

Molecular Rotors for Quantifying Kinetic Effects of Stabilizing
Non-covalent Interactions

by

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DEDICATION

To my late mother.

ACKNOWLEDGMENTS

Life has been an endless journey. For a long time, I didn't imagine I would literally have a PhD or any other sophisticated successes; at least, when I was working for American orders in a toy factory at 13 years old, I didn't. I ambitiously cited PhD as my life goal at ten without the acquaintance of a doctoral degree and the faces of real life; I mean what I already had tasted and would come to my life later: poverty, hunger, diseases, death, and all the darkness coming from humanity and sophistication. Unfortunately, pursuing a doctoral degree has been the least formidable barrier in my life, and time has done aged me to 31.

I was utterly exhausted when I got here after going across mountains to mountains and oceans to oceans. Contradictorily, I am also taking life easy, although I have no idea if I am pretending. While I realize I will eventually start my own, I see the ridiculousness and meaninglessness of what hasn't come. Being discouraged is not my intention. Instead, I am going to explore whatever is on the other side with my timidity and braveness, egotism and uniqueness.

Millions of words that will be said to nobody crowd in my heart. I indulged in seeking my inner universe when I was struggling to live in a tiny spot of this vast universe. Back in the real world, I would appreciate all the kindness and serendipities. I would have a long-long-long list of people who tried to help me. However, I will simply end it with an appreciation to my advisor, Prof. Dr. Ken D. Shimizu. His incredible patience and proficiency significantly promoted my research. I hope I also can be a peaceful and knowledgeable person one day.

ABSTRACT

This thesis describes the development of molecular machines as analytical instruments to measure the strength of non-covalent interactions and to test hypotheses of reaction mechanisms. The first chapter is a review of molecular rotors. The second chapter presents the development of a molecular rotor that can be controlled using electrostatic interactions. Previous examples have used electrostatic interactions to slow down or inhibit molecular motion. Our system is activated and sped up using electrostatic interactions. The third and fourth chapters describe the application of molecular rotors designed to experimentally measure the strength and stability trends for non-covalent pnictogen and chalcogen interactions. Chalcogen bonds involve group VI (oxygen, sulfur) atoms, and pnictogen bonds involve group V (nitrogen). The fifth chapter presents molecular rotors designed to model reaction transition states to test mechanistic hypotheses. For example, the interactions between electron-rich and electron-deficient groups in our rotors were used to test the hypothesis that secondary electrostatic interactions can explain the enhanced reactivity of benzyl and allyl electrophiles in S_N2 reactions.

Techniques used in the described research include organic synthesis, dynamic NMR methods, and DFT calculations. The molecular machines were primarily synthesized via condensation and metal-catalyzed coupling reactions. Dynamic NMR methods, including 2D EXSY and 1D lineshape analysis, were used to measure the rotational barriers. DFT calculations were performed on multiple platforms like Spartan and Q-Chem to reproduce the molecular barriers and analyze the origins of the interactions.

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LIST OF ABBREVIATIONS

CD	Circular dichroism spectroscopy
ChB	Chalcogen bond
DFT	Density Functional Theory
EXSY	Exchange spectroscopy
GS	Ground state
HB	Hydrogen bond
HPLC	High-performance liquid chromatography
KIE	Kinetic isotopic effect
NCI	Non-covalent interaction
NMR	Nuclear magnetic resonance spectroscopy
PnB	Pnictogen bond
SAPT	Symmetry-adapted perturbation theory
TS	Transition state

Chapter 1 Molecular rotors for quantifying non-covalent interactions

1.1 Abstract

This chapter will review the field of rotary molecular machines or molecular rotors designed to study and measure non-covalent interactions (NCIs). These include repulsive steric interactions and stabilizing NCIs such as hydrogen bonds and metal coordination. Molecular rotors can measure the kinetic effects of NCIs. This contrasts with most other molecular machines, like molecular balances, which measure the thermodynamic effects of NCIs. One advantage of measuring kinetic effects is that a broader range of NCI energies can be measured, as they are not limited by the ability to monitor equilibrium ratios.

1.2 Introduction

Molecular rotor molecules consist of a stationary stator and a smaller rotator part where the stator and the rotator can relatively rotate around the bond connected to each other.⁹ One application of molecular rotors or rotary molecular machines is to measure intermolecular or intramolecular non-covalent interactions, which will be the focus of this review. Using or designing molecules to make measurements has been a recent approach. For example, molecular radical clocks were used as early as 1993 to assess radical stabilities and mechanistic pathways (**Figure 1.1a**).¹⁰ Another example is the measurements of axial-equatorial conformational equilibria of substituted cyclohexanes to generate the commonly used steric parameter *A*-value (**Figure 1.1b**).^{11–13} In contrast, using molecular rotors as molecular instruments is relatively new or at least an interesting subset.

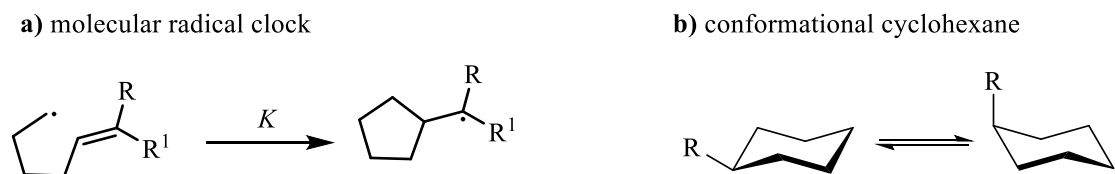
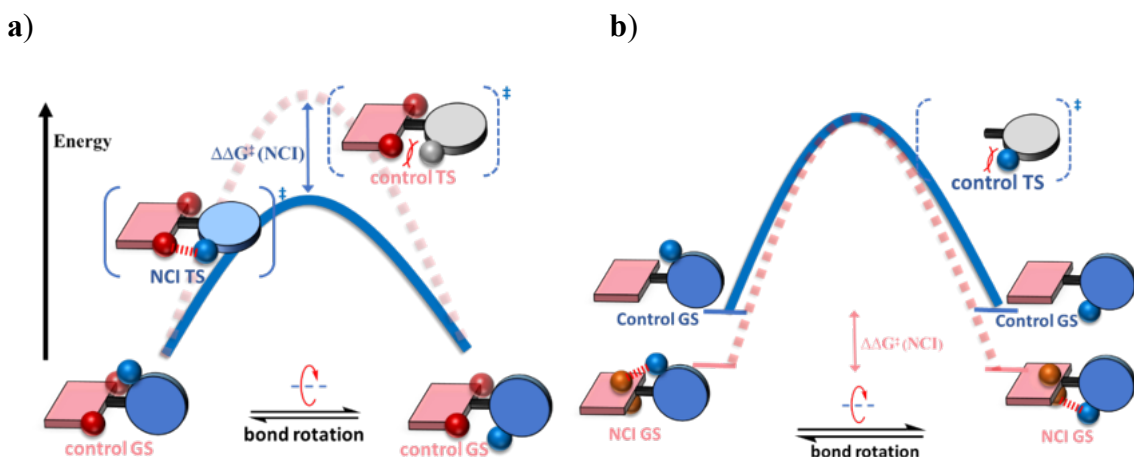


Figure 1.1 a) Molecular radical clock used to measure radical stabilities and mechanistic pathways. b) conformational equilibria of substituted cyclohexanes used to generate an *A*-value.

The critical property resulted in molecular rotors is the rates of bond rotations, thus for NCI applications, the ability of NCIs to change the rates of rotation is assessed. Changes in rotation rates arise from raising or lowering the transition or ground state energies. Specifically, stabilizing TS NCIs will lower the rotational barriers (**Scheme 1.1a**), while stabilizing GS NCIs will raise the rotational barriers (**Scheme 1.1b**). The molecular instrument rotors can be categorized into three basic types: 1. Control rotors, which only form TS steric interactions. 2. NCI rotors, which only form TS interactions. 3. NCI rotors, which only form GS interactions. Some rotors can have characteristics of 2 or more of the basic types. For example, a rotor forms stabilizing NCIs in the bond rotation TS and GS.



Scheme 1.1 Energy diagrams for the rotors with different barriers due to a) the influence of NCIs on the TS structures and b) the influence of NCIs on the GS structures.

In general, a rotational barrier is made up of two components. The first is repulsive steric interaction between the groups forced close together in the bond rotation TS. The second is the stabilizing NCIs that can form between the same groups in TS or GS. Repulsive steric interactions will be the dominant components. Otherwise, there would not be a barrier. Rotors that only form repulsive TS interactions can serve as controls for comparison to isolate the kinetic effects of the NCI rotors.

This review is organized into sections covering rotors that measure specific types of NCIs, such as hydrogen bonding and π -hole interactions. The sections on the particular kinds of NCI measurements proceeded by describing the methods used to measure the rates of rotation and rotational barriers. One subset of molecular instrument rotors that will not be covered in this review are molecular rotors designed to measure solvent viscosities via their changes in fluorescence instead of rate changes.^{14–18}

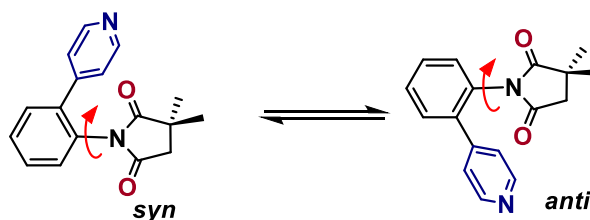
1.3 Measurements of rotational rates

1.3.1 Experimental measurements

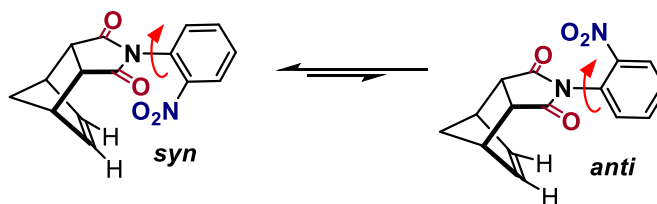
The key to assessing the kinetic effects in the molecular rotors is the measurement and comparison of their rotational barriers. Dynamic NMR is the most common tool for experimentally measuring rotational barriers. Dynamic NMR experiments typically require the rotors to contain diastereotopic or diastereomeric groups, which can allow the differentiation of the rotational isomers and monitor the exchange rate. Diastereotopic groups such as a geminal dimethyl $C(CH_3)_2$ group will have a pair of peaks in a 1:1 ratio that exchanges with bond rotation. An example of rotors with diastereotopic protons is shown in **Scheme 1.2a**, which controlled molecular motions by electrostatic interactions.¹⁹ Diastereomeric groups such as methylene CH_2 in our norbornene rotors will not typically

have a pair of peaks in a 1:1 ratio; the ratios depend on the sizes of different groups that form the NCIs and will exchange with bond rotation.^{1,4,20} An example of rotors with diastereomeric protons is shown in **Scheme 1.2b**. This example is designed to measure nitrogen pnictogen bond interaction.²⁰

a) diastereotopic example



b) diastereomeric example



Scheme 1.2 **a)** A rotor with diastereotopic protons controls molecular motions by electrostatic interactions. **b)** a rotor with diastereomeric protons used to measure the nitrogen pnictogen bond interaction.

The exchange of the diastereotopic or diastereomeric nuclei provides the rate of a rotation. Dynamic NMR typically measures the rates of exchange through 2D EXSY, lineshape analysis (**Figure 1.2a**), and coalescence temperature analysis. The 2D EXSY experiment is the most time-consuming but accurate approach, providing barriers with an error of ± 0.15 to 0.2 kcal/mol.^{21,22} Lineshape analysis^{23–26} and coalescence temperature experiments have ± 1.2 kcal/mol errors.^{27,28} Dynamic NMR methods can measure barriers from 3.0 to 25.5 kcal/mol depending on the temperature limits of the NMR instrument and the solvent system.^{29,30} NMR can also measure rotational barriers following the rate of a

diastereomeric rotor approaching the equilibria over time (**Figure 1.2b**).^{29,31} The real-time NMR method helps measure the barriers higher than 25.0 kcal/mol.³²

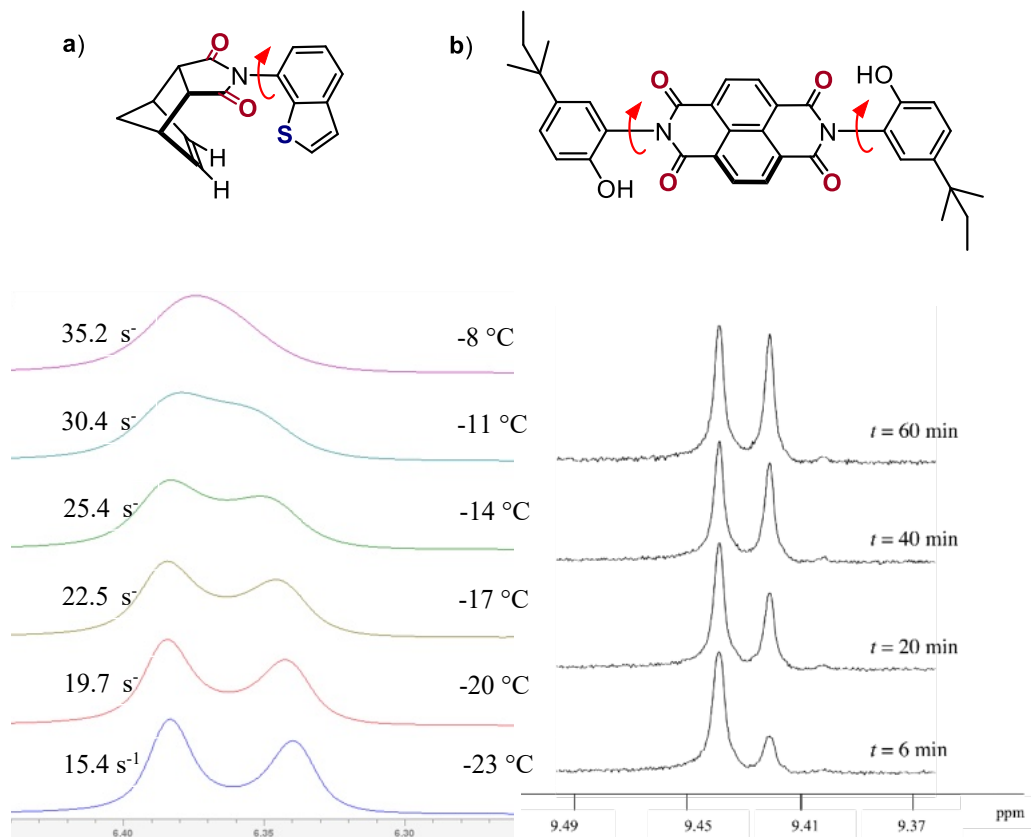


Figure 1.2 a) An example of the NMR method of 1D lineshape analysis at various temperatures. b) an example of the NMR equilibration method at one temperature over time.

Alternatively, HPLC can be used to measure the rates of isomerization, racemization, diastereomerization, or enantiomerization to determine the activation energies of rotations.^{22,33–35} The bottom limit of the measurable barrier is around 20 kcal/mol without cryogenic chromatography.^{33,35,36} The CD has also been used to measure the rates of rotations.³⁵

1.3.2 Theoretical studies

DFT calculations are an accurate method for predicting or reproducing experimental rotational barriers.^{1,20,37,38} For example, in our norbornene succinimide system, a good correlation was shown ($R = 0.966$) between experimentally measured and DFT calculated at a relatively low level of theory (B3LYP-D3, 6-311G*) rotational barriers. Furthermore, the computational barriers reproduced the trends and the specific values of the experimentally measured barriers. The standard deviation of the error between $\Delta G^\ddagger_{\text{exp}}$ and $\Delta G^\ddagger_{\text{calc}}$ was ± 0.88 kcal/mol, the mean absolute error was ± 0.90 kcal/mol, and the root mean square deviation was ± 1.06 kcal/mol (**Figure 1.3**).²⁰

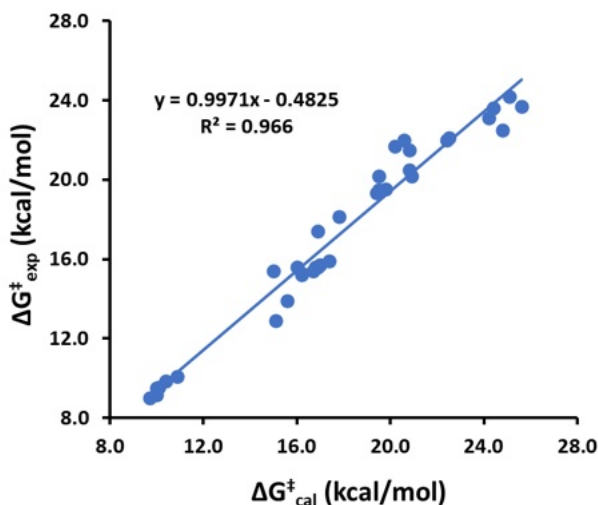


Figure 1.3 The correlation between experimental rotational and DFT-calculated (B3LYP-D3, 6-311G*) rotational barriers in norbornene rotors.

1.4 Steric interactions

The first examples of molecular rotor instruments were designed to measure steric interactions of various-sized groups.^{9,26,33,37,38} The substituent axial-equatorial conformation in cyclohexane skeleton produces steric hindrance called *A*-value of various functional groups, which had a very low energy range of 0-1 kcal/mol. *A*-value could not

predict second-row elements or heavy atoms when they were in axial positions. However, putting the functional groups into the *ortho* positions in the bond rotations to interact with an H atom could confidently measure the steric effects of various groups and heavy atoms.^{26,39} Mislow and Sternhell studied the newer approach to measuring the steric effect.²⁶ Especially, Sternhell measured the rotational barriers of 33 derivatives in the model of 6-(2-R-phenyl)-5-R¹-1,1-dimethylindan by coalescence temperatures with high accuracy of ± 0.5 kcal/mol. The rotational barriers monotonically increased with the van der Waals radius of R¹ (**Figure 1.4a**).²⁶

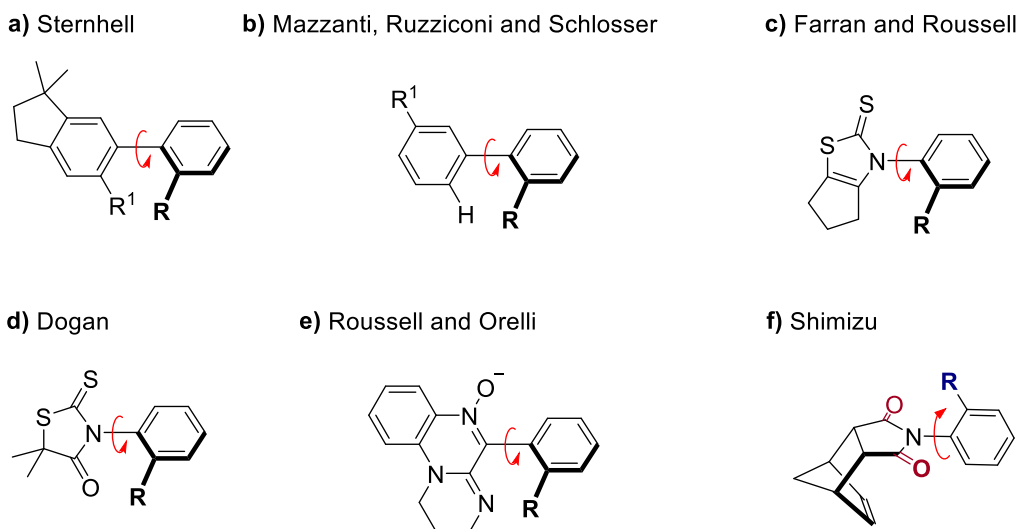


Figure 1.4 The models for measuring serial steric interactions.

A new steric parameter, *B*-values, was developed by Mazzanti, Ruzziconi, and Schlosser based on a biphenyl rotor with a diastereotopic NMR tag (**Figure 1.4b**). The diastereotopic NMR tag R¹ (CH(CH₃)₂, Si(CH₃)₂CH(CH₃)₂, or C(CF₃)₂OH) enabled measurements of the rate of exchange between the enantiomeric rotors. In the biphenyl rotor TS, R groups interacted with non-polar hydrogen. Thus, the barriers did not contain

attractive donor-acceptor or electrostatic interactions. Instead, their data reflected the steric effects of more than 35 R-groups (**Figure 1.4b**).^{37,38}

Farran and Roussel¹⁶ employed *N-ortho*-substituted-aryl-thiazoline-2-thione rotors to investigate the steric interactions of 20 functional groups, which were measured by HPLC (**Figure 1.4c**). The barrier and steric trends of Roussel's rotors were compared with the models of Sternhell,²⁶ Mazzanti,^{37,38} Dogan^{40,41} (**Figure 1.4d**), and Orelli⁴² (**Figure 1.4e**). The steric trends, as measured by the various rotors, showed a strong correlation. Thus, when the R-groups only formed steric interactions in the bond rotation TS, the barriers would monotonically increase with larger sizes. Exceptions to these trends were attributed to the formation of extra stabilization interactions.

Based on this observation, we used the *B*-values for R-groups from Mazzanti's rotors to assess our rotors' steric interactions and isolate the additional stabilizing NCIs. First, we validated this approach by measuring the barriers of norbornene succinimide rotors that had R-groups only formed steric interactions (**Figure 1.4f**). These control rotors correlated well with *B*-values for R-groups from Mazzanti's rotors. Rotors that formed stabilizing TS NCIs fell below the steric control line in the $\Delta G^\ddagger_{\text{exp}}$ vs *B*-values plot (**Figure 1.5**). This allowed both the identification and qualification of NCI rotors. The differences between the experimental barriers and the predicted steric interactions from the steric control line quantified interaction energies for TS NCIs.

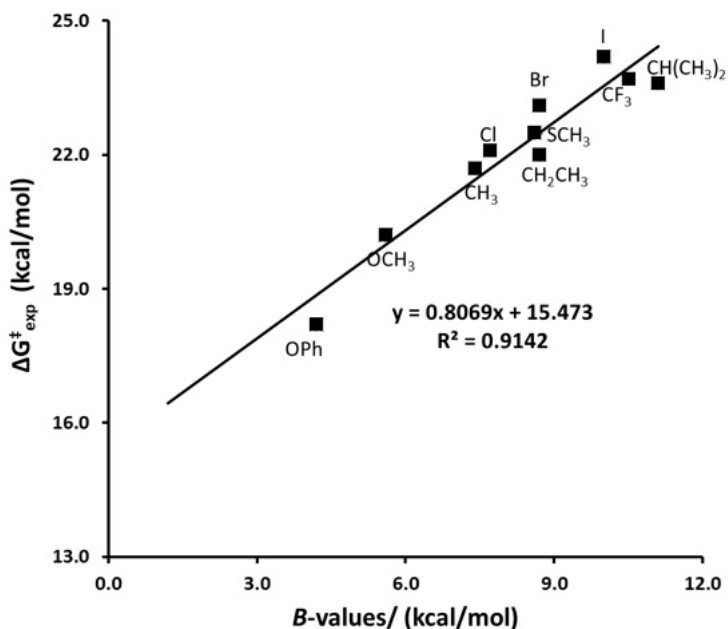


Figure 1.5 The excellent correlation between $\Delta G^\ddagger_{\text{exp}}$ vs. B -values plot.

Rotors have also been designed to measure the steric isotope effects comparing $\text{CH}\cdots\text{CH}$ and $\text{CD}\cdots\text{CD}$ interactions. Wahl (**Figure 1.6a**),⁴³ Leffek (**Figure 1.6b**),⁴⁴ Carter (**Figure 1.6c**),^{45,46} and Boekelheide⁴⁷ observed the kinetic isotope effects (KIE) in different rotors to obtain $K_D/K_H = 1.14$ to 1.20 . The most recent example by Baldrige and Siegel⁴⁸ in 2008 measured the KIE of a penta-aryl corannuleene bowl-inversion rotor, finding a ratio of $K_H/K_D = 1.22$ by VT NMR. Deuterium is sterically smaller due to shorter C-D bond length as the deuterium nuclei are heavier than the proton, which caused the reverse KIE in this case. These studies exemplified the use of molecular rotors to determine and quantify the kinetic isotope effects presented in molecules, especially between deuterated and protonated rotors.

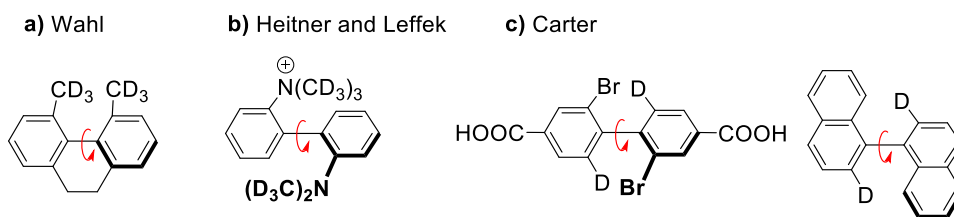


Figure 1.6 Some rotors that studied steric KIE in the 1960s.

1.5 Stabilizing non-covalent interactions (NCIs)

In this section, rotors designed to study and measure multiple types of stabilizing NCIs will be summarized, including 1) hydrogen bonding, 2) n to π^* or π interactions, 3) π stacking interactions, 4) chalcogen bond interactions, 5) pnictogen bond interactions, 6) metal or guest coordination. The last type of rotors investigated the factors that influenced the rotational barriers, which typically formed steric interactions: 7) solvent effects and substituent effects. The rotors assessed the kinetic effects of the NCIs.

While most rotors formed the NCIs in the bond rotation TSs, some rotors formed GS NCIs, like Wegner's London dispersion azobenzene rotors (**Figure 1.7a**).⁴⁹ Halogen bonding (**Figure 1.7b**) and boron triel bonding rotors (**Figure 1.7c**) also formed GS interactions.^{50–52}

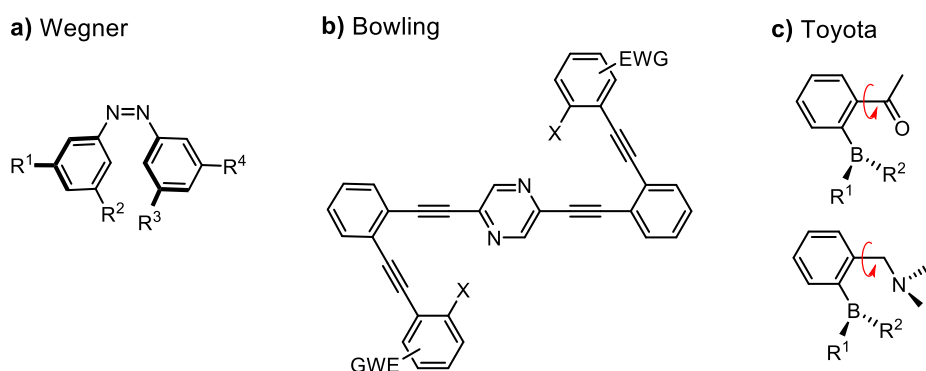


Figure 1.7 Dispersion, chalcogen, and boron bonding interactions in GSs

1.5.1 Hydrogen bonding (HB)

Although hydrogen bonding interactions are one of the earliest NCIs to be identified and studied, important questions remain about their role in kinetic processes such as organic catalysis.⁵³ Roussel explored the influence of hydrogen bonding on the racemization of biaryl atropisomers using iminothiazolines rotors (**Figure 1.8a**).⁵⁴ This work suggests that the OH and imino groups formed a stabilizing interaction in the near planar bond rotation TS. The barriers were measured by HPLC, and the energy gap between OH which was lower, and OCH₃ which was non-HB control, was ~5.7 kcal/mol.

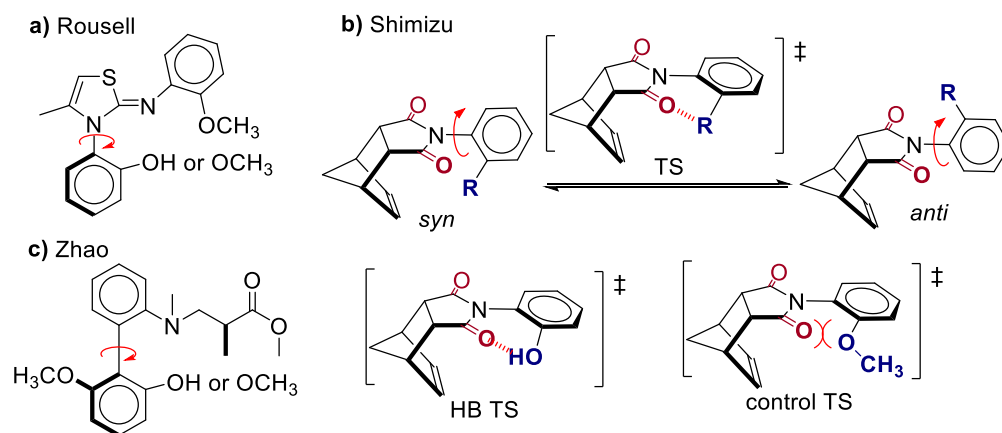


Figure 1.8 The rotors that studied the kinetic effects of hydrogen bonding.

One of our first molecular rotor instruments studied the kinetic effects of hydrogen bonding using norbornene succinimide rotors (**Figure 1.8b**).⁵⁵ Hydrogen bonding OH and non-HB control OCH₃ rotors were designed and synthesized. In the calculated bond rotation TS, the C=O oxygen was well aligned with the σ^* of H-O, and the distance of hydrogen and C=O oxygen atoms was just 1.5 Å, much shorter than the sum of their VDW radii. These suggested the formation of geometrically favorable intramolecular hydrogen bonds. The kinetic effects of neutral C=O...H-O HB were much more significant than expected, lowering the rotational barriers by as much as ~ 10 kcal/mol. The barriers of the

HB rotors were measured in a low-temperature range with coalescence temperatures from -55 °C to -70 °C using dynamic 1D lineshape or coalescence temperature analyses.

Zhao also studied a TS stabilizing intramolecular OH•••N HB using tri-ortho-substituted biaryl rotors (**Figure 1.8c**).⁵⁶ The VT NMR experiments showed that the OH rotor significantly lowered the rotational barriers by 11.1 kcal/mol compared to the OCH₃ rotor, which meant the TS repulsion was reduced by forming stabilizing HB bonding interactions.

1.5.2 n to π^* or π interactions

The n to π and n to π^* interactions are stabilizing interactions between electron-deficient carbonyl carbons and phenyl groups (lone pair acceptors) to interact with another electron-rich atom (lone pair donor). Molecular rotors have been developed to study the kinetic effect of n to π^* (C=O) and n to π interactions (**Figure 1.9**).

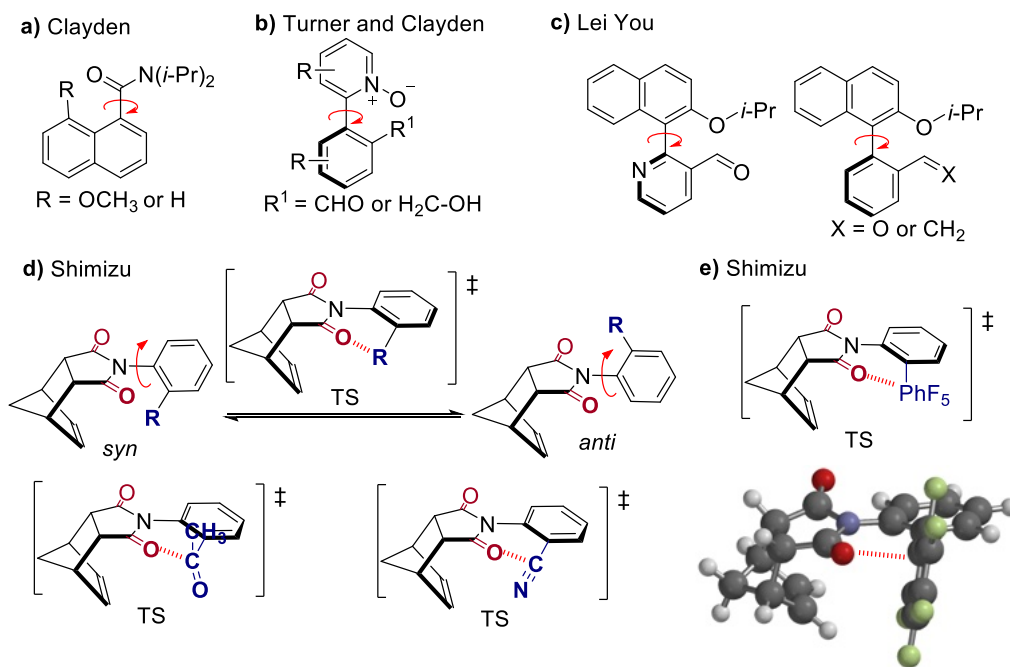


Figure 1.9 The rotor models designed to study n to π^* or π interactions.

Clayden employed chiral atropoisomeric 8-substituted 1-naphthamides rotors to measure the n to π^* ($\text{N/O} \cdots \text{C=O}$) interactions on the racemization. The enantiomers were thermally stable due to GS n to π^* interactions between the peri OCH_3 and $\text{CON}(i\text{-Pr})_2$. Evidence of the presence of stabilizing n to π^* interactions was the higher barriers (25.8 kcal/mol) for the rotor where the OCH_3 group replaced the smaller H-group (17.8 kcal/mol) with the prerequisite that the peri-groups did not significantly contribute to the steric interactions (**Figure 1.9a**).³⁴ Later, Clayden and Turner employed n to π^* ($\text{O} \cdots \text{C=O}$) interactions to design a system capable of the dynamic kinetic resolution (**Figure 1.9b**). In the biaryl N -oxide frameworks, the barrier of aldehyde rotors, which can form n to π^* interactions, have lower barriers (15.7-16.3 kcal/mol) than the benzyl alcohol rotors (27.5-28.8 kcal/mol) which cannot form these interactions.⁵⁷

A study of n to π^* (C=X) was completed in our norbornene succinimide rotors (**Figure 1. 9c**).¹ A series of π^* donors from sp^2 and sp carbons in cyano, alkene, and carbonyl groups were designed and synthesized. VT NMR was employed to measure the rotational barriers. A series of control rotors that did not form n to π^* interactions were used to assess the repulsive steric components of the barriers and isolate the stabilizing n to π^* (C=X) interactions (**Figure 1.9d**), which were up to 8.5 kcal/mol. The origins of the interactions, which contained orbital-orbital interactions with electrostatic interaction contributions, were explored using electrostatic potential (ESP), natural bonding orbital (NBO), and pyramidalization calculations.¹ We also designed a series of norbornene succinimide rotors to study n to $\pi(\text{phenyl})$ interactions.⁴ The carbonyl and phenyl groups differed in the strength of orbital-orbital interaction components. The carbonyl group has strong orbital-orbital interaction components, whereas the phenyl group has a weak or

negligible orbital component and a weaker overall interaction energy.^{4,58} However, the electrostatic components of n to π (phenyl) interactions were more easily modulated via substituents on the phenyl ring. Specifically, electron-withdrawing groups made the phenyl surfaces more electron-deficient, strengthening the interactions with the oxygen lone pair (**Figure 1.7e**).⁴

Lei You explored the kinetic effects of n to π^* in the biaryl-based rotors and developed them into switchable molecular rotors using acid/base stimuli to form and remove hydrogen bonding in the pyridyl ring (**Figure 1.9e**).⁵⁹ The bond rotation TS was accelerated with more substantial n to π^* in the C=O group compared to the C=CH₂ group (**Figure 1.9e**). The n to π^* interaction energies were identified by TS NBO calculations, which could be up to 9.4 kcal/mol.

1.5.3 π -stacking interactions

Rotors have been used to study the kinetic effects of π -stacking interactions. Pioneering studies by Cozzi and Siegel investigated π -stacking in the ground states of 1,8-diaryl naphthalenes rotors (**Figure 1.10a**).⁶⁰ When studying the substituent effects of the interactions, the $\Delta G^\ddagger_{\text{exp}}$ monotonically increased with σ_{para} values as the more electron-deficient phenyl rings formed stronger π -stacking interactions. A NO₂ group would raise the rotational barrier by 3.4 kcal/mol compared to the OCH₃ group. Likewise, Waters measured an offset- π -stacking of substituted benzyl pyridinium arenes in water (**Figure 1.10b**), where the π -stacking happened in GSs but raised the rotational barriers only slightly (0.1-0.66 kcal/mol).⁶¹

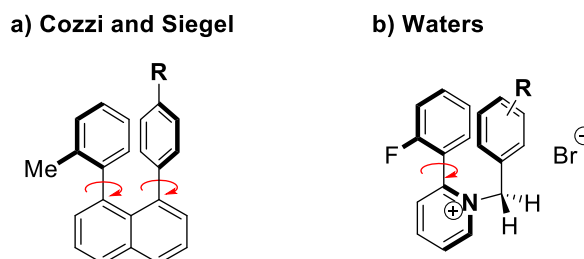


Figure 1.10 Rotors studied π -stacking interactions in GS.

1.5.4 Pnictogen bond (PnB) interactions

The pnictogen bond interaction is the attractive non-covalent interaction between an electrostatically positive part on a pnictogen (Pn) atom (N, P, As, Sb, Bi) and an electrostatically negative part on another atom.⁶² Although pnictogen bond interactions have been well studied in other fields and have many applications, the kinetic effects of PnB have yet to be elaborated in solution-based measurements.²⁰ A few examples of PnB involving the nitrogen of amide groups have been reported.^{63,64}

We developed the nitrogen-centered norbornene succinimide rotors (**Figure 1.11a**) to explore the kinetic effects of nitrogen pnictogen interactions (NPnB). The TS NPnB interactions had a wide range of effects on rotational barriers from +1.8 to -8.4 kcal/mol. Modeling showed the interaction distances shorter than the sum of van der Waals radii of the interacting O and N atoms—the interactions primarily in origins electrostatic with negligible orbital-orbital interactions. The interaction energies would linearly increase as the ESP of the nitrogen increased. A range of functional groups were studied, including amines, amides, nitro, imine, and nitrogen heterocycles. The nitro group and amides formed the strongest PnB which was more robust than the strongest n to π (phenyl) but weaker than the strongest n to π^* ($C=X$) when comparing norbornene succinimide rotors (**Figure 1.9d and e**).²⁰

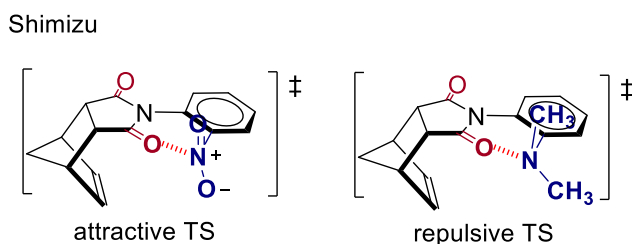


Figure 1.11 The rotor models designed to study nitrogen pnictogen bond interactions.

1.5.5 Chalcogen bond (ChB) interactions

Chalcogen bond interactions are attractive NCI between an electron-rich atom and an electron-poor region of a chalcogen atom (O, S, Se, Te). The strong $\text{N} \cdots \text{Se}$ chalcogen bond interactions were measured in 2-selenobenzylamine derivatives, and the experimental stabilizing interaction energies of $\text{N} \cdots \text{Se}$ chalcogen bond interactions varied from < 7.7 kcal/mol to 18.8 kcal/mol. However, according to the plausible mechanism, the chalcogen bond interactions formed in the ground states (**Figure 1.12a**).⁶⁵

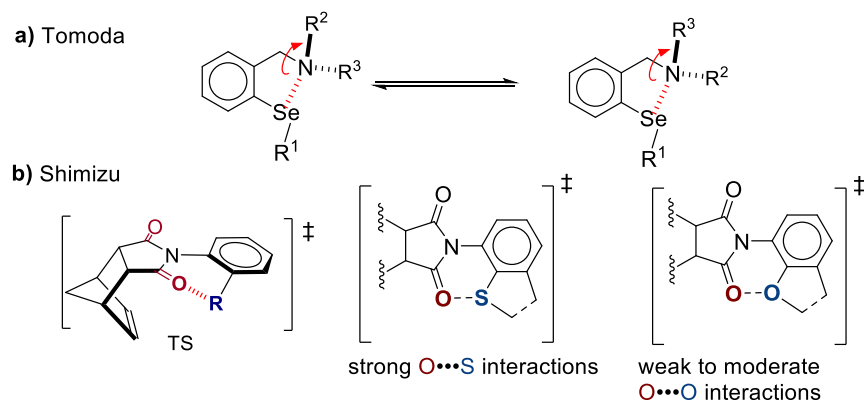


Figure 1.12 a) The model by Tomoda used to study $\text{N} \cdots \text{Se}$ bond interactions in ground states; b) Our work in norbornene succinimide to study oxygen and sulfur chalcogen bond interactions.

A kinetic study was recently conducted in our norbornene succinimide rotors for the smaller oxygen and sulfur chalcogen atoms, which are more challenging to form chalcogen bonds (**Figure 1.12b**). The fused cyclic structures of chalcogen rotors forced the

carbonyl lone pair to align with the σ -holes of the chalcogen atoms in TS. Thus, a short ChB interaction distance (2.5 Å) formed in planar bond rotation TS, which was shorter than the sum of radii of chalcogen atoms (3.04 Å for O...O, and 3.32 Å for O...S). The ChB lowered the rotational barriers by 2.0 to 7.2 kcal/mol. Correlations of calculated parameters with the experimental barriers showed that the ChB was dominated by electrostatics while sulfur ChB was a combination of electrostatic and orbital-orbital interactions.

1.5.6 Guest-accelerated complexation

Some additives could stabilize the transition states of bond rotations by forming Hydrogen bonding. Rebek (**Figure 1.13a**) developed a rotor system to restrict and accelerate the bond rotation TS by protonation and deprotonation.⁶⁶

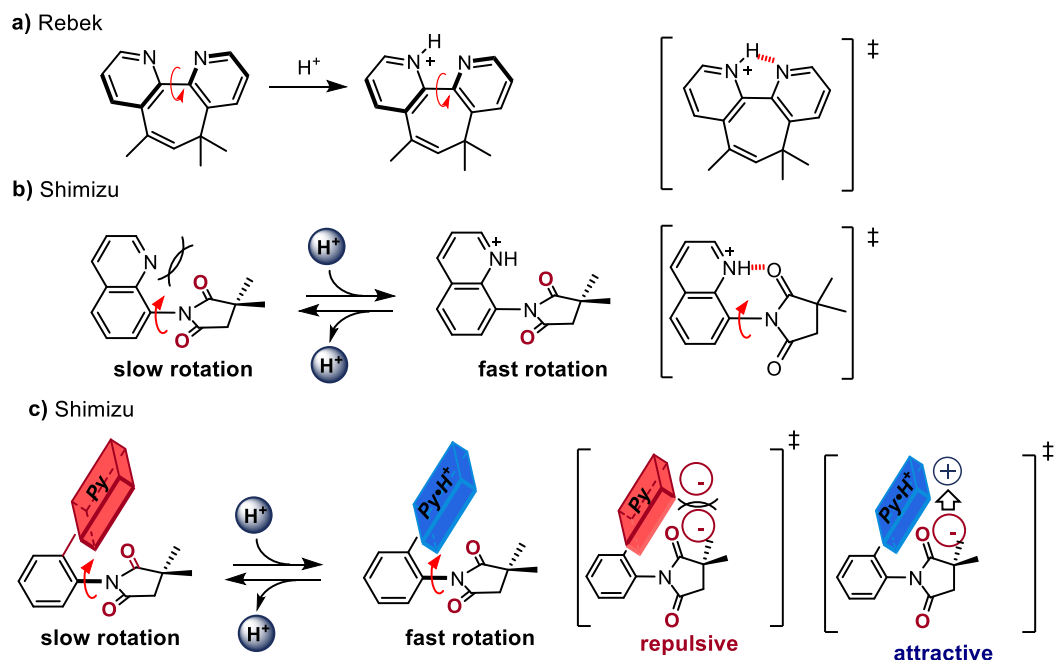


Figure 1.13 a) The rotation acceleration by the proton or metal coordination from Rebek; b) The “proton grease” developed by Shimizu and coworkers; c) electrostatically-gated molecular rotors.

We created a “proton grease” intramolecular HB by pronating the quinolinyl ring in dimethyl succinimide rotors (**Figure 1.13b**);⁶⁷ Other rotors employed similar strategies.^{68,69} In all these rotors, the pronated rotors with intramolecular HB stabilized the TS and lowered the rotational barriers from 4.5 to 10.0 kcal/mol. Our “proton grease” displayed a stabilization of 10.0 kcal/mol.⁶⁷

We also used the same strategy to build up electrostatically-gated molecular rotors.¹⁹ In this case, N-H was not directly involved in the NCIs, but positive-charged aromatic surfaces were created to interact with the carbonyl lone pair. The electrostatic *n* to π (pyridyl) interaction in dimethyl succinimide was gated by the protonation of the pyridyl nitrogen, and the rotational barriers consistently decreased up to 3.2 kcal/mol with the protonation level until complete. Moreover, the cycle of protonation and deprotonation by NaHCO₃ fine powder was reversed by multiplying. Fi-SAPT calculations revealed the electrostatic terms were way more favorable than other terms after the protonation, which did not happen using the phenyl control rotor (**Figure 1.13c**).¹⁹

The intermolecular HB with the solvents in TS would compete with TS intramolecular HB, which decelerated the bond rotations.^{70,71} In the bond rotation TS of our *N*-phenylimide rotors, the intermolecular HB (C=O...H-O) competed with the intramolecular HB (DMSO...H-O) and raised the barriers by more than 10 kcal/mol from nonpolar solvent like CD₂Cl₂ to polar solvent like DMSO, which could be regarded as the interaction energies of the intramolecular HB (**Figure 1.14**).⁷⁰

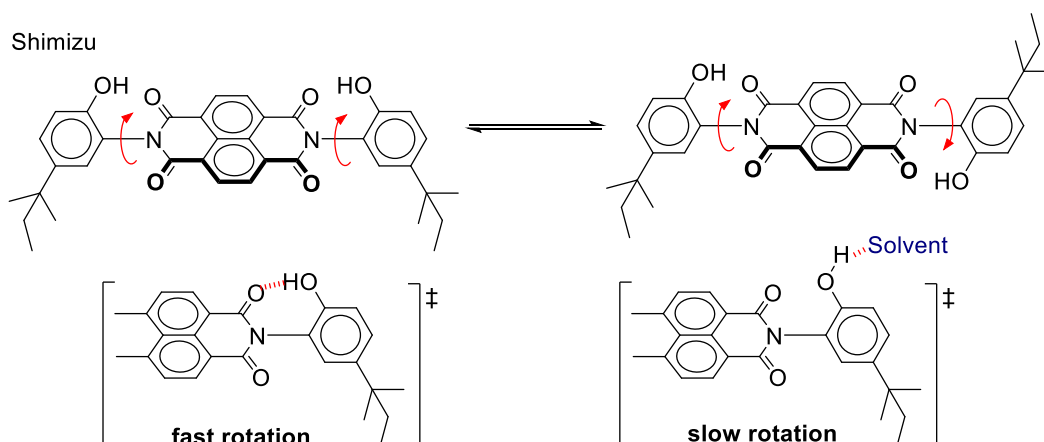


Figure 1.14 The competition and deacceleration of forming hydrogen bonding with the solvent molecules.

The work of Rebek⁶⁶ also referred to metal coordination in TS (**Figure 1.11b**) with a stabilization of 4.0 kcal/mol. The dimethyl succinimide rotors were also used to study the metal coordination in TS by Wang, which accelerated the rotation from the intramolecular electrostatic repulsion between oxygen anion and carbonyl oxygen.⁷² The metal coordination studies were interestingly conducted solidly using giant rotors.⁷³ Ito and Jin employed the crystalline molecular rotors with a central pyrazine rotator connected by implanted transition metals to measure the d to π^* interactions, and they found out that Cu was ~ 4.0 kcal/mol lower than Au in the rotational energy barrier.⁷³ Moreover, Schmittel studied GS metal coordination and exchange in reversible switch rotors; the barriers increased from 0.56-0.64 to 11.3-12.1 kcal/mol by coordinating Cu^+ or Zn^{2+} .⁷⁴

1.5.7 Solvent effect and electronic effects of steric interactions

Some research was conducted to study how environmental factors influenced the bond rotations of steric interactions, including substituent or electronic and solvent effects. Substituent effects have been studied since the 1970s by Harris⁷⁵ and Kishikawa⁷⁶, respectively, on the rotors that only formed steric interactions. However, they proposed

different perspectives for substituent effects. Harris concluded that the half-lives of racemization were raised by electron-withdrawing while being reduced by electron-donating groups with the most significant energy gap of 2.4 kcal/mol between the COOCH₃ and NH₂ group (**Figure 1.15a**).⁷⁵

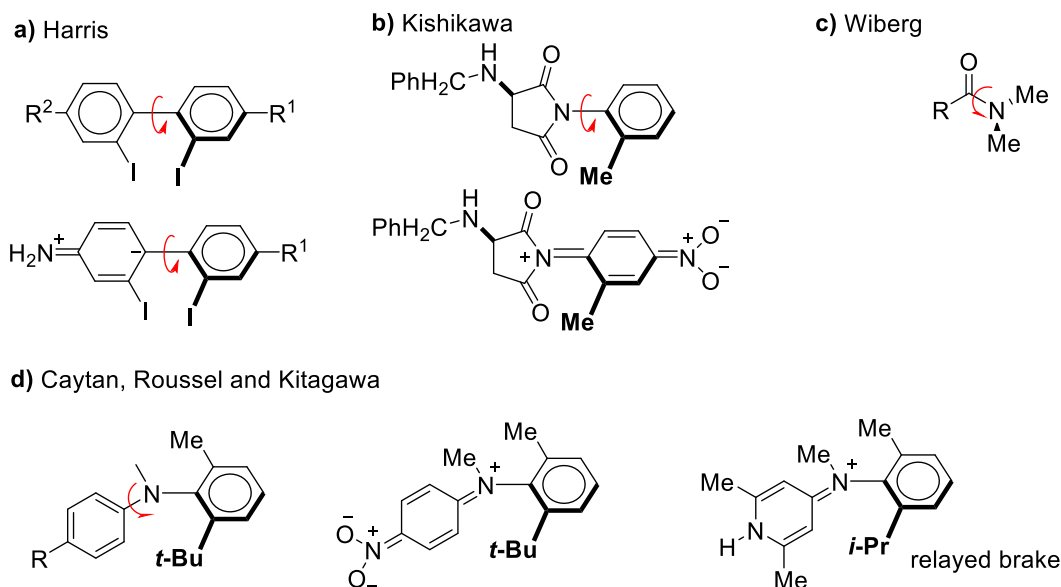


Figure 1.15 The rotor models for studying solvent and electronic effects of steric interactions.

Kishikawa came to an opposite conclusion, stating that the rotational barriers decreased by ~1.0 kcal/mol with the electron-withdrawing capacities of the attached groups (Figure 1.15b).^[66] Kishikawa also proved that the steric interactions of the methyl group would be increased by the solvent polarity up to 2.0 kcal/mol (Figure 1.15b), which was previously observed in amide rotors by Wiberg with a slightly higher increase from 2.3 to 2.7 kcal/mol (**Figure 1.15c**).⁷⁷

Roussel observed the same phenomenon as Harris in an N-C axially chiral aniline system. They enlarged the effects by developing “proton brakes.” After adding MsOH, they observed a remote⁷³ or relayed⁷⁴ brake, with the rotation rates around both N-pyridyl

and N- (i-Pr) phenyl bonds significantly decelerated. Calculations suggested that the steric interactions increased from 4.0 to 5.7 kcal/mol in bond rotational TS (**Figure 1.15d**).

The significant differences in substituent effects were reasonably given out. In the *N*-phenylimide rotor system, the electron-withdrawing substituents stabilized the transition states by conjugating substituted phenyl and *N*-bond rotation (**Figure 1.15b**).⁷⁶ This phenomenon was also observed in our *N*-phenylimide rotor system, which studied HB studies (**Figure 1.8b**).⁵⁵ However, in the N-C axially chiral rotor systems, the co-plane of the substituted phenyl group and nitrogen plane produced the electronic effect to form conformational stability, which increased the rotational barriers (**Figure 1.15d**).⁷⁸ In the biaryl rotors of Harris, the sp^3 character of the biaryl axis would be adjusted by the electron density from the attached groups, where the electron-withdrawing group decreased the character and raised the half-life of racemization (**Figure 1.15a**).^{75,79}

1.6 Conclusion

In summary, molecular rotors have been used to measure steric interaction or further isolate the interaction energies of non-covalent interactions. Intriguing molecular systems were designed, including diastereotopic and diastereomeric rotors, and their rotations were measured by multiple methods. These studies highlighted methods to modulate the dynamic bond rotations and indicated possible applications. In the future, more exciting publications will come out from our research groups and others. Potential topics could be the measurements of non-covalent interactions that are rare. Also, the precise identification and measurement of interactions in a reaction process or supramolecular system will help organic chemists determine organic reaction mechanisms. The last challenging and exciting topic is employing a rotor system to elaborate an organic

reaction mechanism or theory. There may be interesting applications in some switchable and tunable systems.

Chapter 2 Electrostatically-gated molecular rotors

2.1 Abstract

The ability to control molecular-scale motion using electrostatic interactions was demonstrated using an N-phenyl succinimide molecular rotor with an electrostatic pyridyl-gate. Protonation of the pyridyl-gate forms stabilizing electrostatic interactions in the transition state of the bond rotation process that lowers the rotational barrier and increases the rate of rotation by two orders of magnitude. Molecular modelling and energy decomposition analysis confirms the dominant role of attractive electrostatic interactions in lowering the bond rotation transition state.

2.2 introduction

The development and study of synthetic molecular devices and molecular machines are an exciting new area of research.^{80–84} An important challenge in the field is developing effective methods of controlling molecular-scale motion using macroscale inputs and stimuli. For example, stimuli used to control the rates of rotation of molecular rotors have included: light,^{85–90} metal ions,^{91–93} hydrogen bonds,^{94–96} redox,^{97–99} anions,¹⁰⁰ guests,^{95,101,102} and protons.^{67,103–107} The majority of these systems were molecular brakes where the stimuli slowed the rate of rotation. More rare were stimuli that increased or accelerated the rate of rotations.^{94,98,67,99,106,107}

In this work, we demonstrate the use of attractive electrostatic interactions to stabilize transition states, lower barriers, and increase rates of molecular scale motion. The control of molecular-scale motion using electrostatic interactions has the potential of being integrated with existing micro- and nanoscale devices such as memory and transistors that are electrically addressed and controlled.¹⁰⁸ In addition, the electrostatic gating mechanism could be coupled with electron microscopy methods that can manipulate and investigate the electronic states of single molecules.^{109–112}

Electrostatic interactions have been employed to control the thermodynamic equilibria of molecular devices by stabilizing or destabilizing one or more possible states.^{80,113} However, there are few examples that use electrostatic interactions to control the kinetics and rates of molecular motion. The examples we did find used repulsive electrostatic interactions to raise barriers such as preventing pseudorotaxane dethreading.¹¹⁴ Therefore, the goal of this work was to develop a molecular device in which attractive electrostatic interactions lower barriers and increase the rate of molecular motion by forming stabilizing transition state interactions.

2.3 Results and discussion

A challenge in demonstrating electrostatically controlled increases in molecular-scale motion is separating the electrostatic component from other TS interactions in particular the steric interactions. Our recent studies of $C=O \cdots \pi(\text{phenyl})$ interactions using molecular rotors suggested a possible solution.⁵⁸ The substituents on the phenyl gates only modulated the electrostatic interaction as the steric component stayed constant. Thus, in the design of the electrostatically gated rotors **1**, a structurally similar 3- and 4-pyridyl gate was used as the protonation of the pyridyl group would provide larger changes in the

electrostatic interactions due to the presence of the positive charge with minimal change in the steric interactions.

The electrostatically gated molecular rotors are based on the *N*-phenylimide framework, which displays restricted rotation about the central C-N single bond.^{95,115,116} Rotors **1**(3-Py) and **1**(4-Py) have 3- or 4-pyridyl electrostatic gates appended to the *ortho*-position of the *N*-phenyl stator. The electrostatically negative π -face of the neutral pyridyl groups form repulsive electrostatic interactions with the imide C=O oxygen in the bond rotation transition state leading to a high barrier and slow rotation of the succinimide rotor (Figure 2.1a). However, when the pyridyl gate is protonated in **1**(3-Py)•H⁺ and **1**(4-Py)•H⁺, the positively charged pyridinium group forms attractive electrostatic interactions with the imide C=O oxygen lowering the barrier and speeding up rotation of the succinimide rotor. A control rotor **2**(Ph) was also prepared with a phenyl gate, which lacks a basic pyridyl nitrogen and thus cannot be protonated (Figure 2.1b).

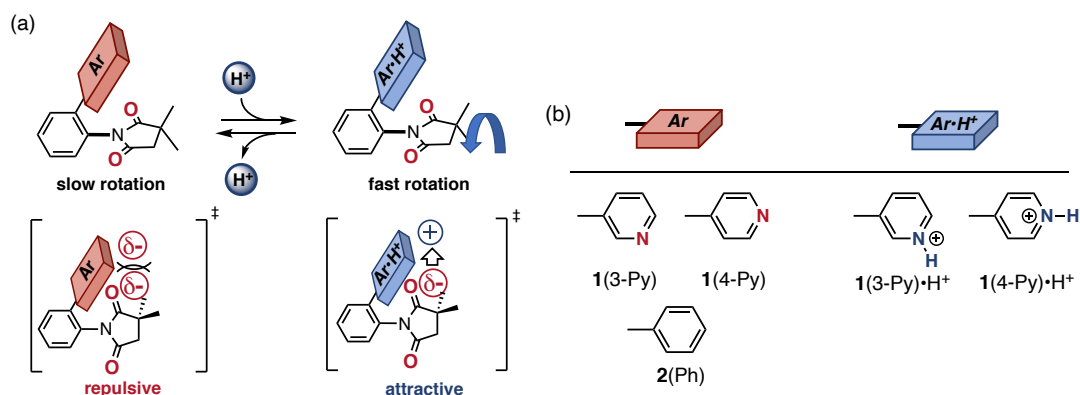


Figure 2.1 a) Schematic representation of the electrostatically-gated rotors **1** which are activated by protonation that lowers the rotational barriers by forming attractive electrostatic interactions in the bond rotation TS and b) chart of the chemical structures of **1**, **1**•H⁺, and control rotor **2**.

Rotors **1** and **2** were synthesized via the thermal condensation of 3,3-dimethylsuccinic anhydride and an *ortho*-substituted aniline (AcOH, 140 °C, 24 h).¹¹⁷ The

dimethyl groups break the symmetry of the succinimide rotor, enabling the rate of rotation to be monitored by ^1H NMR. For example, the succinimide CH_2 protons were diastereotopic in the unprotonated rotors **1**(3-Py), **1**(4-Py), and **2**(Ph), due to slow rotation around the C-N bond at (25 °C) (Figure 2.2, 0 eq. MsOH). However, when the pyridyl groups are protonated with methane sulfonic acid (MsOH), the succinimide CH_2 protons were in fast exchange and collapsed into a singlet due to fast rotation around the C-N bond (Figure 2.2a). By comparison, the ^1H NMR spectra of control rotor **2**(Ph) did not change when MsOH was added. The diastereomeric succinimide CH_2 protons shifted downfield but remained in slow exchange (Figure 2.2b).

The differences in the rates of rotation and rotational barriers were observed by the changes in coalescence temperatures (Figure 2.18 in 2.5 supporting information) and quantitatively measured using EXSY NMR (Table 2.1). The changes in rotational barrier were consistent with the ability of the pyridinium gates to electrostatically lower the rotational barriers of rotors **1**. Initially, the neutral rotors **1**(3-Py), **1**(4-Py), and **2**(Ph) had similar barriers of 18.8 to 20.6 kcal/mol. On the addition of 3 equivalents of MsOH, the rotational barriers of the pyridyl rotors, **1**(3-Py) and **1**(4-Py) decreased by 2.1 and 3.2 kcal/mol. In contrast, the rotational barrier for the control rotor **2**(Ph) increased slightly on addition of MsOH. The changes in barriers correspond to increases in the rates of rotation of 32 and 206 fold for rotors **1**(3-Py)• H^+ and **1**(4-Py)• H^+ respectively (Figure 2.3).

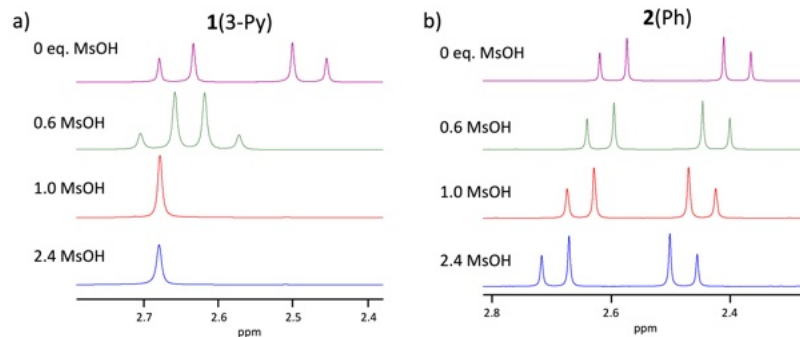


Figure 2.2 ^1H NMR spectra of the succinimide CH_2 protons for a) electrostatically gated rotor **1(3-Py)** and b) control rotor **2(Ph)** with increasing number of equivalents of MsOH. The ^1H NMR spectra for **1(4-Py)** were similar to those of **1(3-Py)**.

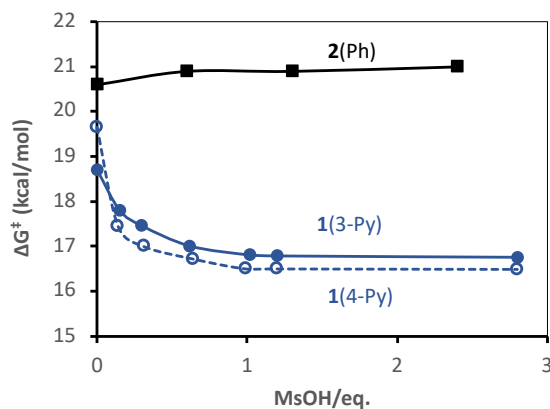


Figure 2.3. Rotational barriers for rotors **1(3-Py)**, **1(4-Py)**, and **2(Ph)** with increasing equivalents of methanesulfonic acid (MsOH) in TCE- d_2 as measured by EXSY ^1H NMR.

To verify that attractive electrostatic interactions were the reason for the lower barriers of the pyridinium rotors, the geometries, rotational barriers, and energy decomposition analyses were calculated. The ground state and TS geometries (B3LYP-D3/6-311G* with a solvent dielectric of 8.42 for TCE) were very similar for the unprotonated and protonated rotors **1** and control rotor **2**. In particular, the TS structures were nearly identical as shown in Figure 2.4 with the $\text{C}=\text{O}$ groups pointing into the π -face of the perpendicular aryl rings. The closest contacts from the oxygen of the $\text{C}=\text{O}$ to the aryl rings were also very similar (2.42 – 2.58 Å). Most importantly, the rigid framework

and the perpendicular geometry of the pyridinium rings prevent the N-H protons of **1**(3-Py)•H⁺ and **1**(4-Py)•H⁺ from forming intramolecular hydrogen bonding interactions that could have provided another explanation for their lower barriers.

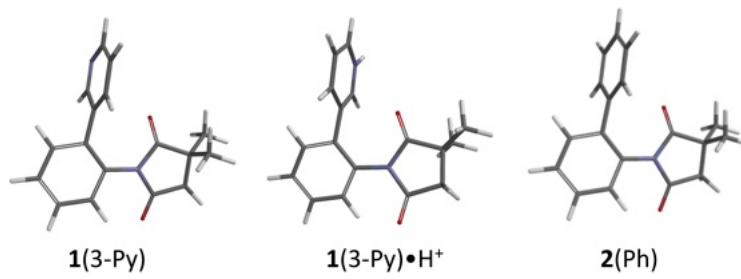


Figure 2.4 Calculated (B3LYP-D3/6-311G*) transition state structures for the unprotonated and protonated electrostatically gated rotor **1**(3-Py) and **1**(3-Py)•H⁺ and control rotor **2**(Ph).

Table 2.1 Experimental and calculated rotational barriers and rates of rotations.

Rotor	$\Delta G_{\text{expt}}^{\ddagger}$ ^a (kcal/mol)	$\Delta G_{\text{calc}}^{\ddagger}$ ^b (kcal/mol)	rotation rate ^c (Hz)
1 (3-Py)	18.8	21.9(20.7)	0.095
1 (4-Py)	19.7	20.1(20.5)	0.025
1 (3-Py)•H ⁺	16.7 ^e	19.0(13.8)	3.02
1 (4-Py)•H ⁺	16.5 ^e	17.5(12.7)	5.14
2 (Ph)	20.6	20.9(22.2)	0.0049

^aRotational barriers measured by EXSY of the ¹H NMR in TCE-d₂. ^b Calculated using B3LYP-D3/6-311G* in 1,1,2,2-tetrachloroethane (dielectric = 8.42) at 298.15 K. Values in parentheses were calculated in the gas phase at 298.15 K. ^c Calculated using $\Delta G_{\text{expt}}^{\ddagger}$ for 298.15 K. ^e **1**(3-Py) and **1**(4-Py) were protonated by the addition of 3 equivalents of MsOH in TCE-d₂.

The calculated rotational barriers ($\Delta G_{\text{calc}}^{\ddagger}$) from the GS and TS structures were also able to reproduce the experimentally observed lower rotational barriers of **1**(3-Py)•H⁺ and **1**(4-Py)•H⁺ (Table 2.1).¹¹⁸ The average difference between the neutral and protonated

rotors for the experimentally measured ($\Delta\Delta G^\ddagger_{\text{expt}}$) and calculated barriers ($\Delta\Delta G^\ddagger_{\text{calc}}$) were very similar (2.7 and 2.8 kcal/mol).

Comparisons of the barriers calculated in solvent (dielectric = 8.42) and the gas phase provided the first evidence for presence of stabilizing TS electrostatic interactions (Table 2.1). The neutral rotors **1**(3-Py), **1**(4-Py), and **2**(Ph) had similar $\Delta G^\ddagger_{\text{calc}}$ values in solvent and the gas phase. In contrast, the positively charged pyridinium rotors **1**(3-Py) $\cdot\text{H}^+$ and **1**(4-Py) $\cdot\text{H}^+$ had very different $\Delta G^\ddagger_{\text{calc}}$ values in solvent and the gas phase. The average change in the barrier ($\Delta\Delta G^\ddagger_{\text{calc}}$) on protonation for rotors **1** was small in solvent (-2.75 kcal/mol) and large (-7.35 kcal/mol) in the gas phase. These differences are consistent with the electrostatic interactions being screened in solvent, which reduces their effect on the rotational barriers.

Direct evidence for the stabilizing electrostatic TS interactions in the pyridinium rotors was provided by energy decomposition analyses of the non-covalent interactions in the transition states (Figure 2.5). The intramolecular interaction energies between the imide carbonyl groups (C=O) and the aromatic pyridyl, pyridinium, and phenyl gates in the TS (B3LYP-D3/6-311G*) were calculated using the functional group interaction analysis method (fi-SAPT(0), jun-cc-pVZT).¹¹⁹ The calculated interaction energy trends mirrored the experimental rotational barrier trends. The neutral rotors, **1**(3-Py), **1**(4-Py), and **2**(Ph), had destabilizing C=O $\cdots$ aryl interactions ($E_{\text{total}} = 11.7$ to 13.6 kcal/mol). Whereas, the positively charged rotors, **1**(3-Py) $\cdot\text{H}^+$, **1**(4-Py) $\cdot\text{H}^+$, had stabilizing interactions ($E_{\text{total}} = -4.4$ and -8.0 kcal/mol). The origins of the differences in the E_{total} values between the neutral and positively charged rotors were evident from an analysis of the component repulsion-exchange, electrostatic, induction, and dispersion (E_{exch} , E_{elec} , E_{ind} ,

and E_{disp}) terms. The E_{exch} , E_{elec} , and E_{disp} terms were similar between the neutral and positively charged rotors. In particular, the similarity in the repulsive E_{exch} terms provided confirmation that the pyridyl gates do not change in size on protonation or deprotonate. Only, the E_{elec} term changed dramatically between the neutral and protonated rotors **1**. For example, the change in the E_{elec} term (ΔE_{elec}) between **1**(3-Py) and **1**(3-Py)•H⁺ was -16.2 kcal/mol which was very similar to the differences in the total interaction energies ($\Delta E_{\text{total}} = -17.1$ kcal/mol). Likewise, the ΔE_{elec} (-18.3 kcal/mol) and ΔE_{total} (109.8 kcal/mol) terms were very similar for **1**(4-Py) and **1**(3-Py)•H⁺. The electrostatic nature of the intramolecular C=O... π (pyridyl) are consistent with our recent study, which found that stabilizing C=O... π (phenyl) interactions in neutral aromatic systems were dominated by electrostatic interactions.⁵⁸

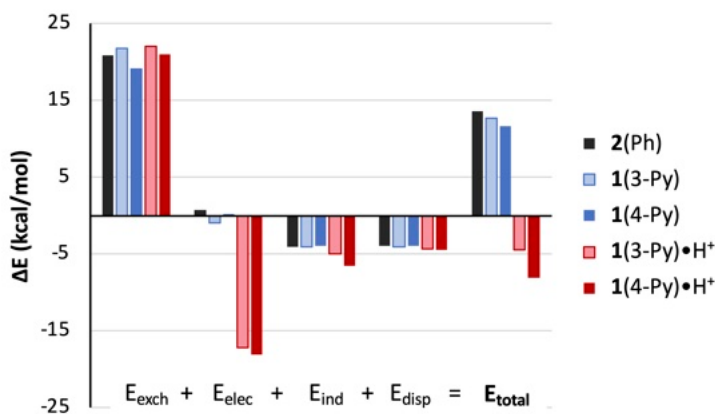


Figure 2.5 The fi-SAPT (SAPT(0), jun-cc-pVDZ) energies for the intramolecular C=O...aryl interactions in the optimized TS structures (B3LYP-D3, 6-311G*) for protonated and unprotonated rotors **1** and control rotor **2**.

Additional SAPT analyses were conducted that included the intramolecular interactions of the pyridyl/pyridinium group in the ground state and transition state (Figure 2.18 in **2.5 supporting information**), leading to the same conclusion. The electrostatic

interactions were the dominant term in the change in barrier on protonation and deprotonation of the pyridyl gate.

Finally, the reversibility of the electrostatic gates were demonstrated by following four protonation-deprotonation cycles using ^1H NMR lineshape analysis at 25 °C (Figure 2.16 in 2.5 supporting information). In each cycle, the rotor **1**(3-Py) in TCE- d_2 was treated with 3 equivalents of MsOH followed by neutralization by washing aqueous NaHCO_3 solutions. The rotor cleanly switched from slow-exchange to fast-exchange and back to slow-exchange without degradation or formation of by-products.

2.4 Conclusions

Molecular pyridyl rotor **1** was designed in which the rate of rotation is accelerated by the formation of attractive through-space electrostatic interactions. Protonation of the pyridyl gates on the stator leads to a positively charged pyridinium aromatic surface that forms stabilizing electrostatic interactions with the electrostatically negative C=O oxygen in the bond rotation transition state. Dynamic NMR and theory concurred that the pyridinium rotors **1**(3-Py)• H^+ and **1**(4-Py)• H^+ had rotational barriers that were 2.7 to 2.8 kcal/mol lower than the neutral pyridyl rotors **1**(3-Py) and **1**(4-Py), leading to increases in the rates of rotation of 32 and 206 times. Computational modelling and energy decomposition analysis were consistent with the formation of stabilizing electrostatic interactions in the TS between the face of the pyridinium gate and the C=O oxygens in **1**(3-Py)• H^+ and **1**(4-Py)• H^+ . Similar attractive through-space electrostatic interactions have recently been demonstrated to be able to control the thermodynamic equilibrium of conformationally flexible molecules,^{120,121} contribute to aromatic interactions,¹²² and have also been hypothesized to play a key role in the kinetic rate enhancement of biological¹²³

and synthetic processes.^{124–126} Thus, this study demonstrates that stabilizing through-space electrostatic interactions can also be used to control and accelerate molecular-scale motion.

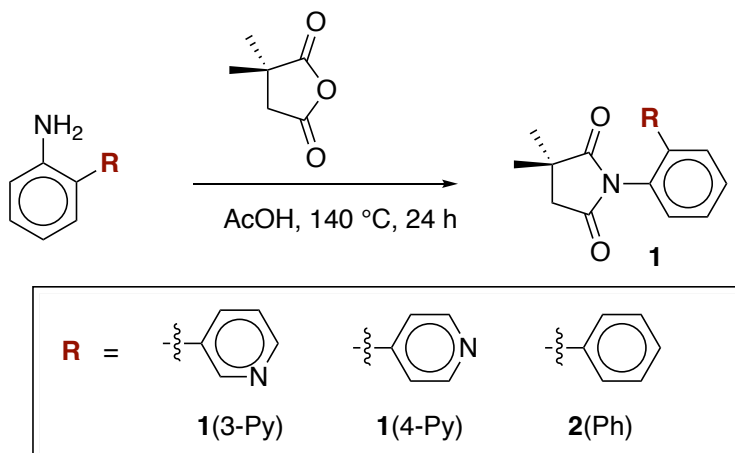
2.5 Supporting information

2.5.1 General experimental procedures

NMR spectra were recorded on a Bruker 400 MHz spectrometer at 25 °C. Chemical shifts are reported in ppm (δ) and were referenced to residual solvent peaks. Chemicals and solvents were purchased from commercial suppliers and used as received. Flash chromatography was performed using silica gel from Sorbent Technologies (60 Å, 200 – 400 mesh). HRMS were measured using a magnetic sector spectrometer (VG 70S) using EI sources.

2.5.2 Synthesis of the molecular rotors

The rotors **1** and **2** were prepared via a thermal condensation between an *ortho*-substituted aniline and 2,2-dimethylsuccinic anhydride (**Scheme 2.1**).



Scheme 2.1 General synthetic route to molecular rotors **1** and **2**.

Rotor **2(Ph)** (*1-([1,1'-biphenyl]-2-yl)-3,3-dimethylpyrrolidine-2,5-dione*): The reactants 3,3-dimethyldihydrofuran-2,5-dione (65 mg, 0.5 mmol) and [1,1'-biphenyl]-2-amine (130 mg, 0.75 mmol) and 3 mL AcOH were added to a reaction tube. The tube was

then sealed and heated to 140 °C for 24 hours. After letting the tube cool to room temperature, 50 mL EtOAc and 50 mL water was added to the reaction mixture. The organic layer was separated, and the solvent was removed under reduced pressure. The crude material was purified by column chromatography (CH₂Cl₂/MeOH = 200:1, v/v) to give **2(Ph)** as a colorless solid (130 mg, 92%). ¹H NMR (400 MHz, chloroform-d) δ 7.55-7.45 (m, 3H), 7.40-7.32 (m, 3H), 7.28-7.22 (m, 3H), 2.59 (d, J = 18.1 Hz, 1H), 2.38 (d, J = 18.1 Hz, 1H), 1.34 (s, 3H), 0.94 (s, 3H). ¹³C NMR (100 MHz, chloroform-d) δ 182.3, 175.4, 141.4, 138.7, 130.9, 130.3, 129.7, 128.7, 128.65, 128.60, 128.3, 127.8, 43.9, 40.4, 25.45, 25.33. HRMS (EI) m/z calculated for [C₁₈H₁₇NO₂]⁺ (M⁺): calculated 279.1259; observed 279.1268.

Rotor **1(3-Py)** (3,3-dimethyl-1-(2-(pyridin-3-yl)phenyl)pyrrolidine-2,5-dione): The reactants 3,3-dimethyldihydrofuran-2,5-dione (65 mg, 0.5 mmol) and 2-(pyridin-3-yl)aniline (102 mg, 0.6 mmol) were and 3 mL AcOH were added to a reaction tube. The tube was then sealed and heated to 140 °C in a silicon oil bath for 24 hours. After letting the tube cool to room temperature, using 50 mL EtOAc and 50 mL water to extract AcOH away. Collecting the organic layer and making second extraction with 50 mL NaH₂CO₃ solution, recollecting the organic layer and drying it under vacuum, the crude material was purified by column chromatography (CH₂Cl₂/MeOH = 200:1, v/v) to give **1(3-Py)** as a colorless solid (100 mg, 72%). ¹H NMR (400 MHz, chloroform-d) δ 8.51 (d, J = 4.34 Hz, 1H), 8.41 (s, 1H), 7.56-7.53 (m, 1H), 7.50-7.43 (m, 2H), 7.38-7.35 (m, 1H), 7.24 (dd, J = 8.2 Hz, J = 4.9 Hz, 1H), 7.20-7.16 (m, 1H), 2.60 (d, J = 18.3 Hz, 1H), 2.42 (d, J = 18.3 Hz, 1H), 1.33 (s, 3H), 0.97 (s, 3H). ¹³C NMR (100 MHz, chloroform-d) δ 182.2, 175.1, 149.0, 148.96, 137.6, 136.3, 134.5, 130.9, 130.4, 129.94, 129.59, 128.9, 123.3, 43.8, 40.4, 25.65,

25.23. HRMS (EI) m/z calculated for $[C_{17}H_{16}N_2O_2]^+$ (M^+): calculated 280.1212; observed 280.1213.

Rotor **1**(4-Py) (*3,3-dimethyl-1-(2-(pyridin-4-yl)phenyl)pyrrolidine-2,5-dione*): The reactants 3,3-dimethyldihydrofuran-2,5-dione (65 mg, 0.5 mmol) and 2-(pyridin-4-yl)aniline (130 mg, 0.75 mmol) and 3 mL AcOH were added to a reaction tube. The tube was then sealed and heated to 140 °C in a silicon oil bath for 24 hours. After letting the tube cool to room temperature, using 50 mL EtOAc and 50 mL water to extract AcOH away. Collecting the organic layer and making second extraction with 50 mL NaH_2CO_3 solution, recollecting the organic layer and drying it under vacuum, the crude material was purified by column chromatography ($CH_2Cl_2/MeOH = 200:1$, v/v) to give **1**(4-Py) as a colorless solid (100 mg, 72%). 1H NMR (400 MHz, chloroform- d) δ 8.61 (dd, $J = 4.6$ Hz, $J = 1.6$ Hz, 2H), 7.57-7.53 (m, 2H), 7.44-7.40 (m, 1H), 7.25-7.22 (m, 1H), 7.188 (dd, $J = 4.7$ Hz, $J = 1.6$ Hz, 2H), 2.61 (d, $J = 18.1$ Hz, 1H), 2.41 (d, $J = 18.1$ Hz, 1H), 1.33 (s, 3H), 0.99 (s, 3H). ^{13}C NMR (100 MHz, chloroform- d) δ 182.2, 175.1, 149.9, 146.6, 138.7, 130.3, 130.0, 129.9, 129.0, 123.5, 43.9, 40.5, 25.46 (d, $J = 15.5$ Hz). HRMS (EI) m/z calculated for $[C_{17}H_{16}N_2O_2]^+$ (M^+): calculated 280.1212; observed 280.122

2.5.3 ^1H and ^{13}C NMR spectra

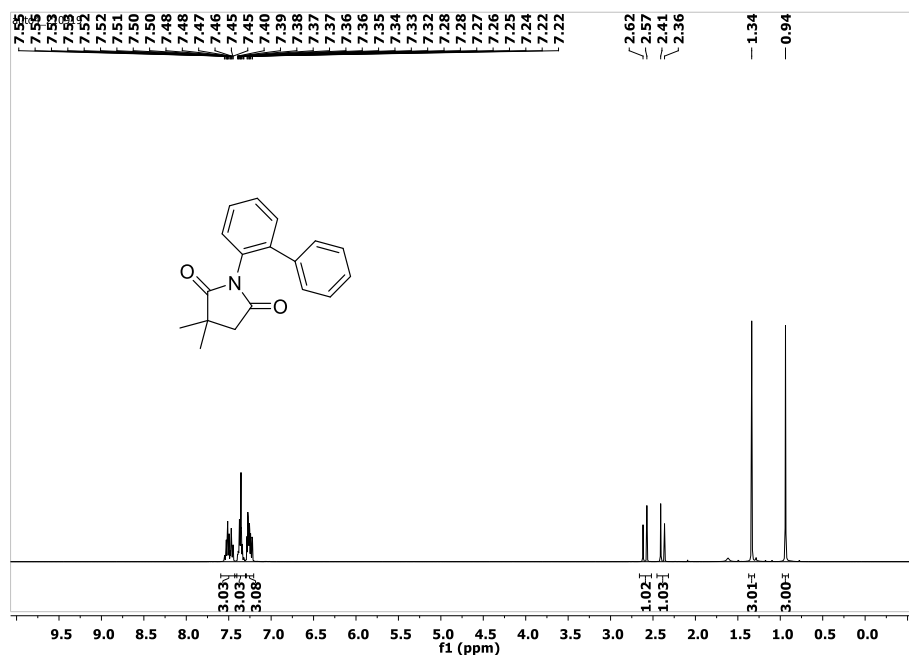


Figure 2.6 ^1H NMR spectra (400 MHz) of rotor **2(Ph)** in CDCl_3 .

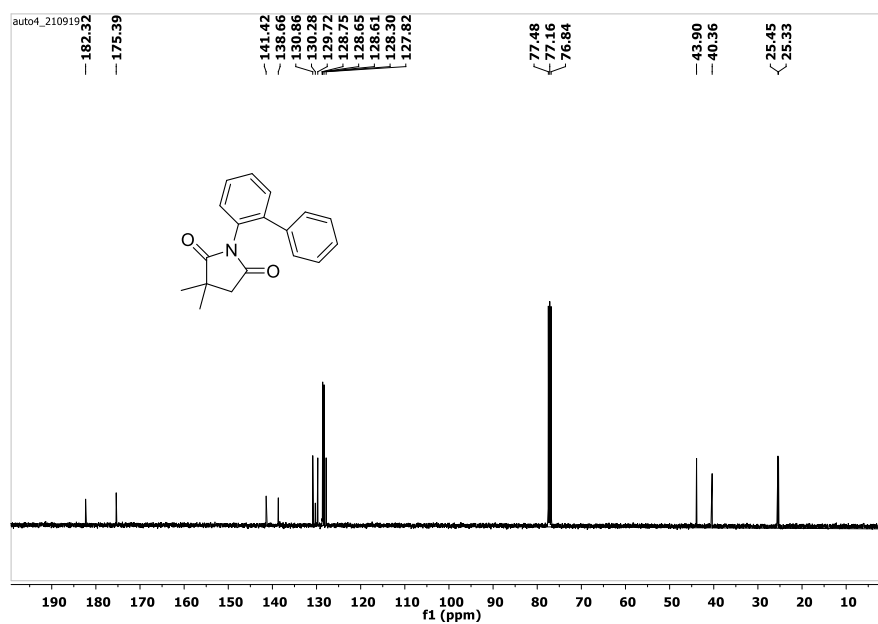


Figure 2.7 ^{13}C NMR spectra (100 MHz) of rotor **2(Ph)** in CDCl_3 .

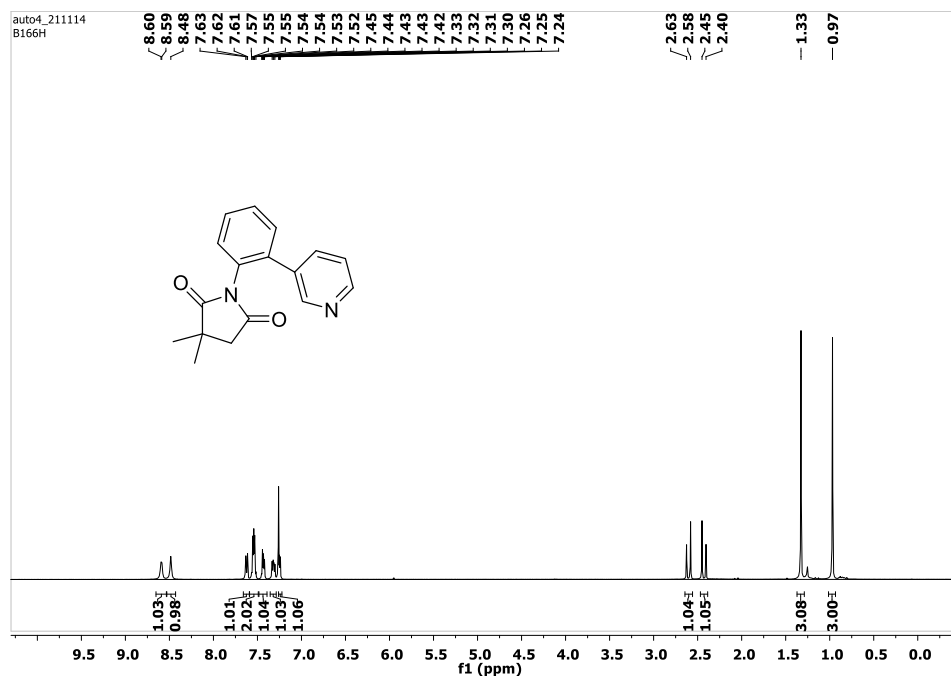


Figure 2.8 ^1H NMR spectra (400 MHz) of rotor 1(3-Py) in CDCl_3 .

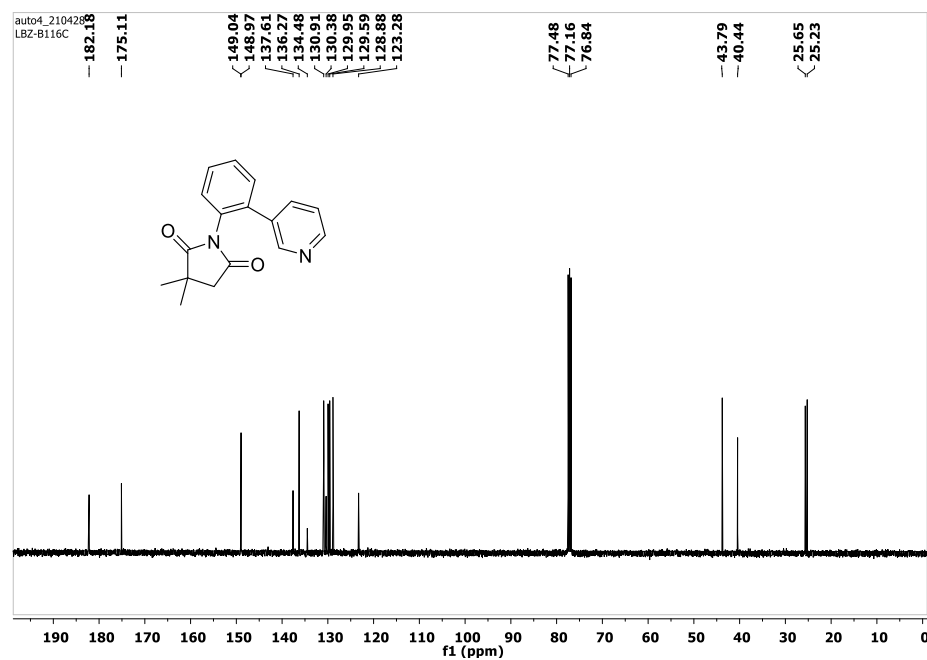


Figure 2.9 ^{13}C NMR spectra (100 MHz) of rotor 1(3-Py) in CDCl_3 .

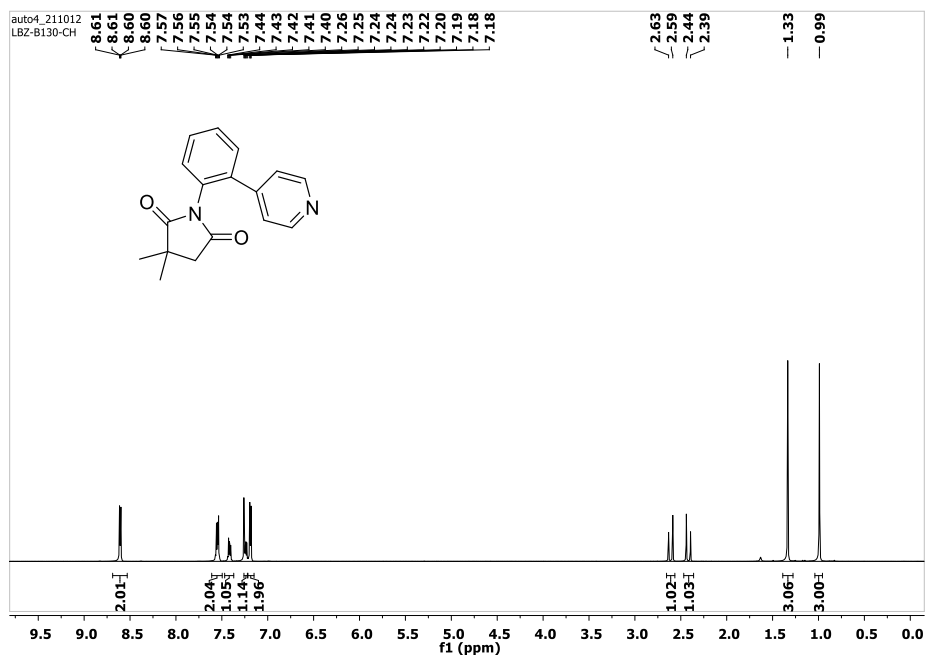


Figure 2.10 ¹H NMR spectra (400 MHz) of rotor 1(4-Py) in CDCl₃.

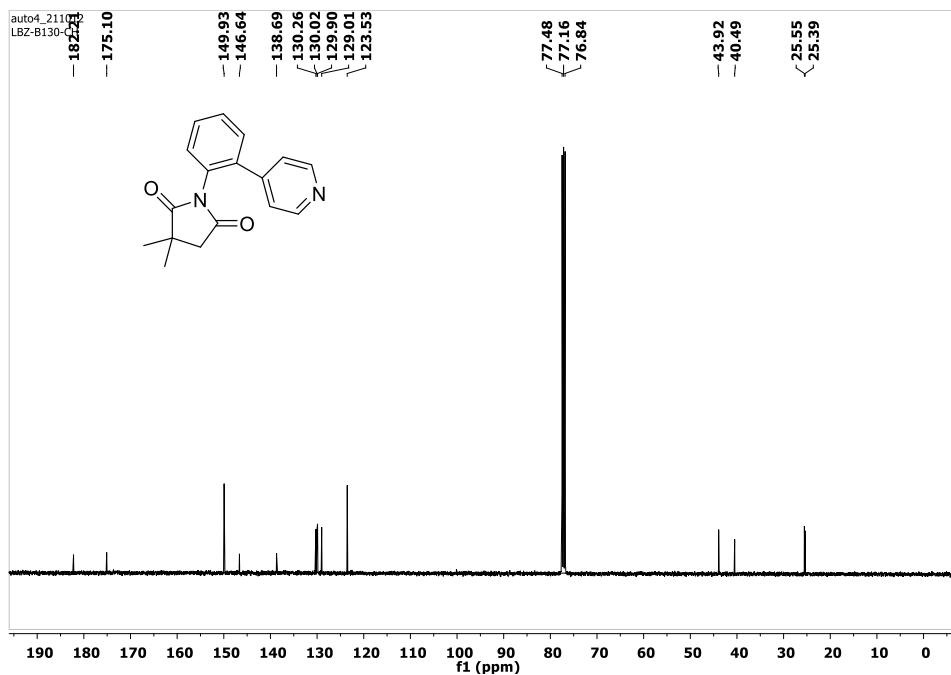


Figure 2.11 ¹³C NMR spectra (100 MHz) of rotor 1(4-Py) in CDCl₃.

2.5.4 Experimental measurement of the rotor rotational barriers

The experimental rotational barriers of the rotors were determined via exchange spectroscopy (EXSY) NMR experiments in TCE-d₂ (Table 2.2). An example of the 2D

NOESY spectra is shown in Figure 2.12 and integration of the crosspeak and diagonal signals were performed using the Bruker Topspin software, and rate constants were calculated using EXSYCalc. The rotational barrier for each rotor were extrapolated to room temperature for consistency. The TS enthalpy ($\Delta H^\ddagger$) and entropy ($\Delta S^\ddagger$) for rotor were obtained using Eyring plots (Figures 2.13 – 2.15).

Table 2.2. The experimentally measured rotational barriers for rotors during titration with MsOH. The experimental barriers were measured by EXSY NMR in TCE-d2.

MsOH/ (eq)	$\Delta G^\ddagger_{\text{expt}}$ 1(3-Py) (kcal/mol)	MsOH (eq)	$\Delta G^\ddagger_{\text{expt}}$ 1(4-Py) (kcal/mol)	MsOH (eq)	$\Delta G^\ddagger_{\text{expt}}$ 2(Ph) (kcal/mol)
0	18.83	0	19.65	0	20.63
0.15	17.80	0.14	17.45	0.6	20.93
0.3	17.45	0.31	17.0	1.3	20.94
0.62	17.0	0.64	16.72	2.4	21.07
1.02	16.80	0.99	16.5		
1.2	16.78	1.2	16.5		
2.8	16.75	2.8	16.49		

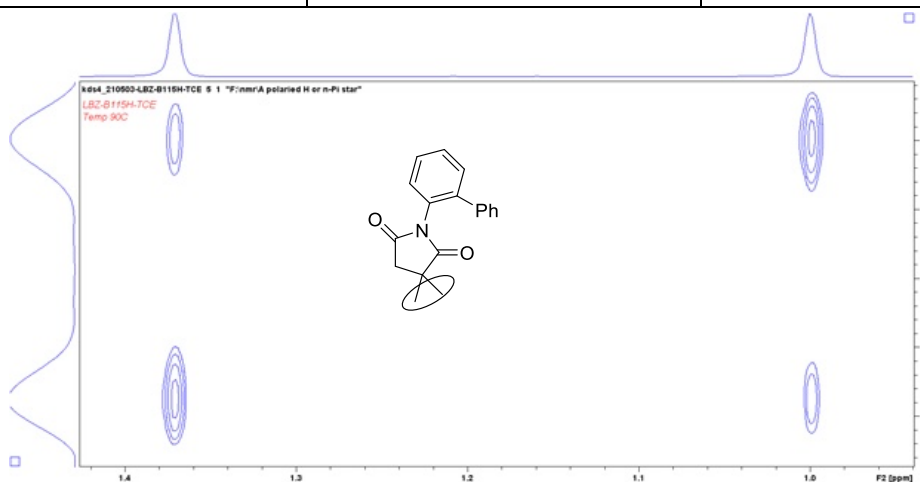


Figure 2.12 2D NMR of diastereotopic methyl groups of **2(Ph)** in TCE-d2 at 90 °C.

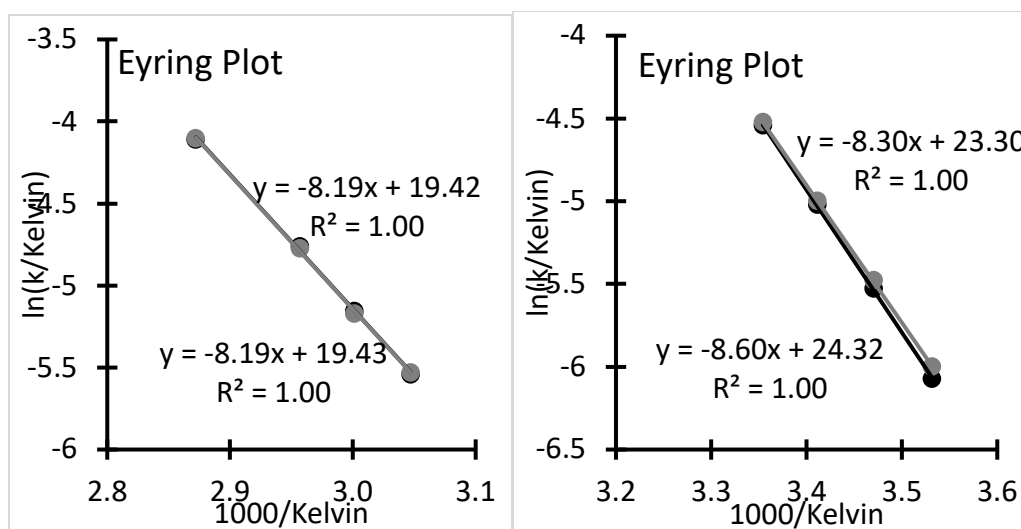


Figure 2.13 Eyring plots for (left) rotors **1(3-Py)** and (right) **1(3-Py)•H⁺** in 2.8 eq. MsOH.

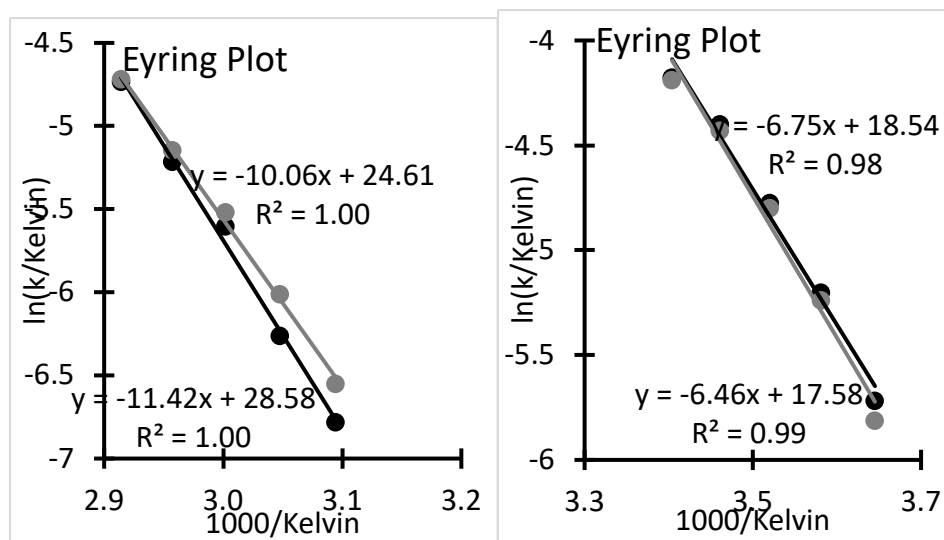


Figure 2.14 Eyring plots for (left) rotor **1(4-Py)** and (right) rotor **1(4-Py)•H⁺** in 2.8 eq. MsOH.

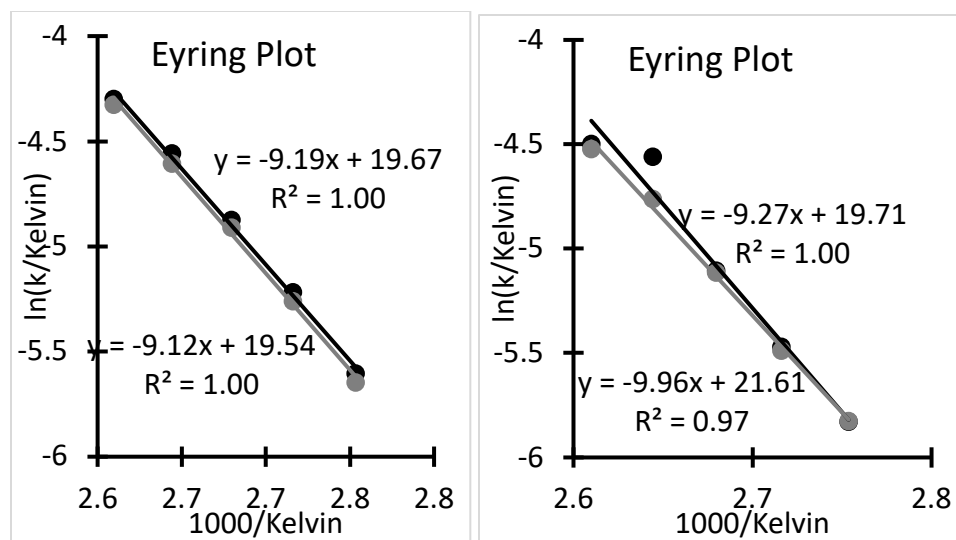
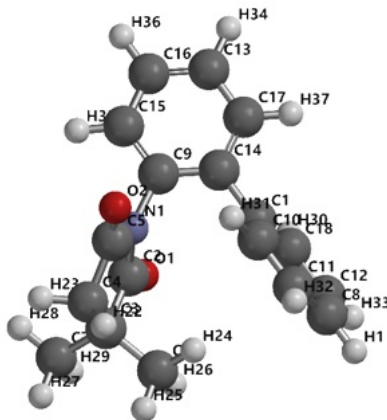


Figure 2.15 Eyring plots for (left) rotor **2(Ph)** and (right) rotor **2(Ph)** in 2.4 eq. MsOH.

2.5.5 Molecular Modeling Studies

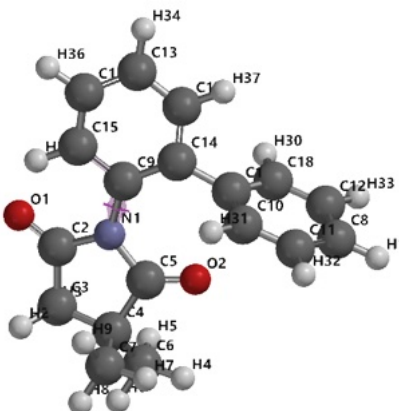
The optimized the ground state (GS) and transition state (TS) for the rotors were calculated (B3LYP-D3(0)/6-311G*) in Spartan '18.¹²⁷ Convergence criteria were 10^{-4} Hartree and 10^{-4} atomic units as the maximum norm of the cartesian gradient. Vibrational analyses were also carried out at the B3LYP-D3(0)/6-311G* level of theory. The free energies were calculated at 298.15 K using the calculated thermodynamic terms. Solvent calculations were performed using the C-PCM continuum solvent model with dielectric of 8.42 to match the dielectric of 1,1,2,2-tetrachloroethylene (TCE). The XYZ coordinates for the GS and TS structures are in **Tables 2.3 – 2.12**.

Table 2.3 The GS structure of rotor **2(Ph)** in solvent and the XYZ coordinates in gas phase (left) and in solvent (right).



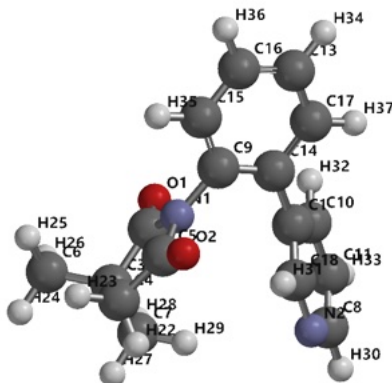
N1	0.511393855	-0.882941210	0.741806000	N1	0.488869277	-0.867428579	0.740306362
C2	1.151406681	0.332079166	1.029756069	C2	1.111251523	0.350425681	1.031875998
C3	0.486528753	0.943530489	2.268594571	C3	0.478383527	0.930899191	2.296462247
C4	-0.433734911	-0.182369035	2.777721420	C4	-0.414954275	-0.215971401	2.809812600
C5	-0.482574541	-1.216881421	1.668609451	C5	-0.448146571	-1.245897024	1.703815732
C6	-0.327500654	2.158349122	1.783025030	C6	-0.361315853	2.149348561	1.864556344
C7	1.557092584	1.370554753	3.276091551	C7	1.571924061	1.343633911	3.286628247
O1	2.040438897	0.814034531	0.376111470	O1	1.977857859	0.852781540	0.353786147
O2	-1.223178269	-2.162957828	1.572865005	O2	-1.141648332	-2.235202863	1.628465787
C1	-0.654282174	0.001691258	-1.730740305	C1	-0.655165365	0.015746048	-1.761984209
C8	-2.337170012	2.237558798	-1.849432365	C8	-2.325615336	2.262238860	-1.926845428
C18	-0.244169958	1.161491595	-2.394476760	C18	-0.262352583	1.139313703	-2.497643060
C10	-1.916374426	-0.027642431	-1.125051229	C10	-1.896610137	0.028232092	-1.112907916
C11	-2.753908905	1.083041478	-1.187803211	C11	-2.727573502	1.143107755	-1.197078243
C12	-1.080891356	2.273893031	-2.451288931	C12	-1.091712307	2.256780733	-2.577211227
C9	0.762140583	-1.635316866	-0.450250416	C9	0.746420859	-1.620282887	-0.451279135
C13	1.325191840	-3.062270326	-2.762940366	C13	1.332909042	-3.057780623	-2.752923527
C14	0.231253980	-1.191433728	-1.668293093	C14	0.225862888	-1.179553770	-1.676994408
C15	1.547702910	-2.781132713	-0.382367732	C15	1.533125312	-2.766349047	-0.369674098
C16	1.825279951	-3.501725435	-1.539557508	C16	1.821284133	-3.493034495	-1.521772280
C17	0.536694341	-1.916907536	-2.823919569	C17	0.545755759	-1.911240733	-2.826961612
H22	-1.448936268	0.143385565	3.010498943	H22	-1.434276132	0.092286104	3.047948540
H23	-0.039417236	-0.670543449	3.673956849	H23	-0.003376587	-0.697076857	3.701562275
H24	-1.095406510	1.863985100	1.063142143	H24	-1.141143024	1.862020934	1.154664280
H25	-0.819853622	2.642606955	2.631181439	H25	-0.839648638	2.595173412	2.740266989
H26	0.326314216	2.884569470	1.297156945	H26	0.272707317	2.901789731	1.391527415
H27	1.095055819	1.841010984	4.148380068	H27	1.119977369	1.769833329	4.185766184
H28	2.142240905	0.513514139	3.621194831	H28	2.181016753	0.485007720	3.581512580
H29	2.244104303	2.083995253	2.818349070	H29	2.226906950	2.093231413	2.838814682
H30	0.741892708	1.192693612	-2.845211362	H30	0.701198276	1.138574222	-2.996359544
H31	-2.236562183	-0.928178056	-0.611060755	H31	-2.214450140	-0.844857257	-0.552232405
H32	-3.733755819	1.043919234	-0.722324551	H32	-3.689250471	1.135379702	-0.694266298
H33	-0.749082039	3.171174057	-2.963659120	H33	-0.773561093	3.123548997	-3.147407922
H34	1.540808837	-3.617457401	-3.670267680	H34	1.557646122	-3.615975630	-3.655939938
H35	1.939510312	-3.098371528	0.577397575	H35	1.918964886	-3.076837969	0.594788730
H36	2.432918302	-4.398753500	-1.486475947	H36	2.428976701	-4.389198520	-1.458760362
H37	0.128472911	-1.585650112	-3.773113036	H37	0.151471764	-1.584348305	-3.783427606
H1	-2.989643803	3.103453983	-1.897604492	H1	1 -2.971710034	3.131682323	-1.990891921

Table 2.4 The TS structure of rotor **2**(Ph) in solvent and the XYZ coordinates in gas phase (left) and in solvent (right).



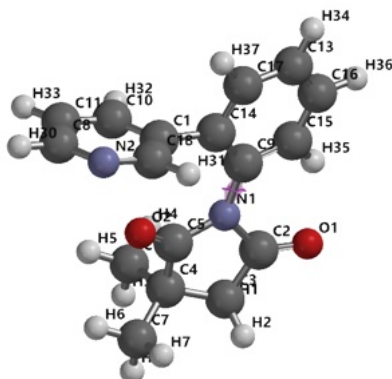
C1	-0.126171779	0.585344422	0.771863203	N1	-0.569494909	0.825259999	0.941146935
C2	-0.588320171	1.124783758	2.011998210	C2	-1.088593627	1.347420464	2.162603432
C3	-0.429720550	0.079975313	3.120266218	C3	-0.701161301	0.437521409	3.303021896
C4	0.574535972	-0.888596986	2.514628222	C4	0.205003433	-0.631693476	2.704478076
C5	0.409489403	-0.717133786	1.022669441	C5	-0.032966846	-0.465690918	1.209316399
C6	-1.805076509	-0.597479103	2.298618581	O1	-1.773812115	2.334003237	2.299734554
C7	0.02297877	0.739414898	4.422246927	O2	0.195168713	-1.320832471	0.395193473
O1	-1.085681641	2.205802797	2.208537148	C1	0.141693107	-0.402195423	-2.012838316
O2	0.674654865	-1.556378543	0.210669101	C8	1.399963292	-2.717657099	-2.975011716
C1	0.540332610	-0.659703444	-2.184711130	C18	-0.614111105	-1.456640556	-2.531668066
C8	1.692673829	-3.023739147	-3.150122088	C10	1.537003442	-0.501015993	-2.020674850
C18	-0.264631117	-1.711052887	-2.627347962	C11	2.161965865	-1.653506496	-2.491385713
C10	1.928899576	-0.787301985	-2.271273748	C12	0.009345664	-2.612266232	-0.982680104
C11	2.501579628	-1.965025440	-2.741728336	C9	-0.722382917	1.478049217	-0.352406175
C12	0.307063607	-2.890294441	-3.095839394	C13	-1.301425571	2.960273805	-2.711342828
C9	-0.296745870	1.239378875	-0.524054151	C14	-0.509249759	0.891990413	-1.632028896
C13	-0.872682717	2.713036807	-2.888417397	C15	-1.110785240	2.833240096	-0.319116389
C14	-0.069923132	0.653894360	-1.801704097	C16	-1.395579236	3.562390168	-1.464632160
C15	-0.735218863	2.578859611	-0.493606822	C17	-0.845306254	1.652981525	-2.768011224
C16	-0.101823957	3.202047538	-1.642480092	H30	-1.696534272	-1.378432995	-2.552258786
C17	-0.393736834	1.414872319	-2.940034155	H31	2.133530343	0.324599383	-1.646256339
H22	0.427124085	-1.936415744	2.777203092	H32	3.245556263	-1.719908149	-2.483868153
H23	1.604256870	-0.618843564	2.772645752	H33	-0.591823743	-3.429741723	-3.384628256
H24	-2.131287971	-1.093352696	2.379620489	H34	-1.541917577	3.499177006	-3.621500883
H25	-1.748619445	-1.353487353	4.086356871	H35	-1.218907396	3.329953618	0.627451543
H26	-2.562935876	0.137364732	3.575818549	H36	-1.696160835	4.600101634	-1.366192064
H27	0.112455312	-0.010793314	5.212415214	H37	-0.699743074	1.184506260	-3.735262924
H28	0.993185049	1.228067220	4.304844449	H1	1.885914115	-3.616687571	-3.340752442
H29	-0.697089157	1.495406332	4.739375336	H2	-0.237284140	1.034634641	4.090289778
H30	-1.344467383	-1.609629601	-2.58411135	H3	-1.625052144	0.019697963	3.712353269
H31	2.560653834	0.036633210	-1.955414320	C6	-0.144345596	-2.056197444	1.324999143
H32	3.582251844	-2.0565671282	-2.793703547	H4	0.476948033	-2.782761846	2.616931885
H33	-0.331422335	-3.705981733	-3.421716142	H5	-1.192012388	-2.289758735	2.934889994
H34	-1.102553709	3.251596140	-3.801788904	H6	0.024149853	-2.166306547	4.216895735
H35	-0.877998315	3.064300520	0.453327611	C7	1.695753551	-0.332100509	2.960233282
H36	-1.357548321	4.328055635	-1.545095973	H7	2.328469652	-1.038276252	4.217675756
H37	-0.229966129	0.945205946	-3.903617321	H8	1.908553920	-0.424161037	4.028149438
H1	2.138582955	-3.943159332	-3.516337382	H9	1.959630746	0.680930635	2.644739696

Table 2.5 The GS structure of rotor **1**(3-Py) in solvent and the XYZ coordinates in gas phase (left) and in solvent (right).



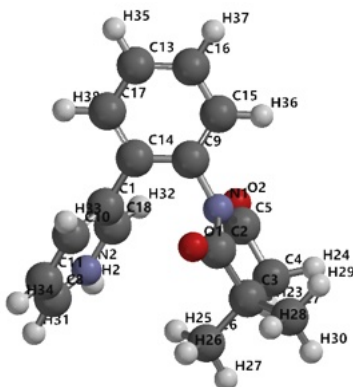
C1	0.012150307	-1.594943932	1.843955588	C3	0.180008255	-1.584515235	1.905516351
C4	1.299946362	-0.832709198	2.212138645	C4	1.364056312	-0.722731694	2.392556880
C5	1.218982811	0.502360328	1.487865999	C5	1.210457579	0.629943329	1.728356106
C6	-0.693231293	-2.248915379	3.034650198	C6	-0.682458642	-2.129314960	3.052380903
C7	0.263781195	-2.632204536	0.927906829	C7	0.633944724	-2.733078012	0.983653860
O1	-2.033582580	-0.613017617	0.792834467	O1	-1.702229132	-0.843257193	0.521546767
O2	2.093780294	1.317948041	1.338484062	O2	1.962024527	1.576262722	1.782620682
C1	0.198957387	0.461301699	-1.831104694	C1	0.171077185	0.458331375	-1.882414001
C8	1.316935034	-1.722305556	-3.038239069	C8	1.403888540	-1.663511370	-3.100553460
C18	-0.538626867	-0.490086881	-2.545137325	C18	1.503400231	0.096870404	-1.644055813
C10	1.579918101	0.269361356	-1.735364110	C10	-0.545870571	-0.306582553	-2.806549374
C11	2.148462803	-0.841469930	-2.349139856	C11	0.079795169	-1.382047584	-3.427414367
N2	-0.005291998	-1.560487284	-3.138570651	N2	2.114728311	-0.939080621	-2.26092960
C9	-0.567559393	1.716272513	0.203932485	C9	-0.473935138	1.703188851	0.212439739
C13	-1.682641083	3.717026274	-1.360074289	C13	-1.593242711	3.754621089	-1.286443376
C14	-0.474819305	1.621064909	-1.190959253	C14	-0.446347652	1.614351188	-1.188104413
C15	-1.200456931	2.793703988	0.811596936	C15	-1.038198091	2.800623502	0.855613970
C16	-1.753133213	3.802576672	0.028147482	C16	-1.590525142	3.83535762	0.105442262
C17	-1.050018939	2.633218217	-1.963064558	C17	-1.029037408	2.65293761	-1.923785322
H22	2.218266686	-1.344686463	1.920546785	H22	2.238666145	-1.135182021	2.124281794
H23	1.368531097	-0.631711629	3.285505498	H23	1.362060723	-0.575700428	3.475419211
H24	-0.068917199	-3.040559079	3.457178294	H24	-0.103125432	-2.838493772	3.648683843
H25	-0.905845190	-1.522935997	3.824164558	H25	-1.024410969	-1.326123337	3.710355946
H26	-1.641113387	-2.687242713	2.717561879	H26	-1.559296655	-2.646340310	2.656823998
H27	0.906742637	-3.433967545	1.103563177	H27	1.232946680	-3.446286144	1.555006706
H28	-0.679919229	-3.069693970	0.398201762	H28	-1.231583720	-3.256889351	0.572234514
H29	0.747459564	-2.182271637	-0.141140472	H29	1.238652985	-2.365271159	0.151117434
H30	1.727510668	-2.600428146	-3.530882435	H30	1.917997131	-2.504654963	-3.557776215
H31	-1.618019759	-0.386004019	-2.621937786	H31	2.106477673	0.680710920	-0.954507455
H32	2.186038579	0.973694942	-1.178054157	H32	-1.583503298	-0.072068905	-3.019696139
H33	3.216754926	-1.021852729	-2.297848585	H33	-0.450031844	-1.999104522	-4.144514887
H34	-2.120896396	4.495101574	-1.976263312	H34	-2.031469557	4.551497320	-1.877755769
H35	-1.271196707	2.823955997	1.892870687	H35	-1.055741664	2.826388549	1.939175449
H36	-2.247689592	6.444473264	0.500353343	H36	-2.028018225	4.691893446	-0.606291165
H37	-0.991074962	2.566623672	-3.044408147	H37	-1.021551440	2.597173779	-3.007234690

Table 2.6 The TS structure of rotor **1**(3-Py) in solvent and the XYZ coordinates in gas phase (left) and in solvent (right).



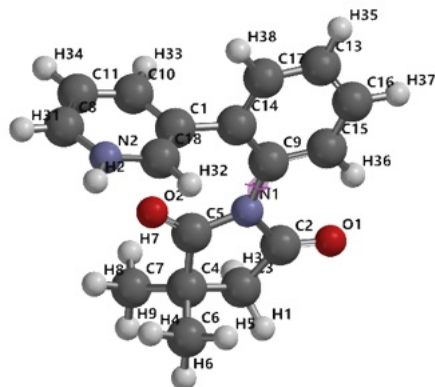
N1	0.081937663	0.603139500	1.105314533	N1	-0.210453572	0.492686750	1.149928862
C2	0.359390802	0.915983703	2.469643852	C2	-0.297662030	0.656742938	2.565385264
C3	0.936226496	-0.311708198	3.147221073	C3	0.193129823	-0.599241606	3.244794361
C4	0.771997408	-1.454310693	2.150336438	C4	0.731643751	-1.497536206	2.136817246
C5	0.606865154	-0.695224874	0.836619364	C5	0.137536793	-0.860864366	0.888385085
O1	0.208489441	1.975542449	3.022251928	O1	-0.730999507	1.614729173	3.160971845
O2	0.887556098	-1.144842609	-0.239123020	O2	-0.014302197	-1.442579927	-0.15402842
C1	-0.205304111	0.230467177	-2.111717223	C1	-0.489416197	0.168069005	-2.087484147
C8	0.369396719	-1.808323114	-3.837220819	C8	-0.119949362	-1.851187580	-3.898263912
C18	-1.037221230	-0.876777730	-2.306973019	C18	-1.534421598	-0.594940107	-2.614054759
C10	0.952607813	0.307519424	-2.881961946	C10	0.799429010	-0.097772001	-2.551877607
C11	1.251461510	-0.734585549	-3.752895369	C11	0.989359226	-1.128279398	-3.465649699
N2	-0.767202505	-1.88189966	-3.13817394	N2	-1.368844781	-1.590426565	-3.490657768
C9	-0.575138922	1.509610070	0.174009382	C9	-0.556342055	1.526182322	0.184858508
C13	-1.899146797	3.471253629	-1.398807619	C13	-1.395233601	3.717237588	-1.424240013
C14	-0.650302648	1.358527235	-1.237815924	C14	-0.765395156	1.347624783	-1.211455799
C15	-1.228338531	2.619391437	0.746159882	C15	-0.677130980	2.835196426	0.693478893
C16	-1.873293059	3.580881647	-0.016669058	C16	-1.087533617	3.908325560	-0.084673504
C17	-1.301254081	2.363566009	-1.975640432	C17	-1.211425777	2.452654959	-1.960283210
H30	0.574112327	-2.642502080	-4.504106940	H30	-0.006457707	-2.665327736	-4.609441864
H31	-1.969108558	-0.952456476	-1.750763433	H31	-2.556101228	-0.396843063	-2.299542930
H32	1.614804645	1.161209795	-2.784342826	H32	1.639339619	0.487694453	-2.193621137
H33	2.151498341	-0.718139357	-4.358369337	H33	1.978135810	-1.369083907	-3.840695339
H34	-2.388785140	4.216270221	-2.016763460	H34	-1.740604539	4.533896716	-2.048792676
H35	-1.211316997	2.751478706	1.812445619	H35	-0.467306379	3.019165542	1.730637585
H36	-2.351357373	4.415223621	0.485703357	H36	-1.167231555	4.888945811	0.372055427
H37	-1.346237706	2.232415672	-3.051312522	H37	-1.385922039	2.295818046	-3.019212132
H1	1.988206304	-0.104057711	3.634698512	H1	0.926816890	-0.328484789	4.006203616
H2	0.430120957	-0.457604262	4.103445572	H2	-0.662591025	-1.046436428	3.758728311
C6	1.961059366	-2.411460823	2.069494140	C6	2.265882739	-1.398686375	2.009537701
H3	2.067886213	-2.968829478	3.003934087	H3	2.734158526	-1.827836967	2.898787399
H4	2.894149539	-1.874403813	1.881152877	H4	2.594386351	-0.360101433	1.918384236
H5	1.818872096	-3.121848235	1.254151948	H5	2.613049463	-1.950760888	1.133227124
C7	-0.537140773	-2.237205907	2.387024561	C7	0.291410432	-2.959163483	2.251807778
H6	-0.703660802	-2.957195286	1.582647244	H6	0.635256500	-3.533574912	1.389931839
H7	-1.405334605	-1.574282541	2.435003415	H7	-0.797397352	-3.040971120	2.304126570
H8	-0.476494890	-2.784821651	3.331399211	H8	0.713187106	-3.404871161	3.155927316

Table 2.7 The GS structure of rotor **1(3-Py)•H⁺** in solvent and the XYZ coordinates in gas phase (left) and in solvent (right).



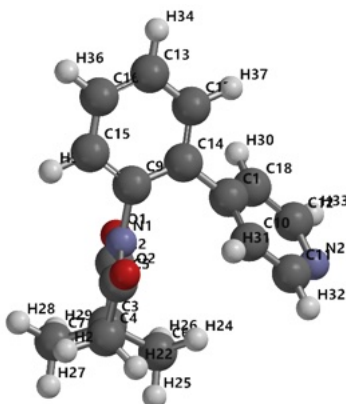
N1	0.354477191	0.700232750	0.935541595	N1	0.375230795	0.685665422	0.946897590
C2	-0.986011532	0.303785691	1.092435402	C2	-0.926376815	0.185431678	1.056778049
C3	-1.041380067	-0.826789169	2.121928076	C3	-0.958879693	-0.869927775	2.159930747
C4	0.410782377	-0.912984439	2.639922816	C4	0.429007539	-0.737654634	2.821040216
C5	1.243947182	-0.119544604	1.652382820	C5	1.244409132	0.161298380	1.916463428
C6	-1.446201770	-2.107698545	1.365615026	C6	-1.139067702	-2.244777572	1.485618255
C7	-2.077700474	-0.501314067	3.203389069	C7	-2.124266100	-0.587879579	3.115723739
O1	-1.899100950	0.743031167	0.441653936	O1	-1.842821892	0.522471212	0.342397929
O2	2.430122702	-0.177193503	1.441952100	O2	2.424019394	0.415007606	1.975697684
C1	0.474759712	-0.005340334	-1.814161397	C1	0.390378048	-0.014519891	-1.860012965
C8	0.072128540	-2.657006539	-2.563918273	C8	-0.159847772	-2.600605056	-2.724427549
C18	1.386447776	-0.999604546	-1.480799102	C18	1.165142897	-1.094379468	-1.462143334
C10	-0.665560505	-0.378416410	-2.536688754	C10	-0.685298930	-0.266760044	-2.722104387
C11	-0.862830294	-1.706418895	-2.918729438	C11	-0.958348449	-1.560645450	-3.158694899
N2	1.159020355	-2.274777184	-1.857448285	N2	0.867957311	-2.333065209	-1.896698338
C9	0.731700899	1.699032224	-0.016145335	C9	0.742394097	1.669502649	-0.023140448
C13	1.247767578	3.688271363	-1.892860593	C13	1.306446699	3.645829498	-1.898964878
C14	0.725774577	1.387854289	-1.381344115	C14	0.707549900	1.354328914	-1.389306417
C15	1.000623501	2.994067073	0.407013220	C15	1.065226657	2.955096211	0.400358399
C16	1.269658015	3.986592121	-0.532416730	C16	1.358118659	3.941341499	-0.537574107
C17	0.972111022	2.392115508	-2.318630074	C17	0.977973352	2.361078680	-2.321122552
H2	1.842707499	-2.978542679	-1.599878445	H2	1.454058075	-3.102567120	-1.587740896
H23	0.798007056	-1.929062431	2.724698376	H23	0.945526350	-1.689226208	2.954731198
H24	0.522187668	-0.445894722	3.623268335	H24	0.372328731	-0.256059767	3.801137272
H25	-0.715118265	-2.369843098	0.591925221	H25	-0.307624451	-2.475353521	0.814305514
H26	-2.417234873	-1.977304530	0.885183432	H26	-2.066004950	-2.270878324	0.909019569
H27	-1.512802713	-2.949672188	2.057965788	H27	-1.182255852	-3.023815217	2.250303361
H28	-3.065613601	-0.373442231	2.757781399	H28	-3.073731956	-0.615788168	2.577276944
H29	-1.827394242	0.419626193	3.735525593	H29	-2.023980275	0.393030067	3.586744046
H30	-2.131187609	-1.311861930	3.934210858	H30	-2.151219493	-1.345755756	3.902308891
H31	-0.005116473	-3.706722071	-2.813029884	H31	-0.300505768	-3.635129462	-3.004393601
H32	2.278423049	-0.806313545	-0.898002617	H32	2.026071119	-1.009280836	-0.814077563
H33	-1.406467403	0.374746878	-2.777473986	H33	-1.316473075	0.554993522	-3.038536841
H34	-1.741537656	-2.006578073	-3.474906110	H34	-1.788497737	-1.767142524	-3.821089283
H35	1.447879476	4.462791022	-2.624177989	H35	1.524280222	4.413197842	-2.633309153
H36	0.980283924	3.220424470	1.466467880	H36	1.067907156	3.176770452	1.460975811
H37	1.482498209	4.996233624	-0.201103158	H37	1.612029352	4.941401126	-0.204918120
H38	0.969950117	2.153521361	-3.377146659	H38	0.949145425	2.124766824	-3.379453309

Table 2.8 The TS structure of rotor **1**(3-Py)•H⁺ in solvent and the XYZ coordinates in gas phase (left) and in solvent (right).



