MECHANISM ELUCIDATION OF ORGANIC REACTIONS:

THE FAILURE AND SUCCESS OF RATE THEORIES

A Dissertation

by

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ABSTRACT

Statistical and nonstatistical rate theories help organic chemists understand reactions. The most widely used statistical rate model is transition state theory (TST). TST is an extremely useful model for describing organic reactions; however, it has some well-known shortcomings. Despite this, reactions are often shoehorned into TST for the explanation of experimental rates and selectivities even when it is clear that TST could not account for experimental observations. Here, we present three mechanistic studies to test the validity of TST and other rate theories, including hydroboration of alkenes, thioboration of alkynes, and 1,5-hydrogen atom transfers (1,5-HAT). These were studied experimentally by the measurement of product ratios and ^{13}C kinetic isotope effects (KIE), and computationally using dynamic trajectories, energy calculations, and tunneling approximations.

The hydroboration of alkenes is a reaction that has long been described by TST; however, it has no enthalpic barrier for reaction. This leads to a nonstatistical energy distribution in the molecule. Other rate theories have been proposed, but these also fail to predict the selectivity. We propose a new nonstatistical model, which does account for the experimental selectivities.

The mechanism of the formal thioboration of alkynes was studied. Through the experimental studies of kinetics and isotope effects, and computational studies, the mechanism was found to occur by simultaneous attacks to both carbons of the alkyne in an Ad_E3 mechanism. This reaction was determined to be governed by TST.

A study of a 1,5-HAT found an extremely large H/D KIE at room temperature of 150. A KIE this large cannot be explained with TST alone, and could only be accounted for by quantum mechanical tunneling. In addition, this 1,5-HAT had a linear Eyring plot across a large range of temperatures. The normal small curvature tunneling (SCT) algorithm was insufficient to describe all of the experimental observations, but by using the large curvature tunneling (LCT) algorithm, the experimental observations were reproduced with striking accuracy.

DEDICATION

I dedicate this work to my wife and best friend, Katie Bailey

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I would like to thank my advisor Dr. Singleton principally for his direction and immeasurable support throughout graduate school. I would like to thank the other members of my committee Dr. Bryk, Dr. Ozerov, and Dr. Powers their guidance and help throughout this process.

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Contributors

This work was supported by a dissertation committee consisting of Dr. Daniel Singleton (advisor), Dr. Oleg Ozerov and Dr. David Powers from the Department of Chemistry, and Dr. Mary Bryk from the Department of Biochemistry and Biophysics.

All the work done in this dissertation was done by the student independently with the exception of the kinetics and synthesis of the molecules in Chapter IV for the kinetic isotope studies were done by two students (Darius Faizi and Adena Issaian) as a collaboration with Dr. Blum from UC-Irvine.

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NOMENCLATURE

CCNM	Canonical Competitive Nonstatistical Model
CLN	Competitive Localized Noncanonical
CVT	Canonical Variational Transition State Theory
DFT	Density Functional Theory
HPLC	High Performance Liquid Chromatography
IVR	Intramolecular Vibrational Redistribution
IRC	Intrinsic Reaction Coordinate
KIE	Kinetic Isotope Effect
LCT	Large Curvature Tunneling
MEP	Minimum Energy Pathway
NMR	Nuclear Magnetic Resonance
RRKM	Rice-Ramsperger-Kassel-Marcus
RRKM-ME	Rice-Ramsperger-Kassel-Marcus Master Equation
SCT	Small Curvature Tunneling
THF	Tetrahydrofuran
TS	Transition State
TST	Transition State Theory
VTS	Variational Transition State
ZPE	Zero Point Energy

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CHAPTER I

INTRODUCTION

1.1 Chemical Models

The core goal in organic chemistry is the design and synthesis of molecules found or derived from nature. Key to the design of syntheses is the knowledge of the mechanisms of organic reactions. This subset of organic chemistry is known as physical organic chemistry.

Physical organic chemists devise experiments (i.e. kinetic studies, isotope effects, crossover experiments, and intermediate trapping)[1–8] to probe the mechanisms of organic reactions and use theoretical studies (i.e. density functional theory computations) to help explain the mechanisms of complex reactions.[9–11] With the knowledge of the mechanism, physical organic chemists can condense the information gained into a chemical model for ease of understanding.

These models allow for a qualitative understanding of chemical reactions, and in some instances, allow for quantitative inferences. One such model is transition state theory (TST). TST is ubiquitous in organic chemistry, and offers an intuitive look at reactions as a whole. TST is a statistical model that is used to understand the rate and selectivity of a chemical reaction. It is generally described as a particular geometry that must be passed through in order to achieve the products. It is more precisely a hypersurface that passes through a saddle point and separates the thermally equilibrated reactants and products on the reaction coordinate.[12] The Eyring equation allows for the calculation of the rate of reaction based on the Boltzmann constant (k$_B$), temperature (T), Planck's constant (h), the universal gas constant (R), and the free energy of the transition state (G‡) shown in equation (1-**1**). The differences in the rate for the two transition states allow for a simple calculation of product ratios.

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^‡}{RT}} \tag{1-1}$$

TST has a few inherent assumptions. One assumption is the reactants must be at thermal equilibrium, that is, there is no excess energy in the reactants. Other very important assumptions are that the reactants can only pass through the transition state once, and a transition state leads to only one product. These assumptions lead to interesting exceptions that will be discussed in section 1.2.

Since TST cannot handle non-thermally equilibrated intermediates in a reaction, the Rice-Ramsperger-Kassel-Marcus (RRKM) theory was introduced to account for excess energy in reactive intermediates. Rice, Ramsperger and Kassel proposed this chemical model in 1927[13] and 1928.[14] Marcus brought these two accounts together and took TST into account as well in 1952.[15] The fundamental tenet of RRKM theory is that the excess energy of an intermediate is statistically distributed throughout the molecules normal modes.[16–18] In the same such calculation, TST assumes complete thermal equilibrium in the system, but by assuming a distribution of excess energy in a molecule is much faster than the reaction itself, RRKM is better equipped to take on reactions with energetic intermediates.

1.2 Dynamic Effects

Transition state theory is a particularly useful model that has been employed to understand many chemical reactions for more than 80 years, but it is only a model to increase understanding of chemistry, not a law that must be obeyed. The failure of TST or other statistical methods, such as RRKM, to predict an outcome or rate of a reaction will be referred to in this text as dynamic effects.

The first of these dynamic effects to be discussed is dynamic matching. This effect has been studied extensively by Carpenter.[19–22] Dynamic matching is the selectivity of a reaction as dictated by the momentum of a shallow intermediate carrying it across a barrier, giving the reaction a different selectivity than is expected by TST. This dynamic effect can be found throughout the literature in reactions such as sigmatropic rearrangements and recombination of diradical intermediates.[19–24] Chapter II will discuss this dynamic effect with regard to the hydroboration reaction.[25]

Another dynamic effect is incomplete intramolecular vibrational redistribution (IVR.) Incomplete IVR occurs when an intermediate in a reaction has gained potential energy from a previous step in the reaction, but it does not have time to distribute the excess energy equally throughout the molecule. Examples of this dynamic effect is found in ozonolysis of alkenes by Hase[26] or vinyl ethers from Quijano and Singleton.[27] The reaction of ozone with a vinyl ether makes a primary ozonide with 57 kcal/mol extra energy that allows for a product ratio for the cleavage of the primary ozonide that cannot be explained using transition state theory. This dissertation will deal with this dynamic effect notably throughout chapter II.

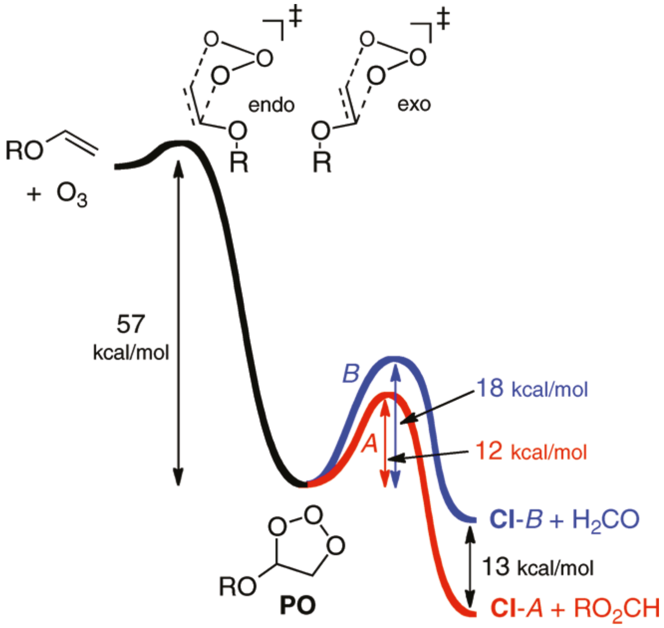

Figure 1.1 The energy curve for ozonolysis of vinyl ethers.[27]

One major shortcoming with TST arises when determining product ratios. TST assumes that one product arises from one transition state, but, in some cases, more than one product can be formed in a downhill path from a single transition state. This is called a bifurcating energy surface. Some examples of this is the Wolff rearrangement of carbenes,[11] Ene reactions,[28] and cycloadditions.[29]

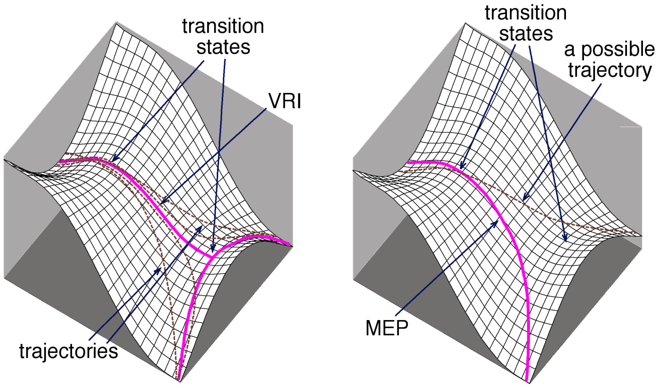

Figure 1.2 A bifurcating energy surface in which a single transition state connects two products.

Transition state theory assumes that a transition state is passed only once. However, it is well known that a small portion of trajectories will return to starting materials after the TS. This in handled well using variational transition state theory, which determines the TS to be at the free energy maximum. Although, under the right circumstances, there can be nonstatistical recrossing. An example of nonstatistical recrossing is the cycloaddition of dichloroketene and cis-2-butene.[30] The presence of a second free energy barrier causes this reaction to "hit a wall" and rebound to starting materials.

A Newtonian kinetic isotope effect is an isotope effect that arises only from the classical laws of physics, which differs from a traditional KIE that arises from ZPE. Some examples of these KIEs can be seen in the dimerization of cyclopentadiene[31] and the dimerization of methacrolein.[32] In Newtonian KIEs, the lighter atoms follow reaction coordinate with more motion than the heavier atoms. This is illustrated in Figure 1.3

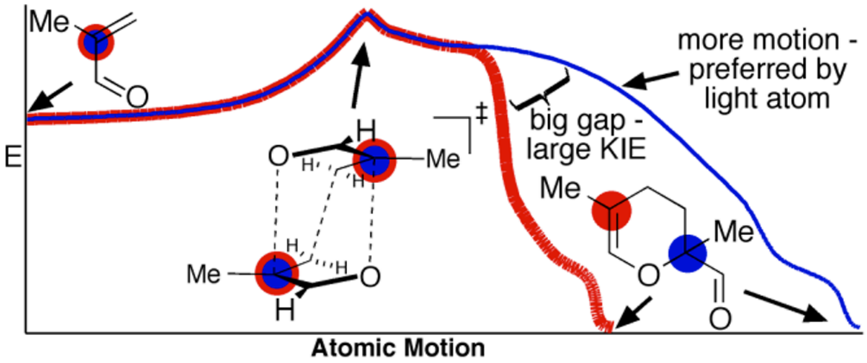

Figure 1.3 Atomic motion reaction coordinate diagram of the dimerization of methacrolein.[32]

An interesting dynamic effect occurs when solvent rearrangement is the major factor in product determination. This occurs in the nitration of toluene.[33] This product ratio of this reaction has long been described as the *meta* position of toluene is less reactive than the *ortho* or *para* due to the electron donating methyl group. However, the Nieves and Singleton showed that the solvent and counterion blocks the approach of the nitronium ion to the toluene, and can only react after favorable rearrangement of the solvent and counterion. Figure 1. 4 is a trace of the atomic motion of a NO_2^+ ion in the the nitration of toluene. This dynamic effect can also be seen in the stabilization of betaine intermediates in the Wittig reaction.[34]

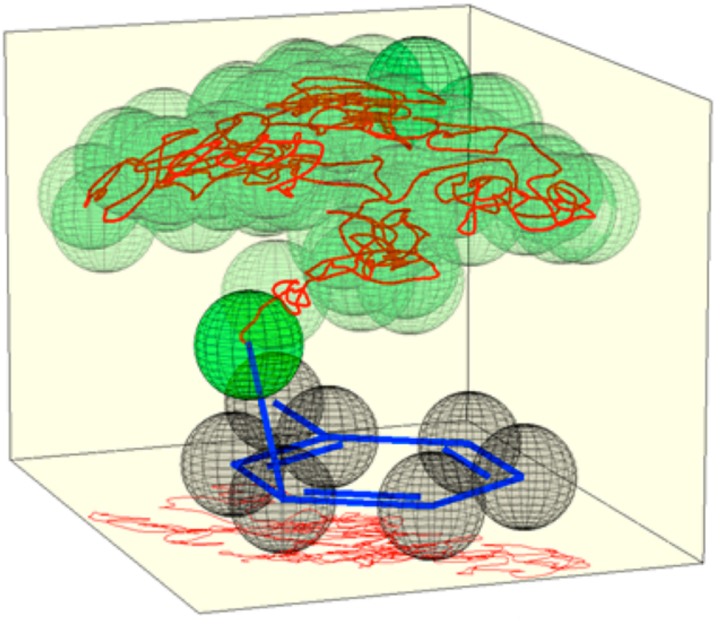

Figure 1. 4 The nitration of toluene. The motion of NO_2^+ is shown with the red line.[33]

1.3 Kinetic Isotope Effects

For the study of reaction mechanisms, one very powerful tool is the measurement of kinetic isotope effects (KIE). These KIEs can give insight into the nature of the transition state of a given reaction.[30–32,35–37] KIEs are the measurement of the difference in rates of different isotopes for a given reaction. They are generally broken down into two categories, which are primary and secondary. Primary KIEs are large effects and occur when the substituted isotope has a bond change in the rate-determining step.[37–39] If the substituted isotope is near the bonding change, but is not itself directly affected, then this is known as a secondary isotope effect.[40–42]

KIEs are dependent on the differences of the vibrational modes of the bond changes in a reaction. Since the vibrational modes differ in energy due to the masses of the isotopes, there is a difference in the rate of zero point energy (ZPE) for each isotopomer. In a KIE, the zero point energy for the lighter isotopomer will have a smaller barrier than that of the heavy isomer as the ZPE gap in the TS shrinks the potential energy well becoming wider as the bonds are broken. A two dimensional illustration of this is shown in Figure 1.5 for a H and D case.

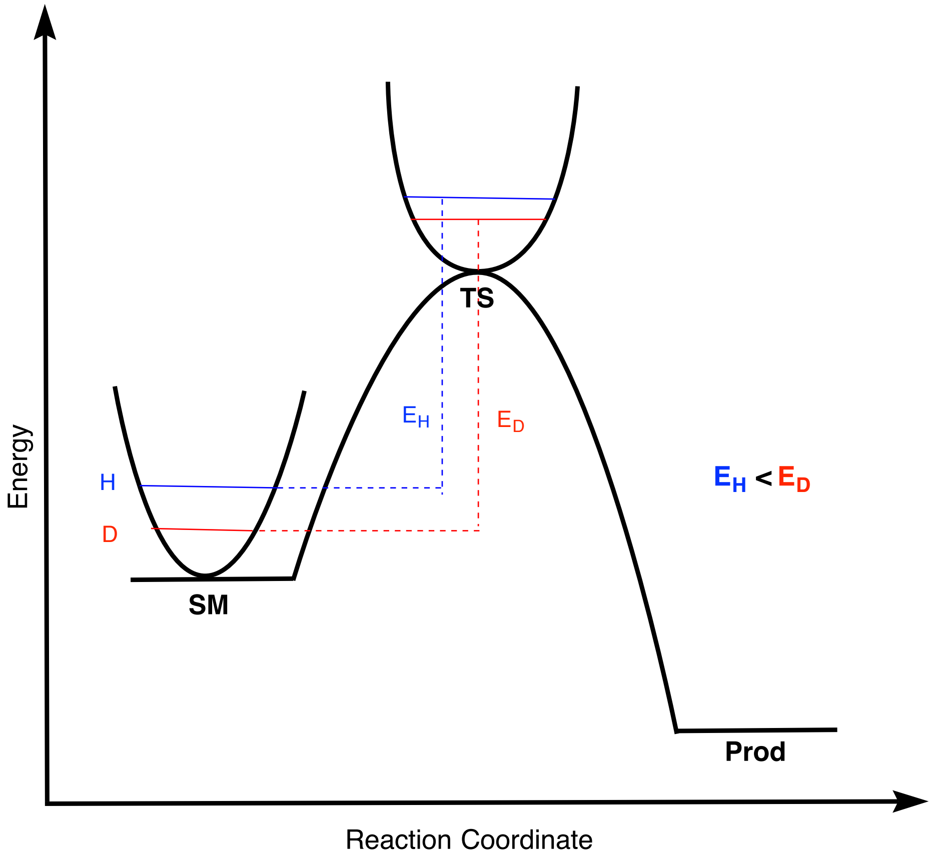

Figure 1.5 The main origin of the kinetic isotope effect is the difference in zero point energy of the isotopes as the starting material approaches the transition state.

The most common isotope effects studied in organic chemistry are hydrogen and carbon KIEs. The traditional method for the determination of a KIE is to synthesize labeled material at the position of interest and measure either its relative rate in a competition with unlabeled material or to measure its absolute rate and compare the labeled rate against the unlabeled rate. This method of determining KIEs is inconvenient, especially for ^{13}C KIEs, since only one KIE can be measured at a time, multiple labeled materials would have to be produced to measure KIEs at all positions, and the errors in rate measurements can be large compared to the magnitude of the rate differences. However, if KIEs are measured at natural abundance, many of the disadvantages to the conventional method are moderated.

In 1995, Singleton developed a nuclear magnetic resonance (NMR) spectroscopy method to measure relative ^{2}H KIEs and ^{13}C KIEs at natural abundance.[43] This method does not require the synthesis of labeled reagents, which reduces the overall synthetic demand in determining a KIE. In addition, KIEs in multiple positions can be determined with one sample.

The original method of KIE determination was used to determine intermolecular KIEs of starting materials. This allows the probing of the rate-limiting step. In these KIEs, the reaction is taken to a high conversion (>80%), and the isotopic composition of the recovered starting material is compared to starting material from the same synthetic lot. The recovered starting material is enriched with the slower reacting isotopomer. The KIE is calculated by equation (1-**2**) where F is reaction conversion and (R/R_0) is the relative isotopic composition. This methodology is quite robust and the KIE precision can exceed the precision of method of analysis. This dissertation will only deal with starting material KIEs.

$$\mathrm{KIE_{SM}} = \frac{\log(1\text{-}F)}{\log[(1\text{-}F)(R\text{-}R_0)]} \tag{1-2}$$

This methodology can be extended to intermolecular product KIEs. This process requires a sample of isolated product at a low conversion (~20%). The sample is compared to a standard of a reaction taken to 100% conversion. The KIE is calculated with equation (1-**3**). This method is subject to errors with respect to the calculation of 100% conversion, and if the product forms some side product.

$$\mathrm{KIE_{Prod}} = \frac{\log(1\text{-}F)}{\log[(1\text{-}(F^{*}R\text{-}R_0)]} \tag{1-3}$$

Intramolecular KIEs can give information about steps after the rate-limiting step if the starting material is symmetrical. It actually gives information about the desymmetrizing step of the mechanism. The KIE is simply the ratio of the two isotopic ratios as shown in equation (1-**4**).

$$\mathrm{KIE_{Intramolecular}} = \frac{R_A}{R_B} \tag{1-4}$$

The ability to correctly predict KIEs through computations is a powerful tool. The method to accomplish this was proposed by Bigeleison and Mayer in 1947.[44,45] This calculation is shown in equation (1-**5**) to (1-**8**). These equations account for the temperature, the fractionation factor, and the frequency of the vibrational mode. These equations are based on TST, and rely on the harmonic approximation. It does not take into account tunneling, but whenever tunneling is not a significant factor, it is effective in predicting KIEs for reactions.

$$KIE_{TST} = \frac{v_1^{\ddagger}(s_2/s_1)f_{GS}}{v_2^{\ddagger}(s_2/s_1)f_{TS}} \tag{1-5}$$

$$(s_2/s_1)f_{GS} = \prod_{i}^{3N-6} \frac{v_{2i}}{v_{1i}} \frac{1-e^{-u_{1i}}}{1-e^{-u_{2i}}} \frac{e^{u_{1i}/2}}{e^{u_{2i}/2}} \tag{1-6}$$

$$(s_2/s_1)f_{TS} = \prod_{i}^{3N-7} \frac{v_{2i}}{v_{1i}} \frac{1-e^{-u_{1i}}}{1-e^{-u_{2i}}} \frac{e^{u_{1i}/2}}{e^{u_{2i}/2}} \tag{1-7}$$

$$u_i = \frac{hv_i}{kT} \tag{1-8}$$

1.4 Computational Chemistry

The ultimate goal of computational chemistry is to reproduce and predict the outcome of chemical reactions. It falls short in this goal, since the solution to Schrodinger's equation is often impossible to solve, and the quantum mechanical calculations employed are models, and therefore, subject to some shortcomings. Often the major question is whether the computations are accurate depictions of actual chemistry. However, chemists are still able to utilize computational studies to help understand reactions. The highest level, *ab initio,* is a robust and highly accurate method for calculating the potential energy of chemical species. Although exact solutions of Schrodinger's equation are impractical to find, *ab initio* calculations with an infinite basis set could be made to converge on the exact solution. So, a lower calculated energy is always more realistic; however, these calculations require a large amount of computer resources to undertake.[46] Another method of computations is density functional theory (DFT), which the energy of the molecules is calculated from the electron density of the molecules. DFT is an extremely effective method for calculations due to it requiring less computer resources than *ab initio* calculations, and many different methods and basis sets have been shown to properly estimate for the energy for many molecular systems.[47] Although in order to do accomplish its task, DFT is heavily parameterized. Such shortcuts render the predictions made by DFT subject to significant error, and researchers tend to use experimental observations to benchmark their calculations. However, a more prudent exercise is to test DFT methods against high level *ab initio* calculations to determine the effectiveness of each basis set.

1.5 Quantum Mechanical Tunneling

The phenomenon of tunneling is a reaction that occurs without passing through the transition state, but rather, it passes through the barrier. The effect of this phenomenon is a rate increase versus what is expected by TST. Tunneling is a factor in all reactions, but usually tunneling involves protons, hydrogen atoms, or hydrides. Heavy atom tunneling does occur, but often is trivial in most reactions; however, it is present in all reactions.[48] For all ^{13}C KIE predictions done in this dissertation, a one-dimensional tunneling (infinite parabola) correction is included to account for the heavy atom tunneling and bring the predicted isotope effects closer to the experimental values. When H atom tunneling is a significant factor on the rate of the reaction, the experimental isotope effect can become quite large.[49–52]

CHAPTER II

FAILURE AND REDEMPTION OF STATISTICAL AND NONSTATISTICAL RATE THEORIES IN THE HYDROBORATION OF TERMINAL ALKENES[*]

2.1 Introduction

Organoboranes are a class of synthetically useful molecules that can be quite easy to make and are synthetically useful. They can tolerate a variety of functional groups, and the boron-carbon bond is strong but can be transformed to liberate organic products. There are pathways to many different functional groups such as alcohols, ketones, alkyl halides, amines and sulfides, or they can be used as a method to reduce carbon-carbon double bonds.[53] The first known synthesis of an organoboranes was in 1859 by reacting diethyl zinc with triethoxyborane.[54] They can also be made from the reaction from transmetallation reactions with Grignard reagents, aluminum, or mercury.[53,55–57] But the most common and robust method to form organoboranes is hydroboration.

Boranes are also very useful for synthesis. They can be used for reduction and hydroboration reactions. The hydroboration reaction is of particular importance due to its unique reactivity in the formation of anti-Markovnikov addition products from

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[*] Adapted with permission from “Failure and Redemption of Statistical and Nonstatistical Rate Theories in the Hydroboration of Alkenes” by Bailey, J.O.; Singleton, D.A. *J. Amer. Chem. Soc.* **2017**, *139*, 15710-15723. Copyright 2017 American Chemical Society.

alkenes. This, of course, differs from ordinary acid additions, which forms predominately Markovnikov addition products.

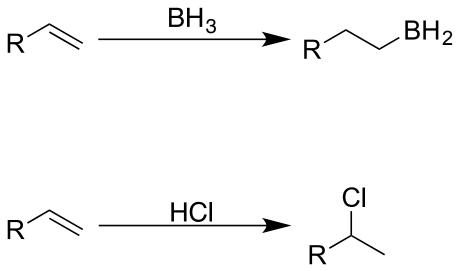
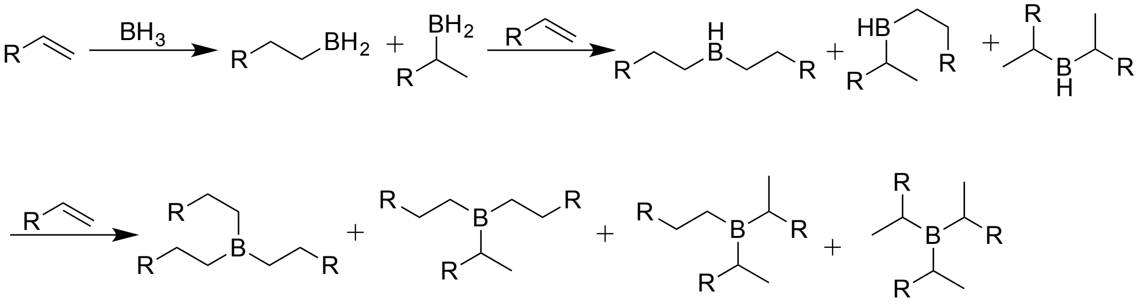


Figure 2.1 Major organic products from common addition reactions.

The hydroboration reaction was first reported in 1956.[58] In this reaction, Brown noticed $NaBH_4$ and $AlCl_3$ could add across a double bond of a simple olefin in an anti-Markovnikov fashion, and the hydroboration product could be easily oxidized to alcohols. Additional investigation led to the discovery that the addition occurs from the same face of the alkene affording syn isomers.[59] An important feature of this reaction is the unique multiple reactivity of a borane. An organoborane can react with up to three alkenes provided it has a reactive boron-hydrogen bond. This effect is shown in Scheme 2.1. This work along with other work with organoboranes earned Brown a shared Nobel Prize in chemistry in 1979 with Georg Wittig.

Scheme 2.1 Consecutive reactions of the hydroboration of an alkene.



The hydroboration reaction has some unique features. First, it is a robust reaction tolerating a wide range of structures with carbon-carbon multiple bonds. Second, the hydroboration of alkenes is only somewhat regioselective, with a significant quantity of the Markovnikov product formed, and the product ratio is more or less constant even over a wide range of temperatures. These peculiar features have sparked a debate in mechanism.

The traditional explanation for the regioselectivity of the hydroboration reaction is the transition state after formation of a π-complex for the formation of the anti-Markovnikov product is lower in energy due to the stabilization of the partial positive charge on the internal carbon atom.[60–63] This description is ubiquitous throughout the literature and textbooks. The assumption here is that TST is applicable at all in this reaction. As will be seen later, TST is insufficient to explain the major observations of the reaction.

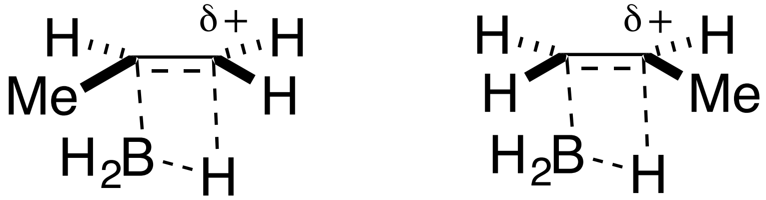


Figure 2.2 Idealized transition states of the Markovnikov (left) anti-Markovnikov (right) addition of BH_3 to propene.

The unique nature of the hydroboration reaction, as well as, the importance in the field of organic chemistry has made this reaction of great interest to chemists. Singleton and Oyola set out to explain some of the more peculiar aspects of hydroboration. The first step to understanding the hydroboration of alkenes was to accurately measure the product ratio. Oyola measured the product ratio for propene-d_6 as 10% Markovnikov alcohols after oxidative work up. The 10% Markovnikov product amount was different from the earlier work of Brown, which was 6% of the minor Markovnikov product.[60] In the Brown work, all the reaction proceeded through the trisubstituted borane, and subsequently had steric effects involved in the final product ratios. Oyola and Singleton took care to ensure that under their reaction conditions (100 equiv. of BH_3) only unsubstituted BH_3 molecules reacted with the propene-d_6. In this way, the energetics of the reaction would be more apparent. The key observation of the Oyola and Singleton study was that TST predicts the product ratios for hydroboration at 99:1 anti-Markovnikov: Markovnikov. The extreme disagreement of TST to experiment showed clearly that dynamic effects must be important to understand fully the hydroboration reaction. When the hydroboration of propene was studied computationally, they noticed that there was no enthalpic barrier to the reaction (Figure 2.3). This finding showed that there was excess energy available to the reaction, which allowed more minor product to be formed than would be predicted by TST.[25]

Singleton and Oyola also employed dynamic trajectories to help understand the hydroboration of propene. The trajectory studies found that reactions started at **INT** formed only 1% Markovnikov product. But, reactions started from the **VTS**, formed 13% Markovnikov product. In their trajectory studies started from **VTS**, they found that trajectories, which form product quickly, formed Markovnikov product 20% of the time. This led Oyola and Singleton to surmise that there were the dynamic effects, dynamic matching and incomplete IVR, in the reaction.

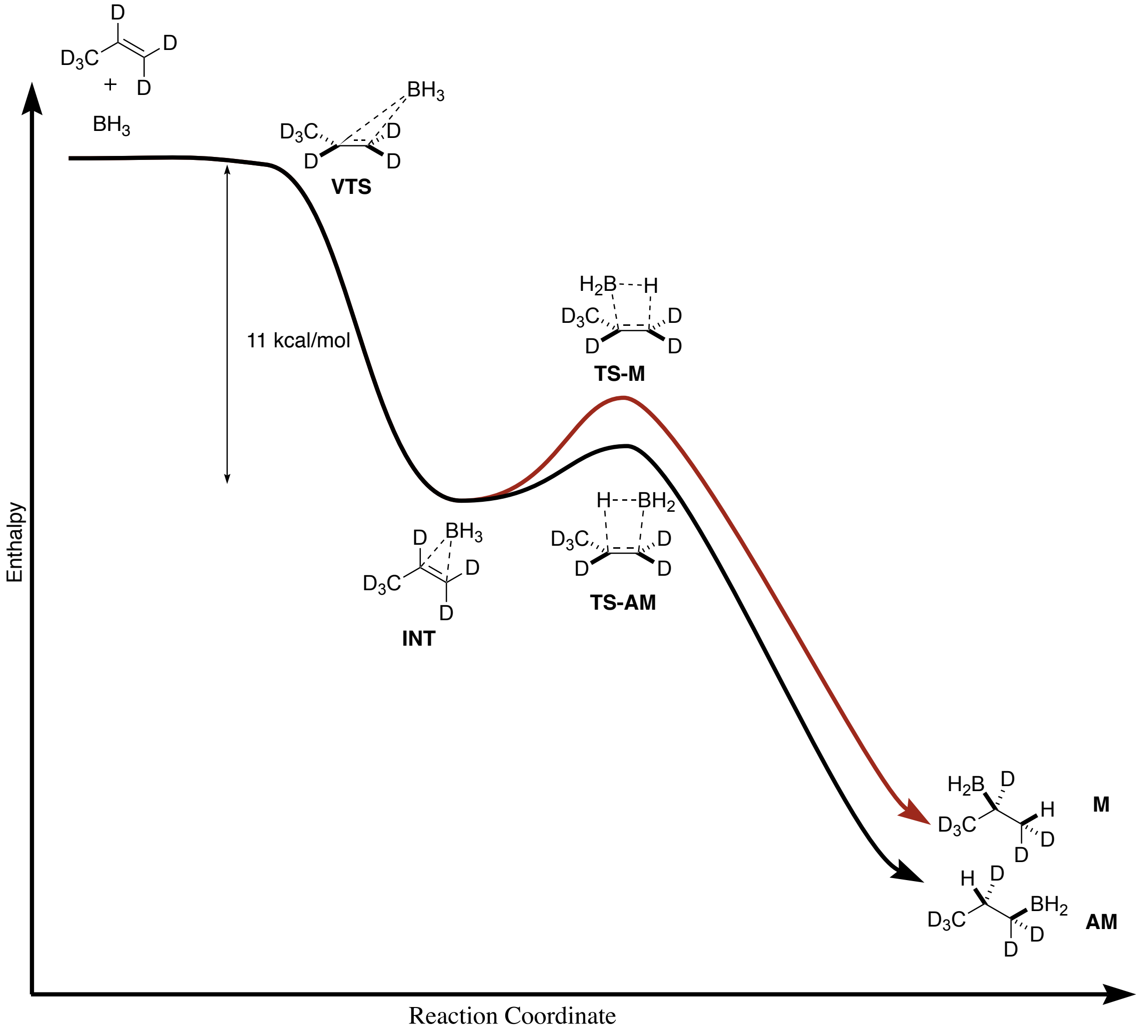


Figure 2.3 The enthalpy curve of the hydroboration of propene-d_6

The key conclusions of Oyola and Singleton directly contradict the use of TST in the hydroboration of alkenes. They argue that the formation of the π-complex would be rate determining, and it would be formed with a significant amount (11 kcal/mol) of excess energy. The product determining transition states are then low enough to allow the "hot" π-complex to pass through them directly without reaching thermal equilibrium. This is the dynamic effect, dynamic matching, discussed in chapter 1. If the π-complex is long lived enough, the reaction was still did not follow TST, since it still retains a significant portion of the excess energy. The excess energy would be statistically distributed, and the selectivity approached the value predicted by RRKM theory.

After the work by Oyola and Singleton, two computational groups discussed the selectivity of the hydroboration reaction with two different models. Glowaki *et al.* proposed that the preexisting fully statistical weak collision RRKM-ME model could account for the observation of the hydroboration reaction.[64,65] Truhlar *et al.* proposed a new nonstatistical model based on a combination of TST and nonstatistical phase space theory called canonical competitive nonstatistical model (CCNM).[66] Both of these models have a distinct advantage over dynamic trajectories in computational time required.

The RRKM theory was discussed previously, but the Glowaki method uses the master equation model (ME). This procedure has been shown to accurately describe reactions in the gas phase, and are now beginning to be applied to reactions in condensed phases.[67–69] The master equation simulates the change in energy of reactive intermediates i.e. allowing them to cool by collisional cooling with a bath gas. In terms of the hydroboration reaction, a model without the collisional cooling predicts lower selectivity than is experimentally observed, but if the π-complex is cooled completely. The selectivity is too high when compared to experiment. Since the RRKM-ME calculation has a cooling model built in, the question is not whether the experimental results can be matched, but it is whether the model can accurately predict selectivities of a diverse range of alkene reactants with a single, representative cooling model. Glowaki chose to use the commonly applied single exponential down model to describe the collisional cooling.[18,70–75] This model allows for small amounts of energy to be transferred versus collisions with the bath gas. The single exponential down model is commonly applied for its ease to apply as it depends only on the average energy transferred per collision, E_{down}. This value may be able to be measured, but often it is used as an adjustable parameter to bring the results onto the proper scale. There is concern that the single exponential down model does not adequately describe bimolecular reactions where the products are much lower in energy than free starting materials over a potential well, which describes the hydroboration reaction.[18] In these cases, a better description of the collisional energy transfer is by a double exponential down or a combination of the double and single exponential down model.[76–78] Despite the different methods, this study will continue to use the exponential down model to determine the rates of the hydroboration of alkenes to adequately test the RRKM-ME model suggested by Glowaki.

Using the program Mesmer,[79] Glowaki calculated the product ratios for the hydroboration of propene at a large number of pressures. From here, he used the pressure in solution to report the product ratio for propene at 25 ºC. The values in the bracketed section (shown in Figure 2.4) do agree with the experimental value of 90% anti–Markovnikov product formed. This analysis was also repeated for the higher temperature measurement in the Oyola and Singleton paper; however, a mistake was made. Instead of the 70 ºC value from the experimental work of Singleton, Glowaki used

95 ºC which is a most likely a mistake of the addition of 70 ºC to the original temperature of 25 ºC instead of using 70 ºC.

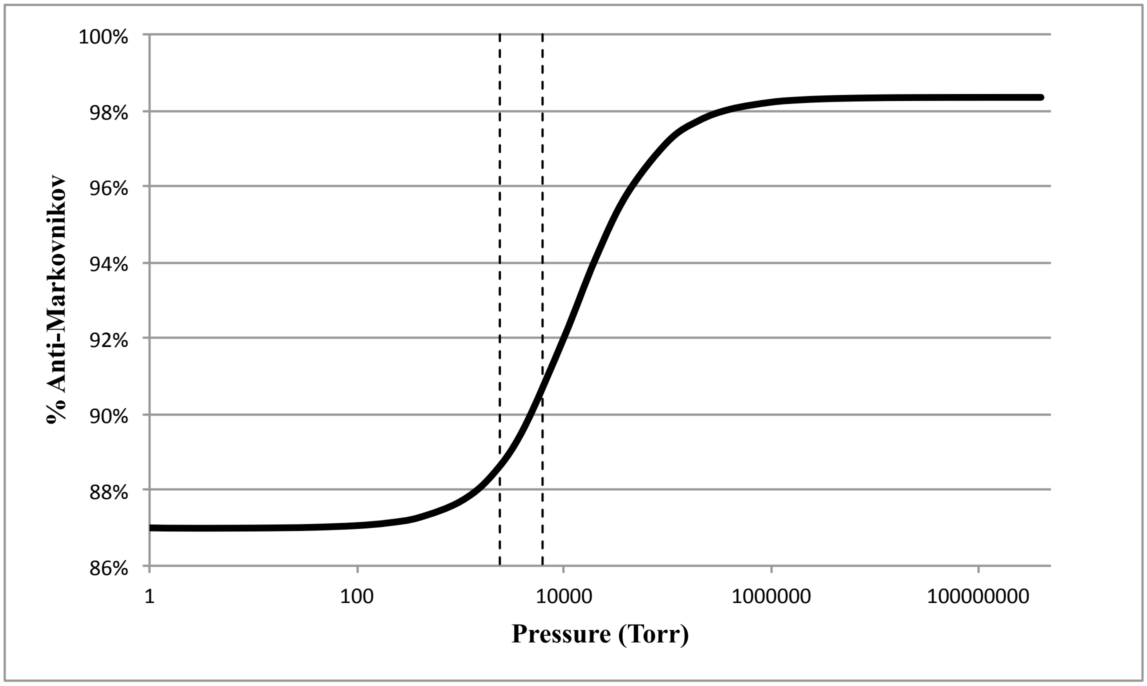


Figure 2.4 Results for RRKM-ME calculation for propene.

The work done by Truhlar *et al.* is a more inventive approach to the understanding of hydroborations. The CCNM model divides the hydroboration reaction into 2 mechanisms, direct and indirect. The indirect mechanism assumes that the intermediate π-complex is formed, but completely equilibrates before the reaction occurs. The product ratios for this mechanism are described by the energies of the transition states and temperatures from in an ordinary CVT method. In the direct mechanism, on the other hand, the products are weighted based on their energy levels modeled on phase space theory. Using this method of calculations,[66] based on calculations of transition states and equilibrium product ratios, Truhlar predicted 8-9% Markovnikov product for the hydroboration of propene.

Glowaki's use of RRKM-ME calculations makes intuitive sense. The hydroboration reaction seems to fit the mold of the RRKM model. It is a reaction that forms an intermediate with excess energy that could be cooled by solvent. Truhlar's CCNM model is more innovative and attempts to explain some of the observations of Oyola and Singleton, that of a direct and indirect mechanism. However, these models, like all models, simplify reality and are subject to discrepancies. These discrepancies will be discussed in the next section.

2.2 Experimental Results and Discussion

The usefulness of a chemical model cannot be determined if it can only be applied to a single data point, but rather it must be applicable to an extensive series. To more rigorously test the model proposed by Oyola and Singleton, as well as to determine the efficacy of the Glowaki and Truhlar models, a variety of alkenes were studied. From the previous work with ozonolysis,[27] the length of the alkyl chain of terminal alkenes were varied to determine the change in selectivity in the hydroboration reaction. The length of alkyl chains was varied to specifically show the shortcoming of the RRKM-ME model. Terminal alkenes would make an ideal substrate for study, since alkyl chains could take up varying amounts of energy based on their size, but should have similar steric and electronic effects. It was believed that RRKM-ME, with its assumption of a statistical energy distribution throughout the molecule, would over estimate the effect of cooling that the larger alkenes were expected to have. In order to probe the validity of the Truhlar model, 3,3-dimethyl-1-butene was studied. This alkene was chosen as a specific case in which the CCNM model was believed to be inadequate since it uses the equilibrium product ratio, and a sterically encumbered alkene would test this method fully.

Our hypothesis was that alkyl chains can take up a small amount of energy very quickly through a process called ballistic energy redistribution.[80–87] Normal energy relaxation occurs by diffusive energy redistribution and through intermolecular energy transfer is the method by which almost all molecules reorganize their energy. In diffusive energy, excess energy is redistributed through anharmonic excitation with excited modes.[88] Energy is also lost through molecular collisions, which is intermolecular energy transfer. When a collision occurs, a random amount of energy is transferred between the two molecules. The energy transfer is completely random with the trend being that higher energy is transferred to lower energy overall, but on an individual basis this is not consistently true. Ballistic energy redistribution is energy taken up from one portion of a molecule by vibrational modes in a different portion of the same molecule. On the timescale of molecular motion, energy vibrations are much faster than molecular collisions. With the ballistic energy distribution in an alkyl chain, the pi complex should be cooled by a small amount, which should be apparent experimentally as a decrease in the Markovnikov product. The speed at which energy is redistributed varies with the substituents. For instance fluorinated alkyl chains undergo IVR at a speed of 3.85 Å/ps while alkyl chains have been measured at 10.0 Å/ps.[81,87]

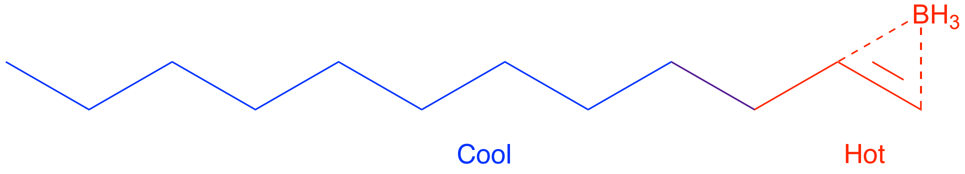


Figure 2.5 Visualization of our hypothesis.

Experimentally, the contribution from the diboration and triboration product should be minimized since their formation will sterically favor the formation of the anti-Markovnikov product.[60] In order to keep multiple hydroborations from occurring, 10 equivalents of BH_3 were used and a dilute solution of alkene was added slowly to the borane solution. In this way, the alkene will be more likely to encounter an unsubstituted borane molecule rather than a mono- or di-substituted borane, which kinetically competes with the formation of free borane.[89] This effect is that a substituted borane appears to react faster than free borane.

The first task was to determine the best analytical technique for the measurement of the product ratios. The first method attempted was ^1H NMR in $CDCl_3$. While this method is fastest and required no synthesis of materials, the peaks from the secondary alcohol were completely overlapped with that of the major primary alcohol. However, the doublet of the methyl peak from the secondary alcohol was visible, but still slightly overlapped with the methylene multiplet of the major alcohol (Figure 2.6a). When C_6D_6 was used as the NMR solvent, the doublet resolved from the multiplet allowing for the quantification of the minor product (Figure 2.6b). It should be noted that the alkenes used must be 99% pure, since the impurities contained are other alkenes that cause significant fluctuations in the ratios.

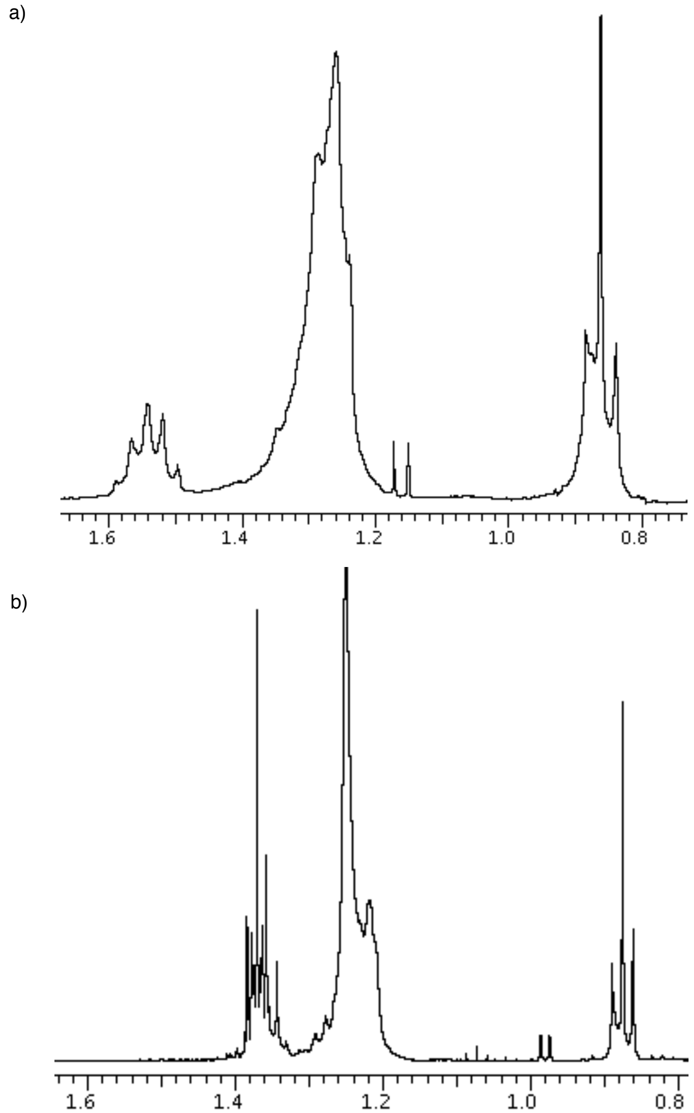
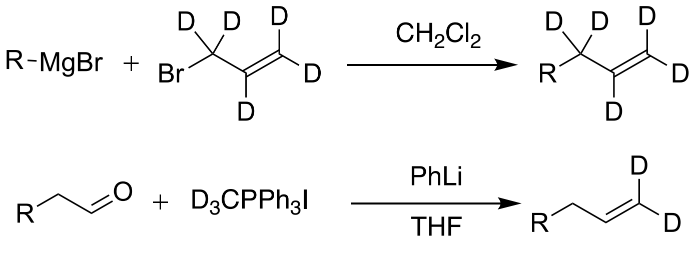


Figure 2.6 a) Spectrum of 1-octanol and 2-octanol in $CDCl_3$ (doublet at 1.14). b) Spectrum of 1-dodecanol and 2-dodecanol in C_6D_6 (doublet at 0.99).

While the 1H NMR shown above was a capable technique of determining the product ratios, other analytical methods were tested for their usefulness. High performance liquid chromatography seemed an ideal method to quantify a product ratio since the UV-Vis detector is very sensitive. The product alcohols, however, did not contain a chromophore. Synthesis of a benzoyl ester from the product alcohol mixture and benzoyl chloride is a simple and clean reaction. Unfortunately, dodecyl benzoate and larger esters could not be separated with HPLC, and any chemical transformation that does not produce 100% of the new product could introduce significant errors in the measurement, therefore this method was rejected.

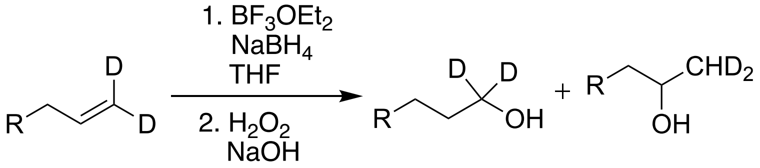
Taking inspiration from Oyola and Singleton, labeling alkenes with deuterium was considered as a simple way to measure product ratios. Two methods were considered for isotopic labeling. The first was the synthesis of d7-alkenes with perdeutero allyl bromide, and the second was labeling only the terminal position of an alkene to make d2-alkenes with a Wittig reaction (Scheme 2.2). The first method, while most closely resembling Oyola and Singleton's work, was deemed too costly to perform.

Scheme 2.2 The methods for deuteration of alkenes



The second method is significantly more tractable. The labeled Wittig salt is easily made and purified from commercially available CD_3I. Two different approaches were considered for the Wittig reaction. The first was the use of dimsyl sodium as the base; however, the formation of the ylide was reversible leading to very low deuterium incorporation. Whenever butyl lithium or phenyl lithium was used, though, the deuterium incorporation was much higher, but still not >85%.

Scheme 2.3 The hydroboration of terminally deuterated alkenes



The product peaks from the terminally deuterium labeled hydroboration reaction are completely resolved from each other, since the major product's label is directly next to the alcohol, while the minor's label is on a methyl group (Scheme 2.3). However, the low amount of deuterium incorporation allows the residual THF solvent peak to potentially have a significant effect on the integration of the major product, and most unfortunately, the minor product is very small and very difficult to satisfactorily integrate (Figure 2.7), and subsequently, this method was also precluded.

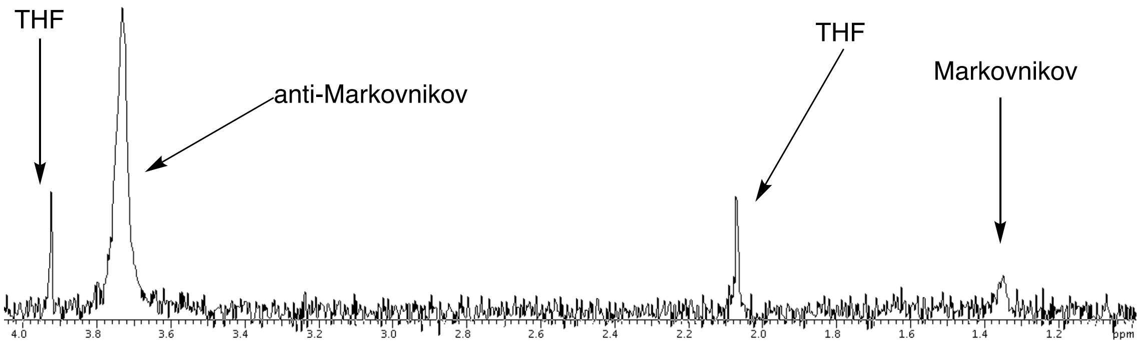
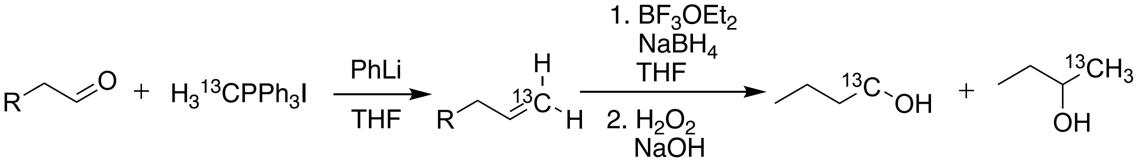


Figure 2.7 The ^{2}H NMR spectrum of products from the hydroboration of 1-tridecene.

Since the Singleton group is most versed in the integration of natural abundance ^{13}C NMR spectra, this analysis was conducted. Using the integrable ^{13}C NMR technique that is used for carbon kinetic isotope effects, the product ratios should have been easily and precisely quantified by integrating the same carbon peaks for both products. However, by the very nature of the reaction, there is a 10% impurity, which is the minor product. These small peaks are usually within 5 Hz of many of the major product peaks rendering the minor product peaks non integrable. Unfortunately, the most easily integrable peak for the minor product corresponds to a non-integrable peak for the major product.

Scheme 2.4 The ^{13}C Labeled hydroboration reaction



The unfortunate chemical shifts of natural abundance ^{13}C NMR led to the labeling of the alkene with ^{13}C. This method had a most unfortunate overlapping of peaks shown in Figure 2.8. These peaks are inherent to many of the major and minor alcohol peaks, which render this method impossible to precisely use, especially considering the significant cost of $^{13}CH_3I$ After the different analytical methods were tested for their usefulness, the decision was made to return to ^{1}H NMR.

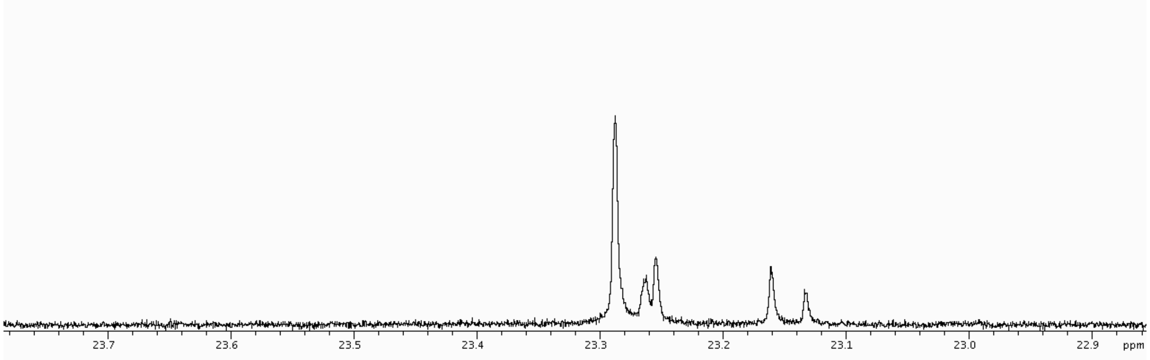
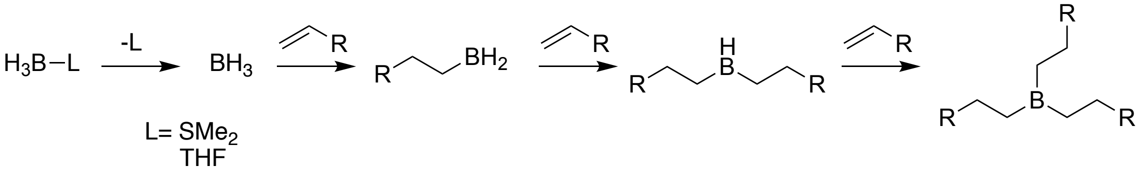


Figure 2.8 The ^{13}C labeled peak of 2-octanol (leftmost peak) and overlapping peaks

Another important issue to consider is the choice of borane source. Some BH_3 sources have a significant barrier for the alkene and borane to approach i.e. ammonia-borane complex. This allows the reaction regioselectivity to be completely understandable by TST.[90] Another effect of the ligand is the rate for the dissociation of the ligand. The amount of free borane in solution is important since it is only the first addition to the alkene that is dynamic (see Scheme 2.5.) A commonly used borane source is commercial borane-tetrahydrofuran complex (BH_3•THF). This particular BH_3

source has a unique issue of decomposition. Over time, the tetrahydrofuran (THF) can undergo a ring opening reaction to give 1-butanol upon hydrolysis.[91] This causes experimental difficulty since the major product in the reaction is a primary alcohol. For these reasons, two BH_3 sources were chiefly used. The first was freshly made BH_3•THF by reduction of boron trifluoride diethyl etherate (BF_3•OEt_2) with sodium borohydride ($NaBH_4$) in THF,[53] and the second was borane-methyl sulfide complex (BH_3•SMe_2).

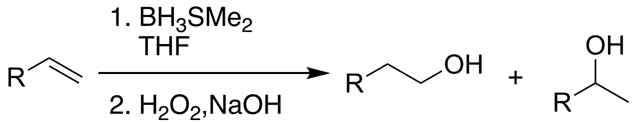
Scheme 2.5 The complete hydroboration of an alkene.



BH_3• SMe_2 has a distinct advantage in ease of use and number of solvents. However, after extensive measurements, it was speculated that the rates of addition for mono- and di-substituted organoboranes were competing significantly with the formation of unhindered BH_3 due to consistent measurement of ~7-8% Markovnikov product with both excess alkene or excess borane as shown in

Table 2.1, which was experimentally seen by Brown when stoichiometric amounts of borane were used.[60]

Table 2.1 The hydroboration of terminal alkenes with 10 equiv. BH_3•SMe_2. These measurements are the average of two trials.

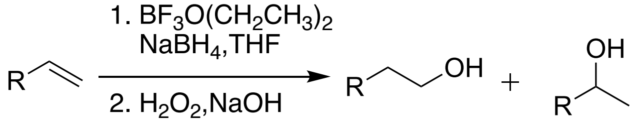


Alkene	% Markovnikov
1-pentene	8.7
1-octene	7.0
1-dodecene	7.0

The true measure of the utility of BH_3•SMe_2 came with the measurement of propene-d6. Using a 100-fold excess of the borane, the product ratio for propene-d6 was measured to be 8.6 ± 0.3%. Care was taken to exactly reproduce the conditions by Oyola and Singleton, but the product ratio disagreed significantly from their reported ratio of 10.0 ± 0.3%. At this point, it was clear that the mono- and di-substituted borane additions were kinetically competing with the free borane, and the borane source used for further studies was freshly prepared BH_3•THF.

With the analytical method and appropriate borane source determined, the effect of the length of an alkyl chain has on the hydroboration reaction was determined. It is important to note that any losses from the products would disproportionally affect the minor Markovnikov product due to its small quantity. This procedure used 10 equiv. of freshly prepared borane to 1 equiv. of alkene in THF. The data collected are shown in Table 2.2. It can be seen clearly that the effect of the length of alkyl chain on the product ratios is to make the hydroboration reaction more selective as the length of the alkyl chain is increased (The ratios seen with BH_3SMe_2 follow a similar trend). While the changes to the product ratio are small, the changes are statistically significant, as the values in Table 2.2 are the averages of 6 independent experiments.

Table 2.2 Experimental data of Markovnikov product with 10 equiv. of freshly prepared borane



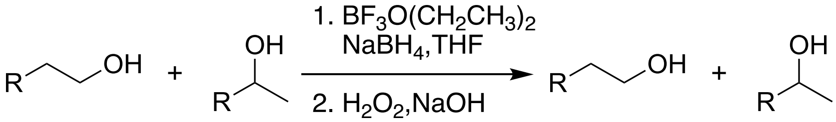
Alkene	% Markovnikov
propene-d6[a]	10.0 ± 0.3%
1-hexene[b,d]	10.7 ± 0.5%
1-octene[b,d]	9.8 ± 0.4%
1-dodecene[b,d]	9.2 ± 0.2%
3,3-dimethyl-1-butene[c,d]	11.2 ± 0.4%

[a] From Oyola and Singleton.[25] [b] Measured by ^1H NMR in benzene-d6. [c] Measured by ^1H NMR in $CDCl_3$.[d] Errors are reported as 95% confidence intervals of 6 measurements.

The trend seen by increasing the length of the alkyl chain cannot be accounted for by a nonpolar interaction, as the hydroboration of hexene with added pentane showed no change in the product ratio, nor should it be a steric effect, since the extra carbons are a long distance away from the reactive double bond. Since the longer alkyl chains make the reaction more selective, it can be said to have a cooling effect on the reaction leading to a small be important increase in selectivity as the length of the alkyl chain increases. Also, 3,3-dimethyl-1-butene showed a lower selectivity than that of the unhindered, unbranched alkenes. This observation also lends credence to the assumption that the straight chain alkenes are actually unhindered.

An important task was to determine whether the reaction conditions or the workup process affected the product ratios. A known mixture of each of the product alcohols were subjected to the hydroboration procedure from Table 2.2 without the alkene and reisolated. The recovered alcohol ratio was compared to the original alcohol ratio. None of the ratios differed in any appreciable amounts. The results of this control study are summarized in Table 2.3.

Table 2.3 Control Reaction Results



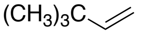
	Standard (%M)	**Reaction 1 (%M)**	**Reaction 2 (%M)**
hexanol	11.7%	11.7%	11.5%
octanol	12.3%	12.2%	12.2%
dodecanol	6.0%	6.0%	5.8%

Now the question that must be answered is whether these product ratios can be explained by the RRKM-ME assumption of cooling from the solvent or from the CCNM model, or if these results require a deeper understanding of the reaction. To ascertain efficacy of these models, all of the product ratios for the alkenes were calculated with both methods as well as TST and are discussed in the next section.

2.3 Computational Models Results and Discussion

The previous studies by Oyola and Singleton determined that B3LYP/6-31G* is comparable to CCSDT/aug-cc-pvqz near the π-complex and the transition structures. This method and basis set were utilized throughout the process for DFT calculations. For 1-dodecene and 1-octene the highest level single point energies could only be calculated at the CCSD(T)/aug-cc-pvdz level. The basis set was extended to aug-cc-pvtz when the alkene was 1-hexene or 3,3-dimethyl-1-butene. With propene and selected 1-butene structures, the basis set could be extended to aug-cc-pvqz. The differences in energies from the aug-cc-pvtz energies to aug-cc-pvqz energies showed were not significant. The CVT energies were calculated using interpolated single point energies (VTST-ISPE)[92] using CCSD(T)/aug-cc-pvtz calculations energies from the program GAUSSRATE/POLYRATE.[93,94] Tunneling was accounted for by the small curvature tunneling approximation.[95] Table 2.4 is a collection of statistical and non-statistical methods for the prediction of the % Markovnikov for the hydroboration of terminal alkenes.

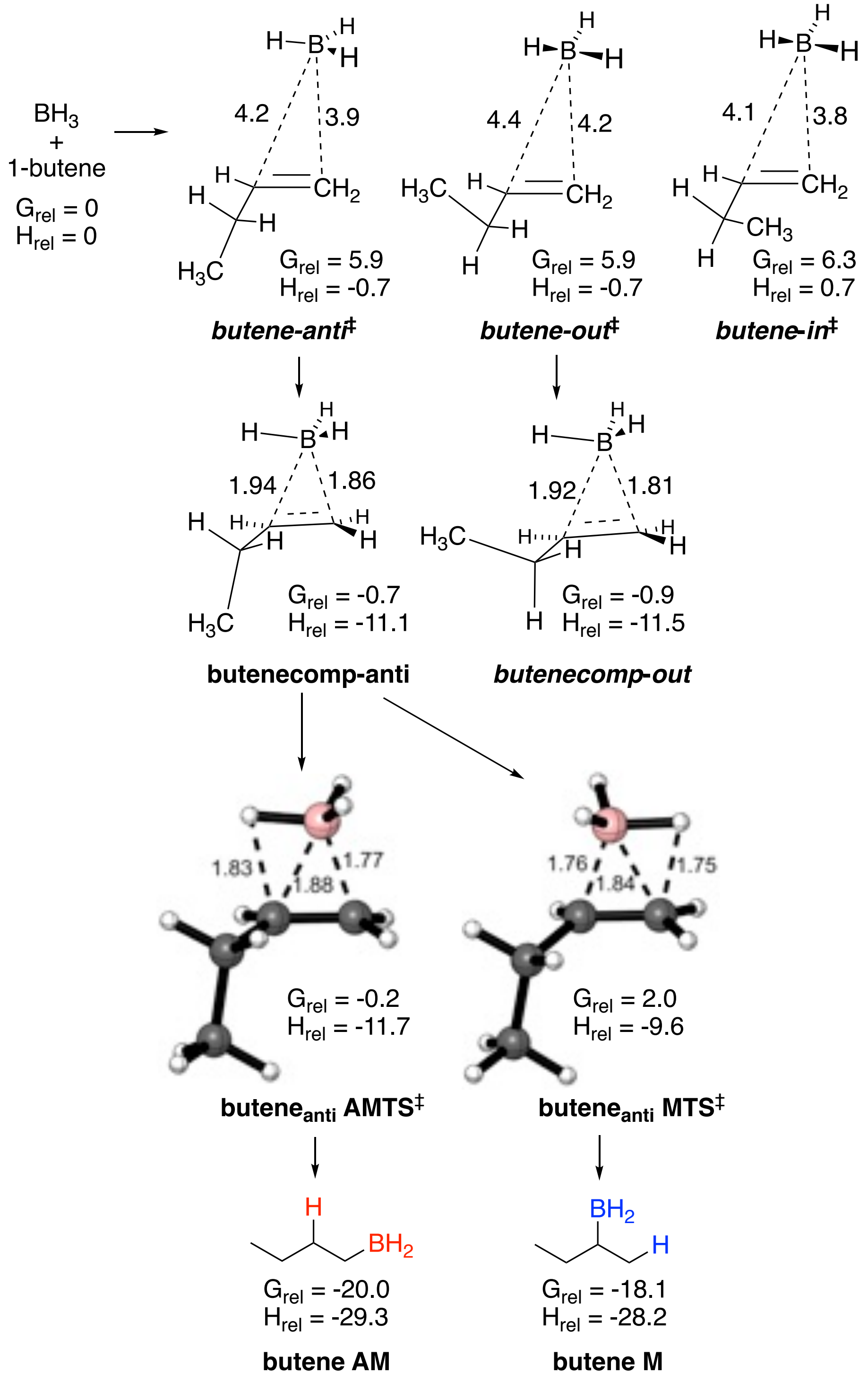
Table 2.4 Experimental and Predicted Selectivities for the hydroboration of alkenes (25 ºC unless noted)

Alkene	Experimental Markovnikov	TST	CVT/ SCT	statistical CCNM	nonstatistical CCNM	best-fit RRKM-ME	Localized RRKM-ME
propene	10.0 ± 0.3%	1.4%	2.2%	4.2%	3.3%	13.0%	8.7%
propene (70 °C)	11.2 ± 0.3%	2.4%	3.5%	6.4%	5.2%	13.7%	10.3%
1-butene	–	1.9%	2.8%	5.6%	4.4%	11.7%	10.9%
1-hexene	10.7 ± 0.5%	2.0%	2.8%	6.2%	4.1%	9.5%	10.9%
1-octene	9.8 ± 0.4%	2.1%	2.9%	6.1%	4.5%	6.8%	10.6%
1-dodecene	9.2 ± 0.2%	2.2%	2.9%	6.2%	4.5%	5.7%	10.1%
	11.2 ± 0.4[f]	1.8%	2.6%	1.9%	1.7%	8.6%	11.4%

From the previous work done by Singleton and Oyola, it suggests that the approach of the BH_3 to the alkene is by free BH_3, rather than by solvent-complexed BH_3. As shown in Figure 2.3, the approach of the BH_3 is enthalpically barrierless, but the CVT transition structures were determined as the maximum on the free energy using CCSD(T)/aug-cc-pvdz single points on B3LYP/6-31G* optimized structures in steepest decent mass weighted coordinates using Truhlar's no saddle method.[96] These structures are very approximate since the free energy calculations for loosely associated molecules are imperfect. The dynamic trajectories performed that will be discussed later show that the VTSs are viable in this case. Three CVT TSs were found for the addition of BH_3 and 1-butene. The BH_3 can approach 1-butene in its most stable conformation from either face of the alkene. This gives rise to the **butene-anti**‡ and **butene-out**‡ conformers shown in Scheme 2.6. If the BH_3 approaches the higher energy conformer of butene, than **butene-in**‡ is formed.

The addition is in a non-Curtin-Hammet realm since the alkyl groups cannot interconvert between conformers within the 1 ps reaction time of the addition.[97] Because of this, it is necessary to follow each of the conformer's mechanistic paths. For all of the alkenes studied, both the *anti* and *out* approaches were weighted evenly, while the inclusion of the *in* conformer of 1-butene showed no appreciable effect on the predicted product ratios, and it was subsequently not calculated for the larger alkenes. For the remainder of the alkyl chains, all were assumed to be in an extended anti conformations. This assumption was tested by a conformational analysis of 1-dodecene. In structures within 2.5 kcal/mol of the lowest energy conformation, none had any significant steric hindrance of the alkene (within 6 Å). In addition, conformers had little effect on the free energy of the transition structures.

Scheme 2.6 Conformations of the hydroboration of butene. Energies are CCSD(T)aug-cc-pvtz//6-31G*



The intrinsic reaction coordinate for the vartiational transition structures **butene-anti**‡ and **butene-out**‡ lead directly to the π-complexes **butenecomp-anti**, and **butenecomp-out**. These are examples of **INT** derived from butene from Figure 2.3. As seen in Scheme 2.6, the π-complexes free energies are very near to the free energy of free starting materials, but the barriers going forward are very low and the reaction occurs rapidly, so the formation of the π-complexes is rate determining.

The π-complexes then lead to the either the anti-Markovnikov or Markovnikov transition states AMTS and MTS, respectively. In Scheme 2.6, the structures of **butene$_{\mathbf{anti}}$-AMTS** and **butene$_{\mathbf{anti}}$-MTS** are shown as CCSD(T)/aug-cc-pvtz//B3LYP CVT structures. Appendix B contains the structures for the out conformer as well as other alkenes studied. The tunneling corrections increase the formation of the Markovnikov product while the rate of formation of anti-Markovnikov product is little changed. This serves to increase the %Markovnikov in Table 2.4 from ~2% (from 2.2-2.5 kcal/mol difference in the potential energy TSs) in the TST calculations to ~3% in the CVT/SCT predictions. All of these calculations are subject to recognized errors. For instance, all of these calculations were performed in the gas phase, but since the anti-Markovnikov TSs are more polar than the Markovnikov TSs, the inclusion of an implicit solvent model (PCM) actually changes the product ratio even further from the experimental value. Anharmonic frequency calculations also only changed the relative energies by 0.02 kcal/mol. Neither of these known shortcomings can account for the inability of TST or CVT to adequately predict the outcome of the hydroboration of alkenes. It is also important to recognize that the TST predictions also predict a decrease in selectivity in the reaction as the alkyl chain length grows. In addition, TST cannot explain the lower selectivity of 3,3-dimethyl-1-butene versus 1-hexene. All of these factors point to a real effect, and not simply an error in the method of calculations.

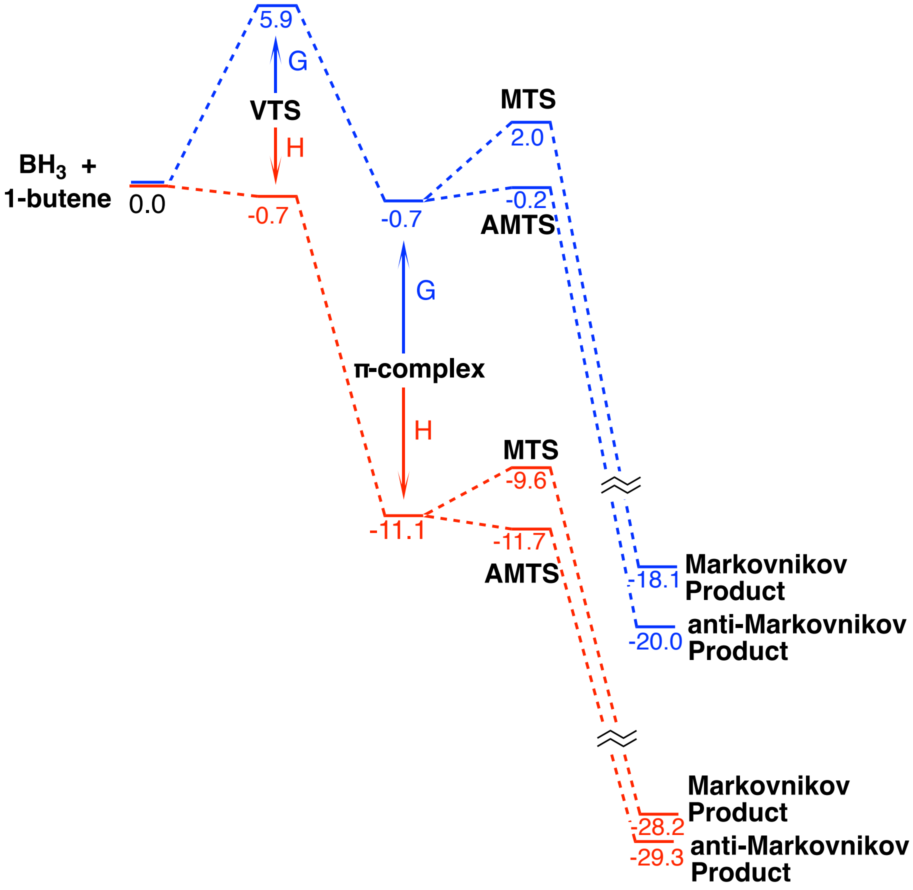


Figure 2.9 Energy diagram (CCSD(T)/aug-cc-pvtz//6-31G*) for the anti conformation of 1-butene.

