MECHANISTIC INVESTIGATIONS INTO THE ORIGIN OF SELECTIVITY IN ORGANIC REACTIONS

A Dissertation

by

JACQUELINE BESINAIZ THOMAS

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

August 2008

Major Subject: Chemistry

MECHANISTIC INVESTIGATIONS INTO THE ORIGIN OF SELECTIVITY IN ORGANIC REACTIONS

A Dissertation

by

JACQUELINE BESINAIZ THOMAS

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Approved by:

Chair of Committee,	Daniel A. Singleton
Committee Members,	David E. Bergbreiter
	Coran Watanabe
	Perla Balbuena
Head of Department,	David H. Russell

August 2008

Major Subject: Chemistry

ABSTRACT

Mechanistic Investigations into the Origin of Selectivity of Organic Reactions.
(August 2008)
Jacqueline Besinaiz Thomas, B.S., Texas A&M University-Kingsville
Chair of Advisory Committee: Dr. Daniel A. Singleton

Detailed mechanistic studies were conducted on several organic reactions that exhibit product selectivity (regio-, peri-, or enantioselectivity). The organic reactions studied were electrophilic aromatic substitutions, Diels-Alder cycloadditions of 1,3-dienes with cyclopentadieneone, Lewis acid catalyzed ene reactions with olefins, chlorinations of alkynes, and the enantioselective intramolecular Stetter reaction. Analyses of these systems were conducted by measurement of kinetic isotope effects, standard theoretical calculations, and in some cases dynamic trajectories.

Mechanistic studies of electrophilic aromatic substitution, Lewis acid catalyzed ene reaction with olefins, the chlorination of alkynes, and the Diels-Alder cycloadditions of 1,3-dienes with cyclopentadienones, suggest that the origin of selectivity is not always a result of selectivity result from a kinetic competition between two closely related pathways to form distinct products. All of these systems involve one transition state on a potential energy surface that bifurcates and leads to two distinct products. In these systems, experimental kinetic isotope effects measured using natural abundance methodology, theoretical modeling of the potential energy surfaces, and trajectory analyses suggests that selectivites (regio- and periselectivities) are a result of influences by momenta and steepest-descent paths on the energy surface. The work here has shown that in order to understand selectivity on bifurcating surfaces, transition state theory is not applicable. In place of transition state energetics, the guiding principles must be those of Newtonian dynamics.

In the mechanistic studies for the enantioselective intramolecular Stetter reaction, the origin of selectivity is a result of multiple transition states and their relative energies. Experimental H/D kinetic isotopes effects had lead to the conclusion that two different mechanisms were operating for reactions where carbenes were generated in situ versus reactions using free carbenes. However, ^{13}C kinetic isotope effects and theoretical modeling of the reaction profile provide evidence for one mechanism operating in both cases.

ACKNOWLEDGEMENTS

I would like to thank my advisor, Dr. Daniel A. Singleton for his guidance and support throughout the course of this research. I would also like to thank my committee member Dr. David E. Bergbreiter for all his guidance throughout the course of my undergraduate and graduate school experiences. To Dr. Coran Watanabe, and Dr. Perla Balbuena thank you for serving on my committee.

Thanks also go to my friends and colleagues and the department faculty and staff for making my time at Texas A&M University a great experience. I also want to extend my gratitude to the National Institute of Health, the National Science Foundation, and Texas A&M University.

Finally, thanks to my family for their encouragement and to my husband for his love and support.

TABLE OF CONTENTS

LIST OF FIGURES

Page

LIST OF TABLES

CHAPTER I

INTRODUCTION

Organic reactions usually produce a mixture of products. Understanding the origin of the product mixture is of great importance because it can offer insight to the mechanism by which the reaction takes place. Distinct products can be the result of independent reactions pathways where each reaction can be considered separate. Sometimes the product mixture is the result of one or more products undergoing a secondary reaction to produce other products, and sometimes the mixture of products are the result of equilibration. In many reactions, however, the interesting cases are those where selectivity results from a kinetic competition between two closely related pathways. In such cases, understanding can be gained by detailed study of the interrelation of the products.

Kinetic selectivity is generally assumed to be controlled within the framework of Transition State Theory (TST). In TST, the rate of a reaction is governed by the energy barrier for formation of the product. This energy barrier is associated with the transition state which is itself technically an energy hypersurface separating starting materials from products. TST then predicts the rates of reactions from this energy hypersurface, including its enthalpy and entropy. Kinetic selectivity is then governed by the relative

---

This dissertation follows the style and format of *The Journal of the American Chemical Society*.

heights of the energy barriers leading to alternative products. In general, the product from a transition state is generally assumed to be the minimum obtained from following the steepest-descent path in mass-weighted coordinates. Such a process by its nature can only lead to a single product. TST for systems with one energy barrier fails to predict in some case the ratio of distinct products. When one transition state can lead to two products, chemistry currently has no qualitative way to predict the ratio of the two. In fact, chemistry has no qualitative theory that predicts that a second product can be formed at all. This dissertation aimed to understand selectivity for systems that proceed through a single transition, and it will be seen that the observed selectivity can be the result of steepest-descent path and Newtonian motion on a bifurcating energy surface.

In order to accurately determine the origin of kinetic selectivity in systems with closely related pathways, physical organic techniques were employed. Such physical organic techniques where determine contributing factors include reaction rate studies, measuring experimental kinetic isotope effects (KIE), predicting theoretical isotope effects, and running dynamic trajectories in some cases.

Kinetic Isotope Effects

Measuring KIEs is a very useful tool for physical organic chemists for probing into a reaction mechanism. Because KIEs are a measure of the change in rate for a reaction resulting from isotopic substitution, the result is correlated with the highest energy barrier or the first irreversible energy barrier in the reaction. Variations in the rate with competing isotopes are caused by differences in their zero-point energies as shown in Figure 1.

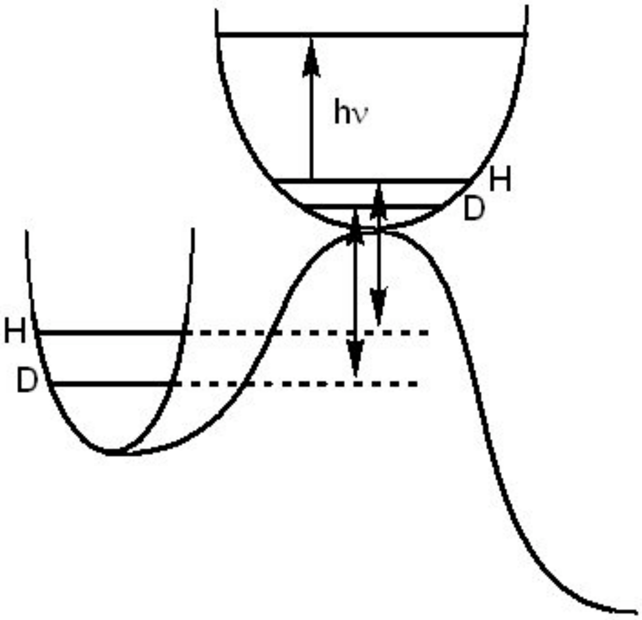


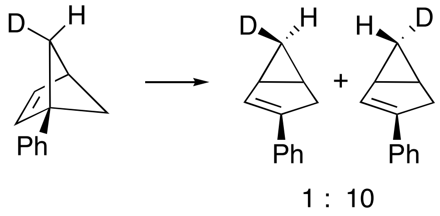
Figure 1. Depiction for the origin of primary isotope effects caused by the zero point energy differences in protium versus deuterium.

The traditional method for measuring KIEs is to measure differences in reaction rates of labeled versus unlabeled material. This method is very useful when labeled material is readily available, however, ^{13}C labeled material is often very expensive and often time consuming to synthesize. For these reasons, all of the ^{13}C KIEs reported in this dissertation were measured at natural abundance using NMR methodology developed by Singleton and co-workers.[1-3] In this method, as a reaction proceeds to high conversion, the unreacted starting material is naturally enriched with slower reacting isotopes, ^{13}C versus ^{12}C, at the reactive centers in the first irreversible step in the reaction. The isotopic content of the recovered unreacted starting material then is compared to that of the original starting material and it is then through a comparison of the relative ^{13}C integrations and taking into account the enhancement that the experimental KIE is obtained. This methodology is very effective in determining the rate-determining step in chemical reactions.

Dynamic Effects

For organic reactions where only one transition state exists on bifurcating energy surfaces, the factors that affect selectivity has been termed “dynamic effects.” Dynamic effects is a term that is used to describe many different phenomena in chemical reactions, however, in the context of this dissertation, dynamic effects is a term used to describe experimental observations that are not understood with current forms of TST. In TST, there is an assumption that intramolecular vibrational energy redistribution (IVR) is fast on the timescale of motion along the reaction coordinate, thus the determining factor in selectivity is relative energy barriers on a hypersurface.[4] This assumption does not hold up for some reactions. It has been shown that selectivity is sometimes controlled by dynamic effects - influences by atomic motion and momenta on a bifurcating energy surface which sometimes cause nonstatistical results.[5]

In 1984 Carpenter brought to light this important phenomena with examples of organic reactions involving diradicals. In one such system, the product ratios for the rearrangement of bicyclo[2.1.1]hexane-5-*d* provided evidence for unusual selectivity. In this rearrangement, one would have expected either pure retention or pure inversion, however, a mixture of both isomers was observed.[6]



In general, on bifurcating energy surfaces (Figure 2), reactants that pass through a rate-limiting transition state can proceed to form two products without an additional barrier. For symmetrical surfaces of this type (Figure 2a), the MEP bifurcates and two products are formed in equal amounts. Such surfaces are typically associated with symmetry breaking and have been analyzed theoretically for many simple reactions.[7-19]

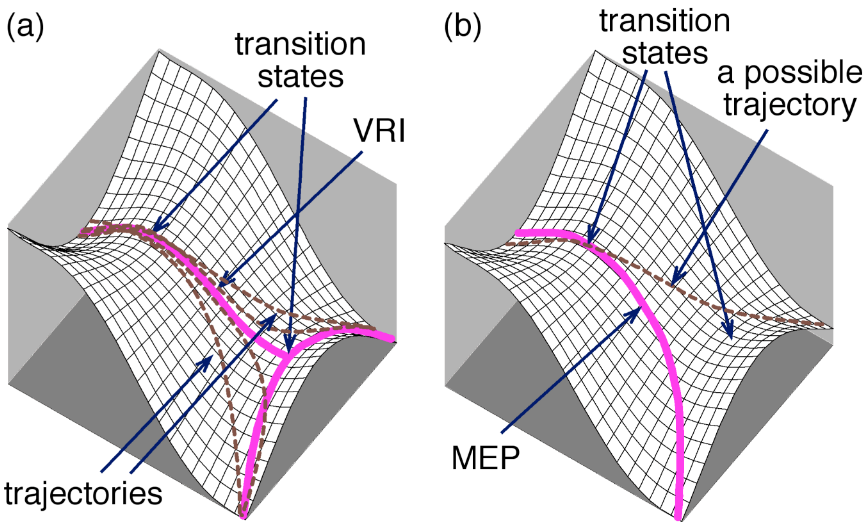


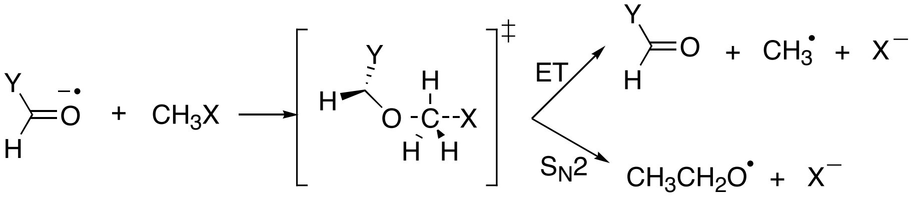
Figure 2. Bifurcating surfaces in which dynamic effects would control selectivity. (a) On a symmetrical surface, the MEP bifurcates at a second transition state. Real trajectories tend to diverge from the MEP in the area of the valley-ridge inflection point (VRI). (b) The surface is unsymmetrical and the MEP does not bifurcate. However, trajectories may afford a product not on the MEP.

One simple reaction of great importance is the gas phase S_N2 reaction of alkyl halides. Hase has conducted studied on S_N2 reactions (eq 1), where X and Y are distinguishable chloride ions. Theoretical results show that both possible ion dipoles, **A** and **B**, exist at the bottom of a deep potential energy well. As a result, this allows each ion dipole to be considered as a distinct and stable intermediate on the potential energy surface. The IVR was slow in this system, and no intermediate was formed during the course of the reaction. Instead, product was formed directly.[20]

$$X^{-} + CH_3Y \longrightarrow \underset{\textbf{A}}{X^{-}\text{---}CH_3Y} \longrightarrow \underset{\textbf{B}}{XCH_3\text{---}Y^{-}} \longrightarrow XCH_3 + Y^{-} \qquad (1)$$

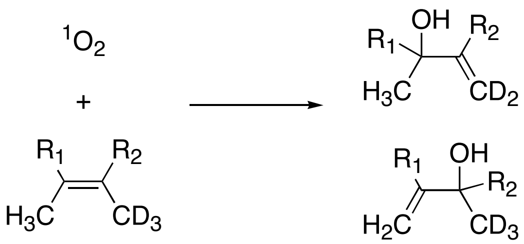
Unsymmetrical bifurcating surfaces (Figure 2b) are far less understood and are potentially more interesting chemically because trajectories may lead to two non-equivalent products.[21-28] Because the MEP does not bifurcate on these surfaces, TST is not able to predict the ratios of products,[29] and presently no qualitative theory exists for predicting the selectivity. As a result, the identity of the major product and the ratio of products can only be understood by consideration of dynamic trajectories.[5]

The electron transfer – substitution mechanism involving ketyl radical anions with alkyl halides has been studied theoretical and found to involve an unsymmetrical bifurcating energy surface.[21, 27, 28] In this reaction, a high-energy transition state was found and is described as an S_N2-like transition state. Trajectory analysis showed that once reactions were past this high-energy transition state on the energy surface, the molecule was able to form two distinct products (eq 2). The product mixture cannot be predicted from TST.

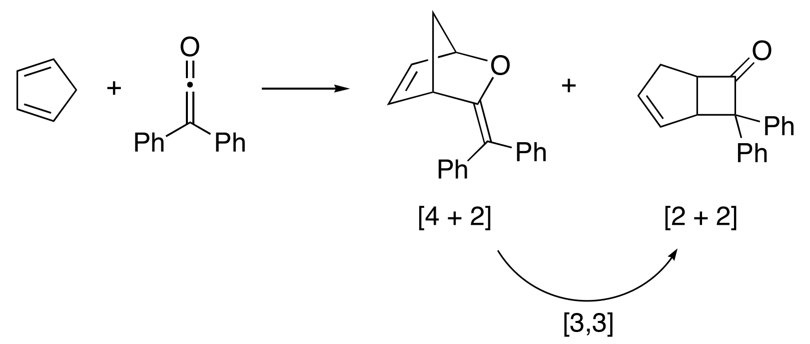


(2)

Singleton and co-workers have also conducted a detailed mechanistic study for the ene reaction of singlet oxygen with simple alkenes. In this study, intermolecular KIEs were obtained for the reaction of singlet oxygen with 2,4-dimethyl-3-isopropyl-2-pentene and intramolecular KIEs were obtained for the reaction with tetramethylethylene. The experimental KIE results suggest that the reaction is taking place via a two-step mechanism since the rate-determining (intermolecular) and the product selectivity-determining (intramolecular) KIEs did not correlate with each other. However, experimentally and theoretically, no intermediate was isolated or predicted to be a minima on the energy surface. This reaction is thought to involve a bifurcating energy hypersurface with an early transition state where singlet oxygen does not decide which olefinic carbon it will react with until it has reached the valley ridge inflection point. The origin of the intramolecular KIE is not a result of a kinetic competition between two high energy barriers for ^{12}C versus ^{13}C, but is a result of symmetry breaking in this symmetrical system.[5, 24, 25]



In a study of the cycloaddition of cyclopentadiene with ketenes, Singleton and Ussing provided evidence that dynamic effects are determining factors in regioselectivities observed for these reactions. Through a detailed kinetic study, they were able to observe the formation of both the [4+2] and [2+2] cycloadducts from the start of the reaction, which an earlier study had overlooked. The kinetic study showed that as the reaction progressed, the [4+2] under went a [3,3] sigmatropic rearrangement to the [2+2] cycloadduct. Also, relatively small experimental intramolecular KIEs were observed for the [2+2] cycloadduct of the diphenylketene reaction. One would have expected to obtain a larger KIE as in the case of the dichloroketene system. This experimental observation of low intramolecular KIE cannot be understood with a TST analysis but can be understood by a trajectory analysis. When starting from one single transition state for the diphenylketene system, quasiclassical trajectories not only afforded both [4+2] and [2+2] products but also many trajectories recrossed to reform starting materials. The trajectory evidence leads to the assumption that in this case, the decision for product determination is not final until it has reached the second transition state (transition state for product rearrangement) on the energy hypersurface, thus giving relatively small KIEs for this system.[5]

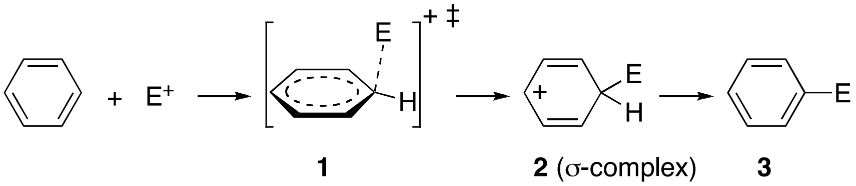


As seen from the examples given, by gathering information such as reaction rates, experimental KIEs, theoretical KIEs, and in some cases, trajectory analysis, selectivity in various reactions one can determine the origin of selectivity in a reaction.

CHAPTER II

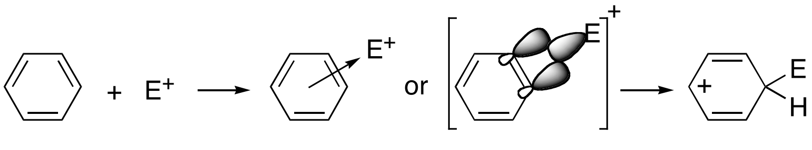
ELECTROPHILIC AROMATIC SUBSTITUTION

The understanding of reactivity and regioselectivity in electrophilic aromatic substitution reactions had a substantial role in arguments in the 1920's and 1930's over the nature of organic structures,[30] then was important again in the 1950's and 1960's in the rise of quantitative physical organic chemistry. The vast observations associated with electrophilic aromatic substitution can usually be understood within a limited mechanistic framework involving electrophilic attack via a transition state resembling **1** to afford an intermediate cation, e. g. **2**, referred to as a σ-complex. This intermediate then loses a proton to form the substituted product **3**. The evidence supporting this simple mechanism is diverse, but a cornerstone observation is a general correspondence between the stability of the intermediate σ-complex, the reactivity of the aromatic, and the regioselectivity of product formation. The relationship between reactivity and selectivity is delineated quantitatively in the "Brown selectivity relationship"."[31] In a series of studies in the 1950's, Brown found that reactivity and isomer selectivity correspond in many simple electrophilic aromatic substitution reactions.[32-41] This correspondence is strong evidence that a single transition state is both rate limiting and product determining, as would be expected for a transition state resembling **1** leading to the σ-complex. A subtle but critical implicit assumption in this analysis is that any particular transition state can only lead directly to a single product. This is not always the case when bifurcating energy surfaces are involved.[14, 42-47] In this chapter, evidence for a bifurcating energy surface will show that under some circumstances play a role in the selectivity and mechanism of electrophilic aromatic substitution reactions.



In considering whether bifurcating surfaces might play a role in electrophilic aromatic substitution, it was best to explore reactions in which the electrophilic addition step has an "early" transition state. When the transition state for the addition of an electrophile to an aromatic is "late," the electrophile will be committed to forming a bond with a particular carbon and no dynamic choice of products is possible. This is the case for most simple electrophilic aromatic substitutions, as recognized by Hammond.[48] An early transition state could in contrast provide the possibility that the ultimate regioselectivity of the attack might not be yet be decided. From Hammond's postulate, an early transition state should result from the combination of highly reactive electrophiles and highly activated aromatics.

Intriguingly, this is exactly the situation that has historically been mechanistically most controversial. Olah observed a series of reactions of strong electrophiles that display low intermolecular substrate selectivity (as a measure of relative reactivity of pairs of aromatics) but high positional (intramolecular) selectivity in product regioselectivity.[49] Based on this breakdown in the Brown selectivity relationship, Olah proposed that the inter- and intramolecular selectivities were determined in different steps, with intermolecular selectivity determined in a rate-limiting formation of a loose π-complex (**4**) (an intermediate first proposed by Dewar[50, 51]) followed by intramolecular selectivity determined in the formation of the σ-complex.



4 (π-complex)

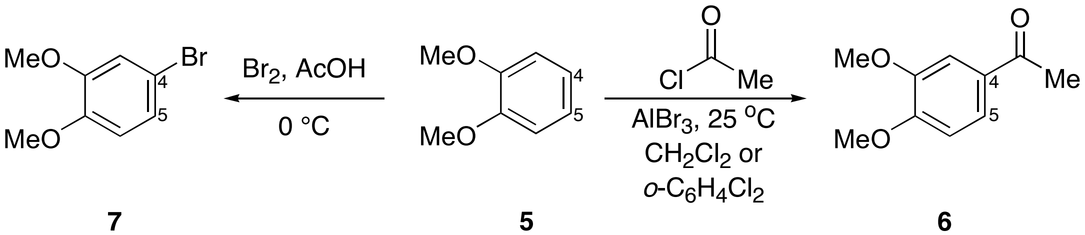
Olah's proposal has been heavily criticized. A real breakdown in the Brown selectivity relationship is unambiguously indicative of the presence of two kinetically distinguishable steps in a reaction, but Ridd suggested that the first of these steps is more likely to be either macroscopic mixing or diffusional encounter.[52] In broad analyses of toluene / benzene rate ratios and selectivities, anomalies were found to be rare.[53, 54] A number of the apparent failures of the Brown selectivity relationship have been proposed to be fallacious.[55, 56] From the perspective of modern kinetic understanding, the rate-limiting formation of a π-complex as a separate step from diffusional encounter is unattractive because other weak complexes are typically formed at encounter-controlled rates.[57] Despite these criticisms, some anomalies in selectivity observations are not readily rationalized or discounted, and this seems particularly the case with aromatics more reactive than toluene in their reactions with strong electrophiles.[58-66]

The Brown relationship between intermolecular substrate selectivity (reactivity) and intramolecular positional selectivity in electrophilic aromatic substitution is analogous to a well-known phenomenon in kinetic isotope effects (KIEs). When a reaction involves a single rate-limiting / product-determining step, intermolecular and intramolecular KIEs must correspond in a consistent manner.[67] If they do not, the rate-limiting and product-determining steps must be separate. In conventional analyses, a lack of correspondence of intermolecular and intramolecular KIEs is considered to be proof of an intermediate, though it has been found that the dynamics of bifurcating energy surfaces can result in a reaction having two kinetically distinguishable steps without an intermediate.[25]

In this chapter, the combination of intermolecular and intramolecular KIEs has been applied as a new and advantageous form of the Brown selectivity relationship for electrophilic aromatic substitution. In the reaction of veratrole with a weak electrophile, the relationship holds, supporting the conventional mechanism. However, the relationship fails with a reactive electrophile, giving unusual intramolecular KIEs that are not rationalizable by a conventional mechanism. The combination of the experimental KIEs, standard theoretical calculations, and trajectory studies support a role for dynamic trajectories in controlling selectivity in some electrophilic aromatic substitutions.

Results

The Friedel-Crafts acylation of veratrole (**5**) was chosen for study. Veratrole is highly reactive in electrophilic aromatic substitution reactions, and this high reactivity was interestingly used by Dewar as an argument for the importance of π-complexes.[51] The C_4 and C_5 positions of veratrole are of course equivalent in the absence of isotopic substitution, and high selectivity for substitution at these positions is typically observed. Particularly high selectivity is observed for acetylation of veratrole, as no product could be detected resulting from substitution at the C_3 position. However, the intermolecular substrate selectivity of acylation is in a medium range among electrophilic aromatic substitution reactions.[68] Under the carefully studied conditions of Rapoport,[69] the acylation of veratrole with acetyl chloride mediated by aluminum bromide affords 3',4'-dimethoxyacetophenone (**6**) at 25 °C with no detectable byproducts at up to 90% conversion.



7 **5** **6**

For comparison with a reaction expected to follow a conventional electrophilic aromatic substitution mechanism, the bromination of veratrole in acetic acid at 0 °C was studied. Under these conditions, the electrophilic attack appears to involve a late transition state for formation of a σ-complex, as the reactivity of diverse aromatics closely parallels the stability of corresponding σ-complexes.[49] As additional mechanistic evidence, bromination in acetic acid follows the Brown selectivity relationship.[31] The bromination of veratrole affords 4-bromoveratrole (**7**) in nearly quantitative yield, accompanied by approximately 0.4% of the isomeric 3-bromoveratrole.

Intermolecular ^{13}C KIEs. Intermolecular KIEs are the measure of the impact of isotopic substitution on the overall reactivity of a molecule, reflecting the transition state for the rate-limiting step in a reaction. The intermolecular ^{13}C KIEs for the Friedel-Crafts acylation of veratrole were determined combinatorially at natural abundance by NMR methodology.[3] Acylations of veratrole mediated by aluminum bromide at 25 °C in CH_2Cl_2 were taken to 82 ± 2% and 86 ± 2% conversion using limiting acetyl chloride, and the unreacted veratrole was recovered by an aqueous workup followed by column chromatography. The recovered veratrole was then analyzed by ^{13}C NMR by comparison with a standard sample of veratrole that was taken from the same reagent bottle. The relative changes in ^{13}C isotopic composition in the aromatic carbons were determined using the methoxy carbons as an internal standard with the assumption that their isotopic composition did not change during the reaction. A problem encountered in this analysis was that the very sharp peak for the quaternary carbons of veratrole was not well integrable, so that the change in isotopic composition at these positions could not be determined. From the changes in isotopic composition of the aromatic carbons, the ^{13}C KIEs were calculated as previously described.[3]

The results are shown in Figure 3. The key observation is that the isotope effects for the aromatic carbons are all very small (Figure 3a), essentially within experimental error of unity. The qualitative interpretation is that the rate-limiting transition state involves little or no bonding of the electrophile to the aromatic carbons. For electrophilic attack to be rate limiting, the transition state would have to be very early. Alternatively, the isotope effects could be considered reasonably consistent with rate-limiting diffusional encounter of the electrophile.

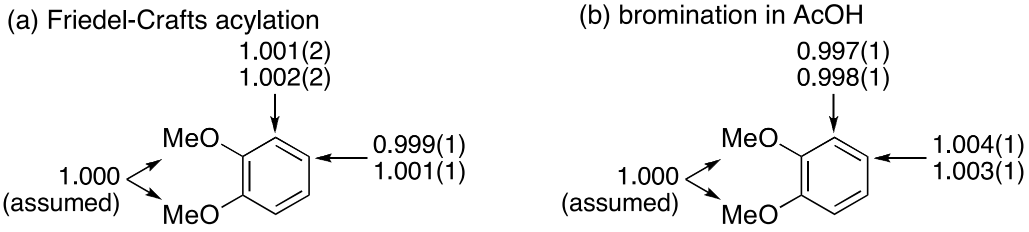


Figure 3. Intermolecular ^{13}C KIEs for electrophilic aromatic substitution reactions. (a) Friedel-Crafts acylation using acetyl chloride / $AlBr_3$ in CH_2Cl_2 at 25 °C. (b) Bromination using Br_2 in acetic acid at 0 °C.

To obtain KIEs for bromination in acetic acid, reactions of natural-abundance veratrole were taken to 77 ± 2% and 74 ± 3% conversion using limiting bromine at 0 °C, and the unreacted veratrole was recovered by removing most of the acetic acid under vacuum, followed by an aqueous workup and fractional vacuum distillation. NMR analysis as before led to the isotope effects shown in Figure 3b.

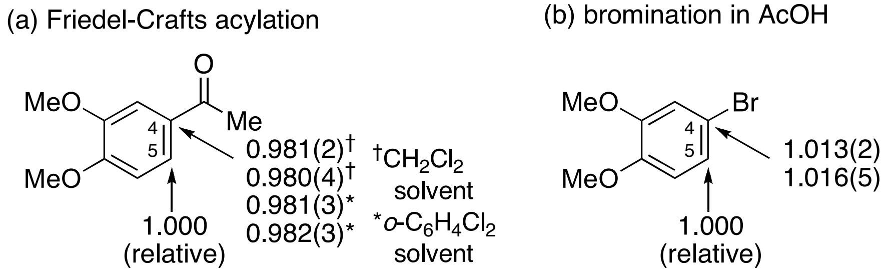
The KIE of $\approx$1.0035 at C_4 / C_5 is quite small for positions expected to exhibit a primary isotope effect, but it should be recognized that the observed isotope effects for the symmetrical veratrole are necessarily an average of the individual isotope effects at the C_4 and C_5 positions. For an unsymmetrical electrophilic attack, the carbon not being attacked would be expected to have a very small isotope effect that would be averaged with that for the carbon being attacked, lowering the overall KIE observed. Overall, the C_4 / C_5 KIE, while small, is qualitatively consistent with a rate-limiting electrophilic attack on one of these carbons. A more quantitative interpretation of the isotope effects will be possible below with the aid of theoretically calculated isotope effects.

Intramolecular ^{13}C KIEs. Intramolecular KIEs reflect the relative facility of two branches of a mechanism that are equivalent, except for isotopic substitution. As such, intramolecular KIEs characterize the first irreversible step undertaken by an initially symmetrical molecule after losing symmetry on the path to product, and this step will be referred to here as the 'product-determining step.'

The intramolecular ^{13}C KIE at C_4 / C_5 for acylation of veratrole was determined from analysis of samples of the product **6** obtained from acylations taken to 46-48% conversion, using methodology for the accurate and precise measurement of the relative integrations of pairs of peaks within a spectrum.[25, 70, 71] This includes high digital resolution, long delays, centering of the peaks of interest within the spectral window, and integration ranges that are a constant multiple of the peak width at half height. A complication in the numerical interpretation of these integrations is that C_4 is subject to three ^1J ^{13}C-^{13}C couplings with satellites not included in the integration range, while C_5 is only subject to two such satellite couplings. To allow for this, the integrations at C_4 was adjusted by the 0.0107(8) natural abundance of ^{13}C.[72] After this correction, the integration of the ^{13}C peak for C_4 of **6** was surprisingly 2% greater than that for C_5. The excess ^{13}C in the acylated carbon was consistent in a total of four samples, two each from reactions in dichloromethane and *o*-dichlorobenzene. The intramolecular KIE, defined as ($^{12}k/^{13}k$ at C_4) / ($^{12}k/^{13}k$ at C_5) was then calculated as the reciprocal of the ratio of ^{13}C composition in the two positions.

The results are shown in Figure 4. The observation of a substantial inverse KIE in this reaction (Figure 4a) is highly unusual and is opposite to what would be expected for a transition state involving carbon-carbon bond formation at C_4. No effect of solvent was observed – allowing for the uncertainties the KIEs in the two solvents were identical.

For comparison, the intramolecular ^{13}C KIE at C_4 / C_5 for bromination in acetic acid (Figure 4b) was determined by analysis of **7** obtained from reactions taken to 91-93% conversion. (No detectable dibromination product was observed in these reactions.) In this case, the ^{13}C composition in the brominated C_4 carbon was less than in C_5 position. This isotopic compositions corresponded to experimental intramolecular KIEs, defined as with **6**, of 1.013-1.016. In this case the normal isotope effect fits with qualitative expectations for a product-determining transition state involving formation of a carbon-bromine bond.


(a) Friedel-Crafts acylation

(b) bromination in AcOH

Figure 4. Intramolecular ^{13}C KIEs, defined as ($^{12}k/^{13}k$ at C_4) / ($^{12}k/^{13}k$ at C_5), for electrophilic aromatic substitution reactions. (a) Friedel-Crafts acylation using acetyl chloride / $AlBr_3$ in either CH_2Cl_2 or *o*-dichlorobenzene at 25 °C. (b) Bromination using Br_2 in acetic acid at 0 °C.

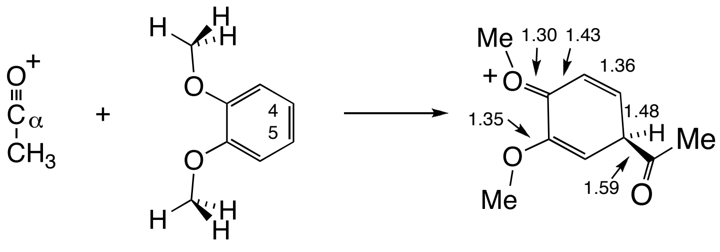
H/D KIEs. In some electrophilic aromatic substitution reactions, loss of a proton from the intermediate σ-complex can be fully or partially rate limiting. This includes Friedel-Crafts acylation reactions under some conditions.[73, 74] Rate-limiting deprotonation of the σ-complex would still not account for inverse isotope effect observed in acylation, as a normal ^{13}C KIE would be expected for the deprotonation step. However, it was important to evaluate this potential complication.

For this reason, the H/D KIEs were studied for veratrole. Veratrole-d_4 was prepared by successive exchange reactions at ≈100 °C with D_2O / H_2SO_4 followed by D_2O / D_2SO_4, and was found to be 98.6% deuterated in the aromatic positions based on NMR analysis. Acylations of 1:1 mixtures of veratrole-d_4 and veratrole-d_0 taken to 7% and 6% conversion (limited by rapid quenching with an excess of an aqueous bicarbonate solution) afforded in both cases a 1.01 : 1 ratio of 6 : 6-d_3 by NMR analysis (using 21.6 s delays, ≈5 x T_1, between $\pi/2$ pulses). Mass spectral analysis of recovered veratrole from each reaction revealed that negligible H / D exchange had occurred in the starting material under these conditions. The k_H/k_D of 1.01 (± ≈5%) rules out rate-limiting deprotonation of a σ-complex.

Theoretical Studies

The Energy Surface for Addition of Acylium Cation to Veratrole. The application of theoretical calculations to mechanistic studies of electrophilic aromatic substitution represents a substantial challenge due to the importance of charge-separated species in the mechanistic pathway. To mitigate this problem, the calculational models here employ a variety of approaches. Initially, the issue of zwitterionic charge separation was avoided by looking at cationic species in the absence of a counterion, either in the gas phase or including implicit or explicit solvent models. Then later, a counterion was included along with implicit or explicit solvent. Ultimately, it is questionable whether any practical theoretical model can adequately and reliably represent the energy surface for the reaction in solution. Instead, the goal was to calculationally explore mechanistic models against which the unusual experimental observations can be interpreted.

In gas-phase DFT calculations (B3LYP/6-31+G**), the addition of acylium cation (**8**) to C_4 / C_5 of veratrole to afford **9** is downhill by 30.6 kcal/mol (pot. E + zpe) and there is no potential energy barrier for the reaction. Solvent will tend to preferentially stabilize the more localized charge of 8 over the delocalized charge of **9**, but **9** is still downhill from **8** + veratrole by 11.9 kcal/mol (B3LYP/6-31+G**/PCM + zpe with full geometry optimization) when a PCM solvent model for CH_2Cl_2 is employed.



8 $E_{rel} = 0$ **5**

9 $E_{rel} = -11.9$
[-30.6 gas phase]

Relaxed energy surfaces for approach of **8** to veratrole were calculated by fixing the C_α-C_4 and C_α-C_5 distances at a grid of values and optimizing the remaining geometrical variables at each point. The B3LYP/6-31+G**/PCM + zpe surface generated in this way is shown in Figure 5. Similar surfaces were obtained for the gas phase (though the surface is more sloping due to the greater exothermicity in the gas phase) and in MP2/6-31+G** calculations in both the gas phase and with a solvent model. The essential feature of each of these surfaces is that the preferred approach of **8** is symmetrical between C_4 and C_5 at long C_α-C_4/C_5 distances. As **8** comes closer to veratrole, its approach ultimately breaks symmetry to afford chiral **9**, but the symmetry breaking is not favored until the C_α-C_4/C_5 distances are less than 2.8 Å.

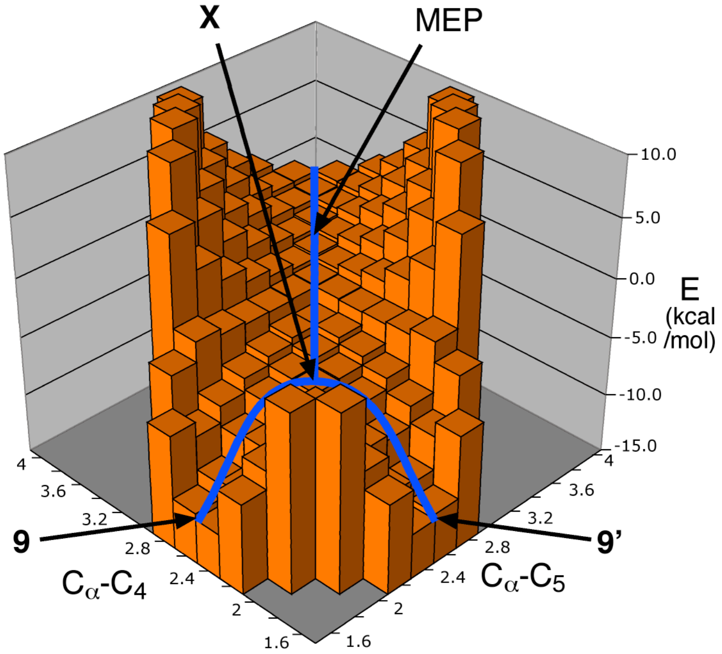
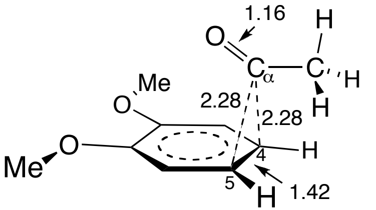
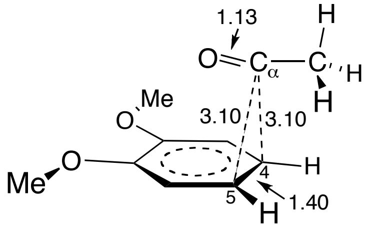


Figure 5. Energy surface (B3LYP/6-31+G**/PCM + zpe) for the approach of acylium ion 8 to veratrole, fixing C_α-C_4 and C_α-C_5 distances at the values specified on the grid. Higher-energy points at the left, right, and front of the grid have been left out for clarity.

In more technical detail, the reaction's minimum-energy path (MEP, the steepest-descent path in mass-weighted coordinates starting from a geometry with C_α-C_4 and C_α-C_5 distances of 3.95 Å) passes through a C_s-symmetric channel in which modes orthogonal to the MEP all have a positive curvature. The MEP then passes a valley-ridge inflection point (VRI) when C_α-C_4 = C_α-C_5 = 2.8 Å, at which one of the modes has a zero curvature. At shorter distances, an orthogonal mode involving side-to-side motion of the acylium ion has a negative curvature, and real trajectories will tend to diverge from the MEP. The MEP itself can only bifurcate at a stationary point, and it proceeds to saddle point **10**‡, the transition structure for a 1,2-migration of the acyl group equilibrating **9** and its enantiomer **9'**.



10‡ E_{rel} = -4.1
(versus **8** + veratrole)



11‡ E_{rel} = -1.3
(versus **8** + veratrole)

Within this calculational model, the addition of acylium cation to veratrole has no meaningful conventional transition state.[75] The canonical variational transition state, that is, the starting materials / product dividing surface for which the free energy is a maximum, can be approximated from entropy estimates based on the unscaled harmonic frequencies. This in itself is problematic due to the inaccuracy of such entropy estimates for loose structures, but following the MEP the free energy reaches an approximate plateau centered on structure **11**‡ with a C_α-C_4 / C_α-C_5 distance of 3.1 Å. It should be noted that the normal mode associated with the imaginary frequency in **11**‡ involves forward / back motion of the acylium ion versus the veratrole, while the imaginary mode in **10**‡ involves side-to-side motion.

Addition in the Presence of Explicit Solvent. The real reaction could be complicated by the presence of solvent molecules in ways that are not accounted for in implicit solvent models. For example, assuming that **8** approaches the veratrole symmetrically, the arrangement of solvent molecules surrounding the reactants as the approach progresses will in any individual case be unsymmetrical. It might be envisioned that the arrangement of solvent molecules could dictate whether **9** or **9’** is formed. In addition, the preference for symmetrical approach could conceivably be lost if explicit solvent best stabilized an unsymmetrical approach. Finally, solvent could certainly affect the position of the variational transition state, and an unsymmetrical transition state would be anticipated if the transition state is sufficiently late.

To study these issues, a calculational model reaction including 22 explicit CH_2Cl_2 molecules was explored in ONIOM calculations using a B3LYP/6-31G* layer for the **8** + veratrole, and using an AM1 layer for the CH_2Cl_2 molecules, shown in Figure 6. Low-energy solvent configurations in the area of the energy surface for attack of **8** on veratrole were obtained by simulated annealing with a maximum temperature of 600 K and confining the molecules to a 14 Å cubic box, fixing the C_α-C_4 / C_α-C_5 distances at 3.1 Å. Of the structures found, **12** was lowest in energy, though the necessarily limited annealing process is unlikely to have found the global minimum. Classical trajectories started statistically at 25 °C from **12** and other low-energy structures invariably resulted in formation of **9** or **9’** within 1000 fs. This supports the idea that **12** is past the variational transition state for addition of **8** to veratrole.

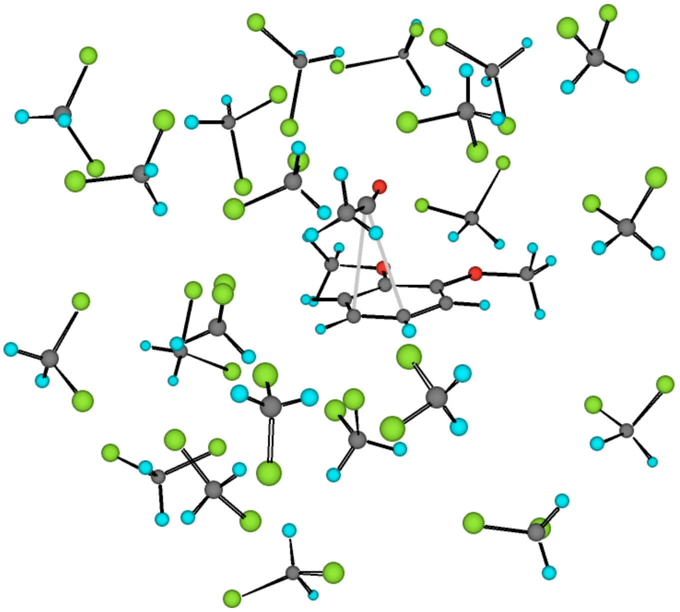
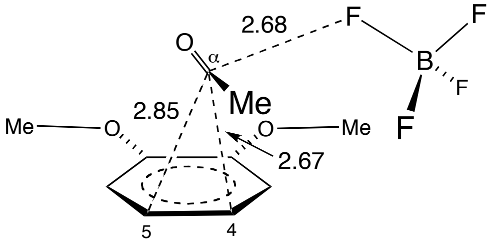


Figure 6. 22 explicit CH_2Cl_2 molecules was explored in ONIOM calculations using a B3LYP/6-31G* layer for the **8** + veratrole, and using an AM1 layer for the CH_2Cl_2 molecules (**12**).

Addition Including the Counterion. The $AlBr_3Cl^-$ counterion involved in this experimental reactions was computationally modeled here for simplicity as BF_4^-, assuming that the choice of the counterion would not qualitatively affect the mechanism. In B3LYP/6-31+G**/PCM calculations, transition structure **13** was located for the reaction of veratrole with an acylium BF_4^- ion pair. Unlike the reaction in the absence of counterion, the reaction including the counterion faces a conventional potential energy barrier. However, with C_α-C_4 at 2.67 Å, the transition structure is still quite early with respect to carbon-carbon bond formation. A notable feature of **13** is that the counterion has imparted asymmetry to the approach of the acylium ion to the veratrole – the C_α-C_4 and C_α-C_5 distances are now unequal. In principle the loosely bound BF_4^- could adopt a position anti to the incoming nucleophilic veratrole, but this would lead to greater charge separation between the BF_4^- and the incipient positive charge on the aromatic ring.



13‡

While structure **13** is a saddle point on the potential energy surface, entropy will also affect the distance between the loosely coordinated counterion and the acylium ion as the attack on veratrole proceeds. To gauge qualitatively the effect of entropy on the looseness of the counterion association, classical trajectories were initiated from **13** at 25 °C, fixing the C_α-C_4 and C_α-C_5 distances but leaving all other motions variable. When this is done, the BF_4 ion traverses its potential energy well over time in a way that reflects both the potential energy and the classical entropy. The average distance between C_α and the nearest fluorine atom over a series of 1 ps trajectories was 3.2 Å. This implies that the counterion association as the acylium ion approaches the veratrole is likely much looser than suggested by **13**. This will tend to decrease the approach asymmetry induced by the counterion.

Predicted Isotope Effects. The ^{13}C KIEs based on **12** and **11**‡ and the bromination derivatives were predicted from scaled theoretical vibrational[76] frequencies using conventional transition state theory by the Bigeleisen and Mayer method.[77-79] Tunneling corrections were applied using a one-dimensional infinite parabolic barrier model.[80] Such KIE predictions have proven highly accurate in reactions not involving hydrogen transfer, so long as the calculation accurately depicts the mechanism and transition state geometry. [2, 21, 23, 26-28, 81, 82] The results are shown in Figure 7.

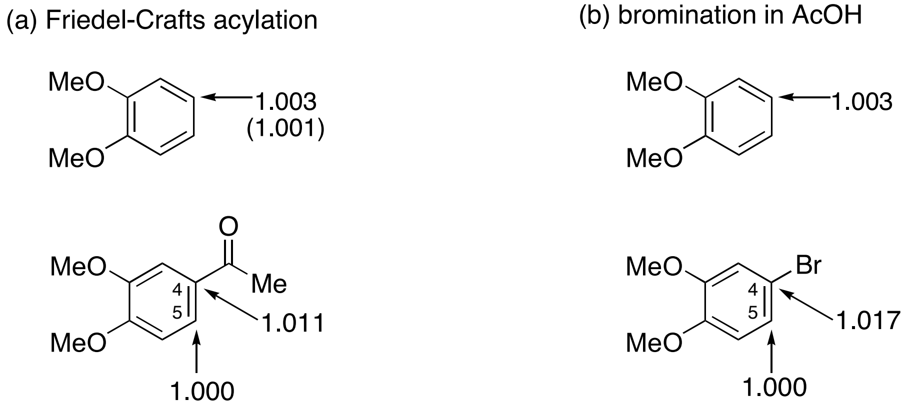


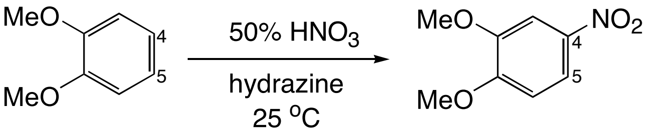
Figure 7. Predicted ^{13}C KIEs based on **11**‡ (**12** in parenthesis), **9** and bromination derivates.

In the case of bromination, the predicted ^{13}C KIEs correlate very well with experimentally measured 13C KIEs. A late transition state is reflective in the KIEs that are observed for the starting material, and the product KIEs are a result of equilibration giving excellent agreement with the Brown selectivity relationship. Meaning, since both starting material and product KIEs correlate nicely with each other, this data is an indication that both the Inter- and intramolecular selectivity for bromination is happening in the same step. On the other hand, in the case of the Friedel-Crafts acylation, when predicting the KIEs form **11**‡ one does not obtain a realistic KIE. The imaginary frequency associated with the transition state overestimates the modes of vibration contribution of the C_4 and C_5 positions. For that reason, the intermolecular KIEs were predicted from **12**. Structure **12** gives a more realistic mode for the solvated veratrole + acylium ion complex, and gives a value that correlates well with what is obtained experimentally. The predicted intramolecular KIEs does not correlate with experimental values, and can not be the result of an equilibration.

Nitrations

Another controversial electrophilic substitution reaction that is notorious for not following the Brown selectivity relationship is that of nitration. To explore this system, a mechanistic study was done similar to that done for Friedel-Crafts acylation.

Many nitration procedures exist in the literature, however, for purposes here, the optimal reaction condition found using 50% aq. HNO_3 at room temperature. Hydrazine was also used in the reaction as an NO^+ scavenger. Also, catalytic amounts of anisole were used (0.01 eq) and was used as an indicator for the presence of NO^+.



5 **14**

Nitration Inter- and Intramolecular ^{13}C KIEs. Inter- and intramolecular KIEs for the nitration of veratrole were determined again combinatorially at natural abundance by NMR methodology.[3] Nitrations of veratrole for intermolecular KIEs were taken to 78 % and 80 % conversion, and the unreacted veratrole was recovered by an aqueous workup followed by column chromatography. The recovered veratrole was then analyzed by ^{13}C NMR by comparison with a standard sample of veratrole that was taken from the same reagent bottle. The relative changes in ^{13}C isotopic composition in the aromatic carbons were determined using the methoxy carbons as an internal standard with the assumption that their isotopic composition did not change during the reaction.

The results are shown in Figure 8. The isotope effects for the aromatic carbons are all very small, essentially unity, just as in the case of Friedel-Crafts acylation.

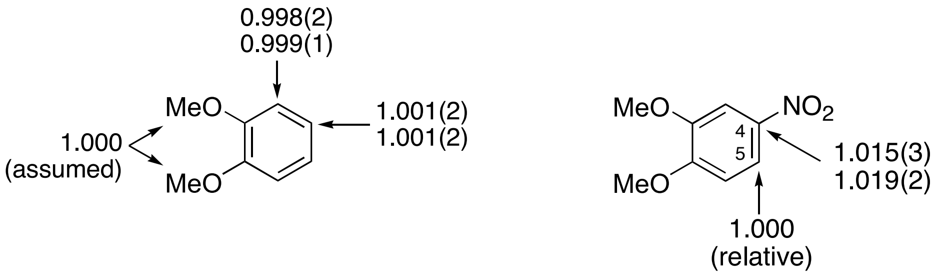
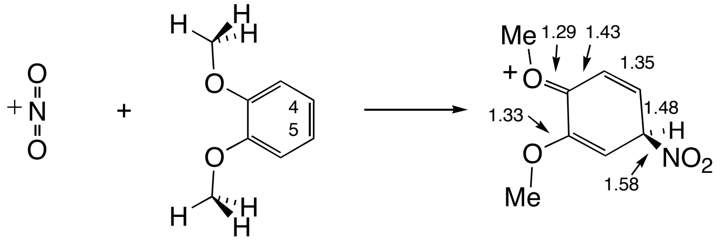


Figure 8. Inter- and intramolecular ^{13}C KIEs for nitration of veratrole using 50% HNO_3 at 25 °C.

The intramolecular ^{13}C KIE at C_4 / C_5 for nitration was determined from analysis of samples of the product **14** obtained from nitrations taken to 50 % conversion, using methodology described above. The ^{13}C composition in the nitrated C_4 carbon was less than in C_5 position. This isotopic composition corresponded to intramolecular KIEs, defined as with **14**, of 1.015-1.019.

Nitration Theoretical Studies. In gas-phase DFT calculations (B3LYP/6-31G*), the addition of nitronium cation (**15**) to C_4 / C_5 of veratrole to afford **16** is downhill by 40.1 kcal/mol (pot. E + zpe) and there is no potential energy barrier for the reaction. With PCM solvent model **16** is still downhill from **15** + veratrole by 20.2 kcal/mol (B3LYP/6-31G*/PCM + zpe with full geometry optimization).



15 E_{rel} = 0 **5**

16 E_{rel} = -20.2
[-40.1 gas phase]

Relaxed energy surfaces for approach of **15** to veratrole were calculated by fixing the C_α-C_4 and C_α-C_5 distances at a grid of values and optimizing the remaining geometrical variables at each point. The B3LYP/6-31G*/PCM + zpe surface generated in this way is shown in Figure 9. Similar surfaces were obtained for the gas phase. As **15** comes closer to the veratrole, its approach ultimately breaks symmetry to afford the chiral **16**, but the symmetry breaking is not favored until the C_α-C_4/C_5 distances are less than 2.4 Å.

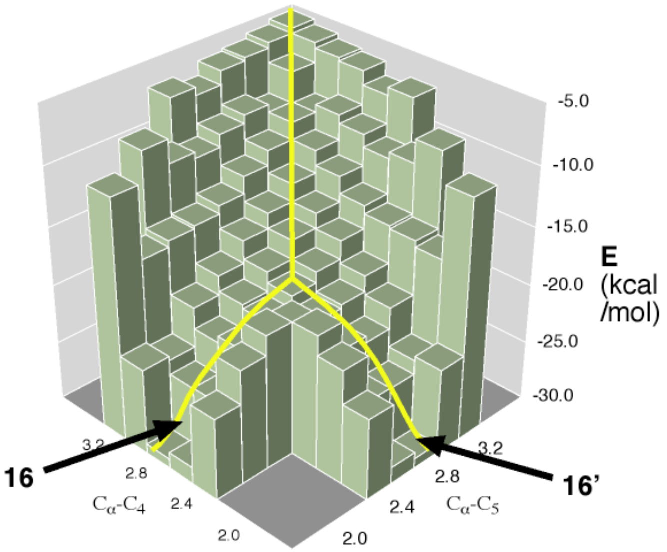


Figure 9. Energy Surface (B3LYP/6-31G*/PCM + zpe) for the approach of nitronium to veratrole, fixing C_α-C_4 and C_α-C_5 distances at the values specified on the grid. High-energy points at the left, right, and front of the grid have been left out for clarity.

Discussion

In the classic mechanism of electrophilic aromatic substitution, Brown identified the relationship that exists between the substrate selectivity and resulting product selectivity.[31] For reactions involving electrophiles with "late," transition states, the electrophile will be committed to forming a bond with a particular carbon and no dynamic choice of products is possible. The bromonium ion is one such electrophile. It has been found through experimental ^{13}C KIEs in the bromination of veratrole that Brown's selectivity relationship holds true. For the bromination of veratrole in acetic acid, a normal intramolecular ^{13}C KIE of ≈1.014 and a normal intermolecular isotope effect of ≈1.007 were observed using natural abundance methodology. These experimental isotope effects are consistent with a conventional electrophilic aromatic substitution mechanism involving a late rate-limiting / selectivity-determining transition state resembling a σ-complex.

This is not the case for Friedel-Crafts acylations. The mechanism supported here for Friedel-Crafts acylations can be described as a “two-step no intermediate” reaction, similar to that of the singlet oxygen ene reaction.[25] Olah was right in the sense that the inter- and intramolecular selectivities were determined in different steps, but in a completely different fundamental. He had proposed a π-complex intermediate where selectivity was determined; our proposal is that selectivity is being influenced by dynamic effects on a bifurcating energy surface.

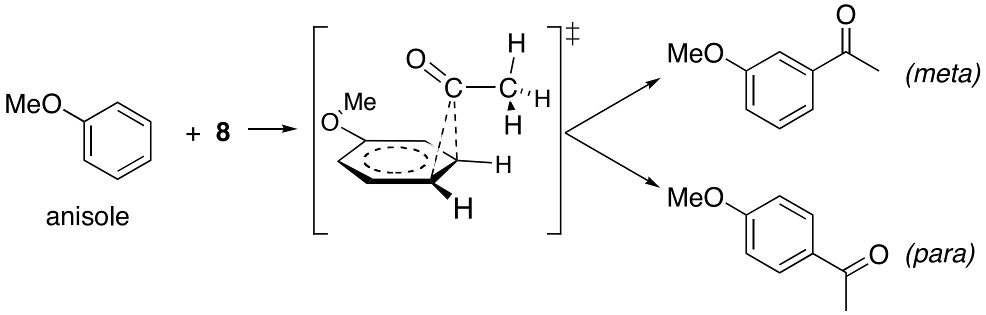
The experimental KIEs (inter- and intramolecular) measured using natural abudance methodology for the Friedel-Crafts acylation of veratrole do not correlate with each other. The inverse intramolecular ^{13}C KIE (≈0.0981) and the lack of an intermolecular ^{13}C KIE (≈1.000) are inconsistent with the conventional electrophilic aromatic substitution mechanism. These data suggest that the rate-determining and selectivity-determining steps are separate. If the rate-determining and selectivity-determining step are different steps on the MEP, this suggests the existence of an intermediate positioned somewhere between a π-complex and **9**. However, upon theoretical examination of the energy surface, and due to the fact that no such intermediate has ever observed in the history of Friedel-Crafts acylations, a long-lived intermediate must be ruled out.

If deprotonation were the rate determining step in Friedel-Crafts acylation, then that might amount for the unusual intramolecular KIE. The experimental H/D KIE is unity and is inconsistent with rate-limiting proton loss from a σ-complex. A deprotonation rate-limiting mechanism cannot be used here to explain the origin of the inverse intramolecular KIE.

Extensive theoretical calculations provide an explanation for the experimental acylation observations. The acylation of veratrole involves a symmetrical early rate-limiting transition state followed by dynamic selectivity on a bifurcating energy surface, which is the origin of the intramolecular isotope effect. It was found that solvent models are necessary for accurately modeling this system due to the charge of the acylium ion.

Nitration is yet another example found in the literature that does not follow the Brown selectivity relationship. The experimental KIEs for the nitration of veratrole are far more difficult to interpret than those of Friedel-Crafts acylation or bromination. A normal intramolecular ^{13}C KIE of ≈ 1.017 was measured, however, no intermolecular ^{13}C KIE was observed. Again here the ^{13}C KIEs are inconsistent with each other, but in a different way from that of Friedel-Crafts acylation. This data can only suggest an early rate-determining step. Because the intramolecular KIE is normal, it cannot be concluded that these two steps are not correlated. Theoretical calculations provide evidence for an early symmetrical rate-limiting transition state followed by dynamic selectivity on a bifurcating energy surface. The mechanism of nitration still remains to be debated.

This type of analysis can be applied to other non-symmetrical systems, such as Friedel-Crafts acylation of anisole. By modeling the energy surface, one might be able to better understand the unusually high amounts of *meta* isomers formed during acylations.



Experimental Section

All reactions were carried out in dried glassware and freshly purified solvent.

