MECHANISMS OF PHOTOINDUCED REACTIONS FROM KINETIC ISOTOPE EFFECTS

A Dissertation

by

KAI-YUAN KUAN

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Chair of Committee,	Daniel A. Singleton
Committee Members,	David Bergbreiter
	David C. Powers
	Dzmitry L. Kurouski
Head of Department,	Simon W. North

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ABSTRACT

Chemists' intuitions rely on statistical assumptions to understand a reaction. Statistical models such as transition state theory are central to account for most of the reaction outcomes. However, failures do exist. This dissertation provides modern interpretations for photochemical reactions: radical-ion mediated cycloaddition and photosensitized di-π-methane rearrangement. These reactions play a fundamental role in understanding key processes in photochemical reactions, including electron transfer and energy transfer. The mechanistic studies of these reactions are based on experimental kinetic isotope effects (KIEs).

The [2 + 2] cycloaddition provides means to construct compounds with cyclobutanes. In 2008, Yoon and coworkers published a novel synthetic method for constructing cyclobutanes from enones through a photoredox process. This method could be applied to either intramolecular or intermolecular cycloadditions. The reaction can be qualitatively understood by a stepwise radical-ion mediated ring closure process. However, the mechanisms of photoredox-promoted reactions are intrinsically complex, involving a combination of photophysical steps, one or more electron-transfer steps leading to activated substrates, chemical conversions of radical ions, chain-transfer steps, and termination steps. We describe a combination of experimental and theoretical studies on the intermolecular cycloaddition of enones. A relatively small kinetic isotope effects at β-carbon were observed from natural abundance approach developed by Singleton in 1995. This qualitatively supports the computational predictions that the first bond

formation is the first irreversible step undergone by the starting materials. Quantitatively, a competitive scheme between electron exchange and bond-formation is proposed. This electron exchange among enones was probed from competitive reactants kinetic study. This study suggests the possibility of ways to control the chemoselectivity.

Another reaction of interest is the di-π-methane rearrangement. This type of reaction was first discovered by Zimmerman and coworkers in 1966. In Zimmerman's study, Bicyclo[2.2.2]octa-2,5,7-triene (barrelene) undergoes rearrangement under UV-light irradiation in the presence of triplet sensitizers such as acetone or acetophenone to afford semibullvalene. The qualitative mechanism can be understood by a stepwise process involving cyclopropyldicarbinyl intermediates. However, some studies reported experimental observations that may require a concerted mechanistic model. In addition, Chung and coworkers computationally predicted a significant heavy atom tunneling effect may be involved in a stepwise di-π-methane rearrangement. Therefore, in this work, we performed comprehensive experimental KIE measurements and theoretical predictions to study the mechanism of the di-π-methane rearrangement. We found the reactions sensitized by low-energy sensitizers undergo a stepwise, significant heavy-atom tunneling path. On the other hand, the reactions sensitized by high-energy sensitizers display a great amount of dynamic effect.

DEDICATION

I dedicate this work to my lovely family, my Mom, Dad, and my sister Niki, who support me all the way here. This thesis is for them.

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NOMENCLATURE

CVT	Canonical Variational Transition State Theory
DCM	Dichloromethane
DFT	Density Functional Theory
DPMR	Di-Π-Methane Rearrangement
dr	Diastereomeric Ratio
FID	Free Induction Decay
HSQC	Heteronuclear Single Quantum Coherence
IC	Internal Conversion
ISC	Intersystem Crossing
IVR	Intramolecular Vibrational Relaxation
KIE	Kinetic Isotope Effect
LED	Light-Emitting Diode
NMR	Nuclear Magnetic Resonance
PCM	Polarizable Continuum Model
PES	Potential Energy Surface
QM	Quantum Mechanics
RDS	Rate-Determining Step
RMS	Root Mean Square
RRKM	Rice-Ramsperger-Kassel-Marcus
rt	Room Temperature

RTG	Redox-Tag Group
SCE	Saturate Calomel Electrode
SCT	Small Curvature Tunneling
SET	Single Electron Transfer
SMD	Solvent Model based on Density
TET	Triplet Energy Transfer
THF	Tetrahydrofuran
TPPT	Triphenylpyrylium Tetrafluoroborate
TS	Transition State
TST	Transition State Theory
bpy	2,2'-bipyridine
ZPE	Zero-Point Energy

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1. INTRODUCTION

A main pursuit of chemical research is to understand why and how transformations occur. All chemical reactions can ultimately be explained by fundamental theories of quantum physics. Unfortunately, the heaven of such perfect theory is too complicated to be applied in chemical systems. Therefore, chemists rely on using models to approach understanding. To achieve broad applicability, assumptions and approximations have to be made but still account for most of the experimental observations. The models built for understanding chemical reactions are called reaction mechanisms. Understanding reaction mechanisms is a key factor in controlling reactions and an important aide for developing novel synthetic methods. It is also an important task in various aspects of improving quality of life such as drug design, industrial production, and material development.

A mechanism is generally regarded as a sequence of steps involving transition states (TS) and intermediates along the reaction path from starting materials to products. Transition state theory (TST) is applied in governing the reactivity and selectivity of a reaction. TST associates the rate of a reaction with the free energy barrier ($\Delta G^{\ddagger}$). The rate constant under TST is expressed by the Eyring equation shown in eq. (1). Complicating issues such as quantum tunneling or recrossing that lead to error versus the semiclassical approximation are hidden in the transmission coefficient (κ) as part of the pre-exponential factor in TST-derived rate constants.

$$k = \kappa \frac{k_B T}{h} exp\left(-\frac{\Delta G^{\ddagger}}{k_B T}\right) \qquad (1)$$

The TST has been successful in providing both qualitative understanding and quantitative prediction of the rate of reactions. However, the simplicity of TST is built on assumptions and approximations. One assumption is that intramolecular vibrational relaxation (IVR) is fast on the time scale of reaction coordinate movement.[1] That is, the TS structure is viewed as another stationary point with properties that can be predicted from its structure. From this standpoint, the history of how a molecule reacts from the reactant region to the TS should affect neither reactivity nor selectivity. However, for reactions experiencing slow IVR, the relative atomistic velocity and momentum at the TS would affect the reaction outcomes. This so-called “dynamic matching” effect could play an important role in mechanistic models. In this case, alternative dynamic methodologies such as trajectory calculations are required to better explain reactions. Throughout the history of mechanistic studies by the Singleton research group, new mechanistic models have been proposed for various types of reactions such as Diels-Alder reactions,[2] ketene cycloadditions,[3] electrophilic aromatic substitution,[4] Wittig reactions,[5] sigmatropic rearrangements,[6] and so forth. Concepts such as bifurcating energy surface, solvent dynamics, non-statistical dynamic matching, entropic intermediates were introduced in order to account for the experimental observations.

Despite limitation and exceptions, TST is centered in chemists’ intuition for predicting reactions. Therefore, the TS structures and intermediates along the reaction coordinate still provide first-order prediction to the mechanism.

The Singleton research group developed methodologies in 1995 to measure ^{13}C kinetic isotope effects (KIEs) at natural abundance.[7] While other nuclei are possible, carbon is a favorable choice due to its precisely quantifiable of spectra and its relevance to most organic reactions.

1.1. Photochemical Reactions

Photochemistry lies at center of life due to its role in photosynthesis Photochemical reactions can achieve chemical transformations without the need for additional reagents or catalyst, making them attractive alternatives to reactions that produce environmentally-hazardous waste.

An example, as seen in the Woodward-Hoffmann rules, that thermally-forbidden reactions can become allowed reactions with irradiation. This provides an additional dimension in controlling reaction selectivity. Therefore, understanding the mechanisms for photoinduced reactions is valuable both in theoretical and in synthetic terms.

A fundamental model for photophysical processes can be illustrated using a Jablonski diagram (Figure 0.5). A molecule absorbs a photon and is excited up to an energy level corresponding to the energy of the absorbed photon (path a). From the Born-Oppenheimer approximation, atom move little during the absorption. Such "vertical" transitions usually result in higher vibrational states of the excited electronic states. After excitation, intramolecular vibration relaxation (IVR) occurs within a few picoseconds. This is faster than other photophysical / chemical events and affords the lowest vibrational level in the S_1 state (path b). The relaxed molecule on the S_1 state can undergo either internal conversion (IC) back to the ground state (by fluorescence, path c, or by radiation-less decay, path d) or intersystem crossing (ISC) to the triplet state (path e). For molecules undergoing ISC, another IVR event would occur because the T_1 state is, in general, lower in energy than the S_1 state (path f). The triplet excited state can undergo phosphorescence (path g), radiationless decay (path h), or chemical reactions (path i).

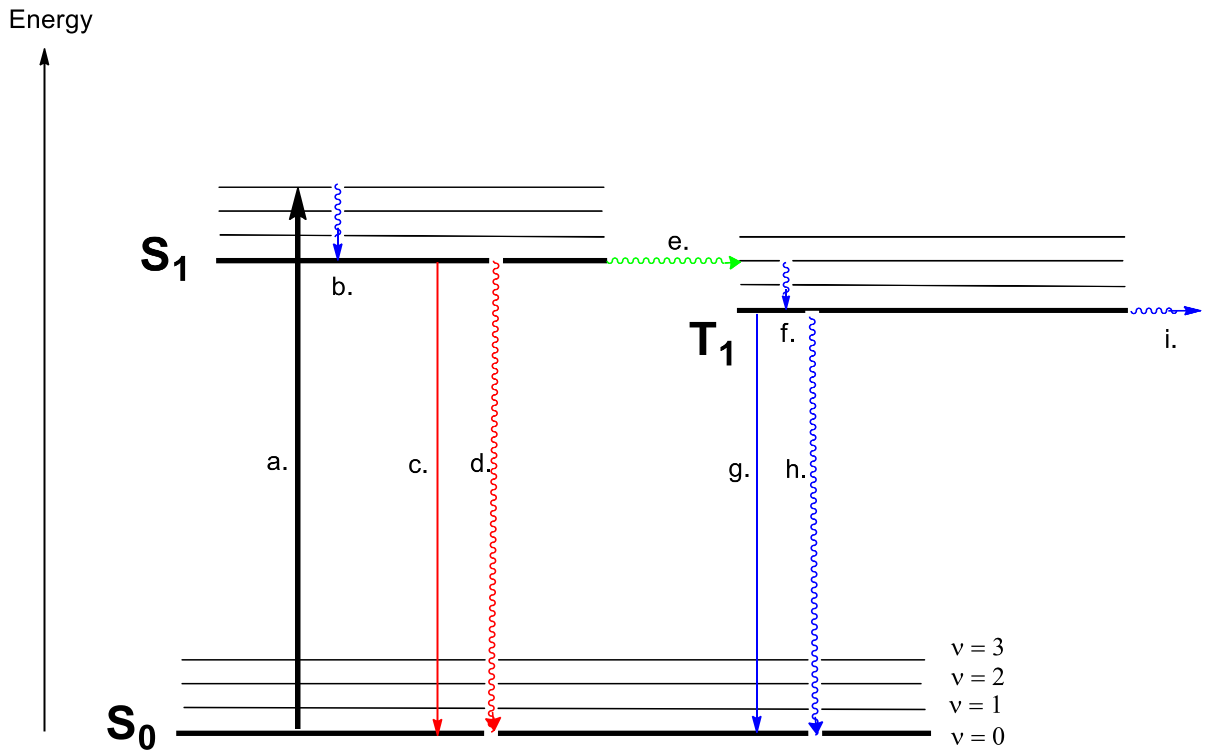

Figure 0.1. Jablonski diagram for some photophysical processes. (a) absorption, (b) vibrational relaxation, (c) fluorescence, (d) non-radiative decay, (e) intersystem crossing, (f) vibrational relaxation, (g) phosphorescence, (h) non-radiative decay, (i) chemical reactions.

1.1.1. Single Electron Transfer in Organic Reactions

Single electron transfer (SET) is a fundamental process that can trigger many important reactions ranging from polymer syntheses to biological reactions.[8] The understanding of electron transfer mechanism had not been fully constructed until pioneer studies by Taube[9–11] and Marcus.[12] SET reactions can be initiated from direct electrochemistry or photochemically using excited-state species. A complete SET process includes the break of solvent cages between donor and acceptor and the electron transfer from donor to acceptor. The rate of the former is approximately that of diffusion, while the latter is hard to estimate from classical rate theories due to the lack of a well-defined transition state. Despite the difficulty of geometrically defining a TS for SET, Marcus theory provides a quantitative tool to estimate the rate of SET.[12] In Marcus theory, the electron transfer barrier ($\Delta G^{\ddagger}_{ET}$) can be calculated from a reorganization energy (λ) and the reaction free energy (ΔG°) (Eq. (1-2)). Reorganization energy is a hypothetical energy required for the reactant to product to adopt the geometry of the product without electron transfer. Marcus theory then assumes that energy arises parabolic versus the distortion. The accuracy of this simple parabolic model makes a surprising prediction that reactions rate can reach of a point of diminishing returns, where additional driving force reduces the rate. This 'Marcus inverted region' prediction has been verified by experiments.[13,14]

$$\Delta G^{\ddagger}_{ET} = \frac{\lambda}{4}\left(1 + \frac{\Delta G^{\circ}}{\lambda}\right)^2 \qquad (1\text{-}2)$$

The SET process is a useful approach to promoting chemical reactions, and it has become very important in organic synthesis. Radicals or radical ions can be generated from closed-shell organic substrates via SET. These open-shelled species can react in many ways, including group transfer, addition, elimination reactions, and additional SET steps.

Recently, visible-light promoted redox reactions have gained attentions since the pioneering photophysical studies with polypyridyl ruthenium complexes in 1982.[15,16] Many visible-light promoted photocatalysts used in synthetic applications are derived from the molecular backbone of ruthenium(II) tris(2,2'-bipyridine) salts (Figure 0.2). The application of such metal complexes in organic synthesis has been reviewed systematically by MacMillan and coworkers.[17]

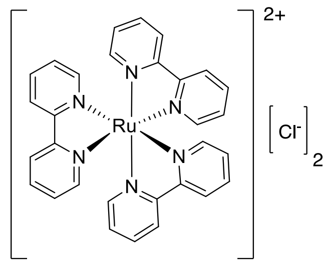

Figure 0.2. Structure of tris(bipyridyl)ruthenium(II) dichloride.

The qualitative mechanisms of photoredox processes are summarized in Figure 0.3. The photoexcited metal complexes can be either reductively quenched or oxidatively quenched depending on their relative potentials versus available electron donors or acceptors. The catalytic cycle can be completed by a back electron transfer from the electron acceptor or to the donor.

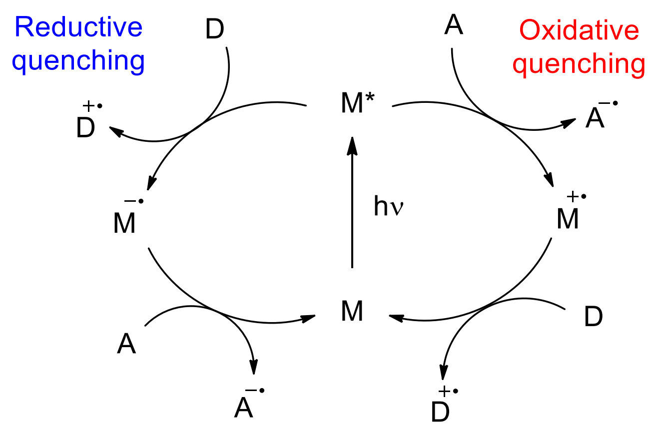

Figure 0.3. General mechanism for photoredox-promoted single electron transfer (M: metal complexes, D: electron donor, A: electron acceptor).

Ion-paring Effects in Electron Transfer

Laboratory electrochemical reactions are usually conducted in solutions of electrolytes. Since SET reactions involve changes in net charges of the reactants and products, an SET step is usually accompanied by shifts in counterion coordination. This can affect the reactivity and selectivity. Marcus discussed the theory of ion-pair effects in 1998.[18] In Marcus's analysis, the electron transfer rate constant (k_{ET}) is controlled by the binding strength of the counterion A tight ion pair may have a major effect on the spectroscopic properties. A loose pair, or a solvent-separated ion-pair, on the other hand, has much less effect.

Different mechanistic schemes could also affect the k_{ET} of SETs involving ion-pairs. A completed electron transfer step may undergo (I) electron transfer first, followed by ion transfer, (II) ion-pair dissociation first, followed by electron transfer, or (III) concerted electron/ion transfer. The kinetics of each pathway are summarized in Table 0.1.

Table 0.1 Reaction scheme of (I) electron transfer first, followed by ion transfer, (II) ion-pair dissociation first, followed by electron transfer, or (III) concerted electron/ion transfer. Adapted from reference 18.

Mechanistic type	Reaction diagram[a]	Rate equation
I	$M^+D^-SA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M^+DSA^- \xrightarrow{k_2} DSA^-M^+$	$\frac{1}{k_{ET}(I)} = \frac{1}{k_1} + \frac{k_{-1}}{k_2 k_1}$
II	$M^+D^-SA \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} M^+ + D^-SA \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} M^+ + DSA^- \xrightarrow{k_5} DSA^-M^+$	$\frac{1}{k_{ET}(II)} = \frac{k_5 k_3}{k_{-3} + \frac{k_4 k_5}{k_{-4} + k_5}}$
III[b]	$M^+D^-SA \rightleftharpoons \left(\begin{matrix} D^-SA \\ M^+ \end{matrix} \rightleftharpoons \begin{matrix} DSA^- \\ M^+ \end{matrix} \right) \longrightarrow DSA^-M^+$	$\frac{1}{k_{ET}(III)} = \frac{1}{k_{diff}^r} + \frac{1}{k_{act}} + \frac{1}{K_{eq} k_{diff}^p}$

a. M: counterion, D: electron donor, A: electron acceptor, S: separator (carbon chain (intramolecular), or solvent (intermolecular)).

b. k_{diff}^r: diffusion rate constant for the M^+ along the reactant's free energy curve. k_{act}, K_{eq}: barrier and equilibrium constant respectively to form the complex in parentheses, k_{diff}^p: diffusion rate constant for the M^+ along the product's free energy curve.

1.1.2. Triplet Energy Transfer in Organic Reactions

Another type of photoinduced reaction is the triplet energy transfer (TT). Triplet-triplet energy transfer may be described as an exchange of electrons between donor and acceptor. This is the "Dexter mechanism" of Figure 0.4c. Triplet energy transfer is similar to electron transfer (ET) and should be governed by the same theory as radiationless transitions. Both long distance ET and TT processes can be described by Fermi's golden rule shown in eq. (1-3), where V is the electron coupling term and FC denotes the Frank-Condon weighted density of states.[19]

$$k = \frac{2\pi}{h}|V|^2(FC) \qquad \text{(1-3)}$$

In organic chemistry, triplet photosensitizers have been widely used to excite organic compounds under mild conditions. This has been applied to many organic synthetic reactions.[20]

In this dissertation, we explore two types of photochemical reactions: (1) photoredox-promoted [2 + 2] cycloadditions of alkenes and (2) photosensitized di-π-methane rearrangement. Detailed mechanistic studies based on KIE measurements combined with theoretical predictions were performed for these reactions. Novel mechanistic models for each types of reactions are proposed.

1.1.3. Photoinduced Electron Transfer and Energy Transfer

Ultraviolet and visible light (UV-vis) light has been used in the excitation of ordinary organic molecules, as most of the HOMO-LUMO energy gaps fall in this energy region. Excited states can undergo electron transfer (photoredox) or energy transfer (photosensitization) depending on the nature of the species and the environment. Photoredox occurs when a photo-excited molecule donates an electron to (oxidative quenching) or accepts (reductive quenching) an electron from substrates. As shown in Figure 0.4, photosensitization can proceed via fluorescence resonance energy transfer (Förster mechanism)[21] or double electron transfer (Dexter mechanism).[22] Due to the spin selection rule, triplet energy transfer usually occurs through the Dexter mechanism pathway (Figure 0.4c).[23]

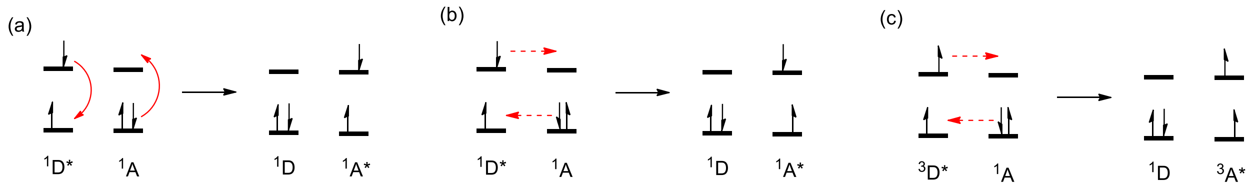

Figure 0.4. Different pathways for photoinduced activation of substrates. (a) Forster resonance energy transfer. (b) Dexter mechanism (singlet energy transfer), (c) Dexter mechanism (triplet energy transfer).

Since solar radiation is an intrinsically simple and green energy source, research on using energy in a more efficient way has become a major pursuit. More specifically, visible-light promoted photoredox reactions have received great attention in recent years in chemistry.[17] Visible photons provide enough energy (35 ~ 70 kcal/mol) to activate a broad range of the organic reactions and can be finely tuned to minimize side products, as opposed to thermal reactions. In 2019, more than a thousand papers have been published using the key word "photoredox," based on Web of Science results. This is more than 50 times higher than in 2008 (Figure 0.5).

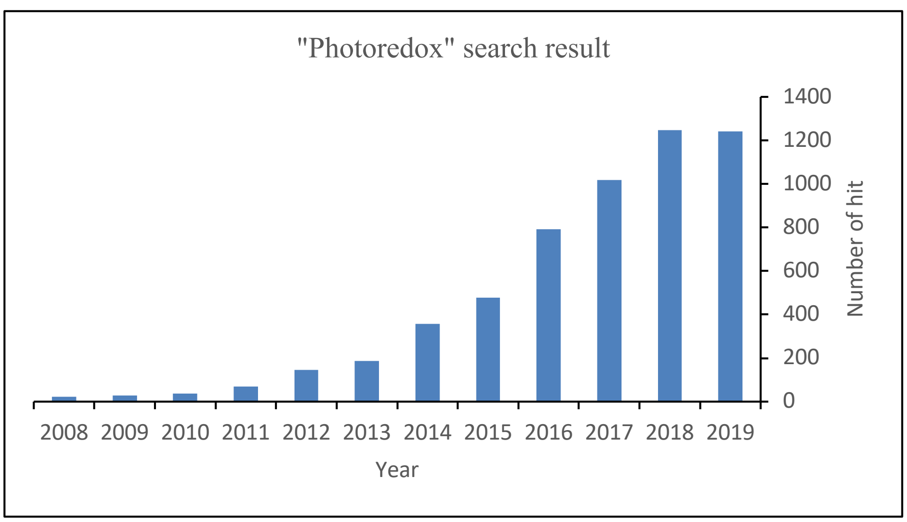

Figure 0.5. Popularity of photoredox chemistry. The bar shows the number of results in Web of Science.

The first application of ruthenium polypyridyl complexes for light-induced organic reactions was performed by Kellogg in 1978. They found that the photo-reduction of sulfonium ions to the corresponding alkanes and thioethers by *N*-substituted 1,4-dihydropyridine can be accelerated by $[Ru(bpy)_3]Cl_2$ (Figure 0.6, condition D).[24] A single electron transfer (SET) mechanism was proposed in this work. Later, the use of $Ru(bpy)^{2+}$ / dihydropyridine catalytic system was extended to the reduction of organic substrates in work by Fukuzumi and Tanaka,[25] and Pac.[26] Despite these early reports, the area of photoredox catalysis was not prominent the twenty-first century.

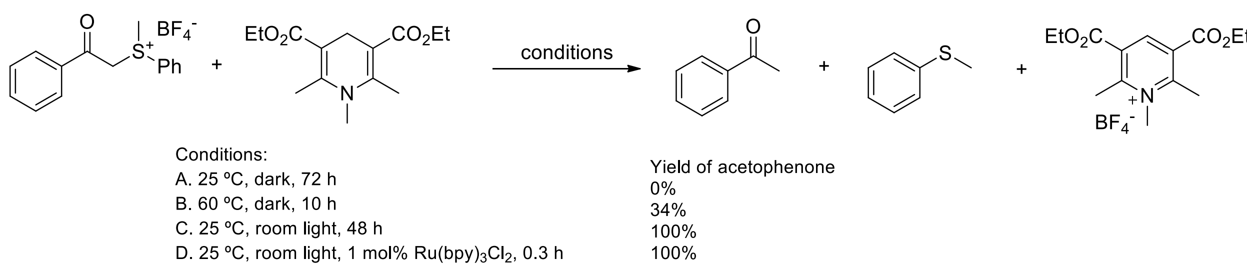

Figure 0.6. Light induced acceleration of reduction reaction of sulfonium ions in an early work by Kellogg and coworkers in 1978.

In 2008, Yoon and coworkers reported a photoinduced intramolecular [2 + 2]-cycloaddition reaction of enones using $Ru(bpy)_3Cl_2$ as the photocatalyst (Figure 0.7).[27] This idea was an extension of the same reaction with an SET mechanism triggered chemically or electrochemically by Krische and Bauld.[28–30] Qualitatively, this reaction undergoes a reductive quenching process (Figure 0.3) where the Hünig base (diisopropylethylamine) reacts with the photoexcited $^*Ru(bpy)_3^{2+}$ species to generate reductant $Ru(bpy)_3^+$. The presence of the lithium salt is also critical for a successful cycloaddition as it stabilizes the relatively unstable radical anion intermediate of the electron-deficient enones.

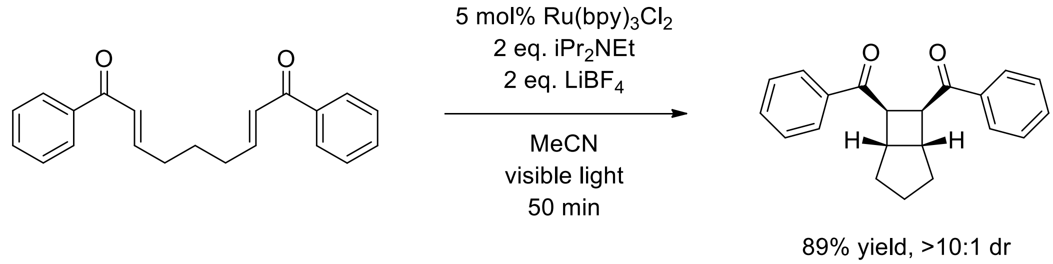

Figure 0.7 Photoinduced intramolecular [2 + 2]-cycloaddition of enones using $Ru(bpy)_3Cl_2$ as the photocatalyst in Yoon's work.

Further research has focused on developing dual catalytic methodologies. Taking advantage of efficient ruthenium photocatalysts, MacMillan has developed the enantioselective alkylation of aldehydes using imidazolidinone as the enantioselective catalyst.[31] Like other enamine-mediated organocatalysts, the imidazolidinone can react with the carbonyl group on the substrate to form the enamine intermediate which induces enantioselectivity. However, this reaction is one of the rare examples of using enamine organocatalysts involving a radical ion pathway. This provides a new strategy for achieving challenging asymmetric α-alkylations.

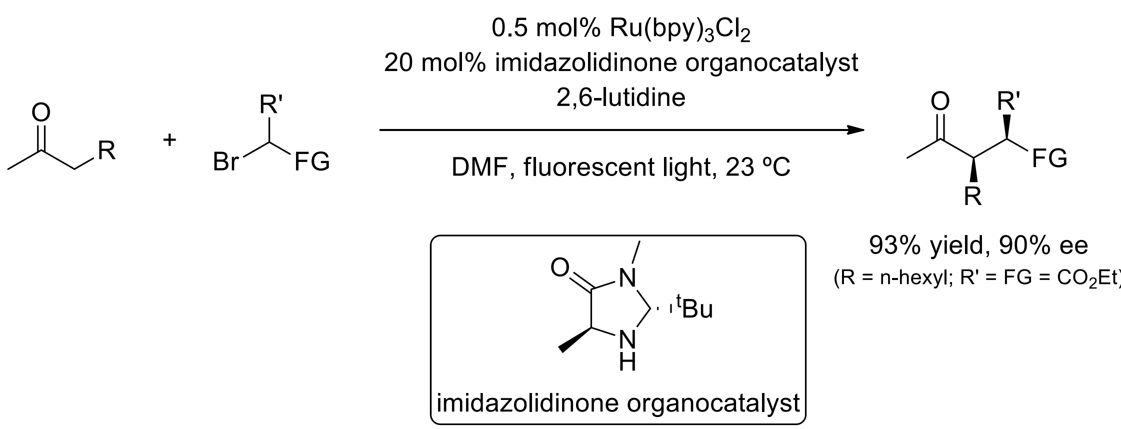

Figure 0.8 Example reaction for photoinduced asymmetric alkylation reaction by MacMillan.

A common way to provide stereochemical control in dual photoredox catalysis is through covalent bond activation, as in the previously mentioned imidazolidinones. However, dual catalysis can also work non-covalently. Ooi and coworkers developed a novel chiral ion-pair strategy to generate asymmetric amines from enantioselective α-coupling between (*N*-arylamino)methanes and (*N*-methanesulfonyl)aldimines (Figure 0.9).[32] Due to the absence of direct bond-formation between chiral agents and substrates, this strategy is particularly useful in further introduction of chirality in sterically encumbered systems.

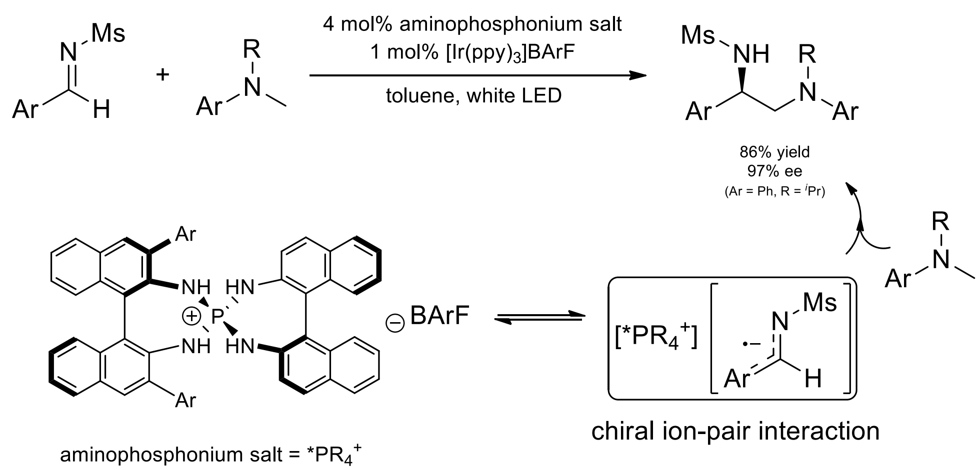

Figure 0.9 Example reaction of noncovalent enantioselective α-coupling between aldimine and aryl amine in the work by Ooi and coworkers (Ms = mesityl group, ppy = 2-(2-pyridyl)phenyl, BArF= $[3,5\text{-}(CF_3)_2C_6H_3]_4B$).

Knowles and Alexanian developed a series of iridium photocatalysts that can facilitate proton-coupled electron transfer (PCET) reactions through non-covalent interactions between the Ir-photocatalyst and a monobasic phosphate (Figure 0.10).[33] PCET involves concerted electron transfer and proton transfer to *different* orbitals in the product. It facilitates the concerted formation of radical species that are kinetically difficult to obtain from stepwise proton transfer-electron transfer (PT-ET) or electron transfer-proton transfer (ET-PT) pathways. They have demonstrated that this exquisitely designed catalyst can be used to activate C-H bonds even for unsubstituted alkanes such as cyclopropane under mild conditions.

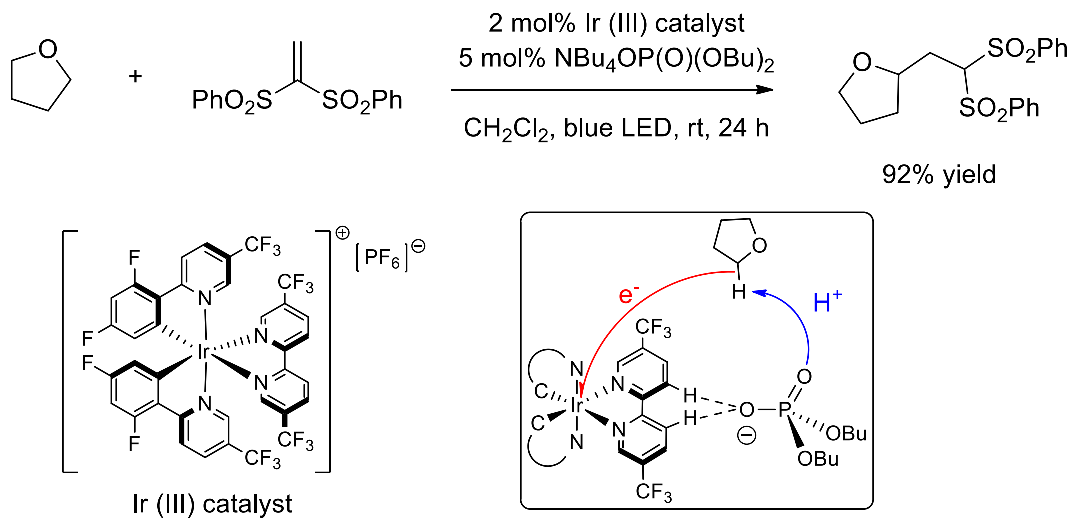

Figure 0.10 C-H activation reaction involving PCET mechanism catalyzed by iridium (III) catalyst developed by Knowles group.

In light of these selected examples of early success using photoredox catalysis in organic reactions, studies in this area have made significant impacts in pharmaceutical industries.[34,35] Due to the increasing importance of these reactions in the community of organic synthesis, it is valuable to study their mechanisms in order to better control the outcomes of photoredox reactions.

1.2. Dynamic Effects and Nonstatistical Dynamics

Chemist relies on transition state theory (TST) or Rice-Ramsperger-Kassel-Marcus (RRKM) theory to understand reactivity and selectivity. However, this understanding is not always feasible even when the transition state is known. In TST and RRKM theory, it is assumed that intermediates live enough time for molecules to reach an equilibrium state for the distribution of internal energy. However, “dynamic effects” occur when a chemical event occurs faster than the time needed to reach this equilibrium state. For these reactions, the consideration of dynamics is required to account for experimental observations. In such cases, analyses must fall back to fundamentals and one needs to consider the detailed dynamics parameters such as the movements and the momenta of atoms or an extended dimensional potential energy surface. These phenomena have been found to play a key role in the understanding the mechanisms of many synthetically valuable reactions.

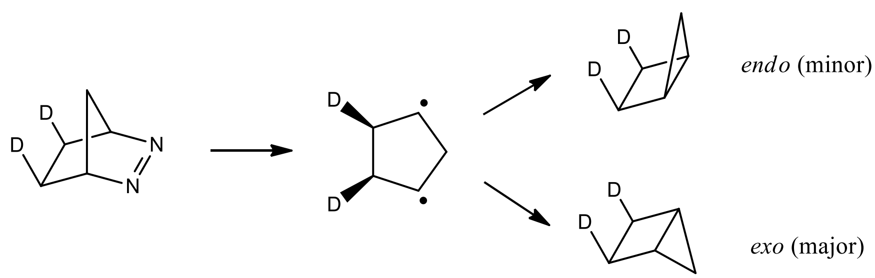

Figure 0.11. Deazetization reaction of 2,3-diazabicyclo[2.2.1]heptane where the *exo* conformation was reported to be the major product. Adapted from reference 37.

A classic example is the thermal decomposition of the 2,3-diazabicyclo[2.2.1]heptane (Figure 0.11). Experiments showed that the *exo* product is favored by 3:1 ratio in the gas phase.[36–38] This differs from a 1:1 ratio predicted from TST due to the equivalent potential energy barriers at the ring-closing step. Molecular dynamics studies revealed that the ring-closing step affording the products dynamically competes with the randomization of the ring flip. A classical trajectories study by Carpenter and coworkers correctly predicted a temperature-independent preference for the *exo* product. It also showed that the vector of atomic displacements at the nitrogen-loss TS points in favor of the *exo* product formation.[39] This local vibrational mode promoted selectivity cannot be expected from TST since it assumes that the intramolecular vibrational relaxation (IVR) is fast in the time scale of reaction coordinate motion. Recently, Rollins et al. used a machine-learning approach to analyze the outcome of quasiclassical trajectory calculations.[40] Supervised classification algorithms such as random forest could predict the outcome of the trajectories from the methylene bridge out-of-plane bending at up to 95% accuracy. This suggests that this nonstatistical product distribution may result from an incomplete relaxation of vibrational energies at an early stage after the nitrogen loss.

The discovery and interpretation of cases where statistical theories fail to predict mechanisms has been the focus in the Singleton group. Historically, several types of nonstatistical dynamics have been discovered such as (1) nonstatistical reaction dynamics, (2) post-TS bifurcation and recrossing, and (3) entropic intermediates. This section will provide a brief introduction of some reactions that require dynamic interpretations.

1.2.1. Nonstatistical Reaction Dynamics

TST assumes that the intermediates of a reaction have equilibrated fully before passing through the next TS. However, for some reactions that are highly exothermic at the rate-limiting step, the intermediates could be formed with large amounts of kinetic energy that cannot be dissipated on timescale of the reaction coordinate. When this occurs, the reactivity or product selectivity can be controlled by certain vibrational modes. In 1972, Polanyi proposed rules to predict different reactivity in terms of the energy partition in triatomic reactions. For reactions with early barriers, translational energy could promote the reaction more effectively than vibrational energy. On the other hand, for reactions with late barriers, vibrational energies could promote the reaction more effectively than translational energy.[41,42] Although this idea has been supported by several following studies on triatomic reactions,[43–45] application to polyatomic molecules seems to be complicated.[46] In 1984, Schatz and coworkers used quasiclassical trajectories to predict that the collision between a hydrogen atom (H) and water to produce dihydrogen (H_2) and hydroxyl radical (OH) could be promoted by the excitation of the O-H vibration of water.[47] Zare and coworkers experimentally demonstrated that reactivity and product selectivity can be controlled by mode-selective excitation by laser.[48] Despite the early reports of the promotion of reactions using local vibrational excitation, the understanding of nonstatistical reaction dynamics has not been extended to the scale of ordinary organic reactions.

More recent studies on nonstatistical reaction dynamics in organic reactions were reported by Kurouchi and Singleton in 2016.[49] They investigated the α-cleavage of alkoxy radicals generated from cycloalkyl hypochlorites with different substituents and ring size. The larger alkyl group substituent contributes more vibrational energy into the alkoxy radical. Since this vibrational energy is not statistically distributed, the observed intramolecular KIEs are lower than those predicted by statistical theories. In 2017, the authors further reported that the history of the formation of the alkoxy radical could be an important factor in controlling the outcomes of the reactions.[50] The experimental intramolecular KIEs change when changing the substituents on the thiophenol leaving groups. These studies show that care must be taken when mechanistically interpreting observations in short-lived intermediates.

1.2.2. Post-Transition State Bifurcation (PTSB) and Recrossing

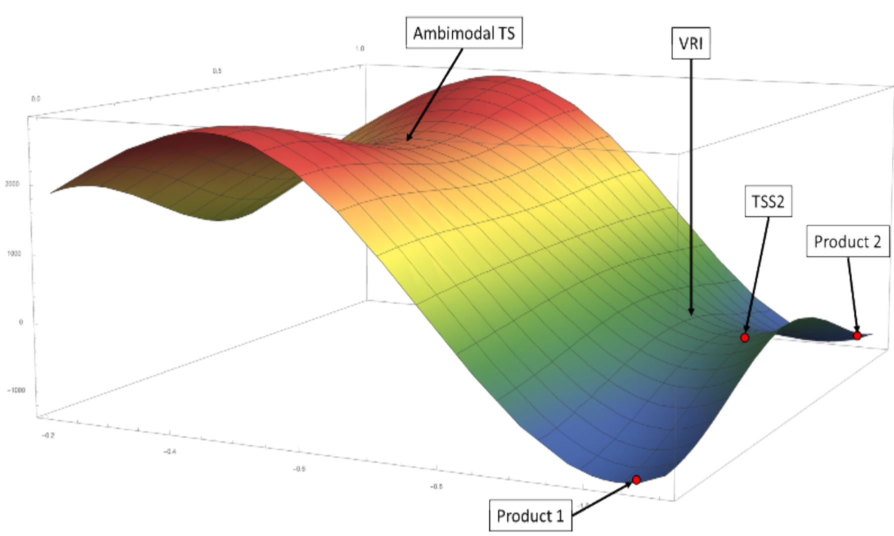

Figure 0.12. A general surface for reactions with post-transition state bifurcation.

Transition states (TSs) connect a set of reactants and with a set of products. Usually, different products are connected by different TSs. However, PTSB occurs when more than one product is formed by a single TS structure. In this case, more than one reaction coordinate would be required to describe the mechanisms. For such reactions, the selectivity-determining point (TSS2) of the products is located behind the first ambimodal TS (Figure 0.12). The experimental and computational demonstration of reactions involving PTSB have been provided by the Singleton group. In one of their studies,[3] experimental KIEs and computational investigations of periselectivity of cycloadditions between ketenes and cyclopentadiene to afford [4 + 2] and [2 + 2] products (Figure 0.13). This reaction was previously proposed as a stepwise [4 + 2] followed by [3,3]-sigmatropic rearrangement mechanism.[51,52] However, the experimental KIEs can only be explained when only one transition state structure is involved. Trajectories showed that nonstatistical recrossing back to starting materials accounts for the late discrimination on the isotope effects.

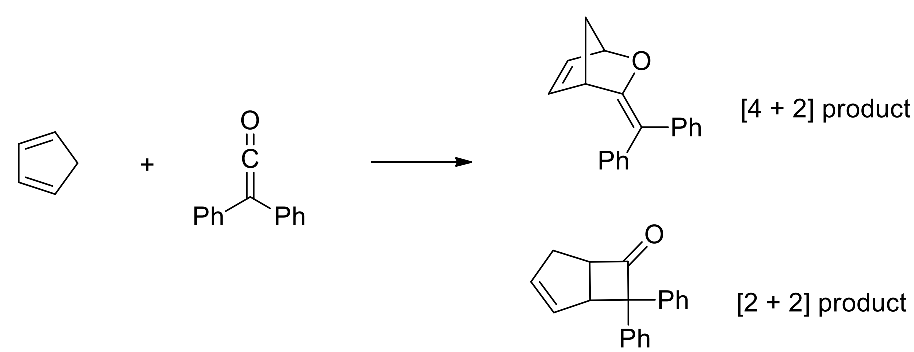

Figure 0.13. Cycloaddition reactions between ketenes and cyclopentadiene in a work by the Singleton group. Adapted from reference 3.

The Singleton group further analyzed factors affecting the product selectivity on a bifurcating surface.[53] In this study a combination of product studies, experimental KIEs and theoretical predictions of the Diels-Alder reaction between 3-methoxycarbonylcyclopentadienones and 1,3-dienes were performed. Depending on the transition state structure, the product selectivity ranges from favoring $[4\pi_{diene} + 2\pi_{dienone}]$ to $[2\pi_{diene} + 4\pi_{dienone}]$ cycloaddition produces. The results suggest that the geometry of the transition state as well as the shape of the energy surface are both critical in predicting product selectivity.

These fundamental studies motivate the exploration of reactions involving complex dynamic behavior. A brief survey for reactions of small organic molecules involving PTSB is summarized by Houk and coworkers.[54] Not limited to small molecule organic reactions, studies on dynamic effect in the biological system are available. An intriguing example for biological PTSB reaction is a Diels-Alderase SpnF found in *Saccharopolyspora spinosa*, which catalyzes the biosynthesis of spinosyn A, a major component of the insecticide spinosad. Its catalytic mechanisms have perplexed researchers since its discovery by Liu and coworkers in 2011.[55] A mechanistic study by Hess and Smentek proposed a "concerted, [but] highly asynchronous" formation of the Diels-Alder cycloadduct (Figure 0.14).[56] Houk, Singleton and coworkers used quantum mechanical (QM) calculations to firstly propose the presence of the [6 + 4]-cycloadduct.[57] A PTSB scheme was also suggested. Yang et al. developed an environment-perturbed transition-state sampling (EPTSS) method to include environmental effect in the trajectory calculations.[58] It showed how enzyme residues and water molecules affect the selectivity of this PTSB reaction.

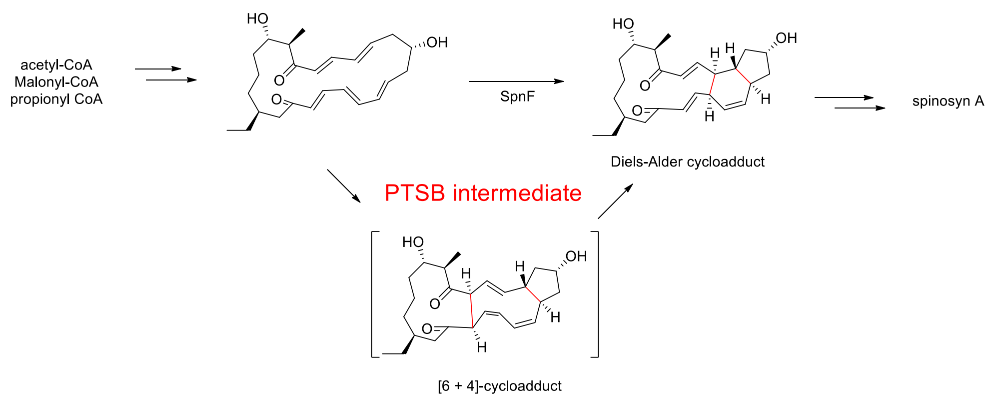

Figure 0.14. Diels-Alder reaction catalyzed by SpnF in the biosynthesis of spinosyn A. in S. spinosa. Adapted from reference 55.

Statistical rate theories assume that the reaction trajectories only pass TS once. In reality, it is possible that the TS can be passed more than once, especially for reactions with bifurcating or flat region on the PES. In contrast to quantum tunneling, recrossing decreases the rate compared to statistical theories. In these cases, an additional correction factors must be included. A common way to estimate the correction factor due to recrossing is to use the variational transition state theory (VTST). VTST looks for the TS structure by minimizing the amount of recrossing. If the recrossing is large, one could observe a large displacement between the TS on PES and the TS predicted from VTST.

The Singleton group reported that dynamic recrossing is an important factor controlling product selectivity of the Diels-Alder reaction between acrolein and methyl vinyl ketone (Figure 0.15).[59] In this study, trajectory calculations show that product selectivity depends on the direction from which trajectories leave the transition state region. It was found that trajectories leading to **DA-2** suffer more recrossing than to **DA-1**. This model accounts for the experimental observation of strong preference to the formation of **DA-1**.

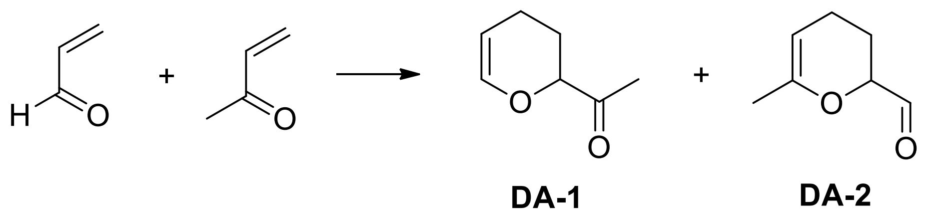

Figure 0.15. Diels-Alder reaction between acrolein and methyl vinyl ketone in a study by the Singleton group. Adapted from reference 59.

Doubleday *et al* reported an unusual H / D KIE on the Bergman cyclization of enediynes (Figure 0.16).[60] The reaction undergoes a 28.3 kcal/mol enthalpic barrier to form *p*-benzyne intermediate, which is only slightly endothermic (+7.7 kcal/mol) than enediyne. Since there is a 20.6 kcal/mol excess energy from TS to the benzyne intermediate, it can easily cross the second barrier to afford enediyne. They proposed competitive scheme between intramolecular vibrational relaxation (IVR) and recrossing back to enediyne. From DFT-based quasiclassical trajectories, they obtained an unusual small H / D KIE (0.79) compared with the one predicted from TST (0.92 ~ 0.93). The decreased KIE implies the slow IVR competes with dynamical recrossing as deuteration increases the rate of IVR in the *p*-benzyne intermediate.

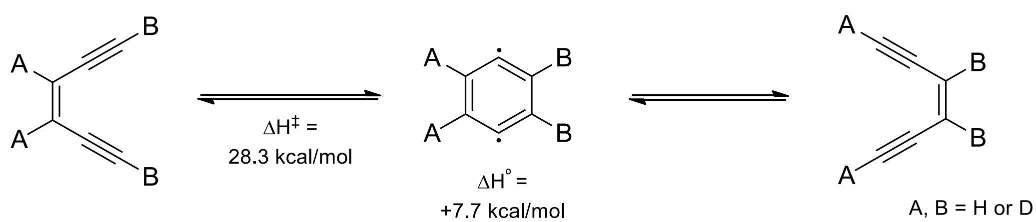

Figure 0.16. Bergman cyclization of enediyne by Doubleday *et al*. The enthalpy is referenced to enediyne reactant (left). Adapted from reference 60.

1.2.3. Entropic Intermediates

Construction of potential energy surface is usually the first step in the computational modelling of a reaction. However, chemical reactions "take place" on the free energy surfaces, which include extra thermal energies and entropy to PES. Entropic intermediates exist when a structure is a minimum on free energy surface but not on PES. This species can transform into another stable structure but it is in some cases a determining factor for product selectivity. Gonzalez-James *et al* reported an unusual heavy-atom intramolecular KIE of the cycloaddition between *cis*-butene and dichloroketene.[61] This reaction is regarded as concerted cycloaddition if predicted from the Woodward-Hoffmann rules. However, the experimental KIE suggests a stepwise bond formation process: The first step suffers from large recrossing and the second step becomes the RDS on the free energy surface. These findings demonstrated that the hidden entropic intermediate can affect experimental observations and the qualitative understanding of the mechanism.

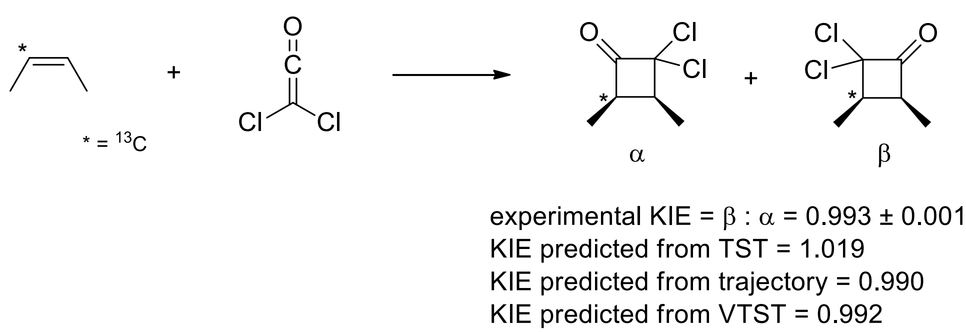

Figure 0.17 Experimental and predicted intramolecular KIE of the cycloaddition between cis-butene and dichloroketene in the work by Gonzalez-James *et al* in reference 61.

Despite the variety of dynamic effects, most reactions occur non-statistically because of shallow intermediate and barrier energies followed by the rate-determining step (RDS). Experimentally, kinetic isotope effects (KIE) not only provide a probe of the TS structure at the rate-limiting step, but can also catch the dynamic behavior after the RDS. Therefore, measuring KIE has been used as a major approach to study the reaction mechanisms in the Singleton group. A modern view of KIEs will be discussed in the next section.

1.3. Kinetic Isotope Effects

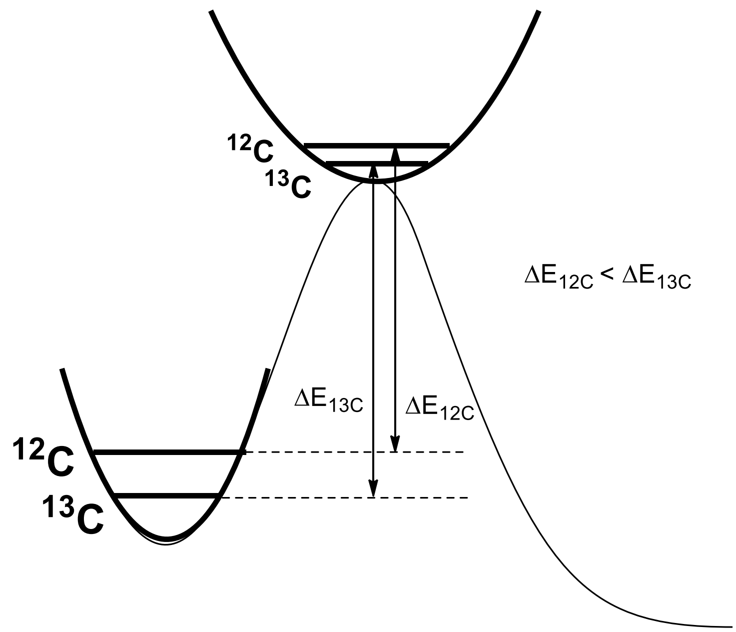

Figure 0.18. The ZPE origin of carbon KIEs. The TS structure is, in general, more loosely bonded than reactant, causing the vibrational energy levels in the TS becomes more closely packed. Therefore, the reaction barrier for ^{13}C-substituted isotopomers becomes larger than all-^{12}C isotopomer.

Kinetic isotope effects (KIEs) are useful kinetic information for understanding the mechanisms of a reaction. A KIE is defined as the change in rate when an atom of the reactant molecules is replaced by one of its isotopes. The origins of KIEs can be classified into three sources. The first source is zero-point energy (ZPE). For an isotope-substituted molecule, the TS structure does not change by any appreciable amount and its potential energy remains unchanged. However, the reaction rate changes due to differing changes in ZPE with isotopic substitution. Vibrational energies, based on quantum theory, are proportional to vibrational frequencies (E =

hν). According to classical mechanics, vibrational frequencies (ν) are proportional to the square root of force constant (k) over the reduced mass (μ) (Eq. (1-4)). Since the TS is more loosely bound than the reactants, the vibrational levels are usually more closely spaced. ^{13}C-substituted isotopomers have slower rates than their all ^{12}C analogues (**Figure 0.18**).

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad (1\text{-}4)$$

The second source of KIEs is tunneling. Tunneling is a quantum mechanical phenomenon arising from wave-particle duality – small particles (raging from electrons, protons, to even light atoms) penetrate through barriers that are classically too high to cross. A systematic review of the tunneling effect in chemistry was made by Bell in 1980.[62] The probability of a particle tunnelling through a barrier can be estimated from the time-independent Schrödinger equation. As an approximation, the probability of tunneling (permeability), G, for a particle with energy W passing through a parabolic barrier (barrier height = V_0) can be described in the following equation:

$$G = \frac{1}{1 + \exp\left(\frac{V_0 - W}{\hbar \nu_{\ddagger}}\right)} \qquad (1\text{-}5)$$

, where $\nu_{\ddagger}$ is the imaginary part of the imaginary frequency at the TS. The $\nu_{\ddagger}$ can also be expressed as $\frac{1}{2\pi}\sqrt{\frac{A}{m}}$, where *A* represents the curvature of the parabolic potential, and *m* is the mass of the particle. That is, the thinner the barrier and the lighter the particle, the more tunneling in the reaction. It can also be derived from the de Broglie equation. Therefore, if a reaction undergoes significant tunneling, the reaction rate of a heavy-isotope substituted isotopomer can be much slower than its non-isotope-labelled analogue. This can result in large KIEs. However, tunneling is relatively less affected by temperature. Therefore, a typical experimental approach to probe tunneling is to measure KIEs under cryogenic temperatures. At low temperatures, reactions from thermal activation can be much inhibited while the tunneling is not slowed down drastically. Experimental H / D KIEs from tunneling effects can range from hundreds to even more than ten thousand.[63]

The third source of KIEs can be attributed to dynamic effects after the rate-determining step. As described in previous section, dynamic effects happen when chemical events (bond-forming or bond-breaking) occur faster than the intramolecular vibrational relaxation or solvent equilibration. In this case, a simple ZPE difference between the TS and the reactants would not be enough to describe the KIEs. Rather, the reaction path after passing the potential energy TS at the RDS is important. The degree of changes in the KIEs depends on how different an intermediate is from its equilibrated state.

KIEs can be categorized, by their magnitude, into two types: primary and secondary. Primary KIEs, usually greater than 1% for ^{13}C, are observed when the isotopic substitution is at bond forming or breaking position, causing large changes in rate between heavy and light isotopomers. On the other hand, secondary carbon KIEs, usually less than 1%, occur when the carbon is close to a bond forming/breaking site and does not influence relative rates as much as in primary KIEs. The rate difference of the isotopomers is used to explain the mechanisms product ratios and the dynamic effects involved in reactions of interest.

1.3.1. Experimental KIEs

Carbon-13 consists naturally as ~1.1% of the overall amount of carbon. The peaks in ^{13}C-NMR represent the ~1.1% of the ensemble of molecules that have ^{13}C-labelled at the corresponding positions. In 1995, Singleton and coworkers developed a methodology to measure KIEs at natural abundance.[7] This method has been used widely and most successfully for determining carbon KIEs. The KIE can be measured intermolecularly or, in some special cases, intramolecularly from quantitative ^{13}C NMR spectroscopy techniques. For intermolecular KIEs, starting materials at high conversion in the reaction of interests are isolated and the ^{13}C NMR spectra are quantitatively compared against starting materials have not been subjected to the reaction (standard). The KIEs are then calculated according to equation below where F indicates the fractional conversion of the reaction and R/R_0 indicates the integration ratio of the peak of interests between the recovered starting material and standard.

$$KIE = \frac{\log(1-F)}{\log\left[(1-F)\left(\frac{R}{R_0}\right)\right]}$$

If a reaction step breaks the symmetry of the molecule, an isotope effect would arise for an isotopomer with only one position substituted by heavy isotope. In this case an intramolecular KIE can be measured. For example, in the ene reaction between hexa-deuterated tetramethylethylene and singlet oxygen,[64] KIEs would arise from the selection between proton and deuterium shifts (Figure 0.19). Since the product is asymmetric, one can calculate the KIE by taking the ratio of the methylene peak (c) and the methyl peak (b).

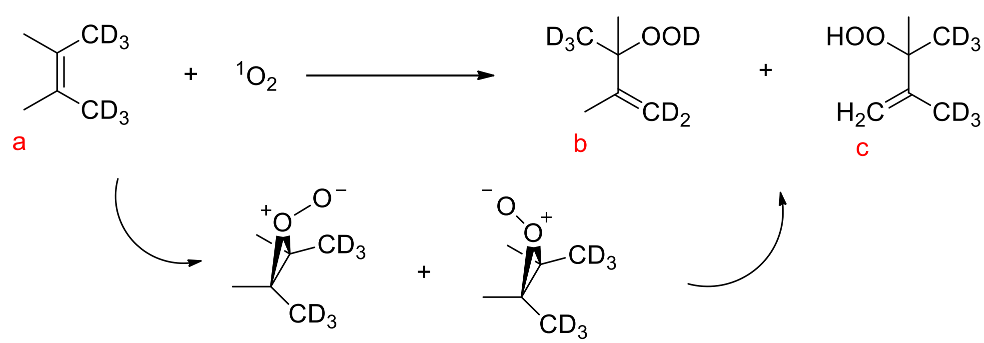

Figure 0.19 Origin of intramolecular KIE in the ene reaction between tetramethyl ethylene and singlet oxygen. Adapted from reference 64.

1.3.2. Theoretical KIEs

The quantitative interpretation of experimental KIEs can be achieved by theoretical predictions. An equation proposed by Bigeleisen and Mayer describes KIEs modelled from vibrational partition functions.[65,66] For an isotope exchange reaction, the equilibrium constant (*K*) can be expressed as the ratio of partition functions (*Q*) of reactants to products.

$$AX + BX^{*} \rightleftharpoons AX^{*} + BX$$

*isotope labelling

$$K = \frac{\prod_i \left(\frac{Q_i^*}{Q_i}\right)_{AX}}{\prod_i \left(\frac{Q_i^*}{Q_i}\right)_{BX}};\, i = translational, vibrational, rotational, electronic, \ldots$$

The partition function can be decomposed into translational, vibrational, rotational and electronic partition functions. However, in isotope exchange reactions, changes in the translational and electronic partition functions upon isotope labelling are negligible. Therefore, the vibrational and rotational partition functions contribute most of the equilibrium constant. Under harmonic oscillator and rigid rotor approximations, the partition function ratio can be reduced into

$$K = \frac{\prod_i^{3n-6} \frac{u_{i,AX^*}}{u_{i,AX}} \frac{1-\exp(-u_{i,AX^*})}{1-\exp(-u_{i,AX})} \frac{\exp\left(\frac{u_{i,AX^*}}{2}\right)}{\exp\left(\frac{u_{i,AX}}{2}\right)}}{\prod_i^{3n-6} \frac{u_{i,BX^*}}{u_{i,BX}} \frac{1-\exp(-u_{i,BX^*})}{1-\exp(-u_{i,BX})} \frac{\exp\left(\frac{u_{i,BX^*}}{2}\right)}{\exp\left(\frac{u_{i,BX}}{2}\right)}} = \frac{\left(\frac{s_{AX^*}}{s_{AX}}\right) f\left(\frac{AX^*}{AX}\right)}{\left(\frac{s_{BX^*}}{s_{BX}}\right) f\left(\frac{BX^*}{BX}\right)}$$

, where $u_i = h\nu_i/kT$, and ν_i refers to normal mode harmonic frequency. This equation permits estimations of kinetic isotope effects from imaginary frequencies of a transition state of a reaction. The tunneling effect and anharmonicity corrections can be made by multiplying extra coefficients. Under the statistical approximation, the rate of a reaction can be described by the Eyring equation, which views the TS as a pseudo-intermediate under steady-state approximation. One can calculate the reaction rate by treating BX as the TS structure at the RDS. To calculate the KIE, the above equation can be rewritten as

$$KIE = \kappa A \frac{\nu_{\ddagger}^{*} f(BX^{*})}{\nu_{\ddagger} f(BX)}$$

, where κ is the tunneling correction, and *A* is anharmonicity correction. The asterisk represents isotopic substitution.

Another computational prediction of KIEs can made under the RRKM theory. RRKM theory estimates a unimolecular reaction rate from summing up rate constants of Boltzmann distributed microcanonical ensemble. The RRKM theory assumes that molecule proceeds to the product once it reaches the TS, and fast IVR rate with respect to the timescale of molecular movements. Under these circumstances, the RRKM rate constant for a molecule with internal energy, *E*, can be expressed as

$$k(E) = \frac{\sigma N^{\ddagger}(E - E_0)}{h\rho(E)}$$

, where $N^{\ddagger}(E - E_0)$ is the sum of states of the energy range from activation energy, E_0, to *E*, σ is the degeneracy of the reaction pathway, $\rho(E)$ is the density of state at energy *E,* and *h* is the Planck's constant. At given canonical temperature, *T*, the rate constant can be estimated from the weighted sum of the Boltzmann distributed density of states at different *E*. That is,

$$k(T) = \int_{E_0}^{\infty} k(E)\rho(E) \exp\left(\frac{-E}{k_B T}\right) dE$$

, where k_B is the Boltzmann constant. The KIE can be calculated by taking the ratio of $k(T)$ of light to heavy isotopomers.

A computationally demanding but more accurate KIE prediction can be made by using the POLYRATE program, developed by Truhlar and coworkers.[67] The previous methods mentioned above only take two points on the reaction potential energy. The POLYRATE program calculates free energy surface using the variational transition state theory (VTST). VTST optimizes the TS position by looking for the minimum of recrossing. It is useful to find the position of free energy barriers in reactions lacking potential energy maximum (entropic barrier). VTST also makes use of quantum mechanical tunneling corrections such that the tunneling correction can be more accurate than the previous methods, particularly when the tunneling effect plays an important role in the reactivity.

2. PHOTOREDOX-PROMOTED [2 + 2]-CYCLOADDITION REACTIONS*

2.1. Introduction

The photophysical and photochemical properties of tris(bipyridyl)ruthenium(II) ($Ru(bpy)_3^{2+}$) was extensively studied since the 1950s. Its relatively long excited state lifetime (~1100 ns) is long enough to diffuse out from the solvent cage and activate substrates bimolecularly. Depending on the nature of the substrates and reaction conditions, the deactivation pathways of the excited $Ru(bpy)_3^{2+}$ varies. It can either undergo single electron transfer (SET) to generate open-shell species or engage in triplet energy transfer (Figure 2.1). Combining with its chemical stability in various conditions, ruthenium polypyridyl complexes have become archetypical catalysts in designing photochemical reactions. Synthetic applications using ruthenium polypyridyl complexes can be found in reactions involving reductions, oxidations, cycloadditions, radical substitutions.[17]

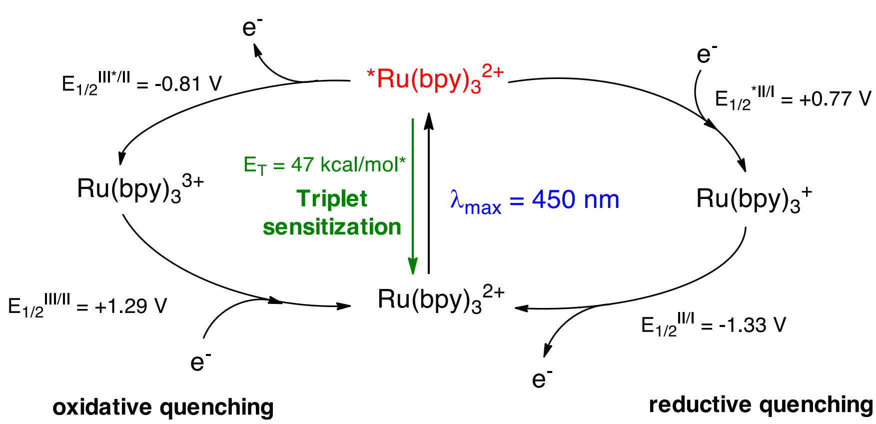

Figure 2.1. Deactivation pathways of photo-excited $Ru(bpy)_3^{2+}$.**[17,68]**

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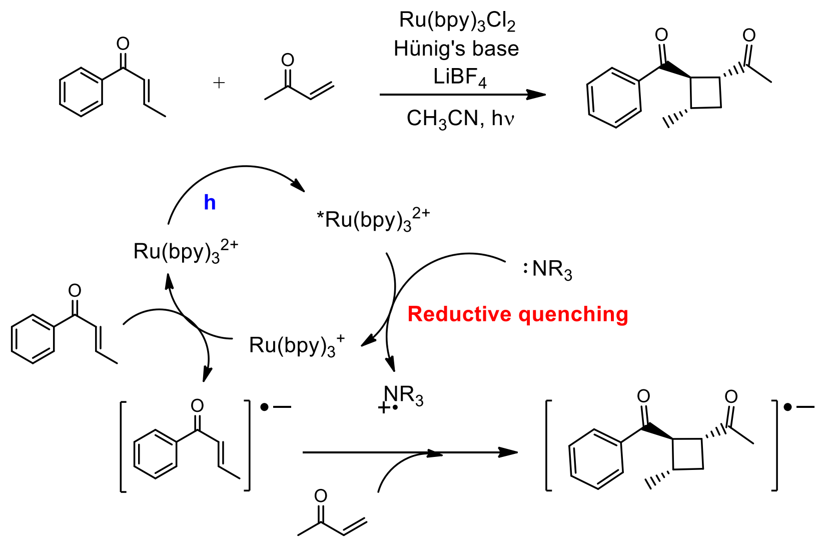
* Adapted with permission from "Isotope Effects and the Mechanism of Photoredox-Promoted [2 + 2] Cycloaddition of Enones" by K.-Y. Kuan and D. A. Singleton. *Journal of Organic Chemistry,* **2021,** *86,* 6305-6313. Copyright 2021 American Chemical Society.

However, the mechanisms of photoredox-promoted reactions are intrinsically complex, involving a combination of photophysical steps, one or more electron-transfer steps leading to activated substrates, chemical conversions of radical ions, chain-transfer steps, and termination steps. Many aspects of these mechanisms are qualitatively understood from general chemical knowledge. In fact, mechanistic understanding is often a key factor in the design and development of these reactions. However, the complexity of the mechanisms leaves some aspects undefined by either qualitative experimental studies or computational studies. The interplay of electron-transfer steps and chemical steps is particularly problematical, as electron-transfer steps are not readily tractable computationally and are often not directly accessible experimentally.

A striking example of the synthetically valuable and complex photoredox reactions developed in recent years is the [2 + 2]-cycloaddition of enones that occurs with visible light in the presence of $Ru^{II}(bpy)_3Cl_2$ as photosensitizer, as developed by Yoon and coworkers.[27,69] The reaction is an extension of earlier work by Kriche and Bauld on cathodic reduction of bis(enones),[30,70] and the reaction is an example of the now broad class of cycloadditions of both anion radicals and cation radicals.[30,70–72] Yoon has recently extended these cycloadditions to enantioselective reactions by employing chiral europium Lewis acid complexes as cocatalysts.[73]



Scheme 2.1. Reductive quenching pathway of intermolecular cycloaddition by Yoon's work.

The basic photophysics of these reactions are well known.[15,16] The triplet excited state of the $^*Ru(bpy)_3^{2+}$ is rapidly formed after excitation, and it is both a reductant and an oxidant. In the presence of an amine the triplet is reduced, and the resulting monovalent $Ru(bpy)^{3+}$ is now a longer-lived strong reductant (E° = -1.33 V).[17] The downhill transfer of an electron to a sufficiently electro-deficient enone such as phenyl propenyl ketone (E° = -1.26 V in the presence of $LiClO_4$ vs. SCE)[28,29,74] may then occur to afford the radical anion of the substrate. It is at this point that the mechanism must first overcome a significant barrier, that for C-C bond formation by the radical anion. The delayed reaction of a reactive intermediate is ripe for mechanistic complications, and the chemoselectivity and success versus failure of reactions may be expected to depend largely on the competition between traversal of the first large-barrier irreversible steps by substrates versus alternative reaction pathways. Such "selectivity-determining" steps can be interrogated by competition reactions, either using electronically differing substrates or using isotopically differing substrates in the measurement of kinetic isotope effects (KIEs). The results of such studies here are surprising and have implications toward the understanding and control of selectivity in these reactions. We describe here a combined experimental and computational study of a photoredox-promoted cycloaddition that elucidates the importance of this interplay in selectivity.

2.2. Experimental Intermolecular KIEs

The photoredox-promoted dimerization of phenyl vinyl ketone (**1**) provided a simple example for study. Under the Yoon conditions (Figure 2.2) including $Ru^{II}(bpy)_3Cl_2$, $LiBF_4$, and diisopropylethylamine in acetonitrile, the dimerization of **1** affords the trans-disubstituted cyclobutane cleanly in 89% yield as the sole cycloadduct (**2**). The ^{13}C KIEs for the dimerization were studied at natural abundance by NMR methodology.[7] Although it was found that **2** can be further ring opened to afford 1,4-dibenzoylbutate upon extend irradiation, it does not affect the intermolecular KIEs based on the enone reactants. Two independent reactions of **1** were taken to 85% and 60% conversion, and the crude unreacted **1** was hydrogenated (H_2 / Pd / C) to propiophenone for final purification and analysis. The propiophenone was then analyzed by ^{13}C NMR in comparison to propiophenone derived from the original **1** that had not been subjected to the reaction conditions. The changes in isotope composition in each position were determined relative to the para phenyl carbon as an "internal standard", with the assumption that the isotopic fractionation in this position was negligible. From the percentage conversions and the changes in isotopic composition, the KIEs were calculated as previously described.[7]

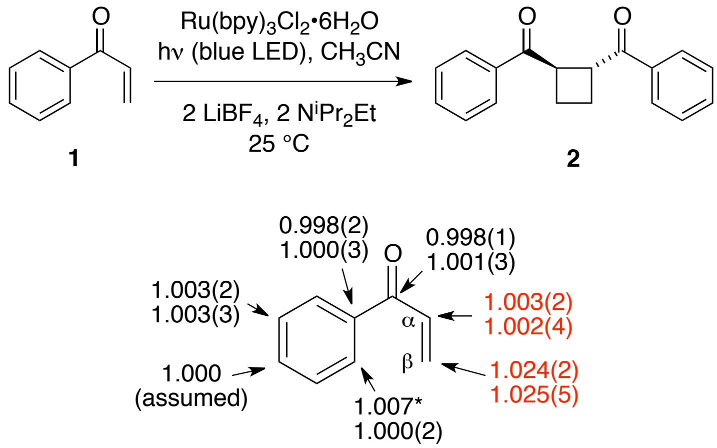
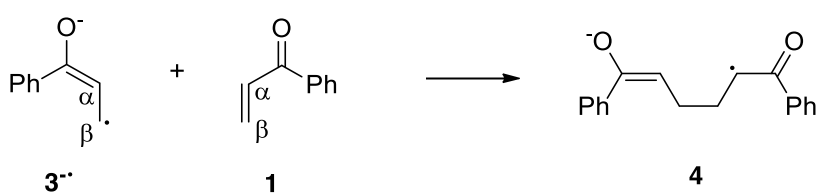


Figure 2.2. The ^{13}C KIEs (k_{12}/k_{13}, 25 °C) for the dimerization of **1**. In one case the measurement was affected by an overlapping impurity, and the resulting KIE is marked with a *.

The resulting KIEs are shown in the bottom part of Figure 2.2. The KIEs reflects the first-irreducible step undergone by the substrate, or selectivity-determining step. In this case, only the β-enone carbon exhibit a substantial ^{13}C KIE, with the remaining carbons essentially within the error of unity. The qualitative interpretation of this observation is that the selectivity-determining step involves C-C bond-formation at the β-enone carbons, as would fit with the reaction of a nominal enone radical anion (**3**$^{-\bullet}$) a neutral enone (eq (2-1)), as previously postulated by Kriche / Bauld and by Yoon.



(2-1)

There is however a substantial limitation on this interpretation because the measured KIE will be the average of KIEs for two molecules of **1**. This does not define the separate KIEs for each reactant; the observed 1.024 could result from the combination of values over a broad range. For example, it could be an average either between 1.023 and 1.025 or 1.000 and 1.048. As a consequence, the observed KIE cannot unambiguously define the selectivity-determining step for enone radical anion $\mathbf{3^{-\bullet}}$.

To define the selectivity-determining step for each component in the cycloaddition, it was necessary to study an unsymmetrical reaction. Yoon and coworkers had previously reported the crossed cycloaddition of 1-phenyl-2-buten-1-one **5** with methyl vinyl ketone (**6**) to afford the cycloadduct **7** in 84% yield (Figure 2.3). In this reaction, the more-conjugated **5** is more easily reduced, and it is expected to be the radical anion in the C_β--C_β bond-forming step, while the unhindered **6** is a more reactive electrophile and is expected to be the neutral component in the reaction.

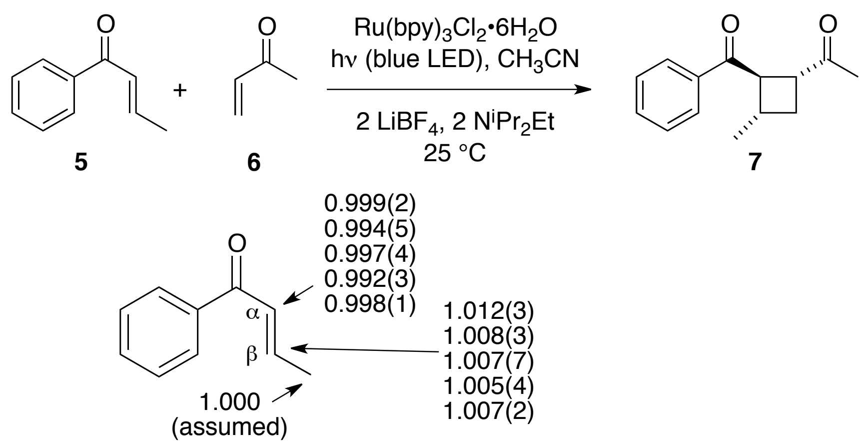


Figure 2.3. ^{13}C KIEs for the cycloaddition of **5** with **6** derived from five independent experiments with conversions from 66% to 92%.

The determination of the KIEs for the reaction of **5** with **6** was significantly more problematic than with the dimerization of **1**. It was first found that the reaction required the use of an excess of **6** to proceed efficiently, and this precluded a measurement of the KIEs for **6**. For **5**, there was an overlap of olefinic and aromatic ^{13}C NMR peaks that prevented a direct analysis of **5**, so recovered unreacted **5** was hydrogenated to afford butyrophenone for the final purification and analysis. Even so, trace (1-3%) inseparable impurity peaks in the aromatic region of the ^{13}C NMR for the butyrophenone prevented the use of an aromatic peak as the internal standard for integrations. Instead, the terminal methyl group was used as the internal standard. The results from a total of five independent KIE determinations are shown in Figure 2.3.

The key observation is that the KIE for the β carbon of **5**, at ~1.008, is much smaller than the composite KIE for **1**. This value is sufficiently small that it could reflect a secondary ^{13}C KIE. In other words, the KIE does not support C_β--C_β bond formation as the selectivity-determining step for the radical anion! A more quantitative interpretation of the KIE will be possible with the aid of computational studies.

The small β KIE for **5** in its reaction with **6** suggests that the KIE observed for the homocoupling of **1** resulted from the combination of a small KIE for the radical anion and a larger KIE for the neutral **1** undergoing bond formation. This assumes that the mechanisms for the homo- and heterocouplings are identical. The observation of very different KIEs (*e.g.,* 1.008 and 1.040, as a possibility) would be rather unusual if both **3**$^{-\bullet}$ and **1** were undergoing a selectivity-determining C_β--C_β bond forming step. This fits with the idea that the radical anion **1** has a separate selectivity-determining step prior to C-C bond formation. An alternative explanation will be considered below after the use of computations to evaluate the expected isotope effect for differing mechanistic scenarios.

