ADVANCES IN SUPRAMOLECULAR CATALYSIS: STUDIES OF BIFURCATED HAMILTON RECEPTORS

by

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A DISSERTATION

Presented to the Department of Chemistry and Biochemistry
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DISSERTATION ABSTRACT

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Bidentate ligands are a commonly used class of ligands in catalysis that generate highly-active and selective catalysts. Such bidentate ligands, however, often suffer from synthetic challenges, which can be alleviated by the use of simpler monodentate ligands that assemble through non-covalent interactions to mimic the structure of bidentate ligands at the metal center. To produce a strongly assembled catalyst complex, the Hamilton receptor motif was utilized. Hamilton receptors form six hydrogen bonds with complementary guests and have binding affinities for barbiturates of up to 10^4 M^{-1} in $CDCl_3$. Complete bifurcation of the Hamilton scaffold produces a modular ligand structure that allows for modification of either end of the supramolecular ligand structure. Similarly, the barbiturate guest can be synthetically altered creating both chiral guests and guests with differing amounts of steric bulk.

Both experimental titration data and density functional theory calculations show that steric bulk discourages binding of the guest while a pre-organized host encourages guest inclusion. Electronic effects on the bifurcated Hamilton system were studied by varying the electron donating or withdrawing ability of the benzamide moiety on the host molecule. Electron withdrawing moieties produce more acidic amide hydrogens on the host which are able to participate in stronger hydrogen bonds with the guest resulting in a stronger host-guest complex.

The effects of substitutions on the barbiturate guest were examined as well, and increased steric bulk on the guest resulted in decreased affinities with the host.

The bifurcated Hamilton receptor ligands were examined in the palladium-catalyzed Heck reaction of iodobenzene with butyl acrylate. $Pd_2(OAc)_4$ was used as a control, and all reaction yields with the diphenylphosphine ligand-stabilized Pd were greater than or equal to those obtained with $Pd_2(OAc)_4$ alone. The reaction rates did not correlate with the determined binding constants, suggesting that phosphine substitution on the guest plays a larger role than affinity of the complex for the guest. Reaction temperatures were varied, and at lower temperatures the yields increased implying that the strength of the hydrogen bonds between the metal complex and the guest does play a secondary role in the catalysis.

This dissertation includes previously published co-authored material.

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CHAPTER I

TRANSLATING TRADITIONAL BIDENTATE LIGANDS TO SUPRAMOLECULAR BIDENTATE LIGANDS

Traditional Catalysis

Catalysts are used to produce many commercially available products, ranging from the rubber found in car tires to complex pharmaceuticals. Such catalysts can be composed of bare metal, metal ions bound by stabilizing ligands, or organocatalysts that do not require a metal. A major benefit of catalysis is that allows access to alternative reaction pathways than the uncatalyzed reaction, often requiring lower temperatures, shorter reaction times, or providing greater product selectivity. These beneficial properties generally reduce the overall amount of energy that is required to carry out the reaction. New strategies for developing active and selective catalysts that provide access to important classes of compounds and reactions are important for energy economy.

Transition metal catalysts can provide new reactivity of known reactions or generate completely new reaction pathways to complex synthetic targets. Catalysts are added to reaction mixtures in small amounts, often as low as 1%, producing minimal waste as opposed to main-group reagents. Transition metal catalysis appeared industrially as early as the 1930s when cobalt complexes were exploited in hydroformylation reactions. Since then, the use of transition metal catalysis in industry has exploded, and catalysts are now commonly used in major industrial processes including the polymerization of alkenes to yield polyethylene and polypropylene, hydrocyanation of butadiene for nylon manufacture, acetic acid production from MeOH and CO, and hydrosilylation in the manufacturing of silicone materials.[1]

Transition metals are used in both heterogeneous and homogenous catalysis. In heterogeneous catalysis, the catalyst is typically a metal or metal oxide surface and is not soluble in the reaction mixture containing the reactants. By contrast, homogenous catalysts are often comprised of a metal ion stabilized by ligand components and are soluble in the same phase that contains the reactants. Commonly-used ligands for transition metal catalysts are often neutral or anionic and can be monodentate, bidentate, or polydentate. Monodentate ligands have one donor moiety that binds to the metal center, whereas bidentate ligands have two donor moieties that attach to the metal canter.[1] Phosphines, PR_3, are an important class of ligands for transition metals because they are one of the few types of ligands in which the electron donating ability and steric bulk can be modulated in a methodical and predictable way. Phosphine ligands can also stabilize a wide variety of metal oxidation states due to the moderate hardness and π-accepting ability of phosphines. This dichotomy means that phosphine based ligands are able to both donate their lone pair to the metal center as well as accept electrons from the metal center through back-bonding.[2] The steric bulk of the ligand can be easily modified by changing the substituents on the phosphine ranging from PMe_3 to more sterically demanding groups like $P(o\text{-tolyl})_3$. Bulky ligands limit the number of phosphines that can bind to a metal center and can encourage the binding of smaller, weakly binding reagents that would usually be excluded by direct competition with smaller phosphine ligands. When smaller substituents are present on the phosphine ligand, the metal center can often bind more ligands, which often limits substrate binding to the metal center.[3,4] Bidentate ligands are subject to the chelate effect making them harder to dissociate from the metal center. This effect produces a more stable complex and also forces the ligands to bind the metal in a cis fashion. Bidentate ligands often produce the most selective and active catalyst for a given reaction.[5] Taken together, the ability to moderate both steric bulk and electron density is paramount to developing active catalyst complexes.

Supramolecular Catalysis

Bidentate ligands have dominated the field of asymmetric transition metal catalysis for years. One challenge when using bidentate ligands, however, is that they are often difficult to synthesize. One way to alleviate this synthetic challenge is to use simpler to make monodentate ligands that can assemble through non-covalent interactions to generate pseudo-bidentate ligands. Taking mondentate ligands and engineering non-covalent interactions between them creates a bidentate ligand from two monodentate ligands as shown in Figure 1.1. The more non-covalent interactions that can be engineered between the two mondentate ligands, the more bidentate nature the assembled ligand will display. Because monodentate ligands are often easier to synthesize, the often modular synthesis makes incorporation of different moieties facile and provides access to a large catalyst library with significantly less effort than for bidentate ligands. Such self-assembled, supramolecular ligands gain their bidentate nature either from directly non-covalent interaction with the other ligand or through binding of a third complementary guest.[6,7]

Briet and co-workers have engineered a hydrogen bonded supramolecular catalyst inspired by DNA base pairing. They prepared the diphenylphosphine derivatives of 2-pyridone and hydroxypyridone shown in Figure 1.2. This system, 6-DPPon, generated quantitative yields and 96:4 linear:branched products in the rhodium catalyzed hydroformylation of terminal alkenes. This assembled system is just as active as Xantphos, a rigid bidentate ligand normally used in hydroformylation reactions.[8] Computational studies were performed and showed that the hydrogen bonding between the self-assembled ligands is active throughout the catalytic cycle. Experimentally, Breit and co-workers found that the hydrogen bonding is necessary for the active catalyst complex, as evidenced by the observation that methylation of the nitrogen interferes with the hydrogen bonding network and results in an inactive catalyst.[9]

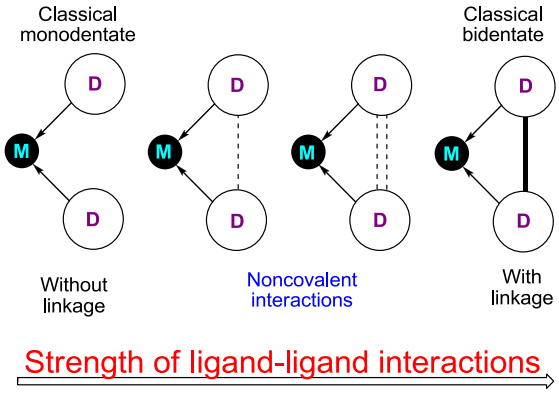


Figure 1.1. Depiction of classical monodentate ligands without any linkage between the ligands, classical bidentate ligands with a covalent linkage between the two ligands, and supramolecular bidentate ligands with noncovalent linkages between the ligands.

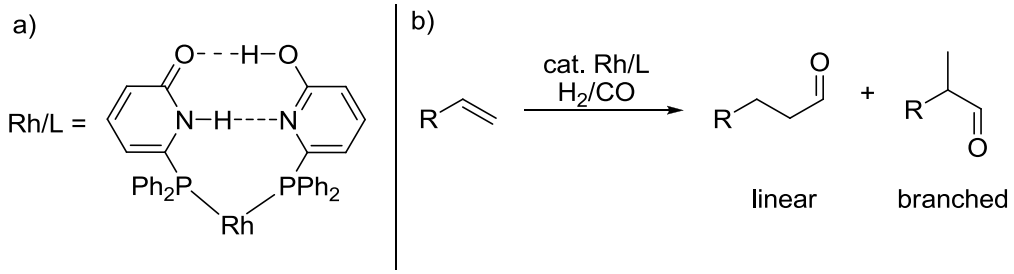


Figure 1.2. a) Hydrogen bonded 6-DPPon system devised by Breit and co-workers. b) The Rh catalyzed hydroformylation that was screen using 6-DPPon.

Another example of self-assembled ligands used for supramolecular catalysis was a three-component ligand system developed by Reek and co-workers. This system produced a hydrogen bonded ligand scaffold that coordinated a metal center in the *trans* geometry as shown in Figure 1.3. The two urea groups on the ligands can either form an intermolecular hydrogen bond or, alternatively, can bind a chloride ion with an association constant of $10^2\ M^{-1}$. Binding of the chloride ion into the self-assembled complex results in the activation of the catalyst by locking the ligands in a *trans* coordination geometry with respect to the metal. Although the *bis*-

urea pocket was not able to abstract chloride from the metal center on its own, the addition of a third equivalent of ligand to the metal center resulted in abstraction of the chloride ion from the metal center. Additionally, chloride abstraction by the bis-urea pocket from the metal center occurred if the metal complex was cooled and CO added. Upon warming, CO migratory insertion occurred creating an acetyl group followed by chloride ion migration to the metal center, regenerating a neutral complex.[10]

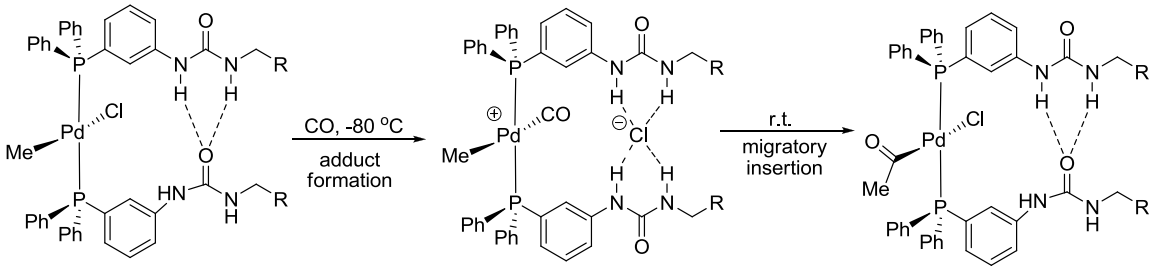


Figure 1.3. Hydrogen bonded *trans* phosphine ligand system developed by Reek et al.

Screening of Supramolecular Catalysts

Trial and error is often a common strategy to determine which catalyst/ligand pairs provide the most active catalytic system. Because this process is often time and material intensive, new methods to generate large libraries and screen them quickly are highly desirable. One benefit of self-assembled ligands is that these supramolecular systems can be used to generate large ligand libraries due to the modular nature of the self-assembly process. For example, Briet and co-workers systematically derivatized their 2-pyridone and hydroxypyridone ligand structure to generate 120 discrete, self-assembled catalyst complexes (Figure 1.4), demonstrating the high level of versatility provided by self-assembled systems. Breit and co-workers applied an iterative deconvolution strategy to the identify the optimal catalyst complex. The ligand library was first divided into 4 groups on the basis of the self-assembly platform, 2 groups of 24 catalyst complexes and 2 groups of 36 catalyst complexes. Each ligand group was

mixed together in the presence of Rh and then the catalyst mixtures were screened in the Rh-catalyzed asymmetric hydrogenation of *N*-acetamidoacrylate. The 4 reaction mixtures were then analyzed by GC to determine the reaction yield and enantioselectivity. The group that displayed the highest activity and enantioselectivity was divided further into 9 groups of four catalyst complexes. After these 9 groups were screened, the most active and selective group of catalysts was again selected and divided further into 4 groups with 1 catalyst complex in each group. This iterative deconvolution stragety yielded 3 catalyst complexes (out of 120 complexes) that displayed quantativie yields and 99% e.e. for the formation of (*R*)-N-acetylaminopropionic acid in just 17 reactions.[11]

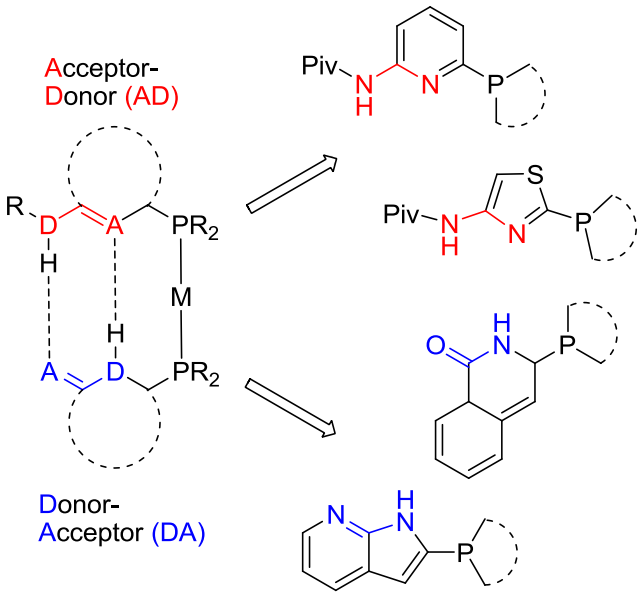


Figure 1.4. Derivatives of the 6-DPPon system created by Breit and colleagues for use in high throughput screening.

Developing a ligand architecture that can bind a third ligand component to generate a three-component, rather than a two component ligand system, would lead to further diversification of the catalyst complexes because both the ligand and guest components can be modified. By modeling the ligand system on well-defined host-guest architectures, this assembly

process can be simplified, thus facilitating generation of strongly-bound catalyst complexes. Quickly discovering a strongly bound metal complex means more time can be spent studying the activity of this new class of catalysts rather than focusing on the engineering of new hydrogen bonded complexes. Additionally, working with a known system provides the researcher with known limitations and reasonable expectations of how to adjust the system to mitigate encountered problems.

Hamilton Receptors

Hamilton receptors are a well-studied host system with high binding affinities for complementary guests of up to 10^5 M^{-1} in $CDCl_3$,[12] shown in Figure 1.5. Due to this strong for affinity for guests, Hamilton receptors have been employed in many supramolecular architectures and have found applications from catalysis to polymers. Both the host and the guest can be modified resulting in a plethora of available constructions. The host has a very modular synthesis and can be either macrocyclic, open, or completely bifurcated depending on the researcher's needs.[13] Different R groups can be appended to the barbiturate fragment which can also modulate the binding affinity of the Hamilton receptor for the barbiturate guest.[14]

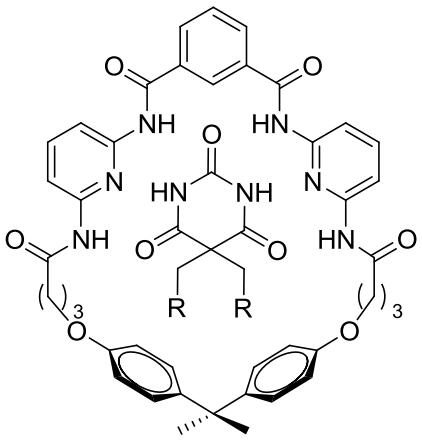


Figure 1.5. Original macrocyclic Hamilon receptor with bound guest.

Demonstrating the versatility of the Hamilton receptor motif, Isied and co-workers created a modified Hamilton host and a decorated barbiturate to probe what effect hydrogen bonding has on the mechanism and rate of photo electron transfer. To that end, they designed a barbituric acid guest with an appended ruthenium (II) polybipyridine derivative and a Hamilton receptor with a nitrogen atom present in the aromatic bridge tethering the hydrogen bonding moieties on the host. The decorated barbituric acid shown in Figure 1.6 is bound by their modified Hamilton receptors up to 2 orders of magnitude more tightly that barbital. Loss of the highly acidic proton on the 5 position of the barbiturate results in an enolate with the net negative charge on the adjacent carbonyl oxygens causing this increase in binding affinity. The system was able to undergo electron transfer from the host to the metal center across the 1.8 nm hydrogen bonded network demonstrating that hydrogen bonded networks do not retard electron transfer.[15]

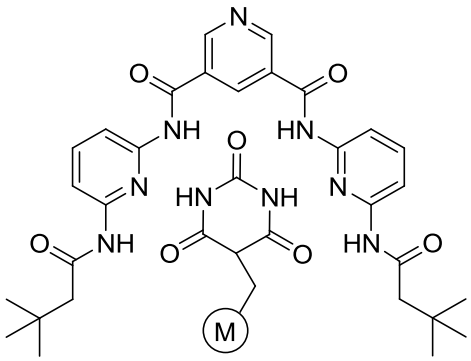


Figure 1.6. Modified Hamilton receptor with barbituric acid guest decorated with ruthenium (II) polybipyridine derivative designed by Iseid and associates.

Skrydstrup and co-workers unilitzed Hamilton receptors to combine molecular recognition and transition metal catalysis in their metal complex picture in figure 1.7. Skrydstrup has used their open Hamilton receptors to aid in the stabilization of their metal complex.

Decorating a barbiturate with a reactive moiety will allow both the ligands to interact with the guest. In this catalyst complex, the positioning of the metal bound aryl group is determined by the molecular recognition event. In the absence of the molecular recognition event, this particular positioning of the aryl group is not favored. The ability to control coordination at the metal center with a molecular recognition event would provide interesting avenues for new catalyst properties and reactivities.[16]

To create a new class of supramolecular ligands for transition metal catalysis, a strongly bound complex with accessible variations is needed. The Hamilton receptor motif is versatile, can be readily modified, and has high affinity for complimentary guests. The malleable nature of the barbiturate guests will generate further diversity in the assembled catalyst complexes. The Hamilton receptors can be macrocyclic, open, or completely bifurcated. Complete bifurcation of the Hamilton receptors allows easy modification of the donor moieties as well as the moieties at the end of the ligand.

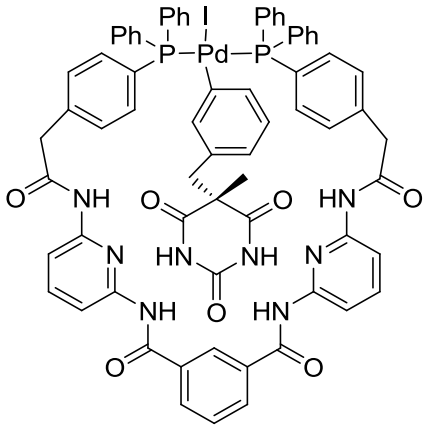


Figure 1.7. Open Hamilton receptor with guest and metal bound created by Skrydstrup and co-workers

The Hamilton receptor motif was used to create a new series of supramolecular bidentate ligands for transition metal catalysis. Triphenylphosphine based anchoring groups were employed

for metal attachment. The binding affinity of Hamilton receptors with varying amounts of steric bulk, pre-organization, and different electronic characteristics has been determined and used to produce a strongly bound metal complex. The binding affinity of the bifurcated Hamilton receptors for a series of synthetically produced barbiturates has also been probed demonstrating how the guest structure plays a role in the overall stability of the complex. The assembled catalyst complexes have been tested in the palladium catalyzed Heck coupling of iodobenzene with butyl acrylate and was found to be catalytically active.

Co-author Information

Chapter II contains work co-authored by Jacqueline M. McGrath and Michael Pluth.

Chapter III contains work co-authored by Jacqueline M. McGrath and Michael Pluth.

CHAPTER II

UNDERSTANDING THE EFFECTS OF PRE-ORGANIZATION, RIGIDITY, AND STERIC INTERACTIONS IN SYNTHETIC BARBITURATE RECEPTORS

The work on the series of Hamilton receptors with varying amounts of pre-organization, rigidity, and steric bulk and with complementary guests was published in volume 79, issue 2, pages 711–719 in *The Journal of Organic Chemistry* in January 2014. Jacqueline M. McGrath performed all the synthesis, purification, and titrations. The computational work was performed by Michael D. Pluth. Michael D. Pluth was the principles investigator for this work.

Preface

Synthetic barbiturate receptors have been utilized for many applications due to their high binding affinities for complementary guests. Although interest in this class of receptors spans from supramolecular to materials chemistry, the effects of receptor steric bulk and pre-organization on guest binding affinity has not been studied systematically. To investigate the roles that steric bulk and pre-organization play in guest binding, we prepared a series of 12 deconstructed Hamilton receptors with varying degrees of steric bulk and pre-organization. Both diethylbarbital and 3-methyl-7-propylxanthine were investigated as guests for the synthetic receptors. The stoichiometry of guest binding was investigated using Job plots for each host-guest pair, and ^{1}H NMR titrations were performed to measure the guest binding affinities. To complement the solution-state studies, DFT calculations at the B3LYP/6-31+G(d,p) level of theory employing the IEF-PCM $CHCl_3$ solvation model were also performed. Calculated guest

binding energies correlated well with the experimental findings and provided additional insight into the factors influencing guest binding. Taken together, the results presented highlight the interplay between pre-organization and steric interactions establishing favorable interactions for self-assembled hydrogen-bonded systems.

Introduction

Hydrogen-bonding interactions are a widely-used structural arrangement found in many synthetic supramolecular structures. Although individual hydrogen bonds are much weaker than covalent bonds, hydrogen-bonding interactions commonly form cooperative networks when multiple donor and acceptor components combine. The fidelity of such networks can be maximized by encoding attractive primary and secondary interactions in the hydrogen-bonding structures[17,18] or by increasing the pre-organization of hydrogen-bonding components to reduce the entropic cost for self-assembly.[19] Similarly, the reversibility of hydrogen-bond formation allows for errors in the assembly process to be repaired, leading to formation of the thermodynamically-favored product. By engineering complementary hydrogen-bonding arrays into geometrically-controlled molecular components, larger self-assembled structures, including foldamers, homo- and hetero-multimeric structures, and cavity-containing 3D supramolecular host molecules can be accessed.[20-31]

One such class of self-assembled hydrogen-bonded host-guest complexes are synthetic barbiturate receptors. Also known as Hamilton receptors, this well-studied class of macrocyclic synthetic receptors bind barbituric acid derivatives in complimentary, pre-organized hydrogen-bonding motifs (Figure 2.1).[32-37] Such receptors typically employ two hydrogen-bond donor-acceptor-donor (DAD) units that align with the two acceptor-donor-acceptor (ADA) faces of the barbiturate. The macrocyclic pre-organization found in most prototypical synthetic barbiturate receptors results in high guest binding affinities ranging from $10^4 - 10^5$ M^{-1}.[32,38] In addition to

binding barbiturates, this class of receptors accommodates other guests with the appropriate complementary hydrogen-bonding arrays including uracils,[39-42] thymines,[39,40,42-46] succinimides,[40,47] glutarimides,[34,40,48] cyanuric acids,[39,49-51] and dipyridine-2-ylamines,[47,48] demonstrating the versatility of the receptor scaffolds. This diversity has resulted in the use of synthetic barbiturate receptors in different applications including catalysis,[16,52,53] electrooptical materials,[50,51,54] and supramolecular dendrimers.[49,55,56] Despite the prevalence of this receptor motif in various disciplines, the impacts of ligand pre-organization, such as the importance of the macrocyclic effect or of ligand flexibility, remain unexplored.

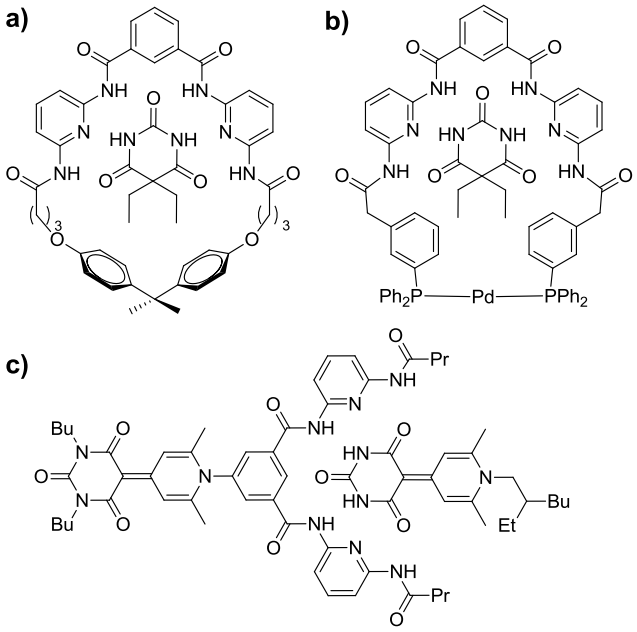


Figure 2.1. Selected examples of synthetic barbiturate receptors. (a) Prototypical Hamilton receptor; (b) chelating *bis*(phosphine) barbiturate receptor; and (c) highly-conjugated non-macrocyclic barbiturate receptor.

Although non-macrocyclic barbiturate receptors have been prepared, studies of such scaffolds have primarily focused on interactions in the solid state. For example, though non-macrocyclic barbiturate receptors have been thoroughly exploited in the solid state to bind nanoparticles to surfaces,[57-59] the solution state binding behavior of these receptors has not been

investigated comprehensively. Investigation of such systems could provide valuable insight into the interplay between steric interactions near the hydrogen-bonding moieties and the requirements of pre-organization required for efficient guest binding.

Toward our goal of understanding the assembly requirements of deconstructed supramolecular systems, and to probe the requirements of ligand rigidity, macrocylization, and pre-organization on barbiturate receptor designs, we have systematically deconstructed barbiturate receptors into simple subunits to determine the effects of ligand bifurcation on barbiturate binding. By measuring the binding affinities and stoichiometries of both barbital and xanthine guests with rigid, flexible, or bifurcated ligands, we directly investigated the pre-organization requirements for self-assembly. To complement the experimental results, we also screened and refined different DFT computational methods to generate a model that correlated well with solution data. Taken together, these results help to establish the requirements for effective barbiturate binding in synthetic host molecules and can be applied to other host-guest systems in which receptor pre-organization is a requirement for self-assembly.

Results and Discussions

To further understand the effect that pre-organization and steric interactions play in determining the guest binding affinities of barbiturate receptors, we deconstructed prototypical macrocyclic barbiturate receptors into more simple subunits (Figure 2.2). The impacts of steric constraints on guest binding were investigated by preparing a library of symmetric (**1a-c**) or unsymmetric (**1d-f**) bifurcated hosts with methyl, phenyl or *tert*-butyl groups on the peripheral amides. Similarly, the role of pre-organization on self-assembly was investigated by preparing two receptor sets with either a flexible alkyl spacer between the two 2,6-dicarboxamido pyridine units (**3a-c**) or a rigid phenyl spacer between the 2,6-diamidopyridine units (**4a-c**). Both barbital (**5**) and 3-methyl-7-propylxanthine (**6**) were used as guests to investigate the structures and stoichiometries of the hydrogen-bonded constructs.

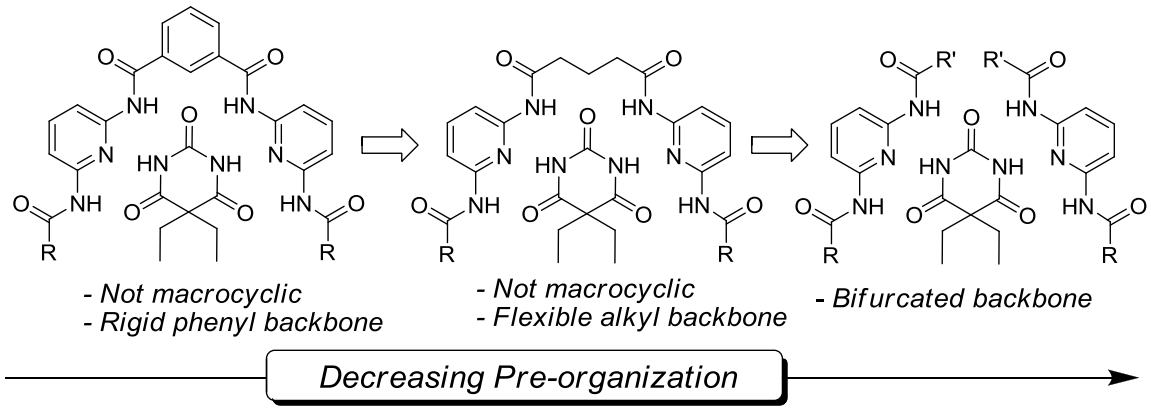
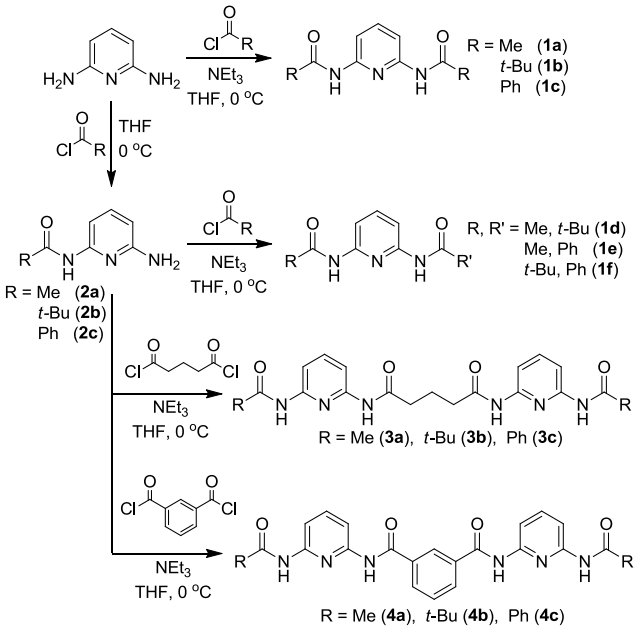


Figure 2.2. Deconstruction of Hamilton receptors to determine effects of pre-organization and steric bulk.

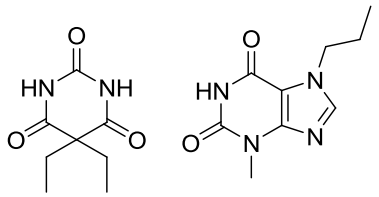
Synthesis. Symmetric 2,6-dicarboxamido pyridine hosts **1a-c** were prepared from 2,6-diaminopyridine by reaction with the desired acid chloride in the presence of triethylamine. To prepare unsymmetric 2,6-dicarboxamido pyridine receptors **1d-f**, 2,6-diaminopyridine was first reacted with one equivalent of the desired acid chloride in the absence of base to afford mono-amido pyridines **2a-c**, followed by installation of a second amide by treatment with a second acid chloride (Scheme 2.1). Non-macrocyclic barbiturate receptors were prepared with both flexible and rigid linkers between the two 2,6-dicarboxamido pyridine units. Treatment of glutaric acid with $SOCl_2$ afforded glutaryl chloride, which was treated with mono-amide **2a-c** to afford the flexible barbiturate receptors **3a-c**. Similarly, treatment of isophthalic acid with $SOCl_2$ generated isophthalolyl chloride, which was treated with monoamines **2a-c** to generate rigid backbone ligands **4a-c**.



Scheme 2.1. Preparation of hydrogen-bonding ligands based on 2,6-dicarboxyamido pyridine scaffolds.

Host-Guest Binding Studies. To obtain binding constants for the deconstructed barbiturate receptors, ^{1}H NMR titrations were performed for each receptor/guest pair. Because guest binding involves hydrogen bonding of the amide N-H groups of both the host and the guest molecules, changes in N-H chemical shift reflect the position of the thermodynamic host-guest equilibrium during the course of the titration. To test the barbiturate binding affinity of each host construct, we used barbital (**5**) as the guest due to its high solubility and previous use as a guest in similar systems.[32,39] Barbital has two hydrogen-bonding ADA faces that can interact with the DAD faces of prototypical barbiturate receptors. For receptors with flexible (**3a-c**) or rigid (**4a-c**) backbones, **5** is expected to form a 1:1 host:guest complex with each face of **5** interacting with each DAD face of the ligand. For bifurcated ligands **1a-f**, either a 1:1 or a 2:1 host:guest complex could be formed, depending on the relative magnitude of the enthalpic gain upon hydrogen bonding and the entropic penalty for assembly of three components. In addition to using **5** as a guest, we also performed titrations with 3-methyl-7-propylxanthine (**6**), which has only one ADA

face, thus simplifying the possible binding modes (Figure 2.3). Furthermore, **6** is less likely to self-aggregate in solution, whereas barbital derivatives, such as **5**, are known to form self-complementary hydrogen-bonded oligomers.[60] Previous studies with similar systems have shown negligible host dimerization.[39,48] For each host-guest system, a Job plot was constructed to determine the stoichiometry of guest binding. After establishing the binding stoichiometry, ^{1}H NMR titrations were performed in triplicate and the N-H chemical shifts of the guest were followed during the titrations. The resulting data was fit to the established binding stoichiometry.[61] Figure 2.4 shows the characteristic shift in the N-H ^{1}H NMR resonances used to quantify guest binding.



5 **6**

Figure 2.3. Barbital (**5**) and 3-methyl-7-propylxanthine (**6**) guests used in the titration studies with ligands **1a-f**, **3a-c**, and **4a-c**.

Job plots of bifurcated barbiturate receptors **1a-f** with **5** and **6** revealed 1:1 binding stoichiometries, suggesting that the entropic penalty to form the three-component system with **5** was too large for the relatively weak binding of **1a-f** with **5** and **6** to overcome. The binding affinities of 2,6-dicarboxamido pyridine hosts **1a-f** for guests **5** and **6** depended greatly on the steric bulk at the periphery of the receptor (Table 2.1). For example, replacing one or both methyl groups of **1a** with *tert*-butyl groups (**1d, 1f**) reduces the binding affinities of **5** and **6** by almost one order of magnitude per *tert*-butyl group. This sizeable reduction in binding affinity is likely due to the more twisted guest approach angle required to avoid disfavorable steric interactions between the host and the guest (*vide infra*). Similar trends are observed for the addition of phenyl

groups, although the magnitude of the decrease in binding affinity is attenuated, which is likely due to rotation of the phenyl group away from the guest to minimize disfavored steric interactions. In all cases, binding constants for **6** were larger than those determined for **5**, which is consistent with the propensity of **5** to form hydrogen-bonded aggregates. Compared to binding affinities of macrocyclic receptors ($K_a \approx 10^4$ M^{-1}), these results demonstrate that complete bifurcation of Hamilton-derived receptors greatly diminishes guest binding affinity, thus suggesting that greater host pre-organization is required to generate high-fidelity guest binding.

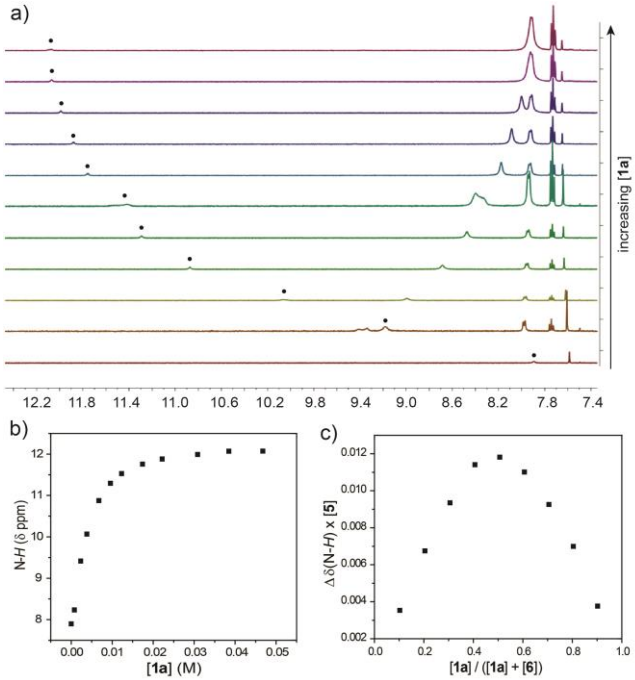


Figure 2.4. Representative ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$) titration data for **1a** with **6**. (a) Stacked ^{1}H NMR titration spectra; (b) Plot of the N-*H* chemical shift data from the ^{1}H NMR titration; and (c) Job plot for **1a** binding to **6** confirming a 1:1 binding stoichiometry.

Table 2.1. Binding constants for **5** and **6** with deconstructed barbituric acid receptors **1a-f**, **3a-c**, and **4a-c**.[a]

	Binding Constant (K_a, M^{-1})			Binding Constant (K_a, M^{-1})	
	5	**6**		**5**	**6**
1a	85 ± 25	490 ± 70	**3a**	70 ± 37[b]	K_{a1} = 1230 ± 280[b] K_{a2} = 184 ± 78[b]
1b	2 ± 1	3 ± 1	**3b**	40 ± 4 – [b,c]	74 ± 15 7 ± 1[b]
1c	7 ± 2	21 ± 3	**3c**	– [b,c]	24 ± 7[b]
1d	17 ± 2	28 ± 2	**4a**	139 ± 18[b]	70 ± 9[b]
1e	29 ± 1	109 ± 14	**4b**	174 ± 3 6 ± 2[b]	40 ± 3 7 ± 5[b]
1f	3 ± 1	6 ± 1	**4c**	4 ± 8[b]	22 ± 10[b]

[a] Titrations were performed in $CDCl_3$ at 25 °C. All measurements are the average of at least three independent titrations. [b] Performed in 5% DMSO in $CDCl_3$ due to poor solubility of either the host or the host-guest complex. [c] Binding constant too low (< 5 M^{-1}) to measure accurately.

To further investigate the degree of pre-organization required for optimal guest binding, receptors **3a-c** and **4a-c** were prepared. These scaffolds employ either flexible (**3a-c**) or rigid (**4a-c**) linkers in the backbone to allow for the degree of pre-organization to be modified. Because both of the 2,6-dicarboxamido pyridine groups in these receptors are tethered together, the entropic penalty for binding **5** should be attenuated. By contrast, hosts **3a-c** and **4a-c** could potentially form either 1:1 or 1:2 host:guest complexes with **6** because **6** does not have entirely complementary interactions to interface with the two DAD faces of the receptor leaving one side of the receptor face free to interact with a second guest. For these receptors, increased steric bulk of the tethered host will reduce the overall binding affinity and more likely result in 1:1 complex formation due to reduced capacity for multiple guests (Figure 2.5).

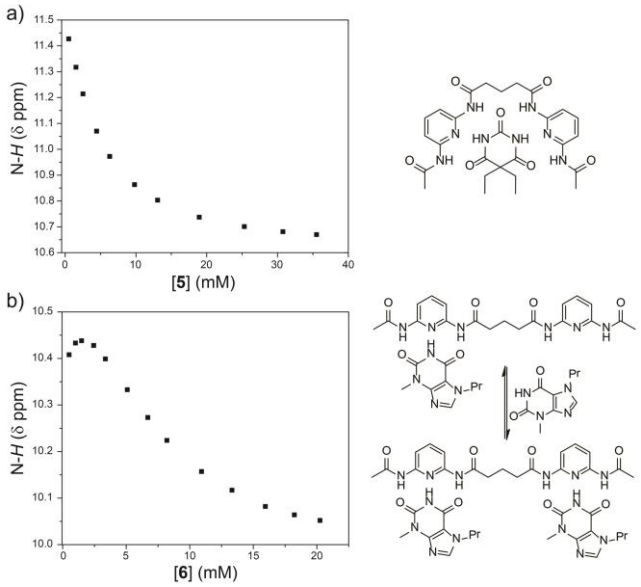


Figure 2.5. Representative ^{1}H NMR (500 MHz, 25 °C, 5% d_6-DMSO in $CDCl_3$) titration data for **1a** with **6.** Graph of the change in N-H chemical shift with changing concentrations of (a) **5** and (b) **6** in the presence of **3a.**

Consistent with the results obtained from bifurcated hosts **1a-f**, steric interactions from the receptor periphery greatly impacted guest binding for the scaffolds with flexible backbones **3a-c**. For example, replacing the methyl groups in **3a** with *tert*-butyl groups (**3b**) resulted in a 60-fold decrease in barbital binding. This observation is consistent with the bifurcated 2,6-dicarboxamido pyridine hosts (**1a-f**) and demonstrates the sensitivity to steric repulsion near the hydrogen-bonding sites. Flexible receptors **3a-c** also maintained higher binding affinity for **6** than for **5,** although the magnitude of this preference was diminished. Job plots of **3a-c** with **5** and **3b,c** with **6** confirmed 1:1 host:guest binding. Investigations of **3a** with **6**, however, revealed two binding events corresponding to the formation of 1:1 and 1:2 host:guest complexes. The first binding event, corresponding to a 1:1 **3a:6** complex, had a K_a of 1230 M^{-1}, which was an order of magnitude greater than binding of a second guest with a K_a of 180 M^{-1}. The difference in K_a values between the first and second guest binding events are consistent with the required

elongation and corresponding entropic penalty of **3a** to accommodate two xanthine guests. Although 2:1 binding was observed with **6**, only 1:1 binding was observed with **5**. If barbital were to form a 1:2 host:guest complex, then the benefits from the chelate effect would need to be sacrificed in order to accommodate two barbital guests.

Job plots of **5** and **6** with **4a-c** confirmed exclusively 1:1 binding and ^{1}H NMR titration data was subsequently fit to a 1:1 model. For **5**, the methyl end capped host (**4a**) had the highest binding affinity, followed by the *tert*-butyl (**4b**), and finally the phenyl (**4c**) analogs. Although phenyl groups are less sterically demanding than *tert*-butyl groups, the requirement of phenyl group rotation to accommodate a bound guest results in a reduction of the conjugation into the amide and thereby reduces the enthalpic gain upon guest binding. As expected, the rigid backbone hosts had lower affinities for **6** than **5** due to constrained binding pockets present in the host constructs and greater steric bulk of **6** in comparison to **5**. Similar to trends observed for other host-guest pairs, steric bulk on the periphery of receptors **4a-c** directly affected the binding affinity toward **6**.[39,48]

The interplay between pre-organization and steric interactions between host and guest is also observed across the different types of receptors. For example, by comparing the binding affinities of **5** with *tert*-butyl substituted receptors **1b**, **3b**, and **4b**, a clear trend is apparent, with the more preorganized structures producing stronger binding. Upon increasing the pre-organization, the binding affinity for **5** increases from 2 M^{-1} for **1**, to 40 M^{-1} for **3b** and finally to 139 M^{-1} for **4b**. This series clearly demonstrates that host pre-organization can offset some of the disfavorable steric interactions present in this series of receptors. A second trend is observed for the same series of host molecules interacting with **6**. In this case, because the xanthine guest cannot form favorable interactions with both sides of the symmetric receptors **3b** and **4b**, the steric influences are more important. The increase of binding affinities from 3 M^{-1} for **1b** to 75 M^{-1} for **3b** is primarily due to the decreased steric bulk from the flexible propyl chain by comparison to a *tert*-butyl group. Replacement of the flexible backbone of **3b** with the rigid phenyl backbone

in **4b** slightly increases the steric encumbrance on the guest due to the inability of the phenyl group in **4b** to completely rotate away from the bound guest. As would be expected from these interactions, the binding constant of **6** with **4b** is lower than for **3b**, but higher than for **1b**. Taken together, these comparisons highlight the delicate balance between pre-organization and minimization of steric interactions for synthetic barbiturate receptors.

To better understand the enthalpic and entropic effects associated with guest binding, we determined ΔH and ΔS using van't Hoff analysis for hosts **1a**, **1c**, and **1e** binding guest **6** (Figure 2.6). The binding enthalpies and entropies (ΔH, ΔS) were determined to be **1a** (4.7 kcal/mol, -4.0 eu), **1c** (3.8 kcal/mol, -6.5 eu), and **1e** (5.8 kcal/mol, -10.1 eu). Both **1a** and **1c** have symmetric amide substituents, whereas **1e** does not. This desymmetrization results in preferential orientation of the guest to minimize the steric interaction between the propyl tail of **6** and the phenyl substituent of **1e**, resulting in a more negative binding entropy than was observed for **1a** or **1c.** Changes in the binding enthalpies are also observed. For example, **1c** has two phenyl substituents that must twist out of conjugation with the amide to allow for guest binding, which results in a lower observed binding enthalpy for **1c** by comparison to **1a** or **1e**.

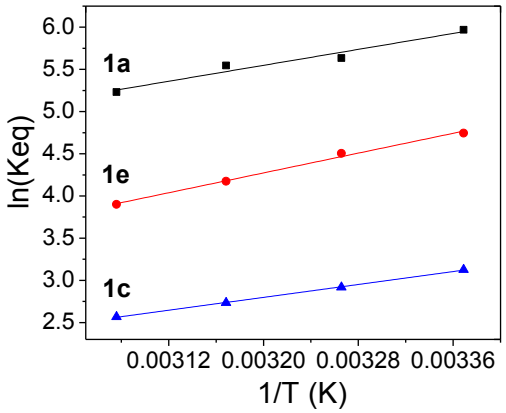


Figure 2.6. Van't Hoff analysis of **1a-1c** with **6.**

Computational Studies on Hydrogen-Bonded Adducts. To gain further insight into the factors influencing host-guest binding, we optimized the structure of each host, guest, and hydrogen-bonded adduct using Gaussian 09 at the B3LYP/6-31+G(d,p) level of theory employing the IEF-PCM $CHCl_3$ solvation model. Based on the computed energies for each of the optimized geometries for each ligand, guest, and host-guest component, binding enthalpies were calculated (Table 2.2). Although the DFT calculations over-estimated the absolute magnitude of the binding energies, good correlation between the experimentally-determined binding affinities determined in $CDCl_3$ and the computed binding enthalpies was observed, suggesting that this computation level of theory can be used to reliably estimate trends in binding affinities of future similar barbiturate-binding scaffolds (Figure 2.7).

Table 2.2 Calculated binding energies for **5** and **6** with **1a-f**, **3a-c**, and **4a-c**.[a]

	$-\Delta H_{binding}$ (kcal/mol)			$-\Delta H_{binding}$ (kcal/mol)	
	5	**6**		**5**	**6**
1a	8.18	8.17	**3a**	10.88	9.40
1b	3.69	5.19	**3b**	5.18	7.41
1c	5.26	6.63	**3c**	3.98	8.53
1d	6.90	7.69	**4a**	12.69	8.13
1e	6.44	7.91	**4b**	7.96	8.17
1f	5.33	6.05	**4c**	10.83	6.96

[a] Calculated using Gaussian 09, B3LYP/6-31+G(d,p), with IEF-PCM solvation model for $CHCl_3$. Binding energies correspond to the difference in ZPE-corrected energies from the host-guest complexes and the isolated host and guest species.

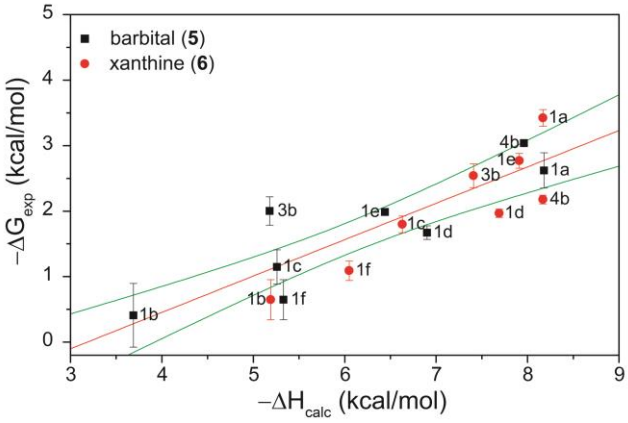


Figure 2.7. Comparison of experimentally-determined binding affinities (□G, kcal/mol) with the calculated binding enthalpies, including linear fit (red) and 95% confidence interval (green).

Having established the validity of this computation model for estimating the magnitude of the binding interactions with the barbiturate-binding hosts, we used the optimized structures to gain insight into the major factors affecting guest binding affinities. By comparing the optimized geometries **1a-f** interacting with **5** and **6**, the steric bulk on the periphery of the receptors greatly affected the approach angle of **5** or **6** to the 2,6-dicarboxamido pyridine scaffolds. Comparing the binding affinities of symmetric **1a-c** with **5**, **1a** forms the strongest interaction with **5** due to the limited repulsive steric interactions. The level of deviation from an ideal co-planar guest approach angle can be compared by measuring the angle between the least squares planes of the pyridine ring of **1a** and the six-membered ring of **5**. Comparing guest approach angles with **5**, **1a** had the lowest approach angle of 15.1^{o} angle, which increases to 32.3^{o} for symmetric *tert*-butyl compound **1b**, and then decreased for the symmetric phenyl complex **1c** (Figure 2.8). These twist angles correlate strongly with both the experimental and computational binding affinities.

Similarly, for hosts tethered with either flexible or rigid backbones, the steric pressure exerted on the guest is greatly dictated by the size of the amide groups (Figure 2.8b). Although the phenyl groups can rotate to minimize steric interactions with the bound barbital, and

potentially generate favorable CH-π interactions, this rotation results in a break of planarity with the amide, thereby reducing the overall conjugation of the system.

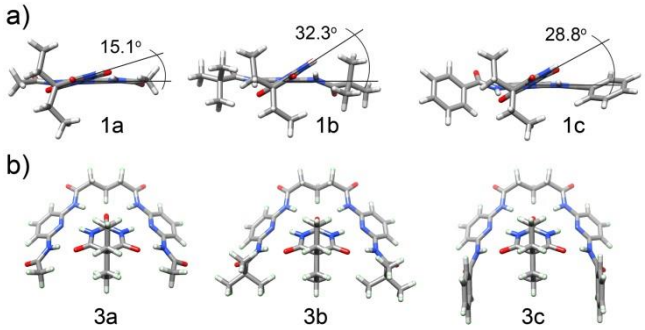


Figure 2.8. Examples of the optimized geometries for host-guest species **1a-c** with **5** (a) and **3a-c** with **5** (b). Changing the steric bulk of the periphery of the receptor influences the twist angel of guest approach and the overall hydrogen-bonding fidelity.

Conclusion

Both experimental titration data and DFT calculations show that both pre-organization and steric bulk play a direct role in the binding affinity of the deconstructed Hamilton receptors. For the least preorganized hosts, **1a-f**, steric bulk had the largest role in influencing guest binding affinity with the least bulky host **1a** maintaining the highest binding affinities toward **5** and **6**, whereas the most bulky host, **1b**, had the smallest guest binding affinities. For hosts **3a-c** with moderate pre-organization, the effects of steric bulk were attenuated. For the most rigid hosts, **4a-c**, steric interactions played a direct role in the guest binding affinities with the bulkiest host having the lowest affinity and the least bulky host having the highest binding affinity.

In addition to steric interactions, pre-organization also played a distinct role in guest binding affinities. The more pre-organized hosts, **4a-c**, had the highest binding affinity for barbital due to the high complementarity with the two hydrogen-bonding faces of **5**. The less pre-organized hosts, **3a-c**, had higher binding affinities for **6** than did **4a-c** due to the flexibility of the ligand backbone, which allowed for two guests to be accommodated. The completely bifurcated

hosts, **1a-f**, had much lower binding affinities than **3a-c** or **4a-c** due to the decreased ligand pre-organization. Importantly, the combined experimental and computational results obtained for the deconstructed barbiturate receptors are also applicable to other hydrogen-bonding systems in which pre-organization must be balanced with disfavorable steric interactions between the host and guest. These results illustrate the important roles that both sterics and pre-organization play in host-guest complexes and how each should be either minimized or maximized in order to obtain the highest affinity for a given host-guest system.

Experimental Section

Materials and Methods. All commercially-available reagents and deuterated solvents were used as received. Anhydrous solvents used for syntheses were collected from a solvent purification system. Reactions were monitored by TLC and the products were purified on an automated flash chromatography instrument. NMR spectra were recorded at the indicated frequencies and chemical shifts are reported in parts per million (δ) and are referenced to residual protic solvent resonances. The following abbreviations are used in describing NMR couplings: (s) singlet, (d) doublet, (t) triplet, (m) multiplet and (b) broad.

General Job Plot Procedure. Job plots were performed in $CDCl_3$ and monitored by ^1H NMR for host molecules **1a-f**, **3b**, **3b**, and **4b**. Job plots with the host molecules **3a**, **3c**, **4a**, and **4c** were performed in 5% DMSO-d_6 in $CDCl_3$ due to poor solubility of the hosts in $CDCl_3$. All Job plots were performed using total (host + guest) concentrations of 10 mM, but compounds **1a-f** were also run at 100 mM total concentrations due to weaker guest binding. For a typical Job plot, 3 mL of a host solution and 3 mL of a guest solution were prepared and then divided between 10 NMR tubes in 10 mol% increments. After equilibration, the ^1H NMR spectrum for each sample was recorded and the shift in the guest N-H resonance was used to construct the Job plot.

General Procedure Binding Constant Determination. Binding studies were performed in $CDCl_3$ for host molecules **1a-f**, **3b**, and **4b** and monitored by ^1H NMR spectroscopy. Due to poor solubility of compounds **3a**, **3c**, **4a**, and **4c** in $CDCl_3$, these compounds were measured in 5% DMSO-d_6 in $CDCl_3$. In order to compare the binding constants obtained in 5% DMSO-d_6 in $CDCl_3$ to those obtained in neat $CDCl_3$, titrations with host molecules **3b** and **4b** were also carried out in 5% DMSO-d_6 in $CDCl_3$. In a typical $CDCl_3$ titration, 2 mL of a 1 mM **5** or **6** was prepared. The guest solution was then divided such that 1 mL was placed into an NMR tube and the other 1 mL was used to create a second solution containing 150-300 mM host. An initial spectrum of the guest was recorded, after which aliquots (5-100 μL) of the host solution were added until the N-H resonance of **5** or **6** no longer shifted. In a typical 5% DMSO-d_6 in $CDCl_3$ titration, 2 mL of a 3 mM host solution was prepared. The host solution was then divided such that 1 mL was placed into an NMR tube and the other 1 mL was used to create a second stock solution containing 25-100 mM guest. An initial spectrum of the host was recorded, after which aliquots (5-100 μL) of **5** or **6** were be added until the N-H resonance of the **5** or **6** no longer shifted.

General van't Hoff Plot Procedure. Stock solutions of **1a**, **1c**, **1e**, and **6** were prepared at concentrations of 24 mM, 120 mM, 86 mM, and 2 mM, respectively. These host concentrations were chosen to ensure complete host-guest complexation at the highest concentration. Six NMR samples of varying host:guest ratios were prepared for each host/guest pair and the N-H resonance of **6** was monitored over the temperature range 298 – 328 K. All temperatures were calibrated using a MeOH temperature standard.[62]

Computational Details. Calculations were performed using the Gaussian 09[63] software package with the GaussView[64] graphical user interface. Graphical representations were produced using the UCSF Chimera package v1.8.[65] Initial conformational searches and optimizations were performed using either the 3-21g or 6-31g basis sets, followed by full geometry optimizations and unscaled frequency calculations at the B3LYP/6-31+G(d,p) level of theory using the IEF-PCM solvation model for chloroform. Frequency calculations were performed on all converged

structures confirmed that they corresponded to local minima. Calculated enthalpies are reported as zero-point corrected enthalpies. In all cases, the lowest energy conformer was used to compare the relative energetics of the calculated species.

Syntheses. ***N,N′*-(Pyridine-2,6-diyl)diacetamide (1a).** A round bottom flask was charged with dry THF (50 mL), 2,6-diaminopyridine (3.0 g, 28 mmol), and triethylamine (9.7 ml, 69 mmol). The flask was then lowered into an ice bath and degassed with N_2. Acetyl chloride (4.3 mL, 61 mmol) was added to an addition funnel containing dry THF (20 mL), and the resultant solution was then slowly added to the diaminopyridine solution while stirring in the ice bath under N_2. Once the addition of the acid chloride was complete, the ice bath was removed, and the reaction was allowed to warm to room temperature overnight while stirring under N_2. The reaction mixture was concentrated by rotary evaporation and the crude product was purified by column chromatography (Si_2O, EtOAc) to afford **1a** as off-white crystals (5.2 g, 96% yield) with spectroscopic properties consistent with literature data.[48] Mp = 201-202 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.91 (d, J = 7.7, 2H), 7.73 (t, J = 7.9, 1H), 7.59 (s, 2H), 2.22 (s, 6H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 168.5, 149.4, 140.9, 109.5, 24.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_9H_{12}N_3O_2$, 194.0930; found 194.0932.

***N,N′*-(Pyridine-2,6-diyl)dipivalamide (1b).** The monosubstituted diaminopyridine **2b** was prepared according to the general procedure outlined for **1a** with the following quantities: 2,6-diaminopyridine (33 mg, 0.30 mmol) in THF (15 mL) and trimethylacetyl chloride (81 µL, 0.66 mmol) in THF (15 mL). The crude product was purified by column chromatography (Si_2O, EtOAc) to afford a tan solid (83 mg, 99% yield) with spectroscopic properties consistent with literature data.[48] Mp = 112-113 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.94 (d, *J* = 7.8, 2H), 7.76 (s, 2H), 7.71 (t, *J* = 7.8, 1H), 1.34 (s, 18H) $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 176.8, 149.6, 140.8, 109.3, 39.8, 27.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{24}N_3O_2$, 278.1869; found 278.1859.

***N,N'*-(Pyridine-2,6-diyl)dibenzamide (1c).** The monosubstituted diaminopyridine **1c** was prepared according to the general procedure outlined for **1a** with the following quantities: 2,6-diaminopyridine (31 mg, 0.28 mmol) in THF (15 mL) and benzoyl chloride (72 µL, 0.62 mmol) in THF (15 mL). The crude product was purified by chromatography (Si_2O, 1:1 EtOAc:DCM) to afford a tan solid (89 mg, 98% yield) with spectroscopic properties consistent with literature data.[66] Mp = 168-170 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.53 (s, 2H), 8.14 (d, *J* = 7.8, 2H), 7.93 (d, *J* = 7.3, 4H), 7.84 (t, *J* = 7.7, 1H), 7.60 (t, *J* = 7.3, 2H), 7.53 (t, *J* = 7.3, 4H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 170.0, 165.5, 149.7, 141.3, 134.1, 133.6, 132.37, 130.0, 128.9, 128.5, 127.2, 110.01. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{16}N_3O_2$, 318.1243; found 318.1247.

***N*-(6-Acetamidopyridin-2-yl)pivalamide (1d).** A round bottom flask was charged with dry THF (75 mL), **2a** (2.9 g, 19 mmol), and triethylamine (5.3 mL, 39 mmol). The flask was then lowered into an ice bath and degassed with N_2. Trimethylacetyl chloride (3.0 mL, 25 mmol) was added to an addition funnel containing dry THF (25 mL) and the resultant acid chloride solution was then slowly added to the diaminopyridine solution while stirring in the ice bath under N_2. Once the addition of the acid chloride was complete, the ice bath was removed and the reaction was allowed to warm to room temperature overnight while stirring under N_2. The reaction was concentrated by rotary evaporation and the crude product was purified by column chromatography (SiO_2, EtOAc) to afford a white crystalline solid (3.88 g, 66%). Mp = 128-129 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.97 (d, *J* = 7.8, 1H), 7.91 (d, *J* = 7.5, 1H), 7.74 (m, 1H), 7.71 (s, 1H), 2.23 (s, 3H), 1.35 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 176.9, 168.4, 149.7, 149.3, 140.9, 109.5, 109.3, 39.8, 27.5, 24.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{18}N_3O_2$, 236.1399; found 236.1402.

***N*-(6-Acetamidopyridin-2-yl)benzamide (1e).** The disubstituted diaminopyridine **1e** was prepared according to the general procedure outlined for **1d** with the following quantities:

benzoyl chloride (1.9 mL, 16 mmol) in THF (25 mL) was added slowly to **2a** (1.9 g, 13 mmol) and triethylamine (3.6 mL, 26 mmol) in THF (50 mL). Purified by column chromatography (Si_2O, EtOAc) to afford a white crystalline solid (2.69 g, 81%). Mp = 195-196 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.34 (s, 1H), 8.10 (d, *J* = 7.8, 1H), 7.96 (d, *J* = 6.4, 1H), 7.92 (d, *J* = 7.8, 2H), 7.79 (m, 1H), 7.61 (t, *J* = 7.3, 1H), 7.53 (t, *J* = 8.3, 2H), 2.24 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 165.4, 149.5, 140.0, 134.2, 132.3, 128.9, 127.1, 109.6, 24.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{14}N_3O_2$, 256.1086; found 256.1097.

***N*-(6-Pivalamidopyridin-2-yl)benzamide (1f).** The disubstituted diaminopyridine **1f** was prepared according to the general procedure outlined for **1d** with the following quantities: trimethylacetyl chloride (0.24 mL, 2.1 mmol) in THF (25 mL) was added slowly to **2c** (0.35 g, 1.6 mmol) and triethylamine (0.34 mL, 2.5 mmol) in THF (50 mL). Purified by column chromatography (Si_2O, CH_2Cl_2) to afford a chalky off-white solid (0.51 g, 82%). Mp = 120-121 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.33 (s, 1H), 8.06 (d, *J* = 8.3, 1H), 7.97 (d, *J* = 8.3, 1H), 7.94 (d, *J* = 4.3, 2H), 7.79 (s, 1H), 7.75 (t, *J* = 8.3, 1H), 7.56 (t, *J* = 7.3, 1H), 7.49 (t, *J* = 6.5, 2H), 1.32 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 176.8, 165.4, 149.8, 149.6, 140.9, 134.2, 132.3, 128.9, 127.1, 109.7, 109.6, 39.8, 27.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{20}N_3O_2$, 298.1556; found 298.1565.

***N*-(6-Aminopyridin-2-yl)acetamide (2a).** A round bottom flask was charged with dry THF (10 mL) and 2,6-diaminopyridine (1.0 g, 9.1 mmol). The flask was then lowered into an ice bath and degassed with N_2. Acetyl chloride (0.32 mL, 4.6 mmol) was added to an addition funnel containing dry THF (20 mL), and the resultant solution was then added slowly to the diaminopyridine solution over the course of 1 hour while stirring at 0 °C under N_2. Once the addition of the acid chloride was complete, the ice bath was removed and the reaction was allowed to warm to room temperature overnight while stirring under N_2. The precipitate from the reaction was filtered, and the resultant filtrate was concentrated by rotary evaporation. The crude

product was purified by column chromatography (SiO_2, EtOAc) to afford a tannish pink solid (0.65 g, 95%), with spectroscopic properties consistent with literature data.[48] Mp = 150-152 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.70 (s, 2H), 7.54-7.46 (m, 2H), 6.27 (d, *J* = 7.8, 1H), 4.32 (s, 2H), 2.18 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 168.4, 157.0, 149.7, 140.2, 104.3, 103.3, 24.7. HRMS (ESI-TOF) m/z: $[M]^+$ Calcd for $C_7H_9N_3O$, 151.0746; found 151.0742.

***N*-(6-Aminopyridin-2-yl)pivalamide (2b).** The monosubstituted diaminopyridine **2b** was prepared according to the general procedure outlined for **2a** with the following quantities: 2,6-diaminopyridine (0.51 g, 4.6 mmol) in THF (10 mL) and trimethylacetyl chloride (0.25 mL, 2.2 mmol) in THF (5 mL). Purified by column chromatography (Si_2O, EtOAc) to afford a tan solid (0.86 g, 97% yield), with spectroscopic properties consistent with literature data.[48] Mp = 131-132 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.73 (s, 1H), 7.59 (d, *J* = 8.3, 1H), 7.46 (t, *J* = 7.8, 1H), 6.26 (d, *J* = 7.81 1H), 4.35 (s, 2H), 1.32 (s, 9H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 168.3, 157.0, 149.8, 104.3, 103.3, 39.7, 27.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{10}H_{16}N_3O$, 194.1293; found 194.1295.

***N*-(6-Aminopyridin-2-yl)benzamide (2c).** The monosubstituted diaminopyridine **2c** was prepared according to the general procedure outlined for **2a** with the following quantities: 2,6-diaminopyridine (2.0 g, 18 mmol) in THF (50 mL) and benzoyl chloride (1.0 mL, 9.0 mmol) in THF (25 mL). Purified by column chromatography (Si_2O, CH_2Cl_2) to afford a white crystalline solid (3.53 g, 92%). Mp = 184-186 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.33 (s, 1H), 7.91 (d, J = 8.0, 2H), 7. 74 (d, J = 8.0, 1H), 7.59-7.50 (m, 4H), 6.32 (d, J = 8.0, 1H), 4.39 (s, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 165.4, 157.1,149.9, 104.3, 134.5, 132.1, 128.8, 127.1, 104.6, 103.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{12}N_3O$, 214.0980; found 214.0974.

***N*^{1},*N*^{5}-*bis*(6-Acetamidopyridin-2-yl)glutaramide (3a).** Glutaric acid (0.21g, 1.6 mmol) was stirred in thionyl chloride (3 mL) for 5 hours at room temperature, after which the thionyl chloride was removed under vacuum. A round bottom flask was charged with dry THF (50 mL),

2a (0.40 g, 2.7 mmol), and triethylamine (1.1 mL, 8.1 mmol). The flask was then lowered into an ice bath and degassed with N_2. The crude glutaroyl chloride was taken up in THF (10 mL) and added to an addition funnel. The resultant acid chloride solution was then slowly added to the diaminopyridine solution while stirring in the ice bath under N_2. Once the addition of the acid chloride was complete, the ice bath was removed and the reaction was allowed to warm to room temperature overnight while stirring under N_2. The reaction mixture was concentrated by rotary evaporation, and the residue was then taken up in EtOAc washed with water and then saturated $NaHCO_3$. The organic layer was concentrated and the resultant residue was then taken up in water (20 mL) and heated to 80 °C until all of the solid was dissolved. Upon cooling, the product crystallized as a white crystalline solid, which was collected by filtration and dried under vacuum (0.70 g, 65%). Mp = 221-222 °C. ^{1}H NMR (300 MHz, DMSO) δ: 10.52 (s, 2H), 10.19 (s, 2H), 8.54 (s, 2H), 8.18 (d, J = 7.3, 2H), 7.83 (s, 6H), 7.70 (t, J = 7.6), 3.36 (s, 4H), 2.14 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, DMSO) δ: 172.2, 169.7, 150.8, 143.3, 109.5 35.8, 24.5, 21.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{23}N_6O_4$, 399.1781; found 399.1799.

***N*^{1},*N*^{5}-*bis*(6-Pivalamidopyridin-2-yl)glutaramide (3b).** The alkyl tethered diaminopyridine **3b** was prepared according to the general procedure outlined for **3a** with the following quantities: glutaroyl dichloride (0.56 g, 3.3 mmol) in THF (20 mL) was added slowly to **2b** (1.1 g, 5.6 mmol) and TEA (1.4 mL, 10 mmol) in THF (50 mL). Purified by column chromatography (Si_2O, DCM with 5% of a 9:1 MeOH:NH_4OH mixture) to afford a white crystalline solid (1.11 g, 41%). Mp = 258 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.95 (d, *J* = 8.1, 2H), 7.90 (s, 2H), 7.86 (d, *J* = 8.7, 2H), 7.77 (s, 2H), 7.71 (t, *J* = 8.1, 2H), 2.55 (t, *J* = 6.9, 4H), 2.16 (m, 2H), 1.33 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 176.9, 170.7, 149.8, 149.2, 140.8, 109.6, 109.3, 39.8, 36.1, 27.5, 20.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{35}N_6O_4$, 483.2720; found 483.2744.

***N*^{1},*N*^{5}-*bis*(6-Benzamidopyridin-2-yl)glutaramide (3c).** The alkyl tethered diaminopyridine **3c** was prepared according to the general procedure outlined for **3a** with the following quantities: glutaroyl dichloride (0.39 g, 2.3 mmol) in THF (20 mL) was added slowly to **2c** (0.81 g, 3.8 mmol) and TEA (1.6 mL, 11 mmol) in THF (50 mL). Purified by column chromatography (Si_2O, 3:2 hexanes:EtOAc) to afford a white crystalline solid (1.38 g, 67%). Mp = 179 °C (dec). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.67 (s, 4H), 8.38 (d, *J* = 8.5, 2H), 7.84 (m, 6H), 7.50 (d, *J* = 8.0, 2H), 7.42 (t, *J* = 7.5, 4H), 6.89 (d, *J* = 8.0, 2H), 2.76 (t, *J* = 7.0, 4H), 2.08 (dd, *J* = 7.5, 8.0, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 173.0, 166.0, 152.0, 148.6,140.5, 134.2, 132.2, 128.6, 127.7, 119.7, 114.0, 32.3, 17.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{27}N_6O_4$, 523.2094; found 523.2106.

***N*^{1},*N*^{3}-*bis*(6-Acetamidopyridin-2-yl)isophthalamide (4a).** Isophthalic acid (0.30 g, 1.8 mmol) was stirred in thionyl chloride (2 mL) at 65 °C with catalytic DMF for 7 hours, after which the excess thionyl chloride was removed under vacuum. A round bottom flask was charged with dry THF (50 mL), **2a** (0.44 g, 3.0 mmol), and triethylamine (1.2 mL 8.9 mmol). The flask was then lowered into an ice bath and degassed with N_2. The crude isophthaloyl chloride was taken up in dry THF (20 mL) and added to an addition funnel. The acid chloride solution was then slowly added to the diaminopyridine solution while stirring in the ice bath under N_2. Once the addition of the acid chloride was complete, the ice bath was removed and the reaction was allowed to warm to room temperature overnight while stirring under N_2. The reaction mixture was concentrated by rotary evaporation and the residue was washed with water and then with saturated $NaHCO_3$. The organic layer was concentrated, and the resultant residue was then taken up in water (20 mL) and heated to 80 °C until all of the solid was dissolved. Upon cooling, the product crystallized as a white crystalline solid, which was collected by filtration and dried under vacuum (1.73 g, 45%). Mp = 161-163 °C. ^{1}H NMR (300 MHz, DMSO) δ: 10.51 (s, 2H), 10.18 (s, 2H), 8.53 (s, 1H), 8.16 (d, *J* = 7.3, 2H), 8.02 (d, *J* = 7.8, 2H), 7.92 (d, *J* = 7.3, 2H), 7.83 (m, 1H), 7.70 (t, *J* = 7.3, 2H),

2.17 (s, 6H). $^{13}C\{^{1}H\}$ NMR (125 MHz, DMSO) δ: 169.8 165.8, 151.1, 150.6, 140.5, 134.7, 161.8, 129.3, 127.9, 129.3, 127.9, 110.9, 110.3, 24.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{21}N_6O_4$, 433.1624; found 433.1615.

***N*^{1},*N*^{3}-*bis*(6-Pivalamidopyridin-2-yl)isophthalamide (4b).** The alkyl tethered diaminopyridine **3e** was prepared according to the general procedure outlined for **3d** with the following quantities: isophthaloyl dichloride (1.0 g, 6.2 mmol) in THF (20 mL) was added slowly to **2b** (2.0 g, 10 mmol) and triethylamine (3.6 mL, 26 mmol) in THF (100 mL). Purified by column chromatography (Si_2O, 3:2 EtOAc:hexanes) to afford a white crystalline solid (2.89 g, 56%). Mp = 135-136 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.10 (s, 2H), 8.46 (s, 2H), 8.20-8.17 (m, 3H), 8.05 (d, J = 8.5, 2H), 7.97 (d, J = 8.0, 2H), 7.86 (t, J = 8, 2H), 7.72 (t, J = 8, 1H), 1.13 (s, 18H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 177.0, 164.2, 149.9, 149.2, 141.0, 134.8, 130.8, 129.6, 125.8, 110.0, 109.0, 39.8, 27.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{28}H_{33}N_6O_4$ 517.2563; found 517.2574.

***N*^{1},*N*^{3}-*bis*(6-Benzamidopyridin-2-yl)isophthalamide (4c).** The alkyl tethered diaminopyridine **4c** was prepared according to the general procedure outlined for **3d** with the following quantities: isophthaloyl dichloride (0.23 g, 1.4 mmol) in THF (20 mL) was added slowly to **2c** (0.0.51 g, 2.4 mmol) and triethylamine (0.71 mL, 7.0 mmol) in THF (50 mL). Purified by column chromatography (Si_2O, 3:2 hexanes:EtOAc) to afford a white crystalline solid (0.88 g, 66%). Mp = 213-215 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.56 (s, 2H), 8.53 (s, 1H), 8.40 (s, 2H), 8.17 (d, *J* = 8.0, 4H), 8.14 (d, *J* = 8.0, 2H) 7.94 (d, *J* = 7.0, 4H), 7.87 (t, *J* = 8.0, 2H), 7.70 (t, *J* = 8.0, 1H), 7.61 (t, *J* = 7.5, 2H), 7.53 (t, *J* = 7.5, 4H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 165.5, 164.2, 149.8, 149.4, 141.2, 134.8, 134.1, 132.4, 130.9, 128.9, 127.2, 110.3, 109.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{25}N_6O_4$, 557.1937; found 557.1940.

Supporting Information. NMR spectra of new compounds, optimized geometries from DFT calculations is available in Appendix A.

CHAPTER III

LINEAR FREE ENERGY RELATIONSHIPS REVEAL STRUCTURAL CHANGES IN HYDROGEN-BONDED HOST-GUEST INTERACTIONS

The work on the series of Hamilton receptors with appended electron withdrawing or electron donating groups and with a complementary guest was published in volume 79, issue 23, pages 11797–11801 in *The Journal of Organic Chemistry* in December 2014. Jacqueline M. McGrath performed all the synthesis, purification, and titrations. The computational work was performed by Michael D. Pluth. Michael D. Pluth was the principles investigator for this work.

Preface

Hydrogen bond strength in host-guest systems is modulated by many factors including pre-organization, steric effects, and electronic effects. To investigate how electronic effects affect barbiturate binding in bifurcated Hamilton receptors, a library of receptors with differing electronic substituents was synthesized and ^{1}H NMR titrations were performed with diethyl barbital. The Hammett plot revealed a clear break between the different electronic substituents suggesting a change in binding conformation. The titration data were complimented with computational studies confirming the change in structure.

Introduction

Host-guest binding plays a key role in many types of chemistry, ranging from molecular recognition to catalysis.[67-72] Understanding how structural changes influence such interactions enables control over guest binding and facilitates the molecular design of synthetic supramolecular complexes. Various factors, including steric and electronic effects as well as host-guest pre-organization, can all affect host-guest complex stability and guest exchange rates.[71,73,74] To better understand the interplay of these forces in hydrogen-bonded systems, we recently investigated barbiturate binding to 2,6-diamidopyridines, a bifurcated form of macrocyclic Hamilton receptors to determine the differential effects of steric interactions and host pre-organization on guest binding affinities.[75] Toward understanding the impacts of electronic substitution on guest binding in hydrogen-bonded systems, we report here binding studies on 2,6-diaminopyridines with barbital that reveal changes in host-guest structure as a function of electronic substitution.

Because 2,6-diamidopyridines bind barbiturates through complementary hydrogen bonding, we chose to use a system in which one of the amides contained a phenyl substituent with an electron withdrawing or donating group in the *para* position. This design allowed for electronic changes in the phenyl substituent to modulate the acidity of the amide N-H as well as the basicity of the pyridine nitrogen (Figure 3.1).[76,77] Inclusion of electron withdrawing groups should acidify the amide, making it a better hydrogen bond donor, whereas electron donating groups should decrease the amide acidity but also increase electron density of the pyridine nitrogen, making it a better hydrogen bond acceptor. Although these two effects are opposing, the acidification of the amide N-H is expected to be a larger effect due to the closer proximity to the substituted phenyl group.

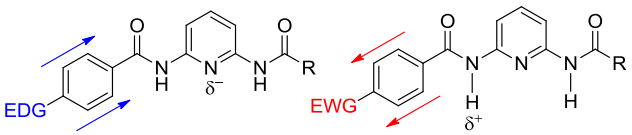
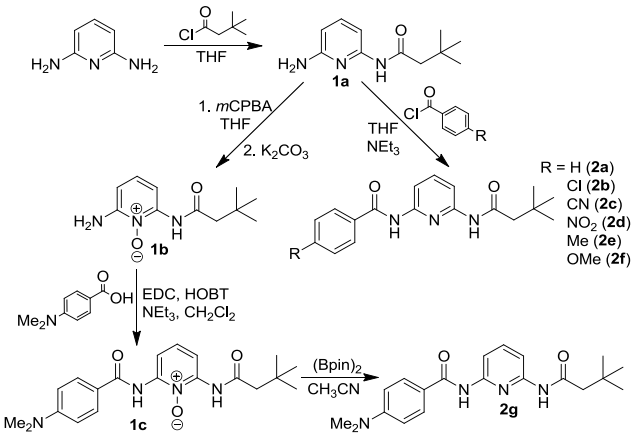


Figure 3.1. Effects of electron donating and electron withdrawing on the electron density of the 2,6-diamidopyridine receptors.