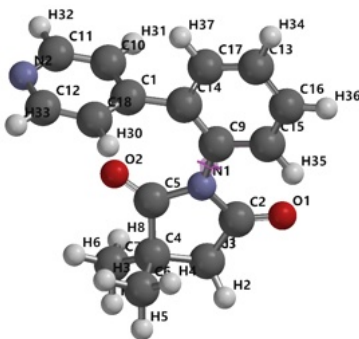
N1	0.217425013	0.790065647	1.136475050	N1	0.269789301	0.756025233	1.138079618
C2	0.275476813	1.212860932	2.525047650	C2	0.410053187	1.151327982	2.510298022
C3	0.013832136	0.008658410	3.396696361	C3	0.048705588	-0.014628327	3.395830304
C4	-0.579141379	-1.053746483	2.477455222	C4	-0.582449188	-1.057268057	2.480717246
C5	-0.194962434	-0.549361363	1.094325756	C5	-0.116115188	-0.603941699	1.107311666
O1	0.508138246	2.315587622	2.929406638	O1	0.789287365	2.219327548	2.922457830
O2	-0.278672189	-1.227866396	0.093565723	O2	-0.101369712	-1.317697460	0.133475528
C1	0.237961910	-0.086479882	-1.997295183	C1	0.286938202	-0.101612085	-2.006902665
C8	-0.427565050	-2.401151757	-3.404731629	C8	-0.413268687	-2.390873140	-3.422562505
C18	-1.062886260	-0.340423142	-2.409504684	C18	-1.032184760	-0.379805916	-2.332911694
C10	1.225246395	-1.000660210	-2.387087907	C10	1.270449961	-0.981416804	-2.469927102
C11	0.891565361	-2.163641382	-3.076673851	C11	0.919335844	-2.134596726	-3.167225672
N2	-1.353951515	-1.476260631	-3.072805321	N2	-1.337007440	-1.502150856	-3.007240909
C9	0.551698336	1.627403801	-0.001946218	C9	0.560388704	1.607664581	-0.003235309
C13	1.315236441	3.463939862	-2.049141395	C13	1.266217953	3.479343350	-2.037518447
C14	0.580749866	1.224819508	-1.368201413	C14	0.628222107	1.205123499	-1.367002399
C15	0.896663357	2.965377339	0.268928332	C15	0.792779495	2.970417926	0.266805083
C16	1.267871705	3.862110493	-0.722823123	C16	1.136151069	3.885876157	-0.718358860
C17	0.969066156	2.156441459	-2.346828170	C17	0.998831116	2.153162687	-2.336851760
H2	-2.318753241	-1.644748920	-3.334261999	H2	-2.313109777	-1.686032848	-3.216772561
H31	-0.777475930	-3.277686325	-3.932205969	H31	-0.778983327	-3.258799948	-3.952751888
H32	-1.887556190	0.326600092	-2.200201123	H32	-1.860985329	0.256598873	-2.057070695
H33	2.257823002	-0.804056123	-2.124211939	H33	2.313025127	-0.769443848	-2.265183240
H34	1.646865596	-2.886461117	-3.357418728	H34	1.670473894	-2.833256587	-3.511728176
H35	1.609436507	4.147478980	-2.837013092	H35	1.548721553	4.173205324	-2.821091544
H36	0.877465202	3.315227552	1.284677658	H36	0.719364897	3.324864445	1.277620196
H37	1.522384752	4.876943411	-0.439187105	H37	1.304036621	4.919327251	-0.435656603
H38	0.989391433	1.827576033	-3.380707666	H38	1.052272323	1.821474300	-3.368055015
H1	-0.620718174	0.303641995	4.232777652	H1	-0.595878075	0.333413441	4.204006350
H3	0.976605507	-0.302220757	3.815254756	H3	0.977846370	-0.376206040	3.846772597
C6	-2.121870896	-1.063988154	2.540376905	C6	-2.124063178	-0.962344165	2.487759205
H4	-2.531861869	-1.738832580	1.786335747	H4	-2.553386343	-1.633257298	1.740320854
H5	-2.541145461	-0.067096810	2.376897147	H5	-2.467579190	0.054453946	2.279062434
H6	-2.449194651	-1.409268270	3.523295484	H6	-2.499749271	-1.252387042	3.471727655
C7	-0.023924468	-2.464792611	2.697035606	C7	-0.129544649	-2.493141876	2.755059251
H7	1.067053318	-2.482291922	2.633614832	H7	0.958953998	-2.580254336	2.712628175
H8	-0.415881167	-3.151731142	1.945689433	H8	-0.555749704	-3.177640861	2.019508528
H9	-0.312396337	-2.831967161	3.684390456	H9	-0.460420962	-2.804850571	3.748606504

Table 2.9 The GS structure of rotor **1**(4-Py) in solvent and the XYZ coordinates in gas phase (left) and in solvent (right).



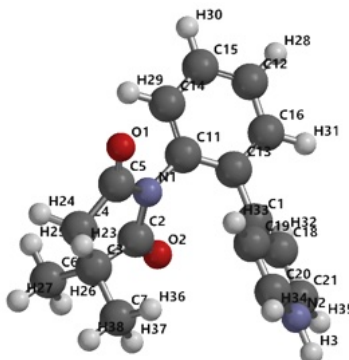
N1	-0.806206936	-0.396631993	0.686564976	N1	-0.786266308	-0.368711984	0.685929558
C2	0.440982253	-0.990673368	0.928384371	C2	0.460153510	-0.948648616	0.940403351
C3	1.037469997	-0.378241010	2.197643534	C3	1.019872916	-0.370745797	2.237421854
C4	-0.073022738	0.563390564	2.705767249	C4	-0.120498400	0.530207759	2.754549620
C5	-1.144919448	0.581046632	1.630734219	C5	-1.179469756	0.537149286	1.674872565
C6	2.303409355	0.389550895	1.778802636	C6	2.278104103	0.437915366	1.873929754
C7	1.381519234	-1.501456498	3.183803195	C7	1.363909732	-1.517878910	3.197005432
O1	0.950635809	-1.823565858	0.223038036	O1	0.992785091	-1.757815989	0.215841255
O2	-2.116559355	1.290444033	1.566180145	O2	-2.196209183	1.191741401	1.632644773
C1	0.056523914	0.731938776	-1.795042620	C1	0.080406043	0.727908007	-1.834590142
N2	2.309554677	2.417039076	-1.881745168	N2	2.343631985	2.395817296	-2.005769229
C18	1.221295173	0.346596590	-2.459019189	C18	1.193228407	0.361796391	-2.594677172
C10	0.046668830	1.987064841	-1.178596343	C10	0.127405968	1.957711194	-1.170461473
C11	1.185984019	2.782676747	-1.255092577	C11	1.267615421	2.746087193	-1.288445102
C12	2.308794308	1.217361136	-2.469929801	C12	2.288377296	1.219975781	-2.644478500
C9	-1.568463500	-0.666275077	-0.494160241	C9	-1.547011670	-0.645966756	-0.495111955
C13	-2.977476648	-1.304156725	-2.799712249	C13	-2.971670793	-1.303687643	-2.787464857
C14	-1.128318275	-0.160921486	-1.724448855	C14	-1.109189414	-0.155350686	-1.734055240
C15	-2.703125484	-1.466328844	-0.412282810	C15	-2.68487493	-1.442536725	-0.398142519
C16	-3.415927749	-1.778474696	-1.565834730	C16	-3.406139216	-1.763407306	-1.545218505
C17	-1.840478021	-0.504730209	-2.876818659	C17	-1.829928232	-0.511508451	-2.879610711
H22	0.264300473	1.585518541	2.886530566	H22	0.190672008	1.556961726	2.954810788
H23	-0.532516858	0.210967039	3.633566206	H23	-0.577095899	0.145762209	3.670476316
H24	2.070555305	1.182517977	1.063610761	H24	2.040349811	1.241331116	1.171879981
H25	2.777056930	0.841942726	2.654162960	H25	2.707343009	0.879704955	2.776340096
H26	3.016584840	-0.287105987	1.305135658	H26	3.025151204	-0.209917316	1.411192567
H27	1.841056766	-1.088616174	4.085885833	H27	1.779457986	-1.116090806	4.124318166
H28	0.488176211	-2.058836344	3.480268565	H28	0.475710167	-2.105846764	3.444574921
H29	2.079872905	-2.205380031	2.727950179	H29	2.101532222	-2.184111412	2.745495193
H30	1.287388541	-0.628014796	-2.929318872	H30	1.214307461	-0.585468192	-3.121617537
H31	-0.836373553	2.330742127	-0.650586963	H31	-0.715036769	2.300043158	-0.580074482
H32	1.198200814	3.764207742	-0.787401785	H32	1.319589794	3.705309605	-0.780540975
H33	3.230564750	0.931656557	-2.970681514	H33	3.166596994	0.946298215	-3.223274244
H34	-3.524744938	-1.551310839	-3.703568755	H34	-3.524252004	-1.557800487	-3.685890903
H35	-3.015857206	-1.845366452	0.554002563	H35	-2.991296694	-1.813683893	0.573261756
H36	-4.304721743	-2.397005117	-1.501982673	H36	-4.296363014	-2.378291390	-1.469659737
H37	-1.507882652	-0.121570497	-3.83580785	H37	-1.500898847	-0.144251536	-3.845864664

Table 2.10 The TS structure of rotor **1**(4-Py) in solvent and the XYZ coordinates in gas phase (left) and in solvent (right).



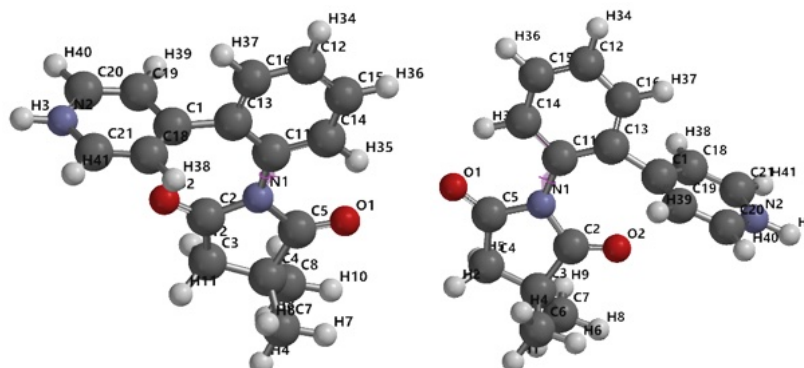
N1	-0.249635531	0.885262648	0.854937501	N1	-0.234519150	0.882771116	0.854652434
C2	-0.440221826	1.579167197	2.087186789	C2	-0.403650190	1.585652541	2.081373600
C3	0.005256305	0.682054832	3.225839345	C3	-0.006461890	0.678160591	3.223971717
C4	0.254462490	-0.687566522	2.602221378	C4	0.251379585	-0.690982662	2.595706141
C5	0.451575736	-0.323970490	1.133780316	C5	0.485098724	-0.312474584	1.141226648
O1	-0.854143349	2.700144940	2.238605133	O1	-0.763231555	2.731873618	2.212948982
O2	1.093487780	-0.970785604	0.354442671	O2	1.174815541	-0.921260720	0.366511629
C1	0.493096454	-0.360360212	-2.060990345	C1	0.508305582	-0.350237310	-2.059648861
N2	1.895877433	-2.615957713	-2.998023200	N2	1.878950482	-2.624598586	-3.003657061
C18	-0.129143944	-1.603894651	-2.180663970	C18	-0.109268019	-1.602139007	-2.106537832
C10	1.823984553	-0.267307293	-2.464166493	C10	1.815485138	-0.259857640	-2.537930777
C11	2.474649353	-1.414588187	-2.908492504	C11	2.453143981	-1.414162322	-2.982115154
C12	0.610938623	-2.688259050	-2.638633885	C12	0.611791334	-2.695058912	-2.572737307
C9	-0.676634233	1.383530830	-0.442957556	C9	-0.670145248	1.375115389	-0.437358254
C13	-1.670507064	2.568776961	-2.826656847	C13	-1.650902323	2.585425444	-2.815537870
C14	-0.310415807	0.852636914	-1.708770419	C14	-0.283862550	0.868670711	-1.706723119
C15	-1.577340619	2.467544026	-0.427018230	C15	-1.606546419	2.428876440	-0.416404633
C16	-2.064573862	3.049839817	-1.586933820	C16	-2.087559206	3.024904482	-1.572899316
C17	-0.814822711	1.480819166	-2.861848568	C17	-0.774775187	1.512645444	-2.857722772
H30	-1.172800275	-1.726751993	-1.910181579	H30	-1.134594945	-1.727556088	-1.775713655
H31	2.350518801	0.679315615	-2.416249029	H31	2.335735575	0.691006898	-2.552098493
H32	3.517459020	-1.366567064	-3.213817378	H32	3.476973971	-1.364621274	-3.344481472
H33	0.145661474	-3.667695785	-2.727892316	H33	0.147400799	-3.677702187	-2.607466577
H34	-2.031861734	3.013754033	-3.747609019	H34	-2.001894876	3.044271312	-3.733372855
H35	-1.890007814	2.881188050	0.514359631	H35	-1.960756792	2.804787157	0.526602416
H36	-2.752532257	3.884835100	-1.505934487	H36	-2.804911831	3.834344591	-1.488585763
H37	-0.521745756	1.063206943	-3.818739071	H37	-0.464178018	1.118543834	-3.819220810
H1	0.917501320	1.111787449	3.650394112	H1	0.895644200	1.094346038	3.681398279
H2	-0.755491014	0.701000274	4.008772170	H2	-0.794918479	0.689689829	3.979106065
C6	-1.002264530	-1.581151763	2.677759656	C6	-1.013103884	-1.577912583	2.635337869
H3	-0.863396958	-2.494792521	2.095224988	H3	-0.863774551	-2.492544617	2.056499251
H4	-1.889279265	-1.067523209	2.296943439	H4	-1.886022777	-1.056690894	2.234098928
H5	-1.195069593	-1.863281443	3.716091042	H5	-1.227238172	-1.855725790	3.670181520
C7	1.474872033	-1.428892556	3.145071335	C7	1.452055438	-1.438609837	3.172070696
H6	1.655166394	-2.340217120	2.572561431	H6	1.629251881	-2.364150702	2.620512173
H7	1.320685557	-1.700241836	4.192747383	H7	1.266059940	-1.691710465	4.218591544
H8	2.376694765	-0.815059731	3.078640399	H8	2.360223889	-0.833089413	3.119422584

Table 2.11 The GS structure of rotor **1(4-Py)•H⁺** in solvent and the XYZ coordinates in gas phase (left) and in solvent (right).



N1	1.215212548	-0.163959449	0.074382964	N1	1.221352037	-0.105651867	0.068784530
C2	0.532586709	0.695595662	0.951424338	C2	0.668177857	0.840616170	0.942603360
C3	0.863963972	0.302295813	2.390459504	C3	0.873848214	0.360469273	2.378569041
C4	1.911733112	-0.817641207	2.239350775	C4	1.789905328	-0.870006589	2.222213443
C5	2.031208515	-1.103941415	0.757217983	C5	1.861047964	-1.159527621	0.741386647
O1	2.676736619	-1.954084880	0.209604425	O1	2.363850131	-2.108192893	0.187767289
O2	-0.231968976	1.561219717	0.598953553	O2	0.090262032	1.839396115	0.581014726
C6	1.395235008	1.534181973	3.136689250	C6	1.501986874	1.482396103	3.212516144
C11	1.185468588	-0.038603287	-1.344756356	C11	1.189729878	0.019409229	-1.353784754
C12	1.174975217	0.397748553	-4.108358947	C12	1.171177880	0.398897937	-4.115389084
C13	-0.037740068	0.060131528	-2.034926725	C13	-0.034546885	0.037320610	-2.041677885
C14	2.384966631	0.058922794	-2.045087008	C14	2.388372318	0.175077394	-2.044185036
C15	2.379412693	0.259107376	-3.422173899	C15	2.381078766	0.349900546	-3.425500625
C16	-0.024119651	0.311395829	-3.414938001	C16	-0.027473773	0.254831446	-3.425356441
C1	-1.332259892	-0.145909774	-1.372180949	C1	-1.324115523	-0.204074635	-1.361259626
N2	-3.783975824	-0.570996036	-0.188864184	N2	-3.7429697	-0.680750555	-0.151753113
C18	-2.393667836	0.759850026	-1.553020534	C18	-2.394422709	0.689686478	-1.515016340
C19	-1.569448435	-1.285045843	-0.578316193	C19	-1.525139712	-1.352902100	-0.580490413
C20	-2.799189097	-1.478511087	0.003184611	C20	-2.746892197	-1.572328810	0.017416362
C21	-3.607333693	0.533192622	-0.951478952	C21	-3.599542125	0.432244512	-0.898456749
H3	-4.684338024	-0.724790438	0.249011379	H3	-4.635750696	-0.855493492	0.298408513
C7	-0.436882307	-0.203874508	3.040250438	C7	-0.508142744	-0.029552362	2.936687525
H23	1.649538118	-1.740907683	2.759721375	H23	1.431741016	-1.756720113	2.747850610
H24	2.899632979	-0.524427794	2.603859995	H24	2.808781298	-0.677996315	2.570324945
H25	2.309142076	1.917068630	2.674995356	H25	2.469093715	1.785221078	2.802703978
H26	0.653953449	2.334627836	3.131693206	H26	0.847502494	2.355677903	3.232713748
H27	1.622162814	1.276864549	4.173742461	H27	1.656591917	1.139365074	4.238082739
H28	1.168784620	0.564807366	-5.179282466	H28	1.158290884	0.545063384	-5.189756045
H29	3.320648527	-0.023219053	-1.508392227	H29	3.320708214	0.168582619	-1.492806184
H30	3.320091240	0.321632594	-3.957029638	H30	3.318477807	0.461179730	-3.958726070
H31	-0.963643760	0.387171306	-3.952929625	H31	-0.968399919	0.273550586	-3.964918586
H32	-2.251571700	1.661863450	-2.132930373	H32	-2.285218906	1.593261711	-2.099868382
H33	-0.797766757	-2.031366044	-0.443364438	H33	-0.742828617	-2.089545338	-0.456163392
H34	-3.044813255	-2.339518552	0.610473917	H34	-2.969995932	-2.438488649	0.624722658
H35	-4.451976304	1.203567371	-1.038279525	H35	-4.460433049	1.082511791	-0.968339586
H36	-0.829095633	-1.084472302	2.519733116	H36	-0.957887275	-0.837468434	2.353112390
H37	-1.201485136	0.575018415	3.021982155	H37	-1.185045494	0.826683585	2.918146274
H38	-0.254177088	-0.484994058	4.079579237	H38	-0.403171371	-0.372643501	3.968423390

Table 2.12 The TS structure of rotor **1**(4-Py)•H⁺ in solvent and the XYZ coordinates in gas phase (left) and in solvent (right).



N1	0.283850500	0.937747087	0.160057111	N1	0.138365601	1.417996688	0.160136779
C2	0.601981353	-0.056564251	1.084435364	C2	0.467606107	0.426635313	1.101584002
C3	1.305370774	0.538709881	2.273589552	C3	1.232366278	1.014509399	2.274080835
C4	1.121765973	2.049164466	2.145189609	C4	1.007886985	2.512834405	2.102867840
C5	0.676648202	2.226465279	0.697194905	C5	0.480862512	2.701120087	0.703408808
O1	0.633940414	3.275598402	0.120854345	O1	0.356800893	3.772245216	0.164070707
O2	0.370173502	-1.240546246	0.944585785	O2	0.211610660	-0.750435315	0.989265169
C11	-0.323395172	0.715113654	-1.133866336	C11	-0.452391213	1.186073387	-1.144612025
C12	-1.492452424	0.511527313	-3.720331163	C12	-1.591571702	0.996980785	-3.750605240
C13	-0.704702834	-0.550200137	-1.656635537	C13	-0.846320181	-0.074739307	-1.670557853
C14	-0.553880419	1.840740382	-1.946189279	C14	-0.644222934	2.310439058	-1.971373327
C15	-1.124679143	1.745662575	-3.207344926	C15	-1.198568308	2.225160148	-3.240840502
C16	-1.276969234	-0.611973242	-2.939503114	C16	-1.406681774	-0.125462983	-2.959996702
C1	-0.620912752	-1.920629834	-1.063384944	C1	-0.773466747	-1.455941781	-1.096796101
N2	-0.666123967	-4.585838392	-0.366129765	N2	-0.808502648	-4.114862659	-0.413275136
C18	-1.740218285	-2.486103028	-0.420083680	C18	-1.897383499	-2.025045683	-0.477394118
C19	0.436290207	-2.783366740	-1.415525655	C19	0.306573585	-2.295109187	-1.414447629
C20	0.403363887	-4.102464617	-1.041306984	C20	0.273867355	-3.620687569	-1.050026210
C21	-1.734750745	-3.810246389	-0.064108604	C21	-1.888120773	-3.355565596	-0.130975942
H3	-0.678112098	-5.562324978	-0.099908007	H3	-0.819830321	-5.095852862	-0.156785110
H34	-1.937605244	0.416510241	-4.703975751	H34	-2.028740240	0.904564296	-4.738444063
H35	-0.271915257	2.813834199	-1.586593417	H35	-0.352673459	3.279856696	-1.612475674
H36	-1.274253863	2.651644988	-3.783598681	H36	-1.316557954	3.132611642	-3.822841951
H37	-1.562690566	-1.584771732	-3.326359722	H37	-1.702474593	-1.095506627	-3.344958879
H38	-2.601889407	-1.875736521	-0.185245857	H38	-2.769704170	-1.425181896	-0.255240855
H39	1.289405164	-2.407654308	-1.964402631	H39	1.174265856	-1.909208443	-1.932514282
H40	1.194030391	-4.806665700	-1.263445075	H40	1.075134764	-4.318454259	-1.250466126
H41	-2.555030795	-4.294798221	0.448771430	H41	-2.712900724	-3.853906930	0.359707800
C7	-0.037756764	2.550743480	3.031418831	H2	1.902115113	3.123535222	2.232279591
H4	0.236866318	2.456719487	4.084359399	H5	0.245048792	2.895769478	2.787281045
H6	-0.951247259	1.971271038	2.866628290	C6	2.714246615	0.629205204	2.080400641
H7	-0.255085706	3.599016650	2.822642710	H1	3.306162631	1.044640469	2.898931260
C8	2.397616295	2.856977642	2.401392855	H4	3.110514909	1.017985291	1.138283890
H1	3.220216986	2.516793018	1.766533019	H6	2.828967516	-0.456618149	2.080828789
H8	2.705794159	2.750493758	3.443830421	C7	0.692701445	0.449613654	3.591926670
H10	2.228734968	3.914040861	2.194988083	H7	1.241260695	0.883090615	4.431272164
H11	0.901123522	0.102765912	3.188431463	H8	0.811729634	-0.634727890	3.622564541
H12	2.356499373	0.238343810	2.213036009	H9	-0.367976760	0.682440136	3.715737245

2.5.6 Energy Decomposition Analyses I

The intramolecular interaction energies between the imide carbonyl groups (C=O) and the aromatic gates (phenyl, pyridyl, and pyridinium) for the optimized (B3LYP-D3/6-311G*) transition states were calculated by functional group interaction analysis method, FI-SAPT (SAPT(0), jun-cc-pVDZ) as implemented in Psi4 (**Table 2.13**).¹¹⁹

Table 2.13 FI-SAPT total and component energies.

Rotor	E _{total}	E _{exch}	E _{elst}	E _{ind}	E _{disp}
phenyl	13.57	20.86	0.74	-4.09	-3.94
3-pyridyl	12.63	21.64	-1.04	-4.02	-3.95
4-pyridyl	11.60	20.51	-0.67	-4.23	-4.01
3-pyridinium	-4.64	20.89	-16.59	-4.76	-4.18
4-pyridinium	-8.04	20.97	-18.06	-6.50	-4.44

2.5.7 Reversibility study

To test the reversibility of the rotors, a sample of rotor **1**(3-Py) was titrated with methanesulfonic acid in TCE-d₂ and then neutralized with sodium bicarbonate through four cycles (**Figure 2.16**). Changes in the rate of rotation were followed by rate of exchange of the succinimide methylene (CH₂) protons in the ¹H NMR spectra at 25 °C (**Figure 2.16**). In the unprotonated pyridyl rotors (0 equiv MsOH), slow rotation was observed as seen by the separate diastereotopic methylene which were two doublets. When methanesulfonic acid (3.0 equiv) was added to form the pyridinium rotors, the rate of rotation increased dramatically and the methylene peaks coalesced into a singlet. The pyridinium rotors were neutralized by washing the solution with aqueous sodium bicarbonate powder. The

methylene protons cleanly reverted to the slowly rotating diastereomeric pair of doublets. This process was repeated through 4 cycles and the spectra cleanly showed the transition from slowly rotating **1**(3-Py) to quickly rotating **1**(3-Py)H⁺ without degradation and the appearance of additional peaks.

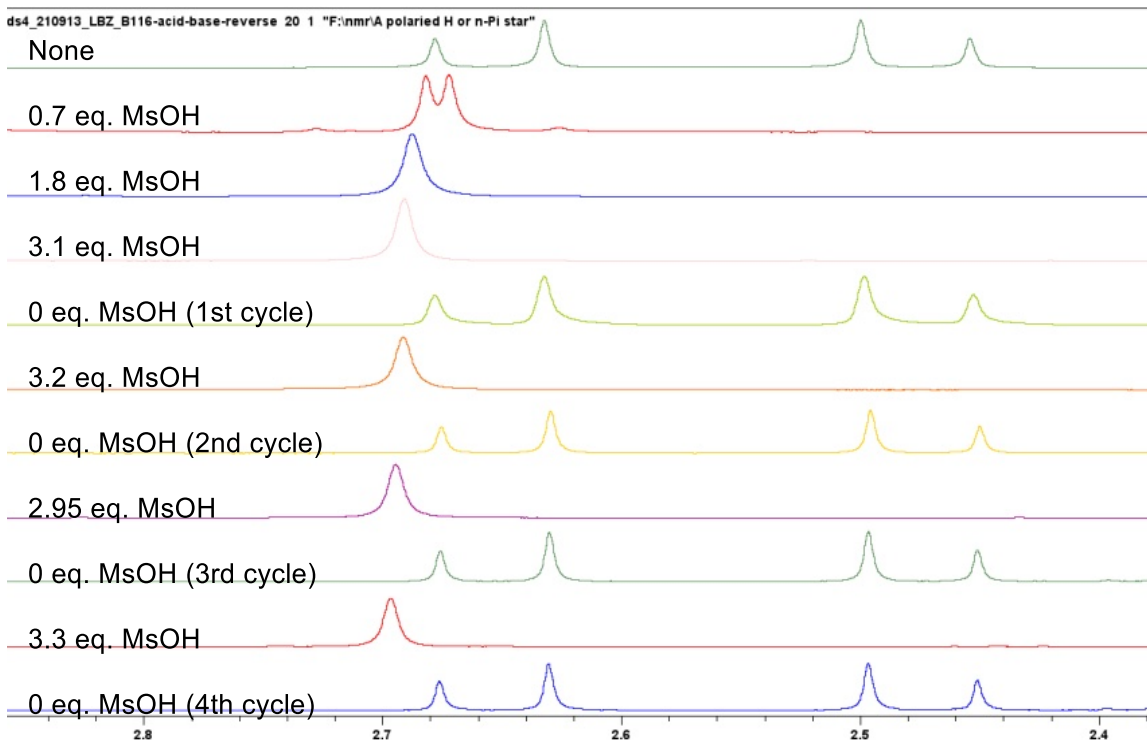


Figure 2.16 ¹H NMR spectra of rotor **1**(3-Py) with various equiv. of MsOH in TCE-d₂ at 25 °C.

2.5.8 Crystallographic structures

X-ray intensity data from a colorless needle were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-II area detector and an Incoatec microfocus source (Mo K α radiation, λ = 0.71073 Å). The raw area detector data frames were reduced, scaled and corrected for absorption effects using the Bruker APEX3, SAINT+ and SADABS programs.¹²⁸ The structure was solved with SHELXT.^{129,130}

F^2 were performed with SHELXL-2018¹²⁸ using OLEX2.¹³¹

electron density peak in the final difference map is $0.36 \text{ e}^-/\text{\AA}^3$, located $0.76 \text{ \AA}$ from C4.

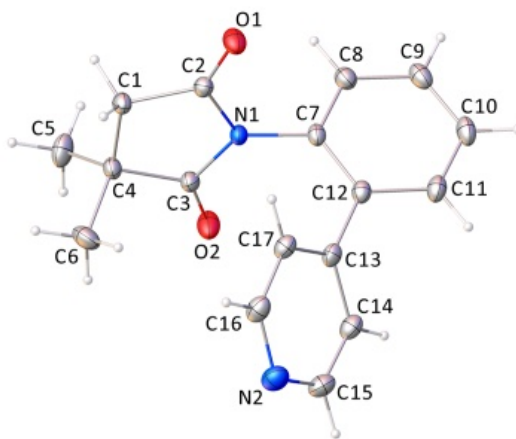


Figure 2.17 Crystal structure of **1**(4-Py) (C₁₇H₁₆N₂O₂).

X-Ray Structure Determination of **1** (4-Py) (C₁₇H₁₆N₂O₂)

X-ray intensity data from a colorless needle were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-II area detector and an Incoatec microfocus source (Mo K α radiation, $\lambda = 0.71073$ Å). The raw area detector data frames were reduced, scaled and corrected for absorption effects using the Bruker APEX3, SAINT+ and SADABS programs.¹²⁸ The structure was solved with SHELXT.^{129,130} Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXL-2018¹²⁸ using OLEX2.¹³¹

The compound crystallizes in the monoclinic system. The pattern of systematic absences in the intensity data was uniquely consistent with the space group $P2_1/n$, which was confirmed by structure solution. The asymmetric unit consists of one molecule. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to carbon were located in difference Fourier maps before being placed in geometrically idealized positions and included as riding atoms with $d(\text{C-H}) = 0.95$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for arene hydrogen atoms, $d(\text{C-H}) = 0.99$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methylene hydrogen atoms, and $d(\text{C-H}) = 0.98$ Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl hydrogens. The methyl hydrogens were allowed to rotate as a rigid group to the orientation of maximum observed electron density. The largest residual electron density peak in the final difference map is $0.36 \text{ e}^-/\text{\AA}^3$, located 0.76 Å from C4.

Table 2.14 Crystal data and structure refinement for rotor **1 (4-Py)**.

Identification code	lbz_b130
Empirical formula	C ₁₇ H ₁₆ N ₂ O ₂
Formula weight	280.32
Temperature/K	100(2)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	5.8248(4)
b/Å	28.7309(17)
c/Å	8.8878(5)
$\alpha/^\circ$	90
$\beta/^\circ$	106.165(2)
$\gamma/^\circ$	90
Volume/Å ³	1428.58(15)
Z	4
$\rho_{\text{calc}}/\text{cm}^{-3}$	1.303
μ/mm^{-1}	0.087
F(000)	592.0
Crystal size/mm ³	0.26 × 0.05 × 0.03
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/ $^\circ$	4.978 to 61.046
Index ranges	-8 ≤ h ≤ 8, -41 ≤ k ≤ 40, -11 ≤ l ≤ 12
Reflections collected	72974
Independent reflections	4356 [R _{int} = 0.0413, R _{sigma} = 0.0160]
Data/restraints/parameters	4356/0/193
Goodness-of-fit on F ²	1.040
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0395, wR ₂ = 0.0977
Final R indexes [all data]	R ₁ = 0.0470, wR ₂ = 0.1024

Table 2.15 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for lbz_b130. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
O1	770.5(13)	4097.2(2)	-294.8(9)	23.23(16)
O2	7207.9(14)	3289.1(3)	2626.5(10)	27.57(18)
N1	4222.3(14)	3785.8(3)	1335.1(9)	14.27(15)
N2	3131.0(17)	3549.4(3)	6746.0(10)	25.05(19)
C1	1353.4(17)	3255.7(3)	-82.9(11)	17.60(18)
C2	1962.3(16)	3762.5(3)	250.9(10)	15.23(17)
C3	5221.7(17)	3348.9(3)	1763.4(11)	16.50(17)
C4	3440.4(16)	2974.8(3)	965.9(11)	16.43(17)
C5	4659.0(19)	2656.6(4)	42.5(14)	27.1(2)
C6	2677(2)	2702.0(4)	2226.8(13)	26.8(2)
C7	5435.1(16)	4212.4(3)	1910.0(11)	15.41(17)
C8	6431.1(17)	4464.7(3)	917.9(11)	19.19(19)
C9	7639.0(18)	4878.6(3)	1429.4(13)	22.2(2)
C10	7846.4(18)	5034.6(3)	2937.1(13)	22.7(2)
C11	6916.0(17)	4773.8(3)	3944.4(12)	20.54(19)
C12	5675.7(16)	4358.1(3)	3454.0(11)	16.12(17)
C13	4744.2(16)	4085.0(3)	4574.2(11)	16.52(17)
C14	6217.8(17)	3992.1(3)	6078.7(11)	20.04(19)
C15	5345.6(19)	3727.3(4)	7098.8(12)	23.4(2)
C16	1705.4(18)	3649.1(4)	5314.1(12)	21.6(2)
C17	2411.7(17)	3912.7(3)	4210.0(11)	18.34(18)

Table 2.16 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for lbz_b130. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^2U_{11}+2hka*b*U_{12}+\dots]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
O1	19.0(3)	17.3(3)	28.9(4)	2.0(3)	-0.7(3)	2.1(3)
O2	22.8(4)	18.3(3)	32.5(4)	-0.8(3)	-7.6(3)	2.7(3)
N1	15.0(3)	11.5(3)	15.0(3)	-0.9(2)	2.1(3)	-0.6(3)
N2	26.0(4)	30.3(5)	19.9(4)	-1.0(3)	8.0(3)	-2.3(4)
C1	17.9(4)	14.3(4)	18.3(4)	0.0(3)	1.3(3)	-2.6(3)
C2	14.5(4)	15.5(4)	15.2(4)	-0.1(3)	3.4(3)	-1.3(3)
C3	19.0(4)	13.2(4)	15.9(4)	-0.4(3)	2.5(3)	0.6(3)
C4	17.6(4)	12.3(4)	18.4(4)	-0.5(3)	3.3(3)	-0.6(3)
C5	23.6(5)	22.6(5)	34.6(6)	-12.4(4)	7.1(4)	0.4(4)
C6	29.0(5)	21.8(5)	28.6(5)	9.8(4)	6.5(4)	-1.3(4)
C7	13.8(4)	12.1(4)	18.8(4)	-0.9(3)	2.0(3)	-0.3(3)
C8	19.1(4)	17.0(4)	20.5(4)	1.9(3)	4.1(3)	-0.8(3)
C9	18.9(4)	17.0(4)	29.6(5)	4.7(4)	4.9(4)	-1.4(3)
C10	17.6(4)	14.8(4)	33.0(5)	-2.2(4)	2.4(4)	-2.8(3)
C11	17.6(4)	17.6(4)	24.0(5)	-5.4(3)	1.8(3)	-1.5(3)
C12	13.3(4)	14.9(4)	19.0(4)	-1.8(3)	2.5(3)	-0.2(3)
C13	15.9(4)	16.3(4)	17.1(4)	-4.3(3)	4.2(3)	0.2(3)
C14	16.4(4)	23.4(4)	18.6(4)	-4.2(3)	2.0(3)	-0.4(3)
C15	22.9(5)	29.2(5)	16.4(4)	-1.4(4)	2.7(4)	0.8(4)
C16	18.4(4)	26.7(5)	20.5(4)	-4.5(4)	6.5(4)	-3.4(4)
C17	15.3(4)	21.8(4)	17.1(4)	-3.8(3)	3.2(3)	-0.6(3)

Table 2.17 Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for lbz_b130.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H1A	1165.29	3185.25	-1201.11	21
H1B	-157.9	3177.99	163.66	21
H5A	3546.79	2410.78	-467.46	41
H5B	6081.07	2515.92	757.75	41
H5C	5130.11	2839.09	-754.58	41
H6A	1876.03	2912.11	2787.65	40
H6B	4091.39	2566.68	2966.74	40
H6C	1576.78	2452.64	1732.8	40
H8	6288.71	4354.79	-112.23	23
H9	8315.83	5052.73	750.46	27
H10	8628.95	5321.22	3282.69	27
H11	7124.31	4879.29	4986.89	25
H14	7804.07	4109.75	6397.42	24
H15	6380.91	3667.88	8112.9	28
H16	116.99	3532.32	5039.18	26
H17	1319.43	3975.09	3217.53	22

2.5.9 Variable Temperature NMR Spectra of the Rotors.

The following equation was used to calculate the rates at coalescence temperatures, $k_c = \pi\Delta\nu/\sqrt{2}$, where k_c is the exchange rate at coalescence temperature and $\Delta\nu$ is the maximum peak separation (25 °C) in Hz: a) **1**(4-Py), 167 Hz at 130 °C; b) **1**(3-Py), 156 Hz at 135 °C; c) **1**(4-Py)•H⁺, 144 Hz at 72 °C; and d) **1**(3-Py)•H⁺, 112 Hz at 85 °C (**Figure 2.18**).

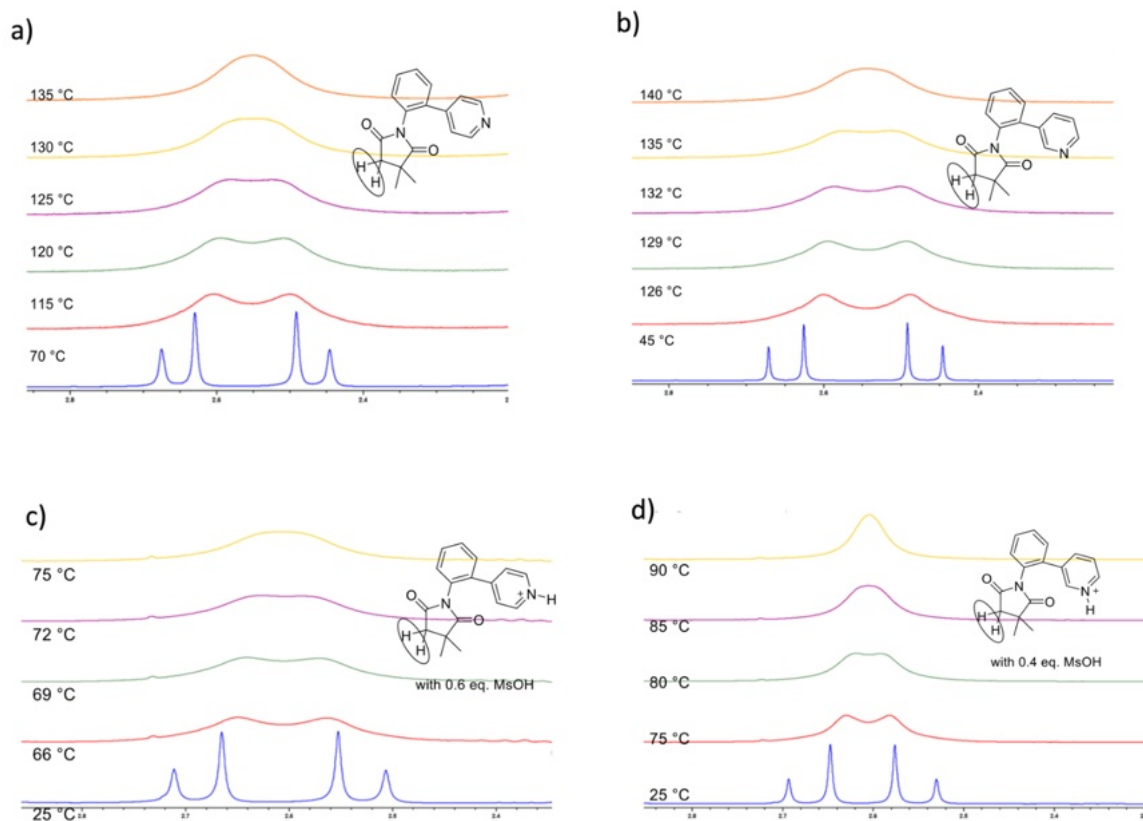


Figure 2.18 Variable temperature ¹H NMR spectra (400 MHz) of rotors a) **1**(4-Py), b) **1**(3-Py), c) **1**(4-Py)•H⁺, and d) **1**(3-Py)•H⁺ in TCE-d₂ highlighting the differences in dynamic behavior when protonated or unprotonated.

2.5.10 Energy Decomposition Analyses II

A more comprehensive FI-SAPT analysis of the effects of protonation on the intramolecular interaction energies in the rotors TS and GS structures were carried out to confirm the dominant role of the electrostatic term to the changes in barrier on protonation.

The results are shown in **Table 2.18**.

Table 2.18 Intramolecular interaction energies (E, kcal/mol) between the pyridyl/pyridinium gates and the dimethylsuccinimide staters calculated using FI-SAPT0(jun-cc-pVDZ).

rotor	GS / TS	E _{total}	E _{elst}	E _{ind}	E _{exch}	E _{disp}
1 (3-Py)	GS	0.960213	1.709445	-1.58873	7.057821	-6.21832
1 (3-Py)•H ⁺	GS	2.504429	5.921008	-3.66906	5.830294	-5.57782
1 (4-Py)	GS	1.523185	2.623817	-1.52361	6.520781	-6.09781
1 (4-Py)•H ⁺	GS	3.012289	6.516217	-3.70031	5.631448	-5.43506
1 (3-Py)	TS	12.11141	3.095865	-2.62218	17.03878	-5.40105
1 (3-Py)•H ⁺	TS	5.887928	-2.57875	-5.23037	19.30853	-5.61148
1 (4-Py)	TS	11.30839	3.756733	-2.67025	15.56096	-5.33906
1 (4-Py)•H ⁺	TS	3.357543	-3.39307	-6.92164	19.39143	-5.71917

To capture more of the intramolecular interactions of the pyridyl and pyridinium gates and also the weak interactions in the GS, the rotor fragment was expanded to include the entire dimethylsuccinimide rotor. Specifically, the intramolecular interaction between the pyridyl/pyridinium (C₅NH₄ or C₅NH₅⁺) and dimethylsuccinimide (C₄H₈NO₂) fragments were calculated. The input structures for the FI-SAPT0(jun-cc-pVDZ) analyses in Psi4² were the solvent GS and TS structures of rotors **1**(3-Py), **1**(4-Py), **1**(3-Py)•H⁺, and **1**(4-Py)•H⁺ found using B3LYP-D3/6-311G* (solvent = TCE).

To check the consistency of the FI-SAPT analysis with the structural and barrier modeling studies conducted using B3LYP-D3/6-311G*, the changes in barrier calculated by both methods were compared. FI-SAPT cannot directly calculate the rotational barriers of the rotors as the method only calculates the interaction energy between structural fragments. However, the relative changes in the rotational barriers can be estimated based on the assumption that the changes in the rotational barriers are due to the intramolecular interactions. Thus, the change in barrier of rotors **1**(3-Py) and **1**(4-Py) on protonation ($\Delta\Delta E^\ddagger$) were calculated using equations 1 and 2 from the FI-SAPT values in Table S18.

$$\Delta\Delta E^\ddagger \text{ for } \mathbf{1}(3\text{-Py}) \rightarrow \mathbf{1}(3\text{-Py})\cdot\text{H}^+ = [E_{(\text{TS } \mathbf{1}(3\text{-Py}))} - E_{(\text{GS } \mathbf{1}(3\text{-Py}))}] - [E_{(\text{TS } \mathbf{1}(3\text{-Py})\cdot\text{H}^+)} - E_{(\text{GS } \mathbf{1}(3\text{-Py})\cdot\text{H}^+)}]$$

equation 2.1

$$\Delta\Delta E^\ddagger \text{ for } \mathbf{1}(4\text{-Py}) \rightarrow \mathbf{1}(4\text{-Py})\cdot\text{H}^+ = [E_{(\text{TS } \mathbf{1}(4\text{-Py}))} - E_{(\text{GS } \mathbf{1}(4\text{-Py}))}] - [E_{(\text{TS } \mathbf{1}(4\text{-Py})\cdot\text{H}^+)} - E_{(\text{GS } \mathbf{1}(4\text{-Py})\cdot\text{H}^+)}]$$

equation 2.2

Table 2.19 Comparison of the calculated $\Delta\Delta G^\ddagger$ and $\Delta\Delta E^\ddagger$ values for the rotational barriers of rotors **1**(3-Py) and **1**(4-Py) on protonation in the gas phase.

	$\Delta\Delta G^\ddagger$ B3LYP-	$\Delta\Delta E^\ddagger$ SAPT0
rotor energy difference	D3/6-311G* (kcal/mol)	(MP2/jun-cc-pVDZ) (kcal/mol)
1 (3-Py) - 1 (3-Py)•H ⁺	-7.8	-8.9
1 (4-Py) - 1 (4-Py)•H ⁺	-9.4	-7.8

The changes in barrier on protonation of the rotors were very similar despite the differences in the two energy calculation methods. The barrier calculation in Table 1 of

the manuscript used B3LYP-D3/6-311G* and included frequency analysis to calculate $\Delta\Delta G^\ddagger$. The FI-SAPT0 analysis in Psi4 uses the equivalent of MP2/jun-cc-pVDZ to calculate $\Delta\Delta E^\ddagger$. The similarity of the $\Delta\Delta G^\ddagger$ and $\Delta\Delta E^\ddagger$ values suggest that the FI-SAPT is accurately capturing the key energy terms in the changes in the rotational barriers.

The advantage of this more comprehensive FI-SAPT analysis is that it captures the energy terms in the GS and TS, whereas the previous SAPT analysis (**Table 2.13**) only captured the energy terms of the TS. The contributing energy terms to the changes in barrier ($\Delta\Delta E^\ddagger$) were examined (**Figure 2.19**). Comparison of the relative contributions of the electrostatic, induction, exchange, and dispersion terms showed that the electrostatic term (E_{elst}) was the dominant component of $\Delta\Delta E^\ddagger$ (E_{total}). This was consistent with the TS only SAPT analysis in **Table 2.13**. The steric exchange term (E_{exch}) was the second largest contributing term, but was much smaller than the electrostatic term.

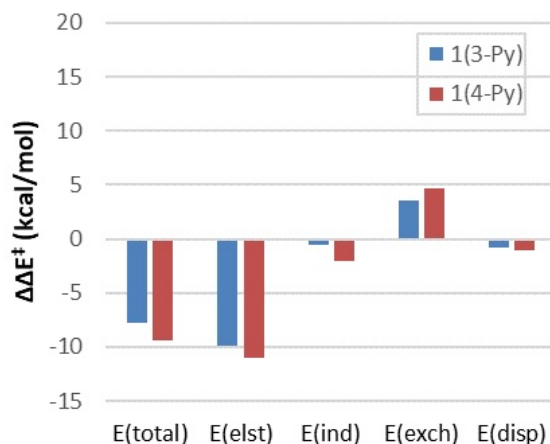


Figure 2.19 The FI-SAPT analysis of the changes in difference in the TS and GS energies of **1(3-Py)** and **1(4-Py)** on protonation.

Interestingly, the electrostatic (E_{elst}) and exchange (E_{exch}) terms have opposite signs. The electrostatic term is negative and stabilizing, which supports the hypothesis that protonation of the pyridyl gate lowers the barrier due to the formation of attractive

electrostatic interactions between the positively charged pyridinium surface and the electrostatically negative oxygen of the succinimide carbonyl. The steric term, on the other hand, is positive and destabilizing. Comparison of the changes in the GS and TS of the FI-SAPT analysis (**Figure 2.18**) reveals that the majority of the destabilizing exchange interactions are in the TS. We hypothesize that the formation of attractive electrostatic interactions in the TS brings the pyridinium gate and succinimide carbonyl closer together leading to the increase in the steric interactions. The overall changes in energy (E_{total}) as well as the component energy terms including exchange (E_{exch}) were much smaller for the GS. This confirms that the majority of the effects of protonation on the rotation barriers are due to changes in the TS energies.

2.5.11 Comparison of the molecular modeling and X-ray structures

The structures for rotor **1**(4-Py) from the crystal structure (**2.5.8 Crystallographic structures**) and from GS molecular modeling (B3LYP-D3/6-311G*) of the GS of **1**(4-Py) were compared. The structures were very similar, which provided support for the ability of the molecular modeling to accurately simulate the geometry and rotational barriers. The 4-pyridyl group is tipped toward the dimethyl groups of the succinimide in both structures. The dihedral angles along the central atropisomeric C-N bond were almost identical. The C(succinimide)-N(succinimide)-C(phenyl)-C(phenyl) dihedrals were 70.67 ° and 71.22° for the calculated and crystal structure respectively.

Chapter 3 Pnictogen bond interactions with Nitrogen acceptors

3.1 Abstract

Stabilizing nitrogen pnictogen bond interactions were measured using molecular rotors. Intramolecular C=O...N interactions were formed in the bond rotation transition states which lowered the rotational barriers and increased the rates of rotation, as measured by EXSY NMR. The pnictogen interaction energies show a very strong correlation with the positive electrostatic potential on nitrogen, which was consistent with a strong electrostatic component. In contrast, the NBO perturbation and pyramidalization analyses show no correlation, suggesting that the orbital-orbital component is minor. The strongest C=O...N pnictogen interactions were comparable to n to π (C=O...C=O) interactions and were stronger than C=O...Ph interactions, when measured using the same *N*-phenylimide rotor system. The ability of the nitrogen pnictogen interactions to stabilize transition states and enhance kinetic processes demonstrates their potential in catalysis and reaction design.

3.2 Introduction

The pnictogen bond is an attractive non-covalent interaction between an electron poor or electrostatically positive region on a pnictogen (Pn) atom (N, P, As, Sb, Bi) and an electron rich or electrostatically negative region on another group (**Figure 3.1a**).^{132–134} The pnictogen bonds have been observed and studied in catalysis,^{135–137} computational,¹³⁸ solution and gas phase experiments,^{139–141} crystal engineering¹⁴² and medicinal chemistry.¹⁴³ Nitrogen pnictogen interactions are of particular interest because nitrogen is one of the most common pnictogens.

Thus, the interaction can impact ligand–protein binding,¹⁴⁴ medical chemistry,¹⁴⁵ organic synthesis^{146,147} and solid-state packing.^{145,148} However, nitrogen generally forms weak pnictogen interactions due to low polarizability and high electronegativity.^{149,150} Accordingly, nitrogen pnictogen interactions have been primarily characterized in the solid-state,^{147,151–154} gas-phase,^{155–157} and computations.^{154,158–160} Only a few examples have been reported of the interaction in the solution.¹⁶¹

Therefore, we were surprised to observe nitrogen pnictogen interactions in solution using our *N*-phenylimide rotors (**Figure 3.1b**). The goal of this study was to confirm that nitrogens can form stabilizing pnictogen interactions in solution and to measure the strengths of the interaction. In addition, the interaction will be compared with other non-covalent interactions measured in our rotor systems including *n* to π (aromatic) and *n* to π (C=O).^{1,4} Finally, the relative contributions of the electrostatic and orbital-orbital components of the interaction will be assessed.

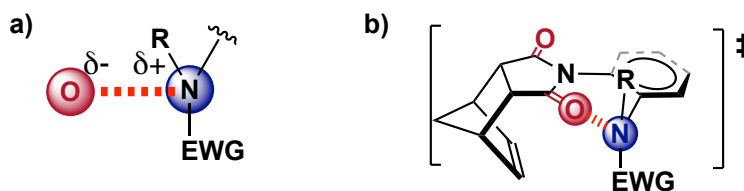


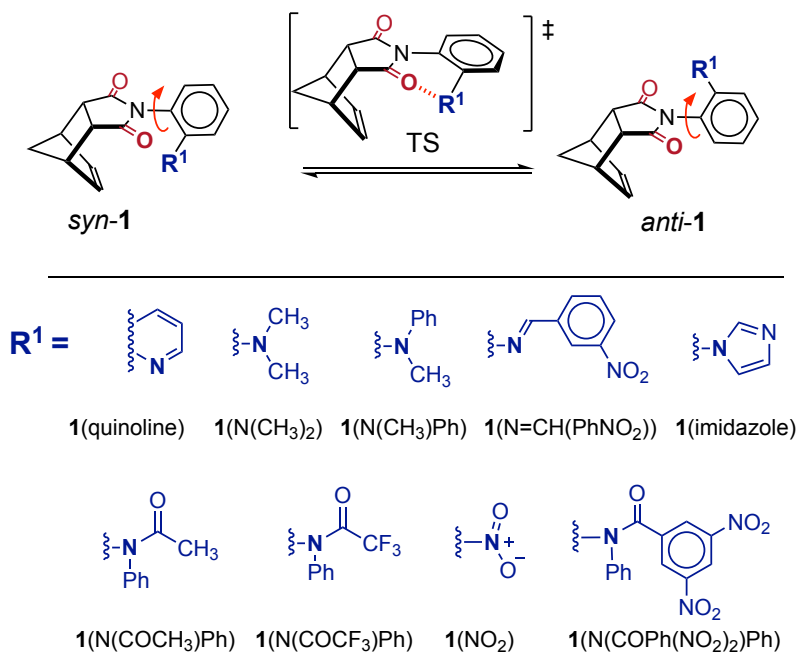
Figure 3.1 a) Representation of the nitrogen pnictogen bond. b) The bond rotation transition state (TS) of a *N*-phenylimide rotor that forms an intramolecular (C=O...N) nitrogen pnictogen bond.

Molecular rotors have been successfully employed to measure the strengths of attractive^{1,4,19,162} and repulsive^{163–165} non-covalent interactions. The rotors are designed to form intramolecular interactions in the bond rotation transition states. Therefore, a stabilizing interaction will lower the TS and rate of rotation will increase. The rate of

rotation and rotational barriers can be easily and accurately measured using dynamic NMR.¹⁶⁶

3.3 Results and discussion

Nitrogen rotors **1** display restricted rotation around the C_(phenyl)-N_(imide) single bond leads to *syn*- and *anti*-conformers (**Scheme 3.1**). Therefore, the rotational barrier can be calculated from the NM measured rate of *syn*- and *anti*-interconversion. In the bond rotation TS, the imide C=O and nitrogen of the R¹-group are forced close together by the rigid *N*-phenyl imide framework. The rigidity of the *N*-phenylimide framework leads to a structurally simple and well-defined TS, which can be accurately modelled.¹



Scheme 3.1 Conformational *syn-anti* equilibrium of the *N*-phenylimide molecular rotors **1** arising from bond rotation around the C-N bond. The R¹-groups are attached at the *ortho*-position of the *N*-phenyl group with the exception of **1**(quinoline) which is fused at the *ortho*- and *meta*-positions.

Rotors **1** were synthesized as previously described via the thermal condensation of cis-5-norbornene-endo-2,3-dicarboxylic anhydride with an *ortho*-substituted aniline.^{1,167}

The *N*-phenylsuccinimide framework was kept constant and only the *ortho*-substituent (R^1) was varied. In **Table 3.1**, the rotors are listed in order of the electrostatic surface potential on the nitrogen (shown in bold) of the R^1 -group from lowest to highest. The R^1 -groups also differed in the geometry and hybridization of the nitrogen centres and the steric sizes and electron withdrawing ability of the groups attached to the nitrogen. The rotational barriers ($\Delta G^\ddagger_{\text{exp}}$) of for each rotor was measured using dynamic ^1H NMR (EXSY) in TCE-d2 (**Table 3.1**) with an accuracy of ± 0.2 kcal/mol^{21,22}

Table 3.1 Comparison of the barriers, parameters, and interaction energies of rotors **1** in units of kcal/mol.

Rotors (R^1)	$\Delta G^\ddagger_{\text{exp}}^{\text{a}}$	$\Delta G^\ddagger_{\text{calc}}^{\text{b}}$	B-value ^c	$E_{\text{steric}}^{\text{d}}$	$E_{\text{int}}^{\text{e}}$
1 (quinoline)	21.3	21.3	<i>4.2</i>	19.5	1.8
1 (N(CH ₃) ₂)	22.0	20.6	6.9	21.3	0.7
1 (N(CH ₃)Ph)	20.2	21.5	<i>6.2</i>	20.9	-0.7
1 (N=CH(PhNO ₂))	19.6	20.0	<i>4.8</i>	20.0	-0.4
1 (imidazole)	19.3	21.5	<i>5.0</i>	20.1	-0.8
1 (N(COCH ₃)Ph)	15.6	16.1	<i>4.9</i>	20.0	-4.4
1 (N(COCF ₃)Ph)	15.4	15.0	<i>4.8</i>	20.0	-4.5
1 (NO ₂)	15.7	17.0	7.6	21.8	-6.1
1 (N(COPh(NO ₂) ₂)Ph)	14.7	16.0	<i>9.5</i>	23.1	-8.4

^ameasured by EXSY ^1H NMR. ^bB3LYP-D3 / 6-311G* (298.15 K). ^cvalues taken from literature or calculated (*italics*).¹⁶⁵ ^dcalculated from equation 1. ^e $E_{\text{int}} = \Delta G^\ddagger_{\text{exp}} - E_{\text{steric}}$.

The first indications that the rotors could form and measure the nitrogen pnictogen interactions was the large variations in barriers ($\Delta G^\ddagger_{\text{exp}}$) of the nitrogen rotors **1** from 21.3 to 14.7 kcal/mol. Usually, the barriers of molecular rotors correlate with the size of the groups adjacent to the atropisomeric bond. For rotors **1**, the size of the R^1 -groups are relatively similar as the steric interaction are most strongly correlated to the first atom

which is nitrogen for all the rotors. The similarity in size was confirmed by comparison of steric B-value parameters (average B-value = 6.0 ± 1.7 kcal/mol), which is based on the barriers of a similar biphenyl rotor.¹⁶⁵ More importantly, the variations in the size of the R¹-groups do not correlate with the measured rotational barriers (**Figure 3.31**). For example, rotor **1**(N(COPh(NO₂)₂)Ph) has the largest R¹-group (B-value = 9.5 kcal/mol) but the lowest barrier. The **1**(quinoline) rotor with the smallest group (B-value = 4.2 kcal/mol) had the highest barrier.

Molecular modelling provided support for the formation of an intramolecular pnictogen interaction and its role in stabilizing the TS structures. We have previously demonstrated that the experimental barriers of the *N*-phenylimide rotors can be accurately calculated even at a modest level of theory (B3LYP-D3/6-311G*).^{1,4} For rotors **1**, the calculated barriers were within ± 1.1 kcal/mol of the experimental barriers (**Table 3.1**). This suggests that the calculated ground state and transition state structures were accurate. Examples are shown in **Figure 3.2** of the TS structures of **1**(NO₂) and **1**(N(CH₃)₂), which highlights the geometry of the interacting C=O imide and the nitrogen of the R¹-groups. The oxygen-nitrogen distances for all the rotors in **Table 3.1** were significantly below the sum of the van der Waals radii (3.07 Å). For example, the C=O oxygen and NO₂ nitrogen of **1**(NO₂) was 2.426 Å. This distance is shorter than typical C=O...NO₂ interactions (2.642 to 2.825 Å) from X-ray and theoretical studies.^{145,160,168}

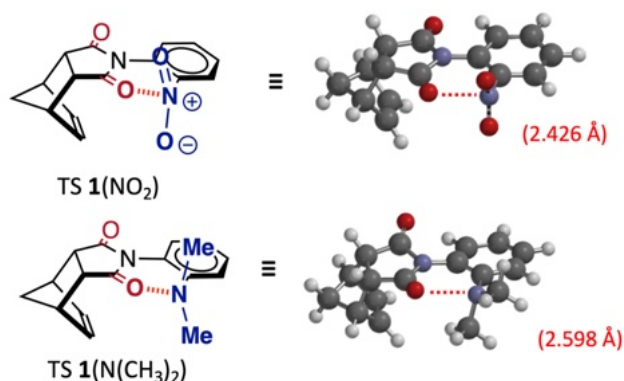


Figure 3.2 Transition state structures (B3LYP-D3/6-311G**) of rotors **1**(NO₂) and **1**(N(CH₃)₂) highlighting the C=O...N interactions and distances.

Next, the pnictogen interaction energies (E_{int}) were assessed. The rotors form minimal steric and non-covalent interactions in the ground states. Thus, the variations in $\Delta G_{\text{exp}}^{\ddagger}$ are due primarily to the interactions in the transition states, and E_{int} can be isolated by subtracting the steric energies (E_{steric}) from the rotational barrier ($E_{\text{int}} = \Delta G_{\text{exp}}^{\ddagger} - E_{\text{steric}}$). We have previously measured E_{steric} in the *N*-phenylimide rotors with R¹-groups (R¹ = CH₃, CH₂CH₃, CH(CH₃)₂, OCH₃, SCH₃, Cl, Br, I, CF₃) that only form steric interactions.^{1,4} The $\Delta G_{\text{exp}}^{\ddagger}$ values of steric rotors showed a good correlation ($R^2 = 0.87$) with Mazzanti's steric parameter (*B*-value).¹⁶⁵ From the trendline, we developed an empirical model for E_{steric} using the *B*-value of the R¹-groups. Equation 1 was used to estimate the E_{steric} for rotors **1**, and in turn, used to find the pnictogen interaction energies, E_{int} (**Table 3.1**).

$$E_{\text{steric}} = 0.677 \times B\text{-value} + 16.7 \quad (\text{eq 3.1})$$

The E_{int} values varied in strength from slightly destabilizing (1.8 kcal/mol) for **1**(quinoline) to strongly stabilizing (-6.1, and -8.4 kcal/mol) for **1**(NO₂) and **1**(N(COPh(NO₂)₂)Ph). The stability trends appeared to correlate to the electrostatic charge of the R¹-group nitrogen. For example, the strongest pnictogen interactions have electron withdrawing groups on the nitrogen such as C=O or electron poor nitrogen such as the NO₂

group in **1**(NO₂). This is consistent with the pnictogen interaction where the electrostatically positive region of the pnictogen atom interacts with the electrostatically negative lone pairs of the imide C=O oxygen.

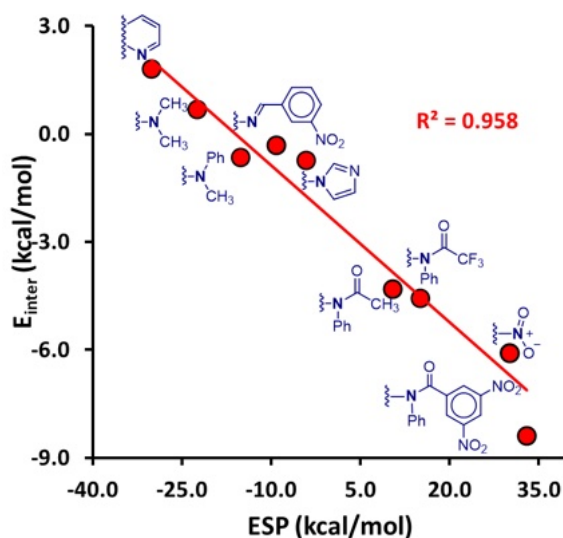


Figure 3.3 Plot of electrostatic surface potentials (ESP, ω B97M-V/6-311+G*) versus the experimentally measured attractive TS interaction energies (E_{int}) for rotors **1**.¹

Qualitative analysis of the electrostatic trends for the C=O...N interactions in the rotors was performed by calculating the electrostatic surface potentials (ESP) of the nitrogen atoms in the R¹-groups at the ω B97M-V/6-311+G* level of theory (see SI). The ESP values showed a strong correlation with E_{int} (**Figure 3.3**, $R^2 = 0.958$). As the ESP value becomes more positive, E_{int} increases linearly. The linear correlation spans a wide range of functional groups (amines, imide, heterocycles, amide) and geometries. For example in **1**(quinoline), the nitrogen is trigonal planar and in the same plane as the cyclic imide ring. In **1**(N(CH₃)₂), the nitrogen is tetrahedral. Finally, in the remaining rotors, the nitrogen is trigonal planar and perpendicular to the cyclic imide. The strong correlation of E_{int} with ESP across the wide range of structures and functional groups suggests that the interaction is primarily electrostatic in nature.

Many pnictogen interactions have a significant orbital-orbital contributions especially with the larger more polarizable members of group 5A elements.¹³⁸ Therefore, we examined the orbital component of the interactions in rotors **1**. The second order perturbation theory analysis of the natural bond orbitals (NBO) were calculated for the C=O...N TS interactions (ω B97M-V/6-311+G*). The E_{int} values were correlated with the NBO perturbation energies as shown in **Figure 3.4**. The NBO interaction energies for rotors **1** were all low (< -5.0 kcal/mol). For example, **1**(N(COPh(NO₂)₂)Ph), which had the strongest interaction, had energies of 0.0 kcal/mol. Only **1**(NO₂) had a small orbital interaction of -4.3 kcal/mol. By comparison rotors which form C=O...C=O interactions which are known to have significant $n \rightarrow \pi^*$ interactions¹⁶⁹ had energies of -16.0 to -18.1 kcal/mol in the *N*-phenylimide rotors.³² Note, the NBO analyses were calculated in the gas phase and, thus, the interaction energies are typically much larger than the experimental interaction energies.

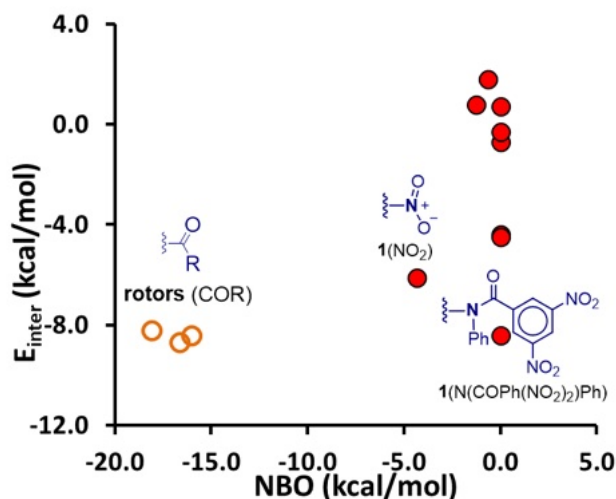


Figure 3.4 Plot of second order perturbation theory analysis of natural bond orbitals (ω B97M-V/6-311+G*) versus E_{int} for rotors **1** (filled red circles) and previously described rotors that form C=O...C=O interactions (open orange circles).

Additional evidence for the absence or weak orbital component was provided by an examination of the geometries of the nitrogens in the TS structures. Strong orbital-orbital interactions lead to a change in the geometry from trigonal planar to pyramidal.^{169,170} For example, $\text{C}=\text{O}\cdots\text{C}=\text{O}$ interactions showed significant pyramidalization ($\Theta = 11.0^\circ$ to 13.0°) in the transition state structures.¹ By comparison, the nitrogen rotors **1** ($\Theta = 4.1^\circ$ to 7.2°) had much smaller degrees of pyramidalization, which was indicative of a weak or minor orbital-orbital interaction.

Using the *N*-phenylimide rotors to study the $\text{C}=\text{O}\cdots\text{N}$ interactions enabled comparison of the magnitude of the pnictogen interaction energies with previously measured non-covalent interactions. Specifically, we have used rotors to study $\text{C}=\text{O}\cdots\text{C}=\text{O}$, $\text{C}=\text{O}\cdots\text{CN}$, and $\text{C}=\text{O}\cdots\pi(\text{aromatic})$ interactions (**Figure 3.5**, blue boxes).^{1,4} The pnictogen interactions in this study spanned a wide range of interaction energies (Figure 5, red boxes), depending on the number and strength of electron withdrawing groups attached to the nitrogen. The strongest pnictogen interactions (-8.4 kcal/mol) were as strong as the $\text{C}=\text{O}\cdots\text{C}=\text{O}$ interactions (-8.2 to -8.7 kcal/mol). The weakest pnictogen interactions were of similar strength to the $\text{C}=\text{O}\cdots\pi(\text{aromatic})$ interactions (-0.3 to -4.5).

The pnictogen interactions of nitro-groups has been recently identified as potentially new non-covalent interaction from gas phase, crystal structure and computational studies.^{155,157,160,168} This study confirms that the nitro-group can form stabilizing interactions in solution where the nitrogen interacts with electrostatically negative groups. However, the nitro-group is not a unique pnictogen bond donor. As seen by Figure 5, the nitro-group falls within the continuum of pnictogen bond donors and are similar in strength to amides with strong electron withdrawing groups.

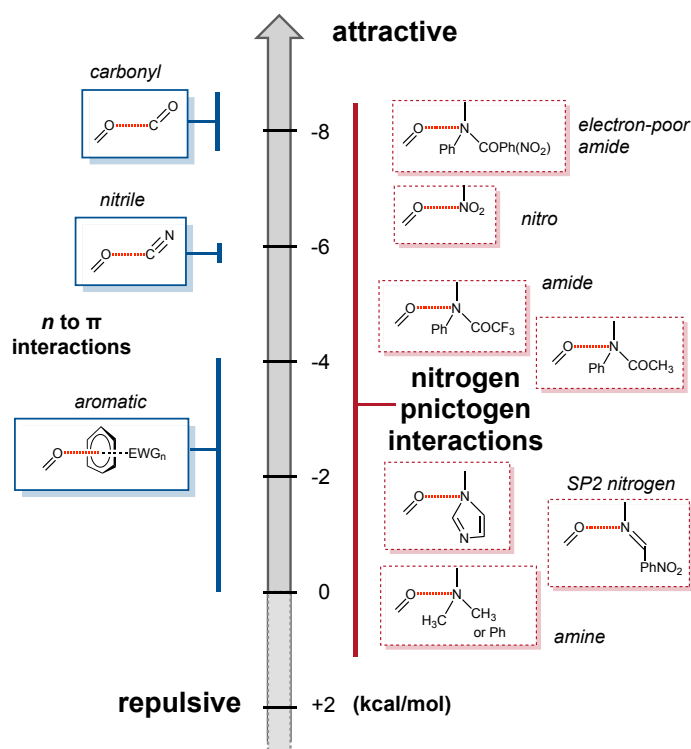


Figure 3.5 Comparison of the relative strengths of the C=O...N nitrogen pnictogen interactions in rotors **1** (red boxes) with the previously studied C=O...C=O, C=O...C $\equiv$ N, and C=O...phenyl interactions (blue boxes).

3.4 Conclusion

In summary, nitrogen pnictogen interactions were formed and measured in solution using a series of molecular rotors. The intramolecular C=O...N interactions in the bond rotation TS lowered the rotational barriers by up to 8 kcal/mol. The ability of common nitrogen containing groups such as NO₂ and amides groups to form pnictogen interactions suggests that the interaction may be present in many systems. The nitrogen pnictogen bond varied widely in strength from slightly destabilizing to strongly stabilizing. Unlike the interactions of the larger pnictogens, the nitrogen interactions are dominated by electrostatics. Thus, ESP and other electrostatic parameters such as Hunter's α and β hydrogen bonding parameters can accurately predict the stability trends.¹⁷¹ The small or

negligible orbital component was somewhat surprising but is consistent with the observed reactivity trends for nitrogen containing functional groups. For example, the nitrogen of NO₂ groups and imines rarely react and form bonds with nucleophiles.¹⁷² The TS interaction energies measured using the molecular rotors are higher than observed in bimolecular systems due to the short distances enforced by the rigid molecular framework and the removal of the steric components of the interactions. Finally, the nitrogen pnictogen interaction has potential in catalysis, as the rotors demonstrate that the interaction can stabilize transition states and affect significant rate enhancements.

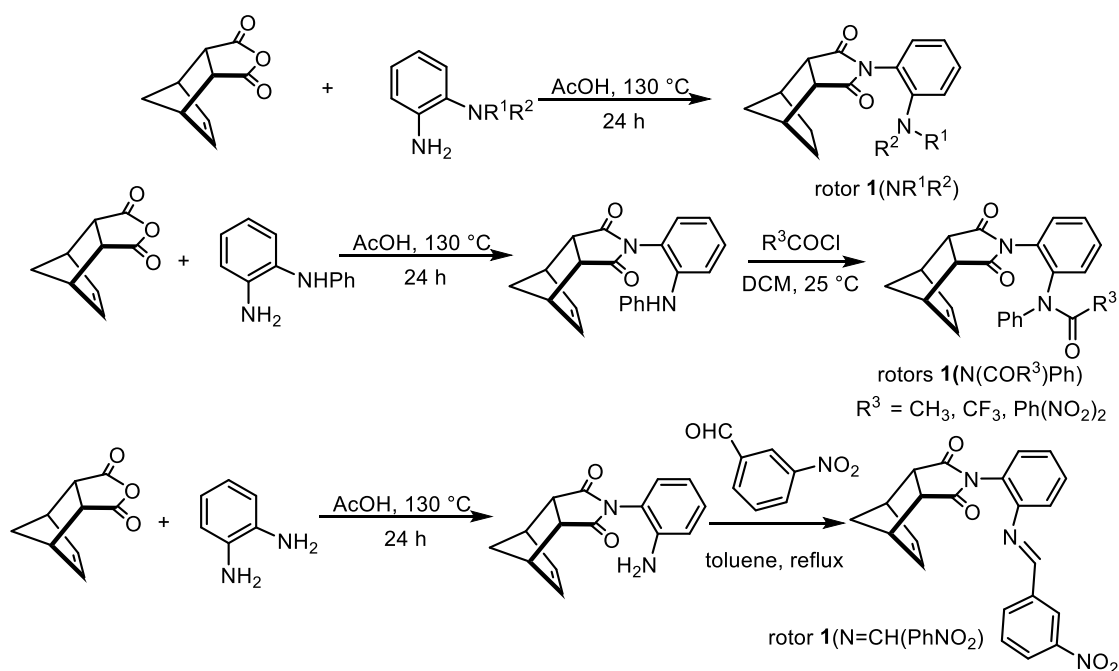
3.5 Supporting information

3.5.1 General experimental procedures

NMR spectra were recorded on a Bruker 400 MHz spectrometer at 25 °C using chloroform-d. Chemical shifts are reported in ppm (δ) and were referenced to residual solvent peaks, ¹H NMR (400 MHz, chloroform-d) δ 7.26 ppm, ¹³C NMR (100 MHz, chloroform-d) δ 77.16 ppm. Chemicals and solvents were purchased from commercial suppliers and used as received. Flash chromatography was performed using silica gel from Sorbent Technologies (60 Å, 200 – 400 mesh). HRMS were measured using a magnetic sector spectrometer (VG 70S) using EI sources.

3.5.2 Synthesis of the molecular rotors

The rotors **1** were prepared via a thermal condensation between an *ortho*-substituted aniline and norbornene anhydride (**Scheme 3.2**), being modified the reports.^{1,4,173,174}



Scheme 3.2 General synthetic route to molecular rotors **1**.

Rotor **1(NO₂)** ((3*aR*,4*S*,7*R*,7*aS*)-2-(2-nitrophenyl)-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoisoindole-1,3(2*H*)-dione): The reactants *cis*-5-norbornene-endo-2,3-dicarboxylic anhydride (82 mg, 0.5 mmol) and 2-nitroaniline (83 mg, 0.6 mmol) and 3 mL AcOH were added to a heavy glass wall pressure vessel. The tube was sealed and heated to 130 °C for 24 hours. After letting the tube cool to room temperature, 50 mL EtOAc and 50 mL water was added to the reaction mixture. The organic layer was separated, and the solvent was removed under reduced pressure. The crude material was purified by column chromatography (hexanes/EtOAc = 10:1 to 2:1, v/v) to give **1(NO₂)** as a colorless solid (130 mg, 92%). ¹H NMR (400 MHz, chloroform-*d*) δ 8.13 (d, *J* = 8.1 Hz, 1H, *major*), 7.98 (d, *J* = 7.1 Hz, 1H, *minor*), 7.69 (t, *J* = 7.7 Hz, 1H, *major* and *minor*), 7.56 (t, *J* = 7.9 Hz, 1H, *major* and *minor*), 7.29 (d, *J* = 7.7 Hz, 1H, *minor*), 7.17 (d, *J* = 7.9 Hz, 1H, *major*), 6.36 (s, 2H, *minor*), 6.29 (s, 2H, *major*), 3.52 (d, *J* = 3.8 Hz, 4H, *major* and *minor*), 1.81

(d, $J = 8.7$ Hz, 1H, *major* and *minor*), 1.64 (d, $J = 8.7$ Hz, 1H, *major* and *minor*). ^{13}C NMR (100 MHz, chloroform- d) δ 175.9, 145.5, 134.8, 134.2, 130.3, 130.0, 126.0, 125.8, 52.9, 52.6, 47.2, 46.4, 45.6. HRMS (EI) m/z calculated for $[\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_4]^+$ (M^+): calculated 284.0797; observed 284.0804.

Rotor **1(N(CH₃)₂)** ((3*aR*,4*S*,7*R*,7*aS*)-2-(2-(dimethylamino)phenyl)-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoisoindole-1,3(2*H*)-dione): The reactants *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride (82 mg, 0.5 mmol) and *N*^{*l*},*N*^{*l*}-dimethylbenzene-1,2-diamine (82 mg, 0.6 mmol) and 3 mL AcOH were added to a heavy walled pressure vessel. The tube was then sealed and heated to 130 °C for 24 hours. After letting the tube cool to room temperature, 50 mL EtOAc and 50 mL water was added to the reaction mixture. The organic layer was separated, and the solvent was removed under reduced pressure. The crude material was purified by column chromatography (hexanes/EtOAc = 10:1 to 2:1, v/v) to give **1(N(CH₃)₂)** as a colorless solid (85 mg, 60%). ^1H NMR (400 MHz, chloroform- d) δ 7.38-7.29 (m, 2H, *major*) and 6.81 (d, $J = 7.7$ Hz, 2H, *minor*), 7.16-7.12 (m, 1H, *major* and *minor*), 7.06-6.97 (m, 1H, *major* and *minor*), 6.28 (s, 2H, *major*), 6.23 (s, 2H, *minor*), 3.48- 3.39 (m, 4H, *major* and *minor*), 2.63 (s, 6H, *major*), 2.51 (s, 6 H, *minor*), 1.78 (d, $J = 8.7$ Hz, 1 H, *major* and *minor*), 1.60 (d, $J = 8.7$ Hz, 1 H, *major* and *minor*). ^{13}C NMR (100 MHz, chloroform- d) δ 177.3, 176.9, 151.3, 134.8, 134.7, 130.4, 130.3, 129.5, 129.4, 125.6, 125.1, 122.7, 122.66, 120.3, 52.8, 52.5, 47.0, 46.1, 45.8, 45.5, 45.3, 44.0. HRMS (EI) m/z calculated for $[\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_2]^+$ (M^+): calculated 282.1368; observed 282.1369.

Rotor **1(N(CH₃)Ph)** (3*aR*,4*S*,7*R*,7*aS*)-2-(2-(methyl(phenyl)amino)phenyl)-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoisoindole-1,3(2*H*)-dione: The reactants *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride (82 mg, 0.5 mmol) and *N*^{*l*}-methyl-*N*^{*l*}-

phenylbenzene-1,2-diamine (100 mg, 0.6 mmol) and 3 mL AcOH were added to a heavy walled pressure vessel. The tube was then sealed and heated to 130 °C for 24 hours. After letting the tube cool to room temperature, 50 mL EtOAc and 50 mL water was added to the reaction mixture. The organic layer was separated, and the solvent was removed under reduced pressure. The crude material was recrystallized from MeOH to give **1(N(CH₃)Ph)** as colorless crystals (50 mg, 61%). ¹H NMR (400 MHz, chloroform-d) δ 7.51-7.31 (m, 2H, *major* and *minor*), 7.26-7.12 (m, 4H, *major*), 6.94 (d, *J* = 1.5 Hz, *J* = 7.9 Hz, 2 H, *minor*), 6.71 (t, *J* = 7.1 Hz, 2 H, *major*), 6.65 (t, *J* = 7.5 Hz, 2 H, *major*), 6.64 (d, *J* = 7.9 Hz, 2 H, *major*), 6.46 (d, *J* = 7.9 Hz, 2 H, *minor*), 6.17 (t, *J* = 1.7 Hz, 2H, *minor*), 5.37 (s, 2H, *major*), 3.34-3.12 (m, 7 H, *major*), 2.78 (dd, *J* = 1.5 Hz, *J* = 3.0 Hz, 1 H, *minor*), 1.65 (d, *J* = 9.0 Hz, 1 H, *major*), 1.60 (d, *J* = 9.0 Hz, 1 H, *minor*), 1.47 (d, *J* = 8.9 Hz, 1 H, *minor*), 1.41 (d, *J* = 8.9 Hz, 1 H, *major*). ¹³C NMR (101 MHz, chloroform-d) δ 176.5, 176.3, 149.6, 147.8, 146.3, 145.0, 134.5, 134.3, 131.4, 130.5, 129.7, 129.65, 128.9, 128.8, 127.7, 127.5, 124.7, 119.2, 117.5, 116.0, 113.5, 52.4, 52.1, 46.6, 45.6, 45.1, 44.8, 39.9, 39.5. HRMS (EI) *m/z* calculated for [C₂₂H₂₀N₂O₂]⁺ (M⁺): calculated 344.1525; observed 344.1520.

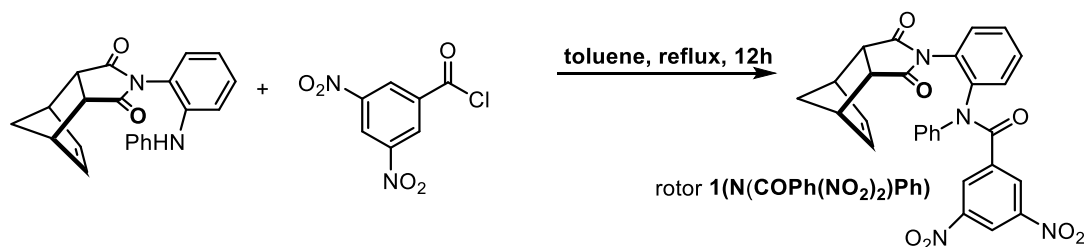
Rotor **1(N(COCH₃)Ph)** (N-(2-((3aR,4S,7R,7aS)-1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-4,7-methanoisindol-2-yl)phenyl)-N-phenylacetamide): The reactants (3aR,4S,7R,7aS)-2-(2-aminophenyl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisindole-1,3(2H)-dione (127 mg, 0.5 mmol) dissolved in 5 mL DCM and acetyl chloride (47 mg, 0.6 mmol) were added dropwise at 25 °C, running for 12 hours.¹ DCM was removed under vacuum. The crude material was purified by column chromatography (hexanes/EtOAc = 10:1 to 2:1, v/v) to give **1(N(COCH₃)Ph)** as a colorless solid (185 mg, quant.). ¹H NMR (400 MHz, chloroform-d) δ 7.51-7.36 (m, 3H, major and minor), 7.26-6.97 (m, 6H, major

and minor), 6.19 (br s, 2H, major and minor), 3.40-2.75 (m, 4H, major and minor), 1.70 (d, J = 8.8 Hz, 1H, major and minor), 1.50 (d, J = 8.8 Hz, 1H, major and minor). ¹H NMR (400 MHz, 1,1,2,2-tetrachloroethane-d₂, at -12 °C) δ 7.57-7.44 (m, 3H, major and minor), 7.27 (t, J = 7.8 Hz, 2 H, major and minor), 7.17 (t, J = 7.4 Hz, 1 H, major and minor), 6.99 (d, J = 7.7 Hz, 2 H, major and minor), 6.94 (d, J = 7.7 Hz, 1 H, major and minor), 6.90 (d, J = 7.7 Hz, 1 H, minor), , 6.20 (s, 2H, minor), 6.16 (s, 2 H, major), 3.37 (br s, 1 H, major and minor), 3.27-3.22 (m, 2H, major and minor), 2.71 (dd, 1H, J = 4.6 Hz, J = 8.0 Hz, minor), 2.15 (s, 3 H, major), 2.04 (s, 3 H, minor), 1.67 (d, J = 8.8 Hz, 1H, major and minor), 1.49 (d, J = 8.8 Hz, 1H, major and minor). ¹³C NMR (100 MHz, chloroform-d) δ 176.0, 175.3, 171.0, 140.9, 140.0, 134.7, 131.1, 130.4, 130.1, 129.3, 128.7, 125.9, 125.3, 52.4, 45.9, 45.2, 23.9. HRMS (EI) m/z calculated for [C₂₃H₂₀N₂O₃]⁺ (M⁺): calculated 372.1474; observed 372.1468.

Rotor **1(N(COCF₃)Ph)** (N-(2-((3aR,4S,7R,7aS)-1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-4,7-methanoisindol-2-yl)phenyl)-2,2,2-trifluoro-N-phenylacetamide):

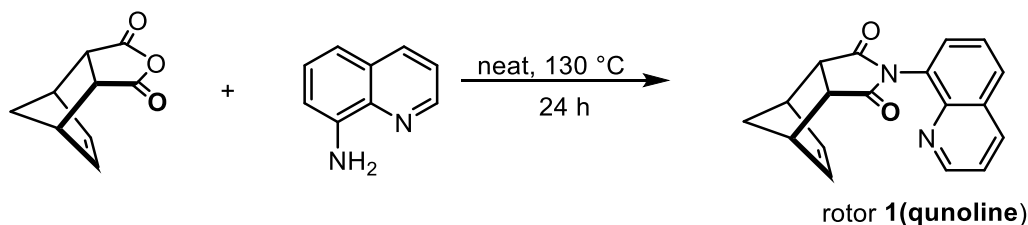
The reactants (3aR,4S,7R,7aS)-2-(2-aminophenyl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisindole-1,3(2H)-dione (127 mg, 0.5 mmol) dissolved in 5 mL DCM and 2,2,2-trifluoroacetic anhydride (126 mg, 0.6 mmol) were added dropwise at 25 °C, running for 12 hours. DCM was removed under vacuum. The crude material was purified by column chromatography (hexanes/EtOAc = 10:1 to 2:1, v/v) to give **1(N(COCF₃)Ph)** as a light green solid (213 mg, quant.). ¹H NMR (400 MHz, chloroform-d) δ 7.56-7.03 (m, 9H, major and minor), 6.27 (br s, 2H, minor), 6.20 (br, 2H, major), 3.46-2.73 (m, 4H, major and minor), 1.76 (br s, 1 H, minor), 1.68 (br s, 1 H, major), 1.60 (br s, 1 H, minor), 1.51 (br s, 1 H, major). ¹H NMR (400 MHz, 1,1,2,2-tetrachloroethane-d₂, at -12 °C) δ 7.57-7.33 (m,

6H, major and minor), 7.29-7.10 (m, 1H, major and minor), 7.06 (d, $J = 7.9$ Hz, 1 H, major and minor), 7.01-6.96 (m, 1H, major and minor), 6.25 (s, 2H, major), 6.17 (t, $J = 8.0$ Hz, 2 H, minor), 3.44-3.21 (m, 4H, major), 2.72 (dd, 4H, $J = 4.7$ Hz, $J = 8.0$ Hz, minor), 1.75 (d, $J = 8.8$ Hz, 1 H, minor), 1.67 (d, $J = 9.0$ Hz, 1 H, major), 1.58 (d, $J = 8.9$ Hz, 1 H, major), 1.48 (d, $J = 8.9$ Hz, 1 H, minor). ^{13}C NMR (100 MHz, chloroform- d) δ 176.0, 139.1 (t, $J = 50.7$ Hz), 134.9, 130.5, 130.0, 129.9, 129.6, 129.1, 128.4, 128.1, 127.4, 125.0, 116.5 (q, $J = 279.7$ Hz), 52.4, 46.1, 45.8, 45.4. HRMS (EI) m/z calculated for $[\text{C}_{23}\text{H}_{17}\text{F}_3\text{N}_2\text{O}_3]^+$ (M^+): calculated 426.1191; observed 426.1183.

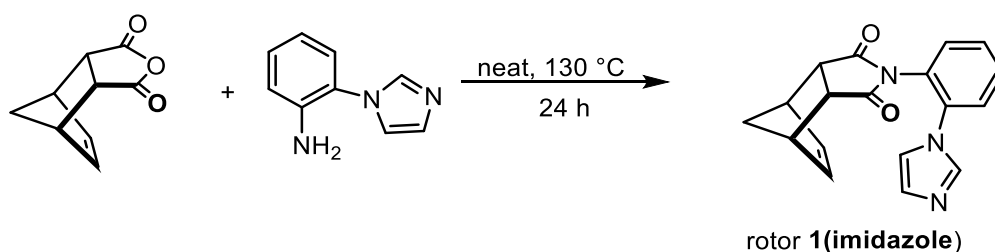


Rotor **1(N(COPh(NO₂)₂)Ph)** (N-(2-((3aR,4S,7R,7aS)-1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-4,7-methanoisindol-2-yl)phenyl)-3,5-dinitro-N-phenylbenzamide): The reactants (3aR,4S,7R,7aS)-2-(2-aminophenyl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisindole-1,3(2H)-dione (138 mg, 0.5 mmol) dissolved and 3,5-dinitrobenzoyl chloride (126 mg, 0.6 mmol) were added into a heavy walled pressure vessel, refluxing in toluene for 12 hours. Toluene was removed under vacuum. The crude material was purified by column chromatography (hexanes/EtOAc = 5:1 to 0:1, v/v) to give **1(N(COPh(NO₂)₂)Ph)** as a light brown solid (100 mg, 40%). ^1H NMR (400 MHz, chloroform- d) δ 9.11-8.56 (m, 3H, major and minor), 7.36-6.91 (m, 9H, major and minor), 6.28 (br, 2H, major and minor), 3.43-2.66 (m, 4H, major and minor), 1.74 (d, $J = 8.9$ Hz, 1 H, major and minor), 1.50 (d, $J = 8.9$ Hz, 1 H, major and minor). ^{13}C NMR (100 MHz,

chloroform-d) δ 176.6, 175.6, 148.2, 140.7, 139.5, 138.8, 134.7, 131.3, 129.9, 129.5, 128.8, 128.2, 127.4, 125.6, 120.3, 52.5, 45.4. HRMS (EI) m/z calculated for $[C_{28}H_{20}N_4O_7]^+$ (H^+): calculated 525.1405; observed 525.1404.



Rotor **1(quinoline)** ((3*aR*,4*S*,7*R*,7*aS*)-2-(quinolin-8-yl)-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoisindole-1,3(2*H*)-dione): The reactants *cis*-5-norbornene-endo-2,3-dicarboxylic anhydride (82 mg, 0.5 mmol) and quinolin-8-amine (86 mg, 0.6 mmol) were added into a heavy walled pressure vessel, running neat at 130 °C for 12 hours. The crude material was purified by column chromatography (hexanes/EtOAc = 5:1 to 2:1, v/v) to give **1(quinoline)** as a light brown solid (140 mg, quant.). 1H NMR (400 MHz, chloroform-*d*) δ 8.88 (dd, J = 1.6 Hz, J = 1.4 Hz, 1 H, *major* and *minor*), 8.18-8.16 (m, 1H, *major* and *minor*), 7.90-7.86 (m, 1H, *major* and *minor*), 7.57 (t, J = 7.6 Hz, 1 H, *major* and *minor*), 7.51-7.39 (m, 2H, *major* and *minor*), 6.44 (s, 2H, *minor*), 6.37 (s, 2H, *major*), 3.66-3.47 (m, 4H, *major* and *minor*), 1.83 (d, J = 8.9 Hz, 1 H, *major* and *minor*), 1.67 (d, J = 8.6 Hz, 1 H, *major* and *minor*). ^{13}C NMR (100 MHz, chloroform-*d*) δ 177.3, 177.1, 150.0, 150.4, 136.2, 135.5, 135.0, 134.8, 130.1, 129.6, 129.5, 129.28, 129.25, 121.9, 121.7, 52.5, 52.0, 46.9, 46.6, 45.46, 45.41. HRMS (EI) m/z calculated for $[C_{18}H_{14}N_2O_2]^+$ (M^+): calculated 290.1049; observed 290.1055.



Rotor **1(imidazole)** ((3*aR*,4*S*,7*R*,7*aS*)-2-(2-(1*H*-imidazol-1-yl)phenyl)-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoisindole-1,3(2*H*)-dione): The reactants *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride (82 mg, 0.5 mmol) and 2-(1*H*-imidazol-1-yl)aniline (96 mg, 0.6 mmol) were added into a heavy walled pressure vessel, running neat for 12 hours. The crude material was purified by column chromatography (hexanes/EtOAc = 5:1 to 2:1, v/v) to give **1(imidazole)** as a colorless solid (145 mg, quant.). ¹H NMR (400 MHz, chloroform-*d*) δ 7.56-7.39 (m, 4H, *major* and *minor*), 7.19-7.07 (m, 1H, *major* and *minor*), 6.94 (br, 1H, *major* and *minor*), 6.25 (t, *J* = 1.7 Hz, 1H, *major*), 5.68 (t, *J* = 1.7 Hz, 1H, *minor*), 3.42-3.24 (m, 4H, *major* and *minor*), 1.74 (d, *J* = 8.9 Hz, 1 H, *major*), 1.67 (d, *J* = 8.9 Hz, 1 H, *minor*), 1.53 (d, *J* = 9.0 Hz, 1 H, *major*), 1.49 (d, *J* = 9.0 Hz, 1 H, *minor*). ¹³C NMR (100 MHz, chloroform-*d*) δ 176.56, 176.52, 138.1, 137.3, 135.8, 135.5, 134.8, 134.5, 130.7, 130.6, 130.5, 130.1, 129.82, 129.80, 129.77, 129.42, 129.21, 129.12, 128.2, 127.5, 121.5, 120.2, 52.9, 52.5, 50.0, 45.90, 45.46, 45.03. HRMS (EI) *m/z* calculated for [C₁₈H₁₅N₃O₂]⁺ (M⁺): calculated 305.1164; observed 305.1170.

Rotor **1(N=CH(PhNO₂))** ((3*aR*,4*S*,7*R*,7*aS*)-2-(2-(((*E*)-3-nitrobenzylidene)amino)phenyl)-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoisindole-1,3(2*H*)-dione): The reactants (3*aR*,4*S*,7*R*,7*aS*)-2-(2-aminophenyl)-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoisindole-1,3(2*H*)-dione (127 mg, 0.5 mmol) dissolved in 5 mL toluene and 3-nitrobenzaldehyde (91 mg, 0.6 mmol) and 1 drop of AcOH were added at room

temperature, refluxing for 12 hours.² Toluene was removed under vacuum, and filtration was performed using MeOH give **1(N=CH(PhNO₂))** as a light-yellow solid (190 mg, quant.). ¹H NMR (400 MHz, chloroform-d) δ 8.75 (s, 1H, minor), 8.67 (s, 1H, major), 8.50 (s, 1H, major), 8.40 (s, 1H, minor), 8.36-8.30 (m, 1H, major and minor), 8.15 (d, J = 7.8 Hz, 1 H, minor), 8.11 (d, J = 7.9 Hz, 1 H, major), 7.69-7.61 (m, 1H, major and minor), 7.46-7.41 (m, 1H, major and minor), 7.34-7.26 (m, 1H, major and minor), 7.17 (d, J = 8.0 Hz, 1 H, major), 7.12 (d, J = 8.0 Hz, 1 H, minor), 7.07 (d, J = 7.8 Hz, 1 H, major), 6.98 (d, J = 7.8 Hz, 1 H, minor), 6.30 (s, 2H, major), 6.00 (s, 2H, minor), 3.47-3.37 (m, 4H, major and minor), 1.78 (d, J = 8.9 Hz, 1 H, major), 1.68 (d, J = 8.9 Hz, 1 H, minor), 1.61 (d, J = 9.0 Hz, 1 H, major), 1.54 (d, J = 9.0 Hz, 1 H, minor). ¹³C NMR (100 MHz, chloroform-d) δ 189.8, 176.7, 176.5, 159.8, 158.8, 149.1, 148.8, 147.3, 134.8, 134.7, 134.6, 134.5, 130.6, 130.5, 130.0, 129.97, 129.4, 128.9, 127.4, 126.1, 125.96, 123.45, 123.42, 118.8, 52.5, 46.8, 46.1, 45.5, 45.0. HRMS (EI) m/z calculated for [C₂₂H₁₇N₃O₄]⁺ (M⁺): calculated 387.1219; observed 387.1226

3.5.3 ¹H and ¹³C NMR spectrum

The ¹H and ¹³C NMR spectrum of new compounds were listed from **Figure 3.6-3.22** as follow:

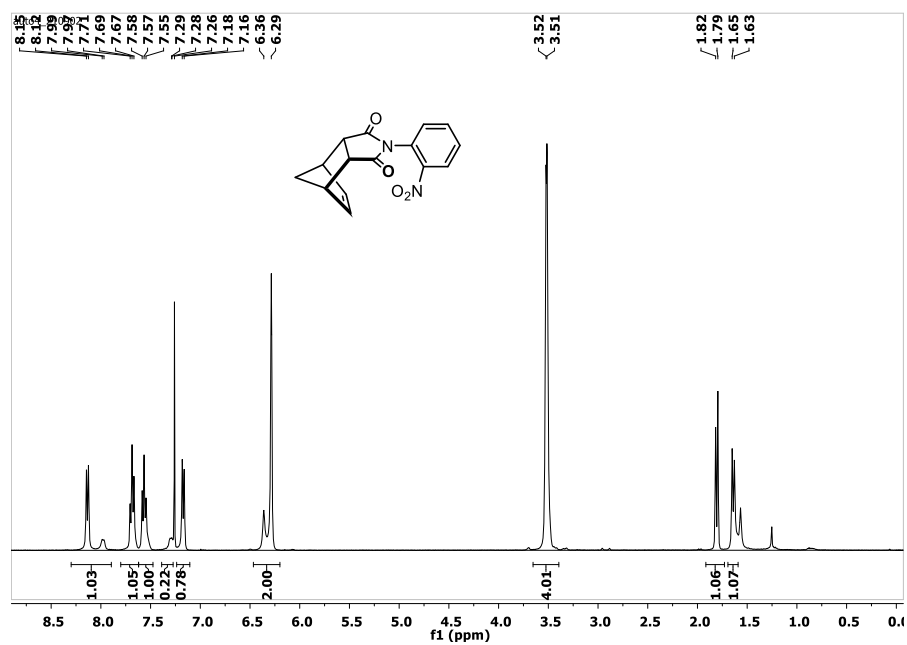


Figure 3.6 ¹H NMR spectra (400 MHz) of rotor 1(NO₂) in CDCl₃.

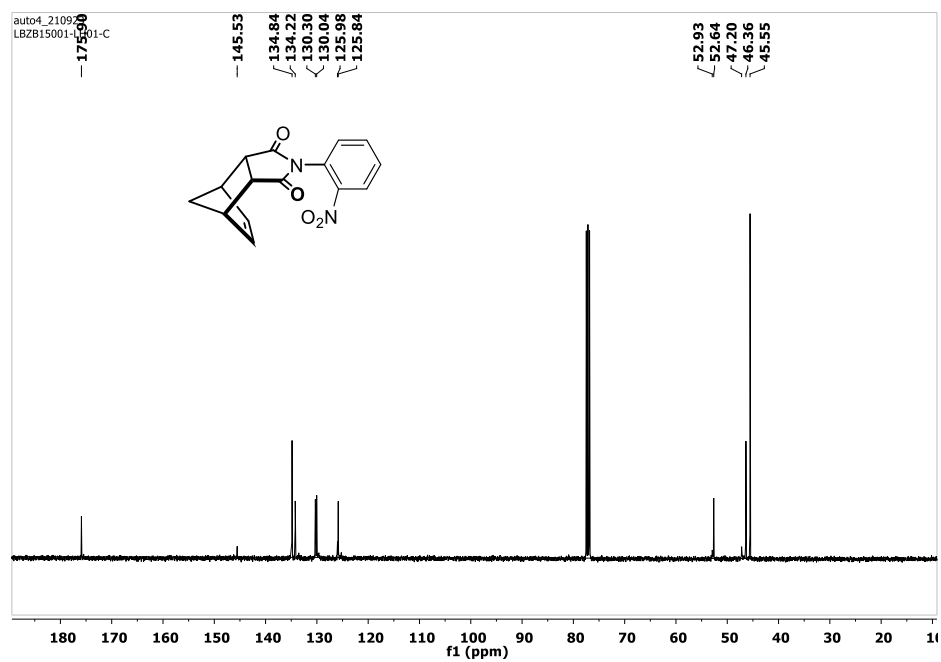


Figure 3.7 ¹³C NMR spectra (100 MHz) of rotor 1(NO₂) in CDCl₃.

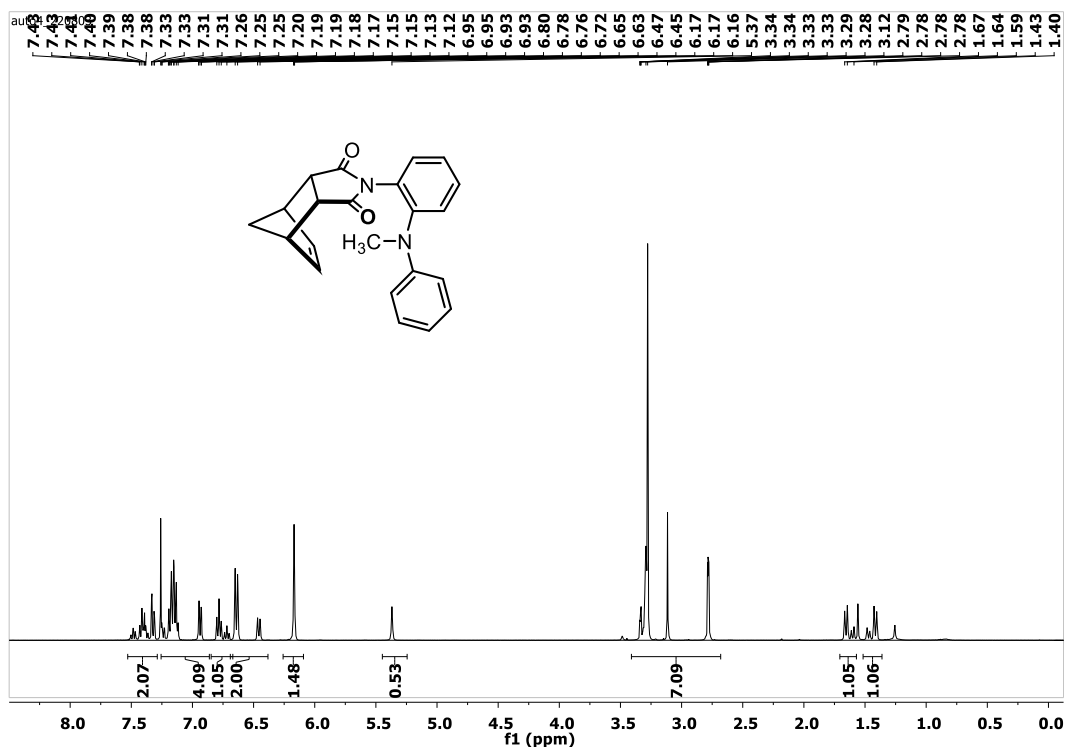


Figure 3.10 ¹H NMR spectra (400 MHz) of rotor 1(N(CH₃)Ph) in CDCl₃.

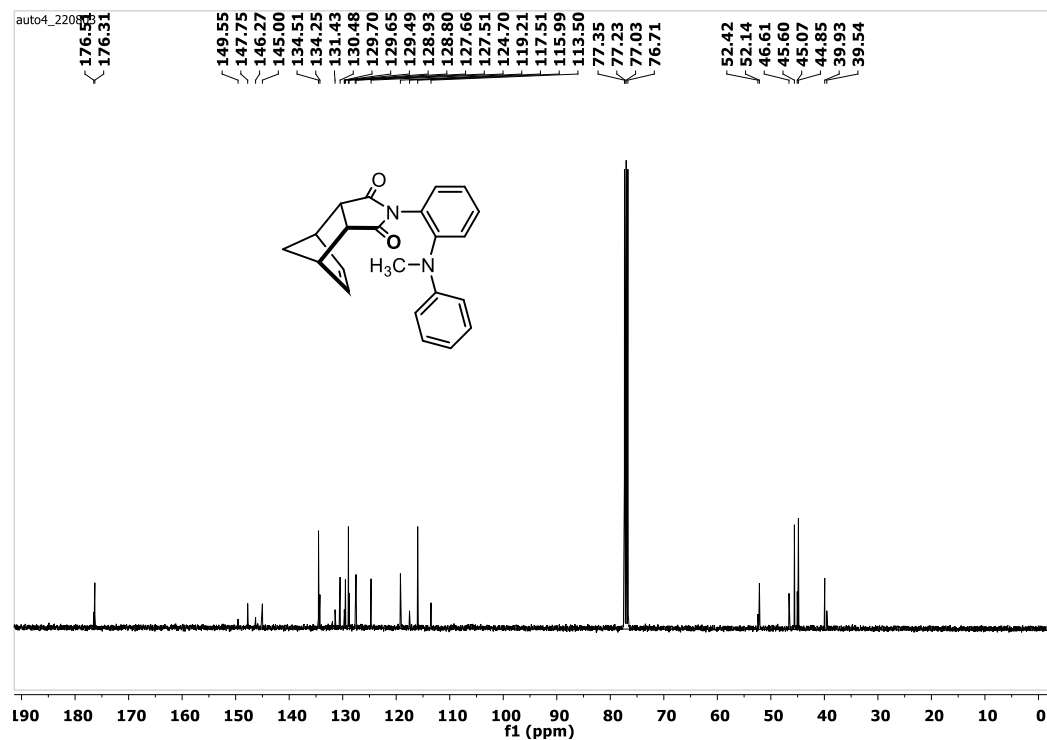
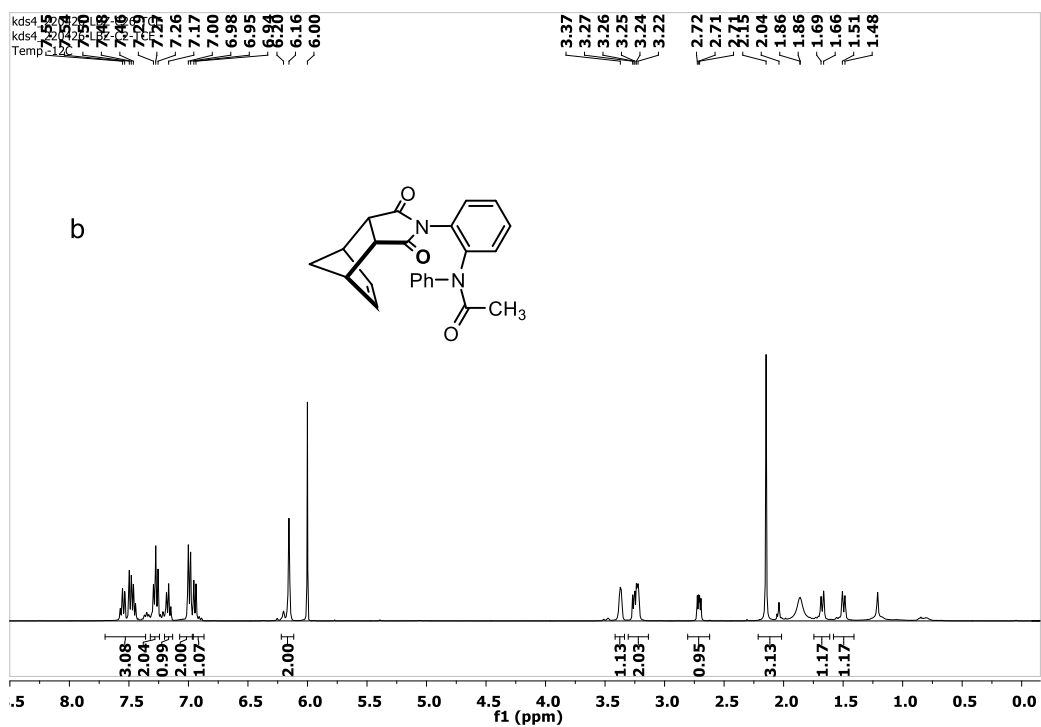
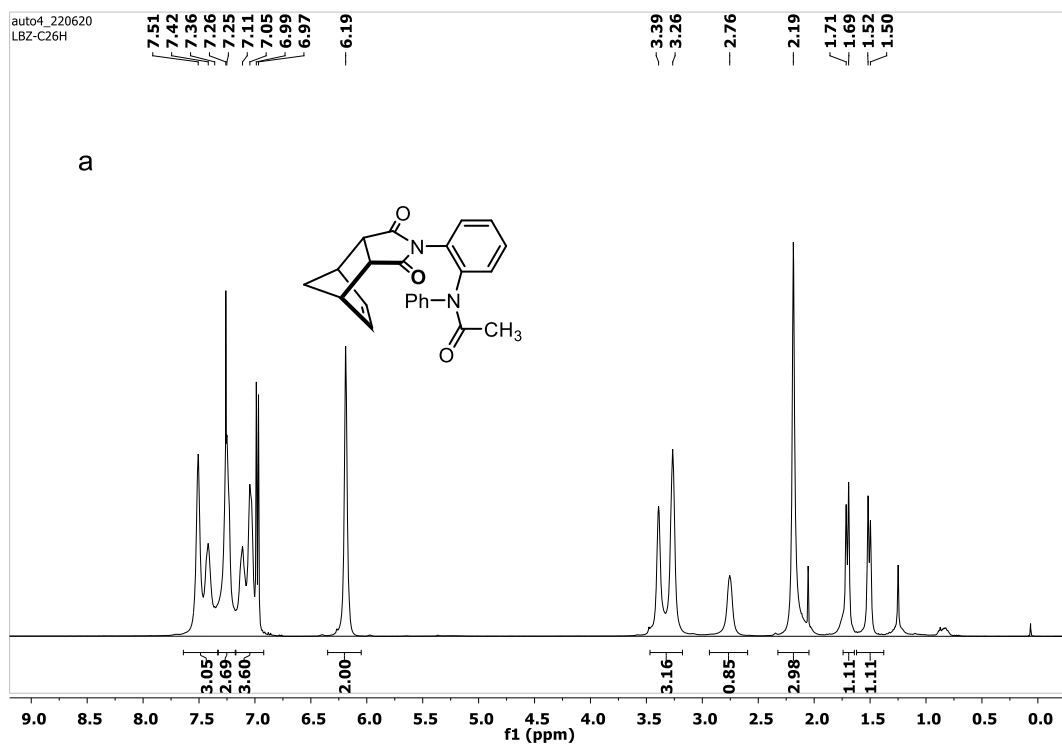


Figure 3.11 ¹³C NMR spectra (100 MHz) of rotor 1(N(CH₃)Ph) in CDCl₃.



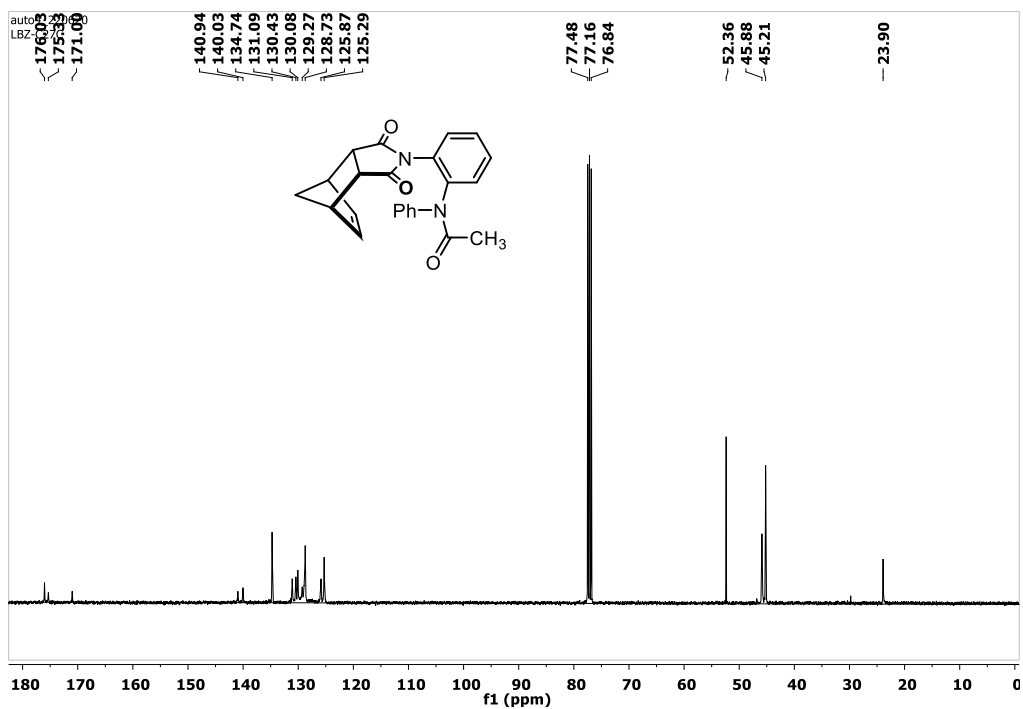
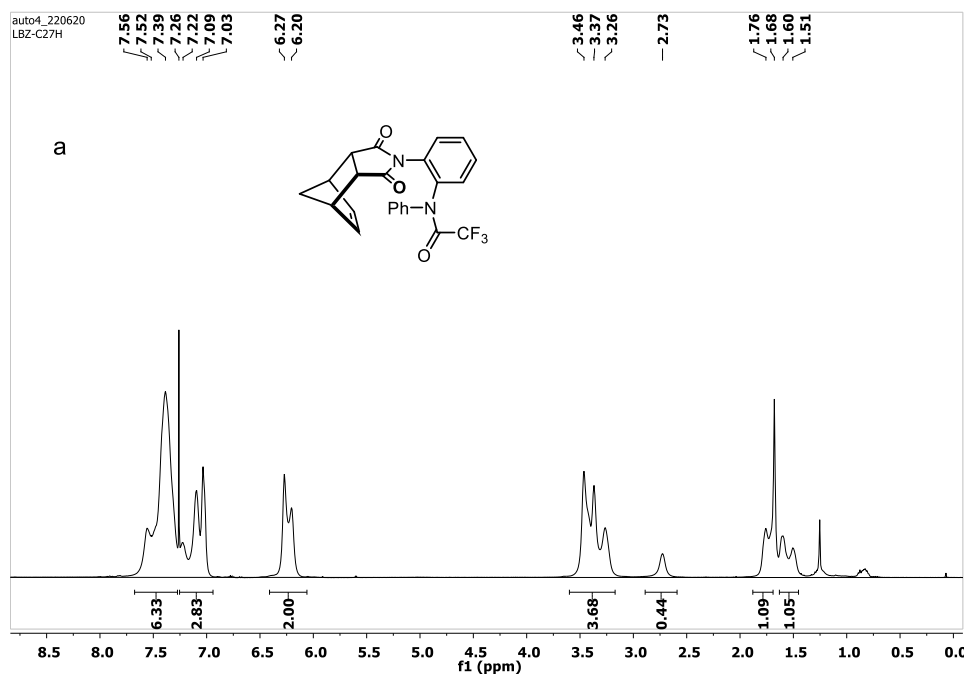


Figure 3.12 a) ^1H NMR spectra (400 MHz) of rotor **1(N(COCH₃)Ph)** in CDCl_3 at 25 °C. **b)** ^1H NMR spectra (400 MHz) of rotor **1(N(COCH₃)Ph)** in TCE-d_2 (solvent residue peak at 6.0 ppm) at -12 °C. **c)** ^{13}C NMR spectra (100 MHz) of rotor **1(N(COCH₃)Ph)** in CDCl_3 .



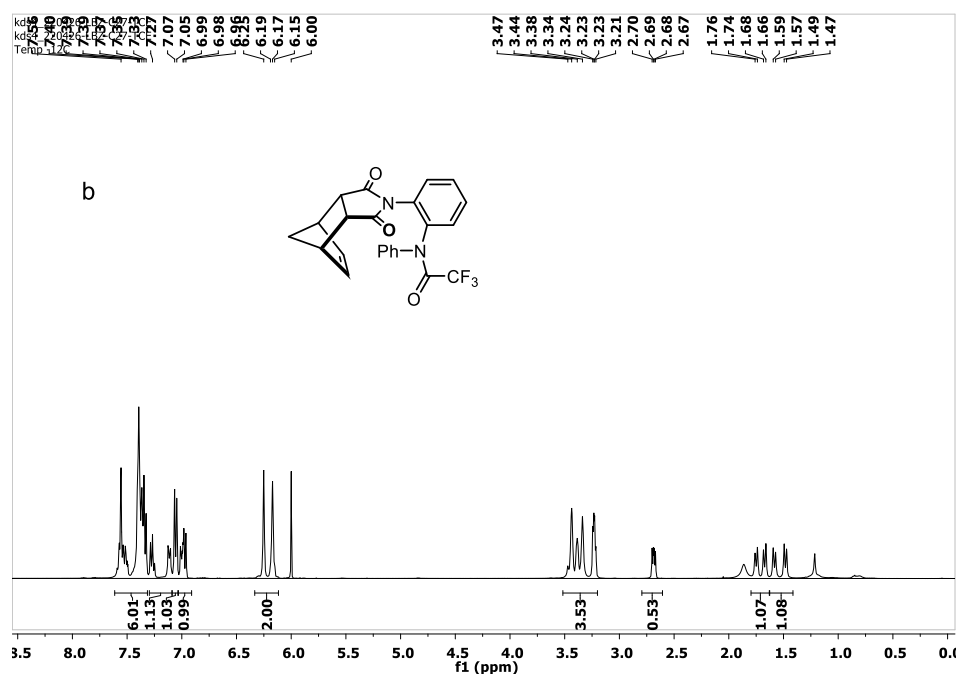


Figure 3.13 a) ^1H NMR spectra (100 MHz) of rotor $1(\text{N}(\text{COCF}_3)\text{Ph})$ in CDCl_3 at 25°C . The peaks are broad due to the slow rotation around the C-N of the amide. b) ^1H NMR spectra (400 MHz) of rotor $1(\text{N}(\text{COCF}_3)\text{Ph})$ in TCE- d_2 (solvent residue peak at 6.0 ppm) at -12°C .

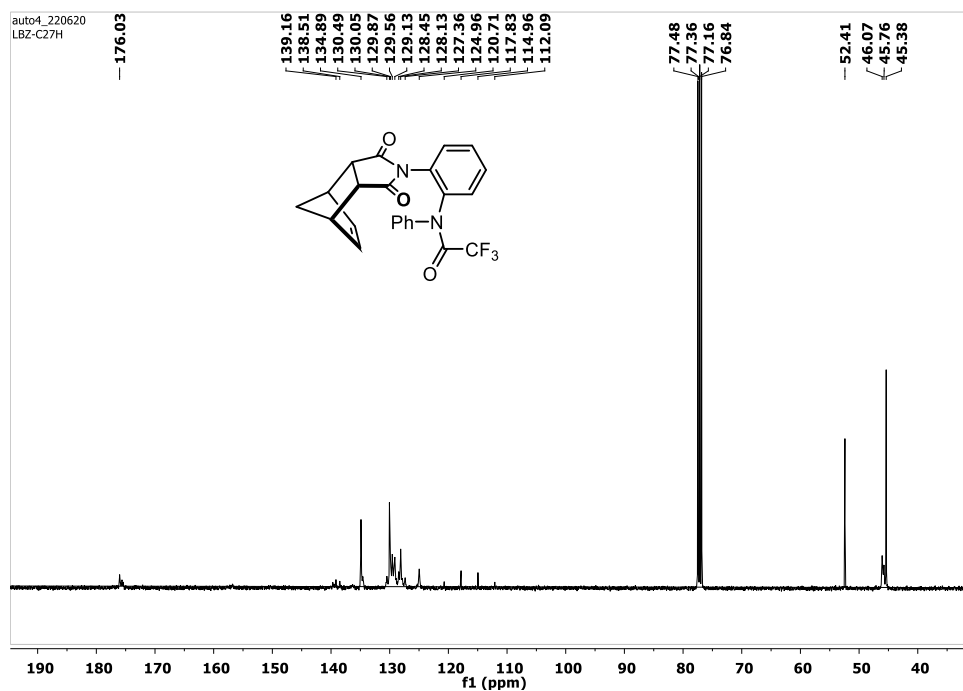


Figure 3.14 ^{13}C NMR spectra (100 MHz) of rotor $1(\text{N}(\text{COCF}_3)\text{Ph})$ in CDCl_3 .

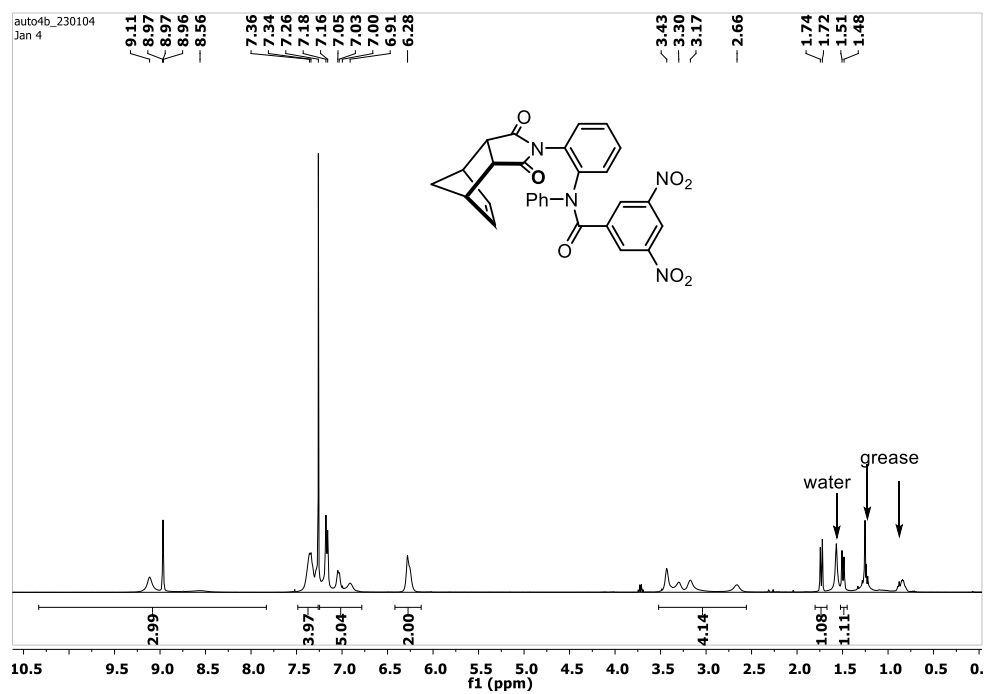


Figure 3.15 ^1H NMR spectra (400 MHz) of rotor **1**($\text{N}(\text{COPh}(\text{NO}_2)_2)\text{Ph}$) in CDCl_3 .

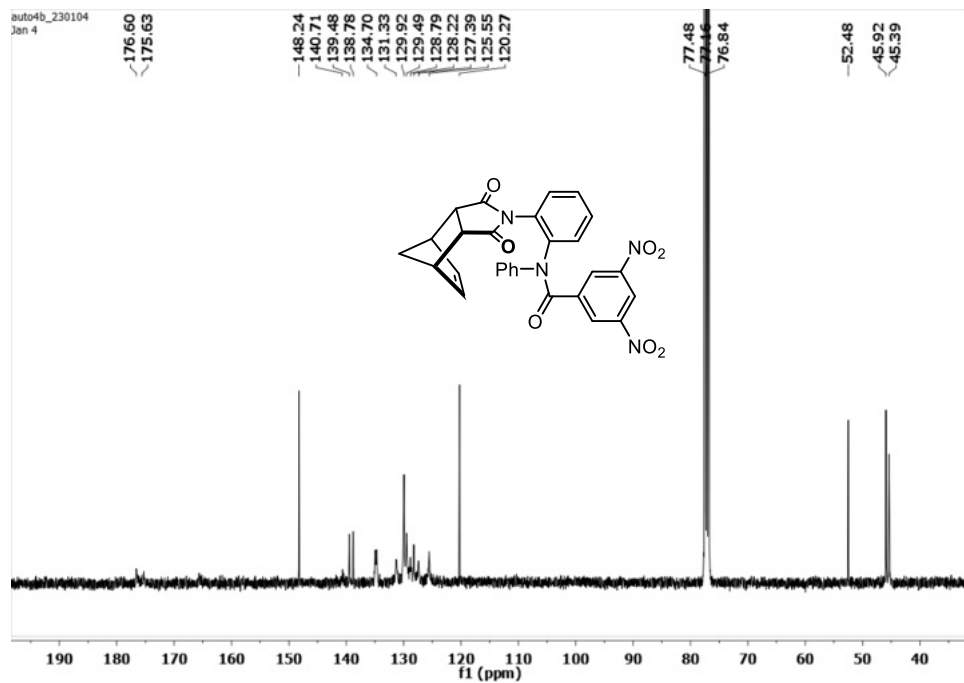
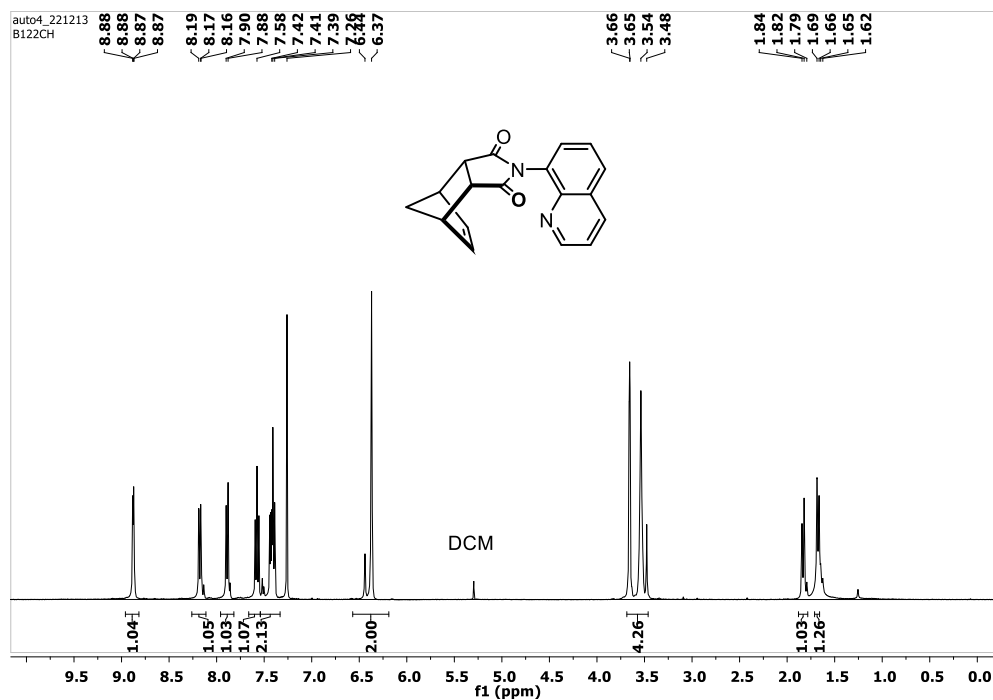


Figure 3.16 ^{13}C NMR spectra (100 MHz) of rotor **1**($\text{N}(\text{COPh}(\text{NO}_2)_2)\text{Ph}$) in CDCl_3 .