2.3. Lithium Coordination

Yoon reported that the photochemical [2 + 2] reactions require the presence of the $LiBF_4$, that an excess of the salt and the diisopropylethylamine was required for high diastereoselectivity, and that the lithium could not be successfully replaced with other cations. To explore the role of lithium coordination in these reactions, we examined its effect on the ^{13}C chemical shifts of **5**, **6**, and diisopropylethylamine in CD_3CN at concentrations similar to that used in the reaction. Initial explorations using $LiBF_4$ were complicated by the partial precipitation of LiF in the presence of amine,[75,76] but it was found that $LiClO_4$ was equally effective and stereoselective in the synthetic reactions, so $LiClO_4$ was used for coordination studies.

In this experiment, two stock solutions (Solution A and B) were prepared:

Solution A: 60.5 mg (0.468 mmol) of diisopropylethylamine dissolved in 2.4 mL of CD_3CN, and

Solution B: 140.36 mg (1.320 mmol) of lithium perchlorate dissolved in 3.3 mL of CD_3CN.

The solutions were transferred to six vials using a 1000-μL micropipette by the volume according to Table 2.1. Samples required >1000 μL of liquid were transferred twice with half amount each.

Table 2.1. Sample preparation methods for coordination study.

Sample #	Solution A (mL)	Solution B (μL)	CD_3CN (μL)	theoretical Li^+ eq.
1	0.4	0	1548.4	0.00
2		96.8	1451.6	0.50
3		193.6	1354.8	0.99
4		387.1	1161.3	1.99
5		774.2	774.2	3.97
6		1548.4	0	7.94

As $LiClO_4$ is added to solutions containing the enones and amine, the carbonyl, α, and β carbons of **5** and **6** shift downfield, upfield, and downfield, respectively, in a pattern and proportion that matches in direction the changes in the calculated chemical shifts for these carbons in going from the neutral structures to structures that are lithium coordinated at their oxygen atoms.

Similarly, the α and β carbons of the diisopropylethylamine shift downfield and upfield, respectively, in line with predicted shift changes. The full ^{13}C spectra for each sample are shown in Figure 2.4, and the expansions are shown in Figure 2.5 and Figure 2.6. Both the carbonyl carbon (position c) of **6** and the α-carbon of amine (position e) show downfield shifts. No saturation of the shift changes could be observed in either case, with maximum shifts in the presence of 8 equivalents of $LiClO_4$ of 2.2 ppm for carbonyl carbon of **6** and 0.4 ppm for the amine α carbons. From this and the calculated shifts for lithium coordination, an order-of-magnitude estimate of the association constants for each is 1 M^{-1}.

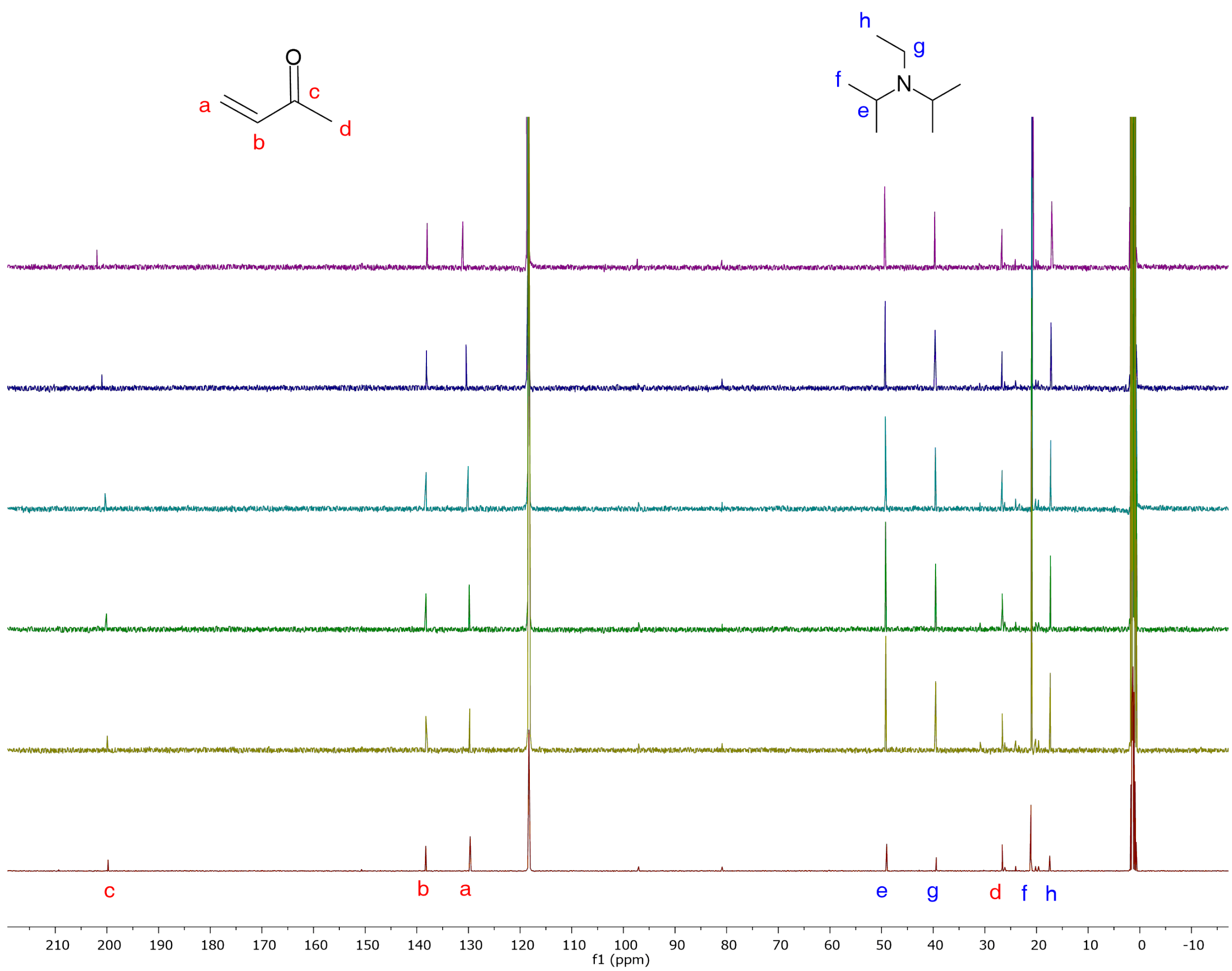


Figure 2.4. Full spectra and peak assignment for samples 1 (bottom) to 6 (top).

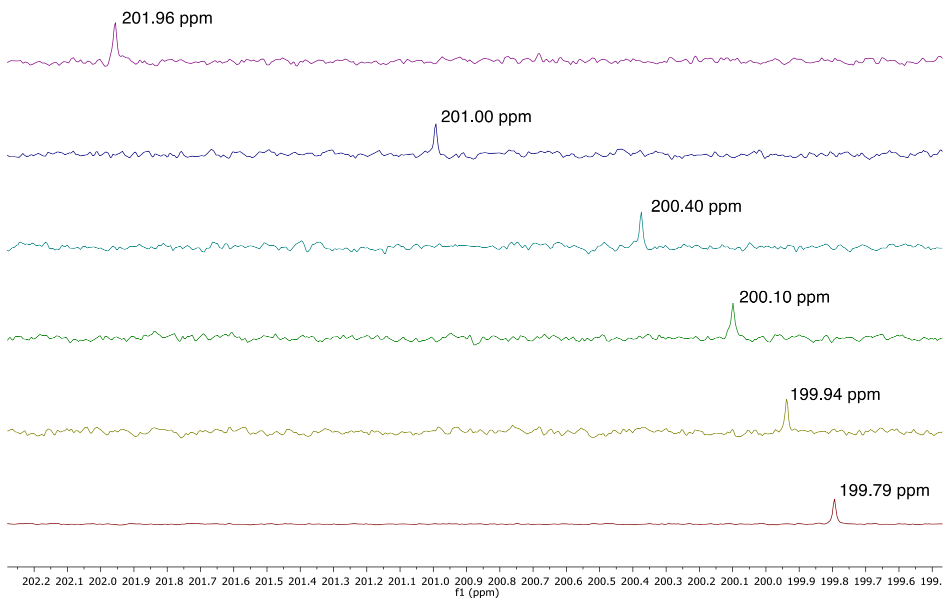


Figure 2.5. Carbonyl peak of **6** (carbon c) for sample 1 (bottom) to 6 (top).

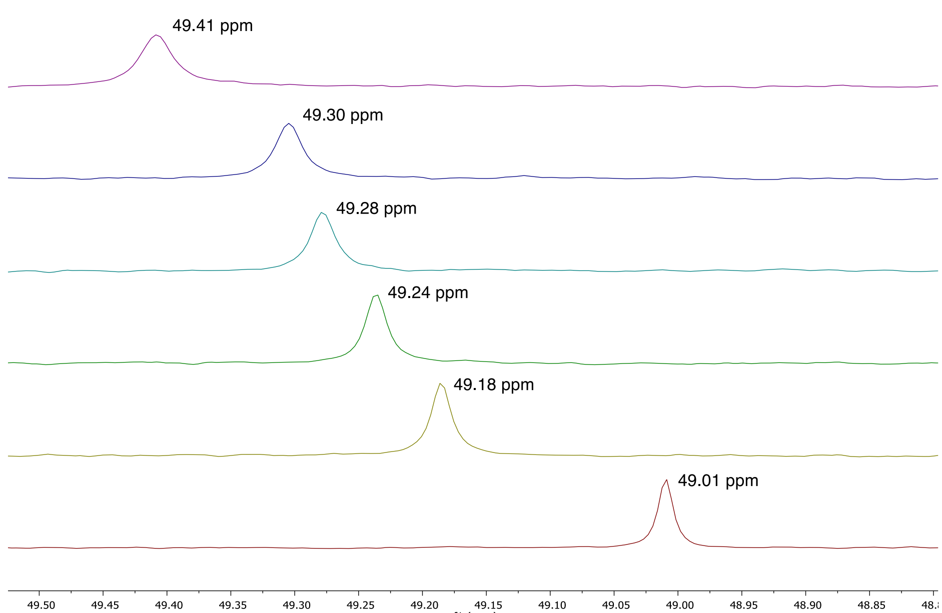


Figure 2.6. Alpha peak for diisopropylethylamine (carbon e) for sample 1 (bottom) to 6 (top).

This is extremely weak coordination, but the reaction conditions would contain significant amounts of lithium-coordinated reactants. Lithium coordination would make **5** a better electron acceptor and make **6** more electrophilic. It is uncertain whether both of these features are required for the success of the reaction, but it is notable that the electrochemical reactions of Krische / Bauld did not require an added lithium salt. Unlike the photochemical reactions, the electrochemical reactions notably involve long-lived anion radicals that cannot readily be quenched by back electron transfer to the original donor.

2.4. Computational Method Selection.

To choose a DFT method suitable for the study of the experimental reactions, the model cycloaddition of **6** with the radical anion of 1-cyano-2-buten-1-one was studied using diverse combinations of DFT methods and basis sets (see Table B.1 in the APPENDIX B). The energetics of the transition states and intermediates along the cycloaddition pathway for the various computational methods were then compared with single-point energies obtained in CCSD(T)/aug-cc-pVDZ energies, ωB97XD calculations employing a 6-311+G(d,p) basis set were chosen because they exhibited the lowest RMS error (1.4 kcal/mol across eight structures, see APPENDIX B) among practical methods. Both common solvent models, polarizable continuum model (PCM) and solvation model based on density (SMD), for acetonitrile were then employed for the exploration of the experimental mechanistic pathways in solution. For simple anionic structures the two solvent models led to qualitatively similar results, while for structures containing lithium counterions and additional coordination there were in cases significant differences, as will be noted. For structures of potential mechanistic relevance, the energies were corrected using DLPNO-CCSD(T)/aug-cc-pVTZ single-point calculations. The final energies reported here are a combination of the DLPNO potential energies and ωB97XD/PCM structures and free energy corrections adjusted to a standard state concentration of 1 M.

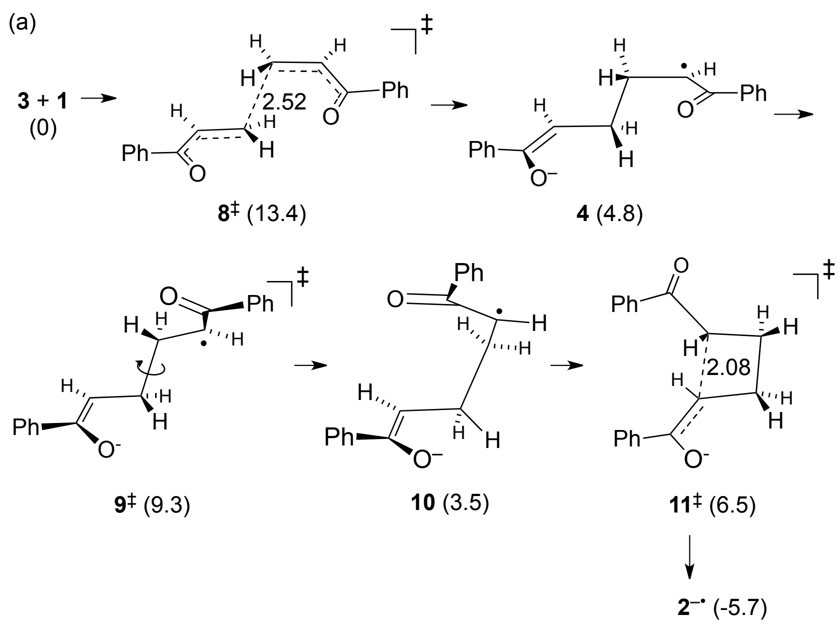
The lithium coordination studies described above provide one way to gauge the accuracy of the computational methods versus experimental observations. The free energy for coordination of **5** with a lithium ion in acetonitrile was calculated with the assumption that a 'free' lithium ion in acetonitrile is coordinated by four solvent molecules and that the **5** would replace one of these, giving rise to a Li(**5**)$(MeCN)_3$ ion. The calculated free energies were -1.7 kcal/mol and -1.1 kcal/mol for the SMD and PCM solvent models, respectively, compared to the experimental value of 0 ± 1 kcal/mol.

2.5. Computational Pathway

The potential involvement of the lithium ion and the amine in the mechanistic pathway complicates substantially computational exploration of these reactions. An additional complication is that several of the mechanistic models explored do not predict the correct major product for the reaction. Despite exhaustive effort on diverse systems including zero, one or two lithium ions, zero to six solvent molecules, and zero to two amine molecules, we ultimately concluded that computations alone could not adequately characterize the mechanism. Instead, we will use computations to aid in the interpretation of the experimental observations.

The important issues with regard to the computational explorations will be described here with reference to the simplified basic mechanisms of Figure 2.7. The effects of counterions, solvent, and amine will then be described as perturbations on these mechanisms. The initial C_β--C_β bond formation of **1** with its radical anion $\mathbf{3}^{-\bullet}$ (Figure 2.7a) and of **6** with the radical anion of **5** ($\mathbf{5}^{-\bullet}$) (Figure 2.7b) may occur by many transition state conformers but the lowest energy transition structures (TSs) invariably orient the olefinic units *anti* to each other, as in $\mathbf{8}^{\ddagger}$ and $\mathbf{12}^{\ddagger}$, and lead to

Z configurations of the incipient enol radical and enolate anion moieties. The corresponding gauche TSs are energetically competitive in structures including lithium counterions but in no case were they the lowest-energy TSs. The resulting distally oriented radical anions **4** and **13** must then undergo conformational interconversion (by TSs **9**‡ and **14**‡) to form gauche radical anions **10** and **15**. These then undergo ring closure via TSs **11**‡ and **16**‡ to afford the closed radical anions of the trans products **2**$^{-\bullet}$ and **7**$^{-\bullet}$. Since **2**$^{-\bullet}$ and **7**$^{-\bullet}$ would be expected to undergo exergonic electron transfers to the starting enones or other electron sinks in solution at a high rate, their formation would be irreversible as would passage over the highest-energy TSs **8**‡ and **12**‡.



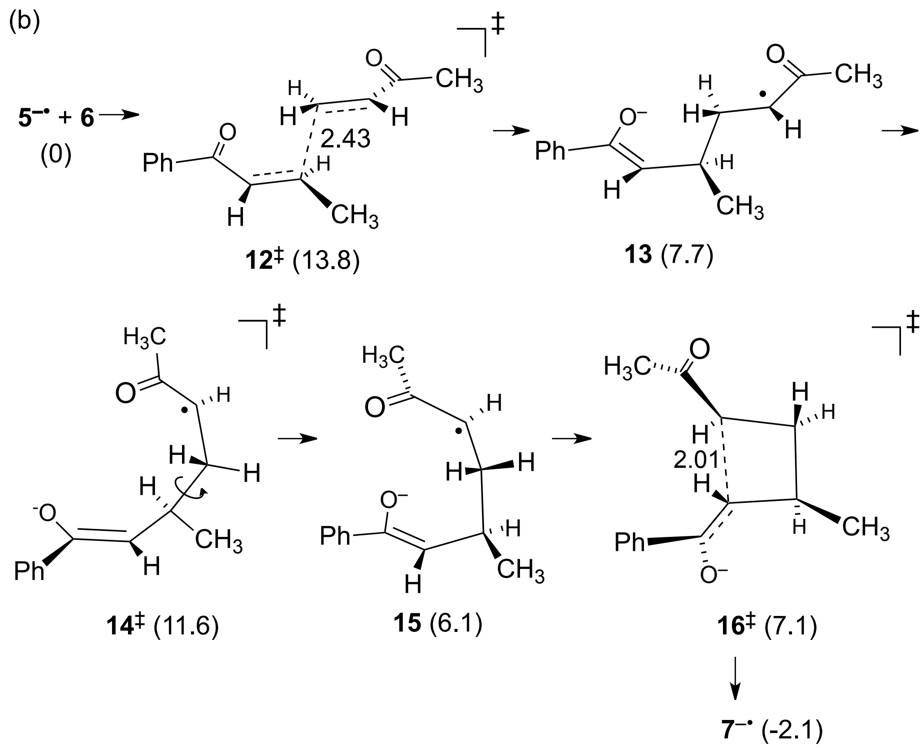


Figure 2.7. Simplified calculated mechanisms for (a) the reactions of **1** with its radical anion $\mathbf{3}^{-\bullet}$ and (b) of **6** with the radical anion of **5** (**5** •). The relative free energies are DLPNO-CCSD(T)/aug-cc-pVTZ//ωB97XD/PCM(acetonitrile) with a 1 M standard state in kcal/mol. Related structures including one or two lithium ions, varying explicit solvent, and on or two coordinating amines are show in the APPENDIX B.

After addition of one or two lithium ions to these parent structures, the energetically preferred structures invariably involve the chelation of a lithium ion by two oxygens. Since $\mathbf{11}^{\ddagger}$ and $\mathbf{16}^{\ddagger}$ can-not provide such chelation, these structures end up higher in energy than ring-closing TSs leading to the alternative cis product. Exhaustive attempts to locate a lower-energy TS for formation of the *trans* product were unsuccessful. In agreement with the many similar observations of Yoon, we have confirmed that product **2** has the *trans* stereochemistry by comparison of its melting point (experimental 92.1 ~ 93.8 ºC) with the known values for the two stereoisomers (95 ~ 97 ºC for *trans*, 121~122 ºC for *cis*).[77] Clearly, the simple solvent model is computationally inadequate. In solution, solvent or amine molecules would specifically coordinate the lithium ions. A series of such structures were located and are presented in the APPENDIX B. With a total of six acetonitrile molecules included, the preferred TS for ring closure was an analog of **11**‡, leading to the correct trans product. This observation should not be overinterpreted in a positive sense; in solution the actual ring closure would occur by an ensemble of structures that cannot be adequately represented by any single or small set of structures, so the calculations cannot be said to actually predict the trans product. The observation does show however that the general mechanism is consistent with the experimentally observed stereochemistry.

For the purpose at hand, the key question is the nature of the selectivity-determining step, that is, the first irreversible step undergone by each reactant. The experimental KIEs will be the ultimate arbiter on this question, but it should be clear that computations predict that the initial C_{β}--C_{β} bond formation is irreversible. In the absence of lithium ions, the highest barriers on the pathway from enone radical anion to product involve **8**‡ and **12**‡. Lithium ion coordination stabilizes the various anionic structures to different extents, but the C_{β}--C_{β} bond formation remains irreversible.

2.6. Calculated KIEs. Disagreement with Experiment

The diverse TSs obtained for the cycloaddition process were used to predict the ^{13}C KIEs for the reaction from the scaled theoretical vibrational frequencies by the method of Bigeleisen and Mayer.[65,78] Tunneling corrections based on a one-dimensional infinite parabolic barrier model were included in the predictions.[79] KIE predictions done in this way have proven highly accurate, so long as the calculation accurately depicts the mechanism and transition state geometry.[80]

The resulting KIE predictions (Table 2.2) fit the qualitative expectation that carbons undergoing sigma-bond formation in the selectivity-determining step should exhibit substantial

KIEs, that is, large at the β carbons for analogs of **8**‡ and **12**‡ and large at the α carbons for analogs of **11**‡ and **16**‡. The α carbons are predicted to exhibit a small ^{13}C KIE for the $C_β$--$C_β$ TSs, in line with observations in other additions to alkenes.[81,82] The inverse ^{13}C KIEs at the β positions for ring-closing TSs are also in line with previous observations and fit with the tighter potential energy well surrounding an sp^3 carbon. Quantitatively, the predictions vary relatively little with the addition of lithium ions or explicit solvation or coordination of the lithium ions. This fits with the general observation that small changes in the calculational model or method lead to only modest changes in the predicted KIEs so long as the mechanism is unchanged and the TS geometry do not change much.[83]

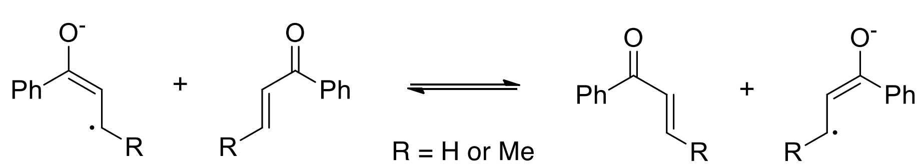
Table 2.2. Predicted ^{13}C KIEs (25 °C) for transition structures in the cycloadditions of **1** with $\mathbf{3^{-\bullet}}$ and of **6** with $\mathbf{5^{-\bullet}}$.

1 + $\mathbf{3^{-\bullet}}$			**6** + $\mathbf{5^{-\bullet}}$		
	α	β		α	β
$C_β$--$C_β$ TSs (analogs of **8**‡)			$C_β$--$C_β$ TSs (analogs of **12**‡)		
no Li^+	1.011	1.034	no Li^+	1.005	1.031
1 Li^+	1.008	1.033	1 Li^+	1.006	1.033
2 Li^+	1.004	1.033	1 Li^+ + 2 MeCN	1.006	1.034
2 Li^+ gauche	1.006	1.043	2 Li^+	1.007	1.030
2 Li^+ + 2 MeCN	1.007	1.034	2 Li^+ + 2 NMe_3	1.006	1.029
2 Li^+ + 2 NMe_3	1.010	1.028			
ring-closing TSs (analogs of **11**‡)			ring-closing TSs (analogs of **16**‡)		
no Li^+	1.035	0.990	no Li^+	1.042	0.992
1 Li^+	1.041	0.990	1 Li^+	1.040	0.992
2 Li^+	1.041	0.990	2 Li^+	1.040	0.993
2 Li^+ + 2 NMe_3	1.035	0.989	2 Li^+ gauche	1.037	0.992
2 Li^+ + 4 MeCN	1.035	0.989	2 Li^+ + 2 NMe_3	1.023	0.994
2 Li^+ + 6 MeCN	1.035	0.989	1 Li^+ + 2 MeCN	1.040	0.993
$C_β$--$C_β$ TSs non-Curtin-Hammett regime			$C_β$--$C_β$ TSs non-Curtin-Hammett regime		
	1.002-1.006	1.014-1.022		1.000	1.000
experimental			experimental		
	1.003	1.024		0.998	1.008

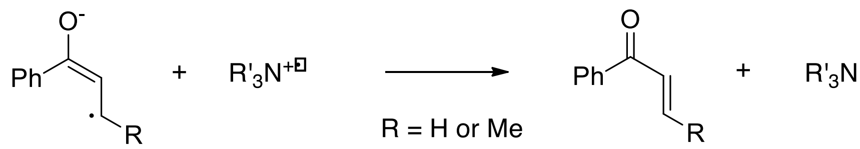
However, none of these predictions fit with experiment. For the C_β--C_β TSs, the predicted KIEs at the β carbon are all larger than those observed, particularly so in the reaction of **6** with **5$^{-•}$**. If the C_β--C_β and ring-closing were competitive as selectivity determining steps, the β carbon KIE would go down but the α carbon KIE would go up, and the agreement with experiment would in fact worsen. This fits with the computational finding that the ring-closing step has a lower barrier and should not be selectivity-determining. Our conclusion is that the experimental KIEs are inconsistent with a mechanism in which the selectivity is determined purely by C-C bond-forming steps.

2.7. An Alternative. Selectivity-Determining Electron Transfer.

An implicit assumption when considering TSs such as **8**‡ or **12**‡ as selectivity-determining is that the electron-transfer steps forming **3$^{-•}$** or **5$^{-•}$** have not themselves predestined particular molecules to react. In other words, it is assumed that the thermoneutral electron transfers between enone radical anions and their starting neutral counterparts (eq (3), (4)) are fast relative to the C-C bond-forming steps, or instead that the deactivation of the radical anions by electron transfer with an amine cation radical (or any other electron acceptor) is faster than C-C bond formation. This may be viewed as a 'Curtin-Hammett assumption', the idea being that the selectivity is determined by the relative heights of competitive bond-forming transition states and not by the ease of formation of their precursors.



(3)

 (4)

The Curtin-Hammett assumption breaks down however if these steps are kinetically competitive with the product-forming steps. In the limit of slow electron exchange or deactivation of intermediate radical anions, the KIEs for **5** would be determined purely by the electron transfer, while the KIEs for **1** would be a 1:1 combination of electron-transfer KIEs for one molecule and C_β--C_β bond formation for the other.

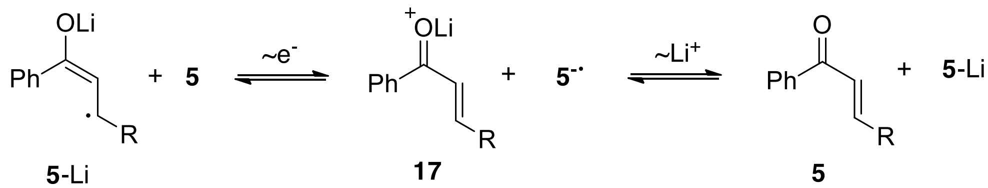
KIEs for electron-transfer reactions can be complex when the electron transfer is intramolecular or thermoneutral, but they tend to approach the equilibrium isotope effect for endergonic reactions and unity for exergonic reactions. The calculated equilibrium isotope effect for electron transfer to **1** would be largest at the carbonyl carbon (1.020), not in line with experiment. The electron transfer from the Ru(I) complex (E_{ox} = -1.33 V versus SCE[84]) to a lithium-coordinated **5** (E_{red} = -1.26 V versus SCE[29]) would be downhill by 1.6 kcal/mol. It would then be expected that the formation of the radical anion of $\mathbf{3}^{-\bullet}$ and $\mathbf{5}^{-\bullet}$ or their lithium-coordinated salts would be iso-topically insensitive, or nearly so. For the purpose of analysis, we will assume that the KIEs for the steps forming these intermediates are unity.

In the limiting case that there is no self-exchange electron transfer between **1** and $\mathbf{3}^{-\bullet}$, the observed KIEs for **1** would be an average of unity and the KIE from Table 2.2 for **1** + $\mathbf{3}^{-\bullet}$, or in the range of 1.001-1.008 for C_α and 1.014-1.020 for C_β. If there is no self-exchange between **5** and $\mathbf{5}^{-\bullet}$, the KIEs expected for **5** would simply be unity.

These limiting-model KIEs are substantially closer to experiment than those in Table 1, though now the predicted KIEs are smaller than the experimental instead of larger. A compromise mechanism in which electron transfer was competitive with C_β--C_β bond formation could readily account for the observed KIEs. The critical question for the remainder of this study is whether the possibility of competitive electron transfer and C_β--C_β bond formation can with-stand logical and experimental scrutiny.

To start, the assumption of slow electron transfer is highly questionable. The self-exchange rates for aromatic radical anions in DMF have typical rate constants in the range of $10^8 – 10^9$ M^{-1} s^{-1},[85,86] while the calculated barriers associated with the C_β--C_β TSs (the analogs of **8**‡ and **12**‡) would lead to rate constants in the range of $10^4 – 10^6$ M^{-1} s^{-1}. Systems in which a high reorganization energy is associated with the self-exchange can exhibit lower rates for electron transfer, for example in the self-exchange of cyclooctatetraene with its radical anion, but there is no reason to expect a high reorganization energy with simple enones and their radical anions.

However, the literature rates for electron transfers similar to that in eq 2 are most commonly measured using large counterions, such as tetraalkylammonium ions, that may be loosely bound or dissociated. The potential effects of tightly bound lithium ions may be more complex, in part because there are multiple possible mechanisms for the overall electron-transfer process.[18,87] Within the possibilities discussed by Marcus,[18] the most easily analyzed is an “electron transfer first” mechanism (eq 4) in which an electron transfer giving **17** + **5**$^{-\bullet}$ is followed by a separate discrete step transferring the counterion. We can estimate a lower bound for the barrier for this mechanism from calculations using a Marcus treatment. For this calculation, the ω-B97XD/PCM-calculated ΔG° for the electron transfer step is +9.9 kcal/mol. The internal reorganization energy λ_i for the electron transfer was estimated as 11.5 kcal/mol based on the average of calculated reorganization energies for self-exchange of **5** with $5^{-\bullet}$ and self-exchange of **5-Li** with **17** (10.9 and 12.1 kcal/mol, respectively, based on the ωB97XD/PCM calculations). The external reorganization energy λ_o, is more difficult to estimate, so we will simply ignore it to obtain a lower-bound $\Delta G^{\ddagger}$ of 10.0 kcal/mol. This barrier would make electron transfer slow enough for plausible competition with C_β--C_β bond formation.

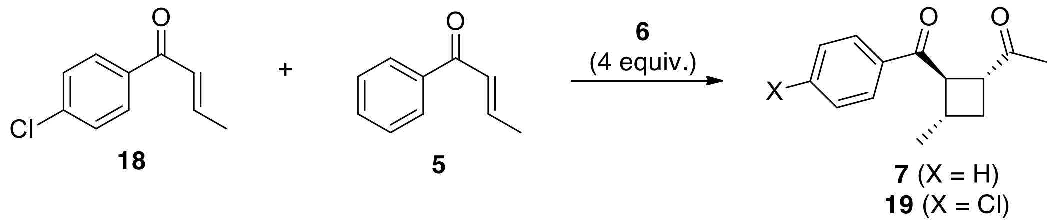


(5)

There are problems with this estimate of the electron-transfer barrier, two being that it assumes a mechanism that is often not the best choice and that it ignores the possibility of electron self-exchange between **5-Li** and **17**. It will be necessary to consider whether there is any other possible explanation for the low KIEs, but first we consider whether other experimental observations can provide information on the rate of electron transfer versus C-C bond formation in these reactions.

2.8. Substituent effect on selectivity.

The relative reactivity of **5** versus the *p*-Cl analog **18** was explored in a competition reaction. The idea of this experiment is that the relative rates of electron transfer versus C–C bond formation ought to have a significant effect on substrate selectivity. If the electron transfer between radical anions (eq (3)) or their lithium-coordinated analogs (eq (5)) is fast, then the competition ought to reflect the equilibrium distribution of the electron between substrates. If instead the electron transfer is slow or competitive with C-C bond formation, then the substrate selectivity should be decreased because the initial electron transfer from the strong reductant $Ru(bpy)_3^+$ should be fast.



In the event, the relative rate for **18** versus **5** under the standard conditions was 2.5 ± 0.2 : 1. The chlorine-substituted analog was more reactive, but it was only moderately so. This observation can be evaluated from two perspectives. The first is electrochemical. The half-wave reduction potential for acetophenone versus *p*-chloroacetophenone is differs by 0.16 V in acetonitrile,[88] corresponding to 3.7 kcal/mol. This is likely to be an overestimate due to the anion-stabilizing effect of lithium coordination. The calculated free energy change for the reaction of **5-Li** + **18** going to **18-Li** + **5** is 1.7 kcal/mol. If this reaction reaches equilibrium for when radical anions are generated under the reaction conditions, then only 6% of the radical anions would be $\mathbf{5}^{-\bullet}$. The calculations predict that the barrier for the reaction of **18-Li** with **6** is slightly lower than that for **5-Li** (9.8 versus 10.2 kcal/mol, respectively), so the calculations are predicting a relative rate ratio of >30. The actual reaction is not as selective as would be expected for a purely rate-limiting C-C bond formation, which fits with the KIE observations.

The second perspective is that of a Hammett relationship. The experimental H/Cl difference of 2.5, and the Hammett sigma value of *p*-Cl is 0.23. This leads to a two-point estimate of the Hammett ρ value for the reaction of 1.7. This is somewhat low. For comparison, the acidity of substituted acetophenones in DMSO has a ρ of 3.55.[89] The latter value represents the effect of a full negative charge at equilibrium, while the relative reactivity of **5** and **18** is kinetic and reflects a partial charge at a transition state, so ρ would be expected to be lower here. However, for early transition states, as consistently calculated, most of the negative charge is retained and a ρ that more closely approaches 3.55 might qualitatively be expected. The computationally predicted ρ assuming full electron equilibration and the **5-Li** / **18-Li** reaction barriers is in fact +6.7. The lower observed ρ fits with the idea that the competition between reactants does not reflect full equilibration of the electrons between reactants, as fits with the observed KIEs.

2.9. An alternative mechanism.

The results so far suggest that electron transfer between reduced reactants occurs at a rate that is competitive with C-C bond formation. Such a competition would be predicted to give rise to KIEs that are in between those predicted for the Curtin-Hammett and non-Curtin Hammett regimes in Table 2.2, which would be fully consistent with the experimental KIEs. While plausible, this mechanism requires a coincidence of similar barriers for independent processes, C-C bond formation and electron transfer, for two different reactions. We therefore considered whether an alternative mechanism that is less reliant on coincidence could be identified.

$$\mathbf{5}\text{-Li} + \mathbf{6} \xrightarrow{k_{diff}} \underset{\mathbf{20}}{[\mathbf{5}\text{-Li}\text{---}\mathbf{6}]} \qquad \mathbf{(6)}$$

$$\mathbf{20}_{12C} + \mathbf{5}_{13C} \underset{k_{-ex}}{\overset{k_{ex}}{\rightleftharpoons}} \mathbf{20}_{13C} + \mathbf{5}_{12C} \qquad \mathbf{(7)}$$

$$\mathbf{20} \xrightarrow{k_{CC}} \mathbf{7}\text{-Li} \qquad \mathbf{(8)}$$

$$\mathbf{7}\text{-Li} + \mathbf{5}\text{-Li}^{+} \xrightarrow{k_{red}} \mathbf{7}\text{-Li}^{+} + \mathbf{5}\text{-Li} \qquad \mathbf{(9)}$$

Previous work from Wiest and Singleton with Diels-Alder reactions of cation radicals had notably observed a similar set of results to that here, particularly finding that the experimental KIEs were much smaller than those predicted.[90] That work faced the identical problem as here of having to account for the discrepancy. Based on kinetic modeling, it was suggested that the suppressed experimental KIEs could be accounted for by the importance of a diene-dienophile cation radical complex.

In an analogous way, we considered the possible role of alkene-alkene complexes in the present reactions. A minimal-complexity kinetic scheme allowing for this possibility is shown in eqs (6) to (9). This scheme is written with only a single lithium ion in the complex **20** and product **7-Li**, but the inclusion of an extra lithium ion would make no essential difference. The real reaction would include both the chain-initiating formation of **5-Li** and chain-termination steps, but these are inconsequential to the observed KIEs. Simulation of this scheme by numerical integration finds that observed KIE does not exceed 90% of the intrinsic KIE (i.e., $(KIE_{obs} - 1)/(KIE_{int} - 1) > 0.9$) unless the rate constant for exchange k_{ex} exceeds the rate constant for CC bond formation k_{CC} by a factor of 250. If the rate constant for exchange were 1×10^{8} M^{-1} s^{-1}, then a k_{CC} of approximately 10^{6} s^{-1} would be consistent with the decreased observed KIEs as well as the calculated barriers. We have no direct evidence for the kinetic importance of 20 or related species, but they provide a plausible explanation of the observations.

2.10. Redox-tag Promoted [2 + 2]-Cycloaddition

Studies on photoinduced redox reactions experienced have become much more popular in recent years. Most of organic reactions catalyzed by redox photosensitizers are initiated by single electron transfer (SET). A common application in organic synthesis is to catalyze cycloadditions from substituted alkenes. Radical ions can be generated from the alkene substrates after being activated by photocatalysts through SET. The first cation radical cycloaddition reaction of alkenes was done by Ledwith in 1969 from the dimerization of *N*-vinylcarbazole in the presence of Fe^{3+} and Ce^{3+}.[91] The reaction was viewed as a stepwise process with cation radicals as the intermediate, which was later supported computationally by Bauld and Pabon in 1982.[92] In addition, it was found that while *trans*-anethole underwent SET-triggered dimerization reaction with moderate yield, *trans*-propenylbenzene gave no yield (a).

In 2001, Chiba and coworkers also reported that the electrocatalytic cycloaddition for *p*-methoxy substituted enol ether gave good yield, but no reaction was found for phenyl substituted enol ether even though the aromatic groups do not directly conjugated with the alkene (Figure 2.8b).[93] These observations suggest that the remotely attached aromatic group play a significant role in the radical ion mediated cycloaddition reactions. Due to the requirement of an electron-donating group, an intramolecular SET process was proposed to be involved in the reactions. Namely, after the first bond formation, the intramolecular SET occur concomitantly with the second bond formation to afford the cyclobutane products. If the molecule lacks an easily oxidized group such as anisolyl group, the intramolecular SET would become difficult and thus inhibit the product formation. A systematic review of this topic can also be found in a review paper published in 2018.[94]

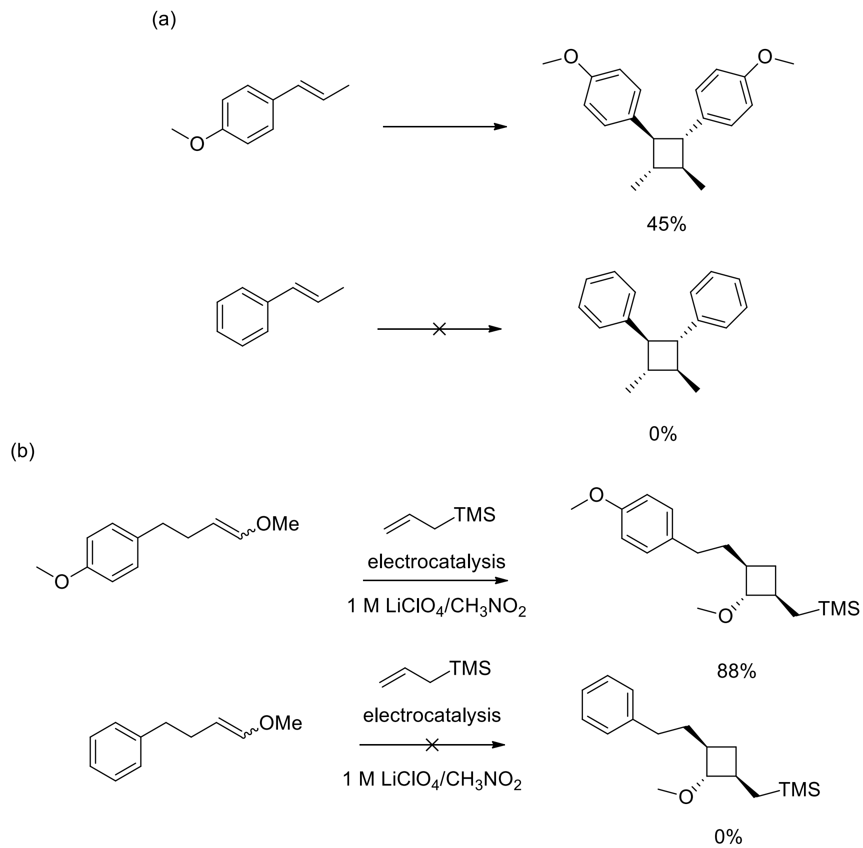
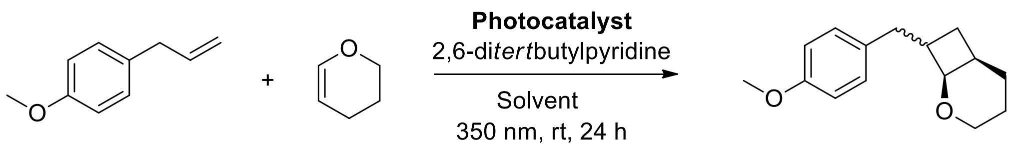


Figure 2.8. (a) SET-triggered dimerization of *trans*-anethole (upper) and unsuccessful reaction for *trans*-propenylbenzene (lower) in a work by Bauld and Pabon.[92] (b) Electrocatalytic cycloaddition of *p*-methoxy aryl enol ether and unsuccessful reaction for phenyl enol ether in a work by Chiba and coworkers.[93]

Reaction Optimization Study

To extend the scope of mechanistic study of radical-ion mediated [2 + 2]-cycloaddition reactions, the best condition for a photochemical induced [2 + 2]-cycloaddition reactions were explored. Two common photocatalysts were used: TPPT and 9,10-dicyanoanthracene (DCNA). The photophysical and photochemical properties of both catalysts have been well-explored to undergo charge transfer under excitation by UV-vis light with wavelength $\lambda = 300 \sim 450$ nm. Table 2.3 summarizes the conditions have been used to optimized the reaction. From entry 1~10, we found that only in nitromethane gave nonzero yield. Furthermore, when $LiClO_4$ was added, the catalyst seems to decompose into brown to black precipitates after overnight irradiation and no yield were observed (entry 10). However, this problem can be prevented by adding excess amount (relative to the TPPT catalyst) of 2,6-di(*tert*-butyl)pyridine (entry 11). Attempt in reducing amount of 2,6-di(*tert*-butyl)pyridine was found to have the same decomposed TPPT (entry 12). Increasing the amount of TPPT or replacing to DCNA showed no effect in enhancing the yields of **3** (entry 13~17**)**. Therefore, condition in entry 11 was chosen as the reaction condition for mechanistic studies in the following sections.

Table 2.3. Reaction scope of photoredox-induced [2 + 2]-cycloaddition between **1** and **2**.



entry	Catalyst (amount, mol%)[a]	2,6-ditertbutylpyridine (eq.)	Solvent / Salt	Yield of 3[c]
1	TPPT (20)	0	DCM	0%
2	TPPT (20)	0	diethyl ether	0%
3	TPPT (20)	0	water	0%
4	TPPT (20)	0	toluene	0%
5	TPPT (20)	0	acetone	0%
6	TPPT (20)	0	methanol	0%
7	TPPT (20)	0	THF	0%
8	TPPT (20)	0	acetonitrile	0%
9	TPPT (20)	0	$MeNO_2$	11%
10	TPPT (20)	0	$MeNO_2$ / $LiClO_4$[b]	0%
11	**TPPT (20)**	**1**	**$MeNO_2$ / $LiClO_4$[b]**	**27%**
12	TPPT (57)	0.75	$MeNO_2$ / $LiClO_4$[b]	0% (catalyst decomposed)
13	TPPT (30)	1	$MeNO_2$ / $LiClO_4$[b]	24%

14	TPPT (60)	2.4	$MeNO_2$ / $LiClO_4$[b]	12%
15	DCNA (20)	0	$MeNO_2$	0%
16	DCNA (20)	0	diethyl ether	0%
17	DCNA (20)	0	DCM	0%

[a] relative to **1**

[b] Saturated solution

[c] sum of all stereoisomers

Here, photoinduced [2 + 2]-cycloaddition reaction between *p*-methoxyallybenzene and dihydropyran was chosen for study. *p*-Methoxyallylbenzene serves as the simplest molecule for a non-conjugated alkene system and the coupling with dihydropyran was reported to afford high yield and high stereospecific cyclobutane products (94% yield, dr 6:1) from electrocatalytic approach.[95] Due to the stepwise mechanism involving cation radicals, the initiation of cation radicals is the key to a success cycloaddition reaction. To the best use of our laboratory instrumentations, we developed a photochemical approach using triphenylpyrylium tetrafluoroborate (TPPT) as the photocatalyst to initiate the cation radical (Figure 2.9). The success of this photoredox-promoted [2 + 2]-cycloaddition reactions of non-conjugated alkenes permits future mechanistic studies on how the proposed intramolecular electron transfer step could affect the selectivity of this type of reactions.

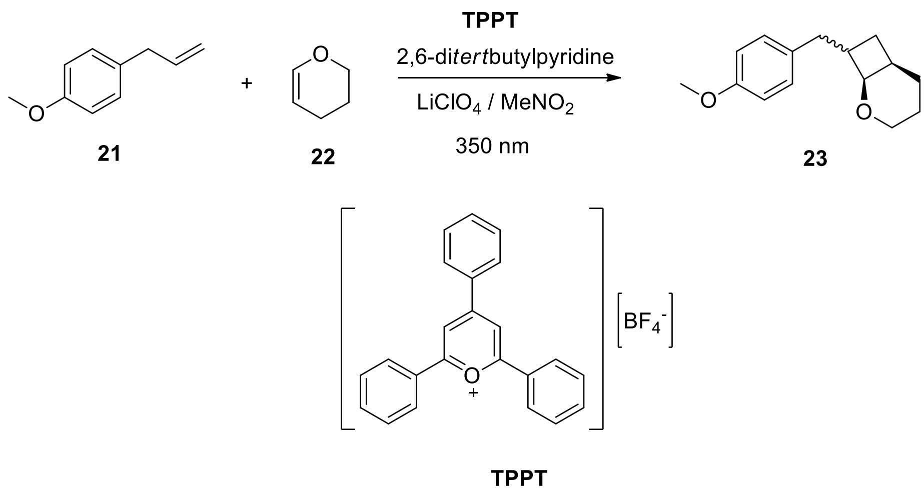


Figure 2.9. Reaction condition for photochemical approach of [2 + 2]-cycloaddition between *p*-methoxyallylbenzene (**21**) and dihydropyran (**22**) in this work.

2.11. Experimental Procedures

2.11.1. General Methods

The enones **1** and **18** were synthesized as described in the following sections. Diisopropylammonium trifluoroacetate was prepared by mixing equimolar amounts of diisoprylamine and trifluoroacetic acid in diethyl ether, followed by filtration and vacuum drying. All other chemicals were commercially available. A Kessil H150B Grow Light (λ_{max} = 450 nm) was used as the blue LED.

2.11.2. Synthesis of Phenyl Vinyl Ketone (1).

By an adaptation of a literature procedure,[96] a mixture of 10.12 g (83 mmol) of acetophenone, 10.50 g (333 mmol equivalent of formaldehyde) of paraformaldehyde, 17.90 g (84 mmol) of diisopropylammonium trifluoroacetate, two drops of 1,4-cyclohexadiene, two drops of trifluoroacetic acid, and 100 mL of tetrahydrofuran was heated at 80 °C in a 250-mL pressure vessel overnight. The mixture was then concentrated on a rotary evaporator, and the residue was dissolved in 200 mL diethyl ether and rinsed with 200 mL of 1 M HCl, 200 mL of 1 M NaOH, and 200 mL of brine. The organic layer was then dried ($MgSO_4$) and concentrated on a rotary evaporator. The residue was chromatographed on multiple silica gel column (initially 40 mm by 350 mm) using 5% of ethyl acetate in hexanes to afford 3.70 g (34%) of **1**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.94 (dd, J = 10.6, 1.5 Hz, 1H), 6.45 (dd, J = 17.2, 1.5 Hz, 1H), 7.17 (dd, J = 17.2, 10.6 Hz, 1H), 7.45 (t, 2H), 7.58 (t, 1H), 7.95 (d, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 127.5, 128.5 (2 carbons), 132.6, 145.0, 190.8.

2.11.3. Synthesis of 4'-Chloro-1-phenylbut-2-en-1-one (18)

By an adaptation of a literature procedure,[97] a mixture of 10.02 g (65 mmol) of 4-chloroacetophenone, 5.28 g (120 mmol) of acetaldehyde, two drops of 50% KOH solution, and 100 mL of methanol was stirred at 25 °C overnight. The reaction mixture was then concentrated on a rotary evaporator. The residue was dissolved in 150 mL of diethyl ether and washed with sequentially with 2 × 150 mL of 1 M HCl and 2 × 150 mL of brine. The organic layer was then dried ($MgSO_4$) and concentrated on a rotary evaporator. A few crystals of $ZnCl_2$ were added into the residue, and it was vacuum distillated (60 °C, 1.5 mm) to afford 0.56 g (4.8%) of **18**. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.01 (dd, J = 6.9, 1.7 Hz, 3H), 6.87 (dq, J = 15.3, 1.6 Hz, 1H), 7.08 (dd, J = 15.3, 7.0 Hz, 1H), 7.44 (m, 2H), 7.87 (m, 2H).

2.11.4. Photodimerization of 1

A mixture of 5.09 g (39 mmol) of freshly prepared **1**, 7.09 g (76 mmol) of $LiBF_4$, 9.78 g (76 mmol) of *N,N*-diisopropylethylamine, 1.0 g of mesitylene (internal standard), 1.42 g (1.9 mmol) of $Ru(bpy)_3Cl_2$•$6H_2O$, and 400 mL of acetonitrile was irradiated under N_2 by a blue LED at 25 °C. The reaction progress was monitored by ^{1}H-NMR analysis of aliquots versus the mesitylene internal standard until a conversion of 85% was reached. The reaction was then concentrated on a rotary evaporator, and the residue was dissolved in 200 mL of diethyl ether. The organic layer was washed by 200 mL of 1 M HCl and 200 mL of brine repeatedly until the aqueous layer is colorless. The organic layer was dried by $MgSO_4$, filtered, and concentrated on a rotary evaporator. The residue was dissolved in 50 mL diethyl ether and 10 mg of palladium on carbon (5 wt% Pd / C) was added. The flask was connected to a balloon with H_2 gas and the reaction was monitored by ^{1}H NMR until 100% conversion. After completion, the reaction mixture was filtered, and concentrated on a rotary evaporator. The residue was chromatographed through a 20 mm by 350 mm column packed with 300 mm height of silica gel using 12.5% of ethyl acetate in hexanes to afford 0.23 g of propiophenone as KIE sample 1.

Spectroscopic information for the dimerization product (**2**, mp = 92.5 ~ 93.8 ºC)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.38 (m, 4H), 4.57 (m, 2H), 7.46 (m, 4H), 7.56 (m, 2H), 7.98 (m, 4H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 22.9, 42.3, 128.6, 128.7, 133.2, 135.2, 199.6

For reproduce experiment, sample 2 was obtained from similar procedures described above but the reaction conversion was monitored until 60% conversion.

2.11.5. Photocycloaddition between 5 and 6

Phenylbut-2-en-1-one (**5**, 5.04 g, 34 mmol), methyl vinyl ketone (**6**, 4.81 g, 68 mmol), $Ru(bpy)_3Cl_2·6H_2O$ (1.37 g, 1.7 mmol), $LiBF_4$ (12.82 g, 137 mmol), *N,N*-diisopropylethylamine (8.80 g, 68 mmol), and mesitylene (1.01 g, 8.3 mmol) were dissolved in 400 mL of acetonitrile. The reaction was proceeded under blue LED in room temperature. The reaction progress was monitored by ^{1}H-NMR until reaching 92% conversion, the reaction mixture was concentrated on a rotary evaporator. The residue was dissolved in 200 mL of diethyl ether, and the organic layer was washed with 200 mL of 1 M HCl and 200 mL of brine repeatedly until the aqueous layer became colorless. The organic layer was dried by $MgSO_4$, filtered, and concentrated on a rotary evaporator. The residue was dissolved in 50 mL diethyl ether 10 mg of palladium on carbon (5 wt% Pd / C) was added. The flask was connected to a balloon filled with H_2 gas and the reaction progress was monitored by ^{1}H NMR until 100% conversion. After completion, the reaction mixture was filtered, and concentrated on a rotary evaporator. The residue was chromatographed through a 20 mm by 350 mm column packed with 300 mm height of silica gel using 12.5% of ethyl acetate in hexanes to afford 0.26 g of butyrophenone.

For reproduce experiment, sample 2-5 was obtained from similar procedures described above but the reaction was monitored until 70, 73, 66, and 82% conversions respectively.

2.11.6. Competition Reaction for the Substituent Effect

A stock solution with 87 mg (0.60 mmol) of **5**, 111 mg (0.61 mmol) of **18**, and 18.3 mg of diphenylmethane (internal standard) were mixed in a 10-mL graduate cylinder. The mixture was diluted by acetonitrile such that the meniscus reaches the 10-mL line. A 2-mL of this solution was transferred into another 10-mL graduate cylinder and diluted by acetonitrile to the 8-mL line to afford two 8-mL solutions with the latter (Kinetics B) 4 times more dilute than the former (Kinetics A). A mixture of 210.4 mg (2.25 mmol) $LiBF_4$, 76.2 mg 6, 23.8 mg (0.032 mmol) $Ru(bpy)_3Cl_2 \cdot 6H_2O$, 18.3 mg of diphenylmethane (internal standard), 140.6 mg (1.08 mmol) of diisopropylethylamine, and 8 mL acetonitrile was further added into both solutions to make kinetic sample A and B.

Both samples were placed equal distance from the blue LED in a cardboard box. During the irradiation, 10-drop aliquots at 0, 10, 20, 30, 40, 50, 60, 90, 120, 180, 240 minutes were taken. Each aliquot was added into a 2 mL $CDCl_3$ solution and washed with distilled water twice. The organic layer was then dried and filtered into NMR tube for kinetic measurements. As shown in Figure 2.10, the product ratio of **19** to **7** was determined by the integration value of the middle peak from the two partially overlapping triplets from the H on the α-carbon close to the aryl side. The cut of the integrals across the spectra was kept the same. The crude integration value was further divided by the total integral of **5**, **7**, **18**, and **19**. The results are shown in Table 2.4.

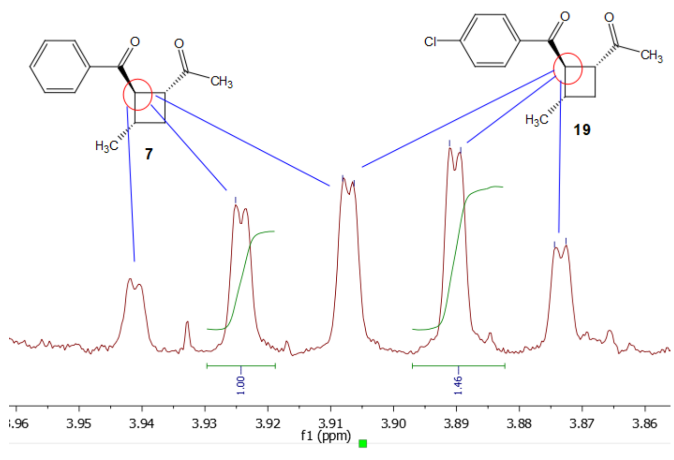


Figure 2.10. The triplets of the cycloaddition products **7** and **19**. The integration was taken around the middle peak of the triplets.

Table 2.4. Experimental kinetics for the relative yields for **7** and **19.**

Cyclobutane product / total of enone + product			
Kinetics A		Kinetics B	
7	**19**	**7**	**19**
0	0	0	0
1.9	3.5	14.7	27.9
3.8	8.3	18.1	36.2
5.8	13.7	29.5	54.7
10.0	24.3	40.8	68.1
12.4	30.5	32.3	59.1

18.2	42.7	44.7	78.1
24.1	55.2	64.2	89.1
35.4	69.8	76.8	93.0
37.6	75.2	83.1	97.3

2.11.7. Kinetic Simulation of Competitive Reactions

By their nature, photochemical reactions of this type are not amendable to an ordinary kinetic study of reaction progress versus time. However, for the purpose at hand of determining the relative reactivity of **5** versus **18** (k_5 / k_{18}), it suffices to model the relative progress of the reaction of one versus that of the other. We assume for the purpose of this analysis that the rate laws for reaction of each, however complex, are the same for both **5** and **18** when the two are mixed together in the same solution (see eqs 10 and 11). We can then divide the two equations to get eq 12. To compare this equation to experimental data for the purpose of determining k_5 / k_{18}, this equation has to be integrated. It is possible to do so analytically, but it is most convenient to do so numerically on an Excel spreadsheet by reintroducing time as an arbitrary and ultimately ignored variable. This lets us separate eq 12 into two unimolecular kinetics equations 13 and 14.

$$-\frac{d[\mathbf{5}]}{dt} = \frac{d[\mathbf{7}]}{dt} = Number\ of\ photons\ absorbed\ \times k_5 \times [\mathbf{5}] \times (arbitrary\ kinetic\ terms) \quad (10)$$

$$-\frac{d[\mathbf{18}]}{dt} = \frac{d[\mathbf{19}]}{dt} = Number\ of\ photons\ absorbed\ \times k_{18} \times [\mathbf{18}] \times (arbitrary\ kinetic\ terms) \quad (11)$$

Divide (10) by (11)

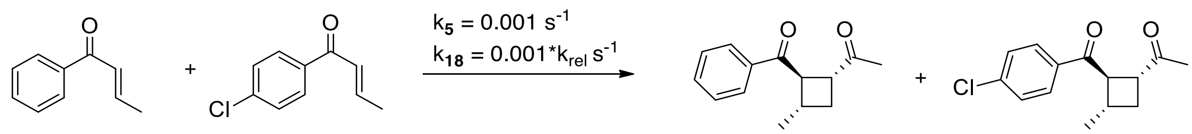
$$\frac{d[\mathbf{5}]}{d[\mathbf{18}]} = \frac{d[\mathbf{7}]}{d[\mathbf{19}]} = \left(\frac{k_5}{k_{18}}\right) \times \left(\frac{[\mathbf{5}]}{[\mathbf{18}]}\right) \quad (12)$$

Separate again using time as arbitrary

$$-\frac{d[\mathbf{5}]}{dt} = \frac{d[\mathbf{7}]}{dt} = k_5 \times [\mathbf{5}] \tag{13}$$

$$-\frac{d[\mathbf{18}]}{dt} = \frac{d[\mathbf{19}]}{dt} = k_{18} \times [\mathbf{18}] \tag{14}$$

The eqs (13) and (14) were integrated numerically in the spreadsheet using an arbitrary timestep of 1 s and an arbitrary $k_{\mathbf{5}}$ of 0.001 s^{-1} (chosen to provide sufficiently small steps for a Euler integration), and applying eqs (15) – (18).



5 **18** **7** **19**

$[\mathbf{5}]_n = [\mathbf{5}]_{n-1} - k_{\mathbf{5}}[\mathbf{5}]_{n-1}$*(timestep) **(15)**

$[\mathbf{18}]_n = [\mathbf{18}]_{n-1} - k_{\mathbf{18}}[\mathbf{18}]_{n-1}$*(timestep) **(16)**

$[\mathbf{7}]_n = k_{\mathbf{5}}[\mathbf{5}]_{n-1}$*(timestep) **(10)**

$[\mathbf{19}]_n = k_{\mathbf{18}}[\mathbf{18}]_{n-1}$*(timestep) **(18)**

The value for $k_{\mathbf{18}}$ was then adjusted until a graph of the simulated conversion of **5** versus the simulated conversion of **18** had a least-squares best fit with the experimental observations. This process was carried out in a total of four reactions, and the value in the main text is an average of the results obtained. Table 2.5 shows selected data from an example simulation, and Figure 2.11 shows an example plot for the relative conversion ratio between **5** and **18**.

Table 2.5 Kinetic simulation of competitive reaction with different rate constants (k_{rel}).

k_{rel}	2.3				2.7			
timestep	**5**	**18**	**7**	**19**	**5**	**18**	**7**	**19**

0	1	1	0	0	1	1	0	0
1	0.999	0.998	0.001	0.002	0.999	0.997	0.001	0.003
2	0.998	0.995	0.002	0.005	0.998	0.995	0.002	0.005
3	0.997	0.993	0.003	0.007	0.997	0.992	0.003	0.008
4	0.996	0.990	0.004	0.010	0.996	0.989	0.004	0.011
5	0.995	0.988	0.005	0.012	0.995	0.987	0.005	0.013
6	0.994	0.986	0.006	0.014	0.994	0.984	0.006	0.016
7	0.993	0.983	0.007	0.017	0.993	0.981	0.007	0.019
8	0.992	0.981	0.008	0.019	0.992	0.979	0.008	0.021
9	0.991	0.979	0.009	0.021	0.991	0.976	0.009	0.024
10	0.990	0.976	0.010	0.024	0.990	0.973	0.010	0.027
		...				...		
100	0.905	0.786	0.095	0.214	0.905	0.763	0.095	0.237
		...				...		
500	0.606	0.301	0.394	0.699	0.606	0.259	0.394	0.741
		...				...		
1000	0.368	0.090	0.632	0.910	0.368	0.067	0.632	0.933
		...				...		
2000	0.135	0.008	0.865	0.992	0.135	0.004	0.865	0.996
		...				...		
2288	0.101	0.004	0.899	0.996	0.101	0.002	0.899	0.998

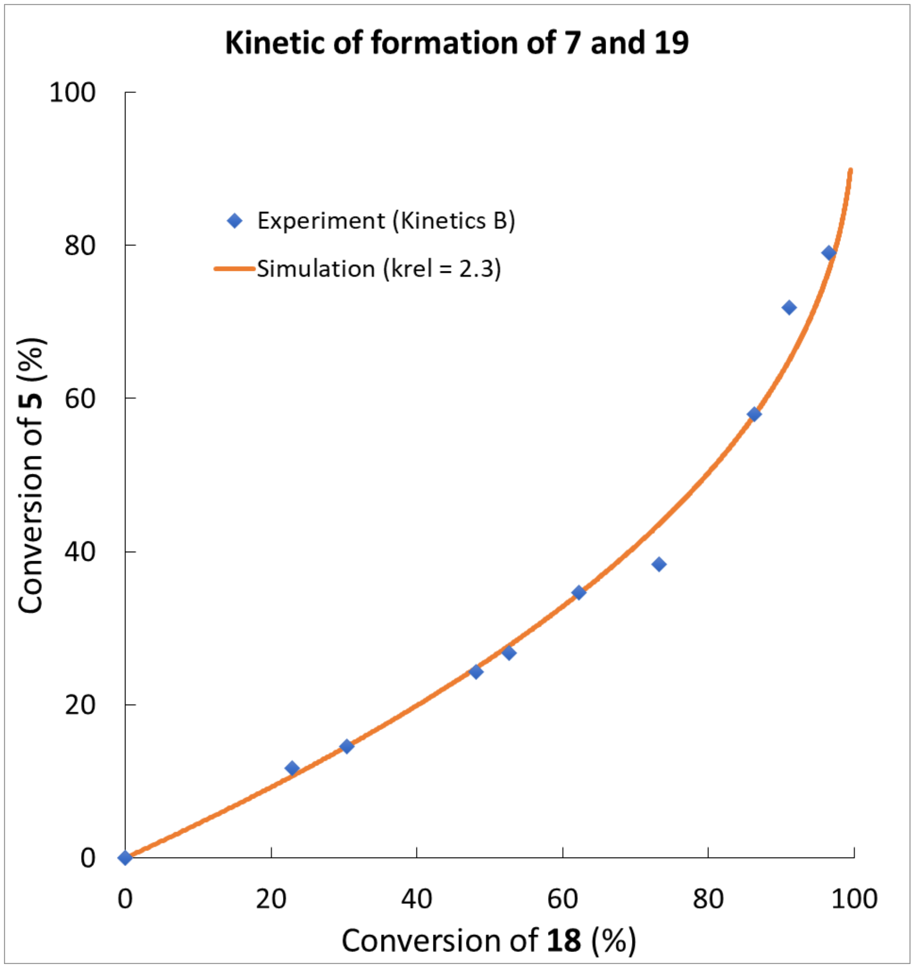


Figure 2.11 Fit of simulated data for the conversion of **18** versus **5**, versus experimental data (k_{rel} = 2.3).

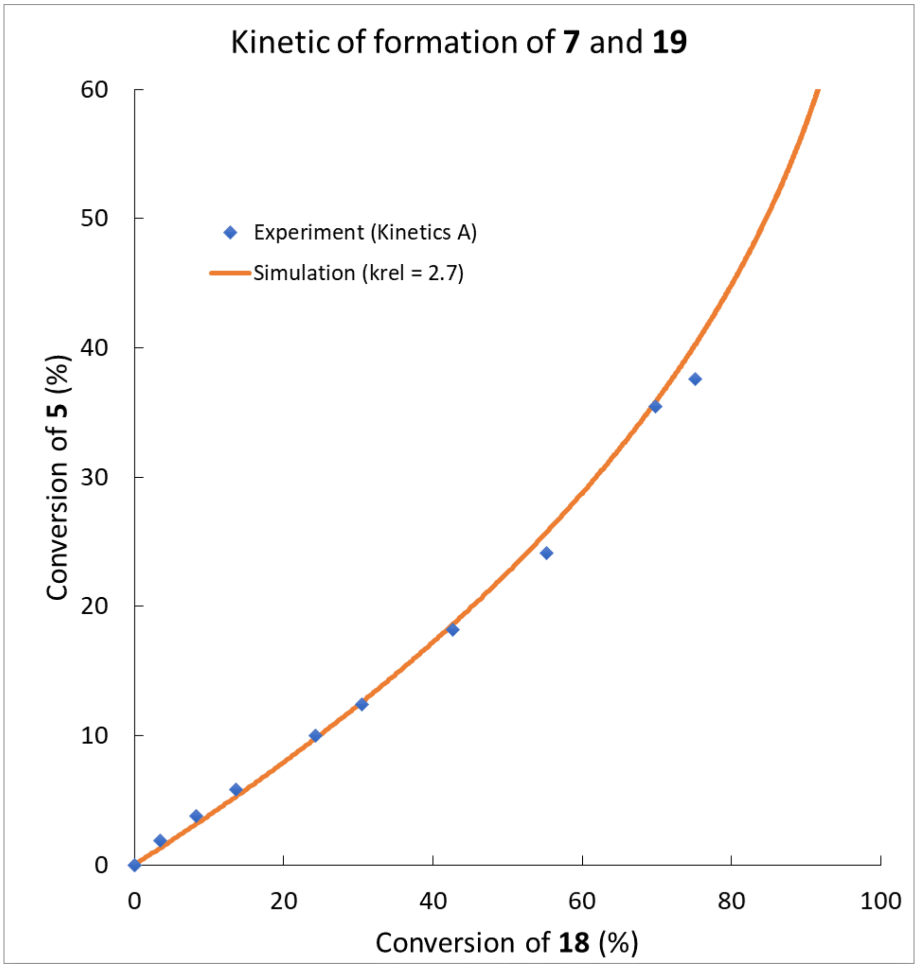


Figure 2.12. Fit of simulated data for the conversion of **18** versus **5**, versus experimental data (k_{rel} = 2.7).

2.11.8. NMR Studies for Lithium Coordination Effects

To investigate the coordination effect on the chemical shifts of the enones, six solutions with 42 mg (60 mmol) of **6**, 162 mg (126 mmol) in test tubes. A mixture of 1.025 g of $LiClO_4$ and 16 mL of CD_3CN were prepared. Then, 0, 0.5, 1, 2, 4, and 8 mL of this mixture was added to the test tubes respectively such that each sample has 0, 0.5, 1, 2, 4, 8 equivalence of Li^+. Additional CD_3CN was added to keep the total volume the same. The solutions were then transferred to NMR tubes for ^{13}C NMR measurements. The full spectra are shown in Figure 2.13. The ^{13}C peaks for the carbonyl of **6** are shown in Figure 2.14. and the diisopropylethylamine α-peak on the isopropyl groups is shown in Figure 2.15. Each spectrum was referenced at the CN carbon of the CD_3CN (118.7 ppm).

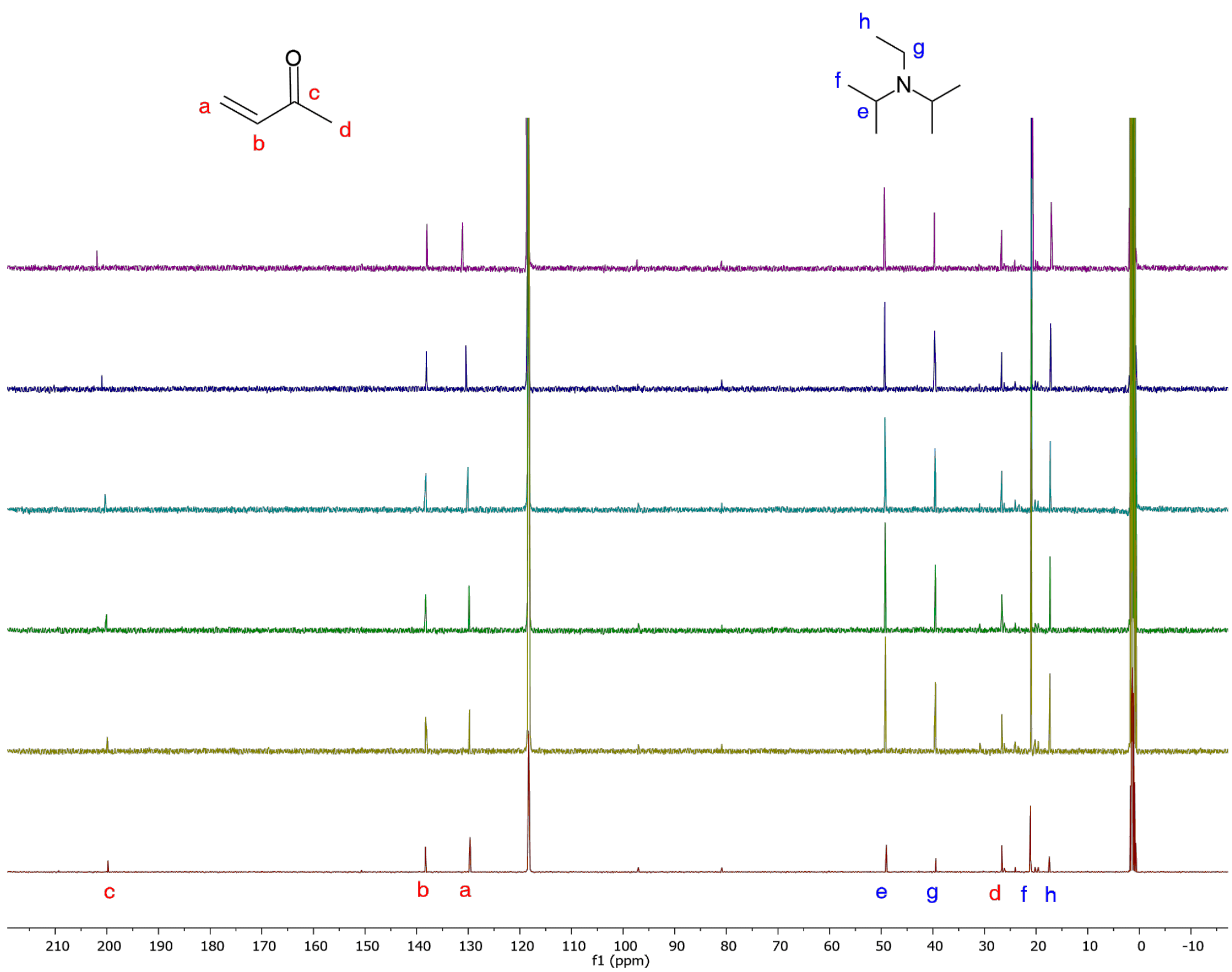


Figure 2.13. Full spectra for samples of 0 (bottom), 0.5, 1, 2, 4, and 8 (top) equivalence of $LiClO_4$

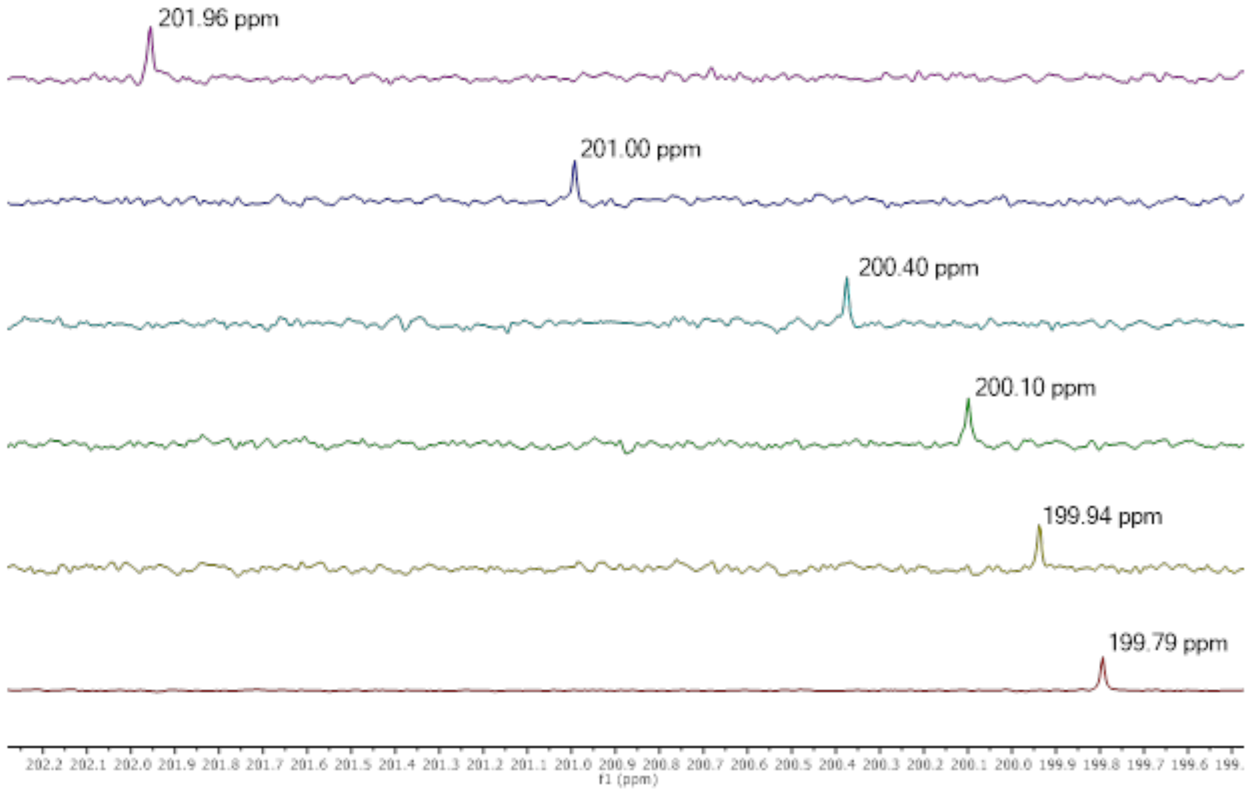


Figure 2.14. Carbonyl peak for **6** with 0 (bottom), 0.5, 1, 2, 4, and 8 (top) equivalence of $LiClO_4$

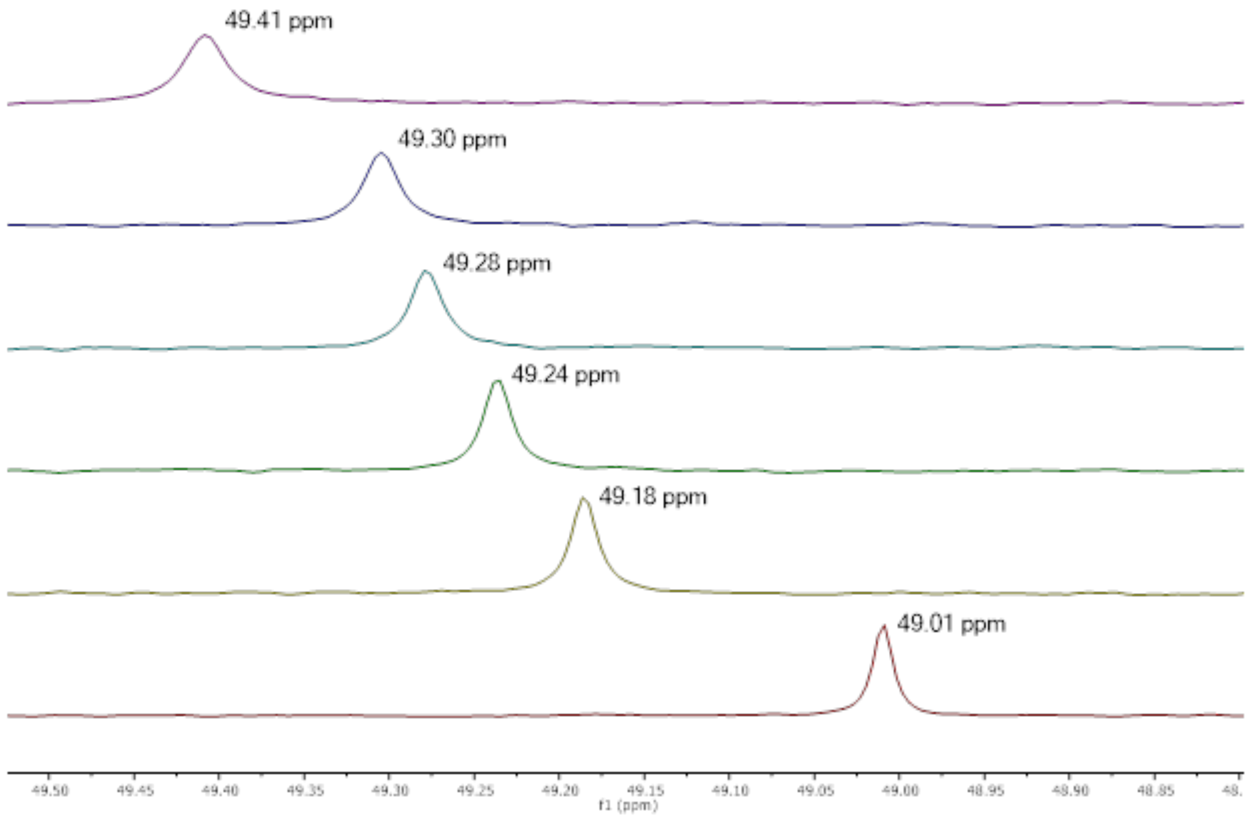


Figure 2.15. Alpha peak for diisopropylethylamine with 0 (bottom), 0.5, 1, 2, 4, and 8 (top) equivalence of $LiClO_4$.