Results and Discussion

To prepare the desired compounds, precursor **1a** was prepared by coupling 3,3-dimethylbutyryl chloride with 2,6-diaminopyridine using excess diaminopyridine as the base in THF (Scheme 3.1). Compounds **2a-f** were prepared by treatment of the corresponding acid chlorides with **1a**. To prepare the *p*-dimethylamino substituted compound, the pyridine nitrogen of **1a** was first oxidized with *m*CPBA to afford **1b**, which was then coupled to *p*-dimethylamino benzoic acid using EDC and HOBT.[78] The resultant *N*-oxide product (**1c**) was then reduced with $(Bpin)_2$ to afford **2g**.[79]



Scheme 3.1. Synthesis of 2,6-diamidopyridines **2a-g**.

To measure the binding affinity of the differently-substituted **2a-g** with diethyl barbital, ^{1}H NMR titrations were performed for each host-guest system in $CDCl_3$. Because the binding involves hydrogen bonding between the receptor and barbital, the N-*H* NMR resonances of the amides on both the host and the guest change during the course of the titration (Figure 3.2). Using the tabulated chemical shift data of the barbital N-*H*, the resultant binding isotherms were fit to a 1:1 model, based on previous studies investigating the binding stoichiometry of compounds such as **2a-g** with diethyl barbital.[75] All measurements were repeated at least in triplicate to ensure reproducibility of the binding affinities.

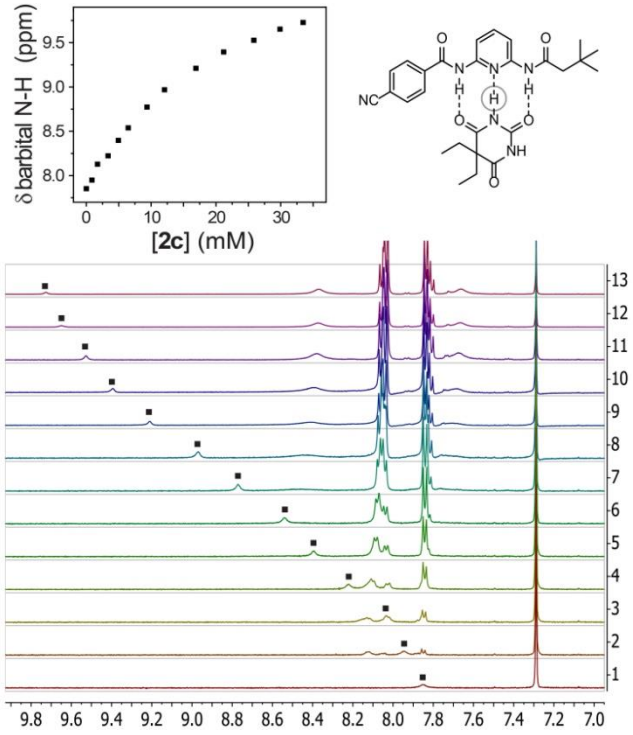


Figure 3.2. Representative ^{1}H NMR (500 MHz, 25 °C, $CDCl_3$) titration of diethyl barbital with **2c**. The stacked ^{1}H NMR titration spectra and tabulated plot of the N-*H* chemical shift data from the ^{1}H NMR titration are shown.

Measurement of the binding constants of **2a-g** with diethyl barbital revealed that electron withdrawing groups result in the highest binding affinity, whereas electron donating groups weakened guest binding. Binding affinities for **2g**, which contained the most electron donating group, were too low to measure reproducibly. These results suggest that acidification of the amide N-*H* plays a larger role in guest binding than increasing the basicity of the pyridine nitrogen, which is consistent with the closer proximity of the amide group to the electronically-substituted phenyl group. To quantitatively compare the impacts of electronic effects on barbiturate binding, we used the experimentally-determined binding affinities to construct a Hammett plot using the corresponding σ_p values for each substituent (Figure 3.3).[80,81] The resultant Hammett plot has a positive slope, which confirms that negative charge buildup is stabilized during the guest binding process; an effect that is consistent with both increased amide acidity and increase electron density on the pyridine nitrogen.[82,83] The slope of the Hammett plot, however, shows a clear break between the electron donating and withdrawing groups, with ρ values of 1.08 ± 0.08 and 0.37 ± 0.02, respectively. This bimodal (or curved) Hammett plot suggests a change in binding conformation between the hosts with electron withdrawing and donating groups, respectively.[84-86] Such a change could be due to the shorter hydrogen bonds formed between host and guest upon acidification of the amides with inclusion of electron withdrawing groups.[76,77,87-90]

To further investigate this non-linear Hammett plot, we used computational studies to determine whether the break in the Hammett plot was related to changes in host-guest structure. Structures for **2a-f** coordinated to diethyl barbital were optimized at B3LYP/6-31+G(d,p) level of theory and the IEF-PCM solvation model for $CHCl_3$, which has been shown to correlate well with experimental binding affinities in similar systems.[75] Calculations using dispersion-corrected functionals were also performed, and provided similar results. For each optimized geometry, the NH-O(barbital) and N-HN(barbital) hydrogen bond lengths were measured and compared to that of **2a** ligated to barbital. As expected, the distal NH of the alkyl amide did not change upon

electronic substitution to the phenyl ring because the alkyl NH is too far away from the electronic modulation to expect a significant contribution. By contrast, the amide NH proximal to the benzene ring changes linearly with electronic substitution. Similarly, the hydrogen bond to the pyridyl nitrogen changes, although not linearly, with electronic substitution. Taken together, the structural difference upon electronic substation are consistent with a change in equilibrium geometry, which would correspond to a bimodal (or curved) Hammett plot, which is consistent with the observed experimental results (Figure 3.4).

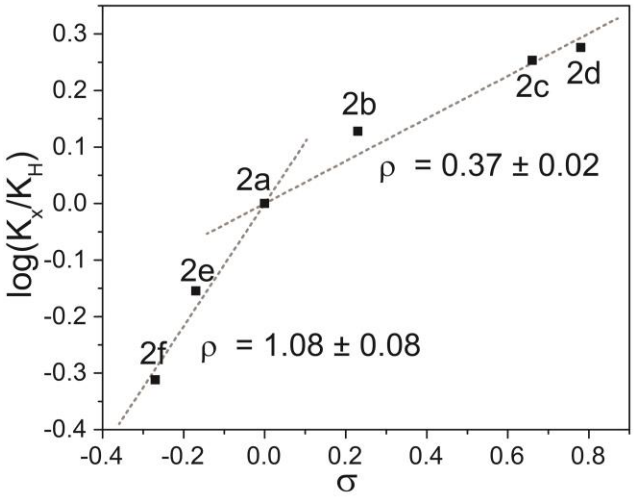


Figure 3.3. Hammett plot of hosts **2a-f** binding diethyl barbital. Binding constants were obtained by following the barbital N-H resonance using ^{1}H NMR spectroscopy (500 MHz, 25 °C, $CDCl_3$).

In conclusion, we have shown that binding of barbiturates to 2,6-diamidopyridines with different electronic structures produces a non-linear Hammett plot, which is characteristic of changes in host-guest structure upon modulation of electronic structure. These results were supported both experimentally, using determined binding affinities, as well as computationally, using structural comparisons of optimized host-guest geometries. Taken together, these studies

highlight how changes in electronic structure in hydrogen bonding assemblies can result not only in change in binding affinities, but also in changes in assembled structure, thus providing insight into the factors controlling structural changes in the hydrogen-bonded complexes between the receptors and barbiturate guest.

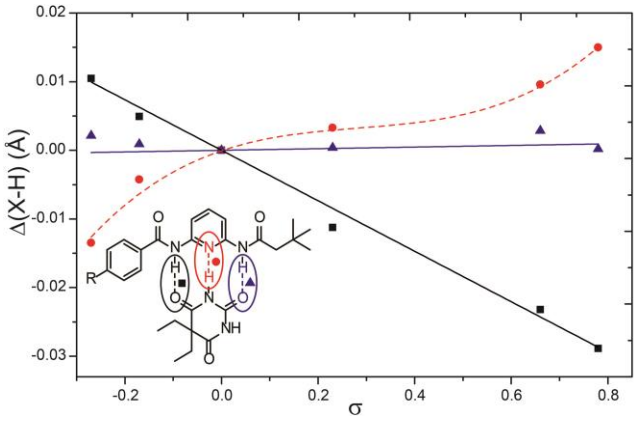


Figure 3.4. Comparison of the NH-O(barbital) and N-HN(barbital) hydrogen bonding distances for **2a-f** hydrogen bonded to diethylbarbital. Calculations were performed in Gaussian using the B3LYP/6-31+G(d,p) level of theory and the IEF-PCM solvation model for $CHCl_3$.

Experimental Section

Materials and Methods. All commercially-available reagents were used as received. Deuterated solvents were used as received. Anhydrous solvents used for syntheses were collected from a solvent purification system. Reactions were monitored by TLC on Silicagel 60 F_{254} plates and the products were purified on an automated chromatography instrument using SiliaFlash F60 SiO_2. NMR spectra were recorded at the indicated frequencies on either 300 MHz or 500 MHz spectrometer. Chemical shifts are reported in parts per million (δ) and are referenced to residual

protic solvent resonances. The following abbreviations are used in describing NMR couplings: (s) singlet, (d) doublet, (t) triplet, (m) multiplet and (b) broad.

General Procedure Binding Constant Determination. Binding studies were performed in $CDCl_3$ for host molecules **2a-g** and were monitored by ^1H NMR spectroscopy. In a typical $CDCl_3$ titration, 2.00 mL of a 1.0 mM of barbital was prepared. The guest solution was then divided such that 1.00 mL was placed into an NMR tube and the other 1.00 mL was used to create a second solution containing 50-75 mM host. An initial spectrum of the guest was recorded, after which aliquots (5-100 µL) of the host solution were added until the N-H resonance of barbital no longer shifted. The resultant curves were fit using a 1:1 model and the K_{assoc} obtained.[61]

Computational Details. Calculations were performed using the Gaussian 09[91] software package using the GaussView[92] 5.0 graphical user interface. Geometry optimizations and unscaled frequency calculations were performed at the B3LYP/6-31+G(d,p) level of theory using the IEF-PCM solvation model for chloroform. Frequency calculations were performed on all converged structures confirmed that they corresponded to local minima. In all cases, the lowest energy conformer was used to compare the relative energetics of the calculated species.

Syntheses. ***N*-(6-Aminopyridin-2-yl)-3,3-dimethylbutanamide (1a)**. A round bottom flask was charged with dry THF (100 mL) and 2,6-diaminopyridine (1.04 g, 9.5 mmol). The flask was then lowered into an ice bath and deoxygenated by sparging with N_2. 3,3-Dimethylbutyryl chloride (0.60 mL, 4.3 mmol) was added to an addition funnel containing dry THF (25 mL), and the resultant solution was then added slowly to the diaminopyridine solution over the course of 1 hour while stirring at 0 °C under N_2. Once the addition of the acid chloride was complete, the ice bath was removed and the reaction was allowed to warm to room temperature overnight while stirring under N_2. The precipitate from the reaction was filtered, and the resultant filtrate was concentrated by rotary evaporation. The crude product was purified by column chromatography (SiO_2, EtOAc) to afford a solid (0.61 g, 69%). Mp = 113-114 °C. ^1H NMR (300 MHz, $CDCl_3$)

δ:7.77 (s, 1H), 7.59 (d, J = 8.0, 1H), 7.48 (t, J = 8.0, 1H), 6.28 (d, J = 7.5, 1H), 4.43 (s, 2H), 2.24 (s, 2H), 1.11 (s, 9H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ:170.3, 156.7, 149.4, 140.5, 104.2, 103.2, 51.7, 31.3, 29.9. HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $[C_{11}H_{17}N_3ONa]^+$, 230.1269; found 230.1275.

2-Amino-6-(3,3-dimethylbutanamido)pyridine 1-oxide (1b). **1a** (0.20 g, 0.97 mmol) was added to a round bottom flask containing THF (75 mL). *m*CPBA (0.22, 1.3 mmol) was then added to the flask and the reaction was allowed to stir overnight at room temperature. The reaction mixture was concentrated and the residue was taken up in EtOAc and washed 3x with 75 mL of saturated K_2CO_3. The organic layer was concentrated using a rotary evaporator to yield the product as a yellow solid (0.18 g, 84%). Mp = 119-120 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.95 (s, 1H), 7.78 (d, J = 8.5, 1H), 7.19 (t, J = 8.5, 1H), 6.48 (d, J = 8.0, 1H), 5.77 (s, 2H), 2.40 (s, 2H), 1.12 (s, 9H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ:170.7, 148.6, 142.5, 130.1, 102.7, 102.1, 51.6, 31.3, 29.8. HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $[C_{11}H_{18}N_3O_2]^+$, 224.1399; found 224.1401.

2-(4-(Dimethylamino)benzamido)-6-(3,3-dimethylbutanamido)pyridine 1-oxide (1c). 4-Dimethylaminobenzoic acid (80 mg, 0.50 mmol) was added to a vial containing HOBT (70 mg, 0.55 mmol.), EDC (0.11 g, 0.55 mmol), NEt_3 (80 µL, 0.59 mmol), and CH_3CN (15 mL). The reaction mixture was allowed to stir for one hour at 50 °C before addition of **1b** (0.10 g, 0.46 mmol). The reaction mixture was stirred overnight at 50 °C, after which the solvent was removed under vacuum. The crude product was purified by column chromatography (SiO_2, 1:1 EtOAc:hexanes) to afford the product as an off-white solid (80 mg, 49%). Mp = 158-159 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 10.63 (s, 1H), 9.85 (s, 1H), 8.31 (d, J = 8.5, 1H), 8.15 (d, J = 8.3, 1H), 7.94 (d, J = 8.5, 2H), 7.42 (t, J = 9.0, 1H), 6.82 (d, J = 8.5, 2H), 3.11 (s, 6H), 2.42 (s, 2H), 1.16 (s, 9H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 170.2, 164.9, 162.9, 149.8, 149.4, 140.9, 129.1, 126.3, 114.1, 109.6, 109.4, 55.5, 51.9, 31.4, 29.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{20}H_{27}N_4O_3]^+$, 371.2079; found 371.2083.

***N*-(6-(3,3-Dimethylbutanamido)pyridin-2-yl)benzamide (2a)**. A round bottom flask was charged with dry THF (30 mL), **1a** (114.5 mg, 0.55 mmol), and NEt_3 (0.12 mL, 0.83 mmol). The flask was then lowered into an ice bath and deoxygenated by sparging with N_2. Benzoyl chloride (70 µL, 0.61 mmol) was added to an addition funnel containing dry THF (10 mL) and the resultant acid chloride solution was then slowly added to the diaminopyridine solution while stirring in the ice bath under N_2. Once the addition of the acid chloride was complete, the ice bath was removed and the reaction was allowed to warm to room temperature overnight while stirring under N_2. The reaction was concentrated by rotary evaporation and the crude product was taken up in EtOAc and washed 3x with 1M NaOH. The organic layer was kept and concentrated under vacuum to afford the product as a white solid (0.15 g, 87%). Mp = 140-141 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.34 (s, 1H), 8.08 (d, *J* = 8.0, 1H), 7.99 (d, *J* = 8.0, 1H), 7.90 (d, *J* = 7.5, 2H), 7.78-7.73 (m, 2H), 7.58 (t, *J* = 7.5, 1H), 7.51 (d, *J* = 8.0, 2H), 2.26 (s, 2H), 1.12 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 170.3, 165.4, 149.6, 140.9, 134.2, 132.3, 128.9, 127.1, 109.7, 109.6, 51.8, 31.4, 29.8. HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $[C_{18}H_{21}N_3O_2Na]^+$, 334.1531; found 334.1532.

4-Chloro-*N*-(6-(3,3-dimethylbutanamido)pyridin-2-yl)benzamide (2b). Disubstituted diaminopyridine **2b** was prepared according to the general procedure outlined for **2a** with the following quantities: 4-chlorobenzoyl chloride (50 µL, 0.37 mmol) in THF (10 mL) was added slowly to **1a** (58.2 mg, 0.281 mmol) and triethylamine (0.10 mL, 0.70 mmol) in THF (30 mL). The solvent was removed and the residue purified by column chromatography (SiO_2, 4:1 hexanes:EtOAc) to afford a white crystalline solid (95 mg, 97%). Mp = 149-151 °C. ^{1}H NMR (500 MHz, DMSO) δ: 10.49 (s, 1H), 10.07 (s, 1H), 8.01 (d, J = 8.5, 2H), 7.88 (d, J = 7.0, 1H), 7.81 (t, J = 7.5, 1H), 7.75 (d, J = 7.0, 1H), 7.60 (d, J = 8.5, 2H), 3.35 (s, 2H), 1.03 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, DMSO) δ: 171.4, 165.3, 151.0, 150.5, 140.4, 137.2, 133.4, 130.3,

128.9, 111.3, 110.3, 49.5, 31.4, 30.1. HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $[C_{18}H_{21}N_3O_2Cl]^+$, 346.1311; found 346.1322.

4-Cyano-*N*-(6-(3,3-Dimethylbutanamido)pyridin-2-yl)benzamide (2c). Disubstituted diaminopyridine **2c** was prepared according to the general procedure outlined for **2a** with the following quantities: 4-cyanobenzoyl chloride (228 mg, 1.38 mmol) in THF (10 mL) was added slowly to **1a** (238 mg, 1.15 mmol) and triethylamine (0.32 mL, 2.29 mmol) in THF (40 mL). The solvent was removed and the residue purified by column chromatography (SiO_2, 1:1 EtOAc:hexanes) to afford a white crystalline solid (0.31 g, 80%). Mp = 202-203 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.27 (s, 1H), 8.07-8.02 (m, 4H), 7.85-7.79 (m, 3H), 7.55 (s, 1H), 2.28 (s, 2H), 1.13 (s, 9H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 170.3, 163.6, 149.6, 148.9, 141.2, 138.1, 132.7, 127.8, 117.8, 115.9, 110.3, 109.7, 51.8, 31.4, 29.8. HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $[C_{19}H_{20}N_4O_2Na]^+$, 359.1484; found 359.1499.

***N*-(6-(3,3-Dimethylbutanamido)pyridin-2-yl)-4-nitrobenzamide (2d).** The disubstituted diaminopyridine **2d** was prepared according to the general procedure outlined for **2a** with the following quantities: 4-nitrobenzoic acid was stirred in thionyl chloride (3 mL) overnight at 65 °C. The thionyl chloride was removed and the residue taken up in THF (10 mL) and was then added slowly to **1a** (126.6 mg, 0.61 mmol) and NEt_3 (0.17 mL, 1.22 mmol) in THF (30 mL). The solvent was removed and the residue purified by column chromatography (SiO_2, 1:1 EtOAc:hexanes) to afford a white crystalline solid (0.20 g, 84 %). Mp = 162-163 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.38 (d, *J* = 9.0, 2H), 8.10 (d, *J* = 8.5, 2H), 8.07-8.02 (m, 2H), 7.81 (t, J = 8.0, 1H), 7.61 (s, 2H), 2.29 (s, 2H), 1.14 (s, 9H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 170.4, 163.5, 150.0, 149.6, 148.9, 141.2, 139.6, 128.4, 124.1, 110.3, 109.7, 51.8, 31.4, 29.8. HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $[C_{20}H_{27}N_4O_2]^+$, 355.2134; found 355.2123.

***N*-(6-(3,3-Dimethylbutanamido)pyridin-2-yl)-4-methylbenzamide (2e)**. Disubstituted diaminopyridine **2e** was prepared according to the general procedure outlined for **2a** with the

following quantities: *p*-tolulic acid was stirred in thionyl chloride (3 mL) overnight at 65 °C. The thionyl chloride was then removed under vacuum and the residue taken up in THF (10 mL) and was then added slowly to **1a** (160.1 mg, 0.77 mmol) and triethylamine (0.22mL, 1.54 mmol) in THF (30 mL). The solvent was removed and the residue purified by column chromatography (SiO_2, 1:1 EtOAc:hexanes) to afford a white crystalline solid (0.22 g, 81%). Mp = 159-161 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.28 (s, 1H), 8.09 (d, *J* = 8.5, 1H), 7.98 (d, J = 7.5, 1H), 7.83 (d, J = 8.0, 2H), 7.78 (t, J = 8.0, 1H), 7.60 (s, 1H), 7.32 (d, J = 8.0, 2H), 2.46 (s, 3H), 2.28 (s, 2H), 1.14 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 170.3, 165.5, 149.6, 149.3, 143.0, 141.1, 131.3, 129.6, 127.1, 109.6, 109.5, 51.8, 31.4, 29.8, 21.6. HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $[C_{19}H_{24}N_3O_2]^+$, 326.1869; found 326.1877.

***N*-(6-(3,3-Dimethylbutanamido)pyridin-2-yl)-4-methoxybenzamide (2f).** Disubstituted diaminopyridine **2f** was prepared according to the general procedure outlined for **2a** with the following quantities: *p*-anisic acid (73.9 mg, 0.489 mmol) was stirred in thionyl chloride (3 mL) at 65 °C overnight. The thionyl chloride was removed under vacuum and the resulting residue taken up in THF (10 mL) was added slowly to **1a** (91.5 mg, 0.442 mmol) and triethylamine (0.12 mL, 0.882 mmol) in THF (30 mL). Purified by column chromatography (SiO_2, 1:1 EtOAc:hexanes) to afford a white crystalline solid (0.18 g, 95%). Mp = 171-172 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.36 (s, 1H), 8.11 (d, *J* = 8.5, 1H), 7.98 (d, *J* = 8.0, 1H), 7.98 (d, *J* = 8.5, 2H), 7.82 (t, *J* = 7.5, 1H), 7.64 (s, 1H), 7.02 (d, *J* = 9.0, 2H), 3.92 (s, 3H), 2.28 (s, 2H), 1.15 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 170.4, 165.0, 162.9, 149.7, 149.4, 141.1, 129.1, 126.2, 114.1, 109.6, 109.4, 55.5, 51.8, 31.4, 29.8. HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $[C_{19}H_{23}N_3O_3Na]^+$, 364.1637; found 364.1635.

4-(Dimethylamino)-*N*-(6-(3,3-dimethylbutanamido)pyridin-2-yl)benzamide (2g). **1c** (48 mg, 0.13 mmol) was placed in a vial in a glovebox. A solution of *bis*(pinacolato)diboron (36 mg, 0.14 mmol) in CH_3CN (10 mL) was then added to **1c** and allowed to stir for 24 hours. The

solvent was then removed and the residue purified using column chromatography (SiO_2, 3:1 EtOAc:hexanes) to afford a white, chalky solid (40 mg, 87%). Mp = 207-209 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.23 (s, 1H), 8.09 (d, *J* = 8.5, 1H), 7.94 (d, *J* = 7.5, 1H), 7.82 (d, *J* = 8.5, 2H), 7.75 (t, *J* = 8.0, 1H), 7.66 (s, 1H), 6.72 (d, *J* = 9.0, 2H), 3.07 (s, 6H), 2.27 (s, 2H), 1.13 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 170.3, 165.3, 152.9, 150.2, 149.4, 140.8, 128.9, 120.4, 111.1, 109.6, 109.0, 51.8, 40.1, 31.4, 29.8. HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $[C_{20}H_{26}N_4O_2Na]^+$, 377.1953; found 377.1966.

Supporting Information NMR spectra of new compounds, titration data, optimized geometries is available in Appendix B.

CHAPTER IV

TOWARD SUPRAMOLECULAR ENANTIOSELECTIVE CATALYSTS: INVESTIGATING INTERACTIONS OF MODIFIED HAMILTON RECEPTORS WITH CHIRAL BARBITURATES

Supramolecular Enantioselective Catalysis

One of our goals is to use barbiturate ligand self-assembly to generate synthetically-simple chiral catalysts by utilizing host-guest interactions. Our approach here is to use achiral ligands that bind to a chiral guest, which results in transfer of chirality from the guest to the entire self-assembled catalyst complex.[93-95] Additionally, use of simple ligand components will enable generation of larger ligand libraries by mixing and matching different ligands with different chiral barbiturates. One added benefit of this approach is that many of the chiral barbiturates can be made in one step, which allows for simple access to enantiomers of different chiral guests.

In nature, enantioselective catalysis is often controlled by enzymes that use chiral cofactors to activate enzymatic systems.[96] Taking inspiration from nature, a chiral co-factor (or guest) can be added to an achiral metal complex creating an enantioselective supramolecular catalyst. Reek and co-workers chose to use a diamidodiindolylmethane anion receptor as the core for their enantioselective supramolecular catalyst system. One benefit of this system is that there is a large library of both natural and synthetic carboxylic acids that can be employed as potential guests. The chiral co-factor, in this case the carboxylic acid, fits in the binding pocket of the ligand and directs the incoming reagent to the metal center through hydrogen bonding. They studied the catalysts in the asymmetric hydrogenation of 2-acet-amidoacrylate using a variety of

both chiral and achiral co-factors. The most active catalyst complex, shown in Figure 4.1, afforded the product with 100% conversion and 98% ee. The metal complexes containing the achiral cofactor produced similar yields, but with no enantioselectivity.[97]

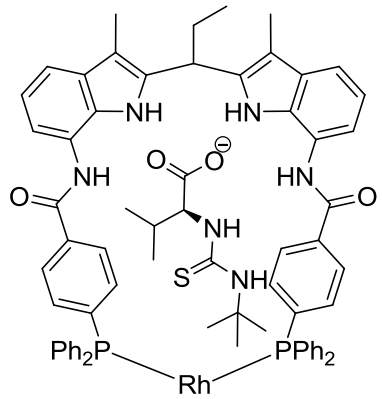


Figure 4.1. Achiral diamidodiindolylmethane anion receptor designed by Reek and co-workers that binds a chiral cofactor to produce a chiral metal complex.

In a similar example of a bound guest transmitting information to a catalyst system, Friexa and co-workers reported an enantioselective supramolecular catalyst in which a commercially available chiral guest binds to the ligand system to transmit chiral information to the catalyst. Even though the chirality center is 13 bonds and 14 Å away from the catalytically active center, chirality transfer is still observed. Additionally, the order of addition of the chiral diols or the achiral ligands did not impact the observed catalysts and both the Δ and Λ diastereomers were able to be formed. Using this self-assembled chiral catalyst complex, the authors were able to demonstrate the rhodium-catalyzed asymmetric hydrogenation of pro-chiral alkenes with full conversion after 3 hours and varying levels of enantioselectivity. The highest observed enantiomeric excess was 92%, with the catalyst system shown in Figure 4.2. The more

electron rich ligands displayed higher enantioselectivites likely due to stronger favored interactions with one product isomer over the other. Conversely, increased steric bulk on the ether oxygen in the ligand reduced the observed ee's.[98]

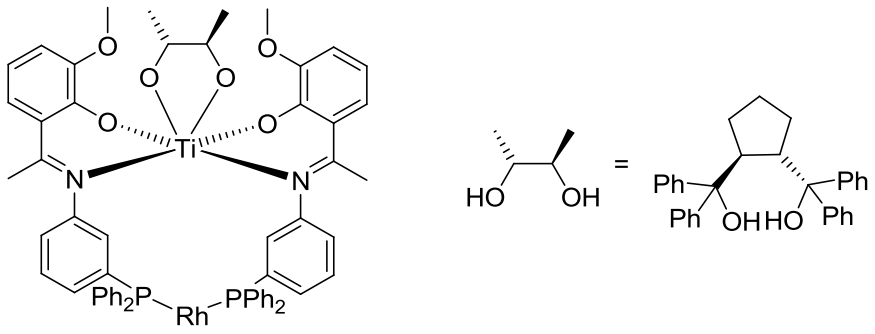


Figure 4.2. Enantioselective supramolecular catalyst developed by Friexa and co-workers.

Based on these demonstrated reports of transfer of chirality from the guest to a catalytically-active site, we reasoned that similar chiral transmission could be obtained from achiral barbiturate-binding ligands used in combination with a chiral barbiturate guest. As a first step toward this goal, the transmission of chiral information from the guest to the host needs to be examined. One simple method to measure chirality of complexes in solution is by using circular dichroism (CD) spectroscopy. Circular dichroism has been used before to investigate chirality and different configurations of supramolecular systems, including molecular tweezers and hydrogen bonded complexes.[99,100] This technique has also been used to determine the chirality of optically inactive cyclodextrose by using an optically-active naphthalene guest and measuring the CD spectrum of the resultant host-guest complex and measuring distinctive Cotton Effects.[101]

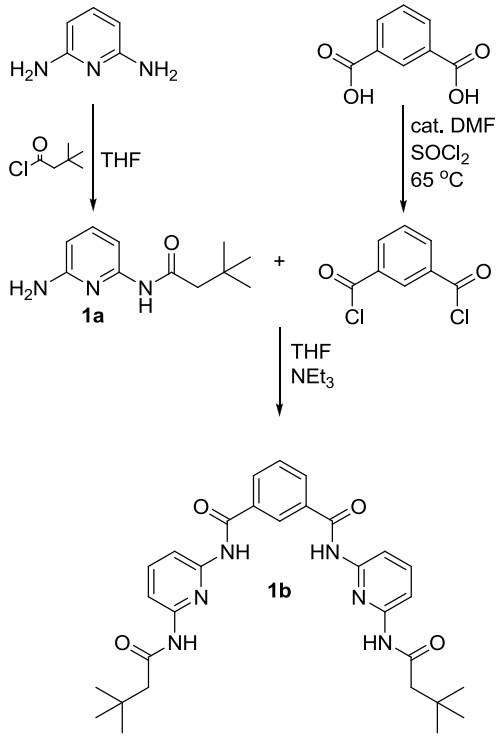
Here we report progress toward transferring chiral information from a barbiturate guest to achiral bifurcated Hamilton receptors, with the ultimate goal of translating the observed

chemistry to generate chiral catalysts. As a model system, we report the preparation of a novel, chiral, BINAP-derivatized barbiturate guest. As a model host system, we chose an open host with rigid backbone to generate a pre-organized pocket for the guest to maximize the binding affinity of the guest and to mimic the pre-organization that would be afforded by binding to a metal complex.[13]

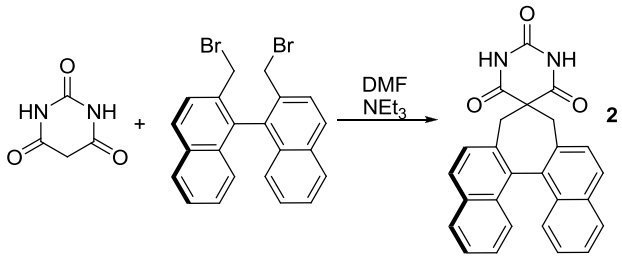
Results and Discussion

A model host was synthesized to assess the effect that a chiral guest would have on an achiral host. We designed the model system such that the host would have a rigid backbone to provide a pre-organized structure to favor tight binding by the guest. The methylene spacer between the amide and the tert-butyl group should also facilitate guest binding while also discouraging self-aggregation of the host. Ideally, the high binding affinity will facilitate measuring the host-guest interactions at concentrations amenable to UV-vis and circular dichroism measurements. To produce the model host, **1a** was prepared by stirring 2,6-diaminopyridine with the 0.5 equivalents of the desired acid chloride as shown in Scheme 4.1. The monosubstituted diaminopyridine **1a** was then treated with 0.5 equiv of isophthaloyl dichloride with NEt_3 and THF. The decorated barbiturate was prepared from barbituric acid and the 2,2'-*bis*(bromomethyl)binapthyl derivative shown in Scheme 4.2.

To measure the affinity of the designed host, **1b**, for complimentary guest **2**, ^{1}H NMR titrations were performed in $CDCl_3$. The N-*H* ^{1}H NMR resonances of the guest were monitored over the course of the titrations. The resultant binding isotherms were fit to a 1:1 model, based on previous studies investigating the binding stoichiometry of similar Hamilton receptors with barbiturate guests.[75] The observed K_{assoc} of **1b** for **2** was measured to be 1254 ± 33 M^{-1}.



Scheme 4.1. Preparation of hydrogen-bonding ligands based on 2,6-dicarboxyamido pyridine scaffolds.



Scheme 4.2. Preparation of guest **2** from barbituric acid.

To test the induction of chirality from the host to the guest, the CD spectra of the host-guest system (Figure 4.3a) was measured and the signal was found to be very small, as shown in Figure 4.3b. This problem is likely due to the similar absorbance maxima of the host and the guest, which makes differentiating free guest from the bound host/guest complex difficult. To overcome this problem, a modified host was synthesized with an attachment point on which a chromophore that absorbs at longer wavelength could be attached. By shifting the host absorbance to a longer wavelength, the absorbance of the chiral barbiturate and the host will be better separated, which will allow for better resolution of their individual CD signals.

The modified host was prepared by stirring **1a** with 0.5 equivalents of 5-nitroisophthaloyl dichloride, NEt_3, and THF as shown in Scheme 4.3. The resultant product was then hydrogenated with Pt(black) in EtOH to afford the amine product. Different reaction conditions for the coupling of dansyl-chloride and **1d** were tried and the attempts were unsuccessful. Fluorescein isothiocyanate was chosen, due to its facile coupling with amines, and was appended to **1d** using CH_3CN as the reaction solvent.

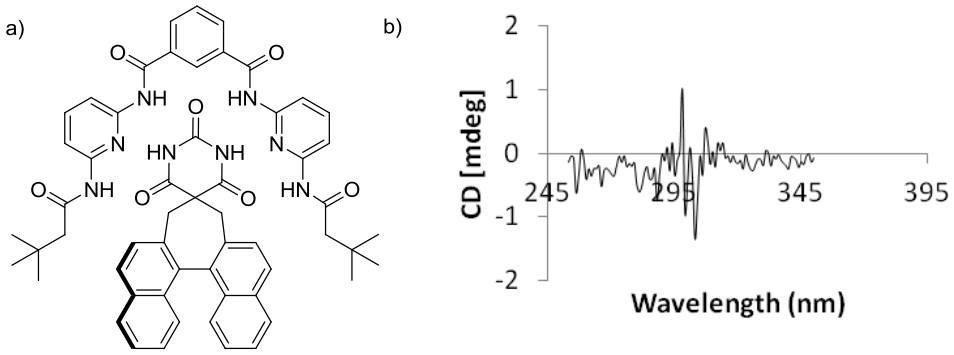
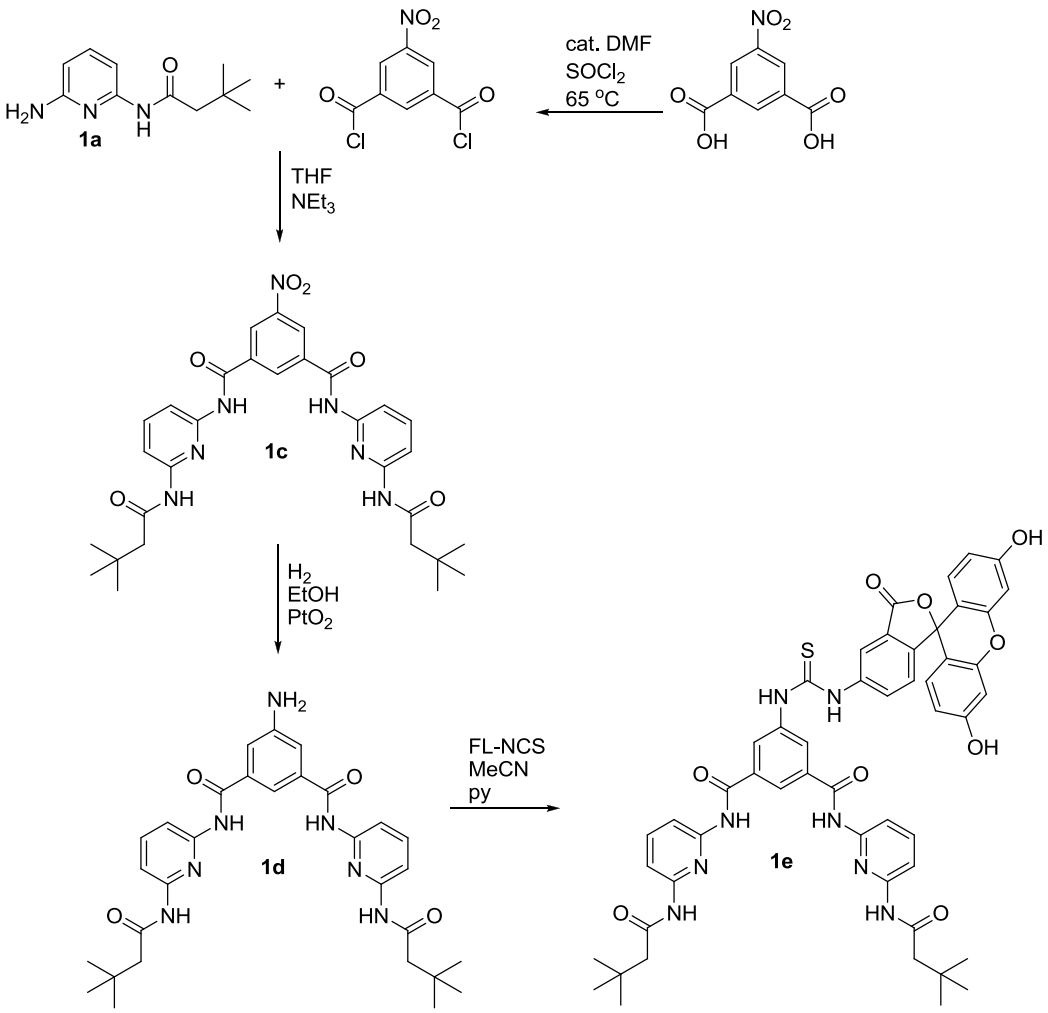


Figure 4.3. a) Nonfunctionalized host, **1b**, with **2**. b) CD spectra of the nonfunctionalized host with guest **2b**.



Scheme 4.3. Synthesis of the open Hamilton receptor with an appended fluorophore.

We chose to append a fluorophore to the host molecule such that its absorption and emission would be outside the range of the chiral guest. Unfortunately, solubility issues of **1e** prevented further study of this system. Several titrations were attempted in both $CDCl_3$ and CD_3CN with varying amounts of DMSO-d_6. At 2-5% DMSO-d_6 in CD_3CN, the binding of 1e with guest 2 was too low to measure. At lower concentrations of 1.5% DMSO-d_6 in CD_3CN, the host was not sufficiently soluble to obtain acceptable ^{1}H NMR spectra for titrations. In the future,

other fluorophores and different attachment points will be explored in hopes to alleviate the solubility issues of the host scaffold

In conclusion, transmission of chiral information from the barbiturate to the achiral Hamilton appears to be a feasible, but a refined system needs to be prepared in which the host solubility is improved while maintaining the optical separation of the host and guest. Solubility issues can be addressed by the addition of a different, less polar fluorophore with fewer hydrogen bond donor or acceptor groups. Ideally, the λ_{max} of the chromophore should be above 500 nm to be out of the cut-off window of the solvent, CH_3CN, and to avoid the absorbance range of the guest. Different attachment points of the chromophore on the host could be exploited as well, such as para to the pyridine nitrogen or perhaps in the place of the ^{t}Bu groups. Once the host molecule is solubilized, the circular dichroism studies can be used to investigate the chiral transmission between the guest and the host molecules.

Experimental Section

Materials and Methods. All commercially-available reagents were purchased from TCI or Aldrich and used as received. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. Anhydrous solvents used for syntheses were collected from a solvent purification system. Reactions were monitored by TLC on Silicagel 60 F_{254} (EMD) plates and the products were purified on an automated chromatography instrument using SiliaFlash F60 SiO_2 (Siliacycle). NMR spectra were recorded at the indicated frequencies on either Varian 300 MHz or Varian 500 MHz spectrometer. Chemical shifts are reported in parts per million (δ) and are referenced to residual protic solvent resonances. The following abbreviations are used in describing NMR couplings: (s) singlet, (d) doublet, (t) triplet, (m) multiplet and (b) broad.

General Procedure for Binding Constant Determination. Binding studies were performed in $CDCl_3$ or CD_3CN with varying amounts of DMSO-d_6 for host molecules **1b** and **1e.** The amide

resonances of the host were monitored by ^{1}H NMR spectroscopy. In a typical $CDCl_3$ titration, 2.00 mL of a 2.0 mM of **1b** or **1e** was prepared. The host solution was then divided such that 1.00 mL was placed into an NMR tube and the other 1.00 mL was used to create a second solution containing 30-50 mM guest, **2**. An initial spectrum of the guest was recorded, after which aliquots (5-100 μL) of the guest solution were added until the amide N-H resonance of the host no longer shifted. The resultant curves were fit using a 1:1 model and the K_{assoc} obtained.[61]

*Synthesis.****N*****-(6-Aminopyridin-2-yl)-3,3-dimethylbutanamide** (**1a**) A round bottom flask was charged with dry THF (100 mL) and 2,6-diaminopyridine (1.0 g, 9.5 mmol). The flask was then lowered into an ice bath and deoxygenated by sparging with N_2. 3,3-Dimethylbutyryl chloride (0.60 mL, 4.3 mmol) was added to an addition funnel containing dry THF (25 mL), and the resultant solution was then added slowly to the diaminopyridine solution over the course of 1 hour while stirring at 0 °C under N_2. Once the addition of the acid chloride was complete, the ice bath was removed and the reaction was allowed to warm to room temperature overnight while stirring under N_2. The precipitate from the reaction was filtered, and the resultant filtrate was concentrated by rotary evaporation. The crude product was purified by column chromatography (SiO_2, EtOAc) to afford a solid (0.61 g, 69%). Mp = 113-114 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.77 (s, 1H), 7.59 (d, J = 8.0, 1H), 7.48 (t, J = 8.0, 1H), 6.28 (d, J = 7.5, 1H), 4.43 (s, 2H), 2.24 (s, 2H), 1.11 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ:170.3, 156.7, 149.4, 140.5, 104.2, 103.2, 51.7, 31.3, 29.9. HRMS (m/z): $[M]^+$ calcd for $[C_{11}H_{17}N_3ONa]^+$, 230.1269; found 230.1275.

***N*^{1},*N*^{3}-bis(6-(3,3-dimethylbutanamido)pyridin-2-yl)isophthalamide (1b)** Isophthalic acid (180 mg, 0.89 mmol) was stirred in thionyl chloride (3 mL) at 65 °C with catalytic DMF for 7 hours, after which the excess thionyl chloride was removed under vacuum. The residue was taken up in THF (10 mL) and then added slowly to a round bottom flask charged with dry THF (30 mL), **1a** (390 mg, 1.87 mmol), and triethylamine (0.15 mL, 2.0 mmol). Once the addition of the acid chloride was complete, the reaction was allowed to stir overnight while under N_2. The

solvent was removed via rotary evaporation and the crude product was purified by column chromatography (SiO_2, 3:2 EtOAc:hexanes) to afford the product as an off-white solid (402 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.51(s, 2H), 8.46 (s, 1H), 8.09 (dd, *J* = 7.5, *J* = 2.0, 2H), 8.36 (d, *J* = 8.0, 2H), 8.00 (d, *J* = 8.0, 2H), 7.83 (s, 2H), 7.77 (t, *J* = 8.5, 2H), 7.62 (t, *J* = 7.5, 1H), 2.29 (s, 4H), (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 170.5, 164.3, 149.7, 149.2, 141.0, 134.7, 130.9, 129.6, 125.8, 110.1, 109.7, 51.7, 31.4, 29.8.

***N*^{1},*N*^{3}-Bis(6-(3,3-dimethylbutanamido)pyridin-2-yl)-5-nitroisophthalamide (1c)** 5-Nitroisophthalic acid (90 mg, 0.43 mmol) was stirred in thionyl chloride (3 mL) at 65 °C with catalytic DMF for 7 hours, after which the excess thionyl chloride was removed under vacuum. The residue was taken up in THF (10 mL) and then added slowly to a round bottom flask charged with dry THF (30 mL), **1a** (186 mg, 0.90 mmol), and triethylamine (0.23 mL, 1.71 mmol). Once the addition of the acid chloride was complete, the reaction was allowed to stir overnight while under N_2. The solvent was removed via rotary evaporation and the crude product was purified by column chromatography (SiO_2, 1:1 EtOAc:hexanes) to afford the product as an off-white solid (231 mg, 92%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.94 (d, J = 1.5, 2H), 8.83 (s, 2H), 8.61 (s, 3H), 8.03 (d, J = 8.0, 2H), 7.81 (t, J = 8.0, 2H), 7.73 (s, 1H), 2.31 (s, 4H), 1.15 (s, 18H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 170.5, 161.9, 149.8, 148.7, 148.7, 141.1, 136.6, 131.4, 125.2, 110.6, 109.8, 52.8, 31.4, 29.8.

5-Amino-*N*^{1},*N*^{3}-bis(6-(3,3-dimethylbutanamido)pyridin-2-yl)isophthalamide (1d). 1b (187 mg, 0.32 mmol) was placed in a Fischer-Porter tube along with platinum black (3.6 mg, 0.016 mmol), EtOH (20 ml), and a stir bar. The tube was pressurized with H_2 and then vented 3x to ensure the headspace was filled with only H_2. The reaction mixture was then allowed to stir for 18 hours at room temperature. Afterwards, the Fischer-Porter tube was vented and the reaction mixture concentrated via rotary evaporation. The crude product was purified by column chromatography (SiO_2, 2:1 EtOAc:hexanes) to afford the product as an off-white solid (171 mg,

97%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.43 (s, 1H), 7.98 (d, J =1.5, 3H), 7.72 (t, J = 1.5, 1H), 7.32 (s, 1H), 7.66 (s, 1H), 4.13 (s, 2H), 2.29 (s, 2H), 1.12 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 171.3, 166.2, 150.9, 150.6, 149.8, 140.5, 135.3, 116.7, 114.3, 110.8, 110.3, 49.6, 31.4, 30.1.

5-(3-(3,6-Dihydroxy-3'-oxo-3'H,10H-spiro[anthracene-9,1'-isobenzofuran]-5'-yl)thioureido)-*N*^{1},*N*^{3}-bis(6-(3,3-dimethylbutanamido)pyridin-2-yl)isophthalamide (1e). The reduced host, **1d** (38 mg, 0.068 mmol), was stirred in CH_3CN and fluorescein isocyanate (29 mg, 0.75 mmol) was added to the reaction mixture. The mixture was allowed to stir for 6 hours and then the solvent was removed via rotary evaporation. The crude product was purified by column chromatography (SiO_2, 1:1 EtOAc:hexanes) to afford the product as an orange, shiny solid (60 mg, 94%).^{1}H NMR (500 MHz, DMSO-$_{d6}$) δ: 10.48 (s, 2H), 10.44 (s, 1H), 10.36 (s, 1H), 10.15 (s, 2H), 10.00 (s, 2H), 8.37 (s, 1H), 8.30 (s, 2H), 8.19 (s, 1H), 7.87-7.08 (m, 5H), 7.26 (d, *J* = 5, 1H), 6.69 (s, 2H), 6.64-6.56 (m, 3H), 2.32 (s, 2H), 1.03 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, DMSO-$_{d6}$) δ:171.4, 165.3, 160.0, 125.3, 151.0, 150.5, 140.6, 140.4, 138.9, 131.5, 129.5, 127.4, 121.3, 121.3, 113.1, 110.9, 110.5, 110.0, 109.9, 102.7, 102.5, 49.6, 31.4, 30.1.

1'H-spiro[dinaptho[7,7]annulene-,6,5',8,7'-pyrimidine]-2',4',6'(3'H)-trione (2). Barbituric acid (322 mg, 2.51 mmol), 2,2'-bis(bromomethyl)biphenyl (854 mg, 2.51 mmol), NEt_3 (0.75 ml, 2.8 mmol), and DMF (50 ml) were added to a round bottom flask along with a stir bar. The reaction mixture was allowed to stir for 2 hours at room temperature. The reaction went from clear and colorless to cloudy and white and finally to clear and yellow upon reaction completion. The DMF was removed under high vacuum with gentle heating. The residue was purified using column chromatography (SiO_2, 3:1 EtOAc:hexanes) to afford an off-white, chalky solid (760 mg, 99%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.98 (s, 2H), 7.47 (d, *J* = 2.5, 2H), 7.38-7.35 (m, 4H), 7.31 (d, *J* = 5, 2H), 3.06 (bd, *J* = 65, 4H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ:171.7, 149.3, 140.1, 134.7, 131.1, 128.2, 127.9, 127.5, 62., 38.0.

Supporting Information NMR spectra of new compounds is available in Appendix C.

CHAPTER V

APPLICATION OF NEW SELF-ASSEMBLED LIGANDS BASED ON BIFURCATED HAMILTON RECEPTORS FOR USE IN SUPRAMOLECULAR CATALYSIS

Introduction

Bidentate ligands are a common class of ligands used in catalysis that often generate highly-active and selective catalysts. Such bidentate ligands, however, often suffer from synthetic challenges, which can often be alleviated by the use of less-active, but simpler monodentate ligands. One strategy to overcome these limitations is to develop and use monodentate ligands that can assemble through non-covalent interactions to mimic the structure of bidentate ligands. Several examples of such catalysts (figure 5.1) have been described in the literature, and much work has been done to illustrate the utility of these ligands in different catalytic processes.[6,7,10,11,102]

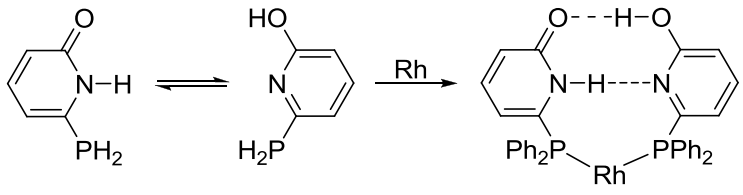


Figure 5.1. 6-DPPon hydrogen bonded catalyst complex developed by Breit and co-workers.

One strategy to improve the fidelity of these self-assembled ligands is to increase the number of hydrogen-bonding interactions between the ligand components.[7] The 6-DPPon system, for example, has four hydrogen bonds that stay intact throughout the entire catalytic cycle as demonstrated by both experimental and computational studies.[9,103] Demonstrating the activity of

this self-assembled catalyst system, the 6-DPPon ligand system has been used in the regioselective hydroformylation of both terminal alkenes and 1,1-disubstituted allenes. Additionally, this catalyst is also more active and selective than the traditional bidentate Xantphos ligand for the regioselective hydroformylation of terminal alkenes. One explanation for this heightened selectivity is that an added benefit of the self-assembled systems allows for the hydrogen bonded catalyst to flex and more easily accommodate incoming reactants at the metal center or stabilize reactive species along the reaction coordinate.[104,105]

Our approach to produce a complex with strong noncovalent interactions between ligand components is to use derivatives of the Hamilton receptor that are able to both bind to a metal catalyst and also bind a barbiturate guest. Hamilton receptors form six hydrogen bonds with complimentary guests and have binding affinities for barbiturates of up to 10^4 M^{-1} in $CDCl_3$. The Hamilton receptor structure has been exploited in many applications from polymers and coatings on nanoparticles to catalysis.[15,16,38,56,106] Previous studies on Hamilton systems have explored how sterics, pre-organization, rigidity, and electronic effects affect guest binding.[13,14] Complete bifurcation of this scaffold produces an easy to modify modular ligand structure that allows for simple modification of either end of the barbiturate-binding ligand as shown in Figure 5.2. Similarly, the barbiturate guest can also be synthetically modified to modulate the steric bulk or chirality of the barbiturate guest (Figure 5.3).

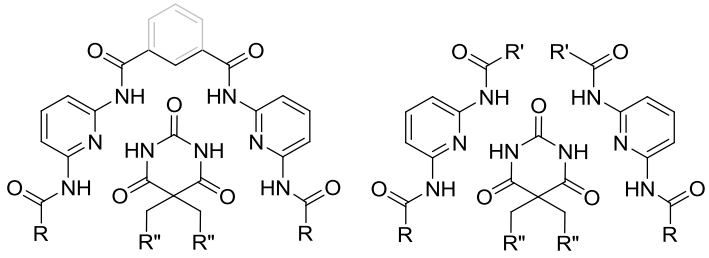


Figure 5.2. Deconstructed Hamilton receptors showing the versatile attachment points of different moieties to both the host and guest.

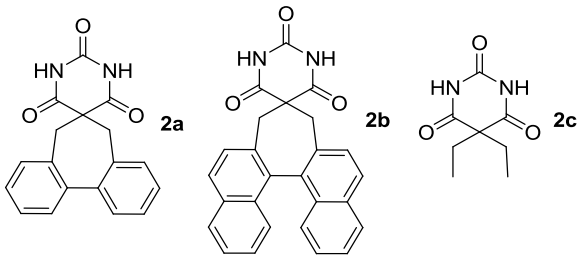


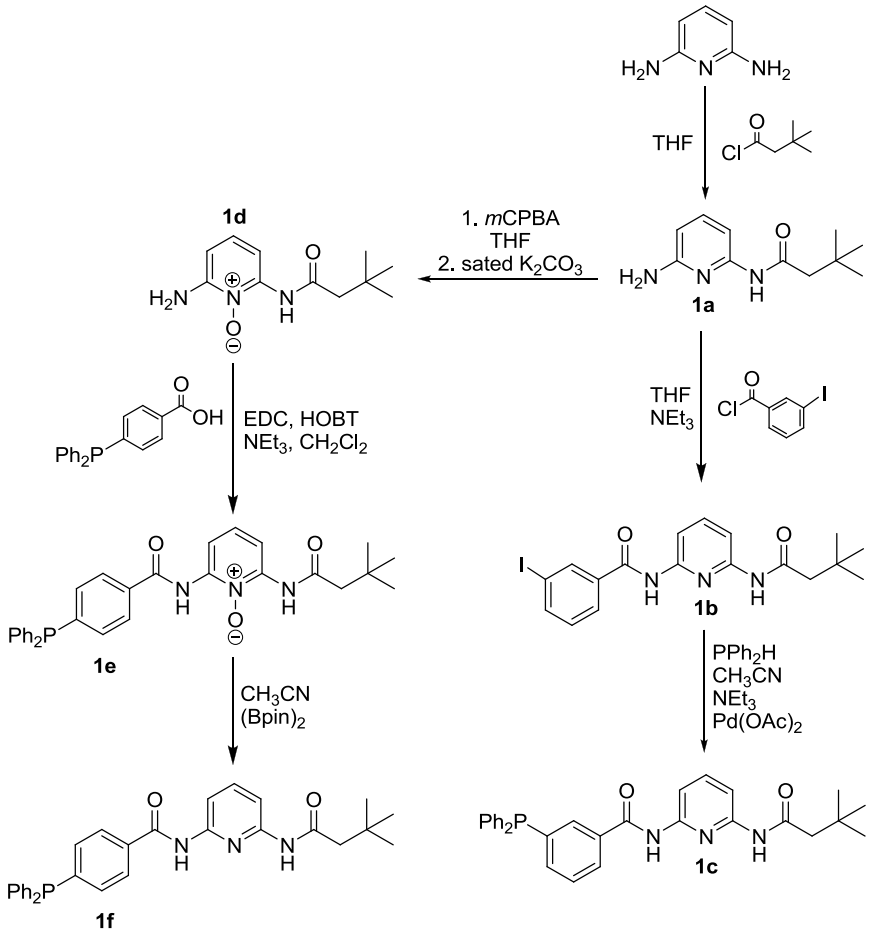
Figure 5.3. The barbiturate guests can also be modified to change the steric bulk or chirality of the guest. The three barbiturates used in our investigations of the Heck reaction are shown here.

The Hamilton receptor motif has been previously employed in the development of a series of diphenyl phosphine based ligands, and these ligands were tested in the palladium catalyzed Heck reaction. The Heck reaction is a versatile C-C bond forming reaction, and the importance of this reaction was recognized in 2010 when Richard F. Heck won the Nobel prize in chemistry along with Ei-ichi Neigshi and Akira Suzuki.[107] Many of the ligands utilized in the Heck reaction, especially for enantioselective Heck couplings, are bidentate phosphine ligands such as BINAP.[108] Due to the strong affinity of Hamilton receptors for complimentary guests, our expectation is that our developed catalyst complexes will behave similarly to a covalently attached bidentate ligand.[12]

Results and Discussion

Synthesis. Pyridyl amide **1a** was prepared by stirring diaminopyridine with the 0.5 equivalents of the desired acid chloride. Bis-amide **1b** was prepared by stirring the 3-iodobenzoyl chloride with **1a** in THF with NEt_3 as a base shown in scheme 5.1. Palladium-mediated cross-coupling between the aryl halide and PPh_2H afforded phosphine **1c**. To prepare compound **1f**, the mono-substituted diaminopyridine **1a** was mixed with *m*-CPBA in THF to oxidize the pyridine

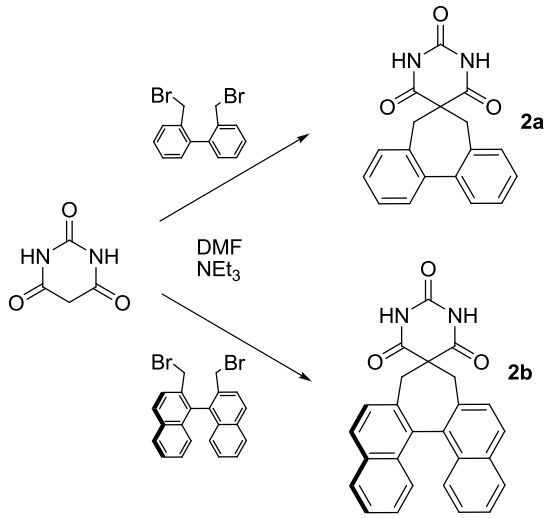
nitrogen to *N*-oxide **1d**, which was coupled to 4-(diphenylphosphino)benzoic acid using EDC and HOBT coupling agents in CH_3CN using NEt_3 as a base to yield **1e**. The *N*-oxide was then reduced using $(Bpin)_2$ to yield **1f.** The synthesis of the guests is shown in scheme 5.2.



Scheme 5.1. Synthesis of bifurcated Hamilton based diphenyl phosphine ligands.

Metal complexes of the developed ligands were prepared by stirring 0.5 equivalents of $Pt(COD)Cl_2$ or $Pd(OAc)_2$ with the desired ligand in CD_2Cl_2 for 1 hr (scheme 5.3). In addition to the more catalytically-relevant Pd complexes, we also chose to prepare Pt complexes because the ^{195}Pt-^{31}P coupling constants can be used to determine whether *cis* or a *trans* phosphine coordination is present. For the $Pt(\mathbf{1f})_2Cl_2$ complex, a $J_{Pt\text{-}P}$ = 1446 Hz was observed. Similarly, the

Pt(**1c**)$_2$Cl$_2$ complex afforded a J_{Pt-P} = 1435 Hz, both of which are consistent *cis* complex formation (Figure 5.4).



Scheme 5.2. Synthesis of guests **2a** and **2b** from barbituric acid.

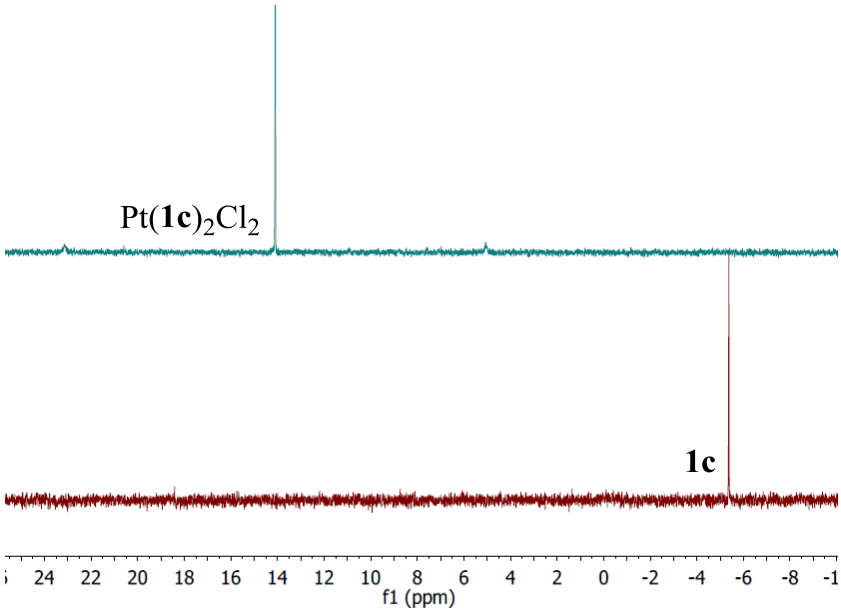
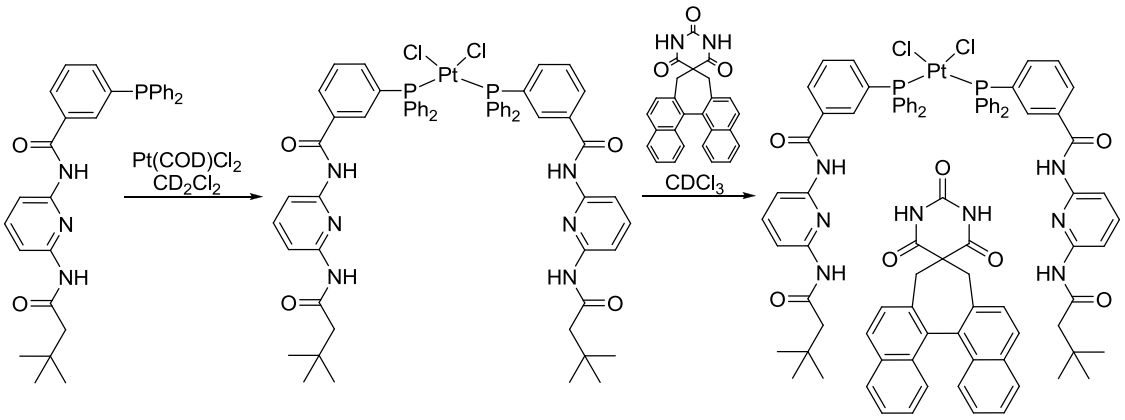


Figure 5.4. $^{31}P\{^1H\}$ NMR spectra of the free ligand **1c** and Pt(**1c**)$_2$Cl$_2$.

There are six hydrogen bonds present between the guest and the host; the strength of the hydrogen bonds can be tuned by adding groups with electron donating or electron withdrawing groups on the benzamide moiety of the host molecule.[14] The stability of the host-guest hydrogen bound complex can also be adjusted by decreasing the steric bulk on the amide moieties of the host.[13] The chosen ligand endcap, 3,3-dimethylbutanamide, lacks steric bulk near the amide N-*H* that participates in guest binding but the endcap displays steric bulk further away from the hydrogen bonding moieties. The structure of 3,3-dimethylbutanamide will encourage guest inclusion due to the lack of bulk near the binding pocket of the host while discouraging self-aggregation of the host molecules due to the bulky ^{t}Bu groups. Binding affinities for the guest can also be tuned by differing placements of the diphenyl phosphine moiety on the benzamide. The *meta* placement of the diphenyl phosphine moiety on the benzamide produces the most accommodating pocket for the barbiturate guests reflected by the high binding affinities of the metal complex Pt(**1c**)$_2$Cl$_2$ for the chosen guests **2a-c**.

Host-Guest Binding Studies. ^{1}H NMR titrations were performed in $CDCl_3$ to determine the binding affinities of metal complexes Pt(**1c**)$_2$Cl$_2$ and Pt(**1f**)$_2$Cl$_2$ for guests **2a-c**. Because binding of the barbiturate involves hydrogen bonding between the receptor and guest, the N-*H* NMR resonances of the barbital were monitored during the course of the titration. Based on the binding stoichiometry found during previous studies of similar systems, the binding isotherms were then fit to a 1:1 model. Each measurement was performed in triplicate to demonstrate their reproducibility and the calculated binding affinities are shown in Table 5.1.



Scheme 5.3. Ligand **1c** binding to Pt and then metal complex Pt(**1c**)$_2$Cl$_2$ binding guest **2b**.

The affinities of Pt(**1c**)$_2$Cl$_2$ and Pt(**1f**)$_2$Cl$_2$ for guests **2a-c** correlate with the steric bulk of the guest. The magnitude of the steric bulk was observed to correlate negatively with binding affinities in similar systems.[13] Both metal complexes Pt(**1c**)$_2$Cl$_2$ and Pt(**1f**)$_2$Cl$_2$ have the highest binding affinity for the smallest guest, **2a**. The slightly larger BINAP-guest **2b**, produces small decrease in the binding affinities of the metal complexes with respect to biphenyl guest **2a**. The bulkiest guest, **2c** produced the lowest binding affinities upon incorporation into the host pocket and also had a larger decrease in the K_{assoc} with respect to the binding affinities with **2a** and **2b**. Overall, the *meta*-substituted phosphine ligand produces the most accommodating pocket for the chosen guests. Extrapolating from these binding affinities, the phosphine ligand **1c** and the guest **2a** would produce the strongest host-guest complex and therefore mimic a bidentate ligand at the metal center.

Palladium-Catalyzed Heck Reaction Screenings. To determine whether the developed ligands were viable ligands for transition metal catalyzed reactions, the metal complexes Pd(OAc)$_2$(**1c**)$_2$ and Pd(OAc)$_2$(**1f**)$_2$, with and without the presence of complementary guests, were used to investigate the Pd-catalyzed Heck coupling of iodobenzene and butyl acrylate. Pd(OAc)$_2$

was used as a control catalyst and it was screened in both the presence and absence of guests **2a-c**. The ligands **1c** and **1f** were also tested without Pd in both the presence and absence of **2a-c**. Each reaction was run in a vial in 1.0 mL of CD_3CN, 5% catalyst loading, 10% guest loading, NEt_3, iodobenzene, and butyl acrylate. The reactions were heated at 80, 70, or 60 ^oC for 24 hrs and protected from light, after which they were allowed to cool to room temperature. Product formation was measured by ^1H NMR spectroscopy. The reactions were run in triplicate and the average of the three runs is shown in Table 5.2.

Table 5.1. Binding affinities of metal complexes Pt(**1c**)$_2$Cl$_2$ and Pt(**1f**)$_2$Cl$_2$ with guests **2a-c**.[a]

	Binding Constant (K_a, M^{-1})		
	2a	**2b**	**2c**
Pt(**1c**)$_2$Cl$_2$	894	661	109
Pt(**1f**)$_2$Cl$_2$	66	64	56

[a] Titrations were performed in $CDCl_3$ at 25 °C. All measurements are the average of at least three independent titrations.

The difference in reactions rates for the two metal complexes Pd(OAc)$_2$(**1c**)$_2$ and Pd(OAc)$_2$(**1f**)$_2$ suggest that the substitution of the diphenyl phosphine moiety on the ligand plays a role in the rate of catalysis. All of the yields for the complex with the para-substituted ligand, **1f**, are significantly greater than for the Pd(OAc)$_2$(**1c**)$_2$ metal complex. All of the reaction rates with the synthesized metal complexes were greater or equal to those found for Pd(OAc)$_2$ alone. This increase in product formation suggests that the ligands are able to assist in the stabilization of the metal center for the Heck reaction. Control reactions confirmed that the ligands alone are not viable catalysts for the Heck reaction in the absence of metal.

Table 5.2. Yields for the Pd catalyzed Heck coupling of iodobenzene and butyl acrylate with the metal complexes $Pd(OAc)_2$(**1c**)$_2$ and $Pd(OAc)_2$(**1f**)$_2$ and either one of the guests **2a-c** or no guest.[a]

		% yields			
	T (^{o}C)	no guest	**2a**	**2b**	**2c**
$Pd(OAc)_2$	80	49	61	58	58
	70	54	55	46	59
	60	41	56	26	56
$Pd(OAc)_2$(**1c**)$_2$	80	62	76	64	58
	70	59	70	62	67
	60	61	71	62	62
$Pd(OAc)_2$(**1f**)$_2$	80	70	70	64	66
	70	69	75	78	84
	60	87	76	80	78

[a]The reaction conditions were as follows: iodobenzene (20 µL), butyl acrylate (35 µL), NEt_3 (35 µL), CD_3CN (1 mL), metal complex (5%), guest (10%). The reaction was allowed to progress for 24 hrs at ether 80, 70, or 60 ^{o}C. The reaction was then allowed to cool and the percent yield was calculated by ^{1}H NMR spectroscopy. All reactions were run in triplicate to ensure reproducibility.

The strength of guest binding does not appear to play a large role in the observed rates of catalysis for the metal complexes $Pd(OAc)_2$(**1c**)$_2$ and $Pd(OAc)_2$(**1f**)$_2$. In the binding studies with the Pt metal complexes, the *meta*-substituted diphenylphosphine ligand had much higher biding affinities for guests **2a-c** than the *para*-substituted diphenyl phosphine ligand. The metal complex $Pd(OAc)_2$(**1f**)$_2$ however, which contains the *para*-substituted diphenyl phosphine ligand, exhibited higher rates of catalysis. To fully examine the effects of binding on the reaction rates, the temperature of the Heck reactions was varied. Three different temperatures were chosen, 80, 70, or 60 ^{o}C. At higher temperatures, the hydrogen bonded host-guest network should be weaker, which would result in decreased binding affinities. Temperature did not affect the control reaction

greatly; the reaction yields were close to one another without the guest and with **2a** and **2c**. Guest **2b** exhibited solubility issues without the presence of the ligands (**1c** and **1f**), and this limited solubility may account for the lower yields in the control reaction with $Pd(OAc)_2$ as the temperature was decreased. The temperature of the reaction did not have a significant impact on the catalysis by metal complex $Pd(OAc)_2(\mathbf{1c})_2$. By contrast, changing the reaction temperature did have a significant effect on the metal complex $Pd(OAc)_2(\mathbf{1f})_2$ and resulted in changes in overall conversion by as much as 18%. Because stronger hydrogen bonded networks can be formed at lower temperatures, this trend suggests that the strength of the hydrogen-bonded network between the ligands **1c** and **1f** and guests **2a-c** in the self-assembled metal complexes plays a secondary role to the diphenyl phosphine substitution on the benzamide moiety of the host.

Conclusion

A series of deconstructed Hamilton receptors were synthesized with diphenyl phosphine moieties for attachment to metal centers. Initial binding studies with Pt showed that the ligands **1c** and **1f** are bound in a *cis* fashion, creating a binding pocket for an incoming guest. The association constants of $Pt(\mathbf{1c})_2Cl_2$ and $Pt(\mathbf{1f})_2Cl_2$ with guests **2a-c** trend negatively with increased steric bulk of the guest. The *meta*-substituted diphenylphosphine ligand in complex $Pt(\mathbf{1c})_2Cl_2$ created the most robust complex with the guest and produced the highest binding affinities of the two metal complexes.

The bifurcated Hamilton receptor ligands are active in the palladium-catalyzed Heck reaction of iodobenzene with butyl acrylate. All reaction yields with the diphenylphosphine ligand-stabilized Pd were greater than or equal to those obtained with $Pd_2(OAc)_4$ alone. Complex $Pd(OAc)_2(\mathbf{1f})_2$ with the *meta*-substituted diphenylphosphine ligand produced higher reaction yields than did complex $Pd(OAc)_2(\mathbf{1c})_2$. These reaction rates do not correlate with the determined

binding constants, suggesting that phosphine substitution on the guest plays a larger role than affinity of the complex for the guest. Reaction temperature was varied and the reaction rates for complex $Pd(OAc)_2$(**1f**)$_2$ increased with decreasing temperature. As lower temperatures encourage the formation of hydrogen bonded networks, the increased reaction rates imply that the strength of the hydrogen bonds between the metal complex and the guest does play a role in the catalysis. Future work with the system will include investigating other metals, different substituents on the guest, different phosphine moieties, and different placement of these moieties on the host.

Experimental Section

Materials and Methods. All commercially-available reagents were purchased from TCI or Aldrich and used as received. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. Anhydrous solvents used for syntheses were collected from a solvent purification system. Reactions were monitored by TLC on Silicagel 60 F_{254} (EMD) plates and the products were purified on an automated chromatography instrument using SiliaFlash F60 SiO_2 (Siliacycle). NMR spectra were recorded at the indicated frequencies on either Varian 300 MHz or Varian 500 MHz spectrometer. Chemical shifts are reported in parts per million (δ) and are referenced to residual protic solvent resonances. The following abbreviations are used in describing NMR couplings: (s) singlet, (d) doublet, (t) triplet, (m) multiplet and (b) broad.

General Procedure Binding Constant Determination. Binding studies were performed in $CDCl_3$ for host molecules **2a-g** and were monitored by ^{1}H NMR spectroscopy. In a typical $CDCl_3$ titration, 2.00 mL of a 1.0 mM of barbital was prepared. The guest solution was then divided such that 1.00 mL was placed into an NMR tube and the other 1.00 mL was used to create a second solution containing 50-75 mM host. An initial spectrum of the guest was recorded, after which aliquots (5-100 μL) of the host solution were added until the N-H resonance of barbital no longer shifted. The resultant curves were fit using a 1:1 model and the K_{assoc} obtained.[61]

General Procedure for Screening of Heck Catalysis. The chosen guest, metal complex or ligand, NEt_3, iodobenzene, butyl acrylate, and CD_3CN were added to a 20 dram vial with a stir bar. The vial was sparged with N_2 for 5 seconds and then allowed to run for 24 hours at 80 °C, 70 °C, or 60 °C. After 24 hours, the reaction mixture was cooled to room temperature and the contents of the vial were transferred to a NMR tube. ^{1}H NMR spectra were obtained and the conversion was measured.

Synthesis. ***N*-(6-Aminopyridin-2-yl)-3,3-dimethylbutanamide (1a)**. A round bottom flask was charged with dry THF (100 mL) and 2,6-diaminopyridine (1.04 g, 9.51 mmol). The flask was then lowered into an ice bath and deoxygenated by sparging with N_2. 3,3-Dimethylbutyryl chloride (0.60 mL, 4.3 mmol) was added to an addition funnel containing dry THF (25 mL), and the resultant solution was then added slowly to the diaminopyridine solution over the course of 1 hour while stirring at 0 °C under N_2. Once the addition of the acid chloride was complete, the ice bath was removed and the reaction was allowed to warm to room temperature overnight while stirring under N_2. The precipitate from the reaction was filtered, and the resultant filtrate was concentrated by rotary evaporation. The crude product was purified by column chromatography (SiO_2, EtOAc) to afford a solid (0.61 g, 69%). Mp = 113-114 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.77 (s, 1H), 7.59 (d, J = 8.0, 1H), 7.48 (t, J = 8.0, 1H), 6.28 (d, J = 7.5, 1H), 4.43 (s, 2H), 2.24 (s, 2H), 1.11 (s, 9H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ:170.3, 156.7, 149.4, 140.5, 104.2, 103.2, 51.7, 31.3, 29.9. HRMS (m/z): $[M]^+$ calcd for $[C_{11}H_{17}N_3ONa]^+$, 230.1269; found 230.1275.

***N*-(6-(3,3-Dimethylbutanamido)pyridin-2-yl)-3-iodobenzamide (1b).** 3-Iodobenzoic acid (425 mg, 1.70 mmol) was stirred in thionyl chloride (3 mL) overnight at 65 °C. The thionyl chloride was then removed under vacuum and the residue was taken up in THF (10 mL) and then added slowly to a round bottom flask charged with dry THF (50 mL), **1a** (329 mg, 1.56 mmol), and NEt_3 (0.32 mL, 2.3 mmol). Once the addition of the acid chloride was complete, the reaction

was allowed to stir overnight while stirring under N_2. The reaction was concentrated by rotary evaporation and the crude reaction mixture was purified by column chromatography (SiO_2, 2:1 EtOAc:hexanes) to afford a white crystalline solid (595 mg, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.34 (s, 1H), 8.25 (s, 1H), 8.05 (d, J = 8.0, 1H), 8.01 (d, J = 8.0, 1H), 7.91 (d, J = 8.0, 1H), 7.87 (d, J = 8.0, 1H), 7.81 (s, 1H) 7.78 (t, J = 8.0, 1H), 7.25 (t, J = 7.5, 1H), 2.28 (s, 2H), 1.13 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 170.4, 163.9, 149.6, 149.2, 141.1, 136.2, 130.5, 126.4, 110.0, 109.7, 94.5, 77.3, 77.1, 76.8, 51.7, 31.4, 29.8.

