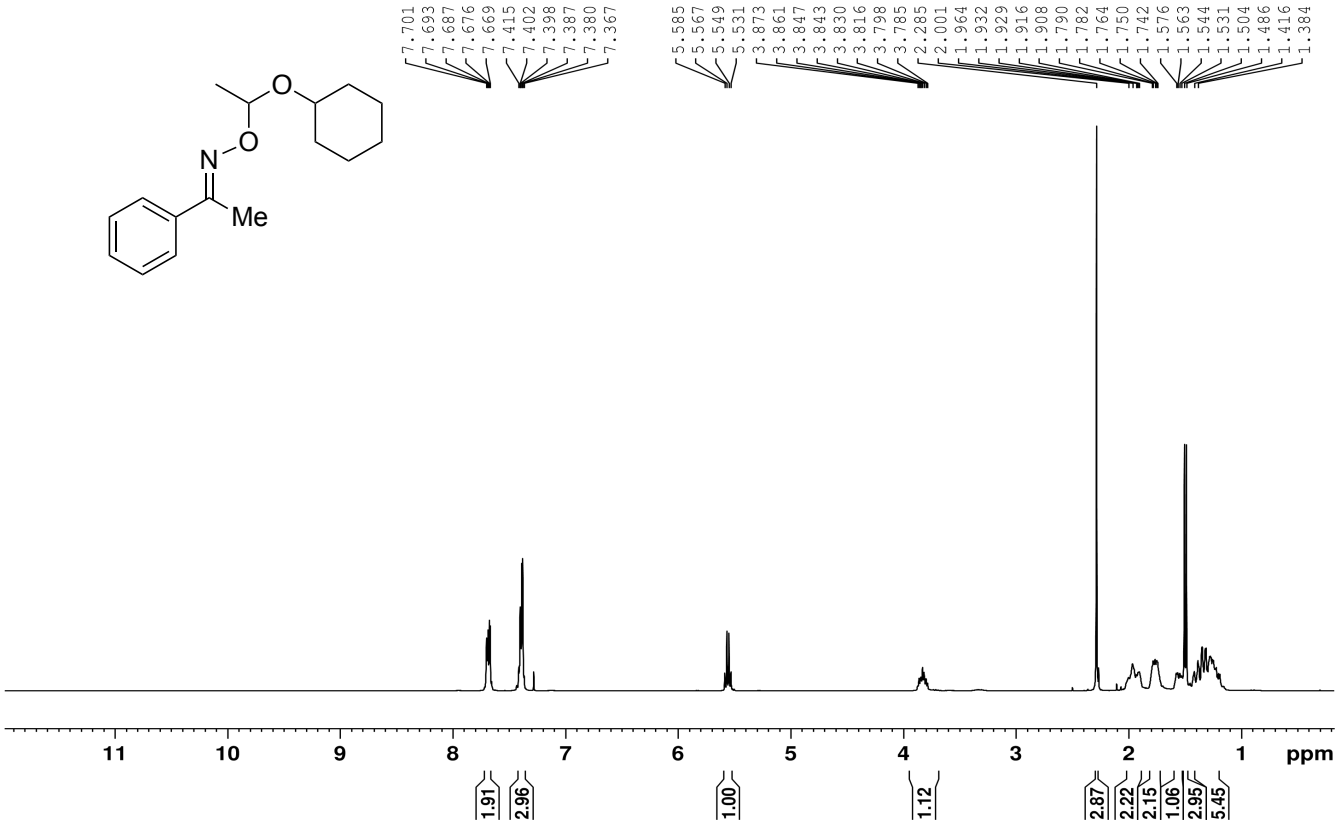
$^{1}$H NMR (300 MHz) Spectrum of **13ab (*E* isomer)** in $CDCl_3$



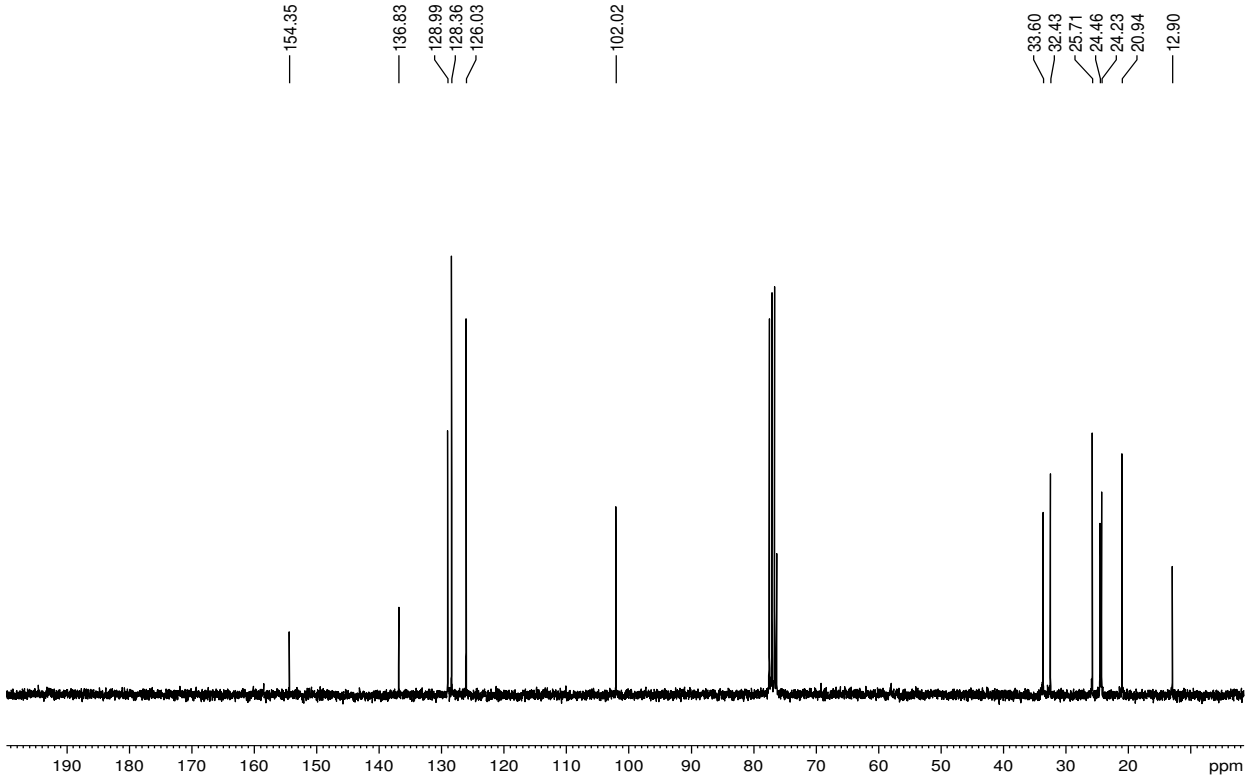

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **13ab (*E* isomer)** in $CDCl_3$



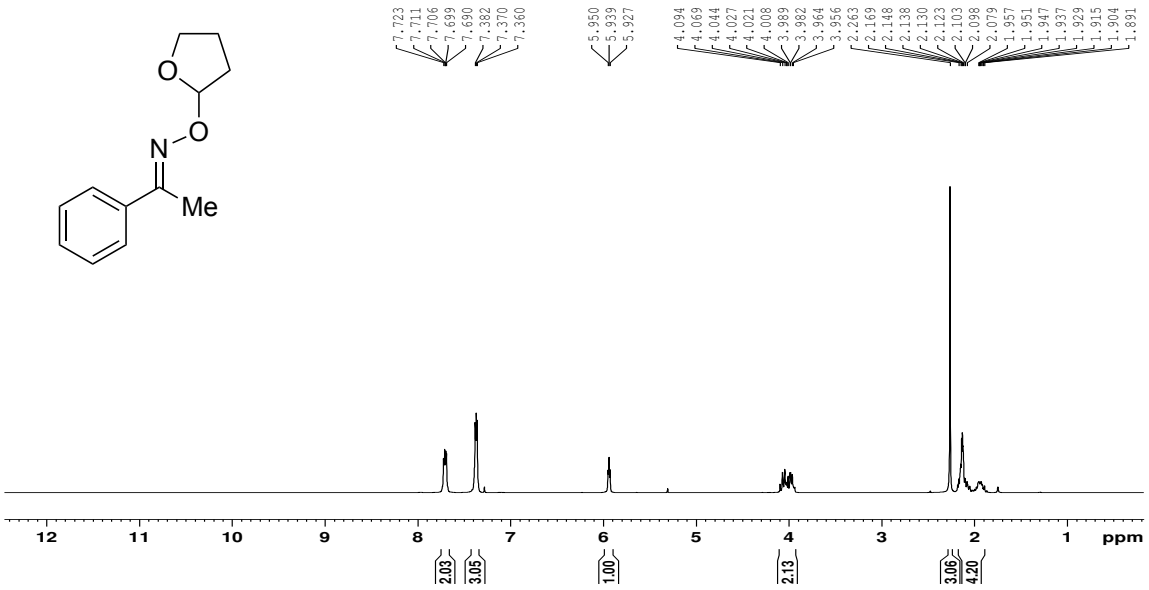
$^{1}$H NMR (300 MHz) Spectrum of **13ac (*E* isomer)** in $CDCl_3$



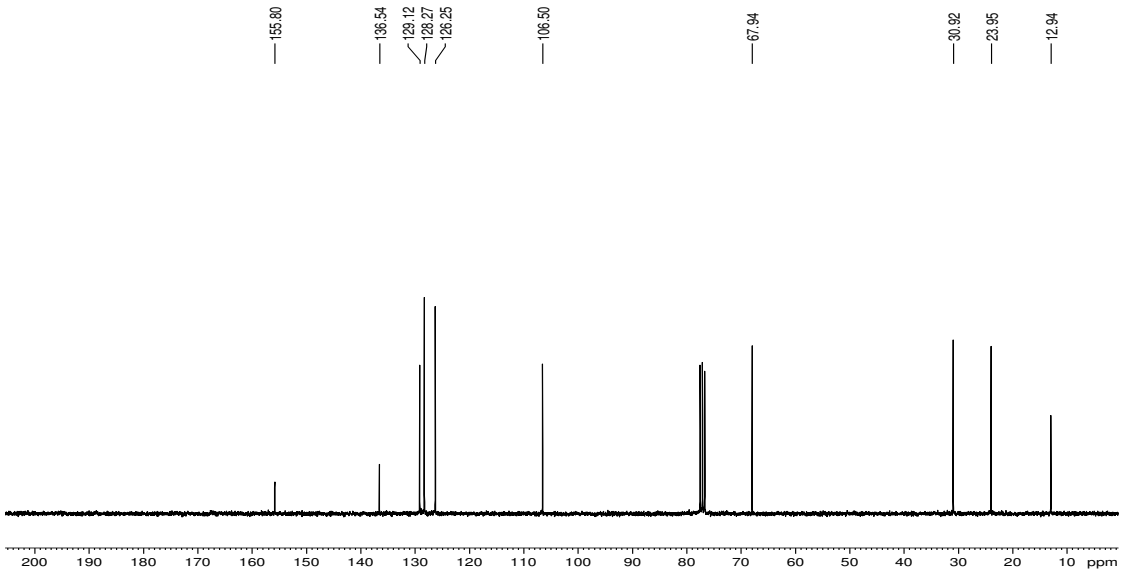

$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **13ac (*E* isomer)** in $CDCl_3$



$^{1}$H NMR (300 MHz) Spectrum of **13ad (*E* isomer)** in $CDCl_3$




$^{13}$C{$^{1}$H} NMR (75.5 MHz) Spectrum of **13ad (*E* isomer)** in $CDCl_3$



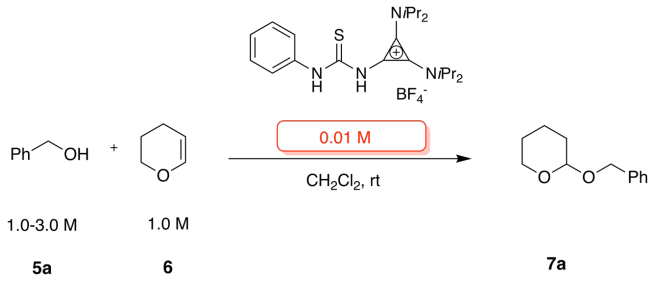
## *8.0 Appendix A*

**Experimental determination of reaction order**

**Reaction order dependence on alcohol concentration**

Three separate reactions were conducted in oven-dried 25.0 mL round-bottom flasks charged with 1 mol% catalyst (0.01 M, 0.05 mmol) (**4**·$BF_4^-$) to which was added benzyl alcohol (1.0, 2.0 or 3.0 M; 5.0, 10.0 or 15.0 mmol in 5.0 mL DCM) (**5a**) and DHP (1.0 M, 5.0 mmol) (**6**) at room temperature under an inert atmosphere. Reaction progress was determined by $^1$H NMR ($CDCl_3$) spectroscopy analyses of aliquots taken periodically. This involved monitoring the disappearance of the signal at 6.37 ppm for DHP and appearance of the signal at 4.51 ppm for the THP-protected product (**7a)**.

***Scheme 14:*** *Investigating reaction order in respect to alcohol concentration.*



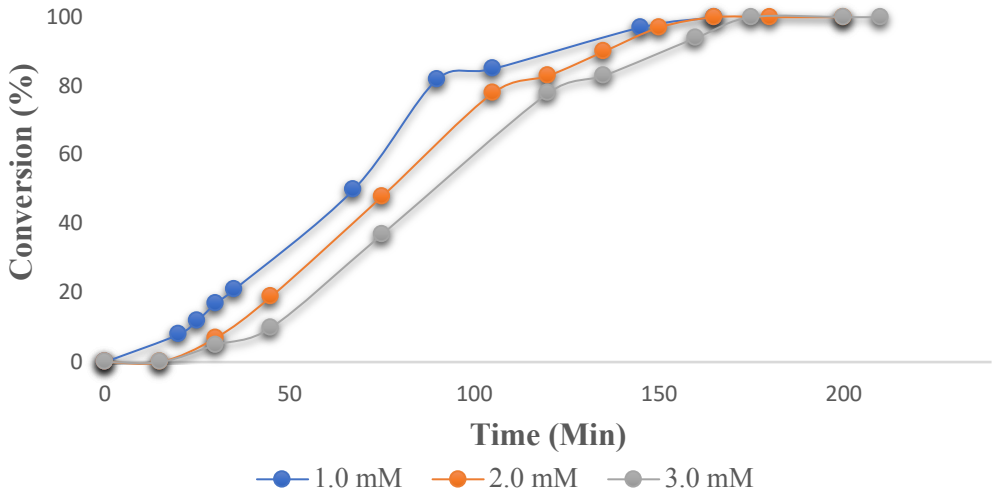



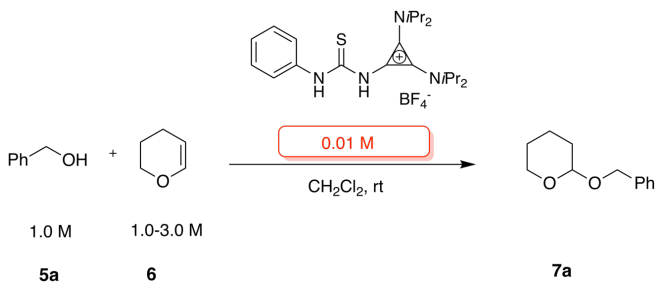
***Figure 35:*** *Plot of time (min) vs conversion (%) for three independent starting concentrations of benzyl alcohol performed under synthetically relevant conditions. The negligible difference in conversion times suggest that the reaction is first-order in benzyl alcohol.*

Plotting the results from these analyses resulted in the curves depicted in Figure 35. As seen, regardless of the initial concentration of benzyl alcohol (1.0, 2.0 or 3.0 M) the reactions went to complete conversion in ~3 hours. To account for these similar rates of reaction, the catalyst must function nearly twice as fast with each incremental increase (i.e., doubling of concentration) in substrate concentration. From these trends a first-order dependence on substrate **5a** is inferred.

**Reaction order dependence on DHP concentration**

Three separate reactions were conducted in oven dried 25.0 mL round-bottom flasks charged with 1 mol% catalyst (0.01 M, 0.05 mmol) (**4**·$BF_4^-$) to which was added DHP (1.0, 2.0 or 3.0 M; 5.0, 10.0 or 15.0 mmol in 5.0 mL DCM) (**6**) and benzyl alcohol (1.0 M, 5.0 mmol) (**5a**) at room temperature under an inert atmosphere. Reaction progress was determined by $^1$H NMR ($CDCl_3$) spectroscopy analyses of aliquots taken periodically. This involved monitoring the disappearance of the signal at 6.37 ppm for DHP and appearance of the signal at 4.51 ppm for the THP-protected product (**7a**).

***Scheme 15.*** *Investigating reaction order in respect to DHP concentration.*



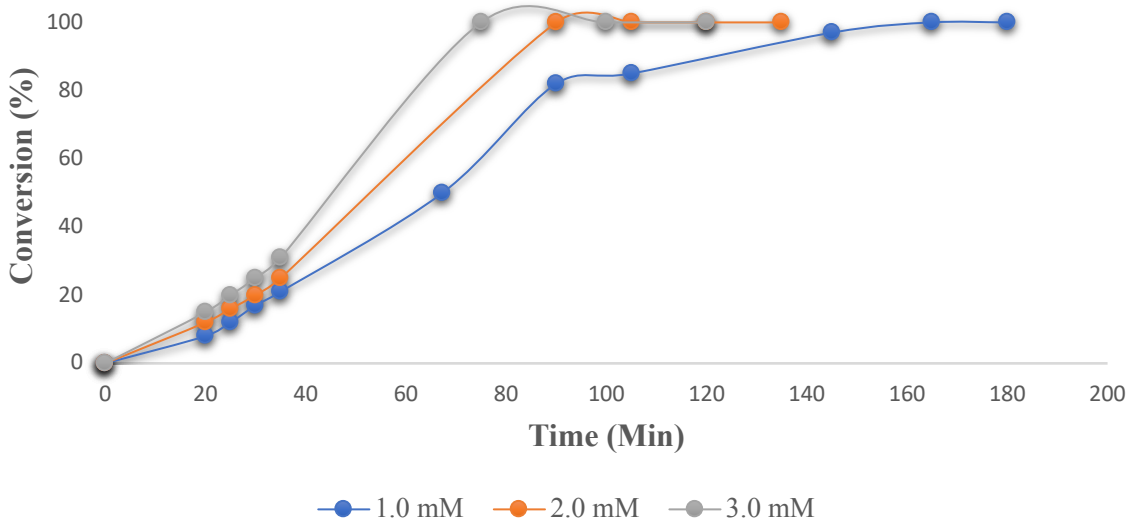



***Figure 36**. Plot of time (min) vs conversion (%) for three independent starting concentrations of DHP performed under synthetically relevant conditions.*

An investigation of the reaction order in DHP revealed a significant decrease in overall reaction time (1.0, 2.0 & 3.0 M; ~ 3, 1.5 and 1.25 H, respectively) with increasing DHP concentration (Figure 36). Plotting the data from these initial rate studies provided first-order dependencies in DHP, as observed from the linear trends in Figure 37. From this, the rate constant ($k$) for each of these reactions was extrapolated. These rate constants were then plotted ($k$ vs [DHP]), and were found to be within standard deviation (Figure 38); therefore, this is in agreement with a first-order reaction dependency on DHP concentration.

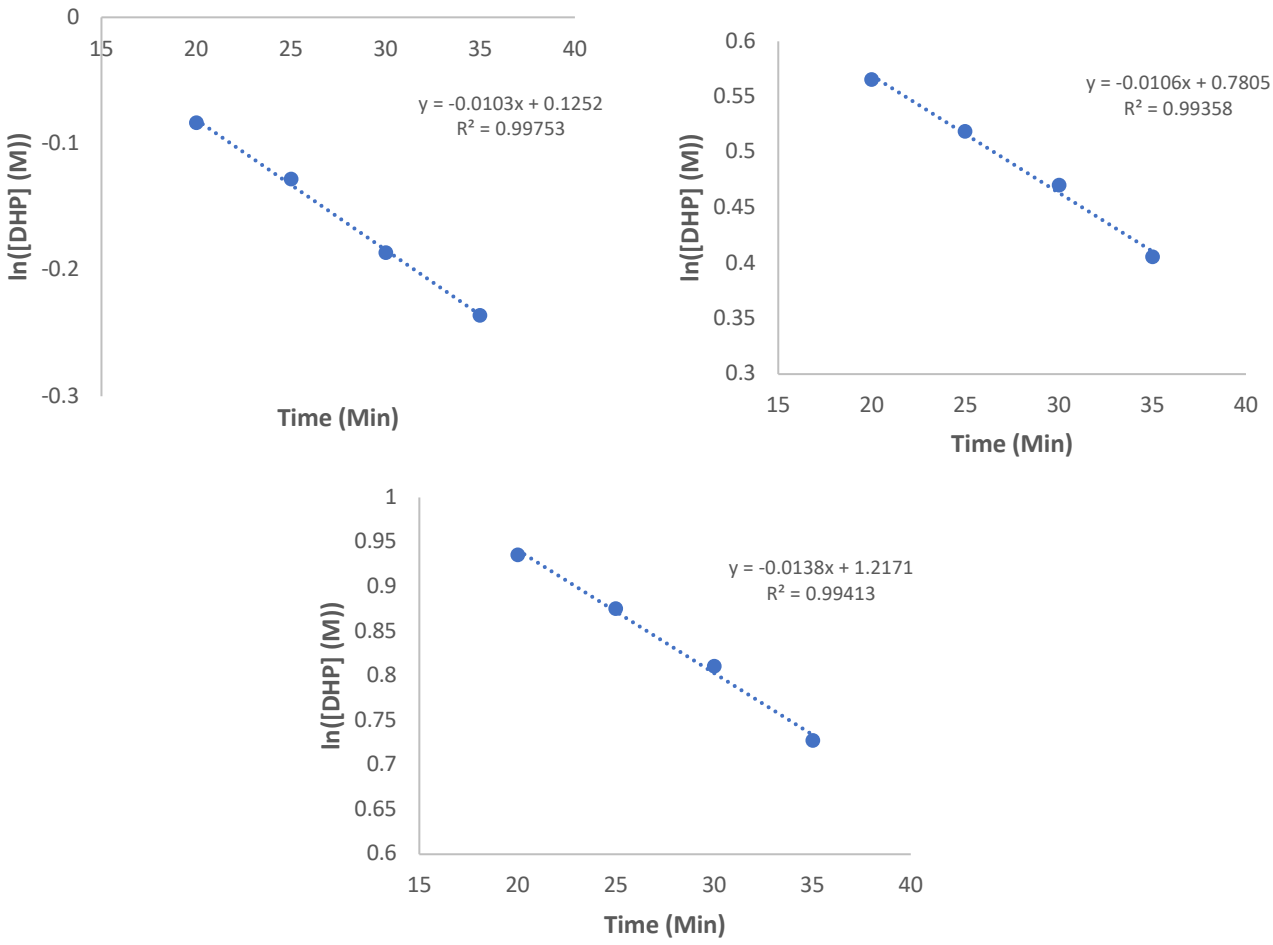



***Figure 37****. Rate constants (k) (top left:* ***1.0 M****, top right:* ***2.0 M****, bottom,* ***3.0 M****) were determined from analysis of the initial rate by implementing first-order kinetics, which invokes taking the natural logarithm of the concentration of substrate plotted against time (min) as fitted to a linear trend.*

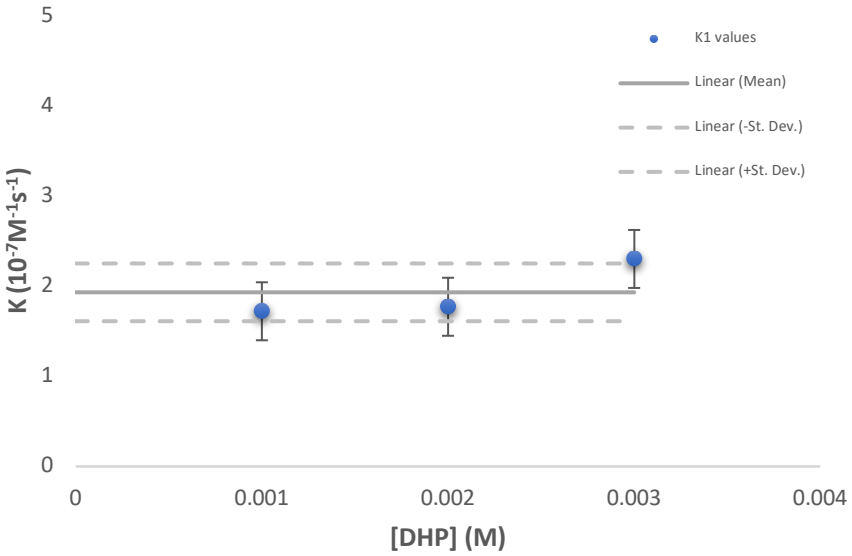



***Figure 38.*** *Rate constants ($M^{-1}s^{-1}$) plotted against the corresponding concentration of DHP (M) with error on fit (Note: error is reported as standard deviation). The mean value of k is represented by the continuous grey line. The standard deviation is represented by the segmented lines above and below the mean value.*

**NMR binding studies**

To further probe the reactivity with respect to alcohol, binding studies were performed. Upon addition of benzyl alcohol (**5a**) (10 equiv.) at room temperature, a minute downfield shift of the N–H hydrogens of the thiourea catalyst **4**·$BF_4^-$ was observed, thus consistent with weak or non-existent alcohol oxygen H-bonding with the N–H hydrogens (Figure 39)**.** By comparison, a measurable downfield shift of the alcohol O–H hydrogen was observed (Figure 40). The large chemical shift in this case was ascribed to non-intermolecular alcohol association. From this, it is apparent that the sulfur of the catalyst engages in H-bonding by way of rapidly exchanging proton transfer, which is consistent with a first-order dependency in alcohol.

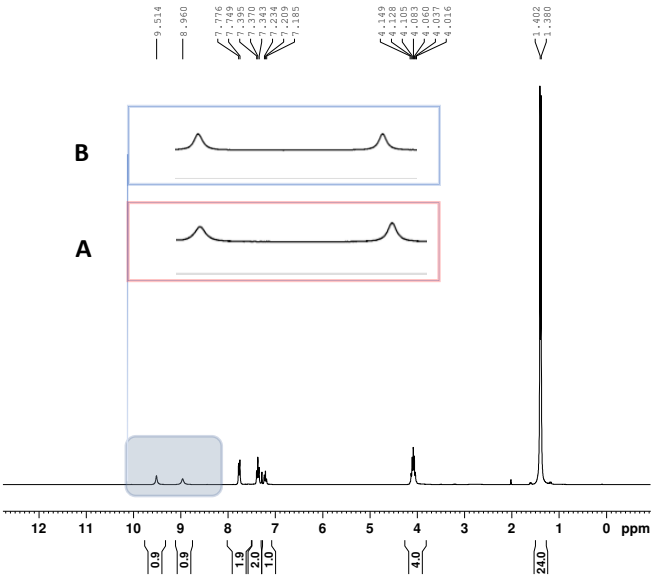



***Figure 39**. (**A**) Comparison $^1H$ NMR spectra at 300 MHz in 0.5 mL $CDCl_3$ at room temperature of **4**·$BF_4^-$ (10 mg, 0.02 mmol) vs. (**B**) titrated variant with benzyl alcohol (10.0 equiv., 22 µL).*

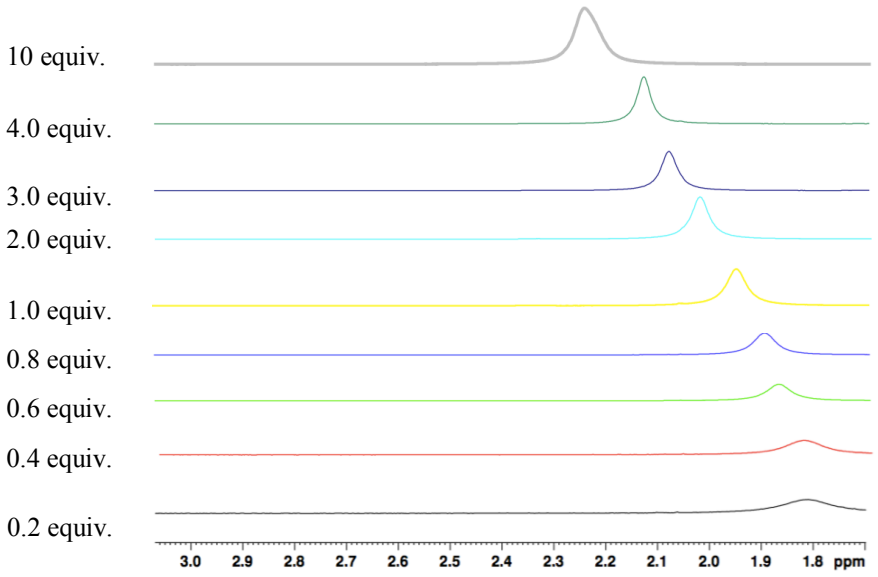



***Figure 40.*** *$^{1}$H NMR spectra at 300 MHz in 0.5 mL $CDCl_3$ at room temperature of thiourea **4**·$BF_4^-$ (10 mg, 0.02 mmol) following subsequent addition of benzyl alcohol aliquots. From this, a noticeable downfield shift of the O–H peak of benzyl alcohol was observed.*

Next, $^{1}$H NMR studies were conducted to investigate binding of the co-catalyst. This involved titration of thiourea **4**·$BF_4^-$ with benzoic acid (up to 2.0 equiv.), which led to broadening and eventual disappearance of the *N*-cyclopropenium hydrogen (Figure 41). This is suggestive of rapid proton exchange between benzoic acid and thiourea **4**·$BF_4^-$ N–H hydrogens. Therefore, this result shows a different binding mode is active relative to alcohol binding, *vide supra*.

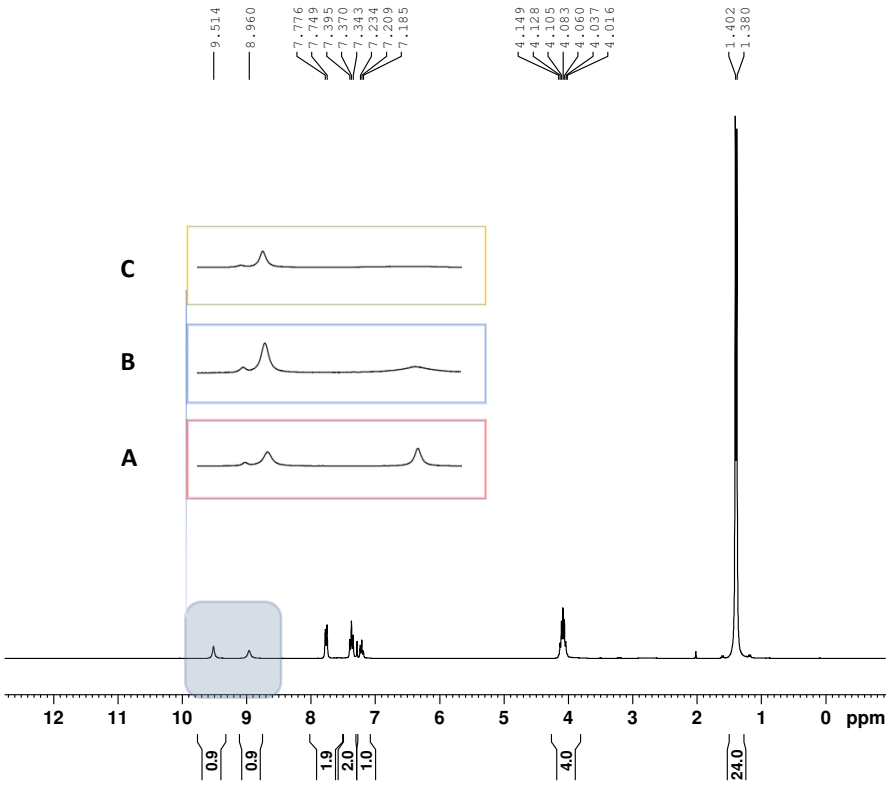



***Figure 41***. *(**A**) Comparison $^{1}H$ NMR spectra at 300 MHz in 0.5 mL $CDCl_3$ at room temperature of thiourea **4**·$BF_4^-$ (10 mg, 0.02 mmol) vs. (**B**) titrations with benzoic acid (1.0 equiv.), and (**C**) (2.0 equiv.).*

Variable temperature $^{1}H$ NMR experiments were proven to be effective in order to further explore the dynamic nature of the catalyst. Utilizing a 1:1 ratio of catalyst to benzoic acid led to the complete disappearance of the *N*-cyclopropenium hydrogen signal upon heating to 312.9 K. Conversely, this signal became sharper and more distinct after cooling the sample (Figure 42). From these events, it is inferred that dynamic low-barrier H-

bonding processes exist between the thiourea and benzoic acid. This renders the catalyst more electron deficient resulting in significantly enhanced reaction rates.

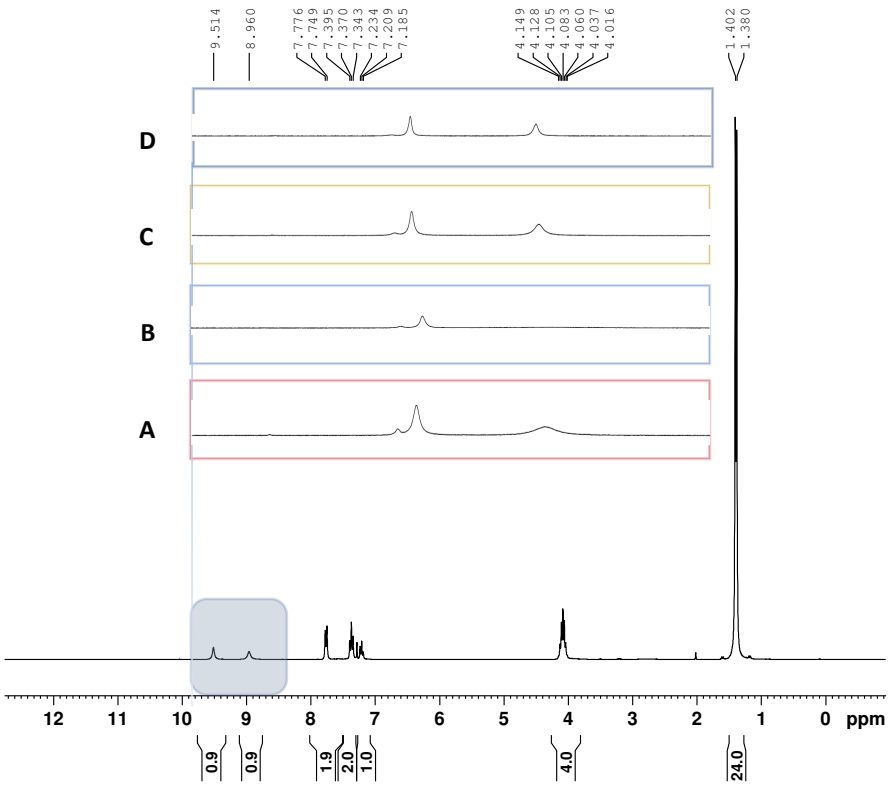



***Figure 42***. *Variable temperature $^{1}H$ NMR spectra at 600 MHz in 0.5 mL $CDCl_3$ of thiourea **4**·$BF_4^-$ (10 mg, 0.02 mmol) with benzoic acid (**A**) (1.0 equiv. at 295.1 K), (**B**) 312.9 K, (**C**) 284.2 K, and (**D**) 273.3 K.*

## X-ray crystallographic analysis

### Crystallogaphic data for $4 \cdot BF_4^-$

Single-crystals of the compound were mounted on a cryoloop with paratone oil and examined on a Bruker APEX II CCD X-ray diffractometer equipped with an Oxford Cryoflex Plus cooler used to maintain cryogenic temperatures for these studies. Data were collected using the APEX-II software,[178] integrated using SAINT[179] and corrected for absorption using a multi-scan approach (SADABS).[180] Final cell constants were determind from full least square refinements of all observed reflections. The structure was solved using intrinsic phasing (SHELX).[181] The structure was refined with full least squares software on $F^2$ using SHELXTL.[182] All hydrogen atoms were added at calculated positions and refined isotropically with a riding model. A summary of the key crystallographic data is presented in Table 10 and select geometries of bond lengths and angles are presented in Tables 11.

***Table 10.*** *Summary of Crystal data for* $4 \cdot BF_4^-$

| | |
|---|---|
| Chemical formula | $C_{22}H_{35}BF_4N_4S$ |
| $M_r$ | 474.41 |
| Crystal system, space group | Orthorhombic, $P2_12_12_1$ |
| Temperature (K) | 150 |
| $a$, $b$, $c$ (Å) | 9.8710 (6), 12.4156 (8), 20.5950 (11) |
| $V$ (Å$^3$) | 2524.0 (3) |
| $Z$ | 4 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.17 |
| Crystal size (mm) | 0.2 × 0.17 × 0.17 |
| Data collection | |
| Diffractometer | Bruker *APEX*-II CCD |

| | |
|---|---|
| Absorption correction | Multi-scan<br>Bruker *SADABS* |
| $T_{min}$, $T_{max}$ | 0.647, 0.746 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 10784, 4399, 4069 |
| $R_{int}$ | 0.039 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.594 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.043, 0.086, 1.61 |
| No. of reflections | 4399 |
| No. of parameters | 297 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.28, −0.21 |
| Absolute structure | Flack x determined using 1533 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259). |
| Absolute structure parameter | 0.01 (5) |

**Computer programs**: Bruker *APEX2*,[178] Bruker *SAINT*,[179] *SHELXS97* (Sheldrick 2008), *SHELXTL,* Bruker *SHELXTL*.[181,182]

***Table 11.*** *Selected geometric parameters for 4·$BF_4^-$*

| Bond | Length (Å) | Bond | Length (Å) |
|---|---|---|---|
| B1—F1 | 1.377 (5) | C17—C22 | 1.395 (4) |
| B1—F2 | 1.417 (5) | C18—C19 | 1.394 (5) |
| B1—F3 | 1.367 (4) | C19—C20 | 1.369 (5) |
| B1—F4 | 1.384 (4) | C20—C21 | 1.372 (5) |
| C1—C2 | 1.437 (4) | C21—C22 | 1.380 (5) |
| C1—C3 | 1.369 (4) | N1—C1 | 1.307 (4) |
| C2—C3 | 1.364 (4) | N1—C4 | 1.493 (4) |
| C4—C5 | 1.507 (4) | N1—C7 | 1.485 (4) |

| | | | |
|---|---|---|---|
| C4—C6 | 1.507 (5) | N2—C2 | 1.302 (4) |
| C7—C8 | 1.517 (5) | N2—C10 | 1.484 (4) |
| C7—C9 | 1.519 (5) | N2—C13 | 1.493 (4) |
| C10—C11 | 1.513 (5) | N3—C3 | 1.393 (4) |
| C10—C12 | 1.527 (5) | N3—C16 | 1.379 (4) |
| C13—C14 | 1.519 (5) | N4—C16 | 1.353 (4) |
| C13—C15 | 1.507 (4) | N4—C17 | 1.418 (4) |
| C17—C18 | 1.389 (5) | S1—C16 | 1.668 (3) |

| | | | |
|---|---|---|---|
| B1—F1 | 1.377 (5) | C17—C22 | 1.395 (4) |
| B1—F2 | 1.417 (5) | C18—C19 | 1.394 (5) |
| B1—F3 | 1.367 (4) | C19—C20 | 1.369 (5) |
| B1—F4 | 1.384 (4) | C20—C21 | 1.372 (5) |
| C1—C2 | 1.437 (4) | C21—C22 | 1.380 (5) |
| C1—C3 | 1.369 (4) | N1—C1 | 1.307 (4) |
| C2—C3 | 1.364 (4) | N1—C4 | 1.493 (4) |
| C4—C5 | 1.507 (4) | N1—C7 | 1.485 (4) |
| C4—C6 | 1.507 (5) | N2—C2 | 1.302 (4) |
| C7—C8 | 1.517 (5) | N2—C10 | 1.484 (4) |
| C7—C9 | 1.519 (5) | N2—C13 | 1.493 (4) |
| C10—C11 | 1.513 (5) | N3—C3 | 1.393 (4) |
| C10—C12 | 1.527 (5) | N3—C16 | 1.379 (4) |
| C13—C14 | 1.519 (5) | N4—C16 | 1.353 (4) |
| C13—C15 | 1.507 (4) | N4—C17 | 1.418 (4) |
| C17—C18 | 1.389 (5) | S1—C16 | 1.668 (3) |
| **Bond** | **Angle ($^0$)** | **Bond** | **Angle ($^0$)** |
| F3—B1—F1 | 111.5 (4) | N1—C4—C6 | 110.1 (3) |

| | | | |
|---|---|---|---|
| F3—B1—F4 | 111.5 (3) | N1—C4—C5 | 110.8 (2) |
| F1—B1—F4 | 108.4 (3) | C6—C4—C5 | 113.1 (3) |
| F3—B1—F2 | 109.3 (3) | N1—C7—C8 | 110.5 (3) |
| F1—B1—F2 | 107.7 (3) | N1—C7—C9 | 110.8 (3) |
| F4—B1—F2 | 108.3 (3) | C8—C7—C9 | 112.9 (3) |
| C1—N1—C7 | 122.2 (2) | N2—C10—C11 | 111.1 (3) |
| C1—N1—C4 | 118.5 (2) | N2—C10—C12 | 110.2 (3) |
| C7—N1—C4 | 119.1 (2) | C11—C10—C12 | 112.6 (3) |
| C2—N2—C10 | 122.9 (2) | N2—C13—C15 | 111.1 (2) |
| C2—N2—C13 | 118.1 (2) | N2—C13—C14 | 110.3 (3) |
| C10—N2—C13 | 119.0 (2) | C15—C13—C14 | 113.2 (3) |
| C16—N3—C3 | 120.1 (2) | N4—C16—N3 | 112.2 (3) |
| C16—N4—C17 | 132.3 (3) | N4—C16—S1 | 128.0 (2) |
| N1—C1—C3 | 150.7 (3) | N3—C16—S1 | 119.9 (2) |
| N1—C1—C2 | 151.2 (3) | C18—C17—C22 | 119.5 (3) |
| C3—C1—C2 | 58.1 (2) | C18—C17—N4 | 125.1 (3) |
| N2—C2—C3 | 150.7 (3) | C22—C17—N4 | 115.4 (3) |
| N2—C2—C1 | 150.8 (3) | C17—C18—C19 | 119.2 (3) |
| C3—C2—C1 | 58.5 (2) | C20—C19—C18 | 121.3 (3) |
| C2—C3—C1 | 63.4 (2) | C19—C20—C21 | 119.2 (3) |
| C2—C3—N3 | 148.0 (3) | C20—C21—C22 | 121.2 (3) |
| C1—C3—N3 | 148.5 (3) | C21—C22—C17 | 119.7 (3) |

Examination of the crystal packing of **4**·$BF_4^-$ reveals that the molecules are backed as a head-to-tail arrangement of dimers that form a herringbone pattern along the *b*-axis. The $BF_4^-$ counterions occupy the spaces in the crystal lattice, and form short contacts with aryl and alkyl hydrogen atoms from adjacent molecules (Figure 43).

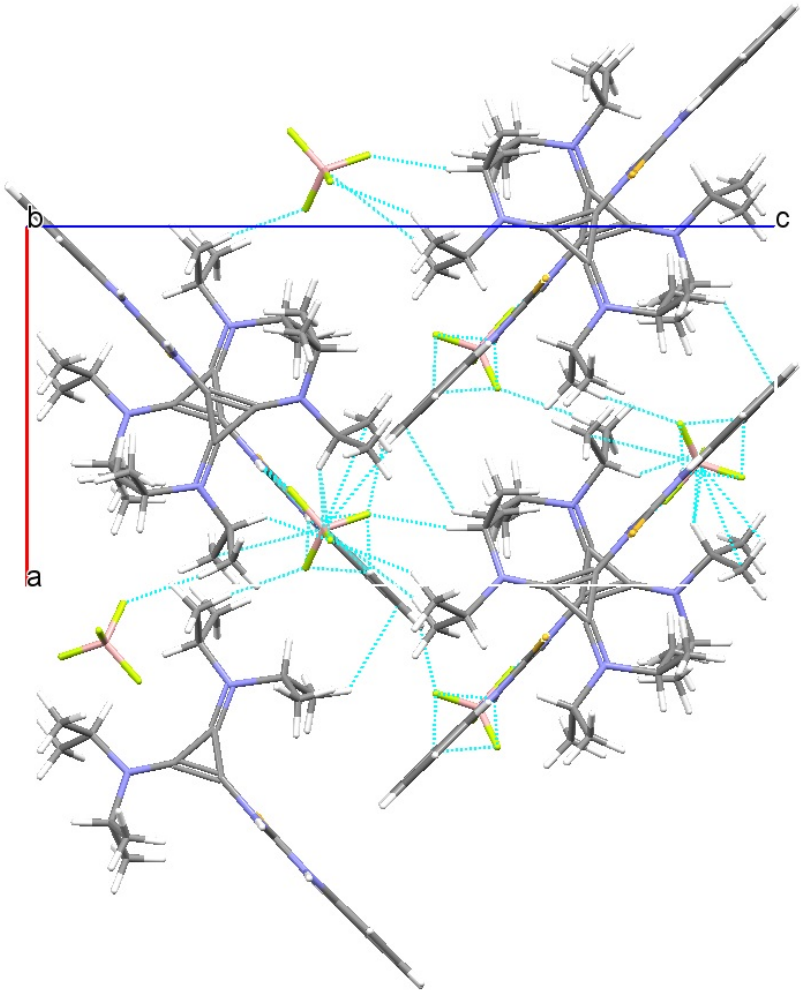



***Figure 43.*** *Packing diagram for* ***4***·$BF_4^-$. *View down the b-axis of the unit cell. Short contacts are shown as blue dashed lines.*

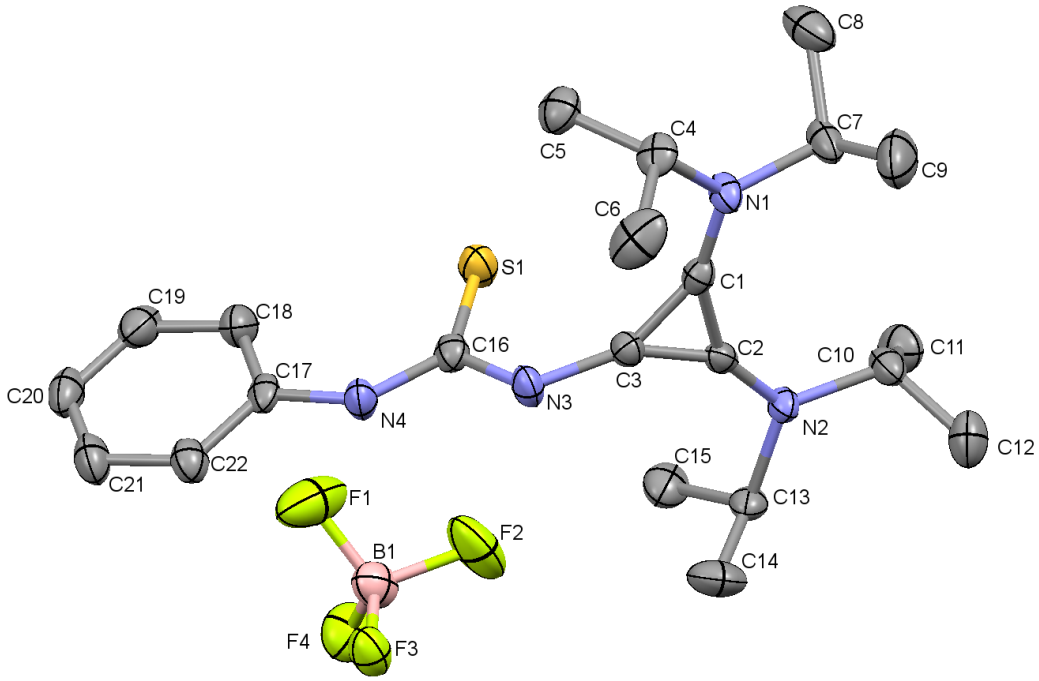



***Figure 44***. *ORTEP plot of the molecular structure of* ***4***·$BF_4^-$ *with appropriate labelling scheme. Thermal ellipsoids are plotted at 50%. H-atoms are omitted for clarity.*

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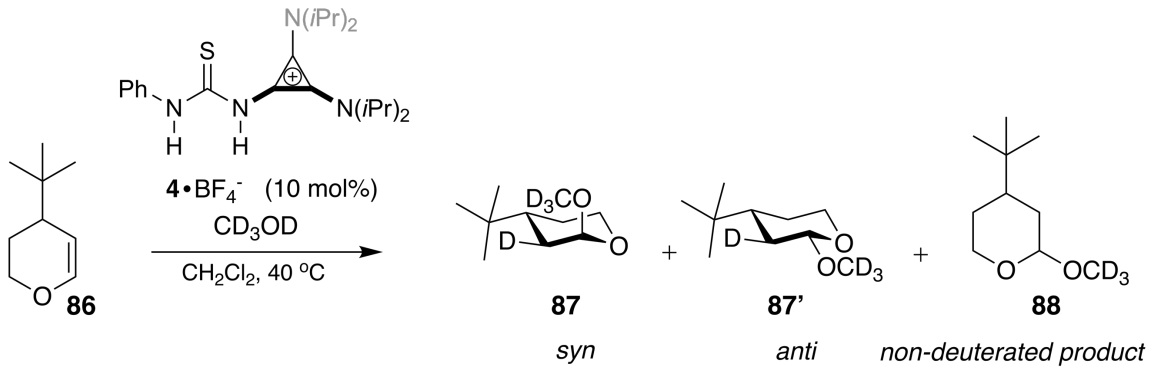
**Probing the stereochemistry of alcohol addition**

It was found that the majority of the products were deuterated in position 3, while any minor byproducts (e.g., protonated products – **88**) arose from the non-deuterated catalyst (Scheme 16). Key to these findings is the kinetically-controlled preference for *syn* product formation over a duration of 48 hours (*syn* : *anti* ratio of 70:30) that is consistent with the computed Brønsted acid mode of catalysis.

***Scheme 16.*** *Investigating the stereochemistry of addition using methanol-d$_4$ and 4-(tert-butyl)-3,4-dihydro-2H-pyran.*




**Experiments investigating alkoxide exchange**

**Probing the stereochemistry of alcohol addition.**

To probe the stereochemistry of alcohol addition, an experiment using methanol-d$_4$ was performed. This involved the use of a 10.0 mL round-bottom flask charged with thiourea **4**·$BF_4^-$ (115 mg, 10 mol%) to which methanol-d$_4$ (114 mg, 3.2 mmol) and 4-(*tert*-butyl)-3,4-dihydro-*2H*-pyran (340 mg, 2.4 mmol) were combined and subsequently diluted in DCM (2.0 mL). The resulting solution was stirred at 40 °C, while monitoring product

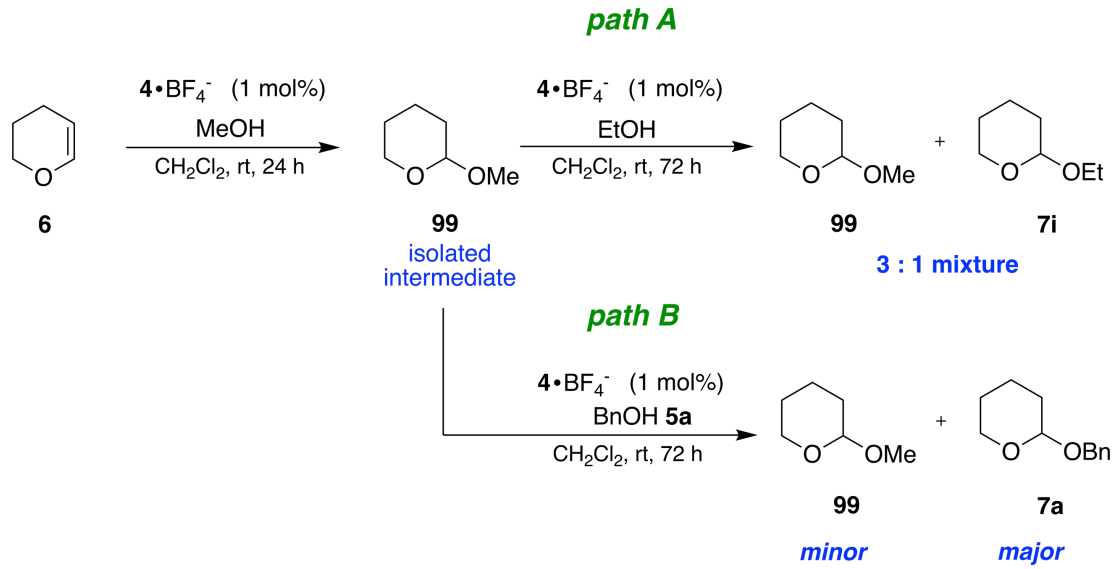
formation with $^{1}H$ NMR spectroscopy over a period of 72 hours (reaction completion). Next, all volatiles (DCM and any residual methanol-$d_4$) were removed *in vacuo,* and the crude product was extracted with diethyl ether, concentrated and analyzed with NMR spectroscopy.

To examine the potential for alkoxide exchange, intermediate **99** was exposed to ethanol, which was allowed to stir for 72 hours. Over the course of the reaction, a distinguishable triplet slowly evolved indicating formation of 2-ethoxytetrahydropyran (**7i**), and, thus, showing that alkoxide exchange had taken place as seen by a 3 : 1 / 2-methoxytetrahydropyran:2-ethoxytetrahydropyran ratio (Scheme 17 – path A). Inspired by the interconversion of alkoxide adducts, *vide infra,* benzyl alcohol (**5a**) was employed anticipating that the $\pi$–system of the benzene ring would impart additional non-covalent interactions upon contact with thiourea **4**·$BF_4^-$. The impetus for this pursuit arising from the proximal cyclopropenyl cation appended to the thiourea, which would presumably participate in catalyst–substrate $\pi$–stacking[183] or cation–$\pi$[184] interactions.

To test this hypothesis, the same reaction parameters were implemented, with the exception of using benzyl alcohol (**5a**) as substrate (120 mg, 1.1 mmol), as opposed to ethanol, which resulted in nearly full interconversion yielding the benzyl adduct (**7a**) after 72 hours (Scheme 17 – path B). A computational study was then performed to examine this exchange process, wherein the stability of the pyranylated products were compared. These calculations demonstrated that both the ethyl and benzyl alkoxide products (**7i**) and (**7a**), respectively were lower in energy than the methyl adduct (**99**). These energetic trends are consistent with the observed experimental product distribution. Taken together, these

results suggest that pyranyl product formation is reversible in the presence of thiourea **4**·$BF_4^-$.

***Scheme 17.*** *Probing the possibility for alkoxide exchange.*

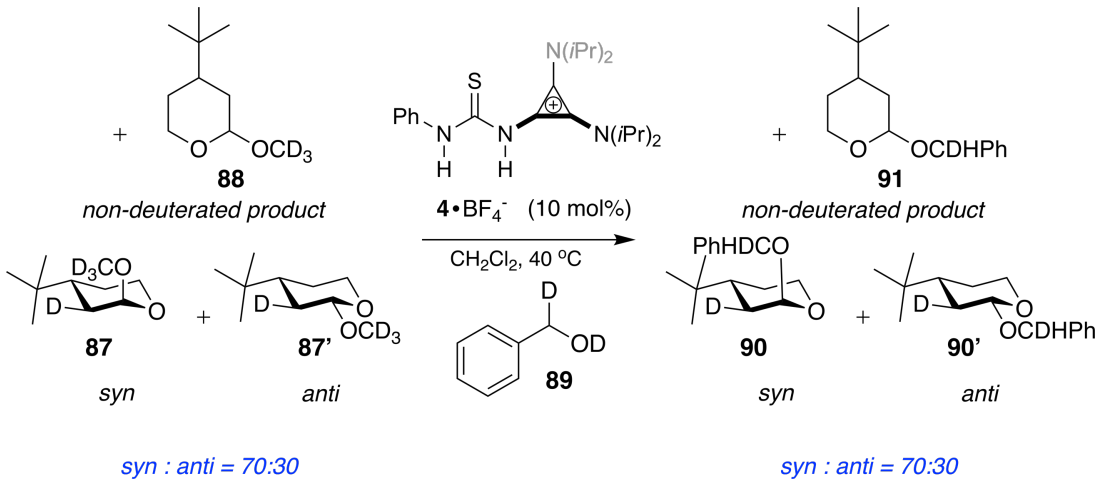



**Experiments investigating epimerization.**

The reaction conditions were then applied to phenyl (*O*,1-$^2H_2$) methanol to distinguish between alkoxide exchange and epimerization. This involved the use of a 5.0 mL round-bottom flask charged with thiourea **4**·$BF_4^-$ (49 mg, 10 mol%) to which phenyl (*O*,1-$^2H_2$) methanol (114 mg, 1.0 mmol) and the deuterated mixture of *syn* and *anti* product isomers (182 mg, 1.0 mmol) were combined and subsequently diluted in dichloromethane (0.75 mL). The resulting solution was stirred at 40 °C, while monitoring product formation with $^1$H NMR spectroscopy over a period of 9 days. Next, DCM was removed *in vacuo* and the crude product was extracted with diethyl ether, concentrated and analyzed with NMR spectroscopy.

Finally, intrigued by the ability of thiourea catalyst **4**·$BF_4^-$ to induce alkoxide exchange, the reaction conditions were subjected to phenyl (*O*,1-$^2H_2$) methanol (**89**) to distinguish between alkoxide exchange and epimerization (Scheme 18). Based on these experimental results, there is an obvious kinetic preference for *syn* product formation as observed from the *syn* : *anti* ratio of 70:30 upon completion of alkoxide interconversion. From this, epimerization is ruled out, and instead, the retention of stereochemistry is ascribed to analogous mechanisms of alcohol addition. Furthermore, the stereochemical outcome is governed by a catalyst-controlled stereoselective reaction scenario. This is in accordance with kinetic control.

***Scheme 18.*** *Investigating the stereochemistry of addition using phenyl (O,1-$^2H_2$) methanol and a mixture of syn and anti product isomers (methyl adduct).*



**Low temperature NMR experimental acquisition.**

NMR spectra were recorded on a Bruker Avance AV I 600 spectrometer ($^1$H 600 MHz) in $CD_2Cl_2$. The observed chemical shifts are reported as $\delta$-values (ppm) relative to tetramethylsilane (TMS). The peaks of interest are denoted by red squares, as determined upon cooling of the sample. This protocol provides experimental evidence demonstrating the conformational orientation of thiourea **4**·$BF_4^-$, which was then compared with the computed results. The equations used to calculate the barrier to interconversion are shown below. The rate constant $k_c$ at the coalescence temperature ($T_c$) was found using the difference in Hz ($\Delta\nu$ – equation 1). The free activation energy ($\Delta G^{\ddagger}$) was determined using equation 2.

$$k_c = \frac{\pi\Delta\upsilon}{\sqrt{2}} \quad (1)$$

$$\Delta G^{\ddagger} = RT_c\left[22.96 + \ln\left(\frac{T_c}{\Delta\upsilon}\right)\right] \quad (2)$$

**Procedure for $^{13}$C KIE experiments.**

Two independent reactions were conducted at either stoichiometric (1:1) or pseudo-first-order conditions to furnish the THP-protected product at high conversion (100%) or low conversion (2%), respectively. The products were analyzed using Jacobsen's DEPT-55 technique.[128] Equation 3 was applied to calculate the KIEs.

$$\mathrm{KIE_{PTD}} = \frac{\ln(1-F)}{\ln[(1-F(R_{\mathrm{PDT}}/R_0))]} \quad (3)$$

(High conversion)

To an oven-dried 10.0 mL round-bottom flask charged with thiourea **4**·$BF_4^-$ (11 mg, 1 mol%); benzyl alcohol (2.3 mmol) and DHP (2.3 mmol) were combined and subsequently diluted in DCM (2.0 mL). The resulting solution was stirred at room temperature under an

inert atmosphere for 3 hours. After removal of the solvent, the crude material was triturated with diethyl ether (1 x 3.0 mL), and concentrated to yield the THP-protected alcohol.

(Low conversion)

To an oven-dried 10.0 mL round-bottom flask charged with thiourea **4**·$BF_4^-$ (~2 mg, 1 mol%); benzyl alcohol (0.37 mmol) and DHP (18.5 mmol) were combined and subsequently diluted in DCM (1.0 mL). The resulting solution was stirred at room temperature under an inert atmosphere for 3 hours. After removal of the solvent, the crude material was subjected to flash chromatography using a hexanes/ethyl acetate (9:1) solvent system to yield the THP-protected alcohol.

## NBO studies

***Table 12.*** *NBO values for selected atoms.*

| Structure | Atom | NBO Charge (e) |
|---|---|---|
| Z,Z-**1-INT$_2$** | $N_3$ | -0.671 |
| | ($N_3$)-H | 0.459 |
| (N-H···O-H Bond) b/w catalyst and pyran | O | -0.795 |
| | H | 0.510 |

**Rotational energy barrier between *E,Z*- and *Z,Z*-conformers**

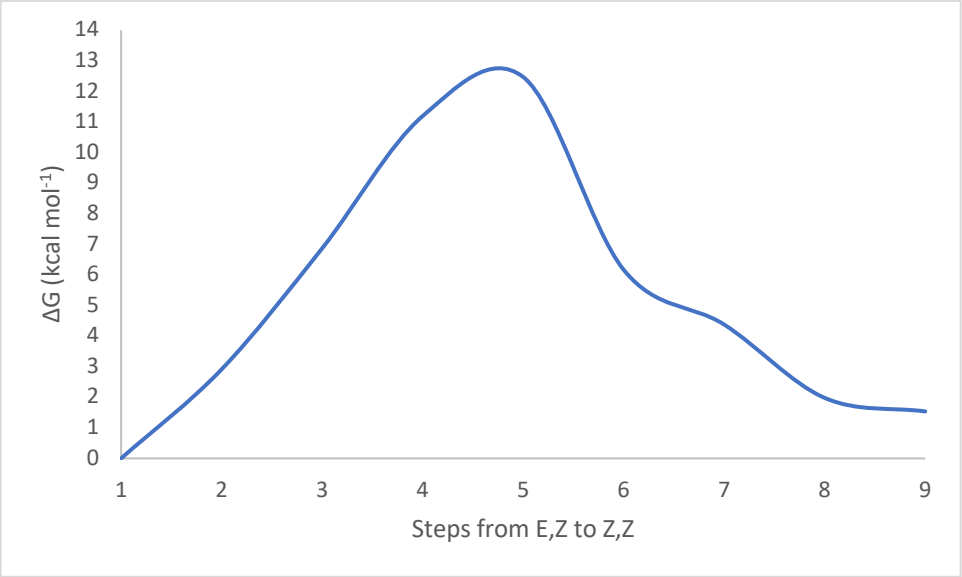



***Figure 45.*** *Plot of energy versus steps in rotation from E,Z-conformer to Z,Z-conformer calculated in the absence of counterion.*

**Conformational search for α- vs. β-stereofacial alcohol addition**

**Computational methods and details:**

Force Field = OPLS3

Dielectric constant = 1.0

Method = PRCG

Convergence threshold = 0.05

Maximum interactions 2500

Mixed torsional/Low-mode sampling

Maximum number of steps = 100

100 steps per rotatable bond

Number of structures to save for each search = 100

Energy window for saving structures 21.0 kJ/mol

Maximum atom deviation Cutoff = 0.5 angstrom

Probability of a torsion rotation/molecule translation = 0.5

Minimum distance for low-mode move = 3.0

Maximum distance for a low-mode move = 6.0

From these searches

(β) Bottom face 49 conformers

(α) Top face 27 conformers

## *9.0 Appendix B*

**NMR binding study**

To probe the reactivity with respect to *trans*-$\beta$-nitrostyrene (**8a**), binding studies were performed. $^{1}$H NMR titrations in $CDCl_3$ using catalyst **4**·$BF_4^-$ and substrate **8a** (up to 20.0 equiv.) at room temperature revealed a downfield shift of the N–H hydrogen atom belonging to **4** ($\Delta\delta$ = 0.04 ppm), thus, consistent with a LUMO-lowering mode of activation (Figure 46). This experimental data is congruent with the computational findings.

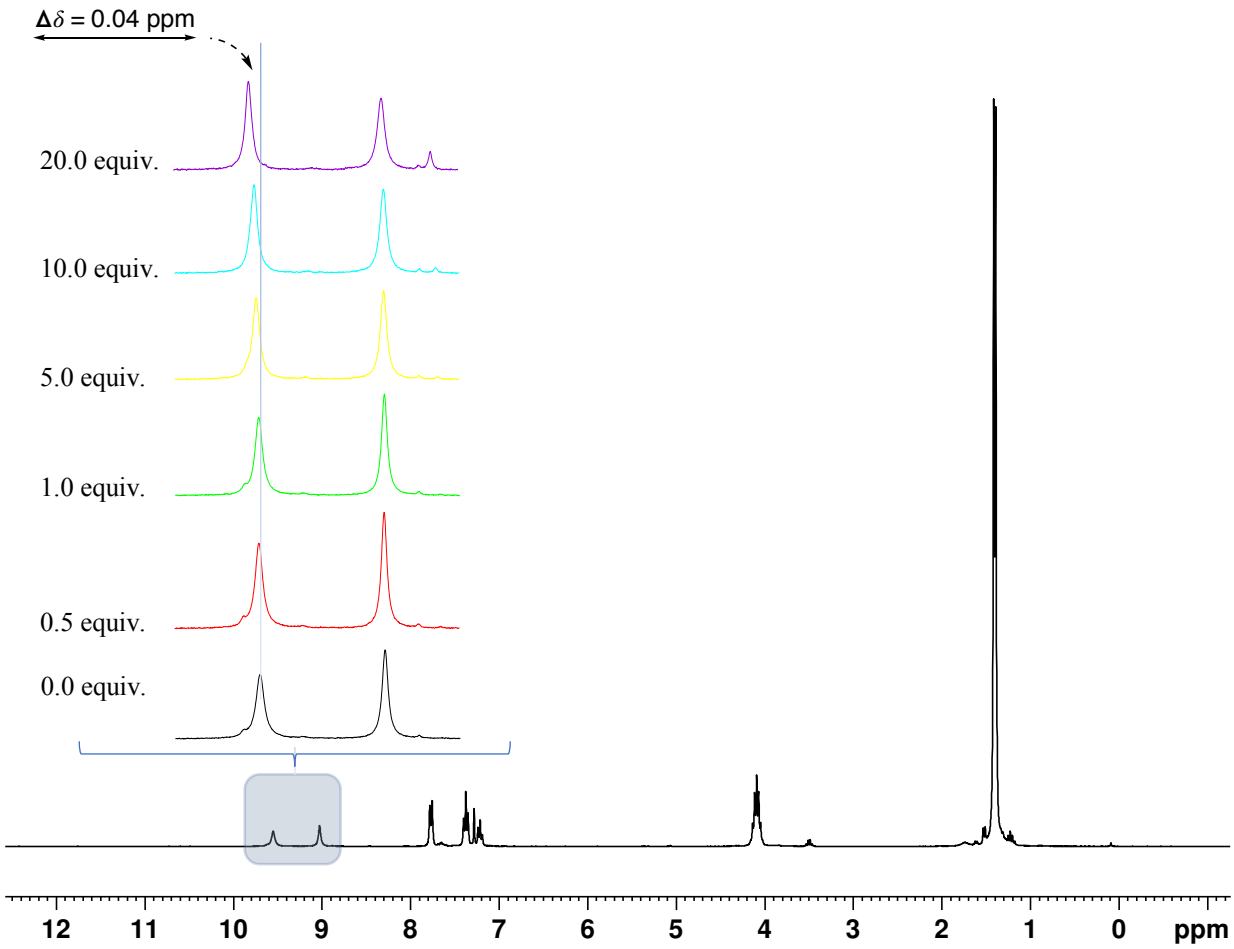


***Figure 46.*** *$^1$H NMR spectra at 300 MHz in 0.5 mL $CDCl_3$ at room temperature of thiourea **4**·$BF_4^-$ (10 mg, 0.02 mmol) following subsequent additions of trans-β-nitrostyrene aliquots. From this, a noticeable downfield shift, that being, 0.04 ppm of the N–H hydrogen atom belonging to the thiourea moiety was observed.*

## VTNA

Exploiting this methodology can help provide key mechanistic facets of reactivity, including catalyst deactivation, the order in catalyst, as well as the order in substrates.[3,4] The order in catalyst can be determined abiding to the normalized time scale method, which is approximated *via* the trapezoid rule, and, thus, removes the kinetic effect of that component from the reaction profile. Notably, VTNA can function to elucidate numerous reaction components irrespective of whether their concentration is constant or variable. To this end, the following equations were used to determine the order in catalyst (eq 4) and the order in substrates (eq 5). The value of "$\gamma$" and "$\beta$" that provides the greatest overlay of the generated curves is the order in the respective component.

$$\sum [\text{cat}]^{\gamma} \Delta t = \sum_{i=1}^{n} \left( \frac{[\text{cat}]_i + [\text{cat}]_{i-1}}{2} \right)^{\gamma} (t_i - t_{i-1}) \tag{4}$$

$$\sum [\text{component}]^{\beta} \Delta t = \sum_{i=1}^{n} \left( \frac{[\text{component}]_i + [\text{component}]_{i-1}}{2} \right)^{\beta} (t_i - t_{i-1}) \tag{5}$$

**Experimental determination for potential product inhibition or catalyst deactivation**

Two separate reactions were conducted in oven-dried 25.0 mL round-bottom flasks charged with 10 mol% catalyst (0.168 M, 0.335 mmol) (**4**·$BF_4^-$) to which was added *trans*-*β*-nitrostyrene (1.68- or 1.00 M; 3.35-, or 2.00 mmol) (**8a**) and 1-methylindole (5.03- or 4.35 M; 10.1- or 8.70 mmol) (**9a**) diluted in 2.0 mL DCM at room temperature under an inert atmosphere. Reaction progress was determined by $^1$H NMR ($CDCl_3$) spectroscopy analyses of aliquots taken periodically. This involved monitoring the disappearance of the signal at 8.00 ppm for (**8a**) and appearance of the signal at 5.21 ppm for the FC alkylated product (**10a**).

***Scheme 19.*** *Probing the potential for product inhibition or catalyst deactivation with respect to trans-β-nitrostyrene concentration.*

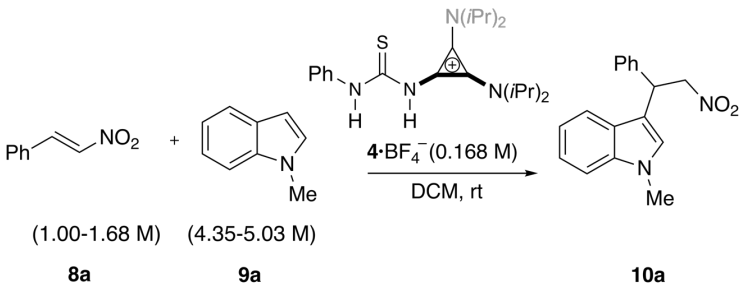



***Table 13***. *$^1$H NMR data probing the potential for product inhibition or catalyst deactivation.*

| Experiment 1: standard conditions | | | |
|---|---|---|---|
| entry | t (h) | [**8a**] (M) | [**10a**] (M) |
| 1 | 0 | 1.68 | 0.00 |
| 2 | 2 | 1.44 | 0.24 |
| 3 | 3 | 1.31 | 0.37 |
| 4 | 4 | 1.23 | 0.45 |
| 5 | 6 | 1.06 | 0.62 |

| | | | |
|---|---|---|---|
| 6 | 8 | 0.924 | 0.76 |
| 7 | 11 | 0.739 | 0.94 |
| 8 | 18 | 0.487 | 1.19 |
| 9 | 24 | 0.336 | 1.34 |
| 10 | 27 | 0.286 | 1.39 |
| 11 | 30 | 0.252 | 1.43 |
| 12 | 35 | 0.202 | 1.48 |

***Table 14***. *$^1$H NMR data for probing the potential for product inhibition or catalyst deactivation.*

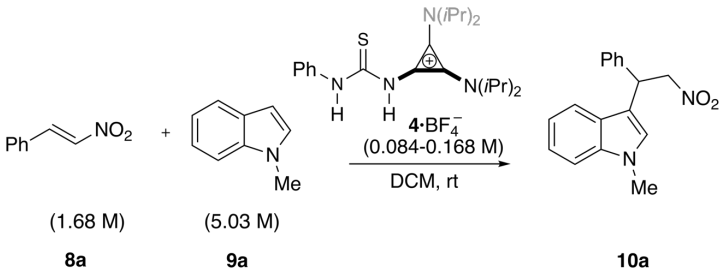
| Experiment 2: reduced concentration | | | | |
|---|---|---|---|---|
| entry | t (h) | time adjusted (h) | [**8a**] (M) | [**10a**] (M) |
| 1 | 0 | 7 | 1.00 | 0.00 |
| 2 | 0.5 | 7.5 | 0.94 | 0.06 |
| 3 | 2 | 9 | 0.83 | 0.17 |
| 4 | 4 | 11 | 0.73 | 0.27 |
| 5 | 6 | 13 | 0.63 | 0.37 |
| 6 | 8 | 15 | 0.54 | 0.46 |
| 7 | 18 | 25 | 0.28 | 0.72 |
| 8 | 23 | 30 | 0.19 | 0.81 |
| 9 | 26 | 33 | 0.16 | 0.84 |
| 10 | 29 | 36 | 0.12 | 0.88 |

**Experimental determination of the order in catalyst**

Having established the robust nature of charged thiourea **4**, this insight was utilized to probe the kinetic order in catalyst. As such, two separate reactions were conducted in oven-dried 25.0 mL round-bottom flasks charged with either 5- or 10 mol% catalyst (0.084- or 0.168 M; 0.168- or 0.335 mmol) (**4**·$BF_4^-$) to which was added *trans*-*β*-nitrostyrene (1.68 M, 3.35 mmol) (**8a**) and 1-methylindole (5.03 M, 10.1 mmol) (**9a**) diluted in 2.0 mL DCM at room temperature under an inert atmosphere. Reaction progress was determined by $^1$H NMR ($CDCl_3$) spectroscopy analyses of aliquots taken periodically. This involved

monitoring the disappearance of the signal at 8.00 ppm for (**8a**) and appearance of the signal at 5.21 ppm for the FC alkylated product (**10a**).

***Scheme 20.*** *Investigating the order in catalyst for thiourea* ***4***·$BF_4^-$.




The order in catalyst was elucidated using the normalized time scale method, wherein data points correlating to the formation of the alkylated product **10a** were plotted against a normalized time scale, $t[\mathrm{cat}]_T^n$.[4b] Since the concentration of the catalyst is constant throughout the course of the reaction, the equation used to determine the time scale is as follows: $t[cat]_o^{\gamma}$. The value of "$\gamma$" that is responsible for the overlay of the curves corresponds to the order in catalyst.

***Table 15***. *$^1$H NMR data corresponding to 10 mol% catalyst loading for determining the order in catalyst.*

| | | Experiment 1: 10 mol% | | | | | |
|---|---|---|---|---|---|---|---|
| entry | t (h) | $tcat^{\gamma}$ ($\gamma$ = 0, 0.5, 0.8, 1) | | | | [**4**·$BF_4^-$] (M) | [**10a**] (M) |
| 1 | 0 | 0 | 0.0000 | 0.0000 | 0.0000 | 0.168 | 0.0000 |
| 2 | 2 | 2 | 0.8197 | 0.4800 | 0.3360 | 0.168 | 0.2352 |
| 3 | 3 | 3 | 1.229 | 0.7200 | 0.5040 | 0.168 | 0.3696 |
| 4 | 4 | 4 | 1.639 | 0.9600 | 0.6720 | 0.168 | 0.4536 |
| 5 | 6 | 6 | 2.459 | 1.440 | 1.008 | 0.168 | 0.6216 |
| 6 | 8 | 8 | 3.279 | 1.920 | 1.344 | 0.168 | 0.756 |
| 7 | 11 | 11 | 4.508 | 2.640 | 1.848 | 0.168 | 0.9408 |
| 8 | 18 | 18 | 7.377 | 4.320 | 3.024 | 0.168 | 1.1928 |
| 9 | 24 | 24 | 9.837 | 5.760 | 4.032 | 0.168 | 1.344 |
| 10 | 27 | 27 | 11.06 | 6.480 | 4.536 | 0.168 | 1.3944 |
| 11 | 30 | 30 | 12.29 | 7.200 | 5.040 | 0.168 | 1.428 |
| 12 | 35 | 35 | 14.34 | 8.400 | 5.880 | 0.168 | 1.4784 |

***Table 16***. *$^1$H NMR data corresponding to 5 mol% catalyst loading for determining the order in catalyst.*

| | | Experiment 2: 5 mol% | | | | | |
|---|---|---|---|---|---|---|---|
| entry | t (h) | $tcat^{\gamma}$ ($\gamma$ = 0, 0.5, 0.8, 1) | | | | [**4**·$BF_4^-$] (M) | [**10a**] (M) |
| 1 | 0 | 0 | 0.0000 | 0.0000 | 0.0000 | 0.084 | 0.0000 |
| 2 | 3 | 3 | 0.8694 | 0.4135 | 0.2520 | 0.084 | 0.2184 |
| 3 | 6 | 6 | 1.738 | 0.8271 | 0.5040 | 0.084 | 0.3864 |
| 4 | 8 | 8 | 2.318 | 1.102 | 0.6720 | 0.084 | 0.4872 |
| 5 | 22 | 22 | 6.376 | 3.032 | 1.848 | 0.084 | 0.9912 |
| 6 | 26 | 26 | 7.535 | 3.584 | 2.184 | 0.084 | 1.092 |
| 7 | 29 | 29 | 8.404 | 3.997 | 2.436 | 0.084 | 1.142 |
| 8 | 46 | 46 | 13.33 | 6.341 | 3.864 | 0.084 | 1.3776 |

## *10.0 Appendix C*

### VTNA

Procedure for determining potential product inhibition or catalyst deactivation.

Two independent reactions were conducted in oven-dried NMR tubes. The first reaction was charged with 3,4-dihydro-*2H*-pyran (**6a**) (1.35 M) to which was diluted in 0.5 mL $CDCl_3$. Next, the addition of acetophenone oxime (**12a**) (0.68 M) and catalyst **11c**·$\mathbf{BF_4^-}$ (5 mol%; 0.034 M) were added to the solution. The next experiment followed the same protocol; however, with a consistent reduction in the initial concentrations of substrates by 0.16 M, i.e., **6a** = 1.19 M and **12a** = 0.52 M. Each respective experiment was placed in a $^1$H NMR 300 MHz spectrometer and allowed to react for ~ 5 hours at 40 ºC. Reaction progress was tracked by monitoring the disappearance of the signal at ~ 7.65 ppm for **12a** and appearance of the signal at ~ 7.71 ppm for product **13a**. Data points were recorded every six minutes.

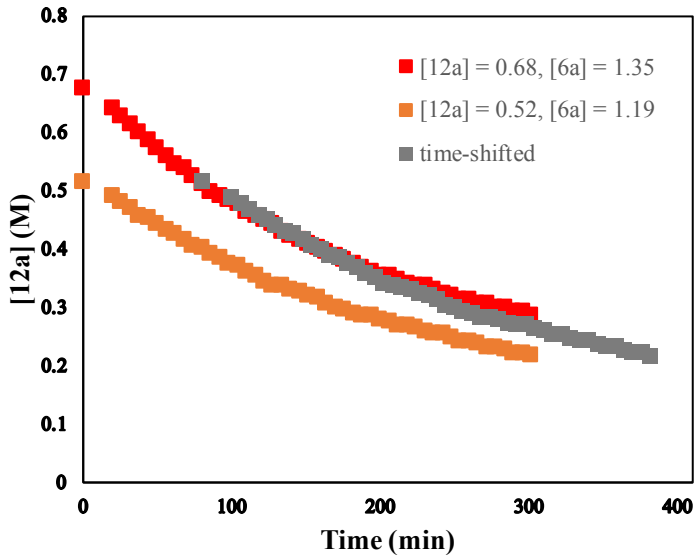



***Figure 47.*** *Plot depicting the absence of catalyst deactivation and product inhibition.*

***Table 17.*** *Data for the determination of the potential product inhibition or catalyst deactivation.*

| **expt 1: [12a] = 0.68 M, [6a] = 1.35 M** | | **expt 2: [12a] = 0.52 M, [6a] = 1.19 M** | | | |
|---|---|---|---|---|---|
| time (min) | [**12a**] (M) | time (min) | [**12a**] (M) | time-shift | [**12a**] (M) |
| 0 | 0.68 | 0 | 0.52 | 80 | 0.52 |
| 20 | 0.646 | 20 | 0.494 | 100 | 0.494 |
| 26 | 0.6324 | 26 | 0.4836 | 106 | 0.4836 |
| 32 | 0.6188 | 32 | 0.4732 | 112 | 0.4732 |
| 38 | 0.6052 | 38 | 0.4628 | 118 | 0.4628 |
| 44 | 0.5916 | 44 | 0.4576 | 124 | 0.4576 |
| 50 | 0.578 | 50 | 0.4472 | 130 | 0.4472 |
| 56 | 0.5644 | 56 | 0.4368 | 136 | 0.4368 |
| 62 | 0.5508 | 62 | 0.4316 | 142 | 0.4316 |
| 68 | 0.544 | 68 | 0.4212 | 148 | 0.4212 |
| 74 | 0.5304 | 74 | 0.4108 | 154 | 0.4108 |
| 80 | 0.5168 | 80 | 0.4056 | 160 | 0.4056 |
| 86 | 0.5032 | 86 | 0.3952 | 166 | 0.3952 |
| 92 | 0.4964 | 92 | 0.39 | 172 | 0.39 |
| 98 | 0.4896 | 98 | 0.3796 | 178 | 0.3796 |
| 104 | 0.4828 | 104 | 0.3744 | 184 | 0.3744 |
| 110 | 0.4692 | 110 | 0.364 | 190 | 0.364 |
| 116 | 0.4624 | 116 | 0.3588 | 196 | 0.3588 |
| 122 | 0.4556 | 122 | 0.3484 | 202 | 0.3484 |
| 128 | 0.4488 | 128 | 0.3432 | 208 | 0.3432 |
| 134 | 0.4352 | 134 | 0.338 | 214 | 0.338 |
| 140 | 0.4284 | 140 | 0.3328 | 220 | 0.3328 |
| 146 | 0.4216 | 146 | 0.3276 | 226 | 0.3276 |
| 152 | 0.4148 | 152 | 0.3224 | 232 | 0.3224 |
| 158 | 0.408 | 158 | 0.3172 | 238 | 0.3172 |
| 164 | 0.4012 | 164 | 0.3068 | 244 | 0.3068 |
| 170 | 0.3944 | 170 | 0.3016 | 250 | 0.3016 |
| 176 | 0.3876 | 176 | 0.2964 | 256 | 0.2964 |
| 182 | 0.3808 | 182 | 0.2912 | 262 | 0.2912 |
| 188 | 0.374 | 188 | 0.286 | 268 | 0.286 |
| 194 | 0.3672 | 194 | 0.286 | 274 | 0.286 |
| 200 | 0.3604 | 200 | 0.2808 | 280 | 0.2808 |
| 206 | 0.3604 | 206 | 0.2756 | 286 | 0.2756 |
| 212 | 0.3536 | 212 | 0.2704 | 292 | 0.2704 |
| 218 | 0.3468 | 218 | 0.2704 | 298 | 0.2704 |

| | | | | | |
|---|---|---|---|---|---|
| 224 | 0.34 | 224 | 0.2652 | 304 | 0.2652 |
| 230 | 0.34 | 230 | 0.26 | 310 | 0.26 |
| 236 | 0.3332 | 236 | 0.2548 | 316 | 0.2548 |
| 242 | 0.3264 | 242 | 0.2548 | 322 | 0.2548 |
| 248 | 0.3196 | 248 | 0.2496 | 328 | 0.2496 |
| 254 | 0.3128 | 254 | 0.2444 | 334 | 0.2444 |
| 260 | 0.3128 | 260 | 0.2444 | 340 | 0.2444 |
| 266 | 0.306 | 266 | 0.2392 | 346 | 0.2392 |
| 272 | 0.306 | 272 | 0.234 | 352 | 0.234 |
| 278 | 0.2992 | 278 | 0.234 | 358 | 0.234 |
| 284 | 0.2992 | 284 | 0.2288 | 364 | 0.2288 |
| 290 | 0.2924 | 290 | 0.2236 | 370 | 0.2236 |
| 296 | 0.2924 | 296 | 0.2236 | 376 | 0.2236 |
| 302 | 0.2856 | 302 | 0.2184 | 382 | 0.2184 |

Procedure for determining the order in catalyst.

Using the data obtained from the first experiment (see above), two additional independent reactions were conducted in oven-dried NMR tubes charged with 3,4-dihydro-*2H*-pyran (**6a**) (1.35 M) to which were diluted in 0.5 mL $CDCl_3$. Next, acetophenone oxime (**12a**) (0.68 M) and catalyst **11c**·$\mathbf{BF_4^-}$ (2.5- or 7.5 mol%; 0.015- or 0.053 M, respectively) were added to the solutions. Each respective experiment was placed in a $^1$H NMR 300 MHz spectrometer and allowed to react for ~ 3–4 hours at 40 °C. Reaction progress was tracked by monitoring the disappearance of the signal at ~ 7.65 ppm for **12a** and appearance of the signal at ~ 7.71 ppm for product **13a**. Data points were recorded every six minutes.

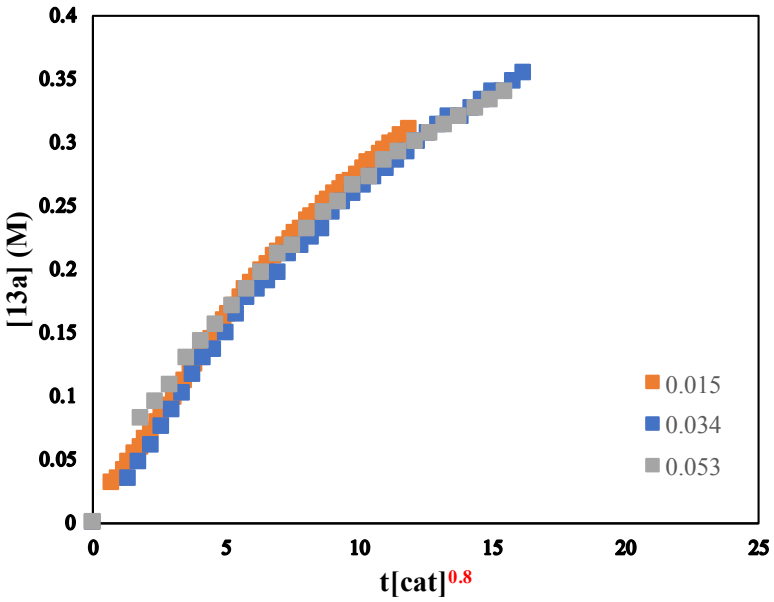



***Figure 48.*** *Normalized time scale plot displaying a 0.8-order dependence in catalyst.*

***Table 18.*** *Data for the determination of the reaction order in catalyst.*

| **catalyst loading: 2.5 mol%** | | | | **catalyst loading: 5 mol%** | | | | **catalyst loading: 7.5 mol%** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| time (min) | [**13a**] (M) | [**11c**·$BF_4^-$] (M) | tcat$^{\gamma}$ $\gamma = 0.8$ | time (min) | [**13a**] (M) | [**11c**·$BF_4^-$] (M) | tcat$^{\gamma}$ $\gamma = 0.8$ | time (min) | [**13a**] (M) | [**11c**·$BF_4^-$] (M) | tcat$^{\gamma}$ $\gamma = 0.8$ |
| 0 | 0 | 0.015 | 0 | 0 | 0 | 0.034 | 0 | 0 | 0 | 0.053 | 0 |
| 36 | 0.030464 | 0.015 | 0.72 | 20 | 0.034 | 0.034 | 1.34 | 32 | 0.0816 | 0.053 | 1.753 |
| 42 | 0.03502 | 0.015 | 0.93 | 26 | 0.0476 | 0.034 | 1.74 | 38 | 0.0952 | 0.053 | 2.325 |
| 48 | 0.041412 | 0.015 | 1.14 | 32 | 0.0612 | 0.034 | 2.14 | 44 | 0.1088 | 0.053 | 2.897 |
| 54 | 0.0476 | 0.015 | 1.34 | 38 | 0.0748 | 0.034 | 2.54 | 50 | 0.1292 | 0.053 | 3.47 |
| 60 | 0.053516 | 0.015 | 1.55 | 44 | 0.0884 | 0.034 | 2.94 | 56 | 0.1428 | 0.053 | 4.042 |
| 66 | 0.05916 | 0.015 | 1.76 | 50 | 0.102 | 0.034 | 3.34 | 62 | 0.1564 | 0.053 | 4.614 |
| 72 | 0.065144 | 0.015 | 1.97 | 56 | 0.1156 | 0.034 | 3.74 | 68 | 0.17 | 0.053 | 5.186 |
| 78 | 0.0714 | 0.015 | 2.18 | 62 | 0.1292 | 0.034 | 4.15 | 74 | 0.1836 | 0.053 | 5.758 |
| 84 | 0.0782 | 0.015 | 2.39 | 68 | 0.136 | 0.034 | 4.55 | 80 | 0.1972 | 0.053 | 6.331 |
| 90 | 0.084116 | 0.015 | 2.59 | 74 | 0.1496 | 0.034 | 4.95 | 86 | 0.2108 | 0.053 | 6.903 |
| 96 | 0.0918 | 0.015 | 2.8 | 80 | 0.1632 | 0.034 | 5.35 | 92 | 0.2176 | 0.053 | 7.475 |
| 102 | 0.09826 | 0.015 | 3.01 | 86 | 0.1768 | 0.034 | 5.75 | 98 | 0.2312 | 0.053 | 8.047 |
| 108 | 0.10472 | 0.015 | 3.22 | 92 | 0.1836 | 0.034 | 6.15 | 104 | 0.2448 | 0.053 | 8.62 |
| 114 | 0.11084 | 0.015 | 3.43 | 98 | 0.1904 | 0.034 | 6.55 | 110 | 0.2516 | 0.053 | 9.192 |
| 120 | 0.117844 | 0.015 | 3.64 | 104 | 0.1972 | 0.034 | 6.95 | 116 | 0.2652 | 0.053 | 9.764 |
| 126 | 0.12444 | 0.015 | 3.85 | 110 | 0.2108 | 0.034 | 7.35 | 122 | 0.272 | 0.053 | 10.34 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 132 | 0.13124 | 0.015 | 4.05 | 116 | 0.2176 | 0.034 | 7.76 | 128 | 0.2856 | 0.053 | 10.91 |
| 138 | 0.13804 | 0.015 | 4.26 | 122 | 0.2244 | 0.034 | 8.16 | 134 | 0.2924 | 0.053 | 11.48 |
| 144 | 0.14484 | 0.015 | 4.47 | 128 | 0.2312 | 0.034 | 8.56 | 140 | 0.2992 | 0.053 | 12.05 |
| 150 | 0.15096 | 0.015 | 4.68 | 134 | 0.2448 | 0.034 | 8.96 | 146 | 0.306 | 0.053 | 12.63 |
| 156 | 0.15844 | 0.015 | 4.89 | 140 | 0.2516 | 0.034 | 9.36 | 152 | 0.3128 | 0.053 | 13.2 |
| 162 | 0.16422 | 0.015 | 5.1 | 146 | 0.2584 | 0.034 | 9.76 | 158 | 0.3196 | 0.053 | 13.77 |
| 168 | 0.17 | 0.015 | 5.3 | 152 | 0.2652 | 0.034 | 10.2 | 164 | 0.3264 | 0.053 | 14.34 |
| 174 | 0.1768 | 0.015 | 5.51 | 158 | 0.272 | 0.034 | 10.6 | 170 | 0.3332 | 0.053 | 14.91 |
| 180 | 0.1836 | 0.015 | 5.72 | 164 | 0.2788 | 0.034 | 11 | 176 | 0.34 | 0.053 | 15.49 |
| 186 | 0.18836 | 0.015 | 5.93 | 170 | 0.2856 | 0.034 | 11.4 | - | - | - | - |
| 192 | 0.19312 | 0.015 | 6.14 | 176 | 0.2924 | 0.034 | 11.8 | - | - | - | - |
| 198 | 0.19856 | 0.015 | 6.35 | 182 | 0.2992 | 0.034 | 12.2 | - | - | - | - |
| 204 | 0.20332 | 0.015 | 6.56 | 188 | 0.306 | 0.034 | 12.6 | - | - | - | - |
| 210 | 0.20944 | 0.015 | 6.76 | 194 | 0.3128 | 0.034 | 13 | - | - | - | - |
| 216 | 0.21352 | 0.015 | 6.97 | 200 | 0.3196 | 0.034 | 13.4 | - | - | - | - |
| 222 | 0.21828 | 0.015 | 7.18 | 206 | 0.3196 | 0.034 | 13.8 | - | - | - | - |
| 228 | 0.22304 | 0.015 | 7.39 | 212 | 0.3264 | 0.034 | 14.2 | - | - | - | - |
| 234 | 0.22814 | 0.015 | 7.6 | 218 | 0.3332 | 0.034 | 14.6 | - | - | - | - |
| 240 | 0.23188 | 0.015 | 7.81 | 224 | 0.34 | 0.034 | 15 | - | - | - | - |
| 246 | 0.23732 | 0.015 | 8.01 | 230 | 0.34 | 0.034 | 15.4 | - | - | - | - |
| 252 | 0.2414 | 0.015 | 8.22 | 236 | 0.3468 | 0.034 | 15.8 | - | - | - | - |
| 258 | 0.24412 | 0.015 | 8.43 | 242 | 0.3536 | 0.034 | 16.2 | - | - | - | - |
| 264 | 0.25092 | 0.015 | 8.64 | - | - | - | - | - | - | - | - |
| 270 | 0.25364 | 0.015 | 8.85 | - | - | - | - | - | - | - | - |
| 276 | 0.2584 | 0.015 | 9.06 | - | - | - | - | - | - | - | - |
| 282 | 0.26248 | 0.015 | 9.27 | - | - | - | - | - | - | - | - |
| 288 | 0.26724 | 0.015 | 9.47 | - | - | - | - | - | - | - | - |
| 294 | 0.26928 | 0.015 | 9.68 | - | - | - | - | - | - | - | - |
| 300 | 0.27404 | 0.015 | 9.89 | - | - | - | - | - | - | - | - |
| 306 | 0.278664 | 0.015 | 10.1 | - | - | - | - | - | - | - | - |
| 312 | 0.28288 | 0.015 | 10.3 | - | - | - | - | - | - | - | - |
| 318 | 0.2856 | 0.015 | 10.5 | - | - | - | - | - | - | - | - |
| 324 | 0.29036 | 0.015 | 10.7 | - | - | - | - | - | - | - | - |
| 330 | 0.29308 | 0.015 | 10.9 | - | - | - | - | - | - | - | - |
| 336 | 0.29784 | 0.015 | 11.1 | - | - | - | - | - | - | - | - |
| 342 | 0.30056 | 0.015 | 11.3 | - | - | - | - | - | - | - | - |
| 348 | 0.30464 | 0.015 | 11.6 | - | - | - | - | - | - | - | - |
| 356 | 0.31008 | 0.015 | 11.8 | - | - | - | - | - | - | - | - |

Procedure for determining the oxime reaction order dependence

Using the data obtained from the first experiment (see above), two additional independent reactions were conducted in oven-dried NMR tubes charged with 3,4-dihydro-*2H*-pyran (**6a**) (1.35 M) to which were diluted in 0.5 mL $CDCl_3$. Next, acetophenone oxime (**12a**) (0.44- or 0.56 M) and catalyst **11c**·$\mathbf{BF_4^-}$ (5 mol%; 0.034 M) were added to the solutions. Each respective experiment was placed in a $^1$H NMR 300 MHz spectrometer and allowed to react for ~ 4 hours at 40 ºC. Reaction progress was tracked by monitoring the disappearance of the signal at ~ 7.65 ppm for **12a** and appearance of the signal at ~ 7.71 ppm for product **13a**. Data points were recorded every six minutes.