2.12. Conclusions

The results here suggest that C_β-C_β bond formation in the photo-redox-promoted [2 + 2] cycloaddition of enones is irreversible but kinetically competitive with electron transfer between the enones. This is supported by the observation of lower C_β KIEs than would be expected if the C-C bond forming step were fully product-determining, and is consistent with a relatively small substituent effect on the selectivity for the cycloaddition. Whether the competition involves simple enone radical anions or alkene-alkene complexes is uncertain. It is notable that the competition between electron transfer and C-C bond formation has now been supported for both anion-radical and cation-radical reactions.[90]

This competition adds a potentially useful complication in the mechanism of photoredox-promoted reactions. That is, if the rates of key intermolecular steps can, as here, be competitive with electron- transfer rates between substrates, then it would seem possible to engineer reactions in which the electron transfer is fully slow compared to the product-determining step. The value of this possibility is that it may be possible to control the chemoselectivity of these reactions through the kinetics of the initial electron transfer, instead of having the reactive ion decided by equilibria. This suggests that there may be ways to influence or control chemoselectivity in these reactions.

3. HEAVY-ATOM TUNNELING AND REACTION DYNAMICS OF DI-Π-METHANE REARRANGEMENT OF BENZOBARRELENE†

3.1. Introduction

The di-π-methane rearrangement (DPMR) is a photochemical reaction of a 1,4-diene functionality to afford vinylcycloprpane.[98] It was firstly discovered by Zimmerman and co-workers in 1967 from the photolysis of barrelene to afford semibullvalene in the presence of acetone as the photosensitizer.[99] The reactions exhibit the advantages of accessing complicated molecular structures containing highly-strained cyclopropane ring, which has been applied in many synthetic strategies.[100,101] A qualitative mechanism of DPMR is shown in Scheme 3.1: The reaction occurs photochemically for molecules with functionality where two unsaturated moieties are bridged by a methylene group. The reaction can occur in both singlet and triplet excited-state manifolds, depending on the substrates. In general, alkenes in rigid rings proceed on triplet surfaces, while acyclic 1,4-diene triplet diradicals are prone to undergo cis-trans isomerization and hence most of acyclic molecules undergo DPMR on singlet surface.[102–105] The substrates can be activated either by direct irradiation or photosensitization to afford singlet or triplet diradicals respectively (diradical I).[98] Diradical I can undergo rearrangement to afford diradical III through concerted or stepwise pathway. The cyclopropane product is obtained from radical recombination of diradical III. However, its mechanistic complexity does not accord with the simplicity of the reaction conditions. It has been a long debate over the existence of the cyclopropyldicarbinyl diradical intermediate (diradical II). Besides, recent studies have shown that quantum mechanical

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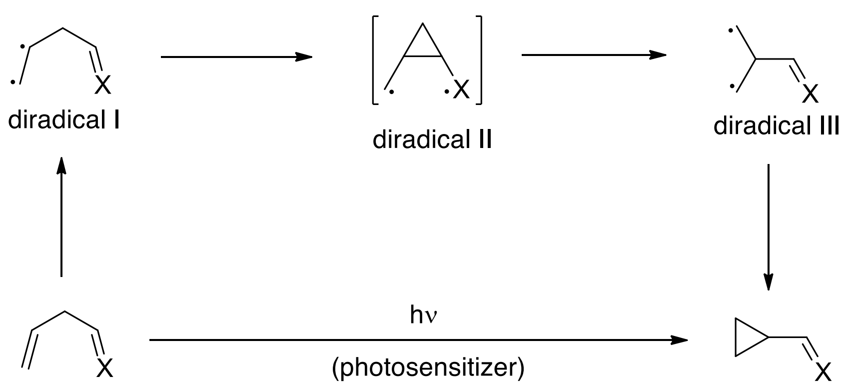
†Adapted with permission from "Vibrationally Hot and Cold Triplets. Sensitizer-Dependent Dynamics and Localized Vibrational Promotion of a Di-π-methane Rearrangement" by K.-Y. Kuan and D. A. Singleton. *Journal of American Chemical Society,* **2020,** *142,* 19885-19888. Copyright 2020 American Chemical Society.

phenomenon[106] and nonstatistical dynamics[107] may play a key role in understanding the reactivity and selectivity of DPMR reactions.

In this chapter, benzobarrelene DPMR was chosen for study because is uniquely breaks symmetry in each of its key mechanistic steps, providing a handle on the molecular energy in its intermediate. In order to address these issues and provide insights into the reaction mechanisms, (1) the background of the mechanistic study of DPMR, (2) the background of reaction dynamics in organic reactions, (3) results from kinetic isotope effect experiments of benzobarrelene DPMR, and (4) comparison and discussion of theoretical computations will be discussed in the following sections.

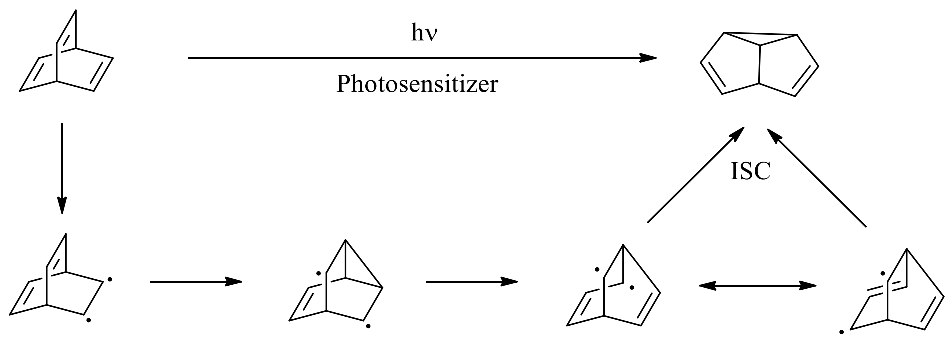


Scheme 3.1. General reaction scheme of a di-π-methane ($X = CH_2$) or oxa-di-π-methane rearrangement (X = O).

3.2. Classical Mechanistic Background of DPMR

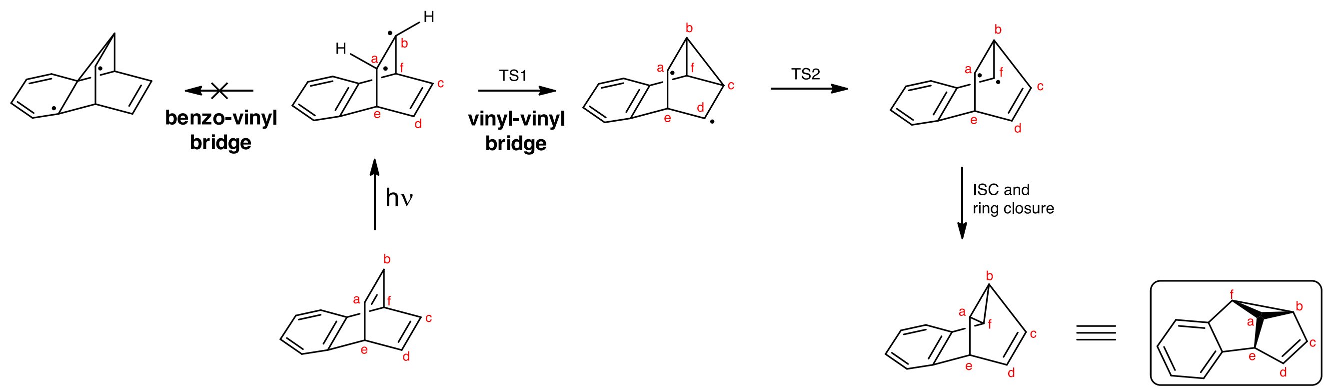
Triplet Photosensitized DPMR

The qualitative mechanism for DPMR was systematically established since the discovery by Zimmerman and co-workers.[99,103,108] The requirement of photosensitizers such as acetone or acetophenone to afford DPMR product suggested the involvement of triplet intermediates. From isotope labelling study and computational results, it was proposed that the photoisomerization of barrelene affords semibullvalene through a cyclopropyldicarbinyl diradical intermediate in a stepwise bond-forming and bond-breaking scenario (Scheme 3.2).



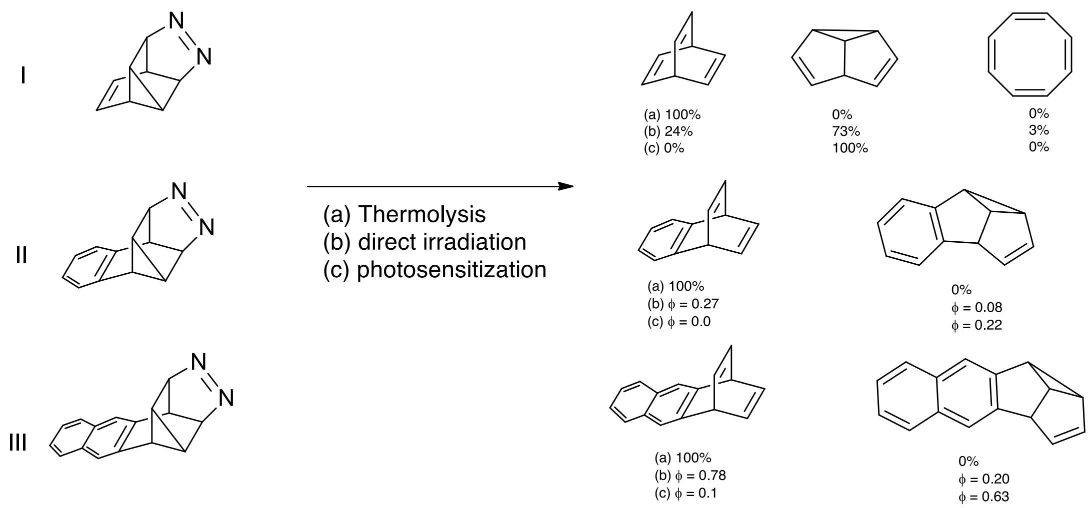
Scheme 3.2. Stepwise mechanism of barrelene DPMR by Zimmerman.

In order to examine the generality of the mechanistic model, the mechanistic study was extended to benzobarrelene DPMR in the later work of the Zimmerman and coworkers in 1968.[103] Similarly, acetone is still required as a photosensitizer to afford benzosemibullvalene as so in the barrelene case. Depending on the energy of the triplet sensitizer energy gap, the triplet energy can theoretically be transferred to either aryl (benzene E_T = 84.2 kcal/mol) or alkenyl (ethylene E_T = 82.1 kcal/mol) groups. However, isotope labelling studies suggested that the isotope distribution pattern of the product can only be explained if the reaction undergoes vinyl-vinyl bridge pathway. (Scheme 3.3), This implies the triplet energy has to be eventually or in large degree distributed into the alkenyl region before reacting further to afford the DPMR products.



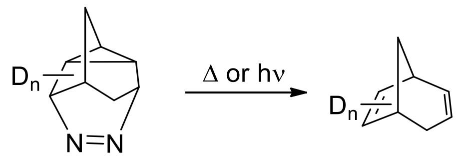
Scheme 3.3. Qualitative reaction mechanism for benzobarrelene DPMR in a work by Zimmerman and coworkers.

The existence of the cyclopropyldicarbinyl diradical intermediate after crossing the TS1 was further supported by a series of mechanistic work after the pioneer work of Zimmerman. In a mechanistic study in 1976,[109] where a series of azo compounds were prepared to work as precursors of the *in situ* cyclopropyldicarbinyl diradical intermediate of DPMR (Scheme 3.4). Upon nitrogen expulsion thermally or photochemically, the yields of DPMR products were maximized in the presence of ketone photosensitizers. This experiment supports the idea that the cyclopropyldicarbinyl diradical is the key intermediate to the success DPMR reactions.



Scheme 3.4. Reaction selectivity of azo precursors upon (a) thermolysis, (b) direct photoirradiation, and (c) photosensitized by benzophenone (I), acetophenone (II), or m-methoxyacetophenone (III). Adapted by reference 109.

However, a kinetic isotope effect (KIE) study by Paquette and Bay[110] reported that the secondary deuterium KIE could not be explained solely from the equilibrium state of the cyclopropyldicarbinyl diradical intermediate. Instead, they suggested a concerted 1,2-aryl shift mechanism from a smaller KIE than what expected from stepwise mechanism. Adam and coworkers[111,112] also questioned the existence of cyclopropyldicarbinyl diradical intermediate by isotope-labelling study of azoalkanes (*vide infra*), which were the precursors for the diradicals at positions of interests. This result suggested that the transformation cannot be explained by a fully stepwise route to afford the DPMR products. Although these studies did not exclude the possibilities of a stepwise process via the cyclopropyldicarbinyl diradical intermediate, they all support the complicated nature on the mechanisms of the DPMR reactions.



Frutos *et al* revealed that the different multiplicity of the excited state can result in the different mechanistic pathways in 2004.[113] Constructed from CASSCF(8,8)/6-31g* level of theory, the DPMR reaction path of barrelene on the triplet surface passes through the cyclopropyldicarbinyl diradical intermediate and has enough energetic gap with the S_0 surface to avoid intersystem crossing until the semibullvalene product is reached. On the other hand, no intermediate was reached on the S_1 surface. Instead, a conical intersection region was found which allows $S_1 \rightarrow S_0$ radiationless transition to occur within the timescale of a few vibrations. For conformationally flexible molecules, the triple state can quickly decay into cis-trans isomerization product, making the S_1 state as the dominant route to reach the DPMR products.

3.3. Nonclassical Mechanisms of DPMR

The molecular energy required to traverse a transition state is initially retained in the products. This excess energy is broadly important in gas-phase reactions, but it can also affect condensed-phase reactions when subsequent steps occur rapidly.[49,50,71,114–116] For common organic reactions in solution, we have probed the initial energy in intermediates and its nonstatistical distribution through their effects on selectivity in subsequent steps. The amount and distribution of excess energy is relatively well understood in the simplest chemical reactions, and its prediction is conceptually straightforward for reactions passing over a simple energy barrier.[117] The disposition of energy in reactions involving electron transfer or changes in electronic state is less well understood.

Houk and coworkers demonstrated a competition scenario of stepwise and concerted DPMR reaction of dibenzobarrelene using quasiclassical trajectory studies.[107,118] From the prediction of statistical TST and RRKM theory, a half-life of more than 400 fs is required for the 1,4-diradical intermediate. However, the majority (~81%) of the trajectories has lifetimes of the 1,4-diradical intermediate no more than 300 fs. There was even 10% of the trajectories with lifetime below 60 fs, which were thought to have significant degree of nonstatistical dynamics.[38]

Despite the great efforts on the existence of the 1,4-diradical intermediate, the mechanistic complexity of DPMR is not limit to it. Chung and coworkers computationally predicted an appreciable amount of heavy-atom tunneling possesses in the DPMR of barrelene, benzobarrelene, and dibenzobarrelene.[106] Significant intramolecular KIEs were predicted under small curvature tunneling (SCT) correction at low temperatures (Table 3.1).

Table 3.1. POLYRATE predicted KIE for the rate-determining rearrangement step of barrelene DPMR in Chung's work.

Barrelene	KIE_{CVT}	$KIE_{CVT+SCT}$
100 K	1.213	3.210
200 K	1.101	1.246
300 K	1.074	1.113

[a]canonical variational transition state theory

[b]canonical variational transition state theory with small curvature tunneling correction

Our initial aim to this project is trying to obtain experimental evidence for the heavy-atom tunneling initially proposed by Chung from intramolecular KIE measurements. The large KIE observed using acetophenone as the photosensitizer at 200 K qualitatively support this idea.

However, the KIEs decreases as the increase energy of the triplet sensitizers, which implies that dynamic effect plays an important role when using high-energy sensitizers. If the reaction undergoes classical stepwise mechanism, the photosensitizers should make no differences in the product selectivity. Although stationary point calculations predict the existence of intermediacy of the cyclopropyldicarbinyl diradicals. The experimental KIEs do not support the presence of fully equilibrated intermediate. In the following sections, we demonstrate how triplet energy transfer in a classical photochemical reaction can afford either a dynamically hot triplet, reacting nonstatistically, or a “cold” triplet, reacting statistically. The results add a potential new avenue to control photoreaction outcome.[119–121] Our data not only provided the first experimental observations for the heavy-atom tunneling for the DPMR, but also the demonstrated the unprecedent sensitizer-dependent dynamics.

3.4. Experimental Methodologies and Results

The triplet reactions are generally carried out through photosensitization. The benzobarrelene di-π-methane was chosen for study because it uniquely breaks symmetry in each of its key mechanistic steps, providing a handle on the molecular energy in its intermediates (Figure 3.1).[50]

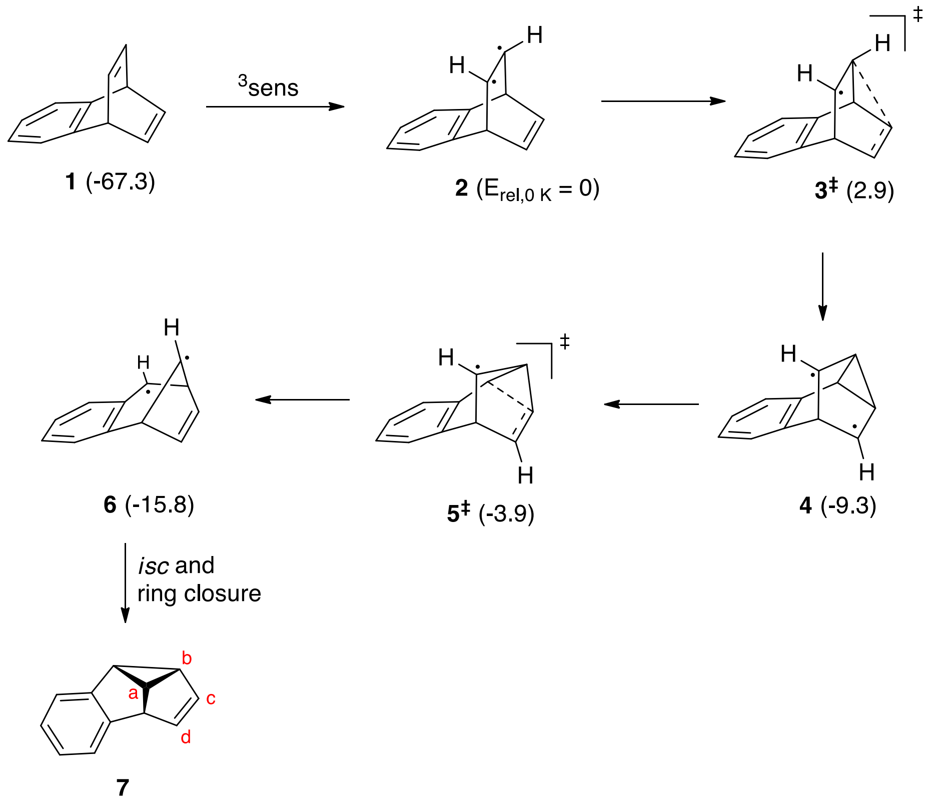


Figure 3.1. Qualitative mechanism for the di-π-methane rearrangement of benzobarrelene (**1**). Relative energies are DLPNO-CCSD(T)/aug-cc-pVTZ//ω-B97XD/6-31+G** + zpe, in kcal.mol.

Qualitatively, the mechanism may be described as involving the ring closure of the homoallylic triplet diradical **2** via transition state (TS) **3**‡ to afford the cyclopropyldicarbinyl diradical **4**, followed by a cyclopropyldicarbinyl ring opening via TS **5**‡ to afford the stabilized triplet diradical **6**.[103] The final product **7** is then formed after intersystem crossing (*isc*) and ring closure of the singlet form of **6**. Although **2** is not symmetrical due to its pyramidalized radical centers, experiment and calculations suggest that the two centers exchange very rapidly under statistical conditions (Figure 3.2). This means that **2** can undergo two equivalent (in a Curtin-

Hammett sense) competitive ring closures. The resulting intermediate **4** has a plane of symmetry and can competitively undergo two equivalent ring-opening steps.

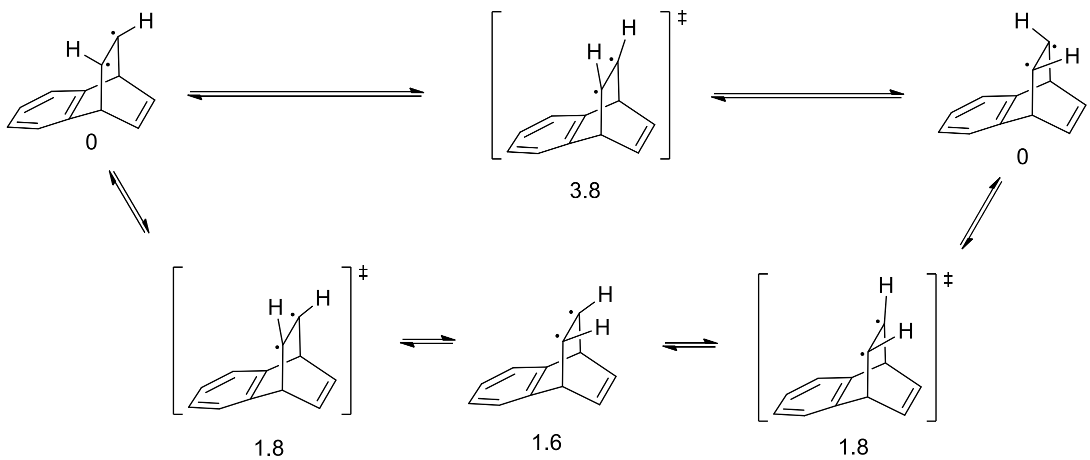


Figure 3.2. Free energy (kcal/mol) for the rapid exchange at the radical center for both concreted (upper) and stepwise (lower) calculated by ω-B97XD/6-31+G**.

The sequential competitive possibilities are indistinguishable without isotopic labeling, but molecules containing a ^{13}C in one of the original olefinic positions of **1** can form **7** with a ^{13}C in any of the four positions *a*, *b*, *c*, and *d*. Each step involves KIEs that unevenly partition the ^{13}C among the possible pathways. The isotopic distribution in **7** is then shaped by the KIEs for each step. Chung recently predicted that heavy-atom tunneling would be extensive in this reaction,[106] leading to unusually high KIEs. However, the KIE in this work represents the rate ratios of non-^{13}C labelled isotopomer to the one with multiple ^{13}C-labelled positions, which are not experimentally reproducible. Despite the overestimation of the KIEs, the KIEs with only one ^{13}C labeled barrelene is still predicted as high as 1.140, suggesting the heavy-atom tunneling may still play an important role in the reaction dynamics. This prediction encourages us to proceed to further studies in order to support the heavy-atom tunneling effect in both experimentally and theoretically.

The ^{13}C isotopic composition of **7** derived from sensitized di-π-methane reactions of **1** was studied at natural abundance using NMR methodology.[7] The measurements focused on ^{13}C in the *d* versus *c* positions of **7**, since this pairing was expected to exhibit the largest difference in isotopic composition. The *d / c* ratio will be described as the *nominal KIE* since it arises from a combination of KIEs for the individual steps. More limited studies on alternative positional pairs were consistent with the *d / c* pairing results (see Section A.2.4 in APPENDIX A). All results (Table 3.2) are based at least twelve measurements on samples from two independent reactions.

Table 3.2. Experimental and predicted nominal KIEs

		nominal KIE (^{13}C in *d* / ^{13}C in *c*)[a]	
sensitizer	**E_T (kcal/mol)**	**200 K**	**300 K**
acetophenone	73.3	1.138(7)	1.075(9)
methyl benzoate	78.3	[b]	1.057(4)
acetone	81.2	1.069(9)	1.037(4)
		1.140[c]	1.071[c]
CVT/SCT-predicted		1.123[d]	1.064[d]
		1.157[e]	1.077[e]

[a]Numbers in parentheses are 95% confidence limits for the last digit(s). [b]The methyl benzoate sensitized reaction at 200 K was not practical. [c]Calculated using the method of reference 42. [d]VTST-ISPE using CASSCF(6,6)+NEVPT2/aug-cc-pVTZ energies along the ω-B97XD/6-31+G** path. [e]Using LC-mPWLYP/6-31+G** calculations.

Strikingly, the observed nominal KIEs vary with the sensitizer. The KIEs are exceptionally high with acetophenone, particularly at 200 K. Despite the limited studies, the KIEs from other carbon pairs also fit qualitatively on the heavy-atom tunneling (see Section A.2.4). However, they are only half as large with acetone, with methyl benzoate in between. In the conventional view of the mechanism, the sensitizers serve only to generate the triplet **2**, and they are not involved in the rearrangement steps. From this, the nominal KIEs with differing sensitizers should be identical. This is decidedly not the case.

3.5. KIE prediction from POLYRATE

The qualitative mechanism for the benzobarrelene di-π-methane rearrangement is illustrated in Scheme 3.3 with the carbons labeled. Due to a large heavy-atom tunneling character suggested by Chung and coworkers, a program called POLYRATE, developed by Isaacson, Truhlar and coworkers, was used to estimate the possibility of transition state recrossing and quantum tunneling.[67,122] Using the benchmark process mentioned in Section 3.11, the calculations were carried out at ωB97XD/6-31+G** level of theory. The POLYRATE rate constants for non-labeled as well as ^{13}C-labelled at each position from *a* to *d* are summarized in Section B.3 and B.4 in APPENDIX B. The calculation of the product isotopic distribution from these rate constants requires a choice between three differing plausible assumptions. We refer to these assumptions as "non-Curtin-Hammett," "partial Curtin-Hammett", and "full Curtin-Hammett."

As noted in the main text, the structure of **2** is not symmetrical due to its pyramidalized radical centers. At the extreme of the "non-Curtin-Hammett" assumption, these non-equivalent centers do not exchange and react inequivalently, so that the choice of which center reacts would be decided by the initial asymmetry adopted by **2** on excitation. (We assume in every case that the choice of which alkene is excited and the initial pyramidalization of the carbons for this alkene are subject to negligible KIEs.) If this were the case, there would be no significant isotope effect for the first step (bond making) of the mechanism. The overall observed isotope effects would be much lower than those experimentally observed with acetophenone (~1.03 at 300 K, ~1.07 at 200 K) since they would arise only from the KIE for the second step. The non-Curtin-Hammett assumption is then inconsistent with the experimental observations.

At the opposite extreme, the full Curtin-Hammett assumption would be that the pyramidal centers of **2** rapidly interconvert and that the excitation can move rapidly between the two olefinic centers. With this assumption, the fraction of ^{13}C in the original olefins that ends up in the a and d positions of **4** is:

$$\text{labeled at a/d in } \mathbf{4} = (r_{a1} + r_{d1}) / (r_{a1} + r_{b1} + r_{c1} + r_{d1}) \qquad (1)$$

while at b and c of **4** is:

$$\text{labeled at b/c in } \mathbf{4} = (r_{b1} + r_{c1}) / (r_{a1} + r_{b1} + r_{c1} + r_{d1}) \qquad (2)$$

where "r" is a calculated rate constant; a, b, c, and d refer to the positions of the ^{13}C in Scheme 3.5, and 1 or 2 refer to first step (2 to 4) versus second (bond breaking) step (4 to 6) in the mechanism. For the second step the ^{13}C in a/d of **4** is partitioned to **6** and ultimately to **7** as:

$$\text{label at a of } \mathbf{6/7} = (\text{labeled at a/d in } \mathbf{4}) \times (r_{a2} / (r_{a2} + r_{d2})) \qquad (3)$$

$$\text{label at d of } \mathbf{6/7} = (\text{labeled at a/d in } \mathbf{4}) \times (r_{d2} / (r_{a2} + r_{d2})) \qquad (4)$$

and the ^{13}C in b/c of **4** is partitioned to **6** and ultimately to **7** as:

$$\text{label at b of } \mathbf{6/7} = (\text{labeled at b/c in } \mathbf{4}) \times (r_{b2} / (r_{b2} + r_{c2})) \qquad (5)$$

$$\text{label at c of } \mathbf{6/7} = (\text{labeled at b/c in } \mathbf{4}) \times (r_{c2} / (r_{b2} + r_{c2})) \qquad (6)$$

The crude rate constants data are summarized in Section B.3 and B.4 in APPENDIX B. The reported nominal KIEs in Table 3.3 and Table 3.4 and the main text are then the ratio of (label at d) / (label at c) from eqs 4 and 6 above.

The "partial Curtin-Hammett" assumption is that the pyramidal centers rapidly interconvert but that the excitation does not move rapidly between the two olefinic centers. If this is the case, then by an analogous process to that above, the label in the various carbons would be defined by eqs 7 to 10.

$$\text{label at a of } \mathbf{6/7} = \left(\frac{r_{b1}}{r_{a1}+r_{b1}} + \frac{r_{c1}}{r_{c1}+r_{d1}}\right)\left(\frac{r_{d2}}{r_{a2}+r_{d2}}\right) \qquad (7)$$

$$\text{label at b of } \mathbf{6/7} = \left(\frac{r_{a1}}{r_{a1}+r_{b1}} + \frac{r_{d1}}{r_{c1}+r_{d1}}\right)\left(\frac{r_{c2}}{r_{b2}+r_{c2}}\right) \qquad (8)$$

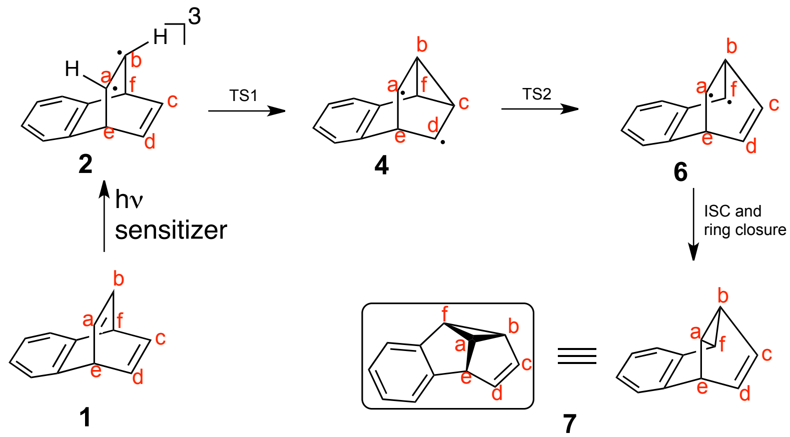
$$\text{label at c of } \mathbf{6}/\mathbf{7} = \left(\frac{r_{a1}}{r_{a1}+r_{b1}} + \frac{r_{d1}}{r_{c1}+r_{d1}}\right)\left(\frac{r_{b2}}{r_{b2}+r_{c2}}\right) \quad (9)$$

$$\text{label at d of } \mathbf{6}/\mathbf{7} = \left(\frac{r_{b1}}{r_{a1}+r_{b1}} + \frac{r_{c1}}{r_{c1}+r_{d1}}\right)\left(\frac{r_{a2}}{r_{a2}+r_{d2}}\right) \quad (10)$$

The results from (eq) 7 to 10 are extremely close to those from (eq) 1 to 6, being consistently slightly smaller but never differing by more than 0.001 at 300 K and 0.003 at 200K. We cannot experimentally distinguish the full Curtin-Hammett and partial Curtin-Hammett possibilities, but the difference is not relevant to the conclusions of the paper.

Multireference character was judged to be of less importance to second step in the mechanism, and the full-path CASSCF calculations for the ISPE calculations in POLYRATE were not carried out. Instead, the first-step CASSCF rate constants were combined with ω-B97XD second-step rate constants for the purpose of isotope effect predictions.

Numerical convergence can be difficult to achieve for the calculation of small isotope effects by this method, and POLYRATE's SSTEP parameter is the key factor. (Other factors contributing to numerical non-convergence are more easily controlled, while calculations with a small SSTEP are costly.) The calculations with differing SSTEP values were carried out to gauge the potential errors due to a lack of numerical convergence, and it appears that the errors are small, 0.004 at 200 K and 0.002 at 300 K.



Scheme 3.5. Reaction scheme for the benzobarrelene DPMR and carbon assignment.

Table 3.3. POLYRATE KIEs (200 K)

KIE (d / c)	SSTEP	TST	CVT	TST/SCT	CVT/SCT
M06-2X	0.01	1.068	1.072	1.142	1.141
ωB97xD	0.01	1.064	1.066	1.110	1.111
ωB97xD	0.005	1.064	1.066	1.114	1.114
ωB97xD	0.0025	1.064	1.066	1.114	1.115
ωB97xD CAS-ISPE	0.0025	1.036	1.035	1.093	1.123
LC-mPWLYP	0.01	1.072	1.072	1.157	1.157

Table 3.4. POLYRATE KIEs (300 K)

KIE (d / c)	SSTEP	TST	CVT	TST/SCT	CVT/SCT
M06-2X	0.01	1.047	1.049	1.073	1.072
ωB97xD	0.01	1.044	1.046	1.062	1.063
ωB97xD	0.005	1.044	1.046	1.063	1.064
ωB97xD	0.0025	1.044	1.046	1.064	1.065
ωB97xD CAS-ISPE	0.0025	1.028	1.027	1.044	1.064
LC-mPWLYP	0.01	1.050	1.050	1.077	1.077

3.6. The Triplet Surface of Benzobarrelene DPMR

Consideration of the theoretical methods validation studies in a later section may be aided by a detailed examination of the energy surface in the area of **2**. We will refer to five structures, though not all five are stationary points in all computational methods. The five structures are:

- **anti-2**, in which the carbons of the excited olefin are pyramidalized and the hydrogens of the pyramidalized carbons are displaced away from each other.
- **syn-2**, in which the hydrogens on the pyramidalized carbons are approximately eclipsed.
- **anti-synTS**, the TS for interconversion of **anti-2** and **syn-2.**
- **anti-TS 3‡**, the TS that connects **anti-2** to intermediate **4.**
- **syn-TS 3‡**, the TS that connects **syn-2** to intermediate **4.**

We also located additional structures in this area, including an analog of **syn-2**, **benzo-syn-2**, with the hydrogens pointing toward the benzene ring, a TS for the formation of **benzo-syn-2**, a TS for a rearrangement involving initial bond formation at the benzene ring (benzo-vinyl bridge pathway, Scheme 3.3), and an unusual TS that accomplishes a front-to-back interconversion of **4**, but these structures were higher in energy and were judged to not be chemically relevant.

The various DFT and *ab initio* computational methods might be described as predicting crudely similar energy surfaces, in that all methods predict that **anti-2** is lowest in energy of the five, and most predict the relative energy of the other four structures versus **anti-2** within a range of ± 2 kcal/mol. However, the surfaces differ qualitatively from the perspective that some predict that the lowest barrier from **anti-2** to **4** is via **anti-TS 3‡** (CASSCF(6,6)+NEVPT2/aug-cc-pVTZ, LC-ωHPBE, LC-mPWLYP, LC-BLYP), some predict that the lowest barrier from **anti-2** to **4** is via **syn-TS 3‡** (most DFT methods), some predict that the lowest barrier from **anti-2** to **4** is via **anti-synTS** (notably DLPNO-CCSD(T)/aug-cc-pVTZ, though this TS is importantly not consistent with the large experimental [13]C KIEs), and some have a single barrier along the syn pathway (the CASSCF(6,6)+NEVPT2/aug-cc-pVTZ energies look this way approximately, though this is unavoidably based on single-point energies instead of a full energy surface search) The variation in possibilities is illustrated diagrammatically in Figure 3.3.

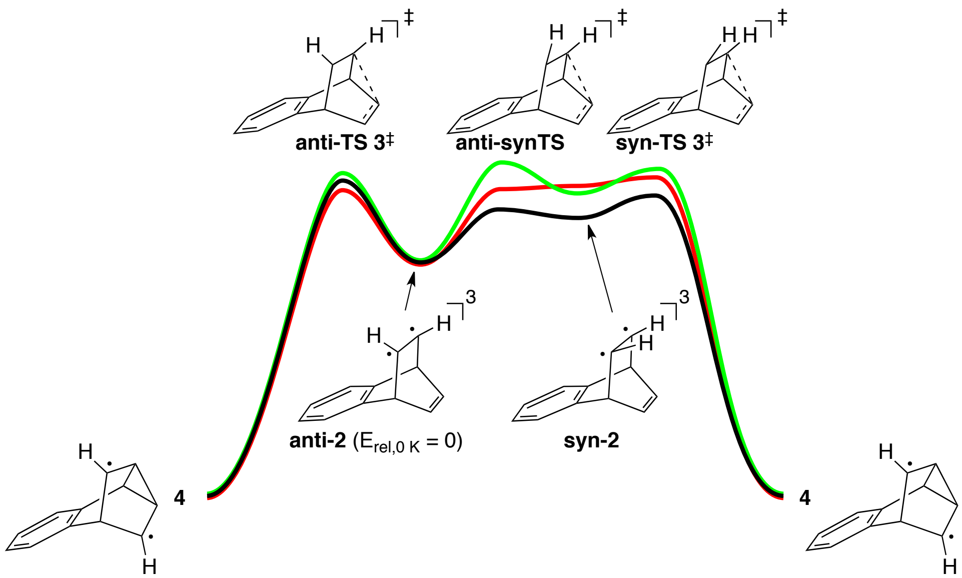


Figure 3.3. Diagrammatic illustration, not to scale, of the variation in the energy surfaces in the area of **2** for various computational methods. The CASSCF+NEVPT2, ω-B97XD, and LC-mPWLYP surfaces are illustrated qualitatively by the red, black, and green curves, respectively.

Figure 3.4 shows the TD-DFT (ω-B97XD/6-31+G**) vertical excitation energy along the reaction coordinate for the reaction of **anti-2** via either **anti-TS 3‡** or **syn-TS 3‡**. The excitation energies are large throughout, but they dip particularly of **syn-TS 3‡** to less than 50 kcal/mol, which is where the CASSCF+NEVPT2 energies disagree modestly with the DFT energies.

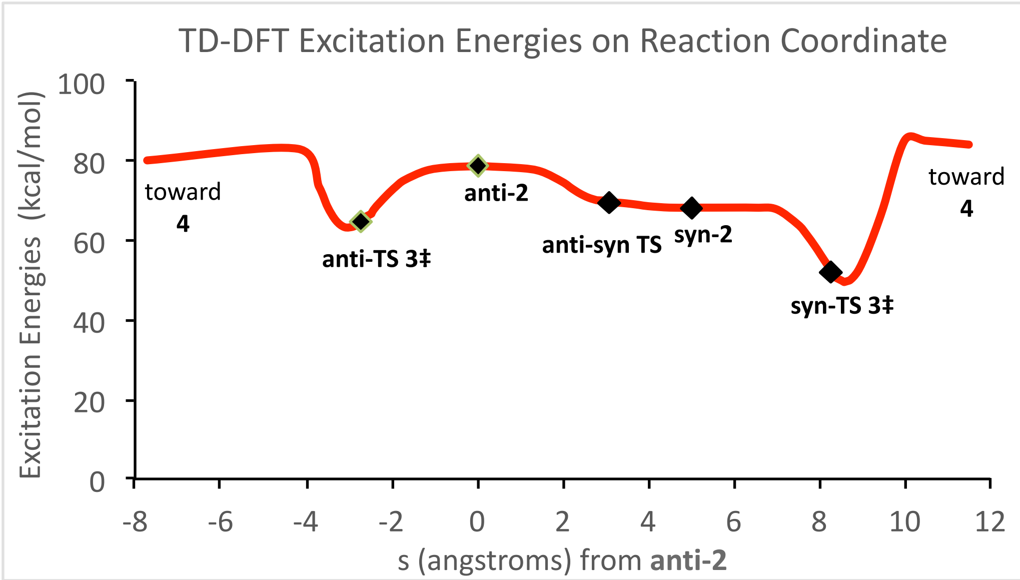


Figure 3.4. A connected plot of the TD-DFT (ω-B97XD/6-31+G**) vertical excitation energies along the POLYRATE / GAUSSRATE minimum energy paths through the three TSs.

Two issues add further to the complexity of understanding this surface. The first is that the zero-point energy (ZPE) along the pathway through **anti-TS 3‡** is lower than that along the pathway through **syn-TS 3‡**, because the olefinic C-H bending vibrations are less constrained in the anti structures. ZPE thus favors the anti process by about ~0.6 kcal/mol. The second is that tunneling adds significantly to the rate of passage through **anti-TS 3‡** (by a factor of ~1.6 at 300 K and ~3 at 200 K) and substantially favors **anti-TS 3‡**, because the barrier though **anti-TS 3‡** is sharper.

These issues potentially affect the detailed accuracy of the trajectory simulations. Quasiclassical trajectories reflect zero-point energy surfaces at short times[123] but do not reflect tunneling. In addition, the ω-B97XD/6-31+G** surface has a lower barrier along the syn pathway when compared to the CASSCF(6,6)+NEVPT2/aug-cc-pVTZ (the relative energies of **anti-TS 3‡** versus **syn-TS 3‡** change by 0.6 kcal/mol in going from CASSCF(6,6)+NEVPT2 to ω-B97XD, favoring the syn). These factors were however considered to be sufficiently minor to allow a qualitative examination of the ω-B97XD/6-31+G** trajectories.

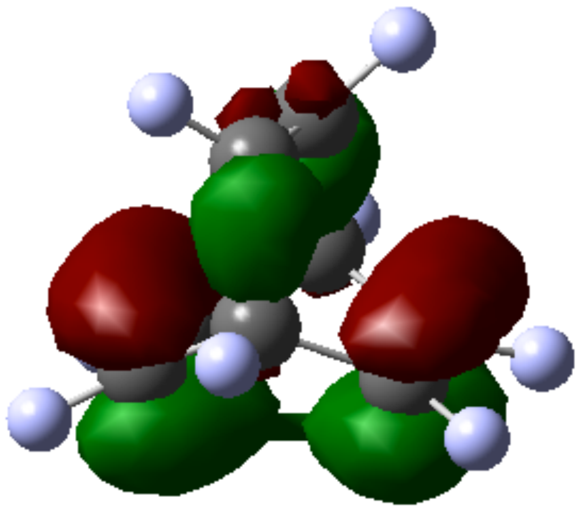
To gain quantitative insight into the experimental intramolecular KIE results in Table 3.2, the KIEs for each position and step in the conventional mechanism were theoretically predicted. Structures based on the mechanism described in Scheme 3.3 were calculated with the 1,4-diradical intermediate being a both potential and free energy minima at ω-B97xD/6-31+G** level of theory. However, a problem was that the energy surface in the area of **2** is complicated by multireference character, particularly for structures in which the olefinic HCCH dihedral angle approaches 0°. The initial conformation for **2** has a large HCCH dihedral angle (**anti-TS 2**) was suggested in Chung's work.[106] However, another conformation with close-to-zero dihedral angle was found to have similar but slightly lower potential energies (**syn-TS 2**) at most of the DFT methods. Despite the small conformational changes, **syn-TS 2** does not give large heavy-atom tunneling as observed experimentally (Table 3.5).

Table 3.5. Single point energies for **syn-TS 2** and **anti-TS 2** at the ωB97xD/6-31+g** optimized geometry.

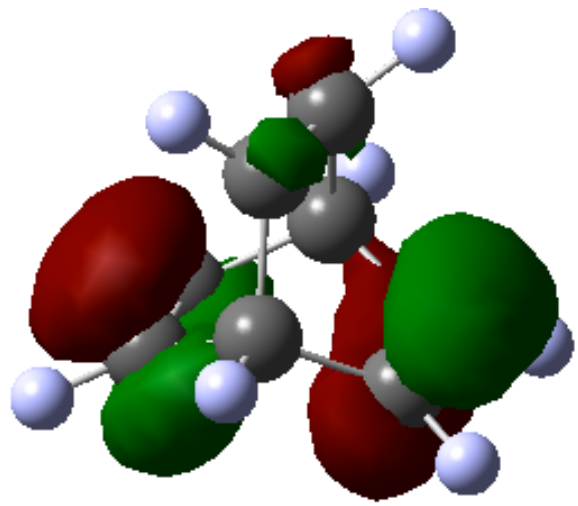
DFT methods	syn-TS 2	anti-TS 2	Δ (anti - syn, kcal/mol)
B1B95	-462.9529615	-462.9500972	1.80
B3LYP	-463.1693071	-463.1660178	2.06
B3P86	-464.6520775	-464.6493496	1.71
B3PW91	-462.9972218	-462.9946935	1.59
B971	-463.0335345	-463.0302556	2.06
B972	-463.0071533	-463.0039882	1.99
B98	-462.9762579	-462.9731419	1.96
BMK	-462.836914	-462.8344204	1.56
CAM-B3LYP	-462.8920554	-462.890931	0.71
HSEH1PBE	-462.6621335	-462.6601135	1.27
LC-BRxPL	-464.0770462	-464.0783319	**-0.81**

LC-mPWLYP	-461.7209061	-461.722286	**-0.87**
LC-UBLYP	-461.714446	-461.7158307	**-0.87**
LC-wHPBE	-462.8275208	-462.8292353	**-1.08**
LC-wPBE	-462.8286308	-462.8303456	**-1.08**
M062X	-462.954579	-462.9540112	0.36
M11	-462.8535767	-462.853886	-0.19
MN12SX	-462.7851532	-462.7821505	1.88
MN15	-462.5907851	-462.5882483	1.59
mPW1LYP	-462.9044088	-462.9015957	1.77
mPW1PBE	-462.8900084	-462.8881733	1.15
mPW1PW91	-463.0698308	-463.0679586	1.17
mPW3PBE	-462.8480855	-462.8455462	1.59
N12SX	-462.970874	-462.9687706	1.32
OHSE1PBE	-462.6630647	-462.6610457	1.27
OHSE2PBE	-463.5415243	-463.5395733	1.22
PBE0	-462.6230102	-462.6230102	0.00
PBE1PBE	-462.6241662	-462.62224	1.21
ωB97xd	-463.0081911	-463.006917	0.80

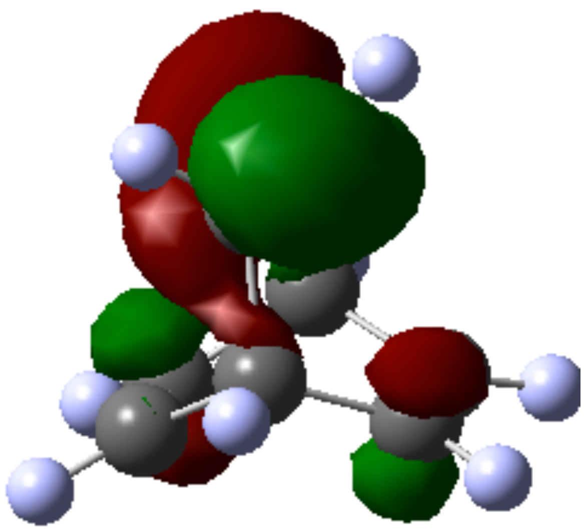
However, some long-range corrected DFTs (LC-DFTs) predict in favor of the experimental results. As shown in the bolded relative energies in Table 3.5, all the LC-DFTs chosen predict in favor of the **anti-TS 2** by around 0.8 to 1.1 kcal/mol. In addition, time-dependent DFTs (TDDFTs) calculations around the surface connecting **anti-TS 2** and **syn-TS 2** show that the T_2-T_1 gap is smaller around the **syn-TS 2** area. This smaller gap may result in a multireference character, which is typically not accurate for conventional DFT methods. The multireference character may explain why most of the DFT methods did not account for the experimental observations. Therefore, we moved to a higher level CASSCF(6,6)+NEVPT2/aug-cc-pVTZ methods to have more accurate longer-range interaction and multireference character. By including the molecular orbitals shown in Figure 3.5, the CASSCF calculation predict in favor of the **anti-TS 2** by 0.7 kcal/mol. In fact, the preference for the **anti-TS 2** is strengthened by the higher entropy resulted from the conformational diversity of the HCCH dihedral angle.



orbital 25



orbital 26



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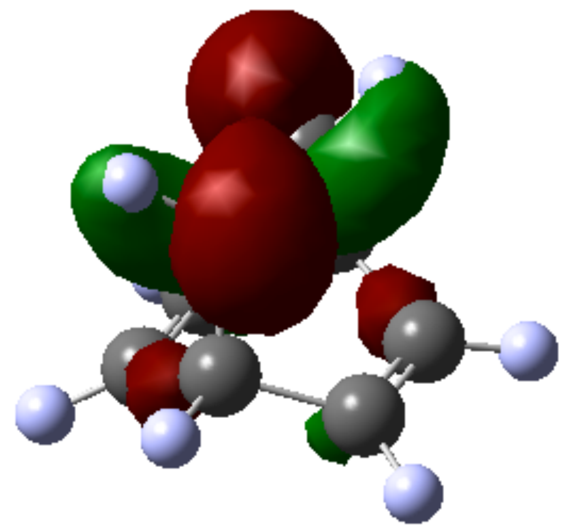

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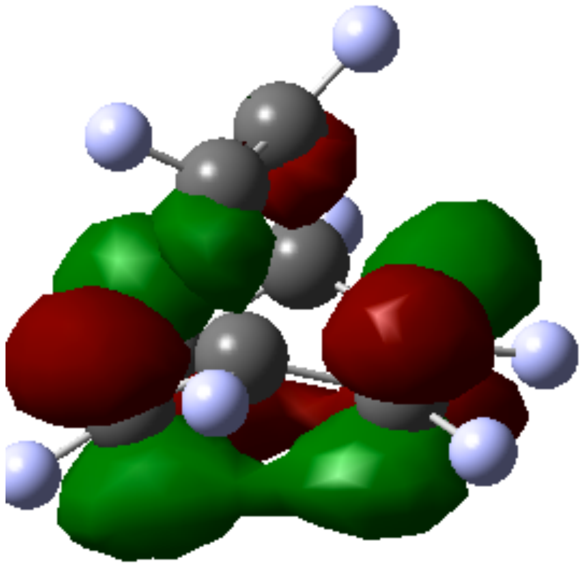
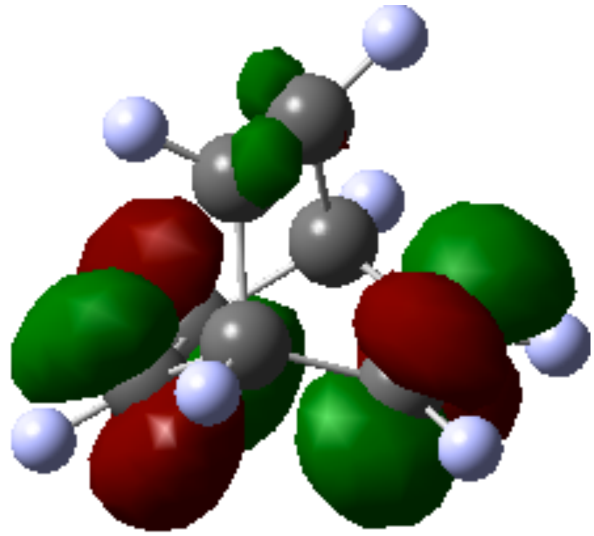


orbital 29



orbital 30

Figure 3.5. Molecular orbitals involved in the CASSCF(6,6)+NEVPV2/aug-cc-pVTZ calculation.

Using the GAUSSRATE / POLYRATE set of programs,[67,124] the rearrangement steps were explored in canonical variational transition state theory (CVT) including small-curvature tunneling (SCT).[125] The predicted nominal KIEs (Table 3.2) derived from the CVT/SCT rate constants varied moderately over a range in calculated barrier heights due to variation in the tunneling contribution to the rate constants.

3.7. Sensitizers Effects on the KIE Results

For the acetophenone-sensitized reactions, the predicted KIEs fit closely with those observed. Importantly, this supports the conventional mechanism involving structures **2** through **7**, the approximate accuracy of the computational energy surface, and Chung's insightful prediction of excited-state heavy-atom tunneling.[106,126,127] The agreement also weighs against the importance of triplet exciplexes in the mechanism, as have other observations.[128] Finally, the agreement does not support the importance of a dynamically concerted combination of the two rearrangement steps, as has been proposed for the reaction of dibenzobarrelene.[107]

Something else is happening for the acetone and methyl benzoate reactions. We considered a singlet-manifold process, but the direct irradiation of **1** did not afford **7**, instead giving benzocyclooctatetraene, as previously reported.[103,129] We also considered whether an unknown photochemical isomerization of **7** could scramble its isotopic composition, but the observed KIE was unchanged for an acetone-sensitized reaction taken to 83% conversion versus one taken to only 10% conversion. Zimmerman's work had excluded the direct involvement of a benzene-centered triplet ($E_T \sim 80.5$ kcal/mol) with acetone as sensitizer.[103]

The hypotheses in our experiments were that triplet sensitization would lead to a vibrationally excited benzobarrelene triplet **2**, that higher-energy sensitizers would afford greater vibrational energy in **2**, and that the low barrier for the reaction of **2** would allow this initial vibrational energy to manifest in the experimental KIEs. The results fit with these ideas. The minimum sensitizer triplet energy (E_T) to success-fully promote the reaction of **1**, albeit with a low quantum yield, is 69 kcal/mol.[109,130] Acetophenone ($E_T = 73.3$ kcal/mol) efficiently promotes the reaction, and the triplet **2** appears to react by an ordinary thermally activated reaction, leading to KIEs that match CVT/SCT predictions. With the higher E_T of methyl benzoate (78.3 kcal/mol), the KIE is decreased. With an E_T of 81.2 kcal/mol, triplet acetone possesses ~12 kcal/mol excess energy beyond the minimum required to bring about the reaction. The greatly reduced KIEs for the acetone reaction then suggest that the fast reaction of vibrationally excited **2** predominates.

For these hypotheses to be correct, the triplet **2** must be formed with sufficient vibrational energy to both react rapidly before thermal cooling and account for the observed KIE. The maximum energy available from the interaction of **1** with the sensitizer can be calculated from a combination of the differences in the E_T (0-0) for the sensitizer versus **1** and the thermal vibrational energies within **1** and the sensitizer. With acetone, this amounts to an average of ~16.8 kcal/mol (~12 from above[130] + 3.2 from **1** + 1.6 from triplet acetone at 25 °C). If this energy is distributed randomly between **2** and acetone based on their vibrational heat capacities, the initial excess energy in **2** would average ~13.0 kcal/mol. This would lead to an RRKM rate constant of 9×10^{11} s^{-1}, or a half-life of 0.8 ps. The RRKM-predicted KIE for this average energy would be 1.031. From this, the available energy is clearly sufficient to account for the observed KIE of 1.037.

3.8. Dynamic Trajectory Studies

Molecular dynamics simulations have been used to probe non-classical mechanisms. Quasiclassical direct-dynamics trajectory calculations provided an alternative estimate of the lifetime of vibrationally excited **2**. However, reactions involve electron transfer or energy transfer are intrinsically complicated because the transition states are not easy to be defined. Several approaches were performed in order to simulate the excess energy retained in the **2**. Depending on the distribution of the triplet energy, the starting point of each trajectory can be sampled from canonical and microcanonical approaches. For the microcanonical approach, the energy retained in the substrate can be distributed either in a Boltzmann way or locally in some vibrational normal modes. From these approaches, we concluded that the approach from the algorithms developed by Frutos and coworkers is the best to describe the nonstatistical triplet energy distribution.

In the Frutos's algorithm, complete potential energy surfaces on both S_0 and T_1 state are calculated such that each point on the S_0 surface corresponds vertically to a point on the T_1 surface. Thus, the driving force ΔE (= $E_T^A - E_T^D$) for the triplet energy transfer (TT) process for each point can be calculated. To get the optimal structure for the acceptor upon TT, the lowest energy structure on the S_0 surface along the path with the same ΔE is obtained. In the next section, we demonstrate the approaches to simulate the reaction dynamics of benzobarrelene DPMR.

3.8.1. Canonical Sampling

In the canonical sampling approach, it is assumed that the energy transferred to a molecule is quickly distributed evenly into vibrational modes. By increasing the temperature in the trajectory simulation, molecules can reach higher vibration energy levels. It is assumed that the triplet energy from the sensitizers is distributed statistically among the normal modes. The excess energies were calculated compared to the zero-point energy of the optimized structure.

The trajectories were initiated from the area of **2** on the ω-B97xD/6-31+G** triplet surface, giving each normal mode its zero-point energy plus a Boltzmann distribution of quantized vibrational energies. The trajectories were then integrated in 1 fs steps until either **6** was formed or a 350-fs time limit was reached. To explore reactions activated by sensitizers with different triplet energies, the trajectories were carried out under three different temperatures: 50 K, 298.15 K, and 518 K. A total of 2538 trajectories were carried were calculated and the results are summarized in Table 3.6. As shown in Table 3.6, the conversions show positive correlation with the temperature, which indicates that the thermal activation of vibrations could enhance the DPMR reaction. These trajectories give us a rough estimation of how much dynamic effect may be involved in the process at different canonical temperatures. To provide clearer picture of how nonstatistical effect would affect the reactivity, we further simulate the dynamics around the onset of energy transfer by running the trajectory with localized energy distribution. This demonstrates the key vibrational normal mode contributes the most to the reactivity and will be discussed in the following sections.

Table 3.6. Trajectory statistics for canonical sampling at different temperatures.

	canonical temperature			
Trajectory count (%)	50 K	298.15 K	518 K	Total
Total	464	1102	972	2538
remain as reactant (**2**)	417 (89.9%)	917 (83.2%)	615 (63.3%)	1979
forms IM	45 (9.7%)	178 (16.2%)	324(33.3%)	547
forms PD	2 (0.4%)	7 (0.6%)	33 (3.4%)	42

3.8.2. Statistical vs. nonstatistical dynamics

To simulate reaction dynamics undergoing statistical cooling after the energy transfer by the photosensitizer, the trajectories were initiated from the area of **2** on the ω-B97XD/6-31+G** triplet surface, giving each normal mode its zero-point energy plus a Boltzmann sampling of 12 to 14 kcal/mol of additional energy. The trajectories were then integrated in 1 fs steps until either **6** was formed or a 350-fs time limit was reached. Out of 525 total trajectories, 204 (39%) underwent formation of either **4** or **6** during this time. This corresponds to a half-life of ~500 fs. The cooling of hot molecules in solution is generally associated with lifetimes of a few picoseconds,[131,132] so the lifetime of excited **2** by either the RRKM or the trajectory method appears consistent with reaction before thermal cooling.

We hypothesized, however, that an initial localization of excess energy in **2** could promote the di-π-methane rearrangement by nonstatistical dynamics. The idea is that the molecular geometry changes in going from **1** to **2** mainly occurs at a single olefinic moiety, with pyramidalization of each carbon and extension of the carbon-carbon distance from 1.33 to 1.49 Å. Relaxation of molecular geometries in the area of **1** to the geometry of **2** would afford **2** with vibrational energy at these carbon centers.

To explore this idea, an approximate transition state for the “nonvertical” triplet energy transfer to **1** was located by the approach of Frutos, within the non-adiabatic formulation of transition state theory and assuming weak coupling.[133–135] To simulate the structure on the onset of triplet excitation of **1,** single-point energies for triplet and singlet structures of benzobarrelene from scanning two internal coordinates were calculated at ω-B97xD/6-31+G** level of theory: (1) H-C-C-H dihedral angle ($\theta_{HCCH,}$ *vide infra*) and (2) C-C bond length ($d_{CC,}$ *vide infra*). The energy maps for the singlet and the corresponding vertical excitation energies were constructed in Table 3.7 and Table 3.8. The structure for the non-statistical trajectories was obtained by minimizing the singlet energy along the path having the same vertical excitation energy with the triplet sensitizers within an error of ± 0.2 kcal/mol.

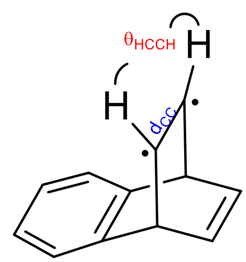


Table 3.7. Singlet energy surface of scanning along d_{cc} and θ_{HCCH} internal coordinates. The outlined number represent the path along the 76.0 ± 0.2 kcal/mol vertical gap energy (see Table 3.8). The highlighted structure represents the final structure of **8**.

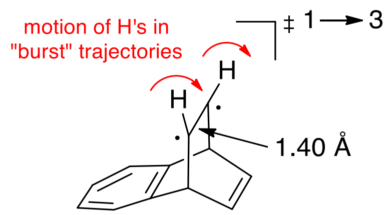
Singlet energy θ_{HCCH} **(º)** d_{CC} **(Å)**	**0.05**	**-0.95**	**-1.95**	**-2.95**	**-3.95**
1.3667	0.83	0.84	0.84	0.86	0.88
1.3692	0.95	0.95	0.96	0.98	1.00
1.3717	1.07	1.07	1.08	1.10	1.12
1.3742	1.20	1.20	1.21	1.23	1.25
1.3767	1.34	1.34	1.35	1.37	1.39
1.3792	1.48	1.48	1.49	1.51	1.53
1.3817	1.63	1.63	1.64	1.66	1.68
1.3842	1.79	1.79	1.80	1.82	1.84
1.3867	1.95	1.95	1.96	1.98	2.00
1.3892	2.12	2.12	2.13	2.15	2.17
1.3917	2.30	2.30	2.31	2.32	2.35
1.3942	2.48	2.48	2.49	2.51	2.53
1.3967	2.67	2.67	2.68	2.69	2.72

1.3992	2.86	2.86	2.87	2.89	2.91
1.4017	3.06	3.06	3.07	3.09	3.11
1.4042	**3.26**	**3.27**	**3.28**	**3.29**	**3.31**
1.4067	3.48	3.48	3.49	3.50	3.52
1.4092	3.69	3.69	3.70	3.72	3.74
1.4117	3.91	3.92	3.93	3.94	3.96
1.4142	4.14	4.14	4.15	4.17	4.19
1.4167	4.37	4.38	4.39	4.40	4.42

Table 3.8. Singlet and triplet vertical gap energy surface of scanning along d_{cc} and θ_{HCCH} internal coordinates. The outlined number represent the path along the 76.0 ± 0.2 kcal/mol vertical gap energy. The highlighted structure represents the final structure of **8**.

gap energy / **d_{CC} (Å)**	**θ_{HCCH} (º)**	**0.05**	**-0.95**	**-1.95**	**-2.95**	**-3.95**
1.367		99.0	99.0	99.0	99.0	99.0
1.369		98.8	98.8	98.8	98.8	98.8
1.372		98.6	98.6	98.6	98.6	98.6
1.374		98.4	98.4	98.4	98.3	98.4
1.377		81.6	81.5	81.5	81.5	81.5
1.379		81.1	81.0	81.0	81.0	81.0
1.382		80.6	80.5	80.5	80.5	80.5
1.384		80.1	80.1	80.0	80.0	80.0
1.387		79.6	79.6	79.5	79.5	79.5
1.389		79.1	79.1	79.1	79.0	79.0
1.392		78.6	78.6	78.6	78.5	78.5
1.394		78.1	78.1	78.1	78.0	78.0
1.397		77.6	77.6	77.6	77.6	77.5
1.399		77.1	77.1	77.1	77.1	77.0
1.402		76.6	76.6	76.6	76.6	76.6
1.404		**76.1**	**76.1**	**76.1**	**76.1**	**76.1**
1.407		75.7	75.7	75.6	75.6	75.6
1.409		75.2	75.2	75.2	75.1	75.1
1.412		74.7	74.7	74.7	74.7	74.6
1.414		74.2	74.2	74.2	74.2	74.2
1.417		73.7	73.7	73.7	73.7	73.7

Within this formalism, the transition state is the lowest-energy geometry of **1** that has an excitation energy that matches the triplet energy of the sensitizer. The vertical excitation of **1** from its lowest-energy geometry requires 95.3 kcal/mol, too high for any of the sensitizers. However, the deformation of **1** to structure **8** by extending the olefinic C-C bond to 1.40 Å drops the excitation energy to ~81 kcal/mol. The barrier for this deformation is only 2.9 kcal/mol. The excitation of **8** to the triplet state then provides a structure with 12 kcal/mol of excess energy that is specifically localized in the area of the olefin due to its distortion relative to **2**.



8

A total of 831 quasiclassical trajectories were initiated from the area of **8** on the triplet energy surface, including only ordinary random thermal energy appropriate for 25 °C. Of these, 485 (58%) afforded either **4** or **6** within ~350 fs. The increased rearrangement relative to **2** initiated statistically supports the role of nonstatistical dynamics in the reaction.

The triplet energy transfer from acetone would then be promoting the di-π-methane rearrangement in two previously unrecognized ways: by supplying excess vibrational energy and by supplying it in a location that is particularly conducive to facilitating the reaction. The latter can be seen in the time course of the decay of the trajectories initiated statistically (with the 12-14 kcal/mol excess energy distributed randomly starting from the area of **2**) versus nonstatistically (from with area of **8** with random thermal energy), as shown in Figure 3.6. While the statistical trajectories decay in an ordinary way, approximately 30% of the nonstatistical trajectories react in a burst of the rearrangement reaction at ~50 fs, with a smaller second burst occurring at ~165 fs. The burst trajectories are recognizable at their outset because they predominantly involve motion of the hydrogens on the excited olefin toward the second olefin, while trajectories that approach the geometry of **2** do not react rapidly. The burst process is unavailable with acetophenone because its low triplet energy leads per force to an initial geometry of **2** that is much closer to its equilibrium structure.

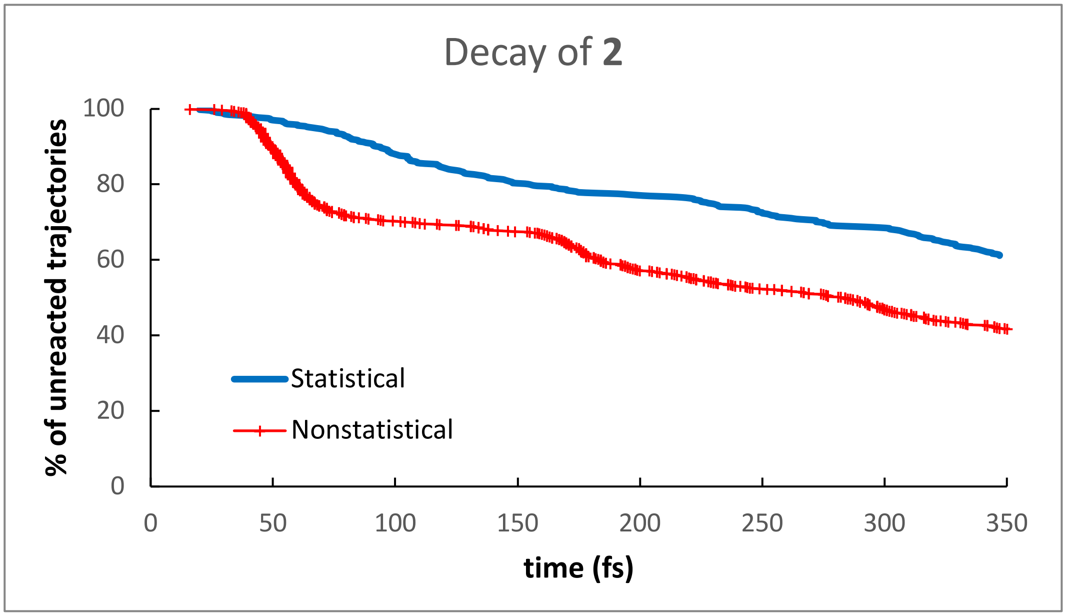


Figure 3.6. Decay of triplet trajectories undergoing the first step of the di-π-methane rearrangement for benzobarrelene.

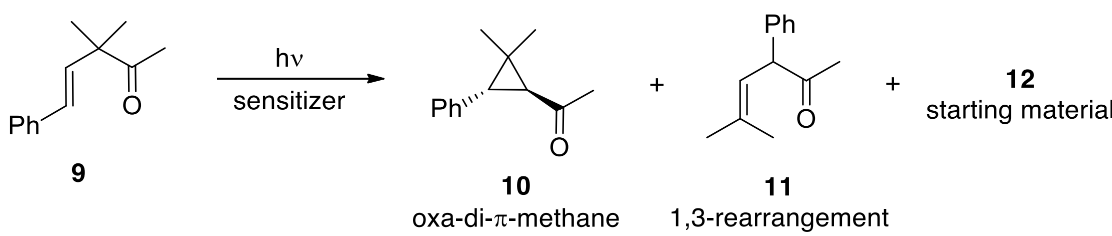
3.9. Technical Comments

3.9.1. Comment on heavy atom tunneling proposed by Chung and coworkers

We note briefly that the Chung paper[106] had based its predictions of exceptional heavy-atom tunneling on transition state **anti-TS 3‡.** However, the apparently unfound **syn-TS 3‡** was actually the lowest-energy transition state for their M06-2X surface. Because the tunneling contribution to the rate for **syn-TS 3‡** is much smaller (this is because the 'floor' for tunneling is the higher-energy **syn-2** structure), this surface if correct would lead to substantially lower tunneling. However, the CASSCF(6,6)+NEVPT2/aug-cc-pVTZ and our experimental KIEs with acetophenone support that **anti-TS 3‡** is actually the preferred transition state and that heavy-atom tunneling through this transition state is substantial, and in this way the general conclusion of the Chung paper is supported qualitatively.

3.9.2. Comment on a prior proposed effect of triplet sensitizers providing vibrational energy

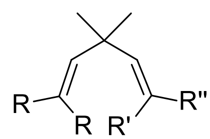
In 2005, Armesto, Ortiz, Agarrabeitia, and El-Boulifi[120,121] reported an intriguing apparent effect of sensitizer energy on the oxa-di-π-methane rearrangement. In the sensitized reaction of β-γ-unsaturated methyl ketone **9**, only starting material was obtained when the reaction was carried out with acetophenone (E_T = 73 kcal/mol). However, only the oxa-di-π-methane product **10** was formed when thioxanthone (E_T = 63 kcal/mol) was the sensitizer. Lower-energy sensitizers provide more and then exclusively the 1,3-rearrangement product **11**.



	E_T	10	11	12
Acetophenone	73	--	--	91%
Thioxanthone	63	50%	--	20%
4-phenylbenzophenone	61	10%	28%	35%
chrysene	57	--	6%	56%

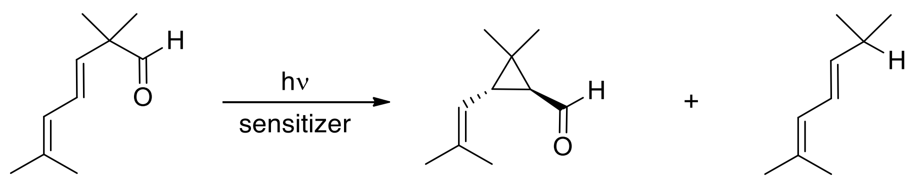
It was proposed in this first paper that acetophenone gave rise to *'"hot" triplet excited states, with a large excess of vibrational energy'* that deactivated *'by E/Z isomerization exclusively'* while *'"warm" triplet excited states'* gave rise to the oxa-di-π-methane rearrangement and *'"cold" triplet excited states'* apparently give rise to the 1,3-rearrangement.

In a later paper,[121] the authors appear to walk away from this explanation based on studies of the di-π-methane reaction of structures of type **13**: *"Although our previous studies with related unsaturated ketones suggested that a possible correlation exists between the triplet energy of the sensitizer and the photoreactivity observed, the observations made in this study demonstrate that this correlation does not apply to dienes 4. Therefore, other factors (still unknown) must play an important role in the outcome of triplet-sensitized reactions of acyclic 1,4-dienes."* No mention of vibrational energy or "hot" triplets appears in this paper. The authors had, as with **9**, observed a degree of sensitizer-dependent results but these results were apparently not viewed as congruent with the hot and cold triplet idea above. A notable observation was that the reaction of **13**, R=Ph, R'=R"=Me, saw improved yields when the ET was both increased and decreased from that of benzophenone.



13

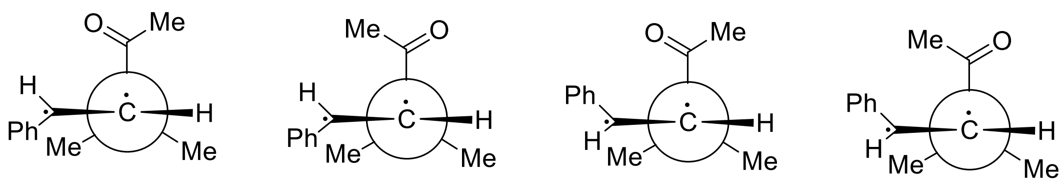
In a third paper,[136] Armesto and Ortiz observed sensitizer-dependent chemistry in competition between the oxa-di-π-methane reaction of **14** to afford **15** and its decarbonylation forming **16** (or isomers). The key observation was that the decarbonylation reaction was observed with a high-energy sensitizer (3-methoxyacetophenone, E_T = 71 kcal/mol) but not with a low-energy triplet sensitizer (4-phenylbenzophenone, E_T = 61 kcal/mol).



14 **15** oxa-di-π-methane **16** decarboxylation only observed with high-energy sensitizer

Of the systems studied in the three papers, we view the results with **14** as most interesting because they fit with chemical intuition and a potentially straightforward physical explanation of the results in terms of the involvement of a “hot” triplet. The authors themselves at this point no longer referred to either the idea of hot triplets nor to any role for excess vibrational energy, but in the reactions of **14**, the possibility that decarbonylation is promoted by vibrational excitation of the triplet **14** on formation seems at least physically plausible and worth future exploration. In contrast, bluntly, we could not discern any simple physical explanation for the results with **9** and **13** that would relate vibrational excitation to the experimental observations. The complete lack of oxa-di-π-methane product from **9** with the highest-energy sensitizer seems particularly difficult to ascribe to a vibrationally activated intermediate.

In all of these systems, a number of potential complications and study limitations hamper the interpretation of the results. At one level, a more quantitative approach than the simple reporting of yields after a set irradiation time would have aided in the analysis of the data. On a different level, a substantial issue is that these acyclic structures are conformationally rich. The singlet ground state of **9** has three available conformations within 0.5 kcal/mol (ω-B97XD/6-31+G**) and these can give rise to a total of four conformations of the triplet of **9**, **17** – **20**. Considering that the conventional explanation of triplet sensitizer-dependent chemistry is the formation of differing mixtures of excited state conformers (see reference 4a in the main text), it is surprising that this issue was apparently not considered in the original work. (One advantage in the choice of benzobarrelene in the current study was the absence of the complication of multiple ground-state conformations.)



17 **18** **19** **20**

Overall, it remains possible that the work of Armesto and Ortiz exhibits the effects of vibrationally excited triplets due to varying sensitizer energies seen in the current paper, but the series of papers on this issue ended up with the authors no longer asserting this, and further work would be required to assess the proposal.

3.9.3. The Triplet Energy of 1

Zimmerman, Amick, and Hemetsberger[130] had reported a triplet energy for benzobarrelene of 79.3 kcal/mol. This is based on the phosphorescence spectrum, as described in the thesis of one of the authors[137] without experimental details. From experiments alone, this value would be very surprising since acetophenone (E_T = 73.3 kcal/mol) is a highly efficient sensitizer for the reaction ($\Phi \sim 0.5$). In addition, in the similar dibenzobarrelene case acetone (E_T = 81.2 kcal/mol) and acetophenone transfer their energy at nearly identical rates.[128] (We note that it is experimentally difficult to obtain benzobarrelene in analytically pure form, and impurities are a conventional source of error in phosphorescence spectra. The absence of experimental details makes this possibility difficult to assess.)

Computationally, the E_T predicted from a series of ab initio composite methods in addition to DLPNO-CCSD(T)/aug-cc-pVTZ//ω-B97XD/6-31+G** calculations is show in Table 3.9. The range of results from these methods is notably large, but all fall much lower than the reported value. It should be noted that these composite methods are highly accurate in their prediction of E_T for acetone (G3 and G3B3 methods find 81.2 and 80.9 kcal/mol, compared to the experimental 81.2 kcal/mol.

For the work in the main text, we have taken the E_T as being ~69 kcal/mol, in line with the lowest-energy sensitizer that promotes the reaction and the average of the computational values. However, a range of ET's within ±3 kcal/mol of this value would make no meaningful difference in the results. For example, the predicted RRKM KIE at a vibrational energy of 10.0 kcal/mol in place of the 13.0 kcal/mol value used in the main text changes to 1.033 from the original 1.031.

Table 3.9. Energies of singlet and triplet benzobarrelene from *ab initio* methods.

Method	multiplicity	E + zpe	E(T)
G1	singlet	-462.350615	
	triplet	-462.234776	72.7
G2	singlet	-462.349055	
	triplet	-462.23463	71.8
G2MP2	singlet	-462.340566	
	triplet	-462.225783	72.0
G3	singlet	-462.889516	
	triplet	-462.778494	69.7
G3B3	singlet	-462.900046	
	triplet	-462.791075	68.4

G3MP2	singlet	-462.441296	
	triplet	-462.329397	70.2
G4	singlet	-462.973157	
	triplet	-462.867682	66.2
G4MP2	singlet	-462.494014	
	triplet	-462.388515	66.2
DLPNO-CCSD(T)/aug-cc-pVTZ	singlet	-462.217392	
+ zpe from ω-B97XD/6-31+G**	triplet	-462.110365	67.2

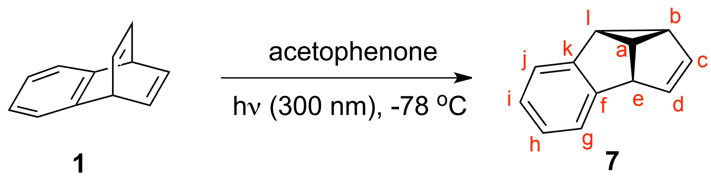
3.10. Experimental Procedures

3.10.1. General Methods

Benzobarrelene (**1**) was prepared as described by Hales[138] and used in each case within one week of preparation. All other chemicals were used as commercially available. The photochemical reactions were conducted in a Rayonet Photochemical Reactor equipped with RPR-3000Å lamps. The internal temperature of reactions was monitored internally using a digital thermometer, and the temperatures reported reflect an approximate average temperature within ~± 5 degrees. The 300 K temperature was obtained using a fan to cool the Rayonet.