***N*-(6-(3,3-Dimethylbutanamido)pyridin-2-yl)-3-(diphenylphosphino)benzamide (1c)**. **1b** (595 mg, 1.36 mmol), diphenylphosphine (0.28 mL, 1.63 mmol), triethylamine (0.23 mL, 1.63 mmol), $Pd(OAc)_2$ (15.3 mg, 0.06 mmol), and CH_3CN (15 mL) were combined in a vial in the glovebox. The reaction mixture was allowed to stir for 48 hrs. The reaction mixture was then concentrated by rotary evaporation and the crude product was purified by column chromatography (dried SiO_2, 1:1 EtOAC:hexanes) to afford a solid (342 mg, 51 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.21 (s, 1H), 8.03 (d, J = 1.5, 1H), 7.98 (d, J = 1.5, 1H), 7.90 (t, J = 1.5, 2H), 7.75 (t, J = 1.5, 1H), 7.58 (s, 1H), 7.48-7.32 (m, 12H), 2.26 (s, 2H), 1.13 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 170.2, 170.2, 164.9, 162.9, 153.4, 149.8, 149.4, 140.9, 129.1, 126.3, 114.1, 110.0, 109.6, 109.4, 55.5, 51.9, 29.8. ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$) δ: -5.3.

2-Amino-6-(3,3-dimethylbutanamido)pyridine 1-oxide (1d). **1a** (0.20 g, 0.97 mmol) was added to a round bottom flask containing THF (75 mL). *m*CPBA (0.22, 1.3 mmol) was then added to the flask and the reaction was allowed to stir overnight at room temperature. The reaction mixture was concentrated and the residue was taken up in EtOAc and washed 3x with 75 mL of saturated K_2CO_3. The organic layer was concentrated using a rotary evaporator to yield the product as a yellow solid (0.18 g, 84%). Mp = 119-120 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.95 (s, 1H), 7.78 (d, *J* = 8.5, 1H), 7.19 (t, *J* = 8.5, 1H), 6.48 (d, *J* = 8.0, 1H), 5.77 (s, 2H), 2.40 (s,

2H), 1.12 (s, 9H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ:170.7, 148.6, 142.5, 130.1, 102.7, 102.1, 51.6, 31.3, 29.8. HRMS (m/z): $[M]^+$ calcd for $[C_{11}H_{18}N_3O_2]^+$, 224.1399; found 224.1401.

2-(3,3-Dimethylbutanamido)-6-(4-(diphenylphosphino)benzamido)pyridine 1-oxide (1e). 1d (397 mg, 1.78 mmol) was added to a vial containing 4-diphenylbenzoic acid (544 mg, 1.78 mmol), HOBT (288 mg, 2.13 mmol.), EDC (410 g, 2.13 mmol), NEt_3 (0.30 mL, 2.13 mmol), and CH_3CN (15 mL). The reaction mixture was stirred overnight in the glovebox, after which the solvent was removed under vacuum. The crude product was purified by column chromatography (dried SiO_2, 1:1 EtOAc:hexanes) to afford the product as an off-white solid (520 mg, 57 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 10.74 (s, 1H), 9.81 (s, 1H), 8.29 (d, *J* = 2, 1H), 8.27 (d, *J* = 2, 1H), 8.22 (d, *J* = 1.5, 2H), 8.20-1.35 (m, 13H), 2.42 (s, 2H), 1.16 (s, 9H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 170.6, 166.5, 137.1, 134.9, 134.0, 133.8, 131.4, 129.3, 128.8, 128.8, 128.6, 128.5, 107.8, 107.7, 51.8, 31.4, 29.8. $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) δ: -5.1.

***N*-(6-(3,3-Dimethylbutanamido)pyridin-2-yl)-4-(diphenylphosphino)benzamide (1f). 1d** (510 mg, 1.00 mmol) was placed in a vial in a glovebox. A solution of *bis*(pinacolato)diboron (279 mg, 1.09 mmol) in CH_3CN (15 mL) was then added to **1f** and allowed to stir for 24 hours. The solvent was then removed and the residue purified using column chromatography (dried SiO_2, 1:1 EtOAc:hexanes) to afford a tan, fluffy solid (413 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.37 (s, 1H), 8.13 (d, J = 8.0, 1H), 8.07 (d, J = 8.0, 1H), 7.99 (d, J = 8.0, 1H), 7.86 (d, J = 8.5, 2H), 7.76 (t, J = 8.0, 1H), 7.70 (s, 1H), 7.42-7.34 (m, 5H), 2.27 (s, 2H), 1.13 (s, 9H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 170.3, 165.1, 140.9, 134.0, 133.9, 133.7, 133.6, 129.2, 128.8, 128.7, 127.0, 127.0, 109.7, 109.6, 83.5, 51.7, 29.8, 25.0. $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) δ: -5.1.

Supporting Information NMR spectra of new compounds, titration data, and unsuccessful amide coupling conditions to create **1f** are available in Appendix D.

APPENDIX A

SUPPLEMENTAL INFORMATION: UNDERSTANDING THE EFFECTS OF PRE-ORGANIZATION, RIGIDITY, AND STERIC INTERACTIONS IN SYNTHETIC BARBITURATE RECEPTORS

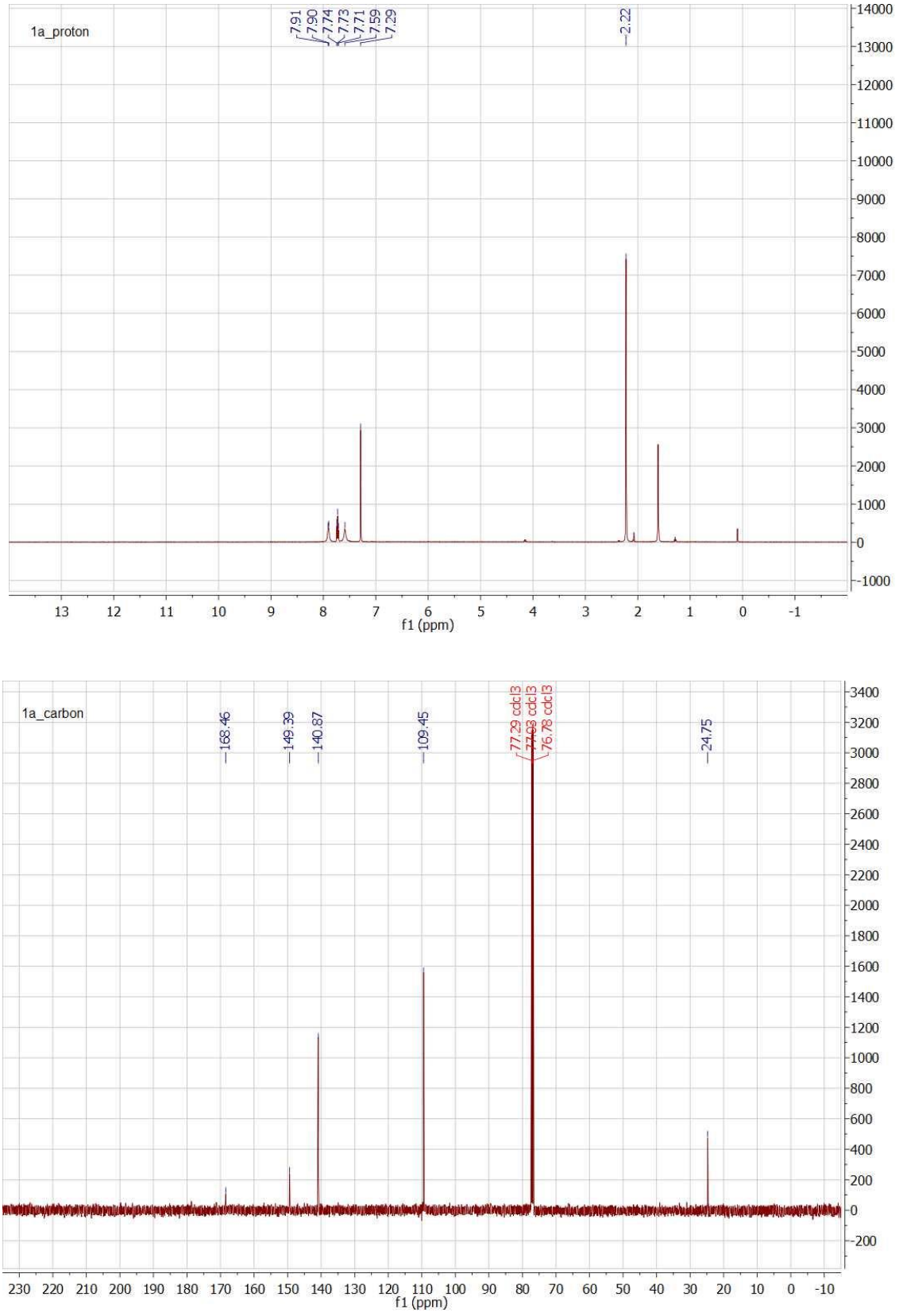


Figure A1. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **1a**.

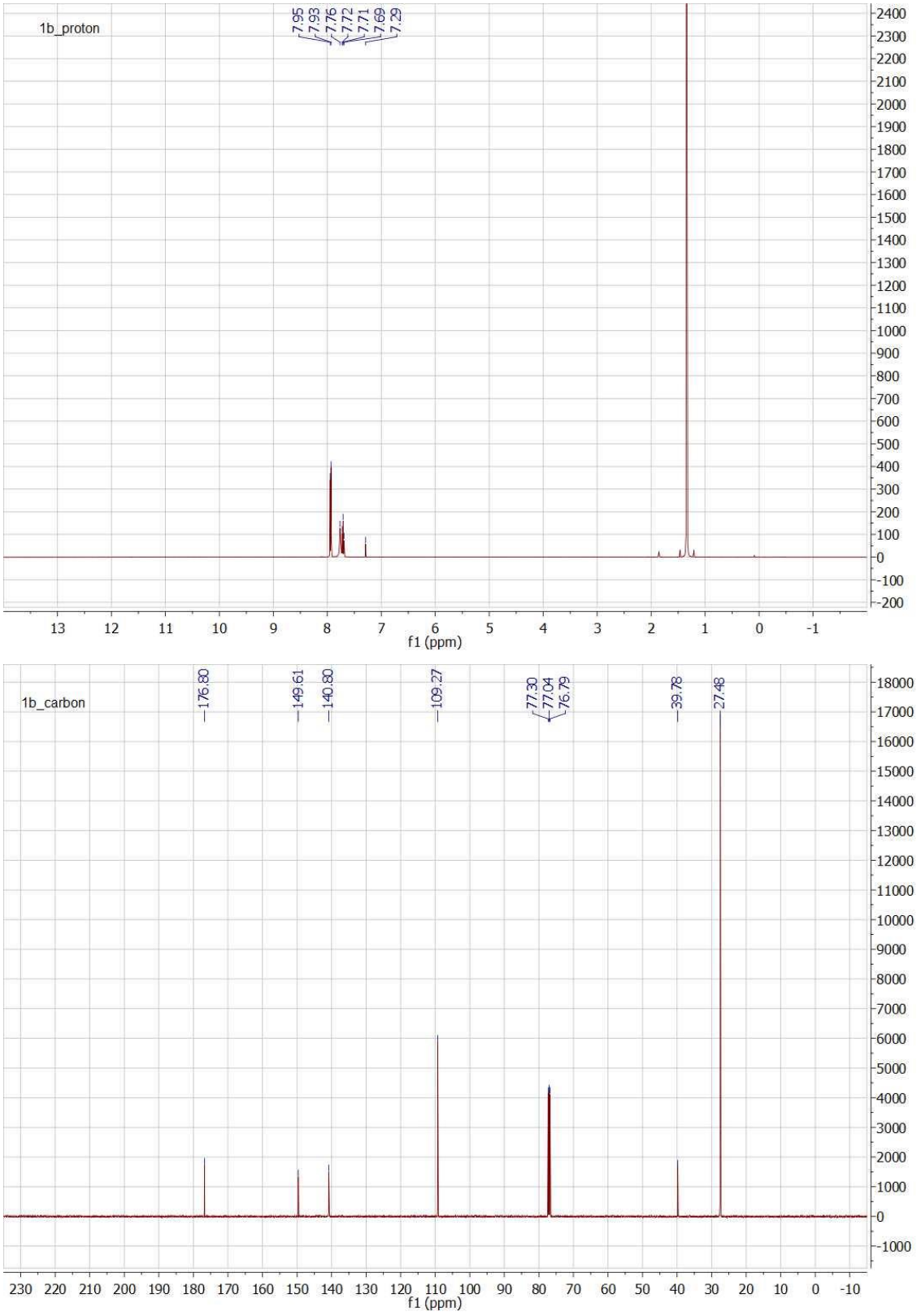


Figure A2. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **1b**.

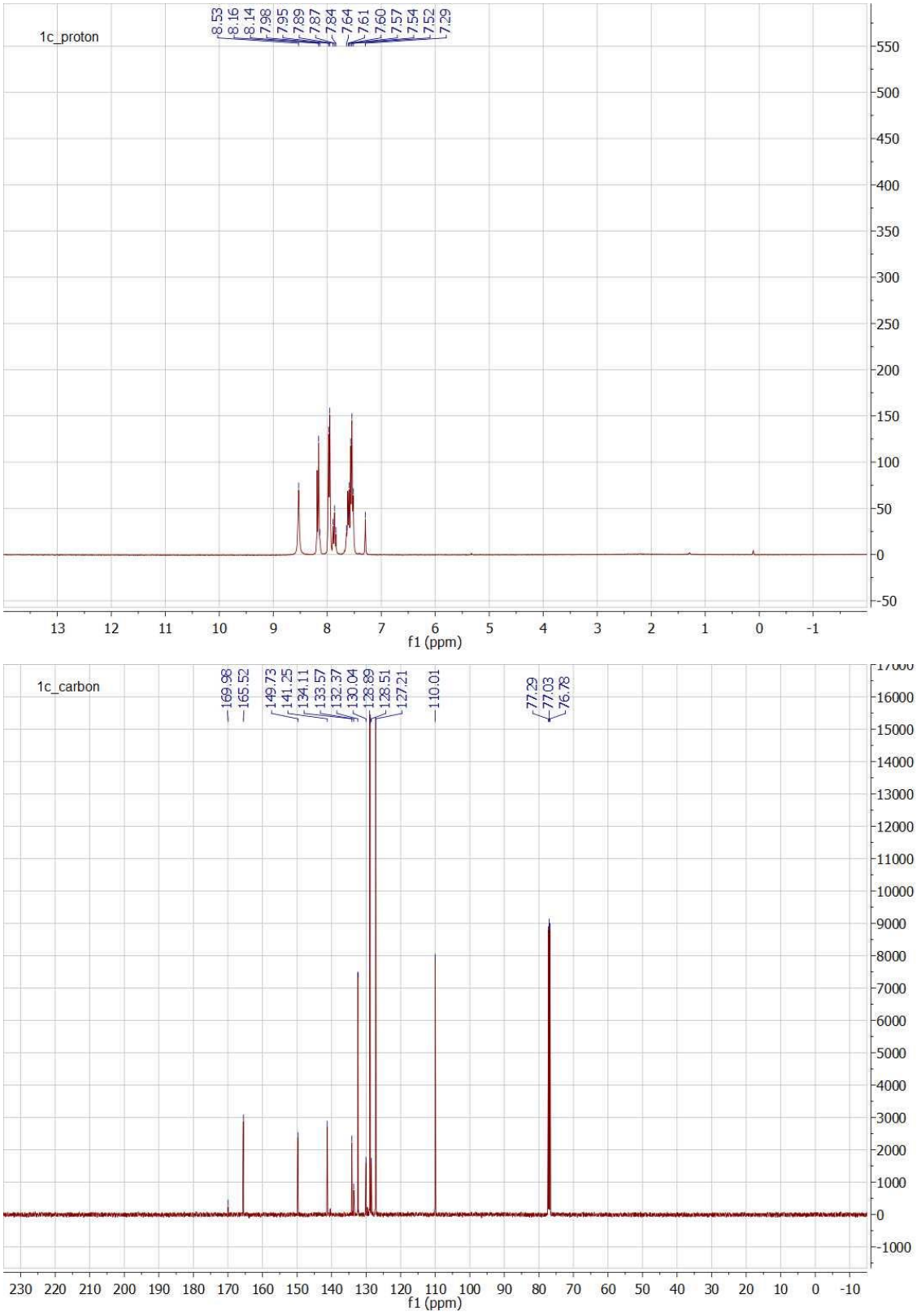


Figure A3. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **1c**.

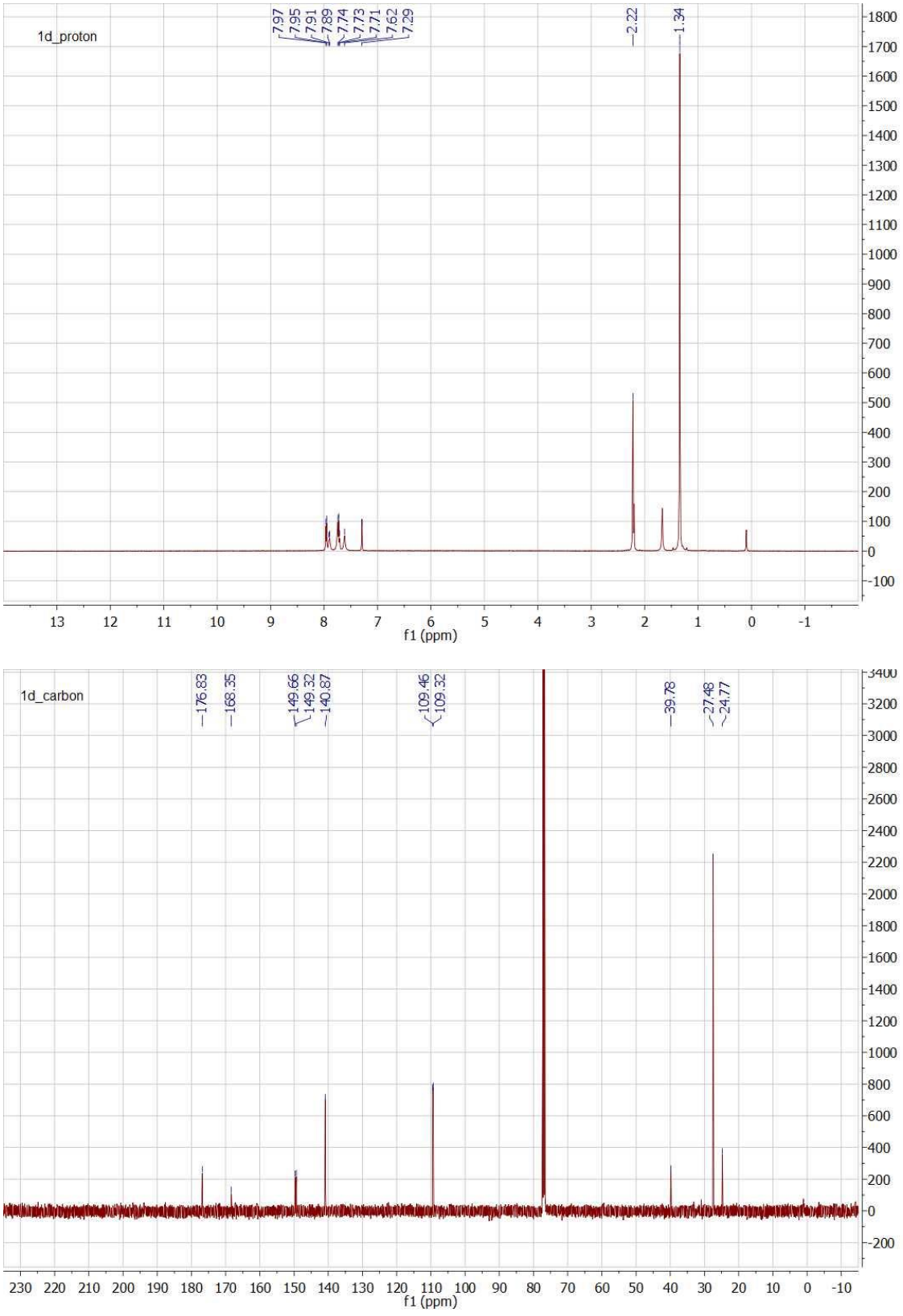


Figure A4. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **1d**.

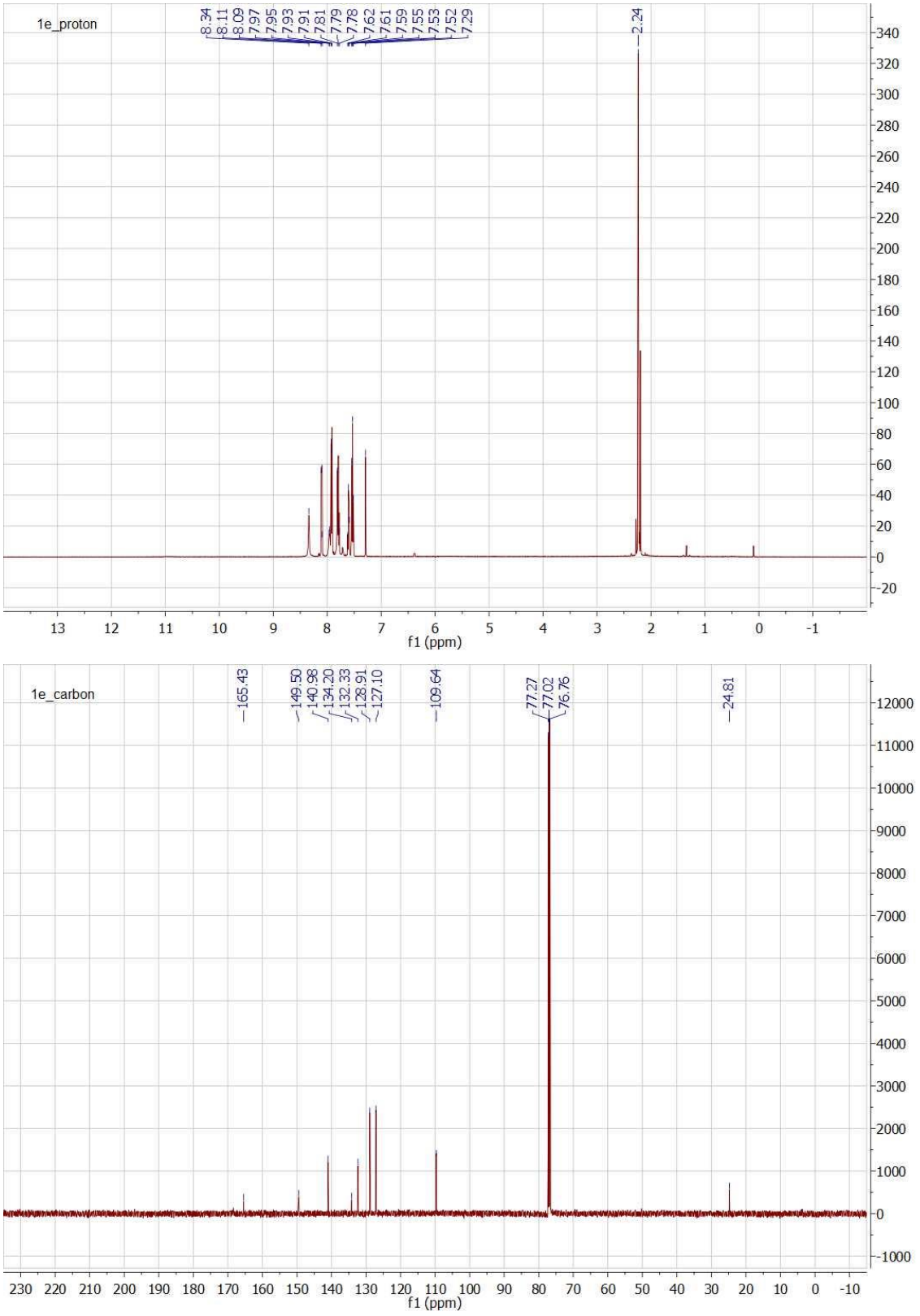


Figure A5. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **1e**.

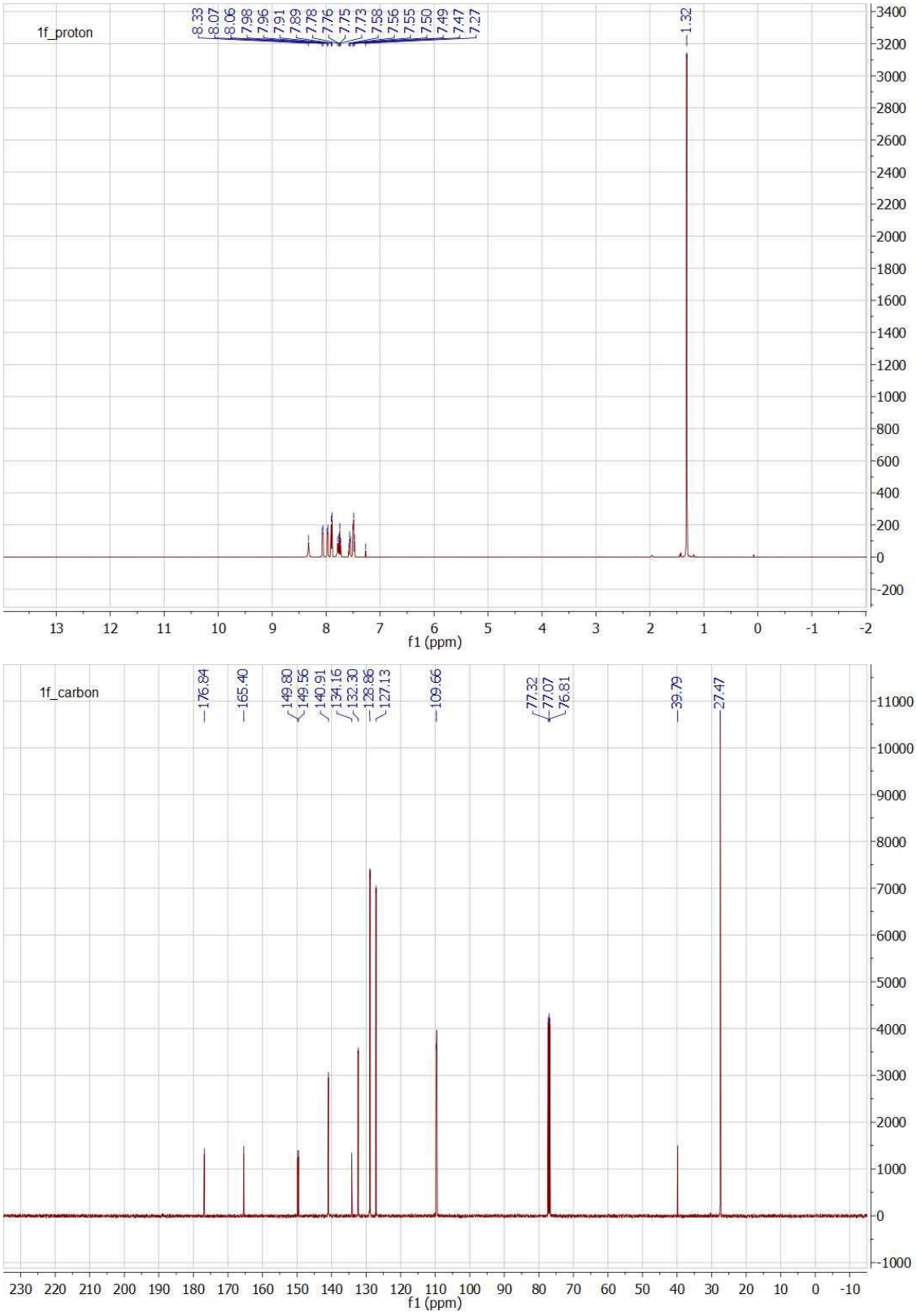


Figure A6. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **1f**.

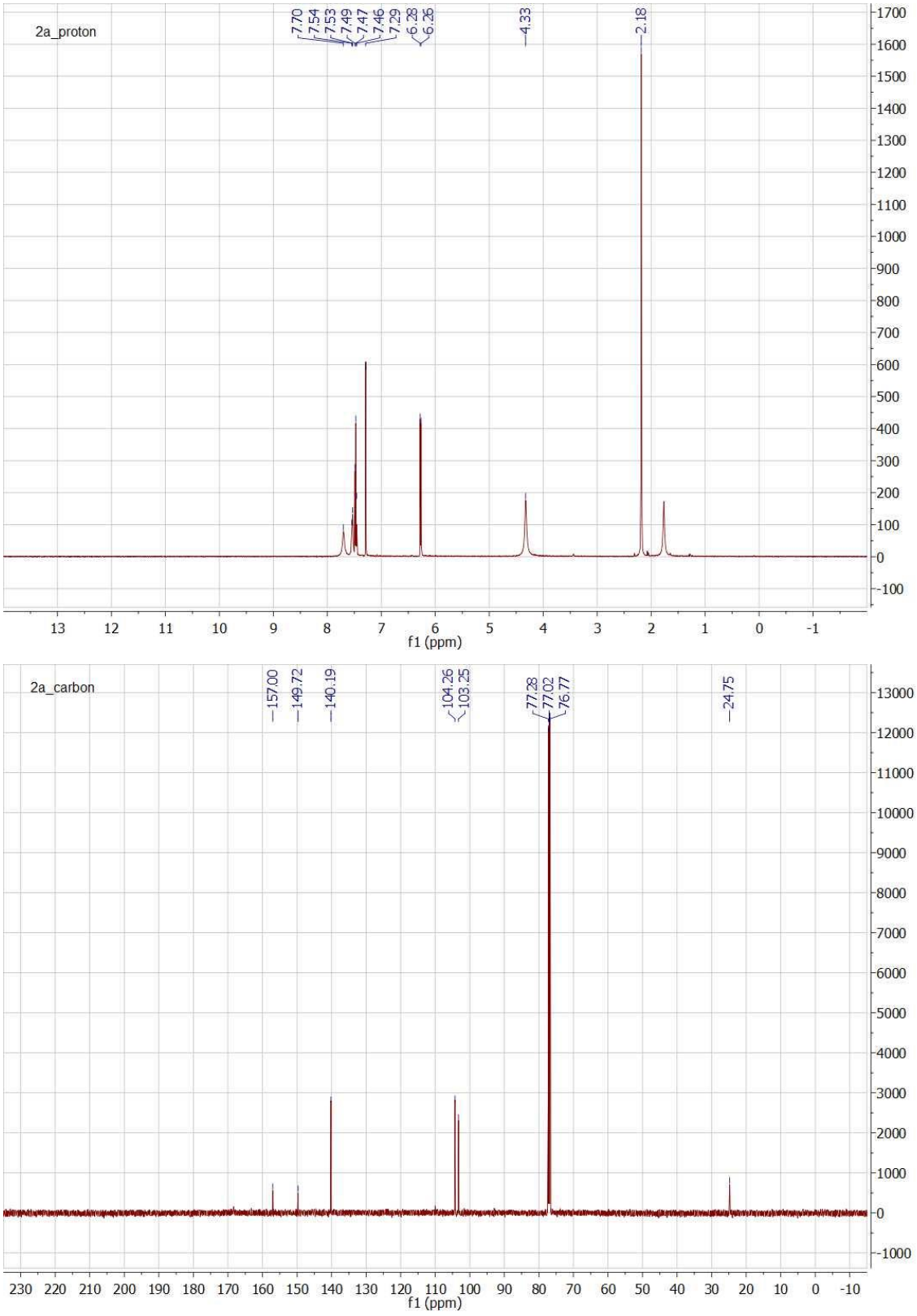


Figure A7. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **2a**.

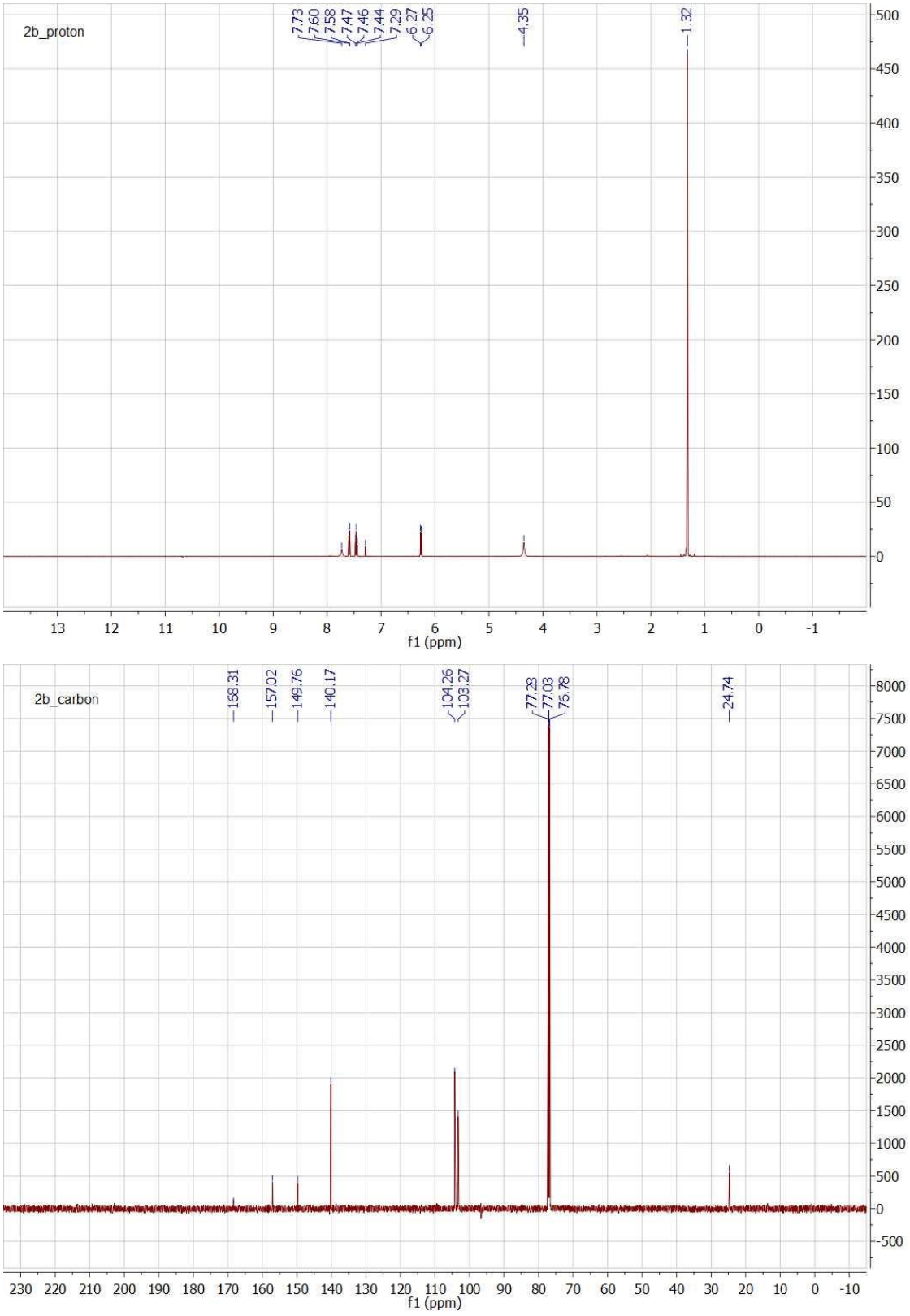


Figure A8. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **2b**

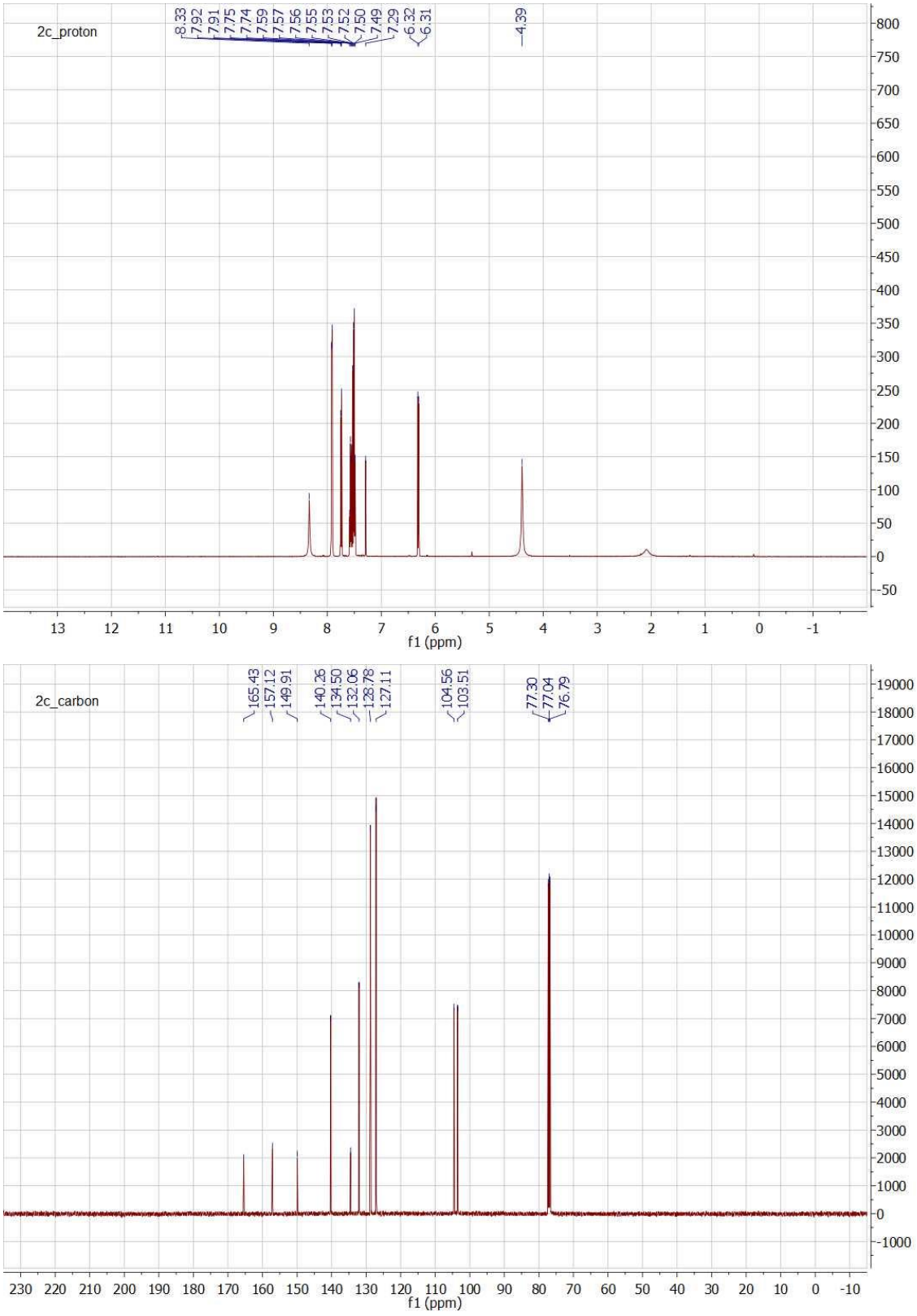


Figure A9. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **2c**.

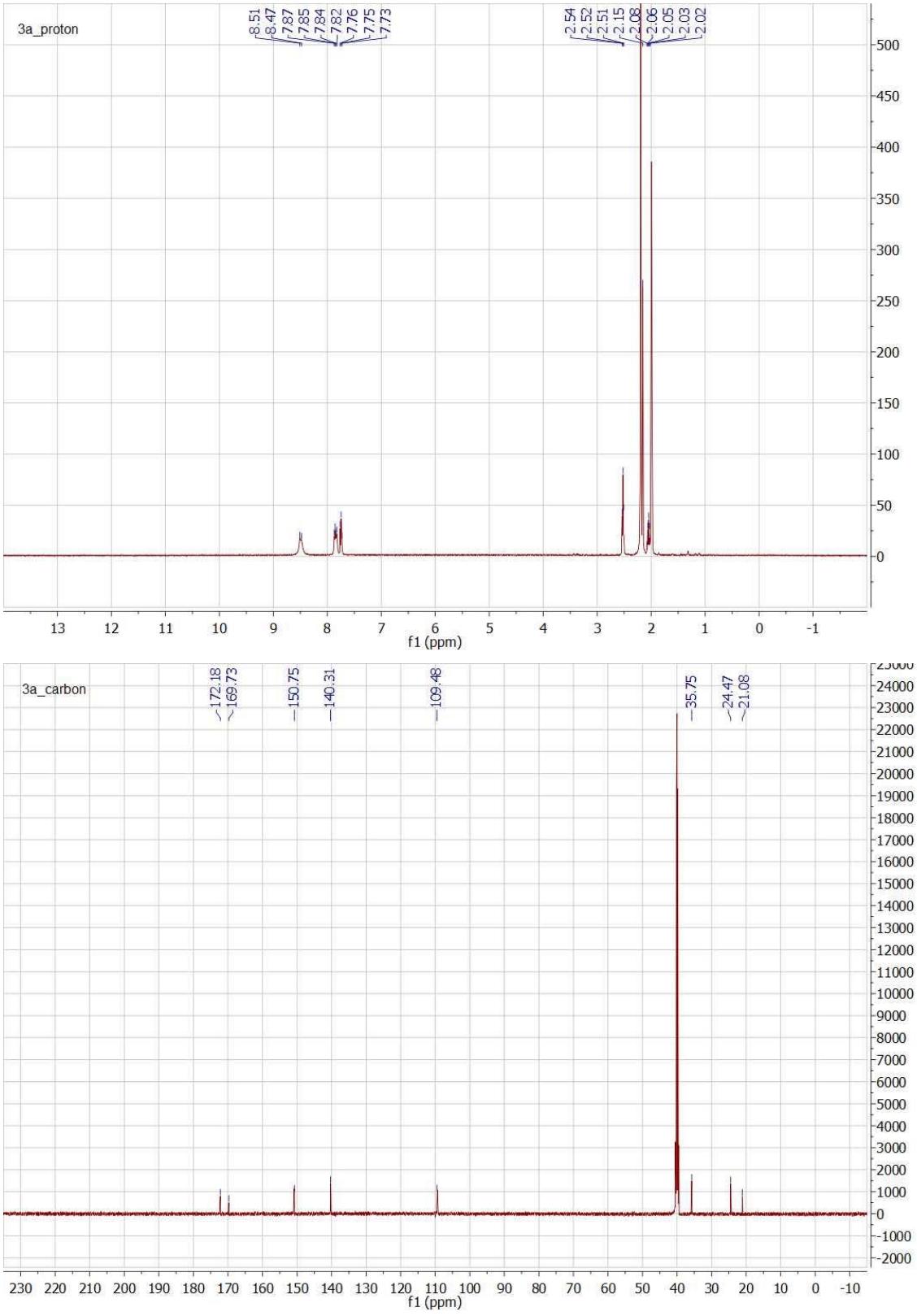


Figure A10. ^{1}H (500 MHz, CD_3CN) and $^{13}C\{^{1}H\}$ (125 MHz, DMSO) NMR spectra of **3a**.

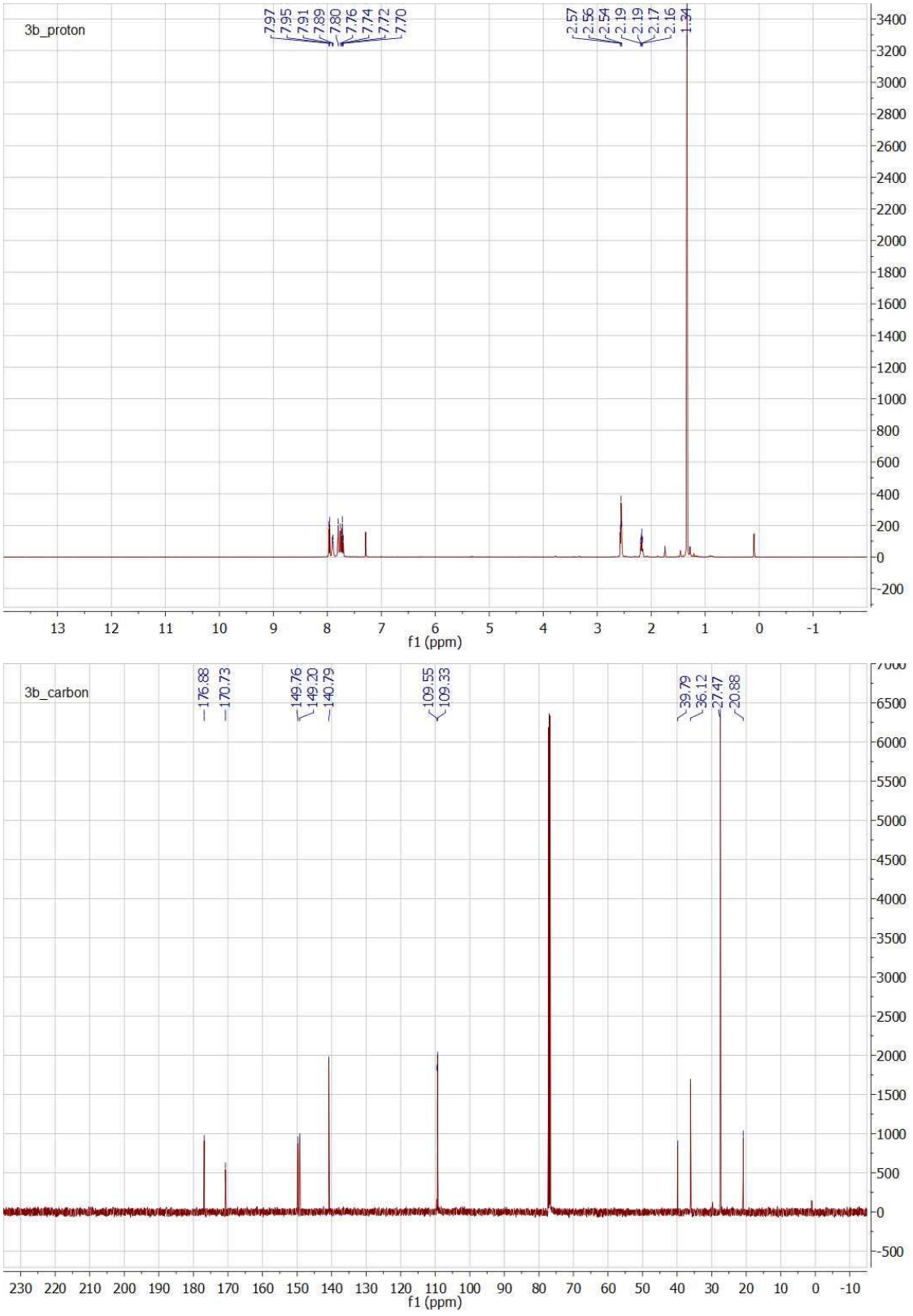


Figure A11. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **3b**.

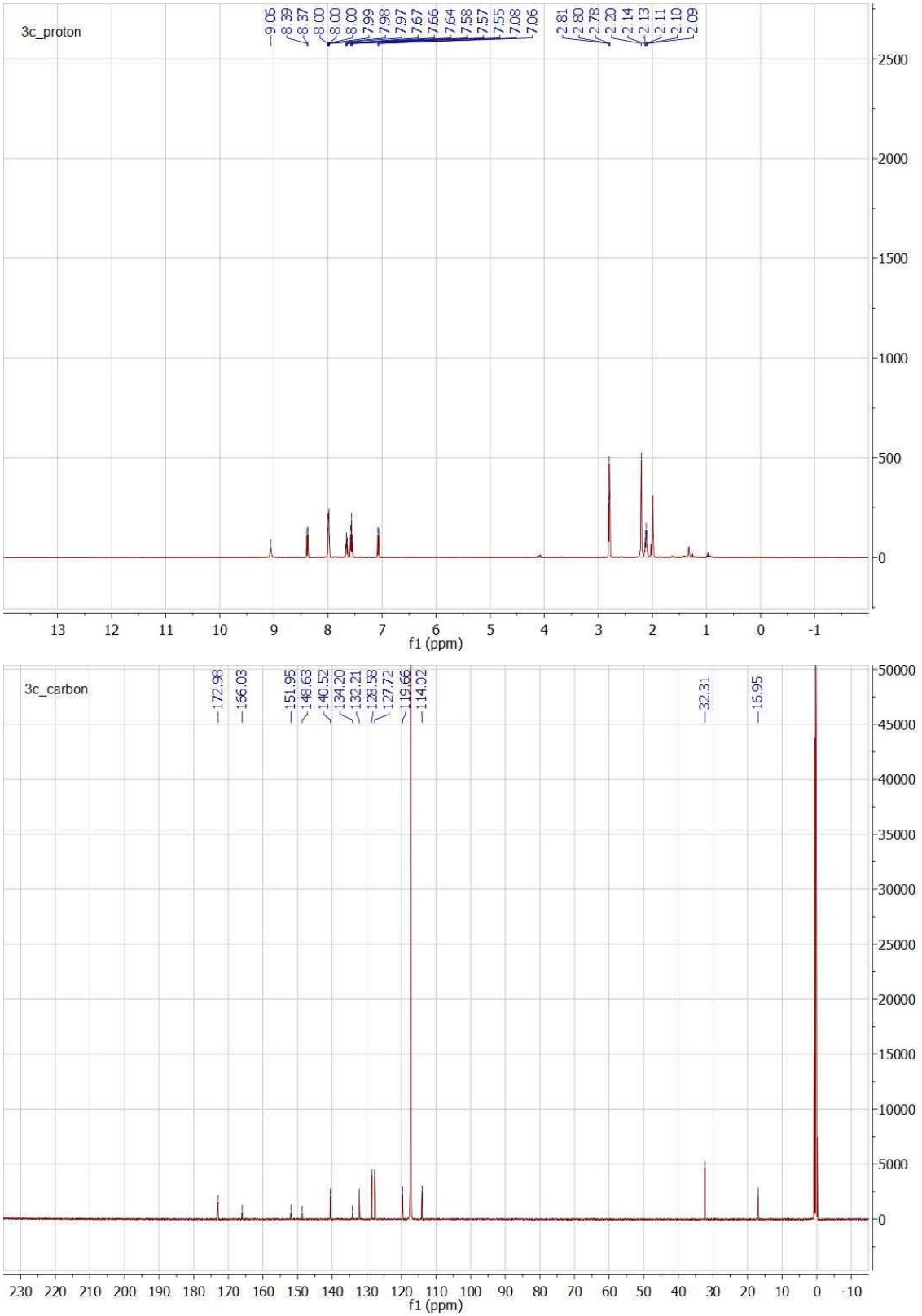


Figure A12. ^{1}H (500 MHz, DMSO) and $^{13}C\{^{1}H\}$ (125 MHz, CD_3CN) NMR spectra of **3c**.

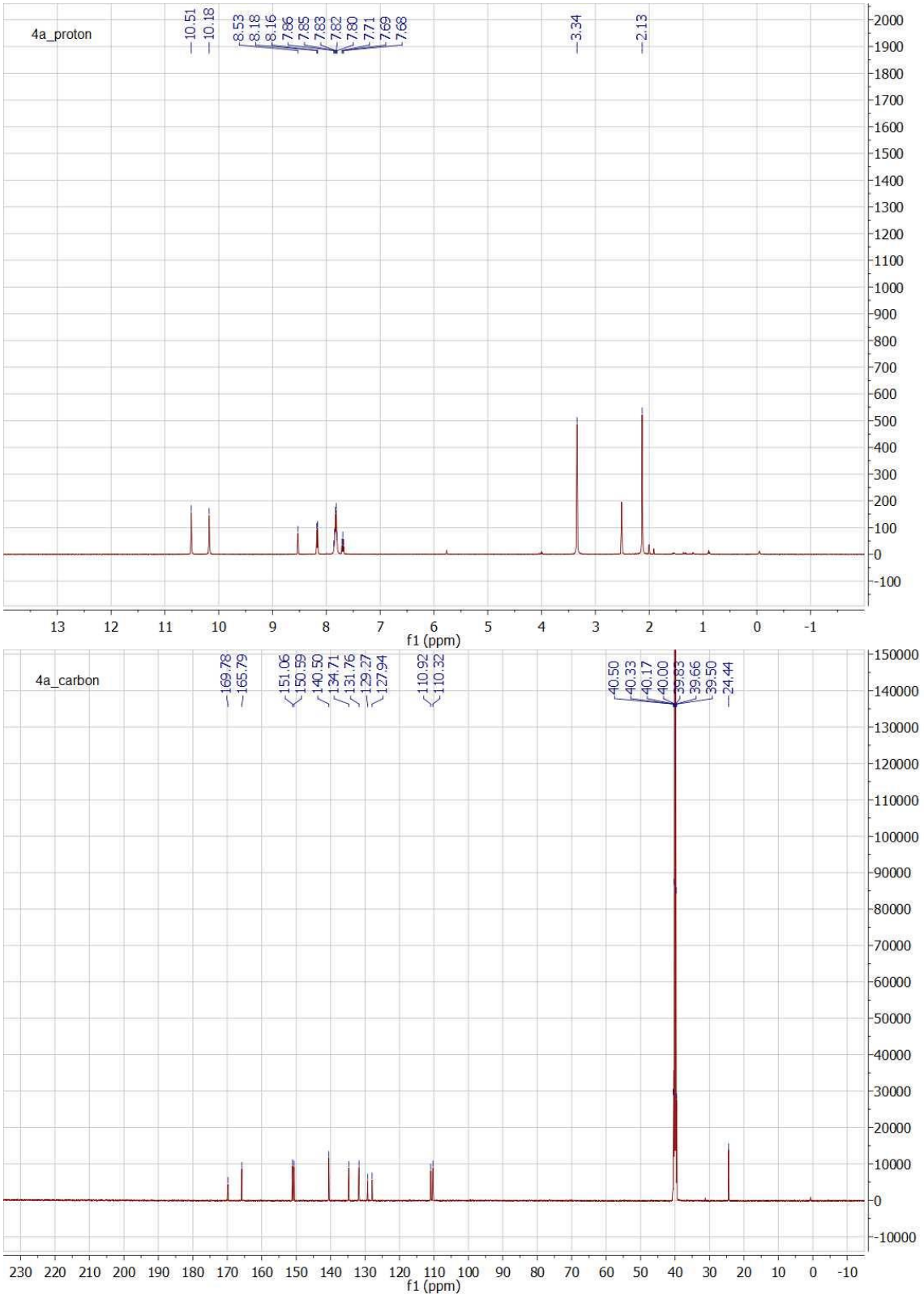


Figure A13. ^{1}H (500 MHz, DMSO) and $^{13}C\{^{1}H\}$ (125 MHz, DMSO) NMR spectra of **4a**.

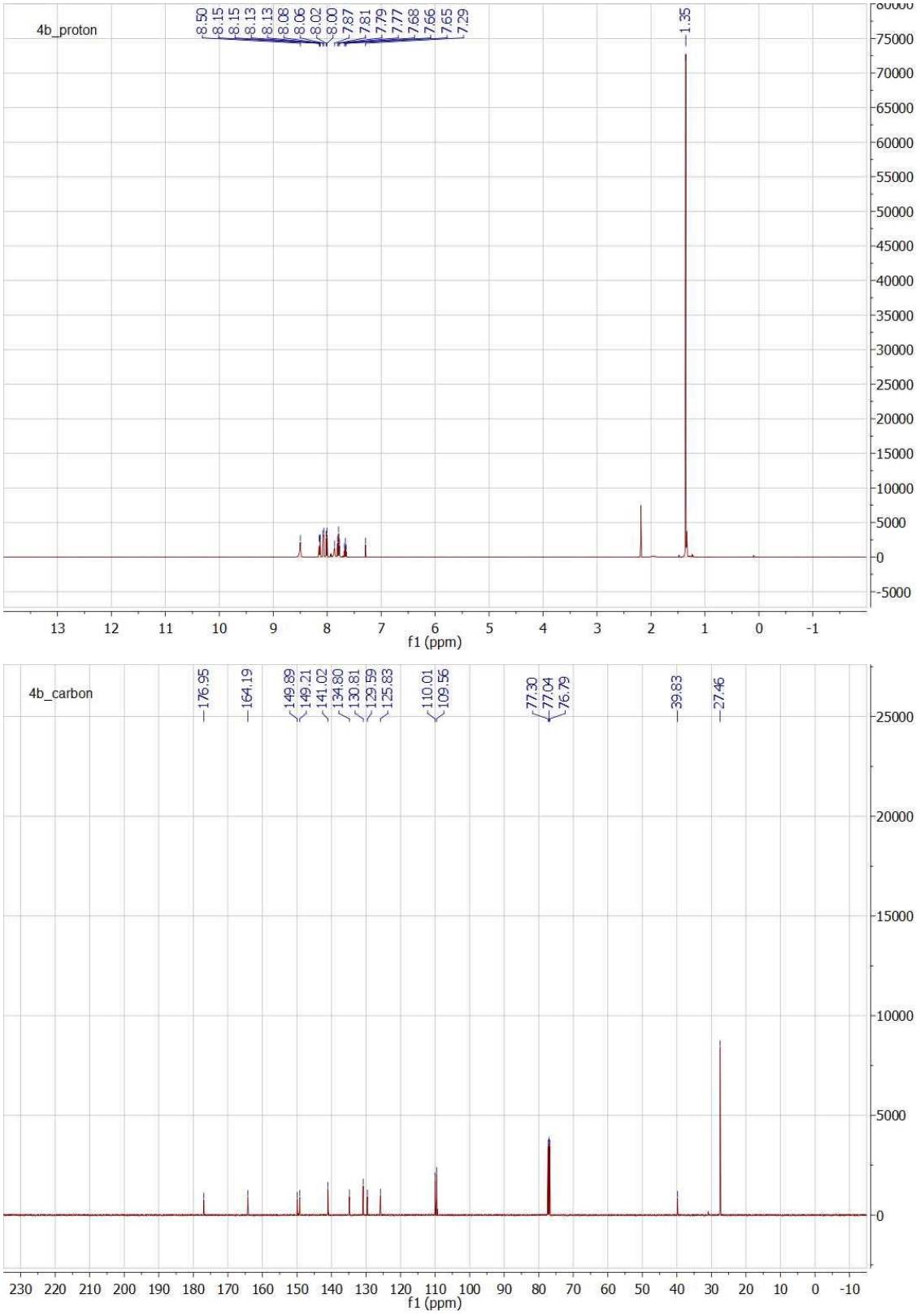


Figure A14. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **4b**.

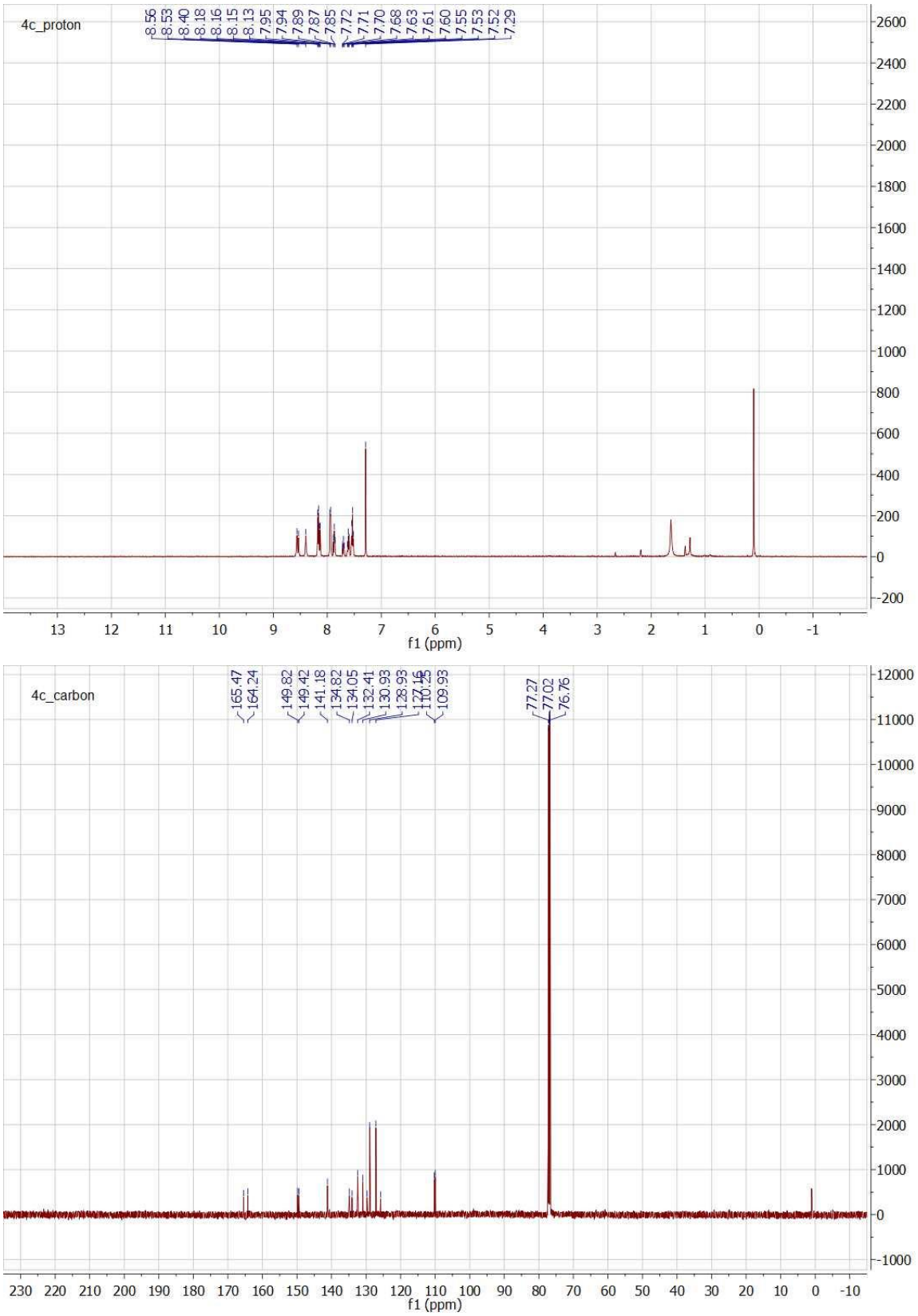


Figure A15. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **4c**.

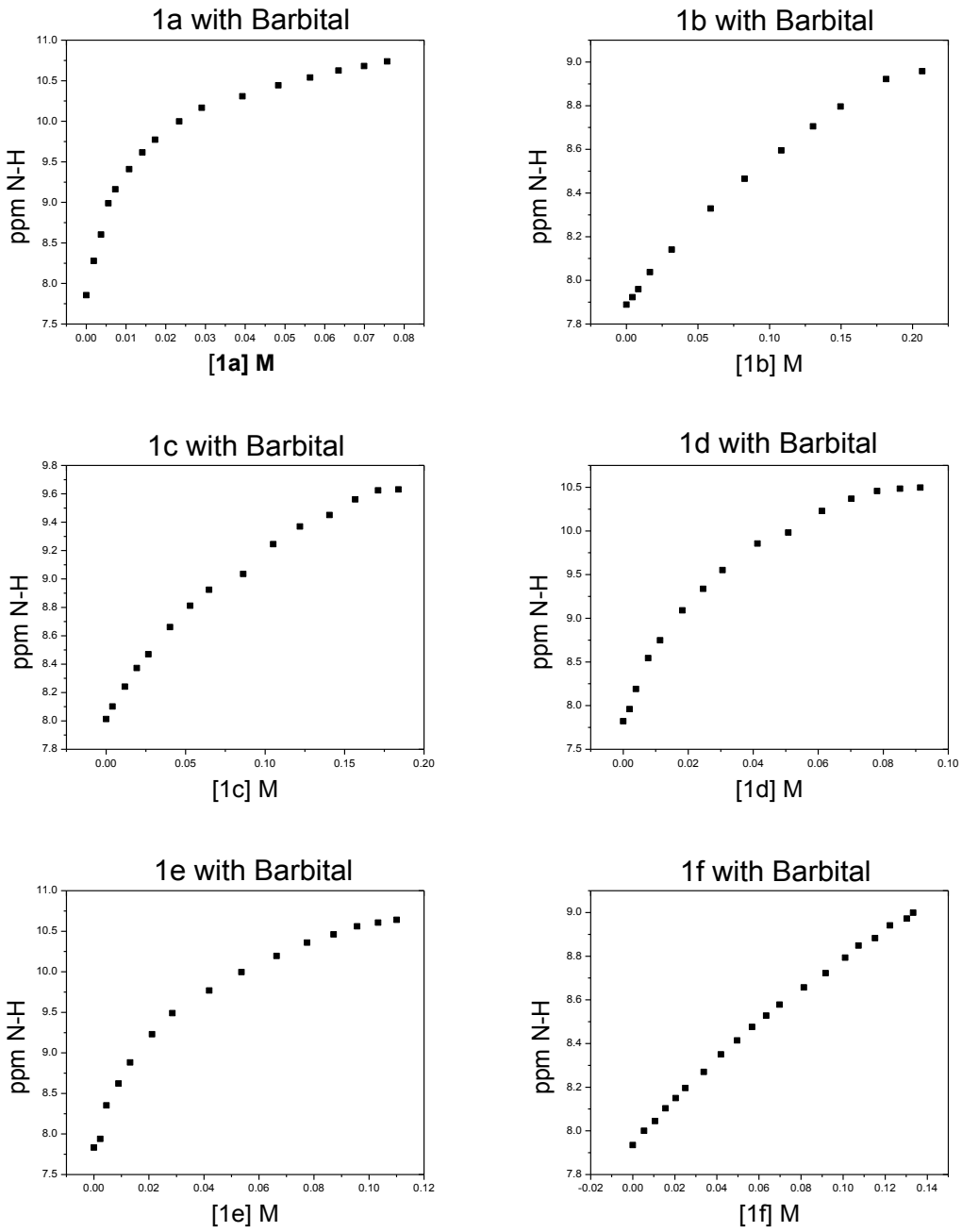


Figure A16. ^{1}H NMR (500 MHz, $CDCl_3$) titration data. Representative binding curves for hosts **1a-f** with **5**.

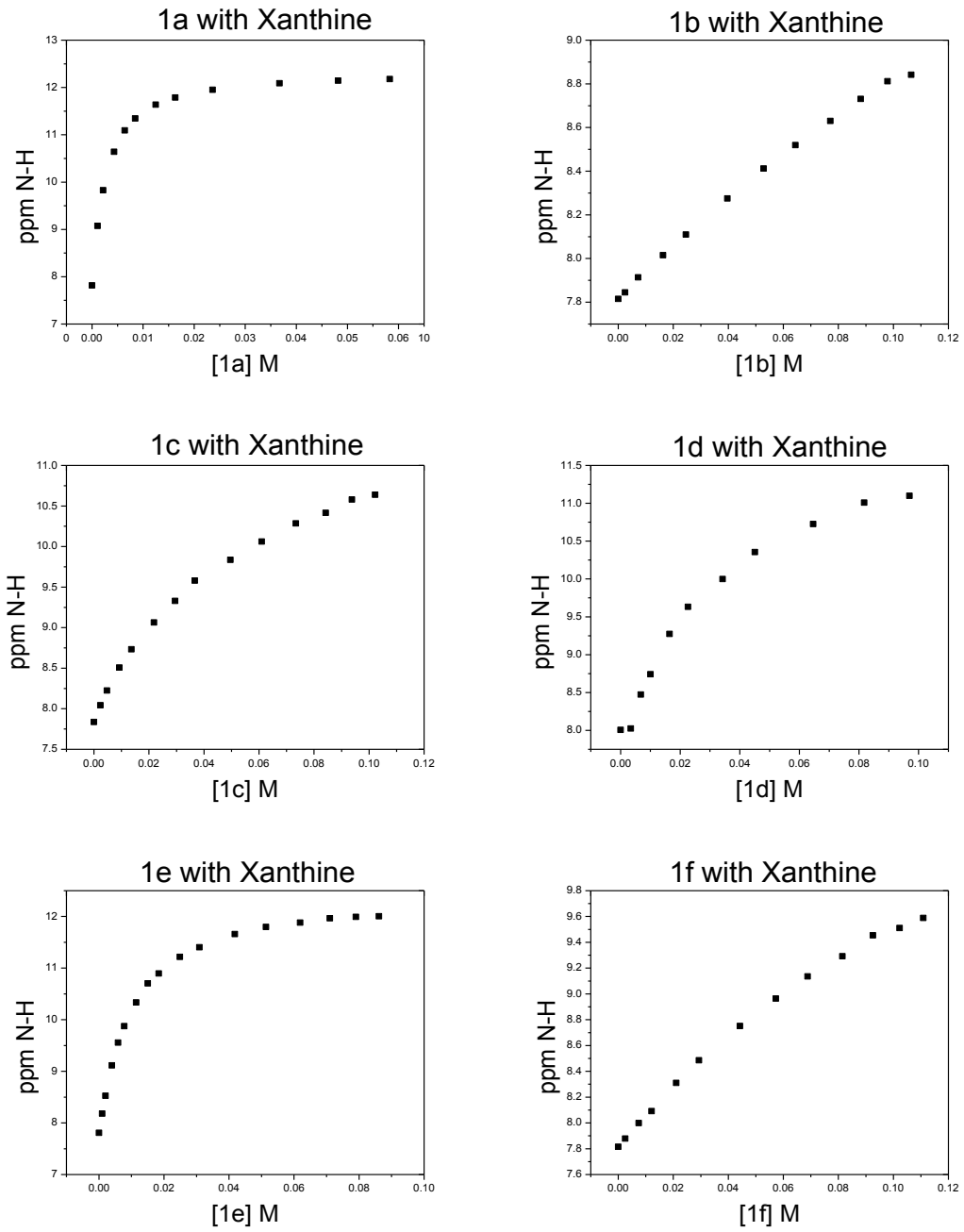


Figure A17. ^{1}H NMR (500 MHz, $CDCl_3$) titration data. Representative binding curves for hosts **1a-f** with **6**.

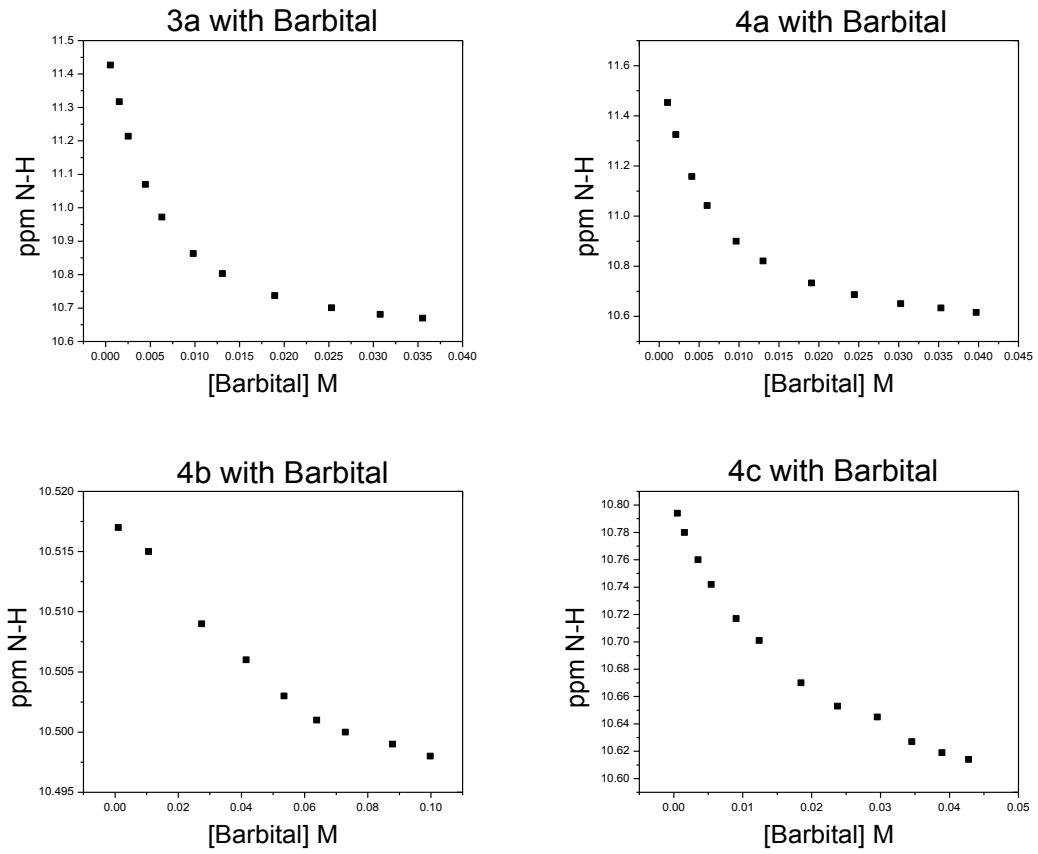


Figure A18. ^{1}H NMR (500 MHz, $CDCl_3$) titration data. Representative binding curves for hosts **3a** and **4a-c** with **5**.

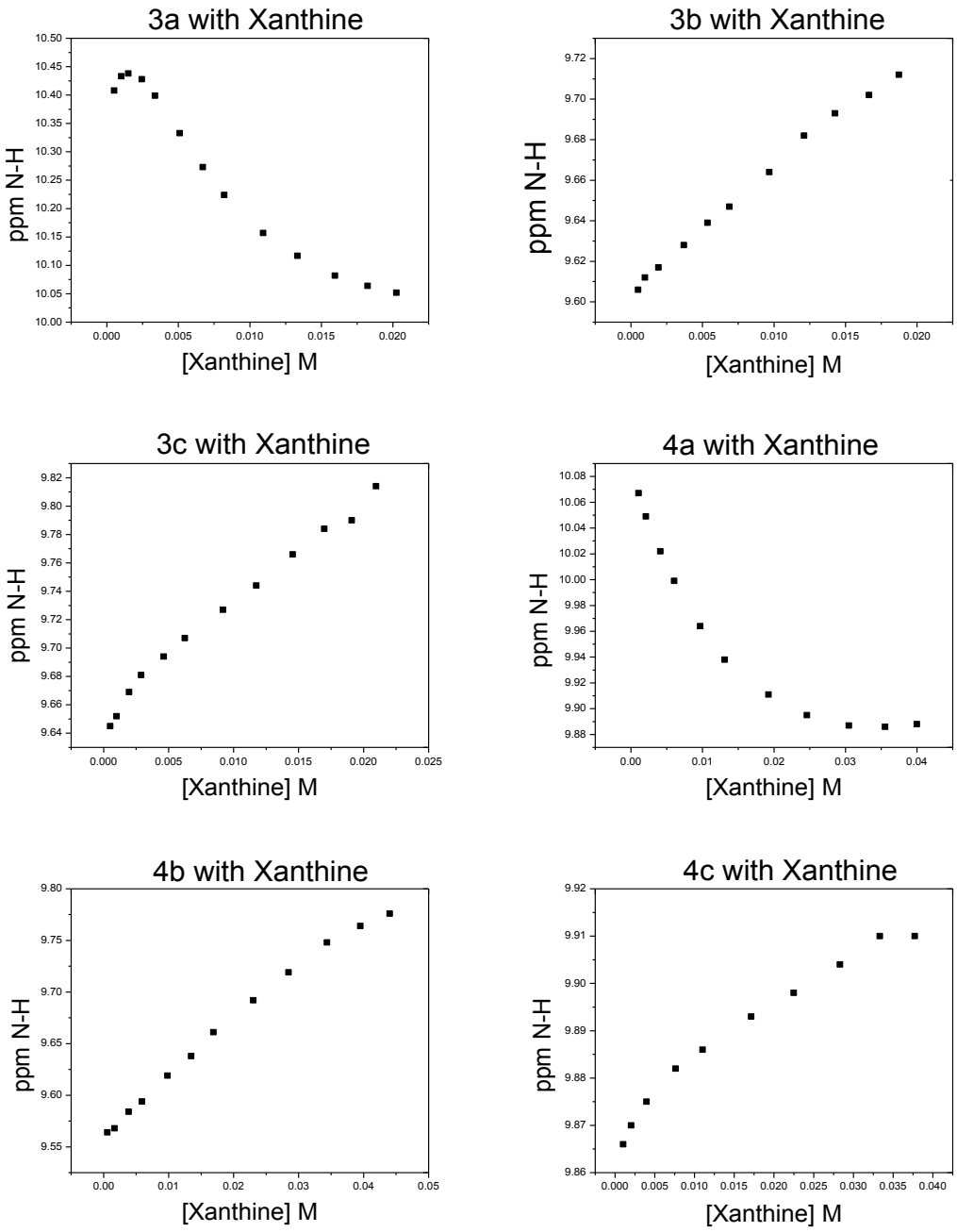


Figure A19. ^{1}H NMR (500 MHz, $CDCl_3$) titration data. Representative binding curves for hosts **3a-c** and **4a-c** with **6**.