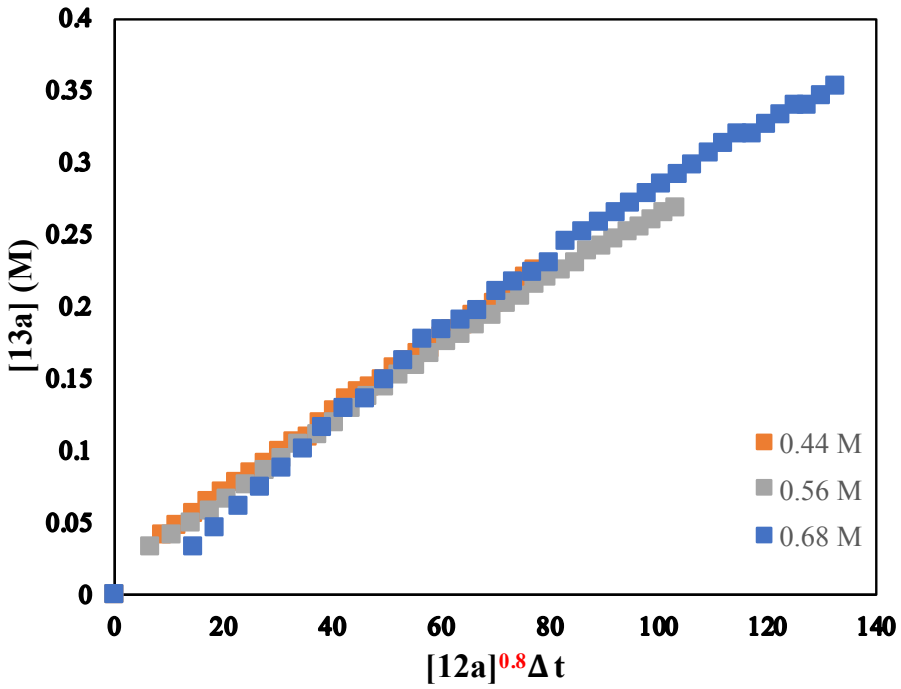



***Figure 49.*** *Plot revealing a 0.8-order dependence in oxime.*

***Table 19.*** *Data for the determination of the reaction order in the oxime component.*

| [12a] = 0.44 M | | | | [12a] = 0.56 M | | | | [12a] = 0.68 M | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| time (min) | [**13a**] (M) | [**12a**] (M) | [**12a**]$^{\beta}$ $\beta = 0.8$ | time (min) | [**13a**] (M) | [**12a**] (M) | [**12a**]$^{\beta}$ $\beta = 0.8$ | time (min) | [**13a**] (M) | [**12a**] (M) | [**12a**]$^{\beta}$ $\beta = 0.8$ |
| 0 | 0 | 0.44 | 0 | 0 | 0 | 0.56 | 0 | 0 | 0 | 0.68 | 0 |
| 32 | 0.04224 | 0.39776 | 8.79069 | 20 | 0.03416 | 0.5258 | 6.869 | 20 | 0.034 | 0.646 | 14.396 |
| 38 | 0.047872 | 0.392128 | 11.6442 | 26 | 0.042504 | 0.5175 | 10.43 | 26 | 0.0476 | 0.6324 | 18.59 |
| 44 | 0.05632 | 0.38368 | 14.4569 | 32 | 0.050232 | 0.5098 | 13.96 | 32 | 0.0612 | 0.6188 | 22.713 |
| 50 | 0.06556 | 0.37444 | 17.2183 | 38 | 0.05824 | 0.5018 | 17.43 | 38 | 0.0748 | 0.6052 | 26.764 |
| 56 | 0.07216 | 0.36784 | 19.9333 | 44 | 0.0672 | 0.4928 | 20.86 | 44 | 0.0884 | 0.5916 | 30.743 |
| 62 | 0.07832 | 0.36168 | 22.611 | 50 | 0.077 | 0.483 | 24.24 | 50 | 0.102 | 0.578 | 34.649 |
| 68 | 0.08448 | 0.35552 | 25.2524 | 56 | 0.086128 | 0.4739 | 27.57 | 56 | 0.1156 | 0.5644 | 38.482 |
| 74 | 0.09152 | 0.34848 | 27.8549 | 62 | 0.09408 | 0.4659 | 30.85 | 62 | 0.1292 | 0.5508 | 42.242 |
| 80 | 0.09944 | 0.34056 | 30.413 | 68 | 0.10416 | 0.4558 | 34.08 | 68 | 0.136 | 0.544 | 45.948 |
| 86 | 0.1056 | 0.3344 | 32.9293 | 74 | 0.11144 | 0.4486 | 37.26 | 74 | 0.1496 | 0.5304 | 49.597 |
| 92 | 0.11 | 0.33 | 35.414 | 80 | 0.1204 | 0.4396 | 40.39 | 80 | 0.1632 | 0.5168 | 53.173 |
| 98 | 0.1188 | 0.3212 | 37.8591 | 86 | 0.12992 | 0.4301 | 43.47 | 86 | 0.1768 | 0.5032 | 56.674 |
| 104 | 0.1276 | 0.3124 | 40.2512 | 92 | 0.1372 | 0.4228 | 46.51 | 92 | 0.1836 | 0.4964 | 60.119 |
| 110 | 0.1364 | 0.3036 | 42.59 | 98 | 0.14448 | 0.4155 | 49.5 | 98 | 0.1904 | 0.4896 | 63.526 |
| 116 | 0.1408 | 0.2992 | 44.8886 | 104 | 0.15344 | 0.4066 | 52.45 | 104 | 0.1972 | 0.4828 | 66.896 |
| 122 | 0.1452 | 0.2948 | 47.1603 | 110 | 0.15904 | 0.401 | 55.35 | 110 | 0.2108 | 0.4692 | 70.209 |
| 128 | 0.1496 | 0.2904 | 49.4051 | 116 | 0.168 | 0.392 | 58.21 | 116 | 0.2176 | 0.4624 | 73.466 |
| 134 | 0.15796 | 0.28204 | 51.6106 | 122 | 0.17584 | 0.3842 | 61.03 | 122 | 0.2244 | 0.4556 | 76.684 |
| 140 | 0.1628 | 0.2772 | 53.7753 | 128 | 0.18144 | 0.3786 | 63.8 | 128 | 0.2312 | 0.4488 | 79.864 |
| 146 | 0.1672 | 0.2728 | 55.9114 | 134 | 0.18816 | 0.3718 | 66.54 | 134 | 0.2448 | 0.4352 | 82.986 |
| 152 | 0.1716 | 0.2684 | 58.0201 | 140 | 0.19488 | 0.3651 | 69.24 | 140 | 0.2516 | 0.4284 | 86.051 |
| 158 | 0.17952 | 0.26048 | 60.0903 | 146 | 0.2016 | 0.3584 | 71.9 | 146 | 0.2584 | 0.4216 | 89.077 |
| 164 | 0.18436 | 0.25564 | 62.1205 | 152 | 0.2072 | 0.3528 | 74.52 | 152 | 0.2652 | 0.4148 | 92.064 |
| 170 | 0.187 | 0.253 | 64.127 | 158 | 0.21504 | 0.345 | 77.11 | 158 | 0.272 | 0.408 | 95.012 |
| 176 | 0.1936 | 0.2464 | 66.1044 | 164 | 0.2212 | 0.3388 | 79.65 | 164 | 0.2788 | 0.4012 | 97.921 |
| 182 | 0.198 | 0.242 | 68.0468 | 170 | 0.22568 | 0.3343 | 82.16 | 170 | 0.2856 | 0.3944 | 100.79 |
| 188 | 0.2024 | 0.2376 | 69.9612 | 176 | 0.23128 | 0.3287 | 84.64 | 176 | 0.2924 | 0.3876 | 103.62 |
| 194 | 0.20856 | 0.23144 | 71.8418 | 182 | 0.238 | 0.322 | 87.09 | 182 | 0.2992 | 0.3808 | 106.41 |
| 200 | 0.2134 | 0.2266 | 73.687 | 188 | 0.24192 | 0.3181 | 89.5 | 188 | 0.306 | 0.374 | 109.16 |
| 206 | 0.22 | 0.22 | 75.4953 | 194 | 0.2464 | 0.3136 | 91.88 | 194 | 0.3128 | 0.3672 | 111.88 |
| 212 | 0.22528 | 0.21472 | 77.265 | 200 | 0.252 | 0.308 | 94.24 | 200 | 0.3196 | 0.3604 | 114.55 |
| - | - | - | - | 206 | 0.25536 | 0.3046 | 96.57 | 206 | 0.3196 | 0.3604 | 117.2 |
| - | - | - | - | 212 | 0.2604 | 0.2996 | 98.87 | 212 | 0.3264 | 0.3536 | 119.83 |
| - | - | - | - | 218 | 0.26544 | 0.2946 | 101.1 | 218 | 0.3332 | 0.3468 | 122.42 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| - | - | - | - | 224 | 0.2688 | 0.2912 | 103.4 | 224 | 0.34 | 0.34 | 124.98 |
| - | - | - | - | - | - | - | - | 230 | 0.34 | 0.34 | 127.51 |
| - | - | - | - | - | - | - | - | 236 | 0.3468 | 0.3332 | 130.02 |
| - | - | - | - | - | - | - | - | 242 | 0.3536 | 0.3264 | 132.49 |

Procedure for determining the vinyl ether reaction order dependence

Using the data obtained from the first experiment (see above), two additional independent reactions were conducted in oven-dried NMR tubes charged with 3,4-dihydro-*2H*-pyran (**6a**) (0.71- or 0.95 M) to which were diluted in 0.5 mL $CDCl_3$. Next, acetophenone oxime (**12a**) (0.68 M) and catalyst **11c**·$\mathbf{BF_4^-}$ (5 mol%; 0.034 M) were added to the solutions. Each respective experiment was placed in a $^1$H NMR 300 MHz spectrometer and allowed to react for ~ 4 hours at 40 ºC. Reaction progress was tracked by monitoring the disappearance of the signal at ~ 7.65 ppm for **12a** and appearance of the signal at ~ 7.71 ppm for product **13a**. Data points were recorded every six minutes.

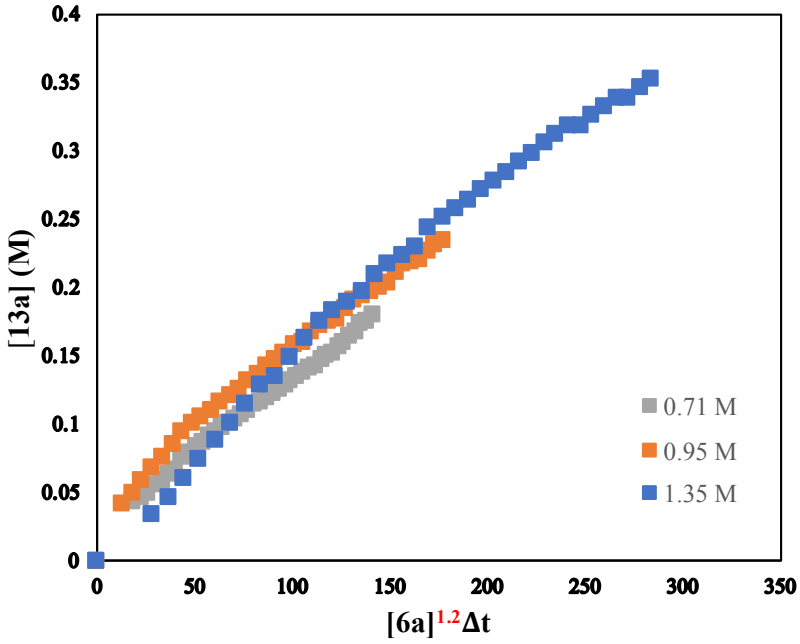


***Figure 50.*** *Plot revealing a 1.2-order dependence in vinyl ether.*

***Table 20.*** *Data for the determination of the reaction order in the vinyl ether component.*

| **[6a] = 0.71 M** | | | | **[6a] = 0.95 M** | | | | **[6a] = 1.35 M** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| time (min) | [**13a**] (M) | [**6a**] (M) | [**6a**]$^{\beta}$ $\beta = 1.2$ | time (min) | [**13a**] (M) | [**6a**] (M) | [**6a**]$^{\beta}$ $\beta = 1.2$ | time (min) | [**13a**] (M) | [**6a**] (M) | [**6a**]$^{\beta}$ $\beta = 1.2$ |
| 0 | 0 | 0.71 | 0 | 0 | 0 | 0.95 | 0 | 0 | 0 | 1.35 | 0 |
| 70 | 0.0442 | 0.6658 | 18.701 | 33 | 0.0425 | 0.9075 | 12.785 | 20 | 0.034 | 1.316 | 28.2375 |
| 76 | 0.04692 | 0.66308 | 22.375 | 39 | 0.05066 | 0.89934 | 18.096 | 26 | 0.0476 | 1.3024 | 36.5276 |
| 82 | 0.050728 | 0.659272 | 26.027 | 45 | 0.059228 | 0.890772 | 23.349 | 32 | 0.0612 | 1.2888 | 44.7144 |
| 88 | 0.05644 | 0.65356 | 29.648 | 51 | 0.06902 | 0.88098 | 28.537 | 38 | 0.0748 | 1.2752 | 52.7982 |
| 94 | 0.059296 | 0.650704 | 33.24 | 57 | 0.07718 | 0.87282 | 33.662 | 44 | 0.0884 | 1.2616 | 60.7793 |
| 100 | 0.063784 | 0.646216 | 36.808 | 63 | 0.08636 | 0.86364 | 38.726 | 50 | 0.102 | 1.248 | 68.6577 |
| 106 | 0.068 | 0.642 | 40.347 | 69 | 0.096016 | 0.853984 | 43.724 | 56 | 0.1156 | 1.2344 | 76.4338 |
| 112 | 0.07616 | 0.63384 | 43.845 | 75 | 0.101456 | 0.848544 | 48.67 | 62 | 0.1292 | 1.2208 | 84.1078 |
| 118 | 0.07956 | 0.63044 | 47.306 | 81 | 0.106216 | 0.843784 | 53.58 | 68 | 0.136 | 1.214 | 91.7053 |
| 124 | 0.085 | 0.625 | 50.737 | 87 | 0.11152 | 0.83848 | 58.455 | 74 | 0.1496 | 1.2004 | 99.2265 |
| 130 | 0.087516 | 0.622484 | 54.142 | 93 | 0.117028 | 0.832972 | 63.293 | 80 | 0.1632 | 1.1868 | 106.646 |
| 136 | 0.09248 | 0.61752 | 57.523 | 99 | 0.122264 | 0.827736 | 68.093 | 86 | 0.1768 | 1.1732 | 113.964 |
| 142 | 0.095064 | 0.614936 | 60.879 | 105 | 0.12716 | 0.82284 | 72.859 | 92 | 0.1836 | 1.1664 | 121.207 |
| 148 | 0.09792 | 0.61208 | 64.218 | 111 | 0.1326 | 0.8174 | 77.588 | 98 | 0.1904 | 1.1596 | 128.399 |
| 154 | 0.101592 | 0.608408 | 67.535 | 117 | 0.13736 | 0.81264 | 82.282 | 104 | 0.1972 | 1.1528 | 135.54 |
| 160 | 0.10472 | 0.60528 | 70.83 | 123 | 0.1428 | 0.8072 | 86.941 | 110 | 0.2108 | 1.1392 | 142.606 |
| 166 | 0.108052 | 0.601948 | 74.104 | 129 | 0.14756 | 0.80244 | 91.565 | 116 | 0.2176 | 1.1324 | 149.597 |
| 172 | 0.11084 | 0.59916 | 77.357 | 135 | 0.153 | 0.797 | 96.153 | 122 | 0.2244 | 1.1256 | 156.537 |
| 178 | 0.11492 | 0.59508 | 80.589 | 141 | 0.15844 | 0.79156 | 100.7 | 128 | 0.2312 | 1.1188 | 163.428 |
| 184 | 0.117232 | 0.592768 | 83.8 | 147 | 0.161092 | 0.788908 | 105.23 | 134 | 0.2448 | 1.1052 | 170.243 |
| 190 | 0.11968 | 0.59032 | 86.996 | 153 | 0.167892 | 0.782108 | 109.72 | 140 | 0.2516 | 1.0984 | 176.983 |
| 196 | 0.12376 | 0.58624 | 90.17 | 159 | 0.1734 | 0.7766 | 114.17 | 146 | 0.2584 | 1.0916 | 183.673 |
| 202 | 0.12614 | 0.58386 | 93.323 | 165 | 0.176052 | 0.773948 | 118.59 | 152 | 0.2652 | 1.0848 | 190.314 |
| 208 | 0.129472 | 0.580528 | 96.458 | 171 | 0.17816 | 0.77184 | 122.99 | 158 | 0.272 | 1.078 | 196.905 |
| 214 | 0.132804 | 0.577196 | 99.572 | 177 | 0.18496 | 0.76504 | 127.37 | 164 | 0.2788 | 1.0712 | 203.446 |
| 220 | 0.135728 | 0.574272 | 102.66 | 183 | 0.19176 | 0.75824 | 131.69 | 170 | 0.2856 | 1.0644 | 209.937 |
| 226 | 0.13872 | 0.57128 | 105.74 | 189 | 0.19448 | 0.75552 | 135.99 | 176 | 0.2924 | 1.0576 | 216.379 |
| 232 | 0.14144 | 0.56856 | 108.79 | 195 | 0.19856 | 0.75144 | 140.26 | 182 | 0.2992 | 1.0508 | 222.771 |
| 238 | 0.14416 | 0.56584 | 111.83 | 201 | 0.2006 | 0.7494 | 144.51 | 188 | 0.306 | 1.044 | 229.114 |
| 244 | 0.14756 | 0.56244 | 114.85 | 207 | 0.20468 | 0.74532 | 148.74 | 194 | 0.3128 | 1.0372 | 235.408 |
| 250 | 0.15164 | 0.55836 | 117.85 | 213 | 0.211208 | 0.738792 | 152.94 | 200 | 0.3196 | 1.0304 | 241.652 |
| 256 | 0.153 | 0.557 | 120.82 | 219 | 0.2176 | 0.7324 | 157.09 | 206 | 0.3196 | 1.0304 | 247.871 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 262 | 0.157012 | 0.552988 | 123.78 | 225 | 0.21896 | 0.73104 | 161.21 | 212 | 0.3264 | 1.0236 | 254.066 |
| 268 | 0.1598 | 0.5502 | 126.72 | 231 | 0.221 | 0.729 | 165.33 | 218 | 0.3332 | 1.0168 | 260.212 |
| 274 | 0.16524 | 0.54476 | 129.63 | 237 | 0.2278 | 0.7222 | 169.41 | 224 | 0.34 | 1.01 | 266.308 |
| 280 | 0.16864 | 0.54136 | 132.52 | 243 | 0.23256 | 0.71744 | 173.45 | 230 | 0.34 | 1.01 | 272.381 |
| 286 | 0.17476 | 0.53524 | 135.37 | 249 | 0.23528 | 0.71472 | 177.47 | 236 | 0.3468 | 1.0032 | 278.428 |
| 292 | 0.17612 | 0.53388 | 138.2 | - | - | - | - | 242 | 0.3536 | 0.9964 | 284.427 |
| 298 | 0.1802 | 0.5298 | 141.01 | - | - | - | - | - | - | - | - |

**$^1$H NMR titration experiments**

**Catalyst dimerization study**

Three stock solutions of catalyst **11c**·$\mathbf{BF_4^-}$ **(**3x 32.4 mg, 0.05 mmol, 50.1 mM) in $CD_2Cl_2$ (3x 1.0 mL) were prepared in oven-dried 1.0 mL volumetric flasks. A series of solutions at varying concentrations were then prepared in oven-dried NMR tubes by combining the appropriate amount of stock solution with $CD_2Cl_2$ totalling a volume of 0.5 mL. Each respective NMR sample was then recorded on a $^1$H NMR 300 MHz spectrometer.

**Host–guest binding study involving acetophenone oxime**

A stock solution of catalyst **11c**·$\mathbf{BF_4^-}$ **(**32.4 mg, 0.05 mmol, 50.1 mM) in $CD_2Cl_2$ (1.0 mL) and two stock solutions of oxime **12a (**2x 6.8 mg, 0.05 mmol, 50.3 mM) in $CD_2Cl_2$ (2x 1.0 mL) were prepared in oven-dried 1.0 mL volumetric flasks. A series of solutions containing 5 mM of catalyst **11c**·$\mathbf{BF_4^-}$ were combined with 0.1–6 equivalents of oxime **12a**, and were further diluted in the appropriate amount of $CD_2Cl_2$ in separate oven-dried NMR tubes totalling a volume of 0.5 mL. Each respective NMR sample was then recorded on a $^1$H NMR 300 MHz spectrometer.

**Host–guest binding study involving 3,4-dihydro-*2H*-pyran**

A stock solution of catalyst **11c**·$\mathbf{BF_4^-}$ (32.4 mg, 0.05 mmol, 50.1 mM) in $CD_2Cl_2$ (1.0 mL) was prepared in an oven-dried 1.0 mL volumetric flask. A solution containing 5 mM of catalyst **11c**·$\mathbf{BF_4^-}$ (0.5 mL of $CD_2Cl_2$) were titrated in 5–230 equivalents of 3,4-dihydro-*2H*-pyran (**6a**) sequentially in an oven-dried NMR tube. Each respective NMR titration sample was then recorded on a $^1$H NMR 300 MHz spectrometer.

**X-ray Crystallographic Analysis**

Single-crystals of **11c**·$\mathbf{BF_4^-}$ were mounted on a cryoloop with paratone oil and examined on an APEX II CCD X-ray diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). An Oxford Cryostream cooler was used to maintain cryogenic temperatures. Data were collected using the APEX-II software,[178] integrated using SAINT[179] and corrected for absorption using the multi-scan approach (SADABS).[180] Final cell constants were determined from full least squares refinement of all observed reflections. The structures were solved using intrinsic phasing (SHELXT).[185] All structures were refined with full squares refinement on $F^2$ using the SHELXTL software.[186] All hydrogen atoms were added at calculated positions and refined isotropically with a riding model. Both $CF_3$ groups were highly disordered and successfully modelled over two and three positions, respectively. Disordered solvent was removed from the crystallographic model using PLATON/SQUEEZE.[187] A thermal ellipsoid plot of the complex with the appropriate atomic labelling scheme is given in Figure 51. A summary of the experimental crystallographic data for the complex is presented in Table 21. Select bond lengths and angles are provided in Table 22, and a summary of the H-bonding interactions are presented in Table 23.

***Table 21.*** *Select Crystallographic Parameters for* ***11c·BF$_4^-$***.

| | |
|---|---|
| Chemical formula | $C_{27}H_{33}BF_{10}N_4O_2$ |
| $M_r$ | 646.38 |
| Crystal system, space group | Orthorhombic, *Pbca* |
| Temperature (K) | 150 |
| *a*, *b*, *c* (Å) | 7.9774 (7), 29.030 (2), 30.322 (3) |
| *V* (Å$^3$) | 7022.1 (10) |
| *Z* | 8 |
| Radiation type | Mo *K*α |
| μ (mm$^{-1}$) | 0.11 |
| Crystal size (mm) | 0.2 × 0.05 × 0.05 |
| Data collection | |
| Diffractometer | Bruker *APEX*-II CCD |
| Absorption correction | Multi-scan<br>Bruker *SADABS* |
| $T_{min}$, $T_{max}$ | 0.435, 0.786 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 28152, 6853, 4548 |
| $R_{int}$ | 0.085 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.628 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.128, 0.337, 1.06 |
| No. of reflections | 6853 |
| No. of parameters | 413 |
| No. of restraints | 31 |
| H-atom treatment | H-atom parameters constrained<br>$w = 1/[\sigma^2(F_o^2) + (0.0963P)^2 + 55.5373P]$<br>where $P = (F_o^2 + 2F_c^2)/3$ |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.69, −0.46 |

Computer programs: Bruker *APEX2*[178], Bruker *SAINT*[179], *SHELXT* (Sheldrick 2015),[185] *SHELXL2014*(Sheldrick 2014),[185] Bruker *SHELXTL*.[186]

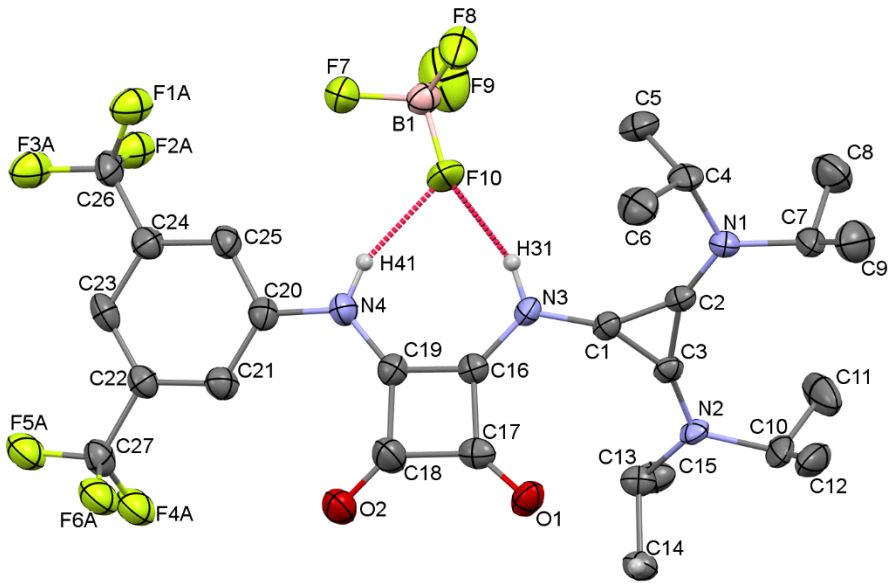



***Figure 51.*** *ORTEP plot of the molecular structure of* ***11c·BF₄⁻*** *with appropriate atomic labelling scheme. Thermal ellipsiods are plotted at 50%. For clarity only select H atoms are shown, and only one orientation of the disordered $CF_3$ groups are shown. Short contacts from F(10) of the $BF_4^-$ counterion to H(41) and H(31) are shown as red dashed lines.*

***Table 22.*** *Selected geometric parameters for* ***11c·BF₄⁻*** *(Å, º)*

| Bond | Length (Å) | Bond | Length(Å) |
|---|---|---|---|
| F1A—C26 | 1.338 (12) | N3—C16 | 1.348 (7) |
| F2A—C26 | 1.386 (11) | N3—C1 | 1.375 (7) |
| F3A—C26 | 1.342 (10) | N4—C19 | 1.360 (8) |
| F1B—C26 | 1.327 (12) | N4—C20 | 1.405 (8) |
| F2B—C26 | 1.381 (10) | C1—C2 | 1.363 (8) |
| F3B—C26 | 1.318 (10) | C1—C3 | 1.369 (8) |
| F4A—C27 | 1.345 (11) | C2—C3 | 1.421 (8) |
| F5A—C27 | 1.327 (10) | C4—C6 | 1.511 (10) |
| F6A—C27 | 1.346 (11) | C4—C5 | 1.519 (10) |
| F4B—C27 | 1.311 (11) | C7—C9 | 1.507 (10) |
| F5B—C27 | 1.313 (12) | C7—C8 | 1.528 (10) |
| F6B—C27 | 1.383 (12) | C10—C12 | 1.494 (11) |
| F4C—C27 | 1.343 (15) | C10—C11 | 1.533 (11) |
| F5C—C27 | 1.390 (15) | C13—C14 | 1.526 (8) |

| | | | |
|---|---|---|---|
| F6C—C27 | 1.334 (15) | C13—C15 | 1.528 (9) |
| F7—B1 | 1.398 (9) | C16—C19 | 1.386 (8) |
| F8—B1 | 1.371 (9) | C16—C17 | 1.476 (8) |
| F9—B1 | 1.343 (9) | C17—C18 | 1.514 (9) |
| F10—B1 | 1.391 (8) | C18—C19 | 1.479 (9) |
| O1—C17 | 1.209 (8) | C20—C21 | 1.386 (9) |
| O2—C18 | 1.221 (8) | C20—C25 | 1.414 (9) |
| N1—C2 | 1.302 (7) | C21—C22 | 1.390 (9) |
| N1—C7 | 1.484 (8) | C22—C23 | 1.383 (9) |
| N1—C4 | 1.496 (7) | C22—C27 | 1.494 (9) |
| N2—C3 | 1.323 (7) | C23—C24 | 1.388 (9) |
| N2—C13 | 1.472 (8) | C24—C25 | 1.389 (9) |
| N2—C10 | 1.497 (8) | C24—C26 | 1.488 (9) |
| **Bond** | **Angle (°)** | **Bond** | **Angle (°)** |
| F9—B1—F8 | 109.2 (6) | N4—C19—C18 | 139.4 (6) |
| F9—B1—F10 | 110.7 (7) | C16—C19—C18 | 91.8 (5) |
| F8—B1—F10 | 110.4 (6) | C21—C20—N4 | 123.3 (6) |
| F9—B1—F7 | 110.1 (6) | C21—C20—C25 | 120.3 (6) |
| F8—B1—F7 | 109.3 (6) | N4—C20—C25 | 116.3 (6) |
| F10—B1—F7 | 107.0 (6) | C20—C21—C22 | 119.1 (6) |
| C2—N1—C7 | 121.9 (5) | C23—C22—C21 | 121.8 (6) |
| C2—N1—C4 | 118.4 (5) | C23—C22—C27 | 119.5 (5) |
| C7—N1—C4 | 119.4 (5) | C21—C22—C27 | 118.6 (5) |
| C3—N2—C13 | 119.5 (5) | C22—C23—C24 | 118.8 (6) |
| C3—N2—C10 | 121.0 (5) | C25—C24—C23 | 121.2 (6) |
| C13—N2—C10 | 119.5 (5) | C25—C24—C26 | 119.1 (6) |
| C16—N3—C1 | 123.3 (5) | C23—C24—C26 | 119.5 (6) |
| C19—N4—C20 | 127.6 (5) | C24—C25—C20 | 118.8 (6) |
| C2—C1—C3 | 62.7 (4) | F3B—C26—F1B | 109.8 (8) |
| C2—C1—N3 | 146.6 (5) | F1A—C26—F3A | 108.7 (8) |
| C3—C1—N3 | 150.3 (5) | F3B—C26—F2B | 104.8 (6) |
| N1—C2—C1 | 148.2 (6) | F1B—C26—F2B | 103.5 (7) |
| N1—C2—C3 | 152.9 (6) | F1A—C26—F2A | 104.2 (8) |
| C1—C2—C3 | 58.9 (4) | F3A—C26—F2A | 104.6 (6) |
| N2—C3—C1 | 149.1 (6) | F3B—C26—C24 | 114.0 (6) |
| N2—C3—C2 | 152.5 (6) | F1B—C26—C24 | 115.2 (8) |
| C1—C3—C2 | 58.4 (4) | F1A—C26—C24 | 112.9 (9) |
| N1—C4—C6 | 111.4 (5) | F3A—C26—C24 | 116.1 (7) |

| | | | |
|---|---|---|---|
| N1—C4—C5 | 111.2 (5) | F2B—C26—C24 | 108.5 (7) |
| C6—C4—C5 | 113.5 (6) | F2A—C26—C24 | 109.3 (6) |
| N1—C7—C9 | 111.9 (6) | F4B—C27—F5B | 109.7 (8) |
| N1—C7—C8 | 110.1 (5) | F5A—C27—F6A | 106.7 (7) |
| C9—C7—C8 | 112.8 (6) | F6C—C27—F4C | 106.3 (10) |
| C12—C10—N2 | 111.3 (6) | F5A—C27—F4A | 106.4 (7) |
| C12—C10—C11 | 117.0 (7) | F6A—C27—F4A | 105.4 (7) |
| N2—C10—C11 | 109.6 (6) | F4B—C27—F6B | 104.7 (8) |
| N2—C13—C14 | 111.4 (5) | F5B—C27—F6B | 104.5 (8) |
| N2—C13—C15 | 111.4 (5) | F6C—C27—F5C | 102.7 (10) |
| C14—C13—C15 | 110.6 (5) | F4C—C27—F5C | 102.1 (10) |
| N3—C16—C19 | 133.8 (5) | F4B—C27—C22 | 112.8 (7) |
| N3—C16—C17 | 132.9 (5) | F5B—C27—C22 | 114.6 (7) |
| C19—C16—C17 | 93.2 (5) | F5A—C27—C22 | 114.9 (6) |
| O1—C17—C16 | 135.6 (6) | F6C—C27—C22 | 115.3 (9) |
| O1—C17—C18 | 137.4 (6) | F6A—C27—C22 | 111.9 (6) |
| C16—C17—C18 | 87.0 (5) | F4C—C27—C22 | 113.7 (9) |
| O2—C18—C19 | 137.7 (7) | F4A—C27—C22 | 111.0 (6) |
| O2—C18—C17 | 134.2 (6) | F6B—C27—C22 | 109.8 (7) |
| C19—C18—C17 | 88.1 (5) | F5C—C27—C22 | 115.2 (9) |
| N4—C19—C16 | 128.9 (6) | | |

***Table 23.*** *Summary of H-bonding interactions present in* ***11c·BF$_4^-$***.

| **Donor-H…Acceptor** | **H…A (Å)** | **D…A (Å)** | **D-H….A (°)** |
|---|---|---|---|
| N3-H31…F10 | 1.95 | 2.760(6) | 153 |
| N4-H41…F10 | 2.02 | 2.867(7) | 160 |
| C4-H4….F6C | 2.43 | 3.373(19) | 157 |
| C13-H13….F1B | 2.51 | 3.287(14) | 134 |
| C14-H14A….O1 | 2.47 | 3.086(8) | 120 |
| C15-H15B…F7 | 2.49 | 3.238(7) | 134 |
| C21-H21…O2 | 2.17 | 3.061(8) | 156 |
| C23-H23…F5A | 2.41 | 2.733(11) | 100 |
| C25-H25…F7 | 2.28 | 3.216(7) | 166 |

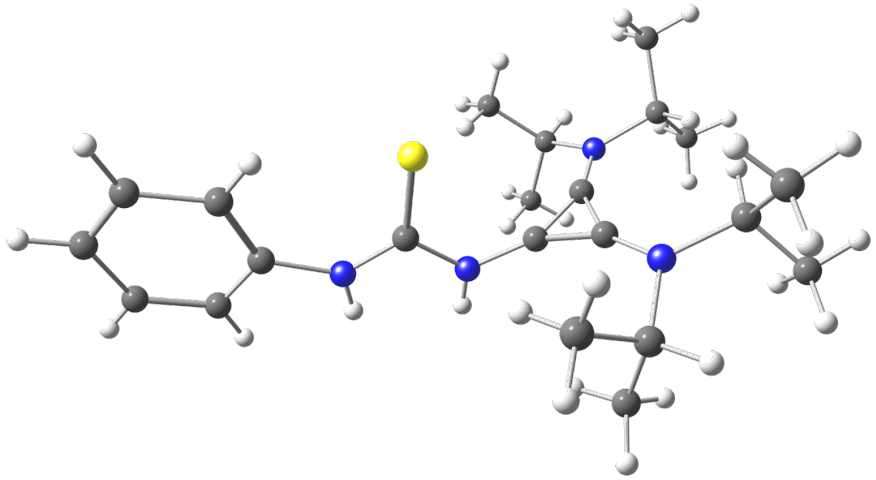
## *11.0 Computational section*

### Computational Methods, Cartesian Coordinates and Energies of Calculated Structures

The following DFT calculations were performed using the Gaussian 16 program.[188] The hybrid B3LYP[189] functional and the dispersion energy corrections by D3[190] version of Grimme's dispersion with the original D3 damping function were used. All the electronic properties were obtained with the 6-311+G(d,2p) basis sets. The solvent effects were taken into account using the Self-Consistent Reaction Field (SCRF) method grounded from the Solvation Model based on Density (SMD).[191] The p$K_a$ calculation was performed using equation $pKa = \Delta G^*_{aq}\ /2.303\ RT$, where $\Delta G^*_{aq}$ was calculated directly from the aqueous Gibbs free energies of the acid and conjugate base in dimethyl sulfoxide (DMSO ε= 46.7), using the solvation corrections to construct the solute cavity made by Lian, P. et al.[192] The interaction energy ($E_{int}$) was calculated using the B3LYP/6-311+G(d,2p) level of theory in chloroform ($CHCl_3$, ε= 4.81) (SMD model) using the following equation: $E_{int} = E_{alcohol-thiourea} - E_{alcohol} - E_{thiourea}$, which corresponds to the difference between the total energy of the supermolecular system (i.e. *alcohol –thiourea*), and the total energy of its fragments (i.e. *alcohol* and *thiourea* isolated). This property is used to determine the stability of an interaction. A negative value indicates that the molecular system is more energetically stable with respect to the isolated fragments, and thus the interaction is favorable. Conversely, if $E_{int}$ is positive, it indicates that the isolated fragments are more stable than in the supermolecule, and therefore the interaction does not favor an increase in stability. Visualization and generation of molecular structures was performed with Chemcraft[193] graphical user interface software.

## Stationary Points

Cartesian coordinates of B3LYP-D3/6-311+G(d,2p) geometries are given below in standard XYZ format. The first line indicates the total number of atoms.



Computed structure thiourea (crystal structure) (**4**)

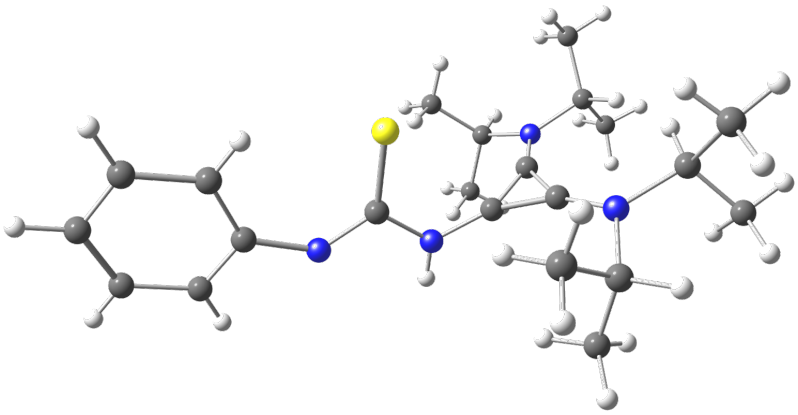
# Freq B3LYP/6-311+G(d,2p) nosymm int=(grid=ultrafine) scf=(maxcycles=200) EmpiricalDispersion=GD3 SCRF=(SMD,Solvent=DiMethylSulfoxide)

---

| | |
|---|---|
| SCF Done: E(RB3LYP) = | -1476.49319421 |
| Zero-point correction= | 0.554438 (Hartree/Particle) |
| Thermal correction to Energy= | 0.574640 |
| Thermal correction to Enthalpy= | 0.575584 |
| Thermal correction to Gibbs Free Energy= | 0.507016 |
| Sum of electronic and zero-point Energies= | -1475.938757 |
| Sum of electronic and thermal Energies= | -1475.918554 |
| Sum of electronic and thermal Enthalpies= | -1475.917610 |
| Sum of electronic and thermal Free Energies= | -1475.986178 |

| | | | |
|---|---|---|---|
| S | 6.368276000 | 10.403776000 | 6.348203000 |
| N | 5.148714000 | 8.153325000 | 2.765703000 |
| N | 2.736241000 | 8.039101000 | 5.592572000 |
| N | 6.351001000 | 7.765461000 | 6.240491000 |
| H | 6.654041000 | 6.968876000 | 6.458592000 |
| N | 7.893839000 | 8.591595000 | 7.680699000 |
| H | 8.058684000 | 7.729953000 | 7.747839000 |
| C | 4.884171000 | 8.044067000 | 4.040739000 |
| C | 3.953336000 | 8.000613000 | 5.134333000 |
| C | 5.297766000 | 7.885148000 | 5.336576000 |
| C | 6.530654000 | 7.837968000 | 2.295725000 |

| | | | |
|---|---|---|---|
| H | 6.514860000 | 7.836727000 | 1.295425000 |
| C | 7.501960000 | 8.905710000 | 2.732133000 |
| H | 7.212740000 | 9.773560000 | 2.380782000 |
| H | 8.394298000 | 8.694645000 | 2.389020000 |
| H | 7.528612000 | 8.941715000 | 3.711219000 |
| C | 6.928455000 | 6.456112000 | 2.745314000 |
| H | 7.055791000 | 6.452387000 | 3.717397000 |
| H | 7.765516000 | 6.197868000 | 2.306640000 |
| H | 6.222678000 | 5.819192000 | 2.506412000 |
| C | 4.097452000 | 8.455024000 | 1.762108000 |
| H | 3.267301000 | 8.703336000 | 2.261331000 |
| C | 4.496241000 | 9.651887000 | 0.918331000 |
| H | 4.753874000 | 10.393099000 | 1.505495000 |
| H | 3.739135000 | 9.923789000 | 0.358353000 |
| H | 5.254333000 | 9.408542000 | 0.345996000 |
| C | 3.776645000 | 7.225879000 | 0.928835000 |
| H | 4.545596000 | 7.004882000 | 0.364532000 |
| H | 2.996836000 | 7.407147000 | 0.364532000 |
| H | 3.581199000 | 6.471011000 | 1.524030000 |
| C | 1.556657000 | 8.282447000 | 4.726141000 |
| H | 1.892271000 | 8.464956000 | 3.801837000 |
| C | 0.788693000 | 9.504142000 | 5.182114000 |
| H | 0.403724000 | 9.336531000 | 6.067287000 |
| H | 0.070084000 | 9.695342000 | 4.543257000 |
| H | 1.395759000 | 10.272667000 | 5.229070000 |
| C | 0.682086000 | 7.032196000 | 4.662090000 |
| H | 1.235849000 | 6.258704000 | 4.423806000 |
| H | -0.015794000 | 7.155110000 | 3.985132000 |
| H | 0.266517000 | 6.878242000 | 5.535936000 |
| C | 2.525989000 | 7.795755000 | 7.050698000 |
| H | 1.538889000 | 7.732436000 | 7.202071000 |
| C | 3.132068000 | 6.463561000 | 7.455390000 |
| H | 2.804351000 | 5.760838000 | 6.856075000 |
| H | 2.873448000 | 6.253738000 | 8.378046000 |
| H | 4.108310000 | 6.516948000 | 7.393605000 |
| C | 3.032371000 | 8.951648000 | 7.873263000 |
| H | 3.988871000 | 9.082011000 | 7.700470000 |
| H | 2.897139000 | 8.760447000 | 8.824958000 |
| H | 2.542770000 | 9.764869000 | 7.630447000 |
| C | 6.918584000 | 8.893294000 | 6.793673000 |
| C | 8.700299000 | 9.396126000 | 8.523035000 |
| C | 8.729912000 | 10.785432000 | 8.511296000 |
| H | 8.167265000 | 11.273365000 | 7.920837000 |
| C | 9.594612000 | 11.454633000 | 9.376698000 |
| H | 9.613367000 | 12.404426000 | 9.374844000 |
| C | 10.416866000 | 10.769291000 | 10.229742000 |
| H | 11.007152000 | 11.237360000 | 10.808256000 |
| C | 10.377382000 | 9.397368000 | 10.239628000 |
| H | 10.942991000 | 8.919367000 | 10.835029000 |
| C | 9.530451000 | 8.700852000 | 9.401412000 |
| H | 9.513670000 | 7.751059000 | 9.422213000 |



Computed structure conjugate base H (4) (**4-H**')

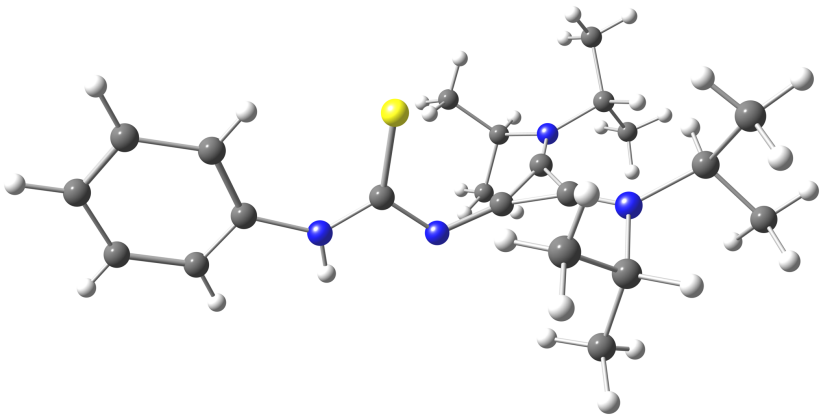
# Freq B3LYP/6-311+G(d,2p) nosymm int=(grid=ultrafine) scf=(maxcycles=200) EmpiricalDispersion=GD3 SCRF=(SMD,Solvent=DiMethylSulfoxide)

---

| | |
|---|---|
| SCF Done: E(RB3LYP) = | -1476.02344061 |
| Zero-point correction= | 0.539773 (Hartree/Particle) |
| Thermal correction to Energy= | 0.559122 |
| Thermal correction to Enthalpy= | 0.560066 |
| Thermal correction to Gibbs Free Energy= | 0.493467 |
| Sum of electronic and zero-point Energies= | -1475.483667 |
| Sum of electronic and thermal Energies= | -1475.464319 |
| Sum of electronic and thermal Enthalpies= | -1475.463375 |
| Sum of electronic and thermal Free Energies= | -1475.529974 |

| | | | |
|---|---|---|---|
| S | 6.368276000 | 10.403776000 | 6.348203000 |
| N | 5.148714000 | 8.153325000 | 2.765703000 |
| N | 2.736241000 | 8.039101000 | 5.592572000 |
| N | 6.351001000 | 7.765461000 | 6.240491000 |
| H | 6.654041000 | 6.968876000 | 6.458592000 |
| N | 7.893839000 | 8.591595000 | 7.680699000 |
| C | 4.884171000 | 8.044067000 | 4.040739000 |
| C | 3.953336000 | 8.000613000 | 5.134333000 |
| C | 5.297766000 | 7.885148000 | 5.336576000 |
| C | 6.530654000 | 7.837968000 | 2.295725000 |
| H | 6.514860000 | 7.836727000 | 1.295425000 |
| C | 7.501960000 | 8.905710000 | 2.732133000 |
| H | 7.212740000 | 9.773560000 | 2.380782000 |
| H | 8.394298000 | 8.694645000 | 2.389020000 |
| H | 7.528612000 | 8.941715000 | 3.711219000 |
| C | 6.928455000 | 6.456112000 | 2.745314000 |
| H | 7.055791000 | 6.452387000 | 3.717397000 |
| H | 7.765516000 | 6.197868000 | 2.306640000 |
| H | 6.222678000 | 5.819192000 | 2.506412000 |
| C | 4.097452000 | 8.455024000 | 1.762108000 |
| H | 3.267301000 | 8.703336000 | 2.261331000 |
| C | 4.496241000 | 9.651887000 | 0.918331000 |

| | | | |
|---|---|---|---|
| H | 4.753874000 | 10.393099000 | 1.505495000 |
| H | 3.739135000 | 9.923789000 | 0.358353000 |
| H | 5.254333000 | 9.408542000 | 0.345996000 |
| C | 3.776645000 | 7.225879000 | 0.928835000 |
| H | 4.545596000 | 7.004882000 | 0.364532000 |
| H | 2.996836000 | 7.407147000 | 0.364532000 |
| H | 3.581199000 | 6.471011000 | 1.524030000 |
| C | 1.556657000 | 8.282447000 | 4.726141000 |
| H | 1.892271000 | 8.464956000 | 3.801837000 |
| C | 0.788693000 | 9.504142000 | 5.182114000 |
| H | 0.403724000 | 9.336531000 | 6.067287000 |
| H | 0.070084000 | 9.695342000 | 4.543257000 |
| H | 1.395759000 | 10.272667000 | 5.229070000 |
| C | 0.682086000 | 7.032196000 | 4.662090000 |
| H | 1.235849000 | 6.258704000 | 4.423806000 |
| H | -0.015794000 | 7.155110000 | 3.985132000 |
| H | 0.266517000 | 6.878242000 | 5.535936000 |
| C | 2.525989000 | 7.795755000 | 7.050698000 |
| H | 1.538889000 | 7.732436000 | 7.202071000 |
| C | 3.132068000 | 6.463561000 | 7.455390000 |
| H | 2.804351000 | 5.760838000 | 6.856075000 |
| H | 2.873448000 | 6.253738000 | 8.378046000 |
| H | 4.108310000 | 6.516948000 | 7.393605000 |
| C | 3.032371000 | 8.951648000 | 7.873263000 |
| H | 3.988871000 | 9.082011000 | 7.700470000 |
| H | 2.897139000 | 8.760447000 | 8.824958000 |
| H | 2.542770000 | 9.764869000 | 7.630447000 |
| C | 6.918584000 | 8.893294000 | 6.793673000 |
| C | 8.700299000 | 9.396126000 | 8.523035000 |
| C | 8.729912000 | 10.785432000 | 8.511296000 |
| H | 8.167265000 | 11.273365000 | 7.920837000 |
| C | 9.594612000 | 11.454633000 | 9.376698000 |
| H | 9.613367000 | 12.404426000 | 9.374844000 |
| C | 10.416866000 | 10.769291000 | 10.229742000 |
| H | 11.007152000 | 11.237360000 | 10.808256000 |
| C | 10.377382000 | 9.397368000 | 10.239628000 |
| H | 10.942991000 | 8.919367000 | 10.835029000 |
| C | 9.530451000 | 8.700852000 | 9.401412000 |
| H | 9.513670000 | 7.751059000 | 9.422213000 |



Computed structure conjugate base H (3) (**4-H)**

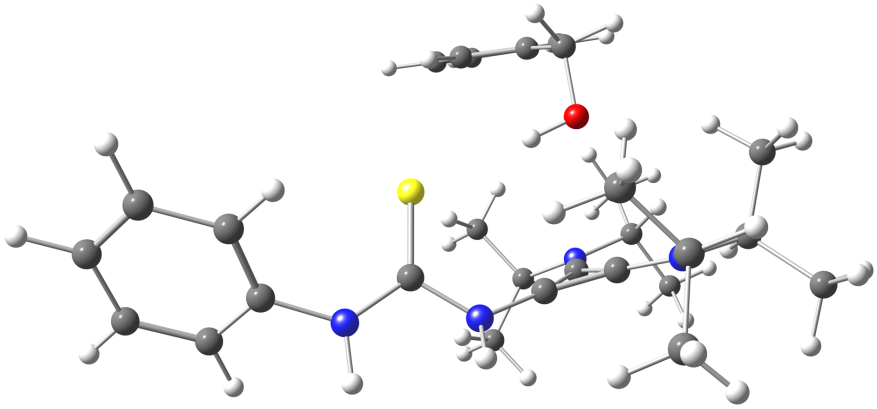
# Freq B3LYP/6-311+G(d,2p) nosymm int=(grid=ultrafine) scf=(maxcycles=200) EmpiricalDispersion=GD3 SCRF=(SMD,Solvent=DiMethylSulfoxide)

---

| | |
|---|---|
| SCF Done: E(RB3LYP) = | -1476.03701651 |
| Zero-point correction= | 0.540103 (Hartree/Particle) |
| Thermal correction to Energy= | 0.559961 |
| Thermal correction to Enthalpy= | 0.560905 |
| Thermal correction to Gibbs Free Energy= | 0.493377 |
| Sum of electronic and zero-point Energies= | -1475.496914 |
| Sum of electronic and thermal Energies= | -1475.477056 |
| Sum of electronic and thermal Enthalpies= | -1475.476112 |
| Sum of electronic and thermal Free Energies= | -1475.543639 |

| | | | |
|---|---|---|---|
| S | 6.368276000 | 10.403776000 | 6.348203000 |
| N | 5.148714000 | 8.153325000 | 2.765703000 |
| N | 2.736241000 | 8.039101000 | 5.592572000 |
| N | 6.351001000 | 7.765461000 | 6.240491000 |
| N | 7.893839000 | 8.591595000 | 7.680699000 |
| H | 8.058684000 | 7.729953000 | 7.747839000 |
| C | 4.884171000 | 8.044067000 | 4.040739000 |
| C | 3.953336000 | 8.000613000 | 5.134333000 |
| C | 5.297766000 | 7.885148000 | 5.336576000 |
| C | 6.530654000 | 7.837968000 | 2.295725000 |
| H | 6.514860000 | 7.836727000 | 1.295425000 |
| C | 7.501960000 | 8.905710000 | 2.732133000 |
| H | 7.212740000 | 9.773560000 | 2.380782000 |
| H | 8.394298000 | 8.694645000 | 2.389020000 |
| H | 7.528612000 | 8.941715000 | 3.711219000 |
| C | 6.928455000 | 6.456112000 | 2.745314000 |
| H | 7.055791000 | 6.452387000 | 3.717397000 |
| H | 7.765516000 | 6.197868000 | 2.306640000 |
| H | 6.222678000 | 5.819192000 | 2.506412000 |
| C | 4.097452000 | 8.455024000 | 1.762108000 |
| H | 3.267301000 | 8.703336000 | 2.261331000 |
| C | 4.496241000 | 9.651887000 | 0.918331000 |

| | | | |
|---|---|---|---|
| H | 4.753874000 | 10.393099000 | 1.505495000 |
| H | 3.739135000 | 9.923789000 | 0.358353000 |
| H | 5.254333000 | 9.408542000 | 0.345996000 |
| C | 3.776645000 | 7.225879000 | 0.928835000 |
| H | 4.545596000 | 7.004882000 | 0.364532000 |
| H | 2.996836000 | 7.407147000 | 0.364532000 |
| H | 3.581199000 | 6.471011000 | 1.524030000 |
| C | 1.556657000 | 8.282447000 | 4.726141000 |
| H | 1.892271000 | 8.464956000 | 3.801837000 |
| C | 0.788693000 | 9.504142000 | 5.182114000 |
| H | 0.403724000 | 9.336531000 | 6.067287000 |
| H | 0.070084000 | 9.695342000 | 4.543257000 |
| H | 1.395759000 | 10.272667000 | 5.229070000 |
| C | 0.682086000 | 7.032196000 | 4.662090000 |
| H | 1.235849000 | 6.258704000 | 4.423806000 |
| H | -0.015794000 | 7.155110000 | 3.985132000 |
| H | 0.266517000 | 6.878242000 | 5.535936000 |
| C | 2.525989000 | 7.795755000 | 7.050698000 |
| H | 1.538889000 | 7.732436000 | 7.202071000 |
| C | 3.132068000 | 6.463561000 | 7.455390000 |
| H | 2.804351000 | 5.760838000 | 6.856075000 |
| H | 2.873448000 | 6.253738000 | 8.378046000 |
| H | 4.108310000 | 6.516948000 | 7.393605000 |
| C | 3.032371000 | 8.951648000 | 7.873263000 |
| H | 3.988871000 | 9.082011000 | 7.700470000 |
| H | 2.897139000 | 8.760447000 | 8.824958000 |
| H | 2.542770000 | 9.764869000 | 7.630447000 |
| C | 6.918584000 | 8.893294000 | 6.793673000 |
| C | 8.700299000 | 9.396126000 | 8.523035000 |
| C | 8.729912000 | 10.785432000 | 8.511296000 |
| H | 8.167265000 | 11.273365000 | 7.920837000 |
| C | 9.594612000 | 11.454633000 | 9.376698000 |
| H | 9.613367000 | 12.404426000 | 9.374844000 |
| C | 10.416866000 | 10.769291000 | 10.229742000 |
| H | 11.007152000 | 11.237360000 | 10.808256000 |
| C | 10.377382000 | 9.397368000 | 10.239628000 |
| H | 10.942991000 | 8.919367000 | 10.835029000 |
| C | 9.530451000 | 8.700852000 | 9.401412000 |
| H | 9.513670000 | 7.751059000 | 9.422213000 |



Computed structure alcohol ⋯ thiourea (OH⋯S) (**5a•4**)

# opt B3LYP/6-311+g(d,2p)  nosymm int=(grid=ultrafine) EmpiricalDispersion=GD3

--Link1--

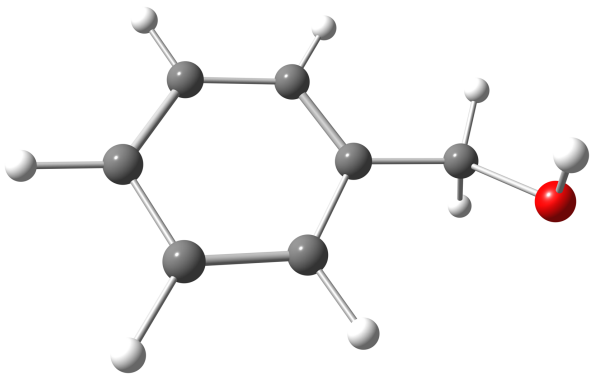
# Freq B3LYP/6-311+g(d,2p) SCRF=(SMD,Solvent=chloroform) nosymm geom=(check,newdefinition) guess=read int=(grid=ultrafine) EmpiricalDispersion=GD3

---

| | |
|---|---|
| SCF Done:  E(RB3LYP) = | -1823.78898963 |
| Zero-point correction = | 0.673512 (Hartree/Particle) |
| Thermal correction to Energy= | 0.709757 |
| Thermal correction to Enthalpy= | 0.710702 |
| Thermal correction to Gibbs Free Energy= | 0.604079 |
| Sum of electronic and zero-point Energies= | -1822.996778 |
| Sum of electronic and thermal Energies= | -1822.960532 |
| Sum of electronic and thermal Enthalpies= | -1822.959588 |
| Sum of electronic and thermal Free Energies= | -1823.066211 |

| | | | |
|---|---|---|---|
| S | 7.629644000 | 10.044777000 | 7.211364000 |
| N | 5.366432000 | 8.354315000 | 2.967661000 |
| N | 3.596522000 | 9.136647000 | 6.132514000 |
| N | 7.006871000 | 7.638485000 | 6.166386000 |
| H | 7.472639000 | 6.856689000 | 5.720622000 |
| N | 8.629377000 | 7.597088000 | 7.761882000 |
| H | 8.410129000 | 6.609006000 | 7.766656000 |
| C | 5.330652000 | 8.403956000 | 4.279552000 |
| C | 4.659604000 | 8.690069000 | 5.506008000 |
| C | 5.928852000 | 8.155323000 | 5.491324000 |
| C | 6.653096000 | 8.020415000 | 2.280319000 |
| H | 6.462354000 | 8.228404000 | 1.227432000 |
| C | 7.794603000 | 8.931967000 | 2.738768000 |
| H | 7.497340000 | 9.980576000 | 2.706951000 |
| H | 8.659072000 | 8.789457000 | 2.086640000 |
| H | 8.110957000 | 8.705553000 | 3.759849000 |
| C | 6.986063000 | 6.531577000 | 2.415516000 |
| H | 7.168706000 | 6.254167000 | 3.458445000 |
| H | 7.893071000 | 6.299621000 | 1.852889000 |
| H | 6.179288000 | 5.902337000 | 2.036485000 |
| C | 4.182172000 | 8.755669000 | 2.150661000 |
| H | 3.368024000 | 8.849187000 | 2.869242000 |
| C | 4.407739000 | 10.118743000 | 1.490555000 |
| H | 4.689490000 | 10.863096000 | 2.237039000 |
| H | 3.491105000 | 10.443366000 | 0.992356000 |
| H | 5.192487000 | 10.074280000 | 0.730753000 |
| C | 3.787235000 | 7.661788000 | 1.154639000 |
| H | 4.543697000 | 7.511802000 | 0.380712000 |
| H | 2.863855000 | 7.953691000 | 0.649581000 |
| H | 3.610223000 | 6.708867000 | 1.657933000 |
| C | 2.517299000 | 9.826474000 | 5.357632000 |
| H | 2.978839000 | 10.071062000 | 4.401430000 |
| C | 2.113670000 | 11.153608000 | 6.002612000 |
| H | 1.627368000 | 11.015018000 | 6.970604000 |
| H | 1.397200000 | 11.657241000 | 5.349450000 |
| H | 2.978324000 | 11.806329000 | 6.125462000 |

| | | | |
|---|---|---|---|
| C | 1.324951000 | 8.893720000 | 5.121553000 |
| H | 1.631013000 | 7.966653000 | 4.630044000 |
| H | 0.588063000 | 9.388790000 | 4.484806000 |
| H | 0.823199000 | 8.631876000 | 6.056293000 |
| C | 3.385250000 | 8.868720000 | 7.594666000 |
| H | 2.308290000 | 8.983306000 | 7.727127000 |
| C | 3.738837000 | 7.423492000 | 7.954887000 |
| H | 3.219759000 | 6.710902000 | 7.309563000 |
| H | 3.435970000 | 7.227428000 | 8.985351000 |
| H | 4.813508000 | 7.238195000 | 7.890208000 |
| C | 4.093604000 | 9.886226000 | 8.492173000 |
| H | 5.177951000 | 9.804247000 | 8.409178000 |
| H | 3.815486000 | 9.702091000 | 9.533113000 |
| H | 3.813072000 | 10.909685000 | 8.243613000 |
| C | 7.784318000 | 8.393963000 | 7.068023000 |
| C | 9.668902000 | 7.987140000 | 8.665740000 |
| C | 10.641626000 | 8.914828000 | 8.295420000 |
| H | 10.600405000 | 9.387702000 | 7.323675000 |
| C | 11.662118000 | 9.224703000 | 9.188294000 |
| H | 12.417347000 | 9.947244000 | 8.903045000 |
| C | 11.723428000 | 8.605648000 | 10.435798000 |
| H | 12.523888000 | 8.848840000 | 11.124006000 |
| C | 10.755615000 | 7.670482000 | 10.793336000 |
| H | 10.796919000 | 7.183791000 | 11.760296000 |
| C | 9.723896000 | 7.361906000 | 9.911332000 |
| H | 8.959689000 | 6.645315000 | 10.192865000 |
| C | 5.793173000 | 13.740522000 | 5.568048000 |
| C | 6.641401000 | 13.944310000 | 6.661111000 |
| C | 4.519101000 | 14.317819000 | 5.589706000 |
| H | 7.641496000 | 13.521722000 | 6.651004000 |
| H | 3.859182000 | 14.186296000 | 4.737856000 |
| C | 6.223552000 | 14.697352000 | 7.756477000 |
| C | 4.098645000 | 15.074771000 | 6.680512000 |
| H | 6.894664000 | 14.852386000 | 8.593432000 |
| H | 3.114151000 | 15.528897000 | 6.677588000 |
| C | 4.950158000 | 15.262592000 | 7.768460000 |
| H | 4.627513000 | 15.857864000 | 8.614846000 |
| O | 5.864355000 | 11.500267000 | 4.548036000 |
| H | 6.339353000 | 11.148373000 | 5.317411000 |
| C | 6.233105000 | 12.886321000 | 4.403152000 |
| H | 7.316831000 | 12.970714000 | 4.261805000 |
| H | 5.749088000 | 13.220151000 | 3.483766000 |



Computed structure benzyl alcohol (**5a**)

# opt B3LYP/6-311+g(d,2p)  nosymm int=(grid=ultrafine) EmpiricalDispersion=GD3

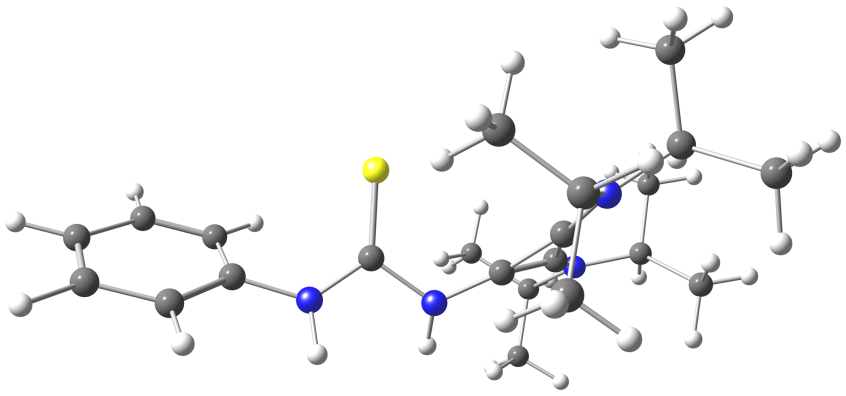
--Link1--

# Freq B3LYP/6-311+g(d,2p) SCRF=(SMD,Solvent=chloroform) nosymm geom=(check,newdefinition) guess=read int=(grid=ultrafine) EmpiricalDispersion=GD3

---

| | |
|---|---|
| SCF Done:  E(RB3LYP) = | -346.902255328 |
| Zero-point correction= | 0.132707 (Hartree/Particle) |
| Thermal correction to Energy= | 0.138986 |
| Thermal correction to Enthalpy= | 0.139930 |
| Thermal correction to Gibbs Free Energy= | 0.102312 |
| Sum of electronic and zero-point Energies= | -346.769549 |
| Sum of electronic and thermal Energies= | -346.763269 |
| Sum of electronic and thermal Enthalpies= | -346.762325 |
| Sum of electronic and thermal Free Energies= | -346.799944 |

| | | | |
|---|---|---|---|
| O | 0.174195000 | -2.755652000 | -1.198857000 |
| C | -0.352459000 | -3.795803000 | -0.371659000 |
| C | 0.659199000 | -4.872738000 | -0.041411000 |
| C | 0.757068000 | -5.391794000 | 1.251888000 |
| C | 1.504185000 | -5.374262000 | -1.038511000 |
| H | 0.115305000 | -5.004200000 | 2.033839000 |
| H | 1.437752000 | -4.967242000 | -2.038714000 |
| C | 1.674254000 | -6.401526000 | 1.546116000 |
| C | 2.424468000 | -6.377506000 | -0.745920000 |
| H | 1.739557000 | -6.793518000 | 2.552434000 |
| H | 3.072545000 | -6.757073000 | -1.524843000 |
| C | 2.510410000 | -6.896288000 | 0.547430000 |
| H | 3.225390000 | -7.675886000 | 0.773865000 |
| H | -0.774085000 | -3.385167000 | 0.552459000 |
| H | -1.179101000 | -4.218359000 | -0.945853000 |
| H | 0.954436000 | -2.393663000 | -0.768466000 |



Computed structure thiourea (optimized) (**4**)

# opt B3LYP/6-311+g(d,2p) nosymm int=(grid=ultrafine) EmpiricalDispersion=GD3

--Link1--

# Freq B3LYP/6-311+g(d,2p) SCRF=(SMD,Solvent=chloroform) nosymm geom=(check,newdefinition) guess=read int=(grid=ultrafine) EmpiricalDispersion=GD3

---

| | |
|---|---|
| SCF Done: E(RB3LYP) = | -1476.84645588 |
| Zero-point correction= | 0.536665 (Hartree/Particle) |
| Thermal correction to Energy= | 0.563687 |
| Thermal correction to Enthalpy= | 0.564631 |
| Thermal correction to Gibbs Free Energy= | 0.481163 |
| Sum of electronic and zero-point Energies= | -1476.248772 |
| Sum of electronic and thermal Energies= | -1476.221750 |
| Sum of electronic and thermal Enthalpies= | -1476.220806 |
| Sum of electronic and thermal Free Energies= | -1476.304274 |

| | | | |
|---|---|---|---|
| C | -0.357796000 | 0.872463000 | -1.449335000 |
| S | -0.236832000 | 1.317198000 | 0.141963000 |
| N | -1.543516000 | 0.282938000 | -1.973811000 |
| H | -1.398146000 | -0.537876000 | -2.547762000 |
| N | 0.580804000 | 0.982847000 | -2.418238000 |
| H | 0.248615000 | 0.910875000 | -3.369688000 |
| C | 1.941146000 | 1.400157000 | -2.280704000 |
| C | 2.437760000 | 2.326103000 | -3.199049000 |
| C | 2.770985000 | 0.860827000 | -1.298047000 |
| C | 3.772490000 | 2.718376000 | -3.130663000 |
| H | 1.784776000 | 2.742266000 | -3.955769000 |
| C | 4.099987000 | 1.268188000 | -1.230730000 |
| H | 2.382632000 | 0.140131000 | -0.595384000 |
| C | 4.604705000 | 2.194627000 | -2.143317000 |
| H | 5.639128000 | 2.503135000 | -2.086577000 |
| C | -2.703350000 | 0.280947000 | -1.240548000 |
| C | -3.660283000 | -0.436066000 | -0.567622000 |
| C | -3.753535000 | 0.982865000 | -0.698789000 |
| H | 4.743834000 | 0.853665000 | -0.467579000 |
| H | 4.155781000 | 3.435684000 | -3.842785000 |

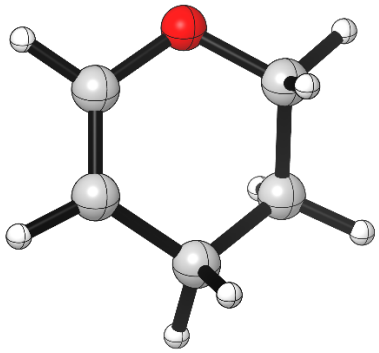
| | | | |
|---|---|---|---|
| N | -4.371935000 | 2.119446000 | -0.479581000 |
| N | -4.071023000 | -1.614421000 | -0.148146000 |
| C | -5.500523000 | 2.199790000 | 0.491278000 |
| H | -5.612264000 | 1.188140000 | 0.871413000 |
| C | -3.947363000 | 3.362407000 | -1.204602000 |
| H | -4.770303000 | 4.055809000 | -1.044620000 |
| C | -5.432695000 | -1.860513000 | 0.409631000 |
| H | -5.554144000 | -2.941377000 | 0.340372000 |
| C | -3.136572000 | -2.779627000 | -0.269847000 |
| C | -1.773554000 | -2.487222000 | 0.358317000 |
| H | -1.217962000 | -1.723865000 | -0.184772000 |
| H | -1.882457000 | -2.149007000 | 1.388118000 |
| H | -1.174614000 | -3.397859000 | 0.357774000 |
| C | -6.523704000 | -1.233049000 | -0.457501000 |
| H | -6.464377000 | -0.148368000 | -0.477434000 |
| H | -6.457658000 | -1.597135000 | -1.482815000 |
| H | -7.503179000 | -1.501381000 | -0.062453000 |
| H | -3.610260000 | -3.565400000 | 0.317485000 |
| C | -3.046296000 | -3.250251000 | -1.723371000 |
| H | -4.030875000 | -3.493197000 | -2.123025000 |
| H | -2.605391000 | -2.480534000 | -2.360171000 |
| H | -2.418576000 | -4.138308000 | -1.794047000 |
| C | -5.498516000 | -1.472943000 | 1.889143000 |
| H | -4.750623000 | -2.018034000 | 2.465179000 |
| H | -5.317234000 | -0.407887000 | 2.033271000 |
| H | -6.481368000 | -1.708141000 | 2.297784000 |
| C | -5.149333000 | 3.109783000 | 1.670951000 |
| H | -5.041303000 | 4.148230000 | 1.357463000 |
| H | -5.950934000 | 3.071497000 | 2.408909000 |
| H | -4.223176000 | 2.793658000 | 2.150139000 |
| C | -6.809253000 | 2.607591000 | -0.191951000 |
| H | -6.793510000 | 3.648953000 | -0.513098000 |
| H | -7.018999000 | 1.985247000 | -1.061728000 |
| H | -7.633418000 | 2.499420000 | 0.513338000 |
| C | -2.675807000 | 3.979258000 | -0.621416000 |
| H | -2.488407000 | 4.938961000 | -1.104432000 |
| H | -2.766671000 | 4.148645000 | 0.449675000 |
| H | -1.812176000 | 3.339541000 | -0.786514000 |
| C | -3.836421000 | 3.102256000 | -2.708133000 |
| H | -2.998477000 | 2.443084000 | -2.938312000 |
| H | -4.750779000 | 2.657783000 | -3.101790000 |
| H | -3.664802000 | 4.045381000 | -3.226314000 |

**Computational Methods**

The following calculations were performed using the Gaussian 09[194] suite of programs at the DFT level employing the range-separated hybrid ωB97X-D functional[195] with a 6-311G(d,p) basis set.[196] This functional was selected as it accounts for dispersion and has been shown to provide accurate thermochemical and kinetic energies. Single-point calculations were also performed at the SMD/ωB97X-D/6-311G(d,p) level on ωB97X-D/6-311G(d,p) optimized geometries. Thermal corrections from the vibrational frequencies at the ωB97X-D/6-311G(d,p) were added to the electronic energies of the abovementioned methods to gain the free energies. All of the optimized geometries (minimum stationary points (reactants, intermediates and products)) were confirmed by frequency computations as minima (zero imaginary frequencies) or transition states (one imaginary frequency) using analytic second derivatives.[197] Intrinsic reaction coordinate calculations were performed to ensure that the transition states found were first-order saddle points connecting the reactants and the products.[198] Solvent dichloromethane (DCM - $\varepsilon$ = 8.93) in these calculations was accounted for by the Self-Consistent Reaction Field (SCRF) method using the Solvation Model based on Density (SMD) model to gain a more accurate treatment of medium/long ranged attractive non-covalent interactions.[199] The Gibbs free energy differences ($\Delta G^{o}$) were taken with respect to the most stable conformer. The 3D images of all optimized geometries were generated with CYLview.[200] GaussView[201] was used to construct all structures prior to geometrical optimization. Monte Carlo conformational searches (MCCS) with an OPLS3[202] force field were performed on the full catalyst systems using Macro-model program in Schrodinger.[203]

## Thiourea Conformers, Methanol, DHP and MTP Optimized Structures

a. Methanol, DHP and MTP Optimized Structures



Optimized Structure of DHP.

---

- Thermochemistry -

---

(0 imaginary frequencies)

Zero-point correction= 0.123525 (Hartree/Particle)

Thermal correction to Energy= 0.128718

Thermal correction to Enthalpy= 0.129662

Thermal correction to Gibbs Free Energy= 0.095132

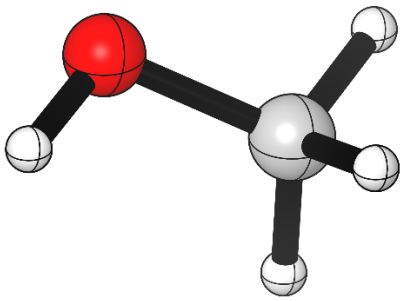
Sum of electronic and zero-point Energies= -270.403457

Sum of electronic and thermal Energies= -270.398264

Sum of electronic and thermal Enthalpies= -270.397320

Sum of electronic and thermal Free Energies= -270.431850

| | | | |
|---|---|---|---|
| H | -0.64766000 | 2.41093800 | 0.09524600 |
| C | 0.91359900 | 1.05500200 | -0.08177700 |
| C | -0.37391700 | 1.36348800 | 0.06244200 |
| C | -1.44414700 | 0.30830200 | 0.12582700 |
| C | -0.86010300 | -1.03348500 | -0.32286700 |
| C | 0.51897700 | -1.21851700 | 0.29381700 |
| H | -1.84990000 | 0.22676900 | 1.14180100 |
| H | -2.28438100 | 0.58826600 | -0.51726100 |
| H | -1.50547500 | -1.86745600 | -0.03494100 |
| H | -0.76026900 | -1.05171300 | -1.41256200 |
| H | 0.44481200 | -1.19741800 | 1.38949700 |
| H | 0.97869200 | -2.15970500 | -0.00740900 |
| O | 1.42560700 | -0.19971800 | -0.11544900 |
| H | 1.69287200 | 1.79932600 | -0.19543900 |



Optimized Structure of Methanol.

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- Thermochemistry -

---

(0 imaginary frequencies)

Zero-point correction= 0.051766 (Hartree/Particle)

Thermal correction to Energy= 0.055076

Thermal correction to Enthalpy= 0.056020

Thermal correction to Gibbs Free Energy= 0.029039

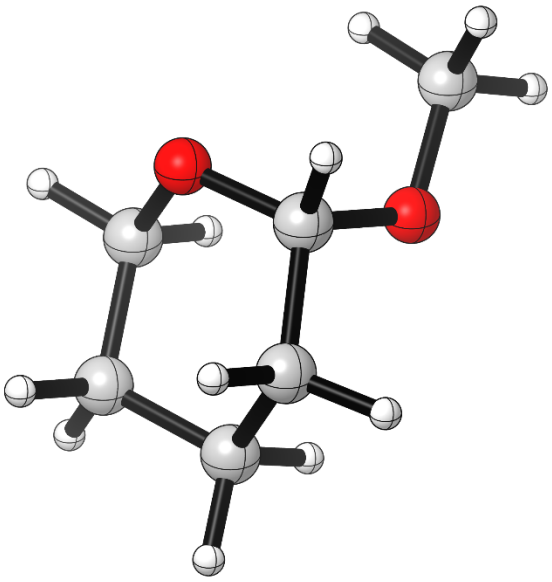
Sum of electronic and zero-point Energies= -115.665488

Sum of electronic and thermal Energies= -115.662178

Sum of electronic and thermal Enthalpies= -115.661234

Sum of electronic and thermal Free Energies= -115.688215

| | | | |
|---|---|---|---|
| C | 0.65848200 | -0.01957300 | 0.00000800 |
| H | 1.02945200 | -0.54148000 | -0.89234200 |
| H | 1.02937400 | -0.54356800 | 0.89115600 |
| H | 1.08204600 | 0.98553300 | 0.00113000 |
| O | -0.74534100 | 0.12146400 | 0.00001600 |
| H | -1.12903900 | -0.75476300 | -0.00011900 |

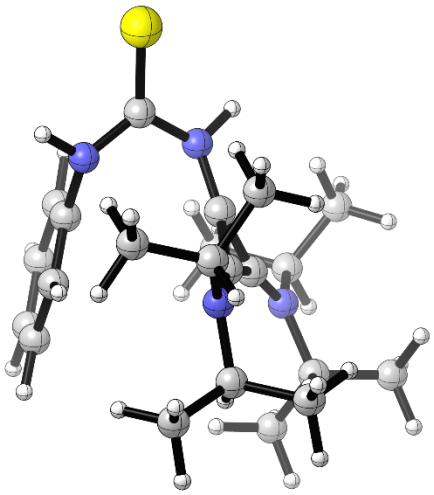


Optimized Structure of MTP.

---
- Thermochemistry -
---
(0 imaginary frequencies)
Zero-point correction= 0.180759 (Hartree/Particle)
Thermal correction to Energy= 0.188582
Thermal correction to Enthalpy= 0.189526
Thermal correction to Gibbs Free Energy= 0.148695
Sum of electronic and zero-point Energies= -386.104437
Sum of electronic and thermal Energies= -386.096615
Sum of electronic and thermal Enthalpies= -386.095670
Sum of electronic and thermal Free Energies= -386.136501

| | | | |
|---|---|---|---|
| H | -1.12543900 | -1.45597400 | 1.44154200 |
| C | 0.56123200 | -0.42583800 | 0.65141900 |
| C | -0.61112100 | -1.38264500 | 0.47788300 |
| C | -1.57807300 | -0.87401100 | -0.59187500 |
| C | -1.96737700 | 0.57307400 | -0.28584000 |
| C | -0.71565000 | 1.42114000 | -0.10893100 |
| H | -1.08956000 | -0.92351500 | -1.56998500 |
| H | -2.46352900 | -1.51358700 | -0.63682200 |
| H | -2.58287100 | 0.99284100 | -1.08724700 |
| H | -2.55599600 | 0.61161200 | 0.63782900 |
| H | -0.17049200 | 1.48610700 | -1.05994100 |
| H | -0.95875900 | 2.43336700 | 0.21654500 |
| O | 0.13807400 | 0.89364700 | 0.90044400 |
| H | 1.15984700 | -0.68535700 | 1.53453400 |
| H | -0.22107200 | -2.37168700 | 0.22820200 |
| C | 2.55432100 | 0.21829500 | -0.41977700 |
| H | 3.17600500 | -0.13813300 | 0.41320900 |
| H | 2.36634800 | 1.28794000 | -0.28167800 |
| H | 3.08788800 | 0.05930000 | -1.35638400 |
| O | 1.35163200 | -0.51402200 | -0.50257900 |

b. Thiourea Conformers



Optimized Structure of Thiourea *E,E*-**4** Conformer.

---

- Thermochemistry -

---

(0 imaginary frequencies)

Zero-point correction= 0.548404 (Hartree/Particle)

Thermal correction to Energy= 0.578341

Thermal correction to Enthalpy= 0.579285

Thermal correction to Gibbs Free Energy= 0.488250

Sum of electronic and zero-point Energies= -1475.778161

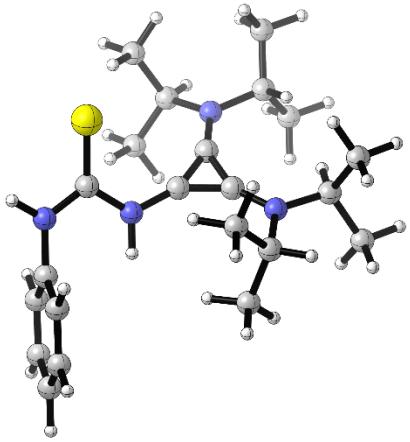
Sum of electronic and thermal Energies= -1475.748223

Sum of electronic and thermal Enthalpies= -1475.747279

Sum of electronic and thermal Free Energies= -1475.838315

| | | | |
|---|---|---|---|
| C | -2.67507200 | -0.90203300 | -1.00755200 |
| S | -3.91896400 | -1.04556400 | -2.07371300 |
| N | -1.34767200 | -1.08138300 | -1.41388600 |
| H | -1.23730600 | -1.54782700 | -2.30246100 |
| N | -2.81900800 | -0.60337800 | 0.31032700 |
| C | -1.94325200 | -1.04565800 | 1.35934100 |
| C | -1.63223700 | -2.39601200 | 1.47994200 |
| C | -1.44525200 | -0.12513000 | 2.27477700 |
| C | -0.80043600 | -2.81980600 | 2.50740400 |
| H | -2.05036700 | -3.10776900 | 0.77690300 |
| C | -0.61691100 | -0.55613800 | 3.30308900 |
| H | -1.70749900 | 0.92049000 | 2.17758400 |
| C | -0.28809200 | -1.90205300 | 3.41713000 |
| H | 0.35092400 | -2.23828800 | 4.22498900 |
| H | -3.78106200 | -0.43535200 | 0.57130100 |
| H | -0.23905900 | 0.15916600 | 4.02441400 |
| H | -0.56661300 | -3.87316400 | 2.60714300 |
| C | -0.31516200 | -0.32929500 | -0.94774000 |
| C | 0.15094000 | 0.85577200 | -0.43761600 |
| C | 1.02292000 | -0.23408900 | -0.65485700 |
| N | -0.02814100 | 2.09222700 | -0.03073300 |

| | | | |
|---|---|---|---|
| N | 2.21985400 | -0.76353800 | -0.64376300 |
| C | 1.07403300 | 2.76115300 | 0.70053800 |
| C | -1.15988000 | 2.91153600 | -0.54970300 |
| C | 3.39997000 | 0.03981100 | -0.25429400 |
| C | 2.38492900 | -2.18931800 | -1.01966900 |
| C | 1.93430200 | 3.60406200 | -0.23788800 |
| H | 1.67807300 | 1.94612100 | 1.10620100 |
| C | 0.54976800 | 3.55816900 | 1.88973500 |
| C | -2.40041100 | 2.84264100 | 0.33216900 |
| H | -0.77738900 | 3.93415200 | -0.52526800 |
| C | -1.47358200 | 2.57504100 | -2.00373200 |
| H | 3.02679600 | 1.05721800 | -0.13664100 |
| C | 3.94994400 | -0.43352400 | 1.08755900 |
| C | 4.45016800 | 0.06379300 | -1.36017300 |
| H | 3.43145100 | -2.41666100 | -0.81292200 |
| C | 1.51987500 | -3.08989000 | -0.14783400 |
| C | 2.13483400 | -2.39060100 | -2.51076800 |
| H | 2.28902400 | 3.01577000 | -1.08854100 |
| H | 1.38098000 | 4.46156400 | -0.62830400 |
| H | 2.80374300 | 3.99163500 | 0.29742900 |
| H | -0.06609500 | 4.40456400 | 1.57724900 |
| H | -0.03734100 | 2.92517100 | 2.55797200 |
| H | 1.39443900 | 3.95885800 | 2.45316500 |
| H | -2.83779900 | 1.84404200 | 0.29844700 |
| H | -2.17681100 | 3.09984700 | 1.36868800 |
| H | -3.14595100 | 3.55069000 | -0.03577500 |
| H | -0.57361300 | 2.60474800 | -2.62261600 |
| H | -1.94712400 | 1.59525000 | -2.10794100 |
| H | -2.17815900 | 3.30988000 | -2.39659300 |
| H | 4.34903600 | -1.44908700 | 1.02244900 |
| H | 4.76506900 | 0.21909900 | 1.40683400 |
| H | 3.17200400 | -0.41785200 | 1.85469500 |
| H | 4.02173400 | 0.41564700 | -2.30101200 |
| H | 5.25624700 | 0.74358500 | -1.07734000 |
| H | 4.89668600 | -0.91955500 | -1.52595400 |
| H | 1.74670200 | -4.13687900 | -0.35822800 |
| H | 1.69980900 | -2.90073500 | 0.91218700 |
| H | 0.45623400 | -2.93260700 | -0.34418000 |
| H | 1.09453100 | -2.17137200 | -2.76948100 |
| H | 2.78084200 | -1.74988500 | -3.11314000 |
| H | 2.32767900 | -3.42951400 | -2.78460100 |



Optimized Structure of Thiourea *E,Z*-**4** Conformer.

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- Thermochemistry -

---

(0 imaginary frequencies)

Zero-point correction= 0.547610 (Hartree/Particle)

Thermal correction to Energy= 0.578095

Thermal correction to Enthalpy= 0.579039

Thermal correction to Gibbs Free Energy= 0.484071

Sum of electronic and zero-point Energies= -1475.780215

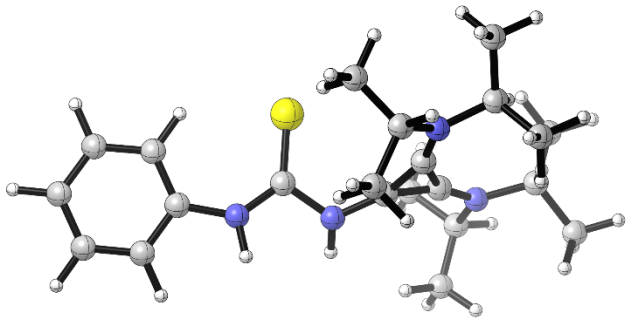
Sum of electronic and thermal Energies= -1475.749730

Sum of electronic and thermal Enthalpies= -1475.748786

Sum of electronic and thermal Free Energies= -1475.843754

| | | | |
|---|---|---|---|
| C | -1.73719900 | -1.38675100 | -1.03634700 |
| S | -0.79976900 | -2.19786500 | -2.13681300 |
| N | -1.21476000 | -0.46175700 | -0.14531700 |
| H | -1.86118600 | 0.16475100 | 0.31816600 |
| N | -3.07339900 | -1.53079300 | -0.93753000 |
| C | -3.92666900 | -0.73012100 | -0.11125900 |
| C | -4.14078900 | -1.08578000 | 1.21703500 |
| C | -4.51949400 | 0.41105100 | -0.64596000 |
| C | -4.95217400 | -0.28889200 | 2.01503100 |
| H | -3.67861900 | -1.98419500 | 1.60943000 |
| C | -5.33450800 | 1.19896000 | 0.15675100 |
| H | -4.34493500 | 0.66500500 | -1.68551400 |
| C | -5.54742900 | 0.85074100 | 1.48583800 |
| H | -6.18558500 | 1.46527900 | 2.10946300 |
| H | -3.48582500 | -2.14688800 | -1.62202300 |
| H | -5.80708400 | 2.08132300 | -0.25765700 |
| H | -5.12764000 | -0.56347000 | 3.04816100 |
| C | 0.11063200 | -0.15220100 | -0.07447200 |
| C | 1.42313800 | -0.50446600 | 0.12587500 |
| C | 1.04060200 | 0.84963700 | -0.05786500 |
| N | 2.38319900 | -1.36706500 | 0.33828100 |
| N | 1.31445100 | 2.12885200 | -0.14159200 |
| C | 3.78141400 | -0.86671400 | 0.36110200 |
| C | 2.09437000 | -2.74991700 | 0.81377300 |
| C | 2.67232200 | 2.64355700 | 0.14263800 |
| C | 0.24591000 | 3.05570200 | -0.58981300 |
| C | 4.20023400 | -0.51277400 | 1.78620400 |

| | | | |
|---|---|---|---|
| H | 3.76685300 | 0.04155600 | -0.24520000 |
| C | 4.75281900 | -1.82825300 | -0.31206900 |
| C | 2.02712100 | -3.75699900 | -0.32879100 |
| H | 2.94578000 | -2.99548200 | 1.45353800 |
| C | 0.84136500 | -2.78757400 | 1.68213600 |
| H | 3.21072600 | 1.80220800 | 0.57963300 |
| C | 3.37503300 | 3.06260500 | -1.14420000 |
| C | 2.63687700 | 3.75051400 | 1.19199100 |
| H | 0.74685700 | 4.01238900 | -0.74337200 |
| C | -0.34237800 | 2.61496900 | -1.92669900 |
| C | -0.81253100 | 3.24033200 | 0.49378200 |
| H | 3.49906500 | 0.19105600 | 2.24337400 |
| H | 4.24810800 | -1.40222200 | 2.41948100 |
| H | 5.19209100 | -0.05567000 | 1.78364100 |
| H | 4.84382300 | -2.77201500 | 0.22992100 |
| H | 4.45307100 | -2.03854500 | -1.33971500 |
| H | 5.74201300 | -1.36691600 | -0.33453500 |
| H | 1.18746500 | -3.52801300 | -0.98533000 |
| H | 2.94219500 | -3.76555300 | -0.92034500 |
| H | 1.88248200 | -4.75819500 | 0.08391900 |
| H | 0.87739800 | -2.03274500 | 2.47175400 |
| H | -0.06488500 | -2.64533000 | 1.08891900 |
| H | 0.76775600 | -3.76820300 | 2.15499400 |
| H | 2.87249600 | 3.91059600 | -1.61720000 |
| H | 4.40080100 | 3.36785300 | -0.92776200 |
| H | 3.40424600 | 2.23914600 | -1.86168500 |
| H | 2.14020000 | 3.41261400 | 2.10386600 |
| H | 3.65898300 | 4.03708300 | 1.44683900 |
| H | 2.12892900 | 4.64706000 | 0.82847900 |
| H | -1.04729000 | 3.36882300 | -2.28253200 |
| H | 0.43955900 | 2.49494100 | -2.67890900 |
| H | -0.88406700 | 1.66911000 | -1.84116800 |
| H | -1.34962200 | 2.30764600 | 0.68963600 |
| H | -0.36664500 | 3.58111100 | 1.42955600 |
| H | -1.54964000 | 3.97932500 | 0.17420200 |



Optimized Structure of Thiourea *Z,Z*-**4** Conformer.

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- Thermochemistry -

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(0 imaginary frequencies)

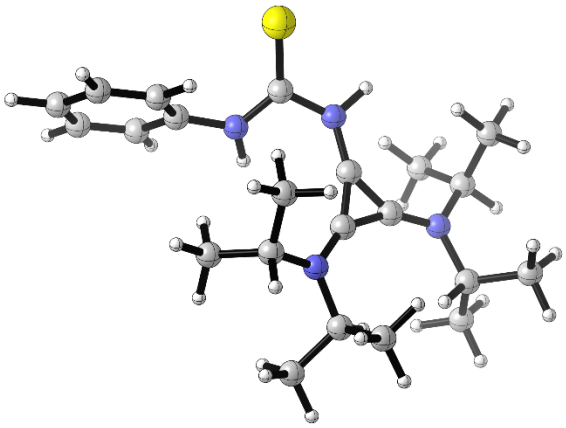
Zero-point correction= 0.547201 (Hartree/Particle)

Thermal correction to Energy= 0.577826

Thermal correction to Enthalpy= 0.578770
Thermal correction to Gibbs Free Energy= 0.483301
Sum of electronic and zero-point Energies= -1475.771861
Sum of electronic and thermal Energies= -1475.741236
Sum of electronic and thermal Enthalpies= -1475.740292
Sum of electronic and thermal Free Energies= -1475.835761

| | | | |
|---|---|---|---|
| C | 1.86398800 | -0.31005200 | 0.05797100 |
| S | 1.62562600 | 0.30685800 | 1.56955500 |
| N | 0.76360300 | -0.76800100 | -0.72160900 |
| H | 0.84943900 | -1.70703900 | -1.08799000 |
| N | 3.00543700 | -0.48496400 | -0.62887500 |
| C | 4.37426500 | -0.38255800 | -0.26307100 |
| C | 4.83592200 | 0.17170800 | 0.92696400 |
| C | 5.28314800 | -0.87334700 | -1.20404000 |
| C | 6.20563300 | 0.21929900 | 1.16246900 |
| H | 4.14417900 | 0.56412100 | 1.65472800 |
| C | 6.64338200 | -0.81272500 | -0.95769400 |
| H | 4.92393900 | -1.30941400 | -2.13178800 |
| C | 7.11176200 | -0.26654100 | 0.23220200 |
| H | 8.17586000 | -0.21762200 | 0.42785600 |
| H | 2.87654600 | -0.74291900 | -1.59737600 |
| H | 6.56122400 | 0.65154600 | 2.09011000 |
| H | 7.33822000 | -1.19496500 | -1.69558200 |
| C | -0.50524000 | -0.37087900 | -0.43124600 |
| C | -1.80755500 | -0.70717900 | -0.17843000 |
| C | -1.40996300 | 0.64604200 | -0.25448800 |
| N | -2.72122900 | -1.63271700 | -0.00505100 |
| N | -1.72956400 | 1.91392500 | -0.18051900 |
| C | -4.15346600 | -1.27767200 | 0.10001600 |
| C | -2.28481500 | -3.03873800 | 0.16837700 |
| C | -3.10916400 | 2.27581900 | 0.22813100 |
| C | -0.81938100 | 2.96680400 | -0.70787900 |
| C | -4.99892900 | -2.08580300 | -0.87969500 |
| H | -4.21357500 | -0.23285700 | -0.20855400 |
| C | -4.63515700 | -1.39395100 | 1.54262400 |
| C | -1.27494100 | -3.16773500 | 1.30461000 |
| H | -3.18480500 | -3.58249000 | 0.45831000 |
| C | -1.78191400 | -3.61950900 | -1.14979100 |
| H | -3.48063000 | 1.40620700 | 0.77426900 |
| C | -3.12798000 | 3.44982600 | 1.19985300 |
| C | -3.99060800 | 2.51089200 | -0.99581100 |
| H | -1.48917000 | 3.77412000 | -1.01271500 |
| C | 0.13543600 | 3.49540200 | 0.35674300 |
| C | -0.07959500 | 2.49157300 | -1.95438900 |
| H | -4.62834100 | -1.97532100 | -1.90089800 |
| H | -5.01983500 | -3.14902400 | -0.62867300 |
| H | -6.02879100 | -1.72495500 | -0.84963300 |
| H | -4.57949100 | -2.42572800 | 1.89992500 |
| H | -4.03295200 | -0.76999100 | 2.20760400 |
| H | -5.67667700 | -1.07499100 | 1.61863500 |
| H | -0.33340000 | -2.65919300 | 1.07894500 |
| H | -1.67237300 | -2.74369900 | 2.22869500 |
| H | -1.05010200 | -4.22151700 | 1.47941200 |
| H | -2.54531100 | -3.55708300 | -1.92694300 |
| H | -0.89417900 | -3.08758000 | -1.50631900 |

| | | | |
|---|---|---|---|
| H | -1.50832800 | -4.66805500 | -1.01861100 |
| H | -2.77688600 | 4.37448600 | 0.73643200 |
| H | -4.15488000 | 3.61899000 | 1.52942500 |
| H | -2.51703100 | 3.24284200 | 2.07988400 |
| H | -3.97558300 | 1.64805100 | -1.66750200 |
| H | -5.02324500 | 2.68764500 | -0.68738400 |
| H | -3.66184100 | 3.38620300 | -1.56178600 |
| H | 0.71626100 | 4.32325600 | -0.05646800 |
| H | -0.39823100 | 3.86119200 | 1.23398300 |
| H | 0.82758400 | 2.71452100 | 0.67585500 |
| H | 0.67779100 | 1.74140200 | -1.71440200 |
| H | -0.76822800 | 2.07833500 | -2.69547000 |
| H | 0.43613000 | 3.34004300 | -2.40703800 |



Optimized Structure of Thiourea *Z,E*-**4** Conformer.