The energy diagram (Figure 2.9) shows the energetics across the CVT surface for the **anti** track of 1-butene. First, the VTS is the first irreversible step in the reaction and is thermally equilibrated. As such, the 10.4 kcal/mol potential energy difference from the

VTS to the **π-complex** is the average excess energy that could be available to promote the hydroboration in the subsequent step. This amount of excess energy far surpasses the potential energy barrier in **AMTS** or **MTS**. TST theory assumes that at the point of the **π-complex** the intermediate would thermally equilibrate before the next step. However, since the experimental evidence shows a large quantity of Markovnikov product formed in the reaction, it is evidence that the **π-complex** is not thermally equilibrated. In the absence of this assumed thermal equilibration, it is clear that TST should not be applied in this case.

The CCNM calculation separates the mechanism into a direct and indirect path. The indirect path is calculated by CVT/SCT for this study. The direct portion is calculated based on the equilibrium product mixture. However, in the hydroboration of alkenes the products are conformationally complex. The transition states are cyclic, and as the reaction progresses to the products, it forms eclipsed conformations that are unstable. This eclipsed product can rotate to afford either gauche or anti conformations at the C_1 and C_2 bond, and trajectories started from **butene-AMTS** do form both of these products. The products can also twist the C_1-BH_2 bond. The CCNM model depends closely on the relative energies of the products. For the calculations in this study, the products formed most often within 200 fs after the hydroboration TSs were used. The proportion of direct to indirect mechanism is heavily reliant on the difference in energies of the two possible transition states, **AMTS** and **MTS**. If the barriers are very low, then the direct mechanism is dominant, but if the barriers are high, than the indirect mechanism will dominate. For the butene anti track, the direct mechanism accounts for 41% and the indirect mechanism, 59%.

The indirect portion of the mechanism described by the CVT/SCT rate constants in this case, and since the CCNM has the direct mechanism, it can only improve upon the CVT/SCT product ratios from Table 2.4. For the statistical CCNM model, the selectivity for the product ratio is the equilibrium constant for the products. For the unbranched alkenes, this favors the anti-Markovnikov product by a factor of 8-15. This less selective direct mechanism brings the predicted product ratios closer to the experimental results, but the statistical CCNM model still predicts a too high selectivity of the hydroboration reaction. Most importantly, the trend in of greater selectivity in experimental values when the alkyl chain is increased is not seen in this CCNM model.

The most intriguing result of the statistical CCNM model is the complete failure to predict the product ratio of 3,3-dimethyl-1-butene. This is due to the equilibrium preference for the anti-Markovnikov product from a factor of 8-15 for the unbranched alkenes to 86.This is reflected in the direct mechanism, making the direct mechanism far too selective when compared to experiment. This was a shortcoming that was foreseen, and 3,3-dimethyl-1-butene was specifically studied as a substrate that would cause CCNM to fail.

The nonstatistical CCNM model allows for a finite intramolecular energy relaxation versus the time that the molecule takes to traverse the distance from the TS to the products in mass weighted coordinates.[98] The longer distance from the transition state to the products allows for less energy relaxation, and decreases the predicted formation of that product. In the Truhlar work, the nonstatistical CCNM calculation improved the value to the experimental result, but the calculation of the distance from the both the AMTS and MTS were assumed to be the same. The actual distance from the AMTS to products is always larger than the distance from the MTS to products (a factor of 1.7 with propene and 2.2-2.7 with 1-hexene). The to form the Markovnikov product, the MTS must only rotate a methyl group, while the formation of the anti-Markovnikov product requires the rotation of a larger -CH_2BH_2 with an additional rotation of the BH_2. This makes the nonstatistical correction favor the formation of the anti-Markovnikov product, and subsequently takes the predicted product ratios away from the experimental observations as seen in Table 2.4. Truhlar had suggested that the inclusion of this nonstatistical correction help bring the CCNM model closer to experiment, but it is not obvious that this is the case when the distance effect is taken into account.

Both the statistical and nonstatistical CCNM computations fall into the same errors for the hydroboration of alkenes as TST and CVT/SCT. They over predict the effect of the high temperature on the selectivity. They also fail to account for the selectivity increase as length of the alkyl chain in increased. The CCNM model fails to accurately allow for the excess energy in the intermediate. The CCNM model cannot be described as a successful physical model for the hydroboration of alkenes. The fact that it can handle the observations of a direct and indirect mechanism as described by Oyola and Singleton is a promising observation, and will be built upon later in this section.

The next model that was studied was the RRKM-ME model. Since the RRKM-ME calculations contain several adjustable parameters, the first factor that must be determined is whether a logical and consistent method for the collisional energy loss can be determined. Glowaki used an exponential down model. Using the program Mesmer[79] utilized by Glowaki, the RRKM-ME calculations were performed utilizing the same energies as TST on a series of alkene with varying alkyl chain lengths as well as 3,3-dimethyl-1-butene.

The RRKM-ME has adjustable parameters some of which can be set based on literature data. The Lennard-Jones parameter for the solvents and reactants is one of these parameters. The Lennard-Jones parameter will affect the collision frequency of the reaction. The Lennard-Jones parameters for THF and each alkene were used when available, but if they could not be found, then the alkane Lennard-Jones parameter was substituted for the alkene. The specific density for THF was set as well. This allowed the RRKM-ME calculations to rely on a single adjustable parameter, E_{down}.

For the "best-fit" RRKM value in Table 2.4 were acquired by minimizing the root mean squared error for the experimental data as a whole using 860 cm^{-1} for E_{down}. The predictions do not match the experimental values very well. RRKM-ME predicts lower selectivity than is experimentally seen for propene by 3%, while at the larger dodecene over predicts the change that increasing the alkyl chain produces by 3.5%. In addition, the change from 25 ºC to 70 ºC is under predicted, only 0.7% versus 1.2% seen in experiment. One important feature that is captured by the RRKM-ME selectivities is the trend in the effect of the alkyl chain, which is not captured by TST or CCNM. Since RRKM theory distributes excess energy statistically throughout the molecule, the correct prediction of the trend was foreseeable. The increased selectivity from 1-hexene/ 1-

octene/1-dodecene that is predicted is much too large. The difference seen in experiment is only 1.5% from 1-hexene to 1-dodecene, while RRKM-ME predicts this change to be 3.8%. If propene is included the number is wrong by nearly 8%. The alkyl chain does make a difference in the result, but the effect is too high when subjected to the statistical energy distribution of RRKM-ME. Unfortunately, even with E_{down} set at 0 the 1-dodecene ratio is still 6.1%. No settings of the adjustable parameter were effective in predicting the amount of Markovnikov product for such a large alkene. If a sufficiently large alkene is assumed, the RRKM-ME prediction should approach the 2.9% Markovnikov amount of CVT/SCT, but as seen by experiment, it is difficult to imagine the experimental number to be that low.

It does seem from the simple RRKM-ME calculations that the excess energy in the π-complexes is non-statistically distributed throughout the molecule. From this springs the idea that perhaps the larger molecules can take up the energy that is statistically expected, but it reacts too quickly for IVR to occur. This could allow the large molecules to behave as smaller molecules do on the fast timescales. It has been seen previously, that treating the larger molecules as smaller molecules can account for this nonstatistical energy distribution in hot intermediates.[27,99] A “local RRKM” model is achieved by replacing the large molecule vibrational frequencies with the small molecule vibrational frequencies.

This “localized RRKM-ME” model treats the large molecule vibrational frequencies as a smaller model, but allows cooling as if the large molecule normally would in the RRKM-ME fashion. The model here substituted the vibrational frequencies of all propene moieties into the calculations for the larger 1-butene, 1-hexene, 1-octene, 1-dodecene, and 3,3-dimethyl-1-butene structures, while keeping the Lennard-Jones parameters constant to allow for cooling. This is a qualitative choice inherent to this model. The E_{down} was modified to best fit the experimental ratios, and the results are shown in Table 2.4. These results are the closest match to any of the models studied so far, and improve upon the simple RRKM-ME predictions. While the room temperature propene ratio is predicted to be too low, the rest of the predictions are within 0.5% of the experimental product ratio observed.

These two RRKM-ME models show the extremes of the continuum of possibilities in the actual reaction, one with complete IVR (RRKM-ME) and the other with no IVR outside of the core atoms (localized RRKM-ME). It is quite intriguing that these results bracket the experimental value in every occasion, but with the localized RRKM-ME model prediction being closer to the experimental value.

One mechanism not discussed thus far is direct transfer of BH_3 from a molecule of THF. This mechanism has been shown by Singleton and Oyola to not be the correct mechanism previously, but this mechanism was briefly studied as well. For this study, a classical single trajectory study was used to measure the excess energy in the π-complex. This was found to have a less energetic π-complex (3.0 kcal/mol) than that of the free BH_3 mechanism (10-11 kcal/mol). When the product ratios are predicted using the localized RRKM-ME calculation (discussed later in this section) with E_{down} set to 0, only 3.6% Markovnikov product was predicted to occur for 1-dodecene. Therefore, this mechanism was dismissed, as it did not account for the experimental results.

2.4 Dynamic Trajectory Results and Discussion

Dynamic trajectories are extremely useful in understanding reactions on the molecular level. For this study, two different QM/MM ONIOM models were employed for the hydroboration of alkenes in explicit solvent. Dynamic trajectories were released from the approximate position for the VTS of the hydroboration of propene, hexene, and dodecene in a sphere THF molecules. The first used B3LYP/6-31G* for the alkene and BH_3 with PM3 for 53 THF molecules in a 24.6 Å diameter sphere with a density about 0.88. While the second, still used B3LYP/6-31G* for the alkene and BH_3, but used the larger PM6-D3H4 for 80 THF molecules in a sphere with its diameter of ~29 Å and a density ~0.91. The second model also included a small dispersion correction based on Grimes' D2 model.[100] It is important to note that PM3 underestimates intramolecular attraction forces, but was used at first only for practical reasons. PM6-D3H4 became computationally feasible with the development of a new program *ProgdynONIOM*. Even though the two models have different molecular forces, the two methods are comparable.

The dynamic trajectories are, by necessity, fully classical due to computational limitations. The exclusion of ZPE and tunneling does cause some concern since the trajectory models simplify reality. The B3LYP surface used for trajectories The simplifications can be tested by calculating the rates using CVT/SCT for both B3LYP and CCSD(T) surfaces. The rates are comparable with values of $1.6 \times 10^{12}\ s^{-1}$ to $2.0 \times 10^{12}\ s^{-1}$ for B3LYP to CCSD(T). In addition, RRKM theory predicts 15.4% Markovnikov with B3LYP energies, but 14.2% with CCSD(T) energies. The RRKM selectivity difference should minimally affect the observations from trajectories, but it does suggest that trajectories will overestimate the amount of Markovnikov products seen.

The initial points for trajectories were obtained from a series of independent structures that had the BH_3 held loosely to the alkene at 3.4 Å from the terminal olefinic carbon and 3.8 Å from the internal olefinic carbon. Those distances were chosen to closely resemble the gas phase VTS for the approach of BH_3 to propene. This choice was arbitrary, but it could easily be checked. If the trajectories were at the VTS, half of the released trajectories would form products, and the other half would recross to starting materials. The actual product forming trajectories, among all the calculations, were 57% with a range 40-70% depending on the alkene or ONIOM model. These values are relatively close to 50% suggesting that the starting points were relatively close to the variational transition state. For all alkenes, each of the starting structures and velocities were extracted from the equilibrating trajectories at 250 fs intervals and integrated forward in time using the Verlet algorithm with no constraints until either the anti-Markovnikov, Markovnikov, or the complex dissociated into separated starting materials separated by 4.5 Å. Trajectories that formed exclusively product or recrossed were disregarded on the basis that the starting structures were not at the variational transition state. The results of the trajectories are shown in Table 2.5.

Table 2.5 Results from dynamic trajectories

Alkene	ONIOM Model	Anti-Markovnikov: Markovnikov (% Mark)
propene VTS	53 THF	115:11 (8.7%)
	80 THF	153:26 (14.5%)
1-hexene VTS	53 THF	108:15 (12.2%)
	80 THF	184:36 (16.4%)
1-dodecene VTS	53 THF	71:10 (12.3%)
	80 THF	108:15 (12.2%)

Dynamic trajectories rely on the results of chance events. As such, trajectories have an uncertainty associated with them, and large numbers of trajectories are necessary for precise predictions. The practical number of trajectories is limited, and the 95% confidence ranges for Table 2.5 are 4-6%. This limits the predictive power of dynamic trajectories for the range of experimental values seen in this report. But in spite of the limitations of the trajectories, overall the results of the trajectories are successful. In every case when the trajectories are started near the VTS, the calculated amounts of the Markovnikov product are near to the experimental results, and significantly different from the TST. But if the starting point for the trajectories is moved to the π-complex then the results shift to 2.9 ± 1.6% Markovnikov (198:6 anti-Markovnikov: Markovnikov) which is within error of the classical TST value.

The product outcomes of dynamic trajectories are only one piece of the information that can be gleaned. The total trajectory time and energy flow are also extremely enlightening. While it is difficult to explain all of the variations of the trajectories proceeding from the VTS to the π-complex (median 450 fs), the lifetime of the π-complex is far easier to describe and is quite interesting. The lifetime of the π-complex was defined in this study as beginning with both the C-B distances were less than 2 Å and ending with the either product formation. Remarkably, ~30% of trajectories have the π-complex lifetime of less than 50 fs. These trajectories react in the first collision of BH_3 / alkene with little to no intermediate. After this initial collision, few complexes react from 50 to 120 fs. This is shown in Figure 2.10. The lull in reactivity is the time the BH_3 takes to rebound and reapproach to the alkene. After this time, the decay continues to proceed but at a much slower rate. The most striking detail from Figure 2.10 is the low selectivity of the reactions occurring in the first collision. Nearly half of the Markovnikov product is formed within the first collision. Overall, 20.2% of the total Markovnikov product is formed in this portion of the reaction. This burst, however, is not sufficient to explain the departure from TST, since even after 1000 fs the ratio is still 4.7% Markovnikov.

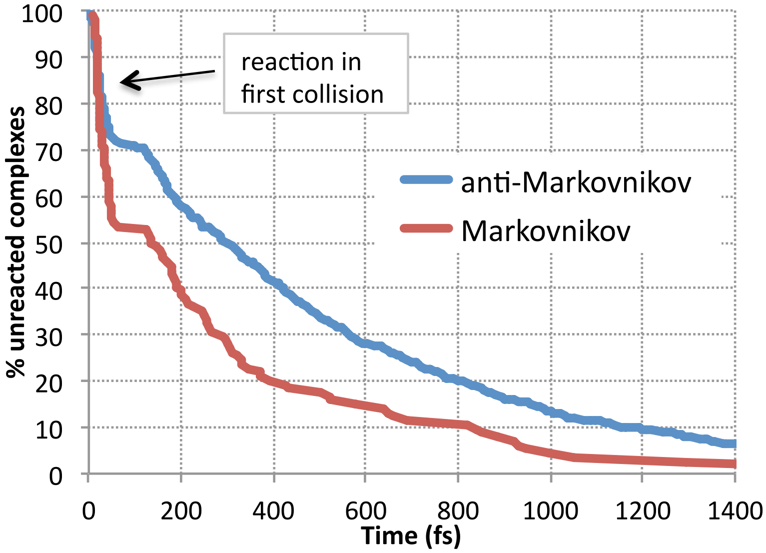


Figure 2.10 Decay of all combined trajectories BH_3 / alkene π-complexes after formation.

An energy analysis of the alkene / BH_3 was performed from the trajectory studies. The entire system (solvent, alkene, and BH_3) has its energy held constant, but the alkene / BH_3 energy can change through interactions with the solvent. The total energy of the alkene /BH_3 can be described as the combination of the potential energies and the atomic kinetic energies in a center of mass frame of the alkene and BH_3. From the full dynamic trajectories, the total energy is computed from the sum of gas phase B3LYP/6-31G* potential energies calculated from the geometries at each point along the trajectory and the kinetic energy calculated from the displacements between three points of a trajectory. The total energy of alkene, $E_{\text{alkene+BH3}}$, was tracked for each trajectory from the VTS until the trajectory passed through a product forming TS (**TS-AM** or **TS-M**). In a similar method, the energy of only the BH_3 and propene portion, E_{local}, of the alkene was also followed. To acquire the propene portion of the alkene, the alkyl chain was deleted and replaced by an H atom in the same direction as the first C atom in the chain with a bond length of 1.100 Å. This value allows a probe into the reactive site of the hydroboration reaction. At the same time, the energy of the alkyl chain , E_{chain}, was calculated by the same replacement of the propene portion of the alkene. For the replaced H atoms in E_{local} and E_{chain}, these were assumed to have no kinetic energy. The averages of the different energies ($E_{alkene=BH3}$, $E_{local,}$ and $E_{chain)}$ for 20 points at the beginning of a trajectory and of points 40 to 21 from end were calculated. These were used to calculate the change in the energies and are summarized in **Table 2.6**. For ease, **Table 2.7** is a list all of the energies for the dynamic trajectories that are discussed in this chapter. From the table, some observations are clear. One is that, the sum of $\Delta E_{local\ avg}$ and $\Delta E_{chain\text{-}avg}$ is close to the $\Delta E_{average}$, but not exact since due to the incomplete modeling of interactions between the two models. Another is that larger alkenes seem to lose more energy over the course of reaction versus the smaller alkenes. The values of $\Delta E_{average}$ in **Table 2.6** vary from -2.8 to 5.4. These values have a quite large distribution. The standard deviations are the following: propene 3.8 kcal/mol, 1-hexene 4.9 kcal/mol, and 1-dodecene 6.7 kcal/mol.

Table 2.6 Energy Results of Dynamic Trajectories

Alkene	ONIOM model	$\Delta E_{average}$ (kcal/mol)	$\Delta E_{local\text{-}avg}$ (kcal/mol)	$\Delta E_{\text{“experimental”}}$ (kcal/mol)	$\Delta E_{chain\text{-}avg}$ (kcal/mol)
propene	53 THF	-4.0 ± 0.7	-4.0 ± 0.7[a]	-3.4	-
	80 THF	-2.8 ± 0.4	-2.8 ± 0.4[a]		-
1-hexene	53 THF	-3.5± 0.6	-4.5 ± 0.9	-4.7	+0.7 ± 0.6
	80 THF	-4.1 ± 0.5	-5.1 ± 0.6		+0.8 ± 0.5
1-dodecene	53 THF	-5.1 ± 1.1	-4.7 ± 1.2	-5.6	-0.5 ± 1.0
	80 THF	-5.4 ± 1.4	-5.4 ± 0.9		+1.0 ± 0.8

[a] the propene $\Delta E_{local\ avg}$ is the same at $\Delta E_{average}$

Table 2.7 Energies of Interest in the Analysis of Dynamic Trajectories

	Full Solute
$E_{alkene+BH3}$	$BH_3 + CH_2{=}CHCH_2R$ kinetic energy + B3LYP/6-31G* potential energy
$\Delta E_{alkene+BH3}$	Change in $E_{alkene+BH3}$ from VTS to TS-AM or TS-M
$\Delta E_{average}$	Average of $\Delta E_{alkene+BH3}$ for a class of trajectories
	Local Area of Reaction
E_{local}	$BH_3 + CH_2{=}CHCH_2$ kinetic energy + B3LYP/6-31G* energy $BH_3 + CH_2{=}CHCH_2H$
ΔE_{local}	Change in E_{local} from VTS to TS-AM or TS-M
$\Delta E_{local\text{-}avg}$	Average of ΔE_{local} for a class of trajectories
	Alkyl Chain
E_{chain}	kinetic energy of R– + B3LYP/6-31G* energy for RH
ΔE_{chain}	Change in E_{chain} from VTS to TS-AM or TS-M
$\Delta E_{chain\text{-}avg}$	Average of ΔE_{chain} for a class of trajectories
$\Delta E_{\text{“experimental”}}$	Average loss in energy for localized RRKM-ME to account for the experimental results

Some individual $E_{alkene+BH3}$ of trajectories are graphed in Figure 2.11a. In Figure 2.11a, the three graphs are examples of the energy fluctuations in $E_{alkene+BH3}$ for trajectories. These three examples were chosen for their diverse characteristics. The first (top left) loses 4 kcal/mol or about $\Delta E_{average}$ for 1-hexene. The second (top right) loses 11 kcal/mol (matched or exceeded by 10% of trajectories), and the third (bottom left) actually gains ~4 kcal/mol (matched or exceeded by 10% of trajectories). Fascinatingly, the $E_{alkene+BH3}$ is constantly variable, with the amount of energy lost or gained is capricious. The solute of the reaction is inside the solvent force field and is continually changing energy randomly (see the standard deviations above) often gaining or losing >5 kcal/mol,[101] but overall, $\Delta E_{alkene+BH3}$ is negative, since the hydroboration reaction is very exothermic and, consequently, tends to lose energy. What seem like hills in Figure 2.11a, appear to be discrete events or collisions with the solvent, but similar artifacts can be modeled with a random walk (Figure 2.11b).

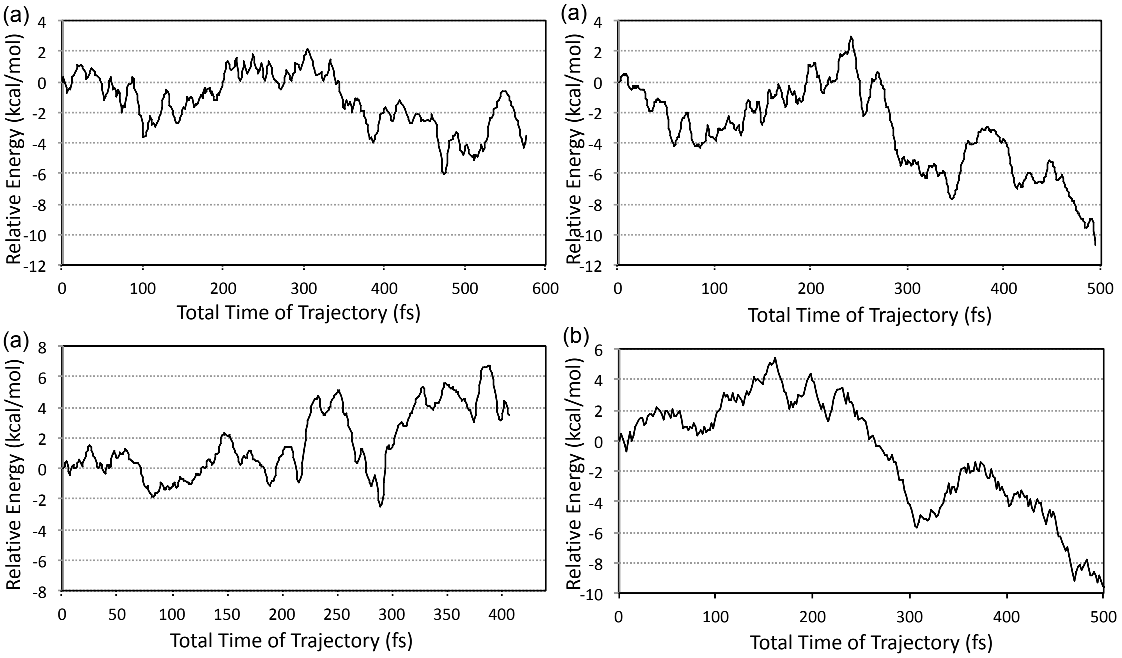


Figure 2.11 (a) Three graphs of $E_{alkene+BH3}$ versus time for trajectories of 1-hexene/BH_3 with product formation is ~500 fs. (b) A biased random walk in the energy, with $E(t+2fs)=E(t)+0.54*\textit{rand}-0.016$, where *rand* is a random number between -1 and 1. The parameters were chosen to mimic $\Delta E_{average}$ and the variation in $\Delta E_{alkene+BH3}$ over 180 fs

Another fact apparent from the trajectory studies is the initial 10-11 kcal/mol excess energy upon the formation of the π-complex is only partially lost before the trajectories form product. This observation makes it clear that transition state theory is clearly inapplicable to the hydroboration of alkenes. While the after the initial burst of product forming reaction, the use of localized RRKM theory seems like a more prudent choice.

The variation in the change of the solute energy, $\Delta E_{alkene+BH3}$, from trajectories gives insight into the energy transfer in and out of the molecular normal modes for the solute. Propene, 1-hexene, and 1-dodecene have 33, 60, and 114 classical modes, respectively, and the average total energies are 33RT, 60RT and 114RT with standard deviations of 3.4, 4.6, and 6.6 kcal/mol, respectively. This random amount of energy shows the energy in the solute is varied randomly before the trajectory can occur. This means that the energies at any of the transition structures (**AMTS** or **MTS**) are uncorrelated with the starting energies. This randomization of energy does take time, but for 1-hexene, the standard deviation of $\Delta E_{\text{alkene+BH3}}$ is 2.9 kcal/mol within 180 fs. This crudely gives a half-life of the decorrelation at 140 fs.

The quantum real system would be subject to a tighter distribution of $\Delta E_{\text{alkene+BH3}}$ because the high-energy normal modes are rarely excited. For the propene, 1-hexene, and 1-dodecene systems, the standard deviations on the Boltzmann-random energies in individual molecules at 25 °C would be 1.6, 2.3, and 3.2 kcal/mol, respectively. These are approximately half of the variations in the classical systems. From Fermi's Golden Rule, the quantum system should be subject to lower rates of energy interchange with solvent than the classical system. However, most of the excess energy will be in low-energy modes that should behave closer to the classical limit seen in the simulations.

An unexpected observation from the energy studies was the small value of $\Delta E_{\text{chain avg}}$. As the BH_3 approaches an alkene, the potential energy lost is converted into kinetic energy in the approaching motion. Some of this energy is redistributed ballistically very quickly (10 Å/ps). The very low values of $\Delta E_{\text{chain avg}}$ seem to show the alkyl chain either does not take up energy or else loses it very quickly.

In order to better understand the nature of the effect of the alkyl chain, single-trajectory studies were carried out on gas phase BH_3 with each alkene conformation in the method of Hase.[26] These trajectories were started with the BH_3 5.0 Å from the olefinic carbons. With no energy given to the normal modes, the BH_3 was allowed to fall into the alkene as with a normal trajectory. Since the motion in the molecules is undeterred by other molecular motions, the trajectory falls directly into the deepest portion of the π-complex well. Figure 2.12 shows the potential energy curve and E_{local} over the time of the trajectory for *anti* conformation of 1-hexene (a) and 1-dodecene (b) *out* conformations of 1-dodecene (c). In both of the *anti* cases, (a) and (b), a persistent π-complex is formed for 2000 fs. Curiously, the *out* case (c) immediately passes over **TSM** and forms the Markovnikov product. This gives a small piece of data that dynamic matching favors the formation of the minor product. The trajectory giving the Markovnikov product is by no mean conclusive; however, it does suggest that dynamic matching favors the formation of the minor product in this reaction. This follows the observation in Figure 2.10 of the trajectories that react in the first collision form a larger percentage of Markovnikov products than in longer-lived trajectories.

The persistent π-complexes in Figure 2.12a and Figure 2.12b allow the study of how fast energy is taken up by the alkyl chain. As the BH_3 approaches the alkene, the potential energy of the reaction falls, while the kinetic energy builds concurrently in the atoms that form the π-complex. The energy transferred out of the complex to the chain is seen in Figure 2.12 as a drop in E_{local}. The loss of energy from the complex does not occur for about 100 fs after the drop in potential energy begins. At this time, the energy transfer seen is very fast, and it is assumed to be ballistic. The fast energy loss takes up ~4 kcal/mol from the 1-hexene, and 6 kcal/mol from 1-dodecene within 100 fs. The alkyl chain for 1-hexene is mostly saturated, but the 1-dodecene continues to take up energy albeit much slower until it reaches an equilibrium value of 8.3 kcal/mol.

The single trajectory studies indicate that ballistic energy transfer is fast and a large amount of energy is transferred to the alkyl chain. The solution phase trajectories and experimental results imply that not all of the 6 kcal/mol energy is actually transferred in this way. In fact, only about half of this amount is transferred ballistically in the case of 1-dodecene. It is clear from the higher experimental selectivities that 1-dodecene redistributes more energy away from the alkene than smaller alkenes. Based on the $\Delta E_{\text{experimental}}$ values, 1-dodecene should take up 0.9 kcal/mol more energy than 1-hexene and 2.2 kcal/mol more than propene, and this accounts for the extra selectivity observed experimentally. The solution phase trajectories show a low amount of energy in the chain by the modestly lower $E_{\text{local avg}}$ for dodecene from propene as well as a small $E_{\text{chain avg}}$. The $E_{\text{chain avg}}$ cannot show the actual amount transferred to the alkyl chain, but rather, it only gives shows a small amount of energy present in the chain at the time the reaction occurs.

The single gas phase trajectories show that ~6 kcal/mol energy can be transferred to the alkyl chain, but why then do the solution phase trajectories and experimental values show only half of that number? The most straightforward response to this is shown in Figure 2.12c. In this graph, the 1-dodecene trajectory passes over **MTS**, immediately while losing only 1.2 kcal/mol. The 1-hexene (not shown) loses only 0.8 kcal/mol at the transition state. The trajectories that immediately form product are all included in the calculations of $\Delta E_{\text{chain avg}}$ and $\Delta E_{\text{local avg}}$. It is possible for the trajectories that do not react within the first collision to not be forced into the lowest potential energy well for the π-complex, and consequently do not have the full energy to redistribute. For trajectories that persist longer than 500 fs, it is possible from the chain to the solvent, but the low $\Delta E_{\text{chain avg}}$ from the solvent phase trajectories suggest the energy is transfer occurs from by direct passage from the π-complex. What is clear from trajectories is that the extra mass of 1-dodecene is a factor in cooling the reaction as seen by the E_{average} for propene is over half of that of 1-dodecene.

When comparing the two values of $\Delta E_{\text{“experimental”}}$ and $\Delta E_{\text{local avg}}$, it is important to note that these numbers are very similar. The calculation of $\Delta E_{\text{“experimental”}}$ is the average amount of energy lost in the localized RRKM-ME calculation to account for the experimental results. This value shows that the localized RRKM-ME model has the ability to predict the amount of energy lost from the propene portion of the alkene as seen in trajectories. This allows the alkyl chain to be looked at like a method to cool the reaction. To measure this, the E_{down} was set to reproduce the experimental value for propene, and the density of THF was altered to fit the localized RRKM-ME value to each of the remaining alkenes. The results were that 1-hexene, 1-octene, 1-dodecene, and 3,3-dimethyl-1-butene were 1.55, 1.81, 1.91, and 1.53 times of the concentration of THF to account for the experimental selectivities. This cooling effect is large for the smaller hexene and 3,3-dimethyl-1-butene, but the alkyl chain effect diminishes as the chain grows. The straight chain 1-hexene and branched chain 3,3-dimethyl-1-butene have a similar cooling effect as well, which does make intuitive sense. The cooling trends seen make qualitative sense, and arise from experimental results and only the assumption of the localized RRKM-ME model.

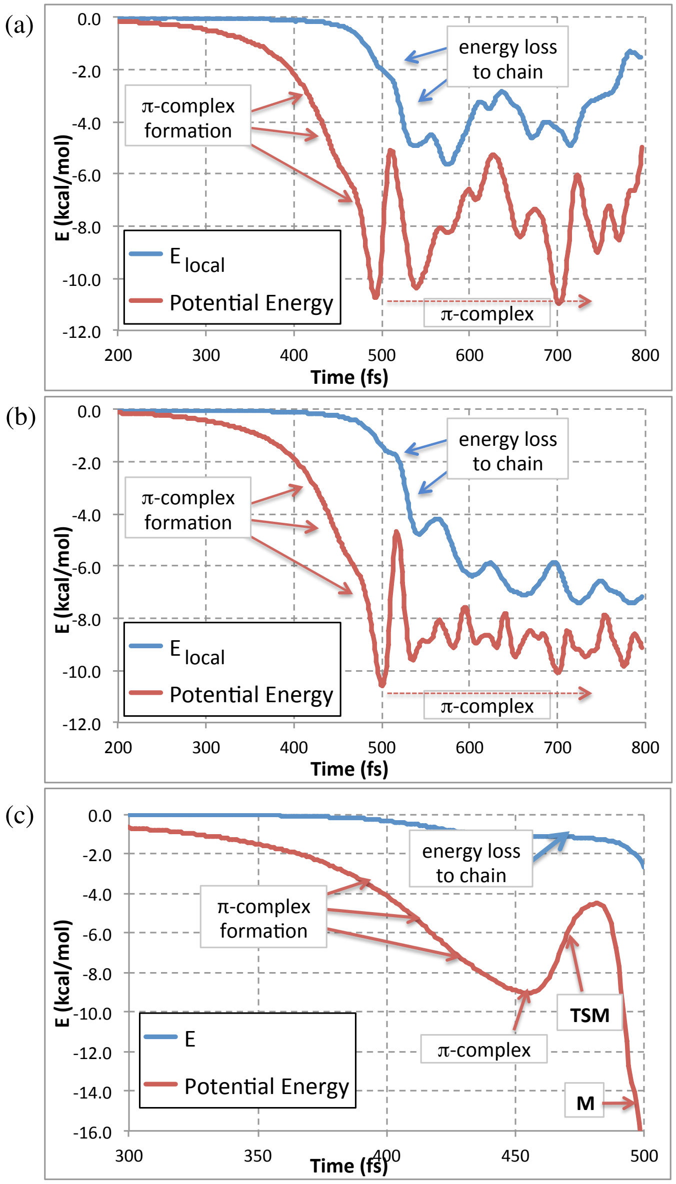


Figure 2.12 Single gas phase trajectory studies of the reaction of BH_3 with alkene. (a) 1-hexene anti approach of BH_3. (b) 1-dodecene anti approach of BH_3. (c) 1-dodecene out approach of BH_3. Both anti approaches form persistent π-complexes, while the out approach immediately passes through the Markovnikov transition state and forms product.

The CCNM model tries to understand the hydroboration of alkenes by a combination of mechanisms that are at two extremes, one of a direct path with no intermediate and the other an entirely thermally equilibrated intermediate. But, the success of the RRKM-ME and localized RRKM-ME calculations suggest that results from the CCNM model could be improved by describing the reaction, not as extremes, but more in the middle as described by the trajectories. This model the "competitive localized noncanonical" (CLN) model attempts to do just that.

The CLN model utilizes the direct and indirect paths directly from the CCNM model that are based on the energies of the π-complex versus the subsequent TSs. This calculation provides k_{dir} and k_{ind}, which are the rate constants for the direct and indirect mechanism, respectively. The branching ratio of the direct mechanism, $R_{A/B}^{loc\,RRKM}$, is based on a localized RRKM model, which is a RRKM-ME model without collisional cooling. This means that the direct portion can only distribute energy throughout the propene portion of the molecule. These predictions should mimic the reactions that react within the first collision as seen in the dynamic trajectory studies. The branching ratio for the indirect mechanism, $R_{A/B}^{RRKM-ME}$, is based on the RRKM-ME calculations with an exponential down model for the collisional energy, and the E_{down} set at the same value for each substrate.

$$k_{\mathrm{A}}^{CLN} = \frac{R_{A/B}^{loc\,RRKM}}{1 + R_{A/B}^{loc\,RRKM}} k_{dir} + \frac{R_{A/B}^{RRKM-ME}}{1 + R_{A/B}^{RRKM-ME}} k_{ind} \tag{2- 1}$$

$$k_{\mathrm{A}}^{CLN} = \frac{R_{A/B}^{loc\,RRKM}}{1 + R_{A/B}^{loc\,RRKM}} k_{dir} + \frac{R_{A/B}^{RRKM-ME}}{1 + R_{A/B}^{RRKM-ME}} k_{ind} \tag{2- 2}$$

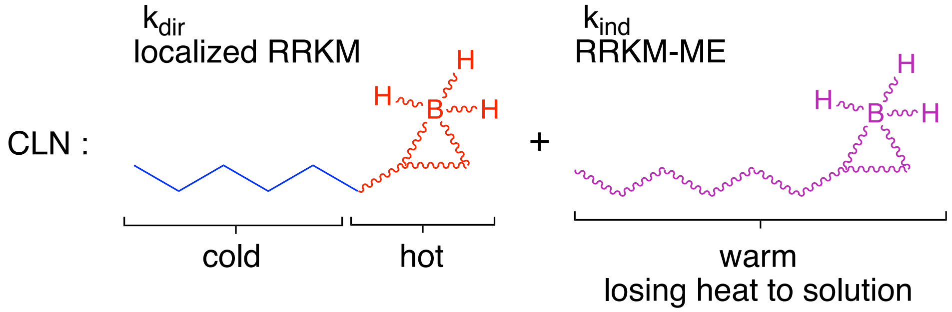
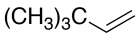


Figure 2.13 Graphical representation of the competitive localized noncanonical model

The results for the CLN model are shown in Table 2.8. The process for determining the best E_{down} was to set to reproduce the propene product ratio at room temperature. The CLN model predicts %Markovnikov for 70 ºC propene and 3,3-dimethyl-1-butene selectivities with very good accuracy. The 1-hexene value is overestimated by 0.9%, but the change from 1-hexene, 1-octene, and 1-dodecene is predicted very well. The CLN model predicts the trends in the experimental data well with only a single adjustable parameter.

Table 2.8 Experimental and CLN model predicted selectivities of the hydroboration of alkenes at 25 ºC (unless noted otherwise)

Alkene	Experimental Markovnikov	Competitive Non-canonical (CLN)
propene	10.0 ± 0.3%	10.0%
propene (70 °C)	11.2 ± 0.3%	11.1%
1-butene	–	12.3%
1-hexene	10.7 ± 0.5%	11.6%
1-octene	9.8 ± 0.4%	10.8%
1-dodecene	9.2 ± 0.2%	10.3%
	11.2 ± 0.4[f]	11.3%

The CLN model gives insight into some of the experimental results as well. The high temperature change in the selectivity of propene is a combination of a low change in the selectivity in the direct (RRKM) mechanism, 0.5%, and a larger change in the indirect (RRKM-ME) mechanism, 1.3%. The 3,3-dimethyl-1-butene result has a lower selectivity than does propene, due to the decrease of the faster reacting, less selective direct mechanism of 3,3-dimethyl-1-butene (33% for 3,3-dimethyl-1-butene and 47% for propene). The length of the alkyl chains contribute to the cooling of the reactive complex, but due to the lower selectivity of the direct mechanism, the predictions more accurately predict the experimental results. The CLN model is a simplification of the complex nature of the hydroboration of alkenes, but it does quantitatively predict the experimental results, as well as, gives a qualitative intuitive explanation of the experimental observations.

2.5 Conclusions

Transition state theory unequivocally fails to explain the regioselectivity observed in the hydroboration of alkenes both quantitatively, and in the qualitative trends in the experimental observations. TST is simply not designed to accept intermediates of reactions that are not a thermal equilibrium. However, TST is used to describe hydroboration to students every year. It is generally very difficult to determine when TST will fail before experiments are conducted, and it was only by the unique failure of TST to describe the product ratios seen that this study could have been done. This failure of TST does not exclude it from being a highly useful model to describe reactions in solution; in fact, it surely is effective in describing most solution phase reactions. But, care must be exercised when TST is applied to reactions when it is possible for an intermediate to contain excess energy, as TST may be invalid but without much experimental evidence to show this.

The CCNM model takes into account two extreme cases for the description of hydroboration of alkenes. The first where there is no intermediate, and the second fully thermally equilibrated reaction. The direct mechanism is supported with evidence from trajectories in this study. Approximately 20% of the trajectories react within the first collision of the BH_3 with the alkene, while the CCNM model estimates 33% of a direct mechanism when propene is the alkene. The failure of the CCNM model is its inability to describe the IVR in the direct mechanism, as well as relying on CVT/SCT rates for the indirect mechanism. The reliance on phase space predicted equilibrium product ratios allowed too much reliance on the sterics of the reaction, allowing the designed failure of 3,3-dimethyl-1-butene. As shown in this study the CCNM model cannot be used to explain the selectivity seen in the hydroboration of terminal alkenes.

RRKM-ME calculations are also insufficient to describe the selectivity of the hydroboration reaction, as it allows too much IVR overall for the reaction. The RRKM-ME calculations are based in the gas phase where collisions with bath gas molecules are easier to define, but this reaction occurs in the constantly changing force field of solution phase physics. The RRKM assumption fails by overestimating the effect of the molecular size.

Trajectories in explicit solvent are successful in the prediction of the approximate selectivity of hydroborations. These studies have few physical assumptions, and contain no adjustable parameters. These studies are impractical due to computational resources to adequately predict the outcome of trajectories within experimental errors, but they are effective in lending insight into the nature of the reaction. A large portion of trajectories was seen to react within the first collision of the BH_3 and alkene. ~50% of Markovnikov product was formed overall was formed in these fast reacting trajectories with the selectivity increasing over time. The energy change in the alkene and BH_3 is continually fluctuating randomly, with the average effect being that less than half of the total energy gained upon the formation of the π-complex is lost before the trajectory crosses either the anti-Markovnikov or Markovnikov transition state. The larger alkenes lose more energy, but the energy does not seem to be stored in the chain. The major source of energy change seems to be loss to the solvent. The alkyl chain can be seen as an additional cooling mechanism on the reaction area instead of a heat sink.

The localized RRKM-ME model is a new semi-statistical rate model that is suggested in this study. The larger alkenes are treated as a mixture of propene normal modes, while keeping the size of the alkene the same. This allows for a nonstatistical but more realistic energy distribution. The CLN model combines the direct vs indirect branching ratio from Truhlar's work, but treats the direct portion of the reaction by a localized RRKM model and the indirect mechanism with the statistical RRKM-ME model. The CLN model allows a good agreement with experimental selectivities with only one adjustable parameter. These two models allow the nonstatistical nature of the hydroboration reaction to be understood by a semi-statistical method. These models could become very useful to describe other reactions with similarly energetic intermediates.

2.6 Experimental and Computational Procedures

Example procedure of hydroboration from freshly prepared BH_3. A flask containing 2.08 g (55 mmol) of $NaBH_4$ was immersed in a 25 °C water bath. The flask was flushed with nitrogen, then 45 mL of THF was added and the solution was stirred rapidly. To this mixture was added dropwise 6.15 mL (50 mmol) of $BF_3O(CH_2CH_3)_2$ and the solution was stirred for 5 min. A solution of 1.1 mL (5 mmol) of 1-dodecene in 5 mL of THF was added dropwise. After 5 min the flask was cooled to 0 °C. The reaction was quenched by the slow addition of 25 mL of water (CAUTION gas evolution), followed by the dropwise addition of 16 mL of 3 M NaOH then 16.0 mL of 30% H_2O_2. The ice bath was removed, and the reaction was stirred at room temperature for 2 h. The aqueous layer was saturated with NaCl, and the organic layer was separated. The aqueous layer was then extracted with 25 mL of THF, and the two organic layers combined. The organic layer was washed twice with saturated NaCl solution, once with saturated NaS_2O_4 solution, and once with saturated NaCl. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure, though the solvent was not completely removed due to concerns about effects on the product ratio (unseen in control reactions). The residue was analyzed directly by ^{1}H NMR spectroscopy. The product ratios were measured using the doublet of the methyl group in the secondary alcohol (**M** product) and the triplet (sometimes a multiplet) of the methylene protons nearest the hydroxyl group in the primary alcohol (**A** product). The secondary methine of the **M** product overlaps with residual THF. All of the alkene product mixtures have nearly identical spectra, but in many spectra a broad peak at 0.6 ppm interferes with the integration of the peak at 0.85.

1-dodecanol ^{1}H NMR (500 MHz, C_6D_6) 3.37 (2H, t, J=6.6 Hz), 1.37 (2H, quin, J=6.8 Hz) overlaps with THF, 1.34-1.21 (18H, m), 0.92 (3H, t, J=7.0)

2-dodecanol ^{1}H NMR (500 MHz, C_6D_6) 1.01(3H, d, J=6.1 Hz)

*Example procedure of the product ratio control reaction***.** A flask containing 2.12 g (55 mmol) of $NaBH_4$ was immersed in a 25 °C water bath. The flask was flushed with nitrogen, then 45 mL of THF was added and the solution was stirred rapidly. To this mixture was added dropwise 6.15 mL (50 mmol) of $BF_3O(CH_2CH_3)_2$ and the solution was stirred for 5 min. A solution of 0.8 mL (5 mmol) of a known mixture of 1- and 2-octanol (standard in Table 2.3) in 5 mL of THF was added dropwise. After 5 min the flask was cooled to 0 °C. The reaction was quenched by the slow addition of 25 mL of water (CAUTION gas evolution), followed by the dropwise addition of 16 mL of 3 M NaOH then 16.0 mL of 30% H_2O_2. The ice bath was removed, and the reaction was stirred at room temperature for 2 h. The aqueous layer was saturated with NaCl, and the organic layer was separated. The aqueous layer was then extracted with 25 mL of THF, and the two organic layers combined. The organic layer was washed twice with saturated NaCl solution, once with saturated NaS_2O_4 solution, and once with saturated NaCl. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was analyzed directly by ^{1}H NMR spectroscopy.

Procedure of hydroboration of hexene with additional pentane with freshly prepared BH_3. A flask containing 2.38 g (55 mmol) of $NaBH_4$ was immersed in a 25 °C water bath. The flask was flushed with nitrogen, then 45 mL of THF was added and the solution was stirred rapidly. To this mixture 0.6 mL of n-pentane was added. Then the dropwise addition of 6.15 mL (50 mmol) of $BF_3O(CH_2CH_3)_2$ formed the borane after the solution was stirred for 5 min. A solution of 0.6 mL (5 mmol) of 1-hexene in 5 mL of THF was added dropwise. After 5 min the flask was cooled to 0 °C. The reaction was quenched by the slow addition of 25 mL of water (CAUTION gas evolution), followed by the dropwise addition of 16 mL of 3 M NaOH then 16.0 mL of 30% H_2O_2. The ice bath was removed, and the reaction was stirred at room temperature for 2 h. The aqueous layer was saturated with NaCl, and the organic layer was separated. The aqueous layer was then extracted with 25 mL of THF, and the two organic layers combined. The organic layer was washed twice with saturated NaCl solution, once with saturated NaS_2O_4 solution, and once with saturated NaCl. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure.

Example procedure of hydroboration of dodecene with BH_3•SMe_2. A 3-neck flask with 100 mL of THF was flushed with nitrogen. Then 2.2 mL (22 mmol) of BH_3•SMe_2 was added. Then 0.5 mL (2.2 mmol) of 1-dodecene was dissolved in 10 mL of THF, and this solution was added dropwise to the stirred borane solution. After 45 min, the flask was cooled to 0 °C. The reaction was quenched by the slow addition of 4.1 mL of water (CAUTION gas evolution), followed by the dropwise addition of 7.6 mL of 3 M NaOH then 7.6 mL of 30% H_2O_2. The ice bath was removed, and the reaction was stirred at room temperature for 8 h. The aqueous layer was saturated with NaCl, and the organic layer was separated. The aqueous layer was then extracted with 50 mL of THF, and the two organic layers combined. The organic layer was washed twice with saturated NaCl solution, once with saturated NaS_2O_4 solution, and once with saturated NaCl. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure.

Example procedure hydroboration of propene-d6 with BH_3•SMe_2. A 3-neck flask with100 mL of THF was flushed with nitrogen. Then 2.7 mL (27 mmol) of BH_3•SMe_2 was added. Then 0.25 mL (0.27 mmol) of condensed propene-d_6 was dissolved in 5 mL of cold THF and added dropwise to the solution. After 1 h, the flask was cooled to 0 ºC. the flask was cooled to 0 °C. The reaction was quenched by the slow addition of 6.5 mL of water (CAUTION gas evolution), followed by the dropwise addition of 9.4 mL of 3M NaOH then 9.4 mL of 30% H_2O_2. The ice bath was removed, and the reaction was stirred at room temperature for 4 h. The aqueous layer was saturated with NaCl. At this point the organic layer was analyzed directly by ^{2}H NMR.

(1,1,2,3,3,3-d_6)-1-propanol ^{1}H NMR (400 MHz, THF) 3.53, 1.56, 0.94

(1,1,1,2,3,3,-d_6)-2-propanol ^{1}H NMR (400 MHz, THF) 3.96, 1.18

Example procedure hydroboration of propene-d6 with BH_3•THF. A 3 neck flask was charged with 270 mL (270 mmol) of 1M BH_3•THF. Then 2.7 mL (27 mmol) of BH_3SMe_2 was added. Then 0.25 mL (0.27 mmol) of condensed propene-d6 was dissolved in 5 mL of cold THF and added dropwise to the solution. After 1 h, the flask was cooled to 0 ºC. the flask was cooled to 0 °C. The reaction was quenched by the slow addition 85 mL of 1:1 3M NaOH: 30% H_2O_2. The ice bath was removed, and the reaction was stirred at room temperature for 7 h. The aqueous layer was saturated with NaCl. At this point the organic layer was analyzed directly by ^{2}H NMR.

Synthesis of (methyl-d_3)triphenylphosphonium iodide To a flask equipped with a reflux condenser, 10.5 g (40 mmol) of triphenylphosphine was added. This was dissolved in 150 mL of toluene. To the flask, 2.5 mL (40.2 mmol) of CD_3I was added in one portion through the condenser. The reaction was refluxed under nitrogen for 20 h. After the reaction had cooled to room temperature, the solid product had precipitated and was filtered. The solid was washed with hexanes and left to dry in the dark. The product is a white fluffy solid and weighed 16.17 g (99% yield).

Example procedure for the synthesis of d_2-alkenes: 1-tridecene-1,1-d_2 To a round bottom flask was added 9.3 g (20 mmol) of (methyl-d_3)triphenylphosphonium iodide and suspended in 60 mL THF. The flask was then placed into a water bath. To this 9.2 mL of 2.5 M butyl lithium in hexanes was added dropwise with a syringe. This was allowed to stir for 15 min until the very orange ylide was formed. Then 5 mL (22.5 mmol) of dodecanal was added in one portion and this was stirred for 12 h. After this time, the solid was filtered off, and the filtrate was washed with 20 mL by water. The organic layer was dried over anhydrous $NaSO_4$ and concentrated under vacuum. The deuterated alkene was purified by column chromatography. The product (1,1-d_2)-1-tridecene was collected after concentration under vacuum as a colorless liquid and weighed 2.998 g. (81% yield, 92% deuterium incorporation).

^{1}H NMR (500 MHz, $CDCl_3$) 5.86-5.77 (1H, m), 4.98 (residual), 4.92 (residual), 2.03 (2H, q, J=6.55) 1.34-1.21 (18H, m), 0.92 (3H, t, J=7.1)

Example procedure for the synthesis of ^{13}C labeled alkenes: 1-tridecene-1-^{13}C. To a round bottom flask was added 4.5 g (11 mmol) of (methyl-^{13}C)triphenylphosphonium iodide and suspended in 30 mL THF. The flask was then placed into a water bath. To this 4.1 mL of 2.5 M butyl lithium in hexanes was added dropwise with a syringe. This was allowed to stir for 30 min until the very orange ylide was formed. Then 3.3 mL (15 mmol) of dodecanal was added in one portion and this was stirred for 8 h. After this time, the solid was filtered off, 5 mL of pentane was added, and the solution was washed with 20 mL by water. The organic layer was dried over anhydrous $NaSO_4$ and concentrated under vacuum. The labeled alkene was purified by column chromatography (pentane). The product (1-^{13}C)-1-tridecene was collected after concentration under vacuum as a colorless liquid and weighed 1.248 g. (67% yield)

^{1}H NMR (500 MHz, $CDCl_3$) 5.86-5.77 (1H, m), 4.98(m), 4.92 (m), 2.03 (2H, q, J=6.55) 1.34-1.21 (18H, m), 0.92 (3H, t, J=7.1)

^{13}C NMR (125 MHz, $CDCl_3$) labeled peak 114.0

Example procedure for the esterification of 1- and 2-dodecanol with Benzoyl Chloride To a flask that was charged with 25 mL of CH_2Cl_2, 2.512 g (20.5 mmol) of 4-dimethylaminopyridine, and 2.3 mL (20 mmol) of benzoyl chloride. To this solution was added the 1.46 g (8.0 mmol) of the product dodecanols from a hydroboration reaction. This reaction stirred for 12h. After this time, the reaction was checked by 1H NMR to ensure complete conversion. The excess benzoyl chloride was quenched with the addition of 10 mL of methanol slowly since quenching the reaction is very exothermic. The reaction was washed with 10 mL of water twice, and with 10 mL of brine. The organic layer was dried over anhydrous sodium sulfate and concentrated under vacuum. ^{1}H NMR (300 MHz, $CDCl_3$) 8.13-7.97 (2H, m), 7.64-7.36 (4H, m), 4.31 (2H, t, J=6.4 Hz), 1.75 (2H, sex, 7.6 Hz), 1.50-1.18 (18H, m), 0.88 (3H, t, 6.1Hz)

General computational methods. Calculations of structures, energies, and frequencies employed default procedures in Gaussian09 unless otherwise noted, with the exception that DFT calculations generally employed an ultrafine grid. Complete structures and energetics are provided in sections below. All absolute energies are in Hartrees. All relative energies are presented in kcal/mol.

Some of the dynamics calculations, including all of the 53-THF ONIOM model calculations, all of the single-trajectory calculations, and all of the steepest-descent paths in mass-weighted coordinates, employed the program suite PROGDYN. PROGDYN consists of a series of component programs written as either Unix shell scripts or awk programs. Gaussian09 was used to calculate the forces at each point in trajectories. A full description of PROGDYN including listings of the subprograms can be found in Appendix B. The latest version of this program can be obtained by emailing Daniel Singleton at singleton@chem.tamu.edu.

Other dynamics calculations employed the new program ProgdynONIOM. ProgdynONIOM is a new program that has adapted PROGDYN to the use of a combination of A. Gaussian09 calculations for the DFT calculations needed for an ONIOM and B. MOPAC2016® for all semi-empirical calculations. A full description of ProgdynONIOM including listings of the subprograms can be found Appendix B.

The TST and CVT/SCT calculations in the main text of Chapter II made use of the programs GAUSSRATE and POLYRATE (These programs were modified in minor ways. In particular, the subroutine *mepout* was modified to output frequencies with higher precision, and the utility program *shuttle* was modified to save copies of all frequency calculations so that data could be extracted from them later. To show the complete set of options selected for these calculations, a sample set of input files for GAUSSRATE / POLYRATE are given in Appendix B, along with some additional details of the calculations.

Initialization of Trajectories in a sphere of 53 THF Molecules. For classical dynamic trajectories inside a sphere of 53 THF molecules, the method for generating starting structures was a bit complicated. First a series of boxes of 53 THF molecules that were generated and equilibrated for a previous study were molded into a 12.3 Å radius sphere using the *sphereon* capability in PROGDYN, using a *sphereforce* parameter of 0.01 (11.8 kcal/mol/Å) during the molding process while the temperature was held at 1000 K. After the sphere formed, the pi complex of dodecene was pushed into the center of the sphere, using the *zeroatom* feature of PROGDYN, while using a harmonic potential to keep the reactive boron and olefinic atoms in place at an approximate location of the VTS (using the applyforce feature in PROGDYN.) When the reactants were in the center of the sphere, the whole system was cooled to 298.15 K using the *thermostat* feature with a *thermostatmult* of 0.999, which removes 0.1% of the energy per fs. After reaching 298.15 K, these "feeder trajectories" were continued up to 42,000 fs. At intervals of 250 fs, points and velocities were extracted and used as the starting point of new trajectories, with no constraints except retention of the sphereforce, integrated forward and backward in time until the products **A** or **M** were formed (defined by a C-B distance < 1.6 Å and a C-H distance < 1.1 Å) or the borane had dissociated (defined by all of the hydrogens of the BH_3 being greater than 4.5 Å from the olefinic carbons). Approximately 65% of the trajectories were extracted after > 30,000 fs after the temperature was equilibrated, but approximately 35% of the trajectories were extracted with <10,000 fs of equilibration. No difference was discerned between the short-equilibration and long-equilibration derived trajectories. A sample set of parameters for the trajectories is given in Appendix B.

A series of feeder trajectories for the reaction of 1-hexene were generated from the feeder trajectories for 1-dodecene by manually deleting the longer chain from geoPlusVel files (generated with the program progdynsam, listed in Appendix B) after 33,000 fs of equilibration. The feeder trajectories were continued with points extracted from 1000 to 16,000 fs after equilibration. Figure 2.14 is a typical starting point for the hydroboration of 1-hexene in 53 THF molecules (1-hexene in green and borane in pink the hydrogens on the solvent have been omitted for clarity and solvent molecules that obscured the alkene were made transparent.)

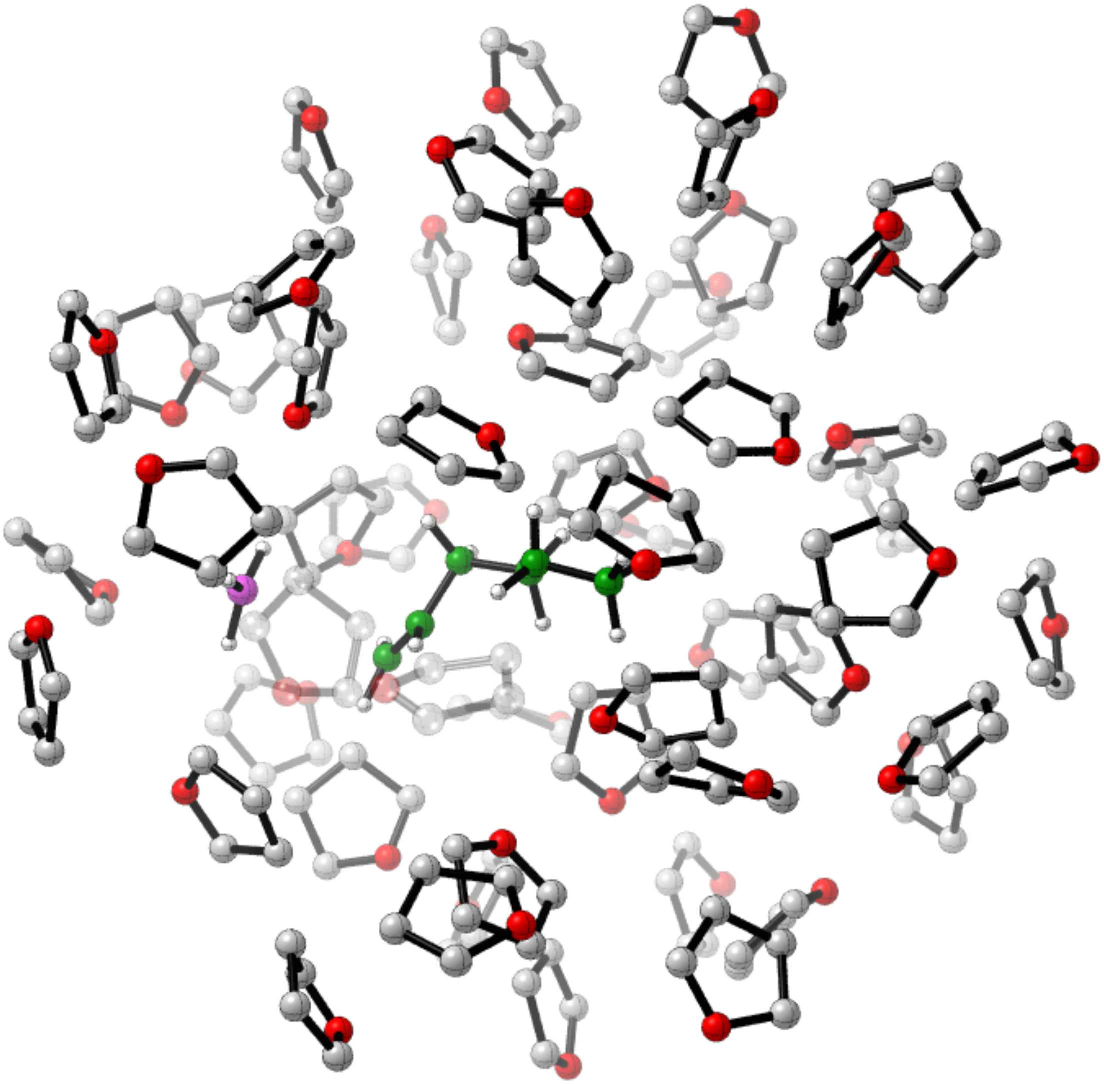


Figure 2.14 An example of a starting point of the hydroboration of 1-hexene in a sphere of 53 THF molecules.

A series of feeder trajectories for the reaction of propene were generated from the feeder trajectories for 1-hexene by manually deleting the longer chain from geoPlusVel files (generated with the program progdynsam, listed in Appendix B) after 16,000 fs of equilibration. The feeder trajectories were continued with points extracted from 1500 to 15,000 fs after equilibration.

Initialization of Trajectories in a sphere of 80 THF Molecules. A series of starting points for the trajectories using 80 THF molecules were generated from scratch, using the program packmol[102] to place each approximate VTS for propene, 1-hexene, and 1-dodecene along with 80 THF molecule inside a sphere with a radius of 14.8 Å. Using ProgdynONIOM, these spheres were equilibrated at 298.15 K with radii 14.5 Å for propene, 14.8 Å for 1-hexene, and 15.0 Å for dodecene. Trajectory starting points were extracted at 250 fs intervals as above with a range from 2250 fs to 24,240 fs for propene, 3500 fs to 32,000 fs for 1-hexene, and 2750 fs to 15250 fs for 1-dodecene. The starting points were then integrated forward and backward in time as above using the ProgdynONIOM program, using B3LYP/6-31G* for the model layer and PM6-D3H4 for the real layer, and including an additional small empirical dispersion correction. Figure 2.15 is a typical starting point for the hydroboration of propene in 80 THF molecules (propene in green and borane in pink the hydrogens on the solvent have been omitted for clarity and solvent molecules that obscured the alkene were made transparent.)

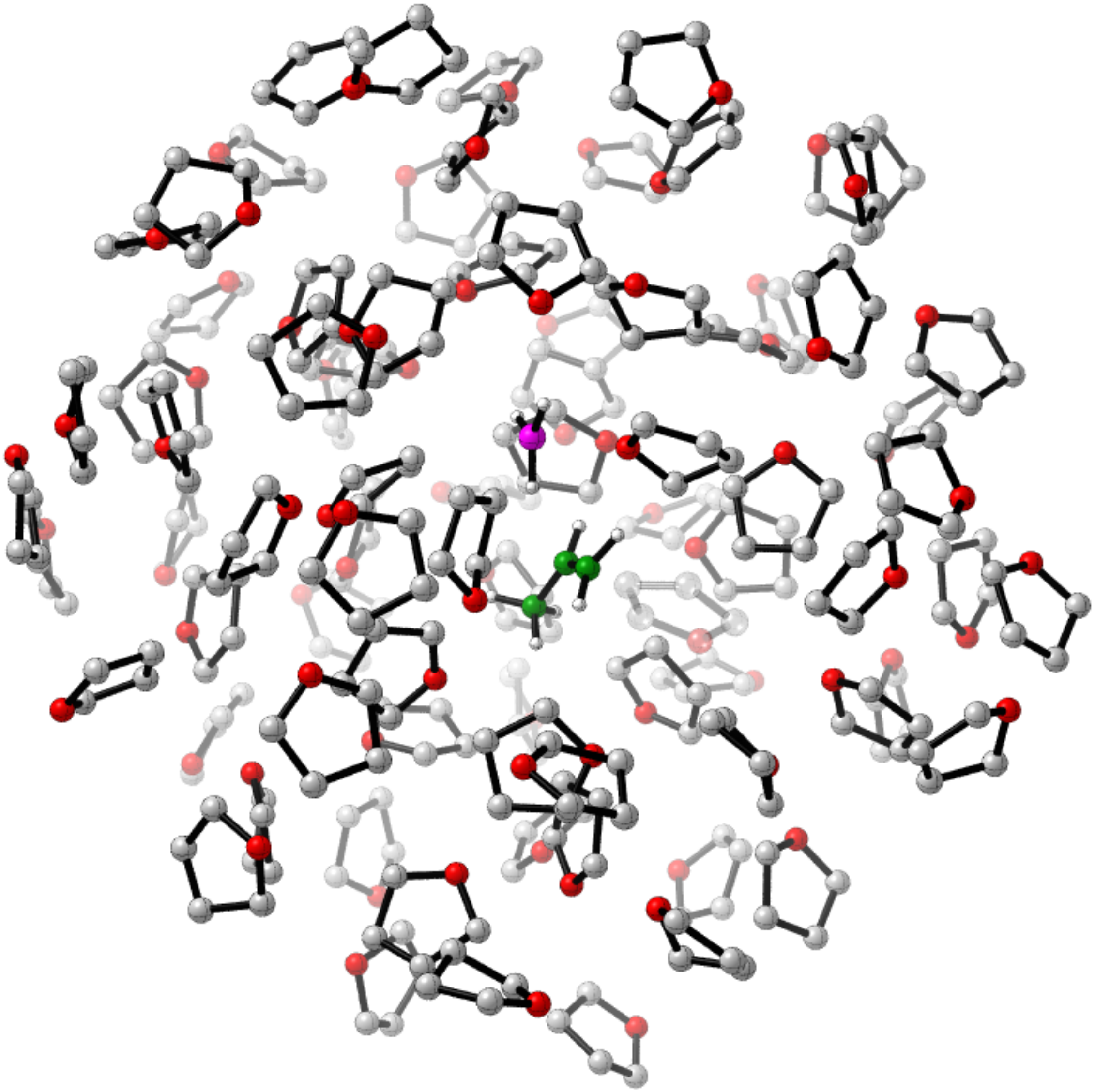


Figure 2.15 An example of a starting point of the hydroboration of propene in a sphere of 80 THF molecules.

Statistical CCNM Calculations

The key numbers that went into the statistical CCNM calculations were:

K The equilibrium ratio of anti-Markovnikov (A): Markovnikov (M), based on their CCSD(T)/aug-cc-pvtz//B3LYP/6-31G* free energies for the initially formed products (ΔG_{AB} in the table below)

k_A The CVT/SCT rate constant (CCSD(T)/aug-cc-pvtz VTST-ISPE) for formation of **A** from **INT**, obtained from POLYRATE, in s^{-1}.

k_B The CVT/SCT rate constant (CCSD(T)/aug-cc-pvtz VTST-ISPE) for formation of **B** from **INT**, obtained from POLYRATE, in s^{-1}.

ΔG_{INT} The free energy for formation of **INT** from separate starting materials (but small changes in this value make no difference in the predicted product ratio in the current case).

$\Delta G^{\ddagger}_{VTS}$ The free energy barrier for the formation of **INT** from separate starting materials (small changes in this value also make no difference in the predicted product ratio in the current case).

The table below shows the numbers used and, in the case of K, their raw-number origin. For 1-octene and 1-dodecene, the same numbers were used as in the 1-hexene case, but the final ratios were adjusted slightly based on the difference seen along the series in corresponding CCSD(T)/aug-cc-pvdz calculations.

Table 2.9 Input numbers for statistical CCNM calculations

propene	**propene 70 °C**	**butene anti**	**butene out**
G **A** product	G **A** product	G **A** product	G **A** product
-144.196604	-144.201910	-183.412376	-183.413089
G **M** product	G **M** product	G **M** product	G **M** product
-144.194312	-144.199625	-183.4098758	-183.4108907
DG_{AB}	DG_{AB}	DG_{AB}	DG_{AB}
-1.44	-1.43	-1.57	-1.38
K at 25 °C	K at 70 °C	K at 25 °C	K at 25 °C
11.33	8.19	14.13	10.2630
k_A	k_A	k_A	k_A
2.004E+12	2.051E+12	2.461E+12	3.936E+12
k_B	k_B	k_B	k_B
4.602E+10	7.328E+10	8.909E+10	8.266E+10
DG_{INT}	DG_{INT}	DG_{INT}	DG_{INT}
-0.6	0.9	-0.7	-0.9
$DG^{\ddagger}_{VTS}$	$DG^{\ddagger}_{VTS}$	$DG^{\ddagger}_{VTS}$	$DG^{\ddagger}_{VTS}$
5.9	5.9	5.9	6.0

hexene anti	**hexene out**	***tert*-butylethylene**
G **A** product	G **A** product	G **A** product
-261.845204	-261.845838	-261.850641
G **M** product	G **M** product	G **M** product
-261.842759	-261.843849	-261.846431
DG_{AB}	DG_{AB}	DG_{AB}
-1.53	-1.25	-2.64
K at 25 °C	K at 25 °C	K at 25 °C
13.33	8.22	86.43
k_A	k_A	k_A
2.317E+12	3.749E+12	2.825E+12
k_B	k_B	k_B
8.112E+10	8.620E+10	7.484E+10
DG_{INT}	DG_{INT}	DG_{INT}
-0.8	-0.9	-0.4
$DG^{\ddagger}_{VTS}$	$DG^{\ddagger}_{VTS}$	$DG^{\ddagger}_{VTS}$
5.9	5.9	5.9

The numbers now needed for the calculation are k_{*1}, k_C, k_{*2}, k_{*2A}, k_{*2B}, and $R_{A/B}$; see reference 66 (Zheng, Papajak, and Truhlar) for a definition of these terms.

From $\Delta G^{\ddagger}_{VTS}$, the k_{*1} was calculated from $k_BT/h \exp(-\Delta G^{\ddagger}_{VTS}/RT)$ and multiplied by $1000*24.465/N_A$ to put k_{*1} in ordinary gas phase units.

The same thing was done with ΔG_{INT} to obtain k_C.

k_{*2A} was calculated as $k_A*\exp(-\Delta G_{INT}/RT)*1000*24.465/N_A$

k_{*2B} was calculated as $k_B*\exp(-\Delta G_{INT}/RT)*1000*24.465/N_A$

k_{*2} was calculated as the minimum of k_C versus $k_{*2A} + k_{*2B}$

$R_{A/B}$ is just K

The final results were then obtained straightforwardly (with no further unit conversions) using the equations in reference 66. These calculations were able to reproduce the results of Zheng, Papajak, and Truhlar.

Nonstatistical CCNM Calculations

The nonstatistical CCNM calculation involves the calculation of a revised $R_{A/B}$, which is plugged into the calculation above in place of the K The key inputs for the calculation are the vibrational frequencies, energies for **AMTS** and **MTS** (their CCSD(T)/aug-CC-pvtz energies and the B3LYP thermal correction to these energies), and a distance factor *l*. In the Zheng, Papajak, and Truhlar paper, *l* was taken as 10.2 Å for both the **A** and **M** pathways, but here *l* was measured based on the POLYRATE calculations for each pathway. The *l* values employed are listed in the table below. Following Zheng, Papajak, and Truhlar, the relaxation time constant was set to τ_{relax} = 100 fs.

The table also lists the $R_{A/B}$ values obtained. Plugging these values into the statistical CCNM calculation above in place of K leads to results in column 6 of Table 2.4. It should be noted that $R_{A/B}$ is in each case greater than K due to the longer *l* values for the **A** pathway.

Table 2.10 POLYRATE-calculated distance factors *l* (in Å) from **AMTS** or **MTS** to their corresponding products.

	A pathway	**M** pathway	$R_{A/B}$
propene	7.46	4.34	17.7
propene at 70 °C	7.46	4.34	12.25
butene out	7.68	4.4	16.215
butene anti	7.52	5.63	17.81
hexene out	10.3	4.72	15.0
hexene anti	12.98	4.76	27.44
octene out	11.68	5.3	10.9
octene anti	11.96	6.21	22.0
dodecene out	15.79	5.93	15.5
dodecene anti	16.25	7.41	19.5
tert-butylethylene	9.06	5.26	130

RRKM-ME Calculations

The program Mesmer[79] was employed for the RRKM-ME calculations. Sample input files are given in Appendix B. The table below shows the Lennard Jones parameters used for the alkenes and THF. The alkene parameters were used when available, but the alkane was substituted when the parameters for a particular alkene was unable to be located. As demonstrated in a sample input, the localized RRKM-ME calculations were carried out by replacing the frequencies of the larger molecules (alkene, complex, both TSs) with that of propene, while leaving the energetics and Lennard Jones parameters unchanged.

Table 2.11 also shows the energies used in Mesmer for **INT**, **AMTS**, and **MTS** in the calculations, relative to zero for the starting BH_3 and alkenes. These energies are CCSD(T)/aug-cc-pvtz//B3LYP/6-31G* + zpe relative energies expressed in kJ/mol. The octene and dodecene numbers were taken from those for hexene. (The B3LYP relative energies for hexene versus octene versus dodecene differed by less than 0.1 kcal/mol.)

Table 2.11 Lennard Jones Parameters[103–105] and Relative Energies for RRKM-ME calculations

	σ	ε/k	**INT** (kJ/mol)	**AMTS** (kJ/mol)	**MTS** (kJ/mol)
propene*	4.50	214.9	-40.931	-40.646	-30.504
Butene* out	4.89	240.8	-43.107	-43.925	-33.917
Butene* anti			-41.868	-42.215	-33.263
Hexene* out	5.5409	265.1	-43.034	-43.930	-34.079
Hexene* anti			-42.457	-42.688	-33.644
Octene** out	6.0263	264.3	-43.034	-43.930	-34.079
Octene** anti			-42.457	-42.688	-33.644
Dodecene** out	6.7697	272.1	-43.034	-43.930	-34.079
Dodecene** anti			-42.457	-42.688	-33.644
3,3-dimethyl-2-butene**	5.689	421	-40.766	-41.348	-32.403
THF	3.57	68.1	N/A	N/A	N/A

*LJ Parameters taken from alkene. **LJ parameters taken from alkane

The CLN Calculation

The table below shows the numerical details of the CLN calculation. The weighting of the direct versus indirect mechanisms was taken from the CCNM calculations. The % **M** for the direct mechanism was taken from a localized RRKM-ME calculation (see the discussion above and the example input file in Appendix B) with the E_{down} set negligibly low. The % **M** for the indirect mechanism was taken from the full RRKM-ME calculations (using all of the molecular frequencies) using an E_{down} of 726.1234 cm^{-1} and a solvent "pressure" of 2093950 Torr (1955440 for THF at 70 °C). These pressures are a factor of 10 greater than the normal pressure; the cooling was increased by raising the pressure instead of the E_{down} due to an apparent numerical issue in Mesmer that limits immediate cooling of the solute by the simple increase in $E_{down.}$ (Technically these are two parameters but adjustments in the two are normally interchangeable, and the same set of results can be obtained with a higher pressure and a lower E_{down}.) It should be noted that the cooling rate is too high to be physical. In the CLN model the fast-reacting trajectories should correspond to the direct mechanism while the indirect mechanism should correspond to slow-reacting trajectories, but the nature of the RRKM-ME calculation is that it starts producing product immediately with no cooling.

