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Enhancing the Kinetics of Hydrazone Exchange Processes: An Experimental and Computational Study†

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The capacity of hydrazone bonds to readily undergo component exchange processes sees their extensive utilization in dynamic combinatorial chemistry. The kinetics of hydrazone exchange are optimal at ~ pH 4.5 which limits the use of hydrazone-based dynamic combinatorial libraries, particularly for any biological targets that are only stable at near-neutral pH values. It would be advantageous if hydrazone exchange proceeded with faster rates at pH values closer to neutral. We evaluated the kinetics of hydrazone exchange for a selection of hydrazones possessing neighbouring acidic or basic functional groups within the carbonyl-derived moiety of the hydrazone that were postulated to lower transition state energies and thus enhance rates. To help rationalize experimental observations, hydrazone exchange was computationally modelled at the M06-2X/6-31G* level of theory, with three possible mechanistic pathways considered. The pathway where hydrazone exchange proceeds by protonation of the hydrazone nitrogen, followed by hydrazide attack (the rate determining step) was computed to have the lowest free energy barrier and predicted the correct experimentally determined order of reactivity for different hydrazones. The computational studies suggest that substrates possessing moieties with ideal spatial orientations of hydrogen bond acceptor groups can stabilize transition states *via* hydrogen bonding interactions and afford significant rate enhancements in hydrazone exchange. To test the model, further substituents were screened computationally, identifying benzodihydropyran as a rate-enhancing moiety which was verified by subsequent experiments. Taken together, these experimental and computational studies suggest that judiciously placed N- or O-hydrogen bond acceptors within the aldehyde-derived moiety of the hydrazone afford up to 8-fold rate enhancements in hydrazone exchange compared to substrates lacking those features, providing a valuable boost to exchange kinetics at near-neutral pH values. We anticipate these findings will be of interest in dynamic combinatorial chemistry, dynamic covalent polymers/materials, functionalized nanoparticles and interlocked molecules, all of which may benefit from hydrazone exchange processes able to operate near-neutral pH values.

Introduction

The field of dynamic combinatorial chemistry[1] requires chemical bonds that readily undergo component exchange processes. One of the most utilized is the hydrazone bond, (Fig. 1) which has optimal exchange kinetics at pH 4.5, being considerably slower at neutral pH.[1b, 2] The requirement to operate at lower pH limits significantly the scope and application of hydrazone-based dynamic combinatorial libraries as many interesting biological templates are only stable at near neutral pH values, and thus it would be advantageous if hydrazone exchange were able to operate on an experimentally useful timescale at pH values closer to neutral.

Inspired by the work[3] of Jencks in the 1960s, Dawson and co-workers demonstrated[4] that aniline can successfully catalyse exchange processes at neutral pH, and aniline catalysis was applied[5] successfully in a hydrazone-based dynamic combinatorial library for the discovery of inhibitors of glutathione *S*-transferase. The relatively high concentrations of aniline required (100 mM) to enhance the rate of component exchange can limit significantly the wider biocompatibility of the organocatalyst approach, and to this end Kool *et al.* have developed[6] improved catalysts which can provide rate enhancements of up to eight times that of aniline catalysis at lower concentrations of catalyst.

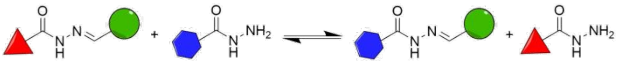

Figure 1. Hydrazones undergo reversible component exchange through transimination processes where a hydrazone reacts with a hydrazide to afford a new hydrazone and hydrazide.

While investigating hydrazone and oxime formation at neutral pH, Kool and co-workers also studied[6a] an alternative approach to

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organocatalysis in which structural modifications of aldehyde components can increase the rate of hydrazone or oxime formation at neutral pH. These structural modifications involve the inclusion of neighbouring acidic or basic functional groups or atoms within the carbonyl-derived moiety of the hydrazone that assist proton transfer within the rate limiting step, thus lowering transition state energies and enhancing the rate of hydrazone formation. We reasoned that these structural modifications may also help increase the rate of hydrazone exchange processes at neutral pH. Thus, in this work, we investigated exchange kinetics for a small pool of hydrazones containing acidic or basic functional groups/atoms and rationalized their observed order of reactivity by computational studies. Our computational model indicates that the rate enhancements likely arise on account of the abilities of neighbouring functional groups/atoms to form stabilizing hydrogen bonds within the transition state. Furthermore, this model correctly identified benzodihydropyran (benzoDHP) as a candidate rate-enhancing group – a prediction that was initially surprising given the absence of any acidic or basic moieties within benzoDHP – which was verified by experiment to be the fastest performing group, demonstrating that useful enhancements in rate can be obtained.

Results and discussion

Experimental hydrazone exchange studies

When considering the application of hydrazone bonds in dynamic combinatorial chemistry, one must take account of several important requirements. It is crucial that equilibria lie very much on the side of product hydrazone, and thus aromatic aldehyde partners are often used as the extended conjugation of the resultant hydrazone ensures product stability, especially important when operating in aqueous solutions. Aliphatic aldehydes, on the other hand, tend to form hydrazones where the equilibrium is less towards the desired hydrazone. Furthermore, acyl hydrazide reaction partners are used to ensure reasonable rates of component exchange as other classes of hydrazides/hydrazines often form hydrazones which undergo component exchange on too slow a timescale to be useful. With these considerations in mind, we focused upon a small pool of hydrazones **1a-f** (Fig. 2) (for synthetic procedures see SI). Hydrazones **1a-c** and **1e-f** contain a basic nitrogen or acidic group either upon or within the aromatic moiety of the carbonyl components which we postulated would likely influence the kinetics of exchange. These specific substrates were chosen based upon the work[6a] of Kool *et al.*, where they displayed relatively high rate enhancements for hydrazone formation and thus are sensible starting points to investigate their influence on hydrazone exchange. Hydrazone **1d** contains no potential rate-enhancing structural features, thus serves as a control.

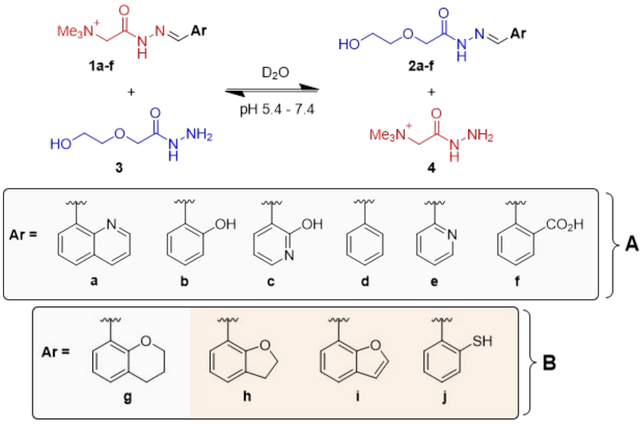

Figure 2. Component exchange of hydrazones **1a-f** with acyl hydrazide **3** to form hydrazones **2a-f** and acyl hydrazide **4**, a process which was studied by ^{1}H NMR spectroscopy. (**A**) Exchange of **1a-f** was studied both experimentally and modelled computationally as a symmetrical exchange process, where $AcNHNH_2$ is both the attacking nucleophile, and hydrazide component of the hydrazone. (**B**) Substrates **h-j** were only studied computationally, and based upon the outcomes of this work, **g** was progressed to experimental study.

Component exchange to form hydrazones **2a**-**f** was accomplished by reaction of hydrazones **1a**-**f** (see SI for characterization) with an excess of acyl hydrazide **3**. Acyl hydrazides **3** and **4** possess hydroxyl and quaternary ammonium groups, respectively, which ensure water solubility of their associated hydrazones. Exchange reactions (see SI for details) were monitored by ^{1}H NMR spectroscopy at room temperature over a range of pH values (5.4-7.4). The mole fraction of each species in solution was determined at each time point from the normalized integrals of diagnostic protons. We found any diagnostic signal could be used as a spectral handle to quantify the rate of component exchange, and for experimental simplicity we chose to utilize those signals associated with the exchange product **4** (Fig. 2). ^{1}H NMR spectroscopic integral analysis afforded kinetics traces (see SI, **Fig S13**) from which the relative rates of hydrazone exchange (Fig. 3) were obtained.

As anticipated, the kinetics of exchange of all examples were faster as the pH decreased. The rates of exchange are 6-7 times faster at the lowest pH investigated (5.4) compared to the highest pH (7.4), observations consistent with component exchange being accelerated by protonation. Component exchange was fastest with hydrazone **1a**, being approximately 8 times faster than control hydrazone **1d** at all pH values investigated, suggesting that the inclusion of a proximal basic nitrogen may catalyse hydrazone exchange. Surprisingly, hydrazones **1b-c** and **1e-f**, all of which possess proximal acid/basic groups, were observed to undergo

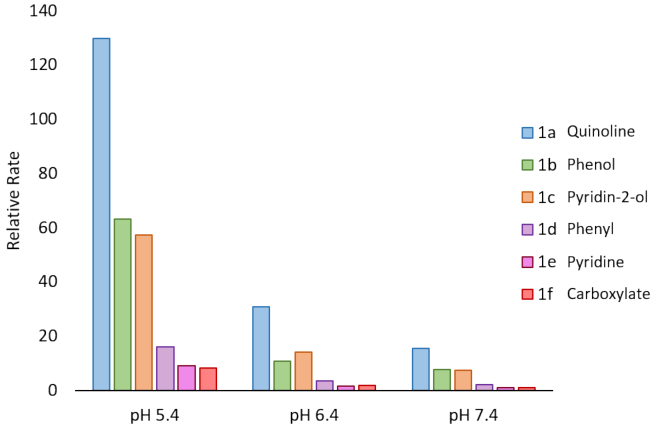

Figure 3: Relative rates of component exchange for hydrazones **1a**-**f**. Rates are presented relative to the slowest exchange process (**1f** at pH 7.4).

slower component exchange processes (at all pH values) than the control hydrazone **1d**. This result was initially surprising, as we had anticipated that the hydrazone containing the most basic group would best catalyse the hydrazone exchange process as it would exhibit the greatest likelihood of being protonated and so be able to transfer a proton in the rate limiting step; the pK_a of the pyridyl nitrogen is estimated to be 5.14[7], which is higher than that of the quinoline (pK_a = 4.85)[7] and the benzoic acid (pK_a = 4.20)[7] suggesting that pyridine **1e** should undergo the fastest hydrazone exchange. Our observed order of reactivity (quinoline > phenol > phenyl > pyridine ≈ carboxylate) does not correlate with the pK_a value of the proximal acid/basic groups, an observation which suggests that the rate enhancement is not caused by protonation of this group.

Computational hydrazone exchange studies

In order to better understand our experimental observations, computational studies were undertaken. To our knowledge, this is the first computational study to explicitly examine the mechanism of hydrazone exchange. Three possible hydrazone exchange mechanisms were considered and studied at the M06-2X/6-31G* level[8] of theory (a level that is expected to produce reasonable agreement with barrier heights). To simplify calculations, the hydrazide employed in modelling the exchange processes was $AcNHNH_2$, which was also used as the hydrazide component within the hydrazone. The overall process modelled was therefore a symmetrical exchange. We considered firstly process (1) (Fig. 4A) in which no protons were added into the system. In the calculated transition state (**P1TS**), proton shuttling between the incoming nucleophile and the hydrazone was required, and a single water molecule can fulfil this role by simultaneously removing a proton from the incoming hydrazine and protonating the hydrazone. This proton shuttling leads to a neutral tetrahedral intermediate (**P1Int**) that would be expected to collapse either to reactants or products through similar barriers. In process (2) (Fig. 4B), groups located within the aldehyde derived moiety of the hydrazone were protonated to give reaction precursors (**P2Prot**) before nucleophilic attack by the hydrazide, a process that proceeds through a similar transition state (**P2TS**) to process (1). This mechanism leads to a protonated intermediate (**P2PI**) that can either rearrange (intramolecular proton transfer) or return a proton to the surrounding environment. The computed energetics (see $\Delta G^{\dagger}$ values in Fig. 4) are those calculated for pH 7, while those for pH 5 (where different) are in brackets. The calculated values reveal that process (2) features a high energy barrier, with $\Delta G^{\dagger}$ values exceeding 30 kcal/mol, indicating that protonation of the functional group/atom within the aldehyde-derived moiety likely impedes the exchange process. We then considered process (3) (Fig. 4C), which represents a specific acid-catalysed reaction in which hydrazone nitrogen (N^1) is protonated prior to nucleophilic attack by the hydrazide. This protonation gives protonated hydrazone (**P3PH**) that is attacked by

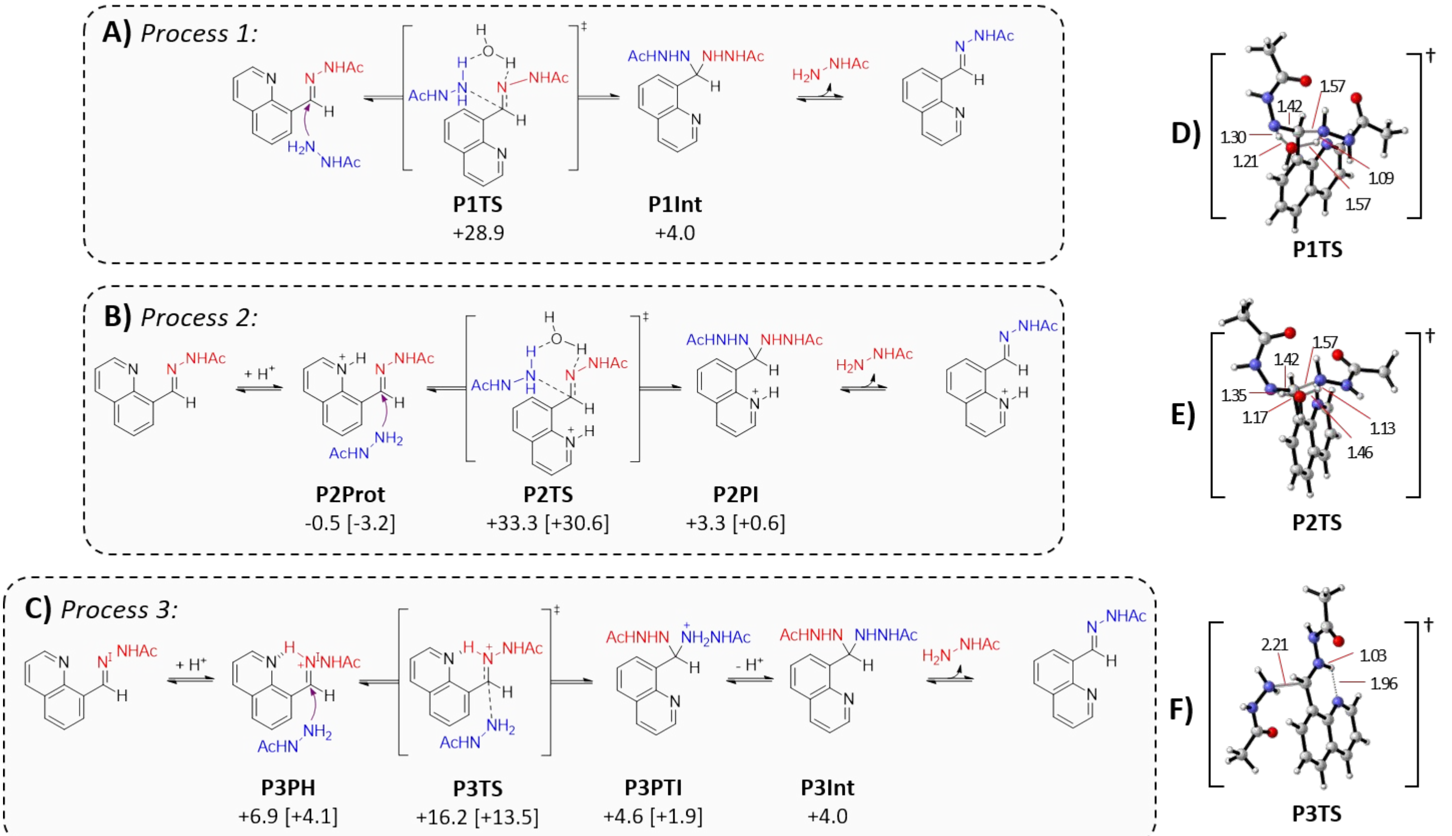

Figure 4: Three mechanisms of hydrazone exchange which were explored computationally. (**A**) Process (1): No protonation of hydrazone prior to hydrazide attack (uncatalysed reaction). (**B**) Process (2): Protonation of proximal acid/base group within aldehyde component of hydrazone. (**C**) Process (3): Protonation of hydrazone nitrogen (N^1) prior to attack. Energetics (kcal/mol) were calculated at pH 7, whilst values for pH 5 are in brackets. Process (3) represents the most likely mechanism for hydrazone exchange, on account of having low energy barriers, relative to Processes (1) and (2). (**D**-**F**) Transition state structures **P1TS**, **P2TS** and **P3TS**, respectively.

hydrazide through transition state **P3TS** to give a protonated tetrahedral intermediate **P3PTI**. For process (3) the calculated free energy barrier (see $\Delta G^{\dagger}$ values) is significantly lower than those obtained for processes (1) and (2), indicating that process (3) constitutes the most likely mechanism for hydrazone exchange. The pathway with the lowest free energy barrier is likely to be the one that is operational but there are significant uncertainties in these comparisons and therefore the ability of each process to explain the relative reactivity of the different hydrazones was also considered.

For process (1), the lowest computed free energy barrier (and therefore fastest reaction) is for carboxylate **1f**† (see SI, Table S19) whilst the highest energy process (and therefore slowest) involves quinoline **1a**, observations that are not consistent with experiment and therefore process (1) was discounted. The energetics calculated for process (2) (SI, Table S20) predict that: (i) the most reactive substrate is control compound **1d** – which is absent of any acid/basic groups to catalyse the reaction; and (ii) the least reactive substrate is **1a** – which was experimentally observed to have the fastest hydrazone exchange kinetics. Process (2) was not consistent with the observed order of reactivity and was discounted. The computed barrier heights for process (3) (SI, Table S21) however, predict an order of reactivity (pH 7.4: **1a** > **1b** > **1d** ≈ **1e** > **1f**; pH 5.4: **1a** ≈ **1b** > **1d** ≈ **1e** > **1f**) that was consistent with the observed relative rates (Fig. 3), further supporting the idea that process (3) constitutes the most likely mechanism of hydrazone exchange.

We then further scrutinized the key species that governs reactivity *via* process (3), the transition state for hydrazide attack (**P3TS**). The origin of the high reactivity of **1a** was revealed in the corresponding transition state structure (Fig. 5A), which features two hydrogen bonds from the quinoline nitrogen to both the incoming hydrazide (N-H distance: 3.18 Å) and the protonated hydrazone (N-H: 1.96 Å), that stabilize the transition state. Crucially, these stabilizing interactions help to lower the energy barrier for hydrazone exchange, thus providing a boost in the exchange kinetics. In the analogous transition states for pyridine **1e** (N-H: 2.93 Å, 2.25 Å) and carboxylate **1f** (O-H: 2.23 Å, 2.21 Å) (Fig. 5B-C) these distances are longer, suggesting that of the two interactions it is the hydrogen bond to the protonated hydrazone that governs reactivity. It has been noted previously[9] that 6-membered ring intramolecular hydrogen bonding interactions (such as those that operate for quinoline **1a**) are slightly favoured over their 5-membered equivalent (as for pyridine **1e**) and much favoured compared to their 7-membered equivalent (carboxylate **1f**). Thus, it is the ideal spatial positioning and orientation of hydrogen bond acceptor atoms/groups within the transition state, rather than simply the presence of acidic or basic moieties, that leads to increased reactivity in hydrazone exchange.

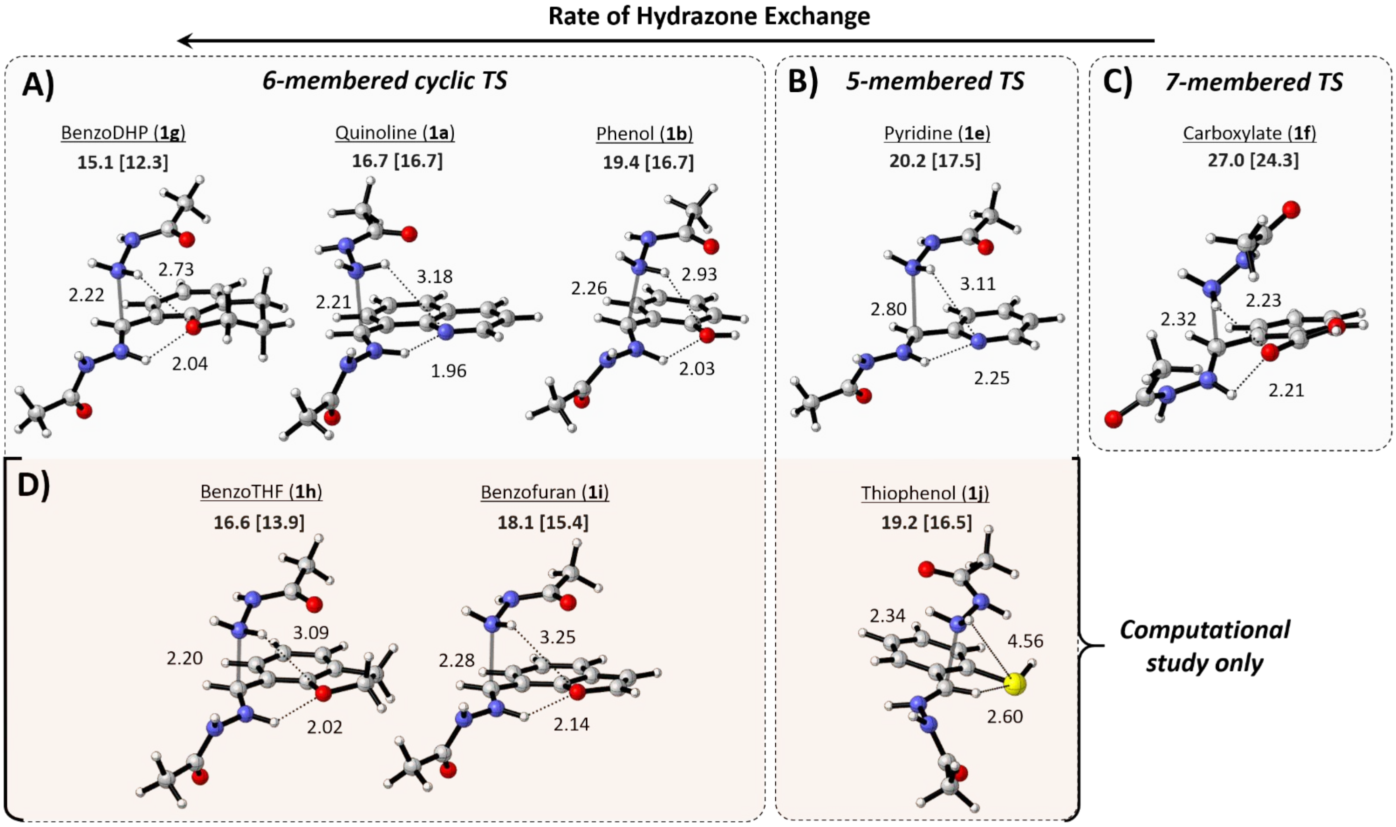

Figure 5: Hydrogen bonding interactions stabilise the transition states for hydrazone exchange. The energy barriers ($\Delta G^{\dagger}$) corresponding to each TS structure were calculated at pH 7.4 and pH 5.4 (brackets). (**A**) 6-membered cyclic TS (benzoDHP **1g**, quinoline **1a**, phenol **1b**) have the lowest energies and exhibit the fastest hydrazone exchange. (**B**) 5-membered cyclic TS (pyridine **1c**, thiophenol **1j**), 7-membered TS (carboxylate **1f**). (**D**) Substrates **1h-j** were only studied computationally.

With this thought in mind, alternative oxygen-containing substrates **1g-i**, and thiophenol **1j** (Fig. 5) were considered computationally as a test of this model, as such substrates contain hydrogen bond acceptors, but lack the suitably acidic/basic groups required to catalyse the reaction *via* intramolecular proton transfer. Amongst these examples, benzoDHP **1g** was predicted to be faster than all the other compounds studied experimentally and was therefore selected for synthesis. The origin of this predicted rate enhancement was clear in the structure of the relevant transition state for **1g** (Fig. 5A). The heterocyclic oxygen atom in this species is positioned in such a way that it can form two stabilizing interactions through a favoured 6-membered ring: one with the protonated hydrazone (2.04 Å, O-H) and a second with the incoming nucleophile (2.73 Å, O-H). Short hydrogen bonding interactions within the transition state indicate stronger stabilizing interactions, the likes of which lower the transition state energy to a greater extent, thus resulting in faster hydrazone exchange. The transition state of benzoDHP **1g** features two such short hydrogen bonds, which are considerably shorter (and therefore presumably stronger) than analogous bond lengths calculated for quinoline **1a** (N-H: 1.96 Å, 3.18 Å) and phenol **1b** (O-H: 2.03 Å, 2.93 Å). This observation suggests that **1g** would offer significantly improved exchange kinetics over quinoline **1a**, an already fast exchanging hydrazone. We then experimentally validated this hypothesis by determining the hydrazone exchange kinetics of benzoDHP **1g** (Fig. 6).

Exchange kinetics of benzoDHP (1g)

Hydrazones **1a**, **1d** and **1g** were exchanged with hydrazide **5** (Fig. 6A) and the kinetics were monitored by ^{1}H NMR spectroscopy and the relative rates of exchange were deduced. It was necessary to study this exchange process with morpholine hydrazide (**5**) instead of glycol hydrazide **3**, as exchange of **1g** with **3** resulted in product precipitation that convoluted the exchange kinetics (see SI, Fig. S14). Gratifyingly, **1g** displayed a 2-fold rate enhancement with respect to quinoline **1a** (Fig. 6B), highlighting the predictive power of our computational model of hydrazone exchange.