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- Thermochemistry -

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(0 imaginary frequencies)

Zero-point correction= 0.547941 (Hartree/Particle)

Thermal correction to Energy= 0.578206

Thermal correction to Enthalpy= 0.579150

Thermal correction to Gibbs Free Energy= 0.486208

Sum of electronic and zero-point Energies= -1475.771922

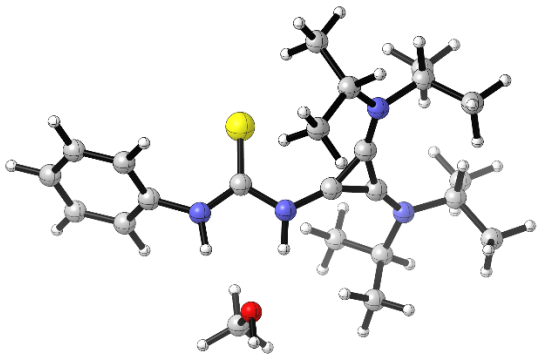
Sum of electronic and thermal Energies= -1475.741657

Sum of electronic and thermal Enthalpies= -1475.740712

Sum of electronic and thermal Free Energies= -1475.833654

| | | | |
|---|---|---|---|
| C | -1.63146500 | -1.76941200 | -0.42887300 |
| S | -2.43186200 | -2.79788500 | -1.42558100 |
| N | -0.22422200 | -1.81905600 | -0.35961700 |
| H | 0.16714300 | -2.66589200 | -0.74736500 |
| N | -2.14163400 | -0.84144700 | 0.41110000 |
| C | -3.50495600 | -0.44938500 | 0.53280800 |
| C | -4.25399200 | -0.10000800 | -0.58550700 |
| C | -4.04658900 | -0.34179100 | 1.80817600 |
| C | -5.55680500 | 0.34443200 | -0.41741800 |
| H | -3.82742500 | -0.18499300 | -1.57602700 |
| C | -5.34743400 | 0.11741900 | 1.96679000 |
| H | -3.45816300 | -0.62691200 | 2.67423800 |

| | | | |
|---|---|---|---|
| C | -6.10605500 | 0.45780800 | 0.85475400 |
| H | -7.12346800 | 0.80832700 | 0.97827100 |
| H | -1.54371900 | -0.55189500 | 1.17180300 |
| H | -6.14535100 | 0.60690400 | -1.28833900 |
| H | -5.77014000 | 0.19849800 | 2.96082700 |
| C | 0.62113500 | -0.78081900 | -0.17271000 |
| C | 0.95102900 | 0.55925200 | -0.15213300 |
| C | 1.92846100 | -0.42812900 | 0.06211600 |
| N | 0.66910000 | 1.84347100 | -0.23602200 |
| N | 3.16683400 | -0.80708200 | 0.28305000 |
| C | 1.75587500 | 2.80682400 | 0.07440100 |
| C | -0.56677600 | 2.34443100 | -0.89725200 |
| C | 4.27855000 | 0.17022000 | 0.27901100 |
| C | 3.44410300 | -2.23866700 | 0.55545700 |
| C | 2.50464300 | 3.20815100 | -1.19467900 |
| H | 2.43437800 | 2.26369000 | 0.73559300 |
| C | 1.25237200 | 4.01236500 | 0.85943600 |
| C | -1.68985600 | 2.59272400 | 0.10408800 |
| H | -0.27096500 | 3.30585000 | -1.32322400 |
| C | -0.99011600 | 1.45323700 | -2.05895400 |
| H | 3.84317300 | 1.09986800 | -0.08608200 |
| C | 4.80756900 | 0.39713100 | 1.69137100 |
| C | 5.36962000 | -0.23281100 | -0.70874300 |
| H | 4.48499900 | -2.26661000 | 0.88088200 |
| C | 2.58977700 | -2.76127400 | 1.70609600 |
| C | 3.32183900 | -3.07460300 | -0.71521000 |
| H | 2.85801100 | 2.33133300 | -1.74409700 |
| H | 1.86836400 | 3.79222500 | -1.86416700 |
| H | 3.36896300 | 3.82602200 | -0.94123200 |
| H | 0.57559600 | 4.63590300 | 0.27105700 |
| H | 0.74394600 | 3.70569500 | 1.77495500 |
| H | 2.10650700 | 4.63292400 | 1.13751400 |
| H | -1.99251000 | 1.67019300 | 0.59707700 |
| H | -1.39632900 | 3.31423500 | 0.86623500 |
| H | -2.56705200 | 2.98511600 | -0.41457900 |
| H | -0.16377600 | 1.28288200 | -2.75286200 |
| H | -1.37371300 | 0.49046800 | -1.71950300 |
| H | -1.79615100 | 1.94363100 | -2.60727800 |
| H | 5.25131500 | -0.51230400 | 2.10476800 |
| H | 5.58353800 | 1.16510100 | 1.68018500 |
| H | 4.00981000 | 0.72397200 | 2.36290200 |
| H | 4.95996500 | -0.36950100 | -1.71167000 |
| H | 6.12447100 | 0.55445900 | -0.75261100 |
| H | 5.87677000 | -1.15335600 | -0.41007600 |
| H | 2.90767000 | -3.77211600 | 1.96785800 |
| H | 2.69945700 | -2.12968400 | 2.59015700 |
| H | 1.52962400 | -2.81195900 | 1.44357200 |
| H | 2.31098000 | -3.03151500 | -1.13156100 |
| H | 4.01265500 | -2.72678600 | -1.48459700 |
| H | 3.54510200 | -4.12136800 | -0.50104400 |



Optimized Structure of *Z,Z*-**4**-**INT**$_1$.

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- Thermochemistry -

---

(0 imaginary frequencies)

Zero-point correction= 0.602340 (Hartree/Particle)

Thermal correction to Energy= 0.637014

Thermal correction to Enthalpy= 0.637958

Thermal correction to Gibbs Free Energy= 0.534908

Sum of electronic and zero-point Energies= -1591.465376

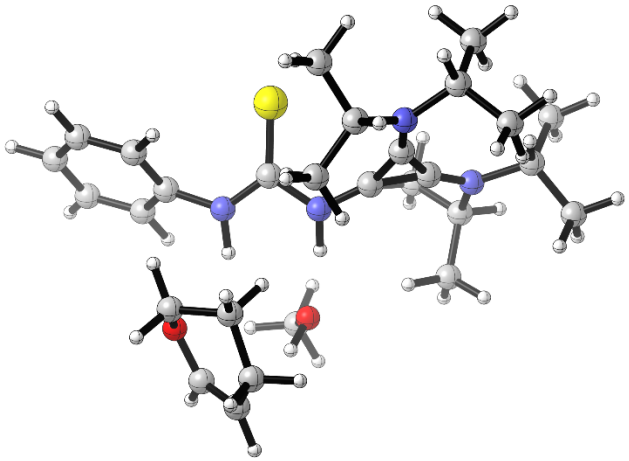
Sum of electronic and thermal Energies= -1591.430702

Sum of electronic and thermal Enthalpies= -1591.429758

Sum of electronic and thermal Free Energies= -1591.532808

| | | | |
|---|---|---|---|
| C | 1.69603800 | -0.20427400 | 0.12460100 |
| S | 1.49794700 | -1.23057500 | -1.16348200 |
| N | 2.86733700 | 0.23386100 | 0.62066600 |
| H | 2.83053100 | 0.93058900 | 1.35682800 |
| N | 0.60924300 | 0.34511600 | 0.80579100 |
| H | 0.77172800 | 1.19848800 | 1.33993900 |
| O | 1.81316400 | 2.64542400 | 1.96899100 |
| H | 1.85734100 | 3.03542800 | 2.84329900 |
| C | 2.11991900 | 3.63202200 | 0.98271400 |
| H | 3.12323600 | 4.03906100 | 1.12968500 |
| H | 2.07899900 | 3.12766100 | 0.01670500 |
| H | 1.38581300 | 4.44186100 | 0.99132100 |
| C | 4.15111600 | -0.03909400 | 0.05444900 |
| C | 4.71713100 | -1.30140900 | 0.17299700 |
| C | 4.83810400 | 0.98977000 | -0.57658900 |
| C | 5.97958700 | -1.53310600 | -0.35415300 |
| H | 4.16582800 | -2.09218400 | 0.66641000 |
| C | 6.10537100 | 0.75481800 | -1.09352000 |
| H | 4.37552200 | 1.96596800 | -0.67222200 |
| C | 6.67484400 | -0.50722800 | -0.98435600 |
| H | 7.66095800 | -0.69257500 | -1.39303300 |
| H | 6.42443400 | -2.51713800 | -0.26824500 |
| H | 6.64274300 | 1.55527600 | -1.58775800 |
| C | -0.67446200 | 0.01684100 | 0.49476200 |
| C | -1.65736900 | -0.92935100 | 0.33358900 |
| C | -1.90724500 | 0.45131600 | 0.09803600 |
| N | -2.06080200 | -2.17422500 | 0.36328100 |
| N | -2.65634500 | 1.47011900 | -0.26312600 |
| C | -3.36783000 | -2.58520700 | -0.19908300 |
| C | -1.26892800 | -3.25380400 | 1.01482600 |

| | | | |
|---|---|---|---|
| C | -4.10785400 | 1.34249900 | -0.50545200 |
| C | -2.01512300 | 2.79969900 | -0.40022900 |
| H | -3.31131500 | -3.67469300 | -0.23874000 |
| C | -3.53405000 | -2.10709900 | -1.63660900 |
| C | -4.50957200 | -2.22643800 | 0.74865700 |
| C | -0.28469400 | -2.72364300 | 2.04655400 |
| H | -2.02338000 | -3.83983600 | 1.55111900 |
| C | -0.59689900 | -4.14387000 | -0.02512000 |
| H | -4.33242900 | 0.28992500 | -0.34679900 |
| C | -4.91072100 | 2.15266000 | 0.50785900 |
| C | -4.45936900 | 1.68716200 | -1.95021900 |
| H | -2.79677300 | 3.45025700 | -0.79416100 |
| C | -1.58748300 | 3.35822100 | 0.95478100 |
| C | -0.87971000 | 2.76122000 | -1.41845100 |
| H | -3.55229200 | -1.02019900 | -1.72275100 |
| H | -2.71233200 | -2.47646300 | -2.25343400 |
| H | -4.47149300 | -2.48778600 | -2.04664500 |
| H | -4.37171000 | -2.71664200 | 1.71509100 |
| H | -4.57462000 | -1.15175600 | 0.93128800 |
| H | -5.46323000 | -2.55888400 | 0.33366700 |
| H | 0.56781500 | -2.23108200 | 1.57800400 |
| H | -0.76337700 | -2.03458200 | 2.74666200 |
| H | 0.10129200 | -3.56841400 | 2.61960500 |
| H | -1.31431200 | -4.53198700 | -0.75203500 |
| H | 0.17284000 | -3.58465900 | -0.55879300 |
| H | -0.13107900 | -4.99904600 | 0.46949100 |
| H | -4.73549200 | 3.22610600 | 0.39784100 |
| H | -5.97753200 | 1.97860400 | 0.35375900 |
| H | -4.66050300 | 1.86288000 | 1.53095500 |
| H | -4.30184600 | 2.74637900 | -2.16764000 |
| H | -3.86319000 | 1.10006100 | -2.65206200 |
| H | -5.51435800 | 1.47179100 | -2.13104500 |
| H | -1.24976200 | 4.39022000 | 0.83437800 |
| H | -2.41814600 | 3.35346300 | 1.66267800 |
| H | -0.76001100 | 2.79117900 | 1.38830100 |
| H | -0.06096900 | 2.11639600 | -1.08851600 |
| H | -1.23325400 | 2.39093200 | -2.38239400 |
| H | -0.47895900 | 3.76688400 | -1.56352200 |



Optimized Structure of *Z,Z*-**4-INT$_2$**.

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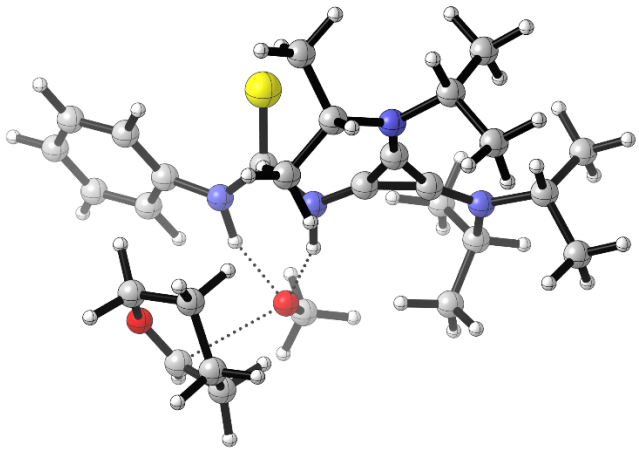
- Thermochemistry -
---
(0 imaginary frequencies)
Zero-point correction= 0.728118 (Hartree/Particle)
Thermal correction to Energy= 0.769320
Thermal correction to Enthalpy= 0.770265
Thermal correction to Gibbs Free Energy= 0.652003
Sum of electronic and zero-point Energies= -1861.890966
Sum of electronic and thermal Energies= -1861.849764
Sum of electronic and thermal Enthalpies= -1861.848820
Sum of electronic and thermal Free Energies= -1861.967081

| | | | |
|---|---|---|---|
| C | -0.98931500 | 0.60747900 | -0.79076700 |
| S | -0.41947200 | 1.94552000 | -1.59467300 |
| N | -2.27069500 | 0.20504500 | -0.70104400 |
| H | -2.47249500 | -0.64654800 | -0.18694000 |
| N | -0.12814200 | -0.26923400 | -0.13671800 |
| H | -0.45042200 | -1.23104500 | 0.02636800 |
| C | -3.88047800 | -2.42429900 | 1.84029600 |
| C | -3.15692900 | -2.66231600 | 2.93718000 |
| C | -2.44342000 | -1.56424800 | 3.67939300 |
| C | -2.44504600 | -0.27366200 | 2.85345400 |
| C | -3.78882800 | -0.10490900 | 2.16148500 |
| H | -2.93420800 | -1.40030600 | 4.64497100 |
| H | -1.41816700 | -1.86973000 | 3.90970400 |
| H | -2.24669700 | 0.59680400 | 3.48322200 |
| H | -1.65615900 | -0.30250700 | 2.09488400 |
| H | -4.60032000 | -0.06137000 | 2.89577200 |
| H | -3.83026600 | 0.78646100 | 1.53705600 |
| O | -4.05363600 | -1.20293800 | 1.27646900 |
| H | -4.39731200 | -3.19960400 | 1.28514700 |
| H | -3.12549700 | -3.67541500 | 3.32070000 |
| O | -1.30467400 | -2.73023100 | 0.26825200 |
| H | -1.83452300 | -2.90146900 | 1.06094200 |
| C | -1.79552200 | -3.50722400 | -0.81724600 |
| H | -2.85885200 | -3.31661900 | -0.99418800 |
| H | -1.23445200 | -3.21059100 | -1.70406800 |
| H | -1.64071800 | -4.57486000 | -0.64093800 |
| C | -3.40997300 | 0.81939300 | -1.29677400 |
| C | -3.70297600 | 2.16121100 | -1.08193600 |
| C | -4.27023700 | 0.02086500 | -2.04039800 |
| C | -4.85519400 | 2.70398800 | -1.63324000 |
| H | -3.02934900 | 2.77507600 | -0.49876700 |
| C | -5.42587300 | 0.56821800 | -2.58011500 |
| H | -4.03043100 | -1.02478500 | -2.19731600 |
| C | -5.71724200 | 1.91178600 | -2.38185300 |
| H | -6.61532500 | 2.34119000 | -2.80933400 |
| H | -5.07970700 | 3.75184700 | -1.47388300 |
| H | -6.09386900 | -0.05464200 | -3.16280000 |
| C | 1.20075700 | -0.00343900 | -0.01787100 |
| C | 2.20971700 | 0.82377100 | 0.40737400 |
| C | 2.48590600 | -0.40350900 | -0.25586000 |
| N | 2.61119700 | 1.92790400 | 0.98831500 |
| N | 3.28617800 | -1.30346400 | -0.78176700 |
| C | 4.02678700 | 2.35917100 | 0.94827800 |

| | | | |
|---|---|---|---|
| C | 1.69071000 | 2.79323500 | 1.77346500 |
| C | 4.75524100 | -1.22968900 | -0.65244800 |
| C | 2.68082500 | -2.45004000 | -1.50423100 |
| H | 4.00690200 | 3.38281700 | 1.32740200 |
| C | 4.54785800 | 2.43438300 | -0.48240100 |
| C | 4.87439200 | 1.53674800 | 1.91630100 |
| C | 0.45711600 | 2.05142600 | 2.26807700 |
| H | 2.28086600 | 3.07190800 | 2.65357600 |
| C | 1.33165900 | 4.05491400 | 0.99550200 |
| H | 4.94859800 | -0.32149300 | -0.08589000 |
| C | 5.30211100 | -2.40704100 | 0.14870200 |
| C | 5.42234600 | -1.07937300 | -2.01729700 |
| H | 3.52691700 | -2.97661800 | -1.94762500 |
| C | 1.98278200 | -3.40580600 | -0.54104200 |
| C | 1.77976800 | -1.97696600 | -2.64059600 |
| H | 4.55651000 | 1.46441800 | -0.98069700 |
| H | 3.92339000 | 3.10588700 | -1.07496100 |
| H | 5.56949000 | 2.81929100 | -0.48510200 |
| H | 4.51223100 | 1.66333100 | 2.93920200 |
| H | 4.84508300 | 0.46934800 | 1.68791400 |
| H | 5.91555600 | 1.86403500 | 1.88275700 |
| H | -0.24708300 | 1.85331100 | 1.45934900 |
| H | 0.71725900 | 1.11014000 | 2.75879300 |
| H | -0.05288700 | 2.68149900 | 2.99924800 |
| H | 2.22273100 | 4.59619500 | 0.66907800 |
| H | 0.73852900 | 3.79705000 | 0.11677900 |
| H | 0.74874000 | 4.72613800 | 1.63017000 |
| H | 5.15056800 | -3.35679300 | -0.37065800 |
| H | 6.37658600 | -2.28169800 | 0.29703500 |
| H | 4.82526100 | -2.46934500 | 1.12956300 |
| H | 5.31159400 | -1.97807800 | -2.62884000 |
| H | 5.00346900 | -0.23479000 | -2.56870400 |
| H | 6.49205000 | -0.90601500 | -1.88327000 |
| H | 1.62699800 | -4.28272600 | -1.08706600 |
| H | 2.66801200 | -3.74705900 | 0.23713300 |
| H | 1.11497300 | -2.94676900 | -0.06158600 |
| H | 0.89173700 | -1.45920900 | -2.26964100 |
| H | 2.31482200 | -1.29810400 | -3.30712700 |
| H | 1.44647200 | -2.83768700 | -3.22446000 |



Optimized Structure of *Z,Z*-**4**-**TS**.

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- Thermochemistry -

---

(1 imaginary frequency = -303.24 Hz)

Zero-point correction= 0.723846 (Hartree/Particle)

Thermal correction to Energy= 0.763874

Thermal correction to Enthalpy= 0.764818

Thermal correction to Gibbs Free Energy= 0.650166

Sum of electronic and zero-point Energies= -1861.840949

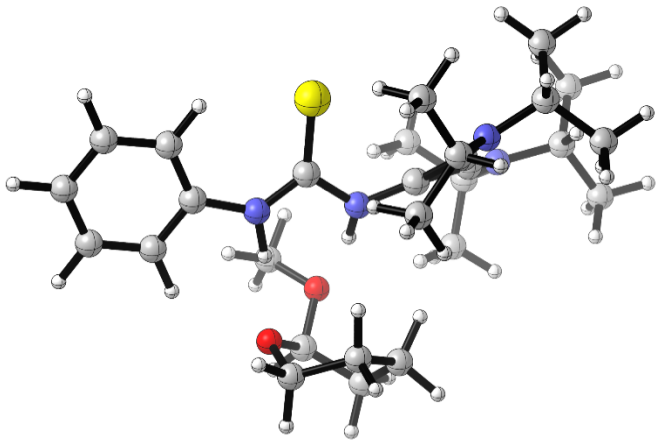
Sum of electronic and thermal Energies= -1861.800921

Sum of electronic and thermal Enthalpies= -1861.799977

Sum of electronic and thermal Free Energies= -1861.914630

| | | | |
|---|---|---|---|
| C | -1.03874800 | 0.63428600 | -0.82301800 |
| S | -0.58966100 | 2.05376400 | -1.56504700 |
| N | -2.27463700 | 0.09674500 | -0.73579700 |
| H | -2.26619900 | -0.87776400 | -0.37925000 |
| N | -0.11993600 | -0.21790500 | -0.21854500 |
| H | -0.48773500 | -1.20829100 | -0.02925600 |
| C | -3.68981100 | -2.04946500 | 1.90988600 |
| C | -2.58791800 | -2.27772000 | 2.80384100 |
| C | -2.15130600 | -1.06712200 | 3.61653400 |
| C | -2.29548500 | 0.18563700 | 2.75134900 |
| C | -3.70964000 | 0.31804400 | 2.23324000 |
| H | -2.75644100 | -0.97593100 | 4.52355900 |
| H | -1.11569100 | -1.19444200 | 3.93343200 |
| H | -2.06549300 | 1.08976600 | 3.31936100 |
| H | -1.60108500 | 0.14390600 | 1.90920000 |
| H | -4.43761600 | 0.52237700 | 3.01960200 |
| H | -3.81654100 | 1.04807400 | 1.43381400 |
| O | -4.19004600 | -0.93184800 | 1.60687300 |
| H | -4.14334000 | -2.87466000 | 1.36394000 |
| H | -2.71018700 | -3.21673100 | 3.34588800 |
| O | -1.54265800 | -2.32556400 | 0.26082900 |
| H | -1.85486800 | -2.50234000 | 1.94030300 |
| C | -1.69613700 | -3.38421200 | -0.63505900 |
| H | -2.43504700 | -4.12303400 | -0.27868200 |
| H | -2.04278000 | -3.04086300 | -1.62462200 |
| H | -0.75952400 | -3.93523500 | -0.80251000 |
| C | -3.50010400 | 0.55129300 | -1.26803500 |
| C | -3.87146500 | 1.89402500 | -1.30063300 |
| C | -4.40177000 | -0.42642400 | -1.69160000 |
| C | -5.13253800 | 2.24373300 | -1.76836100 |
| H | -3.17526000 | 2.65639900 | -0.98235200 |
| C | -5.65950500 | -0.06617200 | -2.14940500 |
| H | -4.10342300 | -1.47004100 | -1.67110700 |
| C | -6.02990200 | 1.27297800 | -2.19247900 |
| H | -7.00892400 | 1.55666400 | -2.55926400 |
| H | -5.41019000 | 3.29076700 | -1.80292800 |
| H | -6.34847400 | -0.83285700 | -2.48393100 |
| C | 1.19811500 | 0.05922900 | -0.14336100 |
| C | 2.24808000 | 0.89469500 | 0.16124300 |
| C | 2.47175600 | -0.42638100 | -0.28810300 |
| N | 2.71518700 | 2.05128400 | 0.58523600 |
| N | 3.23389900 | -1.44353300 | -0.63469600 |

| | | | |
|---|---|---|---|
| C | 4.14624700 | 2.39648400 | 0.45121700 |
| C | 1.89339100 | 3.00992400 | 1.36684400 |
| C | 4.70416200 | -1.40265300 | -0.52027100 |
| C | 2.58036200 | -2.69998800 | -1.07462600 |
| H | 4.18845100 | 3.46760200 | 0.66050300 |
| C | 4.62946800 | 2.22279700 | -0.98482900 |
| C | 4.98249800 | 1.69578000 | 1.52182000 |
| C | 0.67509900 | 2.35658000 | 2.00484600 |
| H | 2.55911500 | 3.32174900 | 2.17998300 |
| C | 1.52726700 | 4.23757600 | 0.53927300 |
| H | 4.93851800 | -0.40179800 | -0.16629400 |
| C | 5.21649200 | -2.39624600 | 0.51838600 |
| C | 5.36690500 | -1.57740300 | -1.88403400 |
| H | 3.40117300 | -3.34530600 | -1.39126000 |
| C | 1.86651400 | -3.38554800 | 0.08862400 |
| C | 1.67793100 | -2.47026800 | -2.28237400 |
| H | 4.54949000 | 1.19489400 | -1.34070400 |
| H | 4.03745000 | 2.85003200 | -1.65418500 |
| H | 5.67633300 | 2.52221800 | -1.06466100 |
| H | 4.67399800 | 2.02061300 | 2.51842500 |
| H | 4.87403000 | 0.61018100 | 1.48431300 |
| H | 6.04039200 | 1.93800000 | 1.40090100 |
| H | -0.07859600 | 2.11046400 | 1.25620900 |
| H | 0.94687800 | 1.45412500 | 2.55938200 |
| H | 0.23072500 | 3.06548800 | 2.70652500 |
| H | 2.41121400 | 4.69908900 | 0.09293100 |
| H | 0.83743500 | 3.96109900 | -0.25798200 |
| H | 1.04958800 | 4.98410000 | 1.17828200 |
| H | 5.02975900 | -3.43087400 | 0.21931700 |
| H | 6.29543500 | -2.27794200 | 0.63837800 |
| H | 4.74353900 | -2.22703600 | 1.48873400 |
| H | 5.20525000 | -2.57717500 | -2.29408200 |
| H | 4.98581700 | -0.84705700 | -2.60127900 |
| H | 6.44514500 | -1.43381700 | -1.78753000 |
| H | 1.52966300 | -4.37745300 | -0.22072000 |
| H | 2.53935600 | -3.50707200 | 0.93981200 |
| H | 0.98242200 | -2.82926500 | 0.41309900 |
| H | 0.81008700 | -1.85561200 | -2.03311500 |
| H | 2.22592100 | -1.98352800 | -3.09161900 |
| H | 1.30509300 | -3.42932900 | -2.64830400 |



Optimized Structure of Z,Z-**4-INT3**.

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- Thermochemistry -

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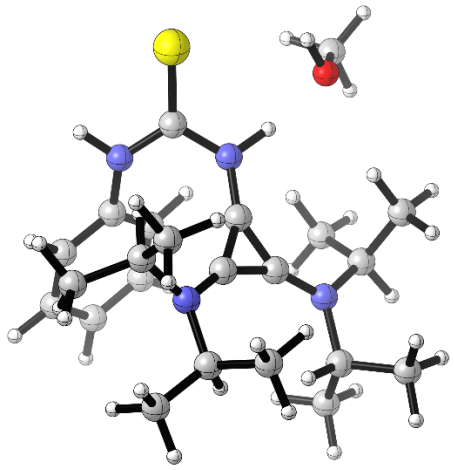
(0 imaginary frequencies)

Zero-point correction= 0.731375 (Hartree/Particle)
Thermal correction to Energy= 0.771006
Thermal correction to Enthalpy= 0.771951
Thermal correction to Gibbs Free Energy= 0.658826
Sum of electronic and zero-point Energies= -1861.908964
Sum of electronic and thermal Energies= -1861.869333
Sum of electronic and thermal Enthalpies= -1861.868389
Sum of electronic and thermal Free Energies= -1861.981514

| | | | |
|---|---|---|---|
| C | -1.26281000 | 0.87192900 | -0.58405400 |
| S | -0.72057700 | 2.20617800 | -1.41042800 |
| N | -2.52067400 | 0.51367700 | -0.27902800 |
| H | -2.61206800 | -0.33679400 | 0.27717600 |
| N | -0.34986700 | -0.09165900 | -0.11708400 |
| H | -0.64901000 | -1.07216000 | -0.14663700 |
| C | -2.22449500 | -3.06902800 | 0.82971900 |
| C | -1.23625600 | -3.54302300 | 1.88194800 |
| C | -0.47786100 | -2.38475900 | 2.53752700 |
| C | -1.43977900 | -1.25971900 | 2.98790900 |
| C | -2.88203800 | -1.59928200 | 2.64349100 |
| H | 0.09127500 | -2.77269900 | 3.38393000 |
| H | 0.26057100 | -1.98550000 | 1.83634500 |
| H | -1.36584600 | -1.07936100 | 4.06296200 |
| H | -1.17932500 | -0.32364300 | 2.48818200 |
| H | -3.27417900 | -2.40599600 | 3.27138600 |
| H | -3.53780600 | -0.73712700 | 2.76718100 |
| O | -3.00107600 | -1.96268200 | 1.26372700 |
| H | -2.91540900 | -3.87078700 | 0.54314000 |
| H | -1.78977800 | -4.10247800 | 2.64075600 |
| O | -1.51461200 | -2.66807500 | -0.31870100 |
| H | -0.55401300 | -4.25024900 | 1.40710900 |
| C | -2.28153900 | -2.65779800 | -1.52154200 |
| H | -2.63241800 | -3.66696500 | -1.75489600 |
| H | -3.13456700 | -1.97734400 | -1.44905000 |
| H | -1.61520600 | -2.31591200 | -2.31270100 |
| C | -3.78040400 | 1.03596200 | -0.67117700 |
| C | -3.97815500 | 2.26491600 | -1.29489100 |
| C | -4.88027700 | 0.22597800 | -0.36576100 |
| C | -5.27197400 | 2.66146200 | -1.61639000 |
| H | -3.14098700 | 2.90365500 | -1.52539700 |
| C | -6.16175700 | 0.63872400 | -0.68899000 |
| H | -4.72354500 | -0.72643200 | 0.13028500 |
| C | -6.36465300 | 1.86076300 | -1.32002800 |
| H | -7.36648200 | 2.18521200 | -1.57389900 |
| H | -5.41804600 | 3.61854200 | -2.10310600 |
| H | -7.00405300 | 0.00183600 | -0.44581800 |
| C | 0.97959800 | 0.16620100 | -0.05939500 |
| C | 2.00978400 | 0.98066500 | 0.34489000 |
| C | 2.25610600 | -0.21742200 | -0.37091700 |
| N | 2.43710000 | 2.06938800 | 0.94061200 |
| N | 3.04107600 | -1.09056500 | -0.96532100 |

| | | | |
|---|---|---|---|
| C | 3.83556100 | 2.53490800 | 0.80754100 |
| C | 1.57676400 | 2.86943400 | 1.85282900 |
| C | 4.51225500 | -1.02535000 | -0.85716000 |
| C | 2.42215900 | -2.21163600 | -1.71295900 |
| H | 3.81392900 | 3.55822800 | 1.18783900 |
| C | 4.26018100 | 2.62514300 | -0.65357500 |
| C | 4.76815700 | 1.73587600 | 1.71543400 |
| C | 0.42537100 | 2.06200200 | 2.43324000 |
| H | 2.24590900 | 3.12549600 | 2.68170300 |
| C | 1.10539100 | 4.15734900 | 1.18654200 |
| H | 4.71753300 | -0.13114100 | -0.27284500 |
| C | 5.06812200 | -2.22230100 | -0.09168300 |
| C | 5.16190200 | -0.84631700 | -2.22696200 |
| H | 3.25744300 | -2.71355900 | -2.20311100 |
| C | 1.75905200 | -3.21186200 | -0.77041200 |
| C | 1.48331000 | -1.69791600 | -2.79962000 |
| H | 4.27320500 | 1.65597300 | -1.15293700 |
| H | 3.57636100 | 3.27426700 | -1.20413900 |
| H | 5.26519800 | 3.04612200 | -0.72105400 |
| H | 4.47503200 | 1.85273600 | 2.76138200 |
| H | 4.75307900 | 0.66809200 | 1.48770000 |
| H | 5.79514000 | 2.09205300 | 1.61153200 |
| H | -0.34842900 | 1.86835900 | 1.68919000 |
| H | 0.77087300 | 1.11367900 | 2.85302000 |
| H | -0.03427300 | 2.63810700 | 3.23810400 |
| H | 1.94100200 | 4.72848700 | 0.77524800 |
| H | 0.40677900 | 3.93216800 | 0.37975400 |
| H | 0.60069500 | 4.78840100 | 1.92155100 |
| H | 4.90666200 | -3.15930200 | -0.63093900 |
| H | 6.14493700 | -2.10282700 | 0.04420300 |
| H | 4.60537300 | -2.30640400 | 0.89440700 |
| H | 5.04815700 | -1.73317700 | -2.85498500 |
| H | 4.73400600 | 0.00730100 | -2.75699000 |
| H | 6.23245400 | -0.67151700 | -2.10185700 |
| H | 1.42452500 | -4.08495800 | -1.33535200 |
| H | 2.45676100 | -3.54846400 | -0.00130200 |
| H | 0.87575800 | -2.78893200 | -0.28903900 |
| H | 0.61880600 | -1.17786000 | -2.37892700 |
| H | 2.00090100 | -1.00743800 | -3.46798600 |
| H | 1.11407600 | -2.53777100 | -3.39206300 |

*E,E*-Conformation



Optimized Structure of *E,E*-**4**-An-**INT1**.

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- Thermochemistry -

---

(0 imaginary frequencies)

Zero-point correction= 0.602894 (Hartree/Particle)

Thermal correction to Energy= 0.636314

Thermal correction to Enthalpy= 0.637258

Thermal correction to Gibbs Free Energy= 0.537826

Sum of electronic and zero-point Energies= -1591.464198

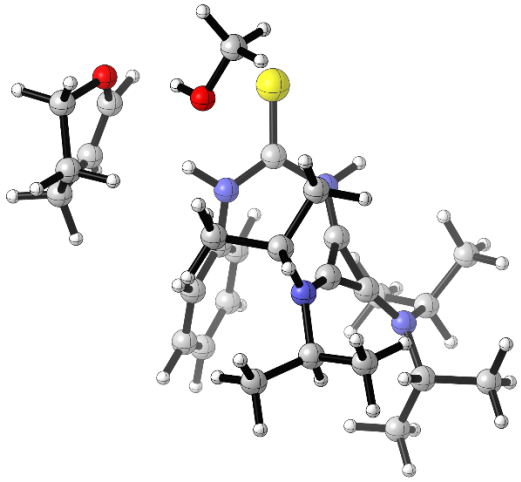
Sum of electronic and thermal Energies= -1591.430778

Sum of electronic and thermal Enthalpies= -1591.429834

Sum of electronic and thermal Free Energies= -1591.529266

| | | | |
|---|---|---|---|
| C | -1.70543000 | 2.14334800 | -0.50602100 |
| S | -2.81206300 | 2.97260100 | -1.41891200 |
| N | -0.81954300 | 2.77203700 | 0.30901300 |
| H | -0.85067700 | 3.77728200 | 0.21223000 |
| N | -1.64481500 | 0.75966400 | -0.53741500 |
| C | -0.21201300 | 2.28230300 | 1.50170700 |
| C | 1.00870000 | 2.83030900 | 1.88298900 |
| C | -0.82810900 | 1.33091200 | 2.31128700 |
| C | 1.63171500 | 2.40014300 | 3.04611900 |
| H | 1.46052900 | 3.60261500 | 1.27166900 |
| C | -0.18955800 | 0.89268200 | 3.46331000 |
| H | -1.80727800 | 0.94861200 | 2.05486100 |
| C | 1.04392100 | 1.41622700 | 3.83160600 |
| H | 1.53056900 | 1.07918500 | 4.73863800 |
| H | -2.48346200 | 0.29438500 | -0.92728300 |
| C | -5.04871500 | -0.27340500 | -0.73967900 |
| H | -5.14040800 | 0.66378900 | -0.18185500 |

| | | | |
|---|---|---|---|
| H | -4.84548300 | -1.08906500 | -0.04526000 |
| H | -5.98617100 | -0.48226200 | -1.26002100 |
| O | -3.95549100 | -0.22799900 | -1.65437000 |
| H | -4.08651300 | 0.51402800 | -2.25335400 |
| C | -0.51993000 | 0.01666200 | -0.40903100 |
| C | 0.83622200 | -0.14865600 | -0.52650200 |
| C | 0.01082400 | -1.21859300 | -0.13065000 |
| N | 2.02860800 | 0.32995500 | -0.82605000 |
| N | -0.17436100 | -2.47215300 | 0.21359600 |
| C | 3.14149300 | -0.65867900 | -0.82936700 |
| C | 2.04498700 | 1.64668800 | -1.52533700 |
| C | 0.97030800 | -3.39417300 | 0.37478700 |
| C | -1.54519500 | -2.95067400 | 0.51595600 |
| C | 3.04910600 | -1.61346000 | -2.02201700 |
| H | 2.99121400 | -1.22701100 | 0.09297400 |
| C | 4.52547500 | -0.03505300 | -0.72477200 |
| C | 2.19528100 | 1.49251900 | -3.03637000 |
| H | 1.83716700 | -2.84272000 | 0.01451600 |
| C | 1.19482700 | -3.72056700 | 1.84883400 |
| C | 0.82093400 | -4.63496000 | -0.49895400 |
| H | -1.40435600 | -3.93874800 | 0.95605300 |
| C | -2.23156700 | -2.07372400 | 1.55870200 |
| C | -2.36614300 | -3.10334800 | -0.76063700 |
| H | 2.04951300 | -2.04480800 | -2.12383700 |
| H | 3.29249900 | -1.10684700 | -2.95695000 |
| H | 3.75844400 | -2.43455500 | -1.89238400 |
| H | 4.80591200 | 0.49706400 | -1.63513500 |
| H | 4.60485900 | 0.64209700 | 0.12528900 |
| H | 5.25008800 | -0.83950000 | -0.58445200 |
| H | 3.19525400 | 1.14629900 | -3.30734600 |
| H | 1.45929900 | 0.79436100 | -3.44149400 |
| H | 2.04308400 | 2.46235500 | -3.51475100 |
| H | 0.35666600 | -4.27956200 | 2.27265300 |
| H | 2.08950000 | -4.33648400 | 1.96047900 |
| H | 1.33069200 | -2.80622600 | 2.43129800 |
| H | -0.01776300 | -5.26109400 | -0.18451500 |
| H | 0.67633300 | -4.36346500 | -1.54684500 |
| H | 1.72606300 | -5.24102100 | -0.42496100 |
| H | -3.15722900 | -2.55209900 | 1.88490400 |
| H | -1.59298500 | -1.92807400 | 2.43255800 |
| H | -2.49324100 | -1.09510300 | 1.14909200 |
| H | -2.55574700 | -2.14065700 | -1.24283300 |
| H | -1.86114100 | -3.75660300 | -1.47424900 |
| H | -3.33651100 | -3.54699300 | -0.52578500 |
| H | 2.57729400 | 2.84023700 | 3.33988000 |
| H | -0.67685600 | 0.15715500 | 4.09297400 |
| H | 1.05023400 | 2.04954500 | -1.32712400 |
| C | 3.04755100 | 2.64614300 | -0.94784200 |
| H | 4.04370600 | 2.53211800 | -1.37406200 |
| H | 2.70804700 | 3.65698600 | -1.18647900 |
| H | 3.11847400 | 2.55477900 | 0.13573900 |



Optimized Structure of *E,E*-**4**-An-**INT**$_2$.

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- Thermochemistry -

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(0 imaginary frequencies)

Zero-point correction= 0.727990 (Hartree/Particle)

Thermal correction to Energy= 0.769375

Thermal correction to Enthalpy= 0.770319

Thermal correction to Gibbs Free Energy= 0.650709

Sum of electronic and zero-point Energies= -1861.880770

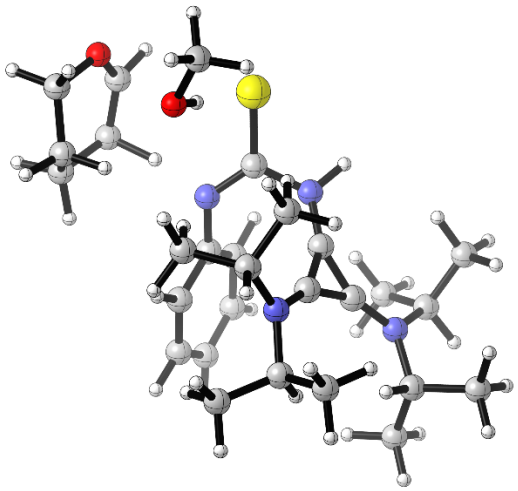
Sum of electronic and thermal Energies= -1861.839385

Sum of electronic and thermal Enthalpies= -1861.838441

Sum of electronic and thermal Free Energies= -1861.958051

| | | | |
|---|---|---|---|
| C | -0.99664100 | -1.11551400 | -1.52635600 |
| S | -2.03686700 | -1.40693500 | -2.77055800 |
| N | 0.37244700 | -0.98142500 | -1.77052700 |
| H | 0.67887500 | -1.30420100 | -2.67625300 |
| N | -1.34853300 | -0.99699500 | -0.22212500 |
| C | -0.57356700 | -1.50528500 | 0.87058200 |
| C | 0.02437900 | -2.75883500 | 0.77878100 |
| C | -0.47540900 | -0.77046100 | 2.04755100 |
| C | 0.74739500 | -3.25944900 | 1.85258800 |
| H | -0.09175400 | -3.34166400 | -0.12819800 |
| C | 0.23981200 | -1.28242600 | 3.12295400 |
| H | -0.96056000 | 0.19371000 | 2.11848500 |
| C | 0.86084400 | -2.52206500 | 3.02526200 |
| H | 1.41274400 | -2.92177200 | 3.86755700 |
| H | -2.35560200 | -1.02436300 | -0.06787100 |
| C | -4.66373300 | -1.50926400 | -0.02070200 |
| C | -4.20580900 | -1.71162800 | 1.21641600 |
| C | -4.30783200 | -0.66538300 | 2.29176300 |
| C | -4.67239200 | 0.68437000 | 1.66965200 |
| C | -5.73808100 | 0.49235400 | 0.60317600 |
| H | -5.06007100 | -0.96319200 | 3.03063200 |
| H | -3.36040000 | -0.59442600 | 2.83546600 |
| H | -5.03471400 | 1.38651600 | 2.42382500 |
| H | -3.79749600 | 1.13784900 | 1.19511700 |
| H | -6.64502800 | 0.04974000 | 1.02892200 |
| H | -5.99332500 | 1.42893900 | 0.11032900 |

| | | | |
|---|---|---|---|
| O | -5.27725700 | -0.37303900 | -0.44520300 |
| H | -4.56956100 | -2.23110900 | -0.82274200 |
| H | -3.76215900 | -2.67438300 | 1.44249500 |
| C | -3.76269700 | 1.99274100 | -2.86622600 |
| H | -4.83027300 | 2.17480200 | -3.03473800 |
| H | -3.40719100 | 1.26625400 | -3.60665900 |
| H | -3.23227600 | 2.93367400 | -3.02465000 |
| O | -3.49857700 | 1.56821300 | -1.54389400 |
| H | -4.03131700 | 0.78094000 | -1.37893800 |
| H | 0.30491600 | -0.71397000 | 4.04353900 |
| H | 1.20698200 | -4.23806800 | 1.77789700 |
| C | 1.21312700 | -0.21092600 | -1.03412100 |
| C | 1.44204500 | 0.89453500 | -0.25219000 |
| C | 2.48574900 | -0.00333000 | -0.56587200 |
| N | 1.04880900 | 1.99079800 | 0.35349700 |
| N | 3.74464000 | -0.36653800 | -0.51467200 |
| C | 1.98626400 | 2.64188300 | 1.29860500 |
| C | -0.14985800 | 2.74481500 | -0.11853000 |
| C | 4.75201700 | 0.47764700 | 0.16351700 |
| C | 4.15332600 | -1.65156800 | -1.13139100 |
| C | 2.79256800 | 3.74121000 | 0.61001900 |
| H | 2.66418800 | 1.84715100 | 1.61873200 |
| C | 1.26855600 | 3.13752900 | 2.54850700 |
| C | -1.41320700 | 2.38568600 | 0.64911600 |
| H | 0.10003500 | 3.78893600 | 0.08459000 |
| C | -0.34588100 | 2.60155100 | -1.62370200 |
| H | 4.23440000 | 1.40608800 | 0.40340800 |
| C | 5.20953500 | -0.17575600 | 1.46369900 |
| C | 5.90673800 | 0.83142900 | -0.76857800 |
| H | 5.19723000 | -1.78468400 | -0.84436500 |
| C | 3.35719600 | -2.81897400 | -0.56213700 |
| C | 4.08277500 | -1.56964200 | -2.65318500 |
| H | 3.29237500 | 3.36487500 | -0.28666100 |
| H | 2.15700800 | 4.57932700 | 0.31449000 |
| H | 3.55342700 | 4.12937900 | 1.29082700 |
| H | 0.56942200 | 3.94641600 | 2.32567200 |
| H | 0.72421700 | 2.32474000 | 3.03301800 |
| H | 2.00572100 | 3.52444900 | 3.25474100 |
| H | -1.69696300 | 1.35820500 | 0.42636700 |
| H | -1.28790100 | 2.51701000 | 1.72519900 |
| H | -2.23703300 | 3.01410100 | 0.30833700 |
| H | 0.58423200 | 2.78417500 | -2.16795100 |
| H | -0.75045200 | 1.62319700 | -1.89072400 |
| H | -1.08290100 | 3.33573200 | -1.95112500 |
| H | 5.73283600 | -1.11717800 | 1.27595800 |
| H | 5.89942800 | 0.48470900 | 1.99290100 |
| H | 4.35797300 | -0.38238700 | 2.11675500 |
| H | 5.54215800 | 1.30452900 | -1.68275600 |
| H | 6.57501700 | 1.53246100 | -0.26486400 |
| H | 6.50016000 | -0.04435900 | -1.04198900 |
| H | 3.75991900 | -3.75894200 | -0.94462000 |
| H | 3.41112000 | -2.83450000 | 0.52814900 |
| H | 2.30424700 | -2.76449300 | -0.84906900 |
| H | 3.05439200 | -1.42067000 | -2.99536800 |
| H | 4.69067300 | -0.74730400 | -3.03391000 |
| H | 4.44496300 | -2.49902700 | -3.09665200 |



Optimized Structure of *E,E*-**4**-An-**TS**$_1$.

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- Thermochemistry -

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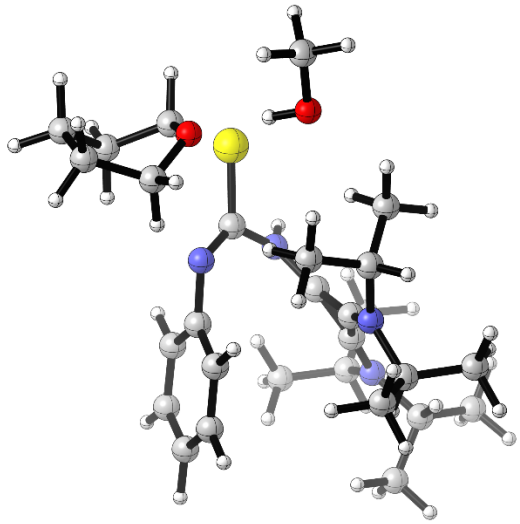
(1 imaginary frequency = -506.37 Hz)
Zero-point correction= 0.722648 (Hartree/Particle)
Thermal correction to Energy= 0.763218
Thermal correction to Enthalpy= 0.764162
Thermal correction to Gibbs Free Energy= 0.648624
Sum of electronic and zero-point Energies= -1861.852291
Sum of electronic and thermal Energies= -1861.811721
Sum of electronic and thermal Enthalpies= -1861.810777
Sum of electronic and thermal Free Energies= -1861.926315

| | | | |
|---|---|---|---|
| C | -1.17845900 | -0.87227500 | -1.24766900 |
| S | -2.36865700 | -0.66931800 | -2.44555200 |
| N | 0.16893600 | -0.81907900 | -1.68713600 |
| H | 0.29593500 | -0.93177100 | -2.68322100 |
| N | -1.42661500 | -1.07680100 | 0.01709700 |
| C | -0.47893800 | -1.60310100 | 0.92723100 |
| C | 0.15970200 | -2.81928600 | 0.67154100 |
| C | -0.25444000 | -0.96733900 | 2.14959600 |
| C | 1.03760900 | -3.36028500 | 1.60061100 |
| H | -0.04067200 | -3.33606300 | -0.26042300 |
| C | 0.63174500 | -1.50858700 | 3.07164100 |
| H | -0.77620900 | -0.04610000 | 2.37090100 |
| C | 1.28865300 | -2.70305900 | 2.79949900 |
| H | 1.97002300 | -3.13048200 | 3.52539200 |
| H | -2.83048400 | -1.55225100 | 0.25078000 |
| C | -4.70948600 | -1.69662500 | -0.49096500 |
| C | -3.92840500 | -1.99327800 | 0.64043300 |
| C | -4.21947900 | -1.20030500 | 1.90366900 |
| C | -4.57815700 | 0.22654100 | 1.49298000 |
| C | -5.71017800 | 0.23494400 | 0.49000600 |
| H | -5.03555800 | -1.65871300 | 2.47073500 |
| H | -3.33756100 | -1.20192000 | 2.54765900 |
| H | -4.88579200 | 0.82623600 | 2.35257200 |

| | | | |
|---|---|---|---|
| H | -3.71464400 | 0.71884900 | 1.04130800 |
| H | -6.66074300 | -0.08328200 | 0.92238900 |
| H | -5.81511700 | 1.20280300 | 0.00884100 |
| O | -5.47876800 | -0.68371100 | -0.62990800 |
| H | -4.67163100 | -2.31223600 | -1.38403300 |
| H | -3.70878300 | -3.05566700 | 0.73967700 |
| C | -4.07921300 | 2.81533500 | -2.22066500 |
| H | -4.80093600 | 2.29647700 | -2.86204700 |
| H | -3.21547600 | 3.10268100 | -2.83329000 |
| H | -4.54719700 | 3.72301400 | -1.83711000 |
| O | -3.69850400 | 2.02900500 | -1.10785300 |
| H | -3.29940000 | 1.21678600 | -1.45365800 |
| H | 0.79566700 | -1.00306600 | 4.01695500 |
| H | 1.51983400 | -4.30827200 | 1.39012200 |
| C | 1.11612100 | -0.14342900 | -0.99371700 |
| C | 1.44710800 | 0.86893100 | -0.12668800 |
| C | 2.43690300 | 0.01570100 | -0.65266900 |
| N | 1.12386300 | 1.89872700 | 0.62507300 |
| N | 3.69280200 | -0.34021700 | -0.78416600 |
| C | 2.12226000 | 2.41702500 | 1.58538500 |
| C | -0.09627600 | 2.70248600 | 0.32862500 |
| C | 4.76864200 | 0.43893500 | -0.13687700 |
| C | 4.02628100 | -1.53251500 | -1.59880500 |
| C | 2.87184100 | 3.62173100 | 1.02078600 |
| H | 2.82827900 | 1.59595400 | 1.73305700 |
| C | 1.48579400 | 2.70147100 | 2.94128200 |
| C | -1.32966900 | 2.20974300 | 1.07028900 |
| H | 0.15073000 | 3.70206200 | 0.69373400 |
| C | -0.34124300 | 2.81222900 | -1.17293200 |
| H | 4.27355300 | 1.31028200 | 0.29257200 |
| C | 5.40525100 | -0.36196100 | 0.99476200 |
| C | 5.78408700 | 0.94782100 | -1.15565100 |
| H | 5.09669100 | -1.68603700 | -1.45403100 |
| C | 3.29755400 | -2.77099700 | -1.09308300 |
| C | 3.77272100 | -1.26469600 | -3.07943900 |
| H | 3.31849600 | 3.39202700 | 0.04962000 |
| H | 2.21043000 | 4.48201200 | 0.89256200 |
| H | 3.66983600 | 3.92035700 | 1.70427500 |
| H | 0.75984800 | 3.51631000 | 2.88862900 |
| H | 0.98615300 | 1.81093500 | 3.32735800 |
| H | 2.26079900 | 2.99668300 | 3.65132200 |
| H | -1.58039300 | 1.19840500 | 0.74762900 |
| H | -1.17935200 | 2.21797300 | 2.15158200 |
| H | -2.18091500 | 2.84495300 | 0.82216100 |
| H | 0.55938900 | 3.13857300 | -1.69913200 |
| H | -0.68967600 | 1.87047900 | -1.60381400 |
| H | -1.12956100 | 3.54525500 | -1.34950700 |
| H | 5.91875900 | -1.24997800 | 0.61686000 |
| H | 6.14482800 | 0.24919700 | 1.51620600 |
| H | 4.64955500 | -0.68348000 | 1.71548500 |
| H | 5.29495100 | 1.52796300 | -1.94112100 |
| H | 6.50883200 | 1.59295700 | -0.65505000 |
| H | 6.34093800 | 0.13174400 | -1.62243800 |
| H | 3.65391700 | -3.65260400 | -1.62977000 |
| H | 3.47068600 | -2.91811900 | -0.02547600 |
| H | 2.21972200 | -2.69126200 | -1.25476100 |

| | | | |
|---|---|---|---|
| H | 2.70860600 | -1.09769200 | -3.27105300 |
| H | 4.32490600 | -0.38924100 | -3.42524400 |
| H | 4.08255800 | -2.12534400 | -3.67540800 |



Optimized Structure of *E,E*-**4**-An-**INT**$_3$.

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- Thermochemistry -

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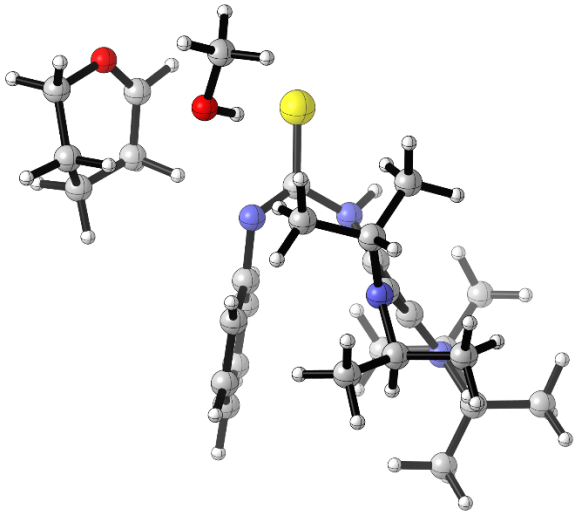
(0 imaginary frequencies)

Zero-point correction= 0.728170 (Hartree/Particle)
Thermal correction to Energy= 0.768994
Thermal correction to Enthalpy= 0.769939
Thermal correction to Gibbs Free Energy= 0.653515
Sum of electronic and zero-point Energies= -1861.878500
Sum of electronic and thermal Energies= -1861.837676
Sum of electronic and thermal Enthalpies= -1861.836732
Sum of electronic and thermal Free Energies= -1861.953155

| | | | |
|---|---|---|---|
| C | -1.15184100 | -1.06528700 | -0.90962800 |
| S | -2.42445100 | -0.76569000 | -2.08346600 |
| N | 0.12775800 | -0.99968500 | -1.52077000 |
| H | 0.27561300 | -1.41320900 | -2.42855900 |
| N | -1.33105800 | -1.24250500 | 0.32907500 |
| C | -0.29108200 | -1.66473500 | 1.18817900 |
| C | 0.31947200 | -2.90495500 | 0.99598200 |
| C | 0.06448600 | -0.89193500 | 2.29357200 |
| C | 1.29320200 | -3.34787300 | 1.88046600 |
| H | 0.01122000 | -3.52677200 | 0.16273600 |
| C | 1.05579900 | -1.33194500 | 3.16023900 |
| H | -0.43962200 | 0.04843700 | 2.46810200 |
| C | 1.67809600 | -2.55863400 | 2.95742000 |
| H | 2.43438700 | -2.90887300 | 3.64952700 |
| H | -3.41457300 | -2.55253500 | 0.14854500 |
| C | -4.03195500 | -0.94238200 | -1.16128700 |
| C | -4.25694700 | -2.29470200 | -0.49484500 |
| C | -5.54963600 | -2.21169700 | 0.32301900 |

| | | | |
|---|---|---|---|
| C | -5.45784500 | -1.10724400 | 1.39773200 |
| C | -4.31383600 | -0.14551900 | 1.09074100 |
| H | -6.38097500 | -1.99987500 | -0.35603100 |
| H | -5.75850500 | -3.18091700 | 0.77815800 |
| H | -6.40230800 | -0.56232500 | 1.45279700 |
| H | -5.28024200 | -1.54035800 | 2.38583800 |
| H | -4.45539300 | 0.82393200 | 1.56767900 |
| H | -3.35146800 | -0.55375300 | 1.40625600 |
| O | -4.25489700 | 0.14658600 | -0.31488800 |
| H | -4.72231500 | -0.83381400 | -2.00435300 |
| H | -4.33048500 | -3.05648800 | -1.27291500 |
| C | -5.05365100 | 3.45670200 | -1.11621500 |
| H | -5.79290500 | 3.26819700 | -0.32771100 |
| H | -5.45440600 | 3.08127700 | -2.06593100 |
| H | -4.92002900 | 4.53512200 | -1.20755600 |
| O | -3.79430100 | 2.89402700 | -0.81205900 |
| H | -3.90216200 | 1.93651500 | -0.74464500 |
| H | 1.32514700 | -0.72264400 | 4.01592600 |
| H | 1.74953700 | -4.31935400 | 1.72809900 |
| C | 1.09423600 | -0.22996600 | -0.96918300 |
| C | 1.41771000 | 0.86906500 | -0.21038800 |
| C | 2.41900300 | 0.01365300 | -0.71148100 |
| N | 1.08494200 | 1.93202800 | 0.48559100 |
| N | 3.68262800 | -0.30148500 | -0.87355800 |
| C | 2.11200300 | 2.56330600 | 1.34389700 |
| C | -0.20375600 | 2.64457500 | 0.23268300 |
| C | 4.74950100 | 0.57866600 | -0.35117900 |
| C | 4.03147400 | -1.56335200 | -1.56600300 |
| C | 2.75496400 | 3.76313700 | 0.65292800 |
| H | 2.86931300 | 1.79030600 | 1.49788600 |
| C | 1.54683300 | 2.90685600 | 2.71771200 |
| C | -1.36136100 | 2.12088300 | 1.07147400 |
| H | -0.00118400 | 3.67263400 | 0.54062400 |
| C | -0.53768800 | 2.67368600 | -1.25363500 |
| H | 4.23866600 | 1.48268500 | -0.01831200 |
| C | 5.43209700 | -0.06600100 | 0.85132200 |
| C | 5.72712200 | 0.98738200 | -1.44865300 |
| H | 5.11157300 | -1.66308700 | -1.45025900 |
| C | 3.37461400 | -2.76333500 | -0.89586800 |
| C | 3.71244000 | -1.46918100 | -3.05515700 |
| H | 3.15803200 | 3.48868800 | -0.32566000 |
| H | 2.03475200 | 4.57152200 | 0.50563700 |
| H | 3.57124300 | 4.15498500 | 1.26376000 |
| H | 0.78076200 | 3.68360100 | 2.66289900 |
| H | 1.11557900 | 2.02271300 | 3.19085400 |
| H | 2.34998100 | 3.28075300 | 3.35577300 |
| H | -1.60441700 | 1.09132100 | 0.80351500 |
| H | -1.13993100 | 2.16946700 | 2.13943100 |
| H | -2.24478000 | 2.72737400 | 0.86310600 |
| H | 0.26733800 | 3.13508000 | -1.83119200 |
| H | -0.72695300 | 1.67258900 | -1.64761600 |
| H | -1.46278400 | 3.23375000 | -1.39880900 |
| H | 5.95542500 | -0.98354900 | 0.56920400 |
| H | 6.17053700 | 0.61817100 | 1.27440000 |
| H | 4.70163300 | -0.31328400 | 1.62555100 |
| H | 5.20464400 | 1.45227400 | -2.28735000 |

| | | | |
|---|---|---|---|
| H | 6.43985300 | 1.71097200 | -1.04811000 |
| H | 6.30305600 | 0.13827400 | -1.82463000 |
| H | 3.74944600 | -3.68609800 | -1.34331900 |
| H | 3.58931500 | -2.78115800 | 0.17411800 |
| H | 2.28855700 | -2.74744800 | -1.01822700 |
| H | 2.63788800 | -1.34034500 | -3.21953800 |
| H | 4.22866600 | -0.62710100 | -3.51906600 |
| H | 4.01744500 | -2.38499400 | -3.56503700 |



Optimized Structure of *E,E*-**4**-An-**TS**$_2$.

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- Thermochemistry -

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(1 imaginary frequency = - 59.09 Hz)

Zero-point correction= 0.724296 (Hartree/Particle)

Thermal correction to Energy= 0.765235

Thermal correction to Enthalpy= 0.766179

Thermal correction to Gibbs Free Energy= 0.648126

Sum of electronic and zero-point Energies= -1861.848532

Sum of electronic and thermal Energies= -1861.807593

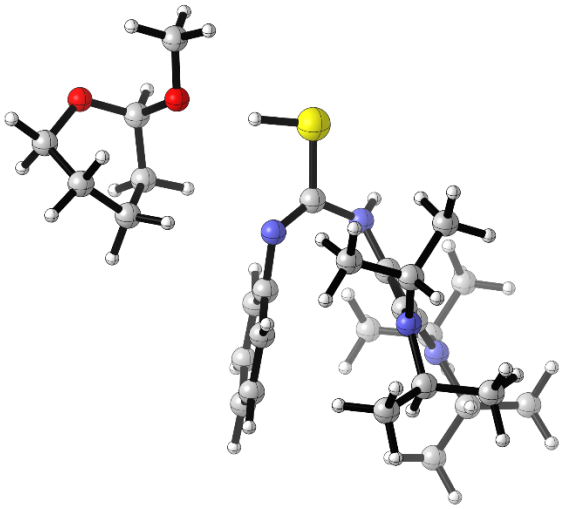
Sum of electronic and thermal Enthalpies= -1861.806649

Sum of electronic and thermal Free Energies= -1861.924702

| | | | |
|---|---|---|---|
| C | -1.04354000 | -0.62884500 | -1.35539400 |
| S | -2.11888000 | -0.37418600 | -2.66295200 |
| N | 0.32075400 | -0.85995400 | -1.71305000 |
| H | 0.48344400 | -1.16742700 | -2.66086000 |
| N | -1.38137400 | -0.60392300 | -0.10641600 |
| C | -0.57507100 | -1.10668000 | 0.92920000 |
| C | -0.08506700 | -2.41745100 | 0.89776700 |
| C | -0.34681500 | -0.33705000 | 2.07435200 |
| C | 0.65037800 | -2.92288900 | 1.96066600 |
| H | -0.28994700 | -3.03510200 | 0.03025400 |
| C | 0.40089600 | -0.84367500 | 3.12867900 |
| H | -0.76413900 | 0.65994000 | 2.12535500 |
| C | 0.91216600 | -2.13617300 | 3.07633900 |
| H | 1.48261200 | -2.53457400 | 3.90687400 |

| | | | |
|---|---|---|---|
| H | -3.18174800 | -1.15143600 | 0.06541900 |
| C | -5.01277300 | -1.17531300 | -0.81686700 |
| C | -4.15111200 | -1.70791100 | 0.21372400 |
| C | -4.67195300 | -1.53973100 | 1.63456600 |
| C | -5.37385500 | -0.18651600 | 1.73205200 |
| C | -6.49596400 | -0.11034900 | 0.72212700 |
| H | -5.36424700 | -2.34789300 | 1.89042300 |
| H | -3.83752600 | -1.59201700 | 2.33431000 |
| H | -5.80816500 | -0.03155900 | 2.72198400 |
| H | -4.66078400 | 0.61537300 | 1.53127500 |
| H | -7.32713200 | -0.77920300 | 0.95084100 |
| H | -6.87228700 | 0.89795900 | 0.56781900 |
| O | -6.06863900 | -0.51511100 | -0.63358300 |
| H | -4.77521100 | -1.33452500 | -1.86727400 |
| H | -3.87813700 | -2.73043100 | -0.07073600 |
| C | -4.45582900 | 2.40771700 | -1.41529600 |
| H | -4.90078400 | 1.99805800 | -2.33016400 |
| H | -3.70930400 | 3.15814800 | -1.69995800 |
| H | -5.23857100 | 2.90649800 | -0.84074200 |
| O | -3.89853400 | 1.39701200 | -0.59939300 |
| H | -3.22114500 | 0.94284300 | -1.12834800 |
| H | 0.57029200 | -0.23044800 | 4.00735200 |
| H | 1.01668900 | -3.94283100 | 1.91778500 |
| C | 1.31303500 | -0.22334800 | -1.05741800 |
| C | 1.71562500 | 0.84572800 | -0.29536900 |
| C | 2.61375500 | -0.18743300 | -0.61265900 |
| N | 1.47360500 | 1.99940100 | 0.29499200 |
| N | 3.81224100 | -0.72368700 | -0.57051800 |
| C | 2.45385200 | 2.50051100 | 1.28114200 |
| C | 0.43924000 | 2.92651200 | -0.24390400 |
| C | 4.92825600 | -0.01920600 | 0.09191400 |
| C | 4.03522800 | -2.04737600 | -1.19592900 |
| C | 3.44316600 | 3.47824800 | 0.64903900 |
| H | 2.99391900 | 1.61224900 | 1.61874900 |
| C | 1.75846500 | 3.08519600 | 2.50568100 |
| C | -0.92637400 | 2.75788900 | 0.40929800 |
| H | 0.82042600 | 3.91920000 | 0.00738900 |
| C | 0.35323000 | 2.84505900 | -1.76522800 |
| H | 4.52690900 | 0.95574200 | 0.36873500 |
| C | 5.34213800 | -0.74847400 | 1.36655300 |
| C | 6.09011400 | 0.21972500 | -0.86780600 |
| H | 5.06286500 | -2.31285000 | -0.94294400 |
| C | 3.11151000 | -3.10399500 | -0.60379300 |
| C | 3.92536600 | -1.95233500 | -2.71511300 |
| H | 3.91707800 | 3.04704500 | -0.23690400 |
| H | 2.95146200 | 4.40688500 | 0.34896300 |
| H | 4.22519700 | 3.73755600 | 1.36625400 |
| H | 1.20016500 | 3.99269200 | 2.26335700 |
| H | 1.07331900 | 2.35744400 | 2.94407300 |
| H | 2.50711800 | 3.35049200 | 3.25478100 |
| H | -1.36085700 | 1.78405500 | 0.18068500 |
| H | -0.86812300 | 2.87538000 | 1.49282500 |
| H | -1.60574700 | 3.52374800 | 0.02712500 |
| H | 1.33954400 | 2.93898700 | -2.22667100 |
| H | -0.11560300 | 1.91778800 | -2.10430400 |
| H | -0.26827400 | 3.66467100 | -2.13092400 |

| | | | |
|---|---|---|---|
| H | 5.75565800 | -1.73659800 | 1.14768000 |
| H | 6.11308500 | -0.17903800 | 1.89020200 |
| H | 4.48766000 | -0.87417900 | 2.03584100 |
| H | 5.75638100 | 0.75207000 | -1.76111500 |
| H | 6.85266600 | 0.82508200 | -0.37350800 |
| H | 6.56545000 | -0.71420800 | -1.17774100 |
| H | 3.36887100 | -4.08607100 | -1.00607200 |
| H | 3.20212400 | -3.13581900 | 0.48350800 |
| H | 2.06639000 | -2.90133000 | -0.85041400 |
| H | 2.91085300 | -1.67844600 | -3.01952000 |
| H | 4.61669500 | -1.20848000 | -3.11511500 |
| H | 4.15532800 | -2.91754600 | -3.17050100 |



Optimized Structure of *E,E*-**4**-An-**INT**$_4$.

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- Thermochemistry -

---

(0 imaginary frequencies)

Zero-point correction= 0.726287 (Hartree/Particle)

Thermal correction to Energy= 0.766382

Thermal correction to Enthalpy= 0.767326

Thermal correction to Gibbs Free Energy= 0.651748

Sum of electronic and zero-point Energies= -1861.876862

Sum of electronic and thermal Energies= -1861.836766

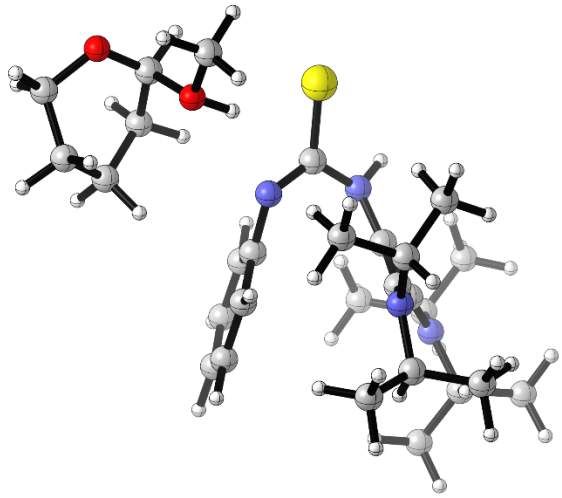
Sum of electronic and thermal Enthalpies= -1861.835822

Sum of electronic and thermal Free Energies= -1861.951400

| | | | |
|---|---|---|---|
| C | -1.02379400 | -0.04235100 | -1.28245700 |
| S | -2.10352300 | 0.29164000 | -2.62558800 |
| N | 0.23163100 | -0.53994200 | -1.71702900 |
| H | 0.26205100 | -1.22310800 | -2.45833500 |
| N | -1.33346200 | 0.17744800 | -0.07597800 |
| C | -0.61826900 | -0.35278600 | 1.01486100 |
| C | -0.45342200 | -1.73267700 | 1.15197900 |
| C | -0.17221300 | 0.48913200 | 2.03434000 |

| | | | |
|---|---|---|---|
| C | 0.18958700 | -2.25337000 | 2.26685700 |
| H | -0.85475200 | -2.39490900 | 0.39258700 |
| C | 0.48951900 | -0.03664800 | 3.13465000 |
| H | -0.35664900 | 1.55162300 | 1.95805800 |
| C | 0.68132000 | -1.40903000 | 3.25464900 |
| H | 1.17557600 | -1.81859800 | 4.12737400 |
| H | -3.36285400 | -1.47128200 | 0.03958900 |
| C | -5.37515800 | -0.94526100 | -0.48859300 |
| C | -4.32009800 | -1.30847900 | 0.53929600 |
| C | -4.19943900 | -0.22366200 | 1.62287600 |
| C | -5.54670500 | 0.48928700 | 1.83627500 |
| C | -6.70150900 | -0.41668100 | 1.44268300 |
| H | -3.85657700 | -0.68748000 | 2.55163700 |
| H | -3.44107100 | 0.50043700 | 1.32539300 |
| H | -5.67049000 | 0.79712900 | 2.87741200 |
| H | -5.59105200 | 1.39077700 | 1.22016500 |
| H | -6.70869200 | -1.32107200 | 2.06578700 |
| H | -7.66328800 | 0.08166500 | 1.56662100 |
| O | -6.64412500 | -0.80516200 | 0.06746500 |
| H | -5.47829300 | -1.71410400 | -1.26504800 |
| H | -4.62152800 | -2.26385000 | 0.97848500 |
| C | -5.86326300 | 0.73511400 | -2.10071500 |
| H | -6.01183900 | -0.01376500 | -2.88962000 |
| H | -5.42701800 | 1.63673600 | -2.53127800 |
| H | -6.82880600 | 0.97286800 | -1.65170200 |
| O | -4.95412000 | 0.26385400 | -1.11882500 |
| H | -3.24921500 | 0.30280300 | -1.87327600 |
| H | 0.83168200 | 0.62889000 | 3.91952200 |
| H | 0.29557000 | -3.32747300 | 2.36876200 |
| C | 1.37088100 | -0.17988200 | -1.08682200 |
| C | 2.06780300 | 0.80134000 | -0.42980900 |
| C | 2.62729200 | -0.47662200 | -0.61733600 |
| N | 2.16503200 | 2.02939600 | 0.03279800 |
| N | 3.62386100 | -1.32092300 | -0.49894500 |
| C | 3.24596600 | 2.33968800 | 0.99498200 |
| C | 1.41090300 | 3.14130800 | -0.61082500 |
| C | 4.89356100 | -0.89714300 | 0.12997900 |
| C | 3.47396700 | -2.70347800 | -1.00946800 |
| C | 4.46495000 | 2.93716500 | 0.29623800 |
| H | 3.51801100 | 1.37650900 | 1.43419000 |
| C | 2.73471900 | 3.21426100 | 2.13457200 |
| C | 0.03656600 | 3.37876500 | 0.00278900 |
| H | 2.02610600 | 4.02328500 | -0.41993200 |
| C | 1.33660900 | 2.95628600 | -2.12341900 |
| H | 4.77831800 | 0.17151500 | 0.31131900 |
| C | 5.08420600 | -1.59676500 | 1.47190400 |
| C | 6.07609000 | -1.07719900 | -0.81670600 |
| H | 4.39372800 | -3.21356400 | -0.72026600 |
| C | 2.30887100 | -3.42161300 | -0.34175000 |
| C | 3.38332200 | -2.71013900 | -2.53264300 |
| H | 4.81517900 | 2.29215000 | -0.51431000 |
| H | 4.24316700 | 3.91982400 | -0.12729200 |
| H | 5.28091200 | 3.06408800 | 1.01117700 |
| H | 2.45052400 | 4.21147700 | 1.79033700 |
| H | 1.87438500 | 2.75121600 | 2.62073000 |
| H | 3.52463700 | 3.33702900 | 2.87808000 |

| | | | |
|---|---|---|---|
| H | -0.62890800 | 2.52967300 | -0.16445900 |
| H | 0.10579700 | 3.56827200 | 1.07482200 |
| H | -0.41642400 | 4.25723400 | -0.46238300 |
| H | 2.32475000 | 2.77211000 | -2.55178600 |
| H | 0.66900400 | 2.13697500 | -2.40231500 |
| H | 0.93411800 | 3.86345000 | -2.57713300 |
| H | 5.20606100 | -2.67604300 | 1.34675000 |
| H | 5.98299600 | -1.21979500 | 1.96413300 |
| H | 4.22788300 | -1.41984700 | 2.12721200 |
| H | 5.90528600 | -0.55851400 | -1.76249500 |
| H | 6.97488800 | -0.66159100 | -0.35696100 |
| H | 6.27629900 | -2.13042800 | -1.02840600 |
| H | 2.29006500 | -4.46724900 | -0.65542300 |
| H | 2.40044800 | -3.38278500 | 0.74477700 |
| H | 1.35120600 | -2.97066800 | -0.61376900 |
| H | 2.48689300 | -2.18661900 | -2.87983200 |
| H | 4.25284200 | -2.22810500 | -2.98266600 |
| H | 3.32838700 | -3.73585200 | -2.90219200 |



Optimized Structure of *E,E*-**4**-An-**TS$_3$-PA**.

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- Thermochemistry -

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(1 imaginary frequency = -317.72 Hz)

Zero-point correction= 0.728079 (Hartree/Particle)

Thermal correction to Energy= 0.767512

Thermal correction to Enthalpy= 0.768456

Thermal correction to Gibbs Free Energy= 0.654958

Sum of electronic and zero-point Energies= -1861.859264

Sum of electronic and thermal Energies= -1861.819831

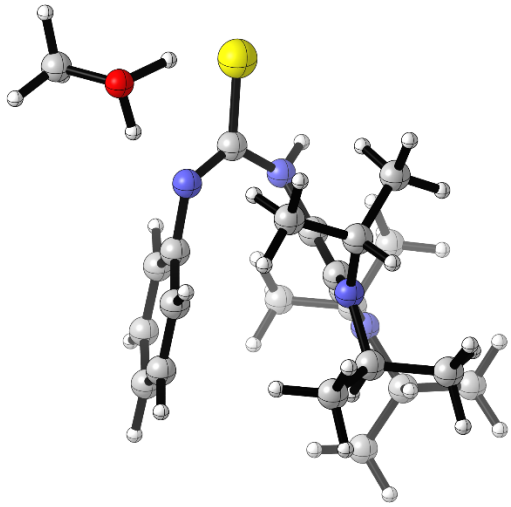
Sum of electronic and thermal Enthalpies= -1861.818887

Sum of electronic and thermal Free Energies= -1861.932384

| | | | |
|---|---|---|---|
| C | -1.02513900 | -0.07878800 | -1.49616200 |
| S | -2.03548400 | 0.34850800 | -2.80577500 |
| N | 0.28796000 | -0.52910000 | -1.82186500 |
| H | 0.42724000 | -0.89749400 | -2.75058200 |
| N | -1.40289200 | 0.00230900 | -0.26087300 |

| | | | |
|---|---|---|---|
| C | -0.74871100 | -0.65644500 | 0.79309100 |
| C | -0.49908700 | -2.03319100 | 0.74339900 |
| C | -0.44930000 | 0.03024100 | 1.97390600 |
| C | 0.06791800 | -2.69008900 | 1.82646900 |
| H | -0.76361400 | -2.58481700 | -0.15231200 |
| C | 0.12974100 | -0.62933200 | 3.04940100 |
| H | -0.68222300 | 1.08468300 | 2.04075200 |
| C | 0.39931300 | -1.99200600 | 2.98177700 |
| H | 0.83689000 | -2.50721400 | 3.82844200 |
| H | -3.28809500 | -1.74646000 | -0.50513700 |
| C | -5.03058300 | -0.55118100 | -0.79995300 |
| C | -4.27737600 | -1.62713200 | -0.06235900 |
| C | -4.20121700 | -1.34962300 | 1.44948400 |
| C | -5.37735100 | -0.47378400 | 1.91535000 |
| C | -6.57805900 | -0.65281700 | 1.00614100 |
| H | -4.20211500 | -2.30433400 | 1.97885600 |
| H | -3.25738400 | -0.85781000 | 1.68417100 |
| H | -5.66866500 | -0.71873900 | 2.93870300 |
| H | -5.08937800 | 0.58085000 | 1.90980100 |
| H | -6.92630900 | -1.69075900 | 1.00452400 |
| H | -7.41097700 | -0.01086900 | 1.28688100 |
| O | -6.27542500 | -0.28842000 | -0.36179900 |
| H | -5.03937100 | -0.66265200 | -1.88467600 |
| H | -4.83247100 | -2.54872300 | -0.26450600 |
| C | -4.75950900 | 1.93465700 | -1.22171900 |
| H | -4.81383000 | 1.78650900 | -2.30047400 |
| H | -4.09147000 | 2.75645600 | -0.97742100 |
| H | -5.74348800 | 2.07947600 | -0.78706600 |
| O | -4.19557800 | 0.75371100 | -0.59635900 |
| H | -3.27844500 | 0.58849600 | -0.98610800 |
| H | 0.35394800 | -0.07854100 | 3.95666600 |
| H | 0.24360800 | -3.75872800 | 1.76804200 |
| C | 1.35289100 | -0.10716600 | -1.11265600 |
| C | 1.90948600 | 0.85116500 | -0.30301600 |
| C | 2.61848900 | -0.31981000 | -0.61754800 |
| N | 1.85303100 | 2.01649500 | 0.31157100 |
| N | 3.69778100 | -1.06448900 | -0.54368300 |
| C | 2.85664000 | 2.30836600 | 1.35680900 |
| C | 1.02805700 | 3.12459000 | -0.24305400 |
| C | 4.88651100 | -0.58650700 | 0.19142100 |
| C | 3.70143800 | -2.40278000 | -1.17732000 |
| C | 4.02423400 | 3.12749500 | 0.80931100 |
| H | 3.22623100 | 1.33023200 | 1.67516400 |
| C | 2.21020000 | 2.95505200 | 2.57687700 |
| C | -0.37861300 | 3.18816100 | 0.34130300 |
| H | 1.56353200 | 4.02843900 | 0.05718500 |
| C | 1.00307500 | 3.09345600 | -1.76865700 |
| H | 4.67735500 | 0.45777200 | 0.42535000 |
| C | 5.04989800 | -1.35431500 | 1.49967700 |
| C | 6.13825900 | -0.61454800 | -0.68043400 |
| H | 4.64213400 | -2.86188400 | -0.86962400 |
| C | 2.56247000 | -3.27089600 | -0.65764600 |
| C | 3.70140800 | -2.27802500 | -2.69823800 |
| H | 4.45739200 | 2.65960100 | -0.07888900 |
| H | 3.71394200 | 4.13984200 | 0.53910100 |
| H | 4.80647400 | 3.21645200 | 1.56664900 |

| | | | |
|---|---|---|---|
| H | 1.81654400 | 3.94932400 | 2.35180500 |
| H | 1.39810000 | 2.33241700 | 2.95654800 |
| H | 2.95695200 | 3.06824200 | 3.36539500 |
| H | -0.95306200 | 2.30039000 | 0.06753100 |
| H | -0.35665200 | 3.27753000 | 1.42874600 |
| H | -0.88819400 | 4.06899000 | -0.05756000 |
| H | 2.01063300 | 3.00516100 | -2.18245900 |
| H | 0.38359500 | 2.27915700 | -2.15340400 |
| H | 0.56733700 | 4.02328300 | -2.13874600 |
| H | 5.25450300 | -2.41273600 | 1.31656400 |
| H | 5.88777800 | -0.94982600 | 2.07141400 |
| H | 4.14445100 | -1.28154600 | 2.10733900 |
| H | 5.98286800 | -0.05992600 | -1.60818600 |
| H | 6.96731900 | -0.15241500 | -0.14081200 |
| H | 6.44157600 | -1.63389800 | -0.93123800 |
| H | 2.65530500 | -4.27980500 | -1.06505800 |
| H | 2.58205700 | -3.32969500 | 0.43210300 |
| H | 1.58961900 | -2.87366000 | -0.95732100 |
| H | 2.77852200 | -1.81044200 | -3.05459100 |
| H | 4.54438600 | -1.67803100 | -3.04555200 |
| H | 3.76955200 | -3.26573600 | -3.15832200 |



Optimized Structure of *E,E*-**4**-An-**TS$_3$**-**MA**.

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- Thermochemistry -

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(1 imaginary frequency = -707.17 Hz)

Zero-point correction= 0.596566 (Hartree/Particle)

Thermal correction to Energy= 0.630160

Thermal correction to Enthalpy= 0.631104

Thermal correction to Gibbs Free Energy= 0.531491

Sum of electronic and zero-point Energies= -1591.442070

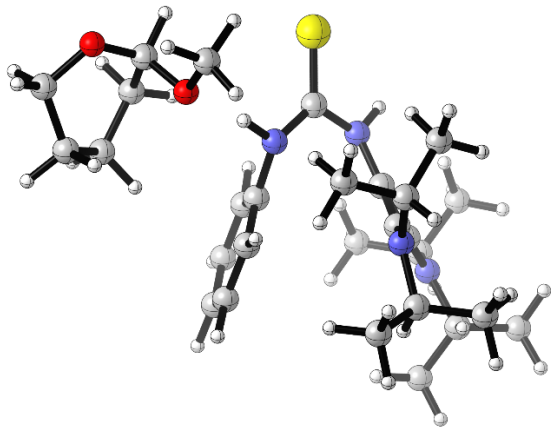
Sum of electronic and thermal Energies= -1591.408476

Sum of electronic and thermal Enthalpies= -1591.407532

Sum of electronic and thermal Free Energies= -1591.507145

| | | | |
|---|---|---|---|
| C | -2.26647700 | -0.66928200 | -0.93660700 |
| S | -3.46826900 | -0.62304100 | -2.18533000 |
| N | -0.97781600 | -1.04482600 | -1.37376600 |
| H | -0.91740200 | -1.59539800 | -2.21720700 |
| N | -2.50435100 | -0.36939000 | 0.29683400 |
| C | -1.59845600 | -0.65107000 | 1.34855200 |
| C | -1.15720500 | -1.95482400 | 1.58184300 |
| C | -1.21575000 | 0.36257300 | 2.22687100 |
| C | -0.31120200 | -2.22702000 | 2.64792700 |
| H | -1.49343500 | -2.75334700 | 0.93002400 |
| C | -0.35798900 | 0.08645200 | 3.28341000 |
| H | -1.59792400 | 1.36349300 | 2.07759800 |
| C | 0.10645600 | -1.20677500 | 3.49444000 |
| H | 0.76077400 | -1.42395100 | 4.33023300 |
| H | -0.06927700 | 0.88266200 | 3.96060000 |
| H | 0.01212100 | -3.24659300 | 2.82456500 |
| C | 0.12701900 | -0.39403500 | -0.93423100 |
| C | 0.68955700 | 0.76916400 | -0.47477900 |
| C | 1.45949300 | -0.40587100 | -0.60032900 |
| N | 0.60645500 | 2.04475400 | -0.16509500 |
| N | 2.60692400 | -1.03444600 | -0.52820800 |
| C | 1.71037400 | 2.66023800 | 0.60550600 |
| C | -0.39651900 | 2.92001600 | -0.83509700 |
| C | 3.83379100 | -0.31935800 | -0.11513100 |
| C | 2.67747400 | -2.47010500 | -0.89004900 |
| C | 2.71715100 | 3.34902900 | -0.31293600 |
| H | 2.19830500 | 1.82463400 | 1.11381400 |
| C | 1.17379600 | 3.58531700 | 1.69195900 |
| C | -1.72223000 | 3.00215100 | -0.08937100 |
| H | 0.06617400 | 3.90898400 | -0.82027100 |
| C | -0.58806900 | 2.52834000 | -2.29722400 |
| H | 3.53364400 | 0.72163200 | 0.00384700 |
| C | 4.32318300 | -0.83553300 | 1.23441000 |
| C | 4.90314300 | -0.36789800 | -1.20196100 |
| H | 3.70704800 | -2.76302400 | -0.68080800 |
| C | 1.75850100 | -3.31305500 | -0.01644400 |
| C | 2.41972600 | -2.66678300 | -2.38089400 |
| H | 3.07905000 | 2.66760600 | -1.08772600 |
| H | 2.27800700 | 4.21916500 | -0.80703200 |
| H | 3.57558600 | 3.69826100 | 0.26512100 |
| H | 0.67236100 | 4.46146200 | 1.27415200 |
| H | 0.47404500 | 3.05435400 | 2.33976000 |
| H | 2.00415500 | 3.94359800 | 2.30345600 |
| H | -2.22460600 | 2.03332500 | -0.07653400 |
| H | -1.58386700 | 3.34528900 | 0.93713800 |
| H | -2.37615000 | 3.71489400 | -0.59668700 |
| H | 0.37102600 | 2.44029500 | -2.81337500 |
| H | -1.13950400 | 1.59048100 | -2.40246400 |
| H | -1.17435100 | 3.29836600 | -2.80139200 |
| H | 4.64025600 | -1.88000900 | 1.17405500 |
| H | 5.18285900 | -0.25054700 | 1.56752200 |
| H | 3.53595600 | -0.75781700 | 1.98809100 |
| H | 4.51957400 | 0.02301100 | -2.14697300 |
| H | 5.75533500 | 0.24434700 | -0.90017000 |
| H | 5.27421300 | -1.38198300 | -1.36940600 |

| | | | |
|---|---|---|---|
| H | 1.91890800 | -4.37218200 | -0.22789000 |
| H | 1.95463500 | -3.13437600 | 1.04199600 |
| H | 0.70703500 | -3.08609400 | -0.21002600 |
| H | 1.39134200 | -2.39972200 | -2.64269900 |
| H | 3.09664500 | -2.05964800 | -2.98441200 |
| H | 2.56393600 | -3.71489800 | -2.64968000 |
| H | -4.60197700 | -0.24767400 | -1.07109000 |
| O | -5.08091000 | 0.01570600 | 0.01612700 |
| H | -4.17991500 | -0.00089100 | 0.45895000 |
| C | -5.88713100 | -1.06794800 | 0.51169900 |
| H | -6.08819900 | -0.89940000 | 1.56856900 |
| H | -6.82122000 | -1.05710300 | -0.04515400 |
| H | -5.37588100 | -2.02316400 | 0.37002800 |



Optimized Structure of *E,E*-**4**-An-**INT**$_5$.

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- Thermochemistry -

---

(0 imaginary frequencies)

Zero-point correction= 0.730400 (Hartree/Particle)

Thermal correction to Energy= 0.770169

Thermal correction to Enthalpy= 0.771113

Thermal correction to Gibbs Free Energy= 0.656411

Sum of electronic and zero-point Energies= -1861.900976

Sum of electronic and thermal Energies= -1861.861207

Sum of electronic and thermal Enthalpies= -1861.860263

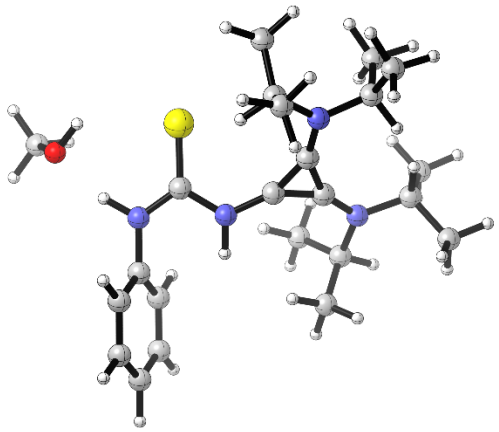
Sum of electronic and thermal Free Energies= -1861.974965

| | | | |
|---|---|---|---|
| C | -0.85985200 | -0.18939500 | -1.90299800 |
| S | -1.76340200 | 0.04318200 | -3.26558200 |
| N | 0.49086900 | -0.55828700 | -2.00174400 |
| H | 0.77542600 | -0.91690000 | -2.90135100 |
| N | -1.31347600 | -0.04019400 | -0.64314400 |
| C | -0.84683300 | -0.74481100 | 0.50573500 |
| C | -0.60804400 | -2.11479700 | 0.44750900 |
| C | -0.72801100 | -0.06830100 | 1.71572400 |
| C | -0.22145700 | -2.79747300 | 1.59218100 |
| H | -0.74915300 | -2.64334600 | -0.48837900 |

| | | | |
|---|---|---|---|
| C | -0.34833500 | -0.75886100 | 2.85929700 |
| H | -0.95108500 | 0.98975400 | 1.75841700 |
| C | -0.08564600 | -2.12268800 | 2.79972800 |
| H | 0.20102800 | -2.66122600 | 3.69503700 |
| H | -3.42057700 | -1.78416700 | -0.71239800 |
| C | -4.87211600 | -0.20157300 | -0.69886700 |
| C | -4.37512500 | -1.55776200 | -0.23192800 |
| C | -4.28359400 | -1.63458500 | 1.30396300 |
| C | -5.28537400 | -0.66764900 | 1.95795500 |
| C | -6.49029700 | -0.46088800 | 1.05387400 |
| H | -4.48854900 | -2.66150400 | 1.61734100 |
| H | -3.27185200 | -1.40203800 | 1.64169000 |
| H | -5.62262700 | -1.04692300 | 2.92557200 |
| H | -4.81081500 | 0.30133900 | 2.12980000 |
| H | -7.00291800 | -1.41604300 | 0.87994100 |
| H | -7.20926400 | 0.22944600 | 1.49571800 |
| O | -6.13640100 | 0.10757200 | -0.21060600 |
| H | -4.94542600 | -0.14751600 | -1.79016000 |
| H | -5.09257200 | -2.29280300 | -0.60660300 |
| C | -4.21012100 | 2.08326400 | -0.75799700 |
| H | -4.11970100 | 2.11975300 | -1.85004000 |
| H | -3.48429700 | 2.76192700 | -0.30941900 |
| H | -5.21786900 | 2.37880200 | -0.46141700 |
| O | -3.91637700 | 0.77962500 | -0.27645500 |
| H | -2.28400600 | 0.31085500 | -0.56877100 |
| H | -0.27024700 | -0.23207700 | 3.80334100 |
| H | -0.04819300 | -3.86625400 | 1.54318200 |
| C | 1.43949800 | -0.09842700 | -1.14793600 |
| C | 1.87891700 | 0.87785600 | -0.29067400 |
| C | 2.63629800 | -0.29334600 | -0.50240200 |
| N | 1.74102000 | 2.04290700 | 0.30450100 |
| N | 3.70595400 | -1.02074600 | -0.29509000 |
| C | 2.64837800 | 2.36679800 | 1.42957000 |
| C | 0.95064300 | 3.13575500 | -0.32964000 |
| C | 4.80384700 | -0.52360400 | 0.56301700 |
| C | 3.80922400 | -2.35857900 | -0.92726000 |
| C | 3.85694100 | 3.17433900 | 0.96034700 |
| H | 2.98845500 | 1.39873200 | 1.80562100 |
| C | 1.89864100 | 3.04502000 | 2.57036100 |
| C | -0.49431900 | 3.18960200 | 0.15029600 |
| H | 1.45456300 | 4.04849500 | -0.00417500 |
| C | 1.03953600 | 3.08239100 | -1.85137400 |
| H | 4.54656900 | 0.51144800 | 0.78797400 |
| C | 4.85396300 | -1.30834300 | 1.87002700 |
| C | 6.13518200 | -0.50905900 | -0.18172000 |
| H | 4.71301200 | -2.80149000 | -0.50703100 |
| C | 2.62925300 | -3.24445900 | -0.54893800 |
| C | 3.99158600 | -2.22997200 | -2.43638600 |
| H | 4.36121900 | 2.68579500 | 0.12207300 |
| H | 3.57008400 | 4.17917700 | 0.64077400 |
| H | 4.57493100 | 3.28294700 | 1.77623500 |
| H | 1.52335200 | 4.03068300 | 2.28549900 |
| H | 1.05961400 | 2.43112600 | 2.90341600 |
| H | 2.57798100 | 3.18448600 | 3.41343400 |
| H | -1.03935600 | 2.30725000 | -0.18585300 |
| H | -0.56027300 | 3.25887100 | 1.23708200 |

| | | | |
|---|---|---|---|
| H | -0.98034900 | 4.07156500 | -0.27335600 |
| H | 2.07636700 | 3.01021200 | -2.18848100 |
| H | 0.46864200 | 2.24893300 | -2.26862700 |
| H | 0.61316500 | 3.99690000 | -2.26685400 |
| H | 5.09700800 | -2.35988800 | 1.69601100 |
| H | 5.62377800 | -0.89671600 | 2.52591800 |
| H | 3.89332700 | -1.26023000 | 2.38867600 |
| H | 6.05992100 | 0.05965100 | -1.11095900 |
| H | 6.89443800 | -0.03824900 | 0.44577800 |
| H | 6.48748100 | -1.51616500 | -0.41720500 |
| H | 2.79391200 | -4.25570000 | -0.92603500 |
| H | 2.50530900 | -3.29143100 | 0.53449600 |
| H | 1.69747100 | -2.87383400 | -0.98322200 |
| H | 3.11278000 | -1.77402600 | -2.90239500 |
| H | 4.86302000 | -1.62023700 | -2.68055900 |
| H | 4.12566200 | -3.21635800 | -2.88438300 |

E,Z Conformation



Optimized Structure of *E,Z*-**4**-An-**INT**$_1$.