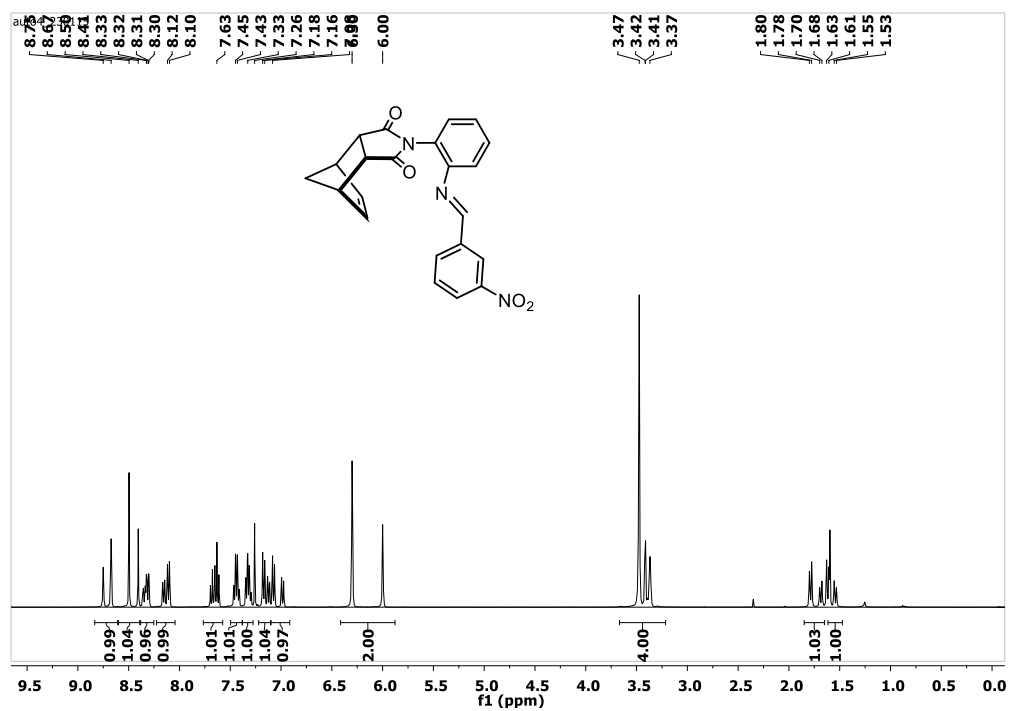


Figure 3.19 ^1H NMR spectra (400 MHz) of rotor **1** ($\text{N}=\text{CH}-(\text{PhNO}_2)$) in CDCl_3 .

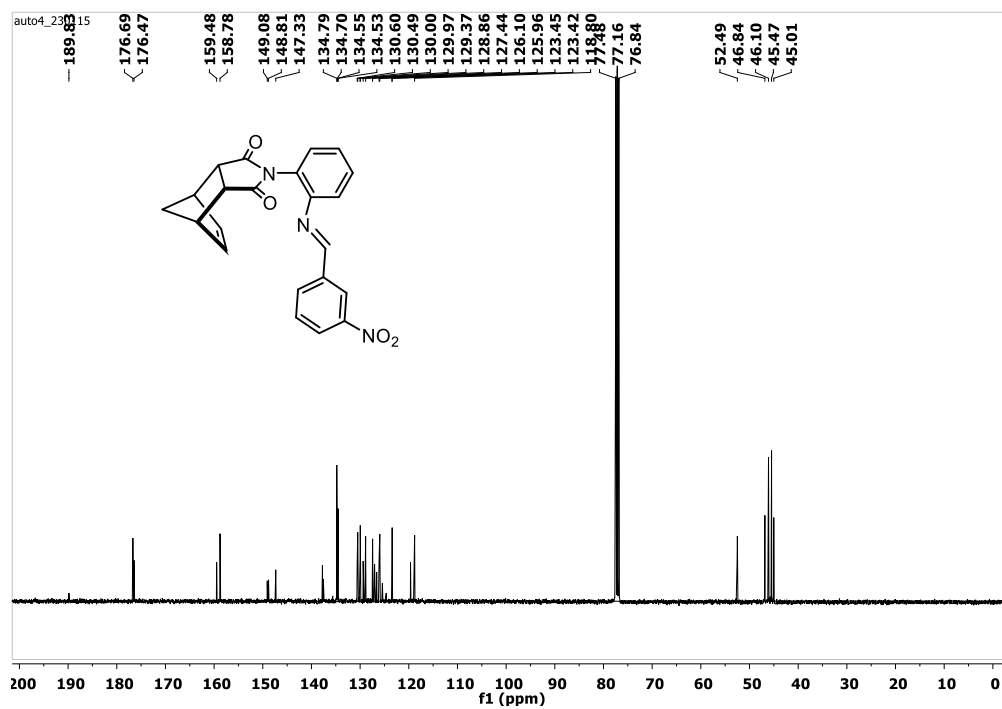


Figure 3.20 ^{13}C NMR spectra (100 MHz) of rotor **1** ($\text{N}=\text{CH}-(\text{PhNO}_2)$) in CDCl_3 .

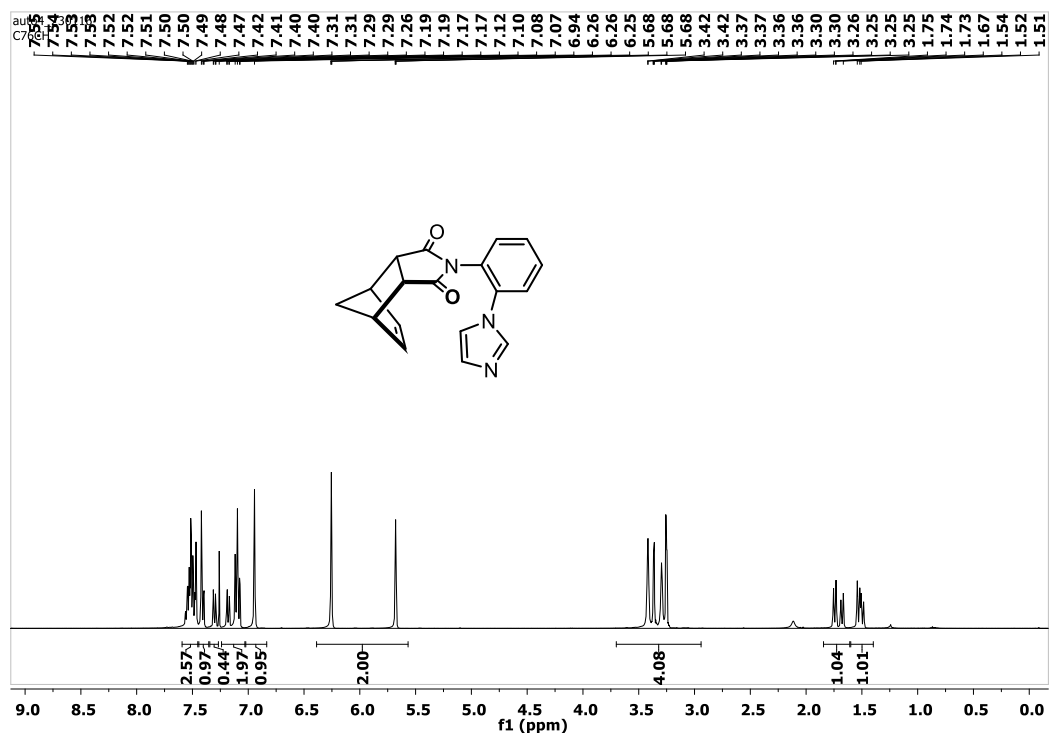


Figure 3.21 ^1H NMR spectra (400 MHz) of rotor **1** (imidazole) in CDCl_3 .

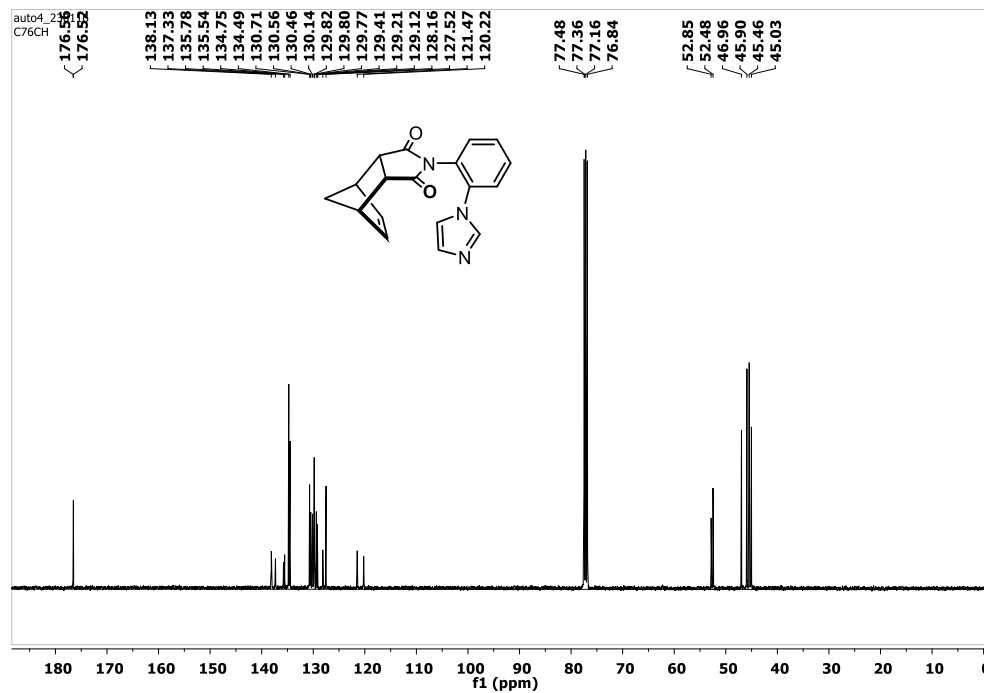
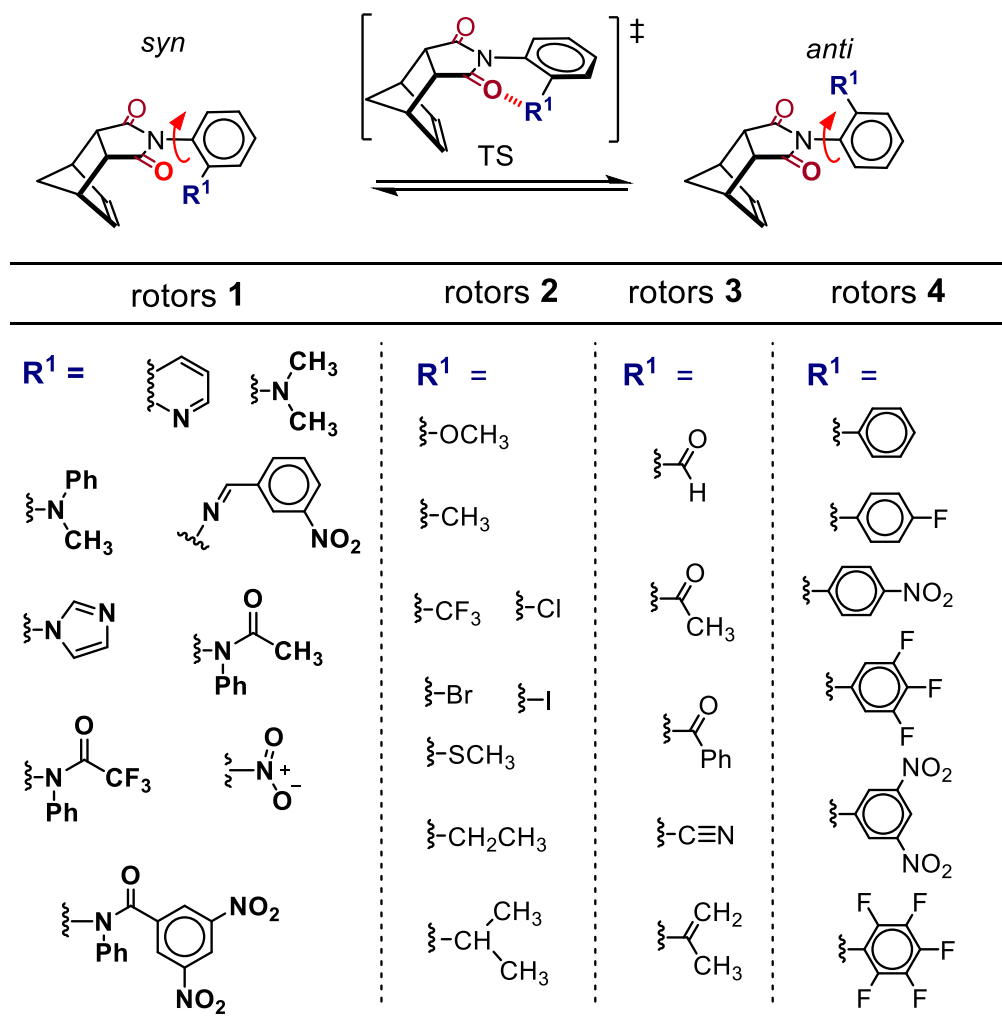


Figure 3.22 ^{13}C NMR spectra (100 MHz) of rotor **1** (imidazole) in CDCl_3 .

3.5.4 Additional Tables and Plots

Rotors **2** were those determined to only have steric interactions in TSs. They were plotted to show the steric trendline using B-values,^{3, 4, 5} which was the steric parameter from Mazzanti, with experimental barriers (**Scheme 3.3**).



Scheme 3.3 Conformational *syn-anti* equilibrium of the *N*-arylimide molecular rotors **1** to **4** (left to right) arising from restricted rotation around the C(aryl)-N(imide) single bond. The rotor numbers (**1-4**) correlated to the type of TS interaction interactions and the R^1 are listed in table form. Rotors **1** form nitrogen pnictogen bond interactions in the bond rotation transition state. Control rotors **2** form varying types of C=O...N interactions. Rotors **2**, **3**, and **4** formed steric, C=O...C=O interactions, and C=O...Ph interactions, respectively.

Rotors 2 kept consistent in the line range to offer a good correlation ($R^2 = 0.87$). Rotors 3 were not further used to discuss the interaction energies, but for the other rotors would have numbers for the interaction energies. Rotors on the line will have 0 interaction energies which means steric effect is dominant. Rotors above the line have extra repulsion with a positive interaction energy, and finally for the rotors below the line do have attractive interaction energies with negative numbers (See **Figure 3.23** and **Table 3.2**).

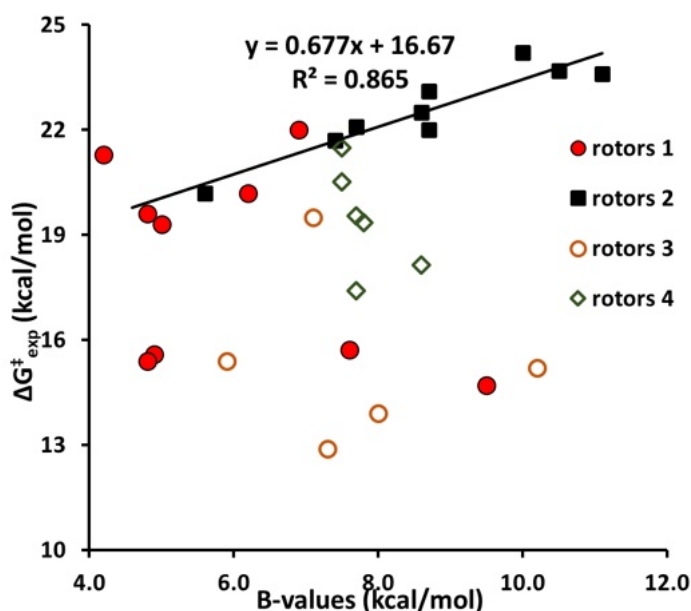


Figure 3.23 Correlation plot of the experimental rotational barriers for rotors versus the steric B-values of the R-groups of the rotors that form C=O...N interactions (**1**, red circles), C=O...R steric interactions (**2**, black squares), C=O...C=O and C=O...C≡N interactions (**3**, orange open circles), and C=O...Ph interactions (**4**, green open diamond

Table 3.2 Experimental barriers, B-values, ESP, calculated barriers, steric predictions, interaction energies and pyramidalization.

Rotors R=	B-value (kcal/mol)	$\Delta G^{\ddagger}_{\text{exp}}$ (kcal/mol)	E_{steric} (kcal/mol)	E_{int} (kcal/mol)	ESP (kcal/mol)	$\Delta G^{\ddagger}_{\text{cal}}$ (kcal/mol)	Θ (deg.)
1(quinoline)	4.2	21.3	19.5	1.8	-30.0	22.5	/
1(N(CH ₃) ₂)	6.9	22.0	21.3	0.7	-22.3	20.6	33.2
1(N(CH ₃)Ph)	6.2	20.2	20.9	-0.7	-15.0	21.5	9.0
1(N=CH-(PhNO ₂))	4.8	19.6	19.9	-0.3	-9.0	20.0	7.4
1(imidazole)	5.0	19.3	20.1	-0.8	-4.0	21.5	4.7
1(N(COCH ₃)Ph)	4.9	15.6	20.0	-4.4	10.5	16.1	4.1
1(N(COCF ₃)Ph)	4.8	15.4	19.9	-4.5	15.3	15.0	7.2
1(NO ₂)	7.6	15.7	21.8	-6.1	30.3	17.0	7.2
1(N(COPh(NO ₂) ₂)Ph)	9.5	14.7	23.1	-8.4	33.0	16.0	11.9
3(C(CH ₂)CH ₃)	7.1	19.5	21.5	-2.0	2.5	19.5	9.4
3(CN)	5.9	15.4	20.7	-5.3	15.0	16.7	15.4
3(CHO)	10.2	15.2	23.6	-8.4	26.5	16.2	11.0
3(COCH ₃)	8.0	13.9	22.1	-8.2	23.8	15.6	13.0
3(COPh)	7.3	12.9	21.6	-8.7	17.5	15.1	11.3
4(Ph)	7.5	21.5	21.8	-0.3	-2.8	20.9	7.3
4(PhF)	7.5	20.5	21.8	-1.2	0.8	20.8	7.1
4(PhF ₃)	7.7	19.5	21.9	-2.3	8.8	19.8	6.9
4(PhF ₅)	7.7	17.4	21.9	-4.5	16.0	16.9	5.8
4(PhNO ₂)	7.8	19.3	22.0	-2.6	10.0	19.4	7.9
4(Ph(NO ₂) ₂)	8.6	18.1	22.5	-4.4	21.2	17.8	6.8

^aExperimental barriers were measured via EXSY, details are provided in Section 3.5.5. ^bB-values were the steric parameters for the R-groups from the literature or calculated.^{1,4,37} The methods of calculating B-values are provided in Section 3.5.7. ^cElectrostatic potential (ESP) were calculated in Spartan18 as described in Section 3.5.10. ^dCalculated barriers (B3LYP-D3/6-311G*) were completed in Spartan18 as described in Section 3.5.6. ^eThe steric values of the R-groups calculated from the B-values using the equation $E_{\text{steric}} = 0.677*(B\text{-value}) + 16.673$. The derivations of this equation are provided in the text of the manuscript. ^fInteraction energies were the attractive component of the interaction of the C=O and R-groups in the transition states based on difference of the experimental barrier and E_{steric} . ^gPyramidalization of the first atom of the R-groups in the TS as were measured by the angle (deg) deviation from the third attached atom from the plane defined by the first atom and two attached atoms.^{1,4}

3.5.5 Experimental measurements of the rotational barriers

The experimental rotational barriers of the rotors were determined via exchange spectroscopy (EXSY) NMR experiments in TCE-d₂. An example of the 2D NOESY spectra is shown in **Figure 3.24**. The integration of the crosspeak and diagonal signals were performed using the Bruker Topspin software, and rate constants were calculated using EXSYCalc. The rotational barrier ($\Delta G^\ddagger_{\text{exp}}$) for each rotor were extrapolated to room temperature for comparison. The TS enthalpy ($\Delta H^\ddagger_{\text{exp}}$) and entropy ($\Delta S^\ddagger_{\text{exp}}$) for rotor were obtained using Eyring plots (**Figures 3.25– 3.29**).

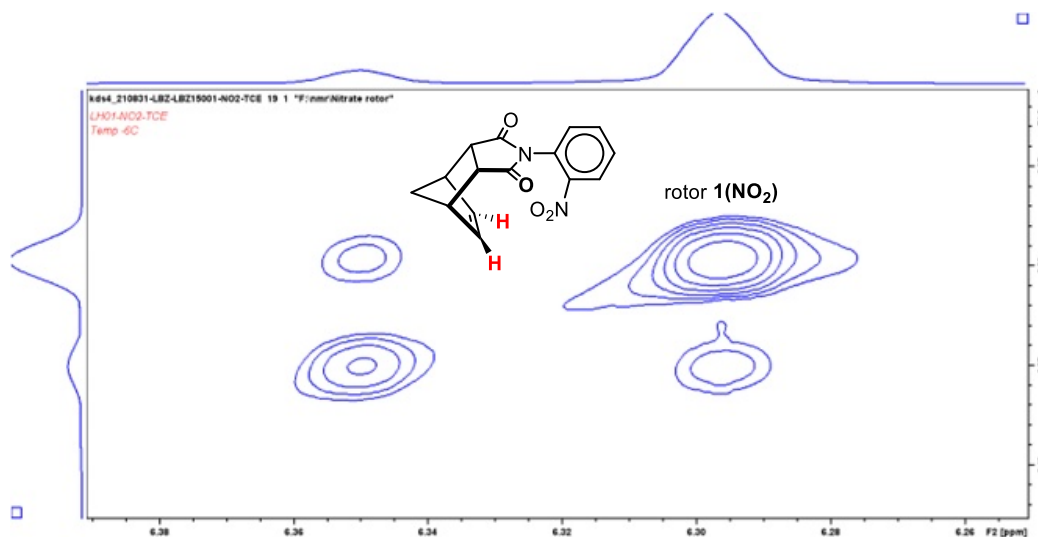


Figure 3.24 2D NMR of diastereomeric alkene protons of **1**(NO₂) in TCE-d₂ at 90 °C.

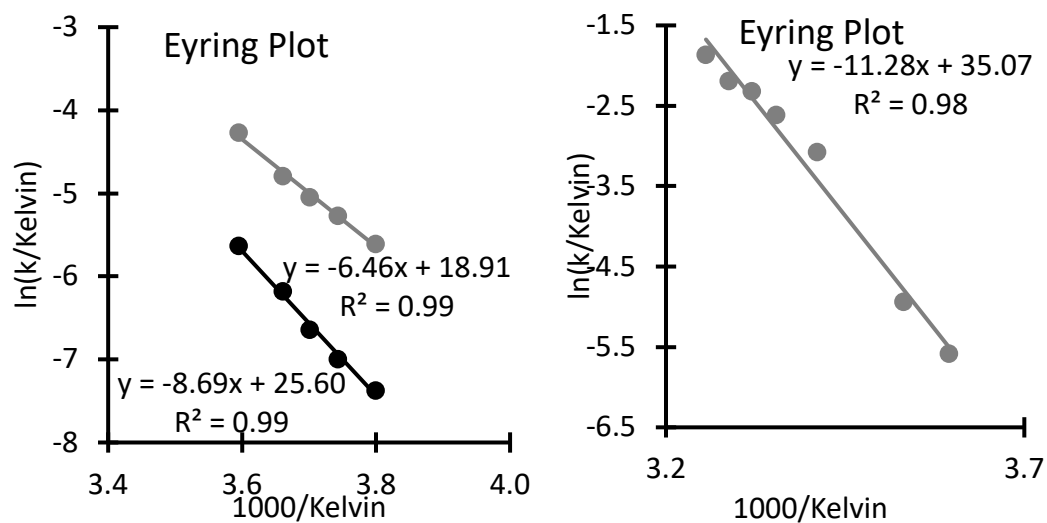


Figure 3.25 Eyring plots for rotor **1**(NO₂) by EXSY ($\Delta G^\ddagger_{\text{exp}} = 15.9$ kcal/mol, left) and lineshape analysis ($\Delta G^\ddagger_{\text{exp}} = 15.6$ kcal/mol, right).

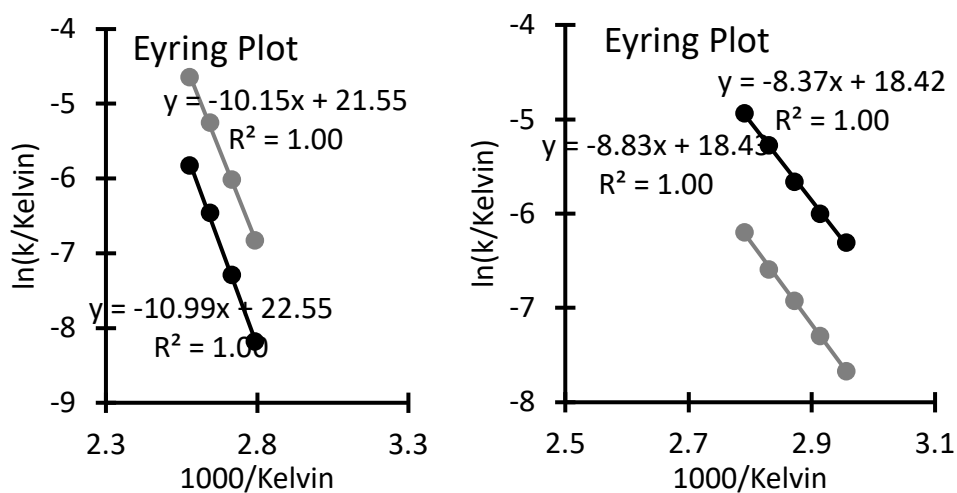


Figure 3.26 Eyring plots for rotor **1**(N(CH₃)₂) (left) and rotor **1**(N(CH₃)Ph) (right) by EXSY.

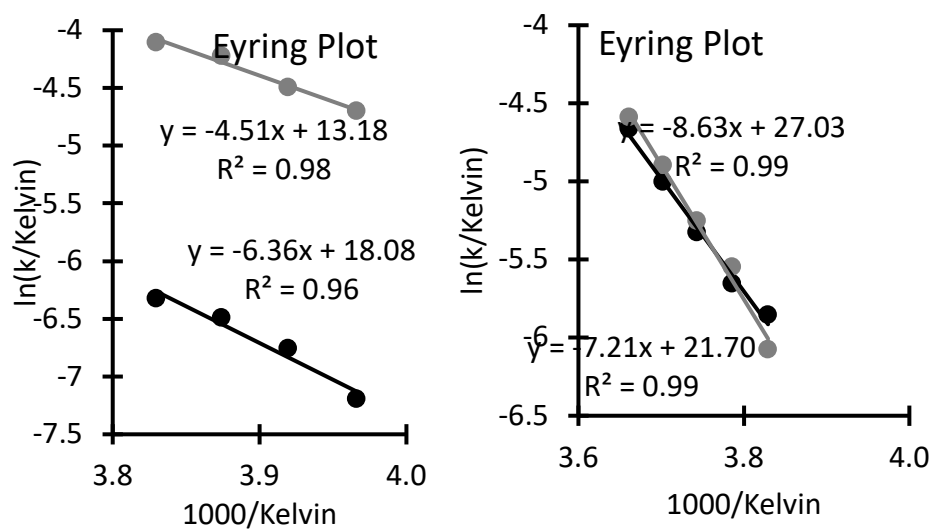


Figure 3.27 Eyring plots for rotor **1**(N(COCH₃)Ph) (left) and rotor **1**(N(COCF₃)Ph) by EXSY.

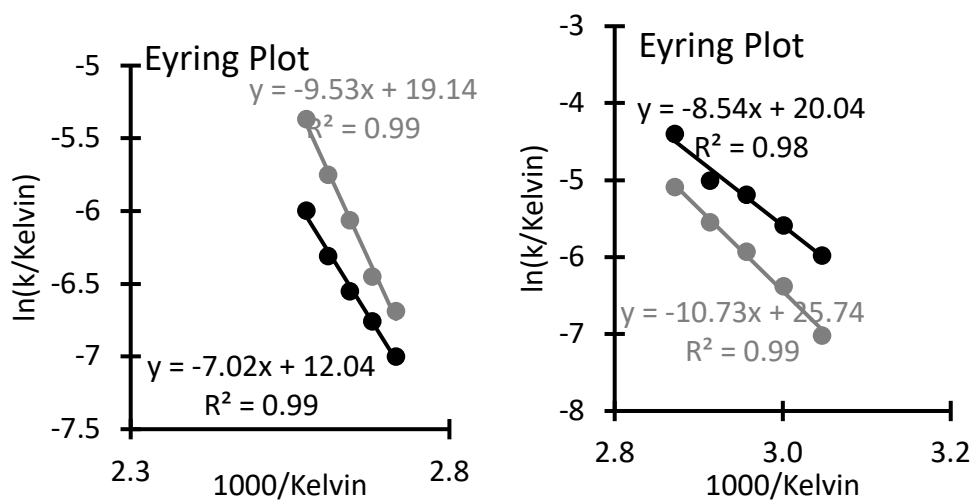


Figure 3.28 Eyring plots for rotor **1**(quinoline) (left) and rotor **1**(N=C-Ph(NO₂)) (right) by EXSY.

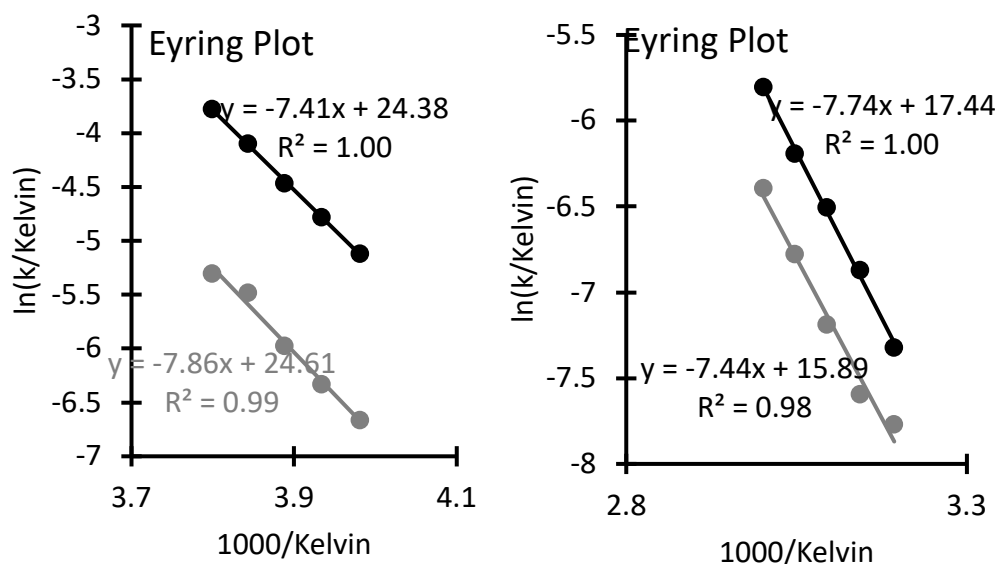


Figure 3.29 Eyring plots for rotor **1**(N(Ph(NO₂)₂) Ph) (left) and rotor **1**(imidazole)) (right) by EXSY.

3.5.6 Molecular Modeling Studies

The optimized the ground state (GS) and transition state (TS) for the rotors were calculated (B3LYP-D3(0)/6-311G*) in Spartan18.^{1,4} Convergence criteria were 10^{-4} Hartree and 10^{-4} atomic units as the maximum norm of the cartesian gradient. Vibrational analyses were also carried out at the B3LYP-D3(0)/6-311G* level of theory. The free energies were calculated at 298.15 K using the calculated thermodynamic terms. To reduce error, the calculated GS energies for the *syn*- and *anti*-conformers were averaged. The XYZ coordinates for the GS and TS structures are in **Tables 3.3 – 3.11**. Transition state structures all had a single imaginary frequency. Ground state structures had zero imaginary frequencies.

With thermodynamic corrections, the calculated barriers ($\Delta G^\ddagger_{\text{cal}}$) reproduced the experimental barriers ($\Delta G^\ddagger_{\text{exp}}$) (**Figure 3.30**), suggesting that the calculated TS and GS

geometries (Tables 3.3 – 3.11) were also accurate. Standard deviation of the error between $\Delta G^\ddagger_{\text{exp}}$ and $\Delta G^\ddagger_{\text{cal}}$ was 0.88 kcal/mol, mean absolute error between $\Delta G^\ddagger_{\text{exp}}$ and $\Delta G^\ddagger_{\text{cal}}$ was 0.90 kcal/mol, root mean square deviation between $\Delta G^\ddagger_{\text{exp}}$ and $\Delta G^\ddagger_{\text{cal}}$ was 1.06 kcal/mol.

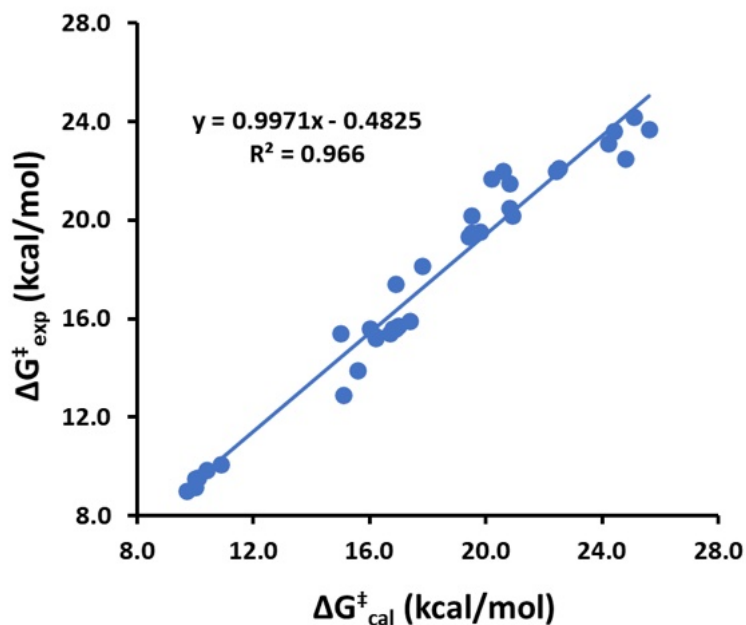
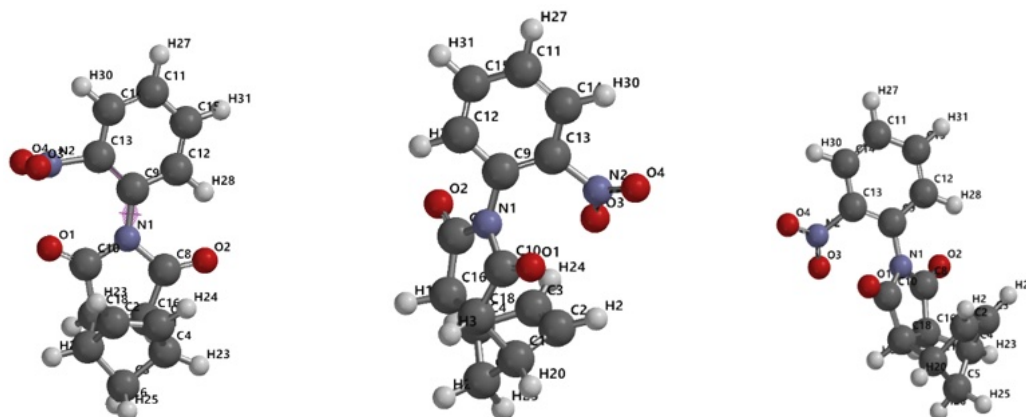


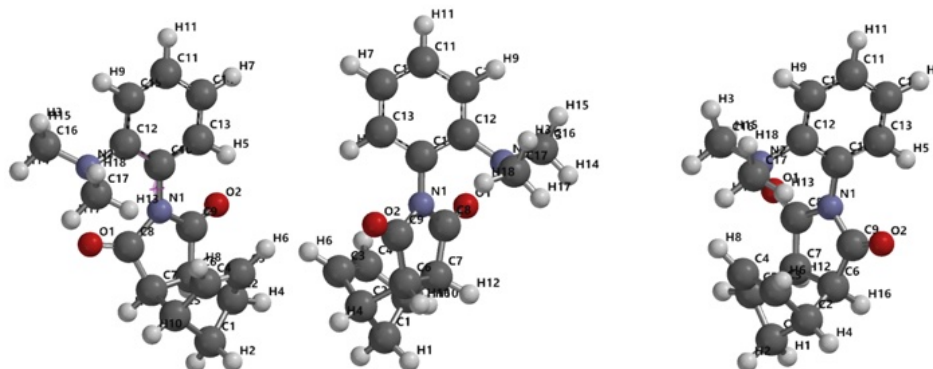
Figure 3.30. Correlation of the calculated ($\Delta G^\ddagger_{\text{cal}}$) and experimental ($\Delta G^\ddagger_{\text{exp}}$) rotational barriers for R¹. Structures were calculated at the B3LYP-D3/6-311G* level of theory with thermodynamic corrections.

Table 3.3 The TS structure (left) and XYZ coordinates of rotor **1**(NO₂), the folded GS structure (middle) and the unfolded GS structure (right).



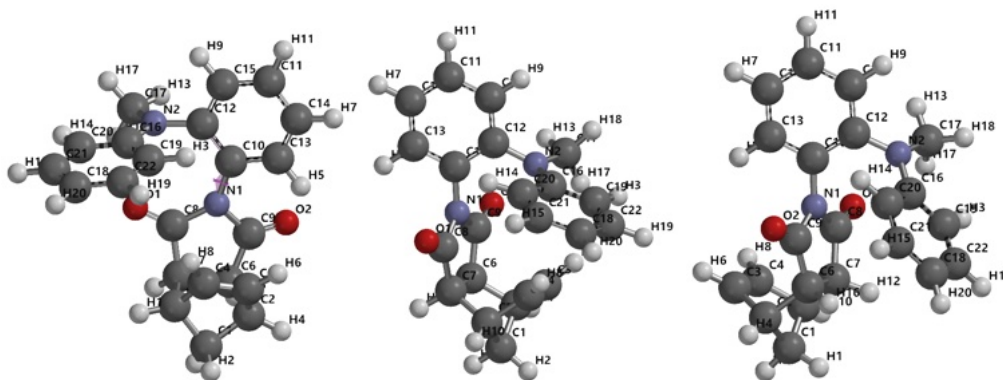
C1	6	0.501914941	1.668526820	-2.536009557	C1	6	0.974453091	1.661669868	-2.336701280	C1	6	0.777762842	1.885340305	-2.273664011
C2	6	-0.951914379	1.333191930	-2.244043062	C2	6	-0.481619444	1.860832160	-1.951286952	C2	6	-0.662187525	2.089999108	-1.828260776
C3	6	-1.144712946	0.051696073	-2.575455206	C3	6	-1.157130197	0.785274570	-2.368033226	C3	6	-1.377231001	1.060604299	-2.294640187
C4	6	0.173396313	-0.496605549	-3.102527940	C4	6	-0.176386336	-0.149294949	-3.058125756	C4	6	-0.437784122	0.151480463	-3.073507643
C5	6	0.747440693	0.774553097	-3.776484590	C5	6	0.806081423	0.882755978	-3.664991145	C5	6	0.546039550	1.202650385	-3.644904318
C16	6	1.159217119	-0.585875477	-1.875352209	C16	6	0.762296874	-0.747201603	-1.944680931	C16	6	0.520095167	-0.536145448	-2.029268854
C18	6	1.360582444	0.873971698	-1.477237304	C18	6	1.513582233	0.497186357	-1.421703661	C18	6	1.324967231	0.652661486	-1.461010133
C8	6	0.577018062	-1.267442395	-0.663194243	C8	6	0.065551329	-1.346467634	-0.741667618	C8	6	-0.180646434	-1.164748997	-0.845083762
N1	7	0.446222605	-0.315524480	0.398738606	N1	7	0.339510867	-0.515553508	0.364324673	N1	7	0.160975353	-0.413793897	0.294595697
C10	6	0.830499460	0.978714684	-0.068926918	C10	6	1.134396055	0.606372970	0.042883824	C10	6	1.007136206	0.681849684	0.018789053
O1	8	0.719566937	2.003233974	0.542022990	O1	8	1.436307924	1.467235562	0.827323655	O1	8	1.370790464	1.480709691	0.841115265
O2	8	0.268110699	-2.432459429	-0.642404974	O2	8	-0.593839651	-2.352741152	-0.694944823	O2	8	-0.920317873	-2.115499651	-0.846897793
C9	6	-0.096001904	-0.622198278	1.701666301	C9	6	-0.105492631	-0.796388323	1.681443923	C9	6	-0.312826795	-0.715444785	1.593561625
C11	6	-1.243101187	-1.454893942	4.187000723	C11	6	-0.777966412	-1.368180181	4.345047440	C11	6	-1.322295086	-1.202579064	4.162168344
C12	6	-0.376185768	-1.973147221	1.998402598	C12	6	0.202134283	-2.035515250	2.242481912	C12	6	-1.684297939	-0.855736343	1.800683648
C13	6	-0.389462460	0.293492006	2.737146830	C13	6	-0.777283520	0.140133517	2.474384984	C13	6	0.544971404	-0.841622586	2.692903090
C14	6	-0.963685171	-0.123292680	3.938730801	C14	6	-1.087599484	-0.127289101	3.802904360	C14	6	0.046350132	-1.058065854	3.972692036
C15	6	-0.928824383	-2.381351189	3.202593794	C15	6	-0.145920621	-2.327200359	3.556506861	C15	6	-2.185123509	-1.113800534	3.071706984
H20	1	0.756038718	2.723848042	-2.602914133	H20	1	1.608731013	2.545627401	-2.338984870	H20	1	1.427926845	2.756793076	-2.239790072
H23	1	0.123050575	-1.413636093	-3.686093221	H23	1	-0.599802103	-0.904217974	-3.718598795	H23	1	-0.900762761	-0.549687145	-3.765431047
H1	1	2.072236439	-1.111268977	-2.160717686	H1	1	1.414360570	-1.507556965	-2.379989776	H1	1	1.133004108	-1.294032592	-2.520120999
H3	1	2.400302916	1.205733063	-1.489622938	H3	1	2.600029387	0.413593996	-1.496450368	H3	1	2.404903297	0.550070203	-1.581660232
H23	1	-1.646635442	1.994384990	-1.742074196	H2	1	-0.851384060	2.648792061	-1.310260884	H2	1	-0.992696197	2.868715162	-1.152583843
H24	1	-2.032062875	-0.545036609	-2.403397412	H24	1	-2.185837564	0.536839330	-2.140475450	H24	1	-2.415037679	0.832438283	-2.084133037
H25	1	0.163851768	1.087860623	-4.644095173	H25	1	0.346267295	1.485816642	-4.449990141	H25	1	0.075668402	1.865630540	-4.373582858
H26	1	1.802094318	0.686521060	-4.056221348	H26	1	1.734876483	0.439649225	-4.038943362	H26	1	1.451964810	0.766200805	-4.077555668
H27	1	-1.685444041	-1.757202454	5.129313720	H27	1	-1.034097097	-1.584943156	5.375782837	H27	1	-1.711432221	-1.387193850	5.156936797
H28	1	-0.166195069	-2.720677900	1.255543710	H28	1	0.715611564	-2.767551449	1.632491614	H28	1	-2.347916990	-0.767834152	0.950589920
H30	1	-1.174941013	0.632872194	4.685457726	H30	1	-1.578980365	0.641130206	4.385344060	H30	1	0.743056328	-1.118516339	4.798140260
H31	1	-1.114652810	-3.438794079	3.357153695	H31	1	0.092918597	-3.301813519	3.967691758	H31	1	-3.254311677	-1.232068318	3.210249148
N2	7	-0.115903056	1.756483997	2.805349296	N2	7	-1.258818882	1.420721215	1.922904100	N2	7	2.015614573	-0.817516459	2.541375326
O3	8	-1.054351489	2.499828989	2.585061979	O3	8	-1.682579106	1.405983642	0.774369597	O3	8	2.486928475	-1.270084464	1.505859605
O4	8	0.982529985	2.074493459	3.222589342	O4	8	-1.252371517	2.392300426	2.659943437	O4	8	2.666712620	-0.390773014	3.480728435

Table 3.4 The TS structure (left) and XYZ coordinates of rotor **1**(N(CH₃)₂), the unfolded GS structure (middle) and the folded GS structure (right).



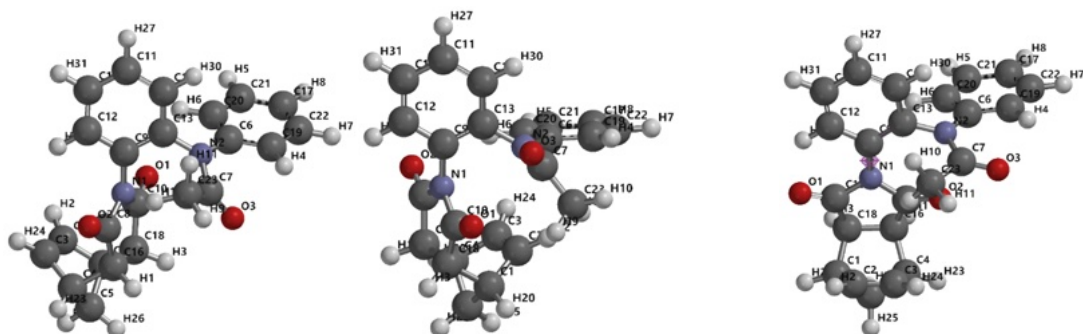
H1	1	1.704052365	-1.243012464	-3.230293923	H1	1	0.986240645	-2.348574485	-3.951860993	H1	1	0.505494925	-2.037847215	-4.212108886
C1	6	2.426825270	-0.954195215	-2.460526124	C1	6	1.766138500	-2.283744238	-3.186024892	C1	6	0.869796904	-2.263328171	-3.204776882
C2	6	2.528104173	0.574679617	-2.242422108	C2	6	2.136285457	-0.829736061	-2.802515684	C2	6	1.713970037	-1.128018685	-2.577444235
C3	6	3.338590491	0.609589111	-0.957964054	C3	6	2.959319330	-1.083875383	-1.547897580	C3	6	1.781492441	-1.607656085	-1.134876788
C4	6	2.977648997	-0.451163181	-0.227361578	C4	6	2.444335369	-2.153650544	-0.932502462	C4	6	0.626429962	-2.221316244	-0.860636428
C5	6	1.934743133	-1.228183786	-1.015889156	C5	6	1.266872032	-2.642440578	-1.765007319	C5	6	-0.230582721	-2.184660115	-2.117052386
H2	1	3.392389320	-1.416748905	-2.674520423	H2	1	2.630021357	-2.875675836	-3.494938851	H2	1	1.388662198	-3.223439974	-3.212490825
H4	1	2.886153063	1.189875815	-3.065301503	H4	1	2.588591806	-0.197062485	-3.563584363	H4	1	2.658644523	-0.870463137	-3.052033631
H6	1	3.980971946	1.426984605	-0.655299411	H6	1	3.738150562	-0.426757250	-1.181234678	H6	1	2.574728946	-1.360899059	-0.441490696
H8	1	3.278081921	-0.677348690	0.788270479	H8	1	2.712526783	-2.547022553	0.039862511	H8	1	0.275615614	-2.561982036	0.102558038
H10	1	1.769723426	-2.262774755	-0.720099582	H10	1	0.929200921	-3.660500825	-1.580911591	H10	1	-1.053474964	-2.895515294	-2.165313898
C6	6	1.023806166	0.870966137	-1.844799494	C6	6	0.716843380	-0.327327098	-2.328475817	C6	6	0.649860772	0.034271677	-2.622252334
C7	6	0.601179889	-0.374569626	-1.072360986	C7	6	0.126965344	-1.565150999	-1.620082540	C7	6	-0.683316650	-0.690844031	-2.333862561
H12	1	-0.181343625	-0.962848790	-1.552209344	H12	1	-0.803610373	-1.930174079	-2.059407855	H12	1	-1.407722241	-0.635237863	-3.148816271
H16	1	0.425080769	1.082138629	-2.731740542	H16	1	0.132872693	0.016135249	-3.184135505	H16	1	0.678892219	0.543851755	-3.587889677
C8	6	0.059404403	0.144412294	0.237998076	C8	6	-0.132114013	-1.129687346	-0.192160026	C8	6	-1.262729951	-0.008094243	-1.111372210
C9	6	0.884266868	2.009317728	-0.862717137	C9	6	0.746101500	0.763824465	-1.275446527	C9	6	0.796726589	1.055577907	-1.508786272
O1	8	-0.714464733	-0.465192105	0.921022793	O1	8	-0.536467273	-1.811212871	0.714798929	O1	8	-2.320472604	-0.240293401	-0.581503654
O2	8	1.043182118	3.166186313	-1.166446806	O2	8	1.131322713	1.899387216	-1.407345831	O2	8	1.723990666	1.801365603	-1.316663157
N1	7	0.558628351	1.489411190	0.429380296	N1	7	0.243764607	0.219104423	-0.086847141	N1	7	-0.350156821	0.975564808	-0.701354282
C10	6	0.671291266	2.297746679	1.636766211	C10	6	0.138722153	0.940867983	1.136077813	C10	6	-0.505563108	1.721786366	0.503927024
C11	6	0.874962392	4.133848365	3.796394569	C11	6	-0.065221696	2.244657274	3.573780227	C11	6	-0.813452983	3.190693104	2.841897082
C12	6	0.162806091	1.954842179	2.924291007	C12	6	-1.127965037	1.126603646	1.702981547	C12	6	-0.503202771	1.053882221	1.735466532
C13	6	1.389617185	3.504983194	1.532076505	C13	6	1.286463605	1.420195094	1.758800677	C13	6	-0.645001775	3.105654113	0.440893937
C14	6	1.486319555	4.409485482	2.580250068	C14	6	1.184142194	2.080294424	2.978168871	C14	6	-0.794345645	3.842444253	1.610227705
C15	6	0.248673797	2.908493219	3.953662026	C15	6	-1.211067433	1.774258820	2.938228002	C15	6	-0.667499504	1.808214425	2.899796544
H5	1	1.841020009	3.776680907	0.595720604	H5	1	2.247615621	1.267360824	1.282560758	H5	1	-0.634012218	3.593152890	-0.527069873
H7	1	2.032405083	5.334469523	2.426535751	H7	1	2.077380683	2.455004856	3.466164435	H7	1	-0.901357781	4.920669069	1.559447778
H9	1	-0.161829667	2.641363172	4.921011010	H9	1	-2.183758669	1.918447827	3.395837661	H9	1	-0.671796067	1.300390049	3.858737962
H11	1	0.919465965	4.838887397	4.620477702	H11	1	-0.148234362	2.750037449	4.530642030	H11	1	-0.936555799	3.759857572	3.757652550
N2	7	-0.381031653	0.693229128	3.224903966	N2	7	-2.269883675	0.666670097	0.976487879	N2	7	-0.305299115	-0.365682927	1.759551453
C16	6	-1.524733265	0.617822877	4.106358292	C16	6	-3.185008439	-0.178929174	1.728697635	C16	6	-1.421169004	-1.114006253	2.327180478
H3	1	-1.268559485	0.632573725	5.181302856	H3	1	-2.622827896	-0.994582452	2.182541546	H3	1	-1.537953555	-0.975006063	3.415438822
H14	1	-2.061776066	-0.314781976	3.908479662	H14	1	-3.911536361	-0.612761841	1.036256778	H14	1	-1.264354023	-2.181287773	2.142451265
H15	1	-2.205180511	1.445236734	3.903409283	H15	1	-3.751519549	0.353698069	2.512326045	H15	1	-2.340123442	-0.817472413	1.823977423
C17	6	0.573164002	-0.383048436	3.415333467	C17	6	-2.929982808	1.719917413	0.212506372	C17	6	0.989514101	-0.748076286	2.308824021
H13	1	1.394804377	-0.294259589	2.703392875	H13	1	-3.471504666	2.444785302	0.845287033	H13	1	1.782757416	-0.203840693	1.792834342
H17	1	0.085532142	-1.345074923	3.241530899	H17	1	-3.648663741	1.268751329	-0.477598544	H17	1	1.150637490	-1.817610089	2.146324846
H18	1	1.006024316	-0.380021582	4.431383828	H18	1	-2.190511263	2.268864337	-0.374028550	H18	1	1.082927937	-0.554797764	3.390607146

Table 3.5 The TS structure (left) and XYZ coordinates of rotor **1(N(CH₃)Ph)**, the folded GS structure (middle) and the unfolded GS structure (right).



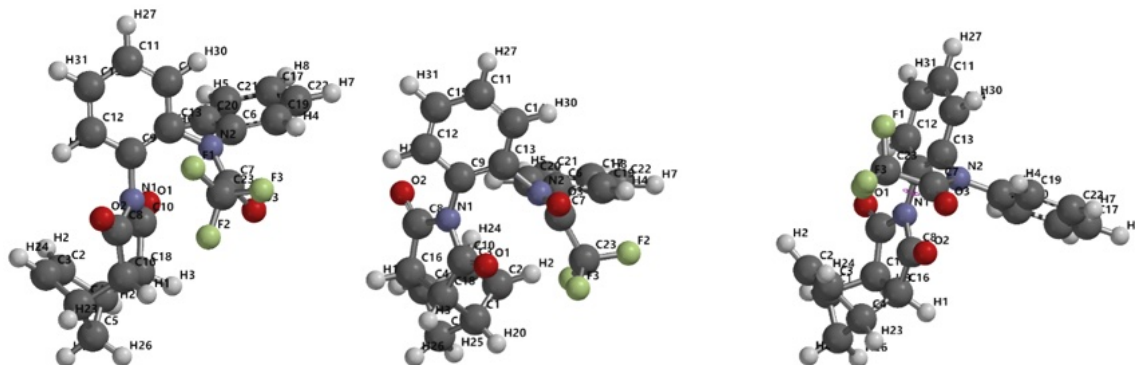
C1	1	0.307082805	-1.296109671	-4.788598540	C1	1	-0.081937223	2.015011835	-4.429194483	H1	1	-0.754601741	-2.297157705	-3.719687464
C1	6	1.067304908	-1.036074967	-4.045167960	C1	6	0.471531267	2.127607597	-3.490603796	C1	6	0.196981079	-1.763999193	-3.815740679
C2	6	1.086005681	0.466882983	-3.673168263	C2	6	-0.435217747	2.379590021	-2.258748611	C2	6	0.077531019	-0.237120892	-3.588679177
C3	6	1.978462567	0.429311467	-2.442204203	C3	6	0.574916153	2.174215261	-1.138877533	C3	6	1.550807011	0.133343494	-3.468726843
C4	6	1.750938407	-0.727386531	-1.810021699	C4	6	1.441944041	1.237545096	-1.535351231	C4	6	2.181841756	-0.893327070	-2.887542206
C5	6	0.708002076	-1.490660146	-2.611763280	C5	6	1.032829684	0.793800008	-2.932552887	C5	6	1.145819517	-1.974245259	-2.609418070
H2	1	2.041655159	-1.401366582	-4.374878811	H2	1	1.241642883	2.891537126	-3.609795440	H2	1	0.661905456	-2.016310616	-4.770806608
H4	1	1.347800094	1.185133256	-4.447689907	H4	1	-1.016780741	3.299301217	-2.232276920	H4	1	-0.513808373	0.340709292	-4.296474412
H6	1	2.582895820	1.257821110	-2.094181979	H6	1	0.517283118	2.629392383	-0.159811057	H6	1	1.960242795	1.106330657	-3.710152634
H8	1	2.114636470	-1.032037303	-0.836245887	H8	1	2.224743684	0.780174399	-0.947600993	H8	1	3.211287588	-0.928876799	-2.553533798
H10	1	0.621889713	-2.556354730	-2.409131851	H10	1	1.787253799	0.271405051	-3.517952943	H10	1	1.525960913	-2.977823972	-2.427756818
C6	6	-0.415554995	0.609849346	-3.171972074	C6	6	-1.317497616	1.079692690	-2.330307247	C6	6	-0.510100367	-0.244540271	-2.129049928
C7	6	-0.668026043	-0.719716686	-2.463988128	C7	6	-0.323430031	-0.001271452	-2.810638302	C7	6	0.212892196	-1.435401462	-1.464023521
H12	1	-1.478654785	-1.316306720	-2.882469230	H12	1	-0.583199442	-0.437600536	-3.777803276	H12	1	-0.466226192	-2.215668248	-1.115524126
H16	1	-1.077957655	0.817341836	-0.012603172	H16	1	-2.163128126	1.227532328	-3.006261894	H16	1	-1.596641154	-0.348546136	-2.138841203
C8	6	-1.005568050	-0.363346670	-1.042122128	C8	6	-0.377241196	-1.096165270	-1.763843137	C8	6	0.930925544	-0.856253373	-0.265186003
C9	6	-0.606401368	1.659945661	-2.105408501	C9	6	-1.847633322	0.578051446	-1.001360657	C9	6	-0.153389737	0.962647755	-1.287929527
O1	8	-1.504828962	-1.133939884	-0.272273524	O1	8	0.225474372	-2.139549036	-1.753454789	O1	8	1.638983533	-1.442163336	0.516968904
O2	8	-0.683780072	2.845207889	-2.305219352	O2	8	-2.614537329	1.136063386	-0.256815794	O2	8	-0.464842321	2.110986982	-1.477429362
N1	7	-0.674252071	1.015048173	-0.827506719	N1	7	-1.298255948	-0.695398254	-0.777805857	N1	7	0.643140611	0.514556888	-0.216304174
C10	6	-0.370098391	1.729781468	0.393799491	C10	6	-1.610560739	-1.483797742	0.369117712	C10	6	1.063230211	1.369514993	0.840684418
C11	6	0.333970493	3.355600331	2.615711445	C11	6	-2.253290206	-3.023289482	2.594853300	C11	6	1.920177661	3.063693834	2.868741696
C12	6	-0.717529863	1.338932263	1.711270305	C12	6	-1.183161329	-1.073584943	1.636926487	C12	6	0.644971789	1.118934042	2.160865226
C13	6	0.399368684	2.900961878	0.252931200	C13	6	-2.332201714	-2.664655411	0.213098053	C13	6	1.864555622	2.467192630	0.541562957
C14	6	0.740434268	3.700209022	1.332707499	C14	6	-2.651576699	-3.436384587	1.325126318	C14	6	2.299221979	3.316386853	1.551468775
C15	6	-0.369949725	2.173852980	2.782036467	C15	6	-1.517464127	-1.851961305	2.745985229	C15	6	1.096104058	1.984023423	3.164336921
H5	1	0.720379715	3.214251686	-0.725526953	H5	1	-2.637192595	-2.970201425	-0.781379110	H5	1	2.145709231	2.636207136	-0.490855333
H7	1	1.326618847	4.596312997	1.157037711	H7	1	-3.212079985	-4.356757018	1.200054997	H7	1	1.929152290	4.165680119	1.311032698
H9	1	-0.654001430	1.833578136	3.771423674	H9	1	-1.174093519	-1.534731132	3.724624865	H9	1	0.769767282	1.805723025	4.183127040
H11	1	0.581314494	3.978276400	3.468726229	H11	1	-2.502212352	-3.622081451	3.464844560	H11	1	2.250232729	3.720461777	3.666700432
N2	7	-1.337485009	0.110511682	2.073610267	N2	7	-0.402736838	0.104758284	1.783628086	N2	7	-0.178621821	0.014644450	2.503764587
C17	6	-2.788987856	0.036394062	2.053806078	C17	6	-1.040598500	1.252187264	2.411728562	C17	6	0.410297747	-1.019070140	3.353303769
H13	1	-3.182543171	1.039049636	1.891808766	H13	1	-2.117113458	1.109759575	2.369519676	H13	1	1.252256707	-0.593540579	3.894247652
H17	1	-3.184159100	-0.333392772	3.006081551	H17	1	-0.820638121	2.168412434	1.857918828	H17	1	0.787493853	-1.858898010	2.762534290
H18	1	-3.145235586	-0.609704846	1.246633759	H18	1	-0.727402762	1.386174556	3.455595934	H18	1	-0.324568152	-1.378991164	4.078102184
C16	6	-0.550440500	-1.027624479	2.226513725	C16	6	0.980978299	0.035931096	1.633002678	C16	6	-1.365889903	-0.260192296	1.816208840
C18	6	1.041893618	-3.363963653	2.395109040	C18	6	3.777908709	-0.062394432	1.222329250	C18	6	-3.765413002	-0.804878599	0.420353779
C19	6	0.854265578	-0.961575421	2.127924381	C19	6	1.802730986	1.127086180	1.971923204	C19	6	-1.887810649	-1.565361141	1.753392557
C20	6	-1.133183260	-2.291788845	2.436730438	C20	6	1.598123840	-1.116944191	1.105740522	C20	6	-2.082821453	0.766862449	1.171755354
C21	6	-0.345112293	-3.433658985	2.510581334	C21	6	2.970583682	-1.154550220	0.903091861	C21	6	-3.253315141	0.492562284	0.478945448
C22	6	1.628669720	-2.113439658	2.212751771	C22	6	3.177480415	1.072101104	1.761750592	C22	6	-3.073888781	-1.823231549	1.068890221
H3	1	1.341625429	-0.007544685	1.971314470	H3	1	1.374123888	2.027479325	2.392597161	H3	1	-1.364474834	-2.389625587	2.219589331
H14	1	-2.209349148	-2.393956393	2.485253257	H14	1	1.002068986	-1.970904671	0.813100121	H14	1	-1.704714666	1.781460389	1.197009053
H15	1	-0.830310258	-4.396685397	2.641471797	H15	1	3.408605658	-2.051226385	0.476024067	H15	1	-3.770491120	1.307242618	-0.018087185
H19	1	2.708701587	-0.026372488	2.131901927	H19	1	3.781836849	1.935493866	2.022949102	H19	1	-3.452866388	-2.840709392	1.040724599
H20	1	1.649493510	-4.261246858	2.445005579	H20	1	4.849121353	-0.096854587	1.056904792	H20	1	-4.687005281	-0.101323299	-0.112561661

Table 3.6 The unfolded GS structure (left) and the unfolded GS structure (middle) and the TS structure (right) and XYZ coordinates of rotor 1(N(COCH₃)Ph).



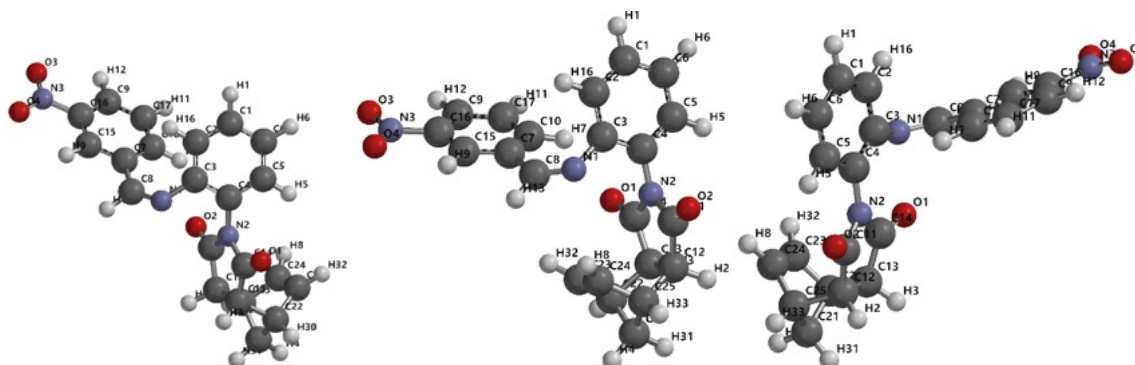
C1	6	-0.011012416	0.300422610	-3.801066189	C1	6	-1.847503373	-1.305363253	-2.308410569	C1	6	1.807491111	-1.314376820	-3.687248700
C2	6	-0.475297283	-1.148418718	-3.808709702	C2	6	-0.554549808	-1.730492962	-1.626224531	C2	6	2.903159687	-1.050374340	-2.662824549
C3	6	0.611165960	-1.924757725	-3.753164223	C3	6	0.466629049	-1.249932210	-2.342632982	C3	6	2.866254998	0.249423607	-2.349542975
C4	6	1.829047276	-1.015760975	-3.710486712	C4	6	-0.119833275	-0.464977215	-3.503412339	C4	6	1.732709002	0.880102293	-3.146754080
C5	6	1.322361968	0.163248285	-4.578856519	C5	6	-1.389987266	-1.305938611	-3.789391440	C5	6	1.803427199	0.037654506	-4.443236052
C16	6	1.822901392	-0.308785501	-2.305503180	C16	6	-0.794130996	0.815665123	-2.880964621	C16	6	0.394863742	0.303200892	-2.544384534
C18	6	0.560292039	0.580386381	-2.362741472	C18	6	-2.007686515	0.250717151	-2.115387261	C18	6	0.425170273	-1.168162653	-2.945914221
C8	6	1.618469786	-1.229363999	-1.121129927	C8	6	0.035484507	1.528974884	-1.829415600	C8	6	0.363021329	0.302238298	-1.034611059
N1	7	0.411277923	-0.865831859	-0.500815066	N1	7	-0.671241982	1.483613350	-0.611133962	N1	7	0.088577835	-1.036975000	-0.568117433
C10	6	-0.318787925	0.096669015	-1.231088856	C10	6	-1.877073024	0.764390957	-0.697803218	C10	6	0.298484756	-1.943163970	-1.660525067
O1	8	-1.452310214	0.418011273	-0.990669954	O1	8	-2.658670299	0.609727639	0.204847567	O1	8	0.386500206	-3.144972337	-1.608059832
O2	8	2.339711587	-2.122621174	-0.749148726	O2	8	1.118037559	2.039904209	-1.974344294	O2	8	0.603037796	1.268836060	-0.372207819
C9	6	-0.095387646	-1.472236724	0.687946366	C9	6	-0.216081712	2.161726211	0.564070145	C9	6	-0.281473340	-1.478552654	0.770376096
C11	6	-1.136068383	-2.636388144	2.991069928	C11	6	0.722158343	3.549323892	2.789612248	C11	6	-1.158854130	-2.566692583	3.264004698
C12	6	-0.432328327	-2.822753027	0.692667198	C12	6	-0.032683062	3.542458196	0.502102139	C12	6	-0.574285651	-2.847886428	0.943381416
C13	6	-0.249784746	-0.698508752	1.848994180	C13	6	0.083168352	1.468194427	1.741491784	C13	6	-0.449316511	-0.653775856	1.913819630
C14	6	-0.784789906	-1.291265152	2.992600093	C14	6	0.543712843	2.172566897	2.851310179	C14	6	-0.883847603	-1.218790855	3.118735889
C15	6	-0.951316737	-3.406121260	1.843054176	C15	6	0.436605389	4.235083585	1.610385357	C15	6	-0.998805925	-3.380174536	2.151726965
H20	1	-0.730538213	1.042705442	-4.140675348	H20	1	-2.743597005	-1.866756904	-2.049253968	H20	1	1.893671424	-2.230266183	-4.268574466
H23	1	2.783969674	-1.468581000	-3.969536106	H23	1	0.547660868	-0.248624211	-4.335206522	H23	1	1.742978301	1.963897666	-3.236095025
H1	1	2.746746152	0.251915778	-2.150867777	H1	1	-1.062726555	1.529099609	-3.663603971	H1	1	-0.475609529	0.851439883	-2.911594238
H3	1	0.764962919	1.642554924	-2.216606721	H3	1	-2.973473314	0.572348302	-2.510185287	H3	1	-0.389608259	-1.476677314	-3.605309709
H2	1	-1.510402524	-1.461365746	-3.750250025	H2	1	-0.494194694	-2.247681782	-0.679137666	H2	1	3.516349992	-1.819833429	-2.210564916
H24	1	0.644266282	-3.001849645	-3.644186415	H24	1	1.515358289	-1.290318407	-2.087604875	H24	1	3.437874697	0.760653720	-1.586019868
H25	1	1.173731542	-0.116319803	-5.623690746	H25	1	-1.158959196	-2.306505958	-4.160128557	H25	1	2.719088233	0.207663929	-5.012655661
H26	1	1.955296015	1.053745761	-4.520897196	H26	1	-2.098768553	-0.819113431	-4.467127717	H26	1	0.936376009	0.169497745	-5.098779151
H27	1	-1.547496807	-3.086857596	3.888030662	H27	1	1.081542112	4.086391122	3.660565652	H27	1	-1.491613899	-2.966016994	4.215724558
H28	1	-0.290305836	-3.404044667	-0.210667738	H28	1	-0.252697863	4.061333948	-0.423295280	H28	1	-0.455974822	-3.520299577	0.114703898
H30	1	-0.920277436	-0.678924983	3.876842786	H30	1	0.752475289	1.621886118	3.760207245	H30	1	-1.003383926	-0.536897522	3.952693744
H31	1	-1.215551863	-4.458075881	1.840983245	H31	1	0.577196739	5.308925829	1.552374996	H31	1	-1.204733621	-4.444127979	2.206385663
N2	7	0.131209061	0.675600935	1.851921095	N2	7	-0.082390006	0.041934683	1.805308661	N2	7	-0.247164177	0.763718448	2.004152450
C7	6	1.478564528	0.999826558	1.618887997	C7	6	-1.248040566	-0.419058417	2.466907654	C7	6	1.037593788	1.243608967	2.268914093
O3	8	1.821133210	2.091106017	1.212442649	O3	8	-1.852306775	0.294150206	3.231682256	O3	8	1.281387284	2.412965857	2.478490463
C6	6	-0.882764584	1.671953909	2.040302352	C6	6	1.044386720	-0.777230567	1.520541740	C6	6	-1.385281588	1.590862856	1.773286693
C17	6	-2.910134697	3.544386777	2.538435411	C17	6	3.273739346	-2.396094869	0.947764967	C17	6	-3.694147571	3.133222769	1.298517739
C19	6	-0.574021378	2.912285120	2.611639504	C19	6	1.289949157	-1.946725891	2.254870505	C19	6	-1.491855144	2.890572885	2.290618718
C20	6	-2.212330181	1.378306044	1.721574991	C20	6	1.960910404	-0.405113311	0.528131364	C20	6	-2.453672908	1.078910901	1.019225564
C21	6	-3.214766549	2.309097553	1.973672604	C21	6	3.063425909	-1.206646582	0.253746261	C21	6	-3.592821639	1.841874577	0.787962243
C22	6	-1.584244921	3.838059043	2.849761595	C22	6	2.381095994	-2.756559265	1.953134261	C22	6	-2.636668812	3.644025953	2.046589057
H4	1	0.449912071	3.161058060	2.850430429	H4	1	0.638833267	-2.219241990	3.076881010	H4	1	-0.678738265	3.308190725	2.861126564
H6	1	-2.457540755	0.438477089	1.248260550	H6	1	1.821940434	0.509007886	-0.033172719	H6	1	-2.406360803	0.074574864	0.616655260
H5	1	-4.239625439	2.064079530	1.713309205	H5	1	3.759410423	-0.895604368	-0.519204792	H5	1	-4.404403059	1.417936845	0.204235652
H7	1	-1.327331847	4.796636530	3.289372706	H7	1	2.543381540	-3.662521552	2.528593800	H7	1	-2.698098404	4.647379923	2.457186849
H8	1	-3.693704718	4.270154963	2.729729743	H8	1	4.130061545	-3.022334421	0.721352942	H8	1	-4.582924595	3.729603049	1.119258892
C23	6	2.490673969	-0.074491921	1.985319642	C23	6	-1.782862717	-1.785572059	2.085580636	C23	6	2.139543178	0.195350671	2.272124075
H9	1	3.466113900	0.406387008	2.032172175	H9	1	-2.743049373	-1.592191334	1.603272094	H9	1	2.238287670	-0.267938656	1.287811666
H10	1	2.545119147	-0.886546910	1.261200138	H10	1	-1.972050716	-2.372670175	2.985848313	H10	1	1.955175454	-0.604682824	2.992227517
H11	1	2.251554934	-0.527203441	2.950137182	H11	1	-1.152605429	-2.354154477	1.406458397	H11	1	3.068620161	0.703230568	2.523083144

Table 3.7 The unfolded GS structure (left) and the folded GS structure (middle) and the TS structure (right) and XYZ coordinates of rotor 1(N(COCF₃)Ph).



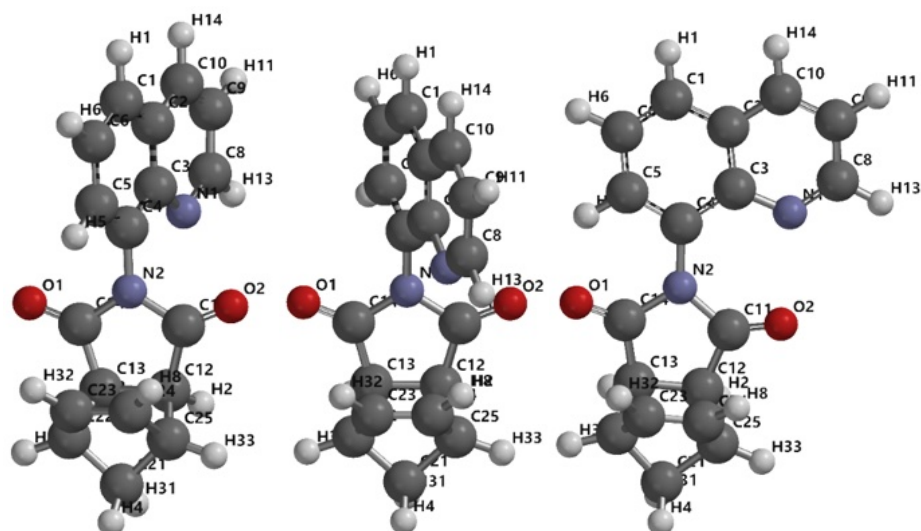
C1	6	0.214069842	0.209076626	-3.853988333	C1	6	-1.631196479	-1.363680451	-2.304871222	C1	6	1.793811800	-1.413272265	-3.684974022
C2	6	-0.453361149	-1.157471472	-3.799098807	C2	6	-0.233362400	-1.631964162	-1.763361590	C2	6	2.848391850	-1.228134721	-2.603461878
C3	6	0.512382542	-2.078922091	-3.724865387	C3	6	0.642607265	-1.019697917	-2.565999747	C3	6	2.889794442	0.070645772	-2.287707155
C4	6	1.848890629	-1.350621052	-3.725198851	C4	6	-0.150278333	-0.293308400	-3.639623969	C4	6	1.851471133	0.781221414	-3.144716337
C5	6	1.500853113	-0.146664286	-4.635846668	C5	6	-1.326161532	-1.284562920	-3.823404168	C5	6	1.926829840	-0.065874615	-4.437369127
C16	6	1.955758989	-0.602358299	-2.345632157	C16	6	-0.901289524	0.880236325	-2.904113500	C16	6	0.445027009	0.301511454	-2.612937844
C18	6	0.839427332	0.461362277	-2.434205422	C18	6	-1.982269239	0.158337265	-2.073930922	C18	6	0.383833970	-1.164280235	-3.019695430
C8	6	1.617714165	-1.447414928	-1.136182767	C8	6	-0.059596743	1.621676929	-1.879205004	C8	6	0.343287871	0.305134250	-1.107480426
N1	7	0.487750338	-0.862888213	-0.511325814	N1	7	-0.681904534	1.480399726	-0.616608153	N1	7	0.025119666	-1.020330047	-0.641772180
C10	6	-0.092736152	0.164832534	-1.281148217	C10	6	-1.844228427	0.687442531	-0.667145475	C10	6	0.130686970	-1.930568298	-1.749745909
O1	8	-1.158706600	0.674101135	-1.047306048	O1	8	-2.591634065	0.498173395	0.257696871	O1	8	0.046921617	-3.133526165	-1.725681678
O2	8	2.162351950	-2.450752529	-0.760793075	O2	8	0.967731780	2.221065850	-2.070603389	O2	8	0.541476732	1.284371793	-0.447218850
C9	6	-0.118895207	-1.404785651	0.660460393	C9	6	-0.207097255	2.154094496	0.552039529	C9	6	-0.296538898	-1.448567614	0.713686905
C11	6	-1.261246270	-2.513961679	2.948178360	C11	6	0.787076211	3.538819554	2.765193973	C11	6	-1.087889882	-2.518373611	3.249989731
C12	6	-0.500207355	-2.744331075	0.676036227	C12	6	0.023558010	3.528256902	0.479015055	C12	6	-0.535018253	-2.822893736	0.923630045
C13	6	-0.292515701	-0.614863758	1.807165079	C13	6	0.072992710	1.470990680	1.742697021	C13	6	-0.445214411	-0.617334799	1.855912490
C14	6	-0.873248760	-1.180433446	2.942424837	C14	6	0.560822677	2.170416954	2.843037530	C14	6	-0.842994776	-1.169069994	3.078348523
C15	6	-1.071922559	-3.300276760	1.813591066	C15	6	0.519643487	4.216982167	1.577888539	C15	6	-0.918785616	-3.345323102	2.149822723
H20	1	-0.395485879	1.033261640	-4.218595226	H20	1	-2.416553081	-2.038294981	-1.969579177	H20	1	1.841225621	-2.333875568	-4.263489640
H23	1	2.726785829	-1.944429470	-3.971339410	H23	1	0.396195569	0.020686461	-4.526641728	H23	1	1.942019095	1.861631125	-3.230104201
H1	1	2.952125407	-0.181768246	-2.206240230	H1	1	-1.308874223	1.601024638	-3.617070032	H1	1	-0.362006314	0.916093618	-3.017531470
H3	1	1.200289426	1.486978016	-2.337427318	H3	1	-3.003717584	0.342751253	-2.410652746	H3	1	-0.410286615	-1.411269588	-3.727256432
H2	1	-1.521655563	-1.315558306	-3.718183971	H2	1	-0.018726261	-2.151809347	-0.842304359	H2	1	3.372616018	-2.038969791	-2.113065233
H24	1	0.392985998	-3.144843482	-3.574341580	H24	1	1.711007135	-0.933426294	-2.425166960	H24	1	3.443680471	0.531719524	-1.480833154
H25	1	1.298598905	-0.443964854	-5.666806037	H25	1	-1.006602066	-2.241313551	-4.240535960	H25	1	2.880789263	0.035589222	-4.958113505
H26	1	2.255679641	0.646005625	-4.624393886	H26	1	-2.155074794	-0.885416641	-4.417220684	H26	1	1.106296981	0.125728781	-5.136593345
H27	1	-1.705887380	-2.940166672	3.840939539	H27	1	1.169403968	4.073294449	3.627645140	H27	1	-1.391511260	-2.909344479	4.214652006
H28	1	-0.338166310	-3.343764232	-0.210666164	H28	1	-0.176253421	4.045402828	-0.450749081	H28	1	-0.418562842	-3.505124320	0.103432032
H30	1	-1.017221819	-0.558155896	3.817820697	H30	1	0.755249609	1.622680512	3.757160474	H30	1	-0.946021780	-0.480227691	3.908336266
H31	1	-1.367505046	-4.343731082	1.812322946	H31	1	0.696085872	5.284496783	1.504723582	H31	1	-1.085392297	-4.414757338	2.227411937
N2	7	0.046238255	0.774108145	1.823528577	N2	7	-0.132850616	0.046114797	1.836072029	N2	7	-0.266291746	0.809343331	1.936131340
C7	6	1.230514914	1.297895916	1.353285546	C7	6	-1.295931094	-0.345871084	2.496034573	C7	6	0.965860727	1.375694629	2.148321201
O3	8	1.374552719	2.426982835	0.945695965	O3	8	-1.916597927	0.353872777	3.251693174	O3	8	1.186854239	2.549041279	2.323101067
C6	6	-1.002919984	1.700652572	2.184985411	C6	6	0.983529294	-0.811051782	1.579689981	C6	6	-1.441612385	1.616561096	1.784681911
C17	6	-3.025975614	3.423887684	3.005331892	C17	6	3.165216132	-2.489010775	1.049056502	C17	6	-3.787097386	3.117487080	1.478896290
C19	6	-0.725278969	2.702385781	3.113773291	C19	6	1.256367290	-1.902160350	2.410506842	C19	6	-1.642330569	2.770353976	2.548641143
C20	6	-2.285960280	1.553223393	1.663231518	C20	6	1.845328464	-0.534323198	0.513628110	C20	6	-2.426967499	1.215316784	0.876001276
C21	6	-3.294693362	2.416670623	2.080895048	C21	6	2.927255799	-1.367357541	0.257372092	C21	6	-3.590385890	1.961973866	0.726761111
C22	6	-1.737059960	3.566876505	3.516995659	C22	6	2.326335248	-2.747111014	2.128796006	C22	6	-2.808891971	3.512286493	2.387700943
H4	1	0.278389758	2.802815936	3.510025570	H4	1	0.641625132	-2.095814729	3.279173749	H4	1	-0.887864406	3.091994281	3.250483793
H6	1	-2.476446485	0.787882616	0.923950887	H6	1	1.671232768	0.319130593	-0.125392803	H6	1	-2.294709843	0.315150244	0.287974830
H5	1	-4.293480164	2.304803570	1.671815419	H5	1	3.583966496	-1.139074054	-0.575785436	H5	1	-4.344236438	1.637645334	0.015976301
H7	1	-1.518312460	4.347640144	4.237677451	H7	1	2.511439910	-3.599306267	2.774334387	H7	1	-2.951464984	4.406184695	2.986767225
H8	1	-3.816116598	4.095536493	3.324618005	H8	1	4.003462025	-3.143604656	0.836097888	H8	1	-4.694326893	3.701232690	1.361409926
C23	6	2.356888088	0.462700712	1.495905596	C23	6	-1.896665343	-1.749729773	2.162689158	C23	6	2.185000058	0.394068763	2.195697272
F1	9	2.400211477	-0.805508890	1.907315682	F1	9	-1.481374275	-2.253176737	0.979715890	F1	9	2.094766986	-0.459439615	3.240246446
F2	9	3.191129458	0.447208123	0.315907012	F2	9	-1.577035035	-2.651394157	3.122488580	F2	9	2.321383038	-0.352950267	1.075064710
F3	9	3.21416854	0.940747467	2.389707696	F3	9	-3.228485966	-1.663887534	2.125519428	F3	9	3.309257397	1.095526258	2.340664225

Table 3.8 The unfolded GS structure (left) and the folded GS structure (middle) and the TS structure (right) and XYZ coordinates of rotor 1($\text{N}=\text{CH}(\text{PhNO}_2)$).



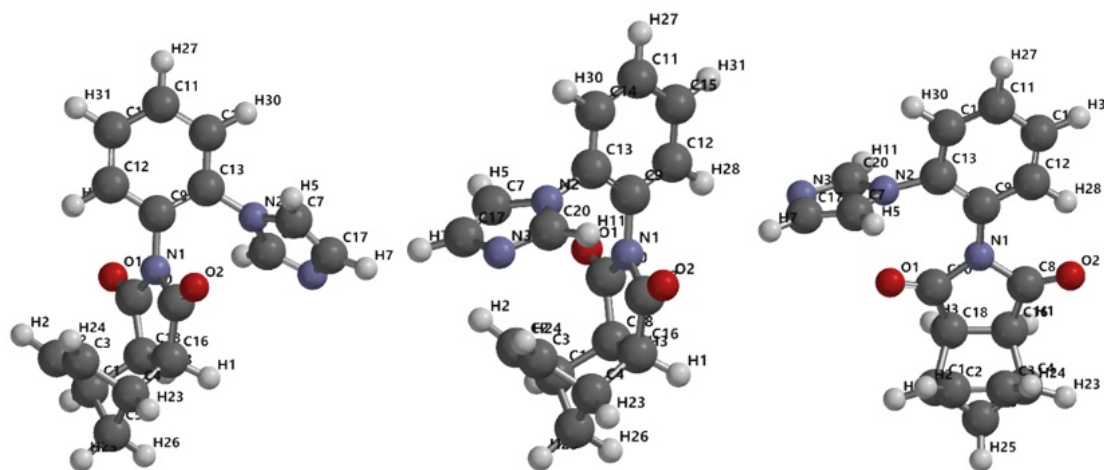
H1	1	-3.536091809	-0.416453202	-3.271954605	H1	1	-4.142216524	0.483236114	-3.018488078	H1	1	-3.490418555	0.452269139	-3.390553434
C1	6	-2.970185504	-0.097755638	-2.402653162	C1	6	-3.377442540	0.818268869	-2.325223428	C1	6	-2.750595681	0.635907991	-2.618636879
C4	6	-1.540325126	0.699316892	-0.162725342	C4	6	-1.430677247	1.661059071	-0.534233290	C4	6	-0.791203214	1.053860484	-0.599435896
C2	6	-2.355293186	-1.051327108	-1.601540131	C2	6	-2.854255155	-0.078642455	-1.402363483	C2	6	-2.439799471	-0.354809919	-1.707402111
C6	6	-2.867613428	1.258637006	-2.095007744	C6	6	-2.926763406	2.136759069	-2.365406135	C6	6	-2.109274715	1.863078529	-2.509026197
C5	6	-2.148001050	1.653278944	-0.972583119	C5	6	-1.949769944	2.551842229	-1.466020449	C5	6	-1.156118145	2.055407548	-1.520726579
C3	6	-1.628154579	-0.667097733	-0.466267756	C3	6	-1.868994560	0.32999376	-0.493479155	C3	6	-1.489659492	-0.183009634	-0.679953156
H6	1	-3.351231772	2.000873363	-2.720142314	H6	1	-3.336875198	2.835320762	-3.086049691	H6	1	-2.340560707	2.677789056	-3.186375695
H5	1	-2.056445408	2.699634016	-0.706864416	H5	1	-1.580177949	3.571096308	-1.475759950	H5	1	-0.659725050	3.007838329	-1.484410117
N1	7	-1.118693535	-1.603787037	0.444977604	N1	7	-1.414314115	-0.523985762	0.519965041	N1	7	-1.482921142	-1.215764182	0.266322249
C8	6	-0.314884706	-2.540652937	0.137097458	C8	6	-0.782817275	-1.608694071	0.318822570	C8	6	-1.055149254	-2.394368818	0.078416855
H13	1	-0.106478734	-3.259613960	0.934079596	H13	1	-0.599251023	-2.212057476	1.212679368	H13	1	-1.260020061	-3.097474558	0.889568916
N2	7	-0.815708185	1.103800317	0.991998812	N2	7	-0.419273173	2.091136423	0.374698352	N2	7	0.244360460	1.387842580	0.362751734
C11	6	0.560617512	0.911514532	1.136434734	C11	6	-0.707896716	2.645500653	1.637717360	C11	6	1.068591247	2.549921359	0.241563369
C12	6	0.968702971	1.474780615	2.481715114	C12	6	0.615155495	2.875983542	2.338591306	C12	6	1.725477389	2.827954171	1.567878534
C13	6	-0.333168499	2.025492674	3.106463959	C13	6	1.704977949	2.443714162	1.330472518	C13	6	1.454483228	1.588131562	2.415256774
C14	6	-1.420643248	1.741869524	2.091792834	C14	6	0.942668586	1.881403983	0.145759535	C14	6	0.622520336	0.678106880	1.544786320
O1	8	-2.588919728	2.020469094	2.166279464	O1	8	1.397434626	1.330217883	-0.829671979	O1	8	0.364910804	-0.460678770	1.821542873
O2	8	1.276429138	0.404183890	0.304799560	O2	8	-1.814441601	2.875057923	2.047742753	O2	8	1.230604666	3.219243159	-0.749091473
C21	6	1.472362228	3.444995969	3.716462642	C21	6	2.439406839	1.971406754	3.552181185	C21	6	1.411245354	3.504608164	3.824065670
C22	6	-0.015986630	3.556360739	3.305610539	C22	6	2.537398003	1.370345069	2.129529877	C22	6	0.667553059	2.156491198	3.665208926
C23	6	0.132895007	4.163194320	1.917558441	C23	6	1.622893325	0.166293431	2.284358196	C23	6	-0.677347296	2.648509679	3.158652010
C24	6	1.262585815	3.687702689	1.383768019	C24	6	0.641722063	0.506432780	3.126077593	C24	6	-0.455497815	3.732710677	2.408221404
C25	6	1.893743332	2.747992939	2.400186150	C25	6	0.890957435	1.938259683	3.574414308	C25	6	1.042622352	3.991773700	2.401101067
H2	1	1.445665626	0.688760643	3.069888080	H2	1	0.679219084	3.922287798	2.642552518	H2	1	2.779650450	3.053493600	1.45126484
H3	1	-0.599077041	1.562449095	4.058090665	H3	1	2.341261789	3.264092654	0.991771426	H3	1	2.346309430	1.051262085	2.739468171
H30	1	-0.702497102	4.057418818	3.984976741	H30	1	3.526450650	1.185183283	1.715509761	H30	1	0.651333694	1.472118125	4.510942370
H33	1	2.946586415	2.513117727	2.257216992	H33	1	0.382015794	2.259592836	4.481149784	H33	1	1.365226249	4.984926158	2.094491926
H4	1	1.947234003	4.418904134	3.849110649	H4	1	2.886521596	1.362779577	4.311124727	H4	1	0.980965722	4.131378860	4.607263009
H31	1	1.636208996	2.832516852	4.608791351	H31	1	2.854831317	2.980718294	3.635152310	H31	1	2.488090515	3.396211545	3.986546556
H32	1	-0.618191819	4.772355300	1.429986097	H32	1	1.693968147	-0.734268175	1.688050824	H32	1	-1.613741427	2.118831570	3.283482738
H8	1	1.619740802	3.827074567	0.371023035	H8	1	-0.257233792	-0.056179483	3.342088751	H8	1	-1.177296457	4.265631827	1.801378694
H16	1	-2.445767164	-2.106816301	-1.832624173	H16	1	-3.208721103	-1.102888489	-1.363335608	H16	1	-2.955626372	-1.307923748	-1.740714892
C7	6	0.387013192	-2.825627607	-1.138891956	C7	6	-0.244723910	-2.203020966	-0.928948672	C7	6	-0.287669342	-2.985472697	-1.043625865
C9	6	1.725618686	-3.480548695	-3.520372033	C9	6	0.810421016	-3.45503474	-3.214489743	C9	6	1.176801694	-4.260342062	-3.088951478
C10	6	0.821988587	-1.818056963	-2.013248858	C10	6	0.164483837	-1.442926081	-2.036959076	C10	6	0.388542426	-2.238294286	-2.022496956
C15	6	0.655407608	-4.162001896	-1.448628789	C15	6	-0.092580946	-3.592765854	-0.963198114	C15	6	-0.209380682	-4.381982170	-1.095491933
C16	6	1.304843860	-4.467918263	-2.637186322	C16	6	0.417466751	-4.194970788	-2.104931461	C16	6	0.508075495	-4.992425171	-2.114353138
C17	6	1.485789204	-2.148991658	-3.189724179	C17	6	0.687841386	-2.069935525	-3.163238313	C17	6	1.111706554	-2.871280818	-3.028386537
H7	1	0.673705071	-0.782113219	-1.743157406	H7	1	0.120415960	-0.363671856	-1.998548802	H7	1	0.353141262	-1.158500717	-1.994932125
H9	1	0.357892014	-4.964254123	-0.784776116	H9	1	-0.369860075	-4.211650732	-0.118733259	H9	1	-0.701290487	-4.999318744	-0.353832116
H11	1	1.825963150	-1.363555069	-3.855029408	H11	1	1.012431898	-1.471890922	-4.007059773	H11	1	1.630377649	-2.278243660	-3.773279701
H12	1	2.236466422	-3.760417216	-4.431761764	H12	1	1.211785766	-3.964000377	-4.080832080	H12	1	1.730887544	-4.776581042	-3.861344472
N3	7	1.565880695	-5.887823430	-2.966640851	N3	7	0.562281079	-5.669474116	-2.133767410	N3	7	0.570591411	-6.473410054	-2.158716219
O3	8	2.131768804	-6.128212557	-4.024238688	O3	8	1.003888199	-6.174831082	-3.156452931	O3	8	1.229733206	-6.983216008	-3.054204274
O4	8	1.198249111	-6.733670050	-2.162289402	O4	8	0.230387662	-6.290895844	-1.133219180	O4	8	-0.040506829	-7.092200969	-1.298104404

Table 3.9 The unfolded GS structure (left) and the folded GS structure (middle) and the TS structure (right) and XYZ coordinates of rotor 1(**quinoline**).



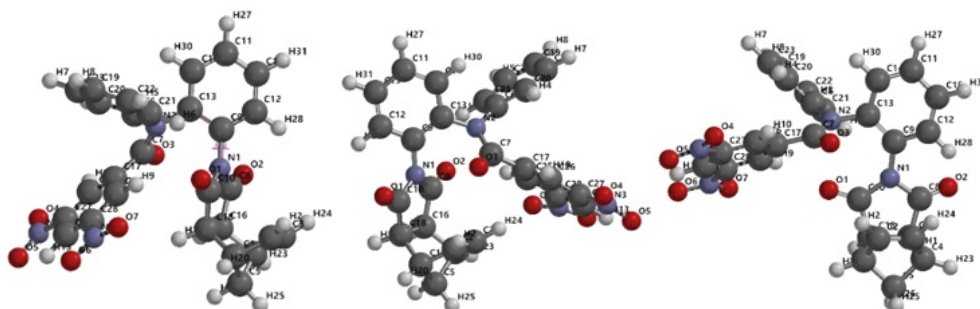
H1	1	-1.461766056	-1.339953128	-4.829619580	H1	1	-2.115322992	-2.100889978	-4.352671966	H1	1	-2.235142035	-1.609786756	-4.576918711
C1	6	-1.180452882	-1.035288621	-3.825918915	C1	6	-1.806242691	-1.820691579	-3.349956657	C1	6	-1.882931953	-1.361163114	-3.580196975
C4	6	-0.445240916	-0.257888149	-1.237555085	C4	6	-0.989967567	-1.100385114	-0.766183476	C4	6	-0.907352105	-0.644535023	-0.977349646
C2	6	-0.949533188	-2.031337323	-2.845297110	C2	6	-0.678703080	-0.978253565	-3.189181821	C2	6	-0.589628176	-1.756632036	-3.177685945
C6	6	-1.053831171	0.294797020	-3.510010669	C6	6	-2.500920058	-2.268097103	-2.254396701	C6	6	-2.675922092	-0.698369422	-2.687004661
C5	6	-0.680616142	0.685880791	-2.205177411	C5	6	-2.086057659	-1.906753956	-0.955245604	C5	6	-2.195198446	-0.351933184	-1.409818320
C3	6	-0.584718707	-1.644084664	-1.520106557	C3	6	-0.259814912	-0.590696262	-1.878427438	C3	6	-0.086428379	-1.445749310	-1.865013112
H6	1	-1.236631509	1.054134139	-4.262456492	H6	1	-3.370077519	-2.905139701	-2.378309665	H6	1	-3.688984482	-0.412207694	-2.950880971
H5	1	-0.577105488	1.734876844	-1.954144877	H5	1	-2.633765799	-2.262720694	-0.090890832	H5	1	-2.863076220	0.200053422	-0.775595622
C9	6	-0.843735280	-4.314999703	-2.091989381	C9	6	1.122498121	0.363471288	-4.053165247	C9	6	1.459129354	-2.960723517	-3.615858017
C10	6	-1.071060456	-3.418808924	-3.104505499	C10	6	0.060370408	-0.471010838	-4.285237651	C10	6	0.237831420	-2.513506740	-4.043697109
H11	1	-0.926489599	-5.384482752	-2.252403769	H11	1	1.710962635	0.771982068	-4.867198955	H11	1	2.111098151	-3.546569094	-4.254775089
H14	1	-1.343774219	-3.755506693	-4.100680522	H14	1	-0.227493550	-0.747911181	-5.295503586	H14	1	-0.125187754	-2.741624591	-5.042016757
N1	7	-0.373643679	-2.542873654	-0.521910615	N1	7	0.787305628	0.248667468	-1.665363858	N1	7	1.104265192	-1.940438252	-1.470441959
C8	6	-0.500505993	-3.818504618	-0.810723098	C8	6	1.438753701	0.697211152	-2.714437983	C8	6	1.836057314	-2.652357093	-2.290835269
H13	1	-0.326083343	-4.515566265	0.006597055	H13	1	2.270213183	1.369398603	-2.511618538	H13	1	2.780435237	-3.017455176	-1.889532747
N2	7	-0.079957992	0.128341244	0.077745477	N2	7	-0.598235261	-0.743388629	0.550557902	N2	7	-0.502685091	-0.157382669	0.334753147
C11	6	1.216814218	-0.042358490	0.590795916	C11	6	0.629702679	-1.132426995	1.116889158	C11	6	0.707140336	-0.410325822	1.110173719
H12	1	1.190836535	0.415899617	2.035252758	H12	6	0.727681463	-0.471388445	2.476906532	H12	6	0.529672006	0.193588574	2.485445646
C13	6	-0.268052233	0.843276371	2.310003009	C13	6	-0.597267188	0.301271702	2.662287631	C13	6	-0.754751784	1.008032239	2.432354328
C14	6	-1.008260847	0.614704260	1.008035707	C14	6	-1.379022555	0.074239823	1.383590226	C14	6	-1.274154033	0.832324275	1.027738014
O1	8	-2.171940210	0.825333381	0.775700942	O1	8	-2.469187387	0.504484125	1.101761183	O1	8	-2.199676157	1.474363879	0.591517402
O2	8	2.158628626	-0.447463641	-0.039290918	O2	8	1.424225369	-1.868934385	0.593906021	O2	8	1.726551442	-0.930594708	0.773714344
C21	6	1.195886739	2.269013863	3.525711251	C21	6	1.168479672	1.523539509	3.690533892	C21	6	0.810614033	2.139255521	3.818571682
C22	6	-0.127485361	2.356395445	2.728586445	C22	6	-0.120131908	1.790693492	2.876577670	C22	6	-0.282079901	2.470586737	2.772602376
C23	6	0.348852520	3.114023566	1.498190511	C23	6	0.482269663	2.243333317	1.555883471	C23	6	0.587375263	2.924786860	1.608824465
C24	6	1.610582434	2.743281009	1.256300714	C24	6	1.623190562	1.571203753	1.378152030	C24	6	1.716111997	2.207511320	1.643847402
C25	6	2.008390233	1.732691094	2.322251455	C25	6	1.817532214	0.661384047	2.580697242	C25	6	1.628608171	1.265774275	2.836133219
H2	1	1.540754267	-0.398830190	2.671557621	H2	1	0.905709471	-1.237035785	3.234115787	H2	1	0.524939810	-0.614284785	3.220405907
H3	1	-0.757500039	0.271685564	3.100513310	H3	1	-1.193316655	-0.037682406	3.512040025	H3	1	-1.530085041	0.678582106	3.128478914
H30	1	-1.007196668	2.751296436	3.233235076	H30	1	-0.882620526	2.431931895	3.314664917	H30	1	-1.091848031	3.135700647	3.065932436
H33	1	3.074857453	1.562492730	2.456463331	H33	1	2.822940564	0.279545181	2.747989858	H33	1	2.564514467	0.832458339	3.182420282
H4	1	1.544600294	3.243451782	3.873408377	H4	1	1.730968894	2.435500195	3.899918611	H4	1	1.355932138	3.023262779	4.153368562
H31	1	1.153469021	1.571348009	4.368096151	H31	1	0.993885045	0.977035832	4.623088094	H31	1	0.435112175	1.586702379	4.686173790
H32	1	-0.284583028	3.735897326	0.877417473	H32	1	-0.024736882	2.869900117	0.833026506	H32	1	0.265279508	3.607597598	0.832839101
H8	1	2.216492669	2.999126323	0.395927923	H8	1	2.216194920	1.528613051	0.475203223	H8	1	2.504463772	2.185058087	0.902326281

Table 3.10 The unfolded GS structure (left) and the folded GS structure (middle) and the TS structure (right) and XYZ coordinates of rotor 1(imidazole).



C1	6	0.516630065	2.301424444	-2.562779589	C1	6	1.885301295	0.207453360	-2.516863808	C1	6	1.094751685	1.124554681	-2.893781126
C2	6	-0.992124298	2.116833082	-2.512703226	C2	6	1.596264177	1.347735917	-1.550232043	C2	6	-0.310035952	1.656712722	-2.648800566
C3	6	-1.261867872	0.869805013	-2.913201968	C3	6	0.353306155	1.780582757	-1.786854744	C3	6	-1.171586022	0.724377472	-3.069393321
C4	6	0.058792678	0.192339793	-3.243632766	C4	6	-0.223158588	0.928243961	-2.907732792	C4	6	-0.364048976	-0.444684273	-3.615305517
C5	6	0.862058151	1.403052363	-3.776570177	C5	6	1.055340630	0.667154361	-3.742434585	C5	6	0.859107432	0.310029458	-4.189797270
C16	6	0.813055218	-0.027979681	-1.878971586	C16	6	-0.438708983	-0.525607828	-2.335344812	C16	6	0.338540309	-1.136611980	-2.387378536
C18	6	1.122855825	1.412762081	-1.411696361	C18	6	1.002837687	-1.017497923	-2.072412457	C18	6	1.295853713	-0.062287565	-1.879174366
C8	6	-0.029669655	-0.636889113	-0.779788143	C8	6	-1.146631116	-0.615572335	-0.999051402	C8	6	-0.567983168	-1.456087260	-1.226128898
N1	7	-0.166944140	0.330514145	0.235897206	N1	7	-0.228832284	-1.130166627	-0.065499123	N1	7	-0.125676884	-0.746517393	-0.061175887
C10	6	0.448590388	1.557680319	-0.061710423	C10	6	1.056616053	-1.356959577	-0.596245725	C10	6	0.831577173	0.252237562	-0.475803434
O1	8	0.423481110	2.527853765	0.652705270	O1	8	1.997533528	-1.752050885	0.042554191	O1	8	1.182602026	1.215783233	0.138042797
O2	8	-0.526291013	-1.732493437	-0.747135654	O2	8	-2.286973523	-0.321418403	-0.742763611	O2	8	-1.520925870	-2.189733638	-1.319109058
C9	6	-0.853154975	0.066014345	1.453321110	C9	6	-0.564810131	-1.389347494	1.294920402	C9	6	-0.662925312	-0.985334517	1.268194808
C11	6	-2.251123902	-0.530563222	3.784594426	C11	6	-1.233903771	-1.923034357	3.947408177	C11	6	-1.814026941	-1.705678542	3.788955363
C12	6	-2.011890216	0.768373546	1.768550795	C12	6	-0.748587431	-2.702849383	1.718406597	C12	6	-1.544261616	-2.077415879	1.422742590
C13	6	-0.372477609	-0.923970419	2.321695851	C13	6	-0.710482767	-0.338812747	2.203835703	C13	6	-0.349628119	-0.270791224	2.456330650
C14	6	-1.082252426	-1.222521175	3.482865267	C14	6	-1.050143707	-0.609202663	3.527669304	C14	6	-0.936683111	-0.642256205	3.673346884
C15	6	-2.710951045	0.472597987	2.933458723	C15	6	-1.078541786	-2.971000087	3.042425715	C15	6	-2.104568029	-2.429329795	2.641437685
H20	1	0.881617707	3.326438338	-2.563623194	H20	1	2.931516233	-0.047409532	-2.675280921	H20	1	1.900636601	1.854891689	-2.883629621
H23	1	0.006663680	-0.701658790	-3.862086359	H23	1	-1.098006722	1.323620640	-3.420688289	H23	1	-0.891244599	-1.140695285	-4.264805654
H1	1	1.702198659	-0.644997054	-2.021600048	H1	1	-0.986803516	-1.134447963	-3.057946206	H1	1	0.822323202	-2.063929546	-2.702715207
H3	1	2.189063039	1.614607877	-1.294184701	H3	1	1.272522078	-1.907872982	-2.645112378	H3	1	2.340971767	-0.377414052	-1.838650897
H2	1	-1.689167010	2.842206044	-2.111570117	H2	1	2.248984342	1.660055810	-0.746325050	H2	1	-0.536786461	2.569180611	-2.112966792
H24	1	-2.221447549	0.367679938	-2.902231145	H24	1	-0.203045715	2.516462480	-1.223507471	H24	1	-2.248275182	0.722581726	-2.953756840
H25	1	0.464499681	1.792147048	-4.716253198	H25	1	1.448370657	1.574979517	-4.203430547	H25	1	0.602517670	0.939292782	-5.044094354
H26	1	1.932869437	1.204621699	-3.885070829	H26	1	0.932389042	-0.108062858	-4.506338861	H26	1	1.694939857	-0.344964895	-4.456302532
H27	1	-2.796297999	-0.768435220	4.691674354	H27	1	-1.495344946	-2.127639982	4.979820733	H27	1	-2.245179542	-1.966438070	4.749099341
H28	1	-2.362672487	1.531947680	1.085072659	H28	1	-0.627845882	-3.506980705	1.001686222	H28	1	-1.815834925	-2.658522862	0.561450325
H30	1	-0.698853412	-1.987517916	4.148581775	H30	1	-1.160782223	0.220508679	4.216393376	H30	1	-0.658206993	-0.056849926	4.541925484
H31	1	-3.617446874	1.018380293	3.171136757	H31	1	-1.217432924	-3.997122626	3.364917835	H31	1	-2.775429386	-3.281412847	2.676996483
N2	7	0.826317902	-1.619529370	2.015971140	N2	7	-0.479541281	1.005757177	1.794788720	N2	7	0.553083050	0.822872788	2.585887542
C7	6	0.971579617	-2.982987920	1.823352439	C7	6	0.701537684	1.706659051	1.963845668	C7	6	0.216776587	2.159194379	2.644328684
C17	6	2.279980547	-3.166027918	1.471530615	C17	6	0.439293903	2.973157623	1.517111660	C17	6	1.393814439	2.822305249	2.866435889
N3	7	2.951056234	-1.962238184	1.440999003	N3	7	-0.862524062	3.073959558	1.079834374	N3	7	2.441418189	1.935527539	2.957246727
C20	6	2.058004125	-1.062043108	1.765697350	C20	6	-1.385965810	1.884771200	1.260141214	C20	6	1.905002909	0.752388302	2.786880058
H5	1	0.131074459	-3.653111589	1.898967751	H5	1	1.579172043	1.226127803	2.363841128	H5	1	-0.800516640	2.484663292	2.499508992
H7	1	2.778330708	-4.094030326	1.231929022	H7	1	1.110822653	3.817621917	1.476017656	H7	1	1.547731475	3.886828770	2.964300101
H11	1	2.225913250	-0.000285360	1.866807969	H11	1	-2.383740992	1.568211876	0.998446151	H11	1	2.422175699	-0.196466553	2.799659527

Table 3.11 The unfolded GS structure (left) and the folded GS structure (middle) and the TS structure (right) and XYZ coordinates of rotor **1**(N(COPh(NO₂)₂)Ph).



C1	6	0.907849285	-0.176746258	-3.771240058	C1	6	-2.159455719	1.260501438	-3.679216680	C1	6	-0.219472452	-0.002780082	-4.010313355
C2	6	0.211799173	-1.454097118	-4.213670737	C2	6	-2.631156186	0.905132041	-2.279629284	C2	6	-1.421051380	-0.808052735	-3.547389546
C3	6	1.067838357	-2.465469740	-4.038607537	C3	6	-2.068319719	-0.260270831	-1.950764830	C3	6	-1.222126302	-2.076298654	-3.921110627
C4	6	2.358223550	-1.888810685	-3.472653191	C4	6	-1.197425481	-0.709323614	-3.111726393	C4	6	0.113868753	-2.147419767	-4.641454570
C5	6	2.367792422	-0.507509398	-4.173250029	C5	6	-2.027413131	-0.155645244	-4.297645029	C5	6	0.134672144	-0.752814754	-5.316055717
C16	6	2.041190046	-1.427524636	-2.002189275	C16	6	0.032045889	0.281237400	-3.211755195	C16	6	1.255488771	-1.903355034	-3.567208528
C18	6	1.051327101	-0.261911448	-2.208005358	C18	6	-0.636104104	1.624684712	-3.561475414	C18	6	1.004320076	-0.465684509	-3.119915198
C8	6	1.298699572	-2.444386632	-1.160351703	C8	6	0.837526377	0.547844184	-1.957216987	C8	6	1.135869532	-2.727012317	-2.312846872
N1	7	0.030993661	-1.889318465	-0.846409378	N1	7	0.617951248	1.872926765	-1.560115233	N1	7	0.560408902	-1.914452988	-1.270696298
C10	6	-0.206401989	-0.664883668	-1.470848094	C10	6	-0.272327443	2.563271228	-2.429561141	C10	6	0.659841822	-0.549963232	-1.654066882
O1	8	-1.246009338	-0.047176100	-1.413178486	O1	8	-0.628281066	3.701068099	-2.285154788	O1	8	0.515909417	0.424188682	-0.962462586
O2	8	1.661182142	-3.540697266	-0.833801118	O2	8	1.574848821	-0.230935968	-1.396422566	O2	8	1.477895317	-3.874743799	-2.203836479
C9	6	-0.881129556	-2.521224927	0.043441320	C9	6	1.311005537	2.540118951	-0.502121918	C9	6	0.034033505	-2.517549336	-0.061484294
C11	6	-2.663216738	-3.793651666	1.764350720	C11	6	2.740338061	3.972096278	1.433483842	C11	6	-0.794419784	-4.025587461	2.203684370
C12	6	-1.349269622	-3.798498513	-0.252340719	C12	6	1.927731037	3.754035382	-0.816513029	C12	6	-0.343896073	-3.870731244	-0.155013350
C13	6	-1.285704799	-1.880945104	1.224823465	C13	6	1.406772888	2.042679283	0.808627761	C13	6	-0.146560943	-1.900084510	1.198043268
C14	6	-2.185360002	-2.525525482	2.073516172	C14	6	2.129155155	2.770348818	1.758523123	C14	6	-0.529362354	-2.671643911	2.300437801
C15	6	-2.239523906	-4.436461311	0.603670364	C15	6	2.635706136	4.469630420	0.137256428	C15	6	-0.738529283	-4.613895850	0.946518476
H20	1	0.475857820	0.759347329	-4.119134884	H20	1	-2.746127853	2.000291400	-4.220161659	H20	1	-0.339010588	1.077752000	-4.051605759
H23	1	3.245874910	-2.512705846	-3.554396010	H23	1	-0.908055016	-1.758828714	-3.132041335	H23	1	0.289636227	-3.022157381	-5.265025350
H1	1	2.952241553	-1.142113370	-1.474118036	H1	1	0.724323051	-0.080308632	-3.975407561	H1	1	2.231755084	-2.083483420	-4.017574961
H3	1	1.403675333	0.689202949	-1.803048652	H3	1	-0.272829666	2.059749896	-4.495729820	H3	1	1.852539567	0.207050923	-3.248721097
H2	1	-0.83035116	-1.517082241	-4.501499378	H2	1	-3.209676891	1.552074670	-1.634202399	H2	1	-2.208390258	-0.430950853	-2.906804844
H24	1	0.868337846	-3.523247631	-4.157986894	H24	1	-2.138413242	-0.764704663	-1.001420169	H24	1	-1.828155933	-2.935198533	-3.659459416
H25	1	2.498509720	-0.583745378	-5.254161415	H25	1	-2.990022153	-0.658469927	-4.408332085	H25	1	-0.633486570	-0.647161654	-6.084468681
H26	1	3.105497241	0.187952780	-3.761091341	H26	1	-1.494398107	-0.171483030	-5.253966190	H26	1	1.109790287	-0.478152958	-5.730231885
H27	1	-3.36045341	-4.282727035	2.436074823	H27	1	3.289448124	4.519512423	2.191558549	H27	1	-1.080081950	-4.596136707	3.080608194
H28	1	-1.009795675	-4.279094972	-1.161030790	H28	1	1.840804697	4.134838002	-1.825260671	H28	1	-0.302724879	-4.372353637	-1.106220996
H30	1	-2.506224616	-2.020557583	2.977002587	H30	1	2.204886733	2.373571725	2.763963732	H30	1	-0.643241295	-2.159943457	3.249152495
H31	1	-2.603755491	-5.428858942	0.361732427	H31	1	3.106036643	5.407812794	-0.135081724	H31	1	-0.996265046	-5.659068491	0.810814510
N2	7	-0.832543447	-0.564527326	1.546349675	N2	7	-0.830404189	0.797690362	1.216293445	N2	7	-0.080848455	-0.490558167	1.460313756
C7	6	0.524457182	-0.289883723	1.549630767	C7	6	-0.524474073	0.582988778	1.017640706	C7	6	-1.138952406	0.264123701	0.983890069
O3	8	1.379405043	-1.156398962	1.572697595	O3	8	-1.316167841	1.453947674	0.764784428	O3	8	-2.096839598	-0.245565990	0.430988096
C6	6	-1.806632979	0.389603481	1.990747551	C6	6	1.648947114	-0.092247926	1.994443305	C6	6	0.881341879	-0.040031576	2.111956481
C19	6	-3.686549076	2.255176308	2.848329364	C19	6	3.217215281	-1.822457223	3.510572088	C19	6	2.780521528	0.806432382	4.272645140
C20	6	-1.644631028	1.024720977	3.222044084	C20	6	1.282738961	-0.396692555	3.306285039	C20	6	0.477670628	0.616767168	3.576711398
C21	6	-2.921304166	0.664600898	1.195117559	C21	6	2.809754707	-0.635234545	1.442770158	C21	6	2.236343810	-0.294801855	2.190852519
C22	6	-3.856702086	1.595907841	1.630261790	C22	6	3.590237080	-1.497147289	2.206036779	C22	6	3.179532018	0.124023199	3.123254454
C23	6	-2.579452729	1.967733214	3.642512117	C23	6	2.061952842	-1.270791564	4.059174139	C23	6	1.427523020	1.051926955	4.495796505
H4	1	-0.792134420	0.776703825	3.845216198	H4	1	0.391320449	0.052640403	3.730906303	H4	1	-0.578722123	0.782795887	3.756272498
H6	1	-3.020652627	0.173737034	0.235185772	H6	1	3.062415141	-0.400859274	0.417379343	H6	1	2.536708259	-0.818607834	1.290174350
H5	1	-4.715618197	1.819359960	1.006328496	H5	1	4.486490230	-1.928884036	1.773320013	H5	1	4.231387540	-0.074234146	2.947126105
H7	1	-2.446469768	2.466643673	4.596560877	H7	1	1.769333797	-1.511345540	5.075758069	H7	1	1.105392210	1.568724827	5.393693437
H8	1	-4.417190441	2.986648871	3.176985152	H8	1	3.826682348	-2.501432514	4.097384633	H8	1	3.519862130	1.138283774	4.993542408
C17	6	0.940497683	1.151460628	1.407450476	C17	6	-1.010601809	-0.835330041	1.248163836	C17	6	-1.087035310	1.762675172	1.136166290
C24	6	1.978481923	3.729683542	0.979708794	C24	6	-2.169853825	-3.393874375	1.351857333	C24	6	-1.184542739	4.574132683	1.225926929
C25	6	0.267408632	2.044519266	0.570507383	C25	6	-0.382001000	-1.911992262	0.616839172	C25	6	0.078328191	2.509232858	0.960694596
C26	6	2.140871599	1.531215024	2.006254719	C26	6	-2.226971002	-1.025909880	1.901956240	C26	6	-2.301539009	2.415903005	1.332910562
C27	6	2.627086914	2.813949014	1.795980878	C27	6	-2.770993703	-2.302429276	1.960242483	C27	6	-2.325931387	3.803988832	1.390908663
C28	6	0.804599953	3.308945309	0.370961806	C28	6	-0.984236384	-3.161805259	0.670373011	C28	6	0.004419072	3.893636994	1.002370717
H9	1	-0.637944181	1.763516552	0.050909229	H9	1	0.528615649	-1.778577720	0.048976393	H9	1	1.023440350	2.032068963	0.759347256
H10	1	2.693416050	0.826530833	2.612377660	H10	1	-2.752826606	-0.189427992	2.341555141	H10	1	-3.217059559	1.847297116	1.423007021
H13	1	2.376059805	4.719929205	0.814273453	H13	1	-2.614923442	-4.377205102	1.393408849	H13	1	-1.221694331	5.652732194	1.258493161
N3	7	3.898654157	3.215377858	2.447565703	N3	7	-4.056494920	-2.509426453	2.674102575	N3	7	-3.622402813	4.48941973	1.615644163
O4	8	4.441471181	2.393130595	3.169540218	O4	8	-4.547032798	-1.541809620	3.235726519	O4	8	-4.606518891	3.785643631	1.789733162
O5	8	4.315805163	4.340242933	2.217128089	O5	8	-4.535420757	-3.633222202	2.653022257	O5	8	-3.620638743	5.711311786	1.613250812
N4	7	0.104509994	4.242185716	-0.548198374	N4	7	-0.359388470	-4.293115024	-0.058743336	N4	7	1.243855209	4.678188128	0.785140051
O6	8	0.560501070	5.370945377	-0.654336551	O6	8	-0.782803562	-5.414776337	0.176648622	O6	8	1.163180621	5.893866693	0.881068702
O7	8	-0.875479193	3.816810433	-1.139689271	O7	8	0.529507786	-4.024692496	-0.853368879	O7	8	2.263964640	4.058587158	0.522828934

3.5.7 B-value calculations

Most B-values were gotten from the previous papers.^{1,4,37} But some groups were not reported in the literature, which had been calculated using the DFT method from Mazzanti (B3LYP/6-31G*) without thermodynamic corrections.³⁷ B-values were consistently calculated (B3LYP/6-31G*) using Spartan18 and listed. Calculated structures and XYZ coordinates were listed from **Table 3.12-3.18**.

The experimental barriers did not correlate with the size of the R¹-groups as measured by the steric B-value parameter. Basically, the smaller steric size of a rotor did not mean a smaller experimental barrier of the rotor because the lower barrier was due to the nitrogen pnictogen bonding interactions (**Figure 3.31**).

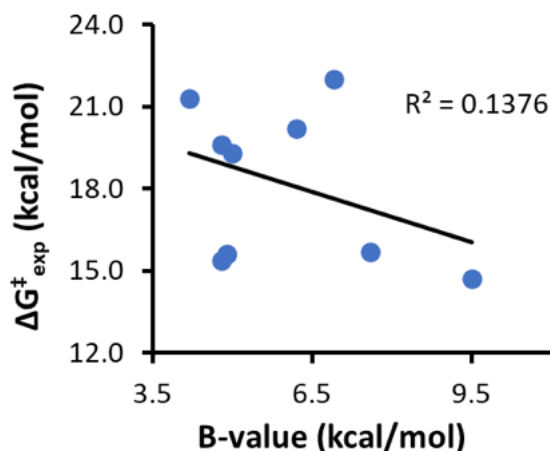
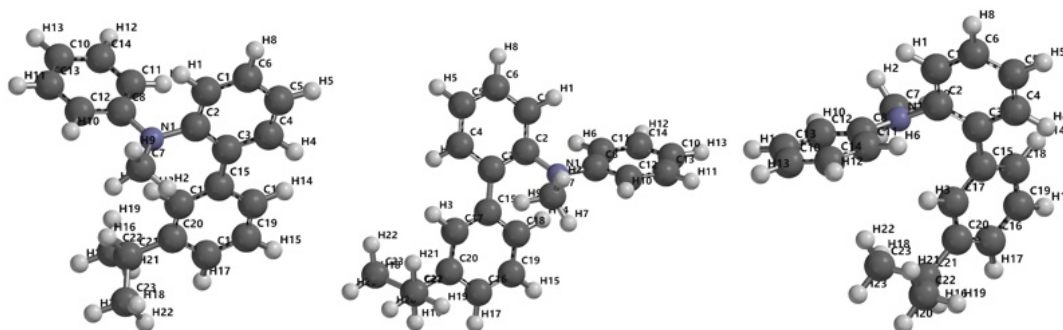


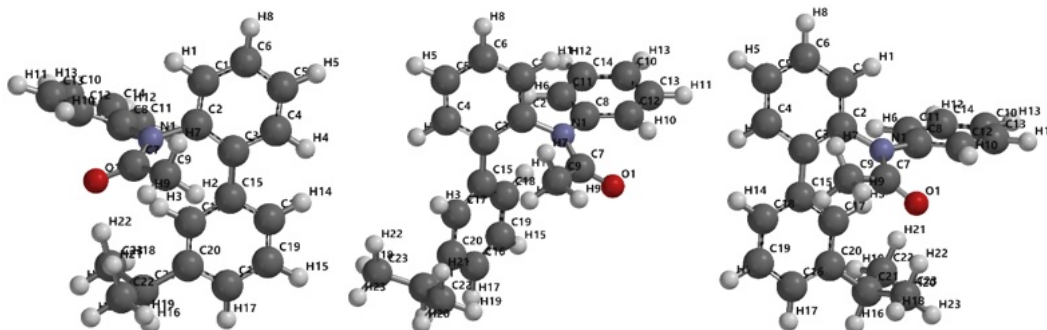
Figure 3.31 Plot showing the poor correlation between $\Delta G^\ddagger_{\text{exp}}$ and B-value.

Table 3.12 The TS structure (N(CH₃)Ph closer to H3, left), the unfolded GS structure (N(CH₃)Ph closer to H14, middle) and the GS structure (N(CH₃)Ph closer to H3, left) and the XYZ coordinates.