Table 2.12. Numerical Details of the CLN calculation

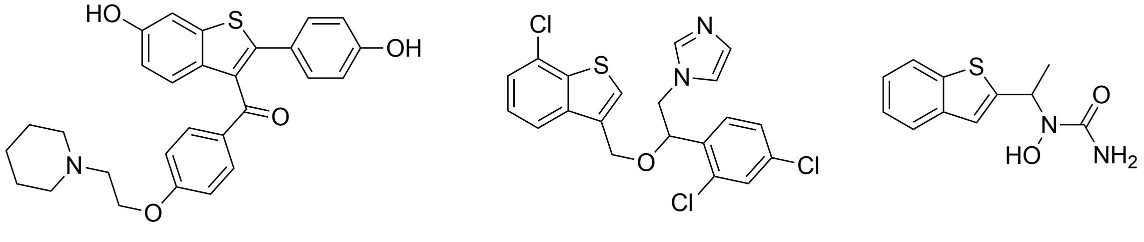
	weighting		localized RRKM (direct)			RRKM-ME (indirect)			% **M**
	direct	indirect	raw	correction	% **M**	raw	correction	% **M**	weighted
propene	0.33	0.67	12.7%	1.14	14.2%	7.0%	1.14	7.9%	10.0%
propene 70°C	0.34	0.66	13.2%	1.13	14.7%	8.5%	1.13	9.5%	11.3%
butene out	0.65	0.35	13.4%	1.14	15.0%	6.3%	1.15	7.2%	12.3%
butene anti	0.41	0.59	15.5%	1.14	17.2%	7.9%	1.15	8.9%	12.3%
hexene out	0.62	0.38	14.1%	1.14	15.7%	5.0%	1.16	5.7%	11.9%
hexene anti	0.39	0.61	15.7%	1.14	17.5%	6.3%	1.16	7.2%	11.2%
octene out	0.62	0.38	14.0%	1.14	15.6%	3.2%	1.17	3.7%	11.1%
octene anti	0.39	0.61	15.5%	1.14	17.3%	5.2%	1.17	6.0%	10.4%
dodecene out	0.62	0.38	13.8%	1.14	15.5%	2.9%	1.21	3.5%	10.9%
dodecene anti	0.39	0.61	15.4%	1.14	17.2%	3.9%	1.21	4.7%	9.6%
3,3-dimethyl-1-butene	0.47	0.53	15.6%	1.14	17.4%	5.0%	1.17	5.8%	11.3%

CHAPTER III

MECHANISTIC STUDIES OF FORMAL THIOBORYLATION REACTION OF ALKYNES[*]

3.1 Introduction

The formation of substituted benzothiophenes is of particular importance in the field of medicinal chemistry. Raloxifene, sertaconazole, and zileuton are bioactive products that treat a range of conditions from osteoporosis to fungal infections.[106–108] All of these drugs contain a benzothiophene core. As with all medicinal chemistry, the ease of functionalization is key to the discovery of new treatments. To this end, the synthesis of borylated benzothiophene derivatives is of synthetic value due to a myriad of downstream synthetic transformations.



Raloxifene Sertaconazole Zileuton

Figure 3.1 Benzothiophene containing bioactive molecules.

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[*] Adapted with permission from “Mechanistic Studies of Formal Thioboration Reactions of Alkynes” by Issaian, A.; Faizi, D.; Bailey, J. O.; Mayer, P.; Berionni, G.; Singleton, D. A.; Blum, S. *J. Org. Chem.* **2017**, *82*, 8165-8178. Copyright 2017 American Chemical Society

The major syntheses of borylated benzothiophene derivatives generally require the use of metal catalysts or require lithiation of the aryl ring followed by trapping an electrophile to close the five-membered ring.[109,110] Ultimately, an ideal synthesis would be high yielding and not use metals or metal catalysts since metals must be removed prior to use due to their toxicity. Recently, it was found that the electrophilic nature of $B(C_6F_6)_3$ was capable of activating an alkyne, with no metal catalyst, to undergo a nucleophilic cyclization.[111–114] This work highlights the multifunctionality of boron as both activating agent, and could theoretically give a synthetic handle for downstream reactions. However, the $B(C_6F_6)_3$ group is a resilient functionalization and resists chemical transformations.

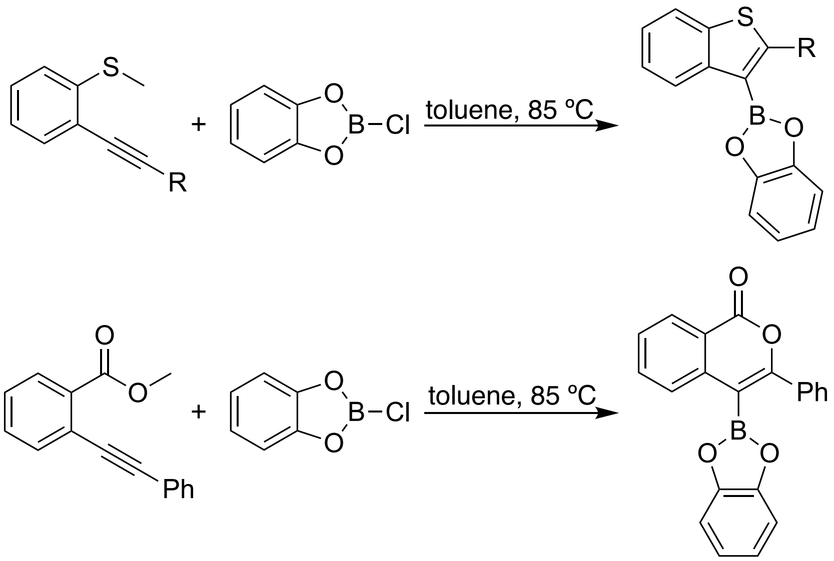
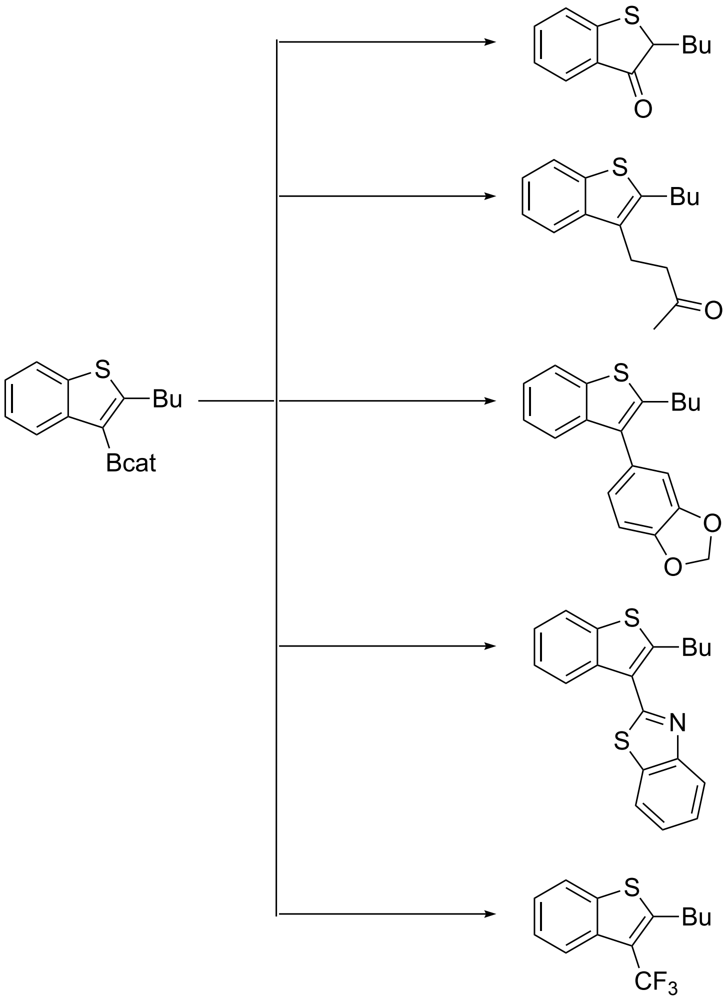


Figure 3.2 The ring closure reaction for the formation of heterocycles using chlorocatecholborane.

Suzanne Blum and coworkers found that commercially available chlorocatecholborane (ClBcat) with *o*-alkynylthioanisoles and *o*-alkynylbenzoates would induce a ring closure reaction with alkynes followed, in the same reaction, by demethylation to form benzothiophene and pyrone derivatives under catalyst free conditions (Figure 3.2).[115,116] These reaction conditions are extremely useful for downstream reactions since the catecholborane moiety can undergo a variety of transformations or be converted to the more stable pinacol derivative. The diversity of the downstream processes makes this method for the formation of borylated benzothiophenes a useful tool for synthesis. While both of these reactions are of interest, this dissertation will only cover the thioboration reaction.

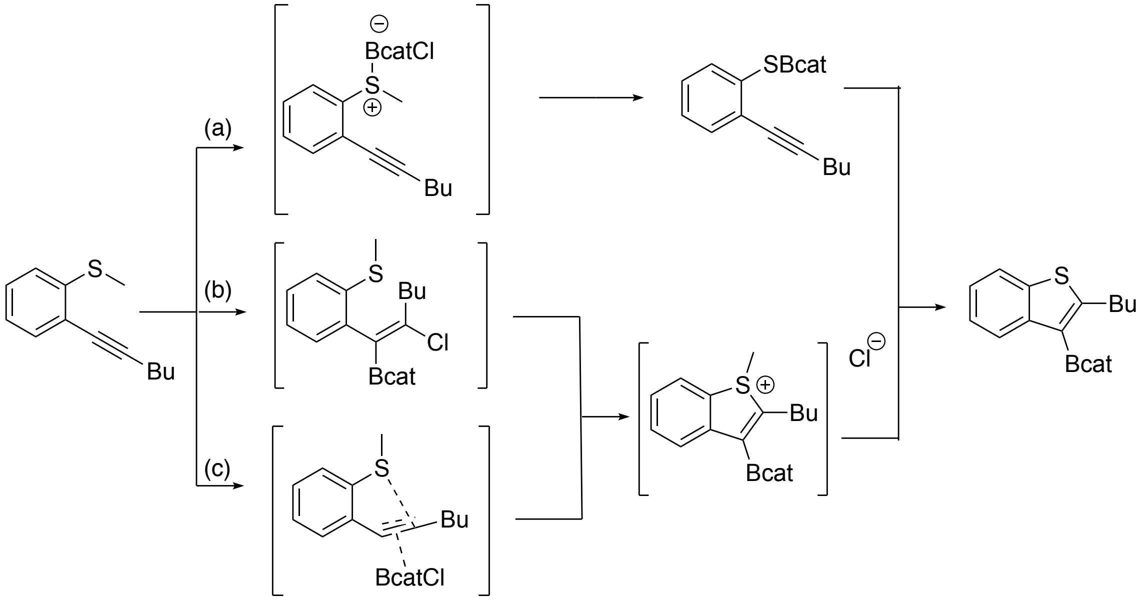
Scheme 3.1 Downstream reaction examples[115]



Other synthetic groups have extended this work to include other transformations. The Fu group used amines to form borylated indole derivatives.[117] Other intriguing work done by Ingleson shows that BCl_3 is sufficiently electrophilic to promote the cyclization reaction with esters, but under the reaction conditions, requires additional reagents to afford the thioborylated product.[118,119]

Several different mechanisms could be imagined for these reactions and are summarized in Scheme 3.2. This dissertation will deal only with the thioboration reaction. The chlorocatecholborane could be attacked by the nucleophilic heteroatom, followed by demethylation in the case of sulfur, and then the alkyne could attack the electrophilic sulfur and close the ring (a). Haloboration of the alkyne could occur followed by nucleophilic attack by sulfur (b). The ClBcat can activate the alkyne, making it more electrophilic, and allowing the sulfur to react in either an Ad_E2 or Ad_E3 type mechanism (c).

Scheme 3.2 Three pathways for the thioboration with ClBcat

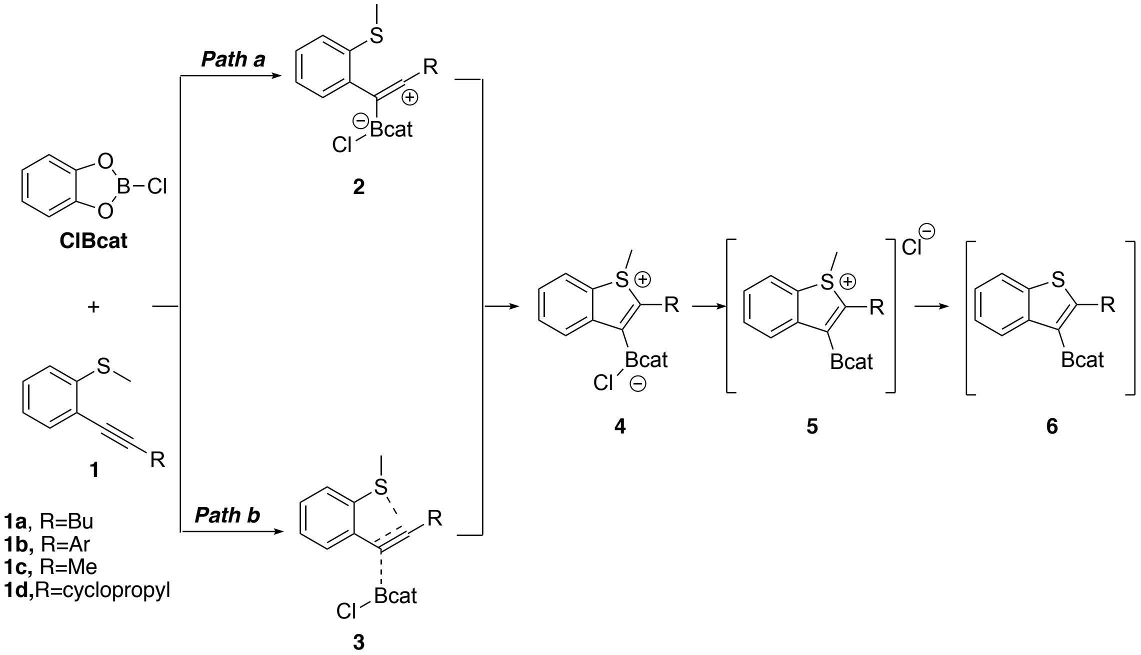


Preliminary studies thioborylation clarified some of the major points of the mechanism. First, in order to determine if (a) was the mechanism the reaction was monitored by ^{11}B NMR showed no significant change in chemical shift that would be present in the case of both (a) and (b). In addition, there was no reaction when ClBcat was mixed with orthoiodothioanisole for 4 h at 100 ºC. The addition of ClBcat to diphenylacetylene was not observed under the reaction conditions. These results convincingly contradict (a) and (b). The mechanism that remains is the activation of the alkyne by the ClBcat.

3.2 Experimental Results and Discussion

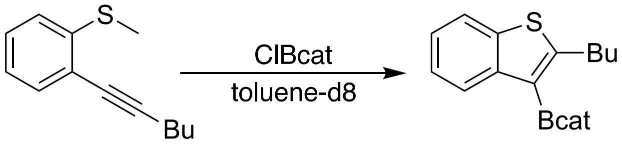
This study was done in collaboration with Prof. Blum at University of California Irvine, and the experiments that follow were done in her lab. Since the preliminary work showed that the mechanism for of this thioboration reaction is the ClBcat activates the alkyne, two additional mechanisms were envisioned. These are shown in Scheme 3.3. The key question is whether the mechanism follows *path a,* which is a complete formation of a vinyl cation with the ring closure happening in a subsequent step, or *path b* which is an Ad_E3 (formal Ad_E2 since the nucleophile is intramolecular) addition. These mechanisms utilize the Lewis acidity of the boron to achieve the reaction, but do not take in to account multiple molecules of ClBcat nor a π-complex of the reagents prior to reaction. After the ring is closed, the chloride must dissociate, followed by demethylation by Cl^- to ultimately form CH_3Cl.

Scheme 3.3 Two possible mechanistic pathways for thioboration with ClBcat



The first experiments done from the Blum group were to conduct kinetics on substrate 1a. The data for the initial rates is summarized in Table 3.1. These data show a second order for the reaction overall, and first order dependence on the **ClBcat** and on the substrate **1a**. Using entries 5, 6, and 7 from Table 3.1 an Eyring analysis was utilized to determine the energies experimentally. From the Eyring plot shown in Figure 3.3, experimental enthalpy ($\Delta H^{\ddagger}$) was determined to be 13.8 ± 1.0 kcal mol^{-1} and entropy ($\Delta S^{\ddagger}$) of -37 ± 3 cal mol^{-1} K^{-1}. While a judgment on the enthalpy of a reaction is difficult to ascertain in an intuitive sense, the entropy can be checked by chemical intuition. A large negative value does indeed fit with a bimolecular reaction forming one product in the rate-determining step. With the experimental $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ terms in hand, the Gibbs free energy (ΔG) can be calculated. At the experimental temperature of 90 ºC, the $\Delta G^{\ddagger}$ is 27.1 ± 0.1 kcal/mol.

Table 3.1 Observed initial reaction rates for the thioboration of 1a.



	Equiv (1a)	Equiv (ClBcat)	T (ºC)	Rate 10^{-6} M/s
1	2.0	1.0	90	6.5 ± 0.5
2	0.5	1.0	90	1.8 ± 0.2
3	1.0	2.0	90	8.0 ± 0.1
4	1.0	0.5	90	2.0 ± 0.3
5	1.0	1.0	90	3.7 ± 0.2
6	1.0	1.0	80	1.8 ± 0.1
7	1.0	1.0	70	1.1 ± 0.1

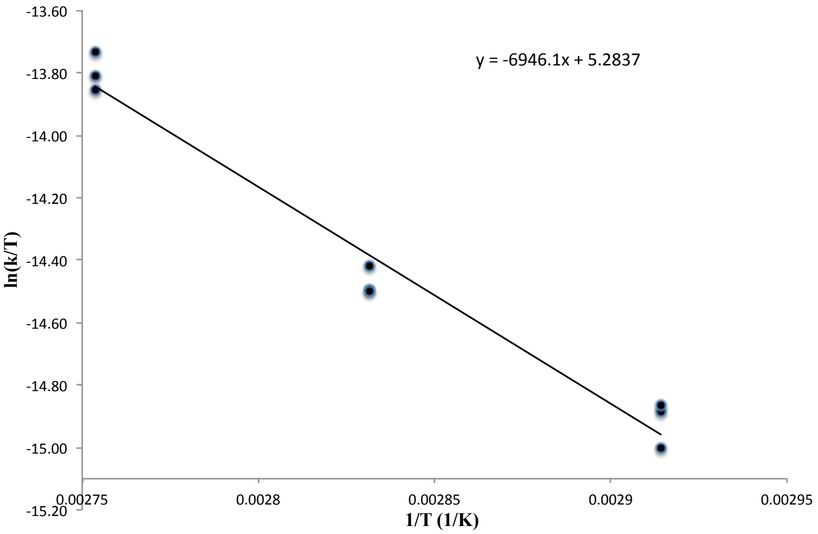


Figure 3.3 The Eyring plot for thioboration of 1a with ClBcat

In order to understand the nature of the transition state for the reaction, a Hammett study was performed. In order to determine charge build up on the external alkynyl carbon, the aryl groups on substrate **1a** were varied *para* to the alkynyl group and the Hammett plot in Figure 3.4 was generated with σ^+ since it gave a better R^2 value for the linear regression vs. σ. A ρ^+ value of -1.7 does indicate a positive charge buildup during the transition state. However, the magnitude of ρ^+ is not large enough to indicate a full cation formation, which is typically larger than -4.0.[120,121]

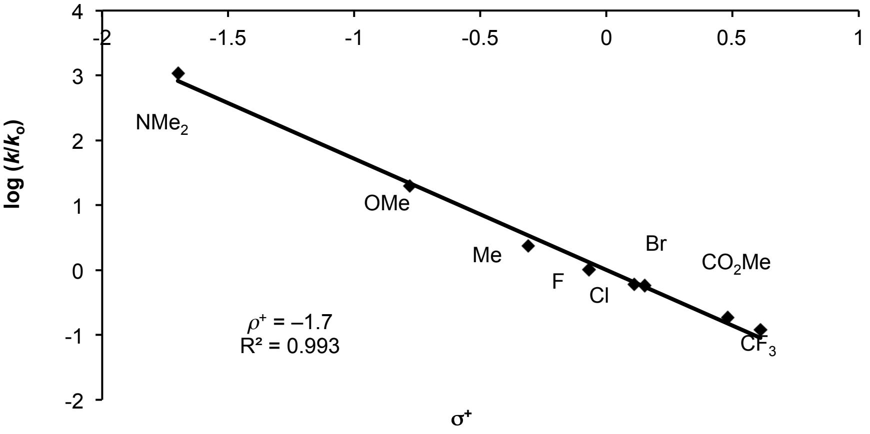


Figure 3.4 Hammett study for thioboration reaction at 100 ºC.

At this point the in the project, the collaboration between Blum and Singleton shifts from the work done by Blum and her students to the work done by Singleton and this student. The ^{13}C isotope effects for the reaction of **1a** reacting to **6a** were measured using NMR methodology developed in the Singleton group.[43] Two independent reactions of **1a** were taken to 75% and 74% conversion, respectively, and **1a** was recovered. In order to determine the difference of isotopic composition, the recovered **1a** was compared to unreacted **1a** from the same synthetic portion. An internal standard for integrals was set as the carbon para to the alkynyl group since it was assumed that the isotopic fractionation was insignificant at this position. Using the change in the isotopic composition at each position and the conversion of the reaction the KIEs were calculated as discussed in Chapter I. These experimental isotope effects are shown in Figure 3.5.

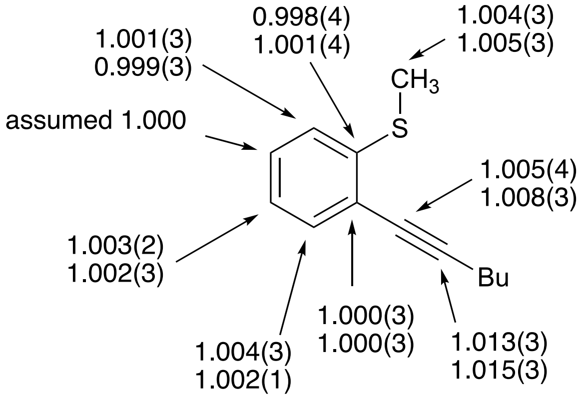


Figure 3.5 The experimental kinetic isotope effects of **1a** for the reaction with **ClBcat** at 85 ºC in toluene. 95% confidence limits on the last digit are shown in parentheses.

The KIEs for the arene are consistently negligible around the ring. There is a small isotope effect on the methylthio carbon. The most important observation is the significant ^{13}C KIE on both carbons on the alkyne. The typical conclusion of this observation is that both of these carbons are undergoing a bonding change during the TS and is consistent with an Ad_E3 mechanism rather than the vinyl cation mechanism from

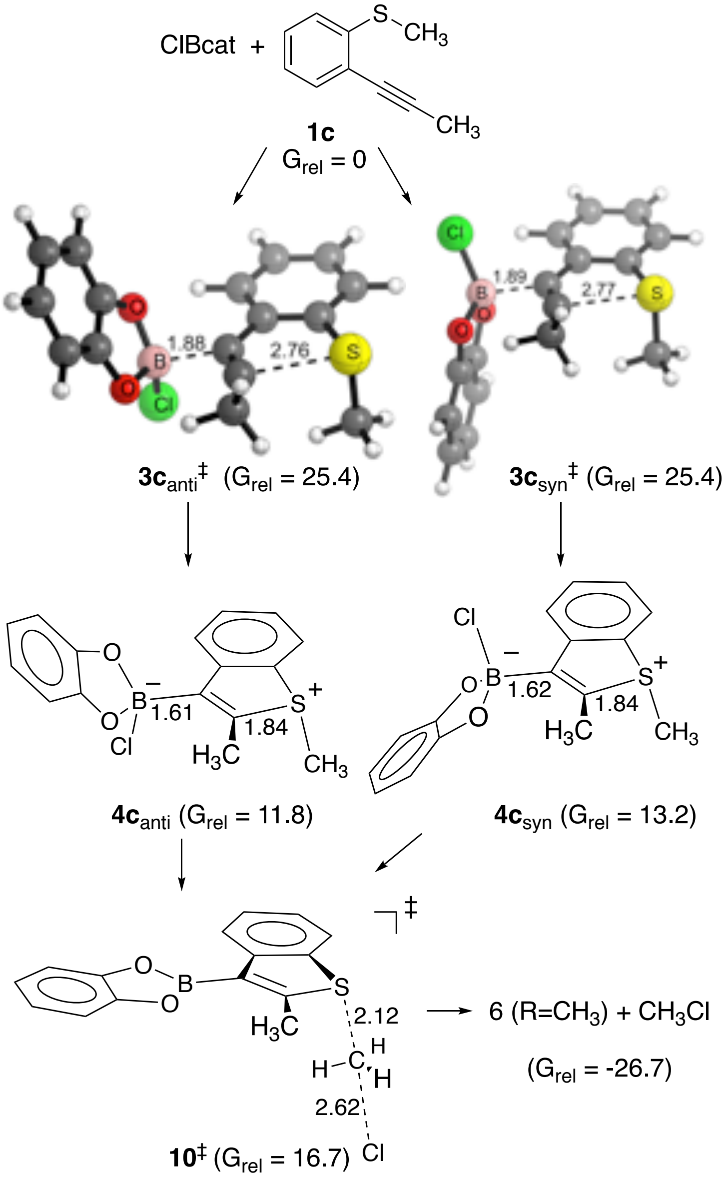
Scheme 3.3, which would show only a significant isotope effect on the internal alkynyl carbon. While general explanation for the KIEs is qualitative, computational studies will allow a quantitative interpretation.

3.3 Computational Results and Discussion

Calculations were employed in order to help understand the experimental results from the thioboration reaction. When computations are employed, the general method is to use high-level *ab intio* methods to benchmark the process. However, this reaction is not easily benchmarked due to the large size of the reaction, but also because there is no logical way to truncate the system down in to a suitable model. That said, it is possible to use many of the experimental observations to determine the efficacy of the computational method. The method used here is B3LYP/6-31+G** with a PCM solvent model (toluene) and Grimme's D3 dispersion corrections, but other methods and their differences will be discussed.

The model studied for the reaction **1c** with **ClBcat** is shown in Scheme 3.4. Two TSs were found that were very close in energy. However, the TSs on the potential energy surface lies in a relatively flat region where entropy changes rapidly. This is a classic example of when classical TST fails, but VTST tends to do well in these cases. Therefore, two very close VTSs (maxima on the free energy surface within 0.1 kcal/mol) were found using the program GAUSSRATE/POLYRATE.[93,94] These VTSs differ in the orientation (syn or anti) of the Bcat group to the SCH_3 group. These VTSs have the 1M standard state energy of 25.4 kcal/mol relative to separate starting materials. This calculation is a bit misleading, since the VTSs is chiral, and has an entropy of mixing as well as the entropy of symmetry for the ClBcat. These effects would lower the observed barrier by 1.5 kcal/mol. The entropy of activation was calculated by the summation of the SCT rate constants at 70 ºC and 90 ºC. After allowing for the 1M standard state, the entropy calculated was 37.4 e. u. which matches the experimental value.

Scheme 3.4 Calculated structures (B3LYP-D3/6-31+G**/PCM(Toluene)) for **1c** reacting with **ClBcat** at 358K.



In both of the VTSs **3c**, the C–B bond (1.88 Å) is significantly more advanced than the C-S bond (2.77 Å). The carbon further from the arene is therefore moving much more in the VTS, which fits nicely with the larger KIE at this position. The negative ρ^+ value from the Hammett study is explained by a Mulliken-charge calculation gain of 0.63 at this external alkynyl location. The VTSs $\mathbf{3c}_{\text{syn}}{}^{\ddagger}$ and $\mathbf{3c}_{\text{anti}}{}^{\ddagger}$ afford the zwitterions $\mathbf{4c}_{\text{syn}}$ and $\mathbf{4c}_{\mathbf{anti}}$**,** respectively. From here, a molecule of **ClBcat** could remove the chloride before ultimately dissociating and demethylating the cation by TS $\mathbf{10}^{\ddagger}$, or the Cl^- could simply dissociate and migrate over to TS $\mathbf{10}^{\ddagger}$. TS $\mathbf{10}^{\ddagger}$ leads the product **6** with relative Gibbs free energy of -26.7 kcal/mol.

Of course, other mechanisms were considered. No transition structures were located for the addition of **ClBcat** without simultaneous attack by the sulfur. Any attempts to optimize the vinyl cation were found to form the ring closed product. It was envisioned that a second molecule of **ClBcat** could enhance reactivity of the electrophilic alkyne. To this effect, a structure that is equivalent to the TS $\mathbf{3c}^{\ddagger}$ with 2 molecules of **ClBcat** was found, but the TS was calculated to be 3.7 kcal/mol higher in energy relative to free starting materials than $\mathbf{3c}^{\ddagger}$ was itself. Three pre-reactive complexes of **ClBcat** and **1c** were located, but these structures were not found to be a minimum on the free energy surface (2.3-2.8 kcal/mol) and cannot be of any kinetic significance of this mechanism.

The predicted KIEs for the VTSs $3c_{\text{anti}}{}^{\ddagger}$ $3c_{\text{syn}}{}^{\ddagger}$ were calculated by applying the Bigeleisen and Mayer method that was designed TST to the two VTSs. A one-dimensional tunneling correction was applied to the predictions, but they were negligible (less than 0.0003) so the SCT corrections were assumed to be not important. The calculated isotope effects are summarized in below Figure 3.6 along side the experimental isotope effects for comparison. The calculated KIEs fit well with the pattern of the experimental isotope effects especially calculating a larger isotope effect for the external alkynyl carbon than that of the internal alkynyl carbon.

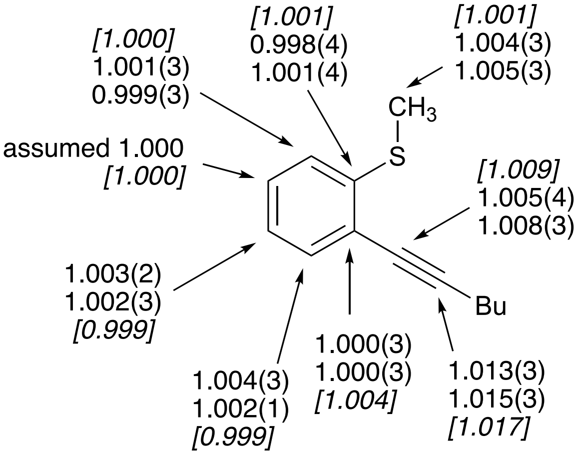


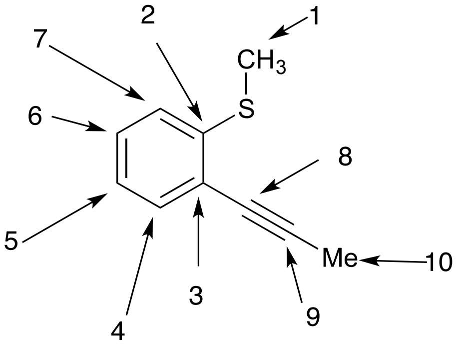
Figure 3.6 Experimental and B3LYP-D3/6-31+G**/PCM(toluene) predicted (italicized and in brackets) ^{13}C kinetic isotope effects of the thioboration of **1c.** 95% confidence limits on the last digit are shown in parentheses for the experimental results

At this point, one of the biggest shortcomings of computational chemistry is demonstrated. Several different methods and basis sets were used, and while all of the calculations do calculate the Ad$_E$3 as the lowest energy pathway, each method calculates a different geometry (Table 3.2) for the TS **3c**‡, which has a range KIEs (Table 3.3) associated with the different geometries. Because there is no objective way to differentiate between the different DFT methods, it is impossible to say that calculations "predict" the KIEs well. However, since the experimental KIEs are consistent an Ad_E3 mechanism, and the computational results are consistent with experimental observations (barrier, molecularity, and entropy), the evidence is quite clear that the mechanism follows Ad_E3 addition.

Table 3.2 The differences in $3c^{\ddagger}$ for several methods. basis sets, and solvent model

Method	Basis Set	Solvent Model	B-C Distance	C-S Distance
b3lyp-d3	6-31+G**	PCM	1.975	2.849
b3pw91	6-31+G**	PCM	1.996	2.882
b97d3	6-31+G**	PCM	2.082	2.894
bp86	6-31+G**	PCM	2.087	2.916
m06	6-311+G(2d,p)	PCM	1.878	2.702
m06	6-311+G(2d,p)	SMD	1.876	2.712
m06	6-31+G**	PCM	1.869	2.729
m11	6-31+G**	PCM	1.857	2.721
pbe	6-311+G(2d,p)	PCM	2.121	2.895
pbe	6-31+G**	PCM	2.128	2.961
tpss	6-31+G**	PCM	2.082	2.894
wb97d	6-311+G(2d,p)	PCM	1.904	2.793
wb97d	6-311+G(2df,p)	PCM	1.896	2.771
wb97d	6-311+G(2df,p)	SMD	1.896	2.782
wb97d	6-311+G(2d,p)	SMD	1.8996	2.801
wb97d	6-31+G**	PCM	1.909	2.851

Table 3.3 Comparison of calculated KIEs from different methods



ANTI TS

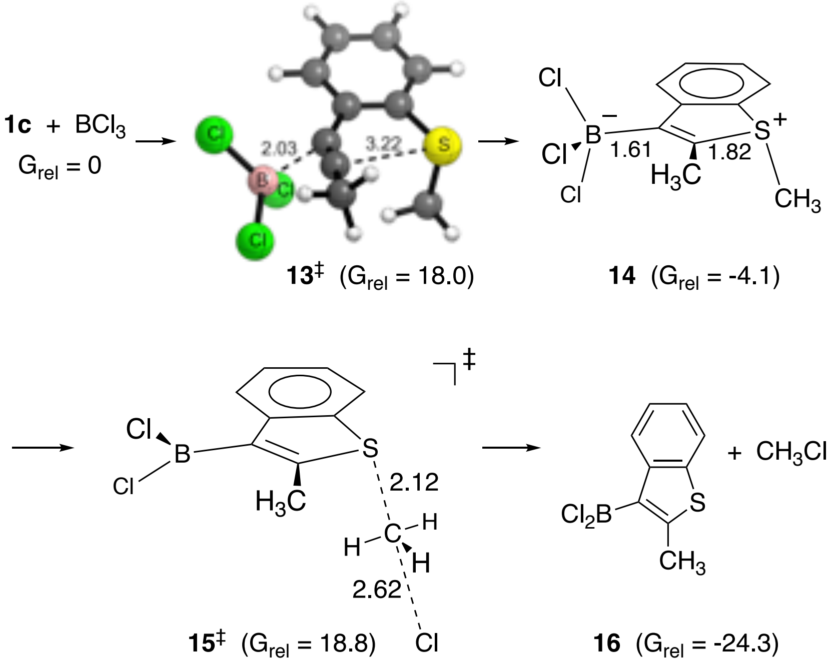
	VTST B3LYP-d3 6-31+G**	VTST M06-2X 6-31+G**	VTST B3PW91-d3 6-31+G**	VTST B97D3 6-31+G**	VTST wB97xD 6-31+G**	TST wB97xD 6-311+G(2d,p)
1	1.001	1.001	1.001	1.001	1.001	1.001
2	1.001	1.000	1.001	1.002	1.000	1.000
3	1.004	1.003	1.003	1.004	1.003	1.003
4	0.999	0.999	0.999	0.999	0.999	0.999
5	0.999	1.000	0.999	0.999	0.999	0.999
6	1.000	1.000	1.000	1.000	1.000	1.000
7	1.000	1.000	1.000	1.000	1.000	0.999
8	1.009	1.006	1.008	1.011	1.008	1.010
9	1.017	1.029	1.018	1.013	1.017	1.015
10	1.003	1.003	1.003	1.001	1.004	1.003

SYN TS

	VTST B3LYP-d3 6-31+G**	VTST M06-2X 6-31+G**	VTST B3PW91-d3 6-31+G**	VTST B97D3 6-31+G**	VTST wB97xD 6-31+G**	TST wB97xD 6-311+G(2d,p)
1	1.001	1.001	1.001	1.001	1.002	1.002
2	1.001	1.000	1.001	1.001	1.000	1.000
3	1.004	1.003	1.003	1.003	1.003	1.003
4	0.999	0.999	0.999	0.999	0.999	0.999
5	0.999	1.000	0.999	0.999	1.000	0.999
6	1.000	1.000	1.000	1.000	1.000	1.000
7	1.000	0.999	1.000	1.000	1.000	0.999
8	1.009	1.007	1.008	1.011	1.008	1.010
9	1.016	1.028	1.017	1.014	1.017	1.015
10	1.003	1.003	1.003	1.001	1.003	1.003

When the electrophile of the thioboration reaction was changed to BCl_3, Ingleson isolated zwitterions like **5** but with Bcat replaced with BCl_3. It was odd that that the BCl_3 did not remove the methyl as ClBcat did. The reaction of **1c** with BCl_3 was investigated with the same method as with ClBcat reaction and is summarized in Scheme 3.5. BCl_3 is a stronger electrophile than ClBcat and actually reacts at room temperature. The calculations reflect this as the TS **13**‡ is only 18.0 kcal/mol rather than 25.4 kcal/mol for the ClBcat TSs 3c‡. **13**‡ is much earlier than **3c**‡ with the C–S distance at 3.22 Å rather than 2.76 Å, but no separate ring closing transition state could be located. The barrier (**15**‡) to the demethylated product is only slightly higher than **13**‡, however, the starting point for this barrier is -4.1 kcal/mol. This barrier is too much to overcome at room temperature, and thus the BCl_3 electrophilicity works against the demethylation reaction by stabilizing the zwitterion too much.

Scheme 3.5 Calculated structures (B3LYP-D3/6-31+G**/PCM(Toluene)) for **1c** reacting with BCl_3 at 298K.



3.4 Conclusions

Through a combination of experimental observations and of computations, the mechanism of the thioboration of alkynes with chlorocatecholborane was determined. Through the preliminary experiments, it was determined that the ClBcat was activating the alkyne. Kinetics studies show a bimolecular rate-determining step. The Hammett studies suggest a concerted reaction with a slight positive charge built up during the rate-determining step. The KIEs clearly show that both alkynyl carbons are undergoing a bonding change during the rate-determining step. DFT calculations show that the demethylation step is accessible when ClBcat is the electrophile, but not with BCl_3.

Overall, the mechanism of the thioboration of an alkyne with ClBcat is consistent with an Ad_E3 addition followed by demethylation by Cl^-.

3.5 Experimental and Computational Procedures

Intermolecular KIE Determination. The ^{13}C spectra were recorded at 125.7 MHz using inverse gated decoupling and calibrated π/2 pulses. The integrations were obtained numerically by a macro provided in Appendix B. A zero-order baseline correction was generally applied, but to avoid any qualitative manipulation no first-order or higher-order baseline correction was ever applied. Six spectra were recorded for each sample and standard.

NMR measurements of the standard: The NMR sample consisted of 355.4 mg of **1a** in a 5 mm NMR tube filled to a height of 5 cm with $CDCl_3$. A 60 s delay was used along with a 10 s acquisition time to collect 403226 points.

NMR measurements of sample 1: The NMR sample consisted of 348.9 mg of **1a** in a 5 mm NMR tube filled to a height of 5 cm with $CDCl_3$. A 60 s delay was used along with a 10 s acquisition time to collect 403226 points.

NMR measurements of sample 2: The NMR sample consisted of 353.1 mg of **1a** in a 5 mm NMR tube filled to a height of 5 cm with $CDCl_3$. A 60 s delay was used along with a 10 s acquisition time to collect 403226 points.

General Computational Procedure. Calculations of structures, energies, and frequencies employed standard procedures in Gaussian09 unless otherwise noted. Complete structures and energetics are provided in Appendix B. All absolute energies are in Hartrees. All relative energies are presented in kcal/mol.

GAUSSRATE Calculations A number of the calculations in the manuscript made use of the programs GAUSSRATE and POLYRATE.[93,94] These programs were modified in minor ways. In particular, the subroutine *mepout* was modified to output frequencies with higher precision, and the utility program *shuttle* was modified to save copies of all frequency calculations so that data could be extracted from them later.

To show the complete set of options selected for these calculations, a sample set of input files for GAUSSRATE / POLYRATE are given in a later Appendix B. For the sake of simplicity, the starting material in these calculations was generally taken to be a minimized loose complex of reactants. Such complexes are not kinetically significant but this does not matter for the purpose at hand.

CHAPTER IV

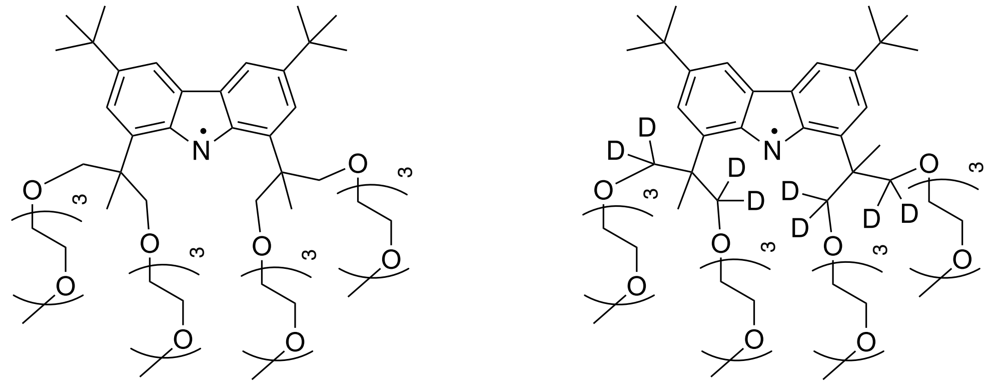
LARGE ISOTOPE EFFECTS CAUSED BY HYDROGEN ATOM TUNNELING IN A 1,5 HYDROGEN ATOM TRANSFER

4.1 Introduction

Tunneling is a phenomenon that affects the rates of all chemical reactions. It is defined as the ability for a molecule to traverse a reaction barrier without having sufficient energy to classically overcome the same barrier. While tunneling is an ever present acceleration of rates, often its contribution to the overall rate is negligible; however, the acceleration of rates due to tunneling play a significant role in many reactions involving a proton, hydrogen, or hydride.[122,123] The effect of tunneling is dependent upon the mass of the atom, and one of the standard observations when tunneling is accelerating a reaction is a large KIE, higher than the classical boundary of 7 based on the difference in ZPE for a C–H bond versus a C–D bond.[49–52,124–128]

The effect of tunneling on the rate of a reaction is generally estimated by a one-dimensional correction. These calculations are generally sufficient to account for the effect of tunneling as seen in the calculations of KIEs.[99,129] This correction is based on the modes of the bond change in the transition state. Multidimensional tunneling corrections are more difficult to apply, but have an intuitive description of the assumptions of the multidimensional models. Small curvature tunneling (SCT) assumes that the molecules move from the edge of a normal mode to the edge of another normal mode after the barrier, i.e. on the concave side of a minimum energy pathway. Large curvature tunneling (LCT) allows departure from the normal modes, and is much more difficult to calculate.

Rajca and coworkers saw an isotope effect on the rates of decomposition of large aminyl radicals (Figure 4.1) while attempting to form a new organic radical contrast agent (ORCA).[130] When the aminyl radical **17-H** was synthesized, the radical decomposed quickly with a half-life for decomposition estimated of ~1 min. When the deuterium isotopologue **17-D** was synthesized, the half-life increased to over 1 h, suggesting that the mechanism for decomposition was a 1,5-hydrogen atom transfer (1,5-HAT) from the polyethylene glycol chain to the nitrogen centered radical.



17-H **17-D**

Figure 4.1 Aminyl radicals synthesized by Rajca and coworkers.

In this study, Rajca measured a KIE for H/D of 150 at room temperature, which is indicative that tunneling was accelerating the rate of the 1,5-HAT. The KIE grew larger as the temperature was lowered, which is a general feature of most reactions, but in this case, the KIE grew very large with KIEs of 360 and 1380 at -20 and -41 ºC, respectively. Another feature of this decomposition was the linear Eyring plot (Figure 4.2) at a large range of temperatures as reactions, which are accelerated by tunneling, generally would approach a constant rate at lower temperatures.[131] These striking features could arise from large curvature tunneling, and this was investigated in the next section.

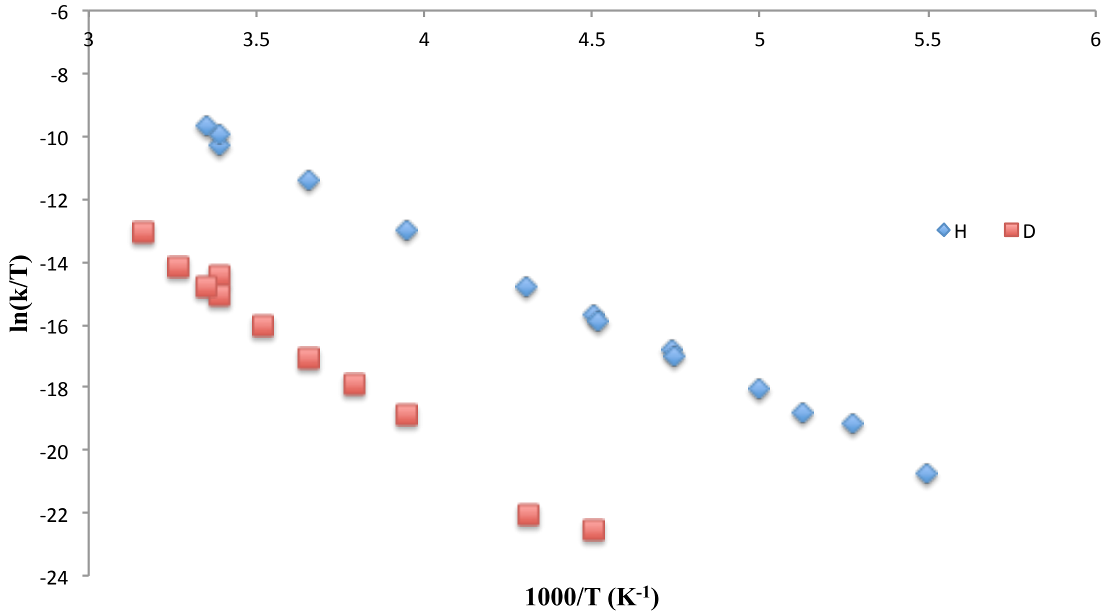


Figure 4.2 Eyring plot for the decay kinetics of 17-H (blue) and 17-D (red).

4.2 Computational Results and Discussion

The radicals **17-H** and **17-D** are too large to make adequate quantum mechanical calculations in a reasonable time frame. In order to approach an accurate prediction, a computational model was devised. For this model, **18** to **20** was used to adequately describe the electronics and structure of the full **17** system in DFT calculations and the path, while **21** to **23** was used for high level CCSD(T)/aug-cc-pvtz and large curvature tunneling calculations. Tunneling was included using either SCT[95] or LCT[132] approximations, and their combination calculated by the micro canonical optimized multidimensional tunneling (μOMT) approximation.[133] The computational method was to use **18** to find the path and SCT predictions using UM06-2X/6-31+G**, and then to extrapolate the results by CCSD(T)/aug-cc-pvtz and LCT calculations on **21**.

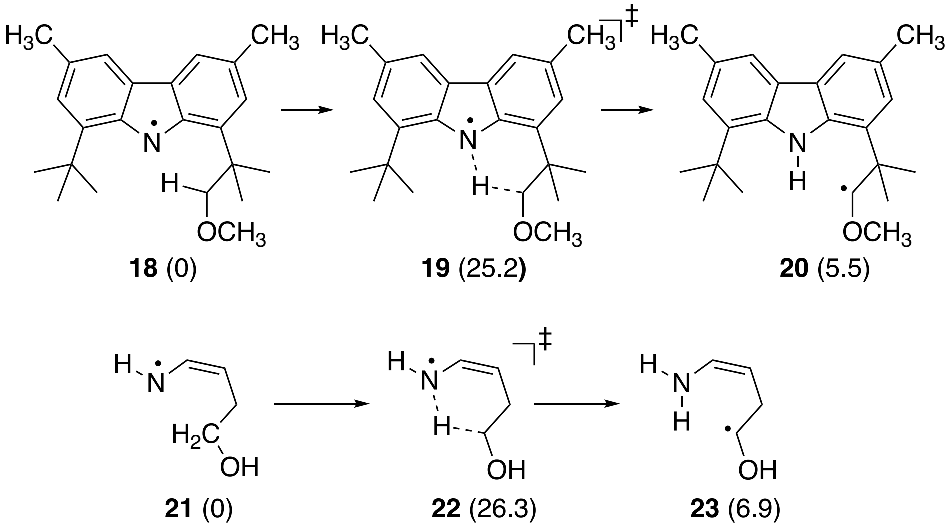


Figure 4.3 The computational model reactions. Values in parentheses are relative energies (kcal/mol).

The first prediction that was calculated was the TST rates for the model reaction. TST underestimates the rate of reaction 17-H by 1000 at 25 ºC and 1 billion at -40 ºC. In addition, the calculated KIE is only 5.6, which is significantly incorrect when compared to the experimental value of 150. With SCT calculations, it predicts a KIE of 49, which is only a factor of 2 from the experimental result. When the SCT calculation is corrected by CCSD(T), the KIE becomes 65 at room temperature. The SCT clearly makes a significant difference in the rate calculation and appears to be quite successful in its prediction. However, when all of the temperatures are calculated, it is seen that SCT greatly overestimates the temperature dependence on the rate than is observed.

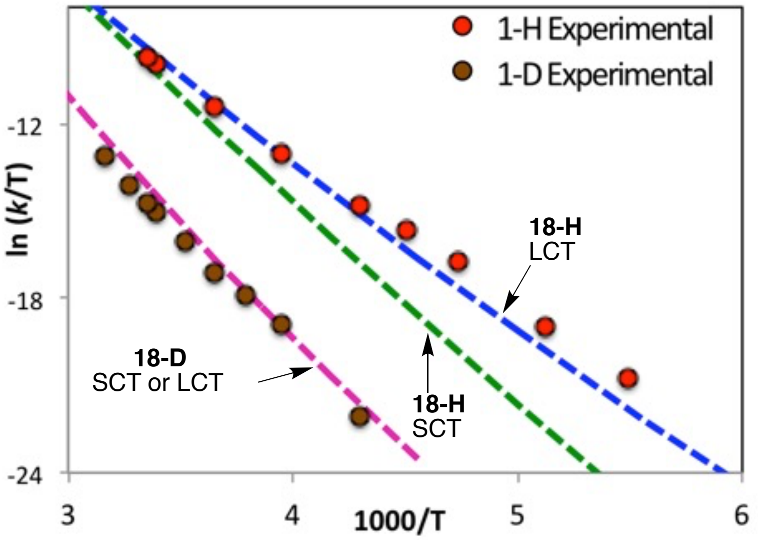


Figure 4.4 Eyring plot for the experimental data of **17-H** and **17-D**[130] versus predicted curves including tunneling models and CCSD(T)/aug-cc-pvtz for **18-H** and **18-D**.

Figure 4.4 is the Eyring plot of the Experimental data from Rajca and the SCT predictions. As seen in the figure, the slope for SCT curve of **17-D** is very close to the experimental data points. The SCT curve for **17-H** is nearly parallel to the **17-D** curve.

This results in the SCT calculations predicting a modest increase in the KIE when compared to the experimental values. The error becomes quite large. At 232 K, the predicted KIE is 140 while the experimental KIE is 1380. This difference for the SCT calculation would equate to a $\Delta\Delta H^{\ddagger}$ for **17-H** versus **17-D** of 2.2 kcal/mol, while the experimental value is 4.9 kcal/mol. These errors in predicting the proper KIE show that SCT is missing an important factor in the reaction.

The next study tried to accurately predict the LCT contribution to the reaction of **17-H**. The LCT algorithm is impractical to apply directly to the large model **18**, so in this case model **21** was used to calculate the LCT path the LCT corrections were then applied back to the predicted rates of model **18**. This added correction was graphed in Figure 4.4. When the LCT corrections are applied to **18-H**, the LCT contribution to the rate is significant when the temperature is below 298 K. But, the acceleration by LCT is negligible for **18-D**. The LCT correction brings the rates in Figure 4.4 into extremely good agreement with the experimental values, bringing the $\Delta\Delta H^{\ddagger}$ to 4.4 kcal/mol for the reaction. These predictions seem to suggest that rising involvement of the LCT pathway occurs as the temperature is decreased, and because of this increase in importance of LCT, the Eyring plot is linear to 182 K.

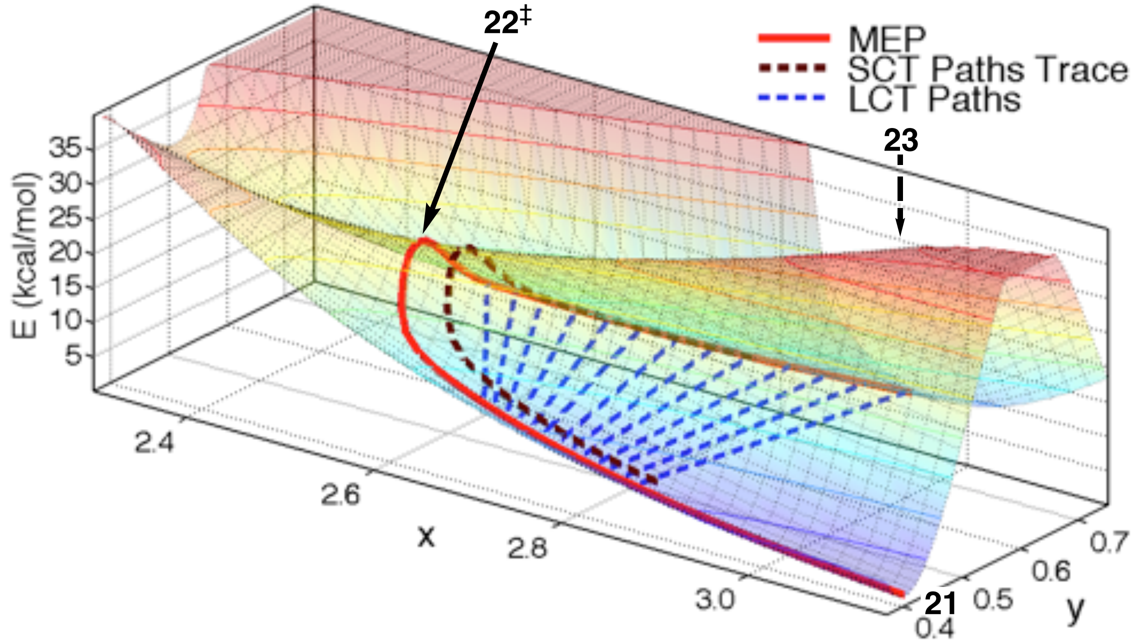


Figure 4.5 A relaxed potential energy surface for the reaction of 15-H, plotted in pseudo-Jacobi coordinates. The MEP and the LCT paths are calculated, but the SCT path is qualitative.

It should be noted that the phenomenon of tunneling is not separable into several different mechanisms such as SCT and LCT, but rather, in this case that the inclusion of the LCT corrections is far more accurate than that of the SCT model. But, the differences in SCT and LCT do provide intuitive explanations for the results in this study. Figure 4.5 is a plot depicting the potential energy surface and tunneling paths for the reaction of **18-H** to **20-H** The SCT uses a curve that is on the inside of the MEP, and it becomes much less accessible outside of the curved area of the TS. This causes the relative rate of SCT to decay rapidly with the decrease in incident energy, though, the SCT rate will grow versus the over the barrier pathway. LCT allows paths that leave the MEP. This causes the LCT to fall away more slowly as the temperature decreases. With the deuterated case, the angle in the Jacobian coordinates is 30º, while the angle in Figure 4.5 is only 24º. This makes the length of the tunneling paths for deuterium longer, and the effect of the LCT diminishes and the SCT path dominates the rate. These factors lead to the unusually large $\Delta\Delta H^{\ddagger}$.

4.3 Conclusions

The experimental observations in a reaction of unusually large KIEs at room temperature, the large temperature dependence of the KIE, and the linear Eyring plot over a wide range of temperatures are signs of large curvature tunneling. In the case of the 1,5-HAT seen by Rajca,[130] the LCT approximation provided an extremely accurate prediction of the tunneling rates. In reactions that see similar experimental effects,[134–136] the LCT approximation should adequately reproduce the rate increase due to tunneling. The LCT calculation is more difficult to apply; however, it should still be applied to more reactions in the literature to help in understanding the nature of tunneling in reactions.

4.4 Computational Methods

General Computational Procedures Calculations of structures, energies, and frequencies employed standard procedures in Gaussian09 unless otherwise noted. Structures used in POLYRATE calculations were optimized using the int(grid=ultrafine) and nosymm options. Complete structures and energetics are provided Appendix B.

CHAPTER V

CONCLUSIONS

The study of mechanisms for organic reactions is of the utmost importance for the design and understanding of new methods for the future of organic chemistry. Physical organic chemists have developed and are continued to develop methods for the elucidation of mechanisms and the formulation of chemical models to understand reactions. Throughout this dissertation, existing chemical models have been examined and challenged, and new models proposed in effort to better explain the nature of organic reactions. In addition, mechanisms of reactions were examined experimentally with the measurement of product ratios and kinetic isotope effects (KIEs). The experimental results were computationally modeled to get a better understand the underlying features of the reaction.

In the study of the hydroboration of terminal alkenes, the failure of transition state theory (TST) was reinforced, while new statistical and nonstatistical models were evaluated to understand which factors were the most important in the reaction. The full reaction mechanism was calculated with high level *ab initio* methods, and the formation of a π-complex was determined to be rate determining, however there was no enthalpic barrier to the reaction, and the excess energy made TST an unreliable method to predict the outcome of the reaction. Rice, Ramsperger, Kassel, and Marcus-Master Equation (RRKM-ME) model, which assumes a statistical distribution of the excess energy, was found to overestimate the effect the size of an alkene has upon the selectivity of the hydroboration reaction. Canonical competitive nonstatistical model (CCNM), which utilizes the statistical and nonstatistical phase space theory equilibrium distribution of products to determine a direct and indirect mechanism, was found to be unable to accurately reproduce the product ratios and fails completely to account for the experimental product ratios for sterically encumbered alkenes. Through studies of dynamic trajectories in explicit solvent, the nonstatistical energy redistribution throughout the molecule was determined to play an important role in the selectivity of the reaction. Using the data collected by the dynamic trajectories, a combination of the CCNM model and RRKM-ME models was proposed. This competitive localized noncanonical (CLN) model was found to successfully describe the selectivity of the hydroboration of alkenes with only one adjustable parameter. The CLN model should be effective in the description of reactions in which a large amount of energy is nonstatistically distributed in a reaction, and this model should be utilized for future analyses of reactions in the future to determine its efficacy.

In a collaboration with Professor Blum at UC-Irvine, the mechanism for the intramolecular formal thioboration of alkynes was studied. In this study, the mechanism was found to follow and Ad_E3 mechanism. This was discovered through extensive kinetic studies, ^{13}C kinetic isotope effects, and computational studies. This reaction can be explained using a variation of TST, which unlike the hydroboration reaction, is quite successful in explaining the experimental observations of the thioboration of alkenes.

A well-documented failure of TST occurs when there is significant tunneling in a reaction. The observation by Rajca of a H/D KIE of 150 at room temperature is a startling example of tunneling in a 1,5-hydrogen atom transfer. This computational study accurately predicted the rates and KIEs seen experimentally by Rajca using the fairly unused large curvature tunneling (LCT) approximation. Other computational predictions of reactions with very large room temperature KIEs with linear Eyring plots of the rate would benefit from the utilization of the more computationally complex LCT approximation

Through these studies, the most common theme was the effectiveness of TST. TST is an extremely effective model for the description of nearly all reactions including the thioboration in this dissertation, but often, reactions that clearly cannot be described by TST are shoehorned into the model. This unfortunate assumption allows misunderstandings of the nature of reactions to endure throughout the field of organic chemistry. Using this work as a guide, hopefully in the future organic chemists will think critically about the experimental observations and determine whether TST is the best model to be used. When the experimental observations are in disagreement with the model, that chemists will study closely the nature of the reaction to prepare new models to enhance the knowledge and predictive power of science.

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APPENDIX A

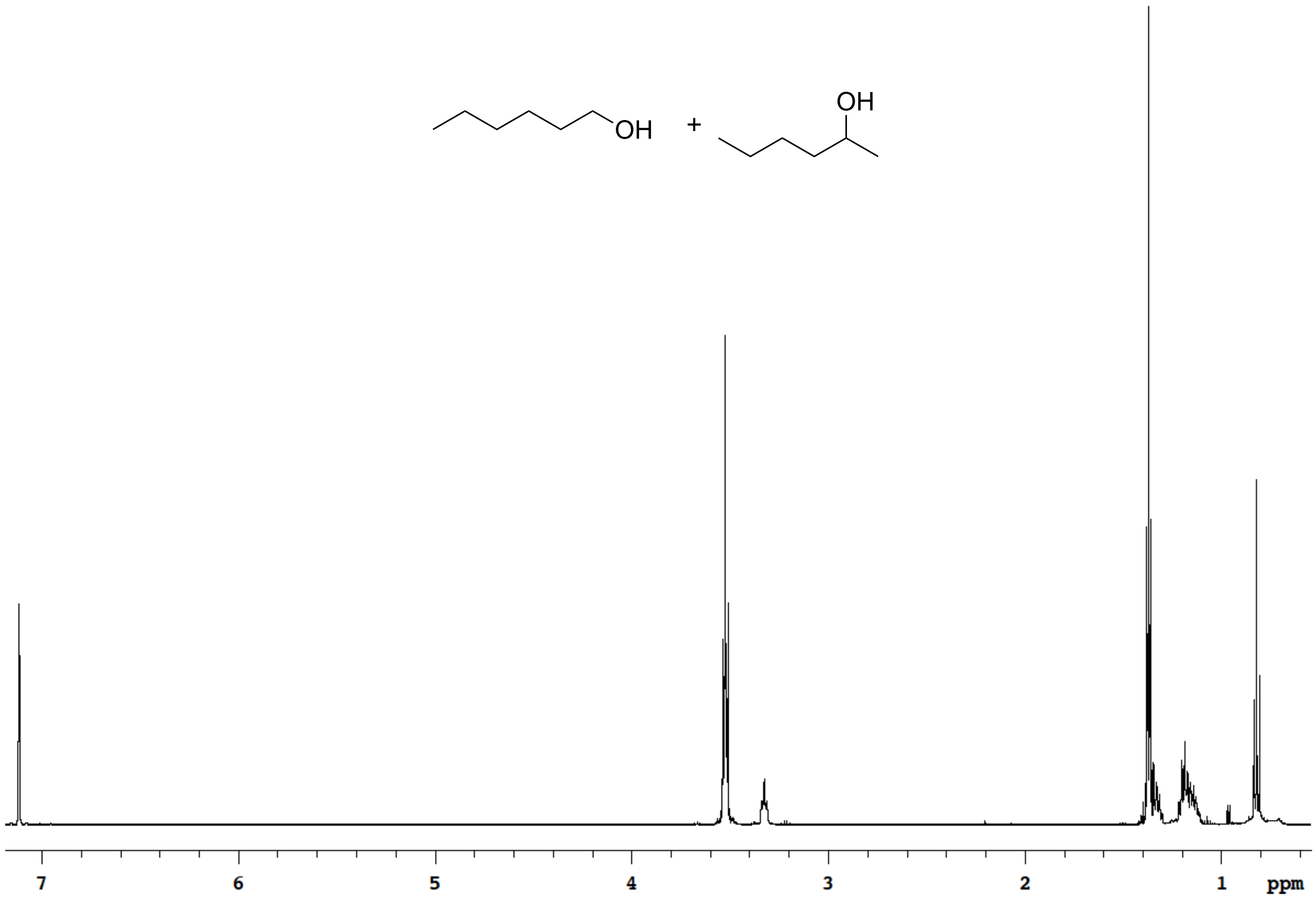
NMR DATA

Table A.1 Raw integrals for determination of product ratios for the hydroboration of alkenes

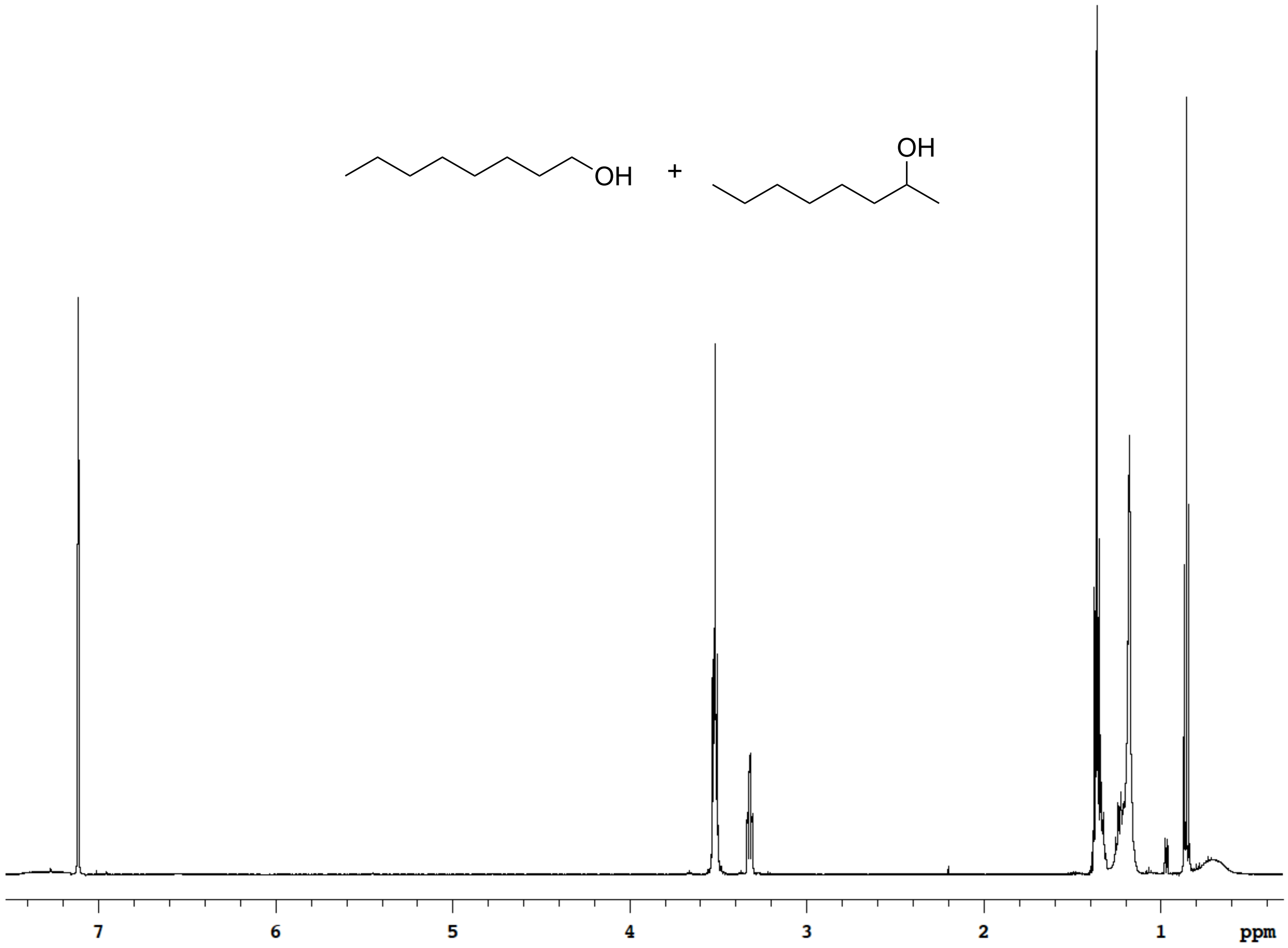
Alkene	**Sample**	**Major Product Peak**	**2 protons**	**Minor Product Peak**	**3 protons**	**% M**
		Raw	Normalized	Raw	Normalized	
1-hexene	1	30.62	15.315	5.32	1.773	10.5
	2	32.46	16.23	5.96	1.986	10.9
	3	33.9	16.95	5.75	1.917	10.2
	4	33.75	16.875	5.85	1.95	10.4
	5	83.92	41.96	16.08	5.36	11.3
	6	34.04	6.35	6.35	2.117	11.1
1-octene	1	34.77	17.385	5.64	1.88	9.8
	2	34.0	17.0	6.01	2.003	10.5
	3	35.34	17.67	5.38	1.793	9.2
	4	34.57	17.285	5.70	1.90	9.9
	5	34.66	17.33	5.66	1.887	9.8
	6	34.75	17.375	5.68	1.893	9.8
1-dodecene	1	34.75	17.375	5.29	1.763	9.2
	2	33.63	16.815	4.98	1.66	9.0
	3	33.01	16.505	4.88	1.627	9.0
	4	34.57	17.285	5.39	1.797	9.0
	5	34.89	17.445	5.33	1.777	8.9
	6	34.80	17.40	5.43	1.81	9.4
		Major Product Peak	9 protons	Minor Product Peak	9 protons	
3,3-dimethyl-2-butene	1	88.96	9.873	11.61	1.29	11.6
	2	85.65	9.517	11.07	1.23	11.4
	3	88.62	9.847	11.38	1.264	11.4
	4	89.40	9.933	10.60	1.117	10.6
	5	89.06	9.896	10.94	1.216	10.9
	6	86.07	9.563	10.83	1.203	11.2

Table A.2 Raw integrals for the determination of ratios of a standard solution of alcohols

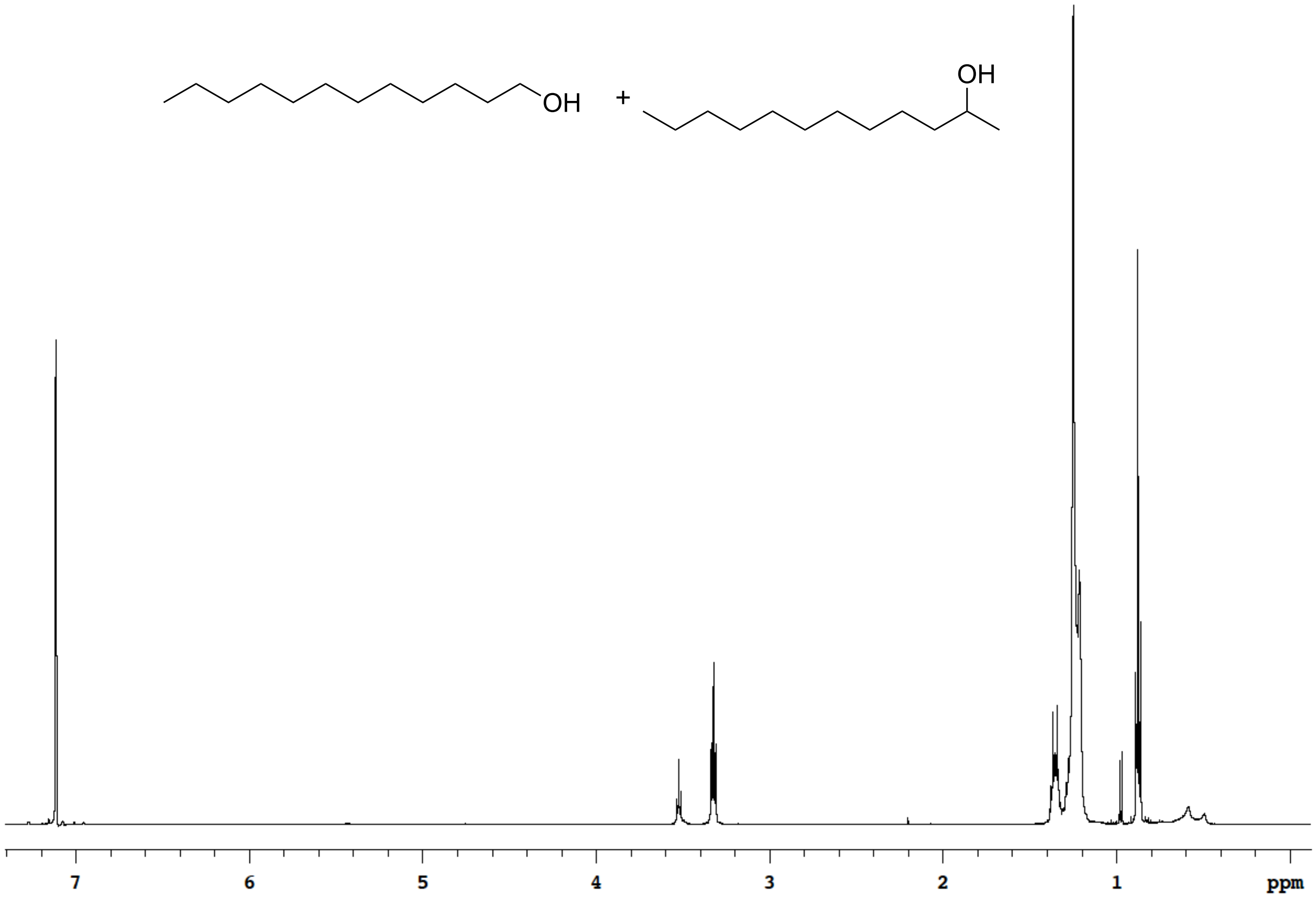
Alkene	**Sample**	**Major Product Peak 1**	**2 protons**	**% M**	**Major Product Peak 2**	**3 protons**	**Minor Product Peak**	**3 protons**	**% M**
		Raw	Norm		Raw	Norm	Raw	Norm	
hexanol	Standard	34.18	17.09	11.7	59.04	19.68	6.77	2.26	11.5
	1	34.42	17.21	11.7	58.75	19.58	6.82	2.27	11.6
	2	34.84	17.72	11.5	58.36	19.45	6.80	2.27	11.7
octanol	Standard	34.28	17.14	12.3	58.53	19.51	7.19	2.40	12.3
	1	34.31	17.16	12.2	58.51	19.50	7.18	2.39	12.3
	2	34.06	17.03	12.2	58.81	19.61	7.13	2.38	12.1
dodecanol	Standard	37.47	18.74	6.0	58.92	19.64	3.61	1.20	6.1
	1	37.33	18.67	5.8	59.25	19.75	3.42	1.14	6.1
	2	37.43	18.72	6.0	58.96	19.65	3.61	1.20	5.8



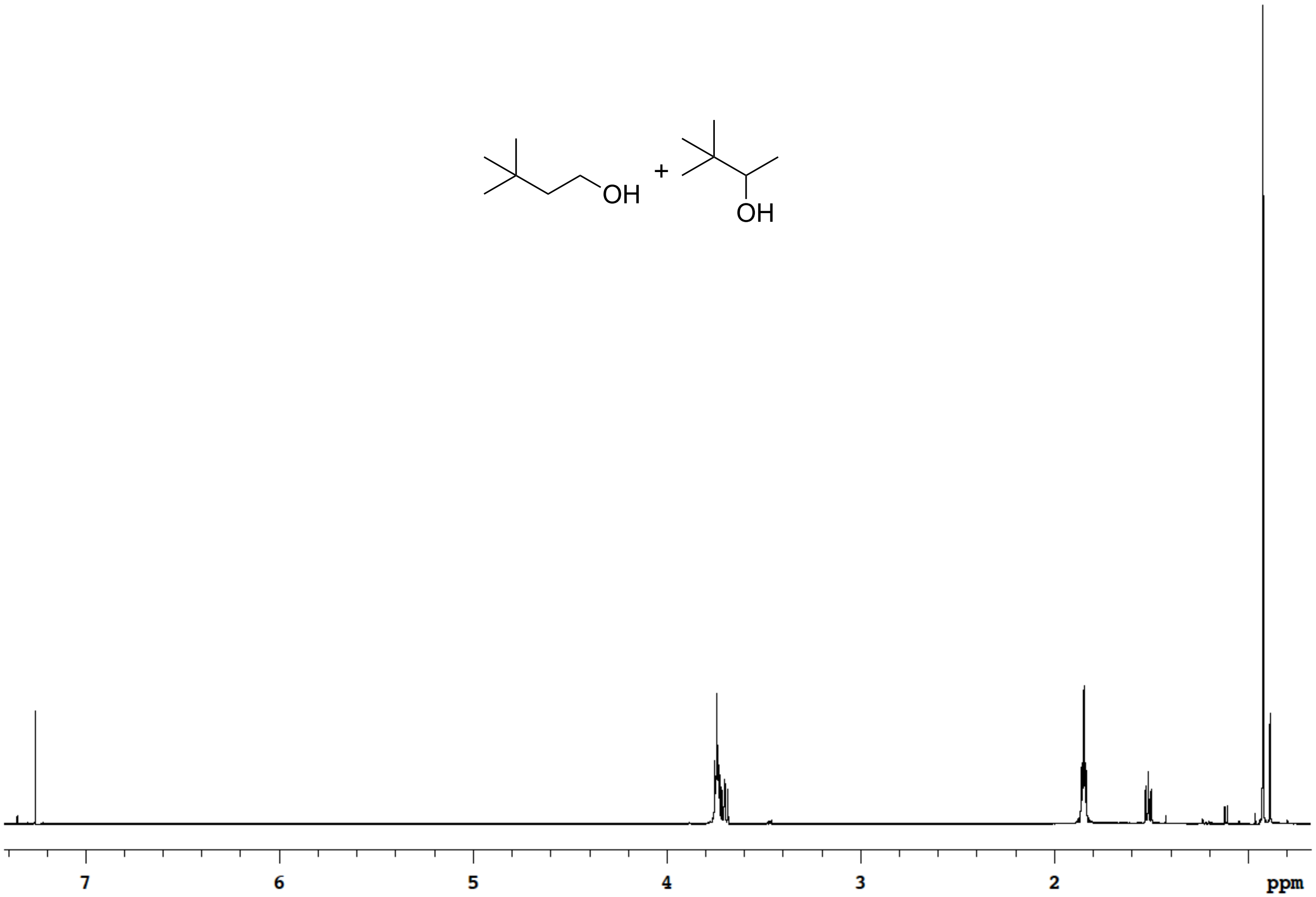
Crude 1H NMR for product ratio determination for the hydroboration of 1-hexene.