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- Thermochemistry -

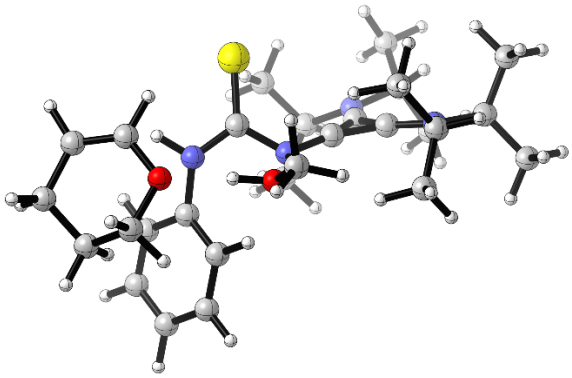
---

(0 imaginary frequencies)
Zero-point correction= 0.602056 (Hartree/Particle)
Thermal correction to Energy= 0.636847
Thermal correction to Enthalpy= 0.637792
Thermal correction to Gibbs Free Energy= 0.533221
Sum of electronic and zero-point Energies= -1591.463325
Sum of electronic and thermal Energies= -1591.428534
Sum of electronic and thermal Enthalpies= -1591.427590
Sum of electronic and thermal Free Energies= -1591.532161

| | | | |
|---|---|---|---|
| C | -1.69895000 | -0.94482800 | 0.27324700 |

| | | | |
|---|---|---|---|
| S | -0.99553400 | -2.23085900 | 1.08507800 |
| N | -3.01681100 | -0.77676700 | 0.14122900 |
| H | -3.60683100 | -1.53307000 | 0.52637900 |
| N | -0.93408200 | 0.06200400 | -0.29718200 |
| C | -3.63938800 | 0.33865000 | -0.49887000 |
| C | -4.22286400 | 0.17675200 | -1.75073700 |
| C | -3.66561100 | 1.57787200 | 0.13902300 |
| C | -4.83174600 | 1.26219200 | -2.36747600 |
| H | -4.19858900 | -0.79593700 | -2.22742500 |
| C | -4.26368500 | 2.66225700 | -0.49131600 |
| H | -3.23739200 | 1.67713300 | 1.13100800 |
| C | -4.84653900 | 2.50419000 | -1.74337300 |
| H | -5.32212000 | 3.34808700 | -2.22849600 |
| H | -1.42075300 | 0.89740400 | -0.59807400 |
| C | -4.78758600 | -2.80617500 | 2.59601100 |
| H | -4.94501500 | -3.77005200 | 3.08769600 |
| H | -5.75495700 | -2.32220500 | 2.46552900 |
| H | -4.15372000 | -2.17643200 | 3.23036000 |
| O | -4.22801600 | -2.97858200 | 1.29934800 |
| H | -3.35675700 | -3.37953400 | 1.39427400 |
| C | 0.42453100 | 0.13319900 | -0.23865400 |
| C | 1.67348900 | -0.41492700 | -0.39073400 |
| C | 1.50506400 | 0.93744700 | -0.00112600 |
| N | 2.46169300 | -1.42407300 | -0.66745600 |
| N | 1.96052600 | 2.11884400 | 0.34699200 |
| C | 3.91729000 | -1.23151800 | -0.42781500 |
| C | 1.81081600 | -2.71318100 | -1.04282000 |
| C | 3.40830700 | 2.38620300 | 0.48362800 |
| C | 0.98217200 | 3.17044800 | 0.71614400 |
| C | 4.25341100 | -1.41021200 | 1.05122800 |
| H | 4.10185900 | -0.19008000 | -0.70196300 |
| C | 4.81156100 | -2.06422400 | -1.33597200 |
| C | 2.13394000 | -3.83331400 | -0.06223100 |
| H | 3.90228200 | 1.47774800 | 0.14003600 |
| C | 3.84429800 | 3.53455800 | -0.42056300 |
| C | 3.78492200 | 2.60113500 | 1.94679200 |
| H | 1.58620000 | 4.01518200 | 1.04944200 |
| C | 0.17937600 | 3.62270100 | -0.49987500 |
| C | 0.10572400 | 2.73093400 | 1.88581400 |
| H | 3.61869900 | -0.77841600 | 1.67887300 |
| H | 4.11726300 | -2.44593500 | 1.36601500 |
| H | 5.29485500 | -1.13421000 | 1.23240300 |
| H | 4.73231600 | -3.13324100 | -1.13845100 |
| H | 4.59870700 | -1.88018400 | -2.38930100 |
| H | 5.84732600 | -1.77505500 | -1.14730700 |
| H | 3.17542800 | -4.15563700 | -0.11657700 |
| H | 1.90498700 | -3.52997500 | 0.96070000 |
| H | 1.50996200 | -4.69673000 | -0.30310200 |
| H | 3.38519100 | 4.48154600 | -0.12566600 |
| H | 4.92621900 | 3.66356600 | -0.35275700 |
| H | 3.58726500 | 3.33397200 | -1.46270200 |
| H | 3.32450600 | 3.50413400 | 2.35597700 |
| H | 3.47894000 | 1.74967900 | 2.55872600 |
| H | 4.86679700 | 2.71680500 | 2.03702100 |
| H | -0.48608700 | 4.44293300 | -0.22388000 |
| H | 0.83860300 | 3.96640100 | -1.29885100 |

| | | | |
|---|---|---|---|
| H | -0.44472100 | 2.81779400 | -0.89867100 |
| H | -0.54895100 | 1.89919800 | 1.61183600 |
| H | 0.71507100 | 2.41971500 | 2.73639200 |
| H | -0.52749000 | 3.56173100 | 2.20372600 |
| H | -5.29514700 | 1.13674700 | -3.33858300 |
| H | -4.29317900 | 3.62488000 | 0.00520000 |
| H | 0.74765700 | -2.50373600 | -0.92336800 |
| C | 2.04426000 | -3.09668600 | -2.50256300 |
| H | 3.03106700 | -3.52417300 | -2.67832600 |
| H | 1.30664300 | -3.85187600 | -2.78318600 |
| H | 1.91049200 | -2.23666100 | -3.16256700 |



Optimized Structure of *E,Z*-**4**-An-**INT**$_2$.

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- Thermochemistry -

---

(0 imaginary frequencies)

Zero-point correction= 0.728291 (Hartree/Particle)

Thermal correction to Energy= 0.769514

Thermal correction to Enthalpy= 0.770458

Thermal correction to Gibbs Free Energy= 0.651821

Sum of electronic and zero-point Energies= -1861.892083

Sum of electronic and thermal Energies= -1861.850859

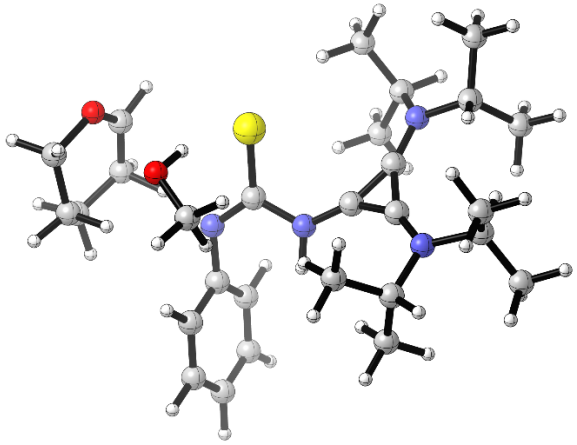
Sum of electronic and thermal Enthalpies= -1861.849915

Sum of electronic and thermal Free Energies= -1861.968552

| | | | |
|---|---|---|---|
| C | -0.81167100 | -0.47210700 | -1.03059100 |
| S | -0.28714800 | -0.66745700 | -2.58947400 |
| N | -0.05114600 | 0.20500100 | -0.05259600 |
| H | -0.44847700 | 1.12687800 | 0.17979700 |
| N | -2.01255100 | -0.89539900 | -0.60429000 |
| C | -2.50666000 | -1.13343300 | 0.71042800 |
| C | -3.13749900 | -2.35942100 | 0.91823600 |
| C | -2.45137200 | -0.19591700 | 1.73676300 |
| C | -3.71026900 | -2.64823200 | 2.14797600 |
| H | -3.17756900 | -3.08452600 | 0.11252200 |
| C | -3.01530600 | -0.50171200 | 2.96953800 |
| H | -2.01550600 | 0.77989900 | 1.57956400 |
| C | -3.64710800 | -1.72015600 | 3.18045400 |
| H | -4.09434700 | -1.94279600 | 4.14156200 |
| H | -2.58705200 | -1.27434100 | -1.34543700 |
| C | -4.23132500 | 0.77853200 | -1.88194900 |

| | | | |
|---|---|---|---|
| C | -5.23662600 | -0.07361900 | -2.05485700 |
| C | -6.28381100 | -0.31052300 | -1.00284800 |
| C | -5.83236100 | 0.27543100 | 0.33679500 |
| C | -5.17523700 | 1.62799700 | 0.12314300 |
| H | -7.23238900 | 0.13722800 | -1.32010700 |
| H | -6.47352800 | -1.38244400 | -0.89808100 |
| H | -6.67681000 | 0.39665300 | 1.01910000 |
| H | -5.11855100 | -0.39458300 | 0.82103800 |
| H | -5.88250600 | 2.34141100 | -0.31403700 |
| H | -4.78148500 | 2.04099400 | 1.05202700 |
| O | -4.04464100 | 1.53925700 | -0.75995900 |
| H | -3.44991900 | 0.95165200 | -2.61268400 |
| H | -5.29984400 | -0.59493000 | -3.00246300 |
| C | -1.59797100 | 3.84847600 | -0.23923700 |
| H | -2.51267600 | 4.36380300 | 0.06732400 |
| H | -1.45754900 | 3.97862600 | -1.31726400 |
| H | -0.75586000 | 4.30180700 | 0.28224900 |
| O | -1.64371400 | 2.47582300 | 0.11864100 |
| H | -2.47662800 | 2.10501100 | -0.22639700 |
| H | -2.97396400 | 0.23285200 | 3.76514900 |
| H | -4.20190300 | -3.60174800 | 2.29886800 |
| C | 1.29250700 | 0.09305800 | -0.06266400 |
| C | 2.40516800 | -0.71180100 | -0.10293600 |
| C | 2.52372800 | 0.67241800 | 0.09845500 |
| N | 2.98011900 | -1.88900300 | -0.22158300 |
| N | 3.24522600 | 1.75351200 | 0.30509300 |
| C | 4.45788300 | -1.94766200 | -0.29098200 |
| C | 2.20019500 | -3.14269800 | -0.05259600 |
| C | 4.69819500 | 1.65391100 | 0.55148300 |
| C | 2.58913400 | 3.07733800 | 0.22250500 |
| C | 5.06049700 | -2.20861500 | 1.08766000 |
| H | 4.76493400 | -0.95616600 | -0.63167000 |
| C | 4.94336100 | -2.94188600 | -1.33982400 |
| C | 1.62931200 | -3.65093000 | -1.37217900 |
| H | 2.92937700 | -3.86832200 | 0.31570700 |
| C | 1.12407100 | -2.99450800 | 1.01972800 |
| H | 4.88892100 | 0.59234900 | 0.71389600 |
| C | 5.49094900 | 2.11336200 | -0.66851400 |
| C | 5.09995400 | 2.38365000 | 1.83015600 |
| H | 3.40502600 | 3.80123400 | 0.25263500 |
| C | 1.86126200 | 3.25156100 | -1.10739400 |
| C | 1.69082500 | 3.31934000 | 1.43238800 |
| H | 4.71203900 | -1.47340100 | 1.81815400 |
| H | 4.79544200 | -3.20293300 | 1.45616500 |
| H | 6.15033500 | -2.15447000 | 1.03820100 |
| H | 4.70234100 | -3.97378400 | -1.07389200 |
| H | 4.51222800 | -2.72237100 | -2.31789600 |
| H | 6.02973000 | -2.87032400 | -1.42168200 |
| H | 0.89673700 | -2.94772200 | -1.77258500 |
| H | 2.40934400 | -3.79416200 | -2.12026500 |
| H | 1.13405400 | -4.61142500 | -1.21014000 |
| H | 1.53585000 | -2.58801500 | 1.94646200 |
| H | 0.30238800 | -2.35388500 | 0.69177900 |
| H | 0.69854300 | -3.97552700 | 1.23807800 |
| H | 5.32851700 | 3.17539400 | -0.87148200 |
| H | 6.56004200 | 1.96975600 | -0.49840400 |

| | | | |
|---|---|---|---|
| H | 5.20311200 | 1.54786600 | -1.55815300 |
| H | 4.52917700 | 2.01870200 | 2.68648700 |
| H | 6.15974900 | 2.21046100 | 2.02721700 |
| H | 4.95630800 | 3.46380300 | 1.74965600 |
| H | 1.48238500 | 4.27236300 | -1.18951200 |
| H | 2.53494800 | 3.06688800 | -1.94634800 |
| H | 1.00686800 | 2.57516500 | -1.19826000 |
| H | 0.82471200 | 2.65082600 | 1.42867600 |
| H | 2.23792100 | 3.16974600 | 2.36467200 |
| H | 1.31626300 | 4.34527700 | 1.42069400 |



Optimized Structure of *E,Z*-**4**-An-**TS**$_1$.

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- Thermochemistry -

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(1 imaginary frequency = -269.60 Hz)

Zero-point correction= 0.722611 (Hartree/Particle)

Thermal correction to Energy= 0.763382

Thermal correction to Enthalpy= 0.764326

Thermal correction to Gibbs Free Energy= 0.646270

Sum of electronic and zero-point Energies= -1861.849215

Sum of electronic and thermal Energies= -1861.808444

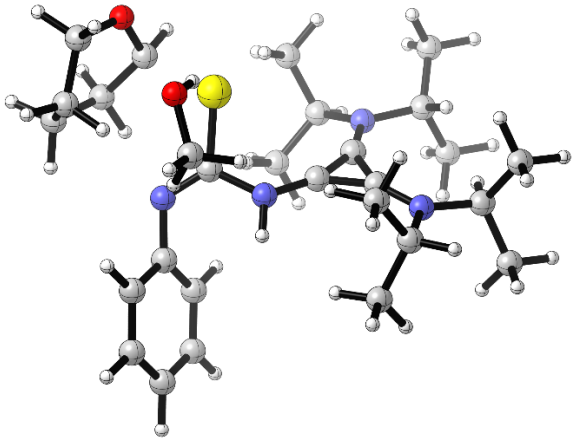
Sum of electronic and thermal Enthalpies= -1861.807500

Sum of electronic and thermal Free Energies= -1861.925557

| | | | |
|---|---|---|---|
| C | 1.14159700 | -0.37736600 | -0.34932300 |
| S | 0.90770400 | -1.89171500 | 0.41135700 |
| N | 0.01415800 | 0.43592700 | -0.58539300 |
| H | 0.20588400 | 1.41186600 | -0.77358400 |
| N | 2.30468400 | 0.09947100 | -0.66834400 |
| C | 2.46356600 | 1.35597000 | -1.29317400 |
| C | 2.12747100 | 1.54449600 | -2.63659500 |
| C | 3.01855600 | 2.41501000 | -0.57128700 |
| C | 2.33464200 | 2.77784100 | -3.24066300 |
| H | 1.71288300 | 0.71464400 | -3.19855800 |
| C | 3.22061400 | 3.64634900 | -1.18160000 |
| H | 3.29093100 | 2.25766800 | 0.46664200 |
| C | 2.87920100 | 3.83233100 | -2.51624300 |
| H | 3.04416600 | 4.79145700 | -2.99209400 |

| | | | |
|---|---|---|---|
| H | 3.46221300 | -0.93373600 | -0.69626800 |
| C | 4.15789700 | -2.57787200 | 0.19253500 |
| C | 4.50373100 | -1.57556600 | -0.73782200 |
| C | 5.57137400 | -0.58400200 | -0.30323000 |
| C | 5.34565500 | -0.28149200 | 1.17644100 |
| C | 5.33827400 | -1.55007200 | 1.99954300 |
| H | 6.57312100 | -0.99061800 | -0.47298700 |
| H | 5.48531100 | 0.32996200 | -0.89369300 |
| H | 6.12001900 | 0.37720000 | 1.57555000 |
| H | 4.37864300 | 0.20829500 | 1.31000300 |
| H | 6.31811400 | -2.02644300 | 2.06382400 |
| H | 4.92183700 | -1.38965500 | 2.98961200 |
| O | 4.45975100 | -2.58547300 | 1.43076400 |
| H | 3.52170600 | -3.41294900 | -0.08564600 |
| H | 4.52431200 | -1.94086300 | -1.76364300 |
| C | 1.91450800 | 0.64969100 | 2.97918600 |
| H | 0.92514000 | 0.50161500 | 3.43040200 |
| H | 1.78161500 | 1.15215200 | 2.00947900 |
| H | 2.49110600 | 1.30893900 | 3.63051700 |
| O | 2.62621800 | -0.55670900 | 2.85118600 |
| H | 2.11764700 | -1.13395000 | 2.26260700 |
| H | 3.65287200 | 4.46223700 | -0.61375700 |
| H | 2.07879600 | 2.91333600 | -4.28524600 |
| C | -1.26694200 | 0.12034900 | -0.29042600 |
| C | -2.36529100 | -0.70747700 | -0.33751800 |
| C | -2.45576900 | 0.59068800 | 0.20332400 |
| N | -2.98327200 | -1.82884200 | -0.63678200 |
| N | -3.12524800 | 1.58151600 | 0.75440900 |
| C | -4.39469300 | -1.96596200 | -0.20246800 |
| C | -2.44420200 | -2.77910700 | -1.64883400 |
| C | -4.58644500 | 1.50558700 | 0.95694800 |
| C | -2.37808200 | 2.77107100 | 1.22375100 |
| C | -5.34854100 | -1.45087500 | -1.27937100 |
| H | -4.47955700 | -1.33475600 | 0.68474400 |
| C | -4.73576600 | -3.38382400 | 0.23966400 |
| C | -1.72581900 | -3.96746900 | -1.01731800 |
| H | -3.33291200 | -3.14399700 | -2.17151600 |
| C | -1.56976000 | -2.06844200 | -2.67681600 |
| H | -4.90543600 | 0.61035000 | 0.42471400 |
| C | -4.92180400 | 1.33674200 | 2.43581900 |
| C | -5.30189800 | 2.69058700 | 0.31485700 |
| H | -3.10481400 | 3.36040400 | 1.78503400 |
| C | -1.25822300 | 2.38066000 | 2.18269600 |
| C | -1.89132200 | 3.61558500 | 0.04901700 |
| H | -5.09528800 | -0.43124700 | -1.58293900 |
| H | -5.32106800 | -2.08397200 | -2.16973000 |
| H | -6.37487400 | -1.45267800 | -0.90509900 |
| H | -4.70251400 | -4.09444000 | -0.58911300 |
| H | -4.05959300 | -3.72517300 | 1.02469900 |
| H | -5.75247200 | -3.39250400 | 0.63784700 |
| H | -0.83497400 | -3.63007700 | -0.48808200 |
| H | -2.36595600 | -4.51057200 | -0.32300800 |
| H | -1.42175300 | -4.66111400 | -1.80542400 |
| H | -2.07569400 | -1.19856400 | -3.10378000 |
| H | -0.61744600 | -1.75741300 | -2.24256500 |
| H | -1.34737900 | -2.76257400 | -3.48917100 |

| | | | |
|---|---|---|---|
| H | -4.61762400 | 2.21063500 | 3.01819600 |
| H | -5.99920000 | 1.21437400 | 2.56491600 |
| H | -4.42317000 | 0.45786200 | 2.85135500 |
| H | -5.05462000 | 2.77174400 | -0.74573500 |
| H | -6.38126500 | 2.55277900 | 0.40437600 |
| H | -5.05351500 | 3.63590800 | 0.80366300 |
| H | -0.80389700 | 3.27945200 | 2.60467500 |
| H | -1.64333600 | 1.77208100 | 3.00351200 |
| H | -0.46908200 | 1.81696400 | 1.67997200 |
| H | -1.17667800 | 3.06809000 | -0.57246100 |
| H | -2.72300900 | 3.92240200 | -0.58748300 |
| H | -1.38762400 | 4.51268300 | 0.41416600 |



Optimized Structure of *E,Z*-**4**-An-**INT**$_3$.

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- Thermochemistry -

---

(0 imaginary frequencies)

Zero-point correction= 0.726911 (Hartree/Particle)

Thermal correction to Energy= 0.768150

Thermal correction to Enthalpy= 0.769094

Thermal correction to Gibbs Free Energy= 0.649656

Sum of electronic and zero-point Energies= -1861.858585

Sum of electronic and thermal Energies= -1861.817347

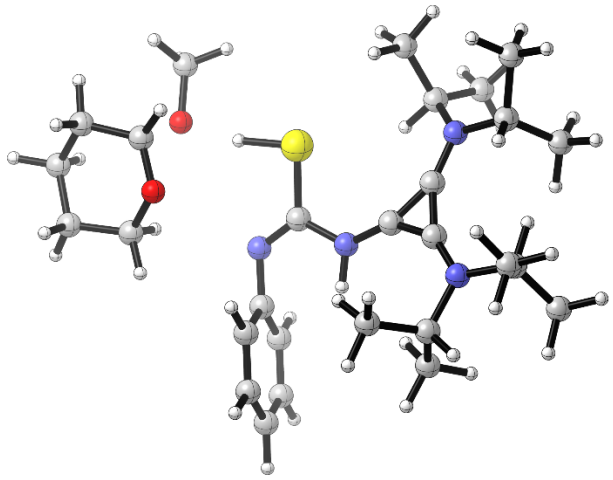
Sum of electronic and thermal Enthalpies= -1861.816402

Sum of electronic and thermal Free Energies= -1861.935840

| | | | |
|---|---|---|---|
| C | 1.41940200 | 0.08088000 | -0.11322400 |
| S | 1.48062400 | -1.40670100 | 0.82700000 |
| N | 0.17641100 | 0.74012600 | 0.04423000 |
| H | 0.21633100 | 1.74755500 | -0.04588000 |
| N | 2.38868200 | 0.59461800 | -0.73680100 |
| C | 2.23477600 | 1.81158200 | -1.43563100 |
| C | 1.35985300 | 1.93505500 | -2.51813900 |
| C | 3.01977700 | 2.89941300 | -1.05436800 |
| C | 1.26242200 | 3.14321000 | -3.19580900 |
| H | 0.77918900 | 1.07623600 | -2.83759300 |
| C | 2.90456100 | 4.10754700 | -1.72926100 |
| H | 3.71965000 | 2.78189000 | -0.23485100 |
| C | 2.02593100 | 4.23500000 | -2.79887300 |
| H | 1.94773900 | 5.17598200 | -3.32967800 |

| | | | |
|---|---|---|---|
| H | 3.15111600 | -1.61072100 | -1.62674000 |
| C | 3.01749500 | -2.50524400 | 0.32884600 |
| C | 3.81927100 | -2.04035100 | -0.88072400 |
| C | 4.97074000 | -1.07767300 | -0.52609100 |
| C | 4.90517200 | -0.64464100 | 0.93533000 |
| C | 4.77551100 | -1.84299000 | 1.85414600 |
| H | 5.92652100 | -1.57700400 | -0.70824800 |
| H | 4.93016600 | -0.20112200 | -1.17243800 |
| H | 5.80844100 | -0.09872100 | 1.21794500 |
| H | 4.06674800 | 0.03590700 | 1.09107200 |
| H | 5.69780100 | -2.43021300 | 1.86147800 |
| H | 4.54610900 | -1.53037100 | 2.87335400 |
| O | 3.73167500 | -2.76370000 | 1.45565800 |
| H | 2.47185300 | -3.41979500 | 0.09897400 |
| H | 4.22646800 | -2.96072600 | -1.30996700 |
| C | 2.37918100 | 1.61521200 | 2.96316900 |
| H | 1.30894500 | 1.77422900 | 3.15555300 |
| H | 2.57260800 | 1.77232500 | 1.89178800 |
| H | 2.93533100 | 2.37049900 | 3.51910000 |
| O | 2.81942200 | 0.35428100 | 3.40773200 |
| H | 2.33840700 | -0.31839000 | 2.91787900 |
| H | 3.51500600 | 4.94957000 | -1.42472200 |
| H | 0.59197600 | 3.22891300 | -4.04328400 |
| C | -1.04931800 | 0.18250700 | 0.06913200 |
| C | -1.96106800 | -0.80204900 | -0.24168100 |
| C | -2.36914300 | 0.38519000 | 0.38908800 |
| N | -2.30285900 | -1.97123700 | -0.74571200 |
| N | -3.28525500 | 1.18484700 | 0.89010600 |
| C | -3.71470900 | -2.39857000 | -0.58273400 |
| C | -1.44503400 | -2.68479400 | -1.72862900 |
| C | -4.72457700 | 0.85808600 | 0.79985200 |
| C | -2.85327500 | 2.43938100 | 1.55043000 |
| C | -4.56204400 | -1.93778700 | -1.76768400 |
| H | -4.05901000 | -1.89550100 | 0.32342300 |
| C | -3.84308100 | -3.89512500 | -0.32562000 |
| C | -0.59571900 | -3.76995000 | -1.07420900 |
| H | -2.15399000 | -3.16173600 | -2.41008100 |
| C | -0.60566400 | -1.72048500 | -2.56125300 |
| H | -4.77915100 | -0.03365700 | 0.17625300 |
| C | -5.29471200 | 0.52359700 | 2.17445500 |
| C | -5.49983700 | 1.95973200 | 0.08292100 |
| H | -3.75685300 | 2.84501300 | 2.00756600 |
| C | -1.85180900 | 2.16324100 | 2.66746400 |
| C | -2.34475100 | 3.45307000 | 0.52822400 |
| H | -4.45598800 | -0.86290100 | -1.93884800 |
| H | -4.27629100 | -2.45549500 | -2.68675700 |
| H | -5.61687300 | -2.15333900 | -1.58360800 |
| H | -3.53665200 | -4.49051800 | -1.18857500 |
| H | -3.25514800 | -4.19972000 | 0.54159000 |
| H | -4.89077300 | -4.12769300 | -0.12540300 |
| H | 0.08364700 | -3.32554200 | -0.34683200 |
| H | -1.20811700 | -4.51365900 | -0.56553600 |
| H | -0.00659000 | -4.28298800 | -1.83843400 |
| H | -1.21562400 | -0.91279700 | -2.97402400 |
| H | 0.21516400 | -1.29077800 | -1.98356700 |
| H | -0.15982100 | -2.26491200 | -3.39535400 |

| | | | |
|---|---|---|---|
| H | -5.25773600 | 1.38445100 | 2.84725000 |
| H | -6.34120300 | 0.22635900 | 2.08045300 |
| H | -4.74338800 | -0.29765500 | 2.63826800 |
| H | -5.07480600 | 2.15921300 | -0.90312900 |
| H | -6.53722300 | 1.64653600 | -0.04973800 |
| H | -5.51169000 | 2.89230900 | 0.65241600 |
| H | -1.63865500 | 3.08807800 | 3.20690400 |
| H | -2.24851500 | 1.43543300 | 3.37812300 |
| H | -0.90366300 | 1.78248800 | 2.27873200 |
| H | -1.45830700 | 3.08789300 | 0.00100500 |
| H | -3.10715000 | 3.67665800 | -0.21957700 |
| H | -2.06971900 | 4.38424800 | 1.02707600 |



Optimized Structure of *E,Z*-**4**-An-**TS$_2$**.

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- Thermochemistry -

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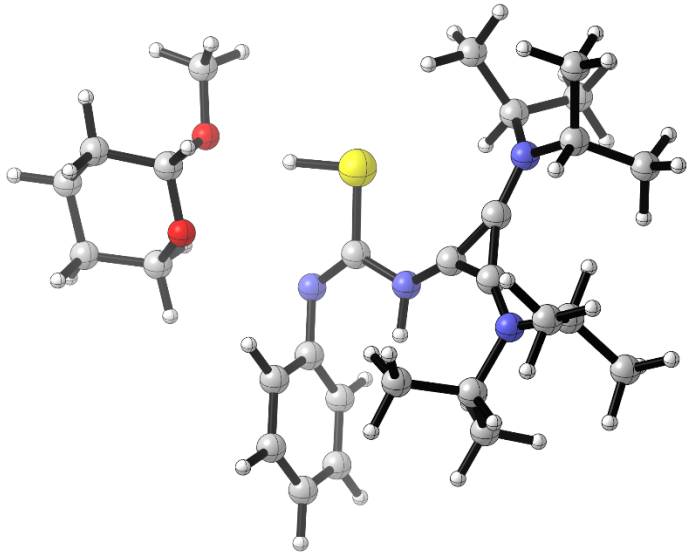
(1 imaginary frequencies = -283.97 Hz)
Zero-point correction= 0.723228 (Hartree/Particle)
Thermal correction to Energy= 0.762111
Thermal correction to Enthalpy= 0.763056
Thermal correction to Gibbs Free Energy= 0.650594
Sum of electronic and zero-point Energies= -1861.852330
Sum of electronic and thermal Energies= -1861.813447
Sum of electronic and thermal Enthalpies= -1861.812502
Sum of electronic and thermal Free Energies= -1861.924964

| | | | |
|---|---|---|---|
| C | 1.06625800 | -0.00601700 | -0.73137300 |
| S | 1.12031800 | -1.72901200 | -0.43440800 |
| N | 2.09025700 | 0.68952800 | -1.00298800 |
| N | -0.20155500 | 0.60706500 | -0.61768700 |
| C | 1.96502900 | 2.08966700 | -1.10177800 |
| C | 1.88168900 | 2.71058100 | -2.34887600 |
| C | 1.94300400 | 2.87068100 | 0.05898200 |
| C | 1.76268000 | 4.09214400 | -2.42889200 |
| H | 1.91515000 | 2.10074700 | -3.24414100 |

| | | | |
|---|---|---|---|
| C | 1.82571800 | 4.25262500 | -0.03230300 |
| H | 2.03013300 | 2.37977100 | 1.02298800 |
| C | 1.73053800 | 4.86789600 | -1.27478800 |
| H | 1.64487800 | 5.94548000 | -1.34593200 |
| H | 6.08517700 | -2.92092000 | 1.43492300 |
| C | 4.42571600 | -1.56589700 | 1.41921000 |
| C | 5.89432100 | -1.85791500 | 1.58637700 |
| C | 6.75427400 | -0.98458700 | 0.67847300 |
| C | 6.31811800 | 0.47102800 | 0.83000700 |
| C | 4.83519900 | 0.59261400 | 0.54130000 |
| H | 7.80930700 | -1.10897300 | 0.92926900 |
| H | 6.61952400 | -1.30323900 | -0.35892800 |
| H | 6.52901300 | 0.82346700 | 1.84552800 |
| H | 6.86253300 | 1.11993500 | 0.13965500 |
| H | 4.45056000 | 1.58656600 | 0.76205300 |
| H | 4.60194900 | 0.35332400 | -0.49741700 |
| O | 4.04495200 | -0.29238100 | 1.37159000 |
| H | 6.12089300 | -1.64701100 | 2.63927200 |
| C | 4.00028400 | -3.62197100 | -0.21131600 |
| H | 2.97412900 | -4.01813100 | -0.19525600 |
| H | 4.53665900 | -4.07423500 | 0.62934100 |
| H | 4.48359000 | -3.94472600 | -1.13669900 |
| O | 3.99844100 | -2.21306700 | -0.14962000 |
| H | 2.56541700 | -1.82019200 | -0.35769000 |
| C | -1.39187400 | 0.11316900 | -0.23652500 |
| C | -2.38116600 | -0.83992300 | -0.12408400 |
| C | -2.61246100 | 0.48315800 | 0.27522100 |
| N | -2.83684100 | -2.07040300 | -0.26579800 |
| N | -3.36825200 | 1.45456600 | 0.74613200 |
| C | -4.19654600 | -2.33458100 | 0.26944700 |
| C | -2.06143100 | -3.00331100 | -1.12744800 |
| C | -4.79373400 | 1.23485300 | 1.06528700 |
| C | -2.77196300 | 2.79866900 | 0.92930100 |
| C | -5.29346600 | -1.95161800 | -0.72617400 |
| H | -4.27330300 | -1.67373400 | 1.13754700 |
| C | -4.37496400 | -3.75017400 | 0.80277000 |
| C | -2.85478000 | -3.47236500 | -2.34374500 |
| H | -4.99041000 | 0.19483600 | 0.80871100 |
| C | -5.05612900 | 1.41371900 | 2.55771600 |
| C | -5.69395400 | 2.10525300 | 0.19336500 |
| H | -3.55509900 | 3.39028600 | 1.40553800 |
| C | -1.58375600 | 2.75841300 | 1.88627500 |
| C | -2.44838600 | 3.45479600 | -0.41155900 |
| H | -5.11482100 | -0.96331400 | -1.15882600 |
| H | -5.36341700 | -2.66934400 | -1.54396800 |
| H | -6.26108900 | -1.93039200 | -0.21822100 |
| H | -4.37129100 | -4.49726900 | 0.00792700 |
| H | -3.60360100 | -4.00322000 | 1.53077700 |
| H | -5.34503400 | -3.81030700 | 1.30046100 |
| H | -3.66413100 | -4.15374000 | -2.07410100 |
| H | -3.27289700 | -2.62932000 | -2.89734400 |
| H | -2.18241200 | -4.01559100 | -3.01096100 |
| H | -4.88486200 | 2.44423900 | 2.87956200 |
| H | -6.09717300 | 1.17171500 | 2.78128300 |
| H | -4.41452200 | 0.75716600 | 3.14956400 |
| H | -5.55290500 | 3.16957200 | 0.39883600 |

| | | | |
|---|---|---|---|
| H | -5.50012200 | 1.92901600 | -0.86704000 |
| H | -6.74108000 | 1.86969300 | 0.39389700 |
| H | -1.24183600 | 3.77534400 | 2.08861100 |
| H | -1.86469000 | 2.29361200 | 2.83343800 |
| H | -0.73472900 | 2.20886700 | 1.47228300 |
| H | -3.34599700 | 3.55183100 | -1.02501700 |
| H | -2.02906800 | 4.44973600 | -0.25091000 |
| H | -1.71484400 | 2.88462600 | -0.98864000 |
| H | 1.69901400 | 4.56638900 | -3.40146200 |
| H | 1.81909600 | 4.84949100 | 0.87297400 |
| H | -1.23772900 | -2.39167700 | -1.49697100 |
| C | -1.43426600 | -4.16005500 | -0.35259800 |
| H | -2.15250100 | -4.94475200 | -0.11475200 |
| H | -0.64911300 | -4.60491500 | -0.96874000 |
| H | -0.97487700 | -3.80543300 | 0.57132700 |
| H | 3.75494300 | -2.12629900 | 2.06876500 |
| H | -0.14961300 | 1.61839500 | -0.64799900 |



Optimized Structure of *E,Z*-**4**-An-**INT**$_4$.

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- Thermochemistry -

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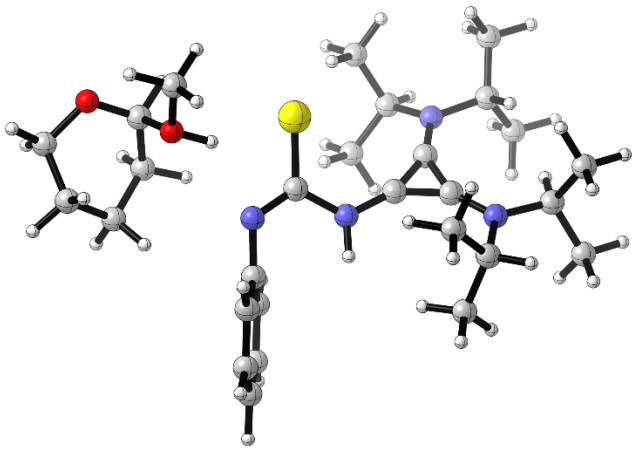
(0 imaginary frequencies)
Zero-point correction= 0.726802 (Hartree/Particle)
Thermal correction to Energy= 0.766493
Thermal correction to Enthalpy= 0.767438
Thermal correction to Gibbs Free Energy= 0.652288
Sum of electronic and zero-point Energies= -1861.872595
Sum of electronic and thermal Energies= -1861.832904
Sum of electronic and thermal Enthalpies= -1861.831960
Sum of electronic and thermal Free Energies= -1861.947109

| | | | |
|---|---|---|---|
| C | -1.01664000 | -0.04141400 | 1.07628000 |
| S | -1.04115500 | -1.79748600 | 0.94923800 |
| N | -2.05557800 | 0.63777100 | 1.30669300 |
| N | 0.23268200 | 0.58292200 | 0.87851900 |
| C | -1.97947500 | 2.04418900 | 1.21181000 |
| C | -1.74291900 | 2.82935300 | 2.34052300 |
| C | -2.15065300 | 2.65187000 | -0.03575200 |
| C | -1.66331300 | 4.21174000 | 2.21488500 |
| H | -1.63154000 | 2.34991700 | 3.30623700 |
| C | -2.07069400 | 4.03382900 | -0.14766300 |
| H | -2.36232500 | 2.02419800 | -0.89529900 |
| C | -1.82137100 | 4.81781800 | 0.97403000 |
| H | -1.76656200 | 5.89605800 | 0.88364700 |
| H | -5.75084800 | -2.79031600 | -2.16309900 |
| C | -4.19444000 | -1.51566100 | -1.36159900 |
| C | -5.59104800 | -1.73380100 | -1.93545500 |
| C | -6.65552800 | -1.18694000 | -0.98664000 |
| C | -6.32388100 | 0.26700500 | -0.65034500 |
| C | -4.90095800 | 0.37622100 | -0.12665300 |
| H | -7.64490200 | -1.26678900 | -1.44215200 |
| H | -6.67234000 | -1.78212000 | -0.06734900 |
| H | -6.42718200 | 0.88459300 | -1.54936600 |
| H | -7.01226700 | 0.66416500 | 0.10050900 |
| H | -4.59697300 | 1.41564700 | -0.01101200 |
| H | -4.79497100 | -0.11765500 | 0.84319000 |
| O | -3.95148300 | -0.19202000 | -1.04252700 |
| H | -5.62650000 | -1.19690200 | -2.88863100 |
| C | -4.07208400 | -3.68137700 | -0.30588400 |
| H | -3.50311200 | -4.02833300 | -1.17856100 |
| H | -5.11048900 | -4.01222700 | -0.40144300 |
| H | -3.64967600 | -4.12643100 | 0.59591000 |
| O | -3.98287000 | -2.27963800 | -0.15495500 |
| H | -2.38829400 | -1.85796400 | 0.59679300 |
| C | 1.39390000 | 0.11757200 | 0.38132800 |
| C | 2.39905100 | -0.80351500 | 0.17884100 |
| C | 2.54906500 | 0.52561700 | -0.24175000 |
| N | 2.90666000 | -2.01731200 | 0.27703700 |
| N | 3.22865800 | 1.51482000 | -0.78304300 |
| C | 4.21306600 | -2.24516800 | -0.39263600 |
| C | 2.23919500 | -2.98043800 | 1.19336500 |
| C | 4.63539400 | 1.33993700 | -1.20073200 |
| C | 2.57367100 | 2.83616000 | -0.93621700 |
| C | 5.39322000 | -1.86139200 | 0.50215300 |
| H | 4.19459000 | -1.56543100 | -1.24906000 |
| C | 4.36397300 | -3.64593500 | -0.97203200 |
| C | 3.16096300 | -3.46959800 | 2.30685700 |
| H | 4.88573700 | 0.31125200 | -0.94508000 |
| C | 4.78775600 | 1.50518300 | -2.70961300 |
| C | 5.56237000 | 2.25230000 | -0.40295200 |
| H | 3.29526300 | 3.44440900 | -1.48343900 |
| C | 1.31416500 | 2.73797600 | -1.79184800 |
| C | 2.33619000 | 3.50528800 | 0.41606300 |
| H | 5.24240100 | -0.88237400 | 0.96542300 |
| H | 5.54810300 | -2.59056700 | 1.29786100 |
| H | 6.30887500 | -1.81881500 | -0.09320800 |
| H | 4.44881900 | -4.40908400 | -0.19742000 |

| | | | |
|---|---|---|---|
| H | 3.53200600 | -3.89901900 | -1.63015500 |
| H | 5.28366600 | -3.67654500 | -1.55991900 |
| H | 3.94301600 | -4.13526000 | 1.93680900 |
| H | 3.62741600 | -2.63529900 | 2.83420300 |
| H | 2.56663700 | -4.03597200 | 3.02672800 |
| H | 4.56675000 | 2.52611600 | -3.03135900 |
| H | 5.81724800 | 1.28794700 | -3.00171500 |
| H | 4.12565600 | 0.82328100 | -3.24778400 |
| H | 5.37924300 | 3.30800500 | -0.61922300 |
| H | 5.43838700 | 2.09224000 | 0.67035800 |
| H | 6.60143800 | 2.04052100 | -0.66293900 |
| H | 0.91559200 | 3.73765700 | -1.97486600 |
| H | 1.53455900 | 2.27155600 | -2.75415300 |
| H | 0.52195400 | 2.16449000 | -1.30386300 |
| H | 3.27532300 | 3.64401100 | 0.95463000 |
| H | 1.87131100 | 4.48242400 | 0.27284200 |
| H | 1.66986100 | 2.92247700 | 1.05816400 |
| H | -1.48355000 | 4.81696400 | 3.09594400 |
| H | -2.21406200 | 4.50040400 | -1.11577100 |
| H | 1.45685000 | -2.38805700 | 1.66971000 |
| C | 1.54747200 | -4.12548600 | 0.45689300 |
| H | 2.24969900 | -4.88461900 | 0.11261600 |
| H | 0.84668100 | -4.60943900 | 1.14149600 |
| H | 0.98052500 | -3.75152900 | -0.39705700 |
| H | -3.42097500 | -1.80373300 | -2.08468600 |
| H | 0.15661700 | 1.59378800 | 0.89160600 |



Optimized Structure of *E,Z*-**4**-An-**TS$_3$**-**PA**.

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- Thermochemistry -

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(1 imaginary frequency = -273.08 Hz)

Zero-point correction= 0.727902 (Hartree/Particle)

Thermal correction to Energy= 0.767538

Thermal correction to Enthalpy= 0.768482

Thermal correction to Gibbs Free Energy= 0.652541

Sum of electronic and zero-point Energies= -1861.856001

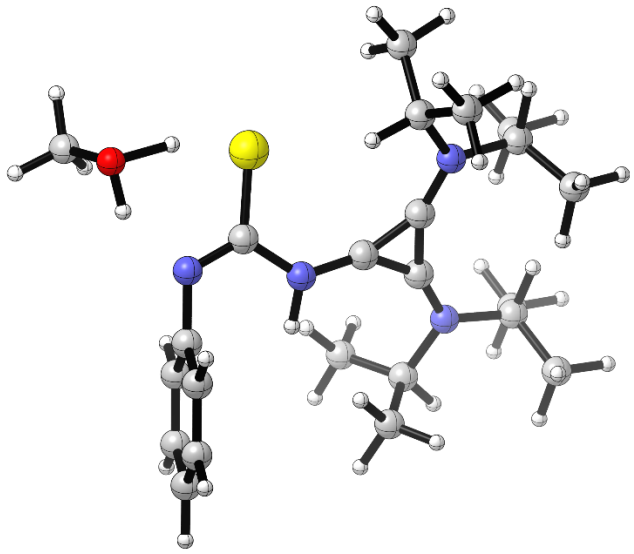
Sum of electronic and thermal Energies= -1861.816366

Sum of electronic and thermal Enthalpies= -1861.815422

Sum of electronic and thermal Free Energies= -1861.931363

| | | | |
|---|---|---|---|
| C | -0.90630700 | 0.12136600 | -0.29647000 |
| S | -0.86504100 | -1.41997700 | -1.06147700 |
| N | 0.31384400 | 0.70011700 | 0.12568400 |
| H | 0.28341300 | 1.70114000 | 0.27357600 |
| N | -2.00042900 | 0.78498200 | -0.15919600 |
| C | -2.03222300 | 2.03152800 | 0.49187800 |
| C | -1.79846900 | 2.14672100 | 1.86708300 |
| C | -2.37519800 | 3.17464800 | -0.23498500 |
| C | -1.89882400 | 3.38199600 | 2.49414200 |
| H | -1.55091500 | 1.25709200 | 2.43695500 |
| C | -2.46839300 | 4.40696400 | 0.39774200 |
| H | -2.57076400 | 3.07612700 | -1.29675400 |
| C | -2.23111700 | 4.51680000 | 1.76333100 |
| H | -2.31433900 | 5.47803400 | 2.25598400 |
| H | -3.32110200 | -0.98764900 | 1.13171200 |
| C | -4.51192900 | -1.91246000 | -0.37724800 |
| C | -4.37650600 | -1.17204300 | 0.92835300 |
| C | -5.19384600 | 0.13173300 | 0.94386400 |
| C | -6.37520200 | 0.06230800 | -0.03894500 |
| C | -6.82730000 | -1.37144900 | -0.23962100 |
| H | -5.55437200 | 0.30621600 | 1.95954900 |
| H | -4.54576800 | 0.96836900 | 0.68367000 |
| H | -7.22108800 | 0.65071700 | 0.32213700 |
| H | -6.08695300 | 0.47949700 | -1.00717400 |
| H | -7.16151600 | -1.81921400 | 0.70188200 |
| H | -7.63370400 | -1.45421000 | -0.96603800 |
| O | -5.76724900 | -2.20348700 | -0.76943900 |
| H | -3.89133400 | -2.80593400 | -0.45711000 |
| H | -4.73963200 | -1.87361300 | 1.68638900 |
| C | -3.92713800 | -1.51263300 | -2.80605300 |
| H | -3.31233500 | -2.41233600 | -2.84706400 |
| H | -3.52025500 | -0.73851700 | -3.45107500 |
| H | -4.96490000 | -1.72446200 | -3.04350600 |
| O | -3.90856500 | -0.97310800 | -1.46045100 |
| H | -2.94985100 | -0.77733900 | -1.20136400 |
| H | -2.73512600 | 5.28606700 | -0.17798900 |
| H | -1.72392200 | 3.45732000 | 3.56151100 |
| C | 1.53966500 | 0.14843700 | 0.03051800 |
| C | 2.44739700 | -0.86584100 | 0.23887800 |
| C | 2.86166800 | 0.38738800 | -0.24623300 |
| N | 2.79131000 | -2.08083600 | 0.61230200 |
| N | 3.78210700 | 1.23690200 | -0.65479400 |
| C | 4.20963600 | -2.47193400 | 0.43223000 |
| C | 1.92300100 | -2.90614700 | 1.49466100 |
| C | 5.21916500 | 0.90573400 | -0.58358400 |
| C | 3.34983100 | 2.52932800 | -1.23473000 |
| C | 5.02910100 | -2.13119500 | 1.67665800 |
| H | 4.56518700 | -1.86988900 | -0.40688600 |
| C | 4.36645100 | -3.93038600 | 0.01929900 |
| C | 1.11496600 | -3.94044000 | 0.71737300 |
| H | 2.62492900 | -3.42876900 | 2.15059000 |
| C | 1.03193300 | -2.03915500 | 2.37873300 |
| H | 5.27406500 | -0.01983800 | -0.01145800 |
| C | 5.79242800 | 0.65078500 | -1.97452100 |

| | | | |
|---|---|---|---|
| C | 5.99655900 | 1.96400600 | 0.19426000 |
| H | 4.25527800 | 2.96726600 | -1.65796500 |
| C | 2.35808400 | 2.32458500 | -2.37665400 |
| C | 2.82825000 | 3.47450500 | -0.15518500 |
| H | 4.90404100 | -1.08232400 | 1.95957100 |
| H | 4.73151800 | -2.74758900 | 2.52864400 |
| H | 6.09028200 | -2.31366200 | 1.49242300 |
| H | 4.04735100 | -4.61844200 | 0.80528600 |
| H | 3.80217200 | -4.14605400 | -0.88920200 |
| H | 5.42195100 | -4.12760200 | -0.17914100 |
| H | 0.40340100 | -3.43949600 | 0.06076800 |
| H | 1.75276500 | -4.59011400 | 0.11860000 |
| H | 0.56056400 | -4.56689700 | 1.42100100 |
| H | 1.60855400 | -1.27175900 | 2.90175000 |
| H | 0.23776400 | -1.56399400 | 1.79910800 |
| H | 0.55592900 | -2.67353800 | 3.12877900 |
| H | 5.75519700 | 1.55033400 | -2.59471300 |
| H | 6.83875200 | 0.34737200 | -1.89799500 |
| H | 5.23958900 | -0.14073400 | -2.48612200 |
| H | 5.56703000 | 2.11337400 | 1.18714700 |
| H | 7.03203500 | 1.63948600 | 0.31501800 |
| H | 6.01476400 | 2.92533700 | -0.32523100 |
| H | 2.15870000 | 3.28111300 | -2.86375200 |
| H | 2.76031400 | 1.63596500 | -3.12248500 |
| H | 1.40280400 | 1.92706900 | -2.02450800 |
| H | 1.93407600 | 3.07578800 | 0.33241900 |
| H | 3.58152000 | 3.64730100 | 0.61524900 |
| H | 2.55918400 | 4.43632400 | -0.59605300 |



Optimized Structure of *E,Z*-**4**-An-**TS$_3$-MA**.

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- Thermochemistry -

---

(1 imaginary frequency = -725.18 Hz)

Zero-point correction= 0.596299 (Hartree/Particle)

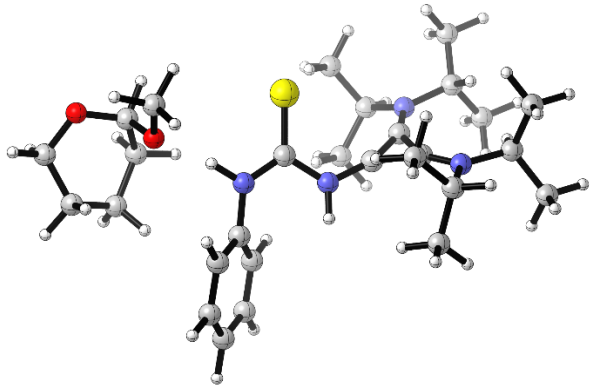
Thermal correction to Energy= 0.630391

Thermal correction to Enthalpy= 0.631335

Thermal correction to Gibbs Free Energy= 0.528663
Sum of electronic and zero-point Energies= -1591.443262
Sum of electronic and thermal Energies= -1591.409169
Sum of electronic and thermal Enthalpies= -1591.408225
Sum of electronic and thermal Free Energies= -1591.510897

| | | | |
|---|---|---|---|
| C | 1.92032800 | 1.02343500 | 0.08929100 |
| S | 1.35153500 | 2.57634200 | 0.63804100 |
| N | 0.96890900 | 0.03010300 | -0.16349700 |
| H | 1.36931700 | -0.89259600 | -0.28524400 |
| N | 3.16967000 | 0.74532100 | -0.05046300 |
| C | 3.54614200 | -0.56839100 | -0.43426000 |
| C | 3.67718000 | -1.56477000 | 0.53548300 |
| C | 3.78735500 | -0.87162000 | -1.77378400 |
| C | 4.03445500 | -2.85545900 | 0.16284100 |
| H | 3.50837200 | -1.31545200 | 1.57770600 |
| C | 4.14653300 | -2.16361200 | -2.13675400 |
| H | 3.69477200 | -0.09000700 | -2.51893500 |
| C | 4.26723800 | -3.15884500 | -1.17313000 |
| H | 4.55387300 | -4.16316400 | -1.46104300 |
| H | 4.33785000 | -2.39111100 | -3.17892400 |
| H | 4.14341000 | -3.62129800 | 0.92223200 |
| C | -0.37744700 | 0.06207000 | -0.06378800 |
| C | -1.62615100 | 0.63333400 | -0.17206100 |
| C | -1.47410000 | -0.73541200 | 0.13217900 |
| N | -2.38710700 | 1.67965900 | -0.40106100 |
| N | -1.91342100 | -1.95060600 | 0.39295200 |
| C | -1.78004300 | 2.94173900 | -0.89224200 |
| C | -3.85238800 | 1.61232400 | -0.21164500 |
| C | -3.35324100 | -2.27709400 | 0.44627400 |
| C | -0.91933800 | -3.02584100 | 0.62770600 |
| C | -2.33510100 | 3.31970000 | -2.26191900 |
| H | -0.71652100 | 2.72937900 | -0.99862400 |
| C | -1.93404400 | 4.05273100 | 0.13949600 |
| C | -4.20117700 | 1.23284800 | 1.22535700 |
| H | -4.19709500 | 2.63687600 | -0.35554800 |
| C | -4.51281500 | 0.76100700 | -1.29584200 |
| H | -3.86912100 | -1.33930800 | 0.25415600 |
| C | -3.73717200 | -3.25891600 | -0.65616900 |
| C | -3.75967800 | -2.75171000 | 1.83877100 |
| H | -1.51394300 | -3.90408600 | 0.88171500 |
| C | -0.13952300 | -3.35826000 | -0.64293600 |
| C | -0.03032000 | -2.71440600 | 1.82869400 |
| H | -2.20008700 | 2.50909500 | -2.98138700 |
| H | -3.39713400 | 3.57668600 | -2.22012400 |
| H | -1.80297200 | 4.19684100 | -2.63498800 |
| H | -2.98077000 | 4.33241300 | 0.28822400 |
| H | -1.50927100 | 3.75048100 | 1.09825400 |
| H | -1.40172300 | 4.94266300 | -0.20267200 |
| H | -3.79524700 | 0.26154600 | 1.51477400 |
| H | -3.80283700 | 1.97739700 | 1.91748700 |
| H | -5.28487700 | 1.19273800 | 1.35128700 |
| H | -4.38426300 | 1.22689300 | -2.27424100 |
| H | -4.08437700 | -0.24142500 | -1.35502400 |
| H | -5.58312600 | 0.66201900 | -1.10356300 |
| H | -3.25451700 | -4.23050600 | -0.52175100 |

| | | | |
|---|---|---|---|
| H | -4.81631600 | -3.42466300 | -0.64182400 |
| H | -3.46317400 | -2.86966800 | -1.63952900 |
| H | -3.48026900 | -2.01882600 | 2.59905900 |
| H | -4.84214100 | -2.88927800 | 1.87738300 |
| H | -3.30009300 | -3.70892600 | 2.09727600 |
| H | 0.55732700 | -4.17597000 | -0.44983900 |
| H | -0.81534800 | -3.66185200 | -1.44446900 |
| H | 0.44917100 | -2.51376500 | -1.01184900 |
| H | 0.62236800 | -1.85617100 | 1.65202400 |
| H | -0.63480100 | -2.50699700 | 2.71391100 |
| H | 0.61017600 | -3.57210000 | 2.04373200 |
| H | 2.84630000 | 3.10573400 | 0.67627000 |
| O | 4.11089100 | 3.12183200 | 0.60760100 |
| H | 4.13678800 | 2.18974700 | 0.25582400 |
| C | 4.70982200 | 3.14506500 | 1.91212000 |
| H | 5.77710200 | 2.94888700 | 1.81513400 |
| H | 4.55965800 | 4.14137500 | 2.32246800 |
| H | 4.24640400 | 2.39943900 | 2.56357800 |



Optimized Structure of *E,Z*-**4**-An-**INT**$_5$.

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- Thermochemistry -

---

(0 imaginary frequencies)

Zero-point correction= 0.729562 (Hartree/Particle)

Thermal correction to Energy= 0.769857

Thermal correction to Enthalpy= 0.770801

Thermal correction to Gibbs Free Energy= 0.650830

Sum of electronic and zero-point Energies= -1861.900872

Sum of electronic and thermal Energies= -1861.860577

Sum of electronic and thermal Enthalpies= -1861.859633

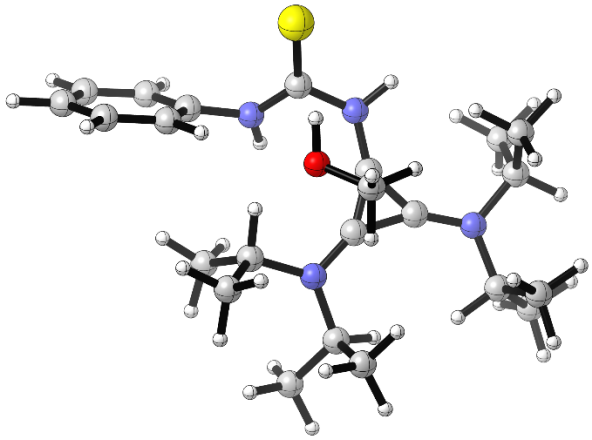
Sum of electronic and thermal Free Energies= -1861.979604

| | | | |
|---|---|---|---|
| C | 0.66451700 | 0.01693500 | 0.46465900 |
| S | 0.40131600 | -1.25430900 | 1.50945400 |
| N | -0.38913800 | 0.66060200 | -0.17667100 |
| H | -0.22831300 | 1.59397800 | -0.53352800 |
| N | 1.87098100 | 0.53134000 | 0.21100700 |
| C | 2.20374500 | 1.52833600 | -0.74569200 |
| C | 1.86552300 | 1.37893000 | -2.09008300 |
| C | 2.96337700 | 2.61892900 | -0.33124500 |

| | | | |
|---|---|---|---|
| C | 2.27339100 | 2.33466200 | -3.01082100 |
| H | 1.31481300 | 0.50286100 | -2.41337400 |
| C | 3.38074500 | 3.56076500 | -1.26169300 |
| H | 3.23392700 | 2.71088000 | 0.71407700 |
| C | 3.03269800 | 3.42424600 | -2.60042300 |
| H | 3.36088900 | 4.15996600 | -3.32454400 |
| H | 3.39970000 | -1.58123200 | -0.70387100 |
| C | 4.63327300 | -1.61193200 | 1.05164600 |
| C | 4.46378200 | -1.61332700 | -0.45743200 |
| C | 5.24361800 | -0.46020900 | -1.11891100 |
| C | 6.44875600 | -0.05163300 | -0.25505900 |
| C | 6.94957900 | -1.23919700 | 0.55214500 |
| H | 5.57981600 | -0.78371500 | -2.10749600 |
| H | 4.59559300 | 0.40360800 | -1.27781000 |
| H | 7.26280000 | 0.33279600 | -0.87405400 |
| H | 6.15881300 | 0.74094800 | 0.43879100 |
| H | 7.27033400 | -2.04637700 | -0.11972300 |
| H | 7.80015000 | -0.96673000 | 1.17753700 |
| O | 5.95923300 | -1.75244900 | 1.44777600 |
| H | 4.08917500 | -2.43800900 | 1.52273200 |
| H | 4.84025200 | -2.57723100 | -0.81071500 |
| C | 4.02915900 | -0.32434500 | 2.96267300 |
| H | 3.36381600 | -1.10170600 | 3.35508300 |
| H | 3.62717600 | 0.65535800 | 3.22101600 |
| H | 5.02697700 | -0.43843100 | 3.39002300 |
| O | 4.08561000 | -0.38844200 | 1.54473400 |
| H | 2.65442500 | 0.14726800 | 0.76500600 |
| H | 3.98034200 | 4.40346100 | -0.93891700 |
| H | 2.01905800 | 2.21311000 | -4.05709700 |
| C | -1.67902400 | 0.23200600 | -0.08895100 |
| C | -2.63164900 | -0.73479200 | -0.29718100 |
| C | -2.97674400 | 0.54240900 | 0.21144900 |
| N | -3.01928300 | -1.92821800 | -0.66776500 |
| N | -3.85389000 | 1.41160100 | 0.65147000 |
| C | -4.44344600 | -2.29910900 | -0.47683000 |
| C | -2.13251200 | -2.80871500 | -1.47786600 |
| C | -5.30645600 | 1.14594400 | 0.56727000 |
| C | -3.36024900 | 2.65880900 | 1.28546700 |
| C | -5.24638500 | -2.01516900 | -1.74412300 |
| H | -4.79948600 | -1.64911700 | 0.32519900 |
| C | -4.60623900 | -3.73276200 | 0.01290500 |
| C | -1.31876400 | -3.76429800 | -0.61251400 |
| H | -2.82034000 | -3.38789200 | -2.09900000 |
| C | -1.24470200 | -1.99279100 | -2.41216400 |
| H | -5.39968400 | 0.25245100 | -0.05125300 |
| C | -5.88725800 | 0.85106200 | 1.94624000 |
| C | -6.03226000 | 2.27568700 | -0.15756000 |
| H | -4.24543600 | 3.12429300 | 1.72135900 |
| C | -2.38624000 | 2.35304600 | 2.41919700 |
| C | -2.78167200 | 3.61195900 | 0.24426200 |
| H | -5.12623600 | -0.97652900 | -2.06444400 |
| H | -4.93282100 | -2.66230600 | -2.56717000 |
| H | -6.30803300 | -2.19930900 | -1.56599400 |
| H | -4.27803600 | -4.46246500 | -0.73050000 |
| H | -4.05381700 | -3.89909000 | 0.93886900 |
| H | -5.66406200 | -3.91890800 | 0.20855700 |

| | | | |
|---|---|---|---|
| H | -0.63442900 | -3.20503000 | 0.02715800 |
| H | -1.95597000 | -4.38438300 | 0.01761300 |
| H | -0.73294900 | -4.42483700 | -1.25621700 |
| H | -1.82721500 | -1.27650500 | -2.99717400 |
| H | -0.46679100 | -1.45904200 | -1.86079700 |
| H | -0.74465700 | -2.66997200 | -3.10660800 |
| H | -5.80170100 | 1.71507600 | 2.61048000 |
| H | -6.94803000 | 0.60698100 | 1.85949500 |
| H | -5.37555500 | 0.00740300 | 2.41556500 |
| H | -5.59676300 | 2.45165600 | -1.14339900 |
| H | -7.08170800 | 2.00644000 | -0.29111400 |
| H | -6.00560400 | 3.21091100 | 0.40693300 |
| H | -2.13135500 | 3.27740400 | 2.94106800 |
| H | -2.82834600 | 1.66237000 | 3.13984300 |
| H | -1.45584700 | 1.91237800 | 2.05112800 |
| H | -1.89173300 | 3.18742000 | -0.22965600 |
| H | -3.51087800 | 3.83698400 | -0.53566500 |
| H | -2.48412300 | 4.54894300 | 0.71877100 |

Z,Z Conformation



Optimized Structure of *Z,Z*-**4**-An-**INT**$_1$.

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- Thermochemistry -

---

(0 imaginary frequencies)

Zero-point correction= 0.603114 (Hartree/Particle)

Thermal correction to Energy= 0.637273

Thermal correction to Enthalpy= 0.638217

Thermal correction to Gibbs Free Energy= 0.538294

Sum of electronic and zero-point Energies= -1591.457405

Sum of electronic and thermal Energies= -1591.423246

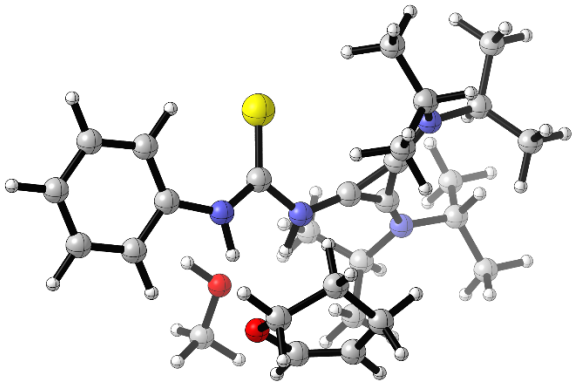
Sum of electronic and thermal Enthalpies= -1591.422301

Sum of electronic and thermal Free Energies= -1591.522225

| | | | |
|---|---|---|---|
| C | 1.46866000 | -1.95857500 | -0.23013700 |

| | | | |
|---|---|---|---|
| S | 2.09035800 | -3.11540300 | 0.77020300 |
| N | 2.13681200 | -0.98878600 | -0.87202100 |
| H | 1.67062400 | -0.53689100 | -1.64584400 |
| N | 0.08600500 | -1.93641900 | -0.50050700 |
| C | 3.48011300 | -0.57744400 | -0.61713700 |
| C | 3.83310500 | -0.11440200 | 0.64620600 |
| C | 4.39214300 | -0.56826300 | -1.66254900 |
| C | 5.11941200 | 0.35822800 | 0.85804500 |
| H | 3.10486000 | -0.11891400 | 1.44907000 |
| C | 5.67510700 | -0.08178200 | -1.44316100 |
| H | 4.10305500 | -0.94658000 | -2.63660300 |
| C | 6.03975900 | 0.37945000 | -0.18496800 |
| H | 7.04213200 | 0.75345700 | -0.01510800 |
| H | -0.37420200 | -2.80167400 | -0.25472200 |
| C | -0.58501600 | -0.38449100 | 2.92995400 |
| H | -1.32278200 | -1.11259800 | 2.56539600 |
| H | -1.00070900 | 0.61824900 | 2.81023800 |
| H | -0.41629400 | -0.55988500 | 3.99675500 |
| O | 0.61602200 | -0.42778100 | 2.18576300 |
| H | 1.01593400 | -1.29874900 | 2.28161900 |
| C | -0.68988300 | -0.82662700 | -0.48166600 |
| C | -0.89064500 | 0.53024000 | -0.37182600 |
| C | -1.97636700 | -0.35111300 | -0.46432700 |
| N | -0.43318000 | 1.75897300 | -0.24166800 |
| N | -3.26650000 | -0.61675300 | -0.46162500 |
| C | -1.43170700 | 2.85763000 | -0.27885500 |
| C | 1.01646000 | 1.92664600 | 0.05423000 |
| C | -4.26604500 | 0.45080600 | -0.24596900 |
| C | -3.70550800 | -2.02848300 | -0.54448800 |
| C | -2.02304600 | 3.12858000 | 1.10374600 |
| H | -2.22734400 | 2.47849100 | -0.92593400 |
| C | -0.91737900 | 4.12238400 | -0.95566800 |
| C | 1.28676800 | 2.74979700 | 1.30738200 |
| H | -3.69476400 | 1.37739200 | -0.20284900 |
| C | -5.23296100 | 0.54636500 | -1.42193100 |
| C | -4.97294300 | 0.27731200 | 1.09540700 |
| H | -4.79487300 | -1.98371200 | -0.57595000 |
| C | -3.23256300 | -2.67905400 | -1.84054000 |
| C | -3.30879900 | -2.81027700 | 0.70591300 |
| H | -2.39987000 | 2.20801500 | 1.55857500 |
| H | -1.28410400 | 3.56294700 | 1.77788000 |
| H | -2.85648000 | 3.83045200 | 1.02059800 |
| H | -0.13425700 | 4.61793500 | -0.38150400 |
| H | -0.54169200 | 3.91281000 | -1.95794000 |
| H | -1.74778300 | 4.82530500 | -1.04693700 |
| H | 1.02287700 | 3.80283400 | 1.19764300 |
| H | 0.76447600 | 2.32977300 | 2.16770200 |
| H | 2.35813800 | 2.69994800 | 1.51466800 |
| H | -5.85960700 | -0.34469300 | -1.50889900 |
| H | -5.90051300 | 1.39868300 | -1.28048500 |
| H | -4.69504500 | 0.68348800 | -2.36226000 |
| H | -5.57503400 | -0.63477900 | 1.12076500 |
| H | -4.25110900 | 0.23895100 | 1.91490000 |
| H | -5.64607500 | 1.11890300 | 1.27048400 |
| H | -3.65125500 | -3.68353500 | -1.92564200 |
| H | -3.55779000 | -2.09869200 | -2.70603400 |

| | | | |
|---|---|---|---|
| H | -2.14369800 | -2.77246600 | -1.88344200 |
| H | -2.22286800 | -2.87221700 | 0.82516000 |
| H | -3.71556300 | -2.34393400 | 1.60509900 |
| H | -3.69113800 | -3.83104500 | 0.64690000 |
| H | 5.40321800 | 0.71502600 | 1.84092500 |
| H | 6.39236100 | -0.07416700 | -2.25477000 |
| H | 1.33762600 | 0.91839500 | 0.29970400 |
| C | 1.81501900 | 2.40544000 | -1.15620400 |
| H | 1.67400600 | 3.46729100 | -1.35813500 |
| H | 2.87835600 | 2.23908200 | -0.96897200 |
| H | 1.53922700 | 1.85248100 | -2.05940900 |



Optimized Structure of *Z,Z*-**4**-An-**INT**$_2$.

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- Thermochemistry -

---

(0 imaginary frequencies)

Zero-point correction= 0.728586 (Hartree/Particle)

Thermal correction to Energy= 0.769970

Thermal correction to Enthalpy= 0.770914

Thermal correction to Gibbs Free Energy= 0.652420

Sum of electronic and zero-point Energies= -1861.889420

Sum of electronic and thermal Energies= -1861.848036

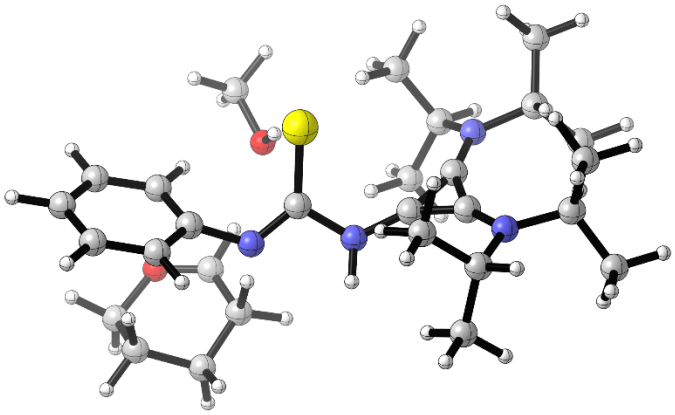
Sum of electronic and thermal Enthalpies= -1861.847092

Sum of electronic and thermal Free Energies= -1861.965586

| | | | |
|---|---|---|---|
| C | -1.39131800 | 0.71678400 | -0.75545300 |
| S | -0.99527400 | 1.97677900 | -1.75184100 |
| N | -0.40841200 | -0.16574100 | -0.26344700 |
| H | -0.68246900 | -1.14942000 | -0.27401200 |
| N | -2.59961300 | 0.32172300 | -0.31857600 |
| C | -3.91566400 | 0.70253000 | -0.67753400 |
| C | -4.25293400 | 1.86499900 | -1.36493300 |
| C | -4.91833100 | -0.18385200 | -0.26782800 |
| C | -5.59112100 | 2.11942400 | -1.64599300 |
| H | -3.48816500 | 2.56047800 | -1.67241900 |
| C | -6.24605000 | 0.08825000 | -0.55108900 |
| H | -4.64795400 | -1.08130300 | 0.28060300 |
| C | -6.58884400 | 1.24215000 | -1.24739100 |
| H | -7.62691600 | 1.45571400 | -1.47089300 |
| H | -2.58622300 | -0.45083700 | 0.34871000 |
| C | -1.60234300 | -2.35665000 | 2.10395700 |
| C | -0.55396400 | -2.06194800 | 2.86669800 |

| | | | |
|---|---|---|---|
| C | -0.44032600 | -0.76310600 | 3.61367700 |
| C | -1.53097800 | 0.21034600 | 3.15961300 |
| C | -2.83682400 | -0.53492400 | 2.94193500 |
| H | -0.51633800 | -0.94922700 | 4.69077600 |
| H | 0.54970000 | -0.32372500 | 3.45261900 |
| H | -1.68160900 | 1.00765000 | 3.89070200 |
| H | -1.24325400 | 0.68192900 | 2.21716100 |
| H | -3.17007200 | -1.02820400 | 3.86087600 |
| H | -3.63085100 | 0.12076200 | 2.58379700 |
| O | -2.68702200 | -1.54327900 | 1.92912400 |
| H | -1.70083100 | -3.27742200 | 1.54382700 |
| H | 0.23131100 | -2.80299800 | 2.95770200 |
| C | -2.17619800 | -3.82550100 | -1.13936300 |
| H | -3.12099900 | -3.98063100 | -0.60919800 |
| H | -1.38027400 | -4.34008900 | -0.60126700 |
| H | -2.24839500 | -4.25431800 | -2.14280700 |
| O | -1.82352400 | -2.44947600 | -1.18540300 |
| H | -2.47565700 | -1.97761900 | -1.70771000 |
| H | -5.84898600 | 3.02531200 | -2.18178500 |
| H | -7.01373000 | -0.60469500 | -0.22784500 |
| C | 0.91587900 | 0.08585900 | -0.30367700 |
| C | 2.16480900 | -0.45772800 | -0.45558800 |
| C | 2.01150800 | 0.89822900 | -0.11665000 |
| N | 2.90754500 | -1.51182000 | -0.72345600 |
| N | 2.59637700 | 2.04580800 | 0.15928200 |
| C | 4.37588600 | -1.46772200 | -0.56603900 |
| C | 2.26294300 | -2.73403800 | -1.25687300 |
| C | 4.07421700 | 2.10191700 | 0.04585300 |
| C | 1.88926300 | 3.15043400 | 0.86052700 |
| C | 4.87705000 | -2.60186700 | 0.32369300 |
| H | 4.58090200 | -0.53626800 | -0.04003100 |
| C | 5.07056800 | -1.42469000 | -1.92377400 |
| C | 1.42224500 | -2.43068900 | -2.49351300 |
| H | 3.08998100 | -3.37338800 | -1.56978700 |
| C | 1.48449700 | -3.46429600 | -0.16626800 |
| H | 4.33106800 | 1.33669000 | -0.68903200 |
| C | 4.57029000 | 3.42812200 | -0.51815700 |
| C | 4.73533900 | 1.76013100 | 1.38063300 |
| H | 2.65221300 | 3.58930800 | 1.50927200 |
| C | 1.38207100 | 4.22576900 | -0.09521900 |
| C | 0.77528400 | 2.62535900 | 1.75745300 |
| H | 4.36962200 | -2.59426400 | 1.29064500 |
| H | 4.73531800 | -3.58230900 | -0.13735500 |
| H | 5.94738100 | -2.47669700 | 0.49898200 |
| H | 4.89775300 | -2.34360300 | -2.49027600 |
| H | 4.71170400 | -0.58260500 | -2.52051900 |
| H | 6.14905500 | -1.31778300 | -1.78983900 |
| H | 0.51696100 | -1.87067200 | -2.25052900 |
| H | 2.00191400 | -1.86753900 | -3.22760600 |
| H | 1.10416800 | -3.36809700 | -2.95482400 |
| H | 2.13150600 | -3.71712000 | 0.67583700 |
| H | 0.65666900 | -2.85788700 | 0.21136600 |
| H | 1.06704200 | -4.39059500 | -0.56748600 |
| H | 4.37730100 | 4.26230600 | 0.15987800 |
| H | 5.65094900 | 3.36515500 | -0.66070700 |
| H | 4.11093000 | 3.64290100 | -1.48398500 |

| | | | |
|---|---|---|---|
| H | 4.36159700 | 0.81339200 | 1.78087000 |
| H | 5.81712500 | 1.67603600 | 1.25455400 |
| H | 4.55013200 | 2.53713700 | 2.12647400 |
| H | 0.94017000 | 5.04173100 | 0.48185000 |
| H | 2.18295600 | 4.64099300 | -0.70564000 |
| H | 0.61703000 | 3.81673000 | -0.75492100 |
| H | -0.07274600 | 2.27409300 | 1.16704400 |
| H | 1.12482700 | 1.81816000 | 2.40646400 |
| H | 0.41393600 | 3.43685400 | 2.39136000 |



Optimized Structure of *Z,Z*-**4**-An-**TS**$_1$.

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- Thermochemistry -

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(1 imaginary frequency = -373.31 Hz)

Zero-point correction= 0.722930 (Hartree/Particle)

Thermal correction to Energy= 0.763533

Thermal correction to Enthalpy= 0.764478

Thermal correction to Gibbs Free Energy= 0.648222

Sum of electronic and zero-point Energies= -1861.842948

Sum of electronic and thermal Energies= -1861.802345

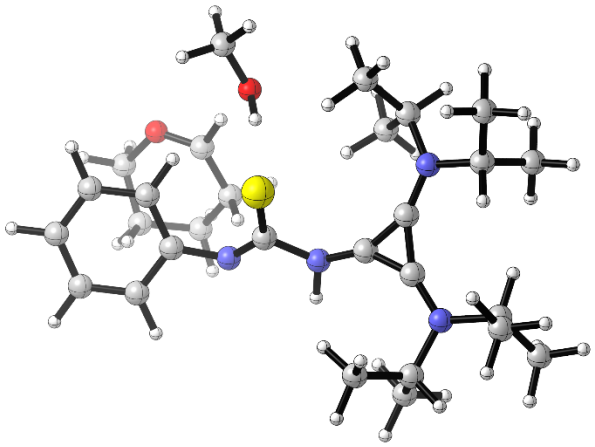
Sum of electronic and thermal Enthalpies= -1861.801401

Sum of electronic and thermal Free Energies= -1861.917656

| | | | |
|---|---|---|---|
| C | 0.80654200 | -0.47955800 | -0.56154100 |
| S | 0.39578500 | 0.41804800 | -1.93953800 |
| N | -0.20273100 | -0.74495500 | 0.40781400 |
| H | -0.04743300 | -1.61638400 | 0.89644700 |
| N | 1.93502200 | -1.03121600 | -0.20237400 |
| C | 3.08899900 | -1.03721200 | -1.01633400 |
| C | 3.62453400 | -2.27293300 | -1.38098100 |
| C | 3.79411500 | 0.12723100 | -1.31837200 |
| C | 4.84768800 | -2.34289700 | -2.03229100 |
| H | 3.07319300 | -3.17356900 | -1.13626200 |
| C | 5.02580800 | 0.05187100 | -1.95757800 |
| H | 3.37751900 | 1.08777600 | -1.04470900 |
| C | 5.55870300 | -1.18030500 | -2.31417400 |
| H | 6.51648500 | -1.23645800 | -2.81777300 |
| H | 2.45452400 | -0.54260000 | 1.15812200 |
| C | 3.58800100 | 1.01846400 | 1.78962800 |
| C | 2.97701900 | -0.18156700 | 2.21216900 |
| C | 3.89470600 | -1.29796400 | 2.68232900 |

| | | | |
|---|---|---|---|
| C | 5.19980800 | -1.23118700 | 1.88651800 |
| C | 5.80241900 | 0.15364200 | 1.97401400 |
| H | 4.09581200 | -1.20548800 | 3.75403000 |
| H | 3.40845000 | -2.26248100 | 2.52538300 |
| H | 5.93316200 | -1.94281700 | 2.27146300 |
| H | 5.01893000 | -1.48234000 | 0.83862100 |
| H | 6.14125400 | 0.40370500 | 2.98139500 |
| H | 6.61673100 | 0.30347800 | 1.26933300 |
| O | 4.84146000 | 1.20470800 | 1.62019000 |
| H | 2.98875200 | 1.87095500 | 1.46369600 |
| H | 2.06704700 | 0.00878100 | 2.78433500 |
| C | 2.36729200 | 3.79258400 | -0.91974900 |
| H | 3.06732900 | 3.45440100 | -1.69223900 |
| H | 2.88712600 | 4.48212900 | -0.25402500 |
| H | 1.54409700 | 4.32839300 | -1.40409300 |
| O | 1.89305300 | 2.71177300 | -0.13365100 |
| H | 1.42076800 | 2.09996200 | -0.72319100 |
| H | 5.25142400 | -3.30787300 | -2.31643600 |
| H | 5.56547500 | 0.96436200 | -2.18529700 |
| C | -1.50480500 | -0.38862800 | 0.24680900 |
| C | -2.49231300 | 0.56320900 | 0.15104700 |
| C | -2.80594900 | -0.81142400 | 0.18018900 |
| N | -2.92309500 | 1.80022000 | 0.07711100 |
| N | -3.66837000 | -1.80400400 | 0.15474600 |
| C | -4.37244400 | 2.03005200 | -0.12939200 |
| C | -2.04301300 | 2.94394300 | 0.43573200 |
| C | -5.12303100 | -1.55318200 | 0.21135400 |
| C | -3.15871700 | -3.18148900 | -0.04347900 |
| C | -5.08358700 | 2.21740200 | 1.20934200 |
| H | -4.74100500 | 1.11941800 | -0.60572400 |
| C | -4.64474900 | 3.17412400 | -1.09862600 |
| C | -1.34966100 | 3.53537000 | -0.78678400 |
| H | -2.72329700 | 3.69147600 | 0.85268800 |
| C | -1.05621700 | 2.56026800 | 1.53308400 |
| H | -5.22374500 | -0.50833600 | 0.50738400 |
| C | -5.76185300 | -1.73834800 | -1.16181600 |
| C | -5.79105100 | -2.39164100 | 1.29730600 |
| H | -4.04458800 | -3.78530500 | -0.24640500 |
| C | -2.24865600 | -3.26895100 | -1.26544100 |
| C | -2.50317900 | -3.71027300 | 1.22864300 |
| H | -4.89392200 | 1.37510300 | 1.88036100 |
| H | -4.75084600 | 3.12996000 | 1.71032600 |
| H | -6.16185800 | 2.30000900 | 1.05591400 |
| H | -4.31991500 | 4.13691200 | -0.69768700 |
| H | -4.15048700 | 3.00593900 | -2.05654200 |
| H | -5.72018800 | 3.23993000 | -1.27516400 |
| H | -0.73370200 | 2.77608700 | -1.26945200 |
| H | -2.06681700 | 3.91394200 | -1.51492800 |
| H | -0.70829000 | 4.36224300 | -0.47349500 |
| H | -1.57002000 | 2.10919900 | 2.38631700 |
| H | -0.29026900 | 1.87551300 | 1.16580000 |
| H | -0.54105600 | 3.45869600 | 1.87615100 |
| H | -5.66815400 | -2.77066800 | -1.50938500 |
| H | -6.82681300 | -1.50082600 | -1.11644500 |
| H | -5.29267400 | -1.08627400 | -1.90265800 |
| H | -5.31519400 | -2.22784700 | 2.26642500 |

| | | | |
|---|---|---|---|
| H | -6.84172700 | -2.10690000 | 1.38052100 |
| H | -5.76131700 | -3.46031500 | 1.07118200 |
| H | -2.00512400 | -4.31439300 | -1.46477500 |
| H | -2.73989800 | -2.85692500 | -2.14894300 |
| H | -1.30789100 | -2.73212300 | -1.11960700 |
| H | -1.62583900 | -3.11438700 | 1.49835500 |
| H | -3.19846000 | -3.68895200 | 2.06948000 |
| H | -2.17046100 | -4.73964300 | 1.08109000 |



Optimized Structure of *Z,Z*-**4**-An-**INT**$_3$.

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- Thermochemistry -

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(0 imaginary frequencies)

Zero-point correction= 0.726072 (Hartree/Particle)

Thermal correction to Energy= 0.767283

Thermal correction to Enthalpy= 0.768227

Thermal correction to Gibbs Free Energy= 0.650427

Sum of electronic and zero-point Energies= -1861.842898

Sum of electronic and thermal Energies= -1861.801687

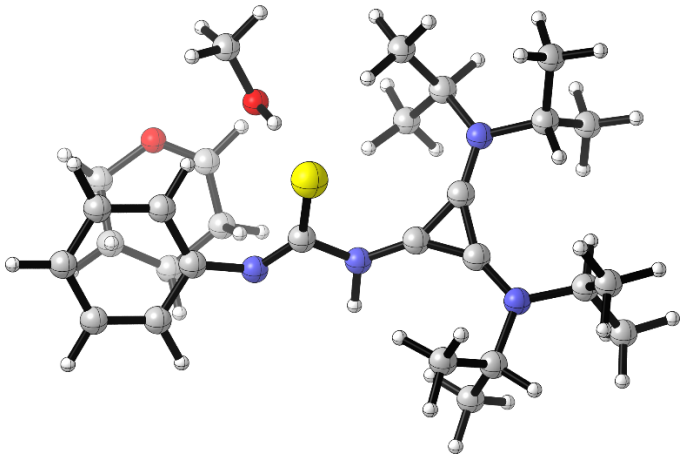
Sum of electronic and thermal Enthalpies= -1861.800743

Sum of electronic and thermal Free Energies= -1861.918543

| | | | |
|---|---|---|---|
| C | 0.73303400 | -0.61896700 | -0.56327800 |
| S | 0.43270900 | 0.48006600 | -1.83895300 |
| N | -0.36933000 | -0.95076900 | 0.28300700 |
| H | -0.26507300 | -1.86154500 | 0.70902200 |
| N | 1.77760300 | -1.30230500 | -0.21516400 |
| C | 2.99692900 | -1.29656600 | -0.89759000 |
| C | 3.64972300 | -2.53099500 | -1.02440500 |
| C | 3.66267100 | -0.14725200 | -1.33895900 |
| C | 4.91532100 | -2.61584500 | -1.58110200 |
| H | 3.13521300 | -3.41892600 | -0.67571100 |
| C | 4.94327900 | -0.23572300 | -1.87903000 |
| H | 3.16937000 | 0.81284100 | -1.28117400 |
| C | 5.57675100 | -1.46358200 | -2.00415900 |
| H | 6.56498000 | -1.53028900 | -2.44372800 |
| H | 2.61515200 | -0.46306100 | 1.44411100 |
| C | 3.91278100 | 1.11531700 | 1.37559200 |
| C | 3.32294500 | 0.03110600 | 2.14956900 |
| C | 4.32080900 | -0.95499200 | 2.75008400 |

| | | | |
|---|---|---|---|
| C | 5.53283400 | -1.06918600 | 1.82727400 |
| C | 6.14838500 | 0.28974000 | 1.60322000 |
| H | 4.63569600 | -0.61886700 | 3.74247100 |
| H | 3.84194500 | -1.92622500 | 2.87327300 |
| H | 6.29918900 | -1.71569100 | 2.25966900 |
| H | 5.24366400 | -1.50150100 | 0.86614300 |
| H | 6.58431900 | 0.72475200 | 2.50397700 |
| H | 6.87594000 | 0.30616400 | 0.79557800 |
| O | 5.14276600 | 1.28101600 | 1.16282400 |
| H | 3.27361400 | 1.88310100 | 0.91402700 |
| H | 2.65469500 | 0.50305100 | 2.88144100 |
| C | 2.41813800 | 3.73981300 | -1.18536800 |
| H | 2.97773400 | 3.28163900 | -2.00869600 |
| H | 3.06293300 | 4.45461900 | -0.67290800 |
| H | 1.56260500 | 4.27999300 | -1.60356800 |
| O | 2.00159600 | 2.77286700 | -0.23400900 |
| H | 1.45628900 | 2.11407000 | -0.70649100 |
| H | 5.39233300 | -3.58385400 | -1.68508300 |
| H | 5.43736200 | 0.66729400 | -2.22150800 |
| C | -1.62680800 | -0.47914300 | 0.16126500 |
| C | -2.54874000 | 0.54330900 | 0.11356400 |
| C | -2.96151600 | -0.79786900 | 0.15335200 |
| N | -2.89656000 | 1.81300700 | 0.07129500 |
| N | -3.89352700 | -1.73045000 | 0.17161700 |
| C | -4.33726000 | 2.12730100 | -0.06765000 |
| C | -1.95155600 | 2.89236700 | 0.46018300 |
| C | -5.32208300 | -1.37773900 | 0.28479400 |
| C | -3.49529600 | -3.13991600 | -0.04484900 |
| C | -4.99117800 | 2.30006800 | 1.30291900 |
| H | -4.77156900 | 1.25686800 | -0.56347400 |
| C | -4.58879300 | 3.32158700 | -0.98036500 |
| C | -1.28570000 | 3.54348600 | -0.74780300 |
| H | -2.57810600 | 3.63718100 | 0.95922400 |
| C | -0.93348100 | 2.39736600 | 1.48243700 |
| H | -5.33734600 | -0.32673500 | 0.57348900 |
| C | -6.02973600 | -1.52650700 | -1.05906600 |
| C | -6.00426600 | -2.15819000 | 1.40482200 |
| H | -4.43208100 | -3.67907200 | -0.19545100 |
| C | -2.66059900 | -3.29772100 | -1.31277000 |
| C | -2.81344000 | -3.71367100 | 1.19390300 |
| H | -4.80826200 | 1.43252000 | 1.94293400 |
| H | -4.60679000 | 3.18517400 | 1.81605800 |
| H | -6.07068800 | 2.42588900 | 1.19273000 |
| H | -4.21178600 | 4.25234900 | -0.55032100 |
| H | -4.12957700 | 3.17313300 | -1.95875300 |
| H | -5.66515200 | 3.43910100 | -1.12134900 |
| H | -0.72280500 | 2.79645700 | -1.30698400 |
| H | -2.01427800 | 4.00325500 | -1.41497800 |
| H | -0.59661600 | 4.31877400 | -0.40454900 |
| H | -1.42754400 | 1.93015600 | 2.33867600 |
| H | -0.23341700 | 1.68778500 | 1.03890200 |
| H | -0.34844300 | 3.24632400 | 1.83920600 |
| H | -6.03212700 | -2.56681600 | -1.39565800 |
| H | -7.07001200 | -1.20475500 | -0.97465800 |
| H | -5.54139200 | -0.92162000 | -1.82705700 |
| H | -5.47893900 | -2.02301400 | 2.35260700 |

| | | | |
|---|---|---|---|
| H | -7.02713300 | -1.79631400 | 1.52743100 |
| H | -6.06181400 | -3.22770300 | 1.18796300 |
| H | -2.48937400 | -4.35795800 | -1.50934300 |
| H | -3.17503900 | -2.86768100 | -2.17432400 |
| H | -1.68343500 | -2.81585100 | -1.22516800 |
| H | -1.87910100 | -3.18802200 | 1.41186300 |
| H | -3.45806100 | -3.63428200 | 2.07104200 |
| H | -2.57152500 | -4.76678500 | 1.03702200 |



Optimized Structure of *Z,Z*-**4**-An-**TS**$_2$.