Preparation of Veratrole-d$_4$. A mixture of 15 g of veratrole in 100 mL of deuterium oxide and 15 mL of concentrated sulfuric acid was prepared and refluxed. Aliquots were periodically removed and analyzed by ^{1}H NMR, and it was observed that after 3 d the deuterium incorporation into the aromatic hydrogens was no longer changing substantially. The reaction mixture was then cooled and extracted with dichloromethane. The organic layer was then washed with 5% sodium bicarbonate, water, and brine, then dried over Na_2SO_4. The volatiles were removed on a rotary evaporator, and the residue was chromatographed on a 55-mm x 300-mm flash silica gel column using 30% EtOAc/hexanes as eluent to afford 17.4 g veratrole-d$_4$: ^{1}H NMR (C_6D_6) δ 6.78 (m, 0.28 H), 6.60 (m, 0.29 H), 3.37 (s, 6 H). The CI-MS m/e 142:141 ($C_8H_6D_4O_2^+$ / $C_8H_7D_3O_2^+$) ion intensity ratio was 65.5:34.5.

Intramolecular Isotope Effects in the Acylation of Veratrole. Example Procedure. A 2 M solution of aluminum bromide in dichloromethane was added to a mixture of 3.102 g (0.022 mol) of veratrole and 0.78 mL (0.011 mol) of acetyl chloride in CH_2Cl_2 while stirring under N_2 at 25 °C. After 4 h the conversion, monitored by NMR analysis of aliquots, was 46%. The reaction mixture was washed successively with 1 M HCl and water, then dried over $MgSO_4$. The volatiles were removed on a rotary evaporator, and the residual oil was chromatographed on a 65-mm x 300-mm flash silica gel column using CH_2Cl_2 as eluent, followed by a second chromatography on a 33 mm x 300 mm flash silica gel column using 20% EtOAc/hexanes as eluent. The resulting crude product was recrystallized from petroleum ether to afford 398 mg of **6**: ^{1}H NMR (C_6D_6) δ 7.56 (d *J*=2.0 Hz, 2 H), 7.31 (dd *J*=2.0, 8.3 Hz, 1 H), 6.44 (d *J*= 8.3 Hz), 3.37 (s, 3 H), 3.34 (s, 3H), 2.23 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 197.0, 153.5, 149.2, 130.7, 123.5, 110.2, 110.1, 56.2, 56.1, 26.4.

An analogous reaction using 3.105 g of veratrole was taken to 48% conversion and 1.09 g of **6** was isolated. Two other analogous reactions were performed in *o*-dichlorobenzene instead of dichloromethane, using 3.182 and 3.188 g of veratrole with the reactions taken to 82% and 86% conversion, affording 0.95 g and 1.02 g of **6**, respectively. Two similar reactions using 0.345 g of veratrole-d_4 and 0.355g of veratrole-d_0 were taken to 48% and 47% conversion, affording 35 mg and 20 mg of **6-d$_3$**.

Intermolecular Isotope Effects in the Acylation of Veratrole. Example Procedure. A 2 M solution of aluminum bromide in dichloromethane was added to a mixture of 20.726 g veratrole (0.15 mol) and 13 mL (0.15 mol) of acetyl chloride in 1.5

L of CH_2Cl_2 while stirring under N_2 at 25 °C. After 8 h the conversion was 82%. The reaction mixture was washed successively with 1 M HCl and water, then dried over $MgSO_4$, and the volatiles were removed using a rotary evaporator. The residue was chromatographed successively on three flash silica gel columns using 20% EtOAc/hexanes as eluent to afford 0.60 g of the unreacted veratole. An analogous reaction using 20.731 g of veratrole was taken to 86% conversion and 1.10 g of veratrole was reisolated.

Intramolecular Isotope Effects in the Bromination of Veratrole. Example Procedure. While stirring, 8 g of bromine (0.05 mol) in 30 mL of acetic acid was added dropwise over 1 h to 6.901 g (0.05 mol) of veratrole in 20 mL of acetic acid at 0 °C. The reaction was monitored by NMR analysis of aliquots, and after 1 h the conversion was 93%. The bulk of the acetic acid was then removed by vacuum distillation, and the resultant oil was taken up in 25 mL of petroleum ether and washed successively with 5% sodium hydroxide and water, then dried over Na_2SO_4. The volatiles were removed on a rotary evaporator and the residue was distilled under vacuum to afford 2.9 g of 4-bromo-1,2-dimethoxy-benzene: ^1H NMR ($CDCl_3$) δ 6.72-6.76 (m, 2 H), 6.71 (d *J*=8.4 Hz, 1 H), 3.83 (s, 3 H), 3.81 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 149.8, 148.4, 123.4, 114.8, 112.7, 112.6, 56.1, 56.0. An analogous reaction using 6.905 g of veratrole was taken to 95% conversion and 2.0 g of 3-bromo-1,2dimethoxy-benzene was isolated.

Intermolecular Isotope Effects in the Bromination of Veratrole. Example Procedure. While stirring, 19 g of bromine (0.12 mol) in 72 mL of acetic acid was added dropwise over 2 h to 20.727 g (0.15 mol) of veratrole in 60 mL of acetic acid at 0

°C. After 2 h the conversion based on NMR analysis was 77%. The reaction was worked up as in the previous procedure, and 4.0 g of the unreacted veratrole was recovered by fractional vacuum distillation. An analogous reaction using 20.730 g of veratrole was taken to 74% conversion, with1.22 g of veratrole recovered.

Intramolecular Isotope Effects in the Nitration of Veratrole. Example Procedure. While stirring, 10 g of hydrazine (0.08 mol) in 544 mL of 50 % nitric acid solution was added and stirred for 30 mins, then 0.2 g of anisole (0.002 mol) was added to the solution and left to stir for an additional hour. Veratrole, 5.5 g (0.04 mol), was then added and the reaction was monitored by NMR analysis of aliquots, and after 30 mins the conversion was 50%. The reaction mixture was then poured over ice and the organics were extracted with chloroform. The combined organic layers were then filtered through a silica plug and then dried over $MgSO_4$ and deactivated charcoal. The volatiles were removed using a rotary evaporator and the residue was crystallized using petroleum ether to afford 2.5 g of 1,2-dimethoxy-4-nitrobenzene: ^{1}H NMR (C_6D_6) δ X.X (m, 2H), 6.60 (m, 1H), 3.12 (s, 3H), 3.11 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 154.7, 149.1, 118.0, 110.1, 106.7, 56.77, 56.6. An analogous reaction using 5.5 g of veratrole was taken to 50% conversion and 2.6 g of 1,2-dimethoxy-4-nitrobenzene.

Intermolecular Isotope Effects in the Nitration of Veratrole. Example Procedure. While stirring, 26 g of hydrazine (0.20 mol) in 1.36 L of 50 % nitric acid solution was added and stirred for 30 mins, then 0.54 g of anisole (0.005 mol) was added to the solution and left to stir for an additional hour. Veratrole, 13.8 g (0.10 mol), was then added and the reaction was monitored by NMR analysis of aliquots, and after 1 hr the conversion was 76 %. The reaction was worked up as in the previous procedure, and 2.1 g of the unreacted veratrole was recovered by fractional vacuum distillation. An analogous reaction using 13.8 g of veratrole was taken to 80% conversion, with 2.4 g of veratrole recovered.

NMR Measurements. Samples were in 5-mm NMR tubes filled with $CDCl_3$ or C_6D_6 to a constant height of 5.0 cm, and the intermolecular KIE measurements involving a comparison of sample versus standard used a constant amount of analyte (400 mg for samples of recovered veratrole from acylation, 650 mg for samples of recovered veratrole from bromination, and 400 mg for samples of recovered veratrole from nitration). ^{13}C NMR spectra were recorded at 125.701 MHz with inverse gated decoupling. A T_1 measurement was performed on each sample to ensure that the relaxation rates did not change from sample to sample. Integrations were determined numerically using a constant integration region for each peak based on peak width. The ^{13}C spectra of **6** were taken using 86.5-s delays between calibrated 90° pulses, 9.000-s acquisition time, and collecting 503 872 points. For comparison of each relevant pair of peaks, a set of spectra was taken with the transmitter centered between the two peaks. The ^{13}C spectra of veratrole were taken using 72-s delays between calibrated 90° pulses, 14.221-s acquisition time, and collecting 512,000 points.

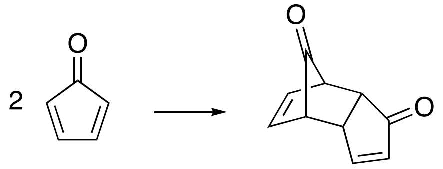
The ^{1}H spectra of **6-d$_3$** were taken using 10-s delays between calibrated 90° pulses, 3.744-s acquisition time, and collecting 41 932 points. The ^{13}C spectra of 3-bromo-1,2-dimethoxy-benzene were taken using 69-s delays between calibrated 90° pulses, 10.669-s acquisition time, and collecting 512 000 points. Six spectra were obtained for each sample. The resulting ^{13}C integrations for the spectra are provided in the Appendix A, along with sample spectra, and the KIEs were calculated as previously described.

CHAPTER III

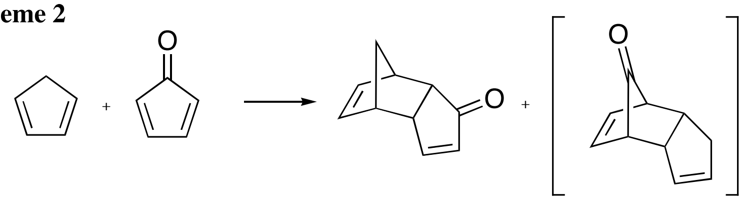
CYCLOPENTADIENONE DIELS-ALDER CYCLOADDITIONS

A unique opportunity to develop an understanding of selectivity on bifurcating energy surfaces was presented by the cycloadditions of 1,3-dienes with a substituted cyclopentadieneone. Cyclopentadienones are extremely reactive in Diels-Alder cycloadditions and readily dimerize in the absence of steric stabilization (Scheme 1).[83] The dimer product is the result of a [4 + 2] cycloaddition, with one molecule acting as the diene and the other as the dienophile.[84] Caramella and co-workers have proposed based on computational studies that the cyclopentadienone dimerization also involves a *C2*-symmetric bispericyclic transition state, similar to the cyclopentadiene case previously mentioned, which involves symmetry breaking to afford two identical products.[85] Early studies found that when free cyclopentadienone is generated in the presence of a diene, the cyclopentadienone acts exclusively as the dienophile and not as a diene in the observed Diels-Alder product (Scheme 2).[86] However, cyclopentadienone can also act as a reactive diene in Diels-Alder cycloadditions with acetylenic dienophiles.[84] The nature of the exclusive periselectivity (selectivity between allowed cycloadditions - here $[4\pi_{\text{dienone}} + 2\pi_{\text{diene}}]$ versus $[2\pi_{\text{dienone}} + 4\pi_{\text{diene}}]$ with cyclopentadiene) remains unclear.

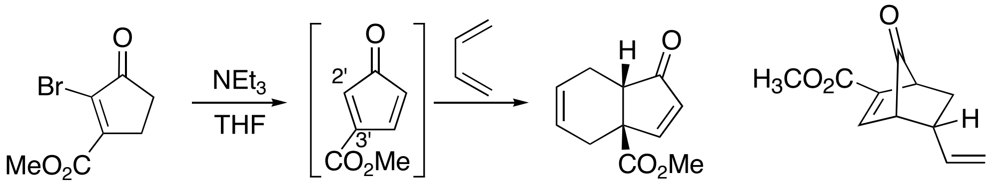
Scheme 1



Scheme 2



Substituted cyclopentadienones are less reactive and have longer lifetimes in solution.[83, 87-90] Recently, Harmata has reported numerous examples of periselective Diels-Alder reactions using **17** as a precursor to cyclopentadienone **18** in the presence of a base. In the presence of various dienes, the ensuing cycloadditions afford good yields of cycloadducts under mild conditions. Mechanistically, these well-behaved reactions provide an excellent opportunity to add to the understanding of cyclopentadienone cycloadditions. The possibility that the periselectivity of these reactions is decided on a bifurcating energy surface was particularly interesting, based on their similarity to both theoretical studies of the parent cyclopentadienone reaction and to the experimental studies of cyclopentadiene/ketene reactions.[5] It will be seen that experimental and calculational studies support this idea. Mechanistically, these well-behaved reactions with broadly variable dienes provide an excellent opportunity for deeper consideration of the nature of their selectivity.



17 **18** [$4\pi_{diene} + 2\pi_{dienone}$] [$2\pi_{diene} + 4\pi_{dienone}$]

Describe here is a mechanistic study of the Diels-Alder cycloaddition of **18** with1,3-dienes using a combination of experimental kinetic isotope effects (KIEs), theoretical calculations, and trajectory calculations. The results define the qualitative ides necessary to understand the dynamically-determined selectivity on bifurcating surfaces, including consideration of the detailed transition structure geometry, of how trajectories cross an unsymmetrical transition state ridge, and of the shape of the energy surface.

Results

Continua of Transition Structures. Based on the hypothesis above that the reactions of **16** with 1,3-dienes would involve bifurcating energy surfaces, we sought to examine a range of reactions that varied from preferring [$4\pi_{diene} + 2\pi_{dienone}$] periselectivity to preferring [$2\pi_{diene} + 4\pi_{dienone}$] periselectivity, with examples exhibiting intermediate selectivity. Toward that end, transition structures for the reaction of **16** with a variety of dienes were surveyed in DFT calculations. From this survey, the reactions of **18** with 2,3-dimethylbutadiene (**19**), 1-vinylcyclohexene (**20**), 2-vinylfuran (**21**), and styrene (**22**) were chosen for further experimental and computational study.

Transition structures for these reactions were located in MPW1K[91] calculations using a 6-31+G** basis set,[92] and depicted in Figure 10. These studies were complicated by a diversity of possible modes for the cycloadditions. For example, a total of 16 transition structures were located for the cycloaddition of vinylcyclohexene with **18** in which vinylcyclohexene plays the 4π-component role in the cycloaddition. These 16 structures arise from the possibility of *endo* versus *exo* orientation of **18** relative to vinylcyclohexene, two possible regiochemical orientations of **18** versus vinylcyclohexene, the possible involvement of the $C_{2'}$=$C_{3'}$ versus $C_{4'}$=$C_{5'}$ double bonds of **18**, and the possibility for attack on vinylcyclohexene from two faces defined by the half-chair conformation of the cyclohexene ring. Fortunately, the consideration of these reactions was simplified by a strong preference for *endo* transition structures (the *exo* transition structures were at least 4 kcal/mol higher in energy), a strong preference for reaction at $C_{2'}$=$C_{3'}$ of **18**, and a strong regioselectivity preference favoring bonding of C_1 of the dienes with $C_{2'}$ of **18**. As a result, the reactions of **19**, **21**, and **22** are predicted to be dominated by the single transition structures **23**, **25**, and **26**, while the reaction of **20** has two low-energy transition structures **24-ax** and **24-eq**. **24-ax** is referred to as "axial" and **24-eq** as "equatorial" based upon the initial orientation of C_4 bond formation on the incipient cyclohexane chair. The axial structure is slightly favored in keeping with related trends in other additions to cyclohexenes.[93]

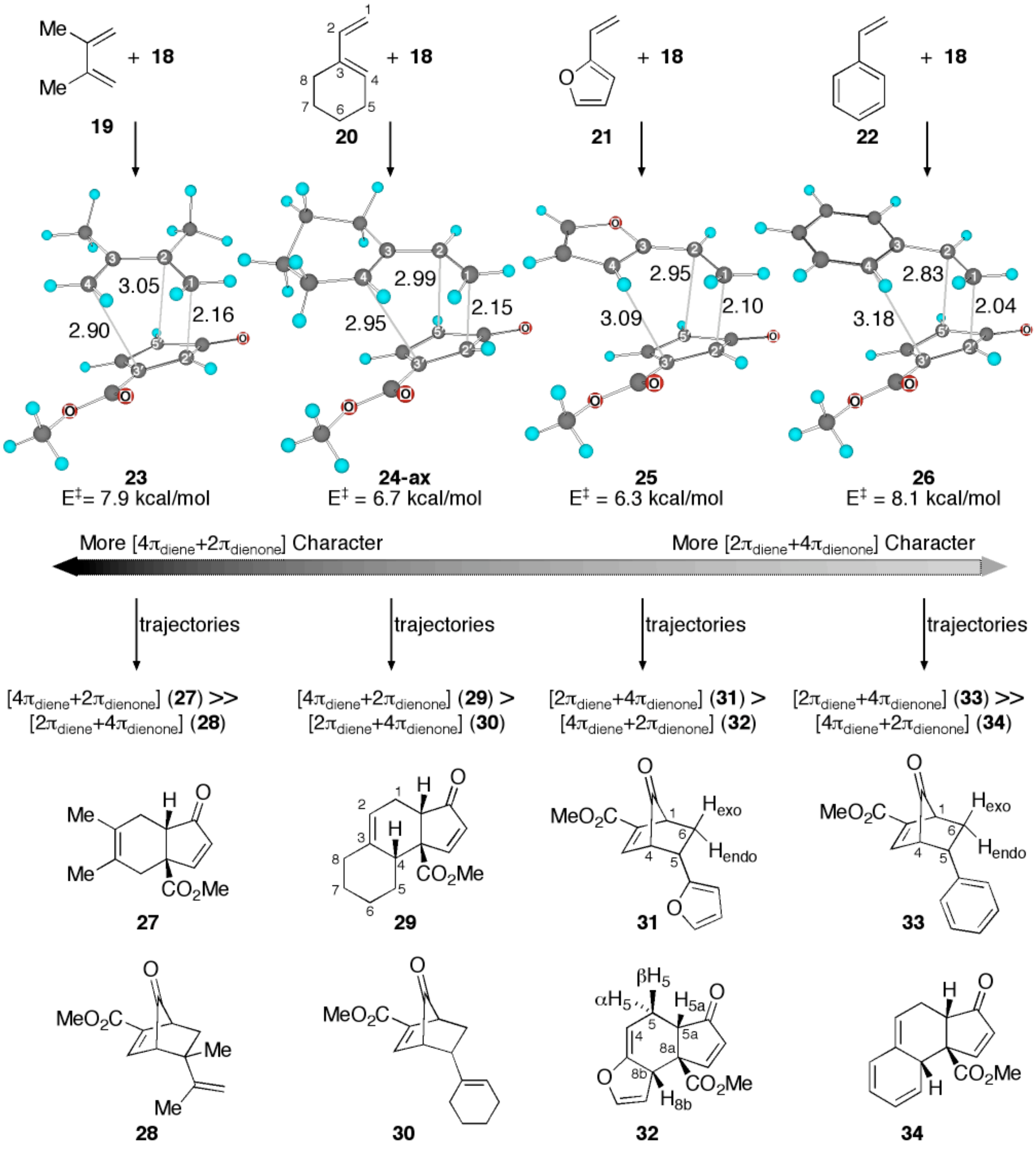


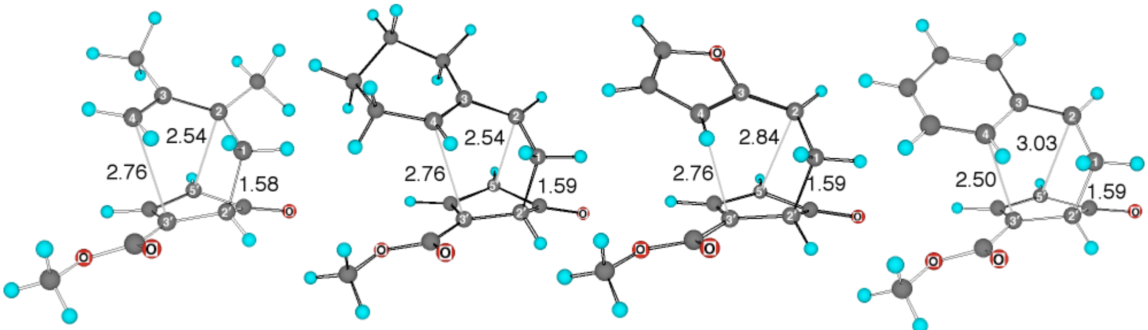
Figure 10. The low-energy transition structures for the reactions of **18** with 2,3-dimethylbutadiene (**19**), 1-vinylcyclohexene (**20**), 2-vinylfuran (**21**), and styrene (**22**), along with a summary of trajectory studies on these structures. Activation barriers (MPW1K/6-31+G** + zpe) are versus separate starting materials in kcal/mol.

The striking feature of these transition structures is that they have qualities of both [$4\pi_{\text{diene}}$ + $2\pi_{\text{dienone}}$] and [$2\pi_{\text{diene}}$ + $4\pi_{\text{dienone}}$] cycloadditions. This bispericyclic character,[85, 94, 95] likely contributing to the low energy of the structures versus alternatives, can be seen in the similarity of the C_4-$C_{3'}$ and C_2-$C_{5'}$ distances in each structure. Based on the C_4-$C_{3'}$ versus C_2-$C_{5'}$ distances, structure **23** may be described as having greater $[4\pi_{\text{diene}} + 2\pi_{\text{dienone}}]$ character while the styrene transition structure **25** is more $[2\pi_{\text{diene}} + 4\pi_{\text{dienone}}]$ in character, with **24-ax** and **25** in between. Notably, the $[4\pi_{\text{diene}} + 2\pi_{\text{dienone}}]$ versus $[2\pi_{\text{diene}} + 4\pi_{\text{dienone}}]$ character of these transition structures seems closely related to the relative stability of the possible products. For **23** and **24-ax**, the $[4\pi_{\text{diene}} + 2\pi_{\text{dienone}}]$ products **27** and **29** are more stable by 22.6 and 10.3 kcal/mol, respectively, than the $[2\pi_{\text{diene}} + 4\pi_{\text{dienone}}]$ products **28** and **30** (MPW1K/6-31+G** + zpe). For **25** and **26**, the $[2\pi_{\text{diene}} + 4\pi_{\text{dienone}}]$ products **31** and **33** are more stable than the $[4\pi_{\text{diene}} + 2\pi_{\text{dienone}}]$ products **32** and **34** by 1.5 and 12.8 kcal/mol, respectively.

This intriguing continuum of transition structures is necessarily subdivided in MEP analyses since a steepest-descent path can only lead to a single product. The MEPs (in mass-weighted coordinates) passing through **23** and **24-ax** lead to the $[4\pi_{\text{diene}} + 2\pi_{\text{dienone}}]$ products **27** and **29**, while the MEPs passing through **25** and **26** lead to $[2\pi_{\text{diene}} + 4\pi_{\text{dienone}}]$ cycloadducts **31** and **33**. It will be seen below that trajectories through these transition structures are not so cleanly subdivided. A search was undertaken for alternative transition state structures that were mainly $[2\pi_{\text{diene}} + 4\pi_{\text{dienone}}]$ in character for reactions of **19** and **20** or mainly $[4\pi_{\text{diene}} + 2\pi_{\text{dienone}}]$ in character for reactions of **21** and **22**. No low-energy structures of these types could be located. Instead, attempts to locate transition structures for the alternative cycloaddition modes invariably reconverged on **23**, **24-ax**, **25**, and **26**. This is consistent with a merging of $[4\pi_{\text{diene}} + 2\pi_{\text{dienone}}]$ and

[$2\pi_{\text{diene}} + 4\pi_{\text{dienone}}$] pathways through the transition structures, and supports the involvement of bifurcating energy surfaces qualitatively resembling those of Figure 2.

A second continuum of transition structures is of importance here. As discussed in the introduction of this chapter, bifurcating energy surfaces are recognizable by the presence of a second geometrically adjacent saddle point without an intervening intermediate. The adjacent saddle points in the systems here are the transition structures for the [3,3]-sigmatropic (Cope) rearrangements interconverting the [$4\pi_{\text{diene}} + 2\pi_{\text{dienone}}$] and [$2\pi_{\text{diene}} + 4\pi_{\text{dienone}}$] products. The transition structures located for these rearrangements are shown in Figure 11 and their geometric proximity to the cycloaddition transition structures of Figure 10 is obvious. However, one difference in the trends in the two continua seems important. While the cycloaddition transition structures geometrically favored the more stable product, the rearrangement transition structures, following Hammond's postulate, more closely resemble the less stable product. As the relative stability of the products changes, the cycloaddition and rearrangement transition structures shift in opposite directions!



35
E = -2.5 kcal/mol

36-ax
E = -2.8 kcal/mol

37
E = -1.4 kcal/mol

38
E = 4.6 kcal/mol

Figure 11. MPW1K/6-31+G** transition structures for the [3,3]-sigmatropic (Cope) rearrangements interconverting the [$4\pi_{\text{diene}} + 2\pi_{\text{dienone}}$] products **27**, **29**, **32**, and **34** and the [$2\pi_{\text{diene}} + 4\pi_{\text{dienone}}$] products **28**, **30**, **31**, and **33**. Energies (MPW1K/6-31+G** + zpe) are versus separate **18** / diene, in kcal/mol, to be on the same scale as the energies of Figure 10.

Product Studies. The reaction of **18** with **19** has been previously reported[88] and affords the [$4\pi_{\text{diene}} + 2\pi_{\text{dienone}}$] product **27** as the only observable cycloadduct except for traces of materials arising from apparent dimerization of **18**. The reaction of **18** with vinylcyclohexene (**20**), also previously reported,[88] affords the single cycloadduct, **29**, though it will be seen that this reaction is more complex than it appears. Product **29** is notably the *endo* isomer that would arise from **24-ax** or **24-eq**, and no traces of either *exo* adducts or the possible alternative regioisomer were observed. For reasons that will be apparent, particular care was taken in attempts to observe the alternative [$2\pi_{\text{diene}} +$ $4\pi_{\text{dienone}}$] product **30** in the reaction mixture, but no evidence for its formation was obtained.

The reaction of 2-vinylfuran (**21**) with **18** was more complicated, affording both the [$2\pi_{diene} + 4\pi_{dienone}$] product **31** and the [$4\pi_{diene} + 2\pi_{dienone}$] product **32** in a total yield of 88% and a ratio of 1.6:1 at 25 °C in 2 days. The stereochemistries of **31** and **32** were assigned from analysis of their ^{1}H NMR coupling constants and COSY spectra. The H_{exo} in **31** was assigned on the basis of a 5.2 Hz coupling constant with the bridgehead hydrogen at C_1, while H_{endo} shows no coupling with this hydrogen. The hydrogen at C_5 was then assigned as *exo* based on a 9.6 Hz coupling with H_{exo} and a 4.6 Hz coupling with H_{endo}.[96, 97] In assigning the stereochemistry of **32**, the observation of relatively small coupling constants to H_{5a} (6.0 and 2.0 Hz) was important. The predicted coupling constants[98] for the *endo* isomer **32**, based on the lowest-energy conformation in MM3 calculations, were 5.6 Hz for H_{5a}-βH_5 and 1.4 Hz for H_{5a}-αH_5, matching well with the observed values. In the alternative *exo* analog of **32**, the predicted coupling constants were 10.0 and 7.6 Hz, matching poorly with the observed values. Notably, the ^{1}H NMR signal for βH_5 exhibited a large long-range coupling of 3.0 Hz with H_{8b}, while no αH_5-H_{8b} coupling was observed.

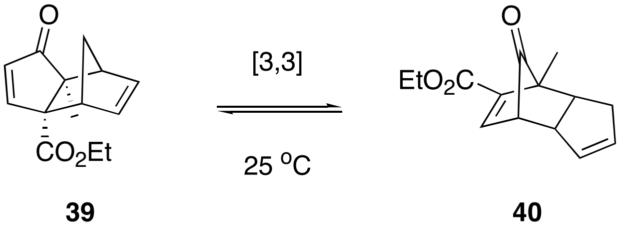
The formation of **32** is particularly striking since the calculational studies were unable to locate any cycloaddition transition structure that leads by a steepest-descent path to **32**. The formation of **32** from **25** will be explained by trajectory studies.

Styrene is somewhat less reactive with **18** than typical 1,3-dienes are, so that dimerization of **18** becomes competitive. With excess styrene at room temperature, the reaction affords **33** as the only styrene adduct in 36% yield. H_{exo} in **33** was assigned from its 4.0 Hz coupling constant with the bridgehead hydrogen at C_1, while H_{endo} was not coupled with this hydrogen. The hydrogen at C_5 was assigned as *exo* based on a 9.8 Hz coupling with H_{exo} versus a 6 Hz coupling with H_{endo}.

Cope Rearrangements and Kinetic versus Thermodynamic Control. Because the [$4\pi_{diene} + 2\pi_{dienone}$] versus [$2\pi_{diene} + 4\pi_{dienone}$] products in these reactions are potentially interconverted by a Cope rearrangement, it was consider here whether the experimental product observations are the result of kinetic or thermodynamic control. In the case of **31** versus **32**, this was readily evaluated experimentally. The ratio of products from the 25 °C reaction was unchanged after 17 days at 25 °C, while isolated **32** underwent no significant isomerization to **31** in 32 days. The combination of these observations indicates that the observed ratio is kinetically controlled.

In the other reactions, the unobserved alternative products **30**, **32**, and **34** are higher in energy and were unable to experimentally determine whether the observed products are the result of kinetic control. As will be seen, the issue of kinetic versus thermodynamic control was of particular interest for the vinylcyclohexene system, and it was considered whether the issue could be resolved from the computational studies. Transition structure **36-ax** for the interconversion of **29** and **30** was predicted to be 28.9 kcal/mol (MPW1K/6-31+G** + ZPE) above **30**. If this barrier were accurate, the rearrangement of **30** at 25 °C would be quite slow, and based on the trajectory studies below, **30** should have been observable.

However, the MPW1K calculations appear to overestimate the barrier in these reactions. In the related [3,3]-sigmatropic rearrangement of **39**, Zwanenburg observed the slow equilibration of **39** and **40** at 25 °C.[99] If one estimates from their observations that the rate constant for the rearrangement is on the order of 10^{-5} s^{-1}, ΔG‡ would be ≈24 kcal/mol. A transition structure was located for the [3,3]-sigmatropic rearrangement of **39**, and the calculated ΔG‡ was 31.0 kcal/mol (MPW1K/6-31+G**, including harmonic thermal energy and entropy estimates). Since MPW1K overestimates this barrier by ≈7 kcal/mol, a similar overestimate of the barrier for the rearrangement of **30** is likely. MP2 single point calculations (MP2/6-31+G**//MPW1K/6-31+G** + ZPE) place the barriers for rearrangement of **30** and **39** at 21.6 and 24.4 kcal/mol, respectively. MP2 tends to underestimate barriers for pericyclic reactions, but if the 2.8 kcal/mol difference in the barrier for **30** versus **39** is correct, **30** would rearrange ≈115 times faster than **39** and it would be difficult to observe under the reaction conditions.



The predicted barrier for rearrangement of **32** is 25.2 kcal/mol (MP2/6-31+G**//MPW1K/6-31+G** + ZPE), in keeping with the observation above of a kinetically controlled product mixture at 25 °C. The situation is less certain with **27**/**28**, as the predicted barrier for rearrangement of **28** is 23.7 kcal/mol, but so little **28** is expected from any prediction (see below) that no effort was made to observe it. The observation of **34** would be very difficult at temperatures conducive to the cycloaddition, as the predicted barrier for its rearrangement is 18.6 kcal/mol, but no **34** is expected from either a conventional calculational analysis or the trajectory studies below.

Experimental Isotope Effects. While synthetic reactions of **17** with vinylcyclohexene mediated by triethylamine have been conducted under refluxing conditions in THF or toluene,[88] the reaction proceeds quite cleanly at room temperature, albeit more slowly, and these conditions were used for the KIE studies here. The ^{13}C KIEs ($k_{^{12}\mathrm{C}}/k_{^{13}\mathrm{C}}$) for the vinylcyclohexene component of the cycloaddition were determined combinatorially at natural abundance by NMR methodology.[3, 70, 100] While it is usually advantageous to analyze recovered starting material when determining KIEs in this way,[3] analysis of the product at low conversion versus 100% conversion[70, 100] was employed here to avoid the need for an excess of **17** in a large-scale reaction. Two reactions were taken to ≈13% conversion and the product **29** was isolated by extractive workup followed by flash chromatography. The samples were then analyzed by ^{13}C NMR in comparison to a standard sample of **29** obtained from a small-scale reaction taken to 100% conversion. The relative changes in ^{13}C isotopic composition in each position were determined using C_7 as an "internal standard" with the assumption that the KIE at C_7 is negligible.

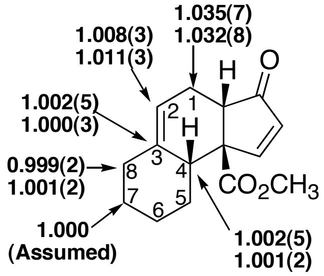


Figure 12. Experimental ^{13}C KIEs for the Diels-Alder reaction of vinylcyclohexene. KIEs at C_5 and C_6 were not determined because of the near-overlap of the ^{13}C peaks.

The results are shown in Figure 12. A large ^{13}C KIE of $\approx$1.033 is observed at C_1. This fits well qualitatively with the expected substantial σ-bond change at the carbon in the cycloaddition transition state. The relatively small ^{13}C KIE at C_4 can be interpreted as the result of the cycloaddition proceeding through a highly asynchronous transition state,[101] and the small ^{13}C KIE is reminiscent of those observed in corresponding positions in Lewis acid catalyzed Diels-Alder reactions.[1] The ^{13}C KIE at C2 is the most difficult to understand, as it is larger than has been observed for the "unreactive" olefinic carbons of the diene in previous studies of carbon KIEs for Diels-Alder reactions.[1, 3, 102] The qualitative suggestion from this isotope effect is that some unusual degree of bonding change is occurring at this carbon in the rate-limiting transition state. A more detailed discussion of this isotope effect will be given below.

Trajectory Studies. Because the simplicity of transition state theory cannot be used to theoretically predict the product ratios that should arise on unsymmetrical bifurcating energy surfaces, one must fall back on the detailed consideration of atomic positions and momenta inherent in trajectory studies. Transition structures **23**, **24-ax**, **24-eq**, **25**, and **26** were used as starting points for quasiclassical direct dynamic trajectories[8, 26, 103-119] on the MPW1K/6-31+G** potential energy surfaces. Trajectories were initialized with all atomic motions freely variable by giving each mode a random sign for its initial velocity, and an initial energy based on a random Boltzmann sampling of vibrational levels appropriate for 298.15 K, including zero-point energy. The mode associated with the imaginary frequency was treated as a translation and given a Boltzmann sampling of translational energy ‘forward’ over the col. The trajectories were propagated employing a Verlet algorithm using 1-fs steps in previously described code[5] and using Gaussian 03[92] to calculate forces at each point until either the [$4\pi_{\text{diene}}$ + $2\pi_{\text{dienone}}$] product (**27**, **29**, **32** or **34**) or the[$2\pi_{\text{diene}}$ + $4\pi_{\text{dienone}}$] product (**28**, **30**, **31**, or **33**) was formed or recrossing occurred to afford the starting materials. All trajectories were complete within 370 fs and the median times for product formation from was **23**, **24** (combined), **25**, and **26** were 70 fs, 109 fs, 129 fs, and 63 fs, respectively.

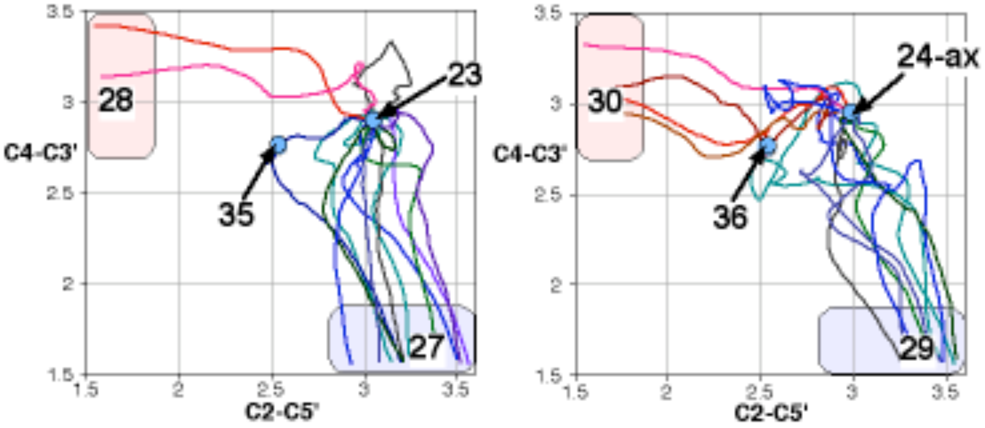
The results are summarized in Table 1 and shown in Figure 13. Trajectories passing through **23** afforded predominantly the [$4\pi_{\text{diene}}$ + $2\pi_{\text{dienone}}$] product **27**, in keeping with experimental observations and the prediction from the MEP passing through **23**. Trajectories passing through **24-ax** or the similar **24-eq** afford a majority of the observed **29**, but the trajectories results predict that a substantial amount (≈25-30%) of the alternative product **30** should also be formed. As discussed above, isomerization of **30** to **29** can account for **30** not being observed. Trajectories passing through **25** preferentially afforded [$2\pi_{\text{diene}}$ + $4\pi_{\text{dienone}}$] product **31** over [$4\pi_{\text{diene}}$ + $2\pi_{\text{dienone}}$] product **32**.

The ratio of trajectories forming **31** versus **32**, at 1.58, is strikingly close experimental observations, though the uncertainty of the predicted ratio based on the necessarily limited number of trajectories is high. All trajectories passing though **26** afforded the [$2\pi_{\text{diene}} + 4\pi_{\text{dienone}}$] product **33**, in keeping with experimental observations and the prediction from the MEP passing through **34**.

Table 1. Results from quasiclassical trajectories starting from transition structures **23**, **24-ax**, **24-eq**, **25**, and **26**, and starting from ridge structures **41** and **42**.

	[$4\pi_{\text{diene}} + 2\pi_{\text{dienone}}$] (Formation of **27**, **29**, **32**, or **34**)	[$2\pi_{\text{diene}} + 4\pi_{\text{dienone}}$] (Formation of **28**, **30**, **31**, or **33**)	Recrossing trajectories
Transition Structure			
23	22	2	2
24-ax	28	10	1
24-eq	18	8	1
25	12	19	2
26	0	10	
Ridge Structure			
41	7	0	12
42	4	7	13

(a) 2,3-dimethylbutadiene (b) 1-vinylcyclohexene



(c) 2-vinylfuran (d) styrene

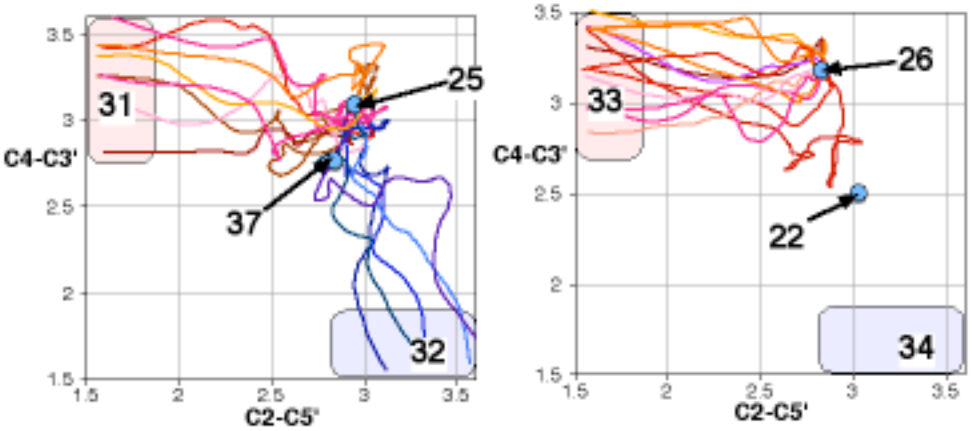


Figure 13. Summary of trajectory studies for reations with 1,3-dienes.

Figure 14 was constructed to display in more detail the qualitative features of the surface involving **24-ax**. On this surface, the paths for formation of observed product **29** versus alternative product **30** have merged into a broad transition state "ridge" with **24-ax** as the low point. This ridge may be roughly defined by the displacement of the atoms along a low-energy transverse vibrational normal mode (70 cm^{-1}). This transverse mode is strikingly anharmonic, which will be seen to have experimental consequences.

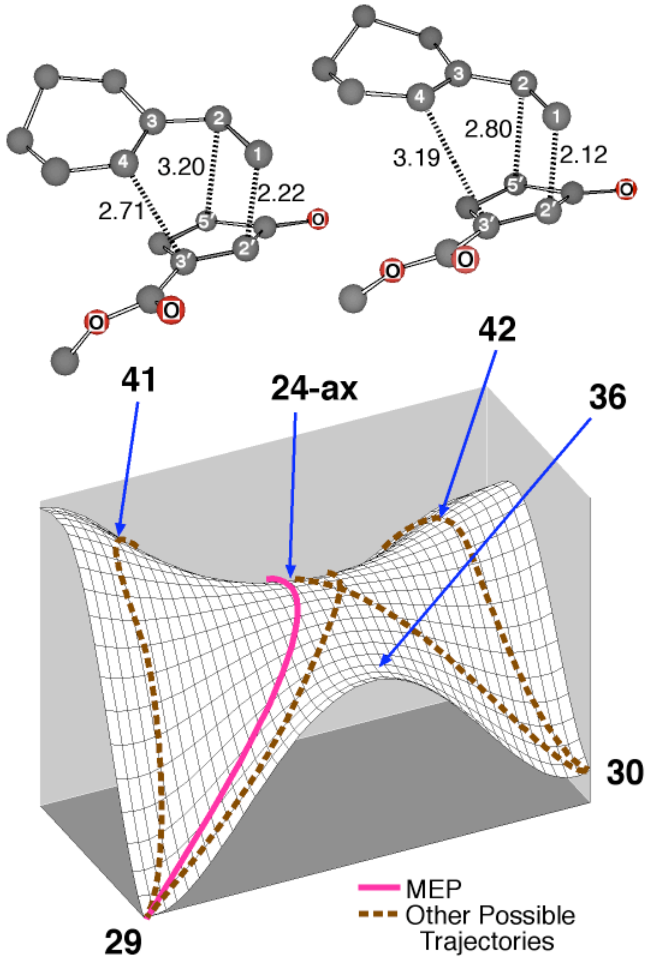


Figure 14. Qualitative energy surface for the reaction of **18** with **20**. Trajectories starting from **18** + **20** (at the back of the surface) could lead to either **29** or **30** through the same transition state area. Due to the anharmonicity of the transition state ridge, more trajectories pass to the right of **24-ax** than to the left, affecting the isotope effects.

On a relaxed potential energy surface (fixing C_1-$C_{2'}$, C_2-$C_{5'}$, and C_4-$C_{3'}$ after extension along the 70 cm^{-1} mode), ridge structure **41** is 1.0 kcal/mol above **24-ax** while ridge structure **42**, displaced equally from **24-ax** in the opposite direction as **41**, is only 0.5 kcal/mol above **24-ax**. The outcome of trajectories should depend on where they cross this ridge, (or more generally, the transition state hypersurface).[120, 121] Trajectories passing through **41** should tend to afford **29**, while trajectories passing through **42** should tend to afford **30**.

Predicted Isotope Effects. For comparison with the experimental KIEs, KIEs were predicted from the computational studies in two ways. The first way employed conventional transition state theory and the second way allowed for the anharmonicity of the transition state ridge.

The ^{13}C KIEs based on **24-ax** were predicted as described earlier. The results are shown in Figure 15. To allow for the anharmonicity of the transition state ridge, a series of 21 equally spaced structures along the 70 cm^{-1} mode for **24-ax** were located and the isotope effects were calculated from a Boltzmann combination of all the predicted isotope effects for the 21 structures (Figure 15a). Because of the asymmetry of the ridge, the Boltzmann combination is weighted toward structures resembling **42**. The results are shown in Figure 15b. Both sets of predicted isotope effects match reasonably with experimental values, but the set of predicted isotope effects allowing for the asymmetry of the transition state match slightly better.

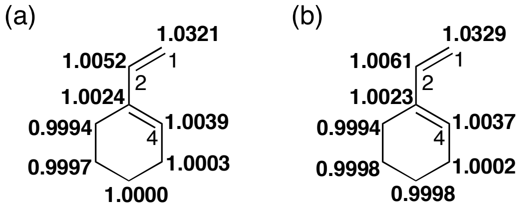
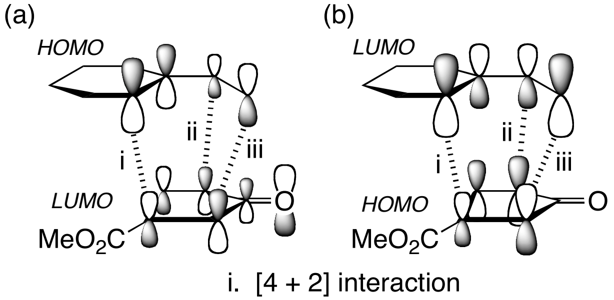


Figure 15. Predicted ^{13}C kinetic isotope effects ($k^{12}\text{C}/k^{13}\text{C}$) for the Diels-Alder reaction of **18** with **20** for both (a) **24-ax** and (b) Boltzmann combination of 21 structures based on **24-ax** located along the transition state ridge.

Discussion

In applying transition state theory to the understanding of the kinetic selectivity between two distinct products in a reaction, and assumption is made that the products arise from two distinct transition states. In the cycloadditions of **17**, the operative transition states would be envisioned as taking on separate "platonic forms" that are recognizably [$4\pi_{\text{diene}} + 2\pi_{\text{dienone}}$] or [$2\pi_{\text{diene}} + 4\pi_{\text{dienone}}$] in character. This assumption is intrinsic in qualitative theory. For example, FMO theory would attempt to account for the selectivity with **18** by examining the various [4 + 2] interactions and identifying the combination with the greatest overlap between the highest-energy HOMO and the lowest energy LUMO. It is not surprising that this simple model of reactivity can fail[122-124] but the emphasis here is that its assumption of the applicability of transition state theory can be incorrect.

In the current reactions, the platonic [$4\pi_{\text{diene}} + 2\pi_{\text{dienone}}$] and [$2\pi_{\text{diene}} + 4\pi_{\text{dienone}}$] forms have merged at the transitions state. The reason for this merging and the strong preference for the resulting transition states over alternatives can be understood from the bispericyclic idea of Caramella.[85, 94] Figure 16 illustrates how the frontier orbital interactions can lead to a transition state with both [$4\pi_{\text{diene}}$ + $2\pi_{\text{dienone}}$] and [$2\pi_{\text{diene}}$ + $4\pi_{\text{dienone}}$] character. Approach of **18** to vinylcyclohexene in the endo orientation that would lead to product **29** maximizes HOMO-LUMO interactions. The $\text{HOMO}_{\text{vinylcyclohexene}}$-$\text{LUMO}_{\mathbf{2}}$ orbital pair in Figure 15a is closer in energy than the $\text{HOMO}_{\mathbf{2}}$-$\text{LUMO}_{\text{vinylcyclohexene}}$ pair of Figure 8b (8.8 eV versus 10.9 eV at HF/6-31++G(2d,p), so this orbital interaction should be more important, but both HOMO-LUMO pairs involve favorable [4 + 2] and [2 + 4] orbital interactions. From the size of the coefficients (HF/STO-3G), it might be expected that the [4 + 2] interaction would be favored by the $\text{HOMO}_{\text{vinylcyclohexene}}$-$\text{LUMO}_{\mathbf{2}}$ orbital pair. but the [2 + 4] interaction is favored by the alternative HOMO-LUMO pair. In the transition structures **24-ax** evolving from these interactions, the [4 + 2] and [2 + 4] character is nearly equal. Only as the energy surface approaches the products is the thermodynamically more stable **29** favored.



i. [4 + 2] interaction
ii. [2 + 4] interaction
iii. interaction for both

Figure 16. Frontier orbital interactions between **18** and vinylcyclohexene. The size of the coefficients depicted is based on an HF/STO-3G calculation.

The experimental of the current system support the bispericyclic nature of the transition state. The C_2 KIE of ≈1.009 is much larger than the KIEs observed at C_3 and C_4 and would be surprisingly large for a simple [$4\pi_{\text{diene}} + 2\pi_{\text{dienone}}$] cycloaddition. However, this strange observation can be qualitatively rationalized once it is understood that a bispericyclic transition state is involved, so that there is some degree of bonding to C_2 at the transition state, even though this bonding does not show up in the observed product. Quantitatively, the close match between experimental and predicted ^{13}C KIEs provides support for the bispericyclic geometries observed in **24-ax**.

When transition state is applicable, the fundamentals of ground-state structural energetics are used implicitly for insight into selectivity. The central goal of the work here is to examine the qualitative ideas that must be considered to understand selectivity on bifurcating surfaces when transition state theory is not applicable. In place of transition state energetics, the guiding principles must be those of Newtonian dynamics.

Experimental Section

Diels-Alder Cycloaddition of 17 and 20 – Low Conversion Reaction. A mixture of 2.59 g (24 mmol) of vinylcyclohexene and 700 mg of **17** was dissolved in 80 mL of dry THF under N_2 at room temperature, then 1.33 mL (9.59 mmol) of triethylamine was added and the reaction was left to stir overnight. An aliquot taken before workup and checked by ^{1}H NMR found that the reaction was at ~13% conversion. The reaction mixture was then poured into 150 mL of saturated aqueous NaCl and extracted with 3 x 60 mL of diethyl ether. The combined organic layers were dried over $MgSO_4$ and concentrated using a rotary evaporator. The resultant oil was chromatographed on a 5 cm x 45 cm flash silica gel column using 20% ethyl acetate/hexanes as eluent to afford 625 mg of **29**. A second reaction performed by an analogous procedure proceeded to 13.2% conversion.

Diels-Alder Cycloaddition of 17 and 20 – High Conversion Reaction. A mixture of 400 mg (3.7 mmol) of vinylcyclohexene and 300 mg of **17** was dissolved in 38 mL of C_6D_6 under N_2 at room temperature, and 1.6 mL (11.5 mmol) of triethylamine was added. The reaction was then heated to reflux. Aliquots were taken every 3 h and checked by ^1H NMR, and additional 300 mg portions of **17** were added until the reaction reached 99.3 ± 0.7% conversion. The reaction mixture was then poured into 50 mL of saturated aqueous NaCl and extracted with 3 x 30 mL of diethyl ether. The combined organic layers were dried over $MgSO_4$ and concentrated on a rotary evaporator. The resultant oil was chromatographed on a 5-cm x 45-cm flash silica gel column using 20% ethyl acetate/hexanes as eluent to afford 610 mg of **29**.

Diels-Alder Cycloaddition of 17 and Styrene. A mixture of 2.93 mL of styrene (25.6 mmol) and 280 mg of **17** was dissolved in 12 mL of dry THF under N_2 at room temperature, and 392 mL (2.8 mmol) of triethylamine was added and left to stir for 3 days at room temperature. The reaction mixture was then poured into 120 mL diethyl ether and washed with 50 mL 2% $CuSO_4$ to remove triethylamine. The organic layer was washed twice with 100 mL of water, dried over $MgSO_4$ with decolorizing charcoal, and concentrated using a rotary evaporator. The resultant oil was chromatographed on a 20-mm x 250-mm flash silica gel column using hexanes to remove the styrene, followed by 5% ethyl acetate/hexanes as eluent to afford 111 mg of **33**: ^{1}H NMR (C_6D_6) δ 6.98 (s, 3H), 6.80 (s, 1H), 6.73 (d *J*=7.0 Hz, 2H), 3.46 (s, 1H), 3.32 (s, 3H), 3.16 (m, 1H), 2.99 (m, 1H), 2.00 (m, 1H), 1.31 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 201.8, 163.3, 141.8, 140.0, 137.5, 128.8, 128.1, 127.2, 56.0, 52.3, 47.9, 39.7, 30.6. HRMS: calculated $[M+Li]^+$ for $C_{15}H_{14}O_3$ 249.1103, found 249.1105.

Diels-Alder Cycloaddition of 17 and 2-vinylfuran. A mixture of 0.82 g of 2-vinylfuran (9 mmol) and 400 mg of **17** was dissolved in 30 mL of C_6D_6 under N_2 at room temperature, and 0.75 mL (5.4 mmol) of triethylamine was added and left to stir for 2 days at room temperature. The reaction mixture was then poured into 100 mL saturated NaCl, then extracted the organic layer with 3 x 100 mL portions of diethyl ether. The combined organic layers were then washed twice with 100 mL of water, dried over $MgSO_4$, and concentrated on a rotary evaporator. The resultant oil was chromatographed on a 20-mm x 400-mm flash silica gel column using hexanes to remove the styrene, followed by 5% ethyl acetate/hexanes as eluent to afford 116 mg of **31** and 80 mg of **32**. **31** ^{1}H NMR (C_6D_6): δ 6.89 (s, 1H), 6.80 (d *J*=4.6 Hz, 1H), 5.89 (m, 1H), 5.45 (m, 1H), 3.35 (m *J*=5.2 Hz, 1H), 3.27 (s, 3H), 3.13 (m, 1H), 3.01 (m, 1H), 1.84 (m *J*=5.2 Hz, 1H), 1.15 (m *J*=4.5, 9.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 200.0, 162.8, 155.4, 142.0, 139.8, 137.8, 110.4, 106.5, 54.0, 51.2, 47.3, 33.2, 28.5. HRMS: calculated $[M+Li]^+$ for $C_{13}H_{12}O_4$ 239.0896, found 239.0901. **32** ^{1}H NMR (C_6D_6): δ 6.91 (d *J*=5.8 Hz, 1H), 6.05 (m *J*=2.2, 2.7 Hz, 1H), 5.88 (d *J*=5.8 Hz, 1H), 5.09 (m *J*=1.2, 2.6, 2.7 Hz, 1H), 5.00 (m *J*=1.2, 3.2, 3.4, 8.0 Hz, 1H), 3.40 (m *J*=2.2, 2.6, 3.0, 3.2, 1H), 3.21 (s, 3H), 2.72 (m *J*=2.0, 8.0, 14.9 Hz, 1H), 2.68 (m *J*=2.0, 6.0 Hz, 1H), 1.71 (m *J*=3.0, 3.4, 6.0, 14.9, 1H). COSY spectrum was consistent with the assigned structure giving couplings between X and Y. HRMS: calculated $[M+Li]^+$ for $C_{13}H_{12}O_4$ 239.0896, found 239.0898.

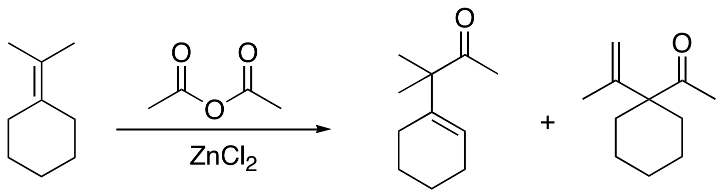
NMR Measurements. NMR samples were prepared using 400 mg of product **29** in a 5-mm NMR tube filled to a 5-cm sample height with $CDCl_3$. The ^{13}C spectra were recorded at 125.895 MHz using inverse gated decoupling, 43.29 s delays, and an 8.493 s acquisition time to collect 512,000 points. Integrations were determined numerically using a constant equal integration region for peaks compared. A zeroth-order baseline correction is generally applied, but in no case was a first-order (tilt) correction applied. Six spectra were obtained for all three independent samples of **29**. The raw integration results are shown in the Appendix A.

CHAPTER IV

ENE REACTION OF ISOPROPYLIDENECYCLOHEXANE

The acylation reaction of olefins catalyzed by Lewis acids, unlike that of aromatics, is postulated to go through a concerted ene type mechanism. A concerted mechanism is proposed to account for experimentally observed regioselectivity in resulting β,γ-unsaturated ketone products.[125-127] However, there have also been arguments for a stepwise mechanisms based on experimental H/D KIEs that support the idea of different rate-determining and product selectivity-determining steps.[128] Deciphering between a concerted and stepwise mechanism is often more complicated than imagined.

Describe here is a mechanistic study of the ene reaction of isopropylidenecyclohexane (**43)** with acetic anhydride catalyzed by zinc chloride using a combination of KIEs, standard theoretical calculations, and trajectory calculations. The results suggest that the nature of regioselectivity in this reaction is far more complicated than previously understood, and thought to involve dynamic effects on a bifurcating energy surface.



43 **44** **45**

Results

Intermolecular and Intramolecular ^{13}C Experimental Isotope Effects. The ene reaction of isopropylidenecyclohexane (**43**) with acetic anhydride catalyzed by zinc chloride proceeds smoothly at room temperature as previously reported in the literature.[128] Similar conditions were used to carry out all reactions. The ^{13}C KIEs for **43** were determined using natural abundance by NMR methodology.[3] Two separate reactions were taken to 85% and 75% conversion and **43** was recovered by extractive workup followed by flash chromatography. Both samples were analyzed by ^{13}C NMR in comparison with unreacted standard of **43**. The relative changes in ^{13}C isotopic composition at each position was then analyzed using C_6 as an internal standard with the assumption that the KIE at C_6 is negligible. In addition, **44** was also isolated by flash chromatography and analyzed by ^{13}C NMR for intramolecular comparison of C_4 with C_8 using NMR methodology.[71]

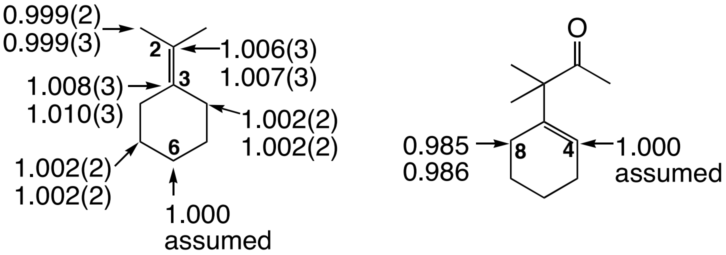
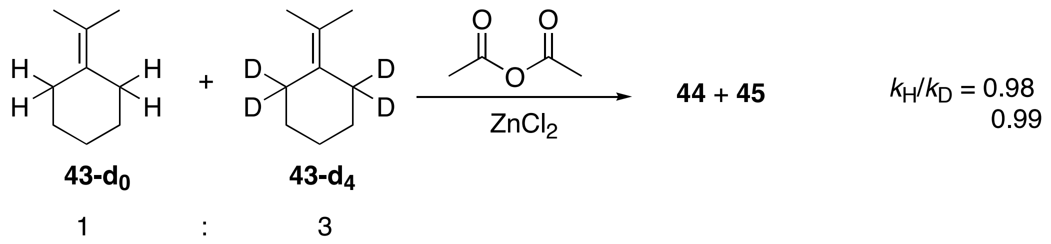


Figure 17. Intermolecular (left) and intramolecular (right) ^{13}C KIEs for the ene reaction of **43** with acetic anhydride catalyzed by zinc chloride.