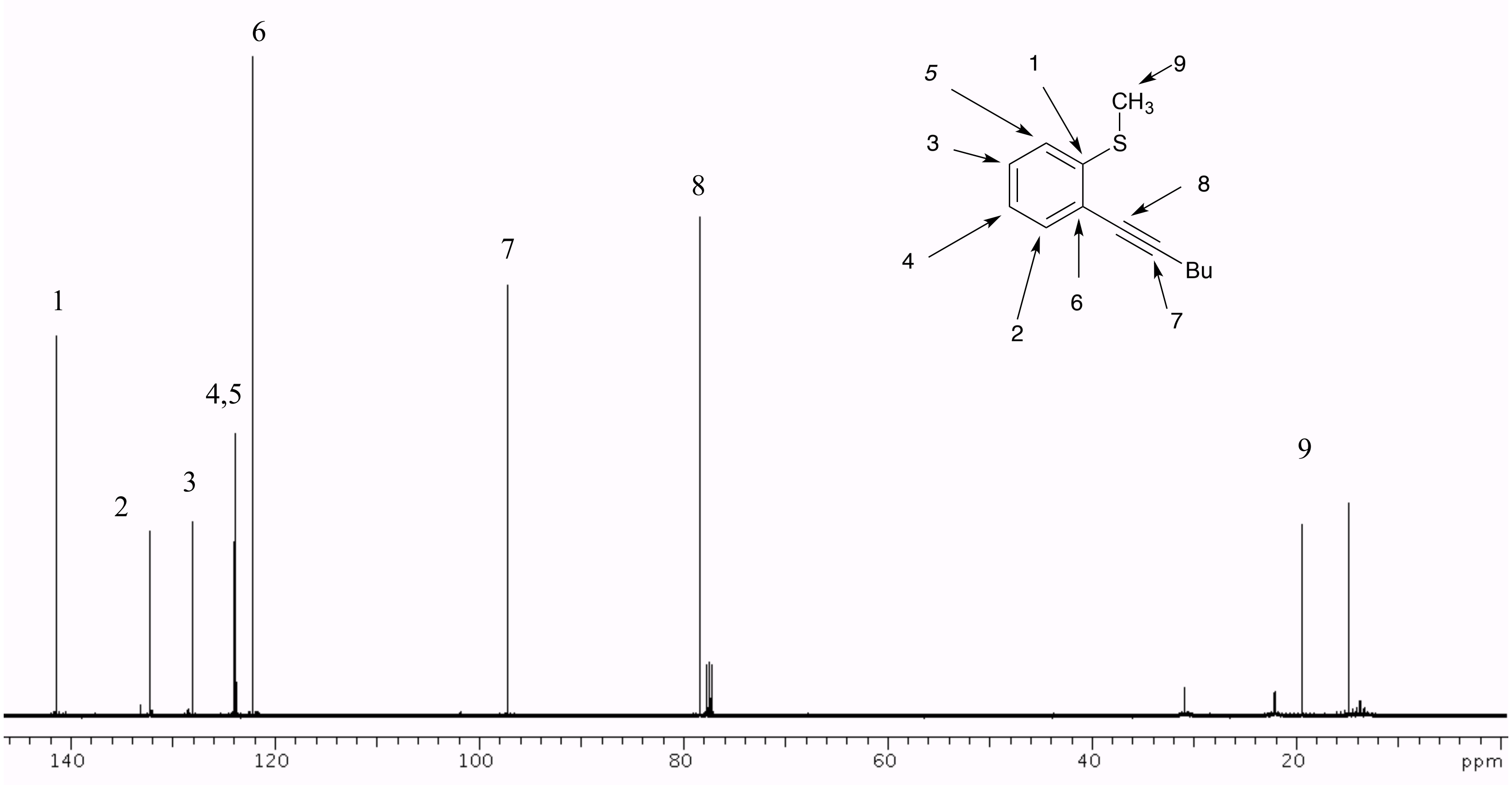
Crude 1H NMR for product ratio determination for the hydroboration of 1-octene.



Crude 1H NMR for product ratio determination for the hydroboration of 1-dodecene



Crude 1H NMR for product ratio determination for the hydroboration of 3,3-dimethyl-1-butene



^{13}C KIE sample for 1a in Chapter III

Table A.3 Raw integrals for the calculation of the ^{13}C isotope effects for the thioboration of 1a

Standard Raw Integrations						
1	1091.18	1089.44	1090.64	1088.47	1090.8	1093.55
2	972.268	976.016	972.353	976.136	973.764	976.845
3	1000	1000	1000	1000	1000	1000
4	1021.56	1028.3	1022.76	1026.92	1026.78	1031.66
5	1020.82	1023.33	1023.52	1022.7	1024.41	1026.92
6	1080.49	1080.26	1077.91	1075.9	1078.53	1080.43
7	1064.36	1071.19	1066.9	1063.02	1066.37	1068.26
8	1096.21	1104.04	1097.88	1097.92	1100.02	1101.94
9	920.274	921.874	920.725	923.025	923.173	925.676

Sample 1 Raw Integrations						
1	1083.45	1087.3	1084.74	1083.58	1088.64	1092.5
2	976.158	979.04	980.845	978.588	979.809	985.946
3	1000	1000	1000	1000	1000	1000
4	1029.25	1030.98	1026.65	1028.93	1033.92	1034.94
5	1023.66	1027.15	1022.11	1027.37	1021.7	1030.06
6	1073.22	1076.98	1077.97	1077.47	1077.14	1086.24
7	1080.85	1085.2	1081.84	1083.46	1085.52	1090.86
8	1100.3	1103.64	1103.26	1103.86	1106.43	1115.74
9	925.245	929.241	929.293	924.716	929.486	933.685

Sample 2 Raw Integrations						
1	1085.81	1085.41	1092.87	1094.08	1091.44	1091.38
2	978.553	977.218	978.755	980.002	976.464	978.116
3	1000	1000	1000	1000	1000	1000
4	1027.69	1025.89	1032.01	1035.95	1030.78	1029.66
5	1022.26	1021.96	1026.23	1023.53	1021.31	1020.42
6	1079.66	1076.97	1086.62	1087.82	1081.79	1080.26
7	1086.19	1081.3	1088.67	1093.6	1088.37	1084.88
8	1108.36	1103.47	1110.98	1111.67	1108.88	1107.38
9	931.337	924.87	927.185	931.375	930.765	931.381

	Average Standard	Average Sample 1	95% conf Sample 1	Average Sample 2	95% conf Sample 2
1	1089.3	1086.7	0.004	1090.2	0.004
2	975.3	980.1	0.004	978.2	0.002
3	1000.0	1000.0	0.000	1000.0	0.000
4	1027.1	1030.8	0.004	1030.3	0.004
5	1023.8	1025.3	0.004	1022.6	0.002
6	1077.4	1078.2	0.004	1082.2	0.004
7	1065.8	1084.6	0.004	1087.2	0.004
8	1098.0	1105.5	0.005	1110.0	0.003
9	924.0	928.6	0.004	929.7	0.003

APPENDIX B

CALCULATED STRUCTURES AND ENERGIES

Calculated Structures for the Hydroboration of Alkenes

CCSD(T)/aug-cc-pvdz structures

For comparison with the B3LYP structures, some structures were obtained that were fully optimized in CCSD(T)/aug-cc-pvdz calculations. Frequency calculations were not performed on these structures.

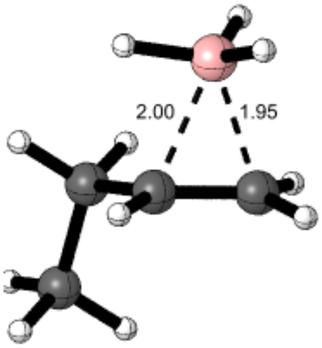
BH_3

CCSD(T)/aug-cc-pvdz
CCSD(T)= -26.5127597

B	0.000000	0.000000	0.000000
H	-1.190245	0.195977	0.000000
H	0.425402	-1.128771	0.000000
H	0.764843	0.932793	0.000000

Butene Complex

CCSD(T)/aug-cc-pvdz
CCSD(T)= -183.3178685

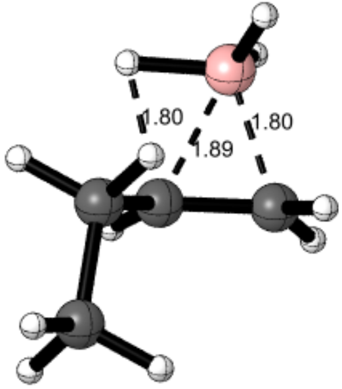


C	0.872374	-0.611238	-0.179042
C	-0.270509	0.129755	0.488708
C	-1.075283	1.033386	-0.184362
B	-2.008908	-0.679742	-0.070006

H	0.969926	-1.619172	0.261853
H	-0.309555	0.106563	1.585449
H	-0.936511	1.199645	-1.257686
H	-1.712910	1.736695	0.356468
H	-1.474090	-1.568357	0.579609
H	-2.025710	-0.935890	-1.255426
H	-2.998715	-0.261038	0.490412
H	0.638526	-0.738640	-1.252216
C	2.191832	0.174788	-0.004906
H	2.429742	0.317957	1.065916
H	3.031803	-0.371202	-0.470312
H	2.121552	1.172001	-0.476424

Butene AMTS

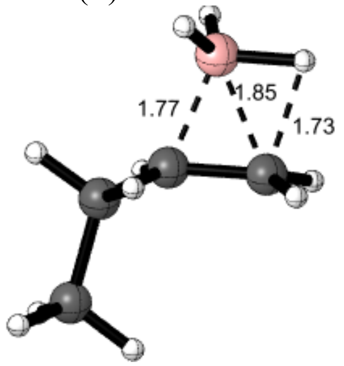
CCSD(T)/aug-cc-pvdz
CCSD(T)= -183.3171005



C	0.886965	-0.638706	-0.171891
C	-0.298413	0.036387	0.498317
C	-1.091854	0.987342	-0.176867
B	-1.979864	-0.575683	-0.108532
H	1.050276	-1.638631	0.269166
H	-0.314203	0.031297	1.595934
H	-0.863866	1.218152	-1.222312
H	-1.651584	1.736421	0.387989
H	-2.955867	-0.341464	0.566378
H	-1.325839	-1.435790	0.510851
H	-2.025128	-0.945248	-1.260568
H	0.651932	-0.781817	-1.242921
C	2.153758	0.229599	-0.009466
H	3.024929	-0.262568	-0.477489
H	2.017483	1.218174	-0.484308
H	2.388456	0.392153	1.059376

Butene MTS

CCSD(T)/aug-cc-pvdz
CCSD(T)= -183.3133853



H	0.952097	1.240983	-1.235950
C	1.133575	0.987328	-0.184525
C	0.317651	0.022117	0.459907
B	1.873858	-0.699600	0.005244
H	1.709454	1.717098	0.393581
C	-0.891542	-0.588434	-0.240219
H	0.279039	0.059579	1.555054
H	2.468227	-0.918525	1.033590
H	2.572232	0.139092	-0.618853
H	1.591111	-1.538462	-0.816951
H	-1.016576	-1.636621	0.089033
H	-0.697227	-0.619288	-1.329462
C	-2.177902	0.212264	0.051398
H	-3.053605	-0.249634	-0.440407
H	-2.379326	0.251551	1.138686
H	-2.085409	1.252576	-0.313910

B3LYP/6-31G structures*

BH_3

B3LYP/6-31G*
E(RB3LYP) = -26.6130000928

Zero-point correction= 0.026503 (Hartree/Particle)
Thermal correction to Energy= 0.029387
Thermal correction to Enthalpy= 0.030331

Thermal correction to Gibbs Free Energy= 0.008948
Sum of electronic and ZPE= -26.586498
Sum of electronic and thermal Energies= -26.583614
Sum of electronic and thermal Enthalpies= -26.582669
Sum of electronic and thermal Free Energies= -26.604053

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 18.440 6.589 45.005

B,0,0.,0.,0.
H,0,0.,0.,1.1938172328
H,0,1.0338760511,0.,-0.5969086164
H,0,-1.0338760511,0.,-0.5969086164

Propene

E(RB3LYP) = -117.907562163

Zero-point correction= 0.080099 (Hartree/Particle)
Thermal correction to Energy= 0.084173
Thermal correction to Enthalpy= 0.085117
Thermal correction to Gibbs Free Energy= 0.055099
Sum of electronic and ZPE= -117.827463
Sum of electronic and thermal Energies= -117.823389
Sum of electronic and thermal Enthalpies= -117.822445
Sum of electronic and thermal Free Energies= -117.852463

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 52.819 12.908 63.178

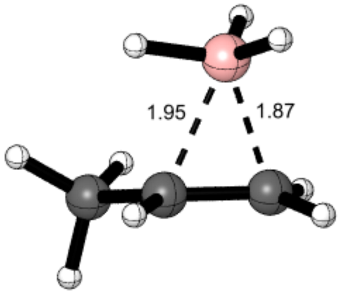
C,0,-0.0316860103,0.,-0.0387837613
C,0,0.0318476871,0.,1.2929722911
C,0,1.2982738493,0.,2.1006617837
H,0,-0.8976095917,0.,1.864679706
H,0,-0.9813004684,0.,-0.5672647441
H,0,0.8664849317,0.,-0.6537040143
H,0,2.18509124,0.,1.4579709445
H,0,1.3514294028,0.8804498739,2.7553276244
H,0,1.3514294028,-0.8804498739,2.7553276244

Propene Complex

B3LYP/6-31G*
E(RB3LYP) = -144.539354036

Zero-point correction= 0.112612 (Hartree/Particle)
Thermal correction to Energy= 0.118633
Thermal correction to Enthalpy= 0.119577
Thermal correction to Gibbs Free Energy= 0.084624
Sum of electronic and ZPE= -144.426742
Sum of electronic and thermal Energies= -144.420721
Sum of electronic and thermal Enthalpies= -144.419777
Sum of electronic and thermal Free Energies= -144.454730

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	74.443	21.094	73.565



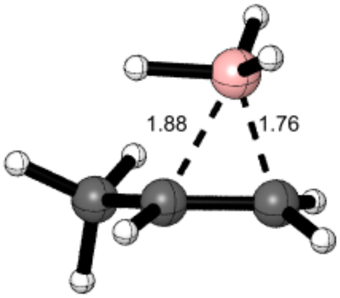
C	0.716835	0.145815	-0.039186
C	-0.056497	0.027531	1.245992
C	0.528086	-0.209957	2.470351
B	0.160630	1.617567	2.355429
H	0.246435	0.848421	-0.732447
H	0.752695	-0.838331	-0.525077
H	-1.130343	-0.115873	1.152808
H	1.605946	-0.303088	2.553882
H	-0.052781	-0.599894	3.297578
H	-0.482056	2.001277	1.397923
H	1.267385	2.079297	2.312445
H	-0.528173	1.731387	3.331479
H	1.744114	0.472159	0.146936

Propene AMTS

B3LYP/6-31G*
E(RB3LYP) = -144.538993703

Zero-point correction= 0.112431 (Hartree/Particle)
Thermal correction to Energy= 0.117611
Thermal correction to Enthalpy= 0.118555
Thermal correction to Gibbs Free Energy= 0.085396
Sum of electronic and ZPE= -144.426563
Sum of electronic and thermal Energies= -144.421382
Sum of electronic and thermal Enthalpies= -144.420438
Sum of electronic and thermal Free Energies= -144.453598

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	73.802	18.766	69.791



C	-0.382938	-0.400571	-1.498259
C	-0.409522	-0.408923	0.008951
C	0.756411	-0.409591	0.785972
B	0.073461	1.207558	0.831833
H	-1.286274	0.046214	-1.923654
H	-0.311532	-1.435961	-1.855533
H	-1.328328	-0.765745	0.468932
H	1.720840	-0.396967	0.287933
H	0.743158	-0.848613	1.777026
H	-0.244627	1.399319	1.971150
H	-0.987926	1.267311	0.204083
H	0.833715	1.910950	0.227519
H	0.487721	0.147763	-1.869757

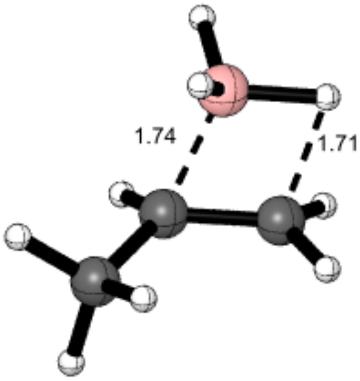
Propene MTS

B3LYP/6-31G*
E(RB3LYP) = -144.535333246

Zero-point correction= 0.112557 (Hartree/Particle)
Thermal correction to Energy= 0.117708
Thermal correction to Enthalpy= 0.118652
Thermal correction to Gibbs Free Energy= 0.085577
Sum of electronic and ZPE= -144.422776

Sum of electronic and thermal Energies= -144.417625
Sum of electronic and thermal Enthalpies= -144.416681
Sum of electronic and thermal Free Energies= -144.449756

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 73.863 18.638 69.613
```



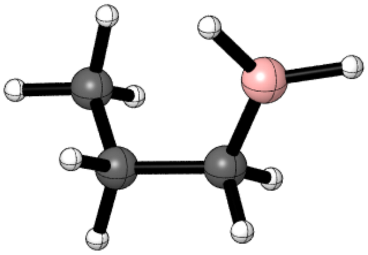
C	-0.365342	0.391568	-1.491184
C	-0.366020	0.391434	0.024379
C	0.827056	0.391911	0.772323
B	-0.135395	-1.165848	0.776756
H	-1.242451	-0.129908	-1.887130
H	-0.381662	1.418843	-1.879316
H	-1.225548	0.866818	0.489737
H	1.786682	0.295416	0.270888
H	0.866123	0.833289	1.763444
H	0.044953	-1.947797	-0.111035
H	0.940226	-1.187863	1.403788
H	-0.973569	-1.294841	1.620789
H	0.524873	-0.107926	-1.887239

Propene AM Product

B3LYP/6-31G*
E(RB3LYP) = -144.571577894

Zero-point correction= 0.114027 (Hartree/Particle)
Thermal correction to Energy= 0.120046
Thermal correction to Enthalpy= 0.120990
Thermal correction to Gibbs Free Energy= 0.085856
Sum of electronic and ZPE= -144.457550
Sum of electronic and thermal Energies= -144.451532
Sum of electronic and thermal Enthalpies= -144.450588
Sum of electronic and thermal Free Energies= -144.485722

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 75.330 20.520 73.946



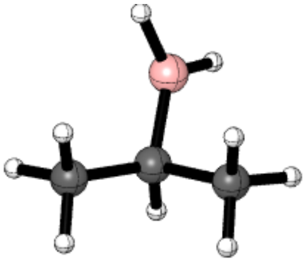
C	-0.167792	0.220722	-0.019849
C	-0.356496	-0.081912	1.470508
C	0.910226	0.202820	2.294993
B	1.348787	1.687735	2.489635
H	-1.079580	0.012484	-0.591237
H	0.639810	-0.386634	-0.447832
H	-0.657525	-1.131773	1.589412
H	1.749961	-0.422325	1.954136
H	0.756645	-0.127992	3.344388
H	0.591850	2.597837	2.293018
H	-1.185950	0.522967	1.860831
H	2.440271	1.944358	2.913593
H	0.091050	1.275360	-0.179061

Propene M Product

B3LYP/6-31G*
E(RB3LYP) = -144.568964309

Zero-point correction= 0.114180 (Hartree/Particle)
Thermal correction to Energy= 0.120349
Thermal correction to Enthalpy= 0.121293
Thermal correction to Gibbs Free Energy= 0.086068
Sum of electronic and ZPE= -144.454784
Sum of electronic and thermal Energies= -144.448615
Sum of electronic and thermal Enthalpies= -144.447671
Sum of electronic and thermal Free Energies= -144.482896

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 75.520 20.980 74.138



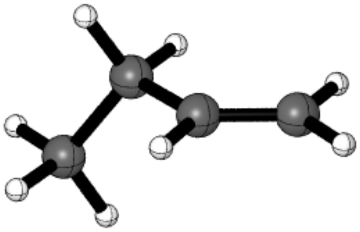
C	0.159981	-0.140557	0.073462
C	0.036717	-0.231314	1.602787
C	1.392401	0.127632	2.285087
B	-0.294887	-1.651000	2.172635
H	-0.793757	-0.359535	-0.421212
H	0.474860	0.861767	-0.246302
H	-0.695073	0.511010	1.952704
H	1.714092	1.127390	1.967061
H	1.320030	0.133932	3.378785
H	0.068138	-2.640813	1.599383
H	2.186205	-0.574959	2.002038
H	-0.837446	-1.778163	3.234045
H	0.897632	-0.858865	-0.305309

Butene Out of plane

B3LYP/6-31G*
E(RB3LYP) = -157.221072411

Zero-point correction= 0.109014 (Hartree/Particle)
Thermal correction to Energy= 0.114265
Thermal correction to Enthalpy= 0.115209
Thermal correction to Gibbs Free Energy= 0.081527
Sum of electronic and ZPE= -157.112059
Sum of electronic and thermal Energies= -157.106807
Sum of electronic and thermal Enthalpies= -157.105863
Sum of electronic and thermal Free Energies= -157.139545

```
    E      CV       S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 71.702 17.643 70.890
```



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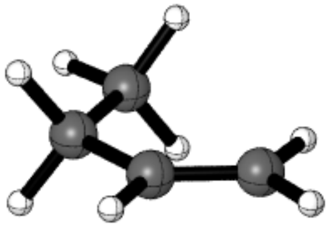
C,0,-0.2598029168,-0.633739236,0.0632469602
C,0,0.7337860797,-0.2745459274,0.8767951623
H,0,-1.0671275963,0.1571428394,-1.7506304772
C,0,-0.4101652809,-1.8605287448,-2.1488352843
H,0,-1.1639950144,-1.0700242903,0.493227837
H,0,1.6551009816,0.1614885252,0.4946947797
H,0,0.6668220106,-0.3978732421,1.9545783381
H,0,0.6846216667,-0.0256903378,-1.7572461408
H,0,-0.4297163855,-1.7324710302,-3.2370516926
H,0,0.4157198966,-2.5357636157,-1.8992145162
H,0,-1.3441170393,-2.3539538145,-1.8536409478

Butene In Plane

B3LYP/6-31G*
E(RB3LYP) = -157.220361409

Zero-point correction= 0.109144 (Hartree/Particle)
Thermal correction to Energy= 0.114277
Thermal correction to Enthalpy= 0.115221
Thermal correction to Gibbs Free Energy= 0.081928
Sum of electronic and ZPE= -157.111217
Sum of electronic and thermal Energies= -157.106085
Sum of electronic and thermal Enthalpies= -157.105141
Sum of electronic and thermal Free Energies= -157.138434

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	71.710	17.565	70.071



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C,0,-0.3307354651,-0.4717965348,0.052946196
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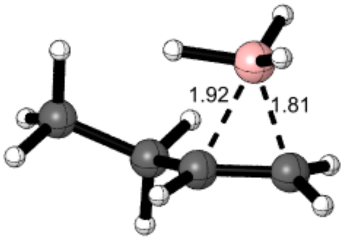
H,0,-0.919667336,0.4372011606,-1.7795646229
C,0,1.0931781515,-0.2925261027,-2.0840670582
H,0,-1.3299982603,-0.5549312968,0.4840237784
H,0,1.7388635287,-0.3538638953,0.5188733164
H,0,0.5883373053,-0.4871728249,1.9560880365
H,0,-0.804983052,-1.3017435413,-1.8490237014
H,0,1.0192459411,-0.253785765,-3.1761350695
H,0,1.6072063914,0.6160643711,-1.7505083316
H,0,1.7236514345,-1.1494580401,-1.8210200153

Butene Complex out

B3LYP/6-31G*
E(RB3LYP) = -183.853110954

Zero-point correction= 0.141268 (Hartree/Particle)
Thermal correction to Energy= 0.148478
Thermal correction to Enthalpy= 0.149422
Thermal correction to Gibbs Free Energy= 0.111190
Sum of electronic and ZPE= -183.711843
Sum of electronic and thermal Energies= -183.704633
Sum of electronic and thermal Enthalpies= -183.703689
Sum of electronic and thermal Free Energies= -183.741921

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	93.171	25.831	80.466



C,0,-0.3771801621,-0.3716153827,-1.484176563
C,0,-0.3945289441,-0.4092893283,0.0251078674
C,0,0.7531878912,-0.3907034679,0.8032921664
B,0,0.0317668119,1.2699971672,0.8456014853
C,0,-1.6453953667,0.1856706063,-2.136187435
H,0,-0.226753556,-1.4113853618,-1.8129822821
H,0,-1.3210316187,-0.7486427122,0.4848363472
H,0,1.7264057725,-0.3262764658,0.3273364681
H,0,0.7419413928,-0.7954877729,1.8084853677

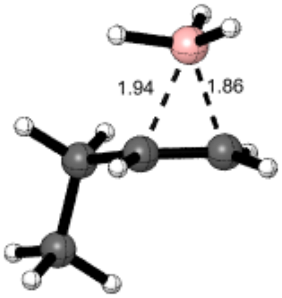
H,0,-0.1985752676,1.4174750092,2.0135274377
H,0,-1.0372019898,1.4030229138,0.2696383391
H,0,0.8421520561,1.9348292665,0.2607316634
H,0,0.50600955,0.1862921006,-1.8172517381
H,0,-1.5863811091,0.1016604105,-3.2264008297
H,0,-2.5359146556,-0.3635563557,-1.8074787245
H,0,-1.7873738047,1.2408753732,-1.8831825699

Butene Complex anti

B3LYP/6-31G*
E(RB3LYP) = -183.852872662

Zero-point correction= 0.141473 (Hartree/Particle)
Thermal correction to Energy= 0.148752
Thermal correction to Enthalpy= 0.149697
Thermal correction to Gibbs Free Energy= 0.111205
Sum of electronic and ZPE= -183.711400
Sum of electronic and thermal Energies= -183.704120
Sum of electronic and thermal Enthalpies= -183.703176
Sum of electronic and thermal Free Energies= -183.741667

```
     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 93.344 25.866 81.012
```



C,0,-0.3583501994,-0.4061427618,-1.4744896255
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C,0,0.7467819809,-0.3572819781,0.8187368401
B,0,-0.0431004037,1.3260580925,0.8027075358
H,0,-1.2462816095,0.1101126378,-1.8552612651
C,0,-0.3060719472,-1.8362280813,-2.040664833
H,0,-1.3098639188,-0.767543844,0.4942658259
H,0,1.723917228,-0.2511723037,0.358402925
H,0,0.7364451245,-0.7051572412,1.8448238467
H,0,-0.2353612561,1.4713321193,1.9780730638
H,0,-1.1126150028,1.4361737255,0.2343352459

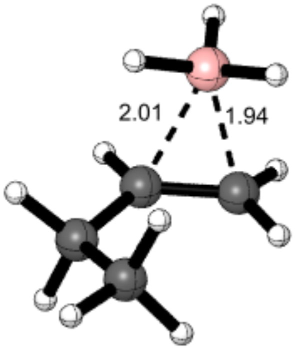
H,0,0.7838774629,1.9690031109,0.2173460353
H,0,0.5139997997,0.1643914657,-1.8129361338
H,0,-0.3065080615,-1.8122544619,-3.1356076743
H,0,0.5972950865,-2.3614960171,-1.7122716422
H,0,-1.1728463361,-2.4258796607,-1.7197469004

Butene Complex in

B3LYP/6-31G*
E(RB3LYP) = -183.851492972

Zero-point correction= 0.141499 (Hartree/Particle)
Thermal correction to Energy= 0.148785
Thermal correction to Enthalpy= 0.149729
Thermal correction to Gibbs Free Energy= 0.111201
Sum of electronic and ZPE= -183.709993
Sum of electronic and thermal Energies= -183.702708
Sum of electronic and thermal Enthalpies= -183.701764
Sum of electronic and thermal Free Energies= -183.740292

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 93.364 25.958 81.089



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C,0,-0.3210936699,-0.4441023498,0.0266201996
C,0,0.8077345336,-0.3113056194,0.7874161584
B,0,-0.1955529704,1.3358045361,0.9510500174
H,0,-1.3079800764,0.0813840175,-1.7878419486
H,0,-0.4831736771,-1.4637506306,-1.8058751062
H,0,-1.2279055788,-0.7923104607,0.5166755877
H,0,1.7699665672,-0.1139620692,0.3286048825
H,0,0.8266906224,-0.6157452696,1.827270748
H,0,-0.7789372529,1.2129160301,1.9907744204
H,0,-0.8788637945,1.6822936352,0.0187030105
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C,0,0.8136776873,0.2260239438,-2.1938132157
H,0,0.6540977454,0.2213271724,-3.2769088346
H,0,0.9471781454,1.2652095012,-1.8761023816
H,0,1.745778013,-0.3153359763,-1.9970454441
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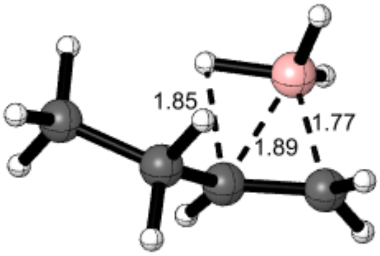
Butene AMTS out

B3LYP/6-31G*
E(RB3LYP) = -183.853079894

Zero-point correction= 0.140980 (Hartree/Particle)
Thermal correction to Energy= 0.147476
Thermal correction to Enthalpy= 0.148420
Thermal correction to Gibbs Free Energy= 0.111643
Sum of electronic and ZPE= -183.712100
Sum of electronic and thermal Energies= -183.705604
Sum of electronic and thermal Enthalpies= -183.704660
Sum of electronic and thermal Free Energies= -183.741437

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 92.543 23.758 77.404
```



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B,0,0.0914724406,1.2089166838,0.8665260158
C,0,-1.6405864945,0.1878308729,-2.1345195559
H,0,-0.2365743355,-1.4240390443,-1.8110634357
H,0,-1.3149161355,-0.7618116758,0.4847825625
H,0,1.7375806519,-0.3976373925,0.3053926384
H,0,0.7593757175,-0.8686259739,1.7882595864
H,0,-0.1895892389,1.3751712341,2.0201298549
H,0,-0.9746933159,1.3192125066,0.2644276607
H,0,0.8754626894,1.8991294902,0.276017252
H,0,0.5111886599,0.1666123923,-1.8204235776
H,0,-1.5837526584,0.1071062611,-3.2250646576
H,0,-2.5359027879,-0.3538693498,-1.8064267162
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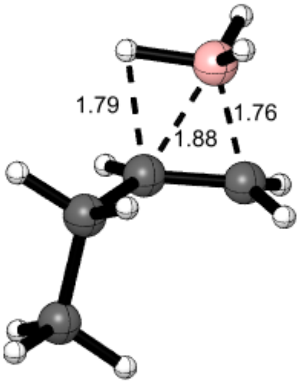
H,0,-1.7728377894,1.2440909542,-1.8789046753

Butene AMTS anti

B3LYP/6-31G*
E(RB3LYP) = -183.852596446

Zero-point correction= 0.141213 (Hartree/Particle)
Thermal correction to Energy= 0.147697
Thermal correction to Enthalpy= 0.148641
Thermal correction to Gibbs Free Energy= 0.111882
Sum of electronic and ZPE= -183.711383
Sum of electronic and thermal Energies= -183.704900
Sum of electronic and thermal Enthalpies= -183.703955
Sum of electronic and thermal Free Energies= -183.740715

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	92.681	23.624	77.366



C,0,-0.377109718,-0.3951255229,-1.4828903688
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B,0,0.0701121363,1.2335128793,0.8479161122
H,0,-1.27270367,0.0991056864,-1.876417694
C,0,-0.296078341,-1.8326155857,-2.0220251904
H,0,-1.3232346219,-0.7442668715,0.4891192732
H,0,1.7258998254,-0.3657746592,0.3112492696
H,0,0.7496489945,-0.8185075976,1.8008446575
H,0,-0.2551777181,1.4216694729,1.9858539
H,0,-0.9832641658,1.298128566,0.2095012432
H,0,0.8408403509,1.9358393807,0.2559144132
H,0,0.4864960436,0.1850941814,-1.827639239
H,0,-0.2903195571,-1.8292399648,-3.1172199451
H,0,0.6143623494,-2.3355229552,-1.6788928733

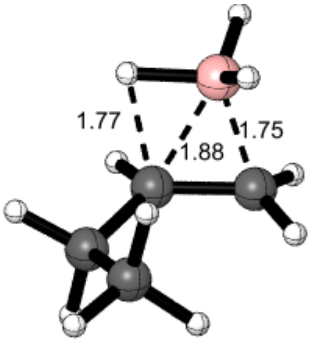
H,0,-1.1540970285,-2.4319356709,-1.6953173143

Butene AMTS in

B3LYP/6-31G*
E(RB3LYP) = -183.850656787

Zero-point correction= 0.141431 (Hartree/Particle)
Thermal correction to Energy= 0.147788
Thermal correction to Enthalpy= 0.148732
Thermal correction to Gibbs Free Energy= 0.112287
Sum of electronic and ZPE= -183.709226
Sum of electronic and thermal Energies= -183.702869
Sum of electronic and thermal Enthalpies= -183.701924
Sum of electronic and thermal Free Energies= -183.738370

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 92.739 23.447 76.706



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B,0,0.0154289969,1.2115041737,0.9582958413
H,0,-1.2974781468,0.0696935305,-1.8546645989
H,0,-0.4097063755,-1.441629525,-1.7791064642
H,0,-1.3010622387,-0.757067691,0.4631693889
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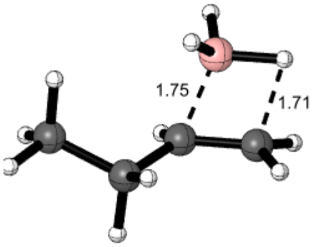
H,0,-0.9660805179,1.2854906409,0.2089731296
H,0,0.8095230111,1.9842062288,0.5031607711
C,0,0.8330893857,0.2854533059,-2.1677042922
H,0,0.730060003,0.2178261736,-3.2557040559
H,0,0.9043577215,1.3428659622,-1.8974061315
H,0,1.7764789171,-0.1997441958,-1.8955730326

Butene MTS out

B3LYP/6-31G*
E(RB3LYP) = -183.849336691

Zero-point correction= 0.141306 (Hartree/Particle)
Thermal correction to Energy= 0.147684
Thermal correction to Enthalpy= 0.148628
Thermal correction to Gibbs Free Energy= 0.112203
Sum of electronic and ZPE= -183.708031
Sum of electronic and thermal Energies= -183.701653
Sum of electronic and thermal Enthalpies= -183.700708
Sum of electronic and thermal Free Energies= -183.737134

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 92.673 23.457 76.664



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C,0,-0.3528953454,0.3744478104,0.0397807696
C,0,0.8354805657,0.4121303924,0.79191366
B,0,-0.0845832688,-1.1706060711,0.8143605506
C,0,-1.5996827297,-0.2893281835,-2.0854697222
H,0,-0.2803105874,1.4006302049,-1.8355918196
H,0,-1.2275564573,0.8330317706,0.4961195438
H,0,1.7994824255,0.3278793954,0.2967140306
H,0,0.8607941696,0.8688597126,1.7765256443
H,0,0.1225614025,-1.9579589028,-0.063202534
H,0,0.9826846208,-1.1631093501,1.4524099676
H,0,-0.9297891411,-1.3121644732,1.6493474871
H,0,0.5477460092,-0.1536653873,-1.8375088923
H,0,-1.5756208876,-0.239576975,-3.1797917213
H,0,-1.672868262,-1.3407773446,-1.7898538477
H,0,-2.5124115506,0.2178614981,-1.7493870111

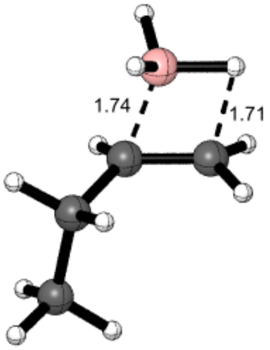
Butene MTS anti

B3LYP/6-31G*

E(RB3LYP) = -183.849344083

Zero-point correction= 0.141251 (Hartree/Particle)
Thermal correction to Energy= 0.147682
Thermal correction to Enthalpy= 0.148626
Thermal correction to Gibbs Free Energy= 0.112019
Sum of electronic and ZPE= -183.708093
Sum of electronic and thermal Energies= -183.701662
Sum of electronic and thermal Enthalpies= -183.700718
Sum of electronic and thermal Free Energies= -183.737325

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 92.672 23.491 77.046



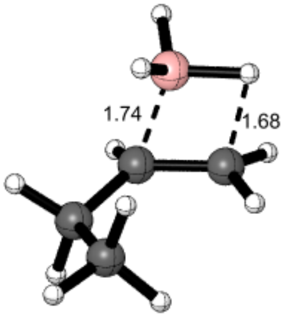
C,0,-0.3632389466,0.3791947665,-1.4765163165
C,0,-0.3653350722,0.3692251437,0.0426127774
C,0,0.8269840137,0.3747598968,0.7911307757
B,0,-0.1287882746,-1.1884688491,0.7919436782
H,0,-1.2301603564,-0.1829950572,-1.8439270409
C,0,-0.3924586511,1.8026105263,-2.0517199589
H,0,-1.2279814428,0.842931971,0.50603138
H,0,1.786960251,0.2788101567,0.2898904538
H,0,0.8658945529,0.8139506558,1.7832684671
H,0,0.0550859964,-1.9663380918,-0.0989309599
H,0,0.943419034,-1.2113515485,1.4229643422
H,0,-0.9713186855,-1.3210745782,1.6311090847
H,0,0.5231546322,-0.1548302158,-1.8408933258
H,0,-0.414017584,1.7832047495,-3.1473678739
H,0,-1.2797320652,2.3506463199,-1.711900613
H,0,0.4893825981,2.3759011544,-1.7414988701

Butene MTS in

B3LYP/6-31G*
E(RB3LYP) = -183.847241490

```
Zero-point correction= 0.141643 (Hartree/Particle)
Thermal correction to Energy= 0.147901
Thermal correction to Enthalpy= 0.148845
Thermal correction to Gibbs Free Energy= 0.112708
Sum of electronic and ZPE= -183.705599
Sum of electronic and thermal Energies= -183.699341
Sum of electronic and thermal Enthalpies= -183.698396
Sum of electronic and thermal Free Energies= -183.734534

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 92.809 23.219 76.058
```



```
C,0,-0.3528460413,0.3499183581,-1.4792010531
C,0,-0.3424777376,0.3701114812,0.0470738925
C,0,0.8328952095,0.3303798225,0.8278857264
B,0,-0.2252213088,-1.1574325504,0.8620880468
H,0,-1.2295293906,-0.2186973194,-1.8123187251
H,0,-0.5152861896,1.3822348365,-1.8233278776
H,0,-1.1780183665,0.9122549822,0.4827848366
H,0,1.8003392287,0.1647534528,0.3634574117
H,0,0.8684585458,0.8129788979,1.7998077389
H,0,-0.0613759659,-1.9963533118,0.024164575
H,0,0.8409024875,-1.2055554969,1.5091205568
H,0,-1.0799192174,-1.2072197922,1.6974936403
C,0,0.8993786987,-0.2061052197,-2.1615043483
H,0,0.7611035755,-0.223472322,-3.247859967
H,0,1.7839232918,0.4088969208,-1.9563471199
H,0,1.1124301802,-1.2301237395,-1.8365203339
```

Butene AM Product out

B3LYP/6-31G*
E(RB3LYP) = -183.884063239

```
Zero-point correction= 0.143186 (Hartree/Particle)
Thermal correction to Energy= 0.150741
Thermal correction to Enthalpy= 0.151685
Thermal correction to Gibbs Free Energy= 0.112041
Sum of electronic and ZPE= -183.740877
Sum of electronic and thermal Energies= -183.733323
Sum of electronic and thermal Enthalpies= -183.732379
Sum of electronic and thermal Free Energies= -183.772023

     E     CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 94.591 25.209 83.438

 C,0,-0.5441999612,-0.4559092773,-1.5451745274
 C,0,-0.4880095734,0.3316807647,-0.2271713403
 C,0,0.8149548338,0.056186284,0.5836276649
 B,0,0.7398733293,0.9144198065,1.889564238
 C,0,-1.8217199414,-0.1905193216,-2.347748795
 H,0,-0.4619663473,-1.5290923808,-1.3244091875
 H,0,-1.3677818514,0.0747288513,0.379674915
 H,0,1.672221946,0.3215903463,-0.0493072236
 H,0,0.8677425476,-1.0216546272,0.7871495942
 H,0,0.2084631551,0.4907239454,2.8776390664
 H,0,-0.5706836159,1.4050822758,-0.4491296544
 H,0,1.1389467932,2.0451563818,1.9095365302
 H,0,0.3346327697,-0.1996692378,-2.1528101926
 H,0,-1.8321287014,-0.7656200254,-3.2807268892
 H,0,-2.7155020403,-0.4682768703,-1.7756228015
 H,0,-1.9131883426,0.8707100845,-2.6099453973
```

Butene AM Product out twisted

```
B3LYP/6-31G*
E(RB3LYP) = -183.885759815

Zero-point correction= 0.142424 (Hartree/Particle)
Thermal correction to Energy= 0.149934
Thermal correction to Enthalpy= 0.150878
Thermal correction to Gibbs Free Energy= 0.111494
Sum of electronic and ZPE= -183.743336
Sum of electronic and thermal Energies= -183.735826
Sum of electronic and thermal Enthalpies= -183.734882
```

Sum of electronic and thermal Free Energies= -183.774265

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 94.085 25.503 82.890
```

```
 C,0,-0.5774236576,-0.4831810864,-1.5387033098
 C,0,-0.559433044,0.3496327181,-0.2505324163
 C,0,0.6489635133,0.0660487511,0.6561489397
 B,0,0.838118962,0.9373465796,1.9369341566
 C,0,-1.7915482117,-0.1987839294,-2.4285637307
 H,0,-0.5551940144,-1.5513940527,-1.2784932165
 H,0,-1.4863329623,0.162426846,0.3107907328
 H,0,1.588331762,0.2395299197,0.0897247399
 H,0,0.7098555842,-1.0051686466,0.9077844328
 H,0,1.6531595915,0.6245712342,2.7586191678
 H,0,-0.5780265297,1.4184255604,-0.5071329255
 H,0,0.2219495889,1.9518752392,2.1105533409
 H,0,0.3459874223,-0.2913344187,-2.104585018
 H,0,-1.7734506421,-0.808462756,-3.3391921607
 H,0,-2.7288171394,-0.4157727725,-1.90126531
 H,0,-1.821457223,0.8546058139,-2.7335704229
```

Butene AM Product out gauche

B3LYP/6-31G*
E(RB3LYP) = -183.885488497

Zero-point correction= 0.142683 (Hartree/Particle)
Thermal correction to Energy= 0.149984
Thermal correction to Enthalpy= 0.150928
Thermal correction to Gibbs Free Energy= 0.112251
Sum of electronic and ZPE= -183.742805
Sum of electronic and thermal Energies= -183.735504
Sum of electronic and thermal Enthalpies= -183.734560
Sum of electronic and thermal Free Energies= -183.773238

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 94.116 25.347 81.404
```

```
 C,0,-0.6187297248,-0.5335321512,-1.5624733584
 C,0,-0.4860032978,0.3730560246,-0.3315539228
 C,0,0.8144821747,0.1268699985,0.4511668812
```

B,0,2.163554007,0.5597213282,-0.2022732215
C,0,-1.9099779499,-0.2993471008,-2.3520525886
H,0,-0.5690420698,-1.584812086,-1.2434158405
H,0,-1.3582441841,0.2190499196,0.3201129696
H,0,0.8119007772,0.7374473168,1.379563681
H,0,0.8584835587,-0.9063956998,0.8275211949
H,0,3.2051744663,0.1588991328,0.2350192018
H,0,-0.5237398325,1.4232882266,-0.6538366885
H,0,2.1972344224,1.3558021321,-1.0995499505
H,0,0.2477825581,-0.3743710099,-2.2213063453
H,0,-1.9742226929,-0.9624852071,-3.2223204823
H,0,-2.7938453381,-0.4819475363,-1.7283049593
H,0,-1.9700298744,0.7340377118,-2.7151515707

Butene AM Product anti

B3LYP/6-31G*
E(RB3LYP) = -183.882835669

Zero-point correction= 0.143228 (Hartree/Particle)
Thermal correction to Energy= 0.150785
Thermal correction to Enthalpy= 0.151729
Thermal correction to Gibbs Free Energy= 0.111532
Sum of electronic and ZPE= -183.739608
Sum of electronic and thermal Energies= -183.732051
Sum of electronic and thermal Enthalpies= -183.731106
Sum of electronic and thermal Free Energies= -183.771304

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	94.619	25.126	84.602

C,0,-0.5151442973,-0.522726232,-1.7665388042
C,0,-0.5615821353,0.1959991121,-0.4053306332
C,0,0.7677709918,0.0989016512,0.4040375462
B,0,0.5886468121,0.9512613497,1.7036279642
H,0,-1.4476154792,-0.3005699716,-2.3037165082
C,0,-0.3403648527,-2.0417730336,-1.6765908597
H,0,-1.3870876385,-0.2163711634,0.1913536583
H,0,1.5890817045,0.4532404244,-0.2326546932
H,0,0.9544925419,-0.9576841438,0.6374318413
H,0,-0.0213036184,0.5113931875,2.6381420976
H,0,-0.8084286823,1.2514059801,-0.5838662555
H,0,0.984959151,2.0806748705,1.775502382

H,0,0.2964150829,-0.0934401955,-2.3704403241
H,0,-0.3665277121,-2.4982605952,-2.6726198226
H,0,0.6146793189,-2.3163251378,-1.2151781638
H,0,-1.1413691872,-2.4972031026,-1.0806664253

Butene AM Product anti twisted

B3LYP/6-31G*
E(RB3LYP) = -183.884555032

Zero-point correction= 0.142658 (Hartree/Particle)
Thermal correction to Energy= 0.150026
Thermal correction to Enthalpy= 0.150971
Thermal correction to Gibbs Free Energy= 0.111977
Sum of electronic and ZPE= -183.741897
Sum of electronic and thermal Energies= -183.734529
Sum of electronic and thermal Enthalpies= -183.733584
Sum of electronic and thermal Free Energies= -183.772578

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 94.143 25.392 82.068

C,0,-0.4432871852,-0.5308326826,-1.83555931
C,0,-0.5577520489,0.278687965,-0.5329254513
C,0,0.6564347021,0.1683586276,0.4057815359
B,0,0.5841137819,0.8820595778,1.790386295
H,0,-1.2904810226,-0.2733374458,-2.4857364986
C,0,-0.4150484661,-2.0503417034,-1.6348681246
H,0,-1.4629032274,-0.0302561453,0.009260808
H,0,1.588649503,0.418840399,-0.124401789
H,0,0.8110842568,-0.8902999203,0.703663807
H,0,1.5798864302,1.0448775887,2.4377012408
H,0,-0.7099817829,1.3357748676,-0.790271673
H,0,-0.461772926,1.2264936122,2.2665263386
H,0,0.461180829,-0.2169926701,-2.3768101447
H,0,-0.3707221875,-2.5747599403,-2.5962219673
H,0,0.4546991452,-2.3696710661,-1.0489394039
H,0,-1.3142518017,-2.395556064,-1.1089276628

Butene AM Product anti gauche

B3LYP/6-31G*
E(RB3LYP) = -183.883997234

Zero-point correction= 0.142852 (Hartree/Particle)
Thermal correction to Energy= 0.150084
Thermal correction to Enthalpy= 0.151028
Thermal correction to Gibbs Free Energy= 0.112434
Sum of electronic and ZPE= -183.741145
Sum of electronic and thermal Energies= -183.733914
Sum of electronic and thermal Enthalpies= -183.732969
Sum of electronic and thermal Free Energies= -183.771563

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 94.179 25.267 81.227

C,0,-0.5623894626,-0.6348083861,-1.8169162967
C,0,-0.5885594061,0.1890273784,-0.5180484541
C,0,0.7442857303,0.1880848448,0.2519916581
B,0,1.9648593461,0.9240975927,-0.3825714847
H,0,-1.4988439582,-0.4591038623,-2.3633094619
C,0,-0.3867781001,-2.1436171709,-1.6072339171
H,0,-1.3974252345,-0.1884116333,0.1245557691
H,0,0.618828939,0.7572211057,1.1984948599
H,0,1.0117646199,-0.8187026951,0.6023979616
H,0,3.0699692112,0.743339289,0.0453037422
H,0,-0.8510356407,1.2259822375,-0.7668449643
H,0,1.8232007244,1.7394512604,-1.2514018788
H,0,0.2418512674,-0.2576963344,-2.4657761302
H,0,-0.419028785,-2.6804663387,-2.5622165978
H,0,0.5701618871,-2.3834980455,-1.1295400172
H,0,-1.1842411381,-2.5483132423,-0.9713157883

Butene AM Product in

B3LYP/6-31G*
E(RB3LYP) = -183.884555027

Zero-point correction= 0.142658 (Hartree/Particle)
Thermal correction to Energy= 0.150026
Thermal correction to Enthalpy= 0.150971
Thermal correction to Gibbs Free Energy= 0.111975
Sum of electronic and ZPE= -183.741897
Sum of electronic and thermal Energies= -183.734529
Sum of electronic and thermal Enthalpies= -183.733584
Sum of electronic and thermal Free Energies= -183.772580

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 94.143 25.392 82.073
```

```
 C,0,-0.4540830725,-0.3519024606,-1.6416426004
 C,0,-0.5002604914,0.5256540927,-0.3795011185
 C,0,0.4115690366,0.0567597048,0.7677787291
 B,0,0.4965598386,0.9412038941,2.0492720212
 H,0,-1.2353043634,-0.0123923236,-2.3353298375
 H,0,-0.7158167228,-1.3854787533,-1.3719494105
 H,0,-1.5361150988,0.5603528628,-0.0153361457
 H,0,1.4696329048,0.0429540391,0.4305634525
 H,0,0.2152744252,-0.9966818498,1.0219601533
 H,0,0.1464636738,2.0886632825,2.0457846783
 H,0,-0.2423543981,1.5606086608,-0.6460912175
 H,0,0.97669639,0.5006947429,3.0555049627
 C,0,0.8950526293,-0.3416423281,-2.3694260673
 H,0,0.8577201208,-0.9523550068,-3.278720172
 H,0,1.1763522999,0.6772542697,-2.6645188066
 H,0,1.701393828,-0.7395788272,-1.7423626211
```

Butene M Product out

```
B3LYP/6-31G*
E(RB3LYP) = -183.882714970
```

```
Zero-point correction= 0.142904 (Hartree/Particle)
Thermal correction to Energy= 0.150308
Thermal correction to Enthalpy= 0.151252
Thermal correction to Gibbs Free Energy= 0.112687
Sum of electronic and ZPE= -183.739811
Sum of electronic and thermal Energies= -183.732407
Sum of electronic and thermal Enthalpies= -183.731463
Sum of electronic and thermal Free Energies= -183.770028
```

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 94.319 25.779 81.167
```

```
 C,0,-0.2310274656,0.1465969499,-1.3961442695
 C,0,-0.3264349594,0.0966749406,0.1390299704
 C,0,1.0053339503,0.5745667248,0.7962104601
 B,0,-0.5429507281,-1.3236843524,0.7609215402
```

```
C,0,-1.5421170727,-0.2325352442,-2.0935844196
H,0,0.0696740984,1.1557422968,-1.7152039991
H,0,-1.1088866491,0.795341485,0.4721132253
H,0,1.2517543942,1.5841341019,0.4443905146
H,0,0.9400728723,0.6106834632,1.8896205605
H,0,-0.1244475808,-2.3040027392,0.2090262816
H,0,1.8464541097,-0.0773304152,0.5290750932
H,0,-1.0412702509,-1.4544350061,1.8432160056
H,0,0.567635157,-0.5313909663,-1.7292101333
H,0,-1.4482131825,-0.1736669269,-3.1839397134
H,0,-1.8444093497,-1.2577470149,-1.8433832002
H,0,-2.3587583434,0.4359997032,-1.7934079165
```

Butene M Product anti

B3LYP/6-31G*
E(RB3LYP) = -183.881372674

```
Zero-point correction= 0.142849 (Hartree/Particle)
Thermal correction to Energy= 0.150340
Thermal correction to Enthalpy= 0.151284
Thermal correction to Gibbs Free Energy= 0.112369
Sum of electronic and ZPE= -183.738524
Sum of electronic and thermal Energies= -183.731033
Sum of electronic and thermal Enthalpies= -183.730089
Sum of electronic and thermal Free Energies= -183.769003
```

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 94.340 25.860 81.902
```

```
C,0,-0.3571391405,0.3358751128,-1.4213799792
C,0,-0.3499296133,0.0750353122,0.1000802985
C,0,0.9818070097,0.5347344077,0.7717723769
B,0,-0.4503769976,-1.4315775326,0.5125363827
H,0,-1.2573458171,-0.1216535568,-1.8549259184
C,0,-0.3235046316,1.8159715353,-1.8230141672
H,0,-1.1558706549,0.6605689864,0.5685255924
H,0,1.8478428544,0.0162082368,0.3415579992
H,0,1.1377667467,1.6095278735,0.6273885484
H,0,-0.0026893764,-2.2928136963,-0.193147084
H,0,0.981616939,0.3498893776,1.8525675385
H,0,-0.897327367,-1.7489822406,1.5786011126
H,0,0.4931619561,-0.1908650075,-1.8776399438
```

H,0,-0.3893554286,1.9285393194,-2.9114011274
H,0,-1.1656873013,2.3640178076,-1.3817452956
H,0,0.5993378226,2.3103030643,-1.4993903336

Butene M Product in

B3LYP/6-31G*
E(RB3LYP) = -183.882116733

Zero-point correction= 0.142595 (Hartree/Particle)
Thermal correction to Energy= 0.149862
Thermal correction to Enthalpy= 0.150807
Thermal correction to Gibbs Free Energy= 0.112551
Sum of electronic and ZPE= -183.739522
Sum of electronic and thermal Energies= -183.732254
Sum of electronic and thermal Enthalpies= -183.731310
Sum of electronic and thermal Free Energies= -183.769566

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	94.040	25.743	80.515

C,0,-0.154764738,0.2992143753,-1.3901527963
C,0,-0.2162341265,0.080073613,0.1384460233
C,0,0.9707717745,0.7077498905,0.8944548019
B,0,-0.658036229,-1.3404876481,0.6075608126
H,0,-1.1109070628,-0.0107865898,-1.8312355876
H,0,-0.0470385637,1.3722886425,-1.605446948
H,0,-1.1336195032,0.6130958663,0.4923657142
H,0,1.0968293236,1.7676563453,0.6383782005
H,0,0.8317270632,0.6356494175,1.9785409402
H,0,-1.3223501812,-2.0411394835,-0.1040769475
H,0,1.9122552713,0.2003835542,0.6552563878
H,0,-0.4352731209,-1.7161560812,1.7242959654
C,0,0.9800845869,-0.4666225807,-2.0817911686
H,0,0.9682676699,-0.2951615093,-3.1642170534
H,0,1.9650126426,-0.1595494093,-1.7121756332
H,0,0.8836211934,-1.5475784028,-1.9165307111

Butene VTS out

B3LYP/6-31G*
E(RB3LYP) = -183.835431471

Zero-point correction= 0.136320 (Hartree/Particle)
Thermal correction to Energy= 0.144696
Thermal correction to Enthalpy= 0.145640
Thermal correction to Gibbs Free Energy= 0.102109
Sum of electronic and ZPE= -183.699111
Sum of electronic and thermal Energies= -183.690735
Sum of electronic and thermal Enthalpies= -183.689791
Sum of electronic and thermal Free Energies= -183.733322

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	90.798	26.059	91.619

C	-1.480381	-0.220345	-0.332966
C	-0.783224	0.877401	0.423973
C	-0.042249	1.844357	-0.121225
B	3.362340	-0.557704	-0.031017
H	-2.565473	-0.138934	-0.168686
C	-1.020604	-1.623500	0.097809
H	-0.903938	0.852955	1.509108
H	0.104322	1.913052	-1.197836
H	0.435430	2.610907	0.482977
H	3.653757	-0.203596	1.070935
H	3.663915	0.109820	-0.973542
H	2.784443	-1.590120	-0.192332
H	-1.316513	-0.086713	-1.409747
H	-1.568672	-2.401014	-0.446138
H	0.049036	-1.761915	-0.094816
H	-1.189257	-1.783402	1.169618

Butene VTS anti

B3LYP/6-31G*
E(RB3LYP) = -183.835794638

Zero-point correction= 0.136313 (Hartree/Particle)
Thermal correction to Energy= 0.144690
Thermal correction to Enthalpy= 0.145634
Thermal correction to Gibbs Free Energy= 0.101929
Sum of electronic and ZPE= -183.699482
Sum of electronic and thermal Energies= -183.691105
Sum of electronic and thermal Enthalpies= -183.690160
Sum of electronic and thermal Free Energies= -183.733866

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	90.794	26.062	91.985

C	1.140149	-0.545135	0.307986
C	0.250544	0.439637	-0.402059
C	-0.502654	1.369684	0.189874
B	-3.807913	-0.740581	-0.035571
C	2.619153	-0.409584	-0.093949
H	0.805053	-1.567183	0.076532
H	0.253265	0.378071	-1.492403
H	-0.530464	1.476826	1.272773
H	-1.111831	2.064444	-0.382359
H	-4.232245	0.217026	-0.608578
H	-3.819114	-0.775926	1.157648
H	-3.394265	-1.672563	-0.656538
C	1.035153	-0.420030	1.393145
H	3.233574	-1.161191	0.414351
H	2.750351	-0.545558	-1.174200
H	3.006939	0.581373	0.166372

Butene VTS in

B3LYP/6-31G*
E(RB3LYP) = -183.835603141

Zero-point correction= 0.136628 (Hartree/Particle)
Thermal correction to Energy= 0.145687
Thermal correction to Enthalpy= 0.146631
Thermal correction to Gibbs Free Energy= 0.100465
Sum of electronic and ZPE= -183.698975
Sum of electronic and thermal Energies= -183.689916
Sum of electronic and thermal Enthalpies= -183.688972
Sum of electronic and thermal Free Energies= -183.735138

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	91.420	27.892	97.164

C	1.387279	-0.116589	-0.711085
C	0.316357	0.913295	-0.454237
C	-0.288962	1.166153	0.709566
B	-3.411007	-0.766963	-0.133942

```
H 2.268712 0.399848 -1.121674
H 1.045096 -0.775760 -1.523510
H 0.032222 1.504974 -1.326128
H -0.050011 0.622519 1.620051
H -1.041458 1.945023 0.796701
H -3.570563 -0.709416 1.047866
H -2.889927 -1.724925 -0.619875
H -3.799847 0.119598 -0.832675
C 1.804831 -0.962735 0.493188
H 2.578856 -1.682873 0.207569
H 2.208636 -0.339134 1.298847
H 0.956282 -1.525777 0.897946
```

Hexene out of plane

```
B3LYP/6-31G*
E(RB3LYP) = -235.848697696

Zero-point correction= 0.166296 (Hartree/Particle)
Thermal correction to Energy= 0.174158
Thermal correction to Enthalpy= 0.175102
Thermal correction to Gibbs Free Energy= 0.134205
Sum of electronic and ZPE= -235.682402
Sum of electronic and thermal Energies= -235.674540
Sum of electronic and thermal Enthalpies= -235.673596
Sum of electronic and thermal Free Energies= -235.714493

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.286 27.305 86.075

 C,0,-0.2291275171,-0.5225229911,-1.373635487
 C,0,-0.2723273257,-0.5858593642,0.1288500625
 C,0,0.6824056838,-0.1438943636,0.9482881913
 H,0,-1.0782877447,0.0769430452,-1.7377937994
 C,0,-0.2921231791,-1.9114492072,-2.0372703673
 H,0,-1.1642069644,-1.0477443155,0.557481658
 H,0,1.5902729952,0.3215692551,0.5687505665
 H,0,0.5949944515,-0.2254375689,2.028582721
 H,0,0.6817906165,-0.000069795,-1.6952657098
 C,0,-0.2967460763,-1.8504852961,-3.5698664475
 H,0,0.5620644638,-2.5115226032,-1.6940522128
 H,0,-1.1936300792,-2.4387083177,-1.6916174352
 C,0,-0.3571900371,-3.2328046141,-4.227665558
```

```
H,0,-1.1520811946,-1.2467054447,-3.9054454344
H,0,0.6027136046,-1.3201963703,-3.913765073
H,0,-0.3586519977,-3.1559873847,-5.3209825262
H,0,0.503846725,-3.8475920003,-3.9379703915
H,0,-1.2639644245,-3.7740366635,-3.9305357572
```

Hexene AM complex out

B3LYP/6-31G*
E(RB3LYP) = -262.480571718

Zero-point correction= 0.198507 (Hartree/Particle)
Thermal correction to Energy= 0.208388
Thermal correction to Enthalpy= 0.209332
Thermal correction to Gibbs Free Energy= 0.163849
Sum of electronic and ZPE= -262.282064
Sum of electronic and thermal Energies= -262.272184
Sum of electronic and thermal Enthalpies= -262.271240
Sum of electronic and thermal Free Energies= -262.316723

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 130.765 35.509 95.728
```

```
C,0,-0.3647606651,-0.3761253023,-1.4686259173
C,0,-0.3847771151,-0.4131110267,0.0399659306
C,0,0.7612097022,-0.3911537928,0.820171694
B,0,0.0408377639,1.2714542171,0.8597179304
C,0,-1.6327408527,0.1744044345,-2.1328558033
H,0,-0.2104635473,-1.4162747466,-1.7976874905
H,0,-1.3118196301,-0.7511598445,0.4992770104
H,0,1.7353630581,-0.3275325722,0.3460603869
H,0,0.7479974304,-0.7934746033,1.8263379614
H,0,-0.1811327874,1.4203369386,2.0292350823
H,0,-1.0312950962,1.4048629903,0.2907507821
H,0,0.8500831796,1.9339346021,0.270412934
H,0,0.5178001497,0.1840917406,-1.8020516989
C,0,-1.5941706939,0.0783010791,-3.6634448872
H,0,-2.5091466273,-0.3736799457,-1.7562138909
H,0,-1.7714899605,1.2211352899,-1.8340800438
C,0,-2.8563363286,0.6349966704,-4.3295535245
H,0,-0.7137811952,0.6197930322,-4.0373485198
H,0,-1.4552675251,-0.9711883515,-3.9602977971
H,0,-2.7994475335,0.5548906951,-5.4208843437
```

H,0,-3.7508456903,0.0913284778,-4.0015769792
H,0,-3.0021190356,1.692842018,-4.0796998161

Hexene AM complex anti

B3LYP/6-31G*
E(RB3LYP) = -262.480552373

Zero-point correction= 0.198733 (Hartree/Particle)
Thermal correction to Energy= 0.208671
Thermal correction to Enthalpy= 0.209615
Thermal correction to Gibbs Free Energy= 0.163918
Sum of electronic and ZPE= -262.281820
Sum of electronic and thermal Energies= -262.271882
Sum of electronic and thermal Enthalpies= -262.270938
Sum of electronic and thermal Free Energies= -262.316635

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	130.943	35.531	96.178

C,0,-0.3602270069,-0.3780400177,-1.4319526845
C,0,-0.3868546048,-0.3949145001,0.0759865279
C,0,0.7452071344,-0.330469415,0.8604103896
B,0,-0.036943336,1.357397751,0.8438765226
H,0,-1.2491802659,0.1369154335,-1.8145971426
C,0,-0.3068209057,-1.808267387,-2.0054654652
H,0,-1.3129175784,-0.7315972159,0.5373874581
H,0,1.7227862764,-0.2293686503,0.3998946422
H,0,0.7334737668,-0.6768715266,1.8869912582
H,0,-0.2260167602,1.5036842137,2.0197766107
H,0,-1.1064551478,1.4732964195,0.276954442
H,0,0.7933353551,1.9953547342,0.2575150259
H,0,0.5120406975,0.1926815786,-1.7729262863
C,0,-0.3113439577,-1.8304527491,-3.5397462984
H,0,0.5926365742,-2.3168945297,-1.6321865891
H,0,-1.1641456142,-2.3866315084,-1.6314121911
C,0,-0.2571842888,-3.2480535392,-4.1178695403
H,0,-1.2117183848,-1.3179105652,-3.9062097176
H,0,0.5434442497,-1.2485733026,-3.9118438277
H,0,-0.261307506,-3.2309225899,-5.2134422473
H,0,0.6501946201,-3.773659266,-3.7962281326
H,0,-1.1183313171,-3.8434723679,-3.7907027544

Hexene M complex out

B3LYP/6-31G*
E(RB3LYP) = -262.480572824

Zero-point correction= 0.198523 (Hartree/Particle)
Thermal correction to Energy= 0.208398
Thermal correction to Enthalpy= 0.209342
Thermal correction to Gibbs Free Energy= 0.163875
Sum of electronic and ZPE= -262.282050
Sum of electronic and thermal Energies= -262.272175
Sum of electronic and thermal Enthalpies= -262.271231
Sum of electronic and thermal Free Energies= -262.316698

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 130.772 35.510 95.693
```

C,0,-0.3962998814,0.320691612,-1.4159351779
C,0,-0.2763705859,0.3970555013,0.086458243
C,0,0.935688073,0.3835027268,0.758215532
B,0,0.2091740047,-1.2744239952,0.9053380683
C,0,-1.7233340981,-0.2369520415,-1.9453736783
H,0,-0.2677511373,1.3507153559,-1.7854860507
H,0,-1.1550344874,0.7541499308,0.620381292
H,0,1.8619574387,0.2966317797,0.1994196436
H,0,1.0179837629,0.8085124266,1.7516668884
H,0,0.9571105104,-1.9560023831,0.2595277835
H,0,0.1026405581,-1.3904598039,2.0946898646
H,0,-0.9132579397,-1.4138092938,0.4467453905
H,0,0.4485151853,-0.2548471122,-1.8145982148
C,0,-1.8262703953,-0.1799280278,-3.4749501566
H,0,-1.8391416677,-1.2746280155,-1.6079538742
H,0,-2.5581320152,0.3271689041,-1.5035719539
C,0,-3.1485588401,-0.7416984596,-4.0066982148
H,0,-1.7083431336,0.8603722989,-3.8106411132
H,0,-0.9880906412,-0.7387862789,-3.9145005591
H,0,-3.1925421843,-0.6898633669,-5.1003361348
H,0,-3.2777096191,-1.7914476359,-3.7168208961
H,0,-4.0049979069,-0.1815991219,-3.6116556816

Hexene M complex anti

B3LYP/6-31G*

E(RB3LYP) = -262.480552376

Zero-point correction= 0.198733 (Hartree/Particle)
Thermal correction to Energy= 0.208671
Thermal correction to Enthalpy= 0.209615
Thermal correction to Gibbs Free Energy= 0.163918
Sum of electronic and ZPE= -262.281820
Sum of electronic and thermal Energies= -262.271882
Sum of electronic and thermal Enthalpies= -262.270938
Sum of electronic and thermal Free Energies= -262.316635

```
     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 130.943 35.531 96.178
```