Despite mechanistic differences between hydrazone exchange and formation processes, we speculate that the rate-enhancing effects observed for proximal acid/base groups upon hydrazone formation may also arise on account of hydrogen bonding interactions which lower the activation energies (by stabilising the transition states). The ability of those groups to facilitate intramolecular proton transfer, as postulated by Kool *et al.*[6a-d], will also be a contributing factor. Preliminary experiments (SI, Fig. S17) revealed that chroman-8-carbaldehyde (the aldehyde from which benzoDHP **1g** was derived) exhibited rapid hydrazone formation, reacting 5-fold faster than quinoline-8-carbaldehyde, and 13-fold faster than benzaldehyde, which lacks any rate-enhancing features. The intriguing observation that the benzoDHP moiety catalyses rapid hydrazone formation, despite its lack of a significantly acidic or basic group to facilitate intramolecular proton transfer processes, supports our hypothesis that hydrogen-bonding interactions play an important role within the context of organocatalysed hydrazone formation, and probably also the mechanistically similar processes of imine and oxime formation.

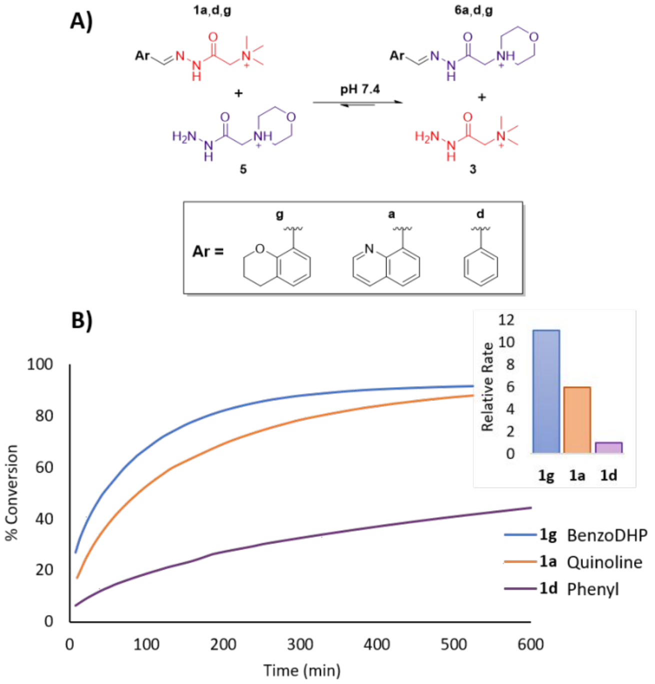

Figure 6: Hydrazone exchange kinetics of **1a**, **1d** and **1g** were studied by ^{1}H NMR spectroscopy. **(A)** Exchange of hydrazones **1a**,**d**,**g** with morpholine hydrazide **5**. (**B**) Kinetic traces of **1a**,**d**,**g** and their relative rates (inset) for hydrazone exchange.

Conclusion

We have demonstrated that the judicial placement of neighbouring hydrogen-bond acceptors within the carbonyl-derived moiety of a hydrazone does lead to enhancements in rates of hydrazone exchange. Computational modelling identified a likely reaction pathway for this process whose energetics were consistent with experimentally determined exchange rates. Modelling supported the hypothesis that the rate-determining step in hydrazone exchange was nucleophilic attack on the protonated hydrazone, which is an important distinction between hydrazone exchange and hydrazone formation, where the rate-limiting step is collapse of the carbinolamine tetrahedral intermediate. Crucially, modelling indicated that the origin of the observed rate enhancements lies in the ability of neighbouring functional groups to form a stabilizing hydrogen bonds within the transition state, and that geometries where 6-membered ring intramolecular hydrogen bonding interactions can be adopted are particularly important. Our confidence in this model was demonstrated by its prediction that a benzoDHP group – containing a very weakly basic but optimally placed oxygen atom that acts as a hydrogen-bond acceptor – displayed fast exchange kinetics, which was gratifyingly supported by experimental observation. Preliminary experiments revealed that chroman-8-carbaldehyde (from which BenzoDHP **1g** was derived) also catalyses rapid hydrazone formation. Surprisingly, chroman-8-carbaldehyde was found to react 5-fold faster than previously reported quinoline-8-carbaldehyde,[6a] despite its lack of an acidic/basic group. These observations suggest that the inclusion of hydrogen-bond acceptor moieties within the aldehyde component may also play an important role in catalysing hydrazone formation, alongside the previously reported[6a-d] catalytic effect of proximal acid/base groups. At neutral pH, benzoDHP **1g** was observed to afford an 8-fold enhancement in the rate of hydrazone exchange, compared to that of control **1d**, and was 16-fold faster than the slowest exchanging hydrazones (**1e**/**1f**). With regards to our own interest in dynamic combinatorial chemistry, our work suggests that valuable gains in rate of exchange can be made that would allow the design of a polymer-scaffolded DCLs operating with reasonable kinetics at near-neutral pH – a crucial requirement for interfacing DCLs with biomacromolecules[10]. Furthermore, given the importance of hydrazone exchange within dynamic covalent polymers[11], materials[12], surfaces[13], molecular machines[14], interlocked molecules[15], cages[16] and functionalized nanoparticles[17], where component exchange processes endow structural adaptivity, we speculate this work will offer insight to the design and optimization of new systems. We also anticipate our work will benefit the development of new organocatalyst for hydrazone/oxime formation and exchange processes, indicating that computational studies, on account of their ability to 'pick winners', might minimise tedious preliminary screenings for catalytic activity.

Conflicts of interest

There are no conflicts of interest.

Acknowledgements

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Notes and references

†Further modelling of **1f** revealed that the carboxylate moiety may ring-close upon the aminal-like intermediate to form a meta-stable 5-membered cyclic structure (Fig. S24), although no evidence of this species was observed during ^{1}H NMR experiments. This meta-stable presented a local minimum on the potential energy surface, making it challenging to reliably compute energetics that were consistent with a single exchange mechanism. Energetics of all other substrates however, were in close agreement with process (3).

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Journal Name

ARTICLE

Supporting Information

Enhancing the Kinetics of Hydrazone Exchange Processes: An Experimental and Computational Study

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General Experimental: All chemicals, including Girard's reagent T (**R1**) were purchased from Sigma-Aldrich or Alfa Aesar and were used as received without further purification. ^{1}H and ^{13}C NMR spectra of synthesised compounds were recorded on a Bruker Avance 300 spectrometer (at 300 and 75 MHz respectively), Bruker Avance 400 spectrometer (at 400 MHz and 100 MHz, respectively), or a Bruker Avance III HD spectrometer (at 500 MHz and 125 MHz, respectively). High-resolution mass spectrometry was performed on a Waters LCT Premier mass spectrometer$^{\alpha}$ or an Agilent 6550 iFunnel Q-TOF LC/MS$^{\beta}$.

Synthetic Procedures:

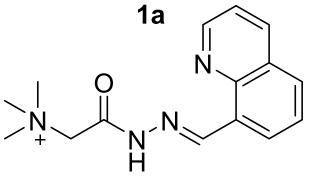
General Procedure for Preparation of Hydrazone Compounds (1a-1g): Aromatic aldehyde (1.00 eqv.) was dissolved in MeOH (2.5 mL) and stirred at rt. Girard's Reagent T (0.9 eqv) was dissolved in MeOH (2.5 mL), then added in one portion to the aldehyde solution. Reactions were judged complete by TLC (7:2 MeOH/2M H_4NCl), evaporated to dryness and the crude residue washed with dichloromethane (7 mL) and sonicated for 5 min. The final products were isolated by filtration and dried for 30 min under high vacuum.

Characterization of Hydrazones 1a-1g:

^{1}H AND ^{13}C NMR spectra of compounds **1a-1g** appear complex on account of *syn*/*anti* isomerization about the C-N amide bond that exhibits hindered rotation, consistent with previous literature reports.[1] The syn/anti ratio was typically in the range 50:50 to 30:70, with the *anti*-isomer being the preferred conformer in most cases.

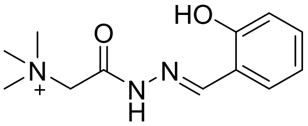
N,N,N-trimethyl-2-oxo-2-(2-(quinolin-8-ylmethylene)hydrazineyl)ethan-1-aminium (**1a**) ^{1}H NMR (D_2O, 400 MHz, ppm) 8.81 + 8.64 (1H, s, Ar-*H*C=N-, *anti* + *syn*), 8.75 + 8.68 (1H, d, Ar, *anti* + *syn*), 8.36 + 8.25 (1H, d, Ar, *anti* + *syn*), 8.10 (1H, d, Ar), 7.96 + 7.87 (1H, d, Ar, *anti* + *syn*), 7.55 (2H, m, Ar), 4.74 + 4.31 (1H, s, -C=N-N-C*H*$_2$-, *syn* + *anti*), 3.43 (9H, s, -N(Me)$_3$). ^{13}C NMR (101 MHz, D_2O) δ 160.91, 150.23, 149.58, 149.30, 147.38, 144.24, 131.94, 131.15, 128.40, 127.05, 126.55, 122.05, 121.87, 63.98, 62.90, 54.49, 54.40. HRMS$^+$ $C_{15}H_{19}N_4O^+$, Theoretical: 271.1559 Actual: 271.1556$^{\beta}$. mp. 159 °C.

1a



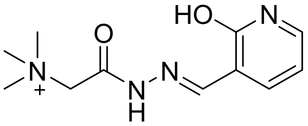
2-(2-(2-hydroxybenzylidene)hydrazineyl)-N,N,N-trimethyl-2-oxoethan-1-aminium (**1b**) ^{1}H NMR (D_2O, 400 MHz, ppm) 8.12 + 7.95 (1H, s, Ar-*H*C=N-, *anti* + *syn*), 7.35 (2H, m, Ar), 6.89 (2H, m, Ar) 4.54 + 4.12 (2H, s, -C=N-N-C*H*$_2$-, *syn* + *anti*), 3.30 + 3.28 ((9H, s, -N(Me)$_3$). ^{13}C NMR (101 MHz, D2O) δ 164.70, 160.08, 156.67, 155.87, 152.76, 148.08, 132.91, 132.53, 131.07, 129.93, 120.64, 120.47, 118.24, 117.48, 116.46, 116.33, 63.88, 62.58, 54.47. HRMS$^+$ $C_{12}H_{18}N_3O_2^+$, Theoretical: 236.1399, Actual: 236.1409.^{β} mp. 206 °C.

1b



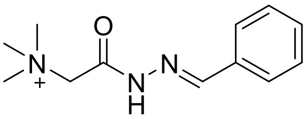
2-(2-((2-hydroxypyridin-3-yl)methylene)hydrazineyl)-N,N,N-trimethyl-2-oxoethan-1-aminium (**1c**) ^{1}H NMR (D_2O, 400 MHz, ppm) 8.35 + 8.10 (1H, s, Ar-*H*C=N-, *anti* + *syn*), 8.25 + 8.20 (1H, d, Ar, *anti* + *syn*) 7.71 + 7.65 (1H, d, Ar, *anti* + *syn*), 6.65 (1H, m, Ar), 4.74 + 4.26 (2H, s, -C*H*$_2$-N(Me)$_3$, *syn* + *anti*) 3.40 (9H, -CH$_2$-N(C*H*$_3$)$_3$. ^{13}C NMR (75 MHz, D2O) δ 165.59, 162.75, 162.70, 160.84, 147.22, 142.60, 141.24, 140.58, 138.26, 137.44, 122.79, 122.24, 108.96, 63.99, 62.82, 54.43, 54.32. HRMS$^+$ $C_{11}H_{17}N_4O_2^+$, Theoretical: 237.1232, Actual: 237.1345.^{β} mp. 159 °C.

1c



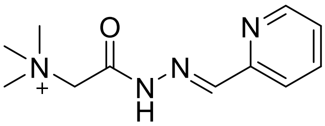
2-(2-benzylidenehydrazineyl)-N,N,N-trimethyl-2-oxoethan-1-aminium (**1d**) ^{1}H NMR (D_2O, 400 MHz, ppm) 8.18 + 7.95 (1H, s, Ar-*H*C=N-, *anti* + *syn*), 7.70 + 7.67 (2H, d, *anti* + *syn*), 7.43 (3H, m, Ar), 4.65 + 4.15 (2H, s, -C=N-N-C*H*$_2$-, *syn* + *anti*), 3.30 + 3.29 (9H, s, -N(Me)$_3$). ^{13}C NMR (101 MHz, D2O) δ 165.61, 160.81, 153.19, 148.32, 133.08, 132.47, 131.74, 131.06, 129.09, 128.99, 127.95, 127.44, 64.06, 62.88, 54.45. HRMS$^+$ $C_{12}H_{18}N_3O^+$, Theoretical: 220.1432, Actual: 220.1450.^{α} mp. 175 °C.

1d



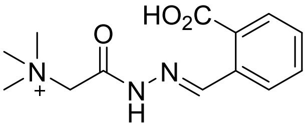
N,N,N-trimethyl-2-oxo-2-(2-(pyridin-2-ylmethylene)hydrazineyl)ethan-1-aminium (**1e**) ^{1}H NMR (D_2O, 400 MHz, ppm) 8.57 (1H, dd, Ar), 8.23 + 8.04 (1H, s, Ar-C*H*=N-N, *anti* + *syn*), 7.95 (2H, m, Ar) 7.51 (1H, dd, Ar), 4.29 (2H, s, -C=N-N-C*H*$_2$-, *anti*), 3.39 (9H, s, -N(Me)$_3$). ^{13}C NMR (101 MHz, D_2O) δ 166.11, 161.38, 150.80, 150.65, 150.60, 149.22, 149.11, 146.17, 138.39, 126.02, 125.63, 122.85, 122.55, 63.87, 62.85, 54.47, 54.34. HRMS$^+$ $C_{11}H_{17}N_4O^+$, Theoretical: 221.1402, Actual: 221.1393.$^\alpha$ mp. 190 °C.

1e



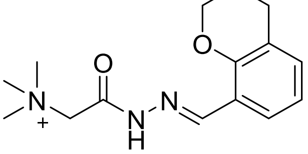
2-(2-(2-carboxybenzylidene)hydrazineyl)-N,N,N-trimethyl-2-oxoethan-1-aminium (**1f**) ^{1}H NMR (D_2O, 400 MHz, ppm) 8.34r + 8.28 (1H, s, br, Ar-HC=N-, *anti* + *syn*), 7.90-7.42 (4H, m, Ar), 4.66 + 4.13 (2H, s, -C=N-N-C*H*$_2$-, *syn* + *anti*), 3.38 + 3.28 (9H, s, -N(Me)$_3$). ^{13}C NMR (101 MHz, D2O) δ 171.26, 161.57, 146.74, 135.37, 133.19, 131.82, 131.07, 130.56, 129.38, 126.67, 63.94, 62.80, 54.33. HRMS$^+$ $C_{13}H_{18}N_3O_3{}^+$, Theoretical: 264.1348, Actual: 264.1355.$^\beta$ mp. 162 °C.

1f



2-(2-(chroman-8-ylmethylene)hydrazineyl)-N,N,N-trimethyl-2-oxoethan-1-aminium (**1g**) ^{1}H NMR (D_2O, 300 MHz, ppm) 8.48 + 8.21 (1H, s Ar-HC=N-, *anti* + *syn*), 7.64 (1H, d, Ar), 7.23 (1H, d, Ar), 6.94 (1H, dd, Ar), 4.67 + 4.21 (2H, s, -C*H*$_2$-N(Me)$_3$, *syn* + *anti*), 4.24 (2H, t, -OC*H*$_2$-), 2.77 (2H, t, -OCH$_2$-CH$_2$-C*H*$_2$-), 1.98 (2H, t, -OCH$_2$-C*H*$_2$-CH$_2$-). ^{13}C NMR (75 MHz, D2O) δ 165.28, 160.41, 153.99, 153.54, 148.98, 144.14, 133.58, 132.86, 124.62, 124.20, 120.48, 120.38, 119.87, 67.23, 64.06, 62.82, 54.41, 54.33, 24.05, 21.41, 21.34. HRMS$^+$ $C_{15}H_{22}N_3O_2{}^+$, Theoretical: 276.1721, Actual: 276.1712.$^\beta$ mp. 173 °C.

1g



^{1}H NMR Spectra:

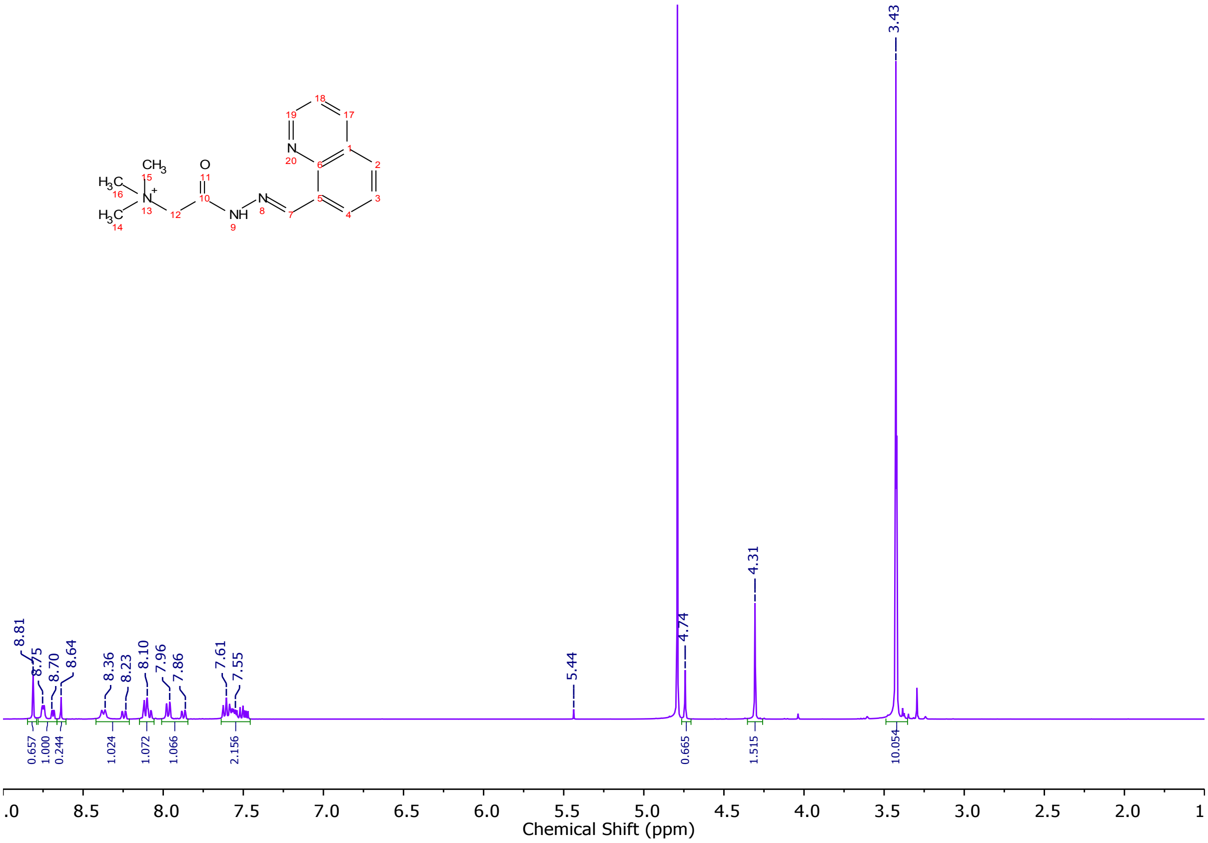


Figure S1: ^{1}H NMR spectrum (400 MHz, D_2O) of **1a**

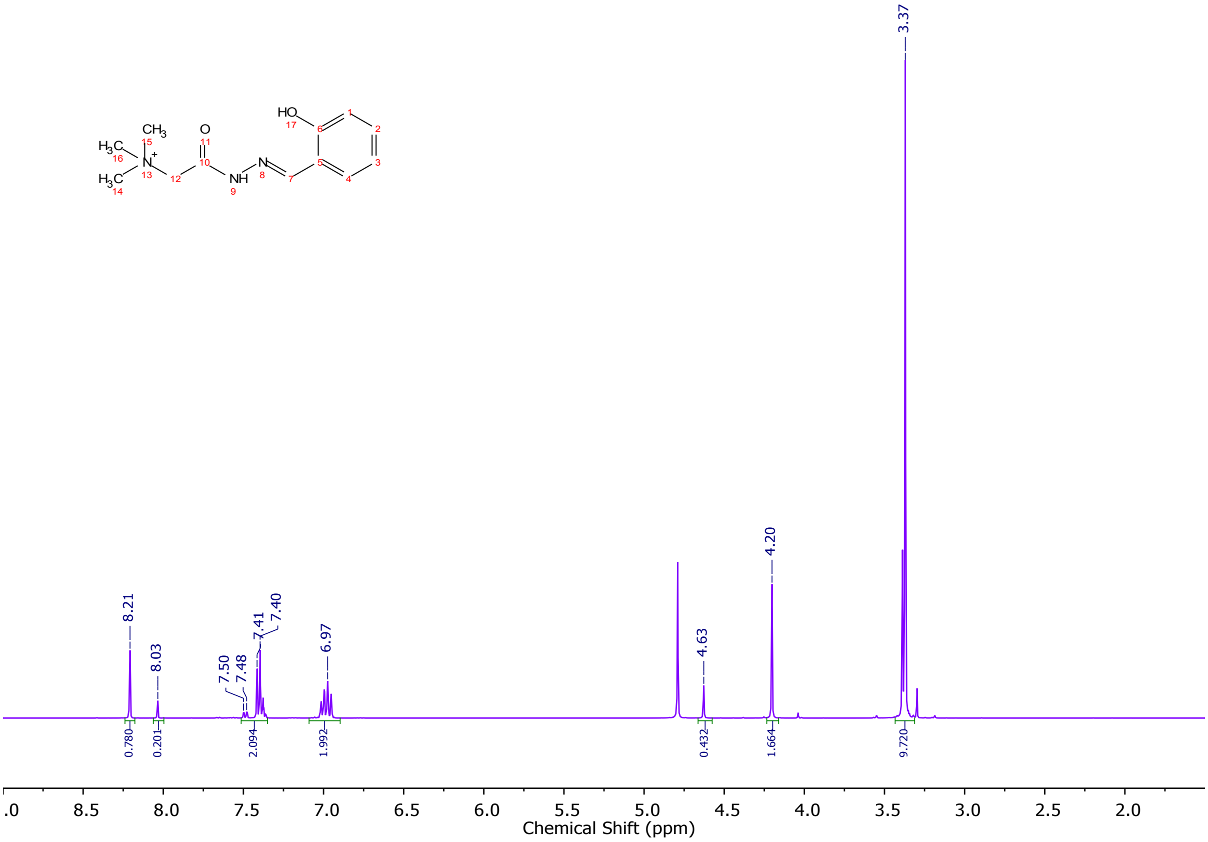


Figure S2: ^{1}H NMR spectrum (400 MHz, D_2O) of **1b**

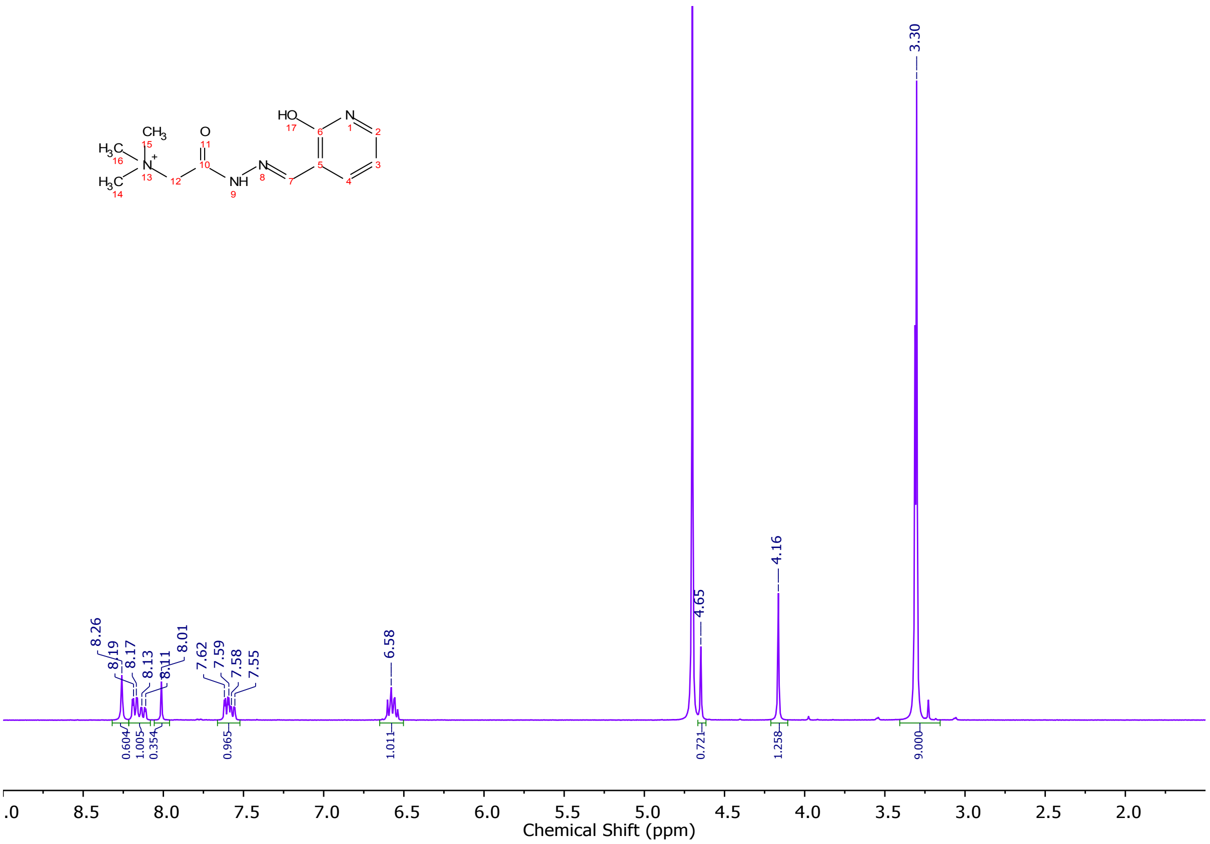


Figure S3: ^{1}H NMR spectrum (300 MHz, D_2O) of **1c**

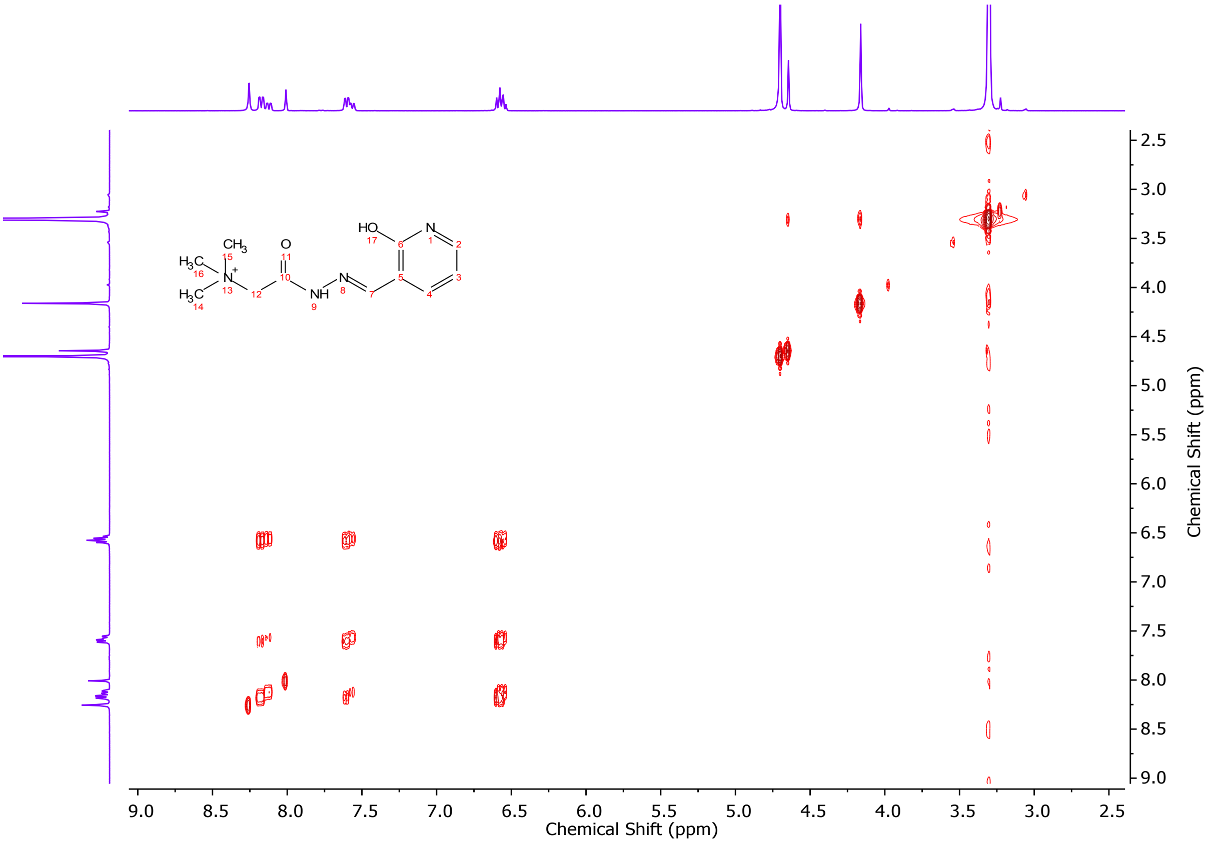


Figure S4: COSY NMR spectrum (300 MHz, D_2O) of **1c**

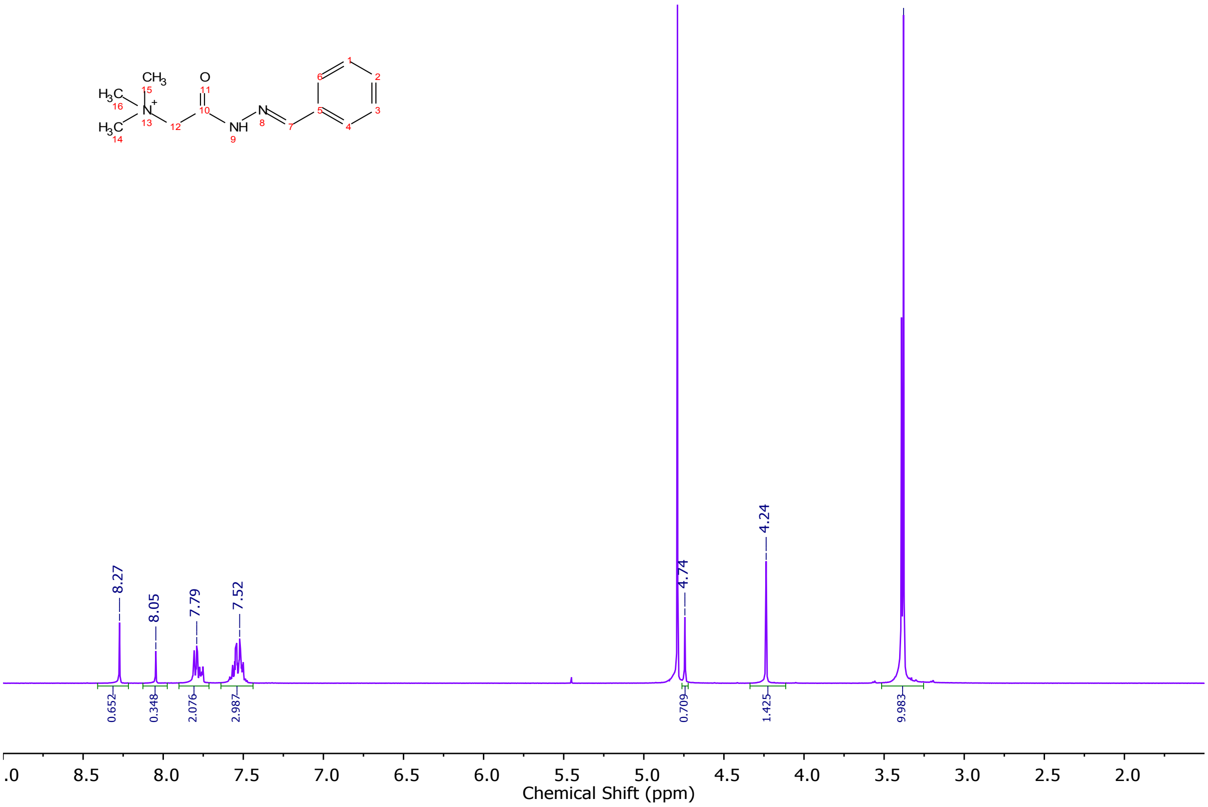


Figure S5: ^{1}H NMR spectrum (400 MHz, D_2O) of **1d**

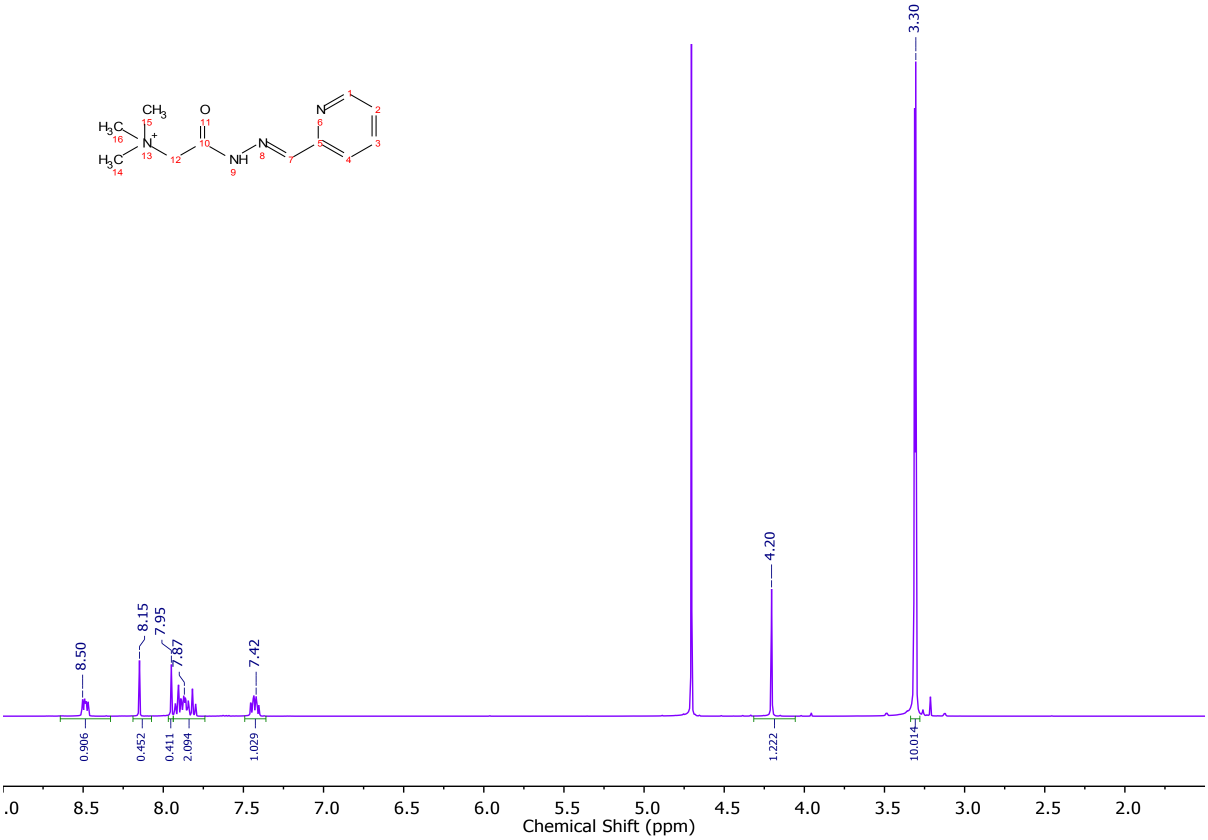


Figure S6: ^{1}H NMR spectrum (400 MHz, D_2O) of **1e**

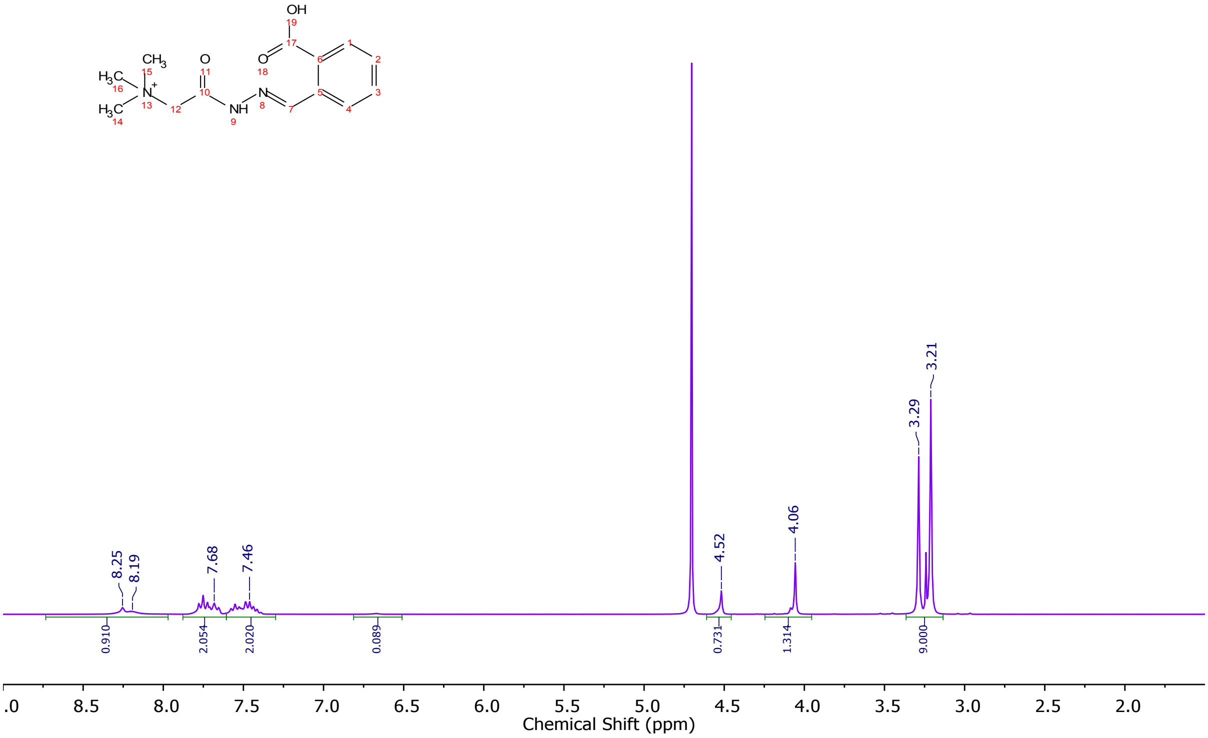


Figure S7: ^{1}H NMR spectrum (300 MHz, D_2O) of **1f**

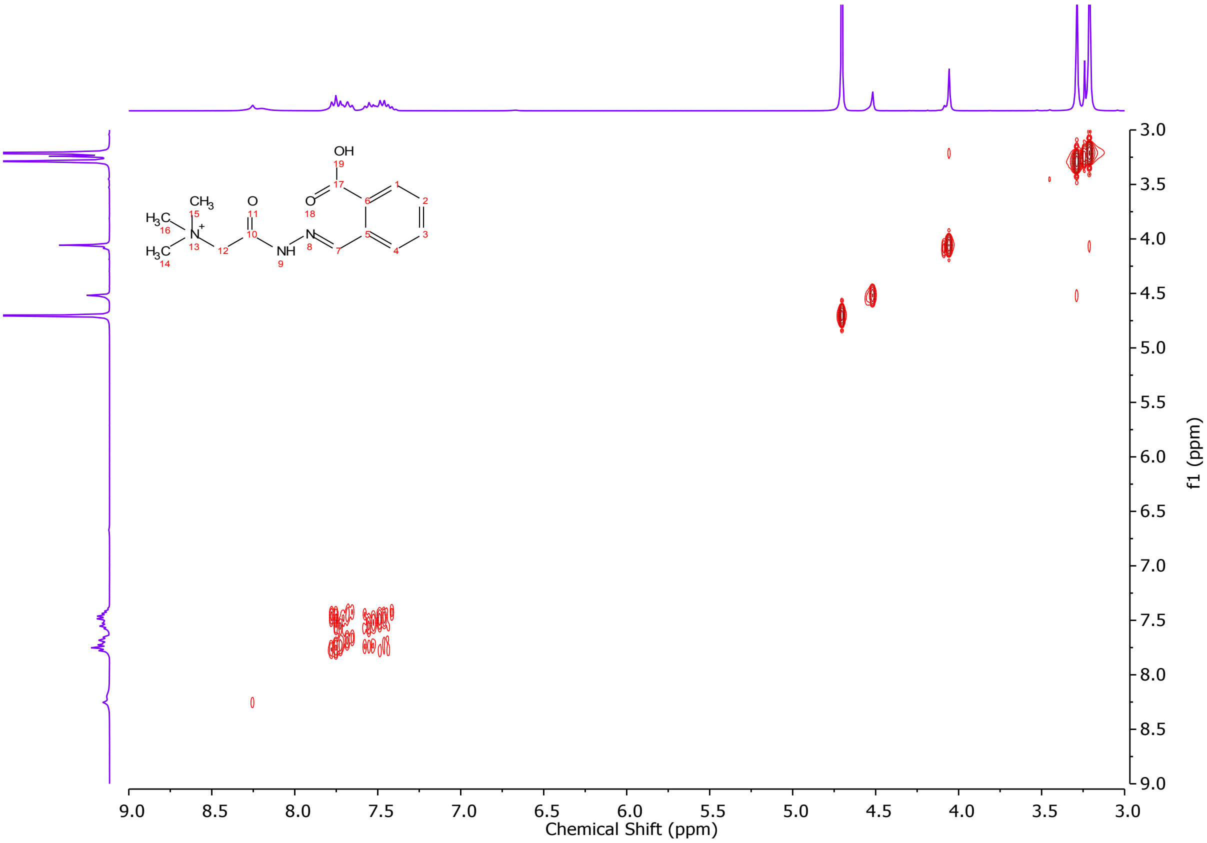


Figure S8: COSY NMR spectrum (300 MHz, D_2O) of **1f**

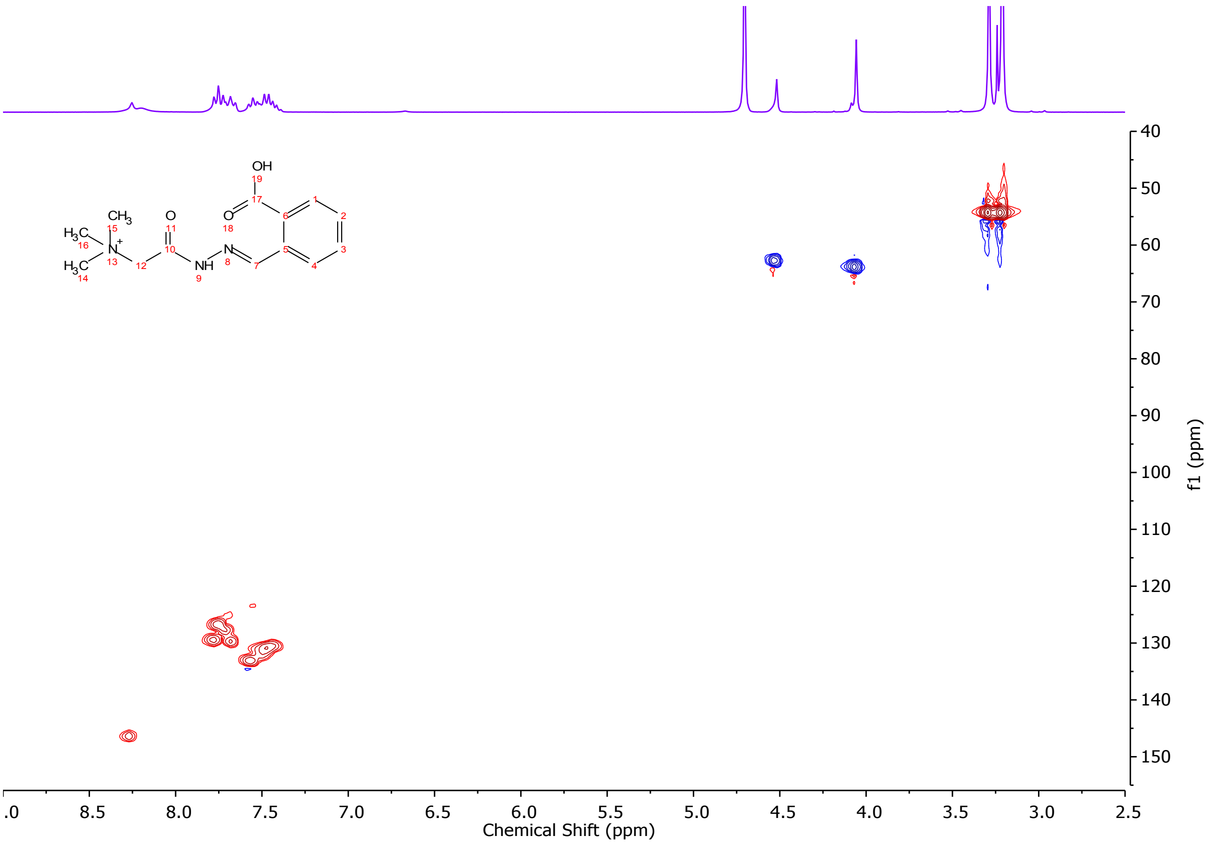


Figure S9: HSQC NMR spectrum (300 MHz ^{1}H, 75 MHz ^{13}C, D$_2$O) of **1f**

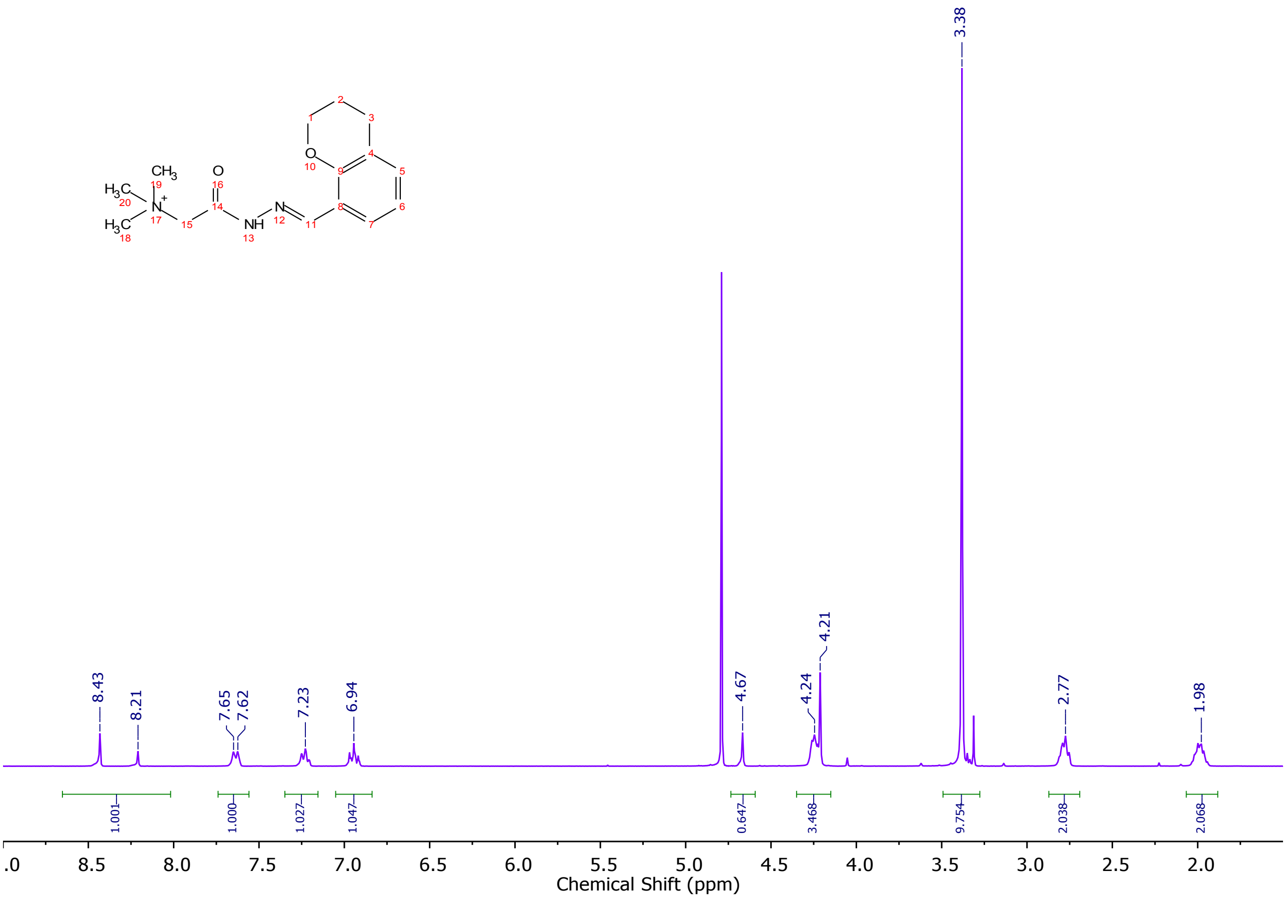


Figure S10: ^{1}H NMR spectrum (300 MHz, D_2O) of **1g**

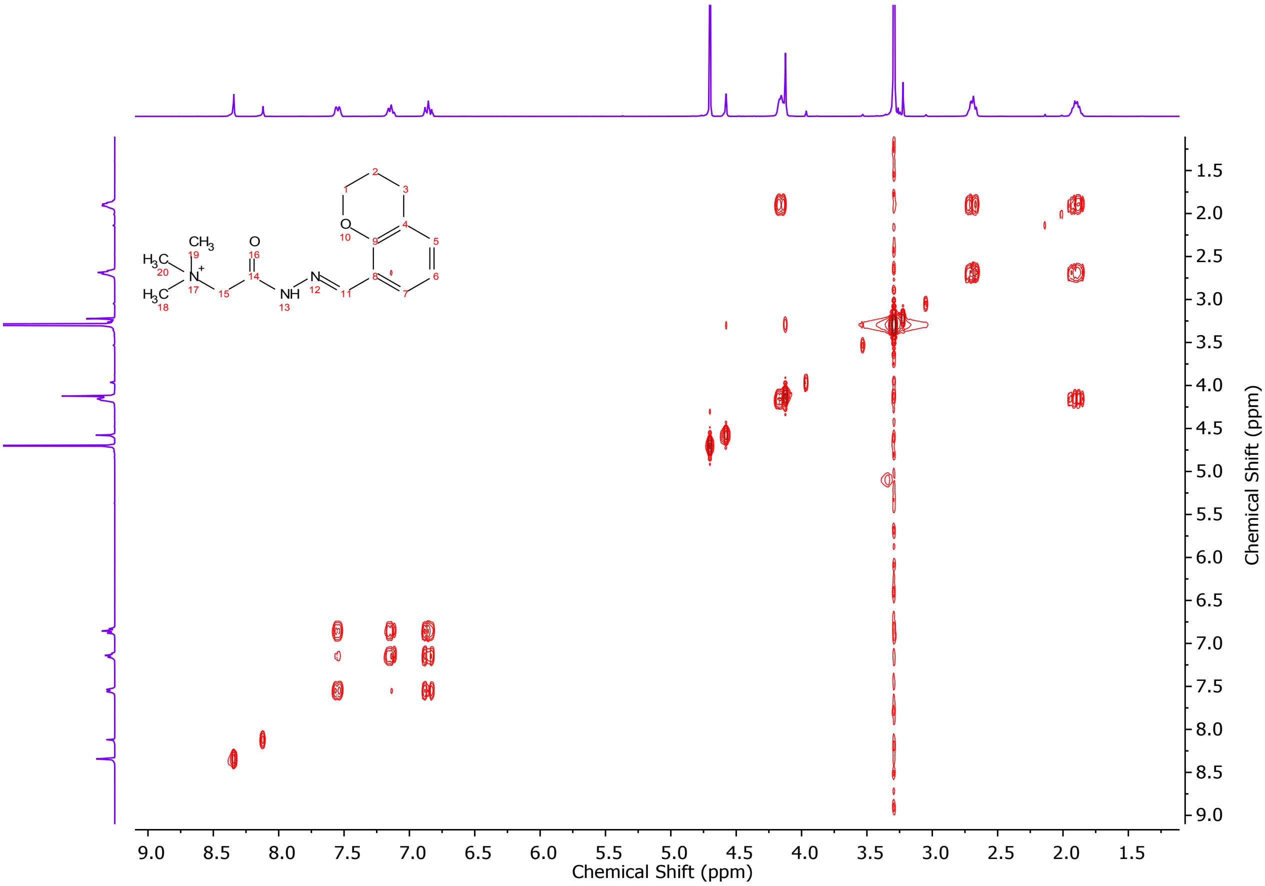
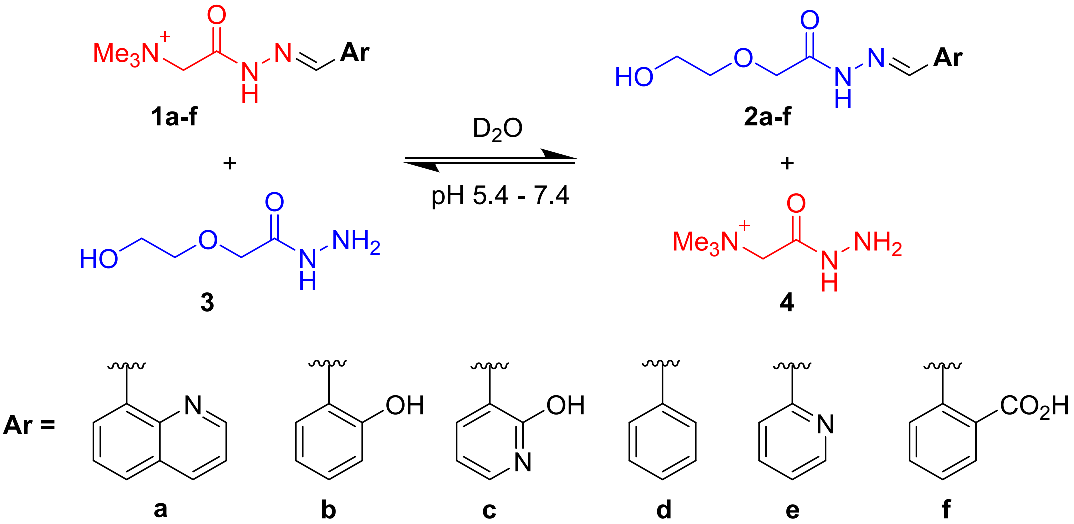