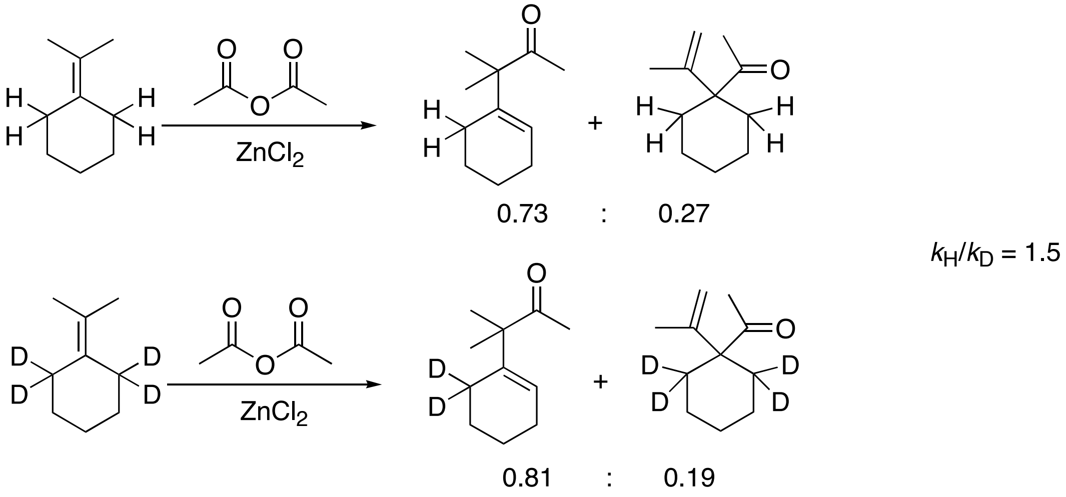
The results show small intermolecular KIEs at the C_2 and C_3 positions of the recovered starting olefin, Figure 17. These results are very similar to those seen in previous studies of ene reactions,[25, 127] and fits well with a mechanism involving an acylium ion attack down the center of the π-bond.

The experimental intramolecular KIEs here are unusual. One would have expected to see an equal amount of ^{13}C at both the C_4 and C_8 positions based on TST, if deprotonation was not the rate-determining step. However, effects upon symmetry breaking have been seen before for reactions that involve bifurcating energy surfaces,[29] and may account for this isotopic selectivity.

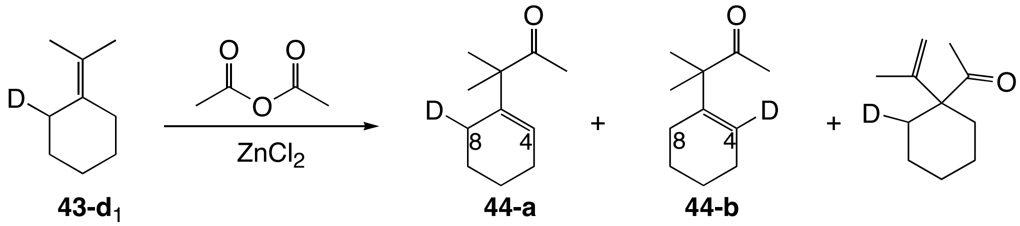
Intermolecular and Intramolecular H/D Experimental Isotope Effects. To explore the possibility of deprotonation being the rate-determining step in the reaction, intermolecular H/D KIEs were obtained. Two reactions of a 1:3 mixture of **43-d$_0$** and **43-d$_4$** was reacted with acetic anhydride catalyzed by zinc chloride and both taken to ≈75% conversion. The mixture of **43** was then isolated by an extractive work up, followed by flash chromatography. Both samples were analyzed by ^1H NMR in comparison with unreacted standard mixture of **43-d$_0$** and **43-d$_4$**. The relative changes in isotopic composition at each position was then analyzed using the isopropylene methyl protons as an internal standard with the assumption that the KIE at those positions are negligible. The absences of a significant H/D KIE ($k_H/k_D \approx 0.99$) suggests that deprotonation is not the rate-determining step in this reaction.



Intramolecular H/D KIEs were also obtained by comparison of the product isomers ratios obtained by GC analyses for 2 sets of independent reactions for **43-d₀** versus **43-d₄**. An intramolecular H/D KIE of 1.5 was obtained. This result suggests that selectivity is in fact decided after the rate-determining step. However, this data does not eliminate the probability of a long-lived intermediate.



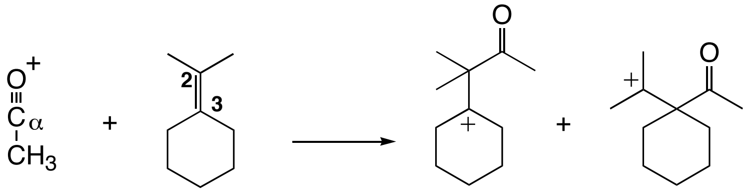
Selectivity in H/D Abstraction? To probe the question about if there is a long-lived intermediate formed following the acylium attack, **43-d₁** was synthesized and used to help clarify this issue. Two separate reactions of **43-d₁** with acetic anhydride catalyzed by zinc chloride were taken to ≈76% and ≈78% conversion. The product mixture of **44-a** and **44-b** was then isolated by an extractive work up, followed by flash chromatography. Both samples were analyzed by ^{2}H NMR to determine relative changes in isotopic composition of C_4 versus C_8 positions.



The results for this experiment are difficult to interpret using TST. By TST, one would expect to have an equal probability of either a proton or deuterium since deprotonation has been ruled out as not being the rate-determining step in this reaction. However, upon analysis of **44** from these reactions shows that there is quantitatively more deuterium at the C_4 position than the C_8 position, 2.13:1 ratio. To interpret these results.

Theoretical Studies

Just as in the case of electrophilic aromatic substitution theoretical calculations are challenging due to the importance of charge separation. Here a more simplistic approach was taken for the modeling process on this system. The ene reaction of **43** with acylium ion was studied using B3LYP calculations using a 6-31+G* basis set. Stationary points and transitions states were located for the reaction of **43** with acylium ion. In the gas-phase DFT calculations, the addition of the acylium ion is downhill by ≈28 kcal/mol (pot. E + zpe) and no potential energy barrier for the reaction.



8 **43** $E_{rel} = 0$ **46** $E_{rel} = -28.6$ **47** $E_{rel} = -27.5$

The intermediates that lead to products **44** and **45**, **46** and **47** respectively are shown in Figure 18. Between these two structures, there is only a difference of 1.13 kcal/mol, with **46** being lower in energy than **47**. By examination of their bond distances with the acyl group, one can predict that the rearrangement would be favorable. The transition state for the rearrangement between **46** and **47** was then located, and found to have a barrier of 1.79 kcal/mol relative to **46**.

Again, if the argument for proton abstraction was made for this reaction, then the barrier should be quite high. The transition state for proton abstraction, **48**, was also located and shown in Figure 18. The barrier was found to be downhill by 0.5 kcal/mol relative to **46**.

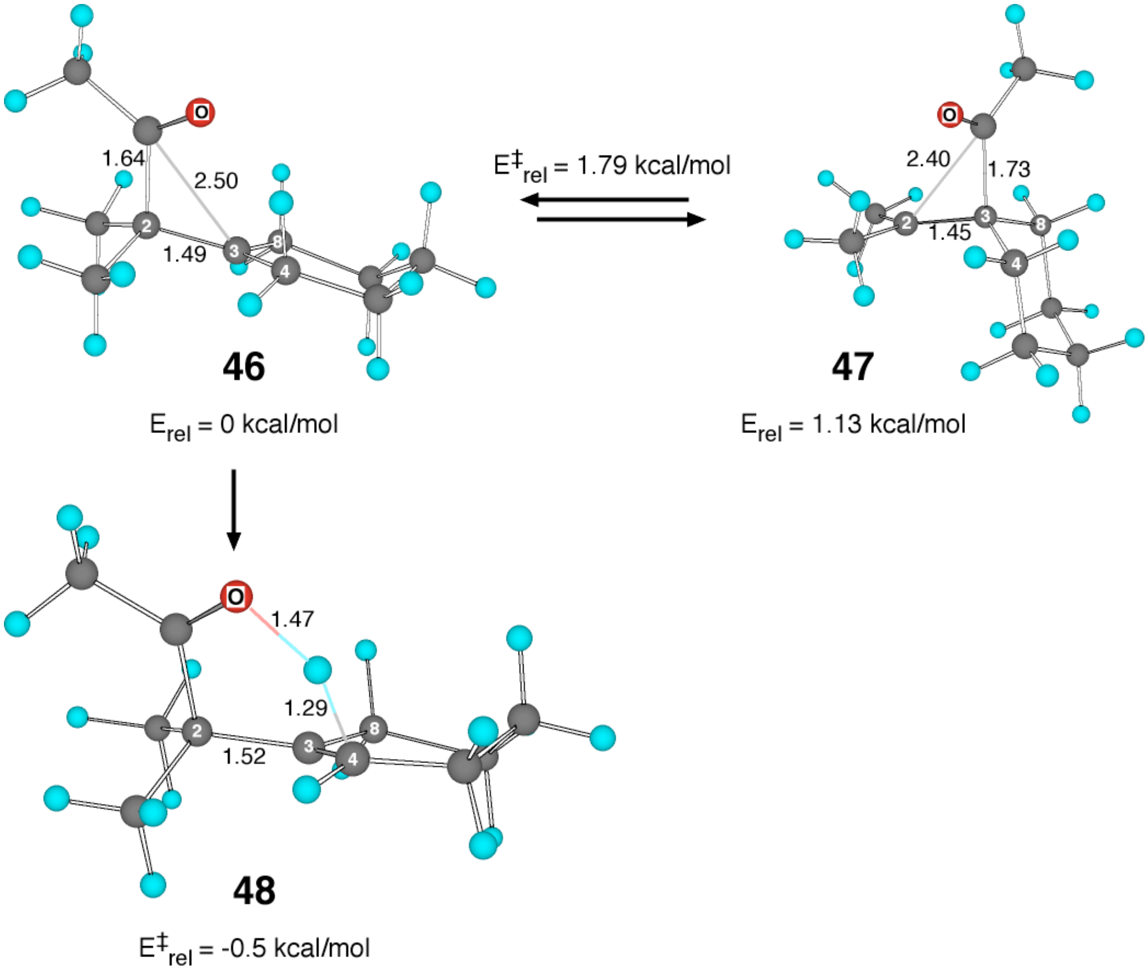


Figure 18. Intermediates **46** and **47** that lead to products **44** (top left) and **45** (top right), and transition state for proton abstraction **48** (bottom left).

The relaxed energy surface was calculated for the reaction of the acylium ion with **43** by fixing the C_α-C_2 and C_α-C_3 distances at a grid of values and optimizing the remaining geometrical variables at each point. The B3LYP/6-31G* +zpe surface generated is shown in Figure19. The surface is amazingly symmetrical as the acylium ion approaches **43**. As the acylium ion approaches **43**, symmetry breaking is only favored after the C_α-C_2 and C_α-C_3 distances are less than 2.4 Å. No conventional transition state can be located within this calculational model.

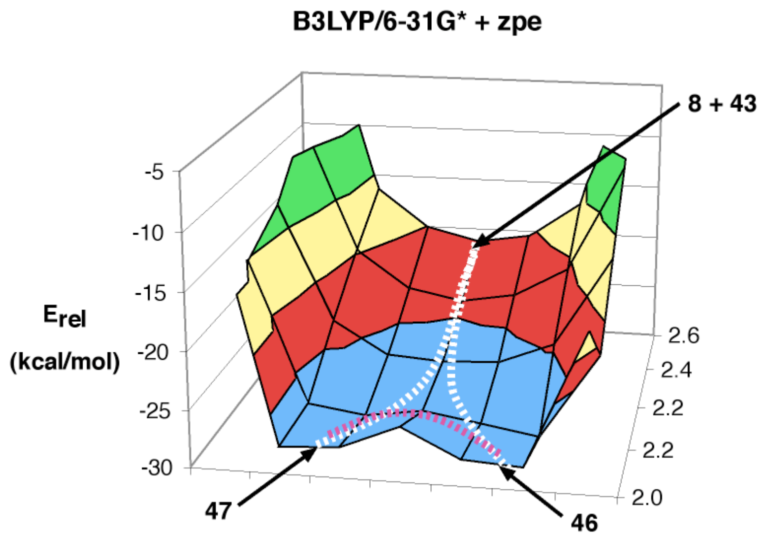
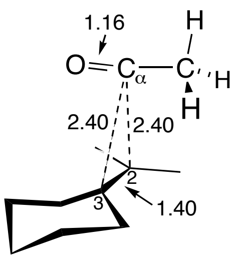
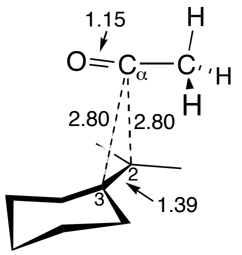


Figure 19. Energy surface for the approach of the acylium ion to **43**, fixing C_α-C_2 and C_α-C_3 distances.

Trajectory Studies. Quasiclassical trajectories were started from structure **49**‡ and **50**‡ on the B3LYP/6-31G* potential energy surface. Trajectories were initialized as previously described for 298.15 K, including zero-point energy. The trajectories were propagated employing a Verlet algorithm using 1-fs steps in previously described code[5] and using Gaussian 03[100] to calculate forces at each point until reaching intermediate **46** or **47**, or recrossing occurred to afford the starting materials. All trajectories were complete within 700 fs and the median time for product formation was 227 fs. Results are shown in Table 2.



49‡ E_{rel} = -26.8
(versus **8** + **43**)



50‡ E_{rel} = -21.3
(versus **8** + **43**)

Table 2. Results of quasiclassical trajectories starting from **49**‡ and **50**‡.

	Formation of **46**	Formation of **47**
49‡	30	39
50‡	2	5

The results for trajectory studies showed no recrossing to starting material in any of the trajectory simulations. Surprisingly, intermediate **47** was favored over **46** giving a ratio of 1:1.10. This preference is contradictory to the selectivity that is observed experimentally (1:0.19).

Predicted Isotope Effects. The ^{13}C and H/D KIEs were predicted based on **49**‡, a comparison of **46** with **47,** and **48** by a standard method described earlier. The results are shown in Figure 20.

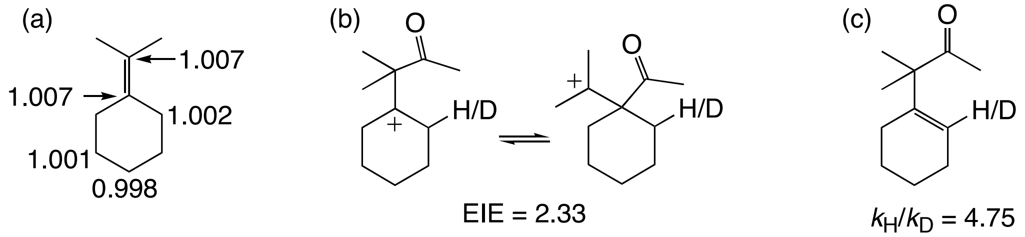


Figure 20. (a) Predicted ^{13}C KIEs based on **50**‡, (b) H/D EIE based on **46** and **47**, and (c) predicted H/D KIE based on transition structure **48**.

^{13}C KIEs for **50**‡ values are within experimental error of values measured experimentally. However, the predicted values would suggest a more synchronous rate-determining step compared to experimental values. The predicted H/D KIE for transition structure **48** shows that if deprotonation were the rate-determining step in this reaction, then a significant experimental KIE would have been obtained. The predicted equilibrium isotope effect (EIE) is calculated to be 2.33. This value is very close to experimentally measure H/D KIE of 2.1.

Discussion

The mechanism for the Lewis acid catalyzed ene reaction of **43** had proven to be a difficult system to interpret. As indicated by the experimental and theoretical results, there is unusual selectivity taking place in this Lewis acid catalyzed ene reaction of **43**. Not only is the observed regioselectivity in these reactions based on product selectivity, but also selectivity is observed in the downhill proton abstraction of **46** to **44**.

The experimental intermolecular ^{13}C KIEs show a slightly smaller KIE at the C_2 position relative to C_3 ($\approx$1.007 versus $\approx$1.010). This information at first did not seem to be unusual, since both experimental values are within experimental error. However, when analyzing the trajectory data, the slightly larger ^{13}C KIE of ≈1.010 suggests that **47** is forming in competition with **46**, with a slight preference for the formation of **47**. This is a clear indication that dynamic effects are influencing the selectivity of the reaction after the initial transition state. However, once the intermediate **47** is formed, the geometry is set up for the enthalpically favored rearrangement to **46** which then leads downhill to the major product **44**. The experimentally observed selectivity in this reaction is a result of the energy barriers associated with the rearrangement of **46** to **47**, however, had this barrier for rearrangement been larger than 1.79 kcal/mol, a different ratio would have been observed in terms of the product selectivity.

Experimental Section

The isopropylidenecyclohexane was prepared according to previously reported procedure.[129]

Ene Reaction of Isopropylidenecyclohexane – High Conversion Reaction. A mixture of 5 g (0.04 mol) of isopropyldienecyclohexane and 0.1 mL of dodecane (internal standard) were dissolved in 400 mL of acetic anhydride under N_2 at room temperature, then 0.54 g (0.004 mol) of dry zinc chloride was added. The reaction was monitored by aliquots taken before workup and checked by GC. After approximately 4 h the reaction was at ~85% conversion. The reaction mixture was then poured into 400 mL of cold saturated aqueous Na_2CO_3 and extracted with 3 x 100 mL of pentane. The combined organic layers were dried over Na_2SO_4. The solution was then concentrated by a distillation. The resultant oil was chromatographed on a 5-cm x 45-cm flash silica gel column using pentane as eluent to afford 2 fractions. Fraction 1 contained dodecane, and fraction 2 contained the recovered **43**. The column was then flushed with diethyl ether to recover a mixture of the two ene products, **44**, which was then set aside. Pentane was then distilled off from fraction 1 and the resultant oil was then vacuum distilled to obtain 630 mg of recovered isopropylidenecyclohexane. The recovered mixture of ene products was then concentrated by rotary evaporator, then the resultant oil was chromatographed on a 5-cm x 45-cm flash silica gel column using dichloromethane as eluent to afford 250 mg of **44**: ^{1}H NMR ($CDCl_3$) δ 5.51 (m, 1 H), 1.92 (m, 2 H), 1.85 (s, 3 H), 1.64 (m, 2 H), 1.41 (m, 4 H), 1.01 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 212.7, 140.3, 122.3, 54.0, 26.1, 25.9, 24.9, 23.5, 23.3, 22.7. A second reaction performed by an analogous procedure proceeded to 75% conversion.

Ene Reaction of Isopropylidenecyclohexane-d_0 vs d_4. A mixture of 0.20 g (0.0016 mol) of **43-d_0** and 0.64 g (0.005 mol) of **43-d_4** and 0.1 mL of dodecane (internal standard) were dissolved in 66 mL of acetic anhydride under N_2 at room temperature, then 0.09 g (0.00066 mol) of dry zinc chloride was added. The reaction was monitored by aliquots taken before workup and checked by GC. After approximately 4 h the reaction was at ~75% conversion. The reaction mixture was then poured into 100 mL of cold saturated aqueous Na_2CO_3 and extracted with 3 x 50 mL of pentane. The combined organic layers were dried over Na_2SO_4. The solution was then concentrated by a distillation. The resultant oil was chromatographed on a 5-cm x 45-cm flash silica gel column using pentane as eluent to afford 2 fractions. Fraction 1 contained dodecane, and fraction 2 contained the recovered isopropylidenecyclohexane. Pentane was then distilled off from fraction 1 and then vacuum distilled to obtain 60 mg of recovered isopropylidenecyclohexane mixture. A second reaction performed by an analogous procedure proceeded to 75% conversion.

Preparations of Isopropylidenecyclohexane-d$_1$. A mixture of 20 g (0.12 mol) of 1-morpholinocyclohexene and 7 mL D_3PO_4 was prepared at 0 ˚C. After stirring for 10 m the reaction mixture was then poured onto 20 mL of H_2O and extracted with 2 x 100 mL of pentane. The combined organic layers were then washed with H_2O and dried over Na_2SO_4. The solution was then concentrated using a rototary evaporator and yielded 6.4 g of cyclohexanone-d$_1$: ^{1}H NMR ($CDCl_3$) δ 2.31 (t, 3 H), 1.84 (m, 4 H), 1.70 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 212.6, 42.3, 27.3, 25.2. The deuterated cyclohexanone was then used to prepare the deuterated isopropylidenecyclohexane which was prepared according to previously reported procedure.[129] ^{1}H NMR ($CDCl_3$) δ 2.15 (t, 3 H), 1.67 (m, 6 H), 1.51 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 132.4, 120.6, 30.6, 28.3, 27.2, 20.1.

Ene Reaction of Isopropylidenecyclohexane-d$_1$. A mixture of 1.5 g (0.012 mol) of **43-d$_1$** and 0.1 mL of dodecane (internal standard) were dissolved in 120 mL of acetic anhydride under N_2 at room temperature, then 0.2 g (0.0012 mol) of dry zinc chloride was added. The reaction was monitored by aliquots taken before workup and checked by GC. After approximately 4hrs the reaction was at ~76% conversion. The reaction mixture was then poured into 100 mL of cold saturated aqueous Na_2CO_3 and extracted with 3 x 60 mL of pentane. The combined organic layers were dried over Na_2SO_4. The solution was then concentrated by a distillation. The resultant oil was chromatographed on a 5-cm x 45-cm flash silica gel column using pentane as eluent to afford 2 fractions. Fraction 1 contained dodecane, and fraction 2 contained the recovered **43**. The column was then flushed with diethyl ether to recover a mixture of the two ene products. The recovered mixture of ene products was then concentrated by rotary evaporator, then the resultant oil was chromatographed on a 5-cm x 45-cm flash silica gel column using dichloromethane as eluent to afford 667 mg of **44**. A second reaction performed by an analogous procedure proceeded to 78% conversion.

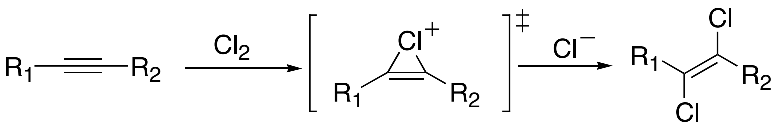
NMR Measurements. Recovered isopropylidenecyclohexane NMR samples were prepared using 360 mg of olefin in a 5-mm NMR tube filled to a 5-cm sample height with $CDCl_3$. The ^{13}C spectra were recorded at 125.698 MHz using inverse gated decoupling, 259.74 s delays, and an 11.648 s acquisition time to collect 512,000 points. Integrations were determined numerically using a constant equal integration region for peaks compared. A zeroth-order baseline correction is generally applied, but in no case was a first-order (tilt) correction applied. Six spectra were obtained for both independent samples of recovered olefin and unreacted olefin.

Product 1 NMR samples were prepared using 530 mg of olefin in a 5-mm NMR tube filled to a 5-cm sample height with $CDCl_3$. The ^{13}C spectra were recorded at 125.697 MHz using inverse gated decoupling, 34.632 s delays, and a 6.40 s acquisition time to collect 512,000 points. Integrations were determined numerically using a constant equal integration region for peaks compared. A zeroth-order baseline correction is generally applied, but in no case was a first-order (tilt) correction applied. Six spectra were obtained for both independent samples of **44**. Recovered mixture of deuterated isopropylidenecyclohexane NMR samples were prepared using 60 mg of olefin in a 5-mm NMR tube filled to a 5-cm sample height with $CDCl_3$. The ^{1}H spectra were recorded at 499.902 MHz, 25.974 s delays, and a 3.0 s acquisition time to collect 48,000 points. Integrations were determined numerically using a constant equal integration region for peaks compared. A zeroth-order baseline correction is generally applied, but in no case was a first-order (tilt) correction applied. Six spectra were obtained for both independent samples of recovered olefin and unreacted olefin. Recovered mixture of **43-d$_1$** NMR samples were prepared using 40 mg of olefin in a 5-mm NMR tube filled to a 5-cm sample height with $CDCl_3$. The ^2H spectra were recorded at 601.337 MHz, 10 s delays, and a 4.00 s acquisition time to collect 5,600 points. Integrations were determined numerically using a constant equal integration region for peaks compared. A zeroth-order baseline correction is generally applied, but in no case was a first-order (tilt) correction applied. Six spectra were obtained for both independent samples of **44**. The raw integration results are shown in the Appendix A.

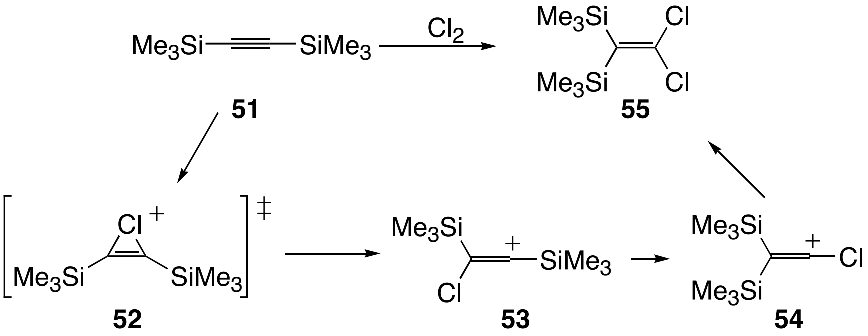
CHAPTER V

CHLORINATION OF ALKYNES

Chlorination of alkynes, like electrophilic aromatic substitution, appears to be another organic reaction of great interest where previous experimental observations for the electrophilic chlorination of alkynes were consistent with a bifurcating energy surface. The reaction is thought to involve an early symmetrical transition state and the regioselectivity is decided later on the energy hypersurface.[130] Unlike bromination, chlorination is not a well-studied system. TST cannot accurately predict the experimentally observed product selectivity that was observed by Yates and co-workers.[130-132] Yates reported that in the chlorination of dialkylacetylenes, the *trans* alkene product was the major product, and for this reason concluded that the reaction passes through a bridged chloronium ion structure.[130] The chloronium ion is not predicted to be a stable intermediate in the reaction, but instead an early transition state.



To investigate the possibility of dynamic effects determining regioselectivity in this reaction, a study was carried out using bis(trimethylsilyl)acetylene (**51**) as the substrate. Bis(trimethylsilyl)acetylene was an excellent substrate to use because it is symmetrical. Secondly, the intermediate does a rapid rearrangement followed by attack of the final nucleophile, in this case a chloride ion, and the carbons of the multiple bond in the final product are now unsymmetrical and easily distinguishable by ^{13}C NMR. The rearrangement of one of the TMS groups is not the rate-determining step in the reaction and has no affect on the ^{13}C content in the product.



Describe here is a mechanistic study of the chlorination of bis(trimethylsilyl)acetylene using KIEs. The results suggest that the nature of the selectivity in this reaction is far more complicated than it appears on the surface, involving dynamically determined regioselectivity on a bifurcating surface.

Results

Experimental Isotope Effects. Intermolecular KIEs for the chlorination of bis(trimethylsilyl)acetylene were determined as previously described.[130] A mixture of 20 mL of bis(trimethylsilyl)acetylene with 3.22 g of 1,3,5-trichlorobenzene (internal standard) in 22 mL of dichloromethane was taken to 82% and 80% conversion by monitoring the addition of chlorine in dichloromethane by ^{1}H NMR. The reactions were then quenched and the starting material for each was isolated and purified by a series of vacuum distillations. The change in isotopic content in the starting material was then measured by comparing these samples to original bis(trimethylsilyl)acetylene samples by ^{13}C NMR. The resulting KIEs are shown in Figure 21.

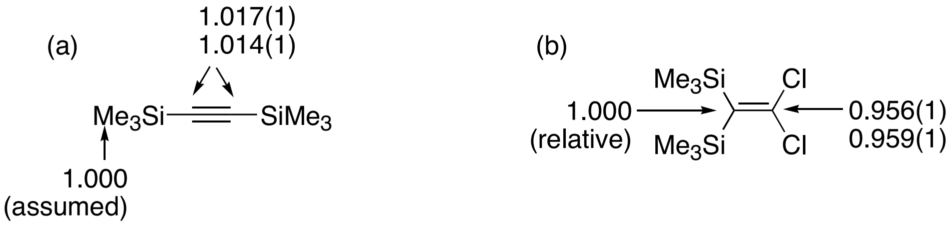


Figure 21. (a) Intermolecular ^{13}C KIEs for the recovered bis(trimethylsilyl)acetylene reactions taken at 82% (top) and 80% (bottom), (b) Intramolecular ^{13}C KIEs for **55**.

As shown in Figure 21a, the recovered starting material shows a significant KIE when compared to original starting material. Since C_1 and C_2 of the starting alkyne are indistinguishable, the only conclusion is that chlorine addition is the rate-determining step in this reaction.

The ^{13}C content of the isolated dichloro product **67** was also analyzed. A mixture of 10 mL of bis(trimethylsilyl)acetylene with 25 mL of dichloromethane was taken to 12.3% and 12.5% conversion by monitoring the addition of chlorine in dichloromethane. The reaction was then stopped and the product was isolated and purified by a series of vacuum distillations. ^{13}C content analyses of **55** are shown in Figure 21b.

As shown in Figure 21b, the product does show different ^{13}C content at the C_1 and C_2 positions in the product. These results indicate that there is selectivitiy in terms of the chlorine preferring to react with ^{13}C versus ^{12}C.

Discussion

Experimental KIEs show that the electrophile, chooses to react with the heavier carbon. This is the same observation as seen in singlet oxygen ene reactions and Friedel-Crafts acylation of veratrole. During the theoretical analysis, it was concluded that a through evaluation of this system could not be done properly. Chlorine ions are very hard to model computationally due to problems of charge separation. Unfortunately, after extensive efforts, no accurate transition state was located. Since a transition state structure could not accurately be located, theoretically predicted KIEs and dynamic simulations could not be done at this time.

Experimental Section

Chlorination of bis(trimethylsilyl)acetylene – High Conversion Reaction. A mixture of 10 mL (0.044 mol) of bis(trimethylsilyl)acetylene and 5.9 mL of isoamyl nitrite (0.044 mol) (radical inhibitor) were dissolved in 25 mL of CH_2Cl_2 under N_2 at room temperature, then 80 mL (0.044 mol) of a 0.4 M chlorine solution in CH_2Cl_2 was added dropwise while stirring. The reaction was monitored by aliquots taken before workup and checked by GC until the reaction was at ~82% conversion. The reaction mixture was then poured into 100 mL of saturated aqueous $NaHSO_3$. The organic layer was then washed with H_2O, saturated NaCl, dried over Na_2SO_4, and concentrated by distillation to remove CH_2Cl_2, and the resultant oil was then vacuum distilled to recover 533mg of bis(trimethylsilyl)acetylene. A second reaction performed by an analogous procedure proceeded to 80% conversion.

Chlorination of bis(trimethylsilyl)acetylene – Low Conversion Reaction. A mixture of 23.6 mL (0.09 mol) of bis(trimethylsilyl)acetylene and 12 mL of isoamyl nitrite (0.09 mol) (radical inhibitor) were dissolved in 200 mL of CH_2Cl_2 under N_2 at room temperature, then 45 mL (0.023 mol) of a 0.5 M chlorine solution in CH_2Cl_2 was added dropwise while stirring. The reaction was monitored by aliquots taken before workup and checked by GC until the reaction was at ~12% conversion. The reaction mixture was then poured into 200 mL of saturated aqueous $NaHSO_3$. The organic layer was then washed with H_2O, saturated NaCl, dried over Na_2SO_4, and concentrated on by distillation. The resultant oil was then vacuum distilled to recover 2.0g of **55**. ^1H NMR ($CDCl_3$): δ 1.23 (s, 6 H). ^{13}C NMR ($CDCl_3$): δ 138.7, 129.2, 2.8. A second reaction performed by an analogous procedure proceeded to ~12% conversion as well.

NMR Measurements. Recovered starting material NMR samples were prepared using 600 mg of bis(trimethylsilyl)acetylene in a 5-mm NMR tube filled to a 5-cm sample height with $CDCl_3$. The ^{13}C spectra were recorded at 125.894 MHz using inverse gated decoupling, 28.860 s delays, and a 8.00 s acquisition time to collect 512,000 points. Integrations were determined numerically using a constant equal integration region for peaks compared. A zeroth-order baseline correction is generally applied, but in no case was a first-order (tilt) correction applied. Six spectra were obtained for two independent samples of recovered bis(trimethylsilyl)acetylene and compared with a standard unreacted sample of bis(trimethylsilyl)acetylene. The raw integration results are shown in the Appendix A.

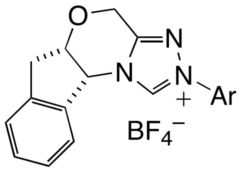
Product NMR samples were prepared using 1.5 g of the **55** in a 10-mm NMR tube filled to a 5-cm sample height with $CDCl_3$. The ^{13}C spectra were recorded at 125.896 MHz using inverse gated decoupling, 151 s delays, and a 8.739 s acquisition time to collect 512,000 points. Integrations were determined numerically using a constant equal integration region for peaks compared. A zeroth-order baseline correction is generally applied, but in no case was a first-order (tilt) correction applied. Six spectra were obtained for two independent samples of recovered **55**. The raw integration results are shown in the Appendix A.

CHAPTER VI

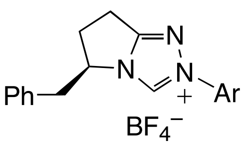
ENANTIOSELECTIVE INTRAMOLECULAR STETTER REACTION

There is no general physical difference in the nature of catalysis by enzymes versus abiological catalysts.[133] However, the evolution of enzymes for both proficiency and specificity tends to raise the importance of binding in the catalysis, so that substrate binding (or product loss) steps are much more often rate limiting in the realm of enzymatic catalysis.[134, 135] This may have the subtle advantage of separating substrate selectivity from the chemical conversion and product selectivity (such as enantioselectivity), so that the two can be affected independently.[136] The need for efficiency also dictates that an enzyme mediating a complex transformation bar loss of intermediates.[137] The mechanism of an organocatalytic reaction can bear each of these traits. The results may impact approaches to the design of new organocatalysts and organocatalytic reactions.

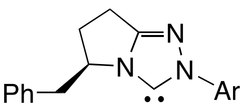
One major class of organocatalytic reactions, modeled on thiamine coenzyme catalysis, achieves reactivity umpolung by changing an electrophilic aldehyde into a nucleophilic acyl anion equivalent. In the example of the Stetter reaction, the intermediate acyl anion equivalent reacts with a Michael acceptor to ultimately afford 1,4-dicarbonyl species.[138-140] Thiazo-, imidazo-, and triazolinylidene carbenes, as well as cyanide catalyze these reactions.[141-143] The Rovis group has focused on the development of chiral triazolinylidene carbenes and precursors, **56-58**.[144-149] These induce the enantioselective cyclization of aromatic and aliphatic aldehydes to diverse activated alkenes, allowing the generation of quaternary stereocenters from β,β-disubstituted Michael acceptors and contiguous stereocenters from α,α,β-trisubstituted acceptors.



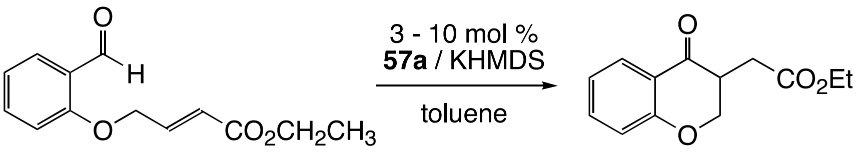
56a Ar = p-$MeOC_6H_4$
56b Ar = Ph
56c Ar = C_6F_5



57a Ar = Ph
57b Ar = p-$CF_3C_6H_4$



58a Ar = Ph
58b Ar = p-$CF_3C_6H_4$



59 **60**

The overall mechanism of these reactions is expected to be analogous to that elucidated by Breslow for thiamine catalysis of the benzoin condensation[150-153], but a detailed study revealed surprising facets, shown in Figure 22.

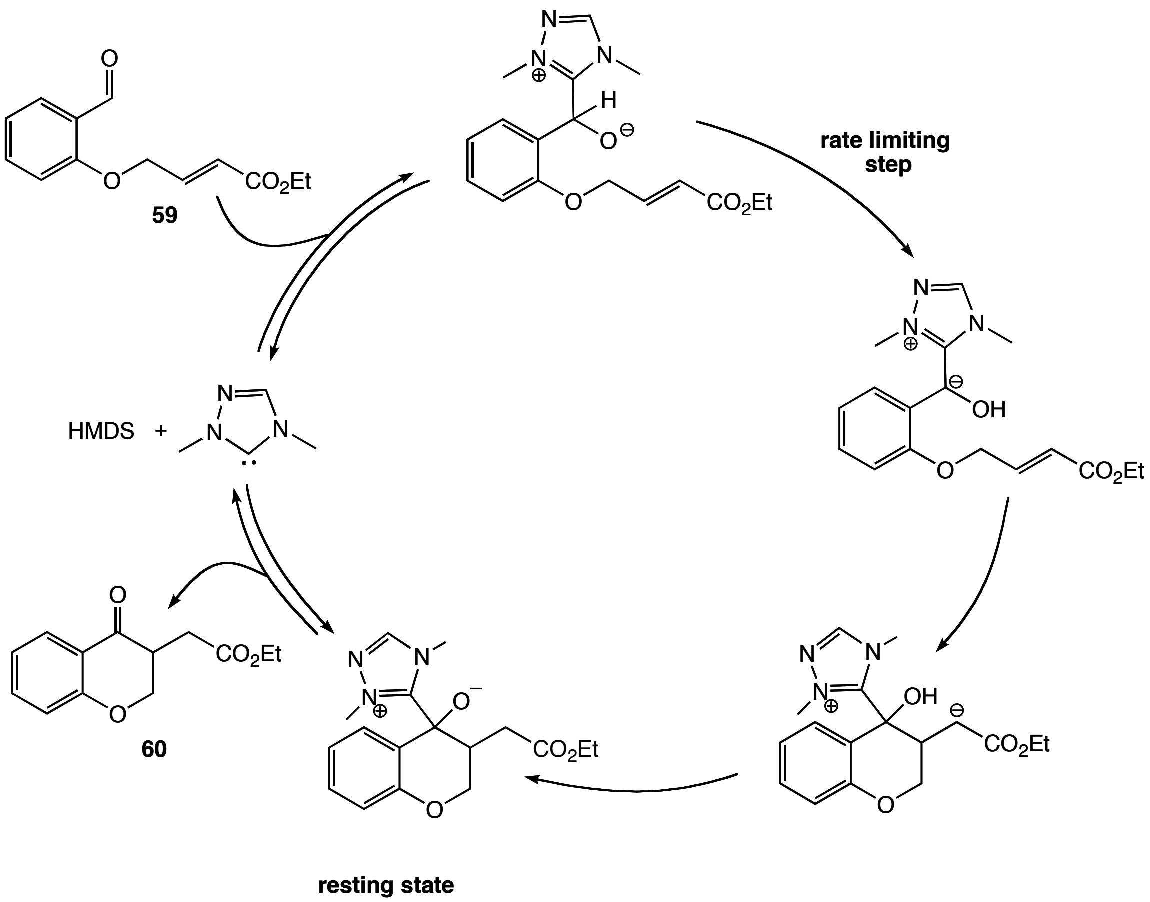


Figure 22. Mechanism based on the benzoin condensation mechanism proposed by Rovis.[149]

Results

Experimental Isotope Effects. For the cyclization of aldehyde **59** to keto-ester **60** mediated by 1:1 **57a** / KHMDS, a standard kinetic analysis found a first-order dependence on aldehyde concentration and a second-order dependence on **57a** / KHMDS. However, KHMDS in excess of **57a** did not increase the rate. Using preformed carbene **58a** in the absence of HMDS, the dependence on carbene is only first order. These observations suggest that the rate law for the **58a** / KHMDS mediated reaction is ν = k[**59**][carbene][HMDS].

The ^{13}C KIEs for the cyclization of **59** were determined by NMR methodology at natural abundance.[1-3] Reactions of **59** mediated by 20 mol % **57a** / 20 mol % KHMDS at 0 °C were taken to ≈80% conversion, and the unreacted **58** was reisolated and analyzed by ^{13}C NMR compared with samples of the original **58**. The change in isotopic composition in each position was determined relative to the methylene group of the ethyl ester, with the assumption that isotopic fractionation of this carbon was negligible, and the KIEs were calculated as previously described. As shown in Figure 23, the aldehydic carbon exhibits a substantial ^{13}C KIE of 1.022, but for the remaining carbons the KIE is negligible.

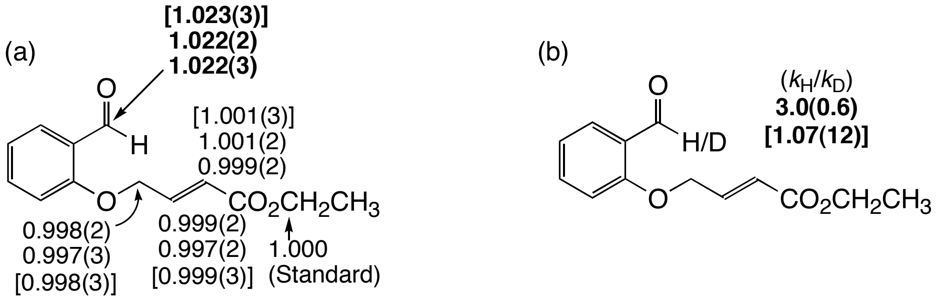


Figure 23. ^{13}C and ^{2}H KIEs for the cyclization of **57** at 27 °C. The ^{13}C KIEs are competitive while the ^{2}H KIEs are based on absolute rates. KIEs for the corresponding reaction using preformed **58a** in the absence of HMDS are shown in brackets.

The ^{2}H KIE for the aldehydic was also measured under these conditions using absolute kinetics. From triplicate runs with **59** and its deuterated isotopologue (Ar-CDO), the k_H/k_D is 3.0 ± 0.6. For the reaction using pre-formed carbene **58a**, the changed rate law is accompanied by a reduction of the ^{2}H KIE to 1.07 ± 0.12. However, the ^{13}C kinetic isotope effects change little, exhibiting a substantial effect at the aldehydic carbon and negligible isotope effects at the other carbons.

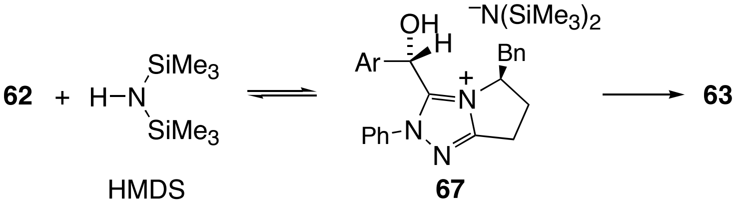
Theoretical Results

The reaction of **58a** with **59** was explored in B3LYP calculations employing a 6-31G* basis set with single-point energies calculated using a PCM solvent model for toluene and a 6-31+G** basis set. The calculationally preferred pathway is shown in Figure 24. Addition of **58a** to **59** occurs preferentially to the *re* face of the aldehyde via transition structure **61** to afford zwitterionic transition structure **62**. The ultimate cyclization requires conversion of **62** to neutral **63**, but the direct intramolecular 1,2-proton transfer has a very high barrier (>40 kcal/mol versus **62**). Instead, the conversion would likely occur by two sequential proton-transfer steps with an acid or base catalyst, as discussed further below. From **63**, the C–C bond-forming transition structure **64** leads to an intermediate ester enolate in the gas-phase calculations, but there is no barrier for proton transfer from the hydroxyl group to the enolate in PCM calculations. As a result, **65** would be formed directly from **64** by a concerted but highly asynchronous cyclization / proton transfer. This concerted process accounts for previous observations of the diastereoselectivity of these reactions.[149] An alternative stepwise cyclization / proton transfer has a predicted barrier that is 0.9 kcal/mol higher in energy, accounting for the observation of some leakage in the diastereoselectivity.[149] The fragmentation of zwitterions **65** into product **60** with regeneration of catalyst **58a** is facile via transition structure **66**.

The best transition structure leading to the enantiomeric product is very similar to **64**, except that the benzyl group of the triazolinylidene moiety is oriented toward the Michael acceptor rather than away. The resulting steric interaction destabilized the transition structure by 1.7 kcal/mol relative to **64**, in excellent agreement with the observed enantioselectivity of 97:3 at 25 °C.

Discussion

This mechanism accounts for the kinetics and kinetic isotope effects in the presence of HMDS, with the rate-limiting proton-transfer converting **62** to **63** being catalyzed by HMDS. The acidity of HMDS is similar to that of alcohols,[154, 155] allowing it to mediate the proton transfer by donation of a proton to **62** to afford ion-pair **67** followed by a second proton transfer affording **63**. In support of this proposal, the calculated formyl-group ^{13}C and ^{2}H KIEs for rate-limiting formation of **63** from **67** (in a simplified model with Ar = Ph and no Bn group) are 1.021 and 2.74, respectively. KIEs were predicted as described previously.



The most striking feature of this mechanism, strongly supported by the ^{13}C KIEs, is that the complex rate-limiting process of binding the catalyst to afford **63** commits the reaction to product formation and is kinetically decoupled from the stereoselectivity-determining cyclization of **63**. This enzyme-like behavior has a series of effects. One effect is that the catalysis is promiscuous, achieving similar reactivity in reactions of diverse Michael acceptors.[147, 149] A second result is that the optimization of stereoselectivity need not incur a cost in reactivity. For example, catalysts derived from **66** versus **67** display relatively similar reactivity, though **66** often leads to substantially greater enantio- and diastereoselectivity.[147] A third effect is that the cyclization of aldehydes of greatly differing intrinsic reactivity, such as salicylaldehyde derivatives versus aliphatic aldehydes, often shows similar stereoselectivity.[147] In each case, the enzyme-like kinetic character of the organocatalytic reaction simplifies the strategy of catalyst design.

Experimental Section

NMR Measurements. NMR samples were prepared using 300 mg of **59** in a 5-mm NMR tube filled to a 5-cm sample height with $CDCl_3$. The ^{13}C spectra were recorded at 125.701 MHz using inverse gated decoupling, 43.00 s delays, and a 9.152 s acquisition time to collect 512,000 points. Integrations were determined numerically using a constant equal integration region for peaks compared. A zeroth-order baseline correction is generally applied, but in no case was a first-order (tilt) correction applied. Six spectra were obtained for all three independent samples of **59**. The raw integration results are shown in the Appendix A.

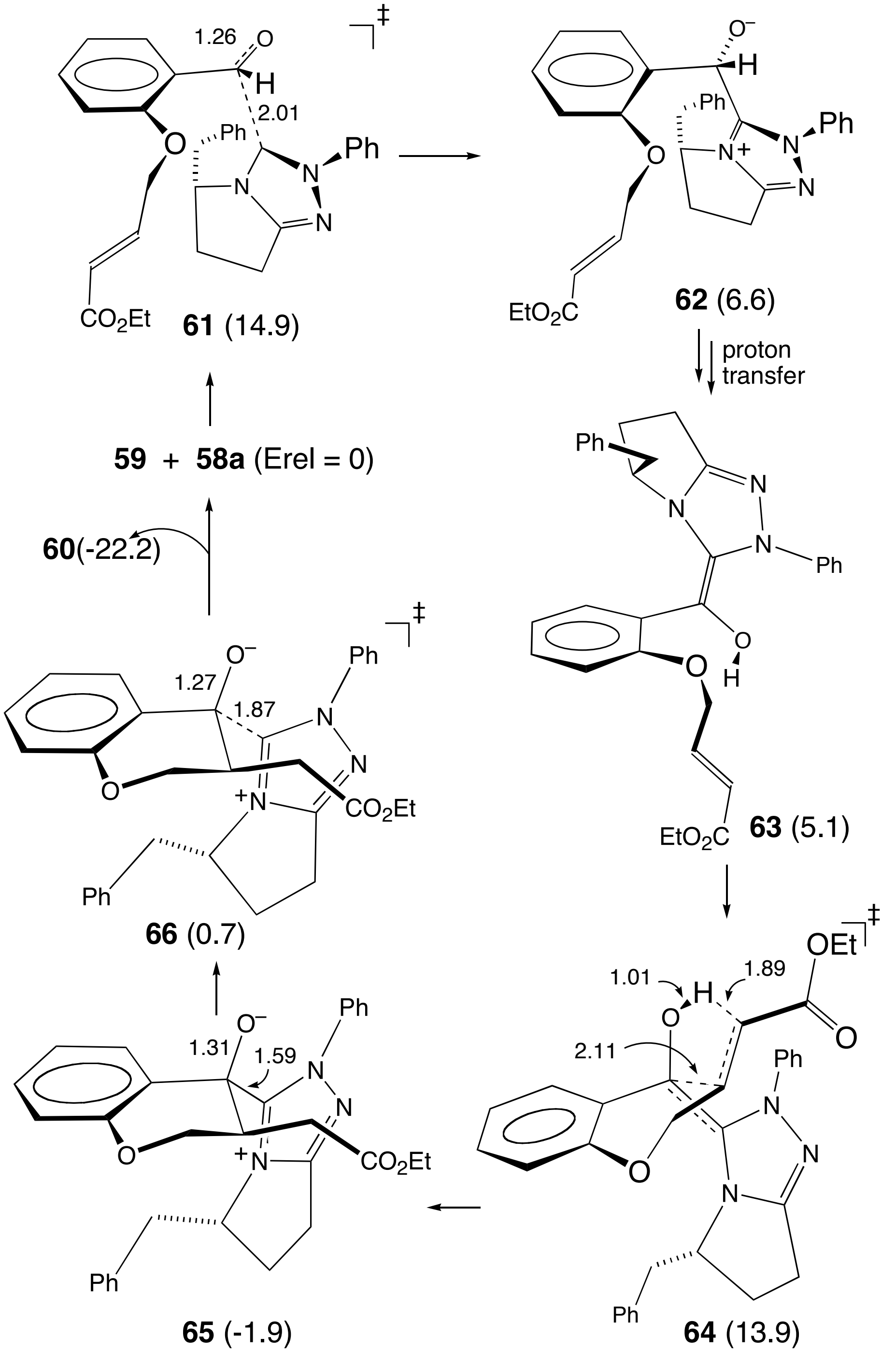


Figure 24. Calculated catalytic cycle for the cyclization of **59** mediated by **58a**. Energies in parentheses are B3LYP/6-31+G**/PCM(toluene) // B3LYP/6-31G* + zpe in kcal/mol relative to **59** + **58a**.

CHAPTER VII

CONCLUSIONS

Detailed mechanistic studies revealed the origin of selectivity for the organic reaction of electrophilic aromatic substitutions, Diels-Alder cycloadditions of **8** with 1,3-dienes, Lewis acid catalyzed ene reactions with **43**, chlorinations of alkynes, and the enantioselective intramolecular Stetter reaction. In all cases studies, with the exception of the Stetter reaction, the reactions all proceeded to product on bifurcating surfaces were selectivity was influenced by steepest-descent paths and atomic motion and momenta.

In the study of electrophilic aromatic substitution reactions, electrophiles that do not follow the Brown selectivity relationship and have early transition states involve dynamic effects on bifurcating energy surfaces. In the case of Friedel-Crafts acyltion, the origin for the regioselectivity (preference for ^{13}C versus ^{12}C) observed by ^{13}C KIEs is the result of symmetry breaking on the downward slope of the bifurcating energy surface. This type of analysis can be applied to other non-symmetrical systems, such as Friedel-Crafts acylation of anisole. By modeling the energy surface, one might be able to better understand the unusually high amounts of *meta* isomers form, and why they do not correlate with the Brown selectivity relationship.

In the Diels-Alder cycloadditions of **18** with various 1,3-dienes, the transition states for the four systems studied would be envisioned having both $[4\pi_{diene} + 2\pi_{dienone}]$ and $[2\pi_{diene} + 4\pi_{dienone}]$ character. The transitions states have ultimately merged into one single transitions state. The reason for this merging and the strong preference for the resulting transition states over alternatives can be understood from the bispericyclic idea of Caramella.[85, 94] The experimental of cycloadditions of **18** with **24** support the bispericyclic nature of the transition state. Trajectory analysis supports the idea that the steepest-descent path is a major contributor to selectivites observed experimentally for cycloadditions of **21** with **18**.

For the mechanism for the Lewis acid catalyzed ene reaction of **43**, the experimental intermolecular ^{13}C KIEs showed a slightly smaller KIE at the C_2 position relative to C_3 ($\approx$1.007 versus $\approx$1.010). This information combined with analyzing the trajectory data leads to the suggestion that **47** is in fact forming in competition with **46**, with a slight preference for the formation of **47**. This is a clear indication that dynamic effects are influencing the selectivity of the reaction after the initial transition state. However, once **47** is formed, the geometry of this intermediate is set up for the enthalpically favored transition state rearrangement to **46.** The observed selectivity in this reaction is a result of the energy barriers associate with the rearrangement of **46** to **47**, however, had this barrier for rearrangement been larger than 1.79 kcal/mol, the regioselectivity may have reflected results similar to the trajectory data.

In the mechanistic studies for the enantioselective intramolecular Stetter reaction, the origin of selectivity is a result of multiple transition states and their relative energies. Experimental H/D KIEs had lead to the conclusion that two different mechanisms were operating for reactions were carbenes were generated in situ versus reactions using free carbenes. However, ^{13}C KIEs and theoretical modeling of the reaction profile provide evidence for one mechanism operating in both cases.

In conclusion, when applying transition state theory to the understanding of the kinetic selectivity between two distinct products in a reaction, an assumption is made that the products arise from two distinct transition states. It has been shown through the mechanistic studies of electrophilic aromatic substitution, Lewis acid catalyzed ene reaction with **43**, the chlorination of alkynes, and the Diels-Alder cycloadditions of 1,3-dienes with **18**, that the origin of selectivity is not always a result of selectivity result from a kinetic competition between two closely related pathways to form distinct products. When TST is applicable, the fundamentals of ground-state structural energetics are used implicity for insight into selectivity. The central goal of the work here was to examine the qualitative ideas that must be considered to understand selectivity on bifurcating surfaces when transition state theory is not applicable. In place of transition state energetics, the guiding principles must be those of Newtonian dynamics for understanding the origin of selectivity.

REFERENCES

1. Singleton, D. A.; Thomas, A. A., *J. Am. Chem. Soc.* **1995,** *117*, 9357-9358.

2. Singleton, D. A.; Merrigan, S. R.; Liu, J.; Houk, K. N., *J. Am. Chem. Soc.* **1997,** *119*, 3385-3386.

3. Singleton, D. A.; Merrigan, S. R.; Beno, B. R.; Houk, K. N., *Tett. Lett.* **1999,** *40*, 5817-5821.

4. Carpenter, B. K., *J. Phys. Chem. A* **2003,** *16*, 858-868.

5. Ussing, B. R.; Hang, C.; Singleton, D. A., *J. Am. Chem. Soc.* **2006,** *128*, 7594-7607.

6. Newman-Evans, R. H.; Carpenter, B. K., *J. Am. Chem. Soc.* **1984,** *106*, 7994-7995.

7. Castaño, O. P., R.; Frutos, L. M.; Luisandrés, J., *J. Comput. Chem.* **2002,** *23*, 732-736.

8. Hrovat, D. A.; Borden, W. T., *J. Am. Chem. Soc.* **1992,** *114*, 5879-5881.

9. Kraus, W. A.; DePristo, A. E., *Theor. Chem. Acta* **1986,** *69*, 309-322.

10. Kumeda, Y.; Taketsugu, T., *J. Chem. Phys.* **2000,** *113*, 477-484.

11. Tachibana, A.; Okazaki, I.; Koizumi, M.; Hori, K.; Yamabe, T., *J. Am. Chem. Soc.* **1985,** *107*, 1190-1196.

12. Taketsugu, T.; Kumeda, Y., *J. Chem. Phys.* **2001,** *114*, 6973-6982.

13. Valtazanos, P.; Elbert, S. T.; Ruedenberg, K., *J. Am. Chem. Soc.* **1986,** *108*, 3147-3149.

14. Valtazanos, P.; Ruedenberg, K., *Theor. Chim. Acta* **1986,** *69*, 281-307.

15. Wenthold, P. G.; Hrovat, D. A.; Borden, W. T.; Lineberger, W. C., *Science* **1996,** *272*, 1456-1459.

16. Windus, T. L.; Gordon, M. S., *Theor. Chim. Acta* **1992,** *83*, 21-30.

17. Windus, T. L.; Gordon, M. S.; Burggraf, L. W.; Davis, L. P., *J. Am. Chem. Soc.* **1991,** *113*, 4356-4357.

18. Yanai, T.; Taketsugu, T.; Hirao, K., *J. Chem. Phys.* **1997,** *107*, 1137-1146.

19. Zhou, C.; Birney, D. M., *Org. Lett.* **2002,** *4*, 3279-3282.

20. Vande Linde, S. R.; Hase, W. L., *J. Am. Chem. Soc.* **1989,** *111*, 2349-2351.

21. Bakken, V.; Danovich, D.; Shaik, S.; Schlegel, H. B., *J. Am. Chem. Soc.* **2001,** *123*, 130-134.

22. Bekele, T.; Lipton, M. A.; Singleton, D. A.; Christian, C. F., *J. Am. Chem. Soc.* **2005,** *127*, 9216-9223.

23. Mann, D. J.; Hase, W. L., *J. Am. Chem. Soc.* **2002,** *124*, 3208-3209.

24. Singleton, D. A.; Hang, C.; Szymanski, M. J.; Greenwald, E. E., *J. Am. Chem. Soc.* **2003,** *125*, 1176-1177.

25. Singleton, D. A.; Hang, C.; Szymanski, M. J.; Meyer, M. P.; Leach, A. G.; Kuwata, K. T.; Chen, J. S.; Greer, A.; Foote, C. S.; Houk, K. N., *J. Am. Chem. Soc.* **2003,** *125*, 1319-1328.