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- Thermochemistry -

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(1 imaginary frequency = -44.43 Hz)

Zero-point correction= 0.725305 (Hartree/Particle)

Thermal correction to Energy= 0.765841

Thermal correction to Enthalpy= 0.766786

Thermal correction to Gibbs Free Energy= 0.651052

Sum of electronic and zero-point Energies= -1861.839806

Sum of electronic and thermal Energies= -1861.799269

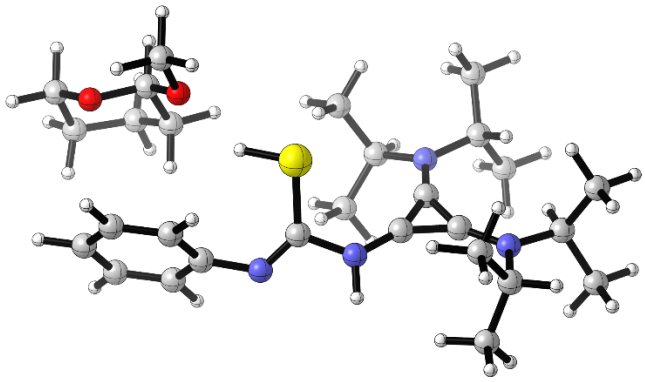
Sum of electronic and thermal Enthalpies= -1861.798325

Sum of electronic and thermal Free Energies= -1861.914058

| | | | |
|---|---|---|---|
| C | 0.74472700 | -0.72568000 | -0.50560000 |
| S | 0.39921700 | 0.18647900 | -1.91249100 |
| N | -0.33261000 | -0.91310500 | 0.42091100 |
| H | -0.23719300 | -1.77180000 | 0.94593000 |
| N | 1.79906200 | -1.34949600 | -0.08856000 |
| C | 2.99336100 | -1.49325000 | -0.81002200 |
| C | 3.66330000 | -2.71262400 | -0.64273700 |
| C | 3.61023500 | -0.49797800 | -1.57653700 |
| C | 4.89814700 | -2.93791100 | -1.23083800 |
| H | 3.18528800 | -3.47896200 | -0.04299300 |
| C | 4.85329200 | -0.72616200 | -2.15823800 |
| H | 3.11599800 | 0.44881500 | -1.72211400 |
| C | 5.50470400 | -1.94134900 | -1.99065100 |
| H | 6.46826300 | -2.11572200 | -2.45470000 |
| H | 2.55121700 | -0.18778500 | 1.35409100 |
| C | 3.58389300 | 1.52593800 | 1.78362200 |
| C | 3.17627400 | 0.19613100 | 2.20010300 |

| | | | |
|---|---|---|---|
| C | 4.32139900 | -0.76708000 | 2.49901400 |
| C | 5.47279500 | -0.50982800 | 1.52977800 |
| C | 5.90308400 | 0.93524500 | 1.57415000 |
| H | 4.65648500 | -0.64275300 | 3.53317400 |
| H | 3.96167600 | -1.78972400 | 2.38677900 |
| H | 6.34244400 | -1.12027200 | 1.78207100 |
| H | 5.17776400 | -0.77283700 | 0.51396200 |
| H | 6.39684500 | 1.21607600 | 2.50557600 |
| H | 6.52256700 | 1.22794700 | 0.73013700 |
| O | 4.75736600 | 1.87508100 | 1.49155200 |
| H | 2.85886100 | 2.32685400 | 1.68526100 |
| H | 2.45043700 | 0.30740900 | 3.01241500 |
| C | 2.68660400 | 3.25562700 | -1.20477000 |
| H | 3.20320200 | 2.76136700 | -2.03515200 |
| H | 3.41261000 | 3.85322600 | -0.65016600 |
| H | 1.92571000 | 3.92724800 | -1.61618000 |
| O | 2.12085300 | 2.31802500 | -0.30632200 |
| H | 1.54196200 | 1.71954800 | -0.82021900 |
| H | 5.38958300 | -3.89510900 | -1.09782700 |
| H | 5.30907700 | 0.05437100 | -2.75793700 |
| C | -1.58829100 | -0.44969900 | 0.24229700 |
| C | -2.48916500 | 0.57802400 | 0.07667400 |
| C | -2.92803800 | -0.74690400 | 0.23373000 |
| N | -2.80836300 | 1.84336900 | -0.09895700 |
| N | -3.87991600 | -1.65479000 | 0.31049400 |
| C | -4.23291600 | 2.17341300 | -0.33214100 |
| C | -1.84974600 | 2.93471000 | 0.21203000 |
| C | -5.30168500 | -1.26125000 | 0.36381900 |
| C | -3.50847200 | -3.08547700 | 0.22165100 |
| C | -4.93703500 | 2.51508400 | 0.98006900 |
| H | -4.67129500 | 1.26288000 | -0.74581600 |
| C | -4.41105600 | 3.26240100 | -1.38368100 |
| C | -1.10577700 | 3.42781600 | -1.02495400 |
| H | -2.47521700 | 3.74746700 | 0.59206000 |
| C | -0.89749900 | 2.53175600 | 1.33382100 |
| H | -5.29588600 | -0.19035700 | 0.56883000 |
| C | -5.98587400 | -1.49954300 | -0.97927400 |
| C | -6.02528100 | -1.93686800 | 1.52532200 |
| H | -4.45389700 | -3.61685300 | 0.10064600 |
| C | -2.65637200 | -3.36644300 | -1.01289400 |
| C | -2.85782400 | -3.56395000 | 1.51627200 |
| H | -4.80889000 | 1.72001300 | 1.71983500 |
| H | -4.54745100 | 3.44135900 | 1.41024400 |
| H | -6.00661400 | 2.65618600 | 0.80889900 |
| H | -4.01543600 | 4.22395800 | -1.04831400 |
| H | -3.92384500 | 2.98824900 | -2.32054200 |
| H | -5.47714600 | 3.39721400 | -1.57735600 |
| H | -0.53041800 | 2.61211900 | -1.46223300 |
| H | -1.78947500 | 3.81475900 | -1.78013600 |
| H | -0.42209200 | 4.23107500 | -0.73878800 |
| H | -1.44542200 | 2.15896300 | 2.20332100 |
| H | -0.18584000 | 1.77360400 | 1.00255000 |
| H | -0.32186500 | 3.40767400 | 1.63881300 |
| H | -6.01727100 | -2.56421300 | -1.22621900 |
| H | -7.01594500 | -1.13785800 | -0.94644500 |
| H | -5.46139000 | -0.97874400 | -1.78423100 |

| | | | |
|---|---|---|---|
| H | -5.51238700 | -1.74733900 | 2.47056700 |
| H | -7.03901100 | -1.53840900 | 1.60173800 |
| H | -6.11015500 | -3.01719300 | 1.38511500 |
| H | -2.50200500 | -4.44225300 | -1.11668100 |
| H | -3.14836000 | -3.00184200 | -1.91671800 |
| H | -1.67208700 | -2.89539500 | -0.94912100 |
| H | -1.91309400 | -3.04365300 | 1.69979400 |
| H | -3.51156500 | -3.39244600 | 2.37326400 |
| H | -2.63985800 | -4.63210100 | 1.45553100 |



Optimized Structure of *Z,Z*-**4**-An-**INT$_4$**.

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- Thermochemistry -

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(0 imaginary frequencies)

Zero-point correction= 0.726617 (Hartree/Particle)

Thermal correction to Energy= 0.766621

Thermal correction to Enthalpy= 0.767565

Thermal correction to Gibbs Free Energy= 0.651762

Sum of electronic and zero-point Energies= -1861.881249

Sum of electronic and thermal Energies= -1861.841246

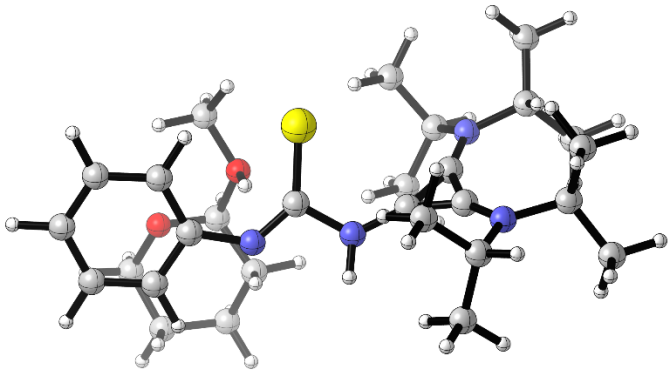
Sum of electronic and thermal Enthalpies= -1861.840301

Sum of electronic and thermal Free Energies= -1861.956105

| | | | |
|---|---|---|---|
| C | 0.19746700 | -1.51149600 | 0.13789000 |
| S | 0.55299600 | -0.62791400 | -1.36148500 |
| N | -1.20030400 | -1.69489800 | 0.28580200 |
| H | -1.44218400 | -2.50098300 | 0.84589300 |
| N | 0.92757100 | -2.04071900 | 1.01500100 |
| C | 2.33315300 | -2.08750200 | 0.99750900 |
| C | 2.99047600 | -1.75385100 | 2.18263900 |
| C | 3.07327400 | -2.51051700 | -0.10707300 |
| C | 4.37510400 | -1.79971200 | 2.24606300 |
| H | 2.40008400 | -1.46747900 | 3.04493700 |
| C | 4.45824500 | -2.55560500 | -0.03301800 |
| H | 2.56827500 | -2.81940100 | -1.01445300 |
| C | 5.11324000 | -2.19453400 | 1.13606800 |
| H | 6.19486500 | -2.22902300 | 1.18405900 |
| H | 3.59062700 | 0.39856900 | 0.62350500 |
| C | 4.41871600 | 1.09133400 | -1.20057700 |
| C | 3.79699100 | 1.36560400 | 0.15573100 |
| C | 4.76810700 | 2.17307300 | 1.01993100 |
| C | 6.13496900 | 1.48670700 | 1.05474700 |

| | | | |
|---|---|---|---|
| C | 6.60789500 | 1.18862800 | -0.36283300 |
| H | 4.87837800 | 3.18158900 | 0.60215500 |
| H | 4.36782900 | 2.29036300 | 2.02987300 |
| H | 6.87283600 | 2.11279600 | 1.56377100 |
| H | 6.05823900 | 0.54437700 | 1.60502000 |
| H | 6.80525700 | 2.12875000 | -0.90213900 |
| H | 7.52493700 | 0.59953700 | -0.36745600 |
| O | 5.64804800 | 0.42361700 | -1.07464900 |
| H | 4.59018300 | 2.03971800 | -1.74856900 |
| H | 2.84970900 | 1.89442500 | 0.01803600 |
| C | 4.00105600 | -0.02540800 | -3.24250100 |
| H | 4.91132700 | -0.62657500 | -3.21404800 |
| H | 4.18969800 | 0.89350000 | -3.81050800 |
| H | 3.19945000 | -0.58662800 | -3.72259700 |
| O | 3.55435500 | 0.28311600 | -1.93175400 |
| H | 1.88043500 | -0.42099300 | -1.17115800 |
| H | 4.87831900 | -1.53530500 | 3.16911000 |
| H | 5.02857500 | -2.86970900 | -0.89820300 |
| C | -2.13045200 | -0.72327900 | 0.16777700 |
| C | -2.53898800 | 0.59340300 | 0.17625000 |
| C | -3.46587500 | -0.44989800 | 0.00067000 |
| N | -2.32578200 | 1.89008500 | 0.26720700 |
| N | -4.69019200 | -0.90030000 | -0.16127400 |
| C | -3.47088900 | 2.79493400 | -0.00002700 |
| C | -1.10886400 | 2.44345100 | 0.92105900 |
| C | -5.85490100 | 0.00771400 | -0.09006800 |
| C | -4.89071700 | -2.34041600 | -0.45137700 |
| C | -4.20484800 | 3.14614400 | 1.29298800 |
| H | -4.13870900 | 2.22071100 | -0.64597700 |
| C | -3.05696600 | 4.03350800 | -0.78606900 |
| C | -0.02211700 | 2.81070400 | -0.08358800 |
| H | -1.45829200 | 3.36026900 | 1.40231700 |
| C | -0.58868400 | 1.52679100 | 2.02325200 |
| H | -5.45558200 | 0.96011900 | 0.25777900 |
| C | -6.47200500 | 0.21060600 | -1.47018400 |
| C | -6.86539800 | -0.46519000 | 0.95102900 |
| H | -5.95004100 | -2.43627100 | -0.69368700 |
| C | -4.08858200 | -2.77446100 | -1.67417700 |
| C | -4.60736700 | -3.19320000 | 0.78188100 |
| H | -4.48333900 | 2.24737800 | 1.85002700 |
| H | -3.58800800 | 3.76946800 | 1.94497900 |
| H | -5.11508100 | 3.70651500 | 1.06782700 |
| H | -2.39946600 | 4.68619100 | -0.20736000 |
| H | -2.55584100 | 3.76249000 | -1.71668100 |
| H | -3.95101300 | 4.60855400 | -1.03524500 |
| H | 0.35854000 | 1.91657700 | -0.57759500 |
| H | -0.38769200 | 3.49916000 | -0.84512700 |
| H | 0.80520000 | 3.29556600 | 0.44085200 |
| H | -1.38140600 | 1.25212100 | 2.72328900 |
| H | -0.13523000 | 0.61585000 | 1.62700200 |
| H | 0.18778100 | 2.05128100 | 2.58306300 |
| H | -6.89243100 | -0.71918300 | -1.86245700 |
| H | -7.28251500 | 0.94016700 | -1.41396200 |
| H | -5.72809100 | 0.57622600 | -2.18218300 |
| H | -6.39351800 | -0.58813500 | 1.92813900 |
| H | -7.66011400 | 0.27729200 | 1.04682800 |

| | | | |
|---|---|---|---|
| H | -7.33502600 | -1.41081400 | 0.66964500 |
| H | -4.33297100 | -3.80817800 | -1.92612100 |
| H | -4.32308600 | -2.14698900 | -2.53653100 |
| H | -3.01174200 | -2.72592800 | -1.49107100 |
| H | -3.55778700 | -3.12345900 | 1.08097500 |
| H | -5.22264000 | -2.88285600 | 1.62797900 |
| H | -4.81718500 | -4.24326400 | 0.56994300 |



Optimized Structure of *Z,Z*-**4**-An-**TS$_3$-PA**.

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- Thermochemistry -

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(1 imaginary frequency = -111.33 Hz)

Zero-point correction= 0.728437 (Hartree/Particle)

Thermal correction to Energy= 0.767631

Thermal correction to Enthalpy= 0.768575

Thermal correction to Gibbs Free Energy= 0.655048

Sum of electronic and zero-point Energies= -1861.839023

Sum of electronic and thermal Energies= -1861.799829

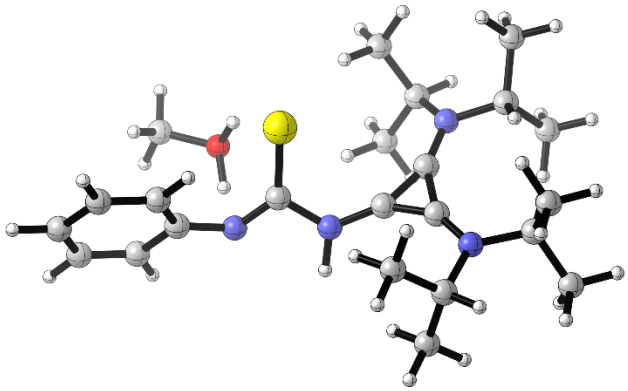
Sum of electronic and thermal Enthalpies= -1861.798885

Sum of electronic and thermal Free Energies= -1861.912412

| | | | |
|---|---|---|---|
| C | 0.66177600 | -0.89363000 | -0.49210000 |
| S | 0.30062200 | -0.16337400 | -1.99868500 |
| N | -0.42765900 | -1.01883400 | 0.42152600 |
| H | -0.32288700 | -1.78004800 | 1.07708400 |
| N | 1.74554800 | -1.37353700 | 0.03971100 |
| C | 2.96562100 | -1.66512400 | -0.59039100 |
| C | 3.95913400 | -2.14856100 | 0.27453400 |
| C | 3.28543500 | -1.52226800 | -1.94805000 |
| C | 5.23312900 | -2.43798700 | -0.17894400 |
| H | 3.68943300 | -2.30247100 | 1.31343000 |
| C | 4.56929400 | -1.81953100 | -2.39726400 |
| H | 2.52971400 | -1.19772700 | -2.64880900 |
| C | 5.55152700 | -2.26086600 | -1.52271800 |
| H | 6.54650400 | -2.48886700 | -1.88652300 |
| H | 2.60554700 | 0.11765500 | 1.74368200 |
| C | 3.62220200 | 1.66694300 | 0.68841000 |
| C | 2.95822900 | 1.13643600 | 1.93783900 |
| C | 3.99963800 | 1.13983200 | 3.06438000 |
| C | 5.25478600 | 0.38878900 | 2.61952500 |
| C | 5.77816600 | 0.96341800 | 1.31422400 |
| H | 4.25808400 | 2.17285600 | 3.32659200 |

| | | | |
|---|---|---|---|
| H | 3.56897600 | 0.68565700 | 3.95781600 |
| H | 6.03757600 | 0.45934000 | 3.37847100 |
| H | 5.02516700 | -0.66954200 | 2.47440900 |
| H | 6.16223700 | 1.98263500 | 1.46047500 |
| H | 6.56672800 | 0.35150400 | 0.88148600 |
| O | 4.75410900 | 0.99603800 | 0.31083300 |
| H | 3.78066100 | 2.75444800 | 0.72998400 |
| H | 2.09633000 | 1.76031400 | 2.18602500 |
| C | 3.19099500 | 1.89266100 | -1.77377000 |
| H | 4.05450900 | 1.27436400 | -2.00287400 |
| H | 3.43683800 | 2.94915700 | -1.69920200 |
| H | 2.35954600 | 1.70620500 | -2.44696300 |
| O | 2.68591200 | 1.51027900 | -0.44336700 |
| H | 2.27816500 | 0.60677300 | -0.46090100 |
| H | 5.97814500 | -2.81619000 | 0.51283100 |
| H | 4.79454600 | -1.71118600 | -3.45271400 |
| C | -1.65241800 | -0.48633600 | 0.24900300 |
| C | -2.47235700 | 0.59315500 | 0.01419600 |
| C | -3.01200200 | -0.67472300 | 0.28663300 |
| N | -2.68643900 | 1.86376800 | -0.26078000 |
| N | -4.02783900 | -1.49584900 | 0.44942200 |
| C | -4.08345700 | 2.29619400 | -0.49595800 |
| C | -1.63497700 | 2.88885300 | -0.04460100 |
| C | -5.41312000 | -0.98870300 | 0.50389400 |
| C | -3.76419900 | -2.95415500 | 0.46050900 |
| C | -4.72436300 | 2.80371300 | 0.79502300 |
| H | -4.60655300 | 1.39487100 | -0.82205100 |
| C | -4.19342900 | 3.30516600 | -1.63294200 |
| C | -0.87058800 | 3.22804000 | -1.32105900 |
| H | -2.18041200 | 3.77785400 | 0.28420400 |
| C | -0.69078200 | 2.48959200 | 1.08598700 |
| H | -5.31802300 | 0.09128400 | 0.62339800 |
| C | -6.15258600 | -1.27551400 | -0.79961400 |
| C | -6.15112800 | -1.51363100 | 1.73220100 |
| H | -4.74810700 | -3.42283100 | 0.40600500 |
| C | -2.97348000 | -3.38285300 | -0.77243200 |
| C | -3.10563400 | -3.37954700 | 1.76928100 |
| H | -4.64264600 | 2.06380400 | 1.59593700 |
| H | -4.25288500 | 3.72793600 | 1.13855800 |
| H | -5.78328900 | 3.01569900 | 0.63101000 |
| H | -3.71291000 | 4.25513100 | -1.38721100 |
| H | -3.75101200 | 2.91242400 | -2.54974900 |
| H | -5.24863900 | 3.51167700 | -1.82277400 |
| H | -0.32738900 | 2.34889200 | -1.67075500 |
| H | -1.53684400 | 3.56273900 | -2.11571100 |
| H | -0.16026300 | 4.03346500 | -1.11365200 |
| H | -1.23879100 | 2.22449800 | 1.99355600 |
| H | -0.05739000 | 1.64725900 | 0.79823700 |
| H | -0.03936500 | 3.33499400 | 1.31878300 |
| H | -6.27002900 | -2.35008300 | -0.96317100 |
| H | -7.15144700 | -0.83485900 | -0.76966300 |
| H | -5.61593700 | -0.85747200 | -1.65485000 |
| H | -5.60085700 | -1.28599700 | 2.64751400 |
| H | -7.13222700 | -1.03890700 | 1.79666300 |
| H | -6.31432400 | -2.59301500 | 1.68335900 |
| H | -2.87857600 | -4.47036400 | -0.78952500 |

| | | | |
|---|---|---|---|
| H | -3.47889400 | -3.06812100 | -1.68761900 |
| H | -1.96476600 | -2.96181100 | -0.77930100 |
| H | -2.12170400 | -2.91598600 | 1.88519900 |
| H | -3.71719400 | -3.09768600 | 2.62832700 |
| H | -2.96321300 | -4.46183800 | 1.78628000 |



Optimized Structure of *Z,Z*-**4**-An-**TS$_3$-MA**.

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- Thermochemistry -

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(1 imaginary frequency = -562.58 Hz)

Zero-point correction= 0.597985 (Hartree/Particle)

Thermal correction to Energy= 0.631601

Thermal correction to Enthalpy= 0.632545

Thermal correction to Gibbs Free Energy= 0.531255

Sum of electronic and zero-point Energies= -1591.409820

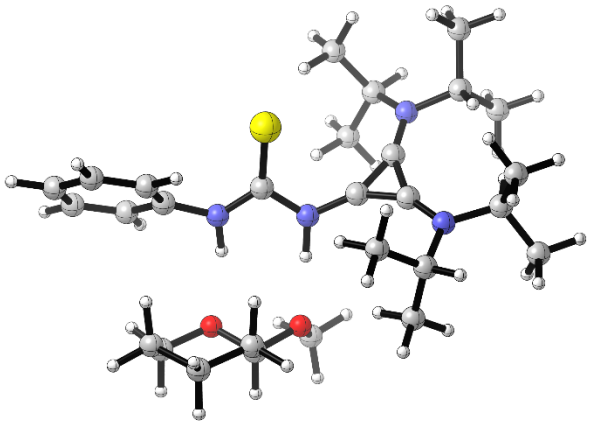
Sum of electronic and thermal Energies= -1591.376205

Sum of electronic and thermal Enthalpies= -1591.375261

Sum of electronic and thermal Free Energies= -1591.476551

| | | | |
|---|---|---|---|
| C | -1.64224600 | -0.16899400 | -0.07054400 |
| S | -1.46044300 | 0.73166400 | 1.36335300 |
| N | -0.49843400 | -0.58624500 | -0.74110800 |
| H | -0.66571600 | -1.28202500 | -1.45566700 |
| N | -2.73785500 | -0.45083000 | -0.76949700 |
| C | -3.99536200 | -0.77312200 | -0.20057700 |
| C | -5.06178000 | -0.81871800 | -1.10740300 |
| C | -4.24275900 | -1.07127500 | 1.14192700 |
| C | -6.34690900 | -1.11695800 | -0.68225300 |
| H | -4.85545000 | -0.63527700 | -2.15679800 |
| C | -5.53280900 | -1.38187100 | 1.55667000 |
| H | -3.43935300 | -1.05876900 | 1.86506700 |
| C | -6.59167800 | -1.39498200 | 0.65779100 |
| H | -7.59326800 | -1.63331200 | 0.99471200 |
| O | -3.23948000 | 2.03357700 | -0.73900500 |
| H | -2.76758000 | 2.00529100 | 0.14079000 |
| H | -7.15600300 | -1.14700100 | -1.40300700 |
| H | -5.70805400 | -1.61271500 | 2.60130300 |
| C | 0.78644900 | -0.28863400 | -0.40516300 |
| C | 1.78828500 | 0.61375000 | -0.14052300 |
| C | 2.04658000 | -0.77757000 | -0.18295300 |

| | | | |
|---|---|---|---|
| N | 2.25726300 | 1.82576000 | 0.03216100 |
| N | 2.85193400 | -1.80848300 | -0.09556800 |
| C | 3.68135900 | 1.97275100 | 0.42539500 |
| C | 1.49925700 | 3.02164600 | -0.42676100 |
| C | 4.31248200 | -1.63298500 | 0.06066200 |
| C | 2.26307200 | -3.17082800 | -0.08310400 |
| C | 4.56861500 | 2.11309100 | -0.80941300 |
| H | 3.92778500 | 1.04277100 | 0.94187400 |
| C | 3.89527500 | 3.09982600 | 1.42803300 |
| C | 0.70158900 | 3.67102200 | 0.69946000 |
| H | 2.27117100 | 3.72049400 | -0.75957400 |
| C | 0.62474800 | 2.69983400 | -1.63406100 |
| H | 4.49466100 | -0.57258800 | -0.11426400 |
| C | 4.74928800 | -1.97953900 | 1.48049600 |
| C | 5.08095000 | -2.40527000 | -1.00752000 |
| H | 3.09056900 | -3.83482500 | 0.17051700 |
| C | 1.20496200 | -3.30741700 | 1.00752500 |
| C | 1.74783200 | -3.55614500 | -1.46602600 |
| H | 4.40889900 | 1.28980100 | -1.51120600 |
| H | 4.37002300 | 3.04972100 | -1.33667900 |
| H | 5.62137500 | 2.11665400 | -0.51844900 |
| H | 3.68792300 | 4.08120400 | 0.99572100 |
| H | 3.27517400 | 2.96395000 | 2.31519200 |
| H | 4.94135200 | 3.09649400 | 1.74062200 |
| H | -0.05553900 | 2.97884200 | 1.07012600 |
| H | 1.33766600 | 3.96654500 | 1.53314600 |
| H | 0.20622400 | 4.56799600 | 0.31943800 |
| H | 1.19442900 | 2.20154400 | -2.42224000 |
| H | -0.22700100 | 2.07291900 | -1.36138500 |
| H | 0.22728500 | 3.63025300 | -2.04308100 |
| H | 4.57950000 | -3.03613100 | 1.70364900 |
| H | 5.81671700 | -1.78497700 | 1.60294600 |
| H | 4.20257200 | -1.38269100 | 2.21451500 |
| H | 4.75521900 | -2.12028600 | -2.01009100 |
| H | 6.14600700 | -2.18317200 | -0.91766800 |
| H | 4.96393700 | -3.48589300 | -0.89703300 |
| H | 0.88726900 | -4.34924900 | 1.08041500 |
| H | 1.60311600 | -3.00233600 | 1.97730100 |
| H | 0.31694000 | -2.70677300 | 0.79399800 |
| H | 0.92864100 | -2.90250400 | -1.77900600 |
| H | 2.53814900 | -3.49531000 | -2.21600200 |
| H | 1.36341500 | -4.57772300 | -1.45173900 |
| H | -3.08605800 | 0.98753900 | -1.00786700 |
| C | -4.63356200 | 2.42513400 | -0.56779400 |
| H | -5.09586600 | 1.80951400 | 0.20243600 |
| H | -4.63612600 | 3.47999300 | -0.30243900 |
| H | -5.11925500 | 2.26888900 | -1.52627300 |



Optimized Structure of *Z,Z*-**4**-An-**INT$_5$**.

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- Thermochemistry -

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(0 imaginary frequencies)

Zero-point correction= 0.730296 (Hartree/Particle)

Thermal correction to Energy= 0.770089

Thermal correction to Enthalpy= 0.771033

Thermal correction to Gibbs Free Energy= 0.655788

Sum of electronic and zero-point Energies= -1861.918663

Sum of electronic and thermal Energies= -1861.878869

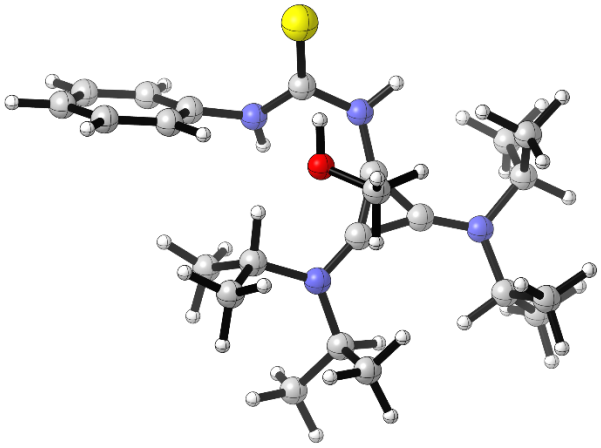
Sum of electronic and thermal Enthalpies= -1861.877925

Sum of electronic and thermal Free Energies= -1861.993170

| | | | |
|---|---|---|---|
| C | 0.92697800 | 1.01534800 | -0.30996400 |
| S | 0.32051200 | 2.07127500 | -1.44036700 |
| N | 0.10244100 | 0.09301300 | 0.33252700 |
| H | 0.51758300 | -0.74223500 | 0.75874800 |
| N | 2.20392900 | 0.89664200 | 0.09075000 |
| C | 3.35270100 | 1.56036700 | -0.41917200 |
| C | 3.60553700 | 1.66936200 | -1.78257800 |
| C | 4.28834800 | 2.01182900 | 0.50667000 |
| C | 4.79598800 | 2.24057700 | -2.21027700 |
| H | 2.87772800 | 1.31606100 | -2.50001000 |
| C | 5.48264400 | 2.56866600 | 0.06945900 |
| H | 4.07493800 | 1.92557500 | 1.56671100 |
| C | 5.73774700 | 2.68735400 | -1.29068400 |
| H | 6.66503300 | 3.12975700 | -1.63416600 |
| H | 2.19132500 | -1.82004700 | -0.71610500 |
| C | 2.58655900 | -2.40214400 | 1.29710000 |
| C | 2.63356700 | -2.67607300 | -0.19378400 |
| C | 4.08865600 | -2.86698700 | -0.63324900 |
| C | 4.94875000 | -1.68910000 | -0.17078300 |
| C | 4.75467900 | -1.44374000 | 1.31773500 |
| H | 4.47694600 | -3.79665300 | -0.20046600 |
| H | 4.14093600 | -2.98012800 | -1.71758800 |
| H | 6.00650000 | -1.88300100 | -0.36540300 |
| H | 4.67906700 | -0.78280700 | -0.72146200 |
| H | 5.14837500 | -2.28242600 | 1.90821500 |
| H | 5.24678600 | -0.52941400 | 1.64616800 |
| O | 3.36752600 | -1.27234400 | 1.63608900 |
| H | 2.95810200 | -3.27021400 | 1.86747200 |

| | | | |
|---|---|---|---|
| H | 2.02916700 | -3.55854300 | -0.41701600 |
| C | 1.07260800 | -2.05737200 | 3.09094400 |
| H | 1.69276600 | -1.27984400 | 3.54053400 |
| H | 1.30504500 | -3.02524400 | 3.54520000 |
| H | 0.01862200 | -1.83139000 | 3.24691000 |
| O | 1.27444500 | -2.11599100 | 1.68050000 |
| H | 2.42455800 | 0.23202100 | 0.83182000 |
| H | 4.98902700 | 2.33302900 | -3.27244000 |
| H | 6.20812000 | 2.91953500 | 0.79379300 |
| C | -1.24594400 | 0.08883900 | 0.14926400 |
| C | -2.46423400 | 0.71575400 | 0.23890300 |
| C | -2.35506000 | -0.61659000 | -0.23064400 |
| N | -3.22555100 | 1.74244900 | 0.52297800 |
| N | -2.88988600 | -1.71819900 | -0.70159400 |
| C | -4.66994800 | 1.66706300 | 0.19684400 |
| C | -2.72226700 | 2.85874000 | 1.37061600 |
| C | -4.35840800 | -1.87916800 | -0.76437400 |
| C | -2.00137200 | -2.76767400 | -1.25937200 |
| C | -5.47269700 | 1.19428600 | 1.40684100 |
| H | -4.74312200 | 0.91948400 | -0.59546600 |
| C | -5.19833500 | 2.97546800 | -0.37915200 |
| C | -2.13108000 | 3.99700700 | 0.54673600 |
| H | -3.61143500 | 3.22323100 | 1.89082700 |
| C | -1.74501700 | 2.35303500 | 2.42699500 |
| H | -4.76124300 | -1.07478700 | -0.14738300 |
| C | -4.86271200 | -1.70441700 | -2.19343900 |
| C | -4.80531300 | -3.19436900 | -0.13330100 |
| H | -2.66828200 | -3.44328300 | -1.79738100 |
| C | -1.01763700 | -2.18431600 | -2.26945500 |
| C | -1.30779300 | -3.54965800 | -0.14825500 |
| H | -5.08405300 | 0.24882300 | 1.79557000 |
| H | -5.44389500 | 1.92987500 | 2.21464000 |
| H | -6.51953900 | 1.04828900 | 1.13175300 |
| H | -5.17271600 | 3.78596300 | 0.35255600 |
| H | -4.62922300 | 3.27733500 | -1.25969100 |
| H | -6.23960000 | 2.83507200 | -0.67587000 |
| H | -1.23571200 | 3.66223000 | 0.02099600 |
| H | -2.84126600 | 4.37806400 | -0.18707000 |
| H | -1.85680400 | 4.81908700 | 1.21226000 |
| H | -2.16020500 | 1.50832800 | 2.98288200 |
| H | -0.79126600 | 2.05628800 | 1.98415900 |
| H | -1.53882100 | 3.15680600 | 3.13576200 |
| H | -4.47222200 | -2.48483100 | -2.85204100 |
| H | -5.95267100 | -1.76716600 | -2.21863600 |
| H | -4.56228300 | -0.73543700 | -2.59966200 |
| H | -4.43913300 | -3.28354100 | 0.89150800 |
| H | -5.89618500 | -3.23059900 | -0.10960200 |
| H | -4.46305300 | -4.06239300 | -0.70184400 |
| H | -0.47083900 | -2.99623900 | -2.75331600 |
| H | -1.53706600 | -1.61267900 | -3.04113700 |
| H | -0.28451200 | -1.52890800 | -1.79232600 |
| H | -0.60740800 | -2.92216900 | 0.40877500 |
| H | -2.03348300 | -3.96904400 | 0.55105200 |
| H | -0.73672400 | -4.37540600 | -0.57943700 |

Z,E Conformation



Optimized Structure of *Z,E*-**4**-An-**INT**$_1$.

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- Thermochemistry -

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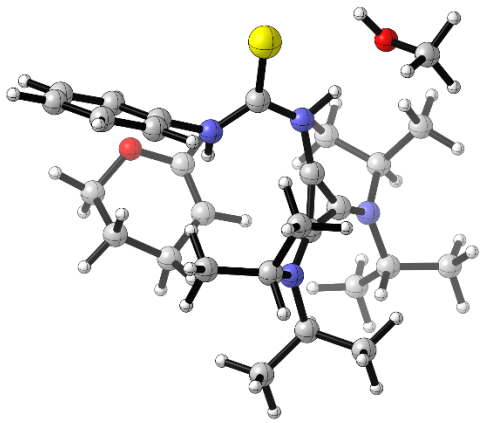
(0 imaginary frequencies)

Zero-point correction= 0.600527 (Hartree/Particle)
Thermal correction to Energy= 0.635884
Thermal correction to Enthalpy= 0.636828
Thermal correction to Gibbs Free Energy= 0.530948
Sum of electronic and zero-point Energies= -1591.455251
Sum of electronic and thermal Energies= -1591.419894
Sum of electronic and thermal Enthalpies= -1591.418950
Sum of electronic and thermal Free Energies= -1591.524830

| | | | |
|---|---|---|---|
| C | 1.49672700 | -0.93537700 | -0.10908500 |
| S | 1.42645500 | -0.17576200 | 1.36234400 |
| N | 2.60021800 | -1.37874300 | -0.73537800 |
| H | 2.52716000 | -1.52649700 | -1.73200000 |
| N | 0.33958900 | -1.21317900 | -0.85179700 |
| C | 3.93131300 | -1.31024400 | -0.21900100 |
| C | 4.28078600 | -2.02500600 | 0.91909800 |
| C | 4.87132300 | -0.55069300 | -0.90390600 |
| C | 5.58594200 | -1.96013100 | 1.38464300 |
| H | 3.53610300 | -2.61654300 | 1.43692200 |
| C | 6.17960300 | -0.50450500 | -0.43890500 |
| H | 4.56969400 | 0.01218600 | -1.77952600 |
| C | 6.53602500 | -1.20376200 | 0.70724000 |
| H | 7.55502900 | -1.16188700 | 1.07270600 |
| H | 0.31673400 | -2.07166700 | -1.38383200 |
| C | 3.76920700 | 2.87153800 | -1.02249300 |
| H | 3.63913600 | 3.67067400 | -0.28300900 |
| H | 3.69156400 | 3.30807400 | -2.01855800 |
| H | 4.77218400 | 2.44521900 | -0.90388800 |
| O | 2.76249600 | 1.88049700 | -0.91693900 |
| H | 2.81209100 | 1.48523800 | -0.04017800 |
| C | -0.85046900 | -0.61571000 | -0.58067900 |
| C | -1.54442300 | 0.53007100 | -0.28471700 |

| | | | |
|---|---|---|---|
| C | -2.19901700 | -0.72036400 | -0.36868300 |
| N | -1.56307600 | 1.81661200 | -0.04918200 |
| N | -3.27186700 | -1.47276500 | -0.28560700 |
| C | -2.75847000 | 2.37628700 | 0.63162000 |
| C | -0.31935500 | 2.57414800 | -0.37471700 |
| C | -4.61177300 | -0.86402500 | -0.13556900 |
| C | -3.10012900 | -2.94302900 | -0.20666000 |
| C | -2.59733700 | 2.35078700 | 2.15167400 |
| H | -3.56234300 | 1.68171100 | 0.38001600 |
| C | -3.17557300 | 3.74291800 | 0.10540900 |
| C | 0.23648700 | 3.35820800 | 0.80492400 |
| H | -4.47989400 | 0.18255800 | -0.41689300 |
| C | -5.61051500 | -1.46758100 | -1.11813500 |
| C | -5.07892800 | -0.93201200 | 1.31457600 |
| H | -4.09010300 | -3.33508800 | 0.02904200 |
| C | -2.67160200 | -3.51397900 | -1.55461100 |
| C | -2.16318500 | -3.32823500 | 0.93466600 |
| H | -2.26133500 | 1.36817100 | 2.49264000 |
| H | -1.87859300 | 3.09452700 | 2.49641000 |
| H | -3.55866200 | 2.56820200 | 2.62333600 |
| H | -2.45587700 | 4.52125300 | 0.36201600 |
| H | -3.31269200 | 3.73160100 | -0.97686600 |
| H | -4.12702100 | 4.01468600 | 0.56693100 |
| H | -0.39064700 | 4.20816500 | 1.08178700 |
| H | 0.37349800 | 2.71444900 | 1.67504600 |
| H | 1.21395100 | 3.74854000 | 0.51569400 |
| H | -5.83200500 | -2.51380800 | -0.89495500 |
| H | -6.55171600 | -0.91813100 | -1.05704500 |
| H | -5.24151500 | -1.39873200 | -2.14339700 |
| H | -5.20096600 | -1.96756500 | 1.64403500 |
| H | -4.36251000 | -0.44211900 | 1.97883500 |
| H | -6.04511100 | -0.43491800 | 1.42343300 |
| H | -2.58088200 | -4.60003800 | -1.49275200 |
| H | -3.39598300 | -3.27039100 | -2.33340100 |
| H | -1.69905800 | -3.11752400 | -1.86284900 |
| H | -1.13828400 | -2.99161000 | 0.75474300 |
| H | -2.50127300 | -2.89560100 | 1.87830600 |
| H | -2.14058900 | -4.41413100 | 1.04419800 |
| H | 5.86354800 | -2.50916800 | 2.27623500 |
| H | 6.91824300 | 0.08145300 | -0.97283000 |
| H | 0.41581600 | 1.80540200 | -0.60918200 |
| C | -0.47169700 | 3.42665100 | -1.63232400 |
| H | -1.04064300 | 4.34056700 | -1.45856300 |
| H | 0.52702100 | 3.70961800 | -1.97152800 |
| H | -0.95100400 | 2.86212300 | -2.43552000 |



Optimized Structure of *Z,E*-**4**-An-**INT**$_2$.

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- Thermochemistry -

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(0 imaginary frequencies)

Zero-point correction= 0.728381 (Hartree/Particle)

Thermal correction to Energy= 0.769422

Thermal correction to Enthalpy= 0.770366

Thermal correction to Gibbs Free Energy= 0.653712

Sum of electronic and zero-point Energies= -1861.890023

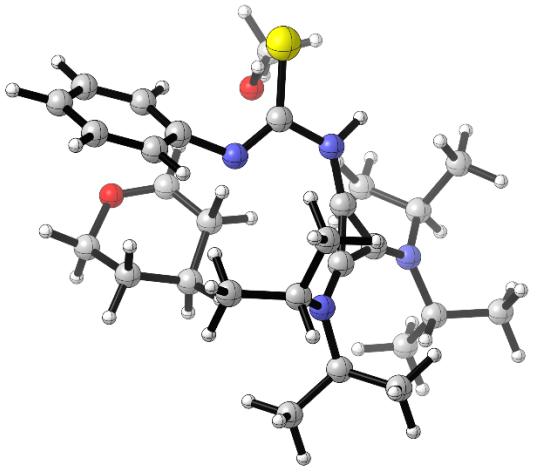
Sum of electronic and thermal Energies= -1861.848982

Sum of electronic and thermal Enthalpies= -1861.848038

Sum of electronic and thermal Free Energies= -1861.964692

| | | | |
|---|---|---|---|
| C | -1.28241700 | 1.89310400 | 0.09339200 |
| S | -2.02861600 | 3.33359900 | 0.42915200 |
| N | 0.10132800 | 1.83181900 | -0.06865800 |
| H | 0.56809300 | 2.74757500 | -0.17881700 |
| N | -1.89462900 | 0.70249300 | -0.07819300 |
| C | -3.30378500 | 0.50016500 | 0.05138600 |
| C | -3.90574100 | 0.59883100 | 1.29997400 |
| C | -4.04985600 | 0.17328500 | -1.07327100 |
| C | -5.26754200 | 0.36835900 | 1.42162200 |
| H | -3.31135400 | 0.86860400 | 2.16455700 |
| C | -5.41126700 | -0.07150800 | -0.93982900 |
| H | -3.56481500 | 0.10867700 | -2.04037900 |
| C | -6.02125600 | 0.02761800 | 0.30364900 |
| H | -7.08470800 | -0.15358700 | 0.40327900 |
| H | -1.38732400 | 0.00665800 | -0.61852500 |
| C | -0.74700500 | -1.02670900 | -2.85292800 |
| C | -0.04220100 | -1.75436600 | -1.98163500 |
| C | -0.63557700 | -2.93252500 | -1.26079700 |
| C | -2.15893400 | -2.91425200 | -1.40489000 |
| C | -2.54425700 | -2.54045700 | -2.82763600 |
| H | -0.22287000 | -3.86755700 | -1.65687200 |
| H | -0.36161800 | -2.89443800 | -0.20278800 |
| H | -2.59267100 | -3.88638700 | -1.16118500 |
| H | -2.60085300 | -2.18784600 | -0.71567200 |
| H | -2.16363300 | -3.28200800 | -3.53892100 |
| H | -3.62373300 | -2.46013200 | -2.94733200 |
| O | -2.02510800 | -1.26008800 | -3.20935200 |

| | | | |
|---|---|---|---|
| H | -0.34622900 | -0.15568500 | -3.35944300 |
| H | 0.99744000 | -1.49300800 | -1.82563900 |
| C | 1.50976500 | 4.76989400 | 1.20760900 |
| H | 1.59524200 | 5.85279600 | 1.32439100 |
| H | 2.50000900 | 4.32903500 | 1.32853900 |
| H | 0.83787400 | 4.37351000 | 1.97639200 |
| O | 1.05834000 | 4.42958500 | -0.09996400 |
| H | 0.14964500 | 4.74168300 | -0.18982500 |
| H | -5.74228700 | 0.45583200 | 2.39145000 |
| H | -5.99734100 | -0.32457400 | -1.81545900 |
| C | 0.88831500 | 0.77213500 | 0.21534100 |
| C | 1.19633900 | -0.38098000 | 0.90208000 |
| C | 2.10642400 | 0.17993900 | -0.01126400 |
| N | 0.91535400 | -1.35060600 | 1.75120400 |
| N | 3.24934300 | 0.17232500 | -0.65908700 |
| C | 1.91722200 | -2.43263100 | 1.91784100 |
| C | -0.16539400 | -1.20432100 | 2.76233700 |
| C | 4.29990600 | -0.81534900 | -0.33075500 |
| C | 3.46783400 | 1.13339700 | -1.77001500 |
| C | 2.93522600 | -2.06058400 | 2.99435100 |
| H | 2.41941000 | -2.50545800 | 0.95048400 |
| C | 1.27849400 | -3.79182000 | 2.18105200 |
| C | -1.46703000 | -1.83831700 | 2.28504900 |
| H | 0.19519400 | -1.76035600 | 3.63072000 |
| C | -0.34660700 | 0.24377800 | 3.20421500 |
| H | 3.97346200 | -1.28660100 | 0.59557300 |
| C | 4.39566900 | -1.88324200 | -1.41632500 |
| C | 5.63627600 | -0.13821200 | -0.04175000 |
| H | 4.38904400 | 0.79719400 | -2.24783300 |
| C | 2.35170200 | 1.04913000 | -2.80607700 |
| C | 3.68556200 | 2.55013000 | -1.24930300 |
| H | 3.39763400 | -1.09098200 | 2.79027200 |
| H | 2.46378600 | -2.00731300 | 3.97910900 |
| H | 3.72467100 | -2.81353100 | 3.04613700 |
| H | 0.75809700 | -3.82821400 | 3.14047900 |
| H | 0.57948700 | -4.06939500 | 1.39131300 |
| H | 2.06622200 | -4.54694700 | 2.21143500 |
| H | -1.83246100 | -1.33801700 | 1.38873100 |
| H | -1.34095700 | -2.89916000 | 2.06636100 |
| H | -2.23440400 | -1.74131000 | 3.05610100 |
| H | 0.60422100 | 0.69192300 | 3.50228400 |
| H | -0.80013700 | 0.86022700 | 2.42666500 |
| H | -1.01528200 | 0.27003500 | 4.06653400 |
| H | 4.71251300 | -1.45523000 | -2.37087900 |
| H | 5.13056400 | -2.63989200 | -1.13424200 |
| H | 3.43222500 | -2.37755100 | -1.56685200 |
| H | 5.53483100 | 0.61117500 | 0.74593800 |
| H | 6.35581400 | -0.88843700 | 0.29192300 |
| H | 6.05556100 | 0.34373000 | -0.92782800 |
| H | 2.59038400 | 1.69778400 | -3.65098100 |
| H | 2.23791100 | 0.02886000 | -3.18042700 |
| H | 1.39564300 | 1.38517200 | -2.39572000 |
| H | 2.77073900 | 2.97686700 | -0.83182700 |
| H | 4.46908600 | 2.57189300 | -0.48977500 |
| H | 3.99092900 | 3.20164500 | -2.07077000 |



Optimized Structure of *Z,E*-**4**-An-**TS$_1$**.

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- Thermochemistry -

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(1 imaginary frequency = -389.29 Hz)

Zero-point correction= 0.723295 (Hartree/Particle)

Thermal correction to Energy= 0.763740

Thermal correction to Enthalpy= 0.764684

Thermal correction to Gibbs Free Energy= 0.649390

Sum of electronic and zero-point Energies= -1861.845928

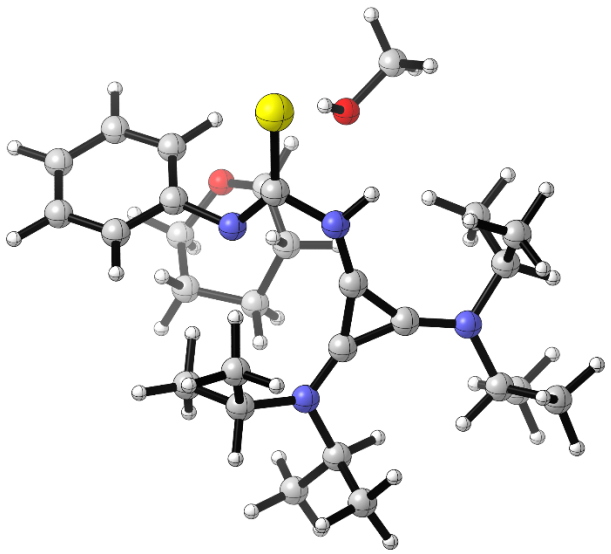
Sum of electronic and thermal Energies= -1861.805483

Sum of electronic and thermal Enthalpies= -1861.804539

Sum of electronic and thermal Free Energies= -1861.919833

| | | | |
|---|---|---|---|
| C | 1.18795200 | 1.00065200 | -1.63964800 |
| S | 2.00021400 | 2.13437700 | -2.59192600 |
| N | -0.21464200 | 1.18415800 | -1.55557100 |
| H | -0.52388400 | 2.08407800 | -1.89106500 |
| N | 1.63674700 | 0.01607800 | -0.90150500 |
| C | 3.02753600 | -0.23627200 | -0.82426600 |
| C | 3.55111200 | -1.42619800 | -1.32705900 |
| C | 3.86904200 | 0.64174000 | -0.13918100 |
| C | 4.88607800 | -1.74578300 | -1.11803800 |
| H | 2.91023300 | -2.08711500 | -1.89707000 |
| C | 5.19911900 | 0.31105200 | 0.08251400 |
| H | 3.48374300 | 1.60111700 | 0.18643300 |
| C | 5.71048000 | -0.88783700 | -0.39854900 |
| H | 6.75155000 | -1.14028600 | -0.23618400 |
| H | 1.18779200 | 0.18021100 | 0.56652400 |
| C | 1.96257300 | 0.95481400 | 2.29874000 |
| C | 0.86337000 | 0.25689600 | 1.75507000 |
| C | 0.66470400 | -1.16245100 | 2.25653300 |
| C | 2.04495700 | -1.80743300 | 2.39059200 |
| C | 2.92635300 | -0.98436600 | 3.30781500 |
| H | 0.14735900 | -1.16507500 | 3.22177400 |
| H | 0.04806600 | -1.72307800 | 1.55361700 |
| H | 1.97836700 | -2.81479800 | 2.80737100 |
| H | 2.51655500 | -1.88872800 | 1.40722500 |
| H | 2.61146300 | -1.03818300 | 4.35145300 |
| H | 3.97716900 | -1.25499200 | 3.23391100 |

| | | | |
|---|---|---|---|
| O | 2.91426000 | 0.44492900 | 2.98255300 |
| H | 2.08647000 | 2.01635600 | 2.09103300 |
| H | -0.00765800 | 0.90723200 | 1.66590000 |
| C | 1.26991300 | 4.67155400 | 0.59711700 |
| H | 2.22112700 | 5.19558300 | 0.46268400 |
| H | 0.90729200 | 4.86247700 | 1.60836900 |
| H | 0.54192100 | 5.07335900 | -0.11664300 |
| O | 1.41946100 | 3.26800300 | 0.45440500 |
| H | 1.72211800 | 3.08749400 | -0.45098000 |
| H | 5.28701200 | -2.66668900 | -1.52565200 |
| H | 5.84168000 | 1.00236000 | 0.61555200 |
| C | -1.12061200 | 0.38784400 | -0.97431500 |
| C | -1.64738500 | -0.83480000 | -0.61815800 |
| C | -2.35417700 | 0.34567500 | -0.36569400 |
| N | -1.59924300 | -2.15165000 | -0.52310900 |
| N | -3.39192500 | 1.01463400 | 0.09533700 |
| C | -2.70522000 | -2.82466000 | 0.19635400 |
| C | -0.69466700 | -2.96080900 | -1.38233200 |
| C | -4.60618700 | 0.31310500 | 0.55842800 |
| C | -3.30267400 | 2.49033200 | 0.19247100 |
| C | -3.82973900 | -3.20888100 | -0.76343300 |
| H | -3.07890100 | -2.08045000 | 0.90416400 |
| C | -2.21886000 | -4.00995500 | 1.02294500 |
| C | 0.60406600 | -3.29845200 | -0.65999500 |
| H | -1.24690700 | -3.88517000 | -1.56879700 |
| C | -0.44085900 | -2.29550700 | -2.73067500 |
| H | -4.47116400 | -0.72580000 | 0.25672500 |
| C | -4.72003600 | 0.36760500 | 2.07922000 |
| C | -5.85409500 | 0.82960800 | -0.15170600 |
| H | -4.18841600 | 2.79013600 | 0.75489900 |
| C | -2.07961300 | 2.92530400 | 0.99690000 |
| C | -3.37692700 | 3.14263700 | -1.18512800 |
| H | -4.16975100 | -2.34545000 | -1.34167100 |
| H | -3.50462000 | -3.97798700 | -1.46840500 |
| H | -4.68183200 | -3.60837800 | -0.20895600 |
| H | -1.82292700 | -4.81356000 | 0.39823500 |
| H | -1.44832700 | -3.70714700 | 1.73472200 |
| H | -3.05980800 | -4.41847600 | 1.58658200 |
| H | 1.15577100 | -2.38052200 | -0.45791700 |
| H | 0.42340600 | -3.82494000 | 0.27855900 |
| H | 1.22364500 | -3.93927800 | -1.29166100 |
| H | -1.37577900 | -2.00287200 | -3.21443200 |
| H | 0.20539200 | -1.42164700 | -2.63211100 |
| H | 0.06833600 | -3.00419500 | -3.38644700 |
| H | -4.84787800 | 1.39340200 | 2.43514700 |
| H | -5.58709000 | -0.20642400 | 2.41262200 |
| H | -3.82758300 | -0.05035200 | 2.55229100 |
| H | -5.74558400 | 0.75194700 | -1.23537100 |
| H | -6.71757100 | 0.23308500 | 0.14926900 |
| H | -6.07140800 | 1.86996500 | 0.10234500 |
| H | -2.12173900 | 4.00279200 | 1.16967000 |
| H | -2.06641200 | 2.42927100 | 1.97112000 |
| H | -1.13509100 | 2.71889900 | 0.48470500 |
| H | -2.54553400 | 2.83369800 | -1.82465200 |
| H | -4.30472100 | 2.88032100 | -1.69587800 |
| H | -3.33285000 | 4.22929100 | -1.08906500 |



Optimized Structure of *Z,E*-**4**-An-**INT**$_3$.

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- Thermochemistry -

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(0 imaginary frequencies)

Zero-point correction= 0.725700 (Hartree/Particle)

Thermal correction to Energy= 0.766822

Thermal correction to Enthalpy= 0.767766

Thermal correction to Gibbs Free Energy= 0.650947

Sum of electronic and zero-point Energies= -1861.845240

Sum of electronic and thermal Energies= -1861.804118

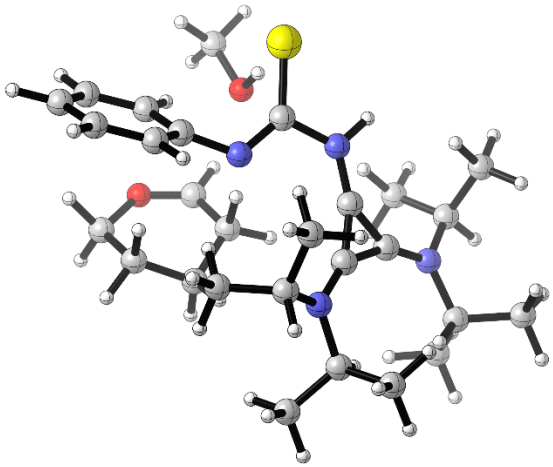
Sum of electronic and thermal Enthalpies= -1861.803173

Sum of electronic and thermal Free Energies= -1861.919993

| | | | |
|---|---|---|---|
| C | 1.06913200 | 1.10209800 | -1.71055800 |
| S | 1.80107400 | 2.46664400 | -2.42117200 |
| N | -0.35041700 | 1.20067900 | -1.61946300 |
| H | -0.69734200 | 2.11489300 | -1.86966700 |
| N | 1.55355100 | 0.01813900 | -1.19186800 |
| C | 2.93510500 | -0.18867100 | -1.06031100 |
| C | 3.49138900 | -1.38523400 | -1.52100300 |
| C | 3.75064500 | 0.69374700 | -0.34329200 |
| C | 4.81138900 | -1.70648000 | -1.23894100 |
| H | 2.87703600 | -2.05305100 | -2.11205300 |
| C | 5.06770100 | 0.36168500 | -0.04979900 |
| H | 3.35857500 | 1.66185200 | -0.05389700 |
| C | 5.60246300 | -0.84443800 | -0.48542500 |
| H | 6.63441500 | -1.09535700 | -0.27075700 |
| H | 1.12140100 | 0.22307700 | 0.68800800 |
| C | 2.17877100 | 1.01020200 | 2.23317000 |
| C | 1.04026000 | 0.21924600 | 1.81141400 |
| C | 1.04564400 | -1.21277800 | 2.32596800 |
| C | 2.47757300 | -1.74088300 | 2.23916500 |
| C | 3.40498700 | -0.87570900 | 3.06269500 |
| H | 0.68634900 | -1.25330200 | 3.35919300 |
| H | 0.37329700 | -1.81782800 | 1.71801600 |

| | | | |
|---|---|---|---|
| H | 2.55350700 | -2.76089400 | 2.62176500 |
| H | 2.81513900 | -1.75296000 | 1.19921700 |
| H | 3.25733000 | -0.98474900 | 4.13781600 |
| H | 4.45455500 | -1.02013000 | 2.81702500 |
| O | 3.20411000 | 0.56933300 | 2.81661900 |
| H | 2.18413100 | 2.08299900 | 2.02581500 |
| H | 0.13431700 | 0.80301900 | 2.00229900 |
| C | 0.99220200 | 4.66340500 | 0.82286000 |
| H | 1.87269100 | 5.26294000 | 0.57231300 |
| H | 0.74645900 | 4.82647600 | 1.87349700 |
| H | 0.14983900 | 5.00335200 | 0.21005600 |
| O | 1.23598200 | 3.27704900 | 0.64484000 |
| H | 1.47276300 | 3.13566300 | -0.29258500 |
| H | 5.22906600 | -2.63293700 | -1.61652400 |
| H | 5.68490900 | 1.06201400 | 0.50241400 |
| C | -1.19346500 | 0.36591600 | -1.00385100 |
| C | -1.64396800 | -0.87013600 | -0.58899700 |
| C | -2.40756900 | 0.27601000 | -0.35843900 |
| N | -1.53134300 | -2.18149800 | -0.44237600 |
| N | -3.46590200 | 0.90655800 | 0.11480600 |
| C | -2.59739000 | -2.86735900 | 0.32265500 |
| C | -0.63809900 | -2.99311700 | -1.31085900 |
| C | -4.64233200 | 0.16358600 | 0.60727500 |
| C | -3.43965100 | 2.38526200 | 0.18811500 |
| C | -3.73001300 | -3.32382600 | -0.59582300 |
| H | -2.98193500 | -2.11379400 | 1.01457100 |
| C | -2.05259900 | -4.00744700 | 1.17615800 |
| C | 0.69533600 | -3.26985500 | -0.62693500 |
| H | -1.16918500 | -3.93906500 | -1.44375600 |
| C | -0.45701200 | -2.36865400 | -2.68968400 |
| H | -4.46272900 | -0.87627900 | 0.33467300 |
| C | -4.75121700 | 0.25442800 | 2.12684200 |
| C | -5.91701000 | 0.60234000 | -0.10842400 |
| H | -4.33418800 | 2.65656100 | 0.75132000 |
| C | -2.23200000 | 2.87819800 | 0.98216400 |
| C | -3.55239400 | 3.01540800 | -1.19734700 |
| H | -4.10491900 | -2.49645400 | -1.20424200 |
| H | -3.39849600 | -4.11414000 | -1.27379400 |
| H | -4.55955900 | -3.72105200 | -0.00641700 |
| H | -1.64489000 | -4.81890500 | 0.56939400 |
| H | -1.27545800 | -3.65669800 | 1.85841700 |
| H | -2.86538500 | -4.42369400 | 1.77463200 |
| H | 1.21860600 | -2.32796900 | -0.46483400 |
| H | 0.56233000 | -3.78439800 | 0.32654300 |
| H | 1.31703000 | -3.90207500 | -1.26506900 |
| H | -1.42039100 | -2.13837000 | -3.15131100 |
| H | 0.15098400 | -1.46398100 | -2.63839800 |
| H | 0.06217700 | -3.07920700 | -3.33592800 |
| H | -4.91850100 | 1.28328900 | 2.45636500 |
| H | -5.59256900 | -0.34520400 | 2.48044700 |
| H | -3.84041300 | -0.11464400 | 2.60564200 |
| H | -5.80838400 | 0.50410500 | -1.19040600 |
| H | -6.74996900 | -0.02721000 | 0.21086000 |
| H | -6.18222500 | 1.63717700 | 0.12162600 |
| H | -2.30367800 | 3.95832600 | 1.12626400 |
| H | -2.20845000 | 2.40839000 | 1.96915400 |

| | | | |
|---|---|---|---|
| H | -1.27944900 | 2.68008300 | 0.48227300 |
| H | -2.71450700 | 2.73731400 | -1.84202800 |
| H | -4.47141200 | 2.70254100 | -1.69553200 |
| H | -3.55929800 | 4.10412800 | -1.11580100 |



Optimized Structure of *Z,E*-**4**-An-**TS**$_2$.

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- Thermochemistry -

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(1 imaginary frequency = -39.39 Hz)

Zero-point correction= 0.726261 (Hartree/Particle)

Thermal correction to Energy= 0.766376

Thermal correction to Enthalpy= 0.767321

Thermal correction to Gibbs Free Energy= 0.653395

Sum of electronic and zero-point Energies= -1861.841574

Sum of electronic and thermal Energies= -1861.801458

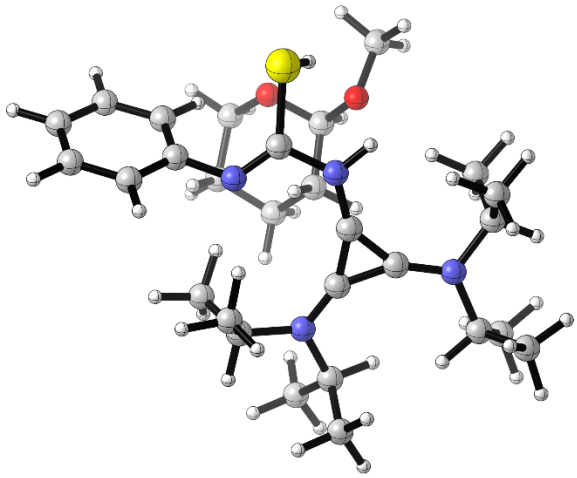
Sum of electronic and thermal Enthalpies= -1861.800514

Sum of electronic and thermal Free Energies= -1861.914440

| | | | |
|---|---|---|---|
| C | -1.13612200 | -0.87289100 | -1.67846500 |
| S | -1.99670000 | -2.04615000 | -2.56410800 |
| N | 0.26522400 | -1.13418500 | -1.58989900 |
| H | 0.52912000 | -2.03848600 | -1.95275200 |
| N | -1.51635700 | 0.17080600 | -1.01523900 |
| C | -2.87943300 | 0.53023200 | -0.96970800 |
| C | -3.29845100 | 1.72438300 | -1.55499600 |
| C | -3.80426900 | -0.22343400 | -0.24147500 |
| C | -4.60687800 | 2.16507900 | -1.39932100 |
| H | -2.59203500 | 2.29907100 | -2.14208000 |
| C | -5.10936000 | 0.22319000 | -0.08381400 |
| H | -3.49266500 | -1.17269000 | 0.17662400 |
| C | -5.51606300 | 1.42430900 | -0.65430700 |
| H | -6.53624300 | 1.76945800 | -0.53626800 |
| H | -0.98853300 | -0.39546800 | 0.79318100 |
| C | -1.76897600 | -1.31544900 | 2.44602900 |
| C | -0.73269700 | -0.46741300 | 1.88676600 |
| C | -0.74969300 | 0.94784800 | 2.45781800 |
| C | -2.18146600 | 1.47238000 | 2.38610000 |

| | | | |
|---|---|---|---|
| C | -3.14847200 | 0.55310400 | 3.10506600 |
| H | -0.37830200 | 0.95091200 | 3.48751900 |
| H | -0.09000200 | 1.57879200 | 1.86204700 |
| H | -2.26669700 | 2.45827200 | 2.84816900 |
| H | -2.48276700 | 1.57113900 | 1.34242900 |
| H | -3.16385500 | 0.69551200 | 4.18555000 |
| H | -4.15953400 | 0.61899200 | 2.70843600 |
| O | -2.82872600 | -0.88961900 | 2.97442900 |
| H | -1.68863800 | -2.39628000 | 2.43199400 |
| H | 0.22580300 | -0.98737200 | 1.93838300 |
| C | -3.24019100 | -3.97598100 | 0.56929300 |
| H | -4.15114100 | -3.55631800 | 0.12911100 |
| H | -3.41482200 | -4.15823800 | 1.63220400 |
| H | -3.02176500 | -4.93274600 | 0.08641000 |
| O | -2.14644700 | -3.07620200 | 0.45473200 |
| H | -2.05454800 | -2.85880700 | -0.49495700 |
| H | -4.91881200 | 3.09075800 | -1.86933900 |
| H | -5.81873300 | -0.38226500 | 0.47088900 |
| C | 1.20172800 | -0.39924800 | -0.98528800 |
| C | 1.75659400 | 0.77505300 | -0.51874400 |
| C | 2.44970000 | -0.43065000 | -0.40138100 |
| N | 1.73723300 | 2.07815000 | -0.28348800 |
| N | 3.48383100 | -1.15939700 | -0.02296300 |
| C | 2.86883800 | 2.64269400 | 0.48608000 |
| C | 0.87042800 | 3.00172500 | -1.06347200 |
| C | 4.72650400 | -0.52675200 | 0.46108100 |
| C | 3.36809300 | -2.63440400 | -0.06387900 |
| C | 3.99285500 | 3.10586700 | -0.43946700 |
| H | 3.23398600 | 1.81814300 | 1.10356700 |
| C | 2.41800500 | 3.74146600 | 1.44221600 |
| C | -0.42878300 | 3.30292700 | -0.32610100 |
| H | 1.45269800 | 3.92351500 | -1.14006000 |
| C | 0.62782700 | 2.49514000 | -2.48074700 |
| H | 4.60076600 | 0.53864100 | 0.26820000 |
| C | 4.89517600 | -0.73207900 | 1.96387600 |
| C | 5.93890900 | -0.99068200 | -0.34146000 |
| H | 4.26488300 | -3.00444300 | 0.43575700 |
| C | 2.16332900 | -3.11780700 | 0.74179700 |
| C | 3.37983300 | -3.15431200 | -1.49881400 |
| H | 4.29666100 | 2.30966300 | -1.12432000 |
| H | 3.68495000 | 3.96508600 | -1.04039700 |
| H | 4.86468900 | 3.40830200 | 0.14529100 |
| H | 2.03443900 | 4.61603500 | 0.91242900 |
| H | 1.64534000 | 3.38106800 | 2.12464900 |
| H | 3.27175800 | 4.06880400 | 2.03898000 |
| H | -1.00508200 | 2.38429300 | -0.22199000 |
| H | -0.24275800 | 3.73505500 | 0.65912800 |
| H | -1.02502100 | 4.01688200 | -0.89871000 |
| H | 1.56818100 | 2.25078100 | -2.98101200 |
| H | -0.02584700 | 1.62162900 | -2.48541500 |
| H | 0.13477800 | 3.27916400 | -3.05891400 |
| H | 5.01838200 | -1.78980700 | 2.21165500 |
| H | 5.78378200 | -0.20615600 | 2.31908200 |
| H | 4.02818600 | -0.35013200 | 2.50928600 |
| H | 5.78939100 | -0.81753400 | -1.40902400 |
| H | 6.82213900 | -0.43285800 | -0.02399500 |

| | | | |
|---|---|---|---|
| H | 6.15050300 | -2.05171800 | -0.18739900 |
| H | 2.17755600 | -4.20710700 | 0.81188100 |
| H | 2.19802000 | -2.71238700 | 1.75669800 |
| H | 1.21300800 | -2.83514400 | 0.28009300 |
| H | 2.54204200 | -2.75925200 | -2.07936800 |
| H | 4.30061400 | -2.86984500 | -2.01038300 |
| H | 3.30339300 | -4.24333100 | -1.50780200 |



Optimized Structure of *Z,E*-**4**-An-**INT**$_4$.

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- Thermochemistry -

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(0 imaginary frequencies)

Zero-point correction= 0.726739 (Hartree/Particle)

Thermal correction to Energy= 0.766823

Thermal correction to Enthalpy= 0.767767

Thermal correction to Gibbs Free Energy= 0.654513

Sum of electronic and zero-point Energies= -1861.893184

Sum of electronic and thermal Energies= -1861.853101

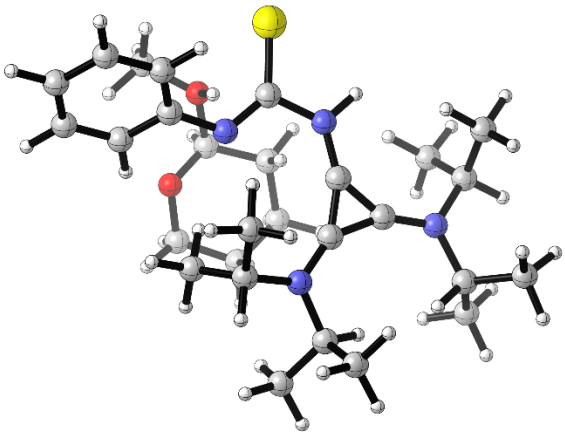
Sum of electronic and thermal Enthalpies= -1861.852156

Sum of electronic and thermal Free Energies= -1861.965410

| | | | |
|---|---|---|---|
| C | -1.28596400 | -0.57873000 | -1.69131600 |
| S | -2.18458600 | -2.03522800 | -2.24933700 |
| N | 0.10222900 | -0.78028900 | -1.68569500 |
| H | 0.41578500 | -1.67284700 | -2.03375200 |
| N | -1.74267800 | 0.54036800 | -1.35625800 |
| C | -3.10932900 | 0.84194900 | -1.19497100 |
| C | -3.61206800 | 1.98086000 | -1.82055900 |
| C | -3.92432300 | 0.09450100 | -0.34543600 |
| C | -4.93611000 | 2.34863600 | -1.62522600 |
| H | -2.96390200 | 2.56349100 | -2.46474700 |
| C | -5.24242300 | 0.48075600 | -0.14468800 |
| H | -3.51955200 | -0.77543400 | 0.15823200 |
| C | -5.75458900 | 1.60222000 | -0.78539800 |
| H | -6.78590300 | 1.89483700 | -0.62927500 |
| H | -0.60601400 | -0.45848800 | 0.93110300 |
| C | -1.04561800 | -2.34308900 | 1.79752600 |
| C | -0.35758200 | -0.99239400 | 1.85173800 |

| | | | |
|---|---|---|---|
| C | -0.87220200 | -0.19995200 | 3.05477800 |
| C | -2.39931500 | -0.12779700 | 3.01354100 |
| C | -2.98903000 | -1.52398900 | 2.85117000 |
| H | -0.54966300 | -0.68852400 | 3.98193800 |
| H | -0.43851600 | 0.80274200 | 3.05742900 |
| H | -2.79349800 | 0.32667800 | 3.92617300 |
| H | -2.71997500 | 0.49474700 | 2.17183200 |
| H | -2.80170200 | -2.12650000 | 3.75227100 |
| H | -4.06579200 | -1.48871500 | 2.68589800 |
| O | -2.44338200 | -2.19061600 | 1.71667200 |
| H | -0.80551600 | -2.92648200 | 2.70637400 |
| H | 0.72620600 | -1.13664000 | 1.89316000 |
| C | -0.96314100 | -4.42888400 | 0.70992100 |
| H | -2.04409000 | -4.56869600 | 0.78866800 |
| H | -0.47013800 | -4.91841900 | 1.55685900 |
| H | -0.59966300 | -4.86972100 | -0.21798500 |
| O | -0.63019100 | -3.04559200 | 0.66955200 |
| H | -1.86232700 | -2.70618700 | -1.12308800 |
| H | -5.32846200 | 3.22557900 | -2.12664500 |
| H | -5.87507400 | -0.10471000 | 0.51270700 |
| C | 1.02442400 | -0.02647700 | -1.05451500 |
| C | 1.48382000 | 1.06677500 | -0.34891900 |
| C | 2.33109700 | -0.01048300 | -0.63726700 |
| N | 1.35884500 | 2.22922400 | 0.26116400 |
| N | 3.49457000 | -0.62608800 | -0.56604500 |
| C | 2.47685600 | 2.68110000 | 1.12173100 |
| C | 0.23748000 | 3.16680500 | -0.00368100 |
| C | 4.70042000 | 0.08143700 | -0.08730500 |
| C | 3.58403500 | -2.04970900 | -0.96153100 |
| C | 3.35914600 | 3.68945400 | 0.39099600 |
| H | 3.05992600 | 1.78281400 | 1.33254400 |
| C | 1.97846400 | 3.19924400 | 2.46738200 |
| C | -0.99845500 | 2.80105600 | 0.81348400 |
| H | 0.60730100 | 4.13011500 | 0.35326900 |
| C | -0.01629200 | 3.31583300 | -1.49892400 |
| H | 4.40658800 | 1.12755100 | 0.00098100 |
| C | 5.12523500 | -0.42931500 | 1.28581100 |
| C | 5.82563800 | 0.02147000 | -1.11720200 |
| H | 4.60877100 | -2.34258400 | -0.72904800 |
| C | 2.65519700 | -2.91380300 | -0.11390600 |
| C | 3.38382000 | -2.22426100 | -2.46429300 |
| H | 3.72328100 | 3.28228100 | -0.55608500 |
| H | 2.81385500 | 4.61137300 | 0.17379400 |
| H | 4.22180000 | 3.95362100 | 1.00692400 |
| H | 1.40235700 | 4.12180500 | 2.36884900 |
| H | 1.36051300 | 2.45277400 | 2.97017500 |
| H | 2.83704900 | 3.41807500 | 3.10547000 |
| H | -1.29945800 | 1.77360000 | 0.61793800 |
| H | -0.80967500 | 2.92083300 | 1.88190800 |
| H | -1.83482800 | 3.44733600 | 0.53911300 |
| H | 0.90122300 | 3.60508500 | -2.01748800 |
| H | -0.40750400 | 2.39377600 | -1.92862500 |
| H | -0.75971700 | 4.09910300 | -1.66065700 |
| H | 5.42107400 | -1.48115000 | 1.24512100 |
| H | 5.98281500 | 0.13982800 | 1.65040700 |
| H | 4.31299700 | -0.33159400 | 2.01076200 |

| | | | |
|---|---|---|---|
| H | 5.48903400 | 0.39649300 | -2.08586400 |
| H | 6.65658800 | 0.64463100 | -0.78067800 |
| H | 6.21306400 | -0.99159600 | -1.24982800 |
| H | 2.80336800 | -3.96773700 | -0.35913400 |
| H | 2.87234400 | -2.77987200 | 0.94849300 |
| H | 1.59716700 | -2.68308700 | -0.26361700 |
| H | 2.39101500 | -1.89945200 | -2.78838600 |
| H | 4.11812400 | -1.64398300 | -3.02563400 |
| H | 3.49475900 | -3.27522100 | -2.73806900 |



Optimized Structure of *Z,E*-**4**-An-**TS$_3$-PA**.

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- Thermochemistry -

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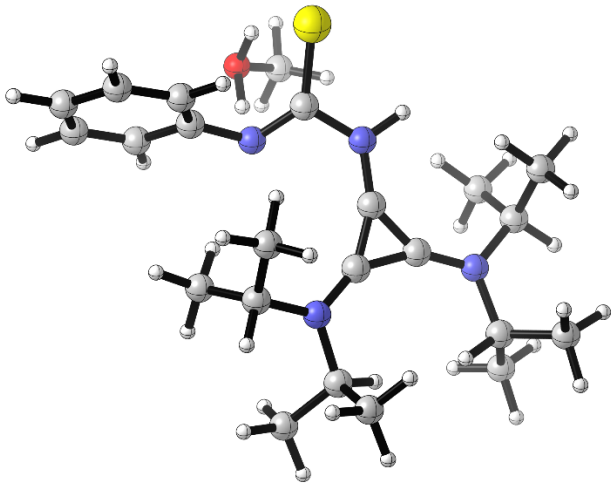
(1 imaginary frequency = -363.40 Hz)
Zero-point correction= 0.729072 (Hartree/Particle)
Thermal correction to Energy= 0.768091
Thermal correction to Enthalpy= 0.769035
Thermal correction to Gibbs Free Energy= 0.658830
Sum of electronic and zero-point Energies= -1861.845824
Sum of electronic and thermal Energies= -1861.806806
Sum of electronic and thermal Enthalpies= -1861.805862
Sum of electronic and thermal Free Energies= -1861.916067

| | | | |
|---|---|---|---|
| C | -1.33445100 | -1.20724200 | -1.32616800 |
| S | -2.13874200 | -2.63496800 | -1.80507400 |
| N | 0.08456300 | -1.32572900 | -1.33168400 |
| H | 0.40569100 | -2.23978300 | -1.61672000 |
| N | -1.77518000 | -0.08595600 | -0.83853900 |
| C | -3.09778800 | 0.35239300 | -1.05375600 |
| C | -3.73033500 | 0.24379500 | -2.29774500 |
| C | -3.76287100 | 1.02510600 | -0.02435100 |
| C | -4.99659700 | 0.77413400 | -2.48984300 |
| H | -3.22680800 | -0.26131000 | -3.11205900 |
| C | -5.03602200 | 1.54688200 | -0.22141500 |
| H | -3.27209000 | 1.13224100 | 0.93401700 |
| C | -5.66179900 | 1.42230700 | -1.45409500 |
| H | -6.65093900 | 1.83519400 | -1.61189400 |
| H | -0.26379900 | -1.33515200 | 1.10655500 |
| C | -1.90874100 | -1.45982900 | 2.42991200 |
| C | -0.46303800 | -1.75636000 | 2.09352800 |

| | | | |
|---|---|---|---|
| C | 0.45099600 | -1.08323000 | 3.11991700 |
| C | 0.09949100 | 0.40054400 | 3.21993000 |
| C | -1.37881800 | 0.55809200 | 3.53611200 |
| H | 0.33557300 | -1.56161100 | 4.09916100 |
| H | 1.49226700 | -1.22218700 | 2.82232000 |
| H | 0.68424900 | 0.88983900 | 4.00315700 |
| H | 0.31836900 | 0.90250100 | 2.27142000 |
| H | -1.60574200 | 0.16430900 | 4.53600000 |
| H | -1.70287300 | 1.59639400 | 3.49167900 |
| O | -2.19273100 | -0.12035600 | 2.57091200 |
| H | -2.27049700 | -2.04534000 | 3.28569000 |
| H | -0.31221100 | -2.83640300 | 2.04782200 |
| C | -4.18814200 | -1.92295800 | 1.41910100 |
| H | -4.51432100 | -0.92337000 | 1.69153500 |
| H | -4.43913900 | -2.67545500 | 2.16224100 |
| H | -4.53705900 | -2.20324700 | 0.42811800 |
| O | -2.72244400 | -1.93134700 | 1.31260900 |
| H | -2.41178700 | -1.56860100 | 0.43737900 |
| H | -5.46902000 | 0.67879900 | -3.46082200 |
| H | -5.53431200 | 2.06269900 | 0.59236300 |
| C | 1.01325700 | -0.44053500 | -0.94641500 |
| C | 1.50909900 | 0.79144000 | -0.56061400 |
| C | 2.35206500 | -0.31646500 | -0.65314300 |
| N | 1.40297100 | 2.07292800 | -0.25686800 |
| N | 3.53421900 | -0.89812100 | -0.54348400 |
| C | 2.59009400 | 2.74764700 | 0.31267100 |
| C | 0.22853400 | 2.89386100 | -0.64891700 |
| C | 4.75711300 | -0.09652300 | -0.33896500 |
| C | 3.62138100 | -2.37249000 | -0.61545900 |
| C | 3.36208400 | 3.50202900 | -0.76740400 |
| H | 3.21901300 | 1.94557500 | 0.70362000 |
| C | 2.22756000 | 3.63249100 | 1.50145400 |
| C | -0.87215800 | 2.79381400 | 0.40085000 |
| H | 0.60811100 | 3.91809600 | -0.66601600 |
| C | -0.24248200 | 2.56347300 | -2.06009300 |
| H | 4.45297800 | 0.93881900 | -0.49323400 |
| C | 5.27754700 | -0.25039300 | 1.08705900 |
| C | 5.81602900 | -0.40582600 | -1.39410000 |
| H | 4.65421300 | -2.60884400 | -0.35450500 |
| C | 2.72655800 | -3.03177500 | 0.43171300 |
| C | 3.36681300 | -2.88072900 | -2.03199000 |
| H | 3.62936700 | 2.84006400 | -1.59536400 |
| H | 2.77158300 | 4.32707200 | -1.17331500 |
| H | 4.27998900 | 3.92477800 | -0.35249800 |
| H | 1.60836100 | 4.48343400 | 1.21009900 |
| H | 1.69819200 | 3.06250100 | 2.26771200 |
| H | 3.14332100 | 4.03093600 | 1.94292000 |
| H | -1.15792900 | 1.74973100 | 0.52704300 |
| H | -0.54116100 | 3.20529400 | 1.35733300 |
| H | -1.75539800 | 3.34685300 | 0.07505600 |
| H | 0.58210500 | 2.64092700 | -2.77340600 |
| H | -0.68021600 | 1.56621800 | -2.10832200 |
| H | -1.01634600 | 3.27441900 | -2.35530800 |
| H | 5.57358800 | -1.28279900 | 1.29237500 |
| H | 6.15490200 | 0.38119200 | 1.24119400 |
| H | 4.51422700 | 0.03729500 | 1.81503400 |

| | | | |
|---|---|---|---|
| H | 5.40836500 | -0.28983200 | -2.40020500 |
| H | 6.65036000 | 0.28946800 | -1.28222500 |
| H | 6.21918100 | -1.41649200 | -1.29380800 |
| H | 2.88544600 | -4.11177900 | 0.42934300 |
| H | 2.96033700 | -2.65333300 | 1.42976200 |
| H | 1.66554100 | -2.85603300 | 0.23514500 |
| H | 2.36382800 | -2.62438500 | -2.38421200 |
| H | 4.08290900 | -2.45162200 | -2.73466300 |
| H | 3.46254000 | -3.96773500 | -2.06712000 |



Optimized Structure of *Z,E*-**4**-An-**TS$_3$-MA**.

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- Thermochemistry -

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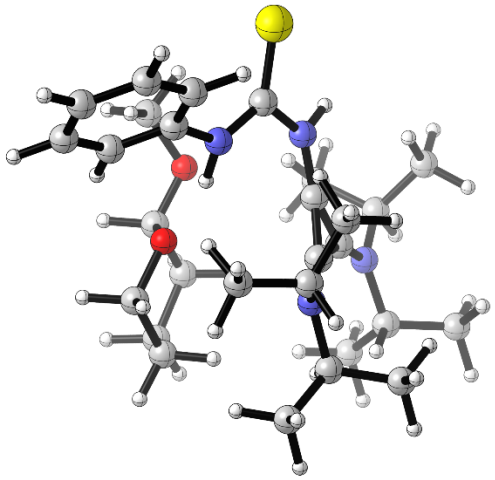
(1 imaginary frequency = -453.03 Hz)
Zero-point correction= 0.599373 (Hartree/Particle)
Thermal correction to Energy= 0.632729
Thermal correction to Enthalpy= 0.633673
Thermal correction to Gibbs Free Energy= 0.534554
Sum of electronic and zero-point Energies= -1591.411199
Sum of electronic and thermal Energies= -1591.377843
Sum of electronic and thermal Enthalpies= -1591.376899
Sum of electronic and thermal Free Energies= -1591.476018

| | | | |
|---|---|---|---|
| C | -1.55083000 | -1.41943300 | -0.58610800 |
| S | -2.38483800 | -2.68327400 | -1.35892200 |
| N | -0.15787700 | -1.48825700 | -0.66253900 |
| H | 0.19748700 | -2.33096600 | -1.09205600 |
| N | -2.01715400 | -0.48624400 | 0.23549800 |
| C | -3.28692400 | 0.11618100 | 0.02210700 |
| C | -3.82224700 | 0.35419300 | -1.24576300 |
| C | -3.96844700 | 0.59758400 | 1.14229200 |
| C | -5.01746100 | 1.04583500 | -1.37856400 |
| H | -3.31121000 | -0.00681500 | -2.12943700 |
| C | -5.16692000 | 1.28215000 | 1.00318200 |
| H | -3.54043100 | 0.44860500 | 2.12851800 |

| | | | |
|---|---|---|---|
| C | -5.69866000 | 1.51027400 | -0.25938600 |
| H | -6.63400900 | 2.04488200 | -0.37162000 |
| O | -3.02755400 | -2.37954300 | 1.58810900 |
| H | -3.20939500 | -2.75752700 | 0.67649900 |
| H | -5.42226000 | 1.21887500 | -2.36905700 |
| H | -5.68175700 | 1.64408600 | 1.88552500 |
| C | 0.75142400 | -0.54310900 | -0.32622400 |
| C | 1.19596700 | 0.74159100 | -0.08952800 |
| C | 2.09193900 | -0.33937500 | -0.12073400 |
| N | 1.03188600 | 2.03652100 | 0.05892900 |
| N | 3.30874500 | -0.84048600 | -0.04900100 |
| C | 2.19688300 | 2.85104900 | 0.47832900 |
| C | -0.22606900 | 2.72064500 | -0.34192800 |
| C | 4.49044700 | 0.04404800 | 0.04268900 |
| C | 3.48474400 | -2.30987800 | -0.03604700 |
| C | 2.86798100 | 3.49672300 | -0.73132400 |
| H | 2.89059800 | 2.14499500 | 0.93888100 |
| C | 1.82917300 | 3.86569300 | 1.55566800 |
| C | -1.24230000 | 2.70122200 | 0.79377700 |
| H | 0.07473100 | 3.75349400 | -0.53133300 |
| C | -0.76303000 | 2.16123700 | -1.65384100 |
| H | 4.11303900 | 1.04759900 | -0.15258400 |
| C | 5.08922400 | 0.00775100 | 1.44528800 |
| C | 5.51098000 | -0.26718500 | -1.04830300 |
| H | 4.53547400 | -2.46775600 | 0.21163400 |
| C | 2.65410900 | -2.95929600 | 1.06750500 |
| C | 3.22919300 | -2.91340800 | -1.41452700 |
| H | 3.14788000 | 2.74677000 | -1.47605100 |
| H | 2.20422200 | 4.21905200 | -1.21294000 |
| H | 3.77004700 | 4.02983200 | -0.42316500 |
| H | 1.14628600 | 4.63350900 | 1.18560600 |
| H | 1.37196900 | 3.37762500 | 2.41798700 |
| H | 2.73766800 | 4.37006800 | 1.89076000 |
| H | -1.42046600 | 1.67435700 | 1.11035000 |
| H | -0.89301900 | 3.28391200 | 1.64733500 |
| H | -2.19246000 | 3.12010300 | 0.45590900 |
| H | -0.00240900 | 2.20175500 | -2.43741000 |
| H | -1.10978800 | 1.13452000 | -1.54114000 |
| H | -1.62093200 | 2.75431800 | -1.97429900 |
| H | 5.48166800 | -0.98374400 | 1.68679600 |
| H | 5.91739500 | 0.71575700 | 1.51800200 |
| H | 4.34215200 | 0.27367200 | 2.19717100 |
| H | 5.05324200 | -0.21940600 | -2.03835400 |
| H | 6.31453000 | 0.47068600 | -1.00907900 |
| H | 5.96726900 | -1.25173600 | -0.92002100 |
| H | 2.89588700 | -4.02160700 | 1.13523100 |
| H | 2.86390500 | -2.49620900 | 2.03395000 |
| H | 1.58135800 | -2.87680200 | 0.87164200 |
| H | 2.20498000 | -2.73107700 | -1.75300200 |
| H | 3.90356500 | -2.49051300 | -2.16052600 |
| H | 3.38205000 | -3.99405600 | -1.38776700 |
| H | -2.49061500 | -1.50251300 | 1.25980300 |
| C | -2.19946000 | -3.28814200 | 2.35647500 |
| H | -2.76641700 | -4.20475000 | 2.49863300 |
| H | -1.26847000 | -3.48607000 | 1.82433000 |
| H | -2.01342500 | -2.80703300 | 3.31272700 |



Optimized Structure of *Z,E*-**4**-An-**INT**$_5$.

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- Thermochemistry -

---

(0 imaginary frequencies)

Zero-point correction= 0.731368 (Hartree/Particle)

Thermal correction to Energy= 0.770700

Thermal correction to Enthalpy= 0.771645

Thermal correction to Gibbs Free Energy= 0.660142

Sum of electronic and zero-point Energies= -1861.915232

Sum of electronic and thermal Energies= -1861.875899

Sum of electronic and thermal Enthalpies= -1861.874955

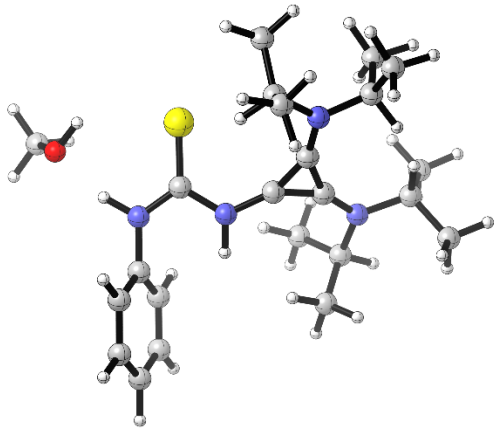
Sum of electronic and thermal Free Energies= -1861.986458

| | | | |
|---|---|---|---|
| C | -1.70186600 | -1.56610100 | -1.24336900 |
| S | -2.56040900 | -2.67232000 | -2.11256100 |
| N | -0.29918900 | -1.60871200 | -1.29742400 |
| H | 0.07300100 | -2.48747100 | -1.62488400 |
| N | -2.15248900 | -0.59793900 | -0.42181500 |
| C | -3.50088100 | -0.19631100 | -0.23509100 |
| C | -4.36384000 | 0.00599000 | -1.30743700 |
| C | -3.91667200 | 0.09090600 | 1.06299500 |
| C | -5.64762200 | 0.47483900 | -1.06931200 |
| H | -4.04036500 | -0.20916800 | -2.31672400 |
| C | -5.20045600 | 0.56850300 | 1.28853500 |
| H | -3.22808600 | -0.05351600 | 1.88786200 |
| C | -6.07174400 | 0.75722300 | 0.22423900 |
| H | -7.07590500 | 1.12347700 | 0.39975400 |
| H | 1.88057500 | -0.71860800 | 1.94301700 |
| C | -0.08885300 | -1.09865700 | 2.62824000 |
| C | 1.37446100 | -0.81512700 | 2.90839200 |
| C | 1.52960000 | 0.47064800 | 3.72134200 |
| C | 0.79365900 | 1.61801700 | 3.03101100 |
| C | -0.64633700 | 1.22075800 | 2.74643300 |
| H | 1.11458800 | 0.32298500 | 4.72498800 |
| H | 2.58712100 | 0.71023800 | 3.85502200 |
| H | 0.81267800 | 2.52485400 | 3.64144200 |

| | | | |
|---|---|---|---|
| H | 1.28318800 | 1.84824200 | 2.07909600 |
| H | -1.19530500 | 1.07045300 | 3.68688500 |
| H | -1.17486400 | 1.97440400 | 2.16244600 |
| O | -0.69353600 | 0.02309400 | 1.97491200 |
| H | -0.63666000 | -1.27191300 | 3.57047300 |
| H | 1.80701500 | -1.67389600 | 3.42647600 |
| C | -1.43712900 | -2.89058100 | 1.87438800 |
| H | -2.29589200 | -2.23544700 | 1.70509000 |
| H | -1.52954400 | -3.37515700 | 2.85157500 |
| H | -1.41872800 | -3.65076000 | 1.09533500 |
| O | -0.20683600 | -2.18007900 | 1.78288000 |
| H | -1.52095200 | -0.30683400 | 0.32733200 |
| H | -6.32192000 | 0.62213900 | -1.90455500 |
| H | -5.52017500 | 0.78556800 | 2.30086300 |
| C | 0.57182000 | -0.63070200 | -0.99393400 |
| C | 0.92792600 | 0.68931700 | -0.83526000 |
| C | 1.88820500 | -0.32678400 | -0.74402300 |
| N | 0.65363700 | 1.98394500 | -0.80758100 |
| N | 3.12276600 | -0.75992700 | -0.58990600 |
| C | 1.77277600 | 2.90198900 | -0.48463100 |
| C | -0.53123400 | 2.54707300 | -1.51562400 |
| C | 4.24346300 | 0.18108700 | -0.38685900 |
| C | 3.40231800 | -2.21028300 | -0.73678000 |
| C | 2.59033300 | 3.23281400 | -1.73223600 |
| H | 2.39931500 | 2.34804700 | 0.21848700 |
| C | 1.30258900 | 4.15418900 | 0.24661400 |
| C | -1.68477200 | 2.83644900 | -0.56283700 |
| H | -0.17415800 | 3.49926900 | -1.91482600 |
| C | -0.94861800 | 1.70246800 | -2.71450000 |
| H | 3.79392700 | 1.17245100 | -0.39678300 |
| C | 4.88536800 | -0.03494100 | 0.98030200 |
| C | 5.24512600 | 0.12073700 | -1.53638800 |
| H | 4.47387500 | -2.30919400 | -0.55812100 |
| C | 2.67920200 | -3.03562100 | 0.32093500 |
| C | 3.13039600 | -2.67147000 | -2.16680800 |
| H | 2.93336700 | 2.32486900 | -2.23576600 |
| H | 2.00258800 | 3.81438000 | -2.44679700 |
| H | 3.46714100 | 3.82671700 | -1.46427300 |
| H | 0.68649500 | 4.79763000 | -0.38500400 |
| H | 0.73820600 | 3.90172100 | 1.14562300 |
| H | 2.17686300 | 4.73469700 | 0.54763900 |
| H | -2.04157000 | 1.92614500 | -0.08426000 |
| H | -1.39343300 | 3.54809200 | 0.21066500 |
| H | -2.52354400 | 3.26480600 | -1.11582100 |
| H | -0.09673900 | 1.48070900 | -3.36199700 |
| H | -1.42308400 | 0.76860900 | -2.41498700 |
| H | -1.67953500 | 2.26124800 | -3.30133200 |
| H | 5.34940200 | -1.02145600 | 1.05849800 |
| H | 5.66643400 | 0.70974900 | 1.14660700 |
| H | 4.14269100 | 0.05910200 | 1.77615600 |
| H | 4.75192200 | 0.29407200 | -2.49554800 |
| H | 6.00597100 | 0.89191200 | -1.39970000 |
| H | 5.76012700 | -0.84193200 | -1.58210200 |
| H | 2.88535800 | -4.09594100 | 0.16161600 |
| H | 3.02606600 | -2.76911500 | 1.32096700 |
| H | 1.59676200 | -2.89016300 | 0.30620900 |

| | | | |
|---|---|---|---|
| H | 2.07679800 | -2.56602300 | -2.44016800 |
| H | 3.71775100 | -2.09259400 | -2.88198200 |
| H | 3.39437800 | -3.72453400 | -2.27879400 |

E,Z Conformation



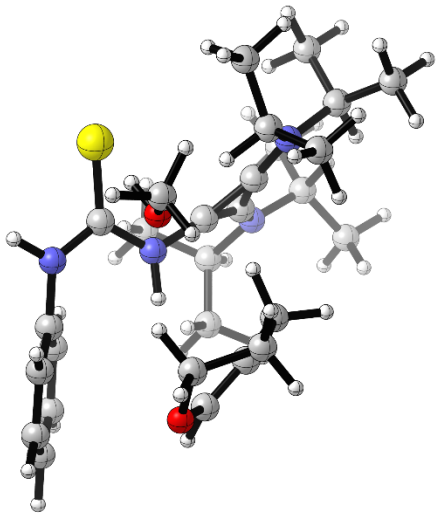
Optimized Structure of *E,Z*-**4**-Cy-**INT**$_1$.