3.10.2. Di-π-methane Rearrangements of 1

3.10.2.1. Acetophenone-Sensitized Reaction at 200 K



A mixture of 1.0 g (6.5 mmol) of freshly prepared **1** and 7.8 g (65 mmol) of acetophenone was prepared in 300 mL of anhydrous diethyl ether. The mixture was placed in a 500-mL Pyrex® bottle equipped with a cold finger (see Figure 3.7). The reaction mixture was added to the external container with dry ice /acetone filled in the inner container. The reaction was irradiated by 300 nm light while at -70 ºC until 75% conversion was reached based on ^{1}H NMR analysis of an aliquot. This required ~10-12 h. The reaction mixture was concentrated on a rotary evaporator, and most of the acetophenone was then removed by vacuum distillation (60 ºC, 1.3 Torr). The crude benzosemibullvalene product (**7**) was further purified on a 20 mm by 400 mm basic alumina column using petroleum ether as eluent to afford 312 mg (31%) of **7**. The ^{1}H and ^{13}C NMR spectra were in accord with previous report,[103] and the important peak assignments were confirmed based on HSQC spectra.

^{1}H NMR ($CDCl_3$, 500 MHz): 7.20-7.10 (m, 2H), 6.94-6.87 (m, 2H), 5.62 (ddd, J = 5.1, 2.2, 0.57 Hz, 1H), 5.23 (dd, J = 5.1, 2.5 Hz, 1H), 3.92 (dd, J = 6.3, 2.3 Hz, 1H), 3.3 (qd, J = 6.3, 0.57 Hz), 3.1 (t, J = 6.6 Hz, 1H), 2.7 (td, J = 6.6, 0.44 Hz, 1H)

^{13}C NMR (CDCl3, 125 MHz): 150.1 (f / k), 137.1 (f / k), 135.5 (d), 126.0 (h / i), 125.2 (h / i), 125.1 (g), 121.0 (c), 120.8 (j), 53.8 (e), 47.7 (a), 39.6 (b), 37.4 (l).

Of note, the relative positions of carbons c and j change with solvent: ^{13}C NMR (acetone-D_6, 125 MHz): 150.4 (f / k), 137.5 (f / k), 135.7 (d), 126.0 (g / h / i), 125.3 (g / h / i), 125.2 (g / h / i), 121.1 (j), 120.9 (c), 53.9 (e), 47.9 (a), 39.7 (b), 37.5 (l).

Figure 3.7. Experimental set-up for low temperature photolysis.

3.10.2.2. Acetone-Sensitized Reaction at 200 K

A mixture of 1.0 g (6.5 mmol) of 1 in 20 mL of acetone was added to a 30-cm × 1-cm quartz tube. The reaction mixture was cooled in a dry ice / isopropanol bath in a 30-cm × 10-cm quartz tube. The reaction was irradiated by 300 nm light while at -70 ºC until 75% conversion was reached based on ^{1}H NMR analysis of an aliquot. This required ~25-30 h. The reaction mixture was concentrated on a rotary evaporator. The residue was chromatographed on a 20 mm by 400 mm alumina column using petroleum ether as eluent to afford 478 mg (48%) of **7**.

3.10.2.3. Acetophenone-Sensitized Reaction at 300 K

A mixture of 1.0 g (6.5 mmol) of 1 and 7.8 g (65 mmol) of acetophenone in 20 mL of anhydrous diethyl ether was added to a 30-cm by 1-cm quartz tube. The reaction was irradiated by 300 nm light until 75% conversion was reached based on ^{1}H NMR analysis of an aliquot. This required 5 h. The reaction mixture was concentrated on a rotary evaporator and vacuum distilled to remove most of the acetophenone (60 ºC, 1.3 Torr). The residue was chromatographed on a 20 mm by 400 mm alumina column using petroleum ether as eluent to afford 291 mg (29%) of **7**.

3.10.2.4. Acetone-Sensitized Reaction at 300 K

A mixture of 1.0 g (6.5 mmol) of **1** in 20 mL of acetone was placed in a 30-cm by 1-cm quartz tube and was irradiated with 300 nm light until 75% conversion measured by ^{1}H NMR, which took 3 days. The reaction mixture was concentrated on a rotary evaporator to remove acetone. The residue was chromatographed on a 20 mm by 400 mm alumina column using petroleum ether to afford 267 mg (27%) of **7**.

3.10.2.5. Methyl-Benzoate Sensitized Reaction at 300 K

A 1.0 g (6.5 mmol) of **1** was dissolved in 20 mL of methyl benzoate in a 30-cm by 1-cm quartz tube. The reaction was irradiated by 300 nm light until 75% conversion was reached based on ^{1}H NMR analysis of an aliquot. Because of minimal absorption of the nominally 300 nm light, this required 21 days. Most of the methyl benzoate was then removed by vacuum distillation (80 ºC, 1.3 Torr), and the crude benzosemibullvalene product (**7**) was chromatographed through a 20 mm by 400 mm alumina column using petroleum ether as eluent to afford 353 mg (35%) of **7**.

3.11. Computational Procedures

3.11.1. General Procedures

The calculations of DFT or MP2 structures, energies, and frequencies employed default procedures in Gaussian16[139] unless otherwise noted. CASSCF+NEVPT2 and DLPNO-CCSD(T) energies were calculated using ORCA 4.0.1.[140] Calculations of KIEs including small-curvature tunneling (SCT) employed the GAUSSRATE / POLYRATE set of programs.[67,124] Complete structures and energetics are provided in sections below, as well as additional details on the calculations and relevant program input files. All absolute energies are in Hartrees. All relative energies are presented in kcal/mol.

Calculations of trajectories employed the program suite PROGDYN. PROGDYN consists of a series of component programs written as either Unix shell scripts or awk programs. Gaussian16 was used to calculate the forces at each point in trajectories. A detailed description of PROGDYN's subprograms, inputs and outputs can be found in the Supporting Information for a recent paper[141] A full listing of the subprograms of PROGDYN can be found as a permanent public dataverse set at:

https://dataverse.harvard.edu/dataset.xhtml?persistentId=doi:10.7910/DVN/TQZR7E.

A later section contains PROGDYN usage details and configuration parameters.

Calculations of KIEs based on RRKM microcanonical rate constants made use of the QCPE RRKM program. A complete description of the theory and parameters used in the program can be found in https://cdssim.chem.ttu.edu/RRKM/Doc/RRKM_manual.pdf.

3.11.2. Computational Methods Validation Studies

To explore the accuracy of computational methods for the di-π-methane rearrangement, a series of structures were first optimized in gas-phase unrestricted ω-B97XD/6-31+G(d,p) calculations. Single-point energies for each of these structures were then calculated in DLPNO-CCSD(T)/aug-cc-pVTZ calculations, and the energetics were then calculated in a series of DFT calculations, as shown in Table 3.10 and Table 3.11. The ωB97xD/6-31+G(d,p) was chosen as the working optimization method based on it being closest to getting the relative energy of **anti-TS 3‡** versus **anti-2** compared to the DLPNO-CCSD(T) calculation. As the course of the research evolved, we opted to prefer the use of the CASSCF+NEVPT2/aug-cc-pVTZ calculations as a primary standard, but the ωB97xD/6-31+G(d,p) remained a good choice by this measure.

Table 3.10 DFT methods exploration based on **anti TS 3‡.** All structures are calculated based on ω-B97XD/6-31+G** optimized structures.

Method	Basis set	anti-2	anti-TS 3‡	ΔE (kcal/mol)
DLPNO-CCSD(T)	aug-cc-pVTZ	-462.2902453	-462.2834899	4.2
M062X	6-31+G*	-462.9354833	-462.9259711	6.0
M062X	6-311+G**	-463.0541951	-463.0456957	5.3
B3LYP	6-311+G**	-463.2535836	-463.2481255	3.4
ωB97xD	6-31+G**	-462.2906565	-462.2839465	4.2
ωB97xD	6-311+G**	-463.0916214	-463.085059	4.1
B3PW91	6-311+G**	-463.0768334	-463.0728114	2.5
mPW-PW91	6-311+G**	-463.1862855	-463.1850827	0.8
mPW1PW91	6-311+G**	-463.1495836	-463.1450156	2.9
TPSSTPSS	6-311+G**	-463.3428364	-463.3402876	1.6
X3LYP	6-311+G**	-463.0256911	-463.0200753	3.5
BMK	6-311+G**	-462.9172207	-462.9127703	2.8
CAM-B3LYP	6-311+G**	-462.9820031	-462.9744447	4.7
PBE-PBE	6-311+G**	-462.6482521	-462.6476336	0.4
HSEH1PBE	6-311+G**	-462.7402267	-462.735966	2.7
B-VP86	6-311+G**	-463.2710588	-463.2696253	0.9
APFD	6-311+G**	-462.8700168	-462.8658807	2.6
HCTH407	6-311+G**	-463.1904571	-463.1889651	0.9
S-VWN	6-311+G**	-460.590683	-460.5945364	-2.4
TPSSh	6-311+G**	-463.2957222	-463.2920062	2.3
LC-wPBE	6-311+G**	-462.9151693	-462.9072067	5.0
B3P86	6-311+G**	-464.7332953	-464.7295526	2.3
HISSbPBE	6-311+G**	-462.7264665	-462.72017	4.0
tHCTHhyb	6-311+G**	-463.1768547	-463.1733083	2.2

Table 3.11. DFT methods exploration of **syn-TS 3‡.** All structures are calculated based on ω-B97XD/6-31+G** optimized structures.

Method	Basis set	syn-TS 3‡	anti-TS 3‡	ΔE (kcal/mol)
DLPNO-CCSD(T)	aug-cc-pVTZ	**-462.2902453**	**-462.2834899**	4.2
ω-B97XD	6-31+G**	-463.0081911	-463.006917	0.8
M062X	6-31+G**	-462.954579	-462.9540112	0.4
B3LYP	6-31+G**	-463.1693071	-463.1660178	2.1
HSEH1PBE	6-31+G**	-462.6621335	-462.6601135	1.3
OHSE2PBE	6-31+G**	-463.5415243	-463.5395733	1.2
OHSE1PBE	6-31+G**	-462.6630647	-462.6610457	1.3
LC-wPBE	6-31+G**	-462.8286308	-462.8303456	-1.1
CAM-B3LYP	6-31+G**	-462.8920554	-462.890931	0.7
M11	6-31+G**	-462.8535767	-462.853886	-0.2
N12SX	6-31+G**	-462.970874	-462.9687706	1.3
MN12SX	6-31+G**	-462.7851532	-462.7821505	1.9
B3P86	6-31+G**	-464.6520775	-464.6493496	1.7
B3PW91	6-31+G**	-462.9972218	-462.9946935	1.6
B1B95	6-31+G**	-462.9529615	-462.9500972	1.8
mPW1PW91	6-31+G**	-463.0698308	-463.0679586	1.2
mPW1LYP	6-31+G**	-462.9044088	-462.9015957	1.8
mPW1PBE	6-31+G**	-462.8900084	-462.8881733	1.2
mPW3PBE	6-31+G**	-462.8480855	-462.8455462	1.6
B98	6-31+G**	-462.9762579	-462.9731419	2.0
B971	6-31+G**	-463.0335345	-463.0302556	2.1
B972	6-31+G**	-463.0071533	-463.0039882	2.0
PBE1PBE	6-31+G**	-462.6241662	-462.62224	1.2
LC-wHPBE	6-31+G**	-462.8275208	-462.8292353	-1.1
MN15	6-31+G**	-462.5907851	-462.5882483	1.6
PBE0	6-31+G**	-462.6230102	-462.6230102	0.0
BMK	6-31+G**	-462.836914	-462.8344204	1.6

LC-mPWLYP	6-31+G**	-461.7209061	-461.722286	-0.9
LC-UBLYP	6-31+G**	-461.714446	-461.7158307	-0.9
LC-BRxPL	6-31+G**	-464.0770462	-464.0783319	-0.8

The LC-mPWLYP/6-31+G** calculations require some particular comment. As we note in a previous section, the CASSCF+NEVPT2/aug-cc-pVTZ calculations predict that the lowest barrier from **anti-2** to **4** is via **anti-TS 3‡.** This was true of LC DFT methods, though most DFT calculations predict the opposite (Table 3.11). Because the LC-mPWLYP/6-31+G** calculations get this aspect of the surface right, we explored them in more detail and carried out KIE calculations with them. Those are retained for the main text, but the LC-mPWLYP/6-31+G** calculations appear to overestimate the barrier for **anti-TS 3‡** leading to an overestimate of tunneling and the predicted KIE.

There is little polarity in **anti-2**; its B3LYP/6-31+G** dipole moment is within 2% of that for **1**, and the barrier ω-B97XD/6-31+G** barrier for passing over **anti-TS 3‡** was decreased by only 0.1 kcal/mol employing a PCM solvent model.

3.12. Conclusion

The much-sought promotion of specific reactions in complex molecules by direct vibrational excitation has historically proven daunting, in part due to the rapidity of vibrational energy redistribution and in part due to the large barriers that stable ground-state molecules must overcome for reaction. In contrast, the idea that direct photochemical excitation leads to excited states that include vibrational excitations that influence subsequent reactions is well established.[142,143] The results here support the viability of an indirect process for vibrational activation, one that is not limited by chromophores and that is potentially controllable by the choice of sensitizer. This suggests new opportunities for controlling and driving photochemical reactions, along with the study of localized vibrational effects on reactions, which we intend to pursue.

4. CONCLUSION

Integrating experimental ^{13}C KIEs, physical organic techniques, and theoretical calculations, mechanisms for important of photochemical induced organic reactions were elucidated. The mechanisms of photoredox reaction are intrinsically complicated, which involving multiple electron transfer processes. The intermolecular ^{13}C KIEs obtained from natural abundance approach cannot be fully explained by any simple coordination models. Therefore, an alternative slow electron transfer model is proposed, where the rate of the electron exchange between activated and neutral enones competes with the bond-forming rate at the first irreversible step. This idea is supported both by competition kinetic study and by several computational methodologies. The mechanistic model provides a new opportunity to engineer the stereochemical outcomes of the photoredox reactions. In the future of our study, we continue to extend the mechanistic study on radical cation mediated [2 + 2]-cycloaddition of redox-tag promoted alkenes.

Typical primary ^{13}C KIEs fall within the range of 1.010 ~ 1.060. Reactions with significant heavy-atom tunneling effect may go beyond this range. In the di-π-methane rearrangement of benzobarrelene, the intramolecular KIE can be as high as 1.138 sensitized by acetophenone at 200 K, indicating significant heavy-atom tunneling involved in this reaction. However, using triplet photosensitizers with higher energies such as acetone and methyl benzoate, the KIEs were found largely decrease away from tunneling effects models to only 1.037 at 300 K. This suggests nonstatistical dynamic effect may be involved in this reaction. The RRKM predicted a 1.030 as the lower-limit for the KIE on the extreme of full dynamic effect, in line with the trend of experimental KIEs. Furthermore, quasiclassical trajectory studies show that decent amount of the trajectories undergoes slow intramolecular vibrational relaxation relative to the chemical events, leading to nonstatistical dynamic effects. Structures with elongated C-C bond length at the triplet diradical center promotes the reaction by an extra ~15% of the total trajectories within 350 fs. The changes in the selectivity from different photosensitizers are not predictable from classical rate theories as the qualitative arrow-pushing mechanisms are not changed. This study not only provides a new concept in the fundamentals of organic chemistry but also demonstrates a potential strategy to engineer chemoselectivity from sensitizers.

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A. APPENDIX A

A.1. Photoredox-Promoted [2 + 2]-Cycloaddition of Enones

A.1.1. Intermolecular ^{13}C NMR KIE Methods and Integration Results

A.1.1.1. NMR Details for KIE Measurements

NMR samples of 200 mg of recovered **21** or **22** at certain conversions in 5 mm NMR tubes that were filled to a constant height of 5 cm with $CDCl_3$. The ^{13}C spectra were recorded at 125.70 MHz using inverse gated decoupling. The acquisitions used a 160 s (**1**) or a 125 s (**2**) delay between calibrated π/2 pulses and a 7.55 s (for both **1** and **2**) acquisition time to collect 524288 points. Integrations were determined numerically using a macro. A zero-order baseline correction was generally applied, but to avoid any qualitative manipulation no first-order or higher-order baseline was ever applied. The integration of the measurement was determined by the average of all measurements. This integration was divided by the one from standards of the same compound not subjected to reaction taken from the same lot and from the same NMR parameters.

A.1.1.2. Calculation of KIEs and Errors

The isotope effects were calculated from the average adjusted integrations divided by the 1000 value assigned to para carbon (S1) or methyl carbon (S2). The 95% confidence ranges were calculated from the standard deviations and number of measurements in a normal way (See: http://www.iupac.org/publications/analytical_compendium/Cha02sec3.pdf).

A.1.1.3. Crude Integration Values for KIE Measurements

A.1.1.3.1. Photodimerization of phenyl vinyl ketone (1)

recovered S1, 85% conversion, sample 1								
	spectrum							
position	**1**	**2**	**3**	**4**	**5**	**6**	**Average**	**σ**
carbonyl	996.169	998.854	995.868	997.734	998.2	997.797	997.437	1.2
ipso	990.537	990.655	991.696	989.756	990.793	989.945	990.5637	0.7
para	1000	1000	1000	1000	1000	1000	1000	0.0
meta	1952.16	1953.1	1953.4	1952.12	1943.57	1945.92	1950.043	4.2
ortho	2044.38	2047.98	2046.39	2050.22	2048.31	2045.71	2047.162	2.1
alpha	1020.19	1022.14	1021.29	1021.34	1020.4	1018.48	1020.641	1.3
beta	1025.45	1028.74	1027.11	1030.97	1028.57	1030.23	1028.512	2.0

sample 1, standard								
	spectrum							
position	**1**	**2**	**3**	**4**	**5**	**6**	**Average**	**σ**
carbonyl	1003.42	1001.68	996.758	1003.31	1001.6	1000.62	1001.23	2.4
ipso	997.055	994.468	990.754	998.26	997.142	993.775	995.2423	2.8
para	1000	1000	1000	1000	1000	1000	1000	0.0
meta	1938.88	1938.76	1935.84	1946.41	1936.56	1934.1	1938.424	4.3
ortho	2027.1	2019.64	2012.59	2022.33	2020.13	2018.18	2019.996	4.8
alpha	1013.55	1014.44	1010.9	1020.68	1015.47	1014.04	1014.846	3.2
beta	984.361	983.534	982.373	989.027	984.097	984.22	984.602	2.3

recovered S1, 60% conversion, sample 2								
	spectrum							
position	**1**	**2**	**3**	**4**	**5**	**6**	**Average**	**σ**
carbonyl	980.296	983.588	982.088	979.201	980.95	982.843	981.4943	1.6

ipso	986.473	990.776	987.782	983.103	986.477	989.595	987.3677	2.7
para	1000	1000	1000	1000	1000	1000	1000	0.0
meta	2019.39	2026.3	2022.86	2014.32	2025.26	2022.54	2021.778	4.4
ortho	2022.65	2025.77	2025.2	2018.59	2025.05	2022.38	2023.271	2.7
alpha	1003.86	1005.89	1008.73	1001.65	1006.53	1003.72	1005.064	2.5
beta	1000.59	1006.17	999.266	997.452	999.675	998.692	1000.307	3.1

sample 2, standard								
	spectrum							
position	**1**	**2**	**3**	**4**	**5**	**6**	**Average**	**σ**
carbonyl	979.425	979.513	977.941	982.271	981.365	981.024	980.2565	1.6
ipso	986.96	987.79	985.146	987.524	988.655	986.568	987.1072	1.2
para	1000	1000	1000	1000	1000	1000	1000	0.0
meta	2014.61	2016.84	2015.94	2016.75	2018.99	2014.41	2016.256	1.7
ortho	2024.25	2022.54	2021.48	2025.98	2028.32	2022.21	2024.132	2.6
alpha	1001.79	1006.85	1004.49	1002.63	1005.15	999.115	1003.337	2.7
beta	980.649	976.44	977.604	977.772	977.076	978.421	977.9937	1.5

A.1.1.3.2. Photocycloaddition between phenyl propanone (5) and methyl vinyl ketone (6)

recovered **S2**, 92% conversion, sample 1								
	spectrum							
position	**1**	**2**	**3**	**4**	**5**	**6**	**Average**	**σ**
carbonyl	1035.85	1037.59	1036.2	1027.56	1035.62	1020.01	1032.138	6.9
ipso	988.964	993.653	998.978	980.178	993.671	980.482	989.321	7.7
para	1003.09	1003.91	1000.44	995.048	1001.97	992.904	999.559	4.5
meta	2126.44	2129.23	2124.73	2120.05	2134.69	2122.01	2126.192	5.3
ortho	1994.12	1996.28	1989.94	1975.43	1986.6	1976.32	1986.449	8.9

alpha	988.927	976.66	981.742	973.539	984.62	972.746	979.7057	6.5
beta	999.867	1002.09	998.66	996.354	1013.95	999.695	1001.77	6.3
methyl	1000	1000	1000	1000	1000	1000	1000	0.0

sample 1, standard

	spectrum							
position	**1**	**2**	**3**	**4**	**5**	**6**	**Average**	**σ**
carbonyl	1008.03	1002.58	1005.82	1006.01	1003.98	1006.42	1005.474	1.9
ipso	993.014	994.203	990.411	990.908	993.017	990.434	991.9978	1.6
para	995.102	988.573	992.212	994.07	993.15	993.418	992.7542	2.3
meta	2000.89	1998.06	1998.04	2000.04	1999.73	2003.29	2000.005	2.0
ortho	1960.85	1953.36	1955.9	1957.02	1957.16	1958.32	1957.103	2.5
alpha	983.592	980.88	983.779	975.201	986.996	979.773	981.7035	4.1
beta	968.62	973.611	973.691	971.241	973.049	975.555	972.6278	2.4
methyl	1000	1000	1000	1000	1000	1000	1000	0.0

recovered **S2**, 70% conversion, sample 2

	spectrum							
position	**1**	**2**	**3**	**4**	**5**	**6**	**Average**	**σ**
carbonyl	1033.01	1031.03	1031.24	1037.8	1032.19	1034.9	1033.362	2.6
ipso	987.153	986.108	983.11	994.753	985.673	991.393	988.0317	4.3
para	1028.57	1023.24	1015.57	1028.31	1024.44	1020.88	1023.5	4.9
meta	2113.5	2105.84	2107.74	2113.96	2104.21	2106.37	2108.604	4.1
ortho	2005.95	2002.93	1994.35	2011.14	1994.71	1979.96	1998.172	11.0
alpha	983.414	980.772	982.122	989.674	981.945	987.069	984.166	3.5
beta	980.175	981.713	977.479	982.045	981.961	977.177	980.0917	2.2
methyl	1000	1000	1000	1000	1000	1000	1000	0.0

sample 2, standard								
	spectrum							
position	**1**	**2**	**3**	**4**	**5**	**6**	**Average**	**σ**
carbonyl	1008.89	1006.34	1002.28	1004.33	1009.35	1007.27	1006.409	2.7
ipso	995.215	991.351	990.166	993.526	993.842	991.287	992.5645	1.9
para	998.434	995.324	995.911	999.564	999.195	999.661	998.0148	1.9
meta	2005.23	2007.32	1998.69	2000.49	2009.49	2005.24	2004.41	4.1
ortho	1989.35	1985.11	1975.95	1985.83	1985.64	1983.69	1984.262	4.5
alpha	991.143	990.739	988.709	991.202	993.258	990.898	990.9915	1.4
beta	971.645	969.52	971.586	967.805	972.688	969.611	970.4758	1.8
methyl	1000	1000	1000	1000	1000	1000	1000	0.0

recovered **S2**, 73% conversion, sample 3								
	spectrum							
position	**1**	**2**	**3**	**4**	**5**	**6**	**Average**	**σ**
carbonyl	1020.94	1023.49	1009.96	1013.85	1015.8	1017.12	1016.86	4.9
ipso	987.52	984.019	978.141	989.739	980.117	987.756	984.5487	4.6
para	978.825	975.881	965.909	967.017	970.539	968.838	971.1682	5.1
meta	2130.35	2127.48	2112.25	2115.57	2112.57	2107.94	2117.695	9.1
ortho	1997.52	1991.81	1977.71	1983.91	1985.88	1991.79	1988.103	7.0
alpha	982.761	977.266	963.579	975.959	972.797	968.51	973.4787	6.8
beta	983.497	980.005	965.966	978.684	977.488	977.089	977.1215	5.9
methyl	1000	1000	1000	1000	1000	1000	1000	0.0

sample 3, standard

	spectrum							
position	**1**	**2**	**3**	**4**	**5**	**6**	**Average**	**σ**
carbonyl	1016.72	1004.64	1010.67	1006.88	1003.25	1007.05	1008.201	4.9
ipso	997.683	979.079	987.278	987.016	985.003	982.25	986.3848	6.3
para	976.434	964.668	974.519	969.771	966.415	963.5	969.2178	5.3
meta	2018.75	1993.72	2013.1	2015.02	2007.1	2007.93	2009.269	8.8
ortho	1997.43	1978.38	1993.78	1985	1983.72	1980.64	1986.494	7.5
alpha	985.867	970.736	977.974	978.863	972.999	976.768	977.2012	5.3
beta	976.49	962.727	970.799	969.981	960.752	965.347	967.6827	5.8
methyl	1000	1000	1000	1000	1000	1000	1000	0.0

recovered **S2**, 66% conversion, sample 4

	spectrum							
position	**1**	**2**	**3**	**4**	**5**	**6**	**Average**	**σ**
carbonyl	984.471	986.529	991.582	988.151	987.888	982.518	986.8565	3.2
ipso	990.056	989.336	991.005	995.368	993.525	984.059	990.5582	3.9
para	997.752	1003.9	1010.1	1003.38	1000.85	996.803	1002.131	4.8
meta	2107.63	2117.53	2120.36	2120.17	2115.21	2107.59	2114.747	5.8
ortho	1958.81	1967.03	1965.89	1969.82	1962.64	1955.67	1963.311	5.3
alpha	982.786	986.568	979.612	988.629	980.93	978.977	982.917	3.9
beta	971.905	979.767	980.683	983.238	976.845	973.229	977.6112	4.4
methyl	1000	1000	1000	1000	1000	1000	1000	0.0

sample 4, standard

	spectrum							
position	**1**	**2**	**3**	**4**	**5**	**6**	**Average**	**σ**
carbonyl	995.66	992.849	993.186	992.664	992.385	992.397	993.1902	1.2

ipso	993.292	994.502	994.421	992.827	994.519	992.821	993.7303	0.8
para	986.942	983.652	986.021	982.792	987.414	987.247	985.678	2.0
meta	2065.14	2059.99	2064.6	2060.52	2062.58	2060.45	2062.213	2.3
ortho	1948.2	1945.63	1950.14	1943.44	1948.12	1943.31	1946.471	2.8
alpha	995.089	992.882	991.514	989.954	991.569	990.586	991.9323	1.8
beta	974.643	972.721	972.587	971.486	974.352	969.858	972.6078	1.8
methyl	1000	1000	1000	1000	1000	1000	1000	0.0

recovered **S2**, 82% conversion, sample 5

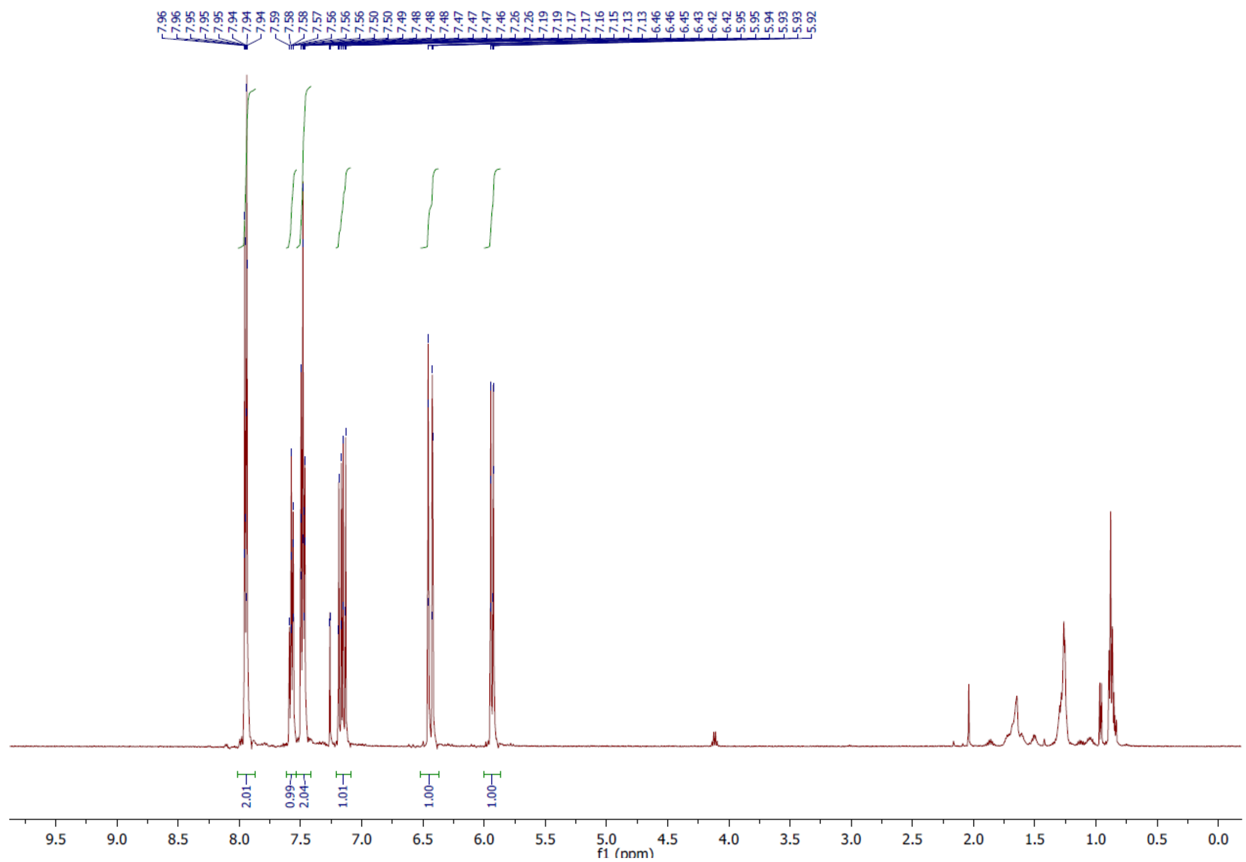
	spectrum							
position	**1**	**2**	**3**	**4**	**5**	**6**	**Average**	**σ**
carbonyl	1003.7	1007.94	998.129	1005.69	1003.71	1005.78	1004.158	3.3
ipso	956.562	960.611	957.42	960.814	960.118	958.956	959.0802	1.8
para	947.169	949.178	943.777	941.583	942.565	944.014	944.7143	2.9
meta	1972.78	1975.63	1964.09	1969.01	1968.44	1968.58	1969.756	4.0
ortho	1934.23	1941.06	1931.61	1935.71	1934.77	1935.76	1935.524	3.1
alpha	995.835	996.169	993.254	993.5	995.349	989.812	993.9865	2.4
beta	988.73	988.099	985.806	986.823	986.083	986.526	987.0112	1.2
methyl	1000	1000	1000	1000	1000	1000	1000	0.0

sample 5, standard

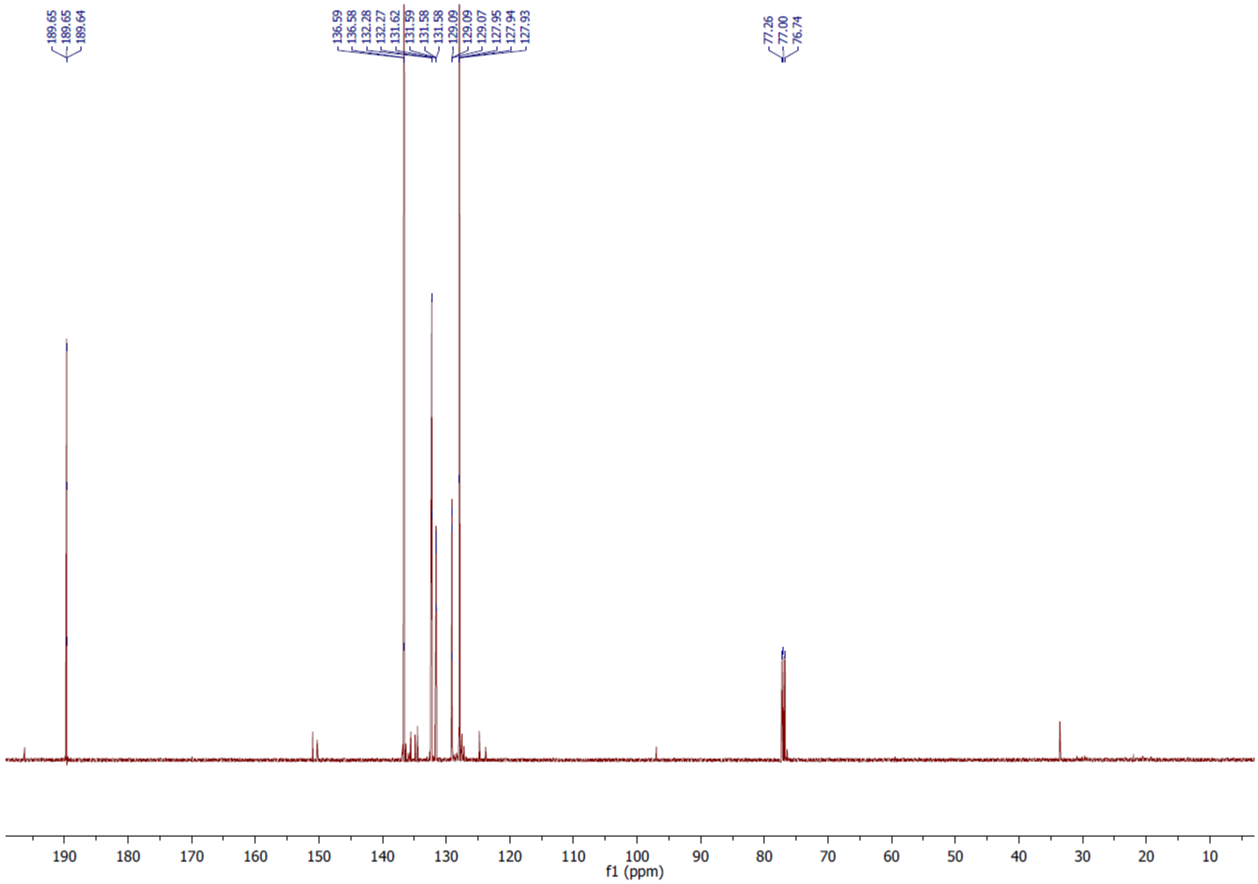
	spectrum							
position	**1**	**2**	**3**	**4**	**5**	**6**	**Average**	**σ**
carbonyl	1008.25	1009.96	1010.55	1010.47	1012.34	1008.56	1010.021	1.5
ipso	977.302	976.993	977.224	975.183	979.602	976.885	977.1982	1.4
para	954.077	955.553	956.009	951.794	958.415	954.41	955.043	2.2
meta	1935.9	1941.08	1940.32	1938.62	1942.99	1937.88	1939.464	2.5

ortho	1950.38	1953.62	1954.61	1950.08	1958.97	1951.42	1953.178	3.4
alpha	999.635	998.373	996.248	992.41	1001.04	998.223	997.6548	3.0
beta	975.146	976.197	973.938	974.709	977.791	976.399	975.6967	1.4
methyl	1000	1000	1000	1000	1000	1000	1000	0.0

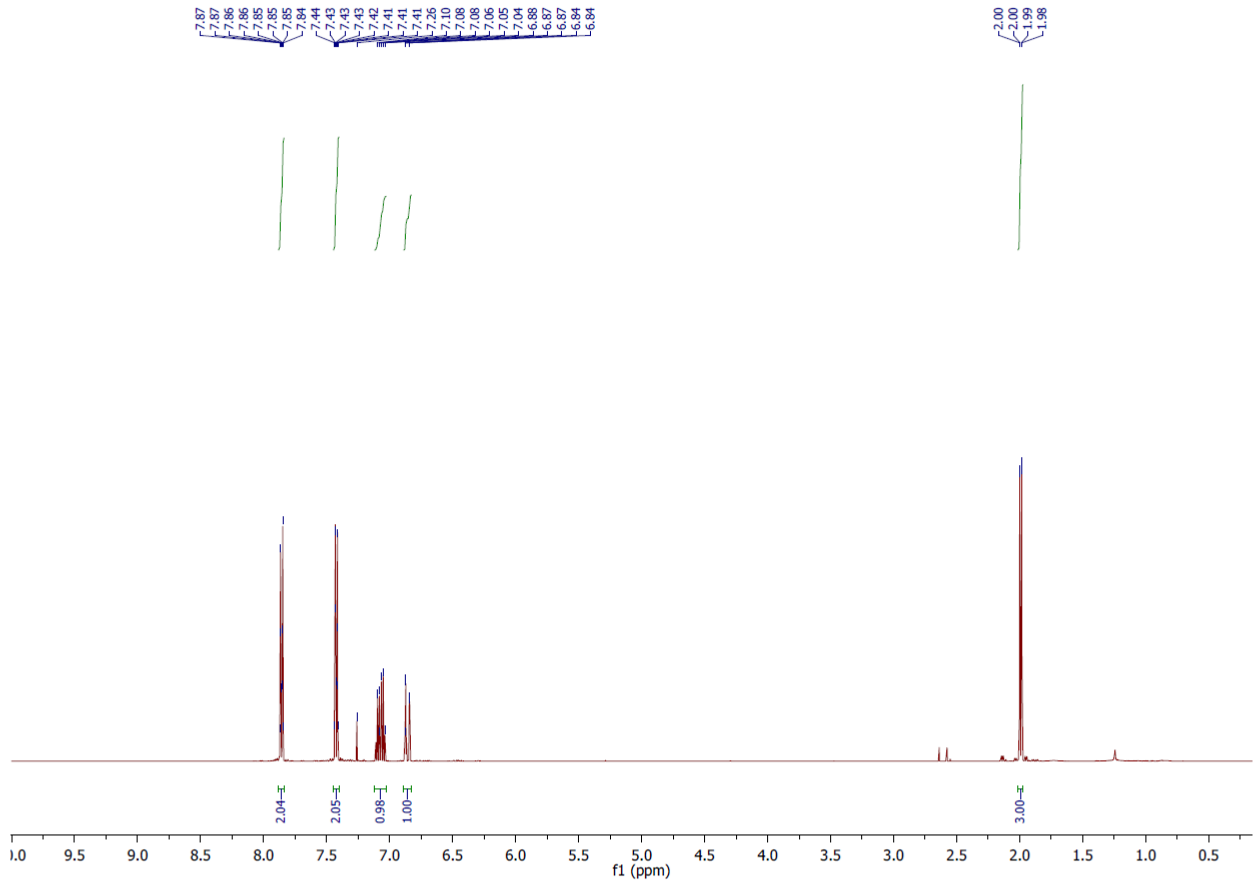
A.1.2. Phenyl vinyl ketone **(1)** – ^{1}H NMR (500 MHz, $CDCl_3$, full spectrum)



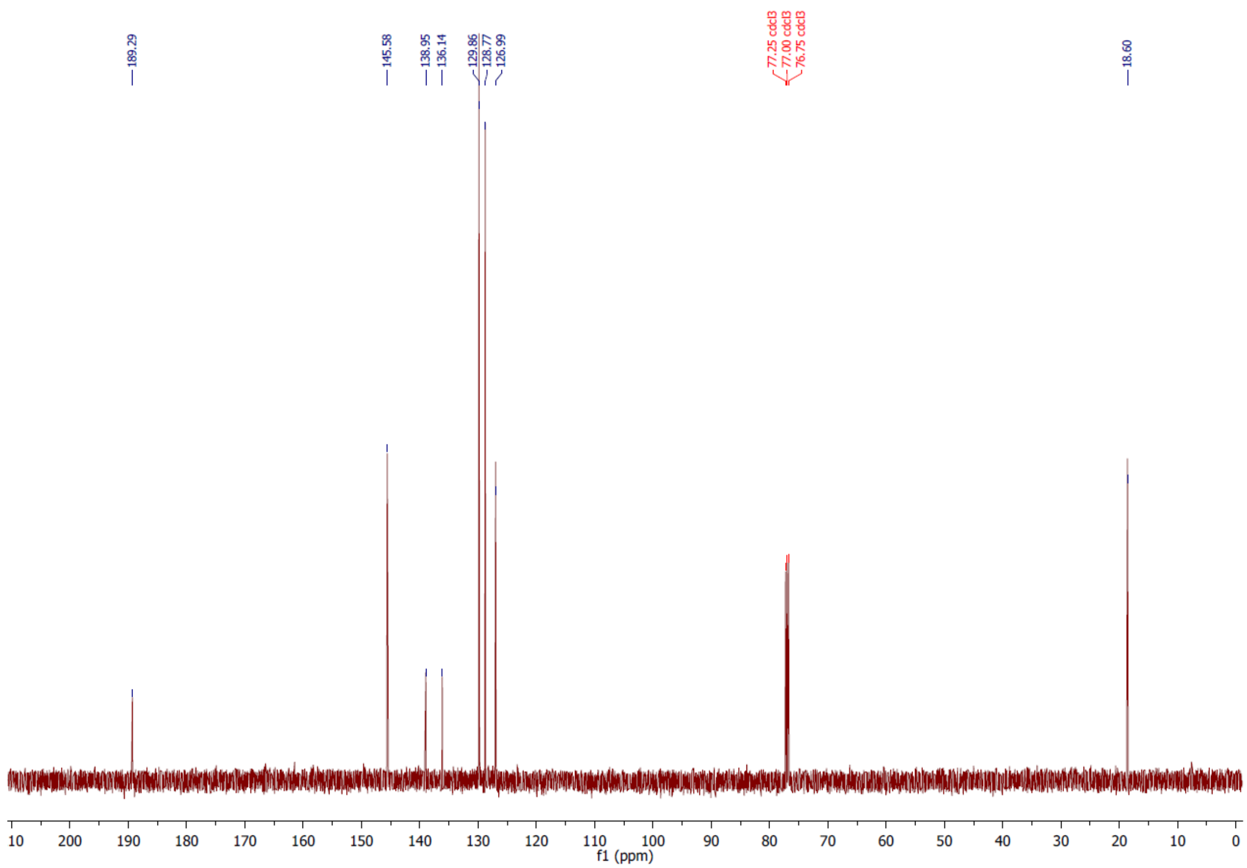
A.1.3. Phenyl vinyl ketone **(1)** – ^{13}C NMR (125 MHz, $CDCl_3$, full spectrum)



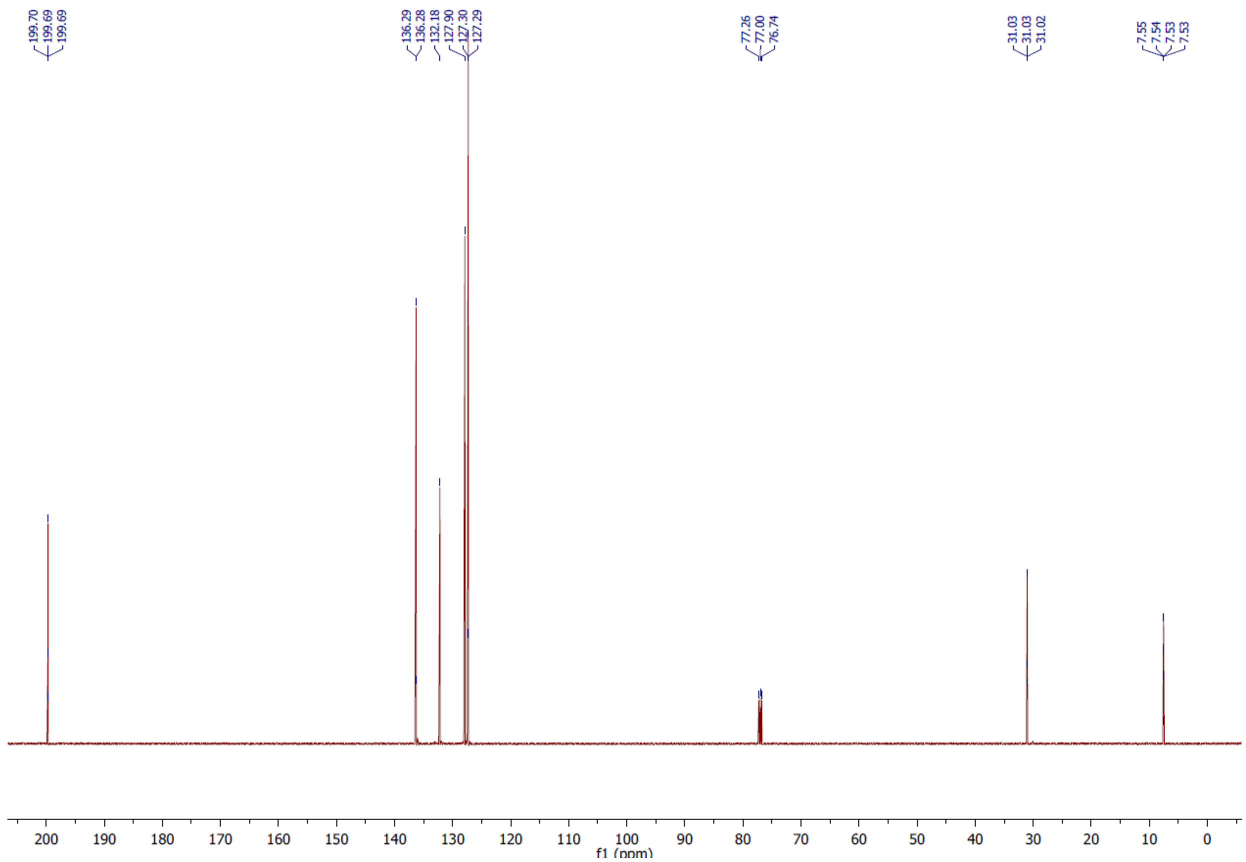
A.1.4. 4’-Chloro-1-phenylbut-2-en-1-one **(18)** – ^{1}H NMR (500 MHz, $CDCl_3$, full spectrum)



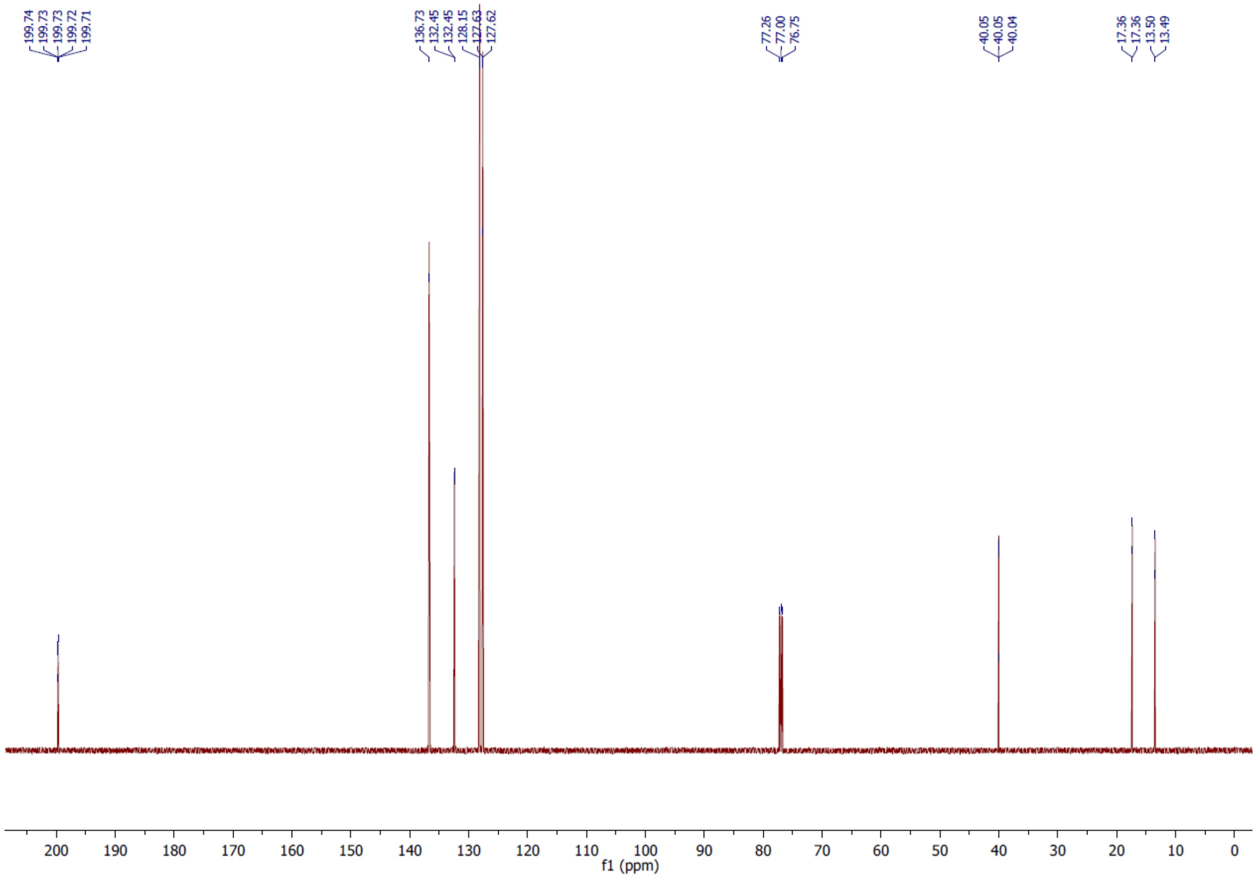
A.1.5. 4'-Chloro-1-phenylbut-2-en-1-one **(18)** – ^{13}C NMR (125 MHz, $CDCl_3$, full spectrum)



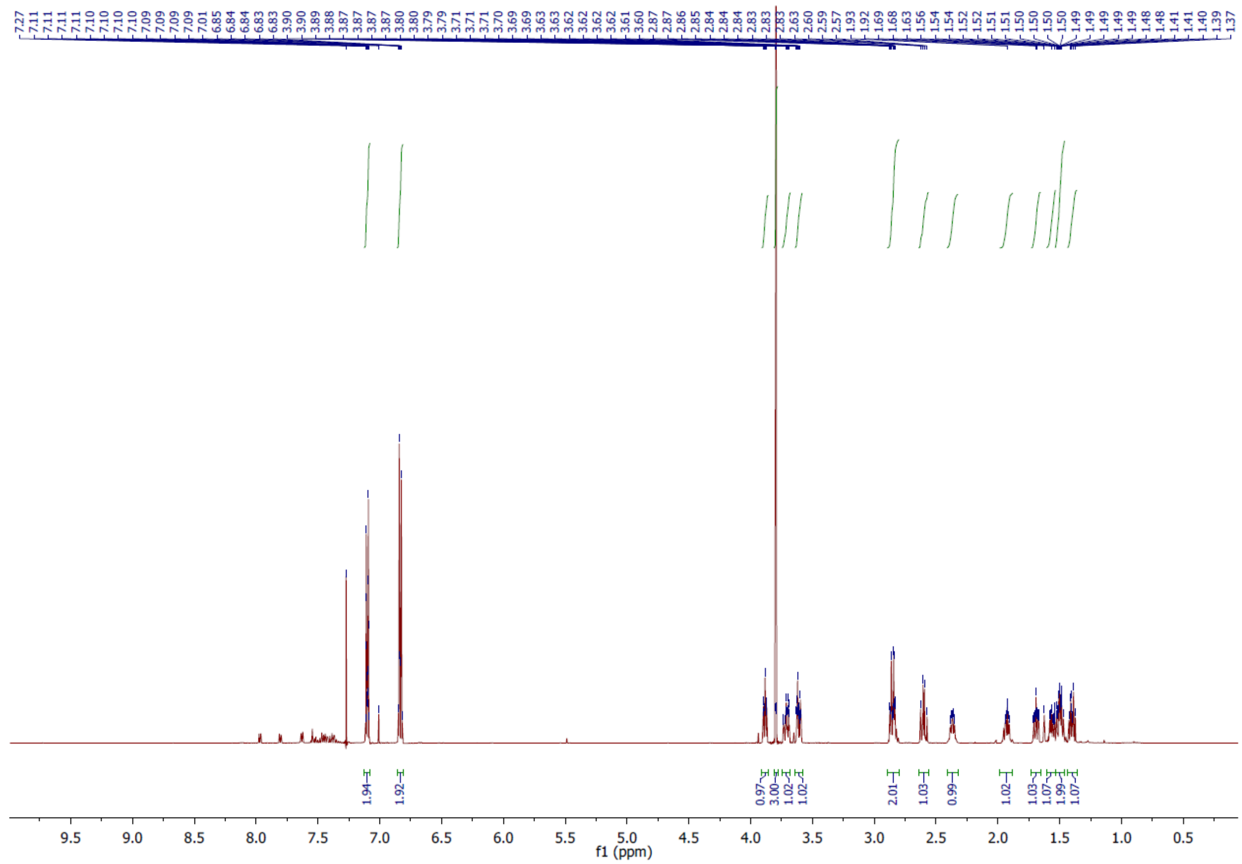
A.1.6. Propiophenone – ^{13}C NMR for KIEs (125 MHz, $CDCl_3$, Full Spectrum)



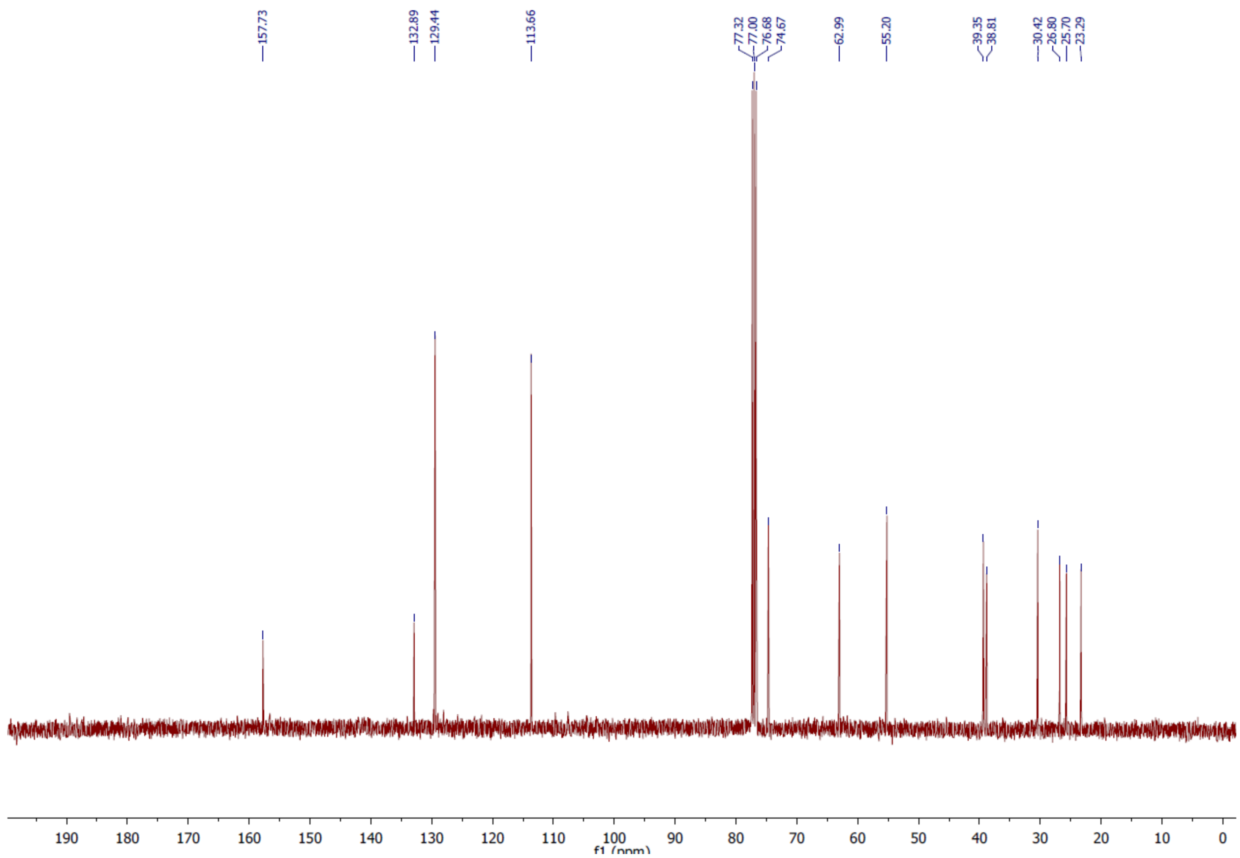
A.1.7. Butyrophenone – ^{13}C NMR for KIEs (125 MHz, $CDCl_3$, Full Spectra)



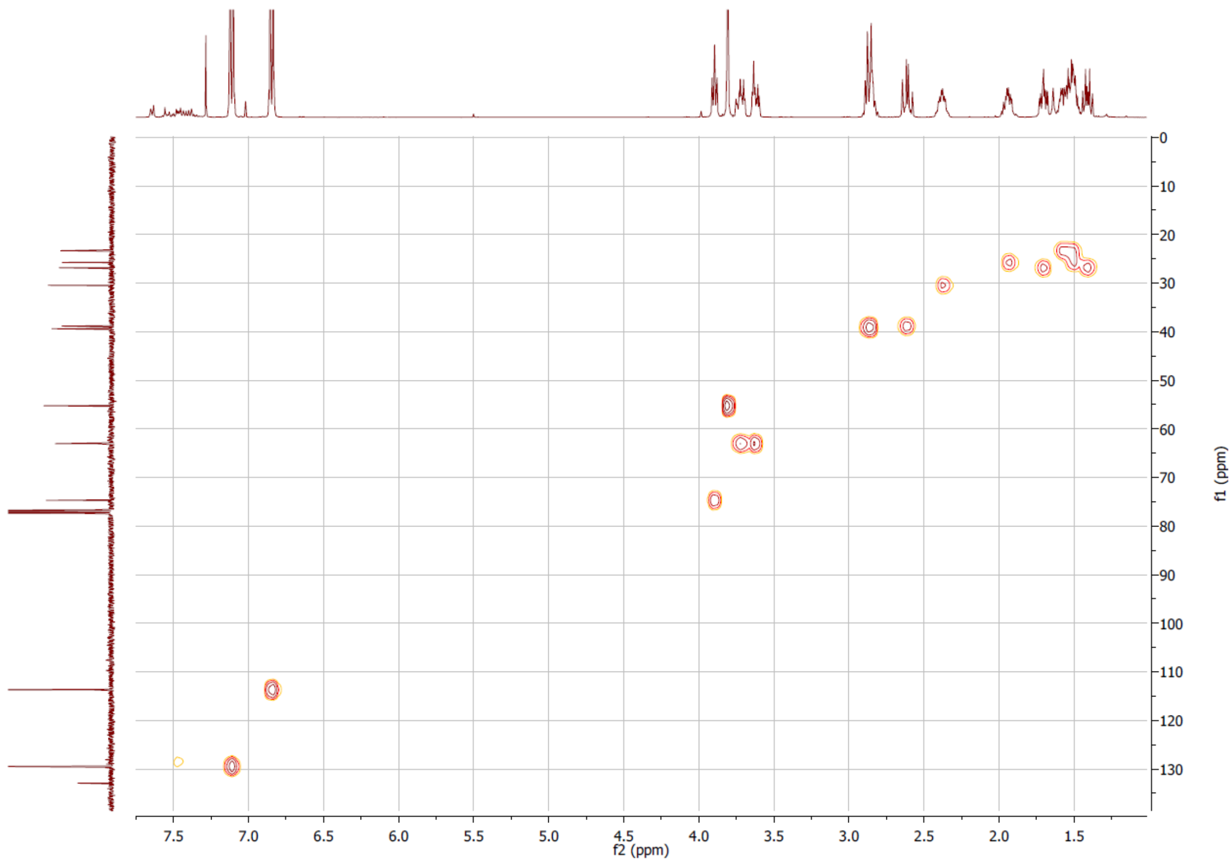
A.1.8. ***trans*-23** – ^{1}H NMR (500 MHz, $CDCl_3$)



A.1.9. *trans*-**23** – ^{13}C NMR (125 MHz, $CDCl_3$)

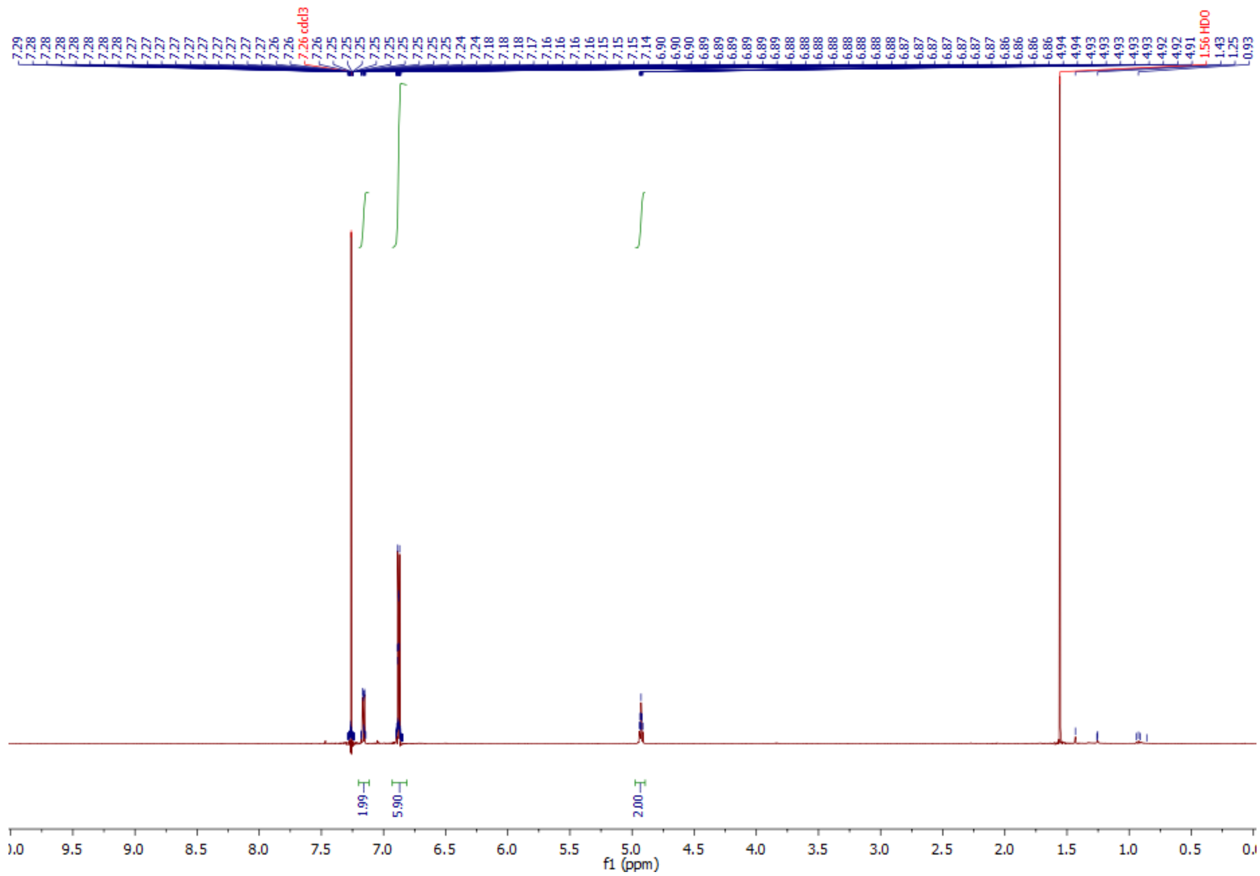


A.1.10. ***trans*-23** – HSQC

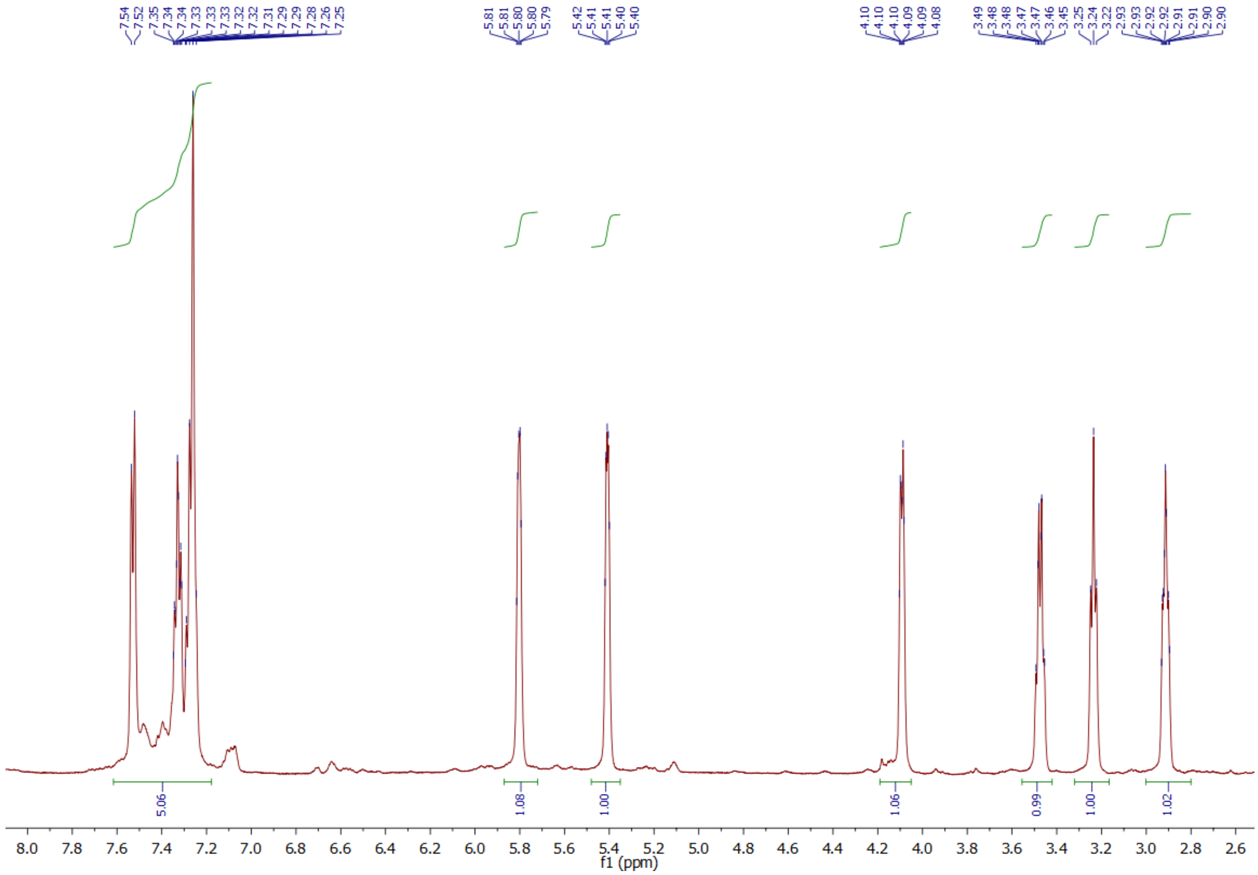


A.2. Heavy-atom Tunneling and Nonstatistical Dynamics of Di-π-methane Rearrangement of Benzobarrelene

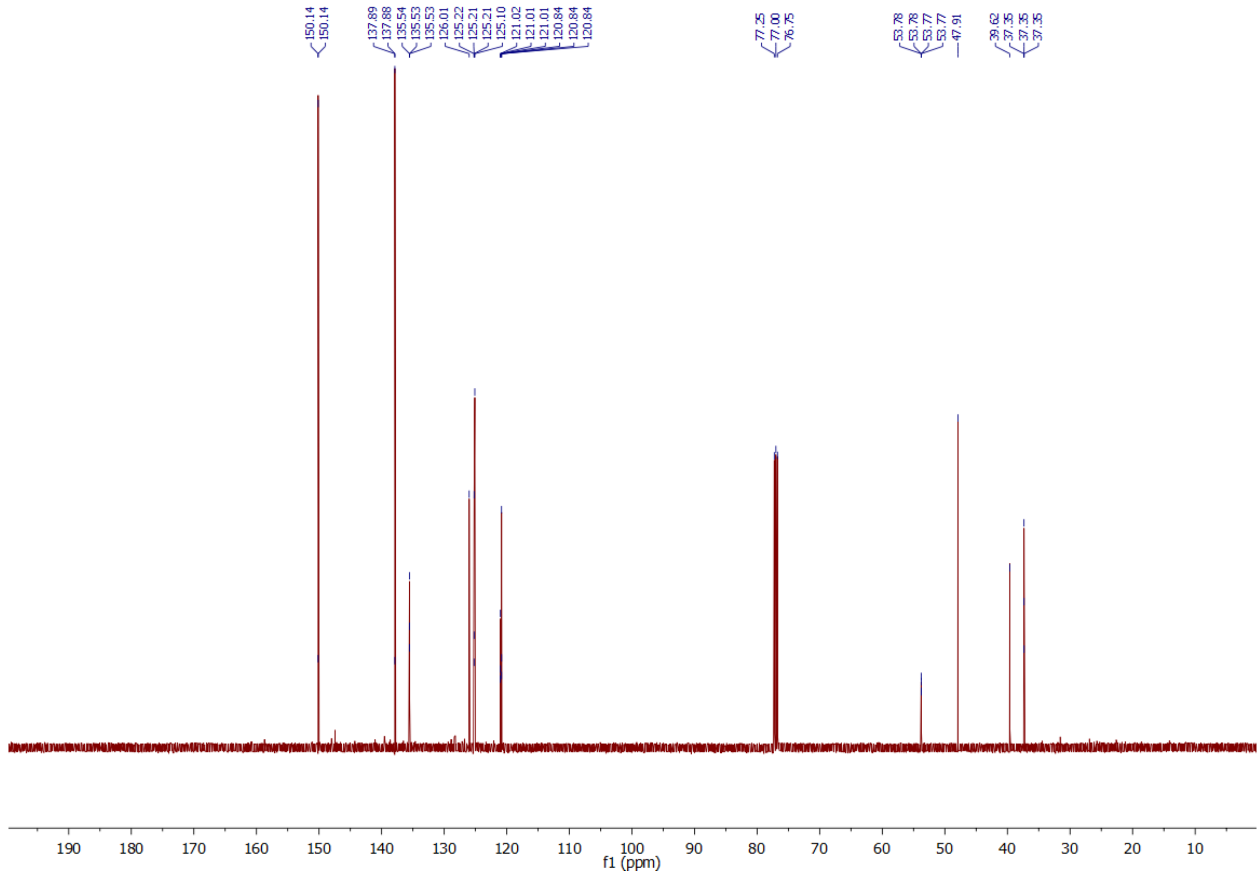
A.2.1. Benzobarrelene (**1**) – ^{1}H NMR (500 MHz, $CDCl_3$)



A.2.2. Benzosemibullvalene (**7**) – ^{1}H NMR (500 MHz, $CDCl_3$)



A.2.3. Benzosemibullvalene (**7**) – ^{13}C NMR (125 MHz, $CDCl_3$)



A.2.4. KIE Measurement

A.2.4.1. NMR Details for KIE Measurements

The ^{13}C spectra were recorded at 125.7 MHz using inverse gated decoupling and calibrated π/2 pulses. The delay between pulses ranged from 36.5 to 41.5 s, and the number of points collected per FID ranged from 387,000 to 524,000. The FID acquisition times ranged from 6.5 to 8.4 s. The integrations were obtained numerically by a macro provided in a later section. A zero-order baseline correction was generally applied, but to avoid any qualitative manipulation no first-order or higher-order baseline correction was ever applied.

For each KIE measurement, the center of the spectrum was placed at the middle of the two peaks of interests, which were carbons 3 and 7 in most cases. The spectral widths were set to ensure that no peak of 7 was within 10% of the spectral edge. T_1 measurements were carried out on each sample, and the relaxation time between each pulse was set to be more than 7 times T_1.

The integration ranges for each peak of interest were chosen based on the T_1 measurements with the goal of including an equal percentage of each peak's integration, typically 99.7% for each. For calculating this percentage, it was assumed that each peak's shape was a combination of a Lorentzian, based on the T_1 with a width of $1/(\pi T_1)$, with narrower gaussian broadenings from imperfect shims.

For the integrations of the peaks for carbon 3 versus carbon 7 (see the assignments below) for **7**, the integration of carbon 7 was set to 1000 and the integration of carbon 3 was recorded. The raw results are at the top of Table A.1. Because of the close proximity of carbons g and c, in some of the spectra the integration range of carbon c included a satellite peak from carbon g. For these spectra, the integrations were adjusted by an assumed natural abundance of ^{13}C of 1.07%. (Any reasonable choice makes no more than round-off changes in the KIEs.)

Table A.1 Intramolecular KIE results for **7** obtained from di-π-methane rearrangement.

Sensitizer	acetophenone	acetone	methyl benzoate	acetophenone	acetone
temperature	300 K	300 K	300 K	200 K	200 K
entry			Raw Integration Results		
1	1075.32	1017.48	1036.07	1142.03	1057.58
2	1073.66	1025.87	1049.39	1135.64	1049.77
3	1051.91	1017.36	1044.68	1153.22	1102.29
4	1084.72	1020.13	1047.65	1149.24	1059.80
5	1086.11	1029.69	1059.56	1141.58	1063.81
6	1061.32	1028.31	1047.28	1144.82	1045.76
7	1061.16	1038.96	1051.52	1115.39	1046.77
8	1052.25	1016.23	1054.90	1121.77	1071.11
9	1053.04	1024.06	1039.69	1144.90	1074.81
10	1063.98	1030.09	1055.04	1138.88	1080.74
11	1054.50	1029.37	1059.37	1136.29	1077.51
12	1042.48	1023.97	1053.04	1137.37	1076.14
13		1029.72	1055.38		1074.03
14		1028.94	1054.87		1058.27
15					1072.97
	Integration Results Adjusted for Satellite of Carbon g Overlapping with Carbon c				
1	1086.83	1028.37	1047.16	1142.03	1057.578
2	1085.15	1036.84	1060.62	1135.64	1049.773
3	1063.17	1028.24	1055.86	1153.22	1102.293
4	1096.33	1031.04	1058.86	1149.24	1059.802
5	1097.74	1040.71	1070.90	1141.58	1063.808
6	1072.67	1039.32	1058.49	1144.82	1045.763
7	1072.52	1050.07	1062.77	1115.39	1046.774

8	1063.51	1027.10	1066.19	1121.77	1071.112
9	1064.31	1035.02	1039.69	1144.90	1074.811
10	1075.37	1041.11	1055.04	1138.88	1080.744
11	1065.78	1040.38	1059.37	1136.29	1077.512
12	1053.63	1034.93	1053.04	1137.37	1076.137
13		1040.74	1055.38		1074.031
14		1039.95	1054.87		1069.59
15					1084.45
average	1074.75	1036.70	1057.02	1138.43	1068.95
std. deviation	14.0	6.4	7.6	10.7	15.4
Nominal KIE	1.075	1.037	1.057	1.138	1.069
95% confidence	0.009	0.004	0.004	0.007	0.009

Table A.2 shows data from a limited study of the alternative atom pairings a versus c and b versus c. Based on our original protocol for obtaining intramolecular KIEs by NMR (reference 8a in the main text), the exploration of a different pairing required new sets of spectra with each centered on the peaks of interest. These results are consistent with the large KIEs seen in the d / c measurements and consistent with the statistical predictions for the acetophenone KIEs. As was true of the d / c results, this supports the conventional mechanism involving structures 2 through 7 and the approximate accuracy of the computational energy surface. The results for a / c and b / c are not completely independent of the results for d / c since all depend on the integration of c, albeit in separate sets of spectra. However, it should be noted that the large KIEs cannot be the result of an impurity under c since this would decrease the measured KIEs.

Table A.2. Intramolecular KIE results for **7** obtained from di-π-methane rearrangement for other carbon pairs

sensitizer	acetophenone	acetophenone
temperature	200 K	200 K
carbon pair	a / c	b / c
entry	Raw Integration Results	
1	1130.499	1121.897
2	1127.635	1097.316
3	1132.455	1098.161
4	1129.099	1089.346
5	1124.03	1095.864
6	1137.271	1097.538
7	1131.205	1105.697
8	1136.77	1107.238
9	1137.198	1100.674
10	1140.05	1098.05
11	1133.962	1120.465
12	1127.426	1108.488
average	1132.30	1103.39
std. deviation	4.7	9.4
Nominal KIE	1.132	1.103
95% confidence	0.003	0.005

CVT/SCT-predicted	1.124[a]	1.113[a]
	1.108[b]	1.105[b]
	1.141[c]	1.141[c]

[a]Calculated using the method of main text reference 7. [b]VTST-ISPE using CASSCF(6,6)+NEVPT2/aug-cc-Pvtz energies along the ω-B97XD/6-31+G** path. [c]Using LC-Mpwlyp/6-31+G** calculations.

B. APPENDIX B

B.1. Computational Methods Validation Studies

To explore the accuracy of computational methods for the photoredox-promoted [2 + 2]-cycloaddition reaction, a series of structures between the reaction of the 1-cyano-2-buten-1-one and **6** along the same mechanistic pathway as Figure 2.7(b) were first optimized in gas-phase unrestricted ω-B97XD/6-311+G(d,p) calculations. Single-point energies for each of these structures were then calculated in uCCSD(T)/aug-cc-pVDZ calculations, and the energetics were then calculated in a series of DFT calculations, as shown in Table B.1. The ω-B97XD/6-311+G(d,p) was chosen as the working optimization method on it being the smallest root-mean-square error compared to the uCCSD(T)/aug-cc-pVDZ calculation.

Table B.1. DFT methods exploration based on the [2 + 2]-cycloaddition of the 1-cyano-2-buten-1-one.