26. Sun, L.; Song, K.; Hase, W. L., *Science* **2002,** *296*, 875-878.

27. Yamataka, H.; Aida, M., *Bull. Chem. Soc. Jpn.* **2002,** *75*, 2555-2569.

28. Yamataka, H.; Aida, M.; Dupuis, M., *Chem. Phys. Lett.* **1999,** *300*, 583-587.

29. Gonzalez-Lafont, A.; Moreno, M.; Lluch, J. M., *J. Am. Chem. Soc.* **2004,** *126*, 13089-13094.

30. Brock, W. H., *The History of Chemistry*. W. W. Norton & Company: New York, 1992; p 506-569.

31. Brown, H. C.; Nelson, K. L., *J. Am. Chem. Soc.* **1953,** *75*, 6292-6299.

32. Brown, H. C.; Jensen, F. R., *J. Am. Chem. Soc.* **1958,** *80*, 2291-2296.

33. Brown, H. C.; Jungk, H., *J. Am. Chem. Soc.* **1955,** *77*, 5584-5589.

34. Brown, H. C.; Jungk, H., *J. Am. Chem. Soc.* **1956,** *78*, 2182-2184.

35. Brown, H. C.; Marino, G.; Stock, L. M., *J. Am. Chem. Soc.* **1959,** *81*, 3310-3314.

36. Brown, H. C.; Okamoto, Y., *J. Am. Chem. Soc.* **1957,** *79*, 1913-1917.

37. Brown, H. C.; Smoot, C. R., *J. Am. Chem. Soc.* **1956,** *78*, 6255-6259.

38. Brown, H. C.; Young, H. L., *J. Org. Chem.* **1957,** *22*, 719-723.

39. Brown, H. C.; Young, H. L., *J. Org. Chem.* **1957,** *22*, 724-730.

40. Jensen, F. R.; Marino, G.; Brown, H. C., *J. Am. Chem. Soc.* **1959,** *81*, 3303-3307.

41. McGary, J. C. W.; Okamoto, Y.; Brown, H. C., *J. Am. Chem. Soc.* **1955,** *77*, 3037-3043.

42. Bosch, E.; Moreno, M.; Lluch, J. M.; Bertran, J., *J. Chem. Phys. Lett.* **1989,** *160*, 543-548.

43. Metiu, H.; Ross, J.; Silbey, R.; George, T. F., *J. Chem. Phys.* **1974,** *61*, 3200-3209.

44. Quapp, W., *J. Mol. Struct.* **2004,** *695-696*, 95-101.

45. Quapp, W.; Hirsch, M.; Heidrich, D., *Theor. Chem. Accounts* **1998,** *100*, 285-299.

46. Quapp, W.; Hirsch, M.; Heidrich, D., *Theor. Chem. Accounts* **2004,** *112*, 40-51.

47. Ramquet, M. N.; Dive, G.; Dehareng, D., *J. Chem. Phys.* **2000,** *112*, 4923-4934.

48. Hammond, G. S., *J. Am. Chem. Soc.* **1955,** *77*, 334-338.

49. Olah, G. A., *Acc. Chem. Res.* **1970,** *4*, 240-248.

50. Dewar, M. J. S., *J. Chem. Soc.* **1946**, 406-408.

51. Dewar, M. J. S., *J. Chem. Soc.* **1946**, 777-781.

52. Ridd, J. H., *Acc. Chem. Res.* **1970,** *4*, 248-253.

53. DeHaan, F. P.; Covey, W. D.; Delker, G. L.; Baker, N. J.; Feigon, J. F.; Miller, K. D.; Stelter, E. D., *J. Am. Chem. Soc.* **1979,** *101*, 1136-1136.

54. Santiago, C.; Houk, K. N.; Perrin, C. L., *J. Am. Chem. Soc.* **1979,** *101*, 1337-1340.

55. Darbeau, R. W.; White, E. H., *J. Org. Chem.* **2000,** *65*, 1121-1131.

56. DeHaan, F. P.; Djaputra, M.; Grinstaff, M. W.; Kaufman, C. R.; Keithly, J. C.; Kumar, A.; Kuwayama, M. K.; Macknet, K. D.; Na, J.; Patel, B. R.; Pinkerton, M. J.; Tidwell, J. H.; Villahermosa, R. M., *J. Org. Chem.* **1997,** *62*, 2694-2703.

57. Gorman, A. A.; Hamblett, I.; Lambert, C.; Spencer, B.; Standen, M. C., *J. Am. Chem. Soc.* **1988,** *110*, 8053-8059.

58. Barnett, J. W.; Moodie, R. B.; Schofield, K.; Taylor, P. G.; Weston, J. B., *J. Chem. Soc. Perkin Trans. II* **1979,** *6*, 747-755.

59. Darbeau, R. W.; Siso, L. M.; Trahan, G. A.; Nolan, R. S., *Letters Org. Chem.* **2005,** *2*, 139-144.

60. Draper, M. R.; Ridd, J. H., *Chem. Commun.* **1978**, 445-446.

61. Eberson, L.; Hartshorn, M. P.; Radner, F., *Acta Chem. Scand.* **1994,** *48*, 937-950.

62. Eberson, L.; Radner, F., *Acc. Chem. Res.* **1987,** *20*, 53-59.

63. Kochi, J. K., *Acc. Chem. Res.* **1992,** *25*, 39-47.

64. Olah, G.; Narang, S. C.; Olah, J. A., *Proc. Natl. Acad. Sci. USA* **1981,** *78*, 3298-3300.

65. Olah, G. A.; Olah, J. A.; Ohyama, T., *J. Am. Chem. Soc.* **1984,** *106*, 5284-5290.

66. Perrin, C. L., *J. Am. Chem. Soc.* **1977,** *99*, 5516-5518.

67. Intermolecular and intramolecular KIEs will not in general be equal, in part because they are usually measured in different substrates and in part because the former is typically an absolute value while the latter is by its nature a relative KIE.

68. Rys, P.; Skrabal, P.; Zollinger, H., *Angew. Chem. Int. Ed. Engl.* **1972,** *11*, 874.

69. Buckley, T. F., III; Rapoport, H., *J. Am. Chem. Soc.* **1980,** *102*, 3056-3062.

70. Singleton, D. A.; Schulmeier, B. E., *J. Am. Chem. Soc.* **1999,** *121*, 9313-9317.

71. Singleton, D. A.; Szymanski, M. J., *J. Am. Chem. Soc.* **1999,** *121*, 9455-9456.

72. De Laeter, J. R.; Böhlke, J. K.; De Biévre, P.; Hidaka, H.; Peiser, H. S.; Rosman, K. J. R.; Taylor, P. D. P., *Pure Appl. Chem.* **2000,** *75*, 683-800.

73. Denney, D. B.; Klemchuk, P. P., *J. Am. Chem. Soc.* **1958,** *80*, 6014-6016.

74. Olah, G. A.; Kuhn, S. J.; Flood, S. H.; Hardie, B. A., *J. Am. Chem. Soc.* **1964,** *86*, 2203-2209.

75. Within the DFT/PCM calculational model of the ion/molecule approach, artifactual potential energy saddle points occur at longer intermolecular separations.

76. The calculations used the program QUIVER (Saunders, M.; Laidig, K. E.; Wolfsberg, M. *J. Am. Chem. Soc.* **1989**, *111*, 8989-8994). MPW1K frequencies were scaled by 0.9614 (Scott, A. P.; Radom, L. J. *Phys. Chem.* **1996**, *100*, 16502-16513). The exact choice of scaling factor makes little difference in the calculated KIE – varying the scaling factor from 0.93 to 0.97 changes the 13C KIEs by less than 0.001.

77. Bigeleisen, J., *J. Chem. Phys.* **1949,** *17*, 675-678.

78. Bigeleisen, J.; Mayer, M. G., *J. Chem. Phys.* **1947,** *15*, 261-267.

79. Wolfsberg, M., *Acc. Chem. Res.* **1972,** *5*, 225-233.

80. Bell, R. P., *The Tunnel Effect in Chemistry*. Chapman & Hall: London, 1980; p 60-63.

81. DelMonte, A. J.; Haller, J.; Houk, K. N.; Sharpless, K. B.; Singleton, D. A.; Strassner, T.; Thomas, A. A., *J. Am. Chem. Soc.* **1997,** *119*, 9907-9908.

82. Meyer, M. P.; DelMonte, A. J.; Singleton, D. A., *J. Am. Chem. Soc.* **1999,** *121*, 10865-10874.

83. Ogliaruso, M. A.; Romanelli, M. G.; Becker, E., *I. Chem. Rev.* **1965,** *65*, 261-367.

84. Gaviña, F.; Costero, A. M.; Gil, P.; Palazón, B.; Luis, S. V., *J. Am. Chem. Soc.* **1981,** *103*, 1797-1798.

85. Quadrelli, P.; Romano, S.; Toma, L.; Caramella, P., *J. Org. Chem.* **2003,** *68*, 6035-6038.

86. DePuy, C. H.; Eilers, I. K.; Morris, G. F., *J. Org. Chem.* **1964,** *29*, 3503-3507.

87. Harmata, M.; Barnes, C. L.; Brackley, J.; Bohnert, G.; Kirchhoefer, P.; Kurti, L.; Rashatasakhon, P., *J. Org. Chem.* **2001,** *66*, 5232-5236.

88. Harmata, M.; Gomez, M., *Eur. J. Org. Chem.* **2006**, 2273-2277.

89. Harmata, M.; Pinguan, Z.; Schreiner, P. R.; Navarro-Vázquez, A., *Angew. Chem. Int. Ed.* **2006,** *45*, 1966-1971.

90. Nantz, M. H.; Fuchs, L. P., *J. Org. Chem.* **1987,** *52*, 5298-5299.

91. Lynch, B. J.; Fast, P. L.; Harris, M.; Truhlar, D. G., *J. Phys. Chem. A* **2000,** *104*, 4811-4815.

92. Frisch, M. J. e. a. *Gaussian 03, Revision C.02*, Gaussian, Inc.: Wallingford CT, 2004.

93. Boren, B.; Hirschi, J. S.; Reibenspies, J. H.; Tallant, M. D.; Singleton, D. A.; Sulikowski, G. A., *J. Org. Chem.* **2003,** *68*, 8991-8995.

94. Caramella, P.; Quadrelli, P.; Toma, L., *J. Am. Chem. Soc.* **2002,** *124*, 1130-1131.

95. Quadrelli, P.; Romano, S.; Toma, L.; Caramella, P., *Tett. Lett.* **2002,** *43*, 8785-8789.

96. Jackman, L. M.; Sternhell, S., *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*. Pergamon Press: Oxford, 1969; p 280-304.

97. Laszlo, P.; Schleyer, P. v. R., *J. Am. Chem. Soc.* **1964,** *86*, 1171-1179.

98. Haasnoot, C. A. G.; de Leeuw, F. A. A. M.; Altona, C., *Tetrahedron* **1980,** *36*, 2783-2792.

99. Klunder, A. J. H.; Lange, J. H. M.; Zwanenburg, B., *Tett. Lett.* **1987,** *28*, 3027-3030.

100. Frantz, D. E.; Singleton, D. A.; Snyder, J. P., *J. Am. Chem. Soc.* **1997,** *119*, 3385-3386.

101. Beno, B. R.; Houk, K. N.; Singleton, D. A., *J. Am. Chem. Soc.* **1996,** *118*, 9984-9985.

102. Singleton, D. A.; Schulmeier, B. E.; Hang, C.; Thomas, A. A.; Leung, S. W.; Merrigan, S. R., *Tetrahedron* **2001,** *57*, 5149-5160.

103. Cho, Y. J.; Vande Linde, S. R.; Zhu, L.; Hase, W. L., *J. Chem. Phys.* **1992,** *96*, 8275-8287.

104. Hase, W. L., *Science* **1994,** *266*, 998-1002.

105. Li, G.; Hase, W. L., *J. Am. Chem. Soc.* **1999,** *121*, 7124-7129.

106. Sun, L.; Chang, E.; Song, K.; Hase, W. L., *Can. J. Chem.* **2004,** *82*, 891-899.

107. Sun, L.; Hase, W. L.; Song, K., *J. Am. Chem. Soc.* **2001,** *123*, 5753-5756.

108. Vande Linde, S. R.; Hase, W. L., *J. Chem. Phys.* **1990,** *93*, 7962-7980.

109. Vande Linde, S. R.; Hase, W. L., *J. Phys. Chem. A* **1990,** *94*, 6148-6150.

110. Wang, H.; Hase, W. L., *J. Am. Chem. Soc.* **1995,** *117*, 9347-9356.

111. Wang, Y.; Hase, W. L.; Wang, H., *J. Chem. Phys.* **2003,** *118*, 2688-2695.

112. Carpenter, B. K., *J. Am. Chem. Soc.* **1996,** *118*, 10329-10330.

113. Debbert, S. L.; Carpenter, B. K.; Hrovat, D. A.; Borden, W. T., *J. Am. Chem. Soc.* **2002,** *124*, 7896-7897.

114. Doubleday, C., *J. Phys. Chem. A* **2001,** *105*, 6333-6341.

115. Doubleday, C., Jr.; Bolton, K.; Hase, W. L., *J. Am. Chem. Soc.* **1997,** *119*, 5251-5252.

116. Doubleday, C., Jr.; Bolton, K.; Hase, W. L., *J. Phys. Chem. A* **1998,** *102*, 3648-3658.

117. Doubleday, C.; Li, G.; Hase, W. L., *Phys. Chem. Chem. Phys.* **2002,** *4*, 304-312.

118. Doubleday, C.; Nendel, M.; Houk, K. N.; Thweatt, D.; Page, M., *J. Am. Chem. Soc.* **1999,** *121*, 4720-4721.

119. Hrovat, D. A.; Fang, S.; Borden, W. T.; Carpenter, B. K., *J. Am. Chem. Soc.* **1997,** *119*, 5253-5254.

120. Truhlar, D. G.; Garrett, B. C.; Klippenstein, S. J., *J. Chem. Phys.* **1996,** *100*, 12771-12800.

121. Truhlar, D. G.; Hase, W. L.; Hynes, J. T., *J. Chem. Phys.* **1983,** *87*, 2664-2682.

122. Alston, P. V.; Gordon, M. D.; Ottenbrite, R. M.; Cohen, T., *J. Org. Chem.* **1983,** *48*, 5051-5054.

123. Kahn, S. D.; Pau, C. F.; Overman, L. E.; Hehre, W. J., *J. Am. Chem. Soc.* **1986,** *108*, 7381-7396.

124. Takasu, K.; Mizutani, S.; Ihara, M., *J. Org. Chem.* **2002,** *67*, 2881-2884.

125. Hoffmann, H. M. R.; Tsushima, T., *J. Am. Chem. Soc.* **1977,** *99*, 6008-6011.

126. Orfanopoulos, M.; Stephenson, L. M., *J. Org. Chem.* **1981,** *46*, 2200-2201.

127. Singleton, D. A.; Hang, C., *J. Am. Chem. Soc.* **2000,** *65*, 895-899.

128. Beak, P.; Berger, K. R., *J. Am. Chem. Soc.* **1980,** *102*, 3848-3856.

129. Adam, W.; Baeza, J.; Liu, J.-C., *J. Am. Chem. Soc.* **1972,** *94*, 2000-2006.

130. Yates, K.; Go, T. A., *J. Org. Chem.* **1980,** *45*, 2385-2391.

131. Yates, K.; Pincock, J. A., *J. Am. Chem. Soc.* **1968,** *90*, 5643-5644.

132. Yates, K.; Pincock, J. A., *Canadian J. Chem.* **1970,** *48*, 3332-3348.

133. Knowles, J. R. N., *Nature* **1991,** *350*, 121-124.

134. Cleland, W. W., *Accounts Chem. Res.* **1975,** *8*, 145-151.

135. Knowles, J. R.; Albery, W. J., *Accounts Chem. Res.* **1977,** *10*, 105-111.

136. Karbstein, K.; Herschlag, D., *Proc. Natl. Acad. Sci. USA* **2003,** *100*, 2300-2305.

137. Knowles, J. R., *Phil. Trans. R. Soc. B* **1991,** *332*, 115-121.

138. Seebach, D., *Angew. Chem., Int. Ed. Engl.* **1979,** *18*, 239-258.

139. Stetter, H., *Angew. Chem., Int. Ed. Engl.* **1976,** *15*, 639-648.

140. Stetter, H.; Kuhlmann, H., *Org. React.* **1991,** *40*, 407-496.

141. Enders, D.; Balensiefer, T., *Acc. Chem. Res.* **2004,** *37*, 534-541.

142. Johnson, J. S., *Angew. Chem., Int. Ed. Engl.* **2004,** *43*, 1326-1328.

143. Pohl, M.; Lingen, B.; Müller, M., *Chem.—Eur. J.* **2002,** *8*, 5288-5295.

144. Kerr, M. S.; Read de Alaniz, J.; Rovis, T., *J. Am. Chem. Soc.* **2002,** *124*, 10298-10299.

145. Kerr, M. S.; Read de Alaniz, J.; Rovis, T., *J. Org. Chem.* **2005,** *70*, 5725-5728.

146. Kerr, M. S.; Rovis, T., *Synlett* **2003**, 1934-1936.

147. Kerr, M. S.; Rovis, T., *J. Am. Chem. Soc.* **2004,** *126*, 8876-8877.

148. Liu, Q.; Rovis, T., *J. Am. Chem. Soc.* **2006,** *128*, 2552-2553.

149. Read de Alaniz, J.; Rovis, T., *J. Am. Chem. Soc.* **2005,** *127*, 6284-6289.

150. Breslow, R. J., *J. Am. Chem. Soc.* **1958,** *80*, 3719-3726.

151. Dudding, T.; Houk, K. N., *Proc. Natl. Acad. Sci. U.S.A.* **2004,** *101*, 5770-5775.

152. Knight, R. L.; Leeper, F. J., *J. Chem. Soc., Perkin Trans. 1* **1998**, 1891-1893

153. Sheehan, J. C.; Hunneman, D. H., *J. Am. Chem. Soc.* **1966,** *88*, 3666-3667.

154. Bordwell, F. G., *Acc. Chem. Res.* **1988,** *21*, 456-463.

155. Grimm, D. T.; Bartmess, J. E., *J. Am. Chem. Soc.* **1992,** *114*, 1227-1231.

APPENDIX A

TABLE OF CONTENTS

Electrophilic Aromatic Substitution

Intermolecular ^{13}C NMR KIE Sample Integration Results for Acylation of Veratrole

Standard C13 KIE's

#	Initial Int.1	Initial Int. 2	Initial Int. 3	Initial Int. 4	Initial Int. 5	Initial Int. 6	<Int>
1	1022.080	1021.680	1021.640	1022.600	1019.940	1020.27	1021.36
2	1098.320	1098.070	1099.400	1100.170	1099.810	1100.87	1099.44
3	1088.520	1089.930	1085.930	1092.790	1088.660	1091.63	1089.57
4	1000.000	1000.000	1000.000	1000.000	1000.000	1000.00	1000

Sample2 Percent Conversion = 82%

#	Final Int. 1	Final Int. 2	Final Int. 3	Final Int. 4	Final Int. 5	Final Int. 6	<Int>
1	1013.83	1008.510	1010.470	1004.390	1004.390	1010.43	1008.67
2	1095.25	1093.220	1098.270	1093.610	1098.180	1099.08	1096.26
3	1092.57	1086.610	1091.140	1091.240	1093.620	1091.13	1091.05
4	1000.00	1000.0	1000.000	1000.0	1000.000	1000.0	1000

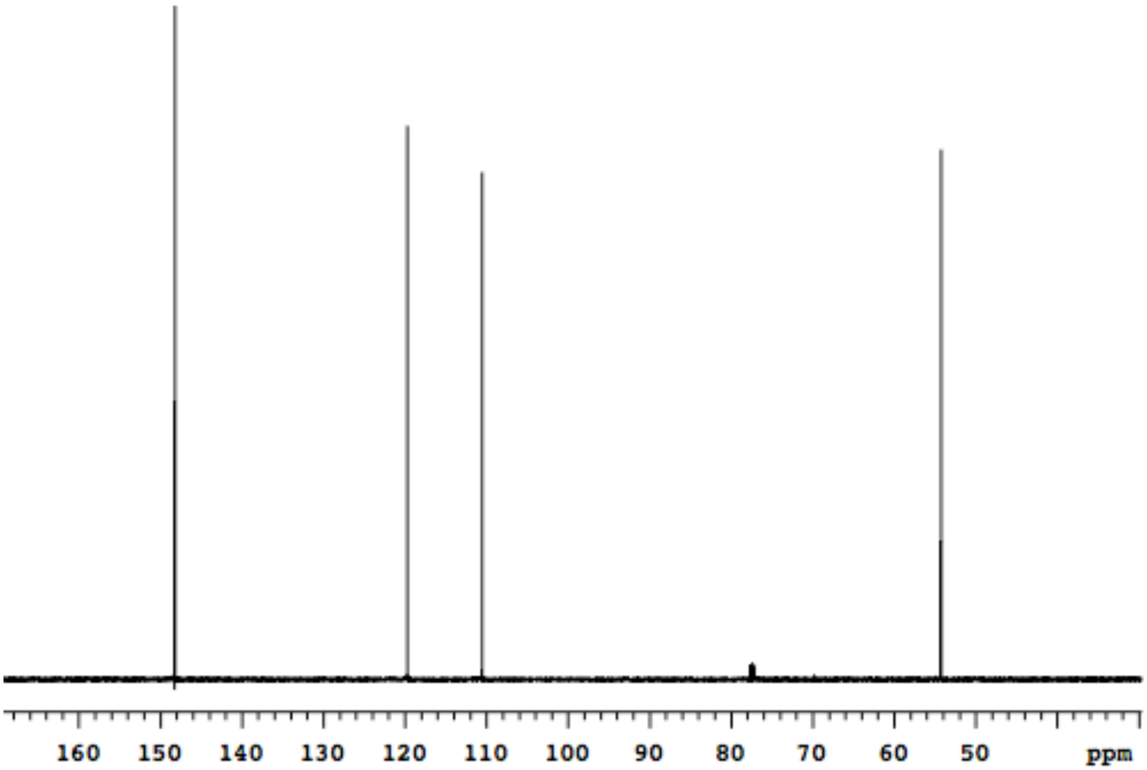
#	SD Init	RSD Init	SD Final	RSD Final
1	1.043157	0.1021332	3.7316377	0.36995
2	1.081443	0.0983631	2.5675935	0.23421
3	2.446284	0.2245169	2.3949732	0.21951
4	0	0	0	0

#	Enhancement	% Conv	SD of Conv	KIE	SD of KIE
1	0.9876	0.18	0.0010	0.993	0.002
2	0.9971	0.18	0.0010	0.998	0.001
3	1.0014	0.18	0.0010	1.001	0.002
4	1.0000	0.18	0.0010	1.000	#DIV/0!

Intermolecular ^{13}C NMR KIE Sample Integration Results for Acylation of Veratrole

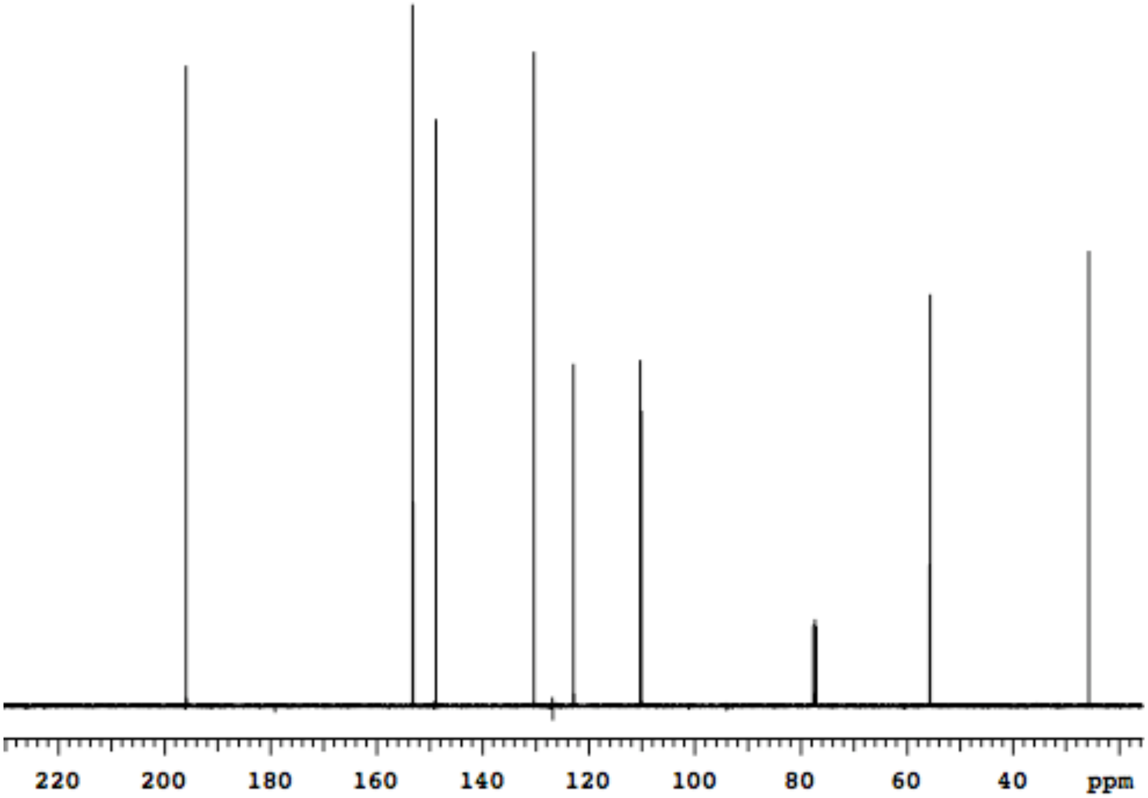
Cut	6	7					
1	1000	1008.690					
2	1000	1010.880					
3	1000	1006.550					
4	1000	1009.230					
5	1000	1004.720					
6	1000	1012.290	13C ratio			ADJUSTED	
Ave	1000	1008.727	1.008726667	0.991	(3)	**0.981**	**3**
Stdev	0	2.770564323	13C ratio uncertainty				
			0.002746596				
			adjuster 13 ratio				
			1.019426667				
			adj ratio uncertainty				
			0.002860732				

Veratrole (5) – ^{13}C NMR for KIEs



^{13}C NMR (CDCl$_3$) δ 149.4, 119.8, 110.1, 54.3.

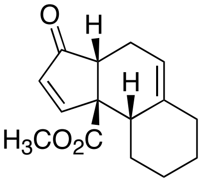
3,4-dimethoxyacetophenone (6) - ^{13}C NMR for KIEs

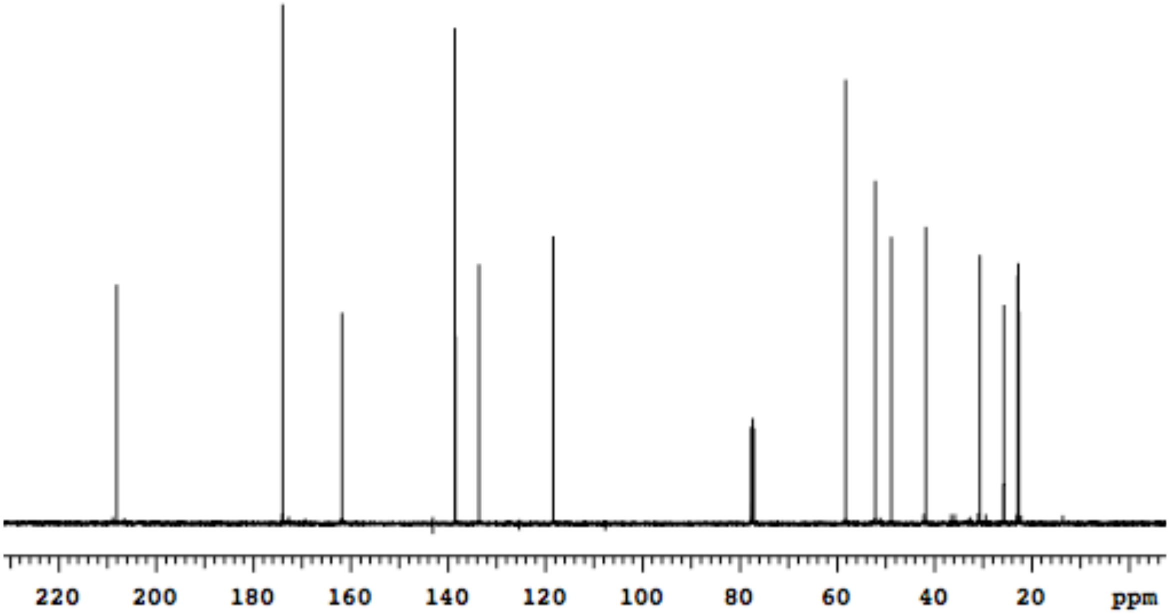


^{13}C NMR ($CDCl_3$) δ 195.8, 153.0, 148.8, 130.2, 122.7, 110.25, 110.1, 55.7, 55.6, 25.8.

Diels-Alder Reaction of 1,3-dienes with 17

Sample ^{13}C NMR for 29





^{13}C NMR (CDCl$_3$) δ 208.3, 174.2, 161.9, 138.7, 133.6, 118.6, 58.1, 52.4, 49.0, 42.2, 30.9, 25.8, 22.9, 22.8, 22.7.

NMR Sample Integration Results for 29

Standard
1

	1	2	3	4	5	6	Ave	Std
C2	1090.65	1096.83	1098.40	1096.43	1097.72	1098.96	1096.49	3
C3	1094.54	1096.83	1101.34	1099.60	1097.71	1099.76	1098.29	2
C4	1010.62	1015.78	1011.30	1014.24	1012.02	1013.49	1012.90	2
C7	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00	0
C8	965.42	972.60	970.56	971.84	968.23	969.84	969.75	3
C5	975.65	981.46	978.35	975.66	974.22	978.78	977.35	3
C6	999.40	1004.14	1002.84	1007.27	1003.29	1003.62	1003.42	3
C1	952.32	953.80	952.82	956.91	948.99	950.71	952.59	3

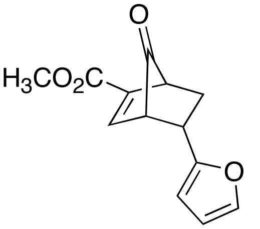
Sample
1

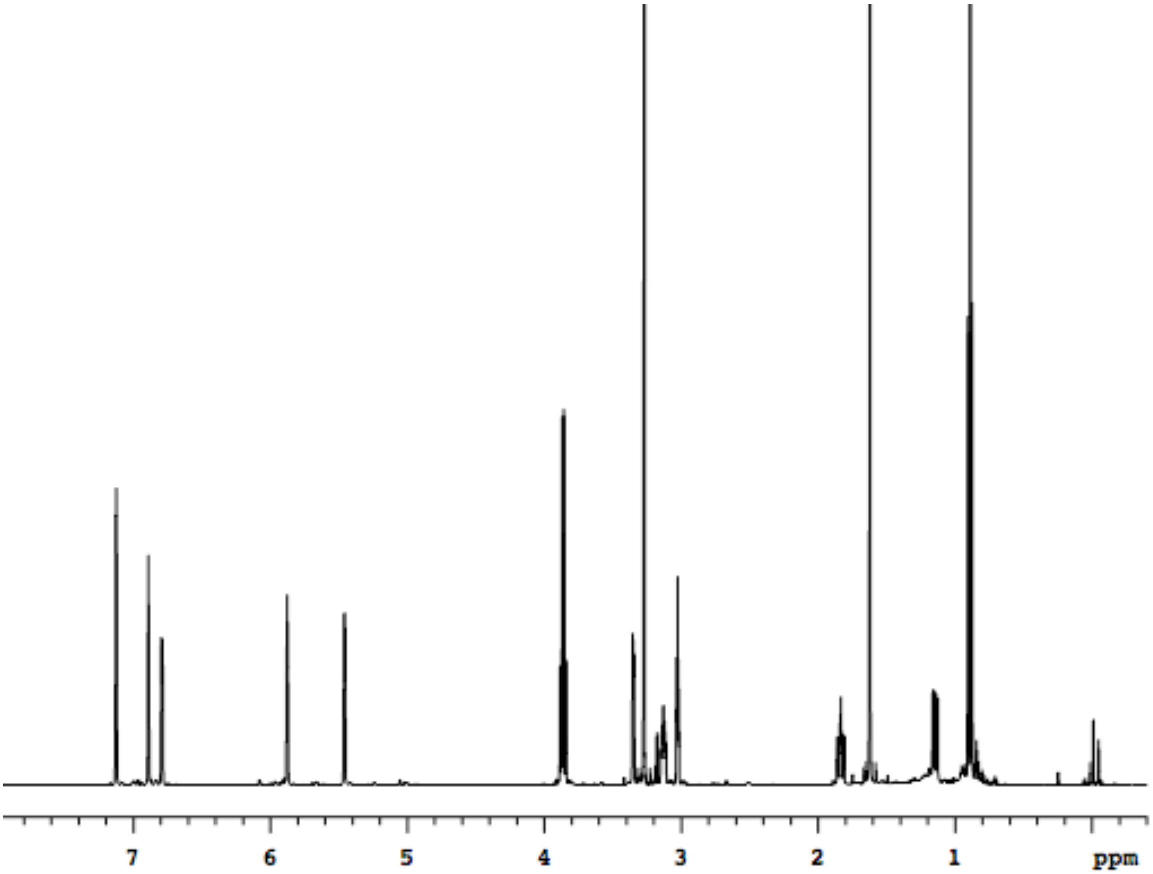
	1	2	3	4	5	6	Ave	Std
C2	1084.09	1091.68	1085.57	1086.28	1090.03	1092.40	1088.34	3
C3	1090.50	1095.03	1095.40	1095.74	1099.24	1097.68	1095.59	3
C4	1008.87	1015.53	1010.27	1008.02	1013.76	1006.83	1010.54	3
C7	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00	0
C8	968.62	972.89	971.30	968.22	973.64	968.48	970.52	2
C5	980.92	976.62	974.77	979.37	985.20	974.56	978.57	4
C6	996.57	1004.89	1002.91	999.01	1001.23	1001.19	1000.96	3
C1	919.21	931.52	924.30	924.49	921.58	920.20	923.55	4

	C^{12}/C^{13}	**Corrected for 99.3% conversion**	
C2	1.007	1.008	3
C3	1.002	1.002	5
C4	1.002	1.002	5
C7	1.000	1.000	
C8	0.999	0.999	2
C5	0.999	0.999	4
C6	1.002	1.002	4
C1	1.031	1.035	7

Spectra of 31

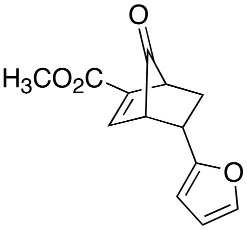
31 - ^1H in C_6D_6

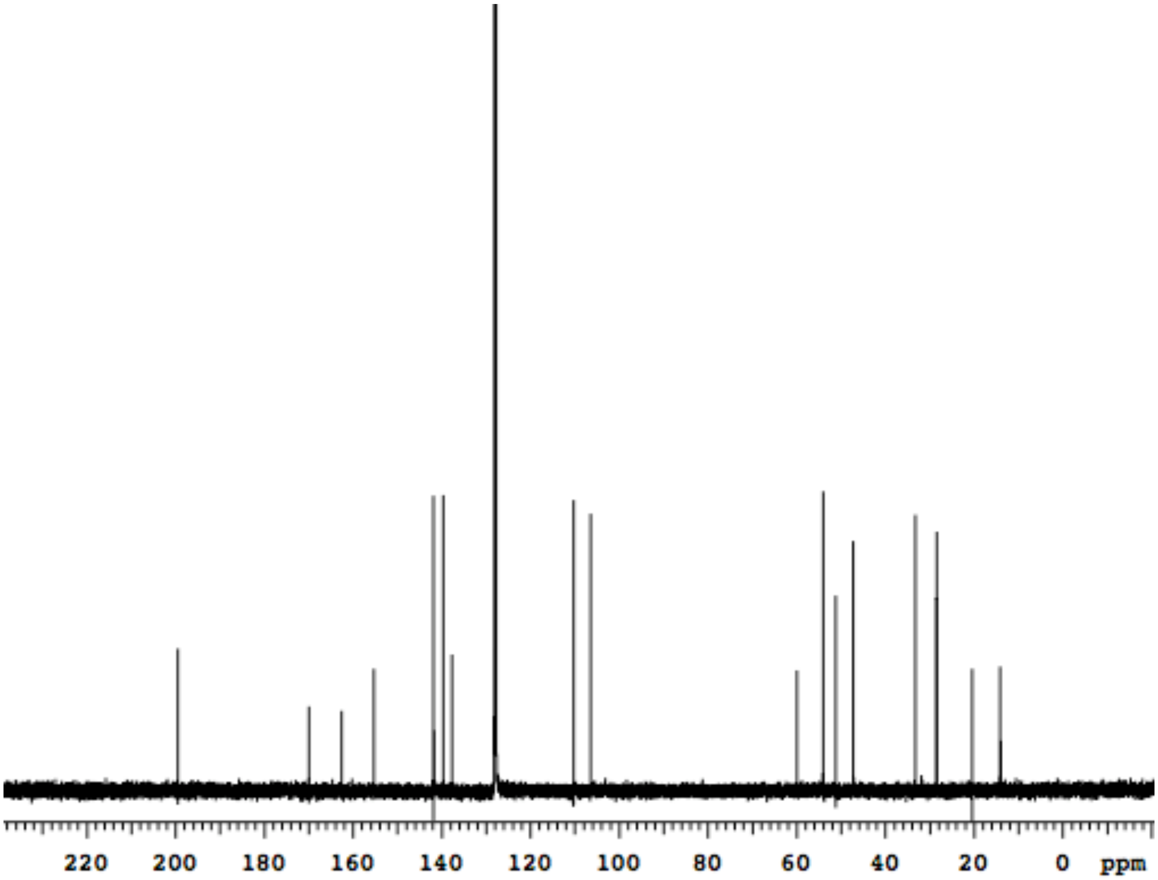




^{1}H NMR (C6D6) d 6.91 (s, 1H), 6.80 (s, 1H), 5.89 (m, 1H), 5.45 (d, 1H), 3.35 (m, 1H), 3.27 (s, 3H), 3.13 (m, 1H), 3.01 (m, 1H), 1.84 (m, 1H), 1.15 (m, 1H).

31 – ^{13}C in C_6D_6

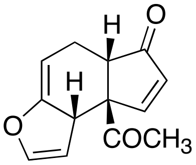


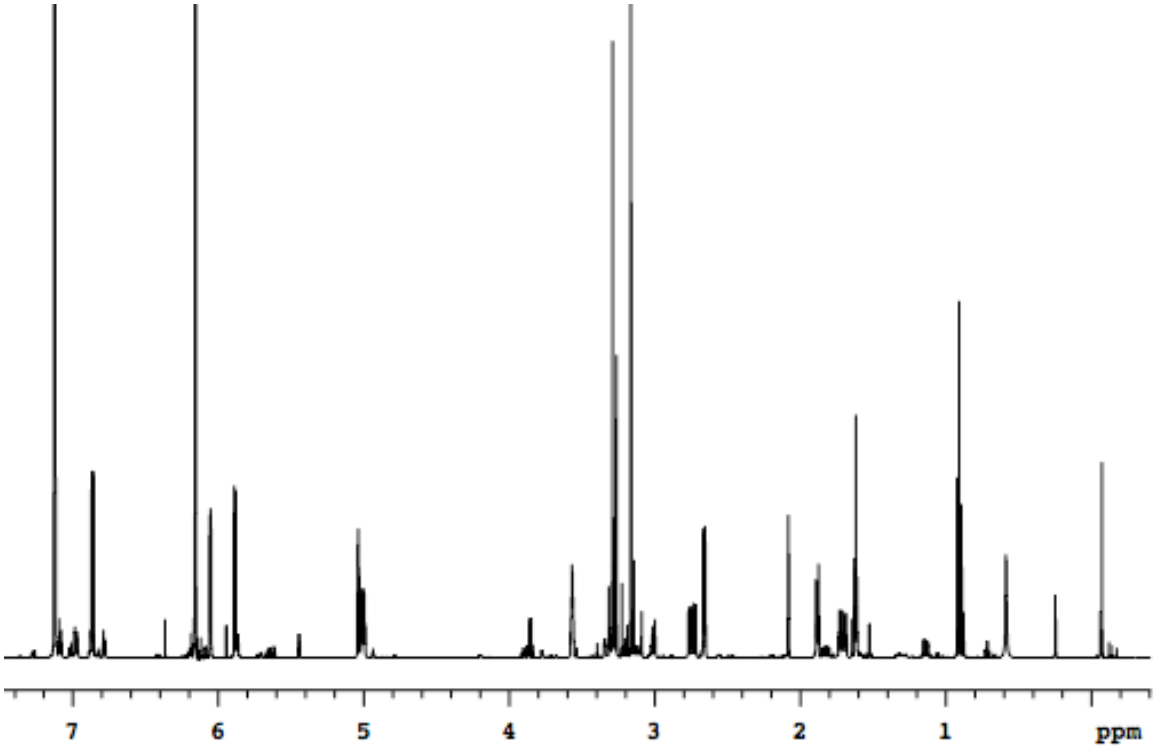


^{13}C NMR ($CDCl_3$) δ 200.0, 162.8, 155.4, 142.0, 139.8, 137.8, 110.4, 106.5, 54.0, 51.2, 47.3, 333.2, 28.5.

Spectra of 32

32 - ^1H in C_6D_6

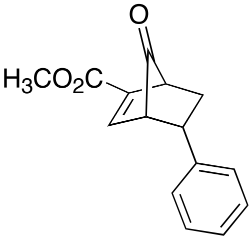


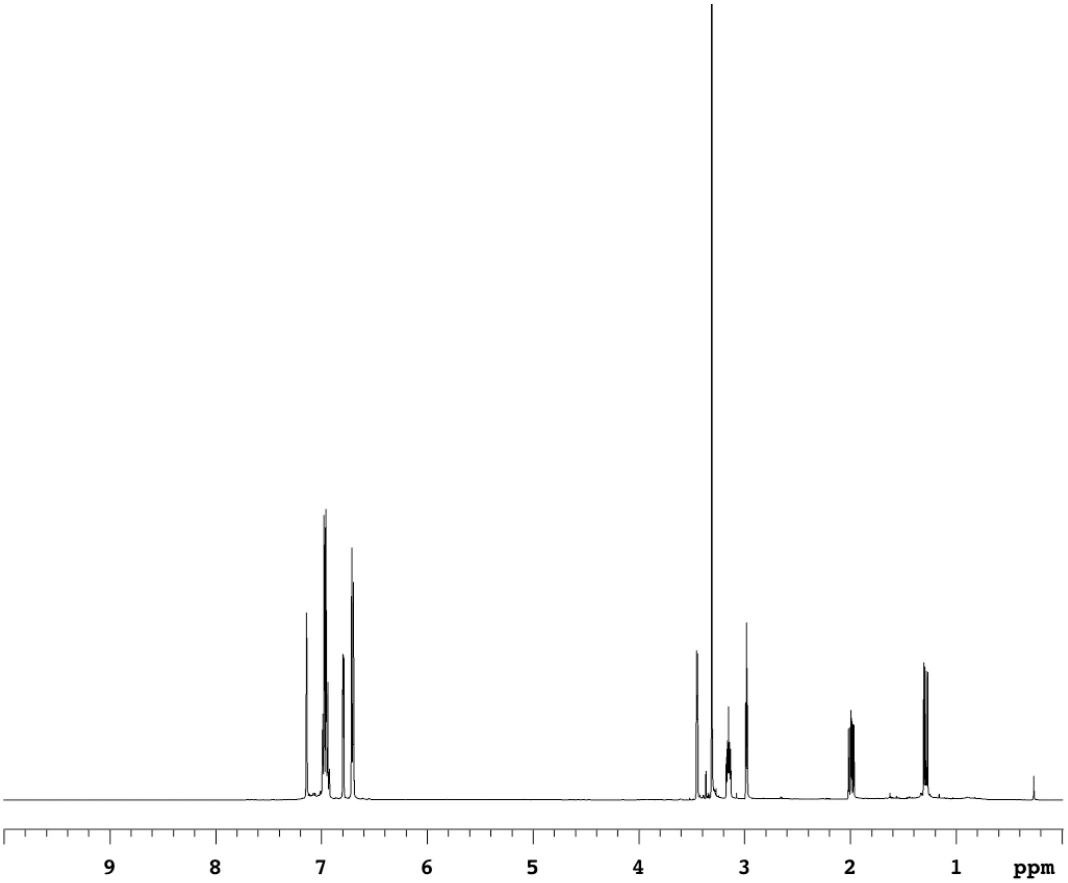


^{1}H NMR (C_6D_6) δ 6.91 (d, 1H), 6.10 (m, 1H), 5.90 (d, 1H), 5.09 (m, 1H), 5.00 (m, 1H), 3.40 (m, 1H), 3.21 (s, 3H), 2.72 (m, 1H), 2.68 (m, 1H), 1.71 (m, 1H).

Spectra of 33

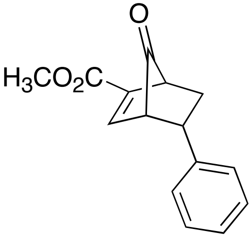
33 - ^1H in C_6D_6

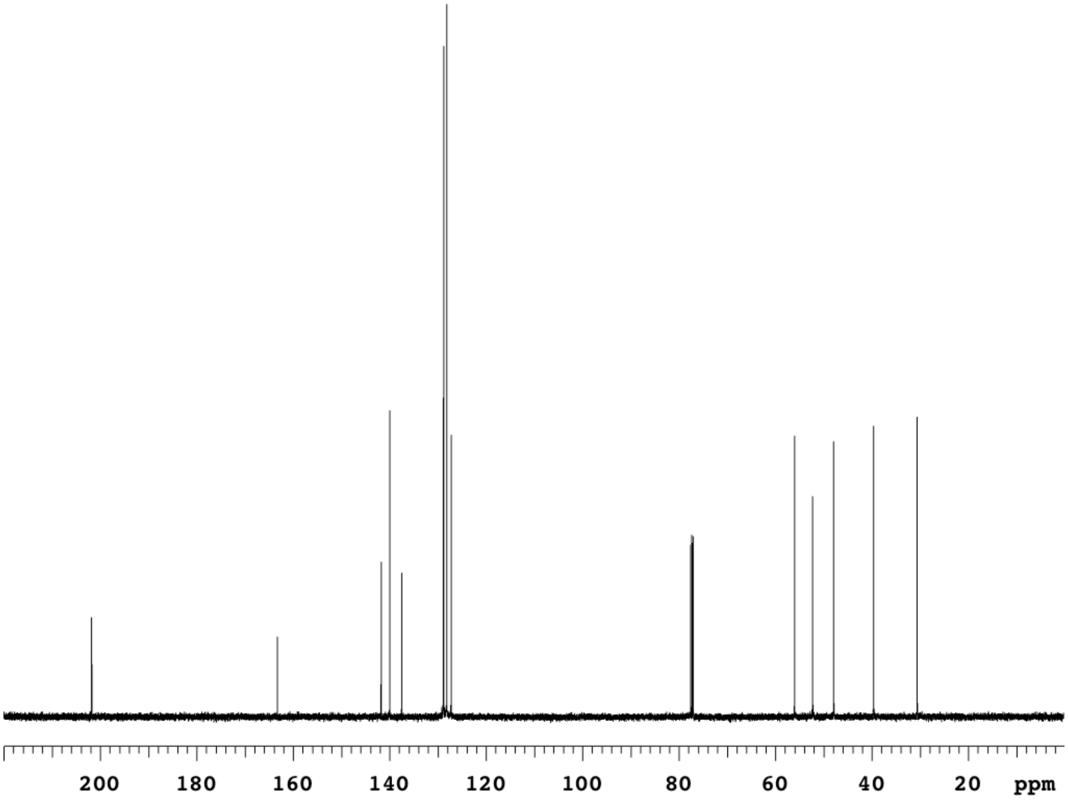




^{1}H NMR (C6D6) d 6.91 (s, 3H), 6.80 (s, 1H), 6.72 (d, 2H), 3.46 (s, 1H), 3.32 (s, 3H), 3.16 (m, 1H), 2.99 (m, 1H), 2.00 (m, 1H), 1.31 (m, 1H).

33 – ^{13}C in C_6D_6

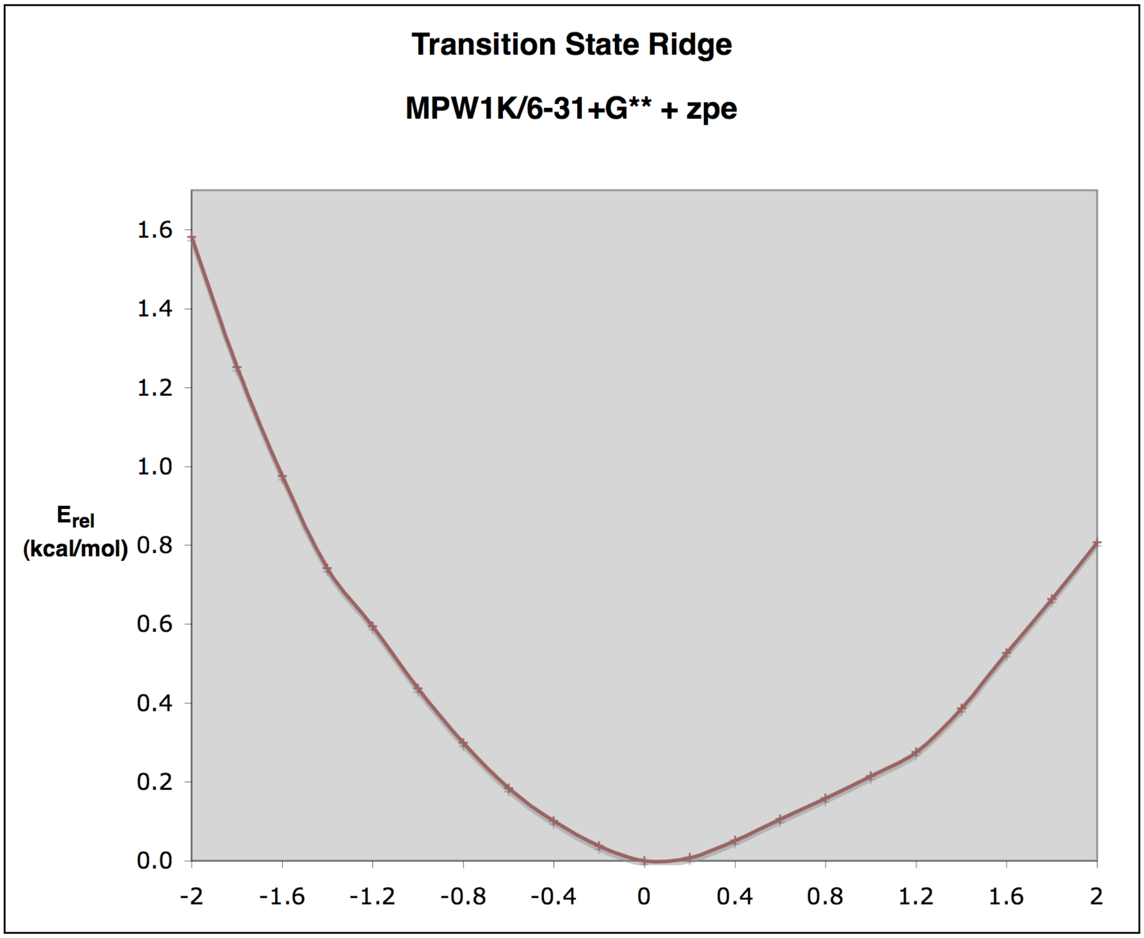




^{13}C NMR ($CDCl_3$) δ 201.8, 163.3, 141.8, 140.0, 137.5, 128.8, 128.1, 127.2, 56.0, 52.3, 47.9, 39.7, 30.6.

Transition State Ridge for 24-ax

Graph of Transition State Ridge for 24-ax



Method for predicting ^{13}C KIEs based on transition state ridge

^{13}C KIEs were predicted for each of the 21 structures generated from scaled theoretical vibrational frequencies[1] using conventional Bigeleisen Mayer method.[2, 3] Tunneling corrections were applied using a one-dimensional infinite parabolic barrier model.[4] The individual KIEs were then calculated using a Boltzmann combination of all the predicted isotope effects and their relative energies.

	Erel + ZPE	BFx	BFx/SBF
-2	1.5813	0.0705	0.0059
-1.8	1.2519	0.1225	0.0102
-1.6	0.9752	0.1949	0.0162
-1.4	0.7417	0.2883	0.0240
-1.2	0.5943	0.3691	0.0307
-1	0.4374	0.4802	0.0400
-0.8	0.2993	0.6053	0.0504
-0.6	0.1845	0.7339	0.0611
-0.4	0.1010	0.8441	0.0703
-0.2	0.0377	0.9388	0.0782
0	0.0000	1.0000	0.0833
0.2	0.0082	0.9864	0.0822
0.4	0.0515	0.9173	0.0764
0.6	0.1061	0.8371	0.0697
0.8	0.1588	0.7663	0.0638
1	0.2152	0.6970	0.0581
1.2	0.2755	0.6300	0.0525
1.4	0.3859	0.5235	0.0436
1.6	0.5265	0.4136	0.0344
1.8	0.6633	0.3288	0.0274
2	0.8076	0.2581	0.0215
Total		12.006	1.0000

	^{13}C KIE
C1	1.033
C2	1.0056
C3	1.002
C4	1.004
C5	1.002
C6	1.000
C7	0.998
C8	0.999

Ene Reaction of Isopropylidenecyclohexene

Intermolecular ^{13}C NMR KIE Sample Integration Results

Standard C13 KIE's

#	Initial Int.1	Initial Int. 2	Initial Int. 3	Initial Int. 4	Initial Int. 5	Initial Int. 6	<Int>
1	983.269	977.452	985.930	978.857	980.898	978.390	980.799
2	1018.940	1020.720	1024.840	1023.430	1023.180	1023.310	1022.403
3	2019.510	2016.650	2025.170	2021.530	2023.760	2018.070	2020.782
4	2004.450	1999.850	2010.390	2009.550	2008.260	2006.560	2006.510
5	1000.000	1000.000	1000.000	1000.000	1000.000	1000.000	1000.000
6	1978.580	1970.630	1982.970	1980.050	1980.200	1979.580	1978.668

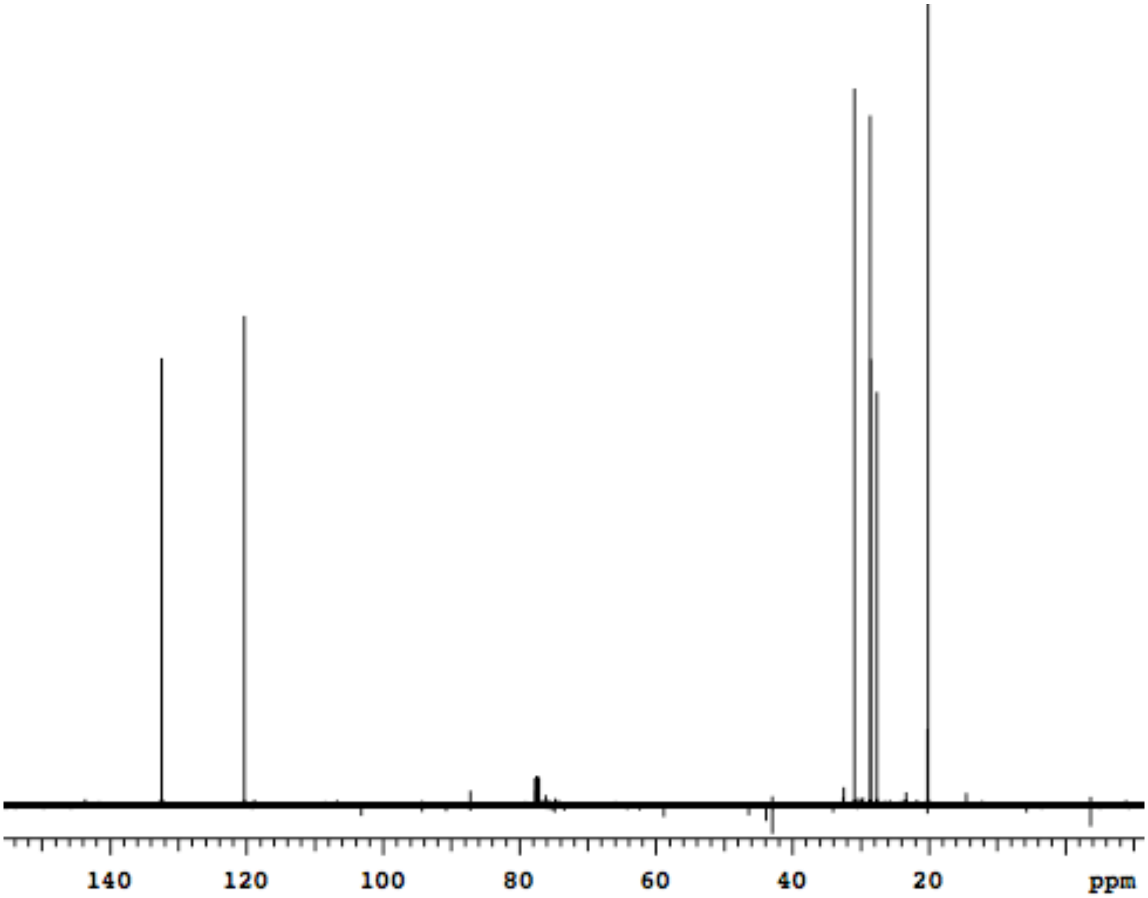
Sample1 Percent Conversion = 85%

#	Final Int. 1	Final Int. 2	Final Int. 3	Final Int. 4	Final Int. 5	Final Int. 6	<Int>
1	988.383	998.444	996.441	994.243	997.584	993.505	994.767
2	1029.950	1033.650	1033.690	1036.050	1041.570	1026.190	1033.517
3	2022.280	2024.330	2026.680	2030.900	2036.750	2029.090	2028.338
4	2004.720	2005.170	2011.820	2014.570	2023.400	2014.240	2012.320
5	1000.000	1000.000	1000.000	1000.000	1000.000	1000.000	1000.000
6	1973.260	1974.770	1970.710	1981.690	1985.050	1968.620	1975.683

#	SD Init	RSD Init	SD Final	RSD Final
1	3.2624	0.3326	3.6573	0.3677
2	2.1562	0.2109	5.2483	0.5078
3	3.3084	0.1637	5.1653	0.2547
4	3.8977	0.1943	6.9375	0.3448
5	0.0000	0.0000	0.0000	0.0000
6	4.2003	0.2123	6.4054	0.3242

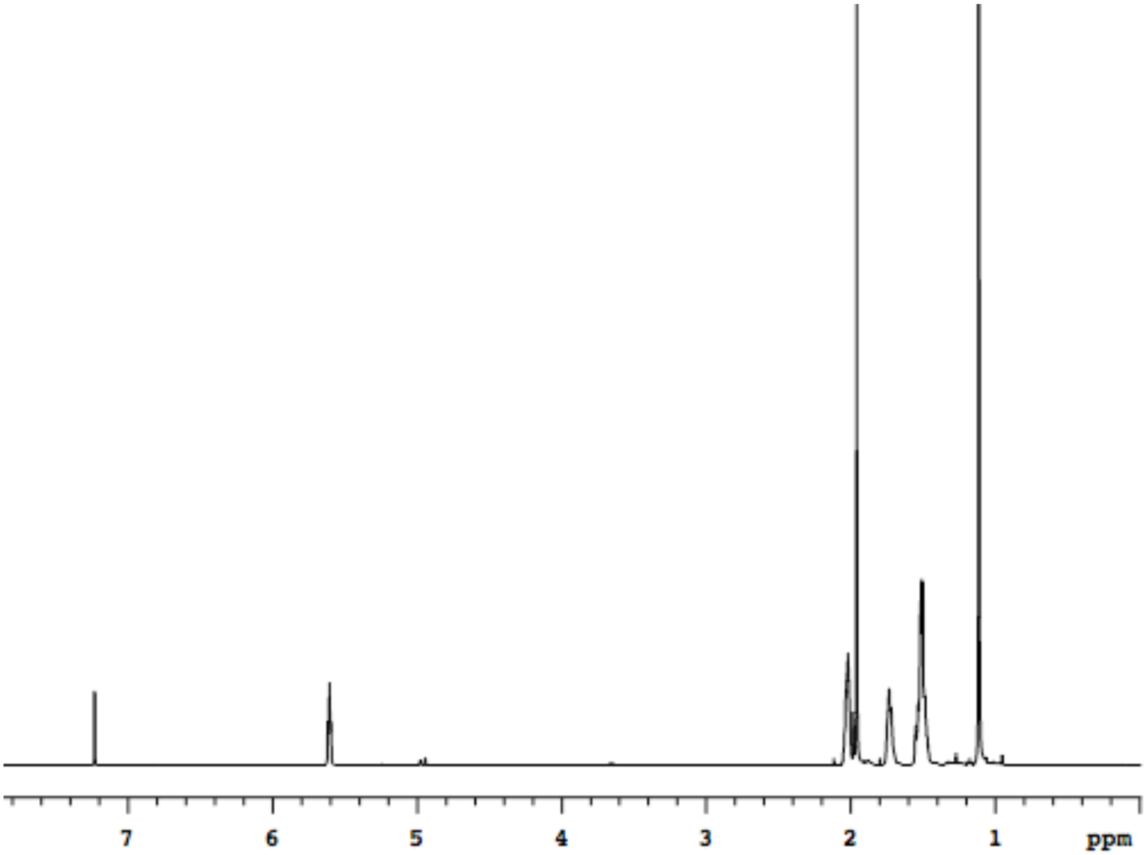
	Enhancement	% Conv	SD of Conv	KIE	SD of KIE
1	1.0142	0.15	0.0010	1.008	0.0027
2	1.0109	0.15	0.0010	1.006	0.0029
3	1.0037	0.15	0.0010	1.002	0.0016
4	1.0029	0.15	0.0010	1.002	0.0021
5	1.0000	0.15	0.0010	1.000	#DIV/0!
6	0.9985	0.15	0.0010	0.999	0.0020

Isopropylidenecyclohexene (43) – ^{13}C NMR for KIEs



^{13}C NMR (CDCl$_3$) δ 132.2, 120.3, 30.8, 28.5, 27.5, 20.1.