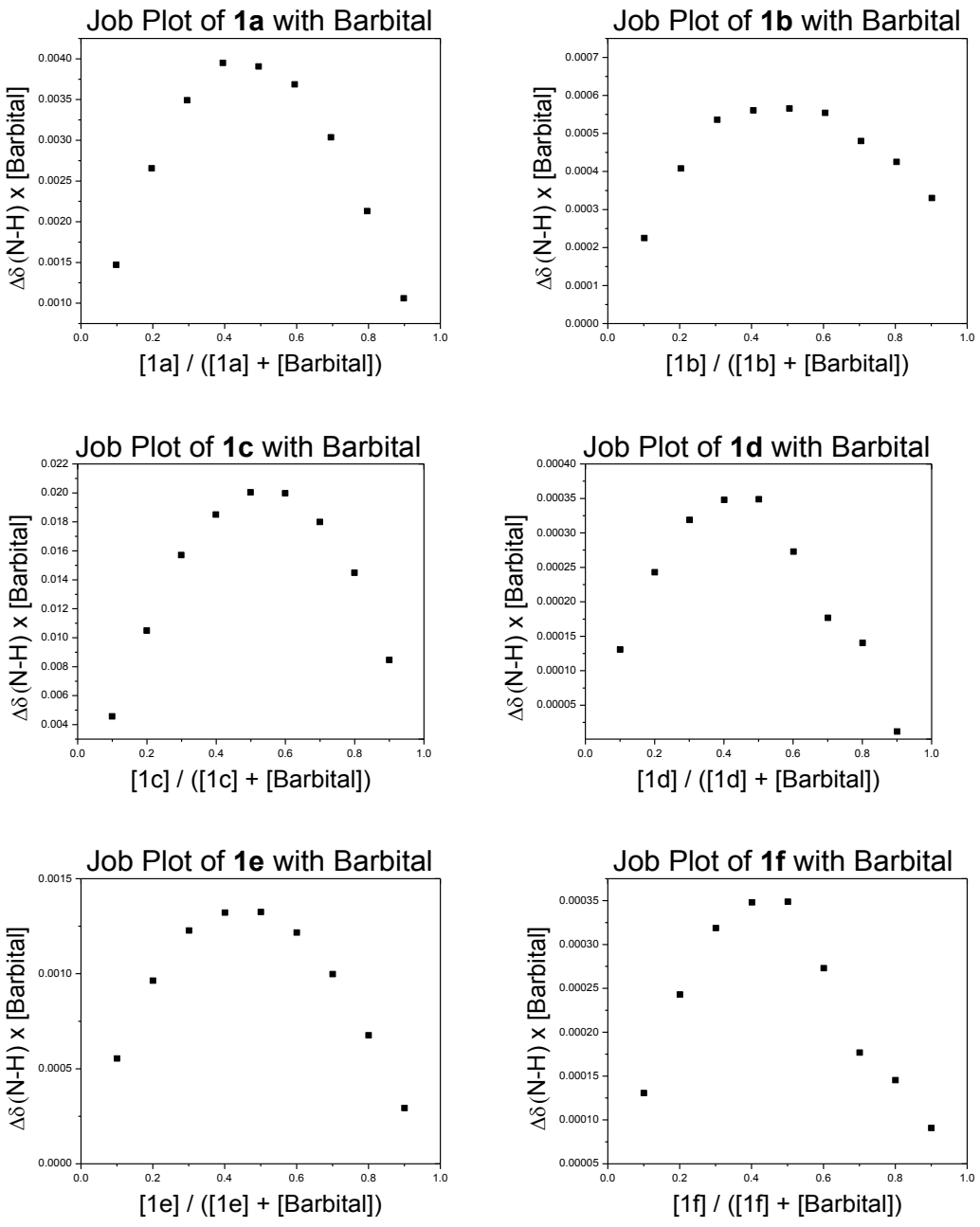


Figure A20. Job plots for hosts **1a-f** with **5**. ^{1}H NMR (500 MHz, $CDCl_3$) data.

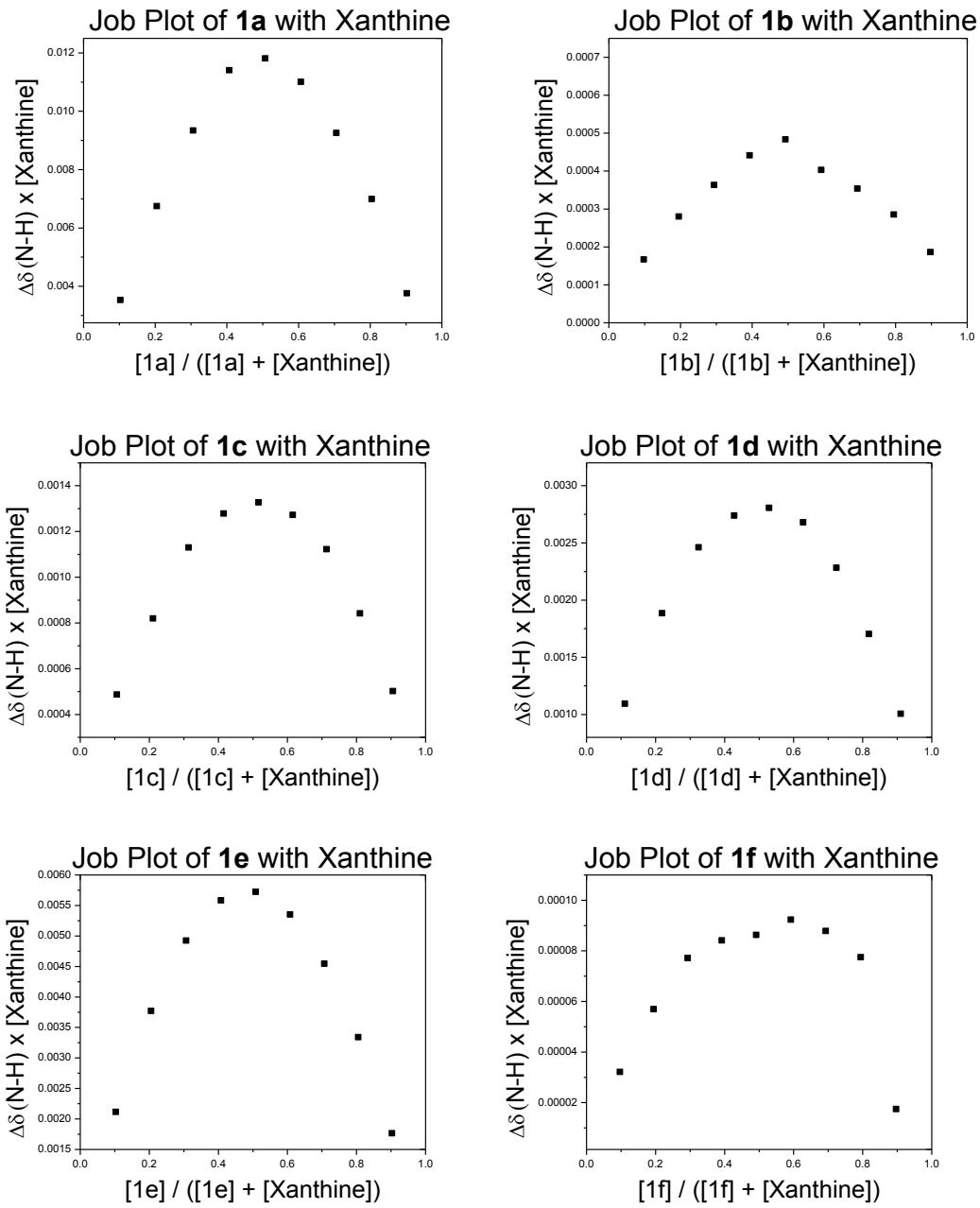


Figure A21. Job plots for hosts **1a-f** with **6**. ^{1}H NMR (500 MHz, $CDCl_3$) data.

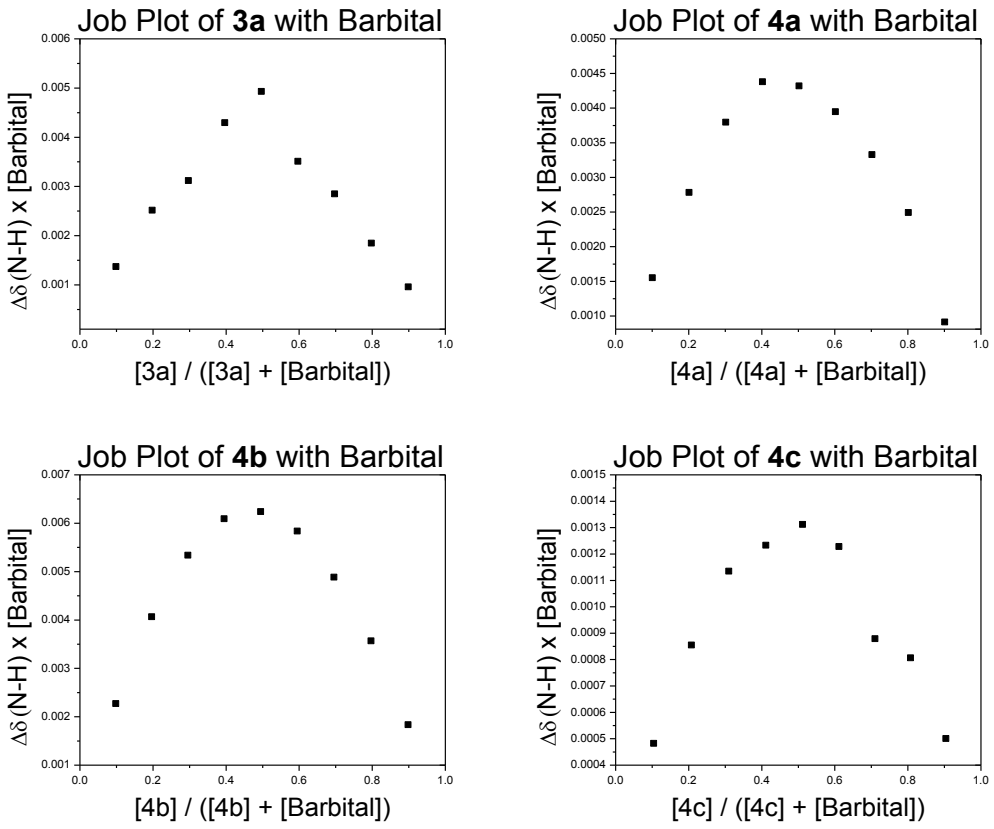


Figure A22. Job plots for hosts **3a** and **4a-c** with **5**. ^{1}H NMR (500 MHz, $CDCl_3$) data.

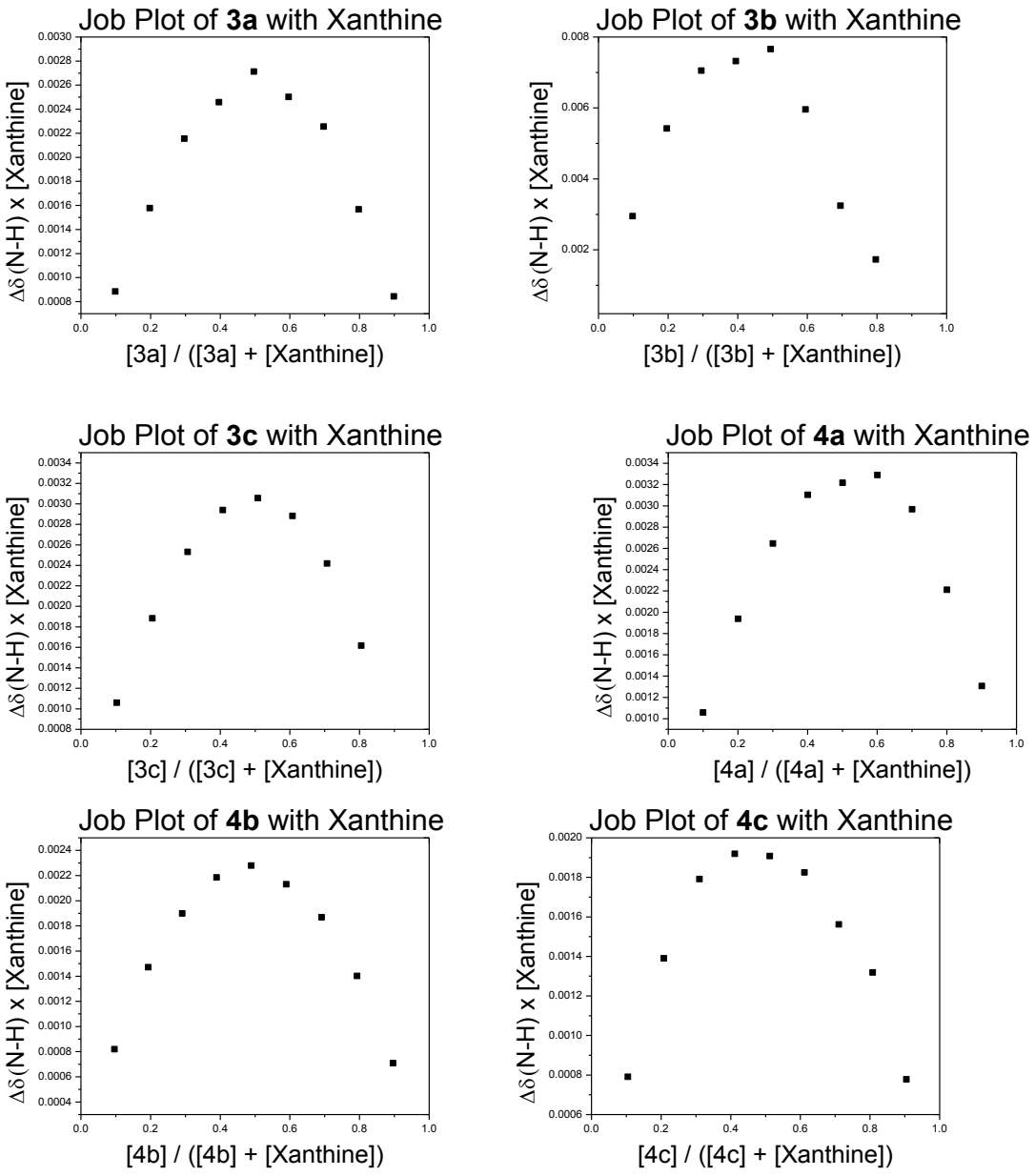


Figure A23. Job plots for hosts **3a-c** and **4a-c** with **6**. ^{1}H NMR (500 MHz, $CDCl_3$) data.

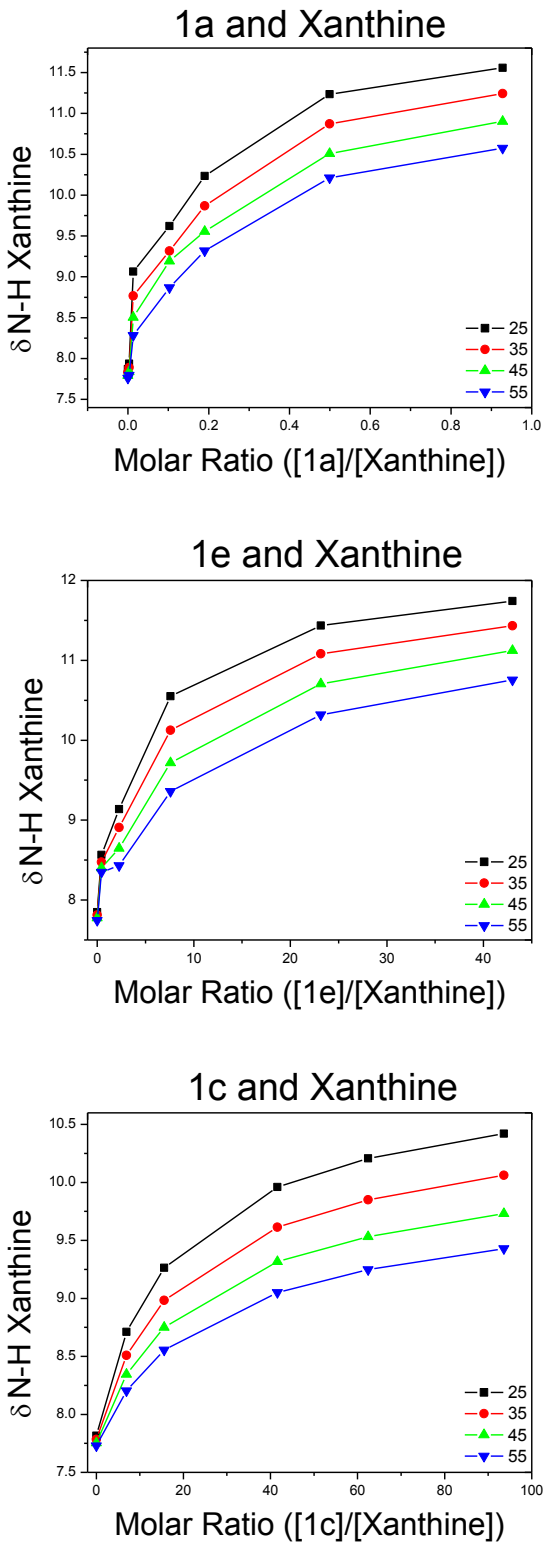


Figure A24. ^{1}H (600 MHz, $CDCl_3$) Temperature dependent binding curves for hosts **1a, 1c,** and **1e** with **6**.

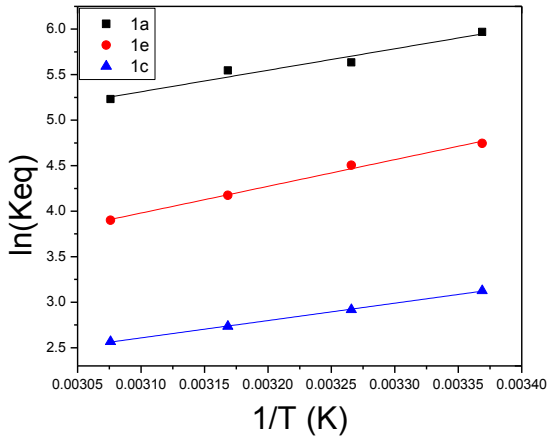
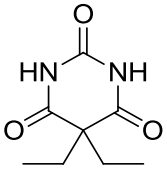
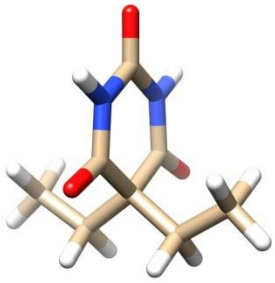


Figure A25. Van't Hoff plot of **1a**, **1c**, and **1e** with **6**.

Computational Details.





Calculated Enthalpy: -647.171052 Hartree

Zero Point Energy: 0.203653 Hartree

Lowest Frequency: 34.7 cm^{-1}

Coordinates:

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N	-1.35841700	-0.00201400	1.16878100
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C	-2.10319000	-0.00487900	-0.00003300
C	0.85119500	0.00210000	-0.00003900
O	0.53956400	0.00187000	2.39282700
N	-1.35862900	-0.00469900	-1.16871700
O	-3.32340900	-0.00755700	0.00019500
C	0.02233300	-0.00203200	-1.28621000
C	1.75570700	1.27587500	-0.00135800
C	1.76530700	-1.26462000	0.00120400
H	-1.89473100	-0.00704800	-2.03094200

O	0.53928700	-0.00241500	-2.39292900
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H	2.39754800	1.20545700	-0.88428700
H	2.40713700	-1.19093600	-0.88147500
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H	0.37831000	2.73235400	-0.88964500
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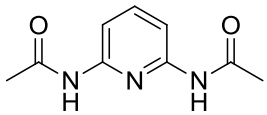
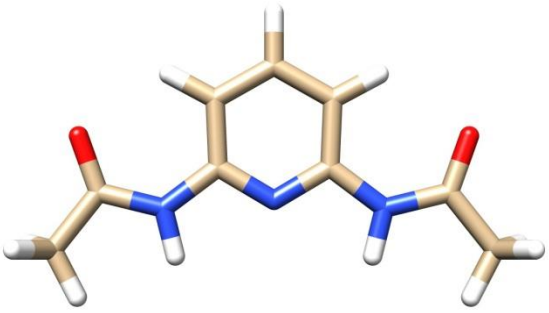
H	0.39910900	-2.73268500	-0.88527600
H	1.75519700	-3.42742700	0.00312200
H	0.39867000	-2.73112200	0.88963900





Calculated Enthalpy: -664.199545 Hartree

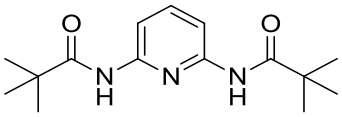
Zero Point Energy: 0.197983 Hartree

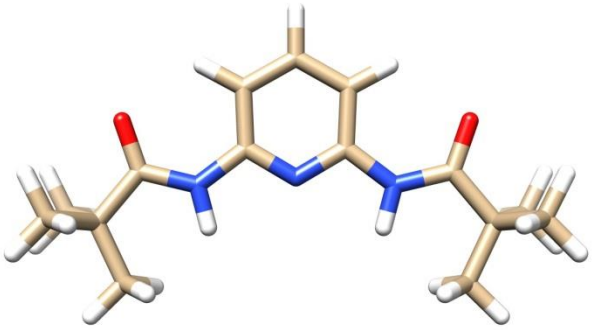
Lowest Frequency: 35.9 cm^{-1}

Coordinates:

Atom	x	y	z
C	-1.15356600	0.11858300	-0.00003900
C	-1.21497300	1.51917700	-0.00003300
C	0.00000000	2.20301500	-0.00004200
C	1.21497300	1.51917700	-0.00003500
C	1.15356600	0.11858300	-0.00004100
N	0.00000000	-0.56306900	-0.00003900
H	0.00000000	3.28885600	-0.00003700
H	-2.16726900	2.02763300	-0.00000500
H	2.16726900	2.02763300	-0.00000900
N	2.27917700	-0.72345100	-0.00003000
C	3.61563000	-0.39763900	0.00002300
H	2.03488900	-1.70571100	-0.00006100
O	4.02987600	0.76099200	0.00009400
N	-2.27917700	-0.72345100	-0.00002600
C	-3.61563000	-0.39763900	0.00003000
H	-2.03488900	-1.70571100	-0.00005800
O	-4.02987600	0.76099200	0.00009300
C	-4.56275100	-1.58180700	0.00000600
C	4.56275100	-1.58180700	0.00001000
H	5.20547800	-1.51371400	0.88233000

H	5.20563400	-1.51357600	-0.88218300
H	4.05898400	-2.55103900	-0.00010500
H	-4.05898400	-2.55103900	-0.00011100
H	-5.20563000	-1.51357200	-0.88218900
H	-5.20548200	-1.51371900	0.88232300





Calculated Enthalpy: -899.927978 Hartree

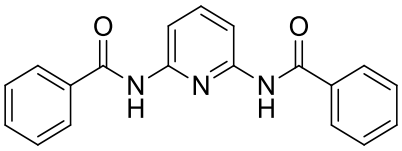
Zero Point Energy: 0.367218 Hartree

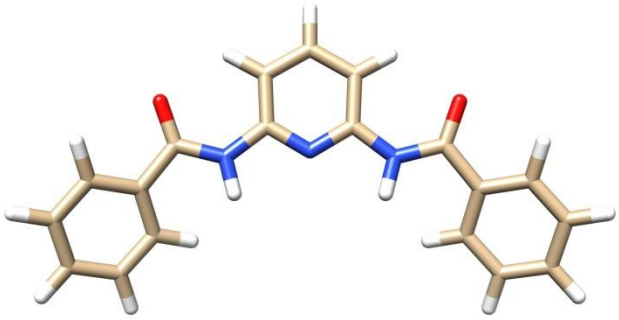
Lowest Frequency: 26.1 cm^{-1}

Coordinates:

Atom	x	y	z
C	-1.15460900	0.76440800	0.00002800
C	-1.21541000	2.16508400	-0.00001500
C	0.00000100	2.84843700	0.00004900
C	1.21541200	2.16508400	0.00012700
C	1.15461100	0.76440800	0.00012500
N	0.00000100	0.08401900	0.00008800
H	0.00000100	3.93433100	0.00003700
H	-2.16757300	2.67353800	-0.00012600
H	2.16757500	2.67353700	0.00020400
N	2.27670200	-0.08235500	0.00009900
C	3.61300900	0.23592400	0.00033000
H	2.02109500	-1.06042700	-0.00010200
O	4.01665100	1.39929800	0.00075500
N	-2.27670000	-0.08235500	0.00008700
C	-3.61300800	0.23592500	-0.00045700
H	-2.02109300	-1.06042700	0.00040500
O	-4.01664800	1.39930000	-0.00123900
C	-4.61119200	-0.94735300	0.00008800
C	4.61119000	-0.94735400	-0.00013400
C	-5.48841000	-0.79765300	1.26450300
H	-5.97572400	0.18007100	1.28534700
H	-6.26115400	-1.57365900	1.27085700
H	-4.89180100	-0.90594800	2.17722500
C	-3.95317000	-2.34055000	-0.00021600
H	-3.34099800	-2.51165900	-0.89323800
H	-3.34033400	-2.51181300	0.89232300
H	-4.73568400	-3.10585600	0.00004600
C	-5.48991900	-0.79789400	-1.26325200
H	-6.26271000	-1.57385600	-1.26844900

H	-5.97718100	0.17985500	-1.28379300
H	-4.89442500	-0.90647900	-2.17667100
C	5.48879200	-0.79750100	-1.26425000
H	5.97607600	0.18024100	-1.28486500
H	6.26156300	-1.57348100	-1.27042700
H	4.89247300	-0.90573900	-2.17716900
C	5.48953300	-0.79804900	1.26350600
H	6.26229900	-1.57403600	1.26887600
H	5.97682400	0.17968200	1.28427700
H	4.89374900	-0.90669400	2.17672700
C	3.95316600	-2.34054900	-0.00022700
H	3.34074300	-2.51181200	0.89259500
H	3.34057900	-2.51165600	-0.89296600
H	4.73567700	-3.10585800	-0.00038400





Calculated Enthalpy: -1047.586813 Hartree

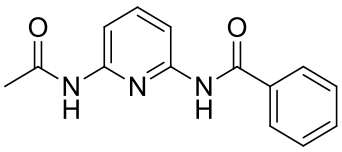
Zero Point Energy: 0.304762 Hartree

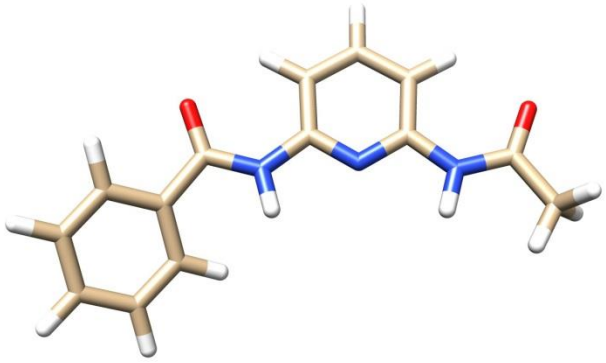
Lowest Frequency: 22.6 cm^{-1}

Coordinates:

Atom	x	y	z
C	-1.15397300	1.24390100	-0.07048900
C	-1.21511400	2.63855800	-0.20370800
C	0.00001600	3.31862200	-0.27064600
C	1.21514000	2.63856200	-0.20354200
C	1.15398500	1.24390600	-0.07033400
N	0.00000300	0.56583500	-0.00576100
H	0.00002100	4.39951500	-0.37395800
H	-2.16675100	3.14607500	-0.24645000
H	2.16678000	3.14608300	-0.24615200
N	2.27652700	0.40333500	0.00296200
C	3.61310400	0.73070500	-0.00146500
H	2.02645100	-0.57036800	0.11760100
O	4.02043100	1.89364600	-0.01802000
N	-2.27652100	0.40332500	0.00265200
C	-3.61309900	0.73068900	-0.00194400
H	-2.02645400	-0.57037300	0.11734900
O	-4.02042400	1.89363400	-0.01824300
C	-4.56050400	-0.43442000	0.03001600

C	-5.84376100	-0.20992900	0.55278200
C	-4.23303100	-1.70887700	-0.46152200
C	-6.77585200	-1.24589300	0.60458200
H	-6.09457500	0.78060200	0.91657000
C	-5.17175600	-2.74207200	-0.41855200
H	-3.26409700	-1.90158600	-0.91285600
C	-6.44158500	-2.51499600	0.11977600
H	-7.76216100	-1.06386500	1.02053000
H	-4.91283700	-3.72009700	-0.81251600
H	-7.16874600	-3.32074700	0.15532800
C	4.56050400	-0.43441400	0.03020400
C	4.23292400	-1.70881800	-0.46140100
C	5.84385700	-0.20999500	0.55276600
C	5.17163500	-2.74203600	-0.41869000
H	3.26390500	-1.90146300	-0.91258200
C	6.77593600	-1.24598300	0.60430800
H	6.09475100	0.78049600	0.91660700
C	6.44156100	-2.51503400	0.11944000
H	4.91262800	-3.72001900	-0.81270000
H	7.76232000	-1.06401300	1.02010300
H	7.16871300	-3.32080300	0.15479000





Calculated Enthalpy: -855.893148 Hartree

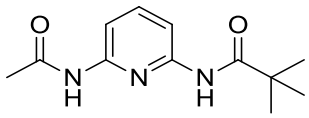
Zero Point Energy: 0.251404 Hartree

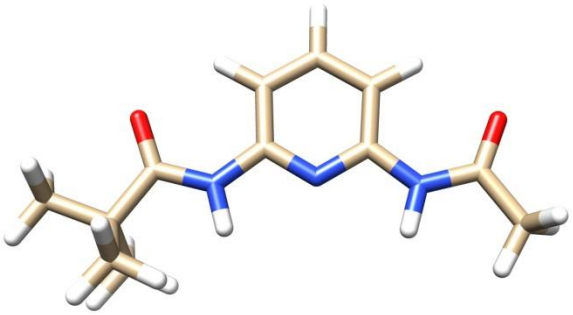
Lowest Frequency: 27.6 cm^{-1}

Coordinates:

Atom	x	y	z
C	0.43558900	0.72663500	-0.04610200
C	0.74250500	2.08876500	-0.17521100
C	2.09402900	2.42869800	-0.21459900
C	3.08827900	1.45532800	-0.12577500
C	2.66290900	0.12576800	0.00447400
N	1.37150800	-0.22851100	0.04206300
H	2.37769200	3.47199700	-0.31518000
H	-0.04332000	2.82620400	-0.23656400
H	4.14044200	1.69534800	-0.15389400
N	3.52901700	-0.97630500	0.10940500
C	4.90409400	-1.01279400	0.10569000
H	3.03618800	-1.85583200	0.19930400
O	5.60767400	-0.00847600	0.00389600

N	-0.86832400	0.20699200	-0.00124200
C	-2.07272700	0.87208500	-0.02097500
H	-0.88235800	-0.79872200	0.10926100
O	-2.16152900	2.10123000	-0.03191200
C	-3.29243300	-0.00433700	-0.01288900
C	-4.48065900	0.54636300	0.49238200
C	-3.30215500	-1.31824200	-0.50937400
C	-5.65197900	-0.20978000	0.52232000
H	-4.46943500	1.56661200	0.86033300
C	-4.47899900	-2.06998200	-0.48839400
H	-2.41037600	-1.75617100	-0.94811500
C	-5.65381500	-1.52036000	0.03266900
H	-6.56292400	0.22263900	0.92505100
H	-4.47835500	-3.08023600	-0.88603600
H	-6.56706800	-2.10761700	0.05119100
C	5.50692800	-2.39833400	0.23295000
H	4.76709600	-3.19243000	0.35707100
H	6.10169000	-2.60280900	-0.66218100
H	6.18677400	-2.40512900	1.08931300





Calculated Enthalpy: -782.063410 Hartree

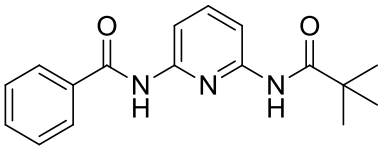
Zero Point Energy: 0.282535 Hartree

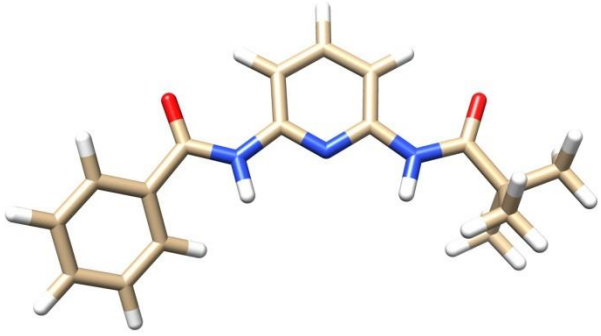
Lowest Frequency: 12.8 cm^{-1}

Coordinates:

Atom	x	y	z
C	-2.14945200	0.19008000	-0.00180200
C	-2.42529800	1.56436200	0.00216200
C	-1.32901500	2.42600300	0.00275300
C	-0.02380400	1.93660200	-0.00074100
C	0.13178000	0.54254900	-0.00481700
N	-0.90538800	-0.30705300	-0.00529800
H	-1.49506100	3.49911100	0.00600600
H	-3.44450400	1.91991400	0.00485000
H	0.83891900	2.58524700	-0.00058900
N	1.37039600	-0.11823900	-0.00775800
C	2.64603000	0.40225500	-0.01448600
H	1.26825900	-1.12489300	-0.00875100
O	2.86318900	1.61230600	-0.02220400
N	-3.13377300	-0.81396600	-0.00200700
C	-4.50406500	-0.69494500	0.00316400

H	-2.74353700	-1.74792600	-0.00704000
O	-5.09016600	0.38712200	0.00891800
C	3.77898000	-0.65246100	0.00185000
C	3.71961700	-1.44646500	1.32957600
H	2.79505200	-2.02365700	1.43287800
H	4.55547800	-2.15296900	1.36928300
H	3.80014100	-0.77781100	2.19295100
C	5.13000000	0.07611900	-0.09428000
H	5.94054600	-0.65971500	-0.07617900
H	5.20694200	0.65137400	-1.02116500
H	5.27071800	0.76723500	0.74074600
C	3.63380800	-1.61575500	-1.19994700
H	3.63214600	-1.06880700	-2.14851800
H	4.48003200	-2.31055800	-1.21168600
H	2.72062400	-2.21848100	-1.15449400
C	-5.25953400	-2.00958500	-0.00388000
H	-5.86129800	-2.06112200	-0.91612700
H	-4.61425000	-2.88945000	0.04625900
H	-5.94732600	-2.02065800	0.84599100





Calculated Enthalpy: -973.757019 Hartree

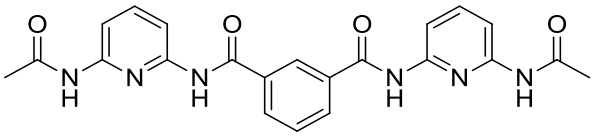
Zero Point Energy: 0.335968 Hartree

Lowest Frequency: 24.1 cm^{-1}

Coordinates:

Atom	x	y	z
C	-0.61481300	1.09876700	-0.05742900
C	-0.52310100	2.49418300	-0.15603800
C	0.75982300	3.03841400	-0.20244200
C	1.89253900	2.22790600	-0.14900700
C	1.67982400	0.84498200	-0.04812500
N	0.45745700	0.29662600	-0.00476100
H	0.87878500	4.11498100	-0.27984400
H	-1.41365800	3.10307700	-0.18945500
H	2.89455800	2.62747800	-0.18117700
N	2.70396300	-0.11273500	0.01943500
C	4.07120000	0.05857400	0.00247000
H	2.34386100	-1.05563300	0.09133300
O	4.59438600	1.16759300	-0.08571800
N	-1.82394700	0.38512500	-0.01203900
C	-3.11544200	0.85940700	0.00847900

H	-1.68414900	-0.61407500	0.06673800
O	-3.39167300	2.05996100	0.04495800
C	-4.18592600	-0.19392100	-0.00209100
C	-4.00847000	-1.46484700	-0.57287500
C	-5.42789800	0.13827000	0.56133300
C	-5.05438000	-2.39046800	-0.56781600
H	-3.07318800	-1.73293400	-1.05560100
C	-6.46710800	-0.79154500	0.57549700
H	-5.56224500	1.12698000	0.98665700
C	-6.28249600	-2.05852500	0.01135500
H	-4.91124700	-3.36579800	-1.02280900
H	-7.42041000	-0.52838300	1.02378000
H	-7.09334100	-2.78086300	0.01736200
C	4.89237200	-1.24931200	0.10435800
C	4.56722600	-1.96992400	1.43493400
H	3.52591600	-2.30343200	1.49129100
H	5.20066800	-2.85796500	1.53117600
H	4.76218000	-1.32048600	2.29468800
C	6.38841300	-0.89396200	0.07251100
H	6.98036800	-1.81169200	0.15049900
H	6.65795300	-0.38697200	-0.85801100
H	6.65921200	-0.23574500	0.90242300
C	4.56193500	-2.17163800	-1.09367500
H	4.76004000	-1.66885800	-2.04604400
H	5.18989900	-3.06764300	-1.04735900
H	3.51859300	-2.50375100	-1.09665000



Calculated Enthalpy: -1479.615505 Hartree

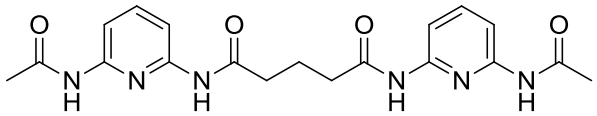
Zero Point Energy: 0.402147 Hartree

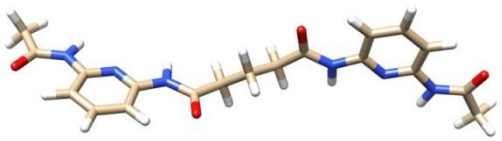
Lowest Frequency: 10.4 cm^{-1}

Coordinates:

Atom	x	y	z
C	-0.65180900	-3.79901700	-1.02086300
C	0.69103900	-3.71626800	-0.65912600
C	1.24053100	-2.48773600	-0.25943600
C	0.42040000	-1.35586400	-0.20188300
C	-0.93853900	-1.43930400	-0.53524500
C	-1.46831200	-2.66702300	-0.95900800
H	-1.06559000	-4.74427100	-1.35710100
H	1.32931100	-4.59241800	-0.68911500

H	0.79815400	-0.39384000	0.12810000
H	-2.50506500	-2.75071100	-1.27029400
C	2.69527000	-2.47014800	0.12431700
O	3.25951600	-3.48608000	0.53296000
N	3.32876700	-1.26129400	-0.02771600
H	2.81618400	-0.50481300	-0.46328700
C	-1.74297900	-0.17175600	-0.44470500
O	-1.20387000	0.93325400	-0.52691400
N	-3.09252000	-0.34171700	-0.25549200
H	-3.43842700	-1.27881200	-0.09298900
C	4.65492900	-0.90857600	0.27730800
C	5.58563300	-1.76924500	0.87521700
N	4.93834700	0.35629600	-0.06028500
C	6.85665200	-1.24981200	1.11847400
H	5.31616900	-2.78394800	1.12587600
C	6.16745900	0.83020000	0.18236000
C	7.17914900	0.06285400	0.77773400
H	7.60971500	-1.88036300	1.58137500
H	8.15638500	0.48571300	0.95562800
C	-4.10861000	0.62710400	-0.18067400
C	-3.90369700	2.00371000	-0.34491200
N	-5.31157600	0.08858900	0.05927200
C	-5.02837200	2.82269500	-0.25031800
H	-2.91535500	2.39533400	-0.53132300
C	-6.37559600	0.89783300	0.14720200
C	-6.29201400	2.28985000	-0.00167900
H	-4.91714900	3.89595600	-0.37134400
H	-7.17650900	2.90378200	0.07647700
N	6.32161100	2.16659200	-0.22324700
C	7.42418400	2.98522100	-0.13875500
H	5.47962300	2.55298200	-0.63123800
O	8.50006500	2.62388000	0.33652700
N	-7.56824900	0.19988100	0.40109400
C	-8.84934600	0.68161100	0.54478400
H	-7.43091300	-0.79985500	0.48006700
O	-9.13532000	1.87572800	0.46813200
C	7.22112900	4.38835700	-0.67624500
H	6.22872600	4.55999500	-1.09910500
H	7.38968500	5.10025300	0.13711400
H	7.97574800	4.57991900	-1.44409600
C	-9.90402300	-0.37516200	0.80837500
H	-9.51011800	-1.39338800	0.84290800
H	-10.39350500	-0.14917900	1.76003100
H	-10.66332800	-0.31215700	0.02376600





Calculated Enthalpy: -1366.496158 Hartree

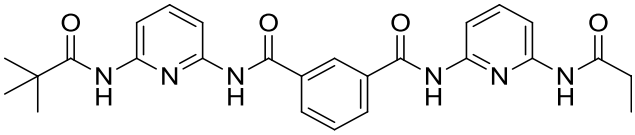
Zero Point Energy: 0.407015 Hartree

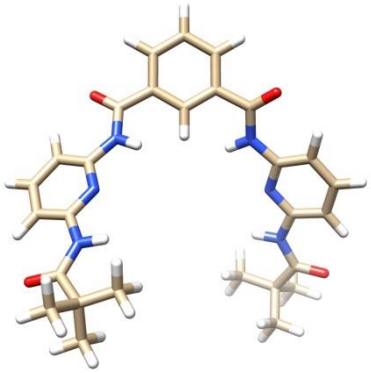
Lowest Frequency: 2.1 cm^{-1}

Coordinates:

Atom	x	y	z
C	1.20370300	0.36396100	-0.89629200
C	-0.00559400	-0.03914600	-0.03912600
C	-1.20485400	-0.44794100	-0.90830400
H	0.26291500	-0.87419400	0.61551700
C	2.35804300	0.88679700	-0.04994700
O	2.18995800	1.73237300	0.82762600
N	3.58645900	0.35420300	-0.36265400
H	3.62433900	-0.33673100	-1.10167000
C	-2.37047800	-0.95854300	-0.07033100
O	-2.21869600	-1.81640900	0.79835400
N	-3.58834000	-0.39897100	-0.37701300
H	-3.61329100	0.30025000	-1.10875800
C	4.85127600	0.64327100	0.17922700
C	5.07358000	1.55053200	1.22449800
N	5.83518600	-0.04789400	-0.41169400
C	6.39300200	1.71885100	1.64245700
H	4.24983200	2.08418600	1.67385200
C	7.09430200	0.13193500	0.00961500
C	7.43648400	1.01362300	1.04460900
H	6.61185400	2.41147200	2.44955400
H	8.46505500	1.12734900	1.35204300
C	-4.85796700	-0.66716300	0.16442900
C	-5.09758100	-1.58094800	1.20012800
N	-5.82810400	0.05101400	-0.41695900
C	-6.41957600	-1.72608700	1.61864400
H	-4.28450200	-2.13670800	1.64205500
C	-7.09001000	-0.10673000	0.00481300
C	-7.44900500	-0.99251900	1.03059200
H	-6.65162100	-2.42288100	2.41843400
H	-8.47918100	-1.08822600	1.33882100
N	8.01915300	-0.65530100	-0.69782400
C	9.38404900	-0.74537900	-0.55170600
H	7.58379400	-1.23097600	-1.40751300
O	10.02053700	-0.09499600	0.27642400
N	-7.99897900	0.70807700	-0.69187800
C	-9.36128100	0.82618500	-0.54192000
H	-7.55260700	1.28200400	-1.39608000

O	-10.01014900	0.18078000	0.28047600
C	-10.02238300	1.82513100	-1.47141000
H	-9.33256900	2.29822000	-2.17399600
H	-10.80875300	1.31216300	-2.03197500
H	-10.50088700	2.60028700	-0.86571700
C	10.06429900	-1.72144400	-1.49157500
H	10.53803700	-2.50660100	-0.89483500
H	9.38728900	-2.18391700	-2.21340000
H	10.85587100	-1.19309100	-2.02980500
H	-1.51218900	0.38734700	-1.54722600
H	-0.91654700	-1.27157600	-1.57496700
H	-0.28178600	0.80024700	0.60669700
H	1.52228100	-0.47653900	-1.52279600
H	0.92178900	1.17971100	-1.57553500





Calculated Enthalpy: -1715.343379 Hartree

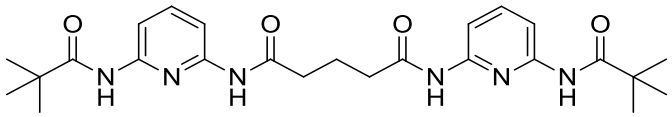
Zero Point Energy: 0.571304 Hartree

Lowest Frequency: 7.0 cm^{-1}

Coordinates:

Atom	x	y	z
C	0.00002200	6.28387600	0.00003700
C	1.05214700	5.58835900	0.59607500
C	1.06978600	4.18633100	0.57971200
C	0.00007400	3.48995800	-0.00002100
C	-1.06966500	4.18631400	-0.57972700
C	-1.05207700	5.58834400	-0.59603100
H	0.00000200	7.36919000	0.00005900
H	1.87196600	6.11845500	1.06851600
H	0.00009700	2.40421000	-0.00004700
H	-1.87191400	6.11843000	-1.06845200
C	2.23428600	3.49334000	1.23116400
O	2.83134500	4.00227600	2.18027400
N	2.57177100	2.27783900	0.68582400
H	2.11502700	1.99857500	-0.17340200
C	-2.23413400	3.49330900	-1.23122100
O	-2.83123300	4.00229100	-2.18028000
N	-2.57165300	2.27782200	-0.68587200
H	-2.11492500	1.99855500	0.17336200
C	3.56571600	1.36801200	1.08897500
C	4.35331500	1.51578300	2.23870900
N	3.67338700	0.32539400	0.25528400

C	5.28124200	0.50768900	2.49813500
H	4.23828400	2.37708700	2.87910400
C	4.57599000	-0.62823500	0.52463700
C	5.41527300	-0.58846000	1.64757100
H	5.91246400	0.57888600	3.37873400
H	6.12729100	-1.37936300	1.82753900
C	-3.56563600	1.36803000	-1.08900900
C	-4.35321400	1.51581100	-2.23875700
N	-3.67336300	0.32543600	-0.25529600
C	-5.28118200	0.50775200	-2.49817100
H	-4.23813800	2.37709500	-2.87916900
C	-4.57600300	-0.62816100	-0.52464000
C	-5.41527200	-0.58837200	-1.64758500
H	-5.91239000	0.57895700	-3.37878000
H	-6.12732200	-1.37924800	-1.82754400
N	4.58167700	-1.65228500	-0.43707100
C	5.35780800	-2.78537400	-0.50127300
H	3.90943800	-1.49332500	-1.17541700
O	6.19844700	-3.05974600	0.35534600
N	-4.58174800	-1.65218700	0.43709500
C	-5.35792000	-2.78524700	0.50131000
H	-3.90951800	-1.49323300	1.17545000
O	-6.19854000	-3.05962100	-0.35532800
C	5.13274000	-3.71669600	-1.71644200
C	-5.13287000	-3.71657800	1.71647400
C	-4.03203900	-3.24715800	2.68657500
H	-3.04920900	-3.19083000	2.20410500
H	-4.26396100	-2.27696500	3.14121900
H	-3.94357800	-3.96809200	3.50527600
C	-6.47917500	-3.80191100	2.47256200
H	-7.27584900	-4.14414000	1.80769000
H	-6.39018500	-4.50897300	3.30400600
H	-6.76705000	-2.82815600	2.88422200
C	-4.76265300	-5.11018600	1.15870200
H	-4.66856400	-5.82357100	1.98419300
H	-5.53281400	-5.47116100	0.47287400
H	-3.80727400	-5.08346400	0.62281100
C	4.03183300	-3.24731400	-2.68647700
H	3.04903100	-3.19102400	-2.20394400
H	4.26368900	-2.27711100	-3.14113400
H	3.94335100	-3.96824900	-3.50517400
C	4.76262600	-5.11033700	-1.15868600
H	4.66854300	-5.82370800	-1.98418900
H	5.53283600	-5.47128200	-0.47289700
H	3.80726600	-5.08367900	-0.62275800
C	6.47901200	-3.80193500	-2.47260100
H	7.27573700	-4.14415900	-1.80778500
H	6.39001300	-4.50896400	-3.30407300
H	6.76682500	-2.82815000	-2.88423200



Calculated Enthalpy: -1602.224302 Hartree

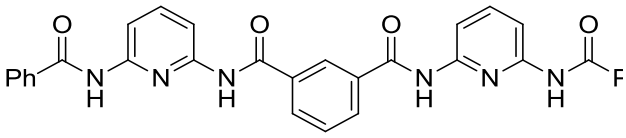
Zero Point Energy: 0.576508 Hartree

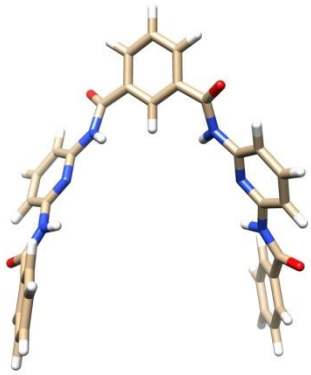
Lowest Frequency: 28.6 cm^{-1}

Coordinates:

Atom	x	y	z
C	1.17991400	0.51035800	-0.58874200
C	0.00710300	0.06008200	0.29518300
C	-1.17932200	-0.43516600	-0.54480200
H	0.33124000	-0.74357000	0.96384000
C	2.30127400	1.14363400	0.22623100
O	2.08270800	2.02523500	1.05612200
N	3.55872600	0.66589300	-0.05736200
H	3.63720400	-0.06486100	-0.75353300
C	-2.28671100	-1.02875800	0.31805800
O	-2.05081000	-1.84364100	1.20901700
N	-3.55348700	-0.59813400	0.00206500
H	-3.64631200	0.07924600	-0.74452200
C	4.80430600	1.05889500	0.46394300
C	4.97305900	2.04411200	1.44678800
N	5.82642400	0.38698800	-0.08195900
C	6.28038000	2.31374800	1.84942100
H	4.11963900	2.55897000	1.86144400
C	7.07378000	0.66459000	0.32285500
C	7.36302000	1.63097900	1.29674000
H	6.45881200	3.06943100	2.60850800
H	8.38303600	1.82286800	1.59280400
C	-4.79141600	-0.97967700	0.54931000
C	-4.94149200	-1.89695500	1.59868700
N	-5.82632200	-0.36926900	-0.04276500
C	-6.24368300	-2.16469000	2.01882500
H	-4.07843300	-2.36366200	2.04889200
C	-7.06846200	-0.64405500	0.37964800
C	-7.33933200	-1.54525100	1.41913900
H	-6.40771900	-2.86845000	2.82933000
H	-8.35557800	-1.73709500	1.72793100
N	8.03937200	-0.11635700	-0.33552500
C	9.40705700	-0.10982400	-0.20157800
H	7.62886700	-0.75915100	-0.99910300
O	9.99129600	0.64188100	0.57921000
N	-8.04858200	0.07003600	-0.33117000
C	-9.41704400	0.02980600	-0.21137700

H	-7.64932300	0.68231500	-1.02961900
O	-9.98830700	-0.69341800	0.60506200
C	-10.22826100	0.93991200	-1.16477100
C	10.20038600	-1.09591200	-1.09269000
H	-1.56200800	0.37400000	-1.17679200
H	-0.84876300	-1.23722500	-1.21866400
H	-0.30688800	0.89769000	0.92595000
H	1.55053600	-0.33032400	-1.18573600
H	0.83890400	1.27889400	-1.29533200
C	-11.11821100	1.84406600	-0.28113900
H	-11.76391400	2.45994600	-0.91587900
H	-11.74906800	1.24358000	0.37851500
H	-10.51238300	2.51490600	0.33819300
C	-9.37032800	1.82220400	-2.09190600
H	-8.73061200	2.51420300	-1.53200100
H	-8.74716600	1.23054100	-2.77273200
H	-10.02915000	2.43261800	-2.71725700
C	-11.11973800	0.01186800	-2.02271800
H	-11.74868300	-0.61811500	-1.38888500
H	-11.76812400	0.61519000	-2.66695200
H	-10.51522200	-0.63860100	-2.66474000
C	9.32592100	-2.00594100	-1.97658100
H	8.66393100	-2.64815700	-1.38424400
H	8.72379400	-1.43761000	-2.69526500
H	9.97291700	-2.66765700	-2.56076700
C	11.12482800	-0.24340900	-1.99360100
H	11.77035600	0.39989400	-1.39053300
H	11.75708100	-0.90043900	-2.60007700
H	10.54438700	0.39022000	-2.67351700
C	11.05756500	-1.97176200	-0.15058000
H	11.69671300	-2.63476200	-0.74325000
H	11.69398800	-1.35157100	0.48503800
H	10.42836700	-2.59495600	0.49462600





Calculated Enthalpy: -1863.001971 Hartree

Zero Point Energy: 0.509137 Hartree

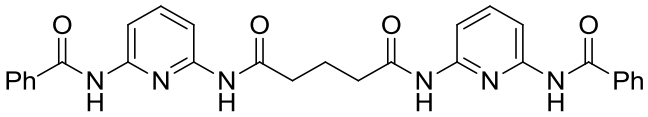
Lowest Frequency: 5.7 cm^{-1}

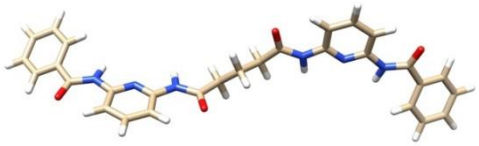
Coordinates:

Atom	x	y	z
C	-0.00005400	6.70541300	-0.00000200
C	-1.00529800	6.00985800	-0.67196100

C	-1.02364000	4.60779600	-0.65785000
C	-0.00003500	3.91159300	0.00001500
C	1.02355800	4.60781900	0.65787500
C	1.00520000	6.00988000	0.67196600
H	-0.00006000	7.79072400	-0.00001000
H	-1.78799600	6.53976400	-1.20380300
H	-0.00001600	2.82586100	0.00001400
H	1.78789300	6.53980300	1.20379800
C	-2.13571700	3.91623100	-1.39673000
O	-2.66632500	4.43264900	-2.38057600
N	-2.50525800	2.69345400	-0.88980800
H	-2.10533900	2.40362000	-0.00618000
C	2.13564100	3.91627100	1.39675500
O	2.66627200	4.43271700	2.38057300
N	2.50517000	2.69348800	0.88983800
H	2.10523900	2.40365300	0.00621500
C	-3.45720700	1.78020600	-1.37661400
C	-4.17083000	1.94292000	-2.57193800
N	-3.60385000	0.71819400	-0.57400500
C	-5.06319500	0.92733400	-2.91409700
H	-4.02800500	2.81981600	-3.18504400
C	-4.47052900	-0.24210000	-0.92389000
C	-5.23355200	-0.19093500	-2.09972300
H	-5.63642800	1.00931000	-3.83255800
H	-5.91474800	-0.99046100	-2.34861800
C	3.45714700	1.78025200	1.37661800
C	4.17077400	1.94295000	2.57194200
N	3.60380700	0.71826300	0.57398200
C	5.06316000	0.92737200	2.91407400
H	4.02793500	2.81982500	3.18507300
C	4.47050900	-0.24202000	0.92384100
C	5.23353400	-0.19087200	2.09967100
H	5.63639600	1.00933500	3.83253500
H	5.91475000	-0.99039200	2.34854100
N	-4.52901600	-1.28334100	0.01541200
C	-5.25432500	-2.45303400	-0.02355700
H	-3.89673100	-1.14340800	0.79313600
O	-5.95341900	-2.77882400	-0.98441800
N	4.52903200	-1.28324600	-0.01547200
C	5.25432700	-2.45294200	0.02355400
H	3.89676300	-1.14332000	-0.79321200
O	5.95337700	-2.77869900	0.98445800
C	5.12592700	-3.32749200	-1.18994300
C	5.34733000	-4.70350200	-1.02294500
C	4.82918800	-2.82960800	-2.46932300
C	5.24971000	-5.57040100	-2.11086800
H	5.59127700	-5.07836700	-0.03480300
C	4.74328200	-3.69830200	-3.55951800
H	4.69899200	-1.76439000	-2.63650500
C	4.94637400	-5.06981800	-3.38169000
H	5.41148500	-6.63463500	-1.96886500

H	4.52563500	-3.30196000	-4.54656100
H	4.87501300	-5.74404200	-4.22995700
C	-5.12586300	-3.32756600	1.18994700
C	-5.34734000	-4.70356800	1.02299100
C	-4.82899100	-2.82966900	2.46929200
C	-5.24966600	-5.57045000	2.11092300
H	-5.59138500	-5.07844100	0.03487700
C	-4.74302800	-3.69834700	3.55949600
H	-4.69872400	-1.76445500	2.63644000
C	-4.94619700	-5.06985600	3.38170900
H	-5.41150200	-6.63467900	1.96895500
H	-4.52527600	-3.30199700	4.54651200
H	-4.87479200	-5.74406800	4.22998200





Calculated Enthalpy: -1749.883075 Hartree

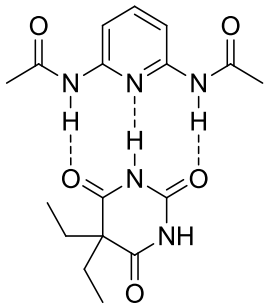
Zero Point Energy: 0.513581 Hartree

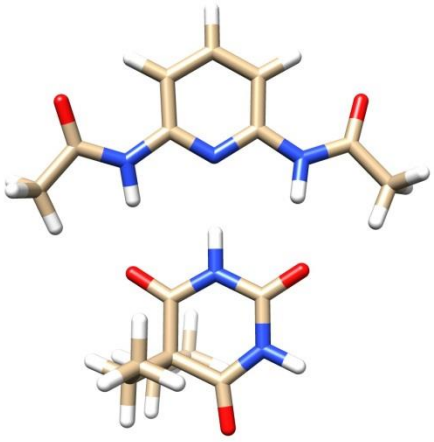
Lowest Frequency: 23.7 cm^{-1}

Coordinates:

Atom	x	y	z
C	1.21588400	-0.40863800	0.36266400
C	0.00004300	-1.27050100	0.00013800
C	-1.21587900	-0.40857100	-0.36194200
H	0.24186600	-1.92245900	-0.84401000
C	2.38939600	-1.23324900	0.87019000
O	2.23626600	-2.26182100	1.53275000
N	3.62381900	-0.71835400	0.56397000
H	3.65630000	0.12702800	0.00683800
C	-2.38932200	-1.23303000	-0.86987700
O	-2.23611300	-2.26135900	-1.53279400
N	-3.62378600	-0.71826400	-0.56359900
H	-3.65634100	0.12691200	-0.00616000
C	4.89994800	-1.17938800	0.92799600
C	5.14255800	-2.33386900	1.68447100
N	5.87596700	-0.38554500	0.46663700
C	6.47443600	-2.64376500	1.95142000
H	4.32287100	-2.94338200	2.03408000
C	7.14878700	-0.70826400	0.73870700
C	7.51101600	-1.83887600	1.48343600
H	6.70911200	-3.52995800	2.53298900
H	8.55019200	-2.06188000	1.67186300

C	-4.89986400	-1.17919200	-0.92792900
C	-5.14236300	-2.33340000	-1.68485700
N	-5.87595300	-0.38553700	-0.46639200
C	-6.47420300	-2.64322800	-1.95207100
H	-4.32262300	-2.94276600	-2.03459700
C	-7.14873400	-0.70818500	-0.73872600
C	-7.51085500	-1.83853300	-1.48390800
H	-6.70879400	-3.52921200	-2.53399000
H	-8.55000500	-2.06149200	-1.67253200
N	8.05379600	0.21834300	0.19838700
C	9.42594200	0.22015600	0.24192700
H	7.59070700	0.95233600	-0.32185000
O	10.07627700	-0.69623800	0.75900100
N	-8.05383300	0.21819400	-0.19816800
C	-9.42597200	0.21998600	-0.24189500
H	-7.59083000	0.95202200	0.32238000
O	-10.07620300	-0.69607100	-0.75969600
H	-1.52295700	0.20010600	0.49672200
H	-0.95287300	0.29524900	-1.16443600
H	-0.24171300	-1.92291800	0.84395100
H	1.52290700	0.20050500	-0.49568900
H	0.95280400	0.29474300	1.16551700
C	10.10151600	1.40051100	-0.38283200
C	11.43712700	1.24239800	-0.78628200
C	9.47563200	2.64641200	-0.55816400
C	12.12682600	2.30158100	-1.37425700
H	11.91616700	0.28152800	-0.63486300
C	10.17134900	3.70816700	-1.13900900
H	8.45955200	2.81589500	-0.21459400
C	11.49502100	3.53677800	-1.55356200
H	13.15622700	2.16528300	-1.69128200
H	9.68178900	4.66954400	-1.26006500
H	12.03305400	4.36317000	-2.00819900
C	-10.10163200	1.40029100	0.38286100
C	-9.47565300	2.64607900	0.55866000
C	-11.43740100	1.24225900	0.78581900
C	-10.17143100	3.70779800	1.13949600
H	-8.45943300	2.81549600	0.21546900
C	-12.12716300	2.30140600	1.37378600
H	-11.91650800	0.28148000	0.63403800
C	-11.49526500	3.53648600	1.55356400
H	-9.68179100	4.66908800	1.26092200
H	-13.15668800	2.16517000	1.69043600
H	-12.03334800	4.36285000	2.00819400





Calculated Enthalpy: -1311.381458 Hartree

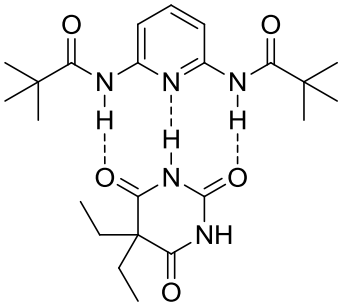
Zero Point Energy: 0.403814 Hartree

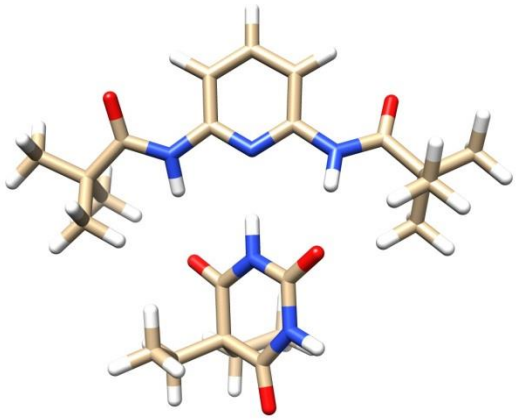
Lowest Frequency: 21.0 cm^{-1}

Coordinates:

Atom	x	y	z
H	2.74571600	-3.13392900	-0.78799400
N	2.55355100	-2.17377400	-0.51887300
C	3.64603800	-1.36390700	-0.24105000
C	1.22129300	-1.82058000	-0.45569800
C	3.37142800	0.08436200	0.16592600
O	4.77592800	-1.81556300	-0.32808600
N	0.95420300	-0.51843400	-0.08788400
O	0.32546100	-2.61872300	-0.71022600
C	1.88813400	0.44574300	0.22028900
C	3.99554300	0.33048000	1.57704500
C	4.07183000	1.02691800	-0.86596000
H	-0.04636100	-0.25180900	-0.04777300
O	1.51418100	1.57387700	0.52775800
H	5.06993000	0.15074800	1.47919000
H	3.85662200	1.39168400	1.80238200
H	3.93326600	2.04951900	-0.50349400
H	5.14105400	0.80158500	-0.81911300
N	-2.02223400	0.27941300	0.00457500
C	-2.99479700	-0.65664200	-0.00150900
C	-2.38175700	1.58000100	0.04203300
C	-4.35935000	-0.33552100	0.03432200
N	-2.53096600	-1.98096100	-0.06935400
C	-3.71987300	1.99809500	0.07062300
N	-1.30572900	2.48286300	0.07280400
C	-4.70118900	1.01229000	0.06801300
H	-5.09984300	-1.11982200	0.03478300
C	-3.25581700	-3.14641900	0.06914800
H	-1.53684600	-2.09339100	-0.26412300
H	-3.95822500	3.04982300	0.09343900
C	-1.34127000	3.85510300	-0.06257100
H	-0.38465700	2.07164200	0.22318800

H	-5.74826200	1.29883500	0.09283100
O	-4.46417900	-3.17849700	0.30360100
C	-2.45444200	-4.42417200	-0.08539200
O	-2.37343200	4.49883700	-0.25331200
C	0.00509900	4.54560000	0.03264100
H	-1.39437400	-4.25924000	-0.27911700
H	-2.88678000	-5.00280500	-0.90727700
H	-2.57152400	-5.01579500	0.82733400
H	-0.04993900	5.29692600	0.82579800
H	0.18688300	5.07567600	-0.90726200
H	0.83494300	3.86745800	0.23222800
C	3.42210500	-0.52639200	2.71036400
H	3.93020000	-0.28430700	3.64847000
H	2.35265600	-0.34493400	2.86345400
H	3.56612800	-1.59701700	2.52883700
C	3.57482000	0.90873000	-2.31064000
H	2.51191700	1.15756100	-2.40318800
H	4.12829700	1.60369300	-2.94897700
H	3.72697100	-0.09742300	-2.71586700





Calculated Enthalpy: -1547.103162 Hartree

Zero Point Energy: 0.572622 Hartree

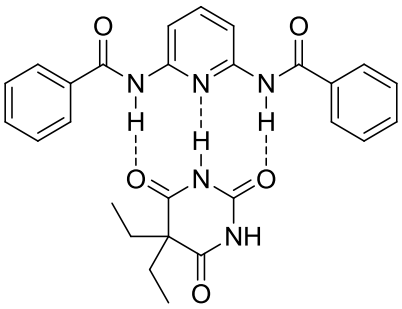
Lowest Frequency: 18.0 cm^{-1}

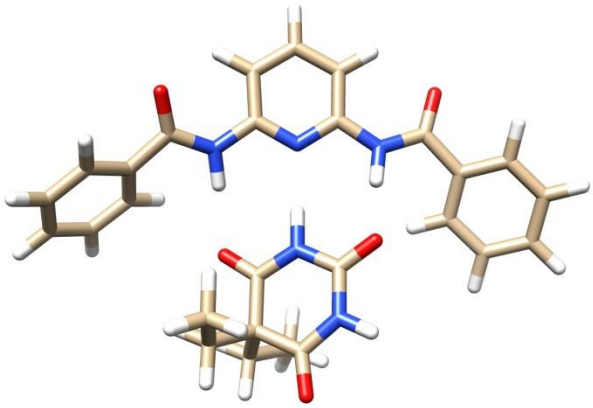
Coordinates:

Atom	x	y	z
H	1.36290100	3.79444000	-1.58922900
N	0.67258000	3.26578400	-1.06456100
C	-0.33535000	3.98635500	-0.43993600
C	0.87493100	1.90081400	-1.00442400
C	-1.38701500	3.20197100	0.34659000
O	-0.36598300	5.20230300	-0.53863800
N	-0.05053400	1.18013800	-0.28284900
O	1.83036000	1.36112000	-1.55333500
C	-1.15272100	1.69078600	0.36487600
C	-1.39462800	3.71714000	1.82121900
C	-2.78315900	3.48444900	-0.29603400
H	0.11128400	0.15384400	-0.22369300

O	-1.92096200	0.92611400	0.94083900
H	-1.64476200	4.78100300	1.78052800
H	-2.21465000	3.20327100	2.33119900
H	-3.52212600	2.95002500	0.30784600
H	-2.97268500	4.55522900	-0.17863400
N	0.46314300	-1.76251200	-0.06017900
C	1.73181400	-2.22085100	-0.07244000
C	-0.54709400	-2.65645600	0.00410800
C	2.04388400	-3.58571500	-0.03746700
N	2.73556200	-1.23469400	-0.16314200
C	-0.32739300	-4.04021400	0.05299200
N	-1.83777400	-2.09583400	0.06748800
C	0.98882400	-4.48857700	0.02698300
H	3.07236000	-3.91126200	-0.05442500
C	4.03806600	-1.35653400	0.28917000
H	2.45839800	-0.36218000	-0.60920100
H	-1.16086900	-4.72238300	0.10348700
C	-3.03688400	-2.74669900	-0.17080900
H	-1.87218100	-1.11813900	0.35069100
H	1.19323100	-5.55449400	0.05760300
O	4.43153400	-2.35965400	0.88139900
C	4.97299900	-0.15483000	0.01288000
O	-3.08186300	-3.91271100	-0.55840400
C	-4.32324100	-1.92256000	0.07462200
C	6.37634100	-0.49822700	0.54244800
C	4.45091900	1.09872400	0.75416100
C	5.05691300	0.11080700	-1.50911900
C	-5.54002400	-2.82734400	-0.18832300
C	-4.36639700	-1.43033700	1.54104200
C	-4.37055400	-0.72360500	-0.90112500
H	6.78420800	-1.38407200	0.04794000
H	7.04944000	0.34447000	0.35266700
H	6.36047000	-0.69353600	1.61793400
H	3.47679300	1.42484900	0.38292600
H	4.36911300	0.91300300	1.83053200
H	5.15402000	1.92579100	0.60719900
H	5.77009000	0.92132100	-1.69531700
H	5.41308300	-0.77788800	-2.04145600
H	4.09764000	0.40957300	-1.93743100
H	-5.54806900	-3.69311300	0.47960400
H	-6.45711900	-2.25300600	-0.02012600
H	-5.54874400	-3.19849900	-1.21659500
H	-5.31668100	-0.91557200	1.72050600
H	-4.30453500	-2.27275900	2.23852200
H	-3.56253600	-0.72813300	1.77200000
H	-3.56059900	-0.01341900	-0.72249200
H	-4.31697100	-1.06149400	-1.94167400
H	-5.31585200	-0.18607100	-0.76935200
C	-2.91918400	3.09016800	-1.77046000
H	-2.74449800	2.02078100	-1.93014800
H	-3.93228000	3.30998700	-2.11997200

H	-2.22581300	3.64776400	-2.40907200
C	-0.08698100	3.51598400	2.59388600
H	-0.19341900	3.90987300	3.60897800
H	0.18075700	2.45751600	2.68178400
H	0.75068100	4.04421000	2.12564000





Calculated Enthalpy: -1694.764702 Hartree

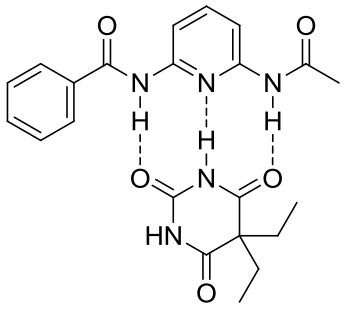
Zero Point Energy: 0.509962 Hartree

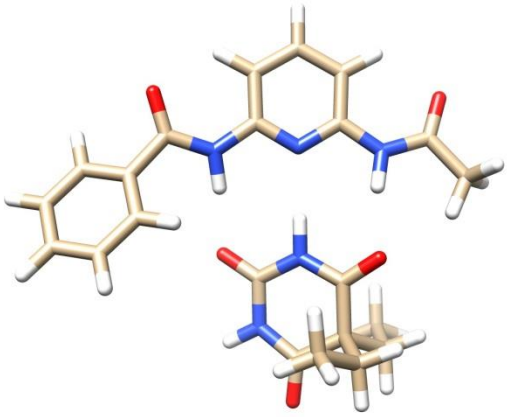
Lowest Frequency: 9.1 cm^{-1}

Coordinates:

Atom	x	y	z
C	-0.70786000	-2.70288600	0.06840800
C	-0.65389800	-4.10332200	0.06631000
C	0.60141900	-4.69913900	0.04378100
C	1.75803500	-3.92367100	0.02157400
C	1.60513900	-2.53080900	0.02428800
N	0.39475000	-1.93112100	0.04615200
H	0.68284200	-5.78179000	0.04423300
H	-1.56202200	-4.68683000	0.07905400
H	2.74393200	-4.36022000	-0.00124800
N	2.69168500	-1.63934700	-0.00444900
C	4.03259200	-1.93622300	0.13317000
H	2.46376200	-0.68436700	-0.27868100
O	4.47383100	-3.08331500	0.22703900
N	-1.93028600	-2.00995000	0.14962000
C	-3.15208600	-2.47460300	-0.29965800
H	-1.88538100	-1.04483600	0.47987100
O	-3.27731400	-3.51319500	-0.95063500
C	-4.34366200	-1.63482100	0.05137600
C	-5.42550300	-1.62743700	-0.84392700
C	-4.44279100	-0.92798500	1.25918700
C	-6.57906000	-0.90272400	-0.54742100
H	-5.34887600	-2.19294300	-1.76667200
C	-5.60744300	-0.21874800	1.56254800
H	-3.62595100	-0.94260100	1.97265300
C	-6.67317300	-0.19854300	0.65877300

H	-7.40601100	-0.89183400	-1.25114600
H	-5.68179200	0.31427100	2.50564400
H	-7.57562700	0.35781000	0.89483200
C	4.95437600	-0.75225500	0.17369100
C	4.60286900	0.46277900	0.78075000
C	6.24224400	-0.90715100	-0.36284600
C	5.52472500	1.51038300	0.84093300
H	3.62322400	0.58793800	1.23017800
C	7.15468100	0.14641300	-0.31845200
H	6.51425000	-1.85586300	-0.81330000
C	6.79787800	1.35758400	0.28510900
H	5.24982800	2.44236300	1.32577000
H	8.14384200	0.02260100	-0.74892700
H	7.51127100	2.17538700	0.32742400
H	0.19943700	0.00539800	-0.09637900
N	0.09241800	1.03199200	-0.22095600
C	-1.05001400	1.62194500	0.26992400
C	1.11769800	1.66715500	-0.88933200
C	-1.25484000	3.12143800	0.05965500
O	-1.88146000	0.93520500	0.85675500
N	0.95661700	3.02339500	-1.09956700
O	2.11596400	1.06282400	-1.26472300
C	-0.11044800	3.80879600	-0.68816300
C	-2.56945300	3.32796700	-0.76112100
C	-1.41765300	3.80442300	1.45409200
H	1.71351600	3.49047600	-1.58981500
O	-0.11373400	5.00559400	-0.92789900
H	-3.38198200	2.89821200	-0.16845000
H	-2.73566200	4.40759300	-0.81913900
H	-1.64780500	4.85659800	1.26425900
H	-2.29530300	3.35343200	1.92596300
C	-0.20589300	3.69366100	2.38559700
H	0.68579200	4.16356900	1.95639500
H	-0.41844600	4.20248800	3.33052400
H	0.03579000	2.65193900	2.62412900
C	-2.56935300	2.72141600	-2.16845600
H	-3.52677700	2.92397500	-2.65744600
H	-1.78331900	3.14958300	-2.80005300
H	-2.43826900	1.63409900	-2.14830600





Calculated Enthalpy: -1503.073615 Hartree

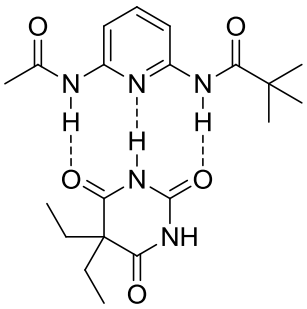
Zero Point Energy: 0.456643 Hartree

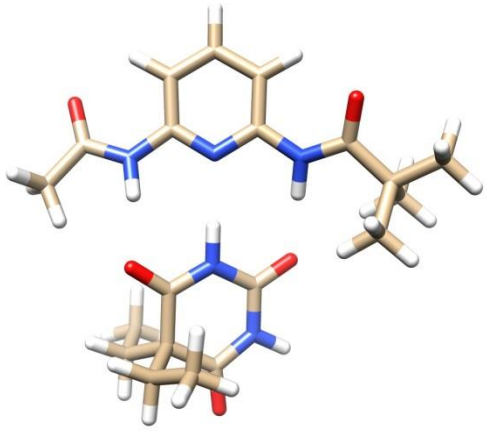
Lowest Frequency: 11.6 cm^{-1}

Coordinates:

Atom	x	y	z
C	0.64725900	-2.55489200	0.09752000
C	0.99659100	-3.90667900	0.21634800
C	2.34977400	-4.22315700	0.25399900
C	3.31560000	-3.22371000	0.17129200
C	2.87080000	-1.90104800	0.04899900
N	1.56193800	-1.57013800	0.01587100
H	2.65734600	-5.25997500	0.34973000
H	0.23221300	-4.66689700	0.27465700
H	4.37233200	-3.43966200	0.19905000
N	3.74928600	-0.81291400	-0.08379600
C	5.10777900	-0.78548300	0.14953900
H	3.33152800	0.05528300	-0.41776700
O	5.75150300	-1.75326800	0.55563100
N	-0.69632300	-2.13559500	0.10943900
C	-1.77399500	-2.88128300	-0.32862500
H	-0.86618900	-1.16429600	0.37524800
O	-1.65037500	-3.96193400	-0.90803400
C	-3.13023100	-2.30061800	-0.06005900
C	-4.16221500	-2.60430300	-0.96286800
C	-3.41640800	-1.53971200	1.08322700
C	-5.45498600	-2.13311400	-0.73872100
H	-3.93718900	-3.21040500	-1.83411100
C	-4.71646700	-1.08377900	1.31458000
H	-2.63705400	-1.31560200	1.80310000
C	-5.73532900	-1.37296100	0.40284300
H	-6.24420300	-2.36241200	-1.44848200
H	-4.93210400	-0.50649400	2.20864700
H	-6.74426300	-1.01332100	0.58281500
C	5.77869400	0.54496100	-0.12997700
H	5.08709700	1.32859600	-0.44182300
H	6.30805900	0.86154600	0.77324300

H	6.52830100	0.39440800	-0.91292900
H	1.00532300	0.32072500	-0.12163500
N	0.71222000	1.31528900	-0.18937100
C	-0.54360500	1.64038900	0.27384900
C	1.63091800	2.18852100	-0.72958400
C	-1.01360100	3.09157500	0.18133600
O	-1.26046800	0.76329300	0.74584500
N	1.23108500	3.50574500	-0.83297300
O	2.74278300	1.81826700	-1.09490400
C	0.01530800	4.04229500	-0.43243300
C	-2.30906400	3.13651800	-0.69227500
C	-1.35728700	3.59584700	1.61945300
H	1.91040700	4.14585500	-1.23299300
O	-0.20003600	5.23486100	-0.57507000
H	-3.05408700	2.51914400	-0.18260400
H	-2.66479100	4.17067600	-0.67110200
H	-1.77321300	4.60123200	1.50834600
H	-2.15281900	2.94813000	1.99865800
C	-2.14453200	2.66904100	-2.14241500
H	-3.10423300	2.73942800	-2.66281000
H	-1.42822900	3.28666800	-2.69496800
H	-1.81685200	1.62565700	-2.20447300
C	-0.18522300	3.62101400	2.60634800
H	-0.52788000	3.99074500	3.57730700
H	0.23796500	2.62359600	2.76822400
H	0.61914700	4.28437900	2.27049200





Calculated Enthalpy: -1429.242804 Hartree

Zero Point Energy: 0.488112 Hartree

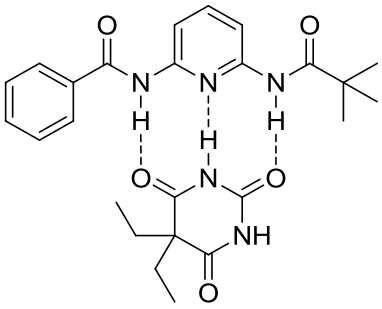
Lowest Frequency: 18.1 cm^{-1}

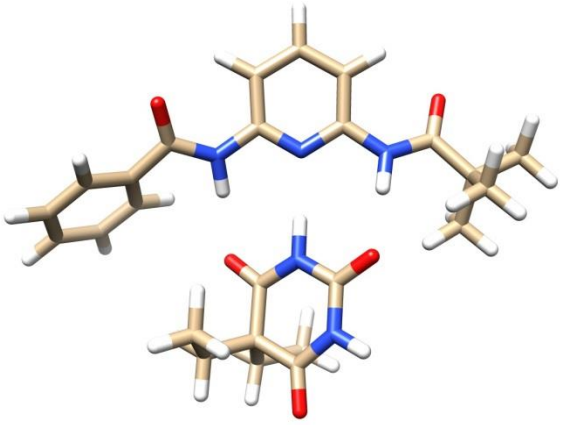
Coordinates:

Atom	x	y	z
C	0.73760000	2.85775000	0.04013700
C	1.65710500	3.91155900	-0.04168700
C	3.00547000	3.58087400	-0.13859700
C	3.41325200	2.25147200	-0.14939400

C	2.42130300	1.26433600	-0.06607000
N	1.10869000	1.55982400	0.02133900
H	3.74773700	4.37045100	-0.20614500
H	1.31346900	4.93420500	-0.02937900
H	4.45356300	1.97413800	-0.21630400
N	2.72552800	-0.10987000	-0.10685200
C	3.93074300	-0.69660400	0.23740300
H	1.96968400	-0.71389400	-0.42357600
O	4.87756700	-0.04002300	0.66670100
N	-0.64484000	3.06533300	0.18565400
C	-1.34897800	4.23970300	0.02498200
H	-1.18835400	2.25059200	0.47106200
O	-0.83616200	5.30261700	-0.32589900
C	4.01898800	-2.23001400	0.04960600
C	2.94697700	-2.93650100	0.91305200
H	1.92975900	-2.69532900	0.59573800
H	3.06967200	-4.02151800	0.82557500
H	3.05539000	-2.66968100	1.96988600
C	5.41317800	-2.69726800	0.50258400
H	5.49062300	-3.78136200	0.36920800
H	6.20398400	-2.21989100	-0.08213700
H	5.59035600	-2.46509800	1.55633800
C	3.82764700	-2.58170900	-1.44572600
H	4.57876900	-2.07855800	-2.06434400
H	3.95070700	-3.66189400	-1.58093000
H	2.83598400	-2.31204100	-1.81596000
C	-2.83335600	4.14239100	0.31774000
H	-3.38252300	4.51731400	-0.55047200
H	-3.16911800	3.13248600	0.55612400
H	-3.06075300	4.80412600	1.15936600
H	-0.29296900	0.17173300	-0.06257800
N	-1.03790500	-0.54777400	-0.15207600
C	-2.27756800	-0.26835400	0.37651900
C	-0.68125800	-1.69574800	-0.82722700
C	-3.38456900	-1.31548700	0.26090700
O	-2.47128400	0.81166100	0.92923300
N	-1.67012000	-2.64828800	-0.97341700
O	0.45163200	-1.86124100	-1.26590500
C	-2.96911000	-2.58177200	-0.48998200
C	-3.83801100	-1.71881600	1.70135200
C	-4.59872100	-0.67679500	-0.48679500
H	-1.40303800	-3.49357800	-1.46881900
O	-3.73535300	-3.51372700	-0.67224700
H	-4.21243500	-0.80906100	2.17947000
H	-4.68347100	-2.40240700	1.58259600
H	-5.40155000	-1.41934400	-0.47270800
H	-4.92663400	0.17555500	0.11503900
C	-4.32413500	-0.23026000	-1.92646000
H	-5.23122200	0.20304000	-2.35807600
H	-3.54113500	0.53407200	-1.97834600
H	-4.02701500	-1.06811700	-2.56630400

C	-2.75979100	-2.36560800	2.57674900
H	-1.91048700	-1.69479400	2.74606600
H	-3.17953500	-2.61231700	3.55642300
H	-2.38071300	-3.29660600	2.14102300





Calculated Enthalpy: -1620.935150 Hartree

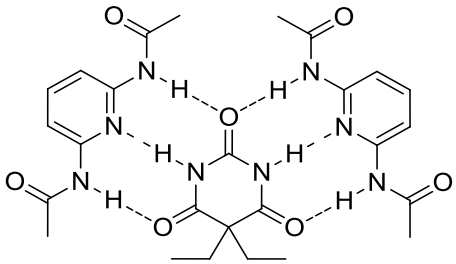
Zero Point Energy: 0.541042 Hartree

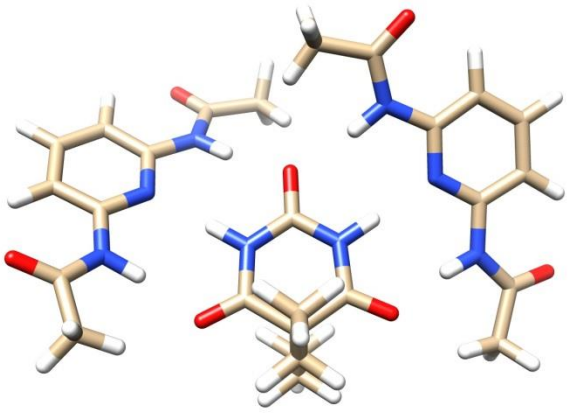
Lowest Frequency: 10.9 cm^{-1}

Coordinates:

Atom	x	y	z
C	-0.02893400	-2.61262200	-0.00292800
C	0.23463500	-3.98690100	-0.05611800
C	1.56610200	-4.38641500	-0.09516500
C	2.59002400	-3.44388100	-0.07901700
C	2.23108200	-2.09076900	-0.02559800
N	0.94552200	-1.68248100	0.00873800
H	1.80984800	-5.44354600	-0.13745400
H	-0.57563600	-4.70054500	-0.06840000
H	3.62959300	-3.73150100	-0.10424600
N	3.18516000	-1.05599900	-0.04717700
C	4.50867900	-1.14721900	0.34523600
H	2.84788500	-0.16248900	-0.40007300
O	4.98106900	-2.18147200	0.81316900
N	-1.34077700	-2.11307300	0.10309200
C	-2.48039200	-2.72926900	-0.37640000
H	-1.43854500	-1.17387800	0.49136900
O	-2.45121900	-3.73590900	-1.08656600
C	-3.78167900	-2.09770300	0.01930200
C	-4.86054100	-2.20130800	-0.87359400
C	-3.97330800	-1.48016900	1.26445700
C	-6.10579400	-1.67258200	-0.53635500
H	-4.70940800	-2.69841500	-1.82609100
C	-5.22683100	-0.96795700	1.60739800
H	-3.15721300	-1.41410300	1.97582200
C	-6.29171700	-1.05602500	0.70666800
H	-6.93174900	-1.74568700	-1.23753800

H	-5.37046100	-0.50402400	2.57857300
H	-7.26411400	-0.65226400	0.97335700
C	5.35966000	0.13142000	0.16039900
H	0.45344900	0.18481600	-0.09282500
N	0.16740500	1.17896600	-0.20905600
C	-1.03114100	1.57281600	0.34149300
C	1.03832200	1.97536400	-0.91932300
C	-1.49184100	3.01770400	0.15204500
O	-1.70979900	0.75901500	0.96160100
N	0.64719900	3.28654400	-1.10978600
O	2.10437100	1.54550600	-1.34811000
C	-0.51352100	3.88567100	-0.64128300
C	-2.85826800	3.00048200	-0.60839200
C	-1.70492000	3.66423800	1.55703000
H	1.29261200	3.87192900	-1.63125200
O	-0.72463200	5.06579800	-0.87011600
H	-3.55934600	2.44194600	0.01823400
H	-3.20587400	4.03671600	-0.65309400
H	-2.10849000	4.66586100	1.38395600
H	-2.47907400	3.07745600	2.05969100
C	-2.81955000	2.39882400	-2.01690500
H	-3.82122900	2.42285500	-2.45603200
H	-2.15697700	2.95927500	-2.68537600
H	-2.49312500	1.35335500	-2.00813600
C	-0.45539300	3.74852200	2.43973100
H	-0.71008600	4.21453000	3.39629600
H	-0.04007200	2.75912200	2.66036100
H	0.33189700	4.35692900	1.98122900
C	4.75173200	1.29913000	0.97301600
H	3.76461300	1.59212000	0.60726300
H	4.66720900	1.03857200	2.03357800
H	5.40496900	2.17471900	0.89238900
C	5.42697600	0.49729700	-1.34205700
H	6.08032600	1.36702600	-1.47252700
H	5.84686900	-0.32838300	-1.92677800
H	4.44822600	0.75195500	-1.75489100
C	6.78179700	-0.15071300	0.67538100
H	7.25086600	-0.96996100	0.12397900
H	7.39515900	0.74756600	0.54905800
H	6.77692200	-0.42076700	1.73494200





Calculated Enthalpy: -1975.591030 Hartree

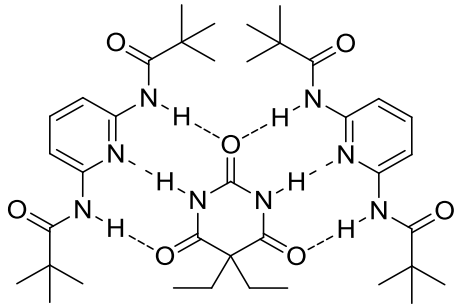
Zero Point Energy: 0.603281 Hartree

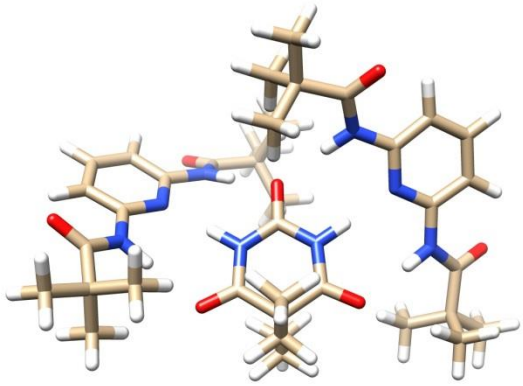
Lowest Frequency: 19.2 cm^{-1}

Coordinates:

Atom	x	y	z
C	4.91497100	0.20283400	-0.00252100
C	6.12666300	0.89974700	0.10149000
C	6.08249800	2.19260300	0.61390800
C	4.87539100	2.76603100	1.00264600
C	3.71542000	1.99511200	0.85068500
N	3.73110800	0.73938200	0.35903900
H	7.00202300	2.76141200	0.71274200
H	7.04891500	0.43293100	-0.20785400
H	4.81485600	3.76467700	1.40677000
N	2.43456200	2.47726300	1.17046600
C	2.10687700	3.58296100	1.92679300
H	1.65626000	1.94488500	0.78680600
O	2.93905600	4.32335300	2.44939600
N	4.83615000	-1.12340900	-0.45790800
C	5.80140300	-1.85347300	-1.11862700
H	3.96413100	-1.60988500	-0.25030900
O	6.90224300	-1.40265800	-1.43468300
C	5.40776600	-3.27896400	-1.45249700
C	0.61981100	3.82941100	2.08860600
H	0.39823300	4.84544200	1.75010400
H	0.37549700	3.77943900	3.15401200
H	-0.00521800	3.12086300	1.54322200
H	4.43253300	-3.56835100	-1.05900200
H	6.17435500	-3.95009400	-1.05525700
H	5.40659300	-3.39143300	-2.54114000
H	2.04840800	-0.29355700	0.16512300
N	1.16998800	-0.84567900	0.09212300
C	1.27618900	-2.22072800	0.07078600
C	-0.00001000	-0.12964500	0.00002100
C	-0.00001300	-3.05496500	-0.00007900
O	2.38531800	-2.74353900	0.11044200
N	-1.17001000	-0.84567300	-0.09211000

O	-0.00000800	1.10409700	0.00004500
C	-1.27621600	-2.22072200	-0.07083800
C	0.06725900	-3.96627400	-1.26923600
C	-0.06728500	-3.96645400	1.26894500
H	-2.04843200	-0.29354700	-0.16508200
O	-2.38534900	-2.74352600	-0.11048500
H	0.94813800	-4.60341800	-1.15027000
H	-0.81430200	-4.61276400	-1.23770000
H	-0.94815900	-4.60358800	1.14988300
H	0.81428000	-4.61293400	1.23732700
N	-3.73110400	0.73937400	-0.35898300
C	-3.71540300	1.99509600	-0.85064600
C	-4.91496100	0.20286300	0.00264500
C	-4.87535700	2.76605000	-1.00255100
N	-2.43454800	2.47719500	-1.17051500
C	-6.12663800	0.89981300	-0.10130300
N	-4.83615000	-1.12338300	0.45802400
C	-6.08246100	2.19266400	-0.61373500
H	-4.81481500	3.76468800	-1.40669400
C	-2.10686900	3.58282100	-1.92694800
H	-1.65624400	1.94483700	-0.78683400
H	-7.04888600	0.43302800	0.20809600
C	-5.80139300	-1.85343400	1.11877100
H	-3.96415200	-1.60987500	0.25037700
H	-7.00197300	2.76150100	-0.71252100
O	-2.93905200	4.32318400	-2.44958600
C	-0.61980200	3.82926700	-2.08876700
O	-6.90220900	-1.40259700	1.43487700
C	-5.40777600	-3.27894000	1.45260000
H	0.00523600	3.12023700	-1.54401900
H	-0.39808000	4.84500400	-1.74946000
H	-0.37564400	3.78014900	-3.15424300
H	-6.17438700	-3.95004700	1.05536200
H	-5.40657800	-3.39143500	2.54124000
H	-4.43255800	-3.56833700	1.05907300
C	0.12940100	-3.22886900	-2.61096600
H	0.17463700	-3.95485400	-3.42792600
H	-0.75475500	-2.60449600	-2.77884500
H	1.01772100	-2.59265900	-2.69072700
C	-0.12944300	-3.22923400	2.61077600
H	-0.17469500	-3.95533100	3.42763500
H	0.75471500	-2.60489000	2.77875300
H	-1.01776100	-2.59302900	2.69061000





Calculated Enthalpy: -2447.035754 Hartree

Zero Point Energy: 0.940410 Hartree

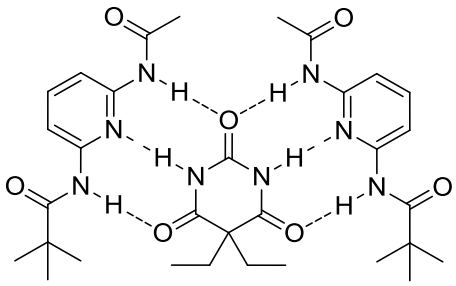
Lowest Frequency: 10.2 cm^{-1}

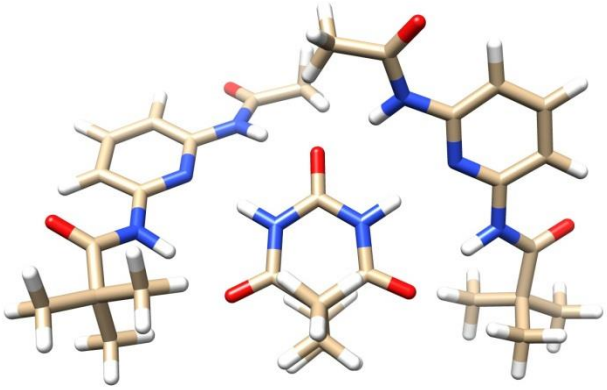
Coordinates:

Atom	x	y	z
C	4.75660400	0.38909400	0.72206700
C	5.88639500	1.14416800	1.06561800
C	5.69008300	2.29512100	1.82168700
C	4.41225800	2.67264900	2.22115400
C	3.34292900	1.85614100	1.83480200
N	3.50854300	0.74094400	1.09519200
H	6.54368100	2.90408100	2.10336600
H	6.86828300	0.83271200	0.74580500
H	4.23729400	3.55851400	2.81197100
N	2.00836100	2.17061600	2.16405500
C	1.58829200	2.88316200	3.27397900
H	1.30579500	1.82783600	1.51390200
O	2.38017200	3.29846500	4.11716800
N	4.84445700	-0.82082800	0.00702100
C	5.90211000	-1.24064200	-0.78205600
H	4.05431200	-1.45190700	0.12577800
O	6.87164900	-0.52027300	-1.01012300
C	5.79256100	-2.67072800	-1.36045700
C	0.06384900	3.11666100	3.39806700
C	7.06247700	-2.96621400	-2.17741800
H	7.96114400	-2.89922100	-1.55819100
H	6.99904600	-3.97979500	-2.58697200
H	7.17602100	-2.26479700	-3.00842200
C	4.56101800	-2.76970700	-2.29039400
H	3.62259400	-2.62903200	-1.74960900
H	4.61543300	-2.02878200	-3.09520100
H	4.53127100	-3.76412400	-2.74871600
C	5.68040100	-3.69520000	-0.20568200
H	5.67220800	-4.70862400	-0.62152200
H	6.53760600	-3.61758300	0.47192500
H	4.76519700	-3.56989400	0.37770200

C	-0.19736300	3.97199700	4.65034400
H	0.30128000	4.94271000	4.58116900
H	-1.27414300	4.14299200	4.75172700
H	0.16169100	3.47593400	5.55577400
C	-0.46381300	3.86761100	2.15319300
H	-1.52531000	4.09844700	2.29350300
H	0.06936700	4.81352400	2.00943200
H	-0.37370500	3.27730900	1.23852600
C	-0.66219800	1.75925600	3.55589700
H	-0.55760100	1.12572400	2.67155800
H	-0.28220500	1.20811400	4.42264500
H	-1.73214900	1.93526300	3.70960200
H	1.98508200	-0.28400400	0.53520800
N	1.13588700	-0.83884200	0.29275000
C	1.25440300	-2.21175300	0.25427100
C	0.00002200	-0.12333600	0.00001500
C	-0.00005200	-3.04840400	0.00041700
O	2.35294900	-2.72746800	0.43406000
N	-1.13587400	-0.83886700	-0.29252500
O	0.00005600	1.11044400	-0.00015000
C	-1.25446200	-2.21176600	-0.25368000
C	0.23827000	-3.95991200	-1.24653400
C	-0.23841500	-3.95952500	1.24765100
H	-1.98504400	-0.28405800	-0.53512800
O	-2.35303200	-2.72747000	-0.43333300
H	1.12322700	-4.56396000	-1.02717100
H	-0.61751300	-4.63823200	-1.30873500
H	-1.12348200	-4.56350100	1.02853400
H	0.61727200	-4.63795500	1.30997200
N	-3.50849700	0.74086400	-1.09527900
C	-3.34274400	1.85601400	-1.83492500
C	-4.75659500	0.38924300	-0.72205000
C	-4.41195700	2.67271300	-2.22119600
N	-2.00814400	2.17026900	-2.16428900
C	-5.88627800	1.14450900	-1.06553000
N	-4.84460100	-0.82063800	-0.00695800
C	-5.68981800	2.29541900	-1.82162800
H	-4.23688500	3.55854500	-2.81203100
C	-1.58806100	2.88252000	-3.27439500
H	-1.30558900	1.82752800	-1.51409800
H	-6.86819500	0.83323200	-0.74563100
C	-5.90237700	-1.24037000	0.78199500
H	-4.05444500	-1.45173500	-0.12554300
H	-6.54333000	2.90453000	-2.10324100
O	-2.37992500	3.29758100	-4.11772100
C	-0.06358800	3.11570000	-3.39869400
O	-6.87193200	-0.51995900	1.00986500
C	-5.79295400	-2.67041600	1.36052200
C	0.19763000	3.97106300	-4.65095200
C	0.66214800	1.75814900	-3.55671500
C	0.46440800	3.86645100	-2.15384600

C	-7.06303000	-2.96581700	2.17726400
C	-5.68058500	-3.69498400	0.20585700
C	-4.56159600	-2.76932900	2.29071700
H	-0.30076600	4.94189300	-4.58162400
H	1.27443600	4.14180400	-4.75249400
H	-0.16168700	3.47515900	-5.55636400
H	0.55753600	1.12458500	-2.67240300
H	0.28191100	1.20714600	-4.42344400
H	1.73211500	1.93393600	-3.71056000
H	1.52593100	4.09707600	-2.29429800
H	-0.06855400	4.81246400	-2.00993700
H	0.37430800	3.27609900	-1.23920800
H	-7.96157600	-2.89888600	1.55785500
H	-6.99968000	-3.97935400	2.58693700
H	-7.17673300	-2.26431100	3.00817200
H	-5.67249000	-4.70837500	0.62177900
H	-6.53765500	-3.61741200	-0.47192800
H	-4.76526700	-3.56974600	-0.37736200
H	-3.62306200	-2.62869500	1.75011200
H	-4.61618000	-2.02834800	3.09546000
H	-4.53194800	-3.76371500	2.74911300
C	-0.41831800	-3.22310700	2.57910900
H	-0.60706100	-3.94618500	3.37802100
H	0.47525700	-2.65506900	2.85852000
H	-1.26867500	-2.53318500	2.55744900
C	0.41839900	-3.22389300	-2.57818100
H	0.60712700	-3.94721700	-3.37687300
H	-0.47507800	-2.65582000	-2.85783600
H	1.26884100	-2.53407200	-2.55663400





Calculated Enthalpy: -2211.313713 Hartree

Zero Point Energy: 0.771756 Hartree

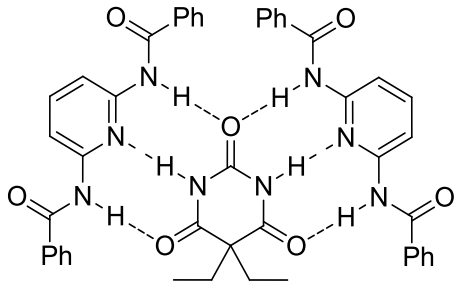
Lowest Frequency: 8.2 cm^{-1}

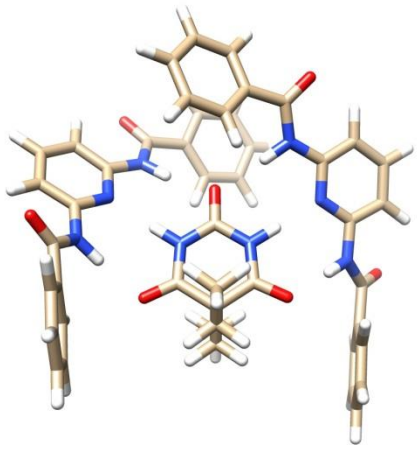
Coordinates:

Atom	x	y	z
C	3.50860400	2.29305500	1.62136000

C	4.59811200	2.96126800	2.19367200
C	5.86535300	2.43033200	1.97078800
C	6.03101000	1.28129900	1.20517400
C	4.88129000	0.67948000	0.67486500
N	3.64339600	1.17271700	0.88070200
H	6.73457600	2.91922000	2.40007400
H	4.44132700	3.85111600	2.78344800
H	7.00468300	0.85701600	1.01578700
N	4.93399100	-0.50833400	-0.07873000
C	6.01705500	-0.97794500	-0.80102200
H	4.08111100	-1.06440900	-0.07314400
O	7.07008300	-0.34875400	-0.88172800
N	2.18591000	2.75406800	1.74239100
C	1.69147200	3.70081000	2.61539600
H	1.51617000	2.34791000	1.09197000
O	2.37666500	4.27082100	3.46371800
C	5.82424200	-2.34399500	-1.50081300
C	5.58524300	-3.44123600	-0.43548500
H	4.65945500	-3.28597700	0.12312400
H	5.51629100	-4.41604900	-0.93064300
H	6.41762600	-3.48363000	0.27527400
C	7.10421500	-2.67362100	-2.28815800
H	6.98292900	-3.64261200	-2.78354600
H	7.30964000	-1.91863300	-3.05212900
H	7.97490100	-2.72834200	-1.62955500
C	4.63152300	-2.27816300	-2.48363200
H	4.76977500	-1.47766100	-3.21848200
H	4.55847000	-3.22573900	-3.02827900
H	3.67838800	-2.12055800	-1.97299100
C	0.21582800	4.00892100	2.45547700
H	0.11495000	5.03825300	2.09628700
H	-0.29939400	3.33958800	1.76497800
H	-0.25760100	3.95789000	3.43933800
H	2.03080600	0.19179400	0.33222100
N	1.16076000	-0.35439600	0.16739100
C	1.27123700	-1.72920000	0.13783200
C	0.00004900	0.36122500	0.00002700
C	-0.00003500	-2.56478100	0.00018300
O	2.37924600	-2.24638300	0.22907100
N	-1.16070200	-0.35434700	-0.16727200
O	0.00008300	1.59597100	-0.00002500
C	-1.27126100	-1.72913800	-0.13748800
C	0.12682200	-3.47687100	-1.26336000
C	-0.12693800	-3.47684200	1.26373200
H	-2.03072200	0.19186700	-0.33214900
O	-2.37930900	-2.24626400	-0.22857700
H	1.02086300	-4.08954200	-1.11723100
H	-0.73771000	-4.14674300	-1.25481400
H	-1.02099500	-4.08949000	1.11760700
H	0.73757500	-4.14673900	1.25521700
N	-3.64330300	1.17285000	-0.88067100

C	-3.50843400	2.29320700	-1.62129000
C	-4.88123600	0.67969900	-0.67484400
C	-4.59789500	2.96152600	-2.19356600
N	-2.18571200	2.75413300	-1.74234000
C	-6.03091600	1.28163900	-1.20510900
N	-4.93402100	-0.50815200	0.07868300
C	-5.86517600	2.43068700	-1.97068100
H	-4.44104600	3.85138000	-2.78331700
C	-1.69124600	3.70087000	-2.61533600
H	-1.51597200	2.34791900	-1.09195100
H	-7.00462000	0.85743300	-1.01572000
C	-6.01718100	-0.97784700	0.80078000
H	-4.08115300	-1.06425000	0.07312800
H	-6.73436600	2.91966200	-2.39993400
O	-2.37643800	4.27094800	-3.46361500
C	-0.21558300	4.00891100	-2.45545300
O	-7.07020900	-0.34865100	0.88144700
C	-5.82448200	-2.34399300	1.50041500
H	-0.11465000	5.03823700	-2.09625900
H	0.29962800	3.33955000	-1.76497500
H	0.25781500	3.95786900	-3.43932800
C	-5.58509700	-3.44107000	0.43500300
C	-7.10466100	-2.67381500	2.28734100
C	-4.63204900	-2.27820700	2.48359000
H	-4.65907300	-3.28574900	-0.12319300
H	-5.51637600	-4.41596400	0.93003200
H	-6.41719700	-3.48332400	-0.27609600
H	-6.98344800	-3.64286100	2.78264000
H	-7.31036800	-1.91893900	3.05134600
H	-7.97514800	-2.72851600	1.62847200
H	-4.77060100	-1.47784200	3.21853300
H	-4.55905700	-3.22586500	3.02810400
H	-3.67878300	-2.12041400	1.97325100
C	0.20527800	-2.74179800	-2.60537500
H	0.30908300	-3.46752700	-3.41725800
H	-0.69746400	-2.15529500	-2.80653800
H	1.06841400	-2.06941500	-2.65760600
C	-0.20539800	-2.74172700	2.60572400
H	-0.30921500	-3.46742400	3.41763300
H	0.69734600	-2.15522200	2.80687200
H	-1.06853300	-2.06933900	2.65791900





Calculated Enthalpy: -2743.17543424 Hartree

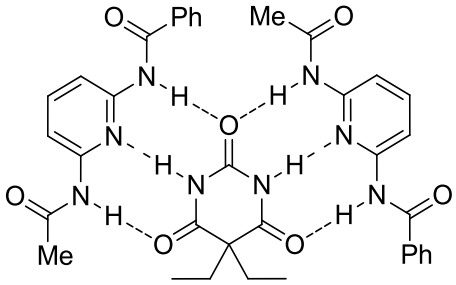
Lowest Frequency: 11.8 cm^{-1} (6-31g(d))

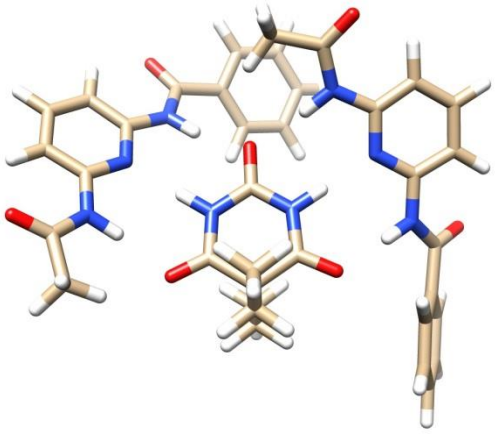
Coordinates:

Atom	x	y	z
C	4.69163300	-0.33888700	-0.95956900
C	5.86599000	-1.06098100	-1.20673400
C	5.73476700	-2.35810400	-1.68851500
C	4.47582700	-2.91013200	-1.91228800
C	3.35768400	-2.11131700	-1.63811700
N	3.46413000	-0.84836000	-1.17014600
H	6.62230700	-2.94864200	-1.89412900
H	6.83251300	-0.61543400	-1.02368800
H	4.34495800	-3.91589600	-2.27889200
N	2.03550300	-2.55528200	-1.81112900
C	1.60794200	-3.71272000	-2.43119100
H	1.32810900	-2.01595000	-1.31402800
O	2.37228600	-4.57094300	-2.87624700
N	4.72829600	0.99848600	-0.51948600
C	5.70994900	1.54993500	0.28184000
H	3.90719500	1.56901300	-0.72555800
O	6.60459000	0.88067200	0.80123600
C	5.62811800	3.03194900	0.49436900
C	6.10498500	3.54646100	1.71095200
C	5.16386500	3.91393600	-0.49304500
C	6.09444400	4.92064600	1.94581400
H	6.48046800	2.85938400	2.46196900
C	5.17223000	5.29166600	-0.26235700
H	4.81476200	3.53506900	-1.44752700
C	5.62981300	5.79668800	0.95776400
H	6.45386000	5.30955800	2.89385300
H	4.82490800	5.96834300	-1.03727500
H	5.63093300	6.86797300	1.13660600
C	0.12019900	-3.87356500	-2.54508400
C	-0.74860600	-2.79266300	-2.75869600
C	-0.40047900	-5.17646500	-2.49852000
C	-2.11932100	-3.01266500	-2.91275900
H	-0.35989800	-1.78250300	-2.83436300
C	-1.77149200	-5.39216500	-2.63393600

H	0.27881400	-6.00946200	-2.35151600
C	-2.63404300	-4.31009600	-2.84256200
H	-2.78320900	-2.17216200	-3.09125400
H	-2.16712300	-6.40192400	-2.58005300
H	-3.70110900	-4.47804900	-2.95444600
H	1.92275100	0.21427600	-0.71823600
N	1.09185600	0.77341400	-0.43091700
C	1.19085200	2.14691600	-0.46903500
C	0.00001600	0.05694900	0.00002300
C	-0.00000100	2.98152200	0.00003800
O	2.22695200	2.66921400	-0.86835200
N	-1.09182800	0.77339800	0.43097600
O	0.00002400	-1.17501800	0.00002300
C	-1.19085400	2.14689900	0.46907400
C	0.46544400	3.89264700	1.18161900
C	-0.46544000	3.89271300	-1.18149400
H	-1.92274200	0.21424900	0.71824100
O	-2.22698100	2.66917600	0.86835000
H	1.25969700	4.53426600	0.79005800
H	-0.38351100	4.53414800	1.43494500
H	-1.25967500	4.53432900	-0.78989300
H	0.38352400	4.53420700	-1.43480300
N	-3.46411400	-0.84837300	1.16996300
C	-4.69161400	-0.33894000	0.95926600
C	-3.35766600	-2.11134300	1.63789700
C	-5.86596900	-1.06109800	1.20626500
N	-4.72827300	0.99845000	0.51924200
C	-4.47580600	-2.91021300	1.91191700
N	-2.03548400	-2.55524800	1.81105800
C	-5.73474300	-2.35823200	1.68801700
H	-6.83249000	-0.61558800	1.02312000
C	-5.70993400	1.54996200	-0.28202800
H	-3.90717900	1.56897100	0.72537000
H	-4.34493600	-3.91598200	2.27850800
C	-1.60794000	-3.71266700	2.43116800
H	-1.32806600	-2.01590500	1.31400200
H	-6.62228200	-2.94881400	1.89350700
O	-6.60457300	0.88073700	-0.80147700
C	-5.62811800	3.03199600	-0.49443800
O	-2.37229000	-4.57094900	2.87609900
C	-0.12020100	-3.87341900	2.54525900
C	-6.10500500	3.54660100	-1.71097400
C	-5.16386900	3.91390900	0.49304500
C	0.74849500	-2.79246300	2.75904500
C	0.40057700	-5.17628000	2.49872300
C	-6.09448600	4.92080600	-1.94572200
H	-6.48048700	2.85958200	-2.46204300
C	-5.17225500	5.29165700	0.26247000
H	-4.81475400	3.53496900	1.44749300
C	2.11920200	-3.01237200	2.91330300
H	0.35970100	-1.78233500	2.83470500

C	1.77158500	-5.39188700	2.63433100
H	-0.27863700	-6.00931800	2.35158900
C	-5.62985800	5.79677300	-0.95760500
H	-6.45391800	5.30979200	-2.89372500
H	-4.82493600	5.96827500	1.03744100
C	2.63402700	-4.30976300	2.84312800
H	2.78300300	-2.17183000	3.09193800
H	2.16729700	-6.40161500	2.58046700
H	-5.63099400	6.86807300	-1.13635900
H	3.70108900	-4.47764500	2.95516500
C	-0.95723800	3.15603800	-2.43194500
H	-1.25808800	3.88264000	-3.19238000
H	-0.17643400	2.52712900	-2.87355900
H	-1.82852800	2.52607800	-2.22253800
C	0.95721000	3.15590800	2.43204500
H	1.82849200	2.52594200	2.22262300
H	1.25806100	3.88247100	3.19251700
H	0.17638900	2.52699300	2.87362000





Calculated Enthalpy: -2359.68515203 Hartree

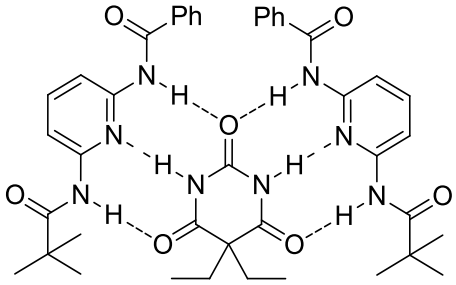
Lowest Frequency: 14.5 cm^{-1} (6-31g(d))

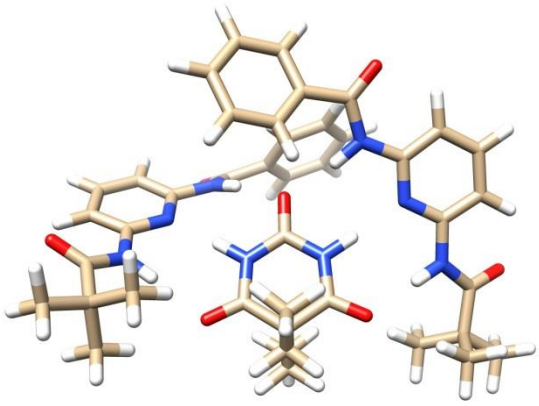
Coordinates:

Atom	x	y	z
C	-4.61035400	-0.76675100	0.76200200
C	-5.93706000	-1.21174000	0.84636400
C	-6.94101200	-0.30243100	0.52660600
C	-6.63249900	0.99825900	0.14286700
C	-5.27708500	1.35352600	0.09372000
N	-4.28444900	0.48884700	0.38892300
H	-7.98004400	-0.61329600	0.57828000
H	-6.15101000	-2.22534700	1.14622600
H	-7.39181700	1.72150700	-0.11019000
N	-4.84220800	2.64790500	-0.23637400
C	-5.58270600	3.68725300	-0.76105000
H	-3.86247700	2.85057600	-0.03914400
O	-6.77553900	3.59896400	-1.05120200
N	-3.50819900	-1.58999700	1.05231300
C	-3.51542000	-2.84927000	1.61931000

H	-2.61063500	-1.24952900	0.71393900
O	-4.54399200	-3.47848500	1.87317500
C	-2.16425500	-3.42805300	1.92295900
C	-2.01691700	-4.82155200	1.83491700
C	-1.07866800	-2.64687300	2.34767700
C	-0.79493400	-5.42096400	2.13828400
H	-2.86599100	-5.42194700	1.52573300
C	0.13869500	-3.25133000	2.66975800
H	-1.18466400	-1.57245900	2.45670500
C	0.28570100	-4.63659900	2.55702600
H	-0.68576100	-6.49790700	2.05295200
H	0.96938100	-2.64157400	3.01202000
H	1.23541300	-5.10366900	2.80040900
C	-4.81621600	4.97822400	-0.97111300
H	-3.77505600	4.92909600	-0.65045100
H	-4.85747200	5.23490300	-2.03397700
H	-5.32811000	5.77442100	-0.42281800
H	-2.40453400	1.04386300	0.09290800
N	-1.41596600	1.32068200	-0.06978600
C	-1.10070100	2.66119300	-0.02807700
C	-0.54237400	0.29726200	-0.35716700
C	0.35047300	3.07894200	-0.25130300
O	-1.98359300	3.48485200	0.19211300
N	0.76869100	0.63523600	-0.58906400
O	-0.92605400	-0.87342100	-0.39965100
C	1.28742700	1.91217100	-0.55956000
C	0.40625400	4.09085900	-1.43939800
C	0.85900300	3.79054300	1.04595300
H	1.42239100	-0.14769000	-0.80305100
O	2.48274500	2.08569400	-0.77195500
H	-0.20915700	4.94829900	-1.15271000
H	1.44146200	4.43655200	-1.50958800
H	1.87667400	4.13200400	0.83693600
H	0.23304300	4.67672100	1.18393200
N	2.63457300	-1.59113600	-1.24747600
C	3.95511400	-1.47917100	-1.01298400
C	2.17931000	-2.70464800	-1.86040100
C	4.87689000	-2.46701600	-1.38064800
N	4.36506000	-0.27254300	-0.41287900
C	3.02522800	-3.74324800	-2.26937500
N	0.78467600	-2.74939700	-2.02035700
C	4.38746600	-3.60272700	-2.01682500
H	5.92884900	-2.33940300	-1.17228400
C	5.44342100	-0.13354000	0.43910700
H	3.75061900	0.53088000	-0.54840600
H	2.61763400	-4.61309900	-2.76107500
C	0.05052300	-3.58874100	-2.83120100
H	0.25454300	-2.09656000	-1.44500000
H	5.07340200	-4.38757000	-2.32036200
O	6.09871500	-1.09380000	0.84779500
C	5.78069500	1.26661000	0.85760000

O	0.55393400	-4.42808200	-3.57742000
C	-1.45178600	-3.40829800	-2.74402500
C	6.38930400	1.44125800	2.11135300
C	5.57571200	2.38073600	0.02965200
H	-1.75693300	-2.56740300	-2.11947000
H	-1.84383100	-3.27483100	-3.75589100
H	-1.88763400	-4.32810100	-2.34169800
C	6.76438700	2.71331000	2.54105100
H	6.56290500	0.57159100	2.73618700
C	5.96790100	3.65212200	0.45607900
H	5.13104900	2.26301500	-0.95214500
C	6.55565800	3.82210200	1.71259900
H	7.22391100	2.84041300	3.51667200
H	5.81838300	4.50719000	-0.19626800
H	6.85621700	4.81218100	2.04287100
C	-0.05598200	3.54048000	-2.79282600
H	0.01762400	4.32288000	-3.55388800
H	0.56263900	2.70109500	-3.12832900
H	-1.09955100	3.20805400	-2.76795400
C	0.84247800	2.93358800	2.31603000
H	1.22659100	3.51612700	3.15842500
H	-0.16991900	2.60889700	2.57981000
H	1.47488200	2.04422600	2.22101700





Calculated Enthalpy: -2595.57582733 Hartree

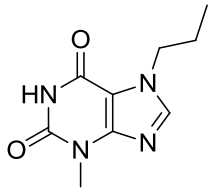
Lowest Frequency: 10.1 cm^{-1} (6-31g(d))

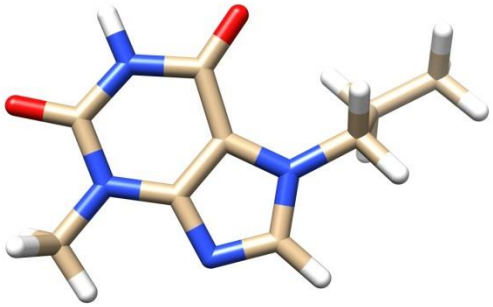
Coordinates:

Atom	x	y	z
C	-3.25669300	-1.66755400	1.93535400
C	-4.27476200	-2.39693300	2.56020900
C	-5.58306800	-1.96010000	2.38258000
C	-5.85519900	-0.83628100	1.60753400
C	-4.77189700	-0.16866600	1.02177300
N	-3.49587300	-0.57662100	1.18306200
H	-6.39993400	-2.50000400	2.85148700
H	-4.03963100	-3.26558000	3.15747400
H	-6.86199000	-0.47984700	1.45441800
N	-4.92877100	1.00520200	0.26096200

C	-6.07132700	1.40812400	-0.40670800
H	-4.11277700	1.61406600	0.23217800
O	-7.08565500	0.71415800	-0.44131800
N	-1.90872100	-2.06713100	2.01423900
C	-1.32550400	-2.71332400	3.08755300
H	-1.29948000	-1.76503300	1.25485000
O	-1.90980200	-2.89538100	4.15676200
C	0.08151300	-3.18604700	2.87961500
C	0.54744200	-3.64829500	1.63947000
C	0.93244600	-3.22511200	3.99584700
C	1.85068000	-4.13621600	1.51839200
H	-0.10681000	-3.65236700	0.77399800
C	2.23894600	-3.69484800	3.86767000
H	0.55772400	-2.88438400	4.95529200
C	2.70000600	-4.15323000	2.62811300
H	2.20068600	-4.50508600	0.55914700
H	2.89561400	-3.70914600	4.73235900
H	3.71512400	-4.52630300	2.52916800
C	-5.99637200	2.78481200	-1.10746400
C	-5.76334200	3.89148300	-0.05058700
H	-4.80014900	3.78966600	0.45473900
H	-5.77950600	4.86998200	-0.54288600
H	-6.55561200	3.88297200	0.70569900
C	-7.33351200	3.04151800	-1.82388500
H	-7.29340700	4.01449300	-2.32469800
H	-7.53835300	2.27393200	-2.57532700
H	-8.16896700	3.04960300	-1.11883800
C	-4.85495900	2.79036800	-2.15162500
H	-4.98849400	1.98887200	-2.88639400
H	-4.86071000	3.74412400	-2.69027600
H	-3.86978400	2.68055900	-1.69134500
H	-2.00569700	0.43562900	0.52008800
N	-1.17369200	1.00992300	0.26514600
C	-1.32974200	2.37844400	0.22857500
C	-0.01892100	0.32534400	-0.03073400
C	-0.10123000	3.25020600	-0.02866600
O	-2.44058700	2.86542100	0.41507400
N	1.09706500	1.07538300	-0.32355300
O	0.01768600	-0.90587200	-0.04443600
C	1.17025500	2.45070700	-0.31208900
C	-0.38092000	4.18114400	-1.25060200
C	0.13559500	4.13929800	1.23652300
H	1.96218600	0.54752700	-0.55540700
O	2.24525200	2.99982800	-0.53095500
H	-1.26764400	4.77013600	-0.99994000
H	0.46466600	4.87109000	-1.32206600
H	0.99783300	4.77436900	1.01413300
H	-0.73864400	4.78989800	1.33063300
N	3.55654300	-0.45722300	-1.14158200
C	3.42539400	-1.63189000	-1.79566500
C	4.79676200	0.02183500	-0.91597400

C	4.52360600	-2.37424600	-2.24975300
N	2.09482700	-2.04910600	-1.98322400
C	5.95379200	-0.64926500	-1.33888300
N	4.85030800	1.26737600	-0.26161300
C	5.79246300	-1.85463300	-2.01099500
H	4.37128400	-3.31108300	-2.76145900
C	1.64098700	-3.13520400	-2.70581100
H	1.40061200	-1.56339600	-1.41824300
H	6.92847100	-0.23335600	-1.13901300
C	5.93514600	1.79668900	0.41863200
H	3.99886100	1.82360600	-0.31134000
H	6.66709200	-2.39864600	-2.35451300
O	2.38201700	-3.96930500	-3.22918300
C	0.14984700	-3.24910000	-2.83312900
O	6.98361800	1.17164900	0.56306700
C	5.75159400	3.22191500	0.99119100
C	-0.40746800	-4.53661600	-2.88598800
C	-0.68493500	-2.13115400	-2.97898500
C	5.44750800	4.21553400	-0.15552600
C	7.05940900	3.64088800	1.68541700
C	4.60696900	3.22742200	2.03172700
C	-1.78237900	-4.70198000	-3.05065500
H	0.24615100	-5.39794600	-2.79634600
C	-2.05904300	-2.29937300	-3.16424100
H	-0.26333200	-1.13140800	-2.98077600
H	4.49877200	4.00485400	-0.65372300
H	5.38917400	5.23030500	0.25323600
H	6.24584000	4.20180000	-0.90546200
H	6.93953700	4.64767200	2.09903200
H	7.31593300	2.95998700	2.50139300
H	7.89824300	3.65355000	0.98418700
H	4.80157400	2.50801500	2.83445700
H	4.53135400	4.22289000	2.48264800
H	3.63817600	2.99495300	1.58417100
C	-2.61112800	-3.58308400	-3.19176100
H	-2.20700200	-5.70101300	-3.07528800
H	-2.69629300	-1.42968400	-3.29271100
H	-3.68066800	-3.71176600	-3.32900000
C	0.36376900	3.37885200	2.54705000
H	0.54074400	4.09008100	3.35915500
H	-0.50454800	2.77358700	2.82790100
H	1.23680400	2.71933400	2.49633800
C	-0.58551500	3.46554100	-2.58990900
H	-0.79361200	4.20002900	-3.37346200
H	0.30446200	2.90569300	-2.89667800
H	-1.43315800	2.77233200	-2.56068600





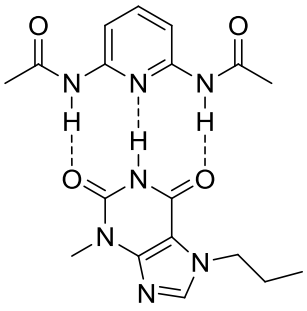
Calculated Enthalpy: -719.536629 Hartree

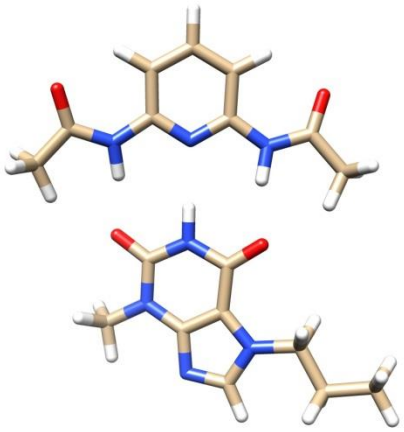
Zero Point Energy: 0.217365 Hartree

Lowest Frequency: 45.1 cm^{-1}

Coordinates:

Atom	x	y	z
N	-0.52789100	2.20072800	-0.07571800
C	0.78805000	2.10607000	-0.28191200
H	1.45751800	2.95121100	-0.36428300
N	1.23180400	0.83273500	-0.38972800
C	0.11040000	0.02810600	-0.23382700
C	-0.07062100	-1.39221000	-0.27411300
O	0.77733700	-2.27049400	-0.45026500
N	-1.42348600	-1.71821000	-0.07768700
H	-1.64980200	-2.70665600	-0.08971700
C	-2.51959800	-0.87758800	0.11992800
N	-2.24698200	0.47851700	0.13371500
C	-0.94667600	0.90995300	-0.04669200
C	2.62556000	0.40083300	-0.56611200
H	2.63311300	-0.40126000	-1.30778700
H	3.16647300	1.25533300	-0.98264500
O	-3.65390100	-1.32915900	0.27132100
C	-3.35579500	1.41761400	0.33219600
H	-4.08086000	1.31810300	-0.47853200
H	-3.85341900	1.20934500	1.28136800
H	-2.94338800	2.42438700	0.34001400
C	3.27450400	-0.06816900	0.74093500
H	2.69619000	-0.90680700	1.14287200
H	3.22594600	0.74468300	1.47575600
C	4.72979300	-0.49566300	0.52195400
H	5.18147700	-0.82388800	1.46297000
H	4.79628700	-1.32773600	-0.18780600
H	5.33516500	0.33043600	0.13112900





Calculated Enthalpy: -1383.747148 Hartree

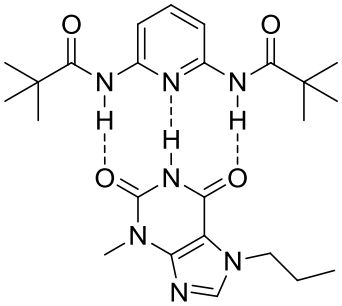
Zero Point Energy: 0.417397 Hartree

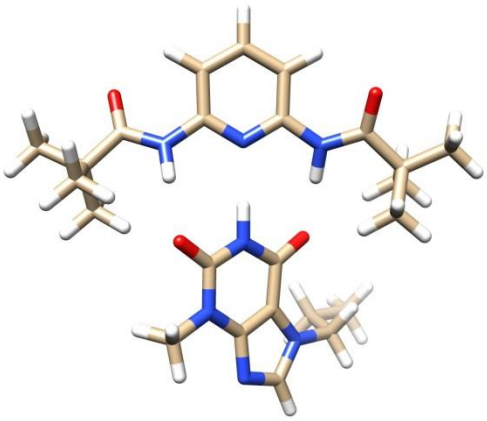
Lowest Frequency: 11.4 cm^{-1}

Coordinates:

Atom	x	y	z
N	3.85245300	-2.66997800	-0.27812800
C	4.64968400	-1.62578600	-0.02988000
H	5.72513800	-1.69272200	0.02655000
N	3.98303100	-0.46126400	0.14661800
C	2.63702400	-0.77581000	0.00298300
C	1.44697400	0.01025100	0.06677100
O	1.34345800	1.22924400	0.27487000
N	0.30889900	-0.77084400	-0.14602200
H	-0.59939300	-0.28168700	-0.10590300
C	0.23298600	-2.13126800	-0.40073200
N	1.42319800	-2.82304000	-0.46390800
C	2.60601000	-2.14041700	-0.25715500
C	4.52644300	0.87978800	0.44039000
H	4.14917400	1.55880100	-0.32921300
H	4.10423100	1.20325600	1.39650200
O	-0.86058100	-2.68796100	-0.56248300
C	1.39521400	-4.26554800	-0.73361900
H	0.86183900	-4.78471000	0.06540000
H	0.88976600	-4.45424600	-1.68234000
H	2.42440200	-4.61478600	-0.78220900
C	6.05229700	0.92213900	0.48904700
H	6.46519100	0.57777800	-0.46666000
H	6.42084000	0.24340000	1.26728000
C	6.54855700	2.34452200	0.77686100
H	7.64153100	2.36896800	0.81154900
H	6.22204100	3.04446400	0.00003500
H	6.17465000	2.71004400	1.73949500
N	-2.40211200	0.70950500	0.00060000
C	-3.55602200	0.02498000	0.14068800

C	-2.45299700	2.05600000	-0.05966600
C	-4.80616600	0.65505200	0.23044400
N	-3.40477800	-1.37132900	0.16618300
C	-3.65561100	2.77412300	0.01427300
N	-1.20030600	2.68151400	-0.17921000
C	-4.83080300	2.04433700	0.16255500
H	-5.70278100	0.06691900	0.34846600
C	-4.35330500	-2.32256400	0.47290700
H	-2.47814300	-1.72431900	-0.08325400
H	-3.64857000	3.85124700	-0.04314500
C	-0.93682500	4.00621300	-0.45063800
H	-0.38485100	2.08111900	-0.03504800
H	-5.78075000	2.56664400	0.22649700
O	-5.51180900	-2.05794800	0.79917300
C	-3.87407900	-3.75853300	0.38677900
O	-1.80830000	4.85550700	-0.64523200
C	0.53417100	4.37018800	-0.50786600
H	-2.82759700	-3.85462900	0.09695700
H	-4.50232900	-4.28702100	-0.33668600
H	-4.02937600	-4.23201600	1.36084100
H	0.71256900	5.18973000	0.19435700
H	0.75600300	4.74619300	-1.51155700
H	1.20026800	3.53889400	-0.27631300





Calculated Enthalpy: -1619.471342 Hartree

Zero Point Energy: 0.586121 Hartree

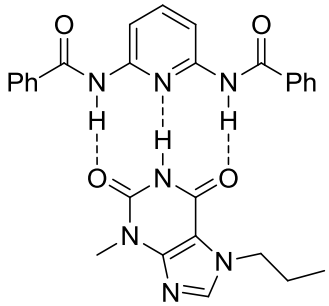
Lowest Frequency: 12.2 cm^{-1}

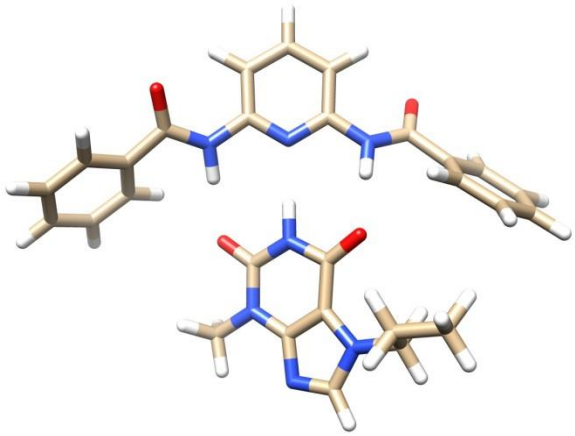
Coordinates:

Atom	x	y	z
N	-1.93065900	4.42767100	1.08279200
C	-3.08040900	4.17867700	0.45104700
H	-3.90125100	4.87847000	0.37515500
N	-3.14383900	2.94496400	-0.10060400
C	-1.92654400	2.34086000	0.18661900

C	-1.40096700	1.03804500	-0.07676100
O	-1.95227100	0.09150200	-0.66076400
N	-0.11156400	0.89748600	0.43537600
H	0.35471300	-0.01482200	0.27105500
C	0.64105700	1.81879400	1.14417700
N	0.05261900	3.03939400	1.40408300
C	-1.21641600	3.28654300	0.91780600
C	-4.24648100	2.40207000	-0.90734800
H	-4.41378500	1.37029600	-0.59001000
H	-5.13561000	2.98484400	-0.65072000
O	1.79050400	1.54750100	1.51472700
C	0.80334600	4.04633200	2.16297200
H	1.12878600	3.62195500	3.11400400
H	1.68023600	4.36800500	1.59681400
H	0.14297500	4.89328500	2.33686400
C	-3.97044600	2.46622000	-2.41375000
H	-3.06763200	1.88698100	-2.63554400
H	-3.76770900	3.50669700	-2.69533400
C	-5.15196100	1.92131200	-3.22342200
H	-4.94101700	1.97274700	-4.29576500
H	-5.35528400	0.87404900	-2.97363100
H	-6.06548100	2.49691500	-3.03455300
N	1.21945500	-1.71670400	-0.05884200
C	2.54598600	-1.78457000	-0.29047200
C	0.49313700	-2.85126800	-0.09096600
C	3.20152300	-2.99320800	-0.56288300
N	3.23120700	-0.55761400	-0.19227400
C	1.06171100	-4.10266600	-0.36237000
N	-0.89004400	-2.68449900	0.12500800
C	2.43219000	-4.15192300	-0.59646700
H	4.26487200	-3.00912900	-0.74384300
C	4.45668300	-0.25428000	-0.75623900
H	2.76013400	0.16037600	0.35986700
H	0.44747100	-4.98936600	-0.38146500
C	-1.76075000	-3.64669100	0.60108200
H	-1.26006400	-1.75954900	-0.09914400
H	2.90704800	-5.10531700	-0.80782200
O	5.06360800	-1.05100300	-1.47101400
C	5.02274500	1.15103700	-0.44147700
O	-1.37823100	-4.76836200	0.93215500
C	-3.24925300	-3.23377600	0.69778800
C	6.40246800	1.28405100	-1.10996100
H	6.33533800	1.16719300	-2.19495500
H	6.81221600	2.27621800	-0.89316400
H	7.10265300	0.53229700	-0.73527500
C	4.08049300	2.23642900	-1.01473000
H	4.52261700	3.22486600	-0.84743500
H	3.94388600	2.10697300	-2.09391000
H	3.09963200	2.22775100	-0.53435100
C	5.18208200	1.32489400	1.08777900
H	4.22543500	1.29720500	1.61380100

H	5.83220700	0.54712500	1.50338300
H	5.64678500	2.29546100	1.29418500
C	-3.40812600	-2.05347400	1.68556000
H	-3.00681400	-2.30989900	2.67204300
H	-2.91179000	-1.14726300	1.33141900
H	-4.47264800	-1.82337600	1.80555900
C	-4.05608800	-4.43497200	1.22121000
H	-5.11211800	-4.15434500	1.29560100
H	-3.97373900	-5.29502800	0.55097700
H	-3.71097100	-4.74874700	2.21013100
C	-3.77584000	-2.83997000	-0.70280100
H	-3.64840300	-3.66315300	-1.41441900
H	-4.84683700	-2.61791800	-0.63616100
H	-3.27578800	-1.95456300	-1.10130800





Calculated Enthalpy: -1767.132706 Hartree

Zero Point Energy: 0.523436 Hartree

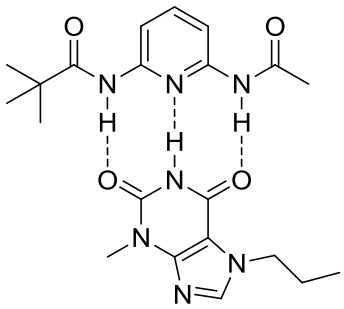
Lowest Frequency: 8.0 cm^{-1}

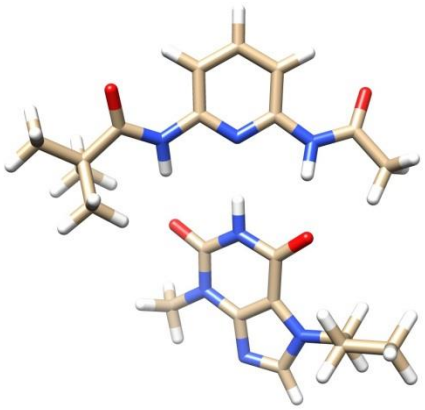
Coordinates:

Atom	x	y	z
N	0.63815900	-4.70969800	-1.03013400
C	1.84945900	-4.76268900	-0.47080100
H	2.46583300	-5.65003400	-0.42861800
N	2.26202100	-3.58415100	0.04978800
C	1.22700200	-2.68731600	-0.18104100
C	1.06984100	-1.29268900	0.09044400
O	1.87365000	-0.52375700	0.64145500
N	-0.16372300	-0.82432900	-0.36046400
H	-0.36121100	0.18224500	-0.20441900
C	-1.16584900	-1.52085400	-1.01426300
N	-0.93573600	-2.85727700	-1.26732700
C	0.25398600	-3.42133300	-0.84984700
C	3.51578600	-3.33822500	0.77660800
H	4.20947800	-4.12940400	0.47809500

H	3.91910600	-2.38401300	0.43000500
O	-2.21720600	-0.95916200	-1.34916700
C	-1.96498200	-3.63824400	-1.96268300
H	-2.89341400	-3.62287400	-1.38872300
H	-2.14940600	-3.21358500	-2.95153500
H	-1.60104900	-4.65905200	-2.05795900
C	3.32754600	-3.32598600	2.29789200
H	2.88499900	-4.27936700	2.61089500
H	2.61711500	-2.53522600	2.56171900
C	4.65663700	-3.09749000	3.02593500
H	4.50653600	-3.08669200	4.10966700
H	5.38011100	-3.88834100	2.79653800
H	5.10420000	-2.13884600	2.74145200
N	-0.71583400	2.04763800	0.06600200
C	-1.97430300	2.49344700	0.24007800
C	0.29490300	2.93616800	0.07839900
C	-2.27501200	3.84727000	0.43486400
N	-2.97810200	1.50942000	0.15755800
C	0.09140500	4.30884500	0.26544600
N	1.58507500	2.38612900	-0.05417900
C	-1.21622700	4.75044500	0.44401600
H	-3.29708800	4.16735700	0.57294300
C	-4.19462900	1.55703500	0.80653200
H	-2.73463800	0.66059900	-0.36102100
H	0.92750000	4.99248700	0.26713900
C	2.66560300	3.02773200	-0.62321000
H	1.68937900	1.40203000	0.21023100
H	-1.41207200	5.80804600	0.59165600
O	-4.48000600	2.42856200	1.63136900
O	2.57519100	4.11791500	-1.19256500
C	3.98640900	2.32475600	-0.51501700
C	4.92487100	2.53691700	-1.53789200
C	4.33915200	1.53921800	0.59231000
C	6.18915200	1.95360100	-1.46619600
H	4.65025500	3.16199900	-2.38098800
C	5.61401600	0.97281500	0.67127100
H	3.63341200	1.38021500	1.40000800
C	6.53774200	1.17232000	-0.35824600
H	6.90443500	2.11361900	-2.26746500
H	5.88592000	0.38141300	1.54046400
H	7.52684900	0.72785500	-0.29541600
C	-5.17517400	0.47564600	0.46000700
C	-6.10097100	0.09564200	1.44548100
C	-5.24528700	-0.10982000	-0.81309800
C	-7.06701900	-0.87108300	1.16992600
H	-6.05195600	0.56668700	2.42151000
C	-6.22560400	-1.06566900	-1.09169600
H	-4.55099600	0.18260900	-1.59242000
C	-7.13278900	-1.45260700	-0.10171700
H	-7.77123900	-1.16669500	1.94192400
H	-6.28098600	-1.50385700	-2.08372100

H	-7.89110800	-2.19887200	-0.32042600





Calculated Enthalpy: -1501.610436 Hartree

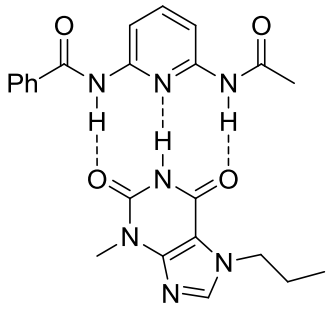
Zero Point Energy: 0.501761 Hartree

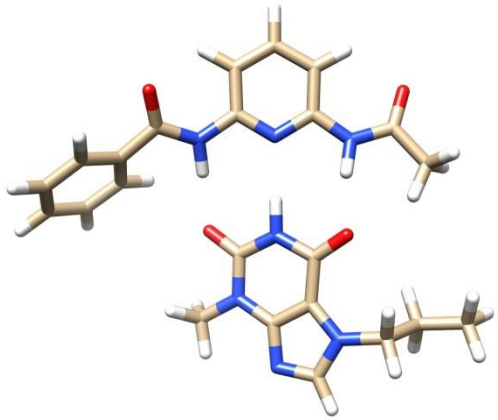
Lowest Frequency: 16.6 cm^{-1}

Coordinates:

Atom	x	y	z
N	-3.54201200	3.24305600	-0.98189800
C	-4.58524400	2.53588600	-0.54012800
H	-5.60561500	2.89372800	-0.52701800
N	-4.25936200	1.29778100	-0.10295200
C	-2.88416900	1.19129400	-0.26552500
C	-1.95901200	0.12815100	-0.03412000
O	-2.19523500	-1.01017400	0.40240300
N	-0.65867500	0.50156400	-0.37428100
H	0.08133700	-0.21055000	-0.24390300
C	-0.21804800	1.70364600	-0.90485500
N	-1.17156900	2.67397800	-1.13241000
C	-2.48808200	2.40698100	-0.81139300
C	-5.17134100	0.30755500	0.48792600
H	-6.17874100	0.57829400	0.16004000
H	-4.92570100	-0.66681400	0.05946000
O	0.98037300	1.88571400	-1.15250600
C	-0.75652300	3.96104700	-1.70267700
H	-0.05054400	4.45563800	-1.03260000
H	-0.27773000	3.80055500	-2.67039100
H	-1.64715200	4.57393300	-1.82398000
C	-5.09199200	0.26128400	2.01791100
H	-5.31168600	1.25913500	2.41656100
H	-4.06805600	0.00998800	2.31458000
C	-6.06962000	-0.76648000	2.59812600
H	-6.00779000	-0.78365300	3.69033200
H	-7.10517600	-0.53229800	2.32560600
H	-5.84558500	-1.77598100	2.23580000
N	1.48960700	-1.60734000	-0.10084000

C	2.79507500	-1.29216600	0.00636600
C	1.14413100	-2.90295400	-0.25086900
C	3.81035700	-2.25817200	-0.04388900
N	3.06989000	0.08312200	0.13735300
C	2.08808400	-3.93710200	-0.31118700
N	-0.24178700	-3.13065700	-0.30805000
C	3.43110500	-3.58630700	-0.20687600
H	4.84533500	-1.96730800	0.04634600
C	4.19708100	0.63995200	0.71233800
H	2.34744300	0.70874100	-0.22214300
H	1.76701500	-4.95954700	-0.43624800
C	-0.89531000	-4.28815700	-0.66815300
H	-0.83537700	-2.34519600	-0.03081100
H	4.19200900	-4.35966100	-0.25305400
O	5.09085300	-0.04937500	1.20244500
C	4.27151000	2.18546800	0.70740600
O	-0.32158100	-5.31741100	-1.02849600
C	-2.40832600	-4.21946800	-0.59358100
H	-2.75131000	-4.96876000	0.12668300
H	-2.81451300	-4.49567200	-1.57103300
H	-2.78677700	-3.23891300	-0.30261000
C	3.06679400	2.77927300	1.47550200
H	2.11526700	2.56689300	0.98269600
H	3.02522300	2.39329100	2.49995800
H	3.17467300	3.86818900	1.53064300
C	4.28886000	2.69988000	-0.75231800
H	4.40340700	3.78964600	-0.74980200
H	5.13394200	2.27547100	-1.30553800
H	3.36742600	2.46310900	-1.28849600
C	5.57253700	2.61375800	1.40832300
H	6.45229200	2.21543400	0.89573800
H	5.63811000	3.70694800	1.40979200
H	5.60315400	2.26458900	2.44421400





Calculated Enthalpy: -1575.440945 Hartree

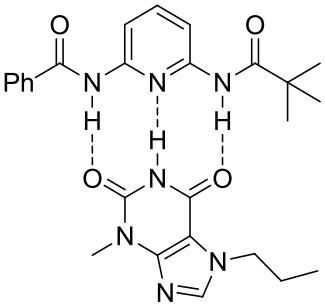
Zero Point Energy: 0.470304 Hartree

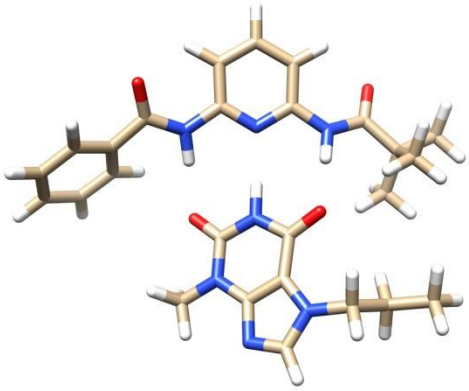
Lowest Frequency: 11.0 cm^{-1}

Coordinates:

Atom	x	y	z
N	-2.46876900	4.16698200	-0.17381400
C	-3.66068200	3.80436200	0.30699500
H	-4.48273900	4.48475100	0.48154700
N	-3.76214600	2.48206100	0.57408200
C	-2.53198300	1.93406100	0.23380100
C	-2.00857000	0.60679500	0.29808100
O	-2.58523900	-0.42537400	0.67847000
N	-0.68642200	0.55882100	-0.14394500
H	-0.21815700	-0.36387100	-0.11656600
C	0.10578100	1.59695100	-0.60823200
N	-0.46536400	2.85203600	-0.64305400
C	-1.77005900	3.00562100	-0.21784700
C	-4.95628300	1.77357300	1.05790400
H	-4.63045100	1.05157700	1.81000500
H	-5.58338100	2.52004400	1.55331600
O	1.27144100	1.39473300	-0.96995500
C	0.33562900	3.98536300	-1.12023200
H	1.22566400	4.09759800	-0.49858400
H	0.64141200	3.81526300	-2.15449800
H	-0.28103500	4.87931900	-1.05587100
C	-5.72932000	1.07410200	-0.06589500
H	-5.06673700	0.35400500	-0.55801400
H	-6.01682900	1.81854600	-0.81815000
C	-6.97336400	0.35797500	0.47102500
H	-7.51648500	-0.13427400	-0.34127600
H	-6.70360900	-0.40900100	1.20552500
H	-7.66160800	1.06041800	0.95503400
N	0.67538100	-2.13579600	-0.06550300
C	2.01637300	-2.24150500	-0.03595800
C	-0.06242100	-3.26422800	-0.12912400
C	2.67960700	-3.47566800	-0.07462700
N	2.72142100	-1.02269900	-0.01396000
C	0.51100300	-4.54200300	-0.17703700
N	-1.45087700	-3.05008800	-0.10798500
C	1.90083900	-4.62501900	-0.14917200
H	3.75808600	-3.51956000	-0.04609100
C	3.96838200	-0.83414700	0.54669600
H	2.21624100	-0.19896300	-0.35297800
H	-0.11765200	-5.41707100	-0.23427000
C	-2.45052900	-3.95681200	-0.38152400
H	-1.75377700	-2.11208400	0.16667300
H	2.38071300	-5.59832000	-0.18626900
O	4.54906900	-1.70224900	1.20270800
O	-2.24529400	-5.12120300	-0.72860000
C	-3.86024900	-3.42053600	-0.22617300
H	-4.36753800	-4.00636000	0.54672700

H	-4.39723800	-3.58360000	-1.16507800
H	-3.89745000	-2.36357000	0.03998400
C	4.60173800	0.50631800	0.31722700
C	5.46909200	0.99746600	1.30657300
C	4.42039900	1.23848100	-0.86537200
C	6.12636700	2.21380300	1.12645700
H	5.61880900	0.41569600	2.20998600
C	5.09498500	2.44778400	-1.05141500
H	3.76743000	0.86642300	-1.64666100
C	5.94271100	2.94058200	-0.05576400
H	6.78555400	2.59190800	1.90223100
H	4.95910800	3.00163900	-1.97553100
H	6.46261300	3.88311000	-0.20124900





Calculated Enthalpy: -1693.301937 Hartree

Zero Point Energy: 0.554690 Hartree

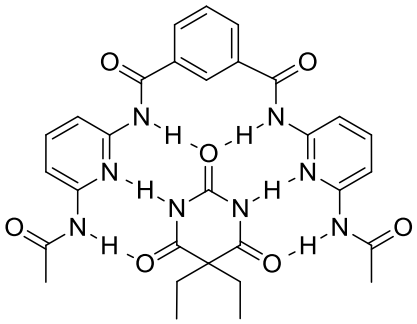
Lowest Frequency: 12.5 cm^{-1}

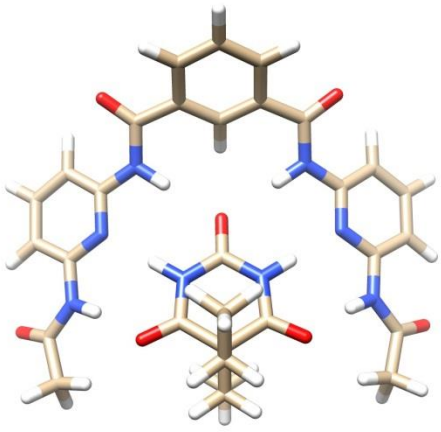
Coordinates:

Atom	x	y	z
N	-0.71814100	-4.82923000	0.17645600
C	-1.90564000	-4.83742000	-0.43383900
H	-2.46546300	-5.73153100	-0.67164600
N	-2.36540900	-3.60486100	-0.74977900
C	-1.39565600	-2.71534300	-0.30445900
C	-1.28341500	-1.29109200	-0.35488500
O	-2.09793500	-0.47153600	-0.80838500
N	-0.08340000	-0.85653600	0.20796800
H	0.10371100	0.16207400	0.16422900
C	0.93277100	-1.61312600	0.76790700
N	0.74692200	-2.97968500	0.80377800
C	-0.40281500	-3.51238700	0.25445100
C	-3.65324800	-3.28833300	-1.38426800
H	-3.47554700	-2.49951900	-2.11870600
H	-3.96520100	-4.18812900	-1.92198500