Figure S11: COSY NMR spectrum (300 MHz, D_2O) of **1g**

Kinetics Studies

Exchange Kinetics Procedure: Hydrazones **1a-1g** (23.4 mM) were dissolved in 500 µL deuterated buffer solution (pD = 5.8-7.8), and hydrazide residue **3**, **5** (117 mM, 5.0 eqv., dissolved in 500 µL buffer) was added, and solution mixed thoroughly by rapidly pipetting up and down 10 times. The sample was loaded into the NMR spectrometer to monitor the exchange kinetics over a minimum of 16 h at 25 °C. The kinetics traces were corrected for the time delay between initial mixing of reagents, and the time at which the first spectrum was acquired.

Study 1: Hydrazones **1a-f** (23.4 mM) were exchanged with hydrazide **3** (117 mM) in buffered D_2O at pD 7.8 (, pD 6.8 and pD 5.8. See **S13** for kinetics traces.



Scheme S12: Hydrazones **1a-f** undergoing component exchange with hydrazide **3** to afford product hydrazones **2a-f**.

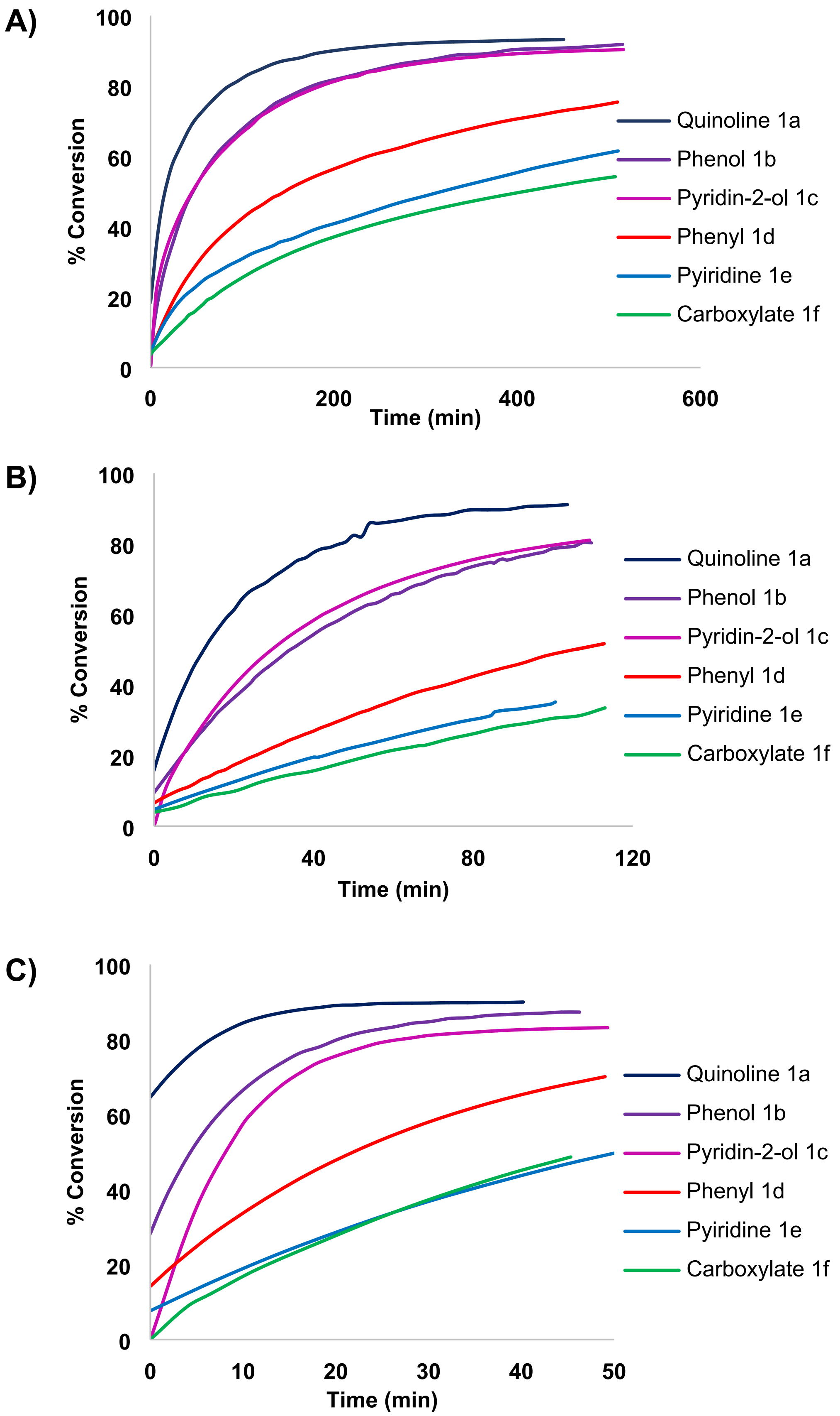


Figure S13: Kinetics traces of hydrazones **1a-1f** reacting with hydrazide **3** at pD 7.8 (**A**), pD 6.8 (**B**) and pD 5.4 (**C**).

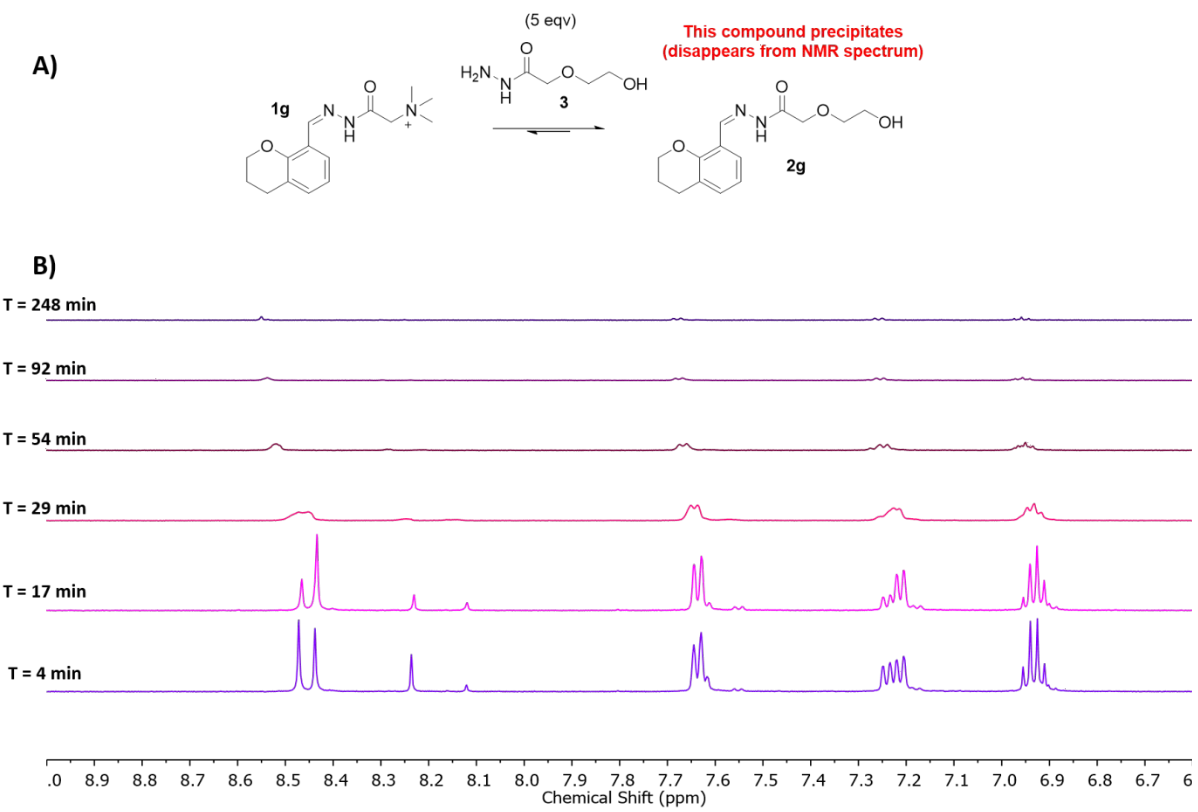
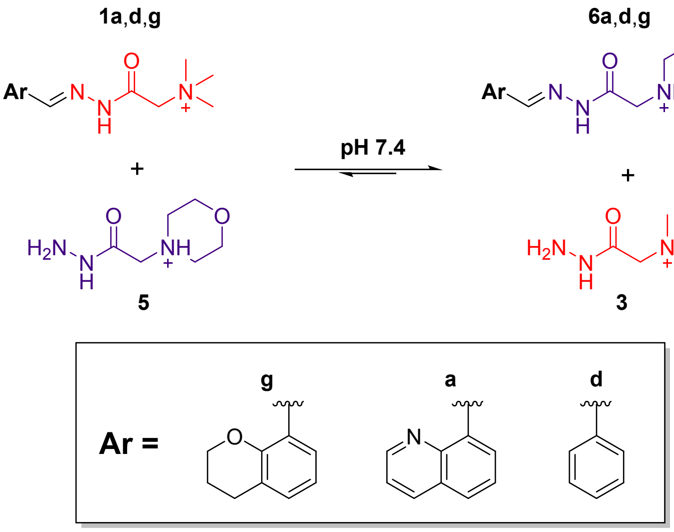


Figure S14: Hydrazone exchange of **1g** with hydrazide **3** (**A**) resulted in precipitation of the product hydrazone (**2g**), which led to signal broadening in the ^{1}H NMR spectra. (**B**). Convolution of the NMR spectra ultimately prevented accurate monitoring of the hydrazone exchange kinetics, thus an alternative exchange process was investigated (see **S15** and **S16**).

Study 2: Hydrazones **1a**, **1d**, and **1f** (23.4 mM) were exchanged with hydrazide **4** (117 mM) in buffered D_2O at pD 7.8. See **Fig. S16** for kinetics traces.



Scheme S15: Hydrazones **1a**,**d**,**g** undergoing component exchange with hydrazide **5** to afford product hydrazones **6a**,**d**,**g**.

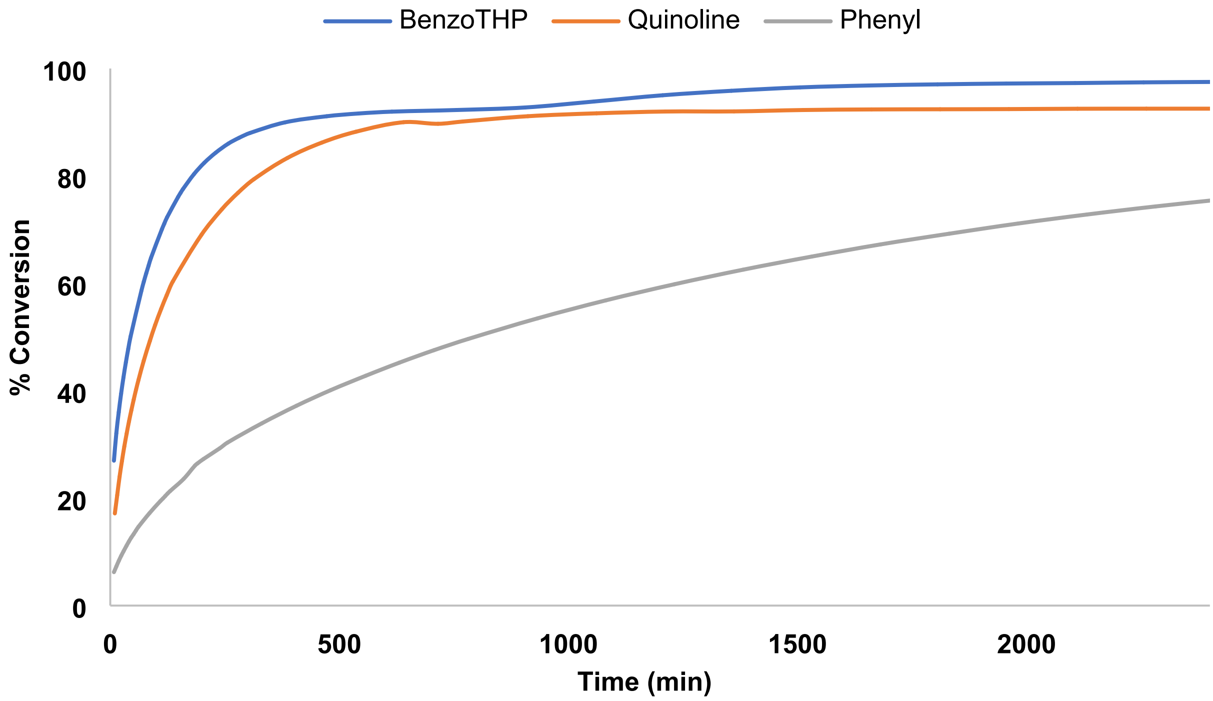


Figure S16: Kinetics traces of BenzoDHP **1g**, Quinoline **1a** and Phenyl **1d** reacting with hydrazide **5** at pD 7.8.

Study 3: Hydrazone formation kinetics of aldehydes **6**-**8** with Girard's Reagent T was studied by ^{1}H NMR spectroscopy. Hydrazone formation was observed to be significantly faster than hydrazone exchange under similar conditions.

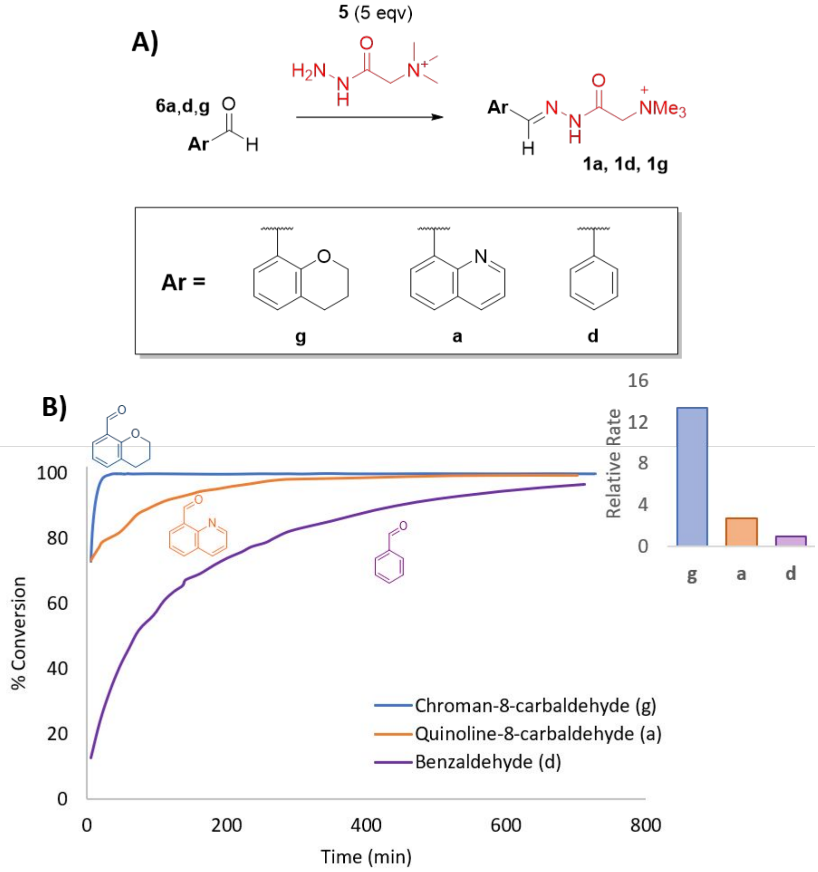


Figure S17: (**A**) Hydrazone formation of aromatic aldehydes **a**,**d**,**g** with Girard's Reagent T (**5**). 1H NMR monitored the reaction kinetics at pD 7.8. (**B**) Kinetics traces of hydrazone formation of aldehydes **a**,**d**,**g**. Inset shows the relative rates of hydrazone formation.

Computational Studies

Hydrazone Exchange Studies: In order to gain insights to our experimental observations, computational studies were undertaken. Reaction mechanisms were studied at the M06-2X/6-31G* level of theory. To simplify the calculations, the hydrazide employed in modelling the exchange processes was $AcNHNH_2$, which was also used as the hydrazide component within the hydrazone. The process modelled is therefore a symmetrical exchange but provided the mechanistic insight required. Protonation free energies were computed using H_3O^+ as the proton source and corrected by adding the difference between the computed and experimental values of K_w. Corrections to 1 M concentrations were applied using an ideal gas approximation. Concentrations of H^+ and ^-OH that are appropriate to the pH were applied and water was assumed to be present at 55.5 M.

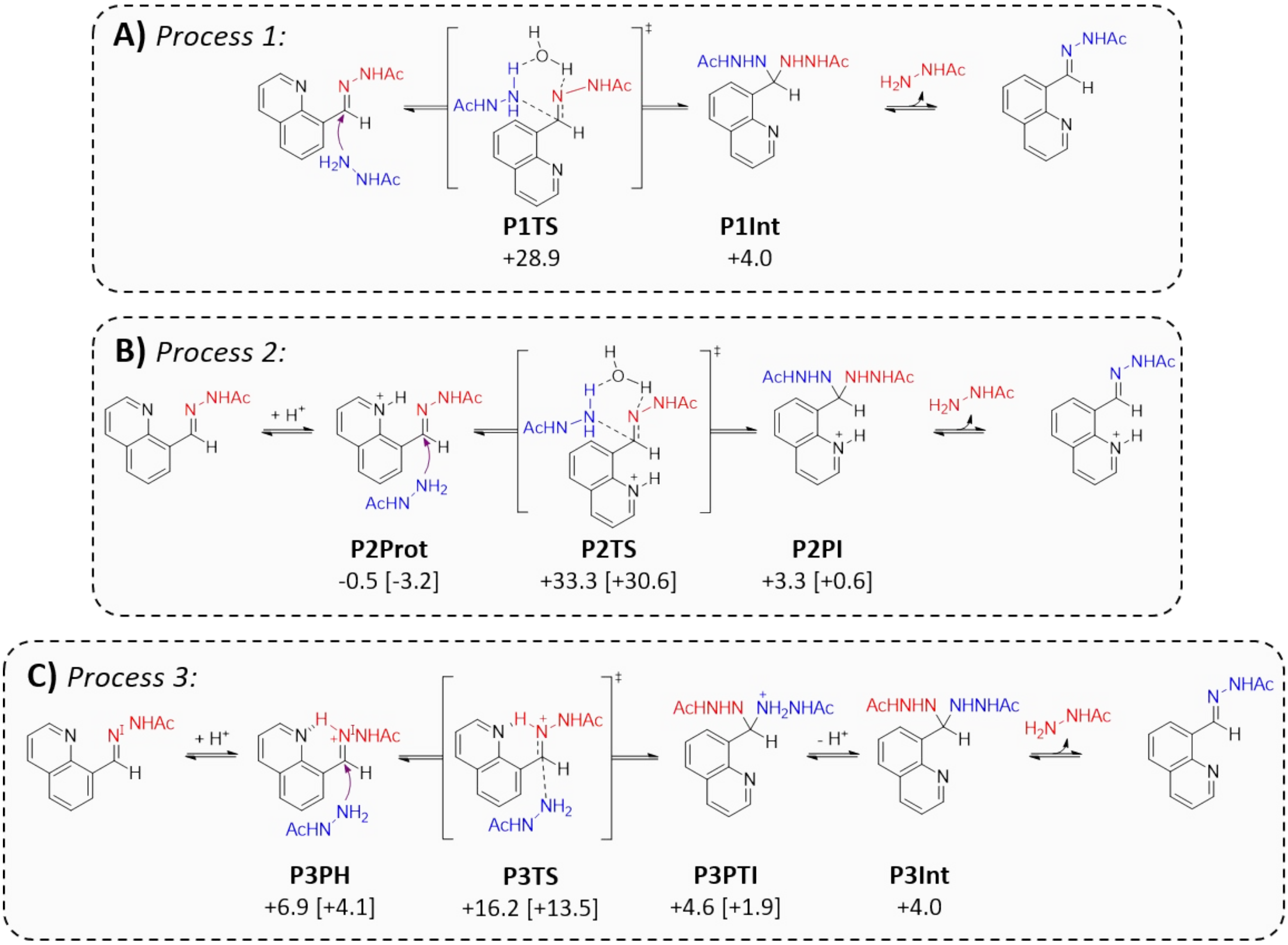


Figure S18: Three mechanisms of hydrazone exchange which were explored computationally. (**A**) Process (1): No protonation of hydrazone prior to hydrazide attack (uncatalysed reaction). (**B**) Process (2): Protonation of proximal acid/base group within aldehyde component of hydrazone. (**C**) Process (3): Protonation of hydrazone nitrogen (N^1) prior to attack. See tables **S19-21** for energetics.

Process 1:

Table S19: Free energies computed for intermediates and transition states of **1a-f** at pH 7.4. Values computed at pH 5.4 are in brackets (where given).

Substrate	P1TS	P1Int
quinoline **1a**	+28.9	+4.0
phenyl **1d**	+27.1	+3.0
pyridine **1e**	+26.2	+3.7
carboxylate **1f**	+23.0	+3.0

Process 20:

Table S21: Free energies computed for intermediates and transition states of **1a-f** at pH 7.4. Values computed at pH 5.4 are in brackets (where given).

Substrate	P2Prot	P2TS	P2PI	ΔG†
quinoline **1a**	-0.5 [-3.2]	+33.3 [+30.6]	+3.3 [+0.6]	+33.8 [+33.8]
phenyl **1d**	0.0	+27.1	+3.0	+27.1
pyridine **1e**	+3.4 [+0.7]	+33.2 [+30.5]	+3.2 [+0.5]	+33.2 [+30.5]
carboxylate **1f**	-16.2 [-19.0]	+15.3 [+12.7]	-14.4 [-17.1]	+31.6 [+31.6]

Process 3:

Table S21: Free energies computed for intermediates and transition states of **1a-f** at pH 7.4. Values computed at pH 5.4 are in brackets (where given).

Substrate	P3PH	P3TS	P3PTI	ΔG†
quinoline **1a**	+6.8 [+4.1]	+16.2 [+13.5]	+4.6 [+1.9]	+16.7 [+16.7]
phenol **1b**	+11.1 [+8.3]	+19.4 [+16.7]	+23.2 [+20.4]	+19.4 [+16.7]
phenyl **1d**	+15.0 [+12.2]	+20.3 [+17.6]	+7.9 [+5.2]	+20.3 [+17.6]
pyridine **1e**	+13.4 [+10.6]	+20.2 [+17.5]	+6.7 [+3.9]	+20.2 [+17.5]
carboxylate **1f**	-4.3 [-9.8]	+10.8 [+5.3]	+4.3 [-1.1]	+27.0[a] [+24.3]

[a] *this is the free energy relative the lowest free energy state available pre-rate-limiting transition state,* **P2Prot**

Hydrazone Formation versus Hydrazone Exchange: In order to gain insight to the mechanistic differences between hydrazone exchange and hydrazide, both reactions were studied in an identical way, with three possible mechanisms being considered: Process (1) hydrazide directly attacks the unprotonated aldehyde (**Fig. S23A**); process (2) protonation of acid/base groups within the aldehyde, followed by hydrazide attack; process (3) protonation of the aldehyde, followed by hydrazide attack.