Computational method	**S1 + 6**	**S2‡**	**S3**	**S4‡**	**S5**	**S6‡**	**S7**
uCCSD(T)/aug-cc-pVDZ	-553.2912945	-553.2959667	-553.3173203	-553.3109036	-553.3140795	-553.3044103	-553.3202623
E_rel (kcal/mol)	0	-2.9	-16.3	-12.3	-14.3	-8.2	-18.2
uM06-2X-D3/6-311+G**	-554.65843	-554.67041	-554.68279	-554.67565	-554.67851	-554.67265	-554.6851
E_rel (kcal/mol)	0.0	-7.5	-15.3	-10.8	-12.6	-8.9	-16.7
uB3LYP-D3/6-311+G**	-554.93103	-554.94352	-554.95171	-554.94424	-554.94298	-554.93951	-554.94641
E_rel (kcal/mol)	0.0	-7.8	-13.0	-8.3	-7.5	-5.3	-9.7
uMPW1PW91/6-311+G**	-554.75374	-554.76089	-554.77432	-554.76697	-554.76609	-554.7656	-554.77704
E_rel (kcal/mol)	0.0	-4.5	-12.9	-8.3	-7.7	-7.4	-14.6
UB3LYP/6-311+G**	-554.91914	-554.9214	-554.93041	-554.92282	-554.92044	-554.91771	-554.92463
E_rel (kcal/mol)	0.0	-1.4	-7.1	-2.3	-0.8	0.9	-3.4
UB3PW91/6-311+G**	-554.68406	-554.6895	-554.70158	-554.69407	-554.69209	-554.69242	-554.70225
E_rel (kcal/mol)	0.0	-3.4	-11.0	-6.3	-5.0	-5.2	-11.4
UB-VP86/6-311+G**	-554.94294	-554.95408	-554.96373	-554.95582	-554.95186	-554.95287	-554.95839

E_rel (kcal/mol)	0.0	-7.0	-13.0	-8.1	-5.6	-6.2	-9.7
UCAM-B3LYP/6-311+G**	-554.62941	-554.63017	-554.64427	-554.63731	-554.63844	-554.63262	-554.64569
E_rel (kcal/mol)	0.0	-0.5	-9.3	-5.0	-5.7	-2.0	-10.2
UHCTH407/6-311+G**	-554.83712	-554.84138	-554.85167	-554.84383	-554.83984	-554.83849	-554.84687
E_rel (kcal/mol)	0.0	-2.7	-9.1	-4.2	-1.7	-0.9	-6.1
UHSEH1PBE/6-311+G**	-554.29513	-554.30518	-554.31867	-554.311	-554.30986	-554.30924	-554.32062
E_rel (kcal/mol)	0.0	-6.3	-14.8	-10.0	-9.2	-8.9	-16.0
US-VWN/6-311+G**	-551.88354	-551.91723	-551.93087	-551.92236	-551.9194	-551.92522	-551.93491
E_rel (kcal/mol)	0.0	-21.1	-29.7	-24.4	-22.5	-26.2	-32.2
UM062X/6-311+G**	-554.65805	-554.66936	-554.68175	-554.67457	-554.67745	-554.67165	-554.68411
E_rel (kcal/mol)	0.0	-7.1	-14.9	-10.4	-12.2	-8.5	-16.4
UmPW1PW91/6-311+G**	-554.75368	-554.76089	-554.77432	-554.76697	-554.76609	-554.7656	-554.77704
E_rel (kcal/mol)	0.0	-4.5	-12.9	-8.3	-7.8	-7.5	-14.7
UPBE-PBE/6-311+G**	-554.22834	-554.24362	-554.254	-554.24607	-554.24231	-554.24405	-554.25078
E_rel (kcal/mol)	0.0	-9.6	-16.1	-11.1	-8.8	-9.9	-14.1
UTPSS-TPSS/6-311+G**	-554.99638	-555.00716	-555.01556	-555.00781	-555.004	-555.00498	-555.01025
E_rel (kcal/mol)	0.0	-6.8	-12.0	-7.2	-4.8	-5.4	-8.7
UwB97XD/6-311+G**	**-554.706**	**-554.716**	**-554.731**	**-554.724**	**-554.726**	**-554.721**	**-554.736**
E_rel (kcal/mol)	**0.0**	**-6.1**	**-15.7**	**-11.6**	**-12.9**	**-9.6**	**-19.1**
UB3LYP/6-311+G(2d,p)	-554.93271	-554.93418	-554.94298	-554.9354	-554.93291	-554.93003	-554.93656
E_rel (kcal/mol)	0.0	-0.9	-6.4	-1.7	-0.1	1.7	-2.4
UwB97XD/6-311+G(d,2p)	-554.70997	-554.71975	-554.73491	-554.72833	-554.73045	-554.7253	-554.74036
E_rel (kcal/mol)	0.0	-6.1	-15.7	-11.5	-12.9	-9.6	-19.1
UM06HF/6-311+G(d,2p)	-554.72793	-554.74063	-554.75444	-554.74728	-554.75117	-554.74445	-554.75748
E_rel (kcal/mol)	0.0	-8.0	-16.6	-12.1	-14.6	-10.4	-18.5
UM06HF/6-311+G(d,p)	-554.71603	-554.72889	-554.74297	-554.73581	-554.73966	-554.73265	-554.74587
E_rel (kcal/mol)	0.0	-8.1	-16.9	-12.4	-14.8	-10.4	-18.7
UM06HF/6-311+G(2d,p)	-554.74216	-554.75241	-554.76612	-554.75896	-554.76245	-554.75536	-554.76794
E_rel (kcal/mol)	0.0	-6.4	-15.0	-10.5	-12.7	-8.3	-16.2
UwB97XD/6-311+G(2d,p)	-554.71909	-554.72789	-554.74316	-554.73651	-554.73855	-554.73322	-554.74806
E_rel (kcal/mol)	0.0	-5.5	-15.1	-10.9	-12.2	-8.9	-18.2
UM06HF/6-311+G(2d,2p)	-554.75697	-554.76669	-554.78011	-554.77297	-554.77647	-554.76958	-554.78203
E_rel (kcal/mol)	0.0	-6.1	-14.5	-10.0	-12.2	-7.9	-15.7
UwB97XD/6-311+G(2d,2p)	-554.72422	-554.73283	-554.74802	-554.74137	-554.74342	-554.73804	-554.75284
E_rel (kcal/mol)	0.0	-5.4	-14.9	-10.8	-12.0	-8.7	-18.0
UwB97XD/6-311++G(d,p)	-554.70606	-554.71584	-554.73109	-554.72449	-554.72662	-554.72133	-554.73648

E_rel (kcal/mol)	0.0	-6.1	-15.7	-11.6	-12.9	-9.6	-19.1
UwB97XD/6-311++G(2d,p)	-554.71926	-554.72803	-554.7433	-554.73667	-554.73871	-554.73335	-554.74822
E_rel (kcal/mol)	0.0	-5.5	-15.1	-10.9	-12.2	-8.8	-18.2
UB3LYP/6-31G(d)	-554.73077	-554.73862	-554.74888	-554.74085	-554.73824	-554.7376	-554.74428
E_rel (kcal/mol)	0.0	-4.9	-11.4	-6.3	-4.7	-4.3	-8.5
uwb97xd/6-31++g(2d,p)	-554.60405	-554.61373	-554.62967	-554.62305	-554.62507	-554.62026	-554.63573
E_rel (kcal/mol)	0.0	-6.1	-16.1	-11.9	-13.2	-10.2	-19.9
ub2plypd3/6-311+g(2d,2p)	-553.78487	-553.78192	-553.79827	-553.79131	-553.79357	-553.78031	-553.79445
E_rel (kcal/mol)	0.0	1.9	-8.4	-4.0	-5.5	2.9	-6.0
umbk/6-311+d(d,p)	-554.56313	-554.57702	-554.59096	-554.58389	-554.58521	-554.58325	-554.59949
E_rel (kcal/mol)	0.0	-8.7	-17.5	-13.0	-13.9	-12.6	-22.8
uwb97xd/aug-cc-pvdz	-554.62302	-554.63382	-554.65021	-554.64364	-554.64564	-554.64146	-554.65745
E_rel (kcal/mol)	0.0	-6.8	-17.1	-12.9	-14.2	-11.6	-21.6
um062x/aug-cc-pvdz	-554.58467	-554.59657	-554.60964	-554.60246	-554.60507	-554.6004	-554.61337
E_rel (kcal/mol)	0.0	-7.5	-15.7	-11.2	-12.8	-9.9	-18.0
UwB97XD/6-311++g(2d,2p)	-554.72435	-554.73294	-554.74813	-554.74149	-554.74353	-554.73814	-554.75296
E_rel (kcal/mol)	0.0	-5.4	-14.9	-10.8	-12.0	-8.7	-18.0

B.2. Example input for POLYRATE calculation

B.2.1. First Step of the Di-π-methane Rearrangement

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First step of benzobarrelene dipimethane rearrangement
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  3  C
  4  C
  5  C
  6  C
  7  C
  8  C
  9  C
  10  C
  11  H
  12  H
  13  H
  14  H
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  16  H
  17  C
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  19  H
  20  H
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  22  H
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 NOSUPERMOL
 INPUNIT AU

 WRITEFU31

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 OPTTS   OHOOK

 *SECOND

 HESSCAL HHOOK

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 SPECIES   NONLINRP
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3    0.67348465    -1.314923624    -0.118198974
4    0.622560713    1.336037939    -0.032369618
5    2.862308291    2.695528013    0.007720947
6    5.167745939    1.406133402    -0.041016275
7    -1.957283545    -2.490562433    -0.047278441
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9    -3.39726049    1.300914767    2.326297394
10    -2.955158404    -1.47702861    2.470869973
11    7.014645254    -2.212488999    -0.145365188
12    2.994861753    -4.651421106    -0.17781323
13    2.821626415    4.74874881    0.076849315
14    6.92693359    2.462824633    -0.022652874
15    -1.888950088    -4.552144282    -0.134258005
16    -2.053022531    4.487569182    -0.002869771
17    -3.537772723    1.233460901    -2.119944843
18    -3.516697668    -1.291309008    -2.141392735
19    -4.538842156    -2.440336948    -3.497091593
20    -4.61610895    2.392896081    -3.424437751
21    -2.06112381    -2.259045791    4.15308375
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3 0.779454953 -1.305540177 0.000178305
4 0.69330251 1.35220506 0.00006732
5 2.937703873 2.721975581 -0.000496935
6 5.254641329 1.462125426 -0.000948189
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11 7.13829826 -2.143226689 -0.001189239
12 3.135379045 -4.609438033 -0.00018298
13 2.878065902 4.776245322 -0.000584292
14 7.000273688 2.541246519 -0.001387379
15 -1.666708136 -4.628601174 0.000882344
16 -1.955245619 4.571902548 0.000496977
17 -3.962785001 1.131613943 -1.434506032
18 -3.251723444 -1.446135897 -2.206752457
19 -2.932929911 -2.015254232 -4.147946745
20 -5.286027702 2.261745026 -2.51574529
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13 2.903573644 4.744788982 0.035666542
14 7.005464183 2.457247352 -0.003662208
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 INH     10
 NSTEPS  99999
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 COORD  CART

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 ZCT
 SCT

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   BOTHK
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   CVT

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  500
  568
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B.2.2. Second Step of the Di-π-methane Rearrangement

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 Second step of benzobarrelene dipimethane rearrangement
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   3  C
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   6  C
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   9  C
  10  C
  11  H
  12  H
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 END

 NOSUPERMOL
 INPUNIT AU

 WRITEFU31

# MICROCANONICAL RATE CONSTANT

# MDMOVIE ON

*OPTIMIZATION

 OPTMIN  OHOOK
 OPTTS   OHOOK

 *SECOND

 HESSCAL HHOOK
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SPECIES   NONLINRP
STATUS 2

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4     0.69330251     1.35220506     0.00006732
5     2.937703873     2.721975581     -0.000496935
6     5.254641329     1.462125426     -0.000948189
7     -1.818961906     -2.567594344     0.000816448
8     -1.85613721     2.521105165     0.000577053
9     -3.962145451     1.131754777     1.436733335
10     -3.250741081     -1.445921075     2.208913873
11     7.13829826     -2.143226689     -0.001189239
12     3.135379045     -4.609438033     -0.00018298
13     2.878065902     4.776245322     -0.000584292
14     7.000273688     2.541246519     -0.001387379
15     -1.666708136     -4.628601174     0.000882344
16     -1.955245619     4.571902548     0.000496977
17     -3.962785001     1.131613943     -1.434506032
18     -3.251723444     -1.446135897     -2.206752457
19     -2.932929911     -2.015254232     -4.147946745
20     -5.286027702     2.261745026     -2.51574529
21     -2.931080202     -2.014847803     4.150021718
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ELEC
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END


*PROD1
SPECIES   NONLINRP
STATUS 2

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3     -0.756312387     -1.18534335     -0.160050411
4     -0.795699142     1.516941344     -0.311607047
5     -3.15940324     2.752441587     -0.14054668
6     -5.380360797     1.391699321     0.115518261
7     1.828364361     -2.474921033     -0.245425324
8     1.496642239     2.876221621     -0.643370275
9     3.952975102     1.405600676     -0.798955615
10     3.371444985     -1.033893426     -2.159040588
11     -7.057888701     -2.314135992     0.418470673
12     -2.948066062     -4.563543135     0.181817593
13     -3.208766779     4.804683011     -0.23711147
14     -7.175908387     2.379245447     0.228381136
15     1.629930265     -4.503067951     -0.596763241
16     1.487302081     4.928141115     -0.645208481
17     4.455871667     0.388442537     1.872318659
18     3.238637459     -1.796147659     2.182367977
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19    3.058266467    -2.863219336    3.923048986
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21    2.960953513    -1.092067532    -4.168662891
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 END


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 STATUS 2
 GEOM
1    5.321282028    -1.235620455    -0.05792103
2    3.046453754    -2.564165338    0.085798377
3    0.764194835    -1.274489995    0.166366506
4    0.728509584    1.40155421    0.132139472
5    3.020874185    2.709023583    -0.069408831
6    5.29875031    1.398270402    -0.147818134
7    -1.84036997    -2.528205316    0.181179512
8    -1.702804043    2.661452788    0.243050298
9    -3.996782129    1.279945892    1.180426323
10    -3.330039265    -1.237738909    2.250647002
11    7.101716368    -2.254023665    -0.117242388
12    3.04824737    -4.619775696    0.114853871
13    3.007487587    4.763284662    -0.128269187
14    7.06484198    2.435609993    -0.277969464
15    -1.68554191    -4.583568825    0.340097362
16    -1.831940958    4.675841687    -0.126823291
17    -4.185783514    0.78591035    -1.624951642
18    -3.19272272    -1.56798817    -2.16360133
19    -2.903645894    -2.352396986    -4.031960057
20    -5.126560142    2.049892981    -2.92832789
21    -2.936712149    -1.538278083    4.239378865
22    -5.44225304    2.414481904    2.104614634
 END

 ELEC
 3 0.00
 END

# end of start section

*PATH

 SCALEMASS  1.00

 RODS ON

 INTMU   3
 SSTEP   0.01
 INH     10
 NSTEPS  99999
 RPM pagem
 SIGN    PRODUCT


 SRANGE
```

```
  SLP   2.60
  SLM  -2.20
 END

 COORD  CART

 PRPATH
  COORD 9 25
  INTERVAL 1
  XMOL
 END

 PRSAVERP

 #SPECSTOP
 #PERCENTDOWN 99.
 #END

*TUNNEL

QUAD
 NQE   40
 NQTH  40
END

 ZCT
 SCT

 *RATE
   GTLOG
   BOTHK
   SIGMAF 1
   TST
   CVT

  TEMP
  77
  100
  120
  200
  300
  400
  487
  500
  568
```

B.3. POLYRATE rate constants for predicting KIEs of DPMR of benzobarrelene (200 K)

^{13}C position	N/A

Method	Step	SSTEP	TST	CVT	TST/SCT	CVT/SCT
M06-2X	Bond-forming	0.01	3.1691E+07	2.9618E+07	9.9549E+07	1.0053E+08
ωB97xD	Bond-forming	0.01	5.9521E+09	5.7173E+09	1.3065E+10	1.2920E+10
ωB97xD	Bond-forming	0.005	5.9521E+09	5.7204E+09	1.2861E+10	1.2722E+10
ωB97xD	Bond-forming	0.0025	5.9521E+09	5.7206E+09	1.2714E+10	1.2577E+10

ωB97xD CAS-ISPE	Bond-forming	0.0025	6.6449E+09	6.5444E+09	8.8883E+09	2.0640E+10
LC-mPWLYP	Bond-forming	0.01	5.8533E+07	5.8341E+07	2.0215E+08	2.0242E+08
M06-2X	Bond-breaking	0.01	5.4460E+02	5.2793E+02	1.4791E+03	1.4788E+03
ωB97xD	Bond-breaking	0.01	3.3390E+04	3.3381E+04	8.8258E+04	8.8290E+04
LC-mPWLYP	Bond-breaking	0.01	4.9995E+00	4.9957E+00	2.2184E+01	2.2168E+01

^{13}C position	a					
Method	**Step**	**SSTEP**	**TST**	**CVT**	**TST/SCT**	**CVT/SCT**
M06-2X	Bond-forming	0.01	3.1801E+07	2.9712E+07	9.9857E+07	1.0085E+08
ωB97xD	Bond-forming	0.01	5.9673E+09	5.7296E+09	1.3109E+10	1.2964E+10
ωB97xD	Bond-forming	0.005	5.9673E+09	5.7327E+09	1.2906E+10	1.2766E+10
ωB97xD	Bond-forming	0.0025	5.9673E+09	5.7329E+09	1.2772E+10	1.2633E+10
ωB97xD CAS-ISPE	Bond-forming	0.0025	7.4814E+09	7.4008E+09	1.0735E+10	2.2447E+10
LC-mPWLYP	Bond-forming	0.01	5.8781E+07	5.8582E+07	2.0246E+08	2.0274E+08
M06-2X	Bond-breaking	0.01	5.4514E+02	5.2854E+02	1.4804E+03	1.4800E+03
ωB97xD	Bond-breaking	0.01	3.3442E+04	3.3434E+04	8.8365E+04	8.8397E+04
LC-mPWLYP	Bond-breaking	0.01	5.0114E+00	5.0075E+00	2.2226E+01	2.2211E+01

^{13}C position	b					
Method	**Step**	**SSTEP**	**TST**	**CVT**	**TST/SCT**	**CVT/SCT**
M06-2X	Bond-forming	0.01	3.0848E+07	2.8740E+07	9.1536E+07	9.2547E+07
ωB97xD	Bond-forming	0.01	5.8033E+09	5.5626E+09	1.2383E+10	1.2240E+10
ωB97xD	Bond-forming	0.005	5.8033E+09	5.5656E+09	1.2126E+10	1.1989E+10
ωB97xD	Bond-forming	0.0025	5.8033E+09	5.5658E+09	1.2010E+10	1.1875E+10
ωB97xD CAS-ISPE	Bond-forming	0.0025	7.3118E+09	7.2355E+09	1.0211E+10	2.1241E+10
LC-mPWLYP	Bond-forming	0.01	5.6944E+07	5.6734E+07	1.8645E+08	1.8672E+08
M06-2X	Bond-breaking	0.01	5.5175E+02	5.3511E+02	1.4872E+03	1.4866E+03
ωB97xD	Bond-breaking	0.01	3.3974E+04	3.3968E+04	8.9080E+04	8.9108E+04
LC-mPWLYP	Bond-breaking	0.01	5.0732E+00	5.0689E+00	2.2242E+01	2.2226E+01

^{13}C position	c

Method	Step	SSTEP	TST	CVT	TST/SCT	CVT/SCT
M06-2X	Bond-forming	0.01	3.0414E+07	2.8410E+07	9.2003E+07	9.2954E+07
ωB97xD	Bond-forming	0.01	5.7263E+09	5.4988E+09	1.2291E+10	1.2152E+10
ωB97xD	Bond-forming	0.005	5.7263E+09	5.5017E+09	1.2095E+10	1.1961E+10
ωB97xD	Bond-forming	0.0025	5.7263E+09	5.5019E+09	1.1947E+10	1.1814E+10
ωB97xD CAS-ISPE	Bond-forming	0.0025	7.3789E+09	7.2769E+09	1.0119E+10	2.0555E+10
LC-mPWLYP	Bond-forming	0.01	5.5996E+07	5.5819E+07	1.8564E+08	1.8589E+08
M06-2X	Bond-breaking	0.01	5.1469E+02	4.9881E+02	1.3352E+03	1.3356E+03
ωB97xD	Bond-breaking	0.01	3.1755E+04	3.1748E+04	8.0748E+04	8.0777E+04
LC-mPWLYP	Bond-breaking	0.01	4.7058E+00	4.7019E+00	1.9489E+01	1.9475E+01

^{13}C position	d

Method	Step	SSTEP	TST	CVT	TST/SCT	CVT/SCT
M06-2X	Bond-forming	0.01	3.0942E+07	2.8984E+07	9.7104E+07	9.8007E+07
ωB97xD	Bond-forming	0.01	5.8119E+09	5.5908E+09	1.2765E+10	1.2625E+10
ωB97xD	Bond-forming	0.005	5.8119E+09	5.5938E+09	1.2561E+10	1.2426E+10
ωB97xD	Bond-forming	0.0025	5.8119E+09	5.5940E+09	1.2428E+10	1.2295E+10
ωB97xD CAS-ISPE	Bond-forming	0.0025	7.1467E+09	7.0316E+09	1.0240E+10	2.1855E+10
LC-mPWLYP	Bond-forming	0.01	5.7090E+07	5.6922E+07	1.9692E+08	1.9717E+08
M06-2X	Bond-breaking	0.01	5.5208E+02	5.3586E+02	1.5024E+03	1.5015E+03
ωB97xD	Bond-breaking	0.01	3.3845E+04	3.3839E+04	8.9583E+04	8.9611E+04
LC-mPWLYP	Bond-breaking	0.01	5.0698E+00	5.0652E+00	2.2523E+01	2.2507E+01

B.4. POLYRATE rate constants for predicting KIEs of DPMR of benzobarrelene (300 K)

^{13}C position	N/A

Method	Step	Stepsize	TST	CVT	TST/SCT	CVT/SCT
M06-2X	Bond-forming	0.01	2.3170E+09	2.2334E+09	3.5484E+09	3.5944E+09
ωB97xD	Bond-forming	0.01	8.3485E+10	8.0466E+10	1.1509E+11	1.1287E+11
ωB97xD	Bond-forming	0.005	8.3485E+10	8.0504E+10	1.1430E+11	1.1213E+11

ωB97xD	Bond-forming	0.0025	8.3485E+10	8.0509E+10	1.1378E+11	1.1162E+11
ωB97xD CAS-ISPE	Bond-forming	0.0025	8.6894E+10	8.5795E+10	8.0056E+10	1.3996E+11
LC-mPWLYP	Bond-forming	0.01	3.3905E+09	3.3852E+09	5.5338E+09	5.5413E+09
M06-2X	Bond-breaking	0.01	1.5213E+06	1.5011E+06	2.2258E+06	2.2345E+06
ωB97xD	Bond-breaking	0.01	2.2743E+07	2.2742E+07	3.3529E+07	3.3534E+07
LC-mPWLYP	Bind-breaking	0.01	6.4808E+04	6.4740E+04	1.1375E+05	1.1360E+05

^{13}C position	a

Method	**Step**	**Step size**	**TST**	**CVT**	**TST/SCT**	**CVT/SCT**
M06-2X	Bond-forming	0.01	2.3212E+09	2.2370E+09	3.5535E+09	3.5998E+09
ωB97xD	Bond-forming	0.01	8.3604E+10	8.0553E+10	1.1530E+11	1.1307E+11
ωB97xD	Bond-forming	0.005	8.3604E+10	8.0591E+10	1.1449E+11	1.1230E+11
ωB97xD	Bond-forming	0.0025	8.3604E+10	8.0596E+10	1.1399E+11	1.1183E+11
ωB97xD CAS-ISPE	Bond-forming	0.0025	9.4921E+10	9.4099E+10	9.1458E+10	1.4929E+11
LC-mPWLYP	Bond-forming	0.01	3.3980E+09	3.3926E+09	5.5407E+09	5.5484E+09
M06-2X	Bond-breaking	0.01	1.5217E+06	1.5016E+06	2.2265E+06	2.2351E+06
ωB97xD	Bond-breaking	0.01	2.2757E+07	2.2757E+07	3.3547E+07	3.3552E+07
LC-mPWLYP	Bind-breaking	0.01	6.4882E+04	6.4813E+04	1.1386E+05	1.1371E+05

^{13}C position	b

Method	**Step**	**Step size**	**TST**	**CVT**	**TST/SCT**	**CVT/SCT**
M06-2X	Bond-forming	0.01	2.2686E+09	2.1827E+09	3.4008E+09	3.4485E+09
ωB97xD	Bond-forming	0.01	8.1842E+10	7.8738E+10	1.1147E+11	1.0924E+11
ωB97xD	Bond-forming	0.005	8.1842E+10	7.8775E+10	1.1049E+11	1.0831E+11
ωB97xD	Bond-forming	0.0025	8.1842E+10	7.8780E+10	1.1002E+11	1.0785E+11
ωB97xD CAS-ISPE	Bond-forming	0.0025	9.3230E+10	9.2433E+10	8.8776E+10	1.4439E+11
LC-mPWLYP	Bond-forming	0.01	3.3182E+09	3.3123E+09	5.3138E+09	5.3215E+09
M06-2X	Bond-breaking	0.01	1.5320E+06	1.5120E+06	2.2361E+06	2.2445E+06
ωB97xD	Bond-breaking	0.01	2.2964E+07	2.2963E+07	3.3757E+07	3.3761E+07

LC-mPWLYP	Bind-breaking	0.01	6.5340E+04	6.5267E+04	1.1424E+05	1.1409E+05

^{13}C position	c

Method	**Step**	**Step size**	**TST**	**CVT**	**TST/SCT**	**CVT/SCT**
M06-2X	Bond-forming	0.01	2.2483E+09	2.1665E+09	3.3967E+09	3.4420E+09
ωB97xD	Bond-forming	0.01	8.1143E+10	7.8172E+10	1.1085E+11	1.0866E+11
ωB97xD	Bond-forming	0.005	8.1143E+10	7.8208E+10	1.1009E+11	1.0794E+11
ωB97xD	Bond-forming	0.0025	8.1143E+10	7.8212E+10	1.0949E+11	1.0736E+11
ωB97xD CAS-ISPE	Bond-forming	0.0025	9.3683E+10	9.2634E+10	8.9181E+10	1.4266E+11
LC-mPWLYP	Bond-forming	0.01	3.2829E+09	3.2780E+09	5.2802E+09	5.2872E+09
M06-2X	Bond-breaking	0.01	1.4639E+06	1.4445E+06	2.1076E+06	2.1165E+06
ωB97xD	Bond-breaking	0.01	2.1969E+07	2.1969E+07	3.1946E+07	3.1950E+07
LC-mPWLYP	Bind-breaking	0.01	6.2207E+04	6.2138E+04	1.0678E+05	1.0664E+05

^{13}C position	d

Method	**Step**	**Step size**	**TST**	**CVT**	**TST/SCT**	**CVT/SCT**
M06-2X	Bond-forming	0.01	2.2808E+09	2.2015E+09	3.4939E+09	3.5372E+09
ωB97xD	Bond-forming	0.01	8.2196E+10	7.9309E+10	1.1337E+11	1.1121E+11
ωB97xD	Bond-forming	0.005	8.2196E+10	7.9347E+10	1.1257E+11	1.1046E+11
ωB97xD	Bond-forming	0.0025	8.2196E+10	7.9351E+10	1.1209E+11	1.0999E+11
ωB97xD CAS-ISPE	Bond-forming	0.0025	9.2203E+10	9.1100E+10	8.8441E+10	1.4640E+11
LC-mPWLYP	Bond-forming	0.01	3.3352E+09	3.3306E+09	5.4413E+09	5.4481E+09
M06-2X	Bond-breaking	0.01	1.5346E+06	1.5153E+06	2.2477E+06	2.2556E+06
ωB97xD	Bond-breaking	0.01	2.2941E+07	2.2940E+07	3.3839E+07	3.3842E+07
LC-mPWLYP	Bind-breaking	0.01	6.5388E+04	6.5312E+04	1.1480E+05	1.1465E+05

B.5. RRKM Calculations

RRKM calculations were based on the frequencies in optimized structures for **2**, **3**‡, **4**, and **5**‡ including ^{13}C in the relevant positions. An example input file is given below. The threshold energy barriers in each calculation were the differences between the zero-point level energies for the **3**‡ versus **2** or **5**‡ versus **4**. The nominal KIE was then calculated using eqs 7 through 10 in Section 3.5.

Tunneling corrections for the RRKM rate constants were estimated using the equation below for the transmission coefficient (G), where V_0 is the classical E+zpe barrier, E is the microcanonical energy, and ν* is the imaginary frequency of the transition state. It was found that the tunneling correction was negligible in the high-energy realm of interest, and the reported nominal KIE in the main text is not tunneling corrected.

$$G = \frac{1}{1 + \exp\left[\frac{2\pi(V_0 - E)}{h\nu^*}\right]}$$

B.5.1. Example RRKM input for unlabeled isotopomer