O	1.95542000	-1.07509000	1.21134100
C	1.79626400	-3.82758200	1.38101700
H	2.69862700	-3.78111300	0.76715500
H	2.03214400	-3.48215500	2.38855200
H	1.42089700	-4.84827900	1.41194900
C	-4.72550700	-2.85969400	-0.37678100
H	-4.37774500	-1.96724200	0.15398900
H	-4.85255300	-3.65378800	0.36913200
C	-6.06108200	-2.56922000	-1.06976300
H	-6.81841500	-2.27045900	-0.33872600
H	-5.96208700	-1.75764400	-1.79914800
H	-6.43776900	-3.45277400	-1.59780000
N	0.50258800	2.05177300	-0.07419400
C	1.76810900	2.45036800	-0.30555500
C	-0.48849900	2.96236300	-0.14222200
C	2.09746500	3.77578800	-0.61965900
N	2.74850900	1.45277400	-0.14942600
C	-0.25487100	4.30910500	-0.44873500
N	-1.78385700	2.45304300	0.07733400
C	1.05974400	4.69953800	-0.68705300
H	3.12321900	4.05701200	-0.80443300
C	3.99689900	1.44913300	-0.73763500
H	2.46869100	0.62368300	0.38233300
H	-1.07441400	5.00979700	-0.49242300
C	-2.86740300	3.16568100	0.55336400
H	-1.90777700	1.46363100	-0.14260700
H	1.27740300	5.73553700	-0.92849000
O	4.33914500	2.26625200	-1.59586900
O	-2.78282500	4.35240500	0.86742300
C	-4.19663500	2.38311700	0.67094900
C	4.94329900	0.38189900	-0.27274200
C	5.90754900	-0.07868800	-1.18408000
C	4.94754800	-0.10880200	1.04155900
C	6.84648900	-1.03268500	-0.79416600
H	5.90966800	0.32048400	-2.19288500
C	5.90145900	-1.05053800	1.43501900
H	4.22255800	0.24907400	1.76377300
C	6.84684100	-1.51891900	0.51855300
H	7.58085300	-1.39191800	-1.50900900
H	5.90593300	-1.41508400	2.45787300
H	7.58454500	-2.25452600	0.82596700
C	-4.02262800	1.17899900	1.62681300
H	-3.32633900	0.43440900	1.23361900
H	-3.66717600	1.50505700	2.61036400
H	-4.99067000	0.68521500	1.76664100
C	-4.63706400	1.89891100	-0.73161000
H	-5.61167200	1.40437100	-0.65411300
H	-4.74392100	2.74402900	-1.42050100
H	-3.93336000	1.18389100	-1.16370000
C	-5.27038000	3.32542300	1.24184100
H	-5.42380300	4.19445300	0.59647400

H	-6.21855300	2.78362500	1.32440600
H	-4.99427200	3.69164200	2.23457000





Calculated Enthalpy: -2126.803698 Hartree

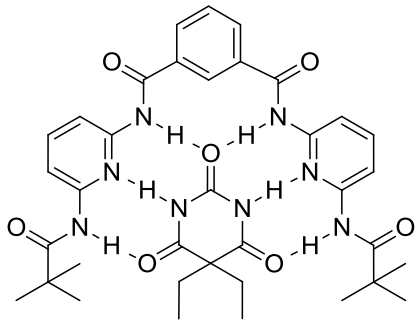
Zero Point Energy: 0.608889 Hartree

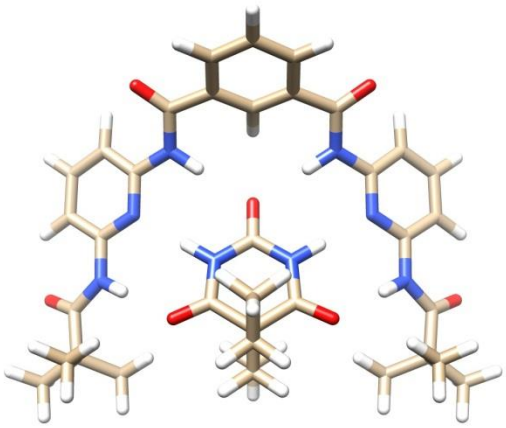
Lowest Frequency: 13.2 cm^{-1}

Coordinates:

Atom	x	y	z
C	0.00014000	5.74818300	1.92849800
C	1.20934100	5.23102900	1.46328500
C	1.21614700	4.18842000	0.52479500
C	0.00014000	3.68774900	0.04256600
C	-1.21586800	4.18848000	0.52473000
C	-1.20906100	5.23108800	1.46322200
H	0.00014100	6.55147900	2.65849100
H	2.15534100	5.62388700	1.81965300
H	0.00013900	2.93144300	-0.73068100
H	-2.15506000	5.62399100	1.81954000
C	2.55215100	3.66636500	0.07622500
O	3.54974100	4.38779200	0.08463900
N	2.58287600	2.33690700	-0.29381300
H	1.73894700	1.78243800	-0.16421000
C	-2.55187200	3.66648900	0.07608800
O	-3.54943200	4.38795800	0.08446300
N	-2.58263900	2.33703200	-0.29395300
H	-1.73875000	1.78251600	-0.16428900
C	3.71764700	1.61981100	-0.72108700
C	4.78887900	2.24390900	-1.37120900
N	3.67739100	0.29435600	-0.48261500
C	5.85040400	1.44142200	-1.77720400
H	4.78003200	3.30964900	-1.54170800
C	4.72314600	-0.46286900	-0.87612800
C	5.83947000	0.07114600	-1.53499700
H	6.69768500	1.88880900	-2.28767300
H	6.65061100	-0.57341400	-1.83580600

C	-3.71743800	1.61999800	-0.72126500
C	-4.78855700	2.24414700	-1.37152200
N	-3.67732500	0.29455900	-0.48268600
C	-5.85012800	1.44173200	-1.77753600
H	-4.77959400	3.30987300	-1.54210600
C	-4.72312800	-0.46259600	-0.87620900
C	-5.83934800	0.07147400	-1.53521000
H	-6.69732400	1.88915700	-2.28811000
H	-6.65053200	-0.57303000	-1.83602200
N	4.61451100	-1.82267200	-0.54080300
C	5.41386500	-2.86802600	-0.95639400
H	3.86686700	-2.06028900	0.11000200
O	6.34783600	-2.74017400	-1.74746800
N	-4.61465400	-1.82237800	-0.54074900
C	-5.41419200	-2.86766900	-0.95614500
H	-3.86699500	-2.06002500	0.11002600
O	-6.34819400	-2.73978700	-1.74717900
C	5.06484200	-4.21815100	-0.36250300
H	5.92612800	-4.57247700	0.21225600
H	4.18585700	-4.20138000	0.28273700
H	4.90548100	-4.92517700	-1.18154500
C	-5.06524100	-4.21779200	-0.36220700
H	-4.90540000	-4.92473100	-1.18123800
H	-4.18653600	-4.20094900	0.28341000
H	-5.92673700	-4.57229200	0.21212200
O	0.00005500	0.68709300	-0.28151600
C	0.00001900	-0.44255700	0.20871900
N	1.17385700	-1.09783000	0.49390700
N	-1.17385800	-1.09776600	0.49389300
H	2.04718800	-0.60536300	0.22200700
C	1.27969800	-2.34672900	1.06689400
C	-1.27977300	-2.34666500	1.06687100
H	-2.04716000	-0.60525200	0.22198900
C	-0.00005900	-3.08147700	1.46292100
O	2.38979300	-2.83620400	1.25014000
O	-2.38989400	-2.83609300	1.25007600
C	-0.00010000	-4.48601000	0.78180500
C	-0.00008300	-3.27535000	3.01631300
H	0.88224200	-5.01560200	1.15128000
H	-0.88220900	-5.01572000	1.15166800
H	-0.88256500	-3.87596600	3.25543600
H	0.88251800	-3.87576600	3.25549900
C	-0.00026700	-1.98722400	3.84589100
H	0.88731800	-1.37432100	3.65555700
H	-0.88797200	-1.37452100	3.65546900
H	-0.00029100	-2.23677600	4.91090200
C	-0.00045500	-4.47205100	-0.75048200
H	0.88645400	-3.97476500	-1.15782800
H	-0.00047900	-5.49831900	-1.12926800
H	-0.88761600	-3.97487400	-1.15742000





Calculated Enthalpy: -2363.30207755 Hartree

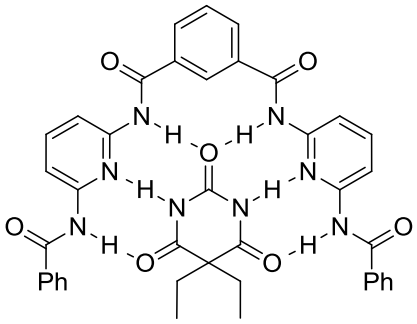
Lowest Frequency: 12.4 cm^{-1} (6-31g(d))

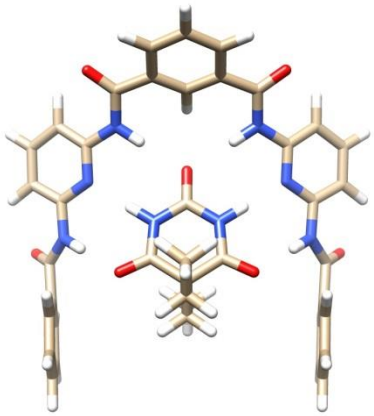
Coordinates:

Atom	x	y	z
C	-0.00007600	6.16880500	2.03295600
C	1.20928900	5.67238500	1.54596100
C	1.21612100	4.67430400	0.56022700
C	0.00011900	4.19890600	0.05388900
C	-1.21598300	4.67437200	0.55992400
C	-1.20934700	5.67245600	1.54565400
H	-0.00015000	6.93808000	2.79874700
H	2.15550600	6.04601200	1.92177900
H	0.00019400	3.48072800	-0.75491000
H	-2.15563700	6.04614000	1.92123100
C	2.55095700	4.16364100	0.09614300
O	3.56101700	4.86300300	0.17681100
N	2.56814400	2.86603700	-0.37292700
H	1.71597800	2.31407200	-0.30638600
C	-2.55072400	4.16375600	0.09551200
O	-3.56076800	4.86318000	0.17584500
N	-2.56785100	2.86609800	-0.37340500
H	-1.71572000	2.31411100	-0.30659900
C	3.71490600	2.17595900	-0.81994800
C	4.73824900	2.83767000	-1.50488100
N	3.73464300	0.85435800	-0.55924400
C	5.82582000	2.07783000	-1.92169400
H	4.67514900	3.89911900	-1.69343500
C	4.80805200	0.13693400	-0.95675600
C	5.88205600	0.71443500	-1.65257700
H	6.64087400	2.55117100	-2.46046800
H	6.71720000	0.10669400	-1.96099000
C	-3.71454100	2.17600400	-0.82059500
C	-4.73762500	2.83763500	-1.50599200
N	-3.73447000	0.85447400	-0.55956200
C	-5.82512100	2.07777700	-1.92296800
H	-4.67438200	3.89903500	-1.69477900

C	-4.80783400	0.13704600	-0.95719400
C	-5.88155800	0.71445400	-1.65352400
H	-6.63996300	2.55104500	-2.46212700
H	-6.71665100	0.10670000	-1.96205100
N	4.78714000	-1.21687500	-0.57486200
C	5.68496200	-2.20744200	-0.94300800
H	4.06372000	-1.46145400	0.09772400
O	6.56201900	-2.01544600	-1.78231000
N	-4.78717100	-1.21664800	-0.57488800
C	-5.68522600	-2.20714500	-0.94264900
H	-4.06381100	-1.46114000	0.09779200
O	-6.56229500	-2.01523300	-1.78195800
C	5.52324200	-3.57511500	-0.23842300
C	-5.52374000	-3.57462600	-0.23763300
O	0.00011100	1.21199100	-0.55269600
C	0.00007000	0.14199200	0.05873000
N	1.17353100	-0.47679600	0.41730100
N	-1.17343600	-0.47672300	0.41728100
H	2.05407900	-0.01561500	0.11927700
C	1.28100000	-1.65190800	1.13075200
C	-1.28099300	-1.65179600	1.13078400
H	-2.05394900	-0.01550100	0.11923000
C	-0.00002200	-2.35735500	1.57652200
O	2.39222600	-2.10367900	1.38228200
O	-2.39225100	-2.10345900	1.38236000
C	-0.00009700	-3.80070500	0.97725100
C	-0.00000700	-2.45493600	3.13606000
H	0.88203200	-4.30828800	1.37738500
H	-0.88219200	-4.30825200	1.37750800
H	-0.88274400	-3.03801200	3.41415300
H	0.88275100	-3.03798300	3.41414600
C	-6.67068500	-4.49384000	-0.69430600
H	-6.65463000	-4.64677400	-1.77648600
H	-6.56709100	-5.46771100	-0.20464100
H	-7.64679500	-4.07718700	-0.43025200
C	-5.59861000	-3.39825200	1.29771900
H	-4.76938400	-2.80929600	1.69598600
H	-6.53888900	-2.91928400	1.59159500
H	-5.56100400	-4.38322300	1.77566600
C	-4.17474200	-4.21257300	-0.64560000
H	-4.09664400	-5.21070500	-0.20094500
H	-4.10535900	-4.32175200	-1.73326200
H	-3.32048300	-3.62892000	-0.29658200
C	5.59834900	-3.39924200	1.29697500
H	6.53876800	-2.92056600	1.59088300
H	4.76929900	-2.81022500	1.69552000
H	5.56058500	-4.38435100	1.77462400
C	6.66991200	-4.49444600	-0.69554800
H	6.56617800	-5.46844400	-0.20616500
H	6.65365500	-4.64704300	-1.77777200
H	7.64615600	-4.07808900	-0.43152000

C	4.17404200	-4.21261800	-0.64641000
H	4.10447000	-4.32140600	-1.73409900
H	4.09578700	-5.21088700	-0.20208900
H	3.31996500	-3.62889800	-0.29706000
C	-0.00003500	-1.11511000	3.87945600
H	0.88764000	-0.51643100	3.64765100
H	-0.88772600	-0.51646200	3.64763100
H	-0.00004300	-1.29235500	4.95888500
C	-0.00021100	-3.87583000	-0.55360000
H	0.88556200	-3.40262300	-0.99013300
H	-0.00020500	-4.92221800	-0.87245400
H	-0.88608200	-3.40267700	-0.98999400





Calculated Enthalpy: -2510.90307058 Hartree

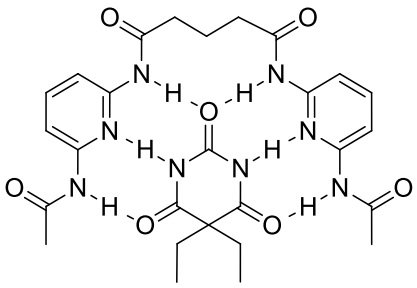
Lowest Frequency: 10.2 cm^{-1} (6-31g(d))

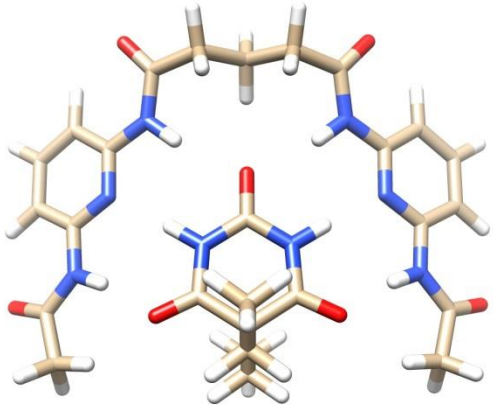
Coordinates:

Atom	x	y	z
C	0.00002200	6.72462400	1.89766000
C	1.20925700	6.20395900	1.43651900
C	1.21631700	5.15567400	0.50433000
C	0.00001300	4.65332600	0.02423800
C	-1.21628600	5.15568100	0.50433300
C	-1.20921800	6.20396600	1.43652200
H	0.00002500	7.53266100	2.62241700
H	2.15534400	6.59766900	1.79165600
H	0.00001100	3.89306000	-0.74499100
H	-2.15530100	6.59768100	1.79166100
C	2.55337700	4.62594800	0.06674200
O	3.55734000	5.33832800	0.09366400
N	2.57890300	3.29921300	-0.31150600
H	1.72540100	2.75251300	-0.21432900
C	-2.55335000	4.62596100	0.06675100
O	-3.55730600	5.33835100	0.09366700
N	-2.57888300	3.29922800	-0.31150200
H	-1.72538500	2.75252300	-0.21432300
C	3.71257300	2.57436900	-0.72782400

C	4.80092500	3.18785900	-1.35722900
N	3.65090500	1.24626600	-0.50249800
C	5.85747600	2.37354900	-1.75636700
H	4.80970400	4.25506900	-1.51878900
C	4.68578400	0.47774700	-0.89340800
C	5.81907700	1.00217100	-1.52967800
H	6.71977700	2.81353100	-2.24758200
H	6.62713700	0.35304300	-1.83134500
C	-3.71255500	2.57438900	-0.72782800
C	-4.80090000	3.18788300	-1.35724300
N	-3.65089500	1.24628600	-0.50250100
C	-5.85745300	2.37357600	-1.75638600
H	-4.80967400	4.25509100	-1.51880600
C	-4.68577500	0.47777100	-0.89341700
C	-5.81906200	1.00219900	-1.52969400
H	-6.71974800	2.81356000	-2.24760800
H	-6.62712200	0.35307300	-1.83136600
N	4.57871900	-0.88651400	-0.56703900
C	5.21138900	-1.92787800	-1.22094700
H	3.90846300	-1.12570500	0.16410200
O	5.84045000	-1.77579900	-2.26918400
N	-4.57871800	-0.88649000	-0.56704800
C	-5.21139700	-1.92784800	-1.22095500
H	-3.90846200	-1.12568600	0.16409300
O	-5.84046200	-1.77576200	-2.26918900
O	0.00000400	1.64850500	-0.39069300
C	0.00000200	0.55078100	0.17090200
N	1.17310200	-0.08226900	0.49984800
N	-1.17310200	-0.08226200	0.49985000
H	2.04930200	0.39288500	0.20223300
C	1.28077500	-1.28341300	1.16740100
C	-1.28078100	-1.28339900	1.16741400
H	-2.04929900	0.39289800	0.20223800
C	-0.00000500	-2.00541300	1.58695000
O	2.39219100	-1.74438300	1.40509100
O	-2.39219900	-1.74437500	1.40508500
C	-0.00001000	-3.42798100	0.93841800
C	-0.00000300	-2.16298300	3.14180700
H	0.88283300	-3.94726500	1.32143400
H	-0.88290800	-3.94722900	1.32135700
H	-0.88254100	-2.75687800	3.39664500
H	0.88256600	-2.75682900	3.39665300
C	-5.09049100	-3.27719000	-0.57905900
C	-5.01587400	-3.45273500	0.81097300
C	-5.12476700	-4.40428600	-1.41632400
C	-4.96918200	-4.73909300	1.35352600
H	-5.01361500	-2.59487000	1.47447900
C	-5.05988900	-5.68658500	-0.87309100
H	-5.20184500	-4.26019300	-2.48880900
C	-4.98398200	-5.85645000	0.51433400
H	-4.92506600	-4.86623900	2.43096300

H	-5.07453300	-6.55236900	-1.52833600
H	-4.94294700	-6.85547200	0.93849000
C	5.09046500	-3.27722100	-0.57905700
C	5.01585000	-3.45277000	0.81097500
C	5.12472400	-4.40431300	-1.41632600
C	4.96914000	-4.73913000	1.35352200
H	5.01360500	-2.59490900	1.47448500
C	5.05982900	-5.68661400	-0.87309900
H	5.20180200	-4.26021600	-2.48881100
C	4.98392300	-5.85648400	0.51432500
H	4.92502500	-4.86628100	2.43095900
H	5.07445800	-6.55239500	-1.52834800
H	4.94287400	-6.85550800	0.93847600
C	-0.00004800	-0.85440600	3.93913400
H	-0.00005700	-1.07507500	5.01058800
H	0.88742500	-0.24668700	3.73138900
H	-0.88754800	-0.24673400	3.73136500
C	0.00006100	-3.45619800	-0.59393200
H	0.88743500	-2.97151500	-1.01496900
H	0.00006300	-4.49309200	-0.94242400
H	-0.88725800	-2.97149000	-1.01505400





Calculated Enthalpy: -2013.681691 Hartree

Zero Point Energy: 0.613519 Hartree

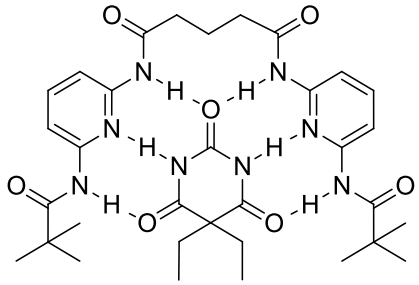
Lowest Frequency: 10.4 cm^{-1}

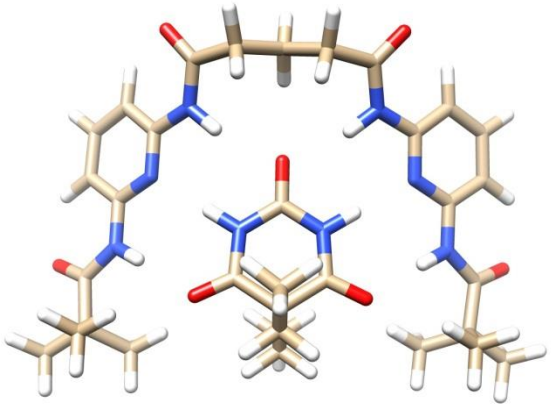
Coordinates:

Atom	x	y	z
C	1.26657000	4.30415000	1.28440500
C	-0.00007100	4.28660300	0.40294100
C	-1.26666400	4.30412100	1.28447900
H	-0.00010100	5.14973900	-0.27073000
C	2.54488800	3.98038200	0.52540300
O	3.35511300	4.84541000	0.19826000
N	2.70625300	2.63405300	0.26089100

H	1.93848400	2.02874300	0.53939900
C	-2.54501200	3.98033400	0.52553700
O	-3.35521400	4.84536200	0.19834000
N	-2.70637200	2.63400200	0.26103400
H	-1.93860300	2.02870000	0.53955200
C	3.80065600	1.98038500	-0.32698800
C	4.83337500	2.67151800	-0.97501300
N	3.77296200	0.63677100	-0.21138900
C	5.87133000	1.91496600	-1.50947800
H	4.80787500	3.74807400	-1.04108700
C	4.79726400	-0.07217700	-0.73125200
C	5.87612100	0.52833700	-1.39689200
H	6.68992300	2.41314900	-2.02003700
H	6.67075300	-0.08056400	-1.79829400
C	-3.80074400	1.98032000	-0.32688500
C	-4.83350500	2.67144400	-0.97485400
N	-3.77298300	0.63670000	-0.21137200
C	-5.87142700	1.91487300	-1.50935900
H	-4.80806000	3.74800600	-1.04085700
C	-4.79725700	-0.07226600	-0.73126600
C	-5.87614900	0.52823700	-1.39686000
H	-6.69005000	2.41304900	-2.01987600
H	-6.67075600	-0.08067700	-1.79828900
N	4.70345800	-1.45897000	-0.53137400
C	5.54508000	-2.44939500	-0.99583900
H	3.92163100	-1.76843700	0.04424600
O	6.52190700	-2.23662700	-1.71403200
N	-4.70338500	-1.45906600	-0.53146700
C	-5.54495300	-2.44950500	-0.99599800
H	-3.92154900	-1.76852600	0.04414800
O	-6.52179500	-2.23674300	-1.71417200
O	0.00002000	1.09786600	0.52014300
C	0.00001800	-0.12738300	0.62044100
N	1.17322900	-0.84758100	0.67953300
N	-1.17319200	-0.84758500	0.67948300
H	2.04893200	-0.32212800	0.51689400
C	1.27813100	-2.20888000	0.87367200
C	-1.27809400	-2.20888400	0.87362600
H	-2.04889800	-0.32214000	0.51682200
C	0.00001700	-3.02697300	1.03874800
O	2.38723900	-2.73030100	0.91286100
O	-2.38720200	-2.73030600	0.91278700
C	0.00004300	-4.16316100	-0.03428000
C	-0.00001100	-3.67778800	2.46124400
H	0.88245700	-4.77864900	0.16040600
H	-0.88245100	-4.77857800	0.16027400
H	-0.88234500	-4.32261800	2.50885100
H	0.88237700	-4.32253800	2.50892900
H	1.40386000	5.28907200	1.73698000
H	1.14553400	3.57703800	2.09642300
H	-0.00008000	3.38959400	-0.22078600

H	-1.14556900	3.57700600	2.09648600
H	-1.40394700	5.28903700	1.73706700
C	5.19244100	-3.85482000	-0.55063100
H	4.26718900	-3.91711800	0.02214400
H	5.11807200	-4.48923600	-1.43823800
H	6.01854600	-4.23815800	0.05658200
C	-5.19222800	-3.85494300	-0.55089600
H	-4.26704000	-3.91721000	0.02198500
H	-6.01837200	-4.23843300	0.05616500
H	-5.11767800	-4.48925400	-1.43856400
C	0.00018000	-3.68823700	-1.49091100
H	0.88718900	-3.09146900	-1.72919600
H	0.00021000	-4.55271000	-2.16119300
H	-0.88675000	-3.09141500	-1.72934500
C	-0.00011300	-2.69889300	3.63974100
H	0.88769000	-2.05706000	3.64239300
H	-0.88797600	-2.05714000	3.64230500
H	-0.00013500	-3.25690200	4.58055800





Calculated Enthalpy: -2249.400834 Hartree

Zero Point Energy: 0.782929 Hartree

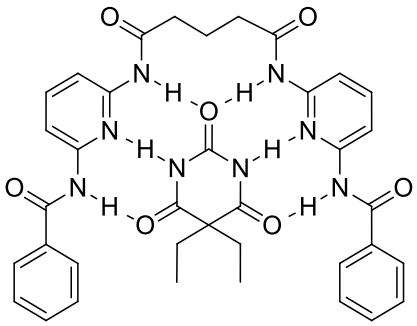
Lowest Frequency: 10.8 cm^{-1}

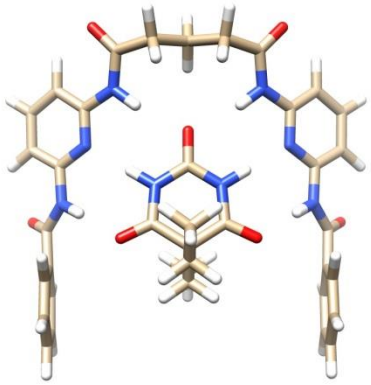
Coordinates:

Atom	x	y	z
C	1.28886700	4.75598600	1.35558300
C	0.07238500	4.83775200	0.40969900
C	-1.24197300	4.85174700	1.22074000
H	0.13873300	5.73821600	-0.20966800
C	2.60068100	4.44603200	0.64874000
O	3.45748700	5.30496700	0.44762900
N	2.73633500	3.12066500	0.28353500
H	1.93213300	2.52449200	0.46189700
C	-2.47754000	4.53849000	0.38903900
O	-3.27032400	5.40674700	0.02913800
N	-2.62327300	3.19537700	0.10228500
H	-1.87248300	2.58797300	0.41725800

C	3.84843300	2.48531300	-0.29481200
C	4.88160800	3.20746700	-0.90488500
N	3.83451200	1.13767200	-0.21355100
C	5.93911400	2.47973500	-1.43867300
H	4.84297800	4.28497000	-0.94277900
C	4.87950500	0.45411900	-0.72957700
C	5.96026500	1.09191400	-1.36012100
H	6.76047700	3.00019400	-1.92188000
H	6.77199400	0.50937500	-1.76344500
C	-3.68953900	2.55290100	-0.54930100
C	-4.59289200	3.25127900	-1.35958500
N	-3.76660600	1.22397300	-0.32776900
C	-5.61640900	2.51839900	-1.94993100
H	-4.48462700	4.31520000	-1.50388200
C	-4.78710100	0.53921700	-0.88897200
C	-5.73644000	1.15145700	-1.72393400
H	-6.33439300	3.01835300	-2.59299100
H	-6.52919200	0.56710900	-2.16096900
N	4.82009400	-0.94143800	-0.55500900
C	5.70709800	-1.89031400	-1.04257700
H	4.05861600	-1.26698100	0.03605700
O	6.63537200	-1.59590200	-1.79276500
N	-4.84170700	-0.82421500	-0.54469500
C	-5.80896800	-1.74890200	-0.90999000
H	-4.12291100	-1.12867800	0.10753500
O	-6.70419400	-1.48070800	-1.70872900
O	0.03642700	1.66368600	0.32328700
C	0.01738600	0.45575400	0.55468400
N	1.17882100	-0.27008400	0.69276700
N	-1.16666600	-0.23410000	0.68759500
H	2.06638900	0.21746000	0.48325500
C	1.26296100	-1.60052200	1.04794600
C	-1.29485600	-1.55753300	1.05620600
H	-2.03710400	0.27762400	0.46943400
C	-0.02819500	-2.35718800	1.35604700
O	2.36316300	-2.13296800	1.12617800
O	-2.41204500	-2.05023700	1.14853600
C	-0.05500600	-3.67138300	0.51820800
C	-0.02844800	-2.72621300	2.87888300
H	0.82454300	-4.25158000	0.81035400
H	-0.93910600	-4.23176500	0.83429700
H	-0.92483500	-3.32877500	3.05279600
H	0.83978700	-3.37126100	3.04318500
H	1.42762500	5.70275700	1.88305600
H	1.10411000	3.97941300	2.10781200
H	0.07684800	3.98055600	-0.26709500
H	-1.17001100	4.11537200	2.03023900
H	-1.40129300	5.83147700	1.67702200
C	5.46725000	-3.35258800	-0.59624500
C	-5.70257500	-3.15083000	-0.26317900
C	4.12253100	-3.85600500	-1.17210300

H	4.11278500	-3.77947800	-2.26475400
H	3.98719700	-4.91040900	-0.90724300
H	3.26915800	-3.30385100	-0.77438000
C	6.60507200	-4.22362100	-1.15854000
H	7.58013400	-3.89975000	-0.78405800
H	6.44522500	-5.26263800	-0.85184100
H	6.63668300	-4.18586100	-2.25046600
C	5.47595200	-3.45311600	0.94746900
H	5.38116000	-4.50467600	1.23975200
H	6.41898100	-3.07560000	1.35757100
H	4.65170900	-2.90831500	1.41142200
C	-4.44380500	-3.86965300	-0.80561500
H	-3.52129200	-3.36218600	-0.51742800
H	-4.40520100	-4.88644200	-0.39930800
H	-4.47867000	-3.94465400	-1.89786500
C	-5.64970800	-3.03987500	1.27867200
H	-6.52635200	-2.50638400	1.66205200
H	-5.65431300	-4.04591900	1.71211900
H	-4.75030600	-2.53513400	1.63699500
C	-6.94893800	-3.96243100	-0.66067800
H	-7.02732000	-4.07206600	-1.74514500
H	-6.88353100	-4.96034000	-0.21458900
H	-7.86690300	-3.48564200	-0.30516900
C	0.00583800	-1.54298800	3.85186200
H	0.90862700	-0.93474300	3.73001300
H	-0.86619500	-0.88964700	3.73873200
H	0.00138400	-1.91467100	4.88061700
C	-0.07428800	-3.47549800	-1.00129300
H	-0.09189200	-4.44916700	-1.49973500
H	-0.95979200	-2.92366600	-1.33411600
H	0.81319700	-2.94328600	-1.35956600





Calculated Enthalpy: -2397.77756054 Hartree

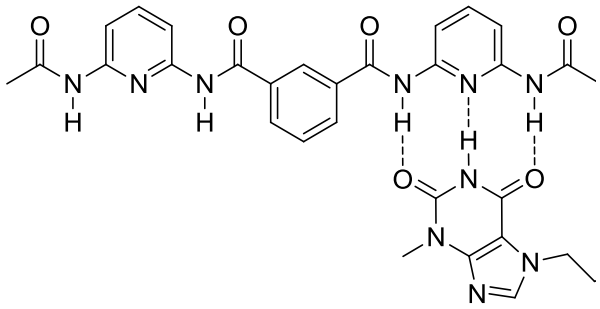
Lowest Frequency: 15.8 cm^{-1}

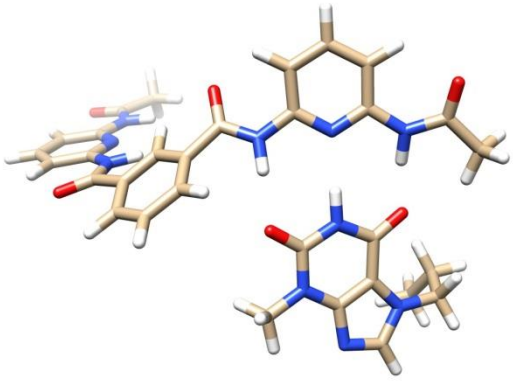
Coordinates:

Atom	x	y	z

C	1.23947900	5.40896200	1.08794500
C	-0.04432500	5.32992500	0.22365400
C	-1.30391500	5.37263400	1.12506800
H	-0.06638600	6.15971600	-0.49142200
C	2.50643900	4.99186000	0.35971400
O	3.38472000	5.81947600	0.02425200
N	2.60430600	3.62881100	0.13401700
H	1.78935800	3.06838500	0.37902500
C	-2.58335900	4.94781800	0.42388000
O	-3.48117200	5.76680400	0.12050400
N	-2.66670500	3.58671700	0.18265600
H	-1.83807900	3.03610200	0.40301100
C	3.68366000	2.92339500	-0.42358000
C	4.74059600	3.55675400	-1.09365800
N	3.62432400	1.57089000	-0.26638000
C	5.75240600	2.75325400	-1.61803300
H	4.74976400	4.63073600	-1.18375900
C	4.62797500	0.80670800	-0.77803300
C	5.71239300	1.36839100	-1.47225700
H	6.58148800	3.21202700	-2.14529600
H	6.47690000	0.73082800	-1.88446800
C	-3.74567800	2.87214900	-0.36328900
C	-4.82757400	3.49679300	-1.00082200
N	-3.65860400	1.51869000	-0.23038300
C	-5.83461100	2.68315000	-1.51895700
H	-4.85845500	4.57184100	-1.07199500
C	-4.65681500	0.74415700	-0.73650100
C	-5.76528700	1.29685300	-1.39896900
H	-6.68291100	3.13502300	-2.02098300
H	-6.52611800	0.65221600	-1.80709500
N	4.52887100	-0.57329700	-0.52218600
C	5.20395100	-1.57665200	-1.20096000
H	3.84935200	-0.85599500	0.18738300
O	5.87408500	-1.36031400	-2.24246700
N	-4.52539700	-0.63839400	-0.50928500
C	-5.17683200	-1.64120300	-1.21136000
H	-3.83952700	-0.91913100	0.19491800
O	-5.85568800	-1.41444400	-2.24493600
O	-0.01866200	2.18730200	0.36849600
C	-0.00978500	0.95429100	0.61273600
N	1.17239700	0.26110800	0.75359500
N	-1.18200400	0.24583400	0.76122700
H	2.05322500	0.75861900	0.48573700
C	1.27727600	-1.05623400	1.15389500
C	-1.26785200	-1.07208400	1.16322600
H	-2.07168000	0.73142400	0.49925700
C	0.01057800	-1.83142600	1.48993000
O	2.40722600	-1.58200700	1.24993300
O	-2.39081900	-1.61135800	1.26768000
C	0.01583900	-3.17930300	0.69098200
C	0.01850400	-2.16082800	3.02909700

H	0.90617600	-3.73080000	1.00837300
H	-0.86516000	-3.74172700	1.01522900
H	-0.86079900	-2.78563000	3.21781000
H	0.90866600	-2.77198100	3.21147500
H	1.39479400	6.42940100	1.44712700
H	1.11576700	4.76145500	1.96595800
H	-0.04010000	4.40354900	-0.35632200
H	-1.14461600	4.71093200	1.98672500
H	-1.46486700	6.38381300	1.50728100
C	-5.03120800	-3.03275400	-0.69013400
C	-4.84954900	-3.32659500	0.67258800
C	-5.15881100	-4.08803400	-1.61247000
C	-4.77940300	-4.65671800	1.10019700
H	-4.77749800	-2.52895900	1.40111600
C	-5.07626300	-5.41395800	-1.18460700
H	-5.32301400	-3.85046900	-2.65720100
C	-4.88573300	-5.70139000	0.17429800
H	-4.64899500	-4.87509000	2.15489800
H	-5.16444200	-6.22069500	-1.90469600
H	-4.82822300	-6.73213300	0.50909700
C	5.09593900	-2.95685400	-0.64232800
C	5.24036800	-4.03311500	-1.53741000
C	4.93378800	-3.21799300	0.72941900
C	5.19290500	-5.34863200	-1.07364500
H	5.38944600	-3.81974100	-2.58959500
C	4.89889500	-4.53735100	1.19300700
H	4.84938200	-2.40237400	1.43660000
C	5.02135800	-5.60373900	0.29422600
H	5.29352600	-6.17219300	-1.77275800
H	4.78308600	-4.73042800	2.25432700
H	4.99096200	-6.62617200	0.65690700
C	0.00876400	-3.02455100	-0.83655900
H	0.89349900	-2.48734400	-1.19699000
H	0.01287700	-4.01236100	-1.30873600
H	-0.88532500	-2.49826400	-1.18991700
C	0.01222600	-0.94067100	3.96107900
H	0.89471300	-0.30738200	3.81385200
H	-0.88253300	-0.32292000	3.82204000
H	0.01989500	-1.27252300	5.00435200





Calculated Enthalpy: -2199.163337 Hartree

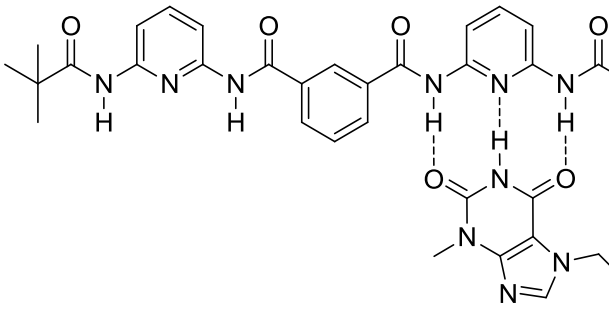
Zero Point Energy: 0.621259 Hartree

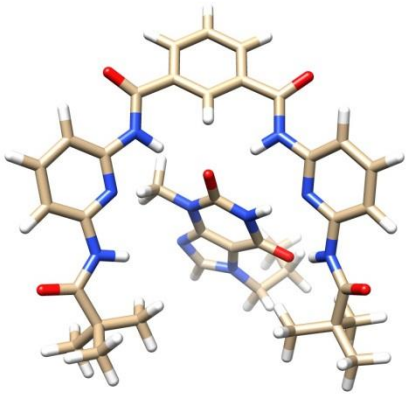
Lowest Frequency: 5.14 cm^{-1}

Coordinates:

Atom	x	y	z
C	-1.42081500	-0.85207300	-4.11855400
C	-0.65955500	-1.49050400	-3.13538100
C	-1.22307500	-1.76343300	-1.88196100
C	-2.54898300	-1.38798700	-1.62371000
C	-3.30499500	-0.72442100	-2.59600600
C	-2.73427700	-0.47161500	-3.85449200
H	-0.98579100	-0.65613300	-5.09345600
H	0.35924300	-1.78622800	-3.35637400
H	-2.97089300	-1.66298500	-0.66251000
H	-3.33427100	0.02009100	-4.61242500
C	-0.50323800	-2.52714500	-0.80638400
O	-1.12971900	-3.25296300	-0.03114500
N	0.86226300	-2.35857100	-0.75075200
H	1.27600600	-1.58607300	-1.28203700
C	-4.73091500	-0.29932200	-2.38225300
O	-5.50413900	-0.15017500	-3.32996700
N	-5.09109200	-0.08062400	-1.07395100
H	-4.36974300	-0.13197800	-0.36596800
C	1.73623400	-3.07663500	0.09062100
C	1.46371300	-4.39293100	0.48523600
N	2.86159000	-2.42869200	0.44125800
C	2.41262500	-5.03972900	1.26966000
H	0.54618700	-4.87722200	0.18610200
C	3.76647200	-3.07155000	1.20911000
C	3.58468800	-4.39039000	1.64788300
H	2.23864700	-6.06230500	1.59044900
H	4.33757200	-4.86824900	2.25528000
C	-6.34463100	0.26661400	-0.54290500
C	-7.51448200	0.41033000	-1.30203900
N	-6.30795200	0.44143500	0.78494700

C	-8.67669300	0.74747300	-0.60951600
H	-7.49804100	0.26612100	-2.37158300
C	-7.43843900	0.76621400	1.42587000
C	-8.66751800	0.93392800	0.77199800
H	-9.60664100	0.86748100	-1.15707800
H	-9.55494200	1.19532900	1.32841000
N	4.88637200	-2.29835400	1.55619800
C	6.06490600	-2.72613200	2.12706100
H	4.80731500	-1.29324000	1.38116100
O	6.30878400	-3.90321100	2.39701100
N	-7.25123400	0.91622600	2.81068200
C	-8.16425000	1.24237100	3.78653500
H	-6.29499900	0.75042500	3.09834400
O	-9.35203000	1.46486200	3.55473500
C	7.07457100	-1.63042800	2.40812100
H	6.74131800	-0.63985900	2.09658400
H	7.28281100	-1.62179900	3.48243100
H	8.00805100	-1.88234600	1.89634400
C	-7.60113200	1.30773900	5.19283300
H	-8.11901900	0.56779800	5.81011100
H	-6.52545600	1.12535900	5.24675200
H	-7.81846800	2.29515900	5.60931900
H	3.23180500	-0.59015200	-0.20716600
N	3.42726700	0.36705000	-0.54858100
C	4.33186700	1.12567400	0.19521300
C	2.76116000	0.71607400	-1.71179600
C	4.50103600	2.42975300	-0.36247900
O	4.88087700	0.64435200	1.19962100
N	2.99521100	1.97961100	-2.21124500
O	1.99234100	-0.07902100	-2.26789700
N	5.28785600	3.51740200	-0.00379500
C	3.86068300	2.81673600	-1.53483200
C	2.31762600	2.39506300	-3.44527100
C	5.06646200	4.45716400	-0.95127000
C	6.13993200	3.65487900	1.18841900
N	4.21007900	4.07417500	-1.90166900
H	2.61625200	1.74626200	-4.27119700
H	1.23612700	2.33071800	-3.31340700
H	2.60838800	3.42219200	-3.65493200
H	5.55378000	5.42169900	-0.92036400
H	6.76033300	2.75877400	1.25528800
H	6.79476700	4.50987800	0.99802700
C	5.34538300	3.85576300	2.48508800
H	6.08018700	3.88259700	3.29895200
H	4.72280800	2.97184600	2.65986400
C	4.49371800	5.12839500	2.50993700
H	3.97976300	5.22690300	3.47107800
H	5.10962100	6.02417900	2.36769500
H	3.72740700	5.11814300	1.72738100





Calculated Enthalpy: -2435.68169928 Hartree

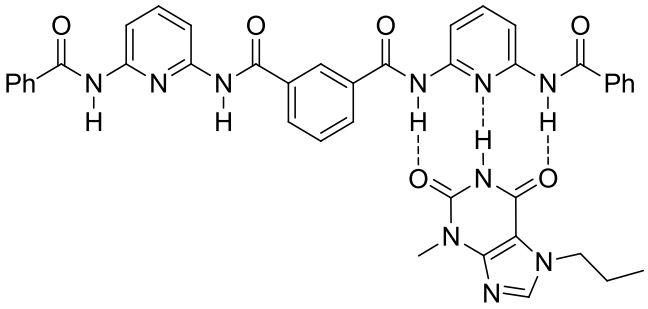
Lowest Frequency: 9.3 cm^{-1} (6-31g(d)

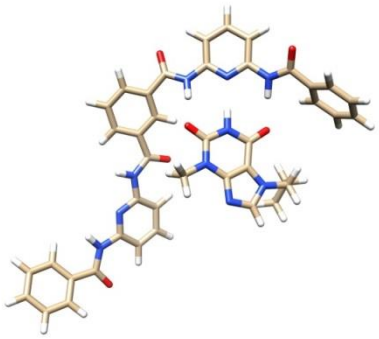
Coordinates:

Atom	x	y	z
C	2.76392100	-5.84196600	-1.58713700
C	1.50573400	-5.79476300	-0.98545200
C	1.17737300	-4.73969500	-0.12164200
C	2.12697000	-3.74680700	0.14502100
C	3.38645900	-3.78465400	-0.46459800
C	3.70476500	-4.84486900	-1.32561300
H	3.01190700	-6.65713200	-2.25961900
H	0.77044200	-6.56959700	-1.17438100
H	1.89699100	-2.96432100	0.85720900
H	4.68899600	-4.87627900	-1.78063700
C	-0.17577000	-4.74365100	0.52726100
O	-0.77106400	-5.79842300	0.75216200
N	-0.68755700	-3.50002600	0.83487900
H	-0.21291700	-2.68374600	0.44620500
C	4.43409900	-2.74222000	-0.20112000
O	5.63504500	-3.01304000	-0.26383600
N	3.95035100	-1.48791600	0.09481200
H	2.95319000	-1.31573100	-0.02401100
C	-1.86048300	-3.23399400	1.56608800
C	-2.41524800	-4.16111800	2.45716800
N	-2.37107900	-2.00153200	1.38198400
C	-3.54024200	-3.76700200	3.17551700
H	-1.97911200	-5.14183800	2.57122000
C	-3.46048900	-1.63960000	2.08760700
C	-4.08322300	-2.49747400	3.00421300
H	-3.99923600	-4.45813200	3.87583900
H	-4.95323200	-2.17098700	3.55299300
C	4.67799800	-0.34132100	0.45862600
C	6.06030000	-0.32682400	0.70013100
N	3.90931300	0.75132800	0.56924200
C	6.62419100	0.89060600	1.07701800
H	6.64770900	-1.22541300	0.59074800
C	4.47651600	1.90976100	0.93386000

C	5.84581000	2.04027400	1.20353500
H	7.69028800	0.94429100	1.27620600
H	6.25959200	2.99378000	1.49402500
N	-3.95251900	-0.35044800	1.80716900
C	-4.67269800	0.45079800	2.67232500
H	-3.74188000	0.00075500	0.87128600
O	-4.93124300	0.10244600	3.82359400
N	3.54757400	2.96265700	1.01388300
C	3.75183100	4.28321900	1.33394700
H	2.60544600	2.66362600	0.80195700
O	4.86476300	4.73305400	1.60817800
C	-5.13273100	1.81647200	2.10903300
C	2.50665300	5.20269100	1.34040100
H	-1.63292300	-0.84809500	-0.03123700
N	-1.31136600	-0.28812700	-0.84149100
C	-2.29478500	0.45734000	-1.49625900
C	0.03145300	-0.40640200	-1.15475300
C	-1.76334900	1.13229700	-2.63730300
O	-3.45598500	0.48399200	-1.06090200
N	0.48591600	0.30983600	-2.24003000
O	0.77719400	-1.13177000	-0.47772200
N	-2.32441400	1.98755800	-3.57722500
C	-0.41510600	1.06296200	-2.96870200
C	1.90210100	0.22242700	-2.62089700
C	-1.30670400	2.35653100	-4.38904800
C	-3.74200700	2.35956200	-3.71660300
N	-0.12922500	1.82282800	-4.05432300
H	2.52920400	0.53314400	-1.78362100
H	2.14987100	-0.80363900	-2.90143000
H	2.05745400	0.88436400	-3.47016900
H	-1.45894800	3.02472800	-5.22530100
H	-4.09961100	2.67213300	-2.73337400
H	-3.76611900	3.22814300	-4.38072300
C	-4.61512900	1.22608100	-4.26960300
H	-5.64731200	1.59687700	-4.26208300
H	-4.58465200	0.38274200	-3.57146100
C	-4.23553600	0.77127400	-5.68186300
H	-4.91599100	-0.01301800	-6.02749100
H	-4.29142200	1.60038900	-6.39691300
H	-3.21969700	0.36298000	-5.71714900
C	-3.90625100	2.65383300	1.67477100
H	-3.21065900	2.79381200	2.50936100
H	-3.36531400	2.19715200	0.84248400
H	-4.24221500	3.64405200	1.34754400
C	-5.88964700	2.57290200	3.21456900
H	-6.22267000	3.54069500	2.82485800
H	-6.76814100	2.01562000	3.55066200
H	-5.25394200	2.75149000	4.08622800
C	-6.08175800	1.58973700	0.90744000
H	-6.94186000	0.97686400	1.19850600
H	-6.46242500	2.55714200	0.56092700

H	-5.57929500	1.10721700	0.06610200
C	2.79379100	6.36065100	0.35726100
H	1.96798100	7.07945200	0.38363700
H	3.71651800	6.87974200	0.62708000
H	2.89227500	5.99413600	-0.67070100
C	1.19397000	4.50615300	0.93463500
H	1.23491300	4.10902400	-0.08620500
H	0.91980400	3.69844800	1.62326100
H	0.37845100	5.23568900	0.96101000
C	2.36619000	5.76215200	2.77535000
H	3.28283900	6.26960300	3.08570500
H	1.54053400	6.48078800	2.81159600
H	2.15271200	4.96371000	3.49467900





Calculated Enthalpy: -2583.27619881Hartree

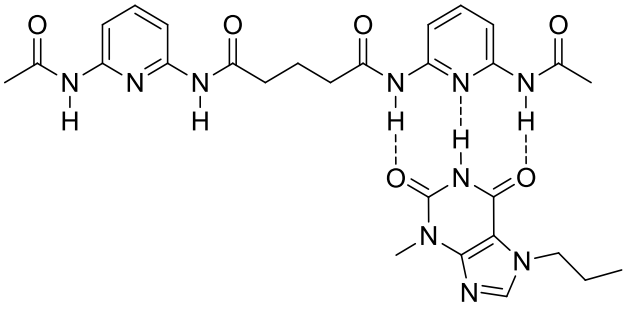
Lowest Frequency: 8.7 cm^{-1}

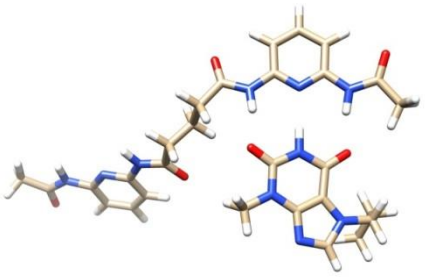
Coordinates:

Atom	x	y	z
C	1.93214300	5.34421300	0.19207300
C	0.54785700	5.47606000	0.10255100
C	-0.28629400	4.39021400	0.41204300
C	0.28251700	3.18601100	0.83552500
C	1.67431200	3.04550400	0.92502100
C	2.49792500	4.13368400	0.60035600
H	2.57409900	6.18676600	-0.04438500
H	0.09988100	6.41616800	-0.20064400
H	-0.33624300	2.34406200	1.12106400
H	3.57732600	4.06696700	0.69767500
C	-1.77345600	4.60669700	0.35050700
O	-2.25194900	5.71283500	0.61166300
N	-2.52057400	3.50504900	0.00441500
H	-2.01599200	2.69827000	-0.37346000
C	2.19801500	1.72091200	1.40383100
O	1.50880700	0.96897100	2.09507200
N	3.47616200	1.41189900	1.00149300
H	3.93514100	2.03556500	0.34998000
C	-3.92407400	3.39982200	-0.01875200
C	-4.77878600	4.50709000	0.05581500

N	-4.38031700	2.13550200	-0.13302100
C	-6.15029800	4.26470400	0.01192100
H	-4.37298800	5.50267800	0.14252200
C	-5.70756400	1.92521900	-0.17444800
C	-6.64074600	2.96959600	-0.10465400
H	-6.84322500	5.09855500	0.07039200
H	-7.69976300	2.76297700	-0.14348600
C	4.25968400	0.28883300	1.31712400
C	3.86285700	-0.73278300	2.19140600
N	5.44571200	0.29952700	0.69419700
C	4.77118400	-1.76949800	2.40106300
H	2.89530300	-0.70370800	2.66882300
C	6.29960300	-0.71039000	0.91097500
C	6.01105800	-1.78528500	1.76449800
H	4.50681900	-2.58151100	3.07167200
H	6.72569900	-2.58141500	1.90779100
N	-6.10396700	0.57577300	-0.23523400
C	-7.28268700	0.11313300	-0.78546000
H	-5.41095100	-0.11758900	0.06217200
O	-8.06264800	0.83591500	-1.40954100
N	7.50144500	-0.56223600	0.20059800
C	8.58235400	-1.41187600	0.13135900
H	7.51656200	0.27321200	-0.37015600
O	8.60909000	-2.51139900	0.68695000
H	-3.15817500	0.63573200	-0.34657300
N	-2.52301400	-0.16373400	-0.51935600
C	-2.97855200	-1.41659100	-0.10991700
C	-1.34454100	0.15790700	-1.17208500
C	-2.03547600	-2.44176300	-0.43035200
O	-4.08179500	-1.53369900	0.44607200
N	-0.50567600	-0.88750900	-1.49604200
O	-1.07114700	1.33502800	-1.44235200
N	-2.04059300	-3.81941200	-0.25309400
C	-0.85897400	-2.16889600	-1.11922900
C	0.74918000	-0.60461600	-2.20162000
C	-0.89776200	-4.26608100	-0.82315100
C	-3.04248900	-4.62453200	0.46317100
N	-0.15167700	-3.29976400	-1.36414100
H	0.53803600	-0.06647600	-3.12724600
H	1.40363500	0.00462800	-1.57471200
H	1.22843300	-1.55606400	-2.42244100
H	-0.63744500	-5.31539600	-0.82944100
H	-4.02749300	-4.32107300	0.10290700
H	-2.87280900	-5.66263100	0.16327800
C	-2.96192500	-4.47701000	1.98792300
H	-3.79621500	-5.05681500	2.40145900
H	-3.15074400	-3.43097800	2.25226400
C	-1.64185700	-4.95640300	2.59867600
H	-1.66312900	-4.85222000	3.68790900
H	-1.45520700	-6.01190900	2.36776200
H	-0.79040400	-4.37428100	2.23015700

C	9.73893400	-0.91608200	-0.68790900
C	10.01218100	0.44662600	-0.89105700
C	10.59618000	-1.87820500	-1.24462600
C	11.11848600	0.83671100	-1.64902200
H	9.39359100	1.21434400	-0.43539600
C	11.69366000	-1.48649300	-2.01057100
H	10.38723700	-2.92823100	-1.07064000
C	11.95694900	-0.12770900	-2.21531600
H	11.32828100	1.89267800	-1.78930800
H	12.34401300	-2.23922000	-2.44575300
H	12.81444200	0.17790100	-2.80738200
C	-7.57976500	-1.34304700	-0.58189400
C	-7.21123800	-2.03459300	0.58153300
C	-8.32535000	-2.00436100	-1.57135800
C	-7.58154000	-3.37125300	0.74900600
H	-6.65257300	-1.53294500	1.36374300
C	-8.67606700	-3.34416900	-1.41077200
H	-8.62340100	-1.45692700	-2.45938300
C	-8.30713300	-4.02988000	-0.24742500
H	-7.30627000	-3.89463300	1.65980200
H	-9.24181500	-3.85146800	-2.18656400
H	-8.59007700	-5.07041000	-0.11659000





Calculated Enthalpy: -2086.045516 Hartree

Zero Point Energy: 0.626626 Hartree

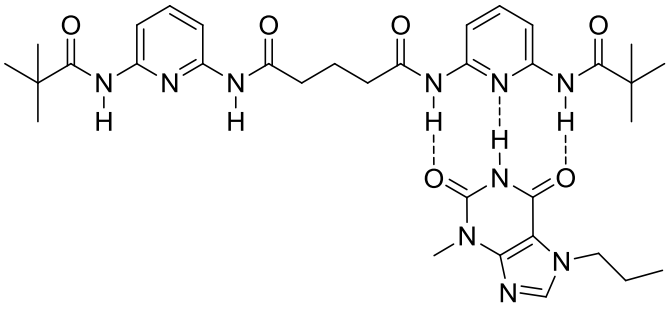
Lowest Frequency: 3.3 cm^{-1}

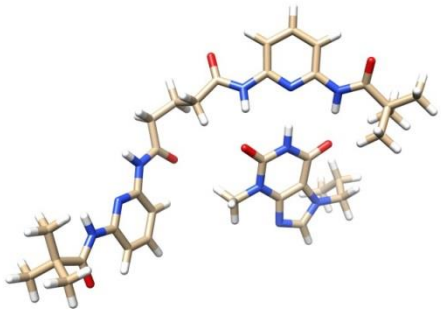
Coordinates:

Atom	x	y	z
C	-0.17379000	-3.38381900	0.82366600
O	0.12431200	-4.48584400	0.35912200
N	-1.42019800	-2.81021600	0.70786700
H	-1.52759500	-1.88180200	1.12440600
C	3.70196500	-0.15222800	0.35647000
O	3.17582800	0.67350600	-0.38945200
N	5.05925100	-0.36485900	0.41165500

H	5.39803900	-1.06886300	1.05541800
C	-2.56324000	-3.33944600	0.08608800
C	-2.65365900	-4.67762600	-0.32417900
N	-3.57731600	-2.46219900	-0.05701300
C	-3.85430100	-5.09540900	-0.88980400
H	-1.81324300	-5.34210800	-0.19748600
C	-4.72935900	-2.89080000	-0.61174100
C	-4.91842700	-4.21204800	-1.04262400
H	-3.96234200	-6.12539700	-1.21643300
H	-5.86062300	-4.51225500	-1.47384700
C	6.09371200	0.27029600	-0.29756700
C	5.89220000	1.26939900	-1.26003500
N	7.30733700	-0.18287800	0.04395000
C	7.03024000	1.79509100	-1.87019500
H	4.89501300	1.60276800	-1.50439500
C	8.38459900	0.33884500	-0.55805700
C	8.30524500	1.34265100	-1.53372400
H	6.92146300	2.57093700	-2.62205700
H	9.20047900	1.73419600	-1.99261100
N	-5.71557000	-1.89873400	-0.74375300
C	-7.04507300	-2.06344300	-1.06396100
H	-5.40285800	-0.93575200	-0.59788700
O	-7.57120500	-3.15751200	-1.27564500
N	9.58709700	-0.22924900	-0.10317700
C	10.88187600	0.04877300	-0.47569600
H	9.44378700	-0.94033300	0.60282400
O	11.17647300	0.89132600	-1.32272600
C	-7.85112400	-0.78102500	-1.13529800
C	11.94188400	-0.76273400	0.24327300
H	-3.34797800	-0.50645700	0.50333500
N	-3.22056600	0.48813700	0.75031600
C	-4.13644800	1.38725800	0.20092100
C	-2.14989700	0.75342100	1.58957500
C	-3.84199800	2.73092200	0.58421600
O	-5.06514200	0.98124300	-0.51533400
N	-1.94061100	2.06996200	1.93834200
O	-1.42250400	-0.16011800	2.00081200
N	-4.45983100	3.94663800	0.31813200
C	-2.78685500	3.03880900	1.43563100
C	-0.81769700	2.40271800	2.82305900
C	-3.75064200	4.87406400	1.00168800
C	-5.61232200	4.19122400	-0.56443600
N	-2.72832900	4.36781700	1.69592200
H	-0.93510100	1.89224200	3.78091100
H	0.12156200	2.09071900	2.36248600
H	-0.81985200	3.48033600	2.97190900
H	-4.01027300	5.92318700	0.97463300
H	-6.37895400	3.45524400	-0.31406300
H	-5.99319400	5.18264500	-0.30347400
C	-5.26453900	4.11619100	-2.05666100
H	-6.20903200	4.23294900	-2.60198800

H	-4.89854000	3.10946500	-2.28512500
C	-4.25971100	5.17355200	-2.52344100
H	-4.07742900	5.08073400	-3.59850700
H	-4.63022300	6.18798400	-2.33414400
H	-3.29454100	5.06669200	-2.01669400
C	0.85537400	-2.53472500	1.55607000
H	0.37153200	-1.81800900	2.22495400
H	1.45073900	-3.22600800	2.16134300
C	1.77123400	-1.78411900	0.56947500
H	1.18200100	-1.07637700	-0.02200800
H	2.22050400	-2.49976300	-0.12853300
C	2.88041400	-1.01447700	1.30581000
H	2.42825500	-0.33189300	2.03647600
H	3.51681700	-1.70944200	1.86435200
H	-7.26597800	0.11517200	-0.92769100
H	-8.29032100	-0.70580000	-2.13461800
H	-8.67625600	-0.85399100	-0.42038500
H	12.59152600	-0.07640900	0.79444700
H	11.53617600	-1.50259800	0.93685800
H	12.55754400	-1.27164900	-0.50344100





Calculated Enthalpy: -2321.771100 Hartree

Zero Point Energy: 0.795514 Hartree

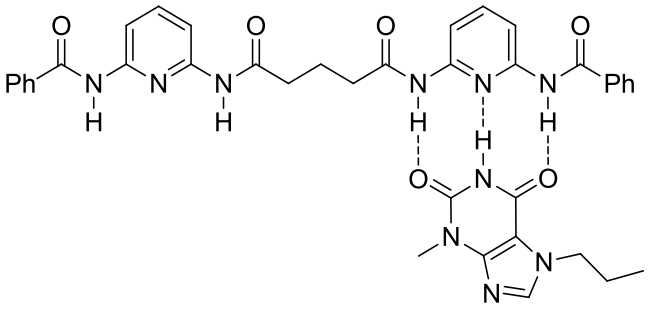
Lowest Frequency: 6.2 cm^{-1}

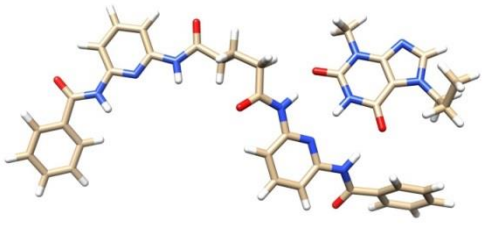
Coordinates:

Atom	x	y	z
C	0.85377400	3.70653300	-1.28658300
O	1.15177600	4.75720200	-1.85739100
N	1.74957500	2.94163700	-0.57465300
H	1.38474400	2.07426100	-0.17252500
C	-3.08853200	1.52007200	-2.34398600
O	-2.42762600	0.54545000	-2.70066800
N	-4.25810400	1.41721200	-1.62629900
H	-4.70577200	2.27761200	-1.33515800

C	3.10139600	3.21738100	-0.30697800
C	3.68446300	4.47186300	-0.53241900
N	3.78481000	2.18126600	0.22129600
C	5.02296300	4.62948400	-0.18348000
H	3.10264500	5.27201000	-0.96301800
C	5.07686900	2.35777000	0.55573200
C	5.74428600	3.57630100	0.36941000
H	5.50976100	5.58641500	-0.34617300
H	6.78087200	3.67992400	0.65080200
C	-4.96663500	0.27100200	-1.22690200
C	-4.60985700	-1.03860800	-1.57839800
N	-6.04129600	0.56040600	-0.48161600
C	-5.43478100	-2.06240900	-1.11508300
H	-3.73515800	-1.22627300	-2.18253200
C	-6.81733100	-0.44221600	-0.04606300
C	-6.55859900	-1.78953900	-0.33624200
H	-5.19833800	-3.09217700	-1.36598000
H	-7.21060100	-2.56604000	0.03369300
N	5.72163500	1.21671800	1.07293200
C	6.80456100	1.21304800	1.93087900
H	5.32378900	0.32147800	0.78405800
O	7.31106300	2.25338300	2.34988100
N	-7.90016500	0.01239600	0.72587500
C	-8.91009200	-0.70482700	1.32070200
H	-7.90329900	1.01773400	0.83281400
O	-8.98976500	-1.93055800	1.23477200
C	7.34535600	-0.17871900	2.33665700
C	-9.96349900	0.10102500	2.11861200
H	2.95343700	0.38642700	0.25949300
N	2.52796500	-0.55088900	0.15204800
C	3.41332700	-1.60718700	-0.06498700
C	1.14359800	-0.57965100	0.19355900
C	2.71519800	-2.83546800	-0.27832400
O	4.63904600	-1.41314500	-0.04461700
N	0.53751200	-1.80214600	0.00247800
O	0.49258000	0.45513100	0.39343500
N	3.14081500	-4.13776400	-0.50906400
C	1.32740800	-2.91116800	-0.22749900
C	-0.92876400	-1.87950100	0.02203000
C	2.01409900	-4.88284300	-0.58533700
C	4.52243900	-4.60976100	-0.69306600
N	0.89078100	-4.18107000	-0.41700500
H	-1.30332100	-1.61499700	1.01335500
H	-1.34328300	-1.18990800	-0.71519300
H	-1.21012900	-2.90242900	-0.21909000
H	2.04831900	-5.94858200	-0.76379700
H	5.12324100	-4.19524200	0.11901600
H	4.49276500	-5.69681100	-0.57523300
C	5.12076000	-4.22626500	-2.05267000
H	6.16527700	-4.56087100	-2.03841300
H	5.14704700	-3.13430100	-2.13320500

C	4.39461500	-4.83815700	-3.25426200
H	4.88850100	-4.55101200	-4.18770000
H	4.38981700	-5.93329600	-3.20241900
H	3.35498700	-4.49881100	-3.31541500
C	-0.57381500	3.17139300	-1.30120600
H	-0.61733900	2.16423600	-0.87971200
H	-1.14768500	3.82932300	-0.63321400
C	-1.19066100	3.20984400	-2.70841300
H	-0.69703200	2.47131500	-3.34885400
H	-1.00970900	4.19433300	-3.14883400
C	-2.70206400	2.94929700	-2.71123600
H	-3.21299800	3.66762500	-2.05948400
H	-3.09281000	3.11516800	-3.72419700
C	-11.33881100	-0.19246700	1.47588500
H	-11.53578100	-1.26698200	1.45405900
H	-12.12893200	0.29558100	2.05630300
H	-11.38724800	0.18856500	0.44961000
C	-9.94100100	-0.43920500	3.56738300
H	-10.72144700	0.05348900	4.15688700
H	-10.12079900	-1.51682200	3.58301000
H	-8.97700900	-0.24318900	4.04995500
C	-9.72543700	1.62310100	2.14050600
H	-8.77374800	1.88884000	2.61539400
H	-9.76121600	2.06576700	1.13824200
H	-10.51691600	2.10060100	2.72652600
C	6.23467600	-1.00218200	3.03083200
H	5.83991800	-0.47188500	3.90428000
H	5.40579800	-1.23124500	2.35707100
H	6.65307900	-1.95406700	3.37621400
C	8.51245400	0.01732900	3.31984900
H	8.90393700	-0.96221100	3.61427400
H	9.32496200	0.59305000	2.86847200
H	8.19042500	0.54558900	4.22161100
C	7.85824000	-0.92031800	1.07859200
H	8.63359000	-0.33717100	0.56951500
H	8.30131600	-1.87661600	1.37878800
H	7.05743900	-1.13219400	0.36650200





Calculated Enthalpy: -2469.431201 Hartree

Zero Point Energy: 0.73304 Hartree

Lowest Frequency: 6.6 cm^{-1}

Coordinates:

Atom	x	y	z
C	-0.41844600	0.80242800	1.47149400
O	-1.27516200	0.17060700	2.09159100
N	0.71495300	0.23444400	0.93506900
H	1.33146900	0.86238000	0.41219600
C	-4.01649500	2.95305500	-0.33288300
O	-4.17941100	4.16457900	-0.47970400
N	-5.05336000	2.05045900	-0.29042800
H	-4.81916200	1.07527000	-0.15166800
C	1.12176600	-1.10885400	0.99304000
C	0.28101400	-2.14510100	1.42148900
N	2.38592300	-1.32399100	0.57143800
C	0.79204700	-3.44064600	1.39816500
H	-0.72174600	-1.92744400	1.75481700
C	2.85527500	-2.58411100	0.55288900
C	2.08862000	-3.68434200	0.96007700
H	0.17032900	-4.26817700	1.72620000
H	2.50109500	-4.68189700	0.92889900
C	-6.43712200	2.27185400	-0.39270500
C	-7.02231800	3.53004100	-0.59509500
N	-7.15051300	1.14362300	-0.28027000
C	-8.41348400	3.57217400	-0.67535200
H	-6.40837100	4.41388300	-0.68109900
C	-8.48635700	1.21184900	-0.36036900
C	-9.18073300	2.41396500	-0.55778000
H	-8.90942300	4.52563900	-0.83050900
H	-10.25882700	2.42434300	-0.60958800
N	4.19480900	-2.73013900	0.14174200
C	4.70494100	-3.83639500	-0.50690300
H	4.79595200	-1.90655100	0.24080400
O	3.99920600	-4.76808900	-0.90019300
N	-9.09718800	-0.04612100	-0.22996300
C	-10.43411800	-0.37061200	-0.22890400
H	-8.42811300	-0.78773800	-0.06725900
O	-11.33128200	0.47164200	-0.29867800
H	3.55602600	0.19665300	0.09433000
N	4.17794500	0.99369300	-0.12801900
C	5.54697400	0.76915000	0.02538300
C	3.53359700	2.14917600	-0.53776400
C	6.30526500	1.93593100	-0.30070000
O	5.96555100	-0.33737800	0.39862200
N	4.32911100	3.22540000	-0.86723100
O	2.29742800	2.20066000	-0.59991300

N	7.66887000	2.20064400	-0.32874800
C	5.69979400	3.10693600	-0.74249800
C	3.69506000	4.47181400	-1.31273400
C	7.78519600	3.47592500	-0.76528800
C	8.76385700	1.30424300	0.07569800
N	6.61594600	4.06411700	-1.02992100
H	3.04081300	4.26813500	-2.16169400
H	3.10460300	4.90392800	-0.50168200
H	4.48457000	5.16097700	-1.60480900
H	8.74887800	3.95154200	-0.88317100
H	8.59080200	0.33786000	-0.40204000
H	9.67996100	1.73219800	-0.34114400
C	8.88463700	1.13687800	1.59567100
H	9.67463800	0.39478500	1.76444000
H	7.95831600	0.69507100	1.97825500
C	9.21712900	2.42894900	2.34791000
H	9.32546700	2.23209400	3.41899800
H	10.15720100	2.86684700	1.99228700
H	8.42917600	3.18078900	2.23070000
C	-0.51857600	2.31302500	1.27667800
H	-0.06821100	2.76732900	2.16991800
H	0.09080600	2.63271400	0.42628700
C	-1.96193300	2.81171600	1.13829900
H	-1.95854800	3.90571400	1.16262200
H	-2.54799700	2.46577800	1.99582100
C	-2.63167800	2.34520000	-0.16925600
H	-2.03619000	2.68234800	-1.02569700
H	-2.67277400	1.25193800	-0.20386200
C	6.19030000	-3.85710600	-0.71672000
C	7.09328900	-3.28985900	0.19461100
C	6.68204400	-4.54466400	-1.83826900
C	8.46928200	-3.40639300	-0.01814800
H	6.73104300	-2.77127100	1.07493400
C	8.05525200	-4.64277800	-2.05821900
H	5.97700100	-4.99732100	-2.52746400
C	8.95269100	-4.07568600	-1.14570700
H	9.16197400	-2.97862300	0.70053700
H	8.42618800	-5.16583600	-2.93459900
H	10.02291000	-4.16123300	-1.31051400
C	-10.73936800	-1.83714800	-0.12043500
C	-11.98145700	-2.20073400	0.42306500
C	-9.86203800	-2.84183300	-0.56047400
C	-12.33122900	-3.54500700	0.54656800
H	-12.65959400	-1.41874400	0.74730600
C	-10.21907600	-4.18720300	-0.44598900
H	-8.91373600	-2.58981100	-1.02611900
C	-11.45022500	-4.54166800	0.11300400
H	-13.28989600	-3.81554000	0.97875100
H	-9.53879300	-4.95562500	-0.80021600
H	-11.72423600	-5.58848500	0.20444800

APPENDIX B

SUPPLEMENTAL INFORMATION: LINEAR FREE ENERGY RELATIONSHIPS REVEAL STRUCTURAL CHANGES IN HYDROGEN-BONDED HOST-GUEST INTERACTIONS

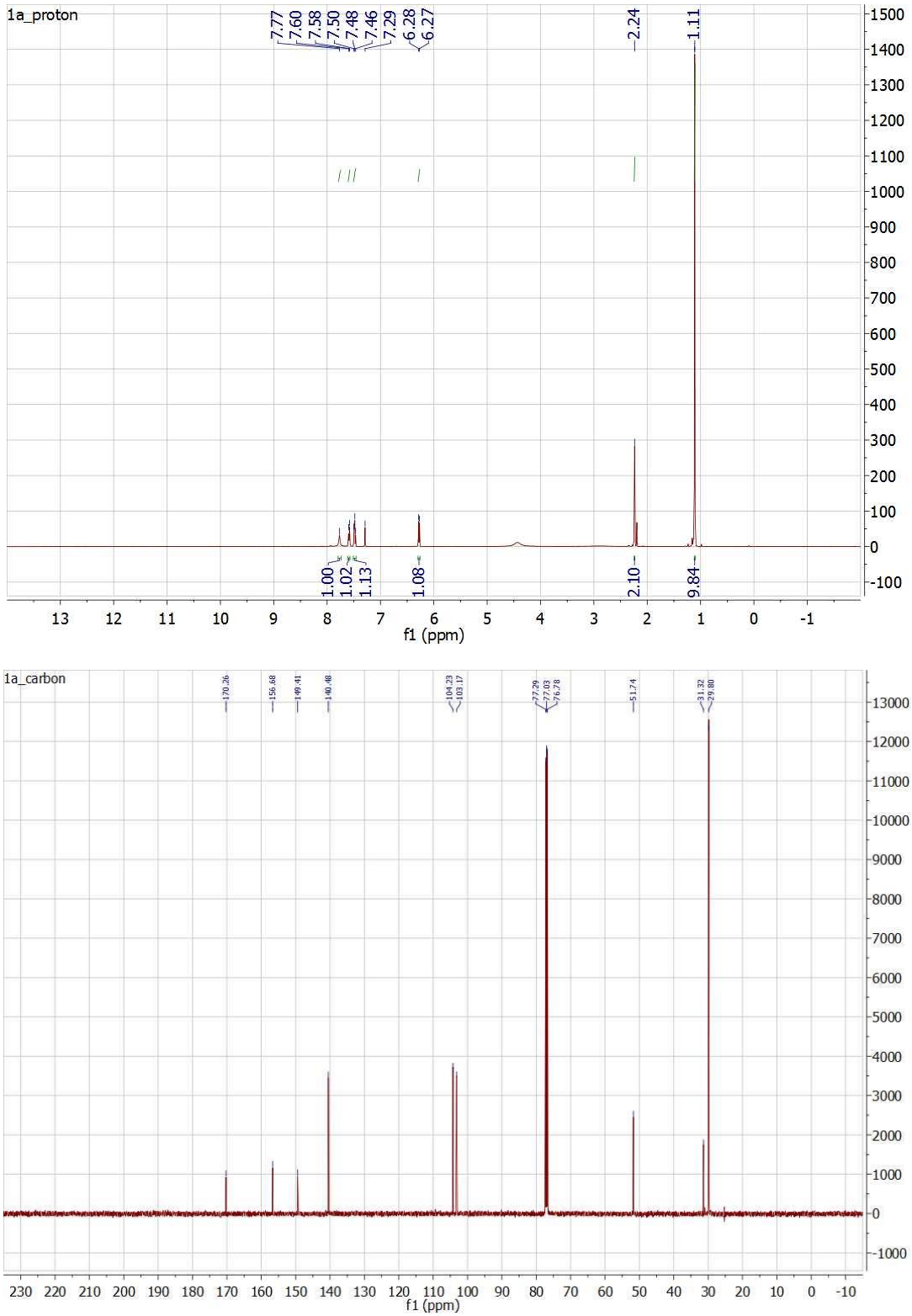


Figure B1. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **1a**.