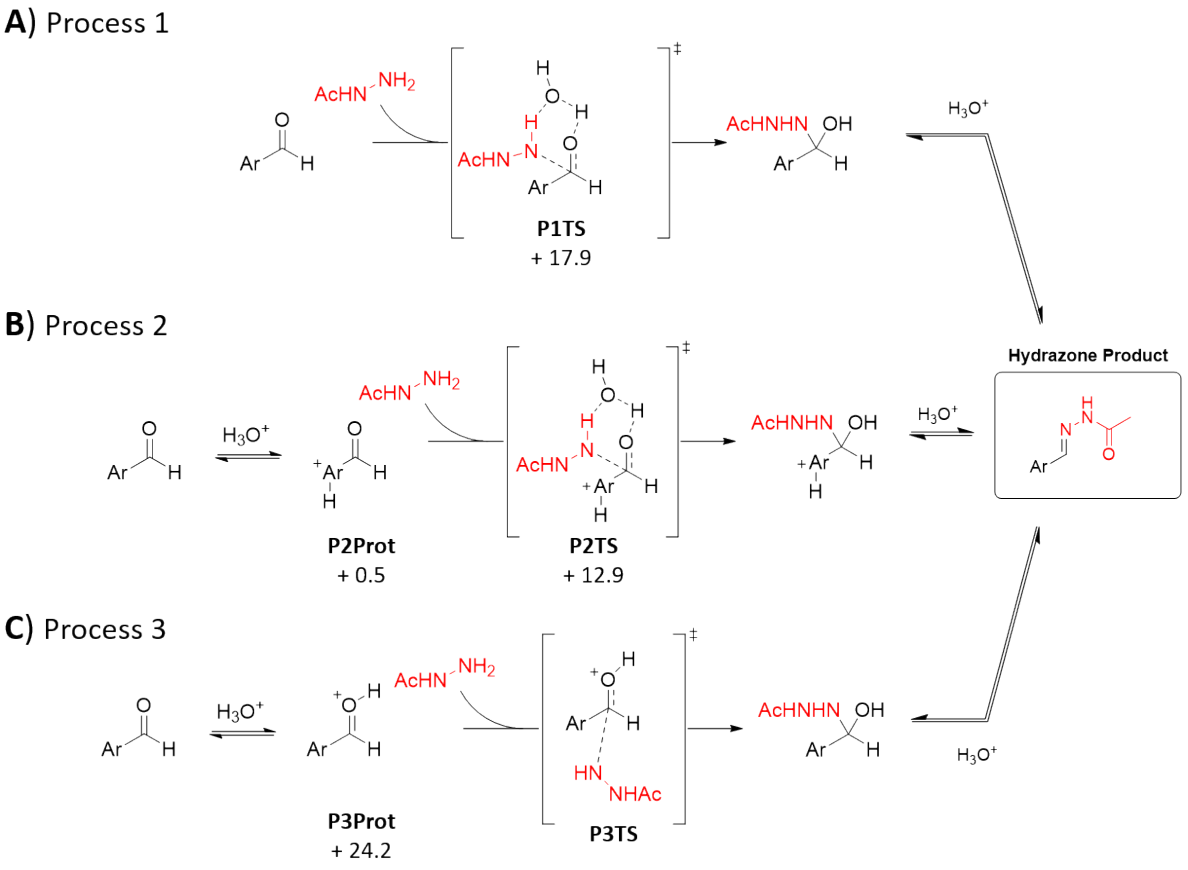


Figure S22: Three potential mechanisms of hydrazone formation were explored computationally for quinoline-8-carbaldehyde (Ar = quinoline). Free energy barriers (kcal/mol) were calculated relative to the lowest energy species. (**A**) No protonation prior to hydrazide attack on aldehyde (uncatalysed reaction). (**B**) Protonation of proximal acid/base group within the aromatic aldehyde, and subsequent hydrazide attack to form the hemiaminal intermediate. (**C**) Protonation of aldehyde oxygen prior to hydrazide attack.

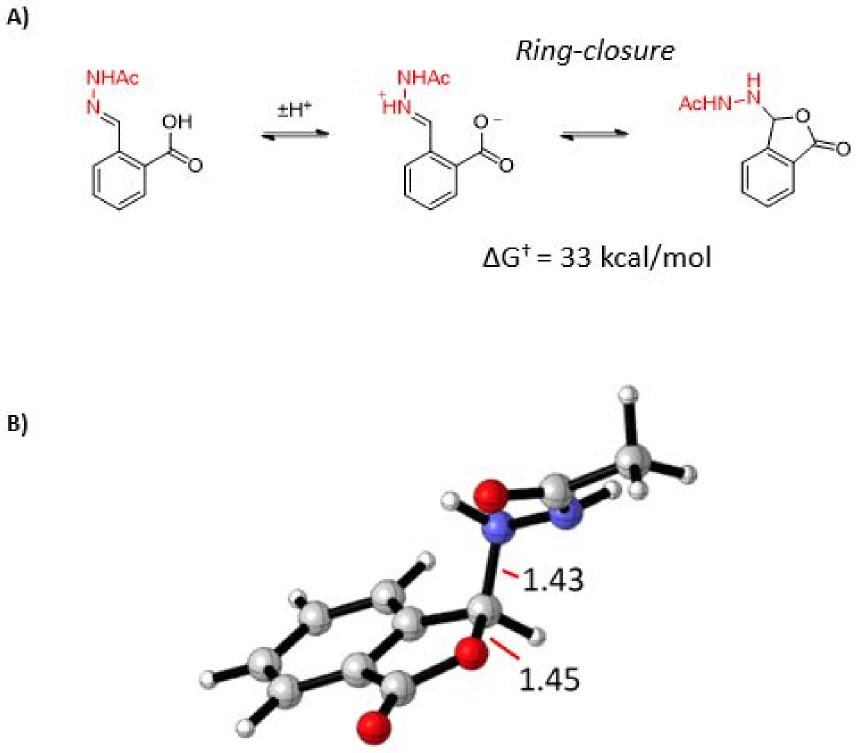


Figure S23: Computational modelling revealed that hydrazone **1f** forms a meta-stable cyclic intermediate, formed by carboxylate ring-closing upon tetrahedral (aminal) intermediate to form a 5-membered ring (**A**). Annotations indicate key bond lengths: 1.45 Å (O-C), 1.43 Å (C-N) are shown for the computed structure of the ring-closed intermediate (**B**).

Computational data

Below are geometries obtained at the M06-2X/6-31G* level in Gaussian09 with solvation incorporated using the IEFPCM model for water (geometry optimization and second derivatives were also computed with solvation included). In most cases, many conformations were considered and only the lowest energy structure has been included here for each species. Energies are in Hartrees.

Reactants

QUINOLINE
SCF energy = -703.088841077
Zero-point correction = 0.214283
Thermal correction to Energy = 0.227883
Thermal correction to Enthalpy = 0.228827
Thermal correction to Gibbs Free Energy = 0.172008
G(1M) = -702.914

Coordinates:

6	-4.15556	1.4352	0.001235
6	-4.09601	0.06806	-0.000217
6	-2.83085	-0.57378	-0.000646
6	-1.6715	0.249945	0.000396
6	-2.93969	2.16357	0.002259
1	-5.10133	1.96513	0.001614
1	-4.99851	-0.537225	-0.001039
1	-2.96909	3.25161	0.003443
6	-0.379329	-0.36608	-0.000151
6	-0.289798	-1.74416	-0.001545
1	0.693589	-2.20411	-0.002368
6	-1.44392	-2.55463	-0.002398
1	-1.33587	-3.63428	-0.003642
6	-2.69333	-1.98364	-0.002072
1	-3.58872	-2.59877	-0.002935
7	-1.74856	1.61163	0.001872
6	0.816638	0.485613	-0.000506
1	0.661402	1.56648	-0.003577
7	1.98586	-0.034851	0.001887
7	3.0374	0.818708	-0.000988
1	2.88756	1.8269	-0.006822
6	4.33581	0.374509	-0.001295
6	4.52913	-1.12072	0.00763
1	4.04216	-1.57727	-0.857223
1	4.08196	-1.55817	0.903722
1	5.59898	-1.32378	-0.012794
8	5.25193	1.18148	-0.00674

PYRIDINE

SCF energy = -549.505184199
Zero-point correction = 0.167229
Thermal correction to Energy = 0.177973
Thermal correction to Enthalpy = 0.178917
Thermal correction to Gibbs Free Energy = 0.129579
G(1M) = -549.373

Coordinates:

6	-0.001175	0.914593	2e-06
1	-0.081175	2.00576	0.000114
7	-1.02	0.14441	-8.1e-05
7	-2.23952	0.726063	-2.2e-05
1	-2.33245	1.74124	0.000173
6	-3.39838	-0.01427	-3e-06
6	-3.23226	-1.51218	-0.000234
1	-2.67249	-1.83532	0.880737
1	-2.67197	-1.83506	-0.880952
1	-4.22389	-1.96272	-0.000572
8	-4.47621	0.556314	0.000222
6	1.36451	0.363645	7e-06
6	1.60994	-1.01382	0.000157
6	3.60141	0.844373	-8.3e-05
6	2.92717	-1.44978	0.000131
1	0.777351	-1.70844	0.00027
6	3.94963	-0.503475	2e-06
1	4.37359	1.61034	-0.000237
1	3.15492	-2.51101	0.000226
1	4.9929	-0.798738	-2.8e-05
7	2.34063	1.28223	-9.5e-05

CARBOXYLIC ACID
SCF energy = -721.504519988
Zero-point correction = 0.181256
Thermal correction to Energy = 0.194798
Thermal correction to Enthalpy = 0.195742
Thermal correction to Gibbs Free Energy = 0.139045
G(1M) = -721.362

Coordinates:

```
6 0.407293 0.391287 0.202965
1 0.306242 1.44982 0.440838
7 1.54908 -0.159156 0.0232
7 2.6365 0.642521 0.196524
1 2.51948 1.61807 0.467132
6 3.91422 0.186843 0.024927
6 4.05831 -1.26125 -0.372687
1 3.55003 -1.45094 -1.32119
1 3.60316 -1.91279 0.377193
1 5.12066 -1.48325 -0.466602
8 4.86082 0.942605 0.194321
6 -0.83019 -0.403395 0.085347
6 -0.740462 -1.80394 0.119903
6 -3.22965 -0.609324 -0.050512
6 -1.87656 -2.59716 0.045374
1 0.240053 -2.25983 0.217354
6 -3.13311 -1.99566 -0.038671
1 -4.19593 -0.118198 -0.100766
1 -1.78505 -3.67899 0.067525
1 -4.02982 -2.60671 -0.086821
6 -2.09607 0.207977 -0.00535
6 -2.31639 1.73162 -0.09414
8 -1.36135 2.41801 -0.53352
8 -3.446 2.13655 0.25974
```

PHENYL

SCF energy = -533.467137249
Zero-point correction = 0.179020
Thermal correction to Energy = 0.189916
Thermal correction to Enthalpy = 0.190860
Thermal correction to Gibbs Free Energy = 0.141260
G(1M) = -533.323

Coordinates:

6	-0.023479	0.909808	-1.1e-05
1	-0.13557	1.99993	3.2e-05
7	-1.04082	0.135999	-6.5e-05
7	-2.26301	0.721474	-6.8e-05
1	-2.35342	1.7368	3.2e-05
6	-3.42162	-0.013962	-2.1e-05
6	-3.25917	-1.51279	-7.8e-05
1	-2.69973	-1.83729	0.880609
1	-2.69957	-1.83724	-0.880678
1	-4.25177	-1.96133	-0.000171
8	-4.50056	0.557213	7.1e-05
6	1.34475	0.37623	8e-06
6	1.60008	-1.00208	3e-05
6	3.72896	0.801701	2.7e-05
6	2.90791	-1.4685	4.9e-05
1	0.76458	-1.69508	3.3e-05
6	3.97615	-0.568721	4.7e-05
1	4.55546	1.50522	2.7e-05
1	3.09884	-2.53716	6.7e-05
1	4.99715	-0.937469	6.3e-05
6	2.41838	1.27201	9e-06
1	2.22354	2.34141	-4e-06

PHENOL

SCF energy = -608.671411256
Zero-point correction = 0.183918
Thermal correction to Energy = 0.195541
Thermal correction to Enthalpy = 0.196486
Thermal correction to Gibbs Free Energy = 0.145794
G(1M) = -608.523

Coordinates:

6	-0.070578	1.07555	-5e-06
1	-0.188446	2.16394	-4e-06
7	-1.09196	0.299915	-2e-05
7	-2.32549	0.861044	-3.1e-05
1	-2.42711	1.87449	1e-05
6	-3.47188	0.105688	-1.1e-05
6	-3.28424	-1.39057	-7.3e-05
1	-2.72443	-1.70887	0.883617
1	-2.72435	-1.7088	-0.88374
1	-4.26952	-1.85477	-0.000132
8	-4.55884	0.659324	-1.8e-05
6	1.29108	0.549822	1e-05
6	1.57139	-0.834903	2.4e-05
6	3.67734	1.02082	2.7e-05
6	2.89909	-1.27089	3.8e-05
6	3.93939	-0.352072	4e-05
1	4.49137	1.73725	2.8e-05
1	3.08735	-2.3396	5e-05
1	4.9645	-0.709556	5.2e-05
6	2.36154	1.45623	1.3e-05
8	0.604353	-1.77569	2.7e-05
1	-0.269419	-1.32828	2.5e-05
1	2.13931	2.52037	2e-06

BENZOFURAN

SCF energy = -684.843775903
Zero-point correction = 0.195711
Thermal correction to Energy = 0.208640
Thermal correction to Enthalpy = 0.209584
Thermal correction to Gibbs Free Energy = 0.154143
G(1M) = -684.687

Coordinates:

6	0.616325	0.54991	0.00012
1	0.51589	1.63971	0.000251
7	1.76013	-0.022252	2.3e-05
7	2.85181	0.777953	0.000105
1	2.75395	1.79248	0.000245
6	4.12657	0.267849	-1.7e-05
6	4.24305	-1.23512	-0.000263
1	3.75341	-1.65748	-0.881048
1	3.75339	-1.65778	0.880363
1	5.30135	-1.49255	-0.000296
8	5.08161	1.02779	2.9e-05
6	-0.615356	-0.242092	4.8e-05
6	-0.642727	-1.63951	-1.6e-05
6	-3.08531	-0.297104	-1.8e-05
6	-1.85002	-2.34857	-8.2e-05
1	0.301757	-2.1739	-1.1e-05
6	-3.07878	-1.69653	-8.4e-05
1	-1.82126	-3.43337	-0.000128
1	-4.00741	-2.25787	-0.000132
6	-1.86181	0.385677	4.5e-05
8	-2.06808	1.7297	9.8e-05
6	-4.09626	0.736911	7e-06
6	-3.42624	1.90889	5.5e-05
1	-5.1687	0.610487	-2.1e-05
1	-3.75088	2.93851	8.3e-05

DIHYDROBENZOPYRAN

SCF energy = -725.349234326
Zero-point correction = 0.249153
Thermal correction to Energy = 0.263568
Thermal correction to Enthalpy = 0.264512
Thermal correction to Gibbs Free Energy = 0.206526
G(1M) = -725.14

Coordinates:

6	0.91059	0.429891	-0.065375
1	0.74276	1.50723	-0.137271
7	2.09065	-0.061008	0.001569
7	3.12223	0.820369	-0.03228
1	2.94693	1.82092	-0.116577
6	4.4295	0.414118	0.033009
6	4.66074	-1.07108	0.155311
1	4.23489	-1.59695	-0.702738
1	4.17477	-1.46249	1.05222
1	5.73501	-1.24376	0.205031
8	5.32613	1.24284	-0.009094
6	-0.26852	-0.442466	-0.053286
6	-0.150838	-1.83564	-0.064505
6	-1.55208	0.135229	-0.039758
6	-1.28134	-2.64132	-0.061034
6	-2.70313	-0.666241	-0.026929
6	-2.54332	-2.0511	-0.038943
1	-1.1832	-3.72172	-0.071
1	-3.43418	-2.67455	-0.0235
1	0.843471	-2.27078	-0.081265
8	-1.60429	1.49655	-0.011929
6	-4.07758	-0.036325	0.021818
6	-3.98495	1.42072	0.468568
6	-2.86829	2.09602	-0.306645
1	-3.05027	2.02172	-1.38718
1	-2.75394	3.14785	-0.040535
1	-4.9275	1.94658	0.293556
1	-3.75876	1.48189	1.53898
1	-4.53835	-0.083902	-0.973164
1	-4.72109	-0.613518	0.693228

DIHYDROBENZOFURAN
SCF energy = -686.048925520
Zero-point correction = 0.219162
Thermal correction to Energy = 0.232825
Thermal correction to Enthalpy = 0.233769
Thermal correction to Gibbs Free Energy = 0.176627
G(1M) = -685.869

Coordinates:

6	-0.676316	0.518686	-0.000684
1	-0.561051	1.60705	-0.004647
7	-1.82946	-0.035933	0.003027
7	-2.90812	0.786328	-0.00279
1	-2.79012	1.79857	-0.012793
6	-4.19096	0.30244	0.003509
6	-4.33693	-1.19826	0.019225
1	-3.86065	-1.61999	0.907684
1	-3.85048	-1.64075	-0.85335
1	-5.39999	-1.43527	0.016419
8	-5.13307	1.07969	-0.002837
6	0.545605	-0.285828	-0.00079
6	0.543204	-1.69207	-0.037269
6	2.99061	-0.378592	0.025083
6	1.72616	-2.4172	-0.044243
1	-0.414172	-2.20299	-0.067085
6	2.96643	-1.7613	-0.008503
1	1.69132	-3.50105	-0.077568
1	3.89064	-2.3316	-0.00769
6	1.79242	0.335558	0.028456
8	1.96943	1.68193	0.074012
6	4.11899	0.620159	0.120815
6	3.37551	1.94183	-0.154099
1	4.91416	0.445978	-0.607293
1	3.66822	2.76057	0.5029
1	3.48928	2.2539	-1.19685
1	4.56665	0.607208	1.12022

CARBOXYLATE

SCF energy = -721.504519988
Zero-point correction = 0.181256
Thermal correction to Energy = 0.194798
Thermal correction to Enthalpy = 0.195742
Thermal correction to Gibbs Free Energy = 0.139045
G(1M) = -721.362

Coordinates:

6	0.407293	0.391287	0.202965
1	0.306242	1.44982	0.440838
7	1.54908	-0.159156	0.0232
7	2.6365	0.642521	0.196524
1	2.51948	1.61807	0.467132
6	3.91422	0.186843	0.024927
6	4.05831	-1.26125	-0.372687
1	3.55003	-1.45094	-1.32119
1	3.60316	-1.91279	0.377193
1	5.12066	-1.48325	-0.466602
8	4.86082	0.942605	0.194321
6	-0.83019	-0.403395	0.085347
6	-0.740462	-1.80394	0.119903
6	-3.22965	-0.609324	-0.050512
6	-1.87656	-2.59716	0.045374
1	0.240053	-2.25983	0.217354
6	-3.13311	-1.99566	-0.038671
1	-4.19593	-0.118198	-0.100766
1	-1.78505	-3.67899	0.067525
1	-4.02982	-2.60671	-0.086821
6	-2.09607	0.207977	-0.00535
6	-2.31639	1.73162	-0.09414
8	-1.36135	2.41801	-0.53352
8	-3.446	2.13655	0.25974

Addition transition states

QUINOLINE

SCF energy = -1043.87944049
Zero-point correction = 0.332513
Thermal correction to Energy = 0.353279
Thermal correction to Enthalpy = 0.354224
Thermal correction to Gibbs Free Energy = 0.282715
G(1M) = -1043.59

Coordinates:

6	0.891846	-0.039226	0.416038
1	1.46389	-0.824501	0.915382
7	1.47799	1.24894	0.610844
7	2.80189	1.14766	1.06839
7	0.988073	-0.398485	-1.10981
1	1.04019	0.587173	-1.62993
7	0.007137	-1.24383	-1.64222
1	3.00461	1.65909	1.91677
6	3.80202	0.506483	0.441835
6	5.16153	0.613306	1.09538
1	5.86799	1.0108	0.362735
1	5.49899	-0.388208	1.37365
1	5.16657	1.25141	1.98089
8	3.6436	-0.159332	-0.592018
1	-0.824538	-0.748016	-1.94621
6	-0.083061	-2.50869	-1.10938
6	-1.3587	-3.23913	-1.43355
1	-2.08138	-3.02865	-0.637456
1	-1.16184	-4.31083	-1.45174
1	-1.78673	-2.91982	-2.3856
8	0.820891	-2.96306	-0.428956
8	1.37278	2.03993	-1.74094
1	1.45392	1.85551	-0.583963
1	0.479662	2.40845	-1.8236
6	-0.543959	-0.146741	0.884809
6	-2.11732	-1.03578	2.52504
6	-2.91451	0.51555	0.855383
6	-3.14536	-0.306748	1.98866
1	-2.28822	-1.67976	3.38145
1	-4.14645	-0.354855	2.40775
1	1.9253	-0.807782	-1.22302
6	-1.61191	0.593783	0.291597
6	-0.819675	-0.954494	1.96405
1	-0.01807	-1.5426	2.40314
6	-3.94848	1.26275	0.236944
6	-3.66938	2.008	-0.877475
1	-4.43338	2.5882	-1.38194
6	-2.34777	1.99285	-1.38163
1	-2.11092	2.55646	-2.28219
7	-1.3562	1.3245	-0.832989
1	-4.95155	1.22469	0.653415

PYRIDINE
SCF energy = -890.297666291
Zero-point correction = 0.284428
Thermal correction to Energy = 0.302895
Thermal correction to Enthalpy = 0.303839
Thermal correction to Gibbs Free Energy = 0.236113
G(1M) = -890.059

Coordinates:

6	0.062209	0.379999	0.307849
1	0.406631	-0.030226	1.26347
7	0.717066	1.59962	-0.047433
7	2.00312	1.72624	0.491695
7	0.391744	-0.67641	-0.761325
1	0.206411	-0.12696	-1.70628
7	-0.237938	-1.92125	-0.649422
1	2.13515	2.52829	1.09377
6	3.0767	0.985707	0.166373
6	4.38448	1.4174	0.787379
1	5.10691	1.59334	-0.013179
1	4.76486	0.600858	1.40584
1	4.29737	2.31885	1.39632
8	3.02388	-0.006585	-0.574019
1	-1.22135	-1.8938	-0.897726
6	0.287992	-2.81493	0.246135
6	-0.551506	-4.04191	0.488378
1	-1.31828	-4.18271	-0.274792
1	-1.0346	-3.94374	1.46464
1	0.1037	-4.91355	0.518298
8	1.36814	-2.60859	0.776599
8	0.289128	1.20074	-2.45164
1	0.590801	1.60408	-1.33671
1	-0.626958	1.48766	-2.58789
6	-1.44165	0.604364	0.313502
6	-3.47966	0.358528	-0.70748
6	-3.36029	1.62792	1.31261
6	-4.12261	1.1114	0.265605
1	-4.03572	-0.065024	-1.53968
1	-3.8246	2.21945	2.09526
1	-5.19089	1.28529	0.204883
1	1.42535	-0.791734	-0.708361
7	-2.16419	0.10426	-0.690792
6	-1.99641	1.37604	1.33567
1	-1.35813	1.77099	2.11943

CARBOXYLATE

SCF energy = -1062.30449348
Zero-point correction = 0.299565
Thermal correction to Energy = 0.320110
Thermal correction to Enthalpy = 0.321054
Thermal correction to Gibbs Free Energy = 0.249793
G(1M) = -1062.05

Coordinates:

6	0.561929	-0.050273	0.44805
1	0.981203	-0.903554	0.985528
7	1.36105	1.12632	0.627539
7	2.64279	0.821239	1.11164
7	0.635414	-0.466022	-1.05598
1	0.792479	0.496111	-1.61282
7	-0.433509	-1.22433	-1.55685
1	2.90987	1.31079	1.95518
6	3.53326	-0.003972	0.538105
6	4.8692	-0.114388	1.23903
1	5.66003	0.059043	0.505732
1	4.98569	-1.13236	1.61996
1	4.98351	0.590294	2.06492
8	3.29515	-0.670514	-0.479954
1	-1.19591	-0.591239	-1.8555
6	-0.650131	-2.4412	-0.974053
6	-2.00035	-3.04227	-1.27057
1	-2.67769	-2.7667	-0.454874
1	-1.91458	-4.12881	-1.29839
1	-2.41823	-2.67433	-2.20943
8	0.194002	-2.97571	-0.267974
8	1.35325	1.875	-1.73228
1	1.42828	1.69639	-0.546658
1	0.576737	2.45632	-1.81592
6	-0.884649	0.115328	0.880409
6	-2.56463	-0.480179	2.5406
6	-3.07147	1.14313	0.839293
6	-3.4592	0.41416	1.96088
1	-2.85256	-1.06448	3.40891
1	-3.77077	1.83601	0.37784
1	-4.4554	0.540454	2.37411
1	1.53079	-0.969869	-1.13381
6	-1.79984	0.997489	0.28018
6	-1.28975	-0.620585	1.99805
1	-0.587643	-1.31683	2.45069
6	-1.50727	1.77482	-1.00076
8	-1.60379	1.11521	-2.0741
8	-1.21844	2.98224	-0.892584