```
 C,0,-0.2731431039,0.3127647331,-1.4356890497
 C,0,-0.4324472638,0.3696757617,0.0630628106
 C,0,0.6278426269,0.4430761013,0.9413783597
 B,0,0.0210417156,-1.3154213211,0.9218212566
 H,0,-1.0700643751,-0.300670242,-1.8720927897
 C,0,-0.3118686516,1.7241244982,-2.0552720898
 H,0,-1.423907333,0.6233499188,0.4325149155
 H,0,1.6469842892,0.4289467594,0.5684065745
 H,0,0.4925741001,0.8155081758,1.9498412353
 H,0,-0.9784708389,-1.5555653443,0.2722077558
 H,0,0.9581542325,-1.8819615323,0.4308845812
 H,0,-0.2540671941,-1.4467785374,2.0824049353
 H,0,0.6776838956,-0.1756553844,-1.6810657607
 C,0,-0.1850189521,1.7021330633,-3.5843097754
 H,0,-1.2515196135,2.2226048533,-1.7759872118
 H,0,0.4969059053,2.3320698272,-1.6270797582
 C,0,-0.2213455874,3.100882164,-4.2079548664
 H,0,0.7522955388,1.1999548995,-3.8617293821
 H,0,-0.9949078357,1.090394598,-4.0056469448
 H,0,-0.1283891552,3.0522996567,-5.2986376803
 H,0,-1.1623931076,3.6146006604,-3.9763108685
 H,0,0.5980947081,3.7250506907,-3.8311492472
```

Hexene AMTS out

B3LYP/6-31G*
E(RB3LYP) = -262.480534863

Zero-point correction= 0.198224 (Hartree/Particle)

Thermal correction to Energy= 0.207390
Thermal correction to Enthalpy= 0.208334
Thermal correction to Gibbs Free Energy= 0.164327
Sum of electronic and ZPE= -262.282311
Sum of electronic and thermal Energies= -262.273145
Sum of electronic and thermal Enthalpies= -262.272201
Sum of electronic and thermal Free Energies= -262.316208

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 130.139 33.424 92.621

C,0,-0.3649953691,-0.3850131299,-1.4692803645
C,0,-0.3813605319,-0.4158781411,0.040395255
C,0,0.7800984408,-0.4264670858,0.8155284036
B,0,0.1034863465,1.2082511002,0.8826407518
C,0,-1.6287819183,0.1771031756,-2.1313664585
H,0,-0.2205185226,-1.4275399304,-1.7942913342
H,0,-1.3057054403,-0.7613689907,0.5000056433
H,0,1.7469330419,-0.4011038135,0.3227688628
H,0,0.7665107755,-0.8687685904,1.8050892806
H,0,-0.1776472493,1.3761065551,2.0360619685
H,0,-0.9631927052,1.3177603301,0.281247948
H,0,0.8864551559,1.8985531182,0.2907520737
H,0,0.5221638475,0.1661021495,-1.8057258777
C,0,-1.5928463303,0.0854033808,-3.6623070008
H,0,-2.5096250649,-0.3642126269,-1.7553195051
H,0,-1.7587694233,1.224789078,-1.8302276765
C,0,-2.8511701418,0.6543260526,-4.3253377829
H,0,-0.7083683546,0.6206125851,-4.035527793
H,0,-1.4629387872,-0.9643377698,-3.9621377219
H,0,-2.7962028354,0.5766875996,-5.4169302021
H,0,-3.7497468286,0.1171586034,-3.9977684604
H,0,-2.9879201052,1.7126953504,-4.0725300099

Hexene AMTS anti

B3LYP/6-31G*
E(RB3LYP) = -262.480231959

Zero-point correction= 0.198486 (Hartree/Particle)
Thermal correction to Energy= 0.207622
Thermal correction to Enthalpy= 0.208566
Thermal correction to Gibbs Free Energy= 0.164637

```
Sum of electronic and ZPE= -262.281746
Sum of electronic and thermal Energies= -262.272610
Sum of electronic and thermal Enthalpies= -262.271666
Sum of electronic and thermal Free Energies= -262.315595

      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 130.285 33.271 92.458

 C,0,-0.3800775629,-0.3644044607,-1.4411646563
 C,0,-0.4067225728,-0.3550189803,0.0698707765
 C,0,0.7576651977,-0.3582333449,0.8490056257
 B,0,0.0794883643,1.2625137215,0.8893708635
 H,0,-1.2768987181,0.1278008865,-1.8368421551
 C,0,-0.2972193849,-1.802444104,-1.9875117973
 H,0,-1.3281337864,-0.7058126073,0.5308474931
 H,0,1.7230489106,-0.3478694546,0.3522674935
 H,0,0.7438118155,-0.7934215433,1.8418062204
 H,0,-0.2454652673,1.4549225968,2.026806168
 H,0,-0.974927403,1.3301628047,0.2518378026
 H,0,0.8509600162,1.9616945246,0.2945065715
 H,0,0.4833661177,0.2161165017,-1.7883242474
 C,0,-0.2937761338,-1.8540427771,-3.5211251435
 H,0,0.609530701,-2.2870305288,-1.6006696733
 H,0,-1.1454086966,-2.3898565711,-1.6065430747
 C,0,-0.2096600859,-3.2812542096,-4.0712332894
 H,0,-1.2018032708,-1.3660214629,-3.9021149313
 H,0,0.5516357397,-1.2631564329,-3.9004780789
 H,0,-0.2084288755,-3.2857649965,-5.1669313825
 H,0,0.7058606889,-3.782968578,-3.7348620534
 H,0,-1.0609507936,-3.8865819837,-3.7364955316
```

Hexene MTS out

```
B3LYP/6-31G*
E(RB3LYP) = -262.476805871

Zero-point correction= 0.198521 (Hartree/Particle)
Thermal correction to Energy= 0.207574
Thermal correction to Enthalpy= 0.208518
Thermal correction to Gibbs Free Energy= 0.164880
Sum of electronic and ZPE= -262.278285
Sum of electronic and thermal Energies= -262.269232
Sum of electronic and thermal Enthalpies= -262.268288
```

Sum of electronic and thermal Free Energies= -262.311926

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 130.255 33.138 91.844

C,0,-0.3411059745,0.3643463123,-1.4645292592
C,0,-0.3444098569,0.3741765232,0.0547800297
C,0,0.8423013054,0.4175468244,0.8091867716
B,0,-0.0680911215,-1.1706074975,0.8289232189
C,0,-1.5881267243,-0.2810747396,-2.0817703981
H,0,-0.2662747001,1.4045104978,-1.8195205747
H,0,-1.2218142294,0.8275093472,0.5108609032
H,0,1.8077917138,0.3391181222,0.3159734545
H,0,0.8628744854,0.8737349195,1.7941728457
H,0,0.146610162,-1.9559495497,-0.0484979726
H,0,0.9965796768,-1.1568198676,1.4710266361
H,0,-0.9153518108,-1.3177522163,1.6608952388
H,0,0.5589777129,-0.1520734407,-1.8232884273
C,0,-1.5954969166,-0.2367285984,-3.6148784242
H,0,-1.6576881583,-1.3221266619,-1.7408269298
H,0,-2.4859754937,0.2279859895,-1.7002425282
C,0,-2.8444213571,-0.8777723194,-4.2284562222
H,0,-1.5175357872,0.807479171,-3.9506742508
H,0,-0.6986916738,-0.7460006455,-3.9958592753
H,0,-2.8204395382,-0.8336993605,-5.3233100412
H,0,-2.9309904479,-1.932062509,-3.9386726622
H,0,-3.7564602658,-0.3678693011,-3.8942691325

Hexene MTS anti

B3LYP/6-31G*
E(RB3LYP) = -262.476928679

Zero-point correction= 0.198501 (Hartree/Particle)
Thermal correction to Energy= 0.207598
Thermal correction to Enthalpy= 0.208542
Thermal correction to Gibbs Free Energy= 0.164745
Sum of electronic and ZPE= -262.278428
Sum of electronic and thermal Energies= -262.269331
Sum of electronic and thermal Enthalpies= -262.268387
Sum of electronic and thermal Free Energies= -262.312184

E CV S

```
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 130.270 33.152 92.179

 C,0,-0.3617153221,0.3515808445,-1.434093677
 C,0,-0.364492235,0.3382705522,0.0844589755
 C,0,0.8275460684,0.3482393256,0.8337149139
 B,0,-0.120676204,-1.2194539585,0.8315511102
 H,0,-1.229854595,-0.2086053813,-1.8045029213
 C,0,-0.388797963,1.7757961155,-2.0142325663
 H,0,-1.2293916114,0.8063524771,0.5491136157
 H,0,1.7881904248,0.2580886603,0.3327077683
 H,0,0.8637870382,0.786491456,1.8263715082
 H,0,0.0680192874,-1.9959423265,-0.0594169185
 H,0,0.9514008975,-1.2367137837,1.4634349105
 H,0,-0.96258799,-1.3573480762,1.670515472
 H,0,0.5245237707,-0.1826258062,-1.8011004509
 C,0,-0.4277343523,1.8028086995,-3.5476032973
 H,0,-1.2637861876,2.3137344129,-1.6199261589
 H,0,0.4926098649,2.3303770873,-1.6598557196
 C,0,-0.4564121907,3.2215430411,-4.1251425021
 H,0,0.4457640737,1.2639824307,-3.941546551
 H,0,-1.3093798495,1.2466802563,-3.8963342154
 H,0,-0.4835840666,3.2068283722,-5.2206259376
 H,0,-1.3384444636,3.7733809833,-3.777479322
 H,0,0.4304036053,3.7915656179,-3.8216550364
```

Hexene AM Product out

```
B3LYP/6-31G*
E(RB3LYP) = -262.511491848

Zero-point correction= 0.200428 (Hartree/Particle)
Thermal correction to Energy= 0.210650
Thermal correction to Enthalpy= 0.211594
Thermal correction to Gibbs Free Energy= 0.164747
Sum of electronic and ZPE= -262.311064
Sum of electronic and thermal Energies= -262.300842
Sum of electronic and thermal Enthalpies= -262.299898
Sum of electronic and thermal Free Energies= -262.346744

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 132.185 34.856 98.597
```

C,0,-0.5334907687,-0.4527907969,-1.5298491473
C,0,-0.477446635,0.3347908225,-0.2117710334
C,0,0.8260237601,0.0589123939,0.5988591115
B,0,0.7508320031,0.9174299938,1.904628456
C,0,-1.8097301949,-0.1930332485,-2.3401774452
H,0,-0.4508747621,-1.527021817,-1.3097898441
H,0,-1.3564035237,0.0780831295,0.3960874985
H,0,1.6832220984,0.324059891,-0.0342103226
H,0,0.8787304642,-1.0188911467,0.8023919943
H,0,0.2199836206,0.4940029467,2.8931847421
H,0,-0.5594699907,1.4083115404,-0.4326307187
H,0,1.1504858393,2.048003903,1.9249993376
H,0,0.3459579655,-0.1969608772,-2.1384090611
C,0,-1.8682870886,-0.9783295393,-3.6569979734
H,0,-2.6880965278,-0.4467004589,-1.7278885842
H,0,-1.8915963452,0.8828008012,-2.5561658906
C,0,-3.1444756245,-0.7153572592,-4.462117814
H,0,-0.9904629918,-0.7249603428,-4.268651339
H,0,-1.7862645829,-2.0532953111,-3.4411003911
H,0,-3.1552507007,-1.2902921267,-5.3953310181
H,0,-4.0389164106,-0.9925011109,-3.8902999311
H,0,-3.2370026038,0.3460366134,-4.724206626

Hexene AM Product out twisted

B3LYP/6-31G*
E(RB3LYP) = -262.513174556

Zero-point correction= 0.199653 (Hartree/Particle)
Thermal correction to Energy= 0.209835
Thermal correction to Enthalpy= 0.210780
Thermal correction to Gibbs Free Energy= 0.164171
Sum of electronic and ZPE= -262.313522
Sum of electronic and thermal Energies= -262.303339
Sum of electronic and thermal Enthalpies= -262.302395
Sum of electronic and thermal Free Energies= -262.349004

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 131.674 35.161 98.096

C,0,-0.5960746333,-0.462559135,-1.5081953712
C,0,-0.5562304085,0.3560512731,-0.2113563777
C,0,0.6764916762,0.0746440567,0.6630430932

B,0,0.886970923,0.9331917633,1.9490667328
C,0,-1.832346348,-0.1868222189,-2.3731728903
H,0,-0.5565552721,-1.5343579678,-1.2613431229
H,0,-1.4668548934,0.1530641946,0.3704668242
H,0,1.6002864927,0.2643001567,0.0765971341
H,0,0.7543092146,-0.9986743592,0.9006006593
H,0,1.7245118222,0.6198048244,2.747594687
H,0,-0.5911238239,1.4275095376,-0.4541785172
H,0,0.2645298302,1.9390184837,2.1490929709
H,0,0.3122079675,-0.2551104768,-2.0944180043
C,0,-1.8704724602,-1.0051427191,-3.6703450323
H,0,-2.7400083372,-0.3954007804,-1.787045556
H,0,-1.8718860276,0.8847855074,-2.6200579268
C,0,-3.1087919225,-0.7232727196,-4.5273748215
H,0,-0.9642174905,-0.7962274423,-4.2566407407
H,0,-1.8318027478,-2.0758558557,-3.4238575327
H,0,-3.1061392804,-1.3222751782,-5.4452808294
H,0,-4.0308098671,-0.9561943842,-3.9803938705
H,0,-3.156763414,0.3331604397,-4.8192705081

Hexene AM Product out gauche

B3LYP/6-31G*
E(RB3LYP) = -262.512935487

Zero-point correction= 0.199927 (Hartree/Particle)
Thermal correction to Energy= 0.209891
Thermal correction to Enthalpy= 0.210835
Thermal correction to Gibbs Free Energy= 0.164940
Sum of electronic and ZPE= -262.313008
Sum of electronic and thermal Energies= -262.303045
Sum of electronic and thermal Enthalpies= -262.302101
Sum of electronic and thermal Free Energies= -262.347996

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 131.708 35.003 96.595

C,0,-0.1378092593,-0.0415812204,-1.0238276961
C,0,-0.3656469647,-0.5028429668,0.4219068208
C,0,0.8695434884,-0.2935463252,1.3138760663
B,0,1.2763522724,1.1669554191,1.6820544543
C,0,-1.3572134991,-0.2380183754,-1.9326274758
H,0,0.7216268794,-0.5845098377,-1.4457601813

```
H,0,-0.6563698789,-1.5631851948,0.4171841718
H,0,1.7279584213,-0.8724113481,0.9407773411
H,0,0.6824625475,-0.7315069604,2.3178632302
H,0,0.4989979909,2.0761712108,1.5869619472
H,0,-1.2170797039,0.0483012415,0.8453685164
H,0,2.3587715966,1.3968186959,2.1429597626
H,0,0.1463718775,1.0221011654,-1.0223409596
C,0,-1.1269627262,0.2212944149,-3.3782386778
H,0,-1.6434911453,-1.3005489679,-1.9316068388
H,0,-2.2153450486,0.3070268517,-1.5117168663
C,0,-2.350677452,0.0218669393,-4.2782822914
H,0,-0.8408900549,1.2827827916,-3.3792803937
H,0,-0.2701508999,-0.3241106868,-3.7990711704
H,0,-2.154292886,0.3589894184,-5.3025385831
H,0,-2.6401388476,-1.0352878711,-4.3253529213
H,0,-3.2147637075,0.5838166059,-3.9026632548
```

Hexene AM Product anti

```
B3LYP/6-31G*
E(RB3LYP) = -262.510212130

Zero-point correction= 0.200470 (Hartree/Particle)
Thermal correction to Energy= 0.210694
Thermal correction to Enthalpy= 0.211639
Thermal correction to Gibbs Free Energy= 0.164074
Sum of electronic and ZPE= -262.309742
Sum of electronic and thermal Energies= -262.299518
Sum of electronic and thermal Enthalpies= -262.298574
Sum of electronic and thermal Free Energies= -262.346139

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 132.213 34.793 100.109

C 0.125155 1.011974 -0.108236
C 1.558147 0.670588 0.341220
C 2.186104 -0.542530 -0.411459
B 3.662955 -0.686723 0.084645
H -0.177902 1.944089 0.390556
C -0.919398 -0.070741 0.189641
H 1.559737 0.472886 1.422049
H 2.110678 -0.359325 -1.491351
H 1.593854 -1.437449 -0.179673
```

H	3.899442	-1.200677	1.142435
H	2.184420	1.560909	0.191239
H	4.582804	-0.227619	-0.532482
H	0.129029	1.229430	-1.186244
C	-2.344459	0.339566	-0.206076
H	-0.658245	-0.998971	-0.336840
H	-0.896735	-0.311567	1.263393
C	-3.387393	-0.743737	0.087207
H	-2.616198	1.263382	0.324126
H	-2.364819	0.587283	-1.276977
H	-4.393097	-0.421901	-0.206405
H	-3.161708	-1.669137	-0.457081
H	-3.414968	-0.988433	1.156250

Hexene AM Product anti twisted

B3LYP/6-31G*
E(RB3LYP) = -262.511949830

Zero-point correction= 0.199889 (Hartree/Particle)
Thermal correction to Energy= 0.209922
Thermal correction to Enthalpy= 0.210867
Thermal correction to Gibbs Free Energy= 0.164608
Sum of electronic and ZPE= -262.312061
Sum of electronic and thermal Energies= -262.302027
Sum of electronic and thermal Enthalpies= -262.301083
Sum of electronic and thermal Free Energies= -262.347342

	E KCal/Mol	CV Cal/Mol-K	S Cal/Mol-K
Total	131.728	35.056	97.359

```
C,0,-0.5958185086,-0.4798390738,-1.774306171
C,0,-0.6595561644,0.2616536888,-0.4283145967
C,0,0.6599679712,0.2845761226,0.3632029525
B,0,0.6588384715,0.9410260896,1.7777157894
H,0,-1.536419398,-0.3073258348,-2.3169533547
C,0,-0.3631031768,-1.9926872805,-1.6630879433
H,0,-1.447818579,-0.1825840822,0.1959961891
H,0,1.4839429931,0.6731126471,-0.2557542515
H,0,0.9837637544,-0.7525079866,0.5928023557
H,0,-0.3599580273,1.1352435666,2.3807071355
H,0,-0.975830079,1.2968906949,-0.6152266834
H,0,1.6945143399,1.2098936387,2.3182949174
```

```
H,0,0.1973039275,-0.0355671406,-2.394811239
C,0,-0.3603430716,-2.708395219,-3.0204949444
H,0,0.5923598084,-2.1901091893,-1.1563298898
H,0,-1.1434569783,-2.4326539588,-1.02343612
C,0,-0.1286733767,-4.2186692474,-2.9082352204
H,0,-1.3164742901,-2.5212153116,-3.5297464239
H,0,0.415815372,-2.2654889715,-3.6608665979
H,0,-0.1337578417,-4.6993377063,-3.8932539147
H,0,0.8370124367,-4.43792289,-2.4359678231
H,0,-0.9082965831,-4.6953955557,-2.3011921658
```

Hexene M Product out

B3LYP/6-31G*
E(RB3LYP) = -262.510287083

```
Zero-point correction= 0.200137 (Hartree/Particle)
Thermal correction to Energy= 0.210209
Thermal correction to Enthalpy= 0.211153
Thermal correction to Gibbs Free Energy= 0.165402
Sum of electronic and ZPE= -262.310150
Sum of electronic and thermal Energies= -262.300078
Sum of electronic and thermal Enthalpies= -262.299134
Sum of electronic and thermal Free Energies= -262.344885
```

```
     E      CV        S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 131.908 35.437 96.291
```

```
C,0,-0.2083390633,0.1546515203,-1.3511170921
C,0,-0.3012414715,0.102711348,0.1840642456
C,0,1.0328123194,0.5761826616,0.8397054425
B,0,-0.5196955154,-1.3192375278,0.8013955981
C,0,-1.5194912198,-0.2240813681,-2.0528109537
H,0,0.0916226352,1.1646543063,-1.6713133369
H,0,-1.0811713702,0.8023986626,0.5201827773
H,0,1.2797584777,1.5868922655,0.49165452
H,0,0.9699814107,0.6081105954,1.933480264
H,0,-0.0867979725,-2.2955037593,0.2533826973
H,0,1.8721677989,-0.0759742184,0.5681195291
H,0,-1.0330827828,-1.4554918937,1.8759653252
H,0,0.5900855405,-0.5233698973,-1.6874813364
C,0,-1.4399762616,-0.1589150074,-3.5831638505
H,0,-1.8139154348,-1.2415851788,-1.7511503322
```

H,0,-2.3242783454,0.4403717536,-1.7033640955
C,0,-2.7538757899,-0.5371512252,-4.2744940108
H,0,-1.1455960385,0.8561935796,-3.8858749916
H,0,-0.6374085055,-0.8242762111,-3.9318577953
H,0,-2.6636965385,-0.479937124,-5.3652892675
H,0,-3.0562316842,-1.5602193902,-4.0186991054
H,0,-3.5682871883,0.1328091086,-3.9720682311

Hexene M Product anti

B3LYP/6-31G*
E(RB3LYP) = -262.508738171

Zero-point correction= 0.200076 (Hartree/Particle)
Thermal correction to Energy= 0.210248
Thermal correction to Enthalpy= 0.211192
Thermal correction to Gibbs Free Energy= 0.165011
Sum of electronic and ZPE= -262.308662
Sum of electronic and thermal Energies= -262.298490
Sum of electronic and thermal Enthalpies= -262.297546
Sum of electronic and thermal Free Energies= -262.343727

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	131.932	35.530	97.195

C,0,-0.3490356871,0.3070417162,-1.3802250331
C,0,-0.3428622786,0.0450423044,0.141141667
C,0,0.990450478,0.4962023586,0.8157680754
B,0,-0.4504170363,-1.4619403894,0.5502331173
H,0,-1.2471369925,-0.1546230037,-1.8164302154
C,0,-0.3229573221,1.7868712206,-1.7902870388
H,0,-1.1466160856,0.6323070639,0.6107788239
H,0,1.854924673,-0.0210334887,0.3810043675
H,0,1.1488591691,1.5717009235,0.680274076
H,0,-0.0003925783,-2.3232557755,-0.1538516323
H,0,0.9900745764,0.3024810616,1.8950181049
H,0,-0.9056291997,-1.7800503635,1.6126598468
H,0,0.5044834132,-0.2158585055,-1.8369039988
C,0,-0.4160163316,1.9951689244,-3.307943572
H,0,-1.1571263731,2.3131599385,-1.3016503882
H,0,0.5953513673,2.2656905412,-1.422930833
C,0,-0.3904144159,3.4709596896,-3.7188718693
H,0,0.4130838986,1.4643926145,-3.7973590269

H,0,-1.3377571143,1.5267627418,-3.6816658644
H,0,-0.4589778612,3.5853529712,-4.8067836394
H,0,-1.2280401852,4.0212682659,-3.2726601562
H,0,0.536217886,3.9580301905,-3.3906728111

Octene

B3LYP/6-31G*
E(RB3LYP) = -314.476138238

Zero-point correction= 0.223511 (Hartree/Particle)
Thermal correction to Energy= 0.234065
Thermal correction to Enthalpy= 0.235009
Thermal correction to Gibbs Free Energy= 0.186900
Sum of electronic and ZPE= -314.252627
Sum of electronic and thermal Energies= -314.242073
Sum of electronic and thermal Enthalpies= -314.241129
Sum of electronic and thermal Free Energies= -314.289238

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 146.878 36.963 101.254
```

C,0,-0.2944469466,-0.6765622381,-1.491431893
C,0,-0.3056153614,-0.6697562418,0.0129584671
C,0,0.604107414,-0.0800169584,0.7894616744
C,0,-1.5400923394,-0.0094626394,-2.1057967252
H,0,-0.2421865316,-1.7162575503,-1.8509763859
H,0,-1.1454758668,-1.1864496258,0.4822040688
H,0,1.4574555639,0.4488285237,0.3686831862
H,0,0.5359193032,-0.1042462522,1.8739422744
H,0,0.6117045356,-0.1747429152,-1.8563820327
C,0,-1.5564584304,-0.055120728,-3.6388726931
H,0,-2.4437269788,-0.5013038439,-1.7166492928
H,0,-1.5908342811,1.0341141067,-1.7657926863
C,0,-2.7931916104,0.6090883697,-4.257322392
H,0,-0.6500563129,0.4334837509,-4.0263645712
H,0,-1.5016776407,-1.1025467839,-3.9714649366
C,0,-2.81105702,0.5650765883,-5.7907868054
H,0,-3.700183139,0.120665506,-3.870579331
H,0,-2.8482639111,1.6563491407,-3.9245079072
C,0,-4.0491753901,1.2305243092,-6.4003780249
H,0,-1.9051526147,1.0535511983,-6.1772445535
H,0,-2.756591726,-0.4813728185,-6.1234058644

```
H,0,-4.0320162776,1.1825466171,-7.4952384491
H,0,-4.9702634765,0.7413576081,-6.0599997636
H,0,-4.1123409616,2.287732877,-6.114296363
```

Octene AM Complex out

```
B3LYP/6-31G*
E(RB3LYP) = -341.108029610

Zero-point correction= 0.255697 (Hartree/Particle)
Thermal correction to Energy= 0.268292
Thermal correction to Enthalpy= 0.269236
Thermal correction to Gibbs Free Energy= 0.216499
Sum of electronic and ZPE= -340.852332
Sum of electronic and thermal Energies= -340.839738
Sum of electronic and thermal Enthalpies= -340.838793
Sum of electronic and thermal Free Energies= -340.891530

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 168.356 45.173 110.994
```

```
C,0,-0.3409097785,-0.3812106956,-1.4251300466
C,0,-0.3585485866,-0.4184004183,0.0834555439
C,0,0.7886958276,-0.3954388892,0.8618713693
B,0,0.0665631672,1.2660711219,0.9040796019
C,0,-1.6110366806,0.1672945919,-2.0872565176
H,0,-0.1853378487,-1.4210827529,-1.7544090817
H,0,-1.2845138664,-0.7574602848,0.5442185545
H,0,1.7619526508,-0.330714643,0.3860510858
H,0,0.777625841,-0.7984774774,1.8677768938
H,0,-0.1554423529,1.4137873715,2.0737462652
H,0,-1.0057114752,1.3987587391,0.3351227293
H,0,0.8747560516,1.9302727214,0.3152348041
H,0,0.5402376212,0.1804571039,-1.759791316
C,0,-1.5749208737,0.0694434731,-3.6177683542
H,0,-2.4854267829,-0.3816221236,-1.7074962811
H,0,-1.7499206011,1.2138736425,-1.7883593025
C,0,-2.836921708,0.6232236657,-4.2914027179
H,0,-0.6949710618,0.6111090587,-3.9950098508
H,0,-1.4357205043,-0.9808768815,-3.9147927319
C,0,-2.8049819447,0.5290541861,-5.8223662353
H,0,-3.7179639544,0.0832052529,-3.9135619419
H,0,-2.9753181947,1.6735660651,-3.9955000807
```

```
C,0,-4.0685032286,1.0843662361,-6.4877985124
H,0,-1.9249215169,1.0690367031,-6.1996194412
H,0,-2.6665979269,-0.5208181832,-6.1178079998
H,0,-4.0147173002,1.0029173054,-7.579383421
H,0,-4.962307104,0.5412661299,-6.1567628509
H,0,-4.2145848682,2.142768981,-6.2394001642
```

Octene AM Complex anti

B3LYP/6-31G*
E(RB3LYP) = -341.108015153

Zero-point correction= 0.255923 (Hartree/Particle)
Thermal correction to Energy= 0.268573
Thermal correction to Enthalpy= 0.269517
Thermal correction to Gibbs Free Energy= 0.216575
Sum of electronic and ZPE= -340.852092
Sum of electronic and thermal Energies= -340.839443
Sum of electronic and thermal Enthalpies= -340.838498
Sum of electronic and thermal Free Energies= -340.891440

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 168.532 45.194 111.426
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```
C,0,-0.3566475059,-0.3367819557,-1.3734206055
C,0,-0.3856904452,-0.3545344416,0.1344353966
C,0,0.7448659225,-0.2909276199,0.9210986852
B,0,-0.0363657235,1.3973606109,0.9040910086
H,0,-1.2444589609,0.179334202,-1.7570719124
C,0,-0.3042243709,-1.7670927061,-1.9472984608
H,0,-1.3127220712,-0.6910680485,0.5940216725
H,0,1.7233956555,-0.1899274025,0.4625681202
H,0,0.7310317917,-0.6379955817,1.9474308494
H,0,-0.2274294613,1.5429474539,2.0797873134
H,0,-1.1048704466,1.5140051539,0.3354447839
H,0,0.795217245,2.0354685941,0.3197455266
H,0,0.5167551809,0.2330317295,-1.7129224248
C,0,-0.3098094324,-1.7883865227,-3.4814123722
H,0,0.5950746026,-2.2755726358,-1.5737746138
H,0,-1.1616107186,-2.3443948935,-1.572051821
C,0,-0.257275322,-3.2041274839,-4.069719448
H,0,-1.2105396212,-1.2746555564,-3.848038899
H,0,0.545411808,-1.2064715934,-3.8551180831
```

C,0,-0.2630495402,-3.228992517,-5.6037548106
H,0,0.6435980898,-3.7178898098,-3.7024213577
H,0,-1.1124197064,-3.786073842,-3.6947624751
C,0,-0.2105682513,-4.6455774515,-6.1845552416
H,0,-1.1633544722,-2.7156945803,-5.9703356117
H,0,0.5914464358,-2.6475274889,-5.9780886283
H,0,-0.216096325,-4.6290884675,-7.2803140187
H,0,0.6967462282,-5.1723663163,-5.8640762983
H,0,-1.0713415852,-5.2411198294,-5.8561732737

Octene M Complex out

B3LYP/6-31G*
E(RB3LYP) = -341.108030745

Zero-point correction= 0.255712 (Hartree/Particle)
Thermal correction to Energy= 0.268300
Thermal correction to Enthalpy= 0.269244
Thermal correction to Gibbs Free Energy= 0.216529
Sum of electronic and ZPE= -340.852319
Sum of electronic and thermal Energies= -340.839731
Sum of electronic and thermal Enthalpies= -340.838786
Sum of electronic and thermal Free Energies= -340.891502

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 168.361 45.174 110.948

C,0,-0.3951456916,0.3196005674,-1.4253373012
C,0,-0.2788673509,0.3972254441,0.0772945911
C,0,0.9315638366,0.3843006791,0.7520157135
B,0,0.2048318284,-1.2734058948,0.8998985561
C,0,-1.7215931493,-0.2370824992,-1.957543293
H,0,-0.2645582607,1.3492223908,-1.795228646
H,0,-1.1588391855,0.7546353888,0.6088635136
H,0,1.8591108769,0.2969357145,0.1954078276
H,0,1.0115770322,0.8104657749,1.7451649376
H,0,0.9551212682,-1.9559449827,0.2578037172
H,0,0.0943954061,-1.3877269028,2.089075696
H,0,-0.9158871068,-1.4137802499,0.4374682036
H,0,0.4501917268,-0.2569800247,-1.8213536557
C,0,-1.8208733701,-0.1789779928,-3.4873626712
H,0,-1.8382035928,-1.2745477954,-1.6200772831
H,0,-2.5562839966,0.3275844361,-1.5165115781

C,0,-3.1401918559,-0.741108003,-4.0317980733
H,0,-1.7036458099,0.8623673831,-3.8229965039
H,0,-0.9803626115,-0.7363811333,-3.9265424885
C,0,-3.2438888313,-0.6868452123,-5.5614425416
H,0,-3.2567100427,-1.7824636333,-3.6971368932
H,0,-3.9817021097,-0.1853301614,-3.5917293639
C,0,-4.5640228729,-1.2502761775,-6.0972228751
H,0,-3.1273862827,0.3540481836,-5.8956263492
H,0,-2.4033649802,-1.2426312919,-6.0008394489
H,0,-4.6071960485,-1.1974776005,-7.1910568033
H,0,-4.6925092793,-2.3008907202,-5.8091016724
H,0,-5.4224305467,-0.6926406867,-5.7026803144

Octene M Complex anti

B3LYP/6-31G*
E(RB3LYP) = -341.108015150

Zero-point correction= 0.255923 (Hartree/Particle)
Thermal correction to Energy= 0.268573
Thermal correction to Enthalpy= 0.269517
Thermal correction to Gibbs Free Energy= 0.216575
Sum of electronic and ZPE= -340.852092
Sum of electronic and thermal Energies= -340.839443
Sum of electronic and thermal Enthalpies= -340.838498
Sum of electronic and thermal Free Energies= -340.891440

```
    E      CV        S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 168.532 45.194 111.426
```

C,0,-0.2705948779,0.2737625512,-1.3755712887
C,0,-0.4323880307,0.3313072471,0.1228610255
C,0,0.626123313,0.4054302527,1.0032612553
B,0,0.020274724,-1.3533928962,0.9833261989
H,0,-1.066189395,-0.3407244636,-1.8128455563
C,0,-0.3102366512,1.6850932439,-1.9956086568
H,0,-1.4246340874,0.5847063683,0.4904185626
H,0,1.6460284862,0.3915291509,0.6323539839
H,0,0.4887251403,0.7783094698,2.0112732935
H,0,-0.9780094836,-1.5942071611,0.3320913166
H,0,0.9585165899,-1.9199158214,0.4945309684
H,0,-0.256879014,-1.4842504933,2.1435112662
H,0,0.6811321607,-0.2136170587,-1.619409313

C,0,-0.1843516235,1.6621043955,-3.524534846
H,0,-1.2499402676,2.182565101,-1.7151125875
H,0,0.4983821092,2.2928683922,-1.5671747761
C,0,-0.2211857561,3.0585476307,-4.1583934965
H,0,0.7535284225,1.1598698865,-3.8035074745
H,0,-0.994469343,1.0491574123,-3.9460257969
C,0,-0.0958498075,3.0390926158,-5.6873894483
H,0,-1.1591013436,3.5608570543,-3.8781689766
H,0,0.589012871,3.671559221,-3.7362235738
C,0,-0.1334736869,4.4365831004,-6.3138089252
H,0,0.8413212849,2.5372138255,-5.9670655553
H,0,-0.9055931303,2.4266207658,-6.1088146071
H,0,-0.0419483314,4.388485039,-7.4048173441
H,0,-1.0742608844,4.9505156964,-6.0809380901
H,0,0.6858956125,5.061873474,-5.938204558

Octene AMTS out

B3LYP/6-31G*
E(RB3LYP) = -341.107994089

Zero-point correction= 0.255429 (Hartree/Particle)
Thermal correction to Energy= 0.267303
Thermal correction to Enthalpy= 0.268247
Thermal correction to Gibbs Free Energy= 0.217014
Sum of electronic and ZPE= -340.852565
Sum of electronic and thermal Energies= -340.840691
Sum of electronic and thermal Enthalpies= -340.839747
Sum of electronic and thermal Free Energies= -340.890980

```
      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 167.735 43.083 107.829
```

C,0,-0.3512903699,-0.387725426,-1.4485208456
C,0,-0.3679076734,-0.419227746,0.0611131546
C,0,0.793237393,-0.4286266476,0.8366208399
B,0,0.1142680129,1.205314321,0.9049429316
C,0,-1.6158583271,0.1731952852,-2.1104809191
H,0,-0.20553011,-1.4299724384,-1.7737904679
H,0,-1.2920216098,-0.765726556,0.5204412899
H,0,1.7602021454,-0.4015527575,0.3441986887
H,0,0.7799761102,-0.8713786534,1.8259852474
H,0,-0.1681440054,1.371559564,2.0583020445

H,0,-0.9515747856,1.3145023461,0.3021134494
H,0,0.8974571647,1.89707968,0.3150010832
H,0,0.5352986228,0.1645069845,-1.7845617904
C,0,-1.5803384631,0.079230608,-3.6412825395
H,0,-2.495668244,-0.3681347202,-1.7324029876
H,0,-1.7454766089,1.2209139254,-1.8097282574
C,0,-2.8368974084,0.6464508166,-4.3138075025
H,0,-0.6951626008,0.6135322577,-4.0167308329
H,0,-1.4509219441,-0.9716195843,-3.940680179
C,0,-2.8057018068,0.5554147262,-5.8448950681
H,0,-3.7231032973,0.1140062048,-3.9372103431
H,0,-2.9653783399,1.6974500371,-4.0155768246
C,0,-4.0636431566,1.1243979858,-6.5089825897
H,0,-1.9203935625,1.0877082779,-6.2208449803
H,0,-2.6774684476,-0.4951101552,-6.1426294457
H,0,-4.0107545413,1.0448618366,-7.6007514157
H,0,-4.962786023,0.5893602272,-6.1791991121
H,0,-4.1995351234,2.1836626004,-6.258360628

Octene AMTS anti

B3LYP/6-31G*
E(RB3LYP) = -341.107694481

Zero-point correction= 0.255659 (Hartree/Particle)
Thermal correction to Energy= 0.267511
Thermal correction to Enthalpy= 0.268455
Thermal correction to Gibbs Free Energy= 0.217265
Sum of electronic and ZPE= -340.852036
Sum of electronic and thermal Energies= -340.840183
Sum of electronic and thermal Enthalpies= -340.839239
Sum of electronic and thermal Free Energies= -340.890429

```
      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 167.866 42.939 107.739
```

C,0,-0.3784836878,-0.3222277427,-1.3830329686
C,0,-0.4059888601,-0.3142552621,0.1279726239
C,0,0.7579666393,-0.3181332336,0.9078947119
B,0,0.0799296256,1.3023949207,0.9495059306
H,0,-1.27450292,0.1713115836,-1.7787915557
C,0,-0.297048037,-1.7602093839,-1.9303017329
H,0,-1.3276115215,-0.6656854555,0.5880619995

H,0,1.72363377,-0.3074001751,0.4117059485
H,0,0.7435090452,-0.7545891355,1.9001385443
H,0,-0.2454979947,1.4939464107,2.0869763593
H,0,-0.9744640575,1.3701843699,0.3118269038
H,0,0.8512575119,2.0023729674,0.3553846982
H,0,0.485791929,0.2576284002,-1.7291464697
C,0,-0.2932274918,-1.8102567391,-3.4639147764
H,0,0.6088617712,-2.2454546294,-1.5426618984
H,0,-1.1460542549,-2.3461380553,-1.5492173425
C,0,-0.2116674206,-3.2356559103,-4.0246471993
H,0,-1.2006844467,-1.3198722496,-3.8457912408
H,0,0.5537093904,-1.2201256904,-3.8436042104
C,0,-0.2071347126,-3.2900185523,-5.5578315183
H,0,0.6957858921,-3.7260570451,-3.64192059
H,0,-1.0585267349,-3.8257808161,-3.643638515
C,0,-0.1256280161,-4.7164671169,-6.1107556815
H,0,-1.1140138869,-2.8000831964,-5.9399336793
H,0,0.6391934996,-2.7005885384,-5.938245771
H,0,-0.1244650222,-4.7212797535,-7.2066353538
H,0,0.7888937995,-5.2205132195,-5.7745917682
H,0,-0.9776778083,-5.3209427518,-5.7760014481

Octene MTS out

B3LYP/6-31G*
E(RB3LYP) = -341.104247031

Zero-point correction= 0.255715 (Hartree/Particle)
Thermal correction to Energy= 0.267478
Thermal correction to Enthalpy= 0.268422
Thermal correction to Gibbs Free Energy= 0.217555
Sum of electronic and ZPE= -340.848532
Sum of electronic and thermal Energies= -340.836769
Sum of electronic and thermal Enthalpies= -340.835825
Sum of electronic and thermal Free Energies= -340.886692

```
    E      CV        S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 167.845 42.801 107.059
```

C,0,-0.3290877325,0.369830234,-1.4432260285
C,0,-0.3319898216,0.378544129,0.0761102862
C,0,0.85489748,0.4227702606,0.8301813984
B,0,-0.0540801004,-1.1661802418,0.8497603872

C,0,-1.5754560679,-0.2772433945,-2.0604422299
H,0,-0.2560393556,1.4103993075,-1.7973045905
H,0,-1.2097020171,0.830791902,0.5326862197
H,0,1.8202995162,0.3455225213,0.3365979204
H,0,0.8753461427,0.8784667079,1.8153971036
H,0,0.1606027784,-1.9513877508,-0.0278364057
H,0,1.0110140545,-1.1518547676,1.491151981
H,0,-0.9007473077,-1.3141217567,1.6822057626
H,0,0.5717548257,-0.1447284791,-1.8026688724
C,0,-1.5832092627,-0.230908316,-3.5935332558
H,0,-1.6423459229,-1.3184587685,-1.7198840786
H,0,-2.4733781665,0.2299880871,-1.6770535685
C,0,-2.8293915245,-0.8727876299,-4.2166025086
H,0,-1.507534922,0.8144590218,-3.9291401104
H,0,-0.6848736053,-0.7378988415,-3.9764922623
C,0,-2.8393777494,-0.8321802105,-5.7501280353
H,0,-2.9057601619,-1.9177294157,-3.8812057991
H,0,-3.7286492805,-0.3662028983,-3.8351526051
C,0,-4.0874889379,-1.4749331625,-6.3636916137
H,0,-2.7629696489,0.2121848063,-6.0852376161
H,0,-1.9415054026,-1.3393521705,-6.131243984
H,0,-4.0644938824,-1.4304485806,-7.4586171087
H,0,-4.1725891094,-2.5298249062,-6.0748821018
H,0,-5.0003708177,-0.966922687,-6.0288082839

Octene MTS anti

B3LYP/6-31G*
E(RB3LYP) = -341.104376064

Zero-point correction= 0.255688 (Hartree/Particle)
Thermal correction to Energy= 0.267494
Thermal correction to Enthalpy= 0.268438
Thermal correction to Gibbs Free Energy= 0.217426
Sum of electronic and ZPE= -340.848689
Sum of electronic and thermal Energies= -340.836883
Sum of electronic and thermal Enthalpies= -340.835938
Sum of electronic and thermal Free Energies= -340.886950

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 167.855 42.813 107.362

C,0,-0.3569607338,0.311338275,-1.3750662513

```
C,0,-0.3603695449,0.2978089387,0.143492401
C,0,0.8314625812,0.3079653877,0.8931704089
B,0,-0.1165406903,-1.2598004332,0.8904718877
H,0,-1.2244695983,-0.2493993313,-1.7460327907
C,0,-0.3848185497,1.7359451694,-1.9546777688
H,0,-1.2254389791,0.7658522764,0.6078865121
H,0,1.7922619312,0.2180269146,0.3924128769
H,0,0.8673570938,0.7463132743,1.8858017645
H,0,0.0729133603,-2.0363532867,-0.0002971088
H,0,0.9553060105,-1.2765685646,1.5228873667
H,0,-0.9586520714,-1.3980340216,1.7291934848
H,0,0.529849028,-0.2221502687,-1.7416766654
C,0,-0.422092335,1.7628977356,-3.4880777163
H,0,-1.2607079464,2.2721114228,-1.5603142763
H,0,0.4955788557,2.2905940915,-1.5983012661
C,0,-0.4522428327,3.179927265,-4.0747310939
H,0,0.4529581972,1.2248896469,-3.88218437
H,0,-1.3030342733,1.2051856057,-3.8388677441
C,0,-0.4895671063,3.2082547874,-5.6081308313
H,0,-1.3276773611,3.7179653598,-3.6812021023
H,0,0.4286162186,3.7382168605,-3.7236493394
C,0,-0.5190912167,4.6269195482,-6.1859159873
H,0,0.3850738156,2.6707049467,-6.0013824958
H,0,-1.3701823033,2.6514608562,-5.9588592878
H,0,-0.5456115936,4.6129570555,-7.2814984876
H,0,-1.4016221493,5.178262203,-5.8385204518
H,0,0.3670641931,5.197596285,-5.8815636674
```

Octene AM Product out

B3LYP/6-31G*
E(RB3LYP) = -341.138930733

```
Zero-point correction= 0.257623 (Hartree/Particle)
Thermal correction to Energy= 0.270562
Thermal correction to Enthalpy= 0.271506
Thermal correction to Gibbs Free Energy= 0.217411
Sum of electronic and ZPE= -340.881308
Sum of electronic and thermal Energies= -340.868369
Sum of electronic and thermal Enthalpies= -340.867424
Sum of electronic and thermal Free Energies= -340.921520

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

Total 169.780 44.529 113.853

```
C,0,-0.5094610366,-0.4410400137,-1.4878382397
C,0,-0.4500974142,0.3450507738,-0.1690198529
C,0,0.8545437694,0.0667762275,0.6388854791
B,0,0.7825635035,0.923983226,1.9455962377
C,0,-1.7870733145,-0.1788174961,-2.2955320062
H,0,-0.4277120285,-1.5155417896,-1.2690371628
H,0,-1.3282554294,0.0886385653,0.4401369734
H,0,1.7108498375,0.3316373308,0.0044883707
H,0,0.9063414463,-1.011316786,0.8411200324
H,0,0.2525979468,0.5000934793,2.9344194007
H,0,-0.5312794576,1.4189014949,-0.3886384091
H,0,1.183191055,2.0542020924,1.966138203
H,0,0.3691266302,-0.1855135759,-2.0976753361
C,0,-1.8478264691,-0.963355773,-3.613190513
H,0,-2.6641578147,-0.4323708827,-1.6817892623
H,0,-1.867619649,0.8971526658,-2.5101176828
C,0,-3.1248862905,-0.7026938022,-4.4228576289
H,0,-0.970758021,-0.7100975008,-4.2270554906
H,0,-1.7671392058,-2.0393593988,-3.3988898512
C,0,-3.1864408459,-1.4865471823,-5.7401881958
H,0,-4.0023938798,-0.9560611413,-3.8094257694
H,0,-3.2059426878,0.3733179641,-4.6376639763
C,0,-4.464313684,-1.2210335588,-6.5428499192
H,0,-2.3098823855,-1.2331634283,-6.3532927416
H,0,-3.1058150007,-2.5616769323,-5.525593834
H,0,-4.4775145215,-1.7948766618,-7.4766018619
H,0,-5.3573495458,-1.4977985949,-5.9689565958
H,0,-4.555365507,-0.1591843013,-6.8029483673
```

Octene AM Product out twisted

B3LYP/6-31G*
E(RB3LYP) = -341.140605183

Zero-point correction= 0.256842 (Hartree/Particle)
Thermal correction to Energy= 0.269736
Thermal correction to Enthalpy= 0.270680
Thermal correction to Gibbs Free Energy= 0.216853
Sum of electronic and ZPE= -340.883763
Sum of electronic and thermal Energies= -340.870870
Sum of electronic and thermal Enthalpies= -340.869925
Sum of electronic and thermal Free Energies= -340.923752

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 169.262 44.822 113.287

C,0,-0.5367399874,-0.3764195518,-1.5040037653
C,0,-0.5026029357,0.4011592371,-0.181986384
C,0,0.7890651419,0.1958810755,0.62601815
B,0,0.889425501,0.8409814137,2.0433927936
C,0,-1.8226661329,-0.1610118848,-2.3121566627
H,0,-0.4133656829,-1.4500550262,-1.2949589176
H,0,-1.3653901595,0.1120079621,0.434618138
H,0,1.6755937453,0.4516471372,0.0234319921
H,0,0.933431302,-0.8864277459,0.8287981873
H,0,-0.0725173607,1.280353937,2.6097524124
H,0,-0.6323324125,1.4727594787,-0.3913103621
H,0,1.9413504887,0.8628727881,2.6181303059
H,0,0.3307066697,-0.0876127729,-2.1166370346
C,0,-1.8557685788,-0.9401798716,-3.6334155976
H,0,-2.6892996302,-0.4496690966,-1.6988217556
H,0,-1.9442874276,0.9124206817,-2.5208450755
C,0,-3.1417266522,-0.7243623842,-4.4414969269
H,0,-0.9891191353,-0.6514077196,-4.2467383852
H,0,-1.7343185758,-2.0136593447,-3.4247740048
C,0,-3.1753501841,-1.5034200292,-5.7626901863
H,0,-4.0090320849,-1.013179425,-3.828952177
H,0,-3.2638008088,0.348954819,-4.6511046084
C,0,-4.4628681822,-1.2820193072,-6.5631250942
H,0,-2.3092751726,-1.2145048546,-6.3751699274
H,0,-3.0542310948,-2.5759100281,-5.5534287994
H,0,-4.4558438353,-1.851262754,-7.4997648754
H,0,-5.3446061369,-1.5946304992,-5.9900732359
H,0,-4.5940116776,-0.2230542345,-6.8180182035

Octene AM Product out gauche

B3LYP/6-31G*
E(RB3LYP) = -341.140367888

Zero-point correction= 0.257128 (Hartree/Particle)
Thermal correction to Energy= 0.269798
Thermal correction to Enthalpy= 0.270742
Thermal correction to Gibbs Free Energy= 0.217620
Sum of electronic and ZPE= -340.883240

Sum of electronic and thermal Energies= -340.870570
Sum of electronic and thermal Enthalpies= -340.869626
Sum of electronic and thermal Free Energies= -340.922748

```
     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 169.301 44.659 111.806
```

```
C,0,-0.1235532101,-0.0436638207,-0.9869425958
C,0,-0.3483469887,-0.5036301268,0.4596861497
C,0,0.8890071433,-0.2945842634,1.3486894709
B,0,1.2980607396,1.1658059138,1.7148251698
C,0,-1.3447281016,-0.2427829508,-1.8930961216
H,0,0.7356637748,-0.5861069506,-1.4098692978
H,0,-0.6397083741,-1.5638067763,0.4564976352
H,0,1.7460296989,-0.8746335166,0.9742381093
H,0,0.7037257899,-0.7314270051,2.3535156809
H,0,0.5212249535,2.0756146129,1.6211256653
H,0,-1.1984556619,0.0483735657,0.8846839851
H,0,2.3818451814,1.3950304202,2.1728442733
H,0,0.1594464663,1.0203044186,-0.9871551926
C,0,-1.1176614671,0.216052675,-3.3394144897
H,0,-1.628584949,-1.3058136506,-1.8897846181
H,0,-2.202385476,0.3009539815,-1.4698991253
C,0,-2.3390459466,0.015718268,-4.2456931986
H,0,-0.8341208128,1.2791292963,-3.3425431453
H,0,-0.2593091309,-0.3273269777,-3.7620375674
C,0,-2.112826493,0.4744971238,-5.6920448991
H,0,-2.623140631,-1.0473711897,-4.24349785
H,0,-3.197962688,0.5590002391,-3.823897531
C,0,-3.3373555261,0.270586749,-6.5900222342
H,0,-1.8298930501,1.5368455345,-5.6945184607
H,0,-1.2550166857,-0.0685629354,-6.1138693455
H,0,-3.1437761432,0.6075085266,-7.6149042422
H,0,-3.6235927868,-0.7875063564,-6.6357921164
H,0,-4.202654625,0.8300551951,-6.2134291081
```

Octene AM Product anti

B3LYP/6-31G*
E(RB3LYP) = -341.137655648

Zero-point correction= 0.257706 (Hartree/Particle)
Thermal correction to Energy= 0.270637

Thermal correction to Enthalpy= 0.271582
Thermal correction to Gibbs Free Energy= 0.216764
Sum of electronic and ZPE= -340.879950
Sum of electronic and thermal Energies= -340.867018
Sum of electronic and thermal Enthalpies= -340.866074
Sum of electronic and thermal Free Energies= -340.920891

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	169.827	44.433	115.372

C	1.462429	1.071545	-0.062977
C	2.859198	0.575832	0.355094
C	3.353009	-0.671785	-0.440354
B	4.813850	-0.978387	0.028408
H	1.261185	2.015325	0.464532
C	0.318160	0.091198	0.223523
H	2.854168	0.347534	1.429883
H	3.282677	-0.450204	-1.513375
H	2.676721	-1.509370	-0.224665
H	5.010536	-1.545213	1.067164
H	3.569912	1.402969	0.220505
H	5.767534	-0.596260	-0.589796
H	1.474067	1.317175	-1.134850
C	-1.063148	0.655495	-0.135881
H	0.477851	-0.842895	-0.332197
H	0.333193	-0.180969	1.289767
C	-2.215136	-0.317750	0.144990
H	-1.231380	1.588048	0.423160
H	-1.075178	0.934432	-1.200135
C	-3.596225	0.246405	-0.212748
H	-2.048772	-1.250035	-0.415327
H	-2.203291	-0.598160	1.208957
C	-4.741071	-0.731430	0.071045
H	-3.762744	1.177587	0.347444
H	-3.608477	0.525953	-1.275929
H	-5.712608	-0.299299	-0.194809
H	-4.621245	-1.659221	-0.502006
H	-4.776695	-1.002527	1.133486

Octene AM Product twisted

B3LYP/6-31G*
E(RB3LYP) = -341.139382863

```
Zero-point correction= 0.257084 (Hartree/Particle)
Thermal correction to Energy= 0.269822
Thermal correction to Enthalpy= 0.270766
Thermal correction to Gibbs Free Energy= 0.217280
Sum of electronic and ZPE= -340.882299
Sum of electronic and thermal Energies= -340.869561
Sum of electronic and thermal Enthalpies= -340.868617
Sum of electronic and thermal Free Energies= -340.922103

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 169.316 44.715 112.571
```

```
C,0,-0.606685888,-0.4058003521,-1.7308458184
C,0,-0.648780993,0.3240555412,-0.3776677028
C,0,0.6782835541,0.3240944427,0.4015611768
B,0,0.6980722545,0.9677184303,1.8218155361
H,0,-1.5499889943,-0.2166769814,-2.2631099367
C,0,-0.3918140954,-1.9225552797,-1.6352241151
H,0,-1.4364273406,-0.1163275541,0.2501431881
H,0,1.5010457988,0.7085263802,-0.2215665031
H,0,0.9917929407,-0.7188044333,0.6187067443
H,0,-0.3127541756,1.168591469,2.4359219774
H,0,-0.9542964275,1.36467409,-0.5522691282
H,0,1.7418487423,1.219486113,2.3550168187
H,0,0.1861425632,0.0342723296,-2.3546431128
C,0,-0.4102132808,-2.6253171055,-2.9992977141
H,0,0.565440384,-2.1354324878,-1.1385103966
H,0,-1.1719189965,-2.3576189819,-0.9921816433
C,0,-0.1972624478,-4.1419639116,-2.9121588596
H,0,-1.3688505422,-2.4214342706,-3.4992634607
H,0,0.3661373063,-2.1863401191,-3.6436488364
C,0,-0.2179739287,-4.8445240536,-4.2758437071
H,0,0.7624698666,-4.3467919528,-2.4142553713
H,0,-0.9725136091,-4.5817269037,-2.2668285698
C,0,-0.0043040711,-6.3586232263,-4.179829267
H,0,-1.1771646907,-4.6409913851,-4.773002044
H,0,0.5567177996,-4.4056005241,-4.9207206729
H,0,-0.024638564,-6.8300732478,-5.1691078565
H,0,0.9628622992,-6.5940801277,-3.7185951518
H,0,-0.7841014639,-6.8311238979,-3.5697225733
```

Octene M Product out

B3LYP/6-31G*
E(RB3LYP) = -341.137723334

Zero-point correction= 0.257330 (Hartree/Particle)
Thermal correction to Energy= 0.270109
Thermal correction to Enthalpy= 0.271054
Thermal correction to Gibbs Free Energy= 0.218096
Sum of electronic and ZPE= -340.880393
Sum of electronic and thermal Energies= -340.867614
Sum of electronic and thermal Enthalpies= -340.866670
Sum of electronic and thermal Free Energies= -340.919627

```
    E      CV        S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 169.496 45.096 111.458
```

```
C,0,-0.1744725895,0.1627135332,-1.2883983245
C,0,-0.2666550058,0.1088842488,0.2467799586
C,0,1.0675596567,0.5818383666,0.9024752067
B,0,-0.4846452422,-1.3138886633,0.8623009417
C,0,-1.486273358,-0.2155215174,-1.9895821594
H,0,0.1251800881,1.1730777632,-1.6076172346
H,0,-1.0466147988,0.8079571983,0.5841359705
H,0,1.3142056224,1.5929935001,0.5555070099
H,0,1.005140221,0.6124530348,1.9963123266
H,0,-0.0520380967,-2.2894474861,0.3127934118
H,0,1.9069336922,-0.0698435197,0.6298004438
H,0,-0.9973551861,-1.4515615512,1.937026336
H,0,0.6238475328,-0.5148009589,-1.6259442669
C,0,-1.4066867303,-0.1501262854,-3.520015068
H,0,-1.7802861456,-1.2327256371,-1.6870660726
H,0,-2.2900143277,0.4492791133,-1.6388925535
C,0,-2.7185497702,-0.527002494,-4.2202212088
H,0,-1.1117657729,0.8654666457,-3.8237390923
H,0,-0.6038289634,-0.8159857999,-3.8698290814
C,0,-2.6384307514,-0.4612878504,-5.7508517601
H,0,-3.0142031615,-1.5425245914,-3.9167209161
H,0,-3.5218669925,0.1389941985,-3.8709321035
C,0,-3.9525208388,-0.8390806384,-6.4421697262
H,0,-2.3435407473,0.5533756545,-6.054464922
H,0,-1.8364335736,-1.1272848947,-6.0999441291
H,0,-3.8624317633,-0.7824857665,-7.5330473239
```

H,0,-4.2556009495,-1.8617567772,-6.1856445886
H,0,-4.766496048,-0.1684858254,-6.1399870739

Octene M Product anti

B3LYP/6-31G*
E(RB3LYP) = -341.136173158

Zero-point correction= 0.257278 (Hartree/Particle)
Thermal correction to Energy= 0.270155
Thermal correction to Enthalpy= 0.271099
Thermal correction to Gibbs Free Energy= 0.217726
Sum of electronic and ZPE= -340.878896
Sum of electronic and thermal Energies= -340.866018
Sum of electronic and thermal Enthalpies= -340.865074
Sum of electronic and thermal Free Energies= -340.918447

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 169.525 45.187 112.333

C,0,-0.3467487331,0.2615548894,-1.3243644087
C,0,-0.3388302568,-0.0012366398,0.1969464776
C,0,0.9960493635,0.4476996943,0.8698707317
B,0,-0.4476542901,-1.5083631388,0.6051812613
H,0,-1.2457820251,-0.1989431,-1.7598082119
C,0,-0.3195475662,1.7418933408,-1.7332300959
H,0,-1.1411797586,0.5868185805,0.6679737197
H,0,1.8591671991,-0.0696206398,0.4325710826
H,0,1.155182906,1.523293973,0.7360101861
H,0,0.0021776216,-2.3694812764,-0.0992904048
H,0,0.9975849002,0.2521830236,1.9488170396
H,0,-0.9036774237,-1.8269690559,1.6671246751
H,0,0.5056844191,-0.2619343451,-1.7823383237
C,0,-0.4098023312,1.9508544512,-3.2509514759
H,0,-1.154340814,2.2671325372,-1.2448436697
H,0,0.5982146748,2.2193060273,-1.3631100573
C,0,-0.3839285064,3.4262300745,-3.6703944274
H,0,0.4206341131,1.42012186,-3.7401512385
H,0,-1.3313747887,1.4825293493,-3.6277900937
C,0,-0.4741300297,3.6352738623,-5.1875679112
H,0,-1.2142407039,3.9579716522,-3.1818151335
H,0,0.5379873417,3.8952503899,-3.2948758683
C,0,-0.4477729356,5.1112585773,-5.5976012397

H,0,0.3558730428,3.1047576381,-5.6757294625
H,0,-1.3953914849,3.1673841134,-5.5630678678
H,0,-0.5135122472,5.2265356974,-6.6856005028
H,0,-1.2866130346,5.6612082609,-5.1532089936
H,0,0.477871348,5.5982312032,-5.2664977866

Dodecene

B3LYP/6-31G*
E(RB3LYP) = -471.730998629

Zero-point correction= 0.337861 (Hartree/Particle)
Thermal correction to Energy= 0.353864
Thermal correction to Enthalpy= 0.354808
Thermal correction to Gibbs Free Energy= 0.292254
Sum of electronic and ZPE= -471.393138
Sum of electronic and thermal Energies= -471.377134
Sum of electronic and thermal Enthalpies= -471.376190
Sum of electronic and thermal Free Energies= -471.438744

```
      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 222.053 56.286 131.656
```

C,0,-0.2212353662,-0.6549953277,-1.35033435
C,0,-0.2516434576,-0.6148043944,0.153264092
C,0,0.6304551222,0.0188570427,0.9270406498
C,0,-1.4779325093,-0.0387646042,-1.994626376
H,0,-0.1341757685,-1.7005002293,-1.6854573824
H,0,-1.0819013589,-1.1454541689,0.6240259376
H,0,1.4732180017,0.5631578704,0.5046377626
H,0,0.5492051904,0.0169602289,2.0108922496
H,0,0.6744638712,-0.1350602897,-1.7157285539
C,0,-1.4738009022,-0.1195872887,-3.5263489717
H,0,-2.3717101621,-0.5479488226,-1.6050011486
H,0,-1.5632121995,1.010304952,-1.6793132173
C,0,-2.7216761982,0.4942713739,-4.1741921499
H,0,-0.5771496023,0.3863130115,-3.9142574974
H,0,-1.3846541184,-1.1722058835,-3.8340972131
C,0,-2.7189201675,0.4146266577,-5.7063842689
H,0,-3.6182475019,-0.0116290806,-3.7859932787
H,0,-2.8103427535,1.5464511357,-3.8654507358
C,0,-3.966544716,1.0286274444,-6.3546451283
H,0,-1.8221301275,0.9203220559,-6.0943941245

H,0,-2.6301242634,-0.6377208791,-6.0149808894
C,0,-3.964171705,0.9491823648,-7.8867912994
H,0,-4.8633165816,0.5230273416,-5.9664357022
H,0,-4.0552160687,2.0809380432,-6.0459573797
C,0,-5.2114136404,1.5631723988,-8.5353916424
H,0,-3.0672840419,1.4547008246,-8.2749470002
H,0,-3.8755388785,-0.1032046516,-8.1954353496
C,0,-5.2095237136,1.4840232841,-10.0674947087
H,0,-6.1089676144,1.0579454859,-8.1480841213
H,0,-5.3006681328,2.6158564072,-8.2275836
C,0,-6.4585382859,2.099416461,-10.706772174
H,0,-4.31325031,1.9894247633,-10.4547258795
H,0,-5.1211108036,0.4322954469,-10.3752936441
H,0,-6.4267422335,2.0271203653,-11.8000024505
H,0,-7.3693992224,1.5917950323,-10.3658332556
H,0,-6.5554517802,3.1606146283,-10.4459091985

Dodecene AM Complex out

B3LYP/6-31G*
E(RB3LYP) = -498.362901587

Zero-point correction= 0.370076 (Hartree/Particle)
Thermal correction to Energy= 0.388111
Thermal correction to Enthalpy= 0.389055
Thermal correction to Gibbs Free Energy= 0.321948
Sum of electronic and ZPE= -497.992825
Sum of electronic and thermal Energies= -497.974790
Sum of electronic and thermal Enthalpies= -497.973846
Sum of electronic and thermal Free Energies= -498.040953

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	243.543	64.490	141.239

C,0,-0.2719020926,-0.4063114042,-1.2985564901
C,0,-0.2876683708,-0.439568139,0.2100920718
C,0,0.858746364,-0.4109829628,0.9874674223
B,0,0.1336974969,1.2561055491,1.0185843254
C,0,-1.5427082241,0.1408981681,-1.9606241639
H,0,-0.1173546387,-1.4470771092,-1.6255368526
H,0,-1.2133914283,-0.7761403567,0.6731366816
H,0,1.8322360632,-0.3435448067,0.5125475318
H,0,0.8484127383,-0.8051910041,1.9968420859

H,0,-0.0719491773,1.4077354696,2.1909003696
H,0,-0.944376829,1.3874801879,0.462481259
H,0,0.9412861922,1.9128369058,0.4206312316
H,0,0.608964143,0.1541240047,-1.6359480427
C,0,-1.5070887038,0.0412768279,-3.4910584783
H,0,-2.4166460893,-0.4079764655,-1.5797573523
H,0,-1.6816854151,1.1876856731,-1.6628451511
C,0,-2.7699136406,0.5936669447,-4.1646393854
H,0,-0.6276783756,0.5832467094,-3.8690642788
H,0,-1.3672197484,-1.00922049,-3.7870810162
C,0,-2.7368478839,0.5004728293,-5.6956331607
H,0,-3.649635292,0.0519362974,-3.7864668601
H,0,-2.9092870945,1.6433288238,-3.8671411504
C,0,-3.9994253921,1.0525083625,-6.3700542751
H,0,-1.8571020077,1.0426696741,-6.0730153057
H,0,-2.5959719216,-0.549497779,-5.9928284999
C,0,-3.9661882685,0.9618407367,-7.9012043738
H,0,-4.8791132767,0.509681126,-5.9932319068
H,0,-4.1407128719,2.1019085099,-6.0715328742
C,0,-5.2283440608,1.5138325183,-8.5761326914
H,0,-3.0864416014,1.5048236229,-8.2777303085
H,0,-3.8245473607,-0.0876716009,-8.1997573094
C,0,-5.1952865362,1.4245364717,-10.107304281
H,0,-6.1087203042,0.9707310028,-8.2008538581
H,0,-5.3708569782,2.5633433779,-8.2778221024
C,0,-6.4594258686,1.9779051959,-10.7730088759
H,0,-4.3162307437,1.9678501266,-10.4824337735
H,0,-5.0535055672,0.3759134429,-10.4056367375
H,0,-6.4046163099,1.8999790348,-11.8649180086
H,0,-7.3521511682,1.4313430927,-10.4445482574
H,0,-6.6093317559,3.0352214318,-10.5217331571

Dodecene AM Complex anti

B3LYP/6-31G*
E(RB3LYP) = -498.362892192

Zero-point correction= 0.370283 (Hartree/Particle)
Thermal correction to Energy= 0.388390
Thermal correction to Enthalpy= 0.389334
Thermal correction to Gibbs Free Energy= 0.321956
Sum of electronic and ZPE= -497.992609
Sum of electronic and thermal Energies= -497.974502
Sum of electronic and thermal Enthalpies= -497.973558

Sum of electronic and thermal Free Energies= -498.040936

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 243.719 64.510 141.810

C,0,-0.3581887032,-0.2426525659,-1.2335044486
C,0,-0.3859305054,-0.2618102855,0.2744025359
C,0,0.7452495612,-0.1966275631,1.0600683607
B,0,-0.0393241439,1.4900526241,1.0458704941
H,0,-1.2466623811,0.2730233495,-1.6161814819
C,0,-0.3051744834,-1.6723735361,-1.8085514134
H,0,-1.311876348,-0.6005896386,0.7345272732
H,0,1.72307314,-0.0931935862,0.6005765467
H,0,0.7332204951,-0.5448699366,2.0860273792
H,0,-0.2295486935,1.6339546034,2.2219192915
H,0,-1.1086390382,1.6052616379,0.4784494923
H,0,0.7903127668,2.1306447213,0.4614608703
H,0,0.5145339717,0.3280272301,-1.5733083631
C,0,-0.3085169652,-1.692167653,-3.3427206969
H,0,0.5935549875,-2.1813237863,-1.4343091565
H,0,-1.1631799907,-2.2498481933,-1.4350056085
C,0,-0.2563612137,-3.1076463356,-3.932048462
H,0,-1.2081496392,-1.1772961908,-3.7103924327
H,0,0.5477760924,-1.1106679683,-3.714557639
C,0,-0.2585649332,-3.1304721153,-5.4661171308
H,0,0.6428968742,-3.6221801005,-3.5622413064
H,0,-1.1130841401,-3.6881019161,-3.558750663
C,0,-0.2076560348,-4.5451627709,-6.0574834986
H,0,-1.1573659496,-2.6146118776,-5.8353591503
H,0,0.598328004,-2.549865191,-5.8388085089
C,0,-0.2095121294,-4.5685357268,-7.5914687783
H,0,0.6909516015,-5.0610973499,-5.6876372299
H,0,-1.0647815455,-5.1254429105,-5.6845418006
C,0,-0.1594484787,-5.982705565,-8.183699854
H,0,-1.1078671228,-4.0519542329,-7.9611075064
H,0,0.6478460987,-3.9884267243,-7.9641999041
C,0,-0.1611847591,-6.0066433511,-9.7176487885
H,0,0.7388790759,-6.5001215576,-7.8147607501
H,0,-1.0169237637,-6.5634351409,-7.8117912299
C,0,-0.1113900864,-7.4224788833,-10.3005995819
H,0,-1.0589079545,-5.4901408402,-10.0863891523
H,0,0.6959596187,-5.427185426,-10.0893647509
H,0,-0.1138286153,-7.4050959789,-11.3964828764

H,0,0.7933385911,-7.9525261925,-9.9779970881
H,0,-0.9747762601,-8.0158950758,-9.9750639919

Dodecene M Complex out

B3LYP/6-31G*
E(RB3LYP) = -498.362901457

Zero-point correction= 0.370068 (Hartree/Particle)
Thermal correction to Energy= 0.388106
Thermal correction to Enthalpy= 0.389050
Thermal correction to Gibbs Free Energy= 0.321930
Sum of electronic and ZPE= -497.992834
Sum of electronic and thermal Energies= -497.974795
Sum of electronic and thermal Enthalpies= -497.973851
Sum of electronic and thermal Free Energies= -498.040971

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 243.540 64.490 141.266

C,0,-0.363469385,0.331430797,-1.3771488312
C,0,-0.2452235386,0.4044257617,0.1255660452
C,0,0.9661096602,0.3893813944,0.7985324886
B,0,0.2399985182,-1.2691967128,0.941006233
C,0,-1.6906924855,-0.2234163143,-1.9093505855
H,0,-0.2330432861,1.362052256,-1.744283771
H,0,-1.1245304217,0.7598741865,0.6595445708
H,0,1.8929221108,0.3040561982,0.2403810595
H,0,1.0473992958,0.8119570827,1.7931138936
H,0,0.9889051744,-1.9488930892,0.2942752562
H,0,0.1328198851,-1.3881610511,2.1300458606
H,0,-0.8820023054,-1.4079297212,0.4812550021
H,0,0.4811734196,-0.2442715447,-1.7759172342
C,0,-1.7901170761,-0.1647606254,-3.4391025985
H,0,-1.8082910695,-1.2608793053,-1.5722326437
H,0,-2.5246389005,0.3419808138,-1.4678232229
C,0,-3.1104720543,-0.7251646533,-3.9833001286
H,0,-1.671447396,0.8764021503,-3.7747065103
H,0,-0.9504657143,-0.7232826117,-3.8784421173
C,0,-3.2125597348,-0.6728794232,-5.5131645218
H,0,-3.2284989938,-1.7654715166,-3.6463151653
H,0,-3.9504151888,-0.1668944189,-3.543723596
C,0,-4.5326273007,-1.2332947392,-6.0582474937

```
H,0,-3.0932983611,0.3677603842,-5.8499933467
H,0,-2.3724040578,-1.2313804026,-5.9519831266
C,0,-4.6347713514,-1.1830234217,-7.5882030908
H,0,-4.6519709895,-2.2734636331,-5.7204335351
H,0,-5.3728016429,-0.6744521235,-5.6197226079
C,0,-5.9543875041,-1.7435125416,-8.1338482979
H,0,-4.5151365067,-0.1427322998,-7.9260631174
H,0,-3.7944570691,-1.7419403689,-8.0264232343
C,0,-6.0568315297,-1.6943442469,-9.6637693527
H,0,-6.0748037427,-2.7838743572,-7.7963349317
H,0,-6.7954551586,-1.1846504539,-7.696663515
C,0,-7.3775698917,-2.2560102737,-10.2000213457
H,0,-5.9371819253,-0.6548565968,-10.001206779
H,0,-5.2170319395,-2.2533603295,-10.1006788558
H,0,-7.4194541827,-2.2068761259,-11.2941748168
H,0,-7.5094980882,-3.3053679969,-9.9085235401
H,0,-8.2351062724,-1.6948921258,-9.8084194962
```

Dodecene M Complex anti

```
B3LYP/6-31G*
E(RB3LYP) = -498.362892191

Zero-point correction= 0.370283 (Hartree/Particle)
Thermal correction to Energy= 0.388390
Thermal correction to Enthalpy= 0.389334
Thermal correction to Gibbs Free Energy= 0.321956
Sum of electronic and ZPE= -497.992609
Sum of electronic and thermal Energies= -497.974502
Sum of electronic and thermal Enthalpies= -497.973558
Sum of electronic and thermal Free Energies= -498.040937

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 243.719 64.510 141.811
```

```
C,0,-0.2750027945,0.1839793561,-1.2328776393
C,0,-0.4356554107,0.2430644231,0.2656609991
C,0,0.6237135957,0.3156275097,1.1451847294
B,0,0.014105693,-1.4418434646,1.1277036875
H,0,-1.0713932835,-0.4300944069,-1.6692547151
C,0,-0.3138655765,1.5947504702,-1.8540123819
H,0,-1.4270887427,0.4988525679,0.6337563225
H,0,1.6432451446,0.2991774565,0.7733576493
```

```
H,0,0.4880253407,0.6898542343,2.1529310166
H,0,-0.985253131,-1.6812478565,0.4775929096
H,0,0.9506449586,-2.011061479,0.6387558774
H,0,-0.2623930133,-1.5709251545,2.2882534229
H,0,0.6761527084,-0.3043610693,-1.4770347868
C,0,-0.1855927895,1.5704906952,-3.3827484813
H,0,-1.2540443609,2.0923022548,-1.5752772395
H,0,0.4940883427,2.202941365,-1.4249239099
C,0,-0.2226565803,2.9666048067,-4.0176494537
H,0,0.7531388933,1.0688129421,-3.6597766199
H,0,-0.9944264044,0.9565048796,-3.8051507713
C,0,-0.0935621657,2.9454794446,-5.5463027982
H,0,-1.1618387097,3.467241322,-3.7391639252
H,0,0.5856524557,3.5802775006,-3.5931381656
C,0,-0.1316083805,4.3406251492,-6.1833087649
H,0,0.8457513719,2.4447282403,-5.824164579
H,0,-0.9013352535,2.3305493299,-5.9701641157
C,0,-0.0022299379,4.3200823594,-7.7118701496
H,0,-1.071142199,4.8410345054,-5.905205452
H,0,0.675912653,4.9556269031,-5.7588642597
C,0,-0.0409880475,5.7145997323,-8.3497883139
H,0,0.9374995824,3.8198733562,-7.9897506067
H,0,-0.8094542653,3.704468567,-8.1360629837
C,0,0.0884508035,5.6946319164,-9.878324382
H,0,-0.98082365,6.2153902853,-8.0727600169
H,0,0.7661870561,6.3310208744,-7.9263249982
C,0,0.0484528553,7.0910417897,-10.5070850564
H,0,1.0278159791,5.1950782021,-10.155235809
H,0,-0.71823273,5.0791862291,-10.3015732237
H,0,0.1431511868,7.0423632854,-11.597924727
H,0,-0.894461006,7.6025281736,-10.2771998304
H,0,0.8647568117,7.7193583038,-10.1296954578
```