```
0,0.1,301
0
-1,0,1,10
0
0
0
1.0
60,0
124.4239,170.2000,276.0117,318.3819,354.9149,377.6504,430.3171
505.0296,513.3253,534.4443,579.4522,631.5954,653.8064,655.8322
722.5026,772.1473,777.7874,798.5469,811.0521,833.2601,898.4797
901.3637,931.9622,959.7746,966.7662,969.6294,976.2146,1001.0930
1009.4800,1064.2046,1101.0508,1132.5956,1138.2221,1185.7406,1190.4919
1191.4661,1221.6087,1227.9069,1246.5392,1268.5326,1302.3970,1328.9446
1354.7775,1376.2255,1382.9124,1509.4858,1524.5552,1661.8962,1678.1694
1687.4079,3134.8019,3137.0392,3152.6303,3164.7169,3199.0546,3203.5555
3216.7188,3221.6750,3231.3673,3246.5708
404.05,404.05,643.28
0
2.918
59,0
124.9097,166.6127,194.8289,345.5069,377.4768,420.2073,455.2271
469.3747,521.0664,534.9264,556.7006,591.9112,653.4248,667.3212
682.1649,776.8157,784.4243,789.9482,814.8841,865.0691,899.4059
910.7498,947.2153,963.2776,969.3937,975.2466,1009.8379,1014.9739
```

1066.1782,1084.7793,1123.3590,1142.1735,1166.5325,1191.3429,1197.5879
1227.3338,1238.7689,1264.1512,1269.8335,1301.7233,1337.4495,1358.1468
1371.3809,1392.1804,1496.7868,1512.2880,1537.9647,1668.2771,1691.5781
3138.0274,3158.4226,3197.6031,3201.6456,3216.0041,3219.4989,3230.6306
3231.0659,3240.3116,3258.3600
402.44,402.44,665.75
0

B.6. Calculated Structures and Complete Energies

B.6.1. Photoredox-Promoted [2 + 2]-Cycloaddition of Enones

B.6.1.1.1. acetonitrile

./acetonitrile
opt
E(UwB97XD) = -132.750733762

Zero-point correction= 0.045509 (Hartree/Particle)
Thermal correction to Energy= 0.049093
Thermal correction to Enthalpy= 0.050037
Thermal correction to Gibbs Free Energy= 0.021520
Sum of electronic and ZPE= -132.705225
Sum of electronic and thermal Energies= -132.701641
Sum of electronic and thermal Enthalpies= -132.700697
Sum of electronic and thermal Free Energies= -132.729214

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 30.806 10.287 60.020

C,0,-1.3527283941,0.1958642772,-0.0589726088
C,0,0.1006861005,0.2039229311,-0.0135622874
H,0,-1.7467059075,-0.2456526598,0.8568097965
H,0,-1.6899058311,-0.3904487638,-0.9141231808
H,0,-1.723403712,1.2167565903,-0.153880095
N,0,1.2507777442,0.2098676251,0.0222783755

B.6.1.1.2. BF_4^-

./BF4
opt
E(UwB97XD) = -424.643440739

Zero-point correction= 0.013589 (Hartree/Particle)
Thermal correction to Energy= 0.018037
Thermal correction to Enthalpy= 0.018981
Thermal correction to Gibbs Free Energy= -0.014072
Sum of electronic and ZPE= -424.629852
Sum of electronic and thermal Energies= -424.625404
Sum of electronic and thermal Enthalpies= -424.624460
Sum of electronic and thermal Free Energies= -424.657513

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 11.318 14.733 69.567

B,0,0.6774430596,0.5284716477,0.1739951596
F,0,1.4772615259,0.2029821355,1.290430147
F,0,-0.5609758357,1.0416696821,0.6159114396
F,0,0.4570022044,-0.6303764825,-0.6010405026
F,0,1.3363190459,1.5000130172,-0.6096662437

B.6.1.1.3. 18-Li

./cLiClPPK-1
E(UwB97XD) = -929.357328882

Zero-point correction= 0.164612 (Hartree/Particle)
Thermal correction to Energy= 0.177390
Thermal correction to Enthalpy= 0.178334
Thermal correction to Gibbs Free Energy= 0.124708
Sum of electronic and ZPE= -929.192717
Sum of electronic and thermal Energies= -929.179939
Sum of electronic and thermal Enthalpies= -929.178995
Sum of electronic and thermal Free Energies= -929.232620

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 111.314 46.398 112.865

C,0,2.9869214437,-1.0933210107,-0.0917785997
C,0,1.8520649232,-1.7583644565,-0.5341329827
C,0,0.6307266476,-1.1006790162,-0.4980025813
C,0,0.5451465053,0.2162598139,-0.0408790338
C,0,1.706613272,0.8659544563,0.3857051264
C,0,2.9289286235,0.2158323432,0.3723326356
Cl,0,4.5252090629,-1.9198346171,-0.1197430211
H,0,1.9198124321,-2.7745551015,-0.90035398
H,0,-0.247051964,-1.6230446411,-0.8570653831
H,0,1.6452560326,1.8877070275,0.7400220829
H,0,3.8257963325,0.7147411207,0.7163235463
C,0,-0.7416526043,0.9686979054,-0.0198065894
C,0,-2.008976893,0.2216281108,-0.0113842312
H,0,-1.9783857666,-0.8521046822,0.1317476118
C,0,-3.1809804037,0.8487697318,-0.1621048443
H,0,-3.1683012881,1.9272279001,-0.3047142284
C,0,-4.5122451322,0.1858700223,-0.1550069211
H,0,-5.1421471088,0.6232296382,0.6257604656
H,0,-5.0240550162,0.3677299796,-1.1051640635
H,0,-4.4361608365,-0.8899113043,0.008394428
O,0,-0.7245867251,2.1961838708,0.0042089487
Li,0,-0.247839537,4.1163339088,0.0137736141

B.6.1.1.4. 5-Li

./cLiPPK-1
E(UwB97XD) = -469.750586063

Zero-point correction= 0.174122 (Hartree/Particle)
Thermal correction to Energy= 0.185819
Thermal correction to Enthalpy= 0.186763
Thermal correction to Gibbs Free Energy= 0.135965
Sum of electronic and ZPE= -469.576464
Sum of electronic and thermal Energies= -469.564767
Sum of electronic and thermal Enthalpies= -469.563823
Sum of electronic and thermal Free Energies= -469.614621

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 116.603 42.670 106.912

C,0,3.0116359264,-1.1153372527,-0.004918378
C,0,1.8681092707,-1.7758325508,-0.4397963918
C,0,0.6449070561,-1.1170174196,-0.4494910914
C,0,0.5614738961,0.2169764948,-0.0401107922
C,0,1.7192595865,0.8769331366,0.3833319123

C,0,2.9358551821,0.2121858006,0.4093802885
H,0,3.9633447615,-1.6341857552,0.0119070855
H,0,1.9257289808,-2.8063407598,-0.7697549475
H,0,-0.2334711962,-1.6431846252,-0.8024322406
H,0,1.6570402518,1.9093825019,0.7054894246
H,0,3.8255677197,0.726427706,0.7531208036
C,0,-0.7251501924,0.9695451038,-0.0659684425
C,0,-1.9911691232,0.2198497489,-0.0122922842
H,0,-1.9568393828,-0.8460388645,0.1802640397
C,0,-3.1666360479,0.8344013687,-0.1856793038
H,0,-3.1585239871,1.905697217,-0.3750550595
C,0,-4.494463248,0.1656579775,-0.1443430732
H,0,-5.1242881584,0.6297081847,0.6210852772
H,0,-5.0120785731,0.3060557692,-1.0984829467
H,0,-4.4122150914,-0.9025276788,0.0611846408
O,0,-0.7168429952,2.1972649631,-0.1179490373
Li,0,0.0328473642,4.0147309339,-0.4213574834

B.6.1.1.5. 1-Li

./cLiPVK-1
E(UwB97XD) = -430.429777859

Zero-point correction= 0.146060 (Hartree/Particle)
Thermal correction to Energy= 0.156193
Thermal correction to Enthalpy= 0.157138
Thermal correction to Gibbs Free Energy= 0.109140
Sum of electronic and ZPE= -430.283718
Sum of electronic and thermal Energies= -430.273584
Sum of electronic and thermal Enthalpies= -430.272640
Sum of electronic and thermal Free Energies= -430.320638

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	98.013	37.194	101.020

C,0,3.0097055094,-1.1337103525,0.0047352273
C,0,1.8203449587,-1.8506157395,0.0765794772
C,0,0.6027535311,-1.1824608465,0.0484836031
C,0,0.5700834594,0.2126962681,-0.033155552
C,0,1.7719990011,0.9266961173,-0.0904027261
C,0,2.9849225879,0.256333938,-0.0813760233
H,0,3.9582488338,-1.6585027958,0.016101122
H,0,1.8394352251,-2.9311499913,0.1530321423
H,0,-0.3132070449,-1.7566543346,0.1153943247
H,0,1.7416112998,2.0077370861,-0.152450277
H,0,3.9115017603,0.8150725703,-0.1404130767
C,0,-0.7069475661,0.9735859013,-0.035563882
C,0,-1.9618256031,0.2792765804,-0.4134139294
H,0,-1.887337375,-0.6983286113,-0.8732549949
C,0,-3.1531827631,0.8358032849,-0.2045272642
H,0,-3.2471228356,1.8104763022,0.2623870809
H,0,-4.065946119,0.3258762253,-0.4889607113
O,0,-0.7054216681,2.1642924148,0.2565023076
Li,0,-1.3532861916,4.0122919828,0.3917811517

B.6.1.1.6. 1-Li NMe_3

./cLiPVK-NMe3
opt
E(UwB97XD) = -604.912151594

Zero-point correction= 0.270294 (Hartree/Particle)
Thermal correction to Energy= 0.286723
Thermal correction to Enthalpy= 0.287667

Thermal correction to Gibbs Free Energy= 0.225449
Sum of electronic and ZPE= -604.641858
Sum of electronic and thermal Energies= -604.625429
Sum of electronic and thermal Enthalpies= -604.624484
Sum of electronic and thermal Free Energies= -604.686702

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 179.921 60.487 130.949

C,0,4.4419194209,-0.8559430585,-0.0749943267
C,0,4.0792099657,0.2915943906,-0.771392362
C,0,2.8224005359,0.8518745123,-0.5817294609
C,0,1.9145838637,0.256214987,0.2990639968
C,0,2.283938789,-0.9041493363,0.9872266027
C,0,3.5436321159,-1.4529463848,0.8069744012
H,0,5.4256676987,-1.2879662605,-0.2188742391
H,0,4.774709035,0.7516461261,-1.4632059034
H,0,2.5503111482,1.7401501822,-1.1389320508
H,0,1.5751290317,-1.3624771766,1.6662366776
H,0,3.8275699077,-2.3469257918,1.3494923124
C,0,0.5476537996,0.8025464674,0.503365037
C,0,0.2617370011,2.1979565614,0.0872815265
H,0,1.0942907966,2.8884465502,0.0202692728
C,0,-0.970823352,2.5960975617,-0.2172108273
H,0,-1.810674101,1.9106661021,-0.1900107231
H,0,-1.171248527,3.615836403,-0.5238354582
O,0,-0.3197706278,0.1029780386,1.0147907118
Li,0,-2.1320914451,-0.0078560493,1.8859722084
N,0,-4.110144025,-0.4274904548,1.2031460955
C,0,-4.3267657171,0.2020258695,-0.0985318591
H,0,-3.5930311449,-0.1705477949,-0.8167846911
H,0,-4.2107579651,1.2843592619,-0.008921614
H,0,-5.3352273303,-0.0056621163,-0.4893381986
C,0,-4.2569106953,-1.8787418747,1.0971921373
H,0,-4.0571755217,-2.3409952534,2.0661752075
H,0,-3.5412192352,-2.2703016033,0.3714313083
H,0,-5.2714750661,-2.1632364946,0.7774494134
C,0,-5.0469354155,0.1079645533,2.1906240218
H,0,-4.9074559827,1.186930597,2.2848915952
H,0,-4.8611694886,-0.3527029441,3.1629643673
H,0,-6.0928774691,-0.0861455703,1.9063248208

B.6.1.1.7. (p-Cl)-12‡ gauche

./ClPPKhetero-cisTS1-1
E(UwB97XD) = -1153.19141346

Zero-point correction= 0.250971 (Hartree/Particle)
Thermal correction to Energy= 0.268656
Thermal correction to Enthalpy= 0.269601
Thermal correction to Gibbs Free Energy= 0.201635
Sum of electronic and ZPE= -1152.940443
Sum of electronic and thermal Energies= -1152.922757
Sum of electronic and thermal Enthalpies= -1152.921813
Sum of electronic and thermal Free Energies= -1152.989779

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 168.584 64.217 143.046

C,0,-0.2121774379,-0.3528987693,0.9162146316
C,0,3.3814671639,-0.3785433199,-0.9503081472
C,0,1.0542818133,-0.9094254348,1.0270469553
C,0,2.026970987,-0.1505129645,-0.9737677995
C,0,4.324152514,0.6018076367,-0.4833569706

H,0,3.7693488986,-1.3502316006,-1.2408289189
C,0,-1.2297384548,-0.9148056323,0.1034464957
H,0,-0.4049779318,0.585079696,1.428140109
C,0,2.0484852039,-0.458565608,2.0495066569
H,0,1.1836782218,-1.9148904893,0.6380515998
H,0,1.6527103456,0.8473536914,-0.779923523
H,0,1.3498926829,-0.8320838304,-1.4727779318
C,0,5.7910754068,0.2137235641,-0.4470847227
O,0,4.0042745204,1.7457934946,-0.1144405724
O,0,-1.1023665849,-2.0079466043,-0.5148060781
H,0,1.8704408629,0.5760260181,2.3560197267
H,0,3.070562744,-0.530965139,1.6617181138
H,0,1.9975823208,-1.089203138,2.9461098225
H,0,6.3792989822,0.9616267405,-0.9857111192
H,0,5.9809738964,-0.770779062,-0.8777746593
H,0,6.1365079644,0.2138053404,0.5914414919
C,0,-2.5434653191,-0.1922508058,-0.0096362895
C,0,-3.678740947,-0.9191203312,-0.3847268811
C,0,-2.690196625,1.1826434546,0.2093818481
C,0,-4.919874279,-0.3120077143,-0.5171232242
H,0,-3.5757890568,-1.981145872,-0.5719403768
C,0,-3.9222438578,1.8092210135,0.0735089148
H,0,-1.8321841673,1.7909831791,0.4690975819
C,0,-5.0286408324,1.0518433493,-0.2849931696
H,0,-5.7909334324,-0.8914583518,-0.7985299665
H,0,-4.0170783983,2.8760470965,0.2348867924
Cl,0,-6.5905972048,1.8357903928,-0.4589503899

B.6.1.1.8. (p-Cl)-12‡

./ClPPKhetero-transTS1-5
E(UwB97XD) = -1153.19108770

Zero-point correction= 0.250525 (Hartree/Particle)
Thermal correction to Energy= 0.268340
Thermal correction to Enthalpy= 0.269284
Thermal correction to Gibbs Free Energy= 0.200876
Sum of electronic and ZPE= -1152.940562
Sum of electronic and thermal Energies= -1152.922748
Sum of electronic and thermal Enthalpies= -1152.921804
Sum of electronic and thermal Free Energies= -1152.990212

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	168.386	64.416	143.977

C,0,0.6119143852,0.8414667602,0.8281906347
C,0,4.1820093688,0.4873457442,-1.0998668267
C,0,1.9752295661,0.8220698654,1.0752091535
C,0,2.8157219929,0.3784783712,-1.1092254102
C,0,5.0421220537,-0.5849454656,-0.6708176304
H,0,4.6483913515,1.4338026468,-1.3550665939
C,0,-0.1557002748,-0.3343817858,0.6206592329
H,0,0.1370300446,1.8071945813,0.6807535167
C,0,2.7461081391,2.0535236459,1.4356685015
H,0,2.4233951839,-0.1296857356,1.3424528513
H,0,2.2060772472,1.181266335,-1.5049627762
H,0,2.3336995013,-0.5837135767,-0.9868253007
C,0,6.5392977328,-0.3378347178,-0.6684742131
O,0,4.6208114462,-1.6914123251,-0.2975494424
O,0,0.3305293348,-1.4996582445,0.6685915677
H,0,2.3000097414,2.9497352044,0.9933900173
H,0,3.7845207887,1.9810641053,1.095700066
H,0,2.7724411023,2.1980824504,2.5235260632
H,0,6.9105793507,-0.3910056116,0.3596024928
H,0,6.8109971567,0.6317676858,-1.0887983411

H,0,7.0384824508,-1.1279633038,-1.235837864
C,0,-1.6135773254,-0.19220039,0.2864627973
C,0,-2.3685179387,0.9525341655,0.5731443604
C,0,-2.2669590773,-1.2677897204,-0.3258135655
C,0,-3.7163223809,1.0300234994,0.2486860132
H,0,-1.9130968534,1.7970231278,1.0762735415
C,0,-3.6121486232,-1.2064619055,-0.6630768929
H,0,-1.6969408034,-2.1637636785,-0.5398223175
C,0,-4.3250604289,-0.0518979554,-0.3725742534
H,0,-4.2871173338,1.9201401157,0.4837859627
H,0,-4.0996176771,-2.0447221728,-1.1461637525
Cl,0,-6.0296892217,0.0399482849,-0.7878915923

B.6.1.1.9. 13-2Li gauche

./Li2PPKhetero-cisIM1-1
opt
E(UwB97XD) = -708.610837385

Zero-point correction= 0.269735 (Hartree/Particle)
Thermal correction to Energy= 0.288211
Thermal correction to Enthalpy= 0.289155
Thermal correction to Gibbs Free Energy= 0.222089
Sum of electronic and ZPE= -708.341102
Sum of electronic and thermal Energies= -708.322626
Sum of electronic and thermal Enthalpies= -708.321682
Sum of electronic and thermal Free Energies= -708.388748

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	180.855	69.025	141.152

C,0,-0.747834132,-1.2158424266,-0.3427785511
C,0,-1.9708176374,1.0381729451,-1.1026350103
C,0,-2.2166843587,-1.2706286235,-0.0938057983
C,0,-2.8536746483,-0.182870066,-0.9943608596
C,0,-1.7175735044,1.8828353639,-0.0707619103
H,0,-1.4916313432,1.2373557197,-2.0552797734
C,0,0.1949590048,-0.6770932587,0.5821000156
H,0,-0.3869992199,-1.5689163633,-1.3042036756
C,0,-2.7999565765,-2.6607323338,-0.3521397851
H,0,-2.3994146074,-0.9990478509,0.9468792529
H,0,-3.8474292805,0.0594805857,-0.5993132489
H,0,-3.0035756704,-0.6054410288,-1.9936984074
C,0,-0.7531688644,3.0333046426,-0.2367412555
O,0,-2.2490464355,1.7590804325,1.125112436
O,0,-0.1301810837,-0.3574414853,1.7434651657
H,0,-2.5986861726,-2.9823698729,-1.3788809571
H,0,-3.8841708018,-2.6467178947,-0.2099043164
H,0,-2.3780539376,-3.404707141,0.328519703
H,0,-0.3546036128,3.1003229325,-1.2507305623
H,0,0.0827915611,2.9073254115,0.4602913642
H,0,-1.2416201452,3.9810968794,0.0129232962
C,0,1.6164491412,-0.5003489864,0.1575069028
C,0,1.9557711858,-0.2163938428,-1.1672734528
C,0,2.6253044588,-0.5806944612,1.1198872593
C,0,3.285172584,-0.0222326514,-1.5230127296
H,0,1.1808377058,-0.1150210013,-1.9185320814
C,0,3.9542526757,-0.4034841381,0.7601906041
H,0,2.3580612395,-0.7926555058,2.1485546727
C,0,4.286225634,-0.1223001192,-0.5625347022
H,0,3.5379552838,0.2128072571,-2.5505107831
H,0,4.732637314,-0.482728761,1.5105103331
H,0,5.323775607,0.021569965,-0.842124488
Li,0,-1.6333352272,0.6376329389,2.5401121006
Li,0,-3.1360161361,3.2004127387,2.0030892418

B.6.1.1.10. 15-2Li gauche

./Li2PPKhetero-cisIM2-2
opt
E(UwB97XD) = -708.611960646

Zero-point correction= 0.269424 (Hartree/Particle)
Thermal correction to Energy= 0.287776
Thermal correction to Enthalpy= 0.288720
Thermal correction to Gibbs Free Energy= 0.222695
Sum of electronic and ZPE= -708.342537
Sum of electronic and thermal Energies= -708.324185
Sum of electronic and thermal Enthalpies= -708.323240
Sum of electronic and thermal Free Energies= -708.389265

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	180.582	69.165	138.961

C,0,-0.4760030291,-1.2998577751,-0.2222947241
C,0,-2.1280836149,0.4604207664,-1.4335442929
C,0,-1.9368149746,-1.560839038,0.0324250719
C,0,-2.7797765362,-0.823281501,-1.0442442452
C,0,-1.8425154199,1.5023782995,-0.4937274296
H,0,-1.7765248448,0.5955408937,-2.4509673108
C,0,0.3337819995,-0.6294604362,0.6369780046
H,0,-0.0721608186,-1.6428895109,-1.1706532442
C,0,-2.286153767,-3.0488312753,0.0666315625
H,0,-2.184437526,-1.1233523306,1.0015064431
H,0,-3.793253106,-0.6461707134,-0.6637629269
H,0,-2.8728110039,-1.4545570931,-1.9324916987
C,0,-0.9160869358,2.6139114967,-0.9098685296
O,0,-2.3005013185,1.4698451175,0.6619005781
O,0,-0.0307713247,-0.2239152098,1.8348308736
H,0,-2.0068707526,-3.5351598277,-0.8742211387
H,0,-3.3596413263,-3.2012785505,0.2185383574
H,0,-1.7525160124,-3.5536147273,0.8768013701
H,0,-1.0263083859,2.8679635727,-1.9653257366
H,0,0.1130754596,2.2692227354,-0.7556716323
H,0,-1.0828608189,3.4956336667,-0.2912400376
C,0,1.7432950903,-0.3019011819,0.2413592273
C,0,2.105217156,-0.0630445918,-1.0887784681
C,0,2.7317325008,-0.1956314997,1.2239126589
C,0,3.4182841973,0.2430163066,-1.4280539956
H,0,1.3483054107,-0.096991465,-1.8647818205
C,0,4.0464818549,0.1050885442,0.8870305395
H,0,2.4621592598,-0.3522811932,2.2620841034
C,0,4.3967189702,0.3240374174,-0.4418525504
H,0,3.6756384107,0.4307841605,-2.4649098837
H,0,4.7993091633,0.1727912989,1.6650809237
H,0,5.4207852978,0.5646757368,-0.7047724791
Li,0,-1.3984538564,0.9804578998,2.3593577573
Li,0,0.0439606014,-1.4089399924,3.3382746731

B.6.1.1.11. 7-2Li gauche

./Li2PPKhetero-cisPD-3
E(UwB97XD) = -708.620394000

Zero-point correction= 0.270269 (Hartree/Particle)
Thermal correction to Energy= 0.288348
Thermal correction to Enthalpy= 0.289293
Thermal correction to Gibbs Free Energy= 0.223721
Sum of electronic and ZPE= -708.350125

Sum of electronic and thermal Energies= -708.332046
Sum of electronic and thermal Enthalpies= -708.331101
Sum of electronic and thermal Free Energies= -708.396673

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 180.941 68.027 138.006

C,0,0.725792455,1.1080014588,-0.0155128092
C,0,1.4801265533,0.2984710946,-1.1573124599
C,0,2.0934699714,1.5543754501,0.5455574208
C,0,2.7821698863,1.0215568764,-0.7304338008
C,0,1.4402737574,-1.1805664618,-0.9063419983
H,0,1.1264743869,0.5148597826,-2.1652183867
C,0,-0.2299264907,0.367442385,0.8833234175
H,0,0.2265345608,1.9545747904,-0.4970554955
C,0,2.2550686058,3.0228688384,0.8893373916
H,0,2.3612808982,0.9441173248,1.4093144823
H,0,3.0361237684,1.8161823486,-1.4352721861
H,0,3.6539472865,0.3824748235,-0.5823289153
C,0,0.7035934825,-2.024849732,-1.8996532755
O,0,1.9396272799,-1.6727321676,0.0964552629
O,0,0.1992175909,-0.0303289453,2.057831702
H,0,1.6144551942,3.2999720641,1.7323420569
H,0,3.2894249919,3.2527457814,1.1622973938
H,0,1.982417428,3.6540014338,0.0370979246
H,0,1.1177708418,-1.8734235783,-2.9002412808
H,0,0.7403876006,-3.0779837681,-1.6258881642
H,0,-0.3361132414,-1.6799017838,-1.9304656054
C,0,-1.5318031919,0.0242485255,0.4187823247
C,0,-2.4110813689,-0.7509394534,1.2280745507
C,0,-2.0151337645,0.4006224286,-0.8685241333
C,0,-3.672914229,-1.1037168674,0.7867332788
H,0,-2.0709660467,-1.07476257,2.2049143395
C,0,-3.2802231284,0.0387593019,-1.294569117
H,0,-1.3867504205,0.9759732847,-1.5391977672
C,0,-4.1288603371,-0.714845196,-0.4772896404
H,0,-4.3154289557,-1.6956415,1.431434294
H,0,-3.6138916601,0.343982023,-2.2814642475
H,0,-5.1189298558,-0.9952884514,-0.8177914736
Li,0,-0.5238452871,0.6646539907,3.6919293812
Li,0,1.5636714377,-1.3961735319,2.0877955353

B.6.1.1.12. 12‡-2Li gauche

./Li2PPKhetero-cisTS1-3
opt=(calcfc,ts,modredundant,noeigentest)
E(UwB97XD) = -708.586884672

Zero-point correction= 0.267157 (Hartree/Particle)
Thermal correction to Energy= 0.285658
Thermal correction to Enthalpy= 0.286602
Thermal correction to Gibbs Free Energy= 0.219387
Sum of electronic and ZPE= -708.319728
Sum of electronic and thermal Energies= -708.301226
Sum of electronic and thermal Enthalpies= -708.300282
Sum of electronic and thermal Free Energies= -708.367497

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 179.253 69.046 141.466

C,0,-0.3289760236,-1.6738771656,-0.0558514435
C,0,-2.1577695181,0.6818285229,-1.1260338173
C,0,-1.6890272865,-1.9309465848,0.20657945
C,0,-2.8651789988,-0.4280136859,-0.6742332134

C,0,-1.8499118511,1.8056905501,-0.3122364943
H,0,-1.7474501867,0.6705956793,-2.1303240724
C,0,0.4371413559,-0.8007088381,0.7064854869
H,0,0.1050202566,-2.0783972387,-0.9640704573
C,0,-2.3384628838,-3.1549371196,-0.3851649279
H,0,-2.0216287237,-1.6913973775,1.2129683931
H,0,-3.2556983434,-1.1033921955,-1.4266658061
H,0,-3.4816419083,-0.3142934662,0.2127505628
C,0,-1.1001885123,2.9634459665,-0.9263356295
O,0,-2.1682436438,1.8858904524,0.8995549295
O,0,0.0005467653,-0.1959900989,1.7577060375
H,0,-1.977859735,-4.0500101036,0.1337536779
H,0,-3.4253538187,-3.1294059365,-0.2801814886
H,0,-2.0931131114,-3.2631619986,-1.4451936284
H,0,-0.9491029191,2.8470036547,-1.9998223708
H,0,-1.6424055618,3.8929507508,-0.735070323
H,0,-0.1232833605,3.0505600991,-0.4403143038
C,0,1.845101637,-0.5065932104,0.3009954616
C,0,2.3731160642,0.7626527475,0.5575390081
C,0,2.6592598624,-1.4578920229,-0.321844444
C,0,3.6755978327,1.078338502,0.1909140934
H,0,1.7468643372,1.5058561296,1.0391093542
C,0,3.9650319618,-1.1457939448,-0.6791895365
H,0,2.277677349,-2.4554162509,-0.5087253973
C,0,4.4772098625,0.1238102823,-0.4274884719
H,0,4.0660638206,2.0707827899,0.3870214722
H,0,4.5879181256,-1.8986181855,-1.1493022111
H,0,5.496423991,0.365129832,-0.7074859189
Li,0,-1.643907178,0.6552487122,2.2937850666
Li,0,1.080410343,0.0360207526,3.3661909623

12‡-2Li 2NMe₃ gauche

./Li2PPKhetero-cisTS1-NMe3-temp
opt=modredundant
E(UwB97XD) = -1057.56087314

Zero-point correction= 0.515802 (Hartree/Particle)
Thermal correction to Energy= 0.546932
Thermal correction to Enthalpy= 0.547876
Thermal correction to Gibbs Free Energy= 0.453793
Sum of electronic and ZPE= -1057.045071
Sum of electronic and thermal Energies= -1057.013941
Sum of electronic and thermal Enthalpies= -1057.012997
Sum of electronic and thermal Free Energies= -1057.107080

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	343.205	115.286	198.015

C,0,-0.7256795883,-0.9633044582,0.521134292
C,0,-2.6660230118,0.9068456233,-1.0353148697
C,0,-2.0696941848,-1.2884194573,0.812534579
C,0,-3.3397664498,0.1795014257,-0.063675197
C,0,-1.8672856691,2.0437098505,-0.7167767374
H,0,-2.6365542029,0.540918987,-2.0560347003
C,0,0.0182590859,-0.0579692576,1.257880399
H,0,-0.2980967083,-1.3371522099,-0.4037547493
C,0,-2.6596156941,-2.5440331783,0.2263611478
H,0,-2.4025305066,-1.0397117847,1.8174798096
H,0,-4.0811250586,-0.544042211,-0.3811016964
H,0,-3.5551671818,0.6701916688,0.8790297952
C,0,-1.0630346164,2.7088331523,-1.8051240453
O,0,-1.7917388387,2.5165545665,0.4418083313
O,0,-0.4049041711,0.5197189531,2.3327428465
H,0,-2.1837661713,-3.4210824729,0.6799221047
H,0,-3.7325630637,-2.6193577682,0.4123279897

H,0,-2.4875958232,-2.5954898332,-0.8523938776
H,0,-1.3115446305,2.3364981721,-2.7994652414
H,0,-1.2162753129,3.7900077409,-1.7708815979
H,0,-0.0007274276,2.5213260084,-1.6144839499
C,0,1.3758487112,0.333946705,0.7731068527
C,0,1.7499101681,1.6781137496,0.8480439137
C,0,2.2797229277,-0.5918413398,0.2474768346
C,0,2.9958368794,2.0915689731,0.3940555368
H,0,1.045350377,2.3968150137,1.2516349695
C,0,3.5344772073,-0.1812125625,-0.1884914565
H,0,2.009786719,-1.6413192443,0.20225133
C,0,3.8946487882,1.1613845838,-0.1200946189
H,0,3.2680298261,3.1401510804,0.4436005647
H,0,4.2350966604,-0.9122646879,-0.576269736
H,0,4.8720894758,1.4808322565,-0.4634901201
Li,0,-1.7935243925,1.8447735526,2.2373150568
Li,0,0.6948181805,0.7163015519,3.9156412792
N,0,2.6854671022,1.0776444497,4.5316883256
C,0,3.584050827,0.1971531297,3.785801108
H,0,3.5306084016,0.4305421025,2.7213407725
H,0,3.2845134216,-0.8434307033,3.9290809651
H,0,4.6279820946,0.3090517063,4.1192012171
C,0,2.7389451683,0.7693026046,5.9595112141
H,0,2.0414131125,1.4099595874,6.5035291649
H,0,3.7485009593,0.9237978217,6.3716277016
H,0,2.4544390877,-0.2724848585,6.1231636877
C,0,3.0353077125,2.4781820171,4.3012280498
H,0,2.9719444585,2.7023728344,3.2353432043
H,0,4.056806475,2.7032209195,4.6465093228
H,0,2.3385065176,3.1259598945,4.8377006999
N,0,-3.201096237,1.8859276248,3.824705156
C,0,-4.4431895798,1.2059198453,3.4635846234
H,0,-4.2340419791,0.1648069071,3.2065459045
H,0,-4.8968219014,1.6957567391,2.5991727727
H,0,-5.169193857,1.2191263554,4.2916782468
C,0,-3.4620227168,3.2913012686,4.1350323359
H,0,-2.5219796123,3.7985752808,4.363169766
H,0,-4.1374088309,3.4005863849,4.9978433007
H,0,-3.9184012475,3.7795991759,3.271629222
C,0,-2.5732588239,1.218394969,4.9634309553
H,0,-2.324325387,0.1894165223,4.6960381381
H,0,-3.2353028217,1.2059492289,5.8432936012
H,0,-1.6540046464,1.7411250429,5.234215505

16‡-2Li 2NMe₃ gauche

./Li2PPKhetero-cisTS2-1-2NMe3-temp
opt=(modredundant,calcfc)
E(UwB97XD) = -1057.56947696

Zero-point correction= 0.517401 (Hartree/Particle)
Thermal correction to Energy= 0.548036
Thermal correction to Enthalpy= 0.548980
Thermal correction to Gibbs Free Energy= 0.455612
Sum of electronic and ZPE= -1057.052076
Sum of electronic and thermal Energies= -1057.021441
Sum of electronic and thermal Enthalpies= -1057.020497
Sum of electronic and thermal Free Energies= -1057.113865

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	343.898	113.845	196.509

C,0,1.248889,-0.464123,1.225862
C,0,1.212205,-2.518746,1.011704
C,0,-0.195766,-0.770359,1.563424
C,0,-0.033553,-2.271238,1.840765
C,0,1.144899,-2.792083,-0.371684

H,0,2.128583,-2.811338,1.511699
C,0,1.61838,0.349817,0.133598
H,0,1.940133,-0.504383,2.062228
C,0,-0.807146,0.082882,2.663989
H,0,-0.769848,-0.653979,0.641868
H,0,0.175597,-2.451082,2.899519
H,0,-0.894839,-2.8834,1.557253
C,0,2.43755,-2.941842,-1.133862
O,0,0.067114,-2.800451,-1.026719
O,0,0.765246,0.793402,-0.709686
H,0,-0.809832,1.140203,2.384858
H,0,-1.840806,-0.213004,2.867682
H,0,-0.238959,-0.019197,3.594295
H,0,2.338169,-3.708559,-1.905122
H,0,2.651964,-1.98876,-1.632174
H,0,3.281688,-3.177159,-0.483979
C,0,3.059032,0.650745,-0.103337
C,0,3.403895,1.654537,-1.016327
C,0,4.092439,-0.049165,0.534064
C,0,4.733819,1.962177,-1.272011
H,0,2.608388,2.188966,-1.521797
C,0,5.422662,0.256704,0.27681
H,0,3.860937,-0.856118,1.219388
C,0,5.750767,1.265644,-0.624831
H,0,4.979421,2.746513,-1.979914
H,0,6.207886,-0.300435,0.776119
H,0,6.789943,1.501454,-0.825253
Li,0,-1.796362,-2.652851,-1.119419
Li,0,-0.787731,1.830744,-0.475661
N,0,-2.423561,3.136913,0.031483
C,0,-1.863281,4.481872,-0.1044
H,0,-1.443594,4.608577,-1.104664
H,0,-1.065714,4.624296,0.627665
H,0,-2.627506,5.25872,0.05426
C,0,-3.472345,2.92381,-0.965033
H,0,-3.051425,3.007682,-1.969376
H,0,-4.284943,3.66025,-0.864094
H,0,-3.898275,1.925508,-0.848133
C,0,-2.955862,2.945786,1.379145
H,0,-3.775388,3.649417,1.594529
H,0,-2.165589,3.102296,2.115634
H,0,-3.335591,1.928473,1.491176
N,0,-3.684137,-1.692662,-0.75917
C,0,-4.010863,-0.919573,-1.955466
H,0,-4.042355,-1.580312,-2.824246
H,0,-3.243318,-0.161228,-2.126429
H,0,-4.986562,-0.416727,-1.863066
C,0,-3.624152,-0.819389,0.409118
H,0,-3.324577,-1.393356,1.288489
H,0,-4.59615,-0.342314,0.613529
H,0,-2.882343,-0.035426,0.243117
C,0,-4.671954,-2.750901,-0.548825
H,0,-4.685355,-3.421243,-1.410712
H,0,-5.683776,-2.339904,-0.407831
H,0,-4.40636,-3.330812,0.337557

16‡-2Li gauche

./Li2PPKhetero-cisTS2-3
E(UwB97XD) = -708.605566047

Zero-point correction= 0.269270 (Hartree/Particle)
Thermal correction to Energy= 0.287049
Thermal correction to Enthalpy= 0.287993
Thermal correction to Gibbs Free Energy= 0.223109
Sum of electronic and ZPE= -708.336296
Sum of electronic and thermal Energies= -708.318517
Sum of electronic and thermal Enthalpies= -708.317573

Sum of electronic and thermal Free Energies= -708.382458

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 180.126 67.072 136.561

C,0,-0.6364150666,-1.0818755676,-0.1829386971
C,0,-1.8184763376,0.1988728892,-1.2004387056
C,0,-2.0022519213,-1.5301087095,0.3138082474
C,0,-2.8377671352,-0.843638706,-0.7752688923
C,0,-1.6495428999,1.4110594636,-0.477509889
H,0,-1.4594643593,0.198737218,-2.2239137195
C,0,0.3478199561,-0.5562568485,0.6850093035
H,0,-0.2775224635,-1.6133778806,-1.0595117583
C,0,-2.1616741402,-3.0334637013,0.4844445907
H,0,-2.1977163247,-1.0317918877,1.2646230252
H,0,-3.041171655,-1.5262659083,-1.6049948353
H,0,-3.7859221703,-0.4267070149,-0.4276321647
C,0,-0.6220265982,2.3988648143,-0.9694046612
O,0,-2.2057655091,1.6243371834,0.6282973658
O,0,0.0557724946,-0.2230570844,1.9088161135
H,0,-1.4729725669,-3.416672898,1.2442745241
H,0,-3.1809688573,-3.283978201,0.7927463218
H,0,-1.9543242412,-3.5565768358,-0.4546581231
H,0,-0.9784326061,3.4187422409,-0.8120783116
H,0,0.2881359116,2.2661544199,-0.3715220038
H,0,-0.3625653443,2.2531675882,-2.0185150671
C,0,1.7103339139,-0.2696945048,0.1913195451
C,0,2.7153871812,0.0694491216,1.1086500872
C,0,2.0411720474,-0.292836997,-1.1734303189
C,0,4.0055169042,0.3542859962,0.6823822532
H,0,2.4656498841,0.1029527433,2.1621619
C,0,3.3305772488,-0.00342535,-1.5974266447
H,0,1.2832426778,-0.512584953,-1.9160815593
C,0,4.3215788125,0.318535375,-0.6731741882
H,0,4.7689022548,0.6069901681,1.4102720819
H,0,3.5613913041,-0.0194246729,-2.6569957016
H,0,5.3280031957,0.544780308,-1.00683371
Li,0,-1.1972747142,1.2551069787,2.2883618758
Li,0,-0.3372698757,-1.5648487873,3.254309716

B.6.1.1.13. 13-2Li

./Li2PPKhetero-transIM1-1
E(UwB97XD) = -708.612439824

Zero-point correction= 0.270244 (Hartree/Particle)
Thermal correction to Energy= 0.288369
Thermal correction to Enthalpy= 0.289313
Thermal correction to Gibbs Free Energy= 0.223661
Sum of electronic and ZPE= -708.342196
Sum of electronic and thermal Energies= -708.324071
Sum of electronic and thermal Enthalpies= -708.323126
Sum of electronic and thermal Free Energies= -708.388778

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 180.954 68.811 138.176

C,0,-0.210189385,1.1342125116,0.2832826657
C,0,3.4656116776,0.6222472362,-0.631980214
C,0,1.2501454443,1.1874543255,0.5042492769
C,0,2.0041097823,0.866125411,-0.8379250014
C,0,3.9695664497,-0.6042235262,-0.3518719081
H,0,4.1446835895,1.4669209522,-0.6711121072
C,0,-0.9185584366,-0.1087506314,0.2203292306

H,0,-0.7507814865,2.0627885759,0.1365767726
C,0,1.6938048139,2.5309907969,1.0796778617
H,0,1.5241046643,0.3879488244,1.2005861081
H,0,1.5413942024,-0.0153520494,-1.293446519
H,0,1.836959836,1.7053969352,-1.521614146
C,0,5.4537852941,-0.7951082579,-0.1372462112
O,0,3.242553892,-1.6992480485,-0.2519360086
O,0,-0.3104758834,-1.189865716,0.3360109086
H,0,1.2092351988,2.7312217007,2.0384941239
H,0,2.7746397992,2.5364136466,1.2356922774
H,0,1.4447822622,3.3463498056,0.392924969
H,0,6.0076795159,0.1410642983,-0.228000031
H,0,5.6349538344,-1.2159959628,0.8571991063
H,0,5.8555004392,-1.5061503075,-0.8672641027
C,0,-2.4011190805,-0.1240347827,0.0502661277
C,0,-3.1019268362,-1.2662165808,0.4489374576
C,0,-3.1057792639,0.9481701598,-0.504700326
C,0,-4.4802627476,-1.3315084607,0.3082340492
H,0,-2.553877347,-2.0974477384,0.8759379824
C,0,-4.4849310014,0.8756260156,-0.6576053008
H,0,-2.5878406934,1.8371798869,-0.843737233
C,0,-5.174589199,-0.2601281207,-0.2476057592
H,0,-5.01436101,-2.2176188057,0.631155175
H,0,-5.0201587514,1.7080736077,-1.0992271449
H,0,-6.2511454783,-0.3126827141,-0.3631928598
Li,0,1.4614187779,-2.0674901512,0.2550612439
Li,0,3.8319971266,-3.4280828361,-0.8192804635

B.6.1.1.14. 7-2Li

./Li2PPKhetero-transPD-4
opt
E(UwB97XD) = -708.614481389

Zero-point correction= 0.270102 (Hartree/Particle)
Thermal correction to Energy= 0.288208
Thermal correction to Enthalpy= 0.289152
Thermal correction to Gibbs Free Energy= 0.223167
Sum of electronic and ZPE= -708.344379
Sum of electronic and thermal Energies= -708.326274
Sum of electronic and thermal Enthalpies= -708.325330
Sum of electronic and thermal Free Energies= -708.391314

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	180.853	68.154	138.877

C,0,1.0078849577,-0.4873494339,0.2510760889
C,0,2.0182916802,0.3510725053,-0.6446451198
C,0,2.1621806414,-1.5027931947,0.4462255882
C,0,3.1704875122,-0.4105588096,0.0237803395
C,0,1.8611807692,1.818893059,-0.4713472486
H,0,1.8658927527,0.060859483,-1.6866737679
C,0,-0.277355668,-0.9350263265,-0.3754792191
H,0,0.8542416987,0.0484071253,1.1904114016
C,0,2.3053547224,-2.1592507967,1.8046501624
H,0,2.0837428938,-2.2553118511,-0.3427418486
H,0,4.0059490045,-0.7043889229,-0.6133368617
H,0,3.5493616974,0.1415304415,0.8879795616
C,0,0.758707809,2.4696037764,-1.253832206
O,0,2.5522004483,2.4525200962,0.3183755859
O,0,-0.1920059263,-1.8122068248,-1.3187288503
H,0,2.3858647189,-1.4054790996,2.5949269029
H,0,3.1992261249,-2.7891090882,1.8468029394
H,0,1.438782886,-2.7899748582,2.0269389947
H,0,1.0377374877,2.4800354405,-2.3120908472

H,0,0.5789442556,3.4893856401,-0.914313367
H,0,-0.154890676,1.8725518351,-1.1715525928
C,0,-1.5342719844,-0.3612420964,-0.0007414186
C,0,-2.7313886408,-0.7964443525,-0.6441348417
C,0,-1.6885297613,0.6581004898,0.9864333717
C,0,-3.9652664212,-0.2616908446,-0.3223648334
H,0,-2.6602683779,-1.5626764382,-1.4070555744
C,0,-2.9293084984,1.183231265,1.2958339795
H,0,-0.8237463101,1.049051217,1.5098578192
C,0,-4.0887598074,0.7348998009,0.6513570277
H,0,-4.8507691121,-0.6228317124,-0.8372704805
H,0,-3.0002144111,1.958530651,2.0528464893
H,0,-5.0578253836,1.1529710906,0.8985201574
Li,0,-0.6716555731,-3.2612841722,-2.3245776027
Li,0,2.4327444909,4.1759949058,1.3051002702

B.6.1.1.15. 12‡-2Li

./Li2PPKhetero-transTS1-1
E(UwB97XD) = -708.588763379

Zero-point correction= 0.266781 (Hartree/Particle)
Thermal correction to Energy= 0.285182
Thermal correction to Enthalpy= 0.286126
Thermal correction to Gibbs Free Energy= 0.220060
Sum of electronic and ZPE= -708.321983
Sum of electronic and thermal Energies= -708.303582
Sum of electronic and thermal Enthalpies= -708.302638
Sum of electronic and thermal Free Energies= -708.368704

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	178.954	69.463	139.048

C,0,-0.4602289038,1.4273473968,0.3756064361
C,0,3.3765554971,0.5837412169,-0.8096586443
C,0,0.8455543833,1.6709850113,0.7194697922
C,0,2.0548997671,0.8041018779,-1.1800891041
C,0,3.8608133837,-0.6268804352,-0.2945376033
H,0,4.0885836473,1.3983682557,-0.8989050522
C,0,-1.0192226062,0.1148461715,0.4395271898
H,0,-1.0677529887,2.2451276223,0.0063939572
C,0,1.4232684884,3.0482694563,0.7925600478
H,0,1.384514165,0.9011098278,1.2581578648
H,0,1.3631230904,-0.0271947293,-1.2499866153
H,0,1.7815467467,1.7098289085,-1.7065717959
C,0,5.3261934324,-0.7781321214,0.0208892731
O,0,3.1125776589,-1.6580247777,-0.0915281739
O,0,-0.3410751278,-0.8866190449,0.7646022167
H,0,1.2581545065,3.4624198772,1.7942687512
H,0,2.5013330353,3.0330545681,0.6213414885
H,0,0.9566844404,3.7217987435,0.0701521079
H,0,5.8850357285,0.1426379197,-0.1509362201
H,0,5.452730942,-1.0799992114,1.0654612423
H,0,5.7618043053,-1.5696324202,-0.5992388246
C,0,-2.4666090728,-0.0990840869,0.120211893
C,0,-3.0814227955,-1.2656914082,0.5856483586
C,0,-3.2211497511,0.8020876139,-0.6375894259
C,0,-4.4191270748,-1.5191103928,0.3168561227
H,0,-2.4943875362,-1.9668724319,1.1663594239
C,0,-4.5573834752,0.54207107,-0.9178829463
H,0,-2.7691890913,1.7029332391,-1.0344874086
C,0,-5.161595586,-0.6153459817,-0.4378627589
H,0,-4.883916121,-2.4228609972,0.6946441664
H,0,-5.1271903095,1.2440032902,-1.5160296312
H,0,-6.2057742629,-0.8129215559,-0.6525313705

Li,0,1.3807039896,-1.7387419126,0.7801911514
Li,0,3.6418394986,-3.5247585595,-0.3441619084

B.6.1.1.16. 12‡-2Li 2NMe3

./Li2PPKhetero-transTS1-NMe3-temp2
opt=(calcfc,modredundant)
E(UwB97XD) = -1057.56161296

Zero-point correction= 0.514727 (Hartree/Particle)
Thermal correction to Energy= 0.546156
Thermal correction to Enthalpy= 0.547100
Thermal correction to Gibbs Free Energy= 0.450684
Sum of electronic and ZPE= -1057.046886
Sum of electronic and thermal Energies= -1057.015457
Sum of electronic and thermal Enthalpies= -1057.014513
Sum of electronic and thermal Free Energies= -1057.110929

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	342.718	116.189	202.926

C,0,-2.6766675011,1.4683870524,-0.0874857697
C,0,0.9275297874,2.471460209,-1.6190954151
C,0,-1.5215300868,2.1853809574,0.1275867396
C,0,-0.3688924007,2.052721776,-1.9026744516
C,0,1.9153002081,1.6167626825,-1.1145461878
H,0,1.1839585146,3.5193944717,-1.7334943952
C,0,-2.6702634628,0.0447771691,-0.1435737758
H,0,-3.5969405673,1.9990373119,-0.3029936152
C,0,-1.5164564107,3.6628411117,0.3621831339
H,0,-0.6622403684,1.6468431835,0.5053692889
H,0,-0.5897492866,0.993415489,-1.9659024414
H,0,-1.0632175271,2.7252477773,-2.3912955224
C,0,3.2958557085,2.1457588221,-0.8276390563
O,0,1.7051985455,0.3681283412,-0.8822326802
O,0,-1.6126827946,-0.628299563,-0.0867742608
H,0,-1.7155926268,3.864493919,1.4214434286
H,0,-0.5448426145,4.0995413026,0.124243429
H,0,-2.287998667,4.166711648,-0.2247229272
H,0,3.3813086162,3.2158482823,-1.0188728233
H,0,3.5548260633,1.9528870922,0.2185760638
H,0,4.033592293,1.6245203759,-1.44711622
C,0,-3.9637385485,-0.6870513471,-0.3150128191
C,0,-3.9441833552,-1.9736563893,-0.8605685041
C,0,-5.1899497109,-0.1348800817,0.0675264345
C,0,-5.12384724,-2.6835898637,-1.0405667364
H,0,-2.9928175767,-2.4056132254,-1.1475552064
C,0,-6.3693852398,-0.8499140699,-0.1012512626
H,0,-5.2289082462,0.8487117931,0.5209192347
C,0,-6.3403910258,-2.12316819,-0.6613412226
H,0,-5.0955931089,-3.6752873964,-1.4779391377
H,0,-7.3118143009,-0.4127454125,0.2085402022
H,0,-7.2623894552,-2.6769002516,-0.7985413581
Li,0,0.2708257415,-0.4474141012,0.1437969881
Li,0,3.0496186364,-1.0338298182,-0.9771786248
N,0,5.0840778207,-1.553878365,-0.6194620098
C,0,5.1859542373,-2.9965368749,-0.4056895267
H,0,6.2267615232,-3.3095871568,-0.2292304485
H,0,4.8078309352,-3.5266148341,-1.2822808144
H,0,4.5856340483,-3.2838438671,0.4600586729
C,0,5.5526189468,-0.828290843,0.5596889515
H,0,6.6156434352,-1.0287132844,0.7660462029
H,0,4.9693770108,-1.1267435342,1.4330959776
H,0,5.4257167751,0.245550171,0.4072574523
C,0,5.850356221,-1.1558766852,-1.8002086802

H,0,5.4716591359,-1.6795336035,-2.6802417208
H,0,6.9211515539,-1.3863456093,-1.6874667931
H,0,5.7440105913,-0.0814139023,-1.964189658
N,0,0.7875334907,-0.074281697,2.1909280097
C,0,2.1626768094,-0.5611992547,2.2678583738
H,0,2.809178716,0.0924624258,1.6791295872
H,0,2.2263086687,-1.5707652712,1.8535065651
H,0,2.5346475889,-0.5857084262,3.3041217164
C,0,-0.1103389484,-0.9296705865,2.9649907408
H,0,0.14848768,-0.9366893498,4.0355120458
H,0,-0.0572287313,-1.9536341964,2.588023723
H,0,-1.1368477955,-0.5757364649,2.8516273038
C,0,0.7269286816,1.3028968997,2.6752540857
H,0,1.303966818,1.9544448584,2.0137135916
H,0,1.1325896067,1.3922887886,3.6952294707
H,0,-0.3079618116,1.6487816048,2.6881496516

B.6.1.1.17. 12‡-2Li

./Li2PPKhetero-transTS2-1
E(UwB97XD) = -708.601488481

Zero-point correction= 0.268921 (Hartree/Particle)
Thermal correction to Energy= 0.286969
Thermal correction to Enthalpy= 0.287913
Thermal correction to Gibbs Free Energy= 0.221362
Sum of electronic and ZPE= -708.332567
Sum of electronic and thermal Energies= -708.314519
Sum of electronic and thermal Enthalpies= -708.313575
Sum of electronic and thermal Free Energies= -708.380126

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	180.076	67.213	140.068

C,0,0.8820976049,-0.7876720319,0.3818830451
C,0,1.9719130012,0.3560418153,-0.8858495611
C,0,2.1679403634,-1.5922721392,0.3063281934
C,0,3.0574592723,-0.4506959371,-0.2023474825
C,0,1.7322422839,1.7256445014,-0.6266263605
H,0,1.6165199485,-0.0257706072,-1.8387560655
C,0,-0.3463457015,-1.2405104111,-0.1509154295
H,0,0.8406320399,-0.0950249437,1.2177071853
C,0,2.5869438717,-2.2717938947,1.602199514
H,0,2.0497624778,-2.340109243,-0.4827864362
H,0,3.8818265818,-0.7494930549,-0.8561494852
H,0,3.4658232303,0.1219426109,0.6350804166
C,0,0.7476912782,2.4715802768,-1.4978330173
O,0,2.2616857583,2.3367282689,0.3439711757
O,0,-0.4127836635,-2.2577343921,-0.9162731604
H,0,2.6761238695,-1.5382308498,2.410412537
H,0,3.5566858583,-2.765957457,1.487631381
H,0,1.855967281,-3.0261401266,1.9080908101
H,0,1.2947160577,3.1437805958,-2.1677018305
H,0,0.0904185568,3.0860435975,-0.877419394
H,0,0.1408825616,1.798216193,-2.1055155287
C,0,-1.5884724551,-0.4574088023,0.1058770796
C,0,-2.8276759774,-1.0061320917,-0.2479751327
C,0,-1.5746596978,0.8268674128,0.6692576115
C,0,-4.0096612997,-0.3096494091,-0.0338067653
H,0,-2.8538482958,-1.993488097,-0.6926166491
C,0,-2.7562326174,1.5269943978,0.8771670385
H,0,-0.6364279061,1.2992598631,0.9342181608
C,0,-3.9804419074,0.9624298547,0.5307714412
H,0,-4.9572310096,-0.7602789834,-0.3086294568
H,0,-2.7198686566,2.5212075675,1.3091002936

H,0,-4.9022493533,1.5088252781,0.6959659649
Li,0,-0.9933533451,-3.7764617284,-1.8032805347
Li,0,2.2419429889,4.0701999669,1.1652284418

B.6.1.1.18. 16‡-2Li 2NMe3

./Li2PPKhetero-transTS2-1-2NMe3-temp
opt=(modredundant,calcfc)
E(UwB97XD) = -1057.57495372

Zero-point correction= 0.515099 (Hartree/Particle)
Thermal correction to Energy= 0.546549
Thermal correction to Enthalpy= 0.547494
Thermal correction to Gibbs Free Energy= 0.451899
Sum of electronic and ZPE= -1057.059854
Sum of electronic and thermal Energies= -1057.028404
Sum of electronic and thermal Enthalpies= -1057.027460
Sum of electronic and thermal Free Energies= -1057.123055

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 342.965 115.264 201.195

C,0,0.8401263458,-0.8108449474,-1.8189254008
C,0,0.3163447003,-2.5289151231,0.0384250324
C,0,1.4046849616,-2.1632966031,-2.1360089581
C,0,0.5454024318,-3.1393457692,-1.3204512162
C,0,-0.8894575914,-2.0033269882,0.4541637309
H,0,1.1460081119,-2.520180712,0.7378539654
C,0,1.6238588625,0.3187967958,-1.4963496551
H,0,-0.2332396084,-0.6915440728,-1.9184345579
C,0,1.4288300224,-2.4571142204,-3.6382651094
H,0,2.4310734271,-2.194462564,-1.7571495424
H,0,1.023842204,-4.1238095543,-1.261662051
H,0,-0.4211004907,-3.2726817299,-1.8181908078
C,0,-0.9927713823,-1.4072579416,1.8440901059
O,0,-1.9519987314,-1.962427161,-0.2673326769
O,0,2.8802868138,0.2722982819,-1.4768982162
H,0,0.4184207708,-2.4098347363,-4.0568379884
H,0,1.824975302,-3.4601758819,-3.8232908489
H,0,2.0552025354,-1.7396705531,-4.1754059732
H,0,-1.8549273507,-1.839174269,2.361771511
H,0,-1.1612881295,-0.3268224425,1.7779649794
H,0,-0.0978258059,-1.5759687755,2.4455215155
C,0,0.9431115701,1.6057155771,-1.1469044303
C,0,1.6191333286,2.8093737238,-1.3575272585
C,0,-0.334344339,1.6354969516,-0.5805869689
C,0,1.0336617622,4.0203153285,-1.0127909793
H,0,2.6047713752,2.7916114317,-1.8083785174
C,0,-0.9139325275,2.8466803985,-0.2236695704
H,0,-0.8684723822,0.7083709703,-0.3993093261
C,0,-0.2336822294,4.0411261541,-0.4394399071
H,0,1.5649359149,4.9481815568,-1.1922534226
H,0,-1.8981249619,2.864342533,0.2295312517
H,0,-0.6911855498,4.9838619163,-0.161721727
Li,0,4.1938394145,1.0561998104,-0.2721098472
Li,0,-3.7848707906,-1.8774080572,0.0556457493
N,0,-4.7293344582,-0.1514824256,0.8579057148
C,0,-3.8814736277,0.9732933903,0.475849899
H,0,-3.7689758218,1.0028566492,-0.6103516615
H,0,-2.8933214548,0.8454523712,0.9207237351
H,0,-4.2996120669,1.9354321494,0.8132514125
C,0,-6.0564561462,-0.0201551831,0.2609603811
H,0,-5.9698819492,0.0127243865,-0.827284418
H,0,-6.5670605913,0.8957057952,0.5983951587
H,0,-6.671262548,-0.8803885377,0.5338160574

C,0,-4.8243857041,-0.2485913118,2.3123975849
H,0,-3.8266587612,-0.375497812,2.7373842333
H,0,-5.4319995672,-1.1136229582,2.5858758532
H,0,-5.280458034,0.6524275073,2.7524159405
N,0,3.707969826,0.0902138282,1.5699150879
C,0,2.3070101512,0.3405450849,1.901540148
H,0,1.6618461367,-0.0828402573,1.1301867121
H,0,2.123253136,1.4159021412,1.9602360251
H,0,2.0318241576,-0.1166424056,2.8658383249
C,0,4.5784945867,0.5780456868,2.6364473725
H,0,5.624334977,0.4287819145,2.3591353319
H,0,4.3909001303,0.0563749561,3.5885258026
H,0,4.4093555361,1.6462968929,2.7889306864
C,0,3.9264450895,-1.3352941841,1.3337833291
H,0,3.324220063,-1.6569188293,0.481773614
H,0,3.6550071773,-1.9429383758,2.2118718022
H,0,4.978651779,-1.5126698007,1.1005429878

B.6.1.1.19. LiF

./LiF
opt
E(UwB97XD) = -107.500406895

Zero-point correction= 0.001211 (Hartree/Particle)
Thermal correction to Energy= 0.003773
Thermal correction to Enthalpy= 0.004717
Thermal correction to Gibbs Free Energy= -0.018444
Sum of electronic and ZPE= -107.499196
Sum of electronic and thermal Energies= -107.496634
Sum of electronic and thermal Enthalpies= -107.495689
Sum of electronic and thermal Free Energies= -107.518851

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 2.368 6.148 48.747

F,0,-1.8125316829,-1.0059248115,0.
Li,0,-3.5204283171,-1.4156451885,0.

B.6.1.1.20. 6-Li

./LiMVK-1
E(UwB97XD) = -238.719125409

Zero-point correction= 0.091710 (Hartree/Particle)
Thermal correction to Energy= 0.099053
Thermal correction to Enthalpy= 0.099997
Thermal correction to Gibbs Free Energy= 0.060890
Sum of electronic and ZPE= -238.627416
Sum of electronic and thermal Energies= -238.620073
Sum of electronic and thermal Enthalpies= -238.619129
Sum of electronic and thermal Free Energies= -238.658236

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 62.156 24.516 82.308

C,0,-0.818521723,1.3292843845,-0.02100787
H,0,-0.393717714,1.7939745323,0.8721438136
H,0,-0.3584029975,1.8052518543,-0.8901766355
H,0,-1.8934194291,1.500059554,-0.0415896459
C,0,-0.5329823061,-0.1455917618,-0.0237809661
O,0,-1.4409404079,-0.9685305465,-0.0254243361
C,0,0.8613250358,-0.6330547355,-0.021026099

H,0,0.9627670136,-1.7135702271,-0.044081251
C,0,1.9310112575,0.1590995887,0.0190220287
H,0,1.8532758049,1.2407190299,0.0468042597
H,0,2.9315686478,-0.2576073513,0.0286229479
Li,0,-3.4528431818,-0.9531643215,0.1908437537

B.6.1.1.21. 6-Li 2CH_3CN

./LiMVK-2ACN
E(UwB97XD) = -504.232160809

Zero-point correction= 0.185888 (Hartree/Particle)
Thermal correction to Energy= 0.203699
Thermal correction to Enthalpy= 0.204643
Thermal correction to Gibbs Free Energy= 0.134999
Sum of electronic and ZPE= -504.046272
Sum of electronic and thermal Energies= -504.028462
Sum of electronic and thermal Enthalpies= -504.027518
Sum of electronic and thermal Free Energies= -504.097161

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	127.823	55.918	146.578

C,0,0.4777665089,1.462823193,0.0674575681
H,0,0.1023531778,1.8298721617,-0.8909623737
H,0,-0.1532956212,1.8874490846,0.8521945324
H,0,1.5046760548,1.795308947,0.205157275
C,0,0.4145312325,-0.0370673921,0.1075021069
O,0,1.4227480727,-0.7122376703,0.2763367825
C,0,-0.8800266292,-0.7302429233,-0.055486234
H,0,-0.8230746637,-1.8133604203,-0.0103058582
C,0,-2.0420630759,-0.1079308886,-0.2445331406
H,0,-2.1207041302,0.972860593,-0.2920332322
H,0,-2.9615656642,-0.6702993957,-0.358888046
Li,0,3.3872736361,-0.4311353429,0.4850601701
N,0,3.8992517184,1.0959084441,-0.9718495077
N,0,4.2798229997,-2.377146498,0.8048403591
C,0,4.0702436963,1.9366504101,-1.7349419735
C,0,4.8358448544,-3.3733822424,0.9336910277
C,0,4.2800465574,3.0016256409,-2.6974287181
H,0,5.2100575031,2.8265036971,-3.2386482963
H,0,4.3401544484,3.9569433713,-2.1753265962
H,0,3.4484860557,3.0248412304,-3.4018948668
C,0,5.5420276896,-4.6303371628,1.0942705831
H,0,6.2539506829,-4.7537228702,0.277732419
H,0,4.8294883398,-5.4552657833,1.0809654
H,0,6.0767465561,-4.6285781834,2.0444006194

B.6.1.1.22. 6-Li NMe_3

./LiMVK-NMe3
opt
E(UwB97XD) = -413.200444287

Zero-point correction= 0.215175 (Hartree/Particle)
Thermal correction to Energy= 0.229229
Thermal correction to Enthalpy= 0.230173
Thermal correction to Gibbs Free Energy= 0.172767
Sum of electronic and ZPE= -412.985269
Sum of electronic and thermal Energies= -412.971215
Sum of electronic and thermal Enthalpies= -412.970271
Sum of electronic and thermal Free Energies= -413.027678

E CV S

KCal/Mol Cal/Mol-K Cal/Mol-K
Total 143.843 48.127 120.822

C,0,-2.708610168,-0.5508093427,-0.3454892919
H,0,-2.8501984186,-0.9383413896,-1.3574382028
H,0,-3.6901222479,-0.5135352517,0.1328236476
H,0,-2.2920854641,0.4532699019,-0.3985997866
C,0,-1.7848404664,-1.4485043981,0.4271206723
O,0,-0.7235453941,-1.0320947564,0.8764090839
C,0,-2.1444679159,-2.8621667682,0.6593091461
H,0,-1.4128275291,-3.428001451,1.2275705427
C,0,-3.2646345233,-3.4316913921,0.2183865294
H,0,-4.0092718915,-2.8866853298,-0.3518879661
H,0,-3.4733986936,-4.4762492055,0.418664935
Li,0,0.3085686301,0.7024934098,0.8352742077
N,0,0.842499141,2.7381407994,1.1694922633
C,0,-0.343542752,3.5827822771,1.0347839018
H,0,-1.1059533092,3.2648328611,1.7491623598
H,0,-0.7507386651,3.4882404417,0.0260009503
H,0,-0.1111524483,4.6432190667,1.2202313648
C,0,1.8586015073,3.1232389167,0.1913631599
H,0,1.4542486271,3.0289581476,-0.8185865315
H,0,2.7250012336,2.4647055281,0.2815170896
H,0,2.1927310616,4.162127526,0.339217384
C,0,1.3815788597,2.8275001183,2.5258256864
H,0,0.6209398884,2.5211479128,3.2469032562
H,0,1.7020764512,3.8523526209,2.7702226814
H,0,2.241964487,2.1623697569,2.6254229168

B.6.1.1.23. 13-Li gauche

./LiPPKhetero-cisIM1-2
E(UwB97XD) = -701.115671101

Zero-point correction= 0.266734 (Hartree/Particle)
Thermal correction to Energy= 0.283756
Thermal correction to Enthalpy= 0.284700
Thermal correction to Gibbs Free Energy= 0.221302
Sum of electronic and ZPE= -700.848937
Sum of electronic and thermal Energies= -700.831915
Sum of electronic and thermal Enthalpies= -700.830971
Sum of electronic and thermal Free Energies= -700.894369

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 178.060 64.326 133.433

C,0,0.4662231124,1.2492109369,0.1105271092
C,0,2.1248360033,0.0538837639,-1.2099986523
C,0,1.8242462835,1.8030087756,0.4636088052
C,0,2.7476494724,1.3173250838,-0.6715287696
C,0,2.131362343,-1.1550249498,-0.5064241478
H,0,1.6960288757,0.0600322583,-2.2055705203
C,0,-0.2136034124,0.3042570696,0.8735979374
H,0,-0.0398423791,1.6975556661,-0.7385830722
C,0,1.8284602861,3.318213374,0.6515201404
H,0,2.143905363,1.337424767,1.398374354
H,0,3.7754756329,1.1644150576,-0.3249426611
H,0,2.7789640563,2.0692423396,-1.4665254919
C,0,1.3803007886,-2.3397980983,-1.0672104714
O,0,2.6933798478,-1.2919702128,0.6209232983
O,0,0.2428940339,-0.1928595408,1.9538206125
H,0,1.4744577796,3.8198357278,-0.2555679658
H,0,2.838250048,3.6831146207,0.8643408037
H,0,1.1779363764,3.6151607308,1.4792321945
H,0,1.0551186508,-2.1846936149,-2.097058767

H,0,0.4941682493,-2.512873565,-0.4461963255
H,0,2.0023253075,-3.2367477554,-1.0128113382
C,0,-1.5492854923,-0.1943471674,0.4012497778
C,0,-1.9038450641,-0.2199513356,-0.9507711076
C,0,-2.4604886874,-0.6814161915,1.3412483225
C,0,-3.1448436894,-0.7042009983,-1.3486229728
H,0,-1.1966455777,0.1156723391,-1.700850116
C,0,-3.7046759821,-1.1579957734,0.94623421
H,0,-2.1802415196,-0.6805243373,2.3881054844
C,0,-4.0518968983,-1.169738968,-0.4015384082
H,0,-3.4006339086,-0.7243226885,-2.4023651022
H,0,-4.4039498139,-1.5231964229,1.6905357339
H,0,-5.0199317178,-1.5471063457,-0.7119232668
Li,0,1.9729306321,-0.8960325451,2.3614703733

B.6.1.1.24. 15-Li gauche

./LiPPKhetero-cisIM2-2
E(UwB97XD) = -701.115494051

Zero-point correction= 0.266326 (Hartree/Particle)
Thermal correction to Energy= 0.283588
Thermal correction to Enthalpy= 0.284532
Thermal correction to Gibbs Free Energy= 0.220028
Sum of electronic and ZPE= -700.849168
Sum of electronic and thermal Energies= -700.831906
Sum of electronic and thermal Enthalpies= -700.830962
Sum of electronic and thermal Free Energies= -700.895466

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	177.954	64.553	135.760

C,0,0.7715467111,1.1072060197,-0.3365387279
C,0,2.057677613,-0.8189473887,-1.0842816024
C,0,2.2238306755,1.3744384435,-0.0263498285
C,0,2.9958989066,0.3426510614,-0.8739992547
C,0,1.708781044,-1.7115715517,-0.0642046449
H,0,1.6644138525,-1.0053234881,-2.0771791361
C,0,-0.1539766247,0.646620915,0.594235573
H,0,0.4240497932,1.3804097022,-1.3279717846
C,0,2.6419033627,2.8189030428,-0.29145968
H,0,2.3890732758,1.151323187,1.0297386379
H,0,3.2485765882,0.7795056325,-1.8455453361
H,0,3.934865191,0.0424178525,-0.3962876181
C,0,0.6595081459,-2.7648369084,-0.3341265623
O,0,2.1887491798,-1.6414774357,1.1053770925
O,0,0.1258814025,0.4162851381,1.8158615293
H,0,2.0866893268,3.5137150216,0.3454221645
H,0,3.7100402159,2.9595066701,-0.0976050921
H,0,2.451873888,3.0901117829,-1.3356432896
H,0,0.4200254552,-2.860896401,-1.3942212541
H,0,0.9907699078,-3.731118289,0.0541277605
H,0,-0.2545738198,-2.4867743034,0.2027172985
C,0,-1.5607412075,0.3610957498,0.1506521111
C,0,-2.5902626069,0.4107311965,1.093501519
C,0,-1.8746994456,0.0058568415,-1.1645400137
C,0,-3.9033485015,0.1373588926,0.7298065978
H,0,-2.3464377188,0.6662546118,2.1180355365
C,0,-3.1865783285,-0.2756383513,-1.5286782574
H,0,-1.0861368128,-0.0795143411,-1.9035659723
C,0,-4.2064209323,-0.2062253808,-0.5844202505
H,0,-4.6912844061,0.1891473246,1.473343885
H,0,-3.4109806099,-0.5582028934,-2.5514289598
H,0,-5.2294507725,-0.4268850307,-0.8682818481
Li,0,1.4501352514,-0.6868473229,2.6213174078

B.6.1.1.25. 7-Li gauche

./LiPPKhetero-cisPD-1
opt
E(UwB97XD) = -701.123270860

Zero-point correction= 0.267751 (Hartree/Particle)
Thermal correction to Energy= 0.284361
Thermal correction to Enthalpy= 0.285305
Thermal correction to Gibbs Free Energy= 0.222865
Sum of electronic and ZPE= -700.855520
Sum of electronic and thermal Energies= -700.838910
Sum of electronic and thermal Enthalpies= -700.837966
Sum of electronic and thermal Free Energies= -700.900406

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 178.439 63.181 131.415

C,0,-0.9175720884,-0.6760000259,-0.3599051412
C,0,-2.0245593357,0.2942320824,-0.9778575684
C,0,-2.0724691108,-1.4460243284,0.3347257903
C,0,-3.0864003643,-0.7534778945,-0.6027090794
C,0,-2.088298905,1.6010701734,-0.2491648144
H,0,-1.8713812417,0.4920846504,-2.0406571357
C,0,0.1785740906,-0.1002022531,0.4858536547
H,0,-0.5320482536,-1.2796591114,-1.1816587507
C,0,-1.992467369,-2.9596410276,0.3424336132
H,0,-2.1921991639,-1.0665780554,1.3528825921
H,0,-3.3421616213,-1.3786092441,-1.4620550353
H,0,-4.0002871263,-0.3699250122,-0.1469401401
C,0,-1.1276453269,2.6554630192,-0.7210084004
O,0,-2.8575707725,1.804554791,0.6823648701
O,0,-0.1809027462,0.5447874875,1.5494778857
H,0,-1.1382347772,-3.3031936077,0.9343053948
H,0,-2.8977332594,-3.4022475375,0.7692707665
H,0,-1.8758435813,-3.3456412877,-0.6757731264
H,0,-1.4402678438,3.0041990951,-1.7103928763
H,0,-1.1008318034,3.4966621311,-0.0294184895
H,0,-0.1305536148,2.2184377482,-0.8304517627
C,0,1.5591553884,-0.1953289102,0.1237619214
C,0,2.5431718425,0.4003132198,0.9683536103
C,0,2.0471167163,-0.8476503556,-1.0470038288
C,0,3.8910431598,0.3419421089,0.6657926105
H,0,2.2065394326,0.9075514652,1.8643802231
C,0,3.3985871688,-0.8965081233,-1.3355780593
H,0,1.3582222421,-1.3185921344,-1.7384987087
C,0,4.344223495,-0.3062053345,-0.4880937114
H,0,4.6062966989,0.80908882,1.3367104483
H,0,3.7273466767,-1.4029891053,-2.2381337123
H,0,5.4019102432,-0.3500834151,-0.7217715156
Li,0,-1.5424338495,1.4488129718,2.4204554756

B.6.1.1.26. 12‡-Li gauche

./LiPPKhetero-cisTS1-1
E(UwB97XD) = -701.092652372

Zero-point correction= 0.264153 (Hartree/Particle)
Thermal correction to Energy= 0.281430
Thermal correction to Enthalpy= 0.282374
Thermal correction to Gibbs Free Energy= 0.217679
Sum of electronic and ZPE= -700.828499
Sum of electronic and thermal Energies= -700.811223

Sum of electronic and thermal Enthalpies= -700.810279
Sum of electronic and thermal Free Energies= -700.874974

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 176.600 64.530 136.162

C,0,0.1879379784,1.6025647384,0.3210827338
C,0,2.6784011378,-0.0258877338,-0.8827290544
C,0,1.4047033604,2.2226318475,0.6099682723
C,0,2.9909680146,0.750005115,0.2233922825
C,0,1.9258313667,-1.2245673214,-0.7902668246
H,0,2.9179948169,0.3400733422,-1.8759145248
C,0,-0.3594572196,0.598233426,1.1346397248
H,0,-0.2863681263,1.8192354557,-0.6302568393
C,0,1.8626138062,3.390084903,-0.2206228648
H,0,1.7290256431,2.2062628228,1.6459260345
H,0,2.888437736,0.3106111597,1.2094914313
H,0,3.7282106272,1.5394015624,0.1319905231
C,0,1.5016247402,-1.924063469,-2.0604962214
O,0,1.5940494875,-1.7595994935,0.3012413832
O,0,0.1618239218,0.2330693832,2.2327818083
H,0,1.7929331903,3.1620044398,-1.288165911
H,0,2.8922025241,3.674826668,0.0048548405
H,0,1.2299431671,4.2644209045,-0.0282243852
H,0,1.8420382061,-1.4103897269,-2.9604976217
H,0,0.4088896976,-1.9888317005,-2.0800788853
H,0,1.8864100017,-2.9480963104,-2.064648223
C,0,-1.6092807303,-0.1072504697,0.6950947204
C,0,-1.9539869914,-0.2659180207,-0.6509350645
C,0,-2.4390182432,-0.6719742716,1.6679176039
C,0,-3.1043976926,-0.9583332902,-1.0109389223
H,0,-1.3088202827,0.1285897398,-1.4275334671
C,0,-3.5952852648,-1.3537444757,1.3103773649
H,0,-2.1645604791,-0.5672055826,2.7111199758
C,0,-3.9326406895,-1.4992265965,-0.0321163357
H,0,-3.3514309263,-1.0807548401,-2.0597627164
H,0,-4.2332539672,-1.7745384311,2.0799317528
H,0,-4.8305922369,-2.0377551992,-0.3141003095
Li,0,1.1240824263,-1.4483265753,2.1237777191

B.6.1.1.27. 12‡-Li 2CH_3CN gauche

./LiPPKhetero-cisTS1-1-2ACN-temp
opt=modredundant
E(UwB97XD) = -966.608962163

Zero-point correction= 0.358881 (Hartree/Particle)
Thermal correction to Energy= 0.386293
Thermal correction to Enthalpy= 0.387238
Thermal correction to Gibbs Free Energy= 0.297580
Sum of electronic and ZPE= -966.250081
Sum of electronic and thermal Energies= -966.222669
Sum of electronic and thermal Enthalpies= -966.221725
Sum of electronic and thermal Free Energies= -966.311382

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 242.403 95.827 188.701

C,0,-0.5808353025,-1.3665970247,-0.9455258315
C,0,-2.7295074256,0.8720567146,0.0827259914
C,0,-1.9098856656,-1.800586514,-0.9537331966
C,0,-3.0587311592,-0.4506351962,0.3470608457
C,0,-1.6555037173,1.5309214375,0.7309195538
H,0,-3.2415382755,1.4034133181,-0.712996029

C,0,0.2527211575,-1.5112586103,0.1735010651
H,0,-0.2063607688,-0.8131144861,-1.8009961252
C,0,-2.7019094982,-1.7541486585,-2.230969281
H,0,-2.1700365644,-2.5844155631,-0.2483382494
H,0,-2.6635299145,-0.915990594,1.2435070018
H,0,-3.9986700283,-0.8494203949,-0.0184706283
C,0,-1.287303631,2.9327144263,0.301057608
O,0,-0.9831351707,1.0186349641,1.6643421458
O,0,-0.1218237204,-2.0447596167,1.2621626473
H,0,-2.6075427633,-0.7771235695,-2.7135951235
H,0,-3.7618961208,-1.954874739,-2.062762699
H,0,-2.331534322,-2.5079775802,-2.9357096141
H,0,-1.9434701775,3.3230070187,-0.4782057452
H,0,-0.2575211431,2.9323389905,-0.0703608521
H,0,-1.3183217348,3.6029060641,1.1648934539
C,0,1.6594845073,-0.9956296451,0.1047539203
C,0,1.9811783583,0.2017845051,-0.5376870395
C,0,2.6745730046,-1.7086346954,0.7473737684
C,0,3.291599855,0.6691088049,-0.5468296406
H,0,1.198426533,0.7854163722,-1.0097611159
C,0,3.9863219017,-1.2550809246,0.7204538612
H,0,2.4215786771,-2.6251901204,1.2678878391
C,0,4.2991437144,-0.0616808736,0.0740215182
H,0,3.5246360224,1.6091189527,-1.0348991341
H,0,4.7667790297,-1.8270794691,1.2104757825
H,0,5.3214160116,0.3000420208,0.0634854902
Li,0,-0.5317688254,-0.6173229718,2.5458671481
N,0,1.2770779267,-0.0476322608,3.5593779609
N,0,-2.001593032,-1.2862215687,3.892412671
C,0,2.3657897318,0.3177700283,3.573590127
C,0,-2.8493030848,-1.6744755627,4.5624425203
C,0,3.7399373609,0.7827119879,3.5848528246
H,0,3.8957499788,1.4511808236,4.4321276243
H,0,3.9463688513,1.3138167624,2.655049684
H,0,4.4129595867,-0.0714766984,3.6634090169
C,0,-3.9212829166,-2.1666967858,5.407422998
H,0,-4.7096387526,-1.4164812487,5.4721913328
H,0,-3.5344901754,-2.3726628215,6.4056677417
H,0,-4.3287283183,-3.0836749979,4.9811061628

B.6.1.1.28. 16‡-Li gauche

./LiPPKhetero-cisTS2-1
E(UwB97XD) = -701.110637438

Zero-point correction= 0.266443 (Hartree/Particle)
Thermal correction to Energy= 0.282903
Thermal correction to Enthalpy= 0.283848
Thermal correction to Gibbs Free Energy= 0.220891
Sum of electronic and ZPE= -700.844194
Sum of electronic and thermal Energies= -700.827734
Sum of electronic and thermal Enthalpies= -700.826790
Sum of electronic and thermal Free Energies= -700.889747

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	177.525	62.314	132.504

C,0,0.8686774223,0.8027651896,-0.3556263351
C,0,1.9212183181,-0.6822309183,-1.1291292721
C,0,2.2689839984,1.2577833735,0.0416788188
C,0,3.0353925479,0.3287350255,-0.9105572477
C,0,1.7388312661,-1.7681586112,-0.2298760611
H,0,1.5300268683,-0.8273497101,-2.1309544481
C,0,-0.1288718982,0.466408216,0.6007916079
H,0,0.5160178798,1.2518670868,-1.2799093217

C,0,2.5213572302,2.7522399684,-0.0898054763
H,0,2.4523761231,0.9505021641,1.0728766506
H,0,3.2772877926,0.8364519273,-1.8487284547
H,0,3.9528567843,-0.0982146523,-0.4985653855
C,0,0.6087952915,-2.7255883425,-0.5098419312
O,0,2.3651335557,-1.8663293963,0.8587753035
O,0,0.1816150732,0.1426109689,1.8028648145
H,0,1.8811978011,3.3226985592,0.5896248361
H,0,3.5632614258,2.9914275967,0.1443181192
H,0,2.3198931518,3.0911753998,-1.1114791498
H,0,0.4171737204,-2.8488109341,-1.5771139491
H,0,0.8052768685,-3.6954716836,-0.0504623275
H,0,-0.2998931525,-2.3104616247,-0.0534590152
C,0,-1.5517869053,0.3721809921,0.1910655456
C,0,-2.535222649,0.2281486339,1.1817240503
C,0,-1.9706840743,0.3945882394,-1.1496567634
C,0,-3.8800120491,0.1311674635,0.8505739912
H,0,-2.2215379751,0.1938664451,2.2180456467
C,0,-3.3154236541,0.29096874,-1.4793810489
H,0,-1.2434522088,0.4717988294,-1.9493896174
C,0,-4.2801910739,0.1630969091,-0.4828831352
H,0,-4.6212590607,0.0277600377,1.6360575995
H,0,-3.6117925019,0.3049624248,-2.5228140578
H,0,-5.329789172,0.0825762553,-0.7426357374
Li,0,1.607216256,-0.9455465729,2.4354087513

B.6.1.1.29. 16‡-Li 2CH₃CN gauche

./LiPPKhetero-cisTS2-1-2ACN-temp
E(UwB97XD) = -966.625265818

Zero-point correction= 0.360844 (Hartree/Particle)
Thermal correction to Energy= 0.387801
Thermal correction to Enthalpy= 0.388746
Thermal correction to Gibbs Free Energy= 0.297249
Sum of electronic and ZPE= -966.264421
Sum of electronic and thermal Energies= -966.237464
Sum of electronic and thermal Enthalpies= -966.236520
Sum of electronic and thermal Free Energies= -966.328017

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	243.349	93.564	192.572

C,0,-0.9094718063,-0.8092967367,-0.3774745899
C,0,-1.8426369293,0.758300998,-1.1411603091
C,0,-2.3417736845,-1.152506752,0.0160404717
C,0,-3.0255900476,-0.1779411609,-0.9529195656
C,0,-1.6049635057,1.8092518618,-0.2136415329
H,0,-1.4265262768,0.8950655933,-2.1340959296
C,0,0.1132468303,-0.5711032574,0.5821555395
H,0,-0.5942367749,-1.2753202729,-1.3074345886
C,0,-2.7081016334,-2.6244128062,-0.0988458301
H,0,-2.509154509,-0.817307553,1.0409334156
H,0,-3.2734453873,-0.6717783191,-1.8972132017
H,0,-3.9255158917,0.3061436476,-0.565694504
C,0,-0.4020863595,2.6900679574,-0.4370375659
O,0,-2.2527281703,1.9278213627,0.8596781213
O,0,-0.1655856985,-0.2500280277,1.7914238651
H,0,-2.1245350394,-3.2334592871,0.5979123527
H,0,-3.7687703878,-2.7792944467,0.1225016737
H,0,-2.5190167841,-2.9930325906,-1.1128009459
H,0,-0.1308750876,2.7749425568,-1.4906294697
H,0,-0.5704207002,3.6809447792,-0.0118074401
H,0,0.4454576748,2.2351163422,0.092728286
C,0,1.5374342663,-0.5873729998,0.1672865711

C,0,2.53331563,-0.5983081522,1.1558341256
C,0,1.9462607676,-0.5674251137,-1.1762180865
C,0,3.8796402963,-0.6167340907,0.8176322476
H,0,2.2271194963,-0.5973012026,2.1951489704
C,0,3.2934272803,-0.5773262129,-1.5126024495
H,0,1.2100529235,-0.5209707191,-1.9704358642
C,0,4.2696718712,-0.6076701071,-0.5194338152
H,0,4.6306175126,-0.63793799,1.6004518837
H,0,3.5841415426,-0.554640801,-2.5575180952
H,0,5.3207716898,-0.6201272451,-0.7852905049
Li,0,-1.5099678578,0.9533103487,2.4065435984
N,0,-3.1010312953,0.0000504461,3.4603278103
N,0,-0.6217423222,2.4166006377,3.7070814013
C,0,-0.055390616,3.2325386012,4.2833990824
C,0,-3.9755077407,-0.6130618346,3.8822301362
C,0,0.6628798576,4.2647497346,5.0081818425
H,0,0.0640073744,5.175265902,5.0371574642
H,0,1.6088754724,4.4695902562,4.5063314048
H,0,0.8591947555,3.9277711755,6.0262455323
C,0,-5.0800293126,-1.3921206254,4.4099764768
H,0,-5.6263547251,-0.8021690872,5.1461976102
H,0,-4.6959940419,-2.2964814589,4.8823376242
H,0,-5.7521026558,-1.6666733502,3.5965167808

B.6.1.1.30. 13-Li

./LiPPKhetero-transIM1-4
E(UwB97XD) = -701.116254538

Zero-point correction= 0.266666 (Hartree/Particle)
Thermal correction to Energy= 0.283898
Thermal correction to Enthalpy= 0.284842
Thermal correction to Gibbs Free Energy= 0.219856
Sum of electronic and ZPE= -700.849589
Sum of electronic and thermal Energies= -700.832356
Sum of electronic and thermal Enthalpies= -700.831412
Sum of electronic and thermal Free Energies= -700.896398

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	178.149	64.526	136.774

C,0,-0.2252426904,1.0488509034,0.3563493043
C,0,3.4108996934,0.5753782073,-0.7492147969
C,0,1.2617673322,1.0714912738,0.5104076392
C,0,1.9575772111,0.7788476391,-0.8765533984
C,0,3.9608256704,-0.6592758736,-0.2784590522
H,0,4.0971801263,1.3899454027,-0.9546358834
C,0,-0.9090275266,-0.1242561223,0.2181962107
H,0,-0.7464566209,1.9996477708,0.3284986079
C,0,1.7678767605,2.3865847742,1.0998592597
H,0,1.5641075448,0.253207476,1.176458916
H,0,1.4848220974,-0.1202130646,-1.2833285352
H,0,1.7426692551,1.6167894455,-1.5440193299
C,0,5.4525555234,-0.8093879243,-0.1417257836
O,0,3.2222121574,-1.6133733834,0.030874934
O,0,-0.3485165048,-1.2945125742,0.2493667894
H,0,1.2989454558,2.5756961566,2.0692402378
H,0,2.8524883333,2.3749176394,1.2437957721
H,0,1.5237543882,3.2253536591,0.4389651297
H,0,5.9967908074,0.0380813741,-0.5578485101
H,0,5.7020511839,-0.9043568066,0.9189043768
H,0,5.7716191234,-1.7281049379,-0.6384188293
C,0,-2.4056758405,-0.1113906377,0.0459838037
C,0,-3.1410862818,-1.2399687403,0.4186919017
C,0,-3.1004338704,0.9767107474,-0.4941541148

C,0,-4.5247847478,-1.2746871239,0.281945798
H,0,-2.6076979222,-2.0949097821,0.8173386053
C,0,-4.4830058764,0.9441829344,-0.6363472246
H,0,-2.5564538857,1.8538731006,-0.8260252816
C,0,-5.2037953211,-0.1811105913,-0.2460645012
H,0,-5.0739735734,-2.1601953255,0.5844696139
H,0,-4.9980373311,1.7975207976,-1.064691193
H,0,-6.2817579492,-0.208261697,-0.3618176733
Li,0,1.3155602782,-2.0912297174,0.2952112071

B.6.1.1.31. 15-Li

./LiPPKhetero-transIM2-1
E(UwB97XD) = -701.114730727

Zero-point correction= 0.267126 (Hartree/Particle)
Thermal correction to Energy= 0.284084
Thermal correction to Enthalpy= 0.285028
Thermal correction to Gibbs Free Energy= 0.221116
Sum of electronic and ZPE= -700.847605
Sum of electronic and thermal Energies= -700.830647
Sum of electronic and thermal Enthalpies= -700.829703
Sum of electronic and thermal Free Energies= -700.893615

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	178.265	64.328	134.514

C,0,-0.725439923,-1.3901903074,-0.2463139221
C,0,-2.5684419145,0.8978457903,0.6274367141
C,0,-2.1530144168,-1.5649940541,0.1734184332
C,0,-3.0154531946,-0.2848526572,-0.1345568699
C,0,-1.7550741779,1.962391791,0.1274397695
H,0,-2.8091458498,0.9481398617,1.685085139
C,0,0.145867575,-0.6314101159,0.4732572757
H,0,-0.4178204137,-1.8438993747,-1.1824294418
C,0,-2.8009738175,-2.7731636747,-0.5022945775
H,0,-2.1943678356,-1.7000600547,1.2603379865
H,0,-4.0517782009,-0.5165325935,0.1398360291
H,0,-2.9851351843,-0.1074800471,-1.2131012978
C,0,-1.4581363529,2.0520057627,-1.3468047185
O,0,-1.2611247295,2.7947230322,0.9166627776
O,0,-0.1697702573,-0.0729146483,1.6057308344
H,0,-2.7930896146,-2.6571569873,-1.5916800485
H,0,-3.8398846893,-2.9021990828,-0.1849837829
H,0,-2.2541515049,-3.6888101755,-0.2609493461
H,0,-0.8816312349,1.1710896909,-1.6472898592
H,0,-0.8816514495,2.9529326945,-1.5524530423
H,0,-2.3768454276,2.0591263268,-1.9389166079
C,0,1.5468884303,-0.3849037927,-0.0213199793
C,0,2.5229445497,0.0235010845,0.8921303113
C,0,1.9178845805,-0.511508795,-1.3651521573
C,0,3.8299417743,0.2725594142,0.4873192291
H,0,2.2392536135,0.1448993071,1.931325939
C,0,3.2227480633,-0.262290576,-1.7739497689
H,0,1.1772466194,-0.7903980089,-2.1061364885
C,0,4.1878074508,0.1277897065,-0.8490245068
H,0,4.5707562388,0.5822838,1.2169920542
H,0,3.4857197279,-0.3639245786,-2.8215750173
H,0,5.2049747477,0.3259791983,-1.1685731288
Li,0,-0.1689813721,1.6313464139,2.3480306684

B.6.1.1.32. 7-Li

./LiPPKhetero-transPD-4

E(UwB97XD) = -701.123094253

Zero-point correction= 0.267638 (Hartree/Particle)
Thermal correction to Energy= 0.284578
Thermal correction to Enthalpy= 0.285522
Thermal correction to Gibbs Free Energy= 0.221609
Sum of electronic and ZPE= -700.855456
Sum of electronic and thermal Energies= -700.838517
Sum of electronic and thermal Enthalpies= -700.837572
Sum of electronic and thermal Free Energies= -700.901485

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 178.575 63.347 134.516

C,0,0.9674862451,-0.5811577323,0.119996682
C,0,2.0426889207,0.3814272687,-0.5224026967
C,0,2.071344055,-1.6712334851,0.130862836
C,0,3.1382427017,-0.5615555146,-0.0062013093
C,0,1.9653746793,1.8004050488,-0.0506944437
H,0,1.9322712409,0.3378317988,-1.6094743815
C,0,-0.3047734472,-0.8281694829,-0.6360029677
H,0,0.7868144396,-0.2610795425,1.1487175969
C,0,2.1299886211,-2.6109487984,1.3186405235
H,0,2.0011958455,-2.2324049101,-0.8048068609
H,0,3.9892905889,-0.7484123848,-0.6634138183
H,0,3.5027227516,-0.2322759006,0.9709012049
C,0,0.8535475694,2.6241888265,-0.6479186129
O,0,2.7200953191,2.2541607026,0.7910060135
O,0,-0.1975698154,-1.4351133315,-1.7720211657
H,0,2.1992726275,-2.0477380398,2.2551622194
H,0,2.9999908931,-3.2722549619,1.2574923107
H,0,1.2336804605,-3.2376486965,1.3672576236
H,0,1.0762487107,2.8100293027,-1.7033062539
H,0,0.7488603623,3.5745388243,-0.1253581222
H,0,-0.0870145111,2.0656253237,-0.6140171697
C,0,-1.5687201859,-0.359731955,-0.1585370538
C,0,-2.749021548,-0.5883556653,-0.9298616506
C,0,-1.7503545444,0.3616162756,1.0609732035
C,0,-3.989494219,-0.1425335316,-0.5123837222
H,0,-2.6607068867,-1.1223485082,-1.8684421814
C,0,-2.9972241039,0.8007265531,1.4634860454
H,0,-0.9003050984,0.5874732821,1.6940334094
C,0,-4.1392441988,0.5581128428,0.6891751752
H,0,-4.8600637811,-0.3392475686,-1.1315887198
H,0,-3.0867481043,1.3487745724,2.3966992057
H,0,-5.1129159275,0.9093164236,1.011098348
Li,0,-0.7412896604,-2.7149170361,-2.9660612676

B.6.1.1.33. 12‡-Li 2CH3CN

./LiPPKhetero-transTS1-1-2ACN-temp
opt=modredundant
E(UwB97XD) = -966.613353995

Zero-point correction= 0.357393 (Hartree/Particle)
Thermal correction to Energy= 0.385339
Thermal correction to Enthalpy= 0.386283
Thermal correction to Gibbs Free Energy= 0.294634
Sum of electronic and ZPE= -966.255961
Sum of electronic and thermal Energies= -966.228015
Sum of electronic and thermal Enthalpies= -966.227071
Sum of electronic and thermal Free Energies= -966.318720

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K

Total 241.804 96.867 192.891

C,0,0.0041014094,1.2350971994,0.3475067114
C,0,-3.8865932044,0.0364059422,0.5031359238
C,0,-1.2348425243,1.8219901246,0.209304055
C,0,-2.6495857918,-0.0402789117,1.0466641783
C,0,-4.2101442843,-0.5753138003,-0.7730098983
H,0,-4.6724409067,0.6018437333,0.9936505776
C,0,0.4711941255,0.2275305061,-0.5343142974
H,0,0.6044675061,1.5040581907,1.2111310793
C,0,-1.7219094028,2.9443752976,1.0732411312
H,0,-1.7826768121,1.6259534357,-0.7051869341
H,0,-2.444773829,0.3679060211,2.0281719306
H,0,-1.8902917325,-0.6749665066,0.6112975075