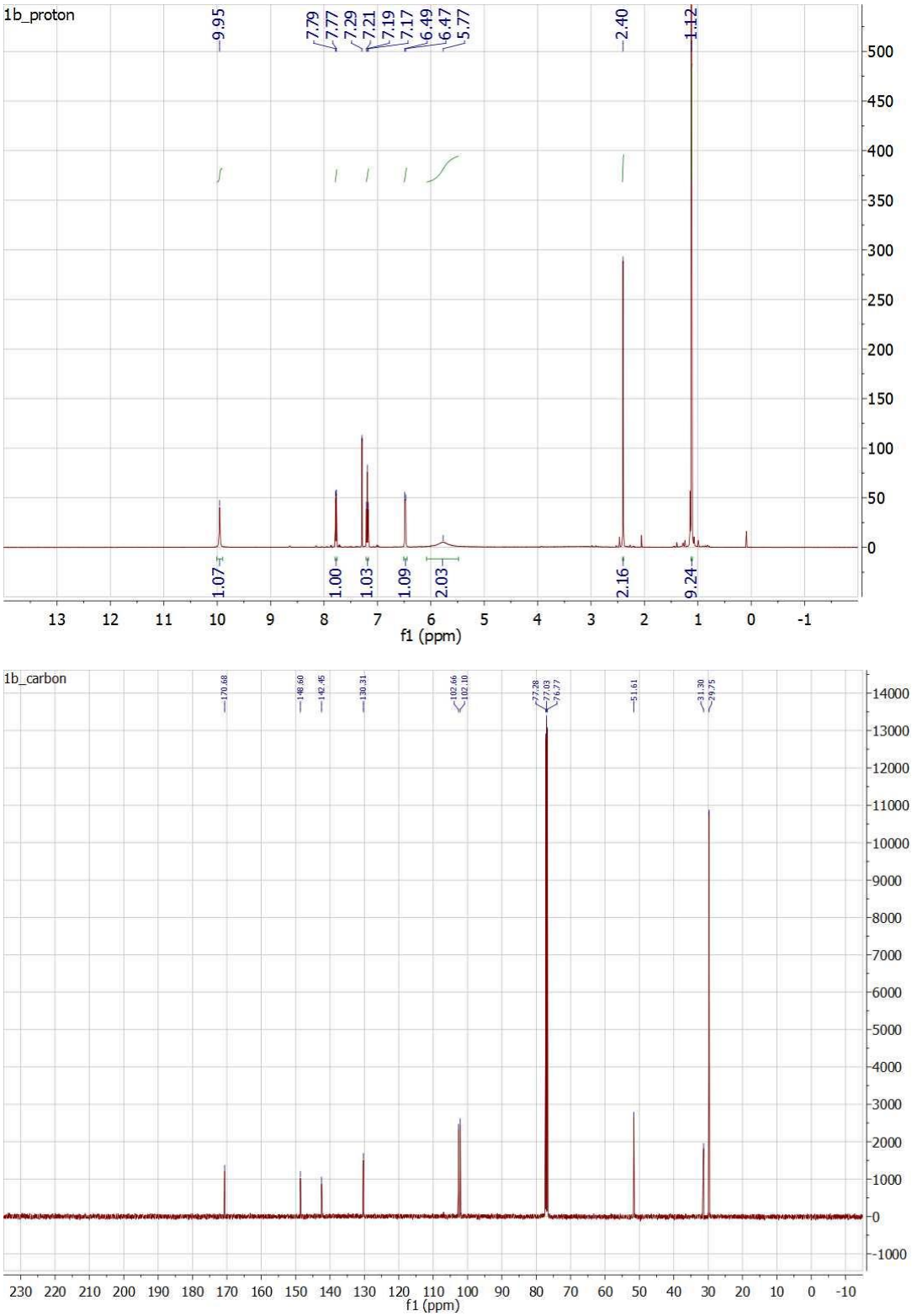


Figure B2. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **1b**.

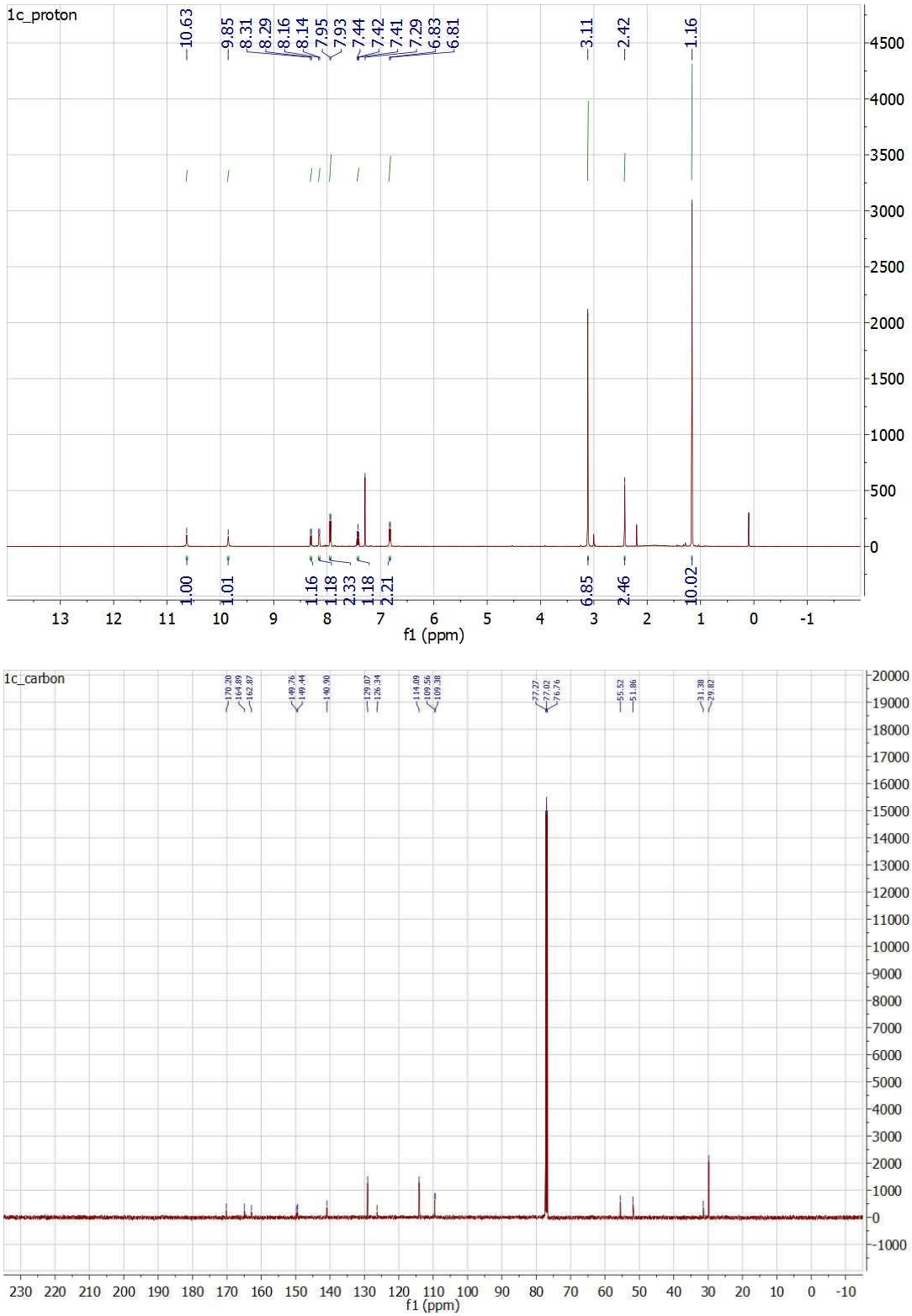


Figure B3. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **1c**.

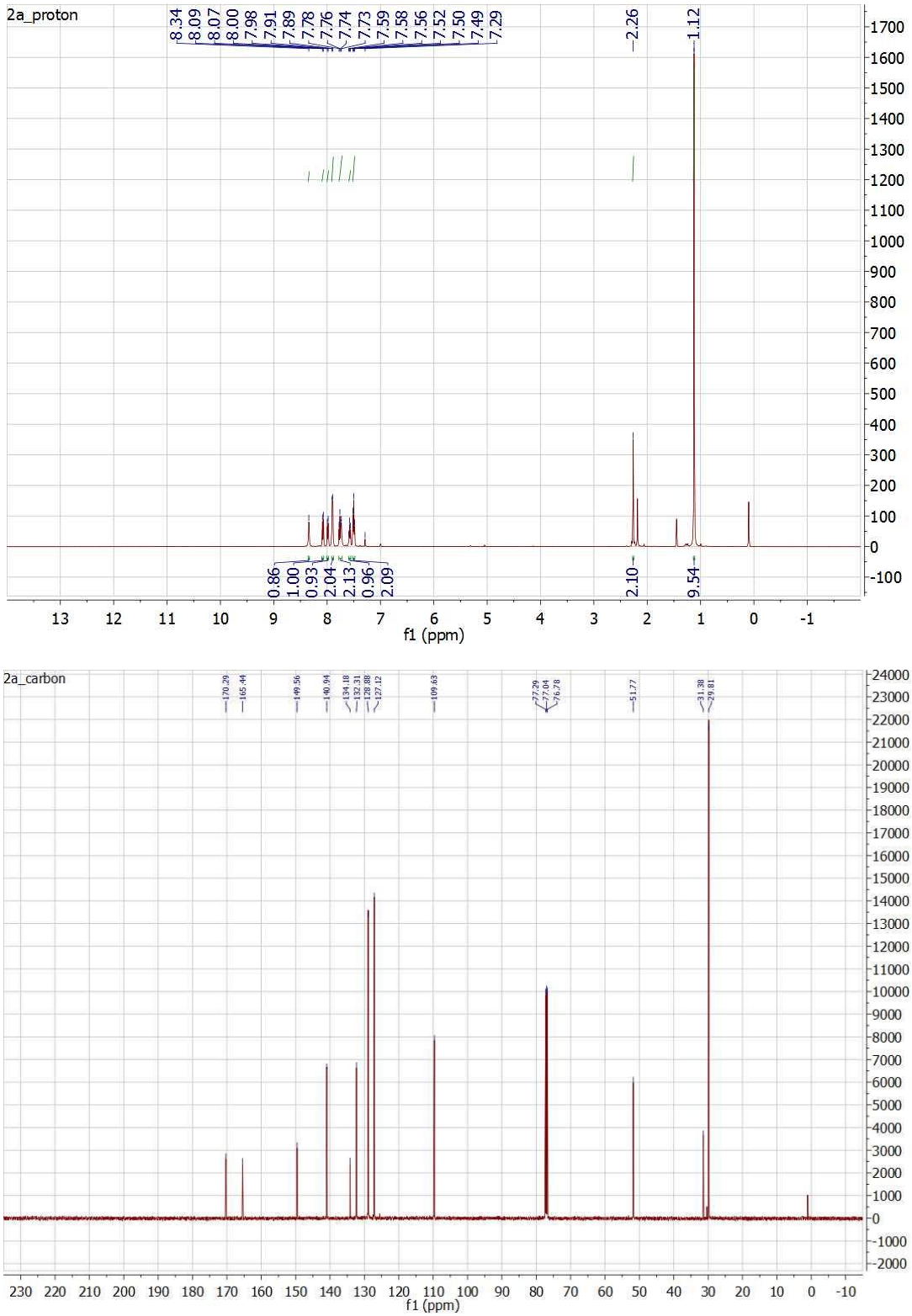


Figure B4. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **2a**.

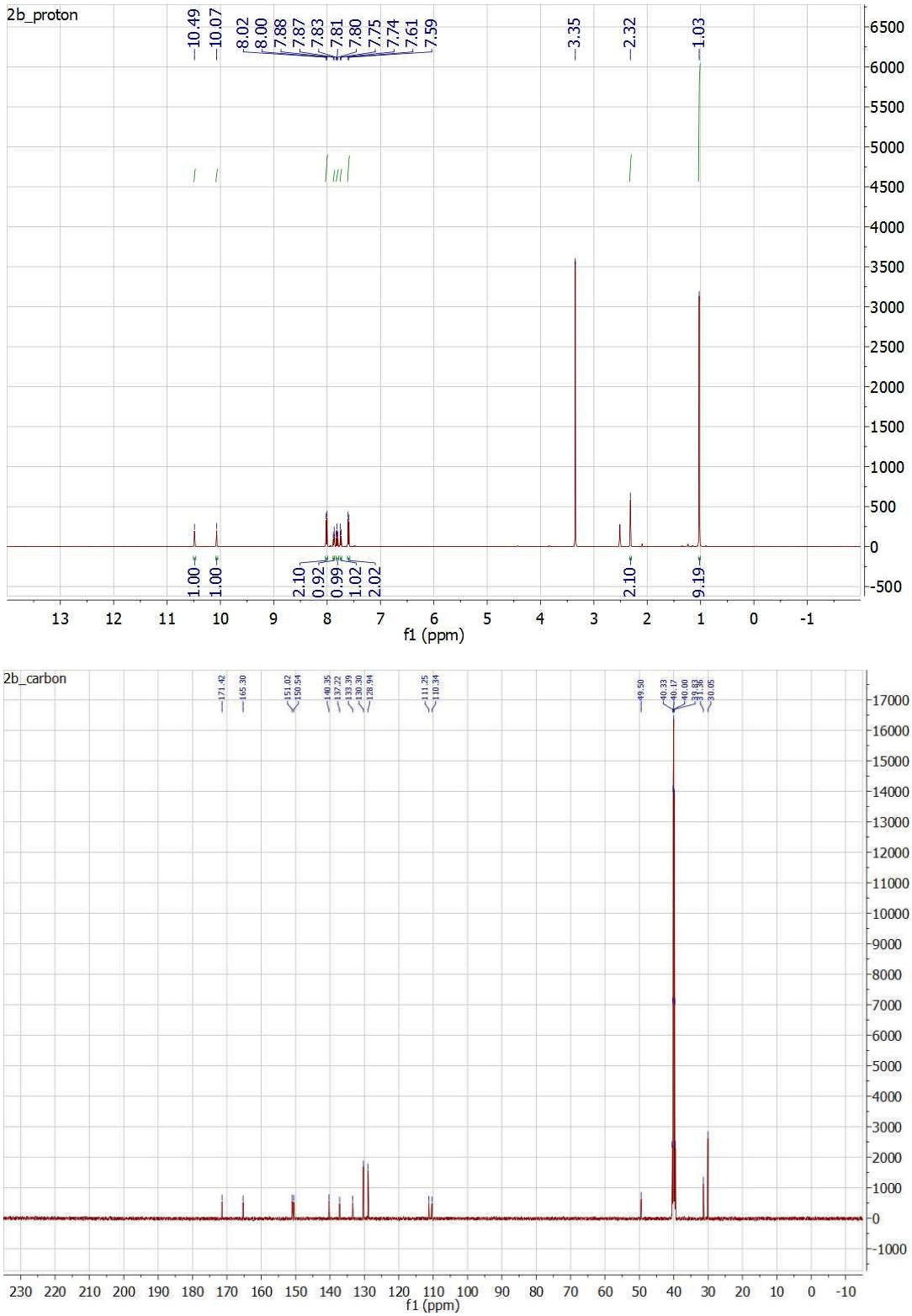


Figure B5. ^{1}H (500 MHz, DMSO) and $^{13}C\{^{1}H\}$ (125 MHz, DMSO) NMR spectra of **2b**.

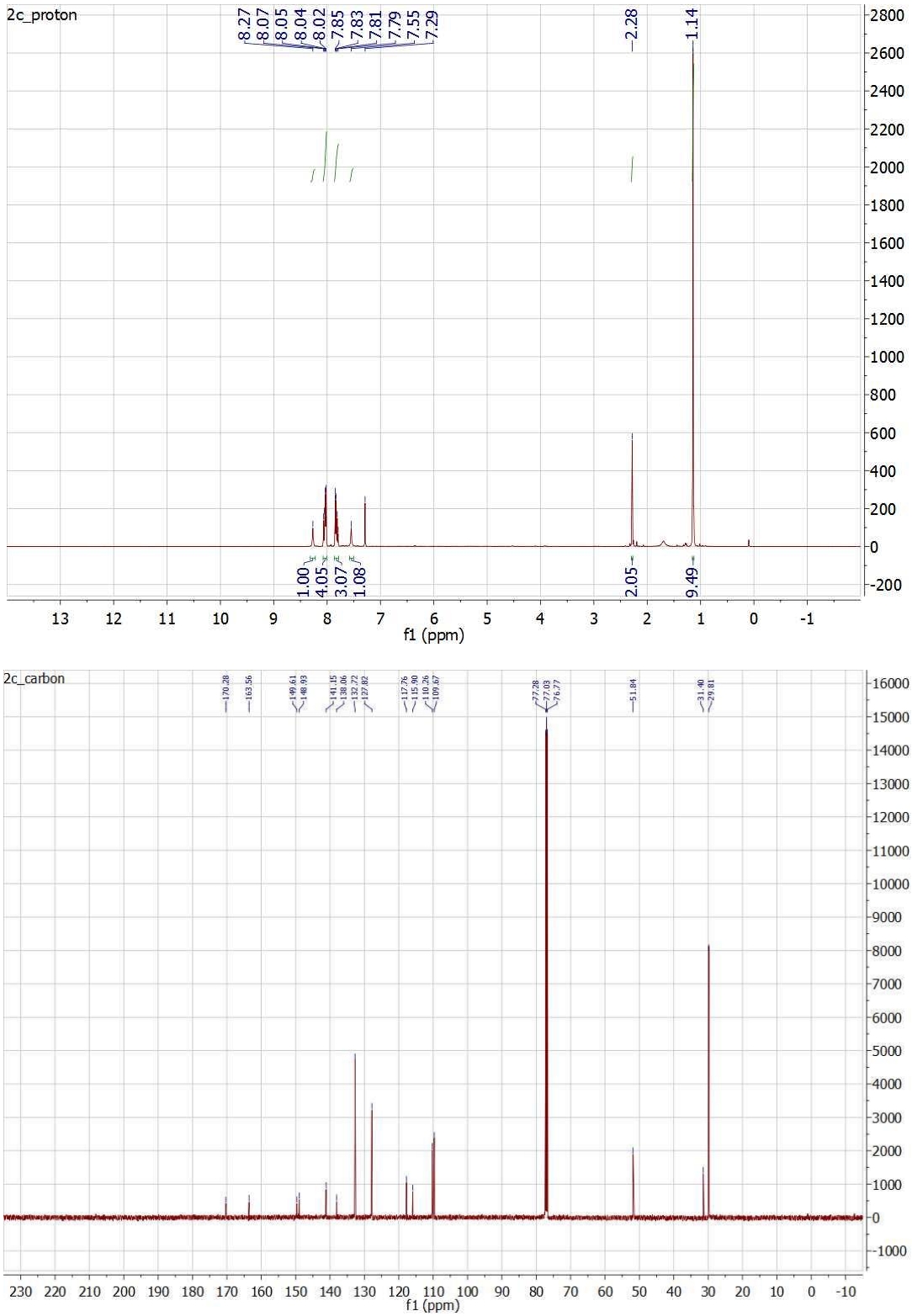


Figure B6. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **2c**.

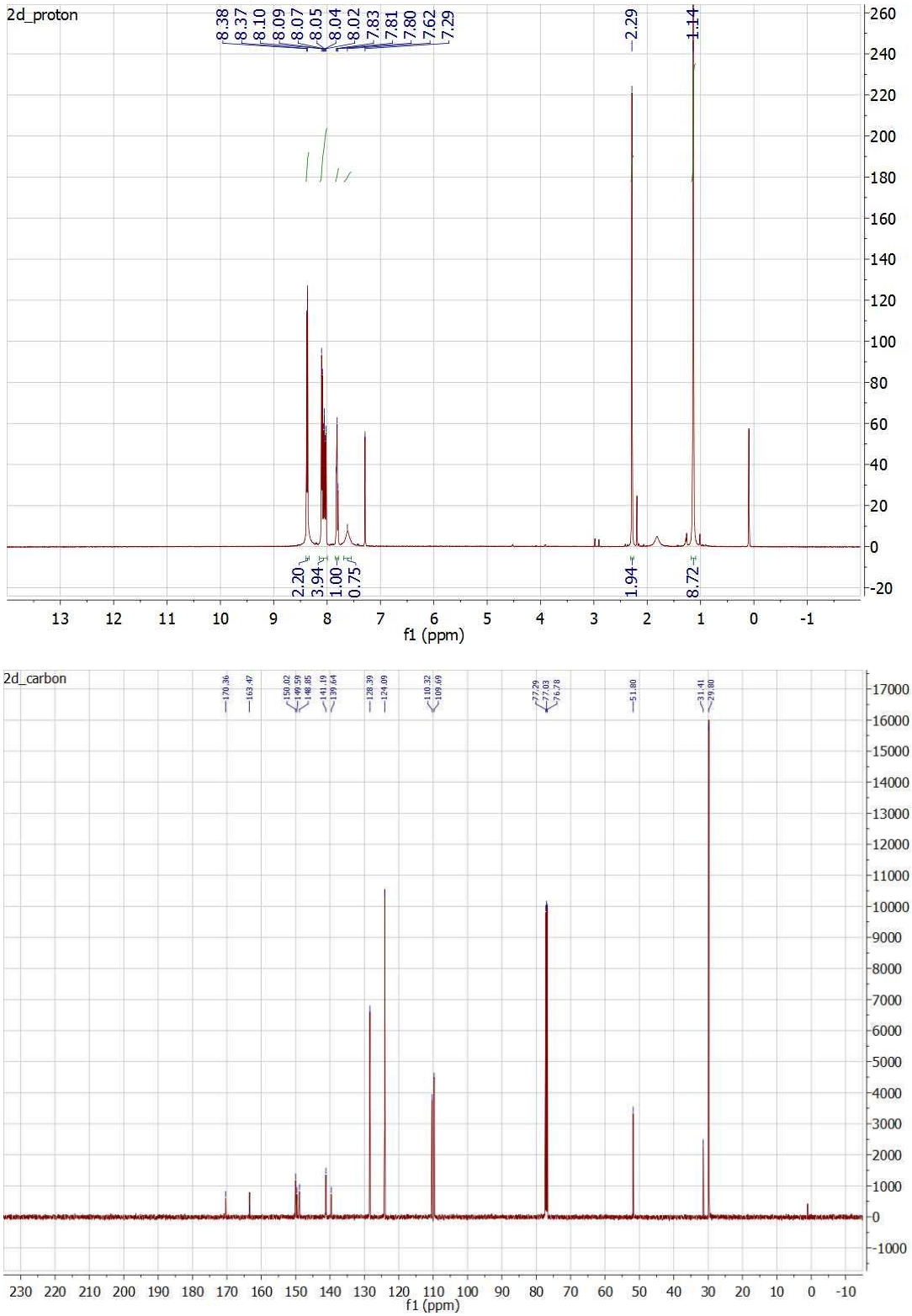


Figure B7. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **2d**.

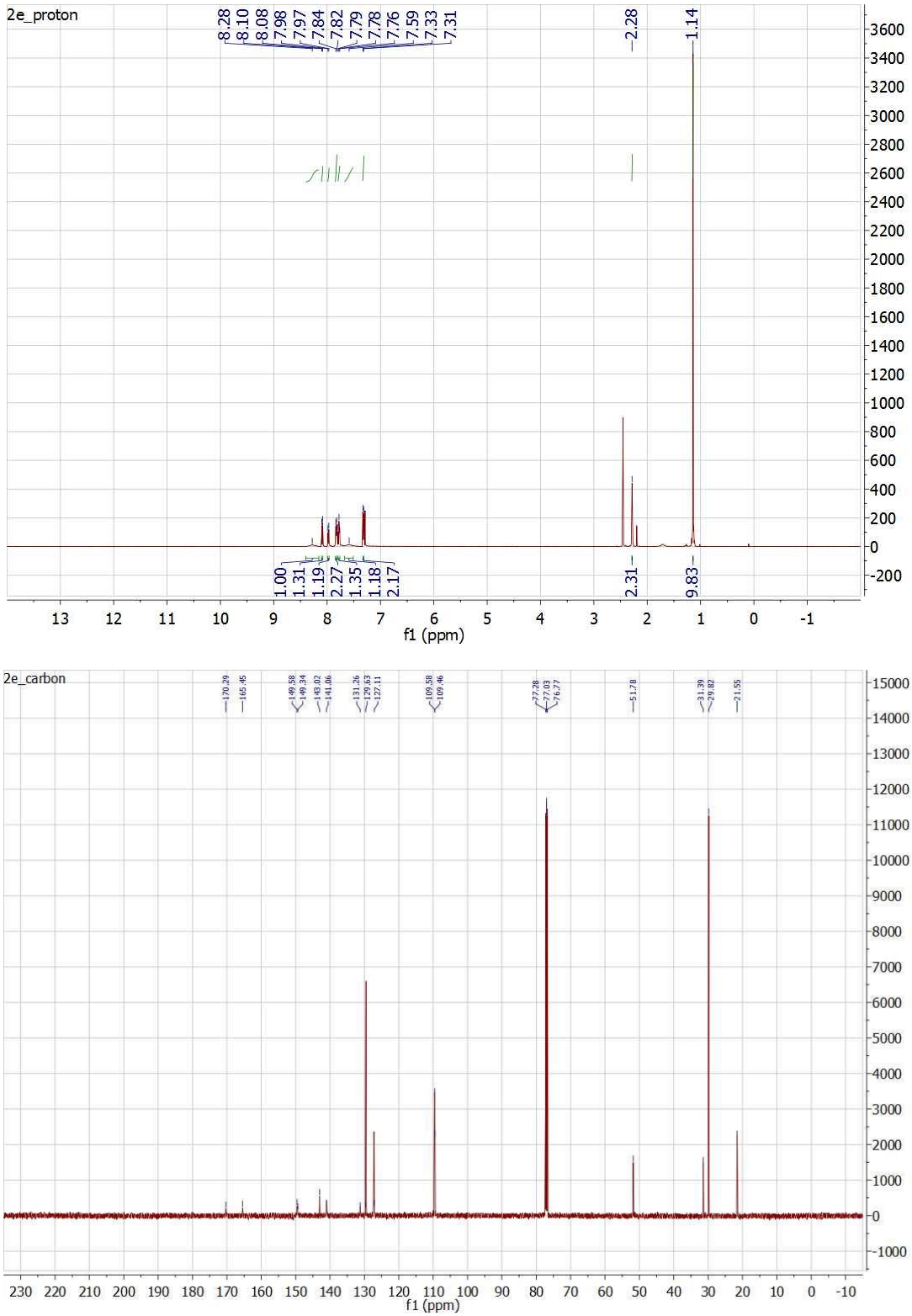


Figure B8. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **2e**.

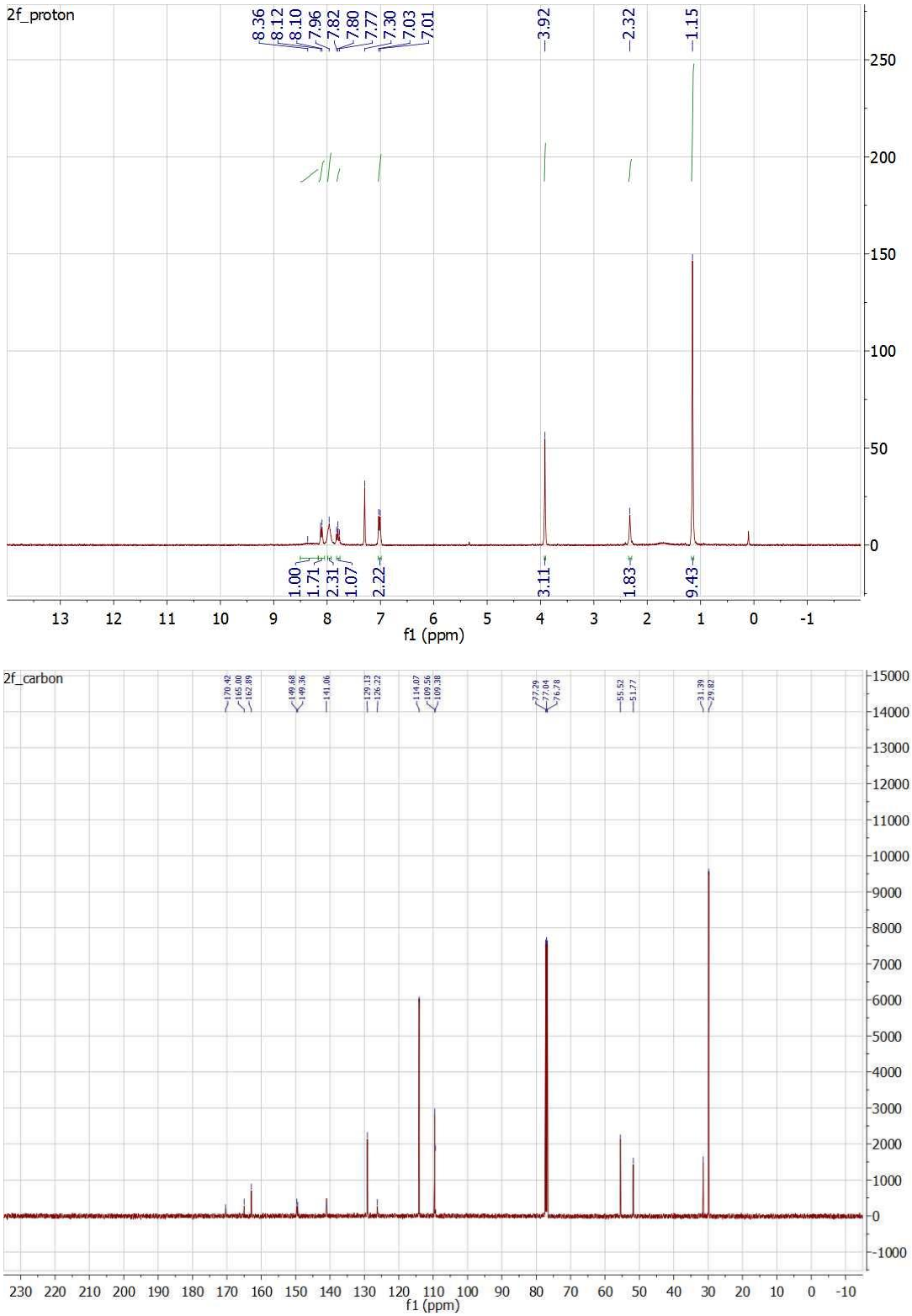


Figure B9. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **2f**.

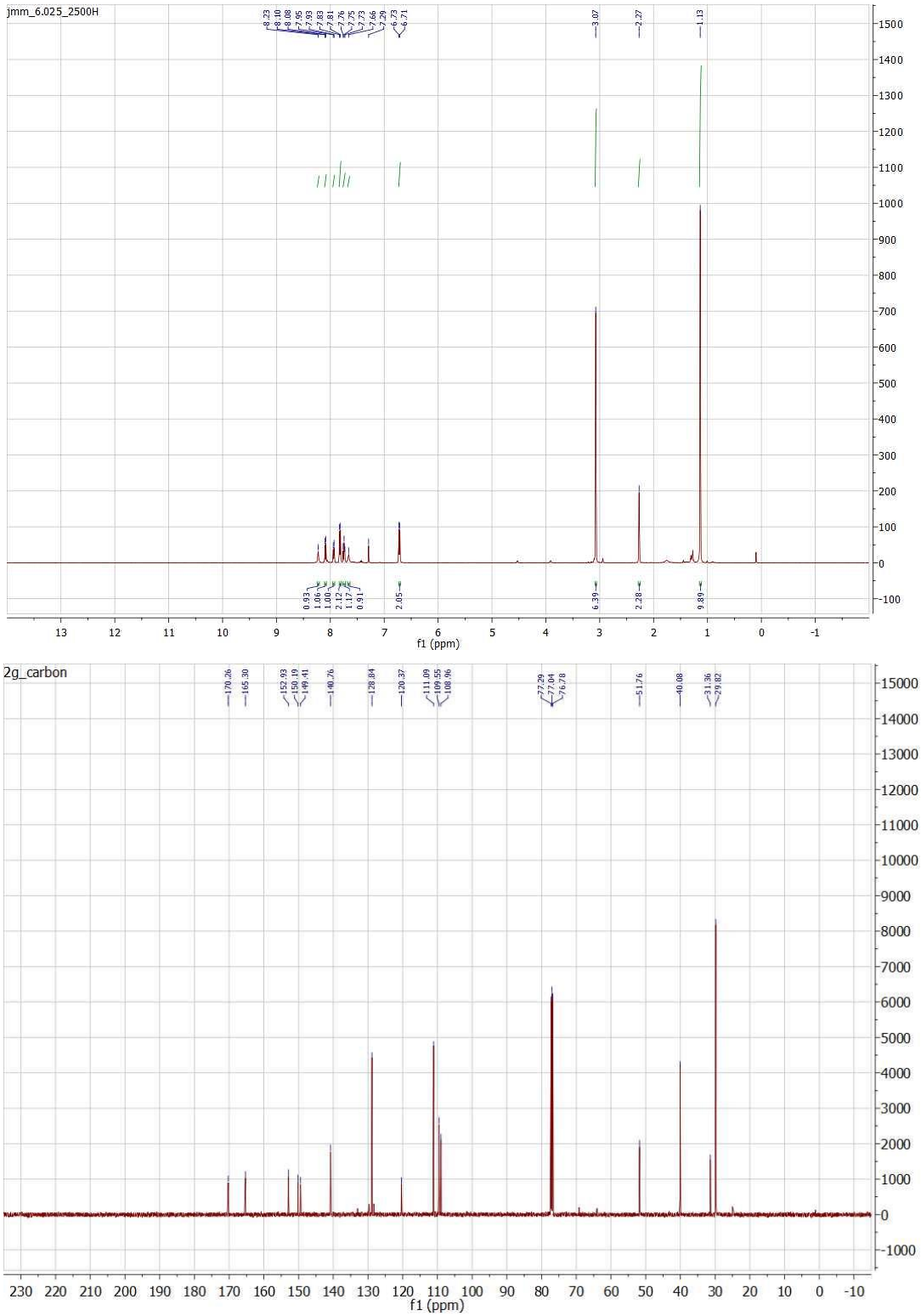


Figure B10. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **2g**.

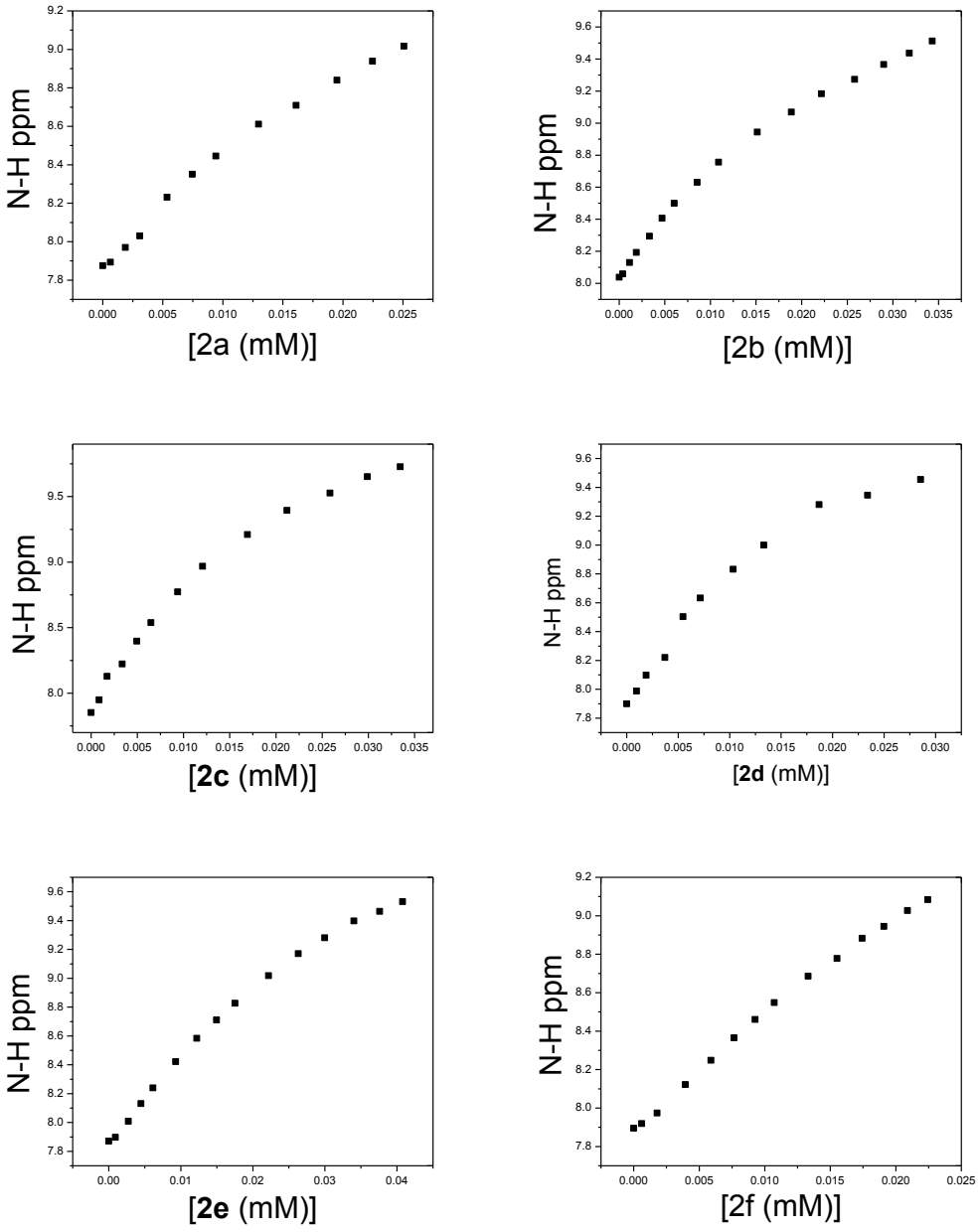


Figure B11. ^{1}H NMR (500 MHz, $CDCl_3$) titration data. Representative binding curves for hosts **2a-f** with **5**.

Calculated Geometries

Diethyl barbital

Sum of electronic and zero point energies: -646.9674167 Hartree
Lowest Frequency: 34.7 cm^{-1}
Coordinates: B3LYP/6-31+G(d,p) IEF-PCM $CHCl_3$

Atom	x	y	z
H	-1.89457700	-0.00259900	2.03104700
N	-1.35841700	-0.00201400	1.16878100
C	0.02232300	0.00064400	1.28614000
C	-2.10319000	-0.00487900	-0.00003300
C	0.85119500	0.00210000	-0.00003900
O	0.53956400	0.00187000	2.39282700
N	-1.35862900	-0.00469900	-1.16871700
O	-3.32340900	-0.00755700	0.00019500
C	0.02233300	-0.00203200	-1.28621000
C	1.75570700	1.27587500	-0.00135800
C	1.76530700	-1.26462000	0.00120400
H	-1.89473100	-0.00704800	-2.03094200
O	0.53928700	-0.00241500	-2.39292900
H	2.39809200	1.20683800	0.88129000
H	2.39754800	1.20545700	-0.88428700
H	2.40713700	-1.19093600	-0.88147500
H	2.40675900	-1.18942600	0.88403600
C	1.00972200	2.61449100	-0.00214600
H	1.72948100	3.43846400	-0.00266000
H	0.37831000	2.73235400	-0.88964500
H	0.37836200	2.73336000	0.88524600
C	1.02934200	-2.60881600	0.00222700
H	0.39910900	-2.73268500	-0.88527600
H	1.75519700	-3.42742700	0.00312200
H	0.39867000	-2.73112200	0.88963900

2a

Sum of electronic and zero point energies: -1013.047193 Hartree
Lowest Frequency: 20.7 cm^{-1}
Coordinates: B3LYP/6-31+G(d,p) IEF-PCM $CHCl_3$

Atom	x	y	z
N	0.045100	0.412300	-0.263000
C	-1.053800	1.152000	-0.060000
C	1.237000	1.023200	-0.312200
C	-1.019500	2.543700	0.106900
N	-2.226300	0.378800	-0.041700
C	1.392300	2.408800	-0.160600
N	2.295500	0.126600	-0.532200
C	0.232900	3.153800	0.050000
H	-1.929100	3.100400	0.273300
C	-3.528600	0.773500	0.161300
H	-2.042100	-0.609500	-0.156300
H	2.371700	2.860000	-0.208600

C	3.645100	0.374300	-0.662600
H	1.985300	-0.834000	-0.607400
H	0.306600	4.230100	0.173100
O	-3.845800	1.934200	0.427900
C	-4.555600	-0.317200	0.051100
O	4.125800	1.505900	-0.601100
C	4.497200	-0.865600	-0.892400
C	-5.765300	-0.138600	0.740600
C	-4.372000	-1.474400	-0.723600
H	3.866700	-1.701500	-1.216500
H	5.174700	-0.628300	-1.719700
C	-6.764000	-1.109900	0.676800
H	-5.906500	0.764200	1.324900
C	-5.377900	-2.440700	-0.794800
H	-3.465800	-1.619800	-1.304300
C	-6.572200	-2.264100	-0.090400
H	-7.691300	-0.966700	1.223100
H	-5.230500	-3.325500	-1.406500
H	-7.351600	-3.018300	-0.144100
C	5.347400	-1.331200	0.332700
C	4.440900	-1.591900	1.551600
H	3.949700	-0.675300	1.896300
H	3.662300	-2.328900	1.321100
H	5.031500	-1.983800	2.387100
C	6.044300	-2.645800	-0.073000
H	6.683200	-2.501000	-0.951900
H	6.675800	-3.012400	0.744200
H	5.313700	-3.428100	-0.310100
C	6.417500	-0.283100	0.693500
H	7.089000	-0.098900	-0.152900
H	5.968600	0.672600	0.975900
H	7.024300	-0.640800	1.533400

2b

Sum of electronic and zero point energies: -1472.650801 Hartree

Lowest Frequency: 14.0 cm^{-1}

Coordinates: B3LYP/6-31+G(d,p) IEF-PCM $CHCl_3$

Atom	x	y	z
N	0.829900	0.634000	-0.285200
C	-0.173800	1.497100	-0.077900
C	2.084200	1.102300	-0.342800
C	0.021600	2.875700	0.083900
N	-1.428800	0.864800	-0.051800
C	2.399300	2.461600	-0.198800
N	3.031700	0.089300	-0.561700
C	1.335900	3.336700	0.016000
H	-0.815700	3.534800	0.255900
C	-2.669400	1.404200	0.193000
H	-1.360900	-0.136900	-0.178300
H	3.424000	2.796300	-0.255200

C	4.401500	0.180300	-0.688800
H	2.614100	-0.830200	-0.629300
H	1.534500	4.397600	0.134000
O	-2.846300	2.587400	0.487400
C	-3.819500	0.443800	0.092100
O	5.007700	1.250300	-0.634100
C	5.109900	-1.149200	-0.904300
C	-4.980300	0.745600	0.819900
C	-3.799100	-0.706500	-0.711800
H	4.405000	-1.894600	-1.290700
H	5.861100	-0.974900	-1.681700
C	-6.092600	-0.091500	0.770700
H	-5.001200	1.642800	1.428700
C	-4.910100	-1.547900	-0.779800
H	-2.935300	-0.947400	-1.323700
C	-6.044600	-1.233900	-0.030900
H	-6.983600	0.139300	1.343800
H	-4.895600	-2.428600	-1.411900
C	5.822400	-1.744500	0.352700
C	4.810000	-1.978000	1.491000
H	4.373400	-1.038700	1.847100
H	3.991900	-2.633800	1.169100
H	5.302300	-2.457100	2.344400
C	6.429500	-3.097700	-0.070700
H	7.142800	-2.972700	-0.893500
H	6.963200	-3.557000	0.769000
H	5.653000	-3.798700	-0.398800
C	6.950200	-0.815500	0.840800
H	7.691600	-0.646700	0.051600
H	6.567200	0.160500	1.150600
H	7.464500	-1.269300	1.695800
Cl	-7.445200	-2.294000	-0.105200

2c

Sum of electronic and zero point energies: -1105.294665 Hartree

Lowest Frequency: 17.0 cm^{-1}

Coordinates: B3LYP/6-31+G(d,p) IEF-PCM $CHCl_3$

Atom	x	y	z
N	0.669300	0.600100	-0.287200
C	-0.342000	1.453400	-0.079800
C	1.918600	1.081400	-0.347200
C	-0.162600	2.833700	0.080100
N	-1.591900	0.807800	-0.053500
C	2.218600	2.444800	-0.205700
N	2.877000	0.079200	-0.564600
C	1.146800	3.308900	0.009700
H	-1.006400	3.484500	0.252000
C	-2.833700	1.334700	0.197700
H	-1.515000	-0.193300	-0.182700
H	3.239600	2.790300	-0.264400

C	4.245900	0.186600	-0.695000
H	2.470900	-0.845900	-0.627200
H	1.334300	4.372000	0.125900
O	-3.029500	2.512500	0.497200
C	-3.976100	0.359300	0.094200
O	4.837800	1.264800	-0.649700
C	4.970300	-1.135600	-0.900800
C	-3.961900	-0.746300	-0.770400
C	-5.112800	0.610200	0.877400
H	4.272700	-1.894700	-1.273400
H	5.713800	-0.960900	-1.685500
C	-5.060000	-1.599700	-0.842100
H	-3.113600	-0.934900	-1.420600
C	-6.210300	-0.241800	0.823900
H	-5.123500	1.477300	1.528100
C	-6.185600	-1.353200	-0.038000
H	-5.051600	-2.446800	-1.519000
H	-7.082500	-0.053100	1.440100
C	5.698600	-1.706900	0.358300
C	4.698200	-1.930700	1.509100
H	4.257800	-0.989200	1.854900
H	3.882000	-2.597100	1.204900
H	5.202000	-2.392900	2.365100
C	6.312100	-3.061600	-0.050800
H	7.015800	-2.943500	-0.882900
H	6.858300	-3.503600	0.790100
H	5.537900	-3.773700	-0.359800
C	6.823900	-0.762700	0.822700
H	7.556800	-0.599900	0.024300
H	6.436300	0.214800	1.122100
H	7.349000	-1.200600	1.679200
C	-7.315400	-2.235800	-0.101700
N	-8.231000	-2.952900	-0.151800

2d

Sum of electronic and zero point energies: -1217.554891 Hartree

Lowest Frequency: 14.9 cm^{-1}

Coordinates: B3LYP/6-31+G(d,p) IEF-PCM $CHCl_3$

Atom	x	y	z
N	1.089300	0.666300	-0.287500
C	0.114500	1.565000	-0.099600
C	2.357600	1.094100	-0.354900
C	0.349900	2.939600	0.032700
N	-1.161700	0.972100	-0.062700
C	2.713200	2.446700	-0.239800
N	3.274300	0.049500	-0.550900
C	1.678100	3.358600	-0.044100
H	-0.466600	3.628000	0.189100
C	-2.379900	1.556700	0.170100
H	-1.126200	-0.034000	-0.171000

H	3.747500	2.748800	-0.303000
C	4.646000	0.100500	-0.688300
H	2.831200	-0.859600	-0.596000
H	1.909500	4.415100	0.051100
O	-2.530300	2.748600	0.437300
C	-3.563200	0.627400	0.088500
O	5.279800	1.155200	-0.665400
C	5.317900	-1.252100	-0.872400
C	-4.682000	0.937800	0.876700
C	-3.601300	-0.487400	-0.764000
H	4.588100	-1.993400	-1.218200
H	6.056300	-1.122900	-1.670700
C	-5.817600	0.135400	0.840400
H	-4.650400	1.812000	1.516700
C	-4.735700	-1.294300	-0.819700
H	-2.766100	-0.720000	-1.416400
C	-5.824100	-0.972200	-0.009400
H	-6.682700	0.357000	1.452100
H	-4.783000	-2.150500	-1.480200
C	6.041900	-1.821000	0.390200
C	5.047300	-1.987200	1.555600
H	4.641800	-1.024600	1.885600
H	4.206000	-2.632000	1.274000
H	5.544600	-2.447800	2.416200
C	6.606000	-3.203300	0.002700
H	7.308700	-3.123600	-0.834800
H	7.141900	-3.648500	0.848500
H	5.806600	-3.894200	-0.289800
C	7.203100	-0.906000	0.823200
H	7.930800	-0.782600	0.013200
H	6.851500	0.089000	1.108700
H	7.724100	-1.345400	1.681500
N	-7.021900	-1.824600	-0.058700
O	-7.008100	-2.801600	-0.811600
O	-7.979300	-1.520100	0.656400

2e

Sum of electronic and zero point energies: -1052.34178 Hartree

Lowest Frequency: 15.5 cm^{-1}

Coordinates: B3LYP/6-31+G(d,p) IEF-PCM $CHCl_3$

Atom	x	y	z
N	0.457100	0.549600	-0.284800
C	-0.588400	1.361000	-0.072800
C	1.687000	1.079000	-0.340300
C	-0.458500	2.747200	0.095500
N	-1.810000	0.669800	-0.047700
C	1.936600	2.450700	-0.189400
N	2.682100	0.113100	-0.563900
C	0.831400	3.271800	0.030000
H	-1.327300	3.363400	0.270700

C	-3.079200	1.147800	0.191900
H	-1.695600	-0.327100	-0.177100
H	2.944000	2.834500	-0.243700
C	4.045900	0.268200	-0.688300
H	2.308400	-0.824800	-0.635700
H	0.978100	4.340600	0.153500
O	-3.308400	2.322400	0.488700
C	-4.178000	0.134000	0.082000
O	4.601800	1.365200	-0.631400
C	4.814800	-1.027500	-0.903100
C	-5.368200	0.380600	0.786000
C	-4.090300	-1.023900	-0.705200
H	4.141200	-1.809400	-1.272400
H	5.546400	-0.826100	-1.692600
C	-6.428600	-0.517900	0.720600
H	-5.444900	1.280800	1.386300
C	-5.162900	-1.915300	-0.774600
H	-3.205100	-1.230000	-1.300000
C	-6.347200	-1.683600	-0.061200
H	-7.336000	-0.313700	1.283300
H	-5.078300	-2.799900	-1.399900
C	5.570500	-1.576200	0.349700
C	4.588300	-1.820700	1.511900
H	4.127200	-0.889200	1.858000
H	3.786100	-2.509200	1.219700
H	5.113000	-2.265500	2.364600
C	6.213400	-2.916500	-0.061400
H	6.903600	-2.784200	-0.902600
H	6.780800	-3.341200	0.774400
H	5.453600	-3.649100	-0.358200
C	6.676700	-0.602400	0.799000
H	7.396900	-0.424600	-0.007700
H	6.267500	0.365900	1.098900
H	7.221400	-1.023900	1.651600
C	-7.509600	-2.643800	-0.136000
H	-7.817700	-2.969300	0.863800
H	-8.380700	-2.169000	-0.602600
H	-7.257600	-3.532400	-0.720600

2f

Sum of electronic and zero point energies: -1127.547005 Hartree

Lowest Frequency: 12.4 cm^{-1}

Coordinates: B3LYP/6-31+G(d,p) IEF-PCM $CHCl_3$

Atom	x	y	z
N	0.860900	0.609600	-0.281000
C	-0.156000	1.457000	-0.068900
C	2.110300	1.093000	-0.318400
C	0.025000	2.835400	0.118600
N	-1.402400	0.812300	-0.066600
C	2.410000	2.452200	-0.147800

N	3.070800	0.093400	-0.546500
C	1.334200	3.311500	0.071800
H	-0.821500	3.481700	0.293600
C	-2.656400	1.336000	0.165900
H	-1.322000	-0.185600	-0.210800
H	3.431500	2.798600	-0.188500
C	4.439800	0.200500	-0.663600
H	2.663100	-0.828900	-0.633700
H	1.519800	4.372400	0.210400
O	-2.837500	2.515700	0.479100
C	-3.793200	0.374500	0.028300
O	5.035300	1.275400	-0.585800
C	5.162400	-1.118000	-0.900000
C	-3.732400	-0.816900	-0.720900
C	-4.999000	0.697700	0.665200
H	4.462700	-1.867800	-1.287000
H	5.903900	-0.927500	-1.683000
C	-4.834700	-1.655400	-0.816300
H	-2.835600	-1.089400	-1.269200
C	-6.111700	-0.138800	0.586400
H	-5.057900	1.619500	1.233700
C	-6.032300	-1.326000	-0.158000
H	-4.793500	-2.566100	-1.404600
H	-7.023000	0.140000	1.100700
C	5.893700	-1.717500	0.343900
C	4.897900	-1.955800	1.495800
H	4.466400	-1.017700	1.861600
H	4.074900	-2.609900	1.183400
H	5.402600	-2.438100	2.340200
C	6.495700	-3.068600	-0.093500
H	7.195100	-2.940000	-0.927600
H	7.043800	-3.529800	0.735800
H	5.714800	-3.769600	-0.411200
C	7.028100	-0.789800	0.819100
H	7.759100	-0.620000	0.020300
H	6.649000	0.185700	1.135300
H	7.553400	-1.245400	1.666300
O	-7.052900	-2.211600	-0.306700
C	-8.307400	-1.931800	0.322600
H	-8.958900	-2.765300	0.061600
H	-8.198600	-1.878200	1.411300
H	-8.737600	-0.997600	-0.054800

2a-Barbital

Sum of electronic and zero point energies: -1660.226464 Hartree

Lowest Frequency: 8.7 cm^{-1}

Coordinates: B3LYP/6-31+G(d,p) IEF-PCM $CHCl_3$

Atom	x	y	z
N	-0.595500	1.673200	-0.307100
C	0.378700	2.601900	-0.311000

C	-1.873000	2.075800	-0.478600
C	0.124500	3.967800	-0.488100
N	1.690000	2.106500	-0.175500
C	-2.223400	3.419100	-0.669300
N	-2.822800	1.044000	-0.410300
C	-1.197100	4.360000	-0.670400
H	0.935100	4.681300	-0.481000
C	2.746200	2.785800	0.399200
H	1.834200	1.130300	-0.438300
H	-3.256900	3.695200	-0.810300
C	-4.144200	1.078800	-0.811800
H	-2.496300	0.170700	0.002400
H	-1.431900	5.410100	-0.815300
O	2.615300	3.871900	0.966800
C	4.087400	2.122000	0.301600
O	-4.658100	2.059300	-1.351800
C	-4.924900	-0.198400	-0.542300
C	4.473000	1.350300	-0.804700
C	5.006700	2.350900	1.338100
H	-5.481200	-0.420500	-1.459600
H	-4.237200	-1.029000	-0.357800
C	5.759700	0.809500	-0.867400
H	3.784000	1.183200	-1.625200
C	6.284100	1.795100	1.281300
H	4.706700	2.965500	2.180300
C	6.663900	1.024100	0.176300
H	6.054900	0.224500	-1.733300
H	6.984700	1.967000	2.092900
H	7.662000	0.598700	0.127100
C	-5.938200	-0.121900	0.645800
C	-7.069500	0.880700	0.349400
H	-6.686300	1.896000	0.218500
H	-7.609300	0.607600	-0.564800
H	-7.789000	0.887900	1.176500
C	-6.545100	-1.530200	0.812100
H	-5.774600	-2.269800	1.058900
H	-7.286900	-1.534300	1.619000
H	-7.047300	-1.855900	-0.106400
C	-5.216500	0.276200	1.948400
H	-4.394100	-0.411800	2.174200
H	-4.804700	1.289900	1.890100
H	-5.916300	0.253200	2.791400
H	-0.166000	-0.228000	-0.123700
N	0.065700	-1.237900	-0.033300
C	1.324400	-1.638600	-0.422200
C	-0.928000	-2.050400	0.467900
C	1.703200	-3.113400	-0.296000
O	2.116800	-0.808500	-0.857700
N	-0.608400	-3.386300	0.609700
O	-2.035100	-1.613500	0.767100
C	0.593500	-3.995600	0.277900

C	2.080300	-3.652800	-1.713000
C	2.953100	-3.224000	0.635200
H	-1.342700	-3.981700	0.980500
O	0.733900	-5.196100	0.445800
H	2.930700	-3.058600	-2.059500
H	2.428500	-4.680400	-1.575100
C	0.955400	-3.615900	-2.753000
H	3.246900	-4.277600	0.642100
H	3.755700	-2.658800	0.153300
C	2.751500	-2.726300	2.070600
H	1.319200	-4.014100	-3.704800
H	0.097200	-4.226300	-2.451300
H	0.601900	-2.596000	-2.940100
H	3.680600	-2.845500	2.635700
H	2.484500	-1.664500	2.103700
H	1.974800	-3.291700	2.597100

2b-barbital

Sum of electronic and zero point energies: -2119.83084 Hartree

Lowest Frequency: 6.8 cm^{-1}

Coordinates: B3LYP/6-31+G(d,p) IEF-PCM $CHCl_3$

Atom	x	y	z
N	-1.051700	-1.670500	0.309300
C	-0.065800	-2.586700	0.313500
C	-2.324400	-2.090400	0.475700
C	-0.301500	-3.956100	0.485800
N	1.239400	-2.072000	0.183700
C	-2.657100	-3.439300	0.660700
N	-3.287500	-1.071500	0.409300
C	-1.618700	-4.366400	0.662200
H	0.518300	-4.658900	0.479400
C	2.307700	-2.736500	-0.382500
H	1.366200	-1.091900	0.442300
H	-3.687300	-3.729600	0.797300
C	-4.610700	-1.127000	0.803800
H	-2.971200	-0.190700	0.004800
H	-1.840000	-5.419900	0.802800
O	2.201200	-3.826600	-0.946900
C	3.638500	-2.052100	-0.280500
O	-5.113700	-2.118200	1.334100
C	-5.407100	0.141500	0.539400
C	4.006200	-1.257300	0.814300
C	4.572000	-2.285200	-1.302300
H	-5.971200	0.349400	1.455300
H	-4.729700	0.982500	0.364600
C	5.281900	-0.695400	0.886900
H	3.312100	-1.081100	1.628000
C	5.842300	-1.716100	-1.251300
H	4.293200	-2.917300	-2.138400
C	6.183700	-0.925300	-0.151600

H	5.569400	-0.091300	1.740000
H	6.558000	-1.887100	-2.047600
C	-6.413200	0.059700	-0.654600
C	-7.533700	-0.958200	-0.369600
H	-7.138900	-1.969400	-0.242200
H	-8.081600	-0.696600	0.543100
H	-8.248800	-0.969600	-1.200600
C	-7.036100	1.461600	-0.815900
H	-6.273500	2.211500	-1.055400
H	-7.774300	1.461200	-1.626000
H	-7.546200	1.776300	0.102100
C	-5.679800	-0.321900	-1.955600
H	-4.864800	0.377400	-2.173000
H	-5.256000	-1.330900	-1.901100
H	-6.375400	-0.302600	-2.802100
Cl	7.789900	-0.210900	-0.071200
H	-0.645700	0.239400	0.128700
N	-0.425400	1.251800	0.040100
C	0.831800	1.664600	0.419300
C	-1.431800	2.055300	-0.451600
C	1.193800	3.143400	0.296100
O	1.637200	0.840700	0.844100
N	-1.128300	3.395000	-0.589500
O	-2.535100	1.606200	-0.745800
C	0.069100	4.016200	-0.263000
C	1.580300	3.680700	1.711400
C	2.432700	3.271600	-0.647800
H	-1.872000	3.984000	-0.951800
O	0.194500	5.219100	-0.424800
H	2.442900	3.096700	2.044600
H	1.912700	4.713600	1.574700
C	0.468700	3.623000	2.764800
H	2.714500	4.328400	-0.653400
H	3.246900	2.714000	-0.176300
C	2.221900	2.777400	-2.083000
H	0.838900	4.021400	3.714100
H	-0.401500	4.223100	2.477100
H	0.131600	2.597500	2.951100
H	3.144000	2.908700	-2.656800
H	1.965400	1.713000	-2.118000
H	1.434200	3.336800	-2.599500

2c-barbital

Sum of electronic and zero point energies: -1752.474457 Hartree

Lowest Frequency: 7.0 cm^{-1}

Coordinates: B3LYP/6-31+G(d,p) IEF-PCM $CHCl_3$

Atom	x	y	z
N	-0.973200	-1.674800	0.307200
C	-0.001500	-2.605600	0.320800
C	-2.252000	-2.074800	0.473900

C	-0.255700	-3.969800	0.502600
N	1.311500	-2.107900	0.188400
C	-2.604000	-3.418100	0.668000
N	-3.200600	-1.043500	0.399600
C	-1.579600	-4.359800	0.678900
H	0.554000	-4.684200	0.503500
C	2.373400	-2.792400	-0.357500
H	1.448600	-1.125100	0.433600
H	-3.638500	-3.692600	0.804400
C	-4.525800	-1.079500	0.791800
H	-2.870600	-0.167300	-0.004000
H	-1.816300	-5.409000	0.826500
O	2.272900	-3.899200	-0.887600
C	3.709800	-2.106300	-0.278400
O	-5.042700	-2.061900	1.324700
C	-5.304900	0.198000	0.520600
C	4.095000	-1.324200	0.819700
C	4.619000	-2.332500	-1.323600
H	-5.868100	0.416600	1.434400
H	-4.616300	1.029500	0.343800
C	5.369500	-0.764400	0.871300
H	3.413300	-1.158600	1.645500
C	5.887100	-1.764100	-1.291700
H	4.320500	-2.958000	-2.157500
C	6.266400	-0.976500	-0.189000
H	5.671200	-0.168600	1.725700
H	6.584400	-1.928400	-2.105900
C	-6.309400	0.124100	-0.675300
C	-7.442500	-0.879600	-0.389700
H	-7.059900	-1.895100	-0.258100
H	-7.989400	-0.608600	0.520800
H	-8.155500	-0.885400	-1.222300
C	-6.915300	1.532700	-0.842300
H	-6.143400	2.273100	-1.081800
H	-7.651500	1.538700	-1.654300
H	-7.424100	1.856000	0.073500
C	-5.577700	-0.270200	-1.973500
H	-4.753200	0.418100	-2.190500
H	-5.167000	-1.284500	-1.915400
H	-6.270700	-0.244100	-2.821800
C	7.576000	-0.391400	-0.144700
N	8.637400	0.085800	-0.110400
H	-0.538100	0.234100	0.115400
N	-0.303400	1.243100	0.033800
C	0.961300	1.634200	0.409500
C	-1.301800	2.065500	-0.444000
C	1.338900	3.110700	0.311900
O	1.760100	0.793400	0.814300
N	-0.981300	3.402300	-0.567500
O	-2.411500	1.633200	-0.738700
C	0.225400	4.004000	-0.237500

C	1.720400	3.620200	1.739300
C	2.584300	3.243100	-0.621900
H	-1.718000	4.005200	-0.921200
O	0.366700	5.206500	-0.387000
H	2.577600	3.025100	2.067300
H	2.060200	4.653200	1.622400
C	0.602500	3.551100	2.785300
H	2.876200	4.297100	-0.608500
H	3.390700	2.670400	-0.155500
C	2.376300	2.774800	-2.066300
H	0.969700	3.931500	3.743100
H	-0.262900	4.160800	2.503500
H	0.258600	2.524600	2.952700
H	3.302400	2.906700	-2.633500
H	2.109200	1.713700	-2.120300
H	1.596700	3.350400	-2.577100

2d-barbital

Sum of electronic and zero point energies: -1864.735918 Hartree

Lowest Frequency: 3.7 cm^{-1}

Coordinates: B3LYP/6-31+G(d,p) IEF-PCM $CHCl_3$

Atom	x	y	z
N	-1.234000	-1.681600	0.299200
C	-0.258500	-2.608900	0.302500
C	-2.511500	-2.089400	0.455800
C	-0.507300	-3.976800	0.462100
N	1.052300	-2.101300	0.183500
C	-2.858500	-3.437300	0.627500
N	-3.464800	-1.061600	0.396700
C	-1.830500	-4.374700	0.627200
H	0.305100	-4.687800	0.454900
C	2.128900	-2.777900	-0.340000
H	1.178400	-1.116000	0.426100
H	-3.892300	-3.718100	0.756200
C	-4.788900	-1.109100	0.792000
H	-3.139600	-0.177700	0.006300
H	-2.063400	-5.427000	0.757200
O	2.055100	-3.891600	-0.859100
C	3.455600	-2.071900	-0.248900
O	-5.300500	-2.102000	1.310100
C	-5.573100	0.170100	0.544600
C	3.823800	-1.301100	0.863200
C	4.371200	-2.270200	-1.294700
H	-6.132700	0.372400	1.464500
H	-4.887900	1.006400	0.378200
C	5.089200	-0.721500	0.929400
H	3.136000	-1.158300	1.688000
C	5.631400	-1.683700	-1.250900
H	4.086100	-2.887700	-2.138800
C	5.969700	-0.915900	-0.134200

H	5.391400	-0.132000	1.785500
H	6.342900	-1.817300	-2.055700
C	-6.583100	0.112400	-0.647500
C	-7.712400	-0.898500	-0.372200
H	-7.326900	-1.915000	-0.258400
H	-8.255500	-0.643200	0.545100
H	-8.429600	-0.893000	-1.201300
C	-7.193200	1.521900	-0.789500
H	-6.424100	2.267700	-1.021200
H	-7.933300	1.538800	-1.597700
H	-7.698100	1.829700	0.133700
C	-5.856700	-0.259600	-1.955200
H	-5.034500	0.433800	-2.164700
H	-5.444000	-1.273900	-1.915400
H	-6.553700	-0.221000	-2.799800
N	7.301200	-0.295200	-0.074900
O	8.071000	-0.480600	-1.020900
O	7.582700	0.382900	0.916900
H	-0.809100	0.235700	0.113400
N	-0.578400	1.245000	0.028000
C	0.690700	1.639400	0.384400
C	-1.584600	2.063900	-0.439400
C	1.062900	3.116800	0.280800
O	1.497100	0.800800	0.778800
N	-1.268200	3.400600	-0.572400
O	-2.697100	1.628200	-0.718100
C	-0.057300	4.005100	-0.263200
C	1.449100	3.630400	1.706000
C	2.303000	3.252600	-0.658900
H	-2.010000	4.000700	-0.920000
O	0.081400	5.206500	-0.423400
H	2.308200	3.037100	2.032000
H	1.787300	4.663400	1.585100
C	0.335000	3.563000	2.756200
H	2.590100	4.307900	-0.649500
H	3.114500	2.684900	-0.195000
C	2.089800	2.780100	-2.101200
H	0.706400	3.944000	3.712000
H	-0.530900	4.173200	2.477200
H	-0.009100	2.536900	2.926200
H	3.012000	2.915200	-2.673800
H	1.827300	1.717600	-2.151400
H	1.304600	3.350900	-2.608900

2e-barbital

Sum of electronic and zero point energies: -1699.521137 Hartree

Lowest Frequency: 8.1 cm^{-1}

Coordinates: B3LYP/6-31+G(d,p) IEF-PCM $CHCl_3$

Atom	x	y	z
N	-0.824500	-1.664100	0.325300

C	0.160200	-2.581600	0.336900
C	-2.097800	-2.079500	0.498700
C	-0.079400	-3.948800	0.525400
N	1.466000	-2.074500	0.196600
C	-2.433400	-3.424800	0.700800
N	-3.058500	-1.058500	0.418400
C	-1.396500	-4.354200	0.710400
H	0.739200	-4.653200	0.524500
C	2.524100	-2.743900	-0.389500
H	1.603000	-1.098000	0.461000
H	-3.463900	-3.711300	0.843100
C	-4.382700	-1.105500	0.808600
H	-2.739100	-0.185400	-0.000100
H	-1.619700	-5.405500	0.864200
O	2.391800	-3.827100	-0.963500
C	3.859900	-2.075000	-0.296800
O	-4.889900	-2.087100	1.353100
C	-5.176200	0.159600	0.519600
C	4.245500	-1.281100	0.791500
C	4.789100	-2.315600	-1.323200
H	-5.744400	0.383700	1.429000
H	-4.496600	0.996600	0.333700
C	5.530500	-0.735600	0.845300
H	3.558800	-1.096800	1.610400
C	6.060700	-1.753600	-1.270700
H	4.498600	-2.944800	-2.158000
C	6.456800	-0.954400	-0.183100
H	5.815800	-0.133600	1.703900
H	6.761200	-1.940200	-2.081000
C	-6.176100	0.059300	-0.678000
C	-7.299900	-0.951900	-0.381800
H	-6.907100	-1.961300	-0.234700
H	-7.852300	-0.673900	0.523300
H	-8.010300	-0.976700	-1.216400
C	-6.796000	1.459100	-0.866700
H	-6.030800	2.203800	-1.114400
H	-7.529600	1.446200	-1.680900
H	-7.310800	1.790100	0.042900
C	-5.436600	-0.346000	-1.968500
H	-4.620100	0.348800	-2.194400
H	-5.013600	-1.353900	-1.893600
H	-6.128000	-0.341500	-2.818700
C	7.845500	-0.363800	-0.129100
H	8.607200	-1.151700	-0.101100
H	8.048800	0.248100	-1.015300
H	7.978700	0.265100	0.755200
H	-0.415000	0.237100	0.142200
N	-0.192900	1.249200	0.048500
C	1.057900	1.665100	0.446900
C	-1.189800	2.048800	-0.466600
C	1.425500	3.141700	0.308800

O	1.853300	0.846400	0.898200
N	-0.882200	3.387000	-0.614000
O	-2.290000	1.599400	-0.772900
C	0.311100	4.009900	-0.276900
C	1.795500	3.697300	1.721200
C	2.677000	3.252600	-0.620700
H	-1.619400	3.972800	-0.994300
O	0.441100	5.210800	-0.450800
H	2.648900	3.112400	2.075700
H	2.136800	4.726000	1.574400
C	0.667900	3.662400	2.758400
H	2.962300	4.308400	-0.637800
H	3.482800	2.698800	-0.130800
C	2.483400	2.738300	-2.051300
H	1.025300	4.074200	3.706800
H	-0.194400	4.262000	2.447100
H	0.322500	2.641600	2.955500
H	3.413100	2.859200	-2.615100
H	2.225200	1.674200	-2.074100
H	1.703700	3.291900	-2.585900

2f-barbital

Sum of electronic and zero point energies: -1774.72628 Hartree

Lowest Frequency: 8.3 cm^{-1}

Coordinates: B3LYP/6-31+G(d,p) IEF-PCM $CHCl_3$

Atom	x	y	z
N	-1.039100	-1.654200	0.348500
C	-0.036500	-2.551300	0.391200
C	-2.307400	-2.092500	0.501300
C	-0.253800	-3.920700	0.591500
N	1.261400	-2.020300	0.271700
C	-2.620900	-3.441300	0.712300
N	-3.285500	-1.091100	0.388200
C	-1.566100	-4.349900	0.754300
H	0.578300	-4.608900	0.616300
C	2.340400	-2.672900	-0.298900
H	1.373400	-1.040800	0.534900
H	-3.648300	-3.746800	0.836800
C	-4.613700	-1.155700	0.761000
H	-2.975700	-0.219900	-0.041500
H	-1.771800	-5.403600	0.916300
O	2.227300	-3.756400	-0.878200
C	3.662200	-1.987600	-0.185900
O	-5.110000	-2.136600	1.316900
C	-5.426200	0.088900	0.437500
C	4.007100	-1.133400	0.878000
C	4.628400	-2.262400	-1.163600
H	-6.007700	0.322300	1.336100
H	-4.759300	0.933600	0.240600
C	5.273900	-0.568700	0.951500

H	3.295000	-0.918100	1.666400
C	5.898200	-1.688900	-1.111900
H	4.374200	-2.934800	-1.976100
C	6.226200	-0.835300	-0.046500
H	5.548200	0.079100	1.777800
H	6.615400	-1.913400	-1.891900
C	-6.411000	-0.054300	-0.768200
C	-7.521200	-1.077400	-0.461700
H	-7.113000	-2.076300	-0.287600
H	-8.088300	-0.788700	0.430900
H	-8.221600	-1.132800	-1.303200
C	-7.051400	1.330400	-0.995100
H	-6.295600	2.082300	-1.249500
H	-7.774300	1.287600	-1.817900
H	-7.583300	1.672400	-0.099500
C	-5.649900	-0.476200	-2.040700
H	-4.844900	0.229100	-2.275400
H	-5.207600	-1.473100	-1.936100
H	-6.332000	-0.506600	-2.897800
O	7.433700	-0.226600	0.107600
C	8.455800	-0.467000	-0.863800
H	8.143700	-0.126200	-1.857200
H	9.317600	0.112500	-0.533600
H	8.721000	-1.529200	-0.902400
H	-0.666300	0.244400	0.158200
N	-0.462100	1.260500	0.060700
C	0.762100	1.708300	0.504000
C	-1.456200	2.033200	-0.498900
C	1.103400	3.190900	0.363400
O	1.556500	0.911600	0.995000
N	-1.171200	3.376000	-0.651000
O	-2.534900	1.557200	-0.839600
C	-0.005500	4.028300	-0.275200
C	1.405700	3.770200	1.782300
C	2.386900	3.317100	-0.519500
H	-1.905900	3.941700	-1.065000
O	0.105600	5.229800	-0.458000
H	2.251800	3.203300	2.180900
H	1.737800	4.801900	1.636100
C	0.235700	3.731800	2.771200
H	2.652500	4.378000	-0.538000
H	3.184400	2.784100	0.005800
C	2.254900	2.784100	-1.950100
H	0.546500	4.161000	3.728300
H	-0.621000	4.314600	2.415700
H	-0.103600	2.708800	2.967700
H	3.202600	2.914300	-2.481000
H	2.014700	1.715700	-1.970300
H	1.486400	3.318800	-2.518900

APPENDIX C

SUPPLEMENTAL INFORMATION: TOWARD SUPRAMOLECULAR ENANTIOSELECTIVE CATALYSTS: INVESTIGATING INTERACTIONS OF MODIFIED HAMILTON RECEPTORS WITH CHIRAL BARBITURATES

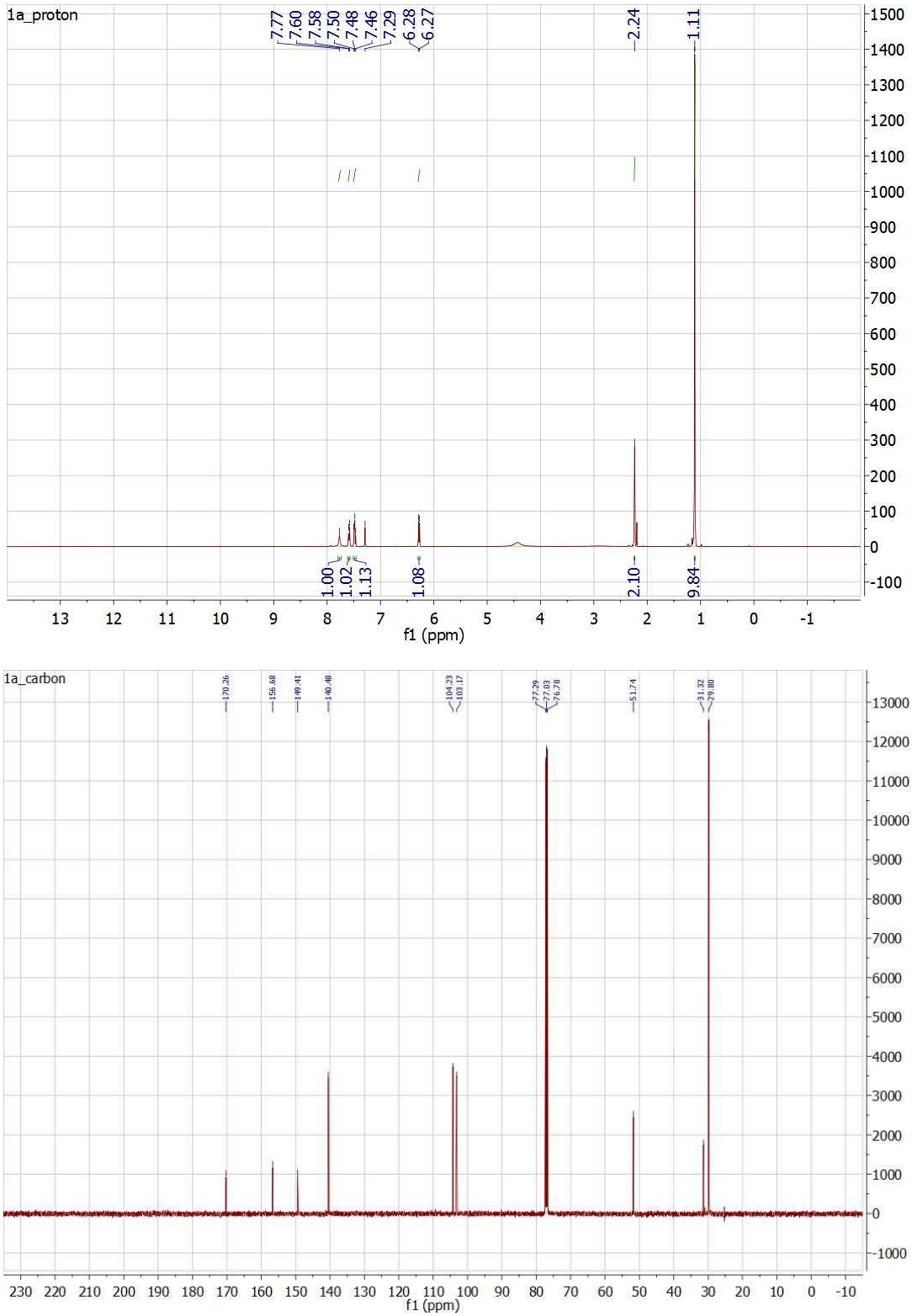
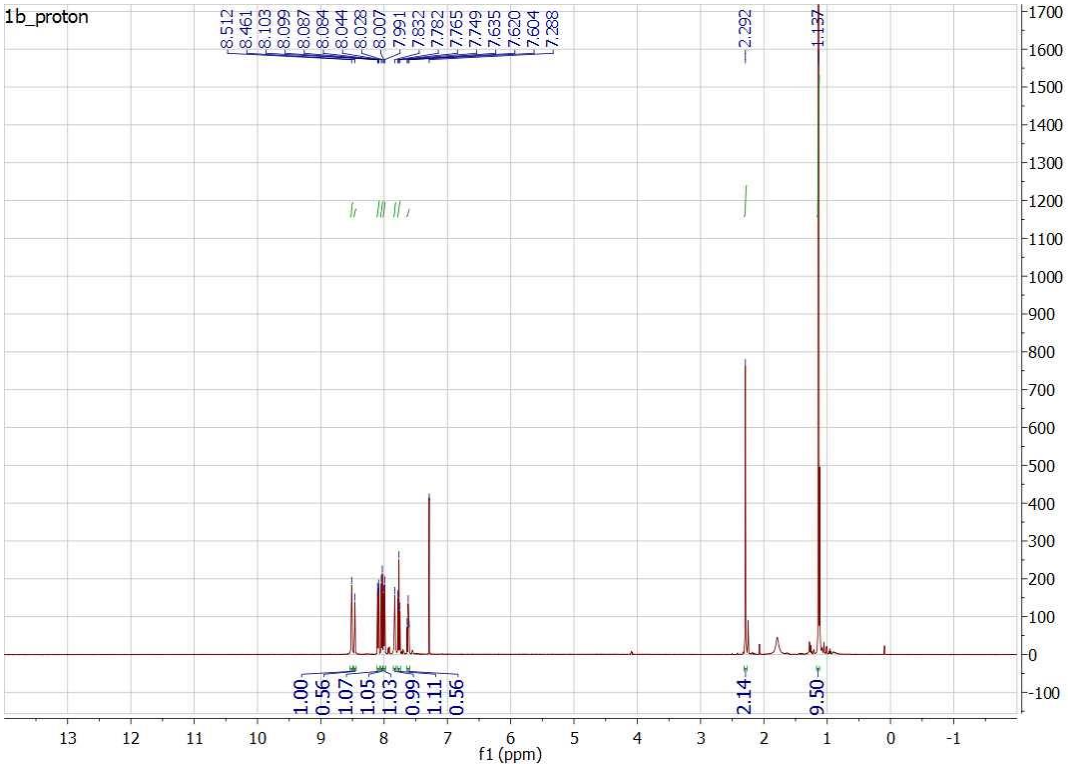


Figure C1. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **1a**.