---
- Thermochemistry -
---

(0 imaginary frequencies)
Zero-point correction= 0.602056 (Hartree/Particle)
Thermal correction to Energy= 0.636847
Thermal correction to Enthalpy= 0.637792
Thermal correction to Gibbs Free Energy= 0.533221
Sum of electronic and zero-point Energies= -1591.463325
Sum of electronic and thermal Energies= -1591.428534
Sum of electronic and thermal Enthalpies= -1591.427590
Sum of electronic and thermal Free Energies= -1591.532161

| | | | |
|---|---|---|---|
| C | -1.69895000 | -0.94482800 | 0.27324700 |
| S | -0.99553400 | -2.23085900 | 1.08507800 |
| N | -3.01681100 | -0.77676700 | 0.14122900 |
| H | -3.60683100 | -1.53307000 | 0.52637900 |
| N | -0.93408200 | 0.06200400 | -0.29718200 |
| C | -3.63938800 | 0.33865000 | -0.49887000 |
| C | -4.22286400 | 0.17675200 | -1.75073700 |
| C | -3.66561100 | 1.57787200 | 0.13902300 |
| C | -4.83174600 | 1.26219200 | -2.36747600 |
| H | -4.19858900 | -0.79593700 | -2.22742500 |
| C | -4.26368500 | 2.66225700 | -0.49131600 |
| H | -3.23739200 | 1.67713300 | 1.13100800 |
| C | -4.84653900 | 2.50419000 | -1.74337300 |
| H | -5.32212000 | 3.34808700 | -2.22849600 |
| H | -1.42075300 | 0.89740400 | -0.59807400 |
| C | -4.78758600 | -2.80617500 | 2.59601100 |

| | | | |
|---|---|---|---|
| H | -4.94501500 | -3.77005200 | 3.08769600 |
| H | -5.75495700 | -2.32220500 | 2.46552900 |
| H | -4.15372000 | -2.17643200 | 3.23036000 |
| O | -4.22801600 | -2.97858200 | 1.29934800 |
| H | -3.35675700 | -3.37953400 | 1.39427400 |
| C | 0.42453100 | 0.13319900 | -0.23865400 |
| C | 1.67348900 | -0.41492700 | -0.39073400 |
| C | 1.50506400 | 0.93744700 | -0.00112600 |
| N | 2.46169300 | -1.42407300 | -0.66745600 |
| N | 1.96052600 | 2.11884400 | 0.34699200 |
| C | 3.91729000 | -1.23151800 | -0.42781500 |
| C | 1.81081600 | -2.71318100 | -1.04282000 |
| C | 3.40830700 | 2.38620300 | 0.48362800 |
| C | 0.98217200 | 3.17044800 | 0.71614400 |
| C | 4.25341100 | -1.41021200 | 1.05122800 |
| H | 4.10185900 | -0.19008000 | -0.70196300 |
| C | 4.81156100 | -2.06422400 | -1.33597200 |
| C | 2.13394000 | -3.83331400 | -0.06223100 |
| H | 3.90228200 | 1.47774800 | 0.14003600 |
| C | 3.84429800 | 3.53455800 | -0.42056300 |
| C | 3.78492200 | 2.60113500 | 1.94679200 |
| H | 1.58620000 | 4.01518200 | 1.04944200 |
| C | 0.17937600 | 3.62270100 | -0.49987500 |
| C | 0.10572400 | 2.73093400 | 1.88581400 |
| H | 3.61869900 | -0.77841600 | 1.67887300 |
| H | 4.11726300 | -2.44593500 | 1.36601500 |
| H | 5.29485500 | -1.13421000 | 1.23240300 |
| H | 4.73231600 | -3.13324100 | -1.13845100 |
| H | 4.59870700 | -1.88018400 | -2.38930100 |
| H | 5.84732600 | -1.77505500 | -1.14730700 |
| H | 3.17542800 | -4.15563700 | -0.11657700 |
| H | 1.90498700 | -3.52997500 | 0.96070000 |
| H | 1.50996200 | -4.69673000 | -0.30310200 |
| H | 3.38519100 | 4.48154600 | -0.12566600 |
| H | 4.92621900 | 3.66356600 | -0.35275700 |
| H | 3.58726500 | 3.33397200 | -1.46270200 |
| H | 3.32450600 | 3.50413400 | 2.35597700 |
| H | 3.47894000 | 1.74967900 | 2.55872600 |
| H | 4.86679700 | 2.71680500 | 2.03702100 |
| H | -0.48608700 | 4.44293300 | -0.22388000 |
| H | 0.83860300 | 3.96640100 | -1.29885100 |
| H | -0.44472100 | 2.81779400 | -0.89867100 |
| H | -0.54895100 | 1.89919800 | 1.61183600 |
| H | 0.71507100 | 2.41971500 | 2.73639200 |
| H | -0.52749000 | 3.56173100 | 2.20372600 |
| H | -5.29514700 | 1.13674700 | -3.33858300 |
| H | -4.29317900 | 3.62488000 | 0.00520000 |
| H | 0.74765700 | -2.50373600 | -0.92336800 |
| C | 2.04426000 | -3.09668600 | -2.50256300 |
| H | 3.03106700 | -3.52417300 | -2.67832600 |
| H | 1.30664300 | -3.85187600 | -2.78318600 |
| H | 1.91049200 | -2.23666100 | -3.16256700 |



Optimized Structure of *E,Z*-**4**-Cy-**INT**$_2$.

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- Thermochemistry -

---

(0 imaginary frequencies)

Zero-point correction= 0.727291 (Hartree/Particle)

Thermal correction to Energy= 0.768940

Thermal correction to Enthalpy= 0.769885

Thermal correction to Gibbs Free Energy= 0.650424

Sum of electronic and zero-point Energies= -1861.885849

Sum of electronic and thermal Energies= -1861.844199

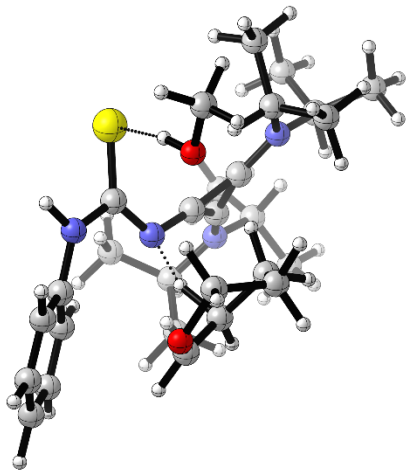
Sum of electronic and thermal Enthalpies= -1861.843255

Sum of electronic and thermal Free Energies= -1861.962716

| | | | |
|---|---|---|---|
| C | -1.09573900 | 0.18933600 | -1.87789700 |
| S | -0.05668300 | 0.93416800 | -2.96362900 |
| N | -2.40943000 | 0.04555900 | -2.11740900 |
| H | -2.72967100 | 0.46766900 | -2.97584300 |
| N | -0.66769700 | -0.32792700 | -0.68694000 |
| C | -3.33357100 | -0.72867100 | -1.34915400 |
| C | -4.45922600 | -0.11795000 | -0.81416100 |
| C | -3.11450900 | -2.09393300 | -1.16951400 |
| C | -5.36925900 | -0.87514700 | -0.08755900 |
| H | -4.61020500 | 0.94556700 | -0.95661300 |
| C | -4.01711900 | -2.83859800 | -0.42543300 |
| H | -2.24972300 | -2.56369600 | -1.62441900 |
| C | -5.14605200 | -2.23003100 | 0.11500400 |
| H | -5.85418900 | -2.81587200 | 0.68865800 |
| H | -1.34350200 | -0.59634100 | 0.02972800 |
| C | -2.70764200 | -0.37765700 | 2.29218400 |
| C | -1.38583900 | -0.17128700 | 2.33845700 |
| C | -0.80297000 | 1.21799400 | 2.34607600 |
| C | -1.90675000 | 2.23388600 | 2.64033900 |
| C | -3.14209700 | 1.87855400 | 1.82941300 |
| H | -0.00990800 | 1.28387500 | 3.09733200 |
| H | -0.35101400 | 1.46559100 | 1.37927900 |
| H | -2.15814500 | 2.22253300 | 3.70483000 |
| H | -1.58522100 | 3.24572700 | 2.38311300 |

| | | | |
|---|---|---|---|
| H | -3.96842700 | 2.56195600 | 2.02093000 |
| H | -2.89799800 | 1.89719200 | 0.76066700 |
| O | -3.64022200 | 0.57897700 | 2.16306100 |
| H | -0.74365400 | -1.03295600 | 2.48439600 |
| C | -1.56866600 | 4.42190200 | -0.69752800 |
| H | -0.65154400 | 4.98760000 | -0.90234100 |
| H | -1.92300300 | 4.68973600 | 0.29892400 |
| H | -2.33183500 | 4.71532000 | -1.42575900 |
| O | -1.34147400 | 3.02461300 | -0.69922000 |
| H | -1.03844600 | 2.75370100 | -1.57363700 |
| C | 0.65053600 | -0.35418400 | -0.30914300 |
| C | 1.82634200 | 0.27268100 | 0.00798100 |
| C | 1.70071300 | -1.14680000 | 0.05736900 |
| N | 2.55178900 | 1.35045100 | 0.14442200 |
| N | 2.17537500 | -2.34953500 | 0.25804800 |
| C | 4.00520700 | 1.16487800 | 0.40449300 |
| C | 1.88424000 | 2.64557100 | -0.17693100 |
| C | 3.57872600 | -2.57886400 | 0.66384200 |
| C | 1.29458700 | -3.50772200 | -0.04067200 |
| C | 4.74237200 | 0.79905500 | -0.88194800 |
| H | 4.05203900 | 0.31430100 | 1.08945200 |
| C | 4.65575200 | 2.32937900 | 1.13735300 |
| C | 2.49013300 | 3.31831100 | -1.40196700 |
| H | 4.00594400 | -1.58459700 | 0.79568800 |
| C | 3.64696600 | -3.30973100 | 2.00080100 |
| C | 4.35985800 | -3.28187000 | -0.44256200 |
| H | 1.90286800 | -4.38783400 | 0.17070600 |
| C | 0.08512800 | -3.53824100 | 0.88880800 |
| C | 0.90778900 | -3.53330200 | -1.51655900 |
| H | 4.27768700 | -0.06073600 | -1.37267000 |
| H | 4.74216300 | 1.63119300 | -1.58783500 |
| H | 5.78046400 | 0.54310900 | -0.65757400 |
| H | 4.68802500 | 3.23761700 | 0.53477000 |
| H | 4.15119800 | 2.54461900 | 2.07942600 |
| H | 5.68727700 | 2.05259800 | 1.36368000 |
| H | 3.50009900 | 3.69184100 | -1.22090500 |
| H | 2.50651700 | 2.63372000 | -2.25134600 |
| H | 1.86908600 | 4.17534400 | -1.67359500 |
| H | 3.23264900 | -4.31887700 | 1.93222700 |
| H | 4.68796000 | -3.40551500 | 2.31542700 |
| H | 3.10246500 | -2.76400900 | 2.77431300 |
| H | 3.99166100 | -4.29579000 | -0.61829400 |
| H | 4.30044200 | -2.72511300 | -1.38024900 |
| H | 5.41065200 | -3.36115100 | -0.15708400 |
| H | -0.46808200 | -4.46745000 | 0.73800600 |
| H | 0.39208400 | -3.48938100 | 1.93569600 |
| H | -0.60144500 | -2.71255300 | 0.68596800 |
| H | 0.29804000 | -2.66603600 | -1.78472500 |
| H | 1.79231500 | -3.53933300 | -2.15610100 |
| H | 0.32622700 | -4.43255300 | -1.73037900 |
| H | -6.24324600 | -0.39830800 | 0.33752400 |
| H | -3.85174400 | -3.90027100 | -0.28499600 |
| H | 0.86793300 | 2.35397000 | -0.44024600 |
| C | 1.76644800 | 3.57799200 | 1.02699100 |
| H | 2.68741500 | 4.12070100 | 1.23878400 |
| H | 0.98951200 | 4.31460000 | 0.81125000 |

| | | | |
|---|---|---|---|
| H | 1.46439300 | 3.03068900 | 1.92194100 |
| H | -3.15803000 | -1.36094300 | 2.37387800 |



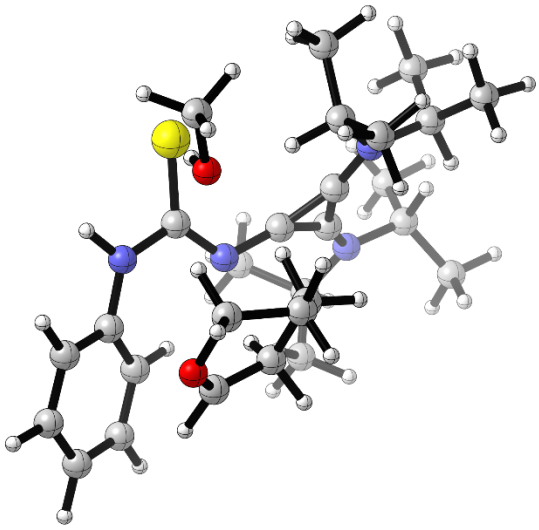
Optimized Structure of *E,Z*-**4**-Cy-**TS**$_1$.

---
- Thermochemistry -
---
(1 imaginary frequency = -664.73 Hz)
Zero-point correction= 0.723417 (Hartree/Particle)
Thermal correction to Energy= 0.763687
Thermal correction to Enthalpy= 0.764632
Thermal correction to Gibbs Free Energy= 0.650510
Sum of electronic and zero-point Energies= -1861.859816
Sum of electronic and thermal Energies= -1861.819545
Sum of electronic and thermal Enthalpies= -1861.818601
Sum of electronic and thermal Free Energies= -1861.932723

| | | | |
|---|---|---|---|
| C | -1.12351300 | 0.11873200 | -1.60401000 |
| S | -0.25338100 | 1.04600800 | -2.73090900 |
| N | -2.46720100 | -0.02447100 | -1.77882600 |
| H | -2.82967500 | 0.49545900 | -2.56312500 |
| N | -0.60961000 | -0.49989700 | -0.53067700 |
| C | -3.35686200 | -0.92625300 | -1.14429300 |
| C | -4.66850600 | -0.50927000 | -0.92556200 |
| C | -2.97548000 | -2.21956200 | -0.78253100 |
| C | -5.58438600 | -1.36535200 | -0.32846300 |
| H | -4.96510300 | 0.49318000 | -1.21447500 |
| C | -3.89207000 | -3.06213200 | -0.16938300 |
| H | -1.96945200 | -2.55884900 | -0.98461500 |
| C | -5.19729400 | -2.64016800 | 0.06674000 |
| H | -5.91129200 | -3.30767000 | 0.53378900 |
| H | -1.37580500 | -0.39760900 | 0.75295000 |
| C | -3.06166000 | -0.15238800 | 1.91740500 |
| C | -1.66036100 | -0.09776100 | 1.94132600 |
| C | -0.99940100 | 1.26102300 | 2.18410300 |
| C | -2.03995400 | 2.29469700 | 2.60844400 |
| C | -3.25322400 | 2.19274400 | 1.71039700 |
| H | -0.22256900 | 1.16142300 | 2.94402800 |
| H | -0.52449500 | 1.61102400 | 1.26441300 |
| H | -2.33933100 | 2.14441300 | 3.65045900 |

| | | | |
|---|---|---|---|
| H | -1.63505600 | 3.30404200 | 2.51771300 |
| H | -4.06725000 | 2.85092100 | 2.00302300 |
| H | -2.98068800 | 2.36058500 | 0.66536300 |
| O | -3.84020100 | 0.85289000 | 1.78773500 |
| H | -1.22910700 | -0.96911800 | 2.43497500 |
| C | -1.42850700 | 4.58281700 | -0.94819600 |
| H | -0.43877000 | 4.94742300 | -1.24792500 |
| H | -1.74587800 | 5.14215900 | -0.06639600 |
| H | -2.13538600 | 4.78471800 | -1.75971100 |
| O | -1.40207800 | 3.21146600 | -0.59765700 |
| H | -1.11425900 | 2.70005800 | -1.37109400 |
| C | 0.72023500 | -0.42301700 | -0.27938900 |
| C | 1.88589400 | 0.25455300 | 0.01055400 |
| C | 1.83023300 | -1.15347100 | 0.06188800 |
| N | 2.57318000 | 1.36764300 | 0.15830700 |
| N | 2.36514200 | -2.34211900 | 0.24824800 |
| C | 4.02902600 | 1.22775000 | 0.41289000 |
| C | 1.87443000 | 2.63489500 | -0.18174400 |
| C | 3.79842300 | -2.51617100 | 0.55008600 |
| C | 1.50799600 | -3.52784800 | 0.01592600 |
| C | 4.78334700 | 0.88269800 | -0.87049900 |
| H | 4.10420500 | 0.37950700 | 1.09917700 |
| C | 4.64543600 | 2.41188500 | 1.14521400 |
| C | 2.46658900 | 3.31562000 | -1.40977100 |
| H | 4.20149500 | -1.50682400 | 0.63370500 |
| C | 3.99569100 | -3.21845400 | 1.89044700 |
| C | 4.52494500 | -3.21275300 | -0.59752200 |
| H | 2.14623200 | -4.38845200 | 0.22139900 |
| C | 0.34060700 | -3.56026600 | 0.99963400 |
| C | 1.04988600 | -3.60174100 | -1.43835500 |
| H | 4.33421800 | 0.02101200 | -1.37198300 |
| H | 4.77815600 | 1.71969000 | -1.57052600 |
| H | 5.82338700 | 0.63890600 | -0.64002700 |
| H | 4.65141600 | 3.32037800 | 0.54186800 |
| H | 4.13245300 | 2.61417700 | 2.08599700 |
| H | 5.68463000 | 2.16732500 | 1.37405200 |
| H | 3.46536400 | 3.71849500 | -1.22897300 |
| H | 2.50386000 | 2.62138900 | -2.25069300 |
| H | 1.82291200 | 4.15112600 | -1.69533600 |
| H | 3.61123100 | -4.24152400 | 1.87085000 |
| H | 5.06024900 | -3.27479600 | 2.12670900 |
| H | 3.49225700 | -2.67615800 | 2.69384300 |
| H | 4.18086100 | -4.24175600 | -0.73024500 |
| H | 4.37689100 | -2.67616700 | -1.53721100 |
| H | 5.59610400 | -3.25006800 | -0.38865200 |
| H | -0.20561700 | -4.50003600 | 0.89271500 |
| H | 0.69710600 | -3.48597200 | 2.02966800 |
| H | -0.35887000 | -2.74353000 | 0.80195300 |
| H | 0.40818100 | -2.75436000 | -1.69484300 |
| H | 1.90301000 | -3.60429900 | -2.11933800 |
| H | 0.48019600 | -4.51916800 | -1.60245100 |
| H | -6.60156600 | -1.02960300 | -0.16596300 |
| H | -3.59000800 | -4.06688800 | 0.10359000 |
| H | 0.87520500 | 2.30708200 | -0.46463800 |
| C | 1.71035800 | 3.57775800 | 1.00911400 |
| H | 2.61126400 | 4.15022900 | 1.23014800 |

| | | | |
|---|---|---|---|
| H | 0.91343600 | 4.28723000 | 0.77577600 |
| H | 1.41727900 | 3.02813900 | 1.90668300 |
| H | -3.60094400 | -1.09770200 | 1.94122000 |



Optimized Structure of *E,Z*-**4**-Cy-**INT3**.

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- Thermochemistry -

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(0 imaginary frequencies)

Zero-point correction= 0.726499 (Hartree/Particle)

Thermal correction to Energy= 0.767764

Thermal correction to Enthalpy= 0.768709

Thermal correction to Gibbs Free Energy= 0.651185

Sum of electronic and zero-point Energies= -1861.860769

Sum of electronic and thermal Energies= -1861.819504

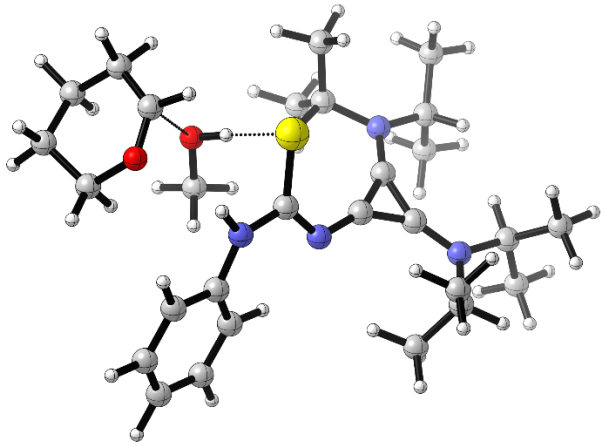
Sum of electronic and thermal Enthalpies= -1861.818560

Sum of electronic and thermal Free Energies= -1861.936083

| | | | |
|---|---|---|---|
| C | -1.05863800 | -0.14875900 | -1.58291900 |
| S | -0.40145500 | 1.00240000 | -2.66632000 |
| N | -2.40027100 | -0.41653200 | -1.72086200 |
| H | -2.83417900 | 0.12654500 | -2.45108700 |
| N | -0.41419000 | -0.81574900 | -0.63824200 |
| C | -3.22572900 | -1.34017100 | -1.05933500 |
| C | -4.59754100 | -1.06107400 | -1.01653400 |
| C | -2.75720700 | -2.52414100 | -0.47889900 |
| C | -5.47747800 | -1.93004100 | -0.38717600 |
| H | -4.97212400 | -0.15516200 | -1.48203300 |
| C | -3.64509600 | -3.37604600 | 0.16599300 |
| H | -1.70649500 | -2.76351700 | -0.53899200 |
| C | -5.00486700 | -3.08622000 | 0.22529600 |
| H | -5.69027100 | -3.76551100 | 0.71720100 |
| H | -1.52486400 | -0.81661800 | 1.20901700 |
| C | -3.38786100 | -0.17496900 | 1.79336100 |
| C | -1.94376100 | -0.17196500 | 2.00476400 |

| | | | |
|---|---|---|---|
| C | -1.29201100 | 1.20691100 | 1.99165500 |
| C | -2.27059200 | 2.26651000 | 2.48872100 |
| C | -3.52707200 | 2.21370900 | 1.65587000 |
| H | -0.38546600 | 1.18934400 | 2.59697700 |
| H | -1.00107500 | 1.45628000 | 0.96904200 |
| H | -2.50538000 | 2.12674000 | 3.54908800 |
| H | -1.84415100 | 3.26427800 | 2.36968300 |
| H | -4.34795200 | 2.81532300 | 2.03647600 |
| H | -3.31818200 | 2.43821800 | 0.60626000 |
| O | -4.10546100 | 0.84024000 | 1.65013500 |
| H | -1.78591500 | -0.73970200 | 2.93343900 |
| C | -1.94814700 | 4.38979200 | -1.28844200 |
| H | -0.95283700 | 4.83487400 | -1.40373600 |
| H | -2.52230400 | 5.01111500 | -0.59860900 |
| H | -2.44938500 | 4.39790500 | -2.26137700 |
| O | -1.87990300 | 3.08417700 | -0.74342900 |
| H | -1.47415500 | 2.49934100 | -1.41112200 |
| C | 0.85864300 | -0.51383200 | -0.34656100 |
| C | 1.89239600 | 0.33943200 | -0.00255500 |
| C | 2.07195000 | -1.04872200 | 0.02244600 |
| N | 2.38370900 | 1.55206100 | 0.20735100 |
| N | 2.79103500 | -2.14135000 | 0.21077600 |
| C | 3.82635200 | 1.63382800 | 0.53586300 |
| C | 1.52632300 | 2.70135900 | -0.17113200 |
| C | 4.22761700 | -2.08124200 | 0.52920400 |
| C | 2.13449100 | -3.44675800 | -0.02208600 |
| C | 4.69753800 | 1.42918500 | -0.70381200 |
| H | 3.99794300 | 0.79720000 | 1.21997100 |
| C | 4.21226200 | 2.88834800 | 1.30849100 |
| C | 2.06535100 | 3.46576600 | -1.37461500 |
| H | 4.45219500 | -1.02158900 | 0.65013600 |
| C | 4.53196600 | -2.78235200 | 1.85043000 |
| C | 5.07332400 | -2.60756100 | -0.62780500 |
| H | 2.91026600 | -4.19534800 | 0.14775800 |
| C | 1.01981300 | -3.67509900 | 0.99680600 |
| C | 1.64696900 | -3.57985000 | -1.46264900 |
| H | 4.40425900 | 0.52687400 | -1.24722300 |
| H | 4.61956200 | 2.27419100 | -1.38987000 |
| H | 5.74585900 | 1.32360200 | -0.41270900 |
| H | 4.12381000 | 3.79379000 | 0.70673700 |
| H | 3.61413600 | 3.00405900 | 2.21302400 |
| H | 5.25888700 | 2.79711700 | 1.60598600 |
| H | 2.98801300 | 4.00589400 | -1.15107200 |
| H | 2.23768900 | 2.78560900 | -2.21024500 |
| H | 1.32149900 | 4.20078100 | -1.69126400 |
| H | 4.34197700 | -3.85712000 | 1.79061800 |
| H | 5.58546600 | -2.65047300 | 2.10587700 |
| H | 3.92618100 | -2.36893100 | 2.65983700 |
| H | 4.90642600 | -3.67475200 | -0.79655500 |
| H | 4.84380500 | -2.07355900 | -1.55255100 |
| H | 6.13401000 | -2.47083000 | -0.40636600 |
| H | 0.58572500 | -4.66848700 | 0.86204500 |
| H | 1.40473900 | -3.60162000 | 2.01653800 |
| H | 0.22297000 | -2.93722300 | 0.86442900 |
| H | 0.85212200 | -2.86144900 | -1.67902700 |
| H | 2.46374700 | -3.41703600 | -2.16861200 |

| | | | |
|---|---|---|---|
| H | 1.24734700 | -4.58304900 | -1.62738600 |
| H | -6.53634400 | -1.69987700 | -0.37406200 |
| H | -3.26771800 | -4.29106800 | 0.60840600 |
| H | 0.60438600 | 2.22951800 | -0.50799300 |
| C | 1.16654500 | 3.61462400 | 1.00120000 |
| H | 1.93890600 | 4.35160000 | 1.22311300 |
| H | 0.25098300 | 4.15321600 | 0.74420300 |
| H | 0.97468000 | 3.03474800 | 1.90698300 |
| H | -3.94782100 | -1.11196200 | 1.76987000 |



Optimized Structure of *E,Z*-**4**-Cy-**TS$_2$**.

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- Thermochemistry -

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(1 imaginary frequency = -65.27 Hz)

Zero-point correction= 0.728155 (Hartree/Particle)

Thermal correction to Energy= 0.768097

Thermal correction to Enthalpy= 0.769042

Thermal correction to Gibbs Free Energy= 0.654409

Sum of electronic and zero-point Energies= -1861.854060

Sum of electronic and thermal Energies= -1861.814118

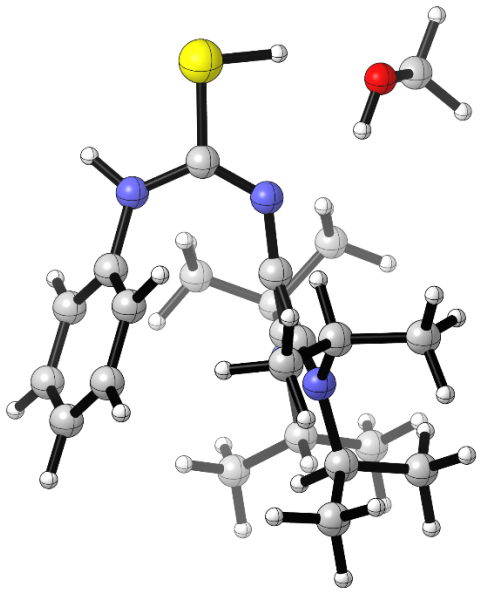
Sum of electronic and thermal Enthalpies= -1861.813173

Sum of electronic and thermal Free Energies= -1861.927806

| | | | |
|---|---|---|---|
| C | -0.78391900 | 0.63744200 | -1.00325000 |
| S | -0.83573600 | -0.77651100 | -2.01252400 |
| N | -1.94768600 | 1.35398200 | -0.92933100 |
| H | -2.62107100 | 1.08621900 | -1.62657600 |
| N | 0.24673600 | 1.07664000 | -0.32467100 |
| C | -2.35669400 | 2.39129300 | -0.07443800 |
| C | -1.66804800 | 2.77760200 | 1.07718600 |
| C | -3.56965500 | 3.01787300 | -0.38548900 |
| C | -2.20067200 | 3.76652500 | 1.89579100 |
| H | -0.72112900 | 2.31725500 | 1.31227400 |
| C | -4.08788300 | 4.00245800 | 0.44092400 |
| H | -4.09458500 | 2.74389500 | -1.29646400 |
| C | -3.40697300 | 4.38172300 | 1.59229200 |
| H | -3.80730300 | 5.15446300 | 2.23691500 |
| H | -3.64523800 | -3.46896100 | -0.81468200 |
| C | -4.04963600 | -1.53784400 | -1.44951000 |
| C | -4.51196800 | -2.80523400 | -0.87000400 |

| | | | |
|---|---|---|---|
| C | -5.25013300 | -2.66714100 | 0.45653100 |
| C | -6.06145700 | -1.37221300 | 0.46653900 |
| C | -5.16893100 | -0.19038200 | 0.17444800 |
| H | -5.89908300 | -3.52912500 | 0.61124100 |
| H | -4.50853100 | -2.65156400 | 1.25599600 |
| H | -6.86871900 | -1.41390100 | -0.27184000 |
| H | -6.52693900 | -1.20787500 | 1.44035200 |
| H | -5.69803900 | 0.74182200 | -0.00376600 |
| H | -4.39410100 | -0.03437300 | 0.92494300 |
| O | -4.40519400 | -0.39286400 | -1.07684500 |
| H | -5.14976800 | -3.22948200 | -1.66449100 |
| C | -1.95058400 | -0.95326500 | 1.75605300 |
| H | -2.55342300 | -1.28093500 | 2.60510500 |
| H | -2.13075500 | 0.11288600 | 1.57979900 |
| H | -0.89550500 | -1.08405000 | 2.01774700 |
| O | -2.31326900 | -1.74918200 | 0.63901600 |
| C | 1.39387800 | 0.39113500 | -0.27034600 |
| C | 2.17669700 | -0.72765800 | -0.05878500 |
| C | 2.76390200 | 0.53180100 | -0.20974500 |
| N | 2.30327900 | -2.02743400 | 0.17304800 |
| N | 3.80212800 | 1.34406100 | -0.27002000 |
| C | 3.67434900 | -2.53749000 | 0.39774500 |
| C | 1.05401500 | -2.77486400 | 0.44316300 |
| C | 5.17732600 | 0.85528200 | -0.07803300 |
| C | 3.55269600 | 2.77334800 | -0.56785600 |
| C | 4.16291100 | -2.23773900 | 1.81662800 |
| H | 4.29277500 | -1.97214900 | -0.30499700 |
| C | 3.85237500 | -4.00446800 | 0.02908600 |
| C | 0.96769100 | -3.30187100 | 1.87307400 |
| H | 5.07705200 | -0.20658700 | 0.14672900 |
| C | 5.99885700 | 0.99468600 | -1.35732400 |
| C | 5.83953100 | 1.52169200 | 1.12517400 |
| H | 4.54123400 | 3.23465100 | -0.60383100 |
| C | 2.89479700 | 2.94259600 | -1.93461500 |
| C | 2.75091100 | 3.43521800 | 0.54997100 |
| H | 4.00952600 | -1.18509200 | 2.07057100 |
| H | 3.63768700 | -2.84589900 | 2.55524300 |
| H | 5.23112700 | -2.45338200 | 1.90067600 |
| H | 3.29996100 | -4.67028900 | 0.69396800 |
| H | 3.54728100 | -4.19711300 | -0.99990300 |
| H | 4.91086600 | -4.25584900 | 0.12243500 |
| H | 1.66475200 | -4.12186500 | 2.05824200 |
| H | 1.16503500 | -2.51074100 | 2.60059300 |
| H | -0.04196900 | -3.68185800 | 2.04729100 |
| H | 6.14820900 | 2.04367700 | -1.62619300 |
| H | 6.98551100 | 0.54742200 | -1.21784700 |
| H | 5.50640900 | 0.49244400 | -2.19290000 |
| H | 5.98165200 | 2.59379500 | 0.96695300 |
| H | 5.23925700 | 1.38313600 | 2.02712700 |
| H | 6.82423500 | 1.08125300 | 1.29630800 |
| H | 2.80271600 | 4.00480200 | -2.17126000 |
| H | 3.48872400 | 2.46452100 | -2.71655500 |
| H | 1.88988400 | 2.51255000 | -1.94163400 |
| H | 1.73948300 | 3.02232200 | 0.59600200 |
| H | 3.23974000 | 3.29493900 | 1.51681600 |
| H | 2.66441200 | 4.50745700 | 0.36056700 |

| | | | |
|---|---|---|---|
| H | -1.65451700 | 4.05974500 | 2.78517000 |
| H | -5.02219500 | 4.48426200 | 0.17630700 |
| H | 0.28413600 | -2.01381500 | 0.32805200 |
| C | 0.73788300 | -3.84239100 | -0.60121700 |
| H | 0.89156900 | -3.44535100 | -1.60543400 |
| H | 1.32616000 | -4.75155700 | -0.47516800 |
| H | -0.31710400 | -4.11293200 | -0.50256100 |
| H | -3.40457100 | -1.51653300 | -2.32835100 |
| H | -1.73418500 | -1.52110700 | -0.11310100 |



Optimized Structure of *E,Z*-**4**-Cy-**INT**$_4$.

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- Thermochemistry -

---

(0 imaginary frequencies)

Zero-point correction= 0.599660 (Hartree/Particle)

Thermal correction to Energy= 0.634038

Thermal correction to Enthalpy= 0.634982

Thermal correction to Gibbs Free Energy= 0.533050

Sum of electronic and zero-point Energies= -1591.451587

Sum of electronic and thermal Energies= -1591.417209

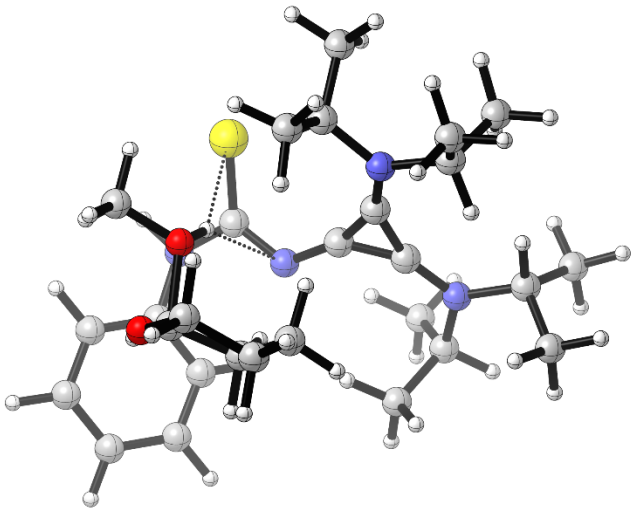
Sum of electronic and thermal Enthalpies= -1591.416265

Sum of electronic and thermal Free Energies= -1591.518197

| | | | |
|---|---|---|---|
| C | 2.53445600 | -0.74138000 | 0.84437900 |
| S | 4.19314500 | -1.32232300 | 0.74619700 |
| N | 2.23119000 | -0.20876500 | 2.05616300 |
| H | 3.00373400 | -0.08893100 | 2.69465400 |
| N | 1.74525300 | -0.85919100 | -0.17754000 |
| C | 0.93081900 | 0.04247900 | 2.58655700 |
| C | 0.65801700 | 1.29039400 | 3.13711400 |
| C | -0.03643900 | -0.95784800 | 2.60097900 |
| C | -0.59619000 | 1.54877900 | 3.67293200 |
| H | 1.42770900 | 2.05275700 | 3.14411100 |

| | | | |
|---|---|---|---|
| C | -1.29449200 | -0.68547100 | 3.12065800 |
| H | 0.20042200 | -1.94100500 | 2.20905900 |
| C | -1.57942000 | 0.56665200 | 3.65228300 |
| H | -2.55702200 | 0.76747000 | 4.07366900 |
| O | 3.46061900 | -1.81246000 | 2.30156500 |
| H | 4.14034500 | -1.59388300 | -0.59302800 |
| C | 0.51430800 | -0.30648000 | -0.2643100 |
| C | -0.82876300 | -0.52127100 | -0.4378900 |
| C | -0.29103100 | 0.76788700 | -0.57695400 |
| N | -1.83642400 | -1.37268600 | -0.4751000 |
| N | -0.40883400 | 2.04515700 | -0.86532600 |
| C | -3.17770200 | -0.82319000 | -0.76680400 |
| C | -1.45239400 | -2.81295300 | -0.46786700 |
| C | -1.73594400 | 2.66361500 | -1.05716600 |
| C | 0.81829600 | 2.86182300 | -1.01291100 |
| C | -3.32795600 | -0.52230700 | -2.25818000 |
| H | -3.21505700 | 0.12201500 | -0.21687300 |
| C | -4.32442300 | -1.67035600 | -0.23402200 |
| C | -1.72496500 | -3.46336200 | -1.82184300 |
| H | -2.45383400 | 1.85642400 | -0.90710500 |
| C | -1.98952000 | 3.72738700 | 0.00747200 |
| C | -1.91025700 | 3.18762500 | -2.47952800 |
| H | 0.46861100 | 3.83722800 | -1.35376500 |
| C | 1.53548600 | 3.04894700 | 0.31831200 |
| C | 1.73445500 | 2.28050300 | -2.08600100 |
| H | -2.49474200 | 0.08268200 | -2.62623200 |
| H | -3.36943000 | -1.43929100 | -2.84787400 |
| H | -4.25208500 | 0.03346600 | -2.43414300 |
| H | -4.41092900 | -2.62604900 | -0.75343800 |
| H | -4.22192500 | -1.85446600 | 0.83595400 |
| H | -5.25772500 | -1.12768700 | -0.39559600 |
| H | -2.79429800 | -3.57801700 | -2.01144300 |
| H | -1.28442100 | -2.88411100 | -2.63596600 |
| H | -1.28033700 | -4.46051200 | -1.83692600 |
| H | -1.29340500 | 4.56483200 | -0.08839200 |
| H | -2.99984900 | 4.12764700 | -0.09832600 |
| H | -1.88592200 | 3.30222400 | 1.00859500 |
| H | -1.23839000 | 4.02257500 | -2.69337400 |
| H | -1.72506800 | 2.40040600 | -3.21371600 |
| H | -2.93168900 | 3.54880700 | -2.61575700 |
| H | 2.36533500 | 3.74843300 | 0.19741800 |
| H | 0.85516400 | 3.44321400 | 1.07499200 |
| H | 1.94609600 | 2.10183500 | 0.67723400 |
| H | 2.14290600 | 1.31565700 | -1.77209900 |
| H | 1.20179800 | 2.14643400 | -3.02987400 |
| H | 2.57534000 | 2.95498300 | -2.25963600 |
| H | -0.80229700 | 2.51785100 | 4.11158800 |
| H | -2.05049400 | -1.46133100 | 3.13541500 |
| H | -0.36782100 | -2.78683700 | -0.33473900 |
| C | -2.02008200 | -3.62866300 | 0.69154800 |
| H | -3.07420400 | -3.86987300 | 0.56123200 |
| H | -1.47445900 | -4.57300900 | 0.75277000 |
| H | -1.89633500 | -3.10706400 | 1.64121200 |
| H | 2.62380500 | -1.55496100 | -1.89354000 |
| C | 3.83587600 | -0.82744300 | -3.24963000 |
| H | 4.01241700 | 0.14938700 | -2.78161900 |

| | | | |
|---|---|---|---|
| H | 4.76297400 | -1.16086600 | -3.71416200 |
| H | 3.07871200 | -0.71539700 | -4.03306100 |



Optimized Structure of *E,Z*-**4**-Cy-**TS$_3$-PA**.

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- Thermochemistry -

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(1 imaginary frequency = -101.65 Hz)

Zero-point correction= 0.729627 (Hartree/Particle)

Thermal correction to Energy= 0.768801

Thermal correction to Enthalpy= 0.769745

Thermal correction to Gibbs Free Energy= 0.657465

Sum of electronic and zero-point Energies= -1861.859081

Sum of electronic and thermal Energies= -1861.819908

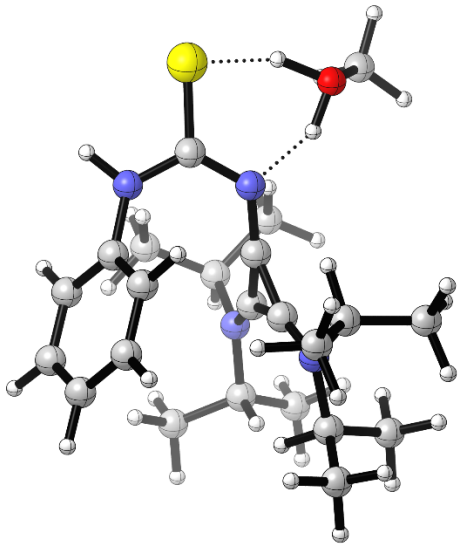
Sum of electronic and thermal Enthalpies= -1861.818964

Sum of electronic and thermal Free Energies= -1861.931244

| | | | |
|---|---|---|---|
| C | 1.23662800 | 0.30342800 | -2.06465000 |
| S | 0.70780500 | -0.96197100 | -3.08355500 |
| N | 2.55903500 | 0.66783800 | -2.18178400 |
| H | 3.03052300 | 0.17066200 | -2.92159300 |
| N | 0.53456700 | 0.94400100 | -1.13809000 |
| C | 3.39523900 | 1.25069700 | -1.20703900 |
| C | 4.68891400 | 0.73369800 | -1.07747600 |
| C | 2.99315000 | 2.29758800 | -0.37717700 |
| C | 5.55203100 | 1.22599300 | -0.10825500 |
| H | 5.02242300 | -0.05201600 | -1.74941200 |
| C | 3.85898200 | 2.77012900 | 0.60140700 |
| H | 2.01255000 | 2.72933700 | -0.50514500 |
| C | 5.13292500 | 2.23498700 | 0.75122900 |
| H | 5.80304500 | 2.61755300 | 1.51133500 |
| H | 1.26513700 | 0.54746900 | 0.96346500 |
| C | 2.58398500 | -1.08586900 | 1.30389600 |
| C | 1.56116000 | -0.09836700 | 1.79016400 |
| C | 0.38702100 | -0.77296700 | 2.49070200 |
| C | 0.92179800 | -1.78271700 | 3.50533900 |
| C | 1.86805200 | -2.75919600 | 2.83342100 |

| | | | |
|---|---|---|---|
| H | -0.22860600 | -0.01715600 | 2.98197900 |
| H | -0.25183700 | -1.27411400 | 1.75620200 |
| H | 1.44891700 | -1.25962800 | 4.30925700 |
| H | 0.11068600 | -2.35142100 | 3.96641500 |
| H | 2.39428000 | -3.38620100 | 3.54925600 |
| H | 1.33558700 | -3.40255700 | 2.12569500 |
| O | 2.92837700 | -2.09168100 | 2.10085300 |
| H | 2.11528700 | 0.53470100 | 2.49280800 |
| C | 2.78034900 | -2.73788900 | -0.71076800 |
| H | 2.17747000 | -3.22990200 | -1.46904800 |
| H | 3.15744900 | -3.44110500 | 0.02594300 |
| H | 3.59015700 | -2.16944400 | -1.16792900 |
| O | 1.89958100 | -1.82691400 | 0.00342900 |
| H | 1.46052800 | -1.23294200 | -0.64302900 |
| C | -0.70905700 | 0.58797900 | -0.80137300 |
| C | -1.73903200 | -0.28170300 | -0.46508300 |
| C | -1.85639800 | 1.08961100 | -0.22210300 |
| N | -2.26361800 | -1.49603100 | -0.32603200 |
| N | -2.49327900 | 2.15365600 | 0.23226600 |
| C | -3.63904200 | -1.55507100 | 0.22265000 |
| C | -1.56400500 | -2.62389000 | -0.98349500 |
| C | -3.89344000 | 2.08826000 | 0.68582400 |
| C | -1.76746700 | 3.44369900 | 0.25540600 |
| C | -4.68970600 | -1.21233500 | -0.83487600 |
| H | -3.65670200 | -0.77814600 | 0.99234800 |
| C | -3.95738200 | -2.86124300 | 0.93826600 |
| C | -2.34301900 | -3.20994200 | -2.15581000 |
| H | -4.20143400 | 1.05579700 | 0.52692200 |
| C | -4.00830200 | 2.39987100 | 2.17536100 |
| C | -4.79475800 | 2.96914300 | -0.17612800 |
| H | -2.48498400 | 4.16978800 | 0.64101900 |
| C | -0.58752300 | 3.37926000 | 1.22311300 |
| C | -1.35131900 | 3.87892200 | -1.14690300 |
| H | -4.43679200 | -0.28775500 | -1.36093900 |
| H | -4.78206800 | -2.00595800 | -1.57743600 |
| H | -5.66571000 | -1.07774700 | -0.36134600 |
| H | -4.01566200 | -3.70654800 | 0.25109800 |
| H | -3.22362600 | -3.08380400 | 1.71427900 |
| H | -4.93425400 | -2.76186100 | 1.41563300 |
| H | -3.23590600 | -3.75356300 | -1.83835200 |
| H | -2.63242600 | -2.42488200 | -2.85663400 |
| H | -1.70134500 | -3.91303600 | -2.69223900 |
| H | -3.71490100 | 3.43013300 | 2.39339600 |
| H | -5.04207400 | 2.27618100 | 2.50503700 |
| H | -3.37640500 | 1.73028100 | 2.76412900 |
| H | -4.57788500 | 4.03171900 | -0.04019000 |
| H | -4.67763700 | 2.72577400 | -1.23421800 |
| H | -5.83951500 | 2.81039300 | 0.09945000 |
| H | -0.10505600 | 4.35688600 | 1.29192200 |
| H | -0.91831700 | 3.08935800 | 2.22346400 |
| H | 0.15765000 | 2.66041700 | 0.87221800 |
| H | -0.60375500 | 3.19981200 | -1.56479600 |
| H | -2.21255000 | 3.91034100 | -1.81736100 |
| H | -0.91201800 | 4.87820000 | -1.10748700 |
| H | 6.55225500 | 0.81729600 | -0.02520400 |
| H | 3.53626600 | 3.58272200 | 1.24261700 |

| | | | |
|---|---|---|---|
| H | -0.68528800 | -2.15180000 | -1.42349300 |
| C | -1.06935900 | -3.69633600 | -0.01137900 |
| H | -1.85355200 | -4.37965700 | 0.31420000 |
| H | -0.30690000 | -4.29727400 | -0.51501300 |
| H | -0.61549500 | -3.24468100 | 0.87368100 |
| H | 3.47445000 | -0.64199900 | 0.85962400 |



Optimized Structure of *E,Z*-**4**-Cy-**TS$_3$-MA**.

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- Thermochemistry -

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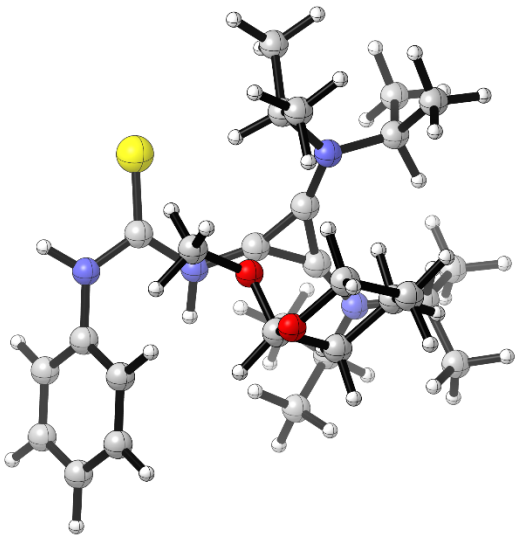
(1 imaginary frequency = -384.83 Hz)
Zero-point correction= 0.597671 (Hartree/Particle)
Thermal correction to Energy= 0.630953
Thermal correction to Enthalpy= 0.631898
Thermal correction to Gibbs Free Energy= 0.532509
Sum of electronic and zero-point Energies= -1591.443428
Sum of electronic and thermal Energies= -1591.410145
Sum of electronic and thermal Enthalpies= -1591.409201
Sum of electronic and thermal Free Energies= -1591.508590

| | | | |
|---|---|---|---|
| C | 2.63573700 | -0.50746800 | 0.74403700 |
| S | 4.29636300 | -0.96540800 | 0.62629400 |
| N | 2.30975100 | 0.27382700 | 1.80737000 |
| H | 3.10253300 | 0.55306200 | 2.36703400 |
| N | 1.74933300 | -0.91718900 | -0.16139900 |
| C | 1.02700600 | 0.47464500 | 2.39689800 |
| C | 0.66059800 | 1.76238600 | 2.77634600 |
| C | 0.17353200 | -0.59640900 | 2.64975400 |
| C | -0.57296100 | 1.98525400 | 3.37273500 |
| H | 1.34702700 | 2.58328800 | 2.60950000 |
| C | -1.06416100 | -0.36296400 | 3.23372600 |
| H | 0.48467000 | -1.60356700 | 2.39446800 |
| C | -1.44546000 | 0.92567200 | 3.58885000 |
| H | -2.40643800 | 1.09806300 | 4.05825000 |
| O | 3.29970100 | -2.31357300 | -1.62728400 |
| H | 3.94118800 | -1.92010200 | -0.79781700 |

| | | | |
|---|---|---|---|
| C | 0.51840700 | -0.36729500 | -0.29338100 |
| C | -0.83121500 | -0.58873900 | -0.37254300 |
| C | -0.29983200 | 0.68134500 | -0.66127000 |
| N | -1.83744400 | -1.43291000 | -0.25059500 |
| N | -0.44334100 | 1.92774200 | -1.05625300 |
| C | -3.19614700 | -0.91714800 | -0.54948300 |
| C | -1.45408100 | -2.86643900 | -0.11595900 |
| C | -1.78560000 | 2.52627000 | -1.20382000 |
| C | 0.75425900 | 2.70878800 | -1.44831400 |
| C | -3.43248800 | -0.78085400 | -2.05322600 |
| H | -3.20354800 | 0.08213300 | -0.10514800 |
| C | -4.31035700 | -1.69103600 | 0.14100800 |
| C | -1.82274300 | -3.67882200 | -1.35496100 |
| H | -2.48047500 | 1.76070200 | -0.85714000 |
| C | -1.93181500 | 3.74199600 | -0.29363400 |
| C | -2.11076500 | 2.83313000 | -2.66331900 |
| H | 0.35697400 | 3.60673500 | -1.92349200 |
| C | 1.58736100 | 3.13473500 | -0.24658200 |
| C | 1.58143900 | 1.95253100 | -2.48447900 |
| H | -2.61411400 | -0.23720300 | -2.53271700 |
| H | -3.52211400 | -1.75640000 | -2.53393600 |
| H | -4.35766800 | -0.22936500 | -2.23682600 |
| H | -4.42722900 | -2.69925000 | -0.25963500 |
| H | -4.14884200 | -1.75098100 | 1.21768800 |
| H | -5.25097700 | -1.16398500 | -0.03008600 |
| H | -2.90257500 | -3.80179900 | -1.45895400 |
| H | -1.43639500 | -3.21189300 | -2.26359600 |
| H | -1.38609000 | -4.67637300 | -1.27262400 |
| H | -1.25479300 | 4.54779600 | -0.58976500 |
| H | -2.95010700 | 4.13150500 | -0.35395000 |
| H | -1.72199200 | 3.47435200 | 0.74447000 |
| H | -1.48464300 | 3.63498800 | -3.06222500 |
| H | -1.97902200 | 1.94880300 | -3.29055100 |
| H | -3.14946500 | 3.15934600 | -2.74779900 |
| H | 2.39920200 | 3.78751800 | -0.57465200 |
| H | 0.97734900 | 3.67973600 | 0.47530700 |
| H | 2.03232400 | 2.26901600 | 0.24889500 |
| H | 2.04604200 | 1.06657000 | -2.04169900 |
| H | 0.96450500 | 1.64436400 | -3.33169500 |
| H | 2.38156300 | 2.59507500 | -2.85703700 |
| H | -0.84801900 | 2.98895900 | 3.67515400 |
| H | -1.72663900 | -1.19481900 | 3.44150700 |
| H | -0.36296800 | -2.83229200 | -0.06202300 |
| C | -1.93370400 | -3.52341900 | 1.17590300 |
| H | -2.99802400 | -3.75476700 | 1.16317000 |
| H | -1.39597600 | -4.46488700 | 1.30963500 |
| H | -1.72243200 | -2.89000600 | 2.03780200 |
| H | 2.45743700 | -1.87747400 | -1.22733500 |
| C | 3.65543600 | -1.67337300 | -2.86948500 |
| H | 3.78357700 | -0.59934200 | -2.71833700 |
| H | 4.58702500 | -2.11889000 | -3.20966800 |
| H | 2.86694700 | -1.87051600 | -3.59326100 |



Optimized Structure of *E,Z*-**4**-Cy-**INT**$_5$.

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- Thermochemistry -

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(0 imaginary frequencies)

Zero-point correction= 0.731752 (Hartree/Particle)

Thermal correction to Energy= 0.771119

Thermal correction to Enthalpy= 0.772063

Thermal correction to Gibbs Free Energy= 0.659882

Sum of electronic and zero-point Energies= -1861.907295

Sum of electronic and thermal Energies= -1861.867928

Sum of electronic and thermal Enthalpies= -1861.866983

Sum of electronic and thermal Free Energies= -1861.979165

| | | | |
|---|---|---|---|
| C | 1.93985000 | -1.31077500 | -1.74895400 |
| S | 1.07587100 | -2.26736500 | -2.78921900 |
| N | 3.23278300 | -1.54767700 | -1.43533000 |
| H | 3.65597600 | -2.29488200 | -1.96543400 |
| N | 1.43649900 | -0.16728800 | -1.15523700 |
| C | 4.07356400 | -0.75948400 | -0.59483300 |
| C | 3.72684900 | -0.52559700 | 0.73567500 |
| C | 5.25368400 | -0.23672800 | -1.11505000 |
| C | 4.55354700 | 0.25368100 | 1.53440400 |
| H | 2.81891800 | -0.96031900 | 1.13652700 |
| C | 6.08473400 | 0.52259700 | -0.30221200 |
| H | 5.51224300 | -0.42281700 | -2.15123200 |
| C | 5.73348500 | 0.77657500 | 1.01840200 |
| H | 6.38282400 | 1.37366500 | 1.64695600 |
| H | -0.02172600 | 1.04792700 | 1.80475600 |
| C | 0.27256700 | -0.86801400 | 2.72396600 |
| C | -0.41728300 | 0.48810800 | 2.65422600 |
| C | -1.93462700 | 0.31920300 | 2.57107900 |
| C | -2.40743400 | -0.56406200 | 3.72681800 |
| C | -1.63053700 | -1.87296300 | 3.74874600 |
| H | -2.42989200 | 1.29342900 | 2.61112500 |
| H | -2.19973500 | -0.14853100 | 1.61624700 |
| H | -2.25211100 | -0.03912900 | 4.67499200 |
| H | -3.47618200 | -0.78080300 | 3.64537400 |

| | | | |
|---|---|---|---|
| H | -1.83902400 | -2.44134100 | 4.65445800 |
| H | -1.90985200 | -2.49564100 | 2.88987800 |
| O | -0.22025700 | -1.66712600 | 3.75518200 |
| H | -0.15586300 | 1.03880300 | 3.56329500 |
| C | 0.68350400 | -2.77468000 | 1.36610900 |
| H | 0.69206400 | -3.04511300 | 0.30938700 |
| H | 0.08614600 | -3.49928000 | 1.92554000 |
| H | 1.70880500 | -2.80330900 | 1.75586100 |
| O | 0.13575700 | -1.47002700 | 1.45239400 |
| C | 0.14632700 | 0.21341000 | -1.05767100 |
| C | -1.21353900 | 0.01773700 | -0.99919900 |
| C | -0.65026200 | 1.27712600 | -0.74002600 |
| N | -2.28561200 | -0.73671500 | -1.08226700 |
| N | -0.73438200 | 2.54442900 | -0.38511500 |
| C | -3.58717100 | -0.02991300 | -1.19015800 |
| C | -2.09360400 | -2.20255300 | -1.24957900 |
| C | -2.01731900 | 3.10744000 | 0.08550400 |
| C | 0.44670400 | 3.42075100 | -0.55935100 |
| C | -3.91057200 | 0.33698900 | -2.63874300 |
| H | -3.43652600 | 0.90319900 | -0.64518400 |
| C | -4.73397000 | -0.75427300 | -0.49969100 |
| C | -2.66732800 | -2.73094500 | -2.55718000 |
| H | -2.61628400 | 2.24209200 | 0.37462800 |
| C | -1.83270100 | 3.94789000 | 1.34570900 |
| C | -2.72851700 | 3.85859200 | -1.03475500 |
| H | 0.06384400 | 4.43474100 | -0.43623400 |
| C | 1.49399300 | 3.17679000 | 0.52498500 |
| C | 1.01795700 | 3.31738300 | -1.97080900 |
| H | -3.06230900 | 0.83684300 | -3.11392100 |
| H | -4.16465300 | -0.54125900 | -3.23279000 |
| H | -4.76421900 | 1.01883800 | -2.66181100 |
| H | -5.00331200 | -1.68132700 | -1.00747300 |
| H | -4.49748300 | -0.97630400 | 0.54220100 |
| H | -5.61201000 | -0.10534600 | -0.51843700 |
| H | -3.75946800 | -2.71779800 | -2.57147100 |
| H | -2.29091200 | -2.16190900 | -3.40916300 |
| H | -2.35052900 | -3.76872400 | -2.68225000 |
| H | -1.29666600 | 4.88013100 | 1.15324300 |
| H | -2.81396800 | 4.21640700 | 1.74185200 |
| H | -1.29787700 | 3.38771200 | 2.11565300 |
| H | -2.13674100 | 4.71384500 | -1.37300600 |
| H | -2.90599100 | 3.20397000 | -1.89167700 |
| H | -3.69110300 | 4.23879500 | -0.68576700 |
| H | 2.32702300 | 3.87222900 | 0.40489300 |
| H | 1.07067800 | 3.31618700 | 1.52092400 |
| H | 1.90552400 | 2.16321100 | 0.47686300 |
| H | 1.47095400 | 2.34133000 | -2.16348800 |
| H | 0.24112100 | 3.48796400 | -2.71885600 |
| H | 1.79538700 | 4.07152500 | -2.10716300 |
| H | 4.28626000 | 0.43161400 | 2.56942400 |
| H | 7.00611000 | 0.92384400 | -0.70661100 |
| H | -1.01209700 | -2.30769400 | -1.31993500 |
| C | -2.54309700 | -2.99823100 | -0.02779400 |
| H | -3.62443400 | -3.11605000 | 0.03839300 |
| H | -2.10540200 | -3.99783300 | -0.08530600 |
| H | -2.17433700 | -2.51989300 | 0.87956400 |

| | | | |
|---|---|---|---|
| H | 1.34030600 | -0.76066500 | 2.95839400 |
| H | 2.10074400 | 0.43715400 | -0.68840000 |

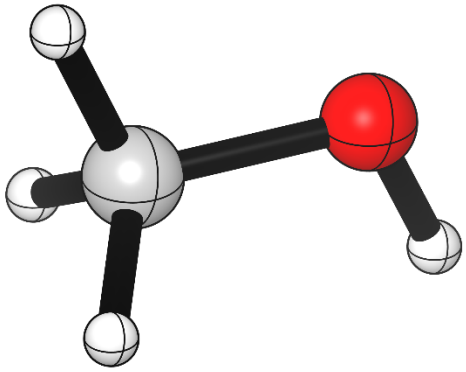
***Table 24.*** *Energy for all structures at TZVP and 6-311G(d,p) basis sets with thermal corrections and quasi-harmonic approximation adjustments to both TZVP and 6-311G(d,p) energies. All values are in kcal mol$^{-1}$.*

| Structure | TZVP Energy | Gibbs Free Energy Correction (TZVP) | 6-311G(d,p) Energy | Gibbs Free Energy Correction (6-311G(d,p)) | Quasi-Harmonic Approximation Adjusted Energy (TZVP) | Quasi-Harmonic Approximation Adjusted Energy (6-311G(d,p)) |
|---|---|---|---|---|---|---|
| MeOH | -72624.20071 | -72605.98501 | -72612.57677 | -72594.36107 | -72605.99002 | -72597.47924 |
| DHP | -169775.2694 | -169715.5741 | -169760.6547 | -169700.9594 | -169715.6153 | -169701.0002 |
| MTP | -242419.5935 | -242326.2874 | -242399.177 | -242305.8709 | -242326.4628 | -242306.0459 |
| E,E-4 | -926496.2265 | -926189.8496 | -926452.0687 | -926145.6918 | -926189.7402 | -926145.5824 |
| E,Z-4 | -926496.6179 | -926192.8634 | -926451.2628 | -926147.5082 | -926191.8925 | -926146.5375 |
| Z,Z-4 | -926492.7109 | -926189.4395 | -926447.3232 | -926144.0518 | -926188.4074 | -926143.0197 |
| Z,E-4 | -926495.0403 | -926189.9448 | -926450.1953 | -926145.0998 | -926189.4378 | -926144.5928 |
| Pathway 1 | | | | | | |
| Z,Z-1-INT1 | -999128.315 | -998792.6602 | -999077.5048 | -998741.8501 | -998792.3091 | -998741.4992 |
| Z,Z-4-INT2 | -1168911.578 | -1168502.446 | -1168848.181 | -1168439.049 | -1168501.831 | -1168438.434 |
| Z,Z-4-TS | -1168879.085 | -1168471.106 | -1168816.262 | -1168408.283 | -1168470.583 | -1168407.759 |
| Z,Z-4-INT3 | -1168922.778 | -1168509.364 | -1168860.363 | -1168446.949 | -1168509.115 | -1168446.701 |
| Pathway 2 - An | | | | | | |
| E,E-4-An-INT1 | -999127.0463 | -998793.0852 | -999072.9582 | -998738.997 | -998789.3122 | -998738.9051 |
| E,E-4-An-INT2 | -1168905.985 | -1168497.665 | -1168842.373 | -1168434.053 | -1168496.611 | -1168432.999 |
| E,E-4-An-TS1 | -1168882.623 | -1168475.611 | -1168819.311 | -1168412.3 | -1168475.379 | -1168412.068 |
| E,E-4-An-INT3 | -1168902.09 | -1168492.009 | -1168838.698 | -1168428.617 | -1168491.658 | -1168428.266 |
| E,E-4-An-TS2 | -1168883.396 | -1168476.697 | -1168820.346 | -1168413.647 | -1168475.99 | -1168412.94 |
| E,E-4-An-INT4 | -1168901.839 | -1168492.867 | -1168838.368 | -1168429.396 | -1168492.11 | -1168428.639 |
| E,E-4-An-TS3-PA | -1168891.163 | -1168480.177 | -1168828.421 | -1168417.435 | -1168479.553 | -1168416.811 |

| | | | | | | |
|---|---|---|---|---|---|---|
| E,E-4-An-TS3-MA | -999107.6866 | -998774.176 | -999056.6096 | -998723.099 | -998773.9547 | -998722.8775 |
| E,E-4-An-INT5 | -1168920.928 | -1168509.03 | -1168858.189 | -1168446.291 | -1168508.265 | -1168445.526 |
| E,Z-4-An-INT1 | -999126.0935 | -998791.4973 | -999074.0016 | -998739.4054 | -998790.7014 | -998738.6095 |
| E,Z-4-An-INT2 | -1168909.942 | -1168500.925 | -1168846.833 | -1168437.815 | -1168500.194 | -1168437.085 |
| E,Z-4-An-TS1 | -1168882.137 | -1168476.602 | -1168817.581 | -1168412.047 | -1168475.543 | -1168410.987 |
| E,Z-4-An-INT3 | -1168893.103 | -1168485.444 | -1168828.396 | -1168420.737 | -1168484.238 | -1168419.530 |
| E,Z-4-An-TS2 | -1168884.827 | -1168476.58 | -1168819.927 | -1168411.68 | -1168476.013 | -1168411.113 |
| E,Z-4-An-INT4 | -1168899.388 | -1168490.077 | -1168835.194 | -1168425.883 | -1168489.131 | -1168424.937 |
| E,Z-4-An-TS3-PA | -1168889.999 | -1168480.53 | -1168825.856 | -1168416.387 | -1168479.235 | -1168415.091 |
| E,Z-4-An-TS3-MA | -999108.1475 | -998776.4114 | -999056.034 | -998724.298 | -998775.7469 | -998723.6336 |
| E,Z-4-An-INT5 | -1168920.722 | -1168512.326 | -1168856.733 | -1168448.337 | -1168510.177 | -1168446.187 |
| Z,E-4-An-INT1 | -999124.8228 | -998787.0433 | -999074.3158 | -998736.5363 | -998787.1623 | -998736.6549 |
| Z,E-4-An-INT2 | -1168912.417 | -1168502.213 | -1168848.924 | -1168438.72 | -1168502.07 | -1168438.577 |
| Z,E-4-An-TS1 | -1168885.107 | -1168477.615 | -1168822.049 | -1168414.557 | -1168477.443 | -1168414.385 |
| Z,E-4-An-INT3 | -1168887.948 | -1168479.479 | -1168824.922 | -1168416.453 | -1168479.285 | -1168416.259 |
| Z,E-4-An-TS2 | -1168887.396 | -1168477.391 | -1168824.352 | -1168414.347 | -1168477.268 | -1168414.224 |
| Z,E-4-An-INT4 | -1168909.98 | -1168499.273 | -1168846.89 | -1168436.183 | -1168499.149 | -1168436.059 |
| Z,E-4-An-TS3-PA | -1168888.691 | -1168475.275 | -1168826.279 | -1168412.863 | -1168475.294 | -1168412.883 |
| Z,E-4-An-TS3-MA | -999093.9807 | -998758.5481 | -999043.2312 | -998707.7986 | -998758.389 | -998707.6393 |
| Z,E-4-An-INT5 | -1168929.241 | -1168515.001 | -1168867.417 | -1168453.178 | -1168514.777 | -1168452.954 |
| Z,Z-4-An-INT1 | -999121.7656 | -998788.5957 | -999070.2989 | -998737.1291 | -998787.8281 | -998736.3618 |
| Z,Z-4-An-INT2 | -1168910.254 | -1168500.861 | -1168846.963 | -1168437.57 | -1168500.257 | -1168436.966 |
| Z,Z-4-An-TS1 | -1168880.133 | -1168473.374 | -1168816.595 | -1168409.835 | -1168473.078 | -1168409.539 |
| Z,Z-4-An-INT3 | -1168883.765 | -1168475.622 | -1168820.092 | -1168411.949 | -1168475.248 | -1168411.574 |
| Z,Z-4-An-TS2 | -1168882.218 | -1168473.682 | -1168818.405 | -1168409.87 | -1168473.401 | -1168409.588 |
| Z,Z-4-An-INT4 | -1168904.284 | -1168495.303 | -1168839.843 | -1168430.863 | -1168494.359 | -1168429.917 |
| Z,Z-4-An-TS3-PA | -1168881.908 | -1168470.866 | -1168818.274 | -1168407.231 | -1168469.841 | -1168406.207 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Z,Z-4-An-TS3-MA | -999090.3865 | -998757.024 | -999039.1985 | -998705.836 | -998756.2498 | -998705.0621 |
| Z,Z-4-An-INT5 | -1168928.83 | -1168517.323 | -1168865.999 | -1168454.492 | -1168516.386 | -1168453.555 |
| Pathway 2- Cy | | | | | | |
| E,Z-4-Cy-INT1 | -999126.0935 | -998791.4973 | -999074.0016 | -998739.4054 | -998790.7014 | -998738.6095 |
| E,Z-4-Cy-INT2 | -1168907.24 | -1168499.098 | -1168843.775 | -1168435.634 | -1168498.482 | -1168435.017 |
| E,Z-4-Cy-TS1 | -1168887.459 | -1168479.264 | -1168824.69 | -1168416.495 | -1168479.339 | -1168416.57 |
| E,Z-4-Cy-INT3 | -1168892.324 | -1168483.705 | -1168829.522 | -1168420.903 | -1168483.385 | -1168420.584 |
| E,Z-4-Cy-TS2 | -1168891.755 | -1168481.113 | -1168828.299 | -1168417.658 | -1168480.414 | -1168416.959 |
| E,Z-4-Cy-INT4 | -1168890.695 | -1168496.511 | -1168765.091 | -1168370.907 | -1168496.196 | -1168430.287 |
| E,Z-4-Cy-TS3-PA | -1168894.233 | -1168481.674 | -1168831.215 | -1168418.656 | -1168481.123 | -1168418.104 |
| E,Z-4-Cy-TS3-MA | -999109.604 | -998775.4546 | -999058.5815 | -998724.4321 | -998775.1012 | -998724.0785 |
| E,Z-4-Cy-INT5 | -1168925.145 | -1168511.07 | -1168861.773 | -1168447.697 | -1168510.771 | -1168447.399 |

## Pyranylation product energies



Optimized Structure of MeOH.
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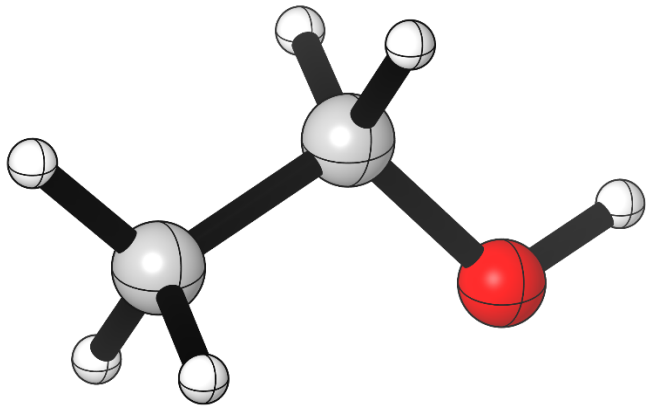
- Thermochemistry -
---
(0 imaginary frequencies)
Zero-point correction= 0.051761 (Hartree/Particle)
Thermal correction to Energy= 0.055076
Thermal correction to Enthalpy= 0.056020
Thermal correction to Gibbs Free Energy= 0.029029
Sum of electronic and zero-point Energies= -115.665493
Sum of electronic and thermal Energies= -115.662178

Sum of electronic and thermal Enthalpies= -115.661234
Sum of electronic and thermal Free Energies= -115.688225

| | | | |
|---|---|---|---|
| C | -0.65848600 | -0.01956200 | 0.00000100 |
| H | -1.02940500 | -0.54247300 | 0.89176100 |
| H | -1.02938900 | -0.54257800 | -0.89170500 |
| O | 0.74535300 | 0.12143700 | 0.00000100 |
| H | 1.12896600 | -0.75460500 | -0.00000400 |
| H | -1.08208100 | 0.98552700 | -0.00006800 |



Optimized Structure of EtOH.

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- Thermochemistry -

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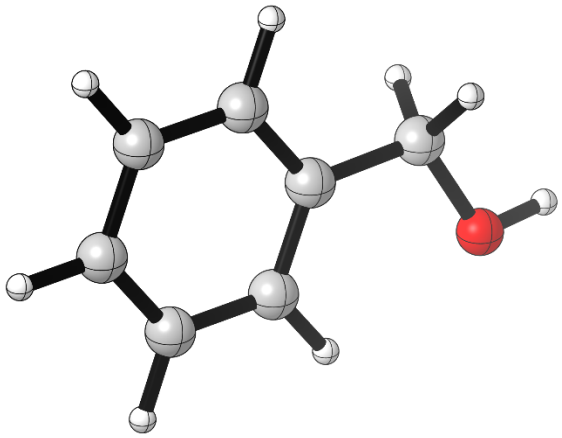
(0 imaginary frequencies)
Zero-point correction= 0.080577 (Hartree/Particle)
Thermal correction to Energy= 0.084854
Thermal correction to Enthalpy= 0.085798
Thermal correction to Gibbs Free Energy= 0.055208
Sum of electronic and zero-point Energies= -154.954306
Sum of electronic and thermal Energies= -154.950030
Sum of electronic and thermal Enthalpies= -154.949086
Sum of electronic and thermal Free Energies= -154.979675

| | | | |
|---|---|---|---|
| C | 0.08772500 | 0.54621800 | 0.00007000 |
| H | 0.13728900 | 1.19389800 | -0.88720800 |
| H | 0.13741500 | 1.19366100 | 0.88751300 |
| O | 1.14526800 | -0.39624300 | -0.00012900 |
| C | -1.21748900 | -0.22112600 | 0.00006100 |
| H | 1.97341500 | 0.08239500 | -0.00024000 |
| H | -1.28157300 | -0.85777200 | 0.88519600 |
| H | -2.06842100 | 0.46476500 | 0.00020100 |
| H | -1.28168800 | -0.85755400 | -0.88522000 |



Optimized Structure of BnOH.

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- Thermochemistry -

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(0 imaginary frequencies)

Zero-point correction= 0.134121 (Hartree/Particle)

Thermal correction to Energy= 0.141295

Thermal correction to Enthalpy= 0.142239

Thermal correction to Gibbs Free Energy= 0.102038

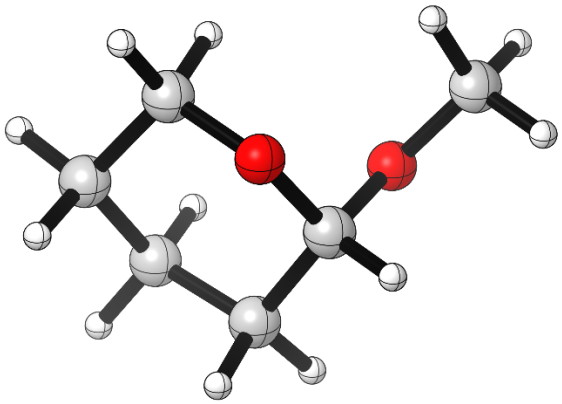
Sum of electronic and zero-point Energies= -346.608470

Sum of electronic and thermal Energies= -346.601297

Sum of electronic and thermal Enthalpies= -346.600352

Sum of electronic and thermal Free Energies= -346.640554

| | | | |
|---|---|---|---|
| C | -1.89903800 | 0.62532200 | 0.06335800 |
| H | -2.11364300 | 1.11282500 | 1.02590300 |
| H | -2.10895800 | 1.35668200 | -0.73036800 |
| O | -2.68077700 | -0.53828500 | -0.09748400 |
| C | -0.43272300 | 0.27329500 | 0.02279500 |
| C | -0.00606000 | -1.04957500 | 0.03425800 |
| C | 0.51697800 | 1.29348300 | -0.01073000 |
| C | 1.35265000 | -1.34688600 | 0.01500600 |
| H | -0.74567900 | -1.83939700 | 0.05366300 |
| C | 1.87217400 | 0.99715300 | -0.02650200 |
| H | 0.19245800 | 2.33037100 | -0.02644200 |
| C | 2.29493100 | -0.32810700 | -0.01380400 |
| H | 1.67429400 | -2.38259100 | 0.02203000 |
| H | 2.60057800 | 1.79995700 | -0.05248500 |
| H | 3.35353300 | -0.56162600 | -0.02928500 |
| H | -3.59984100 | -0.29805900 | 0.01057300 |



Optimized Structure of DHP-MeOH (Axial).

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- Thermochemistry -

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(0 imaginary frequencies)

Zero-point correction= 0.180759 (Hartree/Particle)

Thermal correction to Energy= 0.188582

Thermal correction to Enthalpy= 0.189526

Thermal correction to Gibbs Free Energy= 0.148695

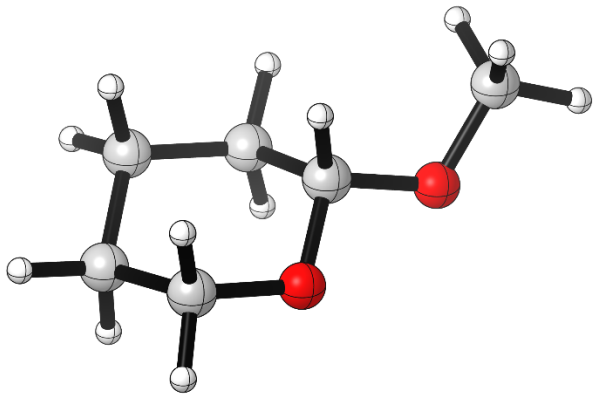
Sum of electronic and zero-point Energies= -386.104437

Sum of electronic and thermal Energies= -386.096615

Sum of electronic and thermal Enthalpies= -386.095670

Sum of electronic and thermal Free Energies= -386.136501

| | | | |
|---|---|---|---|
| H | -1.12543900 | -1.45597400 | 1.44154200 |
| C | 0.56123200 | -0.42583800 | 0.65141900 |
| C | -0.61112100 | -1.38264500 | 0.47788300 |
| C | -1.57807300 | -0.87401100 | -0.59187500 |
| C | -1.96737700 | 0.57307400 | -0.28584000 |
| C | -0.71565000 | 1.42114000 | -0.10893100 |
| H | -1.08956000 | -0.92351500 | -1.56998500 |
| H | -2.46352900 | -1.51358700 | -0.63682200 |
| H | -2.58287100 | 0.99284100 | -1.08724700 |
| H | -2.55599600 | 0.61161200 | 0.63782900 |
| H | -0.17049200 | 1.48610700 | -1.05994100 |
| H | -0.95875900 | 2.43336700 | 0.21654500 |
| O | 0.13807400 | 0.89364700 | 0.90044400 |
| H | 1.15984700 | -0.68535700 | 1.53453400 |
| H | -0.22107200 | -2.37168700 | 0.22820200 |
| C | 2.55432100 | 0.21829500 | -0.41977700 |
| H | 3.17600500 | -0.13813300 | 0.41320900 |
| H | 2.36634800 | 1.28794000 | -0.28167800 |
| H | 3.08788800 | 0.05930000 | -1.35638400 |
| O | 1.35163200 | -0.51402200 | -0.50257900 |



Optimized Structure of DHP-MeOH (Equatorial).

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- Thermochemistry -

---

(0 imaginary frequencies)

Zero-point correction= 0.179964 (Hartree/Particle)

Thermal correction to Energy= 0.187903

Thermal correction to Enthalpy= 0.188847

Thermal correction to Gibbs Free Energy= 0.147471

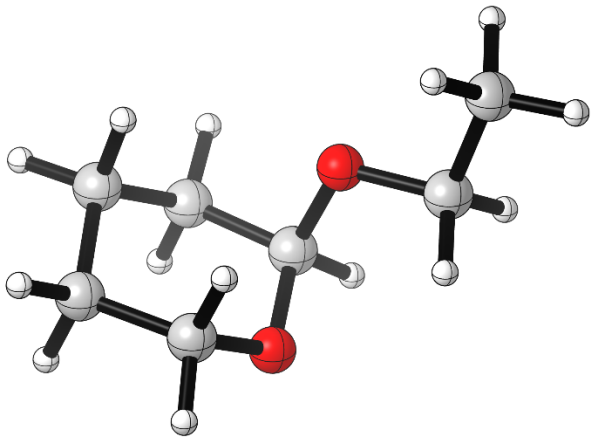
Sum of electronic and zero-point Energies= -386.095617

Sum of electronic and thermal Energies= -386.087678

Sum of electronic and thermal Enthalpies= -386.086734

Sum of electronic and thermal Free Energies= -386.128110

| | | | |
|---|---|---|---|
| H | -0.04673600 | 1.18393000 | -1.40356400 |
| C | 0.57294900 | -0.14111300 | 0.13213100 |
| C | -0.04739700 | 1.18185800 | -0.30913200 |
| C | -1.47309100 | 1.30968600 | 0.23092500 |
| C | -2.27829600 | 0.06289900 | -0.13728200 |
| C | -1.51466600 | -1.18850200 | 0.28169100 |
| H | -1.44204500 | 1.41297400 | 1.32320000 |
| H | -1.95083500 | 2.21253700 | -0.15750100 |
| H | -3.26149100 | 0.07210400 | 0.34262000 |
| H | -2.43724100 | 0.03148900 | -1.22031400 |
| H | -1.44711900 | -1.23382400 | 1.38170600 |
| H | -2.01233400 | -2.09571900 | -0.06231600 |
| O | -0.21534000 | -1.22428900 | -0.27658800 |
| H | 0.66863200 | -0.16066100 | 1.23787800 |
| H | 0.57716700 | 2.01391300 | 0.02977600 |
| C | 2.89502600 | 0.16052100 | 0.29011300 |
| H | 2.95226800 | -0.30008300 | 1.28636600 |
| H | 2.83696900 | 1.25099500 | 0.41031600 |
| H | 3.80417100 | -0.07843600 | -0.26075700 |
| O | 1.81927100 | -0.35337500 | -0.45317300 |



Optimized Structure of DHP-EtOH (Axial).

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- Thermochemistry -

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(0 imaginary frequencies)

Zero-point correction= 0.209412 (Hartree/Particle)

Thermal correction to Energy= 0.218468

Thermal correction to Enthalpy= 0.219412

Thermal correction to Gibbs Free Energy= 0.175333

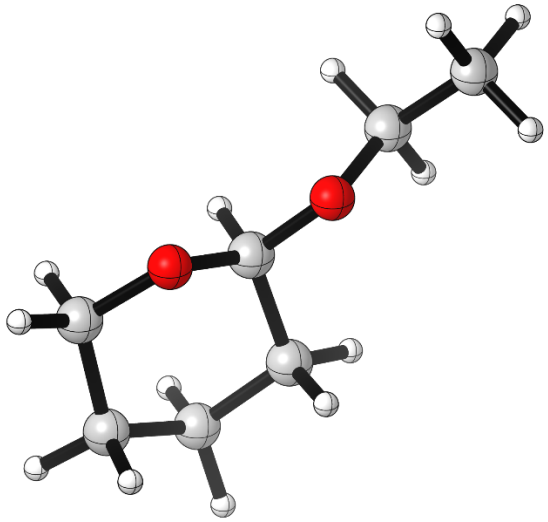
Sum of electronic and zero-point Energies= -425.393203

Sum of electronic and thermal Energies= -425.384147

Sum of electronic and thermal Enthalpies= -425.383203

Sum of electronic and thermal Free Energies= -425.427282

| | | | |
|---|---|---|---|
| H | 1.85685900 | -1.45915900 | -1.23979700 |
| C | 0.02622900 | -0.43189100 | -0.88092400 |
| C | 1.12514000 | -1.38474000 | -0.42898200 |
| C | 1.80378800 | -0.86646000 | 0.83972900 |
| C | 2.25826200 | 0.57791200 | 0.62324700 |
| C | 1.08721200 | 1.42397900 | 0.14175200 |
| H | 1.09022300 | -0.90555500 | 1.66852400 |
| H | 2.65002000 | -1.50510500 | 1.10633300 |
| H | 2.66419700 | 1.00594900 | 1.54488500 |
| H | 3.05172900 | 0.60767500 | -0.13206000 |
| H | 0.32812300 | 1.49781000 | 0.93182500 |
| H | 1.40375300 | 2.43296300 | -0.12559600 |
| O | 0.50067800 | 0.88506800 | -1.03750100 |
| H | -0.35156300 | -0.70007100 | -1.87587100 |
| H | 0.68919000 | -2.37410700 | -0.27437400 |
| C | -2.17880900 | 0.20092500 | -0.30870600 |
| H | -2.56743200 | -0.20155600 | -1.25616400 |
| H | -1.94222200 | 1.25848200 | -0.47183900 |
| O | -1.00903800 | -0.50831900 | 0.05960500 |
| C | -3.19674000 | 0.03706500 | 0.79888200 |
| H | -4.12528100 | 0.55355200 | 0.54375800 |
| H | -3.41776300 | -1.02006700 | 0.96077200 |
| H | -2.81344500 | 0.45445200 | 1.73277300 |



Optimized Structure of DHP-EtOH (Equatorial).

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- Thermochemistry -

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(0 imaginary frequencies)

Zero-point correction= 0.208533 (Hartree/Particle)

Thermal correction to Energy= 0.217773

Thermal correction to Enthalpy= 0.218717

Thermal correction to Gibbs Free Energy= 0.174003

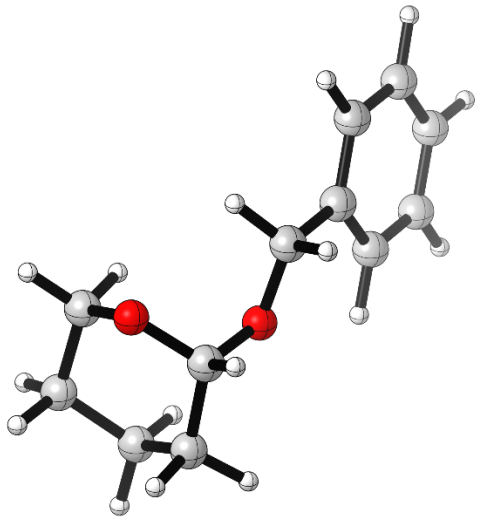
Sum of electronic and zero-point Energies= -425.384606

Sum of electronic and thermal Energies= -425.375367

Sum of electronic and thermal Enthalpies= -425.374423

Sum of electronic and thermal Free Energies= -425.419137

| | | | |
|---|---|---|---|
| H | -0.50183900 | 1.20079900 | -1.37679800 |
| C | 0.08317700 | -0.10270300 | 0.19021800 |
| C | -0.55623900 | 1.19879800 | -0.28374300 |
| C | -2.00971500 | 1.28280500 | 0.18662400 |
| C | -2.75776600 | 0.01026500 | -0.21240500 |
| C | -1.97527600 | -1.21646200 | 0.24421600 |
| H | -2.03458900 | 1.39084000 | 1.27865600 |
| H | -2.49669800 | 2.16892500 | -0.22806200 |
| H | -3.76077400 | -0.01060900 | 0.22432200 |
| H | -2.86868600 | -0.02843100 | -1.30117300 |
| H | -1.95893100 | -1.25889800 | 1.34636500 |
| H | -2.42865900 | -2.13852700 | -0.12103700 |
| O | -0.65091000 | -1.21215600 | -0.25210300 |
| H | 0.12449300 | -0.11833200 | 1.29872900 |
| H | 0.02678500 | 2.04862100 | 0.08390800 |
| C | 2.40114100 | 0.20473500 | 0.49527900 |
| H | 2.37479500 | -0.31576500 | 1.46414700 |
| H | 2.27753200 | 1.27980300 | 0.69306500 |
| O | 1.36204700 | -0.27103100 | -0.33397600 |
| C | 3.71749700 | -0.04721200 | -0.20702800 |
| H | 4.55030600 | 0.30139900 | 0.40864600 |
| H | 3.84518900 | -1.11450300 | -0.39779000 |
| H | 3.74507600 | 0.47882600 | -1.16332100 |



Optimized Structure of DHP-BnOH (Axial).

---

- Thermochemistry -

---

(0 imaginary frequencies)

Zero-point correction= 0.262742 (Hartree/Particle)

Thermal correction to Energy= 0.274008

Thermal correction to Enthalpy= 0.274953

Thermal correction to Gibbs Free Energy= 0.224261

Sum of electronic and zero-point Energies= -617.048075

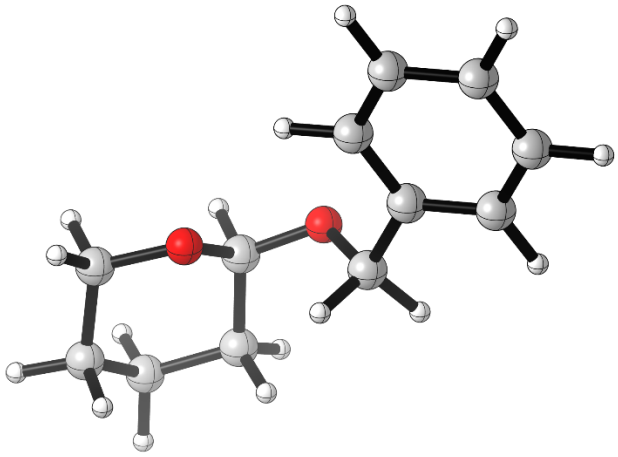
Sum of electronic and thermal Energies= -617.036808

Sum of electronic and thermal Enthalpies= -617.035864

Sum of electronic and thermal Free Energies= -617.086556

| | | | |
|---|---|---|---|
| H | -3.72894600 | 0.50925200 | -1.45102600 |
| C | -1.84416700 | -0.37185800 | -1.01207100 |
| C | -2.76718300 | 0.83837600 | -1.04468300 |
| C | -2.96286600 | 1.41287500 | 0.35893700 |
| C | -3.39551500 | 0.29840100 | 1.31314100 |
| C | -2.41605400 | -0.86435400 | 1.23448800 |
| H | -2.02059300 | 1.84721500 | 0.70690800 |
| H | -3.70460200 | 2.21541500 | 0.33879100 |
| H | -3.44774100 | 0.66217800 | 2.34369400 |
| H | -4.39445700 | -0.05874900 | 1.03831000 |
| H | -1.43440200 | -0.55561800 | 1.61713300 |
| H | -2.75968700 | -1.71923800 | 1.81778700 |
| O | -2.28121500 | -1.34789400 | -0.09931800 |
| H | -1.82992100 | -0.89133300 | -1.97841500 |
| H | -2.35053800 | 1.58119900 | -1.72854300 |
| C | 0.44041000 | -0.90416000 | -0.76281700 |
| H | 0.53210800 | -1.26645400 | -1.79901400 |
| H | 0.15964400 | -1.76241000 | -0.14167700 |
| O | -0.55677700 | 0.09186800 | -0.69958700 |
| C | 1.75986200 | -0.34396500 | -0.30045000 |
| C | 1.99170400 | 1.02728900 | -0.25899500 |
| C | 2.78186900 | -1.21571700 | 0.07106300 |
| C | 3.22780300 | 1.51739500 | 0.14672000 |

| | | | |
|---|---|---|---|
| H | 1.19580100 | 1.70557700 | -0.53924800 |
| C | 4.01834400 | -0.72698200 | 0.46991500 |
| H | 2.60677300 | -2.28747800 | 0.05120300 |
| C | 4.24481600 | 0.64413300 | 0.50991000 |
| H | 3.39557200 | 2.58832200 | 0.17976900 |
| H | 4.80328000 | -1.41740500 | 0.75784500 |
| H | 5.20750400 | 1.02913600 | 0.82678700 |



Optimized Structure of DHP-BnOH (Equatorial).

---

- Thermochemistry -

---

(0 imaginary frequencies)

Zero-point correction= 0.262530 (Hartree/Particle)

Thermal correction to Energy= 0.274632

Thermal correction to Enthalpy= 0.275577

Thermal correction to Gibbs Free Energy= 0.222728

Sum of electronic and zero-point Energies= -617.042306

Sum of electronic and thermal Energies= -617.030204

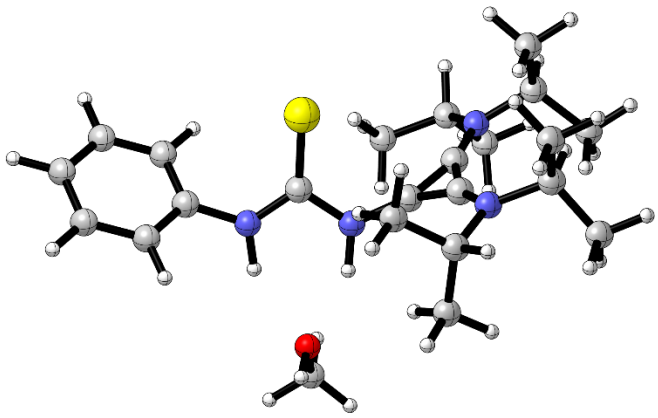
Sum of electronic and thermal Enthalpies= -617.029260

Sum of electronic and thermal Free Energies= -617.082108

| | | | |
|---|---|---|---|
| H | 2.13159900 | -1.58242000 | -0.83612400 |
| C | 1.58905600 | -0.26063000 | 0.77091600 |
| C | 2.53934400 | -1.27232600 | 0.13179700 |
| C | 3.92229600 | -0.64809100 | -0.06747000 |
| C | 3.79407600 | 0.66919800 | -0.83248300 |
| C | 2.77405300 | 1.56745300 | -0.14408500 |
| H | 4.37777300 | -0.45455500 | 0.91189300 |
| H | 4.58406500 | -1.34200100 | -0.59144500 |
| H | 4.75714200 | 1.18465700 | -0.89277300 |
| H | 3.45947100 | 0.47335100 | -1.85694700 |
| H | 3.14983700 | 1.86388500 | 0.84876300 |
| H | 2.58387900 | 2.47574000 | -0.71693100 |
| O | 1.52174900 | 0.92323300 | -0.00303500 |
| H | 1.94759500 | -0.00799700 | 1.78002400 |
| H | 2.58802100 | -2.15696700 | 0.77212800 |
| C | -0.43994600 | -1.04982900 | -0.21182400 |

| | | | |
|---|---|---|---|
| H | -0.50868900 | -2.13887200 | -0.31214200 |
| H | 0.06714200 | -0.65133900 | -1.09556200 |
| O | 0.29903200 | -0.72839900 | 0.96097100 |
| C | -1.81758400 | -0.44516100 | -0.12915900 |
| C | -2.95005700 | -1.20147000 | -0.40925400 |
| C | -1.96224300 | 0.90260600 | 0.19785100 |
| C | -4.21401300 | -0.62107800 | -0.37542500 |
| H | -2.84579000 | -2.25515100 | -0.65011800 |
| C | -3.22171900 | 1.48160100 | 0.23572500 |
| H | -1.07406600 | 1.48272300 | 0.42245800 |
| C | -4.35192900 | 0.72172700 | -0.05327300 |
| H | -5.09044200 | -1.22111200 | -0.59394700 |
| H | -3.32608100 | 2.53090300 | 0.48912300 |
| H | -5.33571700 | 1.17647500 | -0.02179000 |

## Higher energy conformers



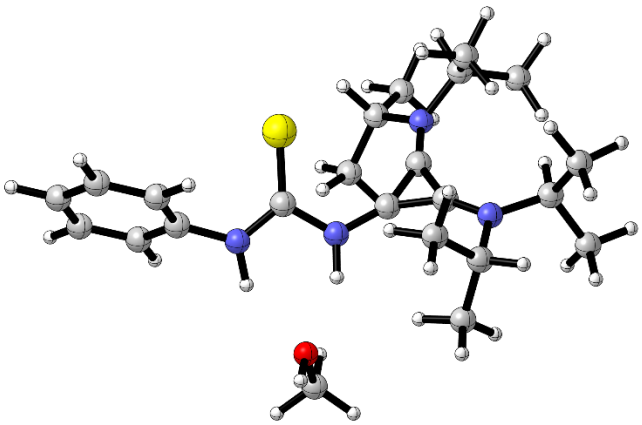
Optimized Higher Energy Structure of *Z,Z*-**4-INT$_1$** (1).