44-d₁ – ¹H NMR



^{1}H NMR ($CDCl_3$) δ 5.6 (m, 0.8 H), 2.02 (m, 1H), 1.96 (s, 3H), 1.73 (m, 1.8 H), 1.51 (m, 4H), 1.11 (m, 6H).

Chlorination of Bis(trimethylsilyl)acetylene

Intermolecular ^{13}C NMR KIE Sample Integration Results

Standard 1 C13 KIE's

#	Initial Int.1	Initial Int. 2	Initial Int. 3	Initial Int. 4	Initial Int. 5	Initial Int. 6	<Int>
1	2330.07	2327.14	2328.48	2325.58	2327.62	2328.57	2327.91
2	6000	6000	6000	6000	6000	6000	6000

Percent Conversion = 85.4% 82%

Sample 1

#	Final Int. 1	Final Int. 2	Final Int. 3	Final Int. 4	Final Int. 5	Final Int. 6	<Int>
1	2396.74	2397.88	2399.11	2398.17	2388.79	2394.98	2395.94
2	6000	6000	6000	6000	6000	6000	6000

#	SD Init	RSD Init	SD Final	RSD Final
1	1.518683641	0.065238074	3.78072	0.1577
2	0	0	0	0

#	Enhancement	% Conv	SD of Conv	KIE	SD of KIE
1	1.029225786	0.18	0.001	1.01708	0.0010609
2	1	0.18	0.001	1	0

Standard 2 C13 KIE's

#	Initial Int.1	Initial Int. 2	Initial Int. 3	Initial Int. 4	Initial Int. 5	Initial Int. 6	<Int>
1	2331.65	2327.52	2328.15	2326.38	2330.51	2333.72	2329.65
2	6000	6000	6000	6000	6000	6000	6000

Percent Conversion = 85.4% 80%

Sample 2

#	Final Int. 1	Final Int. 2	Final Int. 3	Final Int. 4	Final Int. 5	Final Int. 6	<Int>
1	2377.93	2382.29	2383.09	2377.89	2383.06	2378.23	2380.41
2	6000	6000	6000	6000	6000	6000	6000

#	SD Init	RSD Init	SD Final	RSD Final
1	2.785108615	0.11955026	2.64546	0.1111
2	0	0	0	0

#	Enhancement	% Conv	SD of Conv	KIE	SD of KIE
1	1.021788634	0.2	0.001	1.01357	0.0010647
2	1	0.2	0.001	1	0

Intramolecular ^{13}C NMR for KIEs for Prodcut 55

Sample 1

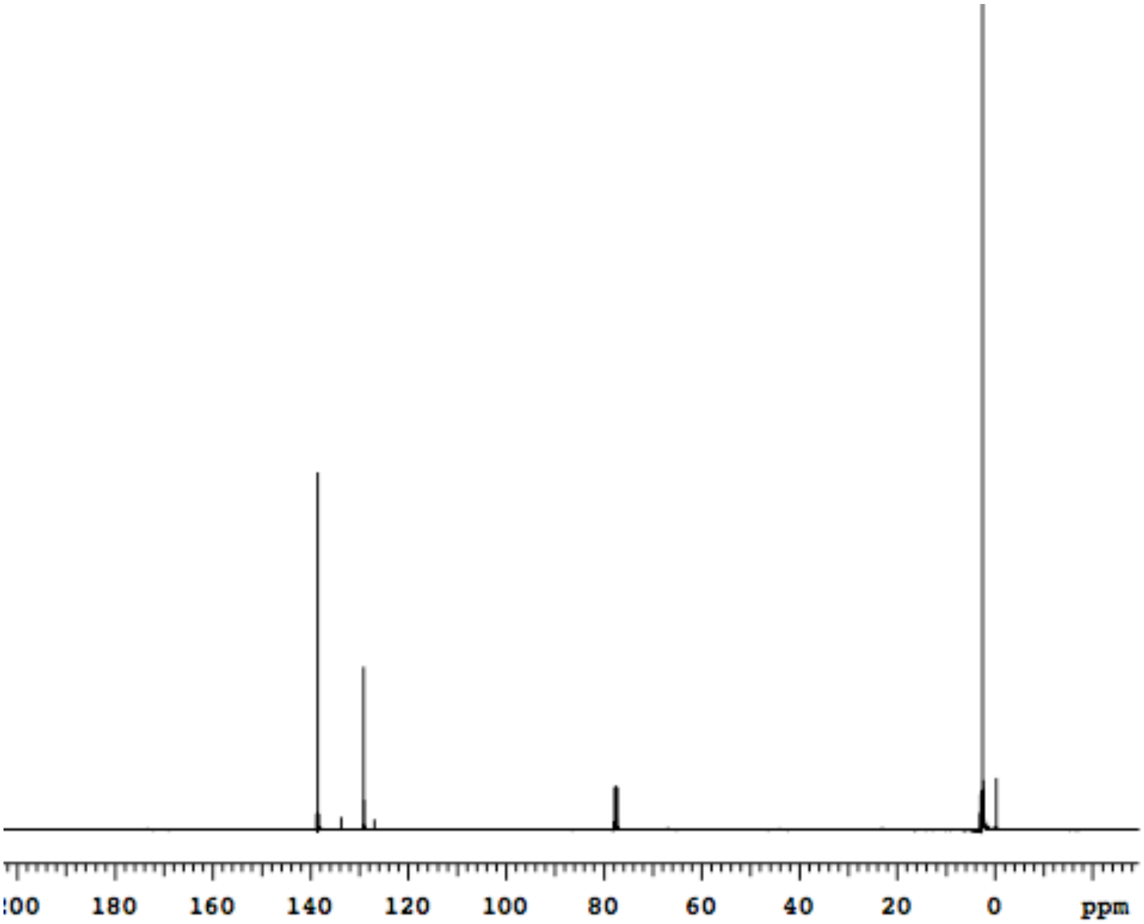
	fid1	fid2	fid3	fid4	fid5	Fid6	AVERAGE	STDEV
1	989.384	987.843	989.501	987.318	985.81	987.382	987.873	1.395670448
2	1031.12	1031.26	1032.1	1034.12	1030.69	1031.97	1031.876667	1.220830318
3	6000	6000	6000	6000	6000	6000	6000	0

Sample 2

	fid1	fid2	fid3	fid4	fid5	Fid6	AVERAGE	STDEV
1	988.619	990.742	986.597	985.323	986.505	988.017	987.6338333	1.921838122
2	1032.55	1037.92	1032.61	1030.98	1030.27	1031.3	1032.605	2.758555782
3	6000	6000	6000	6000	6000	6000	6000	0

13C Content	KIE
1.045	0.957

Prodcut 55 – ^{13}C NMR for KIEs



^{13}C NMR (CDCl$_3$) δ 138.7, 129.2, 2.8.

Enantioselective Intramolecular Stetter Reaction

Intermolecular ^{13}C NMR KIE Sample Integration Results for 59

Standard			C13 KIE's				
#	**Initial Int.1**	**Initial Int. 2**	**Initial Int. 3**	**Initial Int. 4**	**Initial Int. 5**	**Initial Int. 6**	**<Int>**
1	885.19	880.28	886.38	883.81	881.85	878.65	882.69
2	986.80	990.34	996.42	983.62	987.13	984.48	988.13
3	975.41	974.73	978.61	975.53	977.65	973.80	975.96
4	985.08	983.65	984.41	978.39	983.43	981.08	982.67
5	1009.79	1007.50	1008.59	1005.02	1010.58	1006.49	1007.99
6	1001.96	998.99	1002.96	996.39	1000.65	998.31	999.88
7	1022.95	1026.46	1029.51	1024.18	1026.61	1020.91	1025.10
8	993.74	993.71	994.67	991.53	994.35	989.45	992.91
9	1005.85	1005.85	1011.81	1007.18	1008.80	1001.91	1006.90
10	1007.50	1009.27	1014.10	1005.96	1010.61	1006.63	1009.01
11	1004.48	1004.53	1011.11	1003.62	1008.43	1003.59	1005.96
12	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00
13	907.03	904.44	908.28	902.93	903.79	904.08	905.09

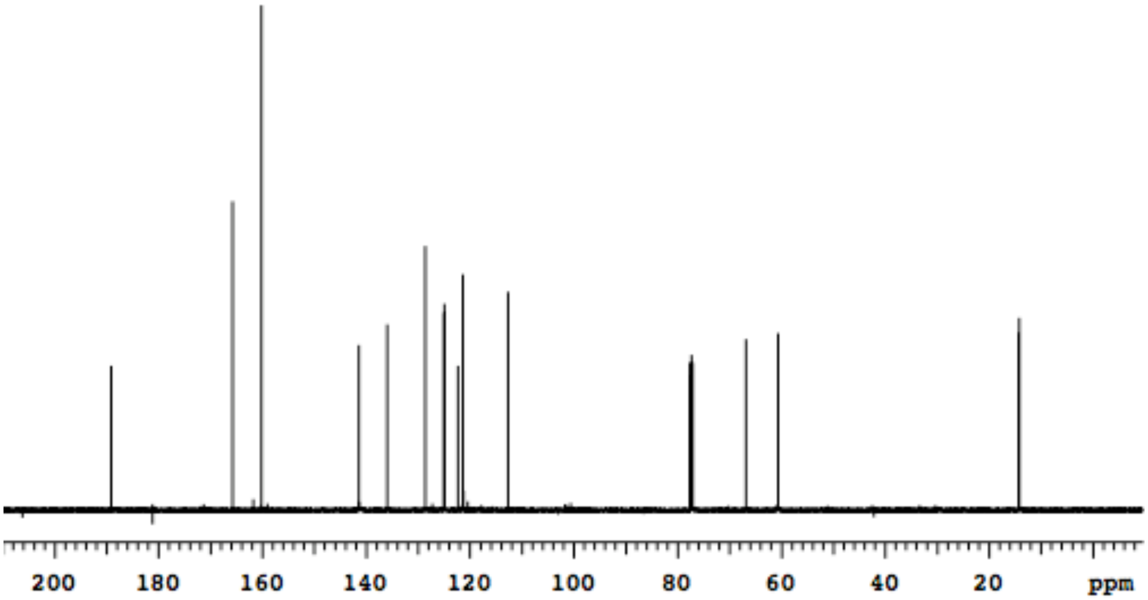
Sample2			Percent Conversion = 75%				
#	**Final Int. 1**	**Final Int. 2**	**Final Int. 3**	**Final Int. 4**	**Final Int. 5**	**Final Int. 6**	**<Int>**
1	907.08	905.93	909.94	911.71	909.22	910.86	909.12
2	977.32	980.67	981.36	981.19	980.04	983.79	980.73
3	974.31	972.98	978.25	978.00	976.89	980.30	976.79
4	978.93	978.27	981.34	978.30	976.61	978.95	978.73
5	1008.34	1011.08	1010.01	1009.37	1011.39	1013.31	1010.58
6	1003.01	1002.05	1003.69	1004.62	1001.51	1005.91	1003.47
7	1002.08	1002.92	1002.57	1003.83	1003.00	1005.14	1003.26
8	990.63	990.59	991.54	995.55	989.86	989.19	991.23
9	1002.05	1002.18	1006.96	1008.70	1003.14	1008.86	1005.32
10	999.80	1001.52	1004.20	1003.93	1001.01	1002.33	1002.13
11	1002.43	998.55	1004.10	1002.76	997.32	1003.82	1001.50
12	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00
13	901.77	903.08	905.07	905.87	897.19	907.60	903.43

#	**SD Init**	**RSD Init**	**SD Final**	**RSD Final**
1	2.9636	0.3357	2.2253	0.2448
2	4.6885	0.4745	2.1011	0.2142
3	1.8194	0.1864	2.7033	0.2768
4	2.4999	0.2544	1.5377	0.1571
5	2.0808	0.2064	1.7422	0.1724

6	2.4412	0.2441	1.6372	0.1631
7	3.0546	0.2980	1.0871	0.1084
8	2.0165	0.2031	2.2610	0.2281
9	3.3134	0.3291	3.2235	0.3206
10	3.0252	0.2998	1.7111	0.1707
11	3.0967	0.3078	2.8550	0.2851
12	0.0000	0.0000	0.0000	0.0000
13	2.0851	0.2304	3.6825	0.4076

Enhancement	**% Conv**	**SD of Conv**	**KIE**	**SD of KIE**
1.0299	0.25	0.0010	1.022	0.003
0.9925	0.25	0.0010	0.995	0.004
1.0009	0.25	0.0010	1.001	0.002
0.9960	0.25	0.0010	0.997	0.002
1.0026	0.25	0.0010	1.002	0.002
1.0036	0.25	0.0010	1.003	0.002
0.9787	0.25	0.0010	0.985	0.002
0.9983	0.25	0.0010	0.999	0.002
0.9984	0.25	0.0010	0.999	0.003
0.9932	0.25	0.0010	0.995	0.002
0.9956	0.25	0.0010	0.997	0.003
1.0000	0.25	0.0010	1.000	#DIV/0!
0.9982	0.25	0.0010	0.999	0.003

59 – ^{13}C NMR for KIEs



^{13}C NMR ($CDCl_3$) δ 189.1, 165.7, 160.2, 141.4, 136.1, 128.7, 125.0, 122.4, 121.3, 112.6, 66.9, 60.8, 14.2.

APPENDIX B

TABLE OF CONTENTS

Veratrole (4)

E(RB+HF-LYP) = -461.328204758

```
Zero-point correction=                          0.164964 (Hartree/Particle)
Thermal correction to Energy=                       0.174406
Thermal correction to Enthalpy=                     0.175350
Thermal correction to Gibbs Free Energy=        0.130466
Sum of electronic and zero-point Energies=          -461.163240
Sum of electronic and thermal Energies=            -461.153799
Sum of electronic and thermal Enthalpies=          -461.152855
Sum of electronic and thermal Free Energies=        -461.197738

               E (Thermal)           CV              S
                KCal/Mol       Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total             109.441          35.681          94.466

C,0,-1.2429954366,0.1496965187,-1.2466042476
C,0,-2.2068186632,0.8162677423,-0.4726111231
C,0,-1.9410144657,1.1207264339,0.8577943705
C,0,-0.7087324675,0.7616213726,1.4277946875
C,0,0.2563902767,0.0989207659,0.6679236863
C,0,-0.0149921709,-0.2118385696,-0.6904271277
H,0,-2.6799524926,1.6368044966,1.4670214711
O,0,1.481932538,-0.2898641676,1.1346947017
C,0,1.802540065,-0.0000590243,2.495557226
O,0,0.9827620741,-0.8613202054,-1.3635544919
C,0,0.7591898483,-1.1958967097,-2.7333544042
H,0,-1.4647311863,-0.0809709547,-2.2829634409
H,0,-3.1578153675,1.0894565663,-0.9248279227
H,0,-0.5160334116,1.0058453543,2.4668386613
H,0,2.8088256158,-0.3912536266,2.6511137629
H,0,1.7967036831,1.0802593011,2.6843462558
H,0,1.106681114,-0.4964352362,3.1826921906
H,0,1.6681192093,-1.6988145537,-3.0661685471
H,0,-0.095443775,-1.8744209859,-2.8429279145
H,0,0.594687798,-0.2976265552,-3.3406846012
```

3,4-dimethoxyacetophenone (6)

E(RB+HF-LYP) = -613.977970517

```
Zero-point correction=                          0.202619 (Hartree/Particle)
Thermal correction to Energy=                       0.215007
```

```
Thermal correction to Enthalpy=              0.215951
Thermal correction to Gibbs Free Energy=        0.163516
Sum of electronic and zero-point Energies=         -613.775351
Sum of electronic and thermal Energies=            -613.762964
Sum of electronic and thermal Enthalpies=          -613.762019
Sum of electronic and thermal Free Energies=        -613.814454

               E (Thermal)          CV             S
                KCAL/MOL      CAL/MOL-KELVIN   CAL/MOL-KELVIN
TOTAL              134.919           46.088           110.359
```

```
C,0,0.7860327886,-0.7017780426,-1.131904038
C,0,-0.4375384704,-0.3461703823,-1.7010049274
C,0,-1.4096944087,0.3185476333,-0.9440424713
C,0,-1.1710673833,0.6374962567,0.3954460974
C,0,0.0686729927,0.2764915492,0.9698719499
C,0,1.0403851447,-0.3818298861,0.2325269571
O,0,2.2569983989,-0.764317024,0.7069779399
C,0,2.5673350024,-0.4707613869,2.065305514
O,0,1.7866544331,-1.3451152757,-1.7818014535
C,0,1.5976049436,-1.694315415,-3.1487281558
C,0,-2.150631625,1.3434274094,1.2725371702
H,0,-0.6453231935,-0.5828125258,-2.7373772121
H,0,-2.3457404561,0.5763627589,-1.4244260547
H,0,0.2279063755,0.5352181702,2.0089061533
H,0,3.5731095503,-0.8597554808,2.2271599079
H,0,2.5570884419,0.6100118473,2.252072852
H,0,1.8676578982,-0.965366622,2.7500506204
H,0,2.5176686058,-2.1933963084,-3.4540137725
H,0,0.7511483538,-2.3811813697,-3.2711692692
H,0,1.4414787721,-0.8036185824,-3.7696533286
O,0,-1.8721919914,1.5913862277,2.4426926649
C,0,-3.5120745076,1.772413708,0.7448083189
H,0,-3.7052152065,1.5269676324,-0.2991698644
H,0,-4.2817619018,1.3058517542,1.3676948736
H,0,-3.6038508267,2.8549586411,0.8780733945
```

Acylium Ion (8)

E(RB+HF-LYP) = -153.020663268

```
Zero-point correction=                   0.044271 (Hartree/Particle)
Thermal correction to Energy=                 0.047847
Thermal correction to Enthalpy=               0.048791
```

```
Thermal correction to Gibbs Free Energy=        0.020197
Sum of electronic and zero-point Energies=          -152.976392
Sum of electronic and thermal Energies=             -152.972817
Sum of electronic and thermal Enthalpies=           -152.971873
Sum of electronic and thermal Free Energies=        -153.000466

                E (Thermal)           CV               S
                 KCal/Mol      Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total               30.024           10.404           60.180
```

```
C,0,0.0535407511,-0.0081031881,-0.2006565859
C,0,-0.3146842661,0.0477167902,1.178954807
O,0,0.3431228139,-0.052042625,-1.2852795567
H,0,-1.2794592429,-0.4681576379,1.2961932035
H,0,0.4709200766,-0.454913589,1.7628128763
H,0,-0.3995691326,1.1061462499,1.4674492558
```

Intermediate 9

E(RB+HF-LYP) = -614.371445010

```
Zero-point correction=                    0.212884 (Hartree/Particle)
Thermal correction to Energy=                0.226386
Thermal correction to Enthalpy=              0.227330
Thermal correction to Gibbs Free Energy=        0.172484
Sum of electronic and zero-point Energies=          -614.158561
Sum of electronic and thermal Energies=             -614.145059
Sum of electronic and thermal Enthalpies=           -614.144115
Sum of electronic and thermal Free Energies=        -614.198961

                E (Thermal)           CV               S
                 KCal/Mol      Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total              142.059           49.619          115.433
```

```
C,0,1.1417392803,0.1776803102,0.1373835765
C,0,0.8019501716,-0.1752270483,-1.2304506516
C,0,-0.5372100565,-0.0603977297,-1.7063888237
C,0,-1.5218895323,0.3610308052,-0.8672901936
C,0,-1.2565018412,0.710559997,0.5410884404
C,0,0.1517992104,0.5846544311,0.9790954937
O,0,1.7993594515,-0.5879176288,-1.9578810218
C,0,1.6217367962,-0.9922498927,-3.3443635687
C,0,-2.2655321711,0.0540580403,1.5746427315
C,0,-3.7028788898,-0.0788788114,1.1483589165
```

```
O,0,2.4482247496,0.0400504375,0.4305944149
C,0,2.8750855188,0.3460026881,1.7677647318
O,0,-1.8606855735,-0.2751072929,2.6658968651
H,0,-0.7733631011,-0.2985485545,-2.7383252366
H,0,-2.5307036222,0.4729181724,-1.2592046716
H,0,0.3598798966,0.8259620152,2.0153876227
H,0,3.950054812,0.169987878,1.7750728978
H,0,2.6668280746,1.3941298808,2.0091592516
H,0,2.3837028992,-0.3144563816,2.490527939
H,0,2.6159267182,-1.2899468939,-3.6712849667
H,0,0.930783599,-1.8366164603,-3.397180006
H,0,1.2622440129,-0.14464543,-3.9322739425
H,0,-3.7963646807,-0.9043999013,0.4314779322
H,0,-4.3169805759,-0.2970104674,2.0234211048
H,0,-4.060285629,0.8314589372,0.654760926
H,0,-1.5452005177,1.7872698998,0.6461962382
```

Structure 11‡

E(RB+HF-LYP) = -614.351931262

```
Zero-point correction=                        0.210227 (Hartree/Particle)
Thermal correction to Energy=                    0.224364
Thermal correction to Enthalpy=                  0.225308
Thermal correction to Gibbs Free Energy=         0.167895
Sum of electronic and zero-point Energies=         -614.141704
Sum of electronic and thermal Energies=            -614.127568
Sum of electronic and thermal Enthalpies=          -614.126623
Sum of electronic and thermal Free Energies=       -614.184036

                E (Thermal)          CV              S
                 KCal/Mol      Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total               140.790          49.973         120.835
```

```
C,0,-0.0515169787,-1.4189256909,0.9079879665
C,0,0.9601832926,-0.7195492824,0.248060217
C,0,0.9454738114,0.708150694,0.2467848902
C,0,-0.080385545,1.3869211635,0.9054977734
C,0,-1.0981474552,0.6724673148,1.5596706247
C,0,-1.0842999379,-0.7257586164,1.5596953911
O,0,1.9989612037,-1.2939937763,-0.4090824091
C,0,2.08902902,-2.7226645525,-0.421990198
O,0,1.9719282416,1.302841677,-0.4118799622
C,0,2.0345625011,2.7328253099,-0.4244085586
```

```
C,0,-2.560002916,-0.0412372904,-1.0779091334
O,0,-1.6137015134,-0.1197836281,-1.6895462047
C,0,-3.8721565172,0.0584444387,-0.5030522069
H,0,-1.8466185543,-1.2868046234,2.0978752893
H,0,-0.0987753872,2.4712006353,0.9274091235
H,0,-1.8704201119,1.2184050966,2.0992531942
H,0,-0.0478304331,-2.5033572552,0.9296331423
H,0,2.990055605,-2.9531420503,-0.9906838417
H,0,2.1831423216,-3.1196969162,0.5950731922
H,0,1.2180170359,-3.1680059303,-0.9163333555
H,0,2.9298286974,2.9807918335,-0.9948423768
H,0,1.1541796848,3.161864205,-0.9166894578
H,0,2.1231839596,3.131336755,0.592628774
H,0,-3.9388164343,0.9969016781,0.0620022357
H,0,-4.5957622054,0.048950269,-1.3330349552
H,0,-4.0321113851,-0.798181458,0.1638808458
```

Structure 12

E(RB+HF-LYP) = -614.244202375

```
Zero-point correction=                           0.847367 (Hartree/Particle)
Thermal correction to Energy=                    0.984587
Thermal correction to Enthalpy=                  0.985532
Thermal correction to Gibbs Free Energy=         0.520351
Sum of electronic and zero-point Energies=          -614.374072
Sum of electronic and thermal Energies=             -614.236852
Sum of electronic and thermal Enthalpies=           -614.235908
Sum of electronic and thermal Free Energies=        -614.701088

                E (Thermal)         CV               S
                 KCal/Mol     Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total              617.838         385.733          979.054
```

```
C,0,0.7033913049,1.6427655754,2.1241537396
C,0,0.5116247247,0.3205001338,2.560396008
C,0,1.9585451727,-0.0380852009,-0.1576674508
O,0,2.9939201857,-0.0871447882,0.3111349298
C,0,0.8356139646,-0.078550558,-1.069629944
C,0,1.5245301645,-0.3428635766,3.2631197777
C,0,1.9043668867,2.309220494,2.4015632247
H,0,-0.4382554645,-0.179447881,2.3883627385
H,0,-0.1021181968,2.1744167455,1.6237795139
H,0,0.0356912961,-0.6896739413,-0.6303686316
```

```
H,0,0.4793223902,0.9454938958,-1.2251165896
H,0,1.1709704724,-0.5193936311,-2.0223046822
C,0,2.733652999,0.3034829586,3.5272366037
H,0,1.3657869931,-1.3615222246,3.6028038232
O,0,3.7752024994,-0.2307210508,4.1903199192
C,0,2.9245827929,1.6549775277,3.0926818538
H,0,2.0321071366,3.3385457685,2.0880234262
O,0,4.1162078692,2.1924191193,3.4190815559
C,0,3.6884118423,-1.5865513775,4.6382523655
H,0,4.6380828831,-1.7896092136,5.1328325167
H,0,2.8625448383,-1.7153034248,5.3474525033
H,0,3.5619351182,-2.2716027197,3.791087308
C,0,4.3928533757,3.5383493729,3.0295707546
H,0,5.4033750666,3.7433006928,3.3806242502
H,0,4.3557645865,3.6496234714,1.938346184
H,0,3.6905119197,4.2343957318,3.5018551054
C,0,6.970338916,0.7183320524,4.2164751408
H,0,5.869407052,0.745868727,4.024802741
H,0,7.2580517068,1.3098630425,5.1143104749
Cl,0,7.4467548558,-0.9361253421,4.4848331874
Cl,0,7.7776755459,1.4240700432,2.8347003871
C,0,1.901629699,2.8471397077,-3.9754101218
Cl,0,0.9846833745,1.4006616831,-4.2974143002
H,0,1.3161547126,3.7223304781,-4.3376320135
Cl,0,2.1973848798,3.0727524481,-2.2649097186
H,0,2.8904430623,2.7614356234,-4.482617558
Cl,0,6.0067085287,-4.9974024905,-0.6453321901
C,0,6.5717755708,-3.6914510242,0.3558554968
H,0,6.9729040532,-2.8885287179,-0.3046292816
Cl,0,5.2891695264,-2.9939764644,1.3216691044
H,0,7.3460763068,-4.0873011094,1.0522233265
Cl,0,-6.8653958616,0.3157173143,6.026662844
C,0,-5.7152436926,1.4918595431,5.4563760812
H,0,-5.5596139404,2.2417070901,6.264088922
H,0,-4.7772062218,0.9544268348,5.1886628425
Cl,0,-6.2682103981,2.3417017271,4.0356868338
Cl,0,2.2698801463,-7.3872149184,-2.1932652709
C,0,0.7967977885,-7.9325327176,-1.436612858
H,0,0.9248905777,-9.0039199915,-1.1634909098
Cl,0,0.429825157,-7.0440405109,0.0194951803
H,0,-0.0401283198,-7.7736737928,-2.1554466192
Cl,0,-2.905086997,1.6796107193,1.8477360033
C,0,-4.12635722,2.4564321257,0.866884669
H,0,-4.0239857764,3.556887984,1.0030686472
```

```
Cl,0,-3.9391551043,2.0927983078,-0.825860602
H,0,-5.122529407,2.0809160193,1.199284453
Cl,0,-3.2646268344,-5.5793002316,1.2137643162
C,0,-4.9344953509,-5.7586247839,1.6711173789
H,0,-5.365785319,-6.6076935938,1.0947095386
H,0,-4.9765932345,-5.9297055894,2.7710599457
Cl,0,-5.8810411372,-4.334316311,1.3157946546
Cl,0,1.5473017771,-3.0645754409,0.5642162782
C,0,2.3621678193,-3.9383325426,-0.7217356617
Cl,0,2.7585144512,-2.87976867,-2.0556586196
H,0,3.3122392581,-4.3521971782,-0.3084500526
H,0,1.6702749526,-4.7320514793,-1.0913200972
Cl,0,-3.9203607185,6.3656308813,1.001521694
C,0,-4.0924633665,6.9744056994,2.6262162448
Cl,0,-2.7172312955,6.6041653101,3.6320473135
H,0,-4.1902069103,8.082121029,2.569239484
H,0,-4.9889720266,6.4957905854,3.0809928783
Cl,0,-7.8572255083,5.2454363675,-4.520890711
C,0,-8.7014581634,5.3627566329,-6.0421130185
Cl,0,-8.9894583469,3.8041027669,-6.7674703027
H,0,-9.688025291,5.8430356455,-5.8529699848
H,0,-8.0715240725,5.9574283193,-6.7411725446
Cl,0,-7.196049421,-1.8520441485,-0.3446349076
C,0,-7.9771011086,-0.410642172,0.2472959703
Cl,0,-7.1873209724,0.2481338232,1.6572211768
H,0,-7.9444313681,0.3579727842,-0.5603114154
H,0,-9.0199748053,-0.6764383699,0.5321241507
Cl,0,5.1963338825,4.312691423,-4.8411316116
C,0,6.0543404015,4.7673205324,-3.390711273
Cl,0,7.5667512864,3.9215727318,-3.2127687925
H,0,6.2726317407,5.8574214236,-3.4508812656
H,0,5.4113658402,4.51604187,-2.5159239005
Cl,0,1.3270655507,8.5366602141,1.802760797
C,0,0.9457218858,7.9406562174,3.3968933131
Cl,0,1.732444691,6.427478142,3.7592109394
H,0,1.2951873209,8.6952152272,4.1374923272
H,0,-0.1553158871,7.7786556556,3.4480238564
Cl,0,-0.284025797,-4.6729473982,-3.2712670981
C,0,-2.0129544839,-4.91694588,-3.279529857
Cl,0,-2.4546585948,-6.5864075331,-3.0608214967
H,0,-2.4467934192,-4.3282132916,-2.4392361217
H,0,-2.3990443895,-4.581439785,-4.2689732969
Cl,0,-3.7318272602,-1.5929637097,4.3135447007
C,0,-5.0535474028,-2.6888139877,4.6323339791
```

H,0,-5.6884163129,-2.2382671288,5.4292433242
H,0,-5.6117218686,-2.8406038286,3.6798934987
Cl,0,-4.5030079589,-4.2469921009,5.1885562636
Cl,0,9.2792773658,-1.1372663512,0.1953312417
C,0,10.0126029555,-1.5260205616,1.7343235733
H,0,9.4941986382,-0.9270737717,2.5188606628
Cl,0,9.8533144731,-3.2106579175,2.142874949
H,0,11.0975814948,-1.2878164833,1.6628793045
Cl,0,-9.5963782347,1.9261002115,-2.2720265697
C,0,-8.6189625048,1.5523246488,-3.6665943737
Cl,0,-7.022444021,1.0010049366,-3.2316781442
H,0,-9.1224946993,0.7353653683,-4.2309467997
H,0,-8.5146268109,2.4808532123,-4.2756273909
Cl,0,-0.7137706829,-1.2815389831,-4.8956144925
C,0,-2.1877019623,-1.0899408158,-5.815687197
Cl,0,-3.5217707351,-1.9688236543,-5.1257865631
H,0,-2.449945509,-0.0081843375,-5.8216198221
H,0,-1.9999641694,-1.4850424914,-6.8397399329
Cl,0,4.048435425,7.7323354029,-2.079250778
C,0,3.5294253681,7.1520399664,-0.5248245826
Cl,0,4.0915325949,5.5282611867,-0.1943506807
H,0,3.9477501925,7.8221983697,0.2603470484
H,0,2.416043432,7.134184838,-0.5104015281
Cl,0,-1.7265457936,-2.0846907484,0.5723812587
C,0,-3.3198179054,-1.7055205559,-0.0527655926
Cl,0,-3.3464939275,-1.6564786875,-1.7917825085
H,0,-4.0149480535,-2.5051039324,0.2942761847
H,0,-3.604766051,-0.6996231396,0.3322892214
Cl,0,0.1170218613,-2.6407286339,5.9580900477
C,0,-0.6050896651,-3.893633285,4.9842458739
H,0,-0.4709779232,-4.8639700934,5.5131449579
H,0,-1.6808015517,-3.6416695458,4.8330627572
Cl,0,0.1461147924,-4.0289499352,3.4143610551
Cl,0,5.8208302354,-0.3374204981,-1.5919133485
C,0,6.4626536428,1.1495300548,-0.9435820985
H,0,7.1046651343,1.6210096066,-1.7234869038
Cl,0,5.1952721937,2.2862928834,-0.5346936661
H,0,7.0239098253,0.9116633187,-0.0102218525

Structure 13‡

E(RB+HF-LYP) = -1038.97884803

Zero-point correction= 0.229571 (Hartree/Particle)

```
Thermal correction to Energy=                 0.248428
Thermal correction to Enthalpy=               0.249372
Thermal correction to Gibbs Free Energy=      0.180811
Sum of electronic and zero-point Energies=        -1038.749277
Sum of electronic and thermal Energies=           -1038.730420
Sum of electronic and thermal Enthalpies=         -1038.729476
Sum of electronic and thermal Free Energies=      -1038.798037

                E (Thermal)          CV                S
                 KCal/Mol      Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total              155.891           67.504          144.300

C,0,1.2006111347,0.6938083821,0.1124591576
C,0,0.6927204083,-0.6501011366,0.1943913655
C,0,-0.5569891262,-0.8434093892,0.7157159598
C,0,-1.4185045576,0.2692333264,1.1339400595
C,0,-0.8601909407,1.612025782,0.9745304596
C,0,0.4036799025,1.8103950298,0.4999594847
O,0,1.5182791398,-1.6036506552,-0.2765199143
C,0,1.0072771921,-2.9482906437,-0.3445681466
C,0,-1.9564556748,0.0874170262,2.6404610921
C,0,-3.4293860672,0.3052520045,2.8272646935
O,0,2.4253647544,0.802530769,-0.3599571077
C,0,3.0610513495,2.0869999135,-0.5068460308
O,0,-1.176864405,-0.2084778742,3.5107648046
H,0,-0.9900105601,-1.8326410842,0.7942209976
H,0,-2.3504783191,0.1891538374,0.5183502104
H,0,0.7997950317,2.8134480406,0.3947520218
H,0,4.0512872766,1.8639615412,-0.9014716549
H,0,2.5060737076,2.7079606632,-1.2161827187
H,0,3.1466030248,2.5839310251,0.4639675058
H,0,1.7878192473,-3.5221149747,-0.8438457117
H,0,0.8413522842,-3.3460829334,0.6631664274
H,0,0.0778618043,-2.978245811,-0.9221086674
H,0,-3.9537423294,-0.5209273025,2.3293572787
H,0,-3.6723334956,0.3294114788,3.8914754462
H,0,-3.758185147,1.2267863583,2.332006463
H,0,-1.4740172906,2.4670289328,1.2474329615
B,0,-3.5290218917,-1.8383235418,-0.5494840262
F,0,-2.3632305072,-2.0661875043,-1.31726204
F,0,-3.2617780153,-2.2488674804,0.7942214559
F,0,-3.7567670456,-0.4143215917,-0.501774917
F,0,-4.6290818843,-2.487068188,-1.06541391
```

Transition State for bromination of veratrole

E(RB+HF-LYP) = -3032.71631708

```
 Zero-point correction=                           0.167904 (Hartree/Particle)
 Thermal correction to Energy=                    0.178667
 Thermal correction to Enthalpy=                  0.179611
 Thermal correction to Gibbs Free Energy=         0.130355
 Sum of electronic and zero-point Energies=         -3032.548413
 Sum of electronic and thermal Energies=            -3032.537650
 Sum of electronic and thermal Enthalpies=          -3032.536706
 Sum of electronic and thermal Free Energies=       -3032.585962

                E (Thermal)             CV                S
                 KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total             112.115             39.367            103.667
```

```
C,0,0.3408200797,-0.2642036517,1.6014965648
C,0,1.4002627088,-0.3164311731,0.6734047357
C,0,1.1384114473,-0.6489033486,-0.6423643132
C,0,-0.2480469131,-0.9527061969,-1.0773383095
C,0,-1.2902816626,-0.9060252664,-0.170667989
C,0,-1.0294203841,-0.5645933236,1.1715855255
O,0,2.0221528457,-0.7575373993,-1.6072862367
C,0,3.4188300857,-0.4877367402,-1.3489793316
O,0,-0.3363955909,-1.274269847,-2.3472126189
C,0,-1.6207547409,-1.5919917014,-2.9300807735
Br,0,-0.8729393375,1.692611058,1.6007215937
H,0,0.5607547247,-0.265901582,2.6632479477
H,0,-2.3032457173,-1.1424681596,-0.4693533664
H,0,-1.7737176922,-0.7773075055,1.9308336153
H,0,2.4082823591,-0.1100037833,1.008814903
H,0,3.9135968155,-0.6239779647,-2.3085590868
H,0,3.5434443351,0.5407327479,-0.998535136
H,0,3.8081364993,-1.2005059973,-0.6164253127
H,0,-1.4117928881,-1.7909238724,-3.9793224151
H,0,-2.0390879408,-2.4817032386,-2.4508756843
H,0,-2.2984754471,-0.7393212927,-2.8314270531
```

Brominated Intermediate

E(RB+HF-LYP) = -3032.72680832

```
 Zero-point correction=                           0.168328 (Hartree/Particle)
 Thermal correction to Energy=                    0.179727
```

```
Thermal correction to Enthalpy=                0.180671
Thermal correction to Gibbs Free Energy=        0.129668
Sum of electronic and zero-point Energies=        -3032.558480
Sum of electronic and thermal Energies=           -3032.547082
Sum of electronic and thermal Enthalpies=         -3032.546137
Sum of electronic and thermal Free Energies=       -3032.597141

                E (Thermal)          CV              S
                 KCal/Mol       Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total              112.780          40.909          107.345
```

```
C,0,-0.9980786635,-0.3524144552,0.9878794324
C,0,-0.9089750329,1.121929732,1.0217866053
C,0,0.1969188874,1.7814126525,0.5922326444
C,0,1.3166711621,1.0396392741,0.0988097986
C,0,1.3045311085,-0.4210689323,0.0649035661
C,0,0.1876461078,-1.0751018806,0.4913753477
O,0,2.403289759,1.5806843076,-0.3497782627
C,0,2.5990160508,3.0228706806,-0.4090275632
O,0,2.4339212372,-0.9543446811,-0.4044093456
C,0,2.5256399704,-2.3857939055,-0.5032890821
Br,0,-2.5420006195,-0.7105039208,-0.2728884918
H,0,-1.7692786035,1.6665298446,1.3976693073
H,0,0.1323375974,-2.156787797,0.4756410896
H,0,-1.369579325,-0.7587333627,1.9333121879
H,0,0.2366076824,2.8636891209,0.6117637069
H,0,3.590624809,3.1441413232,-0.8393480958
H,0,1.8420736252,3.4706880486,-1.0564167665
H,0,2.5647803498,3.4405751702,0.5994895866
H,0,3.5154667122,-2.5823087068,-0.9119468477
H,0,2.4320273558,-2.8456503358,0.4865477495
H,0,1.7570559643,-2.774062083,-1.180138333
```

Nitronium Ion (15)

E(RB+HF-LYP) = -204.711826770

```
Zero-point correction=                     0.010297 (Hartree/Particle)
Thermal correction to Energy=               0.013280
Thermal correction to Enthalpy=              0.014225
Thermal correction to Gibbs Free Energy=       -0.006787
Sum of electronic and zero-point Energies=          -204.701530
Sum of electronic and thermal Energies=            -204.698546
Sum of electronic and thermal Enthalpies=           -204.697602
```

```
Sum of electronic and thermal Free Energies=        -204.718614

                 E (Thermal)           CV              S
                  KCal/Mol        Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total               8.334             7.024           44.223

N,0,0.0003552638,0.,0.0001841139
O,0,-0.5194916683,-0.0000000002,1.0028920518
O,0,0.5191808125,0.0000000002,-1.0030531515
```

Transition Structure for Nitration of veratrole

E(RB+HF-LYP) = -666.098606034

```
Zero-point correction=                          0.178672 (Hartree/Particle)
Thermal correction to Energy=                        0.191197
Thermal correction to Enthalpy=                      0.192141
Thermal correction to Gibbs Free Energy=        0.139660
Sum of electronic and zero-point Energies=          -665.919934
Sum of electronic and thermal Energies=             -665.907409
Sum of electronic and thermal Enthalpies=           -665.906465
Sum of electronic and thermal Free Energies=        -665.958946

                 E (Thermal)           CV              S
                  KCal/Mol        Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total              119.978            45.397          110.456

C,0,0.7278060875,-0.5859152881,1.3356326253
C,0,0.6578247224,0.7731156788,1.6255292134
C,0,0.5447831949,1.7457759705,0.572341979
C,0,0.5029993467,1.3504334426,-0.7610748172
C,0,0.5205550488,-0.0099230177,-1.0687874561
C,0,0.6360003661,-1.0045829552,0.0082320917
N,0,-1.5624758306,1.3580153673,1.4210141728
O,0,0.4519620815,-0.5331178101,-2.2717026774
C,0,0.3465019587,0.3175699276,-3.4355496114
O,0,0.6509595267,-2.2480835709,-0.414682474
C,0,0.7709551537,-3.3399877601,0.5248455596
H,0,0.7576575064,1.1182881285,2.6496628423
H,0,0.427846862,2.0931874073,-1.5453743765
H,0,0.5623081423,2.800340839,0.8283471115
H,0,0.8226735076,-1.3077654014,2.1371251286
H,0,0.7548053963,-4.2397662214,-0.0870044635
H,0,1.7177763252,-3.266795315,1.0672182948
```

```
H,0,-0.077085859,-3.3354714119,1.2155272666
H,0,0.3053887502,-0.3668040934,-4.2806332253
H,0,-0.5700390359,0.9121412805,-3.3838083927
H,0,1.2270443335,0.9616997248,-3.5113280384
O,0,-2.11905083,0.5546063283,0.7391479147
O,0,-1.8883208266,2.1823352404,2.2167561288
```

Nitrated Intermediate (16)

E(RB+HF-LYP) = -666.105681341

```
 Zero-point correction=                           0.180067 (Hartree/Particle)
 Thermal correction to Energy=                    0.192689
 Thermal correction to Enthalpy=                  0.193634
 Thermal correction to Gibbs Free Energy=         0.140186
 Sum of electronic and zero-point Energies=          -665.925614
 Sum of electronic and thermal Energies=             -665.912992
 Sum of electronic and thermal Enthalpies=           -665.912048
 Sum of electronic and thermal Free Energies=        -665.965496

                     E (Thermal)             CV                S
                      KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                  120.914             45.730           112.490
```

```
C,0,0.54700098,-1.3462367722,0.0888946372
C,0,0.4667045551,-0.9502321021,1.4652852469
C,0,0.2031800186,0.3398405949,1.7834698566
C,0,0.0914876597,1.3795492501,0.7348354526
C,0,0.092497818,0.9178562351,-0.6708184565
C,0,0.3489857692,-0.3804902163,-0.9914748482
O,0,0.4271270976,-0.9185886306,-2.2076929395
C,0,0.2042809464,-0.0694817925,-3.3487080613
O,0,0.7652314069,-2.5575088678,-0.302549988
C,0,0.9730677804,-3.6659010802,0.6228450633
N,0,-1.1261880713,2.3370444539,1.0510575399
O,0,-1.2949860961,2.5903026783,2.2285115146
O,0,-1.7389772653,2.7642740328,0.0938441266
H,0,0.0902778172,0.6577873669,2.8148469145
H,0,-0.0864567087,1.6641143245,-1.4342470923
H,0,0.9344330076,2.0789571016,0.8857233366
H,0,0.5839552393,-1.6950306334,2.2433604767
H,0,1.1465728826,-4.5253871668,-0.0207055027
H,0,1.8489280621,-3.4663528361,1.2436293093
H,0,0.0744304638,-3.8119465036,1.2257115627
```

```
H,0,0.3117761171,-0.7203140959,-4.2147115658
H,0,-0.805269976,0.3536966252,-3.3195975732
H,0,0.954275285,0.7279062384,-3.3842876984
```

Cyclopentadienone (18)

E(RmPW+HF-PW91) = -495.841570165

```
 Zero-point correction=                           0.121366 (Hartree/Particle)
 Thermal correction to Energy=                    0.130359
 Thermal correction to Enthalpy=                  0.131303
 Thermal correction to Gibbs Free Energy=         0.086500
 Sum of electronic and zero-point Energies=          -495.720204
 Sum of electronic and thermal Energies=             -495.711211
 Sum of electronic and thermal Enthalpies=           -495.710267
 Sum of electronic and thermal Free Energies=        -495.755070

                     E (Thermal)             CV                S
                      KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                  81.802             31.705            94.296
```

```
C,0,-1.6469433811,0.2760461494,-1.873013
C,0,-1.6470070407,0.1340208897,-0.5499729562
C,0,-0.243324331,0.0173935535,-0.0586991006
C,0,0.606874061,0.0885936242,-1.0826042364
H,0,-2.4928748619,0.1010515463,0.115943507
H,0,-2.4825305381,0.3857892847,-2.5409178084
C,0,0.0610952097,-0.150017072,1.3718796062
O,0,-0.7890219295,-0.2026216181,2.2223960393
O,0,1.3615108546,-0.2351279654,1.6134657135
C,0,1.7243069477,-0.3979784756,2.9761972337
H,0,1.3757087992,0.4459253309,3.5639876748
H,0,1.2945740385,-1.311769313,3.3755664913
H,0,2.8057480377,-0.4490159662,2.9868432883
C,0,-0.2238327465,0.2597436126,-2.3248131489
O,0,0.1918288404,0.3612441971,-3.4466995793
H,0,1.68084804,0.0384222219,-1.0706497242
```

Dimethylbutadiene (19)

E(RmPW+HF-PW91) = -234.583787244

```
 Zero-point correction=                           0.145780 (Hartree/Particle)
 Thermal correction to Energy=                    0.152752
```

```
Thermal correction to Enthalpy=                0.153697
Thermal correction to Gibbs Free Energy=        0.115510
Sum of electronic and zero-point Energies=          -234.438008
Sum of electronic and thermal Energies=             -234.431035
Sum of electronic and thermal Enthalpies=           -234.430091
Sum of electronic and thermal Free Energies=         -234.468277

                E (Thermal)          CV              S
                 KCal/Mol       Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total               95.854           25.844          80.371
```

```
C,0,-0.0038573835,-0.0270518923,0.0219907483
C,0,-0.0061341183,-0.0356398007,1.3576694389
C,0,1.2903032575,0.0607381166,-0.7295919961
H,0,0.9178097617,0.0201036641,1.9139785026
H,0,-0.9140145963,-0.0975897271,1.9365768519
H,0,1.3202767116,0.946554416,-1.3631627086
H,0,2.1301543267,0.1100457399,-0.042490879
H,0,1.432507932,-0.805661432,-1.3746372798
C,0,-1.2587070416,-0.1026767459,-0.7498607228
C,0,-1.2564069807,-0.0941442577,-2.0855499732
C,0,-2.5528699746,-0.1906501971,0.0017031515
H,0,-2.1803329589,-0.1499259804,-2.6418859372
H,0,-0.3485141301,-0.0322298835,-2.6644387812
H,0,-2.6952017792,0.6756545008,0.646847306
H,0,-3.3927063264,-0.2399350574,-0.6854235809
H,0,-2.5827406999,-1.0765424634,0.6351588595
```

Dimethylbutadiene [4+2] product (27)

E(RmPW+HF-PW91) = -730.514146845

```
Zero-point correction=                     0.274391 (Hartree/Particle)
Thermal correction to Energy=                  0.289919
Thermal correction to Enthalpy=                0.290863
Thermal correction to Gibbs Free Energy=        0.231354
Sum of electronic and zero-point Energies=          -730.239756
Sum of electronic and thermal Energies=             -730.224228
Sum of electronic and thermal Enthalpies=           -730.223284
Sum of electronic and thermal Free Energies=         -730.282793

                E (Thermal)          CV              S
                 KCal/Mol       Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total              181.927           57.696          125.248
```

```
C,0,-2.5445568246,0.8957823862,-0.1832952812
C,0,-2.2432178563,-0.1178915395,0.912289294
C,0,-0.8605201288,0.2793429868,1.4409355347
C,0,-0.5345348666,1.5490797584,0.696401097
C,0,-1.4601442617,1.8883377225,-0.1970041121
C,0,-2.3090804711,-1.537051319,0.3611303113
C,0,-1.1714594384,-1.8049595683,-0.5886109221
C,0,0.0522318641,-1.4264395265,-0.2073801615
C,0,0.2017988627,-0.8115636075,1.158174763
C,0,1.315862021,-1.5868074792,-0.9888123063
H,0,0.3793367123,2.0884854689,0.8959698343
O,0,-3.5041941132,0.863655214,-0.911832876
H,0,0.100147021,-1.5901348522,1.9201137809
C,0,-1.5339647296,-2.4664995635,-1.8772519545
H,0,-3.2662978532,-1.6614121049,-0.1415933204
H,0,-2.2908397724,-2.248054693,1.1910699761
C,0,-0.8685332883,0.5313178649,2.9358942831
H,0,-2.9886482371,0.0070066281,1.6968157292
H,0,-1.4455990029,2.7369182517,-0.8611767184
O,0,0.2636841885,1.1052526057,3.3360548895
O,0,-1.7545729575,0.2333665271,3.6887331574
C,0,0.3728287596,1.3546247381,4.7293441538
H,0,1.3390928276,1.8231549693,4.8698091252
H,0,-0.4232477548,2.0153485243,5.0591721568
H,0,0.3154601277,0.4243784915,5.2866048739
H,0,1.1942245341,-0.3833800311,1.2877456713
H,0,2.0430092896,-2.1778100157,-0.4291833455
H,0,1.1650207214,-2.0704245166,-1.9479968925
H,0,1.7775014145,-0.6153237917,-1.1738441375
H,0,-0.6802576705,-2.6650687861,-2.5167786083
H,0,-2.0353268694,-3.4163899128,-1.6850134631
H,0,-2.2396882475,-1.8474628295,-2.4323735324
```

Dimethylbutadiene [2+4] product (28)

E(RmPW+HF-PW91) = -730.473795517

```
 Zero-point correction=                           0.274451 (Hartree/Particle)
 Thermal correction to Energy=                    0.289535
 Thermal correction to Enthalpy=                  0.290479
 Thermal correction to Gibbs Free Energy=         0.232135
 Sum of electronic and zero-point Energies=          -730.199345
 Sum of electronic and thermal Energies=             -730.184261
```

```
Sum of electronic and thermal Enthalpies=          -730.183317
Sum of electronic and thermal Free Energies=        -730.241660

                E (Thermal)           CV               S
                 KCal/Mol      Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total              181.686           57.647          122.795
```

```
C,0,1.1813900665,-2.611344809,1.5513470579
C,0,0.4739968964,-1.5492465563,2.3290701861
C,0,-0.2103978845,-2.1365656839,3.3238739856
C,0,0.0079765543,-3.618009484,3.242367117
C,0,1.4549112958,-3.5304163703,2.7555016171
O,0,2.4674389009,-3.9925333114,3.1759217736
C,0,-0.6761311309,-4.1339415244,1.9559293585
C,0,0.1834847462,-3.5592820769,0.7831488892
C,0,-1.0394466747,-1.4953701468,4.3471982783
O,0,-1.635299792,-2.0960087342,5.2044969506
O,0,-1.0674636863,-0.16950752,4.2242894372
C,0,-1.8472402514,0.5181334146,5.1881628898
C,0,-0.6447253177,-2.8530973499,-0.2760064779
C,0,-1.5333935058,-1.7102281977,0.1251174622
C,0,-0.6168094425,-3.2190874174,-1.5566734533
H,0,-1.7133245836,-3.8139961017,1.9191846355
H,0,-0.6697317501,-5.2215992703,1.9238443419
H,0,-0.1829275948,-4.1795528661,4.147927635
H,0,-2.8844813195,0.2000103675,5.1364460836
H,0,-1.468970958,0.3290442632,6.1885295669
H,0,-1.7594516335,1.5691622544,4.941660172
H,0,0.5340213307,-0.4897509921,2.1425109333
H,0,2.0365470004,-2.3018246766,0.9613759189
C,0,1.019841524,-4.6897200409,0.1863494583
H,0,-2.1988148125,-1.4490752062,-0.6933805924
H,0,-2.1437108933,-1.9371318832,0.9963060214
H,0,-0.9562189394,-0.8209986137,0.3729425852
H,0,1.5935613541,-5.1980440893,0.9582162162
H,0,0.3820515672,-5.4327867793,-0.2874069945
H,0,1.7262412653,-4.317016603,-0.5527986853
H,0,-1.233178683,-2.7105935697,-2.2837286688
H,0,0.0021763514,-4.0167374255,-1.9323136995
```

Dimethylbutadiene Transition Structure 23

E(RmPW+HF-PW91) = -730.413031682

```
Zero-point correction=                    0.268756 (Hartree/Particle)
Thermal correction to Energy=                  0.285083
Thermal correction to Enthalpy=                0.286027
Thermal correction to Gibbs Free Energy=       0.225161
Sum of electronic and zero-point Energies=        -730.144276
Sum of electronic and thermal Energies=           -730.127949
Sum of electronic and thermal Enthalpies=         -730.127004
Sum of electronic and thermal Free Energies=        -730.187871

                E (Thermal)         CV              S
                 KCal/Mol      Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total               178.892          60.271          128.104

C,0,-0.0117595167,0.1992149228,-0.6930606012
 C,0,-1.0248076885,-0.7198553999,-0.5813800252
 C,0,-2.2671419201,0.0496706496,-0.1915347478
 C,0,-1.790914968,1.4036159136,0.1392418485
 C,0,-0.4964094159,1.4862704449,-0.2251609598
 O,0,-3.3975631327,-0.3712413707,-0.1947872927
 C,0,1.2976758804,-0.0958597946,-1.2555703998
 O,0,1.7048066883,-1.2090338247,-1.4927099822
 O,0,2.0144239729,1.0060610348,-1.4931819093
 C,0,3.2981828224,0.7918531849,-2.0512514047
 C,0,-0.9487176134,-1.6596364739,1.3636151208
 C,0,-0.9986330187,-0.6291694757,2.2722427737
 C,0,0.1659528293,0.1953552386,2.5158536164
 C,0,1.3279369796,-0.0209463371,1.8644415977
 H,0,2.1662071392,0.6444433791,2.0102778952
 C,0,0.0396939327,1.3594573097,3.4539097703
 C,0,-2.2720839176,-0.366234599,3.0165972568
 H,0,-1.8228035309,-2.2813487431,1.2335032069
 H,0,-1.0571848585,-1.6718535489,-1.0843561709
 H,0,0.1268311684,2.3642195765,-0.1782579059
 H,0,-2.4257327387,2.1866760387,0.5152478798
 H,0,3.7268820416,1.7768720389,-2.1914610349
 H,0,3.9145629513,0.2014946493,-1.3788766466
 H,0,3.2197117867,0.2729905126,-3.002162117
 H,0,1.5084549864,-0.8855697624,1.2486693959
 H,0,-0.0127949356,-2.103462858,1.0652455163
 H,0,-2.4816192438,0.6933605347,3.1297921871
 H,0,-3.1169428592,-0.8274875966,2.512981077
 H,0,-2.2103384211,-0.7927001269,4.0200317216
 H,0,0.992545244,1.8678015944,3.5692634249
 H,0,-0.687978902,2.0841106825,3.0902776043
```

```
H,0,-0.2899867421,1.0378072057,4.4409313049
```