PHENYL

SCF energy = -874.255679535
Zero-point correction = 0.296010
Thermal correction to Energy = 0.314803
Thermal correction to Enthalpy = 0.315747
Thermal correction to Gibbs Free Energy = 0.247103
G(1M) = -874.006

Coordinates:

6	0.284689	0.378406	0.320764
1	0.552979	-0.266753	1.16146
7	1.19212	1.45735	0.136448
7	2.43852	1.23106	0.736465
7	0.40151	-0.559074	-0.946362
1	0.523864	0.136926	-1.78045
7	-0.605056	-1.50934	-1.15968
1	2.72948	1.94303	1.3931
6	3.28832	0.230375	0.456545
6	4.6126	0.272103	1.18329
1	5.41447	0.223617	0.442853
1	4.69236	-0.612854	1.81954
1	4.74156	1.16668	1.79512
8	3.02449	-0.69929	-0.321347
1	-1.44045	-1.14462	-1.60288
6	-0.701035	-2.53587	-0.247714
6	-1.96935	-3.3414	-0.343309
1	-2.75486	-2.82405	0.21805
1	-1.80124	-4.32059	0.103465
1	-2.30201	-3.45248	-1.37746
8	0.195951	-2.7421	0.551339
8	1.1455	1.45234	-2.3341
1	1.25662	1.64971	-1.15565
1	0.524611	2.09351	-2.70854
6	-1.16204	0.798093	0.413398
6	-2.03193	0.112277	1.26256
6	-1.65385	1.84273	-0.372939
6	-3.37841	0.466958	1.33147
1	-1.65026	-0.700697	1.87741
6	-2.99773	2.19748	-0.30561
1	-0.977691	2.3777	-1.03223
6	-3.86247	1.51028	0.546137
1	-4.045	-0.070618	1.9988
1	-3.37129	3.01212	-0.918325
1	-4.91025	1.78952	0.597379
1	1.32722	-1.01633	-0.834365

Addition intermediates

QUINOLINE
SCF energy= -967.529528342
Zero-point correction = 0.312536
Thermal correction to Energy = 0.332013
Thermal correction to Enthalpy = 0.332957
Thermal correction to Gibbs Free Energy = 0.263609
G(1M) = -967.263

Coordinates:

6	-0.383984	-0.155987	-0.507082
1	-0.992262	-0.796928	-1.15655
7	-0.557307	1.20194	-1.00774
7	-1.89365	1.50316	-1.28333
7	-0.839224	-0.3221	0.898863
7	-1.41062	-1.5812	1.08795
1	-1.55606	0.380613	1.09017
1	-2.16104	1.41939	-2.25377
6	-2.77442	1.94816	-0.358494
6	-4.18043	2.16095	-0.859271
1	-4.77523	1.30676	-0.522903
1	-4.24315	2.22842	-1.94697
1	-4.58785	3.06771	-0.410042
8	-2.45178	2.14867	0.812071
1	-0.887814	-2.23494	1.65325
6	-2.69004	-1.83475	0.710641
6	-3.21286	-3.2093	1.05611
1	-2.44492	-3.86847	1.46481
1	-3.63294	-3.65927	0.15414
1	-4.01941	-3.10482	1.78638
8	-3.37066	-0.989491	0.137039
1	-0.181852	1.87123	-0.336392
6	1.05934	-0.59909	-0.614349
6	3.44823	-0.301398	-0.110476
6	2.69771	-2.27193	-1.29126
6	3.72016	-1.54129	-0.747633
1	2.89819	-3.22059	-1.77851
1	4.74711	-1.89309	-0.794025
6	1.36532	-1.79293	-1.22042
6	2.11205	0.177494	-0.03845
1	0.564856	-2.38727	-1.65376
6	2.77681	2.071	1.08414
1	2.49507	3.01182	1.55333
6	4.13827	1.68182	1.06584
6	4.4687	0.495823	0.466313
1	4.88803	2.32147	1.51763
1	5.49924	0.153261	0.422747
7	1.80085	1.3639	0.561976

PYRIDINE

SCF energy= -813.945592233
Zero-point correction= 0.265193
Thermal correction to Energy= 0.282094
Thermal correction to Enthalpy= 0.283038
Thermal correction to Gibbs Free Energy= 0.218650
G(1M)= -813.724

Coordinates:

6	-0.210432	0.35462	0.098124
1	0.104381	-0.043254	1.07311
7	0.351785	1.69295	0.013145
7	1.65053	1.77437	0.519754
7	0.277179	-0.520706	-0.987522
7	0.25992	-1.86319	-0.594491
1	1.25284	-0.277547	-1.16672
1	1.72917	2.23909	1.41374
6	2.75555	1.51048	-0.220724
6	4.07161	1.71691	0.486392
1	4.54256	0.73772	0.607509
1	3.96556	2.18363	1.46694
1	4.71946	2.32967	-0.143205
8	2.68394	1.11979	-1.38321
1	-0.630702	-2.32216	-0.734025
6	1.22587	-2.35778	0.218529
6	1.03974	-3.79208	0.65466
1	0.132479	-4.24523	0.251265
1	1.00355	-3.82334	1.74636
1	1.90644	-4.37376	0.332044
8	2.20471	-1.68724	0.53944
1	0.353838	2.02258	-0.953141
6	-1.73425	0.417345	0.066063
6	-2.42288	1.53162	0.54608
6	-3.81365	1.51725	0.525869
1	-1.86825	2.38697	0.912859
6	-3.69292	-0.673631	-0.410203
6	-4.46833	0.391842	0.037255
1	-4.37649	2.37382	0.884018
1	-4.16568	-1.5737	-0.796594
1	-5.55053	0.335051	0.000897
7	-2.35794	-0.670468	-0.40191

CARBOXYLATE

SCF energy= -985.944934950
Zero-point correction= 0.279167
Thermal correction to Energy= 0.298577
Thermal correction to Enthalpy= 0.299521
Thermal correction to Gibbs Free Energy= 0.228937
G(1M)= -985.713

Coordinates:

6	0.683301	-0.261981	-0.001845
1	1.00677	0.264181	0.899776
7	1.82372	-0.245111	-0.912807
7	2.97399	-0.792769	-0.345162
7	0.296088	-1.65903	0.30871
7	-0.85961	-1.69706	1.11498
1	1.0478	-2.07208	0.861227
1	3.06751	-1.79794	-0.230267
6	4.08003	-0.040926	-0.074753
6	3.95859	1.44191	-0.333998
1	3.12474	1.86886	0.228935
1	3.76377	1.62853	-1.39275
1	4.89283	1.91642	-0.035726
8	5.09295	-0.567409	0.365926
1	-0.95988	-0.89979	1.76386
6	-2.01583	-2.22009	0.616881
6	-1.90319	-3.08691	-0.616103
1	-1.11067	-3.82986	-0.505375
1	-1.65142	-2.46888	-1.48221
1	-2.86323	-3.57601	-0.780501
8	-3.08428	-2.01996	1.18661
1	1.61506	-0.754591	-1.76903
6	-0.499046	0.465966	-0.612412
6	-1.24063	1.41266	0.112808
6	-0.855741	0.184285	-1.93563
6	-2.28627	2.08423	-0.529579
6	-1.91874	0.836791	-2.55166
1	-0.304129	-0.562768	-2.50133
6	-2.63564	1.79966	-1.84455
1	-2.82716	2.83558	0.036947
1	-2.18001	0.597243	-3.57785
1	-3.46276	2.32183	-2.31627
6	-1.00785	1.74779	1.59524
8	-1.23284	2.92503	1.93268
8	-0.644857	0.80071	2.35154

PHENYL

SCF energy= -797.906499987
Zero-point correction= 0.277051
Thermal correction to Energy= 0.294172
Thermal correction to Enthalpy= 0.295116
Thermal correction to Gibbs Free Energy=0.230057
G(1M)= -797.673

Coordinates:

6	-0.297196	0.269397	0.129011
1	0.032167	-0.072746	1.11889
7	0.142527	1.65847	0.031511
7	1.45421	1.84981	0.473612
7	0.305043	-0.583798	-0.914325
7	0.519837	-1.87912	-0.441264
1	1.21109	-0.189015	-1.17289
1	1.53679	2.24238	1.40078
6	2.54707	1.67608	-0.305911
6	3.87009	1.92307	0.373317
1	4.34419	0.949358	0.525431
1	3.77161	2.42339	1.33815
1	4.50541	2.51661	-0.286099
8	2.4623	1.32681	-1.48215
1	-0.053725	-2.60813	-0.842656
6	1.62696	-2.17153	0.291131
6	1.80842	-3.62797	0.647142
1	0.955055	-4.24624	0.363268
1	1.96882	-3.70616	1.72446
1	2.70471	-4.0028	0.146207
8	2.42213	-1.29957	0.627118
1	0.066677	1.99739	-0.928201
6	-1.81602	0.229058	0.072362
6	-2.54037	0.862293	1.08762
6	-2.50478	-0.41878	-0.950592
6	-3.93011	0.847893	1.08047
1	-2.00265	1.3728	1.88285
6	-3.90068	-0.434582	-0.959743
1	-1.94387	-0.905493	-1.74142
6	-4.61576	0.196699	0.052938
1	-4.48039	1.3428	1.87501
1	-4.42698	-0.942188	-1.76258
1	-5.7014	0.182796	0.045814

Reactants - protonated on aromatic

QUINOLINE
SCF energy= -703.536921399
Zero-point correction= 0.228374
Thermal correction to Energy= 0.241955
Thermal correction to Enthalpy= 0.242899
Thermal correction to Gibbs Free Energy= 0.186184
G(1M)= -703.348

Coordinates:

6	2.31843	-2.63748	0.004844
6	3.17857	-1.56305	0.009867
6	2.68541	-0.237005	0.006561
6	1.28388	-0.036427	-0.001907
6	0.943443	-2.39125	-0.003816
1	2.67686	-3.65829	0.007302
1	4.253	-1.71999	0.016606
1	0.199896	-3.17905	-0.008532
6	0.733769	1.28057	-0.005103
6	1.61976	2.33997	-0.000231
1	1.22145	3.35029	-0.002557
6	3.01931	2.15425	0.007684
1	3.66895	3.02177	0.011035
6	3.54774	0.890346	0.011389
1	4.62029	0.727045	0.018115
7	0.482045	-1.14819	-0.006897
6	-0.706168	1.55848	-0.012078
1	-1.01637	2.60666	-0.011
7	-1.5381	0.589338	-0.018616
7	-2.8612	0.816585	-0.025048
1	-3.21917	1.76831	-0.007146
6	-3.71122	-0.274191	-0.012281
6	-5.17312	0.088244	0.044585
1	-5.4022	0.962204	-0.56954
1	-5.44617	0.315844	1.07968
1	-5.75807	-0.765961	-0.294155
8	-3.28493	-1.41263	-0.021204
1	-0.537215	-0.966585	-0.013347

PYRIDINE

SCF energy= -549.948571229
Zero-point correction= 0.181067
Thermal correction to Energy= 0.191890
Thermal correction to Enthalpy= 0.192834
Thermal correction to Gibbs Free Energy= 0.143472
G(1M)= -549.802

Coordinates:

6	-0.014349	1.10418	1.9e-05
1	-0.108285	2.19004	3.9e-05
7	-1.00363	0.292237	2e-05
7	-2.24372	0.771991	4.6e-05
1	-2.41919	1.77659	5.6e-05
6	-3.35257	-0.067105	4.4e-05
6	-3.07221	-1.54505	-1.9e-05
1	-2.49178	-1.82552	0.882347
1	-2.49179	-1.82544	-0.882415
1	-4.02755	-2.06755	-3.7e-05
8	-4.45837	0.432271	2.1e-05
6	1.32793	0.52691	-1e-06
6	2.49368	1.2817	-3e-06
6	2.60527	-1.47583	-3.8e-05
6	3.72418	0.633662	-2.3e-05
1	2.42439	2.36286	1e-05
6	3.78654	-0.760219	-4e-05
1	2.55176	-2.55655	-5e-05
1	4.63779	1.2175	-2.5e-05
1	4.73142	-1.28755	-5.6e-05
7	1.43481	-0.819648	-1.7e-05
1	0.557185	-1.34412	-1.5e-05

CARBOXYLIC ACID

SCF energy= -721.976329582
Zero-point correction= 0.194215
Thermal correction to Energy= 0.208022
Thermal correction to Enthalpy= 0.208966
Thermal correction to Gibbs Free Energy= 0.151850
G(1M)= -721.821

Coordinates:

6	0.440634	0.396328	0.273443
1	0.339285	1.43337	0.592269
7	1.58529	-0.125504	0.040657
7	2.66833	0.660966	0.241248
1	2.56083	1.61922	0.571643
6	3.94599	0.216048	0.004169
6	4.07819	-1.20216	-0.489337
1	3.55314	-1.32734	-1.43941
1	3.63495	-1.90054	0.22454
1	5.13803	-1.41824	-0.617292
8	4.89044	0.964022	0.197943
6	-0.775637	-0.425793	0.126413
6	-0.658971	-1.8208	0.171772
6	-3.18431	-0.69629	-0.078833
6	-1.7767	-2.639	0.077604
1	0.32816	-2.25305	0.295716
6	-3.04717	-2.07748	-0.043874
1	-4.16609	-0.248555	-0.180295
1	-1.65771	-3.71728	0.112491
1	-3.92508	-2.71152	-0.107505
6	-2.06197	0.135852	-0.005216
6	-2.25694	1.60922	-0.126983
8	-1.40142	2.40812	-0.442605
8	-3.51789	1.98448	0.135366
1	-3.56859	2.94721	-0.006076

Addition transition states - protonated on aromatic

QUINOLINE

SCF energy= -1044.31943225
Zero-point correction= 0.345286
Thermal correction to Energy= 0.365461
Thermal correction to Enthalpy= 0.366406
Thermal correction to Gibbs Free Energy= 0.296578
G(1M)= -1044.02

Coordinates:

6	0.820396	0.475027	0.157046
1	0.864997	-0.227232	0.994151
7	1.83284	1.46446	0.256332
7	2.86997	1.09171	1.11841
7	1.13724	-0.38838	-1.11786
1	1.49787	0.382196	-1.85487
7	0.144445	-1.2319	-1.63072
1	3.05434	1.74176	1.87107
6	3.67679	0.029074	0.966208
6	4.79587	-0.098959	1.97144
1	5.74401	-0.136181	1.42961
1	4.68024	-1.04439	2.50657
1	4.82535	0.721221	2.69058
8	3.52048	-0.825107	0.080045
1	-0.128376	-1.06364	-2.59113
6	-0.104304	-2.41049	-0.996952
6	-0.964164	-3.39285	-1.73933
1	-1.68006	-3.82833	-1.04078
1	-0.320482	-4.1941	-2.11356
1	-1.49155	-2.93989	-2.5798
8	0.347383	-2.60597	0.12975
8	2.26681	1.58743	-2.17054
1	2.19469	1.73076	-1.0117
1	1.76122	2.28166	-2.61837
6	-0.564732	1.07074	-0.013812
6	-3.01115	1.03476	0.336783
6	-1.98146	2.91763	-0.761219
6	-3.1111	2.29957	-0.293219
1	-4.08907	2.75978	-0.388571
1	1.99578	-0.910651	-0.838831
6	-0.717988	2.30503	-0.606378
6	-1.73556	0.423566	0.454447
6	-2.75015	-1.44653	1.53683
6	-4.1417	0.360737	0.853969
6	-4.01819	-0.869638	1.45834
1	0.170677	2.82983	-0.939112
1	-2.04575	3.88823	-1.23989
1	-5.11524	0.833269	0.764531
1	-4.87046	-1.40115	1.86036
1	-2.56792	-2.41994	1.97558
7	-1.68734	-0.811328	1.05559
1	-0.793106	-1.31194	1.09284

PYRIDINE

SCF energy= -890.732752319

Zero-point correction= 0.297880

Thermal correction to Energy= 0.316627

Thermal correction to Enthalpy= 0.317571

Thermal correction to Gibbs Free Energy= 0.249266

G(1M)= -890.48

Coordinates:

6	0.201719	0.39532	0.224122
1	0.505029	-0.087235	1.15842
7	0.969521	1.54769	-0.097046
7	2.20486	1.56942	0.557992
7	0.386359	-0.680717	-0.874014
1	0.459643	-0.091152	-1.83112
7	-0.556774	-1.71547	-0.848794
1	2.39212	2.40589	1.09427
6	3.16181	0.631494	0.435592
6	4.45876	0.915184	1.15363
1	5.2737	0.859475	0.428196
1	4.62321	0.135864	1.90158
1	4.47704	1.89111	1.64163
8	2.99809	-0.419871	-0.198055
1	-1.09769	-1.84291	-1.69608
6	-0.301177	-2.75983	0.013962
6	-1.2037	-3.95236	-0.141542
1	-2.1693	-3.68393	-0.573529
1	-1.3469	-4.41134	0.836653
1	-0.714794	-4.67806	-0.798341
8	0.598744	-2.6669	0.829405
8	0.976695	1.0937	-2.51892
1	1.04798	1.53744	-1.4201
1	0.403103	1.63095	-3.08445
6	-1.26528	0.754245	0.255449
6	-3.24809	0.879603	1.55849
6	-3.2594	1.70131	-0.682913
6	-3.93313	1.46813	0.518314
1	-3.68106	0.660763	2.52543
1	-3.77816	2.16289	-1.51573
1	-4.97307	1.73803	0.647935
1	1.35303	-1.02719	-0.700198
7	-1.95386	0.540943	1.39052
6	-1.92282	1.34782	-0.811897
1	-1.3718	1.5253	-1.72751
1	-1.47321	0.100081	2.17361

CARBOXYLIC ACID
SCF energy= -1062.76183422
Zero-point correction= 0.312487
Thermal correction to Energy= 0.333740
Thermal correction to Enthalpy= 0.334684
Thermal correction to Gibbs Free Energy= 0.261820
G(1M)= -1062.5

Coordinates:

6	-0.486333	-0.000527	-0.450497
1	-0.946013	-0.782817	-1.05732
7	-1.18319	1.24145	-0.568584
7	-2.4576	1.08193	-1.13037
7	-0.657912	-0.512595	1.01503
1	-0.695027	0.374758	1.64384
7	0.246759	-1.4821	1.46413
1	-2.64435	1.65453	-1.94252
6	-3.43395	0.298223	-0.643164
6	-4.74868	0.347797	-1.3854
1	-5.54232	0.571415	-0.668841
1	-4.94984	-0.639303	-1.80922
1	-4.76498	1.09071	-2.18469
8	-3.28239	-0.452713	0.331846
1	1.10101	-1.09671	1.85348
6	0.208303	-2.70535	0.840553
6	1.36948	-3.61093	1.15205
1	2.13983	-3.45836	0.389398
1	1.03175	-4.64601	1.10258
1	1.80283	-3.40562	2.1325
8	-0.716275	-2.9955	0.099586
8	-1.25097	1.84792	1.82338
1	-1.26941	1.73203	0.602042
1	-0.662629	2.59225	2.01673
6	0.979991	0.087216	-0.830929
6	2.68119	-0.549576	-2.45028
6	3.17935	1.12369	-0.797886
6	3.57224	0.361558	-1.89528
1	2.97609	-1.15689	-3.29968
1	3.87007	1.82907	-0.345727
1	4.56931	0.478446	-2.30625
1	-1.62833	-0.879033	1.01988
6	1.90391	0.974849	-0.255006
6	1.39699	-0.674395	-1.92358
1	0.695649	-1.37033	-2.376
6	1.61592	1.77095	0.9789
8	1.5319	0.972157	2.0618
8	1.53326	2.9716	1.04466
1	1.3252	1.52236	2.84128

Addition intermediates - protonated on aromatic

QUINOLINE

SCF energy= -967.977639934
Zero-point correction= 0.326177
Thermal correction to Energy= 0.345651
Thermal correction to Enthalpy= 0.346595
Thermal correction to Gibbs Free Energy= 0.277577
G(1M)= -967.697

Coordinates:

6	-0.443754	0.446609	-0.411479
1	-0.982653	0.317454	-1.35599
7	-0.889864	1.72055	0.132262
7	-2.27024	1.90155	0.055439
7	-0.757788	-0.707601	0.473219
7	-1.06784	-1.84804	-0.270948
1	-1.56513	-0.454895	1.05319
1	-2.57803	2.51548	-0.685751
6	-3.1473	1.40378	0.961638
6	-4.59845	1.68308	0.673381
1	-5.01985	0.770995	0.240128
1	-4.74643	2.50785	-0.025716
1	-5.11477	1.89395	1.61061
8	-2.77658	0.748238	1.93365
1	-0.432986	-2.63062	-0.193024
6	-2.30967	-1.98256	-0.819951
6	-2.57386	-3.29267	-1.51917
1	-1.69868	-3.94343	-1.55095
1	-2.90433	-3.08136	-2.53838
1	-3.38698	-3.80701	-1.00139
8	-3.13592	-1.08245	-0.742158
1	-0.58074	1.86514	1.09356
6	1.04538	0.548308	-0.724099
6	3.45195	0.26501	-0.225142
6	2.77013	1.44647	-2.21116
6	3.77482	0.976319	-1.40574
1	3.00403	1.99099	-3.11896
1	4.81914	1.13925	-1.65144
6	1.41932	1.23138	-1.86129
6	2.08734	0.050664	0.101305
1	0.639297	1.62725	-2.50601
6	2.74018	-1.12555	2.06565
1	2.38697	-1.67308	2.9309
6	4.09737	-0.920161	1.79513
6	4.44295	-0.236823	0.65271
1	4.84076	-1.30907	2.47823
1	5.48786	-0.070456	0.40814
7	1.81401	-0.653383	1.24737
1	0.796236	-0.839373	1.38879

PYRIDINE

SCF energy= -814.394547595

Zero-point correction= 0.279141

Thermal correction to Energy= 0.296013

Thermal correction to Enthalpy= 0.296957

Thermal correction to Gibbs Free Energy= 0.233725

G(1M)= -814.158

Coordinates:

6	-0.316589	0.212351	0.259327
1	0.008083	-0.165979	1.23437
7	0.065933	1.61155	0.191232
7	1.396	1.84105	0.532815
7	0.22147	-0.640082	-0.815409
7	0.648742	-1.88313	-0.348644
1	0.997466	-0.14824	-1.26829
1	1.54292	2.24361	1.44788
6	2.41098	1.71071	-0.358275
6	3.78592	1.99575	0.182157
1	4.26401	1.02902	0.364726
1	3.77112	2.56559	1.11271
1	4.36133	2.53338	-0.572515
8	2.20882	1.36179	-1.51925
1	0.16495	-2.68971	-0.718641
6	1.84827	-2.01776	0.289399
6	2.24765	-3.43549	0.617035
1	1.45191	-4.15791	0.428468
1	2.53736	-3.48028	1.66862
1	3.12097	-3.6998	0.015216
8	2.5346	-1.04536	0.571041
1	-0.114293	2.0045	-0.733213
6	-1.83919	0.180587	0.21265
6	-2.6601	0.776465	1.1571
6	-4.03866	0.694331	0.998422
1	-2.20895	1.29578	1.99419
6	-3.72836	-0.545971	-1.02148
6	-4.58215	0.026563	-0.101773
1	-4.69546	1.15081	1.7307
1	-4.05154	-1.08035	-1.90503
1	-5.65225	-0.049482	-0.245068
7	-2.40132	-0.446778	-0.828734
1	-1.72731	-0.845833	-1.49464

CARBOXYLIC ACID

SCF energy= -986.419659617
Zero-point correction= 0.292253
Thermal correction to Energy= 0.312013
Thermal correction to Enthalpy= 0.312957
Thermal correction to Gibbs Free Energy= 0.242683
G(1M)= -986.174

Coordinates:

6	-0.042632	-0.129207	0.328733
1	-0.341879	0.007915	-0.712444
7	-0.23882	1.16925	0.972352
7	-1.34502	1.84894	0.456156
7	-0.877564	-1.17083	0.958364
7	-1.22415	-2.15726	0.031554
1	-1.74004	-0.718998	1.27265
1	-1.12554	2.43344	-0.340381
6	-2.61625	1.61113	0.852866
6	-3.68301	2.33449	0.071867
1	-4.14668	1.60303	-0.59646
1	-3.28975	3.16032	-0.523609
1	-4.44298	2.70591	0.760816
8	-2.87605	0.859636	1.79256
1	-0.853601	-3.08291	0.195694
6	-2.189	-1.93528	-0.899927
6	-2.53408	-3.11723	-1.77485
1	-1.86728	-3.9683	-1.62572
1	-2.49099	-2.80215	-2.81944
1	-3.56054	-3.42472	-1.55886
8	-2.74085	-0.844657	-1.00772
1	-0.369793	1.06032	1.97825
6	1.43725	-0.477418	0.371633
6	3.74674	0.038546	-0.188067
6	3.24499	-1.91924	1.10947
6	4.17826	-1.10015	0.485414
1	4.46616	0.688322	-0.673478
1	3.56834	-2.80545	1.64692
1	5.23588	-1.33934	0.523499
6	1.88753	-1.60348	1.05444
6	2.38746	0.354229	-0.255849
1	1.1616	-2.23038	1.55992
6	1.98272	1.56918	-1.02676
8	0.89977	1.7714	-1.53542
8	2.98462	2.4557	-1.13763
1	2.65604	3.19222	-1.68447

Reactants - protonated on hydrazone

QUINOLINE

SCF energy= -703.525684514
Zero-point correction= 0.227900
Thermal correction to Energy= 0.241456
Thermal correction to Enthalpy= 0.242400
Thermal correction to Gibbs Free Energy= 0.186548
G(1M)= -703.336

Coordinates:

6	0.62866	1.58958	7.9e-05
1	0.938577	2.63197	0.000393
7	1.54052	0.678645	-0.000262
7	2.87896	0.872876	0.000134
1	3.23094	1.82339	0.004467
6	3.67278	-0.26437	-0.000102
6	5.14863	0.00966	0.001029
1	5.4263	0.59003	0.884855
1	5.42813	0.582238	-0.887352
1	5.67593	-0.942789	0.005667
8	3.14547	-1.35862	-0.002064
6	-0.783052	1.26956	-0.0001
6	-1.2758	-0.078023	5.9e-05
6	-1.67719	2.32632	-0.000296
6	-2.67614	-0.292462	0.000206
6	-3.06847	2.10415	-0.000364
1	-1.29906	3.34441	-0.000384
6	-3.55749	0.821134	-5.6e-05
1	-3.74372	2.95167	-0.000782
1	-4.62788	0.637241	3e-06
6	-0.849511	-2.34132	0.00024
6	-3.13578	-1.63227	0.000462
6	-2.22519	-2.65789	0.000429
1	-0.104823	-3.13275	0.000118
1	-2.53726	-3.69539	0.000619
1	-4.20422	-1.82762	0.00068
7	-0.388611	-1.10739	1e-06
1	1.2285	-0.32669	-0.000389

PYRIDINE

SCF energy= -549.931673027
Zero-point correction= 0.179955
Thermal correction to Energy= 0.190534
Thermal correction to Enthalpy= 0.191478
Thermal correction to Gibbs Free Energy= 0.142423
G(1M)= -549.786

Coordinates:

6	0.091007	1.12056	0.008245
1	-0.029057	2.1991	0.011179
7	-0.946466	0.365978	0.012313
7	-2.24554	0.731307	0.024162
1	-2.46752	1.72039	-0.015066
6	-3.17853	-0.30279	0.008983
6	-4.6071	0.147716	-0.031505
1	-4.83983	0.524679	-1.03184
1	-4.78685	0.947831	0.689832
1	-5.24435	-0.706622	0.19089
8	-2.78269	-1.44958	0.017106
1	-0.817529	-0.661002	0.01199
6	1.40859	0.486491	0.000877
6	2.56168	1.26308	-0.002419
6	3.78731	0.596719	-0.007075
1	2.50245	2.34608	-0.000961
6	2.56792	-1.47449	-0.005009
6	3.79146	-0.789877	-0.008292
1	4.71563	1.15688	-0.009524
1	2.54271	-2.56019	-0.005984
1	4.71998	-1.34895	-0.011751
7	1.39657	-0.855293	-0.00054

CARBOXYLIC ACID

SCF energy= -722.402725011
Zero-point correction= 0.206918
Thermal correction to Energy= 0.221016
Thermal correction to Enthalpy= 0.221960
Thermal correction to Gibbs Free Energy= 0.164024
G(1M)= -722.236

Coordinates:

6	0.240828	1.28279	-0.027506
1	0.422007	2.3546	-0.041196
7	1.28482	0.534242	-0.02695
7	2.55913	0.987456	-0.046715
1	2.71119	1.98949	-0.020009
6	3.57447	0.040278	0.002447
6	4.95678	0.623691	0.041902
1	5.13735	1.06681	1.02569
1	5.07647	1.40299	-0.714311
1	5.67462	-0.176416	-0.13084
8	3.28961	-1.13854	0.019193
1	1.18044	-0.513988	-0.016917
6	-1.16283	0.87866	-0.0095
6	-2.01516	1.99337	-0.001278
6	-1.74983	-0.418933	0.000357
6	-3.39904	1.8648	0.017059
1	-1.58111	2.98791	-0.009086
6	-3.13954	-0.525429	0.017967
6	-3.9637	0.598757	0.02678
1	-4.02178	2.75209	0.02315
1	-3.58639	-1.51117	0.025127
1	-5.04059	0.473235	0.041032
6	-0.980395	-1.69843	-0.007755
8	0.235302	-1.809	-0.014676
8	-1.75794	-2.77164	-0.006748
1	-1.18517	-3.56131	-0.011961

PHENYL

SCF energy= -533.889342364
Zero-point correction= 0.192610
Thermal correction to Energy= 0.203942
Thermal correction to Enthalpy= 0.204886
Thermal correction to Gibbs Free Energy= 0.154163
G(1M)= -533.732

Coordinates:

6	0.183028	-0.237924	-0.523806
1	0.588495	-1.22343	-0.732953
7	1.02913	0.738752	-0.609254
7	2.37354	0.499515	-0.748419
1	2.86336	1.20141	-1.29204
6	3.02677	-0.186347	0.28759
6	4.52396	-0.087798	0.215274
1	4.84012	0.852354	0.677434
1	4.87428	-0.099399	-0.818885
1	4.95704	-0.920892	0.76707
8	2.39382	-0.801962	1.11319
1	0.752386	1.70763	-0.447665
6	-1.21438	-0.090632	-0.208165
6	-2.02256	-1.22497	-0.388857
6	-1.77918	1.11455	0.248035
6	-3.38623	-1.14937	-0.141761
1	-1.57793	-2.15512	-0.729714
6	-3.13972	1.17883	0.495119
1	-1.16701	1.99166	0.434477
6	-3.94194	0.050849	0.296514
1	-4.01229	-2.02265	-0.286576
1	-3.579	2.1035	0.85207
1	-5.00716	0.109694	0.495289

PHENOL

SCF energy= -609.097565398
Zero-point correction= 0.196470
Thermal correction to Energy= 0.209010
Thermal correction to Enthalpy= 0.209954
Thermal correction to Gibbs Free Energy= 0.156448
G(1M)= -608.938

Coordinates:

6	-0.012607	1.06496	0.036674
1	-0.150448	2.14364	0.042564
7	-1.08343	0.341166	0.04915
7	-2.35953	0.810932	0.079584
1	-2.5023	1.80971	-0.017302
6	-3.36153	-0.140776	0.005009
6	-4.75368	0.410016	-0.085777
1	-5.02171	0.505467	-1.1423
1	-4.84275	1.3886	0.388541
1	-5.43668	-0.296897	0.384632
8	-3.06097	-1.3195	0.003037
1	-1.04898	-0.688632	0.044963
6	1.32941	0.551003	0.012113
6	2.38212	1.48594	-0.006354
6	1.63405	-0.827871	0.005869
6	3.69829	1.06655	-0.031322
1	2.14239	2.54503	-0.000665
6	2.96039	-1.24891	-0.020247
6	3.97877	-0.304027	-0.038291
1	4.50377	1.79107	-0.045513
1	3.1869	-2.31064	-0.025026
1	5.00913	-0.643708	-0.057827
8	0.591327	-1.68537	0.026617
1	0.887392	-2.6106	0.023524

BENZOFURAN

SCF energy= -685.272495918
Zero-point correction= 0.209459
Thermal correction to Energy= 0.222561
Thermal correction to Enthalpy= 0.223505
Thermal correction to Gibbs Free Energy= 0.168737
G(1M)= -685.101

Coordinates:

6	-0.430076	1.45856	0.042347
1	-0.700453	2.51131	0.054951
7	-1.39154	0.595622	0.040142
7	-2.72106	0.878539	0.059385
1	-3.00298	1.83366	-0.132038
6	-3.57162	-0.217231	0.013499
6	-5.02654	0.121129	-0.109364
1	-5.25524	0.329712	-1.15883
1	-5.28475	1.00037	0.483978
1	-5.61061	-0.737764	0.21805
8	-3.09534	-1.3342	0.067523
1	-1.22892	-0.423078	0.040788
6	0.95464	1.07646	0.020422
6	1.95721	2.05729	0.003781
6	1.38769	-0.255393	0.00819
6	3.30831	1.70561	-0.024037
1	1.66913	3.10379	0.011506
6	2.73141	-0.630967	-0.02052
6	3.70871	0.371403	-0.036727
1	4.0568	2.48956	-0.037111
1	4.76245	0.11392	-0.058931
8	0.586376	-1.34315	0.020654
6	2.71933	-2.07711	-0.026448
6	1.42188	-2.44084	-0.001653
1	3.57068	-2.74057	-0.046137
1	0.91818	-3.39472	0.00472

DIHYDROBENZOPYRAN
SCF energy= -725.784554268
Zero-point correction= 0.262844
Thermal correction to Energy= 0.277615
Thermal correction to Enthalpy= 0.278559
Thermal correction to Gibbs Free Energy= 0.219844
G(1M)= -725.562

Coordinates:

6	0.724367	-1.57829	0.053777
1	1.07071	-2.60857	0.086625
7	1.631	-0.656746	0.046949
7	2.97537	-0.853863	0.081411
1	3.32329	-1.80419	0.030151
6	3.7602	0.283716	0.017237
6	5.23754	0.030091	-0.045358
1	5.52054	-0.152276	-1.08647
1	5.52799	-0.836449	0.551385
1	5.75558	0.919689	0.310882
8	3.22275	1.37503	-0.003121
6	-0.691564	-1.33452	0.016355
6	-1.53537	-2.4597	0.022428
6	-1.25846	-0.038766	-0.03485
6	-2.90758	-2.30191	-0.018808
6	-2.64729	0.129531	-0.063613
6	-3.44485	-1.01341	-0.055285
1	-3.55968	-3.16722	-0.013518
1	-4.52411	-0.88387	-0.069349
1	-1.09345	-3.45073	0.060363
8	-0.391337	0.99772	-0.033613
6	-3.24329	1.51804	-0.073416
6	-2.22101	2.53702	0.425703
6	-0.90916	2.31793	-0.30067
1	-1.03411	2.41356	-1.38475
1	-0.122193	2.99392	0.032519
1	-2.56521	3.55818	0.243732
1	-2.05831	2.42331	1.50282
1	1.37957	0.341586	0.016647
1	-3.55354	1.77598	-1.09326
1	-4.14417	1.531	0.546562

DIHYDROBENZOFURAN
SCF energy= -686.482760246
Zero-point correction= 0.233282
Thermal correction to Energy= 0.246985
Thermal correction to Enthalpy= 0.247929
Thermal correction to Gibbs Free Energy= 0.191973
G(1M)= -686.288

Coordinates:

6	-0.476873	1.49474	0.025932
1	-0.767447	2.54243	0.018755
7	-1.42602	0.615557	0.033716
7	-2.7604	0.882957	0.041889
1	-3.05326	1.82882	-0.175115
6	-3.59902	-0.21877	0.027996
6	-5.05852	0.10066	-0.102224
1	-5.31885	0.128747	-1.16454
1	-5.30672	1.06436	0.345788
1	-5.62986	-0.693067	0.378209
8	-3.11653	-1.33215	0.111271
1	-1.23519	-0.398812	0.050698
6	0.912255	1.14153	0.017765
6	1.90337	2.1491	-0.006827
6	1.35068	-0.188273	0.020253
6	3.24505	1.81911	-0.028972
1	1.59253	3.18939	-0.01166
6	2.69851	-0.530832	6e-05
6	3.65053	0.471135	-0.022201
1	3.99213	2.60404	-0.050975
1	4.70743	0.222977	-0.033889
8	0.519863	-1.24613	0.044688
6	2.79092	-2.03678	0.051878
6	1.31755	-2.45723	-0.130729
1	3.18885	-2.36982	1.01461
1	3.42464	-2.44668	-0.737033
1	0.966334	-3.17596	0.607459
1	1.111	-2.82617	-1.1368

CARBOXYLATE

SCF energy= -721.984949019
Zero-point correction= 0.197089
Thermal correction to Energy= 0.209889
Thermal correction to Enthalpy= 0.210833
Thermal correction to Gibbs Free Energy= 0.156563
G(1M)= -721.825

Coordinates:

6	-0.162059	-0.459981	0.822991
1	-0.320763	-0.75691	1.86241
7	-1.05835	-1.21307	-0.0068
7	-2.3997	-1.01506	0.342462
1	-2.84156	-1.81759	0.773689
6	-3.16511	-0.151573	-0.394225
6	-4.64325	-0.194286	-0.090953
1	-5.0137	0.829928	-0.023384
1	-4.8695	-0.725086	0.835429
1	-5.15903	-0.686667	-0.919968
8	-2.67409	0.579999	-1.24053
1	-0.946585	-0.93376	-0.983379
6	1.26188	-0.61545	0.357113
6	1.76727	0.64029	0.065737
6	2.03064	-1.75606	0.174384
6	3.06123	0.82691	-0.405135
6	3.33282	-1.58314	-0.295951
6	3.84455	-0.31016	-0.579922
1	3.43714	1.82067	-0.626592
1	3.96372	-2.45308	-0.448795
1	4.86184	-0.214268	-0.944575
1	1.63584	-2.74447	0.385771
6	0.703296	1.63659	0.327573
8	-0.39313	0.971003	0.771596
8	0.726133	2.83391	0.200191

Addition transition states - protonated on hydrazone

QUINOLINE

SCF energy= -967.951891105
Zero-point correction= 0.322615
Thermal correction to Energy= 0.342690
Thermal correction to Enthalpy= 0.343634
Thermal correction to Gibbs Free Energy= 0.272421
G(1M)= -967.676

Coordinates:

6	1.18273	0.455889	-0.276951
1	1.62457	1.32455	-0.753974
7	2.01432	-0.304934	0.395643
7	3.30842	0.104915	0.617216
7	0.290566	1.79104	1.24702
7	-0.730916	2.64153	0.802804
1	0.943006	2.3255	1.82289
1	3.57842	0.189722	1.59
6	4.2523	-0.091439	-0.378198
6	5.67097	0.135661	0.075618
1	6.07151	-0.806768	0.461352
1	5.73476	0.887133	0.865149
1	6.26798	0.445333	-0.781604
8	3.92585	-0.401401	-1.50493
1	-0.446527	3.34798	0.136362
6	-2.00899	2.1623	0.824697
6	-3.03659	3.01722	0.131896
1	-2.59891	3.86158	-0.403496
1	-3.74044	3.39226	0.878933
1	-3.59045	2.38795	-0.568818
8	-2.27547	1.12077	1.41222
1	1.67168	-1.19071	0.783749
6	-0.120061	-0.003797	-0.751062
6	-0.751912	0.762922	-1.71053
6	-0.788262	-1.14323	-0.197189
6	-2.05154	0.44378	-2.16191
1	-0.241369	1.62645	-2.12822
6	-2.09752	-1.44971	-0.645678
6	-2.71332	-0.634322	-1.63179
1	-2.51957	1.06132	-2.92049
1	-3.71793	-0.884424	-1.96092
1	-0.176123	1.10455	1.84857
6	-2.74548	-2.56899	-0.070204
6	-2.09608	-3.30333	0.888449
1	-2.55838	-4.16518	1.35488
6	-0.79227	-2.91568	1.26729
1	-0.25569	-3.48263	2.02362
1	-3.74947	-2.82778	-0.394441
7	-0.157237	-1.88332	0.751812

PYRIDINE

SCF energy= -814.361273051
Zero-point correction= 0.274959
Thermal correction to Energy= 0.292709
Thermal correction to Enthalpy= 0.293653
Thermal correction to Gibbs Free Energy= 0.227499
G(1M)= -814.131

Coordinates:

6	0.962851	-0.028829	-0.236559
1	1.24149	0.533172	-1.11774
7	1.82346	-0.131171	0.726464
7	3.05784	0.466221	0.67081
7	-0.374014	1.90456	0.33202
7	-1.59856	2.05405	-0.344805
1	0.05138	2.82694	0.431389
1	3.36983	0.867599	1.5475
6	3.97157	0.009298	-0.279059
6	5.37532	0.498466	-0.04933
1	5.86628	-0.161101	0.672731
1	5.38768	1.51579	0.347377
1	5.91782	0.459236	-0.993
8	3.61338	-0.692674	-1.19889
1	-1.51661	2.20334	-1.34222
6	-2.69172	1.42643	0.172862
6	-3.91755	1.42074	-0.703499
1	-3.7021	1.69103	-1.73891
1	-4.64483	2.1277	-0.29551
1	-4.36001	0.422918	-0.669569
8	-2.66486	0.942865	1.29961
1	1.59476	-0.734839	1.5208
6	-0.252335	-0.847619	-0.183942
6	-2.28954	-1.6425	-1.12998
6	-1.56837	-2.1973	1.09315
6	-2.52122	-2.29682	0.070842
1	-2.99979	-1.70928	-1.94738
1	-1.71941	-2.70936	2.0391
1	-3.41827	-2.88569	0.225463
1	-0.639405	1.59075	1.27054
7	-0.450568	-1.49486	0.97274
6	-1.12369	-0.888192	-1.26682
1	-0.895922	-0.353338	-2.18291

CARBOXYLIC ACID
SCF energy= -986.821527902
Zero-point correction= 0.302144
Thermal correction to Energy= 0.322535
Thermal correction to Enthalpy= 0.323479
Thermal correction to Gibbs Free Energy= 0.251561
G(1M)= -986.567

Coordinates:

6	-1.13621	-0.190654	0.61469
1	-1.51052	-0.0983	1.62979
7	-1.85433	0.416428	-0.282254
7	-2.9136	1.21707	0.103126
7	0.516538	1.49839	1.12464
7	1.83204	1.02714	1.11071
1	0.357341	2.11739	1.9209
1	-2.76454	2.21246	-0.041998
6	-4.23026	0.768108	-0.056933
6	-4.41456	-0.715573	-0.234898
1	-3.98006	-1.26814	0.603311
1	-3.9289	-1.05938	-1.15282
1	-5.48297	-0.917117	-0.289284
8	-5.12731	1.57747	0.005905
1	1.97874	0.128194	1.5559
6	2.94623	1.74344	0.755284
6	2.69277	3.11273	0.171511
1	2.1449	3.748	0.873265
1	2.10226	3.03811	-0.74836
1	3.65465	3.56823	-0.0584
8	4.05539	1.25011	0.875715
1	-1.55121	0.42939	-1.25897
6	-0.146702	-1.24303	0.355018
6	0.530065	-3.45386	1.10149
6	1.64235	-2.42147	-0.769251
6	1.47439	-3.50991	0.086571
1	0.409124	-4.28113	1.79178
1	2.41001	-2.44703	-1.53347
1	2.10186	-4.38661	-0.031545
1	0.337675	2.01438	0.26418
6	0.841111	-1.28923	-0.656359
6	-0.259355	-2.3154	1.24582
6	1.12127	-0.122165	-1.54273
8	0.355323	0.803984	-1.73867
8	2.32306	-0.183179	-2.10521
1	2.42598	0.590574	-2.69076
1	-0.987186	-2.26728	2.04981

PHENYL
SCF energy= -798.320269593
Zero-point correction= 0.286939
Thermal correction to Energy= 0.304951
Thermal correction to Enthalpy= 0.305895
Thermal correction to Gibbs Free Energy= 0.238278
G(1M)= -798.079

Coordinates:

6	-0.92629	-0.093754	0.127998
1	-1.19336	0.387216	1.06174
7	-1.86131	-0.102167	-0.782376
7	-3.05869	0.535669	-0.558277
7	0.275725	1.91532	-0.286641
7	1.46126	2.02823	0.461235
1	-0.180617	2.82825	-0.309144
1	-3.31852	1.22877	-1.25033
6	-4.00299	-0.094603	0.244857
6	-5.35848	0.557919	0.213478
1	-5.95352	0.090546	-0.576908
1	-5.29377	1.6289	0.012826
1	-5.85023	0.387184	1.17073
8	-3.70969	-1.06601	0.907495
1	1.33445	2.00889	1.46464
6	2.61474	1.55831	-0.094267
6	3.79583	1.46224	0.836171
1	3.54168	1.67993	1.87517
1	4.56363	2.16331	0.499668
1	4.20529	0.451619	0.766298
8	2.66911	1.27384	-1.28517
1	-1.77304	-0.630864	-1.64734
6	0.287501	-0.888514	0.051473
6	1.04389	-1.0118	1.22429
6	0.739417	-1.47198	-1.14154
6	2.24036	-1.72017	1.20782
1	0.685729	-0.563464	2.14683
6	1.93477	-2.17328	-1.15178
1	0.18235	-1.36638	-2.06779
6	2.68581	-2.29548	0.019891
1	2.82313	-1.81756	2.11752
1	2.28951	-2.61862	-2.07473
1	3.6226	-2.84316	0.0034
1	0.593149	1.71022	-1.23913

PHENOL

SCF energy= -873.525343997
Zero-point correction= 0.291503
Thermal correction to Energy= 0.310377
Thermal correction to Enthalpy= 0.311322
Thermal correction to Gibbs Free Energy= 0.242179
G(1M)= -873.28

Coordinates:

6	0.922517	0.045785	0.3743
1	1.29261	-0.132687	1.37815
7	1.79646	-0.161623	-0.584218
7	3.03088	-0.691069	-0.291667
7	-0.20488	-1.90663	0.474432
7	-1.50862	-1.81724	0.98628
1	0.256412	-2.72283	0.878364
1	3.25198	-1.5667	-0.751053
6	4.02473	0.159214	0.172735
6	5.39379	-0.467151	0.208232
1	5.87903	-0.306004	-0.759235
1	5.34833	-1.54136	0.397934
1	5.98272	0.022961	0.982906
8	3.76865	1.2914	0.523691
1	-1.57033	-1.38416	1.90024
6	-2.52186	-1.63302	0.086249
6	-3.84665	-1.22814	0.674966
1	-3.84659	-1.23472	1.76619
1	-4.61591	-1.90934	0.305759
1	-4.08653	-0.221272	0.320647
8	-2.33497	-1.80811	-1.11193
1	1.58602	0.085152	-1.5494
6	-0.287449	0.83274	0.214821
6	-0.87835	1.38031	1.36391
6	-0.925325	0.991206	-1.02916
6	-2.0553	2.10649	1.27809
6	-2.11119	1.71694	-1.11726
6	-2.66383	2.27303	0.031035
1	-2.49955	2.53493	2.16875
1	-2.59552	1.83809	-2.08145
1	-3.58769	2.83707	-0.048755
1	-0.32625	-2.07715	-0.529473
8	-0.343681	0.396407	-2.09419
1	-0.899202	0.477281	-2.88646
1	-0.392899	1.23457	2.32503

BENZOFURAN

SCF energy= -949.702123937
Zero-point correction= 0.303656
Thermal correction to Energy= 0.323377
Thermal correction to Enthalpy = 0.324321
Thermal correction to Gibbs Free Energy= 0.252855
G(1M)= -949.446

Coordinates:

6	-1.1785	-0.208818	-0.590601
1	-1.67388	-0.727235	-1.40363
7	-1.92192	0.05049	0.46004
7	-3.20094	-0.445535	0.54696
7	-0.146851	-2.16123	-0.036443
7	1.18872	-2.27382	-0.455371
1	-0.629254	-3.03918	-0.232756
1	-3.38222	-1.05288	1.33773
6	-4.22382	0.240311	-0.095483
6	-5.60172	-0.234795	0.28212
1	-5.93316	0.316538	1.16731
1	-5.61731	-1.3017	0.513373
1	-6.28318	-0.021738	-0.540758
8	-3.98357	1.122	-0.891814
1	1.32222	-2.16206	-1.45359
6	2.15138	-1.8238	0.406797
6	3.53892	-1.7145	-0.168684
1	3.54975	-1.741	-1.25992
1	4.14253	-2.54253	0.213194
1	3.9825	-0.779775	0.180076
8	1.88049	-1.58771	1.57821
1	-1.58277	0.638936	1.2199
6	0.083043	0.460555	-0.833592
6	0.661631	0.440591	-2.10703
6	0.845621	1.03556	0.185991
6	1.92576	0.996483	-2.33675
6	2.12094	1.57384	-0.011413
6	2.66603	1.55939	-1.30138
1	2.33783	0.970933	-3.33914
1	3.65413	1.96753	-1.48745
1	-0.093343	-2.05334	0.981669
8	0.492176	1.10538	1.4883
1	0.114856	-0.015904	-2.92688
6	2.55995	1.99135	1.30057
6	1.55474	1.68114	2.14512
1	1.42177	1.80037	3.20917
1	3.49994	2.45256	1.5639

DIHYDROBENZOPYRAN

SCF energy= -990.213879702
Zero-point correction= 0.357549
Thermal correction to Energy= 0.378516
Thermal correction to Enthalpy= 0.379460
Thermal correction to Gibbs Free Energy= 0.306658
G(1M)= -989.904

Coordinates:

6	-1.31037	-0.523502	-0.434903
1	-1.82568	-1.36383	-0.88883
7	-2.07075	0.258459	0.301395
7	-3.35408	-0.12025	0.618563
7	-0.376566	-1.872	1.05983
7	0.82357	-2.47099	0.651347
1	-0.966472	-2.57305	1.51059
1	-3.51901	-0.336027	1.59519
6	-4.39182	0.273988	-0.213071
6	-5.75955	0.025309	0.368482
1	-6.05177	0.894012	0.966255
1	-5.777	-0.857827	1.01026
1	-6.47126	-0.094094	-0.44771
8	-4.17851	0.757384	-1.30445
1	0.769887	-2.95519	-0.237294
6	1.99129	-1.8654	1.02166
6	3.22564	-2.34631	0.308324
1	3.55883	-1.55606	-0.372237
1	3.05409	-3.2603	-0.262716
1	4.01197	-2.51535	1.04584
8	2.00067	-0.996383	1.88672
1	-1.70414	1.12705	0.685231
6	-0.029303	-0.118328	-0.990612
6	0.419843	-0.75939	-2.15273
6	0.812283	0.79611	-0.326734
6	1.66946	-0.46236	-2.67431
6	2.08591	1.08549	-0.831209
6	2.48317	0.45565	-2.00991
1	2.01335	-0.942995	-3.58291
1	3.46669	0.689737	-2.41059
1	-0.104531	-1.18148	1.76841
1	-0.226205	-1.48279	-2.64213
8	0.321489	1.34049	0.810051
6	2.98667	2.04464	-0.091458
6	2.16011	2.94254	0.825909
6	1.2311	2.07633	1.65405
1	1.79096	1.3446	2.24361
1	0.586717	2.66348	2.30844
1	2.80476	3.51888	1.4946
1	1.56787	3.65126	0.236664
1	3.70297	1.46897	0.509249
1	3.56708	2.6339	-0.807395