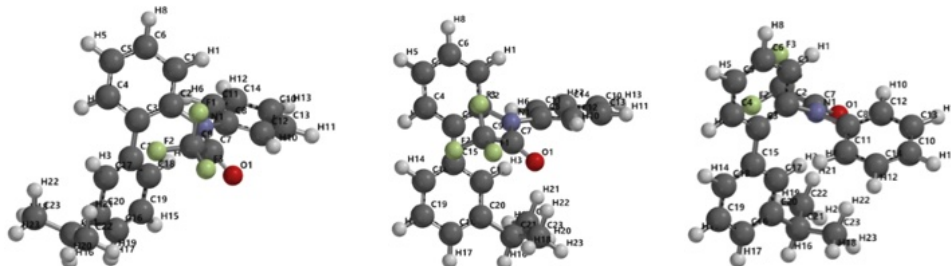
H1	1	1.905513676	3.421813460	0.952575703	H1	1	-3.826937868	0.392833829	-0.957857906	H1	1	1.574574309	3.487874232	-1.026363831
C1	6	1.922469146	2.528807250	1.571201177	C1	6	-3.145801863	0.748419619	-0.190261623	C1	6	2.062236009	2.755348174	-0.389479007
C4	6	1.900665783	0.243646545	3.094135233	C4	6	-1.369111052	1.661133857	1.731883568	C4	6	3.304273240	0.846473920	1.191410986
C2	6	1.080469496	1.468203860	1.203659938	C2	6	-1.826196602	0.274440981	-0.195385774	C2	6	1.565628514	1.444607243	-0.378080046
C6	6	2.750947326	2.460958256	2.683195590	C6	6	-3.579513447	1.658429149	0.770311286	C6	6	3.159442241	3.115722952	0.388831812
C5	6	2.721870856	1.302997998	3.458741042	C5	6	-2.682815848	2.123830368	1.733133863	C5	6	3.788717257	2.152086751	1.178144281
C3	6	1.067332614	0.258396101	1.951267909	C3	6	-0.914887085	0.724963506	0.787718705	C3	6	2.184007565	0.465169694	0.432885090
H5	1	3.338873650	1.218166640	4.349232588	H5	1	-3.005797026	2.835657621	2.487974249	H5	1	4.647763926	2.416833012	1.788692559
H4	1	1.910972458	-0.628348178	3.734412809	H4	1	-0.677716502	2.002131436	2.497589497	H4	1	3.778764956	0.102995369	1.825902440
H8	1	3.390388428	3.298528565	2.947533642	H8	1	-4.607077615	2.011870788	0.756902135	H8	1	3.527858414	4.137853855	0.367583774
N1	7	0.211455414	1.711836736	0.083058377	N1	7	-1.399561663	-0.616102305	-1.228875042	N1	7	0.471902004	1.102743464	-1.232012337
C8	6	0.769992201	1.954170743	-1.182431838	C8	6	-2.091057148	-1.806921998	-1.479373765	C8	6	-0.768462085	1.728506356	-1.101005001
C10	6	1.867566649	2.321274249	-3.765506338	C10	6	-3.409819865	-4.272439391	-1.934722566	C10	6	-3.325183361	2.915344612	-0.791110285
C11	6	1.994065264	1.352664729	-1.543929214	C11	6	-2.810060483	-2.451451532	-0.447717362	C11	6	-1.134382917	2.370905538	0.103839121
C12	6	0.112185396	2.746939250	-2.142694449	C12	6	-2.049813585	-2.429457830	-2.743315072	C12	6	-1.716864516	1.699379354	-2.145738268
C13	6	0.658687500	2.918493006	-3.415957071	C13	6	-2.699122553	-3.645694530	-2.956811455	C13	6	-2.973416544	2.281717848	-1.982302975
C14	6	2.528506945	1.538901144	-2.813679884	C14	6	-3.458148347	-3.659478287	-0.679554681	C14	6	-2.389724293	2.952753812	0.246224196
H6	1	2.514965066	0.730737114	-0.823553934	H6	1	-2.853290583	-1.997694957	0.536823763	H6	1	-0.428205820	2.410421612	0.925926492
H10	1	-0.822792882	3.239722132	-1.901247681	H10	1	-1.521285792	-1.963905117	-3.567193342	H10	1	-1.474077945	1.227227947	-3.090788123
H11	1	0.127592626	3.536351636	-4.135962150	H11	1	-2.649906334	-4.100511484	-3.943354541	H11	1	-3.680790030	2.240716830	-2.807173766
H12	1	3.471620010	1.059270854	-3.063331856	H12	1	-4.000894086	-4.130624346	0.136390360	H12	1	-2.639464299	3.437406046	1.187083440
H13	1	2.288624458	2.460853486	-4.756858303	H13	1	-3.915540214	-5.217499370	-2.109981654	H13	1	-4.304096527	3.370223768	-0.672120458
C15	6	0.277630381	-0.977570192	1.614275626	C15	6	0.496291832	0.250332816	0.856152135	C15	6	1.698214928	-0.942131024	0.510472385
C16	6	-1.173652088	-3.351050540	1.016731089	C16	6	3.164510604	-0.587321369	1.062956729	C16	6	0.812717927	-3.595126200	0.720960407
C17	6	-0.633155516	-1.052298856	0.540086130	C17	6	1.540617504	1.179290445	0.973136296	C17	6	0.343856256	-1.236286744	0.731095913
C18	6	0.440472406	-2.157703509	2.370441667	C18	6	0.812771394	-1.118957489	0.841672241	C18	6	2.606999654	-2.007327575	0.399699514
C19	6	-0.273354684	-3.316246208	2.078498335	C19	6	2.138855075	-1.528440730	0.947765796	C19	6	2.163821344	-3.324382755	0.504680082
C20	6	-1.356031466	-2.209364414	0.229320215	C20	6	2.881370154	0.782471819	1.076105392	C20	6	-0.117284951	-2.553792454	0.837887530
H3	1	-0.772752086	-0.187847596	-0.091320948	H3	1	1.294703336	2.238552979	0.967994426	H3	1	-0.360024069	-0.416890290	0.834093504
H14	1	1.140452092	-2.203984914	3.195017152	H14	1	0.019833262	-1.855240046	0.758626546	H14	1	3.657681526	-1.799265643	0.215744133
H15	1	-0.116409507	-4.203217655	2.687432539	H15	1	2.376834200	-2.589175249	0.946138702	H15	1	2.873696857	-4.142668101	0.413815552
H17	1	-1.723706021	-4.263981525	0.801572281	H17	1	4.197050776	-0.921025784	1.141329590	H17	1	0.474030657	-4.625929367	0.800378255
C21	6	-2.324967746	-2.203814090	-0.946755766	C21	6	4.006120982	1.805933449	1.168466854	C21	6	-1.595435645	-2.855391220	1.054396924
H16	1	-2.275312164	-1.204158321	-1.399205288	H16	1	4.935725644	1.244961553	1.337138156	H16	1	-1.679793355	-3.937241117	1.227561283
C22	6	-1.923114050	-3.220315836	-2.031583323	C22	6	4.170119279	2.582023836	-0.153136867	C22	6	-2.168830594	-2.144195485	2.293696511
H19	1	-0.905737810	-3.033464533	-2.391744752	H19	1	4.334841074	1.899574555	-0.994147078	H19	1	-1.590682259	-2.383404950	3.192997969
H20	1	-2.605585335	-3.160122040	-2.887758826	H20	1	5.023022633	3.269246883	-0.097730675	H20	1	-3.207768404	-2.450796693	2.463182517
H21	1	-1.960290211	-4.247746495	-1.649451026	H21	1	3.275430836	3.175968434	-0.375488035	H21	1	-2.164301778	-1.055145343	2.169465706
C23	6	-3.778960326	-2.431005428	-0.490865495	C23	6	3.828405392	2.770767965	2.354811451	C23	6	-2.424964725	-2.524519567	-0.202394393
H18	1	-4.078209601	-1.695927371	0.264495328	H18	1	3.729943022	2.225435693	3.299799230	H18	1	-2.045366993	-3.061537760	-1.079034772
H22	1	-3.908848745	-3.429033307	-0.055021526	H22	1	2.935302095	3.395181324	2.233284751	H22	1	-2.394983060	-1.451799437	-0.425900475
H23	1	-4.467360139	-2.348302754	-1.340609940	H23	1	4.690540493	3.443439928	2.436930181	H23	1	-3.474811518	-2.807819935	-0.058255797
C7	6	-1.066058964	2.325521133	0.427161514	C7	6	-0.520553185	-0.062631580	-2.251096713	C7	6	0.775917470	0.324875395	-2.425114975
H2	1	-1.389959057	1.939019530	1.395833381	H2	1	-1.076970018	0.332544618	-3.116143549	H2	1	0.892946754	0.957553434	-3.318892852
H7	1	-1.828739877	2.064241644	-0.314898884	H7	1	0.180511938	-0.825464609	-2.605983593	H7	1	-0.013850304	-0.409865413	-2.617889013
H9	1	-1.008321458	3.423987858	0.494489120	H9	1	0.059077237	0.750600552	-1.812904610	H9	1	1.707714185	-0.219278143	-2.262996000

Table 3.13 The GS structure (N(COCH₃)Ph closer to H3, left) and the unfolded GS structure (N(COCH₃)Ph closer to H14, middle) and the TS structure (N(COCH₃)Ph closer to H3, right) XYZ coordinates.



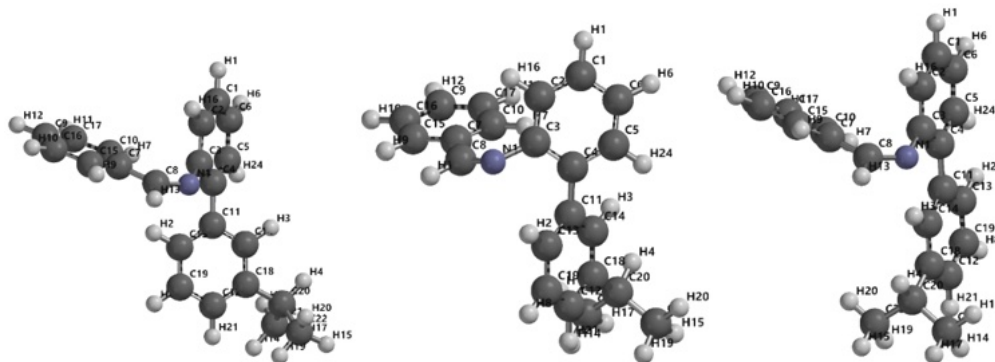
H1	1	0.951326319	3.571065133	-1.512479102	H1	1	1.464257979	3.437485534	-1.234581251	H1	1	0.077381646	3.787516500	0.998331947
C1	6	0.989423745	3.029199388	-0.571918265	C1	6	1.946067617	2.764674224	-0.531247018	C1	6	0.434765652	2.987769984	1.640561055
C4	6	1.067361026	1.604374136	1.799107056	C4	6	3.137694509	1.005491397	1.242146472	C4	6	1.306020438	0.903555124	3.202485871
C2	6	0.428670256	1.746708178	-0.520356760	C2	6	1.435310338	1.467584147	-0.398647539	C2	6	0.215512710	1.670898674	1.215918427
C6	6	1.585093846	3.599441738	0.548577532	C6	6	3.044138145	3.184433094	0.212795331	C6	6	1.080870127	3.275883796	2.835604295
C5	6	1.625057415	2.878002819	1.742701627	C5	6	3.642846562	2.294696874	1.106161427	C5	6	1.511604379	2.211107439	3.624587855
C3	6	0.451848488	1.006283947	0.682692885	C3	6	2.025830949	0.553749457	0.504973966	C3	6	0.670990340	0.563943269	1.985043365
H5	1	2.080310528	3.308499912	2.630368245	H5	1	4.495841310	2.605819425	1.702879233	H5	1	2.012878336	2.392243342	4.571693074
H4	1	1.078102029	1.055315267	2.735977190	H4	1	3.591720276	0.327324079	1.958345102	H4	1	1.656601497	0.117421676	3.857413452
H8	1	2.015494366	4.595037483	0.488282001	H8	1	3.427391863	4.194092336	0.095736507	H8	1	1.237318096	4.305045967	3.145195262
N1	7	-0.162453419	1.232341287	-1.730809974	N1	7	0.290931381	1.123450905	-1.204978775	N1	7	-0.486922681	1.552033932	-0.042545329
C7	6	0.458718613	0.196905647	-2.443815201	C7	6	0.393188052	0.179166056	-2.235504720	C7	6	-1.865724730	1.342467057	-0.080889648
O1	8	-0.069892031	-0.342415584	-3.403039485	O1	8	-0.589408844	-0.269289888	-2.806900994	O1	8	-2.459563596	1.154911068	-1.134502825
C9	6	1.850355201	-0.214546075	-1.988619053	C9	6	1.794195475	-0.249764158	-2.640307583	C9	6	-2.595534718	1.328538033	1.251710264
H2	1	1.798424844	-0.861571992	-1.107262138	H2	1	2.148928699	-1.054697003	-1.988062626	C8	6	0.277533281	1.719418339	-1.248361905
H7	1	2.484157350	0.641715141	-1.741450746	H7	1	2.520093750	0.566191057	-2.596901157	C10	6	1.820631770	2.052866982	-3.569213859
H9	1	2.294607604	-0.782409999	-2.807753023	H9	1	1.726245334	-0.638962187	-3.657756599	C11	6	1.562351453	1.166162669	-1.331540556
C8	6	-1.377439732	1.850104286	-2.180417258	C8	6	-0.959903940	1.744693100	-0.873663516	C12	6	-0.226242813	2.453841178	-2.331409550
C10	6	-3.737912984	3.157722188	-2.997499012	C10	6	-3.371845798	3.022409839	-0.176087813	C13	6	0.544435247	2.612456201	-3.481523420
C11	6	-2.224593358	2.461671310	-1.240721688	C11	6	-1.195671860	2.162797484	0.446352058	C14	6	2.325535837	1.333391224	-2.486753704
C12	6	-1.725967844	1.907559076	-3.540511490	C12	6	-1.945064426	1.985962232	-1.845979136	H6	1	1.963761031	0.601560044	-0.497491256
C13	6	-2.895963859	2.554403535	-3.933304114	C13	6	-3.135497546	2.616343729	-1.490657870	H10	1	-1.219190934	2.880604381	-2.278580470
C14	6	-3.390994813	3.107997557	-1.648776517	C14	6	-2.391791614	2.794197814	0.788207102	H11	1	0.140753341	3.182182183	-4.314257316
H6	1	-1.967789916	2.446120003	-0.187345597	H6	1	-0.439781628	2.004858403	1.207664081	H12	1	3.316587999	0.890220010	-2.537269197
H10	1	-1.095069263	1.436225162	-4.279265998	H10	1	-1.786400452	1.664695980	-2.865213538	H13	1	2.413664858	2.175624980	-4.471219835
H11	1	-3.146040418	2.586885751	-4.990590024	H11	1	-3.885039516	2.792504607	-2.257696461	C15	6	0.546373502	-0.891799412	1.614379592
H12	1	-4.027238038	3.572862100	-0.900241562	H12	1	-2.550598258	3.105584800	1.817276649	C16	6	0.346435787	-3.655381296	0.977993875
H13	1	-4.647742633	3.659009595	-3.315403453	H13	1	-4.304508372	3.511360658	0.090737947	C17	6	-0.108187785	-1.350657360	0.454251472
C15	6	-0.104493445	-0.370703682	0.829043043	C15	6	1.563988970	-0.851630219	0.699002247	C18	6	1.117118946	-1.887778889	2.440682877
C16	6	-1.087086351	-2.972075384	1.216820380	C16	6	0.755907466	-3.511505728	1.103108296	C19	6	1.016488718	-3.238108346	2.128034021
C17	6	0.657267503	-1.346161418	1.494563660	C17	6	0.205229856	-1.193135118	0.778063627	C20	6	-0.221034383	-2.708102289	0.123504438
C18	6	-1.378517810	-0.727018644	0.356279056	C18	6	2.517079931	-1.878575570	0.828985415	H3	1	-0.537616779	-0.645857201	-0.237541015
C19	6	-1.860566670	-2.018614974	0.553189642	C19	6	2.112983940	-3.195737247	1.032483584	H14	1	1.661894603	-1.628274516	3.339638539
C20	6	0.186914641	-2.650237784	1.696821827	C20	6	-0.217574746	-2.513698718	0.972378281	H15	1	1.469910473	-3.971739609	2.790194788
H3	1	1.649952097	-1.078752361	1.848263766	H3	1	-0.542922872	-0.414174370	0.693175415	H17	1	0.271521782	-4.714451276	0.742053503
H14	1	-1.998363245	0.003610750	-0.150585164	H14	1	3.574763404	-1.643928444	0.748670583	C21	6	-0.940691922	-3.133020424	-1.151513727
H15	1	-2.849325262	-2.382409663	0.187524925	H15	1	2.859118014	-3.980492954	1.127102094	H16	1	-0.928459301	-4.231653667	-1.171775666
H17	1	-1.475164703	-3.977954391	1.361070603	H17	1	0.447651109	-4.543659331	1.254510230	C22	6	-2.414397899	-2.682692192	-1.165149798
C21	6	1.039061999	-3.696591863	2.404720090	C21	6	-1.699888401	-2.863091346	1.000289789	H19	1	-2.948643532	-3.050264165	-0.281595941
H16	1	0.424478278	-4.602885059	2.492300327	H16	1	-1.777259304	-3.911288605	1.321281242	H20	1	-2.921884036	-3.072631097	-2.055620701
C22	6	2.287158620	-4.067273403	1.581584427	C22	6	-2.494165132	-2.013463902	2.008768044	H21	1	-2.502712104	-1.590819775	-1.187730346
H19	1	2.011209948	-4.422252405	0.582624759	H19	1	-2.062995903	-2.078991530	3.014097767	C23	6	-0.204092262	-2.637494593	-2.411036172
H20	1	2.857770361	-4.860309038	2.079776856	H20	1	-3.533255692	-2.359357874	2.059742920	H18	1	0.838121694	-2.975948009	-2.422246227
H21	1	2.953927242	-3.205330664	1.457087907	H21	1	-2.516380121	-0.957047047	1.718062866	H22	1	-0.203077100	-1.543140938	-2.466816244
C23	6	1.423058256	-3.263925815	3.831719632	C23	6	-2.312988737	-2.764234444	-0.412078104	H23	1	-0.696706099	-3.014938718	-3.314906182
H18	1	0.533973077	-3.034476664	4.429286383	H18	1	-1.798554721	-3.430993215	-1.112908782	H2	1	-2.245570205	0.512998940	1.893251141
H22	1	2.059200830	-2.370693364	3.822379784	H22	1	-2.236654832	-1.747251424	-0.812562401	H7	1	-2.455237372	2.264504010	1.803110046
H23	1	1.979691311	-4.060451165	4.339402020	H23	1	-3.373252215	-3.044596908	-0.391262391	H9	1	-3.655573346	1.185586770	1.035851730

Table 3.14 The GS structure (N(COCF₃)Ph closer to H3, left) and the GS structure (N(COCF₃)Ph closer to H14, middle) and the TS structure (N(COCF₃)Ph closer to H3, right) XYZ coordinates.



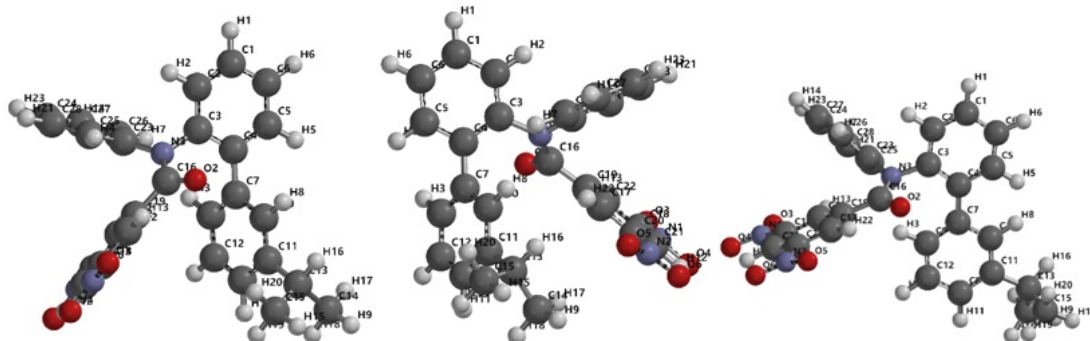
H1	1	1.130645278	3.530974400	-1.471366585	H1	1	1.560333756	3.391859227	-1.293159888	H1	1	0.024530337	3.782904384	1.034183874
C1	6	1.078983336	3.030480500	-0.509603687	C1	6	2.002672814	2.733040833	-0.552309649	C1	6	0.412527003	2.985702953	1.660463967
C4	6	0.950587571	1.685187470	1.911963769	C4	6	3.097324124	0.988527634	1.307083487	C4	6	1.340426096	0.904134234	3.194523168
C2	6	0.481519795	1.768635946	-0.444103333	C2	6	1.472528744	1.447546938	-0.404158952	C2	6	0.213068000	1.668151206	1.234646291
C6	6	1.609544713	3.623509096	0.631608654	C6	6	3.077392780	3.154600076	0.222446971	C6	6	1.070461185	3.275759058	2.847913938
C5	6	1.544605130	2.942967976	1.848442869	C5	6	3.624490360	2.277437589	1.160355163	C5	6	1.529187754	2.212715475	3.622198582
C3	6	0.395877533	1.067666433	0.776688294	C3	6	2.010116496	0.541104203	0.536841769	C3	6	0.695216438	0.561155781	1.984973630
H5	1	1.953711036	3.391890969	2.749368113	H5	1	4.458140482	2.590589952	1.782760622	H5	1	2.035560622	2.396123343	4.565871352
H4	1	0.892283264	1.162375170	2.862041585	H4	1	3.515312359	0.330969744	2.054001268	H4	1	1.705466996	0.119009126	3.842037912
H8	1	2.074852231	4.602834074	0.569167279	H8	1	3.482373550	4.154134796	0.094737105	H8	1	1.209867170	4.305133438	3.163940245
N1	7	-0.066060665	2.19200974	-1.667880274	N1	7	0.324334755	1.111276227	-1.219617347	N1	7	-0.492042736	1.551803545	-0.030456605
C7	6	0.574152687	0.192182309	-2.334891669	C7	6	0.398718869	0.193992079	-2.249645513	C7	6	-1.850934492	1.350496865	-0.119223921
O1	8	0.082596889	-0.498964401	-3.205433494	O1	8	-0.555675815	-0.348796497	-2.772752124	O1	8	-2.458905321	1.173369458	-1.160188991
C9	6	2.097029784	-0.008620532	-2.039043007	C9	6	1.809183914	-0.075159716	-2.863077125	C9	6	-2.672313519	1.353600264	1.205023957
C8	6	-1.316524910	1.757908076	-2.138622586	C8	6	-0.938563981	1.708051927	-0.864967414	C8	6	0.281370345	1.706663262	-1.240592299
C10	6	-3.723551700	2.931615081	-3.015682072	C10	6	-3.352524203	2.958130066	-0.146419899	C10	6	1.810522209	1.994944400	-3.568957592
C11	6	-2.121533852	2.491770236	-1.252966349	C11	6	-1.155585831	2.134316992	0.453501578	C11	6	1.534809654	1.091539076	-1.339758373
C12	6	-1.728091832	1.624491356	-3.475403608	C12	6	-1.937751149	1.926145164	-1.826554333	C12	6	-0.196954858	2.484748396	-2.302478680
C13	6	-2.920210572	2.208963196	-3.898298480	C13	6	-3.131131291	2.544261499	-1.461064898	C13	6	0.567481404	2.621025968	-3.459505055
C14	6	-3.312918484	3.069221611	-1.691365360	C14	6	-2.356119956	2.751964477	0.805802213	C14	6	2.291748481	1.236461113	-2.502306202
H6	1	-1.816868200	2.625294977	-0.222042127	H6	1	-0.385299009	1.995375987	1.203225336	H6	1	1.915545174	0.497348413	-0.517380835
H10	1	-1.133342917	1.056549577	-4.175158329	H10	1	-1.792361353	1.602097742	-2.847634341	H10	1	-1.164937530	2.964358132	-2.231859760
H11	1	-3.218881092	2.092092961	-4.936541245	H11	1	-3.893241275	2.703765332	-2.218889754	H11	1	0.185007366	3.222467985	-4.279461296
H12	1	-3.917520698	3.630858474	-0.984339092	H12	1	-2.504282741	3.071680362	1.833613368	H12	1	3.257923736	0.744238405	-2.571619160
H13	1	-4.652783947	3.799859000	-3.355121401	H13	1	-4.287416996	3.437159361	0.129678453	H13	1	2.397577234	2.096954021	-4.477338945
C15	6	-0.198116432	-0.294778616	0.916053666	C15	6	1.531982918	-0.857715852	0.742093240	C15	6	0.579996821	-0.892996015	1.610613488
C16	6	-1.234214555	-2.875220085	1.273714420	C16	6	0.713073087	-3.508912361	1.178554676	C16	6	0.387062349	-3.653468686	0.960286601
C17	6	0.571218251	-1.309102452	1.504906251	C17	6	0.172443995	-1.196706725	0.796566544	C17	6	-0.094605573	-1.351360354	0.463445936
C18	6	-1.507458292	-0.594877254	0.508624488	C18	6	2.480512499	-1.882704193	0.909885541	C18	6	1.173881590	-1.887932498	2.418764015
C19	6	-2.018034956	-1.878065373	0.692625136	C19	6	2.071890473	-3.194375860	1.128932969	C19	6	1.074062864	-3.237593800	2.100499636
C20	6	0.076509474	-2.606366727	1.684598290	C20	6	-0.255500506	-2.514174495	1.008989496	C20	6	-0.201332290	-2.704952496	0.121969842
H3	1	1.592091140	-1.081036103	1.797076725	H3	1	-0.576733454	-0.422056939	0.682601997	H3	1	-0.546483756	-0.649806028	-0.215271239
H14	1	-2.132144425	0.171728040	0.063461555	H14	1	3.538956798	-1.651311228	0.836757746	H14	1	1.732589734	-1.629105856	3.308997468
H15	1	-3.034296455	-2.101146202	0.378989802	H15	1	2.815553937	-3.977767836	1.249406801	H15	1	1.542407542	-3.971903855	2.750804981
H17	1	-1.641068002	-3.875618794	1.403726482	H17	1	0.401017596	-4.537818855	1.343016074	H17	1	0.314818268	-4.711538992	0.719525728
C21	6	0.950870512	-3.704143793	2.276985317	C21	6	-1.738624886	-2.859873971	1.018663970	C21	6	-0.929642992	-3.117750933	-1.152061837
H16	1	0.324794570	-4.602897338	2.362134212	H16	1	-1.823117086	-3.905285073	1.346567085	H16	1	-0.924212400	-4.216030778	-1.181501913
C22	6	2.127472379	-4.049289041	1.344196171	C22	6	-2.541616178	-2.000555642	2.012159829	C22	6	-2.400424185	-2.658321375	-1.162725665
H19	1	1.770645385	-4.347330866	0.352515751	H19	1	-2.122739371	-2.062653805	3.022869857	H19	1	-2.938215077	-3.025573562	-0.281651881
H20	1	2.718847715	-4.874122428	1.758933891	H20	1	-3.583189549	-2.340156848	2.053167844	H20	1	-2.909906635	-3.038348376	-2.056184358
H21	1	2.796269627	-3.190566853	1.210787066	H21	1	-2.552999849	-0.945345668	1.715633840	H21	1	-2.484003474	-1.566068418	-1.179832639
C23	6	1.446783912	-3.355845982	3.692530870	C23	6	-2.332799420	-2.769353822	-0.401818608	C23	6	-0.189983352	-2.614909744	-2.407450770
H18	1	0.608269821	-3.156981741	4.369162592	H18	1	-1.811308531	-3.442927092	-1.090516287	H18	1	0.847303053	-2.968087283	-2.427060112
H22	1	2.088901036	-2.467080795	3.685903835	H22	1	-2.245382384	-1.755663025	-0.808264285	H22	1	-0.172076154	-1.519667142	-2.445376524
H23	1	2.033035177	-4.183624510	4.108807744	H23	1	-3.394824153	-3.043936528	-0.394261951	H23	1	-0.690568138	-2.969723981	-3.316012374
F1	9	2.767636272	1.148001844	-2.240492195	F1	9	1.656237939	-0.730483890	-4.015878867	F1	9	-3.952386286	1.101215055	0.925287518
F2	9	2.372131396	-0.433251041	-0.789882601	F2	9	2.604081829	-0.818409166	-2.071428833	F2	9	-2.254125274	0.421766779	2.083081938
F3	9	2.581748875	-0.917455719	-2.886777334	F3	9	2.450114893	1.084116882	-3.127494773	F3	9	-2.606365537	2.561350146	1.807203061

Table 3.15 The GS structure (N=C-Ph(NO₂) closer to H2, left) and the GS structure (N=C-Ph(NO₂) closer to H3, middle) and the TS structure (N=C-Ph(NO₂) closer to H3, right) XYZ coordinates.



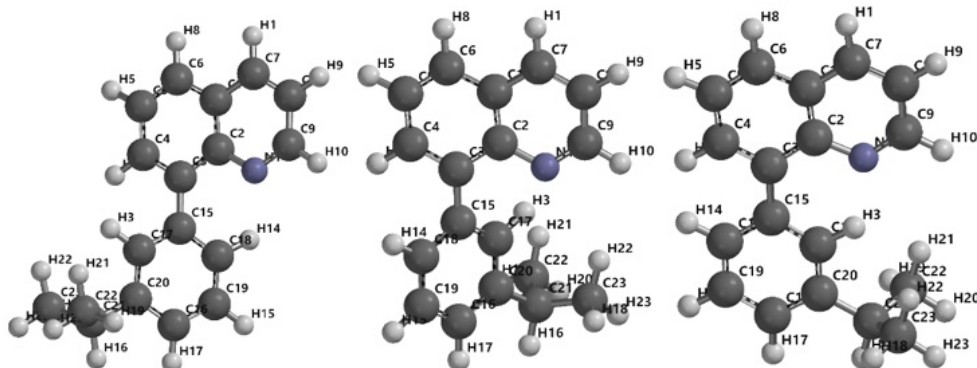
H1	1	-1.603551397	-2.537161599	-4.121671327	H1	1	-2.920874588	-2.041140357	-4.129743902	H1	1	-1.928991139	-1.009876978	-4.913371131
C1	6	-1.404873727	-1.909209517	-3.256971923	C1	6	-2.607030096	-1.514639018	-3.232187923	C1	6	-1.669134171	-0.479593638	-4.001263615
C4	6	-0.894660293	-0.307165018	-0.988805937	C4	6	-1.805438486	-0.171168132	-0.879270321	C4	6	-1.028649459	0.894454283	-1.576466688
C2	6	-0.699678821	-2.429554104	-2.176789693	C2	6	-2.287304720	-2.237702661	-2.086356144	C2	6	-1.662431114	-1.148045414	-2.786197883
C6	6	-1.852433550	-0.587244480	-3.224363387	C6	6	-2.524603544	-0.121769048	-3.220513642	C6	6	-1.325411709	0.871222640	-4.027587972
C5	6	-1.593571509	0.192862899	-2.099868233	C5	6	-2.128723305	0.528488474	-2.053507232	C5	6	-1.016435717	1.523749583	-2.840353086
C3	6	-0.426686988	-1.644004594	-1.041957767	C3	6	-1.874050814	-1.586732951	-0.912651164	C3	6	-1.328679160	-0.498560199	-1.582351130
H6	1	-2.396766097	-0.167007310	-4.065363100	H6	1	-2.779144952	0.455052707	-4.105164931	H6	1	-1.299116226	1.418995776	-4.965333492
N1	7	0.143793846	-2.250462389	0.090429033	N1	7	-1.649968320	-2.361940171	0.240984084	N1	7	-1.433623983	-1.287021161	-0.415817706
C8	6	1.315056756	-2.755952657	0.155491931	C8	6	-0.583444423	-3.012722217	0.502878080	C8	6	-0.669543048	-2.287052763	-0.184354060
H13	1	1.530126651	-3.295620195	1.084863690	H13	1	-0.627200133	-3.610603968	1.420457314	H13	1	-0.955228704	-2.907148674	0.673150964
H16	1	-0.363662218	-3.462388097	-2.184224242	H16	1	-2.347728070	-3.322110813	-2.080694042	H16	1	-1.925429376	-2.200167362	-2.735538279
C7	6	2.468686106	-2.723035057	-0.774714301	C7	6	0.718486526	-3.127182362	-0.193356600	C7	6	0.562647766	-2.734205151	-0.877407151
C9	6	4.780925774	-2.738494897	-2.376618218	C9	6	3.247879609	-3.503328775	-1.364097300	C9	6	2.896453776	-3.681805976	-2.113000794
C10	6	2.596135021	-1.831104000	-1.856126559	C10	6	1.140791330	-2.311124630	-1.259588623	C10	6	1.476450897	-1.836166228	-1.455201026
C15	6	3.528966991	-3.606465099	-0.505458530	C15	6	1.593799505	-4.122050876	0.277922561	C15	6	0.851659332	-4.107681609	-0.901436956
C16	6	4.670638488	-3.623862244	-1.303114283	C16	6	2.843618749	-4.316694497	-0.304046348	C16	6	2.000539752	-4.581589029	-1.532236105
C17	6	3.744632167	-1.839691461	-2.643824820	C17	6	2.395691745	-2.500216675	-1.833074659	C17	6	2.637495498	-2.309570741	-2.060686117
H7	1	1.801545499	-1.128667044	-2.075635274	H7	1	0.496949850	-1.525737403	-1.633248551	H7	1	1.285500828	-0.769703783	-1.414306068
H9	1	3.450283180	-4.286127369	0.340119565	H9	1	1.280603678	-4.749036702	1.109812550	H9	1	0.159047819	-4.805815636	-0.436221154
H10	1	5.475154588	-4.320206639	-1.083010635	H10	1	3.501822994	-5.095520847	0.071089628	H10	1	2.200495627	-5.649082386	-1.563915019
H11	1	3.830922558	-1.140970643	-3.471441581	H11	1	2.711215656	-1.858372002	-2.651117966	H11	1	3.342534079	-1.604712774	-2.493134761
H12	1	5.671970005	-2.743605635	-2.998578008	H12	1	4.224016135	-3.646312531	-1.819943858	H12	1	3.798523259	-4.046402751	-2.596915518
C20	6	-2.768270611	3.006808283	2.303678997	C20	6	0.935253859	3.561832286	1.105055342	C20	6	-0.262964709	1.165342990	3.437684397
H4	1	-3.629567741	2.756356227	1.669288926	H4	1	1.216847870	3.571661890	0.043021923	H4	1	-0.536942523	0.114632182	3.272353300
C21	6	-2.534214721	4.524281602	2.183294858	C21	6	2.222819892	3.346427013	1.921512351	C21	6	-1.288745004	1.759172743	4.420412510
H14	1	-1.687582362	4.847728887	2.800566943	H14	1	2.015362940	3.342682087	2.998110600	H14	1	-1.070232524	2.811763159	4.636626466
H17	1	-3.419538364	5.079095410	2.516658999	H17	1	2.942783218	4.149734837	1.724437194	H17	1	-1.275266698	1.213730221	5.371817307
H18	1	-2.320055206	4.811689288	1.148013417	H18	1	2.696633991	2.391500487	1.669679048	H18	1	-2.303040901	1.706442820	4.009796544
C22	6	-3.133944537	2.615733102	3.748011820	C22	6	0.300592119	4.928156085	1.427375108	C22	6	1.155537279	1.180187756	4.037856605
H15	1	-4.026097296	3.159627823	4.081020202	H15	1	1.013691988	5.740369924	1.241408523	H15	1	1.179873215	0.632955568	4.988097420
H19	1	-2.320772394	2.852606808	4.444689190	H19	1	-0.002912268	4.985594139	2.479611818	H19	1	1.495234322	2.204285973	4.234209812
H20	1	-3.337565287	1.542321962	3.826320220	H20	1	-0.589708276	5.107753086	0.814632130	H20	1	1.877596772	0.714776334	3.357684312
H24	1	-1.925475716	1.227274042	-2.074820532	H24	1	-2.086010783	1.613838957	-2.030762494	H24	1	-0.748064991	2.570434451	-2.908839883
C11	6	-0.672535458	0.572224493	0.190264309	C11	6	-1.373764166	0.585977512	0.328759496	C11	6	-0.697369364	1.692073083	-0.351967875
C12	6	-0.312956712	2.311763191	2.369602698	C12	6	-0.590103003	2.115430168	2.553141126	C12	6	-0.025178562	3.221266926	1.947121113
C13	6	0.584185504	0.701323136	0.799549177	C13	6	-1.881377675	0.297113026	1.605098749	C13	6	-0.423750900	3.073343663	-0.437499595
C14	6	-1.737284406	1.335438275	0.699213351	C14	6	-0.464997324	1.649864030	0.199759897	C14	6	-0.641238081	1.124641964	0.937117637
C18	6	-1.581819681	2.206011764	1.781834322	C18	6	-0.058510978	4.223218525	1.292768788	C18	6	-0.310649478	1.858569939	2.081333698
C19	6	0.757532291	1.565563715	1.879985443	C19	6	-1.491381209	1.062017348	2.703347939	C19	6	-0.092419215	3.818762907	0.689837280
H2	1	1.433638400	0.147585636	0.413490581	H2	1	-2.580504837	-0.522328658	1.731059020	H2	1	-0.474045284	3.595202695	-1.385367943
H3	1	-2.720356676	1.227974435	0.246257665	H3	1	-0.049554845	1.868644781	-0.781805254	H3	1	-0.884006500	0.079921883	1.063863198
H8	1	1.738544222	1.662141853	2.338614375	H8	1	-1.897950960	0.835890424	3.686064285	H8	1	-0.113262884	4.881012468	0.582128814
H21	1	-0.158816278	2.981587217	3.212098638	H21	1	-0.296573878	2.698087505	3.423143404	H21	1	0.243735542	3.817260351	2.815679526

Table 3.16 The GS structure (N(Ph)(Ph(NO₂)₂) closer to H3, left) and the GS structure (N(Ph)(Ph(NO₂)₂) closer to H8, middle) and the TS structure (N(Ph)(Ph(NO₂)₂) closer to H3, right) XYZ coordinates.



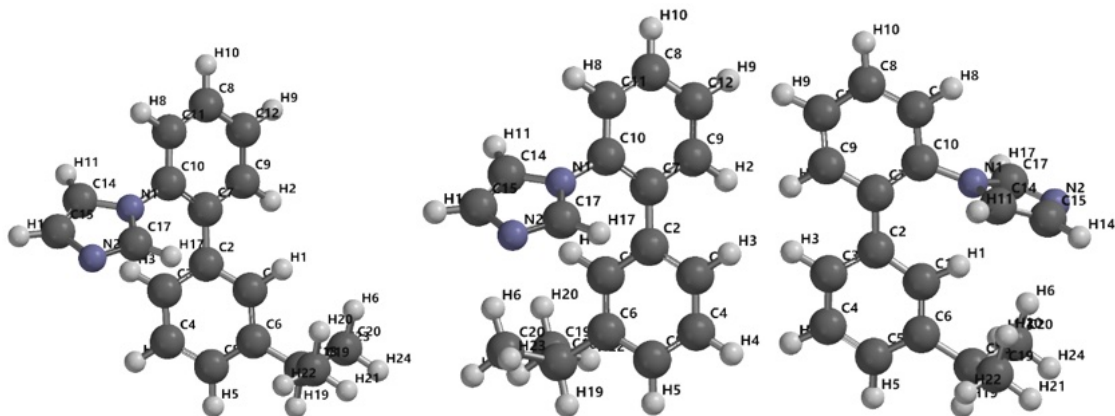
H1	1	1.870027272	1.281371263	-5.612110932	H1	1	1.739510298	2.238407667	-5.465660229	H1	1	1.999656199	1.484043960	-5.055062221
C1	6	1.876423002	1.192263407	-4.529490334	C1	6	1.734525979	2.156505760	-4.382510473	C1	6	1.893509659	1.428411148	-3.975684293
C4	6	1.876838856	0.948922802	-1.717841116	C4	6	1.702291918	1.927484924	-1.564529277	C4	6	1.592115119	1.248201440	-1.125018882
C2	6	0.857613462	0.493544958	-3.886365651	C2	6	0.755585757	1.395483219	-3.749453507	C2	6	0.904511411	0.639792098	-3.404859260
C6	6	2.888676959	1.786716174	-3.775677378	C6	6	2.691269456	2.820727220	-3.615145545	C6	6	2.724734587	2.155327617	-3.127979635
C5	6	2.879490945	1.666439293	-2.387232871	C5	6	2.665773761	2.705522189	-2.227190619	C5	6	2.564950888	2.060793407	-1.751521877
C3	6	0.853088507	0.370546950	-2.494513020	C3	6	0.733598765	1.278131896	-2.356823304	C3	6	0.739644046	0.546623243	-2.018281562
H2	1	0.051040023	0.045314297	-4.458437232	H2	1	-0.009594481	0.891413985	-4.331722264	H2	1	0.228443951	0.074534292	-4.038511117
H6	1	3.686243917	2.337912954	-4.265929043	H6	1	3.459416332	3.421666434	-4.093716050	H6	1	3.499664329	2.800977465	-3.531717070
H5	1	3.674180400	2.115573692	-1.798260926	H5	1	3.421439144	3.207278899	-1.629582890	H5	1	3.228712602	2.659081684	-1.143226301
C17	6	-1.395203193	-1.541609297	0.635023381	C17	6	-1.669167452	-0.853040932	0.588375527	C17	6	-3.959968882	0.137304449	-0.763598986
C18	6	-3.826954066	-0.471457613	1.416042557	C18	6	-4.156676558	0.180714627	1.227683961	C18	6	-3.820794188	-2.444416783	0.202295068
C19	6	-1.886994704	-0.401331306	-0.007485762	C19	6	-2.105456363	0.325707298	-0.024859947	C19	6	-2.726039521	-0.529190876	-0.776645292
C20	6	-2.137300151	-2.113810148	1.664402085	C20	6	-2.495220390	-1.483201159	1.515628481	C20	6	-5.091820032	-0.511883624	-0.283644657
C21	6	-3.366449892	-1.608387705	2.071336176	C21	6	-3.753742357	-0.996404349	1.848656824	C21	6	-5.059400740	-1.817654608	0.192811937
C22	6	-3.105137608	0.150571628	0.401602634	C22	6	-3.353296392	0.857913656	0.315420396	C22	6	-2.658023798	-1.827365901	-0.254189067
H12	1	-3.934947471	-2.070854050	2.866443973	H12	1	-4.387906031	-1.504745317	2.561835128	H12	1	-5.951875951	-2.316583371	0.544746259
H13	1	-3.477583726	1.057322081	-0.058607056	H13	1	-3.686204916	1.791528436	-0.120368539	H13	1	-1.734071664	-2.383406209	-0.192911285
C7	6	1.921661770	0.840658524	-0.230082958	C7	6	1.751346593	1.846306372	-0.076592874	C7	6	1.558947165	1.196767106	0.378978993
C8	6	2.020973658	0.702882911	2.568631729	C8	6	1.958895767	1.742687961	2.720559810	C8	6	1.568547140	1.201347088	3.227060828
C9	6	2.094133786	-0.393170270	0.412054254	C9	6	1.757291035	0.027406536	0.679270569	C9	6	0.597347669	0.486601502	1.123976512
C10	6	1.808793051	1.997174034	0.554653689	C10	6	1.846311846	0.619694436	0.598951468	C10	6	2.535798365	1.880728634	1.134616939
C11	6	1.853540175	1.951196674	1.952213312	C11	6	1.948551629	0.544004817	1.993653069	C11	6	2.557929509	1.906317002	2.531767864
C12	6	2.142766465	-0.457841560	1.805320427	C12	6	1.861589711	2.971017953	2.067835144	C12	6	0.606741273	0.490230112	2.517152913
H3	1	2.207003712	-1.299545389	-0.176090163	H3	1	1.658709664	3.984259911	0.175332674	H3	1	-0.167026724	-0.086504617	0.629346949
H8	1	1.650810722	2.951446113	0.058525633	H8	1	1.866424303	-0.304499445	0.025673023	H8	1	3.331762996	2.421151514	0.637177542
H10	1	2.276043699	-1.418869289	2.295427619	H10	1	1.859619247	3.891420429	2.645940266	H10	1	-0.156935137	-0.069501961	3.051148360
H11	1	2.055036992	0.633450807	3.652955813	H11	1	2.039500368	1.720722364	3.803934470	H11	1	1.551368197	1.197129769	4.31282081
C13	6	1.679479300	3.227982871	2.764131986	C13	6	2.089154772	-0.813543653	2.672920439	C13	6	3.621366630	2.731797560	3.247495980
H16	1	1.672426902	4.061873644	2.048920499	H16	1	1.758212188	-1.572566579	1.950845877	H16	1	4.465212898	2.840506166	2.551496844
C14	6	2.843421962	3.469505270	3.741451087	C14	6	1.198277945	-0.959790445	3.918078970	C14	6	4.163743431	2.063849662	4.521573761
H9	1	2.719785488	4.430898097	4.253647443	H9	1	1.234292765	-1.988526914	4.292828331	H9	1	4.994692268	2.649645860	4.930521744
H17	1	3.805723501	3.482634374	3.218022148	H17	1	0.154104965	-0.720162555	3.690991409	H17	1	4.527208004	1.050082299	4.320567952
H18	1	2.892581932	2.691079554	4.512397809	H18	1	1.523694016	-0.301038875	4.731643830	H18	1	3.398112230	1.998202465	5.303671294
C15	6	0.324221316	3.243508950	3.497678374	C15	6	3.563916737	-1.110245290	3.010666120	C15	6	3.092024873	4.148071381	3.552844739
H15	1	0.181858555	4.192967403	0.4027524851	H15	1	3.670840566	-2.112851798	3.441820401	H15	1	3.866895654	4.759059796	4.031654271
H19	1	0.263900035	2.435811891	4.237348141	H19	1	3.953853190	-0.386646183	3.736635306	H19	1	2.228422846	4.105453700	4.227418736
H20	1	-0.505190409	3.116827190	2.793641107	H20	1	4.192925608	-1.054900525	2.115283957	H20	1	2.772020463	4.657075408	2.637141306
H22	1	-0.442592659	-1.975451441	0.364550517	H22	1	-0.703150694	-1.282892740	0.362823758	H22	1	-4.019045861	1.160048451	-1.114272533
N3	7	-0.222831044	-0.350799370	-1.858761823	N3	7	-0.312361819	0.487898976	-1.750480905	N3	7	-0.352850730	-0.321932708	-1.604541404
C16	6	-1.071804781	0.368314574	-1.018133800	C16	6	-1.230705106	1.150683022	-0.939398030	C16	6	-1.556797542	0.294647254	-1.292119637
O2	8	-1.115970015	1.588602379	-1.013411112	O2	8	-1.306955716	2.368473542	-0.892819621	O2	8	-1.683523023	1.508899143	-1.361231524
N1	7	-5.126089098	0.099834880	1.823788760	N1	7	-5.485775318	0.733239936	1.558203117	N1	7	-3.733892119	-3.831644054	0.701365212
O3	8	-5.518643006	1.096805035	1.222669860	O3	8	-5.834779655	1.754349963	0.971369298	O3	8	-2.617423948	-4.341476280	0.769998269
O4	8	-5.730246759	-0.461842789	2.734795870	O4	8	-6.155518210	0.132519549	2.395404307	O4	8	-4.785041133	-4.388169167	1.008651340
N2	7	-1.948850969	-3.299309290	2.355613796	N2	7	-2.019647535	-2.717815059	2.169213007	N2	7	-6.381415588	0.208977543	-0.269375227
O5	8	-0.474251251	-3.683940679	2.025839991	O5	8	-0.870282215	-3.083649035	1.925932116	O5	8	-6.383543306	1.374486534	-0.656442618
O6	8	-2.99606772	-3.823534775	3.216976933	O6	8	-2.801857929	-3.301607560	2.914620203	O6	8	-7.365908736	-0.407242778	0.133264900
C23	6	-0.538020569	-1.661830266	-2.339161253	C23	6	-0.533783629	-0.832267323	-2.262406119	C23	6	-0.208514157	-1.716780382	-1.922910818
C24	6	-1.134593870	-4.233567518	-3.282832656	C24	6	-0.944406819	-3.418961927	-2.359747955	C24	6	0.047050546	-4.447140139	-2.467655232
C25	6	-1.847959332	-1.991624752	-2.711472925	C25	6	-1.795459616	-1.213718601	-2.737674394	C25	6	0.720842054	-2.488237778	-1.214180133
C26	6	0.477758148	-2.619089409	-2.470974874	C26	6	0.529965859	-1.743705657	-2.319744706	C26	6	-0.985160674	-2.306747401	-2.927068683
C27	6	0.177398909	-3.894949638	-2.942749860	C27	6	0.322022603	-3.027996799	-2.817896094	C27	6	-0.860816718	-3.671531071	-3.190700882
C28	6	-2.143464836	-3.277730838	-3.165632768	C28	6	-1.999612671	-2.507195151	-3.218912265	C28	6	0.842239445	-3.850334122	-1.486371839
H4	1	-2.629465961	-1.240189302	-2.655472371	H4	1	-2.610837888	-0.496942476	-2.737496108	H4	1	1.320521509	-2.021430309	-0.438826159
H7	1	1.498112957	-2.356584423	-2.211110861	H7	1	1.515495480	-1.439440305	-1.981652195	H7	1	-1.691231986	-1.699533916	-3.486431177
H14	1	0.972224071	-4.629486098	-3.036758767	H14	1	1.152127723	-3.727806305	-2.852671515	H14	1	-1.474282832	-4.126424505	-3.963322760
H21	1	-3.164333291	-3.522249943	-3.445236114	H21	1	-2.984143659	-2.793769097	-3.577939539	H21	1	1.547408846	-4.449595060	-0.917399303
H23	1	-1.365792318	-5.231397515	-3.643798831	H23	1	-1.103992571	-4.423239925	-3.641036295	H23	1	0.133258295	-5.511439181	-2.665857319

Table 3.17 The GS structure (quinoline closer to H3, left) and the GS structure (quinoline closer to H14, middle) and the TS structure (quinoline closer to H3, right) XYZ coordinates.



C1	6	-0.890973304	3.567754937	0.033380816	C1	6	-0.114945357	3.419614748	0.738194713	C1	6	-0.096069808	3.415938432	0.725000043
C4	6	-0.052217255	1.485391998	1.697032073	C4	6	-2.020652329	2.089746098	-0.812516736	C4	6	-2.378118662	2.076380949	-0.104288877
C2	6	-1.020405813	2.207060717	-0.403638791	C2	6	-0.140456124	1.985144488	0.713255945	C2	6	-0.026748377	2.010306958	0.423911424
C6	6	-0.342465849	3.853871187	1.309371211	C6	6	-1.052878269	4.160674446	-0.025346611	C6	6	-1.314652793	4.123967757	0.601942231
C5	6	0.069806258	2.826006096	2.124085545	C5	6	-1.990702022	3.501680084	-0.784499081	C5	6	-2.438003354	3.452604322	0.190182927
C3	6	-0.584282743	1.145281349	0.461562080	C3	6	-1.125379765	1.313304329	-0.091009421	C3	6	-1.220770107	1.306176410	-0.009584376
H5	1	0.485417687	3.036766256	3.105721438	H5	1	-2.710065367	4.061301249	-1.376194630	H5	1	-3.386528680	3.972722060	0.087351961
H4	1	0.262010194	0.689072628	2.365549324	H4	1	-2.755173786	1.591989131	-1.438891191	H4	1	-3.304631363	1.615358550	-0.419648915
H8	1	-0.256661051	4.890222886	1.627670913	H8	1	-1.015191891	5.247203132	0.000218180	H8	1	-1.341222547	5.185469407	0.835359622
N1	7	-1.526095778	1.896453310	-1.631658781	N1	7	0.734519444	1.241816768	1.451631275	N1	7	1.162366032	1.352443828	0.550095255
C15	6	-0.663955972	-0.288525923	0.072328146	C15	6	-1.223364683	-0.169236814	-0.164765614	C15	6	-1.288102616	-0.157250086	-0.348788759
C16	6	-0.764011278	-3.030102405	-0.516743498	C16	6	-1.468341850	-2.952307129	-0.412202232	C16	6	-1.473796681	-2.919924635	-0.983947081
C17	6	0.441901335	-1.121631299	0.298778802	C17	6	-0.097595788	-0.976019728	-0.386626413	C17	6	-0.177435985	-1.018877639	-0.271544169
C18	6	-1.830208258	-0.856090332	-0.467463855	C18	6	-2.481838653	-0.786558882	-0.066800564	C18	6	-2.506156125	-0.741959093	-0.765612700
C19	6	-1.874875572	-2.217572963	-0.753217260	C19	6	-2.600540158	-2.168725160	-0.186433084	C19	6	-2.594578216	-2.093633255	-1.075224197
C20	6	0.414698514	-2.492377638	0.010878917	C20	6	-0.201162865	-2.365269022	-0.516858047	C20	6	-0.250262296	-2.383668288	-0.580350368
H3	1	1.352283399	-0.676456629	0.691639410	H3	1	0.874564886	-0.502750814	-0.457774705	H3	1	0.764990233	-0.597529999	0.040482959
H14	1	-2.694087136	-0.230024254	-0.655654566	H14	1	-3.361784004	-0.179169977	0.127038981	H14	1	-3.411224267	-0.154222540	-0.857739908
H15	1	-2.784013874	-2.651575347	-1.161893047	H15	1	-3.577175211	-2.637703171	-0.096895004	H15	1	-3.549649821	-2.505878869	-1.391312792
H17	1	-0.811494568	-4.092238154	-0.747877073	H17	1	-1.567425116	-4.031785729	-0.505146677	H17	1	-1.553094434	-3.977519537	-1.226584951
C21	6	1.636025992	-3.372966863	0.244573241	C21	6	1.031937303	-3.220305778	-0.780174829	C21	6	0.990578071	-3.262843341	-0.471718969
H16	1	1.334078659	-4.405550541	0.021447367	H16	1	0.699358811	-4.267245807	-0.806216990	H16	1	0.690728267	-4.281014125	-0.756922490
C22	6	2.786980131	-3.012420839	-0.714876545	C22	6	1.660104346	-2.903412791	-2.151215016	C22	6	2.096083047	-2.816476535	-1.446841821
H19	1	2.467015896	-3.082945049	-1.760142404	H19	1	0.928997175	-3.020545891	-2.958709200	H19	1	1.730856468	-2.799842997	-2.479669475
H20	1	3.639248171	-3.687836019	-0.570871733	H20	1	2.505719519	-3.571510018	-2.355859447	H20	1	2.953691987	-3.498736727	-1.398415696
H21	1	3.138809536	-1.988178108	-0.542659882	H21	1	2.033679895	-1.873061569	-2.186344054	H21	1	2.455402049	-1.809832489	-1.203353462
C23	6	2.110257915	-3.338476517	1.709389197	C23	6	2.074690409	-3.093550373	0.346128251	C23	6	1.523077736	-3.324058102	0.972279932
H18	1	1.299494697	-3.604271574	2.396668081	H18	1	1.643396196	-3.360149836	1.317135581	H18	1	0.749782775	-3.673828975	1.665083191
H22	1	2.472450618	-2.341673657	1.988324908	H22	1	2.454790428	-2.068241483	0.422590732	H22	1	1.854049270	-2.335939748	1.312904519
H23	1	2.934982546	-4.044143502	1.865306120	H23	1	2.929531918	-3.754220946	0.157005997	H23	1	2.378648403	-4.006844958	1.041129342
C7	6	-1.316609103	4.588446821	-0.855969117	C7	6	0.864785925	4.047015917	1.549787286	C7	6	1.086979034	4.074702143	1.148686253
H1	1	-1.227670643	5.628395030	-0.549334038	H1	1	0.906155428	5.133421381	1.584428405	H1	1	1.038702040	5.136841788	1.377977589
C8	6	-1.828378448	4.250942886	-2.084920981	C8	6	1.738422901	3.277766352	2.279234973	C8	6	2.262296849	3.376371539	1.263606689
H9	1	-2.161619504	5.006455054	-2.790241571	H9	1	2.498361538	3.725018011	2.913080227	H9	1	3.184299441	3.850828455	1.585302059
C9	6	-1.909916469	2.877933678	-2.421940032	C9	6	1.624250049	1.868736867	2.192691350	C9	6	2.237534882	1.999984812	0.945962781
H10	1	-2.305518930	2.585002780	-3.394604413	H10	1	2.301407068	1.237337916	2.768057652	H10	1	3.150979549	1.409784476	1.024290174

Table 3.18 The GS structure (imidazole closer to H3, left) and the GS structure (quinoline closer to H1, middle) and the TS structure (imidazole closer to H31, right) XYZ coordinates.



H1	1	-0.859029312	1.099959236	-1.183311213	H1	1	-0.618191823	-0.112608436	-0.814507471	H1	1	0.346064791	0.565941846	-0.375603263
C1	6	-0.967815857	0.719033010	-0.170686521	C1	6	-0.659315946	-0.555041214	0.176262898	C1	6	-0.365350624	0.642682642	0.428873520
C4	6	-1.217103562	-0.294670935	2.398727588	C4	6	-0.750047093	-1.704274405	2.704275551	C4	6	-2.203276427	0.956507658	2.470559305
C2	6	0.181359486	0.295398466	0.512598679	C2	6	0.538079152	-0.934406866	0.800006947	C2	6	-1.004609005	-0.510786133	0.923839442
C6	6	-2.242656356	0.647909276	0.406046551	C6	6	-1.901768836	-0.734463682	0.795232402	C6	6	-0.611409997	1.926792472	0.934933248
C5	6	-2.349234007	0.135093031	1.703303706	C5	6	-1.929850870	-1.314211298	2.069925873	C5	6	-1.547177078	2.076213386	1.960108347
C3	6	0.042542602	-0.219066311	1.812299424	C3	6	0.479261682	-1.517568596	2.075570469	C3	6	-1.931924917	-0.311671193	1.971238872
H5	1	-3.328245775	0.068009935	2.172708758	H5	1	-2.884998044	-1.457807800	2.570204000	H5	1	-1.759280451	3.064448583	2.361774447
H3	1	0.918303390	-0.549199330	2.362357644	H3	1	1.398818669	-1.804110043	2.578769786	H3	1	-2.453021892	-1.144981385	2.424827144
H4	1	-1.318772776	-0.688330387	3.406574406	H4	1	-0.787860071	-2.148387501	3.695587664	H4	1	-2.929687333	1.069250002	3.271436104
C7	6	1.518842418	0.454826953	-0.126802618	C7	6	1.852156313	-0.765452229	0.115675784	C7	6	-0.740802666	-1.898686472	0.406614465
C8	6	4.056418489	0.914795986	-1.293749566	C8	6	4.329720305	-0.592443246	-1.240322610	C8	6	-0.333811003	-4.626298778	-0.406359307
C9	6	1.854518854	1.694801409	-0.697430600	C9	6	2.722198286	-1.865391154	0.028697846	C9	6	-1.507610020	-2.975999405	0.906405965
C10	6	2.491180340	-0.566838255	-0.180666357	C10	6	2.274420751	0.444110402	-0.477678687	C10	6	0.239437419	-2.266159743	-0.554059527
C11	6	3.743518036	-0.331791583	-0.758350567	C11	6	3.499977775	0.521658475	-1.147410326	C11	6	0.431231362	-3.597676182	-0.941350268
C12	6	3.101393207	1.931462390	-1.270524840	C12	6	3.941607097	-1.790608064	-0.640075380	C12	6	-1.316343152	-4.298936857	0.524996621
H2	1	1.121178397	2.494559165	-0.652339347	H2	1	2.406369956	-2.806007938	0.470535146	H2	1	-2.295356540	-2.781986302	1.621685442
H8	1	4.457667122	-1.148610155	-0.802285010	H8	1	3.803915619	1.473157336	-1.573090443	H8	1	1.201804673	-3.802654947	-1.678591416
H9	1	3.328042419	2.908541459	-1.687824433	H9	1	4.580511727	-2.667277048	-0.699038992	H9	1	-1.942280246	-5.073032714	0.960610463
H10	1	5.033553745	1.082883358	-1.737395353	H10	1	5.277621128	-0.517804081	-1.765430719	H10	1	-0.168656508	-5.654429896	-0.713955606
N1	7	2.229500311	-1.873634461	0.329531689	N1	7	1.481269334	1.628484122	-0.397898045	N1	7	1.109095555	-1.326443298	-1.202555969
C14	6	3.001883015	-2.565156678	1.252366421	C14	6	1.053318451	2.407565558	-1.464355445	C14	6	0.869266850	-0.664603320	-2.395069525
C15	6	2.390055818	-3.781825389	1.406668320	C15	6	0.347222996	3.441196630	-0.905844062	C15	6	1.981534035	0.107988202	-2.616733470
N2	7	1.270866465	-3.871634048	0.606542119	N2	7	0.324490693	3.331853100	0.468304020	N2	7	2.903144519	-0.061727419	-1.605915905
C17	6	1.203377274	-2.719205824	-0.019138767	C17	6	1.008913969	2.243606861	0.736890612	C17	6	2.352297713	-0.928337621	-0.782824004
H11	1	3.872275002	-2.115051464	1.705706635	H11	1	1.280025920	2.139305546	-2.485223710	H11	1	-0.053821128	-0.800381367	-2.938511401
H14	1	2.689135182	-4.599251040	2.049243212	H14	1	-0.147825334	4.258318789	-1.413698093	H14	1	2.175287669	0.771959844	-3.449015418
H17	1	0.453006290	-2.429502164	-0.741365827	H17	1	1.209349676	1.845276001	1.721602413	H17	1	2.784198250	-1.301060313	0.136434030
C18	6	-3.482362988	1.092239994	-0.360036480	C18	6	-3.192150687	-0.321723400	0.098411553	C18	6	0.136177451	3.133936490	0.380538184
H19	1	-4.327576801	1.034138709	0.339591912	H19	1	-4.009509102	-0.487156333	0.813479123	H19	1	-0.219487519	4.011563594	0.937789143
C19	6	-3.791220980	0.143795293	-1.534409410	C19	6	-3.475321115	-1.201745133	-1.134829764	C19	6	-0.177960034	3.371708688	-1.108611073
H20	1	-2.982763239	0.151789373	-2.275904461	H20	1	-2.699827317	-1.072666514	-1.899533943	H20	1	0.169537141	2.533248774	-1.723075015
H21	1	-4.714137134	0.447042978	-2.043055185	H21	1	-4.437398064	-0.932146007	-1.586403036	H21	1	0.325314209	4.277776849	-1.466693177
H22	1	-3.915074781	-0.888011247	-1.188184369	H22	1	-3.508380816	-2.263882011	-0.867829176	H22	1	-1.254752957	3.490562529	-1.274072467
C20	6	-3.382373308	2.551632912	-0.840001613	C20	6	-3.198963648	1.172037508	-0.276617377	C20	6	1.656415911	3.023329804	0.610622625
H6	1	-2.576426148	2.678783892	-1.572802214	H6	1	-2.431862237	1.401123724	-1.025102055	H6	1	2.089659937	2.186894131	0.050737206
H23	1	-3.187118322	3.233624282	-0.005184858	H23	1	-3.005206807	1.805689905	0.594995164	H23	1	1.887522781	2.875602997	1.671622533
H24	1	-4.316706517	2.861458162	-1.322817455	H24	1	-4.170771689	1.453799043	-0.699537921	H24	1	2.158629126	3.939444855	0.277349705

3.5.8 Energy decomposition analyses

The intramolecular interaction between the imide carbonyl groups (C=O) and the R¹-groups on the *N*-phenyl rotors in the optimized (B3LYP-D3/6-311G*) transition states were calculated using the functional group interaction analysis method, FI-SAPT (SAPT(0)/jun-cc-pVDZ) as implemented in Psi4.^{119,175} SAPT(0) is the default SAPT level and jun-cc-pVDZ, which contained the diffuse function, should cover all the atoms involved in our rotors. This energy decomposition analysis provided a total interaction energy (E_{SAPT}) as well as the component terms: exchange-repulsion (E_{SAPT-repl}), electrostatic (E_{SAPT-elst}), induction (E_{SAPT-ind}), and dispersion (E_{SAPT-disp}) (**Table 3.19**).

Table 3.19 Fi-SAPT of all the rotors involved in this paper. All units in kcal/mol.

Rotors (R=)	E _{elst}	E _{exch}	E _{ind}	E _{disp}	E _{total}	E _{int}
1(quinoline)	8.6	17.5	-3.6	-2.2	22.5	1.8
1(N(CH ₃) ₂)	3.7	17.9	-3.2	-3.2	15.2	0.7
1(N=CH(PhNO ₂))	3.3	15.7	-3.3	-2.7	13.0	-0.3
1(N(CH ₃)Ph)	0.4	19.0	-3.7	-5.3	10.4	-0.7
1(imidazole)	2.4	16.8	-2.8	-4.1	16.5	-0.8
1(NPhCOCH ₃)	-3.4	20.2	-3.4	-5.3	8.1	-4.4
1(NPhCOCF ₃)	-3.0	18.5	-3.3	-5.2	6.9	-4.5
1(NO ₂)	-3.5	12.3	-3.1	-2.6	3.1	-6.1
1(N(COPhNO ₂) ₂)Ph)	-9.5	20.0	-4.2	-6.1	0.2	-8.4
3(C(CH ₂)CH ₃)	-0.2	19.7	-3.9	-3.6	12.0	-2.0
3(CN)	-1.5	14.1	-3.8	-2.2	6.6	-5.3
3(CHO)	-6.0	15.7	-4.8	-2.7	2.2	-8.4
3(COCH ₃)	-5.9	17.5	-5.1	-3.8	2.7	-8.2
3(COPh)	-4.2	20.6	-6.2	-4.8	5.4	-8.7
4(Ph)	0.8	21.3	-4.2	-4.0	13.9	-0.3
4(PhF)	-0.5	22.0	-4.1	-4.1	13.3	-1.2
4(PhF ₃)	-2.4	21.2	-4.1	-4.2	10.6	-2.3
4(PhF ₅)	-7.5	22.1	-4.0	-4.5	6.1	-4.5
4(PhNO ₂)	-2.3	21.3	-4.5	-4.3	10.3	-2.6
4(Ph(NO ₂) ₂)	-6.6	22.8	-4.4	-4.5	7.3	-4.4

From **Figure 3.32**, the interaction energies perfectly coordinated with the $E_{\text{total-SAPT}}$ of TSs, which proved that the interactions mainly happened in the TSs. The SAPT electrostatic term ($E_{\text{SAPT-elst}}$) was strongly linearly correlated with the experimental interaction energies (E_{inter}) for the $\text{C}=\text{O}\cdots\text{C}=\text{O}/\text{C}\equiv\text{N}$ interaction in rotor **3**, $\text{C}=\text{O}\cdots\text{aromatic}$ interaction in rotor **4**, and the $\text{C}=\text{O}\cdots\text{N}$ interactions in rotors **1** (**Figure 3.32**). This analysis corroborates the strong correlation of E_{int} with the electrostatic parameter ESP shown in the manuscript, that was used to draw the conclusion that all three types of interactions have a strong electrostatic component. However, only rotors **3** had stronger orbital-orbital interaction components, therefore, rotors **3** shown a moderate correlation for E_{int} and $E_{\text{SAPT-ind}}$ which also matched the fact that the nitrogen pnictogen bond of rotors **1** and rotors **4** had minor orbital-orbital components (**Figure 3.32**).

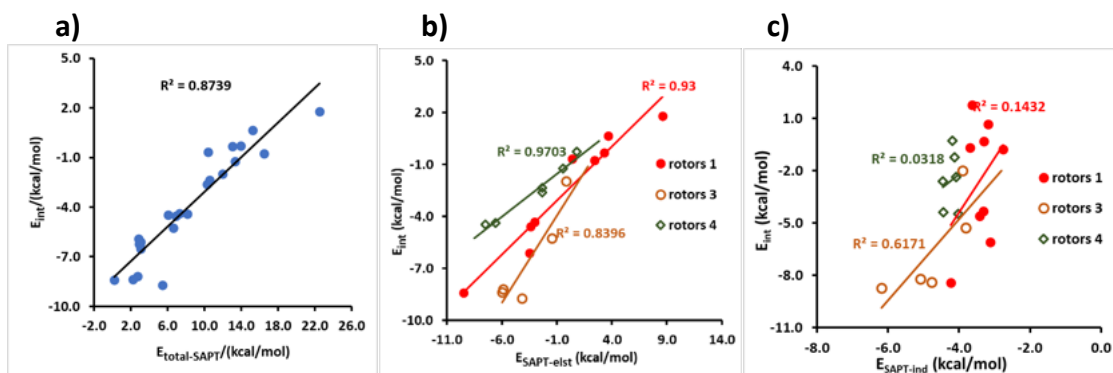


Figure 3.32 a) The correlations between interaction energies E_{int} and total terms of SAPT E_{SAPT} for rotors **1**, **3** and **4** as defined on **Scheme 3.3**. b) The correlations between E_{int} and $E_{\text{SAPT-elst}}$ for rotors **1**, **3**, and **4**. c) The correlations between E_{int} and $E_{\text{SAPT-ind}}$ for rotors **1**, **3**, and **4**.

3.5.9 Second order perturbation theory analysis in natural bond orbital (NBO) basis

Q-Chem version 5.4, which incorporates the NBO version 5.4 program, were used to perform natural bond orbital (NBO) calculations on the transition state structures (B3LYP-D3/6-311G*). The specific term that was analyzed in the text and SI was second

order perturbation theory analysis in natural bond orbital basis (NBO). The NBO calculations were performed at the ω B97M-V/6-311+G* level of theory. A couple of methods and basic sets were tried and compared. As the levels of theory were increased (left to right in **Table 3.20**), the NBO perturbation energies (NBO_{SOPT}) changed. The changes leveled off starting at the ω B97M-V/6-311+G* level of theory which was with a diffuse function. Thus, this level of theory was used to calculate all interaction types in **Table 3.20b**. NBO_{SOPT} energies for the intramolecular C=O lone pair to *N*-phenyl R¹-group interactions provided a measure of the orbital-orbital component of the n→ π^* interactions. The NBO_{SOPT} energies for the new nitrogen rotors **1** were compared with previously measured NBO_{SOPT} energies for rotors **3** and **4**^{1,4} (**Table 3.20b**).

Table 3.20 a) determination of the theory level for NBO_{SOPT} energies.

Rotors	B3LYP/ 6311G*	B3LYP/ 6311+G*	ω B97M-V/ 6-311G*	ω B97M-V/ 6-311+G*	ω B97M-V/ 6-311++G*	ω B97M-V/ 6- 311++G**
1 (NO ₂)	-3.61	-3.86	-4.05	-4.32	-4.33	-4.32
3 (CHO)	-13.10	-14.29	-16.50	-16.04	-16.04	-16.08

b) NBO_{SOPT} (ω B97M-V/6-311+G*) between the C=O lone pair and the R¹-groups in the TS structures of rotors **1**, **3**, and **4** as defined on **Scheme 3.3**.

rotors 3 and 4 R-groups	NBO (kcal/mol)	rotors 1 R-groups	NBO (kcal/mol)
3 (CN)	-8.8	1 (NO ₂)	-4.32
3 ((C=CH ₂)CH ₃)	-5.8	1 (N(COCH ₃)Ph)	0
3 (COPh)	-16.64	1 (N(COCF ₃)Ph)	0
3 (COCH ₃)	-18.1	1 (N(CH ₃) ₂)	0
3 (CHO)	-16.04	1 (N(CH ₃)Ph)	0
4 (Ph)	-3.5	1 (quinoline)	-0.66
4 (PhF)	-3.2	1 (N=CH-(PhNO ₂))	-1.3
4 (PhF ₃)	-3.94	1 (imidazole)	0
4 (PhF ₅)	-3.49	1 (N(COPh(NO ₂) ₂)Ph)	0
4 (PhNO ₂)	-4.8		
4 (Ph(NO ₂) ₂)	-4.21		

The orbital-orbital components were analyzed by plotting E_{int} and NBO_{SOPT} of rotors **1**, **3** and **4**. Rotors **3** had much larger NBO_{SOPT} and showed perfect correlation in E_{int} and NBO_{SOPT} , which meant the orbital-orbital components played another key role in the $n \rightarrow \pi^*$ interactions of rotors **3**. Reversely, rotors **1** and **4** had small even no NBO_{SOPT} energies and NBO_{SOPT} randomly spread out, therefore rotors **1** and **4** had the minor or negligible orbital-orbital components (**Figure S29**).

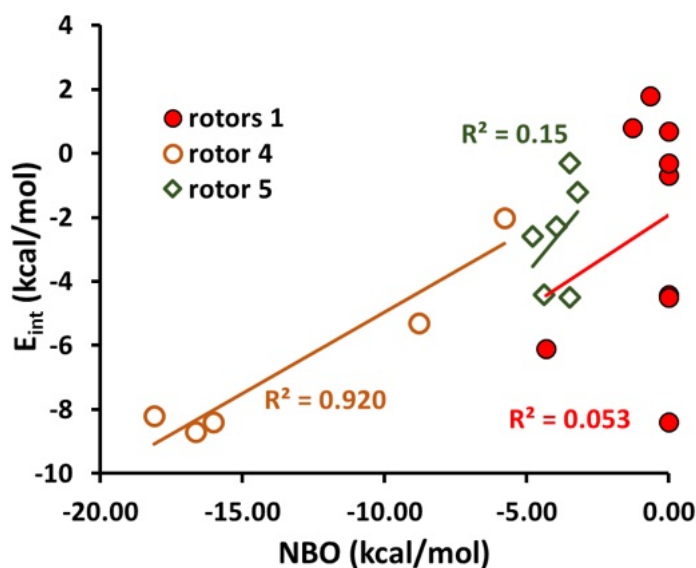


Figure 3.33 Plots of E_{int} and NBO_{SOPT} of rotors **1**, **3** and **4** as defined on **Scheme 3.3**.

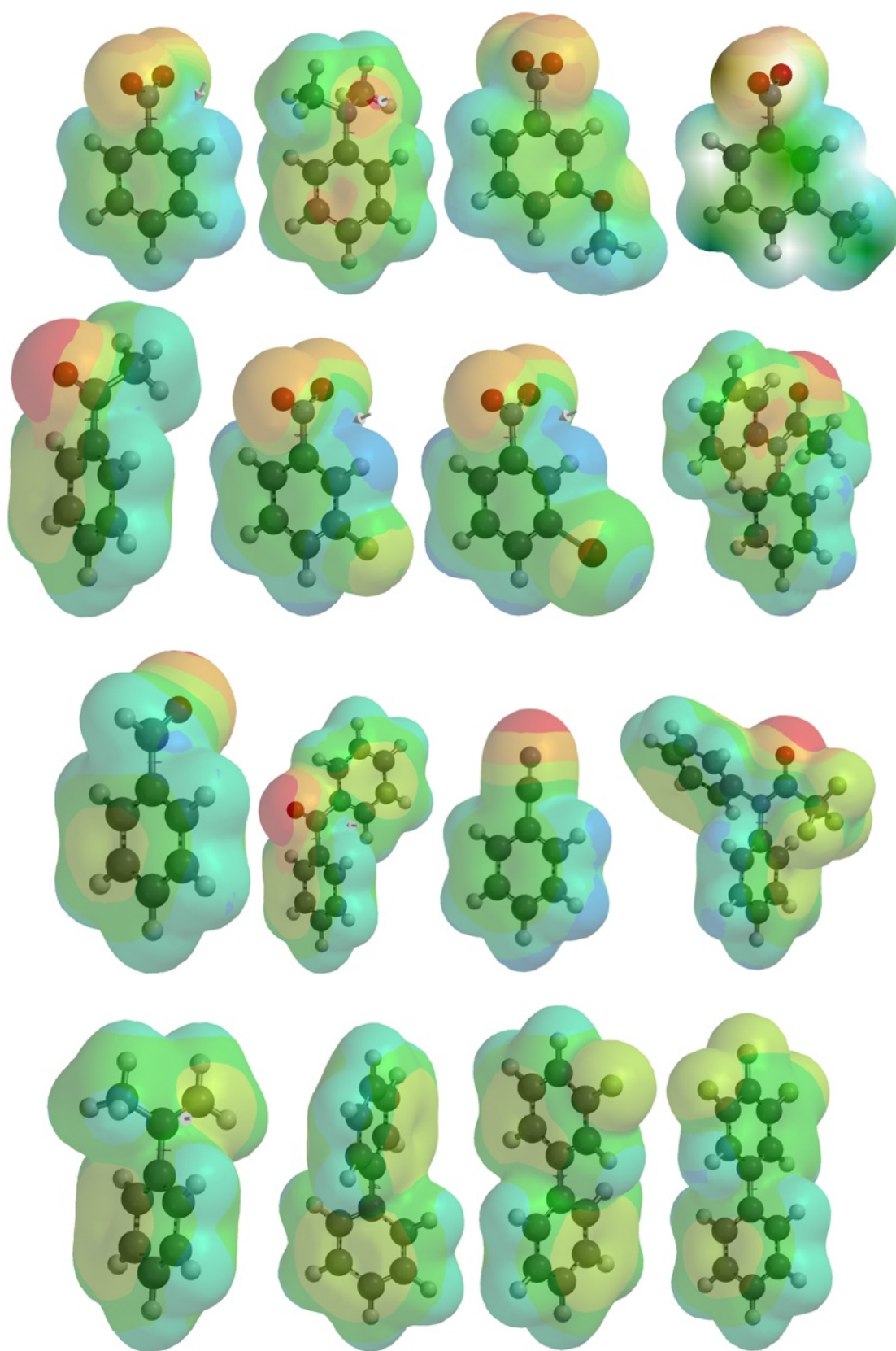
3.5.10 ESP calculations

A series of methods and basic sets were performed to determine the theory level of electrostatic potential maps (ESP) calculations (**Table 3.21**). The ESP values changed with increasing size of the basis set (left to right, **Table 3.21**). A basic set with a diffuse function (+) was necessary, but the methods did not change the outcomes obviously. ESP tended to be steady since the level of $\omega\text{B97M-V/6-311+G}^*$ which was with a diffuse function.

To be consistent with NBO perturbation energies, electrostatic potential maps were calculated with geometry optimization at the ω B97M-V/6-311+G* level of theory for the R¹-groups of the molecular rotors attached to a benzene ring (**Table 3.2**). The R¹-group to phenyl bond was twisted to a perpendicular geometry to mimic the transition state geometry of the R¹-group. The negative to positive regions of the molecules were shown from red, orange, yellow, green, blue-green to blue (-200 to +200 kcal/mol). The ESP value was calculated at a point on the surface for the first atom of the R¹-group. Some figures showed the arrows for the position on the surface for the ESP calculations. For planar R¹-groups the ESP was measured on either side of the first attached atom and the average of the two values was used as the ESP (**Figure 3.34**). All the three types of rotors showed the significance in the relationship between E_{int} and ESP, especially rotors **1** and **4** had perfect correlation ($R^2 = 0.95$, $R^2 = 0.95$). Rotors **3** was less correlated but still good ($R^2 = 0.83$), the electrostatic component was still strong in the interactions (**Figure 3.35**).

Table 3.21 determination of the theory level for ESP.

Rotors R=	B3LYP-			ω B97M-V/ 6311G*	ω B97M-V / 6311+G*	ω B97M-V/ 6311++G**
	B3LYP/ 631G*	D3/ 6311G*	B3LYP-D3/ 6311+G*			
1 (NO ₂)	24.5	27.5	30.0	27.5	30.3	29.5
3 (COCH ₃)	20.7	22.8	24.0	22.0	23.8	23.8



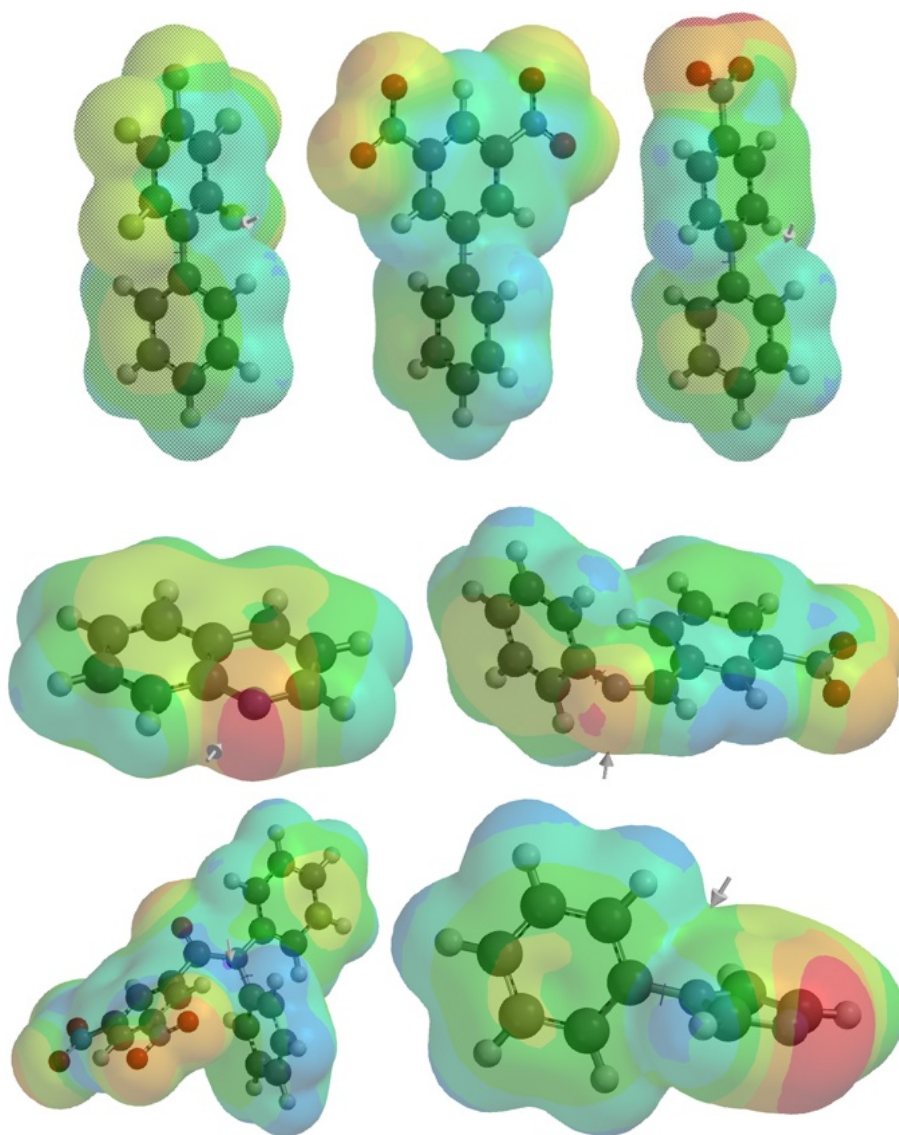


Figure 3.34. ESP maps used to generate the ESP values in **Table 3.2**.

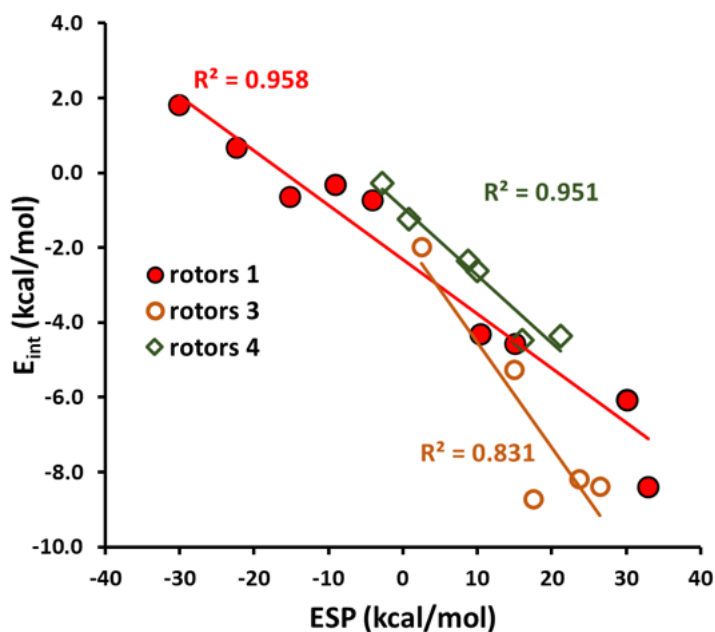


Figure 3.35 Plots of E_{int} and ESP of rotors **1**, **3** and **4** as defined on **Scheme 3.3**.

3.5.11 X-Ray crystal structures

X-Ray Structure Determination of rotor **1** (NO_2) ($\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_4$):

X-ray intensity data from a colorless plate were collected at 300(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-II area detector and an Incoatec microfocus source (Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$). The raw area detector data frames were reduced, scaled and corrected for absorption effects using the Bruker APEX3, SAINT+ and SADABS programs.¹²⁸ The structure was solved with SHELXT.^{129,130} Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXL-2018¹²⁸ using OLEX2.¹³¹

The compound crystallizes in the monoclinic system (**Figure 3.36**). The pattern of systematic absences in the intensity data was consistent with the space group $P2_1/c$, which

was confirmed by structure solution. The asymmetric unit consists of one molecule. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to carbon were located in difference Fourier maps before being placed in geometrically idealized positions and included as riding atoms with $d(\text{C-H}) = 0.98 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methine hydrogen atoms, $d(\text{C-H}) = 0.93 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methine hydrogen atoms, $d(\text{C-H}) = 0.97 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methylene hydrogen atoms. The largest residual electron density peak in the final difference map is $0.22 \text{ e}^-/\text{\AA}^3$, located $1.10 \text{ \AA}$ from O4.

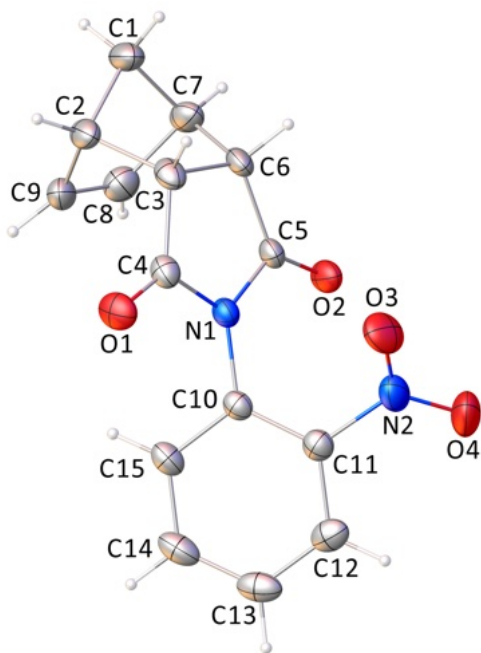


Figure 3.36 Crystal structure of rotor **1**(NO₂) (C₁₅H₁₂N₂O₄).

Table 3.22 Crystal data and structure refinement for rotor **1**(NO₂).

CCDC deposit number	2208130
Identification code	0921LH_nitro
Empirical formula	C ₁₅ H ₁₂ N ₂ O ₄
Formula weight	284.27
Temperature/K	300(2)
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	11.3394(3)
b/Å	17.6877(4)
c/Å	6.74600(10)
α /°	90
β /°	91.9520(10)
γ /°	90
Volume/Å ³	1352.25(5)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.396
μ/mm^{-1}	0.103
F(000)	592.0
Crystal size/mm ³	0.3 × 0.22 × 0.06
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	4.606 to 56.622
Index ranges	-15 ≤ h ≤ 15, -23 ≤ k ≤ 23, -8 ≤ l ≤ 8
Reflections collected	110334
Independent reflections	3351 [R _{int} = 0.0456, R _{sigma} = 0.0136]
Data/raints/parameters	3351/0/191
Goodness-of-fit on F ²	1.076
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0492, wR ₂ = 0.1340

X-Ray Structure Determination of rotor 2(N(COCH₃)Ph) (C₂₃H₂₀N₂O₃):
(CCDC deposit number 2208129)

X-ray intensity data from a colorless plate were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-II area detector and an Incoatec microfocus source (Mo K α radiation, λ = 0.71073 Å). The raw area detector data frames were reduced, scaled and corrected for absorption effects using the Bruker APEX3, SAINT+ and SADABS programs.¹²⁸ The structure was solved with SHELXT.^{129,130} Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXL-2018¹²⁸ using OLEX2.¹³¹

The compound crystallizes in the orthorhombic system (**Figure 3.37**).

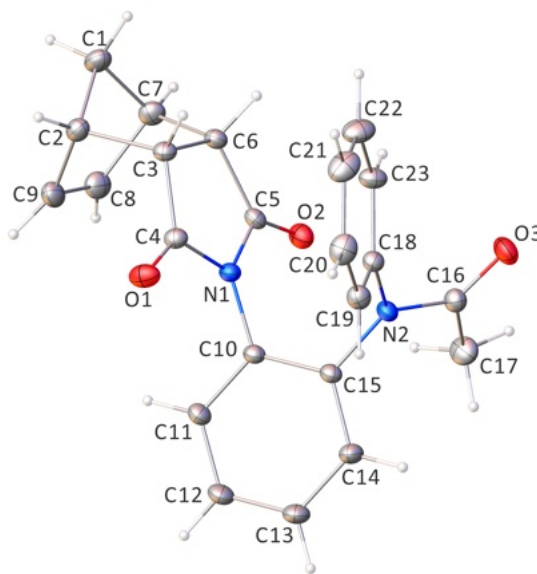


Figure 3.37 Crystal structure of rotor 2(N(COCH₃)Ph) (C₂₃H₂₀N₂O₃).

The pattern of systematic absences in the intensity data was uniquely consistent with the space group $P2_12_12_1$, which was confirmed by structure solution. The asymmetric unit consists of one molecule.

All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to carbon were located in difference Fourier maps before being placed in geometrically idealized positions and included as riding atoms with $d(\text{C-H}) = 1.00 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methine hydrogen atoms, $d(\text{C-H}) = 0.95 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for arene hydrogen atoms and $d(\text{C-H}) = 0.99 \text{ \AA}$, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methylene hydrogen atoms and $d(\text{C-H}) = 0.98 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl hydrogens.

The methyl hydrogens were allowed to rotate as a rigid group to the orientation of maximum observed electron density. The largest residual electron density peak in the final difference map is $0.36 \text{ e}^-/\text{\AA}^3$, located $0.67 \text{ \AA}$ from C10. The final Flack x parameter was $-0.09(12)$, providing good support for the assignment of the correct absolute structure in a light atom structure.

Table 3.23 Crystal data and structure refinement for rotor **2**(N(COCH₃)Ph) (C₂₃H₂₀N₂O₃).

CCDC deposit number	2208129
Identification code	lbz_c26
Empirical formula	C ₂₃ H ₂₀ N ₂ O ₃
Formula weight	372.41
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	P212121
a/Å	8.8868(4)
b/Å	10.9089(5)
c/Å	19.0879(8)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	1850.48(14)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.337
μ/mm^{-1}	0.089
F(000)	784.0
Crystal size/mm ³	0.46 × 0.25 × 0.09
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	5.056 to 67.642
Index ranges	-13 ≤ h ≤ 13, -17 ≤ k ≤ 17, -29 ≤ l ≤ 29
Reflections collected	106598
Independent reflections	7419 [R _{int} = 0.0337, R _{sigma} = 0.0145]
Data/restraints/parameters	7419/0/254
Goodness-of-fit on F ²	1.102
Final R indexes [I ≥ 2 σ (I)]	R1 = 0.0300, wR2 = 0.0823

X-Ray Structure Determination of rotor **2**(N(COCF₃)Ph) (C₂₃H₁₇N₂O₃F₃)

X-ray intensity data from a colorless block were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-II area detector and an Incoatec microfocus source (Mo K α radiation, $\lambda = 0.71073$ Å).

The raw area detector data frames were reduced, scaled and corrected for absorption effects using the Bruker APEX3, SAINT+ and SADABS programs.¹²⁸ The structure was solved with SHELXT.^{129,130} Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXL-2018¹²⁸ using OLEX2.¹³¹

The compound crystallizes in the orthorhombic system (**Figure 3.38**).

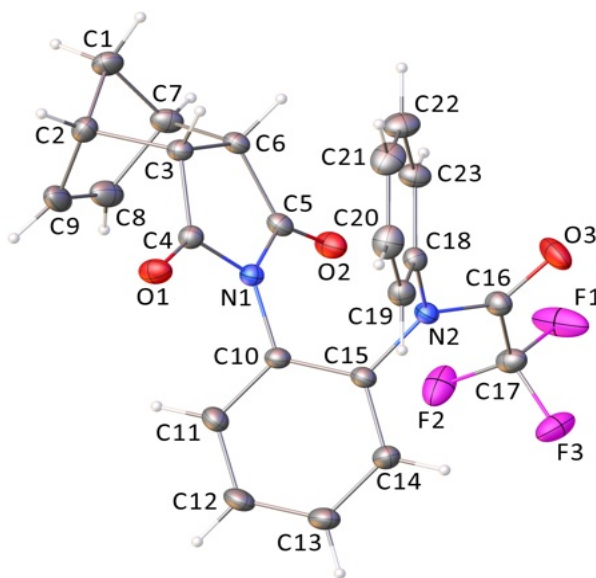


Figure 3.38 Crystal structure of rotor **2**(N(COCF₃)Ph) (C₂₃H₁₇N₂O₃F₃).

The pattern of systematic absences in the intensity data was uniquely consistent with the space group $P2_12_12_1$, which was confirmed by structure solution.

The asymmetric unit consists of one molecule. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to carbon were located in difference Fourier maps before being placed in geometrically idealized positions and included as riding atoms with $d(\text{C-H}) = 1.00 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methine hydrogen atoms, $d(\text{C-H}) = 0.95 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for arene hydrogen atoms and $d(\text{C-H}) = 0.99 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methylene hydrogen atoms.

The largest residual electron density peak in the final difference map is $0.29 \text{ e}^-/\text{\AA}^3$, located $0.67 \text{ \AA}$ from C14. The final Flack x parameter was $0.25(19)$, providing good support for the assignment of the correct absolute structure for a light atom structure.

Table 3.24 Crystal data and structure refinement for rotor 2(N(COCH₃)Ph) (C₂₃H₁₇N₂O₃F₃).

CCDC deposit number	2208127
Identification code	lbz_c27
Empirical formula	C ₂₃ H ₁₇ F ₃ N ₂ O ₃
Formula weight	426.38
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	9.2451(6)
b/Å	10.9843(8)
c/Å	19.0974(13)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/Å ³	1939.4(2)
Z	4
$\rho_{\text{calc}}/\text{cm}^{-3}$	1.460
μ/mm^{-1}	0.117
F(000)	880.0
Crystal size/mm ³	0.44 × 0.24 × 0.18
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/ $^\circ$	4.896 to 65.182
Index ranges	-13 ≤ h ≤ 13, -16 ≤ k ≤ 16, -27 ≤ l ≤ 28
Reflections collected	29748
Independent reflections	6893 [R _{int} = 0.0343, R _{sigma} = 0.0328]
Data/restraints/parameters	6893/0/281
Goodness-of-fit on F ²	1.023
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0362, wR ₂ = 0.0824

X-Ray Structure Determination, rotor 2(NCH₃Ph) (C₂₂H₂₀N₂O₂)

X-ray intensity data from a colorless plate were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-II area detector and an Incoatec microfocus source (Mo K α radiation, $\lambda = 0.71073$ Å). The raw area detector data frames were reduced, scaled and corrected for absorption effects using the Bruker APEX3, SAINT+ and SADABS programs.¹²⁸ The structure was solved with SHELXT.^{129,130} Subsequent difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXL-2018¹²⁸ using OLEX2.¹³¹

The compound crystallizes in the monoclinic system. The pattern of systematic absences in the intensity data was consistent with the space groups $P2_1$ and $P2_1/m$; intensity statistics were consistent with an acentric structure.

The space group $P2_1$ was eventually confirmed by obtaining a stable structure solution and refinement and further by using ADDSYM on a hypothetical non-disordered structure.^{176–178} The asymmetric unit consists of two crystallographically independent molecules. They were numbered similarly except for label suffixes A or B. Initially a normal refinement of just the two molecules were refined, resulting in a rather unsatisfactory $R1$ value of 0.074. Subsequent examination of the difference electron density map showed a clearly defined pattern of small residual density peaks near the two molecules, consistent with the presence of a different conformation for each.

The residual peaks were nearly superimposed on the primary molecules but deviated most obviously at the tetrahydro-1H-4,7-methanoisindole-1,3(2H)-dione substituent part of the molecule. Smaller peaks were also observed around the methylphenylamine grouping.

These observations were attributed to whole-molecule disorder affecting both independent molecules. For the final model, two entire molecules with different conformations and occupancies were refined for each independent site. The minor component of molecule “A” was given atom label suffixes “C”, and those of molecule “B” were given label suffixes “D” (**Figure 3.39**).

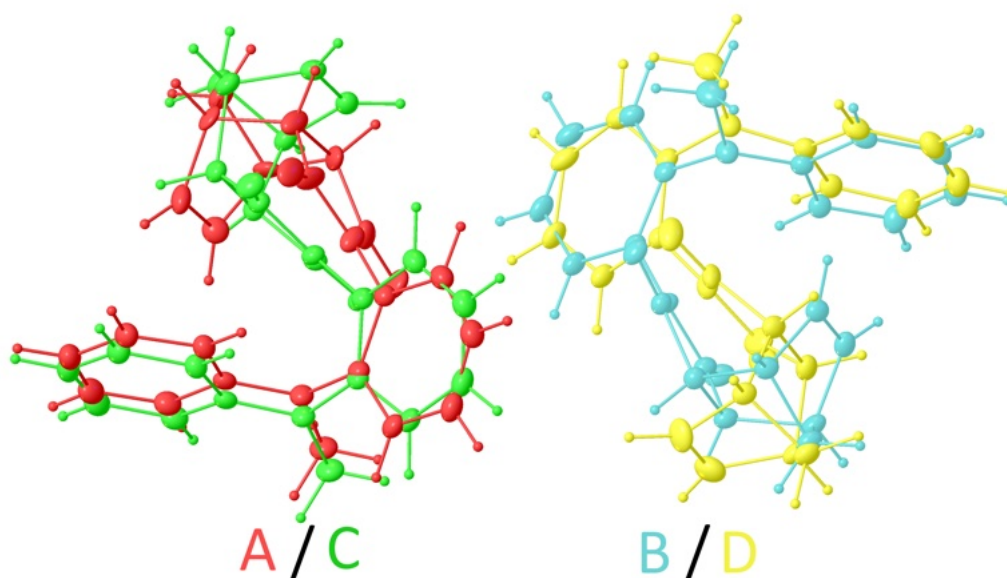


Figure 3.39 Mixed crystal structures of rotor 2(NCH₃Ph) (C₂₂H₂₀N₂O₂).

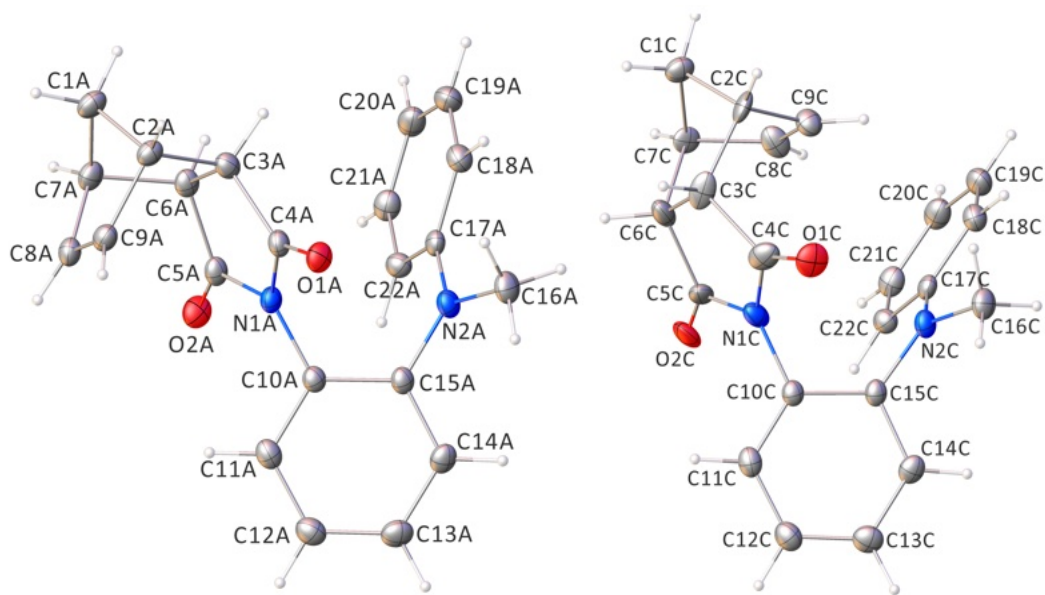
Fractional occupancies for each independent molecule were constrained to sum to one and refined to $A/C = 0.870(3)/0.130(3)$ and $B/D = 0.884(2)/0.116(2)$. The overall geometry of each minor component was restrained to be similar to that of the major using SHELX SAME instructions, technically accomplished by restraining the 1,2- and 1,3-distances of the minor to be the same as the corresponding distances in the major components. This allows for some flexibility in conformation.

In total, 151 distance restraints were applied. Nearly overlapping atoms were given equal displacement parameters for stability. With this treatment, chemically sensible minor

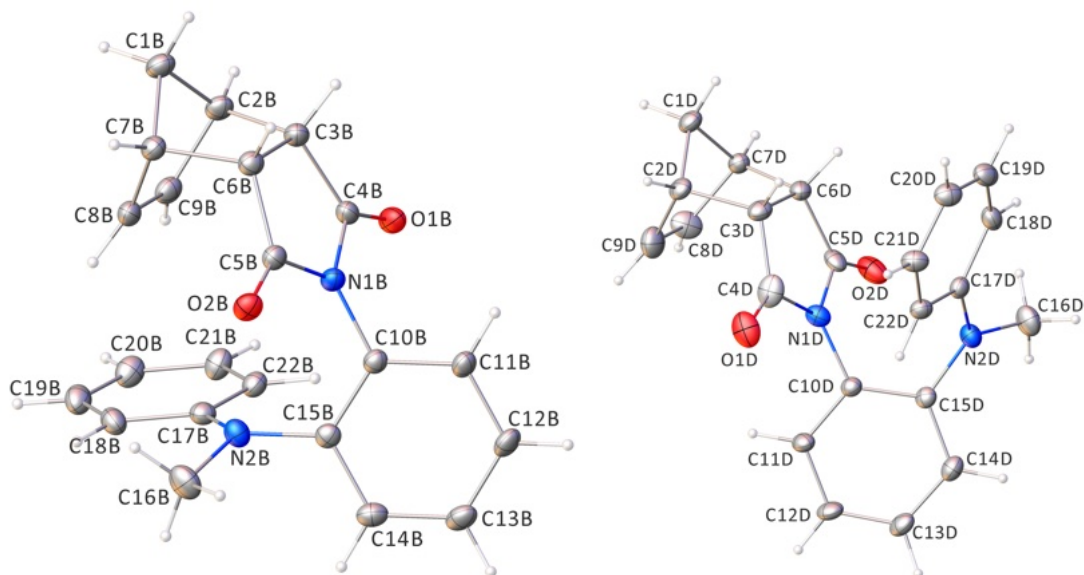
conformation molecular structures were refined, and the *R*1-value decreased to 0.038. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to carbon were placed in geometrically idealized positions and included as riding atoms with $d(\text{C-H}) = 1.00 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methine hydrogen atoms, $d(\text{C-H}) = 0.95 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for arene hydrogen atoms, $d(\text{C-H}) = 0.99 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methylene hydrogen atoms, and $d(\text{C-H}) = 0.98 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl hydrogens.

The methyl hydrogens were allowed to rotate as a rigid group to the orientation of maximum observed electron density. The largest residual electron density peak in the final difference map is $0.21 \text{ e}^-/\text{\AA}^3$ located $0.57 \text{ \AA}$ from H16e. Because of the absence of heavy atoms in the structure, the absolute structure could not be reliably determined and no Flack *x* parameter is reported.

Asymmetric unit of the crystal. Displacement ellipsoids drawn at the 40% probability level. Two crystallographically independent but chemically similar molecules. Each exists in two conformations, which are disordered in the same crystallographic site and appear superimposed on each other in the structure solution. A whole-molecule disorder model was refined, giving fractional occupancies of: A/C = 0.870(3)/0.130(3) and B/D = 0.884(2)/0.116(2) (Figure 3.40).



a) A, 87.0% and C, 13%.



b) B, 88.4% and D, 11.6%.

Figure 3.40 Ratio of mixed crystal structures of rotor **2**(NCH₃Ph) (C₂₂H₂₀N₂O₂).

Table 3.25 Crystal data and structure refinement for rotor 2(NCH₃Ph) (C₂₂H₂₀N₂O₂).

CCDC deposit number	2208128
Identification code	lbz_c40
Empirical formula	C ₂₂ H ₂₀ N ₂ O ₂
Formula weight	344.40
Temperature/K	100(2)
Crystal system	monoclinic
Space group	P2 ₁
a/Å	8.3948(3)
b/Å	7.9262(3)
c/Å	25.6547(10)
$\alpha/^\circ$	90
$\beta/^\circ$	90.0270(10)
$\gamma/^\circ$	90
Volume/Å ³	1707.03(11)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.340
μ/mm^{-1}	0.087
F(000)	728.0
Crystal size/mm ³	0.24 × 0.1 × 0.06
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/ $^\circ$	4.764 to 58.358
Index ranges	-11 ≤ h ≤ 11, -10 ≤ k ≤ 10, -35 ≤ l ≤ 35
Reflections collected	64965
Independent reflections	9208 [R _{int} = 0.0381, R _{sigma} = 0.0264]
Data/restraints/parameters	9208/151/739
Goodness-of-fit on F ²	1.068

Chapter 4 Transition State Stabilizing Effects of Oxygen and Sulfur Chalcogen Bond Interactions

4.1 Abstract

Non-covalent chalcogen bond (ChB) interactions have found utility in many fields, including organocatalysis. To assess the potential of ChB interactions of the most abundant chalcogens (oxygen and sulfur) in catalysis, the kinetic effect of S and O ChBs were experimentally measured using a series of molecular rotors. The rotors were designed to form stabilizing ChB interactions in their bond rotations in transition states. The lower rotational barriers and increased rates of rotation were monitored by 2D EXSY ¹HNMR. Despite the lack of the strong electron-withdrawing groups, a properly oriented sulfur lowered the rotational barriers of by as much as -7.2 kcal/mol. Oxygen rotors also could form ChB interactions but required electron withdrawing groups. These findings suggest that ChB interactions can be used to design efficient catalysts for a variety of reactions. The geometric propensities of the interactions showed that the oxygen and sulfur interactions had different orbital-orbital components the corresponded to their polarizabilities. The strong correlation between the strength of the interactions and ESP provides a valuable tool for the rational design of future ChB catalysts.

4.2 Introduction

The chalcogen bond (ChB) is an attractive interaction between an electron-poor region on a chalcogen atom (O, S, Se, Te) with an electron-rich region of a second group.^{179–181} ChBs are relatively new non-covalent interactions.

Yet, they have already found applications in molecular recognition,^{182–185} drug design,^{186–188} crystal engineering,^{180,189,190} and organic semiconductors.¹⁹¹ A particularly promising application has been in organocatalysis.^{192–195} For example, Matile has developed a organocatalyst which activates pyridines, quinolines, and imines for reduction using selenium chalcogen bonds (**Figure 4.1a**).^{2,192} Elsewhere, Smith proposed that intramolecular sulfur chalcogen bonding interactions were essential in an isothioureacatalyzed asymmetric annulation reaction (**Figure 4.1b**).³ Additional examples of chalcogen bonding promoted or catalyzed reactions include: enantioselective acylation of alcohols,^{196–198} hydrogenation,¹⁹² bromination,¹⁹⁹ halide abstraction,²⁰⁰ Michael addition,²⁰¹ Rauhut-Currier-type reactions,¹⁹⁵ ketone cyanosilylation,²⁰² and Diels-Alder reactions.²⁰³

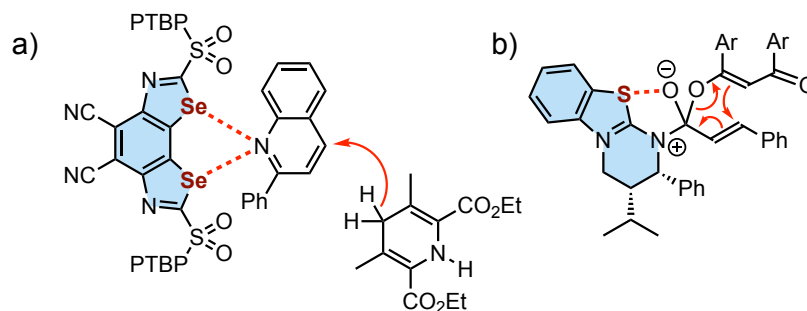


Figure 4.1 Examples of chalcogen bonding (ChB) interactions in organocatalysis, highlighting the role of the ChB interaction (dotted line) in the key transition state or intermediate complexes.^{2,3}

While there have been experimental and theoretical studies of chalcogen bonding interactions,^{180,189,190,204–207} few have directly examined their abilities to effect reaction rates²⁰⁸ and kinetics⁶⁵ via the stabilization of transition states and intermediates. Most studies have focused on the ChB interactions of thermodynamically stable structures such

as those in host-guest complexes or self-assembly.^{183,209,210} The stability trends for non-covalent interactions formed in transition states may differ due to their hypervalent atoms and distorted bond lengths and angles. Therefore, the goal of this study was to quantitatively assess the catalytic abilities of the ChB interaction and compare them to other common non-covalent interactions used in organocatalysts such as hydrogen bonding and $n \rightarrow \pi^*$ interactions. We were particularly interested in the smallest chalcogens, oxygen and sulfur, which are the most abundant and commonly found in organic frameworks.

Measuring the kinetic effects of non-covalent interactions is challenging as transition states are unstable structures that are difficult to probe. In addition, transition state structures and mechanisms can change over the course of a study. Thus, we developed a simple kinetic model system based on an *N*-phenylsuccinimide molecular rotor (**Figure 4.2**).^{1,4,6,19} Rotation of the central $N_{\text{imide}}-C_{\text{phenyl}}$ single bond is a unimolecular kinetic process with a single barrier and a well-defined planar transition state where interacting groups are forced close together. Rotors which can form stabilizing intramolecular ChBs in the TS will have lower rotational barriers and spin faster. The TS stabilizing effects of the ChB (E_{int}) can be quantified by comparing the barrier to control rotors that cannot form stabilizing TS interactions (E_{steric}).

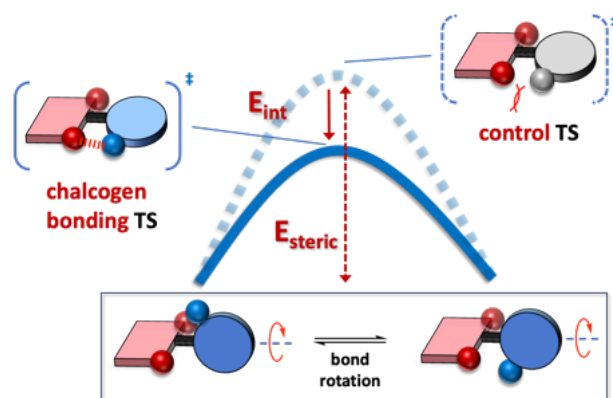


Figure 4.2 Schematic representation of the energy profile of the bond rotation process that highlights the strategy of isolating the stabilizing chalcogen bonding (ChB) interactions (E_{int}) in the TS by comparison with a steric control rotor which measures the steric component of the rotational barrier (E_{steric}).

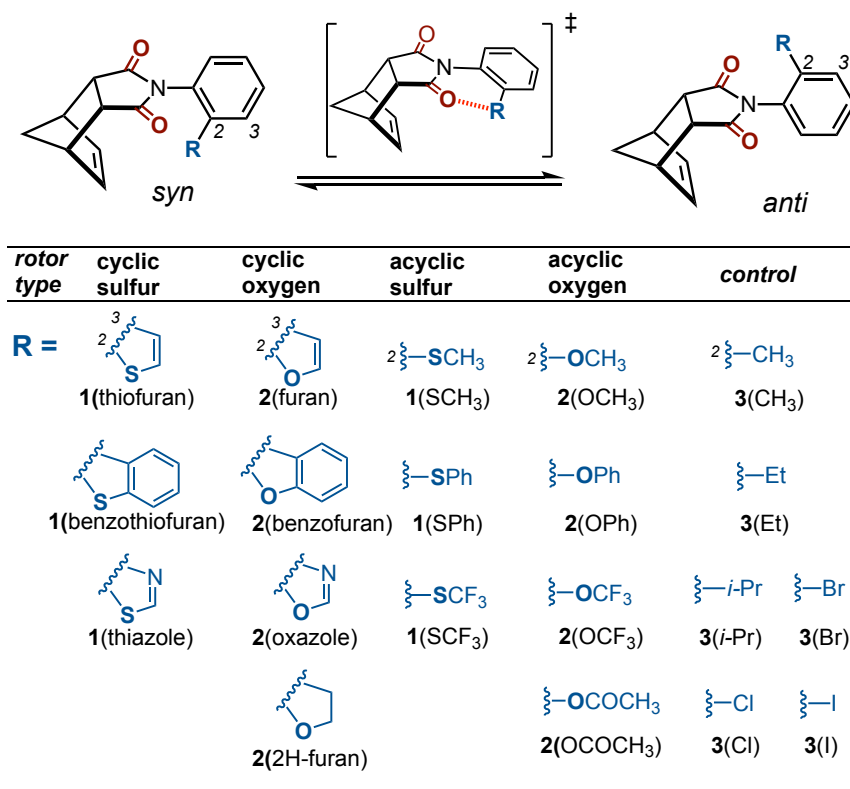
We have successfully employed *N*-phenylsuccinimide rotors to measure and study the kinetic effects other non-covalent interactions such as hydrogen bonding and $n \rightarrow \pi^*$ interactions.^{1,4,6,19} This provides support for the effectiveness of the molecular rotors approach and also provides the opportunity to compare the kinetic effects of the ChB interactions with other non-covalent interactions that have been used in organocatalysts.

The larger chalcogens (Se, Te) are known to form stronger ChB interactions as they are more polarizable which enables the formation of a larger σ -hole. Our main question was whether the smaller chalcogens (S, O) also had potential in organocatalysis by measuring their abilities to affect kinetic processes. While the weaker ChB interactions of sulfur and oxygen would mitigate their utility, this is offset by their greater abundance and ease of incorporation into organic frameworks.

Therefore, our objectives were to employ the molecular rotors to: 1) measure the TS stabilizing abilities sulfur and oxygen ChB interactions, 2) examine the influence of interaction geometry and electron withdrawing groups 3) compare the kinetic effects of

ChB interactions with other non-covalent interactions and 4) to develop predictive models to guide researches in designing new ChB organocatalysts.

N-phenylsuccinimide sulfur rotors **1** and oxygen rotors **2** were designed to measure the TS stabilizing effects of the sulfur ChB and oxygen ChB interactions (**Scheme 4.1**). Due to the steric interactions of the imide C=O groups, the rotors display restricted rotation leading the formation of *syn*- and *anti*-conformers (**Scheme 4.1**). The imide C=O groups can also form TS stabilizing chalcogen bonding interactions with the sulfur or oxygen atoms in the 2-position of the *N*-phenyl unit of rotors **1**.



Scheme 4.1 Conformational *syn-anti* equilibrium of the *N*-phenylsuccinimide molecular rotors **1** arising from bond rotation around the C-N bond. The R-groups are attached at the 2-position of the *N*-phenyl unit with the all the cyclic structures which were fused at the *ortho*- and *meta*-positions.

There are two general classes of ChB rotors: cyclic and acyclic. The cyclic rotors have a chalcogen heterocycle fused to the 2- and 3-positions of the *N*-phenyl unit. The cyclic constraint fixes the geometry of chalcogen atom at the 2-position into a favorable geometry for the ChB interaction (*vide infra*). The acyclic rotors allow greater conformational freedom of the chalcogen group, and in most cases, the rotors adopt a poor ChB geometry, with the chalcogen σ -hole is perpendicular to the imide oxygen lone pair. In addition to exploring the importance of chalcogen atom size and geometry, variations in conjugation and electron withdrawing abilities of the groups attached to the sulfur and oxygen atoms assessed the role of electrostatics and σ -hole size.

To assist in separating the stabilizing ChB and destabilizing steric components of the rotational barriers, control rotors **3** were designed that lack chalcogen atoms and cannot form ChB interactions. Therefore, the rotational barriers of rotors **3** provided a direct measure of the steric component. We have previously successfully utilized this set of control rotors to isolate the TS stabilizing of $n \rightarrow \pi^*$,¹ $n \rightarrow \pi(\text{aromatic})$,⁴ and pnictogen interactions.⁵

4.3 Results and Discussion

The new ChB rotors **1** and **2** were synthesized by thermal condensation of the appropriate *ortho*-substituted aniline with *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride to form the *N*-phenylsuccinimide rotors (**Figure 4.3**, more details in section 4.5.2).^{1,5,211} The imide cyclization reaction is high yielding, does not require additional reagents or catalysts, and functional group tolerant, enabling the rapid assembly of rotors with a variety of chalcogen groups. The structures of several of the rotors (**1**(benzothiofuran), **1**(thiazole), **1**(SPh), **2**(benzofuran)) were also confirmed by X-ray

crystallography (ESI). As expected, the steric interactions between the imide carbonyl and the R-groups in the 2-position lead to distinct *syn*- or *anti*-conformers.

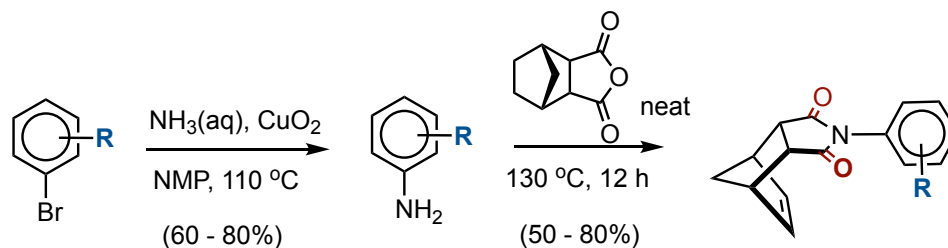


Figure 4.3 General scheme for the two-step synthesis of the chalcogen rotors.

The rotational barriers ($\Delta G^\ddagger_{\text{exp}}$) were measured using 2D EXSY NMR in TCE-d₂. All rotors displayed restricted rotation, as separate peaks were observed in the NMR spectra for the *syn*- and *anti*-conformers below their coalescence temperatures (-50 to >140 °C). The rates of exchange between the *syn*- and *anti*-conformers was measured over a range of temperatures using 2D EXSY of the ¹H NMR spectra of the norbornene alkene protons.^{1,5} The resulting $\Delta H^\ddagger_{\text{exp}}$ and $\Delta S^\ddagger_{\text{exp}}$ values from the Eyring plots were used to calculate $\Delta G^\ddagger_{\text{exp}}$ at a common temperature (298.15 K) to allow direct comparisons. The error in $\Delta G^\ddagger_{\text{exp}}$ was estimated as ± 0.2 kcal/mol based on previous literature precedence.^{21,22}

The NMR measured rotational barriers ($\Delta G^\ddagger_{\text{exp}}$) of the chalcogen rotors varied from 12.0 to 24.2 kcal/mol (**Table 4.1**). In general, the sulfur rotors **1** had higher barriers than the oxygen rotors **1**, which is consistent with the larger size of the sulfur atoms, leading to greater steric interactions in the TS. The cyclic rotors had lower barriers than the acyclic rotors due to the constraints provided by the fused 5-membered rings moving the chalcogen atom away from the opposing C=O oxygen.

Table 4.1 Measured parameters ($\Delta G^\ddagger_{\text{exp}}$, E_{steric} , E_{int}) for molecular rotors **1**, **2**, and **3** and the steric parameter B-value for the R-groups in the 2-position of the *N*-phenylsuccinimide rotors. The values for all parameters are in units of kcal/mol.

rotors	type	$\Delta G^\ddagger_{\text{exp}}^{\text{a}}$	<i>B</i> -value ^b	$E_{\text{steric}}^{\text{c}}$	$E_{\text{int}}^{\text{d}}$
1 (thiofuran)	cyclic	14.9	<i>5.2</i>	19.7	-4.8
(benzothiofuran)	cyclic	14.9	<i>5.5</i>	19.9	-5.0
1 (thiazole)	cyclic	12.0	<i>4.6</i>	19.2	-7.2
2 (furan)	cyclic	15.0	<i>1.9</i>	17.0	-2.0
2 (benzofuran)	cyclic	14.9	<i>2.0</i>	17.1	-2.2
2 (oxazole)	cyclic	12.0	<i>1.5</i>	16.7	-4.7
2 (2H-furan)	cyclic	15.8	<i>1.6</i>	16.8	-1.0
1 (SCH ₃)	acyclic	22.5	8.6	22.4	+0.1
1 (SPh)	acyclic	21.8	8.3	22.2	-0.4
1 (SCF ₃)	acyclic	21.8	8.2	22.1	-0.3
2 (OCH ₃)	acyclic	20.2	5.6	20.0	+0.2 ^f
2 (OPh)	acyclic	18.2	4.2	18.9	-0.7 ^f
2 (OCF ₃)	acyclic	17.9	5.5	19.9	-2.0
2 (OCOCH ₃)	acyclic	16.3	5.4	19.8	-3.5
3 (CH ₃)	acyclic	21.7 ^e	7.4	21.4	f
3 (Et)	acyclic	22.0 ^e	8.7	22.5	f
3 (<i>i</i> -Pr)	acyclic	23.6 ^e	11.1	24.4	f
3 (Cl)	acyclic	22.1 ^e	7.7	21.7	f
3 (Br)	acyclic	23.1 ^e	8.7	22.5	f
3 (I)	acyclic	23.7 ^e	10.0	23.5	f
3 (CF ₃)	acyclic	24.2 ^e	10.5	23.9	f

^ameasured by EXSY ¹H NMR. ^bvalues from literature or calculated (*italics*) at the B3LYP / 6-31G*. ¹⁶⁵ ^ccalculated from equation 2. ^dcalculated from equation 1. ^evalues previously reported.^{1,5} ^frotor was used to calculate the steric trendline.

Confirmation that the rotors formed stabilizing chalcogen interactions were provided by analysis of the experimental and computational rotational barriers. The first indications of the ChB interactions were provided by comparison of $\Delta G^\ddagger_{\text{exp}}$ values for structurally similar pairs of sulfur and oxygen rotors. The barriers for the sulfur rotors were expected to be higher, due to the larger size and steric interactions of the sulfur versus oxygen atoms. However, the more polarizable sulfur atom is known to form stronger ChB interactions than the less polarizable oxygen atom.²⁰⁶ Therefore, if the sulfur rotors had

similar or lower barriers than the oxygen rotors, this could be an indication of the presence of additional TS stabilizing ChB interactions in the sulfur rotors. This was what was observed when comparing similar cyclic sulfur and oxygen rotors. For example, the sulfur rotor **1**(thiofuran) and the oxygen rotor **2**(furan) had very similar $\Delta G^\ddagger_{\text{exp}}$ values (14.9 and 15.0 kcal/mol). The two other pairs of structurally similar cyclic chalcogen rotors also had similar barriers that went against the steric trends. The rotors **1**(benzothiofuran) and **2**(benzofuran) had the same barriers (14.9 and 14.9 kcal/mol). Likewise, the rotor pair **1**(thiazole) and **2**(oxazole) had the same barriers (12.0 and 12.0 kcal/mol).

In contrast, the $\Delta G^\ddagger_{\text{exp}}$ values for the acyclic chalcogen rotors followed the expected steric trends and did not show evidence of stabilizing ChB interactions. For example, rotor **1**(SCH₃) had a higher barrier versus the oxygen rotor **2**(OCH₃) (22.5 vs 20.2 kcal/mol). The other acyclic sulfur and oxygen pairs (**1**(SPh) and **2**(OPh), **1**(SCF₃) and **2**(OCF₃)) also followed the steric trends with the sulfur rotors having a higher barrier than the oxygen rotors. These initial comparisons suggest that the cyclic chalcogen rotors form TS stabilizing ChB interactions. Whereas, the acyclic chalcogen rotors do not. These conclusions were corroborated by the computational analyses below.

Computational studies provided further support for the formation of TS stabilizing ChB interactions in the cyclic sulfur rotors and an explanation for the absence of ChB interactions in the acyclic sulfur rotors. The ground state and transition state structures were calculated at the B3LYP-D3/6-311G* level of theory. The ground state structures were consistent with the x-ray structures. Support for the accuracy of the transition state structures was provided by the ability to reproduce the measured barriers (**Table 4.2**) with a good level of accuracy (± 1.1 kcal/mol). The accuracy was similar for

rotors which formed and did not form ChB interactions (see SI). The level of accuracy and ability to model TS interactions were consistent with our previous computational studies of *N*-phenylsuccinimide rotors.^{1,5}

Analyses of the cyclic sulfur rotor TS structures were consistent with the formation of stabilizing chalcogen interactions (**Figure 4.4**). The distances between the C=O oxygen and the sulfur atoms (**Table 4.2**) were significantly shorter than the sum of the VDW radii for S and O, which is 3.32 Å. For example, the distances (2.535 to 2.580 Å) for **1**(thiofuran), **1**(benzothiofuran), and **1**(thiazole) fall within the range for ChB bonds observed in crystallographic and theory studies (2.4-3.0 Å).^{186,208,212} These distances were also similar to the intramolecular chalcogen bonds in the organocatalysts such as the *N*-acyl isothioureia systems highlighted in Figure 1b.²⁰⁸

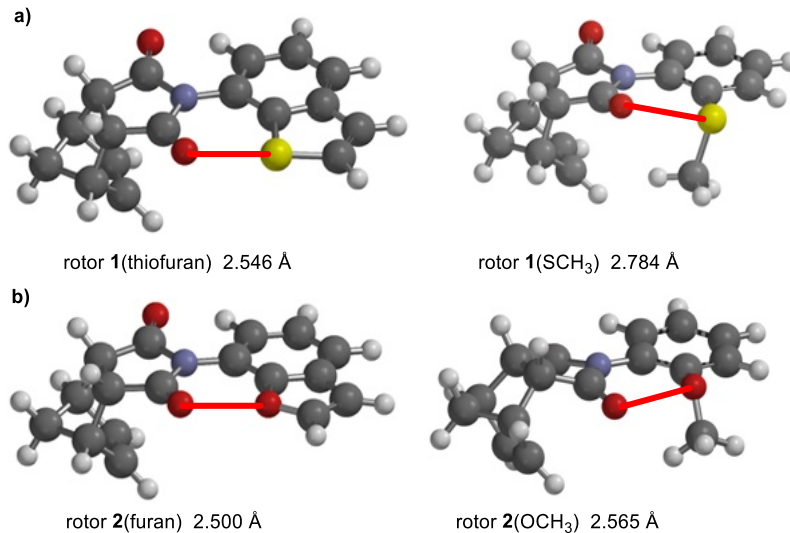


Figure 4.4 **a)** Comparison of the C=O...chalcogen TS distances of cyclic rotor **1**(thiofuran) and acyclic rotor **1**(SCH₃). **b)** Comparison of the C=O...chalcogen TS distances of cyclic rotor **2**(furan) and acyclic rotor **2**(OCH₃).

Comparison of the TS conformations of the cyclic and acyclic sulfur rotors **1** confirmed the importance of the interaction geometry in forming a strong ChB interaction

(Figure 4.4). Theoretical studies have shown that a strong ChB interaction adopt a geometry where the σ -hole of the chalcogen is aligned with the lone pair of the ChB acceptor.^{181,213,214} The TS structures of the cyclic chalcogen rotors are constrained in a favorable ChB geometry with near linear O...S-C angles from 175° to 178°. This is consistent with the cyclic **1** rotors forming stabilizing ChB interactions.

Table 4.2 Measurements from the calculated TS structures (B3LYP-D3/6-311G*).

Rotors (R =)	angle ^a O...Ch-C (deg)	distance ^a O...Ch (Å)	NBO ^b (kcal/mol)	ESP ^c (kcal/mol)
1 (thiofuran)	177.7	2.546	-6.5	12.5
1 (benzothiofuran)	177.8	2.535	-6.9	15.0
1 (thiazole)	175.1	2.580	-5.8	22.0
2 (furan)	152.3	2.503	-0.5	-12.5
2 (benzofuran)	151.4	2.500	-0.5	-10.0
2 (oxazole)	157.7	2.512	-0.6	7.5
2 (2H-furan)	146.6	2.510	0.0	-15.0
1 (SCH ₃)	76.0 ^d (160.0) ^e	2.591 ^d (2.784) ^e	0.0 ^d (-3.7) ^e	-22.0 ^d (3.0) ^e
1 (SPh)	77.1	2.814	0.0	-17.5
1 (SCF ₃)	87.7	2.783	0.0	-14.0
2 (OCH ₃)	74.0	2.565	0.0	-22.5
2 (OPh)	75.0	2.527	0.0	-17.5
2 (OCF ₃)	89.7	2.524	0.0	-5.0
2 (OCOCH ₃)	74.7	2.579	0.0	0.5

^aCh = oxygen or sulfur. ^bsecond order NBO perturbation energies calculated at the ω B97M-V/6-311+G* level of theory for the sum of orbital interactions between the C=O oxygen lone pairs and the chalcogen atom. ^ccalculated at the ω B97M-V/6-311+G* level of theory at the position on the chalcogen atom closest to the C=O oxygen in the TS. ^dperpendicular TS of **1**(SCH₃). ^eplanar TS of **1**(SCH₃).