Dodecene AMTS out

B3LYP/6-31G*
E(RB3LYP) = -498.362865029

Zero-point correction= 0.369767 (Hartree/Particle)
Thermal correction to Energy= 0.387099
Thermal correction to Enthalpy= 0.388043
Thermal correction to Gibbs Free Energy= 0.322385
Sum of electronic and ZPE= -497.993098
Sum of electronic and thermal Energies= -497.975767

Sum of electronic and thermal Enthalpies= -497.974822
Sum of electronic and thermal Free Energies= -498.040480

```
      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 242.908 62.408 138.188
```

```
C,0,-0.3236879024,-0.3980625653,-1.3978416192
C,0,-0.3386581574,-0.426474597,0.1118904565
C,0,0.8234274384,-0.4340282694,0.8859754288
B,0,0.1446982621,1.2002249515,0.9509902886
C,0,-1.5889910792,0.1612495783,-2.0597797252
H,0,-0.177968621,-1.4409060077,-1.7212134039
H,0,-1.2621993541,-0.7720338729,0.5730712875
H,0,1.7897684934,-0.4081049659,0.3922658516
H,0,0.8114127882,-0.8743892069,1.8764242596
H,0,-0.1349971103,1.3694754757,2.1045933979
H,0,-0.9226510806,1.3078299088,0.3506304886
H,0,0.9266280691,1.8903724026,0.3574914032
H,0,0.5624408703,0.1537094158,-1.7358496419
C,0,-1.5534341469,0.0671178749,-3.5905887207
H,0,-2.4681633142,-0.3809688872,-1.6814781828
H,0,-1.7197149842,1.2089012399,-1.7592639231
C,0,-2.8112229078,0.6324098519,-4.2628571338
H,0,-0.6691986956,0.6028829195,-3.966089904
H,0,-1.4222735424,-0.9834807056,-3.8900112566
C,0,-2.7786619469,0.543046249,-5.7940554295
H,0,-3.6957412935,0.097388304,-3.886329319
H,0,-2.9414884387,1.6824746699,-3.9625678784
C,0,-4.0358651816,1.1087929961,-6.4671921199
H,0,-1.8937754604,1.0779180529,-6.1698554656
H,0,-2.6476525137,-0.5074015597,-6.0940263164
C,0,-4.0036667236,1.0207996287,-7.9985062299
H,0,-4.920785788,0.5738762267,-6.0913187322
H,0,-4.1667892711,2.1589379554,-6.1665674386
C,0,-5.2602082549,1.5869481061,-8.672169268
H,0,-3.118481167,1.5555329549,-8.3740805123
H,0,-3.8727505335,-0.0295114126,-8.2991173915
C,0,-5.2284766794,1.4997092901,-10.2034898865
H,0,-6.1460838722,1.052439295,-8.2975000614
H,0,-5.3917136155,2.6374146064,-8.3721730789
C,0,-6.4868344224,2.0675575589,-10.8679074888
H,0,-4.3437807135,2.0342222281,-10.5780007812
H,0,-5.0979362611,0.4501034614,-10.5034841388
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H,0,-6.4332719155,1.9906324371,-11.9599468569
H,0,-7.3852571639,1.5301311706,-10.5399014365
H,0,-6.6253048089,3.12605824,-10.615055521

Dodecene AMTS anti

B3LYP/6-31G*
E(RB3LYP) = -498.362572824

Zero-point correction= 0.370040 (Hartree/Particle)
Thermal correction to Energy= 0.387337
Thermal correction to Enthalpy= 0.388281
Thermal correction to Gibbs Free Energy= 0.322733
Sum of electronic and ZPE= -497.992532
Sum of electronic and thermal Energies= -497.975236
Sum of electronic and thermal Enthalpies= -497.974292
Sum of electronic and thermal Free Energies= -498.039840

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	243.057	62.247	137.957

C,0,-0.3815365944,-0.226083658,-1.2443896071
C,0,-0.4085660196,-0.2196072494,0.2666352732
C,0,0.7556388777,-0.223028978,1.0461906821
B,0,0.0759217859,1.3967167639,1.0897756886
H,0,-1.2779104873,0.2674144951,-1.6393829454
C,0,-0.2995574835,-1.6634975805,-1.7931024702
H,0,-1.329655855,-0.5725240921,0.7266639195
H,0,1.7210793132,-0.21084705,0.549593753
H,0,0.7420036262,-0.660592314,2.0379608337
H,0,-0.2494032447,1.5867494293,2.2275386587
H,0,-0.9787391515,1.4639942621,0.4524565405
H,0,0.8463106064,2.0981620242,0.4961754932
H,0,0.4823546344,0.3545285225,-1.5902094006
C,0,-0.2944083652,-1.7116667044,-3.3268660176
H,0,0.6061016145,-2.1490871157,-1.4053206872
H,0,-1.1489255602,-2.2498270097,-1.4134562351
C,0,-0.2128397839,-3.1367610067,-3.8891166376
H,0,-1.2013889766,-1.2205992407,-3.7088807015
H,0,0.5531381579,-1.1214575723,-3.7049576935
C,0,-0.2060450735,-3.1885401123,-5.4225169008
H,0,0.6937119146,-3.6273565194,-3.5049298899
H,0,-1.0607278001,-3.7259797746,-3.5094148365

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C,0,-0.1256444858,-4.6130266998,-5.9865989171
H,0,-1.1121756285,-2.6965726735,-5.806219215
H,0,0.6420876723,-2.5993129722,-5.8016710242
C,0,-0.1184442095,-4.6654073587,-7.5199059123
H,0,0.7802932698,-5.1049970899,-5.602306334
H,0,-0.9739732399,-5.2019977452,-5.6072304281
C,0,-0.0390100219,-6.0894221258,-8.0848337657
H,0,-1.0240881838,-4.1726415837,-7.9040073284
H,0,0.7302074377,-4.0767181173,-7.8990554671
C,0,-0.0317230466,-6.1423855985,-9.6180699509
H,0,0.8666432805,-6.5829771349,-7.7014055537
H,0,-0.887713951,-6.6787786959,-7.7064221946
C,0,0.0473518957,-7.568051282,-10.1736393724
H,0,-0.9367216948,-5.6497220451,-10.0013452583
H,0,0.8167389506,-5.5544459895,-9.9963106539
H,0,0.0508106561,-7.571663347,-11.2696583331
H,0,0.9598220573,-8.0750390066,-9.8361174371
H,0,-0.8068288935,-8.1709790537,-9.8413576735
```

Dodecene MTS out

B3LYP/6-31G*
E(RB3LYP) = -498.359107146

Zero-point correction= 0.370043 (Hartree/Particle)
Thermal correction to Energy= 0.387268
Thermal correction to Enthalpy= 0.388213
Thermal correction to Gibbs Free Energy= 0.322884
Sum of electronic and ZPE= -497.989064
Sum of electronic and thermal Energies= -497.971839
Sum of electronic and thermal Enthalpies= -497.970895
Sum of electronic and thermal Free Energies= -498.036223

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 243.015 62.126 137.496
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```
C,0,-0.3012388767,0.3828980325,-1.3937950127
C,0,-0.3021797345,0.3904788861,0.1255672143
C,0,0.8857576455,0.4359080214,0.877991572
B,0,-0.0206590166,-1.1544669785,0.8972969678
C,0,-1.5476558605,-0.2650290969,-2.0100346267
H,0,-0.229658595,1.4237673061,-1.7473031489
H,0,-1.1799424383,0.8410125284,0.5837410364
```

H,0,1.8505161356,0.3606005915,0.3828640888
H,0,0.9069989363,0.890919332,1.8635135655
H,0,0.1944463354,-1.9384059966,0.0186962887
H,0,1.0452756397,-1.1386397496,1.537358088
H,0,-0.8658791055,-1.3047998769,1.73077957
H,0,0.5996639665,-0.1305494981,-1.7546880034
C,0,-1.5565666183,-0.2183719787,-3.5431198237
H,0,-1.6134201127,-1.3063699555,-1.6696088894
H,0,-2.4456632508,0.2414183385,-1.625789763
C,0,-2.8028029312,-0.8613838337,-4.1653641028
H,0,-1.4820366499,0.8270907291,-3.8785954458
H,0,-0.6580629356,-0.7244614543,-3.9267996216
C,0,-2.8129696959,-0.8204087741,-5.6989410279
H,0,-2.8774828727,-1.906032269,-3.8290996081
H,0,-3.7016060421,-0.355281818,-3.78259217
C,0,-4.0591032519,-1.4634237598,-6.3214046298
H,0,-2.737609913,0.2246558735,-6.0349386919
H,0,-1.9140828067,-1.3266587598,-6.0813753282
C,0,-4.069346053,-1.4230843,-7.8550295514
H,0,-4.1343492198,-2.5082992036,-5.9852784442
H,0,-4.9580874079,-0.957310393,-5.9390098797
C,0,-5.3148325157,-2.0665277235,-8.4779256797
H,0,-3.9943250639,-0.3780447488,-8.1911580103
H,0,-3.1701176909,-1.9289492228,-8.2372936017
C,0,-5.3255313026,-2.0264296936,-10.0114965217
H,0,-5.3903490356,-3.1118811659,-8.1427405865
H,0,-6.2147979215,-1.5611441341,-8.0964494555
C,0,-6.5724381491,-2.6716002977,-10.6250103599
H,0,-5.2512028299,-0.9819766238,-10.3466508854
H,0,-4.4266744303,-2.5317082014,-10.3928657806
H,0,-6.5499666772,-2.6267268972,-11.7199547553
H,0,-6.6553525676,-3.7268368878,-10.3366222704
H,0,-7.4863150861,-2.1656453463,-10.2896877153

Dodecene MTS anti

B3LYP/6-31G*
E(RB3LYP) = -498.359240752

Zero-point correction= 0.370052 (Hartree/Particle)
Thermal correction to Energy= 0.387311
Thermal correction to Enthalpy= 0.388255
Thermal correction to Gibbs Free Energy= 0.322829
Sum of electronic and ZPE= -497.989189

```
Sum of electronic and thermal Energies= -497.971930
Sum of electronic and thermal Enthalpies= -497.970986
Sum of electronic and thermal Free Energies= -498.036412

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 243.041 62.128 137.701

 C,0,-0.349602522,0.2174704162,-1.235527872
 C,0,-0.3540986941,0.2036421693,0.2830395188
 C,0,0.8372028549,0.2105961525,1.0336372665
 B,0,-0.1149857629,-1.3545580537,1.0301010733
 H,0,-1.2174542898,-0.3422747406,-1.6071855308
 C,0,-0.3756328719,1.6422052302,-1.8149145793
 H,0,-1.2182455886,0.6739608829,0.7468581003
 H,0,1.7981281054,0.1182293888,0.5335633119
 H,0,0.8735206314,0.6488782096,2.0262882236
 H,0,0.0732181607,-2.131771409,0.1396274387
 H,0,0.9563728237,-1.3739985929,1.6633439406
 H,0,-0.9580170481,-1.4905997699,1.8682596016
 H,0,0.5368782487,-0.3168883316,-1.6016893804
 C,0,-0.410763868,1.6691198055,-3.3484555316
 H,0,-1.2518265447,2.1787984445,-1.4218103636
 H,0,0.5046407208,2.1962502695,-1.4573216631
 C,0,-0.4408233245,3.086445568,-3.9351034089
 H,0,0.4651111948,1.1315628758,-3.7412305873
 H,0,-1.2910286111,1.1110983769,-3.7003249193
 C,0,-0.4756081519,3.1139065273,-5.4687315658
 H,0,-1.31732121,3.6230353721,-3.5423821609
 H,0,0.4391017993,3.6445686525,-3.5819068239
 C,0,-0.5070484834,4.530885007,-6.0561221616
 H,0,0.4011374667,2.577527962,-5.8612634141
 H,0,-1.3550977505,2.5550292237,-5.8216171613
 C,0,-0.5418547087,4.5585335884,-7.5897083903
 H,0,-1.3839342626,5.0670304352,-5.6635207677
 H,0,0.3723686154,5.089879991,-5.7029554819
 C,0,-0.5742309529,5.9750686326,-8.1776515529
 H,0,0.3352896051,4.0227136776,-7.9822739646
 H,0,-1.4209784831,3.999008728,-7.9427261367
 C,0,-0.6091320979,6.0032089924,-9.7111676382
 H,0,-1.4514720661,6.5115515698,-7.785876828
 H,0,0.304875371,6.5354166285,-7.8254238065
 C,0,-0.6416197104,7.4215826346,-10.2896553194
 H,0,0.267720984,5.46807567,-10.102861637
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H,0,-1.4876956963,5.4439613802,-10.0633101144
H,0,-0.6659311803,7.4074429645,-11.385353304
H,0,-1.5263749051,7.9705052276,-9.9440149928
H,0,0.2422552029,7.994884243,-9.9835734172
```

Dodecene AM Product out

B3LYP/6-31G*
E(RB3LYP) = -498.393791063

Zero-point correction= 0.371965 (Hartree/Particle)
Thermal correction to Energy= 0.390365
Thermal correction to Enthalpy= 0.391309
Thermal correction to Gibbs Free Energy= 0.322757
Sum of electronic and ZPE= -498.021826
Sum of electronic and thermal Energies= -498.003427
Sum of electronic and thermal Enthalpies= -498.002482
Sum of electronic and thermal Free Energies= -498.071035

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 244.957 63.848 144.280
```

```
C,0,-0.4335878381,-0.411648145,-1.3676885469
C,0,-0.3725357582,0.3736905167,-0.0485016042
C,0,0.9326993833,0.0942391785,0.7580975723
B,0,0.8623458864,0.9508199276,2.0652906554
C,0,-1.7119066436,-0.1480303992,-2.1738261005
H,0,-0.3523337069,-1.4863457094,-1.1496521622
H,0,-1.2502586858,0.1174835251,0.5613709561
H,0,1.7885769022,0.3589425758,0.1230592241
H,0,0.9840458342,-0.9839878671,0.9597236435
H,0,0.3324083187,0.5269279007,3.054127776
H,0,-0.453274039,1.4477196104,-0.2674186378
H,0,1.2630363966,2.0810169114,2.0858053148
H,0,0.4445184166,-0.1563330628,-1.9783121343
C,0,-1.7744567225,-0.931529433,-3.4914934949
H,0,-2.5885483233,-0.4014128098,-1.5592558894
H,0,-1.7919351727,0.928196976,-2.3876711198
C,0,-3.0519234641,-0.6696184048,-4.2995511736
H,0,-0.8978027579,-0.678522153,-4.1061684735
H,0,-1.6942085603,-2.0077857169,-3.2779687005
C,0,-3.1152124114,-1.4526290846,-5.6171459362
H,0,-3.9285518734,-0.9225806362,-3.6847610544
```

```
H,0,-3.1321383811,0.4066959997,-4.5129686366
C,0,-4.3925448996,-1.1914113085,-6.4261874979
H,0,-2.2384451706,-1.1999435738,-6.2319012107
H,0,-3.0347112088,-2.5289738218,-5.4038471507
C,0,-4.4558290012,-1.9745737625,-7.7440215378
H,0,-5.2693006799,-1.4441023072,-5.8114464673
H,0,-4.4730417626,-0.1150837672,-6.6394930304
C,0,-5.73276141,-1.7137675831,-8.5533389993
H,0,-3.5789317513,-1.7218666984,-8.3586318955
H,0,-4.3752039476,-3.0509074526,-7.53057149
C,0,-5.7963624017,-2.496772805,-9.8712251749
H,0,-6.6103809784,-1.966642169,-7.9396418898
H,0,-5.8140872215,-0.6375656206,-8.7677247546
C,0,-7.0744541906,-2.2303996124,-10.672722697
H,0,-4.9200165115,-2.2436956573,-10.4849238954
H,0,-5.7159266944,-3.5721317014,-9.6572400846
H,0,-7.0889075795,-2.8037212932,-11.606805405
H,0,-7.9672001603,-2.5069031061,-10.0981913008
H,0,-7.1652212302,-1.1683374599,-10.9321859953
```

Dodecene AM Product out twisted

B3LYP/6-31G*
E(RB3LYP) = -498.395462935

Zero-point correction= 0.371183 (Hartree/Particle)
Thermal correction to Energy= 0.389535
Thermal correction to Enthalpy= 0.390479
Thermal correction to Gibbs Free Energy= 0.322212
Sum of electronic and ZPE= -498.024280
Sum of electronic and thermal Energies= -498.005928
Sum of electronic and thermal Enthalpies= -498.004984
Sum of electronic and thermal Free Energies= -498.073251

```
      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 244.437 64.144 143.680
```

```
C,0,-0.4972833284,-0.4102167355,-1.3405759111
C,0,-0.4321650583,0.3942409127,-0.0359154405
C,0,0.8227644296,0.1116341623,0.8059376694
B,0,1.058580496,0.957946926,2.0956186059
C,0,-1.755765719,-0.1331635655,-2.172803429
H,0,-0.4448156838,-1.4843702601,-1.1068314506
```

```
H,0,-1.3273892605,0.1785315333,0.5649332321
H,0,1.73108442,0.3142144684,0.1998801356
H,0,0.9133404647,-0.9636644643,1.0294756632
H,0,1.9157421549,0.640798819,2.8715377506
H,0,-0.4799020632,1.4680725738,-0.2657426528
H,0,0.4362325124,1.9586906345,2.3200067364
H,0,0.395436191,-0.1900467153,-1.9457153834
C,0,-1.8188694823,-0.9376164723,-3.4777296546
H,0,-2.647155866,-0.3542121259,-1.566851915
H,0,-1.8075262346,0.9409100561,-2.4057377318
C,0,-3.077848771,-0.6601929719,-4.3094918157
H,0,-0.9275752194,-0.716546944,-4.0837863712
H,0,-1.7672403656,-2.0116813305,-3.2447107797
C,0,-3.141015117,-1.4646017773,-5.6143894145
H,0,-3.9691212901,-0.8812306562,-3.7034121632
H,0,-3.1294272602,0.4138794762,-4.5424322051
C,0,-4.3999883592,-1.1871405978,-6.4461452599
H,0,-2.2497047532,-1.2435730611,-6.2204438419
H,0,-3.0894472268,-2.53868231,-5.3814092936
C,0,-4.463242098,-1.9915161423,-7.7510511091
H,0,-5.2912815451,-1.4081502314,-5.8400844696
H,0,-4.4515439973,-0.1130710936,-6.6791153016
C,0,-5.7219693591,-1.7143645602,-8.5829585978
H,0,-3.5719175421,-1.7704626309,-8.357122653
H,0,-4.4116501699,-3.0656179309,-7.5180488438
C,0,-5.7855883782,-2.5184375869,-9.8879626768
H,0,-6.6139852485,-1.9356263589,-7.9777955478
H,0,-5.7742747216,-0.6403760411,-8.8168082267
C,0,-7.0457214562,-2.2355735397,-10.7122706507
H,0,-4.8948787774,-2.2968967482,-10.4931488471
H,0,-5.7340682145,-3.5915449795,-9.6545569027
H,0,-7.0610451514,-2.8243673161,-11.6366577184
H,0,-7.952969022,-2.4807284284,-10.1462387865
H,0,-7.1075119285,-1.1763179866,-10.991108748
```

Dodecene AM Product out gauche

B3LYP/6-31G*
E(RB3LYP) = -498.395226700

Zero-point correction= 0.371466 (Hartree/Particle)
Thermal correction to Energy= 0.389593
Thermal correction to Enthalpy= 0.390537
Thermal correction to Gibbs Free Energy= 0.322994

```
Sum of electronic and ZPE= -498.023761
Sum of electronic and thermal Energies= -498.005634
Sum of electronic and thermal Enthalpies= -498.004690
Sum of electronic and thermal Free Energies= -498.072233

     E     CV      S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 244.473 63.982 142.156

 C,0,-0.069353893,-0.0539527698,-0.8655846333
 C,0,-0.2919939611,-0.5132096511,0.5816090609
 C,0,0.9465524953,-0.3034425249,1.4687593614
 B,0,1.3550939353,1.1571991332,1.8344469775
 C,0,-1.2918969348,-0.2534721206,-1.7697875273
 H,0,0.7892192011,-0.5966374313,-1.2895121755
 H,0,-0.5831605437,-1.5734469427,0.5793341354
 H,0,1.8033755288,-0.8829547633,1.0930497923
 H,0,0.7629945199,-0.7403186213,2.4738996163
 H,0,0.5772480709,2.0663553684,1.7426973937
 H,0,-1.1416043773,0.0388414931,1.007540861
 H,0,2.4395841546,1.3872791107,2.2903732867
 H,0,0.2137279918,1.0100038479,-0.8667570209
 C,0,-1.0668935362,0.2040767879,-3.2168493612
 H,0,-1.5760706409,-1.3164263332,-1.7651815978
 H,0,-2.1487869478,0.2908352297,-1.3457471048
 C,0,-2.2901503189,0.0033158145,-4.1207910581
 H,0,-0.7828856574,1.2670024407,-3.2213307539
 H,0,-0.209464024,-0.3399965931,-3.6403887107
 C,0,-2.065694086,0.4608157458,-5.5678950186
 H,0,-2.5741735343,-1.0596533306,-4.1161669942
 H,0,-3.1475439991,0.5472488997,-3.6970819626
 C,0,-3.2888541167,0.2595421551,-6.4718598279
 H,0,-1.7820114335,1.5238553374,-5.5725015471
 H,0,-1.2080234067,-0.0828418284,-5.991482561
 C,0,-3.0646662299,0.7170678195,-7.9189956276
 H,0,-3.5724854706,-0.8035277396,-6.4672274208
 H,0,-4.1465232129,0.8031147336,-6.0482046006
 C,0,-4.287457372,0.515758051,-8.8231594361
 H,0,-2.7811791009,1.7801981326,-7.9236104712
 H,0,-2.2068637358,0.1735872164,-8.3426125809
 C,0,-4.063799399,0.9731991827,-10.2703367355
 H,0,-4.5714781704,-0.5473556225,-8.8195486479
 H,0,-5.1458362556,1.0592647353,-8.4004824438
 C,0,-5.2898807452,0.7686766762,-11.1660564555
```

H,0,-3.7807114241,2.0355226382,-10.2742722552
H,0,-3.2067672596,0.4296977174,-10.6931793878
H,0,-5.0980815789,1.1046532492,-12.1915992215
H,0,-5.576383966,-0.2894159087,-11.2103949658
H,0,-6.1544815654,1.3285616646,-10.78845038

Dodecene AM Product anti

B3LYP/6-31G*
E(RB3LYP) = -498.392460367

Zero-point correction= 0.371865 (Hartree/Particle)
Thermal correction to Energy= 0.390337
Thermal correction to Enthalpy= 0.391282
Thermal correction to Gibbs Free Energy= 0.321135
Sum of electronic and ZPE= -498.020595
Sum of electronic and thermal Energies= -498.002123
Sum of electronic and thermal Enthalpies= -498.001179
Sum of electronic and thermal Free Energies= -498.071325

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	244.940	63.825	147.636

C	4.060443	-1.018098	0.026312
C	5.418154	-0.394639	-0.347276
C	5.793427	0.859829	0.500398
B	7.230662	1.303779	0.070157
H	3.947310	-1.956686	-0.535574
C	2.843815	-0.126137	-0.250704
H	5.412040	-0.129011	-1.413450
H	5.725119	0.594175	1.563503
H	5.052863	1.645634	0.301674
H	7.395534	1.922957	-0.943961
H	6.192704	-1.164750	-0.227411
H	8.203166	0.979678	0.692191
H	4.074202	-1.298311	1.089639
C	1.508112	-0.811688	0.067965
H	2.917909	0.800187	0.335224
H	2.852386	0.179397	-1.307947
C	0.285037	0.073767	-0.203825
H	1.424630	-1.737200	-0.521029
H	1.503223	-1.123244	1.123167
C	-1.050549	-0.610161	0.115922

H	0.368927	0.999213	0.385282
H	0.289890	0.385415	-1.258983
C	-2.273619	0.275404	-0.155551
H	-1.134618	-1.535685	-0.473050
H	-1.055131	-0.921743	1.171122
C	-3.609363	-0.407719	0.165255
H	-2.189037	1.201194	0.432941
H	-2.269322	0.586535	-1.210879
C	-4.832455	0.477647	-0.105747
H	-3.694070	-1.333520	-0.423268
H	-3.613479	-0.718885	1.220620
C	-6.168432	-0.204814	0.215295
H	-4.748668	1.403751	0.482634
H	-4.829572	0.788913	-1.161195
C	-7.384346	0.686421	-0.057991
H	-6.252756	-1.129683	-0.373100
H	-6.171761	-0.515326	1.269933
H	-8.321537	0.170671	0.180871
H	-7.346588	1.603649	0.542719
H	-7.428012	0.984924	-1.112773

Dodecene AM Product twisted

B3LYP/6-31G*
E(RB3LYP) = -498.394245935

Zero-point correction= 0.371463 (Hartree/Particle)
Thermal correction to Energy= 0.389642
Thermal correction to Enthalpy= 0.390586
Thermal correction to Gibbs Free Energy= 0.322796
Sum of electronic and ZPE= -498.022783
Sum of electronic and thermal Energies= -498.004604
Sum of electronic and thermal Enthalpies= -498.003660
Sum of electronic and thermal Free Energies= -498.071450

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	244.504	64.027	142.676

C,0,-0.603390437,-0.2567646407,-1.6368105009
C,0,-0.6319326232,0.4656726555,-0.2792197519
C,0,0.6971193356,0.4432177927,0.4961908074
B,0,0.7294860967,1.0784128477,1.9199764267
H,0,-1.5452948054,-0.0515450853,-2.1655593857

```
C,0,-0.4091055001,-1.7768527234,-1.5505247242
H,0,-1.423764545,0.0323188895,0.3482213701
H,0,1.5233096988,0.8199126598,-0.1271112759
H,0,0.9969576637,-0.605071534,0.706562365
H,0,-0.2768476754,1.2893468717,2.5380870286
H,0,-0.923808005,1.5113320877,-0.4469340258
H,0,1.7780046259,1.313125539,2.4516638982
H,0,0.1938855966,0.1760364472,-2.2600489814
C,0,-0.4359453565,-2.4711114252,-2.9188372431
H,0,0.5449443461,-2.0057414731,-1.0547469522
H,0,-1.1952905139,-2.2053009629,-0.9104386719
C,0,-0.2435582706,-3.9911214527,-2.8398932316
H,0,-1.391151797,-2.2512419106,-3.418532876
H,0,0.346996401,-2.0389674155,-3.5597843976
C,0,-0.2693323528,-4.6849753189,-4.2080106659
H,0,0.7117173483,-4.2106314048,-2.3399600753
H,0,-1.0265537647,-4.4232511318,-2.1989955336
C,0,-0.0776094319,-6.2050975324,-4.1287939229
H,0,-1.2241750364,-4.4651627119,-4.7085021568
H,0,0.5141920049,-4.2532667235,-4.848543672
C,0,-0.1013047817,-6.8990259592,-5.4968893621
H,0,0.8766492318,-6.424806475,-3.6270886955
H,0,-0.8618618569,-6.6369023387,-3.4892256336
C,0,0.0897523986,-8.4190616895,-5.4178067832
H,0,-1.0552895157,-6.678902595,-5.9989759247
H,0,0.6834216952,-6.4675644013,-6.1361692252
C,0,0.0669631371,-9.1134418437,-6.7856152957
H,0,1.0436340973,-8.6401484049,-4.9156943357
H,0,-0.6951580475,-8.8516226418,-4.7793119931
C,0,0.2585433763,-10.6309749124,-6.6971542154
H,0,-0.8862842048,-8.8934045224,-7.2872027057
H,0,0.8516219979,-8.6819884107,-7.4234575618
H,0,0.2372545631,-11.0965626123,-7.6892069219
H,0,1.2195782909,-10.8827298322,-6.2317230255
H,0,-0.5313653846,-11.0957697048,-6.0941611723
```

Dodecene M Product out

B3LYP/6-31G*
E(RB3LYP) = -498.392581165

Zero-point correction= 0.371668 (Hartree/Particle)
Thermal correction to Energy= 0.389911
Thermal correction to Enthalpy= 0.390855

```
Thermal correction to Gibbs Free Energy= 0.323416
Sum of electronic and ZPE= -498.020913
Sum of electronic and thermal Energies= -498.002670
Sum of electronic and thermal Enthalpies= -498.001726
Sum of electronic and thermal Free Energies= -498.069165

      E       CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 244.673 64.420 141.938
```

```
C,0,-0.0930899827,0.1777187104,-1.1420279436
C,0,-0.1855330434,0.1290249745,0.3932879494
C,0,1.149259828,0.6024493297,1.0474949948
B,0,-0.4052222545,-1.2913118551,1.0138722445
C,0,-1.4051000709,-0.2012233825,-1.8424500429
H,0,0.2076332473,1.1868155323,-1.4642471341
H,0,-0.9645839765,0.8302790348,0.7281859939
H,0,1.3974324798,1.6119499915,0.6967960131
H,0,1.0867061681,0.6372444584,2.1412038137
H,0,0.0271775357,-2.2692232511,0.468363184
H,0,1.9877405691,-0.0514523035,0.7774037275
H,0,-0.9189749189,-1.4247138451,2.0886446421
H,0,0.7046080299,-0.5016074978,-1.4773821661
C,0,-1.3261762918,-0.1356633744,-3.3729448693
H,0,-1.6985073706,-1.2184985759,-1.5395942323
H,0,-2.2089224445,0.4633423134,-1.4914659995
C,0,-2.6382187751,-0.5136109831,-4.0726546337
H,0,-1.0323322248,0.880267726,-3.6764659914
H,0,-0.522826388,-0.8006169665,-3.7232583814
C,0,-2.5588603174,-0.4445380949,-5.6032694655
H,0,-2.9312754257,-1.5299675273,-3.7699514911
H,0,-3.4417127775,0.1505054052,-3.7206262743
C,0,-3.8704978696,-0.822793894,-6.3035317218
H,0,-2.2660213822,0.5719614836,-5.9058323569
H,0,-1.755054021,-1.1082463661,-5.9552570782
C,0,-3.7914657428,-0.7523798885,-7.8340980967
H,0,-4.1628736869,-1.8395888596,-6.0016180999
H,0,-4.6744945365,-0.1596424696,-5.9508513283
C,0,-5.1026412773,-1.1307278871,-8.5347995241
H,0,-3.4992434989,0.26455903,-8.1358872264
H,0,-2.9872782024,-1.4153296479,-8.1867955118
C,0,-5.0242063008,-1.059840591,-10.0653064331
H,0,-5.3953129879,-2.1479974434,-8.2342217334
H,0,-5.9075894869,-0.4681906948,-8.1826962326
```

C,0,-6.3377505748,-1.4393352146,-10.7568059617
H,0,-4.7326656883,-0.0433150839,-10.3659100052
H,0,-4.2204980068,-1.7222153148,-10.4174241793
H,0,-6.2490097027,-1.378698308,-11.8476065352
H,0,-6.6374456347,-2.4638356742,-10.5035255253
H,0,-7.1535399951,-0.7723629949,-10.4514803876

Dodecene M Product anti

B3LYP/6-31G*
E(RB3LYP) = -498.391030888

Zero-point correction= 0.371618 (Hartree/Particle)
Thermal correction to Energy= 0.389954
Thermal correction to Enthalpy= 0.390899
Thermal correction to Gibbs Free Energy= 0.323100
Sum of electronic and ZPE= -498.019412
Sum of electronic and thermal Energies= -498.001076
Sum of electronic and thermal Enthalpies= -498.000132
Sum of electronic and thermal Free Energies= -498.067931

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	244.700	64.511	142.694

C,0,-0.3354962949,0.1515342907,-1.1977726974
C,0,-0.3386649082,-0.1140827407,0.3229756865
C,0,0.9899244094,0.3367316753,1.0071793087
B,0,-0.4464333493,-1.622216673,0.7275937622
H,0,-1.2319100932,-0.3075489354,-1.6401090675
C,0,-0.3044035077,1.6325069474,-1.604158461
H,0,-1.1460018543,0.4712495563,0.7887928934
H,0,1.8577986954,-0.1766219676,0.5746464629
H,0,1.1466483875,1.4132452407,0.8778625686
H,0,0.0136779915,-2.4803353688,0.0261016723
H,0,0.9842421788,0.137898335,2.0855326585
H,0,-0.9119071975,-1.9444402549,1.7843305703
H,0,0.5196322598,-0.3718624514,-1.6507593929
C,0,-0.3940193416,1.8436027238,-3.1217221842
H,0,-1.1381157872,2.1591430761,-1.1153951576
H,0,0.6144255725,2.1070357358,-1.2329342722
C,0,-0.3637631919,3.3195108862,-3.5395337848
H,0,0.4345212315,1.3107338114,-3.6117295391
H,0,-1.3171825651,1.3785205196,-3.4985805448

```
C,0,-0.4595574496,3.5295511376,-5.0563251391
H,0,-1.1899481471,3.8532718138,-3.0464784012
H,0,0.5614734414,3.7836731712,-3.1665863818
C,0,-0.4287284556,5.0052079771,-5.475036274
H,0,0.365982619,2.9950355962,-5.5495983953
H,0,-1.3852332288,3.0659863846,-5.4288337107
C,0,-0.5275015991,5.2149128777,-6.9916458068
H,0,-1.2532354635,5.5400706885,-4.9803856904
H,0,0.4977946498,5.4684266679,-5.1041615498
C,0,-0.4961593219,6.6901637003,-7.4111021796
H,0,0.296601059,4.6795190811,-7.4864509603
H,0,-1.4543725228,4.7520657916,-7.3621865434
C,0,-0.5963408599,6.9001747322,-8.9274978249
H,0,-1.3197821233,7.2266011087,-6.9163718699
H,0,0.4311347499,7.1536623372,-7.0420984843
C,0,-0.5638273349,8.376115233,-9.3375014313
H,0,0.2266604838,6.3646841468,-9.4220619837
H,0,-1.5233090876,6.4381760401,-9.2962179075
H,0,-0.6373227152,8.4921536569,-10.4249435669
H,0,-1.3956554323,8.9312495195,-8.8864111606
H,0,0.3674411031,8.8570919317,-9.0134842207
```

3,3-dimethyl-1-butene

B3LYP/6-31G*
E(RB3LYP) = -235.848211652

```
Zero-point correction= 0.165444 (Hartree/Particle)
Thermal correction to Energy= 0.173116
Thermal correction to Enthalpy= 0.174060
Thermal correction to Gibbs Free Energy= 0.134831
Sum of electronic and ZPE= -235.682768
Sum of electronic and thermal Energies= -235.675096
Sum of electronic and thermal Enthalpies= -235.674152
Sum of electronic and thermal Free Energies= -235.713381
```

```
     E      CV       S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.632 28.798 82.565
```

```
C,0,-0.4118512738,-0.4450293739,0.0317746888
C,0,0.8112195042,0.3311164217,-0.4221043473
C,0,1.8568817256,0.714319284,0.3115216974
H,0,0.8015506325,0.5911387846,-1.4833395294
```

H,0,1.9415536164,0.4950576989,1.372267287
H,0,2.6796500852,1.2705265106,-0.1301827223
C,0,-1.6650530226,0.4137943536,-0.2569544839
H,0,-1.7271419869,0.6815963649,-1.3188038321
H,0,-1.6468081741,1.3434104137,0.3230708367
C,0,-0.365277198,-0.7937895693,1.528022037
H,0,-0.3199045294,0.1086112568,2.1484062218
H,0,-1.2633862472,-1.3524371007,1.8161761064
H,0,0.5054993758,-1.4147548984,1.7676318315
C,0,-0.493796756,-1.7478779604,-0.7972761013
H,0,-0.5270955633,-1.5332126005,-1.8724072527
H,0,0.375285038,-2.3885669142,-0.6097586188
H,0,-1.397827556,-2.31409523,-0.5409194372
H,0,-2.5789216706,-0.1342674414,0.0039386183

3,3-dimethyl-1-butene AM complex

B3LYP/6-31G*
E(RB3LYP) = -262.478426404

Zero-point correction= 0.197689 (Hartree/Particle)
Thermal correction to Energy= 0.207474
Thermal correction to Enthalpy= 0.208418
Thermal correction to Gibbs Free Energy= 0.164472
Sum of electronic and ZPE= -262.280737
Sum of electronic and thermal Energies= -262.270953
Sum of electronic and thermal Enthalpies= -262.270009
Sum of electronic and thermal Free Energies= -262.313954

C	-0.341726	-0.564176	0.029673
C	0.939852	0.125302	-0.431458
C	1.749246	0.943784	0.331116
B	2.668963	-0.629369	0.052094
H	1.039454	0.198573	-1.513543
H	1.562475	1.074855	1.390883
H	2.361066	1.705001	-0.138226
H	2.045066	-1.559537	-0.421074
H	2.907120	-0.905311	1.196316
H	3.545572	-0.310655	-0.701265
C	-1.470032	0.470741	-0.217988
H	-1.521866	0.766208	-1.272850
H	-1.317397	1.375388	0.380566
C	-0.315334	-0.947939	1.518790
H	-0.204467	-0.071869	2.167315
H	-1.257728	-1.436909	1.790127

H	0.503563	-1.640347	1.735155
C	-0.620814	-1.814826	-0.825796
H	-0.618093	-1.574177	-1.896051
H	0.130263	-2.591621	-0.652409
H	-1.604380	-2.230941	-0.579866
H	-2.439506	0.038493	0.055625

3,3-dimethyl-1-butene M complex

B3LYP/6-31G*
E(RB3LYP) = -262.478425589

Zero-point correction= 0.197670 (Hartree/Particle)
Thermal correction to Energy= 0.207459
Thermal correction to Enthalpy= 0.208404
Thermal correction to Gibbs Free Energy= 0.164444
Sum of electronic and ZPE= -262.280756
Sum of electronic and thermal Energies= -262.270966
Sum of electronic and thermal Enthalpies= -262.270022
Sum of electronic and thermal Free Energies= -262.313982

	E KCal/Mol	CV Cal/Mol-K	S Cal/Mol-K
Total	130.183	37.113	92.522
H	-0.133388	-0.021587	0.163865
C	0.000763	-0.036562	1.239487
C	1.259507	0.085687	1.794613
B	0.156208	1.687657	1.868020
H	-0.813365	-0.466437	1.810850
C	2.584416	0.114770	1.036577
H	1.359496	-0.150771	2.853056
H	-0.582987	1.707940	2.811833
H	-0.112261	2.279086	0.858110
H	1.263469	2.051151	2.215803
C	3.661189	0.850061	1.857388
H	3.747179	0.431326	2.867651
H	4.639192	0.754388	1.372199
H	3.431190	1.915773	1.951949
C	2.465788	0.754451	-0.357024
H	1.771095	0.206425	-1.003124
H	2.125122	1.791823	-0.289321
H	3.444246	0.746887	-0.850343
C	2.999223	-1.372402	0.889549
H	3.968107	-1.441085	0.381478

H	3.098724	-1.861743	1.865954
H	2.264253	-1.933500	0.302248

3,3-dimethyl-1-butene AMTS

B3LYP/6-31G*
E(RB3LYP) = -262.478350849

Zero-point correction= 0.197457 (Hartree/Particle)
Thermal correction to Energy= 0.206451
Thermal correction to Enthalpy= 0.207395
Thermal correction to Gibbs Free Energy= 0.165186
Sum of electronic and ZPE= -262.280894
Sum of electronic and thermal Energies= -262.271900
Sum of electronic and thermal Enthalpies= -262.270956
Sum of electronic and thermal Free Energies= -262.313165

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	129.550	34.954	88.837

C	-0.39371	-0.3548	-1.24716
C	-0.37206	-0.41788	1.64054
C	1.76587	-0.49423	3.18391
B	0.37322	2.53332	3.5421
H	-2.12699	-1.11572	2.4592
H	3.63413	-0.33215	2.35815
H	1.67915	-1.46015	4.98825
H	-0.46066	2.58971	5.64758
H	-1.43614	2.87505	2.12665
H	1.97682	3.96792	2.83343
C	-0.25576	-3.16187	-2.0728
H	1.50014	-4.04808	-1.42806
H	-1.84364	-4.25795	-1.31614
C	1.8578	1.09793	-2.37268
H	1.85774	3.0733	-1.76398
H	3.67103	0.25595	-1.8358
H	1.74645	1.05837	-4.44019
C	-2.88661	0.79225	-2.21896
H	-4.52967	-0.18317	-1.415
H	-3.03167	2.79779	-1.7306
H	-3.00064	0.62581	-4.27997
H	-0.32598	-3.29358	-4.13876

3,3-dimethyl-1-butene MTS

B3LYP/6-31G*
E(RB3LYP) = -262.474866098

Zero-point correction= 0.197690 (Hartree/Particle)
Thermal correction to Energy= 0.206531
Thermal correction to Enthalpy= 0.207476
Thermal correction to Gibbs Free Energy= 0.165730
Sum of electronic and ZPE= -262.277176
Sum of electronic and thermal Energies= -262.268335
Sum of electronic and thermal Enthalpies= -262.267391
Sum of electronic and thermal Free Energies= -262.309136

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	129.600	34.617	87.861

1	-2.033963	-0.064144	-1.136644
C	-1.958249	-0.201199	-0.062333
C	-0.705233	-0.187853	0.581555
B	-1.523150	1.331853	0.834836
H	-2.813391	-0.686123	0.398522
C	0.652810	-0.205156	-0.141469
H	-0.671570	-0.692879	1.545011
H	-1.828534	1.397597	1.989630
H	-2.603155	1.355258	0.218273
H	-0.887566	2.173905	0.270853
C	1.695389	0.534048	0.720030
H	1.740610	0.112552	1.731828
H	2.695043	0.448058	0.277121
H	1.448315	1.596247	0.810398
C	0.604249	0.425671	-1.543490
H	-0.049895	-0.134260	-2.222942
H	0.257777	1.463390	-1.508358
H	1.606654	0.422015	-1.986687
C	1.073878	-1.687916	-0.274806
H	2.057416	-1.770086	-0.753125
H	1.139231	-2.173359	0.706621
H	0.354519	-2.251451	-0.881078

3,3-dimethyl-1-butene AM product

B3LYP/6-31G*
E(RB3LYP) = -262.509891549

Zero-point correction= 0.199480 (Hartree/Particle)
Thermal correction to Energy= 0.209518
Thermal correction to Enthalpy= 0.210462
Thermal correction to Gibbs Free Energy= 0.165119
Sum of electronic and ZPE= -262.310411
Sum of electronic and thermal Energies= -262.300374
Sum of electronic and thermal Enthalpies= -262.299430
Sum of electronic and thermal Free Energies= -262.344773

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 131.474 36.376 95.432

C	-0.036435	0.137150	-0.178928
C	-0.032264	0.697700	1.273493
C	1.238084	0.401988	2.128363
B	0.986896	1.066069	3.522662
H	-0.916406	0.296252	1.789171
H	2.115122	0.821353	1.620954
H	1.372508	-0.683723	2.203957
H	0.422132	0.471064	4.397482
H	-0.181605	1.785253	1.212483
H	1.280944	2.211293	3.723405
C	0.068410	-1.399048	-0.175496
H	1.024406	-1.742412	0.234704
H	-0.735316	-1.850466	0.419741
C	1.119674	0.734511	-1.002011
H	1.078082	1.831006	-1.007332
H	2.097746	0.436815	-0.608518
H	1.067717	0.394483	-2.043492
C	-1.374875	0.545378	-0.827372
H	-2.227355	0.133926	-0.272779
H	-1.487496	1.636334	-0.854035
H	-1.439142	0.177906	-1.858847
H	-0.011412	-1.793472	-1.195820

3,3-dimethyl-1-butene AM product twisted

B3LYP/6-31G*
E(RB3LYP) = -262.511424891

Zero-point correction= 0.198740 (Hartree/Particle)
Thermal correction to Energy= 0.208713

```
Thermal correction to Enthalpy= 0.209657
Thermal correction to Gibbs Free Energy= 0.164800
Sum of electronic and ZPE= -262.312685
Sum of electronic and thermal Energies= -262.302712
Sum of electronic and thermal Enthalpies= -262.301768
Sum of electronic and thermal Free Energies= -262.346625

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 130.969 36.679 94.410

 C,0,-0.0632225984,0.1315710258,-0.1939656446
 C,0,-0.1222358206,0.6807507604,1.2570829676
 C,0,1.087068551,0.4079087244,2.1684142277
 B,0,1.099790024,1.0864480866,3.5730834756
 H,0,-1.021739135,0.2694609083,1.7378507555
 H,0,2.0132957542,0.8144626352,1.7109745806
 H,0,1.3005149779,-0.6670422946,2.2576933978
 H,0,0.3764209575,2.0062484656,3.8374548867
 H,0,-0.2839215381,1.7670555984,1.2076801681
 H,0,1.8877951613,0.7310029238,4.4037570072
 C,0,0.0598752139,-1.40465383,-0.1958454527
 H,0,0.9995907642,-1.7407005949,0.2568500954
 H,0,-0.7653726597,-1.8688570566,0.3589570855
 C,0,1.1225820011,0.7442775741,-0.9637549307
 H,0,1.0682238534,1.840365093,-0.9687496738
 H,0,2.0863601607,0.4573900539,-0.5274668438
 H,0,1.1241792819,0.4068456371,-2.0074679977
 C,0,-1.3738867509,0.526014123,-0.9035558607
 H,0,-2.2459950264,0.103986256,-0.3886405985
 H,0,-1.4977115658,1.6158276817,-0.9311949125
 H,0,-1.3884313029,0.161712288,-1.9381906206
 H,0,0.0323276968,-1.7950440593,-1.220610112
```

3,3-dimethyl-1-butene M Product

```
B3LYP/6-31G*
E(RB3LYP) = -262.506415301

Zero-point correction= 0.199209 (Hartree/Particle)
Thermal correction to Energy= 0.209123
Thermal correction to Enthalpy= 0.210068
Thermal correction to Gibbs Free Energy= 0.166035
Sum of electronic and ZPE= -262.307206
```

Sum of electronic and thermal Energies= -262.297292
Sum of electronic and thermal Enthalpies= -262.296348
Sum of electronic and thermal Free Energies= -262.340380

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	131.227	37.015	92.675

H	-0.242538	0.482038	0.128128
C	-0.065528	-0.071344	1.057390
C	1.210412	0.420409	1.812566
B	0.863528	1.916851	2.123504
H	0.020854	-1.131664	0.795365
C	2.556949	0.132298	1.073262
H	1.233832	-0.147187	2.756072
H	0.131112	2.179125	3.035730
H	-0.959443	0.036135	1.682131
H	1.223787	2.822197	1.425950
C	3.695987	0.763468	1.901162
H	3.708967	0.366380	2.924272
H	4.675037	0.556083	1.451732
H	3.586795	1.853943	1.963976
C	2.582077	0.724567	-0.349175
H	1.832713	0.256150	-0.997545
H	2.396349	1.803948	-0.343170
H	3.562505	0.559271	-0.812488
C	2.808024	-1.387375	0.987012
H	3.786890	-1.593703	0.536681
H	2.797071	-1.848001	1.982998
H	2.055605	-1.895845	0.373548

3,3-dimethyl-1-butene M product Twisted

further than the structure above
B3LYP/6-31G*
E(RB3LYP) = -262.506000861

Zero-point correction= 0.198932 (Hartree/Particle)
Thermal correction to Energy= 0.208835
Thermal correction to Enthalpy= 0.209779
Thermal correction to Gibbs Free Energy= 0.165325
Sum of electronic and ZPE= -262.307069
Sum of electronic and thermal Energies= -262.297166
Sum of electronic and thermal Enthalpies= -262.296222

Sum of electronic and thermal Free Energies= -262.340676

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 131.046 36.943 93.563
```

```
 H,0,-0.190210443,0.0502965361,0.0546302282
 C,0,-0.0489086835,-0.2362545166,1.1033596582
 C,0,1.167541137,0.4883756227,1.734750188
 B,0,0.8480067987,1.9960735746,2.02140955
 H,0,0.0549616751,-1.3254025032,1.1341532294
 C,0,2.5476000413,0.1630864315,1.0684472512
 H,0,1.2271014582,0.1056058746,2.7790693717
 H,0,-0.2409905762,2.2843339576,2.4331554661
 H,0,-0.9694187848,0.0245280811,1.6360032452
 H,0,1.6414765013,2.8846507253,1.9030182444
 C,0,3.6860695712,0.6889799236,1.9664488093
 H,0,3.665072958,0.2073594335,2.9528275063
 H,0,4.6634319517,0.4769489815,1.5160928153
 H,0,3.62008022,1.7711031631,2.1195069752
 C,0,2.6509488942,0.8302833388,-0.3182935254
 H,0,1.8645435634,0.4791963731,-0.9968811531
 H,0,2.5713095053,1.9212996263,-0.2430173484
 H,0,3.6147590708,0.6004509505,-0.7890256434
 C,0,2.7406678612,-1.3599152379,0.9065360973
 H,0,3.7527501983,-1.5813340324,0.5462251762
 H,0,2.6079178092,-1.8822349675,1.8628439079
 H,0,2.0374442727,-1.7921733364,0.1868949506
```

Table B.1 CCSD(T) Energies for the hydroboration of alkenes

CCSD(T)	aug-cc-pvdz E	aug-cc-pvdz E+ZPE	aug-cc-pvtz E	aug-cc-pvtz E+ZPE	Relative E aug-cc-pvtz	Relative E+ZPE aug-cc-pvtz
BH_3	-26.51255	-26.48605	-26.539	-26.513	0	0
propene	-117.57779	-117.49772	-117.69021	-117.61013	0	0
INT	-144.11042	-143.99781	-144.250904	-144.13829	-8.8	-9.5
TSA	-144.10975	-143.99732	-144.2506139	-144.13818	-8.5	-9.4
TSM	-144.10975	-143.99321	-144.2506139	-144.13432	-5.9	-7.0
A	-144.14328	-144.02925	-144.282465	-144.16843	-28.5	-28.4
M	-144.14108	-144.02691	-144.280373	-144.16620	-27.1	-27.0
Butene Out of Plane	-156.78338	-156.67436	-156.93245	-156.82344	0	0
Butene In Plane	-156.78307	-156.67393	-156.93237	-156.82323	0	0
INT out	-183.31640	-183.17513	-183.49366	-183.35240	-9.2	-10.0
INT anti	-183.31639	-183.17492	-183.49343	-183.35196	-9.1	-9.7
TSA out	-183.31632	-183.17534	-183.49372	-183.35274	-9.4	-10.2
TSA anti	-183.31588	-183.17466	-183.49330	-183.35209	-8.9	-9.8
TSM out	-183.31257	-183.17126	-183.49024	-183.34893	-6.8	-7.8
TSM anti	-183.31227	-183.17102	-183.48993	-183.34868	-6.7	-7.7
A out	-183.34764	-183.20445	-183.52365	-183.38046	-27.6	-27.6
A out twisted	-183.34919	-183.20677	-183.52511	-183.38269	-29.1	-29.0
A out gauche	-183.34954	-183.20686	-183.52534	-183.38266	-29.1	-29.0
A anti	-183.34683	-183.20361	-183.52286	-183.37963	-27.1	-27.1
A anti twisted	-183.34839	-183.20573	-183.52435	-183.38170	-28.4	-28.4
A anti gauche	-183.34844	-183.20559	-183.52428	-183.38143	-28.4	-28.2
M out	-183.34770	-183.20479	-183.52358	-183.38067	-27.8	-27.8
M anti	-183.34623	-183.20339	-183.52225	-183.37940	-27.0	-27.0
Hexene out of plane	-235.19561	-235.02932	-235.41801	-235.25171	0	0
A INT out	-261.72874	-261.53024	-261.97918	-261.78068	-9.3	-10.0
A INT anti	-261.72895	-261.53022	-261.97919	-261.78046	-9.3	-9.9
M INT out	-261.72874	-261.53021	-	-	-9.3	-
M INT anti	-261.72895	-261.53022	-	-	-9.3	-
TSA out	-261.72862	-261.53040	-261.97924	-261.78102	-9.4	-10.2
TSA anti	-261.72839	-261.52990	-261.97903	-261.78054	-9.1	-9.9
TSM out	-261.72493	-261.52640	-261.97579	-261.77726	-6.9	-7.9
TSM anti	-261.72474	-261.52623	-261.975601	-261.77710	-6.8	-7.8
A out	-261.75980	-261.55937	-	-	-27.6	-
A out twisted	-261.76137	-261.56172	-262.01051	-261.81086	-29.1	-29.0
A out gauche	-261.76173	-261.56181	-262.01078	-261.81085	-29.1	-29.0
A anti	-261.75913	-261.55866	-262.00831	-261.80784	-27.2	-27.1
A anti twisted	-261.76067	-261.56078	-262.00981	-261.80992	-28.5	-28.4
M out	-261.76019	-261.56005	-262.00925	-261.80911	-28.0	-27.9
M anti	-261.75862	-261.55854	-262.00777	-261.80770	-27.1	-27.0
Octene out of plane	-313.60786	-313.38435	-	-	0	-

Table B.1 cont.

CCSD(T)	aug-cc-pvdz E	aug-cc-pvdz E+ZPE	aug-cc-pvtz E	aug-cc-pvtz E+ZPE	Relative E aug-cc-pvtz	Relative E+ZPE aug-cc-pvtz
A INT anti	-340.14126	-339.88534	-	-	-9.4	-
M INT out	-340.13703	-339.88531	-	-	-9.4	-
M INT anti	-340.14127	-339.88535	-	-	-9.4	-
TSA out	-340.14091	-339.88549	-	-	-9.5	-
TSA anti	-340.14070	-339.88504	-	-	-9.2	-
TSM out	-340.13720	-339.88149	-	-	-7.0	-
TSM anti	-340.13703	-339.88135	-	-	-6.9	-
A out	-340.17397	-339.91443	-	-	-27.6	-
A out twisted	-340.17361	-339.91677	-	-	-29.1	-
A out gauche	-340.17205	-339.91684	-	-	-29.1	-
A anti	-340.17139	-339.91369	-	-	-27.2	-
A anti twisted	-340.17293	-339.91585	-	-	-28.5	-
M out	-340.17244	-339.91511	-	-	-28.1	-
M anti	-340.17091	-339.91363	-	-	-27.1	-
Dodecene out of plane	-470.43237	-470.09451	-	-	0	-
A INT out	-496.96556	-496.59549	-	-	-9.4	-
A INT anti	-496.96582	-496.59554	-	-	-9.4	-
M INT out	-496.96556	-496.59549	-	-	-9.4	-
M INT anti	-496.96582	-496.59554	-	-	-9.4	-
TSA out	-496.96544	-496.59568	-	-	-9.5	-
TSA anti	-496.96525	-496.59521	-	-	-9.2	-
TSM out	-496.96172	-496.59168	-	-	-7.0	-
TSM anti	-496.96157	-496.59152	-	-	-6.9	-
A out	-496.99657	-496.62460	-	-	-27.6	-
A out twisted	-496.99813	-496.62695	-	-	-29.1	-
A out gauche	-496.99848	-496.62702	-	-	-29.2	-
A anti	-496.99591	-496.62404	-	-	-27.3	-
A anti twisted	-496.99745	-496.62599	-	-	-28.5	-
M out	-496.99696	-496.62529	-	-	-28.1	-
M anti	-496.99543	-496.62382	-	-	-27.1	-
3,3-dimethyl-2-butene	-235.20211	-235.03667	-235.42319	-235.25775	0	0
A INT	-261.73508	-261.53739	-261.98354	-261.78585	-9.2	-9.5
M INT	-261.73507	-261.53740	-	-	-9.2	-
TSA	-261.73479	-261.53733	-261.98353	-261.78607	-9.2	-9.6
TSM	-261.73120	-261.53351	-261.98035	-261.78266	-6.8	-7.5
A	-261.76658	-261.56710	-	-	-27.8	-
A twisted	-261.76788	-261.56914	-262.01544	-261.81670	-29.1	-28.8
M	-261.76473	-261.56580	-262.01208	-261.81314	-27.0	-26.6
M twisted	-261.76499	-261.56578	-262.01247	-261.81326	-27.0	-26.7

Table B.2 CCSD(T)/aug-cc-pvtz energies for selected structures

CCSD(T)/aug-cc-pvqz	**Potential E**	**Relative E**
BH_3	-26.545123	0
propene	-117.718677	0
INT	-144.285478	-13.6
TSA	-144.285580	-13.7
TSM	-144.281762	-11.3
Butene	-156.9702597	0
INT	-183.5373791	-13.8
TSA	-183.5375532	-13.9
TSM	-183.5341261	-11.8

Calculated Structures for the Thioboration of Alkynes

298K
all structures below use chlorocatecholborane as the electrophile

Chlorocatecholborane

*B3LYP-D3/6-31+G** PCM(toluene)*

E(RB3LYP) = -866.710762259

Zero-point correction= 0.094441 (Hartree/Particle)
Thermal correction to Energy= 0.101690
Thermal correction to Enthalpy= 0.102634
Thermal correction to Gibbs Free Energy= 0.061860
Sum of electronic and ZPE= -866.616321
Sum of electronic and thermal Energies= -866.609072
Sum of electronic and thermal Enthalpies= -866.608128
Sum of electronic and thermal Free Energies= -866.648902

```
      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 63.812 28.236 85.816
```

C,0,-0.0200799947,0.,-0.008716364
C,0,-0.0646267346,0.,1.3742570282
C,0,1.1749370718,0.,2.035087767
C,0,2.3844600188,0.,1.3255535618

```
C,0,2.412547373,0.,-0.0788847656
C,0,1.1836803379,0.,-0.7148946678
H,0,-1.0065834829,0.,1.9110424102
H,0,1.1937392117,0.,3.1202045505
H,0,3.3224304251,0.,1.8714770765
H,0,3.3407622663,0.,-0.6391016234
O,0,0.9097783023,0.,-2.0753119568
B,0,-0.4698947429,0.,-2.15457076
O,0,-1.0739091594,0.,-0.9116306843
Cl,0,-1.3550388924,0.,-3.6637245719
```

*ωB97xD/6-31+G** PCM(toluene)*

```
E(RwB97XD) = -866.545379566

Zero-point correction= 0.095815 (Hartree/Particle)
Thermal correction to Energy= 0.102974
Thermal correction to Enthalpy= 0.103918
Thermal correction to Gibbs Free Energy= 0.063303
Sum of electronic and ZPE= -866.449564
Sum of electronic and thermal Energies= -866.442405
Sum of electronic and thermal Enthalpies= -866.441461
Sum of electronic and thermal Free Energies= -866.482077

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 64.617 27.798 85.483

C,0,-0.0182199316,0.,-0.0101532194
C,0,-0.0624671224,0.,1.3687327924
C,0,1.1730056993,0.,2.0266879423
C,0,2.3781220104,0.,1.3197259467
C,0,2.4064828116,0.,-0.0796985332
C,0,1.1812791384,0.,-0.7137571046
H,0,-1.0034409876,0.,1.9060986396
H,0,1.1926366041,0.,3.1111928318
H,0,3.3152431854,0.,1.8659510938
H,0,3.334578949,0.,-0.6389897159
O,0,0.9110762424,0.,-2.0661607176
B,0,-0.4634725385,0.,-2.1438078562
O,0,-1.066657049,0.,-0.9061747101
Cl,0,-1.3459650114,0.,-3.6488583895
```

ωB97xD/6-311+G(2d,p) PCM(toluene)

E(RwB97XD) = -866.670745453

Zero-point correction= 0.095411 (Hartree/Particle)
Thermal correction to Energy= 0.102559
Thermal correction to Enthalpy= 0.103503
Thermal correction to Gibbs Free Energy= 0.062914
Sum of electronic and ZPE= -866.575334
Sum of electronic and thermal Energies= -866.568186
Sum of electronic and thermal Enthalpies= -866.567242
Sum of electronic and thermal Free Energies= -866.607831

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 64.357 27.784 85.427

C,0,-0.0142518312,0.,-0.0093526195
C,0,-0.0574611075,0.,1.3639995163
C,0,1.1728128811,0.,2.0204983783
C,0,2.3727637033,0.,1.3166341504
C,0,2.4002802066,0.,-0.0776082429
C,0,1.1804953889,0.,-0.7102417983
H,0,-0.9965237484,0.,1.9012462644
H,0,1.1922393838,0.,3.1030924669
H,0,3.3081536634,0.,1.8619932062
H,0,3.3275719422,0.,-0.6349329909
O,0,0.9113557676,0.,-2.0608668097
B,0,-0.4605911192,0.,-2.1385110666
O,0,-1.062034872,0.,-0.903076602
Cl,0,-1.3426082585,0.,-3.6420848526

ωB97xD/6-311+G(2df,p) PCM(toluene)

E(RwB97XD) = -866.684856448

Zero-point correction= 0.095556 (Hartree/Particle)
Thermal correction to Energy= 0.102679
Thermal correction to Enthalpy= 0.103623
Thermal correction to Gibbs Free Energy= 0.063085
Sum of electronic and ZPE= -866.589301
Sum of electronic and thermal Energies= -866.582178
Sum of electronic and thermal Enthalpies= -866.581234
Sum of electronic and thermal Free Energies= -866.621771

```
     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 64.432 27.691 85.318
```

```
 C,0,-0.014175221,0.,-0.0094047504
 C,0,-0.0571774627,0.,1.3633651463
 C,0,1.1725782464,0.,2.0192660036
 C,0,2.3718028951,0.,1.3158313216
 C,0,2.3995941851,0.,-0.0776662877
 C,0,1.1804220897,0.,-0.7102028329
 H,0,-0.9960627439,0.,1.900707083
 H,0,1.1922326052,0.,3.1017985427
 H,0,3.3070260109,0.,1.8613629118
 H,0,3.3268869162,0.,-0.634782421
 O,0,0.9110762552,0.,-2.0590043878
 B,0,-0.4607420437,0.,-2.1387746304
 O,0,-1.060263381,0.,-0.9024163581
 Cl,0,-1.3409963514,0.,-3.6392903406
```

ωB97xD/6-311+G(2d,p) SMD(toluene)

```
E(RwB97XD) = -866.678540465
```

```
Zero-point correction= 0.095549 (Hartree/Particle)
Thermal correction to Energy= 0.102674
Thermal correction to Enthalpy= 0.103618
Thermal correction to Gibbs Free Energy= 0.063095
Sum of electronic and ZPE= -866.582992
Sum of electronic and thermal Energies= -866.575867
Sum of electronic and thermal Enthalpies= -866.574923
Sum of electronic and thermal Free Energies= -866.615445
```

```
     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 64.429 27.720 85.287
```

```
 C,0,-0.0144323817,0.,-0.0095719271
 C,0,-0.0577232913,0.,1.3637677366
 C,0,1.1724997228,0.,2.0199652637
 C,0,2.3722635926,0.,1.3159460256
 C,0,2.4000533726,0.,-0.0779963669
 C,0,1.1802793531,0.,-0.7105070533
 H,0,-0.9970102159,0.,1.9013286527
 H,0,1.1922797749,0.,3.1027168823
```

```
 H,0,3.3077865784,0.,1.8615511615
 H,0,3.3281572393,0.,-0.6346924906
 O,0,0.9120651407,0.,-2.0601394778
 B,0,-0.4595788273,0.,-2.1375583049
 O,0,-1.0613427905,0.,-0.902480376
 Cl,0,-1.3430952677,0.,-3.6415407257
```

ωB97xD/6-311+G(2df,p) SMD(toluene)

E(RwB97XD) = -866.692641889

```
Zero-point correction= 0.095697 (Hartree/Particle)
Thermal correction to Energy= 0.102797
Thermal correction to Enthalpy= 0.103741
Thermal correction to Gibbs Free Energy= 0.063270
Sum of electronic and ZPE= -866.596945
Sum of electronic and thermal Energies= -866.589845
Sum of electronic and thermal Enthalpies= -866.588901
Sum of electronic and thermal Free Energies= -866.629372
```

```
     E      CV        S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 64.506 27.627 85.179
```

```
 C,0,-0.0143521506,0.,-0.0096134374
 C,0,-0.0574334361,0.,1.3631401671
 C,0,1.1722680519,0.,2.0187328151
 C,0,2.3712990325,0.,1.315145196
 C,0,2.3993631541,0.,-0.0780475967
 C,0,1.1802028477,0.,-0.7104591517
 H,0,-0.9965401485,0.,1.9007939362
 H,0,1.192280957,0.,3.1014232464
 H,0,3.3066574694,0.,1.860919457
 H,0,3.3274604384,0.,-0.6345408664
 O,0,0.9117884678,0.,-2.0582885023
 B,0,-0.4597314427,0.,-2.1378302939
 O,0,-1.0595845915,0.,-0.9018223692
 Cl,0,-1.3414766492,0.,-3.6387636001
```

*PBEPBE/6-31+G** PCM(toluene)*

E(RPBE-PBE) = -866.016393623

```
Zero-point correction= 0.091932 (Hartree/Particle)
```

```
Thermal correction to Energy= 0.099384
Thermal correction to Enthalpy= 0.100329
Thermal correction to Gibbs Free Energy= 0.059209
Sum of electronic and ZPE= -865.924461
Sum of electronic and thermal Energies= -865.917009
Sum of electronic and thermal Enthalpies= -865.916065
Sum of electronic and thermal Free Energies= -865.957185

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 62.365 29.149 86.544

 C,0,-0.0258610259,0.,-0.0111813922
 C,0,-0.0700873902,0.,1.3788220208
 C,0,1.174947153,0.,2.0408534555
 C,0,2.3894944485,0.,1.3283966599
 C,0,2.4192334893,0.,-0.0813884419
 C,0,1.1843755354,0.,-0.7211378014
 H,0,-1.0179580691,0.,1.9220012226
 H,0,1.1940699988,0.,3.1342002013
 H,0,3.3344933776,0.,1.8786150065
 H,0,3.3559009689,0.,-0.6436721856
 O,0,0.9156126707,0.,-2.0878989367
 B,0,-0.4748651614,0.,-2.1630415263
 O,0,-1.0877395977,0.,-0.9126758576
 Cl,0,-1.3594143978,0.,-3.6711034249
```

PBEPBE/6-311+G(2d,p) PCM(toluene)

```
E(RPBE-PBE) = -866.142577637

Zero-point correction= 0.091649 (Hartree/Particle)
Thermal correction to Energy= 0.099089
Thermal correction to Enthalpy= 0.100033
Thermal correction to Gibbs Free Energy= 0.058938
Sum of electronic and ZPE= -866.050929
Sum of electronic and thermal Energies= -866.043489
Sum of electronic and thermal Enthalpies= -866.042545
Sum of electronic and thermal Free Energies= -866.083640

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 62.179 29.112 86.491
```

```
C,0,-0.0218089431,0.,-0.0099327715
C,0,-0.0649300856,0.,1.3742887646
C,0,1.1746832076,0.,2.034094915
C,0,2.3837239928,0.,1.3248437756
C,0,2.4126822481,0.,-0.079135406
C,0,1.1834365042,0.,-0.716938372
H,0,-1.0107972765,0.,1.9172948892
H,0,1.1939926745,0.,3.1253208831
H,0,3.3268010586,0.,1.874173157
H,0,3.3482111288,0.,-0.6397584022
O,0,0.9158208752,0.,-2.0819845722
B,0,-0.4716525532,0.,-2.1576656595
O,0,-1.0826812768,0.,-0.9096997142
Cl,0,-1.3552795547,0.,-3.6641124869
```

PBEPBE/6-311+G(2d,p) SMD(toluene)

E(RPBE-PBE) = -866.150292527

Zero-point correction= 0.091710 (Hartree/Particle)
Thermal correction to Energy= 0.099128
Thermal correction to Enthalpy= 0.100073
Thermal correction to Gibbs Free Energy= 0.059041
Sum of electronic and ZPE= -866.058583
Sum of electronic and thermal Energies= -866.051164
Sum of electronic and thermal Enthalpies= -866.050220
Sum of electronic and thermal Free Energies= -866.091251

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 62.204 29.070 86.357
```

```
C,0,-0.0216383541,0.,-0.0102224739
C,0,-0.0651189663,0.,1.373874302
C,0,1.174276552,0.,2.033474872
C,0,2.3831112043,0.,1.3240743444
C,0,2.4126596392,0.,-0.0795766406
C,0,1.183509231,0.,-0.7174080634
H,0,-1.0114137459,0.,1.9168269427
H,0,1.193852689,0.,3.1248577119
H,0,3.3261843741,0.,1.8738632659
H,0,3.3491834413,0.,-0.6392605152
O,0,0.9164174749,0.,-2.0812214053
B,0,-0.4707978946,0.,-2.156448013
```

```
 O,0,-1.081742892,0.,-0.9088151813
 Cl,0,-1.356280753,0.,-3.6632301461
```

*M062X/6-31+G** PCM(toluene)*

```
E(RM062X) = -866.510069515

Zero-point correction= 0.095670 (Hartree/Particle)
Thermal correction to Energy= 0.102856
Thermal correction to Enthalpy= 0.103801
Thermal correction to Gibbs Free Energy= 0.063130
Sum of electronic and ZPE= -866.414399
Sum of electronic and thermal Energies= -866.407213
Sum of electronic and thermal Enthalpies= -866.406269
Sum of electronic and thermal Free Energies= -866.446940

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 64.543 27.893 85.599

 C,0,-0.0186530236,0.,-0.009529343
 C,0,-0.063077915,0.,1.3700530223
 C,0,1.1732306599,0.,2.0278618169
 C,0,2.378958451,0.,1.3205637464
 C,0,2.4081943697,0.,-0.0795474047
 C,0,1.1823474628,0.,-0.7141500974
 H,0,-1.005257293,0.,1.9056848565
 H,0,1.1931447172,0.,3.1122815961
 H,0,3.315852614,0.,1.8670316216
 H,0,3.3355666634,0.,-0.6404322831
 O,0,0.9091858273,0.,-2.0665525726
 B,0,-0.4649695173,0.,-2.1458727212
 O,0,-1.0661088035,0.,-0.9076199785
 Cl,0,-1.346212213,0.,-3.6489852591
```

M062x/6-311+G(2d,p) PCM(toluene)

```
E(RM062X) = -866.651429912

Zero-point correction= 0.095489 (Hartree/Particle)
Thermal correction to Energy= 0.102654
Thermal correction to Enthalpy= 0.103598
Thermal correction to Gibbs Free Energy= 0.062964
Sum of electronic and ZPE= -866.555941
```

```
Sum of electronic and thermal Energies= -866.548776
Sum of electronic and thermal Enthalpies= -866.547832
Sum of electronic and thermal Free Energies= -866.588466

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 64.416 27.817 85.521
```

```
 C,0,-0.0149191612,0.,-0.0083880513
 C,0,-0.0583265793,0.,1.3656940262
 C,0,1.1733064356,0.,2.0221367892
 C,0,2.3739828918,0.,1.3178327934
 C,0,2.4020588541,0.,-0.077528259
 C,0,1.1814654655,0.,-0.7102159606
 H,0,-0.9978483839,0.,1.9009061054
 H,0,1.1930627356,0.,3.1038540062
 H,0,3.3085344765,0.,1.8629412081
 H,0,3.3277220034,0.,-0.6363758008
 O,0,0.9094085592,0.,-2.0620059682
 B,0,-0.4615511993,0.,-2.1402752642
 O,0,-1.0621803103,0.,-0.9054177922
 Cl,0,-1.3425137877,0.,-3.6423688321
```

M062x/6-311+G(2d,p) SMD(toluene)

```
E(RM062X) = -866.659281108

Zero-point correction= 0.095616 (Hartree/Particle)
Thermal correction to Energy= 0.102758
Thermal correction to Enthalpy= 0.103702
Thermal correction to Gibbs Free Energy= 0.063136
Sum of electronic and ZPE= -866.563665
Sum of electronic and thermal Energies= -866.556523
Sum of electronic and thermal Enthalpies= -866.555579
Sum of electronic and thermal Free Energies= -866.596145

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 64.481 27.755 85.378
```

```
 C,0,-0.0147801564,0.,-0.0087099457
 C,0,-0.0585266401,0.,1.3653561554
 C,0,1.1729361022,0.,2.0216377322
 C,0,2.3734269353,0.,1.3171639025
```

C,0,2.4019915394,0.,-0.0779333963
C,0,1.1815026618,0.,-0.7107003735
H,0,-0.9984587753,0.,1.9006589755
H,0,1.1929199538,0.,3.1035655902
H,0,3.3080627924,0.,1.862628617
H,0,3.3286685963,0.,-0.6359097921
O,0,0.9100490928,0.,-2.0614731618
B,0,-0.4607445425,0.,-2.1392058715
O,0,-1.0613511958,0.,-0.9047039243
Cl,0,-1.343494364,0.,-3.6415855076