---
- Thermochemistry -
---
(0 imaginary frequencies)
Zero-point correction= 0.601833 (Hartree/Particle)
Thermal correction to Energy= 0.636808
Thermal correction to Enthalpy= 0.637752
Thermal correction to Gibbs Free Energy= 0.532055
Sum of electronic and zero-point Energies= -1591.460281
Sum of electronic and thermal Energies= -1591.425306
Sum of electronic and thermal Enthalpies= -1591.424362
Sum of electronic and thermal Free Energies= -1591.530059

| | | | |
|---|---|---|---|
| C | 1.69297600 | 0.18626800 | -0.13401300 |
| S | 1.36577300 | 0.71678100 | -1.67655500 |
| N | 2.90457700 | -0.06954500 | 0.39397400 |
| H | 2.91873600 | -0.50761800 | 1.30963800 |
| N | 0.67253100 | -0.07593300 | 0.77761300 |
| H | 0.89183200 | -0.66348400 | 1.58195000 |

| | | | |
|---|---|---|---|
| O | 2.00776900 | -1.43223600 | 2.90335400 |
| H | 2.18545000 | -2.36543300 | 3.03029700 |
| C | 2.11812200 | -0.75070100 | 4.15638100 |
| H | 3.11740700 | -0.86829200 | 4.58162900 |
| H | 1.94340000 | 0.30516500 | 3.95297000 |
| H | 1.36878500 | -1.10754000 | 4.86725000 |
| C | 4.16390400 | 0.04015500 | -0.26305800 |
| C | 4.56755100 | 1.23235700 | -0.85237600 |
| C | 5.01285300 | -1.06088400 | -0.24678400 |
| C | 5.82095600 | 1.31097400 | -1.44165200 |
| H | 3.90164900 | 2.08492200 | -0.85453400 |
| C | 6.27166700 | -0.96958800 | -0.82563800 |
| H | 4.68329800 | -1.98818100 | 0.20969600 |
| C | 6.67534200 | 0.21446900 | -1.42876900 |
| H | 7.65409400 | 0.28410600 | -1.88788100 |
| H | 6.13376200 | 2.23738900 | -1.90814400 |
| H | 6.93294600 | -1.82778800 | -0.81273200 |
| C | -0.64302500 | 0.05511500 | 0.41129000 |
| C | -1.71594000 | 0.86530700 | 0.14061300 |
| C | -1.79350700 | -0.55877300 | 0.00755400 |
| N | -2.26633000 | 2.04668600 | 0.02558600 |
| N | -2.39782300 | -1.68424100 | -0.28576600 |
| C | -3.62549700 | 2.20610700 | -0.54579200 |
| C | -1.59443700 | 3.29110000 | 0.49458000 |
| C | -3.81206500 | -1.75300500 | -0.70848000 |
| C | -1.61859400 | -2.94502900 | -0.17767000 |
| H | -3.77559000 | 3.28666200 | -0.58828500 |
| C | -4.69747200 | 1.63700300 | 0.38219000 |
| C | -3.66698400 | 1.70107100 | -1.98562800 |
| C | -0.11136600 | 3.10710300 | 0.75892200 |
| H | -1.70517900 | 3.99926500 | -0.33283400 |
| C | -2.31611500 | 3.83852300 | 1.72462900 |
| H | -4.15389700 | -0.72193200 | -0.74530600 |
| C | -3.93842400 | -2.32957700 | -2.11551200 |
| C | -4.65753800 | -2.49341500 | 0.32282800 |
| H | -2.31212900 | -3.72823800 | -0.48504200 |
| C | -0.43528000 | -2.95548900 | -1.13866000 |
| C | -1.21864900 | -3.22137800 | 1.26901500 |
| H | -4.52630300 | 0.58598100 | 0.62007600 |
| H | -4.71920400 | 2.18389100 | 1.32620800 |
| H | -5.68106800 | 1.72233600 | -0.08411300 |
| H | -2.94490200 | 2.24635600 | -2.59636600 |
| H | -3.43020700 | 0.63888300 | -2.06851500 |
| H | -4.66146500 | 1.85727000 | -2.40826800 |
| H | 0.07030500 | 2.45325000 | 1.61582600 |
| H | 0.40474800 | 2.70425100 | -0.11295400 |
| H | 0.31903200 | 4.08282500 | 0.98962900 |
| H | -3.36726900 | 4.05901900 | 1.52952200 |
| H | -2.25842500 | 3.12211100 | 2.54891500 |
| H | -1.83963300 | 4.76727800 | 2.04394000 |
| H | -3.65430400 | -3.38373100 | -2.15776800 |
| H | -4.97698300 | -2.25826700 | -2.44493400 |
| H | -3.31561700 | -1.77591400 | -2.82160800 |
| H | -4.37230000 | -3.54537900 | 0.40515500 |
| H | -4.56346900 | -2.03214200 | 1.30888400 |
| H | -5.70865100 | -2.46092700 | 0.02897600 |

| | | | |
|---|---|---|---|
| H | 0.04669000 | -3.93512200 | -1.11415800 |
| H | -0.75900400 | -2.75850500 | -2.16196400 |
| H | 0.31267600 | -2.20575000 | -0.87220600 |
| H | -0.49355100 | -2.48892000 | 1.63419500 |
| H | -2.08848400 | -3.20657700 | 1.92884200 |
| H | -0.75322700 | -4.20687500 | 1.33840200 |

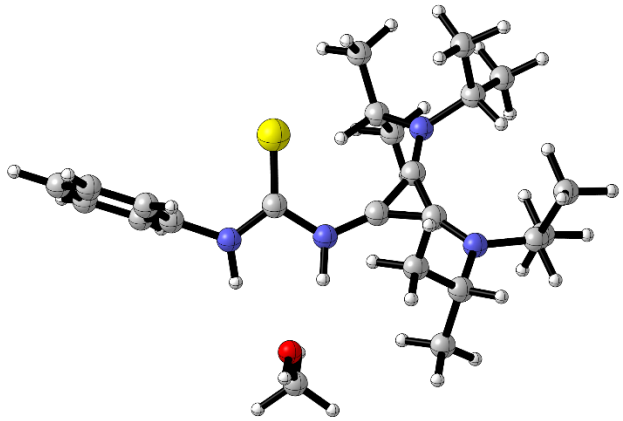


Optimized Higher Energy Structure of *Z,Z*-**4-INT$_1$** (2).

---
- Thermochemistry -
---
(0 imaginary frequencies)
Zero-point correction= 0.601828 (Hartree/Particle)
Thermal correction to Energy= 0.636818
Thermal correction to Enthalpy= 0.637763
Thermal correction to Gibbs Free Energy= 0.531900
Sum of electronic and zero-point Energies= -1591.460746
Sum of electronic and thermal Energies= -1591.425756
Sum of electronic and thermal Enthalpies= -1591.424812
Sum of electronic and thermal Free Energies= -1591.530675

| | | | |
|---|---|---|---|
| C | 1.75691800 | 0.01039700 | -0.16593300 |
| S | 1.56789900 | 1.32662300 | -1.15609800 |
| N | 2.91652900 | -0.56696300 | 0.18851400 |
| H | 2.87155100 | -1.34851000 | 0.83444200 |
| N | 0.66321800 | -0.66017600 | 0.40076900 |
| H | 0.81855300 | -1.60091300 | 0.76225300 |
| O | 1.79494700 | -2.89730800 | 1.71544900 |
| H | 2.03466000 | -3.78447300 | 1.44277400 |
| C | 1.68185700 | -2.84509800 | 3.14006500 |
| H | 2.63216100 | -3.09063000 | 3.61947900 |
| H | 1.41327300 | -1.81934900 | 3.39155500 |
| H | 0.90025100 | -3.51897500 | 3.49958100 |
| C | 4.21442500 | -0.17242400 | -0.26235800 |
| C | 5.13235800 | 0.29132900 | 0.67033900 |
| C | 4.56367000 | -0.29936300 | -1.60093900 |
| C | 6.41575700 | 0.62947300 | 0.25959900 |
| H | 4.83844600 | 0.39606700 | 1.70877400 |

| | | | |
|---|---|---|---|
| C | 5.84305300 | 0.05146900 | -2.00608100 |
| H | 3.83371700 | -0.65788700 | -2.31599800 |
| C | 6.77015400 | 0.51279800 | -1.07811100 |
| H | 7.76954200 | 0.78163600 | -1.39892000 |
| H | 7.13478300 | 0.99118800 | 0.98474400 |
| H | 6.11755300 | -0.04010400 | -3.05008600 |
| C | -0.60478900 | -0.21424500 | 0.26227300 |
| C | -1.50163400 | 0.82416300 | 0.23770000 |
| C | -1.91076800 | -0.50145200 | -0.03837800 |
| N | -1.77574200 | 2.10788500 | 0.34673400 |
| N | -2.79815100 | -1.40719700 | -0.38394900 |
| C | -0.82235400 | 3.02463200 | 1.04439700 |
| C | -2.82596300 | 2.71242000 | -0.51617200 |
| C | -4.24460100 | -1.10700600 | -0.36839000 |
| C | -2.33516400 | -2.78371400 | -0.67562600 |
| H | -0.15318800 | 3.43976300 | 0.28400000 |
| C | 0.00223200 | 2.27984300 | 2.08817400 |
| C | -1.57576900 | 4.16112100 | 1.73577400 |
| C | -4.18151900 | 2.78331100 | 0.18019800 |
| H | -2.47413100 | 3.73066300 | -0.69017700 |
| C | -2.89022800 | 2.04402100 | -1.88637900 |
| H | -4.30714500 | -0.03923600 | -0.15958600 |
| C | -4.88585900 | -1.36417400 | -1.72898300 |
| C | -4.94939500 | -1.85434200 | 0.76023500 |
| H | -3.23263800 | -3.32421100 | -0.97891800 |
| C | -1.35934100 | -2.79221500 | -1.84775600 |
| C | -1.77783900 | -3.47025800 | 0.56986700 |
| H | -0.65079400 | 1.75311400 | 2.79104100 |
| H | 0.70907400 | 1.57864300 | 1.65162800 |
| H | 0.58560200 | 3.00709200 | 2.65462600 |
| H | -2.16559700 | 4.77447600 | 1.05451700 |
| H | -2.23408600 | 3.77244200 | 2.51739500 |
| H | -0.84610400 | 4.82223000 | 2.20630300 |
| H | -4.55454600 | 1.78825600 | 0.43296300 |
| H | -4.12820600 | 3.35993500 | 1.10357500 |
| H | -4.91324000 | 3.25784600 | -0.47751600 |
| H | -1.89625300 | 1.97556100 | -2.33406300 |
| H | -3.32270200 | 1.04314900 | -1.84199400 |
| H | -3.52321000 | 2.64053500 | -2.54587300 |
| H | -4.93010400 | -2.43027100 | -1.96475800 |
| H | -5.91216700 | -0.99158600 | -1.72243600 |
| H | -4.34307300 | -0.85695900 | -2.52913900 |
| H | -4.92254800 | -2.93598100 | 0.60177600 |
| H | -4.48956000 | -1.63272000 | 1.72583300 |
| H | -5.99885800 | -1.55597700 | 0.80323400 |
| H | -1.09985500 | -3.82087300 | -2.10644400 |
| H | -1.80228100 | -2.31895100 | -2.72591100 |
| H | -0.43289800 | -2.26405100 | -1.60466300 |
| H | -0.83634100 | -3.02189100 | 0.89789600 |
| H | -2.48970000 | -3.42401000 | 1.39588800 |
| H | -1.57809600 | -4.52150800 | 0.35062000 |

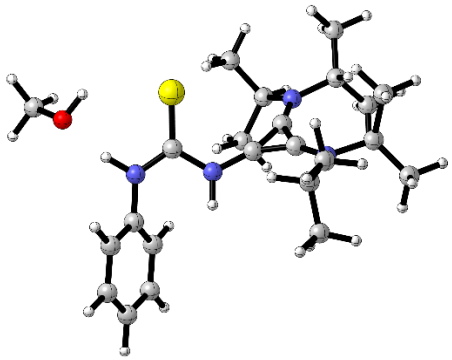


Optimized Higher Energy Structure of *Z,Z*-**4**-**INT**$_1$ (3).

---
- Thermochemistry -
---
(0 imaginary frequencies)
Zero-point correction= 0.602102 (Hartree/Particle)
Thermal correction to Energy= 0.637039
Thermal correction to Enthalpy= 0.637983
Thermal correction to Gibbs Free Energy= 0.532983
Sum of electronic and zero-point Energies= -1591.461183
Sum of electronic and thermal Energies= -1591.426246
Sum of electronic and thermal Enthalpies= -1591.425302
Sum of electronic and thermal Free Energies= -1591.530302

| | | | |
|---|---|---|---|
| C | -1.79059800 | 0.00961900 | -0.17782400 |
| S | -1.62128000 | -1.42415200 | -0.98901700 |
| N | -2.95112000 | 0.59659600 | 0.15617500 |
| H | -2.91311000 | 1.48259600 | 0.64946300 |
| N | -0.69418900 | 0.78944000 | 0.21489900 |
| H | -0.87706400 | 1.75361600 | 0.49438100 |
| O | -1.85134100 | 3.15915500 | 1.27740500 |
| H | -2.07852100 | 3.99199600 | 0.86050500 |
| C | -1.76420500 | 3.34082400 | 2.69352700 |
| H | -2.70927200 | 3.70559200 | 3.10190700 |
| H | -1.54940000 | 2.36201300 | 3.12100300 |
| H | -0.95758900 | 4.03091100 | 2.95415300 |
| C | -4.24318800 | 0.04733700 | -0.12636200 |
| C | -4.92760100 | -0.61739400 | 0.88159300 |
| C | -4.80892300 | 0.21274100 | -1.38339800 |
| C | -6.19605200 | -1.12246300 | 0.62854700 |
| H | -4.46086500 | -0.74578400 | 1.85139500 |
| C | -6.07486600 | -0.29895800 | -1.63212400 |
| H | -4.25222600 | 0.72469200 | -2.15936200 |
| C | -6.76849600 | -0.96389800 | -0.62738400 |
| H | -7.75629300 | -1.36285600 | -0.82501900 |
| H | -6.73413800 | -1.64412900 | 1.41089700 |
| H | -6.52072600 | -0.17855900 | -2.61209900 |
| C | 0.59164000 | 0.40887800 | 0.07663900 |
| C | 1.58334600 | -0.54320900 | 0.10618600 |
| C | 1.88353900 | 0.80862400 | -0.15738700 |

| | | | |
|---|---|---|---|
| N | 1.96792200 | -1.78765700 | 0.27935000 |
| N | 2.71023100 | 1.79711100 | -0.43525500 |
| C | 1.02792400 | -2.69421000 | 0.99683700 |
| C | 3.25776000 | -2.19897900 | -0.32640700 |
| C | 4.16784300 | 1.71914900 | -0.18835100 |
| C | 2.15912000 | 3.09460800 | -0.88964700 |
| H | 0.08399400 | -2.14846100 | 0.98931800 |
| C | 1.44445400 | -2.89141700 | 2.45402800 |
| C | 0.76982100 | -4.00680200 | 0.27145600 |
| C | 3.06642100 | -2.82732800 | -1.70710600 |
| H | 3.78595400 | -1.25823600 | -0.48263100 |
| C | 4.12279400 | -3.04882200 | 0.59493300 |
| H | 4.46877600 | 2.76057200 | -0.04380800 |
| C | 4.49309200 | 0.98902200 | 1.11037600 |
| C | 4.90766700 | 1.18435400 | -1.41084400 |
| H | 3.01390400 | 3.61376900 | -1.33004800 |
| C | 1.11680600 | 2.91998900 | -1.98840800 |
| C | 1.64782100 | 3.91502300 | 0.29238300 |
| H | 2.32704500 | -3.52378200 | 2.55519300 |
| H | 1.64682600 | -1.93198300 | 2.93665500 |
| H | 0.62709700 | -3.37497100 | 2.99407900 |
| H | 0.44433500 | -3.82882600 | -0.75393200 |
| H | 1.64138400 | -4.66450200 | 0.26550900 |
| H | -0.03403400 | -4.53350800 | 0.78999300 |
| H | 2.64229100 | -3.82943300 | -1.64845200 |
| H | 2.41044400 | -2.21157800 | -2.32675000 |
| H | 4.03659900 | -2.90414600 | -2.20450500 |
| H | 4.27466600 | -2.56522700 | 1.56194600 |
| H | 3.69719600 | -4.03919600 | 0.76243800 |
| H | 5.09921400 | -3.18875700 | 0.12642000 |
| H | 4.22824300 | -0.06888700 | 1.08189300 |
| H | 5.56615000 | 1.05172800 | 1.29999200 |
| H | 3.97220300 | 1.44970900 | 1.95287100 |
| H | 4.63308200 | 0.14957100 | -1.62851200 |
| H | 4.67764800 | 1.78372300 | -2.29477000 |
| H | 5.98664800 | 1.22210700 | -1.24666300 |
| H | 0.86090500 | 3.89703400 | -2.40296200 |
| H | 1.50319400 | 2.29774200 | -2.79788100 |
| H | 0.19450100 | 2.46675800 | -1.61763300 |
| H | 0.76358700 | 3.45090500 | 0.74038400 |
| H | 2.41481400 | 4.01460800 | 1.06394400 |
| H | 1.36711100 | 4.91782000 | -0.03803700 |

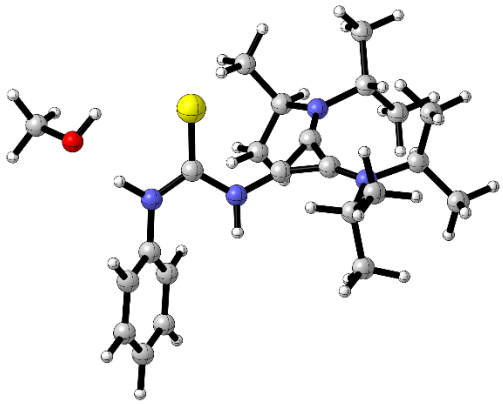


Optimized Higher Energy Structure of *E,Z*-**4**-Cy-**INT$_1$** (1).

---
- Thermochemistry -
---
(0 imaginary frequencies)
Zero-point correction= 0.602876 (Hartree/Particle)
Thermal correction to Energy= 0.637412
Thermal correction to Enthalpy= 0.638357
Thermal correction to Gibbs Free Energy= 0.533917
Sum of electronic and zero-point Energies= -1591.458339
Sum of electronic and thermal Energies= -1591.423802
Sum of electronic and thermal Enthalpies= -1591.422858
Sum of electronic and thermal Free Energies= -1591.527297

| | | | |
|---|---|---|---|
| C | -1.79693300 | -0.52214200 | -0.61005500 |
| S | -1.23325300 | -1.63392800 | -1.72753600 |
| N | -3.09178800 | -0.27257500 | -0.39658100 |
| H | -3.73570700 | -0.71657100 | -1.07091200 |
| N | -0.91556300 | 0.24652400 | 0.13616600 |
| C | -3.64118800 | 0.66998100 | 0.51738300 |
| C | -4.51859100 | 1.63604600 | 0.03148600 |
| C | -3.35503700 | 0.60085600 | 1.88024300 |
| C | -5.09704400 | 2.54150800 | 0.91056900 |
| H | -4.74458100 | 1.66497400 | -1.02834000 |
| C | -3.92495600 | 1.52276800 | 2.74876000 |
| H | -2.70990600 | -0.18512200 | 2.25634300 |
| C | -4.79543700 | 2.49296500 | 2.26669200 |
| H | -5.24748000 | 3.20260600 | 2.94898000 |
| H | -1.26653700 | 1.09916700 | 0.55483100 |
| C | -5.23525600 | -2.72617800 | -2.06106300 |
| H | -5.54098700 | -3.27026400 | -2.95881600 |
| H | -6.12948200 | -2.43340400 | -1.51189100 |
| H | -4.62438600 | -3.38056900 | -1.42978800 |
| O | -4.54214700 | -1.52950200 | -2.39983800 |
| H | -3.73151000 | -1.76987900 | -2.86032800 |
| C | 0.43767400 | 0.07726200 | 0.08691200 |
| C | 1.65793000 | 0.65741400 | -0.11441000 |
| C | 1.55462100 | -0.69647400 | 0.29655000 |
| N | 2.35520200 | 1.72100300 | -0.43936700 |
| N | 2.15239800 | -1.81236200 | 0.62462500 |
| C | 3.83335800 | 1.67368000 | -0.29568700 |
| C | 1.56843300 | 2.87362600 | -0.96466700 |

| | | | |
|---|---|---|---|
| C | 3.63073000 | -1.88669000 | 0.51628900 |
| C | 1.41434900 | -2.90950100 | 1.30977300 |
| C | 4.52489100 | 1.26908900 | -1.59678900 |
| H | 4.00161600 | 0.88146800 | 0.43667500 |
| C | 4.42138400 | 2.94235100 | 0.31132700 |
| C | 2.13593800 | 3.43969400 | -2.26091500 |
| H | 3.90312700 | -1.10568400 | -0.19492500 |
| C | 4.28649300 | -1.58506600 | 1.86168700 |
| C | 4.09786800 | -3.20985500 | -0.07841300 |
| H | 2.17204800 | -3.39991000 | 1.92551600 |
| C | 0.34583900 | -2.35922200 | 2.24876700 |
| C | 0.84281300 | -3.92374000 | 0.32563700 |
| H | 4.05990700 | 0.38104700 | -2.03288400 |
| H | 4.49510400 | 2.06647400 | -2.33987600 |
| H | 5.57464400 | 1.04174900 | -1.39604000 |
| H | 4.34600400 | 3.80016000 | -0.35822200 |
| H | 3.94258400 | 3.18960100 | 1.25998900 |
| H | 5.48288700 | 2.77272700 | 0.50230300 |
| H | 3.09445200 | 3.93932300 | -2.11259900 |
| H | 2.25465200 | 2.66044800 | -3.01540200 |
| H | 1.43756200 | 4.18311600 | -2.65033600 |
| H | 4.06483800 | -2.36125300 | 2.59831400 |
| H | 5.37156500 | -1.54025700 | 1.74652900 |
| H | 3.94413000 | -0.62802200 | 2.26497700 |
| H | 3.87842300 | -4.05582000 | 0.57675900 |
| H | 3.63770200 | -3.38919000 | -1.05132700 |
| H | 5.18044800 | -3.17224400 | -0.21430600 |
| H | -0.04746300 | -3.17619200 | 2.85601100 |
| H | 0.75433100 | -1.60212300 | 2.92303100 |
| H | -0.49403900 | -1.93179000 | 1.69553800 |
| H | 0.07602700 | -3.45909000 | -0.29589700 |
| H | 1.61396800 | -4.33581400 | -0.32493400 |
| H | 0.38964800 | -4.74950700 | 0.87927100 |
| H | -5.78574300 | 3.28801100 | 0.53351200 |
| H | -3.70749000 | 1.46543100 | 3.80870900 |
| H | 0.59981000 | 2.43310400 | -1.21547000 |
| C | 1.32779200 | 3.94392700 | 0.09864300 |
| H | 2.22936600 | 4.51400200 | 0.32235900 |
| H | 0.57296200 | 4.64652100 | -0.26181800 |
| H | 0.96094700 | 3.49969300 | 1.02752500 |

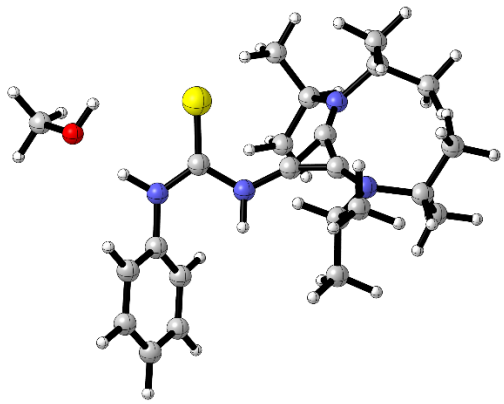


Optimized Higher Energy Structure of *E,Z*-**4**-Cy-**INT**$_1$ (2).

---
- Thermochemistry -
---
(0 imaginary frequencies)
Zero-point correction= 0.602864 (Hartree/Particle)
Thermal correction to Energy= 0.637406
Thermal correction to Enthalpy= 0.638350
Thermal correction to Gibbs Free Energy= 0.533873
Sum of electronic and zero-point Energies= -1591.458350
Sum of electronic and thermal Energies= -1591.423808
Sum of electronic and thermal Enthalpies= -1591.422864
Sum of electronic and thermal Free Energies= -1591.527341

| | | | |
|---|---|---|---|
| C | -1.79719900 | 0.52238800 | 0.60993700 |
| S | -1.23368300 | 1.63446600 | 1.72721100 |
| N | -3.09201000 | 0.27275900 | 0.39628400 |
| H | -3.73606100 | 0.71683400 | 1.07043700 |
| N | -0.91571300 | -0.24643100 | -0.13598100 |
| C | -3.64102900 | -0.67022500 | -0.51749100 |
| C | -4.51756400 | -1.63694300 | -0.03133600 |
| C | -3.35524800 | -0.60091100 | -1.88041100 |
| C | -5.09561000 | -2.54281700 | -0.91026700 |
| H | -4.74318100 | -1.66606500 | 1.02856500 |
| C | -3.92472900 | -1.52323400 | -2.74877900 |
| H | -2.71072400 | 0.18550300 | -2.25664300 |
| C | -4.79441300 | -2.49403300 | -2.26647200 |
| H | -5.24614600 | -3.20398500 | -2.94864500 |
| H | -1.26659800 | -1.09918500 | -0.55449500 |
| C | -5.23508300 | 2.72682700 | 2.06116500 |
| H | -5.54021900 | 3.27097000 | 2.95908800 |
| H | -6.12967100 | 2.43418600 | 1.51251200 |
| H | -4.62448700 | 3.38113900 | 1.42954400 |
| O | -4.54195400 | 1.53006200 | 2.39956100 |
| H | -3.73092600 | 1.77036500 | 2.85942600 |
| C | 0.43751500 | -0.07711400 | -0.08655400 |
| C | 1.65777600 | -0.65728400 | 0.11475800 |
| C | 1.55449300 | 0.69654300 | -0.29634900 |
| N | 2.35509700 | -1.72087100 | 0.43964100 |
| N | 2.15223900 | 1.81236900 | -0.62466100 |
| C | 3.83323100 | -1.67355200 | 0.29574700 |

| | | | |
|---|---|---|---|
| C | 1.56838700 | -2.87349300 | 0.96502500 |
| C | 3.63056000 | 1.88679300 | -0.51623300 |
| C | 1.41415100 | 2.90931600 | -1.31007600 |
| C | 4.52497300 | -1.26908100 | 1.59677800 |
| H | 4.00140100 | -0.88129600 | -0.43659100 |
| C | 4.42112800 | -2.94222000 | -0.31139600 |
| C | 2.13603300 | -3.43957200 | 2.26120200 |
| H | 3.90295000 | 1.10588900 | 0.19510300 |
| C | 4.28642700 | 1.58505600 | -1.86155600 |
| C | 4.09758000 | 3.21006100 | 0.07833400 |
| H | 2.17188900 | 3.39969900 | -1.92579300 |
| C | 0.34580400 | 2.35877700 | -2.24910200 |
| C | 0.84238100 | 3.92370200 | -0.32621300 |
| H | 4.06010100 | -0.38104600 | 2.03300500 |
| H | 4.49524800 | -2.06652300 | 2.33980700 |
| H | 5.57470900 | -1.04178400 | 1.39589100 |
| H | 4.34578600 | -3.80004900 | 0.35813500 |
| H | 3.94219300 | -3.18941900 | -1.26000500 |
| H | 5.48261400 | -2.77263800 | -0.50249900 |
| H | 3.09451700 | -3.93922400 | 2.11276000 |
| H | 2.25486200 | -2.66032900 | 3.01567400 |
| H | 1.43768700 | -4.18297900 | 2.65071000 |
| H | 4.06478400 | 2.36116500 | -2.59826900 |
| H | 5.37149200 | 1.54030500 | -1.74632100 |
| H | 3.94412800 | 0.62796000 | -2.26477700 |
| H | 3.87810600 | 4.05592800 | -0.57695600 |
| H | 3.63735200 | 3.38948500 | 1.05120300 |
| H | 5.18015600 | 3.17254200 | 0.21428400 |
| H | -0.04749800 | 3.17560000 | -2.85654500 |
| H | 0.75443100 | 1.60158000 | -2.92317200 |
| H | -0.49410000 | 1.93139300 | -1.69587100 |
| H | 0.07525500 | 3.45925400 | 0.29506500 |
| H | 1.61332700 | 4.33567900 | 0.32466200 |
| H | 0.38959900 | 4.74951900 | -0.88008900 |
| H | -5.78369000 | -3.28980400 | -0.53303900 |
| H | -3.70757700 | -1.46575200 | -3.80878400 |
| H | 0.59979300 | -2.43296500 | 1.21593400 |
| C | 1.32762100 | -3.94379500 | -0.09825700 |
| H | 2.22915200 | -4.51392200 | -0.32201900 |
| H | 0.57277400 | -4.64634100 | 0.26226300 |
| H | 0.96073800 | -3.49956000 | -1.02712500 |

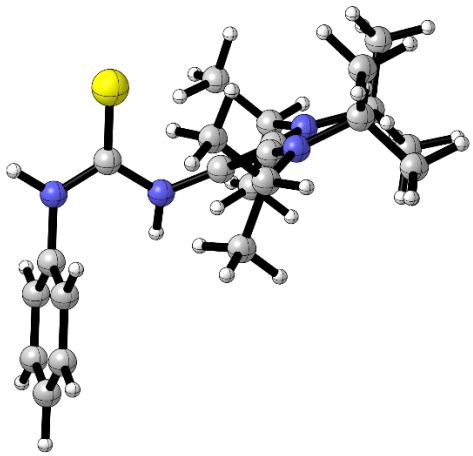


Optimized Higher Energy Structure of *E,Z*-**4**-Cy-**INT**$_1$ (3).

---
- Thermochemistry -
---
(0 imaginary frequencies)
Zero-point correction= 0.601940 (Hartree/Particle)
Thermal correction to Energy= 0.636917
Thermal correction to Enthalpy= 0.637861
Thermal correction to Gibbs Free Energy= 0.531739
Sum of electronic and zero-point Energies= -1591.456368
Sum of electronic and thermal Energies= -1591.421391
Sum of electronic and thermal Enthalpies= -1591.420447
Sum of electronic and thermal Free Energies= -1591.526569

| | | | |
|---|---|---|---|
| C | -1.72335200 | -0.76920800 | -0.41042200 |
| S | -1.19392600 | -2.09765200 | -1.27394300 |
| N | -3.01051100 | -0.46961600 | -0.21660100 |
| H | -3.67373200 | -1.04132300 | -0.76493900 |
| N | -0.82331300 | 0.15010800 | 0.11967900 |
| C | -3.52672100 | 0.69022100 | 0.42834500 |
| C | -4.37483400 | 1.52691400 | -0.29267400 |
| C | -3.23210000 | 0.96488900 | 1.76296300 |
| C | -4.91747100 | 2.64735800 | 0.32113800 |
| H | -4.60648800 | 1.28833100 | -1.32440900 |
| C | -3.76716800 | 2.09824300 | 2.36277500 |
| H | -2.61039200 | 0.28115200 | 2.33002700 |
| C | -4.60853500 | 2.93967100 | 1.64468600 |
| H | -5.03390500 | 3.81521800 | 2.12000500 |
| H | -1.17987000 | 1.07184000 | 0.34350700 |
| C | -5.32576100 | -3.10913700 | -1.35067500 |
| H | -5.68637800 | -3.77715900 | -2.13738800 |
| H | -6.18569200 | -2.64986000 | -0.86462100 |
| H | -4.76311300 | -3.68927300 | -0.61160700 |
| O | -4.54169500 | -2.05280800 | -1.89597600 |
| H | -3.76603500 | -2.43379000 | -2.31938700 |
| C | 0.52283200 | 0.00555000 | 0.06985800 |
| C | 1.70496600 | 0.64931500 | -0.16016000 |
| C | 1.68512200 | -0.70579900 | 0.27251800 |
| N | 2.22717800 | 1.78810300 | -0.57612200 |
| N | 2.28929800 | -1.81464100 | 0.62494100 |
| C | 1.26022000 | 2.75058600 | -1.16881800 |

| | | | |
|---|---|---|---|
| C | 3.54663800 | 2.29621800 | -0.13015100 |
| C | 1.63883100 | -2.82798100 | 1.50200700 |
| C | 3.65036500 | -2.15692000 | 0.14473800 |
| C | 0.74136000 | 3.73464400 | -0.12291700 |
| H | 0.42627700 | 2.13628900 | -1.51775000 |
| C | 1.85085300 | 3.43840100 | -2.39433100 |
| C | 4.69858800 | 1.77006700 | -0.97768900 |
| H | 2.43907900 | -3.11721400 | 2.19246000 |
| C | 0.50970300 | -2.23524800 | 2.33330700 |
| C | 1.19280000 | -4.06164600 | 0.72385900 |
| H | 3.70940900 | -3.23862800 | 0.27785200 |
| C | 3.78344400 | -1.88351800 | -1.34838900 |
| C | 4.74571300 | -1.54191200 | 1.00823100 |
| H | 0.30636200 | 3.21282900 | 0.73478000 |
| H | 1.53757900 | 4.38571700 | 0.24750900 |
| H | -0.02950400 | 4.37331200 | -0.55893400 |
| H | 2.67089600 | 4.11303100 | -2.13692500 |
| H | 2.21313400 | 2.70405800 | -3.11589600 |
| H | 1.07706400 | 4.03799100 | -2.87757100 |
| H | 4.86471300 | 0.70338400 | -0.83243100 |
| H | 4.50778500 | 1.94571900 | -2.03796200 |
| H | 5.62052400 | 2.28907800 | -0.70638500 |
| H | -0.37560700 | -2.03401400 | 1.72755900 |
| H | 0.22164700 | -2.96094500 | 3.09548300 |
| H | 0.82015200 | -1.31943300 | 2.84289700 |
| H | 0.37581000 | -3.80834500 | 0.04822800 |
| H | 2.00696600 | -4.49675200 | 0.14058500 |
| H | 0.84625700 | -4.82435000 | 1.42472700 |
| H | 4.77581900 | -2.18015400 | -1.69345800 |
| H | 3.03740900 | -2.45304800 | -1.90657000 |
| H | 3.65028300 | -0.82699400 | -1.58941700 |
| H | 4.81296000 | -0.46265700 | 0.88016900 |
| H | 4.57164700 | -1.75251400 | 2.06612700 |
| H | 5.71275300 | -1.96957100 | 0.73527200 |
| H | -5.58212100 | 3.29433500 | -0.23859200 |
| H | -3.54557300 | 2.30887600 | 3.40227600 |
| H | 3.48985800 | 3.37164500 | -0.30514100 |
| C | 3.72485600 | 2.10161400 | 1.37277300 |
| H | 3.68253900 | 1.04886800 | 1.65947100 |
| H | 4.69276400 | 2.49442500 | 1.68982100 |
| H | 2.94446100 | 2.63323400 | 1.92240700 |



Optimized Structure of *E,Z-Z,Z*-Rotation-1

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- Thermochemistry -

---

(0 imaginary frequencies)

Zero-point correction= 0.546925 (Hartree/Particle)

Thermal correction to Energy= 0.577671

Thermal correction to Enthalpy= 0.578615

Thermal correction to Gibbs Free Energy= 0.483133

Sum of electronic and zero-point Energies= -1475.778956

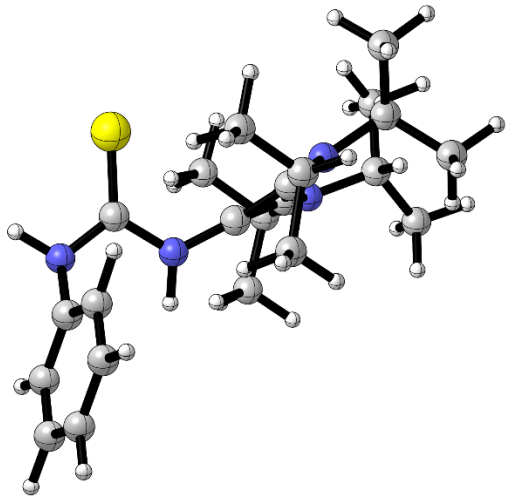
Sum of electronic and thermal Energies= -1475.748209

Sum of electronic and thermal Enthalpies= -1475.747265

Sum of electronic and thermal Free Energies= -1475.842748

| | | | |
|---|---|---|---|
| C | 1.82730300 | -0.20014500 | 1.50089100 |
| S | 0.99198400 | 0.36151100 | 2.81935400 |
| N | 1.20521500 | -0.49200600 | 0.30151500 |
| H | 1.71642200 | -1.00822900 | -0.40268600 |
| N | 3.16116300 | -0.41924300 | 1.48124000 |
| C | 3.96088300 | -0.33762400 | 0.29221000 |
| C | 4.57442400 | -1.48219900 | -0.20229300 |
| C | 4.11361400 | 0.88680800 | -0.35423000 |
| C | 5.34842000 | -1.40103600 | -1.35505700 |
| H | 4.44974700 | -2.42272600 | 0.32201300 |
| C | 4.88295000 | 0.95913000 | -1.50653700 |
| H | 3.64109500 | 1.77158500 | 0.05851400 |
| C | 5.49919700 | -0.18382100 | -2.00680000 |
| H | 6.10387200 | -0.12226800 | -2.90369500 |
| H | 3.61559500 | -0.23861500 | 2.36488500 |
| H | 5.01259200 | 1.91043000 | -2.00860900 |
| H | 5.83494100 | -2.28881500 | -1.74060000 |
| C | -0.12340300 | -0.23169800 | 0.08571700 |
| C | -1.38673700 | -0.71578800 | -0.11490300 |
| C | -1.12480300 | 0.68492700 | -0.10595900 |
| N | -2.20998800 | -1.72374500 | -0.22496900 |
| N | -1.56371300 | 1.90908500 | -0.20662800 |
| C | -3.61534900 | -1.52323500 | -0.64394400 |
| C | -1.72416700 | -3.08076400 | 0.13626000 |
| C | -3.02057600 | 2.16211200 | -0.32643500 |
| C | -0.60004600 | 3.03504900 | -0.34924300 |
| C | -3.95913000 | -2.39069000 | -1.85114400 |

| | | | |
|---|---|---|---|
| H | -3.67139200 | -0.48265400 | -0.96794400 |
| C | -4.56511600 | -1.72676600 | 0.53126500 |
| C | -1.21665500 | -3.11484300 | 1.57392700 |
| H | -2.60418800 | -3.72199300 | 0.07169200 |
| C | -0.69315200 | -3.57749700 | -0.87163200 |
| H | -3.49817500 | 1.25186900 | 0.04146900 |
| C | -3.47355400 | 3.29907900 | 0.58236700 |
| C | -3.40692100 | 2.37688300 | -1.78647400 |
| H | -1.17860600 | 3.83322100 | -0.81862300 |
| C | -0.09173900 | 3.51627300 | 1.00438600 |
| C | 0.53560700 | 2.66961900 | -1.29982200 |
| H | -3.25643200 | -2.22037700 | -2.66947500 |
| H | -3.95866600 | -3.45572800 | -1.60771300 |
| H | -4.96119400 | -2.13870500 | -2.20333600 |
| H | -4.52704000 | -2.75448100 | 0.90193600 |
| H | -4.31523100 | -1.05661300 | 1.35726600 |
| H | -5.59268400 | -1.52599700 | 0.22163700 |
| H | -0.32385000 | -2.49783600 | 1.70633000 |
| H | -1.98055300 | -2.76027700 | 2.26842700 |
| H | -0.95630800 | -4.13993400 | 1.84468700 |
| H | -1.08128100 | -3.53157900 | -1.89077200 |
| H | 0.22546200 | -2.98600300 | -0.81911000 |
| H | -0.42768100 | -4.61310700 | -0.65132400 |
| H | -3.04730700 | 4.26004600 | 0.28590700 |
| H | -4.55941600 | 3.39134600 | 0.51886200 |
| H | -3.20785900 | 3.10257700 | 1.62231500 |
| H | -3.10607000 | 1.52580100 | -2.40344700 |
| H | -4.48811600 | 2.50087600 | -1.87587700 |
| H | -2.93706700 | 3.27559600 | -2.19441500 |
| H | 0.57647300 | 4.36882700 | 0.86294200 |
| H | -0.91024800 | 3.83083300 | 1.65263400 |
| H | 0.45973100 | 2.72315500 | 1.51416600 |
| H | 1.20736500 | 1.92585700 | -0.86292500 |
| H | 0.15240600 | 2.28576100 | -2.24847800 |
| H | 1.12688100 | 3.56269800 | -1.50974100 |



Optimized Structure of *E,Z-Z,Z*-Rotation-2

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- Thermochemistry -

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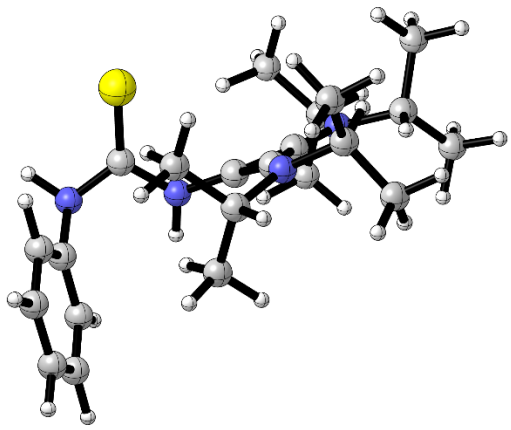
(0 imaginary frequencies)
Zero-point correction= 0.547697 (Hartree/Particle)
Thermal correction to Energy= 0.578209
Thermal correction to Enthalpy= 0.579153
Thermal correction to Gibbs Free Energy= 0.484461
Sum of electronic and zero-point Energies= -1475.775189
Sum of electronic and thermal Energies= -1475.744677
Sum of electronic and thermal Enthalpies= -1475.743733
Sum of electronic and thermal Free Energies= -1475.838426

| | | | |
|---|---|---|---|
| C | 1.73121000 | -0.88863500 | 1.33727100 |
| S | 0.99570700 | -0.41052900 | 2.73982400 |
| N | 1.07736700 | -0.89450100 | 0.12122600 |
| H | 1.50939100 | -1.37227900 | -0.65837100 |
| N | 3.03158000 | -1.28169500 | 1.23331800 |
| C | 3.89059500 | -0.75847700 | 0.20297800 |
| C | 4.64257500 | -1.63513200 | -0.56787000 |
| C | 3.97474200 | 0.61691800 | -0.00084100 |
| C | 5.49053900 | -1.13182900 | -1.54844400 |
| H | 4.56471500 | -2.70139300 | -0.38949500 |
| C | 4.81413100 | 1.11106300 | -0.98873200 |
| H | 3.39668100 | 1.28825700 | 0.62557300 |
| C | 5.57294100 | 0.23802600 | -1.76204300 |
| H | 6.23527000 | 0.62754900 | -2.52577800 |
| H | 3.46939600 | -1.37397500 | 2.14035400 |
| H | 4.89046400 | 2.18056200 | -1.14570900 |
| H | 6.08615300 | -1.81164300 | -2.14566000 |
| C | -0.18913300 | -0.38808500 | -0.03356300 |
| C | -1.52600700 | -0.61906500 | -0.21518500 |
| C | -1.01163500 | 0.70601400 | -0.09695600 |
| N | -2.52542900 | -1.44327300 | -0.37168700 |
| N | -1.21722800 | 1.99323000 | -0.06550800 |
| C | -3.87969100 | -0.94649700 | -0.70498400 |
| C | -2.29333900 | -2.89453400 | -0.14658300 |
| C | -2.60118400 | 2.52536100 | -0.04577900 |
| C | -0.06073300 | 2.92674300 | -0.14871100 |
| C | -4.40725200 | -1.60108500 | -1.97817400 |
| H | -3.74757600 | 0.11591100 | -0.91726300 |
| C | -4.82206300 | -1.10066200 | 0.48352700 |
| C | -1.83680000 | -3.15254900 | 1.28517700 |
| H | -3.26870900 | -3.36196400 | -0.28680000 |
| C | -1.33549700 | -3.46141700 | -1.18853800 |
| H | -3.22837700 | 1.67418900 | 0.22678600 |
| C | -2.78070100 | 3.57609900 | 1.04463000 |
| C | -3.00738700 | 3.02352600 | -1.42857700 |
| H | -0.50143600 | 3.88575900 | -0.42675600 |
| C | 0.63661600 | 3.07492200 | 1.19803900 |
| C | 0.89418600 | 2.51437800 | -1.26389400 |
| H | -3.70274300 | -1.47875300 | -2.80343600 |
| H | -4.60282100 | -2.66709600 | -1.84152600 |
| H | -5.35095600 | -1.13077400 | -2.26068600 |
| H | -4.98603200 | -2.15349200 | 0.72762300 |
| H | -4.42159900 | -0.60193200 | 1.36928900 |
| H | -5.79377000 | -0.66167900 | 0.24878700 |
| H | -0.86871500 | -2.68742500 | 1.49070300 |

| | | | |
|---|---|---|---|
| H | -2.56001000 | -2.76217100 | 2.00381900 |
| H | -1.73359400 | -4.22660000 | 1.45107200 |
| H | -1.68368900 | -3.25443700 | -2.20229000 |
| H | -0.33187900 | -3.04459900 | -1.06720800 |
| H | -1.25420400 | -4.54289700 | -1.06610200 |
| H | -2.21078700 | 4.48543800 | 0.84121600 |
| H | -3.83427000 | 3.85701300 | 1.09711100 |
| H | -2.48364900 | 3.18471700 | 2.01911600 |
| H | -2.91381600 | 2.23206800 | -2.17677700 |
| H | -4.04521300 | 3.36277200 | -1.41461800 |
| H | -2.38861800 | 3.86732600 | -1.74509900 |
| H | 1.44417600 | 3.80587200 | 1.11532200 |
| H | -0.05413200 | 3.41808100 | 1.96921000 |
| H | 1.06053200 | 2.12339800 | 1.52703300 |
| H | 1.41807400 | 1.58445800 | -1.02727700 |
| H | 0.36714600 | 2.39265200 | -2.21301500 |
| H | 1.65257900 | 3.28872800 | -1.39426300 |



Optimized Structure of *E,Z-Z,Z*-Rotation-3

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- Thermochemistry -

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(0 imaginary frequencies)

Zero-point correction= 0.548082 (Hartree/Particle)

Thermal correction to Energy= 0.578388

Thermal correction to Enthalpy= 0.579332

Thermal correction to Gibbs Free Energy= 0.486199

Sum of electronic and zero-point Energies= -1475.770696

Sum of electronic and thermal Energies= -1475.740391

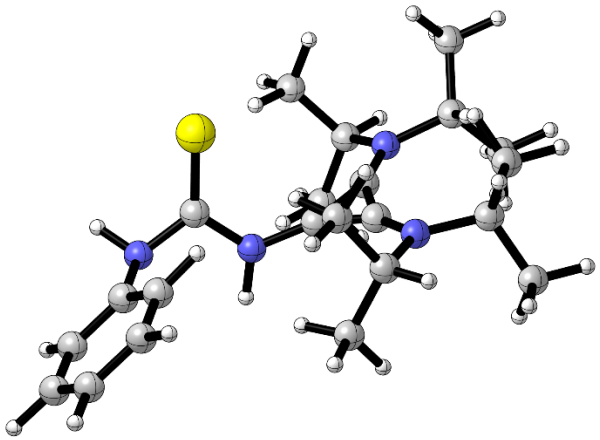
Sum of electronic and thermal Enthalpies= -1475.739447

Sum of electronic and thermal Free Energies= -1475.832580

| | | | |
|---|---|---|---|
| C | 1.52520500 | -1.64898200 | 1.04202700 |
| S | 0.99796600 | -1.24994800 | 2.55160700 |
| N | 0.76310400 | -1.45167100 | -0.08701600 |

| | | | |
|---|---|---|---|
| H | 1.08019300 | -1.85711200 | -0.95671600 |
| N | 2.78284500 | -2.13147400 | 0.73341700 |
| C | 3.62469000 | -1.24417600 | -0.04189100 |
| C | 3.80691200 | -1.47501600 | -1.39878900 |
| C | 4.22504800 | -0.15174400 | 0.57655300 |
| C | 4.57586100 | -0.59370700 | -2.15040800 |
| H | 3.37012400 | -2.35761800 | -1.85361100 |
| C | 5.00617300 | 0.71564200 | -0.17569000 |
| H | 4.07669000 | 0.01383300 | 1.63832600 |
| C | 5.17487200 | 0.50106600 | -1.53939300 |
| H | 5.78710300 | 1.17798300 | -2.12326000 |
| H | 3.24480700 | -2.44063700 | 1.57959000 |
| H | 5.48588600 | 1.56010600 | 0.30524000 |
| H | 4.72414300 | -0.77469800 | -3.20825700 |
| C | -0.32087700 | -0.60762900 | -0.10619200 |
| C | -1.67369600 | -0.43569100 | -0.20931500 |
| C | -0.79415300 | 0.67580700 | -0.03084000 |
| N | -2.87087900 | -0.93068900 | -0.36001300 |
| N | -0.60843800 | 1.95899800 | 0.10092100 |
| C | -4.04688900 | -0.04857500 | -0.53819000 |
| C | -3.04123600 | -2.40706400 | -0.29710200 |
| C | -1.77363100 | 2.87020000 | 0.21125000 |
| C | 0.77069800 | 2.51770300 | 0.01275100 |
| C | -4.81048600 | -0.39851500 | -1.81193200 |
| H | -3.63290800 | 0.95237200 | -0.67246300 |
| C | -4.92498300 | -0.05973200 | 0.70802100 |
| C | -2.56778100 | -2.95175900 | 1.04589400 |
| H | -4.11653700 | -2.57071800 | -0.37507100 |
| C | -2.36323300 | -3.08101900 | -1.48501300 |
| H | -2.61149500 | 2.22672600 | 0.48708200 |
| C | -1.59518700 | 3.87739900 | 1.34189200 |
| C | -2.06691400 | 3.52848800 | -1.13285900 |
| H | 0.62221700 | 3.57696200 | -0.20443600 |
| C | 1.51147700 | 2.38088100 | 1.33723700 |
| C | 1.54288400 | 1.90666300 | -1.15215800 |
| H | -4.14930500 | -0.39375100 | -2.68098100 |
| H | -5.29466800 | -1.37551100 | -1.74647000 |
| H | -5.59505600 | 0.34269500 | -1.97563700 |
| H | -5.35966600 | -1.04789200 | 0.87993800 |
| H | -4.35293300 | 0.22254700 | 1.59500800 |
| H | -5.74900100 | 0.64668800 | 0.58902600 |
| H | -1.49121200 | -2.81819600 | 1.18186000 |
| H | -3.07921300 | -2.45570600 | 1.87315200 |
| H | -2.78007700 | -4.02104600 | 1.10369200 |
| H | -2.72072500 | -2.66959100 | -2.43089900 |
| H | -1.27724100 | -2.96142100 | -1.43520500 |
| H | -2.57390100 | -4.15188700 | -1.47342100 |
| H | -0.78819800 | 4.58554900 | 1.14139000 |
| H | -2.51582900 | 4.45385200 | 1.44985900 |
| H | -1.39563900 | 3.37477500 | 2.28976300 |
| H | -2.23498900 | 2.77847300 | -1.91028000 |
| H | -2.95980900 | 4.15265400 | -1.05856200 |
| H | -1.24038500 | 4.16976900 | -1.44979600 |
| H | 2.50044600 | 2.83637300 | 1.25026500 |
| H | 0.97711600 | 2.87354600 | 2.15056000 |
| H | 1.64307500 | 1.32940600 | 1.60053300 |

| | | | |
|---|---|---|---|
| H | 1.80665000 | 0.86299700 | -0.96370900 |
| H | 0.97622400 | 1.97322000 | -2.08398400 |
| H | 2.48172800 | 2.44682600 | -1.28451100 |



Optimized Structure of *E,Z-Z,Z*-Rotation-4

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- Thermochemistry -

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(0 imaginary frequencies)

Zero-point correction= 0.547304 (Hartree/Particle)

Thermal correction to Energy= 0.576924

Thermal correction to Enthalpy= 0.577868

Thermal correction to Gibbs Free Energy= 0.486057

Sum of electronic and zero-point Energies= -1475.762748

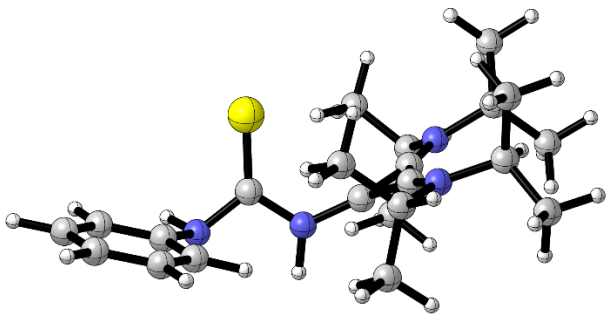
Sum of electronic and thermal Energies= -1475.733128

Sum of electronic and thermal Enthalpies= -1475.732184

Sum of electronic and thermal Free Energies= -1475.823995

| | | | |
|---|---|---|---|
| C | 1.61246900 | -1.59891900 | 0.35948800 |
| S | 1.08254400 | -1.74134900 | 1.90923200 |
| N | 0.89997100 | -0.95491500 | -0.62084800 |
| H | 1.33883100 | -0.86549700 | -1.52794200 |
| N | 2.87222800 | -1.96090300 | -0.12273100 |
| C | 3.91711500 | -0.96996700 | -0.15178800 |
| C | 5.10236900 | -1.30634900 | -0.80134000 |
| C | 3.77170400 | 0.28652300 | 0.42454000 |
| C | 6.14183400 | -0.39055200 | -0.85762500 |
| H | 5.20070800 | -2.28258000 | -1.26250300 |
| C | 4.81196300 | 1.20591200 | 0.34353100 |
| H | 2.86839400 | 0.54157900 | 0.96361500 |
| C | 5.99838300 | 0.87278600 | -0.29314400 |
| H | 6.80906400 | 1.58905200 | -0.34558000 |
| H | 3.19797000 | -2.77379800 | 0.38812200 |
| H | 4.69634200 | 2.18118500 | 0.80246100 |
| H | 7.06502800 | -0.66128200 | -1.35596300 |
| C | -0.32332700 | -0.35800400 | -0.40969400 |
| C | -1.68013800 | -0.49018600 | -0.26437000 |
| C | -1.04441800 | 0.79021900 | -0.22364500 |
| N | -2.76400900 | -1.20872700 | -0.20631100 |
| N | -1.10326700 | 2.08727800 | -0.09997400 |

| | | | |
|---|---|---|---|
| C | -4.06585800 | -0.57329000 | 0.11603800 |
| C | -2.70857800 | -2.65703700 | -0.55160100 |
| C | -2.40036900 | 2.80318900 | -0.09208300 |
| C | 0.16346300 | 2.84166300 | 0.09675000 |
| C | -4.87401400 | -0.34378900 | -1.15654300 |
| H | -3.80973300 | 0.39151000 | 0.55783200 |
| C | -4.82839200 | -1.35720300 | 1.17822000 |
| C | -2.17161600 | -3.48089700 | 0.61219900 |
| H | -3.74730100 | -2.93409400 | -0.73919400 |
| C | -1.92701500 | -2.88611300 | -1.84061900 |
| H | -3.15064700 | 2.03644800 | -0.29112900 |
| C | -2.67810000 | 3.42213800 | 1.27290600 |
| C | -2.46823600 | 3.81338400 | -1.23370800 |
| H | -0.12799800 | 3.89235400 | 0.07838500 |
| C | 0.75516900 | 2.52231000 | 1.46627600 |
| C | 1.14278700 | 2.60381500 | -1.04764100 |
| H | -4.31823000 | 0.27154600 | -1.86891000 |
| H | -5.12311400 | -1.28984100 | -1.64410400 |
| H | -5.81143900 | 0.16394300 | -0.92090400 |
| H | -5.14768800 | -2.33836100 | 0.82022800 |
| H | -4.22719300 | -1.48991900 | 2.07911400 |
| H | -5.72829200 | -0.80163500 | 1.44873700 |
| H | -1.14153300 | -3.19964300 | 0.84417100 |
| H | -2.77224000 | -3.34352700 | 1.51214800 |
| H | -2.18681600 | -4.54103500 | 0.35055500 |
| H | -2.28886800 | -2.24146800 | -2.64504500 |
| H | -0.85683100 | -2.71524700 | -1.69745300 |
| H | -2.05041700 | -3.92381500 | -2.15480600 |
| H | -1.95060900 | 4.20117200 | 1.51461800 |
| H | -3.66670200 | 3.88523500 | 1.27462200 |
| H | -2.64903400 | 2.66644700 | 2.06118500 |
| H | -2.26690800 | 3.33427900 | -2.19403600 |
| H | -3.46787900 | 4.25038500 | -1.27249300 |
| H | -1.75989000 | 4.63408400 | -1.09931600 |
| H | 1.69956400 | 3.05363900 | 1.60056600 |
| H | 0.07678900 | 2.82000300 | 2.26769500 |
| H | 0.94929300 | 1.45099700 | 1.57191300 |
| H | 1.56859200 | 1.59835900 | -1.01337700 |
| H | 0.66372800 | 2.76139900 | -2.01625000 |
| H | 1.97672400 | 3.30278100 | -0.96250000 |



Optimized Structure of *E,Z-Z,Z*-Rotation-5

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- Thermochemistry -

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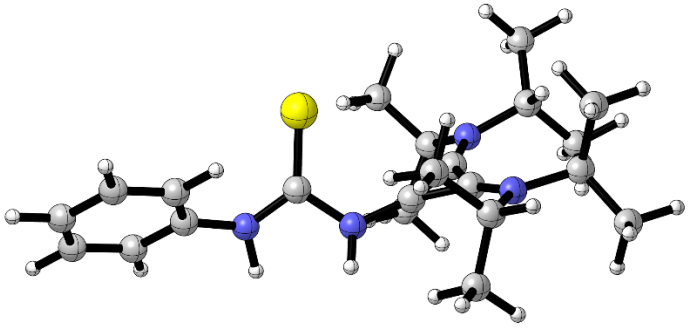
(0 imaginary frequencies)
Zero-point correction= 0.546939 (Hartree/Particle)
Thermal correction to Energy= 0.576622
Thermal correction to Enthalpy= 0.577566
Thermal correction to Gibbs Free Energy= 0.485288
Sum of electronic and zero-point Energies= -1475.758072
Sum of electronic and thermal Energies= -1475.728389
Sum of electronic and thermal Enthalpies= -1475.727444
Sum of electronic and thermal Free Energies= -1475.819722

| | | | |
|---|---|---|---|
| C | 1.65172700 | -1.45137300 | -0.07734500 |
| S | 1.28562600 | -1.70304300 | 1.49874700 |
| N | 0.81729100 | -0.82548400 | -0.96307100 |
| H | 1.16700900 | -0.70303300 | -1.90447200 |
| N | 2.88846100 | -1.75223700 | -0.71081700 |
| C | 3.97307600 | -0.88346400 | -0.35223200 |
| C | 5.14060100 | -1.41257600 | 0.18524400 |
| C | 3.87000500 | 0.48873900 | -0.56583200 |
| C | 6.20118200 | -0.57251000 | 0.49983600 |
| H | 5.22272000 | -2.47974500 | 0.36277700 |
| C | 4.92648800 | 1.32347100 | -0.23113400 |
| H | 2.97219900 | 0.90751400 | -1.00537200 |
| C | 6.09748200 | 0.79757500 | 0.30060500 |
| H | 6.92352900 | 1.45036200 | 0.55427600 |
| H | 3.14087200 | -2.70304100 | -0.46575300 |
| H | 4.83852200 | 2.39049800 | -0.40100000 |
| H | 7.10852600 | -0.99519300 | 0.91444200 |
| C | -0.40641700 | -0.29973600 | -0.60493400 |
| C | -1.72388700 | -0.49860300 | -0.28437900 |
| C | -1.13440500 | 0.80455100 | -0.25561700 |
| N | -2.76013700 | -1.26765600 | -0.11518000 |
| N | -1.21049700 | 2.08838300 | -0.04543200 |
| C | -4.02604300 | -0.71164800 | 0.42436800 |
| C | -2.69558300 | -2.69563200 | -0.53549700 |
| C | -2.50891500 | 2.75529100 | 0.20831600 |
| C | 0.04587000 | 2.88604700 | -0.05840500 |
| C | -5.03504000 | -0.48862000 | -0.69689900 |
| H | -3.75215700 | 0.25244500 | 0.85671300 |
| C | -4.57432500 | -1.56823900 | 1.56057000 |
| C | -1.97894600 | -3.54738900 | 0.50508100 |
| H | -3.73863300 | -3.00987200 | -0.60069000 |
| C | -2.08236400 | -2.83381700 | -1.92468500 |
| H | -3.26299500 | 1.98112900 | 0.05676800 |
| C | -2.59059000 | 3.25118600 | 1.64735500 |
| C | -2.76795800 | 3.85105000 | -0.82173100 |
| H | -0.26266900 | 3.90187800 | 0.19084700 |
| C | 1.00706900 | 2.40245700 | 1.02141200 |
| C | 0.66178800 | 2.90293100 | -1.45318100 |
| H | -4.63009800 | 0.17402200 | -1.46609900 |
| H | -5.31821600 | -1.43149500 | -1.17161700 |
| H | -5.94368300 | -0.03482700 | -0.29620300 |
| H | -4.89575000 | -2.55393400 | 1.21684600 |
| H | -3.83244200 | -1.69611200 | 2.35070700 |
| H | -5.44711900 | -1.07229200 | 1.98921800 |
| H | -0.94069900 | -3.22734100 | 0.61972500 |
| H | -2.46354800 | -3.48252000 | 1.47973200 |

| | | | |
|---|---|---|---|
| H | -1.98373000 | -4.59307100 | 0.19030700 |
| H | -2.56481800 | -2.16532000 | -2.64151400 |
| H | -1.00794800 | -2.63222300 | -1.91298100 |
| H | -2.21470100 | -3.85894300 | -2.27449500 |
| H | -1.84019100 | 4.02019600 | 1.84840700 |
| H | -3.57144100 | 3.69362000 | 1.83197300 |
| H | -2.44104700 | 2.43291200 | 2.35541800 |
| H | -2.70510900 | 3.45692200 | -1.83816300 |
| H | -3.77017100 | 4.25741400 | -0.67353900 |
| H | -2.06349100 | 4.68034800 | -0.72512300 |
| H | 1.88563000 | 3.05001700 | 1.04899800 |
| H | 0.53275900 | 2.42608800 | 2.00431400 |
| H | 1.35771800 | 1.38474500 | 0.83489800 |
| H | 0.97955200 | 1.90210300 | -1.75836000 |
| H | -0.04450800 | 3.28230000 | -2.19395900 |
| H | 1.54539700 | 3.54392500 | -1.46096300 |



Optimized Structure of *E,Z-Z,Z*-Rotation-6

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- Thermochemistry -

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(0 imaginary frequencies)

Zero-point correction= 0.547186 (Hartree/Particle)

Thermal correction to Energy= 0.577743

Thermal correction to Enthalpy= 0.578687

Thermal correction to Gibbs Free Energy= 0.483791

Sum of electronic and zero-point Energies= -1475.765377

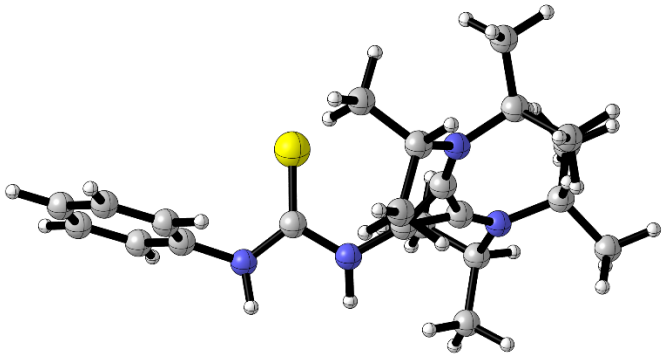
Sum of electronic and thermal Energies= -1475.734820

Sum of electronic and thermal Enthalpies= -1475.733876

Sum of electronic and thermal Free Energies= -1475.828773

| | | | |
|---|---|---|---|
| C | 1.89312000 | -0.26152200 | -0.07761800 |
| S | 1.58869800 | -0.77814700 | 1.45609900 |
| N | 0.87181900 | 0.24044400 | -0.90207000 |
| H | 1.11613200 | 0.99700400 | -1.52669200 |
| N | 3.05328300 | -0.41696300 | -0.76898100 |
| C | 4.36045700 | -0.05631400 | -0.31622200 |
| C | 5.44684900 | -0.66381700 | -0.93656000 |
| C | 4.55744500 | 0.89417300 | 0.67867900 |
| C | 6.73658000 | -0.30768500 | -0.56919700 |
| H | 5.28044500 | -1.41973500 | -1.69630900 |
| C | 5.85165200 | 1.23116400 | 1.05031100 |
| H | 3.71163400 | 1.36169100 | 1.16720900 |

| | | | |
|---|---|---|---|
| C | 6.94255900 | 0.63714600 | 0.42821300 |
| H | 7.94976700 | 0.90708600 | 0.72122400 |
| H | 2.95341400 | -0.38296900 | -1.77481700 |
| H | 6.00534400 | 1.96871800 | 1.82895000 |
| H | 7.58153200 | -0.78052600 | -1.05499800 |
| C | -0.44430100 | 0.13798300 | -0.54931400 |
| C | -1.52104100 | -0.65593200 | -0.24470900 |
| C | -1.63124200 | 0.75725000 | -0.26736700 |
| N | -2.08343000 | -1.81917900 | -0.04694900 |
| N | -2.32473400 | 1.85906000 | -0.12500500 |
| C | -3.47418300 | -1.86334300 | 0.46963300 |
| C | -1.42983600 | -3.07202600 | -0.51861700 |
| C | -3.79004500 | 1.81514800 | 0.07842300 |
| C | -1.60170200 | 3.15417200 | -0.09120000 |
| C | -4.47236600 | -2.01388400 | -0.67502900 |
| H | -3.62676000 | -0.89635400 | 0.95367500 |
| C | -3.64787000 | -2.92922000 | 1.54522700 |
| C | -0.51258900 | -3.68056000 | 0.53557500 |
| H | -2.26010300 | -3.75741200 | -0.70301000 |
| C | -0.71085800 | -2.85248600 | -1.84574400 |
| H | -4.07444900 | 0.78187800 | -0.12596200 |
| C | -4.14608600 | 2.14869100 | 1.52346200 |
| C | -4.51747600 | 2.69422300 | -0.93403800 |
| H | -2.35395800 | 3.89306200 | 0.18772700 |
| C | -0.52324900 | 3.15174500 | 0.98757200 |
| C | -1.06694800 | 3.51602300 | -1.47293100 |
| H | -4.34410900 | -1.22491000 | -1.42128800 |
| H | -4.35921700 | -2.97778000 | -1.17741800 |
| H | -5.49308700 | -1.95994100 | -0.29046700 |
| H | -3.52884600 | -3.93895200 | 1.14603500 |
| H | -2.93647700 | -2.78646200 | 2.36008100 |
| H | -4.65650700 | -2.85577300 | 1.95620000 |
| H | 0.33030200 | -3.01877300 | 0.74157900 |
| H | -1.03835700 | -3.86845700 | 1.47160100 |
| H | -0.12072400 | -4.63207000 | 0.16890400 |
| H | -1.36457700 | -2.37728200 | -2.58123500 |
| H | 0.18836600 | -2.24381500 | -1.72052500 |
| H | -0.39580200 | -3.81765300 | -2.24557300 |
| H | -3.88485000 | 3.18103800 | 1.77100000 |
| H | -5.22080500 | 2.03523800 | 1.67924200 |
| H | -3.62436200 | 1.48680100 | 2.21886400 |
| H | -4.24227500 | 2.42969000 | -1.95709000 |
| H | -5.59430300 | 2.55334600 | -0.82344800 |
| H | -4.31235500 | 3.75629100 | -0.78019100 |
| H | -0.06751700 | 4.14130300 | 1.05619100 |
| H | -0.94716600 | 2.90105700 | 1.96176300 |
| H | 0.27132400 | 2.43276600 | 0.76902300 |
| H | -0.31598400 | 2.79403800 | -1.80827900 |
| H | -1.86727100 | 3.54203200 | -2.21418100 |
| H | -0.58934400 | 4.49707600 | -1.44562600 |



Optimized Structure of *E,Z-Z,Z*-Rotation-7

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- Thermochemistry -

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(0 imaginary frequencies)

Zero-point correction= 0.546433 (Hartree/Particle)

Thermal correction to Energy= 0.576441

Thermal correction to Enthalpy= 0.577385

Thermal correction to Gibbs Free Energy= 0.483912

Sum of electronic and zero-point Energies= -1475.768761

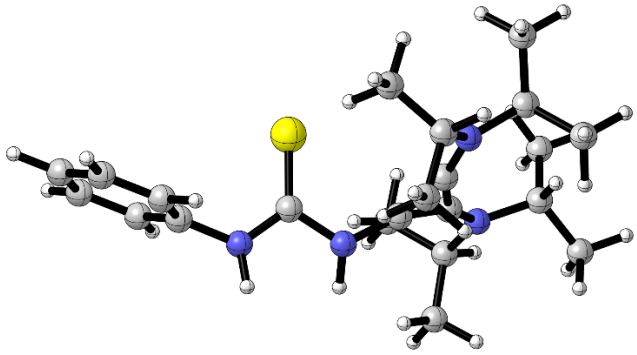
Sum of electronic and thermal Energies= -1475.738752

Sum of electronic and thermal Enthalpies= -1475.737808

Sum of electronic and thermal Free Energies= -1475.831282

| | | | |
|---|---|---|---|
| C | -1.83672700 | -0.62168400 | 0.14839300 |
| S | -1.68455900 | -0.06946000 | -1.40070500 |
| N | -0.72527300 | -0.76021200 | 0.99208500 |
| H | -0.74639700 | -1.49086900 | 1.69063000 |
| N | -2.96553300 | -1.13069400 | 0.69476400 |
| C | -4.27771900 | -0.67893600 | 0.30576400 |
| C | -5.15416100 | -1.57702000 | -0.28266500 |
| C | -4.65921600 | 0.63278500 | 0.55973100 |
| C | -6.43544000 | -1.15748800 | -0.61963000 |
| H | -4.82757200 | -2.59089400 | -0.47975200 |
| C | -5.93791000 | 1.04648600 | 0.21713100 |
| H | -3.95613000 | 1.32352700 | 1.01227900 |
| C | -6.82605100 | 0.15164600 | -0.37010800 |
| H | -7.82478600 | 0.47796600 | -0.63468400 |
| H | -2.91088900 | -1.38855800 | 1.67198000 |
| H | -6.24214600 | 2.06842700 | 0.40880900 |
| H | -7.12577900 | -1.85344600 | -1.08054500 |
| C | 0.51658300 | -0.33988600 | 0.59624800 |
| C | 1.80540300 | -0.65037200 | 0.25810800 |
| C | 1.35530800 | 0.69725800 | 0.27770000 |
| N | 2.74288000 | -1.54158400 | 0.06248200 |
| N | 1.60902000 | 1.96472400 | 0.09405500 |
| C | 4.14350000 | -1.13254900 | -0.18647200 |
| C | 2.36389700 | -2.97608900 | 0.01327400 |
| C | 2.91773500 | 2.36941900 | -0.47565400 |
| C | 0.66799500 | 3.00358500 | 0.59728500 |
| C | 5.10257200 | -1.82492300 | 0.77700600 |
| H | 4.17403300 | -0.06538700 | 0.03981400 |
| C | 4.51442000 | -1.33870100 | -1.65117500 |
| C | 1.28938700 | -3.22289600 | -1.04067400 |

| | | | |
|---|---|---|---|
| H | 3.26994300 | -3.49715800 | -0.29837500 |
| C | 1.97201900 | -3.48408200 | 1.39652600 |
| H | 3.30544500 | 1.47198000 | -0.96181700 |
| C | 2.75732000 | 3.42886200 | -1.55975200 |
| C | 3.87971300 | 2.79420200 | 0.63008400 |
| H | 1.28778600 | 3.89384100 | 0.72317800 |
| C | -0.43846600 | 3.30673700 | -0.40603300 |
| C | 0.11703800 | 2.62701200 | 1.96867000 |
| H | 4.80554900 | -1.66072100 | 1.81483300 |
| H | 5.16542400 | -2.90068000 | 0.59686700 |
| H | 6.10514600 | -1.41477900 | 0.64135400 |
| H | 4.48060900 | -2.39635200 | -1.92567200 |
| H | 3.83409000 | -0.79242900 | -2.30895000 |
| H | 5.53061000 | -0.98312100 | -1.83305000 |
| H | 0.33969300 | -2.74991200 | -0.77578900 |
| H | 1.59976000 | -2.83567700 | -2.01296500 |
| H | 1.11051400 | -4.29517200 | -1.13987300 |
| H | 2.76665900 | -3.31016300 | 2.12403500 |
| H | 1.06368300 | -2.99014800 | 1.75466800 |
| H | 1.76819900 | -4.55572100 | 1.35727700 |
| H | 2.38819000 | 4.37507400 | -1.15787600 |
| H | 3.73130900 | 3.62295500 | -2.01280200 |
| H | 2.07721600 | 3.09009300 | -2.34286500 |
| H | 3.99690400 | 2.00552200 | 1.37830900 |
| H | 4.86171200 | 3.01484900 | 0.20647800 |
| H | 3.52890700 | 3.69589700 | 1.13831700 |
| H | -1.07195800 | 4.10819300 | -0.01891200 |
| H | -0.03451800 | 3.62812000 | -1.36634700 |
| H | -1.05746000 | 2.42395200 | -0.57581300 |
| H | -0.58336200 | 1.78982500 | 1.90639800 |
| H | 0.91868400 | 2.36813200 | 2.66465600 |
| H | -0.42698500 | 3.47836200 | 2.38124700 |



Optimized Structure of *E,Z-Z,Z*-Rotation-8

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- Thermochemistry -

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(0 imaginary frequencies)

Zero-point correction= 0.546839 (Hartree/Particle)

Thermal correction to Energy= 0.577604

Thermal correction to Enthalpy= 0.578549

Thermal correction to Gibbs Free Energy= 0.483102

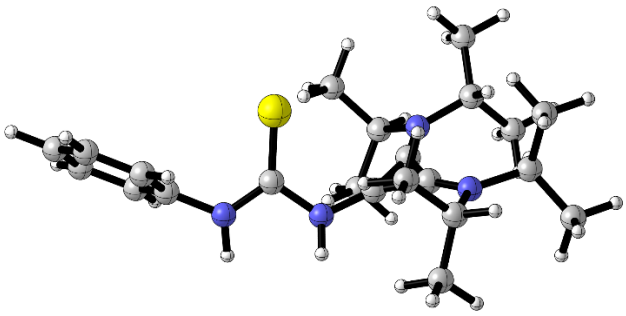
Sum of electronic and zero-point Energies= -1475.772273

Sum of electronic and thermal Energies= -1475.741508

Sum of electronic and thermal Enthalpies= -1475.740564
Sum of electronic and thermal Free Energies= -1475.836010

| | | | |
|---|---|---|---|
| C | 1.85954400 | -0.43257000 | -0.27607400 |
| S | 1.74136500 | 0.09667500 | 1.28235800 |
| N | 0.72273000 | -0.66125600 | -1.07549600 |
| H | 0.75497000 | -1.46349300 | -1.69038100 |
| N | 2.99237500 | -0.79471100 | -0.91019000 |
| C | 4.30463400 | -0.53240700 | -0.38646000 |
| C | 4.96225400 | -1.53016400 | 0.31740600 |
| C | 4.90250600 | 0.70029500 | -0.61125500 |
| C | 6.23844500 | -1.28868400 | 0.80776600 |
| H | 4.47049300 | -2.48107100 | 0.48345700 |
| C | 6.18031400 | 0.93382600 | -0.12198200 |
| H | 4.36637700 | 1.47058500 | -1.15432200 |
| C | 6.84650300 | -0.05898000 | 0.58730300 |
| H | 7.84240400 | 0.12737300 | 0.97112400 |
| H | 2.94076900 | -0.92448600 | -1.91139000 |
| H | 6.65449100 | 1.89302200 | -0.29102200 |
| H | 6.75770300 | -2.06147300 | 1.36148200 |
| C | -0.52044500 | -0.29787100 | -0.63827300 |
| C | -1.78460200 | -0.66731100 | -0.26700300 |
| C | -1.39562400 | 0.69608100 | -0.28230900 |
| N | -2.67501600 | -1.60402400 | -0.05567700 |
| N | -1.70134600 | 1.94910000 | -0.07220900 |
| C | -4.08487100 | -1.26398900 | 0.23948600 |
| C | -2.22823300 | -3.01875800 | -0.02932900 |
| C | -3.01343900 | 2.27813700 | 0.53715700 |
| C | -0.83758000 | 3.03985500 | -0.60164600 |
| C | -5.03911100 | -1.99996600 | -0.69614400 |
| H | -4.17516900 | -0.19894200 | 0.01999500 |
| C | -4.39855600 | -1.49376100 | 1.71416200 |
| C | -1.11127700 | -3.22332200 | 0.98915100 |
| H | -3.09789100 | -3.58433000 | 0.30748200 |
| C | -1.85908500 | -3.50039700 | -1.42822900 |
| H | -3.33174200 | 1.36096800 | 1.03702200 |
| C | -2.88476700 | 3.34878400 | 1.61434000 |
| C | -4.03301300 | 2.64028500 | -0.53894800 |
| H | -1.51529400 | 3.88833600 | -0.71865900 |
| C | 0.27069200 | 3.42254200 | 0.37232400 |
| C | -0.29453900 | 2.69034600 | -1.98331500 |
| H | -4.78683300 | -1.81429800 | -1.74218500 |
| H | -5.03801500 | -3.07863800 | -0.52229300 |
| H | -6.05701000 | -1.64528100 | -0.52355900 |
| H | -4.29335300 | -2.54802000 | 1.98374100 |
| H | -3.73191300 | -0.90962300 | 2.35323900 |
| H | -5.42816700 | -1.20019200 | 1.92831400 |
| H | -0.19254000 | -2.70563300 | 0.69959600 |
| H | -1.40845100 | -2.85658900 | 1.97344900 |
| H | -0.88146900 | -4.28707700 | 1.07450200 |
| H | -2.68560400 | -3.36201600 | -2.12719200 |
| H | -0.98989400 | -2.96029200 | -1.81597200 |
| H | -1.60167900 | -4.56094200 | -1.40375000 |
| H | -2.57789100 | 4.31230300 | 1.20145100 |
| H | -3.85699100 | 3.49160000 | 2.08980900 |
| H | -2.16936300 | 3.05022800 | 2.38207900 |

| | | | |
|---|---|---|---|
| H | -4.12273200 | 1.84476100 | -1.28371400 |
| H | -5.01399600 | 2.80025800 | -0.08653400 |
| H | -3.75491800 | 3.56114800 | -1.05794200 |
| H | 0.82244000 | 4.27763200 | -0.02493000 |
| H | -0.12805000 | 3.70028800 | 1.34812700 |
| H | 0.96707900 | 2.59377700 | 0.51182300 |
| H | 0.45087800 | 1.89219900 | -1.93390200 |
| H | -1.09467300 | 2.38669600 | -2.66279700 |
| H | 0.19448600 | 3.56881800 | -2.40763600 |



Optimized Structure of *E,Z-Z,Z*-Rotation-9

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- Thermochemistry -

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(0 imaginary frequencies)

Zero-point correction= 0.546621 (Hartree/Particle)

Thermal correction to Energy= 0.577436

Thermal correction to Enthalpy= 0.578380

Thermal correction to Gibbs Free Energy= 0.482853

Sum of electronic and zero-point Energies= -1475.772996

Sum of electronic and thermal Energies= -1475.742181

Sum of electronic and thermal Enthalpies= -1475.741237

Sum of electronic and thermal Free Energies= -1475.836765

| | | | |
|---|---|---|---|
| C | -1.86129300 | -0.41135300 | -0.27727200 |
| S | -1.74169800 | 0.12570000 | 1.27796200 |
| N | -0.72351200 | -0.66044300 | -1.07079300 |
| H | -0.76007300 | -1.47398500 | -1.67029600 |
| N | -2.99511000 | -0.74458200 | -0.92549800 |
| C | -4.30900700 | -0.52305700 | -0.39310500 |
| C | -5.02962000 | 0.59433300 | -0.79129400 |
| C | -4.84727400 | -1.44251700 | 0.49588500 |
| C | -6.31021500 | 0.79103000 | -0.29092000 |
| H | -4.58897600 | 1.30718600 | -1.47948300 |
| C | -6.12269200 | -1.23383300 | 1.00057600 |
| H | -4.26391000 | -2.30544700 | 0.79345400 |
| C | -6.85426600 | -0.11947600 | 0.60659200 |
| H | -7.85071600 | 0.03977800 | 1.00092800 |
| H | -2.93976200 | -0.85092200 | -1.92890400 |
| H | -6.54631800 | -1.94389400 | 1.70040800 |
| H | -6.87929000 | 1.66027800 | -0.59770100 |
| C | 0.51988800 | -0.29590900 | -0.63753600 |
| C | 1.39445000 | 0.69714800 | -0.27697800 |
| C | 1.78578100 | -0.66506300 | -0.27205100 |
| N | 1.69986500 | 1.94899900 | -0.05744600 |

| | | | |
|---|---|---|---|
| N | 2.67734500 | -1.60300600 | -0.06895300 |
| C | 3.01394900 | 2.27098200 | 0.55179100 |
| C | 0.84108000 | 3.04589000 | -0.58263500 |
| C | 4.08706900 | -1.26444800 | 0.22813000 |
| C | 2.23149400 | -3.01798100 | -0.05429200 |
| C | 4.03455000 | 2.63197500 | -0.52384900 |
| H | 3.32869600 | 1.35111200 | 1.04894100 |
| C | 2.89139600 | 3.33920300 | 1.63202400 |
| C | -0.25862900 | 3.44096300 | 0.39616600 |
| H | 1.52544400 | 3.88839600 | -0.70486700 |
| C | 0.28671400 | 2.70003200 | -1.96066100 |
| H | 4.17665500 | -0.19775700 | 0.01691700 |
| C | 4.40135600 | -1.50504700 | 1.70100200 |
| C | 5.04180100 | -1.99254200 | -0.71311100 |
| H | 3.10017200 | -3.58576100 | 0.28140600 |
| C | 1.11138500 | -3.23085500 | 0.95904300 |
| C | 1.86742600 | -3.48935400 | -1.45810000 |
| H | 4.11966700 | 1.83909900 | -1.27197400 |
| H | 3.76096500 | 3.55632400 | -1.03898700 |
| H | 5.01669200 | 2.78516800 | -0.07155700 |
| H | 2.58918400 | 4.30540300 | 1.22198900 |
| H | 2.17516700 | 3.04217400 | 2.39956300 |
| H | 3.86474000 | 3.47575600 | 2.10707800 |
| H | -0.96719500 | 2.62249400 | 0.53425600 |
| H | 0.14628800 | 3.71000300 | 1.37175500 |
| H | -0.79886500 | 4.30519600 | 0.00287600 |
| H | 1.07988600 | 2.38953400 | -2.64521100 |
| H | -0.46525100 | 1.90844500 | -1.90624400 |
| H | -0.19784500 | 3.58234300 | -2.38208800 |
| H | 4.29713400 | -2.56137700 | 1.96277200 |
| H | 5.43076800 | -1.21223900 | 1.91716000 |
| H | 3.73438100 | -0.92620900 | 2.34455100 |
| H | 4.78910200 | -1.79954600 | -1.75772200 |
| H | 6.05938800 | -1.63809100 | -0.53818400 |
| H | 5.04190500 | -3.07246000 | -0.54709500 |
| H | 0.88106600 | -4.29522600 | 1.03483700 |
| H | 1.40546100 | -2.87229800 | 1.94727600 |
| H | 0.19371000 | -2.71061100 | 0.67070500 |
| H | 1.00185300 | -2.94411300 | -1.84688700 |
| H | 2.69752100 | -3.34803500 | -2.15218500 |
| H | 1.60736300 | -4.54942400 | -1.44248100 |

**Computational Methods**

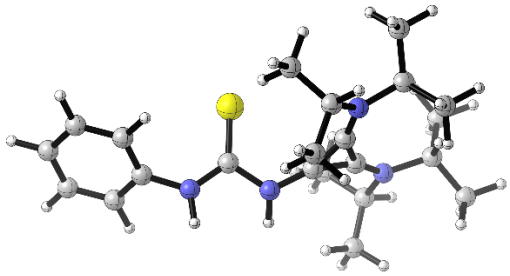
Quantum mechanical calculations were performed using Gaussian 09.[194] The following geometry optimizations were performed using the ωB97XD functional[195] with a 6-31G(d)/def2-SV basis set. The optimized geometries were verified as transition state structures (one imaginary frequency) or minima (zero imaginary frequencies) by frequency calculations. Intrinsic reaction coordinate calculations were performed to confirm that all transition state structures were linked to relevant minima. The energies of the ωB97XD/6-31G(d)/def2-SV optimized structures were further refined by single point calculations performed at the ωB97XD/6-311+G(d,p)/def2-SV level of theory using the integral equation formalism polarizable continuum model (IEFPCM) with the default parameters of dichloromethane (ε = 8.9) to account for solvent.[204] The thermal corrections to the Gibbs free energies (temperature = 298.15 K) computed at the lower level of theory (ωB97XD/6-31G(d)/def2-SV) were added to the electronic energies obtained from the single point calculations to provide the final reported Gibbs free energies. The 3D images of all optimized geometries were generated with CYLview.[200] GaussView5[201] was used to construct all structures prior to optimization and to visualize the output from the Gaussian 09 calculations. The reported non-covalent interaction (NCI) plot (isovalue = 0.3, min = -0.05 and max = 0.05 was calculated using the B3LYP-D3[205] functional with a LAVP*+ basis set using the program Jaguar of the Schrödinger software package.[206]

## Optimized Structures

***Table 25.*** *Gibbs free energy, enthalpies and entropies for all optimized structures.*

| Structure | Gibbs Free Energy (a.u.) | H (a.u.) | S (cal/mol*K) |
|---|---|---|---|
| **4** | -1475.551358 | -1475.456688 | 199.249 |
| **8a** | -513.873247 | -513.826630 | 98.112 |
| **4•8a** | -1989.441285 | -1989.316470 | 262.695 |
| **9a** | -402.865756 | -402.824343 | 87.162 |
| **9b** | -516.168702 | -516.122965 | 96.261 |
| **9d** | -363.590981 | -363.553484 | 78.919 |
| **TS1** | -2392.335045 | -2392.202496 | 278.974 |
| **4•10a'** | -2392.351427 | -2392.220051 | 276.504 |
| **10a** | -916.757514 | -916.691224 | 139.519 |

**4**

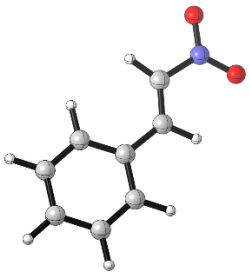


---
- Thermochemistry -
---
Zero-point correction= 0.551934 (Hartree/Particle)
Thermal correction to Energy= 0.582455
Thermal correction to Enthalpy= 0.583399
Thermal correction to Gibbs Free Energy= 0.488729
Sum of electronic and zero-point Energies= -1475.488153
Sum of electronic and thermal Energies= -1475.457632
Sum of electronic and thermal Enthalpies= -1475.456688
Sum of electronic and thermal Free Energies= -1475.551358

| | | | |
|---|---|---|---|
| S | -1.69970300 | -0.30899800 | 1.31375000 |
| N | 1.80773500 | -1.91374600 | -0.14908800 |
| N | 2.61538100 | 1.68714500 | -0.00654400 |
| N | -0.75695500 | 0.62026000 | -1.01742000 |
| N | -3.02522900 | 0.47708700 | -0.89355900 |
| C | 1.43853700 | -0.66507300 | -0.30681900 |
| C | 1.76442000 | 0.71355300 | -0.24241100 |
| C | 0.50948000 | 0.30142100 | -0.60940500 |
| C | 0.99764200 | -3.02616800 | -0.71739400 |
| H | 1.72299200 | -3.82671000 | -0.89049100 |
| C | -0.06595900 | -3.52536800 | 0.25659200 |
| H | 0.36821100 | -3.82108700 | 1.21404300 |
| H | -0.56854000 | -4.39756500 | -0.17273200 |
| H | -0.81384500 | -2.75046900 | 0.44564400 |
| C | 0.40425800 | -2.64167900 | -2.07032900 |
| H | -0.37841700 | -1.88251000 | -1.96952200 |
| H | -0.05345900 | -3.52511900 | -2.52332700 |
| H | 1.17404200 | -2.26940200 | -2.75379700 |
| C | 3.14108500 | -2.19797600 | 0.43726800 |
| H | 3.41424400 | -1.28597800 | 0.97579300 |
| C | 3.08032700 | -3.32102900 | 1.46888500 |
| H | 2.35457100 | -3.09589700 | 2.25449800 |
| H | 4.06457100 | -3.42938700 | 1.93323000 |
| H | 2.82514000 | -4.28393400 | 1.01627500 |
| C | 4.17184200 | -2.45877500 | -0.65996500 |
| H | 3.94235000 | -3.37484900 | -1.21404400 |
| H | 5.16563300 | -2.58010500 | -0.21901600 |
| H | 4.20898200 | -1.62996200 | -1.37508300 |
| C | 4.04561700 | 1.40523700 | 0.25066000 |
| H | 4.18156300 | 0.35166900 | -0.00559100 |
| C | 4.37940700 | 1.60073000 | 1.72793500 |
| H | 4.24372500 | 2.64326800 | 2.03439200 |
| H | 5.42430100 | 1.33634000 | 1.91400600 |
| H | 3.74409200 | 0.97291700 | 2.36088900 |

| | | | |
|---|---|---|---|
| C | 4.94527800 | 2.21779700 | -0.67869500 |
| H | 4.68906800 | 2.04170700 | -1.72743000 |
| H | 5.98601800 | 1.91866500 | -0.52591500 |
| H | 4.88415000 | 3.29218500 | -0.47947200 |
| C | 2.09641700 | 3.07305800 | 0.10003900 |
| H | 2.94710800 | 3.67080600 | 0.43510400 |
| C | 1.65559800 | 3.59844100 | -1.26402700 |
| H | 2.46644900 | 3.53897000 | -1.99499100 |
| H | 1.34079200 | 4.64223300 | -1.17984600 |
| H | 0.80404500 | 3.02855300 | -1.65327500 |
| C | 1.00416100 | 3.17233900 | 1.16308000 |
| H | 0.10679800 | 2.60738000 | 0.88732400 |
| H | 0.71282100 | 4.21809400 | 1.29536900 |
| H | 1.35971500 | 2.79013900 | 2.12406200 |
| C | -1.87483700 | 0.26037400 | -0.22981900 |
| C | -4.35100200 | 0.35972100 | -0.36305300 |
| C | -4.81409700 | -0.85579200 | 0.13159600 |
| H | -4.15773600 | -1.71825800 | 0.15012400 |
| C | -6.11830100 | -0.94207600 | 0.60491400 |
| H | -6.48395200 | -1.88460300 | 0.99897000 |
| C | -6.95458600 | 0.17107800 | 0.56866800 |
| H | -7.97242600 | 0.09591800 | 0.93742500 |
| C | -6.48633500 | 1.37886100 | 0.05950900 |
| H | -7.13525700 | 2.24803100 | 0.02965700 |
| C | -5.17880300 | 1.47793600 | -0.40443000 |
| H | -4.79868800 | 2.41950100 | -0.79039200 |
| H | -0.83957800 | 1.47843700 | -1.55067400 |
| H | -2.96165300 | 0.73010800 | -1.87172200 |

**8a**

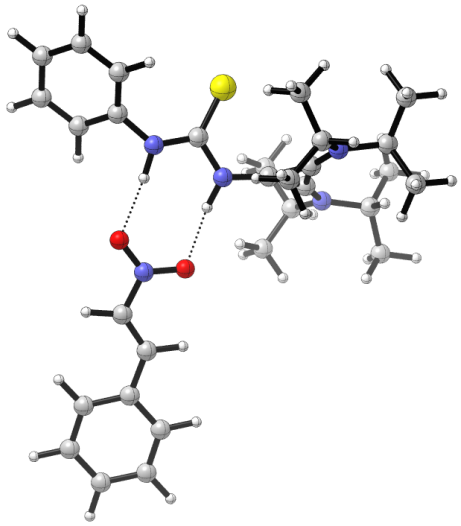


---
- Thermochemistry -
---
Zero-point correction= 0.138818 (Hartree/Particle)
Thermal correction to Energy= 0.147927
Thermal correction to Enthalpy= 0.148871
Thermal correction to Gibbs Free Energy= 0.102255
Sum of electronic and zero-point Energies= -513.836683
Sum of electronic and thermal Energies= -513.827575
Sum of electronic and thermal Enthalpies= -513.826630
Sum of electronic and thermal Free Energies= -513.873247

| | | | |
|---|---|---|---|
| O | -3.81781500 | 0.92852600 | -0.05385500 |
| N | -2.98538000 | 0.03231700 | -0.00522300 |
| O | -3.24480800 | -1.16183900 | 0.05466400 |
| C | -1.59806800 | 0.45741000 | -0.02237000 |
| H | -1.50808200 | 1.53278300 | -0.07816300 |

| | | | |
|---|---|---|---|
| C | -0.61836000 | -0.44595200 | 0.02179200 |
| H | -0.92414900 | -1.48888200 | 0.06493400 |
| C | 0.81990600 | -0.17395000 | 0.01294900 |
| C | 1.70048600 | -1.26220900 | -0.02026400 |
| C | 1.35293900 | 1.12310200 | 0.03785000 |
| C | 3.07621000 | -1.06459800 | -0.03483500 |
| H | 1.29823600 | -2.27163700 | -0.03747700 |
| C | 2.72590400 | 1.32015100 | 0.02490900 |
| H | 0.69263200 | 1.98427900 | 0.07246900 |
| C | 3.59158500 | 0.22732100 | -0.01237000 |
| H | 3.74523800 | -1.91895600 | -0.06197500 |
| H | 3.12556100 | 2.32923400 | 0.04646500 |
| H | 4.66559800 | 0.38581600 | -0.02212900 |