In contrast, the acyclic sulfur rotors had difficulty adopting a favorable ChB interaction geometry (Figure 5). The TS structures of **1**(SCH₃), **1**(CF₃) and **1**(SPh) had the thioether group twisted out of the plane of the *N*-phenyl group. This perpendicular geometry avoids the destabilizing steric interactions between the R-group of the thioether

and adjacent C-H groups of the phenyl ring (**Figure 4.5**). However, in doing so, the sulfur σ -hole is out of alignment with the oxygen lone pair as the $O\cdots S-C$ bond angles were far from linear (76.0° to 87.7°) as shown in Table 2. The absence of strong ChB interactions in the acyclic sulfur rotors was evident from the consistently longer $C=O\cdots S$ distances (2.78 to 2.81 Å) in comparison to the cyclic rotors (2.54 to 2.58 Å). The shorter distances for the cyclic sulfur rotors are even more impressive given the framework constraints that favor the opposite trends. The fused five-membered rings of the cyclic rotors pull the sulfur away from the opposing $C=O$ group in the TS due to the smaller C_3-C_2-S bond angle favoring longer $S\cdots O$ distances (**Figure 4.5**). By comparison, the acyclic rotor has larger C_3-C_2-S bond angles favoring shorter ChB distances.

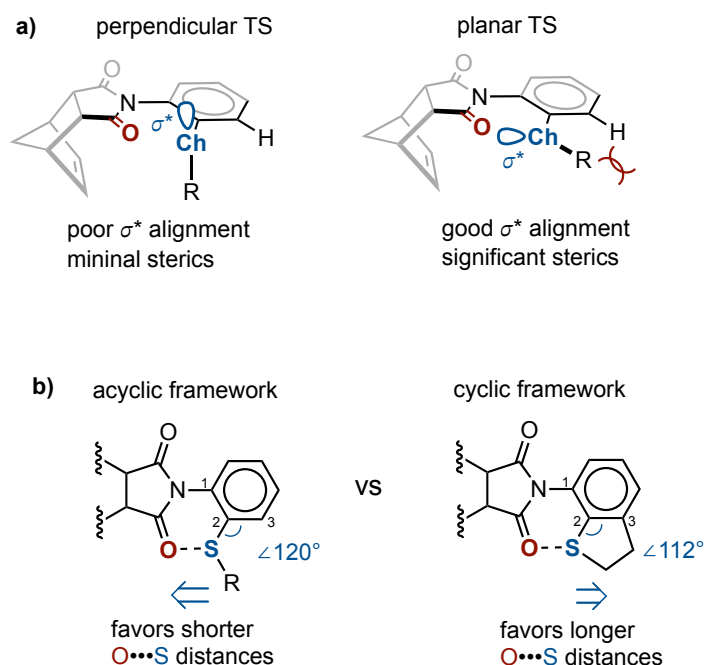


Figure 4.5 Comparison of the geometric variations in the TS structures of the acyclic chalcog rotors.

The one outlier in the trends for the acyclic sulfur rotors was **1**(SCH₃) which has perpendicular and planar TS structures that are very close in energy. A comparison of the

two TS geometries provided further proof for the importance of proper alignment of the σ -hole in the sulfur ChB interaction. The planar TS has good alignment of the sulfur σ -hole with the C=O oxygen with a ChB bond angle of 160° . The presence of a stabilizing ChB interaction was evident from the short S $\cdots$ O distance of 2.59 Å. In contrast, the perpendicular TS had poor alignment with a bond angle of 76° and a much longer S $\cdots$ O distance of 2.78 Å, indicative of a weaker ChB interaction. While **1**(SCH₃) has the ability to form a ChB interaction in the planar TS, the TS stabilizing effects of the interaction are offset by the additional steric interactions that are formed by the CH₃ and thus, the similarity in the energies of the perpendicular and planar geometries. For the other acyclic rotors **1**(Ph) and **1**(CF₃), the destabilizing steric interactions in the planar geometry are larger and thus the perpendicular geometry is favored.

To better understand the trends and to evaluate its potential in effecting reaction rates, we quantitatively measured the magnitude of the TS stabilization by the ChB interactions. Our approach relies on decomposing the rotational barrier ($\Delta G^\ddagger_{\text{exp}}$) into a destabilizing steric (E_{steric}) and a stabilizing non-covalent component (E_{int}). Thus, E_{int} can be isolated by subtracting E_{steric} from $\Delta G^\ddagger_{\text{exp}}$ (equation 4.1). Therefore, the key to measuring E_{int} is to find appropriate steric control rotors to measure E_{steric} . In the above studies, pairwise comparisons were used where the ChB forming rotors were compared with structurally similar rotors that either do not form or form weaker ChB interactions. The difficulty with this analysis is that there are not always structurally similar control rotors available for comparison.

$$E_{\text{int}} = \Delta G^\ddagger_{\text{exp}} - E_{\text{steric}} \quad (\text{equation 4.1})$$

$$E_{\text{steric}} = 0.8061(B\text{-value}) + 15.47 \quad (\text{equation 4.2})$$

$$E_{\text{int}} = \Delta G_{\text{exp}}^{\ddagger} - 0.8061(B\text{-value}) - 15.47 \quad (\text{equation 4.3})$$

Therefore, a systematic approach was employed to generate an ideal steric control for each chalcogen rotor. The barriers from a previously measured series of control rotors **3** were used to generate equation 4.2 for E_{steric} for any size R-group.^{1,5} Rotors **3** have R-groups that lack a chalcogen atom and cannot form ChB or other stabilizing non-covalent interactions with the C=O group. Thus, we assumed that their barriers were due only to the steric component, E_{steric} . The size of the R-groups in rotors were quantitatively assessed using Mazzanti's steric parameter, *B*-value (**Table 4.1**), which was chosen because the parameter is based on the rotational barrier of a similar biaryl molecular rotor.¹⁶⁵ Confirmation of the ability of *B*-value to assess the steric size of the R-groups in the *N*-phenylsuccinimide rotors as provided by the good linear correlation of the $\Delta G_{\text{exp}}^{\ddagger}$ values of rotors **3** with *B*-value gave a linear correlation (**Figure 4.6**, black filled squares) with *B*-value demonstrating that the rotational barriers of the control rotors **3** were primarily due to the steric size of their R-groups.

A limitation in the series of control rotors **3** was the lack of rotors with small R-groups (*B*-values < 7.4 kcal/mol) that would be close to the size of the R-groups in the chalcogen rotors **1** and **2**. Therefore, the acyclic oxygen rotors **2**(OCH₃) and **2**(OPh) were added to the steric control group (**Figure 4.6**, open triangles). We reasoned that these rotors were unlikely to form ChB interactions as they were acyclic rotors, which do not adopt the proper TS geometry. In addition, they contain the least polarizable and smallest chalcogen, oxygen, which was unlike to form ChB interactions without attached electron-withdrawing

groups.^{212,215} These hypotheses were confirmed as the rotational barriers for **2**(OCH₃) and **2**(OPh) fell on the steric trendline and extended the line to lower *B*-values. In addition, all of the ChB forming rotors had barriers that were lower than predicted by the steric trendline. The distance from the steric trendline, as calculated using equation 4.3, provided the TS stabilization energy by the ChB interaction.

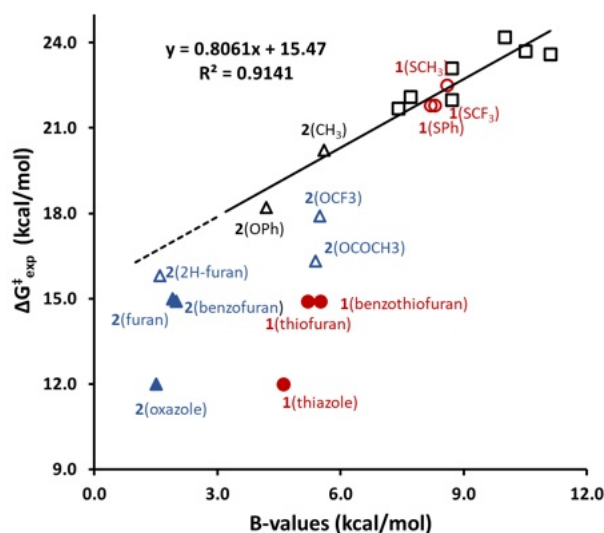


Figure 4.6 Quantitative analysis of the measured rotational barriers ($\Delta G^\ddagger_{\text{exp}}$) versus the steric parameter (*B*-value) to isolate the repulsive steric and attractive ChB components of the rotational barriers.

The steric trendline (black solid line) was generated from the control rotors **3** (open black squares) and acyclic oxygen rotors **2**(OCH₃) and **2**(OPh) (open black triangles). Deviations from the steric trendline on the y-axis provides a measure of the ChB interaction energy (E_{int}) for the cyclic sulfur rotors **1** (filled red circles), acyclic sulfur rotors **1** (open red circles), cyclic oxygen rotors **2** (filled blue triangles) and acyclic oxygen rotors **2** with electron withdrawing groups (open blue triangles).

A key assumption in the above analysis was that variations in the rotational barriers were due only to variations in energy of the TS energies and that the ground state energies stay constant. This assumption was supported by energy decomposition analyses (SI, Section 4.5.13) that showed that the calculated intramolecular TS interactions were strongly correlated with the experimentally measured interaction energies. More directly, the excellent correlation ($R^2 = 0.914$) of the $\Delta G^\ddagger_{\text{exp}}$ values for the steric control rotors **3** and non-interacting acyclic oxygen rotors **2**(OCH₃) and **2**(OPh) with the steric parameter *B*-value provided strong support for the ability to accurately model the barriers by examination of the TS interactions. This assumption was also supported by our previous studies that used a similar series of steric control rotors to successfully isolate the stabilizing TS interactions in the *N*-phenylsuccinimide rotors.^{1,4-6,19}

Equation 4.3, which is derived from a combination of equations 1 and 2, was used to calculate the ChB interaction energies (E_{int}) for each of the chalcogen rotors (**Table 4.1**). The cyclic sulfur rotors **1**(thiofuran), **1**(benzothiofuran), **1**(thiazole), which had the best σ -hole alignment, had the strongest E_{int} values (-4.8 to -7.2 kcal/mol) which is consistent with the formation of strong stabilizing ChB interactions. In contrast, the acyclic sulfur rotors **1**(SCH₃), **1**(SPh), **1**(SCF₃) which had poor σ -hole alignment had very small E_{int} values of 0.1 to -0.4 kcal/mol. Thus, the analysis provided quantitative data to support our initial pairwise analyses.

The quantitative analyses also provided the means to answer the question of whether oxygen can form effective ChB interactions.^{212,215} Oxygen is the least polarizable and most electronegative chalcogen and thus generally forms the weakest ChB interactions. However, oxygen is also the most abundant chalcogen and thus has considerable potential

in ChB catalyst design. The E_{int} values (-1.1 to -4.7 kcal/mol) suggest that cyclic oxygen rotors **2**(2H-furan), **2**(furan), **2**(benzofuran), and **2**(oxazole) form weak to moderate ChB interactions. However, these E_{int} values have a higher degree of uncertainty than for the larger sulfur rotors. The cyclic oxygen rotors have very low B -values (1.5 to 2.1 kcal/mol) which extend below the range of the range of the experimentally measured B -values (4.2 to 11.5 kcal/mol) for the steric control rotors. Thus, their E_{int} values are based on extrapolations of the steric trendline which have higher degrees of uncertainty (See section 4.5.5). For example, the confidence interval for E_{int} is ± 1.0 to ± 1.5 kcal/mol in the low B -value range for the cyclic oxygen rotors (**Figure 4.37** regression confidence line), which is similar in magnitude to the E_{int} values (-1.0 to -4.7 kcal/mol). So there was a high degree of uncertainty in establishing that the oxygen rotors were forming ChB interactions. For comparison, the confidence interval in the B -value range for the cyclic sulfur rotors is much smaller ± 0.6 to ± 0.8 kcal/mol especially comparison to the E_{int} values (-4.8 to -7.2 kcal/mol).

To better address the question of whether oxygen can form ChB interactions, oxygen rotors that formed stronger ChB interactions, which would be outside of our uncertainty range, were examined. Electronegative and electron withdrawing groups are known to enhance the strength of ChB interactions by increasing the size of the σ -hole and the increasing the electrostatic positive charge of the chalcogen atom.^{180,216} For example, the cyclic sulfur rotor which formed the strongest ChB interaction ($E_{\text{int}} = -7.2$ kcal/mol) was **1**(thiazole) which had an electronegative nitrogen in conjugation with the chalcogen sulfur atom. The oxygen rotors with enhanced ChB interactions included cyclic (**2**(oxazole)) and acyclic (**2**(OCF₃) and **2**(OCOCH₃)) rotors.

The E_{int} values for cyclic oxygen rotors with electronegative groups showed an enhancement in the strength of the ChB, which was similar to the enhancement observed for the cyclic sulfur rotors. The conjugated electronegative nitrogen in **2**(oxazole) strengthened the intramolecular ChB interaction by 2.7 kcal/mol in comparison to **2**(furan) which lacked the heterocyclic nitrogen. A similar increase of 2.4 kcal/mol was observed for the analogous sulfur pair of **1**(thiazole) and **1**(thiofuran). More importantly, the strength of the oxygen ChB interaction was $E_{\text{int}} = -4.7$ kcal/mol, which was larger than the error of the analysis.

Interestingly, the electron withdrawing groups also enhanced the strength of the ChB interactions for the acyclic oxygen rotors. For example, the E_{int} of **2**(OCF₃) with a CF₃ electron withdrawing group was -2.2 kcal/mol lower than **2**(OCH₃). Likewise, the acetyl group lowered the $\Delta G_{\text{exp}}^{\ddagger}$ of **2**(OCOCH₃) lower the barrier even further by -3.7 kcal/mol in comparison to **2**(OCH₃).

The analogous electron withdrawing group trends were not observed for in the acyclic sulfur rotors, which provided insight into the relative contributions of the orbital-orbital ($n \rightarrow \sigma^*$) and electrostatic components. For the acyclic sulfur rotors, attaching a CF₃ group had only a small influence as the E_{int} of **1**(SCF₃) and **1**(SCH₃), which only differed by -0.3 kcal/mol. The origins of these differences in electron withdrawing groups trends for the sulfur and oxygen ChB interactions were investigated further in the next section.

In summary, the oxygen ChB interactions could be observed and measured by the molecular rotors. Oxygen formed weaker ChB interactions in comparison to sulfur as expected. In the absence of electron withdrawing groups, the oxygen ChB interactions were

difficult to observe. However, with electron withdrawing groups the oxygen ChB interactions could be as strong as sulfur ChB interactions.

To assess the magnitude of the orbital component of the ChB interactions, Natural Bonding Orbital (NBO) analyses were performed on the TS structures. The second order perturbation interaction energies of the donor orbitals on the C=O oxygen and acceptor orbitals on the chalcogens were calculated for rotors **1** and **2** (**Table 4.2**), providing a comparison of the $n \rightarrow \sigma^*$ interactions.^{181,217} The NBO interaction energies were consistent with the experimental observations of the ChB interactions in the sulfur rotors **1**. A stabilizing NBO interaction (-5.8 to -6.9 kcal/mol) was observed for the cyclic sulfur rotors (**1**(thiofuran), **1**(benzothiofuran), **1**(thiazole)), which form ChB interactions. In contrast, the acyclic sulfur rotors, which do not form ChB interactions, had negligible NBO interaction energies (0.0 kcal/mol). The acyclic sulfur rotor **1**(SCH₃) was again an exception, as the NBO interaction energies depended on the TS geometry and the alignment of the sulfur σ^* (**Figure 4.8**). The planar TS had an NBO interaction energy similar to the cyclic sulfur rotors; whereas, the perpendicular TS had an NBO interaction energy of zero.

In contrast, the NBO interaction energies for the oxygen rotors did not correlate with the observed E_{int} values. This is consistent with the oxygen ChB interaction having a small or negligible orbital component. The cyclic oxygen rotors had small NBO energies of 0.0 to -0.6 kcal/mol. Even **2**(oxazole) which showed moderate TS stabilization ($E_{\text{int}} = -4.7$ kcal/mol) had a very NBO energy of only -0.6 kcal/mol. Similarly, the acyclic oxygen rotor NBO energies were low regardless of the observed stabilization energies (E_{int}). For example, even the oxygen rotors with electron withdrawing groups (**2**(OCF₃) and

2(OCOCH₃)) and modest E_{int} values (-2.0 and -3.5) had negligible NBO energies (0.0 kcal/mol).

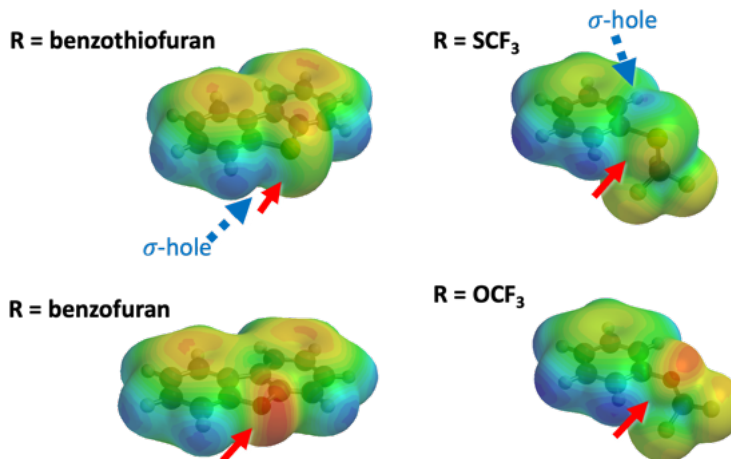


Figure 4.7 Examples of the ESP surfaces generated for the *N*-phenyl units of rotors **1**(benzothiofuran), **1**(SCF₃), **2**(benzofuran), **2**(OCF₃). The calculations were performed without the norborene succinimide units to allow visualization of the interacting surface on the chalcogen atom. The position on the surface of the chalcogen used to estimate the ESP for each rotor is highlighted with a red arrow and corresponds to the approximate position of the C=O oxygen in the TS. The σ -hole of the sulfur R-groups are highlighted with a blue arrow. The oxygen R-groups did not have clearly defined σ -holes.

Next, we look for a simple parameter which could accurately predict the ChB interaction energies. This could be a useful tool for researchers designing new systems based on ChB interactions or optimize existing systems. The variability of the orbital component ruled out the use of NBO interaction energies. However, the ChB interactions of oxygen and sulfur rotors all appeared to have a strong electrostatic component. Therefore, we explored the ability of electrostatic potential (ESP) to predict the ChB interactions energies. Of the many electrostatic parameters, ESP has been shown to be effective in predicting non-covalent interaction trends as best highlighted by the work of

Hunter.¹⁷¹ ESP describes the electrostatic potential energy at points on a molecular surface and therefore provides a measure of interaction energies and geometry.

The ability of ESP to predict the ChB interaction energies was tested by correlating ESP with the experimentally measured E_{int} values. The ESP energies (**Table 4.2**) were calculated at the position on the surface of the chalcogen atom with the closest contact to the C=O oxygen in the TS structures. Examples are shown in Figure 8. The norbornene succinimide portions of the rotors were deleted because they blocked the region of the chalcogen unit that was involved in the ChB interaction.

An excellent correlation was observed between the chalcogen ESP and rotor E_{int} with an $R^2 = 0.964$ (**Figure 4.7**). The ESP trendline included both sulfur and oxygen rotors and also the cyclic and acyclic rotor, demonstrating the generality of the predictive parameter across different types of chalcogen bonding interactions. Thus, ESP was an excellent predictor of the ability of ChB interactions to stabilize the bond rotation transition states.

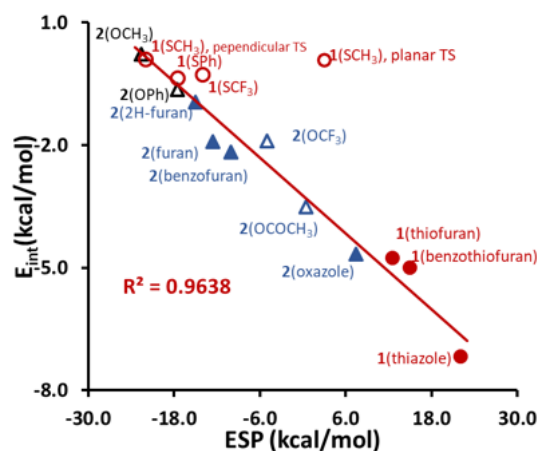


Figure 4.8 Plot of electrostatic surface potentials (ESP, ω B97M-V/6-311+G*) versus the experimentally measured stabilizing TS interaction energies (E_{int}) for rotors **1** and **2**: acyclic oxygen rotors **2**(OCH₃) and **2**(OPh) (open black triangles), acyclic sulfur rotors **1**

(open red circles), cyclic oxygen rotors **2** (filled blue triangles), acyclic oxygen rotors **2** with electron withdrawing groups (open blue triangles) and cyclic sulfur rotors **1** (filled red circles).

The ability of ESP to simultaneously predict the ChB interaction energies of rotors that had strong and weak orbital components was surprising. For example, the cyclic sulfur rotors that have a significant orbital component such as **1**(benzothiofuran), **1**(thiofuran), and **1**(thiazole) fell on the same ESP trendline as the acyclic rotors that lack an orbital component such as **2**(OCF₃) and **2**(OCOCH₃). In the case of the cyclic sulfur rotors, the position on the sulfur atom used to measure the ESP coincided with the σ -hole. An example is shown in Figure 8 (R = benzothiofuran) where the ESP position (red arrow) is the same as the σ -hole (blue arrow). However, the ESP position for the other types of rotors either did not correlate with the σ -hole (**Figure 4.7**, R = SCF₃) or the rotors lacked a σ hole (Figure 8, R = benzofuran or OCF₃). Thus, the effectiveness of ESP in predicting the ChB interaction energies regardless of the degree of orbital overlap suggest that the ESP values were either providing some measure of the orbital component or were correlated with the orbital interaction energies.

The only outlier from the E_{int} vs ESP plot (**Figure 4.8**, open red circle) was, again, the planar TS of rotor **1**(SCH₃). An analysis of this deviation provided insight in the origins of the effectiveness of ESP as a predictive parameter. The ESP value for the planar TS of **1**(SCH₃) was +3.0 kcal/mol, which fell well off the trendline. By comparison, the ESP value for the perpendicular TS of **1**(SCH₃) was -22.0 kcal/mol which fell on the trendline. We hypothesized that the differences were due to ESP analysis only taking into account the TS stabilizing interactions. This is effective for the majority of the chalcogen R-groups, which adopt geometries that avoid strong repulsive interactions. The ESP of the planar TS

is more positive than the perpendicular TS by 25.0 kcal/mol. This difference is consistent with the planar TS forming a chalcogen bonding interaction with the imide oxygen; whereas the perpendicular TS not having the proper orbital alignment to form an interaction. However, the planar TS of **1**(SCH₃) also forms form modest steric interactions (**Figure 4.6**). Therefore, the ESP value does not directly correlate to the rotational barrier.

The above analyses revealed that sulfur and oxygen can form stabilizing ChB interactions, but the interactions differ in the balance of their orbital-orbital and electrostatic components, leading to different stability trends. The sulfur and oxygen ChB interactions both have strong electrostatic components. This is evident from the ability of the electrostatic parameter, ESP, to accurately predict the interaction energies, E_{int} , as shown in **Figure 4.8**. In contrast, the sulfur and oxygen ChB interactions have different orbital-orbital components as seen from the NBO secondary perturbation energies as shown in **Table 4.2**. The more polarizable sulfur had a well-defined σ^* and could form strong orbital-orbital interactions; whereas the less polarizable oxygen had a smaller σ^* and could not form strong orbital-orbital interactions. The differences in the orbital components are most clearly perceived in cyclic sulfur and oxygen rotors, which have their σ^* -orbitals aligned with the C=O oxygen lone pairs. The cyclic sulfur rotors **1** have significant NBO energies (-6.9 to -5.8 kcal/mol) as shown in **Table 4.2**. However, the cyclic oxygen rotors **2**, which have similar lone-pair to σ^* -orbital geometries, displace low or negligible NBO energies (-0.6 to 0 kcal/mol).

The differences in the orbital components are consistent with the differences in the polarizabilities of the sulfur and oxygen atoms. The more polarizable sulfur enables the formation of a significant σ^* -orbital. This can be seen by a well-formed σ -hole in the

electrostatic surface maps of the sulfur groups (**Figure 4.7**, R = benzothiofuran). In contrast, the less polarizable oxygens lead to smaller σ^* -orbitals, and the corresponding oxygen σ -holes are not visible in the electrostatic surface maps (**Figure 4.7**, R = benzofuran).

These differences in the orbital-orbital and electrostatic component of the sulfur and oxygen ChB interactions also explain the different trends for the acyclic rotors. The significant orbital component of the sulfur ChB interaction leads to greater geometric constraints, requiring alignment of the donor lone pair with the chalcogen σ -hole. The importance of proper geometry is evident from the large differences in the interaction energies of the cyclic and acyclic sulfur rotors which have good and poor σ -hole alignments. In contrast, oxygen ChB interactions can adopt a wider variety of geometries. The electron-withdrawing effects of substituents are not focused on the σ -hole and are instead distributed more evenly across the oxygen atom surface.

Our study of ChB interactions using the *N*-phenylsuccinimide rotors provided the opportunity to compare with non-covalent interactions. We have previously measured the TS stabilizing effects of $n \rightarrow \pi^*(\text{CO})$,¹ $n \rightarrow \pi(\text{Ph})$,⁴ pnictogen bonds,⁵ and hydrogen bonding interactions.⁶ The interactions were measured using the same rotor framework and formed interactions with the same succinimide C=O oxygens. What differs is the complementary acceptor group (S, O, N, C=O, Ph, HO) which has electrostatically positive π - or σ -hole region.

The relative TS stabilizing abilities of the interactions are shown in **Figure 4.9**. The C=O...HO-Ph hydrogen bonds were the strongest. However, the remaining interactions, including the sulfur and oxygen chalcogen interactions, spanned a broad and overlapping

range of interaction energies. The stability trends revealed some general trends. First, electronegative accepting groups and electron-withdrawing groups on the accepting groups enhanced the strength of the interactions. This is consistent with the interactions originating from donor-acceptor orbital-orbital and electrostatic interactions. For example, when comparing different types of pnictogen interactions, the electron-poor nitrogen of amides forms the strongest interactions, and the electron-rich nitrogen of amines form weaker interactions.⁵ For the $n \rightarrow \pi^*$ interactions, the electron-poor carbonyl groups form stronger interactions than phenyl groups.^{1,4} The same trends were observed for the ChB interactions. The electron withdrawing groups on the chalcogen atom such as CF_3 in rotors **2**(OCF_3) or conjugated electronegative nitrogen atoms in rotors **1**(thiazole) and **2**(oxazole) increase the strength of the interaction.

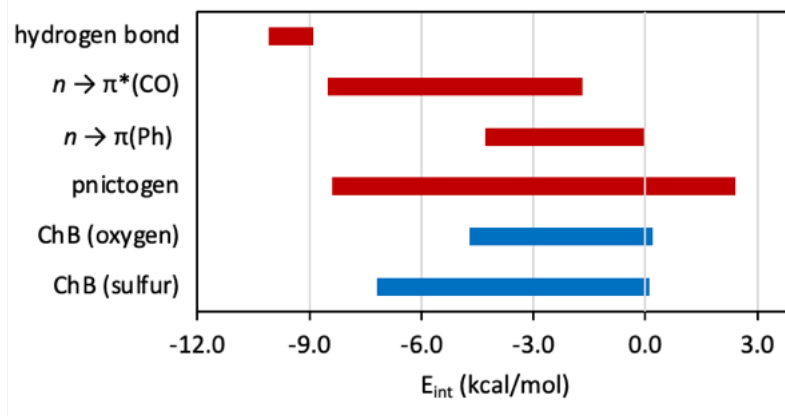


Figure 4.9 Comparison of the TS stabilizing effects (E_{int}) measured in the *N*-phenylsuccinimide rotors of the oxygen and sulfur chalcogen bonding interactions in this study (blue bars) versus the previously measured $n \rightarrow \pi^*(\text{CO})$,¹ $n \rightarrow \pi(\text{Ph})$,⁴ pnictogen,⁵ and hydrogen bonding interactions⁶ (red bars).

4.4 Conclusions

This study has demonstrated the potential of the chalcogen bonding interactions of oxygen and sulfur in facilitating kinetic processes and organocatalysis. Using *N*-

phenylsuccinimide molecular rotors, the transition state stabilizing effects of chalcogen bonding interactions were measured and compared. Rotors with variations in the chalcogen atom orientation and electron-withdrawing groups were synthesized. The rotational barriers were measured using dynamic NMR. The formation of the intramolecular ChB interactions in the bond rotation transition states were verified from the experimental rotational barrier trends and computational modeling of the TS structures.

Evidence for the ChB interactions were provided by the short atom-atom distances and correlation with proper alignment of the chalcogen σ -hole. The more polarizable sulfur rotors formed strong ChB interactions as expected. However, the oxygen rotors could also form ChB interactions if appropriate electronegative or electron withdrawing groups were present. Given the higher availability and better-established chemistry for incorporation of oxygen and sulfur functional into organic frameworks, these results suggest that new organic catalysts could be designed that utilize oxygen and sulfur ChB interactions.

The oxygen and sulfur ChB interactions had different geometric constraints due to the different strengths of their orbital-orbital components. The sulfur ChB interaction has a strong orbital component and thus is restricted to geometries where the lone pair donor orbital is aligned with the sigma-hole of the sulfur atom. The less polarizable oxygen atom does not form a significant sigma-hole in our systems and thus does not have a significant orbital component.

However, this allows the oxygen ChB interaction to form in a wider array of geometries as the effects of electron withdrawing groups are more uniformly distributed on the chalcogen atom surface of the less polarizable oxygen. The ESP energy calculated at the interacting point on the surface of the chalcogen atom was an excellent predictive

parameter for the strength and geometry of the interaction. Therefore, ESP can be used in designing and optimizing organocatalysts and reactions that involve ChB interactions.

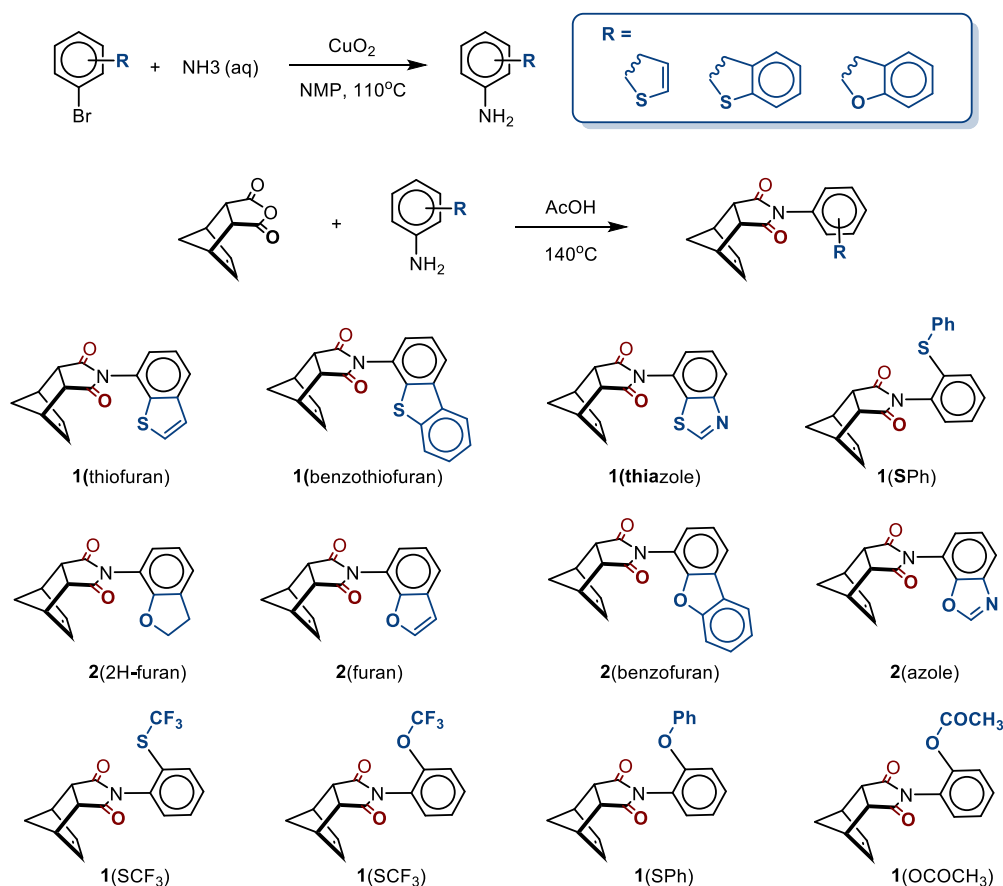
4.5 Supporting information

4.5.1 General experimental procedures

NMR spectra were recorded on a Bruker 400 MHz spectrometer at 25 °C. Chemical shifts are reported in ppm (δ) and were referenced to residual solvent peaks, ^1H NMR (400 MHz, chloroform- d) δ 7.26 ppm, ^{13}C NMR (100 MHz, chloroform- d) δ 77.16 ppm. Chemicals and solvents were purchased from commercial suppliers and used as received. Flash chromatography was performed using silica gel from Sorbent Technologies (60 Å, 200 – 400 mesh). HRMS were measured using a magnetic sector spectrometer (VG 70S) using EI.

4.5.2 Synthesis of the molecular rotors

Rotors **1** were prepared via a thermal condensation between an *ortho*-substituted aniline and norbornene anhydride (**Scheme 4.2**). The rotors **1**(SCH₃), **2**(OCH₃), **3**(CH₃), **3**(Et), **3**(*i*-Pr), **3**(Br), **3**(Cl), and **3**(I) were synthesized as previously described.^{1,20,211}



Scheme 4.2 General synthetic route (top) and chart (bottom) of the oxygen and sulfur chalcogen rotors.

4.5.3 ¹H and ¹³C NMR spectra

The NMR data and spectrum for new rotors are listed in the following section (Figure 4.10 to 4.35):

Rotor **1**(thiofuran) (*3aR,4S,7R,7aS*)-2-(benzo[*b*]thiophen-7-yl)-3*a,4,7,7a*-tetrahydro-1*H*-4,7-methanoisindole-1,3(2*H*)-dione: *cis*-5-Norbornene-endo-2,3-dicarboxylic anhydride (100 mg, 0.6 mmol), benzo[*b*]thiophen-7-amine (100 mg, 0.67 mmol), and acetic acid (2 mL) were added to a heavy wall glass pressure vessel with a magnetic stir bar. The pressure vessel was then capped and heated to 130 °C in a silicon

oil bath for 12 hours. After letting the pressure vessel cool to room temperature, the crude material was purified by column chromatography (ethyl acetate/hexanes = 1:5 to 1:2, v/v) to give **1**(thiofuran), as a yellow powder (132 mg, 75%). **¹H NMR** (400 MHz, CDCl₃) δ 7.85 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.44 – 7.35 (m, 3H), 7.09 (d, *J* = 5.8 Hz, 1H, *ArH*), 6.44 (br s, 2H *syn* and *anti*), 3.54 – 3.52 (m, 4H *syn* and *anti*), 1.83 (d, *J* = 8.8 Hz, 1H *syn* and *anti*), 1.63 (d, *J* = 8.8 Hz, 1H *syn* and *anti*). **¹³C NMR** (101 MHz, CDCl₃) δ 176.1, 141.7, 137.4, 135.2, 126.9, 126.8, 124.9, 124.6, 124.2, 124.0, 52.5, 46.4, 45.6. **HRMS** (ESI) calcd. for [C₁₇H₁₃NO₂S]⁺ (M⁺): 295.0667, observed: 295.0675.

Rotor **1**(benzothiofuran) (*3aR,4S,7R,7aS*)-2-(benzo[*b*]thiophen-7-yl)-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoisoindole-1,3(2*H*)-dione: *cis*-5-Norbornene-endo-2,3-dicarboxylic anhydride (40 mg, 0.24 mmol), dibenzo[*b,d*]thiophen-4-amine (40 mg, 0.2 mmol), and acetic acid (2 mL) were added to a heavy wall glass pressure vessel with a magnetic stir bar. The pressure vessel was then capped and heated to 130 °C in a silicon oil bath for 12 hours. After letting the pressure vessel cool to room temperature, the crude material was purified by column chromatography (ethyl acetate/hexanes = 1:5 to 1:2, v/v) to give **1**(benzothiofuran), as a yellow powder (53 mg, 75%). **¹H NMR** (400 MHz, CDCl₃) δ 8.20 – 8.13 (m, 2H *syn* and *anti*), 7.83 – 7.81 (m, 1H *syn* and *anti*), 7.54 – 7.44 (m, 3H *syn* and *anti*), 7.21 (br s, 1H *syn* and *anti*), 6.55 (br s, 2H *syn*), 6.39 (br s, 2H *anti*), 3.57 – 3.55 (m, 4H *syn* and *anti*), 1.86 (d, *J* = 8.8 Hz, 1H), 1.67 (d, *J* = 8.8 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 176.0, 139.2, 137.8, 135.4, 127.4, 127.1, 125.3, 124.8, 122.8, 122.4, 121.9, 52.5, 46.7, 45.6. **HRMS** (ESI) calcd. for [C₂₁H₁₅NO₂S]⁺ (M⁺): 345.0823; observed 345.0812.

Rotor **1**(thiazole) (*3aR,4S,7R,7aS*)-2-(benzo[d]thiazol-7-yl)-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoisoindole-1,3(2*H*)-dione: *cis*-5-Norbornene-*endo*-2,3-dicarboxylic anhydride (190 mg, 1.2 mmol) and benzo[d]thiazol-7-amine (150 mg, 1 mmol), and acetic acid (5 mL) were added to a heavy wall glass pressure vessel with a magnetic stir bar. The pressure vessel was then capped and heated to 130 °C in a silicon oil bath for 12 hours. After letting the pressure vessel cool to room temperature, the crude material was purified by column chromatography (ethyl acetate/hexanes = 1:5 to 1:2, v/v) to give **1**(thiazole), as a white powder (236 mg, 80%). **¹H NMR** (400 MHz, CDCl₃) δ 8.98 (s, 1H), 8.17 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.62 – 7.55 (m, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 6.40 (s, 2H *syn* and *anti*), 3.58 – 3.50 (m, 4H *syn* and *anti*), 1.84 (d, *J* = 8.8, 1H *syn* and *anti*), 1.65 (d, *J* = 8.9 Hz, 1H *syn* and *anti*). **¹³C NMR** (100 MHz, chloroform-*d*) δ 175.7, 155.0, 154.2, 135.2, 131.8, 126.7, 125.2, 124.5, 76.8, 52.6, 46.3, 45.7. **HRMS** (ESI) calcd. for [C₁₆H₁₂N₂O₂S]⁺ (M⁺): 296.0619; observed 296.0631.

Rotor **1**(SPh) (*3aR,4S,7R,7aS*)-2-(2-(phenylthio)phenyl)-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoisoindole-1,3(2*H*)-phenylthio: *cis*-5-Norbornene-*endo*-2,3-dicarboxylic anhydride (246 mg, 1.5 mmol) and 2-(phenylthio)aniline (300 mg, 1.5 mmol), and acetic acid (5 mL) were added to a heavy wall glass pressure vessel with a magnetic stir bar. The pressure vessel was then capped and heated to 130 °C in a silicon oil bath for 12 hours. After letting the pressure vessel cool to room temperature, AcOH was removed by an extraction with water, the crude material was recrystallized from MeOH to give **1**(SPh) as a light-yellow crystal (422 mg, 80%). **¹H NMR** (400 MHz, chloroform-*d*) δ 7.31 – 6.95 (m, 9H), 6.28 (s, 2H *syn*), 6.11 (s, 2H *anti*), 3.56 – 3.41 (m, 4H *syn* and *anti*), 1.76 (d, *J* = 8.8 Hz, 1H *syn* and *anti*), 1.57 (d, *J* = 8.6 Hz, 1H *syn* and *anti*). **¹³C NMR** (100 MHz,

chloroform-d) δ 176.5, 176.4, 135.5, 135.4, 135.2, 134.8, 134.7, 134.7, 133.8, 133.2, 132.5, 131.7, 131.1, 130.1, 129.3, 129.1, 128.4, 128.2, 127.6, 127.2, 52.6, 52.4, 47.0, 46.0, 45.4, 45.3. **HRMS** (ESI) calcd. for $[\text{C}_{21}\text{H}_{17}\text{NO}_2\text{S}]^+$ (M^+): 347.0980; observed 347.0992.

Rotor **1**(SCF₃) (*3aR,4S,7R,7aS*)-2-(2-((trifluoromethyl)thio)phenyl)-*3a,4,7,7a-tetrahydro-1H-4,7-methanoisindole-1,3(2H)-dione*: *cis*-5-Norbornene-endo-2,3-dicarboxylic anhydride (246 mg, 1.5 mmol) and 2-((trifluoromethyl)thio)aniline (300 mg, 1.5 mmol), and acetic acid (5 mL) were added to a heavy wall glass pressure vessel with a magnetic stir bar. The pressure vessel was then capped and heated to 130 °C in a silicon oil bath for 12 hours. After letting the pressure vessel cool to room temperature, the crude material was purified by column chromatography (ethyl acetate/hexanes = 1:5 to 1:2, v/v) to give **1**(SCF₃) as a white powder (422 mg, 83%). **¹H NMR** (400 MHz, chloroform-d) δ 7.84 (d, J = 7.8 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.24 (dd, J = 7.9, 1.3 Hz, 1H, *syn*), 7.13 (dd, J = 7.8, 1.3 Hz, 1H, *anti*), 6.33 (s, 2H, *syn*), 6.31 (s, 2H, *anti*) 3.61 – 3.48 (m, 4H, *syn* and *anti*), 1.83 (d, J = 8.9 Hz, 1H), 1.66 (d, J = 8.9 Hz, 1H, *syn* and *anti*). **¹⁹F NMR** (376 MHz, CDCl₃) δ -41.86 (s), -42.32 (s). **¹³C NMR** (101 MHz, CDCl₃) δ 176.3, 176.1, 138.5, 136.3, 135.2, 134.8, 132.4, 130.2, 129.9, 129.5, 52.9, 52.5, 47.0, 46.1, 45.5. **HRMS** (ESI) calcd. for $[\text{C}_{16}\text{H}_{12}\text{F}_3\text{NO}_2\text{S}]^+$ (M^+): 339.0541; observed 339.0546.

Rotor **2**(2H-furan) (*3aR,4S,7R,7aS*)-2-(2,3-dihydrobenzofuran-7-yl)-*3a,4,7,7a-tetrahydro-1H-4,7-methanoisindole-1,3(2H)-dione*: *cis*-5-Norbornene-endo-2,3-dicarboxylic anhydride (328 mg, 2 mmol) and 2,3-dihydrobenzofuran-7-amine (297 mg, 2.2 mmol) and acetic acid (2 mL) were added to a heavy wall glass pressure vessel with a magnetic stir bar. The pressure vessel was then capped and heated to 130 °C in a silicon oil bath for 12 hours. After letting the pressure vessel cool to room temperature, the AcOH

was removed by extraction. The crude material was washed by MeOH and was filtrated to give **1**(2H-furan), as a yellow powder (500 mg, 90%). **¹H NMR** (400 MHz, CDCl₃) δ 7.18 (d, *J* = 8.4 Hz, 1H), 6.86 – 6.73 (m, 2H), 6.25 (br s, 2H *syn* and *anti*), 4.57 (t, *J* = 8.7 Hz, 2H), 3.50 – 3.35 (m, 4H *syn* and *anti*), 3.22 (t, *J* = 8.6 Hz, 2H), 1.74 (s, 1H), 1.57 (s, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 176.4, 155.5, 134.6, 129.2, 127.1, 126.8, 125.7, 120.7, 114.4, 72.1, 52.3, 51.8, 46.3, 46.0, 45.4, 29.8. **HRMS** (ESI) calcd. for [C₂₁H₁₅NO₂S]⁺ (M⁺): 281.1052; observed 281.1062.

Rotor **2**(furan) (*3aR,4S,7R,7aS*)-2-(benzofuran-7-yl)-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoisoindole-1,3(2*H*)-dione: *cis*-5-Norbornene-endo-2,3-dicarboxylic anhydride (196 mg, 1.2 mmol) and benzofuran-7-amine (135 mg, 1 mmol), and acetic acid (2 mL) were added to a heavy wall glass pressure vessel with a magnetic stir bar. The pressure vessel was then capped and heated to 130 °C in a silicon oil bath for 12 hours. After letting the pressure vessel cool to room temperature, the crude material was purified by column chromatography (ethyl acetate/hexanes = 1:5 to 1:2, v/v) to give **2**(furan), as a yellow powder (231 mg, 83%). **¹H NMR** (400 MHz, TCE-d₂) δ 7.71 – 7.66 (m, 2H), 7.35 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.08 (d, *J* = 6.7 Hz, 1H), 6.86 (d, *J* = 2.1 Hz, 1H), 6.35 (s, 2H *syn* and *anti*), 3.52 (s, 4H *syn* and *anti*), 1.81 (d, *J* = 8.8 Hz, 1H), 1.63 (d, *J* = 8.8 Hz, 1H). **¹³C NMR** (101 MHz, TCE) δ 176.1, 149.1, 145.6, 134.5, 129.2, 123.2, 122.9, 122.2, 116.1, 106.8, 52.0, 46.0, 45.3. **HRMS** (ESI) calcd. for [C₁₇H₁₃NO₃]⁺ (M⁺): calculated 279.0895; observed 279.0892.

Rotor **2**(benzofuran) (*3aR,4S,7R,7aS*)-2-(dibenzo[*b,d*]furan-4-yl)-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoisoindole-1,3(2*H*)-dione : *cis*-5-Norbornene-endo-2,3-dicarboxylic anhydride (98 mg, 0.6 mmol) and dibenzo[*b,d*]furan-4-amine (92 mg, 0.5

mmol), and acetic acid (2 mL) were added to a heavy wall glass pressure vessel with a magnetic stir bar. The pressure vessel was then capped and heated to 130 °C in a silicon oil bath for 12 hours. After letting the pressure vessel cool to room temperature, the crude material was purified by column chromatography (ethyl acetate/hexanes = 1:5 to 1:2, v/v) to give **1**(benzofuran), as a white powder (148 mg, 90%). **¹H NMR** (400 MHz, CDCl₃) δ 7.98 – 7.93 (m, 2H *syn* and *anti*), 7.54 – 7.35 (m, 4H *syn* and *anti*), 7.28 (br s, 1H), 6.43 (br s, 2H *syn* and *anti*), 3.59 (s, 4H *syn* and *anti*), 1.86 (d, *J* = 8.8 Hz, 1H *syn* and *anti*), 1.69 (d, *J* = 8.8 Hz, 1H *syn* and *anti*). **¹³C NMR** (101 MHz, CDCl₃) δ 176.3, 156.3, 134.9, 127.7, 126.4, 124.0, 123.2, 123.1, 121.6, 120.9, 116.6, 112.0, 52.3, 46.5, 45.6. **HRMS** (ESI) calcd. for [C₂₁H₁₅NO₃]⁺ (M⁺): 329.1052; observed 329.1054.

Rotor **2**(oxazole) (*3aR,4S,7R,7aS*)-2-(benzo[d]oxazol-7-yl)-3*a,4,7,7a*-tetrahydro-1*H*-4,7-methanoisoindole-1,3(2*H*)-dione: *cis*-5-Norbornene-endo-2,3-dicarboxylic anhydride (57 mg, 0.35 mmol) and benzo[d]oxazol-7-amine (50 mg, 0.37 mmol) were neatly added to a heavy wall glass pressure vessel with a magnetic stir bar. The pressure vessel was then capped and heated to 130 °C in a silicon oil bath for 12 hours. After letting the pressure vessel cool to room temperature, the crude material was purified by column chromatography (ethyl acetate/hexanes = 1:5 to 1:2, v/v) to give **2**(oxazole) as a white powder (40 mg, 40%). **¹H NMR** (400 MHz, CDCl₃) δ 8.07 (s, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.41 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 6.33 (s, 2H, *syn* and *anti*), 3.52 (s, 4H, *syn* and *anti*), 1.81 (d, *J* = 8.9 Hz, 1H, *syn* and *anti*), 1.63 (d, *J* = 8.9 Hz, 1H, *syn* and *anti*). **¹³C NMR** (101 MHz, CDCl₃) δ 175.9, 152.6, 145.0, 141.8, 134.8, 124.9, 124.6, 121.5, 52.2, 46.3, 45.6. **HRMS** (ESI) calcd. for [C₁₆H₁₂N₂O₃]⁺ (M⁺): 280.0848; observed 280.0836.

Rotor **2**(OPh) (*3aR,4S,7R,7aS*)-2-(2-phenoxyphenyl)-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoisoindole-1,3(2*H*)-dione: *cis*-5-Norbornene-*endo*-2,3-dicarboxylic anhydride (164 mg, 1 mmol) and 2-phenoxyaniline (124 mg, 1 mmol), and acetic acid (5 mL) were added to a heavy wall glass pressure vessel with a magnetic stir bar. The pressure vessel was then capped and heated to 130 °C in a silicon oil bath for 12 hours. After letting the pressure vessel cool to room temperature, the crude material was purified by column chromatography (ethyl acetate/hexanes = 1:5 to 1:2, v/v) to give **2**(OPh), as a white powder (281 mg, 85%). **¹H NMR** (400 MHz, chloroform-*d*) δ 7.43 – 7.01 (m, 9H), 6.28 (s, 2H *syn*), 5.88 (s, 2H *anti*), 3.46 – 3.29 (m, 4H *syn* and *anti*), 1.86 – 1.61 (m, 2H *syn* and *anti*). **¹³C NMR** (100 MHz, chloroform-*d*) δ 176.5, 176.4, 156.8, 156.5, 153.2, 153.0, 134.7, 134.5, 130.7, 130.5, 129.8, 129.8, 129.8, 129.4, 123.9, 123.8, 123.7, 123.6, 123.5, 122.9, 119.6, 119.4, 119.3, 118.9, 52.3, 52.1, 46.6, 46.1, 45.3. **HRMS** (ESI) calcd. for [C₂₁H₁₇NO₃]⁺ (M⁺): 331.1208; observed 331.1194.

Rotor **2**(OCF₃) (*3aR,4S,7R,7aS*)-2-(2-(trifluoromethoxy) phenyl)-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoisoindole-1,3(2*H*)-dione: *cis*-5-Norbornene-*endo*-2,3-dicarboxylic anhydride (328 mg, 2 mmol) and 2-(trifluoromethoxy)aniline (425 mg, 2.4 mmol) were added to a heavy wall glass pressure vessel with a magnetic stir bar. The pressure vessel was then capped and heated to 130 °C in a silicon oil bath for 12 hours. After letting the pressure vessel cool to room temperature, the crude material was dissolved in menthol, and recrystallize to give **2**(OCF₃) as a light-yellow crystals (540 mg, 85%). **¹H NMR** (400 MHz, CDCl₃) δ 7.45 – 7.31 (m, 3H), 7.16 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.05 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.28 (s, 2H, *syn* and *anti*), 6.26 (s, 2H, *syn* and *anti*) 3.54 – 3.39 (m, 4H, *syn* and *anti*), 1.78 (d, *J* = 8.8 Hz, 1H, *syn* and *anti*), 1.60 (d, *J* = 8.2 Hz, 1H, *syn* and

anti). **¹⁹F NMR** (376 MHz, CDCl₃) δ -56.57 (s), -57.36 (s). **¹³C NMR** (101 MHz, CDCl₃) δ 175.9, 175.8, 145.0, 134.7, 134.7, 130.6, 130.6, 130.2, 129.8, 127.3, 127.1, 124.6, 124.2, 121.6, 121.3, 120.3, 120.3, 119.0, 77.4, 77.1, 76.8, 52.5, 52.4, 46.7, 46.0, 45.4, 45.3. **HRMS** (ESI) calcd. for [C₁₆H₁₂F₃NO₃]⁺ (M⁺): 323.0769; observed 323.0767.

Rotor **2**(OCOCH₃) 2-((3*aR*,4*S*,7*R*,7*aS*)-1,3-dioxo-1,3,3*a*,4,7,7*a*-hexahydro-2*H*-4,7-methanoisindol-2-yl) phenyl acetate: (3*aR*,4*S*,7*R*,7*aS*)-2-(2-hydroxyphenyl)-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoisindole-1,3(2*H*)-dione (50 mg, 0.2 mmol) and acetyl chloride (35 mg, 0.4 mmol) were added with toluene to a heavy wall glass pressure vessel with a magnetic stir bar. The pressure vessel was then capped and heated to 120 °C in a silicon oil bath for 12 hours. After letting the pressure vessel cool to room temperature, toluene was removed under vacuum, the crude material was purified by column chromatography (ethyl acetate/hexanes = 1:5 to 1:1, v/v) to give **2**(OCOCH₃) as a white powder (59 mg, quant.). **¹H NMR** (400 MHz, CDCl₃) δ 7.42 – 7.38 (m, 1H, *syn* and *anti*), 7.30 – 7.24 (m, 2H, *syn* and *anti*), 7.16 (d, *J* = 7.6 Hz, 1H, *syn*), 7.06 (d, *J* = 7.6 Hz, 1H, *anti*) 6.26 (s, 2H, *syn* and *anti*), 3.62 – 3.35 (m, 4H, *syn* and *anti*), 2.26 (s, 3H, *syn*), 2.20 (s, 3H, *anti*) 1.79 (d, *J* = 8.4 Hz, 1H, *syn* and *anti*), 1.62 (d, *J* = 8.4 Hz, 1H, *syn* and *anti*). **¹³C NMR** (101 MHz, CDCl₃) δ 176.0, 167.9, 146.0, 134.7, 129.9, 129.3, 128.7, 126.2, 124.0, 52.5, 46.6, 45.9, 45.8, 45.4, 21.4, 21.0. **HRMS** (ESI) calcd. for [C₁₇H₁₅NO₄]⁺ (M⁺): 297.1001; observed 297.1003.

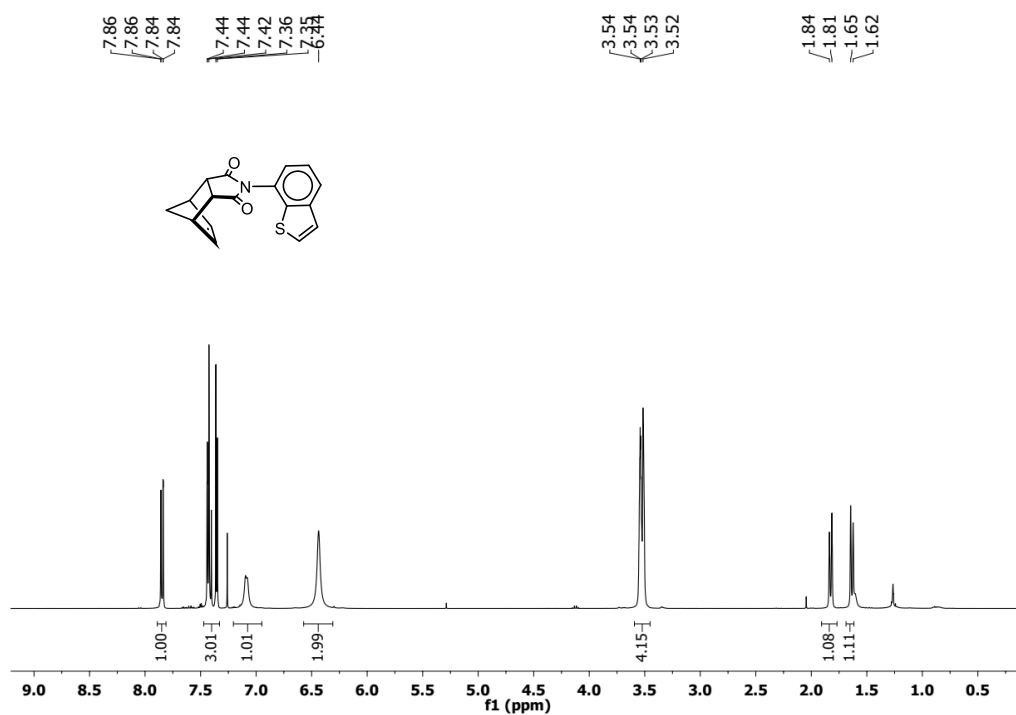


Figure 4.10 ¹H NMR spectra (400 MHz) of rotor 1(thiofuran) in CDCl₃.

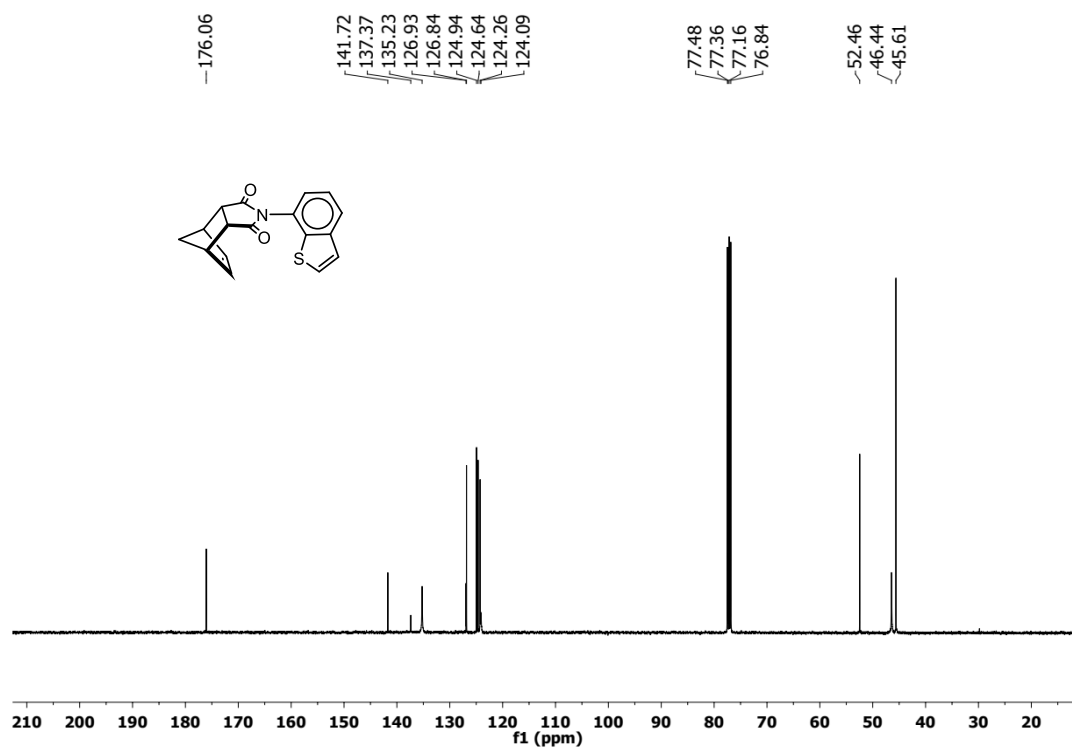


Figure 4.11 ¹³C NMR spectra (100 MHz) of rotor 1(thiofuran) in CDCl₃.

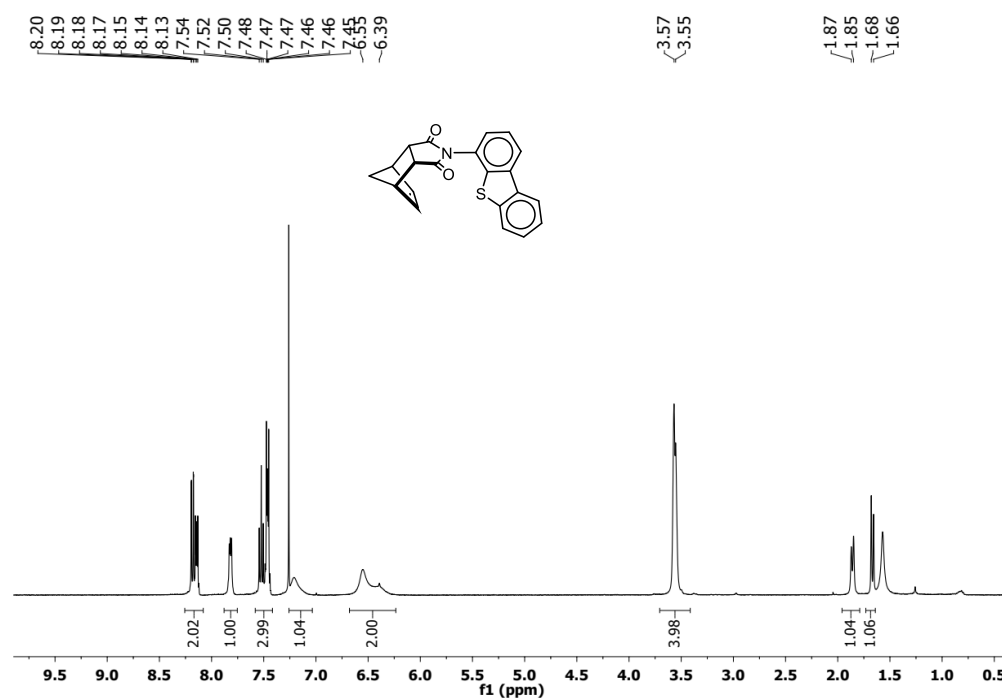


Figure 4.12 ¹H NMR spectra (400 MHz) of rotor 1(benzothiofuran) in CDCl₃.

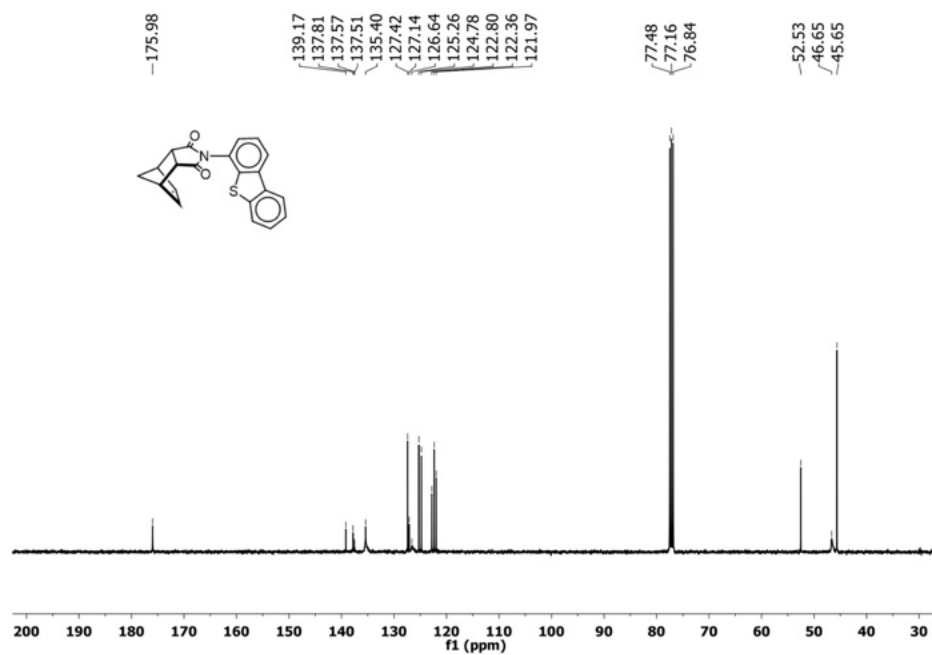
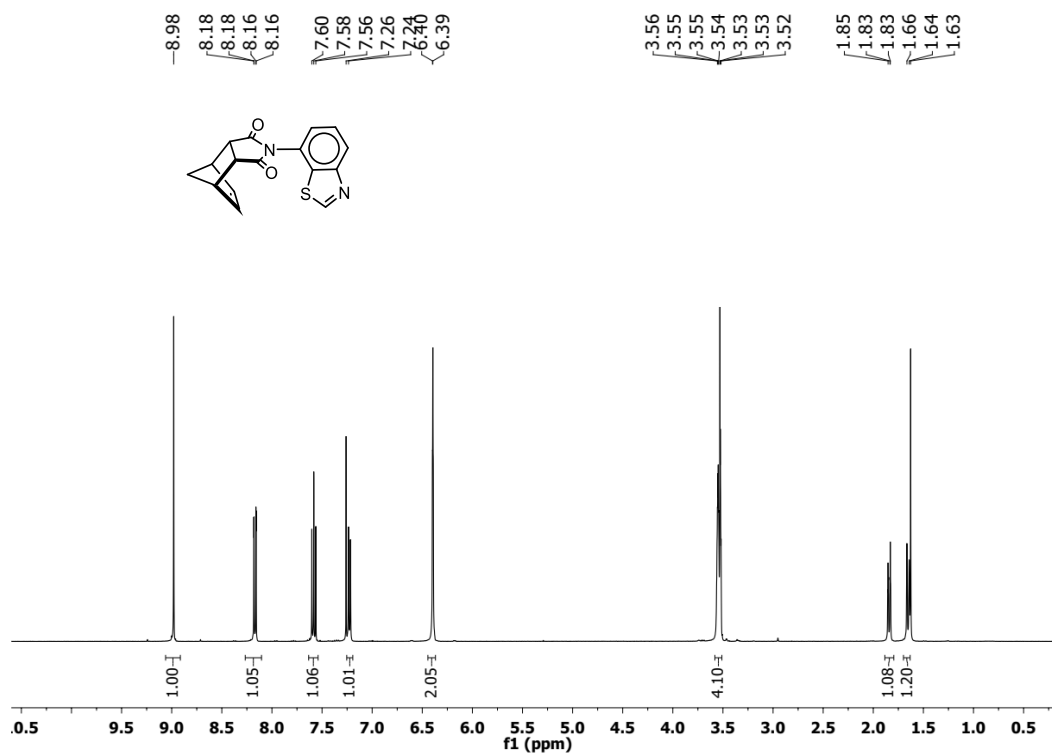


Figure 4.13 ¹³C NMR spectra (100 MHz) of rotor 1(benzothiofuran) in CDCl₃.



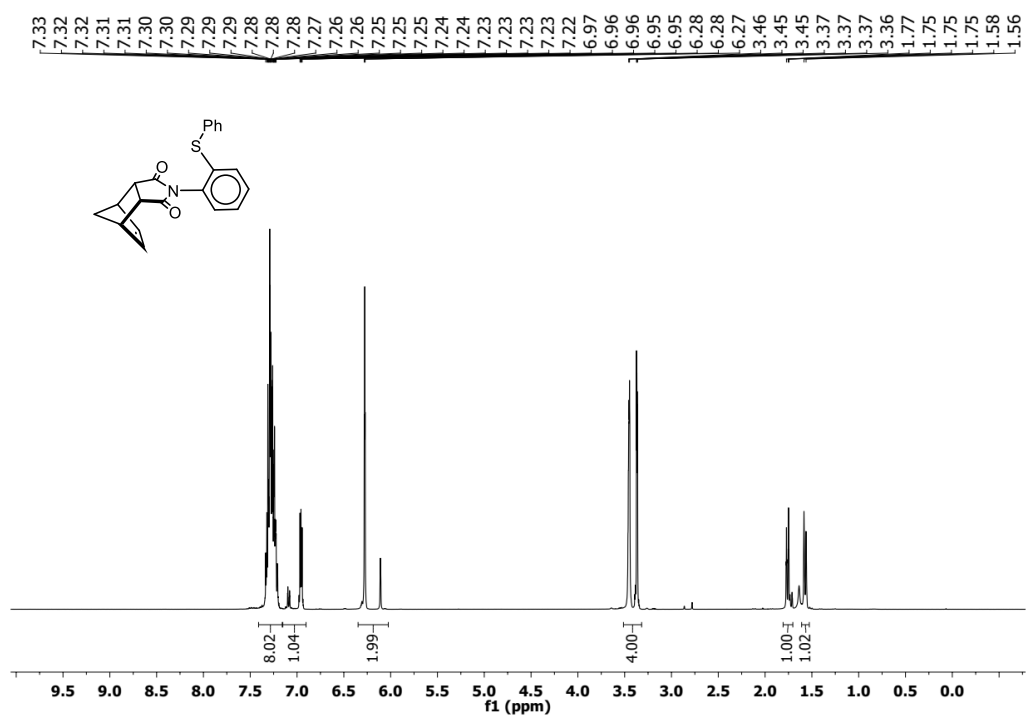


Figure 4.16 ¹H NMR spectra (400 MHz) of rotor 1(SPh) in CDCl₃.

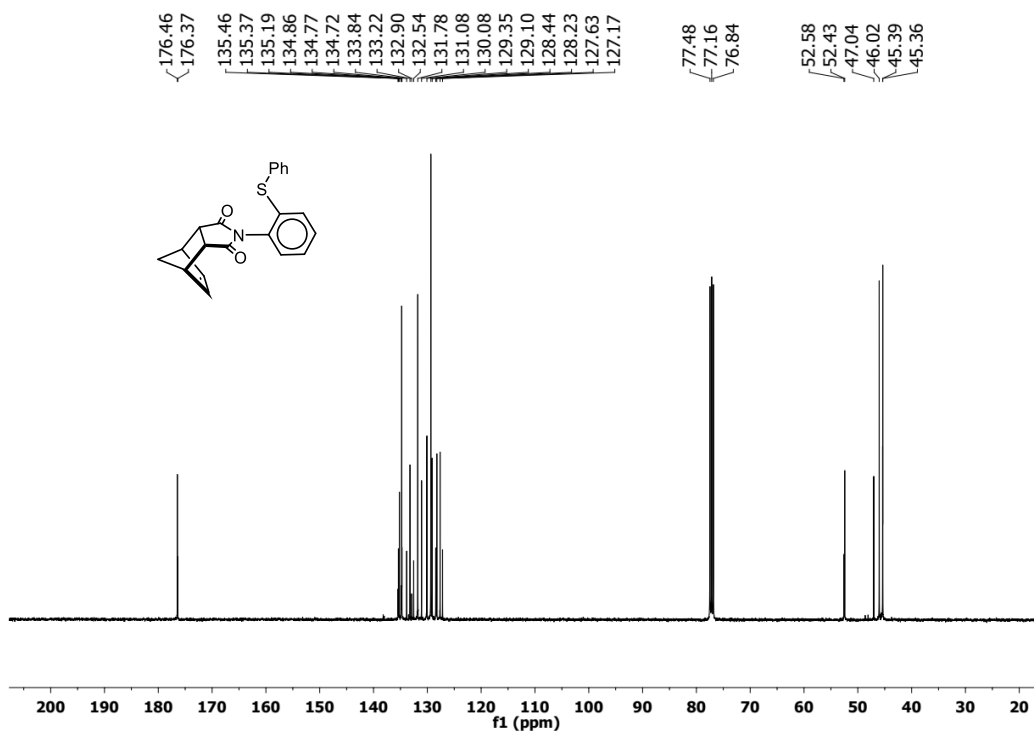


Figure 4.17 ¹³C NMR spectra (100 MHz) of rotor 1(SPh) in CDCl₃.

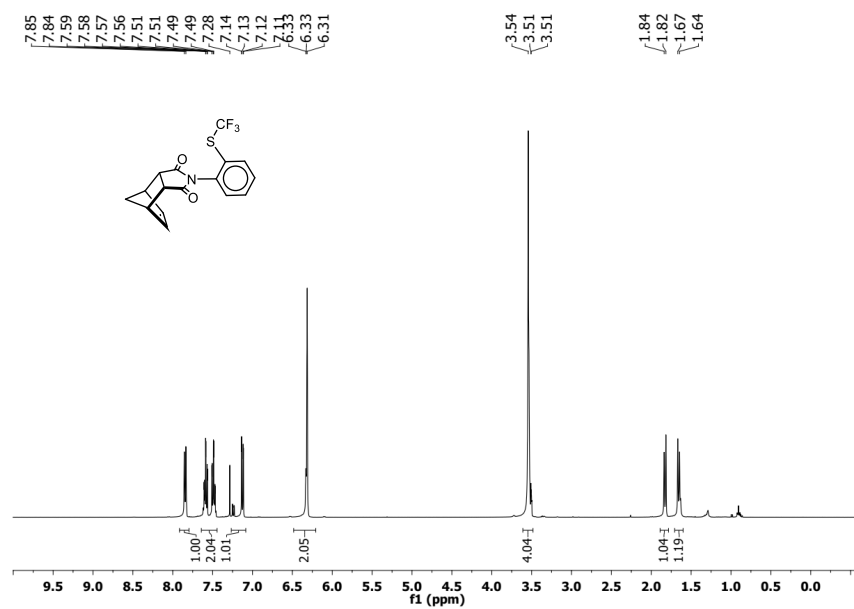


Figure 4.18 ¹H NMR spectra (400 MHz) of rotor **1**(SCF₃) in CDCl₃.

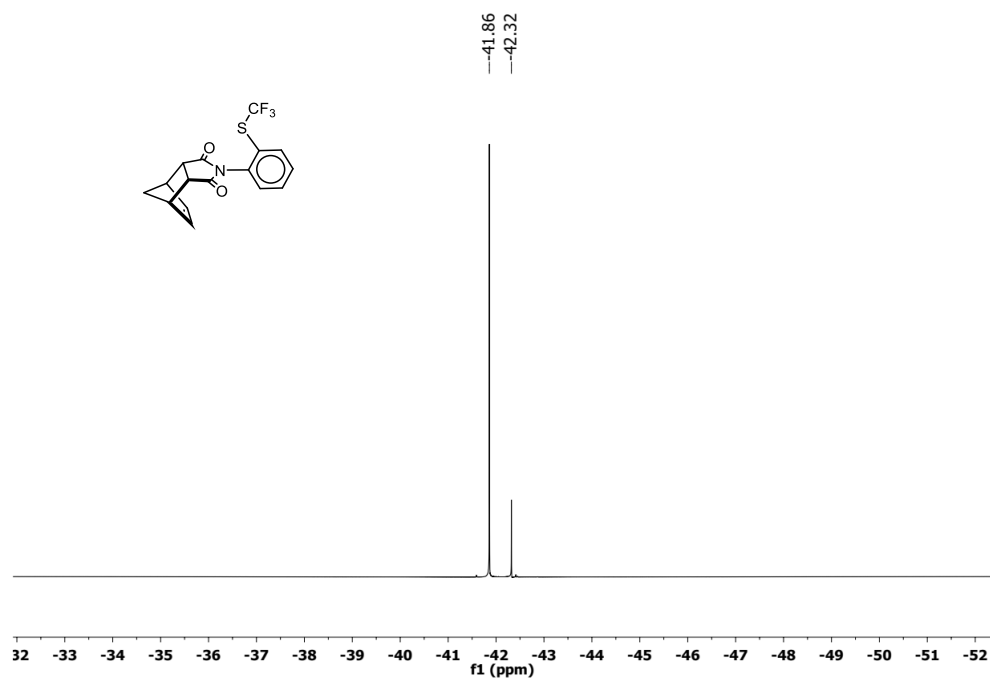


Figure 4.19 ¹⁹F NMR spectra (400 MHz) of rotor **1**(SCF₃) in CDCl₃.

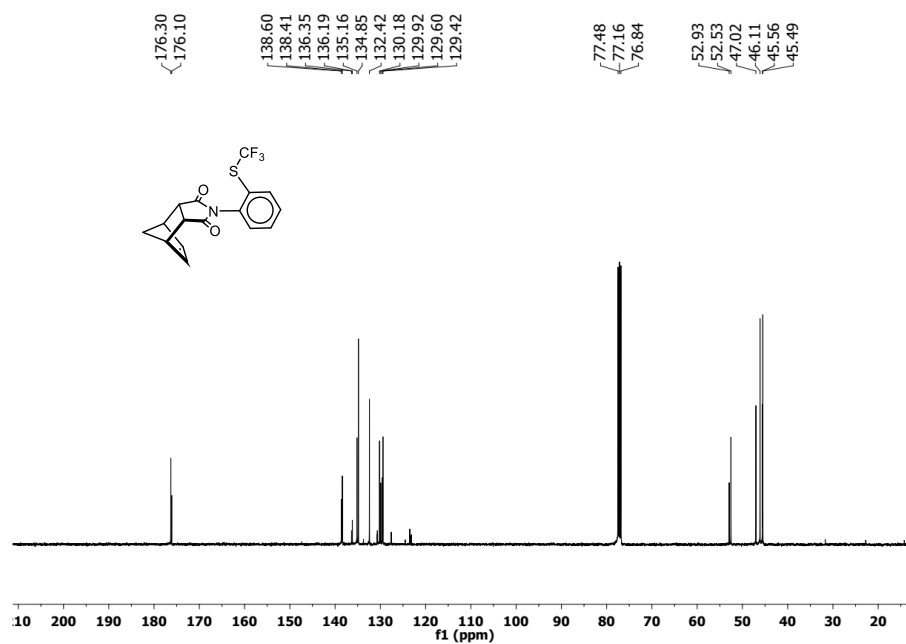


Figure 4.20 ¹³C NMR spectra (100 MHz) of rotor 1(SCF₃) in CDCl₃.

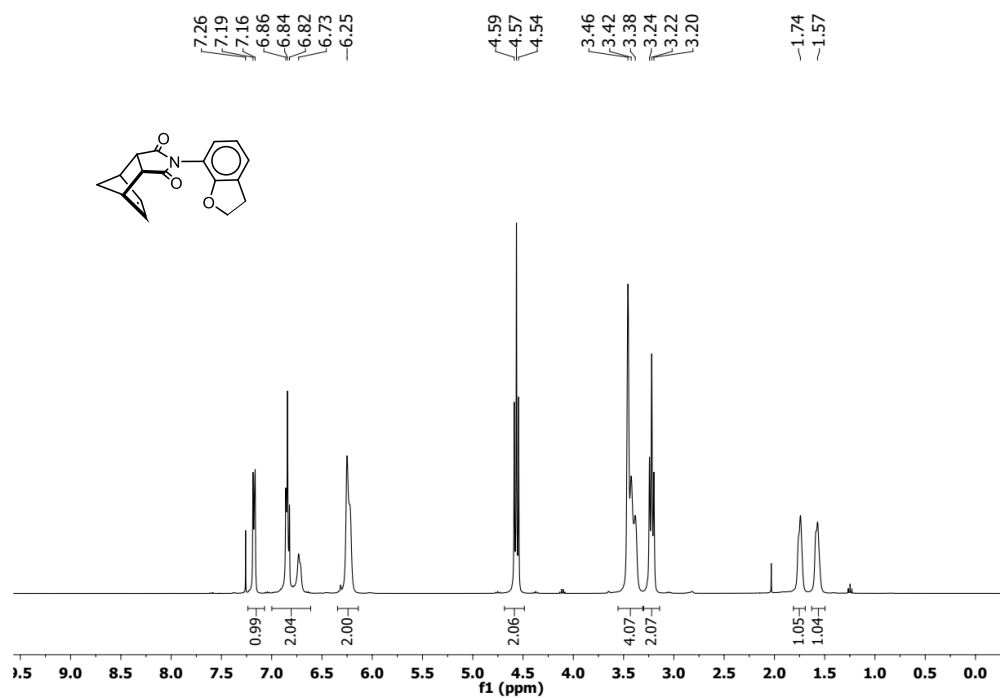


Figure 4.21 ¹H NMR spectra (400 MHz) of rotor 2(2H-furan) in CDCl₃.

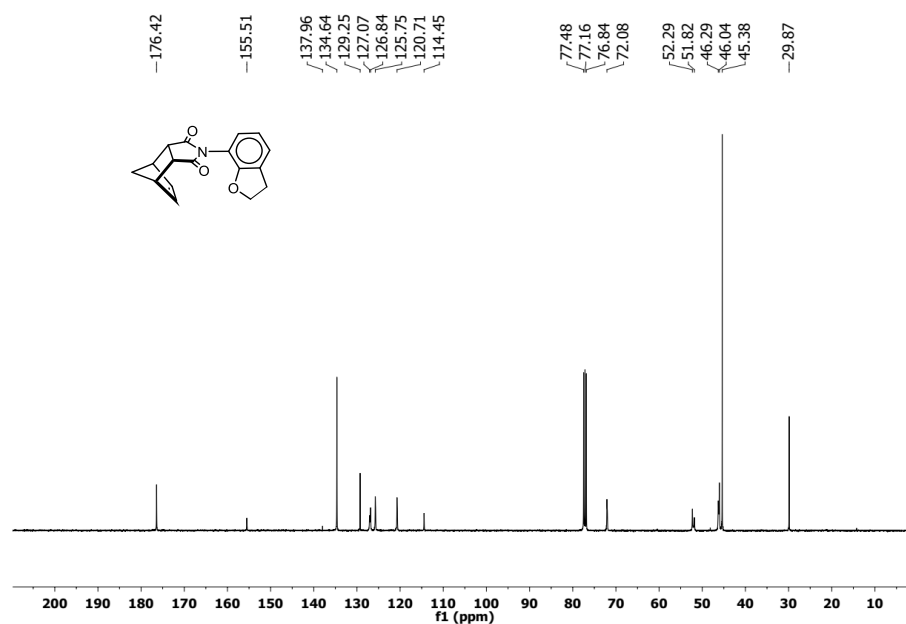


Figure 4.22 ¹³C NMR spectra (100 MHz) of rotor **2**(2H-furan) in CDCl₃.

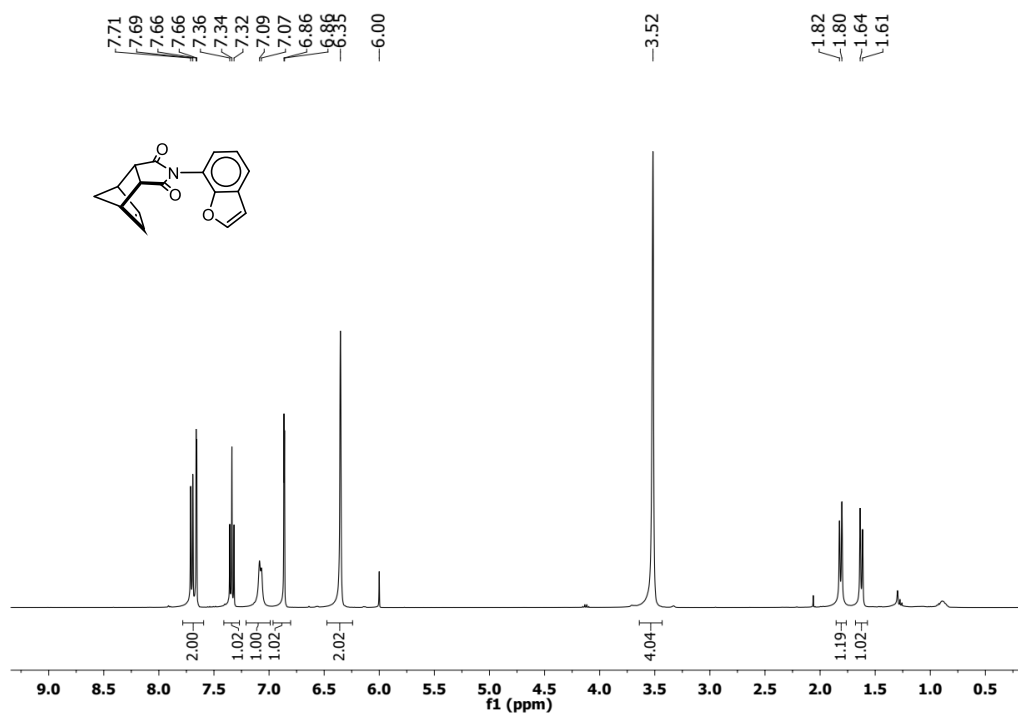


Figure 4.23 ¹H NMR spectra (400 MHz) of rotor **2**(furan) in CDCl₃.

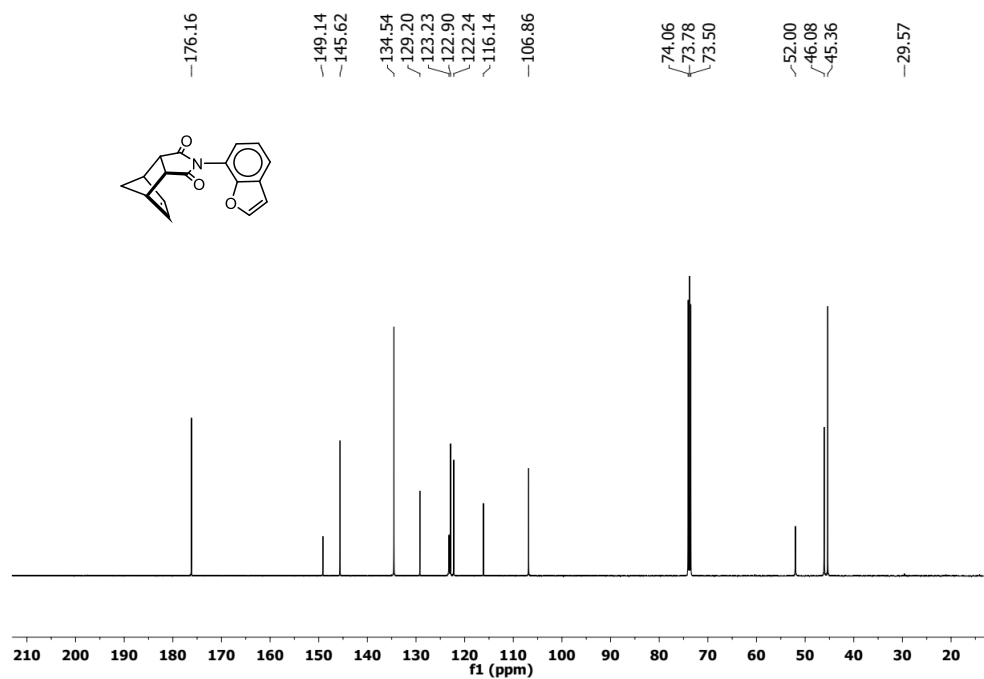


Figure 4.24 ¹³C NMR spectra (100 MHz) of rotor **2**(furan) in CDCl₃.

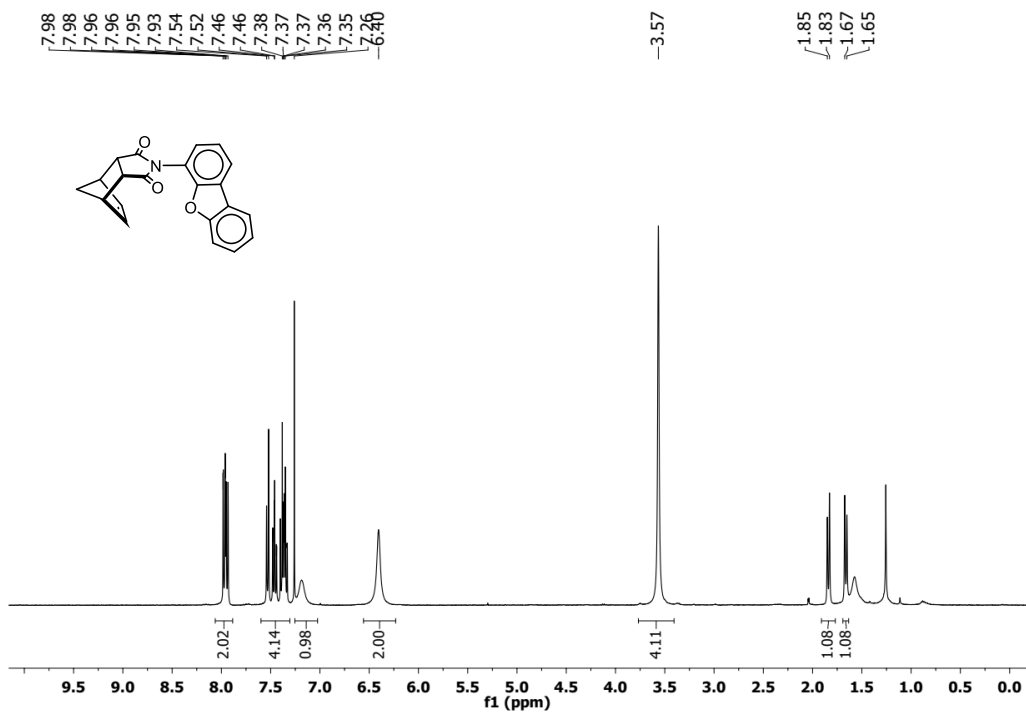


Figure 4.25 ¹H NMR spectra (400 MHz) of rotor **2**(benzofuran) in CDCl₃.

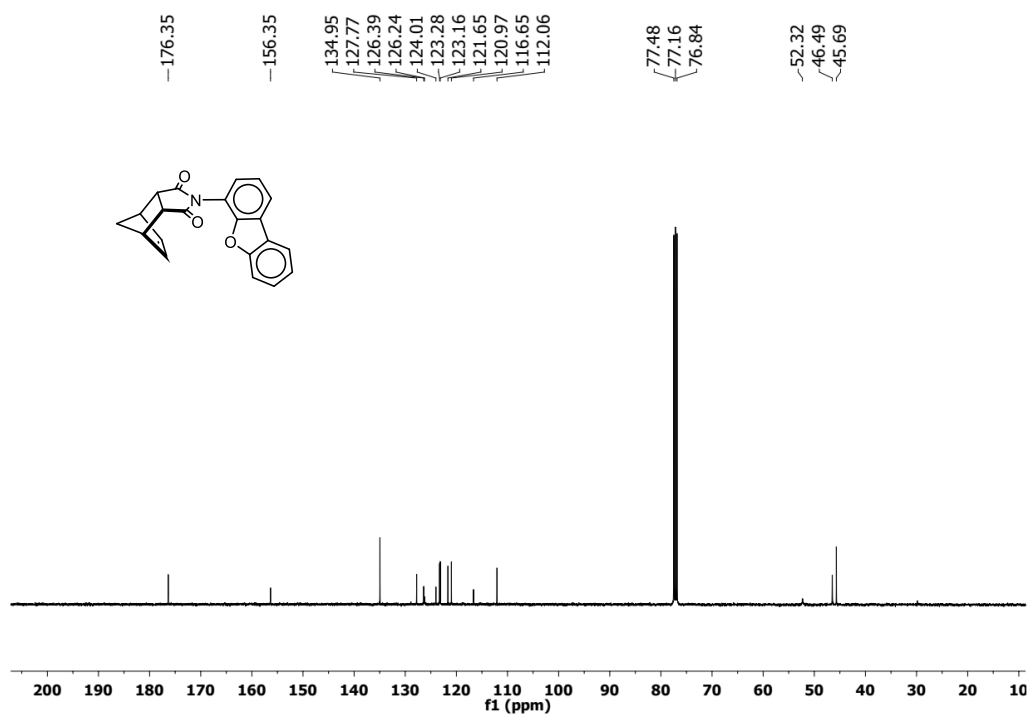


Figure 4.26 ¹³C NMR spectra (100 MHz) of rotor **2**(benzofuran) in CDCl₃.

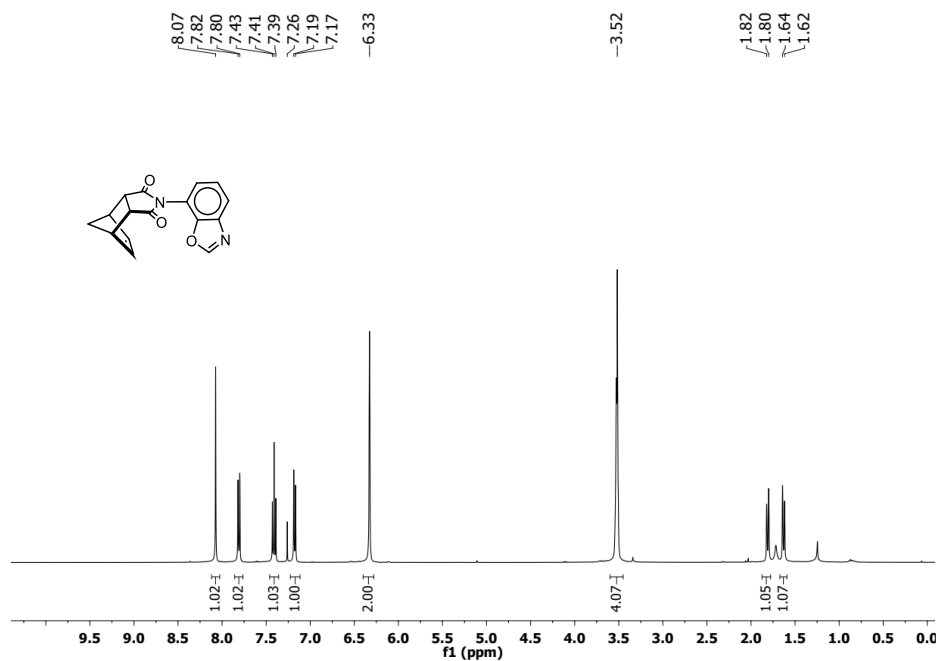


Figure 4.27 ¹H NMR spectra (400 MHz) of rotor **2**(azole) in CDCl₃.

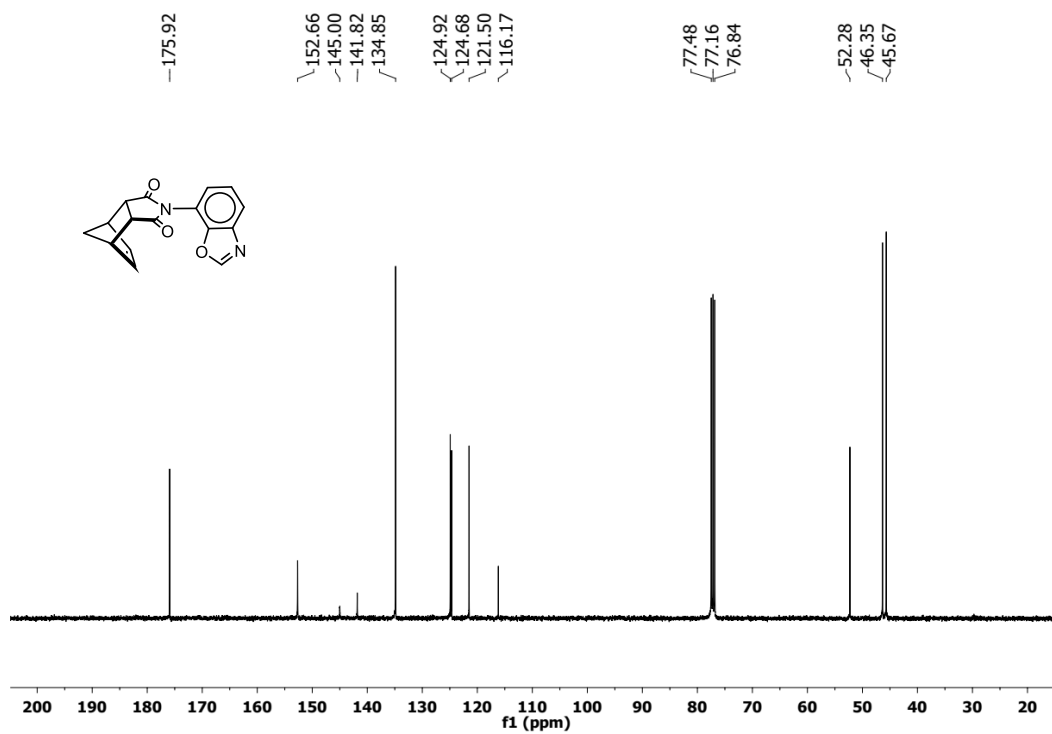


Figure 4.28 ¹³C NMR spectra (100 MHz) of rotor 2(azole) in CDCl₃.

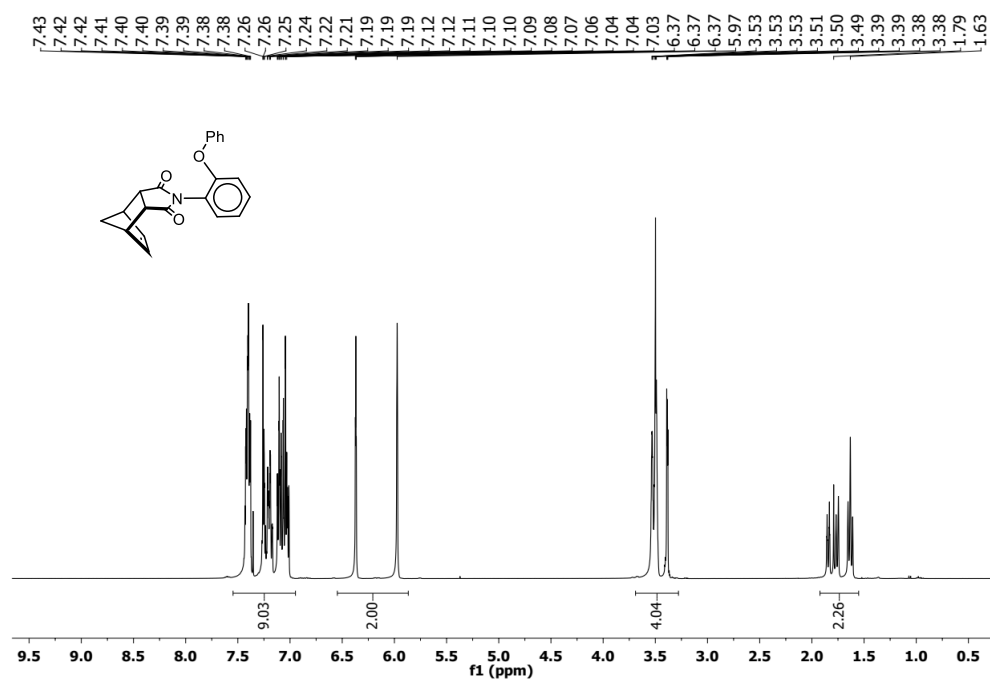


Figure 4.29 ¹H NMR spectra (400 MHz) of rotor 2(OPh) in CDCl₃.

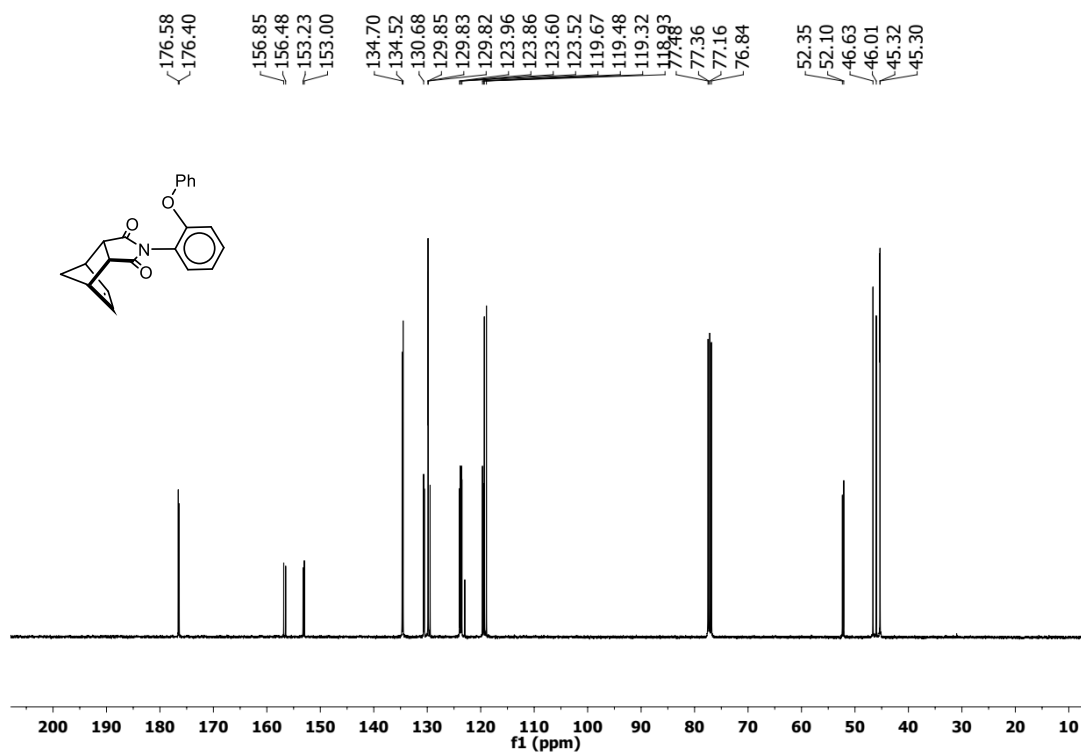


Figure 4.30 ¹³C NMR spectra (100 MHz) of rotor 2(OPh) in CDCl₃.

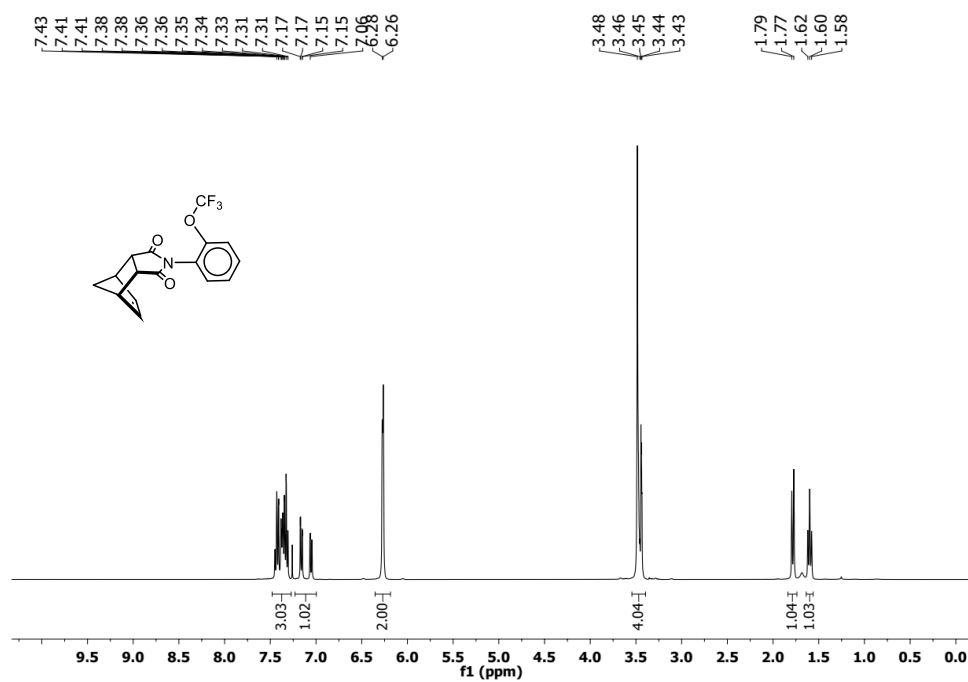


Figure 4.31 ¹H NMR spectra (400 MHz) of rotor 2(OCF₃) in CDCl₃.

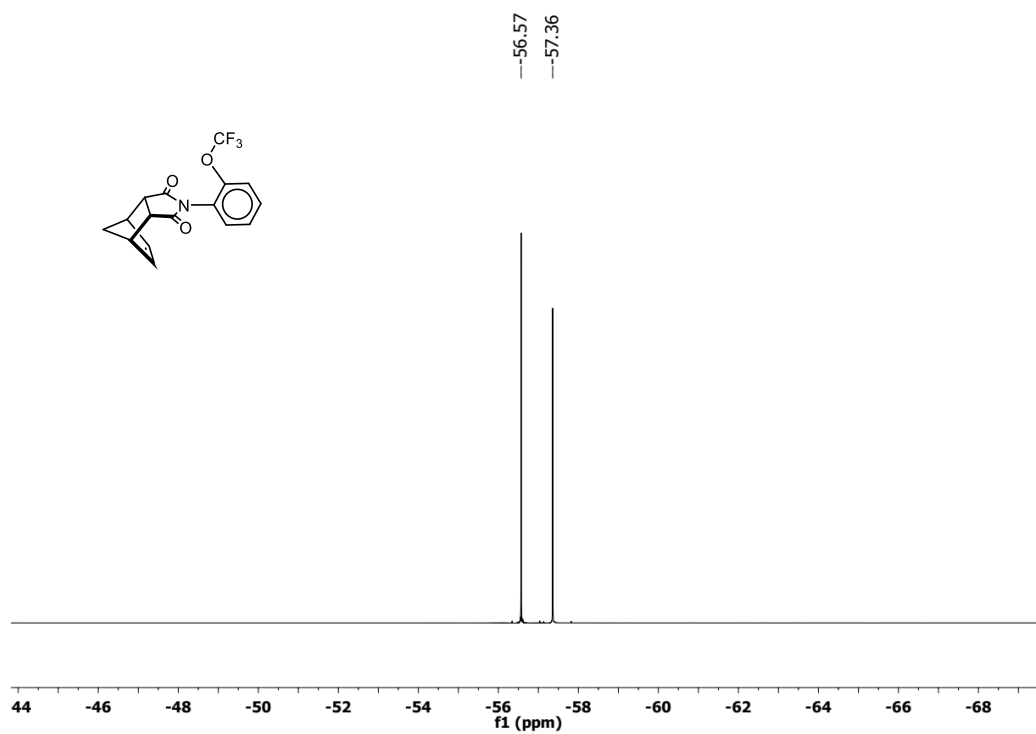


Figure 4.32 ¹⁹F NMR spectra (400 MHz) of rotor 2(OCF₃) in CDCl₃.

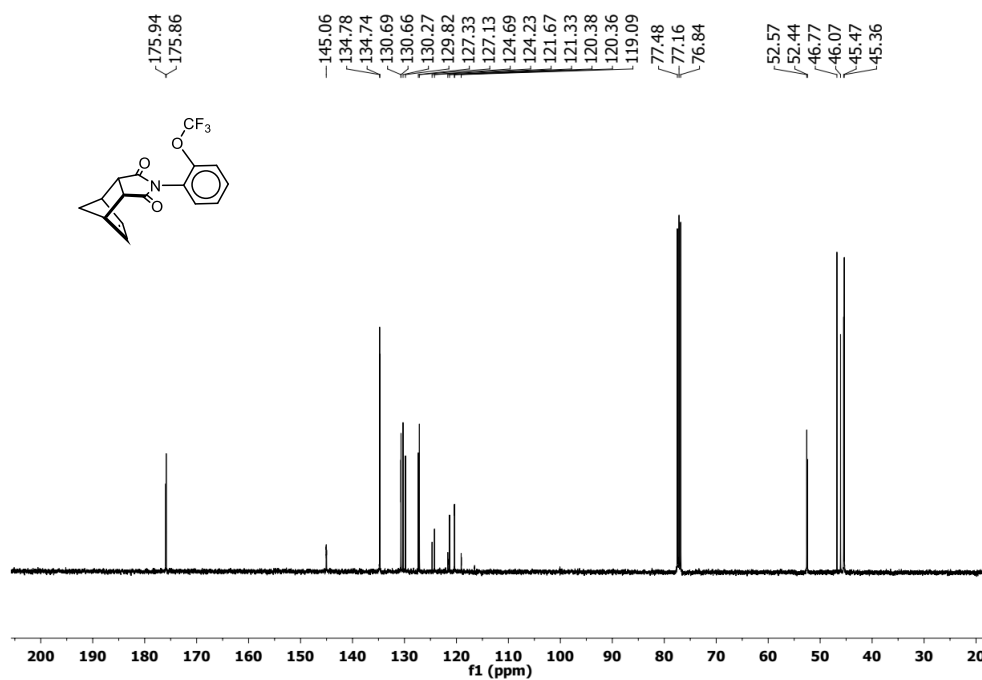


Figure 4.33 ¹³C NMR spectra (100 MHz) of rotor 2(OCF₃) in CDCl₃.

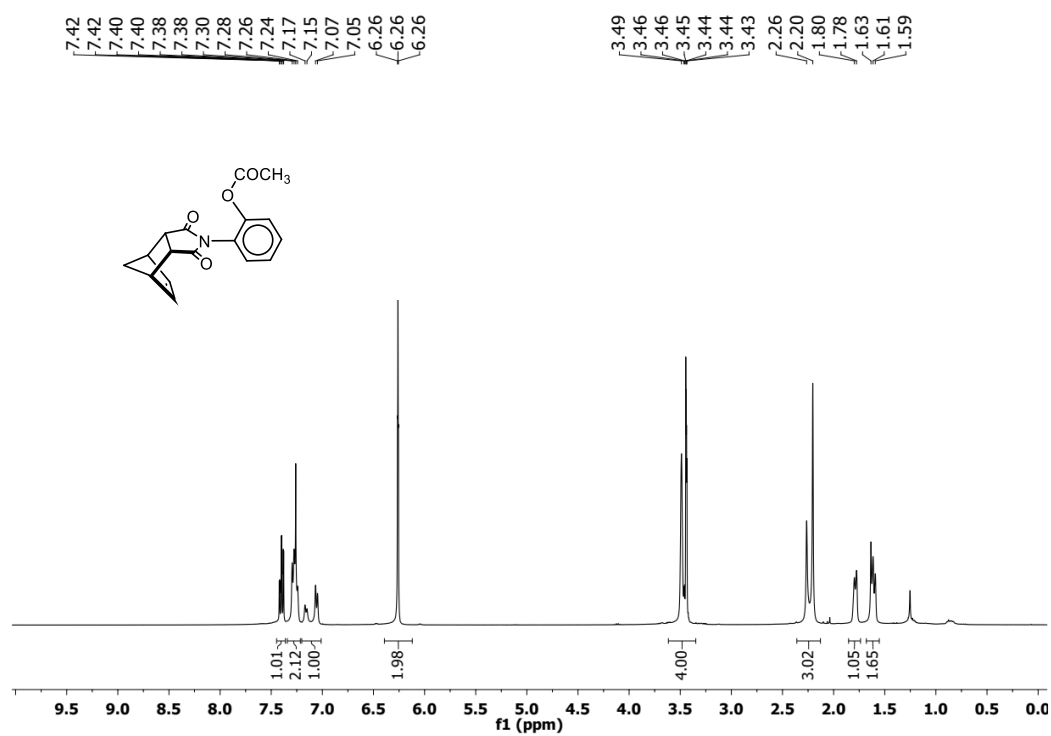


Figure 4.34 ¹H NMR spectra (400 MHz) of rotor **2**(OCOCH₃) in CDCl₃.

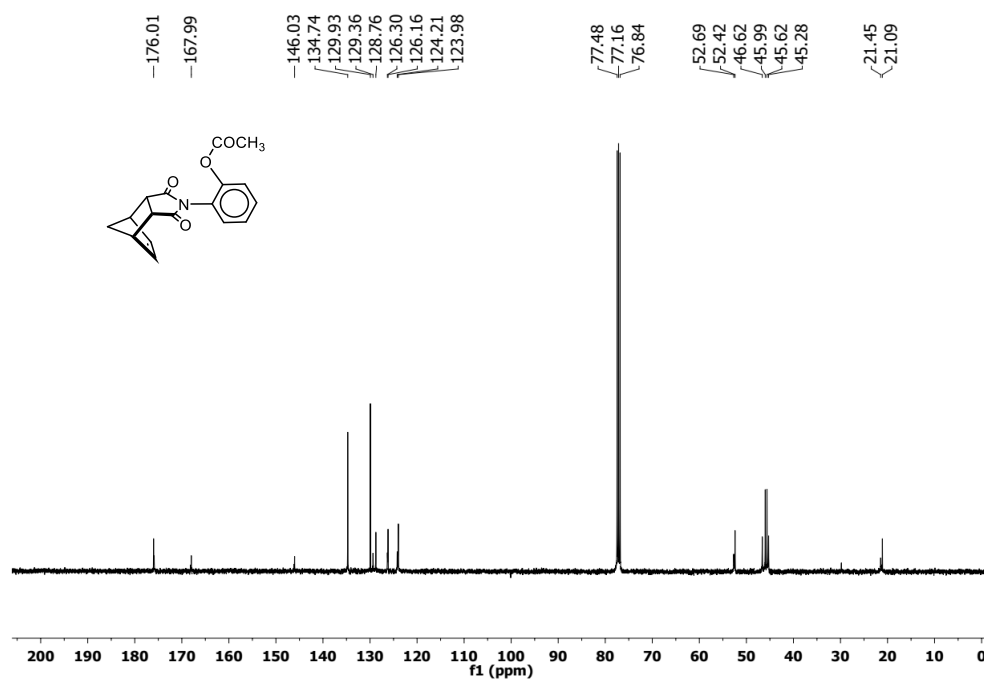
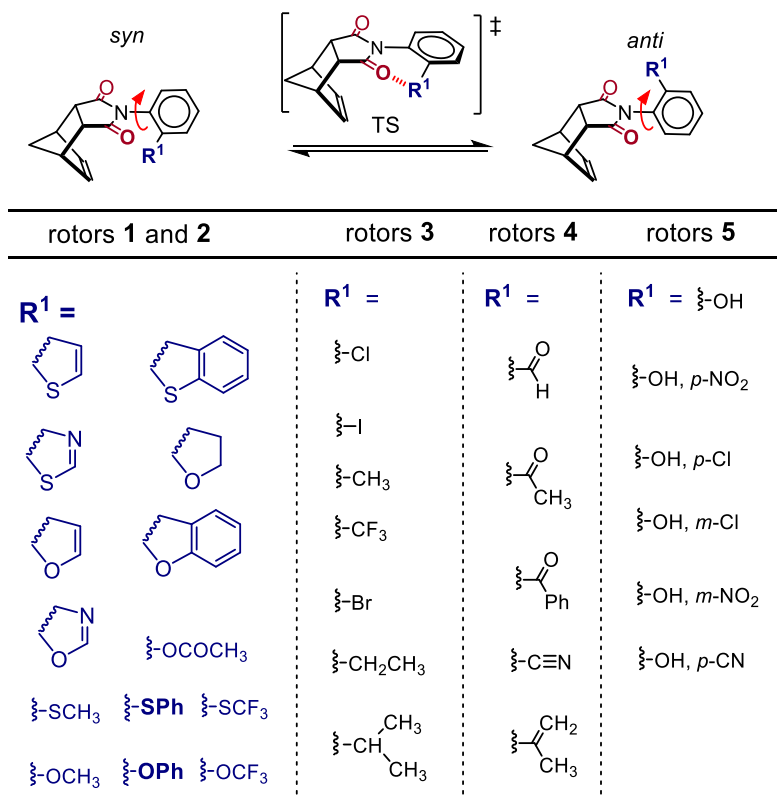


Figure 4.35 ¹³C NMR spectra (100 MHz) of rotor **2**(OCOCH₃) in CDCl₃.

4.5.4 Comparison of the TS stabilizing effects of the ChB interactions with n to $\pi^*(C=O)$, hydrogen bonding.

Rotors **3**, **2**(OCH₃), and **2**(OPh) do not form stabilizing non-covalent interactions in the bond rotation TS (**Scheme 4.3**).



Scheme 4.3 Conformational *syn-anti* equilibrium of the *N*-arylimide molecular rotors (top) and structures of rotors **1** to **5** (bottom). The rotors were each designed to study a different type of non-covalent TS interaction including: chalcogen bonding (rotors **1** and **2**), steric interactions (rotors **3**), C=O $\cdots$ C=O interactions (rotors **4**), and C=O $\cdots$ H-O interactions (rotors **5**).

Therefore, these rotors were used to develop an empirical model for the steric TS interactions in the chalcogen rotors using the trendline from the $\Delta G^\ddagger$ exp versus *B*-value plot (**Figure 4.36**). The values for Mazzanti's steric parameter, *B*-value, were taken from the literature for the corresponding R¹-groups in the *ortho*-position of the rotors.^{3, 4, 5} The

rotational barriers for the steric rotors displayed a good correlation ($R^2 = 0.914$), with B -value. Most of the chalcogen rotors **1** and **2** had rotational barriers that were lower than the steric trendline, which is consistent with the presence of additional TS stabilizing non-covalent interactions. The distance of the barriers from the steric trendline on the y-axis provided a quantitative measure of the non-covalent interaction component of the rotational barrier (See **Figure 4.36** and **Table 4.3**).

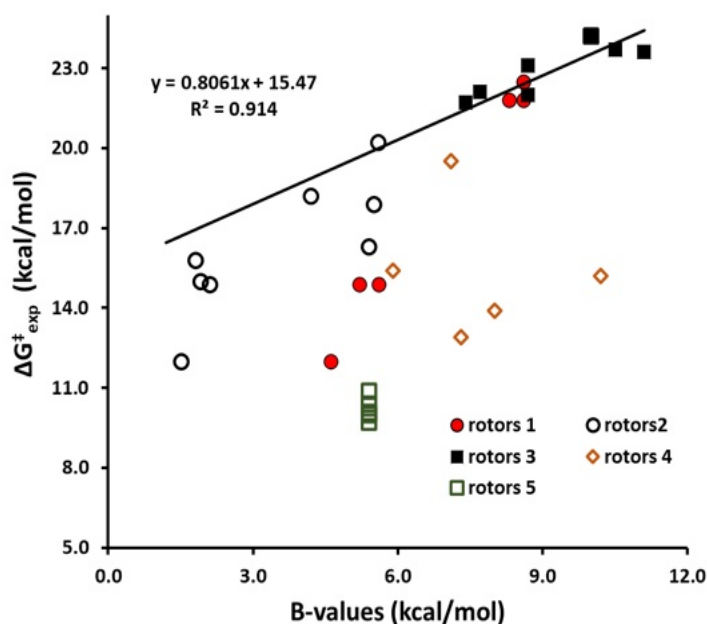


Figure 4.36 Correlation plot of the experimental rotational barriers for rotors versus the steric B -values of the R -groups of the rotors that formed $\text{C}=\text{O}\cdots\text{S}$ interactions (**1**, red filled circles), $\text{C}=\text{O}\cdots\text{O}$ interactions (**2**, black open circles), $\text{C}=\text{O}\cdots\text{R}$ steric interactions (**3**, black squares), $\text{C}=\text{O}\cdots\text{C}=\text{O}$ and $\text{C}=\text{O}\cdots\text{C}\equiv\text{N}$ interactions (**4**, triangle open circles), and $\text{C}=\text{O}\cdots\text{H}-\text{O}$ interactions (**5**, green open squares).

Table 4.3 Experimental barriers,^a *B*-values,^b ESP,^c calculated barriers,^d steric predictions,^e interaction energies.^f

Rotors	R=	$\Delta G^\ddagger_{\text{exp}}$ (kcal/mol)	<i>B</i>-value (kcal/mol)	ESP (kcal/mol)	$\Delta G^\ddagger_{\text{cal}}$ (kcal/mol)	<i>E</i>_{steric} (kcal/mol)	<i>E</i>_{int} (kcal/mol)
1(thiofuran)		14.9	5.2	12.5	14.2	19.7	-4.8
1(benzothiofuran)		14.9	5.5	15.0	14.8	19.9	-5.0
1(thiazole)		12.0	4.6	22.0	12.4	19.2	-7.2
1(SCH ₃)		22.5	8.6	-22.0	24.8	22.4	0.1
1(SPh)		21.8	8.3	-17.0	23.0	22.2	-0.4
1(SCF ₃)		21.8	8.2	-14.0	23.4	22.1	-0.3
2(furan)		15.0	1.9	-12.5	13.0	17.0	-2.0
2(benzofuran)		14.9	2.0	-10.0	13.5	17.1	-2.2
2(oxazole)		12.0	1.5	7.5	11.1	16.7	-4.7
2(2H-furan)		15.8	1.6	-15.0	15.5	16.8	-1.0
2(OCH ₃) ^g		20.2	5.6	-22.5	19.5	20.0	0.2
2(OPh) ^g		18.2	4.2	-17.5	18.3	18.9	-0.7
2(OCF ₃)		17.9	5.5	-5.0	16.6	19.9	-2.0
2(OCOCH ₃)		16.3	5.4	0.5	14.5	19.8	-3.5
3(CH ₃)		21.7	7.4	-	20.2	g	g
3(Et)		22.0	8.7	-	22.4	g	g
3(<i>i</i> -Pr)		23.6	11.1	-	24.4	g	g
3(Cl)		22.1	7.7	-	22.5	g	g
3(Br)		23.1	8.7	-	24.2	g	g
3(I)		23.7	10.0	-	25.1	g	g
3(CF ₃)		24.2	10.5	-	25.6	g	g
4(C(CH ₂)CH ₃)		19.5	7.1	2.5	19.5	21.2	-1.7
4(CN)		15.4	5.9	15.0	16.7	20.2	-4.8
4(CHO)		15.2	10.2	26.5	16.2	23.7	-8.5
4(COCH ₃)		13.9	8.0	23.8	15.6	21.9	-8.0
4(COPh)		12.9	7.3	17.5	15.1	21.4	-8.5
5(OH)		10.9	5.4	67.0	10.1	19.8	-8.9
5(OH, <i>m</i> -Cl)		10.1	5.4	72.5	9.5	19.8	-9.7
5(OH, <i>m</i> -NO ₂)		10.0	5.4	78.5	9.5	19.8	-9.8
5(OH, <i>p</i> -Cl)		10.4	5.4	71.5	9.8	19.8	-9.4
5(OH, <i>p</i> -CN)		10.0	5.4	80.0	9.2	19.8	-9.8
5(OH, <i>p</i> -NO ₂)		9.7	5.4	79.0	9.0	19.8	-10.1

^aExperimental barriers were measured via EXSY, details are provided in Section 4.5.6. ^b*B*-values were the steric parameters for the R-groups from the literature or calculated.^{3, 4, 5} The methods of calculating *B*-values are provided in Section 4.5.8. ^cElectrostatic potential (ESP) were calculated in Spartan18 as described in Section 4.5.11. ^dCalculated barriers (B3LYP-D3/6-311G*) were completed in Spartan18 as described in Section 4.5.7. ^eThe steric values of the R-groups calculated from the *B*-values using the equation $E_{\text{steric}} = 0.8061 \cdot (B\text{-value}) + 15.47$. The derivations of this equation are provided in the text of the manuscript. ^fInteraction energies were the attractive component of the interaction of the C=O and R-groups in the transition states based on difference of the experimental barrier and E_{steric} . ^gThe rotors that were used for building the steric trendline.^{3, 4}

4.5.5 95% Confidence interval analysis of the steric trendline.

The confidence interval (CI) of the steric trendline in the $\Delta G^\ddagger_{\text{exp}}$ versus B -value plot was calculated at the 95% CI (**Figure 4.37**). The data used for the analysis is shown in **Table 4.4**. Numerical values for the $\pm 95\%$ CI for representative data points in the trendline are shown in **Table 4.5**. The values derived from the 95% CI analysis are shown in **Table 4.6**. Finally, the 95% CI values calculated for experimental data points for the chalcogen rotors **1** and **2** (**Table 4.7**).

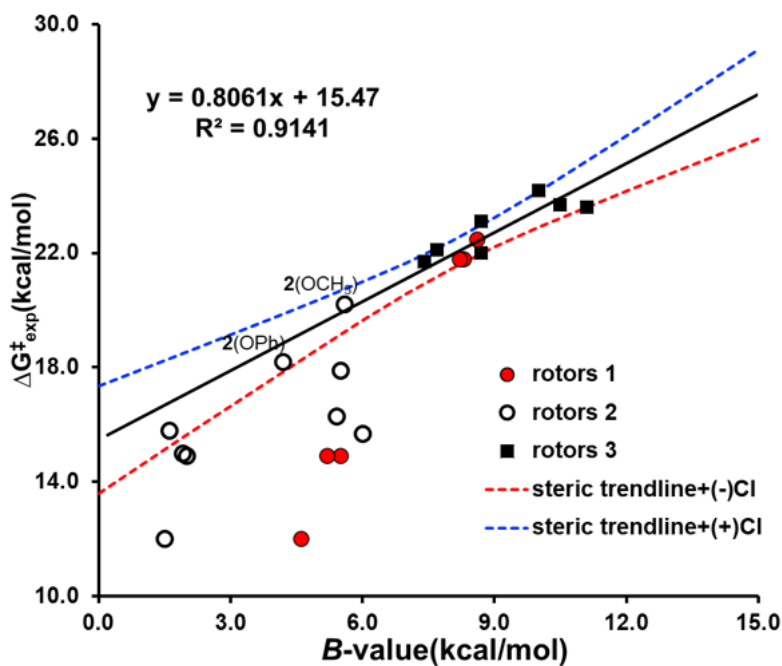


Figure 4.37 The steric trendline (solid black) and the +CI (broken blue) and -CI (broken red) trendlines. The $\Delta G^\ddagger_{\text{exp}}$ values of the chalcogen rotors **1** and **2** are plotted to show whether they fall within the $\pm 95\%$ CI for the steric trendline. Rotor **2**(OCH₃) and **2**(OPh) were in making the steric line.

Table 4.4 The *B*-value and corresponding experimental barriers were used to produce the steric trendline and 95% confidence interval analysis.

	Rotors R= 2-	<i>B</i> -value (kcal/mol)	$\Delta G^\ddagger_{\text{exp}}$ (kcal/mol)
1	CH ₃	7.4	21.7
2	CH(CH ₃) ₂	11.1	23.6
3	Cl	7.7	22.1
4	CH ₂ CH ₃	8.7	22.0
5	Br	8.7	23.1
6	I	10.0	24.2
7	CF ₃	10.5	23.7
8	OCH ₃	5.6	20.2
9	OPh	4.2	18.2

Table 4.5 The regression confidence intervals for the steric trendline.

Regression line confidence interval(CI)			
x(B-value)	CI	y+CI	y-CI
0	1.87	17.34	13.60
2	1.45	18.53	15.63
4	1.04	19.74	17.65
5	0.85	20.35	18.65
6	0.68	20.99	19.63
7	0.54	21.66	20.57
8	0.47	22.39	21.44
9	0.50	23.23	22.22
10	0.62	24.15	22.92
12	0.96	26.10	24.18
15	1.57	29.13	25.99

Table 4.6 The derived values from the 95% confidence interval analysis.

Derived values	
Slope, m	0.806 SLOPE(y,x)
Intercept, b	15.470 INTERCEPT(y,x)
Observations, n	9.000 COUNT(x)
estimate, S_{yx}	0.599 STEYX(y,x)
Average x	8.211 AVERAGE(x)
SSX	41.089 DEVSQ(x)
$t(\alpha, df)$	2.365 TINV(0.05,n-2)

Table 4.7 The fitting of experiment interaction energies in the 95% confidence interval analysis.