*TPSSTPSS/6-31+G** PCM(toluene)*

E(RTPSS-TPSS) = -866.778055784

Zero-point correction= 0.092898 (Hartree/Particle)
Thermal correction to Energy= 0.100301
Thermal correction to Enthalpy= 0.101245
Thermal correction to Gibbs Free Energy= 0.060201
Sum of electronic and ZPE= -866.685158
Sum of electronic and thermal Energies= -866.677755
Sum of electronic and thermal Enthalpies= -866.676811
Sum of electronic and thermal Free Energies= -866.717854

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 62.940 28.880 86.383
```

C,0,-0.0226380528,0.,-0.0087367175
C,0,-0.0695204647,0.,1.379617007
C,0,1.1751569344,0.,2.0402707696
C,0,2.3888800307,0.,1.3282612125
C,0,2.4195354657,0.,-0.0805672985
C,0,1.1848624226,0.,-0.7170786761
H,0,-1.0124415888,0.,1.9192045421
H,0,1.1947577494,0.,3.127862955
H,0,3.3286361496,0.,1.8760894496
H,0,3.3506400091,0.,-0.6402906944
O,0,0.9147317817,0.,-2.0875983571
B,0,-0.4742235981,0.,-2.1621155669
O,0,-1.087013147,0.,-0.9134187839
Cl,0,-1.3591616919,0.,-3.6707108413

*m11/6-31+G** PCM(toluene)*

E(RM11) = -866.450660055

Zero-point correction= 0.095040 (Hartree/Particle)
Thermal correction to Energy= 0.102231
Thermal correction to Enthalpy= 0.103175
Thermal correction to Gibbs Free Energy= 0.062495
Sum of electronic and ZPE= -866.355620
Sum of electronic and thermal Energies= -866.348429
Sum of electronic and thermal Enthalpies= -866.347485
Sum of electronic and thermal Free Energies= -866.388165

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 64.151 27.950 85.619

C,0,-0.0174472049,0.,-0.0078580932
C,0,-0.0620951944,0.,1.3711821093
C,0,1.1737165095,0.,2.0286450629
C,0,2.3794573314,0.,1.3213814574
C,0,2.4087353562,0.,-0.078115058
C,0,1.1832172308,0.,-0.7121970204
H,0,-1.0089400338,0.,1.9091867483
H,0,1.1935875824,0.,3.1185533564
H,0,3.3210863469,0.,1.8705957818
H,0,3.3404345167,0.,-0.6419498335
O,0,0.9083102683,0.,-2.0677527835
B,0,-0.4687749823,0.,-2.1525765267
O,0,-1.0666218977,0.,-0.9091632324
Cl,0,-1.352463829,0.,-3.6591429683

*BP86/6-31+G** PCM(toluene)*

E(RB-P86) = -866.731604605

Zero-point correction= 0.091590 (Hartree/Particle)
Thermal correction to Energy= 0.099065
Thermal correction to Enthalpy= 0.100009
Thermal correction to Gibbs Free Energy= 0.058842
Sum of electronic and ZPE= -866.640014
Sum of electronic and thermal Energies= -866.632540
Sum of electronic and thermal Enthalpies= -866.631596
Sum of electronic and thermal Free Energies= -866.672763

```
     E       CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 62.164 29.241 86.644
```

```
 C,0,-0.026078252,0.,-0.0101104403
 C,0,-0.0711255499,0.,1.3810208495
 C,0,1.1756951279,0.,2.0439764851
 C,0,2.3918607581,0.,1.3305674951
 C,0,2.4216504313,0.,-0.0812340572
 C,0,1.1854091623,0.,-0.7208011637
 H,0,-1.0205449558,0.,1.9220416376
 H,0,1.1946441699,0.,3.137878556
 H,0,3.3374197837,0.,1.880921274
 H,0,3.3571957769,0.,-0.645913908
 O,0,0.9158293641,0.,-2.0905014316
 B,0,-0.4764952501,0.,-2.1658352047
 O,0,-1.0901126175,0.,-0.9137668189
 Cl,0,-1.3631459489,0.,-3.6774542728
```

*B97D3/6-31+G** PCM(toluene)*
E(RB97D3) = -866.447317625

```
Zero-point correction= 0.092261 (Hartree/Particle)
Thermal correction to Energy= 0.099698
Thermal correction to Enthalpy= 0.100643
Thermal correction to Gibbs Free Energy= 0.059517
Sum of electronic and ZPE= -866.355056
Sum of electronic and thermal Energies= -866.347619
Sum of electronic and thermal Enthalpies= -866.346675
Sum of electronic and thermal Free Energies= -866.387800
```

```
     E       CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 62.562 29.045 86.555
```

```
 C,0,-0.0240060077,0.,-0.0091708612
 C,0,-0.0679570255,0.,1.3792748748
 C,0,1.1764678573,0.,2.042303987
 C,0,2.3899839526,0.,1.3304551039
 C,0,2.4186404089,0.,-0.0792934637
 C,0,1.1853476584,0.,-0.7186382853
 H,0,-1.0118294873,0.,1.9200075792
 H,0,1.1946775354,0.,3.1311621464
```

```
H,0,3.3315201911,0.,1.8776920273
H,0,3.3512916886,0.,-0.6391582415
O,0,0.9141423042,0.,-2.0869592165
B,0,-0.4770736754,0.,-2.1666881008
O,0,-1.0861355183,0.,-0.9134669149
Cl,0,-1.3628678823,0.,-3.6767316349
```

*B3PW91/6-31+G** PCM(toluene)*

E(RB3PW91) = -866.495851320

```
Zero-point correction= 0.094873 (Hartree/Particle)
Thermal correction to Energy= 0.102109
Thermal correction to Enthalpy= 0.103053
Thermal correction to Gibbs Free Energy= 0.062309
Sum of electronic and ZPE= -866.400979
Sum of electronic and thermal Energies= -866.393742
Sum of electronic and thermal Enthalpies= -866.392798
Sum of electronic and thermal Free Energies= -866.433542
```

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 64.074 28.160 85.754
```

```
C,0,-0.0202333464,0.,-0.0102870433
C,0,-0.0643747027,0.,1.3709187938
C,0,1.1731987088,0.,2.0295524091
C,0,2.3804579268,0.,1.3213326003
C,0,2.4094804816,0.,-0.0802921097
C,0,1.1823788998,0.,-0.7158024348
H,0,-1.0066048448,0.,1.9078181603
H,0,1.1926088873,0.,3.1150777364
H,0,3.3185366949,0.,1.8679241628
H,0,3.3379352507,0.,-0.6406754414
O,0,0.9118393294,0.,-2.0697897574
B,0,-0.4656200477,0.,-2.1472437803
O,0,-1.0701227665,0.,-0.9071110246
Cl,0,-1.3472784713,0.,-3.6506332712
```

(o-methylthiophenyl)-2-propyne

*B3LYP-D3/6-31+G** PCM(toluene)*

E(RB3LYP) = -785.266955419

Zero-point correction= 0.166509 (Hartree/Particle)
Thermal correction to Energy= 0.178042
Thermal correction to Enthalpy= 0.178986
Thermal correction to Gibbs Free Energy= 0.127649
Sum of electronic and ZPE= -785.100447
Sum of electronic and thermal Energies= -785.088914
Sum of electronic and thermal Enthalpies= -785.087970
Sum of electronic and thermal Free Energies= -785.139307

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	111.723	41.599	108.048

C,0,0.1528285835,0.0336116338,0.0625360246
H,0,-0.1969186933,-0.204561247,1.0696512963
H,0,1.1507756054,0.4744782708,0.1302901292
H,0,0.1845157803,-0.8862831792,-0.5270754443
S,0,-1.0647758474,1.2189428443,-0.6013718475
C,0,-0.4434836121,1.5669201469,-2.2348643542
C,0,-1.1894247594,2.480766189,-3.0300787374
C,0,-0.7393606942,2.7879430762,-4.3274468818
C,0,0.420962734,2.2132391462,-4.8433151327
C,0,1.1493022874,1.31656742,-4.0577746722
C,0,0.7218949385,0.9962153221,-2.7664398354
C,0,-2.3821707321,3.0840932257,-2.5258154117
H,0,-1.3183774401,3.4867552839,-4.9229053915
H,0,0.7521429043,2.4627051665,-5.8464822667
H,0,2.0556300356,0.8601045242,-4.4450651848
H,0,1.3086144331,0.2975869362,-2.1826862753
C,0,-3.3940637822,3.5876245886,-2.0807612454
C,0,-4.6088305975,4.1874411472,-1.5365229047
H,0,-4.7957080249,3.8281812754,-0.5185153805
H,0,-4.5276988427,5.2797424901,-1.4993597135
H,0,-5.4822442765,3.9358647389,-2.1488487704

*ωB97xD/6-31+G** PCM(toluene)*

E(RwB97XD) = -785.091612851

Zero-point correction= 0.168591 (Hartree/Particle)
Thermal correction to Energy= 0.179964

```
Thermal correction to Enthalpy= 0.180908
Thermal correction to Gibbs Free Energy= 0.130046
Sum of electronic and ZPE= -784.923022
Sum of electronic and thermal Energies= -784.911649
Sum of electronic and thermal Enthalpies= -784.910705
Sum of electronic and thermal Free Energies= -784.961567

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 112.929 41.070 107.048

 C,0,0.1549769574,0.039749805,0.0466637053
 H,0,-0.1895521471,-0.2021178016,1.0537836615
 H,0,1.15154935,0.4815753465,0.114550486
 H,0,0.1852408068,-0.8792482131,-0.5428289935
 S,0,-1.0563962536,1.2146467472,-0.6048120133
 C,0,-0.4419238182,1.5637649656,-2.2306315719
 C,0,-1.1848683883,2.4723559021,-3.0193873959
 C,0,-0.7429318274,2.78287381,-4.3117204621
 C,0,0.4135317943,2.2120633493,-4.8299526255
 C,0,1.141789506,1.3182284603,-4.050147288
 C,0,0.7189930188,0.9963321204,-2.7623993467
 C,0,-2.3811522716,3.0763420501,-2.5113146872
 H,0,-1.3245249238,3.4818746003,-4.9037962089
 H,0,0.7420745198,2.46326785,-5.8328376113
 H,0,2.0471412893,0.8637812482,-4.4401580092
 H,0,1.3075119118,0.2973119835,-2.1804659868
 C,0,-3.3909656521,3.5840643344,-2.0780076576
 C,0,-4.6075900577,4.190339156,-1.5443340217
 H,0,-4.79818667,3.834514511,-0.5279525071
 H,0,-4.5182533367,5.2800628801,-1.5138032635
 H,0,-5.4728528077,3.9361558947,-2.1633022026
```

ωB97xD/6-311+G(2d,p) PCM(toluene)

```
E(RwB97XD) = -785.199541908

Zero-point correction= 0.167748 (Hartree/Particle)
Thermal correction to Energy= 0.179125
Thermal correction to Enthalpy= 0.180069
Thermal correction to Gibbs Free Energy= 0.129149
Sum of electronic and ZPE= -785.031794
Sum of electronic and thermal Energies= -785.020417
Sum of electronic and thermal Enthalpies= -785.019473
```

Sum of electronic and thermal Free Energies= -785.070393

```
     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 112.402 41.122 107.171
```

```
 C,0,0.1447877949,0.0497939994,0.0408557755
 H,0,-0.2045918956,-0.1872809606,1.045170398
 H,0,1.1378513936,0.4931434449,0.1080019252
 H,0,0.1726276626,-0.8661494249,-0.5486483899
 S,0,-1.0616693467,1.2234413806,-0.6152449353
 C,0,-0.4445654703,1.5682849621,-2.2360958157
 C,0,-1.1829780657,2.4729641826,-3.0234013878
 C,0,-0.7405836279,2.780389637,-4.3100128357
 C,0,0.4117293912,2.2103604951,-4.8237844142
 C,0,1.1351120181,1.3204177729,-4.044886032
 C,0,0.7119005985,1.001491807,-2.7626691164
 C,0,-2.3773797674,3.0758455576,-2.5157800596
 H,0,-1.3194799653,3.4779066094,-4.902967866
 H,0,0.7416119439,2.459604664,-5.8245861494
 H,0,2.03907458,0.8658913812,-4.4327090792
 H,0,1.2971467519,0.3041718177,-2.1794574308
 C,0,-3.3783085603,3.5756076851,-2.0790473371
 C,0,-4.5915361181,4.1767577318,-1.5398311804
 H,0,-4.7767073884,3.8180900255,-0.5255545061
 H,0,-4.5036527782,5.2645430376,-1.5068418877
 H,0,-5.4567781508,3.9226631942,-2.1553636757
```

ωB97xD/6-311+G(2df,p) PCM(toluene)

E(RwB97XD) = -785.213048537

Zero-point correction= 0.167906 (Hartree/Particle)
Thermal correction to Energy= 0.179235
Thermal correction to Enthalpy= 0.180179
Thermal correction to Gibbs Free Energy= 0.129383
Sum of electronic and ZPE= -785.045143
Sum of electronic and thermal Energies= -785.033813
Sum of electronic and thermal Enthalpies= -785.032869
Sum of electronic and thermal Free Energies= -785.083666

```
     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 112.472 40.988 106.910
```

C,0,0.1418365169,0.0533996417,0.0377235222
H,0,-0.2067124833,-0.1843076415,1.0421247382
H,0,1.1359176896,0.4947759978,0.1052920239
H,0,0.1715593079,-0.8633135532,-0.5507740325
S,0,-1.06018786,1.2235590025,-0.6176958837
C,0,-0.4448832146,1.5676205299,-2.2342665873
C,0,-1.1833977824,2.4723594089,-3.0215613224
C,0,-0.7412372946,2.7797021568,-4.3076476628
C,0,0.4103341375,2.2103173029,-4.8216358445
C,0,1.1336562168,1.3208478188,-4.0436111126
C,0,0.7112450657,1.0016495319,-2.7620175611
C,0,-2.3759226897,3.0742210936,-2.514618878
H,0,-1.3203991016,3.4772397976,-4.9002689417
H,0,0.7398357349,2.4598232098,-5.822411612
H,0,2.0375103401,0.8666080976,-4.4318467063
H,0,1.2971278859,0.3042518108,-2.179567212
C,0,-3.3765623189,3.5740464131,-2.0784600611
C,0,-4.5877427349,4.1745588904,-1.5408401201
H,0,-4.7745056327,3.8169919772,-0.5264718587
H,0,-4.5005609626,5.262430996,-1.5080404599
H,0,-5.4532998199,3.9211565172,-2.1562584278

ωB97xD/6-311+G(2d,p) SMD(toluene)

E(RwB97XD) = -785.209957097

Zero-point correction= 0.167995 (Hartree/Particle)
Thermal correction to Energy= 0.179297
Thermal correction to Enthalpy= 0.180241
Thermal correction to Gibbs Free Energy= 0.129863
Sum of electronic and ZPE= -785.041962
Sum of electronic and thermal Energies= -785.030660
Sum of electronic and thermal Enthalpies= -785.029716
Sum of electronic and thermal Free Energies= -785.080094

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	112.510	41.039	106.030

C,0,0.1529706573,0.0451154305,0.038480617
H,0,-0.1906425874,-0.196912958,1.0446705556
H,0,1.1464884433,0.4884478797,0.107837156
H,0,0.1800286164,-0.8724428256,-0.5495552619

S,0,-1.0576523093,1.2178525399,-0.6094563856
C,0,-0.445548855,1.5672468143,-2.2324330049
C,0,-1.1848634515,2.4721317581,-3.0187950201
C,0,-0.743313734,2.7803464706,-4.3058353778
C,0,0.408581635,2.2111725453,-4.8208471292
C,0,1.1326489508,1.3211366548,-4.0428079291
C,0,0.7108210442,1.0012723291,-2.7606430156
C,0,-2.3796860288,3.0759676247,-2.5124305456
H,0,-1.322767789,3.478117021,-4.8984571288
H,0,0.7371763389,2.4615238995,-5.8220763434
H,0,2.0366920896,0.8670317874,-4.4316867109
H,0,1.2976636378,0.3035031502,-2.1788817906
C,0,-3.3816133789,3.5790022124,-2.0809558368
C,0,-4.5944558221,4.1823167353,-1.5471047767
H,0,-4.7837088139,3.8262587496,-0.532090247
H,0,-4.5059629977,5.2706308411,-1.5155680502
H,0,-5.4592446456,3.9282203403,-2.1642177745

ωB97xD/6-311+G(2df,p) SMD(toluene)

E(RwB97XD) = -785.223443942

Zero-point correction= 0.168147 (Hartree/Particle)
Thermal correction to Energy= 0.179400
Thermal correction to Enthalpy= 0.180344
Thermal correction to Gibbs Free Energy= 0.130090
Sum of electronic and ZPE= -785.055297
Sum of electronic and thermal Energies= -785.044044
Sum of electronic and thermal Enthalpies= -785.043100
Sum of electronic and thermal Free Energies= -785.093354

```
     E      CV        S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 112.575 40.906 105.769
```

C,0,0.1496342769,0.0489636125,0.0354113053
H,0,-0.1930181662,-0.1937974298,1.0417430373
H,0,1.1442928454,0.4901560203,0.105234386
H,0,0.1787130356,-0.869473442,-0.5515293314
S,0,-1.0563387493,1.218159695,-0.6120216201
C,0,-0.4458489792,1.5665913082,-2.2306323962
C,0,-1.185149956,2.4715389895,-3.0171486895
C,0,-0.7438939841,2.779688037,-4.3036211679

C,0,0.4072580378,2.2111456828,-4.8188423948
C,0,1.1312055206,1.3215938095,-4.0416239849
C,0,0.7101739597,1.0014678649,-2.7600884544
C,0,-2.3780712436,3.0742985157,-2.5113568425
H,0,-1.3236924876,3.4774961814,-4.8958182877
H,0,0.735489536,2.4617398575,-5.8200399766
H,0,2.0351487315,0.8677223866,-4.4308346337
H,0,1.2976210364,0.3036287089,-2.1790664022
C,0,-3.3797151572,3.5773731283,-2.0803849449
C,0,-4.5905606641,4.179950824,-1.5479331419
H,0,-4.7812098411,3.8248484,-0.5328373618
H,0,-4.5027617835,5.2683593964,-1.5165386182
H,0,-5.4556649682,3.9264874534,-2.1649244801

*PBEPBE/6-31+G** PCM(toluene)*

E(RPBE-PBE) = -784.552097543

Zero-point correction= 0.162040 (Hartree/Particle)
Thermal correction to Energy= 0.173855
Thermal correction to Enthalpy= 0.174799
Thermal correction to Gibbs Free Energy= 0.123131
Sum of electronic and ZPE= -784.390057
Sum of electronic and thermal Energies= -784.378242
Sum of electronic and thermal Enthalpies= -784.377298
Sum of electronic and thermal Free Energies= -784.428967

```
     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.096 42.801 108.746
```

C,0,0.1558328692,0.0316078602,0.0622738762
H,0,-0.1993397087,-0.2060079519,1.0762008941
H,0,1.16153527,0.4741387578,0.1350682648
H,0,0.1874185241,-0.8976750265,-0.5276461146
S,0,-1.0598289212,1.2157107059,-0.6019218158
C,0,-0.437249076,1.560606634,-2.2309457929
C,0,-1.1918463546,2.4805147924,-3.0259792304
C,0,-0.7402334981,2.7900902245,-4.3306009927
C,0,0.4247197119,2.2139556694,-4.8503316137
C,0,1.158938946,1.3126166343,-4.0637789412
C,0,0.7327881154,0.9885028337,-2.7664921136
C,0,-2.3820319338,3.0783088842,-2.514005673
H,0,-1.3263396202,3.4946932698,-4.9276207689

H,0,0.756473791,2.4668311316,-5.8614091028
H,0,2.0719182879,0.8538921523,-4.4561796038
H,0,1.3232518731,0.2841107838,-2.1763167889
C,0,-3.405971884,3.5912498831,-2.0707123111
C,0,-4.6201868526,4.1951970934,-1.5358963559
H,0,-4.818471283,3.8402032259,-0.5099672451
H,0,-4.5387728682,5.2956518225,-1.5016077303
H,0,-5.4989943882,3.9437396196,-2.1549848405

PBEPBE/6-311+G(2d,p) PCM(toluene)

E(RPBE-PBE) = -784.660623077

Zero-point correction= 0.161333 (Hartree/Particle)
Thermal correction to Energy= 0.173140
Thermal correction to Enthalpy= 0.174084
Thermal correction to Gibbs Free Energy= 0.122442
Sum of electronic and ZPE= -784.499290
Sum of electronic and thermal Energies= -784.487483
Sum of electronic and thermal Enthalpies= -784.486539
Sum of electronic and thermal Free Energies= -784.538181

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.647 42.834 108.690

C,0,0.1418788842,0.0448966062,0.0552701479
H,0,-0.2192223193,-0.1868636409,1.0657988484
H,0,1.1436277295,0.4890461286,0.1273981781
H,0,0.1707463138,-0.881031999,-0.5344711995
S,0,-1.0666680169,1.2270639682,-0.6153891029
C,0,-0.4395017611,1.5655945634,-2.237966625
C,0,-1.1892298002,2.4811283163,-3.0311156369
C,0,-0.7369556179,2.7871998219,-4.3294500642
C,0,0.4237087965,2.2116451067,-4.8440561655
C,0,1.1527506124,1.3144152381,-4.0583849256
C,0,0.7259213818,0.9936709231,-2.7670828506
C,0,-2.3770650115,3.0770817298,-2.518811317
H,0,-1.3197473154,3.4901439091,-4.9279193418
H,0,0.7571229121,2.4622264181,-5.8528197453
H,0,2.064176907,0.8556590526,-4.4484207167
H,0,1.3124349077,0.2911187115,-2.1748985116
C,0,-3.3918710841,3.5812020398,-2.0707023331
C,0,-4.6022126803,4.1790274122,-1.5288351423

H,0,-4.7932738662,3.8201125183,-0.5053776572
H,0,-4.5221507091,5.277167861,-1.4916543859
H,0,-5.4808592629,3.9274343151,-2.1439654533

PBEPBE/6-311+G(2d,p) SMD(toluene)

E(RPBE-PBE) = -784.671062932

Zero-point correction= 0.161464 (Hartree/Particle)
Thermal correction to Energy= 0.173276
Thermal correction to Enthalpy= 0.174220
Thermal correction to Gibbs Free Energy= 0.122810
Sum of electronic and ZPE= -784.509599
Sum of electronic and thermal Energies= -784.497787
Sum of electronic and thermal Enthalpies= -784.496843
Sum of electronic and thermal Free Energies= -784.548253

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.732 42.818 108.201

C,0,0.1481218498,0.0404524392,0.0552703097
H,0,-0.2097379638,-0.1942827795,1.0672375445
H,0,1.1501562138,0.4841528469,0.1309713917
H,0,0.1759963913,-0.8876332884,-0.5317163862
S,0,-1.0624868256,1.2222719483,-0.6115259975
C,0,-0.4396173837,1.5647393705,-2.2359757676
C,0,-1.1906277011,2.4807030557,-3.0280886336
C,0,-0.7391661435,2.7874567912,-4.3266686841
C,0,0.421019206,2.2128353787,-4.8425732835
C,0,1.1508507301,1.3155468378,-4.0579842606
C,0,0.7255145752,0.9937739674,-2.7667184552
C,0,-2.3787892447,3.0772762412,-2.5165004117
H,0,-1.3228523063,3.4906702076,-4.9243446343
H,0,0.7529879213,2.4646096179,-5.8517027928
H,0,2.0622065032,0.857529806,-4.4495014901
H,0,1.3133163562,0.2908575309,-2.1757061224
C,0,-3.3943875845,3.5841183578,-2.0728198063
C,0,-4.603902622,4.1830971686,-1.5348193937
H,0,-4.7982181684,3.8262688429,-0.5107527007
H,0,-4.5240571829,5.281715169,-1.498326579
H,0,-5.4827156203,3.9317794904,-2.1506078467

*M062X/6-31+G** PCM(toluene)*

E(RM062X) = -785.032490473

Zero-point correction= 0.168351 (Hartree/Particle)
Thermal correction to Energy= 0.179750
Thermal correction to Enthalpy= 0.180694
Thermal correction to Gibbs Free Energy= 0.129797
Sum of electronic and ZPE= -784.864140
Sum of electronic and thermal Energies= -784.852741
Sum of electronic and thermal Enthalpies= -784.851797
Sum of electronic and thermal Free Energies= -784.902694

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	112.795	41.222	107.122

C,0,0.1467892426,0.0516280867,0.0341551264
H,0,-0.1924149682,-0.1941109489,1.0414382862
H,0,1.1413096836,0.4975894806,0.0961202317
H,0,0.1751424217,-0.8630146281,-0.5611739087
S,0,-1.0692119686,1.2260936975,-0.6095639187
C,0,-0.4454157094,1.5664998811,-2.2311170649
C,0,-1.1830145607,2.4744271755,-3.0262766052
C,0,-0.7368146545,2.7815051538,-4.3177920888
C,0,0.4214325335,2.206326511,-4.8297210003
C,0,1.1450010328,1.3127482213,-4.0436428867
C,0,0.7168966279,0.9944857679,-2.7555798724
C,0,-2.3803323631,3.0788498002,-2.5174511232
H,0,-1.316597324,3.4803278788,-4.9120921443
H,0,0.7548705052,2.4536607674,-5.8318136189
H,0,2.0509900533,0.8555218365,-4.4289356915
H,0,1.3003148447,0.2961164279,-2.167573049
C,0,-3.3892762193,3.5812312774,-2.0743099812
C,0,-4.6063189651,4.1835954621,-1.5323120584
H,0,-4.7898048063,3.8231986595,-0.5170561035
H,0,-4.5177892154,5.2725329489,-1.4993239448
H,0,-5.4721461909,3.9287255427,-2.1488305837

M062x/6-311+G(2d,p) PCM(toluene)

E(RM062X) = -785.157568513

Zero-point correction= 0.167941 (Hartree/Particle)

```
Thermal correction to Energy= 0.179303
Thermal correction to Enthalpy= 0.180247
Thermal correction to Gibbs Free Energy= 0.129487
Sum of electronic and ZPE= -784.989628
Sum of electronic and thermal Energies= -784.978265
Sum of electronic and thermal Enthalpies= -784.977321
Sum of electronic and thermal Free Energies= -785.028081

     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 112.514 41.175 106.834

 C,0,0.1401138316,0.0585906512,0.0294790897
 H,0,-0.2036289835,-0.1822984487,1.0334534381
 H,0,1.1301089849,0.506797034,0.0899415179
 H,0,0.1653325156,-0.8518802784,-0.5663745817
 S,0,-1.0713837173,1.231580979,-0.6179081452
 C,0,-0.4477463985,1.5701480014,-2.2353141081
 C,0,-1.1821291555,2.4746120449,-3.0281665462
 C,0,-0.7359498228,2.7792583519,-4.3145563381
 C,0,0.4183960521,2.2052976632,-4.8230702843
 C,0,1.1382668031,1.3152126332,-4.0386409478
 C,0,0.7104631945,0.9991173494,-2.7555696367
 C,0,-2.3778306303,3.0782329228,-2.5202959111
 H,0,-1.3129703097,3.4761125587,-4.908957754
 H,0,0.7521604432,2.4511283486,-5.8224865242
 H,0,2.0421150694,0.8588035481,-4.4223139859
 H,0,1.2909471027,0.3028668501,-2.1675131567
 C,0,-3.3782737768,3.5740265858,-2.0761339364
 C,0,-4.5921930158,4.1727025008,-1.5304120967
 H,0,-4.7712668776,3.8105171918,-0.5176979846
 H,0,-4.5040950226,5.2590996018,-1.4961127292
 H,0,-5.4568252865,3.9180129103,-2.1442033787
```

M062x/6-311+G(2d,p) SMD(toluene)

```
E(RM062X) = -785.168077529

Zero-point correction= 0.168182 (Hartree/Particle)
Thermal correction to Energy= 0.179458
Thermal correction to Enthalpy= 0.180402
Thermal correction to Gibbs Free Energy= 0.130174
Sum of electronic and ZPE= -784.999896
Sum of electronic and thermal Energies= -784.988620
```

Sum of electronic and thermal Enthalpies= -784.987676
Sum of electronic and thermal Free Energies= -785.037904

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 112.611 41.082 105.714

C,0,0.1498858161,0.0526709188,0.0273251016
H,0,-0.1877800683,-0.1934148772,1.0331492192
H,0,1.1402129358,0.5012389551,0.0895577407
H,0,0.1742513052,-0.8591199207,-0.5675510604
S,0,-1.0663500895,1.2247865056,-0.6113213991
C,0,-0.4483362135,1.5683740351,-2.2308097359
C,0,-1.1841793903,2.4731932399,-3.0223022317
C,0,-0.7394946164,2.7791313702,-4.3091365909
C,0,0.4144465963,2.2064507829,-4.8196166062
C,0,1.1354859823,1.3162444834,-4.036600142
C,0,0.7096994275,0.9986499471,-2.7534251403
C,0,-2.3803505989,3.0775822056,-2.5154254729
H,0,-1.3177478751,3.4763383303,-4.9024990772
H,0,0.7465466218,2.4537283896,-5.8195542519
H,0,2.0394006368,0.8606488217,-4.4219830406
H,0,1.2921923578,0.3018827251,-2.1672063285
C,0,-3.3820568211,3.5773943202,-2.0777689006
C,0,-4.5959175636,4.1796371068,-1.5392450993
H,0,-4.78042266,3.8209972233,-0.5256600113
H,0,-4.5063645982,5.266536478,-1.5072962382
H,0,-5.4595101849,3.9249879591,-2.1554847345

*TPSSTPSS/6-31+G** PCM(toluene)*

E(RTPSS-TPSS) = -785.338802559

Zero-point correction= 0.164279 (Hartree/Particle)
Thermal correction to Energy= 0.176052
Thermal correction to Enthalpy= 0.176996
Thermal correction to Gibbs Free Energy= 0.125283
Sum of electronic and ZPE= -785.174524
Sum of electronic and thermal Energies= -785.162751
Sum of electronic and thermal Enthalpies= -785.161806
Sum of electronic and thermal Free Energies= -785.213519

E CV S

```
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 110.474 42.388 108.839
```

```
 C,0,0.1436646227,0.0399692115,0.0628446968
 H,0,-0.2128017176,-0.1939490527,1.0710268057
 H,0,1.1426631759,0.4847043572,0.1309662785
 H,0,0.1724880009,-0.8815729779,-0.5290650963
 S,0,-1.0738079593,1.2285200336,-0.6079232016
 C,0,-0.4409987898,1.5665975327,-2.2378504459
 C,0,-1.1891713062,2.4843439262,-3.037857677
 C,0,-0.7340610666,2.7904078485,-4.3403376593
 C,0,0.4309460505,2.2109512273,-4.8532526813
 C,0,1.1598798689,1.3110920027,-4.0619886964
 C,0,0.7292392422,0.9909515007,-2.7663404692
 C,0,-2.3798637997,3.0832441764,-2.5274491617
 H,0,-1.3133863152,3.4906850287,-4.938374206
 H,0,0.7655844754,2.4589232682,-5.8584097257
 H,0,2.0686808845,0.8520734698,-4.4476244411
 H,0,1.3139401324,0.2907053898,-2.1762718
 C,0,-3.3983279608,3.5874063454,-2.0740349196
 C,0,-4.6138088822,4.1839398836,-1.521956344
 H,0,-4.7943348819,3.819255188,-0.5020587259
 H,0,-4.5328143688,5.2787132005,-1.4827717166
 H,0,-5.4900984052,3.93097744,-2.1341248134
```

*m11/6-31+G** PCM(toluene)*

```
E(RM11) = -784.949459434
```

```
Zero-point correction= 0.167156 (Hartree/Particle)
Thermal correction to Energy= 0.178591
Thermal correction to Enthalpy= 0.179535
Thermal correction to Gibbs Free Energy= 0.128056
Sum of electronic and ZPE= -784.782304
Sum of electronic and thermal Energies= -784.770869
Sum of electronic and thermal Enthalpies= -784.769924
Sum of electronic and thermal Free Energies= -784.821404
```

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 112.067 41.261 108.347
```

```
 C,0,0.1450612304,0.0539764613,0.0317816979
 H,0,-0.1906908576,-0.1966273667,1.0440979945
```

```
H,0,1.1436914764,0.5029949338,0.0927859928
H,0,0.173013123,-0.8639657119,-0.5675531521
S,0,-1.0740808952,1.2293754998,-0.609296654
C,0,-0.4458109726,1.5676967829,-2.2330503509
C,0,-1.180765102,2.474032105,-3.0288942487
C,0,-0.7346897604,2.7806672618,-4.3192769358
C,0,0.4237572731,2.2044418029,-4.8292056684
C,0,1.1460742591,1.3113111275,-4.0421139994
C,0,0.7163022212,0.9944952261,-2.7546264211
C,0,-2.3814111409,3.0798118766,-2.5181353059
H,0,-1.3165154832,3.4827391402,-4.9173782985
H,0,0.7600911167,2.4520841016,-5.8361710103
H,0,2.0567366228,0.8513700614,-4.4285508949
H,0,1.3002089706,0.293054211,-2.1608928767
C,0,-3.39024322,3.5813005067,-2.0733838205
C,0,-4.6088639325,4.1838356007,-1.5289960571
H,0,-4.7914046101,3.8208765173,-0.5096710809
H,0,-4.5190225235,5.2771353785,-1.4959926884
H,0,-5.4778267952,3.9273334834,-2.1483302215
```

*BP86/6-31+G** PCM(toluene)*

E(RB-P86) = -785.279455215

Zero-point correction= 0.161506 (Hartree/Particle)
Thermal correction to Energy= 0.173328
Thermal correction to Enthalpy= 0.174273
Thermal correction to Gibbs Free Energy= 0.122657
Sum of electronic and ZPE= -785.117949
Sum of electronic and thermal Energies= -785.106127
Sum of electronic and thermal Enthalpies= -785.105183
Sum of electronic and thermal Free Energies= -785.156798

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 108.765 42.889 108.633
```

```
C,0,0.1437517414,0.0376690378,0.0674860621
H,0,-0.2130471316,-0.1990853482,1.0820211317
H,0,1.1504676529,0.4809691857,0.1392218361
H,0,0.1755562938,-0.8919706533,-0.5240344246
S,0,-1.073930476,1.227073476,-0.6047247635
C,0,-0.4400110651,1.5653230795,-2.2366548172
C,0,-1.1902132731,2.4855428901,-3.0387844309
```

C,0,-0.73404154,2.7921458658,-4.3439485021
C,0,0.4331224312,2.2119423943,-4.858511419
C,0,1.1636352342,1.3102386387,-4.0657654646
C,0,0.7324644398,0.9892584937,-2.7675908879
C,0,-2.3814825042,3.0855991446,-2.5298917372
H,0,-1.3174754316,3.4967089049,-4.9448048737
H,0,0.7693880953,2.4616009514,-5.8695575442
H,0,2.077713778,0.8487458974,-4.4540553507
H,0,1.3216578795,0.2848481731,-2.1755174831
C,0,-3.4032737069,3.590301203,-2.0726951644
C,0,-4.6171960631,4.1864430058,-1.5221730771
H,0,-4.8029035383,3.8223849055,-0.4959808326
H,0,-4.5395136277,5.2879914483,-1.4813035702
H,0,-5.5010581888,3.9342083058,-2.1355886869

*B97D3/6-31+G** PCM(toluene)*

E(RB97D3) = -784.992405029

Zero-point correction= 0.162946 (Hartree/Particle)
Thermal correction to Energy= 0.174818
Thermal correction to Enthalpy= 0.175763
Thermal correction to Gibbs Free Energy= 0.123358
Sum of electronic and ZPE= -784.829459
Sum of electronic and thermal Energies= -784.817587
Sum of electronic and thermal Enthalpies= -784.816642
Sum of electronic and thermal Free Energies= -784.869047

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 109.700 42.634 110.296

C,0,0.1429544952,0.0415261971,0.0606701665
H,0,-0.2110431273,-0.1949486826,1.0705147043
H,0,1.1437913959,0.4844739839,0.1292337824
H,0,0.1738273134,-0.8814926043,-0.5306515419
S,0,-1.0719290457,1.2275478794,-0.6086461456
C,0,-0.442205126,1.5669850524,-2.2368672714
C,0,-1.1899650787,2.4849555324,-3.0379330484
C,0,-0.7335180649,2.7899272968,-4.3401265726
C,0,0.431534782,2.2101454552,-4.8524570349
C,0,1.159563414,1.3104522059,-4.0602187196
C,0,0.7277996921,0.9912261901,-2.7648030466
C,0,-2.3802561625,3.085510749,-2.5315154335

```
H,0,-1.3134390899,3.4909956864,-4.9389151102
H,0,0.7672740067,2.4578575802,-5.8587010533
H,0,2.069559002,0.850497706,-4.4456899793
H,0,1.3123247399,0.2908076811,-2.1741291312
C,0,-3.3988465908,3.588495214,-2.0754708723
C,0,-4.6122605155,4.1830872898,-1.5224810181
H,0,-4.7943367488,3.8187792405,-0.5010987698
H,0,-4.5348788623,5.279570013,-1.481034206
H,0,-5.4923394289,3.9315393338,-2.1325336983
```

*B3PW91/6-31+G** PCM(toluene)*

E(RB3PW91) = -785.065188047

```
Zero-point correction= 0.166904 (Hartree/Particle)
Thermal correction to Energy= 0.178442
Thermal correction to Enthalpy= 0.179386
Thermal correction to Gibbs Free Energy= 0.127989
Sum of electronic and ZPE= -784.898284
Sum of electronic and thermal Energies= -784.886746
Sum of electronic and thermal Enthalpies= -784.885802
Sum of electronic and thermal Free Energies= -784.937199
```

```
      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 111.974 41.589 108.174
```

```
C,0,0.1377042154,0.0500043867,0.050827633
H,0,-0.2142381808,-0.1865153231,1.0577562324
H,0,1.136635369,0.4886928061,0.1232594179
H,0,0.1697369909,-0.8729699323,-0.534535169
S,0,-1.067913908,1.2277550219,-0.6150157681
C,0,-0.4434334406,1.5676664527,-2.236488648
C,0,-1.1862927342,2.4794649295,-3.0320060149
C,0,-0.7367720997,2.785709964,-4.3266417548
C,0,0.4218188475,2.2109761387,-4.8398837225
C,0,1.1474979643,1.3160581493,-4.0540504384
C,0,0.7202501561,0.9967875344,-2.7651946392
C,0,-2.3760049121,3.0797673637,-2.5259630546
H,0,-1.3159628913,3.4847608076,-4.9223489972
H,0,0.7544789246,2.4594352187,-5.8431378257
H,0,2.0542355054,0.8588942814,-4.4404782968
H,0,1.3063433007,0.2978371241,-2.1798441909
C,0,-3.3876782019,3.5810934597,-2.0766769358
```

C,0,-4.5976998876,4.1761519652,-1.5295058999
H,0,-4.7801381646,3.8140102387,-0.5120401341
H,0,-4.517175953,5.2681390483,-1.4906918269
H,0,-5.4717799002,3.9242193648,-2.1401939664

Anti TS with ClBcat

*B3LYP-D3/6-31+G** PCM(toluene)*

E(RB3LYP) = -1651.96117864

Zero-point correction= 0.260690 (Hartree/Particle)
Thermal correction to Energy= 0.280209
Thermal correction to Enthalpy= 0.281153
Thermal correction to Gibbs Free Energy= 0.211430
Sum of electronic and ZPE= -1651.700489
Sum of electronic and thermal Energies= -1651.680970
Sum of electronic and thermal Enthalpies= -1651.680026
Sum of electronic and thermal Free Energies= -1651.749749

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	175.834	73.897	146.744

C,0,-2.3890101531,0.3749515604,2.9888652782
H,0,-2.2033945879,0.911544352,3.9225141707
H,0,-3.4642865986,0.3097818732,2.8125722337
H,0,-1.9023595363,0.8953161361,2.1613412583
S,0,-1.678065114,-1.3089666984,3.1909369495
C,0,-1.9709967081,-1.9713780322,1.5526464516
C,0,-1.0615926038,-1.7184449799,0.4864670714
C,0,-1.3281346285,-2.2701799176,-0.7748583703
C,0,-2.4593511541,-3.0604050728,-0.982366349
C,0,-3.3443317496,-3.3142584071,0.0663602456
C,0,-3.0972881457,-2.7701448384,1.3301725473
C,0,0.1113904263,-0.8988832566,0.7630469978
H,0,-0.6409335065,-2.0879484202,-1.5898689534
H,0,-2.644065723,-3.4789084104,-1.9668923024
H,0,-4.223884815,-3.9306513432,-0.0926534771
H,0,-3.782158744,-2.9626879537,2.1493786272
C,0,0.6301525678,-0.4029768976,1.7877615072
C,0,1.459233753,0.3312744763,2.7148410729

```
H,0,0.8798971508,1.0853341685,3.2577004458
H,0,1.9600234713,-0.3311038613,3.4272543471
H,0,2.2214568052,0.8442451758,2.1126480838
B,0,1.2588611161,-0.2651299425,-0.7146391419
O,0,2.4421465218,0.3652995511,-0.2116563319
O,0,1.6231633127,-1.5051405437,-1.330065202
Cl,0,0.1040013596,0.8227852763,-1.6214057389
C,0,2.9325950606,-1.7151848498,-0.9755496782
C,0,3.7211233681,-2.8282308233,-1.2138638898
C,0,5.0497587532,-2.7779503627,-0.7531358281
C,0,5.5447889796,-1.652049078,-0.0851991592
C,0,4.7324482847,-0.5271376318,0.1513205998
C,0,3.4268195424,-0.5892669976,-0.3056383329
H,0,3.3258059524,-3.6939047125,-1.734252956
H,0,5.7002739289,-3.6308945358,-0.920158049
H,0,6.5745629938,-1.6425686944,0.2585145043
H,0,5.1072464198,0.3529696915,0.6631613685
```

*ωB97xD/6-31+G** PCM(toluene)*

E(RwB97XD) = -1651.61899754

Zero-point correction= 0.264034 (Hartree/Particle)
Thermal correction to Energy= 0.283267
Thermal correction to Enthalpy= 0.284211
Thermal correction to Gibbs Free Energy= 0.214897
Sum of electronic and ZPE= -1651.354964
Sum of electronic and thermal Energies= -1651.335731
Sum of electronic and thermal Enthalpies= -1651.334787
Sum of electronic and thermal Free Energies= -1651.404100

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 177.753 72.821 145.883
```

```
C,0,-3.6678030643,-1.8540122974,0.6734500235
H,0,-3.7453213795,-2.5849579467,1.4808647471
H,0,-2.8210034677,-2.1063961274,0.0317152333
H,0,-4.5909502323,-1.8579558376,0.0923106117
S,0,-3.4202983666,-0.2254412221,1.4524917022
C,0,-3.2175363318,0.7836599222,-0.0011207011
C,0,-1.9609041414,0.8954876554,-0.642445556
C,0,-1.8412997997,1.71104395,-1.7697890415
```

```
C,0,-2.9421912763,2.4100247244,-2.2550960343
C,0,-4.1761954368,2.3037282745,-1.6220480449
C,0,-4.3107773601,1.4924035594,-0.4972979955
C,0,-0.8337234842,0.1522307394,-0.0827504423
H,0,-0.879614296,1.8073092769,-2.2573608594
H,0,-2.8296845273,3.04108355,-3.130369271
H,0,-5.0352910237,2.8491682562,-1.9986633271
H,0,-5.2701077412,1.4056799622,0.0015637423
C,0,-0.6242924964,-0.4911353589,0.9650688965
C,0,-0.0851359679,-1.3021957513,2.0295598046
H,0,-0.0061387658,-0.73968014,2.9622799112
H,0,-0.6816823279,-2.2053675672,2.1805521729
H,0,0.9210928404,-1.5953305975,1.7029098089
B,0,0.7831532597,-0.0844853875,-1.070562528
O,0,1.1765628361,1.267044216,-1.3360233072
O,0,1.8094317002,-0.7075580033,-0.2863709518
Cl,0,0.2058260368,-1.0723045643,-2.4972636871
C,0,2.6310958928,0.3113834258,0.1039233659
C,0,3.7032989363,0.2610928258,0.9715901683
C,0,4.3947391026,1.4610242719,1.199041929
C,0,4.0118340965,2.6456829856,0.5722831827
C,0,2.9210292428,2.6835929348,-0.3095069786
C,0,2.2482925404,1.4977811889,-0.5244443047
H,0,3.9978858225,-0.66747735,1.4483733285
H,0,5.24321258,1.4627883831,1.8755076897
H,0,4.5655831263,3.5581195785,0.7679403497
H,0,2.6164194734,3.5990204703,-0.8042366376
```

ωB97xD/6-311+G(2d,p) PCM(toluene)

E(RwB97XD) = -1651.84913175

```
Zero-point correction= 0.262770 (Hartree/Particle)
Thermal correction to Energy= 0.281983
Thermal correction to Enthalpy= 0.282927
Thermal correction to Gibbs Free Energy= 0.213721
Sum of electronic and ZPE= -1651.586362
Sum of electronic and thermal Energies= -1651.567149
Sum of electronic and thermal Enthalpies= -1651.566205
Sum of electronic and thermal Free Energies= -1651.635411

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

Total 176.947 72.885 145.655

C,0,-3.6705311294,-1.8064026879,0.7515255789
H,0,-3.7253824527,-2.5102451206,1.5818192091
H,0,-2.8637463407,-2.0923723114,0.0779486188
H,0,-4.6206896664,-1.7936433302,0.2211832563
S,0,-3.3402908195,-0.170305039,1.4766231111
C,0,-3.1771107065,0.7996997162,-0.0025184167
C,0,-1.9436100454,0.8744626857,-0.6810200903
C,0,-1.8466528003,1.6603137951,-1.8245049507
C,0,-2.9472640981,2.3632200745,-2.2894186513
C,0,-4.1578467712,2.2910761767,-1.619658353
C,0,-4.2700700542,1.5109815386,-0.4772801521
C,0,-0.8197032038,0.1240323987,-0.1341481178
H,0,-0.9021754936,1.7304405823,-2.3443915257
H,0,-2.8530473552,2.9722542846,-3.1799919007
H,0,-5.017887819,2.8409593415,-1.9818424065
H,0,-5.2127972792,1.452137548,0.0518331878
C,0,-0.6280205714,-0.5187682083,0.9089429551
C,0,-0.0896497238,-1.3391490166,1.9632007929
H,0,-0.0133240016,-0.7885224668,2.9009294454
H,0,-0.6830974489,-2.2440766806,2.1021006413
H,0,0.9159369451,-1.6257058055,1.6346125167
B,0,0.806245793,-0.0708729504,-1.1060128105
O,0,1.1864300635,1.2876921484,-1.3384029603
O,0,1.8290340368,-0.6965992103,-0.3256130432
Cl,0,0.25258691,-1.0379128075,-2.5585401615
C,0,2.6309510273,0.3215142167,0.0956586714
C,0,3.6884666231,0.2667482371,0.9722078219
C,0,4.3603861046,1.4649487733,1.2330440096
C,0,3.973309486,2.6525702712,0.6288470457
C,0,2.8973464458,2.6956681809,-0.2627147051
C,0,2.2434407988,1.5122146154,-0.5108321081
H,0,3.9879508791,-0.666108455,1.4333774321
H,0,5.1984395916,1.462590983,1.9192989395
H,0,4.5126410301,3.5653914224,0.8504620724
H,0,2.5892420461,3.6168190997,-0.7406479525

ωB97xD/6-311+G(2df,p) PCM(toluene)

E(RwB97XD) = -1651.87546945

Zero-point correction= 0.263037 (Hartree/Particle)

```
Thermal correction to Energy= 0.282169
Thermal correction to Enthalpy= 0.283113
Thermal correction to Gibbs Free Energy= 0.214118
Sum of electronic and ZPE= -1651.612433
Sum of electronic and thermal Energies= -1651.593301
Sum of electronic and thermal Enthalpies= -1651.592356
Sum of electronic and thermal Free Energies= -1651.661351

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 177.064 72.679 145.212
```

```
 C,0,-3.6756370388,-1.8029046972,0.7458541075
 H,0,-3.7286462345,-2.5109262935,1.5727195363
 H,0,-2.8767774861,-2.0926314838,0.064107074
 H,0,-4.6295462902,-1.7845948762,0.222037481
 S,0,-3.3313795047,-0.176258141,1.4711111527
 C,0,-3.174285736,0.7954181278,-0.0018159986
 C,0,-1.941728473,0.8718223249,-0.6813839051
 C,0,-1.8464891059,1.6577387746,-1.8239213267
 C,0,-2.9478535994,2.3591636095,-2.2870825771
 C,0,-4.1571379158,2.2860253087,-1.6166183849
 C,0,-4.2678254882,1.5061080814,-0.4749368226
 C,0,-0.8201045518,0.1206426525,-0.1339281306
 H,0,-0.9027073041,1.7289487518,-2.3448193523
 H,0,-2.8551333647,2.9685118638,-3.1775010828
 H,0,-5.0176961655,2.8355431895,-1.9778579942
 H,0,-5.2099449711,1.4467481657,0.0552728831
 C,0,-0.6399994723,-0.5258873619,0.9097844427
 C,0,-0.1065723124,-1.348107964,1.9623273906
 H,0,-0.0426416198,-0.804118521,2.9048111085
 H,0,-0.6928979209,-2.2591902287,2.0907519401
 H,0,0.9044966561,-1.6246424433,1.641639897
 B,0,0.8032816145,-0.0648354885,-1.094901972
 O,0,1.1858549826,1.2945444177,-1.3254277626
 O,0,1.8272997568,-0.6863953014,-0.3108531912
 Cl,0,0.2639359153,-1.0317642654,-2.5502099967
 C,0,2.6332031122,0.328544201,0.102686327
 C,0,3.6948173279,0.273929513,0.9732090457
 C,0,4.3713963748,1.4704028301,1.2262770836
 C,0,3.9851126105,2.6563902764,0.6204899523
 C,0,2.9050937006,2.6999804907,-0.2650952977
 C,0,2.2460356714,1.5186037088,-0.5056822945
 H,0,3.9942916388,-0.6581339029,1.4358102641
```

```
H,0,5.213172228,1.4677541155,1.9078792222
H,0,4.5286606872,3.5681160014,0.8359810157
H,0,2.5978622782,3.620506564,-0.7446368348
```

ωB97xD/6-311+G(2d,p) SMD(toluene)

E(RwB97XD) = -1651.86527592

```
Zero-point correction= 0.262918 (Hartree/Particle)
Thermal correction to Energy= 0.282056
Thermal correction to Enthalpy= 0.283000
Thermal correction to Gibbs Free Energy= 0.214005
Sum of electronic and ZPE= -1651.602358
Sum of electronic and thermal Energies= -1651.583220
Sum of electronic and thermal Enthalpies= -1651.582275
Sum of electronic and thermal Free Energies= -1651.651271
```

```
     E      CV       S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 176.993 72.784 145.213
```

```
C,0,-3.6551579525,-1.819970925,0.7405649536
H,0,-3.7188908759,-2.5268621379,1.5686752243
H,0,-2.8368645814,-2.1024264544,0.0789032229
H,0,-4.5972937121,-1.8228771809,0.1942494968
S,0,-3.3606769047,-0.1800434235,1.4701201264
C,0,-3.1872432211,0.7964851677,-0.0043815383
C,0,-1.9491516057,0.8773771616,-0.6743322803
C,0,-1.8468082656,1.6707263632,-1.8121567039
C,0,-2.9445117746,2.377299508,-2.2781879922
C,0,-4.1585346874,2.3004268137,-1.6157981138
C,0,-4.2773440639,1.511273718,-0.4804990086
C,0,-0.8258764694,0.1252156383,-0.1262425865
H,0,-0.9002542718,1.7450634509,-2.3278268787
H,0,-2.8448087732,2.9923036558,-3.1643079107
H,0,-5.0167425783,2.8534333608,-1.9782276178
H,0,-5.2237616121,1.4486120981,0.0419237791
C,0,-0.6365739131,-0.5226928388,0.9144297109
C,0,-0.1155376254,-1.347886911,1.9715688178
H,0,-0.0165891705,-0.7915420409,2.904476428
H,0,-0.7360297499,-2.2335612338,2.1220160965
H,0,0.8792380907,-1.6724610645,1.6443466956
B,0,0.800388742,-0.0687488712,-1.0884102474
O,0,1.183834609,1.2878167948,-1.3296101258
```

O,0,1.8239583208,-0.6899920226,-0.3042579311
Cl,0,0.2575877384,-1.0459735605,-2.5420931582
C,0,2.631967227,0.3269178137,0.1031261799
C,0,3.6948447391,0.2753650804,0.9733630327
C,0,4.374307791,1.472654124,1.2183922827
C,0,3.9895802252,2.6563530176,0.6055420138
C,0,2.9081480479,2.6965350035,-0.2794570341
C,0,2.2465678022,1.5142206829,-0.511777562
H,0,3.9936728197,-0.6542639564,1.4420250876
H,0,5.2167225479,1.4728700504,1.8996275904
H,0,4.5353874592,3.5684988276,0.8148380161
H,0,2.6019556482,3.6149062903,-0.7645450658

ωB97xD/6-311+G(2df,p) SMD(toluene)

E(RwB97XD) = -1651.89160588

Zero-point correction= 0.263128 (Hartree/Particle)
Thermal correction to Energy= 0.282230
Thermal correction to Enthalpy= 0.283174
Thermal correction to Gibbs Free Energy= 0.213925
Sum of electronic and ZPE= -1651.628478
Sum of electronic and thermal Energies= -1651.609376
Sum of electronic and thermal Enthalpies= -1651.608432
Sum of electronic and thermal Free Energies= -1651.677681

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	177.102	72.605	145.747

C,0,-3.7030379321,-1.7896497447,0.7611816312
H,0,-3.7706846445,-2.4959386643,1.5895696683
H,0,-2.915264611,-2.103933465,0.0767207246
H,0,-4.6590934102,-1.7586309255,0.2401136042
S,0,-3.328929683,-0.1670061872,1.4778973188
C,0,-3.1652468359,0.7978816962,0.0001301317
C,0,-1.9337402187,0.8624740736,-0.6832785214
C,0,-1.8370916549,1.6441553127,-1.8287410456
C,0,-2.9339415935,2.3534111666,-2.2904111318
C,0,-4.1411953103,2.2923277217,-1.6156801084
C,0,-4.254079799,1.5167447513,-0.4714958562
C,0,-0.815290992,0.1030341366,-0.1389449003
H,0,-0.8956681152,1.7068805176,-2.3550358173
H,0,-2.8387673272,2.9586037532,-3.1836675862

```
H,0,-4.9986662575,2.8482958287,-1.9750636933
H,0,-5.1952080252,1.4676221252,0.0619519177
C,0,-0.6353381716,-0.5542582492,0.8978350365
C,0,-0.1177104532,-1.3865518552,1.9485362789
H,0,-0.0271402936,-0.8400741107,2.8880964254
H,0,-0.7326220141,-2.2778473658,2.0875561419
H,0,0.8811681527,-1.7024261178,1.6250626529
B,0,0.815871139,-0.0726029859,-1.0897703481
O,0,1.1898664143,1.2882910865,-1.3251616667
O,0,1.8417986473,-0.6815214072,-0.2980709388
Cl,0,0.2971770951,-1.0518227626,-2.5467675979
C,0,2.6403252213,0.3396222309,0.1100875283
C,0,3.7010850261,0.2974425193,0.9823529817
C,0,4.3706603084,1.4995170513,1.2272553957
C,0,3.9790524353,2.6788237084,0.6123213738
C,0,2.8999598297,2.7101413884,-0.2747749229
C,0,2.2474855757,1.5235357061,-0.506952717
H,0,4.0059655447,-0.6291077853,1.453019465
H,0,5.2114560426,1.5068885238,1.9103700471
H,0,4.5178232355,3.5950852501,0.8216194728
H,0,2.5885326749,3.6256450783,-0.7617839444
```

*PBEPBE/6-31+G** PCM(toluene)*

```
E(RPBE-PBE) = -1650.54812065

Zero-point correction= 0.253570 (Hartree/Particle)
Thermal correction to Energy= 0.273848
Thermal correction to Enthalpy= 0.274793
Thermal correction to Gibbs Free Energy= 0.202856
Sum of electronic and ZPE= -1650.294550
Sum of electronic and thermal Energies= -1650.274272
Sum of electronic and thermal Enthalpies= -1650.273328
Sum of electronic and thermal Free Energies= -1650.345265

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 171.842 76.152 151.403
```

```
C,0,-3.7657800637,-1.8808759604,0.6886546254
H,0,-3.904282074,-2.5923745311,1.516990934
H,0,-2.8762746565,-2.1629131712,0.1058468749
H,0,-4.6593779335,-1.8913911013,0.0477575935
S,0,-3.5481298569,-0.2255447306,1.4549827929
```

```
C,0,-3.2743317548,0.7825259503,-0.00020927
C,0,-1.9815109212,0.887081487,-0.6107205217
C,0,-1.8340418537,1.7233934316,-1.7377090153
C,0,-2.9205031785,2.4468187826,-2.2462807981
C,0,-4.1803539396,2.3523117339,-1.6390610047
C,0,-4.3509904581,1.5222154784,-0.5200361094
C,0,-0.8828384374,0.1405020293,-0.0230038456
H,0,-0.8513778367,1.8159006153,-2.2025044504
H,0,-2.7758961066,3.0903795507,-3.1190759881
H,0,-5.0305604493,2.9184254233,-2.0309578291
H,0,-5.3299516112,1.4399131298,-0.0397815908
C,0,-0.6361749315,-0.5268275571,1.0127196753
C,0,-0.0521782797,-1.3585828737,2.0413980382
H,0,0.0962337439,-0.8044679743,2.9832846602
H,0,-0.6766396195,-2.2458602566,2.2422481375
H,0,0.9339652976,-1.7052689818,1.6790771112
B,0,0.8950492345,-0.143639738,-1.1574377
O,0,1.2242705416,1.2261684448,-1.4042158595
O,0,1.89847202,-0.7442454902,-0.3341538437
Cl,0,0.218811003,-1.1392547362,-2.5027815575
C,0,2.6909431111,0.3092075548,0.0798315459
C,0,3.7612421389,0.287749844,0.9703833912
C,0,4.4171522028,1.5156220256,1.2057107013
C,0,4.0062099843,2.70028009,0.5681349626
C,0,2.9212322045,2.7105992276,-0.3345625924
C,0,2.283000891,1.4939625865,-0.5599826082
H,0,4.0789953384,-0.6382881941,1.4567218142
H,0,5.2629028121,1.5422742453,1.8988406377
H,0,4.536297217,3.6346457595,0.7737190402
H,0,2.595926222,3.6246099063,-0.8377509517
```

PBEPBE/6-311+G(2d,p) PCM(toluene)

E(RPBE-PBE) = -1650.78041746

Zero-point correction= 0.252478 (Hartree/Particle)
Thermal correction to Energy= 0.272790
Thermal correction to Enthalpy= 0.273735
Thermal correction to Gibbs Free Energy= 0.201448
Sum of electronic and ZPE= -1650.527940
Sum of electronic and thermal Energies= -1650.507627
Sum of electronic and thermal Enthalpies= -1650.506683
Sum of electronic and thermal Free Energies= -1650.578969

```
      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 171.179 76.192 152.140
```

```
C,0,-3.7772696544,-1.8295849285,0.7646747568
H,0,-3.8889257112,-2.5151123126,1.6154272709
H,0,-2.9332166407,-2.1467220535,0.1397304873
H,0,-4.7057642298,-1.8150371158,0.1812458142
S,0,-3.4594808122,-0.1731084417,1.4836004432
C,0,-3.2287867114,0.7978220673,0.0023383304
C,0,-1.9615529927,0.8618798674,-0.6520817965
C,0,-1.8398397818,1.6665413027,-1.7974346815
C,0,-2.9264228805,2.3965438295,-2.2805597995
C,0,-4.1599071456,2.3400613703,-1.6296623623
C,0,-4.305718774,1.5419624589,-0.4913207608
C,0,-0.8675402608,0.1035522633,-0.081321685
H,0,-0.8766687968,1.7291118974,-2.3012665552
H,0,-2.8030058355,3.0168589854,-3.1706603847
H,0,-5.0109257761,2.9131327806,-2.0033097582
H,0,-5.2660881882,1.4901185299,0.0242723265
C,0,-0.6411000656,-0.5656276321,0.9483064719
C,0,-0.0629466132,-1.4043814288,1.9704189624
H,0,0.0692593687,-0.8617856082,2.9187070641
H,0,-0.6796951547,-2.2984545385,2.1520873041
H,0,0.9285814793,-1.736428249,1.6152999404
B,0,0.9248546148,-0.1286243876,-1.1911354931
O,0,1.2389432911,1.2467549732,-1.4071507652
O,0,1.9216457697,-0.7291598956,-0.3657759452
Cl,0,0.2760238808,-1.1088590844,-2.5620604469
C,0,2.6943952574,0.3246053711,0.0758340371
C,0,3.7480655745,0.3009934973,0.977067021
C,0,4.3837362928,1.5268945794,1.2418389152
C,0,3.969598408,2.7120151063,0.6216559908
C,0,2.901458376,2.7248389431,-0.2920714957
C,0,2.282488399,1.5105217096,-0.546515034
H,0,4.0696809498,-0.6274888668,1.4518342278
H,0,5.2176081772,1.5517285118,1.9459617369
H,0,4.4847399266,3.6468504137,0.8503951215
H,0,2.5732862596,3.6426380849,-0.7822922583
```

PBEPBE/6-311+G(2d,p) SMD(toluene)

E(RPBE-PBE) = -1650.79652978

```
Zero-point correction= 0.252712 (Hartree/Particle)
Thermal correction to Energy= 0.272929
Thermal correction to Enthalpy= 0.273873
Thermal correction to Gibbs Free Energy= 0.202172
Sum of electronic and ZPE= -1650.543818
Sum of electronic and thermal Energies= -1650.523601
Sum of electronic and thermal Enthalpies= -1650.522657
Sum of electronic and thermal Free Energies= -1650.594358

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 171.266 76.065 150.909

 C,0,-3.7599736177,-1.8354946958,0.7676106183
 H,0,-3.8379980495,-2.5272212433,1.6183380246
 H,0,-2.92613957,-2.1378601837,0.1213367638
 H,0,-4.702451393,-1.8482833867,0.2051634816
 S,0,-3.4687071239,-0.1734418392,1.4814214089
 C,0,-3.2333599104,0.7999306984,0.0017499506
 C,0,-1.9626154642,0.8679849532,-0.6463207108
 C,0,-1.8364256056,1.6803834946,-1.7856435834
 C,0,-2.9202284255,2.4142913203,-2.2688014447
 C,0,-4.1566262092,2.3529116901,-1.6244590709
 C,0,-4.3079118383,1.5470572396,-0.4925663919
 C,0,-0.8715334251,0.1030736776,-0.0773757595
 H,0,-0.8715850512,1.7464287989,-2.2860418889
 H,0,-2.7920318565,3.0404783587,-3.1543586081
 H,0,-5.006284586,2.9284950014,-1.9979080239
 H,0,-5.2715427811,1.4920643215,0.0169724753
 C,0,-0.6515269778,-0.5783515939,0.9456594351
 C,0,-0.0972031393,-1.4333855454,1.9654904175
 H,0,0.0524890152,-0.8957765238,2.9146249675
 H,0,-0.7423106683,-2.3082887265,2.147237444
 H,0,0.883466135,-1.8013960561,1.6148997233
 B,0,0.9286844093,-0.1336132989,-1.18070761
 O,0,1.2431765885,1.239440766,-1.4081894056
 O,0,1.9245022194,-0.7255607304,-0.3479515124
 Cl,0,0.2895647679,-1.1272755034,-2.5489585059
 C,0,2.6977552733,0.3307106329,0.0823637966
 C,0,3.7527738874,0.3158567702,0.9822392808
 C,0,4.3900365803,1.5437840111,1.2326901403
 C,0,3.9765395334,2.722769756,0.6008430144
 C,0,2.9074083587,2.7269496828,-0.3115523762
 C,0,2.2869501185,1.5107263713,-0.5518272082
```

H,0,4.0752395783,-0.6073975763,1.4671408663
H,0,5.2252536382,1.575352372,1.9353404486
H,0,4.4929804888,3.6597290914,0.8188674676
H,0,2.5791451003,3.6399798953,-0.8112506249

*M062X/6-31+G** PCM(toluene)*

E(RM062X) = -1651.52301938

Zero-point correction= 0.263601 (Hartree/Particle)
Thermal correction to Energy= 0.282760
Thermal correction to Enthalpy= 0.283704
Thermal correction to Gibbs Free Energy= 0.214917
Sum of electronic and ZPE= -1651.259418
Sum of electronic and thermal Energies= -1651.240260
Sum of electronic and thermal Enthalpies= -1651.239315
Sum of electronic and thermal Free Energies= -1651.308102

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 177.434 72.957 144.775
```

C,0,-3.6474946302,-1.7834163039,0.7700877956
H,0,-3.6683177279,-2.4992837117,1.5938620213
H,0,-2.8751784886,-2.0670499061,0.0520521643
H,0,-4.6233312594,-1.7595096654,0.2843473473
S,0,-3.2708577998,-0.1516176524,1.4910361252
C,0,-3.1527652651,0.8067540868,-0.002657268
C,0,-1.9291462103,0.8667113877,-0.7111947141
C,0,-1.8486125478,1.632661087,-1.8760607501
C,0,-2.96325601,2.3329366567,-2.3318589303
C,0,-4.1656304822,2.2773457726,-1.6320493988
C,0,-4.2589811943,1.5160579482,-0.4669216222
C,0,-0.8005736034,0.1144530185,-0.167209009
H,0,-0.9105542659,1.6853515398,-2.4157036669
H,0,-2.8868672447,2.9259042963,-3.2371670395
H,0,-5.0322404186,2.8251657842,-1.9874198598
H,0,-5.1914515429,1.4703085284,0.0860644623
C,0,-0.6342850567,-0.5286952863,0.8951362873
C,0,-0.0852085212,-1.3530010334,1.9496756079
H,0,-0.0070046677,-0.8023630418,2.889151717
H,0,-0.675239945,-2.2624255829,2.0897479658
H,0,0.9209154069,-1.6331684028,1.6099813833
B,0,0.7973425922,-0.0560583331,-1.1216902304

```
O,0,1.1789365058,1.3099617611,-1.337515521
O,0,1.8196578222,-0.6928383727,-0.3416662397
Cl,0,0.2722123713,-1.000118104,-2.6028493123
C,0,2.6180132659,0.3243723371,0.1026115326
C,0,3.6729745826,0.2593760654,0.9909897066
C,0,4.3435515791,1.460737623,1.2728526216
C,0,3.9578084417,2.6605261666,0.6774341164
C,0,2.8845535454,2.7146823907,-0.2262434836
C,0,2.2309070868,1.5283825976,-0.4951336167
H,0,3.9694178466,-0.6820929848,1.4409458131
H,0,5.1775793512,1.451020839,1.96674344
H,0,4.4952970131,3.5726411227,0.9147573239
H,0,2.5773354708,3.6413383719,-0.6980587689
```

M062x/6-311+G(2d,p) PCM(toluene)

E(RM062X) = -1651.78689903

```
Zero-point correction= 0.263051 (Hartree/Particle)
Thermal correction to Energy= 0.282140
Thermal correction to Enthalpy= 0.283084
Thermal correction to Gibbs Free Energy= 0.214623
Sum of electronic and ZPE= -1651.523848
Sum of electronic and thermal Energies= -1651.504759
Sum of electronic and thermal Enthalpies= -1651.503815
Sum of electronic and thermal Free Energies= -1651.572277
```

```
     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 177.045 72.850 144.089
```

```
C,0,-3.6120410645,-1.7677828697,0.7926076068
H,0,-3.6171422839,-2.470196819,1.6245573828
H,0,-2.8477935426,-2.048366576,0.0698952798
H,0,-4.5924767222,-1.7470463228,0.3234809788
S,0,-3.233737314,-0.1298427257,1.4924245049
C,0,-3.1361288896,0.8132995671,-0.0072763258
C,0,-1.9254228109,0.8596159721,-0.7295553425
C,0,-1.8576529145,1.6131236809,-1.8970579354
C,0,-2.970835647,2.313748487,-2.3410745638
C,0,-4.1593591739,2.2701135349,-1.6274000778
C,0,-4.2411275339,1.520629157,-0.4597744268
C,0,-0.7982626068,0.1103503096,-0.1877533267
H,0,-0.9303382447,1.6563573727,-2.4502119142
```

H,0,-2.9043555004,2.8985728705,-3.2493263054
H,0,-5.0254700886,2.8187733895,-1.9744204935
H,0,-5.1641740901,1.4841945386,0.1039839724
C,0,-0.632925336,-0.5180385202,0.8731335237
C,0,-0.0841295388,-1.3337642796,1.9315868324
H,0,0.0005412334,-0.7743416272,2.8624909188
H,0,-0.6826659864,-2.2326947948,2.0842893735
H,0,0.916104528,-1.6283718857,1.5952906706
B,0,0.8065539913,-0.0505027022,-1.1492019904
O,0,1.1843823956,1.3144051191,-1.3474944383
O,0,1.8238798969,-0.6942801121,-0.3776951273
Cl,0,0.2662452404,-0.9799946607,-2.6329305954
C,0,2.6110142165,0.3189511618,0.0901139604
C,0,3.6532934371,0.247314498,0.9847562351
C,0,4.3128426952,1.4434959448,1.2902290599
C,0,3.928935099,2.6448599114,0.710481889
C,0,2.8683606753,2.7058312511,-0.2003415642
C,0,2.2257002988,1.5252871352,-0.4921980573
H,0,3.9499841188,-0.6964480362,1.4235052529
H,0,5.1374248211,1.4279649479,1.990946242
H,0,4.4577536958,3.5537822016,0.9661762969
H,0,2.5625289456,3.636052881,-0.6601604961

M062x/6-311+G(2d,p) SMD(toluene)

E(RM062X) = -1651.80318280

Zero-point correction= 0.263276 (Hartree/Particle)
Thermal correction to Energy= 0.282273
Thermal correction to Enthalpy= 0.283217
Thermal correction to Gibbs Free Energy= 0.215096
Sum of electronic and ZPE= -1651.539907
Sum of electronic and thermal Energies= -1651.520910
Sum of electronic and thermal Enthalpies= -1651.519966
Sum of electronic and thermal Free Energies= -1651.588087

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 177.129 72.706 143.372

C,0,-3.6391909846,-1.7644808824,0.7997459756
H,0,-3.644064219,-2.470476787,1.6298328493
H,0,-2.8887494351,-2.0556236751,0.0660514367
H,0,-4.6255165448,-1.7394389288,0.3413276438

```
S,0,-3.2425673638,-0.1303064854,1.4955587024
C,0,-3.1400654701,0.8101654276,-0.0070630014
C,0,-1.9269966065,0.8571594113,-0.7259169079
C,0,-1.8574572919,1.6097456792,-1.8940356712
C,0,-2.9700189672,2.3079633366,-2.3427760306
C,0,-4.1604790462,2.2631479626,-1.632928842
C,0,-4.2443279097,1.5157308685,-0.464324574
C,0,-0.7995464895,0.1064475259,-0.1849317557
H,0,-0.9295100349,1.6538806517,-2.4461976359
H,0,-2.9013293315,2.891002309,-3.2523240403
H,0,-5.0269159645,2.8095449149,-1.9836159052
H,0,-5.1699672236,1.4801901947,0.0958319876
C,0,-0.6345913137,-0.533064914,0.8692612618
C,0,-0.0989944456,-1.3555154974,1.9269219592
H,0,-0.0210017651,-0.8013336274,2.8622571419
H,0,-0.7004759445,-2.2548788121,2.0689130414
H,0,0.9043297894,-1.6544128353,1.6029494268
B,0,0.8115906649,-0.0390236812,-1.1357343051
O,0,1.1851725594,1.3279308749,-1.3297597659
O,0,1.8313299924,-0.6800678418,-0.3646491568
Cl,0,0.2895535058,-0.9707707496,-2.6282616859
C,0,2.622152886,0.3316777415,0.0954915696
C,0,3.6726460057,0.2589136992,0.9802357383
C,0,4.3365105091,1.454153503,1.2792759152
C,0,3.9491360001,2.6555736811,0.7024227765
C,0,2.8803212981,2.7179830897,-0.1987101252
C,0,2.2331479728,1.5382804479,-0.4841807552
H,0,3.9724555298,-0.6854890617,1.4160896342
H,0,5.1677342574,1.4373505151,1.9724013701
H,0,4.4822193175,3.5637655711,0.9528495129
H,0,2.5729720634,3.6493283737,-0.655930785
```

*TPSSTPSS/6-31+G** PCM(toluene)*

E(RTPSS-TPSS) = -1652.10726880

Zero-point correction= 0.256903 (Hartree/Particle)
Thermal correction to Energy= 0.276991
Thermal correction to Enthalpy= 0.277935
Thermal correction to Gibbs Free Energy= 0.206371
Sum of electronic and ZPE= -1651.850366
Sum of electronic and thermal Energies= -1651.830278
Sum of electronic and thermal Enthalpies= -1651.829334
Sum of electronic and thermal Free Energies= -1651.900897

```
      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 173.814 75.366 150.619