Dimethylbutadiene Transition Structure 23-2

E(RmPW+HF-PW91) = -730.405894898

```
 Zero-point correction=                           0.268921 (Hartree/Particle)
 Thermal correction to Energy=                    0.285010
 Thermal correction to Enthalpy=                  0.285954
 Thermal correction to Gibbs Free Energy=         0.225739
 Sum of electronic and zero-point Energies=          -730.136974
 Sum of electronic and thermal Energies=             -730.120885
 Sum of electronic and thermal Enthalpies=           -730.119941
 Sum of electronic and thermal Free Energies=        -730.180156

                E (Thermal)             CV                S
                 KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total             178.846            60.083           126.734
```

```
C,0,2.6336848977,-0.3866484322,-1.2546488084
 C,0,1.307214802,-0.8476410842,-0.7279764333
 C,0,1.0570979712,-0.7840140443,0.6356595637
 H,0,1.8374638425,-0.4073490199,1.281892531
 H,0,3.072178991,0.3587365817,-0.5954819797
 C,0,0.3369759214,-1.4618406841,-1.6053418283
 C,0,-0.8379737585,-1.9329518141,-1.1331649804
 C,0,-0.2998045969,0.7903861332,0.9473122293
 C,0,0.6712547758,1.6519331247,0.1749260044
 C,0,0.1676269967,1.6237648956,-1.2090294517
 C,0,-1.0917970606,1.1189362645,-1.1648019187
 C,0,-1.4052392843,0.6208825545,0.1445066817
 O,0,1.6244400274,2.2459648967,0.6142820257
 H,0,-2.35853943,0.2084561879,0.4233981351
 H,0,2.5670139194,0.0386589076,-2.251302503
 H,0,3.3271951979,-1.2288865956,-1.3054156995
 H,0,0.383387259,-1.4845010077,1.1006086871
 C,0,0.6100042876,-1.4814659782,-3.0800044918
 H,0,-1.5802807731,-2.3289232022,-1.8103689653
 H,0,-1.0639593561,-2.0112646988,-0.0837689093
 H,0,-0.2946337907,0.7509244659,2.024680733
 C,0,-1.9811436873,1.0589459875,-2.340979638
 H,0,0.6559447589,2.0767320019,-2.0532334349
 H,0,-0.1716125929,-2.0172931798,-3.6103344277
 H,0,0.6528046894,-0.470810298,-3.4850571243
```

H,0,1.559578953,-1.9673544116,-3.2995347204
O,0,-1.6327440705,1.2946474963,-3.4681702207
O,0,-3.2254299742,0.7235337281,-2.0131419592
C,0,-4.1466736232,0.6623072985,-3.0886784158
H,0,-5.0965786697,0.3857782082,-2.6479750133
H,0,-4.2211882264,1.6279694571,-3.580072411
H,0,-3.8327273964,-0.0803767395,-3.8165432561

Dimethylbutadiene Cope Transition Structure 35

E(RmPW+HF-PW91) = -730.432384993

```
Zero-point correction=                    0.271521 (Hartree/Particle)
Thermal correction to Energy=                0.286665
Thermal correction to Enthalpy=              0.287609
Thermal correction to Gibbs Free Energy=        0.229882
Sum of electronic and zero-point Energies=         -730.160864
Sum of electronic and thermal Energies=            -730.145720
Sum of electronic and thermal Enthalpies=          -730.144776
Sum of electronic and thermal Free Energies=         -730.202503

              E (Thermal)          CV              S
               KCal/Mol      Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total             179.885           57.669          121.497
```

C,0,0.0769301485,0.2623739472,-0.8417615131
C,0,-0.9660875614,-0.7477822779,-0.5885662079
C,0,-2.2224988498,0.1026118491,-0.4112045381
C,0,-1.7006920693,1.3905637249,0.0131298361
C,0,-0.4111779529,1.5076120657,-0.4963885567
O,0,-3.3651686269,-0.2846974171,-0.4745035087
C,0,1.3633435995,-0.0573779033,-1.4363751832
O,0,1.7678649931,-1.1852762209,-1.6042875539
O,0,2.0676672834,1.0248663731,-1.7803721769
C,0,3.3354331827,0.7700406144,-2.3565018072
C,0,-0.9404597231,-1.3505199081,0.8733071883
C,0,-1.0983081817,-0.2512745162,1.858180026
C,0,0.0519879986,0.4881059114,2.2347666072
C,0,1.2489357658,0.2049737912,1.653896977
H,0,2.1031485436,0.8443091255,1.8262899934
C,0,-0.0756633723,1.6592775538,3.1649229556
C,0,-2.3694065571,-0.1911233392,2.6325194714
H,0,-1.7847839209,-2.0329779543,0.9302952788
H,0,-1.0189119957,-1.5570315318,-1.3083224019
H,0,0.1676158845,2.4158960963,-0.541732838

```
H,0,-2.3240174293,2.194878826,0.3678986455
H,0,3.749693368,1.7415266455,-2.5982927809
H,0,3.9790348575,0.2480264759,-1.6535132352
H,0,3.2341893543,0.1667013647,-3.2539565274
H,0,1.4433184776,-0.7054086425,1.1144609947
H,0,-0.0266442966,-1.9225683524,1.0054634752
H,0,-2.4979763658,0.750918542,3.1553454725
H,0,-3.2278066552,-0.3577794086,1.9826717233
H,0,-2.3740612948,-0.9908973346,3.3785572126
H,0,0.8747042251,2.1759002386,3.2651923049
H,0,-0.8138485992,2.3750806142,2.8048419158
H,0,-0.3834202302,1.3430160477,4.1605817509
```

Vinylcyclohexene (20)

E(RmPW+HF-PW91) = -312.002259823

```
Zero-point correction=                    0.184733 (Hartree/Particle)
Thermal correction to Energy=                0.192255
Thermal correction to Enthalpy=              0.193200
Thermal correction to Gibbs Free Energy=        0.153068
Sum of electronic and zero-point Energies=          -311.817527
Sum of electronic and thermal Energies=            -311.810004
Sum of electronic and thermal Enthalpies=           -311.809060
Sum of electronic and thermal Free Energies=          -311.849191

                E (Thermal)         CV              S
                 KCal/Mol     Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total              120.642          29.208          84.463
```

```
C,0,0.5209305876,-1.0818381664,-0.7304847573
C,0,-0.4823062047,-0.1558153471,-0.1027373415
C,0,-0.0980817638,0.9089000208,0.6130531743
C,0,1.3228141428,1.2711364437,0.8968079604
C,0,2.2761037778,0.129561378,0.5819838156
C,0,1.9236341558,-0.4945417248,-0.7563795162
C,0,-1.9053469149,-0.4346955307,-0.2656766052
C,0,-2.4369105631,-1.4756715364,-0.9055167206
H,0,-3.5070893345,-1.6023400789,-0.963333621
H,0,-1.8324861598,-2.2317792023,-1.3843721212
H,0,-2.5728286153,0.2823159527,0.1981554015
H,0,-0.8624832661,1.5569800335,1.0257573256
H,0,1.4183412614,1.5722789978,1.9415124366
H,0,1.59195176,2.1563722823,0.311635997
```

```
H,0,2.2009571754,-0.6297545946,1.3632208031
H,0,3.3056930946,0.4861948715,0.5850401041
H,0,2.6434701574,-1.2672790249,-1.0249021204
H,0,1.9799556668,0.2710509394,-1.5332901085
H,0,0.5187399725,-2.0298318372,-0.185245845
H,0,0.2032350701,-1.3205558763,-1.7461772615
```

Vinylcyclohexene [4 + 2] Product (29)

E(RmPW+HF-PW91) = -807.917235086

```
Zero-point correction=                        0.313918 (Hartree/Particle)
Thermal correction to Energy=                    0.329530
Thermal correction to Enthalpy=                  0.330474
Thermal correction to Gibbs Free Energy=          0.270207
Sum of electronic and zero-point Energies=          -807.603317
Sum of electronic and thermal Energies=            -807.587705
Sum of electronic and thermal Enthalpies=           -807.586761
Sum of electronic and thermal Free Energies=         -807.647029

              E (Thermal)          CV              S
               KCal/Mol      Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total              206.783          60.678          126.845
```

```
C,0,-2.3576556117,0.8865292332,-0.0664799603
C,0,-2.0496541917,-0.1844269045,0.9731603383
C,0,-0.5665671297,0.0511729754,1.3461648585
C,0,-0.1970557386,1.2891626569,0.5797970799
C,0,-1.1706111165,1.7369159482,-0.2101174526
C,0,-2.3328513703,-1.5801501989,0.4126925832
C,0,-1.3362351763,-1.881368935,-0.6598871349
C,0,-0.0454684703,-1.6360980729,-0.4391208222
C,0,0.3119346247,-1.178753808,0.9561750199
C,0,1.8105279768,-0.9796936151,1.2377639015
C,0,2.6723287627,-0.7511944973,0.0063629086
C,0,2.4120772805,-1.8377916345,-1.0204844935
C,0,0.9867853159,-1.7192974766,-1.5298946783
H,0,0.7797314229,1.7385588492,0.6730245271
O,0,-3.4052687977,0.993982833,-0.6530455202
H,0,3.1075707591,-1.7584446211,-1.8553460101
H,0,2.4602220792,0.2220187149,-0.4435649608
H,0,3.7213104244,-0.7364251703,0.3019153496
H,0,2.181353688,-1.8759605332,1.7360440116
H,0,1.9558968824,-0.1677089039,1.9519929548
```

```
H,0,0.9229035812,-0.8037045031,-2.1251597361
H,0,0.7369436844,-2.5381527297,-2.2037265414
H,0,-0.0398592127,-1.952905911,1.6401476325
H,0,2.5753091606,-2.8168359763,-0.5638600591
H,0,-1.6810577634,-2.2120889358,-1.6306995352
H,0,-3.3494621708,-1.5976998148,0.0277657041
H,0,-2.2793988346,-2.3069201864,1.2264187503
C,0,-0.4441638561,0.2217589294,2.8472969479
H,0,-2.6985317936,-0.0018729953,1.8302758581
H,0,-1.1341591711,2.5887264233,-0.8692772257
O,0,-0.0361428261,1.433666348,3.2073850712
O,0,-0.6967828104,-0.6481667418,3.6369496404
C,0,0.0733731002,1.659435126,4.6054965632
H,0,0.4016807777,2.6858528051,4.7120954388
H,0,-0.8883295081,1.5139205167,5.0879041883
H,0,0.796635029,0.9784178062,5.0441088025
```

Vinylcyclohexene [2 + 4] Product (30)

E(RmPW+HF-PW91) = -807.900272691

```
Zero-point correction=                       0.313391 (Hartree/Particle)
Thermal correction to Energy=                0.329308
Thermal correction to Enthalpy=              0.330253
Thermal correction to Gibbs Free Energy=     0.268591
Sum of electronic and zero-point Energies=        -807.586882
Sum of electronic and thermal Energies=           -807.570964
Sum of electronic and thermal Enthalpies=         -807.570020
Sum of electronic and thermal Free Energies=      -807.631682

                E (Thermal)          CV               S
                 KCal/Mol      Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total             206.644          60.758          129.777
```

```
C,0,1.060251,-2.773748,2.281087
C,0,0.209375,-1.568953,2.582545
C,0,-0.738664,-1.607138,3.517875
C,0,-1.036991,-2.803702,4.36784
C,0,0.061511,-3.851609,4.298949
C,0,0.499599,-4.061549,2.860754
C,0,0.514713,-0.365622,1.733939
C,0,0.083435,1.032896,2.245296
C,0,-0.72297,1.640596,1.07107
C,0,0.069411,1.029247,-0.081348
```

C,0,-0.139438,-0.436365,0.307012
C,0,-1.622976,-0.402242,0.467886
C,0,-1.965968,0.817559,0.910618
O,0,0.693019,1.520549,-0.968706
C,0,-3.304755,1.309526,1.246825
O,0,-3.52396,2.403084,1.70239
O,0,-4.258684,0.414712,0.99665
C,0,-5.580022,0.829457,1.297937
H,0,0.95649,1.644361,2.464351
H,0,1.594389,-0.356638,1.56621
H,0,-1.350463,-0.733232,3.696291
H,0,-0.520511,0.992062,3.145744
H,0,1.180662,-2.872677,1.200214
H,0,2.067686,-2.594614,2.670172
H,0,-0.359731,-4.381899,2.267441
H,0,1.242504,-4.855678,2.792342
H,0,-1.990013,-3.238674,4.051504
H,0,-1.190456,-2.483395,5.399514
H,0,-0.280454,-4.786738,4.741245
H,0,0.917711,-3.517142,4.88855
H,0,-2.294528,-1.22395,0.282697
H,0,0.276847,-1.184972,-0.356092
H,0,-5.84574,1.706939,0.715631
H,0,-6.217335,-0.006472,1.036626
H,0,-5.674487,1.06476,2.354155
H,0,-0.850285,2.715308,1.082697

Vinylcyclohexene Transition Structure 24-ax

E(RmPW+HF-PW91) = -807.833642868

```
 Zero-point correction=                           0.307984 (Hartree/Particle)
 Thermal correction to Energy=                    0.324726
 Thermal correction to Enthalpy=                  0.325671
 Thermal correction to Gibbs Free Energy=         0.263212
 Sum of electronic and zero-point Energies=           -807.525659
 Sum of electronic and thermal Energies=              -807.508917
 Sum of electronic and thermal Enthalpies=            -807.507972
 Sum of electronic and thermal Free Energies=         -807.570431

                     E (Thermal)             CV                S
                      KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                  203.769             63.376            131.455
```

```
C,0,-2.7383958184,0.5977760719,-0.3889297561
C,0,-2.5204059947,0.0810631513,1.0156148572
C,0,-1.2978325126,0.5573198375,1.4212234517
C,0,-0.6393760298,1.1802368192,0.2883101485
C,0,-1.4318986215,1.1445694723,-0.8016292873
C,0,-2.299972567,-1.9247566405,0.2618251714
C,0,-1.2755821078,-1.8373459782,-0.6443227706
C,0,0.1116030959,-1.7581399189,-0.3026838019
C,0,0.518767906,-1.7215980571,0.9884637015
C,0,1.9388774017,-1.5503512144,1.4095487674
C,0,2.8439325841,-1.102593047,0.2732316372
C,0,2.5314658211,-1.8825064067,-0.99183871
C,0,1.0994686955,-1.6288783231,-1.4320938671
H,0,0.3532944226,1.5958818136,0.343787189
O,0,-3.7787529341,0.5922111086,-0.9971962108
H,0,3.2190701151,-1.6126472731,-1.7924254492
H,0,2.6915521558,-0.0378925889,0.0848745641
H,0,3.8882212019,-1.2242612316,0.5580156524
H,0,2.292439515,-2.5021582987,1.8199435257
H,0,1.9833469938,-0.8427229711,2.2386454083
H,0,1.0124186296,-0.6272815606,-1.8609971111
H,0,0.8206071,-2.3213158048,-2.2272722531
H,0,-0.1952340235,-1.9039045579,1.7785952231
H,0,2.6716133331,-2.9488718525,-0.8017893359
H,0,-1.5266782303,-1.765116539,-1.6948252673
H,0,-3.3123844878,-2.0274291439,-0.0988927252
H,0,-2.1227906126,-2.2685766344,1.2695517796
C,0,-0.814098157,0.4914452494,2.7922718457
H,0,-3.3295480832,-0.1882391953,1.6738448624
H,0,-1.2298745809,1.5370547154,-1.7827369932
O,0,0.2885497438,1.2242850658,2.9830316341
O,0,-1.3399839794,-0.1420677322,3.6767004972
C,0,0.7794641265,1.2526500173,4.3115467064
H,0,1.6645288851,1.8770352331,4.2858273227
H,0,0.0372217914,1.6756419582,4.9824145842
H,0,1.0283952226,0.2516024561,4.652468009
```

Vinylcyclohexene Transition Structure 24-eq

E(RmPW+HF-PW91) = -807.833158251

```
Zero-point correction=                 0.307780 (Hartree/Particle)
Thermal correction to Energy=              0.324603
Thermal correction to Enthalpy=            0.325547
```

```
Thermal correction to Gibbs Free Energy=        0.262645
Sum of electronic and zero-point Energies=          -807.525379
Sum of electronic and thermal Energies=             -807.508555
Sum of electronic and thermal Enthalpies=           -807.507611
Sum of electronic and thermal Free Energies=        -807.570513

                E (Thermal)           CV               S
                 KCal/Mol       Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total                203.691           63.452           132.388
```

```
C,0,-2.7677704997,0.560649091,-0.380072992
 C,0,-2.5399550484,0.0455575379,1.0241118973
 C,0,-1.3275902504,0.5493220104,1.4319909115
 C,0,-0.6817109571,1.184373649,0.3015487171
 C,0,-1.4716780426,1.1316435555,-0.7908268188
 C,0,-2.2834627762,-1.9439270503,0.2816078733
 C,0,-1.2688520174,-1.8316229018,-0.6344572532
 C,0,0.1203112237,-1.7270329462,-0.3057715409
 C,0,0.5403708817,-1.7093239913,0.9813916676
 C,0,1.96619755,-1.546970581,1.3917059433
 C,0,2.9358098955,-1.7299024854,0.2348209585
 C,0,2.432989934,-1.0013148094,-0.9990245892
 C,0,1.092852163,-1.561992803,-1.4441830996
 H,0,0.3013801334,1.6220525919,0.3574127425
 O,0,-3.8072369001,0.5343237754,-0.9893655174
 H,0,3.1543718074,-1.0749700326,-1.8119785441
 H,0,3.9261789059,-1.3756853844,0.5181409255
 H,0,3.0342438749,-2.7933821718,0.0080566502
 H,0,2.1894896618,-2.2485497257,2.1970689543
 H,0,2.0879527842,-0.5513689316,1.8304781355
 H,0,0.6470807673,-0.918248042,-2.2029746156
 H,0,1.2408326241,-2.5348119174,-1.9206312981
 H,0,-0.1716440481,-1.8790940229,1.7757031053
 H,0,2.3245063564,0.0611720113,-0.7704659574
 H,0,-1.5327873304,-1.754543227,-1.6812402951
 H,0,-3.2960953746,-2.0669417542,-0.0722026861
 H,0,-2.0917214154,-2.2930286969,1.2847849692
 C,0,-0.8350385943,0.4782928499,2.7988265948
 H,0,-3.3450074233,-0.234476691,1.6830866353
 H,0,-1.27580681,1.5292637247,-1.7711028384
 O,0,0.2606027762,1.2220066437,2.9882327502
 O,0,-1.3462915924,-0.1708693172,3.680792661
 C,0,0.7718464577,1.228272252,4.3093378092
 H,0,1.6387815005,1.877771425,4.287312574
```

```
H,0,0.0292812056,1.6109051842,5.0034962435
H,0,1.0549745771,0.2254481813,4.6167823269
```

Vinylcyclohexene Transition Strucutre 24-endo-3

E(RmPW+HF-PW91) = -807.827045631

```
Zero-point correction=                     0.308064 (Hartree/Particle)
Thermal correction to Energy=                0.324650
Thermal correction to Enthalpy=              0.325594
Thermal correction to Gibbs Free Energy=        0.263459
Sum of electronic and zero-point Energies=          -807.518982
Sum of electronic and thermal Energies=            -807.502396
Sum of electronic and thermal Enthalpies=          -807.501452
Sum of electronic and thermal Free Energies=        -807.563587

                E (Thermal)           CV               S
                 KCal/Mol       Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total              203.721          63.177           130.774
```

```
C,0,0.1964219261,2.49997201,-1.3834262666
C,0,-0.5062293955,1.5048644132,-2.2786404025
C,0,-1.2992546125,0.7324006401,-1.4595426889
C,0,-0.9560712188,1.0132876584,-0.0986828238
C,0,0.0209527041,1.9577913984,-0.0217389331
C,0,1.3552835808,0.5945790665,-2.5140824135
C,0,1.8092799885,0.2976346752,-1.2420183499
C,0,1.3912395829,-0.8527960139,-0.4999834424
C,0,0.421476159,-1.6775061436,-0.9605539007
C,0,-0.1148325416,-2.8480043381,-0.2063348127
C,0,0.3355137885,-2.8788375702,1.2458570512
C,0,1.797072031,-2.4858465591,1.3682313634
C,0,2.0096357626,-1.0715810771,0.8552682279
C,0,-1.625449677,0.3374591721,1.0275871944
O,0,-1.150478384,0.7215923261,2.208806373
C,0,-1.8048152717,0.1755664203,3.3415317953
O,0,0.7372563528,3.5230618347,-1.7181077276
O,0,-2.5198792787,-0.4586526157,0.9002860393
H,0,2.1305083769,-2.5599822923,2.4028444329
H,0,-0.2713298847,-2.1810845454,1.824291463
H,0,0.1608071029,-3.8678322091,1.6678401026
H,0,0.205204532,-3.7615655467,-0.7187247826
H,0,-1.2041771032,-2.8431225519,-0.2643318004
H,0,1.5840978766,-0.3512478542,1.5592912053
```

H,0,3.0751385662,-0.8453360243,0.7991753623
H,0,0.044405198,-1.5467714659,-1.9644020922
H,0,2.4099425038,-3.1798108512,0.7886862385
H,0,2.5405227571,0.9512792923,-0.7864894872
H,0,1.8178723046,1.4100870841,-3.049965899
H,0,0.9507165457,-0.1887778297,-3.1358327436
H,0,-2.0703826289,0.0404458335,-1.7501175859
H,0,-0.6953760377,1.7113006844,-3.3197910301
H,0,0.4476535715,2.3905624731,0.864942344
H,0,-1.30626561,0.6022320013,4.2031631558
H,0,-2.856797437,0.4458383893,3.3375697774
H,0,-1.7196306694,-0.9072545884,3.3502471476

Vinylcyclohexene Transition Strucutre 24-endo-4

E(RmPW+HF-PW91) = -807.828230642

```
Zero-point correction=                      0.308080 (Hartree/Particle)
Thermal correction to Energy=                  0.324750
Thermal correction to Enthalpy=                0.325694
Thermal correction to Gibbs Free Energy=        0.263606
Sum of electronic and zero-point Energies=          -807.520151
Sum of electronic and thermal Energies=            -807.503481
Sum of electronic and thermal Enthalpies=           -807.502537
Sum of electronic and thermal Free Energies=         -807.564625

                E (Thermal)           CV              S
                 KCal/Mol       Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total              203.783           63.430          130.676
```

C,0,1.51459,-0.17666,2.49119
C,0,1.29934,-0.23275,1.00374
C,0,0.58017,-1.27526,0.43673
C,0,0.1908,-2.49544,1.22538
C,0,0.30627,-2.33661,2.73509
C,0,1.5584,-1.56518,3.10941
C,0,1.79944,0.814,0.18617
C,0,1.68268,0.85473,-1.16222
C,0,-1.22046,-0.30367,-0.18559
C,0,-1.57365,0.32781,1.13944
C,0,-1.259,1.75642,0.99213
C,0,-0.97473,1.98526,-0.30268
C,0,-0.9565,0.73837,-1.05515
O,0,-2.05911,-0.23364,2.09286

C,0,-0.91449,0.5855,-2.49979
O,0,-0.84351,-0.47739,-3.07329
O,0,-0.96202,1.75558,-3.14462
C,0,-0.93137,1.67649,-4.55817
H,0,1.64568,-1.48322,4.19209
H,0,-0.56836,-1.80936,3.11146
H,0,0.30907,-3.32292,3.19818
H,0,0.85325,-3.29826,0.88801
H,0,-0.81618,-2.8141,0.95821
H,0,0.70927,0.39278,2.96074
H,0,2.43603,0.36983,2.69202
H,0,0.71986,-1.45654,-0.61987
H,0,2.44671,-2.09505,2.75766
H,0,2.20745,1.67753,0.69614
H,0,1.99402,1.73113,-1.7108
H,0,1.43718,-0.01365,-1.75147
H,0,-1.62642,-1.25174,-0.49683
H,0,-0.77222,2.94313,-0.75358
H,0,-1.33424,2.47297,1.79116
H,0,-0.98614,2.69914,-4.91182
H,0,-0.01208,1.20645,-4.89654
H,0,-1.77584,1.10183,-4.9273

Vinylcyclohexene Transition Strucutre 24-endo-5

E(RmPW+HF-PW91) = -807.823231895

```
Zero-point correction=                           0.308317 (Hartree/Particle)
Thermal correction to Energy=                    0.324726
Thermal correction to Enthalpy=                  0.325670
Thermal correction to Gibbs Free Energy=         0.264147
Sum of electronic and zero-point Energies=          -807.514915
Sum of electronic and thermal Energies=             -807.498506
Sum of electronic and thermal Enthalpies=           -807.497561
Sum of electronic and thermal Free Energies=        -807.559085

                E (Thermal)          CV                S
                 KCal/Mol      Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total              203.769           63.069           129.487
```

C,0,1.6828292883,0.0585933669,2.2670618083
C,0,1.3520131816,-0.2694111346,0.8315159484
C,0,0.6821642814,-1.4255539318,0.5115927662
C,0,0.2143602766,-2.4144491574,1.5229412295

```
C,0,0.3369755454,-1.9180859099,2.9558656262
C,0,1.6410777943,-1.1687049775,3.1616054925
C,0,1.6590574981,0.6728292571,-0.1688511696
C,0,1.2622952769,0.5571446097,-1.4829469799
C,0,-1.3307738418,-0.4388644455,-0.7009050248
C,0,-1.8205400193,-0.1115223316,0.6396423194
C,0,-1.4770270468,1.3275517769,0.8471649159
C,0,-0.9747473629,1.8043511886,-0.295422689
C,0,-0.8492531972,0.7092144071,-1.2962766062
O,0,-2.4480112569,-0.8120944193,1.4067183128
H,0,-0.8833872525,0.9080662389,-2.3550251696
H,0,1.7547330272,-0.8712640543,4.2033723352
H,0,-0.5016239107,-1.2577108025,3.1769007581
H,0,0.2598880812,-2.761414483,3.6408077498
H,0,0.7928752111,-3.3335288529,1.3840881459
H,0,-0.8248427031,-2.6749756644,1.3125702394
H,0,0.9856119997,0.8095022629,2.6435562537
H,0,2.6705213847,0.5200762746,2.2971769369
H,0,0.6912346423,-1.7644101627,-0.5126637595
H,0,2.4836385424,-1.8229464536,2.9249931202
H,0,2.0716107087,1.6199638176,0.1573695808
H,0,1.4915011991,1.3603964477,-2.1675006994
H,0,1.1449872554,-0.4115279196,-1.9427112791
H,0,-1.5664456874,-1.3650374318,-1.1969079594
C,0,-0.6021389411,3.2125831086,-0.5064997791
H,0,-1.6612323437,1.8779854488,1.753776036
O,0,-0.2614534458,3.4535752645,-1.7733061159
O,0,-0.6123413821,4.0605372176,0.3464630686
C,0,0.0790060737,4.7983326661,-2.068157075
H,0,0.3171658943,4.8179513951,-3.1246217077
H,0,-0.7577142294,5.4566237009,-1.8539554987
H,0,0.9346854584,5.112408683,-1.4774911312
```

Vinylcyclohexene Transition Strucutre 24-endo-6

E(RmPW+HF-PW91) = -807.825710863

```
Zero-point correction=                       0.308099 (Hartree/Particle)
Thermal correction to Energy=                0.324708
Thermal correction to Enthalpy=              0.325652
Thermal correction to Gibbs Free Energy=     0.263304
Sum of electronic and zero-point Energies=     -807.517612
Sum of electronic and thermal Energies=        -807.501003
Sum of electronic and thermal Enthalpies=      -807.500059
```

Sum of electronic and thermal Free Energies= -807.562407

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	203.757	63.182	131.223

```
C,0,1.1111911938,-1.5955408623,-1.5215518857
C,0,0.1778196573,-1.6537815579,-0.3413409274
C,0,0.6463493975,-1.6714137059,0.9241870901
C,0,2.0983156632,-1.6716780806,1.2765162072
C,0,2.9823315402,-2.0127564604,0.0871683075
C,0,2.5393511391,-1.2398116863,-1.1424808153
C,0,-1.2331738095,-1.6492766903,-0.6264257115
C,0,-2.2150694604,-1.8030583732,0.336122319
C,0,-2.582657489,0.1121507276,1.1091095628
C,0,-2.7906821964,0.5157605258,-0.3328632239
C,0,-1.4549438004,0.9586995791,-0.7798055164
C,0,-0.7153363825,1.1702704897,0.3458388848
C,0,-1.39097284,0.6769255148,1.5039256722
O,0,-3.825481899,0.5074416166,-0.9480884032
H,0,-0.9993856312,0.7334749257,2.5044701359
C,0,0.6161007358,1.8016950378,0.335033024
H,0,3.203457303,-1.4402053335,-1.9825360929
H,0,4.0247851967,-1.8008491367,0.3230438737
H,0,2.9162229543,-3.083982864,-0.1146682229
H,0,2.2691791536,-2.3731591411,2.0950674865
H,0,2.368176788,-0.6887923042,1.6752752127
H,0,0.7264969975,-0.8717393764,-2.2409362153
H,0,1.0879494966,-2.5659136137,-2.0252782622
H,0,-0.0495201008,-1.7316224845,1.7487679975
H,0,2.6008874605,-0.1691056396,-0.9441064842
H,0,-1.530849322,-1.6104924932,-1.6651966549
H,0,-3.2316130015,-1.9720683651,0.0137069233
H,0,-1.965390313,-2.2191604424,1.2993678418
H,0,-3.4066835516,-0.1357811859,1.7586380255
H,0,-1.2129241565,1.2702515934,-1.7802338758
O,0,1.2185109966,2.1074761138,-0.660699836
O,0,1.0798562708,2.0171674072,1.5644510838
C,0,2.3344997484,2.672369814,1.6400375571
H,0,2.5487982821,2.7781263384,2.696506966
H,0,3.1045212795,2.0817686904,1.1520112132
H,0,2.2831006992,3.6466024229,1.1626827428
```

Vinylcyclohexene Transition Strucutre 24-endo-7

E(RmPW+HF-PW91) = -807.827744820

```
Zero-point correction=                      0.308324 (Hartree/Particle)
Thermal correction to Energy=                   0.324878
Thermal correction to Enthalpy=                 0.325822
Thermal correction to Gibbs Free Energy=        0.264406
Sum of electronic and zero-point Energies=          -807.519421
Sum of electronic and thermal Energies=             -807.502867
Sum of electronic and thermal Enthalpies=           -807.501923
Sum of electronic and thermal Free Energies=        -807.563339

                E (Thermal)          CV              S
                 KCal/Mol      Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total              203.864           63.327         129.261
```

```
C,0,-1.1836275577,1.104999824,-1.2943055058
C,0,-0.0204196814,1.7782362234,-1.3442742345
C,0,0.5579303392,1.776829486,0.0102212675
C,0,-0.2693324762,0.7997231578,0.8012352242
C,0,-1.3725561927,0.5018517438,0.0184581534
O,0,1.4641886195,2.4545070465,0.4356301766
O,0,-2.6963325377,-0.5965510464,1.6346643631
C,0,-2.6000906701,-0.0693902441,0.5505805481
O,0,-3.630777962,0.0500317713,-0.2922429457
C,0,-4.8625950647,-0.4738576659,0.1700887102
C,0,-0.8735639627,-1.8481423033,-0.9274799531
C,0,0.3495179992,-1.4945504412,-1.3937596053
C,0,1.39148517,-0.9784832048,-0.5849299157
C,0,1.1755746872,-0.767366249,0.7722687743
C,0,2.2870081573,-0.3284546966,1.6889511351
C,0,3.6611769377,-0.548327106,1.0723846654
C,0,3.701175044,0.0452378935,-0.3243541537
C,0,2.7124383082,-0.6655366289,-1.2353425641
H,0,-5.5780662637,-0.2867126667,-0.621703326
H,0,-5.1703660922,0.0244377455,1.0847537091
H,0,-4.7787755171,-1.5399489215,0.3621656461
H,0,-1.8943738007,0.9939672611,-2.096902413
H,0,0.3961809258,2.321656703,-2.1742170475
H,0,-0.2875746889,0.8034335477,1.8786450835
H,0,-1.0655273316,-2.0396459867,0.115644279
H,0,-1.6581935335,-2.1285794859,-1.614523725
H,0,0.5132854346,-1.4908964581,-2.4640799926
H,0,0.3892295025,-1.34576611,1.2351897906
```

H,0,2.1795250653,0.7337993721,1.914345262
H,0,2.1957674373,-0.8622224681,2.6343858034
H,0,3.8846815024,-1.6168701092,1.0282740899
H,0,4.4211801242,-0.0908645103,1.7043055206
H,0,3.4568235947,1.1051019273,-0.265106176
H,0,4.7013556638,-0.0296178239,-0.7495452539
H,0,3.1370322522,-1.6225279666,-1.5544397155
H,0,2.5490575678,-0.0943606098,-2.1491726747

Vinylcyclohexene Transition Strucutre 24-endo-8

E(RmPW+HF-PW91) = -807.823713369

```
Zero-point correction=                           0.308528 (Hartree/Particle)
Thermal correction to Energy=                    0.324857
Thermal correction to Enthalpy=                  0.325802
Thermal correction to Gibbs Free Energy=         0.264478
Sum of electronic and zero-point Energies=       -807.515185
Sum of electronic and thermal Energies=          -807.498856
Sum of electronic and thermal Enthalpies=        -807.497912
Sum of electronic and thermal Free Energies=     -807.559235

                 E (Thermal)        CV               S
                  KCal/Mol     Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total              203.851          62.898          129.066
```

C,0,-1.1341650109,1.1079906614,-1.1828208682
C,0,-0.0412714571,1.8374156505,-0.9389495569
C,0,0.2833582156,1.7190353938,0.5132200786
C,0,-0.6655167747,0.7467074615,1.047649685
C,0,-1.5431804137,0.374511999,0.0466381462
O,0,1.1251688457,2.363521348,1.1092523706
C,0,-1.143209873,-1.6141741918,-0.5197462
C,0,0.0623487051,-1.4708579717,-1.1743904194
C,0,1.2579281893,-1.0794453016,-0.5429958438
C,0,1.2979589994,-0.9196387959,0.8215979411
C,0,2.4851055783,-0.4028173983,1.5559315595
C,0,3.7545672135,-0.4301388288,0.7165301358
C,0,3.478209489,0.1128033122,-0.6746930386
C,0,2.4597907488,-0.7554358796,-1.3952405884
C,0,-1.80712179,1.0453194765,-2.4898719838
H,0,0.497074387,2.4518546495,-1.6400684432
H,0,-0.7785916738,0.5569563377,2.1013573195
H,0,-1.1809025634,-1.9296604211,0.511167311

H,0,-2.0198238123,-1.8607606049,-1.100450175
H,0,0.0543272084,-1.4699356918,-2.2574168838
H,0,0.5132472393,-1.3578423832,1.4170782773
H,0,2.2743011869,0.6325802593,1.8511835958
H,0,2.6130943844,-0.9640689876,2.4820964125
H,0,4.1262374859,-1.454496756,0.6397180768
H,0,4.5312369277,0.1529083326,1.2091648107
H,0,3.0999834274,1.1326460934,-0.588458959
H,0,4.3965386742,0.1621771457,-1.2588181802
H,0,2.9306189877,-1.6972296813,-1.6907258077
H,0,2.1352529489,-0.2753161169,-2.3180294306
O,0,-2.9441791003,0.3499360143,-2.4333600131
O,0,-1.401283355,1.5641990697,-3.4963567842
C,0,-3.6709032287,0.2700434265,-3.6486197195
H,0,-4.5552415909,-0.3144917666,-3.4262103245
H,0,-3.9467155299,1.2630378006,-3.9909838451
H,0,-3.0754356343,-0.2147000659,-4.4168432554
H,0,-2.5689640344,0.0886094107,0.2147356

Vinylcyclohexene Transition Strucutre 24-exo-1

E(RmPW+HF-PW91) = -807.825207283

```
Zero-point correction=                        0.307725 (Hartree/Particle)
Thermal correction to Energy=                  0.324497
Thermal correction to Enthalpy=                0.325441
Thermal correction to Gibbs Free Energy=       0.263105
Sum of electronic and zero-point Energies=         -807.517482
Sum of electronic and thermal Energies=            -807.500710
Sum of electronic and thermal Enthalpies=          -807.499766
Sum of electronic and thermal Free Energies=       -807.562102

                 E (Thermal)          CV               S
                  KCal/Mol       Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total              203.625           63.475          131.198
```

C,0,-3.22124,-0.20023,0.13648
C,0,-1.9841,-0.08591,-0.73556
C,0,-1.12825,0.76687,-0.07241
C,0,-1.68084,1.05136,1.2548
C,0,-2.87692,0.4623,1.41328
C,0,0.80834,-0.94006,1.00157
C,0,0.96124,-1.61368,-0.1712
C,0,-0.15498,-2.18718,-0.83546

```
C,0,-1.45058,-2.10592,-0.39718
C,0,2.29899,-1.66734,-0.86055
C,0,3.45095,-1.37484,0.0852
C,0,3.17664,-0.10346,0.86907
C,0,1.92255,-0.25228,1.71588
C,0,-0.03091,1.45505,-0.72437
O,0,0.49551,2.42281,0.04271
C,0,1.47164,3.23374,-0.58321
O,0,-4.26516,-0.70746,-0.18253
O,0,0.35763,1.22794,-1.84692
H,0,-2.03718,-0.17342,-1.80688
H,0,-2.23856,-2.57272,-0.9688
H,0,-1.66068,-1.99036,0.65874
H,0,0.02339,-2.59619,-1.82242
H,0,-0.12602,-1.01313,1.53848
H,0,1.57937,0.72132,2.06893
H,0,2.14621,-0.82891,2.61998
H,0,3.04517,0.72106,0.16762
H,0,4.02329,0.15494,1.50394
H,0,2.4237,-2.64867,-1.31928
H,0,4.37964,-1.28589,-0.47702
H,0,3.57905,-2.20972,0.77802
H,0,-1.16992,1.66104,1.98275
H,0,-3.52179,0.47857,2.27399
H,0,1.03958,3.76418,-1.42752
H,0,1.80276,3.93609,0.17266
H,0,2.30625,2.6367,-0.93859
H,0,2.29526,-0.94244,-1.67828
```

Vinylcyclohexene Transition Strucutre 24-exo-2

E(RmPW+HF-PW91) = -807.816281791

```
Zero-point correction=                          0.307844 (Hartree/Particle)
Thermal correction to Energy=                   0.324481
Thermal correction to Enthalpy=                 0.325425
Thermal correction to Gibbs Free Energy=        0.262846
Sum of electronic and zero-point Energies=      -807.508438
Sum of electronic and thermal Energies=         -807.491801
Sum of electronic and thermal Enthalpies=       -807.490857
Sum of electronic and thermal Free Energies=    -807.553436

                  E (Thermal)        CV               S
                   KCal/Mol     Cal/Mol-Kelvin   Cal/Mol-Kelvin
```

Total	203.615	63.245	131.708

C,0,-0.0326366823,1.3537116023,-2.5942181824
C,0,0.0390471865,1.8338216824,-1.1704424891
C,0,-0.6909199392,0.9425011454,-0.4076725459
C,0,-1.0753058298,-0.1781343444,-1.2747831296
C,0,-0.6470415457,0.0022986027,-2.5367729332
C,0,2.0928086353,1.3636984624,-1.0417459815
C,0,2.3819316005,1.5784963338,0.2858016591
C,0,1.8160285823,0.829712539,1.3348646798
C,0,1.011810028,-0.2514638374,1.075578921
C,0,0.324578796,-1.0331225333,2.1487594844
C,0,0.2649583843,-0.295925821,3.4759026103
C,0,1.6119172024,0.3241782766,3.8004222765
C,0,1.9841710531,1.3474720597,2.742221085
C,0,-1.8947588011,-1.3094335971,-0.7973150604
O,0,-2.0289080751,-2.2654637363,-1.7070390401
C,0,-2.8423228662,-3.3647732686,-1.3303082319
O,0,0.3042825489,1.9548199222,-3.5818126045
O,0,-2.4047105349,-1.3524810288,0.2932487258
H,0,1.5983735477,0.7942617831,4.7831913921
H,0,-0.4914096319,0.4905194027,3.4240095042
H,0,-0.0504454628,-0.9796737577,4.2630275559
H,0,0.8690721558,-1.9754080767,2.2767250722
H,0,-0.6755304275,-1.3116557238,1.8207023098
H,0,1.3641114348,2.2397570581,2.8683647201
H,0,3.0150411579,1.6777000236,2.8743834159
H,0,1.0831827152,-0.7301705831,0.1094854818
H,0,2.3715141526,-0.4601368469,3.8348222958
H,0,2.9122560412,2.4850980001,0.5514749981
H,0,2.5063004811,2.0254324999,-1.7890744206
H,0,1.8811699745,0.3632360533,-1.4005931369
H,0,-1.1584184035,1.1306365281,0.541238972
H,0,0.1482695348,2.8834067422,-0.9599426213
H,0,-0.7707659293,-0.6520620364,-3.3806230279
H,0,-3.8503564581,-3.0302634134,-1.1036828423
H,0,-2.8453078407,-4.0325187565,-2.1827574861
H,0,-2.4289074228,-3.8623717287,-0.4579145052

Vinylcyclohexene Transition Strucutre 24-exo-3

E(RmPW+HF-PW91) = -807.824671615

Zero-point correction= 0.307763 (Hartree/Particle)

```
Thermal correction to Energy=                    0.324395
Thermal correction to Enthalpy=                  0.325339
Thermal correction to Gibbs Free Energy=         0.263558
Sum of electronic and zero-point Energies=          -807.516908
Sum of electronic and thermal Energies=             -807.500276
Sum of electronic and thermal Enthalpies=           -807.499332
Sum of electronic and thermal Free Energies=        -807.561114

                E (Thermal)         CV              S
                 KCal/Mol      Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total             203.561           63.474          130.030

C,0,-1.6218715473,-1.2702424272,-1.3058744741
C,0,-1.034907089,-0.3328141785,-0.2756579537
C,0,-0.6423752927,0.7943519191,-0.9751211219
C,0,-0.8234226622,0.5502937157,-2.4134202621
C,0,-1.3378883757,-0.668876043,-2.6262346887
C,0,1.874616459,0.5881906675,-1.1545416626
C,0,2.0646585487,0.3797811044,0.1734321134
C,0,1.4607330024,-0.6664392804,0.9056704163
C,0,0.6487546606,-1.5949301648,0.2756279279
C,0,0.0483639932,-2.7513908937,1.0188925657
C,0,-0.0832189337,-2.4953064572,2.5098877951
C,0,1.2121098102,-1.9390648896,3.0728885382
C,0,1.5523760246,-0.6183836847,2.4048830151
C,0,-0.4563497668,2.086134778,-0.3350892665
O,0,-0.3823442903,3.0927407245,-1.2145106687
C,0,-0.2152301329,4.3814836005,-0.6539219274
O,0,-2.2437342111,-2.2789779085,-1.0782411906
O,0,-0.3854600418,2.2525314343,0.8599773291
H,0,1.1384756671,-1.7980386758,4.1505339024
H,0,-0.8923822043,-1.7850048154,2.6943300567
H,0,-0.3619917691,-3.4189136102,3.0154841182
H,0,0.6978422077,-3.6161950046,0.8519633119
H,0,-0.9125749873,-3.0143295391,0.5787636679
H,0,0.8670869277,0.1595765646,2.7546435352
H,0,2.5514250324,-0.2858868676,2.6881240347
H,0,0.820069903,-1.7664611308,-0.7810930467
H,0,2.0178275722,-2.6565389598,2.9022040268
H,0,2.5771682397,1.1426180998,0.7452605036
H,0,2.270754162,1.4726732342,-1.6313324956
H,0,1.5149230209,-0.181855772,-1.8171577631
H,0,-1.4026751387,-0.3069660365,0.7359379592
H,0,-0.5577940365,1.2765218604,-3.1646423321
```

H,0,-1.566961858,-1.1451934939,-3.5630771703
H,0,0.7174069721,4.4406964039,-0.0992647588
H,0,-0.2007673849,5.0687111553,-1.4915568461
H,0,-1.0368402899,4.6175624988,0.0161292842

Vinylcyclohexene Transition Strucutre 24-exo-4

E(RmPW+HF-PW91) = -807.817632517

Zero-point correction= 0.307943 (Hartree/Particle)
Thermal correction to Energy= 0.324475
Thermal correction to Enthalpy= 0.325419
Thermal correction to Gibbs Free Energy= 0.263311
Sum of electronic and zero-point Energies= -807.509690
Sum of electronic and thermal Energies= -807.493158
Sum of electronic and thermal Enthalpies= -807.492214
Sum of electronic and thermal Free Energies= -807.554321

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	203.611	63.197	130.717

C,0,0.0943679113,2.33034367,-0.4811930639
C,0,-0.1932098609,0.902957826,-0.7195591087
C,0,-1.3782155782,0.5943307054,-0.0817642344
C,0,-1.8371629551,1.8242226958,0.6266085588
C,0,-0.9630511917,2.8199057843,0.4554290812
C,0,-0.9328884254,-0.6200919539,1.7170494428
C,0,-0.0017233334,-1.5197692746,1.2632310566
C,0,1.2520841523,-1.1506362102,0.7447026503
C,0,1.6201350625,0.174469342,0.7004832324
C,0,2.8886387519,0.6528109161,0.0791840733
C,0,3.5183723984,-0.3730115933,-0.8475510649
C,0,3.5118697522,-1.7483775399,-0.2032334365
C,0,2.0853251167,-2.2014481771,0.0558860521
H,0,-2.074186861,-0.1601537,-0.4024185838
O,0,0.973318917,3.0046388337,-0.9681430428
H,0,4.0227065987,-2.4755592464,-0.8334542294
H,0,2.9601571789,-0.4109005505,-1.7857012825
H,0,4.5319663338,-0.0664162417,-1.1021008637
H,0,3.5831272011,0.8996628308,0.8890253826
H,0,2.70314642,1.5938161018,-0.4421500702
H,0,1.6123884629,-2.4642563579,-0.8954680751
H,0,2.0751436974,-3.1113577241,0.6568320988

```
H,0,1.1478167618,0.8646491039,1.3873393048
H,0,4.0598155779,-1.7074690178,0.7408069862
H,0,-0.3099628861,-2.5496010598,1.1246980734
H,0,-1.9089479932,-0.9682120223,2.0200839302
H,0,-0.6237200543,0.3136237648,2.1620945915
H,0,0.2488658241,0.3633892557,-1.5377343939
C,0,-3.0758160097,1.9524418688,1.4177821019
H,0,-1.0095118916,3.8119162627,0.8696169479
O,0,-3.3800553682,2.9241154964,2.0569577719
O,0,-3.837013722,0.863261788,1.3298538058
C,0,-5.065240114,0.9179375969,2.0377412114
H,0,-5.5557885302,-0.0294371067,1.8512013891
H,0,-4.8851066436,1.0530465287,3.1002517
H,0,-5.6741937005,1.7409084049,1.6754600067
```

Vinylcyclohexene Transition Strucutre 24-exo-5

E(RmPW+HF-PW91) = -807.824368212

```
Zero-point correction=                           0.307648 (Hartree/Particle)
Thermal correction to Energy=                    0.324513
Thermal correction to Enthalpy=                  0.325457
Thermal correction to Gibbs Free Energy=         0.262643
Sum of electronic and zero-point Energies=          -807.516720
Sum of electronic and thermal Energies=             -807.499856
Sum of electronic and thermal Enthalpies=           -807.498912
Sum of electronic and thermal Free Energies=        -807.561725

                E (Thermal)             CV                S
                 KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total             203.635             63.514          132.203
```

```
O,0,-4.344954746,-0.7704197,-0.0602063025
C,0,-3.3011108856,-0.2427532932,0.2238164839
C,0,-2.1003447525,-0.0951358312,-0.696068327
C,0,-1.2400111635,0.7752776415,-0.0589538542
C,0,-1.7447469449,1.0330552956,1.2909312298
C,0,-2.9204643985,0.4150014033,1.491472315
C,0,-0.1727318052,1.4803955833,-0.7380949631
O,0,0.1782076169,1.2761940813,-1.8775718173
O,0,0.3793159429,2.434835431,0.0296034483
C,0,1.3373050441,3.2557751609,-0.6114804343
C,0,-1.5145920853,-2.089106501,-0.4088795786
C,0,-0.2380929952,-2.1429840009,-0.9076725806
```

```
C,0,0.90167238,-1.5700637556,-0.2829174303
C,0,0.7922284192,-0.9253480254,0.9104090195
C,0,1.9306406078,-0.2460805697,1.5960829315
C,0,3.2801883446,-0.6182452409,1.0011734043
C,0,3.216540236,-0.5970049011,-0.5156518847
C,0,2.2097385385,-1.6116649912,-1.0294362396
H,0,-2.1989729245,-0.1664556493,-1.7654940927
H,0,-3.5300657871,0.4087852654,2.3776114436
H,0,-1.2185146559,1.6468543498,2.0044004406
H,0,0.897881571,3.753770756,-1.4712118703
H,0,1.6461689527,3.9840737239,0.129224972
H,0,2.1902102288,2.6720510144,-0.9456452896
H,0,-2.3183418457,-2.5603894864,-0.9543111767
H,0,-1.6772927073,-2.006218772,0.65852864
H,0,-0.1027860994,-2.5248941728,-1.9119622407
H,0,-0.1332155302,-0.9874094272,1.4627074892
H,0,1.7772501446,0.8355243938,1.531305845
H,0,1.8987225329,-0.4824731858,2.6609450956
H,0,4.0481694667,0.0621738661,1.3672325469
H,0,3.560820424,-1.6190303294,1.3358045113
H,0,2.9224742211,0.3971882579,-0.8552423103
H,0,4.1968888171,-0.7991377838,-0.9455276481
H,0,2.019508461,-1.4431449541,-2.0889559421
H,0,2.6256003769,-2.6194126531,-0.9458698338
```

Vinylcyclohexene Transition Strucutre 24-exo-6

E(RmPW+HF-PW91) = -807.824368212

```
Zero-point correction=                     0.307648 (Hartree/Particle)
Thermal correction to Energy=              0.324513
Thermal correction to Enthalpy=            0.325457
Thermal correction to Gibbs Free Energy=   0.262643
Sum of electronic and zero-point Energies=        -807.516720
Sum of electronic and thermal Energies=           -807.499856
Sum of electronic and thermal Enthalpies=         -807.498912
Sum of electronic and thermal Free Energies=      -807.561725

              E (Thermal)         CV              S
               KCal/Mol     Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total           203.635          63.514          132.203
```

```
O,0,-4.344954746,-0.7704197,-0.0602063025
C,0,-3.3011108856,-0.2427532932,0.2238164839
```

```
C,0,-2.1003447525,-0.0951358312,-0.696068327
C,0,-1.2400111635,0.7752776415,-0.0589538542
C,0,-1.7447469449,1.0330552956,1.2909312298
C,0,-2.9204643985,0.4150014033,1.491472315
C,0,-0.1727318052,1.4803955833,-0.7380949631
O,0,0.1782076169,1.2761940813,-1.8775718173
O,0,0.3793159429,2.434835431,0.0296034483
C,0,1.3373050441,3.2557751609,-0.6114804343
C,0,-1.5145920853,-2.089106501,-0.4088795786
C,0,-0.2380929952,-2.1429840009,-0.9076725806
C,0,0.90167238,-1.5700637556,-0.2829174303
C,0,0.7922284192,-0.9253480254,0.9104090195
C,0,1.9306406078,-0.2460805697,1.5960829315
C,0,3.2801883446,-0.6182452409,1.0011734043
C,0,3.216540236,-0.5970049011,-0.5156518847
C,0,2.2097385385,-1.6116649912,-1.0294362396
H,0,-2.1989729245,-0.1664556493,-1.7654940927
H,0,-3.5300657871,0.4087852654,2.3776114436
H,0,-1.2185146559,1.6468543498,2.0044004406
H,0,0.897881571,3.753770756,-1.4712118703
H,0,1.6461689527,3.9840737239,0.129224972
H,0,2.1902102288,2.6720510144,-0.9456452896
H,0,-2.3183418457,-2.5603894864,-0.9543111767
H,0,-1.6772927073,-2.006218772,0.65852864
H,0,-0.1027860994,-2.5248941728,-1.9119622407
H,0,-0.1332155302,-0.9874094272,1.4627074892
H,0,1.7772501446,0.8355243938,1.531305845
H,0,1.8987225329,-0.4824731858,2.6609450956
H,0,4.0481694667,0.0621738661,1.3672325469
H,0,3.560820424,-1.6190303294,1.3358045113
H,0,2.9224742211,0.3971882579,-0.8552423103
H,0,4.1968888171,-0.7991377838,-0.9455276481
H,0,2.019508461,-1.4431449541,-2.0889559421
H,0,2.6256003769,-2.6194126531,-0.9458698338
```

Vinylcyclohexene Transition Strucutre 24-exo-7

E(RmPW+HF-PW91) = -807.821392510

```
Zero-point correction=                     0.307973 (Hartree/Particle)
Thermal correction to Energy=                  0.324632
Thermal correction to Enthalpy=                0.325576
Thermal correction to Gibbs Free Energy=       0.263614
Sum of electronic and zero-point Energies=        -807.513419
```

```
Sum of electronic and thermal Energies=           -807.496760
Sum of electronic and thermal Enthalpies=          -807.495816
Sum of electronic and thermal Free Energies=        -807.557778

                E (Thermal)          CV              S
                 KCal/Mol      Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total              203.710          63.405        130.410

C,0,0.2420962243,2.3264529677,-0.4044743079
C,0,0.0220391265,0.8464169006,-0.6117282808
C,0,-1.2399556726,0.5787392039,-0.1045746189
C,0,-1.7447557278,1.7863089896,0.5654814078
C,0,-0.866305329,2.7929027866,0.4568937849
C,0,-0.8433347986,-0.638470094,2.0268827103
C,0,0.0617331111,-1.5141048743,1.5145129598
C,0,1.2582218949,-1.1240838656,0.8773520276
C,0,1.575625158,0.219802239,0.7479639297
C,0,2.8859794907,0.6813479014,0.1662412636
C,0,3.8470823716,-0.4642742421,-0.115168117
C,0,3.1135729763,-1.6257915571,-0.7588584077
C,0,2.0806793219,-2.1863050238,0.2029620373
C,0,-2.0376443317,-0.5513640349,-0.5540696852
O,0,-3.3227237142,-0.450329548,-0.1903748869
C,0,-4.1612027645,-1.5094244487,-0.6126178783
O,0,1.1190133046,2.9907794955,-0.8985147617
O,0,-1.6094444024,-1.4810580327,-1.1959357727
H,0,3.8074572289,-2.4126590092,-1.0515371524
H,0,4.6572387123,-0.1126207925,-0.7523564041
H,0,4.3041949116,-0.8043991968,0.8167811856
H,0,3.3376132498,1.3932142792,0.8568911155
H,0,2.704130519,1.2529028536,-0.7446124529
H,0,1.4134517235,-2.8798026141,-0.3092327765
H,0,2.5855750345,-2.7682602386,0.979695916
H,0,1.1284006659,0.8965189992,1.4666131085
H,0,2.6229376186,-1.2860402381,-1.6730165405
H,0,-0.2185644591,-2.5565158086,1.4377735351
H,0,-1.7985305555,-0.9897428529,2.3884306263
H,0,-0.5816652551,0.3705823616,2.3016238378
H,0,0.441901151,0.3320942733,-1.4589203235
H,0,-2.6958712203,1.8159121131,1.0723983524
H,0,-0.9394017466,3.7905518409,0.8525767412
H,0,-3.8357256733,-2.4523475936,-0.1813857614
H,0,-5.1551374731,-1.2572760502,-0.2623680368
H,0,-4.1516546712,-1.5977200894,-1.6951303744
```

Vinylcyclohexene Transition Strucutre 24-exo-8

E(RmPW+HF-PW91) = -806.472415852

Zero-point correction= 0.281097 (Hartree/Particle)
Thermal correction to Energy= 0.297289
Thermal correction to Enthalpy= 0.298234
Thermal correction to Gibbs Free Energy= 0.236552
Sum of electronic and zero-point Energies= -806.191318
Sum of electronic and thermal Energies= -806.175126
Sum of electronic and thermal Enthalpies= -806.174182
Sum of electronic and thermal Free Energies= -806.235864

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	186.552	61.983	129.820

C,0,2.1760504119,-2.2002225807,0.269010248
C,0,1.294731742,-1.1491606349,0.894276942
C,0,1.6466358644,0.1803768687,0.8326229691
C,0,2.9271014651,0.6789726911,0.2496926225
C,0,3.8920805918,-0.4369607181,-0.1275978573
C,0,3.1523618112,-1.6137125888,-0.7376319656
C,0,0.0343493102,-1.5163325449,1.3957161459
C,0,-0.9107839119,-0.6102214092,1.8184521961
C,0,-0.1921323329,0.7989595277,-0.6645644991
C,0,0.1260374709,2.2254036039,-0.5282142169
C,0,-0.8915478404,2.7893715375,0.416595431
C,0,-1.7745257415,1.8194776011,0.6781566862
C,0,-1.3598116777,0.539714925,0.0285397585
O,0,0.9949732172,2.8582036709,-1.0838548989
H,0,-2.0846102441,-0.2016514,-0.2587116389
H,0,3.8533079419,-2.3816357823,-1.06252881
H,0,4.6461693844,-0.05476344,-0.813774536
H,0,4.4230248674,-0.7788198814,0.7631461006
H,0,3.3929904353,1.361194838,0.9621112894
H,0,2.6940712136,1.3033189958,-0.6183587654
H,0,1.5566841953,-2.9653411512,-0.1997780625
H,0,2.7359708082,-2.7068640377,1.0595204595
H,0,1.1125343402,0.8818648938,1.4580605794
H,0,2.6123242276,-1.2841481361,-1.6278319765
H,0,-0.2697134057,-2.5482380281,1.2681068638
H,0,-1.8844593458,-0.9660545851,2.1210233216

```
H,0,-0.6079860641,0.3191286104,2.2782267227
H,0,0.2354611751,0.1907488699,-1.4404509204
C,0,-2.9728149779,2.0296626123,1.4932321106
H,0,-0.9084119951,3.8062027308,0.7693122891
O,0,-3.2569106126,2.9905075442,2.1233340647
O,0,-3.7928480344,0.8850445381,1.4923652927
C,0,-5.0879010102,1.0698603951,1.4591960366
H,0,-5.4602272791,0.0307804644,1.5423980176
```

Vinylcyclohexene [2+4] Transition State - High Energy example

E(RmPW+HF-PW91) = -807.826303597

```
Zero-point correction=                      0.307815 (Hartree/Particle)
Thermal correction to Energy=                  0.324665
Thermal correction to Enthalpy=                0.325609
Thermal correction to Gibbs Free Energy=         0.261954
Sum of electronic and zero-point Energies=         -807.518488
Sum of electronic and thermal Energies=           -807.501639
Sum of electronic and thermal Enthalpies=          -807.500694
Sum of electronic and thermal Free Energies=        -807.564350

                E (Thermal)          CV              S
                 KCal/Mol      Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total              203.730          63.256          133.974
```

```
C,0,0.4729421192,2.9572147824,1.1648959354
C,0,1.8143375244,2.4858785137,0.6726761262
C,0,2.4797628268,3.1494383776,-0.2892624231
C,0,2.0015407542,4.4061643663,-0.9326158638
C,0,0.8419076976,5.0358177488,-0.1775946499
C,0,-0.1629895061,3.9718399807,0.2280583509
C,0,2.4257798076,1.3268472475,1.2821408234
C,0,1.5053891282,-0.5943301078,-0.3831419914
C,0,0.1790452276,-0.381606243,-0.1778373262
C,0,-0.1746767604,-0.6743582967,1.1779595195
C,0,0.9714824593,-1.0068694347,1.8765160257
C,0,1.9617079922,0.6916059282,2.4237804024
C,0,2.0408141204,-1.2439854437,0.8274836305
C,0,-1.4841679091,-0.5321053829,1.793766696
O,0,-2.4384481042,-0.2447682826,0.9014769787
C,0,-3.745754893,-0.1116885415,1.4288654094
O,0,3.0676173054,-1.8543056776,0.9760256841
O,0,-1.706125696,-0.6498056408,2.9752848304
```