Rotors R=	x(B-value) (kcal/mol)	(-)CI (kcal/mol)	E _{int} (kcal/mol)	E _{int} (-) CI (kcal/mol)
1(thiofuran)	5.2	-0.8	-4.8	-3.9
1(benzothiofuran)	5.5	-0.8	-5.0	-4.2
1(thiazole)	4.6	-0.9	-7.2	-6.3
1(SCH ₃)	8.6	-0.5	0.1	0.6
1(SPh)	8.3	-0.5	-0.4	0.1
1(SCF ₃)	8.2	-0.5	-0.3	0.2
2(furan)	1.9	-1.5	-2.0	-0.5
2(benzofuran)	2.0	-1.5	-2.2	-0.7
2(oxazole)	1.5	-1.6	-4.7	-3.1
2(2H-furan)	1.6	-1.5	-1.0	0.6
2(OCH ₃)	5.6	-0.7	0.2	1.0
2(OPh)	4.2	-1.0	-0.7	0.3
2(OCF ₃)	5.5	-0.8	-2.0	-1.2
2(OCOCH ₃)	5.4	-0.8	-3.5	-2.7

4.5.6 Experimental measurements of the rotational barriers

The experimental rotational barriers of the rotors were determined via exchange spectroscopy (EXSY) NMR experiments or lineshape analysis in TCE-d₂. An example of the 2D NOESY spectra is shown in **Figure 4.38**. The integration of the crosspeak and diagonal signals were performed using the Bruker Topspin software, and rate constants were calculated using EXSYCalc. The rotational barrier ($\Delta G^\ddagger_{\text{exp}}$) for each rotor were extrapolated to room temperature for comparison. The TS enthalpy ($\Delta H^\ddagger_{\text{exp}}$) and entropy ($\Delta S^\ddagger_{\text{exp}}$) for rotor were obtained using Eyring plots (**Figures 4.39– 4.46**).

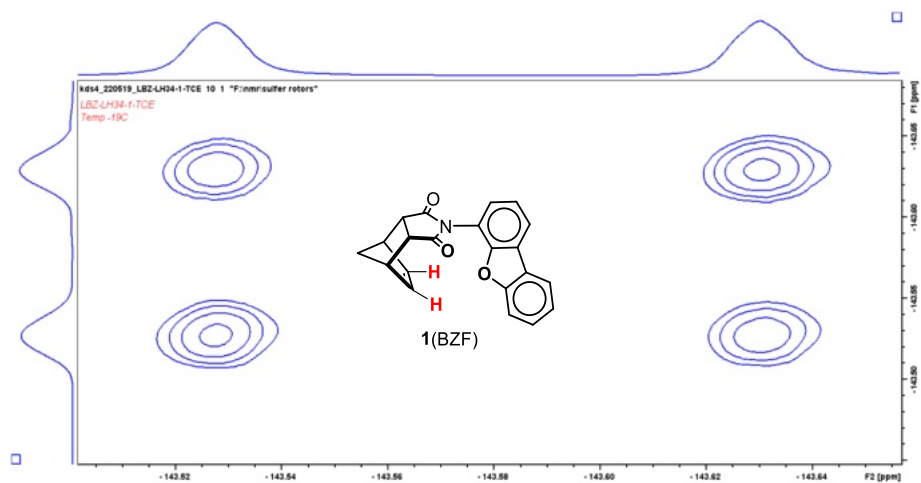


Figure 4.38 2D NMR of diastereomeric alkene protons of **1**(benzothiofuran) in TCE-d₂ at -19 °C.

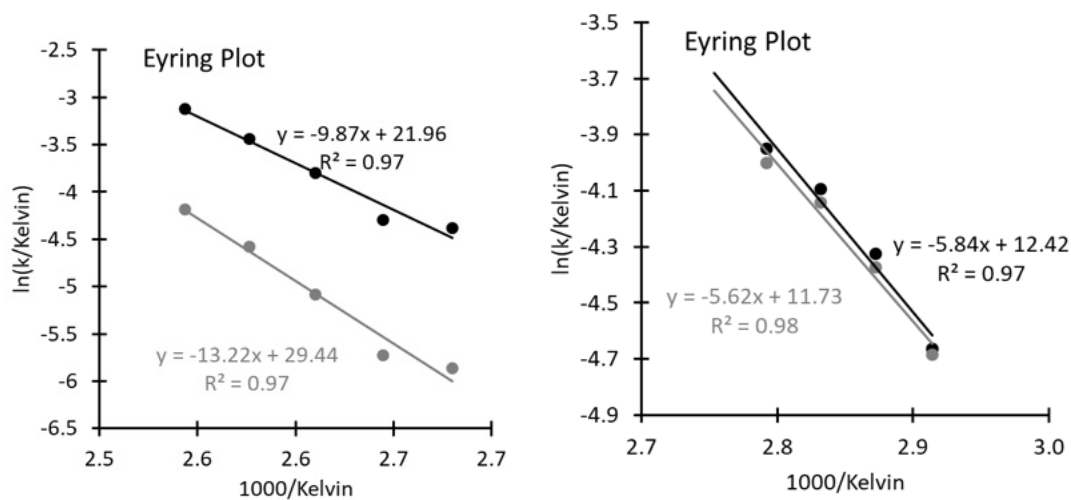


Figure 4.39 Eyring plots for rotor **1**(SPh) (left) and rotor **2**(OPh) (right) by EXSY.

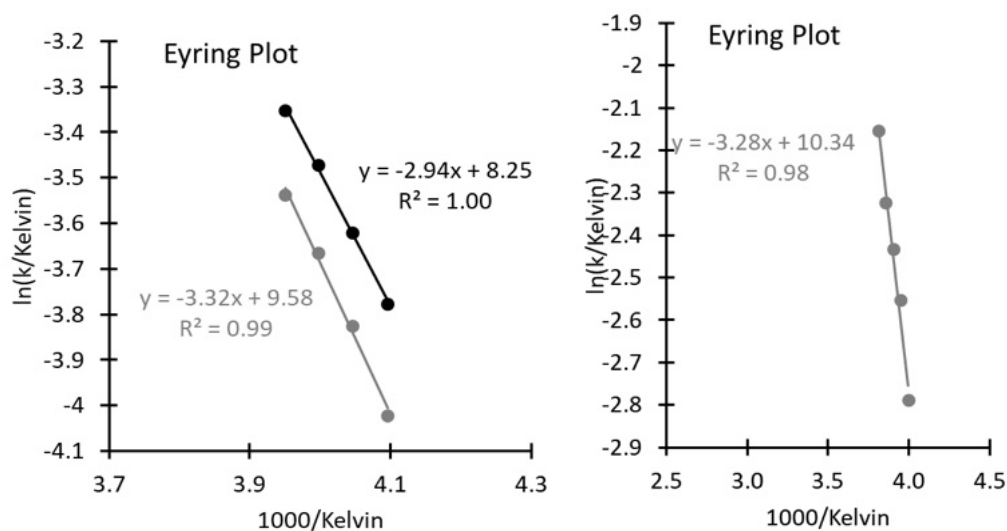


Figure 4.40 Eyring plots for rotor **2**(furan) by EXSY ($\Delta G^\ddagger_{\text{exp}} = 15.0$ kcal/mol, left) and lineshape analysis ($\Delta G^\ddagger_{\text{exp}} = 14.5$ kcal/mol, right).

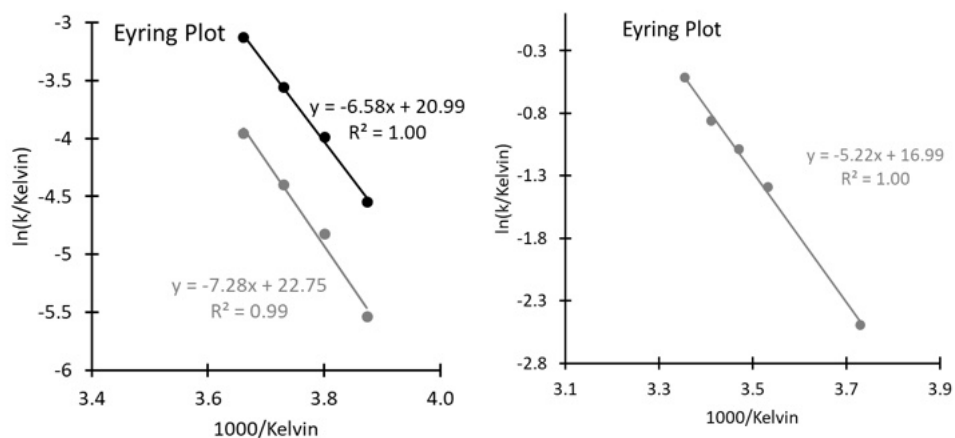


Figure 4.41 Eyring plots for rotor **1**(benzothiofuran) by EXSY ($\Delta G^\ddagger_{\text{exp}} = 14.9$ kcal/mol, left) and lineshape analysis ($\Delta G^\ddagger_{\text{exp}} = 14.4$ kcal/mol, right).

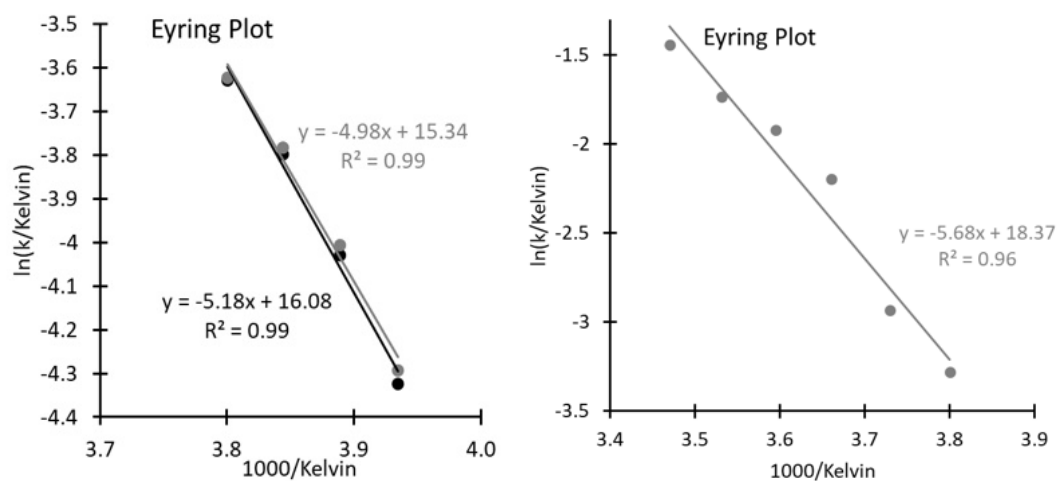


Figure 4.42 Eyring plots for rotor 2(benzofuran) by EXSY ($\Delta G^\ddagger_{\text{exp}} = 14.9$ kcal/mol, left) and lineshape analysis ($\Delta G^\ddagger_{\text{exp}} = 14.5$ kcal/mol, right).

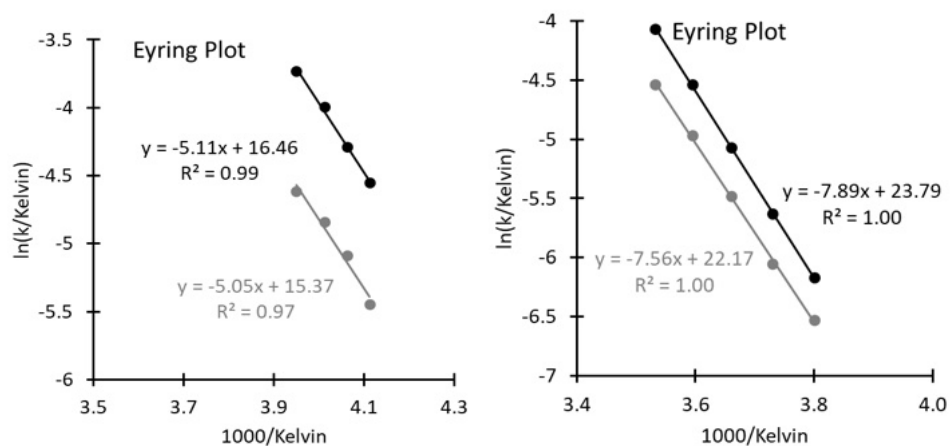


Figure 4.43 Eyring plots for rotor 1(benzothiofuran) (left) and rotor 2(2H-furan) (right) by EXSY.

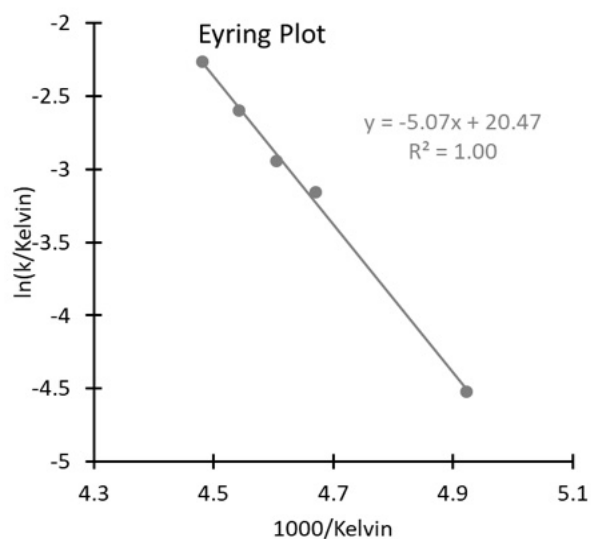


Figure 4.44 Eyring plots for rotor 1(thiazole) by lineshape analysis.

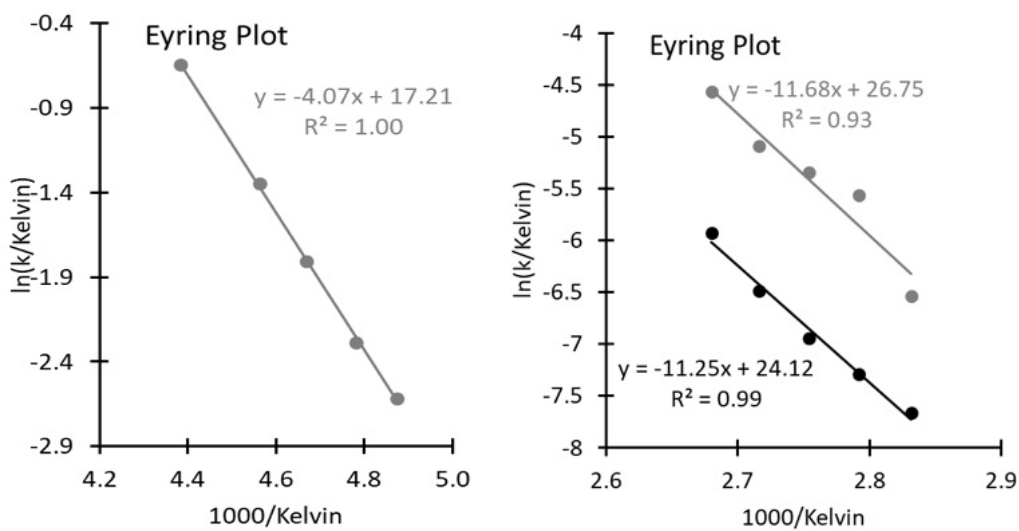


Figure 4.45 Eyring plots for rotor 2(oxazole) by lineshape analysis (left) and Eyring plots for rotor 1(SCF₃) by EXSY (right).

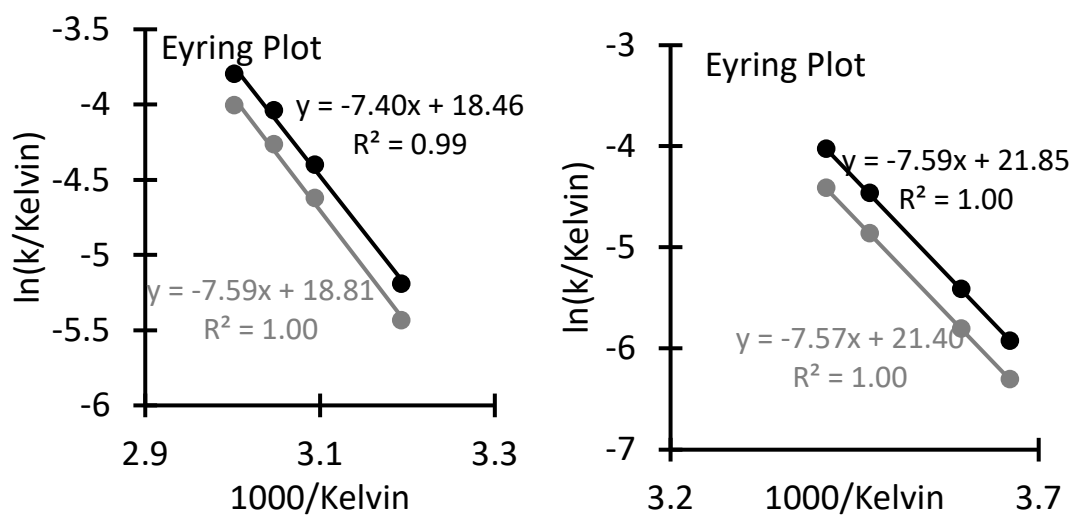


Figure 4.46 Eyring plots for rotor 2(OCF₃) by ESXY (left) and Eyring plots for rotor 2(OCOCH₃) by ESXY (right).

4.5.7 Modeling molecular studies

The optimized the ground state (GS) and transition state (TS) for the rotors were calculated (B3LYP-D3(0)/6-311G*) in Spartan18. Convergence criteria were 10^{-4} Hartree and 10^{-4} atomic units as the maximum norm of the cartesian gradient. Vibrational analyses were also carried out at the B3LYP-D3(0)/6-311G* level of theory. The free energies were calculated at 298.15 K using the calculated thermodynamic terms. To reduce error, the calculated GS energies for the *syn*- and *anti*- conformers were averaged. The XYZ coordinates for the GS and TS structures are in **Tables 4.9 – 4.22**. Transition state structures all had a single imaginary frequency. Ground state structures had zero imaginary frequencies. (Note: all the barrier calculations were not performed in constrained structures.) All the calculated energies of ground states and transition states were listed in **Table 4.8**. All the TS of acyclic Ch rotors that were provided in this section were in perpendicular geometries, details would be discussed in section 4.5.9.

With thermodynamic corrections, the calculated barriers ($\Delta G^\ddagger_{\text{cal}}$) of all the rotors **1** to **5** reproduced the experimental barriers ($\Delta G^\ddagger_{\text{exp}}$) of all the rotors **1** to **5** with an accuracy of ± 1.13 kcal/mol (**Figure 4.47**), suggesting that the calculated TS and GS geometries (**Tables 4.9 – 4.22**) were also accurate. Standard deviation of the error between $\Delta G^\ddagger_{\text{exp}}$ and $\Delta G^\ddagger_{\text{cal}}$ was ± 1.12 kcal/mol, mean absolute error between $\Delta G^\ddagger_{\text{exp}}$ and $\Delta G^\ddagger_{\text{cal}}$ was ± 0.92 kcal/mol, root mean square deviation between $\Delta G^\ddagger_{\text{exp}}$ and $\Delta G^\ddagger_{\text{cal}}$ was ± 1.13 kcal/mol.

Table 4.8 The calculated energies of ground states and transition states and the corresponding calculated barriers.

Rotor R=	energies of folded GS (au)	energies of unfolded GS (au)	energies of GS avg. (au)	energies of TS (au)	$\Delta G^\ddagger_{\text{cal}}$ (kcal/mol)
2(oxazole)	-952.13	-952.13	-952.13	-952.11	11.14
2(furan)	-936.07	-936.06	-936.07	-936.04	13.02
2(benzofuran)	-1089.71	-1089.71	-1089.71	-1089.69	13.51
2(OCOCH ₃)	-1012.53	-1012.53	-1012.53	-1012.50	14.45
2(OCF ₃)	-1197.00	-1197.00	-1197.00	-1196.97	16.91
2(OPh)	-1090.89	-1090.89	-1090.89	-1090.86	19.60
2(2H-furan)	-937.26	-937.26	-937.26	-937.23	15.47
1(thiofuran)	-1259.06	-1259.06	-1259.06	-1259.03	14.18
1(benzothiofuran)	-1412.70	-1412.70	-1412.70	-1412.68	14.76
1(SCF ₃)	-1519.97	-1519.97	-1519.97	-1519.93	22.61
1(SPh)	-1413.87	-1413.87	-1413.87	-1413.83	24.74
1(thiazole)	-1275.12	-1275.12	-1275.12	-1275.10	12.38

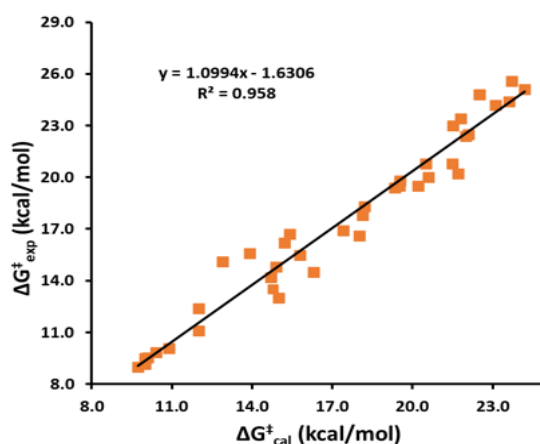
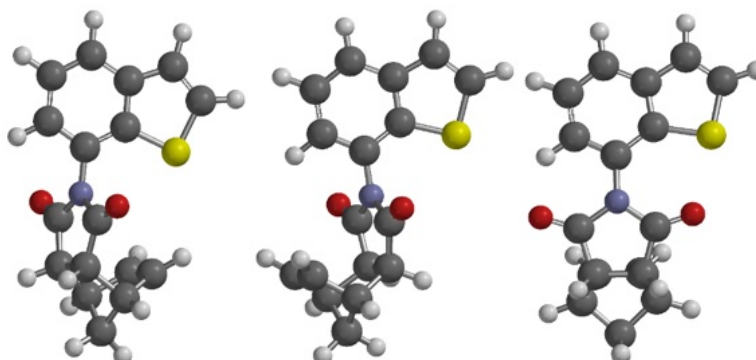


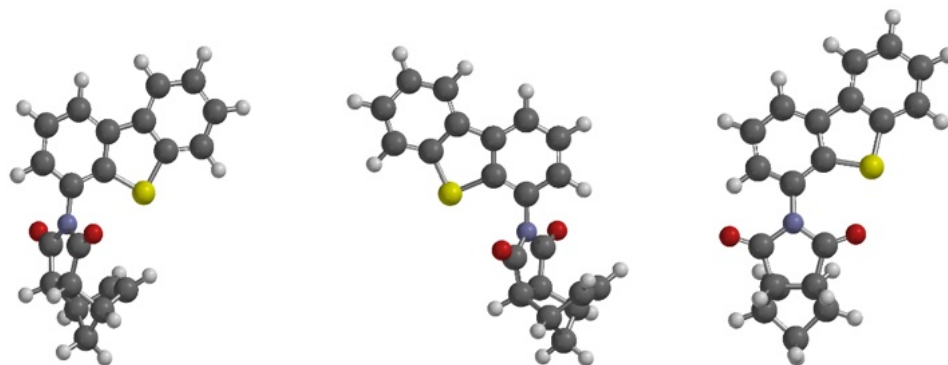
Figure 4.47 Correlation of the calculated ($\Delta G^\ddagger_{\text{cal}}$) and experimental ($\Delta G^\ddagger_{\text{exp}}$) rotational barriers of all the rotors **1** to **5**. Structures were calculated at the B3LYP-D3/6-311G* level of theory with thermodynamic corrections.

Table 4.9 The folded GS structure (left) and XYZ coordinates of rotor 1(thiofuran) the unfolded GS structure (middle) and the lower TS structure (right).



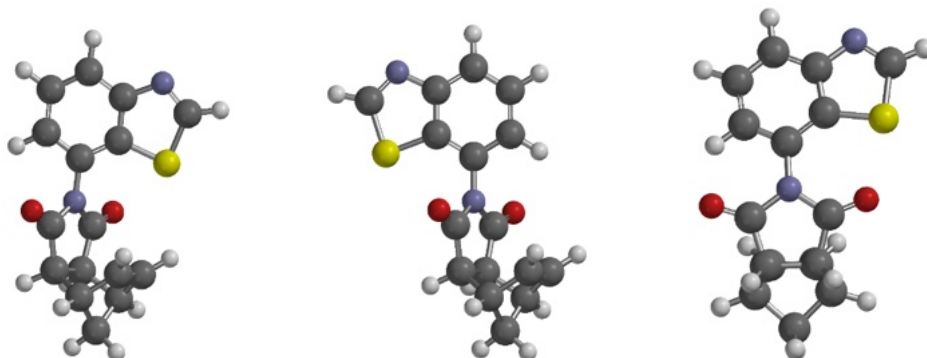
N1	7	-0.596940595	-0.543773887	-0.202518427	N1	7	-0.090614994	-0.264501388	-0.094635773	N1	7	0.686183533	0.280080460	-0.138836714
C2	6	-0.116119174	-1.635936971	0.547114849	C2	6	1.145883101	-0.448320502	0.554839820	C2	6	0.880838187	1.525142766	0.549897234
C3	6	-0.628813553	-1.481613776	1.964006227	C3	6	0.854816253	-0.958113091	1.952656175	C3	6	1.204800278	1.248379042	1.999264360
C4	6	-1.465888406	-0.185180004	1.963322215	C4	6	-0.682853602	-1.043969225	2.053579097	C4	6	1.277482455	-0.269700323	2.116150289
C5	6	-1.400982305	0.341218064	0.543940419	C5	6	-1.203148742	-0.549332412	0.720287873	C5	6	1.008541444	-0.785791231	0.730420853
O1	8	-1.925340186	1.331221485	0.103638374	O1	8	-2.352706246	-0.393662644	0.397816190	O1	8	1.057371993	-1.953099951	0.436530168
O2	8	0.576373768	-2.519360242	0.111974008	O2	8	2.221394399	-0.217969475	0.065249733	O2	8	0.798314488	2.637654536	0.093913039
C1	6	-0.762104089	-1.352933276	-2.491360482	C1	6	-0.862704566	1.473796310	-1.619976080	C1	6	-0.168952918	1.338101186	-2.152457185
C6	6	0.648414960	0.851576864	-3.464809722	C6	6	0.069195080	0.044020942	-3.834164893	C6	6	-0.555236133	-0.998486083	-3.552130998
C7	6	-0.329256489	-0.386205317	-1.594433454	C7	6	-0.222926723	0.261350999	-1.413985851	C7	6	0.182563169	0.149865158	-1.502127923
C16	6	-0.501657043	-1.227866491	-3.862229503	C16	6	-1.033617050	1.978720579	-2.916076064	C16	6	-0.690708908	1.379488239	-3.447789998
C9	6	0.193748350	-0.135772541	-4.352283024	C9	6	-0.571287338	1.278047678	-4.018023118	C9	6	-0.888881427	0.219147622	-4.155663824
C10	6	0.384033197	0.715022226	-2.080584529	C10	6	0.236798221	-0.459080361	-2.522100701	C10	6	-0.017146216	-1.069486798	-2.228486227
C11	6	-0.365598041	-0.394848182	4.059456193	C11	6	0.196833107	-0.404057846	4.168629734	C11	6	0.313130900	0.589181082	4.105918611
C12	6	-0.742896877	0.709795488	3.040787134	C12	6	-1.022202769	-0.096819549	3.264781561	C12	6	0.135730426	-0.617938980	3.153933878
C13	6	0.632156926	1.046634689	2.483952475	C13	6	-0.679702767	1.318955531	2.824066788	C13	6	-1.188042870	-0.257398460	2.500434722
C14	6	1.356572367	-0.077556471	2.480855672	C14	6	0.651503500	1.402210235	2.725733772	C14	6	-1.246825937	1.075410275	2.410638930
C15	6	0.483975636	-1.192156003	3.038416798	C15	6	1.229896969	0.047347735	3.106076739	C15	6	0.039054522	1.634668187	2.999092949
H2	1	-1.195967861	-2.375189523	2.233038043	H2	1	1.365837581	-1.911642441	2.099709675	H2	1	2.124210303	1.772770152	2.262113174
H1	1	-2.512522172	-0.335143015	2.235142390	H1	1	-1.061932295	-2.051605590	2.234456090	H1	1	2.235581269	-0.660182553	2.461579518
H30	1	-1.348522608	1.544661570	3.387645727	H30	1	-2.018304290	-0.253917936	3.673784346	H30	1	0.219665531	-1.620979310	3.567250127
H33	1	0.997395034	-2.087193638	3.384187773	H33	1	2.284317489	0.026882737	3.373850124	H33	1	0.034399887	2.687661944	3.272613632
S1	16	1.072352981	2.040444130	-1.170723690	S1	16	1.002021687	-2.033304959	-2.535813872	S1	16	0.271232721	-2.781570838	-1.838909891
C17	6	1.700910549	2.753386946	-2.639524959	C17	6	1.082848271	-2.003105946	-4.282664450	C17	6	-0.315147472	-3.296784107	-3.392246703
C8	6	1.405324698	2.039559401	-3.750730364	C8	6	0.576070970	-0.869773006	-4.822740414	C8	6	-0.712414163	-2.278115625	-4.181544319
H27	1	-1.300984558	-2.214485985	-2.115433028	H27	1	-1.247402183	2.016020396	-0.765564467	H27	1	-0.025078667	2.272073852	-1.642851516
H28	1	-0.850259028	-1.999332061	-4.540802968	H28	1	-1.543047885	2.926464546	-3.052795397	H28	1	-0.934071755	2.343738204	-3.880691545
H29	1	0.395936966	-0.041849959	-5.414761764	H29	1	-0.715072278	1.665730600	-5.021673019	H29	1	-1.293003339	0.224236491	-5.163254501
H3	1	0.223820259	-0.016687692	4.896576027	H3	1	0.219124921	0.209046370	5.071374582	H3	1	-0.434330130	0.611596068	4.901539083
H31	1	-1.228027358	-0.952273873	4.438754594	H31	1	0.283050276	-1.461030461	4.439865863	H31	1	1.315194028	0.659813971	4.540707472
H32	1	0.902456074	2.000258002	2.049546296	H32	1	-1.409513429	2.063757447	2.531809331	H32	1	-1.880577513	-0.974667612	2.077417361
H4	1	2.336625605	-0.225672564	2.045099246	H4	1	1.229658426	2.228565403	2.331850517	H4	1	-1.997819591	1.664472570	1.899159063
H15	1	1.706915138	2.328009638	-4.750434082	H15	1	0.548244146	-0.675804510	-5.888175417	H15	1	-1.109275015	-2.393694481	-5.182494631
H16	1	2.254867832	3.679242966	-2.576824462	H16	1	1.519542761	-2.844906167	-4.802028497	H16	1	-0.326783082	-4.355585450	-3.619088332

Table 4.10 The folded GS structure (left) and XYZ coordinates of rotor **1**(benzothiofuran) the unfolded GS structure (middle) and the TS (right).



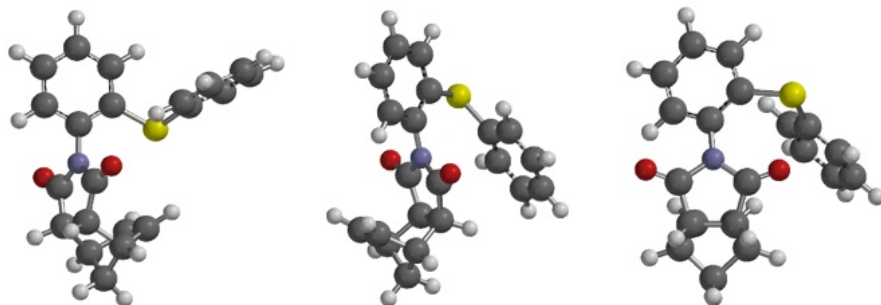
N1	7	1.349453509	-0.814035826	0.517810231	N1	7	0.302289070	0.319606248	0.888090170	N1	7	0.927836887	0.913505501	0.658584864
C2	6	2.262737010	-0.098617056	1.318139589	C2	6	1.375996159	0.712405616	1.713786468	C2	6	1.203710585	2.157977635	1.321699752
C3	6	2.118641572	-0.608872490	2.739289888	C3	6	1.097318812	0.184562848	3.107940323	C3	6	1.505213169	1.890683179	2.776860734
C4	6	1.053601537	-1.725661887	2.674269501	C4	6	-0.273196455	-0.520107965	3.019064703	C4	6	1.523125993	0.372916809	2.915131008
C5	6	0.618125458	-1.787648181	1.225112029	C5	6	-0.720042381	-0.358586142	1.581810307	C5	6	1.218773380	-0.151669525	1.540110714
O1	8	-0.208575790	-2.512775130	0.735726235	O1	8	-1.762889179	-0.710538523	1.094740275	O1	8	1.219831375	-1.323504986	1.263569961
O2	8	3.003825080	0.759936118	0.915479160	O2	8	2.316936813	1.370658604	1.353198478	O2	8	1.199268091	3.262797463	0.840354047
C1	6	2.196185187	-0.973914254	-1.761955541	C1	6	0.140047760	2.044249167	-0.832035058	C1	6	0.051741206	1.992038370	-1.332660380
C6	6	-0.127403938	0.185185371	-2.781345695	C6	6	0.010281074	0.110758435	-2.842696624	C6	6	-0.456799205	-0.334409937	-2.708608049
C7	6	1.190603395	-0.592311048	-0.882292256	C7	6	0.186084053	0.700239554	-0.481085574	C7	6	0.382331450	0.790728560	-0.690142142
C16	6	2.049806100	-0.784005214	-3.139092395	C16	6	0.029789183	2.425411554	-2.172365189	C16	6	-0.504760201	2.048291817	-2.607858830
C9	6	0.894451011	-0.211907864	-3.649605279	C9	6	-0.037967084	1.468267082	-3.174097446	C9	6	-0.762159305	0.889457307	-3.303626347
C10	6	0.029403428	-0.005948134	-1.392370763	C10	6	0.126035575	-0.266868125	-1.487986629	C10	6	0.116372406	-0.420651004	-1.404578579
C11	6	0.841701385	-0.571611182	4.744204877	C11	6	-0.084914556	0.523000338	5.145623064	C11	6	0.589203903	1.297510202	4.891946927
C12	6	-0.062235871	-1.220304680	3.667503700	C12	6	-1.154869974	0.269807100	4.057119609	C12	6	0.376067918	0.078346342	3.962522969
C13	6	-0.672830146	0.023399279	3.041860629	C13	6	-1.323743804	1.679951467	3.509880403	C13	6	-0.936919319	0.465734363	3.303077203
C14	6	0.244306393	0.994948484	3.087435879	C14	6	-0.136697006	2.290831040	3.589353991	C14	6	-0.954521032	1.797627423	3.185978694
C15	6	1.488980644	0.423767217	3.750212336	C15	6	0.853357118	1.302604969	4.190821093	C15	6	0.347230975	2.329388917	3.764782780
H2	1	3.093432776	-0.945051185	3.097386253	H2	1	1.914906648	-0.472369859	3.410864557	H2	1	2.439257715	2.387307195	3.040932185
H1	1	1.418987969	-2.708318889	2.978668814	H1	1	-0.245600986	-1.582194712	3.270348177	H1	1	2.469435107	-0.048300239	3.256337383
H30	1	-0.754074416	-2.001566648	3.976350136	H30	1	-2.064930609	-0.254490597	4.341925419	H30	1	0.431018235	-0.918901830	4.394144833
H33	1	2.206947523	1.142795951	4.139721580	H33	1	1.770922228	1.720864410	4.599358612	H33	1	0.373742013	3.387061893	4.018216649
S1	16	-1.363400409	0.562231515	-0.475097402	S1	16	0.211348625	-2.013742048	-1.278003179	S1	16	0.362237899	-2.141450021	-0.977476954
C19	6	-2.176377234	1.057891073	-1.961801060	C19	6	0.093190064	-2.256004571	-3.021418708	C19	6	-0.292129411	-2.683269502	-2.511087343
C20	6	-1.403979573	0.794067842	-3.109615129	C20	6	-0.016219411	-1.041138293	-3.727451073	C20	6	-0.687471978	-1.622839560	-3.335654438
H27	1	3.094799512	-1.428400654	-1.361979771	H27	1	0.197111721	2.790514865	-0.049488373	H27	1	0.246856314	2.921069022	-0.831395350
H28	1	2.843180699	-1.094019564	-3.810160165	H28	1	-0.002265121	3.478599684	-2.427795304	H28	1	-0.728251492	3.017413132	-3.040052545
H29	1	0.778376674	-0.073509068	-4.719900733	H29	1	-0.120145684	1.767904410	-4.214014687	H29	1	-1.195620484	0.914510314	-4.297442887
H3	1	0.269367152	-0.074329050	5.529404628	H3	1	-0.455534790	1.137185227	5.968334514	H30	1	-0.158159006	1.356688764	5.685485840
H31	1	1.555774331	-1.268944932	5.194018949	H31	1	0.358264978	-0.395388473	5.544399433	H31	1	1.592465785	1.346838472	5.326685189
H32	1	-1.629262252	0.048424332	2.536982301	H32	1	-2.224488744	2.049149492	3.035685860	H32	1	-1.651021417	-0.238368428	2.894026551
H4	1	0.186179978	1.972082434	2.624921990	H4	1	0.128466015	3.264629647	3.197089370	H33	1	-1.686772032	2.398398753	2.661116276
C8	6	-3.440840286	1.640987387	-2.050959853	C8	6	0.091633344	-3.487505407	-3.677730301	C8	6	-0.431447367	-4.015848332	-2.911681966
H5	1	-4.026440722	1.839032197	-1.159511412	H5	1	0.175602554	-4.414653768	-3.120900864	H3	1	-0.122615763	-4.826703901	-2.259695315
C18	6	-3.938364304	1.959209914	-3.308669245	C18	6	-0.022608930	-3.501925372	-5.062106476	C18	6	-0.974462621	-4.279816948	-4.161071140
H6	1	-4.920405615	2.412595917	-3.395682966	H6	1	-0.026759991	-4.450697695	-5.588819038	H5	1	-1.092778289	-5.307590020	-4.489452943
C17	6	-1.928907906	1.120104055	-4.367655572	C17	6	-0.130682167	-1.082937627	-5.123826885	C17	6	-1.231699245	-1.910319996	-4.597649818
H7	1	-1.355960714	0.918166232	-5.267175710	H7	1	-0.218960360	-0.162759316	-5.692178550	H7	1	-1.544064745	-1.110736750	-5.261185202
C21	6	-3.186731408	1.698019607	-4.462655625	C21	6	-0.133430588	-2.304590460	-5.782244099	C21	6	-1.371760514	-3.229291222	-5.002534252
H8	1	-3.593077739	1.948908009	-5.436972136	H8	1	-0.223633973	-2.334702414	-6.863190771	H8	1	-1.792307083	-3.452619177	-5.977709923

Table 4.11 The folded GS structure (left) and XYZ coordinates of rotor **1**(thiazole) the unfolded GS structure (middle) and the TS (right).



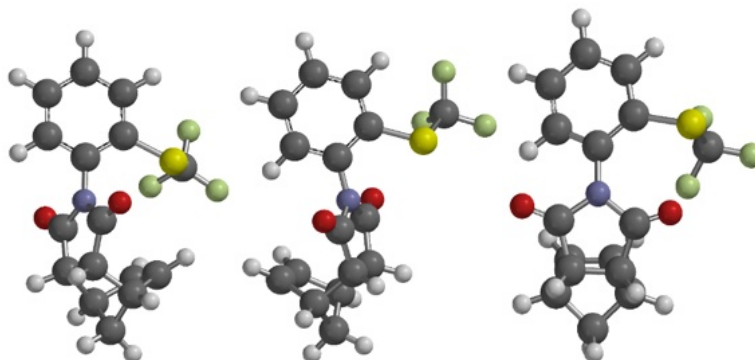
N1	7	0.650664323	0.496431401	-0.312191140	N1	7	-0.148404817	0.245874341	-0.212965363	N1	7	0.249212665	0.817682424	-0.116234207
C2	6	0.022897769	1.420847864	0.547310318	C2	6	0.324503514	-0.575282305	-1.256410669	C2	6	-0.632013146	1.500381166	0.782450407
C3	6	0.563305282	1.195140860	1.944695466	C3	6	-0.253700294	-1.960571069	-1.046012353	C3	6	-0.213531460	1.203631317	2.199680857
C4	6	1.606578733	0.066418541	1.803918439	C4	6	-1.051246816	-1.881535471	0.274504346	C4	6	1.103716794	0.440470241	2.083819541
C5	6	1.621865905	-0.297066146	0.335539083	C5	6	-0.906210392	-0.448820588	0.751737156	C5	6	1.375696058	0.353277562	0.604984297
O1	8	2.311854935	-1.121309145	-0.206254952	O1	8	-1.343492789	0.039248891	1.761349917	O1	8	2.403671051	-0.054361011	0.127211215
O2	8	-0.809769308	2.219960457	0.203112927	O2	8	1.062044641	-0.214294826	-2.136320312	O2	8	-1.574311957	2.193292126	0.492743155
C1	6	1.346671168	0.441092535	-2.644871196	C1	6	1.474673597	2.065113522	-0.033023991	C1	6	-1.268368314	1.021003798	-2.009583358
C6	6	-1.235631410	-0.109489906	-3.507565741	C6	6	-0.556982675	3.970199434	-0.121561410	C6	6	0.366825067	-0.293785266	-3.786005843
C7	6	0.336455409	0.351094087	-1.694405489	C7	6	0.159132553	1.633879952	-0.122205054	C7	6	-0.025802357	0.594036561	-1.524037025
C16	6	1.077969439	0.262555439	-4.007554220	C16	6	1.777254122	3.432189894	0.017698114	C16	6	-1.691886971	0.801944935	-3.322477645
C9	6	-0.206148464	-0.009265135	-4.447884850	C9	6	0.774132971	4.387823462	-0.022685272	C9	6	-0.884021296	0.146336568	-4.222640087
C10	6	-0.965266112	0.067810377	-2.129839222	C10	6	-0.858329298	2.590198856	-0.170415544	C10	6	0.820226295	-0.089375567	-2.447607398
C11	6	0.483484460	-0.183154511	3.884823852	C11	6	-0.067413791	-4.036883162	0.096493096	C11	6	-0.139230730	-0.459072532	3.899232331
C12	6	1.035759954	-1.068552029	2.740430183	C12	6	-0.356759371	-2.967118717	1.178750169	C12	6	0.778574627	-0.956826774	2.756136441
C13	6	-0.266080231	-1.549498362	2.118378673	C13	6	1.056608590	-2.474247458	1.457130175	C13	6	-0.243311683	-1.658528798	1.877131336
C14	6	-1.167364150	-0.571456481	2.254339571	C14	6	1.7444000340	-2.543775227	0.312046310	C14	6	-1.395149525	-0.987251279	1.979407955
C15	6	-0.486187818	0.590023451	2.958232708	C15	6	0.808001373	-3.086416535	-0.758186478	C15	6	-1.169290524	0.174817322	2.932603129
H2	1	0.967825201	2.132426568	2.329730589	H2	1	-0.863068253	2.221772758	-1.913905975	H2	1	-0.157568373	2.136224320	2.761511055
H1	1	2.614239214	0.345037796	2.116892500	H1	1	-2.113556586	-2.107534495	0.159709950	H1	1	1.953282587	0.912036869	2.578262150
H30	1	1.768266610	-1.834536683	2.986978484	H30	1	-0.950660175	-3.261072717	2.041945875	H30	1	1.668816929	-1.524211344	3.019580074
H33	1	-1.137071001	1.338321311	3.406019666	H33	1	1.274676275	-3.486049580	-1.656500149	H33	1	-2.058333813	0.639078362	3.354678948
S1	16	-2.445951778	-0.151972532	-1.225511758	S1	16	-2.583660864	2.370720177	-0.330755678	S1	16	2.422146559	-0.831750028	-2.332850840
C17	6	-3.269317101	-0.457853977	-2.754804061	C17	6	-2.740342931	4.130261644	-0.321710250	C17	6	2.298007345	-1.296562963	-4.011043354
N2	7	-2.553984341	-0.400127053	-3.822213945	N2	7	-1.655614999	4.812553233	-0.204985248	N2	7	1.221819357	-0.970571443	-4.637744917
H27	1	2.357777762	0.636826326	-2.312698960	H27	1	2.264284740	1.324346726	-0.015334941	H27	1	-1.933625424	1.550314806	-1.352313768
H28	1	1.889589054	0.336353406	-4.722627920	H28	1	2.814005775	3.740839293	0.085734930	H28	1	-2.673417055	1.157710205	-3.617753769
H29	1	-0.437896771	-0.153970865	-5.496863486	H29	1	0.991231328	5.448694811	0.010588575	H29	1	-1.178055339	-0.046173326	-5.247753046
H30	1	-0.037110040	-0.761476524	4.650422866	H30	1	0.490140269	-4.891925630	0.483161757	H30	1	-0.562065221	-1.276756374	4.485474041
H31	1	1.241997043	0.451408398	4.353927527	H31	1	-0.965052298	-4.388640543	-0.422209910	H31	1	0.341864925	0.263541658	4.565671923
H32	1	-0.380183186	-2.474159697	1.566374789	H32	1	1.379881512	-2.039274697	2.394410725	H32	1	-0.019477763	-2.476306816	1.203138955
H33	1	-2.166143789	-0.539872516	1.838993801	H33	1	2.746202606	-2.180517023	0.122090060	H33	1	-2.298502639	-1.146794910	1.403605308
H15	1	-4.333096761	-0.667987254	-2.754834502	H15	1	-3.726277858	4.573788563	-0.402162556	H15	1	3.114103438	-1.837451860	-4.479277860

Table 4.12 The folded GS structure (left) and XYZ coordinates of rotor 1(SPh) the unfolded GS structure (middle) and the TS (right).



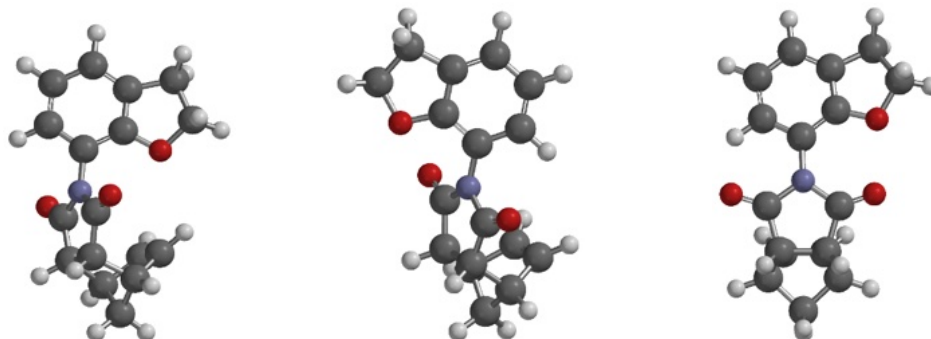
H1	1	-3.711757275	0.181152422	-3.628542615	H1	1	0.658725704	-0.102720360	-5.857001883	H1	1	2.086426566	-1.519411058	-4.912784751
C1	6	-2.736327158	0.160965208	-3.153628424	C1	6	0.505170337	-0.019681812	-4.786102211	C1	6	1.904295439	-1.374129427	-3.853509324
C4	6	-0.244228268	0.105037052	-1.913816645	C4	6	0.090965153	0.171300033	-2.036049903	C4	6	1.431392626	-1.079375712	-1.055193170
C2	6	-2.609490443	0.556155997	-1.829294536	C2	6	-0.093874674	-1.066986470	-4.096302945	C2	6	0.879359643	-2.052974473	-3.217452764
C6	6	-1.612783741	-0.243387693	-3.874247882	C6	6	0.926195387	1.116579826	-4.100531209	C6	6	2.641031983	-0.466414087	-3.107194249
C5	6	-0.372511641	-0.269237022	-3.251728109	C5	6	0.720383003	1.203637896	-2.729087973	C5	6	2.400174253	-0.325504551	-1.750001187
C3	6	-1.363937959	0.535077329	-1.192390586	C3	6	-0.309214222	-0.993167773	-2.715378825	C3	6	0.589516007	-1.910760032	-1.849299372
H2	1	-3.479422049	0.882747613	-1.271220122	H2	1	-0.390926319	-1.965139170	-4.626917057	H2	1	0.229992804	-2.700131303	-3.794637703
H6	1	-1.705012056	-0.540788981	-4.913295396	H6	1	1.408488053	1.930824983	-4.630149284	H6	1	3.413011624	0.139453291	-3.569721714
H5	1	0.511259021	-0.591492140	-3.790450970	H5	1	1.036031004	2.079319374	-2.175189524	H5	1	3.016358698	0.372449808	-1.212514414
N1	7	1.046745831	0.007530702	-1.313056582	N1	7	-0.117487670	0.332198692	-0.637760653	N1	7	1.375730944	-0.849605637	0.370623547
C12	6	2.107223291	0.879242188	-1.623909747	C12	6	0.939792441	0.490661206	0.276024112	C12	6	2.452611923	-0.212781714	1.075798143
C9	6	3.325530586	0.405983818	-0.854878501	C9	6	0.332259143	0.687561152	1.648289708	C9	6	1.914081071	0.368874554	2.354877805
C10	6	2.858344585	-0.836641836	-0.065241523	C10	6	-1.195578510	0.655592782	1.433256702	C10	6	0.527327058	-0.249122125	2.522254285
C13	6	1.395086830	-1.014967293	-0.417879261	C13	6	-1.391214357	0.459002435	-0.055063614	C13	6	0.359908550	-1.166558913	1.336511058
H9	1	4.130446935	0.201697493	-1.564016238	H9	1	0.699568474	-0.098455630	2.309758525	H9	1	2.609190902	0.165084208	3.169426499
O1	8	2.024567689	1.816944592	-2.374568860	O1	8	2.108484027	0.483923857	-0.018202231	O1	8	3.601168705	-0.145025549	0.719281109
O2	8	0.645219726	-1.875497467	-0.027916079	O2	8	-2.430603554	0.438490089	-0.661599736	O2	8	-0.458542397	-2.038178584	1.271964075
C7	6	3.146648500	-0.438749767	1.432076594	C7	6	-1.669216011	2.059464306	1.964692841	C7	6	-0.439515905	1.006888905	2.525880719
H8	1	3.151901761	-1.287551845	2.113243452	H8	1	-2.738054006	2.114271646	2.162328135	H8	1	-1.428515830	0.784100290	2.921358131
H16	1	3.393836188	-1.752240689	-0.324605838	H16	1	-1.694630976	-0.153263482	1.968768608	H16	1	0.393480472	-0.828471333	3.435925650
C8	6	3.826373988	1.381962298	0.274518423	C8	6	0.571100815	2.114635838	2.272625063	C8	6	1.608921256	1.926447860	2.273834403
H10	1	4.451304610	2.191879452	-0.097063120	H10	1	1.541735484	2.224792686	2.752276166	H10	1	2.491119457	2.542077319	2.439308910
C14	6	4.467263965	0.344897695	1.228660695	C14	6	-0.695488985	2.212826699	3.157679270	C14	6	0.462202508	1.989423076	3.312436869
H11	1	5.262072259	-0.246841840	0.763364357	H11	1	-0.777636470	1.407910412	3.895158834	H11	1	0.748053259	1.627131527	4.305151170
H17	1	4.837532428	0.793381155	2.152345685	H17	1	-0.786737659	3.178763849	3.658748100	H17	1	0.026245506	2.986632235	3.396685775
C15	6	2.603284600	1.779808918	1.087291463	C15	6	0.224523518	3.137160009	1.197861539	C15	6	0.825516851	2.180677681	0.996744914
H18	1	2.086869219	2.727397927	0.999598947	H18	1	0.952466307	3.692079778	0.618812014	H18	1	1.241045322	2.610296274	0.093230014
C16	6	2.202177397	0.703217717	1.770570353	C16	6	-1.099668037	3.102110672	1.014241150	C16	6	-0.386001093	1.633523027	1.143871770
H21	1	1.290539203	0.594996138	2.341950090	H21	1	-1.672941133	3.614985850	0.252051524	H21	1	-1.155205810	1.520017440	0.389577814
S1	16	-1.216169921	1.104136402	0.500172406	S1	16	-1.164173238	-2.379775397	-1.972492249	S1	16	-0.928497363	-2.772385078	-1.403438719
C11	6	-2.490849659	0.118349392	1.296911467	C11	6	-0.266248461	-2.657416500	-0.445636832	C11	6	-2.052775506	-1.393493926	-1.163757418
C17	6	-4.423191079	-1.378981486	2.636989304	C17	6	1.055757049	-3.115968543	1.970108237	C17	6	-3.911980923	0.665207138	-0.779185774
C18	6	-3.449759260	0.761026800	2.082331689	C18	6	-0.999689441	-2.842177786	0.729451025	C18	6	-1.995267202	-0.236531935	-1.948206837
C19	6	-2.492711610	-1.276052954	1.181152393	C19	6	1.129520973	-2.713803341	-0.412255042	C19	6	-3.045957449	-1.514511391	-0.186599505
C20	6	-3.467672443	-2.015307895	1.842943537	C20	6	1.784633074	-2.927083500	0.795655337	C20	6	-3.975707478	-0.493082057	-0.006223414
C21	6	-4.408066689	0.007742129	2.760134201	C21	6	-0.336932528	-3.082026649	1.931640520	C21	6	-2.915468431	0.788947897	-1.746996635
H3	1	-3.450850166	1.843344507	2.154329427	H3	1	-2.082195425	-2.778276398	0.700826136	H3	1	-1.234669945	-0.137112877	-2.714043244
H4	1	-1.731593165	-1.766454827	0.585271429	H4	1	1.697514936	-2.557844437	-1.322025694	H4	1	-3.066848524	-2.391201213	0.449740177
H7	1	-3.471790659	-3.096697074	1.748944921	H7	1	2.869010508	-2.940263087	0.817682267	H7	1	-4.742450574	-0.597944059	0.755162645
H12	1	-5.150481425	0.509775345	3.372378578	H12	1	-0.911971537	-3.226452027	2.840966522	H12	1	-2.859375393	1.683800096	-2.359255518
H13	1	-5.175621946	-1.963559479	3.156571623	H13	1	1.572157826	-3.287591706	2.908844528	H13	1	-4.631383498	1.463674462	-0.629629927

Table 4.13 The folded GS structure (left) and XYZ coordinates of rotor **1**(SCF₃) the unfolded GS structure (middle) and the TS (right).



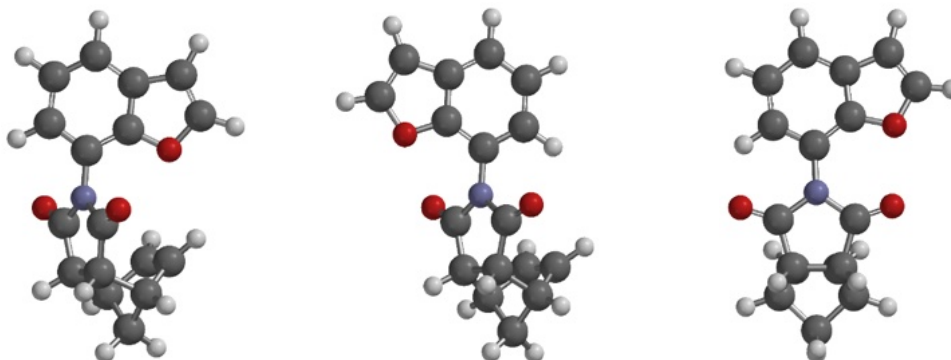
H1	1	0.717952981	-2.106426875	-5.139897270	H1	1	-0.134697642	-1.510964642	-5.183949475	C1	6	-0.536158061	2.619038243	-0.931579463
C1	6	0.730281906	-1.781552406	-4.105197263	C1	6	-0.024494594	-1.183414482	-4.155786757	C2	6	0.625976633	2.200805422	-0.044250382
C4	6	0.747316612	-0.945100195	-1.437756018	C4	6	0.267999003	-0.353515429	-1.512761695	C3	6	0.190823969	2.196568510	1.220299455
C2	6	-0.462733069	-1.678403508	-3.399527557	C2	6	0.893165622	-1.819775208	-3.327901557	C4	6	-1.274737522	2.598101048	1.203793254
C6	6	1.932813749	-1.466416159	-3.478501490	C6	6	-0.783522750	-0.119959607	-3.672576081	C5	6	-1.271172674	3.595493342	0.020383178
C5	6	1.940416713	-1.057605904	-2.149877048	C5	6	-0.632044856	0.295048862	-2.355272936	C16	6	-2.080533451	1.413489169	0.521163839
C3	6	-0.467460480	-1.246735140	-2.071540267	C3	6	1.037889882	-1.419391338	-1.996981940	C18	6	-1.617046646	1.459975863	-0.933967966
H2	1	-1.406039797	-1.917100666	-3.875656337	H2	1	1.497344999	-2.634039496	-3.706684736	C8	6	-1.682679052	0.047590839	1.021688109
H6	1	2.867813697	-1.543256756	-4.022606460	H6	1	-1.491236801	0.385007128	-4.321001869	N1	7	-0.869939177	-0.597291924	0.029141862
H5	1	2.870197060	-0.806698438	-1.655417303	H5	1	-1.212834580	1.119367247	-1.959051303	C10	6	-1.118630197	0.070007992	-1.224592057
N1	7	0.803055472	-0.508772498	-0.085897117	N1	7	0.387967887	0.097232012	-0.167972731	O1	8	-1.036920673	-0.408409719	-2.318337318
C12	6	1.384944118	0.720936364	0.291787715	C12	6	0.967252827	1.333068250	0.168817217	O2	8	-2.017951244	-0.402247251	2.088164861
C9	6	1.315427296	0.812515486	1.801869324	C9	6	0.818833475	1.510807619	1.665395093	C9	6	0.004280234	-1.710219829	0.325240282
C10	6	0.617758593	-0.484762645	2.264324343	C10	6	0.086478185	0.244782272	2.163711675	C11	6	1.702382623	-3.812360194	1.271976701
C13	6	0.360801668	-1.282788757	1.004547255	C13	6	-0.177519391	-0.586351110	0.925080338	C12	6	0.211811283	-1.974154388	1.695895623
H9	1	2.328720327	0.930919914	2.191566703	H9	1	1.805180327	1.658499824	2.108532568	C13	6	0.744289252	-2.523258849	-0.585634907
O1	8	1.851017325	1.521754393	-0.476009681	O1	8	1.460832993	2.096489424	-0.621270632	C14	6	1.558943398	-3.552672790	-0.078566633
O2	8	-0.127035500	-2.380405383	0.912290800	O2	8	-0.785691595	-1.620748283	0.847039629	C15	6	1.025999465	-2.993058874	2.162064767
C7	6	-0.668633362	0.048951574	3.006559505	C7	6	-1.216145464	0.822067784	2.834428895	H20	1	-0.284810363	2.965494550	-1.932317504
H8	1	-1.144987661	-0.700950206	3.635062024	H8	1	-1.714782519	0.116092090	3.495344765	H21	1	1.582215574	1.853095963	-0.410796906
H16	1	1.216193763	-1.091777745	2.946414600	H16	1	0.660248691	-0.347400909	2.878986418	H22	1	0.725059906	1.847287341	2.095080792
C8	6	0.374472547	1.947677854	2.355809480	C8	6	-0.153829178	2.675145290	2.089982567	H23	1	-1.707320059	2.920323575	2.148749476
H10	1	0.850198165	2.925789815	2.392127409	H10	1	0.3111703746	3.658629057	2.072886468	H24	1	-0.692060070	4.496172721	0.230871050
C14	6	-0.045325821	1.290158902	3.692469230	C14	6	-0.627758914	2.114322167	3.452979286	H25	1	-2.271910006	3.874806478	-0.324390614
H11	1	0.797483810	1.051552507	4.349777485	H11	1	0.189020956	1.927536319	4.157159430	H28	1	2.340458891	-4.620219883	1.612311555
H17	1	-0.779845675	1.882393155	4.241194666	H17	1	-1.385466813	2.740699203	3.927431805	H29	1	-0.306011605	-1.382287709	2.427124077
C15	6	-0.931207360	1.850798725	1.582590146	C15	6	-1.428704596	2.511937869	1.273921943	H30	1	2.106886495	-4.150257916	-0.795477083
H18	1	-1.218861635	2.505412718	0.770676798	H18	1	-1.693765929	3.122804554	0.419721157	H31	1	1.121492201	-3.134899171	3.233389806
C16	6	-1.546421303	0.728053391	1.967629097	C16	6	-2.057998479	1.417233325	1.715322405	H1	1	-3.153585873	1.549377974	0.659648438
H21	1	-2.443018036	0.297947517	1.542389624	H21	1	-2.937429829	0.947109941	1.293070848	H3	1	-2.400247088	1.698581881	-1.653803007
S1	16	-2.042273821	-1.092662818	-1.224248004	S1	16	2.252473926	-2.205455829	-0.938127754	S1	16	0.840297754	-2.461398914	-2.386068321
C11	6	-2.499159328	0.560912617	-1.846464117	C11	6	1.567120248	-3.904110224	-0.905012147	C6	6	2.123084585	-1.182691041	-2.542158001
F1	9	-2.755700766	0.587898867	-3.166788966	F1	9	1.687372075	-4.532364676	-2.095898165	F1	9	2.371524733	-0.995709628	-3.847414351
F2	9	-3.617547206	0.941197108	-1.200262800	F2	9	2.285694511	-4.599529411	-0.007102827	F2	9	3.282091879	-1.518423389	-1.942483819
F3	9	-1.550614984	1.486545189	-1.613438508	F3	9	0.281344578	-3.956859595	-0.562459900	F3	9	1.764094833	0.013350346	-2.015148733

Table 4.14 The folded GS structure (left) and XYZ coordinates of rotor **2**(2H-furan) the unfolded GS structure (middle) and the TS (right).



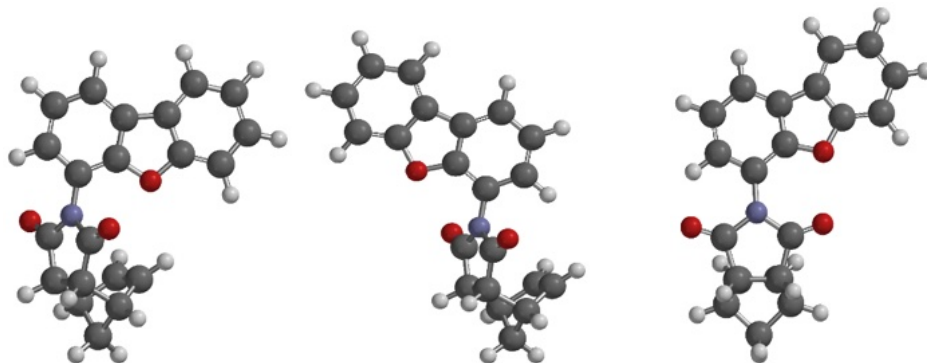
N1	7	-0.501146361	0.985324810	0.279119447	N1	7	0.443563425	0.199185989	0.127569876	N1	7	-0.112027211	0.770966341	0.284578238
C2	6	-1.569109868	0.599807987	1.108090392	C2	6	-0.652990202	0.308698705	1.004315729	C2	6	-1.102923378	1.153984145	1.232003513
C3	6	-1.037825703	0.487612720	2.522688071	C3	6	-0.137318896	0.115355361	2.414417647	C3	6	-0.606638746	0.871313413	2.626475745
C4	6	0.455099964	0.866898435	2.430511867	C4	6	1.373450587	-0.166807951	2.265563705	C4	6	0.837023528	0.410877248	2.457719666
C5	6	0.702894349	1.207099277	0.974775153	C5	6	1.653009755	-0.106279124	0.775967167	C5	6	1.117157041	0.479457125	0.974216637
O1	8	1.729704815	1.581918444	0.470764933	O1	8	2.702742864	-0.313380568	0.221200091	O1	8	2.202607607	0.332113125	0.491963502
O2	8	-2.692201386	0.381466285	0.729371388	O2	8	-1.794740068	0.477473556	0.661730051	O2	8	-2.194675264	1.621682169	1.007851057
C1	6	-1.524826640	1.857302049	-1.782361778	C1	6	0.663809267	-0.859976236	-2.078500651	C1	6	-1.683241212	0.901217378	-1.611312298
C6	6	0.114875988	0.228915221	-3.315029473	C6	6	-0.599266787	1.296201051	-3.277996409	C6	6	0.189422064	0.217915431	-3.485079164
C7	6	-0.599168108	1.032687270	-1.137644900	C7	6	0.280656743	0.226131716	-1.284656530	C7	6	-0.367711700	0.676947379	-1.142018651
C16	6	-1.627491643	1.869480697	-3.170424403	C16	6	0.424007814	-0.864732626	-3.448426730	C16	6	-2.044903495	0.792828288	-2.946827795
C9	6	-0.802544937	1.049927718	-3.948189504	C9	6	-0.220091687	0.218244784	-4.058154773	C9	6	-1.103108568	0.441535811	-3.909162834
C10	6	0.202303915	0.210460479	-1.924171136	C10	6	-0.326357211	1.310347087	-1.909377249	C10	6	0.572690175	0.324061852	-2.135874893
C11	6	0.204034027	-0.880014773	4.026757136	C11	6	0.512133422	-1.478555513	4.056668077	C11	6	-0.153615114	-0.816942764	4.235022471
C12	6	1.185755590	-0.445230443	2.910340409	C12	6	1.530947284	-1.603442248	2.896987152	C12	6	0.824735308	-1.052491769	3.058659413
C13	6	0.903042350	-1.513948471	1.866052832	C13	6	0.786316670	-2.572113606	1.989746344	C13	6	-0.046098280	-1.907531997	2.152314786
C14	6	-0.389143282	-1.843081960	1.960996338	C14	6	-0.521447593	-2.325380051	2.117212371	C14	6	-1.311457516	-1.503197678	2.305125379
C15	6	-1.002251880	-0.995277132	3.064943692	C15	6	-0.681329123	-1.187681267	3.114100497	C15	6	-1.312879985	-0.366645580	3.314920526
H2	1	-1.623788952	1.126032714	3.186461835	H2	1	-0.369948300	0.998485484	3.012384046	H2	1	-0.733926789	1.765709857	3.237857264
H1	1	0.740648460	1.713630199	3.056651536	H1	1	2.015101328	0.548610681	2.782498258	H1	1	1.574157288	1.023200168	2.978305771
H30	1	2.229014505	-0.285820743	3.175855635	H30	1	2.559536341	-1.861093023	3.141539534	H30	1	1.818256738	-1.435497868	3.283312869
H33	1	-1.954357972	-1.332893082	3.470330412	H33	1	-1.668188631	-1.065422096	3.556314330	H33	1	-2.269861323	-0.120421993	3.770806845
O3	8	1.091299053	-0.700828943	-1.447025533	O3	8	-0.725258153	2.449295167	-1.287983414	O3	8	1.889713550	0.021515609	-1.974292737
H27	1	-2.173718260	2.481051826	-1.179718447	H27	1	1.142950066	-1.706961443	-1.603140275	H27	1	-2.442356292	1.190963795	-0.908265430
H28	1	-2.357303643	2.513747945	-3.648003962	H28	1	0.724325010	-1.721591991	-4.041636058	H28	1	-3.074713464	0.987848425	-3.227573322
H29	1	-0.889283544	1.050044942	-5.030477637	H29	1	-0.424916646	0.206133513	-5.124341287	H29	1	-1.372707855	0.343342918	-4.956421797
H3	1	0.475611593	-1.836478265	4.477485323	H3	1	0.392762292	-2.408575598	4.616225190	H3	1	-0.381909608	-1.732530666	4.784700514
H31	1	0.070697835	-0.126815042	4.809600174	H31	1	0.732366923	-0.658499299	4.747297964	H31	1	0.177368667	-0.041740231	4.933682028
H32	1	1.591729480	-1.809779845	1.086008994	H32	1	1.260696315	-3.248755589	1.289747149	H32	1	0.331383411	-2.620947052	1.430051189
H4	1	-0.953760628	-2.473732708	1.285561991	H4	1	-1.331485324	-2.753163698	1.539733621	H4	1	-2.175664525	-1.823497856	1.736038912
C8	6	1.876312977	-1.158736924	-2.582915703	C8	6	-1.623059187	3.125264598	-2.209308945	C8	6	2.509422015	0.036045809	-3.280100483
H6	1	2.823788474	-0.612933718	-2.567695678	H6	1	-2.644946265	2.848899710	-1.930661161	H6	1	2.938078798	1.032479855	-3.438387941
H8	1	2.067834521	-2.221357912	-2.437365653	H8	1	-1.484284692	4.196481968	-2.072056035	H8	1	3.309725588	-0.702439557	-3.264487544
C17	6	1.053645755	-0.828392556	-3.846898793	C17	6	-1.267260866	2.607191286	-3.618805963	C17	6	1.384036675	-0.246490700	-4.280624134
H9	1	1.685590755	-0.479151137	-4.666573829	H9	1	-2.152385024	2.492422993	-4.248751917	H9	1	1.513687991	0.289785285	-5.223734692
H10	1	0.494038401	-1.698935365	-4.207871128	H10	1	-0.573101453	3.277988275	-4.137421400	H10	1	1.300953827	-1.315415718	-4.511442662

Table 4.15 The folded GS structure (left) and XYZ coordinates of rotor **2**(furan) the unfolded GS structure (middle) and the TS (right).



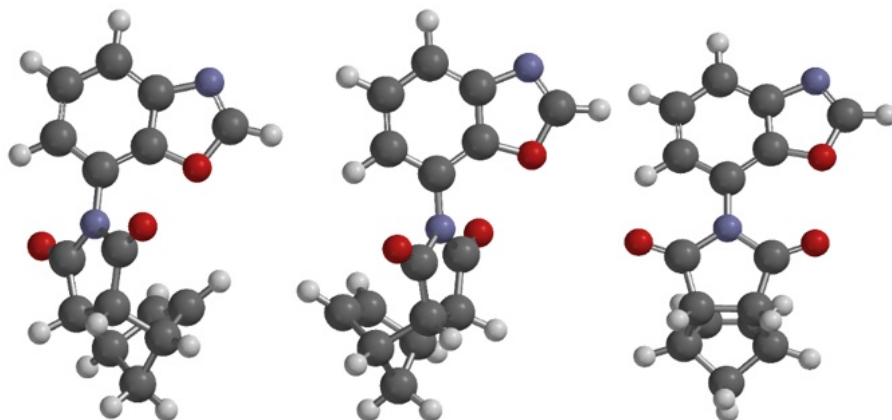
N1	7	0.091636502	1.021068827	-0.051147936	N1	7	0.421379515	0.186182396	-0.097372288	N1	7	-0.067717618	0.748232740	0.051910625
C2	6	-0.915626307	1.334139781	0.880786007	C2	6	-0.395856635	0.898471376	0.805054257	C2	6	-1.097427017	1.038539094	0.992260751
C3	6	-0.335462188	1.143612375	2.266140832	C3	6	0.148495026	0.664142715	2.199321309	C3	6	-0.584975976	0.803935346	2.388588719
C4	6	1.129929836	0.712185942	2.043122491	C4	6	1.343809169	-0.294379765	2.022115173	C4	6	0.893533266	0.465307828	2.230509563
C5	6	1.336729975	0.725120623	0.543634674	C5	6	1.447225398	-0.545993943	0.531365713	C5	6	1.167655930	0.516715747	0.744863324
O1	8	2.354270651	0.511638658	-0.061275519	O1	8	2.229911091	-1.265397253	-0.035299852	O1	8	2.253000264	0.384540699	0.255970057
O2	8	-2.039066123	1.666098769	0.599080760	O2	8	-1.370180698	1.532095655	0.495180226	O2	8	-2.225084299	1.402283810	0.758502182
C1	6	-0.759922630	1.928344261	-2.176551991	C1	6	-0.036711979	-1.145027402	-2.104659890	C1	6	-1.589552154	0.863811648	-1.878645342
C6	6	-0.083401017	-0.424285286	-3.505188000	C6	6	-0.352734076	1.154124210	-3.641589675	C6	6	0.353812839	0.306949067	-3.739911888
C7	6	-0.150809498	0.912674419	-1.445559920	C7	6	0.126170718	0.089847557	-1.483431742	C7	6	-0.289064481	0.679543158	-1.377252053
C16	6	-1.024918712	1.774648939	-3.545813263	C16	6	-0.347010521	-1.232950455	-3.468862709	C16	6	-1.912353526	0.772343565	-3.237263898
C9	6	-0.688634563	0.611129759	-4.225059400	C9	6	-0.514058914	-0.095982909	-4.248726081	C9	6	-0.953359484	0.493894760	-4.190402968
C10	6	0.162215471	-0.257050773	-2.133163944	C10	6	-0.025392034	1.223693269	-2.276563148	C10	6	0.684435170	0.396143999	-2.365075347
C11	6	0.257490055	-0.477009055	3.908587812	C11	6	0.205783752	-0.848556502	4.037994798	C11	6	-0.003077086	-0.815648115	4.022797318
C12	6	1.175016675	-0.730596805	2.688125233	C12	6	0.911657917	-1.562430010	2.859194706	C12	6	1.006112772	-0.980788344	2.860525616
C13	6	0.274937093	-1.626767639	1.851755512	C13	6	-0.290625801	-2.171030047	2.154059787	C13	6	0.225498353	-1.924166390	1.958694196
C14	6	-0.988902117	-1.247760982	2.066546373	C14	6	-1.322707272	-1.336705643	2.313688982	C14	6	-1.072076626	-1.629050112	2.089433050
C15	6	-0.960834132	-0.081922449	3.042676812	C15	6	-0.832919783	-0.147561455	3.127836637	C15	6	-1.186897466	-0.484374412	3.082277454
H2	1	-0.449103744	2.062865975	2.843383623	H2	1	0.406368655	1.621862926	2.654548756	H2	1	-0.790773476	1.687975729	2.993986975
H1	1	1.866541192	1.360403905	2.519656366	H1	1	2.293278835	0.098075802	2.389656416	H1	1	1.573918934	1.151935514	2.735657376
H30	1	2.186501861	-1.089090551	2.869203409	H30	1	1.736975092	-2.235574709	3.082648661	H30	1	2.027090859	-1.269996745	3.101233408
H33	1	-1.895573443	0.155312961	3.546993887	H33	1	-1.597356954	0.468391650	3.596779120	H33	1	-2.167623969	-0.318940581	3.524057860
O3	8	0.706939276	-1.390489951	-1.605501736	O3	8	0.121926713	2.517642421	-1.884414724	O3	8	2.019170717	0.155131446	-2.225016387
C17	6	0.817909456	-2.278274254	-2.647631450	C17	6	-0.123284131	3.279880048	-3.000402845	C17	6	2.526609752	-0.075201137	-3.470092676
C8	6	0.366498393	-1.760912314	-3.810988041	C8	6	-0.412241409	2.525114487	-4.083660036	C8	6	1.578055906	-0.000094490	-4.426883006
H27	1	-1.049705099	2.837061328	-1.666084036	H27	1	0.095833017	-2.044775367	-1.517599789	H27	1	-2.383321986	1.094730571	-1.192563547
H28	1	-1.508486805	2.585384300	-4.079834406	H28	1	-0.460839888	-2.214326351	-3.917905390	H28	1	-2.946370731	0.926700404	-3.529127554
H29	1	-0.902435045	0.499569110	-5.282930165	H29	1	-0.757685692	-0.178191823	-5.302802115	H29	1	-1.199581095	0.419569088	-5.244686018
H3	1	0.079709291	-1.378314652	4.498894246	H3	1	-0.253457195	-1.546764311	4.740552584	H3	1	-0.155129402	-1.739067031	4.585445014
H31	1	0.610361628	0.326766501	4.562485132	H31	1	0.854381860	-0.153264620	4.579659355	H31	1	0.247757392	-0.002300422	4.711179345
H32	1	0.626950886	-2.332597236	1.110867300	H32	1	-0.256917864	-3.063323142	1.541207331	H32	1	0.672354320	-2.616788299	1.255992985
H4	1	-1.874650819	-1.594580665	1.548921281	H4	1	-2.300977810	-1.405061898	1.854627339	H4	1	-1.898055884	-2.032980966	1.516573733
H15	1	0.343565423	-2.262418729	-4.767035878	H15	1	-0.641853331	2.883719708	-5.075635757	H15	1	1.707905737	-0.142397504	-5.489419349
H16	1	1.240328579	-3.235955093	-2.387096065	H16	1	-0.050384771	4.344053384	-2.846565109	H16	1	3.585530064	-0.276489666	-3.494119466

Table 4.16 The folded GS structure (left) and XYZ coordinates of rotor **2**(benzofuran) the unfolded GS structure (middle) and the TS (right).



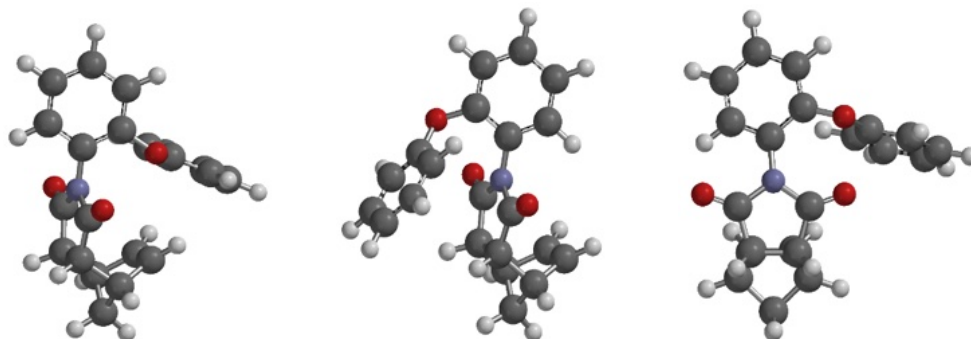
N1	7	-0.273436914	1.612246044	0.689764994	N1	7	0.451870334	-0.397110991	0.681993993	N1	7	-0.021671050	1.173839085	0.737394386
C2	6	-1.336640674	1.668997835	1.610513198	C2	6	-0.442510205	0.075065035	1.661626399	C2	6	-0.672783741	2.058159342	1.649698291
C3	6	-0.759706296	1.452410034	2.991863192	C3	6	0.163158624	-0.231024573	3.017537024	C3	6	-0.176832389	1.793376312	3.048197342
C4	6	0.764408540	1.307592927	2.787302666	C4	6	1.519201128	-0.907091512	2.722572515	C4	6	0.930739504	0.757041933	2.900224647
C5	6	0.991930859	1.466782804	1.297073402	C5	6	1.617219798	-0.980713309	1.212125692	C5	6	1.003302238	0.440045687	1.425219492
O1	8	2.038467191	1.457387164	0.704547713	O1	8	2.496059940	-1.482066799	0.558789941	O1	8	1.795646072	-0.316571518	0.941765781
O2	8	-2.493706597	1.834645721	1.318313819	O2	8	-1.508874330	0.581439554	1.428797084	O2	8	-1.507908538	2.891997890	1.393163297
C1	6	-1.203779724	2.554391716	-1.386253002	C1	6	-0.052796689	-1.729944213	-1.298037172	C1	6	-1.539470295	1.734060682	-1.116657777
C6	6	-0.262314647	0.379763255	-2.842389925	C6	6	-0.443239245	0.537051139	-2.843465006	C6	6	-0.325917029	0.074373420	-2.927776493
C7	6	-0.477181358	1.573212402	-0.713862718	C7	6	0.107215368	-0.482543202	-0.694356429	C7	6	-0.416157942	1.023665071	-0.648982189
C16	6	-1.452946168	2.454905539	-2.760429644	C16	6	-0.394934524	-1.848167216	-2.647804361	C16	6	-2.032939203	1.631224523	-2.418519782
C9	6	-0.987319165	1.373638317	-3.500719108	C9	6	-0.595423389	-0.718161152	-3.432310102	C9	6	-1.436373665	0.798317169	-3.346763806
C10	6	-0.022451114	0.495268503	-1.464020410	C10	6	-0.090251250	0.641289042	-1.486542273	C10	6	0.189089066	0.183844429	-1.612090693
C11	6	0.072266173	-0.167320157	4.522774212	C11	6	0.553292192	-1.912502587	4.655054535	C11	6	-0.244950674	0.343266856	4.926911265
C12	6	1.057761921	-0.146506258	3.327789915	C12	6	1.373259323	-2.322472133	3.407742782	C12	6	0.421905277	-0.455991776	3.779603110
C13	6	0.364386940	-1.120417565	2.387171421	C13	6	0.310292605	-3.081976840	2.627189127	C13	6	-0.811179990	-1.015105598	3.087824461
C14	6	-0.953456931	-0.993483415	2.570073962	C14	6	-0.867205286	-2.497351560	2.870845144	C14	6	-1.788729677	-0.111113190	3.208423788
C15	6	-1.172764382	0.070502841	3.633684152	C15	6	-0.619597191	-1.338395383	3.825374289	C15	6	-1.231266669	1.072704560	3.981732935
H2	1	-1.049461177	2.278130285	3.643883176	H2	1	0.234762214	0.687293824	3.602286277	H2	1	0.135643076	2.737850040	3.495516809
H1	1	1.361569667	2.02708686	3.328667568	H1	1	2.383849666	-0.375822054	3.122999832	H1	1	1.913585508	1.088889783	3.237969782
H30	1	2.112139144	-0.328018004	3.526688587	H30	1	2.322537519	-2.832465118	3.558505187	H30	1	1.206015323	-1.167761243	4.029450177
H33	1	-2.150699008	0.090214651	4.110845621	H33	1	-1.487491030	-0.954818064	4.358048012	H33	1	-1.957293755	1.754342718	4.420474285
O3	8	0.645083918	-0.594728953	-0.969964346	O3	8	0.037564075	1.944820766	-1.091173626	O3	8	1.266476383	-0.653368102	-1.467192895
C19	6	0.846710821	-1.433273870	-2.042789614	C19	6	-0.238197424	2.705307281	-2.208540443	C19	6	1.434446601	-1.314124372	-2.652689192
C18	6	0.311632246	-0.896257353	-3.224247916	C18	6	-0.540415493	1.898852384	-3.316718488	C18	6	0.488262921	-0.911552157	-3.599810345
H27	1	-1.599619825	3.386926751	-0.819648464	H27	1	0.102086366	-2.617156801	-0.695776050	H27	1	-2.046781191	2.397416458	-0.441456125
H28	1	-2.030966773	3.231481546	-3.248876918	H28	1	-0.505773839	-2.835842050	-3.082770042	H28	1	-2.906514509	2.216204956	-2.686345915
H29	1	-1.197814178	1.291979340	-4.562118337	H29	1	-0.859330762	-0.812664197	-4.480699298	H29	1	-1.818570397	0.697197333	-4.357412993
H3	1	0.048008077	-1.132058890	5.033021644	H3	1	0.259279447	-2.768969879	5.265184160	H3	1	-0.750900836	-0.299545112	5.650082983
H31	1	0.248961283	0.631770534	5.249261297	H31	1	1.052091538	-1.167395493	5.282354337	H31	1	0.441483326	1.017580155	5.448626235
H32	1	0.860878347	-1.687749455	1.611046854	H32	1	0.516406594	-3.872998633	1.916493362	H32	1	-0.829841389	-1.928369143	2.506085444
H4	1	-1.741574943	-1.447558241	1.982146202	H4	1	-1.817353126	-2.711269029	2.396948732	H33	1	-2.768447605	-0.139601198	2.747196381
C8	6	1.471209988	-2.668965408	-1.985679494	C8	6	-0.219936178	4.087618488	-2.266836178	C8	6	2.388807095	-2.289898059	-2.901554736
H5	1	1.874394036	-3.052921338	-1.056116142	H5	1	0.017147356	4.681593953	-1.392709541	H3	1	3.100152802	-2.582755823	-2.138736597
C17	6	0.400128537	-1.635915417	-4.407265671	C17	6	-0.839283715	2.493497607	-4.543279961	C17	6	0.482441359	-1.506833356	-4.865097525
H6	1	-0.012020582	-1.252877615	-5.335043232	H6	1	-1.072912636	1.885244882	-5.411462735	H6	1	-0.249509404	-1.220283369	-5.613996048
C20	6	1.552731575	-3.388122498	-3.177115476	C20	6	-0.521334998	4.665093830	-3.499931082	C20	6	2.369993119	-2.872465737	-4.167111458
H7	1	2.033966796	-4.360645651	-3.177386270	H7	1	-0.518747330	5.745756722	-3.591592916	H7	1	3.094036170	-3.644720793	-4.405756426
C21	6	1.022558072	-2.879855700	-4.372038292	C21	6	-0.826694212	3.881329396	-4.622997074	C21	6	1.429799867	-2.487405563	-5.137333793
H8	1	1.098666324	-3.468281105	-5.280468618	H8	1	-1.054991232	4.367668888	-5.565465651	H8	1	1.442213977	-2.967392290	-6.110276103

Table 4.17 The folded GS structure (left) and XYZ coordinates of rotor **2(oxazole)** the unfolded GS structure (middle) and the TS (right).



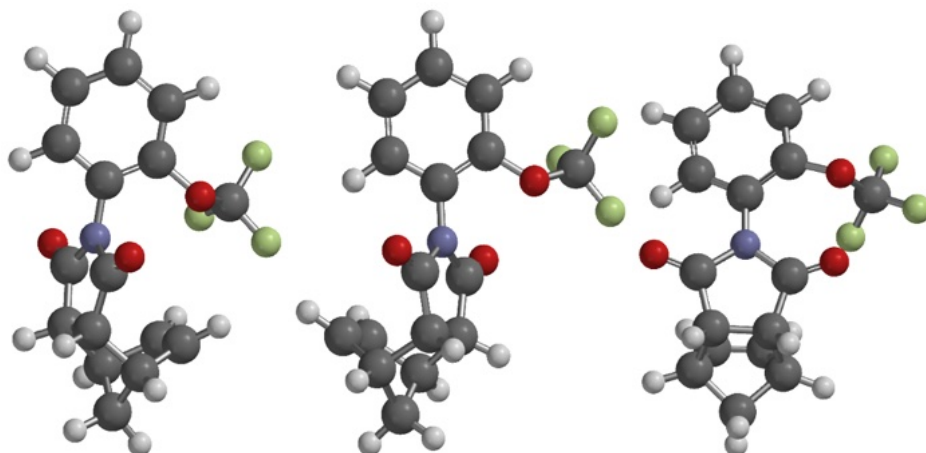
N1	7	-0.294514934	0.910479968	-0.06965590	N1	7	-0.246716944	0.405061033	-0.136899428	N1	7	-0.021600089	0.739857031	-0.102143007
C2	6	-1.383366729	0.658022931	0.78801302	C2	6	-1.316037459	0.136608298	0.738549967	C2	6	-1.055082582	1.024271192	0.835843644
C3	6	-0.844623358	0.553406197	2.19918272	C3	6	-0.764343609	0.127179204	2.147342945	C3	6	-0.537290276	0.798215630	2.232079177
C4	6	0.675670363	0.788313586	2.076638986	C4	6	0.747176080	0.410759630	2.006187797	C4	6	0.942487269	0.458085213	2.072308608
C5	6	0.929825485	1.079415121	0.613751967	C5	6	0.998536091	0.537286623	0.515712077	C5	6	1.211902090	0.500067205	0.586347702
O1	8	1.970202694	1.380481802	0.090489558	O1	8	2.050285697	0.694447847	-0.045925741	O1	8	2.289688986	0.352949790	0.084602490
O2	8	-2.526510967	0.525636549	0.43177480	O2	8	-2.452113782	-0.071314271	0.396178858	O2	8	-2.184762869	1.375020519	0.594925408
C1	6	-1.395929472	1.596571196	-2.16502995	C1	6	-1.016434195	-0.613781589	-2.237507692	C1	6	-1.523536148	0.856921796	-2.051417848
C6	6	0.352670299	0.061480102	-3.660592067	C6	6	-0.024815346	1.506661830	-3.713628515	C6	6	0.436601821	0.314410470	-3.880716298
C7	6	-0.400477655	0.896108195	-1.48339737	C7	6	-0.385549348	0.421159433	-1.548329532	C7	6	-0.229765211	0.673271857	-1.528423759
C16	6	-1.515400706	1.526107626	-3.56097943	C16	6	-1.150077475	-0.586020714	-3.632993244	C16	6	-1.825895225	0.769237241	-3.414883602
C9	6	-0.645529150	0.764876762	-4.33292703	C9	6	-0.654971742	0.467028052	-4.395488960	C9	6	-0.855283323	0.496659836	-4.361509210
C10	6	0.452105782	0.126296259	-2.26783851	C10	6	0.090674715	1.473252155	-2.320222694	C10	6	0.749041648	0.396453102	-2.507431250
C11	6	0.293680249	-0.888168660	3.71947272	C11	6	0.396824162	-1.099601296	3.814149408	C11	6	0.048587766	-0.815482091	3.871923624
C12	6	1.283705254	-0.584695178	2.56971577	C12	6	1.412471135	-0.854538281	2.672904333	C12	6	1.055239800	-0.985643192	2.708198306
C13	6	0.868102153	-1.650033169	1.56578720	C13	6	1.095181575	-2.037547102	1.769400075	C13	6	0.271948767	-1.931385420	1.810665852
C14	6	-0.447085246	-1.847486098	1.70263180	C14	6	-0.214105298	-2.287933565	1.874699815	C14	6	-1.025208352	-1.635156692	1.943271380
C15	6	-0.942584577	-0.908906339	2.79146701	C15	6	-0.802310646	-1.283090427	2.852176276	C15	6	-1.137356742	-0.487153160	2.932921275
H2	1	-1.360003643	1.267736853	2.84335221	H2	1	-1.303653679	0.862460002	2.746961812	H2	1	-0.740875791	1.685343771	2.833657457
H1	1	1.055348165	1.609078388	2.68626545	H1	1	1.073973111	1.326034043	2.503000350	H1	1	1.623991927	1.146956186	2.572783078
H30	1	2.344293410	-0.524295940	2.80535386	H30	1	2.457939313	-0.709659086	2.936837312	H30	1	2.076525702	-1.274618907	2.947594704
H33	1	-1.912676097	-1.136543018	3.22870565	H33	1	-1.773355056	-1.527609529	3.278346984	H33	1	-2.116935088	-0.319680253	3.376269764
O3	8	1.460701432	-0.713565332	-1.88249586	O3	8	0.720275474	2.618025205	-1.922784450	O3	8	2.093947243	0.147489465	-2.411508699
C17	6	1.921373065	-1.225441502	-3.06787185	C17	6	0.959419114	3.274584560	-3.102275386	C17	6	2.500024820	-0.058179378	-3.691835811
N2	7	1.329216792	-0.821089489	-4.13281624	N2	7	0.557181845	2.692379232	-4.173610759	N2	7	1.594558464	0.022303299	-4.598766876
H27	1	-2.106123382	2.178688098	-1.59318126	H27	1	-1.423166796	-1.442013254	-1.671645721	H27	1	-2.327616331	1.082329678	-1.374657678
H28	1	-2.316862417	2.075427328	-4.04289000	H28	1	-1.650869706	-1.413627108	-4.124534050	H28	1	-2.856480101	0.921541725	-3.719159287
H29	1	-0.741523476	0.695673551	-5.41017581	H29	1	-0.752719017	0.487696808	-5.474501596	H29	1	-1.069959855	0.421988762	-5.420980385
H3	1	0.480107277	-1.854484782	4.19183061	H3	1	0.617052658	-2.000424312	4.390719348	H3	1	-0.102759640	-1.736953075	4.437765669
H31	1	0.256610563	-0.106601152	4.48540051	H31	1	0.282989760	-0.248176052	4.492115355	H31	1	0.301254862	-0.000241292	4.557263168
H32	1	1.510581250	-2.054675315	0.79442032	H32	1	1.798069445	-2.492410376	1.082765305	H32	1	0.717127117	-2.627120437	1.109594232
H4	1	-1.088991974	-2.451113413	1.07296591	H4	1	-0.796462114	-2.993855275	1.295339399	H4	1	-1.853008236	-2.041290130	1.374425289
H16	1	2.738009550	-1.926701128	-2.98736884	H16	1	1.469652038	4.220978284	-3.013039649	H16	1	3.550487630	-0.270469739	-3.819007117

Table 4.18 The folded GS structure (left) and XYZ coordinates of rotor **2**(OPh) the unfolded GS structure (middle) and the lower TS structure (right).



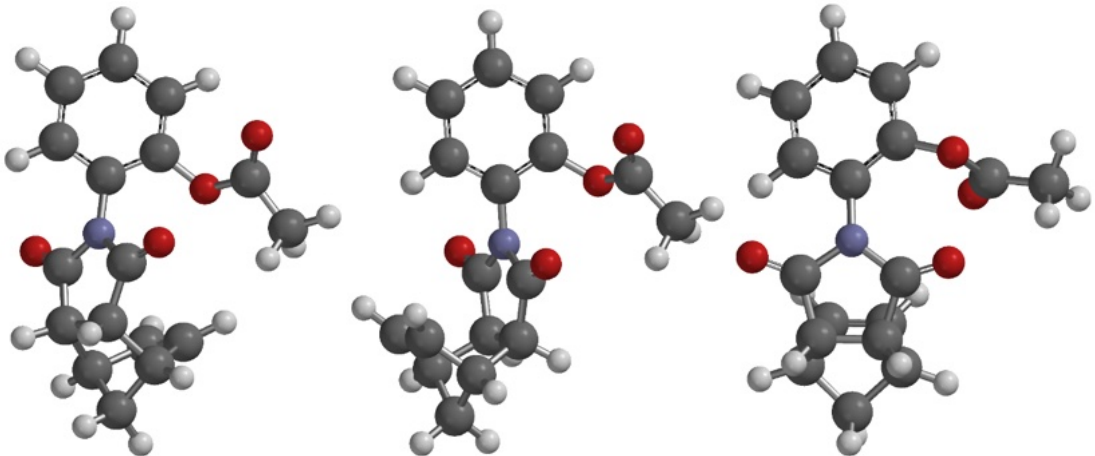
H1	1	1.827817896	-2.146969047	-4.862452804	H1	1	2.643373677	-0.329105316	-5.170419208	H1	1	1.789307752	-0.770118332	-5.049131195
C1	6	1.794638623	-1.753858703	-3.851775912	C1	6	2.225507783	-0.204565333	-4.177050570	C1	6	1.702616234	-0.726687269	-3.968912817
C4	6	1.700497255	-0.751058374	-1.253570027	C4	6	1.154472951	0.092737207	-1.620074275	C4	6	1.468277933	-0.666006015	-1.121427900
C2	6	0.627194976	-1.872160286	-3.105358421	C2	6	1.422760532	-1.205166298	-3.641093163	C2	6	0.693518102	-1.411267963	-3.315630022
C6	6	2.915709913	-1.132693550	-3.304027084	C6	6	2.477997053	0.956777113	-3.448969088	C6	6	2.581559856	0.026020680	-3.200666793
C5	6	2.867201943	-0.636867582	-2.005625053	C5	6	1.944293216	1.098122428	-2.173193811	C5	6	2.464814292	0.050813948	-1.818787836
C3	6	0.579554858	-1.371654458	-1.808528972	C3	6	0.874729097	-1.059250304	-2.369757655	C3	6	0.550327364	-1.381477414	-1.926737998
H2	1	-0.259163353	-2.348981255	-3.508460787	H2	1	1.199931360	-2.112582266	-4.190701860	H2	1	-0.041586366	-1.990634341	-3.862925840
H6	1	3.826441958	-1.039999802	-3.885309667	H6	1	3.092431209	1.744927887	-3.869385606	H6	1	3.376905820	0.596522631	-3.668237833
H5	1	3.729188275	-0.151689348	-1.562313312	H5	1	2.132502073	1.989323161	-1.586874484	H5	1	3.186058944	0.622588829	-1.264667681
N1	7	1.649270206	-0.232555680	0.070727443	N1	7	0.621071617	0.248054507	-0.312540154	N1	7	1.439671515	-0.555296860	0.321289316
C12	6	1.468396674	1.130371784	0.358116100	C12	6	0.914547660	-0.626309347	0.750410314	C12	6	2.504168308	0.046103709	1.064522615
C9	6	1.450798536	1.279546880	1.867640344	C9	6	0.110540890	-0.171712755	1.950380131	C9	6	2.012013491	0.387166946	2.446301705
C10	6	1.590189339	-0.155999640	2.424099159	C10	6	-0.648510279	1.090176266	1.484557814	C10	6	0.647170561	-0.281273442	2.563963706
C13	6	1.696984443	-1.056827066	1.211337702	C13	6	-0.272962642	1.277727634	0.031082099	C13	6	0.417529791	-0.976235865	1.244860823
H9	1	2.261441191	1.947564853	2.166548880	H9	1	-0.547640885	-0.986108116	2.258113491	H9	1	2.749046779	0.062531723	3.181427524
O1	8	1.345987809	1.995439144	-0.473114918	O1	8	1.676274407	-1.555747869	0.681867499	O1	8	3.624280388	0.264717286	0.674273096
O2	8	1.803625528	-2.254607303	1.185011302	O2	8	-0.647415688	2.141166505	-0.721720209	O2	8	-0.467000187	-1.759859858	1.054423749
C7	6	0.274936200	-0.340462646	3.268276449	C7	6	-0.112347006	2.207071536	2.456758451	C7	6	-0.337879329	0.928592110	2.829243683
H8	1	0.318083105	-1.182108107	3.957157507	H8	1	-0.725753157	3.105989530	2.468551594	H8	1	-1.303642210	0.617602734	3.222321420
O3	8	-0.571605444	-1.528406974	-1.064067281	O3	8	0.123618081	-2.105452389	-1.888922777	O3	8	-0.528204283	-2.095512278	-1.453287462
H16	1	2.470407045	-0.303194927	3.053229376	H16	1	-1.733607832	1.001647373	1.556353085	H16	1	0.565109482	-1.015938717	3.365512697
C8	6	0.078930573	1.768126812	2.473820706	C8	6	0.980147287	0.351396652	3.151711924	C8	6	1.681588344	1.925795145	2.647701680
H10	1	-0.050183094	2.848270319	2.440540927	H10	1	1.359657018	-0.440026252	3.795084445	H10	1	2.559790517	2.526132760	2.877456360
C14	6	0.165435920	1.085139592	3.861320176	C14	6	-0.013902791	1.372821034	3.757741921	C14	6	0.583931082	1.786558206	3.730054470
H11	1	1.041782735	1.384827631	4.445567376	H11	1	-0.966014784	0.927683075	4.063224915	H11	1	0.920640156	1.267130407	4.632681083
H17	1	-0.738036317	1.226534421	4.457651549	H17	1	0.413529149	1.935430711	4.589981784	H17	1	0.136876552	2.744628658	4.001665053
C15	6	-1.010154209	0.928664269	1.824587811	C15	6	2.012368074	1.300134231	2.559072714	C15	6	0.837103838	2.372049695	1.464592595
H18	1	-1.660681132	1.268727430	1.030277310	H18	1	3.053525020	1.050196810	2.397256935	H18	1	1.204579560	2.960470299	0.632681920
C16	6	-0.888072293	-0.318954610	2.288312665	C16	6	1.365769022	2.395667174	2.146252167	C16	6	-0.357439222	1.779537702	1.570550638
H21	1	-1.412492711	-1.196085668	1.933501454	H21	1	1.773565699	3.225590993	1.582360210	H21	1	-1.157963270	1.774901916	0.840745987
C17	6	-1.583366814	-0.595786094	-1.199322481	C17	6	-1.110815863	-1.881578941	-1.310206651	C17	6	-1.752290141	-1.468991247	-1.385260400
C18	6	-3.705338961	1.206453609	-1.270146877	C18	6	-3.580113183	-1.571993617	-0.065145253	C18	6	-4.305070769	-0.362381238	-1.147722766
C19	6	-1.398525961	0.657965247	-1.777547371	C19	6	-1.974433609	-0.876089758	-1.739321310	C19	6	-1.961129127	-0.131782806	-1.721355238
C20	6	-2.820612848	-0.962138062	-0.669900598	C20	6	-1.472434076	-2.740165595	-0.274022698	C20	6	-2.812152833	-2.254471883	-0.930111670
C21	6	-3.875532689	-0.057241667	-0.702282967	C21	6	-2.710586067	-2.584060002	0.342219810	C21	6	-4.079802085	-1.700438316	-0.815521735
C22	6	-2.467983072	1.552561410	-1.807029263	C22	6	-3.205819786	-0.723587130	-1.106189224	C22	6	-3.241878550	0.411750641	-1.600993583
H4	1	-0.428321402	0.954186883	-2.153265280	H4	1	-1.674465705	-0.203980533	-2.534510142	H4	1	-1.141665865	0.477449879	-2.081547045
H7	1	-2.931071236	-1.948630066	-0.234133095	H7	1	-0.767953598	-3.501706172	0.038910539	H7	1	-2.612650115	-3.282897345	-0.654272037
H12	1	-4.835208814	-0.341534515	-0.282686076	H12	1	-2.993241145	-3.253031756	1.148944295	H12	1	-4.898568517	-2.315971262	-0.455746042
H13	1	-2.319129119	2.534134996	-2.244778933	H13	1	-3.872151153	0.068646306	-1.431203312	H13	1	-3.400703621	1.451865203	-1.868975131
H14	1	-4.529035530	1.911950151	-1.292027058	H14	1	-4.542443626	-1.449068380	0.420465312	H14	1	-5.297260226	0.066311289	-1.054351094

Table 4.19 The folded GS structure (left) and XYZ coordinates of rotor **2**(OCF₃) the unfolded GS structure (middle) and the TS (right).



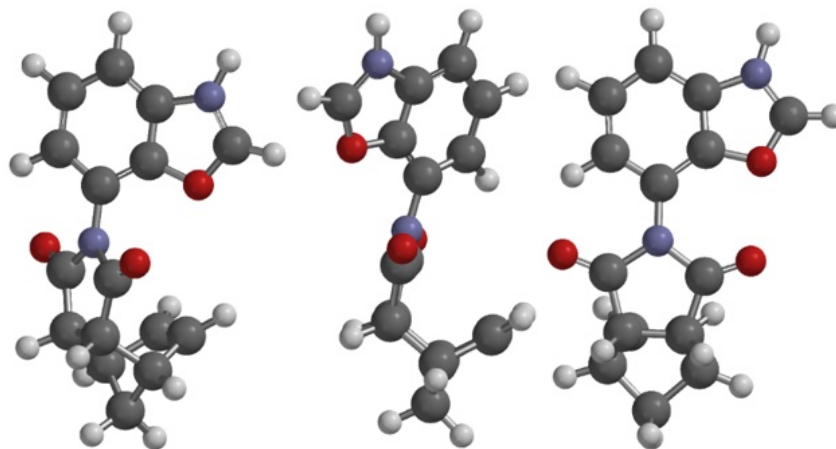
C1	6	-0.405789422	2.678697040	-1.420620644	C1	6	-0.293983698	3.053763885	-0.783914802	C1	6	-0.631200795	2.702426048	-1.030021251
C2	6	0.356803079	2.573016543	-0.109339995	C2	6	0.416852016	2.950787269	0.558946256	C2	6	0.491930148	2.439377007	-0.038826742
C3	6	-0.539801097	2.400662093	0.868320182	C3	6	-0.514980454	2.745646019	1.496584205	C3	6	-0.046313748	2.404520325	1.185572148
C4	6	-1.922943460	2.390123674	0.231642817	C4	6	-1.869715635	2.703216476	0.800125126	C4	6	-1.542277281	2.631748073	1.037181363
C5	6	-1.697000177	3.381560036	-0.935917544	C5	6	-1.621939790	3.716242389	-0.343287094	C5	6	-1.556486547	3.599990019	-0.170662010
C16	6	-2.042379304	1.056665816	-0.601844604	C16	6	-1.909318945	1.374806515	-0.046244903	C16	6	-2.138294203	1.347626124	0.324419543
C18	6	-1.000775654	1.251357213	-1.724749444	C18	6	-0.836063306	1.615863704	-1.129599659	C18	6	-1.546731840	1.412711245	-1.077770371
C8	6	-1.629185095	-0.204892797	0.127989120	C8	6	-1.457512459	0.139830657	0.705891322	C8	6	-1.644612841	0.049025657	0.907507714
N1	7	-0.449318658	-0.676444546	-0.479081531	N1	7	-0.267910912	-0.312390600	0.104866294	N1	7	-0.706221951	-0.552445486	0.006911771
C10	6	-0.025594878	0.100072848	-1.579875843	C10	6	0.178231283	0.505414042	-0.952043341	C10	6	-0.802704222	0.117233705	-1.268080191
O1	8	0.931995632	-0.148455100	-2.262824620	O1	8	1.200549390	0.338159168	-1.564163002	O1	8	-0.407687789	-0.269942214	-2.329051771
O2	8	-2.186532947	-0.740747238	1.050909760	O2	8	-1.982696860	-0.371469317	1.661522260	O2	8	-2.008637167	-0.382002989	1.973229141
C9	6	0.221925681	-1.855327051	-0.060276811	C9	6	0.463452807	-1.434858890	0.577433123	C9	6	0.153201152	-1.652195275	0.391748384
C11	6	1.569113584	-4.178325309	0.709081564	C11	6	1.923755960	-3.627739699	1.475731335	C11	6	1.774745827	-3.798538437	1.377409586
C12	6	-0.427983647	-3.087570351	-0.092907591	C12	6	0.898889463	-1.489751365	1.898733345	C12	6	0.187400733	-2.022321080	1.753340361
C13	6	1.541208566	-1.801536563	0.385985332	C13	6	0.740885500	-2.500707296	-0.280743712	C13	6	1.015526247	-2.393412425	-0.450185421
C14	6	2.226597941	-2.952516107	0.749131331	C14	6	1.474841428	-3.595662319	0.158403044	C14	6	1.784702753	-3.447800521	0.038999264
C15	6	0.238722925	-4.243017302	0.300955552	C15	6	1.628281910	-2.584098509	2.349287253	C15	6	0.972111320	-3.059844123	2.235175485
H20	1	0.128633062	3.112548080	-2.263692060	H20	1	0.264332739	3.513909581	-1.596775150	H20	1	-0.339727267	3.055407170	-2.017332901
H21	1	1.433293634	2.513696538	-0.027657308	H21	1	1.492165539	2.931649456	0.683439429	H21	1	1.509009900	2.193182969	-0.316643526
H22	1	-0.339548045	2.167875382	1.905281894	H22	1	-0.357237089	2.526149880	2.545120761	H22	1	0.446666758	2.131366126	2.110180658
H23	1	-2.768487850	2.562427105	0.894979473	H23	1	-2.746260632	2.844015618	1.429697649	H23	1	-2.088104732	2.916742744	1.934122708
H24	1	-1.520214025	4.403310645	-0.595480270	H24	1	-1.487962757	4.737740248	0.017061270	H24	1	-1.111530855	4.569666667	0.059522991
H25	1	-2.502576355	3.378219033	-1.678138405	H25	1	-2.396386977	3.701510406	-1.117651687	H25	1	-2.550491799	3.746092585	-0.605528341
H28	1	2.096588395	-5.079726629	1.000800881	H28	1	2.497127058	-4.481935680	1.818790741	H28	1	2.381341889	-4.622535072	1.735590815
H29	1	-1.460415460	-3.126902082	-0.418381731	H29	1	0.656246075	-0.668823473	2.561071677	H29	1	-0.440668655	-1.501175405	2.451264821
H30	1	3.257350876	-2.872152422	1.069264045	H30	1	1.676974213	-4.416056093	-0.517073574	H30	1	2.399612606	-3.976356010	-0.677721571
H31	1	-0.278718692	-5.195782955	0.277170127	H31	1	1.965896733	-2.620605965	3.378888812	H31	1	0.936583561	-3.288598744	3.294814156
H1	1	-3.064866014	0.931527106	-0.964564566	H1	1	-2.911290593	1.203738597	-0.444518259	H1	1	-3.228326421	1.362466862	0.360867488
H3	1	-1.426965853	1.224342609	-2.729866180	H3	1	-1.222276707	1.587314089	-2.150436027	H3	1	-2.279463062	1.509327706	-1.879498751
O3	8	2.181180722	-0.556535729	0.435849385	O3	8	0.175910227	-2.420828637	-1.551804741	O3	8	1.137760416	-2.189262869	-1.827219861
C6	6	2.330277709	-0.007750812	1.660115220	C6	6	0.884110725	-2.807181793	-2.639854812	C6	6	2.182445286	-1.451426974	-2.254132181
F1	9	1.163566573	0.110567033	2.323100932	F1	9	2.151862173	-2.386067239	-2.623699882	F1	9	2.284417052	-0.261768937	-1.619548421
F2	9	2.853840108	1.209455670	1.501030261	F2	9	0.270142253	-2.314370713	-3.713644577	F2	9	2.043219471	-1.238446974	-3.555549211
F3	9	3.157998146	-0.718444172	2.453611286	F3	9	0.915029324	-4.157210409	-2.766138682	F3	9	3.368806213	-2.080837550	-2.060085921

Table 4.20 The folded GS structure (left) and XYZ coordinates of rotor **2**(OCOCH₃) the unfolded GS structure (middle) and the TS (right).



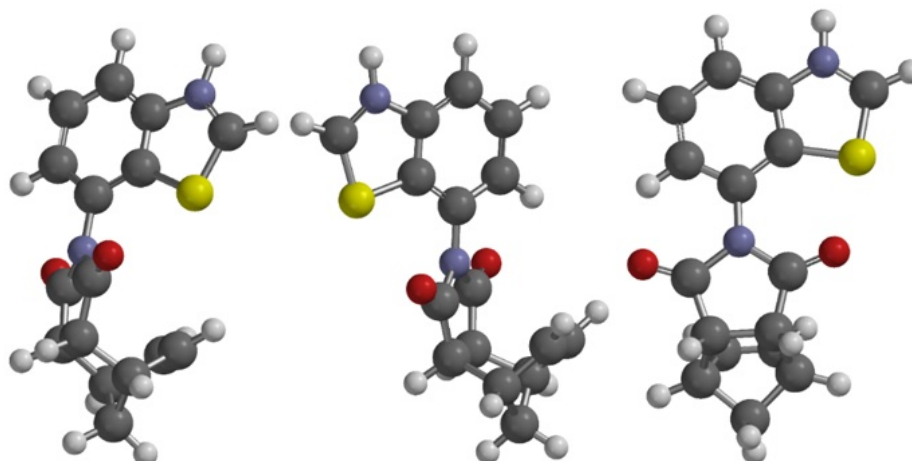
H1	1	1.284793172	-1.347844862	-5.279934500	H1	1	-0.496200473	0.215049055	-5.447790994	H1	1	1.639800676	-0.908750898	-5.060753045
C1	6	1.243660361	-1.073452338	-4.231287589	C1	6	-0.368792172	0.281370082	-4.372588888	C1	6	1.363668013	-0.920563722	-4.012114941
C4	6	1.126726642	-0.383619226	-1.534423665	C4	6	-0.052863085	0.434269556	-1.612280281	C4	6	0.598996363	-0.976674117	-1.263310615
C2	6	0.031454961	-1.142257691	-3.554217096	C2	6	-1.483313627	0.180427465	-3.546490380	C2	6	0.034035681	-0.869589154	-3.634415753
C6	6	2.395950348	-0.653630779	-3.570214480	C6	6	0.899961042	0.466726464	-3.827230444	C6	6	2.324436031	-0.965614453	-3.010715777
C5	6	2.336096670	-0.308916692	-2.225993491	C5	6	1.056727018	0.543184758	-2.448646153	C5	6	1.947437658	-0.991468774	-1.676825403
C3	6	-0.028290194	-0.790542615	-2.209156664	C3	6	-1.324473758	0.263657810	-2.166832300	C3	6	-0.358774874	-0.883254009	-2.296813294
H2	1	-0.869194667	-1.469356285	-4.054476651	H2	1	-2.471740309	0.030033925	-3.956891524	H2	1	-0.757948774	-0.806908499	-4.372098101
H6	1	3.339761609	-0.593707753	-4.100796440	H6	1	1.766246137	0.550296435	-4.474173382	H6	1	3.380383813	-0.987215209	-3.257488517
H5	1	3.220446180	0.031188580	-1.702999589	H5	1	2.033207730	0.693015056	-2.006950592	H5	1	2.725285012	-1.048656480	-0.937528040
N1	7	1.079701565	-0.013430440	-0.160050800	N1	7	0.112465952	0.506100323	-0.200297091	N1	7	0.337294331	-0.990333320	0.158996666
C12	6	1.570938484	1.224739072	0.307520652	C12	6	-0.309978441	-0.498958977	0.683191679	C12	6	1.361756287	-1.268407670	1.124369689
C9	6	1.376773507	1.261440899	1.808129015	C9	6	0.138631316	-0.112470775	2.075861795	C9	6	0.942575776	-0.701934071	2.454789734
C10	6	0.696001748	-0.074892576	2.167743688	C10	6	0.888757123	1.225401482	1.911545719	C10	6	-0.529700818	-0.335169154	2.282473651
C13	6	0.555281667	-0.825099613	0.859545651	C13	6	0.817467910	1.549759487	0.434136969	C13	6	-0.870680111	-0.692158350	0.859731600
H9	1	2.347573907	1.407381259	2.286400842	H9	1	-0.729025262	-0.060376620	2.736202577	H9	1	1.148003245	-1.428300958	3.241252216
O1	8	2.052932591	2.080833911	-0.388340053	O1	8	-0.897455655	-1.503547007	0.363914189	O1	8	2.393868012	-1.854684916	0.921345026
O2	8	0.082979083	-1.923762632	0.699894689	O2	8	1.293297366	2.501072935	-0.129854038	O2	8	-1.994114136	-0.723600801	0.433664160
C7	6	-0.658673628	0.382023703	2.832252644	C7	6	2.339499424	0.888273691	2.429998583	C7	6	-0.557332181	1.226201252	2.551421649
H8	1	-1.148478332	-0.404119088	3.403994770	H8	1	2.936414965	1.770032574	2.654746741	H8	1	-1.555922361	1.607297160	2.755650621
O3	8	-1.222906711	-0.766928576	-1.507605996	O3	8	-2.393084265	0.239479041	-1.287340425	O3	8	-1.737662805	-0.814380333	-2.130897377
H16	1	1.267470772	-0.691153379	2.864467107	H16	1	0.462625102	2.051486093	2.483181082	H16	1	-1.213871779	-0.849987942	2.957130486
C8	6	0.347658191	2.341109830	2.316337373	C8	6	1.236011498	-1.069621621	2.680033873	C8	6	1.623109374	0.690774085	2.800837844
H10	1	0.775327015	3.336810023	2.415630597	H10	1	0.826826521	-1.971040999	3.131912888	H10	1	2.616012241	0.584821350	3.233821366
C14	6	-0.143397199	1.624830886	3.598216219	C14	6	1.967991480	-0.058962284	3.596724380	C14	6	0.499119182	1.287394396	3.680257249
H11	1	0.658662230	1.399399186	4.308365023	H11	1	1.317137769	0.402812269	4.345729385	H11	1	0.247375014	0.672957792	4.550632698
H17	1	-0.941179452	2.168484392	4.107968083	H17	1	2.843587106	-0.489125178	4.086808178	H17	1	0.715136501	2.307820811	4.001991699
C15	6	-0.890065518	2.214413849	1.442771743	C15	6	2.290129924	-1.269111047	1.600756646	C15	6	1.500017994	1.575528924	1.569979595
H18	1	-1.146835858	2.891249276	0.637635032	H18	1	2.385303119	-2.160075547	0.992757041	H18	1	2.304492008	1.778903602	0.873799705
C16	6	-1.484360734	1.056386202	1.747783915	C16	6	2.941551535	-0.110829912	1.452148755	C16	6	0.208306503	1.888027822	1.418201328
H21	1	-2.324999697	0.602534518	1.240763832	H21	1	3.683083893	0.133355650	0.701429297	H21	1	-0.254088143	2.373839942	0.567670523
C11	6	-2.010732321	-1.902074906	-1.462848962	C11	6	-3.298412465	-0.805308743	-1.326216792	C11	6	-2.277578147	0.418986243	-1.864643850
O4	8	-1.839364475	-2.865137940	-2.149659818	O4	8	-3.379728383	-1.588649677	-2.225497983	O4	8	-1.615352588	1.406007641	-1.696576734
C17	6	-3.084483288	-1.726705680	-0.426677087	C17	6	-4.121467016	-0.797995731	-0.069856064	C17	6	-3.775757538	0.324815480	-1.821436567
H3	1	-2.625441755	-1.859762518	0.555876322	H3	1	-3.532548120	-1.294316306	0.705975923	H3	1	-4.156002292	-0.185055180	-2.708541838
H4	1	-3.855913755	-2.480695167	-0.569591084	H4	1	-5.043452034	-1.354229723	-0.229478345	H4	1	-4.200357383	1.323979146	-1.746426118
H7	1	-3.515873119	-0.725734830	-0.473023228	H7	1	-4.334388866	0.218815993	0.261359976	H7	1	-4.055965678	-0.264647632	-0.947431534

Table 4.21 The folded GS structure (left) and XYZ coordinates of rotor **2(oxazole+)** the unfolded GS structure (middle) and the TS (right).



N1	7	-0.323898115	0.777919153	0.042225509	N1	7	-0.270896246	0.448598649	0.035568641	N1	7	-0.092133692	0.716216874	0.037670054
C2	6	-1.416912340	0.623228815	0.949308949	C2	6	-1.310145014	0.308572233	1.004411965	C2	6	-1.128374059	0.988650943	1.006583432
C3	6	-0.840272977	0.567502937	2.341803695	C3	6	-0.654940442	0.287915142	2.363315467	C3	6	-0.563712117	0.794701715	2.382997236
C4	6	0.688582846	0.725597047	2.175389055	C4	6	0.867075105	0.370449656	2.102528359	C4	6	0.919399112	0.464572172	2.193790847
C5	6	0.932898585	0.904680733	0.698852030	C5	6	1.031475241	0.476720982	0.607445131	C5	6	1.156363058	0.462949210	0.707859538
O1	8	1.965991606	1.109054543	0.119006546	O1	8	2.039201528	0.546184717	-0.045179351	O1	8	2.201132206	0.274006845	0.152644199
O2	8	-2.563603283	0.539393020	0.605863591	O2	8	-2.471603183	0.202808942	0.721945784	O2	8	-2.260600865	1.303496161	0.757191883
C1	6	-1.538290881	1.490747558	-1.973085889	C1	6	-1.355453914	-0.555375684	-1.930249221	C1	6	-1.604008954	0.879469066	-1.888068812
C6	6	0.275152751	0.270374805	-3.611926287	C6	6	-0.019100221	1.119298965	-3.629373971	C6	6	0.293867410	0.333399477	-3.727902291
C7	6	-0.476151053	0.828156783	-1.348242197	C7	6	-0.491514623	0.375411170	-1.345821487	C7	6	-0.313422130	0.663262273	-1.360692038
C16	6	-1.682055000	1.535595854	-3.368239790	C16	6	-1.538490868	-0.640713666	-3.319137770	C16	6	-1.926012198	0.819957605	-3.247861831
C9	6	-0.773984569	0.936281112	-4.232107408	C9	6	-0.868490036	0.187494352	-4.212104173	C9	6	-0.982209626	0.542092054	-4.221459519
C10	6	0.408983257	0.202691976	-2.225996929	C10	6	0.148162012	2.192280001	-2.249582068	C10	6	0.640691812	0.386495596	-2.367543851
C11	6	0.261610450	-0.796022985	3.949074679	C11	6	0.483137165	-1.064714992	3.955740066	C11	6	0.079558042	-0.769162244	4.047161092
C12	6	1.248653326	-0.630747678	2.768823884	C12	6	1.408064287	-0.982534302	2.717203205	C12	6	1.063323052	-0.961453747	2.867880794
C13	6	0.775514188	-1.754073777	1.858493730	C13	6	0.842047828	-2.116421975	1.875893563	C13	6	0.272456848	-1.941625032	2.013862485
C14	6	-0.544971760	-1.885887823	2.022924462	C14	6	-0.471711541	-2.185076316	2.116391248	C14	6	-1.025360463	-1.656274597	2.165080319
C15	6	-0.987836968	-0.843819647	3.039633900	C15	6	-0.816380610	-1.092658990	3.119298915	C15	6	-1.131622749	-0.482936034	3.126445008
H2	1	-1.305383453	1.345150105	2.949606931	H2	1	-1.051563054	1.103602944	2.969446124	H2	1	-0.758846674	1.691431084	2.972634899
H1	1	1.110963572	1.575273709	2.712962720	H1	1	1.354253481	1.224426502	2.576067267	H1	1	1.602882778	1.176551672	2.658264147
H30	1	2.313054138	-0.594151648	2.989404820	H30	1	2.483714209	-0.981829438	2.877281991	H30	1	2.092798221	-1.229039320	3.094051086
H33	1	-1.959291502	-0.996120853	3.504106424	H33	1	-1.765736588	-1.189185731	3.640944912	H33	1	-2.102370919	-0.314924123	3.586905374
O3	8	1.495092110	-0.616616997	-1.940189794	O3	8	1.010747340	2.276992668	-1.994443203	O3	8	2.007466238	0.112330954	-2.302183384
H27	1	-2.282224388	1.968001271	-1.351693498	H27	1	-1.900436909	-1.226913372	-1.281738047	H27	1	-2.397581902	1.107533548	-1.197419574
H28	1	-2.534427700	2.061130590	-3.782357512	H28	1	-2.219240156	-1.389586215	-3.706774105	H28	1	-2.955822263	0.998597221	-3.535449080
H29	1	-0.887165855	0.975321595	-5.308263058	H29	1	-1.003991087	0.107944451	-5.283503363	H29	1	-1.221451882	0.491345548	-5.276431079
H3	1	0.414753860	-1.726771762	4.497099376	H3	1	0.630545042	-1.980892988	4.529241808	H3	1	-0.049032801	-1.677934005	4.636738958
H31	1	0.267334598	0.044769864	4.648411423	H31	1	0.563054292	-0.199999227	4.620434354	H31	1	0.335547294	0.063446426	4.708901009
H32	1	1.406470458	-2.279616031	1.152210581	H32	1	1.411474546	-2.692086253	1.156884263	H32	1	0.712493642	-2.676621407	1.350690264
H4	1	-1.217988313	-2.538135489	1.480160126	H4	1	-1.197363300	-2.831711934	1.638520243	H4	1	-1.864693162	-2.109810287	1.652139110
N3	7	1.336649090	-0.506424674	-4.102518899	N3	7	0.794341449	2.137408296	-4.150987448	N3	7	1.482862288	0.028979430	-4.399404768
H7	1	1.556072436	-0.678842068	-5.076077834	H7	1	0.931202756	2.355184341	-5.130535486	H7	1	1.589103027	-0.083521762	-5.400025284
C8	6	2.004674533	-0.995949513	-3.079069556	C8	6	1.363153695	2.773569928	-3.147957068	C8	6	2.443438183	-0.084709536	-3.509880695
H6	1	2.872006350	-1.637690521	-3.105593779	H6	1	2.045407819	3.607889144	-3.201176545	H6	1	3.483873249	-0.311473887	-3.685169525

Table 4.22 The folded GS structure (left) and XYZ coordinates of rotor 1(thiazole) the unfolded GS structure (middle) and the TS (right).