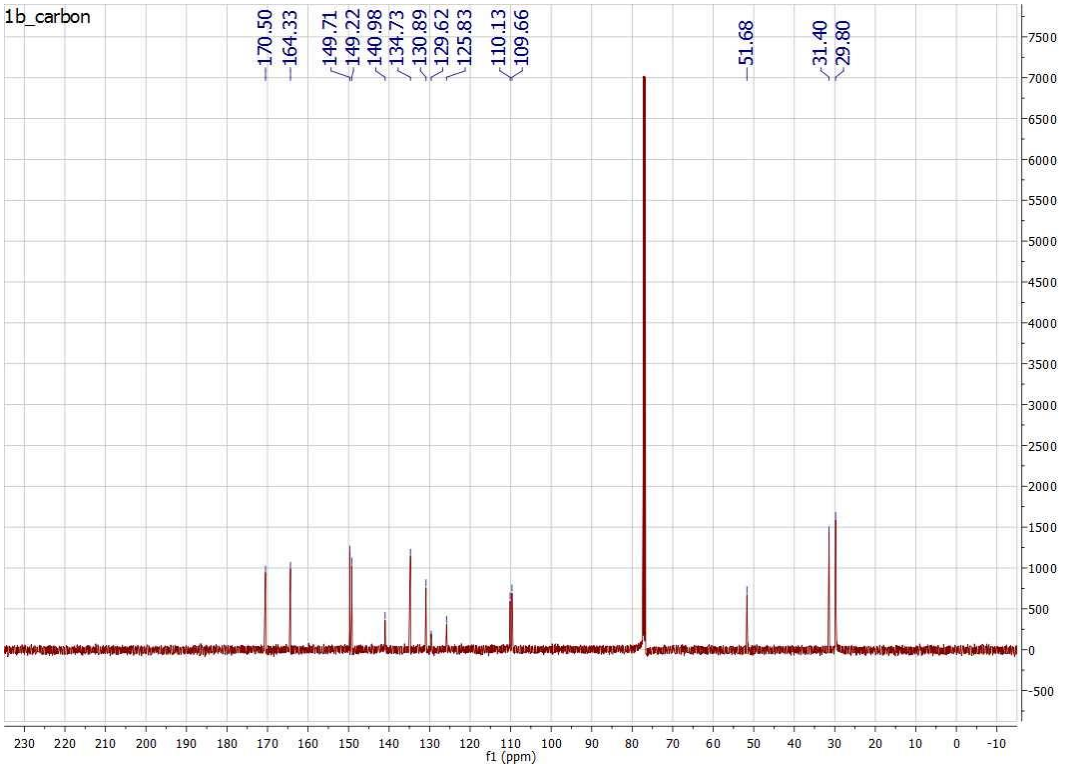


Figure C2. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **1b**.

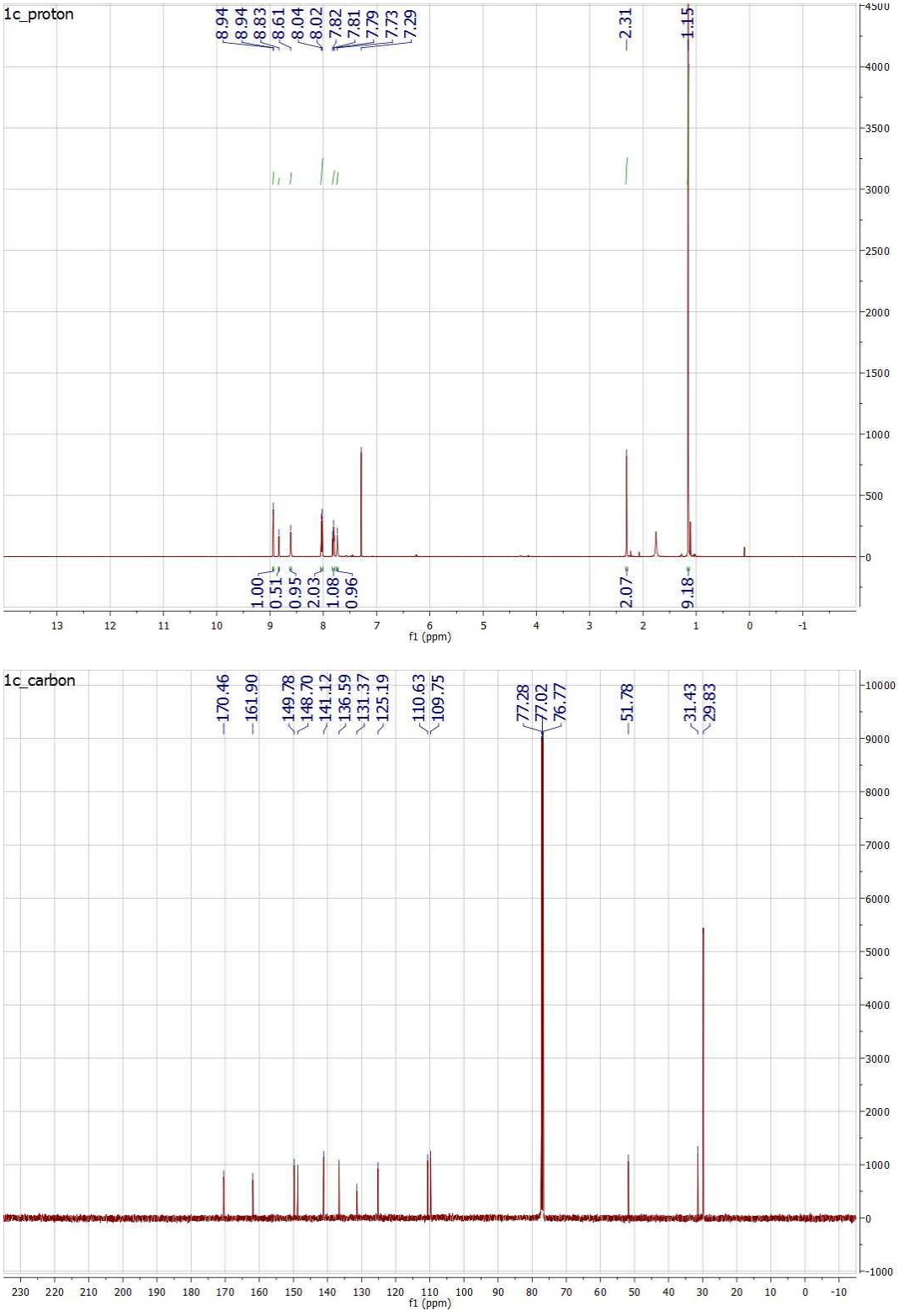


Figure C3. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **1c**.

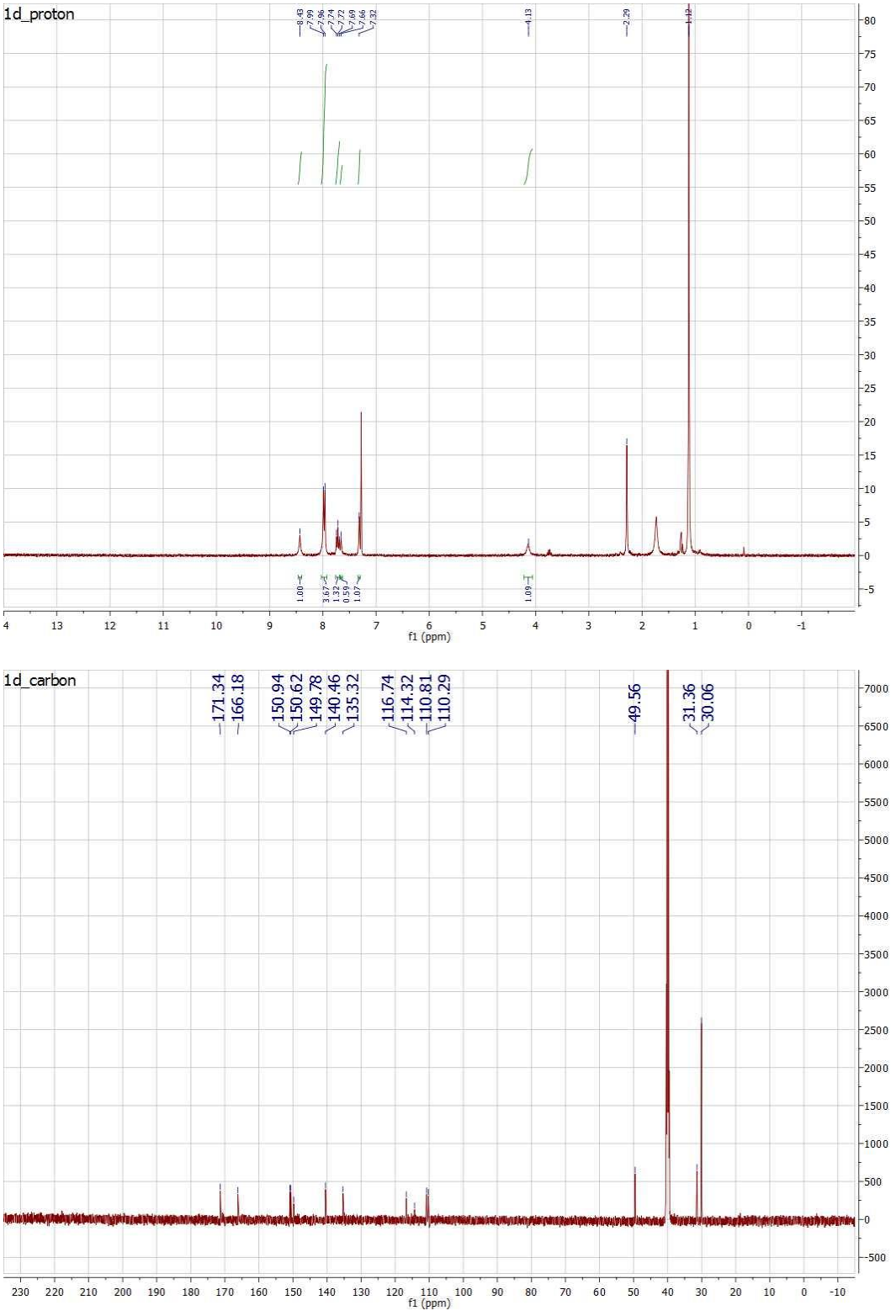


Figure C4. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **1d**.

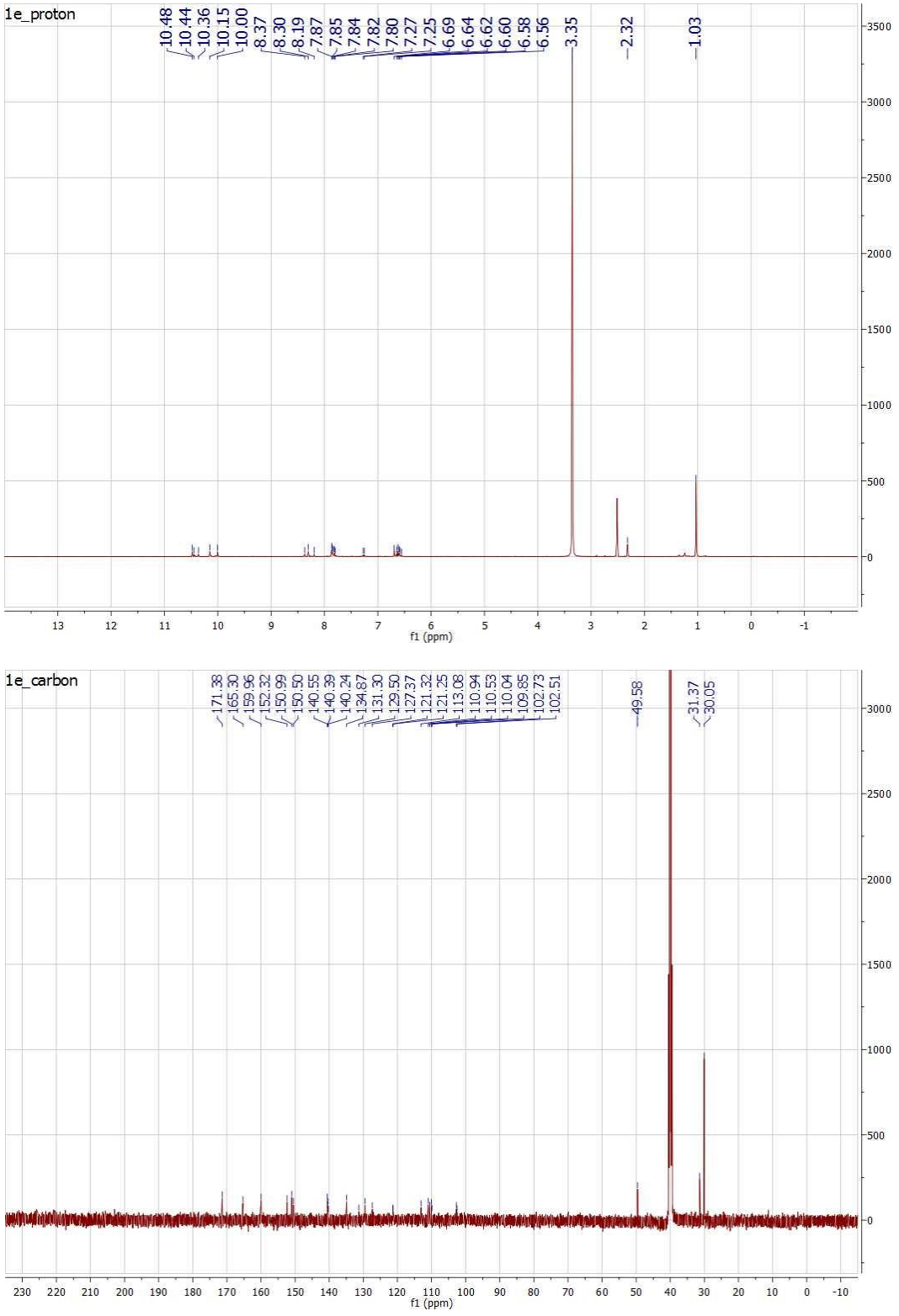


Figure C5. ^{1}H (500 MHz, , DMSO-$_{d6}$) and $^{13}C\{^{1}H\}$ (125 MHz, DMSO-$_{d6}$) NMR spectra of **1e**.

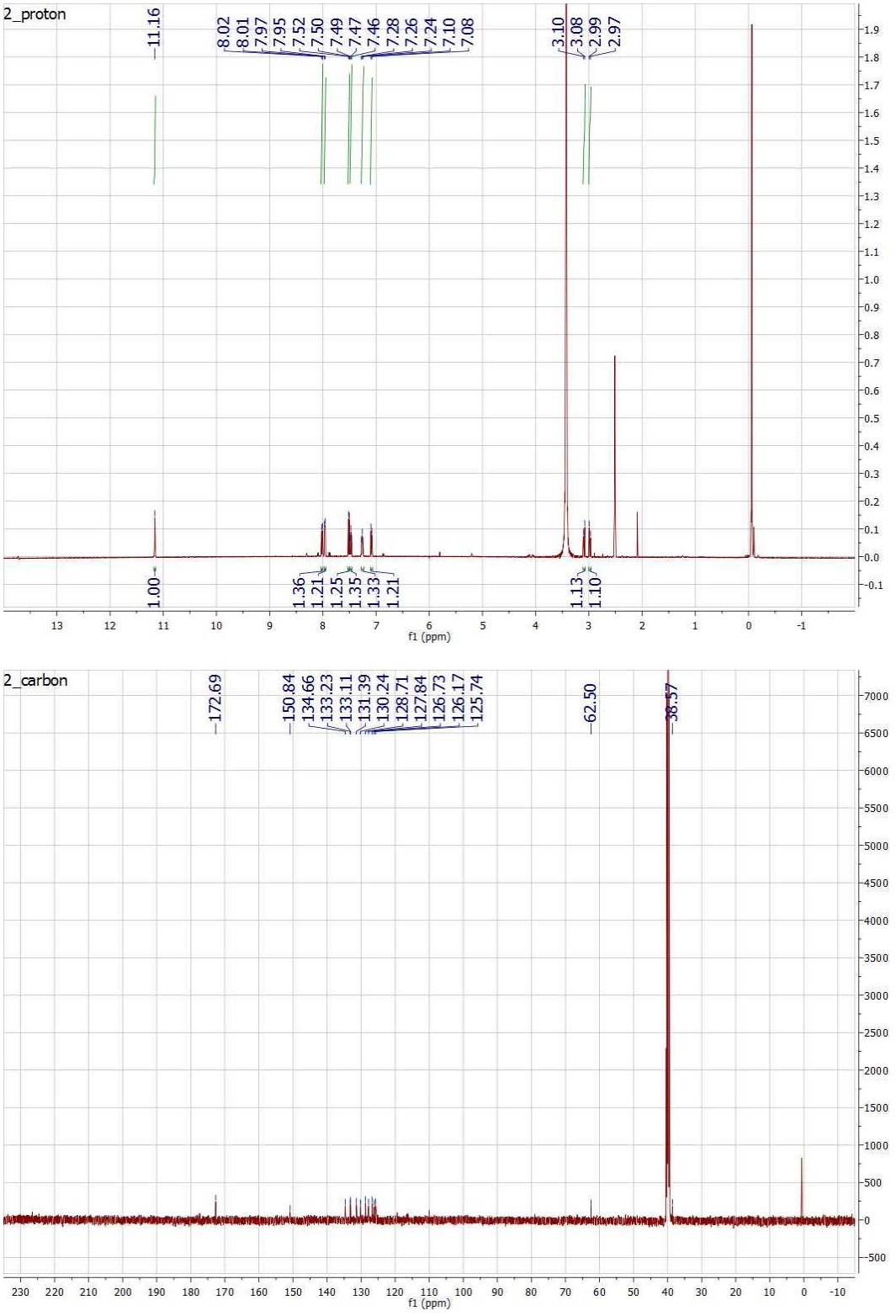
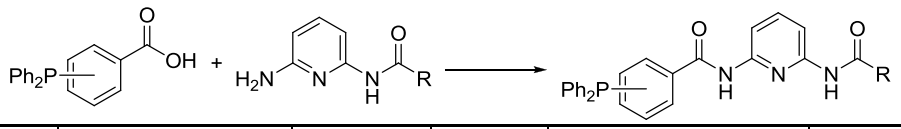


Figure C6. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **2**.

APPENDIX D

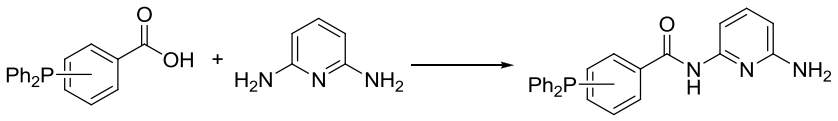
SUPPLEMENTAL INFORMATION: APPLICATION OF NEW SELF-ASSEMBLED LIGANDS BASED ON BIFURCATED HAMILTON RECEPTORS FOR USE IN SUPRAMOLECULAR CATALYSIS

Table D1. Unsuccessful coupling conditions between *para* and *ortho* diphenylphosphinobenzoic acid and monosubstituted 2,6-diaminopyrdine.



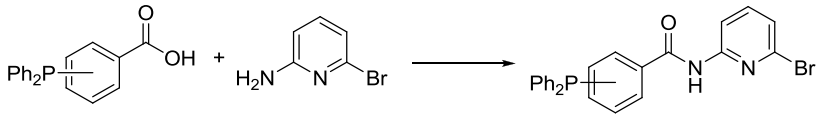
Reaction ID	Coupling agent	Solvent	T (^{o}C)	Additives	Substitution
JMM_1.019	DCC	CH_2Cl_2	rt	2.5 equiv NEt_3 (small scale)	para
JMM_1.023	DCC	CH_2Cl_2	rt	2.5 equiv NEt_3	para
JMM_1.027	DCC	CD_2Cl_2	rt	2.5 equiv NEt_3	para
JMM_1.029	DCC	THF	0 -> rt	3.5 NEt_3	para
JMM_1.031	oxalyl chloride	THF	0 -> rt	1.3 equiv NEt_3	para
JMM_1.033	DCC	CH_2Cl_2	0 -> rt	2.5 equiv NEt_3	para
JMM_1.035	thionyl chloride	CH_2Cl_2	rt	1.2 equiv NEt_3	ortho
JMM_1.045	EDC	THF	rt	2.5 equiv NEt_3	ortho
JMM_1.047	thionyl chloride	pyridine	rt	1.0 equiv NEt_3	ortho
JMM_1.051	thionyl chloride	CH_2Cl_2	rt	1.1 equiv NEt_3	ortho
JMM_1.053	EDC	$CHCl_3$	0 -> rt		ortho
JMM_1.059	CDI	CH_2Cl_2	45		ortho
JMM_1.061	EDC	$CHCl_3$	45	DMAP	ortho
JMM_1.065	DCC	CH_2Cl_2	0 -> rt		ortho
JMM_1.067	cyanuric fluoride	CH_2Cl_2	rt	pyridine, DMAP	para
JMM_1.081	cyanuric chloride	CH_3CN	rt		para
JMM_1.087	cyanuric chloride	DMF	rt	sodium hydride	para
JMM_1.107	thionyl chloride	DMF	rt	NEt_3	para
JMM_1.109	thionyl chloride	CH_2Cl_2	rt	NEt_3	para
JMM_1.115	thionyl chloride	CH_2Cl_2	40	NEt_3	para
JMM_2.005	thionyl chloride	DMF	rt	4 equiv NEt_3	para
JMM_2.017	thionyl chloride	DMF	rt	2 equiv NEt_3	para
JMM_2.189	thionyl chloride	DMF	0 -> rt	1.5 equiv NEt_3	para
JMM_3.049	EDC	CH_2Cl_2	rt	1.2 equiv HOBT, 1.1 equiv NEt_3	para

Table D2. Unsuccessful coupling conditions between *para* diphenylphosphinobenzoic acid and 2,6-diaminopyrdine.



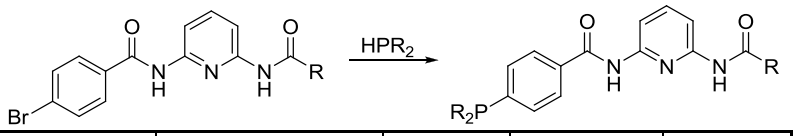
Reaction ID	Coupling agent	Solvent	T (^{o}C)	Additives	Substitution
JMM_1.063	DCC	CH_2Cl_2	rt		para
JMM_2.152	thionyl chloride	THF	0 -> rt	excess diaminopyridine	para
JMM_3.049	EDC	CH_2Cl_2	rt	1.2 equiv HOBT, 1.1 equiv NEt_3	para

Table D3. Unsuccessful coupling conditions between *para* diphenylphosphinobenzoic acid and 2-amino-6-bromopyrdine.



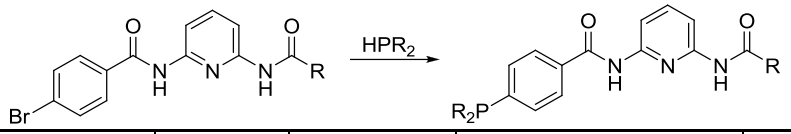
Reaction ID	Coupling agent	Solvent	T (^{o}C)	Additives	Substitution
JMM_1.069	DCC	CH_2Cl_2	0 -> rt		para
JMM_1.071	cyanuric chloride	CH_3CN	rt	1.05 equiv NEt_3	para
JMM_1.073	DCC	CH_2Cl_2	0 -> rt	degassed solutions	para
JMM_1.075	cyanuric chloride	CH_3CN	0 -> rt	1.05 equiv NEt_3	para
JMM_1.077	DCC	CH_2Cl_2	0 -> rt	DMAP, 4-pyrrolidinopyridine	para
JMM_1.091	DCC	DMF	0 -> rt	DMAP	para
JMM_2.154	thionyl chloride	THF	rt	excess aminopyridine	para
JMM_2.158	DCC	THF	rt	2.5 equiv NEt_3	para
JMM_2.158	EDC	THF	rt	2.5 equiv NEt_3	para
JMM_2.164	EDC	THF	60	3.0 equiv NEt_3	para

Table D4. Unsuccessful metal mediated cross-coupling conditions with $Pd_2(OAc)_2$ and CuI.



Reaction ID	Catalyst	Solvent	Additives	T (^oC)
JMM_2.172	10% $Pd(OAc)_2$	CH_3CN	NEt_3	80
JMM_2.172	10% CuI	toluene	Cs_2CO_3	80
JMM_2.185	10% $Pd(OAc)_2$	CH_3CN	NEt_3	65
JMM_3.007	10% $Pd(OAc)_2$	CH_3CN	NEt_3	70
JMM_3.015	10% $Pd(OAc)_2$	CH_3CN	NEt_3	75
JMM_3.016	10% $Pd(OAc)_2$	CH_3CN	NEt_3	85
JMM_3.022	10% $Pd(OAc)_2$	CH_3CN	NEt_3	90
JMM_3.036	10% $Pd(OAc)_2$	CH_3CN	NEt_3	100

Table D5. Unsuccessful metal mediated cross-coupling conditions using $NiCl_2$.



Reaction ID	Catalyst	Solvent	Additives	T (^oC)
RJH_1.031_1	$NiCl_2$	H2O	Zn, Bipy, NEt_3	70
RJH_1.031_2	$NiCl_2$	EtOH	Zn, K_2CO_3, NEt_3	70
RJH_1.031_3	$NiCl_2$	H2O	Zn, K_2CO_3, NEt_3	70
RJH_1.035_1	$NiCl_2$	DMF	Zn, Bipy, K_2CO_3	70
RJH_1.035_2	$NiCl_2$	DMF/THF	Zn, Bipy, NEt_3	70
RJH_1.035_3	$NiCl_2$	THF	Zn, Bipy, K_2CO_3	70
RJH_1.035_4	$NiCl_2$	THF	Zn, Bipy, NEt_3	70
RJH_1.035_5	$NiCl_2$	DMF/THF	Zn, Bipy, K_2CO_3	70

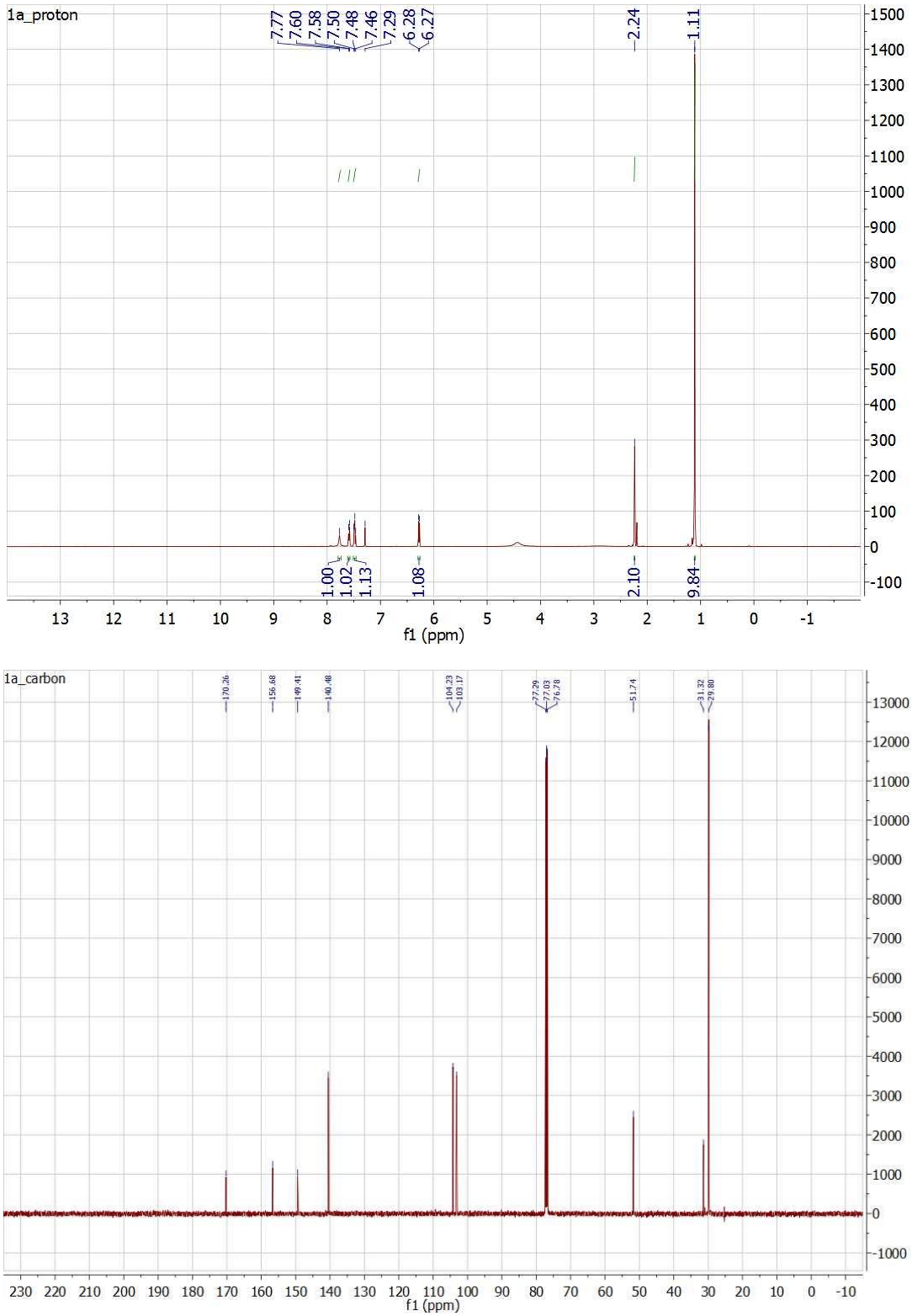


Figure D1. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **1a**.

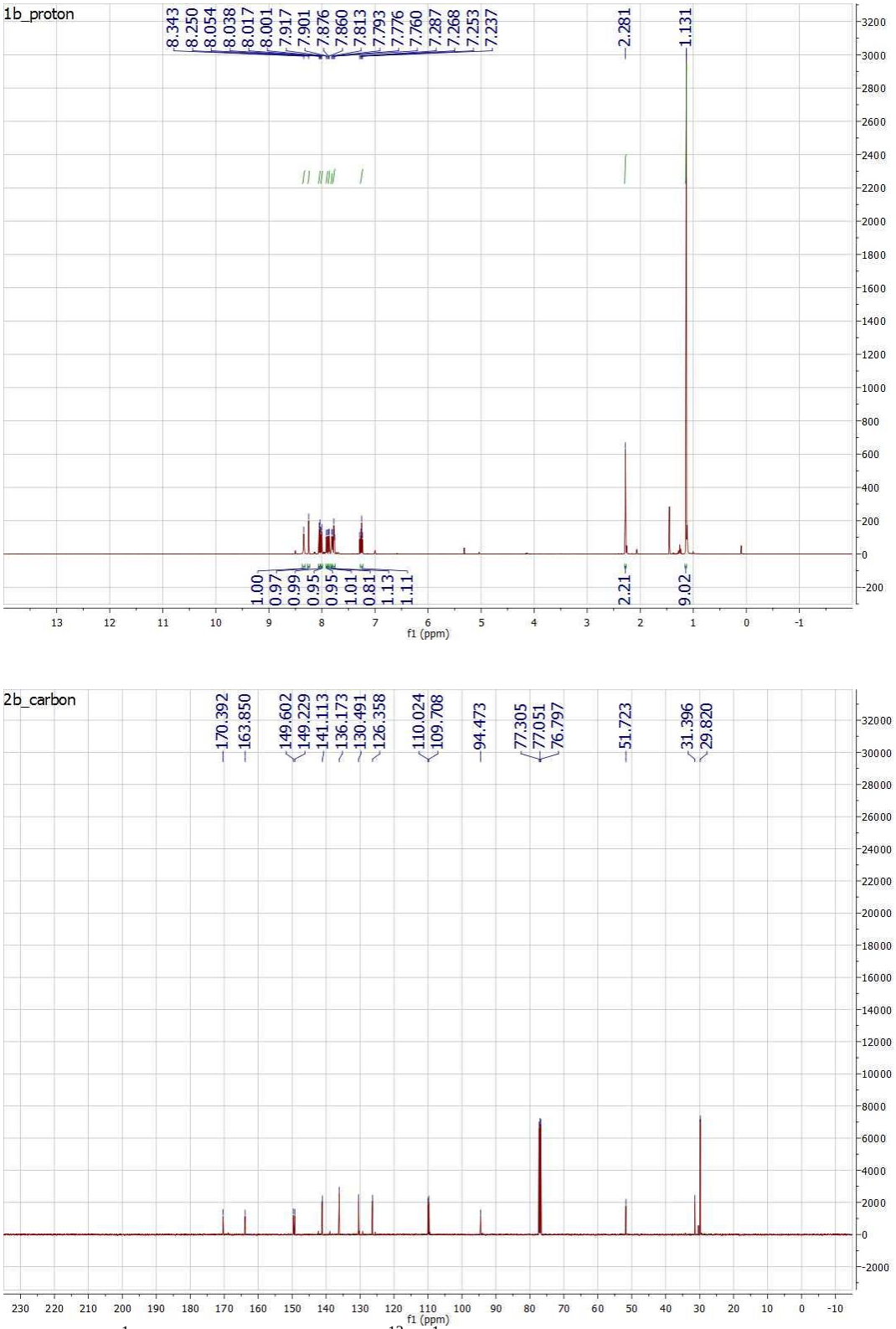
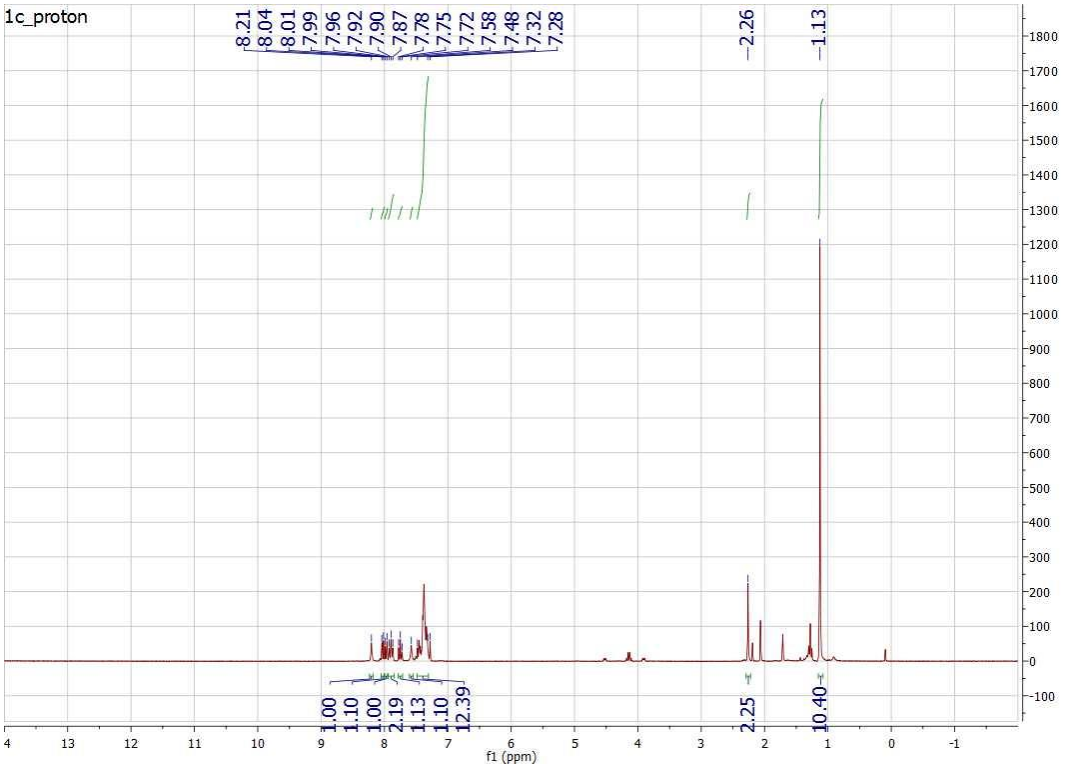
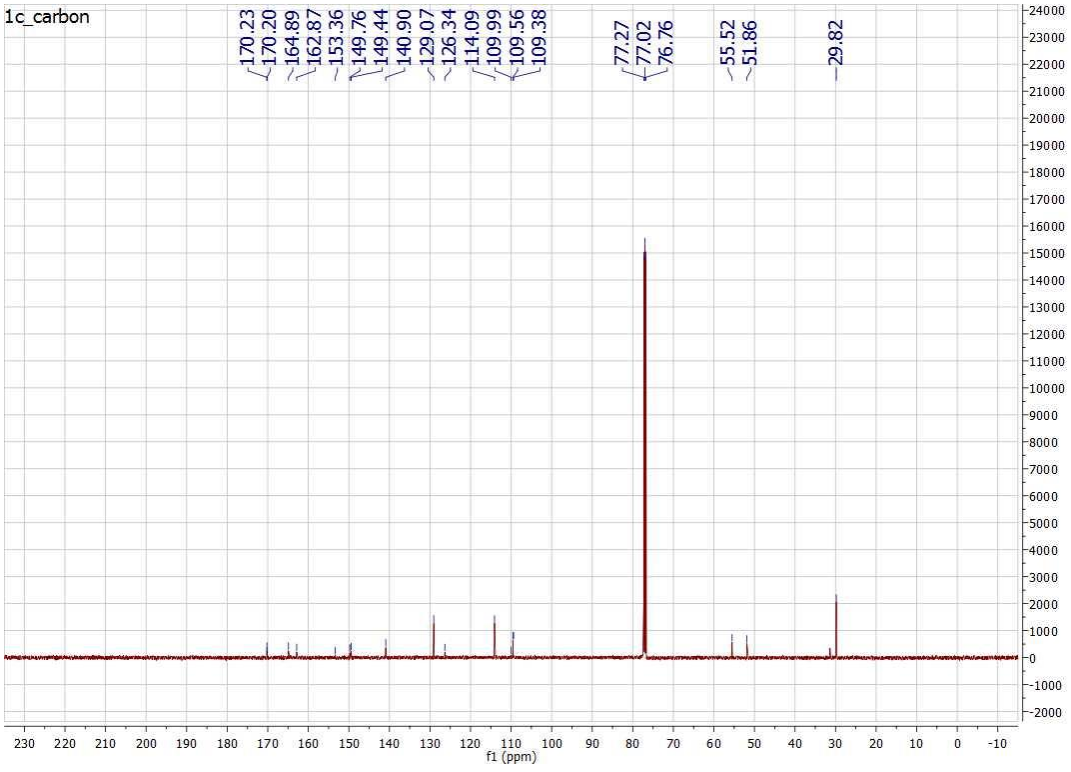


Figure D2. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **1b**.


1c_proton
8.21
8.04
8.01
7.99
7.96
7.92
7.90
7.87
7.78
7.75
7.72
7.58
7.48
7.32
7.28
2.26
1.13
1.00
1.10
1.00
2.19
1.13
1.10
12.39
2.25
10.40
f1 (ppm)


1c_carbon
170.23
170.20
164.89
162.87
153.36
149.76
149.44
140.90
129.07
126.34
114.09
109.99
109.56
109.38
77.27
77.02
76.76
55.52
51.86
29.82
f1 (ppm)

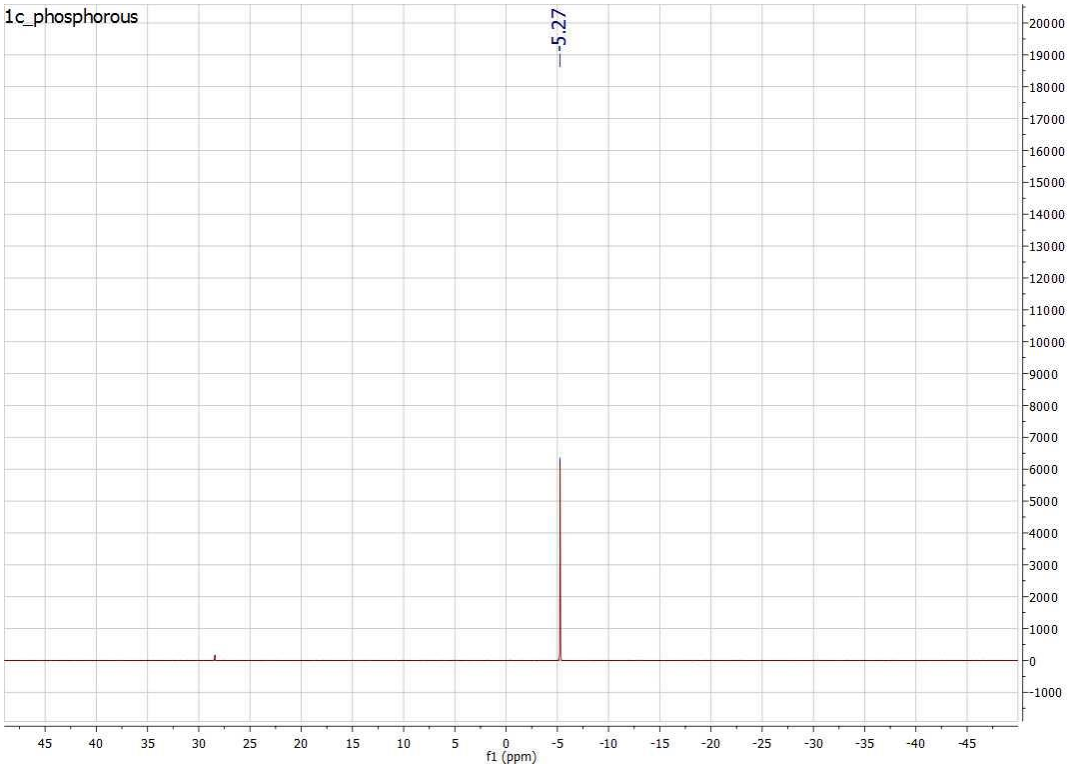


Figure D3. ^{1}H (500 MHz, $CDCl_3$), $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$), and $^{31}P\{^{1}H\}$ (202 MHz, $CDCl_3$) NMR spectra of **1c**.

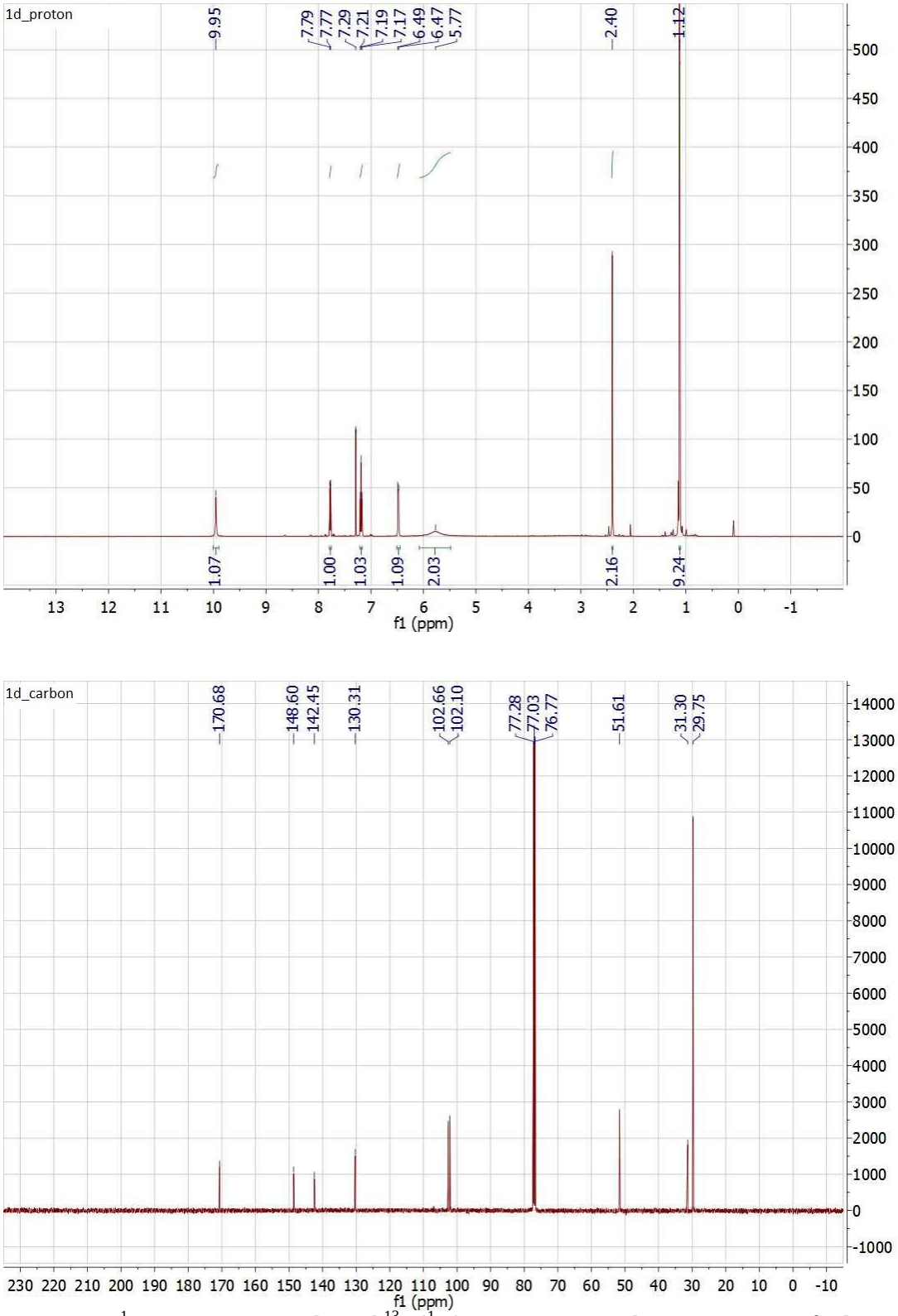
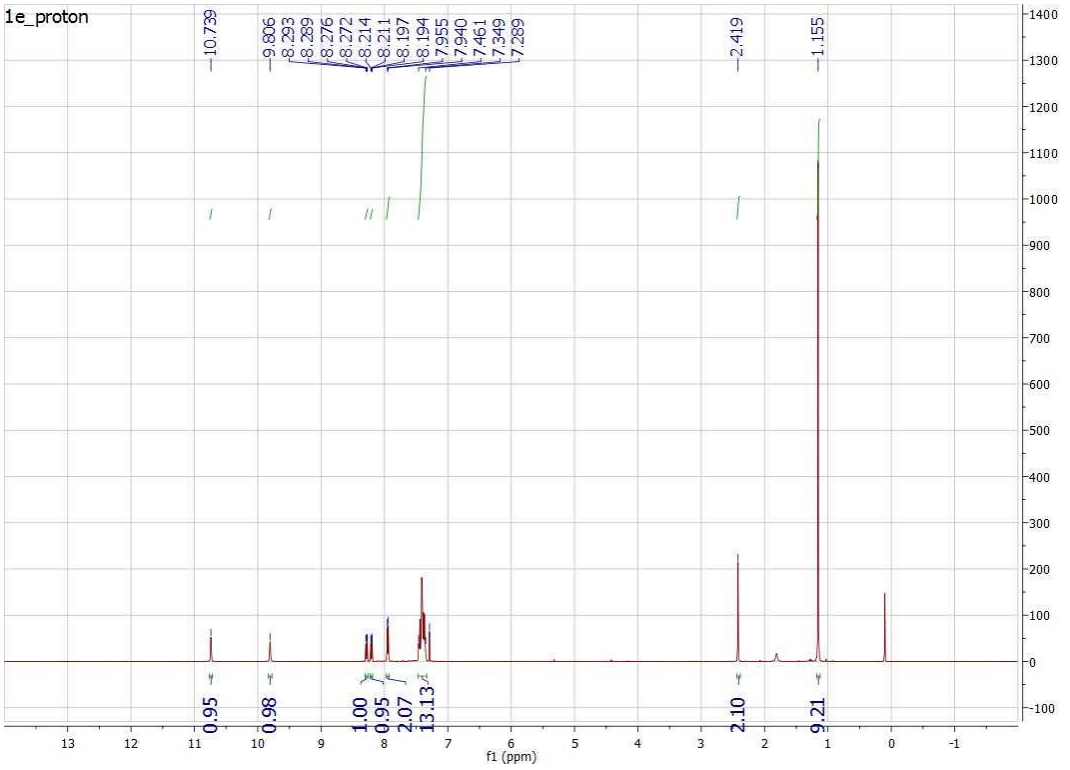
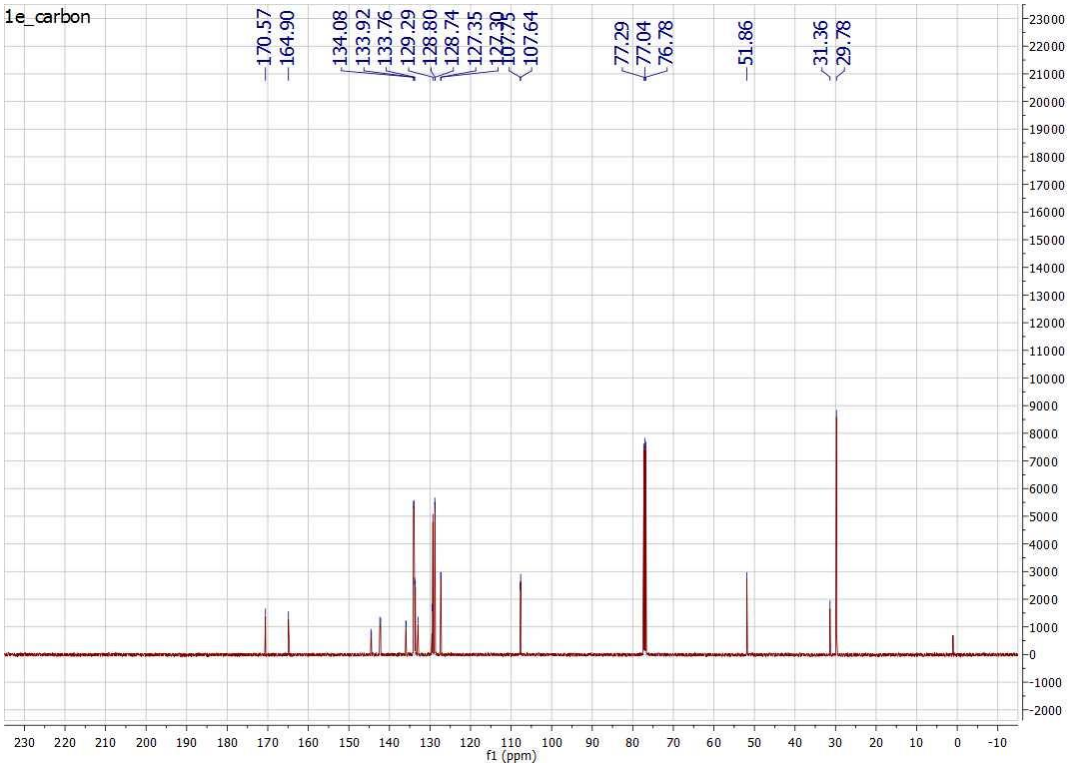


Figure D4. ^{1}H (500 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$) NMR spectra of **1d**.


1e_proton
10.739
9.806
8.293
8.289
8.276
8.272
8.214
8.211
8.197
8.194
7.955
7.940
7.461
7.349
7.289
2.419
1.155
0.95
0.98
1.00
0.95
2.07
13.13
2.10
9.21
f1 (ppm)


1e_carbon
170.57
164.90
134.08
133.92
133.76
129.29
128.80
128.74
127.35
107.75
107.64
77.29
77.04
76.78
51.86
31.36
29.78
f1 (ppm)

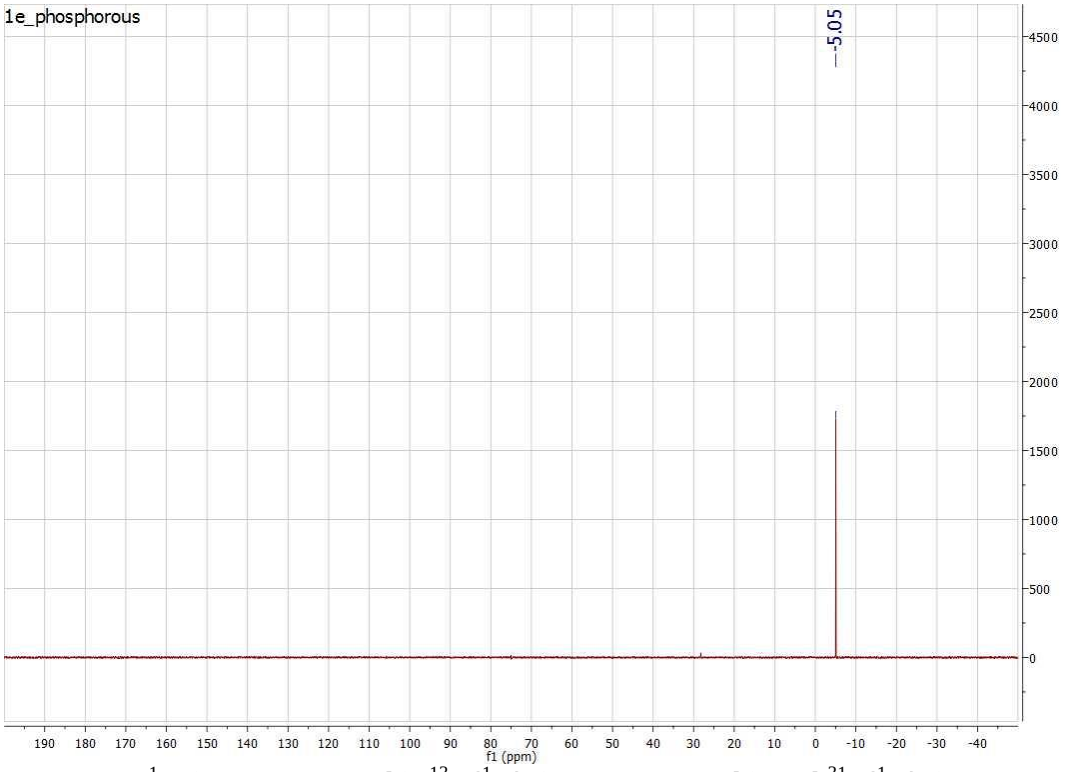
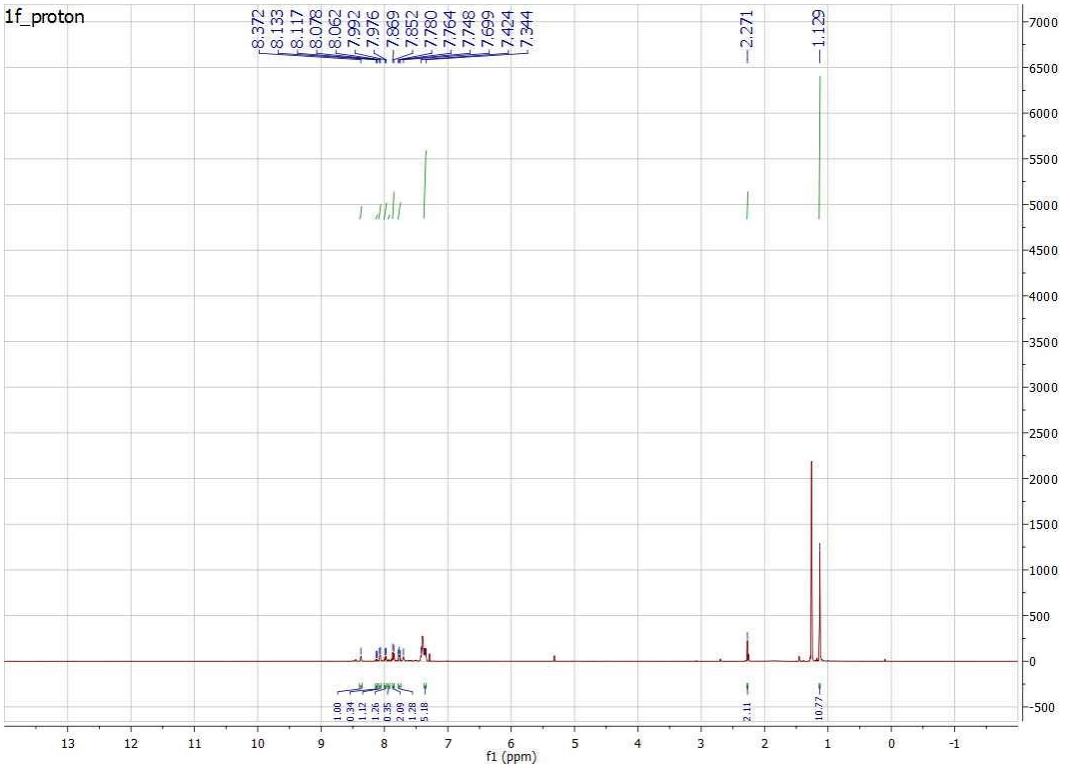
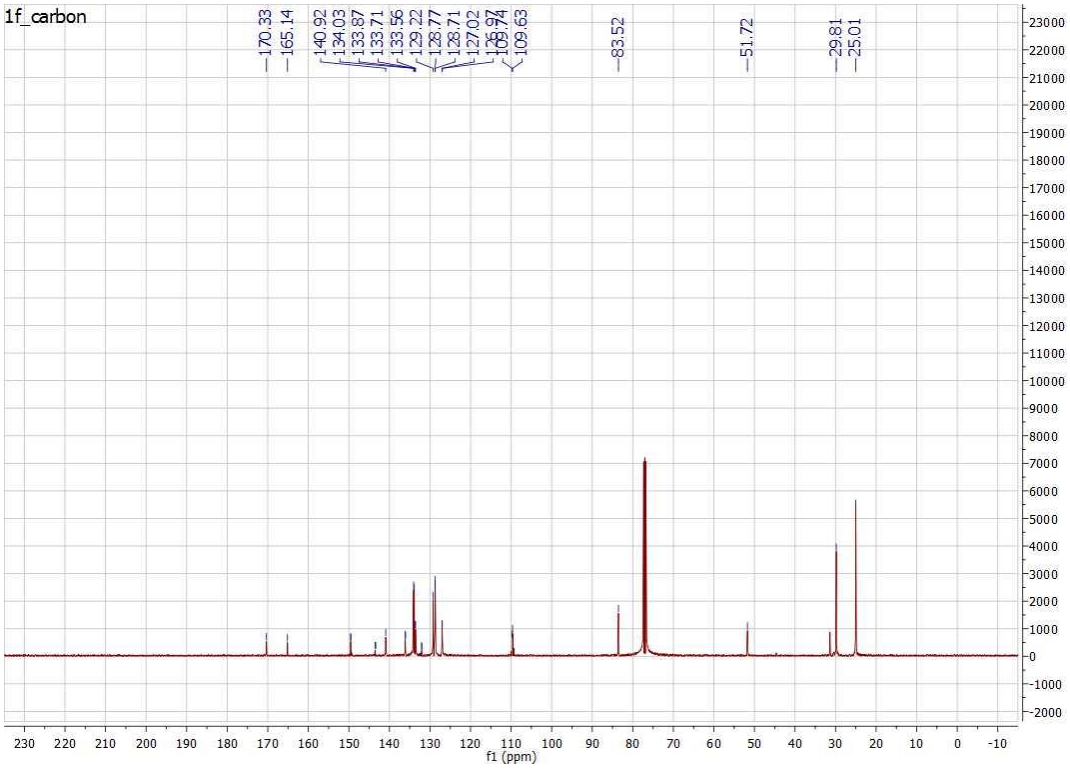


Figure D5. ^{1}H (500 MHz, $CDCl_3$), $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$), and $^{31}P\{^{1}H\}$ (202 MHz, $CDCl_3$) NMR spectra of **1e**.


1f_proton
8.372
8.133
8.117
8.078
8.062
7.992
7.976
7.869
7.852
7.780
7.764
7.748
7.699
7.424
7.344
2.271
1.129
1.00
0.34
1.12
1.26
0.35
2.09
1.28
5.18
2.11
10.77
f1 (ppm)


1f_carbon
170.33
165.14
140.92
134.03
133.87
133.71
133.56
129.22
128.77
128.71
127.02
109.63
83.52
51.72
29.81
25.01
f1 (ppm)

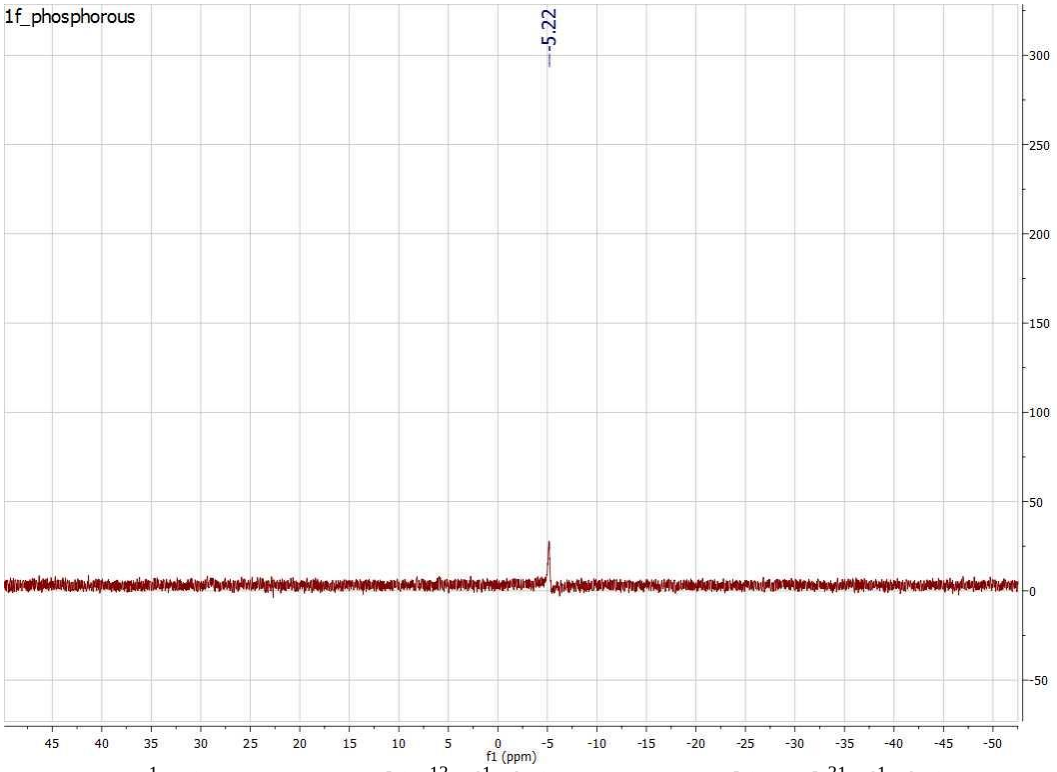


Figure D6. ^{1}H (500 MHz, $CDCl_3$), $^{13}C\{^{1}H\}$ (125 MHz, $CDCl_3$), and $^{31}P\{^{1}H\}$ (202 MHz, $CDCl_3$) NMR spectra of **1f**.

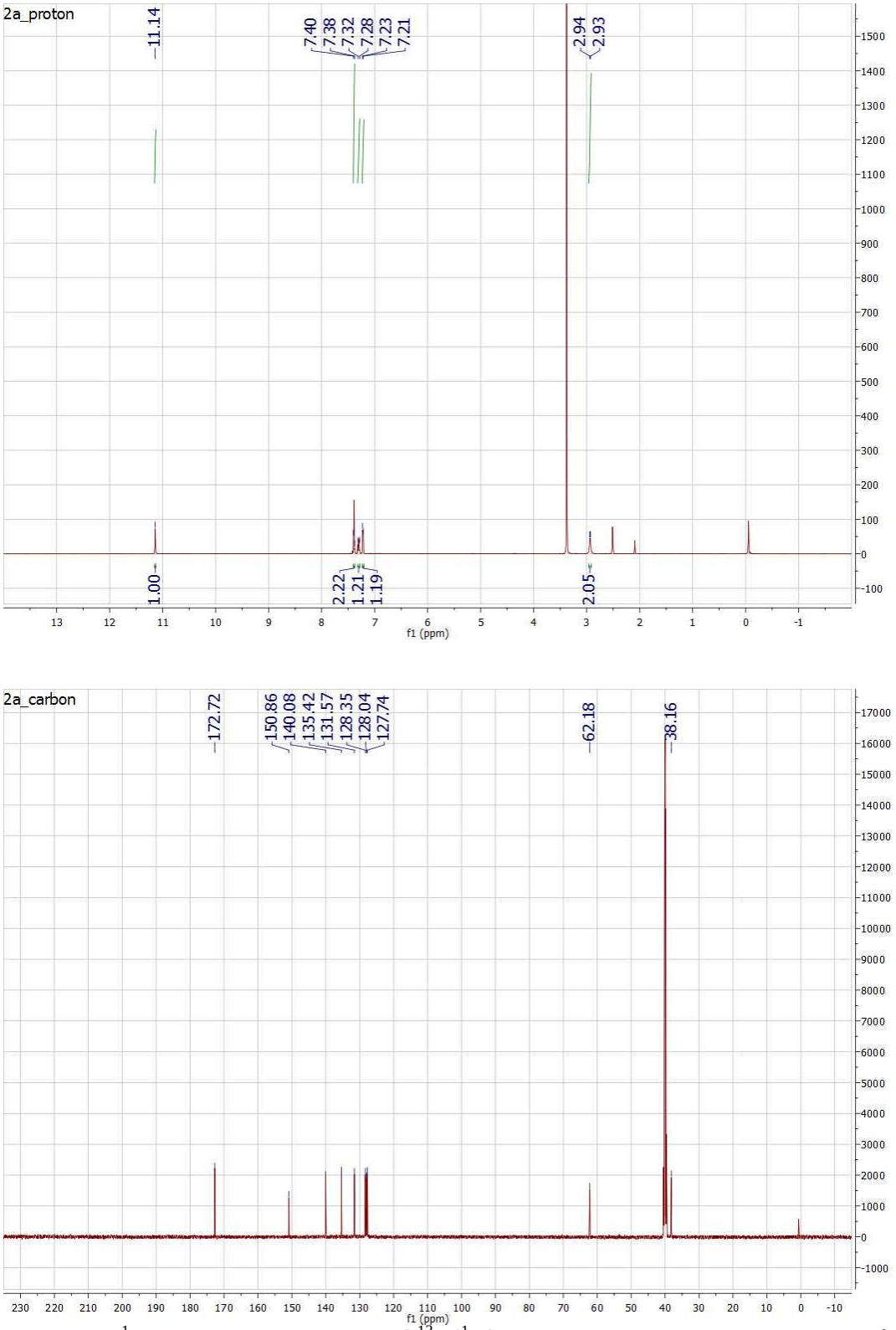


Figure D7. ^{1}H (500 MHz, DMSO-$_{d6}$) and ^{13}C{^{1}H} (125 MHz, DMSO-$_{d6}$) NMR spectra of **2a**.

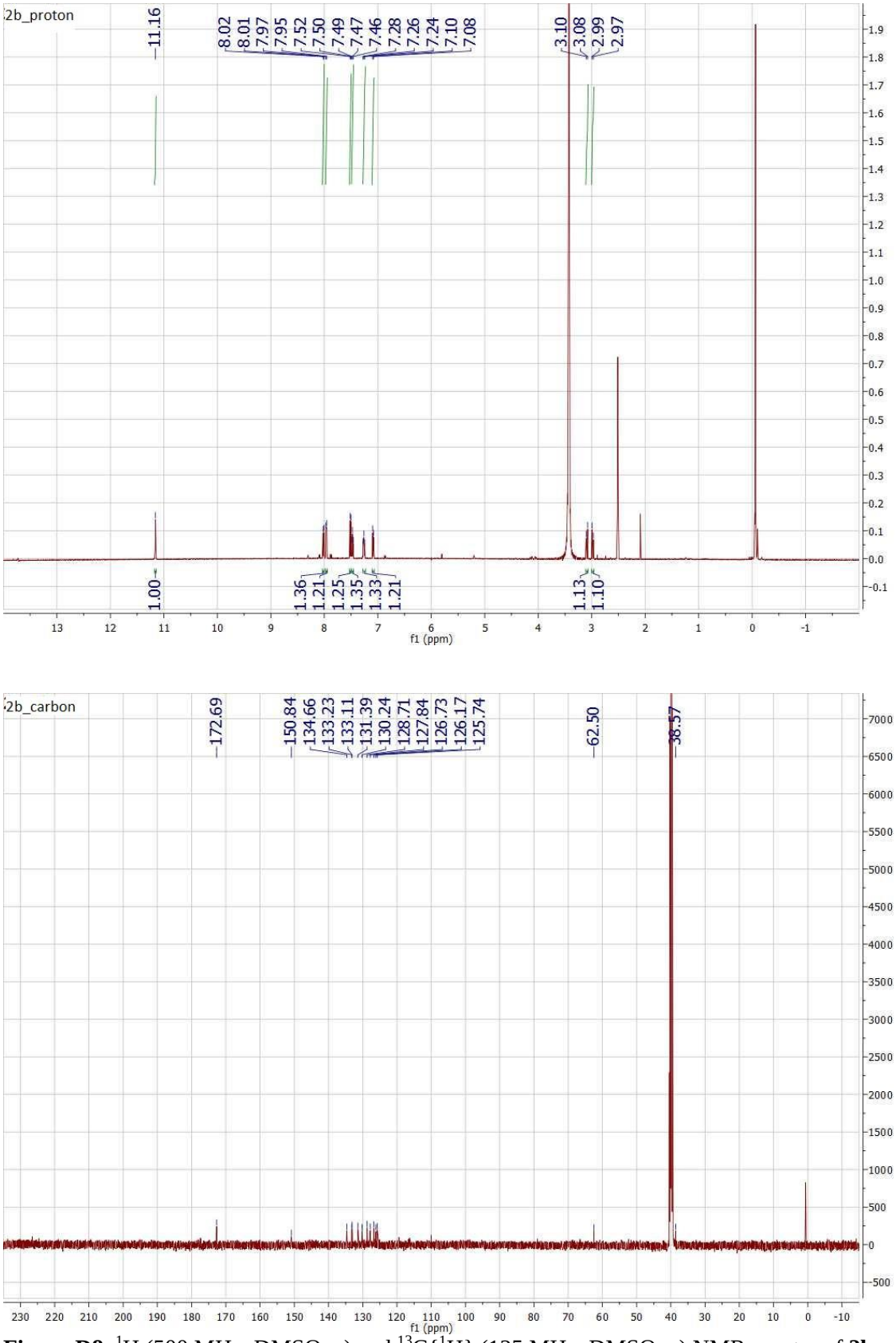


Figure D8. ^{1}H (500 MHz, DMSO-$_{d6}$) and $^{13}C\{^{1}H\}$ (125 MHz, DMSO-$_{d6}$) NMR spectra of **2b**.

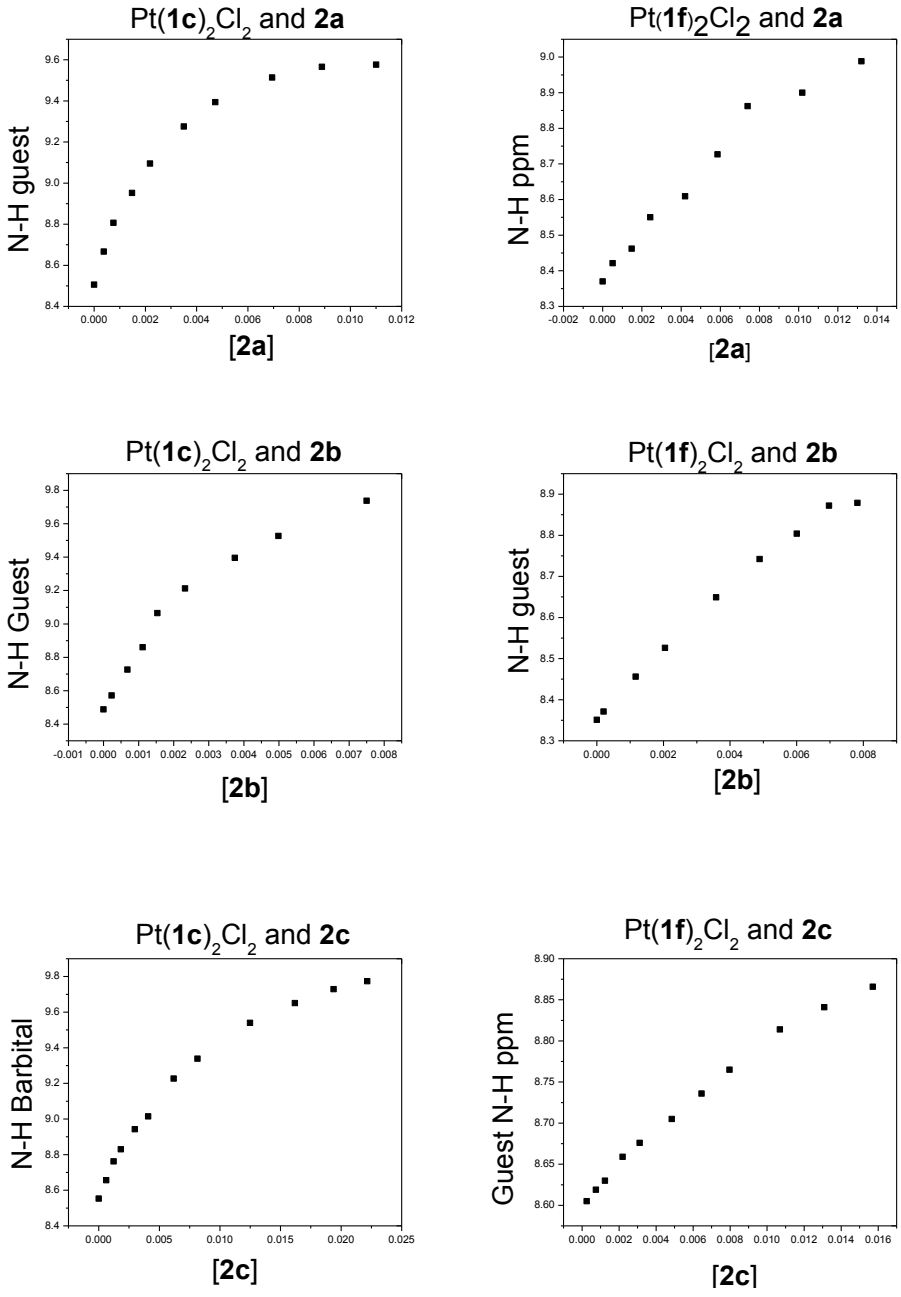


Figure D9. ^{1}H NMR (500 MHz, $CDCl_3$) titration data. Representative binding curve for host Pt(**1c**)$_2$Cl$_2$ and Pt(**1f**)$_2$Cl$_2$ with guests **2a-c**.

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