**4•8a**



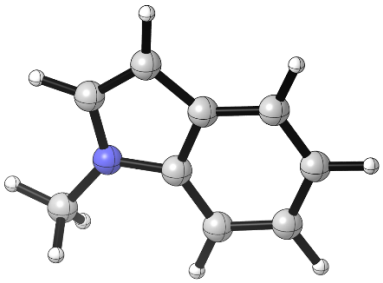
---
- Thermochemistry -
---
Zero-point correction= 0.692486 (Hartree/Particle)
Thermal correction to Energy= 0.733951
Thermal correction to Enthalpy= 0.734895
Thermal correction to Gibbs Free Energy= 0.610080
Sum of electronic and zero-point Energies= -1989.358879
Sum of electronic and thermal Energies= -1989.317414
Sum of electronic and thermal Enthalpies= -1989.316470
Sum of electronic and thermal Free Energies= -1989.441285

| | | | |
|---|---|---|---|
| S | -2.74965500 | 2.18992200 | 0.74575200 |
| N | -3.64553100 | -1.20021700 | -1.41034200 |
| N | -1.76042800 | -2.52102200 | 1.47389900 |
| N | -0.72476100 | 0.65556300 | -0.05699600 |
| N | -0.22912600 | 2.86756400 | 0.02978000 |
| C | -2.65375500 | -1.08210500 | -0.55985200 |
| C | -1.93657800 | -1.60429300 | 0.54800400 |
| C | -1.57254800 | -0.41631300 | -0.03118900 |
| C | -3.69377300 | -0.36198000 | -2.63901000 |
| H | -4.29191500 | -0.94798100 | -3.34315800 |

| | | | |
|---|---|---|---|
| C | -4.38251300 | 0.97833500 | -2.39878300 |
| H | -5.38335700 | 0.84862700 | -1.98062900 |
| H | -4.47629600 | 1.51319000 | -3.34909900 |
| H | -3.80212100 | 1.59366600 | -1.70582300 |
| C | -2.30178200 | -0.19224400 | -3.24300300 |
| H | -1.66417200 | 0.43959700 | -2.61589200 |
| H | -2.39138400 | 0.29670800 | -4.21682500 |
| H | -1.81025400 | -1.15939100 | -3.39001500 |
| C | -4.63264100 | -2.28955200 | -1.22205700 |
| H | -4.52503700 | -2.59301500 | -0.17690800 |
| C | -6.06599500 | -1.79370800 | -1.39449000 |
| H | -6.27647300 | -0.95869400 | -0.72130200 |
| H | -6.75501700 | -2.60873400 | -1.15506200 |
| H | -6.27401500 | -1.48024700 | -2.42196200 |
| C | -4.30638400 | -3.48088600 | -2.12176000 |
| H | -4.41284500 | -3.22436000 | -3.18084400 |
| H | -4.99167700 | -4.30761900 | -1.91213500 |
| H | -3.28154200 | -3.83117600 | -1.95803300 |
| C | -2.51015400 | -3.79401900 | 1.43434100 |
| H | -2.98726400 | -3.81618500 | 0.45121700 |
| C | -3.59480000 | -3.82603600 | 2.50898000 |
| H | -3.16210600 | -3.79258600 | 3.51434900 |
| H | -4.17410300 | -4.75056600 | 2.42904100 |
| H | -4.27834600 | -2.97746900 | 2.40377000 |
| C | -1.56675800 | -4.99388800 | 1.50468700 |
| H | -0.80253800 | -4.93693900 | 0.72415700 |
| H | -2.13855200 | -5.91465300 | 1.35822500 |
| H | -1.06886800 | -5.07099400 | 2.47639100 |
| C | -0.85852900 | -2.21745600 | 2.61281400 |
| H | -1.00296000 | -3.04119000 | 3.31631300 |
| C | 0.60220500 | -2.21250800 | 2.16918200 |
| H | 0.87152300 | -3.15851400 | 1.69042100 |
| H | 1.25284800 | -2.06667100 | 3.03647400 |
| H | 0.80253900 | -1.39908600 | 1.46474000 |
| C | -1.27359500 | -0.92359500 | 3.31012800 |
| H | -1.13948800 | -0.04894500 | 2.66505100 |
| H | -0.66225700 | -0.77607600 | 4.20495000 |
| H | -2.32374200 | -0.96233000 | 3.61336500 |
| C | -1.18826800 | 1.94433000 | 0.21475100 |
| C | -0.27905600 | 4.26038400 | 0.32337600 |
| C | -1.33889000 | 5.06764600 | -0.08308800 |
| H | -2.18222100 | 4.63621000 | -0.60674600 |
| C | -1.30005800 | 6.43003100 | 0.19387100 |
| H | -2.12830000 | 7.05866000 | -0.11729900 |
| C | -0.20867200 | 6.99007600 | 0.85149200 |
| H | -0.18480900 | 8.05519700 | 1.05820500 |
| C | 0.85527600 | 6.17956200 | 1.23702500 |
| H | 1.71305600 | 6.60769100 | 1.74580600 |
| C | 0.82076900 | 4.81452900 | 0.97764400 |
| H | 1.64386700 | 4.17448500 | 1.28305600 |
| H | 0.27797300 | 0.45601200 | -0.06516900 |
| H | 0.69750000 | 2.52797900 | -0.21940900 |
| O | 2.11646500 | -0.15924900 | -0.27623600 |
| N | 2.93479700 | 0.76423800 | -0.33117600 |
| O | 2.61019200 | 1.94941200 | -0.31243300 |
| C | 4.33034800 | 0.48485200 | -0.42435000 |

| | | | |
|---|---|---|---|
| H | 4.92004300 | 1.38897000 | -0.45754600 |
| C | 4.76618000 | -0.78439500 | -0.47514200 |
| H | 4.00858600 | -1.56390700 | -0.44573600 |
| C | 6.14820000 | -1.22110800 | -0.57594400 |
| C | 6.39735200 | -2.59613900 | -0.70044500 |
| C | 7.23482800 | -0.33028100 | -0.55873800 |
| C | 7.69659300 | -3.07240600 | -0.81361200 |
| H | 5.56358100 | -3.29305400 | -0.71258800 |
| C | 8.53052600 | -0.80821600 | -0.66866100 |
| H | 7.07040600 | 0.73740300 | -0.45294900 |
| C | 8.76329200 | -2.17829900 | -0.79851700 |
| H | 7.87717400 | -4.13728700 | -0.91457800 |
| H | 9.36413100 | -0.11403100 | -0.65359200 |
| H | 9.78009100 | -2.54753300 | -0.88699700 |

**9a**

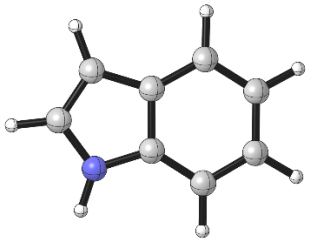


---
- Thermochemistry -
---
Zero-point correction= 0.159838 (Hartree/Particle)
Thermal correction to Energy= 0.167704
Thermal correction to Enthalpy= 0.168648
Thermal correction to Gibbs Free Energy= 0.127235
Sum of electronic and zero-point Energies= -402.833153
Sum of electronic and thermal Energies= -402.825287
Sum of electronic and thermal Enthalpies= -402.824343
Sum of electronic and thermal Free Energies= -402.865756

| | | | |
|---|---|---|---|
| C | -0.72987000 | 1.88464700 | 0.00215500 |
| C | -1.85671500 | 1.11560100 | -0.00377500 |
| N | -1.52410100 | -0.22255900 | -0.01161100 |
| H | -0.69503400 | 2.96472800 | 0.00402700 |
| H | -2.89794500 | 1.40932600 | -0.00484600 |
| C | -0.15152200 | -0.32716800 | -0.00492300 |
| C | 0.65679000 | -1.46793400 | -0.00408600 |
| C | 0.38541400 | 0.98199900 | 0.00107100 |
| C | 2.02803300 | -1.27685000 | -0.00122500 |
| H | 0.22824400 | -2.46600200 | -0.00484400 |
| C | 1.77884800 | 1.14160900 | 0.00374600 |
| C | 2.58458800 | 0.01629300 | 0.00243300 |
| H | 2.68732400 | -2.13990600 | -0.00112400 |
| H | 2.21774500 | 2.13540000 | 0.00763300 |
| H | 3.66471500 | 0.12895600 | 0.00482000 |
| C | -2.44120300 | -1.33558300 | 0.01062500 |
| H | -3.46125200 | -0.95916800 | -0.08766200 |

| | | | |
|---|---|---|---|
| H | -2.24023100 | -2.01696800 | -0.82297400 |
| H | -2.36104300 | -1.89413100 | 0.95012800 |

**9b**



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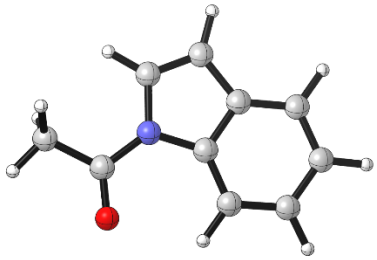
- Thermochemistry -
---

Zero-point correction= 0.131522 (Hartree/Particle)
Thermal correction to Energy= 0.137782
Thermal correction to Enthalpy= 0.138726
Thermal correction to Gibbs Free Energy= 0.101229
Sum of electronic and zero-point Energies= -363.560687
Sum of electronic and thermal Energies= -363.554428
Sum of electronic and thermal Enthalpies= -363.553484
Sum of electronic and thermal Free Energies= -363.590981

| | | | |
|---|---|---|---|
| C | -1.62417900 | 1.16310100 | 0.00003300 |
| C | -2.38154600 | 0.02878100 | -0.00002300 |
| N | -1.56076700 | -1.07782500 | 0.00001900 |
| H | -1.87333300 | -2.03367400 | -0.00077900 |
| H | -1.99801300 | 2.17703900 | 0.00002400 |
| H | -3.45582000 | -0.08973700 | 0.00027300 |
| C | -0.24745300 | -0.66722600 | 0.00000800 |
| C | 0.93363800 | -1.41446300 | 0.00003900 |
| C | -0.24914600 | 0.74768900 | 0.00004600 |
| C | 2.12882900 | -0.71708200 | 0.00002600 |
| H | 0.91510500 | -2.50070800 | 0.00015100 |
| C | 0.97985200 | 1.42503100 | -0.00003400 |
| C | 2.15243400 | 0.69104200 | -0.00003200 |
| H | 3.06630100 | -1.26519700 | 0.00009200 |
| H | 1.00744000 | 2.51112000 | -0.00013900 |
| H | 3.10911600 | 1.20470000 | -0.00013100 |

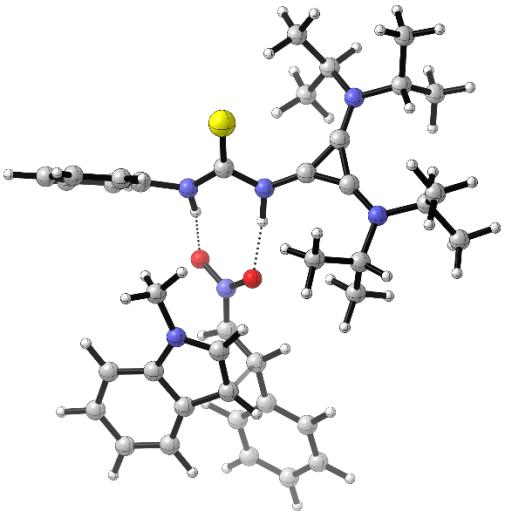
**9d**



---
- Thermochemistry -
---
Zero-point correction= 0.169808 (Hartree/Particle)
Thermal correction to Energy= 0.179352
Thermal correction to Enthalpy= 0.180296
Thermal correction to Gibbs Free Energy= 0.134559
Sum of electronic and zero-point Energies= -516.133454
Sum of electronic and thermal Energies= -516.123910
Sum of electronic and thermal Enthalpies= -516.122965
Sum of electronic and thermal Free Energies= -516.168702

| | | | |
|---|---|---|---|
| C | 0.27411600 | 2.13305600 | -0.00011600 |
| C | -0.98973600 | 1.65497900 | -0.00015500 |
| N | -0.97772300 | 0.25378700 | -0.00000300 |
| H | 0.55649900 | 3.17644200 | -0.00022700 |
| H | -1.92504300 | 2.19302800 | -0.00018800 |
| C | 0.36396200 | -0.16262500 | 0.00004700 |
| C | 0.91765100 | -1.44318500 | 0.00003600 |
| C | 1.16435300 | 0.99677400 | 0.00001700 |
| C | 2.30265000 | -1.53438100 | 0.00006500 |
| H | 0.28688300 | -2.32108000 | -0.00003400 |
| C | 2.55733800 | 0.87665800 | 0.00004100 |
| C | 3.11627100 | -0.39113800 | 0.00008000 |
| H | 2.76517400 | -2.51669400 | 0.00005800 |
| H | 3.18540900 | 1.76280200 | 0.00001200 |
| H | 4.19615400 | -0.50482700 | 0.00008700 |
| C | -2.09618500 | -0.58164800 | -0.00005300 |
| O | -1.98404400 | -1.78830800 | -0.00031600 |
| C | -3.44414400 | 0.10726600 | 0.00031800 |
| H | -4.21014100 | -0.66749200 | 0.00058400 |
| H | -3.56784600 | 0.73670100 | 0.88721200 |
| H | -3.56834100 | 0.73653900 | -0.88663100 |

**TS1**



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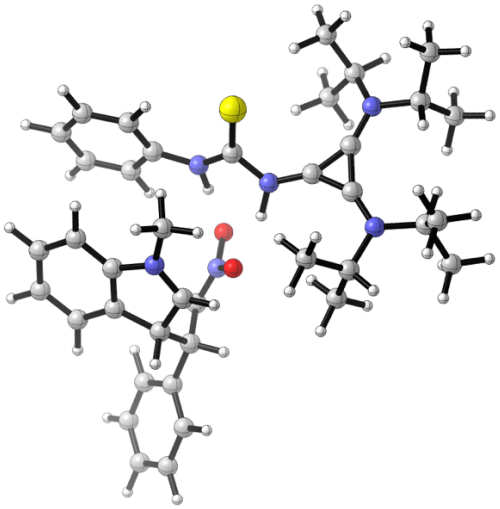
- Thermochemistry -
---
Zero-point correction= 0.857318 (Hartree/Particle)
Thermal correction to Energy= 0.905265
Thermal correction to Enthalpy= 0.906209
Thermal correction to Gibbs Free Energy= 0.773659
Sum of electronic and zero-point Energies= -2392.251387
Sum of electronic and thermal Energies= -2392.203440
Sum of electronic and thermal Enthalpies= -2392.202496
Sum of electronic and thermal Free Energies= -2392.335045

| | | | |
|---|---|---|---|
| S | -3.06544300 | 2.76105500 | -0.74395800 |
| N | -2.90566900 | -2.46143900 | -1.08390500 |
| N | -5.27219900 | -0.35941600 | 0.81481500 |
| N | -1.71995600 | 0.69187700 | 0.30411000 |
| N | -0.61767900 | 2.64736700 | 0.40708600 |
| C | -3.17309500 | -1.35873300 | -0.41770800 |
| C | -4.06865600 | -0.53926000 | 0.31339100 |
| C | -2.76763800 | -0.15238600 | 0.09515700 |
| C | -1.60913400 | -2.59970000 | -1.79153900 |
| H | -1.77622200 | -3.38713700 | -2.53050700 |
| C | -1.23834600 | -1.32907500 | -2.55472800 |
| H | -2.07503500 | -0.97488700 | -3.16385700 |
| H | -0.39908400 | -1.54834900 | -3.22163400 |
| H | -0.92697200 | -0.52349500 | -1.88227400 |
| C | -0.50515100 | -3.04885600 | -0.83548500 |
| H | -0.31399300 | -2.28960800 | -0.07106200 |
| H | 0.42470900 | -3.20001000 | -1.39454300 |
| H | -0.76361800 | -3.98945900 | -0.34295300 |
| C | -3.93904500 | -3.51057100 | -1.23840900 |
| H | -4.68364900 | -3.29964100 | -0.46967000 |
| C | -4.60150900 | -3.40862300 | -2.61108800 |
| H | -5.03070400 | -2.41315500 | -2.76362200 |
| H | -5.40221300 | -4.14930000 | -2.69417400 |
| H | -3.88225000 | -3.59983300 | -3.41456700 |
| C | -3.38574400 | -4.90320600 | -0.94745700 |
| H | -2.64035600 | -5.21677600 | -1.68473300 |

| | | | |
|---|---|---|---|
| H | -4.20773200 | -5.62350700 | -0.98456100 |
| H | -2.93706900 | -4.94703800 | 0.04874000 |
| C | -6.32471200 | -1.35362200 | 0.49194200 |
| H | -6.01794600 | -1.79640900 | -0.45846800 |
| C | -7.68104400 | -0.69783200 | 0.25097500 |
| H | -8.08411300 | -0.23629700 | 1.15750300 |
| H | -8.38865300 | -1.46773800 | -0.06956000 |
| H | -7.61823400 | 0.05886400 | -0.53528200 |
| C | -6.38879000 | -2.44617400 | 1.55913200 |
| H | -5.40857800 | -2.90968800 | 1.71181300 |
| H | -7.09491600 | -3.22315200 | 1.25196100 |
| H | -6.72899600 | -2.04472100 | 2.51921900 |
| C | -5.51215200 | 0.61973600 | 1.90924600 |
| H | -6.30307400 | 0.16313300 | 2.51170500 |
| C | -4.28646600 | 0.77285900 | 2.80603000 |
| H | -3.91558600 | -0.19941800 | 3.14545600 |
| H | -4.56481300 | 1.35872100 | 3.68641000 |
| H | -3.47574600 | 1.30630900 | 2.30051300 |
| C | -6.01031600 | 1.96601100 | 1.38952300 |
| H | -5.23467600 | 2.45448800 | 0.79464500 |
| H | -6.25630400 | 2.61049300 | 2.23963800 |
| H | -6.90703500 | 1.85712400 | 0.77578400 |
| C | -1.75167600 | 2.04450600 | 0.01441600 |
| C | -0.17463500 | 3.96974300 | 0.15106400 |
| C | -0.28819200 | 4.57210100 | -1.10268400 |
| H | -0.78966100 | 4.05418300 | -1.91111200 |
| C | 0.25302000 | 5.83762700 | -1.30493000 |
| H | 0.15852000 | 6.30560900 | -2.27985900 |
| C | 0.92073500 | 6.49727100 | -0.27521800 |
| H | 1.34459100 | 7.48229800 | -0.44271900 |
| C | 1.04880000 | 5.88239400 | 0.96737600 |
| H | 1.57162600 | 6.38375700 | 1.77578900 |
| C | 0.50074800 | 4.62220700 | 1.18365000 |
| H | 0.59675200 | 4.13719700 | 2.15038100 |
| H | -0.78598000 | 0.26145800 | 0.41194200 |
| H | 0.04263900 | 2.08821200 | 0.96516200 |
| O | 0.86672400 | -0.29806100 | 0.29961800 |
| N | 1.71727800 | 0.17099300 | 1.12381100 |
| O | 1.46341100 | 1.23292300 | 1.75674300 |
| C | 2.89186400 | -0.46467100 | 1.29724900 |
| H | 3.57795400 | 0.03650700 | 1.96143400 |
| C | 3.16148100 | -1.64975800 | 0.57299000 |
| C | 4.24460600 | -2.55998900 | 1.01237200 |
| C | 4.15810100 | -3.91290200 | 0.66182600 |
| C | 5.34349800 | -2.12514200 | 1.76238900 |
| C | 5.13925100 | -4.81358200 | 1.05679200 |
| H | 3.30841200 | -4.25859700 | 0.07814000 |
| C | 6.32604700 | -3.02709200 | 2.15751900 |
| H | 5.44577700 | -1.08009600 | 2.03439900 |
| C | 6.22756700 | -4.37130900 | 1.80683800 |
| H | 5.05304400 | -5.86047000 | 0.78351900 |
| H | 7.17215700 | -2.67649100 | 2.74000300 |
| H | 6.99504700 | -5.07305400 | 2.11793800 |
| H | 2.27484300 | -2.16080700 | 0.21013200 |
| C | 3.80612400 | -1.16158800 | -1.32046000 |
| C | 4.92815100 | -0.26779900 | -1.04990300 |

| | | | |
|---|---|---|---|
| C | 2.73935500 | -0.30567500 | -1.69014700 |
| C | 4.40556500 | 1.03253900 | -1.03624300 |
| C | 6.27134900 | -0.46778800 | -0.73859500 |
| H | 1.75580800 | -0.56746600 | -2.04903000 |
| C | 5.15719800 | 2.15141100 | -0.70234000 |
| C | 7.04618000 | 0.64291100 | -0.41804300 |
| H | 6.70205700 | -1.46322600 | -0.74759300 |
| C | 6.49523300 | 1.93147800 | -0.39163500 |
| H | 4.72844600 | 3.14786400 | -0.68701500 |
| H | 8.09760700 | 0.51004500 | -0.18435900 |
| H | 7.12486800 | 2.77586600 | -0.13046700 |
| H | 3.89984100 | -2.16681100 | -1.71084300 |
| C | 2.16246800 | 2.10084400 | -1.47243400 |
| H | 2.11335000 | 2.55268100 | -0.47783700 |
| H | 2.52738700 | 2.83772100 | -2.19095500 |
| H | 1.16725300 | 1.76314100 | -1.75982900 |
| N | 3.05683900 | 0.95852500 | -1.42758600 |

**4•10a'**



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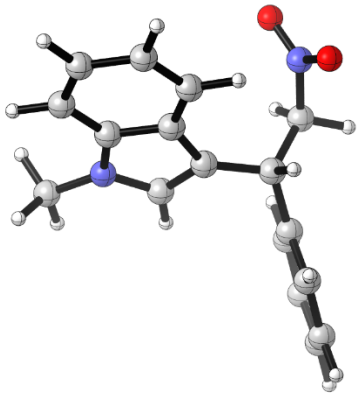
- Thermochemistry -
---
Zero-point correction= 0.858542 (Hartree/Particle)
Thermal correction to Energy= 0.906464
Thermal correction to Enthalpy= 0.907408
Thermal correction to Gibbs Free Energy= 0.776032
Sum of electronic and zero-point Energies= -2392.268917
Sum of electronic and thermal Energies= -2392.220995
Sum of electronic and thermal Enthalpies= -2392.220051
Sum of electronic and thermal Free Energies= -2392.351427

| | | | |
|---|---|---|---|
| S | -2.19408400 | 2.70902600 | -1.03577900 |
| N | -3.50020800 | -2.42421400 | -0.76055300 |

| | | | |
|---|---|---|---|
| N | -5.19494700 | 0.48597900 | 0.74826100 |
| N | -1.49572100 | 0.45064100 | 0.21277600 |
| N | -0.01956800 | 2.11151900 | 0.50104500 |
| C | -3.45821900 | -1.20313100 | -0.26766400 |
| C | -4.08721400 | -0.07919000 | 0.31077100 |
| C | -2.73009900 | -0.09134900 | 0.07831800 |
| C | -2.29207300 | -2.99251900 | -1.40303700 |
| H | -2.64582600 | -3.87947800 | -1.93370900 |
| C | -1.71713700 | -2.03058300 | -2.43987400 |
| H | -2.47947300 | -1.72887100 | -3.16353100 |
| H | -0.90158400 | -2.52236000 | -2.97905700 |
| H | -1.31374400 | -1.12950800 | -1.96596700 |
| C | -1.25669700 | -3.42837100 | -0.36814700 |
| H | -0.83362600 | -2.57244500 | 0.16682100 |
| H | -0.42839000 | -3.93651300 | -0.87279400 |
| H | -1.69151700 | -4.12028300 | 0.35789900 |
| C | -4.74895300 | -3.21483500 | -0.72000100 |
| H | -5.42946100 | -2.64703100 | -0.08491400 |
| C | -5.36637100 | -3.33570800 | -2.11194800 |
| H | -5.52307400 | -2.34825200 | -2.55691900 |
| H | -6.33288100 | -3.84340900 | -2.04289000 |
| H | -4.73010600 | -3.92088000 | -2.78422100 |
| C | -4.53321300 | -4.56939100 | -0.04816000 |
| H | -3.87863200 | -5.22008700 | -0.63661000 |
| H | -5.49794600 | -5.07474000 | 0.05278300 |
| H | -4.10254900 | -4.44556300 | 0.94953300 |
| C | -6.47598000 | -0.22856400 | 0.53020100 |
| H | -6.30455800 | -0.86041000 | -0.34460800 |
| C | -7.61114700 | 0.72316400 | 0.16429400 |
| H | -7.86826700 | 1.39686600 | 0.98746100 |
| H | -8.50170500 | 0.13243200 | -0.06875800 |
| H | -7.35534800 | 1.31944700 | -0.71551600 |
| C | -6.82162000 | -1.11132600 | 1.72990100 |
| H | -5.99452900 | -1.78424300 | 1.97988300 |
| H | -7.70350600 | -1.71776800 | 1.50243500 |
| H | -7.04909100 | -0.50937200 | 2.61566700 |
| C | -5.15840600 | 1.62470900 | 1.70375200 |
| H | -6.03778500 | 1.47476900 | 2.33709900 |
| C | -3.93098500 | 1.56482100 | 2.60938700 |
| H | -3.82749500 | 0.58068100 | 3.07680300 |
| H | -4.04025800 | 2.31091700 | 3.40120700 |
| H | -3.01020500 | 1.79859000 | 2.06698300 |
| C | -5.28785900 | 2.97646500 | 1.00591300 |
| H | -4.41464800 | 3.16537500 | 0.37657300 |
| H | -5.35002900 | 3.76642900 | 1.76115600 |
| H | -6.18506000 | 3.02711900 | 0.38497000 |
| C | -1.18827400 | 1.77658000 | -0.06861100 |
| C | 0.83503800 | 3.22621200 | 0.35573000 |
| C | 0.67506500 | 4.25480400 | -0.57647000 |
| H | -0.17931900 | 4.26768700 | -1.23829400 |
| C | 1.62337600 | 5.27537000 | -0.63918300 |
| H | 1.48941500 | 6.06930100 | -1.36772800 |
| C | 2.72080900 | 5.29025300 | 0.21393800 |
| H | 3.45002700 | 6.09216200 | 0.15841400 |
| C | 2.87573300 | 4.26069600 | 1.14133400 |
| H | 3.73081500 | 4.25002800 | 1.80992500 |

| | | | |
|---|---|---|---|
| C | 1.94663500 | 3.23421100 | 1.21138000 |
| H | 2.07381200 | 2.42152900 | 1.92173600 |
| H | -0.69139100 | -0.18520000 | 0.36672800 |
| H | 0.34414400 | 1.41037700 | 1.17459600 |
| O | 0.90247500 | -0.93527700 | 0.27916000 |
| N | 1.57550200 | -0.61391800 | 1.36339600 |
| O | 1.00135000 | 0.16407200 | 2.20734500 |
| C | 2.77720600 | -1.09052400 | 1.51925900 |
| H | 3.29374100 | -0.77588900 | 2.41269300 |
| C | 3.34692800 | -1.97181600 | 0.46014300 |
| C | 4.65615700 | -2.64080800 | 0.84302800 |
| C | 4.95671200 | -3.87665800 | 0.26302800 |
| C | 5.58403200 | -2.07212900 | 1.71797600 |
| C | 6.15328900 | -4.52773100 | 0.54129900 |
| H | 4.24123400 | -4.33633700 | -0.41476200 |
| C | 6.78351300 | -2.72307200 | 2.00150500 |
| H | 5.39098500 | -1.10938300 | 2.18080100 |
| C | 7.07274200 | -3.95103200 | 1.41451200 |
| H | 6.36377400 | -5.48803200 | 0.08070600 |
| H | 7.49174700 | -2.26534400 | 2.68530200 |
| H | 8.00740100 | -4.45636600 | 1.63684300 |
| H | 2.61635800 | -2.76417500 | 0.24883600 |
| C | 3.49114800 | -1.21012000 | -0.90685100 |
| C | 4.20474300 | 0.12152500 | -0.91121300 |
| C | 2.17502800 | -0.84234400 | -1.52477800 |
| C | 3.36652100 | 1.06014200 | -1.50942300 |
| C | 5.45713100 | 0.52131200 | -0.47329000 |
| H | 1.43168300 | -1.54426600 | -1.87257100 |
| C | 3.69673100 | 2.39002000 | -1.67907000 |
| C | 5.82014600 | 1.86241100 | -0.62884800 |
| H | 6.14631700 | -0.18589200 | -0.02631800 |
| C | 4.95295000 | 2.78195600 | -1.21605900 |
| H | 3.01149600 | 3.10500600 | -2.12112700 |
| H | 6.79517200 | 2.19175700 | -0.28475600 |
| H | 5.25025800 | 3.82053500 | -1.31349100 |
| H | 3.97180900 | -1.91025600 | -1.60461300 |
| C | 1.11741300 | 1.06697300 | -2.66803200 |
| H | 0.73929200 | 1.91298200 | -2.09165400 |
| H | 1.52277000 | 1.42705500 | -3.61593200 |
| H | 0.30998000 | 0.36099000 | -2.85636300 |
| N | 2.17147300 | 0.40185100 | -1.92012400 |

**10a**



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- Thermochemistry -
---
Zero-point correction= 0.303939 (Hartree/Particle)
Thermal correction to Energy= 0.321513
Thermal correction to Enthalpy= 0.322457
Thermal correction to Gibbs Free Energy= 0.256167
Sum of electronic and zero-point Energies= -916.709742
Sum of electronic and thermal Energies= -916.692168
Sum of electronic and thermal Enthalpies= -916.691224
Sum of electronic and thermal Free Energies= -916.757514

| | | | |
|---|---|---|---|
| O | 0.39707100 | 3.42033600 | -0.27282800 |
| N | 0.32147900 | 2.76952100 | 0.76058900 |
| O | 1.12991000 | 2.79547100 | 1.66928000 |
| C | -0.87075700 | 1.87990400 | 0.90346100 |
| H | -1.73663000 | 2.53835400 | 0.80447100 |
| C | -0.88490200 | 0.79532000 | -0.19104800 |
| C | -2.26189200 | 0.15790100 | -0.27216200 |
| C | -2.83392800 | -0.09203400 | -1.52071000 |
| C | -2.96991600 | -0.21637000 | 0.87311400 |
| C | -4.08038200 | -0.69982900 | -1.62596800 |
| H | -2.29335100 | 0.19122000 | -2.42015600 |
| C | -4.21799700 | -0.82548500 | 0.77151300 |
| H | -2.54631200 | -0.03883100 | 1.85830900 |
| C | -4.77770100 | -1.06857200 | -0.47865000 |
| H | -4.51010500 | -0.88156800 | -2.60652900 |
| H | -4.75359700 | -1.10720900 | 1.67340000 |
| H | -5.75199800 | -1.54082800 | -0.55939800 |
| H | -0.70642200 | 1.32009300 | -1.13676600 |
| C | 0.20530200 | -0.22924900 | 0.00345600 |
| C | 1.59030800 | -0.10865600 | -0.37991200 |
| C | 0.07824300 | -1.45832800 | 0.59112100 |
| C | 2.22879300 | -1.30511800 | 0.01816600 |
| C | 2.34724600 | 0.87685400 | -1.03217200 |
| H | -0.80461000 | -1.93999200 | 0.98949500 |
| C | 3.58756300 | -1.54260300 | -0.20687800 |
| C | 3.69241200 | 0.64647600 | -1.25916200 |
| H | 1.89184400 | 1.81191200 | -1.34382700 |
| C | 4.30780100 | -0.55073600 | -0.84937500 |
| H | 4.06064100 | -2.46806300 | 0.10811900 |

| | | | |
|---|---|---|---|
| H | 4.28704000 | 1.40488100 | -1.75906000 |
| H | 5.36651100 | -0.69900900 | -1.03983200 |
| C | 1.53548700 | -3.43267100 | 1.13860200 |
| H | 1.87945200 | -4.10979200 | 0.34900200 |
| H | 2.29330700 | -3.39827200 | 1.92855700 |
| H | 0.61014000 | -3.82953900 | 1.56013600 |
| N | 1.28662200 | -2.11248500 | 0.61311800 |
| H | -0.81255700 | 1.46010900 | 1.90612600 |

**Computational details**

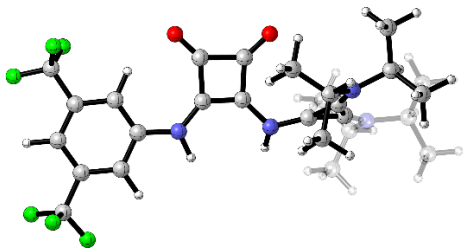
The following DFT calculations were performed using the software package Gaussian 09, Revision E. 01[194] employing the range-separated hybrid ωB97X-D functional[195] with a 6-31G(d)/def2-TZV basis set. This functional was selected as it accounts for dispersion and has been shown to provide accurate thermochemical and kinetic energies. The optimized geometries were verified as transition state structures (one imaginary frequency) or minima (zero imaginary frequencies) by frequency calculations. Intrinsic reaction coordinate calculations[198] were performed to confirm that all transition state structures were linked to relevant minima. The energies of the ωB97X-D/6-31G(d)/def2-TZV optimized structures were further refined by single-point calculations performed at the ωB97X-D/6-311++G(d,p)/def2-TZV level of theory using the integral equation formalism polarizable continuum model (IEFPCM) with the default parameters of dichloromethane (ε= 8.93) to account for solvent.[204] The final reported Gibbs free energies are the summed thermal corrections to the Gibbs free energies computed at the lower level of theory (ωB97X-D/6-31G(d)/def2-TZV) and electronic energies from single-point calculations (ωB97X-D/6-311++G(d,p)/def2-TZV). The keyword (integral=grid=ultrafine) was used for all calculations. The p$K_a$ was calculated in accordance to the method of Xue and Ji[145] at the $SMD_{(DMSO)}$M06-2X/6-311++G(2df,2p)//B3LYP/6-31+G(d) level of theory. Notably, this method has been successfully applied to predict the p$K_a$ values of numerous O–H and N–H acids in DMSO.[207] The 3D images of all optimized geometries were generated with CYLview,[200] and GaussView[201] was used to construct all structures prior to optimization and visualize the output from the Gaussian 09 calculations.

# Cartesian Coordinates and Energies of Calculated Structures

***Table 26.*** *Single-point energies of all structures calculated at the $SMD_{(DMSO)}$M06-2X/6-311++G(2df,2p) level of theory and thermal correction to Gibbs Free Energy and Gibbs Free Energy calculated at the B3LYP/6-31+G(d) level of theory. All energies are reported in Hartrees.*

| Structure | Single-Point Energies (E) $SMD_{(DMSO)}$M06-2X/6-311++G(2df,2p) | Single-Point Energies (E) M06-2X/6-311++G(2df,2p) | Thermal Corrections to Gibbs Free Energies (G) B3LYP/6-31+G(d) | Gibbs Free Energies (G) B3LYP/6-31+G(d) |
|---|---|---|---|---|
| **11c** | -2016.98993189 | -2016.88524360 | 0.492522 | -2016.550047 |
| **$11c_{cy\text{-}H}$** | -2016.53535221 | -2016.49826211 | 0.480739 | -2016.178015 |
| **$11c_{aryl\text{-}H}$** | -2016.52083588 | -2016.46934443 | 0.478187 | -2016.151713 |

Structure **11c**



Number of Imaginary Frequencies = 0

E (Single Point Energy) [$SMD_{(DMSO)}$ M06-2X /6-311++G(2df,2p)] = -2016.98993189

| | |
|---|---|
| Zero-point correction= | 0.574965 (Hartree/Particle) |
| Thermal correction to Energy= | 0.616824 |
| Thermal correction to Enthalpy= | 0.617769 |
| Thermal correction to Gibbs Free Energy= | 0.492522 |
| Sum of electronic and zero-point Energies= | -2016.467604 |
| Sum of electronic and thermal Energies= | -2016.425745 |
| Sum of electronic and thermal Enthalpies= | -2016.424800 |
| Sum of electronic and thermal Free Energies= | -2016.550047 |

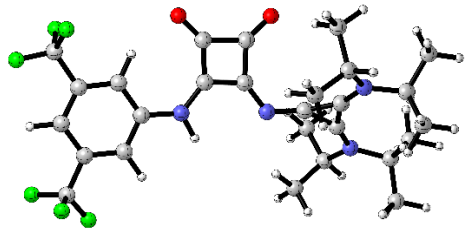
1 1

| | | | |
|---|---|---|---|
| C | 0.91552300 | -0.38234500 | -0.35415800 |
| C | -0.47315600 | -0.25792900 | -0.36787400 |
| C | -0.70735100 | -1.51646900 | -1.09215700 |
| C | 0.82815900 | -1.70854300 | -1.10543700 |
| O | 1.60769900 | -2.51031600 | -1.54706900 |
| O | -1.68383300 | -2.11400400 | -1.48953700 |

| | | | |
|---|---|---|---|
| N | -1.34826700 | 0.72720900 | 0.06726100 |
| H | -1.08698500 | 1.69443100 | -0.10585500 |
| C | -2.70227400 | 0.48088500 | 0.13256300 |
| C | -3.98155300 | 0.82876600 | -0.24746800 |
| C | -3.74780000 | -0.27953700 | 0.62113700 |
| N | -4.22537800 | -1.27863000 | 1.33585600 |
| N | -4.79598700 | 1.62320400 | -0.91587200 |
| C | -4.22796800 | 2.61083100 | -1.88775900 |
| C | -3.45015500 | 3.72199600 | -1.17207100 |
| C | -3.40997800 | 1.91370700 | -2.98061000 |
| H | -2.55011600 | 3.33481800 | -0.67798600 |
| H | -3.12389900 | 4.47445200 | -1.89754500 |
| H | -4.06342700 | 4.22013100 | -0.41524400 |
| H | -2.50645700 | 1.44111700 | -2.57884300 |
| H | -3.99843900 | 1.14211700 | -3.48647700 |
| H | -3.09447400 | 2.64774200 | -3.72951200 |
| C | -6.27735900 | 1.54088000 | -0.72519700 |
| C | -6.97247100 | 1.01135000 | -1.98499000 |
| H | -6.87706300 | 1.70574700 | -2.82702000 |
| H | -6.56268700 | 0.04284200 | -2.29098200 |
| H | -8.04240900 | 0.88381300 | -1.78876300 |
| C | -5.62741200 | -1.75494500 | 1.11357800 |
| C | -5.64636300 | -3.23399300 | 0.70658500 |
| C | -6.52714200 | -1.45412200 | 2.31769700 |
| H | -5.32582000 | -3.89184700 | 1.52132200 |
| H | -6.66971500 | -3.52055100 | 0.44155000 |
| H | -5.00428500 | -3.41428800 | -0.16119100 |
| H | -7.55836900 | -1.74114300 | 2.08564300 |
| H | -6.22579900 | -2.01911900 | 3.20637200 |
| H | -6.51784000 | -0.38806800 | 2.57085000 |
| C | -3.39602800 | -1.92772700 | 2.40461000 |
| C | -2.22712700 | -2.74343800 | 1.84617100 |
| H | -1.43264200 | -2.09431200 | 1.46608200 |
| H | -1.79618400 | -3.34960900 | 2.65038000 |
| H | -2.54164600 | -3.41065500 | 1.03987400 |
| N | 1.87137800 | 0.40647700 | 0.16911100 |
| H | 1.54371600 | 1.18313600 | 0.73524700 |
| H | -5.98525300 | -1.17893500 | 0.25611500 |
| H | -5.10178400 | 3.06490300 | -2.36009500 |
| H | -4.08795700 | -2.61896100 | 2.89016100 |
| C | -2.94802600 | -0.89558300 | 3.44593000 |
| H | -3.80143100 | -0.35633400 | 3.87005600 |
| H | -2.42474100 | -1.40145100 | 4.26420400 |
| H | -2.25420300 | -0.16428700 | 3.01402400 |
| H | -6.41497700 | 0.81541300 | 0.08056900 |
| C | -6.85598600 | 2.87757100 | -0.24403200 |
| H | -6.35783300 | 3.22363700 | 0.66764300 |
| H | -6.77767700 | 3.66214700 | -1.00420200 |
| H | -7.92032800 | 2.74929300 | -0.02062600 |
| C | 3.28786600 | 0.30802500 | 0.10816400 |
| C | 3.95494100 | -0.66512100 | -0.63873000 |
| C | 4.01465300 | 1.26166500 | 0.83364900 |
| C | 5.35316500 | -0.66996100 | -0.64732700 |
| H | 3.40819300 | -1.41557900 | -1.19967600 |
| C | 5.40617900 | 1.23959200 | 0.80852500 |
| H | 3.50081400 | 2.02422500 | 1.41262900 |

| | | | |
|---|---|---|---|
| C | 6.09068000 | 0.27186800 | 0.06786500 |
| H | 7.17384000 | 0.25902200 | 0.04409700 |
| C | 6.18320000 | 2.24141000 | 1.63160500 |
| C | 6.05198300 | -1.74463500 | -1.45297500 |
| F | 6.50773200 | 1.73303400 | 2.84629300 |
| F | 7.33492900 | 2.60233200 | 1.02911600 |
| F | 5.46695300 | 3.37110100 | 1.85626400 |
| F | 7.38755600 | -1.55957600 | -1.49984500 |
| F | 5.82950800 | -2.97237300 | -0.92507000 |
| F | 5.59838200 | -1.77477500 | -2.72878000 |

Structure **11c$_{cy\text{-}H}$**



| | |
|---|---|
| Zero-point correction= | 0.562318 (Hartree/Particle) |
| Thermal correction to Energy= | 0.603574 |
| Thermal correction to Enthalpy= | 0.604518 |
| Thermal correction to Gibbs Free Energy= | 0.480739 |
| Sum of electronic and zero-point Energies= | -2016.096437 |
| Sum of electronic and thermal Energies= | -2016.055181 |
| Sum of electronic and thermal Enthalpies= | -2016.054237 |
| Sum of electronic and thermal Free Energies= | -2016.178015 |

Number of Imaginary Frequencies = 0

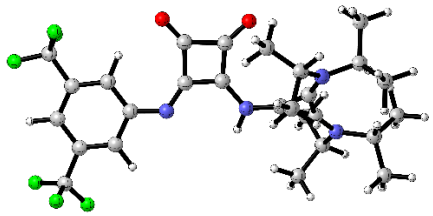
E (Single Point Energy) [SMD$_{(DMSO)}$ M06-2X /6-311++G(2df,2p)] = -2016.53535221

0 1

| | | | |
|---|---|---|---|
| C | 0.92518800 | -0.81136800 | -0.52066000 |
| C | -0.48256600 | -0.77375500 | -0.58522100 |
| C | -0.52078400 | -2.12939300 | -1.21071400 |
| C | 1.00948400 | -2.17481800 | -1.08584200 |
| O | 1.89022200 | -2.97639800 | -1.35703700 |
| O | -1.39371000 | -2.85744400 | -1.64945300 |
| N | -1.30682300 | 0.24031600 | -0.32344300 |
| C | -2.62292900 | 0.10843300 | -0.18923200 |
| C | -3.82741700 | 0.79576300 | -0.30270200 |
| C | -3.80728800 | -0.45764600 | 0.31524000 |
| N | -4.47324900 | -1.42112100 | 0.96874700 |
| N | -4.44933500 | 1.90191800 | -0.73587500 |
| C | -3.67372400 | 2.87909700 | -1.55012500 |
| C | -2.56024100 | 3.54279600 | -0.72692900 |
| C | -3.13603200 | 2.24061600 | -2.83821000 |
| H | -1.80497900 | 2.80689300 | -0.43083000 |
| H | -2.06465800 | 4.31598300 | -1.32605000 |
| H | -2.96398000 | 4.01652100 | 0.17469900 |
| H | -2.38024600 | 1.47962800 | -2.61853000 |

| | | | |
|---|---|---|---|
| H | -3.94224800 | 1.77618100 | -3.41642600 |
| H | -2.66466100 | 3.00771200 | -3.46348100 |
| C | -5.87726200 | 2.15584100 | -0.44061800 |
| C | -6.74556500 | 2.08515100 | -1.70608800 |
| H | -6.49329800 | 2.88255000 | -2.41457000 |
| H | -6.61941400 | 1.12407000 | -2.21627400 |
| H | -7.80401400 | 2.20008500 | -1.44456200 |
| C | -5.94998400 | -1.32503900 | 1.08259900 |
| C | -6.65342200 | -2.65358600 | 0.77339300 |
| C | -6.37946100 | -0.74774600 | 2.44116300 |
| H | -6.43703000 | -3.42226200 | 1.52289800 |
| H | -7.73787600 | -2.49452800 | 0.77155200 |
| H | -6.36136700 | -3.03527100 | -0.20970700 |
| H | -7.46668900 | -0.60800700 | 2.46915700 |
| H | -6.11221900 | -1.41926200 | 3.26519800 |
| H | -5.90372000 | 0.22174400 | 2.62725700 |
| C | -3.75307000 | -2.47699700 | 1.74061200 |
| C | -3.39341900 | -3.68936400 | 0.87220900 |
| H | -2.74078400 | -3.41021000 | 0.04073400 |
| H | -2.87393200 | -4.43919400 | 1.48135000 |
| H | -4.28875100 | -4.15941000 | 0.45420100 |
| N | 1.74397600 | 0.17725700 | -0.06743200 |
| H | 1.24949800 | 1.01220500 | 0.23339900 |
| H | -6.24941000 | -0.62452500 | 0.29852500 |
| H | -4.39884800 | 3.64831600 | -1.83121400 |
| H | -4.47292000 | -2.79710200 | 2.50188200 |
| C | -2.53664800 | -1.91089800 | 2.48435700 |
| H | -2.80960200 | -1.03961400 | 3.09079000 |
| H | -2.13309600 | -2.67906300 | 3.15303300 |
| H | -1.73569100 | -1.61810000 | 1.79937000 |
| H | -6.18037300 | 1.34406400 | 0.22446600 |
| C | -6.08065100 | 3.46924100 | 0.33083700 |
| H | -5.47464700 | 3.48676300 | 1.24282600 |
| H | -5.82013500 | 4.34629300 | -0.27206200 |
| H | -7.13398800 | 3.57019300 | 0.61678000 |
| C | 3.13796200 | 0.22269200 | 0.02574800 |
| C | 3.95929800 | -0.84859800 | -0.35671200 |
| C | 3.72294300 | 1.39911300 | 0.52643400 |
| C | 5.34514500 | -0.72230100 | -0.23163700 |
| H | 3.52062000 | -1.76462800 | -0.74782100 |
| C | 5.10644900 | 1.50005700 | 0.63887200 |
| H | 3.09428500 | 2.23439100 | 0.82139700 |
| C | 5.93743800 | 0.44041300 | 0.26219100 |
| H | 7.01376900 | 0.52229800 | 0.34841000 |
| C | 5.71708400 | 2.74567100 | 1.22711200 |
| C | 6.20545300 | -1.88421700 | -0.66994500 |
| F | 6.90991300 | 3.04842400 | 0.66082900 |
| F | 4.91755400 | 3.83270700 | 1.07971000 |
| F | 5.94538400 | 2.61369400 | 2.56278700 |
| F | 7.51771700 | -1.68969500 | -0.38712600 |
| F | 5.83730900 | -3.04018300 | -0.06686100 |
| F | 6.11884300 | -2.09578400 | -2.00770000 |

Structure **11c$_{aryl-H}$**



| | |
|---|---|
| Zero-point correction= | 0.561308 (Hartree/Particle) |
| Thermal correction to Energy= | 0.602892 |
| Thermal correction to Enthalpy= | 0.603836 |
| Thermal correction to Gibbs Free Energy= | 0.478187 |
| Sum of electronic and zero-point Energies= | -2016.068592 |
| Sum of electronic and thermal Energies= | -2016.027008 |
| Sum of electronic and thermal Enthalpies= | -2016.026064 |
| Sum of electronic and thermal Free Energies= | -2016.151713 |

Number of Imaginary Frequencies = 0

E (Single Point Energy) [SMD$_{(DMSO)}$ M06-2X /6-311++G(2df,2p)] = -2016.52083588

0 1

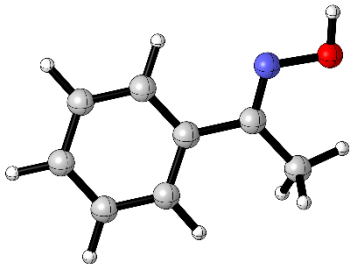
| | | | |
|---|---|---|---|
| C | 1.00512000 | -0.68779200 | -0.33365900 |
| C | -0.41627800 | -0.68636900 | -0.38200800 |
| C | -0.58236700 | -1.94079100 | -1.05907300 |
| C | 0.95676200 | -2.08975600 | -0.99315800 |
| O | 1.75982200 | -2.92146800 | -1.35254000 |
| O | -1.52171100 | -2.59447700 | -1.51535600 |
| N | -1.26284600 | 0.37813800 | -0.08045200 |
| C | -2.59742000 | 0.29593300 | 0.02955200 |
| C | -3.83621200 | 0.87735900 | -0.19873700 |
| C | -3.75001000 | -0.38373200 | 0.41399100 |
| N | -4.37362100 | -1.42775000 | 0.95522100 |
| N | -4.54407100 | 1.89487300 | -0.68535300 |
| C | -3.86782000 | 2.93666500 | -1.51068200 |
| C | -2.90700600 | 3.79219700 | -0.67315400 |
| C | -3.19243200 | 2.32462200 | -2.74456300 |
| H | -2.06438600 | 3.20358700 | -0.29326400 |
| H | -2.48978000 | 4.59721400 | -1.28790400 |
| H | -3.41743200 | 4.24376400 | 0.18332700 |
| H | -2.36489200 | 1.66134000 | -2.47072600 |
| H | -3.90727600 | 1.74731400 | -3.34002400 |
| H | -2.78347100 | 3.12031500 | -3.37686900 |
| C | -6.00055500 | 1.99404600 | -0.40391100 |
| C | -6.83703600 | 1.83157800 | -1.68059000 |
| H | -6.67410200 | 2.65728300 | -2.38251600 |
| H | -6.59740500 | 0.89464300 | -2.19476100 |
| H | -7.90341600 | 1.82211400 | -1.42845700 |
| C | -5.77501200 | -1.72215000 | 0.55071100 |
| C | -5.87406400 | -3.10676300 | -0.10645100 |

| | | | |
|---|---|---|---|
| C | -6.77046800 | -1.54522200 | 1.70566500 |
| H | -5.68065500 | -3.91307000 | 0.60968200 |
| H | -6.88512300 | -3.25487000 | -0.50321200 |
| H | -5.15843000 | -3.19980500 | -0.92911800 |
| H | -7.79299200 | -1.68903300 | 1.33829900 |
| H | -6.60465100 | -2.27731900 | 2.50361800 |
| H | -6.70168500 | -0.54345800 | 2.14488300 |
| C | -3.72333200 | -2.26246500 | 2.01297800 |
| C | -2.49820500 | -3.03693200 | 1.52475700 |
| H | -1.64091000 | -2.37552000 | 1.36997800 |
| H | -2.21361100 | -3.76980800 | 2.28874000 |
| H | -2.68883100 | -3.55958300 | 0.58505800 |
| N | 1.78167800 | 0.26656100 | 0.09236700 |
| H | -6.00843700 | -0.98119300 | -0.22039300 |
| H | -4.67663200 | 3.58555600 | -1.85757400 |
| H | -4.49378600 | -2.98846900 | 2.28529300 |
| C | -3.41036200 | -1.41059600 | 3.25110200 |
| H | -4.30515100 | -0.90459500 | 3.63037100 |
| H | -3.01107500 | -2.04631800 | 4.04918500 |
| H | -2.65099100 | -0.65215000 | 3.02583600 |
| H | -6.21730500 | 1.15023500 | 0.25717800 |
| C | -6.34586800 | 3.27905600 | 0.36217100 |
| H | -5.76074400 | 3.35857900 | 1.28438300 |
| H | -6.16731800 | 4.17710000 | -0.23975300 |
| H | -7.40807800 | 3.27225800 | 0.63113200 |
| C | 3.17265700 | 0.21857700 | 0.07811800 |
| C | 3.97317700 | -0.86312100 | -0.35216900 |
| C | 3.83023200 | 1.37354800 | 0.55187800 |
| C | 5.36628700 | -0.77029700 | -0.30214800 |
| H | 3.50761500 | -1.77047000 | -0.72577900 |
| C | 5.22016800 | 1.45073700 | 0.58944500 |
| H | 3.21893500 | 2.20569400 | 0.88482700 |
| C | 6.01045500 | 0.37823800 | 0.16393600 |
| H | 7.09128800 | 0.43677600 | 0.19327300 |
| C | 5.87447600 | 2.68269600 | 1.15268500 |
| C | 6.18049700 | -1.93507800 | -0.80571800 |
| F | 7.12971600 | 2.87264600 | 0.67361700 |
| F | 5.17324300 | 3.81487900 | 0.87989200 |
| F | 5.98835200 | 2.62770700 | 2.51135600 |
| F | 7.49433300 | -1.83494400 | -0.47466700 |
| F | 5.74141600 | -3.12031700 | -0.31372700 |
| F | 6.13229500 | -2.04073000 | -2.16224500 |
| H | -0.82863600 | 1.29839400 | -0.11791200 |

***Table 27.*** *Single-point energies of all structures calculated at the IEFPCM$_{(DCM)}$ωB97X-D/6-311++G(d,p)/def2-TZV level of theory and thermal correction to Gibbs Free Energy and Gibbs Free Energy calculated at the ωB97X-D/6-31G(d)/def2-TZV level of theory. All energies are reported in Hartrees.*

| Structure | Single-Point Energies (E) IEFPCM$_{(DCM)}$ωB97X-D/6-311++G(d,p)/def2-TZV | Thermal Corrections to Gibbs Free Energies (G) ωB97X-D/6-31G(d)/def2-TZV | Gibbs Free Energies (G) ωB97X-D/6-31G(d)/def2-TZV | Gibbs Free Energies (G) IEFPCM$_{(DCM)}$ωB97X-D/6-311++G(d,p)/def2-TZV//ωB97X-D/6-31G(d)/def2-TZV |
|---|---|---|---|---|
| **12a** | -440.16584496 | 0.122115 | -439.920363 | -440.04373 |
| **6a** | -270.53433179 | 0.096333 | -270.362697 | -270.4379988 |
| **11c** | -2017.01238872 | 0.504297 | -2015.898700 | -2016.508092 |
| **11c•12a** | -2457.20890196 | 0.650746 | -2455.836810 | -2456.558156 |
| **11c$_{cy-H}$•12a** | -2457.20426314 | 0.654273 | -2455.830871 | -2456.54999 |
| **TS1** | -2727.74901860 | 0.767979 | -2726.194263 | -2726.98104 |
| **TS2** | -2727.73670798 | 0.765916 | -2726.180459 | -2726.970792 |

Structure **12a**



| | |
|---|---|
| Zero-point correction= | 0.156963 (Hartree/Particle) |
| Thermal correction to Energy= | 0.165975 |
| Thermal correction to Enthalpy= | 0.166919 |
| Thermal correction to Gibbs Free Energy= | 0.122115 |
| Sum of electronic and zero-point Energies= | -439.885516 |
| Sum of electronic and thermal Energies= | -439.876503 |
| Sum of electronic and thermal Enthalpies= | -439.875559 |
| Sum of electronic and thermal Free Energies= | -439.920363 |

Number of Imaginary Frequencies = 0

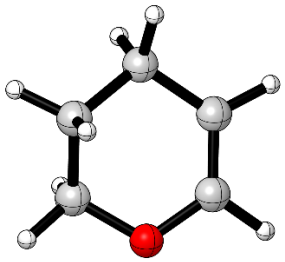
E (Single Point Energy) [IEFPCM$_{(DCM)}$ωB97X-D/6-311++G(d,p)/def2-TZV] = -440.16584496

0 1

| | | | |
|---|---|---|---|
| C | -3.00725200 | -0.20662600 | -0.02542200 |

| | | | |
|---|---|---|---|
| C | -2.19496700 | -1.33169700 | 0.10962100 |
| C | -0.81378800 | -1.20086300 | 0.13154500 |
| C | -0.21403000 | 0.06058500 | 0.01720400 |
| C | -1.03759200 | 1.18249000 | -0.11604700 |
| C | -2.42338400 | 1.04960500 | -0.13893700 |
| H | -4.08809700 | -0.31077600 | -0.03959900 |
| H | -2.64220900 | -2.31699600 | 0.20330300 |
| H | -0.18011100 | -2.07412600 | 0.23979500 |
| H | -0.60196600 | 2.17207200 | -0.21276200 |
| H | -3.04535900 | 1.93330500 | -0.24678900 |
| C | 1.26604900 | 0.20449700 | 0.03116400 |
| C | 1.88525400 | 1.56125500 | 0.22564300 |
| H | 1.38042200 | 2.10053700 | 1.03251000 |
| H | 2.94436300 | 1.47005000 | 0.46330800 |
| H | 1.79058700 | 2.16013600 | -0.68775800 |
| N | 1.93650900 | -0.87517500 | -0.13856900 |
| O | 3.30924700 | -0.67001800 | -0.11850500 |
| H | 3.65109300 | -1.56330800 | -0.24261100 |

Structure **6a**



| | |
|---|---|
| Zero-point correction= | 0.124694 (Hartree/Particle) |
| Thermal correction to Energy= | 0.129848 |
| Thermal correction to Enthalpy= | 0.130792 |
| Thermal correction to Gibbs Free Energy= | 0.096333 |
| Sum of electronic and zero-point Energies= | -270.334335 |
| Sum of electronic and thermal Energies= | -270.329182 |
| Sum of electronic and thermal Enthalpies= | -270.328237 |
| Sum of electronic and thermal Free Energies= | -270.362697 |

Number of Imaginary Frequencies = 0

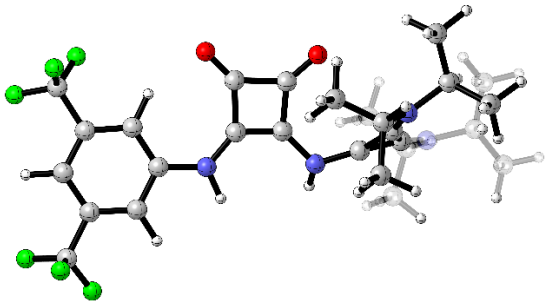
E (Single Point Energy) [IEFPCM$_{(DCM)}$$\omega$B97X-D/6-311++G(d,p)/def2-TZV] = -270.53433179

0 1

| | | | |
|---|---|---|---|
| C | 0.83821600 | -1.05252300 | -0.32247000 |
| C | 1.45283100 | 0.27738400 | 0.12625800 |
| C | 0.40545200 | 1.35727400 | 0.06208100 |
| C | -0.89110000 | 1.07572700 | -0.08166700 |
| C | -0.54760000 | -1.20731600 | 0.29296100 |
| H | 0.74055400 | -1.06980600 | -1.41397200 |
| H | 1.85701000 | 0.18613600 | 1.14418900 |
| H | -0.47480400 | -1.19220900 | 1.39022500 |

| | | | |
|---|---|---|---|
| O | -1.43193500 | -0.16947200 | -0.11491000 |
| H | -1.02836900 | -2.13950500 | -0.01165400 |
| H | 1.46521100 | -1.90224100 | -0.03231600 |
| H | 2.30187300 | 0.53609900 | -0.51765000 |
| H | -1.65848200 | 1.83466200 | -0.19518600 |
| H | 0.70569000 | 2.39936500 | 0.09266900 |

Structure **11c**



| | |
|---|---|
| Zero-point correction= | 0.584726 (Hartree/Particle) |
| Thermal correction to Energy= | 0.625644 |
| Thermal correction to Enthalpy= | 0.626588 |
| Thermal correction to Gibbs Free Energy= | 0.504297 |
| Sum of electronic and zero-point Energies= | -2015.818271 |
| Sum of electronic and thermal Energies= | -2015.777352 |
| Sum of electronic and thermal Enthalpies= | -2015.776408 |
| Sum of electronic and thermal Free Energies= | -2015.898700 |

Number of Imaginary Frequencies = 0

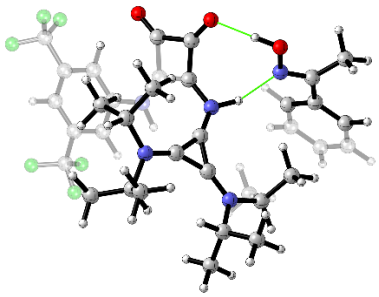
E (Single Point Energy) [IEFPCM$_{(DCM)}$$\omega$B97X-D/6-311++G(d,p)/def2-TZV] = -2017.01238872

1 1

| | | | |
|---|---|---|---|
| C | 0.85281800 | -0.16587000 | -0.31150100 |
| C | -0.51705500 | 0.01747100 | -0.27976100 |
| C | -0.84042200 | -1.22031600 | -0.99150600 |
| C | 0.68050000 | -1.47977700 | -1.07204400 |
| O | 1.40147400 | -2.30525500 | -1.54846900 |
| O | -1.85701600 | -1.77407700 | -1.32977700 |
| N | -1.35089200 | 1.01353200 | 0.21617600 |
| H | -1.13289600 | 1.97051700 | -0.03701800 |
| C | -2.68819100 | 0.70936100 | 0.29432200 |
| C | -3.97715300 | 0.89489800 | -0.14011900 |
| C | -3.65111500 | -0.15900800 | 0.74914800 |
| N | -4.03795200 | -1.21092400 | 1.42793700 |
| N | -4.84984700 | 1.54743900 | -0.87099800 |
| C | -4.35250600 | 2.48873300 | -1.90387800 |
| C | -3.75824200 | 3.73955400 | -1.26092700 |
| C | -3.38725000 | 1.78981100 | -2.85932400 |
| H | -2.87541700 | 3.49542200 | -0.65766500 |
| H | -3.44463600 | 4.44715900 | -2.03336600 |
| H | -4.48462700 | 4.23556600 | -0.61178300 |
| H | -2.45990400 | 1.49507400 | -2.35540300 |

| | | | |
|---|---|---|---|
| H | -3.83912700 | 0.89100600 | -3.28773100 |
| H | -3.11991000 | 2.46604600 | -3.67595600 |
| C | -6.30099400 | 1.28556300 | -0.72536700 |
| C | -6.83063100 | 0.49291300 | -1.91797400 |
| H | -6.75955900 | 1.07028300 | -2.84582100 |
| H | -6.27172500 | -0.43890800 | -2.05194100 |
| H | -7.88494900 | 0.24577400 | -1.76409600 |
| C | -5.33858600 | -1.85000000 | 1.11350900 |
| C | -5.12980400 | -3.30036900 | 0.68188200 |
| C | -6.32849300 | -1.69241400 | 2.26421200 |
| H | -4.76935000 | -3.92545900 | 1.50501700 |
| H | -6.08266500 | -3.71963800 | 0.34639800 |
| H | -4.41409500 | -3.35775600 | -0.14310900 |
| H | -7.29943300 | -2.10510200 | 1.97548500 |
| H | -5.99894600 | -2.22824000 | 3.16021500 |
| H | -6.46486700 | -0.63801800 | 2.52595700 |
| C | -3.17733300 | -1.77332600 | 2.49922400 |
| C | -1.91705400 | -2.43969800 | 1.95636000 |
| H | -1.19722700 | -1.69028400 | 1.61244000 |
| H | -1.43579600 | -3.01029000 | 2.75586300 |
| H | -2.14046100 | -3.11615200 | 1.12862800 |
| N | 1.85227900 | 0.56989600 | 0.19063400 |
| H | 1.57386300 | 1.34763800 | 0.77582200 |
| H | -5.72040900 | -1.30662300 | 0.24488000 |
| H | -5.23710000 | 2.78242000 | -2.47347100 |
| H | -3.79485900 | -2.54115100 | 2.97049200 |
| C | -2.86607700 | -0.70445100 | 3.54379600 |
| H | -3.78344800 | -0.26307500 | 3.94415700 |
| H | -2.30683300 | -1.14800500 | 4.37227300 |
| H | -2.24834100 | 0.09519300 | 3.11830900 |
| H | -6.39018000 | 0.67359300 | 0.17715300 |
| C | -7.07308500 | 2.57961500 | -0.47620100 |
| H | -6.66859500 | 3.12011500 | 0.38433600 |
| H | -7.05854000 | 3.24353300 | -1.34624900 |
| H | -8.11971200 | 2.34022500 | -0.26851900 |
| C | 3.25432900 | 0.39229700 | 0.09025200 |
| C | 3.83547700 | -0.59133800 | -0.70367400 |
| C | 4.05364200 | 1.27321500 | 0.81723000 |
| C | 5.22266100 | -0.68272100 | -0.75303200 |
| H | 3.23079000 | -1.28696400 | -1.27502000 |
| C | 5.43551000 | 1.16592700 | 0.75047900 |
| H | 3.60731100 | 2.04969600 | 1.43186500 |
| C | 6.03312300 | 0.18705700 | -0.03509300 |
| H | 7.11205400 | 0.11125100 | -0.09451300 |
| C | 6.28896600 | 2.08907600 | 1.58619600 |
| C | 5.84128000 | -1.79014000 | -1.57483100 |
| F | 6.51443400 | 1.56423800 | 2.79928300 |
| F | 7.47577300 | 2.31360200 | 1.01328900 |
| F | 5.68636200 | 3.27584500 | 1.77061600 |
| F | 7.10442000 | -1.50455700 | -1.91341200 |
| F | 5.85334600 | -2.94085000 | -0.88717000 |
| F | 5.14820800 | -2.00229800 | -2.70218200 |

Structure **11c·12a**



| | |
|---|---|
| Zero-point correction= | 0.744064 (Hartree/Particle) |
| Thermal correction to Energy= | 0.794992 |
| Thermal correction to Enthalpy= | 0.795936 |
| Thermal correction to Gibbs Free Energy= | 0.650746 |
| Sum of electronic and zero-point Energies= | -2455.743491 |
| Sum of electronic and thermal Energies= | -2455.692564 |
| Sum of electronic and thermal Enthalpies= | -2455.691619 |
| Sum of electronic and thermal Free Energies= | -2455.836810 |

Number of Imaginary Frequencies = 0

E (Single Point Energy) [IEFPCM$_{(DCM)}$$\omega$B97X-D/6-311++G(d,p)/def2-TZV] = -2457.20890196

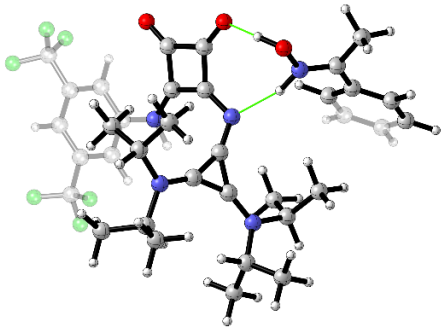
1 1

| | | | |
|---|---|---|---|
| C | -0.84173800 | -1.36139300 | -0.86063100 |
| C | 0.48435800 | -1.29537900 | -1.24539700 |
| C | 0.34870000 | -2.24123200 | -2.34948000 |
| C | -1.16169900 | -2.30120000 | -2.01786300 |
| O | -2.14429100 | -2.79397900 | -2.48583900 |
| O | 1.08396700 | -2.73825800 | -3.16929700 |
| N | 1.58201700 | -0.61750600 | -0.74684700 |
| C | 1.62588100 | 0.72677300 | -0.63866700 |
| C | 2.30065900 | 1.82763700 | -0.15353300 |
| C | 1.14500100 | 1.98771800 | -0.93687500 |
| N | 0.28032800 | 2.80842300 | -1.51450200 |
| N | 3.31746000 | 2.32410800 | 0.51980100 |
| C | 4.21206000 | 1.40069600 | 1.26079400 |
| C | 3.41962300 | 0.51939900 | 2.22037700 |
| C | 5.08869800 | 0.60211200 | 0.29951300 |
| H | 2.77038800 | -0.18300700 | 1.68807700 |
| H | 4.10613500 | -0.08325400 | 2.82065100 |
| H | 2.80886400 | 1.12788300 | 2.89469600 |
| H | 4.48890600 | -0.05523800 | -0.33868700 |
| H | 5.67641500 | 1.26328000 | -0.34296300 |
| H | 5.77399000 | -0.03347900 | 0.86690200 |
| C | 3.58239000 | 3.77949000 | 0.52880300 |
| C | 4.99294600 | 4.09608800 | 0.03482300 |
| H | 5.76286600 | 3.72230400 | 0.71695400 |

| | | | |
|---|---|---|---|
| H | 5.16730700 | 3.66873700 | -0.95682000 |
| H | 5.11612600 | 5.18070900 | -0.03321300 |
| C | 0.33378000 | 4.24892800 | -1.16854600 |
| C | 1.13997500 | 5.03694900 | -2.20099500 |
| C | -1.06330100 | 4.82550700 | -0.94924700 |
| H | 0.63877000 | 5.05304900 | -3.17420900 |
| H | 1.25689800 | 6.07458600 | -1.87452000 |
| H | 2.13653600 | 4.60471800 | -2.34158500 |
| H | -0.97389600 | 5.85892300 | -0.60266900 |
| H | -1.65430100 | 4.84123100 | -1.87012100 |
| H | -1.60972600 | 4.25720100 | -0.19146900 |
| C | -0.53693700 | 2.37529800 | -2.67693900 |
| C | 0.26753400 | 1.49967700 | -3.63464900 |
| H | 0.51694900 | 0.52794400 | -3.19739500 |
| H | -0.32224800 | 1.30688700 | -4.53475500 |
| H | 1.19658400 | 1.99386500 | -3.93431500 |
| N | -1.47164000 | -0.78682700 | 0.17131000 |
| H | -0.87021700 | -0.31648900 | 0.83685700 |
| H | 0.84917900 | 4.29186700 | -0.20435700 |
| H | 4.85620800 | 2.05106900 | 1.85760200 |
| H | -0.76927500 | 3.30253200 | -3.20744400 |
| C | -1.85237300 | 1.73376100 | -2.24629000 |
| H | -2.43018700 | 2.39700300 | -1.59769100 |
| H | -2.45976200 | 1.49896200 | -3.12526100 |
| H | -1.67125800 | 0.80409100 | -1.70510500 |
| H | 2.88430000 | 4.20499200 | -0.19475700 |
| C | 3.28416000 | 4.37574600 | 1.90296400 |
| H | 2.25466100 | 4.16243900 | 2.20785700 |
| H | 3.95780500 | 3.97781300 | 2.66903400 |
| H | 3.41923300 | 5.46091300 | 1.87726300 |
| C | -2.85486300 | -0.68513900 | 0.44551000 |
| C | -3.82822300 | -1.17630200 | -0.41937700 |
| C | -3.22146400 | -0.02392800 | 1.61616200 |
| C | -5.16858500 | -0.99934900 | -0.09220100 |
| H | -3.56060700 | -1.69797900 | -1.33236000 |
| C | -4.56483900 | 0.14331800 | 1.92152200 |
| H | -2.46561300 | 0.36816000 | 2.29052100 |
| C | -5.55098200 | -0.34180100 | 1.07015200 |
| H | -6.59910100 | -0.19976300 | 1.30367300 |
| C | -4.94578200 | 0.81858400 | 3.21664300 |
| C | -6.21581200 | -1.57633000 | -1.01735700 |
| F | -4.03229500 | 1.74187500 | 3.56825000 |
| F | -6.13113000 | 1.42958400 | 3.12289000 |
| F | -5.01996600 | -0.06792200 | 4.21805000 |
| F | -7.40044000 | -0.97455300 | -0.85378100 |
| F | -5.85440800 | -1.43468000 | -2.30101700 |
| F | -6.38539800 | -2.88435200 | -0.78771500 |
| C | 4.56944100 | -2.97006600 | -0.47557400 |
| H | 2.93166800 | -2.57900400 | -2.93299400 |
| O | 3.83325500 | -2.62107000 | -2.55373900 |
| N | 3.60856200 | -2.51786700 | -1.19947600 |
| C | 4.36853200 | -2.89811100 | 0.99245400 |
| C | 5.45675500 | -2.70992100 | 1.85094300 |
| C | 3.09002900 | -3.04996300 | 1.54298600 |
| C | 5.26913600 | -2.65679800 | 3.22880800 |
| H | 6.45814200 | -2.60647900 | 1.44218400 |

| | | | |
|---|---|---|---|
| C | 2.90426500 | -3.00084000 | 2.91959500 |
| H | 2.24960400 | -3.24376500 | 0.88350100 |
| C | 3.99262300 | -2.80230500 | 3.76656800 |
| H | 6.12336400 | -2.51506000 | 3.88348100 |
| H | 1.91153200 | -3.14311400 | 3.33570200 |
| H | 3.84924500 | -2.77955300 | 4.84227600 |
| C | 5.82290700 | -3.55006700 | -1.05918800 |
| H | 5.58073700 | -4.11084800 | -1.96446900 |
| H | 6.51246600 | -2.75026400 | -1.35452500 |
| H | 6.32710900 | -4.20280700 | -0.34478400 |
| H | 2.45925700 | -1.18182800 | -0.75673200 |

Structure **11c$_{cy\text{-}H}$·12a**



| | |
|---|---|
| Zero-point correction= | 0.743861 (Hartree/Particle) |
| Thermal correction to Energy= | 0.794194 |
| Thermal correction to Enthalpy= | 0.795138 |
| Thermal correction to Gibbs Free Energy= | 0.654273 |
| Sum of electronic and zero-point Energies= | -2455.741282 |
| Sum of electronic and thermal Energies= | -2455.690949 |
| Sum of electronic and thermal Enthalpies= | -2455.690005 |
| Sum of electronic and thermal Free Energies= | -2455.830871 |

Number of Imaginary Frequencies = 0

E (Single Point Energy) [IEFPCM$_{(DCM)}$$\omega$B97X-D/6-311++G(d,p)/def2-TZV] = -2457.20426314

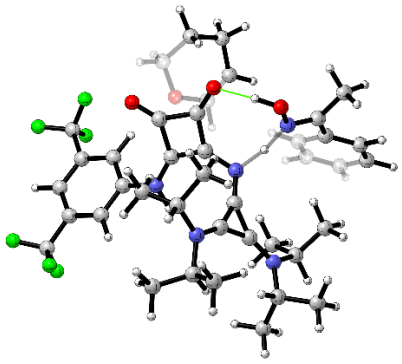
1 1

| | | | |
|---|---|---|---|
| C | 0.47513200 | -1.80571600 | -0.05994000 |
| C | -0.84222800 | -1.75058800 | 0.40792900 |
| C | -0.81783200 | -3.14708200 | 0.83151300 |
| C | 0.62885300 | -3.23728400 | 0.34765800 |
| O | 1.49971000 | -4.06642300 | 0.33675400 |
| O | -1.60914300 | -3.90310800 | 1.37831700 |
| N | -1.81413200 | -0.80596100 | 0.43167600 |
| C | -1.39530700 | 0.44693800 | 0.64465400 |
| C | -1.60301300 | 1.80919000 | 0.48599800 |
| C | -0.51772100 | 1.35203900 | 1.24032300 |
| N | 0.55727300 | 1.63444100 | 1.97291500 |
| N | -2.31257800 | 2.79080000 | -0.04931800 |
| C | -3.34006600 | 2.44716200 | -1.05404500 |
| C | -2.72532600 | 1.67994500 | -2.22324000 |
| C | -4.50669800 | 1.70432200 | -0.40760800 |

| | | | |
|---|---|---|---|
| H | -2.39524800 | 0.68227800 | -1.91166700 |
| H | -3.47066400 | 1.54878800 | -3.01252000 |
| H | -1.87282100 | 2.22500400 | -2.64051200 |
| H | -4.16594800 | 0.75968800 | 0.02908700 |
| H | -4.96387700 | 2.30690700 | 0.38250400 |
| H | -5.26951400 | 1.46999800 | -1.15609900 |
| C | -2.04523000 | 4.19993900 | 0.29546900 |
| C | -3.30376400 | 4.89557700 | 0.81266600 |
| H | -4.06651100 | 4.99919300 | 0.03410900 |
| H | -3.73627200 | 4.34443800 | 1.65280200 |
| H | -3.04997700 | 5.90258000 | 1.15615200 |
| C | 1.03765300 | 3.03459600 | 1.99469100 |
| C | 0.45570000 | 3.81103100 | 3.17782300 |
| C | 2.56247400 | 3.10731300 | 1.94711900 |
| H | 0.85591900 | 3.45082800 | 4.13101000 |
| H | 0.71220800 | 4.87153400 | 3.09489600 |
| H | -0.63540900 | 3.72109100 | 3.21559300 |
| H | 2.87138300 | 4.15478700 | 1.88516000 |
| H | 3.02135100 | 2.68384200 | 2.84599700 |
| H | 2.96002300 | 2.58622400 | 1.07268800 |
| C | 1.03233400 | 0.70338800 | 3.02917800 |
| C | -0.12624300 | -0.04491800 | 3.68487300 |
| H | -0.60574800 | -0.74482900 | 2.99269100 |
| H | 0.25132500 | -0.62785900 | 4.52950700 |
| H | -0.88506900 | 0.64903100 | 4.05971500 |
| N | 1.19852000 | -0.84519900 | -0.66753400 |
| H | 0.69360700 | 0.01161100 | -0.85303400 |
| H | 0.66638000 | 3.47748400 | 1.06460700 |
| H | -3.70602200 | 3.40420900 | -1.43430800 |
| H | 1.46564500 | 1.35873600 | 3.79019100 |
| C | 2.13209200 | -0.24290800 | 2.55218700 |
| H | 2.89683600 | 0.28078400 | 1.97331900 |
| H | 2.61492100 | -0.70874800 | 3.41649100 |
| H | 1.72095100 | -1.04632100 | 1.93728700 |
| H | -1.33201700 | 4.16361300 | 1.12157700 |
| C | -1.39623100 | 4.93925100 | -0.87370000 |
| H | -0.47707700 | 4.43688900 | -1.19262800 |
| H | -2.07021200 | 4.99929800 | -1.73499500 |
| H | -1.14477300 | 5.96255000 | -0.57992000 |
| C | 2.59346900 | -0.74107100 | -0.81691500 |
| C | 3.45650100 | -1.81371400 | -0.60261200 |
| C | 3.10169000 | 0.51112900 | -1.15764000 |
| C | 4.82601600 | -1.60647900 | -0.72282400 |
| H | 3.07292000 | -2.79666300 | -0.34282600 |
| C | 4.47303000 | 0.69410300 | -1.27439700 |
| H | 2.43117100 | 1.35101400 | -1.31772900 |
| C | 5.34919400 | -0.36175300 | -1.05599700 |
| H | 6.41929200 | -0.21841500 | -1.14213600 |
| C | 4.99291200 | 2.04778700 | -1.68555400 |
| C | 5.76177600 | -2.75137100 | -0.41024500 |
| F | 4.23308400 | 3.03519200 | -1.16388700 |
| F | 6.24957100 | 2.24545100 | -1.27784300 |
| F | 4.96419900 | 2.19798000 | -3.01645900 |
| F | 6.93973200 | -2.60628300 | -1.03121800 |
| F | 6.00471500 | -2.81341500 | 0.90861600 |
| F | 5.23952700 | -3.92603900 | -0.78018800 |

| | | | |
|---|---|---|---|
| C | -5.31895300 | -2.31898600 | 0.40706600 |
| H | -2.98071600 | -3.25101500 | 1.95545700 |
| O | -3.86779900 | -2.79849700 | 2.11842500 |
| N | -4.14634300 | -2.20500400 | 0.93318100 |
| C | -5.56738300 | -1.66398100 | -0.88573600 |
| C | -6.83464800 | -1.13560300 | -1.15929600 |
| C | -4.55994000 | -1.59666300 | -1.85678700 |
| C | -7.08356500 | -0.52608700 | -2.38235600 |
| H | -7.62174500 | -1.18712100 | -0.41320900 |
| C | -4.82265200 | -1.00512800 | -3.08523600 |
| H | -3.58482600 | -2.03493300 | -1.66702700 |
| C | -6.07994200 | -0.46511400 | -3.34733200 |
| H | -8.06452500 | -0.11095200 | -2.58772800 |
| H | -4.04834300 | -0.97838400 | -3.84479200 |
| H | -6.28364300 | -0.01009000 | -4.31144300 |
| C | -6.36419400 | -3.10941700 | 1.11950400 |
| H | -5.91169100 | -3.98832700 | 1.58395200 |
| H | -6.79299600 | -2.50814200 | 1.92992800 |
| H | -7.15765500 | -3.40925600 | 0.43557100 |
| H | -3.36675900 | -1.57570700 | 0.58354200 |

Structure **TS1**



| | |
|---|---|
| Zero-point correction= | 0.865773 (Hartree/Particle) |
| Thermal correction to Energy= | 0.922840 |
| Thermal correction to Enthalpy= | 0.923784 |
| Thermal correction to Gibbs Free Energy= | 0.767979 |
| Sum of electronic and zero-point Energies= | -2726.096469 |
| Sum of electronic and thermal Energies= | -2726.039403 |
| Sum of electronic and thermal Enthalpies= | -2726.038458 |
| Sum of electronic and thermal Free Energies= | -2726.194263 |

Number of Imaginary Frequencies = 1

E (Single Point Energy) [IEFPCM$_{(DCM)}$$\omega$B97X-D/6-311++G(d,p)/def2-TZV] = -2727.74901860

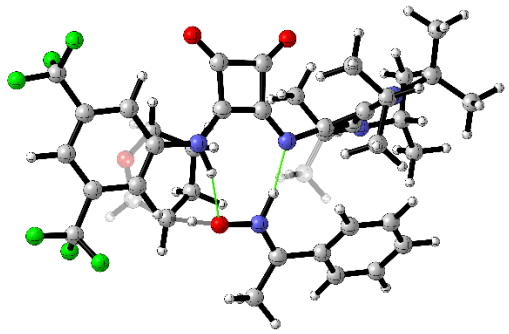
1 1

| | | | |
|---|---|---|---|
| C | 0.65074800 | -0.78205600 | 0.61880000 |
| C | -0.65840900 | -0.78108400 | 1.07254600 |
| C | -0.42121500 | -1.83226900 | 2.05206100 |
| C | 1.06684500 | -1.77924400 | 1.66651500 |

| | | | |
|---|---|---|---|
| O | 2.10255900 | -2.21811300 | 2.08133400 |
| O | -1.10729200 | -2.43494500 | 2.86019400 |
| N | -1.79239900 | -0.09233800 | 0.72272100 |
| C | -1.66819300 | 1.22568500 | 0.54200000 |
| C | -2.17722700 | 2.40859400 | 0.02393500 |
| C | -0.99267400 | 2.41966400 | 0.76689800 |
| N | 0.02225800 | 3.11482300 | 1.28990500 |
| N | -3.11904300 | 3.01971000 | -0.67504500 |
| C | -4.17297300 | 2.20165500 | -1.31453400 |
| C | -3.56692600 | 1.19502500 | -2.28636300 |
| C | -5.07118700 | 1.55049400 | -0.26496800 |
| H | -2.94733700 | 0.45956500 | -1.76340200 |
| H | -4.36131700 | 0.64317000 | -2.79632200 |
| H | -2.95549400 | 1.70131700 | -3.03971600 |
| H | -4.50450300 | 0.85282500 | 0.36015200 |
| H | -5.52536100 | 2.30312000 | 0.38572600 |
| H | -5.86877300 | 0.98556600 | -0.75607500 |
| C | -3.15334500 | 4.49040300 | -0.79261900 |
| C | -4.43228700 | 5.06887300 | -0.18900100 |
| H | -5.32264900 | 4.76578800 | -0.74958800 |
| H | -4.55184600 | 4.75059900 | 0.85102600 |
| H | -4.38757300 | 6.16160100 | -0.21125200 |
| C | 0.15055000 | 4.53458300 | 0.88557000 |
| C | -0.66008800 | 5.45965000 | 1.79775100 |
| C | 1.61225600 | 4.96651000 | 0.78975900 |
| H | -0.21925100 | 5.52489600 | 2.79753700 |
| H | -0.68210200 | 6.47240400 | 1.38372600 |
| H | -1.69233000 | 5.11007900 | 1.90866300 |
| H | 1.65981500 | 5.98726500 | 0.39959400 |
| H | 2.10553600 | 4.96862100 | 1.76663200 |
| H | 2.18472700 | 4.32134400 | 0.11847100 |
| C | 0.65087000 | 2.69872500 | 2.57575000 |
| C | -0.31935400 | 1.92624100 | 3.46648100 |
| H | -0.55668100 | 0.93873400 | 3.06017200 |
| H | 0.13928600 | 1.77091300 | 4.44672600 |
| H | -1.25317300 | 2.47859800 | 3.61119300 |
| N | 1.25646100 | -0.08177800 | -0.34706400 |
| H | 0.70135500 | 0.61742000 | -0.82261700 |
| H | -0.26405800 | 4.57959900 | -0.12707000 |
| H | -4.77679500 | 2.90832600 | -1.88929400 |
| H | 0.86658500 | 3.64156900 | 3.08686800 |
| C | 1.97592100 | 1.96557300 | 2.38795200 |
| H | 2.66039500 | 2.51919100 | 1.74049800 |
| H | 2.46145200 | 1.83638600 | 3.36001000 |
| H | 1.82769900 | 0.97130300 | 1.96305200 |
| H | -2.31581500 | 4.84820400 | -0.19253100 |
| C | -2.92462200 | 4.93091000 | -2.23775500 |
| H | -1.98785600 | 4.52035800 | -2.62727300 |
| H | -3.74001300 | 4.61073700 | -2.89472100 |
| H | -2.87122600 | 6.02226800 | -2.29000800 |
| C | 2.65482300 | -0.03480600 | -0.56753900 |
| C | 3.41844000 | -1.19897900 | -0.55455100 |
| C | 3.24515800 | 1.20030500 | -0.78615200 |
| C | 4.79119200 | -1.09795600 | -0.72064800 |
| H | 2.93430300 | -2.16028700 | -0.43439000 |
| C | 4.62257700 | 1.28180400 | -0.96257700 |

| | | | |
|---|---|---|---|
| H | 2.63692900 | 2.10026600 | -0.78773400 |
| C | 5.40569300 | 0.13755200 | -0.92375100 |
| H | 6.47985200 | 0.20193000 | -1.05249800 |
| C | 5.22092300 | 2.64779900 | -1.17155900 |
| C | 5.65019500 | -2.33741600 | -0.64833000 |
| F | 4.82492000 | 3.17769000 | -2.33966400 |
| F | 4.80763600 | 3.49565200 | -0.20427100 |
| F | 6.55421800 | 2.62972000 | -1.15568400 |
| F | 6.56480500 | -2.34792900 | -1.62829000 |
| F | 6.31000900 | -2.39334400 | 0.51624200 |
| F | 4.91904700 | -3.45674700 | -0.75669500 |
| C | -4.74071500 | -2.10442300 | 0.73324800 |
| H | -2.77733700 | -1.92696800 | 2.93283200 |
| O | -3.72254100 | -1.70085300 | 2.72193900 |
| N | -3.72780400 | -1.61562000 | 1.35781100 |
| C | -4.70425800 | -2.06231500 | -0.74238700 |
| C | -5.88006100 | -1.87799700 | -1.47772400 |
| C | -3.49602700 | -2.28253100 | -1.41378400 |
| C | -5.84297000 | -1.89671600 | -2.86716300 |
| H | -6.82451500 | -1.71891500 | -0.96492400 |
| C | -3.46728400 | -2.31887400 | -2.80274800 |
| H | -2.59161400 | -2.47363600 | -0.84405700 |
| C | -4.63830500 | -2.12382600 | -3.53090600 |
| H | -6.75768300 | -1.75152200 | -3.43265500 |
| H | -2.53226800 | -2.51725000 | -3.31752000 |
| H | -4.61650100 | -2.16234000 | -4.61537000 |
| C | -5.88154900 | -2.72102400 | 1.47636700 |
| H | -5.50400200 | -3.27264600 | 2.34009800 |
| H | -6.54025500 | -1.93531400 | 1.86470200 |
| H | -6.45866100 | -3.38182500 | 0.82910600 |
| C | -0.95008700 | -4.70687400 | -0.58944400 |
| C | -0.61052800 | -5.72235500 | 0.46752300 |
| C | -0.08772700 | -3.76207400 | -0.97009500 |
| H | -1.92116000 | -4.74285300 | -1.07329900 |
| C | 1.68740000 | -4.75996800 | 0.21383300 |
| H | -0.48979900 | -6.71247200 | 0.00830900 |
| H | -1.43861800 | -5.81381700 | 1.17954800 |
| H | -0.31487400 | -2.99887200 | -1.70985800 |
| O | 1.17900800 | -3.62070100 | -0.49740700 |
| C | 0.66956400 | -5.30972300 | 1.20209200 |
| H | 1.96019400 | -5.52048100 | -0.52874100 |
| H | 2.59086000 | -4.40718500 | 0.71232000 |
| H | 1.11074800 | -6.15913900 | 1.73236500 |
| H | 0.44566900 | -4.54527500 | 1.95304700 |
| H | -2.86075400 | -0.84042200 | 0.93013400 |

Structure **TS2**



| | |
|---|---|
| Zero-point correction= | 0.864768 (Hartree/Particle) |
| Thermal correction to Energy= | 0.921704 |
| Thermal correction to Enthalpy= | 0.922648 |
| Thermal correction to Gibbs Free Energy= | 0.765916 |
| Sum of electronic and zero-point Energies= | -2726.081607 |
| Sum of electronic and thermal Energies= | -2726.024671 |
| Sum of electronic and thermal Enthalpies= | -2726.023727 |
| Sum of electronic and thermal Free Energies= | -2726.180459 |

Number of Imaginary Frequencies = 1

E (Single Point Energy) [IEFPCM$_{(DCM)}$$\omega$B97X-D/6-311++G(d,p)/def2-TZV] = -2727.73670798

1 1

| | | | |
|---|---|---|---|
| C | -1.06638300 | -1.49728000 | -0.26163500 |
| C | 0.31305100 | -1.34981100 | -0.11492400 |
| C | 0.45192700 | -2.68975600 | 0.49941400 |
| C | -1.06509900 | -2.85516800 | 0.34128900 |
| O | -1.89031700 | -3.68441000 | 0.64921600 |
| O | 1.38664600 | -3.31212000 | 0.95120500 |
| N | 1.16345200 | -0.32242000 | -0.27714800 |
| C | 2.47199700 | -0.64642400 | -0.13315300 |
| C | 3.66273700 | -0.45924800 | 0.53000800 |
| C | 3.60068600 | -1.30776600 | -0.58464900 |
| N | 4.20176300 | -2.11405500 | -1.43834200 |
| N | 4.33197300 | 0.08497500 | 1.53501600 |
| C | 3.54796000 | 0.62853200 | 2.66324600 |
| C | 2.75210500 | 1.85479100 | 2.22301100 |
| C | 2.66026100 | -0.44805300 | 3.28860500 |
| H | 1.98111800 | 1.56802200 | 1.49835800 |
| H | 2.25587900 | 2.30838800 | 3.08745600 |
| H | 3.40569200 | 2.60051700 | 1.76156900 |
| H | 1.90916100 | -0.80689500 | 2.57662700 |
| H | 3.25095200 | -1.30926500 | 3.61254800 |
| H | 2.14044900 | -0.04145800 | 4.16231200 |
| C | 5.79315000 | -0.08073100 | 1.63436600 |
| C | 6.16454500 | -1.20150400 | 2.60419800 |

| | | | |
|---|---|---|---|
| H | 5.86063000 | -0.95210700 | 3.62671300 |
| H | 5.67764900 | -2.14168600 | 2.32492500 |
| H | 7.24746600 | -1.35855300 | 2.60891600 |
| C | 5.56100700 | -2.61643100 | -1.15578600 |
| C | 5.60149600 | -4.14373600 | -1.14832800 |
| C | 6.58433900 | -1.99595400 | -2.10543600 |
| H | 5.40661500 | -4.56475900 | -2.13979400 |
| H | 6.59539900 | -4.48031400 | -0.83910500 |
| H | 4.86576700 | -4.54681400 | -0.44687500 |
| H | 7.59277000 | -2.33179500 | -1.84611500 |
| H | 6.39701700 | -2.28590200 | -3.14470000 |
| H | 6.55940200 | -0.90234100 | -2.04550800 |
| C | 3.49086700 | -2.53073900 | -2.66794600 |
| C | 2.37435900 | -3.53165800 | -2.38058900 |
| H | 1.53953600 | -3.04514600 | -1.86901300 |
| H | 1.99507300 | -3.94154300 | -3.32153800 |
| H | 2.72167400 | -4.35631200 | -1.75454200 |
| N | -1.95816400 | -0.60861000 | -0.76985300 |
| H | -1.56408800 | 0.28677500 | -1.05350900 |
| H | 5.78338200 | -2.28339500 | -0.13847300 |
| H | 4.28381400 | 0.94396600 | 3.40678100 |
| H | 4.25185900 | -3.02040300 | -3.28150000 |
| C | 2.97738800 | -1.31224200 | -3.43414700 |
| H | 3.78151700 | -0.59186900 | -3.61868500 |
| H | 2.56977600 | -1.62539100 | -4.39955800 |
| H | 2.16977500 | -0.81793400 | -2.88131300 |
| H | 6.11346000 | -0.36018300 | 0.62539400 |
| C | 6.48129500 | 1.24069900 | 1.97465500 |
| H | 6.13804100 | 2.03787800 | 1.30912200 |
| H | 6.29880200 | 1.54777700 | 3.00931600 |
| H | 7.56320800 | 1.12862300 | 1.85774900 |
| C | -3.35207800 | -0.61973100 | -0.70466500 |
| C | -4.08647800 | -1.65771100 | -0.12846700 |
| C | -4.01882800 | 0.50162600 | -1.20889000 |
| C | -5.46788700 | -1.53534900 | -0.02781500 |
| H | -3.58754500 | -2.55341900 | 0.23545700 |
| C | -5.39708900 | 0.60481200 | -1.08190600 |
| H | -3.45482800 | 1.29802200 | -1.68655700 |
| C | -6.13958500 | -0.40766500 | -0.48495400 |
| H | -7.21476800 | -0.32584800 | -0.38853600 |
| C | -6.05909200 | 1.88524200 | -1.51051800 |
| C | -6.22590700 | -2.64081000 | 0.66739100 |
| F | -7.36920100 | 1.74679000 | -1.71244000 |
| F | -5.90494400 | 2.83795000 | -0.55003500 |
| F | -5.51185500 | 2.38610300 | -2.62645700 |
| F | -6.01887900 | -2.58940400 | 1.99549000 |
| F | -7.54681800 | -2.54722000 | 0.46273000 |
| F | -5.82729600 | -3.84702300 | 0.24858000 |
| C | 0.87271700 | 3.34912400 | -0.97123400 |
| H | -1.64820400 | 2.47894300 | 0.30365200 |
| O | -1.10502300 | 2.16072800 | -0.82670600 |
| N | 0.22740700 | 2.24213000 | -0.79636900 |
| C | 2.34411000 | 3.29809100 | -1.00687800 |
| C | 3.08612700 | 4.36172800 | -0.47941000 |
| C | 3.01192700 | 2.20237800 | -1.56681000 |
| C | 4.47462900 | 4.31215600 | -0.48170200 |

| | | | |
|---|---|---|---|
| H | 2.58032600 | 5.22271600 | -0.05284400 |
| C | 4.39988500 | 2.15726800 | -1.56584300 |
| H | 2.44806000 | 1.39946600 | -2.03075500 |
| C | 5.13299300 | 3.20916200 | -1.02274100 |
| H | 5.04385500 | 5.13803500 | -0.06815900 |
| H | 4.90758400 | 1.30605300 | -2.00979600 |
| H | 6.21810500 | 3.18062200 | -1.03811800 |
| C | 0.11762900 | 4.62842000 | -1.11927600 |
| H | -0.87056300 | 4.43138600 | -1.53876900 |
| H | -0.02027500 | 5.09818800 | -0.13745900 |
| H | 0.66550000 | 5.32635300 | -1.75440600 |
| C | -2.10627900 | 2.81941000 | 1.51322500 |
| C | -1.01332800 | 2.35403800 | 2.46201600 |
| C | -3.28911300 | 2.08081300 | 1.50374400 |
| H | -2.25544400 | 3.88945900 | 1.36596400 |
| C | -2.38347900 | 0.27055100 | 2.77548500 |
| H | -1.19010400 | 2.74284100 | 3.47192200 |
| H | -0.04009800 | 2.73576900 | 2.13988400 |
| H | -4.17780900 | 2.41938100 | 0.97516000 |
| O | -3.44881000 | 0.90286500 | 2.00438800 |
| C | -1.00433000 | 0.82422600 | 2.46003900 |
| H | -2.66081300 | 0.42107800 | 3.82171300 |
| H | -2.47639100 | -0.78822100 | 2.53067300 |
| H | -0.30217500 | 0.42543600 | 3.19827900 |
| H | -0.67478700 | 0.46529000 | 1.48129200 |
| H | 0.69915600 | 1.30334900 | -0.62287300 |

## *12.0 Vita*

Ivor Smajlagic was born on February 4, 1994 in Belgrade, Serbia to parents Emir- and Tanya Smajlagic, and shortly after immigrated to Canada, where he was raised in Stoney Creek, Ontario. Here, Ivor completed his secondary school education attending Saltfleet District High School. He then went on to pursue and earn an Honours Bachelor of Science degree in the Biomedical Sciences from Brock University in St. Catharines, Ontario. Following this achievement, Ivor joined Professor Travis Dudding's research group at Brock University initially as a Master's student, wherein he later transitioned to the Doctoral program. Under the mentorship of Professor Dudding, Ivor has successfully contributed to the field of catalysis through his research, and taken his first steps towards being a life-long academic.

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