DIHYDROBENZOFURAN
SCF energy= -950.911968966
Zero-point correction = 0.327943
Thermal correction to Energy= 0.348030
Thermal correction to Enthalpy= 0.348975
Thermal correction to Gibbs Free Energy= 0.277587
G(1M)= -950.631

Coordinates:

6	-1.16538	-0.322629	-0.582395
1	-1.6584	-0.940508	-1.32547
7	-1.93872	0.121767	0.389723
7	-3.21325	-0.368068	0.546034
7	-0.230861	-2.10919	0.292134
7	1.06857	-2.39042	-0.153233
1	-0.77692	-2.97197	0.300362
1	-3.37519	-0.925268	1.3769
6	-4.25466	0.250661	-0.12614
6	-5.62111	-0.215204	0.305076
1	-6.2809	-0.212944	-0.562569
1	-6.01352	0.492053	1.04163
1	-5.60042	-1.21037	0.752709
8	-4.04764	1.07906	-0.987752
1	1.15399	-2.49605	-1.15741
6	2.10251	-1.84957	0.560424
6	3.45492	-1.92585	-0.094883
1	3.41937	-2.36009	-1.09537
1	4.11513	-2.52495	0.536611
1	3.86574	-0.914483	-0.153013
8	1.9114	-1.37186	1.67307
1	-1.59451	0.807727	1.05997
6	0.094872	0.313977	-0.912266
6	0.685344	0.121873	-2.17786
6	0.829265	1.02854	0.034277
6	1.93301	0.649931	-2.46846
6	2.09168	1.54924	-0.239222
6	2.64506	1.37095	-1.49429
1	2.36683	0.497636	-3.45004
1	3.62762	1.77271	-1.72357
1	-0.116698	-1.79436	1.26192
8	0.410737	1.25261	1.29529
1	0.144575	-0.44807	-2.92835
6	2.57819	2.24425	1.00888
6	1.54167	1.77805	2.05106
1	1.15926	2.57659	2.68476
1	3.59034	1.94521	1.28983
1	1.91868	0.95383	2.65827
1	2.56662	3.33093	0.880181

CARBOXYLATE

SCF energy= -986.370214307
Zero-point correction= 0.289713
Thermal correction to Energy= 0.309789
Thermal correction to Enthalpy= 0.310733
Thermal correction to Gibbs Free Energy= 0.238807
G(1M)= -986.128

Coordinates:

6	0.174171	-0.040832	0.274861
7	-0.498093	-0.732358	1.18689
7	-1.84189	-0.971953	1.03213
1	-2.45265	-0.152457	1.07302
6	-2.28163	-2.20019	0.602374
6	-3.77888	-2.26261	0.417586
1	-4.2226	-2.75235	1.28893
1	-3.99736	-2.8676	-0.463206
1	-4.22518	-1.27188	0.305695
8	-1.53031	-3.14057	0.430302
1	-0.098163	-0.915226	2.10303
6	1.62385	0.165067	0.502746
6	2.56312	-0.196362	-0.475325
6	2.0376	0.736352	1.7118
6	3.91173	0.044534	-0.212043
6	3.38812	0.951192	1.9607
6	4.32808	0.604402	0.991747
1	4.626	-0.230773	-0.980953
1	3.70183	1.39405	2.90023
1	5.3846	0.772648	1.17682
1	1.29959	1.03544	2.45348
6	2.17326	-0.895032	-1.79168
8	1.0225	-1.40025	-1.82557
8	3.0452	-0.905518	-2.68249
7	-0.499925	1.88796	0.411464
1	0.256574	2.57509	0.433967
1	-1.0466	1.98628	1.27441
7	-1.36995	2.21085	-0.637527
1	-0.94031	2.41933	-1.52968
6	-2.68721	1.93561	-0.496737
6	-3.54807	2.16543	-1.70569
1	-3.93776	1.20022	-2.03964
1	-3.00918	2.6404	-2.52641
1	-4.39475	2.78942	-1.41353
8	-3.12334	1.52868	0.583539
1	-0.212314	-0.088214	-0.735186

Addition intermediates - protonated on hydrazone

QUINOLINE

SCF energy= -967.973307978
Zero-point correction= 0.325063
Thermal correction to Energy= 0.344730
Thermal correction to Enthalpy= 0.345674
Thermal correction to Gibbs Free Energy= 0.275349
G(1M)= -967.695

Coordinates:

6	-0.475951	0.115083	-0.558731
1	-1.12676	-0.48614	-1.20039
7	-0.817886	1.51558	-0.606085
7	-2.11919	1.78151	-1.01749
7	-0.824277	-0.299495	0.871435
7	-0.967935	-1.67789	1.07705
1	-1.7148	0.196531	1.12364
1	-2.31905	1.80472	-2.01218
6	-3.1366	1.73878	-0.118557
6	-4.50462	2.01319	-0.681
1	-5.04761	1.06527	-0.733909
1	-4.47504	2.4674	-1.67235
1	-5.03636	2.67008	0.009257
8	-2.95571	1.46129	1.0667
1	-0.10324	-2.20117	1.16101
6	-2.13113	-2.23766	0.578644
6	-2.17928	-3.73862	0.617133
1	-1.62577	-4.14294	1.4664
1	-1.73847	-4.12792	-0.305647
1	-3.22199	-4.05096	0.666108
8	-3.01687	-1.51415	0.162631
1	-0.152652	2.08347	-1.11871
6	0.975394	-0.150171	-0.861815
6	1.31037	-0.688852	-2.08252
6	2.00988	0.220114	0.051243
6	2.6615	-0.862553	-2.46151
1	0.523261	-0.977668	-2.77342
6	3.36468	0.057134	-0.33665
6	3.66873	-0.488614	-1.6097
1	2.89029	-1.28915	-3.43181
1	4.71069	-0.607357	-1.89235
1	-0.055832	0.095713	1.46619
6	4.36482	0.456301	0.585825
6	3.9978	0.963903	1.80389
1	4.73319	1.28092	2.53388
6	2.62066	1.05384	2.11321
1	2.30345	1.42195	3.08519
1	5.41079	0.351459	0.311677
7	1.66487	0.702786	1.28165

PYRIDINE

SCF energy= -814.386831614
Zero-point correction = 0.278154
Thermal correction to Energy = 0.295273
Thermal correction to Enthalpy = 0.296217
Thermal correction to Gibbs Free Energy = 0.231505
G(1M) = -814.152

Coordinates:

6	0.155116	0.429615	-0.106954
1	-0.240652	0.036952	-1.04952
7	-0.445181	1.67235	0.248649
7	-1.68028	1.94611	-0.311556
7	-0.304719	-0.568236	0.954613
7	-0.175269	-1.92241	0.602043
1	-1.30911	-0.329032	1.16576
1	-1.71335	2.39027	-1.22322
6	-2.80093	1.40956	0.239284
6	-4.09203	1.75712	-0.448773
1	-4.48316	0.851461	-0.919821
1	-3.97943	2.53824	-1.20148
1	-4.80859	2.07964	0.308968
8	-2.7584	0.667158	1.21997
1	0.789647	-2.24276	0.622717
6	-1.09869	-2.38934	-0.319707
6	-0.804388	-3.76156	-0.855271
1	-0.383953	-4.41139	-0.085498
1	-0.080002	-3.6753	-1.67103
1	-1.72784	-4.18797	-1.24514
8	-2.05554	-1.70128	-0.62011
1	0.16195	2.48128	0.294445
6	1.67081	0.470498	-0.096501
6	2.35238	1.32436	-0.95819
6	3.74201	1.32788	-0.902653
1	1.81184	1.961	-1.65153
6	3.60859	-0.336427	0.811668
6	4.38393	0.484537	-0.000949
1	4.31455	1.97806	-1.55547
1	5.46484	0.456919	0.07229
1	0.253551	-0.412595	1.80437
1	4.06889	-1.01368	1.52471
7	2.27281	-0.345756	0.768944

CARBOXYLIC ACID

SCF energy = -986.836961269
Zero-point correction = 0.306283
Thermal correction to Energy = 0.325973
Thermal correction to Enthalpy = 0.326917
Thermal correction to Gibbs Free Energy = 0.256685
G(1M) = -986.577

Coordinates:

6	-0.669087	0.099894	0.514686
1	-0.510692	0.80951	1.32914
7	-1.92201	-0.611782	0.59098
7	-2.97405	0.255787	0.902896
7	-0.823267	0.986174	-0.731583
7	0.228597	1.90352	-0.972012
1	-1.70152	1.51883	-0.61852
1	-2.98669	0.657937	1.84012
6	-4.23799	0.02659	0.369138
6	-4.32342	-0.919935	-0.800051
1	-4.06079	-1.93297	-0.482982
1	-3.6332	-0.639372	-1.59841
1	-5.34733	-0.904184	-1.17094
8	-5.1935	0.601662	0.850455
1	0.475235	2.3929	-0.11013
6	1.36604	1.51606	-1.70766
6	1.2007	0.481395	-2.78872
1	0.244029	0.560509	-3.31172
1	1.30244	-0.525318	-2.37043
1	2.00631	0.632641	-3.50666
8	2.39921	2.0983	-1.47419
1	-1.84883	-1.37766	1.26152
6	0.503335	-0.830555	0.320784
6	1.80385	-0.533509	0.777492
6	0.277935	-2.0227	-0.370888
6	2.84183	-1.43113	0.512452
6	1.32218	-2.90717	-0.629187
1	-0.723671	-2.25882	-0.716507
6	2.60788	-2.60563	-0.19482
1	3.84052	-1.19895	0.862178
1	1.12561	-3.82501	-1.17254
1	3.42925	-3.28376	-0.398657
1	-0.958079	0.386997	-1.55891
6	2.12763	0.712856	1.54187
8	1.44404	1.71845	1.57941
8	3.27733	0.615007	2.20316
1	3.4406	1.46644	2.65025

PHENYL

SCF energy = -798.344188170
Zero-point correction = 0.290079
Thermal correction to Energy = 0.307473
Thermal correction to Enthalpy = 0.308417
Thermal correction to Gibbs Free Energy = 0.242404
G(1M) = -798.099

Coordinates:

6	-0.47414	0.484776	-0.307171
1	-0.780787	0.321664	-1.34462
7	-1.4418	1.23744	0.445135
7	-2.72603	1.28144	-0.091138
7	-0.511999	-0.913627	0.332137
7	0.183506	-1.88021	-0.407152
1	-1.53057	-1.14358	0.495462
1	-2.96509	2.05562	-0.700792
6	-3.5612	0.227116	0.045619
6	-4.94797	0.414306	-0.504941
1	-5.12404	-0.340456	-1.27432
1	-5.11147	1.40837	-0.922304
1	-5.65991	0.242085	0.305544
8	-3.20583	-0.830968	0.574467
1	-0.375189	-2.42096	-1.05702
6	1.32892	-2.38118	0.188435
6	1.95737	-3.54047	-0.52699
1	1.74346	-3.52324	-1.59682
1	1.56138	-4.468	-0.102797
1	3.03363	-3.51123	-0.35879
8	1.74316	-1.87364	1.21364
1	-1.13087	2.17185	0.686064
6	0.923833	1.02592	-0.213372
6	1.73001	1.05596	-1.35044
6	3.03507	1.53492	-1.26354
1	1.33744	0.705846	-2.30083
6	2.72846	1.94714	1.09682
6	3.53252	1.98245	-0.042316
1	3.66001	1.55798	-2.15006
1	4.5489	2.35698	0.024863
1	-0.036252	-0.868671	1.25182
1	3.11643	2.29187	2.04952
6	1.4269	1.4651	1.01563
1	0.809934	1.42911	1.91088

PHENOL

SCF energy = -873.525161676
Zero-point correction = 0.294847
Thermal correction to Energy = 0.312976
Thermal correction to Enthalpy = 0.313920
Thermal correction to Gibbs Free Energy = 0.247940
G(1M) = -873.274

Coordinates:
6 -0.520341 0.064366 -0.708261
1 -0.484017 -0.33693 -1.72808
7 -1.73538 0.764628 -0.389249
7 -2.86394 0.056249 -0.813615
7 -0.559861 -1.19731 0.172824
7 0.500579 -2.10949 -0.04051
1 -1.45532 -1.68129 -0.002852
1 -3.02644 -0.008707 -1.81837
6 -4.02721 0.097233 -0.053206
6 -3.89615 0.589841 1.3648
1 -3.62769 1.64983 1.37076
1 -3.11474 0.053368 1.90717
1 -4.85653 0.449687 1.85894
8 -5.07108 -0.276438 -0.549929
1 0.638725 -2.2908 -1.03378
6 1.71266 -1.98202 0.666582
6 1.65884 -1.39095 2.0505
1 0.813646 -1.77655 2.62845
1 1.5976 -0.298236 2.00664
1 2.58483 -1.66211 2.55597
8 2.7069 -2.43126 0.148086
1 -1.70661 1.70884 -0.775122
6 0.708976 0.853909 -0.377678
6 1.90453 0.562096 -1.05093
6 0.701956 1.817 0.635694
6 3.08137 1.22199 -0.696844
6 1.87145 2.48237 0.981998
1 -0.225036 2.0293 1.16069
6 3.05786 2.17497 0.314439
1 4.00677 0.981437 -1.21191
1 1.86083 3.22683 1.76994
1 3.97879 2.68117 0.584952
1 -0.572791 -0.911588 1.16208
8 1.85574 -0.392499 -2.01443
1 2.74216 -0.556159 -2.37403

H transfer transition states

QUINOLINE

SCF energy = -967.977639934
Zero-point correction = 0.326177
Thermal correction to Energy = 0.345651
Thermal correction to Enthalpy = 0.346595
Thermal correction to Gibbs Free Energy = 0.277577
G(1M) = -967.697

Coordinates:

6	-0.443754	0.446609	-0.411479
1	-0.982653	0.317454	-1.35599
7	-0.889864	1.72055	0.132262
7	-2.27024	1.90155	0.055439
7	-0.757788	-0.707601	0.473219
7	-1.06784	-1.84804	-0.270948
1	-1.56513	-0.454895	1.05319
1	-2.57803	2.51548	-0.685751
6	-3.1473	1.40378	0.961638
6	-4.59845	1.68308	0.673381
1	-5.01985	0.770995	0.240128
1	-4.74643	2.50785	-0.025716
1	-5.11477	1.89395	1.61061
8	-2.77658	0.748238	1.93365
1	-0.432986	-2.63062	-0.193024
6	-2.30967	-1.98256	-0.819951
6	-2.57386	-3.29267	-1.51917
1	-1.69868	-3.94343	-1.55095
1	-2.90433	-3.08136	-2.53838
1	-3.38698	-3.80701	-1.00139
8	-3.13592	-1.08245	-0.742158
1	-0.58074	1.86514	1.09356
6	1.04538	0.548308	-0.724099
6	3.45195	0.26501	-0.225142
6	2.77013	1.44647	-2.21116
6	3.77482	0.976319	-1.40574
1	3.00403	1.99099	-3.11896
1	4.81914	1.13925	-1.65144
6	1.41932	1.23138	-1.86129
6	2.08734	0.050664	0.101305
1	0.639297	1.62725	-2.50601
6	2.74018	-1.12555	2.06565
1	2.38697	-1.67308	2.9309
6	4.09737	-0.920161	1.79513
6	4.44295	-0.236823	0.65271
1	4.84076	-1.30907	2.47823
1	5.48786	-0.070456	0.40814
7	1.81401	-0.653383	1.24737
1	0.796236	-0.839373	1.38879

PYRIDINE

SCF energy = -814.394547595
Zero-point correction = 0.279141
Thermal correction to Energy = 0.296013
Thermal correction to Enthalpy = 0.296957
Thermal correction to Gibbs Free Energy = 0.233725
G(1M) = -814.158

Coordinates:

6	-0.316589	0.212351	0.259327
1	0.008083	-0.165979	1.23437
7	0.065933	1.61155	0.191232
7	1.396	1.84105	0.532815
7	0.22147	-0.640082	-0.815409
7	0.648742	-1.88313	-0.348644
1	0.997466	-0.14824	-1.26829
1	1.54292	2.24361	1.44788
6	2.41098	1.71071	-0.358275
6	3.78592	1.99575	0.182157
1	4.26401	1.02902	0.364726
1	3.77112	2.56559	1.11271
1	4.36133	2.53338	-0.572515
8	2.20882	1.36179	-1.51925
1	0.16495	-2.68971	-0.718641
6	1.84827	-2.01776	0.289399
6	2.24765	-3.43549	0.617035
1	1.45191	-4.15791	0.428468
1	2.53736	-3.48028	1.66862
1	3.12097	-3.6998	0.015216
8	2.5346	-1.04536	0.571041
1	-0.114293	2.0045	-0.733213
6	-1.83919	0.180587	0.21265
6	-2.6601	0.776465	1.1571
6	-4.03866	0.694331	0.998422
1	-2.20895	1.29578	1.99419
6	-3.72836	-0.545971	-1.02148
6	-4.58215	0.026563	-0.101773
1	-4.69546	1.15081	1.7307
1	-4.05154	-1.08035	-1.90503
1	-5.65225	-0.049482	-0.245068
7	-2.40132	-0.446778	-0.828734
1	-1.72731	-0.845833	-1.49464

Addition intermediates – deprotonated

QUINOLINE
SCF energy = -967.529528342
Zero-point correction = 0.312536
Thermal correction to Energy = 0.332013
Thermal correction to Enthalpy = 0.332957
Thermal correction to Gibbs Free Energy = 0.263609
G(1M) = -967.263

Coordinates:

6	-0.383984	-0.155987	-0.507082
1	-0.992262	-0.796928	-1.15655
7	-0.557307	1.20194	-1.00774
7	-1.89365	1.50316	-1.28333
7	-0.839224	-0.3221	0.898863
7	-1.41062	-1.5812	1.08795
1	-1.55606	0.380613	1.09017
1	-2.16104	1.41939	-2.25377
6	-2.77442	1.94816	-0.358494
6	-4.18043	2.16095	-0.859271
1	-4.77523	1.30676	-0.522903
1	-4.24315	2.22842	-1.94697
1	-4.58785	3.06771	-0.410042
8	-2.45178	2.14867	0.812071
1	-0.887814	-2.23494	1.65325
6	-2.69004	-1.83475	0.710641
6	-3.21286	-3.2093	1.05611
1	-2.44492	-3.86847	1.46481
1	-3.63294	-3.65927	0.15414
1	-4.01941	-3.10482	1.78638
8	-3.37066	-0.989491	0.137039
1	-0.181852	1.87123	-0.336392
6	1.05934	-0.59909	-0.614349
6	3.44823	-0.301398	-0.110476
6	2.69771	-2.27193	-1.29126
6	3.72016	-1.54129	-0.747633
1	2.89819	-3.22059	-1.77851
1	4.74711	-1.89309	-0.794025
6	1.36532	-1.79293	-1.22042
6	2.11205	0.177494	-0.03845
1	0.564856	-2.38727	-1.65376
6	2.77681	2.071	1.08414
1	2.49507	3.01182	1.55333
6	4.13827	1.68182	1.06584
6	4.4687	0.495823	0.466313
1	4.88803	2.32147	1.51763
1	5.49924	0.153261	0.422747
7	1.80085	1.3639	0.561976

PYRIDINE

SCF energy = -813.945592233
Zero-point correction = 0.265193
Thermal correction to Energy = 0.282094
Thermal correction to Enthalpy = 0.283038
Thermal correction to Gibbs Free Energy = 0.218650
G(1M) = -813.724

Coordinates:

6	-0.210432	0.35462	0.098124
1	0.104381	-0.043254	1.07311
7	0.351785	1.69295	0.013145
7	1.65053	1.77437	0.519754
7	0.277179	-0.520706	-0.987522
7	0.25992	-1.86319	-0.594491
1	1.25284	-0.277547	-1.16672
1	1.72917	2.23909	1.41374
6	2.75555	1.51048	-0.220724
6	4.07161	1.71691	0.486392
1	4.54256	0.73772	0.607509
1	3.96556	2.18363	1.46694
1	4.71946	2.32967	-0.143205
8	2.68394	1.11979	-1.38321
1	-0.630702	-2.32216	-0.734025
6	1.22587	-2.35778	0.218529
6	1.03974	-3.79208	0.65466
1	0.132479	-4.24523	0.251265
1	1.00355	-3.82334	1.74636
1	1.90644	-4.37376	0.332044
8	2.20471	-1.68724	0.53944
1	0.353838	2.02258	-0.953141
6	-1.73425	0.417345	0.066063
6	-2.42288	1.53162	0.54608
6	-3.81365	1.51725	0.525869
1	-1.86825	2.38697	0.912859
6	-3.69292	-0.673631	-0.410203
6	-4.46833	0.391842	0.037255
1	-4.37649	2.37382	0.884018
1	-4.16568	-1.5737	-0.796594
1	-5.55053	0.335051	0.000897
7	-2.35794	-0.670468	-0.40191

CARBOXYLIC ACID

SCF energy = -986.419659617
Zero-point correction = 0.292253
Thermal correction to Energy = 0.312013
Thermal correction to Enthalpy = 0.312957
Thermal correction to Gibbs Free Energy = 0.242683
G(1M) = -986.174

Coordinates:

6	-0.042632	-0.129207	0.328733
1	-0.341879	0.007915	-0.712444
7	-0.23882	1.16925	0.972352
7	-1.34502	1.84894	0.456156
7	-0.877564	-1.17083	0.958364
7	-1.22415	-2.15726	0.031554
1	-1.74004	-0.718998	1.27265
1	-1.12554	2.43344	-0.340381
6	-2.61625	1.61113	0.852866
6	-3.68301	2.33449	0.071867
1	-4.14668	1.60303	-0.59646
1	-3.28975	3.16032	-0.523609
1	-4.44298	2.70591	0.760816
8	-2.87605	0.859636	1.79256
1	-0.853601	-3.08291	0.195694
6	-2.189	-1.93528	-0.899927
6	-2.53408	-3.11723	-1.77485
1	-1.86728	-3.9683	-1.62572
1	-2.49099	-2.80215	-2.81944
1	-3.56054	-3.42472	-1.55886
8	-2.74085	-0.844657	-1.00772
1	-0.369793	1.06032	1.97825
6	1.43725	-0.477418	0.371633
6	3.74674	0.038546	-0.188067
6	3.24499	-1.91924	1.10947
6	4.17826	-1.10015	0.485414
1	4.46616	0.688322	-0.673478
1	3.56834	-2.80545	1.64692
1	5.23588	-1.33934	0.523499
6	1.88753	-1.60348	1.05444
6	2.38746	0.354229	-0.255849
1	1.1616	-2.23038	1.55992
6	1.98272	1.56918	-1.02676
8	0.89977	1.7714	-1.53542
8	2.98462	2.4557	-1.13763
1	2.65604	3.19222	-1.68447

PHENYL

SCF energy = -797.906499987
Zero-point correction = 0.277051
Thermal correction to Energy = 0.294172
Thermal correction to Enthalpy = 0.295116
Thermal correction to Gibbs Free Energy = 0.230057
G(1M) = -797.673

Coordinates:

6	-0.297196	0.269397	0.129011
1	0.032167	-0.072746	1.11889
7	0.142527	1.65847	0.031511
7	1.45421	1.84981	0.473612
7	0.305043	-0.583798	-0.914325
7	0.519837	-1.87912	-0.441264
1	1.21109	-0.189015	-1.17289
1	1.53679	2.24238	1.40078
6	2.54707	1.67608	-0.305911
6	3.87009	1.92307	0.373317
1	4.34419	0.949358	0.525431
1	3.77161	2.42339	1.33815
1	4.50541	2.51661	-0.286099
8	2.4623	1.32681	-1.48215
1	-0.053725	-2.60813	-0.842656
6	1.62696	-2.17153	0.291131
6	1.80842	-3.62797	0.647142
1	0.955055	-4.24624	0.363268
1	1.96882	-3.70616	1.72446
1	2.70471	-4.0028	0.146207
8	2.42213	-1.29957	0.627118
1	0.066677	1.99739	-0.928201
6	-1.81602	0.229058	0.072362
6	-2.54037	0.862293	1.08762
6	-2.50478	-0.41878	-0.950592
6	-3.93011	0.847893	1.08047
1	-2.00265	1.3728	1.88285
6	-3.90068	-0.434582	-0.959743
1	-1.94387	-0.905493	-1.74142
6	-4.61576	0.196699	0.052938
1	-4.48039	1.3428	1.87501
1	-4.42698	-0.942188	-1.76258
1	-5.7014	0.182796	0.045814

Others:

WATER

SCF energy= -76.3811217565

Zero-point correction= 0.021452

Thermal correction to Energy= 0.024287

Thermal correction to Enthalpy= 0.025231

Thermal correction to Gibbs Free Energy= 0.003789

G(1M)= -76.3743

G(55.5M)= -76.370525

Coordinates:

8	-0	-0	-0.119699
1	-0	-0.759495	0.478795
1	-0	0.759495	0.478795

HYDRONIUM

SCF energy= -76.7766326997

Zero-point correction= 0.035131

Thermal correction to Energy= 0.037995

Thermal correction to Enthalpy= 0.038939

Thermal correction to Gibbs Free Energy= 0.017025

G(1M)= -76.7566

G(pH 7)= -76.771801

Coordinates:

8	-0	-0	-0.088954
1	-0	-0.929587	0.23721
1	-0.805046	0.464793	0.23721
1	0.805046	0.464793	0.23721

Kw based correction = 19.4559942 kcal/mol

HYDROXIDE

SCF energy= -75.8262734362

Zero-point correction= 0.008337

Thermal correction to Energy= 0.010698

Thermal correction to Enthalpy= 0.011642

Thermal correction to Gibbs Free Energy = -0.007933

G(1M) = -75.8312

G(pH 7) = -75.8463994

Coordinates:

8	-0	-0	-0.108219
1	-0	-0	0.865756

References:

1. B. Levrand, W. Fieber, J. M. Lehn and A. Herrmann, Controlled Release of Volatile Aldehydes and Ketones from Dynamic Mixtures Generated by Reversible Hydrazone Formation, *Helv. Chim. Acta*., 2007, **90**, 2281-2314.