C,0,-5.6315349299,-0.4432407941,-1.2568305433
O,0,-3.3835241543,-1.190343125,-1.4579550339
O,0,-0.2403932681,-0.1615873425,-1.5304350763
H,0,-1.1997601616,2.967758334,2.0343896636
H,0,-2.7959188791,2.8595478674,1.2695294444
H,0,-1.5659410412,3.9169139668,0.5890592039
H,0,-6.3047635328,-0.9653991496,-0.5700611563
H,0,-5.7347264611,-0.8639889992,-2.2561070843
H,0,-5.9325204128,0.6079139293,-1.2634058347
C,0,1.7820229813,-0.4345056131,-0.3173367797
C,0,2.1592798252,-1.4683970092,-1.1911315833
C,0,2.6705226974,-0.1097534659,0.7233569706
C,0,3.356544068,-2.1520132002,-1.0284968208
H,0,1.4791276254,-1.7331059222,-1.9916341379
C,0,3.8683790909,-0.7934122736,0.8839004563
H,0,2.4328609708,0.6826681514,1.4227157629
C,0,4.2212869928,-1.8219187524,0.0116055757
H,0,3.6150601162,-2.950998193,-1.7157617013
H,0,4.532104128,-0.5217207878,1.6978562771
H,0,5.1563262047,-2.3551740555,0.141381932
Li,0,-1.4650984598,-1.5793299743,-1.6653671268
N,0,-0.903885825,-2.8506908838,-3.2997486643
N,0,-0.8286605355,-2.9056566023,-0.0388430172
C,0,-0.3867798936,-3.5695284983,-4.0308989818
C,0,0.0255084527,-3.1629988395,0.6856710786
C,0,0.2706005501,-4.480605042,-4.9497501123
H,0,0.6089288536,-3.9329998639,-5.8295679613
H,0,-0.4291640938,-5.2589966316,-5.254974482
H,0,1.1282568091,-4.9388280511,-4.4565514909
C,0,1.1123887806,-3.4756659221,1.5937789845
H,0,1.5764700045,-4.4172117393,1.2990618328
H,0,0.729323395,-3.5625728616,2.6109354338
H,0,1.8542155494,-2.6756498881,1.5473730072

B.6.1.1.34. 12‡-Li

./LiPPKhetero-transTS1-2
E(UwB97XD) = -701.095752392

Zero-point correction= 0.263572 (Hartree/Particle)
Thermal correction to Energy= 0.281018
Thermal correction to Enthalpy= 0.281962
Thermal correction to Gibbs Free Energy= 0.217049
Sum of electronic and ZPE= -700.832181
Sum of electronic and thermal Energies= -700.814735
Sum of electronic and thermal Enthalpies= -700.813791
Sum of electronic and thermal Free Energies= -700.878704

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 176.341 64.978 136.621

C,0,-0.237331794,1.2711361474,0.5421431307
C,0,3.4311354671,0.1876540206,-0.9477609278
C,0,1.0994349717,1.4325779012,0.8518303824
C,0,2.1095512964,0.4277300181,-1.1801311548
C,0,3.8821184414,-1.0049305882,-0.2818289411
H,0,4.1787051088,0.9222088992,-1.2265712093
C,0,-0.8807096393,0.0120832399,0.5655933243
H,0,-0.7869390451,2.1302473542,0.1698285005
C,0,1.7828323891,2.763212474,0.8891779339
H,0,1.6093615428,0.6120491339,1.3453729305
H,0,1.7911402528,1.3052267927,-1.7283390194
H,0,1.3695646945,-0.3458163688,-1.0181269219
C,0,5.3651777605,-1.2431483625,-0.1466999722
O,0,3.1005813805,-1.8613827973,0.1773075139
O,0,-0.257318258,-1.062192071,0.8656399584
H,0,1.2922928816,3.4862403413,0.2314947988
H,0,2.8314615191,2.6755432414,0.5879552578
H,0,1.7774505165,3.1796790204,1.9046575888
H,0,5.6513545627,-2.0686884256,-0.8059804548
H,0,5.594954156,-1.5477784716,0.8768347923
H,0,5.9559498754,-0.3659438256,-0.4112198405
C,0,-2.316238638,-0.1060882118,0.1840826854
C,0,-2.8157818388,-1.3649473663,-0.1770228203
C,0,-3.2045966043,0.9794264912,0.1802476058
C,0,-4.1438232308,-1.5314535737,-0.5471570075
H,0,-2.1378244282,-2.2099889029,-0.1671063319
C,0,-4.5341135912,0.8118975566,-0.1849988167
H,0,-2.8660098357,1.962945747,0.4850245341
C,0,-5.0117226828,-0.4431466183,-0.5547759747
H,0,-4.5040037951,-2.5143744257,-0.8320237824
H,0,-5.2048559846,1.6642631618,-0.1729315837
H,0,-6.0505219596,-0.5713797694,-0.8377777058
Li,0,1.3348245089,-2.0192517622,0.9890815276

B.6.1.1.35. 16‡-Li

./LiPPKhetero-transTS2-2
E(UwB97XD) = -701.103694934

Zero-point correction= 0.266164 (Hartree/Particle)
Thermal correction to Energy= 0.283044
Thermal correction to Enthalpy= 0.283989
Thermal correction to Gibbs Free Energy= 0.219987
Sum of electronic and ZPE= -700.837531
Sum of electronic and thermal Energies= -700.820651
Sum of electronic and thermal Enthalpies= -700.819706
Sum of electronic and thermal Free Energies= -700.883708

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	177.613	62.529	134.703

C,0,0.977451,-0.65946,0.398191
C,0,2.054561,0.682439,-0.76596
C,0,2.328789,-1.341614,0.289727
C,0,3.148784,-0.097269,-0.072585
C,0,1.695011,2.018931,-0.429634
H,0,1.761652,0.33015,-1.75134
C,0,-0.194855,-1.154319,-0.200659
H,0,0.866667,-0.022279,1.271016
C,0,2.762232,-2.119648,1.525157
H,0,2.294994,-2.013415,-0.573039
H,0,4.038327,-0.283116,-0.683008
H,0,3.456349,0.435614,0.832366
C,0,0.675516,2.713684,-1.31404
O,0,2.135523,2.620714,0.573433

O,0,-0.176728,-2.111979,-1.049314
H,0,2.77961,-1.46792,2.405194
H,0,3.765992,-2.536521,1.394678
H,0,2.076233,-2.94711,1.730484
H,0,1.193145,3.401723,-1.991127
H,0,-0.007257,3.30396,-0.698895
H,0,0.100349,2.007996,-1.917027
C,0,-1.499643,-0.492978,0.090698
C,0,-2.689594,-1.138763,-0.268014
C,0,-1.593042,0.770198,0.692931
C,0,-3.926085,-0.555213,-0.023544
H,0,-2.631402,-2.114085,-0.736543
C,0,-2.829037,1.357222,0.931808
H,0,-0.694786,1.31377,0.960974
C,0,-4.003102,0.697808,0.578001
H,0,-4.833917,-1.079275,-0.302972
H,0,-2.875693,2.338463,1.391705
H,0,-4.966968,1.157945,0.764787
Li,0,-0.695317,-3.322464,-2.351155

B.6.1.1.36. 3-Li

./LiPVK-3
uwb97xd/6-311+g(d,p)
E(UwB97XD) = -430.546367482

Zero-point correction= 0.142933 (Hartree/Particle)
Thermal correction to Energy= 0.153155
Thermal correction to Enthalpy= 0.154099
Thermal correction to Gibbs Free Energy= 0.105828
Sum of electronic and ZPE= -430.403434
Sum of electronic and thermal Energies= -430.393212
Sum of electronic and thermal Enthalpies= -430.392268
Sum of electronic and thermal Free Energies= -430.440539

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	96.106	38.105	101.595

C,0,3.0442184618,-1.1424290041,-0.001448659
C,0,1.8552242785,-1.8541064129,-0.164389311
C,0,0.6325595153,-1.2002290477,-0.1804724928
C,0,0.5475513232,0.2014701412,-0.0343223401
C,0,1.7616073933,0.9006738486,0.1256687545
C,0,2.9831787972,0.2415402156,0.143279282
H,0,3.9976195458,-1.6585587337,0.0110408763
H,0,1.882131003,-2.9326241838,-0.281647644
H,0,-0.2626987283,-1.7956333451,-0.3125026083
H,0,1.7195114556,1.9772504624,0.2374770061
H,0,3.8973038609,0.8126877201,0.2712669773
C,0,-0.7113624204,0.9627724634,-0.0439726895
C,0,-1.9724540942,0.2926413972,-0.145593728
H,0,-1.9665758713,-0.7888252514,-0.2361147728
C,0,-3.1876697933,0.9108138239,-0.132003855
H,0,-3.2756241631,1.9866041777,-0.0281607647
H,0,-4.1057162526,0.3394872916,-0.2124581326
O,0,-0.651042921,2.2500041793,0.0542428155
Li,0,-1.3714323905,3.9051772575,-0.258409714

B.6.1.1.37. 2-Li gauche

./LiPVKhomo-cisPD-2
E(UwB97XD) = -853.520151081

Zero-point correction= 0.294222 (Hartree/Particle)

Thermal correction to Energy= 0.312094
Thermal correction to Enthalpy= 0.313038
Thermal correction to Gibbs Free Energy= 0.246985
Sum of electronic and ZPE= -853.225929
Sum of electronic and thermal Energies= -853.208057
Sum of electronic and thermal Enthalpies= -853.207113
Sum of electronic and thermal Free Energies= -853.273166

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 195.842 70.460 139.020

C,0,-2.1136054851,-0.9757699213,-0.6851986592
C,0,-3.5918402164,-0.6098219886,-0.4685271482
H,0,-3.8348995376,-0.4820951621,0.5862094012
C,0,-3.3522116014,0.7353814103,-1.1892048974
H,0,-4.3162735902,-1.2916167647,-0.9162754151
C,0,-1.8169812248,0.5342395605,-1.0873553525
H,0,-3.6927494764,0.7219232815,-2.2263935932
H,0,-3.7374478193,1.6224539676,-0.6874591649
H,0,-1.2879192183,0.6183373571,-2.0346994675
C,0,-1.1391096326,1.3233457615,0.0103152045
C,0,-1.278992654,-1.4334296178,0.4742009816
H,0,-1.9773937632,-1.6316273649,-1.5452110232
C,0,0.142391493,-1.8075763187,0.2183420544
C,0,0.5988940702,-2.2069448566,-1.0393088995
C,0,1.0530577627,-1.7043139636,1.2738815682
C,0,2.3950195701,-1.9866725471,1.074211895
C,0,2.8405429711,-2.3957703521,-0.1809166957
C,0,1.9405533278,-2.5113139645,-1.2336807251
H,0,-0.0854236281,-2.291754863,-1.8742534331
H,0,0.6972172961,-1.3787430674,2.2440180194
H,0,3.0977788108,-1.8862811549,1.8933540656
H,0,3.8900871956,-2.6179613944,-0.3376460211
H,0,2.2841126719,-2.831234858,-2.2105113465
O,0,-1.7055302938,-1.4051009696,1.6215747803
O,0,-1.8371467523,1.5924002721,1.0692922032
C,0,0.2443070198,1.667350335,-0.0694066109
C,0,0.8603792652,2.3578882346,1.0176114882
C,0,1.0962162618,1.3299545778,-1.1630096217
C,0,2.2047617711,2.6803154836,1.003759976
H,0,0.2444763255,2.623117823,1.8688229582
C,0,2.4381926494,1.659318496,-1.1610478804
H,0,0.704561975,0.7796193659,-2.0100771566
C,0,3.0184396518,2.3394846998,-0.0826402489
H,0,2.6343648915,3.2038957962,1.853212756
H,0,3.0522688861,1.3747553472,-2.0104878432
H,0,4.0732107079,2.5900896178,-0.0886589275
Li,0,-2.3851896806,0.4783777418,2.4664527799

B.6.1.1.38. 6

./MVK-1
E(UwB97XD) = -231.229202861

Zero-point correction= 0.089872 (Hartree/Particle)
Thermal correction to Energy= 0.095668
Thermal correction to Enthalpy= 0.096612
Thermal correction to Gibbs Free Energy= 0.060872
Sum of electronic and ZPE= -231.139331
Sum of electronic and thermal Energies= -231.133535
Sum of electronic and thermal Enthalpies= -231.132591
Sum of electronic and thermal Free Energies= -231.168330

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K

Total 60.032 19.331 75.220

C,0,0.0025060912,-0.0051098787,0.0017821945
H,0,0.0007353933,-0.0073018377,1.0947725448
H,0,1.0454142188,-0.0069845708,-0.3252786544
H,0,-0.4906728628,0.8951289105,-0.3608273068
C,0,-0.7158296799,-1.2202868242,-0.5269528551
O,0,-1.6941406343,-1.1155300541,-1.2461357714
C,0,-0.2222483394,-2.5732657875,-0.1636672682
H,0,-0.7973560243,-3.3918815472,-0.5865858642
C,0,0.8333729335,-2.8078136301,0.6128473809
H,0,1.4228053184,-2.0067397411,1.0462944333
H,0,1.1433433884,-3.8213785513,0.8409637218

B.6.1.1.39. 6-BF_3

./MVK-BF3-1
opt
E(UwB97XD) = -555.828575161

Zero-point correction= 0.104363 (Hartree/Particle)
Thermal correction to Energy= 0.114255
Thermal correction to Enthalpy= 0.115199
Thermal correction to Gibbs Free Energy= 0.067890
Sum of electronic and ZPE= -555.724213
Sum of electronic and thermal Energies= -555.714321
Sum of electronic and thermal Enthalpies= -555.713376
Sum of electronic and thermal Free Energies= -555.760685

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 71.696 34.082 99.569

C,0,-0.1986601658,0.217150954,-0.1891909681
H,0,-0.3539972333,0.2476395253,0.8922078797
H,0,0.8774322143,0.1662405814,-0.3665088696
H,0,-0.6069669591,1.1168735435,-0.6423210369
C,0,-0.8736195298,-0.9817647778,-0.7551038703
O,0,-1.7961404907,-0.7616656351,-1.575057464
C,0,-0.4965000751,-2.3359104264,-0.3785644231
H,0,-1.0416993894,-3.1491396985,-0.838410875
C,0,0.4796347044,-2.5786254679,0.5003858297
H,0,1.0470887993,-1.7901000559,0.9809848614
H,0,0.7372813916,-3.5973592982,0.7643502529
B,0,-2.69795477,-1.8040924049,-2.3287954756
F,0,-3.5397911835,-1.0227334807,-3.0895572303
F,0,-1.8605725661,-2.593275015,-3.1005434032
F,0,-3.3746247467,-2.5366383437,-1.3670052076

B.6.1.1.40. N^iPr_2Et

./NiPr2Et
opt
E(UwB97XD) = -371.033750349

Zero-point correction= 0.263529 (Hartree/Particle)
Thermal correction to Energy= 0.275155
Thermal correction to Enthalpy= 0.276099
Thermal correction to Gibbs Free Energy= 0.227596
Sum of electronic and ZPE= -370.770221
Sum of electronic and thermal Energies= -370.758595
Sum of electronic and thermal Enthalpies= -370.757651
Sum of electronic and thermal Free Energies= -370.806155

E CV S

KCal/Mol Cal/Mol-K Cal/Mol-K
Total 172.662 44.309 102.084

N,0,-1.7161185981,-0.947382191,0.4650673679
C,0,-2.2215594987,-0.5365558279,-0.840261825
H,0,-2.8344222871,0.3537018176,-0.689184559
H,0,-1.4158238427,-0.2319286484,-1.5265156288
C,0,-3.0907800506,-1.5839643933,-1.5299470407
H,0,-3.5276437341,-1.1598441183,-2.4386954933
H,0,-2.520899732,-2.4678961655,-1.8232776649
H,0,-3.9025527661,-1.9048883398,-0.8716618671
C,0,-1.4183472918,0.1681613182,1.3779762515
H,0,-1.042766896,-0.3034985684,2.292081926
C,0,-0.3360677855,1.1340032265,0.8743094074
H,0,-0.1313102371,1.9041782098,1.6234698373
H,0,0.6000311748,0.6083513735,0.6690944082
H,0,-0.6560040129,1.6357970867,-0.0441292234
C,0,-0.6710870352,-1.9929803284,0.4658331125
H,0,-0.0334632083,-1.7756374567,1.3288487803
C,0,-1.2727396445,-3.3801178686,0.7129345176
H,0,-0.4812080147,-4.1295682859,0.8143362838
H,0,-1.8649081616,-3.3766161858,1.6311799098
H,0,-1.9242316972,-3.6873506435,-0.1086486869
C,0,-2.6815955686,0.9304739996,1.7805196227
H,0,-3.4670653945,0.2357583443,2.0871418977
H,0,-2.4585610357,1.594896366,2.6198061391
H,0,-3.0685598204,1.5553237639,0.9706645179
C,0,0.2560182459,-2.0110843816,-0.7566838905
H,0,0.7112291246,-1.0343762692,-0.9357087199
H,0,1.0612262064,-2.7309091313,-0.5874756802
H,0,-0.2675674381,-2.3149077024,-1.6674066998

B.6.1.1.41. 5

./nPPK-1
E(UwB97XD) = -462.260320243

Zero-point correction= 0.172167 (Hartree/Particle)
Thermal correction to Energy= 0.182279
Thermal correction to Enthalpy= 0.183223
Thermal correction to Gibbs Free Energy= 0.135619
Sum of electronic and ZPE= -462.088153
Sum of electronic and thermal Energies= -462.078041
Sum of electronic and thermal Enthalpies= -462.077097
Sum of electronic and thermal Free Energies= -462.124701

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 114.382 37.494 100.190

C,0,1.7090506372,1.0902820689,0.4004261692
C,0,3.0324401182,0.6747461949,0.3882163376
C,0,3.3509179581,-0.6210230716,-0.0113466558
C,0,2.3423807174,-1.49928704,-0.3915910758
C,0,1.0142411563,-1.0891627794,-0.3620480429
C,0,0.6875101375,0.2107078719,0.031747407
H,0,1.4520072962,2.0986999351,0.7022001239
C,0,-0.724687188,0.7113272587,0.0383446306
H,0,3.8170949976,1.3600309382,0.6875396409
H,0,4.3855218213,-0.9449888005,-0.0260774353
H,0,2.5873840277,-2.5052503769,-0.7118660568
H,0,0.2408523533,-1.7825419108,-0.6705537683
O,0,-0.9466958974,1.911251584,-0.0248674787
C,0,-1.820032896,-0.2812928057,0.1363418039
C,0,-3.0916650391,0.0644367538,-0.0820514522
H,0,-1.5715139917,-1.3037966699,0.3996484659

H,0,-3.298682039,1.0985955273,-0.3499273078
C,0,-4.2583279432,-0.857294045,0.0059544421
H,0,-3.9622971684,-1.868357377,0.2902516127
H,0,-4.7802432875,-0.8970242547,-0.9552194573
H,0,-4.9802762907,-0.4803630612,0.7371768272

B.6.1.1.42. 1

./nPVK-2
E(UwB97XD) = -422.940016346

Zero-point correction= 0.144362 (Hartree/Particle)
Thermal correction to Energy= 0.152765
Thermal correction to Enthalpy= 0.153709
Thermal correction to Gibbs Free Energy= 0.110654
Sum of electronic and ZPE= -422.795655
Sum of electronic and thermal Energies= -422.787252
Sum of electronic and thermal Enthalpies= -422.786308
Sum of electronic and thermal Free Energies= -422.829363

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 95.861 32.016 90.617

C,0,-4.0627149603,1.4586829858,0.2673797725
C,0,-4.894420419,0.3657716935,0.0722873662
C,0,-4.3560231815,-0.9178418671,0.0215651267
C,0,-2.9865903815,-1.1048650542,0.1730177883
C,0,-2.154012892,-0.0132688756,0.3912697829
C,0,-2.6883276635,1.2762451212,0.4400642774
H,0,-4.4707896128,2.4623504221,0.2975959593
C,0,-1.8250192933,2.4860056905,0.608708646
H,0,-5.9618197333,0.5121806517,-0.0460454653
H,0,-5.005619809,-1.7709691008,-0.1382926601
H,0,-2.5645848643,-2.1017742774,0.1199931895
H,0,-1.0867398315,-0.164479486,0.5002849074
O,0,-2.1018923184,3.5255131357,0.0326484945
C,0,-0.6367281063,2.4435063689,1.498092275
C,0,-0.5113915131,1.6400720167,2.5523271565
H,0,0.1053915293,3.2087204655,1.2904881555
H,0,-1.2616008759,0.8979238139,2.8030531532
H,0,0.3446939263,1.7192462956,3.2128520748

B.6.1.1.43. 13 gauche

./PPKhetero-cisIM1-5
E(UwB97XD) = -693.601006214

Zero-point correction= 0.263368 (Hartree/Particle)
Thermal correction to Energy= 0.279580
Thermal correction to Enthalpy= 0.280524
Thermal correction to Gibbs Free Energy= 0.216816
Sum of electronic and ZPE= -693.337638
Sum of electronic and thermal Energies= -693.321427
Sum of electronic and thermal Enthalpies= -693.320482
Sum of electronic and thermal Free Energies= -693.384190

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 175.439 60.033 134.084

C,0,0.2690414477,-0.1759023943,0.7226618793
C,0,-3.3501885757,0.5442425726,-0.3378825492
C,0,-1.1675465286,0.2071525262,0.9107297735
C,0,-1.9660111204,0.0472298414,-0.4289397988

C,0,-4.5168016276,-0.2841147136,-0.461167756
H,0,-3.5018323658,1.5988440789,-0.1209574883
C,0,1.1683626842,0.6508697153,0.0953330298
H,0,0.5640221937,-1.1772748945,1.0223182991
C,0,-1.8323426959,-0.5964578721,2.0288084359
H,0,-1.2183614337,1.273518154,1.1658844305
H,0,-1.9562220132,-1.0033588999,-0.7303192856
H,0,-1.4164736021,0.6338786208,-1.1748982636
C,0,-5.8758370464,0.373284924,-0.3596527262
O,0,-4.4310364406,-1.5026652077,-0.6685468906
O,0,0.8970427769,1.813983198,-0.3824645697
H,0,-1.8250584066,-1.6664539504,1.7916053552
H,0,-2.8746501129,-0.2963543663,2.1798176465
H,0,-1.2975660471,-0.4598219004,2.9730946418
H,0,-5.8445430048,1.3036865719,0.2094000207
H,0,-6.587207798,-0.315977894,0.0971333684
H,0,-6.2329797532,0.6058127219,-1.368087476
C,0,2.5894271712,0.156365225,-0.0928340974
C,0,3.3343031628,0.6415400931,-1.1717178001
C,0,3.2072686655,-0.7575530788,0.7683938014
C,0,4.6361196802,0.2100178273,-1.4038081014
H,0,2.8689791461,1.367427517,-1.8288207536
C,0,4.511081054,-1.1874505388,0.545035855
H,0,2.6673783202,-1.1270997962,1.6335808947
C,0,5.2320932259,-0.709731171,-0.5462278046
H,0,5.1876457048,0.5940808211,-2.2560141962
H,0,4.9702546984,-1.8922250227,1.2306119796
H,0,6.2487686408,-1.0453427076,-0.7201798541

B.6.1.1.44. 15 gauche

./PPKhetero-cisIM2-4
E(UwB97XD) = -693.602414014

Zero-point correction= 0.263990 (Hartree/Particle)
Thermal correction to Energy= 0.280079
Thermal correction to Enthalpy= 0.281023
Thermal correction to Gibbs Free Energy= 0.218004
Sum of electronic and ZPE= -693.338424
Sum of electronic and thermal Energies= -693.322335
Sum of electronic and thermal Enthalpies= -693.321391
Sum of electronic and thermal Free Energies= -693.384410

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	175.752	59.756	132.635

C,0,1.6766199162,1.5025049124,-0.7530584664
C,0,1.2750823949,-1.4985170831,-0.6103558897
C,0,2.0074041863,0.6888049773,0.4581088118
C,0,2.3540576594,-0.8047711067,0.1157206376
C,0,0.4245622203,-2.4760564971,-0.0072249421
H,0,1.0803579004,-1.219756857,-1.6388220856
C,0,0.4330758324,1.469375699,-1.3327333711
H,0,2.4660815389,2.1121165639,-1.1826780861
C,0,3.1711846572,1.2881463217,1.2499036741
H,0,1.1234272483,0.6446285974,1.1055678762
H,0,2.5775837031,-1.3378286952,1.0447002403
H,0,3.2606521217,-0.786667545,-0.5023808944
C,0,-0.6824937758,-3.085525271,-0.8403290269
O,0,0.556149416,-2.8262254909,1.1786411375
O,0,-0.5647070177,0.7886472046,-0.8896834111
H,0,4.0724517496,1.3444246315,0.6287557894
H,0,3.4096877614,0.6862580679,2.1323299484
H,0,2.9321638855,2.3020828653,1.5829494249
H,0,-0.6337202758,-2.7866715571,-1.8879564402

H,0,-1.6478773002,-2.771524645,-0.4329284585
H,0,-0.6335458465,-4.1749452426,-0.7709625981
C,0,0.1905086912,2.3005445264,-2.5751603771
C,0,1.1902792554,2.5723882257,-3.5156781978
C,0,-1.0904793756,2.8042722906,-2.8198240724
C,0,0.9247170893,3.3371794093,-4.6468658737
H,0,2.1855670989,2.1671394329,-3.3692006266
C,0,-1.3597749382,3.5754577013,-3.9454481193
H,0,-1.877052541,2.5808284949,-2.1079045773
C,0,-0.3516239413,3.8472757884,-4.8661834693
H,0,1.7156292687,3.5272726354,-5.3650783762
H,0,-2.3599066499,3.9643192923,-4.1074203177
H,0,-0.5602097132,4.4433001224,-5.7479938928

B.6.1.1.45. 7 gauche

./PPKhetero-cisPD-4
E(UwB97XD) = -693.613510049

Zero-point correction= 0.265321 (Hartree/Particle)
Thermal correction to Energy= 0.280597
Thermal correction to Enthalpy= 0.281541
Thermal correction to Gibbs Free Energy= 0.221197
Sum of electronic and ZPE= -693.348189
Sum of electronic and thermal Energies= -693.332913
Sum of electronic and thermal Enthalpies= -693.331969
Sum of electronic and thermal Free Energies= -693.392313

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	176.077	58.302	127.005

C,0,-0.9133180685,0.3978549367,-0.7528132985
C,0,-2.4868143564,0.4091656664,-0.6331741011
C,0,-0.9216133818,1.8249276443,-0.1150081288
C,0,-2.4237805171,1.6776593772,0.2292802591
C,0,-3.1993948034,-0.8021504357,-0.10148728
H,0,-2.9190647793,0.597836096,-1.6228574523
C,0,-0.2001231265,-0.6558542077,0.059682323
H,0,-0.5826026034,0.4116857722,-1.7904485884
C,0,-0.5993157436,2.9409490932,-1.0950758631
H,0,-0.2799299382,1.8916896348,0.7660120642
H,0,-3.0690243463,2.5046453619,-0.0784810893
H,0,-2.5994938154,1.4575964567,1.2828068177
C,0,-2.9111825759,-2.1047427983,-0.8016513998
O,0,-3.9973522108,-0.7332401034,0.8161262752
O,0,-0.5002063946,-0.7336029615,1.3019057468
H,0,0.4432572798,2.8872919077,-1.4242425273
H,0,-0.7625459421,3.9228787178,-0.6394746983
H,0,-1.2354068369,2.876009748,-1.9851070396
H,0,-2.8941504624,-1.9636805528,-1.8857037743
H,0,-3.6487651937,-2.8594761051,-0.5294622525
H,0,-1.9108465606,-2.440997849,-0.5104143619
C,0,0.7347419037,-1.5520760716,-0.5489798125
C,0,1.3809550155,-2.5422960118,0.2615206856
C,0,1.0828245302,-1.5659726198,-1.9384046081
C,0,2.2859902893,-3.4413041917,-0.2675403022
H,0,1.1376359326,-2.5695927524,1.3170822305
C,0,1.9886926507,-2.4741695427,-2.4504949775
H,0,0.6322962429,-0.8548446576,-2.6212742701
C,0,2.6121099317,-3.4289616372,-1.6312775664
H,0,2.7521167471,-4.1723710026,0.3880168421
H,0,2.2201537451,-2.4452915479,-3.5117713535
H,0,3.3230371584,-4.1369893341,-2.0419898285

B.6.1.1.46. 12‡ gauche

./PPKhetero-cisTS1-4
E(UwB97XD) = -693.582535340

Zero-point correction= 0.260462 (Hartree/Particle)
Thermal correction to Energy= 0.276833
Thermal correction to Enthalpy= 0.277777
Thermal correction to Gibbs Free Energy= 0.213948
Sum of electronic and ZPE= -693.322073
Sum of electronic and thermal Energies= -693.305702
Sum of electronic and thermal Enthalpies= -693.304758
Sum of electronic and thermal Free Energies= -693.368588

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 173.715 60.401 134.341

C,0,-0.4179735601,2.3985273237,0.1660653143
C,0,2.7379022047,-0.0582928503,-0.606820361
C,0,0.6407628021,1.7858596961,0.816784195
C,0,1.4932537075,0.4081849685,-0.9464046639
C,0,3.9495744904,0.6265334968,-0.9703915932
H,0,2.8311106737,-0.9471445728,0.0099699053
C,0,-1.657033698,1.746457468,-0.0725386728
H,0,-0.2661216538,3.3995498812,-0.2259538404
C,0,1.8669489892,2.5243885119,1.2475968007
H,0,0.4328829257,0.8511696045,1.3282977473
H,0,1.4027343665,1.2432310644,-1.6301317565
H,0,0.6024820913,-0.1857005757,-0.7862642909
C,0,5.2653266133,0.0440789316,-0.4871172375
O,0,3.9780544736,1.6564505848,-1.6674088609
O,0,-1.9176940652,0.5854340215,0.3484856281
H,0,2.0251014899,3.4252625283,0.6480205099
H,0,2.7574386071,1.8913182211,1.158108422
H,0,1.7930741594,2.8282382355,2.2996084205
H,0,5.8886242557,-0.2110565461,-1.349325808
H,0,5.1348556875,-0.8457340072,0.130897213
H,0,5.8045541735,0.800773107,0.0901127958
C,0,-2.7278676869,2.4799256835,-0.8331692781
C,0,-4.056091956,2.0605394234,-0.689886931
C,0,-2.4675819984,3.5499106573,-1.6997487616
C,0,-5.0886602951,2.6961666268,-1.3677450037
H,0,-4.2624847943,1.2240215107,-0.0324438343
C,0,-3.4983317719,4.1825785517,-2.3846368615
H,0,-1.4498302025,3.885336868,-1.8623327387
C,0,-4.8154495839,3.7627834906,-2.2195590716
H,0,-6.1107585964,2.3579988924,-1.2330624048
H,0,-3.2714983372,5.003202004,-3.0568687557
H,0,-5.6186509111,4.2574171188,-2.754416606

B.6.1.1.47. 16‡ gauche

./PPKhetero-cisTS2-5
E(UwB97XD) = -693.598579420

Zero-point correction= 0.263936 (Hartree/Particle)
Thermal correction to Energy= 0.279048
Thermal correction to Enthalpy= 0.279993
Thermal correction to Gibbs Free Energy= 0.220266
Sum of electronic and ZPE= -693.334643
Sum of electronic and thermal Energies= -693.319531
Sum of electronic and thermal Enthalpies= -693.318587
Sum of electronic and thermal Free Energies= -693.378313

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 175.106 57.459 125.704

C,0,-0.8872066126,0.8033978661,0.2938382622
C,0,-1.8747497739,-0.7558080854,1.0982263547
C,0,-2.3206088396,1.203676798,-0.0136191193
C,0,-2.993096658,0.2680040983,1.003345184
C,0,-1.811352527,-1.8557296015,0.1913345355
H,0,-1.3720059777,-0.9004012032,2.0494565963
C,0,0.0957460477,0.5912437274,-0.7143049303
H,0,-0.5204654578,1.185721563,1.2438324571
C,0,-2.6278489274,2.6906888669,0.0982434789
H,0,-2.5520798356,0.8540564243,-1.022408182
H,0,-3.9560023992,-0.1418521703,0.6861063742
H,0,-3.1316956368,0.773708455,1.9649110755
C,0,-0.592773739,-2.749645575,0.2936510718
O,0,-2.6237789734,-2.0378694123,-0.741277972
O,0,-0.1858408739,0.5256412865,-1.9528908182
H,0,-2.3772965053,3.0630465062,1.097902462
H,0,-3.6910310116,2.8865534377,-0.0757805718
H,0,-2.0537242696,3.2684172766,-0.6325641835
H,0,0.1787430878,-2.3440028575,-0.3731513289
H,0,-0.8286109828,-3.7640892317,-0.0342822612
H,0,-0.1724401171,-2.7730968962,1.3014985792
C,0,1.5060384132,0.3507721138,-0.2859415187
C,0,2.5245275505,0.3745195816,-1.2500768166
C,0,1.869304223,0.0636578566,1.0400374495
C,0,3.8499122504,0.1447227748,-0.9048220766
H,0,2.2519919531,0.5776926471,-2.2790624092
C,0,3.1949016893,-0.169669949,1.3852343898
H,0,1.1084587617,-0.0044052787,1.809027896
C,0,4.1953854473,-0.1272879945,0.4169283554
H,0,4.6182316762,0.1752704998,-1.6706930497
H,0,3.4471787819,-0.3968186424,2.4158914053
H,0,5.2294892363,-0.310434882,0.6873993103

B.6.1.1.48. 14‡ gauche

./PPKhetero-cisTSr-5
E(UwB97XD) = -693.594884329

Zero-point correction= 0.263487 (Hartree/Particle)
Thermal correction to Energy= 0.278987
Thermal correction to Enthalpy= 0.279931
Thermal correction to Gibbs Free Energy= 0.216937
Sum of electronic and ZPE= -693.331397
Sum of electronic and thermal Energies= -693.315897
Sum of electronic and thermal Enthalpies= -693.314953
Sum of electronic and thermal Free Energies= -693.377947

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	175.067	58.092	132.583

C,0,0.2125715143,-0.8141571275,0.2429710003
C,0,-2.9762947291,0.4313142759,-0.8696946034
C,0,-1.2616377477,-0.826605613,0.491438841
C,0,-2.1122431173,-0.7625010871,-0.8571836724
C,0,-4.3112367803,0.4402638277,-0.34008926
H,0,-2.5570526818,1.3764905999,-1.2028914193
C,0,0.9851505732,0.3145644995,0.3710625996
H,0,0.6572584315,-1.7360630733,-0.1231378748
C,0,-1.714957258,-2.0419156994,1.3073184939
H,0,-1.5010257868,0.074107492,1.064255365
H,0,-2.7211976881,-1.6665082045,-0.9376655899
H,0,-1.4182065918,-0.7307630292,-1.697872265
C,0,-5.0587559953,1.7552342951,-0.3062717315
O,0,-4.8410688481,-0.5887435885,0.1021171245

O,0,0.5644282073,1.4857909762,0.700127903
H,0,-1.456965267,-2.9716191743,0.7874378109
H,0,-2.7977125747,-2.0320459854,1.4640112741
H,0,-1.2214571471,-2.0551968849,2.2834016948
H,0,-4.8830954035,2.2369335596,0.6611402301
H,0,-6.1299431905,1.5758380248,-0.4058781318
H,0,-4.7233373407,2.4405259052,-1.0865263312
C,0,2.4679874986,0.1948808916,0.0704858599
C,0,3.1530468558,1.3161532809,-0.4068312258
C,0,3.2000302347,-0.9819526037,0.2657291818
C,0,4.5100471309,1.26065502,-0.7076648636
H,0,2.6002219935,2.2399203319,-0.5356694142
C,0,4.5589136945,-1.0412778351,-0.0264876355
H,0,2.7056423812,-1.8591126325,0.6685502026
C,0,5.2212620473,0.0790922666,-0.5202688347
H,0,5.0148467279,2.1431215817,-1.0874208554
H,0,5.1039647439,-1.9645156974,0.1414004943
H,0,6.2812461129,0.0344714071,-0.7460543671

B.6.1.1.49. 13

./PPKhetero-transIM1-5
E(UwB97XD) = -693.599657913

Zero-point correction= 0.263245 (Hartree/Particle)
Thermal correction to Energy= 0.279618
Thermal correction to Enthalpy= 0.280562
Thermal correction to Gibbs Free Energy= 0.215743
Sum of electronic and ZPE= -693.336413
Sum of electronic and thermal Energies= -693.320040
Sum of electronic and thermal Enthalpies= -693.319096
Sum of electronic and thermal Free Energies= -693.383915

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	175.463	60.139	136.424

C,0,0.2093566089,0.7497283889,-0.352989964
C,0,-3.5268363824,0.6541047955,0.5585482156
C,0,-1.2636852799,0.7287820192,-0.6072639674
C,0,-2.0653839329,0.7162161791,0.7513769822
C,0,-4.2446493009,-0.5840596586,0.4265509794
H,0,-4.0888394609,1.5750418766,0.4328508325
C,0,0.99440998,-0.3782564913,-0.3309686956
H,0,0.6504887848,1.7140114685,-0.1132519084
C,0,-1.7081829457,1.9056476265,-1.4799795055
H,0,-1.5159630891,-0.2080770056,-1.1143577697
H,0,-1.7960219446,1.6244761477,1.3006146736
H,0,-1.7234903601,-0.1538266258,1.3158841354
C,0,-5.7256512626,-0.5169100187,0.1250432718
O,0,-3.6747759017,-1.6779697542,0.5305370394
O,0,0.5947589992,-1.5864922167,-0.5147996031
H,0,-1.4933460181,2.8586907298,-0.9822070354
H,0,-2.781401667,1.876313912,-1.6963832359
H,0,-1.17051608,1.8994454573,-2.4319770814
H,0,-6.1965389936,0.3519956421,0.5886926108
H,0,-6.2174402162,-1.4297901332,0.4619984112
H,0,-5.8641558403,-0.4321434763,-0.9577744064
C,0,2.4717954575,-0.1960311618,-0.0349681999
C,0,3.1534061635,-1.1984502657,0.6616727343
C,0,3.2011300897,0.9262114776,-0.4428812271
C,0,4.5055667163,-1.0771122262,0.9636955947
H,0,2.6030380998,-2.0814574732,0.9658695391
C,0,4.5560400848,1.0494467744,-0.1504816913
H,0,2.7062565336,1.7072180083,-1.0099652951
C,0,5.2155136639,0.049615699,0.5584392224

H,0,5.0078352502,-1.865924131,1.5143885862
H,0,5.1004177336,1.9261194434,-0.486264705
H,0,6.2723008703,0.1433315024,0.7841224425

B.6.1.1.50. 15

./PPKhetero-transIM2-6
E(UwB97XD) = -693.603514921

Zero-point correction= 0.263645 (Hartree/Particle)
Thermal correction to Energy= 0.279610
Thermal correction to Enthalpy= 0.280554
Thermal correction to Gibbs Free Energy= 0.218367
Sum of electronic and ZPE= -693.339870
Sum of electronic and thermal Energies= -693.323905
Sum of electronic and thermal Enthalpies= -693.322961
Sum of electronic and thermal Free Energies= -693.385148

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 175.458 59.914 130.884

C,0,-0.5727765323,1.4796262364,0.0697303358
C,0,-2.6742438178,-0.8108774075,-0.4117154367
C,0,-2.0384219641,1.667446745,-0.1613377083
C,0,-2.8795045004,0.4408500642,0.3495215533
C,0,-1.9459269653,-1.9616909238,0.0232584392
H,0,-3.1342853316,-0.8929715226,-1.3921038913
C,0,0.1812308378,0.6335184524,-0.7028883268
H,0,-0.1440080064,1.9285804674,0.9612392902
C,0,-2.5600976577,2.9358563289,0.5165963273
H,0,-2.2340505088,1.7401665954,-1.2380371187
H,0,-3.9385633004,0.7198082922,0.2637392414
H,0,-2.6616782818,0.3055147247,1.413155186
C,0,-1.1914868044,-1.8997866649,1.3327166325
O,0,-1.9327459267,-3.0041773398,-0.6549977977
O,0,-0.2651888119,-0.030757525,-1.7089375537
H,0,-2.4055809342,2.8871630415,1.6006120227
H,0,-3.6301337495,3.078932543,0.3367931107
H,0,-2.0313995553,3.8184034163,0.1454654634
H,0,-0.5479446942,-1.0156292018,1.3551905131
H,0,-0.593319742,-2.8029092121,1.452985043
H,0,-1.8884524788,-1.8201259999,2.1729512329
C,0,1.6226404377,0.394897386,-0.3124582213
C,0,2.1898110933,-0.8601110947,-0.5516258324
C,0,2.425895646,1.3762634376,0.2779925589
C,0,3.5051780254,-1.1361345928,-0.1945764095
H,0,1.5768830531,-1.6201595374,-1.0228191816
C,0,3.7444403364,1.1074585642,0.6302374998
H,0,2.0176441478,2.3662491058,0.4512204697
C,0,4.2908365094,-0.1519424654,0.3986926841
H,0,3.921024235,-2.1207058986,-0.382808346
H,0,4.3513965772,1.8872696691,1.0786609685
H,0,5.3200986643,-0.3606956837,0.6696272516

B.6.1.1.51. 7$^{-\bullet}$

./PPKhetero-transPD-4
E(UwB97XD) = -693.618418193

Zero-point correction= 0.265103 (Hartree/Particle)
Thermal correction to Energy= 0.280535
Thermal correction to Enthalpy= 0.281479
Thermal correction to Gibbs Free Energy= 0.220449
Sum of electronic and ZPE= -693.353316

Sum of electronic and thermal Energies= -693.337883
Sum of electronic and thermal Enthalpies= -693.336939
Sum of electronic and thermal Free Energies= -693.397969

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 176.038 58.483 128.449

C,0,-1.0484802013,0.2070066413,0.466299343
C,0,-1.5803262457,-0.3215284093,-0.9193222865
C,0,-1.2032742163,1.6387774372,-0.1136969107
C,0,-2.1485723063,1.0765991892,-1.2003282963
C,0,-2.4814153408,-1.5113447038,-0.8238170333
H,0,-0.7099512977,-0.5527884432,-1.5403800427
C,0,0.3086452046,-0.2681006489,0.919706061
H,0,-1.8261033712,0.0533315538,1.2182911731
C,0,-1.70424895,2.7270170404,0.8146587987
H,0,-0.2506009137,1.9240386776,-0.5682492871
H,0,-2.0481229617,1.4656510979,-2.2153774577
H,0,-3.1972110192,1.1374515891,-0.8946946094
C,0,-1.8027761986,-2.8095478533,-0.4680747654
O,0,-3.6884914759,-1.4387396889,-0.9772222544
O,0,1.3001939582,-0.0332573161,0.143785356
H,0,-2.6643558453,2.4460771091,1.260410244
H,0,-1.8440295548,3.6730267854,0.2819746256
H,0,-0.9932516413,2.9017642432,1.6286803209
H,0,-1.1854857918,-3.1322276206,-1.3122966093
H,0,-2.5363544804,-3.5818822774,-0.2380994894
H,0,-1.1275854622,-2.6585875149,0.3803966094
C,0,0.4622296789,-0.9954936993,2.1449159406
C,0,1.7640117762,-1.449946581,2.5329146436
C,0,-0.6031461755,-1.3312998487,3.0400453499
C,0,1.97171907,-2.1594068981,3.7000115463
H,0,2.5967337259,-1.2202281872,1.8784950462
C,0,-0.3774256254,-2.043152657,4.2022801481
H,0,-1.621320378,-1.0340430914,2.8165370106
C,0,0.9102084816,-2.4708144088,4.5604851169
H,0,2.9786895181,-2.481363395,3.9524588902
H,0,-1.2189668888,-2.2757557139,4.8489088099
H,0,1.0774833583,-3.0277228073,5.4755241681

B.6.1.1.52. 12‡

./PPKhetero-transTS1-3
E(UwB97XD) = -693.581890738

Zero-point correction= 0.259741 (Hartree/Particle)
Thermal correction to Energy= 0.276545
Thermal correction to Enthalpy= 0.277489
Thermal correction to Gibbs Free Energy= 0.210386
Sum of electronic and ZPE= -693.322150
Sum of electronic and thermal Energies= -693.305346
Sum of electronic and thermal Enthalpies= -693.304402
Sum of electronic and thermal Free Energies= -693.371504

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 173.535 60.771 141.230

C,0,-0.6261063788,2.2031267951,0.8431429707
C,0,2.461875806,0.0871929772,-0.7928542439
C,0,0.5915583159,1.6519291386,1.2010788207
C,0,1.1377437686,0.4316816078,-0.8241713635
C,0,2.9521247547,-1.0545054325,-0.0633108991
H,0,3.1961332936,0.7285856107,-1.2703915914
C,0,-1.8422610848,1.468173892,0.8329255488

H,0,-0.6387727808,3.23683343,0.5100787222
C,0,1.8289546781,2.4684507192,1.3977622815
H,0,0.5838091791,0.6662044432,1.6547606576
H,0,0.8004132343,1.2662630008,-1.4258388695
H,0,0.3744404615,-0.2488381909,-0.4681534243
C,0,4.4470246725,-1.3150066836,-0.072826787
O,0,2.2173655455,-1.8247722456,0.5752736097
O,0,-1.9305783757,0.2695453417,1.2248528124
H,0,1.7907605859,3.4013567727,0.8268526335
H,0,2.7195876441,1.9098199712,1.0874447442
H,0,1.9672043989,2.7297708947,2.4548212926
H,0,4.8309600922,-1.2447074951,0.9493986914
H,0,4.9961695325,-0.6139623671,-0.7032683539
H,0,4.635248579,-2.3341595069,-0.4217290126
C,0,-3.094001064,2.1564893848,0.3657841013
C,0,-4.3343267593,1.6498438364,0.7745817121
C,0,-3.0901484574,3.2727488047,-0.4824389881
C,0,-5.523232136,2.2472976925,0.3748113637
H,0,-4.347533819,0.7770650021,1.4171508001
C,0,-4.2784785434,3.8673682435,-0.889428541
H,0,-2.1521419846,3.6732698529,-0.8494490026
C,0,-5.5024420487,3.3620044342,-0.459090954
H,0,-6.4708352768,1.8428196566,0.7149541903
H,0,-4.2487532643,4.7261833065,-1.5515998401
H,0,-6.4288928486,3.8289564729,-0.7747503917

B.6.1.1.53. 16‡

./PPKhetero-transTS2-2
E(UwB97XD) = -693.601605544

Zero-point correction= 0.263782 (Hartree/Particle)
Thermal correction to Energy= 0.279168
Thermal correction to Enthalpy= 0.280112
Thermal correction to Gibbs Free Energy= 0.219227
Sum of electronic and ZPE= -693.337823
Sum of electronic and thermal Energies= -693.322438
Sum of electronic and thermal Enthalpies= -693.321494
Sum of electronic and thermal Free Energies= -693.382379

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	175.180	57.541	128.144

C,0,-0.7995921034,0.5246319675,0.7403320929
C,0,-1.8575216601,-0.2257892599,-0.7960665593
C,0,-0.7226649012,1.6807494301,-0.2421715752
C,0,-1.9358666364,1.2611076746,-1.0809186275
C,0,-2.9670976294,-0.9986797968,-0.3500492454
H,0,-1.0761696065,-0.7676175561,-1.323363711
C,0,0.3392486603,-0.2237027836,1.1465463762
H,0,-1.6149042006,0.6145824191,1.4547336087
C,0,-0.745524513,3.0725989336,0.3736191144
H,0,0.1880738297,1.5545069575,-0.8349055708
H,0,-1.900844335,1.5330682757,-2.1409246038
H,0,-2.8584979565,1.6625855221,-0.6506903159
C,0,-2.809117214,-2.5087548467,-0.3129468251
O,0,-4.0377919441,-0.4983342197,0.0708750335
O,0,1.4652012785,-0.1370731695,0.5669945699
H,0,-1.6371723069,3.2050460868,0.9959627911
H,0,-0.7583952734,3.8462611747,-0.4011103942
H,0,0.1340006646,3.2403490239,1.0028899596
H,0,-1.7716130621,-2.8228554246,-0.4448385914
H,0,-3.4108439431,-2.9579790947,-1.1106944001
H,0,-3.181928285,-2.8972977425,0.6382999764
C,0,0.1692013351,-1.2292475727,2.2404552545

C,0,1.3080621312,-1.8068902625,2.8184429568
C,0,-1.0861810275,-1.6566067253,2.6985796881
C,0,1.2010859948,-2.7597945358,3.8229641807
H,0,2.2812617624,-1.4893111862,2.4624714276
C,0,-1.1942513041,-2.6165611401,3.6976638816
H,0,-1.9913072676,-1.2558662398,2.2580235891
C,0,-0.052610789,-3.1723343442,4.2685637951
H,0,2.098476487,-3.1864346482,4.2590137709
H,0,-2.1766776833,-2.9391852895,4.0262255845
H,0,-0.1390521311,-3.9224562774,5.0469381079

B.6.1.1.54. 14‡

./PPKhetero-transTSr-2
E(UwB97XD) = -693.595035766

Zero-point correction= 0.263382 (Hartree/Particle)
Thermal correction to Energy= 0.278901
Thermal correction to Enthalpy= 0.279845
Thermal correction to Gibbs Free Energy= 0.216948
Sum of electronic and ZPE= -693.331654
Sum of electronic and thermal Energies= -693.316135
Sum of electronic and thermal Enthalpies= -693.315190
Sum of electronic and thermal Free Energies= -693.378088

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 175.013 57.950 132.379

C,0,0.153410012,1.0991659825,-0.2748303791
C,0,3.5348565182,-0.0328733699,-0.2089524726
C,0,1.5636433927,1.5084380354,-0.0009480945
C,0,2.5832049688,0.7842444689,-0.9788762633
C,0,3.485765661,-1.4643821429,-0.1474907317
H,0,4.2587990032,0.4780482016,0.4204901532
C,0,-0.6260939412,0.4275261566,0.6369651716
H,0,-0.252698032,1.3492029581,-1.2515293324
C,0,1.7804913385,3.0253289412,-0.0690137411
H,0,1.7915590825,1.1843179905,1.0194711525
H,0,3.1272254723,1.5492677233,-1.5446605796
H,0,2.0349993629,0.1607598938,-1.6851340613
C,0,4.4528324936,-2.1782444579,0.7717124592
O,0,2.6645622202,-2.1176639062,-0.8085441345
O,0,-0.2830541249,0.0958928614,1.8314115638
H,0,1.5298462151,3.4066459702,-1.0653831874
H,0,2.8233494752,3.2903241993,0.1393492042
H,0,1.1448120536,3.5385116698,0.6578852116
H,0,5.3021007219,-1.5526444497,1.0500962669
H,0,4.810791034,-3.0921594683,0.2945879916
H,0,3.9242701278,-2.4635809113,1.6866664003
C,0,-2.0432779646,0.0756133206,0.2252401784
C,0,-3.0385981164,0.0225912994,1.2055256061
C,0,-2.4082110001,-0.2214212816,-1.0923859842
C,0,-4.3562954786,-0.2824113695,0.8821133956
H,0,-2.7587651317,0.2260579235,2.2329516904
C,0,-3.7233545402,-0.5349902046,-1.4206277138
H,0,-1.6521346287,-0.2236878923,-1.8697426997
C,0,-4.7065877004,-0.5621445031,-0.4358979689
H,0,-5.1122997452,-0.3046181313,1.6603533856
H,0,-3.9786773424,-0.7676727414,-2.4493461203
H,0,-5.7322901673,-0.805841506,-0.6909900667

B.6.1.1.55. $5^{-\bullet}$ + 5 gauche

./PPKhomo-cisSM-1

opt
E(UwB97XD) = -924.628253772

Zero-point correction= 0.342458 (Hartree/Particle)
Thermal correction to Energy= 0.364421
Thermal correction to Enthalpy= 0.365365
Thermal correction to Gibbs Free Energy= 0.288492
Sum of electronic and ZPE= -924.285796
Sum of electronic and thermal Energies= -924.263833
Sum of electronic and thermal Enthalpies= -924.262889
Sum of electronic and thermal Free Energies= -924.339762

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 228.677 81.339 161.793

C,0,-0.9192745933,-2.4366971778,-0.3194940652
C,0,3.019283507,-1.2491138776,-0.485393261
C,0,-1.3961339396,-3.5177538964,-0.9848644121
C,0,2.2562448244,-1.9512665358,-1.3335845421
C,0,3.160058018,-1.6404686351,0.9246350545
H,0,3.5238815347,-0.3547789319,-0.8328468272
C,0,-0.8092964975,-1.1051116355,-0.8786907319
H,0,-0.5776708902,-2.594081403,0.7001305669
C,0,-1.4769815151,-4.8968574678,-0.4022010299
H,0,-1.7336243231,-3.3884490651,-2.0104363376
H,0,1.7451771426,-2.8324200021,-0.9553520226
O,0,2.7482296901,-2.7166663519,1.3464824212
O,0,-1.1898911773,-0.8645768191,-2.0786379771
H,0,-1.1107950411,-4.9167170191,0.6285806108
H,0,-0.8838906727,-5.6153854216,-0.9812766809
H,0,-2.5055838027,-5.2780997119,-0.3989940077
C,0,-0.242705227,-0.0229106153,-0.0659531268
C,0,-0.0688634234,1.2503541497,-0.6547829013
C,0,0.1690250296,-0.1555737676,1.281437436
C,0,0.4734866137,2.3135908638,0.0527448078
H,0,-0.3696528399,1.3756244839,-1.6883608839
C,0,0.704441501,0.9104038619,1.9841670977
H,0,0.0794618426,-1.1066734455,1.7917423781
C,0,0.864299352,2.1599627716,1.3824650486
H,0,0.5925890509,3.275756062,-0.4370832842
H,0,1.0185602797,0.7632833045,3.0129053683
H,0,1.293807114,2.9882607789,1.9349885995
C,0,3.8526372194,-0.6962265383,1.8651388164
C,0,4.0572886551,0.6531499084,1.5674046748
C,0,4.2800053913,-1.1877511898,3.1017066486
C,0,4.6804055287,1.4898349392,2.4855300906
H,0,3.701143021,1.072698718,0.6353016443
C,0,4.908348222,-0.3550484534,4.0164434598
H,0,4.1103216159,-2.2326392355,3.3334740922
C,0,5.1107759458,0.9882180487,3.7088174634
H,0,4.8244594913,2.5373994239,2.2462335997
H,0,5.2404745438,-0.7501212113,4.9698793928
H,0,5.6013554173,1.6413498931,4.4219938772
C,0,2.0193585754,-1.5993600446,-2.7589288619
H,0,2.2445132654,-2.4493089875,-3.4109482758
H,0,0.9556449835,-1.361035303,-2.890966988
H,0,2.6188272565,-0.741759754,-3.0727177017

B.6.1.1.56. 4

./PVKhomo-cisIM1-4
E(UwB97XD) = -845.999838992

Zero-point correction= 0.289826 (Hartree/Particle)
Thermal correction to Energy= 0.307454

Thermal correction to Enthalpy= 0.308399
Thermal correction to Gibbs Free Energy= 0.239784
Sum of electronic and ZPE= -845.710013
Sum of electronic and thermal Energies= -845.692385
Sum of electronic and thermal Enthalpies= -845.691440
Sum of electronic and thermal Free Energies= -845.760055

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 192.931 67.306 144.411

C,0,4.8764199897,1.8793604849,-0.5248545667
C,0,3.7599945838,1.0736910863,-0.7179857653
C,0,3.6172863932,-0.1188606372,-0.0050272521
C,0,4.6110027351,-0.489793282,0.9035828177
C,0,5.718619786,0.321855664,1.1073867863
C,0,5.8546445633,1.508347872,0.3913952819
H,0,4.9836154216,2.7958828844,-1.0937879571
H,0,3.0126699106,1.3700219722,-1.4453988284
H,0,4.5014079586,-1.418615745,1.4512961411
H,0,6.4784910606,0.0301552298,1.8235285029
H,0,6.7230373692,2.1390133497,0.5450427055
C,0,2.4445748763,-1.0343850153,-0.2054805641
O,0,2.5669961196,-2.246492385,0.0262517459
C,0,1.1914565209,-0.4823616552,-0.6337093805
C,0,-2.1783554118,-2.1333209915,0.2125635562
C,0,-0.0069936337,-1.3111795167,-0.8507210633
H,0,1.0893822523,0.5964689533,-0.6924001481
C,0,-0.9226917225,-1.3514736476,0.4246936472
H,0,-2.1419685888,-3.2047037518,0.3811818783
H,0,-0.6085421311,-0.894324391,-1.6631721055
H,0,0.2754285847,-2.3351597296,-1.1041085608
H,0,-0.3272561577,-1.7737767662,1.2414822424
H,0,-1.1644241,-0.3185838672,0.6952720389
C,0,-3.3233824619,-1.5559579398,-0.2829752048
O,0,-3.4577261113,-0.3202124044,-0.6115836152
C,0,-4.5346743846,-2.4448711345,-0.4897571058
C,0,-5.4417127442,-2.1292161856,-1.5056715404
C,0,-4.8068975613,-3.5658985949,0.3025869477
C,0,-6.5655591642,-2.9140649175,-1.7406049153
H,0,-5.2491102042,-1.2513305818,-2.1117276707
C,0,-5.9328174504,-4.3509367469,0.0762865685
H,0,-4.1377993945,-3.818249554,1.1180777912
C,0,-6.8176582381,-4.031461361,-0.9499099142
H,0,-7.2493856244,-2.6517383434,-2.5415037623
H,0,-6.1259540715,-5.2105892374,0.7097119019
H,0,-7.6979783895,-4.640474934,-1.1245606929

B.6.1.1.57. 4-2Li gauche

./PVKhomo-cisIM1-inin1Li2
uwb97xd/6-311+g(d,p)
E(UwB97XD) = -860.999135609

Zero-point correction= 0.295195 (Hartree/Particle)
Thermal correction to Energy= 0.315143
Thermal correction to Enthalpy= 0.316087
Thermal correction to Gibbs Free Energy= 0.243601
Sum of electronic and ZPE= -860.703941
Sum of electronic and thermal Energies= -860.683993
Sum of electronic and thermal Enthalpies= -860.683049
Sum of electronic and thermal Free Energies= -860.755534

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 197.755 76.628 152.559

C,0,4.050354434,3.0397275864,-0.0148833723
C,0,3.0141203475,2.1396597701,0.2070604062
C,0,1.8566070042,2.1653064061,-0.578757645
C,0,1.7638678538,3.1379178281,-1.578331154
C,0,2.8000675423,4.0369085042,-1.8067708997
C,0,3.9509801082,3.9912565923,-1.0263226494
H,0,4.9354882874,3.004459704,0.6113836363
H,0,3.1025734721,1.420652001,1.0138208409
H,0,0.8607626301,3.177106676,-2.1760504101
H,0,2.7076761711,4.7771631041,-2.594630248
H,0,4.7585071404,4.6944851423,-1.1977434501
C,0,0.7080521313,1.2080254354,-0.3849096514
O,0,-0.4505212016,1.6240840145,-0.7934390917
C,0,0.9321338164,-0.0229882093,0.1598711646
C,0,-2.2263974248,-1.5204501428,1.7412586222
C,0,-0.1812136693,-0.9995878265,0.3744699384
H,0,1.9299863499,-0.3081725553,0.4710777135
C,0,-1.0589576636,-0.6321142987,1.6217253135
H,0,-3.0739696089,-1.3468699696,1.087291649
H,0,-0.8385417192,-1.0374431777,-0.5018568138
H,0,0.2096199174,-2.0104020709,0.5223287415
H,0,-0.432758008,-0.6871693383,2.5142556455
H,0,-1.3919137817,0.4002590093,1.482572984
C,0,-2.2371944165,-2.6773402302,2.5851354054
O,0,-1.2274380596,-2.9978799754,3.2371009179
C,0,-3.4570197798,-3.5341714655,2.6647432537
C,0,-3.3115654779,-4.86705471,3.0593657892
C,0,-4.7338944986,-3.0411483335,2.3831155094
C,0,-4.4194919214,-5.6962634493,3.1560631056
H,0,-2.320982342,-5.2451515144,3.28219056
C,0,-5.8443634478,-3.8689781675,2.4945169604
H,0,-4.8753455865,-2.0046336558,2.1000825573
C,0,-5.6888985907,-5.1976195686,2.8751284081
H,0,-4.2952750609,-6.7315559305,3.4518518913
H,0,-6.8320384709,-3.4745154384,2.2863825242
H,0,-6.5557674991,-5.8435688951,2.9555392661
Li,0,-2.2309199174,1.3165945177,-1.0956404701
Li,0,0.6103729403,-3.0896043682,3.9134800516

B.6.1.1.58. 10-2Li gauche

./PVKhomo-cisIM2-1Li2
uwb97xd/6-311+g(d,p)
E(UwB97XD) = -861.014397335

Zero-point correction= 0.294815 (Hartree/Particle)
Thermal correction to Energy= 0.314760
Thermal correction to Enthalpy= 0.315704
Thermal correction to Gibbs Free Energy= 0.245076
Sum of electronic and ZPE= -860.719582
Sum of electronic and thermal Energies= -860.699638
Sum of electronic and thermal Enthalpies= -860.698694
Sum of electronic and thermal Free Energies= -860.769321

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 197.515 76.930 148.648

C,0,0.4858362712,-0.2280900601,-1.5376833002
C,0,1.8139133727,0.3764498931,-1.902684636
H,0,2.565809388,-0.4115807283,-1.9509086239
C,0,2.2328954221,1.4367188827,-0.8471779191
H,0,1.7881150309,0.8529342848,-2.8888748895
C,0,1.6890927759,1.0625297941,0.4924663971
H,0,1.8385491839,2.4173540322,-1.120864546

H,0,3.3251739504,1.5264424784,-0.8134008437
H,0,1.0031392935,1.733753924,0.994352716
C,0,1.9748451408,-0.2069550056,1.0881517586
C,0,0.3067137443,-1.5344331286,-1.2045470298
H,0,-0.3589308779,0.4475680794,-1.4480472776
C,0,-1.0224068434,-1.9861481187,-0.6769817581
C,0,-2.2352178687,-1.4565636681,-1.1271399536
C,0,-1.0534361721,-2.9535059296,0.3314573756
C,0,-2.2568768433,-3.3651852116,0.8901118677
C,0,-3.4574025967,-2.8244442114,0.4408333624
C,0,-3.4412849551,-1.8707771974,-0.5732655514
H,0,-2.2373188788,-0.7224364486,-1.9255546842
H,0,-0.116889445,-3.3597358946,0.6966119511
H,0,-2.2565901302,-4.1020094341,1.6860631501
H,0,-4.3985129926,-3.1451578044,0.8737026365
H,0,-4.3726146387,-1.4527795961,-0.9400047289
O,0,1.2492630846,-2.4484657706,-1.2343533259
O,0,2.9514343875,-0.8773747194,0.7014002913
C,0,1.0831765735,-0.7516559212,2.1549799348
C,0,1.5249294955,-1.8430257214,2.906308564
C,0,-0.2067656888,-0.2581353501,2.3668998253
C,0,0.69939073,-2.4221661229,3.8598990101
H,0,2.5213475052,-2.2319219224,2.7325357973
C,0,-1.0329813638,-0.8384304216,3.3193729352
H,0,-0.5891433322,0.5565130991,1.7640067391
C,0,-0.5819359403,-1.919900597,4.0681462515
H,0,1.0533050085,-3.2664729148,4.4405273713
H,0,-2.0366844182,-0.4563436207,3.4649851599
H,0,-1.2303187797,-2.3758888181,4.8078753674
Li,0,2.9356167059,-2.5204669654,-0.3741446838
Li,0,0.9328817009,-4.2136221651,-1.8893677106

B.6.1.1.59. 10 gauche

./PVKhomo-cisIM2-5
E(UwB97XD) = -846.003536688

Zero-point correction= 0.290076 (Hartree/Particle)
Thermal correction to Energy= 0.307266
Thermal correction to Enthalpy= 0.308211
Thermal correction to Gibbs Free Energy= 0.243185
Sum of electronic and ZPE= -845.713461
Sum of electronic and thermal Energies= -845.696270
Sum of electronic and thermal Enthalpies= -845.695326
Sum of electronic and thermal Free Energies= -845.760351

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	192.813	67.037	136.857

C,0,-1.4895205835,1.9461079373,-0.2530011183
C,0,-2.9772070481,1.9077512757,-0.0299947583
H,0,-3.1631185088,1.6186722062,1.0057899349
C,0,-3.4760631679,0.804756305,-0.9808603261
H,0,-3.4660176886,2.8759138922,-0.1987300774
C,0,-2.3115347377,-0.1493153866,-1.1082771506
H,0,-3.7089271014,1.2247596157,-1.9642080553
H,0,-4.3833648141,0.317004757,-0.6090666463
H,0,-1.749117503,-0.156209472,-2.0334852773
C,0,-1.9616930613,-1.054000925,-0.0985516261
C,0,-0.5453245176,1.820399398,0.7804127498
H,0,-1.1356837973,2.1837584391,-1.2502895553
C,0,0.9094621054,1.6916124661,0.4041148626
C,0,1.8865185658,2.112738485,1.3088840366
C,0,1.3188156436,1.1095453762,-0.7985019351
C,0,2.6697096243,0.9572186496,-1.0896929877

C,0,3.6346426896,1.3915816206,-0.1857352011
C,0,3.2377539597,1.9722471949,1.0157739037
H,0,1.5713794297,2.5488792803,2.2502552032
H,0,0.57501393,0.7327471628,-1.490653331
H,0,2.9698822296,0.4850287707,-2.0190484835
H,0,4.6886131524,1.2703871057,-0.4108927201
H,0,3.9834088872,2.3118033728,1.7268235242
O,0,-0.842496761,1.7791699686,2.0032434423
O,0,-2.6163064198,-1.2197305424,0.9660197302
C,0,-0.6608669911,-1.8015416309,-0.2614925678
C,0,0.1225750788,-2.0318277959,0.8711227449
C,0,-0.191123962,-2.2492349802,-1.4986899961
C,0,1.3534633296,-2.669212313,0.7700065163
H,0,-0.242718134,-1.6902650793,1.8328796331
C,0,1.0340138661,-2.8988608736,-1.6022353148
H,0,-0.7899903633,-2.0997687549,-2.3906568791
C,0,1.8151157452,-3.1048331003,-0.4689857519
H,0,1.9561133674,-2.8246376056,1.6585706991
H,0,1.3793416288,-3.2456658279,-2.5703749659
H,0,2.7742519272,-3.6044189917,-0.5502722557

B.6.1.1.60. 10-Li gauche

./PVKhomo-cisIM2-9Li
uwb97xd/6-311+g(d,p)
E(UwB97XD) = -853.517500992

Zero-point correction= 0.293118 (Hartree/Particle)
Thermal correction to Energy= 0.311348
Thermal correction to Enthalpy= 0.312292
Thermal correction to Gibbs Free Energy= 0.245168
Sum of electronic and ZPE= -853.224383
Sum of electronic and thermal Energies= -853.206153
Sum of electronic and thermal Enthalpies= -853.205209
Sum of electronic and thermal Free Energies= -853.272333

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	195.374	71.497	141.274

C,0,4.0646512244,2.2099753857,0.9529859504
C,0,3.0732907265,1.3735198023,0.4570194236
C,0,3.3044744854,0.0028233503,0.3079152048
C,0,4.5484275274,-0.5097647991,0.6828145856
C,0,5.5432139937,0.3257469959,1.1764816656
C,0,5.3041608926,1.6900182072,1.3129148075
C,0,2.2438166175,-0.9444380468,-0.1746579192
O,0,2.3546947378,-2.1698699909,0.1401874811
C,0,1.1606293223,-0.4533980788,-0.9033683544
C,0,-0.0241228079,-1.317314185,-1.2602706192
C,0,-0.7863683515,-1.5531386875,0.0593894238
C,0,-0.4512350213,-0.3743722322,0.9337573465
H,0,3.8621218719,3.2680507024,1.0767140184
H,0,2.099205121,1.7876270648,0.2258551217
H,0,4.7240262773,-1.5746279559,0.5837896372
H,0,6.5055914712,-0.0878418095,1.4577088016
H,0,6.0762054116,2.342658541,1.7053384347
H,0,1.1895644567,0.5659462508,-1.266673837
H,0,-0.8242620525,0.5956032154,0.6268849527
H,0,-0.6560029488,-0.7818202945,-1.9730905807
H,0,0.2768079664,-2.2590860049,-1.730516729
H,0,-0.4418938706,-2.4701475006,0.5396172454
H,0,-1.8657101567,-1.6531038656,-0.0988613318
C,0,0.2765294506,-0.4768301547,2.1208204479
O,0,0.7178852028,-1.5795466876,2.5711037636
C,0,0.6609575371,0.7719427391,2.8607405298

C,0,1.8212778672,0.7477741754,3.6380393003
C,0,-0.0688369493,1.9611465876,2.7858831455
C,0,2.2552094035,1.8843086449,4.3069037203
H,0,2.3889195941,-0.1732764011,3.6942387064
C,0,0.3601554094,3.0988982648,3.4598567831
H,0,-0.9869809733,2.0039137097,2.2110558954
C,0,1.5266395386,3.0664697318,4.2182229092
H,0,3.1669378782,1.8503383514,4.8932361842
H,0,-0.2211039348,4.0121953398,3.3962914661
H,0,1.8625021113,3.9560319146,4.7395427582
Li,0,1.7468989702,-2.9713602802,1.7813366609

B.6.1.1.61. 2-2Li gauche

./PVKhomo-cisPD-2Li2
uwb97xd/6-311+g(d,p)
E(UwB97XD) = -861.018486656

Zero-point correction= 0.296476 (Hartree/Particle)
Thermal correction to Energy= 0.315707
Thermal correction to Enthalpy= 0.316651
Thermal correction to Gibbs Free Energy= 0.246753
Sum of electronic and ZPE= -860.722011
Sum of electronic and thermal Energies= -860.702780
Sum of electronic and thermal Enthalpies= -860.701836
Sum of electronic and thermal Free Energies= -860.771734

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	198.109	75.224	147.112

C,0,1.3867886612,-1.7589496386,-0.4224229939
C,0,2.8650267559,-2.0585584429,-0.1160270696
H,0,3.1369964672,-1.74053543,0.8903175416
C,0,3.2820287672,-1.02095793,-1.1780817481
H,0,3.1820958055,-3.0911619865,-0.2667241038
C,0,1.8594695519,-0.4119215722,-1.1508718708
H,0,3.4920139405,-1.4819999739,-2.1450190223
H,0,4.0993912479,-0.3517005907,-0.9126281646
H,0,1.3954749825,-0.2868752425,-2.1284509752
C,0,1.6947693846,0.8195224255,-0.302449799
C,0,0.4250616196,-1.526126656,0.7002821544
H,0,0.9865284235,-2.4475589873,-1.1641592136
C,0,-1.0407967682,-1.533981458,0.4338142138
C,0,-1.5937761189,-2.0559320327,-0.7379908546
C,0,-1.8821246681,-0.9393314244,1.3797628992
C,0,-3.2470328839,-0.8598678347,1.1559497545
C,0,-3.7898200811,-1.3820075876,-0.0158310931
C,0,-2.9633518403,-1.9834915321,-0.9582272653
H,0,-0.9686685698,-2.5223681438,-1.4884908283
H,0,-1.4466461124,-0.5260124046,2.2811386005
H,0,-3.8897300929,-0.3872616615,1.8895043957
H,0,-4.8574575348,-1.3192315605,-0.1935423313
H,0,-3.3843212492,-2.3935193307,-1.8686558527
O,0,0.8324167465,-1.2167311313,1.8150624026
O,0,2.5814756338,1.0426865684,0.6406987568
C,0,0.5084843586,1.6105299417,-0.3807215725
C,0,0.3159207941,2.6897355871,0.5270381339
C,0,-0.5461248836,1.3601705213,-1.3041871356
C,0,-0.8425850093,3.4458026479,0.5143911013
H,0,1.0989844016,2.9048388067,1.2444224745
C,0,-1.6974663001,2.1251619784,-1.305436839
H,0,-0.4710822081,0.5404941181,-2.008474815
C,0,-1.8667437158,3.1761731784,-0.3978652223
H,0,-0.9565981468,4.2574362311,1.2266667774
H,0,-2.4841357249,1.8960078435,-2.0175280201

H,0,-2.7754437722,3.7672173469,-0.4004596558
Li,0,4.275113567,1.9055819114,0.6131365984
Li,0,2.1478165713,0.2499074463,2.354227642

B.6.1.1.62. 2 gauche

./PVKhomo-cisPD-4
E(UwB97XD) = -846.013675918

Zero-point correction= 0.291711 (Hartree/Particle)
Thermal correction to Energy= 0.308199
Thermal correction to Enthalpy= 0.309144
Thermal correction to Gibbs Free Energy= 0.245972
Sum of electronic and ZPE= -845.721965
Sum of electronic and thermal Energies= -845.705477
Sum of electronic and thermal Enthalpies= -845.704532
Sum of electronic and thermal Free Energies= -845.767704

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 193.398 65.513 132.956

C,0,-0.6309359378,1.9568103386,0.2807810218
C,0,-1.6282453159,3.0047470502,-0.268724561
H,0,-1.8566488191,2.7892697727,-1.3137249187
C,0,-2.7204320717,2.4663050167,0.6789683765
H,0,-1.3407270236,4.053177573,-0.1639214571
C,0,-1.8869020432,1.1898621124,0.8945335772
H,0,-2.7993036398,3.0464339879,1.6006078784
H,0,-3.71490999,2.3201446909,0.256479441
H,0,-1.7392782205,0.8902796161,1.9352178748
C,0,-2.3450369626,-0.0202241897,0.1221859941
C,0,0.2653791134,1.2486248532,-0.7029982296
H,0,-0.075422135,2.3818442071,1.1165356764
C,0,1.6189359054,0.9189167389,-0.3646688672
C,0,2.2395891702,1.192945069,0.8936546255
C,0,2.4287252431,0.2290391277,-1.3205994287
C,0,3.7305370316,-0.1400511859,-1.042187211
C,0,4.3165184807,0.1437810755,0.1989365769
C,0,3.5423197534,0.8147291333,1.1573929507
H,0,1.6864902915,1.697713453,1.6780871402
H,0,1.9873650623,-0.0025354912,-2.2829024782
H,0,4.307716491,-0.662680723,-1.8005195235
H,0,5.3383273617,-0.1480801385,0.4137346967
H,0,3.9705300682,1.0401046659,2.1301821619
O,0,-0.2523483294,0.9075658209,-1.8204850291
O,0,-3.3669717054,-0.0133699196,-0.5455813352
C,0,-1.5259443369,-1.2704203536,0.2339903703
C,0,-1.915939757,-2.399256228,-0.492356475
C,0,-0.3780546757,-1.3378856209,1.0266638568
C,0,-1.1729011611,-3.5685273234,-0.4344991842
H,0,-2.8062149743,-2.341270295,-1.1076498339
C,0,0.3699547762,-2.5091400115,1.0833926961
H,0,-0.0485514377,-0.4798990467,1.597628139
C,0,-0.0236759495,-3.6237039222,0.3529403309
H,0,-1.4831598013,-4.4371769518,-1.0043976735
H,0,1.2642476533,-2.5459036402,1.695354252
H,0,0.5608978857,-4.5361692616,0.3959585688

B.6.1.1.63. 8‡-Li gauche

./PVKhomo-cisTS1-10Li
uwb97xd/6-311+g(d,p)
E(UwB97XD) = -853.493995742

Zero-point correction= 0.290867 (Hartree/Particle)
Thermal correction to Energy= 0.309054
Thermal correction to Enthalpy= 0.309998
Thermal correction to Gibbs Free Energy= 0.243421
Sum of electronic and ZPE= -853.203129
Sum of electronic and thermal Energies= -853.184942
Sum of electronic and thermal Enthalpies= -853.183998
Sum of electronic and thermal Free Energies= -853.250574

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 193.934 71.367 140.122

C,0,-5.4031937181,1.1380786544,-1.6164651908
C,0,-4.1992509036,0.8528434341,-0.982780255
C,0,-4.0987563957,-0.2272239974,-0.1025214152
C,0,-5.2268067059,-1.0184816178,0.1265553104
C,0,-6.4342248455,-0.7249253747,-0.4929531125
C,0,-6.5248770644,0.3532823775,-1.3697605895
C,0,-2.78867044,-0.6143741018,0.5097138237
O,0,-2.5851239443,-1.8403767625,0.7195933277
C,0,-1.8340053569,0.389616765,0.8057334343
C,0,-0.4930634976,0.0744348381,1.0518595807
C,0,0.522186996,-0.1284712121,-0.6816475094
C,0,-0.3293790794,-0.25036135,-1.7938454118
C,0,-0.9621394252,-1.4601219559,-2.1245549845
O,0,-0.6938600909,-2.5673289994,-1.5691907059
C,0,-2.0853081224,-1.4258509451,-3.1181425651
C,0,-3.1622863089,-2.2955999214,-2.9322473449
C,0,-2.126374947,-0.5240114825,-4.1847419142
C,0,-4.2655668801,-2.2503567613,-3.7745502486
C,0,-3.2232877749,-0.4874401167,-5.0379542115
C,0,-4.3000684731,-1.3445571223,-4.830867716
H,0,-5.4622314807,1.9679675822,-2.3118022038
H,0,-3.3232558303,1.4512675446,-1.2061751586
H,0,-5.1439751362,-1.869678724,0.7925220302
H,0,-7.305277263,-1.3411088975,-0.298984988
H,0,-7.4641934579,0.5759169598,-1.8636265406
H,0,-2.1142140739,1.4253726654,0.6513427299
H,0,-0.6987744938,0.6563382419,-2.2589627056
H,0,0.1411845738,0.8479037082,1.4721634003
H,0,-0.2856605108,-0.9253319026,1.4197979241
H,0,1.0896437749,0.7920883416,-0.5938046915
H,0,1.0567513687,-1.019169181,-0.3660042305
H,0,-3.135336583,-2.9885508114,-2.0993468056
H,0,-1.293095833,0.1480808977,-4.3581728971
H,0,-5.1033148104,-2.9175432795,-3.6034387099
H,0,-3.237805256,0.2124914003,-5.8661928986
H,0,-5.1601284415,-1.3077878792,-5.4902811185
Li,0,-1.270120569,-3.1410320147,0.1573365616

B.6.1.1.64. 8‡ gauche

./PVKhomo-cisTS1-2
E(UwB97XD) = -845.980173920

Zero-point correction= 0.285858 (Hartree/Particle)
Thermal correction to Energy= 0.303800
Thermal correction to Enthalpy= 0.304744
Thermal correction to Gibbs Free Energy= 0.234925
Sum of electronic and ZPE= -845.694316
Sum of electronic and thermal Energies= -845.676374
Sum of electronic and thermal Enthalpies= -845.675430
Sum of electronic and thermal Free Energies= -845.745249

E CV S

KCal/Mol Cal/Mol-K Cal/Mol-K
Total 190.637 68.398 146.947

C,0,-4.8377209433,1.4014033629,0.3198051916
C,0,-3.6999536673,0.7154473692,0.727495996
C,0,-3.2329878187,-0.3971481589,0.0135325372
C,0,-3.9600058895,-0.8049304974,-1.1124617429
C,0,-5.093912527,-0.1166318201,-1.5249131814
C,0,-5.5391643632,0.9929957573,-0.8117592877
H,0,-5.1828881938,2.2559165225,0.8920375018
H,0,-3.185624276,1.0440812955,1.6232052694
H,0,-3.6132801429,-1.6734658302,-1.6602117066
H,0,-5.6330538949,-0.4466641446,-2.4067380993
H,0,-6.4247244491,1.5315537998,-1.1306249601
C,0,-2.0137972697,-1.1813130981,0.4032937318
O,0,-1.8747671568,-2.34441135,-0.0666788772
C,0,-1.0430279379,-0.5722966253,1.2517908989
C,0,2.8273769663,-1.4543309721,-0.16573457
C,0,0.1286606259,-1.201530597,1.6126517428
H,0,-1.1832530169,0.4641309012,1.540444804
C,0,1.6115459533,-0.8631200862,-0.3467853317
H,0,2.9660396322,-2.4905363479,-0.4530028771
H,0,0.8350593913,-0.723082312,2.2803275382
H,0,0.2585917873,-2.260218141,1.4275960087
H,0,0.818461157,-1.361665493,-0.8885139965
H,0,1.4847444098,0.1928212228,-0.1462285877
C,0,3.9158831933,-0.7704237989,0.4922291748
O,0,3.8020783814,0.3626620717,0.9848445926
C,0,5.2385756986,-1.4776174973,0.6068875951
C,0,6.0968740203,-1.1311132137,1.6542890067
C,0,5.6557173962,-2.4462929227,-0.3106689779
C,0,7.3330115604,-1.7479388814,1.7930417689
H,0,5.7772306847,-0.3745043558,2.3614856216
C,0,6.8998444119,-3.0535838274,-0.1817323679
H,0,5.0190993085,-2.7151196842,-1.1458437472
C,0,7.7397616307,-2.7107258032,0.872938476
H,0,7.98290229,-1.4775893659,2.6179963649
H,0,7.2157670972,-3.7932475766,-0.9089677794
H,0,8.7080358706,-3.1877388219,0.9757703796

B.6.1.1.65. 8‡-2Li

./PVKhomo-cisTS1gauche-1Li2
uwb97xd/6-311+g(d,p)
E(UwB97XD) = -860.989187644

Zero-point correction= 0.293175 (Hartree/Particle)
Thermal correction to Energy= 0.312807
Thermal correction to Enthalpy= 0.313751
Thermal correction to Gibbs Free Energy= 0.243596
Sum of electronic and ZPE= -860.696013
Sum of electronic and thermal Energies= -860.676381
Sum of electronic and thermal Enthalpies= -860.675437
Sum of electronic and thermal Free Energies= -860.745592

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 196.289 76.349 147.654

C,0,0.4025650745,0.0760370304,-1.499160039
C,0,1.5413257864,0.7726891595,-1.9439148281
H,0,2.3372717015,0.203093456,-2.4124473981
C,0,2.7138351074,1.4526118348,-0.3502097466
H,0,1.3942237776,1.7664508768,-2.3509747466
C,0,2.0326974619,1.201750099,0.8346662239
H,0,2.7967147413,2.4799816371,-0.6860871539

H,0,3.5577834152,0.820128609,-0.6024483578
H,0,1.3522432754,1.9515034847,1.2203356961
C,0,2.0213033639,-0.0929521997,1.4315578801
C,0,0.3991135292,-1.279121408,-1.1824376568
H,0,-0.4659199577,0.6552359137,-1.2075717347
C,0,-0.8004786612,-1.849438358,-0.4974384804
C,0,-2.1026339351,-1.430812647,-0.7848263986
C,0,-0.6056352955,-2.7969349406,0.5106113806
C,0,-1.681866084,-3.3033506056,1.2269854364
C,0,-2.9747626287,-2.8809851114,0.9338837454
C,0,-3.1817461651,-1.9470805969,-0.0773270521
H,0,-2.2757386976,-0.706889146,-1.5735206221
H,0,0.4049938185,-3.103102003,0.7556461743
H,0,-1.5105858917,-4.0190596933,2.0232530663
H,0,-3.8171135919,-3.2752575085,1.4912416172
H,0,-4.1875595813,-1.6201436701,-0.316776542
O,0,1.3949578071,-2.0691434816,-1.3853479616
O,0,2.810114352,-1.0030820371,1.0778505667
C,0,1.0271706829,-0.4079961402,2.50248667
C,0,1.3097970166,-1.4306719255,3.411486407
C,0,-0.2171418776,0.2245956516,2.562249575
C,0,0.3786149156,-1.8002076474,4.3718798076
H,0,2.2676503621,-1.9340725569,3.3521076288
C,0,-1.1553553003,-0.1546041688,3.5144198828
H,0,-0.4747052943,0.9901997111,1.8397100353
C,0,-0.8588746611,-1.1641723486,4.4238103993
H,0,0.6136953741,-2.5893607572,5.0774321158
H,0,-2.1238412306,0.3319734829,3.5387235979
H,0,-1.5916789768,-1.4595536808,5.1664023166
Li,0,3.1738643658,-1.8831278066,-0.6062112237
Li,0,1.2941799017,-3.9619735077,-1.8144822809

B.6.1.1.66. 11‡-Li gauche

./PVKhomo-cisTS2-10Li
uwb97xd/6-311+g(d,p)
E(UwB97XD) = -853.513314358

Zero-point correction= 0.292790 (Hartree/Particle)
Thermal correction to Energy= 0.310509
Thermal correction to Enthalpy= 0.311453
Thermal correction to Gibbs Free Energy= 0.245103
Sum of electronic and ZPE= -853.220524
Sum of electronic and thermal Energies= -853.202805
Sum of electronic and thermal Enthalpies= -853.201861
Sum of electronic and thermal Free Energies= -853.268212

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	194.847	69.485	139.646

C,0,-1.3347657196,1.8145350128,-0.2857971675
C,0,-2.8350617028,1.9167906365,-0.0490768235
H,0,-3.0538470032,1.8229460841,1.0152196527
C,0,-3.2414968031,0.6495240444,-0.8115037868
H,0,-3.2720616383,2.8520254704,-0.4098903978
C,0,-1.886035142,-0.0395377716,-0.7421986496
H,0,-3.5033749796,0.8691737268,-1.8488014848
H,0,-4.0510792759,0.0751646463,-0.3574013092
H,0,-1.3686529216,-0.2477263379,-1.6717682583
C,0,-1.5853665199,-0.878614729,0.3644260122
C,0,-0.3786605494,1.8641181151,0.7643436671
H,0,-1.0106662615,2.1587665942,-1.2618758033
C,0,1.0654368588,2.0861498073,0.4601767482
C,0,1.5282030167,2.609826888,-0.7542088654
C,0,2.0119528862,1.736209898,1.4314066143

C,0,3.3711701237,1.8822639141,1.1924583312
C,0,3.8179647276,2.3888011649,-0.0249724107
C,0,2.8886604928,2.7556832198,-0.9943189851
H,0,0.8300615357,2.9168164698,-1.5237032949
H,0,1.6597056785,1.3297732488,2.37150274
H,0,4.0862783155,1.5944638491,1.9555902665
H,0,4.8794224094,2.5018055997,-0.2152685334
H,0,3.2244712361,3.1622435553,-1.9420102952
O,0,-0.6969370055,1.566593145,1.9567435036
O,0,-2.3681745432,-0.9819973385,1.3611665093
C,0,-0.2573188526,-1.551299556,0.4227172713
C,0,-0.0325961732,-2.5349207179,1.3938750542
C,0,0.8029170344,-1.1929313579,-0.4196361737
C,0,1.2061042167,-3.1492922678,1.5123074333
H,0,-0.8468214148,-2.8069855161,2.0552445247
C,0,2.0452979417,-1.8021697965,-0.2958107007
H,0,0.6753602493,-0.4093967915,-1.1562723517
C,0,2.2528170127,-2.7830707705,0.668652263
H,0,1.3595925748,-3.9134155263,2.2666364341
H,0,2.8576188216,-1.4998604512,-0.9476508164
H,0,3.2234545885,-3.2566537213,0.7656950809
Li,0,-1.8638082148,0.2791935595,2.7849980016

B.6.1.1.67. 11‡ gauche

./PVKhomo-cisTS2-2
E(UwB97XD) = -846.000541968

Zero-point correction= 0.290584 (Hartree/Particle)
Thermal correction to Energy= 0.306996
Thermal correction to Enthalpy= 0.307941
Thermal correction to Gibbs Free Energy= 0.244361
Sum of electronic and ZPE= -845.709958
Sum of electronic and thermal Energies= -845.693546
Sum of electronic and thermal Enthalpies= -845.692601
Sum of electronic and thermal Free Energies= -845.756181

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	192.643	64.612	133.814

C,0,2.3782825646,-2.7318141703,-2.3230173861
C,0,1.708168142,-1.5276847193,-2.4937702704
C,0,1.5640575237,-0.6256984016,-1.4326624626
C,0,2.1061459225,-0.9746441953,-0.1896517382
C,0,2.7690187323,-2.1836971392,-0.0142332539
C,0,2.9099380948,-3.067581089,-1.0794503784
H,0,2.4844467218,-3.4144055491,-3.1595827046
H,0,1.2826826596,-1.2660792264,-3.4557887952
H,0,1.9842105154,-0.3161998869,0.6605332445
H,0,3.1662241957,-2.4399748639,0.9623346299
H,0,3.4255322273,-4.011801939,-0.9417919999
C,0,0.8039764985,0.6478796918,-1.6502654013
O,0,0.0780289203,0.7556786613,-2.6723110114
C,0,0.8926572804,1.6597033471,-0.6462535844
C,0,-0.5019164142,1.4668334657,0.7787101383
C,0,0.1334230092,2.9658821867,-0.8316491977
H,0,1.8098224777,1.6815054117,-0.0674335669
C,0,-1.136912777,2.5473474816,-0.079640783
H,0,0.0981726927,1.8497885548,1.5974448745
H,0,0.6498719075,3.7845713736,-0.3232470083
H,0,-0.0174578824,3.2432518463,-1.8771441398
H,0,-1.6429423707,3.3357512507,0.4880019835
H,0,-1.8581221668,2.0913971283,-0.7594439427
C,0,-1.0775962655,0.1754618056,0.9566845916
O,0,-1.9795212145,-0.2726026343,0.1967385061

C,0,-0.4924966728,-0.7479764477,1.9877386731
C,0,-0.8223185514,-2.1077166265,1.921311419
C,0,0.3860130952,-0.3395831647,3.0016241311
C,0,-0.2813820692,-3.0264139121,2.8108767848
H,0,-1.5008417445,-2.4315325189,1.1416124013
C,0,0.9273691082,-1.2566847648,3.8937859262
H,0,0.6606630676,0.7034133185,3.104900287
C,0,0.6023774512,-2.6076086828,3.8013755997
H,0,-0.5447626483,-4.0757930755,2.7282525578
H,0,1.6073361092,-0.9146503068,4.6667938707
H,0,1.0297037399,-3.3233879697,4.4949089855

B.6.1.1.68. $11^{‡}$-2Li gauche

./PVKhomo-cisTS2-inout16Li2
uwb97xd/6-311+g(d,p)
E(UwB97XD) = -861.007692408

Zero-point correction= 0.295578 (Hartree/Particle)
Thermal correction to Energy= 0.314542
Thermal correction to Enthalpy= 0.315487
Thermal correction to Gibbs Free Energy= 0.247594
Sum of electronic and ZPE= -860.712114
Sum of electronic and thermal Energies= -860.693150
Sum of electronic and thermal Enthalpies= -860.692206
Sum of electronic and thermal Free Energies= -860.760099

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	197.378	74.210	142.892

C,0,0.4875675857,-0.2563427525,-1.4484422798
C,0,1.7852002864,0.3107463821,-2.0045747654
H,0,2.5055564376,-0.4915779592,-2.1658895451
C,0,2.1643911433,1.1689745058,-0.7894708668
H,0,1.6544284164,0.8507563417,-2.946065985
C,0,1.2870204779,0.4530049064,0.2259396852
H,0,1.839971558,2.2046158849,-0.9067009675
H,0,3.2256859976,1.1596948272,-0.5353833709
H,0,0.4910835603,1.0124392318,0.7026482949
C,0,1.7955005941,-0.6753508509,0.9288093
C,0,0.1884928772,-1.6391770629,-1.4532254781
H,0,-0.3587102422,0.4199271732,-1.4913712784
C,0,-1.1710177391,-2.1208443577,-1.1151201075
C,0,-2.3149817772,-1.3134064395,-1.2096985886
C,0,-1.328913321,-3.4325994732,-0.6449110779
C,0,-2.5738823273,-3.9116632612,-0.2619601809
C,0,-3.6964224493,-3.0934215139,-0.3452531328
C,0,-3.5591582618,-1.7934559781,-0.826305436
H,0,-2.243504623,-0.3018398293,-1.5912492859
H,0,-0.4534063795,-4.0646196039,-0.5534101086
H,0,-2.6676682213,-4.9248182246,0.1135960248
H,0,-4.6691466729,-3.4642318037,-0.0425250792
H,0,-4.4285720366,-1.1502986335,-0.9071315186
O,0,1.1308437688,-2.5192915126,-1.5779614042
O,0,2.9205213595,-1.174325603,0.6547795901
C,0,0.9201940247,-1.3774357336,1.914806393
C,0,1.4790817651,-2.3695306775,2.7269387016
C,0,-0.4528438532,-1.1269944464,2.0095857405
C,0,0.6901527737,-3.086888124,3.6154106231
H,0,2.5409716888,-2.5703453464,2.6483608497
C,0,-1.2443558708,-1.8501440903,2.8923143151
H,0,-0.9221791073,-0.3905954936,1.369542165
C,0,-0.6763961496,-2.8313206435,3.6982518381
H,0,1.1389601971,-3.8492671429,4.2424561295
H,0,-2.3096385297,-1.6546367078,2.9409880634

H,0,-1.2954187021,-3.3967195188,4.3858915978
Li,0,2.8377732362,-2.657800442,-0.6366391797
Li,0,1.0588105158,-3.9245630266,-2.9243546748

B.6.1.1.69. 9‡ gauche

./PVKhomo-cisTSr-7
E(UwB97XD) = -845.994456938

Zero-point correction= 0.289292 (Hartree/Particle)
Thermal correction to Energy= 0.306262
Thermal correction to Enthalpy= 0.307206
Thermal correction to Gibbs Free Energy= 0.240310
Sum of electronic and ZPE= -845.705164
Sum of electronic and thermal Energies= -845.688195
Sum of electronic and thermal Enthalpies= -845.687251
Sum of electronic and thermal Free Energies= -845.754147

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 192.182 65.594 140.795

C,0,-1.8088162528,1.4367456975,-0.8635366534
C,0,-0.4868965125,1.9890744793,-1.2829791938
H,0,0.0420359182,1.2519421269,-1.894380014
C,0,0.453660792,2.4087442574,-0.0682627104
H,0,-0.6084485467,2.8795528526,-1.9085872146
C,0,1.7634741827,1.7505104018,-0.1711514852
H,0,-0.0400771292,2.1336283643,0.8628587289
H,0,0.576440319,3.4948272488,-0.0893559746
H,0,2.4556043382,2.0955554737,-0.9327697961
C,0,2.095043234,0.5721089722,0.5736086711
C,0,-2.7888107392,2.2305827833,-0.3136363916
H,0,-1.9560425173,0.364179971,-0.9267747978
C,0,-4.0827633668,1.5654049987,0.1102755247
C,0,-4.620413294,0.4577795143,-0.5542784735
C,0,-4.7891596135,2.0787678415,1.2020099071