H,0,2.0558518188,-0.4864706622,-1.301180321
H,0,0.9743957148,-1.5016148523,2.8339378924
H,0,3.397021893,1.0407902025,0.9008458928
H,0,2.6794689898,0.1260326559,2.9997830417
H,0,1.1553183688,1.1301863175,2.9923180336
H,0,3.4294060729,2.7521704006,-0.6276525311
H,0,2.8325157824,5.1085422187,-1.0185240829
H,0,1.703449641,4.1837419657,-1.9628331771
H,0,1.220040816,5.5325964295,0.7181293821
H,0,0.3692658574,5.8038290429,-0.7884177902
H,0,-1.0308982199,4.4224114871,0.7078465001
H,0,-0.5270484554,3.4613489933,-0.6661210365
H,0,0.5910808269,3.3941174754,2.1605672708
H,0,-0.1894620429,2.100925878,1.2885650969
H,0,-0.5226673672,-0.013898168,-0.9086196329
H,0,-4.3838799857,0.114525193,0.5830618036
H,0,-4.0606370557,-1.0356957549,1.9053285861
H,0,-3.7841427491,0.6908022833,2.1601399135

Vinylcyclohexene Ridge Structure 41

E(RmPW+HF-PW91) = -807.832060986

```
Zero-point correction=                    0.307956 (Hartree/Particle)
Thermal correction to Energy=                0.324671
Thermal correction to Enthalpy=              0.325615
Thermal correction to Gibbs Free Energy=        0.263455
Sum of electronic and zero-point Energies=         -807.524105
Sum of electronic and thermal Energies=            -807.507390
Sum of electronic and thermal Enthalpies=          -807.506446
Sum of electronic and thermal Free Energies=        -807.568606

                E (Thermal)          CV              S
                 KCal/Mol       Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total              203.734            63.454          130.826
```

C,0,-2.3292798816,-1.533185926,-0.5703512115
C,0,-2.1079521591,-0.3844162918,0.3828858398
C,0,-1.2376214396,0.4791737928,-0.2303634157
C,0,-0.780222991,-0.1273314946,-1.4796127365
C,0,-1.3613228974,-1.3238974889,-1.6681008767
C,0,-0.9978792793,-1.6523718744,1.8269234432
C,0,0.0623708083,-2.1000961178,1.0909520442
C,0,1.1488772745,-1.2845199592,0.6593776778

```
C,0,1.1755639349,0.0460202087,0.9338040765
C,0,2.2488263695,0.9652577501,0.4509755127
C,0,3.1001808958,0.3609905371,-0.653583438
C,0,3.4588664932,-1.0765978207,-0.3225206889
C,0,2.201997693,-1.9221247653,-0.2092315042
H,0,-0.0721943181,0.3504608687,-2.1367994845
O,0,-3.1639673529,-2.3964532477,-0.4655076928
H,0,4.1209188361,-1.4945811294,-1.0798887256
H,0,2.5482070581,0.3854093286,-1.5954003846
H,0,3.9966382498,0.9619417489,-0.8014649831
H,0,2.878762198,1.2272936754,1.3076241329
H,0,1.8037310059,1.9037934028,0.1200969931
H,0,1.7820301848,-2.0980535743,-1.2029651603
H,0,2.4429788603,-2.9062265511,0.1941907709
H,0,0.4931238629,0.4543549919,1.6637224731
H,0,4.0042436001,-1.1034315535,0.6234565371
H,0,0.0284545289,-3.1132477012,0.7100565617
H,0,-1.7986726804,-2.3318348032,2.0771890654
H,0,-0.9213990474,-0.7658018429,2.4372688215
C,0,-1.0580764259,1.8627997992,0.1872948796
H,0,-2.8206551673,-0.1115463148,1.1427239773
H,0,-1.2271482898,-2.0078320629,-2.4875968341
O,0,-0.4910243025,2.6137433919,-0.7625683576
O,0,-1.3888940589,2.3051422974,1.2617181312
C,0,-0.3478158898,3.9885297579,-0.4494720719
H,0,0.1252117715,4.4398999547,-1.3133381772
H,0,-1.3192595755,4.440010992,-0.2700381117
H,0,0.2680711307,4.1202830216,0.4357779171
```

Vinylcyclohexene Ridge Structure 42

E(RmPW+HF-PW91) = -807.832628070

```
 Zero-point correction=                           0.307808 (Hartree/Particle)
 Thermal correction to Energy=                    0.324621
 Thermal correction to Enthalpy=                  0.325566
 Thermal correction to Gibbs Free Energy=         0.262403
 Sum of electronic and zero-point Energies=          -807.524820
 Sum of electronic and thermal Energies=             -807.508007
 Sum of electronic and thermal Enthalpies=           -807.507063
 Sum of electronic and thermal Free Energies=        -807.570225

                     E (Thermal)             CV                S
                      KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
```

Total	203.703	63.367	132.938

```
C,0,-2.2470623071,-1.5379173642,-0.5902579187
C,0,-2.173176732,-0.3452950407,0.3383688204
C,0,-1.376685684,0.5850113281,-0.290935228
C,0,-0.7542670246,-0.031622713,-1.4347987032
C,0,-1.1677769679,-1.3131000438,-1.5682183254
C,0,-0.9829163997,-1.5049194374,1.6465389161
C,0,0.0411824999,-1.9883773754,0.8652622334
C,0,1.2503065827,-1.2768223734,0.5561868358
C,0,1.4747705552,-0.0206947765,1.0005758225
C,0,2.6725188878,0.7924735546,0.6428614037
C,0,3.4716303422,0.194757836,-0.5038264206
C,0,3.6108259371,-1.3068777156,-0.3253892191
C,0,2.2447280403,-1.9717460676,-0.3356684678
H,0,-0.0401114941,0.4769995929,-2.0611966831
O,0,-3.0462180477,-2.4379112069,-0.5372074683
H,0,4.2366754022,-1.7330331802,-1.1084721734
H,0,2.960922052,0.3980637571,-1.4472949784
H,0,4.4488184266,0.6718249256,-0.5668374164
H,0,3.3037949333,0.8894618631,1.5323892539
H,0,2.3544724912,1.8084711099,0.402650938
H,0,1.8468912184,-1.9916145143,-1.3537002134
H,0,2.3299033027,-3.0144583844,-0.0269628973
H,0,0.7785813955,0.4320907467,1.6932712054
H,0,4.1099125009,-1.5125169093,0.6240806951
H,0,-0.0547191801,-2.9868989289,0.4597669373
H,0,-1.7776778226,-2.1779995745,1.9314370696
H,0,-0.8284954443,-0.6614376867,2.3018160104
C,0,-1.1869123225,1.9486557697,0.1836619117
H,0,-2.9345620904,-0.1166060146,1.0656243005
H,0,-0.9032965285,-2.0168269858,-2.3380241152
O,0,-0.5070810063,2.7038121723,-0.6852724747
O,0,-1.5955902656,2.3707731831,1.2392174515
C,0,-0.3201954114,4.054623192,-0.3032501953
H,0,0.2374990895,4.515153938,-1.1099403132
H,0,-1.2780405133,4.5502517322,-0.1736917396
H,0,0.2350205845,4.1178065923,0.6284701457
```

Vinylcyclohexene Cope Transition Structure (36-ax)

E(RmPW+HF-PW91) = -807.851279146

Zero-point correction= 0.310392 (Hartree/Particle)

```
Thermal correction to Energy=                0.326081
Thermal correction to Enthalpy=              0.327026
Thermal correction to Gibbs Free Energy=     0.267156
Sum of electronic and zero-point Energies=       -807.540887
Sum of electronic and thermal Energies=          -807.525198
Sum of electronic and thermal Enthalpies=        -807.524254
Sum of electronic and thermal Free Energies=     -807.584123

               E (Thermal)         CV              S
                KCal/Mol     Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total           204.619          60.867          126.007
```

```
C,0,-2.4034962973,-1.4298734976,-0.6123641344
C,0,-2.125442601,-0.3557597329,0.4384884879
C,0,-1.3639373777,0.6516361729,-0.3195504476
C,0,-0.9332672524,0.0841455749,-1.5082690479
C,0,-1.3232501764,-1.2461469541,-1.5752794201
C,0,-1.2230233413,-1.2427858499,1.39360748
C,0,-0.1442763423,-1.8525459458,0.5950332199
C,0,1.0342227698,-1.1545506817,0.3088528504
C,0,1.1543988293,0.1517112578,0.7053624129
C,0,2.2740117689,1.0411223652,0.2897867362
C,0,3.1147581717,0.4623996748,-0.8367616587
C,0,3.3791540623,-1.0139354163,-0.5974573779
C,0,2.0689077605,-1.7833381898,-0.586485734
H,0,-0.3169214004,0.5952880179,-2.2303882244
O,0,-3.2588254221,-2.278023015,-0.5635125205
H,0,4.0384350698,-1.4172449619,-1.3648548402
H,0,2.5873482094,0.582500461,-1.7852217813
H,0,4.0475897318,1.0174865571,-0.9254404917
H,0,2.8993627366,1.229856166,1.1691104041
H,0,1.8669899817,2.0151302409,0.0119255625
H,0,1.6666784999,-1.8303223601,-1.6019766042
H,0,2.2311282201,-2.8158241801,-0.2763053976
H,0,0.4985295716,0.5417778885,1.4681985059
H,0,3.8915856655,-1.1415070801,0.3586274632
H,0,-0.2024444912,-2.9055543543,0.3576784043
H,0,-1.8771498072,-2.0023100849,1.8121121381
H,0,-0.8550929431,-0.6177025629,2.2027348947
C,0,-1.2215199488,2.0288930492,0.1134503837
H,0,-2.9790470176,0.0175264477,0.9928962551
H,0,-1.127543354,-1.9299690343,-2.3846058462
O,0,-0.6512341392,2.8143477136,-0.8091858587
O,0,-1.570064671,2.4417341376,1.196206219
```

```
C,0,-0.5273918692,4.1793877305,-0.4533567537
H,0,-0.0550548605,4.6630749433,-1.3001681734
H,0,-1.5045960288,4.6153809227,-0.2661060604
H,0,0.0820662927,4.29333558,0.4389379551
```

2-vinylfuran (21)

E(RmPW+HF-PW91) = -307.351007957

```
Zero-point correction=                       0.106617 (Hartree/Particle)
Thermal correction to Energy=                    0.112380
Thermal correction to Enthalpy=                   0.113324
Thermal correction to Gibbs Free Energy=         0.077022
Sum of electronic and zero-point Energies=          -307.244391
Sum of electronic and thermal Energies=            -307.238628
Sum of electronic and thermal Enthalpies=          -307.237684
Sum of electronic and thermal Free Energies=        -307.273986

                E (Thermal)          CV              S
                 KCal/Mol       Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total               70.519          21.273           76.404
```

```
C,0,-0.0175396246,0.,-0.0277668173
C,0,0.228530778,0.,1.3018477015
C,0,1.2585008592,0.,-0.656410368
H,0,-0.4051708512,0.,2.1678433697
C,0,2.1813430779,0.,0.3435963451
H,0,1.4692754703,0.,-1.7103739393
C,0,3.6222529851,0.,0.3204163754
O,0,1.5518613502,0.,1.5380241871
H,0,-0.9823991911,0.,-0.5003865074
C,0,4.4106011954,0.,1.3933359088
H,0,4.0552006734,0.,-0.6703910429
H,0,5.4840435487,0.,1.2903223395
H,0,4.0026547287,0.,2.3926274478
```

2-vinylfuran [2+4] product (31)

E(RmPW+HF-PW91) = -803.250868931

```
Zero-point correction=                       0.235292 (Hartree/Particle)
Thermal correction to Energy=                    0.249425
Thermal correction to Enthalpy=                   0.250370
Thermal correction to Gibbs Free Energy=         0.192247
```

Sum of electronic and zero-point Energies= -803.015577
Sum of electronic and thermal Energies= -803.001443
Sum of electronic and thermal Enthalpies= -803.000499
Sum of electronic and thermal Free Energies= -803.058622

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	156.517	52.831	122.329

```
O,0,1.0291352161,-2.5851423225,1.4956100759
C,0,0.4780529347,-1.6467835392,2.2951873921
C,0,-0.0524780857,-2.2381696754,3.3930701231
C,0,0.1919517757,-3.6370861978,3.256706519
C,0,0.5569856291,-0.2326528004,1.8666841645
C,0,0.1061648335,0.0531290736,0.4063786309
C,0,1.2576461304,0.9050371122,-0.1828580989
C,0,1.6762600534,1.6461274518,1.0846269458
C,0,1.9857384951,0.4040879805,1.9301862022
C,0,2.8805914805,-0.2862553791,0.9527120455
C,0,2.4620273747,0.0176525818,-0.2851053142
O,0,1.7193542693,2.8039911737,1.3559267576
C,0,3.0115721848,-0.4467492586,-1.5616114755
O,0,2.5382140168,-0.1736891201,-2.6351585214
O,0,4.0943990181,-1.2049612854,-1.4071707821
C,0,4.6789187243,-1.6879295531,-2.6046875067
H,0,-0.8325036587,0.6023164868,0.3920832835
H,0,-0.0674268617,0.3300757729,2.5596998197
H,0,-0.5577429735,-1.7378798948,4.1993306076
H,0,-0.0246670291,-0.8620387898,-0.1633408869
H,0,3.7062798394,-0.9296485046,1.206705831
H,0,2.3638773809,0.5639623047,2.9325057015
H,0,4.9950615292,-0.8612865311,-3.2343245786
H,0,5.5330299028,-2.2788425872,-2.2973038655
H,0,3.9700947509,-2.3001886959,-3.1546786974
H,0,1.0152894641,1.496754073,-1.0559814569
H,0,-0.0892332236,-4.4215084971,3.9349912863
C,0,0.8508409519,-3.7828850323,2.0876767039
H,0,1.2378328766,-4.6326263467,1.5589240937
```

2-vinylfuran [4+2] product (32)

E(RmPW+HF-PW91) = -803.248056621

Zero-point correction= 0.234794 (Hartree/Particle)

```
Thermal correction to Energy=                   0.248745
Thermal correction to Enthalpy=                 0.249689
Thermal correction to Gibbs Free Energy=        0.192997
Sum of electronic and zero-point Energies=          -803.013263
Sum of electronic and thermal Energies=             -802.999312
Sum of electronic and thermal Enthalpies=           -802.998368
Sum of electronic and thermal Free Energies=        -803.055059

                E (Thermal)             CV                S
                 KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total              156.090            53.398            119.317
```

```
C,0,-2.200210824,1.0772680953,0.1512749294
C,0,-1.8993755953,-0.0725842633,1.1067563119
C,0,-0.3923136822,0.0838247621,1.4478684287
C,0,0.0157799921,1.310363323,0.6707043641
C,0,-0.9679124069,1.8486737969,-0.0425057687
C,0,-2.2856959986,-1.4088571275,0.4570318407
C,0,-1.3213293595,-1.7772235457,-0.6300428631
C,0,-0.0438799355,-1.6437464163,-0.3157102943
C,0,0.417737125,-1.1633102643,1.0263366104
C,0,1.8887255599,-1.0161845327,0.7773577163
C,0,2.132671268,-1.442939673,-0.4543908369
O,0,1.025379569,-1.8468298427,-1.1426381667
H,0,1.0318267245,1.6741590025,0.7072518821
O,0,-3.2765286532,1.2855337561,-0.3472049473
H,0,3.0557643301,-1.5376375386,-0.9979011297
H,0,0.2362333362,-1.919745587,1.794730163
H,0,-1.6540156557,-2.0933797382,-1.6054960575
H,0,-3.29506811,-1.3025765049,0.0666492788
H,0,-2.3221741361,-2.1838927956,1.2269463954
C,0,-0.1853788123,0.318232645,2.935218749
H,0,-2.5154470135,0.0832426221,1.9913958994
H,0,-0.9098996278,2.7146512336,-0.6809320772
O,0,-0.792793321,1.4226405421,3.3489419427
O,0,0.4440109895,-0.4010373115,3.6631679415
C,0,-0.6803597032,1.7136989873,4.7341878882
H,0,-1.2279545033,2.6355480701,4.8850520333
H,0,-1.1118857192,0.9119358029,5.3260407387
H,0,0.3620238794,1.8383857728,5.0115773566
H,0,2.6219462836,-0.6967012704,1.4955026712
```

2-vinylfuran Transition Structure 25

E(RmPW+HF-PW91) = -803.183148908

```
Zero-point correction=                        0.229910 (Hartree/Particle)
Thermal correction to Energy=                   0.244821
Thermal correction to Enthalpy=                 0.245765
Thermal correction to Gibbs Free Energy=        0.186879
Sum of electronic and zero-point Energies=          -802.953239
Sum of electronic and thermal Energies=            -802.938328
Sum of electronic and thermal Enthalpies=          -802.937384
Sum of electronic and thermal Free Energies=        -802.996270

                E (Thermal)           CV              S
                 KCal/Mol      Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total              153.627           55.326          123.937
```

```
C,0,-2.7147678026,0.6086342343,-0.433560283
C,0,-2.5536048229,0.1108241838,0.988579862
C,0,-1.3435007368,0.5984525661,1.4311318859
C,0,-0.6328205806,1.1720221633,0.3112529529
C,0,-1.3821510947,1.1121617803,-0.8111354738
C,0,-2.3322827233,-1.8587392384,0.309325331
C,0,-1.296159469,-1.8247251299,-0.5943688715
C,0,0.0452929349,-1.7999278716,-0.1615687884
H,0,0.3676100675,1.5652638089,0.3890499511
O,0,-3.7336942663,0.6072692745,-1.0763976984
H,0,-1.4827203881,-1.7711609637,-1.6561984754
H,0,-3.3402882348,-1.9726651655,-0.0592498265
H,0,-2.1556850979,-2.2025864138,1.3174139995
C,0,-0.8918713079,0.5237778466,2.8115069561
H,0,-3.3930925249,-0.1142593115,1.625961096
H,0,-1.1282560434,1.4602400267,-1.7967945542
O,0,0.1784822433,1.2878850212,3.0434475137
O,0,-1.4173868546,-0.1490116911,3.6684709129
C,0,0.6645370756,1.2736260658,4.3730891833
H,0,1.5147425998,1.9449780695,4.3834514091
H,0,-0.0999467897,1.6187751763,5.0631396355
H,0,0.9686982309,0.2707646654,4.6602145637
O,0,1.0253332393,-1.6934098119,-1.0925291917
C,0,2.1914759999,-1.6022368614,-0.4415379196
C,0,2.0047243427,-1.6431041711,0.9005026502
C,0,0.6071660012,-1.7718592959,1.0934784922
H,0,3.0697885766,-1.5236254463,-1.0539240291
H,0,0.0844145507,-1.8881241103,2.0251986459
```

```
H,0,2.7698418752,-1.5934474004,1.6529160705
```

2-vinylfuran Transition Structure 25-endo-2

E(RmPW+HF-PW91) = -803.170130373

```
 Zero-point correction=                           0.229677 (Hartree/Particle)
 Thermal correction to Energy=                    0.244506
 Thermal correction to Enthalpy=                  0.245450
 Thermal correction to Gibbs Free Energy=         0.187149
 Sum of electronic and zero-point Energies=         -802.940453
 Sum of electronic and thermal Energies=            -802.925624
 Sum of electronic and thermal Enthalpies=          -802.924680
 Sum of electronic and thermal Free Energies=       -802.982981

                     E (Thermal)             CV                S
                      KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                  153.430             55.461           122.705
```

```
O,0,2.5770492946,-0.7788132942,-1.0985805929
C,0,1.3560835583,-1.040378595,-0.6125919062
C,0,1.3186537448,-0.7605381741,0.7743370748
C,0,2.6909683121,-0.450426908,1.1073149865
C,0,3.3662145815,-0.4315256581,-0.048264102
C,0,0.301151123,-1.4301643105,-1.4433645283
C,0,-0.9075051959,-1.7081810788,-0.8978478324
C,0,0.2130413047,0.8816237941,0.8315098266
C,0,0.9279101115,1.7571590412,-0.1861993359
C,0,0.0285487414,1.8459347147,-1.3363632515
C,0,-1.1480948771,1.2789806208,-0.9918257343
C,0,-1.076606355,0.679074111,0.3208621694
O,0,2.0118333707,2.2686745955,-0.0300403442
C,0,-2.156949058,0.1387703304,1.1121353548
O,0,-2.0019932368,-0.437586002,2.1688626552
O,0,-3.3612302856,0.3150354743,0.556283521
C,0,-4.4560652621,-0.2011353769,1.2902241786
H,0,4.3816225747,-0.1897990488,-0.2967539691
H,0,0.6468646986,-1.2710274497,1.446932893
H,0,0.4470179094,-1.3863774877,-2.5119664084
H,0,-1.766836259,-1.8909070129,-1.5244151997
H,0,-1.0240152957,-1.9084898977,0.1544185968
H,0,0.3874842057,1.0234414295,1.8869159763
H,0,-2.0400600268,1.2509290841,-1.5972228634
H,0,0.2770429503,2.3481741965,-2.2545478488
```

```
H,0,-5.3392609219,0.0406089089,0.7108887859
H,0,-4.3658736679,-1.2771281132,1.4121618108
H,0,-4.5099985583,0.2592775667,2.2725061475
H,0,3.0809165187,-0.2000544601,2.0758179401
```

2-vinylfuran Cope Transition Structure 37

E(RmPW+HF-PW91) = -803.197593831

```
Zero-point correction=                     0.232099 (Hartree/Particle)
Thermal correction to Energy=                0.246022
Thermal correction to Enthalpy=              0.246967
Thermal correction to Gibbs Free Energy=       0.190709
Sum of electronic and zero-point Energies=        -802.965495
Sum of electronic and thermal Energies=          -802.951571
Sum of electronic and thermal Enthalpies=         -802.950627
Sum of electronic and thermal Free Energies=       -803.006885

             E (Thermal)          CV               S
              KCal/Mol      Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total            154.381          53.112          118.404
```

```
C,0,-2.3270231006,-1.4826458437,-0.6657546124
C,0,-2.0802731785,-0.4047639934,0.3933888391
C,0,-1.3576880723,0.6370407808,-0.3479662714
C,0,-0.9648281514,0.1181451554,-1.584528261
C,0,-1.3736835262,-1.1892856663,-1.7243580466
C,0,-1.1955868102,-1.2240514494,1.4310957748
C,0,-0.0748079658,-1.8440007606,0.717230307
C,0,1.0083653989,-1.0601071318,0.4220917688
C,0,1.1934234501,0.3040338857,0.6562048765
C,0,2.3617823882,0.6673664651,-0.0490879016
C,0,2.8040160317,-0.470341586,-0.644655466
O,0,2.0190128713,-1.5145800543,-0.374741791
H,0,-0.3811588616,0.6706348201,-2.3039258497
O,0,-3.1058821962,-2.4012358991,-0.5632610368
H,0,3.6618343934,-0.6731281031,-1.2592058967
H,0,2.826806331,1.6341020464,-0.1002442203
H,0,0.6529170921,0.9001152802,1.3678677162
H,0,-0.0840286886,-2.8868867117,0.4429308411
H,0,-1.8528721731,-1.9720557958,1.8630076232
H,0,-0.8761003973,-0.5346068811,2.2085312242
C,0,-1.2381634165,1.99984744,0.1174437321
H,0,-2.9623285199,-0.0584555996,0.9225906144
```

H,0,-1.1913538446,-1.8370399554,-2.5650996238
O,0,-0.7809308022,2.8411275195,-0.8187886766
O,0,-1.5076698456,2.3615265133,1.2438171123
C,0,-0.6469852413,4.1900257948,-0.4134613987
H,0,-0.2816474958,4.7241395277,-1.2826507382
H,0,-1.6051399397,4.5927417731,-0.0975499895
H,0,0.0569102705,4.2790164292,0.4098273505

Styrene (22)

E(RmPW+HF-PW91) = -309.581745090

```
Zero-point correction=                          0.137208 (Hartree/Particle)
Thermal correction to Energy=                   0.143949
Thermal correction to Enthalpy=                 0.144894
Thermal correction to Gibbs Free Energy=        0.103237
Sum of electronic and zero-point Energies=          -309.444537
Sum of electronic and thermal Energies=             -309.437796
Sum of electronic and thermal Enthalpies=           -309.436851
Sum of electronic and thermal Free Energies=        -309.478508

                E (Thermal)          CV               S
                 KCal/Mol       Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total              90.330           25.319            87.673
```

C,0,-1.0062214476,0.1832772969,-0.0813281236
C,0,0.3723266195,0.1560702596,-0.1831763518
C,0,1.1158648674,1.3374500006,-0.1485022215
C,0,0.4281621673,2.5421175087,-0.0083681807
C,0,-0.9537145888,2.5723750769,0.0939462196
C,0,-1.6772109665,1.3917194615,0.0578178942
H,0,-1.5623724852,-0.7422359985,-0.1103863913
H,0,0.8741524195,-0.7937342743,-0.2905995266
H,0,0.98688278,3.4673517547,0.0205410595
H,0,-1.4634827871,3.5184189683,0.2017813953
H,0,-2.7539830518,1.4095975049,0.1371302689
C,0,2.5777306317,1.3665595688,-0.2522258513
H,0,3.0136338581,2.3573784649,-0.2086250297
C,0,3.3984765698,0.3289889138,-0.3905038942
H,0,3.0488877989,-0.6915334677,-0.4427329963
H,0,4.4651656149,0.4768079609,-0.4565832705

Styrene [2 + 4] Product (33)

E(RmPW+HF-PW91) = -805.481554656

```
Zero-point correction=                     0.266159 (Hartree/Particle)
Thermal correction to Energy=                0.281032
Thermal correction to Enthalpy=              0.281976
Thermal correction to Gibbs Free Energy=        0.222262
Sum of electronic and zero-point Energies=         -805.215396
Sum of electronic and thermal Energies=           -805.200523
Sum of electronic and thermal Enthalpies=          -805.199579
Sum of electronic and thermal Free Energies=        -805.259293

             E (Thermal)          CV              S
              KCal/Mol       Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total            176.350           56.741           125.678
```

```
C,0,-1.4026359936,-1.5440329326,0.4973880419
C,0,0.0121026452,-1.5927306837,0.0110581977
C,0,-0.5778183828,0.6051735681,0.2744856486
C,0,-1.7443273515,-0.2566811085,0.6578495995
H,0,-2.0396179709,-2.3945321708,0.6752778664
C,0,0.0719974379,-1.0218795486,-1.4357047016
H,0,1.1260580511,-1.0222784157,-1.723468727
C,0,-0.3835401371,0.4561988276,-1.2521481858
H,0,0.3713910083,1.1511239757,-1.6135891743
H,0,-1.3138985052,0.6641223512,-1.7735978112
H,0,0.5697419583,-2.5067813141,0.1764642914
H,0,-0.5735268934,1.6154349731,0.6625357924
C,0,0.5216208603,-0.3437510519,0.7420576977
O,0,1.4824340441,-0.1793893353,1.4245198436
C,0,-0.6779023668,-1.8041765279,-2.4839664082
C,0,-1.0182878911,-3.1408168269,-2.3043193403
C,0,-0.990257308,-1.2069969552,-3.70335003
C,0,-1.6625840491,-3.8557077239,-3.3035799931
H,0,-0.7801516913,-3.6387862497,-1.376132784
C,0,-1.6304099242,-1.9179600761,-4.7054011738
H,0,-0.7274398495,-0.1730473512,-3.8767447668
C,0,-1.972955392,-3.2471954637,-4.5085089627
H,0,-1.9211652566,-4.8911165952,-3.1368497167
H,0,-1.8624398338,-1.4313327988,-5.6413727469
H,0,-2.4755283947,-3.8020254307,-5.2866141791
C,0,-3.0359184913,0.2854932622,1.0909241203
O,0,-3.2791283099,1.4631188047,1.1603400199
O,0,-3.9134366518,-0.6662118201,1.3985553112
```

```
C,0,-5.1875745799,-0.2102121025,1.8209327014
H,0,-5.6587034799,0.3795078547,1.039938788
H,0,-5.7664720661,-1.1027138171,2.0243081841
H,0,-5.0965492347,0.3970636831,2.7167835974
```

Styrene [4+2] product (34)

E(RmPW+HF-PW91) = -805.460238490

```
Zero-point correction=                          0.265256 (Hartree/Particle)
Thermal correction to Energy=                       0.280116
Thermal correction to Enthalpy=                     0.281060
Thermal correction to Gibbs Free Energy=            0.222251
Sum of electronic and zero-point Energies=           -805.194982
Sum of electronic and thermal Energies=              -805.180122
Sum of electronic and thermal Enthalpies=            -805.179178
Sum of electronic and thermal Free Energies=         -805.237988

              E (Thermal)        CV              S
               KCal/Mol      Cal/Mol-Kelvin  Cal/Mol-Kelvin
Total            175.775         57.634        123.775
```

```
C,0,-2.2400074515,1.0040942551,0.078302625
C,0,-1.9418922751,-0.1074180351,1.0791149973
C,0,-0.4475421356,0.080363415,1.4422652188
C,0,-0.0502003373,1.3075031674,0.6685986135
C,0,-1.0242553888,1.8044421881,-0.0887764754
C,0,-2.2662507151,-1.4766704115,0.4755934541
C,0,-1.2820093357,-1.8000158814,-0.595172146
C,0,0.0224393151,-1.6238125915,-0.3459111953
C,0,0.4052315336,-1.1600386897,1.0382149366
C,0,1.0555172768,-1.8377299458,-1.3356437466
H,0,0.9540846338,1.6991854965,0.7283757113
O,0,-3.3037443877,1.1636776344,-0.4649672211
H,0,0.1088597063,-1.9302173655,1.7586320077
H,0,-3.2846357847,-1.4529418022,0.0960193246
H,0,-2.2313511873,-2.2276660912,1.2706001243
C,0,-0.3308814837,0.2744659452,2.9428286347
H,0,-2.5826782476,0.0607728824,1.9452469359
H,0,-0.967218633,2.6579205289,-0.7438583499
O,0,-0.4752757826,1.5441673364,3.299017749
O,0,-0.1715373155,-0.6178825406,3.7319910766
C,0,-0.4594374591,1.8030717313,4.6955781966
H,0,-0.5792992319,2.8745346003,4.7959732068
```

H,0,-1.274927659,1.2803399051,5.1864543438
H,0,0.4817819403,1.4803929196,5.1301592403
C,0,1.8708302027,-0.9266209397,1.223159692
H,0,-1.6234576558,-2.1311889816,-1.5658210383
C,0,2.7588312375,-1.1406153729,0.2505723819
H,0,2.1996227896,-0.6119524774,2.2041977615
H,0,3.8115193585,-0.9822241195,0.4362751725
C,0,2.3476834293,-1.6065088996,-1.0626592975
H,0,0.7490301564,-2.1780551946,-2.314872031
H,0,3.1021048872,-1.7645106659,-1.8188549037

Styrene Transition Structure 26

E(RmPW+HF-PW91) = -805.411358366

```
Zero-point correction=                     0.260876 (Hartree/Particle)
Thermal correction to Energy=                 0.276594
Thermal correction to Enthalpy=               0.277538
Thermal correction to Gibbs Free Energy=         0.216558
Sum of electronic and zero-point Energies=          -805.150482
Sum of electronic and thermal Energies=            -805.134764
Sum of electronic and thermal Enthalpies=          -805.133820
Sum of electronic and thermal Free Energies=        -805.194801

              E (Thermal)          CV              S
               KCal/Mol       Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total            173.565          59.171          128.344
```

C,0,-2.7097745915,0.5759351961,-0.4054752941
C,0,-2.5443434919,0.0809454033,1.0209106748
C,0,-1.3622676871,0.6328777626,1.4775607021
C,0,-0.6552108092,1.204863854,0.3653452849
C,0,-1.3812082582,1.089931502,-0.773168097
C,0,-2.2364756795,-1.8167137011,0.3349396629
C,0,-1.2433203107,-1.7363928672,-0.6191267873
C,0,0.1638843077,-1.7634510384,-0.3213036792
H,0,0.330807036,1.6313502084,0.4492610586
O,0,-3.7264842212,0.5591538028,-1.0504303971
H,0,-1.5239290232,-1.6757992615,-1.6613952213
H,0,-3.251085543,-1.9689163983,-0.0023259482
H,0,-2.0146084317,-2.2051134393,1.3178369795
C,0,-0.9167398803,0.5663790156,2.8607976299
H,0,-3.3841576506,-0.1592533709,1.6529055828
H,0,-1.1214652867,1.432739192,-1.7592798195

O,0,0.1327736315,1.3555110656,3.0994438794
O,0,-1.4301827561,-0.1226618228,3.7115066802
C,0,0.6152809371,1.347349027,4.4304637218
H,0,1.4549893339,2.0316671678,4.4437953404
H,0,-0.1565626361,1.6802116067,5.1184650146
H,0,0.9336132515,0.3488550469,4.716944739
C,0,1.0976392117,-1.727850654,-1.3692181885
C,0,2.4509041488,-1.7195921379,-1.1131054629
C,0,2.91233873,-1.7359794815,0.2013601901
C,0,2.0071758576,-1.7722993381,1.2477297292
C,0,0.6434269951,-1.7913548601,0.9948466807
H,0,0.7402236503,-1.7012261834,-2.3889805179
H,0,3.1542327111,-1.6965966482,-1.9321759223
H,0,3.9733464925,-1.7276360059,0.401980056
H,0,2.360328472,-1.7953436955,2.267935841
H,0,-0.0438625096,-1.8539409467,1.8240218875

Styrene Transition Structure 26-endo-2

E(RmPW+HF-PW91) = -805.392979370

```
Zero-point correction=                    0.260446 (Hartree/Particle)
Thermal correction to Energy=                0.276061
Thermal correction to Enthalpy=              0.277005
Thermal correction to Gibbs Free Energy=        0.217386
Sum of electronic and zero-point Energies=          -805.132533
Sum of electronic and thermal Energies=            -805.116919
Sum of electronic and thermal Enthalpies=           -805.115975
Sum of electronic and thermal Free Energies=         -805.175594

              E (Thermal)         CV               S
               KCal/Mol      Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total            173.231           59.473          125.479
```

C,0,2.6410137067,-0.8147448186,-1.0243629511
C,0,1.333589833,-1.1111598163,-0.5943857925
C,0,0.9732794489,-0.8442910182,0.7810259018
C,0,2.0541957108,-0.5623064177,1.696546101
C,0,3.5975762523,-0.4119536647,-0.1359793283
C,0,0.3512938754,-1.5883727232,-1.5009768246
C,0,-0.8992266886,-1.9287952048,-1.1231759285
C,0,-0.0622103192,0.6789536894,0.7313849101
C,0,0.7910570241,1.6332386589,-0.1046883531
C,0,0.1248273307,1.7222516491,-1.4026283657

C,0,-1.0929774037,1.1384695835,-1.2932919136
C,0,-1.2570243704,0.5141886704,-0.0139536577
O,0,1.7891740691,2.1949181383,0.2757135467
C,0,-2.4643347542,-0.0250266509,0.5639232969
O,0,-2.5050785046,-0.6076335766,1.62817678
O,0,-3.5493068542,0.1673769772,-0.1959848639
C,0,-4.7615549327,-0.3393122058,0.3298766575
H,0,2.8808332759,-0.9265377699,-2.0719347176
H,0,0.1876899937,-1.4621884169,1.2009758007
H,0,0.6064528249,-1.5814550809,-2.5522286221
H,0,-1.6455294551,-2.1846421878,-1.8602571876
H,0,-1.1716339148,-2.0897272308,-0.0925932555
H,0,-0.1373675833,0.8521849266,1.795309165
H,0,-1.8566822253,1.1235676232,-2.0544907611
H,0,0.528848915,2.2497587068,-2.2488848233
H,0,-5.5262485644,-0.0844357163,-0.3943164312
H,0,-4.7059813293,-1.4168878955,0.4586013781
H,0,-4.9829956575,0.1169146095,1.2904957225
C,0,3.3068013407,-0.3176980265,1.2477573338
H,0,1.8242885472,-0.491102647,2.7495300859
H,0,4.0924469321,-0.0527680531,1.9386155111
H,0,4.5942434767,-0.1873741115,-0.4846214137

Styrene Cope Transitions Structure (38)

E(RmPW+HF-PW91) = -805.418901378

```
Zero-point correction=                      0.262809 (Hartree/Particle)
Thermal correction to Energy=                  0.277566
Thermal correction to Enthalpy=                0.278510
Thermal correction to Gibbs Free Energy=       0.220600
Sum of electronic and zero-point Energies=        -805.156093
Sum of electronic and thermal Energies=           -805.141335
Sum of electronic and thermal Enthalpies=         -805.140391
Sum of electronic and thermal Free Energies=      -805.198302

                E (Thermal)         CV              S
                 KCal/Mol     Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total             174.175          57.281          121.883
```

C,0,-2.6314079879,0.7568420583,-0.3461807799
C,0,-2.3837082031,-0.0086990773,0.9577286734
C,0,-1.1062561725,0.538714697,1.4392269621
C,0,-0.5574891674,1.3524958813,0.4246898884

```
C,0,-1.3604197298,1.3800771577,-0.680903788
C,0,-2.3535624426,-1.5172431526,0.4501700476
C,0,-1.3349155204,-1.6528191698,-0.5875321255
C,0,0.0105560019,-1.59504697,-0.2681613706
H,0,0.3916391518,1.8553141987,0.5220058671
O,0,-3.6736505181,0.7671639658,-0.9582058033
H,0,-1.6330315942,-1.740156013,-1.6227408158
H,0,-3.3481154108,-1.7297220851,0.0714429805
H,0,-2.161695864,-2.1402212894,1.322051811
C,0,-0.7412379552,0.5365837201,2.8409029015
H,0,-3.190601035,0.0600055681,1.6812865807
H,0,-1.1701622984,1.8952309735,-1.6072372091
O,0,0.2630687334,1.3740981764,3.1240742041
O,0,-1.2693440496,-0.1595216515,3.6810247634
C,0,0.6598988006,1.4142127221,4.4819391532
H,0,1.4667702836,2.1356843446,4.5320465969
H,0,-0.1670226604,1.7268121924,5.1131993275
H,0,1.0022400124,0.437893497,4.8145111633
C,0,1.0179928893,-1.5339081687,-1.2758278483
C,0,2.3148259519,-1.2970160545,-0.9456284949
C,0,2.68297605,-1.1186828323,0.4102603848
C,0,1.7480962149,-1.202853887,1.4052259598
C,0,0.3977009168,-1.4327725379,1.0896905871
H,0,0.7236688875,-1.651475254,-2.3088735109
H,0,3.0710897119,-1.2414488438,-1.7140635093
H,0,3.7195754994,-0.9432524073,0.6579660103
H,0,2.0431067893,-1.1105662225,2.4392109317
H,0,-0.2742612855,-1.7279325365,1.8785934613
```

Zwanenburg Example – [2 + 4] Product 39

E(RmPW+HF-PW91) = -768.593541319

```
Zero-point correction=                          0.282011 (Hartree/Particle)
Thermal correction to Energy=                   0.297091
Thermal correction to Enthalpy=                 0.298035
Thermal correction to Gibbs Free Energy=        0.238989
Sum of electronic and zero-point Energies=         -768.311531
Sum of electronic and thermal Energies=            -768.296451
Sum of electronic and thermal Enthalpies=          -768.295506
Sum of electronic and thermal Free Energies=       -768.354552

                    E (Thermal)            CV                S
                     KCal/Mol       Cal/Mol-Kelvin    Cal/Mol-Kelvin
```

Total	186.427	57.675	124.272

C,0,0.867606,-1.23155,5.374613
C,0,-0.437419,-0.781482,4.756433
C,0,0.16927,0.283298,3.829646
C,0,1.267022,-0.57494,3.203145
C,0,1.850724,-1.099273,4.470997
C,0,0.335027,-1.67609,2.600013
C,0,-0.81647,-1.802054,3.644769
C,0,0.895172,-3.059073,2.512094
C,0,0.252969,-3.912295,3.300822
C,0,-0.868691,-3.279389,4.066603
O,0,-0.154771,1.412016,3.630478
C,0,1.018489,-1.808176,6.716679
O,0,2.294509,-1.885361,7.089629
C,0,2.561853,-2.478609,8.359832
C,0,2.648862,-3.980625,8.257873
O,0,0.099125,-2.181959,7.40206
H,0,2.883026,-1.36899,4.621555
H,0,-0.020033,-1.319241,1.632197
H,0,-1.764818,-1.484674,3.213469
C,0,-1.56067,-0.329275,5.650182
H,0,1.937919,-0.091675,2.503095
H,0,-1.824738,-3.73862,3.810891
H,0,0.491492,-4.962834,3.386704
H,0,1.726486,-3.313893,1.870981
H,0,3.510079,-2.046688,8.665471
H,0,1.787356,-2.175644,9.05892
H,0,2.920396,-4.398955,9.225466
H,0,1.692426,-4.403691,7.962911
H,0,3.405142,-4.276862,7.534384
H,0,-0.749455,-3.402721,5.144038
H,0,-1.980498,-1.162793,6.204904
H,0,-1.214834,0.409793,6.369018
H,0,-2.342329,0.131363,5.049328

Zwanenburg Example – Cope Transition Structure

E(RmPW+HF-PW91) = -768.558900498

Zero-point correction= 0.279095 (Hartree/Particle)
Thermal correction to Energy= 0.294034
Thermal correction to Enthalpy= 0.294978
Thermal correction to Gibbs Free Energy= 0.236912

```
 Sum of electronic and zero-point Energies=          -768.264352
 Sum of electronic and thermal Energies=             -768.249413
 Sum of electronic and thermal Enthalpies=           -768.248469
 Sum of electronic and thermal Free Energies=        -768.306534

E (Thermal)          CV              S
               KCal/Mol       Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total          183.711          57.845          122.165

C,0,-0.7889093049,-3.0898071295,4.432081449
 C,0,0.5902686374,-3.5244615058,4.085615507
 C,0,0.9851668217,-2.9581261349,2.8978721847
 C,0,0.1270566301,-1.9065572156,2.5949623807
 C,0,1.6089728905,0.0122409916,3.4297566885
 C,0,0.2273994255,0.3701014838,3.6692108155
 C,0,-0.2749784326,-0.6335271129,4.7159529611
 C,0,-0.8448504126,-1.7525153944,3.7041218886
 O,0,-0.459356262,1.2143064394,3.1277184726
 C,0,-1.3762329798,-0.1247329344,5.6167838863
 C,0,0.9893040845,-1.1141646895,5.3230488376
 C,0,2.053273138,-0.6990564018,4.5286808796
 C,0,1.120092963,-1.7590724306,6.6155613244
 O,0,0.1934487235,-2.1136968222,7.3201279383
 O,0,2.394110188,-1.920509222,6.9824468149
 C,0,2.621348689,-2.5574076813,8.2369499852
 C,0,4.10901244,-2.6568713275,8.4355975235
 H,0,-0.9876884323,0.6078354104,6.3208690656
 H,0,4.3187617477,-3.1388311514,9.3883687594
 H,0,4.5694904191,-3.2466050292,7.6459958975
 H,0,4.568357294,-1.6708852013,8.4435294264
 H,0,2.1491928611,-1.9698949314,9.0224482005
 H,0,2.150840695,-3.5392345122,8.2262882272
 H,0,-1.8228789093,-0.9310925182,6.1898272739
 H,0,-2.1423892703,0.3564529824,5.0127373696
 H,0,3.0833661834,-0.9614048762,4.7183756722
 H,0,2.2175631707,0.4366894946,2.6454165929
 H,0,0.0811209569,-1.3728760094,1.6562785647
 H,0,1.8708754068,-3.2224543083,2.338345047
 H,0,1.1184579167,-4.3188271749,4.597452964
 H,0,-1.8283612967,-1.4138394542,3.3837672462
 H,0,-1.5070879103,-3.7963297623,4.0046310312
 H,0,-0.9809410716,-3.019856871,5.4989831242
```

Butadiene Transition Structure with 18

E(RB+HF-LYP) = -652.006503369

```
 Zero-point correction=                           0.204584 (Hartree/Particle)
 Thermal correction to Energy=                    0.218374
 Thermal correction to Enthalpy=                  0.219318
 Thermal correction to Gibbs Free Energy=         0.163867
 Sum of electronic and zero-point Energies=          -651.801919
 Sum of electronic and thermal Energies=             -651.788130
 Sum of electronic and thermal Enthalpies=           -651.787186
 Sum of electronic and thermal Free Energies=        -651.842636

                E (Thermal)             CV                S
                 KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total             137.031             50.679            116.706
```

```
C,0,-0.0346168425,0.1623393704,-0.6588861636
 C,0,-1.0421218678,-0.7886482751,-0.4919190443
 C,0,-2.3175151953,-0.004162492,-0.1723694908
 C,0,-1.8599998862,1.3767142877,0.1051061259
 C,0,-0.5496082307,1.4647645909,-0.2554710592
 O,0,-3.4541001982,-0.4460598423,-0.1881235191
 C,0,1.2803877183,-0.1319227505,-1.2333695008
 O,0,1.7177439737,-1.2577036668,-1.4257259853
 O,0,1.9724180614,0.9938344831,-1.5459630196
 C,0,3.2735469696,0.7874969676,-2.1242618987
 C,0,-0.9358233786,-1.6883363711,1.3981453522
 C,0,-0.951375442,-0.6438786637,2.3167138806
 C,0,0.1847834278,0.1803183793,2.5915942633
 C,0,1.4008721926,0.039869539,1.998048251
 H,0,2.1967346615,0.7520993096,2.1917847568
 H,0,0.0285957644,1.0220428926,3.2628988841
 H,0,-1.8930292114,-0.3788013885,2.7894317427
 H,0,-1.8237484378,-2.3044507161,1.2959727604
 H,0,-1.0680920636,-1.7353323833,-1.0184260782
 H,0,0.0583760644,2.361150351,-0.2464152598
 H,0,-2.5116648824,2.1705219748,0.4451360815
 H,0,3.6651325861,1.7856118152,-2.3195220742
 H,0,3.921497985,0.2486504331,-1.4280771217
 H,0,3.1937000367,0.2161668713,-3.0521508122
 H,0,1.6533347139,-0.8071044567,1.3708447787
 H,0,-0.0005087023,-2.1784499895,1.147038241
```

3-vinylfuran Transition Structure with 18

E(RmPW+HF-PW91) = -803.177291140

```
Zero-point correction=                          0.230157 (Hartree/Particle)
Thermal correction to Energy=                       0.245038
Thermal correction to Enthalpy=                     0.245982
Thermal correction to Gibbs Free Energy=            0.187260
Sum of electronic and zero-point Energies=          -802.947134
Sum of electronic and thermal Energies=             -802.932254
Sum of electronic and thermal Enthalpies=           -802.931309
Sum of electronic and thermal Free Energies=        -802.990031

                E (Thermal)         CV               S
                 KCal/Mol      Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total             153.763          55.296          123.591
```

```
C,0,-2.782153638,0.6015964816,-0.4039707058
C,0,-2.5443048441,0.066799822,0.9946860987
C,0,-1.3244333873,0.5703565721,1.3965642795
C,0,-0.6827680758,1.1951713826,0.2624402239
C,0,-1.4807656709,1.1455545492,-0.8263098202
C,0,-2.3332481261,-1.8703431575,0.2556557921
C,0,-1.3126936303,-1.7979071714,-0.6636214786
C,0,0.0519193805,-1.7600762078,-0.2697251557
H,0,0.3085760765,1.6157516496,0.3062368731
O,0,-3.8299339622,0.5949639136,-0.9987365148
H,0,-1.5409887066,-1.7214859816,-1.7165493423
H,0,-3.3479974165,-1.9830342215,-0.0952152111
H,0,-2.1372365472,-2.2468273864,1.2487236854
C,0,-0.8138052818,0.4841848395,2.7554497721
H,0,-3.3503151524,-0.1856817594,1.6643646399
H,0,-1.2825941322,1.5325114116,-1.8103402685
O,0,0.2423326704,1.2744129784,2.9565781439
O,0,-1.2817618594,-0.2233028766,3.6186615519
C,0,0.8004735049,1.2350541158,4.2578362951
H,0,1.6199125727,1.9434624905,4.2479l234106
H,0,0.0601112593,1.5198703132,4.9995896936
H,0,1.1653021587,0.2378726258,4.4878295278
C,0,1.2203118849,-1.6212538838,-1.0961229647
C,0,2.2681760809,-1.5487716217,-0.2578089078
O,0,1.8578588567,-1.6279181272,1.0298951416
C,0,0.5264016728,-1.7466854516,1.0195929747
H,0,1.2516372205,-1.5778062375,-2.1694527901
H,0,3.325537014,-1.4432334709,-0.4059492028
```

H,0,0.053170078,-1.8830845906,1.9735602585

Phenylbutadiene Transition Structure with 18

E(RmPW+HF-PW91) = -882.802103162

```
Zero-point correction=                       0.295473 (Hartree/Particle)
Thermal correction to Energy=                   0.313340
Thermal correction to Enthalpy=                 0.314284
Thermal correction to Gibbs Free Energy=        0.248259
Sum of electronic and zero-point Energies=         -882.506630
Sum of electronic and thermal Energies=            -882.488763
Sum of electronic and thermal Enthalpies=          -882.487819
Sum of electronic and thermal Free Energies=         -882.553844

              E (Thermal)         CV              S
               KCal/Mol     Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total            196.624          67.216          138.961
```

C,0,-2.7887377145,0.5469240076,-0.3524792115
C,0,-2.5037830734,0.0494686822,1.0463022931
C,0,-1.2659041776,0.5331701508,1.3870562549
C,0,-0.6634937484,1.1496536096,0.2169248613
C,0,-1.5065631236,1.099807253,-0.8320962542
C,0,-2.3300640422,-1.9862649242,0.2893012945
C,0,-1.320962339,-1.9004333158,-0.6346215144
C,0,0.0540434212,-1.7950349209,-0.2935126119
C,0,0.5141395789,-1.759244525,0.9818940636
C,0,1.8976600088,-1.5791778002,1.3932015596
H,0,0.3303517645,1.5661460098,0.2228327052
O,0,-3.8547122784,0.5271610805,-0.9139101708
H,0,-0.174639496,-1.9630158598,1.7899385333
H,0,-1.5810111417,-1.8379197541,-1.6817142834
H,0,-3.3510198321,-2.0866194785,-0.0467018988
H,0,-2.1317990245,-2.3107055293,1.2992337907
C,0,-0.7144640356,0.5143469381,2.7371232414
H,0,-3.2801217718,-0.2175335312,1.7437927232
H,0,-1.3512126429,1.4745834208,-1.8284727886
O,0,0.3168787799,1.3480053898,2.8682276477
O,0,-1.1418130255,-0.1598932841,3.6449371651
C,0,0.8901736851,1.424972615,4.1614762522
H,0,1.6801272697,2.1624990361,4.0885275809
H,0,0.1453678709,1.734749766,4.8888779278
H,0,1.2992119513,0.4635351754,4.4559770601

```
C,0,2.2483941387,-1.8854311118,2.7108046324
C,0,3.5537719727,-1.7506003426,3.1516834464
C,0,4.5356227915,-1.2953311008,2.2850889269
C,0,4.1999502379,-0.973930977,0.9758201319
C,0,2.8973716957,-1.1113038963,0.5344984011
H,0,1.4841432688,-2.2386503574,3.3890465391
H,0,3.8046945151,-2.0021065399,4.1716300597
H,0,5.5544721809,-1.1869985094,2.6259181673
H,0,4.9581887425,-0.6093905287,0.2986373015
H,0,2.6531116898,-0.8408508146,-0.4818793732
H,0,0.7502769034,-1.6783660331,-1.1122134543
```

3,3,5,5-tetramethyl-1-vinylcyclohexene Transition Structure with 18

E(RmPW+HF-PW91) = -965.067610296

```
Zero-point correction=                    0.422173 (Hartree/Particle)
Thermal correction to Energy=             0.444484
Thermal correction to Enthalpy=           0.445428
Thermal correction to Gibbs Free Energy=  0.371522
Sum of electronic and zero-point Energies=     -964.645437
Sum of electronic and thermal Energies=        -964.623127
Sum of electronic and thermal Enthalpies=      -964.622182
Sum of electronic and thermal Free Energies=   -964.696088

             E (Thermal)        CV                S
              KCal/Mol     Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total          278.918         85.888          155.548
```

```
C,0,-2.7597713755,0.4914647178,-0.3902058683
C,0,-2.5897926422,0.0645383217,1.0534664459
C,0,-1.4412881356,0.6710193326,1.5028150613
C,0,-0.7576998428,1.2677872778,0.3786480777
C,0,-1.4653427835,1.0927416158,-0.7592848121
C,0,-2.1759142119,-1.9109116002,0.4010018944
C,0,-1.1769567611,-1.7794805254,-0.5305307269
C,0,0.229901287,-1.7063717774,-0.2410288482
C,0,0.7040718841,-1.7556697165,1.0217300475
C,0,2.1535835454,-1.7168651896,1.4062449852
C,0,3.0481246319,-1.4682744503,0.1841732825
C,0,2.5724451587,-2.0511930466,-1.1492292503
C,0,1.1604011459,-1.5324048085,-1.4110763692
H,0,0.1935302163,1.7669070797,0.4653135103
O,0,-3.7631431759,0.3909215985,-1.0494392085
```

```
C,0,3.5044309705,-1.559192379,-2.2512446054
H,0,3.1313211872,-0.3878022802,0.0435610123
H,0,4.0578110183,-1.8227054113,0.4032832147
C,0,2.5040842279,-3.0295903062,2.1215193805
C,0,2.37393135,-0.586170632,2.4149682482
H,0,1.2030045297,-0.4697795033,-1.665884478
H,0,0.7419504463,-2.0338372776,-2.2857891567
H,0,0.0146882754,-1.9014049797,1.8444162613
C,0,2.5697108034,-3.578449226,-1.168239395
H,0,-1.4603282257,-1.7277774827,-1.5735609865
H,0,-3.1824891541,-2.0962910117,0.0573897414
H,0,-1.9580519928,-2.2284998133,1.409125272
C,0,-1.0491726188,0.7266601491,2.9041918769
H,0,-3.4167445292,-0.2284418702,1.679027321
H,0,-1.2263762493,1.4405092117,-1.7489242481
O,0,-0.1193598749,1.6578173666,3.1345783402
O,0,-1.5193566538,0.0367729558,3.7775155037
C,0,0.2719877443,1.811615977,4.4863524891
H,0,1.0201491093,2.5951741694,4.4899570389
H,0,-0.5788630847,2.0968482383,5.0984905349
H,0,0.6889986917,0.886753498,4.8745389805
H,0,3.1636122814,-1.8979648613,-3.2295740407
H,0,3.5539730765,-0.4706455915,-2.2727072855
H,0,4.5161196434,-1.937002709,-2.1038677107
H,0,2.3827076979,-3.93813804,-2.1800502914
H,0,3.5310130276,-3.9789976823,-0.8473964107
H,0,1.7957735256,-3.9959836236,-0.5287619617
H,0,3.4261557373,-0.5353849231,2.6961080013
H,0,2.0825696207,0.3779000205,2.0040117623
H,0,1.793796864,-0.7565502886,3.3209769143
H,0,3.5361232491,-2.9976941788,2.4707339955
H,0,1.8635634998,-3.1724860376,2.9910887538
H,0,2.3927748655,-3.8976683069,1.4798957064
```

Vinylcyclopentene Transition Structure with 18

E(RmPW+HF-PW91) = -768.518464178

```
 Zero-point correction=                           0.277890 (Hartree/Particle)
 Thermal correction to Energy=                    0.293650
 Thermal correction to Enthalpy=                  0.294594
 Thermal correction to Gibbs Free Energy=         0.234325
 Sum of electronic and zero-point Energies=           -768.240574
 Sum of electronic and thermal Energies=              -768.224814
```

Sum of electronic and thermal Enthalpies= -768.223870
Sum of electronic and thermal Free Energies= -768.284139

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	184.268	58.983	126.848

C,0,-2.6624030289,0.5803636192,-0.4495864938
C,0,-2.4855733707,0.0751043511,0.9640402431
C,0,-1.2654514313,0.5373162143,1.3945966267
C,0,-0.5736908443,1.1456635872,0.2729743833
C,0,-1.340132358,1.1095186475,-0.8350981247
C,0,-2.2909697432,-1.9455466563,0.2481405149
C,0,-1.23651444,-1.8876781547,-0.6270864877
C,0,0.1145983206,-1.7968376951,-0.1972889977
C,0,0.5284969546,-1.7356350659,1.0911361681
C,0,2.0087030138,-1.5610901808,1.1918545335
C,0,2.4130587339,-1.1495109814,-0.2295460088
C,0,1.2890796474,-1.6683987086,-1.1322363994
H,0,0.4207978749,1.5533229108,0.3493205965
O,0,-3.6865734241,0.579403595,-1.0848192057
H,0,1.082648278,-1.0062439139,-1.9719803868
H,0,2.4530017615,-0.0627324185,-0.2902504119
H,0,3.3929554388,-1.524049112,-0.5153528103
H,0,2.472097864,-2.5070492022,1.4892108438
H,0,2.2963477061,-0.8282394357,1.945135596
H,0,-0.0960906987,-1.9131988527,1.9525852732
H,0,1.5327067307,-2.6474918271,-1.5512493059
H,0,-1.4378380399,-1.8254499461,-1.6878749762
H,0,-3.2962328657,-2.0369272433,-0.1352004932
H,0,-2.1407531211,-2.2731515945,1.2655835104
C,0,-0.8181097793,0.4860337692,2.7791936099
H,0,-3.3145221753,-0.170336303,1.6068707066
H,0,-1.1095316887,1.4899530358,-1.8146257388
O,0,0.2823941671,1.2152227593,2.9894898194
O,0,-1.3718518985,-0.1338250449,3.6563987916
C,0,0.7503289203,1.2417259142,4.3262033873
H,0,1.6302220897,1.873816408,4.3183012156
H,0,-0.0066968648,1.6543031992,4.9868138981
H,0,1.0032262711,0.240985326,4.6651371229

Isopropylidenecyclohexene (43)