N1	7	-0.071943269	0.891855193	0.042258864	N1	7	0.020517082	0.530089472	0.042188794	N1	7	-0.209305263	0.662060102	0.088007061
C2	6	-1.187633492	1.012320830	0.934791320	C2	6	-0.949234766	1.004844038	0.990057592	C2	6	-1.303580579	0.717156830	1.044863522
C3	6	-0.660485228	0.865714129	2.338170359	C3	6	-0.368896949	0.811291557	2.368202708	C3	6	-0.733842688	0.618749833	2.431362400
C4	6	0.867529020	0.686962016	2.203585663	C4	6	1.027116383	0.189226485	2.152195906	C4	6	0.783591432	0.518038208	2.255050765
C5	6	1.147898888	0.701873356	0.723390741	C5	6	1.210153751	0.099575403	0.662546364	C5	6	1.016719043	0.595247377	0.777049452
O1	8	2.205599828	0.536185277	0.161642544	O1	8	2.181586799	-0.281710196	0.050631634	O1	8	2.102996868	0.586315760	0.241906522
O2	8	-2.319409433	1.174109242	0.574197464	O2	8	-2.023168673	1.440749855	0.685351425	O2	8	-2.468912557	0.807455909	0.777789324
C1	6	-1.092572605	1.793084587	-1.972414237	C1	6	-1.515664391	-0.014746017	-1.759972114	C1	6	-1.667013885	0.720311463	-1.856851155
C6	6	0.206896954	-0.006059727	-3.584688211	C6	6	0.325171965	0.591855269	-3.697348015	C6	6	0.336088560	0.506559406	-3.674081702
C7	6	-0.213446073	0.900835956	-1.361799560	C7	6	-0.251783971	0.396864436	-1.337144068	C7	6	-0.368821524	0.640848329	-1.334930316
C16	6	-1.319897438	1.784138432	-3.355479798	C16	6	-1.852184477	-0.120549434	-3.115345805	C16	6	-1.961802664	0.688092070	-3.221903159
C9	6	-0.678048127	0.885174460	-4.187752343	C9	6	-0.942424122	0.186489390	-4.110253415	C9	6	-0.963911117	0.579992428	-4.163582176
C10	6	0.455017231	-0.013187911	-2.200476205	C10	6	0.692167157	0.688578089	-2.342103575	C10	6	0.682093208	0.532652138	-2.301133539
C11	6	0.082168705	-0.633013620	4.024226987	C11	6	0.050630959	-0.782423997	4.085664885	C11	6	0.134810554	-0.858343505	4.078280190
C12	6	1.125541540	-0.717209184	2.882022073	C12	6	0.905705913	-1.216150592	2.869235640	C12	6	1.129370580	-0.890590922	2.890125508
C13	6	0.468740129	-1.766799269	1.998310273	C13	6	-0.116081479	-2.036086242	2.095857860	C13	6	0.476326014	-1.953947251	2.020781750
C14	6	-0.856161983	-1.612414896	2.097447953	C14	6	-1.319710648	-1.493066603	2.307396212	C14	6	-0.847549179	-1.859147694	2.185678749
C15	6	-1.116980990	-0.461913806	3.059031322	C15	6	-1.128959708	-0.287991597	3.216843932	C15	6	-1.110581590	-0.727961885	3.168358459
H2	1	-0.961215142	1.736365132	2.922736248	H2	1	-0.358707548	1.765549028	2.896201822	H2	1	-1.067785628	1.481487365	3.009388070
H1	1	1.454769472	1.465207390	2.692760974	H1	1	1.848437570	0.761536680	2.585119451	H1	1	1.354304293	1.307522292	2.745196978
H30	1	2.166701255	-0.883574982	3.147852456	H30	1	1.868035076	-1.686316977	3.057100373	H30	1	2.187700140	-1.015713023	3.106240152
H33	1	-2.116258861	-0.400641119	3.483628181	H33	1	-2.015877971	0.091759646	3.718485428	H33	1	-2.092114428	-0.703710298	3.635575597
S1	16	1.588228531	-1.297070066	-1.797576641	S1	16	2.360165205	1.229865262	-2.207681664	S1	16	2.452979452	0.409958314	-2.167028905
H27	1	-1.632417429	2.496092847	-1.355328348	H27	1	-2.264463793	-0.242091927	-1.015823696	H27	1	-2.489667623	0.806573941	-1.169108240
H28	1	-2.023081815	2.492669906	-3.776355998	H28	1	-2.851102081	-0.443697324	-3.383825106	H28	1	-2.998897835	0.749755772	-3.530611248
H29	1	-0.861398447	0.863014539	-5.255832318	H29	1	-1.201273110	0.121526550	-5.160856647	H29	1	-1.169934227	0.552563622	-5.227668393
H3	1	0.023650834	-1.553856629	4.605579541	H3	1	-0.223520791	-1.623193987	4.724199862	H3	1	0.138848424	-1.786864517	4.650045946
H31	1	0.232220010	0.216399555	4.696519255	H31	1	0.512634035	0.002421520	4.691117276	H31	1	0.280766132	-0.010304873	4.753562981
H32	1	1.004205273	-2.461395559	1.362324595	H32	1	0.126975561	-2.862815316	1.439838173	H32	1	1.008843162	-2.609427392	1.342157776
H4	1	-1.626119966	-2.144089104	1.552055004	H4	1	-2.263156883	-1.786562995	1.863717968	H4	1	-1.618330527	-2.416960322	1.668349943
N3	7	0.918571656	-1.019682221	-4.222634300	N3	7	1.375322479	0.977266874	-4.526366447	N3	7	1.454257961	0.396106047	-4.494119032
H7	1	0.879854886	-1.166324853	-5.225006013	H7	1	1.305278932	0.960272005	-5.537503819	H7	1	1.378128532	0.370848157	-5.504786745
C8	6	1.649573069	-1.775141275	-3.420965819	C8	6	2.471115007	1.358737109	-3.892582982	C8	6	2.603546564	0.334193551	-3.854255714
H6	1	2.259903019	-2.589628627	-3.786222025	H6	1	3.365197489	1.668904536	-4.415145954	H6	1	3.550680394	0.250482925	-4.369710928

4.5.8 B-value calculations

When available, the B -values were taken from the literature.^{1,20,165} But the B -value for some R-groups were not reported, and therefore, they were calculated using the DFT method used by Mazzanti (B3LYP/6-31G*) without thermodynamic corrections.^{1,20,165} The R-groups were inserted at the 2'-position of the biaryl rotor, 2-isopropyl biphenyl and their barriers calculated using Spartan18 (B3LYP/6-31G*). Calculated structures and XYZ coordinates were listed from **Table 4.24-4.34**.

The experimental barriers with ChB interaction did not correlate with the size of the R¹-groups as measured by the steric B-value parameter. Basically, the smaller steric size of a rotor did not mean a smaller experimental barrier of the rotor because the lower barrier was due to the ChB interactions (**Figure 4.48**). The computational energies of ground states and transition states were listed in **Table 4.23** in kcal/mol. The B-values were the differences using energies of TS subtracted energies of GS.

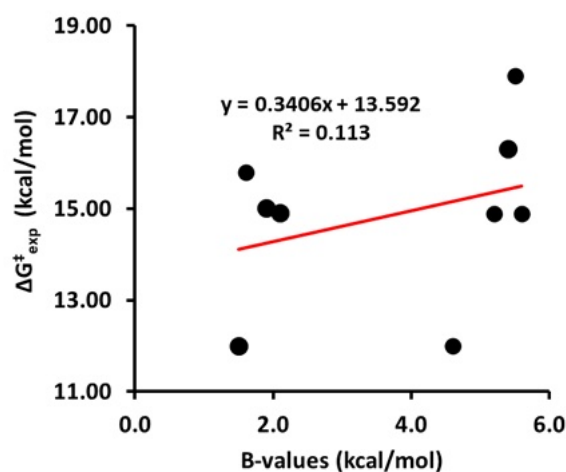
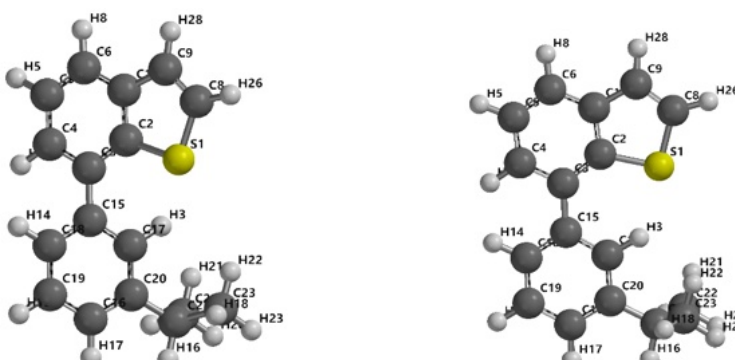


Figure 4.48 Plot showing the poor correlation between $\Delta G^\ddagger_{\text{exp}}$ and B -values.

Table 4.23 The calculated energies of ground states and transition states and the responding B-values.

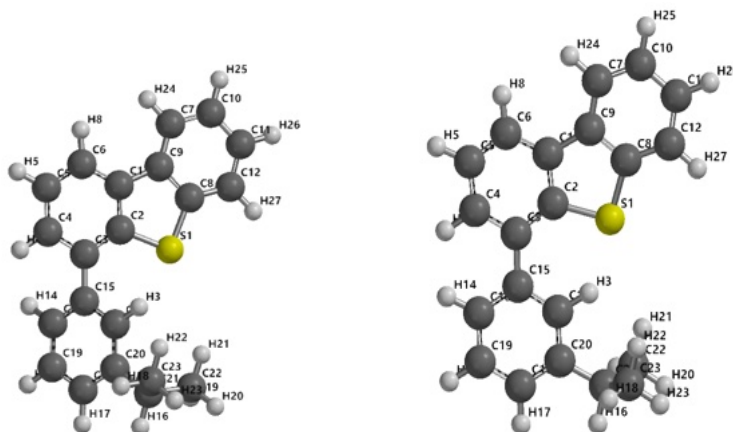
R =	energy of GS (Kcal/mol)	energy of TS (Kcal/mol)	B-value (kcal/mol)
oxazole	-469832.36	-469830.90	1.46
OCOCH ₃	-507733.98	-507728.55	5.43
OPh	-556922.50	-556918.30	4.20
benzofuran	-556180.95	-556178.97	1.98
furan	-459760.60	-459758.74	1.86
2H-furan	-460519.86	-460518.25	1.61
SCF ₃	-826089.74	-826081.58	8.16
benzothiofuran	-758852.44	-758846.91	5.53
thiofuran	-662433.54	-662428.32	5.22
thiazole	-672502.81	-672498.17	4.64

Table 4.24 The folded GS structure (left) and the unfolded GS structure (middle), the TS structure (right), and the XYZ coordinates of **1**(thiofuan).



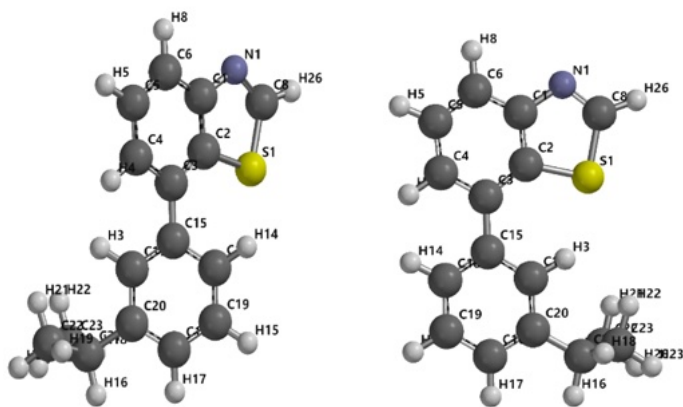
C1	6	0.566128558	3.477620355	0.917925646	C1	6	0.412498647	3.477660173	0.954445445
C4	6	0.528570779	1.322499641	2.689658969	C4	6	1.305341838	1.389307688	2.533168005
C2	6	0.608182740	2.141109002	0.444426594	C2	6	0.271830115	2.128414931	0.516184844
C6	6	0.494162359	3.715529633	2.301927527	C6	6	1.012485277	3.762451484	2.189810429
C5	6	0.477292159	2.638196111	3.174874234	C5	6	1.461599678	2.709613703	2.966761661
C3	6	0.592048332	1.037124630	1.320950079	C3	6	0.706406190	1.030766987	1.311706454
H5	1	0.419734695	2.808151668	4.246504211	H5	1	1.937084609	2.898566862	3.925348636
H4	1	0.497579435	0.492393538	3.389772753	H4	1	1.669020327	0.613880889	3.193701534
H8	1	0.459520182	4.735902111	2.674739862	H8	1	1.120268078	4.793053009	2.517278180
C15	6	0.653695794	-0.373029656	0.850871195	C15	6	0.561465773	-0.420553630	0.963714893
C16	6	0.758369096	-3.041765796	-0.000364468	C16	6	0.281431259	-3.182065201	0.356930426
C17	6	-0.187191228	-0.838299307	-0.170790596	C17	6	-0.065935365	-0.871204207	-0.210713752
C18	6	1.549693071	-1.274968668	1.448207727	C18	6	1.049060748	-1.423586891	1.831604668
C19	6	1.599399248	-2.599567998	1.022228871	C19	6	0.908103832	-2.773028465	1.534480954
C20	6	-0.149200143	-2.168273660	-0.610650020	C20	6	-0.212085466	-2.227855010	-0.533547636
H3	1	-0.901947484	-0.151335923	-0.614705384	H3	1	-0.470317464	-0.162308341	-0.917985380
H14	1	2.217558676	-0.924218980	2.229909666	H14	1	1.545687323	-1.166943158	2.758426129
H15	1	2.301828776	-3.289790367	1.482357165	H15	1	1.291688623	-3.513992685	2.231258236
H17	1	0.805667900	-4.077927546	-0.328342640	H17	1	0.177473591	-4.241012896	0.131592010
C21	6	-1.086840323	-2.664411274	-1.704225152	C21	6	-0.897947834	-2.649571699	-1.827856021
H16	1	-0.814334138	-3.708791444	-1.909470941	H16	1	-0.841857876	-3.745762322	-1.875966869
C22	6	-2.555144750	-2.656654238	-1.236567579	C22	6	-2.389615234	-2.263282022	-1.839625489
H19	1	-2.681860773	-3.240225899	-0.318134877	H19	1	-2.917600827	-2.694768919	-0.982049385
H20	1	-3.208233398	-3.084320476	-2.006705922	H20	1	-2.873536080	-2.622965106	-2.755786364
H21	1	-2.902394609	-1.636217726	-1.034541096	H21	1	-2.517687291	-1.175204389	-1.798630119
C23	6	-0.919484064	-1.877080205	-3.017194124	C23	6	-0.175256495	-2.095880416	-3.070408657
H18	1	0.114970663	-1.918702389	-3.375363982	H18	1	0.884231932	-2.374857243	-3.071435979
H22	1	-1.185343021	-0.821368456	-2.888665802	H22	1	-0.232054172	-1.001214239	-3.110913817
H23	1	-1.568508611	-2.290077643	-3.798611643	H23	1	-0.633563367	-2.485540725	-3.987288752
S1	16	0.746601649	2.110303397	-1.313986952	S1	16	-0.490817490	2.124649923	-1.083362266
C8	6	0.731506412	3.858775035	-1.377101689	C8	6	-0.611003317	3.865978688	-1.103894916
C9	6	0.632915097	4.437356861	-0.154183193	C9	6	-0.106772988	4.437391171	0.014712925
H26	1	0.794670668	4.351519926	-2.338782185	H26	1	-1.058842944	4.352379677	-1.961105740
H28	1	0.610386253	5.510545744	0.004033744	H28	1	-0.100783737	5.507482220	0.199445607

Table 4.25 The folded GS structure (left) and the unfolded GS structure (middle), the TS structure (right), and the XYZ coordinates of **1**(benzothiofuran).



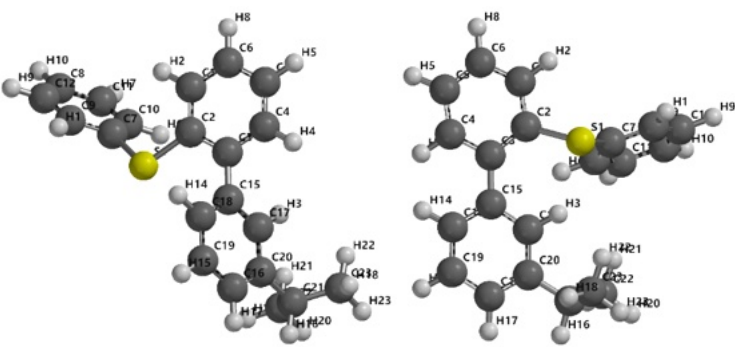
C1	6	0.667449212	-1.492466717	-2.315442669	C1	6	0.550283271	-0.798788929	-2.670304976
C4	6	2.646494153	-1.460359111	-0.352532244	C4	6	2.839349914	0.073642832	-1.381709816
C2	6	0.594264960	-0.593684850	-1.225844270	C2	6	0.493257402	-0.358774907	-1.319816447
C6	6	1.748260069	-2.381055076	-2.402850002	C6	6	1.767600138	-0.803251983	-3.358131403
C5	6	2.731624635	-2.358938873	-1.422498145	C5	6	2.907813357	-0.362746584	-2.704678845
C3	6	1.580857486	-0.558778908	-0.222439618	C3	6	1.650629678	0.091002162	-0.626231638
H5	1	3.572077357	-3.044824224	-1.480343962	H5	1	3.864472624	-0.352697166	-3.219326793
H4	1	3.413948646	-1.468975013	0.416424442	H4	1	3.760320680	0.418290209	-0.930514082
H8	1	1.816627062	-3.076116208	-3.235352312	H8	1	1.813484865	-1.143307735	-4.388698570
C15	6	1.537470855	0.380914358	0.930387130	C15	6	1.696518507	0.558266832	0.797802643
C16	6	1.487804021	2.117545997	3.131171633	C16	6	1.815203752	1.429764817	3.501056949
C17	6	0.379297214	0.529421288	1.707095069	C17	6	0.550041364	0.680343374	1.600326103
C18	6	2.680469696	1.118960435	1.279722601	C18	6	2.922659648	0.898634589	1.413114645
C19	6	2.652246302	1.979859050	2.373557826	C19	6	2.976241640	1.331176776	2.732606726
C20	6	0.333655508	1.394487102	2.808682342	C20	6	0.582833291	1.096574368	2.937707656
H3	1	-0.496972569	-0.062286638	1.458379451	H3	1	-0.423324139	0.454709233	1.193250682
H14	1	3.580762570	1.027758933	0.678488405	H14	1	3.858865433	0.823569870	0.874252448
H15	1	3.538886824	2.552402381	2.633652788	H15	1	3.938151895	1.590283323	3.167895543
H17	1	1.473754222	2.794444187	3.982721992	H17	1	1.869623103	1.762245063	4.535104482
C21	6	-0.939128571	1.553815429	3.631311197	C21	6	-0.702701170	1.163675670	3.753023218
H16	1	-0.696623261	2.218267267	4.471948076	H16	1	-0.435560779	1.551211816	4.745864465
C22	6	-2.055125661	2.230180200	2.811837715	C22	6	-1.731263084	2.131906816	3.139512136
H19	1	-1.731372844	3.205591008	2.432402632	H19	1	-1.307742627	3.134205333	3.013348694
H20	1	-2.950832534	2.381431189	3.426266281	H20	1	-2.615915023	2.211164140	3.782619974
H21	1	-2.338909209	1.615182291	1.949633160	H21	1	-2.068425838	1.785814299	2.155037757
C23	6	-1.421906197	0.216906541	4.223368906	C23	6	-1.317481278	-0.235702453	3.952978795
H18	1	-0.645062286	-0.249619841	4.839053478	H18	1	-0.603308406	-0.920689058	4.423076894
H22	1	-1.695205046	-0.493246841	3.434457622	H22	1	-1.620833392	-0.676211564	2.995684151
H23	1	-2.307900842	0.371691312	4.850362139	H23	1	-2.208037194	-0.178042356	4.590542029
S1	16	-0.818953464	0.472946874	-1.343172040	S1	16	-1.178336078	-0.475600772	-0.71290126
C8	6	-1.323776876	-0.305030646	-2.845450267	C8	6	-1.772177204	-1.076598981	-2.253544977
C9	6	-0.441734398	-1.332923044	-3.242529544	C9	6	-0.740774863	-1.209378626	-3.201417035
C7	6	-0.717018129	-2.046345031	-4.418792801	C7	6	-1.060424550	-1.692028878	-4.480664415
C10	6	-1.845869921	-1.734550663	-5.167764969	C10	6	-2.376775882	-2.020398287	-4.785269775
C11	6	-2.713341543	-0.710221892	-4.756853507	C11	6	-3.392229448	-1.871844809	-3.826743978
C12	6	-2.460439653	0.011647884	-3.593510106	C12	6	-3.098036127	-1.398734598	-2.551385831
H24	1	-0.050870927	-2.842188332	-4.741869892	H24	1	-0.283624921	-1.809443565	-5.231690000
H25	1	-2.059157263	-2.288297829	-6.077776835	H25	1	-2.623103261	-2.393958131	-5.775179842
H26	1	-3.592899723	-0.476766801	-5.350641093	H26	1	-4.417340391	-2.127626453	-4.080171124
H27	1	-3.132849876	0.803222817	-3.275260609	H27	1	-3.879934694	-1.280655480	-1.806425026

Table 4.26 The folded GS structure (left) and the unfolded GS structure (middle), the TS structure (right), and the XYZ coordinates of **1**(thiazole).



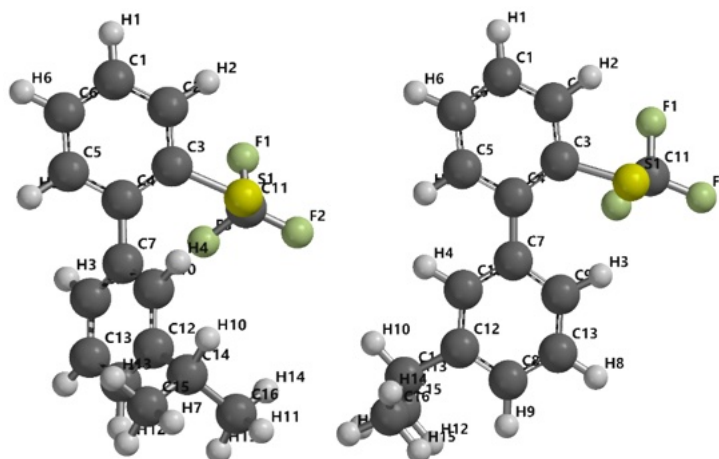
C1	6	1.337655155	3.491288690	1.568088864	C1	6	0.390371660	3.628498819	0.933651908
C4	6	-0.812154658	1.729851790	1.536280762	C4	6	1.305140984	1.565726152	2.517677480
C2	6	1.495666375	2.158262575	1.112755916	C2	6	0.220917317	2.275627803	0.522812530
C6	6	0.085863600	3.933928278	2.018634657	C6	6	1.021757553	3.939180561	2.142829719
C5	6	-0.979343886	3.044924283	1.997234300	C5	6	1.476662800	2.892120535	2.926296044
C3	6	0.422305450	1.247819438	1.082652128	C3	6	0.677637381	1.189002855	1.315733041
H5	1	-1.957869374	3.364492553	2.344355931	H5	1	1.973691692	3.092622233	3.871127930
H4	1	-1.658359095	1.049167708	1.548426557	H4	1	1.682684073	0.798279483	3.179790408
H8	1	-0.023191228	4.956101330	2.366160191	H8	1	1.139277214	4.978643874	2.430563978
C15	6	0.554891279	-0.148821076	0.588237656	C15	6	0.537453743	-0.263080444	0.974920071
C16	6	0.742547029	-2.785039446	-0.349286888	C16	6	0.279416258	-3.023076653	0.365109143
C17	6	-0.394684012	-0.669053676	-0.303472832	C17	6	-0.076448475	-0.715121825	-0.205151956
C18	6	1.607196457	-0.978847049	1.008673666	C18	6	1.023625772	-1.261253304	1.848021021
C19	6	1.696009031	-2.287550399	0.539910324	C19	6	0.895902718	-2.611391805	1.547121892
C20	6	-0.318755687	-1.982292480	-0.784096458	C20	6	-0.215881424	-2.071938413	-0.528135921
H3	1	-1.196678661	-0.019811422	-0.645226883	H3	1	-0.470639046	-0.005305607	-0.918190391
H14	1	2.337962130	-0.608755278	1.721685479	H14	1	1.509204964	-1.000029559	2.779466530
H15	1	2.508876017	-2.925983677	0.876110737	H15	1	1.281253716	-3.350811931	2.244431196
H17	1	0.823042801	-3.807318823	-0.712050927	H17	1	0.184005705	-4.082499040	0.138479201
C21	6	-1.350719182	-2.522188687	-1.766385360	C21	6	-0.896690580	-2.495565939	-1.824129783
H16	1	-1.086872174	-3.569972431	-1.964779431	H16	1	-0.866551420	-3.593252140	-1.856806754
C22	6	-2.773681510	-2.509074144	-1.177343149	C22	6	-2.377907471	-2.072590484	-1.857420459
H19	1	-2.817210713	-3.054180284	-0.228144156	H19	1	-2.924601084	-2.474647800	-0.997415234
H20	1	-3.482171041	-2.975278234	-1.872411377	H20	1	-2.861931768	-2.436237665	-2.771705115
H21	1	-3.119103985	-1.484957178	-0.991796548	H21	1	-2.479522515	-0.981064791	-1.837836064
C23	6	-1.304917544	-1.773114492	-3.112590490	C23	6	-0.146917422	-1.976268283	-3.065468294
H18	1	-0.305101827	-1.817277422	-3.558012849	H18	1	0.901955061	-2.292188456	-3.057947409
H22	1	-1.567911998	-0.715949544	-2.988379951	H22	1	-0.165191471	-0.880728927	-3.113636523
H23	1	-2.015803699	-2.212606318	-3.822403355	H23	1	-0.613029088	-2.355796232	-3.982440739
S1	16	3.156173726	1.937504612	0.575159343	S1	16	-0.602615242	2.302494572	-1.039220666
C8	6	3.464320212	3.617434960	1.015675583	C8	6	-0.627621835	4.058700663	-0.970453145
N1	7	2.474888993	4.286727445	1.505911254	N1	7	-0.099185883	4.602207933	0.072081143
H26	1	4.457132017	4.030568396	0.870427306	H26	1	-1.076223994	4.619743704	-1.784154784

Table 4.27 The folded GS structure (left) and the unfolded GS structure (middle), the TS structure (right), and the XYZ coordinates of **1**(SPh).



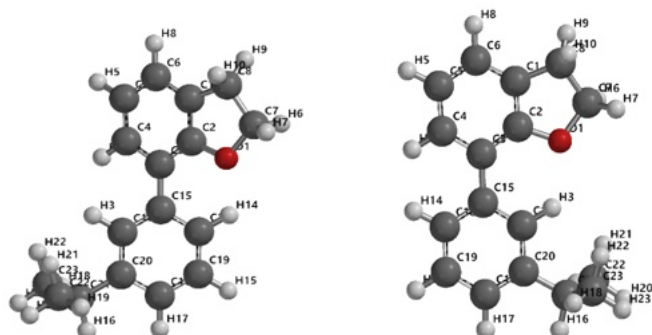
C1	6	-1.347735427	-2.071174431	-2.539637568	C1	6	-0.582253569	-2.312706220	-2.634727012
C4	6	-0.883953675	-3.506841902	-0.208155466	C4	6	0.889251859	-3.484887025	-0.621575302
C2	6	-1.161531018	-1.401944705	-1.327433151	C2	6	-0.421403901	-1.658778353	-1.409902725
C6	6	-1.287554083	-3.461977516	-2.585373623	C6	6	-0.003167956	-3.554129846	-2.861950269
C5	6	-1.055893887	-4.183462994	-1.413006612	C5	6	0.744445847	-4.138368027	-1.839519055
C3	6	-0.925696199	-2.103187395	-0.130431663	C3	6	0.314682277	-2.223911846	-0.340968260
H5	1	-1.004867478	-5.268346502	-1.437102279	H5	1	1.215622466	-5.106314972	-1.985851790
H4	1	-0.687566635	-4.067100916	0.701625155	H4	1	1.482998508	-3.977225053	0.137672912
H8	1	-1.430827245	-3.977227760	-3.531186105	H8	1	-0.136166012	-4.055655943	-3.816333775
C15	6	-0.747668177	-1.426311648	1.182719514	C15	6	0.513419799	-1.593019944	1.005781342
C16	6	-0.377165969	-0.220813851	3.687810995	C16	6	0.940711586	-0.426512253	3.555426377
C17	6	0.101578739	-0.320354327	1.333466001	C17	6	0.012898413	-0.319845622	1.336746366
C18	6	-1.412140432	-1.921094063	2.316975810	C18	6	1.231861123	-2.270406626	2.015035844
C19	6	-1.225821996	-1.320579544	3.559643553	C19	6	1.440140139	-1.695926537	3.263550229
C20	6	0.298889977	0.295402318	2.575356036	C20	6	0.215796755	0.274227028	2.589287656
H3	1	0.630774371	0.058281962	0.464909224	H3	1	-0.564403921	0.221331403	0.604885257
H14	1	-2.090366119	-2.763687973	2.215280638	H14	1	1.634495150	-3.261465777	1.845725757
H15	1	-1.748644961	-1.707065905	4.430851562	H15	1	1.996627429	-2.247133715	4.017598382
C17	1	-0.238632849	0.244268631	4.661489337	H17	1	1.111435993	0.014522445	4.534898601
H21	6	1.212273382	1.506748155	2.717127343	C21	6	-0.354639233	1.655652945	2.888155340
H16	1	1.261558681	1.746729751	3.788295717	H16	1	-0.054605441	1.914405117	3.913347685
C22	6	2.648699601	1.218186984	2.244380654	C22	6	0.222251653	2.733257743	1.950480164
H19	1	3.079860961	0.362116764	2.775127547	H19	1	1.316786127	2.755270077	1.996095723
H20	1	3.291484373	2.088842297	2.420987477	H20	1	-0.151531586	3.726115596	2.228798945
H21	1	2.680188938	0.998380385	1.170833381	H21	1	-0.064655892	2.549999380	0.908503496
C23	6	0.631541676	2.738321177	1.994965906	C23	6	-1.894712047	1.656616180	2.844441808
H18	1	-0.374392453	2.971870388	2.360680348	H18	1	-2.311557526	0.913451834	3.533192393
H22	1	0.561898245	2.570244538	0.913797133	H22	1	-2.262369119	1.423547035	1.838089400
H23	1	1.268015955	3.616639717	2.157811999	H23	1	-2.288589151	2.641413381	3.123556167
O1	8	-1.326334693	-0.027530331	-1.266062220	O1	8	-1.091015368	-0.446085075	-1.276260152
H2	1	-1.550104118	-1.491815289	-3.435273262	H2	1	-1.179166163	-1.822263197	-3.397577035
C7	6	-0.559380709	0.810671352	-2.045937446	C7	6	-0.632539805	0.655491942	-1.975620034
C8	6	0.909131428	2.682144405	-3.511712978	C8	6	0.157116482	2.998701344	-3.270993508
C9	6	-1.063607348	2.102708588	-2.229247808	C9	6	-1.571086575	1.661720255	-2.223016672
C10	6	0.679884284	0.449985185	-2.584665298	C10	6	0.700224375	0.812044376	-2.366956956
C11	6	1.404065723	1.392332302	-3.318646144	C11	6	1.084301368	1.986993659	-3.015732513
C12	6	-0.326384434	3.031890783	-2.959674283	C12	6	-1.170905502	2.829850765	-2.870116225
H1	1	-2.025192749	2.353975887	-1.792970660	H1	1	-2.599222827	1.510325116	-1.908119622
H6	1	1.069125127	-0.551135336	-2.434889255	H6	1	1.424017511	0.030767877	-2.161137823
H7	1	2.366441287	1.109947138	-3.737489913	H7	1	2.122106350	2.110432167	-3.314773174
H9	1	-0.722958286	4.033798644	-3.101040384	H9	1	-1.903390011	3.608896169	-3.064670301
H10	1	1.479008191	3.408165038	-4.084199212	H10	1	0.466190341	3.909601984	-3.775467694

Table 4.28 The folded GS structure (left) and the unfolded GS structure (middle), the TS structure (right), and the XYZ coordinates of **1**(SCF₃).



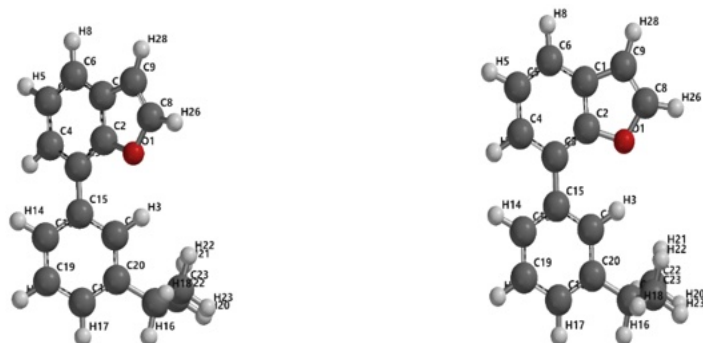
H1	1	-2.219474715	0.766822902	-5.295537729	H1	1	-1.550813419	-1.505509947	-5.526821774
C1	6	-1.935049717	0.746429887	-4.247276303	C1	6	-1.418506169	-1.297208519	-4.469386307
C4	6	-1.188652618	0.703860281	-1.523509292	C4	6	-1.044006452	-0.719252619	-1.669286355
C2	6	-0.812602075	1.451053152	-3.817886949	C2	6	-0.414136719	-0.440336730	-4.039760634
C6	6	-2.688538526	0.022086716	-3.323084054	C6	6	-2.239812776	-1.874778186	-3.506658595
C5	6	-2.317669301	0.006147666	-1.979455492	C5	6	-2.047488020	-1.586362469	-2.161124043
C3	6	-0.433060760	1.425821411	-2.469123671	C3	6	-0.210329248	-0.150157104	-2.680107509
H2	1	-0.217509582	2.021051966	-4.523736671	H2	1	0.244720194	0.026362750	-4.763981257
H6	1	-3.568132365	-0.528319686	-3.645973650	H6	1	-3.038588567	-2.553161829	-3.794508736
H5	1	-2.905941626	-0.556443300	-1.260016668	H5	1	-2.719320798	-2.069324937	-1.465945519
S1	16	1.023183495	2.358447772	-1.967826445	S1	16	1.155702172	1.014379268	-2.441132470
C11	6	2.318110621	1.187892255	-2.494504651	C11	6	2.530699643	-0.170416100	-2.237758244
F1	9	2.339248154	0.988210867	-3.826282080	F1	9	2.747863700	-0.907979290	-3.341631253
F2	9	3.502376557	1.710712386	-2.133825263	F2	9	3.643361715	0.542005937	-1.985490907
F3	9	2.200445583	-0.024446914	-1.922919490	F3	9	2.337893834	-1.028551293	-1.220432497
C7	6	-0.840517553	0.649117963	-0.070677063	C7	6	-0.975781323	-0.502453226	-0.177670166
C8	6	-0.244171877	0.478628245	2.657992193	C8	6	-0.907584968	-0.126756279	2.644838096
C9	6	-1.285714621	1.642126863	0.809053182	C9	6	-1.891870702	-1.147924805	0.681592364
C10	6	-0.100729168	-0.427350627	0.436141758	C10	6	-0.032748859	0.333305244	0.451385535
C12	6	0.208311145	-0.531748089	1.796971070	C12	6	0.019068247	0.535089139	1.833845430
C13	6	-0.983098580	1.554150259	2.168277124	C13	6	-1.855333285	-0.962827363	2.060430863
H3	1	-1.866431272	2.478855364	0.429940293	H3	1	-2.657087704	-1.810572716	0.299881643
H4	1	0.251470074	-1.194536996	-0.249287838	H4	1	0.694301313	0.858580259	-0.144141813
H8	1	-1.328059305	2.328672953	2.848541884	H8	1	-2.580650937	-1.480653523	2.682815752
H9	1	-0.020051796	0.426178229	3.720400464	H9	1	-0.893883346	0.008091934	3.723396140
C14	6	1.016159581	-1.716121240	2.311898023	C14	6	1.077837734	1.460401973	2.420858459
H10	1	1.214687876	-2.366625528	1.449099177	H10	1	1.645000065	1.877188552	1.577863997
C15	6	2.378860085	-1.276658708	2.878996676	C15	6	0.448780241	2.642799030	3.180982858
H7	1	2.965368576	-2.148851631	3.191850543	H7	1	1.224003193	3.338215416	3.523770830
H12	1	2.256339411	-0.626657679	3.753757042	H12	1	-0.103590761	2.300265591	4.064426287
H13	1	2.959222388	-0.725084661	2.131575452	H13	1	-0.249083571	3.197179885	2.543816254
C16	6	0.228857937	-2.545762945	3.342782940	C16	6	2.074084544	0.694799591	3.312035631
H11	1	0.800226232	-3.433975031	3.637212179	H11	1	2.856084752	1.368401065	3.682630580
H14	1	-0.732438124	-2.877149954	2.935116330	H14	1	2.557979018	-0.117425833	2.758387933
H15	1	0.024975868	-1.966534150	4.251316981	H15	1	1.573237314	0.254587081	4.182879535

Table 4.29 The folded GS structure (left) and the unfolded GS structure (middle), the TS structure (right), and the XYZ coordinates of **2**(2H-furan).



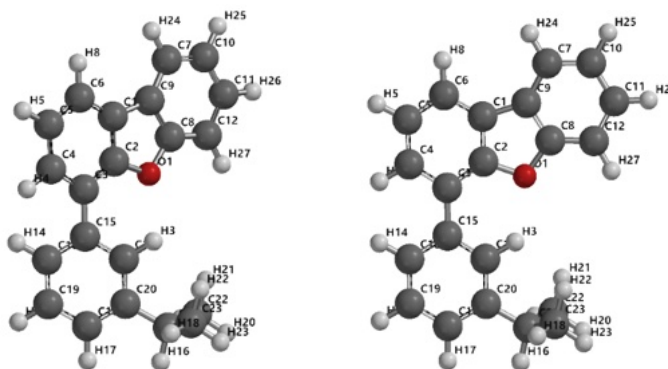
C1	6	0.820986095	2.914925466	2.085363614	C1	6	-0.134690813	3.163618969	1.298126855
C4	6	-0.246344513	2.167090768	-0.353108550	C4	6	1.870770190	1.468996735	2.125285058
C2	6	0.984216056	1.613547767	1.601643188	C2	6	-0.045929692	1.860799114	0.792668756
C6	6	0.119487783	3.856651124	1.345025367	C6	6	0.781557727	3.629419724	2.226783679
C5	6	-0.410808465	3.472233841	0.107835540	C5	6	1.792713273	2.757746189	2.643866001
C3	6	0.451791045	1.183225343	0.377290415	C3	6	0.959896417	0.950274391	1.175304958
H5	1	-0.948185059	4.193319686	-0.501402684	H5	1	2.526766106	3.083275930	3.375523839
H4	1	-0.645578690	1.896262366	-1.326162070	H4	1	2.675919332	0.838256796	2.482360269
H8	1	-0.012635910	4.870459720	1.714605585	H8	1	0.716693650	4.641024334	2.619017938
C15	6	0.587089922	-0.202980263	-0.138623457	C15	6	1.090371616	-0.442007322	0.655502704
C16	6	0.809979801	-2.788456448	-1.212943816	C16	6	1.355169514	-3.086297591	-0.320326154
C17	6	-0.468215191	-0.787452565	-0.857584146	C17	6	0.206011060	-0.969840049	-0.304264074
C18	6	1.762365537	-0.952328267	0.046252072	C18	6	2.119719393	-1.292177689	1.111319764
C19	6	1.866824981	-2.232600559	-0.489914087	C19	6	2.248363130	-2.589644372	0.629633707
C20	6	-0.376861129	-2.072326316	-1.405474556	C20	6	0.321444383	-2.276571217	-0.796485923
H3	1	-1.391410358	-0.225154198	-0.971191694	H3	1	-0.592738712	-0.345755592	-0.677699596
H14	1	2.588418783	-0.528104553	0.605120482	H14	1	2.835993523	-0.951686139	1.849928003
H15	1	2.782211045	-2.801924941	-0.347898351	H15	1	3.053148465	-3.219806035	1.000128001
H17	1	0.904585672	-3.790136209	-1.627075608	H17	1	1.463664479	-4.102885408	-0.692082499
C21	6	-1.537632637	-2.687510940	-2.177604915	C21	6	-0.661543404	-2.804263207	-1.834560711
H16	1	-1.194254742	-3.663822556	-2.546928342	H16	1	-0.372029097	-3.841420555	-2.053893951
C22	6	-2.758574857	-2.941740682	-1.273023328	C22	6	-2.104949976	-2.833917440	-1.298521205
H19	1	-2.493113272	-3.571942336	-0.417413760	H19	1	-2.171409493	-3.412312527	-0.370542233
H20	1	-3.557147953	-3.441882595	-1.834406811	H20	1	-2.780903359	-3.287160036	-2.033843306
H21	1	-3.164507732	-2.000935942	-0.882245488	H21	1	-2.471654969	-1.822077641	-1.088790334
C23	6	-1.931245139	-1.844423785	-3.405236128	C23	6	-0.581273952	-2.014404879	-3.154827871
H18	1	-1.072920231	-1.677391276	-4.065253085	H18	1	0.434660809	-2.030550730	-3.564762883
H22	1	-2.320884559	-0.863572539	-3.107421084	H22	1	-0.864095429	-0.965510603	-3.007052771
H23	1	-2.714867646	-2.349278280	-3.982915687	H23	1	-1.259596102	-2.441683461	-3.903552415
O1	8	1.687789731	0.810912028	2.461163281	O1	8	-1.042622795	1.598479932	-0.116749146
C7	6	2.221693133	1.650541648	3.515443035	C7	6	-2.006459617	2.676752423	-0.050330832
H6	1	3.292460469	1.790356302	3.322806152	H6	1	-2.857367211	2.331962202	0.550776742
H7	1	2.101146743	1.109706764	4.456967394	H7	1	-2.347872559	2.873325811	-1.069185419
C8	6	1.452896625	2.990780682	3.457468690	C8	6	-1.287537291	3.864371941	0.617205689
H9	1	2.121876834	3.849060355	3.582694512	H9	1	-1.943359212	4.402672963	1.309349583
H10	1	0.689367825	3.054891391	4.244148319	H10	1	-0.926829381	4.588994938	-0.125310224

Table 4.30 The folded GS structure (left) and the unfolded GS structure (middle), the TS structure (right), and the XYZ coordinates of **2**(furan).



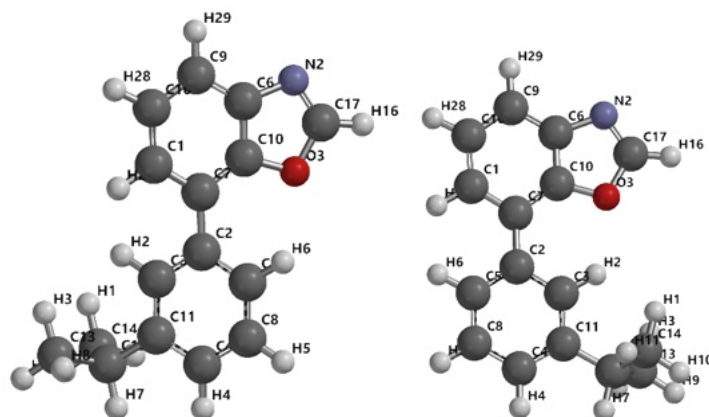
C1	6	-1.345223640	-1.904850482	-3.191389684	C1	6	0.322708205	3.473905115	1.013345083
C4	6	0.946750571	-1.069639905	-1.857979757	C4	6	1.356639808	1.426137076	2.557762059
C2	6	-1.375006382	-1.482728527	-1.848215695	C2	6	0.211578326	2.122256664	0.624855416
C6	6	-0.124079800	-1.909840607	-3.880761273	C6	6	0.978233004	3.804427203	2.205623016
C5	6	1.011228902	-1.489838645	-3.196625162	C5	6	1.488507232	2.760557284	2.966689516
C3	6	-0.253017903	-1.046106122	-1.130417098	C3	6	0.720216762	1.036436409	1.364294203
H5	1	1.973757309	-1.491731574	-3.700879514	H5	1	1.998581697	2.972350476	3.902415593
H4	1	1.862075373	-0.774335805	-1.354110682	H4	1	1.760395430	0.662754425	3.211776554
H8	1	-0.066838644	-2.231983656	-4.916570591	H8	1	1.079032814	4.838268606	2.522859281
C15	6	-0.308250915	-0.583760790	0.278482551	C15	6	0.618200759	-0.395221005	0.963727183
C16	6	-0.338556386	0.297805075	2.941976861	C16	6	0.416903147	-3.118685641	0.241744613
C17	6	0.487489251	0.494676034	0.695217061	C17	6	-0.092541484	-0.803357108	-0.179619375
C18	6	-1.133176681	-1.213313428	1.226469810	C18	6	1.237184539	-1.401319429	1.733174885
C19	6	-1.142201658	-0.773041974	2.546946932	C19	6	1.130612639	-2.741200739	1.379691040
C20	6	0.487070954	0.950175045	2.019126026	C20	6	-0.197148830	-2.149109438	-0.556181831
H3	1	1.103335059	1.002341650	-0.042346817	H3	1	-0.573577652	-0.054816589	-0.794404515
H14	1	-1.756743658	-2.048940662	0.928094319	H14	1	1.818285084	-1.146053368	2.611890004
H15	1	-1.777948412	-1.269759934	3.275489636	H15	1	1.613014818	-3.497231501	1.994228044
H17	1	-0.355920179	0.634490667	3.976361460	H17	1	0.342579556	-4.169217674	-0.030709095
C21	6	1.347201237	2.133174519	2.445887549	C21	6	-0.941175703	-2.550063719	-1.824726428
H16	1	1.176496247	2.283097936	3.520838464	H16	1	-0.950234577	-3.648444242	-1.856703362
C22	6	2.849631394	1.854304068	2.252413017	C22	6	-2.406089125	-2.077440917	-1.824458743
H19	1	3.156447198	0.946460336	2.783157089	H19	1	-2.943467644	-2.452128170	-0.946392738
H20	1	3.449870287	2.690703165	2.630242537	H20	1	-2.925416871	-2.435256574	-2.721678793
H21	1	3.096194272	1.721800334	1.192116896	H21	1	-2.473526284	-0.983225282	-1.816238456
C23	6	0.931528016	3.431378488	1.727916377	C23	6	-0.202018250	-2.059407711	-3.084850932
H18	1	-0.128001443	3.654986605	1.893400806	H18	1	0.828018964	-2.432038001	-3.110121790
H22	1	1.091261078	3.355423507	0.645621082	H22	1	-0.160684427	-0.964096962	-3.116833672
H23	1	1.522193878	4.280370878	2.092584828	H23	1	-0.712820890	-2.402984281	-3.992524569
O1	8	-2.661482851	-1.534957933	-1.371550197	O1	8	-0.463397944	2.052057289	-0.572523012
C8	6	-3.437542566	-1.991448177	-2.406927719	C8	6	-0.776445293	3.340390501	-0.927465989
C9	6	-2.711119385	-2.232295715	-3.524489360	C9	6	-0.331877662	4.239354680	-0.019546258
H26	1	-4.488783831	-2.088616348	-2.179226483	H26	1	-1.320800103	3.439107338	-1.855164630
H28	1	-3.088636691	-2.593998022	-4.470853272	H28	1	-0.449469939	5.313295287	-0.063932354

Table 4.31 The folded GS structure (left) and the unfolded GS structure (middle), the TS structure (right), and the XYZ coordinates of **2**(benzofuran).



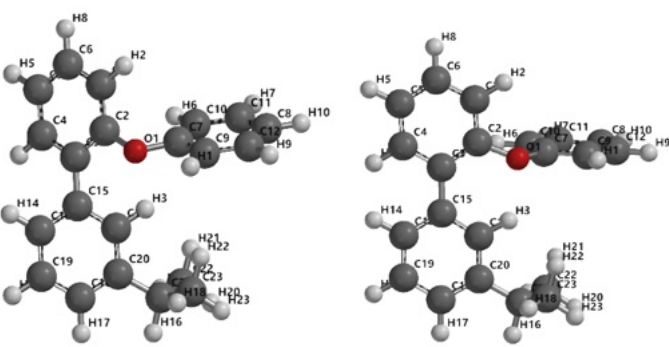
C1	6	0.748099720	-1.002202452	-2.716300334	C1	6	0.754562411	-0.805679507	-2.779623079
C4	6	2.975546906	-0.513088534	-1.135788212	C4	6	2.998165002	0.044309507	-1.412071975
C2	6	0.642859684	-0.354362927	-1.470576768	C2	6	0.680417417	-0.367006320	-1.441065795
C6	6	2.002757685	-1.416797073	-3.174351608	C6	6	1.981590288	-0.816941834	-3.444384515
C5	6	3.110568792	-1.165419985	-2.368712078	C5	6	3.100139096	-0.384425872	-2.739565815
C3	6	1.734785468	-0.078026011	-0.638277649	C3	6	1.786591303	0.074732433	-0.690623446
H5	1	4.097253640	-1.483431543	-2.693399751	H5	1	4.074026213	-0.375938883	-3.220842657
H4	1	3.858225113	-0.354862879	-0.523450119	H4	1	3.909098769	0.369584091	-0.924550392
H8	1	2.109137707	-1.921720147	-4.130263468	H8	1	2.058349652	-1.149356032	-4.475546514
C15	6	1.619129184	0.627276169	0.662431784	C15	6	1.728988473	0.535996313	0.726481444
C16	6	1.431238417	1.938655675	3.134752430	C16	6	1.630792614	1.408709843	3.415154210
C17	6	0.529908330	0.403495762	1.518905971	C17	6	0.520999123	0.581623701	1.445923786
C18	6	2.617598767	1.529159964	1.068879803	C18	6	2.895762402	0.945200842	1.405010087
C19	6	2.522032284	2.176834829	2.296888827	C19	6	2.844046501	1.375176330	2.725935673
C20	6	0.418886575	1.049345527	2.755937280	C20	6	0.453649536	1.008939724	2.778082595
H3	1	-0.243546114	-0.291161855	1.209328963	H3	1	-0.393516836	0.276673549	0.959396707
H14	1	3.453843711	1.739595349	0.408357716	H14	1	3.860243447	0.930653490	0.910715220
H15	1	3.295185496	2.878585317	2.599231443	H15	1	3.759841856	1.685637175	3.222714088
H17	1	1.361669178	2.453069099	4.090796267	H17	1	1.599992250	1.745057395	4.449198497
C21	6	-0.771515628	0.793301255	3.671495197	C21	6	-0.880952884	1.031362120	3.513793192
H16	1	-0.627156086	1.415083901	4.566079825	H16	1	-0.684126617	1.404348839	4.528493580
C22	6	-2.099051063	1.225043965	3.021088034	C22	6	-1.884599067	1.996191907	2.854340451
H19	1	-2.070614746	2.279860546	2.727054921	H19	1	-1.475815401	3.010572167	2.790061221
H20	1	-2.933421687	1.085545554	3.718948671	H20	1	-2.816594169	2.038302517	3.430845235
H21	1	-2.313753166	0.635025931	2.121970898	H21	1	-2.136020374	1.673849883	1.836925229
C23	6	-0.833911995	-0.672650621	4.140312211	C23	6	-1.481503972	-0.380775540	3.648988624
H18	1	0.099168185	-0.970567105	4.630971723	H18	1	-0.786732504	-1.061287277	4.153455955
H22	1	-1.002275091	-1.356428763	3.299745503	H22	1	-1.712067966	-0.808698259	2.666216833
H23	1	-1.655137754	-0.814412662	4.853229193	H23	1	-2.412335876	-0.350707624	4.228124368
O1	8	-0.665439253	-0.008343502	-1.197881707	O1	8	-0.624502002	-0.433740465	-0.987324002
C8	6	-1.409303193	-0.436393009	-2.273039630	C8	6	-1.385160340	-0.913080694	-2.027052480
C9	6	-0.603356447	-1.056542284	-3.244252201	C9	6	-0.598257135	-1.164662107	-3.160570735
C7	6	-1.202784019	-1.549493733	-4.409040482	C7	6	-1.212099675	-1.658711361	-4.316339850
C10	6	-2.581017023	-1.407863848	-4.561435105	C10	6	-2.587651829	-1.880827595	-4.297413833
C11	6	-3.359813443	-0.785064545	-3.571573053	C11	6	-3.348643179	-1.617016559	-3.146585797
C12	6	-2.782905294	-0.285342528	-2.402615227	C12	6	-2.755477134	-1.124579905	-1.983137959
H24	1	-0.607600712	-2.032906938	-5.178867917	H24	1	-0.630666452	-1.864853586	-5.210901357
H25	1	-3.062785800	-1.784459851	-5.459237147	H25	1	-3.081437675	-2.264246124	-5.185743608
H26	1	-4.432036875	-0.688285607	-3.717112945	H26	1	-4.419538271	-1.799141785	-3.160094418
H27	1	-3.370469454	0.199949562	-1.630231256	H27	1	-3.329556784	-0.915244286	-1.086418609

Table 4.32 The folded GS structure (left) and the unfolded GS structure (middle), the TS structure (right), and the XYZ coordinates of **2**(azole).



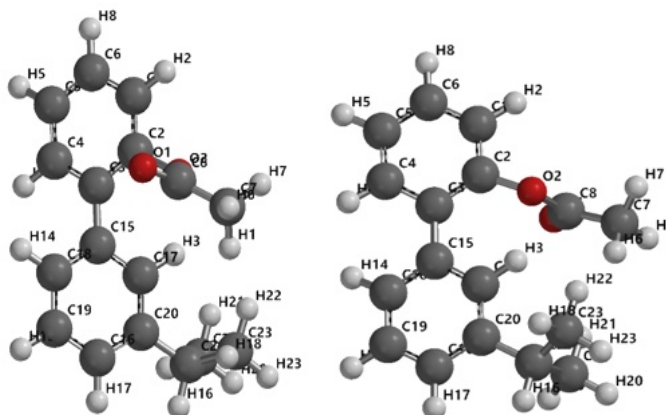
C1	6	-0.904678343	-0.113580976	-2.277592769	C1	6	0.015496470	2.316539711	-2.337117916
C6	6	0.736250200	1.570135155	-3.725296266	C6	6	0.067470431	-0.041369500	-3.748976149
C7	6	-0.094497406	0.762082511	-1.534045381	C7	6	0.023380429	1.140820994	-1.559007580
C16	6	-0.899203911	-0.152001815	-3.681677481	C16	6	0.036322183	2.325442077	-3.739390085
C9	6	-0.079128765	0.685557417	-4.434568219	C9	6	0.063437647	1.146935715	-4.478754951
C10	6	0.706378762	1.592289698	-2.324726617	C10	6	0.048120555	-0.023637065	-2.345629164
O3	8	1.620043203	2.538566835	-1.913485384	O3	8	0.061665922	-1.343424563	-1.938215469
C17	6	2.133911621	3.024074249	-3.085768447	C17	6	0.087064906	-2.055198769	-3.106320809
N2	7	1.670992807	2.510846334	-4.173548230	N2	7	0.092067849	-1.367012056	-4.193911569
H27	1	-1.580600816	-0.771260831	-1.739154574	H27	1	-0.010822513	3.277428428	-1.837392404
H28	1	-1.559599360	-0.851156982	-4.186900817	H28	1	0.030506781	3.282759462	-4.252768219
H29	1	-0.066365253	0.661081841	-5.519099511	H29	1	0.080212975	1.137836028	-5.563343421
H16	1	2.883447916	3.796536355	-2.983441983	H16	1	0.098203338	-3.130807757	-2.997668023
C2	6	-0.094496112	0.782752459	-0.051768812	C2	6	0.008526633	1.167415371	-0.071056541
C4	6	-0.138665439	0.776018433	2.750218859	C4	6	-0.021071093	1.221716478	2.751812047
C3	6	-0.213244328	-0.416424066	0.667592159	C3	6	-0.034693122	-0.015870241	0.688415113
C5	6	0.012384779	1.988706788	0.662029740	C5	6	0.039343703	2.387540062	0.633268364
C8	6	-0.013585194	1.979258506	2.053371197	C8	6	0.022128374	2.410908977	2.022925584
C11	6	-0.236268888	-0.442021688	2.066926823	C11	6	-0.047570403	-0.008615489	2.089202872
H2	1	-0.263277747	-1.350524113	0.114813170	H2	1	-0.058431718	-0.969886351	0.179826912
H6	1	0.104285929	2.928058238	0.126958879	H6	1	0.081827896	3.332867063	0.104900194
H5	1	0.060942315	2.915698172	2.600172619	H5	1	0.045290699	3.365418588	2.542417819
H4	1	-0.154273596	0.781307647	3.837984058	H4	1	-0.031593423	1.250173521	3.839109737
C12	6	-0.339370618	-1.755485518	2.831703844	C12	6	-0.078749421	-1.313540795	2.875931042
H7	1	-0.383863450	-1.501198152	3.899623555	H7	1	-0.120495043	-1.044980216	3.940604509
C13	6	-1.626609697	-2.529065381	2.490377630	C13	6	-1.333560407	-2.150585297	2.564932416
H3	1	-1.644130522	-2.832836955	1.436841230	H3	1	-1.353399535	-2.467368720	1.515477432
H8	1	-2.517833242	-1.920077523	2.677631014	H8	1	-2.249211144	-1.581449464	2.759738695
H9	1	-1.700574754	-3.439198593	3.097355863	H9	1	-1.353424517	-3.054731362	3.184969847
C14	6	0.907807093	-2.634766398	2.619982062	C14	6	1.203831293	-2.139152801	2.660162264
H1	1	1.006494609	-2.938432437	1.571092352	H1	1	1.306862589	-2.446579296	1.612856969
H10	1	0.845667047	-3.545761157	3.227166793	H10	1	1.185066513	-3.046812591	3.275109704
H11	1	1.821661160	-2.099178051	2.899232644	H11	1	2.096195313	-1.562780195	2.927890780

Table 4.33 The folded GS structure (left) and the unfolded GS structure (middle), the TS structure (right), and the XYZ coordinates of **2**(OPh).



C1	6	-1.347735427	-2.071174431	-2.53963756	C1	6	-0.582253569	-2.312706220	-2.634727012
C4	6	-0.883953675	-3.506841902	-0.20815546	C4	6	0.889251859	-3.484887025	-0.621575302
C2	6	-1.161531018	-1.401944705	-1.32743315	C2	6	-0.421403901	-1.658778353	-1.409902725
C6	6	-1.287554083	-3.461977516	-2.58537362	C6	6	-0.003167956	-3.554129846	-2.861950269
C5	6	-1.055893887	-4.183462994	-1.41300661	C5	6	0.744445847	-4.138368027	-1.839519055
C3	6	-0.925696199	-2.103187395	-0.13043166	C3	6	0.314682277	-2.223911846	-0.340968260
H5	1	-1.004867478	-5.268346502	-1.43710227	H5	1	1.215622466	-5.106314972	-1.985851790
H4	1	-0.687566635	-4.067100916	0.70162515	H4	1	1.482998508	-3.977225053	0.137672912
H8	1	-1.430827245	-3.977227760	-3.53118610	H8	1	-0.136166012	-4.055655943	-3.816333775
C15	6	-0.747668177	-1.426311648	1.18271951	C15	6	0.513419799	-1.593019944	1.005781342
C16	6	-0.377165969	-0.220813851	3.68781099	C16	6	0.940711586	-0.426512253	3.555426377
C17	6	0.101578739	-0.320354327	1.33346600	C17	6	0.012898413	-0.319845622	1.336746366
C18	6	-1.412140432	-1.921094063	2.31697581	C18	6	1.231861123	-2.270406626	2.015035844
C19	6	-1.225821996	-1.320579544	3.55964355	C19	6	1.440140139	-1.695926537	3.263550229
C20	6	0.298889977	0.295402318	2.57535603	C20	6	0.215796755	0.274227028	2.589287656
H3	1	0.630774371	0.058281962	0.464909224	H3	1	-0.564403921	0.221331403	0.604885257
H14	1	-2.090366119	-2.763687973	2.21528063	H14	1	1.634495150	-3.261465777	1.845725757
H15	1	-1.748644961	-1.707065905	4.43085156	H15	1	1.996627429	-2.247133715	4.017598382
H17	1	-0.238632849	0.244268631	4.66148933	H17	1	1.111435993	0.014522445	4.534898601
C21	6	1.212273382	1.506748155	2.71712734	C21	6	-0.354639233	1.655652945	2.888155340
H16	1	1.261558681	1.746729751	3.78829571	H16	1	-0.054605441	1.914405117	3.913347685
C22	6	2.648699601	1.218186984	2.24438065	C22	6	0.222251653	2.733257743	1.950480164
H19	1	3.079860961	0.362116764	2.77512754	H19	1	1.316786127	2.755270077	1.996095723
H20	1	3.291484373	2.088842297	2.42098747	H20	1	-0.151531586	3.726115596	2.228798945
H21	1	2.680188938	0.998380385	1.17083338	H21	1	-0.064655892	2.549999380	0.908503496
C23	6	0.631541676	2.738321177	1.99496590	C23	6	-1.894712047	1.656616180	2.844441808
H18	1	-0.374392453	2.971870388	2.36068034	H18	1	-2.311557526	0.913451834	3.533192393
H22	1	0.561898245	2.570244538	0.91379713	H22	1	-2.262369119	1.423547035	1.838089400
H23	1	1.268015955	3.616639717	2.15781199	H23	1	-2.288589151	2.641413381	3.123556167
O1	8	-1.326334693	-0.027530331	-1.26606222	O1	8	-1.091015368	-0.446085075	-1.276260152
H2	1	-1.550104118	-1.491815289	-3.43527326	H2	1	-1.179166163	-1.822263197	-3.397577035
C7	6	-0.559380709	0.810671352	-2.04593744	C7	6	-0.632539805	0.655491942	-1.975620034
C8	6	0.909131428	2.682144405	-3.51171297	C8	6	0.157116482	2.998701344	-3.270993508
C9	6	-1.063607348	2.102708588	-2.22924780	C9	6	-1.571086575	1.661720255	-2.223016672
C10	6	0.679884284	0.449985185	-2.58466529	C10	6	0.700224375	0.812044376	-2.366956956
C11	6	1.404065723	1.392332302	-3.31864614	C11	6	1.084301368	1.986993659	-3.015732513
C12	6	-0.326384434	3.031890783	-2.95967428	C12	6	-1.170905502	2.829850765	-2.870116225
H1	1	-2.025192749	2.353975887	-1.79297066	H1	1	-2.599222827	1.510325116	-1.908119622
H6	1	1.069125127	-0.551135336	-2.43488925	H6	1	1.424017511	0.030767877	-2.161137823
H7	1	2.366441287	1.109947138	-3.73748991	H7	1	2.122106350	2.110432167	-3.314773174
H9	1	-0.722958286	4.033798644	-3.10104038	H9	1	-1.903390011	3.608896169	-3.064670301
H10	1	1.479008191	3.408165038	-4.08419921	H10	1	0.466190341	3.909601984	-3.775467694

Table 4.34 The folded GS structure (left) and the unfolded GS structure (middle), the TS structure (right), and the XYZ coordinates of **2**(OCOCH₃).



C1	6	-3.105359793	1.093010023	1.935945658	C1	6	0.312760707	3.258575647	1.820502831
C4	6	-1.311553981	-0.781512125	2.934798560	C4	6	2.061766619	1.254372139	2.545827860
C2	6	-1.830851527	0.972255700	1.389376594	C2	6	0.311610808	2.043168769	1.139527564
C6	6	-3.487063249	0.263571409	2.989155058	C6	6	1.180308052	3.474608846	2.884009702
C5	6	-2.583669611	-0.672575653	3.493560836	C5	6	2.066650966	2.458943134	3.240437804
C3	6	-0.907003841	0.029541464	1.861974993	C3	6	1.174152006	0.978388328	1.482357873
H5	1	-2.869525770	-1.320608483	4.317319602	H5	1	2.766913303	2.602033986	4.058474734
H4	1	-0.612484494	-1.520873218	3.315958576	H4	1	2.783587974	0.501002613	2.837254539
H8	1	-4.482328843	0.354461106	3.414849790	H8	1	1.168807188	4.421441487	3.415756066
C15	6	0.453670602	-0.128576822	1.274123777	C15	6	1.173541705	-0.375043041	0.842867586
C16	6	3.005159166	-0.510168617	0.188237209	C16	6	1.117440551	-2.975508071	-0.279226220
C17	6	0.613587885	-0.514075913	-0.063721541	C17	6	0.504071432	-0.650723377	-0.363675450
C18	6	1.594416582	0.057574329	2.068757215	C18	6	1.833755189	-1.456489372	1.463249091
C19	6	2.863279255	-0.129248350	1.523280890	C19	6	1.824206565	-2.727110619	0.897504133
C20	6	1.882611664	-0.713454091	-0.623899316	C20	6	0.432032525	-1.936293735	-0.913340376
H3	1	-0.275064577	-0.684762129	-0.664916261	H3	1	0.018089766	0.156657397	-0.887706485
H14	1	1.481636128	0.360965713	3.106103170	H14	1	2.346110815	-1.324458897	2.409068389
H15	1	3.745535513	0.023637699	2.139697865	H15	1	2.356219128	-3.536050994	1.391876009
H17	1	3.999567192	-0.657898465	-0.227885875	H17	1	1.086219124	-3.979846239	-0.696382292
C21	6	2.039364231	-1.171342628	-2.069203148	C21	6	-0.458026138	-2.214810471	-2.119589822
H16	1	3.117002446	-1.198025083	-2.282052105	H16	1	-0.208356337	-3.220935136	-2.482636103
C22	6	1.493244580	-2.598102703	-2.268818224	C22	6	-1.938597860	-2.239022146	-1.681886456
H19	1	1.977048661	-3.305410182	-1.586356768	H19	1	-2.104309775	-2.976603989	-0.889053856
H20	1	1.667841287	-2.939141806	-3.296369249	H20	1	-2.597301472	-2.485336364	-2.523741848
H21	1	0.413654318	-2.637822268	-2.081947544	H21	1	-2.246300048	-1.264208733	-1.286075103
C23	6	1.395478318	-0.190640669	-3.066494683	C23	6	-0.241501845	-1.239081070	-3.288591884
H18	1	1.819354702	0.814968715	-2.962057016	H18	1	0.800096531	-1.246484966	-3.627484569
H22	1	0.311897377	-0.119535064	-2.916395555	H22	1	-0.491375588	-0.207801385	-3.013690163
H23	1	1.565026414	-0.523607459	-4.097365790	H23	1	-0.879152700	-1.512989263	-4.137432445
O2	8	-1.431122457	1.906352056	0.424061638	O2	8	-0.548299323	1.973373710	0.033830387
C8	6	-1.77577131	1.702328424	-0.882809422	C8	6	-1.885625096	1.727034860	0.239312965
H2	1	-3.779446388	1.845745196	1.539310282	H2	1	-0.379135821	4.028492482	1.493930904
O1	8	-2.385900591	0.736952132	-1.277154623	O1	8	-2.368521198	1.497102109	1.317020022
C7	6	-1.256730405	2.833877762	-1.733684513	C7	6	-2.614669059	1.787480571	-1.081843047
H1	1	-1.472208996	3.800101801	-1.269167824	H1	1	-3.677556609	1.603890698	-0.920706383
H6	1	-1.703519824	2.778263208	-2.727012565	H6	1	-2.212240467	1.035841411	-1.769432667
H7	1	-0.167964841	2.743774989	-1.819199689	H7	1	-2.467371618	2.766389576	-1.550313291

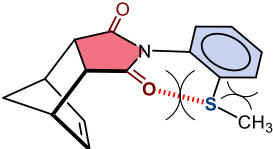
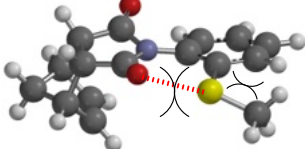
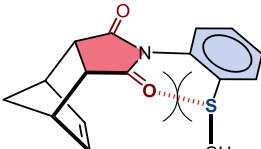
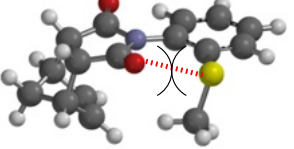
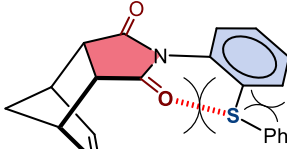
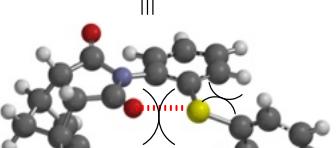
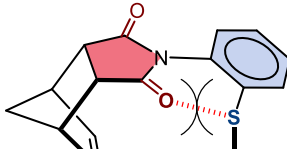
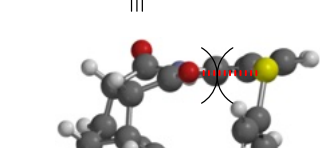
4.5.9 Energy analysis for TSs of acyclic chalcogen rotors.

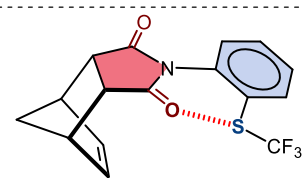
The acyclic chalcogen rotors could have two significantly different transition states (TS): the planar TSI and the perpendicular TSII. The planar TSI was supposed to have the ChB interactions since the σ^* of chalcogen atoms especially sulfur atom aligned with the lone pair of the carbonyl oxygen (the following NBO calculations showed the possibilities), however the *ortho*-group such as OCH₃ or SCH₃ could have extra repulsion against the benzene ring. For sulfur rotors, the perpendicular TSII was more stable than the planar TSI except the TSII of SCH₃ was slightly more unstable than the TSI. For all the oxygen rotors, TSII was always much more stable and the differences between two TSs were larger than in sulfur rotors since C-S-C bond stretched further to reduce part of the steric interactions (C-S-C in rotor SCH₃: 1.811+1.832 Å, C-O-C in rotor OCH₃: 1.347+1.415 Å.) For example, **2**(OPh) was 3.74 kcal/mol more stable in perpendicular TSII than in planar TSI. When the difference got larger, TSII would always be the unique TS in rotor **2**(OCF₃) and **2**(OCOCH₃). With being constrained in TSI, fatal error of geometry optimization occurred; without being constrained in TSI, all the geometries in beginning setup would flip into TSII when the most stable TS was finally computed. Overall, all the acyclic chalcogen rotors did not show very strong stabilizing interactions, therefore they just spread on the steric trendline or slightly dropped off. **Table 4.35** listed the ΔE and ΔG of the modelled planar TSI and perpendicular TSII. **Table 4.36** showed the modelled interaction angles of (C)O...Ch-C of all the chalcogen rotors in this study, cyclic rotors were equally restricted in TSI.

The XYZ coordinates of planar TSI of the acyclic rotors were attached in Table S35-37, perpendicular TSII were shown in section 7. For the convenience, rotors **1**(SCH₃)

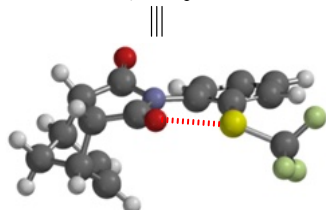
and 2(OCH₃), which were reported earlier,¹ were presented in both TSI and TSII in **Table 4.37-4.39**.

Table 4.35 The ΔE and ΔG of the modelled planar TSI and perpendicular TSII.

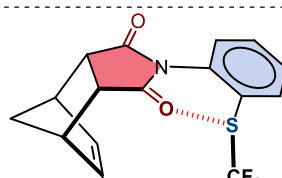
linear TSI	perpendicular TSII	$E_{\text{TSII-TSI}}$ $G_{\text{TSII-TSI}}^*627.5$
 rotor 2(SCH₃) in TSI  E: -767023.43 kcal/mol G: -1222.09535 au	 rotor 2(SCH₃) in TSII  -767022.46 kcal/mol = -0.03kcal/mol -1222.09425 au = +0.69 kcal/mol	
 rotor 2(SCH₃) in TSI  E: -887369.33 kcal/mol G: -1413.83280 au	 rotor 2(SCH₃) in TSII  -887369.94 kcal/mol = -0.61 kcal/mol -1413.83387 au = -0.67 kcal/mol	



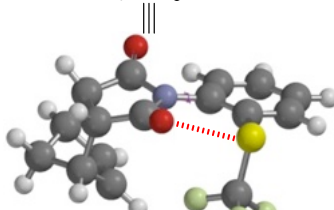
rotor 1(SCF₃) in TSI



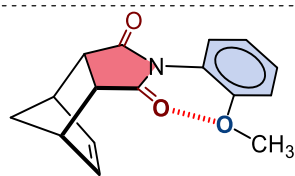
E: -953901.24 kcal/mol
G: -1519.93090 au



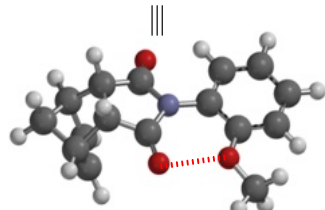
rotor 1(SCF₃) in TSII



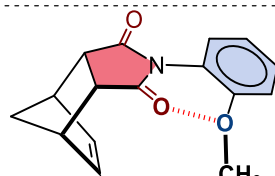
-953901.78 kcal/mol = -0.54 kcal/mol
-1519.93348 au = -1.62 kcal/mol



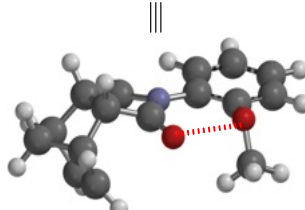
rotor 2(OCH₃) in TSI



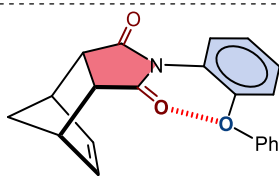
E: -564350.67 kcal/mol
G: -899.112722 au



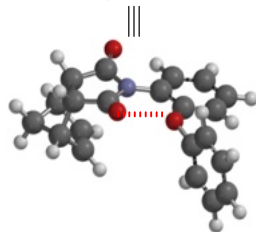
rotor 2(OCH₃) in TSII



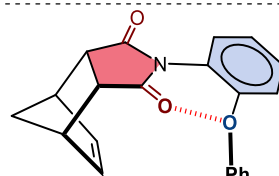
-564352.22 kcal/mol = -1.55 kcal/mol
-899.115024 au = -1.45 kcal/mol



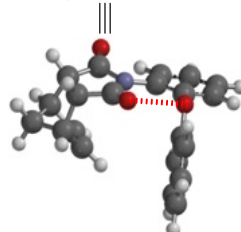
rotor 2(OPh) in TSI



E: -684699.21 kcal/mol
G: -1090.85479 au



rotor 2(OPh) in TSII



-684702.95 kcal/mol = -3.74 kcal/mol
-1090.85888 au = -2.57 kcal/mol

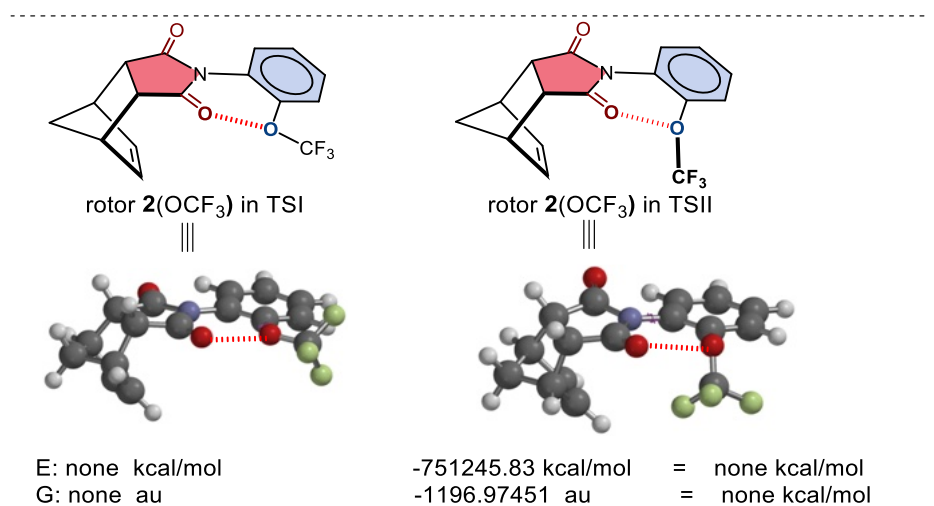


Table 4.36 The interaction angles of chalcogen rotors.

rotors 1 R-groups	Angle of O---Ch- C in planar TSI (degree)	Angle of O---Ch-C in perpendicular TSII (degree)	Distance of O--- Ch-C (Å)
2 (OCH ₃)	162.0	74.0	2.565
2 (OPh)	161.0	75.0	2.527
2 (OCF ₃)	none	89.7	2.524
2 (OCOCH ₃)	none	74.7	2.579
1 (SCF ₃)	159.0	87.7	2.783
1 (SCH ₃)	160.0	76.0	2.591 ^a /2.784
1 (SPh)	162.5	77.1	2.814
2 (2H-furan)	146.6	none	2.51
2 (benzofuran)	151.4	none	2.50
2 (furan)	152.3	none	2.503
2 (oxazole)	157.7	none	2.512
1 (benzothiofuran)	177.8	none	2.535
1 (thiofuran)	177.7	none	2.546
1 (thiazole)	175.1	none	2.58

^aDistance was measured in planar TSI while other acyclic rotors provided the interaction distances in perpendicular TSII.

Table 4.37 XYZ coordinates of planar TSI and perpendicular TSII of rotor **1**(SCH₃).

TSI of SCH ₃				TSII of SCH ₃			
1	0.946429528	-1.141206851	-5.063835274	1	0.952042461	-1.077232698	-5.340117481
6	0.817622833	-0.956400579	-4.002423199	6	0.880791806	-1.017550455	-4.259318898
6	0.515794544	-0.635772961	-1.203838245	6	0.644126585	-0.910244179	-1.411059898
6	-0.161697877	-1.636832880	-3.298253448	6	-0.199431805	-1.573649267	-3.596949714
6	1.591870420	-0.026848437	-3.329681170	6	1.839002018	-0.370315804	-3.499615348
6	1.439830305	0.109157506	-1.959200025	6	1.713807917	-0.323673597	-2.120274273
6	-0.411021075	-1.456035677	-1.925458253	6	-0.373763038	-1.539819879	-2.199496696
1	-0.777540688	-2.330937727	-3.850426086	1	-0.977455568	-2.056520258	-4.174599079
1	2.329610317	0.576571420	-3.846988329	1	2.696907317	0.105001902	-3.963772781
1	2.091756403	0.799660367	-1.456089785	1	2.494800351	0.167993952	-1.573800158
7	0.606763902	-0.444663760	0.233841716	7	0.685754263	-0.732939530	0.038070474
6	1.753025985	0.127310786	0.878142788	6	1.768908641	-0.091001571	0.729547356
6	1.393406378	0.459611325	2.304056058	6	1.343164245	0.240422769	2.135392152
6	0.026793906	-0.180548063	2.535291821	6	-0.016555020	-0.417880457	2.314681006
6	-0.297764295	-0.876667000	1.238893353	6	-0.277307261	-1.145210547	1.018987602
1	2.183599834	0.102596634	2.965079930	1	2.113320439	-0.099095416	2.828837639
8	2.837563667	0.324274822	0.391723542	8	2.868309977	0.170104535	0.307451020
8	-1.165418539	-1.698463864	1.110772467	8	-1.143460372	-1.961221740	0.881167314
6	-0.903837067	1.054073424	2.879466267	6	-0.980441400	0.803710965	2.606516115
1	-1.844221796	0.764933253	3.344604211	1	-1.935286703	0.505165533	3.034930224
1	-0.005771103	-0.911172982	3.343824769	1	-0.072395047	-1.138314562	3.131173606
6	1.121920647	2.001883074	2.555944587	6	1.042587050	1.779797102	2.359282314
1	2.031413798	2.575333143	2.723990969	1	1.936077351	2.367862722	2.558845916
6	0.106757384	1.874730827	3.717982943	6	-0.019135812	1.650219777	3.477941268
1	0.496551287	1.333009874	4.585493478	1	0.341752138	1.124972059	4.367704427
1	-0.292393629	2.839672524	4.036089835	1	-0.446357956	2.612268594	3.766739968
6	0.201550498	2.487971932	1.447783558	6	0.164111692	2.240056091	1.206762284
1	0.517925100	3.078756536	0.597063033	1	0.508355606	2.828659863	0.365457980
6	-0.995246401	1.922754713	1.637680081	6	-1.031548813	1.659383786	1.352665278
1	-1.849855616	1.958717040	0.973323015	1	-1.859591218	1.682352575	0.654817727
16	-1.955511803	-2.173186481	-1.310320176	16	-1.913187848	-2.382586334	-1.761382523
6	-2.911875021	-2.436821023	-2.851066167	6	-3.005905099	-0.971989565	-1.366670764
1	-2.942137167	-1.542064575	-3.474356327	1	-2.736920509	-0.509024939	-0.417026861
1	-3.920799125	-2.649974723	-2.491986153	1	-4.012789441	-1.384862166	-1.280988702
1	-2.575095590	-3.293421668	-3.437125732	1	-2.992286893	-0.234839316	-2.171898493

Table 4.38 XYZ coordinates of planar TSI and perpendicular TSII of rotor 2(OCH₃).

TSI of OCH ₃				TSII of OCH ₃			
1	0.956612726	-1.454635892	-5.296570879	1	0.234813315	-0.199155611	-5.203583279
6	0.872712857	-1.234326581	-4.237334219	6	0.298190176	-0.299250685	-4.124767729
6	0.583361608	-0.625666342	-1.471756453	6	0.434147311	-0.575506621	-1.282182485
6	-0.249332861	-1.643499339	-3.532277722	6	-0.665467204	-1.009926460	-3.423790941
6	1.877730931	-0.565481984	-3.559547261	6	1.334211749	0.285985903	-3.402169512
6	1.728337378	-0.275703754	-2.207803885	6	1.395869704	0.153884230	-2.018985140
6	-0.403436978	-1.386840078	-2.163795584	6	-0.624255928	-1.150091402	-2.030156523
1	-1.020531283	-2.200228280	-4.047114749	1	-1.511471922	-1.457982661	-3.935509760
1	2.781819497	-0.250857234	-4.068947353	1	2.106613351	0.859968581	-3.903524046
1	2.515585630	0.272689186	-1.725861436	1	2.225982912	0.622049228	-1.520981908
7	0.520910810	-0.238067044	-0.065629518	7	0.524997366	-0.579103461	0.159193774
6	1.451327771	0.690539990	0.499016032	6	1.641925687	-0.019081730	0.846697556
6	1.297539559	0.724122772	1.998117124	6	1.192266015	0.449327290	2.204491922
6	0.062795889	-0.121826753	2.294208525	6	-0.211028695	-0.137189981	2.380710545
6	-0.470602362	-0.552273440	0.944225026	6	-0.450911034	-0.963132289	1.143833669
1	2.221320842	0.347536036	2.444019945	1	1.920946743	0.153692692	2.959284898
8	2.244309523	1.381712411	-0.093536014	8	2.766387702	0.088994047	0.422153236
8	-1.569763566	-1.003883949	0.802163596	8	-1.279259751	-1.826020235	1.064479097
6	-0.890538423	0.872584048	3.055699950	6	-1.137937557	1.147073497	2.454180596
1	-1.692099051	0.382078863	3.604055916	1	-2.132645960	0.934473815	2.843726445
8	-1.452617704	-1.886599572	-1.481990292	8	-1.684286925	-1.808525324	-1.468067236
1	0.262459864	-1.013514838	2.893011425	1	-0.345809389	-0.766263054	3.260442261
6	0.930115475	2.132368927	2.595335167	6	0.939600022	2.016397584	2.226867291
1	1.786286667	2.791640680	2.722865531	1	1.845156315	2.593734284	2.406144632
6	0.169572264	1.664244705	3.860768536	6	-0.209176009	2.086374271	3.267590845
1	0.772743903	1.037203982	4.526044270	1	0.054593130	1.706998968	4.262856438
1	-0.259329094	2.492466229	4.428133828	1	-0.619170778	3.095046664	3.372123849
6	-0.227127710	2.672008573	1.767537224	6	0.167397321	2.325101141	0.951720841
1	-0.132492249	3.438064718	1.008383129	1	0.604225525	2.723252412	0.044040265
6	-1.304669199	1.929636490	2.042330041	6	-1.061372800	1.803718793	1.085073577
1	-2.269210867	1.962772176	1.552453473	1	-1.811047562	1.700111455	0.309751746
6	-2.550378959	-2.469990947	-2.157952531	6	-1.509454092	-3.220402487	-1.364662886
1	-2.985322829	-1.783365318	-2.893188820	1	-0.593979169	-3.461757688	-0.815215920
1	-3.282882050	-2.677206096	-1.379874140	1	-1.472575307	-3.676969792	-2.362943048
1	-2.275208062	-3.407702559	-2.655187827	1	-2.367474051	-3.595825428	-0.808822963

Table 4.39 XYZ coordinates of planar TSI of rotor 1(SCF₃), rotor 1(SPh), and rotor 1(OPh).

TSI of SCF ₃					TSI of SPh					TSI of OPh				
1	0.938348491	-1.055154937	-5.054103263		1	1.744519066	-0.628269412	-4.256628614		1	1.884979719	0.013593864	-4.573521778	
6	0.819943362	-0.901767583	-3.986952128		6	1.595865303	-0.437205829	-3.199032816		6	1.778099942	0.012571743	-3.493949486	
6	0.535847909	-0.640404969	-1.179823696		6	1.253771277	-0.090830460	-0.407408372		6	1.479178515	-0.042344096	-0.659047303	
6	-0.106942333	-1.653746350	-3.285763529		6	0.678664367	-1.188232334	-2.485972085		6	0.780768276	-0.739761889	-2.897177718	
6	1.560735284	0.048422882	-3.304319470		6	2.285291887	0.568302052	-2.539834779		6	2.626222745	0.751892241	-2.683406457	
6	1.420910247	0.155163320	-1.930926100		6	2.114805730	0.718338932	-1.173963656		6	2.476584253	0.715477819	-1.303576443	
6	-0.339636263	-1.504201993	-1.908210205		6	0.414208379	-1.003544399	-1.117481716		6	0.605278379	-0.770034324	-1.509823153	
1	-0.683454692	-2.373477236	-3.842938400		1	0.107335089	-1.934520042	-3.020342184		1	0.104260258	-1.328002024	-3.504575037	
1	2.265754362	0.691421287	-3.819473807		1	2.972304823	1.221860739	-3.066211360		1	3.417826787	1.358038826	-3.110234410	
1	2.050749801	0.862266169	-1.421385629		1	2.702611665	1.472377498	-0.682449107		1	3.170026530	1.279042494	-0.707941896	
7	0.627924100	-0.459357104	0.255249993		7	1.325649293	0.132579204	1.026256816		7	1.379665109	0.039060556	0.790415590	
6	1.771186510	0.125806911	0.900516269		6	2.431955067	0.794763945	1.656013788		6	2.325508996	0.763184478	1.579681266	
6	1.389574053	0.489336426	2.313254357		6	2.030791847	1.177056445	3.056973578		6	1.744302330	1.033411964	2.943202942	
6	0.020565388	-0.151963792	2.538094173		6	0.725442680	0.426846735	3.319121238		6	0.455446245	0.222313864	2.996669656	
6	-0.282480099	-0.875052211	1.254402478		6	0.435782547	-0.311642332	2.036567719		6	0.374012910	-0.507866982	1.677573146	
1	2.170040450	0.152042046	2.995633253		1	2.844793002	0.934368488	3.740413260		1	2.479778722	0.773295344	3.705244964	
8	2.857049899	0.305200363	0.414420294		8	3.511595308	1.018704892	1.171349289		8	3.427063846	1.128385338	1.246179829	
8	-1.149203846	-1.701533236	1.125537547		8	-0.408035744	-1.160338132	1.922729992		8	-0.384174079	-1.411032673	1.474346148	
6	-0.922805699	1.087251967	2.829691123		6	-0.308786512	1.583085036	3.640135947		6	-0.661310316	1.323376849	3.211475220	
1	-1.871468032	0.804661628	3.281708490		1	-1.208759946	1.229149763	4.138837379		1	-1.609836880	0.911867816	3.551785644	
1	-0.024709809	-0.860476854	3.365136424		1	0.765601624	-0.287913697	4.141379161		8	-0.392758195	-1.537182110	-0.983108768	
6	1.105033559	2.036763387	2.522359888		6	1.613856419	2.697797615	3.227399092		1	0.411979838	-0.513653108	3.800138907	
1	2.008227316	2.618602063	2.694903337		1	2.465478355	3.364488872	3.347984038		6	1.250599279	2.525329193	3.146643866	
6	0.066799729	1.933845718	3.666799414		6	0.633472720	2.534583372	4.415463422		1	2.050210454	3.208305245	3.427733659	
1	0.440519664	1.418110600	4.556742271		1	1.088496864	2.078508457	5.300681548		6	0.118924338	2.259378181	4.168143332	
1	-0.343855368	2.904762999	3.949462866		1	0.149436447	3.472611046	4.693449854		1	0.461262398	1.764438232	5.082495080	
6	0.204364457	2.492193328	1.385045745		6	0.634021823	3.037107969	2.116460117		1	-0.438669730	3.162268426	4.425169684	
1	0.533188901	3.069692859	0.529742305		1	0.879950647	3.609964412	1.230709138		6	0.428767085	2.901675633	1.925432298	
6	-0.993561711	1.925755831	1.564877410		6	-0.504491464	2.380644324	2.362012367		1	0.776682214	3.536172963	1.119599994	
1	-1.836629126	1.945596848	0.885173092		1	-1.371132982	2.306926383	1.716753754		6	-0.701227416	2.186893591	1.962233834	
16	-1.806815308	-2.356466195	-1.247862260		16	-1.052593133	-1.884344223	-0.491551848		1	-1.460530688	2.120246023	1.192717274	
6	-2.859881911	-2.573252243	-2.737051242		6	-1.979450912	-2.204327579	-2.001832590		6	-1.469971788	-1.942109392	-1.744125899	
9	-2.467993749	-3.546866766	-3.594968973		6	-3.663798752	-2.767265637	-4.162357714		6	-3.698330307	-2.852995455	-3.137195229	
9	-4.055389467	-2.953050267	-2.248666563		6	-2.213630336	-3.526801786	-2.385728716		6	-2.402491091	-1.023524942	-2.225598598	
9	-3.041935966	-1.460124841	-3.466305517		6	-2.596699339	-1.162475371	-2.705658378		6	-1.643839306	-3.308275535	-1.947720903	
					6	-3.424503426	-1.443823048	-3.786146917		6	-2.762474442	-3.761043647	-2.644567812	
					6	-3.060239250	-3.805795039	-3.459618037		6	-3.515864784	-1.486158326	-2.923118564	
					1	-1.734137285	-4.333834479	-1.842466377		1	-2.247216648	0.035841056	-2.050237416	
					1	-2.418744759	-0.136751929	-2.402473441		1	-0.904115666	-3.992787991	-1.548038995	
					1	-3.897864556	-0.630816180	-4.327861321		1	-2.899305072	-4.825836256	-2.803707984	
					1	-3.242483307	-4.836584476	-3.746861833		1	-4.247980261	-0.776016052	-3.295469847	
					1	-4.320350475	-2.984749900	-4.998809686		1	-4.567332393	-3.207437042	-3.680738693	

4.5.10 NBO calculations.

Q-Chem version 5.4.1 which incorporates the NBO version 5.4 program were used to perform natural bond orbital (NBO) calculations on the transition state structures

(B3LYP-D3/6-311G*).²¹⁸ The NBO calculations were performed at the ω B97M-V/6-311+G* level of theory. A couple of methods and basic sets were tried to compare. NBO outcomes tended to be steady since the level of ω B97M-V/6-311+G* which was with a diffuse function (**Table 4.40a**). NBO energies for the intramolecular C=O lone pair to *N*-phenyl R¹-group interactions provided a measure of the orbital-orbital component of the $n \rightarrow \pi^*$ interactions. The NBO interaction energies for the new chalcogen rotors **1** and **2** were compared with previously measured NBO interactions for rotors **4** and **5** (**Table 4.40b**).^{1,20,55}

Table 4.40 a) determination of the theory level for NBO.

rotors R =	B3LYP/ 6311G*	B3LYP/ 6311+G*	ω B97M-V/ 6-311G*	ωB97M-V/ 6-311+G*	ω B97M-V/ 6-311++G*	ω B97M-V/ 6-311++G**
1 (benzothi ofuran)	-5.12	-5.58	-6.76	-6.87	-6.87	-6.87
4 (CHO)	-13.10	-14.29	-16.50	-16.04	-16.04	-16.08
5 (OH)	-36.09	-36.20	-42.94	-42.75	-43.23	-42.32

b) NBO interaction energies (ω B97M-V/6-311+G*) between the C=O lone pair and the R¹-groups in the TS structures of rotors **1**, **3**, and **4**.

rotors 4 and 5 R-groups	NBO (kcal/mol)	rotors 1 and 2 R-groups	NBO (kcal/mol)
4 (CN)	-8.8	1 (benzothiofuran)	-6.87
4 ((C=CH ₂)CH ₃)	-5.8	1 (thiofuran)	-6.54
4 (COPh)	-16.64	1 (thiazole)	-5.82
4 (COCH ₃)	-18.1	2 (2H-furan)	0
4 (CHO)	-16.04	2 (brnzofuran)	-0.52
5 (OH)	-42.75	2 (furan)	-0.51
5 (OH, <i>p</i> -Cl)	-43.65	2 (oxazole)	-0.58
5 (OH, <i>p</i> -CN)	-46.41		
5 (OH, <i>p</i> -NO ₂)	-47.03		
5 (OH, <i>m</i> -Cl)	-44.75		
5 (OH, <i>m</i> -NO ₂)	-44.25		

c) The comparison of the NBO calculations of planar TSI and perpendicular TSII of acyclic chalcogen rotors.

rotors 2 R-groups	Spot NBO in TSII (kcal/mol)	σ -hole NBO in TSI (kcal/mol)
2 (OCH ₃)	0	-0.52
2 (OPh)	0	-0.52
2 (OCF ₃)	0	none
2 (OCOCH ₃)	0	none
1 (SCF ₃)	0	-7.65
1 (SCH ₃)	0	-6.1
1 (SPh)	0	-5.78

The orbital-orbital components were analyzed by plotting E_{int} and NBO of rotors **1**, **2**, **4** and **5**. Rotors **4**($n \rightarrow \pi^*$) had much larger NBO energies and showed perfect correlation in E_{int} and NBO, which meant the orbital-orbital components played another key role in the $n \rightarrow \pi^*$ interactions of rotors **4**($n \rightarrow \pi^*$). However, rotors **5**(HB) had even larger orbital-orbital interaction components than rotors **3**($n \rightarrow \pi^*$). Although rotors **1**(ChB) also showed a good correlation in NBO analysis, the NBO energies were much smaller than rotors **4** and **5**. Thus, the orbital-orbital interaction components of the ChB were not that significant as rotors **4** and **5** (**Figure 4.49a**).

Another interesting analysis was the comparison between the NBO calculations of the planar TSI and the perpendicular TSII (**Table 4.40c**). The planar TSI was showing the supposed orbital-orbital interaction with some NBO energies, which was very similar to the cyclic structures, and at the same time there was no NBO energies of the perpendicular TSII which was closer to the measurements in barriers. Thus, the trend of the perpendicular TSII was better than the planar TSI (**Figure 4.49b**).

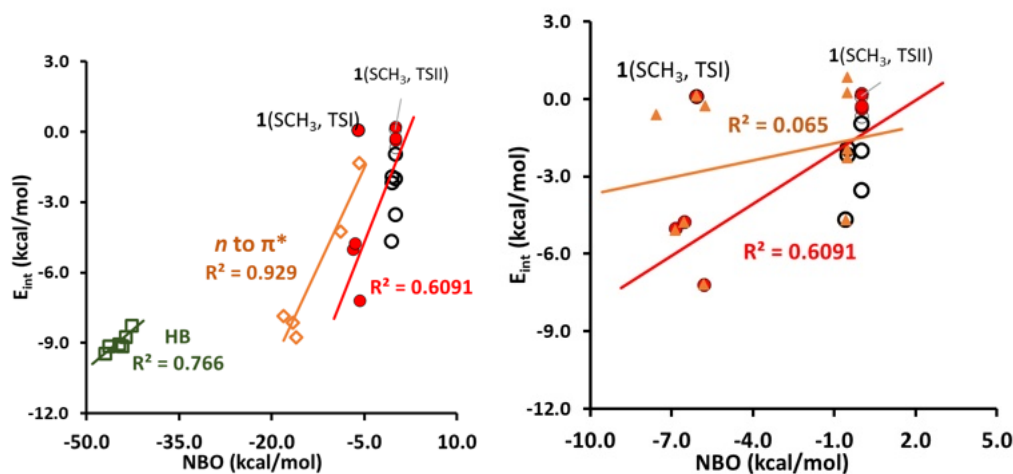


Figure 4.49 a) Plots of E_{int} and NBO of rotors **1** and **2**, **3** and **4**. b) The relative correlations for E_{int} and planar TSI σ -hole NBO or perpendicular TSII spot NBO.

4.5.11 ESP calculations

A series of methods and basic sets were performed to determine the theory level of electrostatic potential maps (ESP) calculations (**Table 4.41**). A basic set with a diffuse function (+) was necessary, but the methods of different levels did not change the outcomes obviously. ESP tended to be steady since the level of ω B97M-V/6-311+G* which has a diffuse function.

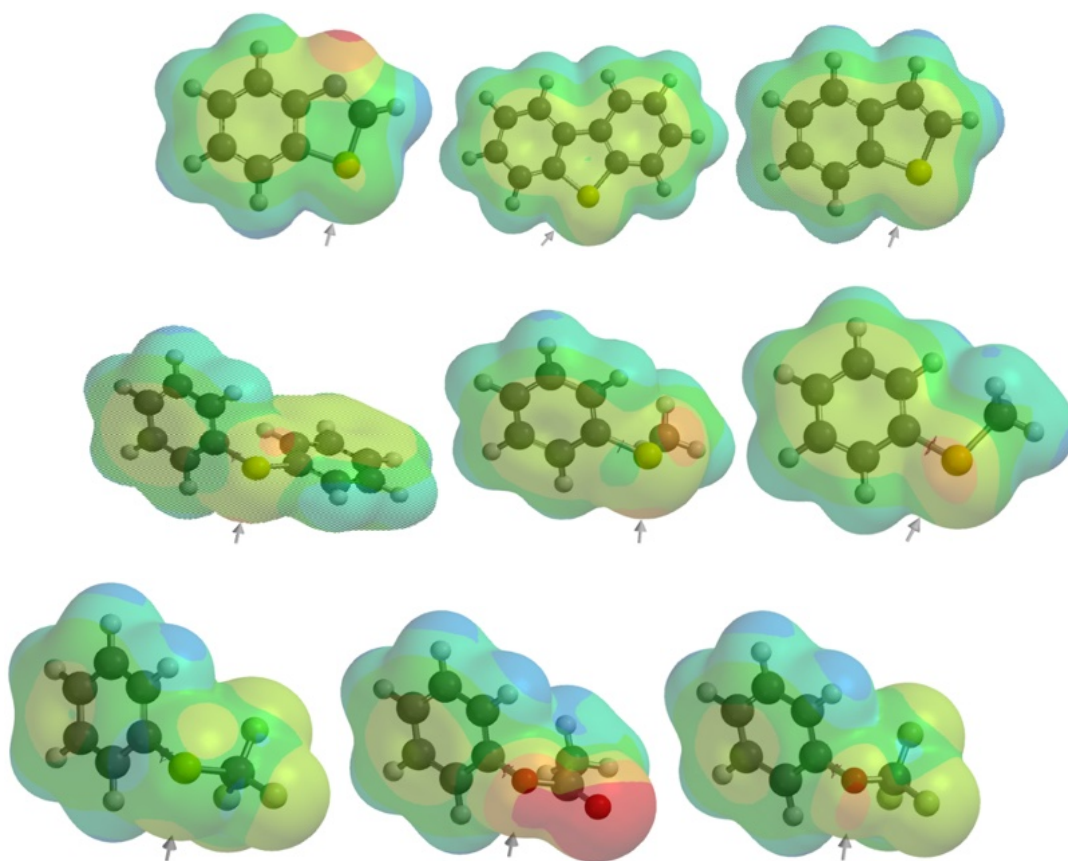
To be consistent with NBO, electrostatic potential maps were calculated with geometry optimization at the ω B97M-V/6-311+G* level of theory for the R^1 -groups of the molecular rotors attached to a benzene ring (**Table 4.41**). The R^1 -group to phenyl bond was twisted to a perpendicular TSII to minimize the transition state geometry of the R^1 -group except **1**(SCH₃) was calculated in planar TSI.

The negative to positive regions of the molecules were shown from red, orange, yellow, green, blue-green to blue (-200 to +200 kcal/mol). The ESP value was calculated at a point on the surface for the first atom of the R^1 -group. Some figures show the arrows

for the position on the surface for the ESP calculations. For planar R¹-groups the ESP was measured on either side of the first attached atom and the average of the two values was used as the ESP (**Figure 4.50**).

Table 4.41 Determination of the theory level for ESP.

Rotors R=	B3LYP-			ω B97M-V/ 6311G*	ω B97M-V/ 6311+G*	ω B97M-V/ 6311++G**
	B3LYP/ 631G*	D3/ 6311G*	B3LYP-D3/ 6311+G*			
1 (benzothiofuran)	10.0	12.0	12.5	12.0	15.0	15.0
3 (COCH ₃)	20.7	22.8	24.0	22.0	23.8	23.8
4 (OH)	65.0	66.3	66.5	67.0	67.0	67.0



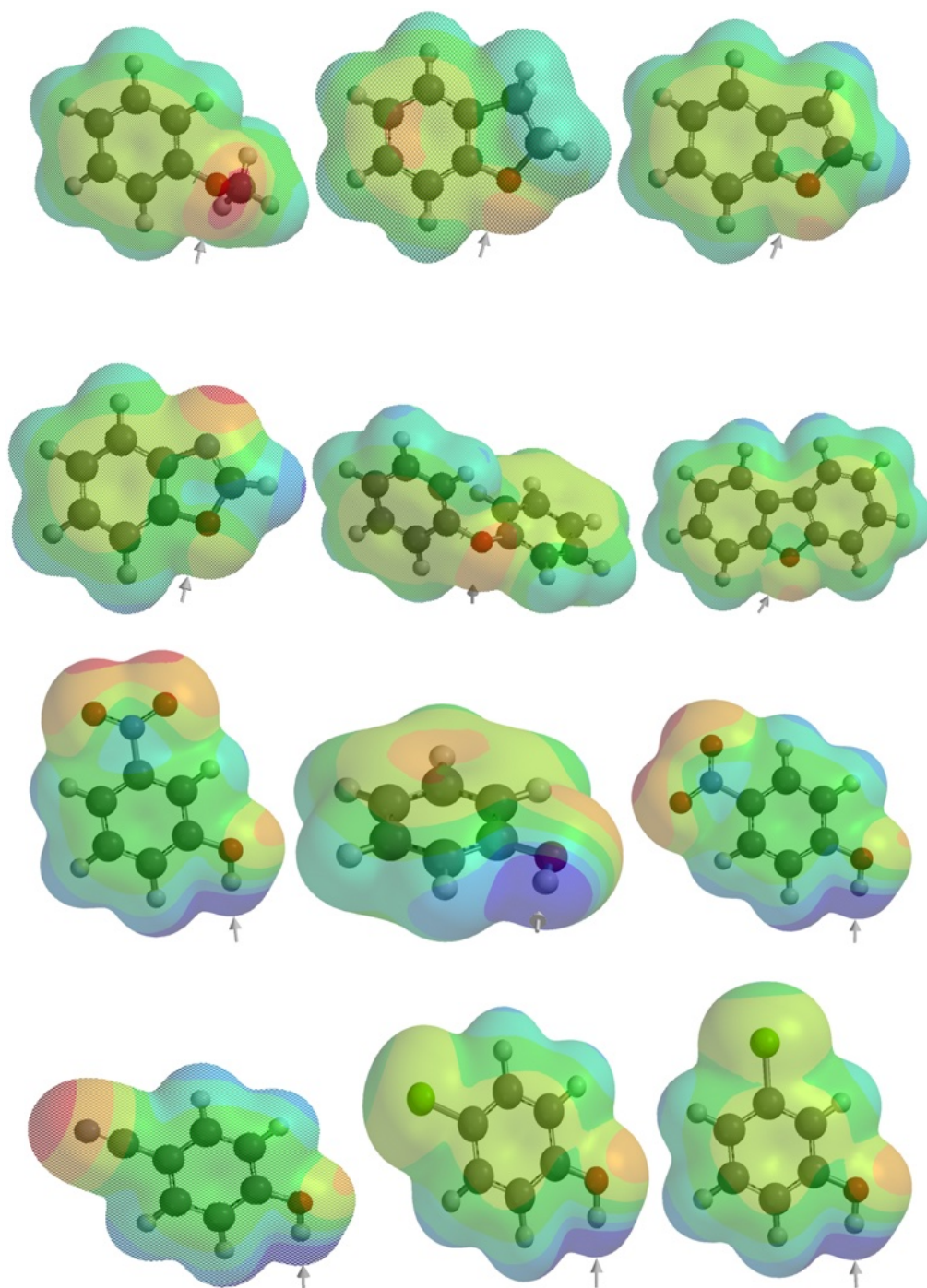


Figure 4.50 ESP maps used to generate the ESP values in **Table 4.3**.

All the three types of rotors showed significance in the relationship between E_{int} and ESP, especially rotors **1**, **3** and **4** had good correlation ($R^2 = 0.964$, $R^2 = 0.867$, $R^2 =$

0.82). the electrostatic component was strong in all the interactions, but rotors **1**(ChB) had a proportion of higher electrostatic components. (**Figure 4.51a**). The planar TSI and the perpendicular TSII of the acyclic rotors **1**(ChB) also could be reflected in the ESP by spot ESP and σ -hole ESP. The σ -hole ESP set of TSI did not show a good relationship with E_{int} , but as aforementioned, the perpendicular TSII showed the excellent correlation between the E_{int} and the spot ESP (**Figure 4.51b**).

The ESP values listed in **Table 4.3** were spot ESP. All cyclic Ch rotors would have the same spot ESP and σ -hole ESP since the interaction spots were the σ -holes. σ -hole ESP in planar TSI and spot ESP in perpendicular TSII was listed in **Table 4.42**.

Table 4.42 The spot ESP and σ -hole ESP for Ch rotors.

rotors 2 R-groups	σ -hole ESP in planar TSI (kcal/mol)	spot ESP in perpendicular TSII (kcal/mol)
2 (OCH ₃)	-12.5	-22.5
2 (OPh)	-10.0	-17.5
2 (OCF ₃)	2.0	-5.0
2 (OCOCH ₃)	5.0	0.5
1 (SCF ₃)	12.5	-12.0
1 (SCH ₃)	3.0	-22.0
1 (SPh)	5.0	-17.5
1 (benzothiofuran)	15.0	15.0
1 (thiofuran)	12.5	12.5
1 (thiazole)	22.0	22.0
2 (2H-furan)	-15.0	-15.0
2 (benzofuran)	-10.0	-10.0
2 (furan)	-12.5	-12.5
2 (oxazole)	7.5	7.5

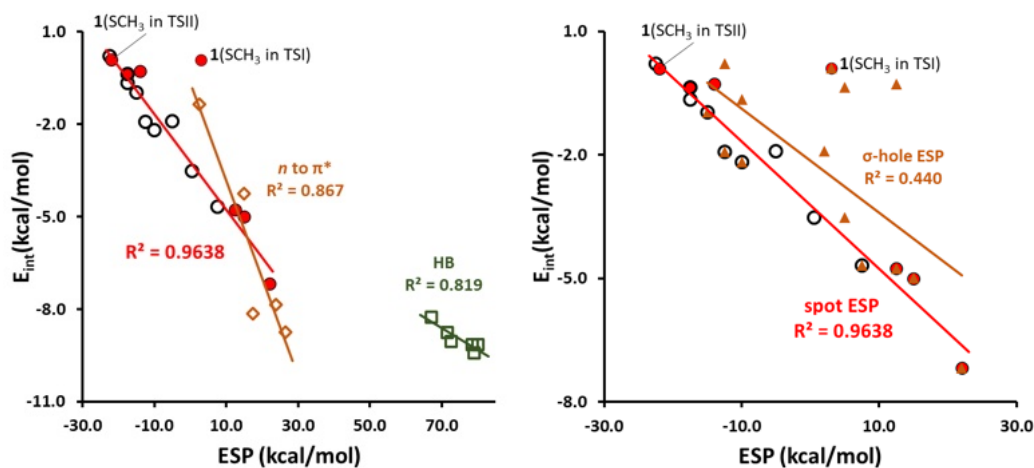


Figure 4.51 a) Plots of E_{int} and ESP of rotors **1**, **3** and **4**. b) The relative correlations for E_{int} and planar TSI σ -hole ESP or perpendicular TSII spot ESP.

4.5.12 Energy decomposed analysis.

The intramolecular interaction between the imide carbonyl groups ($\text{C}=\text{O}$) and the R^1 -groups on the *N*-phenyl rotors in the optimized (B3LYP-D3/6-311G*) transition states were calculated using the functional group interaction analysis method, FI-SAPT (SAPT(0)/jun-cc-pVDZ) as implemented in Psi4.¹⁷⁵ SAPT(0) is the default SAPT level and jun-cc-pVDZ, which contained the diffuse function, should cover all the atoms involved in our rotors. This energy decomposition analysis provided a total interaction energy (E_{SAPT}) as well as the component terms: exchange-repulsion ($E_{\text{SAPT-repl}}$), electrostatic ($E_{\text{SAPT-elst}}$), induction ($E_{\text{SAPT-ind}}$), and dispersion ($E_{\text{SAPT-disp}}$) (**Table 4.43**).

Table 4.43 Fi-SAPT of all the rotors involved in this paper. Acyclic Ch rotors were listed in **Table 4.44**. All units in kcal/mol.

Rotors (R=)	E_{elst}	E_{exch}	E_{ind}	E_{disp}	E_{total}	E_{int}
1(benzothiofuran)	-5.0	21.7	-5.5	-3.1	8.1	-5.1
1(thiofuran)	-4.9	20.2	-5.3	-2.9	7.1	-4.8
1(thiazole)	-6.4	17.3	-4.9	-2.7	3.2	-7.2
2(2H-furan)	8.7	8.9	-2.1	-1.4	14.1	-1.0
2(benzofuran)	6.8	8.6	-2.0	-1.5	11.9	-2.3
2(furan)	6.2	8.0	-1.9	-1.4	10.9	-1.9
2(oxazole)	3.4	7.1	-1.6	-1.3	7.5	-4.7
4(C(CH ₂)CH ₃)	-0.2	19.7	-3.9	-3.6	12.0	-1.7
4(CN)	-1.5	14.1	-3.8	-2.2	6.6	-4.8
4(CHO)	-6.0	15.7	-4.8	-2.7	2.2	-8.5
4(COCH ₃)	-5.9	17.5	-5.1	-3.8	2.7	-8.0
4(COPh)	-4.2	20.6	-6.2	-4.8	5.4	-8.5
5(OH)	-23.6	30.2	-10.0	-3.5	-6.9	-8.9
5(OH, <i>p</i> -Cl)	-23.9	30.4	-10.2	-3.5	-7.2	-9.4
5(OH, <i>p</i> -CN)	-25.0	31.4	-10.8	-3.6	-7.9	-9.8
5(OH, <i>p</i> -NO ₂)	-25.3	31.5	-11.0	-3.6	-8.3	-10.1
5(OH, <i>m</i> -Cl)	-24.3	30.9	-10.4	-3.5	-7.3	-9.7
5(OH, <i>m</i> -NO ₂)	-24.4	30.8	-10.4	-3.5	-7.5	-9.8

From **Figure 4.52**, the interaction energies perfectly coordinated with the $E_{\text{total-SAPT}}$ of TSs, which proved that the interactions mainly happened in the TSs. A few cases might have extra repulsion or stabilization like **2**(OCOCH₃) and **3**(COPh).

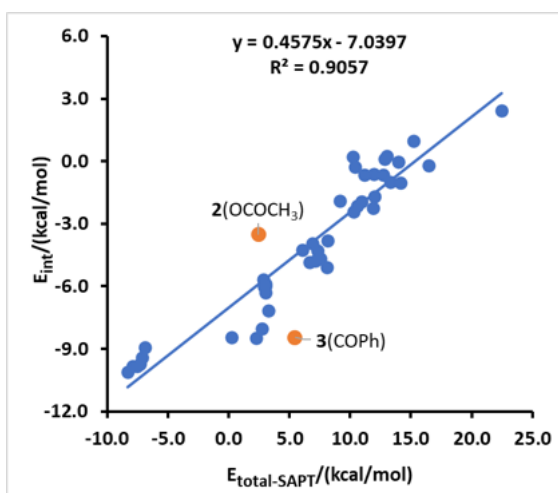


Figure 4.52 The correlations between interaction energies E_{int} and total terms of SAPT E_{SAPT} for rotors **1** and **2**, **4** and **5**.

The energetic geometries of the acyclic rotors (Ch) could also be analyzed by Fi-SAPT. Table S36 listed the different energies of the planar TSI and the perpendicular TSII. Basically, the perpendicular TSII showed the more stable or less unstable electrostatic (more negative or less positive) and less unstable exchange terms (less positive) than the same terms in the planar TSI. More importantly, the total energies of the perpendicular TSII were basically less repulsive (less positive) than in the planar TSI.

Table 4.44 Fi-SAPT of planar rotors **1**(Ch) in planar TSI and perpendicular TSII. All units in kcal/mol.

Rotors (R=)	E_{elst}	E_{exch}	E_{ind}	E_{disp}	E_{total}	Comments
OCH ₃	7.10731	12.85412	-2.28211	-1.68899	15.99034	planar TSI
OCH ₃	2.514859	11.81927	-1.91836	-2.22508	10.1907	perpendicular TSII
OPh	7.580195	12.24564	-2.25954	-1.91702	15.64928	planar TSI
OPh	4.21559	12.76181	-2.52591	-3.30187	11.14962	perpendicular TSII
SCH ₃	-1.73474	21.92557	-4.59278	-2.74424	12.85381	planar TSI
SCH ₃	-2.79594	20.94938	-3.61923	-2.91289	11.62133	perpendicular TSII
SPh	-1.72512	21.80664	-4.73616	-2.78725	12.55811	planar TSI
SPh	-0.66353	21.33996	-4.0354	-3.94293	12.6981	perpendicular TSII
SCF ₃	-6.49674	23.49328	-5.18095	-2.86728	8.948305	planar TSI
SCF ₃	-3.14038	21.54018	-3.59016	-2.85333	11.95632	perpendicular TSII
OCF ₃	0.0119	13.09157	-1.61341	-2.36861	9.121459	perpendicular TSII
OCOCH ₃	-6.0117	14.40953	-2.51971	-3.44697	2.43114	perpendicular TSII

4.5.13 X-Ray crystal structures^{4,128,131,219}

CCDC Deposit numbers for the four crystal structures were: 2287313, 2287314, 2287315, 2287316

X-Ray structures determination, C₂₁H₁₅NO₂S (LBZ-301)

X-ray intensity data from a colorless flat needle were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-II area detector and an Incoatec microfocus source (Mo K α radiation, λ = 0.71073 Å). The raw area detector data

frames were reduced, scaled and corrected for absorption effects using the Bruker APEX3, SAINT+ and SADABS programs. The structure was solved with SHELXT. Subsequent difference Fourier calculations and full-matrix least-squares refinement against F² were performed with SHELXL-2019/23 using OLEX2.

The compound crystallizes in the monoclinic system (**Figure 4.53**). The pattern of systematic absences in the intensity data was uniquely consistent with the space group P2₁/n, which was confirmed by structure solution. The asymmetric unit consists of one molecule. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located in difference Fourier maps before being placed in geometrically idealized positions and included as riding atoms with d(C-H) = 1.00 Å and U_{iso}(H) = 1.2U_{eq}(C) for methine hydrogen atoms, d(C-H) = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C) for arene hydrogen atoms and d(C-H) = 0.99 Å and U_{iso}(H) = 1.2U_{eq}(C) for methylene hydrogen atoms. The largest residual electron density peak in the final difference map is 0.52 e-/Å³, located 0.80 Å from S1.

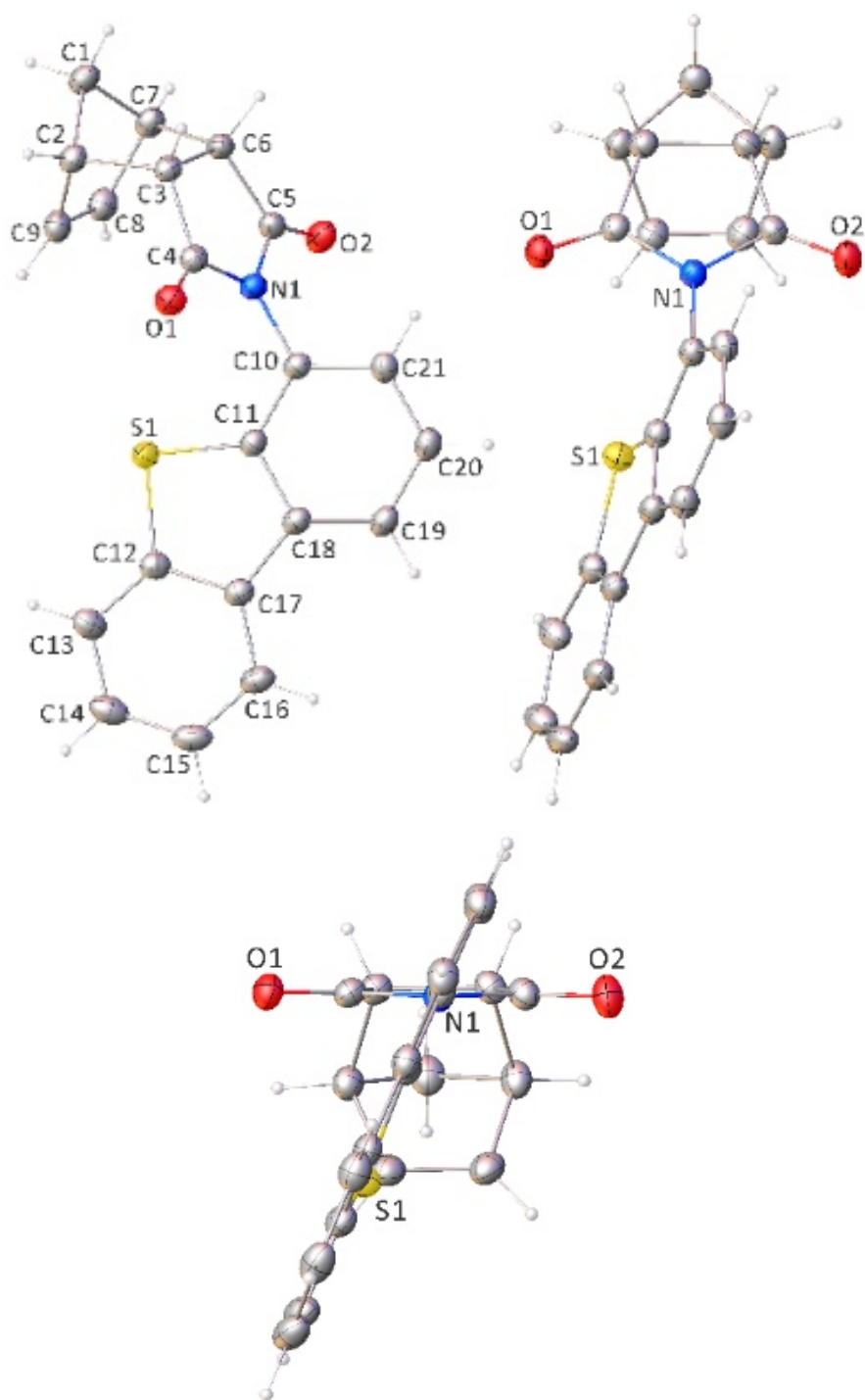


Figure 4.53 Crystal structure of $C_{21}H_{15}NO_2S$ (LBZ-301).

Table 4.45 Crystal data and structure refinement for lbz301.

Identification code	lbz301
Empirical formula	C ₂₁ H ₁₅ NO ₂ S
Formula weight	345.40
Temperature/K	100(2)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	8.3828(4)
b/Å	7.2871(3)
c/Å	26.1103(11)
α /°	90
β /°	93.965(2)
γ /°	90
Volume/Å ³	1591.16(12)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.442
μ/mm^{-1}	0.218
F(000)	720.0
Crystal size/mm ³	0.6 × 0.18 × 0.12
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	5.218 to 65.278
Index ranges	-12 ≤ h ≤ 12, -11 ≤ k ≤ 10, -39 ≤ l ≤ 38
Reflections collected	126393
Independent reflections	5800 [R_{int} = 0.0422, R_{sigma} = 0.0149]
Data/restraints/parameters	5800/0/226
Goodness-of-fit on F ²	1.057
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0403, wR_2 = 0.1034
Final R indexes [all data]	R_1 = 0.0468, wR_2 = 0.1076
Largest diff. peak/hole / e Å ⁻³	0.52/-0.28

X-Ray Structure Determination, C₂₁H₁₅NO₃ (LBZ-3401)

X-ray intensity data from a colorless plate were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-II area detector and an Incoatec microfocus source (Mo K α radiation, $\lambda = 0.71073$ Å). The raw area detector data frames were reduced, scaled and corrected for absorption effects using the Bruker APEX3, SAINT+ and SADABS programs. The structure was solved with SHELXT. Subsequent difference Fourier calculations and full-matrix least-squares refinement against F² were performed with SHELXL-2019/23 using OLEX2.

The compound crystallizes in the orthorhombic system (Figure 4.54). The pattern of systematic absences in the intensity data was uniquely consistent with the space group P_{bca}, which was confirmed by structure solution. The asymmetric unit consists of one molecule. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located in difference Fourier maps before being placed in geometrically idealized positions and included as riding atoms with $d(\text{C-H}) = 1.00$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methine hydrogen atoms, $d(\text{C-H}) = 0.95$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for arene hydrogen atoms and $d(\text{C-H}) = 0.99$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methylene hydrogen atoms. The largest residual electron density peak in the final difference map is 0.41 e-/Å³, located 0.65 Å from C17.

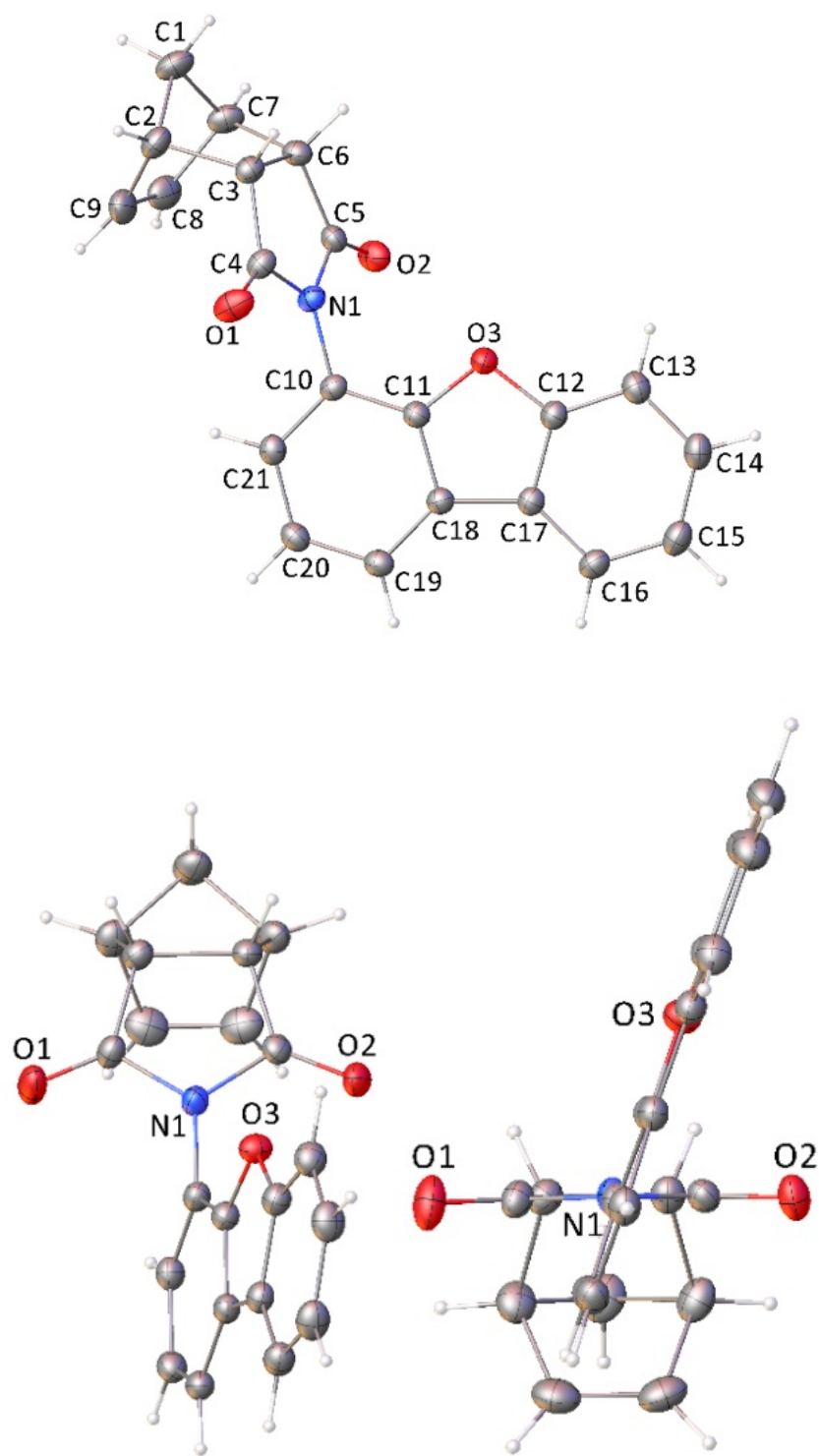


Figure 4.54 Crystal structure of $C_{21}H_{15}NO_3$ (LBZ-3401).

Table 4.46 Crystal data and structure refinement for lbz341.

Identification code	lbz341
Empirical formula	C ₂₁ H ₁₅ NO ₃
Formula weight	329.34
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	Pbca
a/Å	12.6162(5)
b/Å	11.0940(5)
c/Å	22.2223(10)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	3110.3(2)
Z	8
$\rho_{\text{calc}}/\text{cm}^3$	1.407
μ/mm^{-1}	0.095
F(000)	1376.0
Crystal size/mm ³	0.6 × 0.42 × 0.2
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	4.886 to 65.218
Index ranges	-19 ≤ h ≤ 18, -16 ≤ k ≤ 16, -33 ≤ l ≤ 33
Reflections collected	69347
Independent reflections	5676 [R _{int} = 0.0522, R _{sigma} = 0.0239]
Data/restraints/parameters	5676/0/226
Goodness-of-fit on F ²	1.032
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0420, wR ₂ = 0.1095
Final R indexes [all data]	R ₁ = 0.0542, wR ₂ = 0.1185
Largest diff. peak/hole / e Å ⁻³	0.41/-0.20

X-Ray Structure Determination, C₁₆H₁₂N₂O₂S (LBZ57-1)

X-ray intensity data from a colorless block were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-II area detector and an Incoatec microfocus source (Mo K α radiation, $\lambda = 0.71073$ Å). The raw area detector data frames were reduced, scaled and corrected for absorption effects using the Bruker APEX3, SAINT+ and SADABS programs. The structure was solved with SHELXT. Subsequent difference Fourier calculations and full-matrix least-squares refinement against F² were performed with SHELXL-2019/23 using OLEX2.