C,0,-5.9728184293,1.4909990142,1.6358588945
C,0,-6.4884706532,0.3813672313,0.9720807313
C,0,-5.8077329678,-0.129179597,-0.1295284729
H,0,-4.1109481781,0.0587981592,-1.4247132883
H,0,-4.3903907804,2.9494506597,1.7105468405
H,0,-6.4952492442,1.9005158909,2.4944327522
H,0,-7.4137406792,-0.0764450921,1.3048353487
H,0,-6.2078925151,-0.9834753136,-0.6656822189
O,0,-2.690718946,3.4932045361,-0.1037517583
O,0,1.2865564674,0.0528006406,1.3593775021
C,0,3.4366735191,-0.0701552007,0.3631532504
C,0,4.5614095146,0.6593410248,-0.028342866
C,0,3.5635524316,-1.442710909,0.589592979
C,0,5.7888631287,0.0268744955,-0.191879849
H,0,4.4933446191,1.7299082572,-0.1859119035
C,0,4.7857146856,-2.0771762956,0.41236042
H,0,2.6914605761,-2.0061133442,0.9003669892
C,0,5.9022481009,-1.3428737959,0.0220424568
H,0,6.6578471101,0.6053604302,-0.4839405982
H,0,4.8680486068,-3.1454193211,0.5785405868
H,0,6.8587128211,-1.8355664534,-0.1119879231

B.6.1.1.70. 4-Li

./PVKhomo-transIM1-4Li
uwb97xd/6-311+g(d,p)
E(UwB97XD) = -853.514893542

Zero-point correction= 0.292613 (Hartree/Particle)
Thermal correction to Energy= 0.311328
Thermal correction to Enthalpy= 0.312272
Thermal correction to Gibbs Free Energy= 0.242494
Sum of electronic and ZPE= -853.222280
Sum of electronic and thermal Energies= -853.203565
Sum of electronic and thermal Enthalpies= -853.202621
Sum of electronic and thermal Free Energies= -853.272399

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	195.361	71.935	146.860

C,0,-6.1718173,-0.5972008,0.3864187687
C,0,-4.8031527502,-0.6889363548,0.6084777557
C,0,-3.9196583058,0.1423961888,-0.0851296747
C,0,-4.4295479021,1.0664394077,-1.0015067746
C,0,-5.795203589,1.148003555,-1.2318572032
C,0,-6.6693318713,0.3163198994,-0.5368582086
H,0,-6.8500425148,-1.2385826424,0.9369581504
H,0,-4.4344899035,-1.396724382,1.3416049694
H,0,-3.7421339704,1.712945876,-1.5337201907
H,0,-6.1798940851,1.8601365594,-1.9527972166
H,0,-7.7369325685,0.3820325884,-0.7133507487
C,0,-2.4434662713,0.0937245158,0.130084893
O,0,-1.7514432038,1.082254846,-0.1800249821
C,0,-1.8257257784,-1.0866217355,0.6546153907
C,0,1.8751660474,-1.2973965277,-0.3156678183
C,0,-0.3701602276,-1.1474904084,0.866828142
H,0,-2.4249782414,-1.9782234036,0.7974468089
C,0,0.3974230644,-1.4377972155,-0.4755973386
H,0,2.4746195178,-2.1922547071,-0.1994563419
H,0,0.0012508437,-0.1908897321,1.2433959462
H,0,-0.1171422246,-1.9295401543,1.5848993813
H,0,0.1261918633,-2.4395113861,-0.8191707765
H,0,0.0281899652,-0.7255116275,-1.2219852045
C,0,2.458412368,-0.0633135757,-0.2852388251
O,0,1.8066113021,1.0501663273,-0.4293032844
C,0,3.9501102029,0.0549640214,-0.1159482028
C,0,4.6123576562,1.1610920163,-0.6556593768
C,0,4.709908078,-0.8927674657,0.5784390251
C,0,5.9903971146,1.3032654035,-0.5338686892
H,0,4.0271981454,1.9107071824,-1.1755670244
C,0,6.0869936346,-0.7508794175,0.7078227067
H,0,4.2188847294,-1.7427325433,1.039185768
C,0,6.7357313689,0.3461918612,0.148011935
H,0,6.4840469156,2.1654081915,-0.9699763422
H,0,6.6543423844,-1.4949278855,1.2568782003
H,0,7.8095818627,0.4577449809,0.2502646414
Li,0,0.1064276431,1.7466995436,-0.4717082588

B.6.1.1.71. 4-2Li

./PVKhomo-transIM1-4Li2
uwb97xd/6-311+g(d,p)
E(UwB97XD) = -861.013319641

Zero-point correction= 0.295444 (Hartree/Particle)
Thermal correction to Energy= 0.315263
Thermal correction to Enthalpy= 0.316207
Thermal correction to Gibbs Free Energy= 0.245611
Sum of electronic and ZPE= -860.717876
Sum of electronic and thermal Energies= -860.698057
Sum of electronic and thermal Enthalpies= -860.697112
Sum of electronic and thermal Free Energies= -860.767709

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 197.831 76.618 148.582

C,0,-6.1771995222,-0.5984712777,0.459253328
C,0,-4.8030510438,-0.6819068801,0.6473016044
C,0,-3.9401188908,0.1195599393,-0.1047723426
C,0,-4.4739126236,1.0039778757,-1.0461041416
C,0,-5.845240566,1.07413065,-1.2440910244
C,0,-6.6994783454,0.2738834442,-0.4898006121
H,0,-6.8400682207,-1.2141928542,1.0558003898
H,0,-4.4127795372,-1.3570337581,1.400056499
H,0,-3.8019660747,1.6266047055,-1.6246754272
H,0,-6.2501134577,1.7527923861,-1.985875437
H,0,-7.7713956031,0.3318293222,-0.6408081776
C,0,-2.4609188064,0.0788419137,0.078780206
O,0,-1.7782963103,1.0708328655,-0.2384421738
C,0,-1.8293090326,-1.1055596113,0.5815960558
C,0,1.8719758609,-1.2109135165,-0.4246746443
C,0,-0.3675089095,-1.1629334741,0.7718423624
H,0,-2.4269677864,-1.9961447142,0.7363821729
C,0,0.390349871,-1.3484170777,-0.5854402119
H,0,2.4875454183,-2.1006222417,-0.4846148131
H,0,-0.0082677487,-0.2304195129,1.216238027
H,0,-0.1010236803,-1.9874959061,1.4352319981
H,0,0.1352671544,-2.3280231003,-0.9970049885
H,0,0.008708472,-0.6027601498,-1.2925870616
C,0,2.4604355322,-0.0113873315,-0.1983762714
O,0,1.8076910243,1.1291350169,-0.1232653691
C,0,3.9503542562,0.0748971225,-0.0528875489
C,0,4.6391537979,1.145074973,-0.6316462513
C,0,4.6836084865,-0.883842916,0.652114706
C,0,6.0219824091,1.2444309964,-0.5280098953
H,0,4.0808789809,1.8967909432,-1.1799745907
C,0,6.0663401148,-0.7838086424,0.7616618936
H,0,4.1641387203,-1.7068383784,1.130700979
C,0,6.7419020937,0.2789945754,0.169620824
H,0,6.5394436818,2.0750129957,-0.9958120217
H,0,6.6170248925,-1.533574256,1.3193601534
H,0,7.8199401654,0.3570049889,0.2555736384
Li,0,0.0646039771,1.7915851423,-0.492357821
Li,0,2.3911482501,2.5784837424,0.9905639873

B.6.1.1.72. 4

./PVKhomo-transIM1-5
E(UwB97XD) = -845.999041297

Zero-point correction= 0.289834 (Hartree/Particle)
Thermal correction to Energy= 0.307452
Thermal correction to Enthalpy= 0.308397
Thermal correction to Gibbs Free Energy= 0.239527
Sum of electronic and ZPE= -845.709207
Sum of electronic and thermal Energies= -845.691589
Sum of electronic and thermal Enthalpies= -845.690645
Sum of electronic and thermal Free Energies= -845.759515

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 192.929 67.317 144.949

C,0,-5.9433864336,-0.7978851992,-1.1234581896
C,0,-4.594533282,-0.7526706114,-0.7901149712
C,0,-4.140138801,0.1208470527,0.2004656701
C,0,-5.0591223901,0.9496378162,0.8483083035
C,0,-6.4083119519,0.8930495603,0.5268004138

C,0,-6.8535356467,0.0193581411,-0.4618543077
H,0,-6.2830006732,-1.4698623386,-1.9034155561
H,0,-3.8957556975,-1.3856381727,-1.3252582687
H,0,-4.703361429,1.633354089,1.6105045447
H,0,-7.1151375134,1.5312503203,1.0449972072
H,0,-7.9064676225,-0.0223442151,-0.7168026744
C,0,-2.6892168646,0.2234598391,0.5731805554
O,0,-2.2446168313,1.294481448,1.0116931667
C,0,-1.8558870098,-0.9377115813,0.4447347481
C,0,1.8864426865,-0.9476082386,-0.433489204
C,0,-0.4034471206,-0.9222796228,0.6952384806
H,0,-2.3059032911,-1.8641253981,0.1023758392
C,0,0.4065069438,-0.9529699122,-0.6469571846
H,0,2.3681930573,-1.8958238192,-0.2170094214
H,0,-0.1174052639,-0.0297827699,1.253327648
H,0,-0.1172986479,-1.8074934842,1.2731743628
H,0,0.0906636609,-1.8396913326,-1.2092491453
H,0,0.1135089052,-0.0745888807,-1.2297630206
C,0,2.6204743363,0.2143948253,-0.4040495912
O,0,2.1555921548,1.4034657554,-0.5540572825
C,0,4.1111530218,0.1023698204,-0.144867519
C,0,4.7628252303,1.1512740585,0.5102864289
C,0,4.8801727727,-0.9963133274,-0.5445480353
C,0,6.1254148797,1.0965887708,0.7839501388
H,0,4.1786634987,2.0168153493,0.801807372
C,0,6.2450120856,-1.0530307607,-0.2804533788
H,0,4.4088020235,-1.8100996548,-1.0846860971
C,0,6.8747481854,-0.0086115107,0.3904224663
H,0,6.6053370127,1.919105447,1.3043792765
H,0,6.8199199177,-1.9129775136,-0.6084464844
H,0,7.9389960973,-0.0507239498,0.5955737094

B.6.1.1.73. 10

./PVKhomo-transIM2-7
E(UwB97XD) = -846.003767910

Zero-point correction= 0.290170 (Hartree/Particle)
Thermal correction to Energy= 0.307394
Thermal correction to Enthalpy= 0.308338
Thermal correction to Gibbs Free Energy= 0.242107
Sum of electronic and ZPE= -845.713598
Sum of electronic and thermal Energies= -845.696374
Sum of electronic and thermal Enthalpies= -845.695430
Sum of electronic and thermal Free Energies= -845.761661

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	192.893	66.985	139.395

C,0,4.7216064131,0.9305496111,0.8895507267
C,0,3.649917541,0.0526444202,0.7617607397
C,0,2.8166163048,0.0912829652,-0.3613021547
C,0,3.0811521024,1.0529740572,-1.3406241145
C,0,4.154203965,1.9289089052,-1.2202879427
C,0,4.9824869967,1.8708567126,-0.1032558656
C,0,1.6394910509,-0.8368067466,-0.5494788852
O,0,0.653726741,-0.3899047657,-1.2449351922
C,0,1.6653615496,-2.0928204515,0.0033490712
C,0,0.4753095471,-2.9799737701,-0.1193773974
C,0,-0.7196844899,-2.5814852519,0.8228401302
C,0,-1.2540020148,-1.2337385317,0.5544305437
C,0,-1.03315534,-0.1340092864,1.4283937615
O,0,-0.4096456636,-0.2447822076,2.503671591
C,0,-1.6137976661,1.2025139175,1.0600307261
C,0,-2.1197340437,2.0236131906,2.0697899121

C,0,-1.6404266513,1.6503336703,-0.2623866577
C,0,-2.6649095179,3.2642945925,1.7629613596
C,0,-2.1713966191,2.8997349064,-0.5662512354
C,0,-2.6906360326,3.7056377854,0.4425950591
H,0,5.3503936557,0.8867197642,1.7727605021
H,0,3.4474812649,-0.6579619225,1.5557939688
H,0,2.4256006966,1.1028333317,-2.2026001873
H,0,4.343942047,2.6597435343,-1.9997321496
H,0,5.8170949436,2.5562102743,-0.0025333372
H,0,2.5097181475,-2.4211312255,0.5991467809
H,0,-1.8564554699,-1.0774043203,-0.331503284
H,0,0.0876419272,-2.9669966542,-1.1447584819
H,0,0.7329109948,-4.0159961241,0.1220421818
H,0,-1.5122279892,-3.3236441317,0.6650799841
H,0,-0.3832562363,-2.6490921585,1.8597038084
H,0,-2.0888293076,1.6764622925,3.0967384765
H,0,-1.1945928243,1.0301422638,-1.0324848599
H,0,-3.0685031974,3.8881529648,2.553005538
H,0,-2.172228391,3.2496758136,-1.5929090955
H,0,-3.1086234343,4.6771425745,0.2021499792

B.6.1.1.74. 10-Li

./PVKhomo-transIM2-7Li
uwb97xd/6-311+g(d,p)
E(UwB97XD) = -853.510984680

Zero-point correction= 0.292053 (Hartree/Particle)
Thermal correction to Energy= 0.311061
Thermal correction to Enthalpy= 0.312005
Thermal correction to Gibbs Free Energy= 0.240890
Sum of electronic and ZPE= -853.218932
Sum of electronic and thermal Energies= -853.199924
Sum of electronic and thermal Enthalpies= -853.198980
Sum of electronic and thermal Free Energies= -853.270095

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	195.193	72.123	149.673

C,0,3.7421654263,1.59739096,0.9709121994
C,0,2.8557432702,0.5486261657,0.7496723676
C,0,2.4763333466,0.1887470896,-0.5475643197
C,0,2.9926654531,0.9304262232,-1.6136488753
C,0,3.8839903424,1.9753960974,-1.3974789897
C,0,4.2645104829,2.3138295605,-0.1020209633
C,0,1.4966107605,-0.9199797391,-0.8274781184
O,0,0.7576011914,-0.7551992408,-1.8864525761
C,0,1.4376728357,-1.9918185496,0.0105386157
C,0,0.3960989467,-3.0652225074,-0.1157127241
C,0,-0.822213057,-2.8307576298,0.8274562789
C,0,-1.3295331864,-1.4503185592,0.65643557
C,0,-1.1463835251,-0.4260363068,1.6482134863
O,0,-0.8271210192,-0.7023450248,2.8128314963
C,0,-1.3552723729,1.0035941373,1.2506459473
C,0,-1.8231395544,1.9152127579,2.1992577987
C,0,-1.033094609,1.4499586135,-0.0331198349
C,0,-1.9903928315,3.2521171693,1.8641225703
C,0,-1.1834251192,2.7936315376,-0.3597848075
C,0,-1.6687760637,3.6938892075,0.5829586708
H,0,4.0151272916,1.8651545862,1.9861929492
H,0,2.4350718575,0.0186454436,1.5970852097
H,0,2.6784512384,0.676071785,-2.6193826631
H,0,4.2790657184,2.5311328784,-2.241560414
H,0,4.9524164125,3.1343390811,0.0704340307
H,0,2.1071691904,-2.0372452942,0.8629346099

H,0,-1.7689437299,-1.1737507756,-0.2963006261
H,0,0.0341548014,-3.1121395934,-1.1474242393
H,0,0.8072730098,-4.0519938909,0.1228558451
H,0,-1.6062627807,-3.5586798205,0.587256198
H,0,-0.5202502602,-2.9822856537,1.8661517089
H,0,-2.058214043,1.5653989815,3.1981407207
H,0,-0.6222062773,0.7593894372,-0.7650898729
H,0,-2.367397423,3.9517527433,2.6016058818
H,0,-0.9148739046,3.1387895995,-1.3520629832
H,0,-1.7913845876,4.7395027143,0.3231829314
Li,0,-0.6360372309,-1.1597701837,-2.9674330785

B.6.1.1.75. 10-2Li

./PVKhomo-transIM2-inout1Li2
uwb97xd/6-311+g(d,p)
E(UwB97XD) = -861.003271082

Zero-point correction= 0.294806 (Hartree/Particle)
Thermal correction to Energy= 0.315036
Thermal correction to Enthalpy= 0.315981
Thermal correction to Gibbs Free Energy= 0.244074
Sum of electronic and ZPE= -860.708465
Sum of electronic and thermal Energies= -860.688235
Sum of electronic and thermal Enthalpies= -860.687291
Sum of electronic and thermal Free Energies= -860.759197

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	197.688	76.940	151.340

C,0,3.4364251524,1.736372937,0.9421193502
C,0,2.6181521665,0.6377715588,0.7030326452
C,0,2.3828195496,0.1857054151,-0.599194352
C,0,2.9729865546,0.8836436428,-1.6558626093
C,0,3.7977600443,1.9781726888,-1.4210325229
C,0,4.0341112882,2.410013172,-0.1191180358
C,0,1.4695041378,-0.9744821834,-0.8965153917
O,0,0.8072221225,-0.8936209946,-2.0110688327
C,0,1.3836565803,-1.9988604052,0.0006625897
C,0,0.3838895156,-3.1167435702,-0.1202179245
C,0,-0.8303237443,-2.8607023102,0.8091984818
C,0,-1.2349257937,-1.4442547253,0.6270936446
C,0,-1.1330678222,-0.4492803796,1.6486350128
O,0,-0.9273141543,-0.7692745375,2.8352191118
C,0,-1.2689684368,0.9895732777,1.2748734639
C,0,-1.7370094593,1.9010223971,2.2242241989
C,0,-0.8854969495,1.4497884339,0.0119615284
C,0,-1.830381106,3.250923774,1.9160393026
C,0,-0.9629122774,2.8046132596,-0.2876537883
C,0,-1.4378197401,3.7055320459,0.659691462
H,0,3.5967548334,2.076312404,1.9598455371
H,0,2.1333527228,0.1415812914,1.536642422
H,0,2.7720301341,0.5575659168,-2.6699173007
H,0,4.2536682594,2.499360861,-2.2563075435
H,0,4.669193689,3.2693194963,0.0663094382
H,0,1.9948221198,-1.9687173312,0.8966297216
H,0,-1.5261316225,-1.1278189701,-0.3680630585
H,0,0.0331228653,-3.1806511232,-1.1543374437
H,0,0.8203569847,-4.088659349,0.1326013149
H,0,-1.6575617725,-3.5344626095,0.5552321141
H,0,-0.5583625136,-3.0360429332,1.8520643975
H,0,-2.0436499075,1.5427789056,3.1997326294
H,0,-0.4912596111,0.7619786813,-0.7291744467
H,0,-2.2078407277,3.9494848864,2.6539127064
H,0,-0.6459373486,3.1572995722,-1.2625065623

H,0,-1.5022227347,4.7611002416,0.4207667213
Li,0,-0.5593978807,-1.3980817981,-3.1181206727
Li,0,-0.4215581175,-0.1797076387,4.677060691

B.6.1.1.76. 2-Li

./PVKhomo-transPD-1Li
uwb97xd/6-311+g(d,p)
E(UwB97XD) = -853.522937119

Zero-point correction= 0.294208 (Hartree/Particle)
Thermal correction to Energy= 0.312211
Thermal correction to Enthalpy= 0.313156
Thermal correction to Gibbs Free Energy= 0.246145
Sum of electronic and ZPE= -853.228729
Sum of electronic and thermal Energies= -853.210726
Sum of electronic and thermal Enthalpies= -853.209781
Sum of electronic and thermal Free Energies= -853.276792

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	195.916	70.286	141.035

C,0,1.4512525843,2.5153743765,0.6186000915
C,0,1.191210303,1.1573830151,0.7640408342
C,0,2.2353243659,0.2311949861,0.7054708662
C,0,3.5411340519,0.6870753724,0.4992417558
C,0,3.7981360493,2.040335103,0.3418731206
C,0,2.7503960584,2.9576697606,0.4008794383
H,0,0.6345890268,3.2266169696,0.6641182336
H,0,0.1696864312,0.8319457054,0.9155755666
H,0,4.3464391786,-0.0365933266,0.4508928134
H,0,4.8118861683,2.3832303168,0.1689348579
H,0,2.949239829,4.0162724856,0.2756679838
C,0,2.0009035146,-1.2436467219,0.8203174611
O,0,2.932908907,-2.0053405281,1.0236797591
C,0,0.6092798638,-1.7446339666,0.582886688
C,0,0.0780735372,-1.5789293243,-0.8966944976
C,0,0.3516465555,-3.255820012,0.4764992184
H,0,-0.098527405,-1.2648787557,1.2646852025
C,0,-0.5740993875,-2.9761308049,-0.727889892
H,0,0.9238174454,-1.6583857351,-1.5804765814
H,0,1.2593325786,-3.7871103684,0.1840455092
H,0,-0.0837277192,-3.7468900139,1.3478990242
H,0,-0.5100347133,-3.6505293628,-1.5834843689
H,0,-1.6181215988,-2.8735056708,-0.4255912315
C,0,-0.7897981122,-0.3940129048,-1.1953420446
O,0,-1.8829794775,-0.2805577113,-0.5132357266
C,0,-0.3970972216,0.6211748447,-2.1232772136
C,0,-1.2572984219,1.7357900334,-2.3480023057
C,0,0.8409335294,0.6291312097,-2.8295904262
C,0,-0.9060045565,2.762393243,-3.2058536892
H,0,-2.2032590405,1.7655562969,-1.8204003551
C,0,1.1788744996,1.6634684625,-3.6818918343
H,0,1.554657503,-0.1744332455,-2.6915880822
C,0,0.3147766661,2.7463781734,-3.8882008287
H,0,-1.5903998283,3.5939043522,-3.3482918174
H,0,2.1358439724,1.6338823096,-4.1943820987
H,0,0.5883085254,3.5540726248,-4.5575574632
Li,0,-2.9059096622,-0.8721611886,0.9015560325

B.6.1.1.77. 2$^{-•}$

./PVKhomo-transPD-4
E(UwB97XD) = -846.017564245

Zero-point correction= 0.291405 (Hartree/Particle)
Thermal correction to Energy= 0.308126
Thermal correction to Enthalpy= 0.309070
Thermal correction to Gibbs Free Energy= 0.244284
Sum of electronic and ZPE= -845.726160
Sum of electronic and thermal Energies= -845.709439
Sum of electronic and thermal Enthalpies= -845.708494
Sum of electronic and thermal Free Energies= -845.773280

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 193.352 65.699 136.353

C,0,-1.0107766708,1.9663417362,1.6194643497
C,0,0.1081723617,1.2220970812,1.26152279
C,0,0.9955616201,1.7059356558,0.2966424538
C,0,0.7437267839,2.9465856254,-0.2990893263
C,0,-0.3740896709,3.6857523968,0.0554005614
C,0,-1.2558055501,3.1937456631,1.0168587187
H,0,-1.6963286866,1.5796025849,2.3647859367
H,0,0.2703294904,0.2609224145,1.7322789844
H,0,1.4355052175,3.3154366922,-1.0474467334
H,0,-0.563231203,4.6438232113,-0.4155117348
H,0,-2.1319366288,3.7696021359,1.294230995
C,0,2.2002825879,0.9292247751,-0.1394291308
O,0,3.0261582774,1.4379175098,-0.8835247264
C,0,2.3109680956,-0.4961106392,0.300886769
C,0,1.3201260038,-1.5114273531,-0.4045834806
C,0,3.4850389645,-1.3598767416,-0.1830570244
H,0,2.1697443321,-0.5906281984,1.3805120487
C,0,2.4918568186,-2.5249903548,-0.3852401477
H,0,1.1563324493,-1.176433471,-1.4297501565
H,0,3.8800227469,-0.985689505,-1.1296770675
H,0,4.3101122756,-1.5094716833,0.515538104
H,0,2.6143629299,-3.1516267098,-1.2709841754
H,0,2.4231060798,-3.1540063423,0.5040411087
C,0,0.0400755854,-1.8419190574,0.3161708457
O,0,0.1403806264,-2.399334852,1.4649927032
C,0,-1.2284700543,-1.4465919462,-0.2247377663
C,0,-2.4214260172,-1.7189894089,0.5141167389
C,0,-1.4058898681,-0.7433407859,-1.4555590411
C,0,-3.6657022408,-1.3212169561,0.0618075736
H,0,-2.3254260199,-2.243721151,1.4575456235
C,0,-2.6563007195,-0.3514462976,-1.8933678939
H,0,-0.5489549676,-0.4845584331,-2.0666058039
C,0,-3.811371762,-0.6306912204,-1.1479980933
H,0,-4.5448834064,-1.5470586957,0.6595467318
H,0,-2.7410774069,0.188363358,-2.8323569426
H,0,-4.7883623741,-0.3168310374,-1.4980837917

B.6.1.1.78. 2-2Li

./PVKhomo-transPD-outout1Li2
uwb97xd/6-311+g(d,p)
E(UwB97XD) = -861.013302648

Zero-point correction= 0.296026 (Hartree/Particle)
Thermal correction to Energy= 0.315617
Thermal correction to Enthalpy= 0.316561
Thermal correction to Gibbs Free Energy= 0.247080
Sum of electronic and ZPE= -860.717277
Sum of electronic and thermal Energies= -860.697686
Sum of electronic and thermal Enthalpies= -860.696741
Sum of electronic and thermal Free Energies= -860.766223

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 198.053 75.612 146.236

C,0,1.3592079378,2.5279408554,0.5814718459
C,0,1.1354452293,1.1671568706,0.7512830023
C,0,2.1926888652,0.2602099304,0.6334162191
C,0,3.4744130767,0.7404513882,0.3425240885
C,0,3.6934349694,2.0961236945,0.1606763853
C,0,2.6327228425,2.9928746109,0.2792627873
H,0,0.5331017816,3.2233137745,0.672275197
H,0,0.1322911186,0.8231679535,0.9682938576
H,0,4.2922416366,0.0388442739,0.2342602618
H,0,4.6863822519,2.4570584531,-0.0810928346
H,0,2.8019959815,4.0537887974,0.1330438109
C,0,1.9819543692,-1.2088168763,0.7511474489
O,0,2.9349125408,-1.9703452514,0.9003901419
C,0,0.601999783,-1.7336266547,0.5679743122
C,0,0.0379120046,-1.6086955896,-0.9126971961
C,0,0.3462388185,-3.2456853182,0.5014631789
H,0,-0.1066143088,-1.2373524867,1.2348365169
C,0,-0.6236480576,-2.9889054108,-0.6732148796
H,0,0.868261826,-1.7238904433,-1.60994289
H,0,1.2434035617,-3.7811806213,0.1851402557
H,0,-0.0560130423,-3.7179327119,1.3985799089
H,0,-0.6043222535,-3.689697953,-1.5094210382
H,0,-1.6496636636,-2.8552338025,-0.3265760308
C,0,-0.8117635905,-0.416581883,-1.2215021544
O,0,-1.9255675049,-0.3152210032,-0.5767919005
C,0,-0.360463857,0.620749154,-2.1023242021
C,0,-1.1804507029,1.7630796208,-2.3250350683
C,0,0.9047419545,0.6186625591,-2.7568477401
C,0,-0.7656837035,2.8114521685,-3.127004583
H,0,-2.1482493076,1.8072712926,-1.8410992795
C,0,1.3082624013,1.674184024,-3.5526323804
H,0,1.5907329049,-0.2084555225,-2.6192750014
C,0,0.4833102995,2.7876302556,-3.753698888
H,0,-1.4218269606,3.6656077969,-3.2670071638
H,0,2.2855643356,1.6364042808,-4.0243193086
H,0,0.8077362433,3.6123556735,-4.3779346151
Li,0,-3.5913750124,0.2993415428,-0.129254727
Li,0,4.7814212313,-2.5054874429,1.4087216623

B.6.1.1.79. 2-Li

./PVKhomo-transTS1-4Li
uwb97xd/6-311+g(d,p)
E(UwB97XD) = -853.492688677

Zero-point correction= 0.288839 (Hartree/Particle)
Thermal correction to Energy= 0.307862
Thermal correction to Enthalpy= 0.308806
Thermal correction to Gibbs Free Energy= 0.237686
Sum of electronic and ZPE= -853.203850
Sum of electronic and thermal Energies= -853.184827
Sum of electronic and thermal Enthalpies= -853.183882
Sum of electronic and thermal Free Energies= -853.255002

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 193.186 72.915 149.685

C,0,6.2154678571,0.716431761,0.0666439375
C,0,4.8913581871,0.9769770263,0.3949762534
C,0,3.9028790926,-0.0053656564,0.2347776137
C,0,4.2951797058,-1.2601054728,-0.2511796225

C,0,5.6187769914,-1.519730333,-0.5817258671
C,0,6.5871440619,-0.5318566553,-0.4265176372
H,0,6.9631537536,1.4900200319,0.20386175
H,0,4.6357566681,1.9502462534,0.7970695254
H,0,3.5393216707,-2.0273436659,-0.3680035734
H,0,5.8968216095,-2.496862256,-0.9620351252
H,0,7.6216627317,-0.7333367868,-0.6810518771
C,0,2.4684078813,0.2154664557,0.5729749756
O,0,1.7169016099,-0.8086178244,0.6777174219
C,0,1.9649576453,1.5326470655,0.7301551705
C,0,-1.8639553606,1.1769036215,-0.8692594234
C,0,0.6508110956,1.7919860598,1.0470684332
H,0,2.6164119007,2.3675775507,0.4977785336
C,0,-0.5293216169,1.2912342882,-1.1097048055
H,0,-2.5143139394,2.0190769274,-1.0660522105
H,0,0.006540929,1.0050821771,1.4186682746
H,0,0.2935071216,2.8097961063,1.1464312417
H,0,-0.1204931138,2.1846819979,-1.5637012411
H,0,0.1219239001,0.4293621722,-1.0452617376
C,0,-2.4210726891,-0.0273428739,-0.312954746
O,0,-1.705888111,-0.9999008727,0.0035290675
C,0,-3.8992000843,-0.1440027491,-0.1102735189
C,0,-4.4409742424,-1.4164918842,0.100991018
C,0,-4.7572601091,0.960966738,-0.1044312363
C,0,-5.8042296556,-1.5837763159,0.2984109211
H,0,-3.7763358249,-2.2718004188,0.1034864452
C,0,-6.1209621674,0.7943528807,0.1040306242
H,0,-4.3709644403,1.9630155357,-0.2424193267
C,0,-6.6490630776,-0.477247213,0.3015826101
H,0,-6.2096743741,-2.57741662,0.4520937713
H,0,-6.7717282953,1.6611657528,0.1147332617
H,0,-7.7139305662,-0.6051587658,0.4599957245
Li,0,0.0161972549,-1.5981800378,0.6399503738

B.6.1.1.80. 8‡

./PVKhomo-transTS1-5
E(UwB97XD) = -845.979914138

Zero-point correction= 0.285383 (Hartree/Particle)
Thermal correction to Energy= 0.303409
Thermal correction to Enthalpy= 0.304353
Thermal correction to Gibbs Free Energy= 0.233679
Sum of electronic and ZPE= -845.694531
Sum of electronic and thermal Energies= -845.676505
Sum of electronic and thermal Enthalpies= -845.675561
Sum of electronic and thermal Free Energies= -845.746235

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	190.392	68.655	148.746

C,0,-6.3374955356,-0.9215469817,0.0561921989
C,0,-4.9765111478,-1.0563608825,0.3067848229
C,0,-4.1294098486,0.0548217949,0.2532000627
C,0,-4.6795381845,1.3027037344,-0.0542972737
C,0,-6.0362035539,1.4364354986,-0.3177648977
C,0,-6.8708767356,0.3233041354,-0.2615800701
H,0,-6.9835588604,-1.7905137411,0.1135169564
H,0,-4.5835775734,-2.0323393248,0.5665926376
H,0,-4.0248620537,2.165787058,-0.0871489906
H,0,-6.4454849976,2.4099463577,-0.5641410759
H,0,-7.931883335,0.4268621179,-0.4598380059
C,0,-2.6555313171,-0.0299533583,0.5432704312
O,0,-2.0617509735,0.9919572881,0.9186692336
C,0,-1.9856827553,-1.2958547723,0.346370558

C,0,1.9805096777,-0.7359243095,-1.1000613691
C,0,-0.6551558928,-1.4482923132,0.5939851477
H,0,-2.5434223443,-2.1177970798,-0.0876389566
C,0,0.6432395053,-0.6871739303,-1.4228921465
H,0,2.5216498659,-1.6565334135,-1.2920402323
H,0,-0.0955650485,-0.6695718775,1.0954555014
H,0,-0.1736471402,-2.4109057589,0.4810788583
H,0,0.177003705,-1.4901632574,-1.9802126322
H,0,0.0879228174,0.2368378687,-1.3188176691
C,0,2.6621053412,0.3307389707,-0.4402208617
O,0,2.0899948711,1.4054104236,-0.1091284922
C,0,4.1155193122,0.1662040341,-0.1014653869
C,0,4.6821362695,1.0259644518,0.8487346387
C,0,4.9516889338,-0.7846461306,-0.7043227193
C,0,6.0234901488,0.9312647396,1.1974893982
H,0,4.0445449274,1.771295398,1.3096076385
C,0,6.2949762172,-0.8770491599,-0.3608221935
H,0,4.5619338907,-1.4512826042,-1.4646271044
C,0,6.8391624258,-0.0220855892,0.5940975865
H,0,6.4358817795,1.605626126,1.9406978786
H,0,6.9225555551,-1.6158464558,-0.8479088614
H,0,7.8881520542,-0.094299057,0.8593753899

B.6.1.1.81. 8‡-2Li

./PVKhomo-transTS1-inout4Li2
uwb97xd/6-311+g(d,p)
E(UwB97XD) = -860.987140257

Zero-point correction= 0.291949 (Hartree/Particle)
Thermal correction to Energy= 0.312101
Thermal correction to Enthalpy= 0.313046
Thermal correction to Gibbs Free Energy= 0.241012
Sum of electronic and ZPE= -860.695191
Sum of electronic and thermal Energies= -860.675039
Sum of electronic and thermal Enthalpies= -860.674095
Sum of electronic and thermal Free Energies= -860.746128

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	195.847	77.271	151.607

C,0,6.2319988819,0.646870382,0.4621587737
C,0,4.875190426,0.8755781227,0.6571695863
C,0,3.9304455984,-0.057912393,0.2210237629
C,0,4.3721654958,-1.2249290741,-0.4092764828
C,0,5.7265745849,-1.4476728391,-0.6144284315
C,0,6.6603587721,-0.5117276396,-0.1777876823
C,0,2.4623881932,0.1351775642,0.4274627614
O,0,1.7234047763,-0.8699200212,0.3946204861
C,0,1.9395618865,1.4575801203,0.6199215735
C,0,0.6166928136,1.6590878442,0.9035579234
C,0,-0.5410877256,1.4360866072,-1.1205608268
C,0,-1.871369508,1.2545110217,-0.7772448498
C,0,-2.4189514568,-0.0020434784,-0.468959046
O,0,-1.7036346129,-1.0792823571,-0.4653206037
C,0,-3.8603843703,-0.1314197005,-0.1227836371
C,0,-4.296419024,-1.2571842489,0.5883750717
C,0,-4.8148265077,0.8280053707,-0.4906988429
C,0,-5.6322798871,-1.4112333573,0.9362140219
C,0,-6.1504647084,0.6719894062,-0.1457302955
C,0,-6.5662493892,-0.4461715281,0.5725298108
H,0,6.9558196789,1.3728368066,0.8142368122
H,0,4.5596168826,1.7753303224,1.1720499715
H,0,3.6386129307,-1.9506786591,-0.7395597927
H,0,6.0561988483,-2.3518485001,-1.1135549054

H,0,7.7190030634,-0.6866782287,-0.3330196261
H,0,2.585726052,2.3071039749,0.4372575932
H,0,-2.5030580566,2.128964989,-0.6731263416
H,0,-0.0004163009,0.8435335103,1.2552834755
H,0,0.2383265605,2.6580906451,1.0791218855
H,0,-0.1936190217,2.4039707546,-1.4582947964
H,0,0.0733844461,0.5784659043,-1.3661784656
H,0,-3.5700614878,-2.0094853015,0.8735459384
H,0,-4.5211782504,1.6953756606,-1.0699905128
H,0,-5.9450995175,-2.2863472626,1.4951122188
H,0,-6.8723508947,1.4231790655,-0.4464225287
H,0,-7.6097617027,-0.5656596632,0.841037086
Li,0,-0.0361328415,-1.6607051142,0.3273601577
Li,0,-2.1830126274,-2.6095757058,-1.5895102426

B.6.1.1.82. 11‡

./PVKhomo-transTS2-4
E(UwB97XD) = -845.996798824

Zero-point correction= 0.290415 (Hartree/Particle)
Thermal correction to Energy= 0.307018
Thermal correction to Enthalpy= 0.307963
Thermal correction to Gibbs Free Energy= 0.243226
Sum of electronic and ZPE= -845.706384
Sum of electronic and thermal Energies= -845.689780
Sum of electronic and thermal Enthalpies= -845.688836
Sum of electronic and thermal Free Energies= -845.753573

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	192.657	64.733	136.249

C,0,2.3265271453,-2.4727227406,-0.2400567756
C,0,1.788396031,-1.1913905411,-0.2763455313
C,0,2.6125062562,-0.0643837365,-0.1635704391
C,0,3.987387164,-0.2635397672,0.0002327883
C,0,4.5276653637,-1.5430667368,0.027220359
C,0,3.6985001992,-2.6552244151,-0.0936293044
H,0,1.6692006781,-3.3321391096,-0.3179249302
H,0,0.7146537584,-1.0726969063,-0.3655696959
H,0,4.6266550643,0.6057448874,0.10403687
H,0,5.5977478383,-1.6751094785,0.1467620737
H,0,4.1178211961,-3.655017153,-0.067488263
C,0,2.0795762352,1.340548098,-0.1841143847
O,0,2.7776995933,2.2589271625,0.3213614567
C,0,0.7755386356,1.5448277511,-0.7081807385
C,0,-0.6195279888,1.596918514,0.7815988154
C,0,0.1685024259,2.9199957114,-0.912345379
H,0,0.3909312226,0.766012731,-1.3570204824
C,0,-1.1421659618,2.6794871822,-0.1499744451
H,0,0.0478845869,1.9816964429,1.55137608
H,0,0.7846938185,3.6671809062,-0.4076835537
H,0,0.0581621567,3.2141640191,-1.9602800211
H,0,-1.5462838183,3.5511331355,0.3755415319
H,0,-1.9230299585,2.3033024172,-0.8122727757
C,0,-1.2495845585,0.3900743854,1.1933934407
O,0,-0.8725032458,-0.2235782155,2.2330604984
C,0,-2.3595551381,-0.2318824784,0.3943111345
C,0,-3.3794969589,-0.8986481497,1.0843634169
C,0,-2.4051726445,-0.2282126148,-1.0039168261
C,0,-4.4223870899,-1.5140341335,0.4056087707
H,0,-3.3409108717,-0.9264388914,2.1674463659
C,0,-3.4412764319,-0.8576685795,-1.6872350515
H,0,-1.6199507362,0.2515985005,-1.5738760028
C,0,-4.4585945683,-1.4959479918,-0.9870109657

H,0,-5.2089446489,-2.0124175367,0.9621424016
H,0,-3.4498759277,-0.8501105052,-2.7718950046
H,0,-5.2698138217,-1.9800881629,-1.5193294334

B.6.1.1.83. 11‡-Li

./PVKhomo-transTS2-5Li
uwb97xd/6-311+g(d,p)
E(UwB97XD) = -853.506764170

Zero-point correction= 0.292411 (Hartree/Particle)
Thermal correction to Energy= 0.310448
Thermal correction to Enthalpy= 0.311393
Thermal correction to Gibbs Free Energy= 0.244521
Sum of electronic and ZPE= -853.214353
Sum of electronic and thermal Energies= -853.196316
Sum of electronic and thermal Enthalpies= -853.195371
Sum of electronic and thermal Free Energies= -853.262243

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	194.809	69.696	140.743

C,0,2.0223607633,-1.3428644785,1.6967614875
C,0,0.7042427869,-1.2349140095,1.2714660304
C,0,0.2150553666,-2.046014138,0.2407704448
C,0,1.0859205542,-2.969841786,-0.3453271743
C,0,2.4021329935,-3.0840876434,0.0827187675
C,0,2.8774036933,-2.2677238793,1.1054536248
C,0,-1.1825995041,-1.9289177062,-0.3032205305
O,0,-1.4680824264,-2.5165964266,-1.3709728638
C,0,-2.0967459727,-1.0599894563,0.3676091951
C,0,-3.546185104,-0.8857044415,-0.0444895899
C,0,-3.517263314,0.6480181331,-0.1046993618
C,0,-2.0382645625,0.7786250832,-0.4280030883
C,0,-1.150330089,1.6567509836,0.2386474526
O,0,-1.467024669,2.251930154,1.3245832107
C,0,0.2445999859,1.8027789227,-0.259300704
C,0,1.0940764374,2.7227946799,0.3702160621
C,0,0.773236434,1.0302849887,-1.3052267369
C,0,2.4165341038,2.869048492,-0.0281910165
C,0,2.0961040659,1.1730658205,-1.6999287861
C,0,2.9269932278,2.0931165761,-1.065132326
H,0,2.3855551306,-0.694460243,2.4866331749
H,0,0.0715513799,-0.4847956114,1.7291758106
H,0,0.7133159226,-3.5918652396,-1.1504880773
H,0,3.0611448005,-3.8077407662,-0.3848070513
H,0,3.9068144876,-2.3492890139,1.4365694144
H,0,-1.8925771092,-0.8219569841,1.4064242906
H,0,-1.791307591,0.5092841087,-1.4496270208
H,0,-3.7023395511,-1.3170624658,-1.0353043788
H,0,-4.2735958471,-1.3229672381,0.6449849681
H,0,-4.1822841576,1.1153928541,-0.8366591169
H,0,-3.7256713244,1.0798102454,0.8763163393
H,0,0.6971310981,3.3162532273,1.1849904826
H,0,0.1648103093,0.2836996059,-1.800443128
H,0,3.0537008577,3.5887962322,0.4748200491
H,0,2.4838009101,0.5545768527,-2.5022116341
H,0,3.9609501568,2.2008622267,-1.3735204236
Li,0,-2.6549802439,2.9304053407,2.5696232039

B.6.1.1.84. 9‡

./PVKhomo-transTSr-2
E(UwB97XD) = -845.994847073

Zero-point correction= 0.289467 (Hartree/Particle)
Thermal correction to Energy= 0.306289
Thermal correction to Enthalpy= 0.307234
Thermal correction to Gibbs Free Energy= 0.241232
Sum of electronic and ZPE= -845.705380
Sum of electronic and thermal Energies= -845.688558
Sum of electronic and thermal Enthalpies= -845.687613
Sum of electronic and thermal Free Energies= -845.753615

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 192.199 65.488 138.912

C,0,5.5647819019,0.2958197109,0.8061241748
C,0,4.2880002914,-0.2393654002,0.6651598992
C,0,3.5143387371,0.0258397734,-0.4701132586
C,0,4.0572377817,0.8631210334,-1.4495166797
C,0,5.3361802782,1.3930141003,-1.318064689
C,0,6.0983507824,1.1113823156,-0.1876087927
H,0,6.141425486,0.0828152445,1.7003987365
H,0,3.8807248181,-0.8580082768,1.4575622322
H,0,3.4544791033,1.0953154471,-2.3202301957
H,0,5.7388919243,2.0310960563,-2.0980966836
H,0,7.0927647561,1.5304162996,-0.0775341587
C,0,2.115949561,-0.5258339377,-0.6677781304
O,0,1.3033714676,0.2075582372,-1.3410820076
C,0,1.8324463653,-1.7688084416,-0.1510827199
C,0,-1.7630476311,-1.5639896773,0.566673522
C,0,0.4756984175,-2.3804572756,-0.278385272
H,0,2.5878420578,-2.3077092254,0.4113794041
C,0,-0.456144168,-2.107515385,0.9695712888
H,0,-2.3511494744,-2.1283122822,-0.1503418296
H,0,-0.0096327923,-1.9710449295,-1.1689259473
H,0,0.5387706907,-3.4638479032,-0.4195661521
H,0,-0.6025801495,-3.0525905115,1.5074135866
H,0,0.0351060069,-1.415144158,1.6541768039
C,0,-2.2814960394,-0.3187016137,1.0520767966
O,0,-1.7010697784,0.3288616621,1.9369266855
C,0,-3.5809401965,0.1891581163,0.4964306272
C,0,-4.3935511584,0.9853643012,1.3063977061
C,0,-3.9855463439,-0.0840440636,-0.811953833
C,0,-5.5965266542,1.4839445135,0.8250384348
H,0,-4.0737794031,1.2050450437,2.3184479673
C,0,-5.1827005667,0.4281159194,-1.2994194917
H,0,-3.3566906763,-0.6776456048,-1.4659861183
C,0,-5.99330554,1.2067792527,-0.4805749354
H,0,-6.2259284622,2.0906153436,1.4663195995
H,0,-5.4799662879,0.2193944261,-2.3207785538
H,0,-6.9305491053,1.5995958892,-0.8585120158

B.6.1.1.85. 9‡-Li

./PVKhomo-transTSr-5Li
uwb97xd/6-311+g(d,p)
E(UwB97XD) = -853.505430642

Zero-point correction= 0.292478 (Hartree/Particle)
Thermal correction to Energy= 0.310348
Thermal correction to Enthalpy= 0.311293
Thermal correction to Gibbs Free Energy= 0.243794
Sum of electronic and ZPE= -853.212953
Sum of electronic and thermal Energies= -853.195082
Sum of electronic and thermal Enthalpies= -853.194138
Sum of electronic and thermal Free Energies= -853.261636

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 194.747 69.909 142.062

C,0,6.2159374751,-1.090745155,0.1884238468
C,0,4.8282510248,-1.1696288449,0.1970913898
C,0,4.0405129346,-0.0831833591,-0.2024711084
C,0,4.6936602583,1.0915473935,-0.5871990251
C,0,6.0823297399,1.1734489789,-0.6005380266
C,0,6.8518299153,0.0808556249,-0.2144763369
C,0,2.5324527287,-0.1150805286,-0.2142270957
O,0,1.9306544879,1.0383020527,-0.1317359705
C,0,1.8748396267,-1.3027314228,-0.3129307887
C,0,0.3756764461,-1.3927029001,-0.293593141
C,0,-0.2855076283,-0.7637210994,0.9821643881
C,0,-1.0726160103,0.4453563726,0.6796536239
C,0,-0.9110805956,1.7096440372,1.3287157694
O,0,-0.0267349322,1.8961314426,2.1861588601
C,0,-1.8474697102,2.8276697861,0.9957650958
C,0,-2.0679859759,3.8183826514,1.9566599001
C,0,-2.478942525,2.9317524569,-0.2465460988
C,0,-2.9170920356,4.8825714451,1.6886556485
C,0,-3.3158863269,4.0071140788,-0.5198196125
C,0,-3.5416745616,4.9799612085,0.448012407
H,0,6.803985458,-1.9446586312,0.5079115205
H,0,4.3535597104,-2.0834607604,0.5363401536
H,0,4.0912290009,1.9437987492,-0.8792585173
H,0,6.5649010166,2.0939314809,-0.9122301246
H,0,7.9345135966,0.1426531228,-0.2187268942
H,0,2.4335595603,-2.2267518668,-0.4041619831
H,0,-1.8528189227,0.3518744935,-0.0686839458
H,0,-0.057190051,-0.9047036257,-1.1762337807
H,0,0.0790132232,-2.4423603899,-0.3560862424
H,0,0.4699073813,-0.5499056807,1.7385606389
H,0,-0.9776345619,-1.5023389766,1.4095408683
H,0,-1.5712002568,3.7394544866,2.9163262779
H,0,-2.303370818,2.1922256176,-1.0189555716
H,0,-3.0912104524,5.6386131582,2.4456842088
H,0,-3.7899057596,4.0856193702,-1.4913120195
H,0,-4.2006876991,5.8141372295,0.2355380249
Li,0,1.9125722383,1.9324030035,1.515796661

B.6.1.1.86. 5⁻•

./raPPK-1
E(UwB97XD) = -462.354466120

Zero-point correction= 0.168217 (Hartree/Particle)
Thermal correction to Energy= 0.178684
Thermal correction to Enthalpy= 0.179628
Thermal correction to Gibbs Free Energy= 0.129694
Sum of electronic and ZPE= -462.186249
Sum of electronic and thermal Energies= -462.175782
Sum of electronic and thermal Enthalpies= -462.174838
Sum of electronic and thermal Free Energies= -462.224773

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 112.126 38.741 105.097

C,0,-4.030890566,1.4497367517,-0.0854587192
C,0,-4.79348274,0.3377064018,-0.4108319783
C,0,-4.3883203368,-0.9421354999,-0.0325658979
C,0,-3.1947928512,-1.0779501803,0.6826855008
C,0,-2.4283455577,0.0282053015,1.0109649852
C,0,-2.8179967073,1.339895446,0.6382998637

H,0,-4.3550271044,2.4394816749,-0.3843265097
C,0,-2.0667985855,2.5614639342,0.9449537829
H,0,-5.716922929,0.4694382417,-0.9671509868
H,0,-4.983726768,-1.8120420265,-0.2864227374
H,0,-2.8580380964,-2.0639819442,0.9885558423
H,0,-1.5122934635,-0.1348708452,1.5663948125
O,0,-2.5194298356,3.6991844823,0.5543442284
C,0,-0.8255103845,2.4716655475,1.6830702915
C,0,-0.0487572731,3.5329937562,2.0222464724
H,0,-0.4806111105,1.4881154754,1.9934139053
H,0,-0.3752762229,4.5259906947,1.7216503205
C,0,1.2367842818,3.4336885004,2.7873648949
H,0,1.4722008483,2.3951964886,3.0395041929
H,0,1.1969655146,4.0036290621,3.7238448727
H,0,2.0815198878,3.8380887371,2.2161428631

B.6.1.1.87. 3

./raPVK-1
E(UwB97XD) = -423.040853299

Zero-point correction= 0.140775 (Hartree/Particle)
Thermal correction to Energy= 0.149329
Thermal correction to Enthalpy= 0.150273
Thermal correction to Gibbs Free Energy= 0.106294
Sum of electronic and ZPE= -422.900079
Sum of electronic and thermal Energies= -422.891525
Sum of electronic and thermal Enthalpies= -422.890581
Sum of electronic and thermal Free Energies= -422.934560

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	93.705	33.212	92.562

C,0,1.0349519981,1.180505568,0.1477986145
C,0,2.4108834564,0.9990841366,0.1719018865
C,0,2.9625155028,-0.2728122728,0.0325143395
C,0,2.1031029643,-1.3602700746,-0.1347502265
C,0,0.7278870093,-1.1831282812,-0.1575306852
C,0,0.1456901785,0.095908589,-0.0092990998
H,0,0.6110522691,2.1715667092,0.2564669888
C,0,-1.3064228568,0.3669936167,-0.0195061656
H,0,3.0615615733,1.8587763348,0.3009865376
H,0,4.0371707982,-0.4164445439,0.0507092776
H,0,2.5128494934,-2.3582768499,-0.2552616357
H,0,0.1029547849,-2.0564721207,-0.3030767773
O,0,-1.7157354349,1.5825637083,-0.0174615679
C,0,-2.2349821194,-0.7311431733,0.0009999113
C,0,-3.5930476172,-0.5966877271,0.0092207619
H,0,-1.8328891138,-1.739905702,0.0269880993
H,0,-4.0550451154,0.3846984461,-0.0100309011
H,0,-4.2433473109,-1.4645262532,0.0363520121

B.6.1.1.88. 18-Li

./rLiClPPK-1
E(UwB97XD) = -929.470233658

Zero-point correction= 0.161237 (Hartree/Particle)
Thermal correction to Energy= 0.174444
Thermal correction to Enthalpy= 0.175388
Thermal correction to Gibbs Free Energy= 0.119295
Sum of electronic and ZPE= -929.308997
Sum of electronic and thermal Energies= -929.295790
Sum of electronic and thermal Enthalpies= -929.294846

Sum of electronic and thermal Free Energies= -929.350939

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.465 47.472 118.059

C,0,3.0007592915,-1.1067337115,-0.0039722554
C,0,1.8304438365,-1.831518439,-0.2158039467
C,0,0.6118053429,-1.1768517956,-0.2232001709
C,0,0.5126033243,0.2213332572,-0.018885004
C,0,1.7286624901,0.9137754749,0.1894791399
C,0,2.9534581835,0.2663852697,0.1995612652
Cl,0,4.5504707116,-1.9393013002,0.0027785183
H,0,1.8748125944,-2.9019158628,-0.3791562855
H,0,-0.2745698257,-1.7730142633,-0.3998667032
H,0,1.6941260026,1.9830440429,0.3535009194
H,0,3.8674193312,0.8251710577,0.365118157
C,0,-0.7385552888,0.9703932135,-0.0222252657
C,0,-2.0036577383,0.2906615034,-0.1398372236
H,0,-1.9980804066,-0.7937102898,-0.2094256758
C,0,-3.2101214415,0.9105530742,-0.1582783852
H,0,-3.2347012339,1.9952380368,-0.0876238816
C,0,-4.5234337112,0.1986318293,-0.2668049667
H,0,-5.1645697012,0.4039076765,0.598729117
H,0,-5.0851189233,0.523490486,-1.1507095223
H,0,-4.3879033124,-0.8844335669,-0.3342588182
O,0,-0.7030600338,2.2574829849,0.0952975157
Li,0,-0.1466974919,3.9917633221,0.0037154721

B.6.1.1.89. 5-Li

./rLiPPK-1
E(UwB97XD) = -469.860460212

Zero-point correction= 0.170797 (Hartree/Particle)
Thermal correction to Energy= 0.182737
Thermal correction to Enthalpy= 0.183681
Thermal correction to Gibbs Free Energy= 0.130762
Sum of electronic and ZPE= -469.689663
Sum of electronic and thermal Energies= -469.677723
Sum of electronic and thermal Enthalpies= -469.676779
Sum of electronic and thermal Free Energies= -469.729698

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 114.669 43.507 111.378

C,0,3.0481600231,-1.1401037083,-0.012628602
C,0,1.854497297,-1.8521906725,-0.1497104318
C,0,0.6319919012,-1.2005856518,-0.1539933001
C,0,0.5435030717,0.2064152318,-0.0206634262
C,0,1.7654328494,0.9042365698,0.1166702918
C,0,2.9866984515,0.2455607078,0.1203605305
H,0,4.0020976825,-1.655316103,-0.0098186685
H,0,1.8786957266,-2.9323053975,-0.2546489764
H,0,-0.264366144,-1.7989117048,-0.2625067989
H,0,1.7370765892,1.9816421515,0.222041289
H,0,3.9018555766,0.8194034494,0.2283584014
C,0,-0.7123747389,0.9573364084,-0.0166842423
C,0,-1.9748935897,0.2833756187,-0.1554811829
H,0,-1.9695199216,-0.7974046508,-0.2677907775
C,0,-3.1845461634,0.9027164793,-0.1577692393
H,0,-3.2110448274,1.9839491449,-0.0453637503
C,0,-4.496142213,0.1933572829,-0.3032445403
H,0,-5.1414365535,0.3554646683,0.5685645489
H,0,-5.0563901424,0.5554594316,-1.1735641156

H,0,-4.3565010832,-0.8852130679,-0.4200585031
O,0,-0.6774477309,2.2447087148,0.1142591603
Li,0,-0.1512538907,3.9727572573,0.2318039736

B.6.1.1.90. 5-Li 2CH3CN

./rLiPPK-1-2ACN
opt
E(UwB97XD) = -735.378470489

Zero-point correction= 0.265625 (Hartree/Particle)
Thermal correction to Energy= 0.287495
Thermal correction to Enthalpy= 0.288439
Thermal correction to Gibbs Free Energy= 0.210475
Sum of electronic and ZPE= -735.112845
Sum of electronic and thermal Energies= -735.090975
Sum of electronic and thermal Enthalpies= -735.090031
Sum of electronic and thermal Free Energies= -735.167996

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	180.406	74.819	164.090

C,0,3.1016008819,1.1556625504,0.2446431223
C,0,2.4915887694,0.0735871712,-0.3951241904
C,0,1.1117391643,-0.0236680564,-0.4722743027
C,0,0.2690486042,0.9627317103,0.09482895
C,0,0.9097372297,2.0425129939,0.7458013382
C,0,2.2910362126,2.1363824605,0.8159818197
H,0,4.1820304847,1.2290070097,0.295234959
H,0,3.1041801002,-0.6980921972,-0.8503723274
H,0,0.6883403888,-0.8711537486,-0.997942209
H,0,0.2926043938,2.8116714416,1.1915072059
H,0,2.7421443825,2.98514744,1.3210930054
C,0,-1.1906695048,0.9458710198,0.0248831581
C,0,-1.8851599559,-0.1952595104,-0.5098302968
H,0,-1.2936024348,-1.0482461958,-0.8322255186
C,0,-3.2350907156,-0.289490808,-0.6269100662
H,0,-3.8403517165,0.5545344536,-0.3054965965
C,0,-3.9559462173,-1.4867351013,-1.1668060602
H,0,-4.6503658823,-1.9049829797,-0.4281872419
H,0,-4.5586182408,-1.2323939805,-2.0469612908
H,0,-3.2590049815,-2.2788220352,-1.4553947862
O,0,-1.8571467808,1.9660337446,0.4656774857
Li,0,-1.9271643978,3.7770306921,0.0953275536
N,0,-0.7763224101,3.9083958796,-1.8156878582
N,0,-0.7732767217,5.1526631624,1.2962424509
C,0,0.1365449334,3.3631325116,-2.2529372154
C,0,-0.0476346268,5.8122411802,1.8938154211
C,0,1.2930126959,2.6748675915,-2.793344751
H,0,1.9635716002,2.4102668855,-1.9731381395
H,0,1.8109935331,3.3222242847,-3.5016145536
H,0,0.9719361337,1.7639931442,-3.2991174854
C,0,0.8722965139,6.6411359735,2.6498001455
H,0,1.8808967599,6.2352696093,2.5673559303
H,0,0.5727523584,6.6544959317,3.6979832327
H,0,0.8575294464,7.6576057716,2.2559191115

B.6.1.1.91. 5-Li NMe3

./rLiPPK-NMe3
opt
E(UwB97XD) = -644.343587389

Zero-point correction= 0.294146 (Hartree/Particle)

Thermal correction to Energy= 0.312821
Thermal correction to Enthalpy= 0.313765
Thermal correction to Gibbs Free Energy= 0.245123
Sum of electronic and ZPE= -644.049441
Sum of electronic and thermal Energies= -644.030766
Sum of electronic and thermal Enthalpies= -644.029822
Sum of electronic and thermal Free Energies= -644.098464

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 196.298 67.372 144.469

C,0,3.1903201655,0.2076305441,-0.3203944416
C,0,2.3874942064,-0.9354437644,-0.2853705225
C,0,1.0072392564,-0.8374991807,-0.2125773104
C,0,0.3593399689,0.4201316508,-0.169713418
C,0,1.1937743445,1.5588317701,-0.2092071029
C,0,2.5745048695,1.4569320776,-0.2808957377
H,0,4.2695118837,0.1221676065,-0.3777753366
H,0,2.8482354717,-1.9176043553,-0.3189985023
H,0,0.4294710602,-1.754025234,-0.1991311887
H,0,0.723627133,2.5323115684,-0.1747231071
H,0,3.1767120023,2.3604158907,-0.3043367763
C,0,-1.0885383566,0.6100949956,-0.0979707921
C,0,-1.9713678487,-0.512738234,0.0629693974
H,0,-1.5285129581,-1.5026582235,0.1340285925
C,0,-3.3247118836,-0.4242504715,0.1485870693
H,0,-3.7835767378,0.559298677,0.0830329995
C,0,-4.2364280381,-1.5979029469,0.3383750673
H,0,-4.8166534235,-1.5113534464,1.2650111394
H,0,-4.9659370403,-1.6787873287,-0.4763141666
H,0,-3.6774072368,-2.5370162545,0.3814519056
O,0,-1.5695528511,1.8109399727,-0.1624325582
Li,0,-1.5117250955,3.6174368037,-0.3759473468
N,0,-0.1044001092,5.2542909185,-0.5298331286
C,0,0.6607535655,5.3538691532,0.7125805226
H,0,1.2520774409,4.4479448671,0.8611576494
H,0,-0.0225619667,5.4619463631,1.5574536162
H,0,1.3445134348,6.2172850772,0.7019712211
C,0,-0.9160731055,6.4579698903,-0.7168926315
H,0,-1.4974170514,6.3716061784,-1.637274846
H,0,-0.2924285022,7.3634429075,-0.7805725876
H,0,-1.6078259294,6.5715927402,0.1206573727
C,0,0.7939246446,5.0756513383,-1.6705244995
H,0,1.3842104943,4.1662052502,-1.5437672435
H,0,1.4838712598,5.926970174,-1.7811083293
H,0,0.2095069326,4.9808130246,-2.587964979

B.6.1.1.92. 3-Li 2CH$_3$CN

./rLiPVK-2ACN-1
opt
E(UwB97XD) = -696.060865861

Zero-point correction= 0.238205 (Hartree/Particle)
Thermal correction to Energy= 0.258138
Thermal correction to Enthalpy= 0.259082
Thermal correction to Gibbs Free Energy= 0.186530
Sum of electronic and ZPE= -695.822661
Sum of electronic and thermal Energies= -695.802728
Sum of electronic and thermal Enthalpies= -695.801784
Sum of electronic and thermal Free Energies= -695.874336

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 161.984 69.198 152.699

C,0,-2.6718950579,2.0861547937,0.4064799114
C,0,-1.7883839792,2.2776573811,-0.6572898385
C,0,-0.5299047285,1.6973966999,-0.6475244107
C,0,-0.0993797853,0.8942682271,0.4313181518
C,0,-1.0020829406,0.7278143352,1.5010375332
C,0,-2.2616819432,1.3102545644,1.4878094505
H,0,-3.6589758645,2.5342503052,0.3906912679
H,0,-2.0890840351,2.8793362197,-1.508800455
H,0,0.1123804188,1.8521570132,-1.5059989339
H,0,-0.698830148,0.1223257374,2.3455596675
H,0,-2.9318853846,1.153406195,2.326926479
C,0,1.1916001896,0.1936427942,0.4718753319
C,0,2.2014771652,0.462535587,-0.5085903006
H,0,1.9866440993,1.2067282828,-1.2690014775
C,0,3.4211521016,-0.1435644092,-0.5441913764
O,0,1.4118839447,-0.6587833006,1.4170984647
Li,0,0.9084481471,-2.0268993933,2.5236659177
N,0,-1.9496293593,-2.961432916,1.3283054124
C,0,-1.9295295732,-2.3485752243,0.3541092599
C,0,-1.9119146442,-1.5858900562,-0.882453265
H,0,-0.8789405834,-1.4017409059,-1.1800483544
H,0,-2.4058233904,-0.6252972973,-0.7254328379
H,0,-2.4271194826,-2.1432088082,-1.6655123534
H,0,4.1494669905,0.1096465802,-1.3064294895
H,0,3.6928743497,-0.8904374585,0.1938349783
N,0,0.4614143787,-2.3231021272,4.6762625769
C,0,0.1863523621,-2.4117759502,5.7877076314
C,0,-0.1623931875,-2.5227570957,7.1919275225
H,0,0.1745125559,-1.6324704267,7.7235014512
H,0,0.3186027703,-3.4026795416,7.6197821873
H,0,-1.2438153861,-2.6169198053,7.2933698975

B.6.1.1.93. 3-Li NMe$_3$

./rLiPVK-NMe3
opt
E(UwB97XD) = -605.031954804

Zero-point correction= 0.266310 (Hartree/Particle)
Thermal correction to Energy= 0.283166
Thermal correction to Enthalpy= 0.284110
Thermal correction to Gibbs Free Energy= 0.220011
Sum of electronic and ZPE= -604.765644
Sum of electronic and thermal Energies= -604.748789
Sum of electronic and thermal Enthalpies= -604.747844
Sum of electronic and thermal Free Energies= -604.811944

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	177.689	61.881	134.909

C,0,-1.5167019895,0.5196510357,1.4790696664
C,0,-0.6181005469,-0.5351131705,1.3142470442
C,0,0.5707230287,-0.3541735583,0.6244233418
C,0,0.9134165457,0.8970146023,0.067198224
C,0,-0.0104007967,1.9481163822,0.2439521743
C,0,-1.1991227935,1.7623048666,0.9356977699
H,0,-2.4447783142,0.3736504775,2.0203313727
H,0,-0.8487414278,-1.5111099063,1.7288142146
H,0,1.2362755952,-1.2026700305,0.5212340814
H,0,0.235610234,2.9170819362,-0.1727275338
H,0,-1.8848503799,2.5954170402,1.054296211
C,0,2.1595416661,1.1674633045,-0.6643338781
C,0,3.1434751174,0.1416976523,-0.8456884322
H,0,2.9377172577,-0.841661893,-0.4349569928

C,0,4.3281648133,0.316542865,-1.4953867763
H,0,4.5955599849,1.2757271359,-1.9258054865
H,0,5.037493729,-0.4972624105,-1.5962866416
O,0,2.3511128731,2.3547270472,-1.1397275517
Li,0,3.5966509707,3.6925185998,-0.8594644254
N,0,4.1110410411,3.7976744183,1.193301503
C,0,4.8300214819,2.5681873877,1.5168741301
H,0,5.7715240104,2.5348069541,0.9638479559
H,0,4.2288123064,1.7058788742,1.2224934024
H,0,5.0549378892,2.4989859751,2.5937664895
C,0,4.9199057831,4.9703319606,1.5104224549
H,0,4.3788530775,5.8781856679,1.2341505223
H,0,5.8545689725,4.9387308417,0.946013759
H,0,5.1631574228,5.0231780476,2.584142055
C,0,2.8357154103,3.8404419708,1.9048469935
H,0,2.2351699237,2.9718406657,1.6293821637
H,0,2.2859994793,4.7420972012,1.6241099122
H,0,2.9794376347,3.8446280586,2.9974922765

B.6.2. Heavy-atom Tunneling and Reaction Dynamics of Di-π-methane Rearrangement

B.6.2.1.1. acetone-singlet

/home/hanyclose/dipimethane/paper/acetone-singlet-wb97xd
opt
E(UwB97XD) = -193.107950179

Zero-point correction= 0.084320 (Hartree/Particle)
Thermal correction to Energy= 0.089680
Thermal correction to Enthalpy= 0.090624
Thermal correction to Gibbs Free Energy= 0.056175
Sum of electronic and ZPE= -193.023630
Sum of electronic and thermal Energies= -193.018270
Sum of electronic and thermal Enthalpies= -193.017326
Sum of electronic and thermal Free Energies= -193.051776

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	56.275	16.730	72.505

C,0,-1.6466485106,0.1463433668,-0.0212561374
C,0,-0.1592597346,0.1071567622,0.2567602367
H,0,-1.9343258194,-0.6594979678,-0.7044008478
H,0,-1.9242850166,1.1128749894,-0.4425175117
H,0,-2.1957960229,-0.0134959578,0.9135484721
C,0,0.4157731123,-1.2297037578,0.6732386337
O,0,0.5364118429,1.0964748384,0.1510548959
H,0,0.3640414358,-1.9267192965,-0.1708540987
H,0,-0.1711473933,-1.6672892259,1.4873874734
H,0,1.4551257624,-1.1116387349,0.9808372638

B.6.2.1.2. acetone-triplet

/home/hanyclose/dipimethane/paper/acetone-triplet-wb97xd
opt
E(UwB97XD) = -192.984531382

Zero-point correction= 0.082124 (Hartree/Particle)
Thermal correction to Energy= 0.087485
Thermal correction to Enthalpy= 0.088430
Thermal correction to Gibbs Free Energy= 0.053649
Sum of electronic and ZPE= -192.902408
Sum of electronic and thermal Energies= -192.897046
Sum of electronic and thermal Enthalpies= -192.896102

Sum of electronic and thermal Free Energies= -192.930882

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 54.898 17.428 73.202

C,0,-7.4327403373,0.7221137913,-0.018503117
C,0,-6.0345308071,0.3423962121,-0.4643988416
H,0,-8.0506557714,-0.1793162904,-0.0073847933
H,0,-7.8811544461,1.4445414347,-0.7040231885
H,0,-7.425618286,1.1592944845,0.9916133499
C,0,-5.3171565236,-0.7572990185,0.2932573236
H,0,-5.1117977804,-0.458743843,1.3325867
H,0,-4.3693902464,-1.011210452,-0.1865163202
H,0,-5.9537208501,-1.6456880615,0.3016274758
O,0,-5.2660049692,1.3905717293,-0.7055985778

B.6.2.1.3. acetophenone-singlet

/home/hanyclose/dipimethane/paper/acetophenone-singlet-wb97xd
uwB97XD/6-31+g(d,p)
E(UwB97XD) = -384.788408366

Zero-point correction= 0.139325 (Hartree/Particle)
Thermal correction to Energy= 0.147078
Thermal correction to Enthalpy= 0.148023
Thermal correction to Gibbs Free Energy= 0.106603
Sum of electronic and ZPE= -384.649083
Sum of electronic and thermal Energies= -384.641330
Sum of electronic and thermal Enthalpies= -384.640386
Sum of electronic and thermal Free Energies= -384.681806

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 92.293 29.320 87.175

C,0,-2.1025175891,1.370512314,-0.6178558442
C,0,-0.8519649828,1.5916000324,-0.0299896912
C,0,-0.053841012,0.4953530536,0.3133773387
C,0,-0.4993609689,-0.8018326867,0.0726164018
C,0,-1.745543196,-1.0122802304,-0.5129265635
C,0,-2.5470565384,0.076300866,-0.8580697647
H,0,-2.7099255146,2.2308900199,-0.8785053243
C,0,-0.4169464221,3.0080767151,0.2089077718
H,0,-2.0925527045,-2.0237240563,-0.7004723806
H,0,-3.51821636,-0.0868107064,-1.3143794711
H,0,0.9193274673,0.6435586715,0.7702004166
H,0,0.1260215477,-1.6469381587,0.3420166052
O,0,-1.1388311262,3.9376702716,-0.1036581977
C,0,0.9332741563,3.259985235,0.8442999339
H,0,1.7353287704,2.8359604522,0.2314492068
H,0,0.9896562451,2.7938935753,1.8333439822
H,0,1.0799682276,4.3355346317,0.9407755804

B.6.2.1.4. acetophenone-triplet

/home/hanyclose/dipimethane/paper/acetophenone-triplet-wb97xd
opt
E(UwB97XD) = -384.674385854

Zero-point correction= 0.135572 (Hartree/Particle)
Thermal correction to Energy= 0.143991
Thermal correction to Enthalpy= 0.144935
Thermal correction to Gibbs Free Energy= 0.100981
Sum of electronic and ZPE= -384.538813

Sum of electronic and thermal Energies= -384.530395
Sum of electronic and thermal Enthalpies= -384.529451
Sum of electronic and thermal Free Energies= -384.573405

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 90.356 30.997 92.509

C,0,-2.0174658711,1.229026802,-0.0724787523
C,0,-0.6066809819,1.4062108819,-0.0542482799
C,0,-2.5697948984,-0.0240147934,0.1296141684
C,0,0.2083375316,0.2658980746,0.17588627
C,0,-0.3667811933,-0.9786531928,0.3756986752
C,0,-1.7556986344,-1.1392445376,0.3553334013
H,0,-3.6495773078,-0.1379117676,0.1118329253
H,0,-2.1967758966,-2.1177418562,0.5128134059
H,0,1.2889605758,0.3653985515,0.1961448036
H,0,0.274404442,-1.8375809041,0.550005253
H,0,-2.6619389112,2.0853419949,-0.2464201508
C,0,-0.0253241545,2.6808740619,-0.2590701745
O,0,-0.7688008189,3.7512952508,-0.4749481054
C,0,1.4513655948,2.9943623717,-0.2625154856
H,0,1.8959296607,2.7347352557,0.704498912
H,0,1.6193272226,4.0577185676,-0.4432758819
H,0,1.9574136406,2.4266052394,-1.0510309843

B.6.2.1.5. 1

/home/hanyclose/dipimethane/paper/benzobarrelene-singlet
opt
E(UwB97XD) = -463.116771824

Zero-point correction= 0.183499 (Hartree/Particle)
Thermal correction to Energy= 0.191374
Thermal correction to Enthalpy= 0.192319
Thermal correction to Gibbs Free Energy= 0.151008
Sum of electronic and ZPE= -462.933273
Sum of electronic and thermal Energies= -462.925397
Sum of electronic and thermal Enthalpies= -462.924453
Sum of electronic and thermal Free Energies= -462.965764

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 120.089 34.976 86.945

C,0,2.7659340629,-0.595268077,-0.0967894781
C,0,1.5822573984,-1.3461789051,-0.0596057925
C,0,0.3672194617,-0.6868057294,-0.0220152935
C,0,0.3169547059,0.7122837272,-0.0210190193
C,0,1.481537381,1.4572071219,-0.0576047219
C,0,2.7160488929,0.7932314651,-0.0957970981
C,0,-1.0275811456,-1.3150971855,0.0216696095
C,0,-1.1193344999,1.2388042642,0.0235568651
C,0,-1.7377609498,0.6029543123,1.2726866975
C,0,-1.6900222132,-0.7271065319,1.271680411
H,0,3.724885884,-1.1033107756,-0.1264642843
H,0,1.6211124439,-2.432181965,-0.0603870713
H,0,1.4423523887,2.5431980886,-0.0568151899
H,0,3.6360694809,1.3688212691,-0.1246914772
H,0,-0.9964425842,-2.4051213104,0.0211215777
H,0,-1.1664933634,2.3282524319,0.0246191551
C,0,-1.8143796611,0.6020170464,-1.1841097122
C,0,-1.7665467105,-0.7280442555,-1.1851225741
H,0,-2.1785040095,-1.3688445686,-1.955683237
H,0,-2.2713315208,1.2127348231,-1.9537309483
H,0,-2.0531899036,-1.3673292067,2.0668667054

H,0,-2.1458625388,1.214292961,2.0688118764

B.6.2.1.6. 2

/home/hanyclose/dipimethane/paper/benzobarrelene-triplet
opt
E(UwB97XD) = -463.013234922

Zero-point correction= 0.180291 (Hartree/Particle)
Thermal correction to Energy= 0.188616
Thermal correction to Enthalpy= 0.189560
Thermal correction to Gibbs Free Energy= 0.146400
Sum of electronic and ZPE= -462.832944
Sum of electronic and thermal Energies= -462.824619
Sum of electronic and thermal Enthalpies= -462.823675
Sum of electronic and thermal Free Energies= -462.866835

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 118.358 36.377 90.837

C,0,2.7640434681,-0.6462665805,-0.0575187887
C,0,1.5713378298,-1.373830889,-0.0683736103
C,0,0.3592740832,-0.69531679,-0.0613294476
C,0,0.3316715883,0.7072137096,-0.0190975966
C,0,1.5166919914,1.427510018,-0.0000984318
C,0,2.7370801757,0.7458197678,-0.0243438888
C,0,-1.0309090443,-1.319237428,-0.0280302267
C,0,-1.0704860114,1.2834014825,0.017831171
C,0,-1.8020962712,0.6863330577,1.2195201716
C,0,-1.5618464606,-0.7817135887,1.3006625059
H,0,3.7153106361,-1.1691463307,-0.0757824047
H,0,1.5902326683,-2.4602004298,-0.089824632
H,0,1.4959575999,2.5134121637,0.0351216616
H,0,3.6674008786,1.3051951683,-0.0154588368
H,0,-0.9956398109,-2.4093088862,-0.0735572156
H,0,-1.0855130438,2.3743924073,-0.0036267011
C,0,-1.8727123862,0.6531501022,-1.1192697153
C,0,-1.8567848926,-0.6856433944,-1.1347536547
H,0,-2.401779554,-1.291916859,-1.849492838
H,0,-2.4539251622,1.2650168467,-1.8012332296
H,0,-1.1322274491,-1.2136097904,2.2038423903
H,0,-2.7981588332,1.0832562429,1.4159913179

B.6.2.1.7. syn-2

/home/hanyclose/dipimethane/benzobarrelene-triplet-syn
opt
E(UwB97XD) = -463.009071055

Zero-point correction= 0.179337 (Hartree/Particle)
Thermal correction to Energy= 0.188159
Thermal correction to Enthalpy= 0.189104
Thermal correction to Gibbs Free Energy= 0.144813
Sum of electronic and ZPE= -462.829734
Sum of electronic and thermal Energies= -462.820912
Sum of electronic and thermal Enthalpies= -462.819968
Sum of electronic and thermal Free Energies= -462.864258

E CV S

KCal/Mol Cal/Mol-K Cal/Mol-K
Total 118.072 37.399 93.218

C,0,2.7600284795,-0.7199041182,0.0110331894
C,0,1.5465313877,-1.4107239122,0.0053587445
C,0,0.3546069124,-0.6982961193,-0.0196633589
C,0,0.3693476541,0.701788289,-0.0328157299
C,0,1.5760188324,1.3892955843,-0.020948706
C,0,2.7746996388,0.6733001819,-0.0020309376
C,0,-1.0371042581,-1.2899704962,-0.0177687705
C,0,-1.0095788636,1.3225986322,-0.0423220695
C,0,-1.7778530455,0.7939892114,1.1575022714
C,0,-1.7937283062,-0.7228261916,1.171819144
H,0,3.6951554096,-1.2711879242,0.0261991503
H,0,1.5334457602,-2.4972997209,0.0197227487
H,0,1.5858305206,2.4759840725,-0.0270086194
H,0,3.7212305328,1.2049589647,0.0029647247
H,0,-1.0370001263,-2.3801595132,-0.0435515741
H,0,-0.9864785374,2.4118675724,-0.0885833391
C,0,-1.8458065986,0.6908159725,-1.1399789328
C,0,-1.8600485832,-0.6614352,-1.1272769093
H,0,-2.5004268701,-1.2649113364,-1.7615946472
H,0,-2.4734702769,1.2955970477,-1.7856616577
H,0,-2.6663652805,-1.2561157454,1.5398810375
H,0,-2.6392573819,1.3522307492,1.5149102415

B.6.2.1.8. ***anti-TS 3*** ‡

/home/hanyclose/dipimethane/paper/DPM-TS1
opt=(ts,calcfc,noeigentest)
E(UwB97XD) = -463.006916991

Zero-point correction= 0.178187 (Hartree/Particle)
Thermal correction to Energy= 0.186526
Thermal correction to Enthalpy= 0.187470
Thermal correction to Gibbs Free Energy= 0.144187
Sum of electronic and ZPE= -462.828730
Sum of electronic and thermal Energies= -462.820391
Sum of electronic and thermal Enthalpies= -462.819447
Sum of electronic and thermal Free Energies= -462.862730

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 117.047 36.013 91.098

C,0,2.8063312875,-0.6439499163,-0.0310048655
C,0,1.6132437977,-1.3692014389,-0.0356276516
C,0,0.3991548887,-0.6930415654,-0.0317778531
C,0,0.3730150637,0.7085022795,-0.0146966875
C,0,1.5603240934,1.4289663487,-0.0093713625
C,0,2.7801936017,0.7488619864,-0.0183198433
C,0,-0.9809206642,-1.327291917,-0.0121188228
C,0,-1.0062006051,1.3075490724,-0.0095339753
C,0,-1.9094660273,0.6942256764,1.0346926305
C,0,-1.6863428986,-0.7578996031,1.2095808845
H,0,3.7572040403,-1.1679031831,-0.0375380695
H,0,1.6312838439,-2.4558666536,-0.0451531932
H,0,1.5393895928,2.5155116594,0.0024763005
H,0,3.710320378,1.3085998599,-0.0149328165
H,0,-0.935202462,-2.417696166,-0.0262106837
H,0,-1.0247688689,2.3960316342,-0.047046974
C,0,-1.926252548,0.6400016075,-1.0017196741
C,0,-1.8257301578,-0.7266731006,-1.1166749194
H,0,-2.4704950685,-1.3274180568,-1.7455704637
H,0,-2.6578246811,1.2342111363,-1.5386922603
H,0,-1.612995746,-1.2333931779,2.1825073499

H,0,-2.7989958601,1.2181685182,1.3645439503

B.6.2.1.9. ***syn-TS 3‡***

/home/hanyclose/dipimethane/synTS1.log
opt=(ts,calcfc,noeigentest)
Zero-point correction= 0.178063 (Hartree/Particle)
Thermal correction to Energy= 0.186475
Thermal correction to Enthalpy= 0.187419
Thermal correction to Gibbs Free Energy= 0.144071
Sum of electronic and ZPE= -462.830128
Sum of electronic and thermal Energies= -462.821716
Sum of electronic and thermal Enthalpies= -462.820772
Sum of electronic and thermal Free Energies= -462.864120

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	117.015	36.346	91.234

C,0,2.7811379457,-0.6584379951,0.0011035488
C,0,1.577626574,-1.3655557556,-0.0167694196
C,0,0.3746137786,-0.6707450221,-0.0314948151
C,0,0.3697134193,0.7288476766,-0.0266395995
C,0,1.5672048106,1.4330057292,-0.0074104142
C,0,2.776087291,0.7349527525,0.0059502845
C,0,-1.0028952031,-1.2886673588,-0.0456208031
C,0,-1.0068030468,1.3395882393,-0.045315562
C,0,-1.8892668955,0.7571840846,1.0314352848
C,0,-1.8286967082,-0.7183330392,1.0927263403
H,0,3.7238487882,-1.1967816048,0.0116423496
H,0,1.5798341481,-2.4523343843,-0.0189039524
H,0,1.5614788446,2.5197913154,-0.0028177184
H,0,3.714684059,1.2802954842,0.0201298692
H,0,-0.9837437062,-2.3781366871,-0.0651484426
H,0,-1.0045438648,2.4285127454,-0.0717748247
C,0,-1.8854553683,0.7059394146,-1.0963010345
C,0,-1.8490773166,-0.673202657,-1.1386302767
H,0,-2.5363170832,-1.2715353256,-1.7253735842
H,0,-2.5913088956,1.3052029863,-1.6600674991
H,0,-2.6290395659,-1.3011486832,1.535902333
H,0,-2.7216643249,1.3251062948,1.4298649256

B.6.2.1.10. ***anti-synTS***

/home/hanyclose/dipimethane/benzo-wb97xd-TStt-2
opt=(ts,calcfc,noeigentest)
E(UwB97XD) = -463.008784974

Zero-point correction= 0.178812 (Hartree/Particle)
Thermal correction to Energy= 0.187068
Thermal correction to Enthalpy= 0.188012
Thermal correction to Gibbs Free Energy= 0.144912
Sum of electronic and ZPE= -462.829973
Sum of electronic and thermal Energies= -462.821717
Sum of electronic and thermal Enthalpies= -462.820773
Sum of electronic and thermal Free Energies= -462.863873

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 117.387 35.684 90.711

C,0,2.7400505967,-0.7224207235,-0.0561019285
C,0,1.5239859468,-1.4093466186,-0.0297654326
C,0,0.3343567624,-0.6936891636,-0.0303614723
C,0,0.3545770968,0.7072883866,-0.053180086
C,0,1.5632367564,1.3910479007,-0.070895268
C,0,2.7595503418,0.670418383,-0.0767377176
C,0,-1.058159365,-1.2836774473,-0.0029766793
C,0,-1.0297168427,1.3267469255,-0.0141700883
C,0,-1.6838196867,0.7810859312,1.2415605798
C,0,-1.8140615767,-0.7250828409,1.1932446067
H,0,3.6732578314,-1.2771041333,-0.0601142797
H,0,1.5081789928,-2.4957743714,-0.0091749619
H,0,1.5764146555,2.477672654,-0.0821505266
H,0,3.7079472305,1.1984435855,-0.0969816583
H,0,-1.0617409315,-2.3737154262,-0.0418242844
H,0,-1.0053104725,2.4165675777,-0.0481938389
C,0,-1.8850235338,0.7040247098,-1.1044375741
C,0,-1.8979103167,-0.6443675174,-1.0976889054
H,0,-2.5423529074,-1.2465709597,-1.7295395899
H,0,-2.5079526278,1.3128610501,-1.7506261221
H,0,-2.7768789005,-1.1848273232,1.4182071046
H,0,-2.2382944795,1.4019358811,1.9336904126

B.6.2.1.11. 4

/home/hanyclose/dipimethane/paper/DPM-IM
opt
E(UwB97XD) = -463.033276343

Zero-point correction= 0.180078 (Hartree/Particle)
Thermal correction to Energy= 0.188289
Thermal correction to Enthalpy= 0.189234
Thermal correction to Gibbs Free Energy= 0.146306
Sum of electronic and ZPE= -462.853198
Sum of electronic and thermal Energies= -462.844987
Sum of electronic and thermal Enthalpies= -462.844043
Sum of electronic and thermal Free Energies= -462.886970

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 118.153 36.255 90.349

C,0,2.8268853688,-0.6155563176,-0.0004450348
C,0,1.6388018858,-1.3491086147,-0.00014544
C,0,0.4173929804,-0.6869659441,0.000093485
C,0,0.3718920301,0.7190344252,0.0000350479
C,0,1.5596381493,1.4437282974,-0.0002640109
C,0,2.7860352325,0.7765311962,-0.0005038166
C,0,-0.9585930802,-1.3557690641,0.0004316593
C,0,-0.9774698023,1.3377312897,0.0003044725
C,0,-2.0939880827,0.5998314265,0.7639369995
C,0,-1.7130349967,-0.760459662,1.1686677534
H,0,3.781944346,-1.1317645443,-0.0006319482
H,0,1.6649829912,-2.435788169,-0.0000982586
H,0,1.5305919621,2.5302570506,-0.0003105372
H,0,3.7096895359,1.3469429321,-0.0007367561
H,0,-0.8799737664,-2.4454235374,0.0004673701
H,0,-1.0310603837,2.4225175926,0.0002635272
C,0,-2.094327045,0.5997569829,-0.7627602092
C,0,-1.7135537695,-0.7605736393,-1.1675273461
H,0,-1.5980273976,-1.091935437,-2.1927578958
H,0,-2.7949257946,1.1951063614,-1.3364522457

H,0,-1.5970533535,-1.0917214416,2.1938792256
H,0,-2.7943320102,1.1952368165,1.3378819831

B.6.2.1.12. 5‡

/home/hanyclose/dipimethane/paper/DPM-TS2
opt=(ts,calcfc,noeigentest)
E(UwB97XD) = -463.020231267

Zero-point correction= 0.178805 (Hartree/Particle)
Thermal correction to Energy= 0.186787
Thermal correction to Enthalpy= 0.187731
Thermal correction to Gibbs Free Energy= 0.145156
Sum of electronic and ZPE= -462.841426
Sum of electronic and thermal Energies= -462.833444
Sum of electronic and thermal Enthalpies= -462.832500
Sum of electronic and thermal Free Energies= -462.875075

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	117.211	35.195	89.608

C,0,2.8195374171,-0.6532764763,-0.0253333681
C,0,1.6154061103,-1.3563884076,0.0491120982
C,0,0.407809816,-0.672419777,0.0840094756
C,0,0.3894179784,0.7423095939,0.0613008942
C,0,1.6015705234,1.4343137993,-0.0423744725
C,0,2.8080558354,0.7402218711,-0.0778386449
C,0,-0.9715209929,-1.3358496199,0.0920586494
C,0,-0.9016271965,1.4083619501,0.1137001887
C,0,-2.1113986994,0.6778856799,0.6279451795
C,0,-1.7507334527,-0.6512708704,1.189830851
H,0,3.7614681448,-1.1921563322,-0.0512549096
H,0,1.6179371408,-2.4433639916,0.0689966798
H,0,1.5970336466,2.5205923281,-0.0781425624
H,0,3.7425792855,1.2885484843,-0.144992184
H,0,-0.8917724254,-2.4226032585,0.1762380007
H,0,-0.970470275,2.4757015046,-0.0719205025
C,0,-2.2179381271,0.4219590801,-0.8559742367
C,0,-1.6936853003,-0.8292426993,-1.1458946495
H,0,-1.5429091519,-1.2404341209,-2.1363472007
H,0,-2.7333464875,1.0818040471,-1.5407765678
H,0,-1.5862013281,-0.8396730941,2.2451135802
H,0,-2.8690224614,1.2782403094,1.1262367015

B.6.2.1.13. 6

/home/hanyclose/dipimethane/paper/DPM-PD
opt
E(UwB97XD) = -463.037847860

Zero-point correction= 0.179876 (Hartree/Particle)
Thermal correction to Energy= 0.188287
Thermal correction to Enthalpy= 0.189232
Thermal correction to Gibbs Free Energy= 0.145841
Sum of electronic and ZPE= -462.857972

Sum of electronic and thermal Energies= -462.849560
Sum of electronic and thermal Enthalpies= -462.848616
Sum of electronic and thermal Free Energies= -462.892007

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 118.152 36.667 91.323

C,0,-2.8164379541,-0.6586040108,0.1198269053
C,0,-1.5909144835,-1.327458918,0.0456664861
C,0,-0.4030319874,-0.6252645375,-0.0860026208
C,0,-0.4244771264,0.806827248,-0.168152756
C,0,-1.6779762767,1.4602354077,-0.0747683919
C,0,-2.851901798,0.7385575629,0.0631359888
C,0,0.9658878771,-1.3075385258,-0.1300718492
C,0,0.7863927022,1.5240545151,-0.3413678454
C,0,2.0891815271,0.7458879256,-0.4193218935
C,0,1.7794135717,-0.5415952467,-1.1393020725
H,0,-3.7369519125,-1.2238560314,0.2254876778
H,0,-1.5638040889,-2.4130485189,0.0985076195
H,0,-1.70755167,2.5454764695,-0.1255366777
H,0,-3.80241861,1.2593820659,0.1245661708
H,0,0.8625836986,-2.3793349026,-0.319752465
H,0,0.7852161151,2.6103558894,-0.3491064886
C,0,2.3596149313,0.2039610903,0.9915407698
C,0,1.7155973927,-0.9539282259,1.1537885516
H,0,1.6274803513,-1.5228351181,2.0722110948
H,0,2.8956708631,0.7607746075,1.7515385017
H,0,1.6092909118,-0.598093147,-2.2102887006
H,0,2.8973259653,1.3446984007,-0.8453140057

B.6.2.1.14. 7

opt
E(UwB97XD) = -463.114940909

Zero-point correction= 0.183764 (Hartree/Particle)
Thermal correction to Energy= 0.191502
Thermal correction to Enthalpy= 0.192446
Thermal correction to Gibbs Free Energy= 0.151202
Sum of electronic and ZPE= -462.931177
Sum of electronic and thermal Energies= -462.923439
Sum of electronic and thermal Enthalpies= -462.922495
Sum of electronic and thermal Free Energies= -462.963738

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 120.169 34.082 86.804

C,0,-2.7726161279,-0.6393735755,0.4275024392
C,0,-1.5928073691,-1.3593665739,0.2199481043
C,0,-0.4570282231,-0.6784520987,-0.1946038247
C,0,-0.4812731505,0.7136130805,-0.3767312364
C,0,-1.6466192452,1.4317957912,-0.140969457
C,0,-2.7971499379,0.7441373879,0.2538588996
C,0,0.9706610016,-1.1834382647,-0.3680230035
C,0,0.8344877204,1.185012984,-0.8731842385
C,0,2.1549627599,0.9000107297,-0.086160606
C,0,1.6653404805,-0.0393238995,-1.1496918873
H,0,-3.6769088187,-1.1610455569,0.7255180529
H,0,-1.5712835021,-2.4352827501,0.370647931
H,0,-1.6695399661,2.5094824835,-0.2755294482

H,0,-3.7199059984,1.2910273935,0.4215551214
H,0,1.0541515747,-2.1780874445,-0.8107954786
H,0,0.8715553002,2.0459621444,-1.5330844176
C,0,2.1232393888,0.1531924294,1.1969601471
C,0,1.5483301918,-1.04491464,1.0385163869
H,0,1.3291930699,-1.7545692094,1.829154848
H,0,2.4867617755,0.5589373892,2.134176291
H,0,2.1851149502,-0.2111115561,-2.0855895158
H,0,2.9595241254,1.6004487557,-0.2861891078

B.6.2.1.15. 8

After scan r=1.3997 d=0.0471
freq=hpmodes
E(UwB97XD) = -462.989420116

Zero-point correction= 0.177365 (Hartree/Particle)
Thermal correction to Energy= 0.185169
Thermal correction to Enthalpy= 0.186113
Thermal correction to Gibbs Free Energy= 0.143677
Sum of electronic and ZPE= -462.812055
Sum of electronic and thermal Energies= -462.804251
Sum of electronic and thermal Enthalpies= -462.803307
Sum of electronic and thermal Free Energies= -462.845743

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	116.195	33.259	89.315

C -2.743379 0.694543 0.000946
C -1.532546 1.402157 0.000026
C -0.341567 0.699843 0.000896
C -0.341564 -0.699835 0.000875
C -1.532543 -1.402149 -0.000010
C -2.743376 -0.694537 0.000929
C 1.074776 1.284763 -0.001432
C 1.074779 -1.284767 -0.001408
C 1.756653 -0.699839 1.230648
C 1.756653 0.699852 1.230634
H -3.683781 1.236968 0.001568
H -1.532080 2.488890 -0.000949
H -1.532078 -2.488882 -0.000994
H -3.683778 -1.236964 0.001545
H 1.073866 2.375387 -0.016461
H 1.073855 -2.375390 -0.016413
C 1.754473 -0.665107 -1.229189
C 1.754421 0.665075 -1.229228
H 2.164143 1.289639 -2.014198
H 2.164228 -1.289683 -2.014131
H 2.167796 1.318221 2.018771
H 2.167149 -1.318193 2.019135