E(RB+HF-LYP) = -352.623453654

```
Zero-point correction=                       0.230157 (Hartree/Particle)
Thermal correction to Energy=                  0.240133
Thermal correction to Enthalpy=                0.241077
Thermal correction to Gibbs Free Energy=         0.194920
Sum of electronic and zero-point Energies=          -352.393297
Sum of electronic and thermal Energies=            -352.383321
Sum of electronic and thermal Enthalpies=           -352.382377
Sum of electronic and thermal Free Energies=         -352.428533

              E (Thermal)          CV              S
               KCal/Mol       Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total            150.686           37.906          97.145
```

```
C,0,-0.2258543011,-0.7477728634,0.1989320411
C,0,-0.1005862677,-0.1748982275,1.4175514656
C,0,1.1516785767,-0.2385755239,2.2678026394
C,0,-1.1968124518,0.6073263973,2.1115537768
C,0,-1.476152298,-0.6787803885,-0.6621467708
C,0,-1.1806640256,-0.0693998024,-2.049827121
H,0,-1.8542868199,-1.7031069921,-0.8112680363
H,0,-2.2829160636,-0.1210924442,-0.1834870476
C,0,-0.0560627948,-0.8254391458,-2.7712763388
H,0,-2.0942804246,-0.0747974878,-2.6578323684
H,0,-0.8905934838,0.9828334749,-1.922262196
C,0,1.1979282398,-0.9262938271,-1.8914179152
H,0,-0.4048370865,-1.8392535475,-3.0182474196
H,0,0.1833827175,-0.3369519061,-3.7241453717
C,0,0.8733586692,-1.5253186725,-0.5057263274
H,0,1.9633457144,-1.5364539377,-2.387633613
H,0,1.6298753071,0.0748194303,-1.7542842514
H,0,0.5286097418,-2.5616651989,-0.6527203645
H,0,1.7872192429,-1.5878025539,0.0875394762
H,0,1.5107093878,0.7746380217,2.4947806026
H,0,0.933198221,-0.7108919911,3.2355098756
H,0,1.9766225248,-0.7865797639,1.8124987717
H,0,-0.8547867782,1.6270719983,2.3355154823
H,0,-2.1219702934,0.6875554922,1.5407692894
H,0,-1.4420682538,0.1463844594,3.078320721
```

Intermediate 46

E(RB+HF-LYP) = -505.600766372

```
Zero-point correction=                      0.278901 (Hartree/Particle)
Thermal correction to Energy=                    0.292403
Thermal correction to Enthalpy=                  0.293347
Thermal correction to Gibbs Free Energy=         0.239572
Sum of electronic and zero-point Energies=          -505.321865
Sum of electronic and thermal Energies=             -505.308363
Sum of electronic and thermal Enthalpies=           -505.307419
Sum of electronic and thermal Free Energies=        -505.361194

               E (Thermal)           CV              S
                KCal/Mol       Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total              183.486           51.952          113.179

C,0,1.2238249684,-0.4358322459,-1.7464573964
C,0,1.0470921677,-1.4199979703,-0.495306405
C,0,-0.2296488208,-1.0198197766,0.0936068328
C,0,-1.4173601466,-1.2583801447,-0.741793802
C,0,-1.27445124,-0.4288375383,-2.092374421
C,0,0.0886463315,-0.6552673296,-2.7412964256
C,0,-0.3340916881,-0.3815169323,1.4408854158
C,0,-1.3060915768,0.8423493911,1.400939674
C,0,-2.148233055,1.159430253,2.6091783761
C,0,0.9983365548,0.1299594461,2.0374104913
C,0,-0.8737719191,-1.573351619,2.3188237484
O,0,-1.2971017893,1.5398186531,0.403766275
H,0,-1.4380452994,-2.317978544,-1.0294667596
H,0,-2.354090089,-0.9958559492,-0.2494281818
H,0,-2.0945665832,-0.7524866193,-2.7386271128
H,0,-1.4257002358,0.6246698891,-1.8484106055
H,0,0.1530613847,-1.6644282352,-3.1662105609
H,0,0.2044953378,0.0473511492,-3.5755761216
H,0,2.2069963616,-0.6724271935,-2.1631873524
H,0,1.2512462255,0.6019262316,-1.3997003371
H,0,0.9966172635,-2.4306217624,-0.9138213698
H,0,1.8983633877,-1.3312898982,0.1763826853
H,0,-0.1978748186,-2.4324501904,2.2805086609
H,0,-0.904457307,-1.2289247112,3.3560235971
H,0,-1.8741429501,-1.895206573,2.0227027468
H,0,1.6930976084,-0.690842967,2.2351651799
H,0,1.4789730867,0.8606425145,1.3819671253
H,0,0.80530312,0.6205782528,2.9949628814
H,0,-2.9541425455,0.4230357796,2.7138472388
H,0,-1.5646223135,1.1280626699,3.5349644093
H,0,-2.5862044203,2.1502329704,2.4836575133
```

Intermediate 47

E(RB+HF-LYP) = -505.600366433

```
Zero-point correction=                           0.278001 (Hartree/Particle)
Thermal correction to Energy=                    0.291644
Thermal correction to Enthalpy=                  0.292588
Thermal correction to Gibbs Free Energy=         0.238692
Sum of electronic and zero-point Energies=           -505.322366
Sum of electronic and thermal Energies=              -505.308723
Sum of electronic and thermal Enthalpies=            -505.307779
Sum of electronic and thermal Free Energies=         -505.361674

                E (Thermal)          CV                S
                 KCal/Mol       Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total             183.009           52.362           113.432
```

C,0,0.9098862366,-1.6296149014,-0.3771597166
C,0,-0.2705236143,-1.0400557277,0.4235188977
C,0,-1.510009782,-0.9023905144,-0.5102224077
C,0,-1.180122317,-0.0225203136,-1.7315958945
C,0,0.0331070165,-0.5505740288,-2.5079150905
C,0,1.2479982655,-0.7356861944,-1.5891339627
C,0,0.0111051492,0.0809526309,1.3022951804
C,0,-1.0835939367,0.9634467788,1.7507731383
C,0,1.3535622635,0.3426856685,1.8720865437
H,0,-1.7800276827,-1.9072237042,-0.855656754
H,0,-2.3745797813,-0.5242829774,0.0369786058
H,0,-2.0633300403,0.0169512337,-2.3777413627
H,0,-0.9882407736,1.0097976802,-1.4065053447
H,0,-0.2214580721,-1.5133987499,-2.9708471082
H,0,0.2813897285,0.1316762873,-3.3271554572
H,0,2.0787877278,-1.1900908096,-2.1384454101
H,0,1.6068126837,0.2432576209,-1.2411684112
H,0,0.6084978919,-2.6138997538,-0.7506547945
H,0,1.7995708755,-1.7885741892,0.2360534164
H,0,1.7199750208,1.2750833837,1.4092530185
H,0,1.2799093555,0.5721153143,2.9418674505
H,0,2.0964661469,-0.4316286751,1.6936282938
H,0,-1.5618177939,1.4563072669,0.8949372285
H,0,-1.8794251437,0.3338198369,2.1869913584
H,0,-0.7617714515,1.7105263569,2.4763378027
C,0,-0.8177058459,-2.1447504352,1.6434798701

O,0,-1.8655160269,-1.9228258627,2.1664269927
C,0,0.0408861296,-3.3569308615,1.8761462101
H,0,1.0843842522,-3.0811079758,2.0460675898
H,0,-0.3607945484,-3.892104868,2.7378901438
H,0,0.0104000665,-4.0115985162,0.9994629735

Transition Structure 48

E(RB+HF-LYP) = -505.600020244

```
Zero-point correction=                      0.275064 (Hartree/Particle)
Thermal correction to Energy=                  0.287758
Thermal correction to Enthalpy=                0.288702
Thermal correction to Gibbs Free Energy=         0.237103
Sum of electronic and zero-point Energies=          -505.324957
Sum of electronic and thermal Energies=             -505.312262
Sum of electronic and thermal Enthalpies=           -505.311318
Sum of electronic and thermal Free Energies=          -505.362918

              E (Thermal)          CV              S
               KCal/Mol      Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total            180.571           50.148         108.601
```

C,0,1.1282402045,-0.6036359652,-2.0772655743
C,0,1.2088940666,-0.695068966,-0.5445342978
C,0,-0.0492005368,-0.302488795,0.1758109466
C,0,-1.2659603738,-0.2736110428,-0.5118890518
C,0,-1.3774787051,-0.454007539,-2.0166105106
C,0,-0.1778305201,-1.2023569143,-2.6075894784
C,0,-0.0654645274,-0.2433225189,1.6945631179
C,0,-0.8286430953,-1.5479721615,2.1663723326
C,0,-0.6531462703,-2.0432559862,3.5696080337
C,0,-0.9130140801,0.9530969043,2.2370847904
C,0,1.3414150615,-0.1810457288,2.3268654044
O,0,-1.5801526218,-2.1365516653,1.392410007
H,0,-1.4218769287,-1.3635484561,0.1544503063
H,0,-2.1055698326,0.2415411209,-0.0422661677
H,0,-2.318136504,-0.9680441209,-2.2414004773
H,0,-1.4656485982,0.5440913609,-2.4660214923
H,0,-0.2345059145,-2.2675109481,-2.3457783165
H,0,-0.2089719443,-1.1482658688,-3.6994117248
H,0,1.996964127,-1.1114842248,-2.5057677244
H,0,1.2001742768,0.4483225462,-2.3801062031
H,0,1.4754586836,-1.7172266658,-0.2288654194

H,0,2.024735182,-0.0705663858,-0.1604942861
H,0,1.8573398165,0.7260111858,2.0005145829
H,0,1.2679219166,-0.129386183,3.4141576238
H,0,1.964606995,-1.0414155459,2.0715948808
H,0,-0.4864774419,1.8903364444,1.8695747845
H,0,-1.9621408897,0.9093224011,1.9391324357
H,0,-0.8742590048,0.9764001638,3.3283267458
H,0,0.3240680244,-2.5348224582,3.6525706279
H,0,-0.6644228985,-1.2259866749,4.2946745019
H,0,-1.4340466665,-2.7684683121,3.7989956023

Structure 49‡

E(RB+HF-LYP) = -505.561484174

```
Zero-point correction=                     0.279399 (Hartree/Particle)
Thermal correction to Energy=                0.293848
Thermal correction to Enthalpy=              0.294793
Thermal correction to Gibbs Free Energy=        0.238426
Sum of electronic and zero-point Energies=         -505.282085
Sum of electronic and thermal Energies=           -505.267636
Sum of electronic and thermal Enthalpies=          -505.266692
Sum of electronic and thermal Free Energies=        -505.323058

              E (Thermal)          CV              S
               KCal/Mol       Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total            184.393           53.104          118.633
```

C,0,0.0356405286,-0.5804955036,-2.6939055922
C,0,1.2600752269,-0.7530552114,-1.7877362915
C,0,0.9085740646,-1.5704431827,-0.509618549
C,0,-0.2321728067,-0.8842347223,0.2031353422
C,0,-1.4750457765,-0.8118244228,-0.6513155839
C,0,-1.1514987692,0.0165688232,-1.9285811942
C,0,-0.0905467591,-0.1446890588,1.3827707549
C,0,1.22051493,0.020034757,2.108412314
C,0,-0.9633494935,-2.2923555705,2.003851185
O,0,-2.1122042506,-2.200602642,2.1249569136
C,0,-1.1967672337,0.7527039735,1.886256537
C,0,0.1453524145,-3.2002059679,2.3746436462
H,0,-1.761008035,-1.8240977626,-0.9663240943
H,0,-2.3275946743,-0.377531194,-0.1277992439
H,0,-2.0483623713,0.0455808377,-2.5560546212
H,0,-0.9317817087,1.0532234558,-1.6412821172

```
H,0,-0.2509876976,-1.5556347344,-3.1110793658
H,0,0.2912044858,0.0601996902,-3.5450701277
H,0,2.0695746021,-1.2692863851,-2.3144872671
H,0,1.6503497858,0.2277579865,-1.4868714351
H,0,0.586663256,-2.5706726284,-0.8309505198
H,0,1.8008541915,-1.689345015,0.1083157325
H,0,1.5934654554,1.0362456276,1.9169513753
H,0,1.0803785364,-0.0439128792,3.1937231058
H,0,2.0040127455,-0.6752118074,1.8059597682
H,0,-1.2821508781,1.6318374104,1.2338785503
H,0,-2.1764651627,0.2668561329,1.8924713962
H,0,-0.983751787,1.1127573045,2.8958047231
H,0,0.6513371224,-3.5534895598,1.4720239351
H,0,0.870475657,-2.6603586245,2.9901794703
H,0,-0.2776395985,-4.0424731269,2.9321922531
```

Transition Structure 50‡

E(RB+HF-LYP) = -505.551359159

```
Zero-point correction=                     0.278001 (Hartree/Particle)
Thermal correction to Energy=                 0.292274
Thermal correction to Enthalpy=               0.293218
Thermal correction to Gibbs Free Energy=        0.236542
Sum of electronic and zero-point Energies=          -505.273358
Sum of electronic and thermal Energies=            -505.259085
Sum of electronic and thermal Enthalpies=          -505.258141
Sum of electronic and thermal Free Energies=         -505.314817

              E (Thermal)        CV              S
               KCal/Mol     Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total            183.405          51.745        119.286
```

```
C,0,0.043646023,-0.6710038333,-2.6843490223
C,0,1.2437596827,-0.8727657954,-1.7511694236
C,0,0.8264237597,-1.6058806464,-0.4455431962
C,0,-0.2919422315,-0.8430187489,0.2282076407
C,0,-1.508382859,-0.7190372865,-0.6626025877
C,0,-1.1157884909,0.029870706,-1.9661560123
C,0,-0.1538710798,-0.1246021433,1.4070751875
C,0,1.1316055941,-0.0400836611,2.1933006281
C,0,-1.3454797417,-2.5320109703,2.1973071847
O,0,-2.4604420273,-2.2777249347,2.2631737449
C,0,-1.2466586826,0.7953919273,1.9078442708
```

```
C,0,-0.1958252062,-3.3917629021,2.4692634274
H,0,-1.8611403539,-1.7217004214,-0.9445428592
H,0,-2.3397179524,-0.2063726758,-0.1753988165
H,0,-1.9963116072,0.0912445855,-2.6146839802
H,0,-0.8327918866,1.0607801907,-1.7157452188
H,0,-0.2954386069,-1.6469715107,-3.0594243074
H,0,0.3476728939,-0.0887697906,-3.5613607563
H,0,2.0302189537,-1.4540171942,-2.2447334313
H,0,1.6827123337,0.0980432351,-1.4870822645
H,0,0.4632266613,-2.6051021752,-0.7311928286
H,0,1.7007662759,-1.7445301303,0.1944456715
H,0,1.557577316,0.9662939685,2.0745800677
H,0,0.9452667428,-0.1525972569,3.2689497993
H,0,1.8999215592,-0.7526389483,1.8902310221
H,0,-1.296571042,1.7005339596,1.2880042274
H,0,-2.2421293471,0.3405308639,1.8778348509
H,0,-1.0507384099,1.1185992534,2.9337674857
H,0,0.27283216,-3.6738091056,1.5209744598
H,0,0.5304703695,-2.8312583145,3.0672222254
H,0,-0.5464978006,-4.2791222445,3.0123708111
```

Aldehyde 59

E(RB+HF-LYP) = -804.686698943

```
Zero-point correction=                           0.248248 (Hartree/Particle)
Thermal correction to Energy=                    0.265091
Thermal correction to Enthalpy=                  0.266035
Thermal correction to Gibbs Free Energy=         0.200446
Sum of electronic and zero-point Energies=            -804.438451
Sum of electronic and thermal Energies=               -804.421608
Sum of electronic and thermal Enthalpies=             -804.420664
Sum of electronic and thermal Free Energies=          -804.486253

              E (Thermal)         CV                S
               KCal/Mol    Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total            166.347          60.428           138.044

C,0,0.2342922446,-0.5337463178,-0.354846681
O,0,0.5634670918,-0.8204116937,0.7839183559
H,0,0.9933505209,-0.4186744667,-1.1497359714
C,0,-1.1722730605,-0.3195580029,-0.7681212534
C,0,-1.5144942082,0.0124627306,-2.099649692
O,0,-0.4794852089,0.1237694916,-2.9803232407
```

```
C,0,-0.7559894828,0.4908152017,-4.3334080251
C,0,0.5550089009,0.6328562875,-5.040249272
H,0,-1.3909635749,-0.2645001213,-4.8153296401
H,0,-1.2955295377,1.4508500334,-4.3483074465
C,0,0.8247666613,0.0952925093,-6.2331492449
H,0,1.3132022139,1.2404942248,-4.5501502155
C,0,2.1346952707,0.3324747193,-6.8916320318
H,0,0.1111290862,-0.5305053137,-6.7624833468
O,0,3.0352174591,1.0148966021,-6.4445263342
O,0,2.1981019684,-0.3225535229,-8.0720805661
C,0,3.4351721575,-0.1757809679,-8.8071056869
C,0,-2.1897230651,-0.4487118694,0.1862490612
C,0,-3.5244342854,-0.2572908697,-0.1528870082
C,0,-3.849026751,0.0678767781,-1.471859595
C,0,-2.8580626327,0.2030828145,-2.4459922583
H,0,-1.89123183,-0.7035104988,1.1986779083
H,0,-4.304276626,-0.3598602749,0.5954964323
H,0,-4.8874672947,0.2190661289,-1.754954845
H,0,-3.1415806018,0.4523743456,-3.4616365273
C,0,3.3046582554,-0.9797680323,-10.0867418906
H,0,3.6030097828,0.8882449075,-9.0030127593
H,0,4.2597651475,-0.5291156468,-8.1796045612
H,0,4.2256988262,-0.8945216847,-10.6734956975
H,0,3.132324973,-2.0385039077,-9.868254982
H,0,2.4727005994,-0.6133345836,-10.6967039848
```

Carbene catalysis 59b

E(RB+HF-LYP) = -860.361158002

```
Zero-point correction=                           0.314608 (Hartree/Particle)
Thermal correction to Energy=                    0.331063
Thermal correction to Enthalpy=                  0.332007
Thermal correction to Gibbs Free Energy=         0.267889
Sum of electronic and zero-point Energies=            -860.046550
Sum of electronic and thermal Energies=               -860.030095
Sum of electronic and thermal Enthalpies=             -860.029151
Sum of electronic and thermal Free Energies=          -860.093269

              E (Thermal)         CV                S
               KCal/Mol     Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total           207.745          65.729          134.949
```

```
C,0,0.2377646191,-0.849795022,2.0027173704
```

```
C,0,-0.9976175956,-0.2299570909,1.8128978433
C,0,-2.0771446164,-0.9838114142,1.3455060597
C,0,-1.9295001428,-2.3408258481,1.0695273058
C,0,-0.6852980399,-2.9520472043,1.2642403415
C,0,0.4022583894,-2.2083557647,1.7313508785
N,0,-0.5380661233,-4.3409156984,0.9834066194
N,0,0.7205007829,-4.9373716567,1.1760794013
C,0,0.4860705495,-6.1633425706,0.8216294373
C,0,1.2322691527,-7.4577954685,0.7438029885
C,0,-1.1507042542,-7.7025722262,0.0484838377
C,0,0.2683466009,-8.3169480194,-0.1294999247
C,0,-2.0626986421,-7.7573114377,-1.1872902524
C,0,-2.4993987667,-9.1664196926,-1.528576266
C,0,-1.8860628084,-9.8861632594,-2.5622373791
C,0,-2.2745875964,-11.1949257265,-2.8548076008
C,0,-3.2871039464,-11.8065982082,-2.1149413345
C,0,-3.9103315791,-11.0993841833,-1.0843676557
C,0,-3.519648237,-9.791742172,-0.7967277217
N,0,-0.8219725437,-6.3246963021,0.4303376597
C,0,-1.5290606587,-5.1625214619,0.5252935925
H,0,-1.666507751,-8.1815916058,0.8910958964
H,0,1.3580028642,-2.6964961574,1.8764136422
H,0,1.086123562,-0.2755635549,2.3657374985
H,0,-1.1191441745,0.8283980901,2.0263528361
H,0,-3.0451747415,-0.5138424811,1.1929376642
H,0,-2.7552657799,-2.9410178683,0.7061355655
H,0,2.2277822642,-7.354833857,0.3037678147
H,0,1.3593330829,-7.886026259,1.7462573922
H,0,0.2896586746,-9.3766999933,0.1334951798
H,0,0.5623092355,-8.2316841392,-1.1819554855
H,0,-2.9313806968,-7.1212752536,-0.9814240761
H,0,-1.5328741826,-7.3033599017,-2.0334421414
H,0,-1.1023299368,-9.4136102455,-3.1503728091
H,0,-1.7887516625,-11.7336827903,-3.6642003314
H,0,-3.5932596299,-12.8239867986,-2.3429975673
H,0,-4.7061820466,-11.5640174879,-0.5080899744
H,0,-4.018422625,-9.2438922688,0.000303695
```

Product 60

E(RB+HF-LYP) = -804.730198009

```
 Zero-point correction=                           0.251388 (Hartree/Particle)
 Thermal correction to Energy=                    0.266806
```

```
Thermal correction to Enthalpy=                   0.267750
Thermal correction to Gibbs Free Energy=          0.206601
Sum of electronic and zero-point Energies=               -804.478810
Sum of electronic and thermal Energies=                  -804.463392
Sum of electronic and thermal Enthalpies=                -804.462448
Sum of electronic and thermal Free Energies=             -804.523597

                E (Thermal)         CV              S
                 KCal/Mol      Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total              167.423          57.697        128.700

C,0,0.075293942,0.1395574433,0.1911274209
C,0,0.1543457128,0.1332350978,1.5952273326
C,0,1.379802623,0.0421574269,2.2369832136
C,0,2.5531018393,-0.0499695861,1.4711389272
C,0,2.5032823296,-0.0357999387,0.0824414393
C,0,1.2643729549,0.0686146023,-0.5632414883
H,0,-0.7767408844,0.1873244437,2.1509267696
H,0,1.4335886763,0.03504329,3.3214193309
H,0,3.5173956402,-0.1258825455,1.9668191478
H,0,3.4028832721,-0.0924360315,-0.5219057108
O,0,1.2715267621,0.0845281075,-1.9227497614
C,0,-1.2402944542,0.145860113,-0.4840158232
O,0,-2.2988815603,0.2317014843,0.1230385717
C,0,-1.1863963649,-0.0223294804,-2.0056930965
C,0,-2.4484645774,0.5216261262,-2.675443368
H,0,-1.1231121491,-1.1029026177,-2.2034717535
C,0,0.0938554858,0.6138387189,-2.5470110864
H,0,0.2100706057,0.4086530576,-3.6117829337
H,0,0.0743494972,1.7035682415,-2.3885148997
H,0,-3.3212570205,0.2400978631,-2.0756746268
C,0,-2.6392780254,0.0117719531,-4.0903961736
H,0,-2.4521071917,1.6192420463,-2.6935685624
O,0,-3.7093959278,0.5922446807,-4.6680277833
O,0,-1.9387363121,-0.8123992203,-4.6428391891
C,0,-4.0120460109,0.1694904489,-6.019793105
C,0,-5.2298659129,0.9489862569,-6.478117587
H,0,-3.1383629283,0.3593708981,-6.6514169128
H,0,-4.1903524034,-0.9105576092,-6.017898896
H,0,-5.4942777167,0.6563686011,-7.5000801963
H,0,-6.0888246652,0.7502179922,-5.8293699182
H,0,-5.0323242356,2.0256811361,-6.4681732816
```

Transition Structure 61

E(RB+HF-LYP) = -1665.03394722

```
Zero-point correction=                           0.564936 (Hartree/Particle)
Thermal correction to Energy=                    0.598678
Thermal correction to Enthalpy=                  0.599622
Thermal correction to Gibbs Free Energy=         0.494200
Sum of electronic and zero-point Energies=           -1664.469011
Sum of electronic and thermal Energies=              -1664.435269
Sum of electronic and thermal Enthalpies=            -1664.434325
Sum of electronic and thermal Free Energies=         -1664.539747

               E (Thermal)           CV                S
                KCal/Mol       Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total             375.676          128.705           221.880
```

```
C,0,3.854262186,-1.3680482862,0.1915969533
C,0,4.5152505171,-0.5323821545,-0.7204954974
C,0,5.909847022,-0.6279686701,-0.8228078378
C,0,6.6291893717,-1.5274088575,-0.0333569887
C,0,5.9604443688,-2.348100353,0.8751759091
C,0,4.5703295731,-2.2660959079,0.983158462
C,0,3.7418716306,0.4580150129,-1.5664294957
C,0,3.2538307971,1.6963305078,-0.7771426681
C,0,4.3883205467,2.5823145993,-0.1797720476
C,0,4.660285871,3.7136392453,-1.2141275444
C,0,3.345256749,3.7804767666,-1.9204394343
N,0,2.5978498749,2.6579144073,-1.6782891941
C,0,1.3926403001,2.7646485084,-2.2979033041
N,0,1.5128925047,3.9594852852,-2.9320284814
N,0,2.7219114215,4.6190589117,-2.6927128355
C,0,0.5437544125,4.5990493377,-3.7552787964
C,0,-0.3091086602,3.8246070689,-4.5442595941
C,0,-1.2514946509,4.4590592542,-5.3537741853
C,0,-1.3323069304,5.8521274843,-5.3835627777
C,0,-0.4663144583,6.614938933,-4.5964878343
C,0,0.4747465834,5.9948244741,-3.7775163464
C,0,-0.1464991914,2.2377535417,-1.4117591447
O,0,-0.0297459985,2.8761569193,-0.3230143303
C,0,-0.1183629773,0.7040015089,-1.3504904868
C,0,-0.3152389432,-0.1462142606,-2.4565528752
C,0,-0.2911394402,-1.5375296384,-2.295009895
C,0,-0.1318692281,-2.0900829052,-1.0204521225
C,0,0.0059554776,-1.2621256857,0.0910540984
```

```
C,0,0.0160820292,0.1234117898,-0.0892080623
O,0,-0.5333983848,0.4634328342,-3.6723596049
C,0,-0.9535689745,-0.3505334591,-4.7662654116
C,0,-1.5601941404,0.5297820951,-5.8152530678
C,0,-1.2061690722,0.4990704143,-7.1048100245
C,0,-1.8471099238,1.2866514545,-8.1850662793
O,0,-1.5078746368,1.2168533332,-9.3497438688
O,0,-2.8513935232,2.0820556781,-7.744167482
C,0,-3.5315238178,2.8542690105,-8.7619902399
C,0,-4.6756587761,3.5912342794,-8.0919951895
H,0,6.5166402193,-3.0504885867,1.4901736038
H,0,4.0403372604,-2.9079298039,1.6822327575
H,0,2.7710431493,-1.3225802228,0.2701762128
H,0,6.4377587841,0.0011770205,-1.5368086847
H,0,4.3672821315,0.7999542145,-2.4009817092
H,0,2.5371777328,1.397250429,-0.0107052724
H,0,4.0324544479,3.0285490755,0.7537469565
H,0,4.9321581266,4.6629004606,-0.7460473353
H,0,5.4624623988,3.4502007806,-1.9148075772
H,0,1.1527742865,6.5728781248,-3.1609542355
H,0,-0.5242181889,7.6996697186,-4.6150960439
H,0,-2.0622007433,6.3433285939,-6.0213561509
H,0,-1.9057417579,3.8566934574,-5.9773463457
H,0,-0.2187938489,2.744449141,-4.5281882569
H,0,-0.8709087048,2.5848022688,-2.1768874912
H,0,0.1049412729,0.8117797395,0.7466630934
H,0,0.0944189558,-1.68761086,1.0873610836
H,0,-0.1286793552,-3.1712407699,-0.9086351766
H,0,-0.3962047206,-2.1999813979,-3.1467395677
H,0,-0.109229635,-0.9273615619,-5.1687232852
H,0,-1.7170919677,-1.063919988,-4.4209377032
H,0,-2.3624793019,1.1842312262,-5.4830756493
H,0,-0.4031732732,-0.142530205,-7.4583701843
H,0,-3.8828438519,2.1718123789,-9.5419009931
H,0,-2.8119084158,3.5393279802,-9.2219245763
H,0,-4.309453852,4.2702277672,-7.3149821018
H,0,-5.2190199501,4.183728558,-8.8361111903
H,0,-5.3781315767,2.8889584951,-7.6319401968
H,0,7.7098373433,-1.5886310319,-0.1325456975
H,0,5.2797758931,1.995106104,0.0491506992
H,0,2.8599146327,-0.0235565838,-2.0048574561
```

Intermediate 62

E(RB+HF-LYP) = -1665.05258135

```
Zero-point correction=                           0.567140 (Hartree/Particle)
Thermal correction to Energy=                    0.600568
Thermal correction to Enthalpy=                  0.601512
Thermal correction to Gibbs Free Energy=         0.498421
Sum of electronic and zero-point Energies=           -1664.485441
Sum of electronic and thermal Energies=              -1664.452014
Sum of electronic and thermal Enthalpies=            -1664.451069
Sum of electronic and thermal Free Energies=         -1664.554161

                E (Thermal)         CV                S
                 KCal/Mol      Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total             376.862         129.071          216.974
```

```
C,0,0.80891029,0.8318467184,-1.5760277086
N,0,0.5817304695,0.5336481926,-0.2570074956
C,0,1.277044318,-0.5850169522,0.0518365758
N,0,1.8990006936,-0.9119555698,-1.1040843679
N,0,1.6052203076,-0.0279625711,-2.1407404593
C,0,-0.2094186719,1.5590019653,0.4566500984
C,0,1.5475642979,-1.169850264,1.4313741124
O,0,2.5543753233,-0.4032425542,1.8925523124
C,0,2.8733672589,-1.9365214819,-1.3236825633
C,0,0.2722080122,-1.205088243,2.2977511009
C,0,-0.9149423748,-1.8338868837,1.8825021512
O,0,-0.8552238008,-2.4330757706,0.635829672
C,0,-2.0624712052,-2.7881963535,-0.030715729
C,0,-2.788070701,-1.575961737,-0.5389048546
C,0,-4.1099466683,-1.3809192972,-0.5122055499
C,0,-4.6969774536,-0.1416606168,-1.077502192
O,0,-6.0439151282,-0.1785152928,-1.015883738
O,0,-4.0685538905,0.7961891415,-1.5366392722
C,0,0.6698948779,2.3988526734,1.4158297857
H,0,-0.9773273857,1.0574447746,1.04909988
C,0,-0.8378614683,2.3206386909,-0.7512598552
H,0,1.8038342919,-2.2413190835,1.2487271454
C,0,0.3234926661,-0.6452596114,3.5713500997
C,0,-2.0409038901,-1.8490848272,2.7099862745
H,0,-2.7042129839,-3.419922244,0.5964664394
H,0,-1.7294400915,-3.3991848684,-0.8783451417
H,0,-2.1597615038,-0.8083204028,-0.9869543689
H,0,-4.7990065124,-2.1036797258,-0.0834406978
```

```
C,0,-6.7365274871,0.9823866288,-1.5319564475
C,0,-0.7873989546,-0.6730353466,4.4194667454
H,0,1.267387516,-0.1920724968,3.8606862455
H,0,-0.7313132153,-0.2311014135,5.4106208733
C,0,-1.9683904007,-1.2668050385,3.9805949774
H,0,-2.9690891162,-2.3067584157,2.3867415257
H,0,-2.846007856,-1.2866526134,4.6217871746
C,0,2.8455127834,-2.6461032783,-2.525955975
C,0,3.8176181411,-3.6167546775,-2.7604007309
C,0,4.7992212844,-3.8751162459,-1.800418968
C,0,4.8143105916,-3.1514687376,-0.6064356946
C,0,3.8589518042,-2.1652117033,-0.3579283896
H,0,2.0794683041,-2.4267494672,-3.2617729528
H,0,3.8052322904,-4.1729253437,-3.6935921552
H,0,5.5532951112,-4.6350676845,-1.9864098923
H,0,5.5829701213,-3.3430960399,0.1370418087
H,0,3.8600703094,-1.5689485849,0.5561780332
C,0,0.0927328493,2.0807819881,-1.9778532036
H,0,-0.4633046913,1.9598763203,-2.9114808621
H,0,0.8120849735,2.8953164175,-2.1118135807
H,0,-0.9503227388,3.3841499361,-0.5307411289
H,0,-1.8313451692,1.9120610962,-0.9598140652
H,0,1.0995658182,1.7076449801,2.1467109435
C,0,1.7852459189,3.1866862998,0.7608596145
H,0,-0.0147594859,3.0727408631,1.946510759
C,0,3.0402256225,2.5870213808,0.5662518185
C,0,4.069217484,3.2966775701,-0.0559060433
C,0,3.8668159431,4.6105194926,-0.4838541463
C,0,2.6282545026,5.2210660082,-0.2763035433
C,0,1.5976355884,4.5131094992,0.3450917763
H,0,3.1943480194,1.5689251446,0.924435501
H,0,5.0365927353,2.8219107343,-0.1995340169
H,0,4.6719225538,5.1603159861,-0.9647408276
H,0,2.4667852845,6.2500288653,-0.5881591779
H,0,0.6422136311,5.0032717922,0.5242560574
C,0,-8.2242080966,0.7359791357,-1.3686823068
H,0,-6.4007268464,1.865226896,-0.9784372382
H,0,-6.4533791677,1.1220183044,-2.5802086777
H,0,-8.785876824,1.5957367007,-1.7496016723
H,0,-8.5371695518,-0.1535531793,-1.9246047823
H,0,-8.4844893184,0.5939676632,-0.3149640584
```

Transition structure for proton transfer

E(RB+HF-LYP) = -1664.97649539

```
Zero-point correction=                           0.561609 (Hartree/Particle)
Thermal correction to Energy=                    0.595505
Thermal correction to Enthalpy=                  0.596449
Thermal correction to Gibbs Free Energy=         0.491992
Sum of electronic and zero-point Energies=           -1664.414886
Sum of electronic and thermal Energies=              -1664.380990
Sum of electronic and thermal Enthalpies=            -1664.380046
Sum of electronic and thermal Free Energies=         -1664.484504

            E (Thermal)        CV              S
             KCal/Mol      Cal/Mol-Kelvin  Cal/Mol-Kelvin
Total          373.685         130.166         219.850
```

```
C,0,0.4693193553,0.5992151749,2.304703461
N,0,0.7026137487,-0.556591719,1.6131984214
C,0,-0.4861020476,-1.0133470116,1.1075767605
N,0,-1.4036344257,-0.1017560029,1.5990323571
N,0,-0.7875140701,0.922011965,2.3302718881
C,0,2.13143298,-0.8854588811,1.4580732239
C,0,-0.6210787675,-2.2374589292,0.3832976583
O,0,0.5964296433,-3.0594001796,0.3488888466
C,0,-2.8189635684,-0.1027029104,1.5243239807
C,0,-1.5681468816,-2.4386165083,-0.7516776737
C,0,-2.0499582227,-1.4114501368,-1.5953329514
O,0,-1.5712594554,-0.147692121,-1.3458862527
C,0,-2.0411586336,0.9458462066,-2.1082757438
C,0,-1.2278231145,2.1645874262,-1.793193079
C,0,-0.1096244429,2.1485912213,-1.060322177
C,0,0.7204830264,3.3265158553,-0.7425702571
O,0,0.2566522827,4.4782143913,-1.2727263683
O,0,1.7346084908,3.2649961292,-0.0647317212
C,0,2.6203014073,-0.5847405189,0.0240600679
C,0,2.7490549351,0.0193351358,2.5649680335
H,0,-0.4851879967,-3.1593984495,1.1145325124
C,0,-1.9467243681,-3.7538022961,-1.0623024746
C,0,-2.9444435692,-1.6957697449,-2.6338876189
H,0,-3.1055519422,1.1342444129,-1.8951249257
H,0,-1.9609352277,0.7369023714,-3.1877259714
H,0,-1.5911529617,3.0966351888,-2.2201996436
H,0,0.2601865639,1.2197184548,-0.6468379322
C,0,1.0333434003,5.6645081022,-0.9906638356
```

```
C,0,-2.8113714882,-4.0503873115,-2.1121207079
H,0,-1.5326602028,-4.5546346159,-0.4565833155
H,0,-3.0871540178,-5.0811763133,-2.3156439558
C,0,-3.324985102,-3.0133148095,-2.8893059147
H,0,-3.339447513,-0.9000775268,-3.2552112835
H,0,-4.0167795705,-3.2208161427,-3.70124748
C,0,-3.4956468467,1.1249724408,1.5315570593
C,0,-4.8876625893,1.1425866881,1.4971214598
C,0,-5.6132276477,-0.0511496886,1.4547035098
C,0,-4.9314510908,-1.268207035,1.4570460925
C,0,-3.537880458,-1.3028742037,1.4969227949
H,0,-2.9232239185,2.0438773074,1.5760006219
H,0,-5.4076756734,2.096881569,1.5032936408
H,0,-6.6989060917,-0.0314611907,1.4232061194
H,0,-5.4829602804,-2.2039477069,1.4349305654
H,0,-3.0124602253,-2.2492929747,1.514397153
C,0,1.7552654104,1.1999264353,2.7796296033
H,0,1.7069585807,1.5375262176,3.8182193846
H,0,2.00222001,2.0625081789,2.1499392364
H,0,3.7483421479,0.3605434013,2.2858974093
H,0,2.8422866207,-0.5554035117,3.49236821
C,0,0.3471321218,6.8319315013,-1.674254051
H,0,1.089795823,5.7981379607,0.0944841176
H,0,2.0531917542,5.5131896816,-1.3585861033
H,0,0.9066837775,7.7541309272,-1.4836064302
H,0,0.2971148547,6.6776843378,-2.7569463746
H,0,-0.6718714656,6.9635197415,-1.2963194277
H,0,2.2535695915,-1.9497015849,1.651632842
C,0,4.01151514,-1.1248265724,-0.2255583205
H,0,1.9132739754,-1.0721618995,-0.6552585433
H,0,2.5867995003,0.4971291399,-0.1563336908
C,0,5.1301369722,-0.2832453239,-0.2624898484
C,0,6.4096980896,-0.8038774929,-0.471095526
C,0,6.5853914306,-2.1767942856,-0.6455958883
C,0,5.4749693057,-3.0250503396,-0.6150636032
C,0,4.1982272466,-2.5041720236,-0.4086687913
H,0,4.996553818,0.7896727971,-0.1389834078
H,0,7.2666146415,-0.1355094855,-0.5015386994
H,0,7.5796992568,-2.583814718,-0.810592765
H,0,5.6037349546,-4.0948634742,-0.7591556528
H,0,3.3288480197,-3.1580327212,-0.3944046242
```

Intermediate 63

E(RB+HF-LYP) = -1665.04806905

```
Zero-point correction=                           0.565672 (Hartree/Particle)
Thermal correction to Energy=                    0.599915
Thermal correction to Enthalpy=                  0.600859
Thermal correction to Gibbs Free Energy=         0.493413
Sum of electronic and zero-point Energies=           -1664.482397
Sum of electronic and thermal Energies=              -1664.448154
Sum of electronic and thermal Enthalpies=            -1664.447210
Sum of electronic and thermal Free Energies=         -1664.554656

              E (Thermal)        CV              S
               KCal/Mol     Cal/Mol-Kelvin  Cal/Mol-Kelvin
Total            376.452        131.452        226.139
```

```
C,0,4.690115149,-2.4579844809,-2.1173257153
C,0,5.1023134291,-3.7550618827,-2.4302157785
C,0,4.4045774683,-4.8517536635,-1.9236633426
C,0,3.2911463106,-4.6415532639,-1.106609716
C,0,2.8804503564,-3.3449681272,-0.7980665722
C,0,3.5762696222,-2.2327821465,-1.2975843269
C,0,3.140086577,-0.8303864306,-0.9358777303
C,0,3.4704398825,-0.4542161288,0.5286126617
C,0,4.979583317,-0.2152992578,0.8180011861
C,0,5.2278803576,1.3093573131,0.6319796017
C,0,3.838684903,1.8665146066,0.7101255195
N,0,2.9114846606,0.858086254,0.8871977456
N,0,3.3288843202,3.0309055542,0.5132104815
N,0,1.9308517155,2.8091091101,0.5344977305
C,0,1.1442150432,3.7878127836,-0.1209291682
C,0,0.208736387,3.4450661788,-1.1053435422
C,0,1.3608974531,5.1366708859,0.1914517909
C,0,-0.5216266453,4.4454326031,-1.7454063792
C,0,0.6358738843,6.1280002707,-0.4646494472
C,0,-0.3151291781,5.7893356885,-1.4306223371
C,0,1.6350894911,1.4431406734,0.7655763409
C,0,0.4203631802,0.865830549,1.0047787869
O,0,-0.7048521773,1.6816006206,0.958396788
C,0,0.2127678802,-0.5338021026,1.4151557268
C,0,0.9449881275,-1.1360171167,2.4514483132
C,0,0.7086794225,-2.4507607332,2.8579101886
C,0,-0.3016963912,-3.1891112602,2.2470573362
C,0,-1.0732593837,-2.6146627204,1.2303985431
```

```
C,0,-0.8151526466,-1.3081675279,0.8160400118
H,0,0.8106682546,7.1709788285,-0.2134740437
H,0,-0.8850604296,6.5646746824,-1.9352468647
H,0,2.1020163009,5.3903052178,0.9414423428
H,0,-1.2472371672,4.1701552995,-2.506902019
H,0,5.6725762681,1.5475704851,-0.3404974992
H,0,5.8913784675,1.720316257,1.3988316499
H,0,5.1945875107,-0.5006896223,1.8524382611
H,0,5.2341495919,-1.6080300401,-2.5242642984
H,0,5.9662858543,-3.9065671534,-3.0721738397
H,0,4.7222313017,-5.8622567219,-2.1664538992
H,0,2.737777628,-5.4898164081,-0.711791327
H,0,2.0070287861,-3.1929721597,-0.1674645748
H,0,5.609888389,-0.829871904,0.1707745415
H,0,3.0699180205,-1.2291809203,1.185429088
H,0,0.0692194541,2.4041274143,-1.3722465443
H,0,2.0553592345,-0.726873165,-1.0636245849
H,0,3.6091919385,-0.1000491907,-1.6074338287
H,0,1.6961849833,-0.5396598566,2.9609188901
H,0,1.2921598795,-2.8816588276,3.6665781942
H,0,-0.5116544624,-4.2068748444,2.563372838
H,0,-1.8669259738,-3.1977504007,0.777372888
O,0,-1.501187698,-0.6692952083,-0.2007433651
C,0,-2.5312049023,-1.3570814227,-0.9199779741
C,0,-3.841298428,-1.3486849807,-0.1879065128
H,0,-2.6151297029,-0.8248108002,-1.8714172812
H,0,-2.203486043,-2.3820322375,-1.1409947263
C,0,-4.9946007412,-0.9514963231,-0.7351172683
H,0,-3.8473603012,-1.6928222643,0.844475214
C,0,-6.259007961,-0.9991850184,0.0421657266
H,0,-5.0555874514,-0.5814590033,-1.7554536546
O,0,-6.3696655174,-1.4011177534,1.1837227042
O,0,-7.2888896132,-0.5293813759,-0.6962258673
C,0,-8.5784103944,-0.5165632167,-0.0414564116
C,0,-9.5863221866,0.0414784018,-1.0282384533
H,0,-8.8251098322,-1.5373154007,0.2683794424
H,0,-8.5056441901,0.0940487689,0.8642896581
H,0,-10.5797990968,0.0690320218,-0.5676582132
H,0,-9.3177372484,1.0592693383,-1.3287202029
H,0,-9.6406677594,-0.5808753085,-1.927254658
H,0,-1.3747372788,1.2116345645,0.4296277758
```

Transition Structure 64

E(RB+HF-LYP) = -1665.04089390

Zero-point correction= 0.566361 (Hartree/Particle)
Thermal correction to Energy= 0.598825
Thermal correction to Enthalpy= 0.599769
Thermal correction to Gibbs Free Energy= 0.500249
Sum of electronic and zero-point Energies= -1664.474533
Sum of electronic and thermal Energies= -1664.442069
Sum of electronic and thermal Enthalpies= -1664.441124
Sum of electronic and thermal Free Energies= -1664.540645

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	375.769	127.769	209.458

```
C,0,-1.432016333,2.1091778,-0.4798022177
C,0,-0.6217434575,1.7951354431,0.6252390938
C,0,-0.8262490217,2.4957435905,1.8228515219
C,0,-1.8593212623,3.4243320697,1.9378052146
C,0,-2.6902753032,3.6845035613,0.8436615629
C,0,-2.469890952,3.0358668106,-0.3704751937
C,0,0.5052710707,0.8383787227,0.4597708994
O,0,1.5684325139,1.0577404622,1.3502812832
O,0,-1.254165731,1.4558387461,-1.672979438
C,0,0.0612362466,1.4943330416,-2.2646384313
C,0,1.2478106697,1.5025502465,-1.3250310888
C,0,2.4158786609,0.8699746291,-1.7890841918
C,0,3.6695827349,1.1298693136,-1.171148763
O,0,3.8412554697,1.6936968471,-0.0674603859
C,0,0.3140343708,-0.5625389797,0.2230716813
N,0,1.3654106723,-1.4449593289,0.148501983
C,0,0.9037278744,-2.608889588,-0.408146844
N,0,-0.3600889146,-2.5652851754,-0.6942192538
N,0,-0.7461579528,-1.2856978788,-0.2823679143
C,0,2.7338326155,-1.5827450531,0.7006477915
C,0,3.2450784436,-2.7892146639,-0.1330861148
C,0,1.9892628632,-3.636843286,-0.4865736172
C,0,2.6998500668,-1.8228397433,2.2262183444
C,0,4.0928835941,-1.8718746075,2.8192784781
C,0,4.606619637,-3.0521949525,3.3704579265
C,0,5.8955065002,-3.0926853746,3.9075499558
C,0,6.6926280647,-1.9482783263,3.8963880582
C,0,6.1919700221,-0.7645594183,3.3479582247
```

```
C,0,4.9036606261,-0.7248947443,2.8152323029
C,0,-2.1492693545,-1.0407391421,-0.1868753752
C,0,-2.7047749107,-0.5779691432,1.0077895934
C,0,-4.0845863911,-0.3922048687,1.0936819065
C,0,-4.9048406341,-0.6909634869,0.0056758534
C,0,-4.3402241363,-1.1751160551,-1.1775369299
C,0,-2.9626583862,-1.348553204,-1.2802275811
O,0,4.7395233365,0.6583734799,-1.8777456393
C,0,6.0339588555,0.8596580093,-1.2849771152
C,0,7.0601337871,0.2389109742,-2.2167073775
H,0,-4.973658146,-1.4115975881,-2.0278246371
H,0,-5.9796791293,-0.550951588,0.0788873175
H,0,-2.5095648443,-1.7179661702,-2.1932021239
H,0,-4.515331486,-0.0231239772,2.0198846883
H,0,1.8078005972,-4.4361856499,0.2418561168
H,0,2.0516000898,-4.1032086376,-1.4733740163
H,0,3.7037257492,-2.4115705079,-1.0520294757
H,0,3.9878759588,-3.9472242042,3.3886187288
H,0,6.2732197468,-4.0178010049,4.3353822753
H,0,7.6954216226,-1.9760805969,4.3143309423
H,0,6.8041184589,0.133519683,3.3399403769
H,0,4.5246369017,0.2017981547,2.3905012348
H,0,3.9996707938,-3.3586670463,0.4137504041
H,0,3.301949812,-0.6810412733,0.499339504
H,0,1.4094359114,2.4542189075,-0.8167903402
H,0,2.3290230765,1.4740543292,0.8695231083
H,0,0.0945082912,0.6139233889,-2.9124019862
H,0,0.1142948927,2.3871033983,-2.9043505541
H,0,-2.0652659516,-0.3656250544,1.8570275003
H,0,2.1318455479,-0.9974867984,2.6673178155
H,0,2.1611570502,-2.7538246402,2.4456096111
H,0,2.3908094479,0.2006491979,-2.6430239144
H,0,-0.1620910893,2.296100932,2.6574615946
H,0,-2.0150980265,3.9466311568,2.8778891119
H,0,-3.4975894879,4.4070690043,0.9295768569
H,0,-3.0829428856,3.2367095129,-1.243649277
H,0,6.2082068261,1.9325578416,-1.149477268
H,0,6.0584873606,0.3982709721,-0.2911087795
H,0,8.0677800634,0.3699685859,-1.8066747088
H,0,6.8761813063,-0.8334551796,-2.3419079248
H,0,7.0252905862,0.7092791252,-3.2048233845
```

Intermediate 65

E(RB+HF-LYP) = -1665.06708800

```
Zero-point correction=                          0.567927 (Hartree/Particle)
Thermal correction to Energy=                   0.600578
Thermal correction to Enthalpy=                 0.601522
Thermal correction to Gibbs Free Energy=        0.500742
Sum of electronic and zero-point Energies=            -1664.499161
Sum of electronic and thermal Energies=               -1664.466510
Sum of electronic and thermal Enthalpies=             -1664.465566
Sum of electronic and thermal Free Energies=          -1664.566346

              E (Thermal)          CV               S
               KCal/Mol      Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total           376.869          128.022          212.110

C,0,5.0147174936,-0.6699860221,1.9091828379
C,0,4.0983782888,-0.4559749202,0.8718887834
C,0,4.4204134246,-0.9189089483,-0.4133361185
C,0,5.6238628315,-1.5829180489,-0.6488243709
C,0,6.528999384,-1.7918886035,0.3946253916
C,0,6.2224803039,-1.3311445935,1.6749514795
C,0,2.7802108658,0.2483876771,1.1223567517
C,0,1.5873506687,-0.7305190961,1.048757838
N,0,0.2832286913,-0.0374457408,1.1916998118
C,0,-0.2529883301,-0.1824066687,2.4412831617
C,0,0.6201729811,-1.021554299,3.3157851907
C,0,1.5078180796,-1.7190932739,2.247144886
N,0,-1.4082374152,0.4020264048,2.5423889432
N,0,-1.6182855069,0.9215678423,1.2710785115
C,0,-0.6047671847,0.6406672827,0.4219887363
C,0,-0.5965090828,0.8999075063,-1.1466236373
C,0,0.7403809443,1.6305656034,-1.4579319667
C,0,1.6232932112,1.1869203207,-2.4538230265
O,0,1.4049987197,0.0346738839,-3.1638817744
C,0,0.0310125802,-0.3748874575,-3.2070500836
C,0,-0.5362199289,-0.5729003408,-1.8061995241
C,0,1.0395446005,2.8407468301,-0.8170020713
C,0,2.1969545817,3.5605149548,-1.1039237371
C,0,3.0836592368,3.0764014733,-2.0726607581
C,0,2.7948169193,1.896969766,-2.7515331973
O,0,-1.650821648,1.5679709075,-1.5452017193
C,0,-1.9518530868,-1.1523828516,-1.8748065728
C,0,-2.2954386695,-2.092592022,-0.7500606039
```

```
O,0,-3.3498224242,-2.8734472636,-1.0696739335
C,0,-3.8130082181,-3.7778636602,-0.0436723357
C,0,-4.9905395963,-4.5469596255,-0.6132526478
C,0,-2.8866656243,1.5802719382,1.0700536654
C,0,-4.0174624467,0.9455261001,1.5854159057
C,0,-5.2588121383,1.5741382233,1.4877693378
C,0,-5.3607768088,2.8286925879,0.8864574601
C,0,-4.2180632843,3.4529722793,0.3807135749
C,0,-2.9714708459,2.8371707156,0.4718039371
O,0,-1.7361018063,-2.1573352929,0.3326699344
H,0,1.2065562757,-0.3965020682,4.0003251529
H,0,0.0434406074,-1.726021535,3.9193591374
H,0,1.0106167107,-2.6359425194,1.9173822346
H,0,2.5021741665,-1.9779429494,2.6163304241
H,0,1.6076716075,-1.261469237,0.0974486812
H,0,0.1311874271,-1.2571094188,-1.2708426986
H,0,-2.6241598491,-0.2755017518,-1.8351722498
H,0,-0.5624517415,0.384315293,-3.7340588886
H,0,0.0285680865,-1.3049716875,-3.7826218662
H,0,-2.1552171332,-1.6633531401,-2.8230802197
H,0,0.3458943021,3.2160616916,-0.067373006
H,0,2.405985971,4.4912405032,-0.5835745869
H,0,3.9916336312,3.6249630509,-2.3089799499
H,0,3.4514397982,1.5112517906,-3.5259290134
H,0,-2.9898232992,-4.4404978992,0.2436116273
H,0,-4.0921428503,-3.1967866039,0.8417341129
H,0,-3.9160155888,-0.0263339258,2.055146655
H,0,-6.1421537061,1.0801039286,1.8824922971
H,0,-6.3273931106,3.3193315569,0.8104729009
H,0,-4.2938440085,4.4265677721,-0.0946804657
H,0,-2.0918281999,3.2939958793,0.0421880778
H,0,-5.3769079331,-5.24658716,0.1361207033
H,0,-5.7987386101,-3.8667871922,-0.9002502901
H,0,-4.6924409007,-5.1188448511,-1.4978457146
H,0,2.7905855744,0.7288060901,2.1088692727
H,0,2.6286953894,1.0397825253,0.3832846686
H,0,3.7291849118,-0.7485893968,-1.2357596456
H,0,5.8583543457,-1.9315481238,-1.6511111551
H,0,7.4682717287,-2.3057286119,0.2087028674
H,0,6.9226794154,-1.4821783221,2.4924084572
H,0,4.7861732212,-0.3052572557,2.9086564195
```

Transition Structure 66

E(RB+HF-LYP) = -1665.06443380

```
Zero-point correction=                           0.566939 (Hartree/Particle)
Thermal correction to Energy=                    0.599402
Thermal correction to Enthalpy=                  0.600347
Thermal correction to Gibbs Free Energy=         0.498535
Sum of electronic and zero-point Energies=           -1664.497495
Sum of electronic and thermal Energies=              -1664.465031
Sum of electronic and thermal Enthalpies=            -1664.464087
Sum of electronic and thermal Free Energies=         -1664.565899

            E (Thermal)         CV              S
             KCal/Mol      Cal/Mol-Kelvin   Cal/Mol-Kelvin
Total          376.131         126.800         214.280
```

```
C,0,4.8340591958,1.087264963,-2.0984725333
C,0,4.1015975585,0.445152119,-1.0909156517
C,0,4.713536241,0.2441793227,0.1551263934
C,0,6.0167355974,0.6836041586,0.3878027472
C,0,6.7341556933,1.3272940498,-0.6229916271
C,0,6.1400441232,1.5252149672,-1.869681604
C,0,2.6765097323,-0.0098474864,-1.3308813283
C,0,1.6346238366,0.9200437312,-0.6637285444
N,0,0.2569299882,0.4560955142,-0.9422476259
C,0,-0.3386540709,1.1655405361,-1.9516048525
C,0,0.5431296117,2.2695854342,-2.435828963
C,0,1.5724371841,2.3491798652,-1.2722065857
N,0,-1.5298875609,0.7205371022,-2.2107971092
N,0,-1.6837640274,-0.3101285244,-1.2830735837
C,0,-0.6059287279,-0.4827924891,-0.4766854237
C,0,-0.5922640808,-1.2702912434,1.2229464331
C,0,0.7719049104,-1.9756941618,1.2530170293
C,0,1.6829693155,-1.7301050865,2.2927630171
O,0,1.4554007216,-0.7957188395,3.2682137569
C,0,0.0843510847,-0.4177687709,3.4424302113
C,0,-0.544630369,0.0327606249,2.1223788924
C,0,1.0886137117,-2.9739298634,0.3244256293
C,0,2.2897044009,-3.6773905428,0.3842686154
C,0,3.1992096676,-3.3953604881,1.4103724231
C,0,2.8960163517,-2.4305240959,2.3661012993
O,0,-1.6048688556,-2.0131493721,1.3999808154
C,0,-1.9500165198,0.597449751,2.3358945064
C,0,-2.2359321065,1.8599263306,1.5529246487
```

```
O,0,-3.4613676158,2.3390381675,1.8515458792
C,0,-3.8684207284,3.5363843388,1.1525836061
C,0,-5.2727585823,3.8777605109,1.614525463
C,0,-2.9257567473,-1.027032493,-1.3189135898
C,0,-4.0685808979,-0.3472158814,-1.7531253629
C,0,-5.2792651755,-1.0306915111,-1.8394197582
C,0,-5.3514482685,-2.3812834421,-1.492062362
C,0,-4.2041279156,-3.0452156064,-1.0573477227
C,0,-2.98154212,-2.3788402085,-0.9771316464
O,0,-1.4927810891,2.4026820142,0.754846711
H,0,1.0138653791,2.0056673211,-3.3909238191
H,0,-0.0063924863,3.2023975435,-2.582305154
H,0,1.1930139281,3.0383287262,-0.512450234
H,0,2.5574622837,2.692811241,-1.5933575751
H,0,1.8028526742,0.9468239155,0.4137399136
H,0,0.1036596193,0.8072889659,1.7027714561
H,0,-2.6706499739,-0.182634445,2.0507667518
H,0,-0.4796272904,-1.2648295273,3.8571580156
H,0,0.1039440526,0.3931892416,4.1763749191
H,0,-2.1557316009,0.8182598201,3.3918773744
H,0,0.3706814536,-3.1868681859,-0.4644174933
H,0,2.5148041128,-4.441611136,-0.3544335281
H,0,4.1389436969,-3.9376815725,1.4737379386
H,0,3.5706783753,-2.2128896997,3.1890817857
H,0,-3.1559506233,4.3372417479,1.3770956949
H,0,-3.8244535795,3.348228457,0.0747744914
H,0,-3.9963673322,0.6987241167,-2.0260958037
H,0,-6.1670661365,-0.5032337695,-2.1771306307
H,0,-6.2971978558,-2.9120594178,-1.559106127
H,0,-4.2520066574,-4.0939422323,-0.7789472997
H,0,-2.1016557342,-2.8827295813,-0.602014077
H,0,-5.6225054841,4.7827251144,1.1055908895
H,0,-5.9670456724,3.0627329904,1.3868880137
H,0,-5.296582109,4.0581998284,2.6940087679
H,0,2.4741276268,-0.0507275328,-2.4087130769
H,0,2.5297785326,-1.0215849953,-0.938687999
H,0,4.1705074122,-0.2748090965,0.9412615466
H,0,6.4752928711,0.5163466452,1.3589151153
H,0,7.7508596482,1.6655318298,-0.4418199371
H,0,6.6924187274,2.0162984116,-2.6666074083
H,0,4.3809046749,1.2363358811,-3.0766917145
```

VITA

Name:	Jacqueline Besinaiz Thomas
Address:	Department of Chemistry Texas A&M University P.O. Box 30012 College Station, TX 77842
Email Address:	jbesinaiz@gmail.com
Education:	B.S., Chemistry, Texas A&M University-Kingsville, 2003