The compound crystallizes in the orthorhombic system (Figure 4.55). The pattern of systematic absences in the intensity data was consistent with the space groups Pca21 and Pbcn; intensity statistics suggested an acentric structure. The non-centrosymmetric group Pca21 was determined by the solution program XT and was confirmed by structure solution and further with ADDSYM.5 The asymmetric unit consists of one molecule. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to carbon were located in difference Fourier maps before being placed in geometrically idealized positions and included as riding atoms with $d(\text{C-H}) = 1.00$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methine hydrogen atoms, $d(\text{C-H}) = 0.95$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for arene hydrogen atoms and $d(\text{C-H}) = 0.99$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methylene hydrogen atoms. The absolute structure (Flack x) parameter after the final cycle was 0.019(18). The largest residual electron density peak in the final difference map is 0.32 e-/Å³, located 0.74 Å from C6.

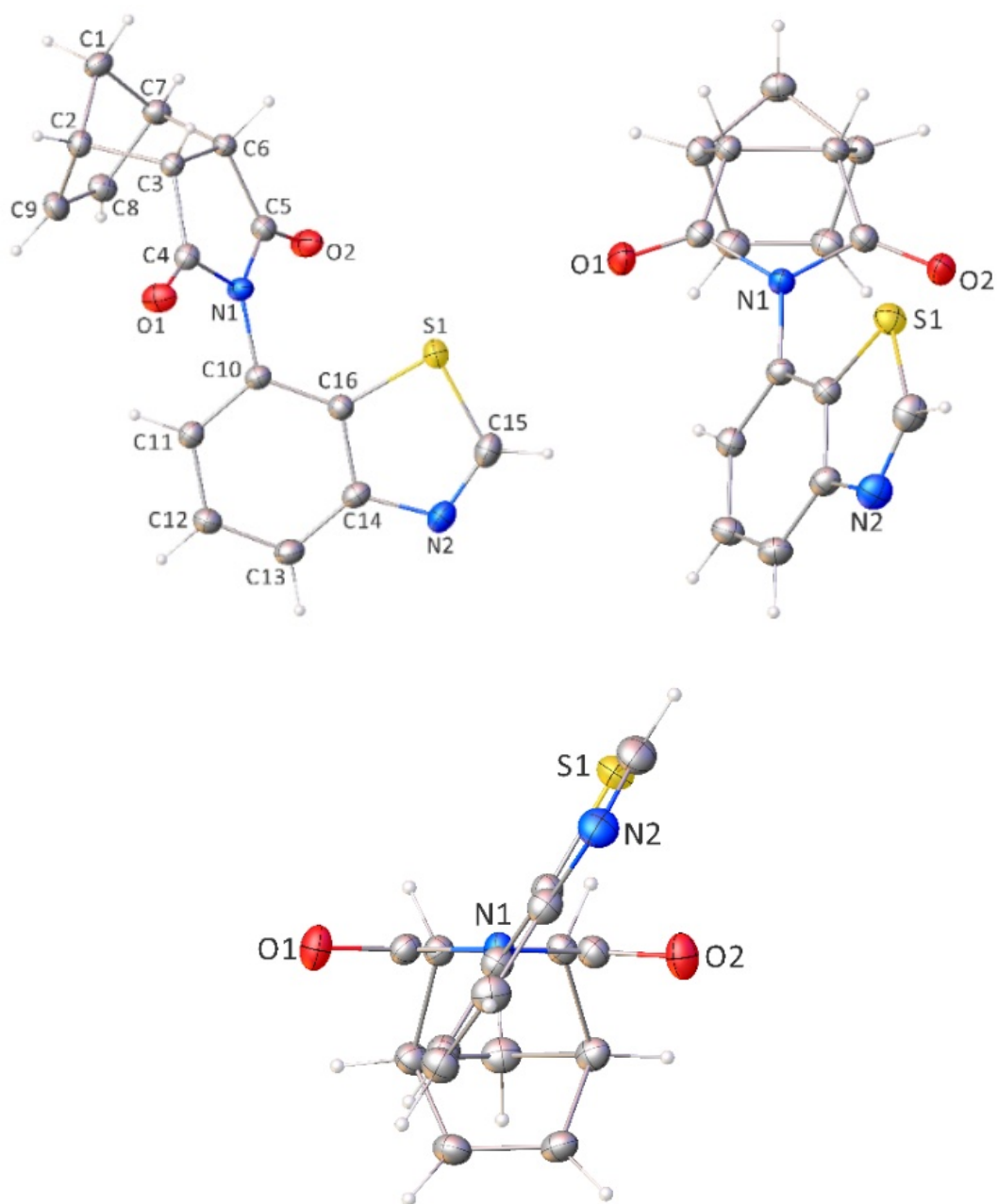


Figure 4.55 Crystal structure of $C_{16}H_{12}N_2O_2S$ (LBZ57-1).

Table 4.47 Crystal data and structure refinement for lbz571.

Identification code	lbz571
Empirical formula	C ₁₆ H ₁₂ N ₂ O ₂ S
Formula weight	296.34
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	Pca2 ₁
a/Å	11.6744(6)
b/Å	10.8063(5)
c/Å	10.2018(5)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	1287.03(11)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.529
μ/mm^{-1}	0.257
F(000)	616.0
Crystal size/mm ³	0.6 × 0.48 × 0.4
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	3.77 to 66.364
Index ranges	-17 ≤ h ≤ 17, -16 ≤ k ≤ 16, -15 ≤ l ≤ 15
Reflections collected	72978
Independent reflections	4914 [R _{int} = 0.0619, R _{sigma} = 0.0246]
Data/restraints/parameters	4914/1/190
Goodness-of-fit on F ²	1.046
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0288, wR ₂ = 0.0762
Final R indexes [all data]	R ₁ = 0.0317, wR ₂ = 0.0778
Largest diff. peak/hole / e Å ⁻³	0.32/-0.28
Flack parameter	0.019(18)

X-Ray Structure Determination, C₂₁H₁₇NO₂S (LBZB162)

X-ray intensity data from a colorless stubby needle were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-II area detector and an Incoatec microfocus source (Mo K α radiation, λ = 0.71073 Å). The raw area detector data frames were reduced, scaled and corrected for absorption effects using the Bruker APEX3, SAINT+ and SADABS programs. The structure was solved with SHELXT. Subsequent difference Fourier calculations and full-matrix least-squares refinement against F² were performed with SHELXL-2019/23 using OLEX2.

The compound crystallizes in the triclinic system (Figure 4.56). The space group P-1 (No. 2) was confirmed by structure solution. The asymmetric unit consists of one molecule. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located in difference Fourier maps before being placed in geometrically idealized positions and included as riding atoms with d(C-H) = 1.00 Å and Uiso(H) = 1.2Ueq(C) for methine hydrogen atoms, d(C-H) = 0.95 Å and Uiso(H) = 1.2Ueq(C) for arene hydrogen atoms and d(C-H) = 0.99 Å and Uiso(H) = 1.2Ueq(C) for methylene hydrogen atoms. The largest residual electron density peak in the final difference map is 0.44 e-/Å³, located 0.70 Å from C15.

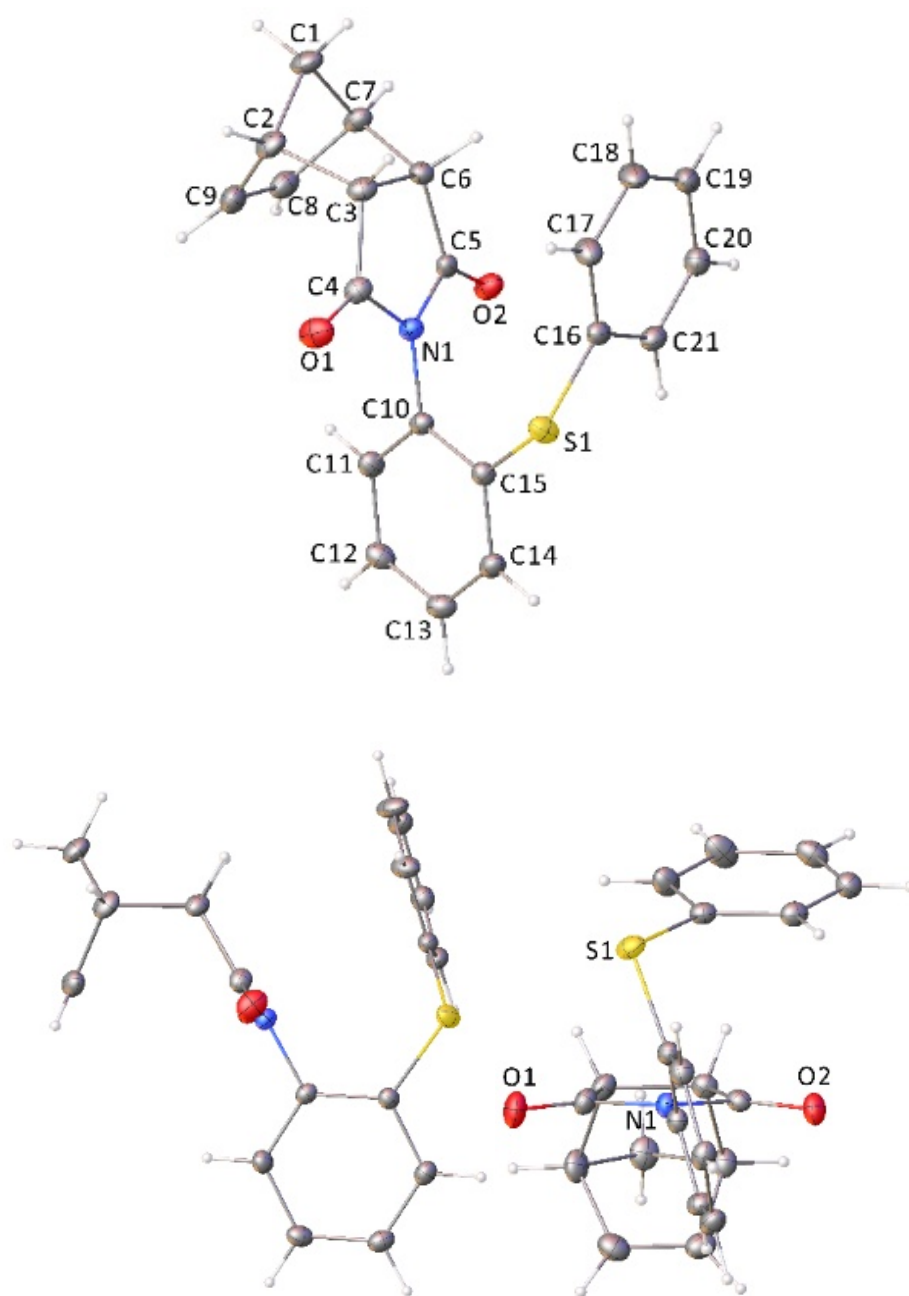


Figure 4.56 Crystal structure of $C_{21}H_{17}NO_2S$ (LBZB162).

Table 4.48 Crystal data and structure refinement for lbz_b162.

Identification code	lbz_b162
Empirical formula	C ₂₁ H ₁₇ NO ₂ S
Formula weight	347.42
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	7.7895(2)
b/Å	9.1850(2)
c/Å	13.0101(3)
α /°	74.3220(10)
β /°	78.8950(10)
γ /°	68.6160(10)
Volume/Å ³	829.89(3)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.390
μ/mm^{-1}	0.209
F(000)	364.0
Crystal size/mm ³	0.28 × 0.18 × 0.16
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	5.248 to 66.388
Index ranges	-11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -20 ≤ l ≤ 20
Reflections collected	23621
Independent reflections	6323 [R _{int} = 0.0380, R _{sigma} = 0.0408]
Data/restraints/parameters	6323/0/226
Goodness-of-fit on F ²	1.021
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0409, wR ₂ = 0.0985
Final R indexes [all data]	R ₁ = 0.0550, wR ₂ = 0.1069
Largest diff. peak/hole / e Å ⁻³	0.44/-0.31

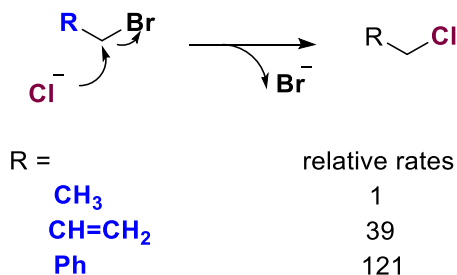
Chapter 5 Confirmation of the Secondary Electrostatic Interaction Hypothesis of the Benzylic S_N2 Effect Using Molecular Rotors

5.1 Abstract

Benzylic and allylic electrophiles are well known to react faster in S_N2 reactions than aliphatic electrophiles. However, the origins of their enhanced reactivity is still being debated. Recently, a new hypothesis was proposed by Galabov, Wu, and Allen that the benzyl and allylic effects are due to secondary electrostatic interactions in the transition state. The sp² carbons of the benzylic and allylic electrophiles form less repulsive or even attractive interactions with the negatively charged nucleophile and leaving group. Therefore, we set out to experimentally test this theoretical hypothesis using a series of molecular rotors, which could form similar secondary electrostatic interactions in the bond rotation transition states but cannot form the primary bonds. The rotational barrier substituent trends matched with experimental and calculated S_N2 rate trends, as rotors with substituents that had sp² or sp carbons at the secondary position had 0.5 to 2.0 kcal/mol lower rotational barriers than rotors with sp³ secondary carbons. The origins of these trends were consistent with the secondary electrostatic interaction hypothesis as the lower barriers for sp² and sp as the trend was observed even when the primary carbon atom was changed to oxygen, sulfur or nitrogen. Further confirmation of the electrostatic nature of barrier trends was provided by an analysis of the NBO charges of the secondary atoms in the bond rotation transition state

5.2 Introduction

The S_N2 reaction is one of the most fundamental in organic chemistry,²²⁰ and accordingly has been the subject of extensive mechanistic studies.²²¹ A well-known trend is the enhanced reactivity of benzylic and allylic electrophiles.^{7,222–227} For example, the S_N2 reactions of benzyl or allyl chloride with cyanide are 39 and 121 times faster than the reaction of ethyl chloride with cyanide (**Scheme 5.1**).⁸ The enhanced reactivity of benzyl and allyl electrophiles is commonly attributed to resonance stabilization of the pyramidal S_N2 transition state.^{220,226} However, recent theoretical studies by Galabov, Wu, and Allen hypothesized that the enhanced reactivity is due to electrostatic interactions in S_N2 transition state between the electronegative nucleophile and leaving group with the secondary carbon which is adjacent to the electrophilic center (**Figure 5.1**).²²⁷ For example, in the S_N2 reaction of ethyl halide, the secondary atom is the sp³ carbon of the methyl group, which has a slightly negative charge and forms repulsive electrostatic interactions with the nucleophile and leaving group. By comparison, in the reaction of a benzyl or allyl halide, the secondary atom is the sp² carbon of the phenyl group, which is less electrostatically negative. Therefore, the secondary electrostatic interaction is less repulsive.



Scheme 5.1 Comparison of the relative rates of S_N2 reactions of benzyl, allyl, and ethyl bromides to form organochlorides.^{7,8}

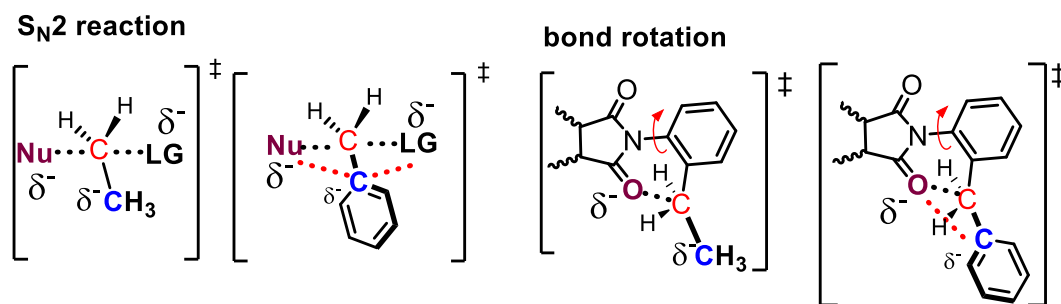


Figure 5.1 Comparison of the transition state structures of the S_N2 reaction (left) and N-C bond in the N-phenylimide rotors (right). The secondary electrostatic interactions in the benzylic electrophiles are highlighted as red broken lines, which are less repulsive interactions than the secondary interactions in the ethyl electrophiles.

Our approach was to design a system where the kinetic effects of the secondary electrostatic interactions could be experimentally isolated and measured in bond rotations. Similar to the S_N2 transition state, the imide carbonyl oxygen and the *ortho*-substituent on the *N*-phenyl rotor can form intramolecular through-space interactions in the bond rotation transition state. The electronegative oxygen of the imide C=O acts as a pseudo-nucleophile, forming close contacts with the electropositive R-group on the *ortho*-position of the opposing *N*-phenylimide, which acts as a pseudo-electrophile (Figure 5.1). Thus, in the bond rotation of the ethyl group, the secondary atom is the sp^3 carbon of the methyl group, forming repulsive electrostatic interactions. By comparison, in the bond rotation of a benzyl, the secondary atom is the sp^2 carbon of the phenyl group and forms a secondary electrostatic interaction, which is less repulsive.

The goal of this study was to experimentally test the secondary electrostatic hypothesis using our N-phenylimide molecular rotors. While the resonance and secondary electrostatic effects can be differentiated in computational studies, the analogous experimental studies are challenging because the charges and resonance effects in the

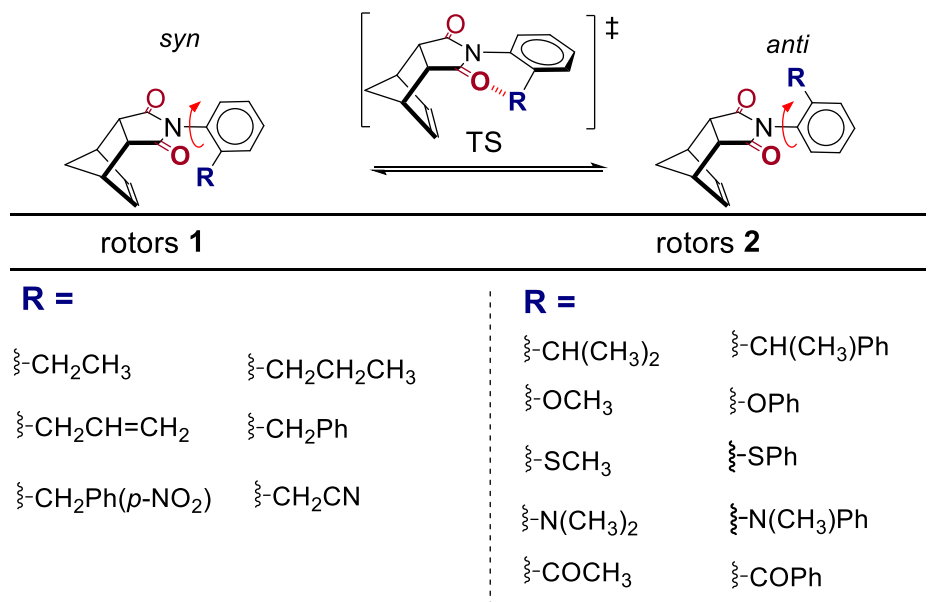
transition state are not as easily isolated. Furthermore, systematic structural changes in the nucleophile or electrophile can lead to changes in the mechanism and transition state structures. Studying the kinetic effects of secondary electrostatic using a molecular rotor addressed many of these challenges. The bond rotation transition state of the rotors mimics the transition state interactions of the S_N2 reaction without forming a bond. This enables the differentiation of the resonance and secondary electrostatic hypotheses.

A series of rotors was designed which contain the R-groups of the S_N2 electrophiles attached at the *ortho*-position of the N-phenyl group (Scheme 5.2). In the bond rotation TS, the alkyl, benzyl, allyl R-groups are brought into proximity to the imide carbonyl oxygen. The lone pairs of the oxygen act as a pseudo-nucleophile and have a similar orientation to an S_N2 nucleophile approaching the reactive CH₂ carbon of 1° alkyl and benzyl S_N2 electrophiles. Due to the lack of the leaving group on the electrophile R-group, the carbonyl oxygen cannot form a new bond with the primary CH₂ group of the electrophile, but it can form secondary interactions with the adjacent sp² or sp³ secondary carbons.

Additional advantages of studying S_N2 mechanism using molecular rotor model systems include: accuracy and the incorporation of non-electrostatic variables such as sterics and solvent effects. The secondary electrostatic interactions are weak and thus require a sensitive system for observation and measurement. Small variations in the rotor transition state energies can be observed via measurement of the rotation barriers using EXSY NMR, which has an accuracy of ±0.2 kcal/mol.^{21,22} Furthermore, the carbonyl oxygen to electrophile interaction also takes into account the steric and solvent effects. The solvent effects are of particular interest as they are not easily assessed in computational studies.

5.3 Results and discussion

Molecular rotors **1** were designed with a variety of electrophile R-groups to examine their influence on the bond rotation TS (**Scheme 5.2**). The first atom of the R-group, which mimics the reactive center of the S_N2 reaction, was kept constant as a CH₂-group. The second atom, which can form secondary electrostatic interactions, was varied. Rotors **1** with R = CH₂CH₃ and CH₂CH₂CH₃ measure the kinetic effects of the alkyl electrophiles. In these rotors, the second atom of the R-groups is an sp³ carbon. Rotors **1** R = CH₂CH=CH₂, CH₂Ph, CH₂Ph(*p*-NO₂), and CH₂CN) represent the benzylic, allylic, and alkynyl electrophiles. The second atom of their R-groups is an sp² or sp carbon.



Scheme 5.2 Conformational *syn-anti* equilibrium based on the rotation of *N*-phenyl imide rotors. Rotors **1** were designed to study the benzylic and allylic effects of regular S_N2 reactions which involve a substitution reaction a sp³ carbon. Rotors **2** were selected for the general benzylic effects where the primary atom was an oxygen, nitrogen, sulfur, or sp² carbon.

Rotors **1** were synthesized via condensation reactions of *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride and 2-substituted aniline. Many of the rotors for this study had

been synthesized in our previous rotor papers which studied the TS effects of various non-covalent interactions.^{1,5} The rotational barriers for rotors **1** were measured by 2D EXSY NMR in TCE-2d (Table 5.1) usually by following the norbornene alkene protons, which displayed distinct peaks for the *syn*- and *anti*-conformers below the rotor's coalescence temperatures (-20 to >140 °C).

To confirm the ability of the rotors to replicate the S_N2 transition states, the experimentally measured rotational barriers ($\Delta G^\ddagger_{\text{exp}}$) were compared with the experimentally measured activation energies ($\Delta\Delta G^\ddagger_{\text{exp}}(\text{S}_{\text{N}}2)$) for the S_N2 reaction of primary bromide electrophiles with a chloride nucleophile (Figure 5.2).^{7,8,228} An excellent correlation between $\Delta G^\ddagger_{\text{exp}}$ and E_a was observed ($R^2 = 0.92$). This suggests that the interactions formed in the bond rotation TS for each electrophile R-group are similar to those in the S_N2 TS.

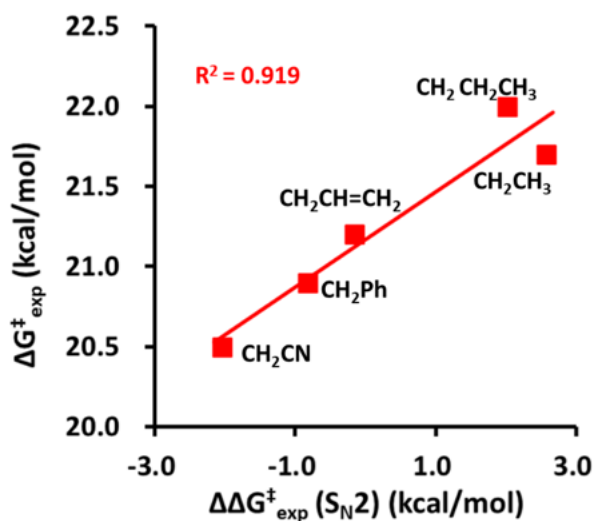


Figure 5.2 Correlation between the NMR-measured rotational barriers ($\Delta G^\ddagger_{\text{exp}}$) for rotors **1** and the experimentally measured free energies of activation ($\Delta\Delta G^\ddagger_{\text{exp}}(\text{S}_{\text{N}}2)$) for the S_N2 reaction of bromide electrophiles relative to the rate of bromomethane.^{7,8,228}

The rotors could also reproduce the calculated reaction barriers (**Figure 5.3a**) from the S_N2 reaction models used to derive the secondary electrostatic interactions. This provides further evidence for bond rotation interactions in the rotors to mimic those in the S_N2 reaction. For example, a plot of the experimentally measured rotational barriers for rotors **1** show a strong linear correlation with the calculated activation energies for the S_N2 reaction of a similar set of electrophiles R-X (X= F or Cl).²²⁷

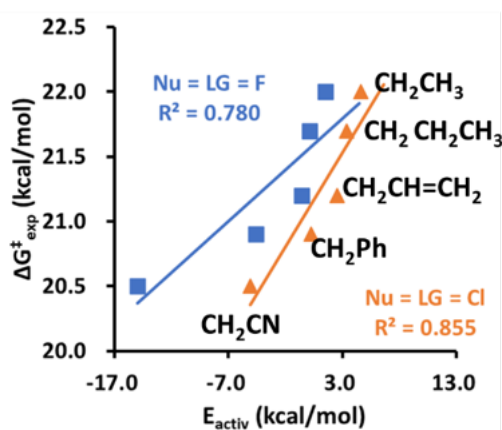


Figure 5.3 The correlations between the theoretical net activation energies of the S_N2 reactions²²⁷ E_{activ} and the experimental rotational barriers $\Delta G^{\ddagger}_{\text{exp}}$. Blue squares and line: Nu = LG = F; Orange triangles and line: Nu = LG = Cl.

The first evidence for the secondary electrostatic interaction in the rotor TS were provided by comparisons of the barriers of rotors with sp^3 versus sp^2 secondary carbons on the R-groups. Rotors **1** with alkyl R-groups (R = CH_2CH_3 and $\text{CH}_2\text{CH}_2\text{CH}_3$) had the highest barriers (22.0 and 21.7 kcal/mol). Rotors **1** with benzyl, allyl, and cyano R-groups (R = $\text{CH}_2\text{CH=CH}_2$, CH_2Ph , $\text{CH}_2\text{Ph}(p\text{-NO}_2)$, and CH_2CN) consistently had lower barriers (21.2 to 20.5 kcal/mol). These trends were consistent with the theoretical studies which found that the sp^3 secondary carbons of alkyl electrophiles formed more repulsive

electrostatic interactions in the S_N2 transition state than the sp² or sp secondary carbons of benzyl, allyl, and alkynyl electrophiles.

Table 5.1 Comparison of the barriers, steric parameters, and interaction energies of rotors **1** in units of kcal/mol.

Rotors (R=)	$\Delta G_{\text{exp}}^{\ddagger}$	<i>B</i> -value	<i>E</i> _{int} ^a
1 (CH ₂ CH ₃)	22.0	8.7 ^b (8.6 ^c)	0
1 (CH ₂ CH ₂ CH ₃)	21.7	8.6 ^c	-0.3
1 (CH ₂ CH=CH ₂)	21.2	9.3 ^c	-0.7
1 (CH ₂ Ph)	20.9	9.3 ^c	-1.1
1 (CH ₂ Ph(<i>p</i> -NO ₂))	20.7	9.3 ^c	-1.3
1 (CH ₂ CN)	20.5	10.0 ^c	-1.5

^a*E*_{int} is defined as the difference in the experimental barriers of a rotor minus the corresponding control rotor **1**(CH₂CH₃), for example, *E*_{int} for **1**(CH₂Ph) = $\Delta G_{\text{exp}}^{\ddagger}(\text{CH}_2\text{Ph}) - \Delta G_{\text{exp}}^{\ddagger}(\text{CH}_2\text{CH}_3)$. ^bExperimental rotational barrier. ^cCalculated rotational barriers at B3LYP-631G*.

As expected, the differences in the secondary interactions of the sp³, sp², and sp were relatively small. Therefore, to provide additional support that the observed trends were due to the secondary electrostatic interactions, a second series of rotors **2** was designed that have primary atoms, which cannot undergo S_N2 reactions such as oxygen, sulfur, nitrogen, and sp² carbon (Scheme 5.2). These rotors will form different primary interactions but similar secondary interactions. This highlights one of the advantages of using a model system. Rotors **2** was designed in pairs where the primary atom was the same and the secondary atom was either an sp³ or sp² carbon. Examples of pairs include: (R = CH(CH₃)₂ and CH(CH₃)Ph, OCH₃ and OPh, SCH₃ and SPh, N(CH₃)₂ and N(CH₃)Ph, COCH₃ and CPh) and sp² carbons (R = CH(CH₃)Ph, OPh, SPh, N(CH₃)Ph, CPh). Rotors **2** were synthesized and their barriers were measured (Table 5.2).

Table 5.2 The experimental rotational barriers and steric parameters of XCH₃ and XPh, and interaction energies of XPh.

Rotors	$\Delta G_{\text{exp}}^{\ddagger}$	<i>B</i> -values	$\Delta\Delta G_{\text{sp}^3\text{-sp}^2}^{\ddagger \text{ a}}$
1 (CH ₂ CH ₃)	22.0	8.7	-
1 (CH ₂ Ph)	20.9	9.3	1.1
2 (CH(CH ₃) ₂)	23.6	11.1	-
2 (CH(CH ₃)Ph)	23.1	11.4	0.5
2 (OCH ₃)	20.2	5.6	-
2 (OPh)	18.2	4.2	2.0
2 (SCH ₃)	22.5	8.6	-
2 (SPh)	21.8	8.3	0.7
2 (N(CH ₃)CH ₃)	22.0	6.9	-
2 (N(CH ₃)Ph)	20.2	6.2	1.8
2 (COCH ₃)	13.9	8.0	-
2 (COPh)	12.9	7.3	1.0

$$^{\text{a}}\Delta\Delta G_{\text{sp}^3\text{-sp}^2}^{\ddagger} = \Delta G_{\text{exp}}^{\ddagger}(\text{X CH}_3) - \Delta G_{\text{exp}}^{\ddagger}(\text{XPh}).$$

Rotors **2** showed the same stability trends as rotors **1** as rotors with R-groups with secondary sp³ carbons consistently had higher barriers than secondary sp² carbons. For example, **2**(OCH₃) and **2**(OPh) had barriers of 20.2 and 18.2 kcal/mol, which equates to a difference of 2.0 kcal/mol. The other sp³ and sp² pairs showed similar differences of 0.7 kcal/mol for **2**(SCH₃) and **2**(SPh), 1.8 kcal/mol for **2**(N(CH₃)₂) and **2**(N(CH₃)Ph), and 1.0 kcal/mol for **2**(COCH₃) and **2**(COPh). This demonstrates that the secondary electrostatic trends are present and are of similar magnitude regardless of the nature of the primary atom. The consistency of the benzylic effect in our rotor model system is evident from a plot comparing the barriers for the secondary sp³ (R = XCH₃) and sp² (R = XPh), where X = CH₂, CH(CH₃), O, S, N(CH₃) and CO (Figure 5.4). From comparison to the 1:1 trendline,

we can see that the sp^2 rotors **2** consistently have barriers that are average 1 kcal/mol lower than the sp^3 rotors **2**.

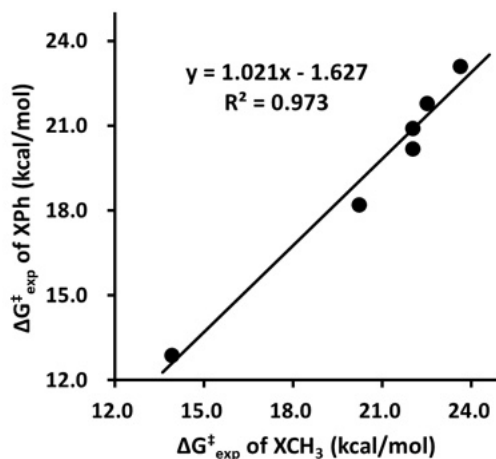


Figure 5.4 The correlations between the experimental barriers of rotors with $R = XCH_3$ and XPh ($X = CH_2, CH(CH_3), O, S, NCH_3, C=O$).

Next, we investigated alternative explanations for the lower barriers of the rotors with secondary sp^2 carbons. Specifically, the trends could be due to differences in steric size of the sp^2 and sp^3 groups. To test this hypothesis, the size of the R-groups were compared (**Table 5.1**). The steric parameter, B -value, was chosen for the comparison because the parameter is derived from the rotational barriers of similar biaryl rotors.¹⁶⁵ The steric parameters were inconsistent with the observed barrier trends for rotors **1**. For example, CH_2Ph is larger than CH_2CH_3 (B -value = 9.3 and 8.7 kcal/mol), which is opposite to the lower measured barrier for **1**(CH_2Ph) versus **1**(CH_2CH_3). Similarly, the B -values could not explain the lower barriers for the allylic or α -cyano rotors, **1**($CH_2CH=CH_2$) and **1**(CH_2CN), as the B -values for the corresponding R-groups (9.3 and 10.0 kcal/mol) were all larger than the B -value of CH_2CH_3 (8.7 kcal/mol). In fact, observed barrier trends are opposite to those predicted by the steric parameters (Figure 5.5b). The plot of the measured

barriers for rotors **1** versus B -value had a negative slope, which means that the barrier is decreasing even though the size of the R-groups is increasing. This rules out sterics as a possible origin for the observed barrier trends.

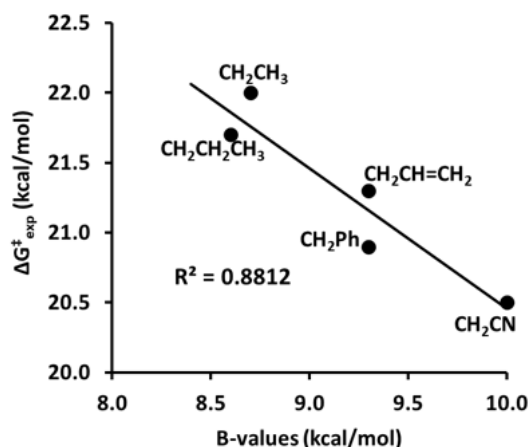


Figure 5.5 The correlations between the B -values and the experimental rotational barriers.

To verify the secondary electrostatic origins of the barrier trends, an analysis was conducted of the charges on the primary and secondary atoms. The atomic NBO charges used were previously calculated by Galabov, Wu, and Allen for the S_N2 electrophiles. The experimentally measured barriers for rotors **1** were plotted against the NBO charges for the primary and secondary atoms of the electrophiles, which are the same as the primary and secondary atoms of the R-groups in **1**. Interestingly both the primary and secondary atom charges are correlated with $\Delta G^\ddagger_{\text{exp}}$ (Figure 5.6). However, only the secondary atom charges were consistent with the barrier trends. The charges on the primary atoms only span a small range (-0.34 to -0.15 kcal/mol). More importantly, the charges become more negative going from CH2CH3 to CH2CN. This is opposite to the expected observed rotors and S_N2 reaction trends. The nucleophile in the S_N2 reaction and the pseudo-nucleophile in the rotors have negative or partial negative charge. Thus, if the primary electrostatic

interactions were the origins of the observed trends, then the strength of the nucleophile-electrophile electrostatic interaction would strengthen as the primary atom became more positive or less negative. However, the opposite trend is observed. The rotors spin slower, and the barriers increase as the primary atom becomes more positive. In contrast, the charge on the secondary atom is consistent with the observed trends. As the charge on the secondary atom becomes more positive, the barrier decreases. This is consistent with a strengthening electrostatic interaction between the nucleophile or pseudo-nucleophile and the secondary carbon of the electrophile.

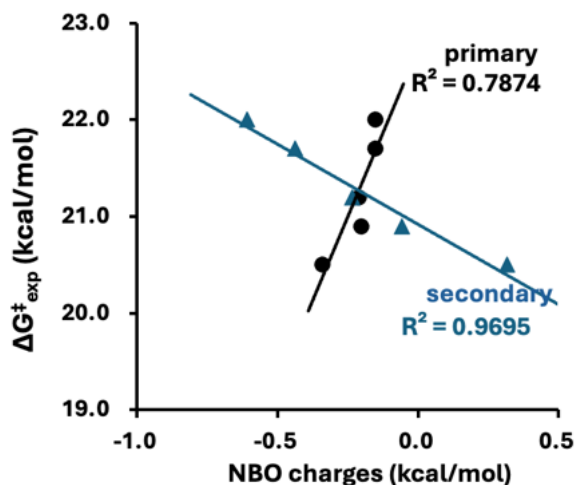


Figure 5.6 The correlations between $\Delta G^\ddagger_{\text{exp}}$ and the calculated NBO charges²²⁷ on the primary and secondary carbons of the electrophiles in the S_N2 reaction where the nucleophile and leaving group are chlorides.

5.4 Conclusion

In conclusion, this study provides strong experimental evidence supporting the secondary electrostatic interaction hypothesis for the benzylic S_N2 effect, using molecular rotors as a model system. The rotors contain an electronegative carbonyl oxygen that makes close contact to electrophilic R-groups at the *ortho*-position of the N-phenyl rotor, which

mimics the nucleophile-electrophile TS interactions. Unlike the S_N2 TS, the rotational barrier TS do not have the possibility for stabilization due to conjugation as the rotors do not form bonds, which rules out the alternative explanation for the benzylic effect. The rotational barriers of the rotors with varying electrophile R-groups were shown to correlate with the experimental and calculated S_N2 rates of the analogous electrophiles. Our results demonstrate that rotors with sp² or sp carbons at the secondary position exhibit significantly lower rotational barriers compared to those with sp³ carbons, mirroring the trends observed in S_N2 reaction rates. This is consistent with the theoretical predictions by Galabov, Wu, and Allen, which attribute the enhanced reactivity of benzylic and allylic electrophiles to favorable electrostatic interactions in the transition state. Furthermore, the correlation between the experimental rotational barriers of the rotors and the calculated activation energies for analogous S_N2 reactions further substantiates the validity of the rotor model in mimicking S_N2 transition states. Additionally, the analysis of NBO charges confirmed that the observed trends are due to secondary electrostatic effects rather than steric factors. Thus, our findings validate the secondary electrostatic interaction hypothesis and contribute to a deeper understanding of the factors influencing S_N2 reaction mechanisms.

5.5 Supporting information

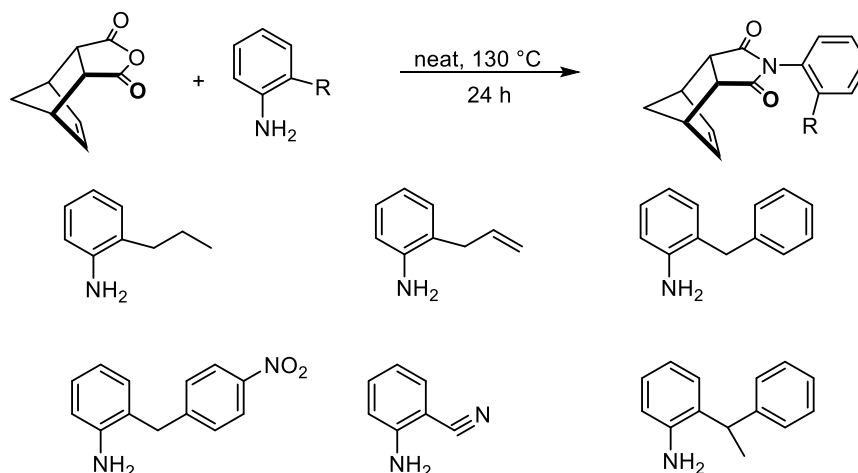
5.5.1 General experimental procedures

NMR spectra were recorded on a Bruker 400 MHz spectrometer at 25 °C. Chemical shifts are reported in ppm (δ) and were referenced to residual solvent peaks, ¹H NMR (400 MHz, chloroform-d) δ 7.26 ppm, ¹³C NMR (100 MHz, chloroform-d) δ 77.16 ppm. Chemicals and solvents were purchased from commercial suppliers and used as received. Flash chromatography was performed using silica gel from Sorbent Technologies (60 Å,

200 – 400 mesh). HRMS were measured using a magnetic sector spectrometer (VG 70S) using EI.

5.5.2 Synthesis of the molecular rotors

Rotors **1** were prepared via a thermal condensation between an *ortho*-substituted aniline and norbornene anhydride (**Scheme 5.3**), most of rotors **2** were earlier reported by similar way.^{1,20,211}



Scheme 5.3 General synthetic route of the rotors **1**.

5.5.3 ¹H and ¹³C NMR spectra

The NMR data and spectrum for new rotors are listed in the following section (**Figure 5.7 to 5.16**):

Rotor **1**(CH₂CH₂CH₃) (*3aR,4R,7S,7aS*)-2-(2-propylphenyl)hexahydro-1*H*-4,7-methanoisindole-1,3(2*H*)-dione: *cis*-5-Norbornene-endo-2,3-dicarboxylic anhydride (164 mg, 1.0 mmol), 2-propylaniline (162 mg, 1.2 mmol), were added to a heavy wall glass pressure vessel with a magnetic stir bar. The pressure vessel was then capped and heated to 130 °C in a silicon oil bath for 24 hours. After letting the pressure vessel cool to room

temperature, the crude material was purified by column chromatography (ethyl acetate/hexanes = 1:5 to 1:2, v/v) to give **1**(CH₂CH₂CH₃), as a colorless solid (142 mg, 50%).

¹H NMR (400 MHz, CDCl₃) δ 7.27 – 7.21 (m, 2H), 7.18 – 7.13 (m, 2H), 6.86 (dd, *J* = 7.8 Hz, *J* = 1.0 Hz, 1H *major*), 6.75 (dd, *J* = 7.8 Hz, *J* = 1.0 Hz, 1H *minor*), 6.24 – 6.21 (m, 2H, *major* and *minor*), 3.43 – 3.37 (m, 4H, *major* and *minor*), 2.31 – 2.23 (m, 2H, *major* and *minor*), 1.75 – 1.70 (m, 1H, *major* and *minor*), 1.58 – 1.39 (m, 3H, *major* and *minor*), 0.87 (t, *J* = 7.4 Hz, 3H *major*), 0.82 (t, *J* = 7.4 Hz, 3H *minor*). ¹³C NMR (101 MHz, CDCl₃) δ 177.3, 177.0, 140.5, 140.2, 135.3, 134.7, 130.97, 130.91, 130.0, 129.5, 128.6, 128.2, 127.0, 126.9, 53.0, 52.4, 46.9, 45.9, 45.5, 45.2, 33.6, 33.3, 23.7, 23.1, 14.18, 14.16.

Rotor **1**(CH₂Ph) (*3aR,4R,7S,7aS*)-2-(2-benzylphenyl)hexahydro-1*H*-4,7-methanoisindole-1,3(2*H*)-dione: *cis*-5-Norbornene-endo-2,3-dicarboxylic anhydride (164 mg, 1.0 mmol), 2-benzylaniline (275 mg, 1.5 mmol), were added to a heavy wall glass pressure vessel with a magnetic stir bar. The pressure vessel was then capped and heated to 130 °C in a silicon oil bath for 24 hours. After letting the pressure vessel cool to room temperature, the crude material was purified by column chromatography (ethyl acetate/hexanes = 1:5 to 1:2, v/v) to give **1**(CH₂Ph), as a colorless solid (345 mg, 80%).

¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.17 (m, 6H), 7.06 (d, *J* = 7.4 Hz, 3H, *major*), 6.87 (d, *J* = 7.4 Hz, 3H, *minor*), 6.25 (s, 2H, *major*), 6.01 (s, 2H, *minor*), 3.87 (s, 2H, *major*), 3.76 (s, 2H, *minor*), 3.47 – 3.40 (m, 4H, *major*), 3.47 – 3.40 (m, 4H, *major*), 3.11 – 3.10 (m, 4H, *minor*), 1.74 (t, *J* = 9.0 Hz, 1 H, *major* and *minor*), 1.77-1.72 (m, 1 H, *major* and *minor*), 1.61 (d, *J* = 4.4 Hz, 1 H, *minor*), 1.52 (d, *J* = 9.0 Hz, 1 H, *major*). ¹³C NMR

(101 MHz, CDCl₃) δ 176.9, 176.6, 139.6, 139.5, 138.7, 138.5, 135.3, 134.7, 131.4, 131.3, 131.0, 129.7, 129.5, 129.3, 128.84, 128.75, 128.6, 127.5, 127.44, 126.5, 126.3, 52.9, 52.3, 46.9, 45.8, 45.3, 38.5, 37.0.

Rotor **1**(CH₂Ph(*p*-NO₂)) (*3aR,4R,7S,7aS*)-2-(2-(4-nitrobenzyl)phenyl)hexahydro-1*H*-4,7-methanoisoindole-1,3(2*H*)-dione: *cis*-5-Norbornene-endo-2,3-dicarboxylic anhydride (82 mg, 0.5 mmol), 2-(4-nitrobenzyl)aniline (136 mg, 0.6 mmol), were added to a heavy wall glass pressure vessel with a magnetic stir bar. The pressure vessel was then capped and heated to 130 °C in a silicon oil bath for 24 hours. After letting the pressure vessel cool to room temperature, the crude material was purified by column chromatography (ethyl acetate/hexanes = 1:5 to 1:2, v/v) to give **1**(CH₂Ph(*p*-NO₂)), as a colorless solid (150 mg, 80%).

¹H NMR (400 MHz, CDCl₃) δ 8.14 – 8.09 (m, 2H), 7.38 – 7.31 (m, 2H), 7.21 (t, *J* = 7.5 Hz, 3H, *major*), 7.08 – 7.03 (m, *minor* for left 3H, and *minor* for right 1H), 6.90 (d, *J* = 7.7 Hz, 1H, *major*), 6.27 (s, 2H, *major*), 5.96 (s, 2H, *minor*), 3.93 (s, 2H, *major*), 3.85 (s, 2H, *minor*), 3.50 – 3.44 (m, 4H, *major*), 3.19 (s, 2H, *minor*), 1.78-1.75 (m, 1 H, *major* and *minor*), 1.61 (d, *J* = 8.8 Hz, 1 H, *minor*), 1.56 (d, *J* = 9.0 Hz, 1 H, *major*). ¹³C NMR (101 MHz, CDCl₃) δ 176.9, 176.7, 147.6, 147.3, 146.8, 137.0, 136.9, 135.3, 134.8, 131.53, 131.42, 131.27, 131.01, 130.00, 129.94, 129.90, 129.70, 129.05, 128.97, 128.24, 123.85, 128.80, 53.1, 52.4, 46.96, 45.8, 45.5, 45.3, 37.9, 36.8.

Rotor **1**(allyl) (*3aR,4R,7S,7aS*)-2-(2-allylphenyl)hexahydro-1*H*-4,7-methanoisoindole-1,3(2*H*)-dione: *cis*-5-Norbornene-endo-2,3-dicarboxylic anhydride (82

mg, 0.5 mmol), 2-allylaniline (136 mg, 0.6 mmol), were added to a heavy wall glass pressure vessel with a magnetic stir bar. The pressure vessel was then capped and heated to 130 °C in a silicon oil bath for 24 hours. After letting the pressure vessel cool to room temperature, the crude material was purified by column chromatography (ethyl acetate/hexanes = 1:5 to 1:2, v/v) to give **1**(allyl), as a colorless solid (150 mg, 80%).

¹H NMR (400 MHz, CDCl₃) δ 7.26 – 7.12 (m, 3H), 6.85 (dd, J = 7.8 Hz, J = 1.0 Hz, 1H, *minor*), 6.74 (dd, J = 7.4 Hz, J = 0.9 Hz, 1H, *major*), 6.17 (t, J = 1.8 Hz, 2H, *major* and *minor*), 5.76 – 5.62 (m, 1H, *major* and *minor*), 4.97 – 4.87 (m, 2H, *major* and *minor*), 3.37 – 3.34 (m, 4H, *major*), 3.28 – 3.27 (m, 4H, *minor*), 3.10 (d, J = 6.8 Hz, 2H, *major*), 3.00 (d, J = 6.4 Hz, 2H, *minor*), 1.70 – 1.63 (m, 1H, *major* and *minor*), 1.49 (t, J = 9.8 Hz, 1H, *major* and *minor*). **¹³C NMR** (101 MHz, CDCl₃) δ 177.1, 176.9, 137.9, 137.6, 135.97, 135.95, 135.37, 134.8, 131.2, 130.6, 130.4, 129.68, 129.62, 128.6, 128.4, 127.49, 127.43, 116.9, 116.5, 52.96, 52.5, 46.9, 45.97, 45.49, 45.34, 36.45, 35.6.

Rotor **1**(CH₂CN) 2-(2-((3*aR*,4*R*,7*S*,7*aS*)-1,3-dioxooctahydro-2*H*-4,7-methanoisoindol-2-yl)phenyl)acetonitrile: *cis*-5-Norbornene-endo-2,3-dicarboxylic anhydride (82 mg, 0.5 mmol), 2-(2-aminophenyl)acetonitrile (136 mg, 0.6 mmol), were added to a heavy wall glass pressure vessel with a magnetic stir bar. The pressure vessel was then capped and heated to 130 °C in a silicon oil bath for 24 hours. After letting the pressure vessel cool to room temperature, the crude material was purified by column chromatography (ethyl acetate/hexanes = 1:5 to 1:2, v/v) to give **1**(CH₂CN), as a colorless solid (150 mg, 80%).

^1H NMR (400 MHz, CDCl_3) δ 7.62 – 7.12 (d, $J = 7.6$ Hz, 3H, *minor*), 7.48 – 7.37 (m, 3H, *minor*), 7.08 (dd, $J = 7.6$ Hz, $J = 1.4$ Hz, 1H, *minor*), 6.98 (dd, $J = 7.1$ Hz, $J = 2.2$ Hz, 1H, *major*), 6.36 (s, 2H, *minor*), 6.30 (s, 2H, *major*), 3.60 (s, 2H, *major*), 3.50 (s, 4H, *major* and *minor*), 3.59 (s, 2H, *minor*), 1.85 (d, $J = 8.6$ Hz, 1 H, *minor*), 1.80 (d, $J = 8.6$ Hz, 1 H, *major*), 1.65 (d, $J = 9.4$ Hz, 1 H, *minor*), 1.62 (d, $J = 9.4$ Hz, 1 H, *major*). **^{13}C NMR** (101 MHz, CDCl_3) δ 176.7, 176.3, 135.6, 134.8, 130.8, 130.7, 130.2, 130.06, 129.83, 129.33, 129.30, 129.10, 128.96, 128.1, 127.99, 116.9, 116.8, 53.2, 52.5, 46.9, 46.1, 45.6, 45.4, 20.9.

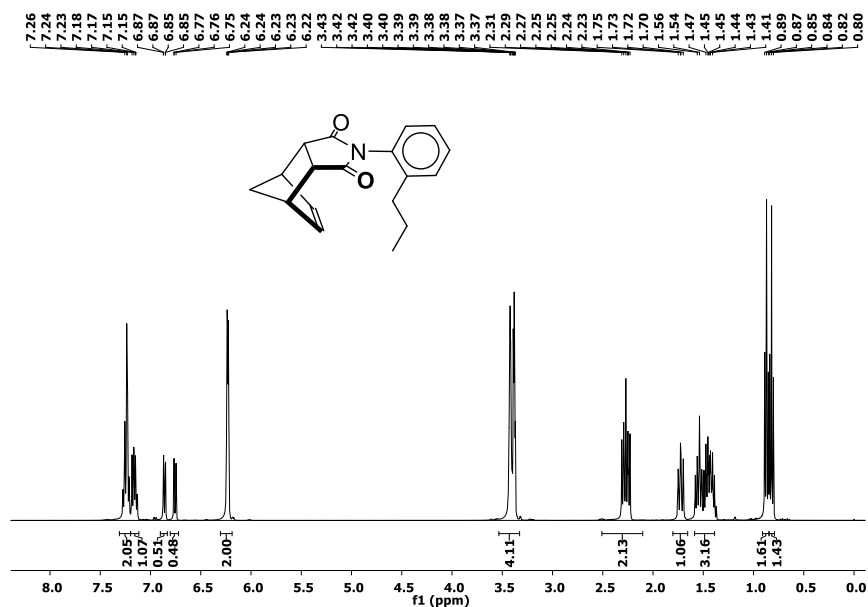


Figure 5.7 ^1H NMR spectra (400 MHz) of rotor 1 ($\text{CH}_2\text{CH}_2\text{CH}_3$) in CDCl_3

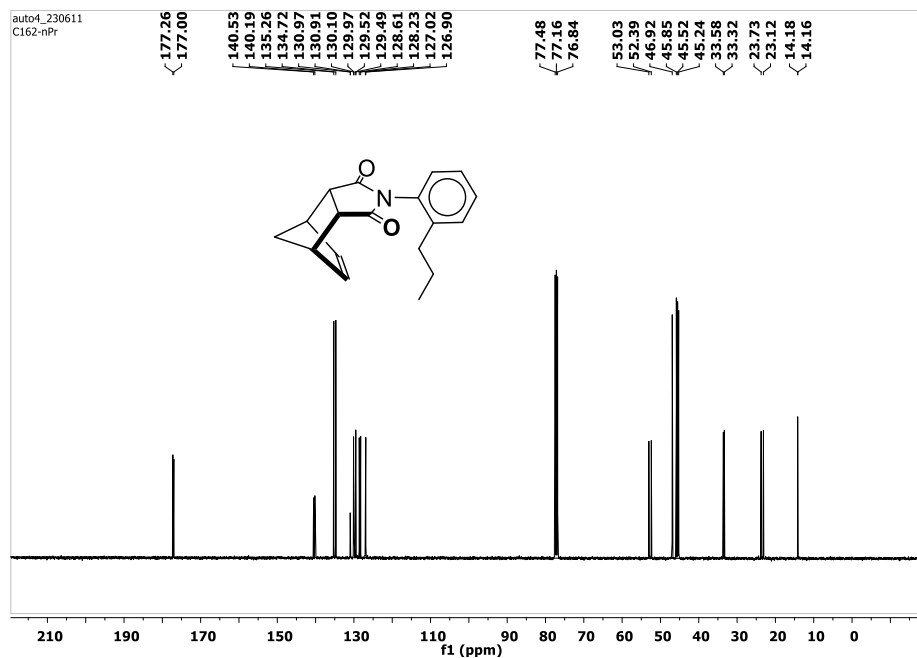


Figure 5.8 ¹³C NMR spectra (100 MHz) of rotor **1**(CH₂CH₂CH₃) in CDCl₃

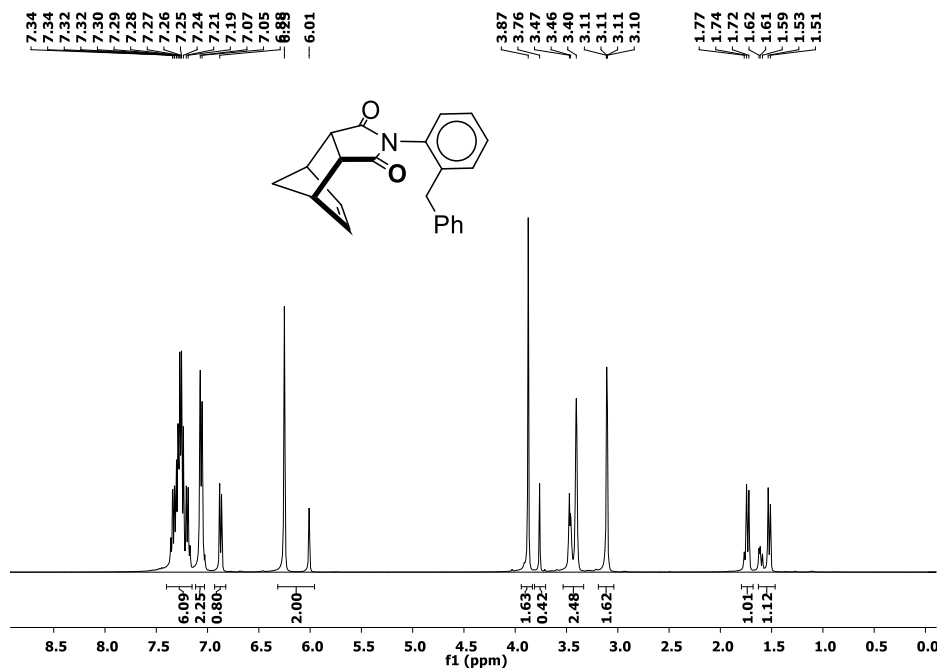


Figure 5.9 ¹H NMR spectra (400 MHz) of rotor **1**(CH₂Ph) in CDCl₃

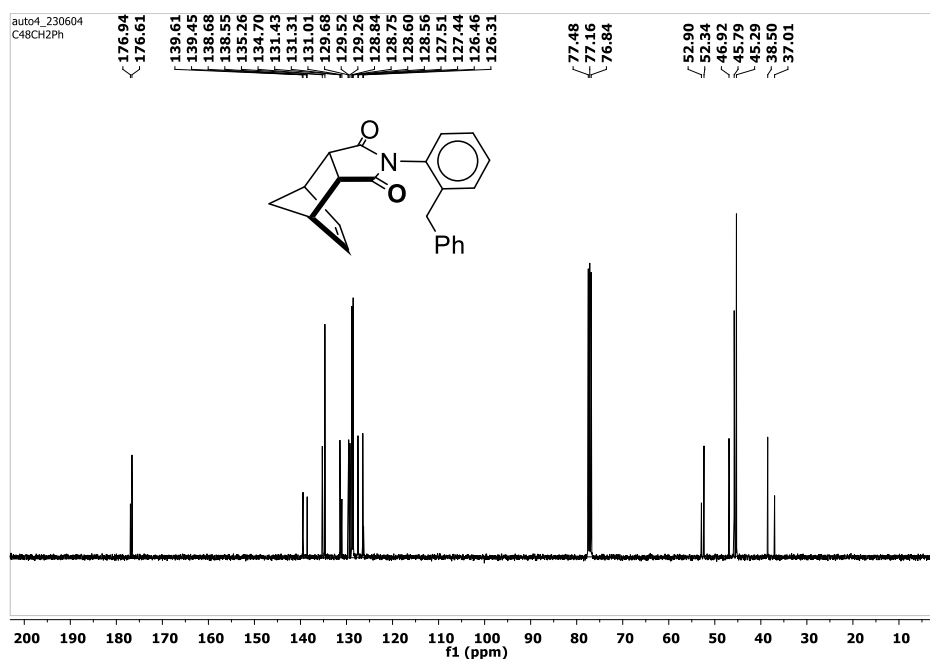


Figure 5.10 ^{13}C NMR spectra (100 MHz) of rotor **1**(CH_2Ph) in CDCl_3

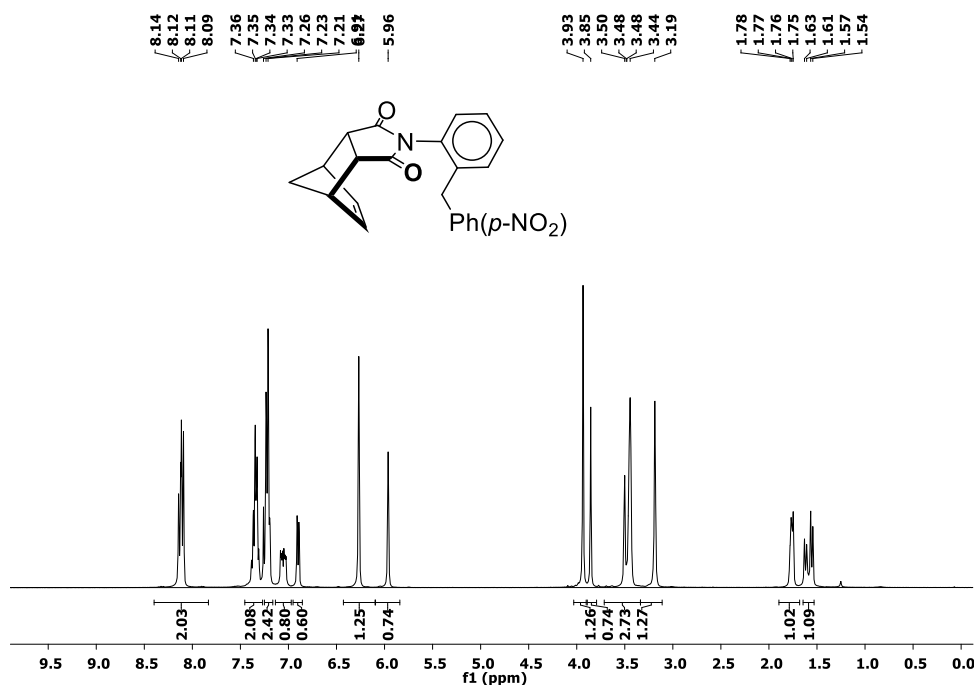


Figure 5.11 ^1H NMR spectra (400 MHz) of rotor **1**($\text{CH}_2\text{Ph}(\text{NO}_2)$) in CDCl_3

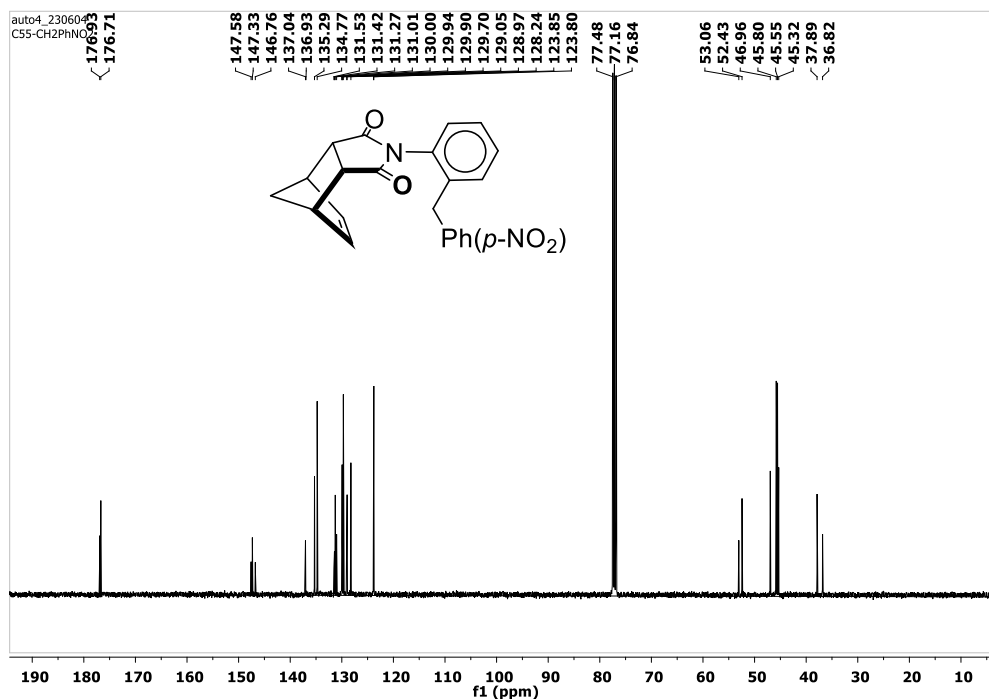


Figure 5.12 ^{13}C NMR spectra (100 MHz) of rotor **1**($\text{CH}_2\text{Ph}(\text{NO}_2)$) in CDCl_3

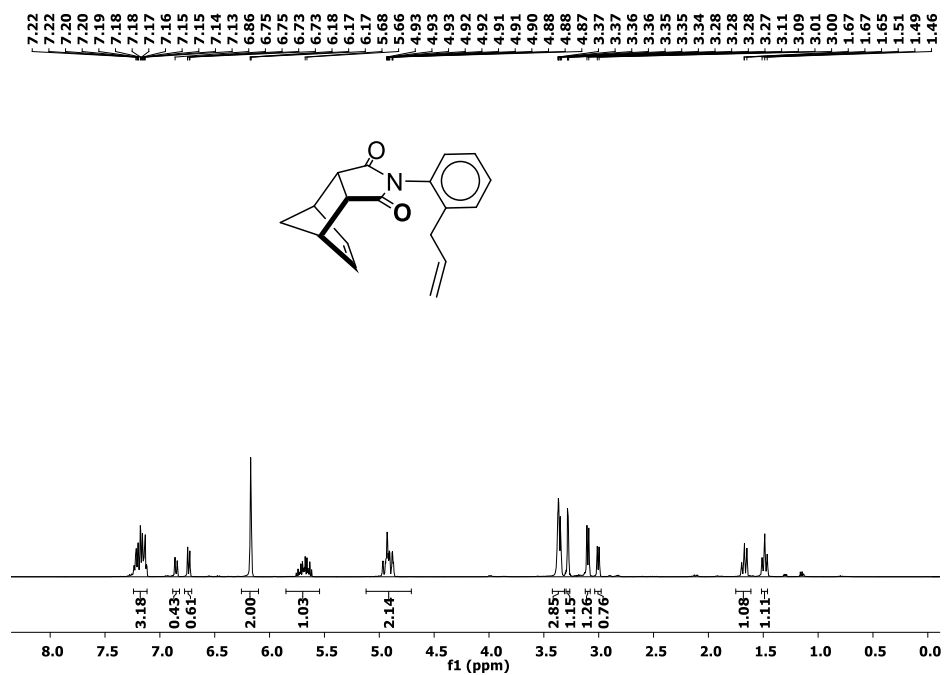


Figure 5.13 ^1H NMR spectra (400 MHz) of rotor **1**(allyl) in CDCl_3

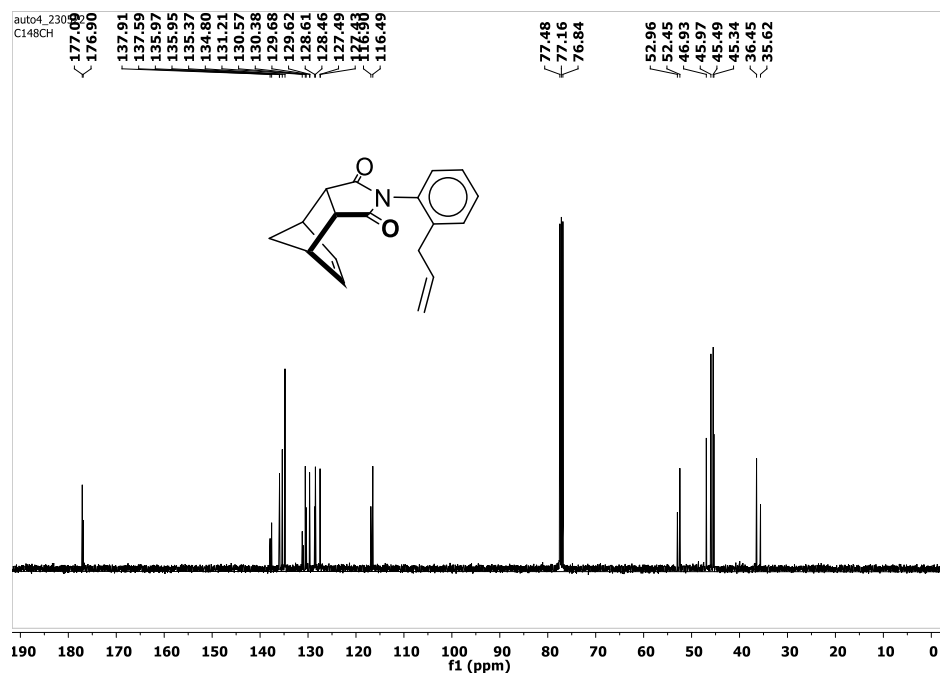


Figure 5.14 ^{13}C NMR spectra (100 MHz) of rotor **1**(allyl) in CDCl_3

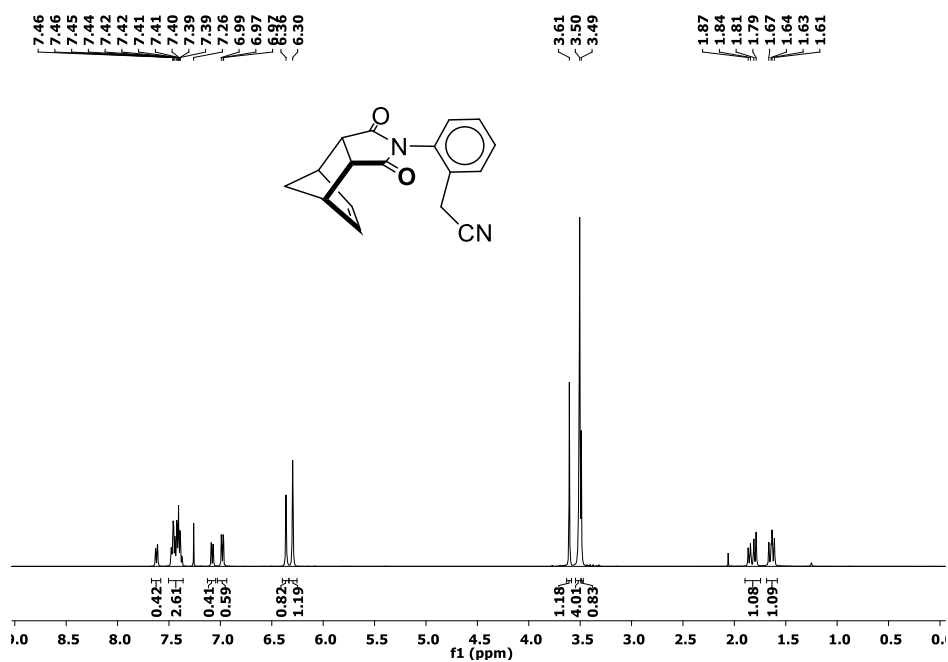


Figure 5.15 ^1H NMR spectra (400 MHz) of rotor **1**(CH_2CN) in CDCl_3

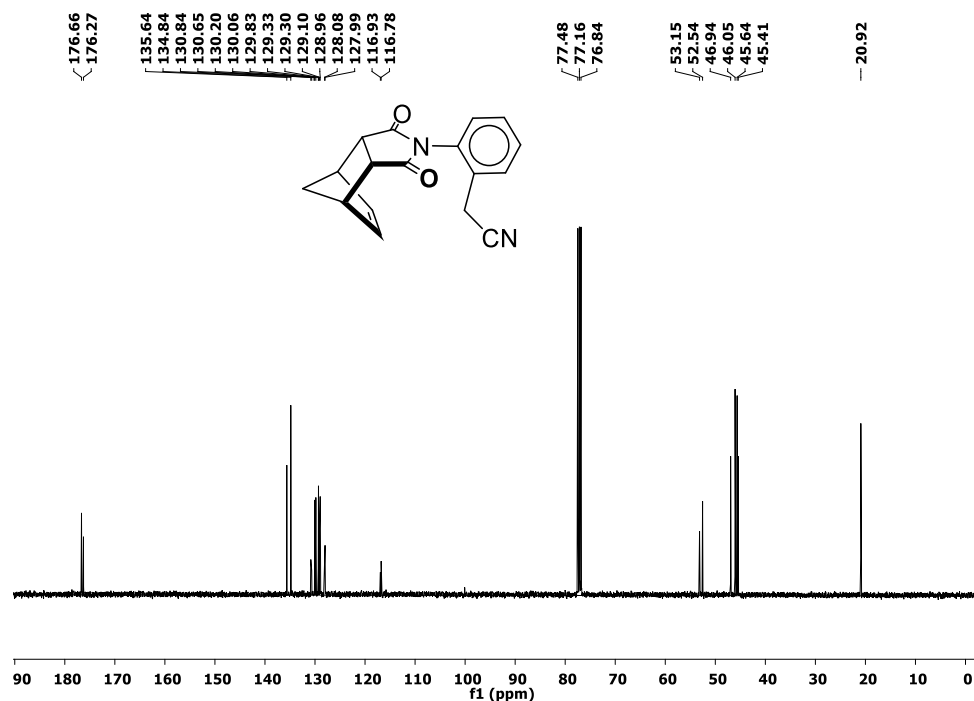


Figure 5.16 ¹³C NMR spectra (100 MHz) of rotor 1(CH₂CN) in CDCl₃

5.5.4 Experimental measurements of the rotational barriers

The experimental rotational barriers of the rotors were determined via exchange spectroscopy (EXSY) NMR experiments in TCE-d₂. An example of the 2D NOESY spectra is shown in **Figure 5.17**. The integration of the crosspeak and diagonal signals were performed using the Bruker Topspin software, and rate constants were calculated using EXSYCalc. The rotational barrier ($\Delta G^\ddagger_{\text{exp}}$) for each rotor were extrapolated to room temperature for comparison. The TS enthalpy ($\Delta H^\ddagger_{\text{exp}}$) and entropy ($\Delta S^\ddagger_{\text{exp}}$) for rotors were obtained using Eyring plots (**Figures 5.18–5.20**).

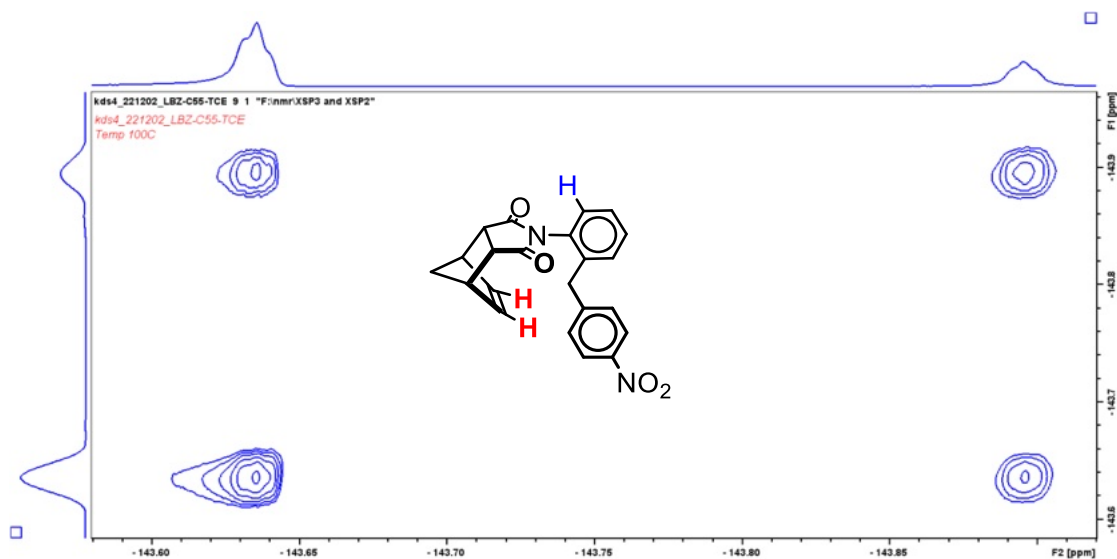


Figure 5.17 2D NMR of diastereomeric alkene protons (red) of **1**(CH₂Ph(NO₂)) in TCE-d₂ at 100 °C. 2D NOESY spectra could be also measured via the *ortho*-phenyl proton (blue).

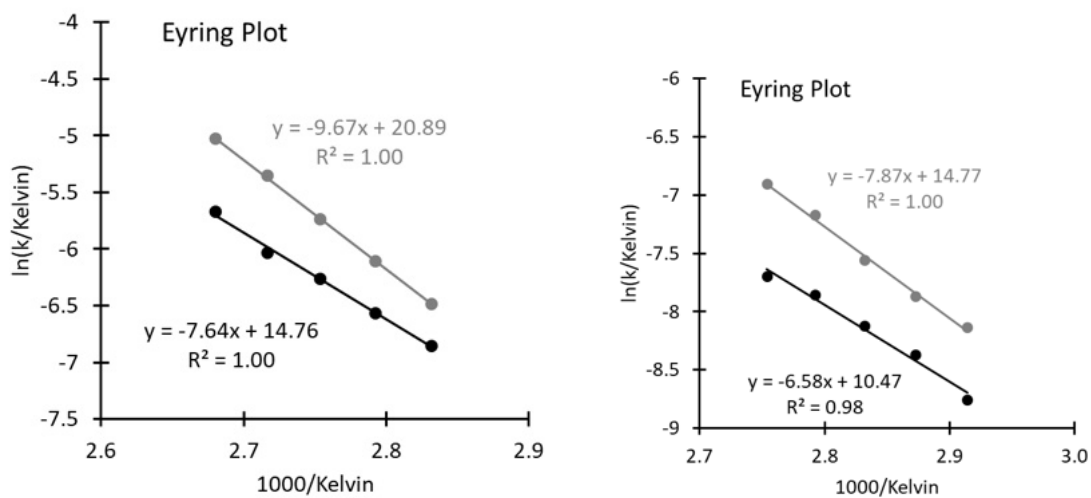


Figure 5.18 Eyring plots for rotor **1**(CH₂Ph(NO₂)) (left) and rotor **1**(CH₂Ph) (right) by EXSY.

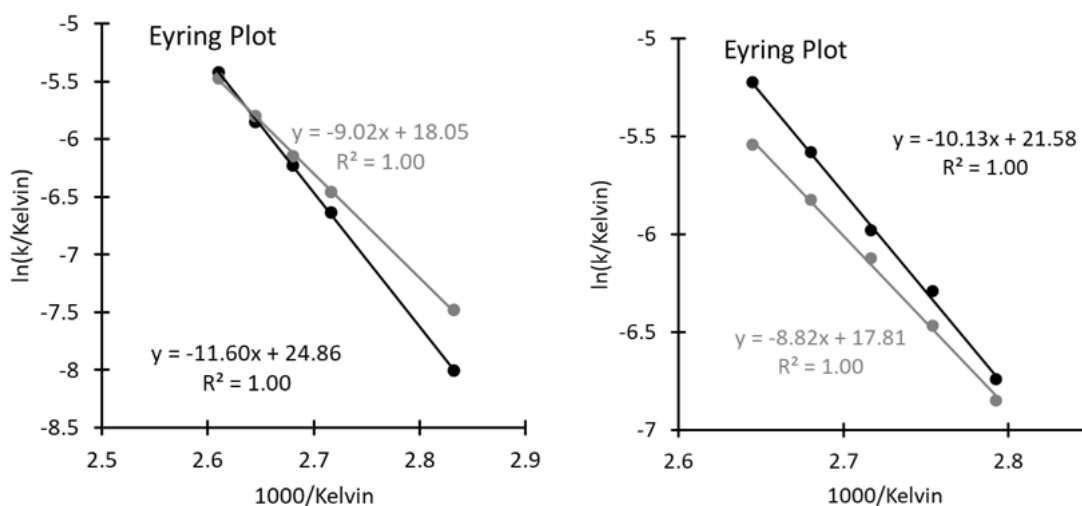


Figure 5.19 Eyring plots for rotor 1(CH₂CH₂CH₃) (left) and rotor 1(allyl) (right) by EXSY.

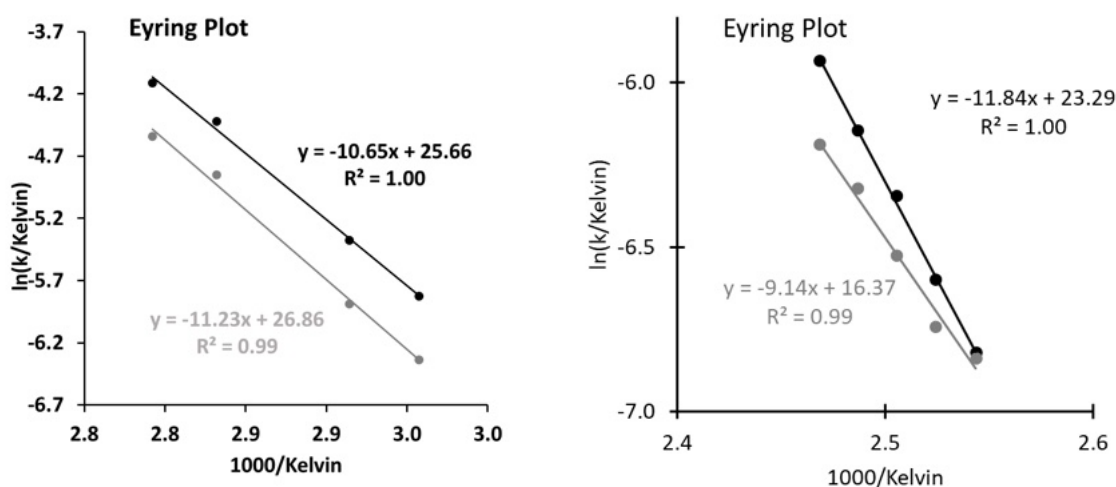


Figure 5.20 Eyring plots for rotor 1(CH₂CN) and 2(CH(CH₃)Ph) by EXSY.

5.5.5 Isolation of interaction energies of overall interactions

When the overall steric and non-covalent interactions are considered, the interaction energies will more complicated to analyze. We successfully employed the steric control line (**Figure 4.6**) and equations (**equation 4.1, 4.2, 4.3**) to isolate many interactions before, herein, the new rotors were placed into the plot to isolate the overall interaction

energies (**Table 5.3**). The trend of overall interaction energies matched the trend of secondary interaction energies. Noticeably, the NO₂ group on the phenyl ring of CH₂Ph(NO₂) did not strengthen the overall interaction energy than CH₂Ph from the electrostatics, which showed again the substituent effects in our system was not obvious. The overall interaction energies of earlier reported rotors can be read from previous chapters.

Table 5.3 Experimental barriers, steric parameters, steric interaction prediction and interaction energies. All in unit of kcal/mol.

rotors (R =)	$\Delta G^\ddagger_{\text{exp}}$	<i>B</i> -value	E _{steric}	E _{inter}
CH ₂ CH ₂ CH ₃	21.7	8.6	22.4	-0.7
allyl	21.3	9.3	23.0	-1.7
CH ₂ Ph	20.9	9.3	23.0	-2.1
CH ₂ Ph(NO ₂)	20.7	8.8	22.6	-1.9
CH ₂ CN	20.5	10	23.5	-3.0

5.5.7 *B*-value calculations

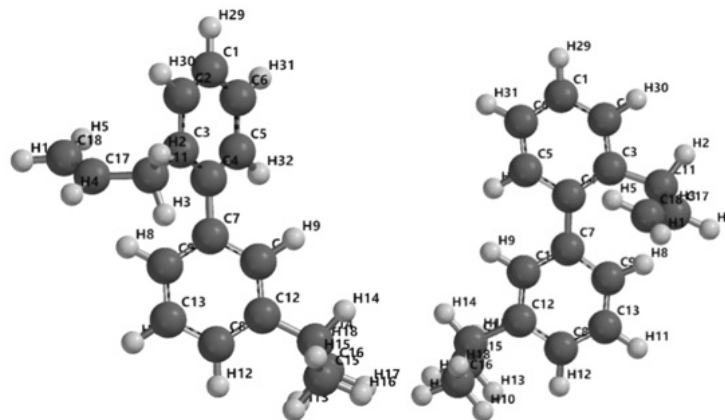
When available, the *B*-values were taken from the literature.^{1,20,165} But the *B*-value for some R-groups were not reported, and therefore, they were calculated using the DFT method used by Mazzanti (B3LYP/6-31G*) without thermodynamic corrections.^{1,20,165} The experimental *B*-values were basically reproduce the calculated *B*-values in the literature, so we think *B*-value was an accurate model when using calculations. The R-groups were inserted at the 2'-position of the biaryl rotor, 2-isopropyl biphenyl and their barriers calculated using Spartan18 (B3LYP/6-31G*). The *B*-values were the differences

using energies of TS subtracted energies of GS (**Table 5.4**). Calculated structures and XYZ coordinates were listed from **Table 5.5-5.10**.

Table 5.4 *B*-values calculations with the TS and GS energies.

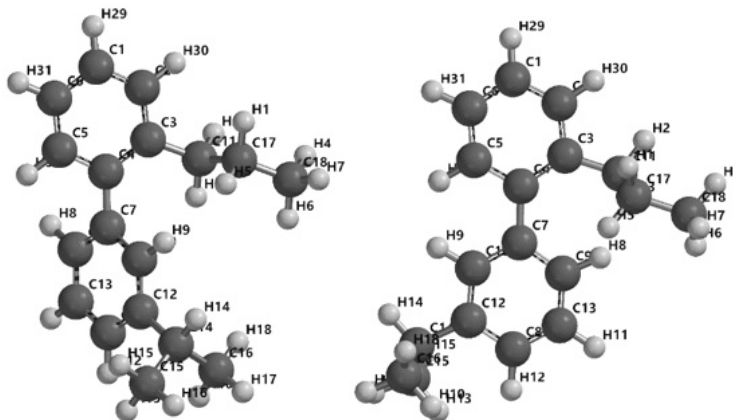
rotors (R =)	GS (kcal/mol)	TS (kcal/mol)	<i>B</i>-value (kcal/mol)
CH ₂ CH ₂ CH ₃	-438749.38	-438740.70	8.68
allyl	-437973.44	-437964.10	9.34
CH ₂ Ph	-534394.96	-534385.62	9.34
CH ₂ Ph(NO ₂)	-662722.92	-662714.10	8.82
CH ₂ CN	-447290.22	-447280.23	9.99
CH(CH ₃)Ph	-559062.99	-559051.62	11.37

Table 5.5 XYZ coordinates of GS (left) and TS structures (right) of rotor **1**(allyl).



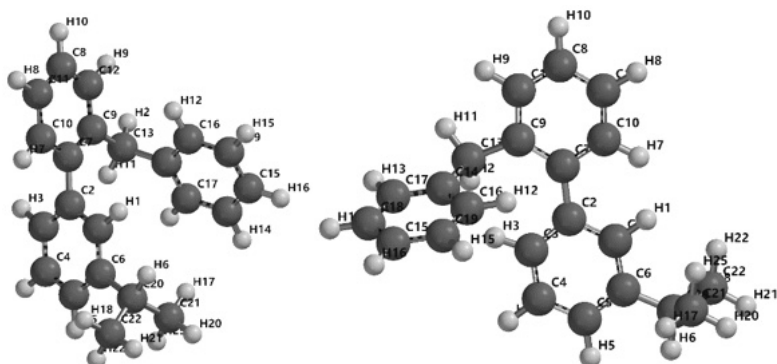
C1	6	0.266655852	-0.252780925	-4.414466476	C1	6	0.391078825	0.062250139	-4.476012843
C4	6	-0.037653033	-0.251323664	-1.612658489	C4	6	-0.011060792	0.304093893	-1.650217705
C2	6	-0.657334045	0.588011477	-3.799448084	C2	6	-0.811690666	0.515609930	-3.949157685
C6	6	1.055470998	-1.094503945	-3.629590352	C6	6	1.418625071	-0.248613908	-3.592025309
C5	6	0.901786502	-1.084574520	-2.245963721	C5	6	1.209293538	-0.120551780	-2.224607888
C3	6	-0.828912141	0.609331189	-2.407322457	C3	6	-1.046047271	0.657973410	-2.571213991
H29	1	0.374441169	-0.245337988	-5.495923967	H29	1	0.522909247	-0.030524671	-5.550487899
H30	1	-1.262536760	1.257084734	-4.407319558	H30	1	-1.616850288	0.781892360	-4.630087759
H31	1	1.783487163	-1.756852225	-4.090584578	H31	1	2.385159359	-0.586175547	-3.956875064
H32	1	1.504248831	-1.748013570	-1.631225062	H32	1	2.049626368	-0.353568274	-1.585449772
C11	6	-1.821653253	1.595881743	-1.822923170	C11	6	-2.427136430	1.202190629	-2.234571640
H2	1	-1.686612864	2.569084426	-2.319869125	H2	1	-2.817453273	1.695326550	-3.136955786
H3	1	-1.594599472	1.777325713	-0.765573351	H3	1	-2.367360934	2.013119235	-1.500685262
C7	6	-0.132435896	-0.302821753	-0.124043233	C7	6	-0.094347939	0.351245612	-0.143043711
C8	6	-0.226136345	-0.463343060	2.678995504	C8	6	-0.127854413	0.433861041	2.710940800
C9	6	-1.346849782	-0.549652050	0.532973210	C9	6	-1.195773812	0.853437495	0.576020906
C10	6	1.025682837	-0.139105150	0.654366290	C10	6	0.977012224	-0.126021977	0.649403194
C12	6	1.002045394	-0.210261753	2.051139799	C12	6	0.988045652	-0.089182837	2.045172269
C13	6	-1.386906480	-0.629688491	1.925343454	C13	6	-1.208610631	0.893896224	1.970048076
H8	1	-2.254468271	-0.689443445	-0.046943015	H8	1	-2.075719653	1.211774732	0.073468598
H9	1	1.967882952	0.068532695	0.151317722	H9	1	1.850563927	-0.562474107	0.181170399
H11	1	-2.331664708	-0.828870099	2.425260857	H11	1	-2.084547363	1.292376365	2.475936699
H12	1	-0.278845346	-0.527530165	3.763141596	H12	1	-0.155051263	0.474279846	3.796920994
C14	6	2.280452713	-0.012179280	2.855764382	C14	6	2.194793421	-0.604872021	2.820552819
H14	1	3.082020841	0.212480427	2.138942678	H14	1	2.940134105	-0.933129306	2.082713696
C15	6	2.174745296	1.186134702	3.817656807	C15	6	2.842520183	0.508560444	3.665006928
H13	1	1.398160943	1.021522478	4.573412783	H13	1	2.152503745	0.877857215	4.433121853
H15	1	1.925911078	2.106491281	3.278089513	H15	1	3.132616246	1.361169170	3.041006865
H16	1	3.123308517	1.344607359	4.344633051	H16	1	3.739627751	0.137247282	4.174785533
C16	6	2.683972246	-1.293113986	3.610256946	C16	6	1.838459968	-1.824506454	3.690529737
H10	1	1.930386377	-1.570322951	4.357410942	H10	1	1.094270845	-1.565085964	4.452699117
H17	1	3.636203153	-1.149989018	4.135291908	H17	1	2.727317737	-2.204611573	4.208139357
H18	1	2.796519065	-2.138457342	2.922631975	H18	1	1.423520041	-2.635670563	3.082387343
C17	6	-3.284230963	1.221398738	-1.938451089	C17	6	-3.465973448	0.187286767	-1.800955262
H4	1	-3.966950855	1.958778003	-1.512776436	H4	1	-4.399718087	0.620189922	-1.437700721
C18	6	-3.791602517	0.118762886	-2.491768114	C18	6	-3.354099731	-1.139237490	-1.876386015
H1	1	-4.864238601	-0.052784629	-2.522333370	H1	1	-4.170722781	-1.791137598	-1.578400863
H5	1	-3.159750594	-0.644477843	-2.937445767	H5	1	-2.448059637	-1.620274244	-2.235189903

Table 5.6 XYZ coordinates of GS (left) and TS structures (right) of rotor **1**(CH₂CH₂CH₃).



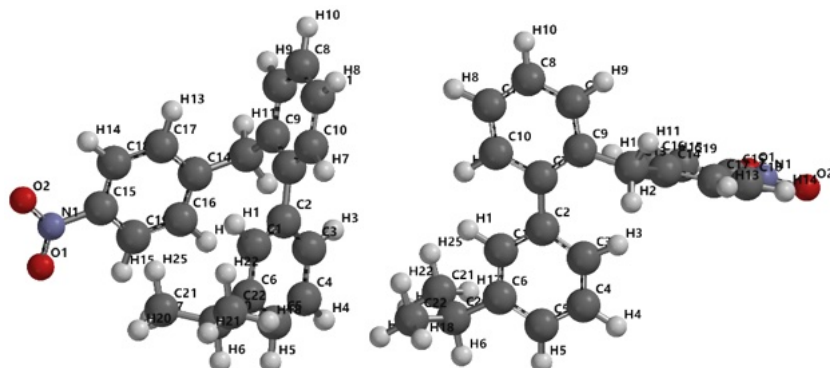
C1	6	-0.412203581	-2.480608497	-3.955350322	C1	6	0.122519014	-0.780812091	-4.409842689
C4	6	0.368283469	-1.551912584	-1.414361470	C4	6	0.205386341	-0.187552979	-1.608741345
C2	6	-0.344171115	-1.116188795	-3.685818251	C2	6	-0.320617267	0.436924748	-3.910508465
C6	6	-0.079737744	-3.394616406	-2.955029633	C6	6	0.608179924	-1.721742131	-3.508455125
C5	6	0.309955722	-2.926672922	-1.703159298	C5	6	0.645155789	-1.416322456	-2.153743991
C3	6	0.039343825	-0.623989861	-2.429141433	C3	6	-0.305176333	0.766947548	-2.544363071
H29	1	-0.713454922	-2.826770027	-4.940713199	H29	1	0.087062601	-0.985241826	-5.476411201
H30	1	-0.580429826	-0.403157844	-4.473399615	H30	1	-0.706684914	1.179450947	-4.605103447
H31	1	-0.123553067	-4.463514554	-3.146659346	H31	1	0.961743709	-2.691236614	-3.849920579
H32	1	0.563104019	-3.633778996	-0.917528296	H32	1	1.037488862	-2.183864737	-1.501277323
C11	6	0.113227326	0.879952936	-2.238100371	C11	6	-0.917275571	2.126837106	-2.237039773
H2	1	0.639035164	1.318688296	-3.097933189	H2	1	-0.933714830	2.704350215	-3.169050411
H3	1	0.712882255	1.119921082	-1.354248291	H3	1	-0.295461998	2.718033760	-1.557872090
C17	6	-1.262789920	1.565590005	-2.118710831	C17	6	-2.370037607	2.039265494	-1.721649250
H1	1	-1.853723363	1.351177885	-3.019471444	H1	1	-2.970486805	1.535166125	-2.489957559
H5	1	-1.820464213	1.125253845	-1.282010473	H5	1	-2.418677056	1.398576862	-0.833704714
C18	6	-1.150184333	3.080596330	-1.924563353	C18	6	-2.972379137	3.412310672	-1.407614370
H4	1	-0.603117493	3.546438718	-2.753650898	H4	1	-2.926134683	4.075265072	-2.280737753
H6	1	-0.615037635	3.323796593	-0.998328156	H6	1	-2.434525807	3.907917962	-0.589166799
H7	1	-2.138732099	3.550987707	-1.871052639	H7	1	-4.022998409	3.325613481	-1.108196125
C7	6	0.808325148	-1.144321708	-0.046068863	C7	6	0.322672318	-0.002926548	-0.113497980
C8	6	1.629413345	-0.450745167	2.550369952	C8	6	0.581930993	0.253142048	2.721016705
C9	6	2.054981220	-1.561740439	0.442559243	C9	6	-0.059653796	1.167536041	0.571637531
C10	6	-0.014639730	-0.382472522	0.798573118	C10	6	0.848698434	-1.031877796	0.703790000
C12	6	0.373642437	-0.024460025	2.094068142	C12	6	0.984820577	-0.930755006	2.090158043
C13	6	2.460222308	-1.212739598	1.730829690	C13	6	0.068625010	1.291225324	1.954697580
H8	1	2.710280252	-2.148048352	-0.196013788	H8	1	-0.469493419	2.010888037	0.046631276
H9	1	-0.995306239	-0.078035477	0.440940021	H9	1	1.175125257	-1.966318781	0.264855285
H11	1	3.431896397	-1.535400465	2.096733753	H11	1	-0.241110423	2.218454689	2.431118729
H12	1	1.962163587	-0.190739331	3.552573260	H12	1	0.670337708	0.362361172	3.798482435
C14	6	-0.554197471	0.804982219	2.972771752	C14	6	1.542144489	-2.098365355	2.896158379
H14	1	-1.477022823	0.969547691	2.399416905	H14	1	1.942943742	-2.829004389	2.178867497
C15	6	-0.942723958	0.063661830	4.264860164	C15	6	2.700449119	-1.672595122	3.818310914
H13	1	-0.067040749	-0.122885083	4.898299511	H13	1	2.357147307	-0.988689643	4.604903768
H15	1	-1.404304180	-0.904442720	4.042014497	H15	1	3.492135168	-1.165392626	3.256176642
H16	1	-1.655827962	0.656026655	4.850656122	H16	1	3.139153837	-2.546065016	4.314257318
C16	6	0.043899678	2.189552244	3.285306738	C16	6	0.429568990	-2.800113033	3.700955970
H10	1	0.966736703	2.103181065	3.871385372	H10	1	-0.012930450	-2.115333751	4.434931537
H17	1	-0.663137252	2.795003667	3.865152679	H17	1	0.829027394	-3.664467818	4.245479827
H18	1	0.284406821	2.732882602	2.364802243	H18	1	-0.374958184	-3.151589741	3.044424567

Table 5.7 XYZ coordinates of GS (left) and TS structures (right) of rotor 1(CH₂Ph).



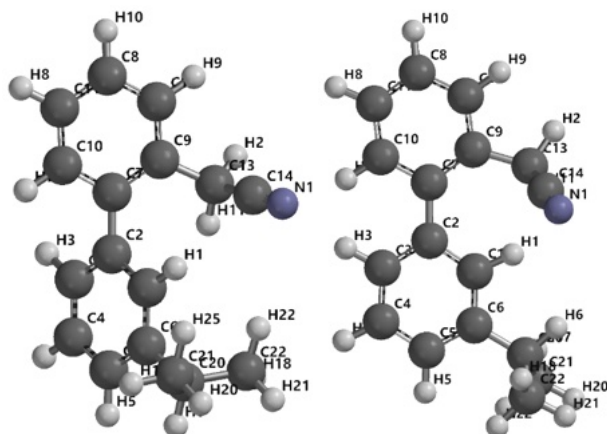
H1	1	0.778151275	0.559891157	1.076528968	H1	1	1.295465278	-0.414053906	2.224033901
C1	6	-0.288491523	0.729449896	0.948823146	C1	6	0.289771627	-0.232776227	1.867435531
C4	6	-3.009478049	1.153105815	0.599654343	C4	6	-2.297721276	0.287877185	1.084758454
C2	6	-0.730053384	1.452107222	-0.168342476	C2	6	-0.068383919	-0.578655230	0.545413213
C6	6	-1.181247339	0.205980347	1.891110583	C6	6	-0.589934562	0.359785590	2.779022188
C5	6	-2.552490715	0.427236947	1.698573576	C5	6	-1.902716394	0.618346807	2.375678736
C3	6	-2.105454181	1.664506491	-0.332599407	C3	6	-1.403181004	-0.293322258	0.189780944
H5	1	-3.271098132	0.030838840	2.411893818	H5	1	-2.603936020	1.081101560	3.066013462
H3	1	-2.462571444	2.234037971	-1.186866400	H3	1	-1.775095272	-0.481694593	-0.800295462
H4	1	-4.075313150	1.322831374	0.468263483	H4	1	-3.312709750	0.491926435	0.753642069
C7	6	0.251980269	2.001487162	-1.157754845	C7	6	0.946950784	-1.188955224	-0.393861622
C8	6	2.081981255	3.124951156	-2.970031860	C8	6	3.047519853	-2.328746645	-1.971619768
C9	6	0.587058710	1.301367514	-2.337940564	C9	6	0.720426852	-1.564671485	-1.754903230
C10	6	0.843918013	3.247245554	-0.907483211	C10	6	2.254611247	-1.405784742	0.099915656
C11	6	1.75591180	3.809484762	-1.800673493	C11	6	3.284471587	-1.955810432	-0.652630038
C12	6	1.496702777	1.885398586	-3.229109874	C12	6	1.776790794	-2.125371283	-2.492793961
H7	1	0.575765832	3.779448480	0.001484078	H7	1	2.495706760	-1.132675181	1.117850138
H8	1	2.201851010	4.776916832	-1.585643106	H8	1	4.265251343	-2.089329653	-0.204013612
H9	1	1.748747410	1.355947538	-4.145483860	H9	1	1.581539057	-2.409035502	-3.524011689
H10	1	2.785000526	3.552444179	-3.680274583	H10	1	3.830620895	-2.767184553	-2.584082386
C13	6	0.005259056	-0.065918357	-2.650769323	C13	6	-0.571472682	-1.417495628	-2.546998921
H2	1	0.079192565	-0.230746162	-3.734978857	H2	1	-1.420389056	-1.824300321	-1.984085586
H11	1	-1.063727092	-0.080698350	-2.413837394	H11	1	-0.493567726	-2.071579829	-3.423307321
C14	6	0.673138117	-1.238111899	-1.936338093	C14	6	-0.906998346	-0.014312726	-3.056533239
C15	6	1.880114166	-3.459916191	-0.691425710	C15	6	-1.631914076	2.534545576	-4.016996742
C16	6	2.059935775	-1.286722578	-1.742776775	C16	6	-0.309836432	1.142986403	-2.542631215
C17	6	-0.098378005	-2.319569321	-1.491779010	C17	6	-1.863601205	0.127266889	-4.072547519
C18	6	0.496908002	-3.422677608	-0.877539202	C18	6	-2.222850881	1.386842711	-4.551290942
C19	6	2.658973045	-2.386413647	-1.126415077	C19	6	-0.673995326	2.406312661	-3.011915556
H12	1	2.673990948	-0.451474590	-2.067969717	H12	1	0.439005938	1.059928332	-1.762542209
H13	1	-1.177674216	-2.296415907	-1.624889419	H13	1	-2.329975225	-0.761687997	-4.493701740
H14	1	-0.121389830	-4.251837104	-0.542510190	H14	1	-2.962147709	1.472557188	-5.343737543
H15	1	3.736714965	-2.402229631	-0.984179912	H15	1	-0.207209439	3.290209356	-2.584021434
H16	1	2.345565424	-4.316175667	-0.210314854	H16	1	-1.914478397	3.518224595	-4.382498575
C20	6	-0.664115187	-0.607375364	3.071140257	C20	6	-0.129197533	0.738666111	4.181563998
H6	1	0.432332544	-0.548993728	3.045847145	H6	1	-1.006254746	1.145931516	4.703573181
C21	6	-1.047943935	-2.093729839	2.932911136	C21	6	0.937746971	1.849601296	4.152254325
H17	1	-0.669834099	-2.511782726	1.993891512	H17	1	0.574407002	2.731405884	3.613196369
H20	1	-0.633256521	-2.679413586	3.762309142	H20	1	1.203890980	2.157109289	5.170695097
C22	6	-1.126233815	-0.041396422	4.426171729	C22	6	0.355563111	-0.480046338	4.986524686
H18	1	-0.852407981	1.014052157	4.531179775	H18	1	-0.411689695	-1.261320046	5.021066448
H21	1	-0.666924151	-0.597974930	5.251917539	H21	1	0.596360423	-0.191810176	6.016636568
H22	1	-2.213938978	-0.118249048	4.542833224	H22	1	1.258778453	-0.919751638	4.546341283
H25	1	-2.137171140	-2.220907323	2.943393761	H25	1	1.854377717	1.509746071	3.655624115

Table 5.8 XYZ coordinates of GS (left) and TS structures (right) of rotor **1**(CH₂Ph(NO₂)).



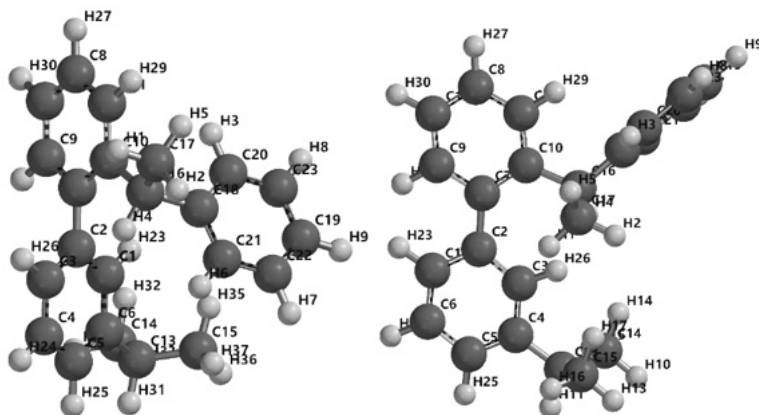
H1	1	0.023663479	-1.323569511	1.130244981	H1	1	1.389246931	-0.585820569	2.445663114
C1	6	-0.446495034	-0.381843250	1.401291019	C1	6	0.380661895	-0.417471112	2.091944784
C4	6	-1.660679420	2.028297472	2.054706677	C4	6	-2.202917194	0.107358776	1.305049942
C2	6	-1.583596348	0.025393696	0.691776316	C2	6	0.027580495	-0.753647143	0.766028316
C6	6	0.103258684	0.396411515	2.429937755	C6	6	-0.504156312	0.153933984	3.011050606
C5	6	-0.520244411	1.609795122	2.743209081	C5	6	-1.816489129	0.413015608	2.605409638
C3	6	-2.193636169	1.242500741	1.034925259	C3	6	-1.303680853	-0.459889340	0.404381000
H5	1	-0.112439916	2.231474314	3.537177364	H5	1	-2.524072526	0.858191305	3.300751606
H3	1	-3.096583539	1.556236667	0.517618361	H3	1	-1.671761376	-0.643287811	-0.589568892
H4	1	-2.141106777	2.965747516	2.323358477	H4	1	-3.217092423	0.316390019	0.974378461
C7	6	-2.150941077	-0.846605014	-0.382013488	C7	6	1.048324303	-1.366112796	-0.164507295
C8	6	-3.266753409	-2.563927775	-2.313006859	C8	6	3.182709759	-2.458612048	-1.733405563
C9	6	-2.181702704	-0.453279851	-1.739698614	C9	6	0.853337794	-1.694427718	-1.542183436
C10	6	-2.665906498	-2.101581520	-0.026681392	C10	6	2.332212139	-1.643953849	0.360634952
C11	6	-3.220330465	-2.958341319	-0.977665868	C11	6	3.377518310	-2.170925840	-0.386517528
C12	6	-2.747186524	-1.322371705	-2.681154554	C12	6	1.928222360	-2.220891124	-2.279187305
H7	1	-2.641540000	-2.396465144	1.018947079	H7	1	2.537683933	-1.451136795	1.404284350
H8	1	-3.618467833	-3.922443915	-0.673190855	H8	1	4.336831226	-2.354573265	0.089827252
H9	1	-2.777901491	-1.018332148	-3.725376452	H9	1	1.760057366	-2.457576752	-3.327053763
H10	1	-3.701177403	-3.215481537	-3.066361670	H10	1	3.981465916	-2.868868133	-2.344733601
C13	6	-1.576750045	0.859575728	-2.216463032	C13	6	-0.433046257	-1.563296948	-2.345890207
H2	1	-1.972296392	1.702445271	-1.642515791	H2	1	-1.283796056	-1.983661855	-1.797513662
H11	1	-1.891663494	1.023569328	-3.255498386	H11	1	-0.334050739	-2.212955156	-3.224237459
C14	6	-0.056532492	0.910497703	-2.160462833	C14	6	-0.800810780	-0.177048996	-2.865719280
C15	6	2.725933530	1.046351523	-2.112074198	C15	6	-1.547030007	2.309238126	-3.883171307
C16	6	0.597296614	2.001988703	-1.572124134	C16	6	-0.091705954	0.979352192	-2.516384704
C17	6	0.720211079	-0.114735292	-2.722594749	C17	6	-1.891852347	-0.055940934	-3.744013911
C18	6	2.109381279	-0.055125123	-2.705402172	C18	6	-2.272421340	1.177706020	-4.258186012
C19	6	1.986617046	2.080599468	-1.542965742	C19	6	-0.459716553	2.226223566	-3.017291578
H12	1	0.010828272	2.796456975	-1.119694817	H12	1	0.754030358	0.907618242	-1.840979578
H13	1	0.229169567	-0.973504716	-3.171008815	H13	1	-2.449604043	-0.944792936	-4.030793144
H14	1	2.717969713	-0.839818396	-3.137922735	H14	1	-3.109854858	1.279340338	-4.937886669
H15	1	2.500399808	2.918627644	-1.088395740	H15	1	0.079020271	3.126149222	-2.745937282
C20	6	1.354243415	-0.051749732	3.175239816	C20	6	-0.044833526	0.503882329	4.422185697
H6	1	1.530917320	0.680305954	3.975196865	H6	1	-0.917408744	0.915659494	4.947883314
C21	6	2.593194032	-0.042795352	2.259376362	C21	6	1.040909980	1.596854805	4.416467059
H17	1	2.754314664	0.945982915	1.816428597	H17	1	0.695605503	2.494177139	3.891691603
H20	1	3.493192535	-0.314132822	2.823778566	H20	1	1.307641576	1.881499250	5.441157347
C22	6	1.172412548	-1.427553144	3.842823177	C22	6	0.418634902	-0.736207890	5.208248302
H18	1	0.306779975	-1.433772308	4.514238761	H18	1	-0.363766514	-1.502523983	5.239181729
H21	1	2.061385538	-1.690047252	4.428106736	H21	1	0.672215245	-0.466245414	6.240296216
H22	1	1.023991169	-2.217156703	3.096843630	H22	1	1.310057030	-1.188649845	4.756816030
H25	1	2.484997611	-0.760896721	1.437687781	H25	1	1.954607958	1.250450727	3.918959990
N1	7	4.192295703	1.116179012	-2.081710815	N1	7	-1.940426981	3.620363562	-4.417033312
O1	8	4.709355110	2.093584262	-1.538449772	O1	8	-1.283928438	4.601696622	-4.066416226
O2	8	4.822122747	0.193508720	-2.600479176	O2	8	-2.904152140	3.659416925	-5.183679435

Table 5.9 XYZ coordinates of GS (left) and TS structures (right) of rotor 1(CH₂CN).



H1	1	0.370498113	-0.436360381	0.896309188	H1	1	-0.022502120	0.514368830	-1.008418389
C1	6	-0.150981305	0.440320983	0.522231447	C1	6	-0.222857813	0.445630624	0.046974926
C4	6	-1.418905830	2.721766869	-0.431045874	C4	6	-0.902508765	0.382438328	2.715580763
C2	6	-0.014014785	0.786203467	-0.830581808	C2	6	0.257265394	-0.638340139	0.8111110901
C6	6	-0.916340269	1.211657999	1.408280740	C6	6	-1.003913429	1.481265952	0.574561075
C5	6	-1.550117538	2.355763732	0.909820748	C5	6	-1.338830405	1.445980546	1.930772994
C3	6	-0.654807114	1.945340759	-1.298688991	C3	6	-0.126547655	-0.635032857	2.170820375
H5	1	-2.150135381	2.968092916	1.579452805	H5	1	-1.945558261	2.233483031	2.370207440
H3	1	-0.561881299	2.222284077	-2.345291554	H3	1	0.160236650	-1.437469482	2.836622901
H4	1	-1.918315006	3.613853584	-0.800421744	H4	1	-1.171124814	0.336857101	3.767934590
C7	6	0.825663356	-0.025710665	-1.759883195	C7	6	1.116562508	-1.754286035	0.268532339
C8	6	2.486135963	-1.447660500	-3.542924410	C8	6	2.705997324	-4.014721359	-0.508772705
C9	6	0.612011274	-1.401574497	-1.990648244	C9	6	1.535255206	-1.937295168	-1.082958486
C10	6	1.868812799	0.611985143	-2.453501412	C10	6	1.571818833	-2.734559492	1.180724395
C11	6	2.693519174	-0.084323467	-3.332838130	C11	6	2.338980425	-3.834790332	0.820153921
C12	6	1.447217383	-2.092476529	-2.875996256	C12	6	2.303138697	-3.058966674	-1.432209864
H7	1	2.038433890	1.670354213	-2.276526392	H7	1	1.329499256	-2.642272995	2.229846338
H8	1	3.497068429	0.434927637	-3.848080723	H8	1	2.646363655	-4.544275675	1.583653663
H9	1	1.272283892	-3.151800715	-3.049879094	H9	1	2.595785139	-3.177691475	-2.472480221
H10	1	3.122600219	-2.004220202	-4.225146629	H10	1	3.300428824	-4.868054456	-0.821587457
C13	6	-0.542769292	-2.163206809	-1.345271778	C13	6	1.263464819	-0.997575930	-2.259411060
H2	1	-0.948498976	-2.891523909	-2.057877294	H2	1	1.948598882	-1.261471701	-3.072732089
H11	1	-1.358426039	-1.482065649	-1.081417086	H11	1	1.487981424	0.045027238	-2.014496766
C20	6	-1.052955277	0.822470176	2.874814694	C20	6	-1.467422394	2.620162689	-0.325563185
H6	1	-1.684564158	1.585653379	3.350112817	H6	1	-1.131392762	2.386480203	-1.345081450
C21	6	0.305655351	0.831791343	3.601498234	C21	6	-0.818798162	3.958086407	0.078075733
H17	1	0.799311821	1.806126469	3.513165613	H17	1	0.274764247	3.889085625	0.065552702
H20	1	0.171461683	0.613023244	4.667395307	H20	1	-1.119081438	4.756124133	-0.611407970
C22	6	-1.759648262	-0.535862057	3.045678264	C22	6	-3.002236535	2.736149578	-0.368376488
H18	1	-2.742416983	-0.535325229	2.560624195	H18	1	-3.459843945	1.795983860	-0.693998639
H21	1	-1.907276630	-0.758410921	4.109057707	H21	1	-3.308061839	3.524880250	-1.065910350
H22	1	-1.170787843	-1.353305629	2.614363209	H22	1	-3.413922772	2.987579006	0.616472964
H25	1	0.982504936	0.073688358	3.190673862	H25	1	-1.120973963	4.260330722	1.088444790
C14	6	-0.152773869	-2.892705755	-0.130649926	C14	6	-0.098065502	-1.087069361	-2.808619408
N1	7	0.162437571	-3.458771435	0.833191709	N1	7	-1.162498601	-1.176041098	-3.264018229

Table 5.10 XYZ coordinates of GS (left) and TS structures (right) of rotor **1**(CH(CH₃)Ph).



C1	6	-0.966920463	0.981334834	0.809767000	C1	6	-2.694708771	1.712381149	1.687452986
C4	6	-0.338626773	3.436271195	-0.327415611	C4	6	-0.045170514	2.503752001	2.035317918
C2	6	-1.049141433	1.132344952	-0.579526487	C2	6	-1.706776856	1.012988519	0.950337369
C6	6	-0.571719110	2.035183008	1.646076296	C6	6	-2.380525012	2.760587237	2.544522246
C5	6	-0.257556274	3.264536445	1.055674004	C5	6	-1.058703522	3.166917404	2.723721895
C3	6	-0.733160266	2.378101893	-1.143881377	C3	6	-0.387011649	1.454058823	1.171473128
C7	6	-1.499736574	-0.010453442	-1.436790121	C7	6	-2.101732196	-0.112315228	0.012644585
C8	6	-2.474271185	-2.120988301	-3.009416477	C8	6	-3.173853379	-2.191162196	-1.641396216
C9	6	-2.867738799	-0.313608694	-1.471878192	C9	6	-3.484767971	-0.390168276	-0.090717969
C10	6	-0.594513956	-0.787104485	-2.197785943	C10	6	-1.237778884	-0.934855455	-0.787363058
C11	6	-1.109627449	-1.829877624	-2.979537692	C11	6	-1.807636430	-1.946178271	-1.577722102
C12	6	-3.36006747	-1.361900491	-2.248639213	C12	6	-4.023052052	-1.392752303	-0.886373396
C13	6	-0.476129287	1.849204057	3.155011684	H23	1	-3.741112417	1.451635897	1.612666126
C14	6	-1.840844554	1.504724086	3.779952596	H25	1	-0.820559412	3.991013703	3.392459892
C15	6	0.586790686	0.801976270	3.538682266	H26	1	0.434944751	0.986973445	0.661069578
H23	1	-1.205934730	0.011969006	1.239612577	H27	1	-3.559239441	-2.988806464	-2.270715485
H24	1	-0.098777700	4.400517903	-0.768607552	H28	1	-4.194281849	0.200216382	0.470688244
H25	1	0.051602262	4.096160788	1.685333973	H29	1	-1.143357605	-2.568150227	-2.165848395
H26	1	-0.806872889	2.513857903	-2.220025493	H30	1	-5.099698825	-1.539998866	-0.908201136
H27	1	-2.838956770	-2.938051425	-3.626614530	C16	6	0.290595619	-0.762276372	-0.923899150
H28	1	-3.550875590	0.292846931	-0.882810989	H4	1	0.698681088	-0.581219147	0.073467542
H29	1	-0.433214233	-2.430263317	-3.579466471	C17	6	0.598988849	0.462256812	-1.814342059
H30	1	-4.425274954	-1.576643724	-2.262101181	H2	1	1.679197646	0.637195188	-1.883021869
H31	1	-0.155879124	2.812190346	3.576821999	H1	1	0.125970274	1.365827423	-1.422328992
H32	1	-2.214956441	0.540506031	3.414638161	H5	1	0.209545073	0.313936096	-2.826468691
H33	1	-1.758960515	1.436579661	4.871380395	C18	6	1.039046272	-2.014246377	-1.394487976
H34	1	-2.591243831	2.266316583	3.540636896	C19	6	2.488042008	-4.317505062	-2.155021085
H35	1	0.323790648	-0.192334386	3.160406744	C20	6	1.440782898	-2.209662725	-2.722742195
H36	1	0.680186342	0.731764728	4.629362992	C21	6	1.378754481	-3.000947802	-0.455916673
H37	1	1.567577682	1.060915450	3.126026558	C22	6	2.093564078	-4.139277427	-0.827001729
C16	6	0.908671791	-0.515558606	-2.128143921	C23	6	2.156025106	-3.348503016	-3.100867778
H4	1	1.032472216	0.567122785	-2.020530007	H3	1	1.200935590	-1.467766951	-3.477577346
C17	6	1.677100827	-0.924833035	-3.403323186	H6	1	1.077988640	-2.871388192	0.581850097
H2	1	2.713859948	-0.579019109	-3.335710235	H7	1	2.349292138	-4.884149018	-0.077666720
H1	1	1.223602764	-0.482965521	-4.298071834	H8	1	2.457731067	-3.470990512	-4.138159597
H5	1	1.709271021	-2.011777423	-3.532824910	H9	1	3.051946660	-5.199201533	-2.447842995
C18	6	1.568920322	-1.147626288	-0.898332686	H12	1	-3.181537361	3.265325732	3.079858272
C19	6	2.899456328	-2.308631593	1.298553630	C13	6	1.415045337	2.908440565	2.200829171
C20	6	1.218959233	-2.424604559	-0.440417241	H11	1	1.446459943	3.704915739	2.957047264
C21	6	2.593296122	-0.461019960	-0.232096250	C14	6	2.276063979	1.741439102	2.717516793
C22	6	3.255653501	-1.034051179	0.853911554	H10	1	3.308778158	2.067659115	2.888556500
C23	6	1.877256033	-3.000768645	0.647380087	H14	1	2.304906151	0.919878557	1.991451151
H3	1	0.415994690	-2.968807870	-0.929983164	H15	1	1.881151367	1.342335925	3.658169396
H6	1	2.870293188	0.537120375	-0.565334759	C15	6	1.996712488	3.482361236	0.895803749
H7	1	4.046887863	-0.482618455	1.355941066	H13	1	3.030892165	3.815170499	1.045396401
H8	1	1.587723464	-3.992032773	0.987603438	H16	1	1.408380473	4.336566068	0.543441043
H9	1	3.411572718	-2.756004323	2.146491608	H17	1	2.001081794	2.727688643	0.099941210

5.5.8 Additional data and figures

As mentioned in the main text, the experimental interaction energies (E_{int}), which was the differences between $\Delta G^{\ddagger}_{\text{exp}}(\text{R})$ and $\Delta G^{\ddagger}_{\text{exp}}(\text{CH}_2\text{CH}_3)$, would also correlate with the calculated parameters in the hypothesis paper. **Table 5.11** showed the calculated net activation energies E_{activ} for the two $\text{S}_{\text{N}}2$ reaction systems: 1) nucleophile (Nu) = leaving group (LG) = F, 2) Nu = LG = Cl.²²⁷ **Table 5.11** additionally showed the experimental activation energies of $\text{S}_{\text{N}}2$ reactions $\Delta\Delta G^{\ddagger}_{\text{exp}}(\text{S}_{\text{N}}2)$.^{7,8,228}

Table 5.11 Net calculated and experimental activation energies for the two $\text{S}_{\text{N}}2$ reaction systems.

R =	$\Delta G^{\ddagger}_{\text{exp}}$ (kcal/mol)	E_{int} (kcal/mol)	net calculated activation energy when Nu=LG= F, $E_{\text{activ}}(\text{F})$ (kcal/mol)	net calculated activation energy when Nu= LG= Cl, $E_{\text{activ}}(\text{Cl})$ (kcal/mol)	^a experimental activation energies of $\text{S}_{\text{N}}2$ reactions, $\Delta\Delta G^{\ddagger}_{\text{exp}}(\text{S}_{\text{N}}2)$ (kcal/mol)
CH_2CH_3	22.0	0.0	1.5	4.6	2.02
$\text{CH}_2\text{CH}_2\text{CH}_3$	21.7	-0.3	0.1	3.4	2.57
$\text{CH}_2\text{CH}=\text{CH}_2$	21.2	-0.8	-0.6	2.5	-0.16
CH_2Ph	20.9	-1.1	-4.6	0.2	-0.82
CH_2CN	20.5	-1.5	-15.0	-5.1	-2.05

^aExperimental activation energies were measured in two systems: CH_2CH_3 , $\text{CH}_2\text{CH}_2\text{CH}_3$, $\text{CH}_2\text{CH}=\text{CH}_2$, and CH_2Ph were reported in *Solvolytic Displacement Reactions*; McGraw-Hill: New York, 1962. The reactions were R-Br reacting with LiCl in acetone. CH_2CN was reported in *J. Am. Chem. Soc.* **1964**, 86, 4645. The reaction was R-Cl reacting with iodide ion. Corresponding $\Delta\Delta G^{\ddagger}_{\text{exp}}(\text{S}_{\text{N}}2)$ were taken from *J. Org. Chem.* **2014**, 79, 867.

The plots in **Figure 5.21a** showed the good correlations between E_{int} and E_{activ} . The plots in **Figure 5.21b** showed a correlation between E_{int} and $\Delta\Delta G^{\ddagger}_{\text{exp}}(\text{S}_{\text{N}}2)$. **Table 5.12** showed the calculated NBO atomic charges in $\text{S}_{\text{N}}2$ reaction transition states, two systems were both calculated for the primary and secondary carbons.²²⁷ The plots with good to

excellent correlations showed the same trend in the main text that the secondary interactions were due to electrostatics (**Figure 5.22**).

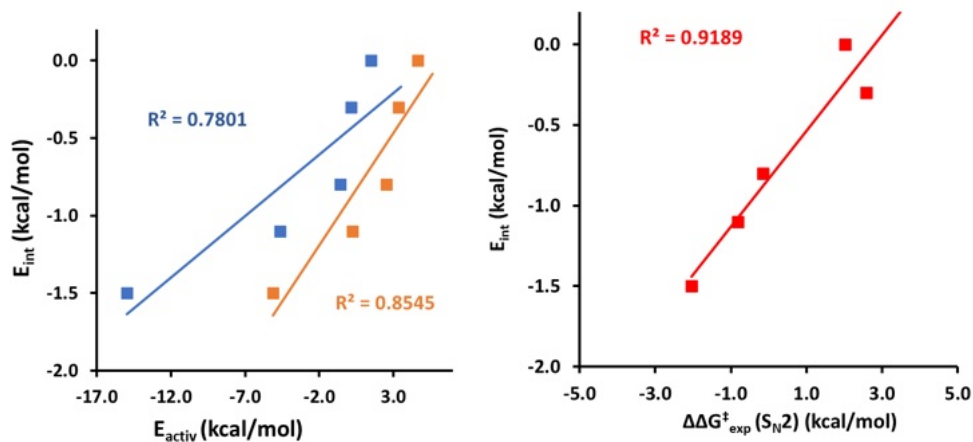


Figure 5.21 a) Good correlations between E_{int} and E_{activ} . b) Excellent correlation between E_{int} and $\Delta\Delta G_{\text{exp}}^{\ddagger}(\text{S}_{\text{N}}2)$.

Table 5.12 Calculated NBO atomic charges for primary and secondary carbons in two $\text{S}_{\text{N}}2$ reaction systems.²²⁷

R =	NBO atomic charge of secondary carbon when Nu=LG= F , (e)	NBO atomic charge of secondary carbon (e)
CH_2CH_3	0.114	-0.595
$\text{CH}_2\text{CH}_2\text{CH}_3$	0.115	-0.422
$\text{CH}_2\text{CH}=\text{CH}_2$	0.063	-0.211
CH_2Ph	0.077	-0.028
CH_2CN	-0.008	0.347
R =	NBO atomic charge of secondary carbon when Nu=LG= Cl , (e)	NBO atomic charge of secondary carbon (e)
CH_2CH_3	-0.153	-0.61
$\text{CH}_2\text{CH}_2\text{CH}_3$	-0.153	-0.438
$\text{CH}_2\text{CH}=\text{CH}_2$	-0.212	-0.236
CH_2Ph	-0.203	-0.059
CH_2CN	-0.34	0.315

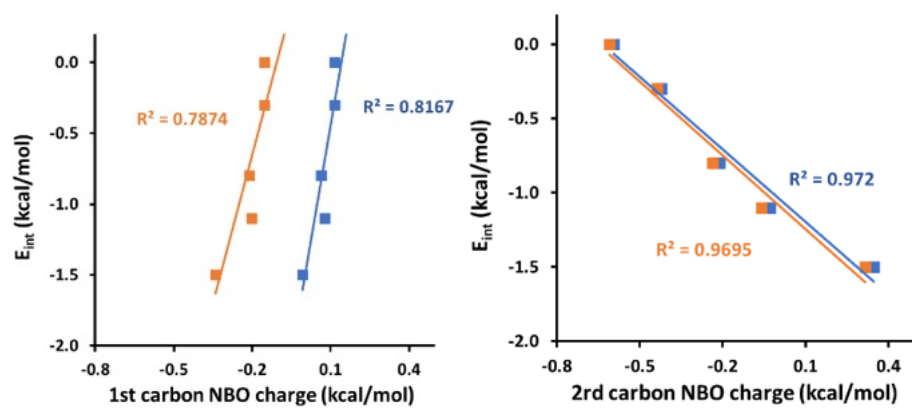


Table.22 Correlations between E_{int} and NBO atomic charges. Orange square: Nu = LG = Cl; Blue square: Nu = LG = F;

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