 C,0,-3.6444825019,-1.8227199836,0.7862847771
 H,0,-3.6986813487,-2.5161784798,1.6318767878
 H,0,-2.793983327,-2.0796229061,0.1471815713
 H,0,-4.5772003255,-1.859801811,0.2161089374
 S,0,-3.4136589044,-0.1385314109,1.5019820506
 C,0,-3.2114732243,0.8145420635,-0.002291784
 C,0,-1.9498181515,0.8786074035,-0.67492893
 C,0,-1.8437269764,1.6609051789,-1.8413189221
 C,0,-2.9462136786,2.3712825271,-2.3307039844
 C,0,-4.1773006015,2.3147169697,-1.6644333733
 C,0,-4.3058275347,1.5376350158,-0.5034443345
 C,0,-0.8371219895,0.135008487,-0.1086012585
 H,0,-0.8883590215,1.7196953613,-2.352448542
 H,0,-2.8381643837,2.9711569014,-3.2321755982
 H,0,-5.0355001452,2.8671511792,-2.0421941372
 H,0,-5.2587660118,1.4850626707,0.0181117825
 C,0,-0.5967710205,-0.5033837301,0.9454701612
 C,0,0.0014081648,-1.3318622604,1.9748224635
 H,0,0.2026660784,-0.760527353,2.8891167992
 H,0,-0.6457993991,-2.1853412007,2.2151084981
 H,0,0.9532669057,-1.7153776584,1.5775491222
 B,0,0.8887638073,-0.1294802383,-1.2420660508
 O,0,1.2220808064,1.2478557656,-1.4481051334
 O,0,1.888683639,-0.7556638337,-0.432720606
 Cl,0,0.2220843892,-1.0857167825,-2.6242735689
 C,0,2.6453829346,0.2959534764,0.0577667581
 C,0,3.6711794465,0.2534116865,0.9955001816
 C,0,4.2910945735,1.4810963913,1.3110884794
 C,0,3.8875074013,2.683143671,0.7044259834
 C,0,2.8454474277,2.7134121334,-0.2459256955
 C,0,2.2437981458,1.4971327308,-0.5493014245
 H,0,3.9791713348,-0.681719738,1.4566925059
 H,0,5.0981618638,1.4940193656,2.0408641727
 H,0,4.3863063711,3.6122914607,0.9725136537
 H,0,2.525351256,3.636898947,-0.7214543424
```

*m11/6-31+G** PCM(toluene)*

E(RM11) = -1651.37973246

Zero-point correction= 0.261752 (Hartree/Particle)
Thermal correction to Energy= 0.280916
Thermal correction to Enthalpy= 0.281860
Thermal correction to Gibbs Free Energy= 0.213089
Sum of electronic and ZPE= -1651.117980
Sum of electronic and thermal Energies= -1651.098816
Sum of electronic and thermal Enthalpies= -1651.097872
Sum of electronic and thermal Free Energies= -1651.166644

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 176.278 73.159 144.742

C,0,-3.6184897412,-1.7791674894,0.7763925186
H,0,-3.6155266894,-2.5031748994,1.5995339328
H,0,-2.8474215384,-2.0460844997,0.0430530359
H,0,-4.6048180401,-1.7729079726,0.3006513093
S,0,-3.2620598248,-0.1403582494,1.4979306402
C,0,-3.1566818239,0.8112003483,-0.0043722558
C,0,-1.9399740825,0.8639799209,-0.7203766526
C,0,-1.8613759336,1.6203005926,-1.8898356907
C,0,-2.9765577075,2.3204056978,-2.3434412603
C,0,-4.1747528212,2.272476862,-1.6360302539
C,0,-4.2641426503,1.5190932857,-0.4661086725
C,0,-0.8069704294,0.1109308125,-0.1772198146
H,0,-0.9199408396,1.6655941974,-2.4355838489
H,0,-2.9037998932,2.9105107912,-3.2574335383
H,0,-5.0459333927,2.8234245757,-1.9921545819
H,0,-5.1975213496,1.4784321194,0.0963175247
C,0,-0.6390865099,-0.5286631715,0.8863735018
C,0,-0.1022113557,-1.351692533,1.9485726893
H,0,-0.0258069598,-0.794957889,2.8896240072
H,0,-0.699781604,-2.2622822335,2.0858533347
H,0,0.9079597589,-1.6368934933,1.610314807
B,0,0.7837994518,-0.0493115141,-1.1212718697
O,0,1.1749533708,1.325224558,-1.323955682
O,0,1.8170631879,-0.6880379026,-0.3409741037
Cl,0,0.2707693942,-0.9821077471,-2.6224088424
C,0,2.6202965059,0.3274852126,0.1056211211
C,0,3.6780698796,0.2561889528,0.9894500086

C,0,4.3518278953,1.4542821621,1.2764561012
C,0,3.9662988956,2.6577245535,0.6892285384
C,0,2.890451441,2.7182317093,-0.210626551
C,0,2.2329153238,1.5357583862,-0.4840076099
H,0,3.975381209,-0.6934915899,1.4340848051
H,0,5.192488682,1.4386242876,1.9707464589
H,0,4.5087991376,3.5722724043,0.930690754
H,0,2.5812850535,3.6520417546,-0.6790168606

*BP86/6-31+G** PCM(toluene)*

E(RB-P86) = -1652.00502035

Zero-point correction= 0.252994 (Hartree/Particle)
Thermal correction to Energy= 0.273138
Thermal correction to Enthalpy= 0.274082
Thermal correction to Gibbs Free Energy= 0.202568
Sum of electronic and ZPE= -1651.752027
Sum of electronic and thermal Energies= -1651.731883
Sum of electronic and thermal Enthalpies= -1651.730939
Sum of electronic and thermal Free Energies= -1651.802452

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 171.396 76.179 150.513

C,0,-3.5858506117,-1.8269650668,0.7863079663
H,0,-3.6328970428,-2.5278067853,1.6346377108
H,0,-2.7104832075,-2.0608612107,0.1606976409
H,0,-4.5095321291,-1.9032376583,0.1931230754
S,0,-3.4297385188,-0.1339224855,1.5023770899
C,0,-3.2296859373,0.8241503631,-0.0024341552
C,0,-1.963568495,0.9017570868,-0.6730080677
C,0,-1.8614237477,1.6899326259,-1.8394276663
C,0,-2.9704679174,2.3935427884,-2.3309993288
C,0,-4.2056072386,2.3234512401,-1.6674220532
C,0,-4.3310209176,1.5395346642,-0.5074199673
C,0,-0.8435470222,0.1710144266,-0.105176883
H,0,-0.8993446011,1.7591354191,-2.3498498327
H,0,-2.8643282787,3.0006357898,-3.235486845
H,0,-5.0728362888,2.8717891094,-2.0487203577
H,0,-5.2915723521,1.4744722723,0.0121950873
C,0,-0.5831739512,-0.4519103806,0.9571675891
C,0,0.0239855669,-1.2714040078,1.9833224977

H,0,0.25910946,-0.6907275093,2.8913529461
H,0,-0.6322916729,-2.1176458633,2.2529727425
H,0,0.9665951441,-1.6789616192,1.56918326
B,0,0.8656728537,-0.1225985974,-1.2668754867
O,0,1.2202297963,1.2555092822,-1.4603405818
O,0,1.8659562129,-0.7741605223,-0.4716770001
Cl,0,0.1663269838,-1.0564980209,-2.6497981631
C,0,2.6296823836,0.2620921866,0.0367813885
C,0,3.6516590477,0.1972702442,0.9815759956
C,0,4.2835657043,1.416000969,1.3200379032
C,0,3.8941706514,2.6333922157,0.7278797874
C,0,2.8551224522,2.6874917297,-0.2289205091
C,0,2.240819599,1.4802983112,-0.555800325
H,0,3.9477367379,-0.7541961788,1.4318966201
H,0,5.0909247133,1.4097302778,2.0588526187
H,0,4.4028762456,3.5590996351,1.0140175676
H,0,2.5424423781,3.625647269,-0.6949452641

*B97D3/6-31+G** PCM(toluene)*

E(RTPSS-TPSS) = -1652.10726938

Zero-point correction= 0.256917 (Hartree/Particle)
Thermal correction to Energy= 0.276996
Thermal correction to Enthalpy= 0.277940
Thermal correction to Gibbs Free Energy= 0.206434
Sum of electronic and ZPE= -1651.850353
Sum of electronic and thermal Energies= -1651.830273
Sum of electronic and thermal Enthalpies= -1651.829329
Sum of electronic and thermal Free Energies= -1651.900836

```
     E      CV        S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 173.818 75.361 150.499
```

C,0,-3.642528512,-1.8281121923,0.770705144
H,0,-3.6926521383,-2.5302586649,1.6093520475
H,0,-2.7949452002,-2.0782295837,0.1250641038
H,0,-4.5778663403,-1.859548909,0.2044968873
S,0,-3.4087066013,-0.1513515937,1.5027422792
C,0,-3.21063923,0.81691416,0.007692971
C,0,-1.9510011991,0.8872167774,-0.6680760087
C,0,-1.847946636,1.681736488,-1.8264515811
C,0,-2.9515120948,2.3977672277,-2.3050564835

```
C,0,-4.1806687171,2.3347846368,-1.6357928745
C,0,-4.3061295748,1.5457004424,-0.4825905911
C,0,-0.8372978238,0.1365436235,-0.1131193454
H,0,-0.8941017171,1.7453893498,-2.3398262358
H,0,-2.845824233,3.0070147506,-3.2005013553
H,0,-5.0396885211,2.8915806337,-2.0051915681
H,0,-5.2574747433,1.4882831524,0.0413634342
C,0,-0.5942435552,-0.5134167524,0.9332028802
C,0,0.0053792589,-1.3550619338,1.950988451
H,0,0.2101123697,-0.7950567493,2.8714962105
H,0,-0.642694574,-2.2102350011,2.1827873048
H,0,0.9554908421,-1.7354297539,1.5465729808
B,0,0.8853341085,-0.1161010247,-1.2539809577
O,0,1.2190085876,1.263318246,-1.4449333245
O,0,1.8869440564,-0.7522584823,-0.4545702982
Cl,0,0.2144917792,-1.0559490206,-2.6454114642
C,0,2.6452114751,0.2932131116,0.0465227785
C,0,3.6729122233,0.2392688214,0.9815798694
C,0,4.2940086623,1.4629177653,1.3102483603
C,0,3.8896757968,2.6721570548,0.7185588128
C,0,2.8456460361,2.7139929287,-0.2291891591
C,0,2.2428504194,1.5015979186,-0.5455632421
H,0,3.9814322946,-0.7013286643,1.4311574193
H,0,5.1025802509,1.4669645979,2.038460431
H,0,4.3894215704,3.5978979015,0.9964890973
H,0,2.5249276801,3.6431307378,-0.6931499736
```

*B3PW91/6-31+G** PCM(toluene)*

E(RB3PW91) = -1651.55006500

```
Zero-point correction= 0.261612 (Hartree/Particle)
Thermal correction to Energy= 0.281141
Thermal correction to Enthalpy= 0.282085
Thermal correction to Gibbs Free Energy= 0.212058
Sum of electronic and ZPE= -1651.288453
Sum of electronic and thermal Energies= -1651.268924
Sum of electronic and thermal Enthalpies= -1651.267980
Sum of electronic and thermal Free Energies= -1651.338007
```

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 176.419 73.769 147.385
```

```
C,0,-3.6197737854,-1.7962022784,0.7691752903
H,0,-3.6767533964,-2.5016462968,1.6019984107
H,0,-2.7744325244,-2.0556917256,0.1274853649
H,0,-4.5493016128,-1.8337988573,0.1974898977
S,0,-3.3883364475,-0.1354845874,1.4912051918
C,0,-3.1971312848,0.82119123,0.0006227824
C,0,-1.9484587958,0.8895360197,-0.6749485144
C,0,-1.8463828929,1.6679087161,-1.8337830128
C,0,-2.946951584,2.3726564149,-2.315385544
C,0,-4.1683995074,2.3116666601,-1.647687156
C,0,-4.289761663,1.537133932,-0.4933238598
C,0,-0.8333132657,0.1486958061,-0.1167683132
H,0,-0.8962634406,1.7289292142,-2.3490535188
H,0,-2.8446406189,2.9727190875,-3.2146852966
H,0,-5.0275986836,2.8612758985,-2.020927656
H,0,-5.2391647429,1.4820501416,0.0300751953
C,0,-0.5830614002,-0.4837057684,0.928978757
C,0,-0.0121084897,-1.3016266853,1.9669442187
H,0,0.1686192842,-0.7301703592,2.8819719146
H,0,-0.655694531,-2.1591563562,2.1884634319
H,0,0.9478563111,-1.6754527189,1.5865838782
B,0,0.83166261,-0.1067391588,-1.1866946194
O,0,1.1939359999,1.2581730583,-1.3968199575
O,0,1.8454051454,-0.7434843145,-0.4089689943
Cl,0,0.1922367355,-1.0501811088,-2.5933897004
C,0,2.6205102243,0.2818389306,0.0620982198
C,0,3.6585773396,0.2239737742,0.9737613942
C,0,4.3018670627,1.433912849,1.2813772913
C,0,3.9071128078,2.636671635,0.6900288817
C,0,2.8518428956,2.6832860697,-0.2349148959
C,0,2.226399959,1.4858865191,-0.5306582225
H,0,3.9597491306,-0.7166494309,1.4233491917
H,0,5.1215180157,1.4310343948,1.9938111592
H,0,4.4236674681,3.5559020004,0.9498356243
H,0,2.5360736775,3.6105992945,-0.7011698342
```

Syn TS with ClBcat

ωB97xD/6-311+G(2d,p) PCM(toluene)

E(RwB97XD) = -1651.84895729

```
Zero-point correction= 0.262896 (Hartree/Particle)
Thermal correction to Energy= 0.282034
Thermal correction to Enthalpy= 0.282979
Thermal correction to Gibbs Free Energy= 0.214196
Sum of electronic and ZPE= -1651.586062
Sum of electronic and thermal Energies= -1651.566923
Sum of electronic and thermal Enthalpies= -1651.565979
Sum of electronic and thermal Free Energies= -1651.634762

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 176.979 72.834 144.766
```

```
C,0,-1.7505275419,-2.913018006,0.8097379637
H,0,-1.5799641788,-3.9266257052,0.4476943372
H,0,-2.332422728,-2.9472174066,1.7287471789
H,0,-0.7957349842,-2.4181366742,0.9823255747
S,0,-2.6874288293,-2.0463454439,-0.4881805443
C,0,-2.7723090941,-0.4224076807,0.226960924
C,0,-1.7233743042,0.5006236974,0.0381124988
C,0,-1.8218838723,1.7624544603,0.6144245744
C,0,-2.9415216126,2.1129417555,1.3528434588
C,0,-3.9755830719,1.2078805605,1.5285681681
C,0,-3.8886386889,-0.0580023305,0.9663071313
C,0,-0.581399749,0.0753305503,-0.7612950779
H,0,-1.0203770231,2.4747003112,0.4825192824
H,0,-3.0029084207,3.1016860001,1.7904984157
H,0,-4.8516838064,1.4820685604,2.1034443401
H,0,-4.6925326616,-0.7705117052,1.101488368
C,0,-0.3194292472,-0.9363888002,-1.4292251545
C,0,0.3044781627,-1.932691481,-2.2619167905
H,0,0.4436290668,-2.8715106468,-1.7236102088
H,0,-0.2645725235,-2.1014344263,-3.1762584704
H,0,1.2892258786,-1.5286853494,-2.5236022336
B,0,1.025051919,1.1076721538,-0.8262305388
O,0,1.2550908454,1.3409014572,0.5655257115
O,0,2.1191213723,0.3431767228,-1.3411176556
Cl,0,0.5450401638,2.5452267556,-1.8463764419
C,0,2.795355352,-0.0926092115,-0.241697768
C,0,3.846593388,-0.9763732463,-0.1815408046
C,0,4.3732627926,-1.2527419312,1.0840560618
C,0,3.8546500658,-0.6563491596,2.2245471022
C,0,2.7863472075,0.2426544647,2.1511128404
C,0,2.2756157595,0.5063043365,0.9022230425
```

H,0,4.2494879112,-1.431243835,-1.0778166979
H,0,5.2021618639,-1.9444732961,1.1721767492
H,0,4.283581413,-0.8894127293,3.1915050461
H,0,2.3767571757,0.7153152785,3.0347156173

ωB97xD/6-311+G(2df,p) PCM(toluene)

E(RwB97XD) = -1651.87528181

Zero-point correction= 0.262864 (Hartree/Particle)
Thermal correction to Energy= 0.282034
Thermal correction to Enthalpy= 0.282978
Thermal correction to Gibbs Free Energy= 0.213841
Sum of electronic and ZPE= -1651.612417
Sum of electronic and thermal Energies= -1651.593248
Sum of electronic and thermal Enthalpies= -1651.592304
Sum of electronic and thermal Free Energies= -1651.661441

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 176.979 72.745 145.510

C,0,-1.8026077703,-2.9226114487,0.7800401426
H,0,-1.6340487245,-3.9330171259,0.4080877805
H,0,-2.3999008455,-2.9651269032,1.6889975788
H,0,-0.8460633215,-2.4406793241,0.9788588313
S,0,-2.7041943313,-2.0304071672,-0.5173919696
C,0,-2.7818877108,-0.4187526555,0.2143445066
C,0,-1.7216867886,0.4950430517,0.0456973705
C,0,-1.8111938546,1.7500734823,0.6361088498
C,0,-2.9329598365,2.103498869,1.3684303043
C,0,-3.9780858153,1.2086414265,1.5239428785
C,0,-3.9004002838,-0.0506956384,0.9477718325
C,0,-0.580195363,0.0642278967,-0.7493217896
H,0,-1.0001058378,2.4542295214,0.5211062656
H,0,-2.987380382,3.0874211761,1.8175230372
H,0,-4.8561581132,1.4860129379,2.0940942247
H,0,-4.7134588233,-0.75565252,1.0671466919
C,0,-0.3303191381,-0.9497331031,-1.4197467619
C,0,0.2866725076,-1.9474087325,-2.2523022669
H,0,0.4137033262,-2.8904307089,-1.7183615793
H,0,-0.2777534059,-2.1071250236,-3.1710800158
H,0,1.2771844639,-1.552666561,-2.5067148927
B,0,1.0203561975,1.0884557223,-0.8175378116

```
O,0,1.2612763571,1.3295821655,0.5722835681
O,0,2.1145977935,0.3207025668,-1.3303792172
Cl,0,0.5438735916,2.5223836612,-1.8406897904
C,0,2.8057389424,-0.0956833918,-0.2357194701
C,0,3.8665202023,-0.9670087276,-0.1766912353
C,0,4.4100813761,-1.2224650411,1.0854180741
C,0,3.8986691665,-0.6180542362,2.2238103243
C,0,2.8204379737,0.268125081,2.1522240184
C,0,2.2921931981,0.5109336142,0.9071354612
H,0,4.2647525297,-1.427904683,-1.0718817179
H,0,5.2474017947,-1.9040565918,1.1722612455
H,0,4.3414860118,-0.8344154879,3.1883262742
H,0,2.416612913,0.7473218989,3.0348752574
```

ωB97xD/6-311+G(2d,p) SMD(toluene)

E(RwB97XD) = -1651.86519069

Zero-point correction= 0.263088 (Hartree/Particle)
Thermal correction to Energy= 0.282161
Thermal correction to Enthalpy= 0.283105
Thermal correction to Gibbs Free Energy= 0.214878
Sum of electronic and ZPE= -1651.602103
Sum of electronic and thermal Energies= -1651.583030
Sum of electronic and thermal Enthalpies= -1651.582086
Sum of electronic and thermal Free Energies= -1651.650313

```
     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 177.059 72.677 143.597
```

```
C,0,-1.5791595436,-2.8682160521,0.8422030422
H,0,-1.3449641331,-3.8662665367,0.4698795247
H,0,-2.121310582,-2.9547387703,1.7827156669
H,0,-0.6563542347,-2.3079274115,0.989580934
S,0,-2.6240835354,-2.0685992021,-0.4138693876
C,0,-2.737930317,-0.4313895782,0.2669824214
C,0,-1.7252457168,0.5179758414,0.0193493007
C,0,-1.8494399595,1.7944378084,0.5562986945
C,0,-2.9616139803,2.1353534115,1.3100173635
C,0,-3.9595608368,1.2037762419,1.5449958077
C,0,-3.8457012011,-0.0776410333,1.0241475632
C,0,-0.5895389074,0.1051463661,-0.7969683643
H,0,-1.0752788562,2.5272584192,0.3785384754
```

H,0,-3.0444217868,3.1369176598,1.7142837543
H,0,-4.8297335207,1.4701859766,2.1328455717
H,0,-4.6231527897,-0.8092198668,1.2054688223
C,0,-0.3356967933,-0.9054488498,-1.4718263859
C,0,0.2716344653,-1.8980123277,-2.3184013044
H,0,0.4652276775,-2.8248826224,-1.775327864
H,0,-0.3398756144,-2.0952352624,-3.199958755
H,0,1.2298301217,-1.4759451431,-2.6434384838
B,0,1.0174899982,1.1143887899,-0.835650125
O,0,1.2338094206,1.3393398416,0.5611505785
O,0,2.1111296862,0.3372827651,-1.3371709713
Cl,0,0.5866004791,2.5696986077,-1.8575650599
C,0,2.759165226,-0.1175694822,-0.2309575707
C,0,3.7932280474,-1.0205732542,-0.1585155487
C,0,4.2932599435,-1.3150398084,1.1138724215
C,0,3.7677884088,-0.7150956741,2.249133224
C,0,2.7169379986,0.2032926701,2.1638649146
C,0,2.2319905713,0.4848108642,0.9084948035
H,0,4.202372515,-1.4784436078,-1.0508019192
H,0,5.1073141108,-2.0234201014,1.2112580995
H,0,4.1757427592,-0.9623144689,3.2219103626
H,0,2.3026988796,0.6788717901,3.0441263929

ωB97xD/6-311+G(2df,p) SMD(toluene)

E(RwB97XD) = -1651.89159072

Zero-point correction= 0.263420 (Hartree/Particle)
Thermal correction to Energy= 0.282382
Thermal correction to Enthalpy= 0.283326
Thermal correction to Gibbs Free Energy= 0.215107
Sum of electronic and ZPE= -1651.628171
Sum of electronic and thermal Energies= -1651.609209
Sum of electronic and thermal Enthalpies= -1651.608265
Sum of electronic and thermal Free Energies= -1651.676483

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	177.197	72.457	143.578

C,0,-1.781025101,-2.9244826947,0.7697283076
H,0,-1.6172044137,-3.9359991475,0.3959226286
H,0,-2.3632934523,-2.9727483513,1.689252344
H,0,-0.8205760055,-2.4462597147,0.9610611118

S,0,-2.7031385726,-2.031725803,-0.5112428071
C,0,-2.7762929974,-0.4198430065,0.2221929984
C,0,-1.7231682559,0.4994293952,0.0383543509
C,0,-1.8148642948,1.756166023,0.6251640404
C,0,-2.9303941564,2.1057382099,1.3685949038
C,0,-3.9674100513,1.2047809375,1.5401657279
C,0,-3.8887553903,-0.0555166794,0.9667027601
C,0,-0.5838839297,0.0712642825,-0.7624886126
H,0,-1.011023703,2.4668195253,0.4988902103
H,0,-2.9853098848,3.0912621404,1.8145643691
H,0,-4.8407903238,1.4781076876,2.1198309012
H,0,-4.6968546652,-0.7643665287,1.0973412859
C,0,-0.3330611352,-0.9404530972,-1.4357589945
C,0,0.2716376967,-1.9451456011,-2.2665708338
H,0,0.4210842897,-2.8790103504,-1.7211347126
H,0,-0.3157265264,-2.123516585,-3.1682293587
H,0,1.2520923387,-1.550816582,-2.55867956
B,0,1.0210416006,1.087516689,-0.8224808256
O,0,1.2557286388,1.3276623508,0.5688986743
O,0,2.1174567497,0.3172607528,-1.3282415163
Cl,0,0.5618614871,2.5252947424,-1.8513463549
C,0,2.8033627407,-0.0972379301,-0.2313918976
C,0,3.8671485792,-0.9646178669,-0.1667772552
C,0,4.4042009985,-1.2188481345,1.0983090156
C,0,3.8833429254,-0.6182948678,2.2343595667
C,0,2.8033925178,0.2651751267,2.1571864051
C,0,2.2828534661,0.5086037687,0.9090278588
H,0,4.2732307301,-1.4235277947,-1.0597947368
H,0,5.2434137302,-1.8979145885,1.1895010822
H,0,4.3208960646,-0.8346154681,3.2015269709
H,0,2.3931863053,0.7426171605,3.0382279519

*PBEPBE/6-31+G** PCM(toluene)*

E(RPBE-PBE) = -1650.54796903

Zero-point correction= 0.253491 (Hartree/Particle)
Thermal correction to Energy= 0.273812
Thermal correction to Enthalpy= 0.274756
Thermal correction to Gibbs Free Energy= 0.202640
Sum of electronic and ZPE= -1650.294478
Sum of electronic and thermal Energies= -1650.274157
Sum of electronic and thermal Enthalpies= -1650.273213
Sum of electronic and thermal Free Energies= -1650.345330

```
      E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 171.819 76.199 151.782
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```
C,0,-1.8400754175,-3.0186391181,0.8235500002
H,0,-1.7612353754,-4.0552644573,0.4620436502
H,0,-2.3385289705,-3.0128047622,1.8038505897
H,0,-0.8341843395,-2.5808344759,0.9042864287
S,0,-2.8506187014,-2.1118699844,-0.414349926
C,0,-2.8338320781,-0.4622992964,0.2849518527
C,0,-1.7472034669,0.4433120365,0.0510262704
C,0,-1.8145140561,1.7353543807,0.614366528
C,0,-2.9226570475,2.1361787083,1.3717252416
C,0,-3.9891233615,1.2524277828,1.5873593553
C,0,-3.9393267156,-0.0411277306,1.0444012586
C,0,-0.6443591332,-0.0089780733,-0.7772981857
H,0,-0.9918044843,2.4318618107,0.4476207935
H,0,-2.9500321373,3.1464727844,1.7904239166
H,0,-4.8580269892,1.5623674711,2.1754380999
H,0,-4.7651869713,-0.7389549492,1.2080634346
C,0,-0.3454337453,-0.9791196197,-1.5173861721
C,0,0.2935450042,-1.9047744662,-2.4260069577
H,0,0.4180608028,-2.9024560053,-1.9712431561
H,0,-0.273479065,-2.0071495954,-3.3662544023
H,0,1.29780691,-1.5056825636,-2.663799408
B,0,1.1329963398,1.161376915,-0.8760736208
O,0,1.2928950916,1.3920369032,0.52556946
O,0,2.2037511727,0.3473948671,-1.3623536546
Cl,0,0.5722932951,2.5134777672,-1.9322354897
C,0,2.86366464,-0.0796543212,-0.2264595974
C,0,3.9294622107,-0.9704782551,-0.1290064084
C,0,4.4324243018,-1.2208438586,1.1664302729
C,0,3.8806455704,-0.5971494161,2.3001463106
C,0,2.8011609454,0.3058133538,2.1900087699
C,0,2.3141126337,0.5462458103,0.9079345935
H,0,4.357406236,-1.4454455335,-1.0157323928
H,0,5.2700654573,-1.9139199545,1.2868372064
H,0,4.2949542361,-0.8130677631,3.2891573009
H,0,2.3675352078,0.7989516086,3.0636740375
```

PBEPBE/6-311+G(2d,p) PCM(toluene)

E(RPBE-PBE) = -1650.78027309

```
Zero-point correction= 0.252525 (Hartree/Particle)
Thermal correction to Energy= 0.272804
Thermal correction to Enthalpy= 0.273748
Thermal correction to Gibbs Free Energy= 0.201812
Sum of electronic and ZPE= -1650.527748
Sum of electronic and thermal Energies= -1650.507469
Sum of electronic and thermal Enthalpies= -1650.506525
Sum of electronic and thermal Free Energies= -1650.578461

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 171.187 76.185 151.402

 C,0,-1.88305028,-3.0204958468,0.795784245
 H,0,-1.7969904772,-4.0453572341,0.4105852429
 H,0,-2.4244329907,-3.031455306,1.7495130706
 H,0,-0.8835132337,-2.5869728292,0.9229276868
 S,0,-2.8363244191,-2.0832700444,-0.4594021836
 C,0,-2.829890371,-0.4500721759,0.2646417572
 C,0,-1.7408245795,0.4489999439,0.0552722016
 C,0,-1.8093669071,1.728807446,0.6307176216
 C,0,-2.9202071735,2.1214285961,1.3781635948
 C,0,-3.9873949348,1.2424699224,1.5702575716
 C,0,-3.937716776,-0.0388004734,1.0133553266
 C,0,-0.6354078329,-0.007284246,-0.7607367649
 H,0,-0.9840618356,2.4232069118,0.481899567
 H,0,-2.9499472621,3.1242292909,1.8091637079
 H,0,-4.8595840889,1.5479610399,2.1518166892
 H,0,-4.7669245002,-0.7333531284,1.1578185085
 C,0,-0.3543982303,-0.9892064185,-1.4788836103
 C,0,0.2779600989,-1.9269105816,-2.3748394709
 H,0,0.4049992682,-2.9155710866,-1.9067721382
 H,0,-0.2937499655,-2.0425652578,-3.3080481456
 H,0,1.2787116046,-1.532003488,-2.6247656593
 B,0,1.1330698056,1.1574510484,-0.8587182775
 O,0,1.306576099,1.3896550029,0.5385273088
 O,0,2.1988616621,0.3465865044,-1.3518322174
 Cl,0,0.5561352729,2.5068678023,-1.9106699599
 C,0,2.8720408034,-0.0728494227,-0.2239095907
 C,0,3.9381618488,-0.9552307127,-0.1356264221
 C,0,4.4551071573,-1.1991318078,1.1492035586
 C,0,3.9165356658,-0.576994273,2.2820822311
 C,0,2.8365673003,0.3175253877,2.1816596973
```

C,0,2.3349430633,0.5513964477,0.9102632638
H,0,4.3574116476,-1.4310575247,-1.023728788
H,0,5.2950530451,-1.8872723049,1.2621152619
H,0,4.3423502605,-0.7880781291,3.2648455888
H,0,2.4124592547,0.8101049473,3.0579855269

PBEPBE/6-311+G(2d,p) SMD(toluene)

E(RPBE-PBE) = -1650.79652978

Zero-point correction= 0.252712 (Hartree/Particle)
Thermal correction to Energy= 0.272929
Thermal correction to Enthalpy= 0.273873
Thermal correction to Gibbs Free Energy= 0.202172
Sum of electronic and ZPE= -1650.543818
Sum of electronic and thermal Energies= -1650.523601
Sum of electronic and thermal Enthalpies= -1650.522657
Sum of electronic and thermal Free Energies= -1650.594358

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 171.266 76.065 150.909

C,0,-3.7599736177,-1.8354946958,0.7676106183
H,0,-3.8379980495,-2.5272212433,1.6183380246
H,0,-2.92613957,-2.1378601837,0.1213367638
H,0,-4.702451393,-1.8482833867,0.2051634816
S,0,-3.4687071239,-0.1734418392,1.4814214089
C,0,-3.2333599104,0.7999306984,0.0017499506
C,0,-1.9626154642,0.8679849532,-0.6463207108
C,0,-1.8364256056,1.6803834946,-1.7856435834
C,0,-2.9202284255,2.4142913203,-2.2688014447
C,0,-4.1566262092,2.3529116901,-1.6244590709
C,0,-4.3079118383,1.5470572396,-0.4925663919
C,0,-0.8715334251,0.1030736776,-0.0773757595
H,0,-0.8715850512,1.7464287989,-2.2860418889
H,0,-2.7920318565,3.0404783587,-3.1543586081
H,0,-5.006284586,2.9284950014,-1.9979080239
H,0,-5.2715427811,1.4920643215,0.0169724753
C,0,-0.6515269778,-0.5783515939,0.9456594351
C,0,-0.0972031393,-1.4333855454,1.9654904175
H,0,0.0524890152,-0.8957765238,2.9146249675
H,0,-0.7423106683,-2.3082887265,2.147237444
H,0,0.883466135,-1.8013960561,1.6148997233

B,0,0.9286844093,-0.1336132989,-1.18070761
O,0,1.2431765885,1.239440766,-1.4081894056
O,0,1.9245022194,-0.7255607304,-0.3479515124
Cl,0,0.2895647679,-1.1272755034,-2.5489585059
C,0,2.6977552733,0.3307106329,0.0823637966
C,0,3.7527738874,0.3158567702,0.9822392808
C,0,4.3900365803,1.5437840111,1.2326901403
C,0,3.9765395334,2.722769756,0.6008430144
C,0,2.9074083587,2.7269496828,-0.3115523762
C,0,2.2869501185,1.5107263713,-0.5518272082
H,0,4.0752395783,-0.6073975763,1.4671408663
H,0,5.2252536382,1.575352372,1.9353404486
H,0,4.4929804888,3.6597290914,0.8188674676
H,0,2.5791451003,3.6399798953,-0.8112506249

*M062X/6-31+G** PCM(toluene)*

E(RM062X) = -1651.52270948

Zero-point correction= 0.263560 (Hartree/Particle)
Thermal correction to Energy= 0.282738
Thermal correction to Enthalpy= 0.283683
Thermal correction to Gibbs Free Energy= 0.214643
Sum of electronic and ZPE= -1651.259150
Sum of electronic and thermal Energies= -1651.239971
Sum of electronic and thermal Enthalpies= -1651.239027
Sum of electronic and thermal Free Energies= -1651.308067

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	177.421	72.980	145.307

C,0,-2.7688388065,0.3562656307,2.6445010021
H,0,-2.8360900483,1.044953607,3.4886968083
H,0,-3.7646448044,-0.0094012077,2.392503477
H,0,-2.324771635,0.865667473,1.7868144018
S,0,-1.7101210118,-1.0316453105,3.1727050135
C,0,-1.6294700454,-1.9325335818,1.6409393161
C,0,-0.6492556625,-1.6017610004,0.674608933
C,0,-0.6094914961,-2.3085895936,-0.5289596604
C,0,-1.5141487125,-3.3412108775,-0.7657770562
C,0,-2.4683504064,-3.6756762695,0.191228844
C,0,-2.5262268871,-2.9701249781,1.3932370961

```
C,0,0.2759349412,-0.5194237095,1.0015908295
H,0,0.1312288162,-2.0494424693,-1.2758648425
H,0,-1.4683063654,-3.885589285,-1.7031026165
H,0,-3.1696730903,-4.4828957761,0.0069365039
H,0,-3.2686403492,-3.2230151941,2.1431014715
C,0,0.4395218654,0.1863617841,2.0235974764
C,0,0.9095344482,1.1762637692,2.968441134
H,0,0.1218101949,1.8913118853,3.2205349575
H,0,1.3017472916,0.7083270729,3.8733631188
H,0,1.7221211715,1.7092203252,2.4568294977
B,0,1.4766163943,0.1503784392,-0.274311672
O,0,0.6051114552,0.4076308352,-1.3843181328
O,0,2.0498441947,1.3961367703,0.1484357668
Cl,0,2.6788013135,-1.2140429676,-0.475737818
C,0,1.320499172,2.3591940426,-0.4911368337
C,0,1.3778873644,3.7289584849,-0.3263227152
C,0,0.5218172209,4.503707203,-1.1261889806
C,0,-0.3423772426,3.9106025157,-2.0449693603
C,0,-0.3916974344,2.5164115144,-2.2055216194
C,0,0.4520676127,1.7635939071,-1.4127199235
H,0,2.0620914844,4.179438254,0.3847189093
H,0,0.5378097438,5.5839488839,-1.0259259341
H,0,-0.990678026,4.5355515083,-2.6502751496
H,0,-1.056444661,2.0435793147,-2.9198762424
```

Pi Complex 1 with ClBcat

*B3LYP-D3/6-31+G** PCM(toluene)*

E(RB3LYP) = -1651.99249944

Zero-point correction= 0.261804 (Hartree/Particle)
Thermal correction to Energy= 0.282616
Thermal correction to Enthalpy= 0.283560
Thermal correction to Gibbs Free Energy= 0.209034
Sum of electronic and ZPE= -1651.730695
Sum of electronic and thermal Energies= -1651.709884
Sum of electronic and thermal Enthalpies= -1651.708939
Sum of electronic and thermal Free Energies= -1651.783466

E CV S

```
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 177.344 75.754 156.854
```

```
C,0,0.7579095079,3.3797465321,-0.876629856
H,0,0.1938073721,4.2635751261,-1.1831133407
H,0,1.5583908865,3.2054381279,-1.5998806312
H,0,1.1726711443,3.5477992738,0.1206727997
S,0,-0.4532290834,2.017203768,-0.8495284309
C,0,0.4988775185,0.6513845543,-0.2193548182
C,0,-0.2097704729,-0.5332287982,0.1199038459
C,0,0.4980782916,-1.6395736538,0.6229358904
C,0,1.8792355041,-1.5898830189,0.7965606888
C,0,2.5719953411,-0.4244887024,0.457747833
C,0,1.8895308759,0.6840531881,-0.0468516232
C,0,-1.6289694724,-0.5982508463,-0.0234481315
H,0,-0.0592927043,-2.5312429773,0.8906192167
H,0,2.4086234528,-2.4511374745,1.1919613649
H,0,3.6493592796,-0.3714906703,0.5861161924
H,0,2.4535842866,1.5739393004,-0.2974411382
C,0,-2.8377583497,-0.6201516382,-0.1398032358
C,0,-4.2909892965,-0.620705627,-0.267469326
H,0,-4.7430767253,0.0384609648,0.4819358473
H,0,-4.596781439,-0.2696848887,-1.2591939065
H,0,-4.6982684176,-1.6260440791,-0.1185825301
B,0,-2.6381011032,-0.4071991717,3.124628861
O,0,-1.3197335048,-0.7159351974,3.396436749
O,0,-2.8304533519,0.9339000739,2.8551507117
Cl,0,-3.9397073655,-1.579795213,3.192589404
C,0,-1.5607825618,1.4894818346,2.9347871197
C,0,-1.1758220952,2.8012272794,2.7279490817
C,0,0.1928511768,3.0777578433,2.8783433615
C,0,1.1108361405,2.0731578377,3.2136861196
C,0,0.7044797583,0.7451463639,3.4176463501
C,0,-0.6458651036,0.4902646188,3.2676293779
H,0,-1.8939684534,3.5655231577,2.4547071842
H,0,0.5449676489,4.0932890824,2.7262809096
H,0,2.1628337526,2.3221502183,3.3097371392
H,0,1.4064125625,-0.0452531887,3.6542269201
```

Pi Complex 2 with ClBcat

*B3LYP-D3/6-31+G** PCM(toluene)*

E(RB3LYP) = -1651.99273912

Zero-point correction= 0.261716 (Hartree/Particle)
Thermal correction to Energy= 0.282575
Thermal correction to Enthalpy= 0.283519
Thermal correction to Gibbs Free Energy= 0.208674
Sum of electronic and ZPE= -1651.731023
Sum of electronic and thermal Energies= -1651.710164
Sum of electronic and thermal Enthalpies= -1651.709220
Sum of electronic and thermal Free Energies= -1651.784066

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 177.318 75.814 157.526
```

```
C,0,-3.1025815413,3.8719911031,0.9140295151
H,0,-4.164519982,3.9347031753,1.159482393
H,0,-2.8727426732,4.6008172306,0.1332615278
H,0,-2.5187958317,4.0723648027,1.8157131681
S,0,-2.8423528656,2.1611043688,0.3389330592
C,0,-1.087724287,2.103357381,0.0284416115
C,0,-0.5404240328,0.8457226563,-0.345489281
C,0,0.8377295108,0.7492330198,-0.6066778947
C,0,1.6700223338,1.8616633302,-0.5026329023
C,0,1.1266618774,3.0928297733,-0.1299244047
C,0,-0.2404434504,3.2139246392,0.1323248608
C,0,-1.373765621,-0.309310112,-0.4414534373
H,0,1.2439903437,-0.218093803,-0.8839417195
H,0,2.7323449122,1.766645194,-0.7046043666
H,0,1.7633576047,3.9684423034,-0.0415509748
H,0,-0.6328775475,4.1812358635,0.4205930526
C,0,-2.1079403787,-1.2747797439,-0.4955643351
C,0,-2.9975084739,-2.4306793774,-0.5348854191
H,0,-2.6996261643,-3.1814545574,0.2063267497
H,0,-4.0283807733,-2.1322528689,-0.3149788871
H,0,-2.9861744273,-2.9087345167,-1.520841105
B,0,-2.8532984711,1.3622754641,3.5168419076
O,0,-2.6314561454,0.0193772867,3.2880947628
O,0,-1.6851327268,2.1027133023,3.5531716864
Cl,0,-4.4373680839,2.047387306,3.8339802356
C,0,-0.6829912244,1.1786065568,3.2871907646
C,0,0.6789430667,1.3898123176,3.1726671824
C,0,1.4597258729,0.2595186914,2.8862944293
```

C,0,0.8839390261,-1.0084893022,2.7268071255
C,0,-0.5009149955,-1.2049907633,2.8441074942
C,0,-1.2566968237,-0.0821935142,3.1270835828
H,0,1.1100935249,2.3781067984,3.2796248483
H,0,2.5326018781,0.375964274,2.7728670086
H,0,1.5195853574,-1.8573778727,2.4959276529
H,0,-0.9616835875,-2.176211907,2.7066985586

Pi Complex 3 with ClBcat

*B3LYP-D3/6-31+G** PCM(toluene)*

E(RB3LYP) = -1651.99106654

Zero-point correction= 0.261521 (Hartree/Particle)
Thermal correction to Energy= 0.282515
Thermal correction to Enthalpy= 0.283460
Thermal correction to Gibbs Free Energy= 0.207526
Sum of electronic and ZPE= -1651.729546
Sum of electronic and thermal Energies= -1651.708551
Sum of electronic and thermal Enthalpies= -1651.707607
Sum of electronic and thermal Free Energies= -1651.783541

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	177.281	75.848	159.816

C,0,-3.6858645106,3.838326833,0.6067101001
H,0,-4.7661489941,3.9956758062,0.5708958247
H,0,-3.2277689143,4.3379197577,-0.2507017948
H,0,-3.2981506685,4.2533409644,1.5406628991
S,0,-3.4610851527,2.0296852436,0.5429471143
C,0,-1.6976468122,1.8365677047,0.6879699727
C,0,-1.1995744066,0.509056007,0.7978286982
C,0,0.1872505671,0.2980601669,0.8906373337
C,0,1.0790310425,1.3679311266,0.8859111281
C,0,0.5857347739,2.6709763998,0.7902549191
C,0,-0.7887853603,2.9040144946,0.6912431284
C,0,-2.0958341205,-0.6016319507,0.8429290298
H,0,0.549434505,-0.72016934,0.9876842267
H,0,2.1460013791,1.1864733887,0.967491619
H,0,1.2681769779,3.516150899,0.7901422293

```
H,0,-1.1398563003,3.9256455168,0.6116228663
C,0,-2.8741712648,-1.5315688617,0.9094112919
C,0,-3.8125914784,-2.6415628834,1.030449496
H,0,-3.814140327,-3.0297129285,2.0552354525
H,0,-4.8307954884,-2.3163401541,0.7919948443
H,0,-3.5478971319,-3.4611643662,0.3534608873
B,0,-3.5475937738,-0.2330153654,3.8704379127
O,0,-2.7755057349,-1.3525294032,4.1226715891
O,0,-2.818637165,0.9383497664,3.9112884408
Cl,0,-5.274960512,-0.2981159685,3.5895862035
C,0,-1.5172270585,0.5317676099,4.1611834383
C,0,-0.3768907395,1.3054874497,4.2688213027
C,0,0.8213713169,0.615175575,4.5098983936
C,0,0.8513979467,-0.7808061169,4.6317015225
C,0,-0.3171002262,-1.5531534387,4.5184257985
C,0,-1.4894961717,-0.8579359678,4.2835723859
H,0,-0.4104699801,2.3816605616,4.1465017553
H,0,1.7459923308,1.1774625901,4.5913838509
H,0,1.7978011894,-1.2801355954,4.8138416133
H,0,-0.3067177368,-2.633814521,4.605222526
```

Anti Zwitterion with ClBcat

*B3LYP-D3/6-31+G** PCM(toluene)*

E(RB3LYP) = -1651.99210253

```
Zero-point correction= 0.263950 (Hartree/Particle)
Thermal correction to Energy= 0.282793
Thermal correction to Enthalpy= 0.283737
Thermal correction to Gibbs Free Energy= 0.216303
Sum of electronic and ZPE= -1651.728153
Sum of electronic and thermal Energies= -1651.709310
Sum of electronic and thermal Enthalpies= -1651.708365
Sum of electronic and thermal Free Energies= -1651.775799
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```
     E      CV       S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 177.455 73.282 141.927
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```
C,0,-3.9330991892,-1.9930661714,0.5090400878
H,0,-3.8192978632,-2.7939890117,1.2414681114
```

H,0,-3.3589207914,-2.1961261322,-0.3953209657
H,0,-4.9892843982,-1.8319678415,0.2899680549
S,0,-3.2839889486,-0.4582081576,1.2819502453
C,0,-3.1645446463,0.6585356211,-0.1018929021
C,0,-1.818193277,0.7720464074,-0.4958165996
C,0,-1.5277189814,1.6247014038,-1.5678180433
C,0,-2.5658919403,2.3197403967,-2.1949969712
C,0,-3.8941443513,2.1902832011,-1.7697155909
C,0,-4.2122877813,1.3513275192,-0.6955770484
C,0,-0.8756401265,-0.0461986731,0.2913903085
H,0,-0.502394706,1.7344414701,-1.8981293503
H,0,-2.3353249817,2.9769934807,-3.0275879743
H,0,-4.6831355761,2.7450104465,-2.2669884892
H,0,-5.2350049124,1.2514572543,-0.3472314043
C,0,-1.4725416112,-0.7625742269,1.267669545
C,0,-0.9655977956,-1.7276730586,2.2890852075
H,0,-1.2209015741,-1.4086613095,3.3061764345
H,0,-1.3768749128,-2.7335054567,2.1362560071
H,0,0.1195585718,-1.7832275261,2.2000053215
B,0,0.6978242798,-0.0788269497,-0.0645869935
O,0,1.2507165668,1.254381243,-0.3213904499
O,0,1.5746174131,-0.7094792603,0.9182653961
Cl,0,0.7639547663,-1.1388880437,-1.7558244008
C,0,2.6730629763,0.0957638319,1.0158994759
C,0,3.8386979368,-0.1255872381,1.7314322809
C,0,4.8258484859,0.8792180986,1.6891012997
C,0,4.6316010501,2.0509484596,0.9514107368
C,0,3.4428336981,2.2653114488,0.2258504246
C,0,2.4778540479,1.2717671944,0.2742352327
H,0,3.9798944657,-1.0411863938,2.296784757
H,0,5.7528630491,0.7354849247,2.2364300833
H,0,5.4091155105,2.8090306897,0.9313818585
H,0,3.2822295462,3.169234359,-0.3528776855

Syn Zwitterion with ClBcat

*B3LYP-D3/6-31+G** PCM(toluene)*

E(RB3LYP) = -1651.99210253

Zero-point correction= 0.263950 (Hartree/Particle)

```
Thermal correction to Energy= 0.282793
Thermal correction to Enthalpy= 0.283737
Thermal correction to Gibbs Free Energy= 0.216303
Sum of electronic and ZPE= -1651.728153
Sum of electronic and thermal Energies= -1651.709310
Sum of electronic and thermal Enthalpies= -1651.708365
Sum of electronic and thermal Free Energies= -1651.775799

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 177.455 73.282 141.927

 C,0,-3.9330991892,-1.9930661714,0.5090400878
 H,0,-3.8192978632,-2.7939890117,1.2414681114
 H,0,-3.3589207914,-2.1961261322,-0.3953209657
 H,0,-4.9892843982,-1.8319678415,0.2899680549
 S,0,-3.2839889486,-0.4582081576,1.2819502453
 C,0,-3.1645446463,0.6585356211,-0.1018929021
 C,0,-1.818193277,0.7720464074,-0.4958165996
 C,0,-1.5277189814,1.6247014038,-1.5678180433
 C,0,-2.5658919403,2.3197403967,-2.1949969712
 C,0,-3.8941443513,2.1902832011,-1.7697155909
 C,0,-4.2122877813,1.3513275192,-0.6955770484
 C,0,-0.8756401265,-0.0461986731,0.2913903085
 H,0,-0.502394706,1.7344414701,-1.8981293503
 H,0,-2.3353249817,2.9769934807,-3.0275879743
 H,0,-4.6831355761,2.7450104465,-2.2669884892
 H,0,-5.2350049124,1.2514572543,-0.3472314043
 C,0,-1.4725416112,-0.7625742269,1.267669545
 C,0,-0.9655977956,-1.7276730586,2.2890852075
 H,0,-1.2209015741,-1.4086613095,3.3061764345
 H,0,-1.3768749128,-2.7335054567,2.1362560071
 H,0,0.1195585718,-1.7832275261,2.2000053215
 B,0,0.6978242798,-0.0788269497,-0.0645869935
 O,0,1.2507165668,1.254381243,-0.3213904499
 O,0,1.5746174131,-0.7094792603,0.9182653961
 Cl,0,0.7639547663,-1.1388880437,-1.7558244008
 C,0,2.6730629763,0.0957638319,1.0158994759
 C,0,3.8386979368,-0.1255872381,1.7314322809
 C,0,4.8258484859,0.8792180986,1.6891012997
 C,0,4.6316010501,2.0509484596,0.9514107368
 C,0,3.4428336981,2.2653114488,0.2258504246
 C,0,2.4778540479,1.2717671944,0.2742352327
 H,0,3.9798944657,-1.0411863938,2.296784757
```

H,0,5.7528630491,0.7354849247,2.2364300833
H,0,5.4091155105,2.8090306897,0.9313818585
H,0,3.2822295462,3.169234359,-0.3528776855

Cation with ClBcat

E(RB3LYP) = -1191.59089211

Zero-point correction= 0.264776 (Hartree/Particle)
Thermal correction to Energy= 0.281750
Thermal correction to Enthalpy= 0.282694
Thermal correction to Gibbs Free Energy= 0.219418
Sum of electronic and ZPE= -1191.326116
Sum of electronic and thermal Energies= -1191.309142
Sum of electronic and thermal Enthalpies= -1191.308198
Sum of electronic and thermal Free Energies= -1191.371474

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 176.801 67.047 133.175

C,0,-3.7353143831,-2.2267525334,0.1651133189
H,0,-3.669615054,-3.0477645366,0.8807640396
H,0,-2.9923846776,-2.3174759955,-0.626797128
H,0,-4.7470850923,-2.1606587457,-0.2374996953
S,0,-3.4375796619,-0.6719784061,1.0977667987
C,0,-3.2564474352,0.568015197,-0.1684656686
C,0,-1.9045203894,0.9500790544,-0.2702803846
C,0,-1.5834893667,1.9553974558,-1.1902963293
C,0,-2.5987057521,2.5276794135,-1.9642665269
C,0,-3.9323917825,2.1254309933,-1.8335704834
C,0,-4.2842714157,1.1334526063,-0.9107102096
C,0,-1.006043946,0.204719855,0.6357590794
H,0,-0.5584382622,2.2863507912,-1.2983759749
H,0,-2.3443524428,3.3047814822,-2.6775656533
H,0,-4.7033352024,2.5876731134,-2.4406046194
H,0,-5.316924437,0.8248813554,-0.7865282121
C,0,-1.6389302342,-0.7190429561,1.4026199526
C,0,-1.1719199064,-1.6829813162,2.4420128071
H,0,-1.6130857835,-1.4497471194,3.4177127051
H,0,-1.4546479299,-2.7112904732,2.1874159421
H,0,-0.0872756105,-1.6384000421,2.5298318956

```
B,0,0.5318109786,0.4557237546,0.7155288776
O,0,1.1895820039,1.4128353868,-0.0367882252
O,0,1.4036419543,-0.2353674212,1.5394311633
C,0,2.6538856263,0.3157869723,1.2938512665
C,0,3.87318649,-0.0128067821,1.860855961
C,0,4.9796972197,0.7255963137,1.4140617178
C,0,4.8486405351,1.7359976044,0.4488560458
C,0,3.6047810125,2.0563979185,-0.1161878871
C,0,2.5237602626,1.3188266657,0.3351761593
H,0,3.9627175972,-0.7945619236,2.6064936127
H,0,5.9593766746,0.5088044741,1.8269234869
H,0,5.7290795076,2.2844470236,0.1306579255
H,0,3.4917989029,2.8353858201,-0.8615097581
```

Chloride Anion

```
E(RB3LYP) = -460.338866325

Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001416
Thermal correction to Enthalpy= 0.002360
Thermal correction to Gibbs Free Energy= -0.015023
Sum of electronic and ZPE= -460.338866
Sum of electronic and thermal Energies= -460.337450
Sum of electronic and thermal Enthalpies= -460.336506
Sum of electronic and thermal Free Energies= -460.353889

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 0.889 2.981 36.586

17 0.000000 0.000000 0.000000
```

S_N2 TS with ClBcat

*B3LYP-D3/6-31+G** PCM(toluene)*

```
E(RB3LYP) = -1651.97480987

Zero-point correction= 0.263472 (Hartree/Particle)
```

```
Thermal correction to Energy= 0.282651
Thermal correction to Enthalpy= 0.283595
Thermal correction to Gibbs Free Energy= 0.212829
Sum of electronic and ZPE= -1651.711338
Sum of electronic and thermal Energies= -1651.692159
Sum of electronic and thermal Enthalpies= -1651.691215
Sum of electronic and thermal Free Energies= -1651.761981

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 177.366 72.139 148.940

 C,0,-3.657877,-2.3758729204,-0.0084831881
 H,0,-3.5328711232,-3.1180083238,0.767940784
 H,0,-2.8354687029,-2.2146879402,-0.6913577836
 H,0,-4.6598633187,-2.2399205261,-0.3923113958
 S,0,-3.4895005084,-0.6138596635,1.15791221
 C,0,-3.3064064077,0.6380480524,-0.0776549483
 C,0,-1.9520593461,1.0165848195,-0.1951446038
 C,0,-1.628981164,2.0083321566,-1.1341093393
 C,0,-2.6394821306,2.5730332701,-1.9144556447
 C,0,-3.9756810729,2.1723741644,-1.7769618768
 C,0,-4.3268712218,1.1936001392,-0.8440565195
 C,0,-1.0631903266,0.2813865445,0.7184444685
 H,0,-0.6012305937,2.3277947786,-1.2523155651
 H,0,-2.3833160034,3.336125128,-2.6427081433
 H,0,-4.7452083175,2.6225300835,-2.3954976611
 H,0,-5.3581891109,0.8782515442,-0.7261254115
 C,0,-1.7274566713,-0.6226353484,1.4961342063
 C,0,-1.2514429777,-1.599328059,2.5234547974
 H,0,-0.1804772592,-1.4915785287,2.6871648999
 H,0,-1.7710763711,-1.4500788201,3.4764143492
 H,0,-1.4466570881,-2.628869696,2.1990706742
 B,0,0.4699690689,0.5031113482,0.7843810391
 O,0,1.1537590447,1.4071639954,-0.0214174897
 O,0,1.3425901289,-0.1590820506,1.6413714996
 Cl,0,-3.8311914161,-4.5644081718,-1.4420784403
 C,0,2.5991234473,0.3456837821,1.3549891765
 C,0,3.8170250016,0.0170218246,1.9252984608
 C,0,4.9392928205,0.6984082634,1.4276456126
 C,0,4.8240157322,1.6565590605,0.409618504
 C,0,3.58093734,1.97828622,-0.1583836038
 C,0,2.4844379932,1.2982081377,0.3434088742
 H,0,3.8938963892,-0.7269794571,2.7101566928
```

H,0,5.9177444735,0.4757244214,1.8409002395
H,0,5.7149234319,2.1612160036,0.0499591783
H,0,3.4794532601,2.7155097678,-0.9468610524

MeCl

E(RB3LYP) = -500.118164465

Zero-point correction= 0.037725 (Hartree/Particle)
Thermal correction to Energy= 0.040757
Thermal correction to Enthalpy= 0.041701
Thermal correction to Gibbs Free Energy= 0.014036
Sum of electronic and ZPE= -500.080440
Sum of electronic and thermal Energies= -500.077408
Sum of electronic and thermal Enthalpies= -500.076464
Sum of electronic and thermal Free Energies= -500.104129

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	25.575	7.763	58.226

C,0,0.1735632714,0.0516803301,0.0157789039
H,0,0.0735198837,0.0590677824,1.1006838309
H,0,1.1150206598,-0.409684304,-0.2803503373
H,0,0.0975096038,1.0626649993,-0.3832635855
Cl,0,-1.1834424188,-0.9351088078,-0.6731778119

Final Product with ClBcat

E(RB3LYP) = -1151.90508486

Zero-point correction= 0.225500 (Hartree/Particle)
Thermal correction to Energy= 0.240529
Thermal correction to Enthalpy= 0.241474
Thermal correction to Gibbs Free Energy= 0.181445
Sum of electronic and ZPE= -1151.679585
Sum of electronic and thermal Energies= -1151.664555
Sum of electronic and thermal Enthalpies= -1151.663611
Sum of electronic and thermal Free Energies= -1151.723640

```
    E     CV      S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 150.934 59.452 126.341

 S,0,-3.4746802953,-0.5883885387,1.1908445119
 C,0,-3.3115633375,0.6332246121,-0.0588248686
 C,0,-1.957459892,1.0248169407,-0.2057260492
 C,0,-1.6513636036,2.0062180209,-1.1699336594
 C,0,-2.6689006733,2.558144495,-1.9423091259
 C,0,-4.0062628909,2.1527859714,-1.7772027085
 C,0,-4.3388558222,1.1853762544,-0.8319783183
 C,0,-1.0656316397,0.3163655714,0.7057373188
 H,0,-0.6246001829,2.3254999528,-1.3044815994
 H,0,-2.4268760216,3.3137322965,-2.6839907007
 H,0,-4.7861662225,2.5955406634,-2.3894509529
 H,0,-5.3683242876,0.8675617389,-0.6988171877
 C,0,-1.7492837346,-0.5736462257,1.5078442854
 C,0,-1.2107179809,-1.5125349635,2.5500008879
 H,0,-0.3908112267,-1.0488500148,3.101369819
 H,0,-1.9867163508,-1.81163411,3.2598133007
 H,0,-0.816613973,-2.4215024431,2.0801391502
 B,0,0.454275858,0.5183018958,0.7680321302
 O,0,1.1619294001,1.4443142698,-0.0061174857
 O,0,1.3301592624,-0.1928160859,1.5965756003
 C,0,2.5884297831,0.3069542946,1.3281307698
 C,0,3.8036590476,-0.0580582191,1.8827316326
 C,0,4.9368042876,0.6270299406,1.4130699521
 C,0,4.8342073421,1.6256946709,0.4343515202
 C,0,3.5937812892,1.9846977837,-0.1191008656
 C,0,2.4864537188,1.3008923753,0.3538296822
 H,0,3.8705064644,-0.8323842235,2.6389969759
 H,0,5.9118290007,0.3755581746,1.8183916549
 H,0,5.7311181648,2.134264715,0.0950931178
 H,0,3.5016155162,2.7553811863,-0.8763877879
```

Dichlorocatecholborate anion

E(RB3LYP) = -1327.07243711

Zero-point correction= 0.093941 (Hartree/Particle)
Thermal correction to Energy= 0.103028

Thermal correction to Enthalpy= 0.103972
Thermal correction to Gibbs Free Energy= 0.058365
Sum of electronic and ZPE= -1326.978496
Sum of electronic and thermal Energies= -1326.969409
Sum of electronic and thermal Enthalpies= -1326.968465
Sum of electronic and thermal Free Energies= -1327.014072

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 64.651 34.409 95.989
```

```
B,0,0.3421440158,-0.1767624003,0.2546403178
O,0,0.0370653539,-0.0195156804,1.6772045567
C,0,1.2313179127,0.0038744965,2.3248861011
C,0,1.4690543149,0.1094702442,3.6865908906
C,0,2.8121192009,0.1076508298,4.1169575622
C,0,3.8622788152,0.0040250421,3.2001918414
C,0,3.6113350891,-0.1015992233,1.8164261397
C,0,2.2883427474,-0.1001796754,1.4020593597
H,0,0.6446692125,0.1875484643,4.3882778075
H,0,3.0294009742,0.186794865,5.1787000296
H,0,4.8893938713,0.0030325656,3.55489305
H,0,4.4178628006,-0.1838106367,1.0947071339
O,0,1.8008436309,-0.1927361037,0.1371761469
Cl,0,-0.4011080881,1.2607250012,-0.7581476894
Cl,0,-0.3919678514,-1.8212217887,-0.4010062479
```

358K
all structures below use chlorocatecholborane as the electrophile

Chlorocatecholborane

*B3LYP-D3/6-31+G** PCM(toluene)*

E(RB3LYP) = -866.710762259

Zero-point correction= 0.094441 (Hartree/Particle)
Thermal correction to Energy= 0.104640
Thermal correction to Enthalpy= 0.105774
Thermal correction to Gibbs Free Energy= 0.053388
Sum of electronic and ZPE= -866.616321
Sum of electronic and thermal Energies= -866.606122

```
Sum of electronic and thermal Enthalpies= -866.604988
Sum of electronic and thermal Free Energies= -866.657374

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 65.663 33.549 91.823

6 0.890078 -0.168989 0.000000
6 2.262297 0.008819 0.000000
6 2.715795 1.338313 0.000000
6 1.821481 2.418400 0.000000
6 0.430714 2.220903 0.000000
6 0.000000 0.905947 0.000000
1 2.943190 -0.834866 0.000000
1 3.783853 1.530884 0.000000
1 2.209923 3.431776 0.000000
1 -0.271104 3.047267 0.000000
8 -1.298887 0.417430 0.000000
5 -1.155872 -0.957098 0.000000
8 0.167844 -1.353973 0.000000
17 -2.503550 -2.072799 0.000000
```

(o-methylthiophenyl)-2-propyne

*B3LYP-D3/6-31+G** PCM(toluene)*

```
E(RB3LYP) = -866.710762259

Zero-point correction= 0.094441 (Hartree/Particle)
Thermal correction to Energy= 0.104640
Thermal correction to Enthalpy= 0.105774
Thermal correction to Gibbs Free Energy= 0.053388
Sum of electronic and ZPE= -866.616321
Sum of electronic and thermal Energies= -866.606122
Sum of electronic and thermal Enthalpies= -866.604988
Sum of electronic and thermal Free Energies= -866.657374

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 65.663 33.549 91.823

6 0.890078 -0.168989 0.000000
```

6	2.262297	0.008819	0.000000
6	2.715795	1.338313	0.000000
6	1.821481	2.418400	0.000000
6	0.430714	2.220903	0.000000
6	0.000000	0.905947	0.000000
1	2.943190	-0.834866	0.000000
1	3.783853	1.530884	0.000000
1	2.209923	3.431776	0.000000
1	-0.271104	3.047267	0.000000
8	-1.298887	0.417430	0.000000
5	-1.155872	-0.957098	0.000000
8	0.167844	-1.353973	0.000000
17	-2.503550	-2.072799	0.000000

Anti TS with ClBcat

*B3LYP-D3/6-31+G** PCM(toluene)*

E(RB3LYP) = -1651.96117864

Zero-point correction= 0.260690 (Hartree/Particle)
Thermal correction to Energy= 0.287847
Thermal correction to Enthalpy= 0.288981
Thermal correction to Gibbs Free Energy= 0.196715
Sum of electronic and ZPE= -1651.700489
Sum of electronic and thermal Energies= -1651.673331
Sum of electronic and thermal Enthalpies= -1651.672198
Sum of electronic and thermal Free Energies= -1651.764463

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	180.627	86.132	161.725

6	3.529894	2.247634	0.587828
1	3.615703	3.334965	0.521241
1	4.498366	1.820442	0.854500
1	2.781588	1.981899	1.337378
16	3.010953	1.650787	-1.072393
6	2.813991	-0.096327	-0.729765
6	1.604911	-0.602244	-0.173078
6	1.494459	-1.979795	0.064724
6	2.546013	-2.843034	-0.245465

6	3.726534	-2.345961	-0.799313
6	3.856674	-0.975127	-1.040539
6	0.533682	0.342265	0.117508
1	0.578377	-2.374481	0.482712
1	2.437001	-3.906187	-0.054735
1	4.544982	-3.016365	-1.043321
1	4.772419	-0.582190	-1.469759
6	0.334143	1.557799	-0.100988
6	-0.203266	2.897875	-0.137903
1	0.474251	3.613037	0.340058
1	-0.419672	3.222689	-1.160024
1	-1.142246	2.873044	0.431710
5	-1.050477	-0.229712	1.149580
8	-2.050470	0.795163	1.165207
8	-1.520024	-1.319849	0.349443
17	-0.297658	-0.628993	2.766158
6	-2.639896	-0.846209	-0.287709
6	-3.401128	-1.465278	-1.264808
6	-4.520354	-0.758999	-1.742905
6	-4.843243	0.510354	-1.249618
6	-4.060635	1.128962	-0.256586
6	-2.961407	0.424553	0.204762
1	-3.141054	-2.450149	-1.637448
1	-5.142701	-1.210126	-2.509553
1	-5.713268	1.030833	-1.637976
1	-4.304706	2.110124	0.136853

Syn TS with ClBcat

*B3LYP-D3/6-31+G** PCM(toluene)*

E(RB3LYP) = -1651.96106080

Zero-point correction= 0.260732 (Hartree/Particle)
Thermal correction to Energy= 0.287861
Thermal correction to Enthalpy= 0.288995
Thermal correction to Gibbs Free Energy= 0.196943
Sum of electronic and ZPE= -1651.700329
Sum of electronic and thermal Energies= -1651.673200
Sum of electronic and thermal Enthalpies= -1651.672066
Sum of electronic and thermal Free Energies= -1651.764117

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 180.635 86.110 161.349

6	-1.818121	2.967955	-0.642766
1	-1.671690	3.968245	-0.228077
1	-2.376532	3.038291	-1.578111
1	-0.848868	2.496052	-0.816210
16	-2.781023	2.010982	0.598561
6	-2.809727	0.407720	-0.200172
6	-1.723787	-0.501876	-0.054161
6	-1.791902	-1.744704	-0.699564
6	-2.910334	-2.094188	-1.457329
6	-3.978852	-1.206094	-1.587994
6	-3.924946	0.042136	-0.960587
6	-0.593660	-0.094845	0.770210
1	-0.968614	-2.439528	-0.604044
1	-2.943287	-3.064398	-1.943261
1	-4.851059	-1.477069	-2.175071
1	-4.750770	0.738585	-1.061606
6	-0.341040	0.878529	1.514731
6	0.290832	1.817834	2.411472
1	0.403308	2.803656	1.948313
1	-0.259589	1.913728	3.352076
1	1.291600	1.417624	2.624744
5	1.071055	-1.157604	0.779617
8	1.274273	-1.317676	-0.628601
8	2.154162	-0.389930	1.317798
17	0.589849	-2.633692	1.740748
6	2.823178	0.103287	0.223642
6	3.875009	1.003252	0.190967
6	4.388236	1.338703	-1.076237
6	3.856078	0.783462	-2.245536
6	2.787633	-0.131421	-2.199024
6	2.292025	-0.453693	-0.946729
1	4.283504	1.422917	1.104223
1	5.213308	2.041136	-1.143784
1	4.273238	1.061247	-3.208597
1	2.367913	-0.570914	-3.097494

Variational TS Syn with ClBcat

E(RB3LYP) = -1651.96141374

Zero-point correction= 0.260698 (Hartree/Particle)
Thermal correction to Energy= 0.280038
Thermal correction to Enthalpy= 0.280982
Thermal correction to Gibbs Free Energy= 0.211988
Sum of electronic and ZPE= -1651.700715
Sum of electronic and thermal Energies= -1651.681376
Sum of electronic and thermal Enthalpies= -1651.680432
Sum of electronic and thermal Free Energies= -1651.749426

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	175.726	73.700	145.210

6	-1.791889	-3.008218	0.835474
1	-1.628094	-4.022444	0.463663
1	-2.370401	-3.045772	1.760287
1	-0.832092	-2.517949	1.008833
16	-2.737999	-2.109481	-0.461535
6	-2.797951	-0.475513	0.266143
6	-1.725314	0.439802	0.070750
6	-1.811290	1.710237	0.656489
6	-2.932278	2.078193	1.402054
6	-3.986714	1.181818	1.581244
6	-3.916851	-0.093946	1.013317
6	-0.582232	0.015231	-0.737973
1	-0.999512	2.412559	0.523839
1	-2.978059	3.070196	1.840556
1	-4.860379	1.467748	2.158876
1	-4.732202	-0.796614	1.150225
6	-0.381104	-1.025859	-1.421633
6	0.266738	-1.990148	-2.280583
1	0.412818	-2.952168	-1.778986
1	-0.279622	-2.138267	-3.216600
1	1.254464	-1.563000	-2.508194
5	1.004310	1.045956	-0.803897
8	1.246317	1.303580	0.593225
8	2.114848	0.278985	-1.314243
17	0.542015	2.495462	-1.840158
6	2.807957	-0.135912	-0.204650

6 3.874044 -1.017501 -0.133877
6 4.404802 -1.279621 1.143984
6 3.876358 -0.671041 2.287737
6 2.795591 0.226938 2.202959
6 2.282227 0.477174 0.941008
1 4.278717 -1.480980 -1.027580
1 5.239730 -1.967136 1.239365
1 4.305449 -0.892819 3.260115
1 2.377960 0.707193 3.081441

Variational TS Anti with ClBcat

E(RB3LYP) = -1651.96141374

Zero-point correction= 0.260698 (Hartree/Particle)
Thermal correction to Energy= 0.280038
Thermal correction to Enthalpy= 0.280982
Thermal correction to Gibbs Free Energy= 0.211988
Sum of electronic and ZPE= -1651.700715
Sum of electronic and thermal Energies= -1651.681376
Sum of electronic and thermal Enthalpies= -1651.680432
Sum of electronic and thermal Free Energies= -1651.749426

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 175.726 73.700 145.210

6 -1.791889 -3.008218 0.835474
1 -1.628094 -4.022444 0.463663
1 -2.370401 -3.045772 1.760287
1 -0.832092 -2.517949 1.008833
16 -2.737999 -2.109481 -0.461535
6 -2.797951 -0.475513 0.266143
6 -1.725314 0.439802 0.070750
6 -1.811290 1.710237 0.656489
6 -2.932278 2.078193 1.402054
6 -3.986714 1.181818 1.581244
6 -3.916851 -0.093946 1.013317
6 -0.582232 0.015231 -0.737973
1 -0.999512 2.412559 0.523839
1 -2.978059 3.070196 1.840556
1 -4.860379 1.467748 2.158876

1	-4.732202	-0.796614	1.150225
6	-0.381104	-1.025859	-1.421633
6	0.266738	-1.990148	-2.280583
1	0.412818	-2.952168	-1.778986
1	-0.279622	-2.138267	-3.216600
1	1.254464	-1.563000	-2.508194
5	1.004310	1.045956	-0.803897
8	1.246317	1.303580	0.593225
8	2.114848	0.278985	-1.314243
17	0.542015	2.495462	-1.840158
6	2.807957	-0.135912	-0.204650
6	3.874044	-1.017501	-0.133877
6	4.404802	-1.279621	1.143984
6	3.876358	-0.671041	2.287737
6	2.795591	0.226938	2.202959
6	2.282227	0.477174	0.941008
1	4.278717	-1.480980	-1.027580
1	5.239730	-1.967136	1.239365
1	4.305449	-0.892819	3.260115
1	2.377960	0.707193	3.081441

Pi Complex 1 with ClBcat

*B3LYP-D3/6-31+G** PCM(toluene)*

E(RB3LYP) = -1651.99249944

Zero-point correction= 0.261804 (Hartree/Particle)
Thermal correction to Energy= 0.290422
Thermal correction to Enthalpy= 0.291556
Thermal correction to Gibbs Free Energy= 0.193339
Sum of electronic and ZPE= -1651.730695
Sum of electronic and thermal Energies= -1651.702077
Sum of electronic and thermal Enthalpies= -1651.700943
Sum of electronic and thermal Free Energies= -1651.799160

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	182.243	87.802	172.156

6	3.404887	-0.497812	-2.083032
1	3.433138	-0.523723	-3.174741

1	4.268374	-1.044488	-1.696017
1	3.429087	0.542680	-1.748860
16	1.827643	-1.286635	-1.620241
6	1.789200	-1.090934	0.148745
6	0.577898	-1.424874	0.813440
6	0.497660	-1.286144	2.210725
6	1.583896	-0.823853	2.950043
6	2.773905	-0.500735	2.292528
6	2.876492	-0.634663	0.906605
6	-0.557724	-1.874536	0.073799
1	-0.438528	-1.531565	2.701350
1	1.502203	-0.716991	4.027195
1	3.629949	-0.140542	2.855955
1	3.810781	-0.373415	0.425251
6	-1.513113	-2.238662	-0.581817
6	-2.655589	-2.654977	-1.387801
1	-3.039425	-1.813044	-1.974582
1	-2.374101	-3.454283	-2.082148
1	-3.470479	-3.021296	-0.754940
5	-2.525406	0.787175	0.167381
8	-1.679599	1.176058	1.187514
8	-2.014167	1.059669	-1.086631
17	-4.112726	0.093895	0.438591
6	-0.769976	1.623440	-0.839189
6	0.178054	2.059733	-1.746128
6	1.358540	2.592125	-1.202654
6	1.558469	2.667699	0.182513
6	0.587163	2.217702	1.090483
6	-0.569327	1.698370	0.539368
1	0.016778	1.982048	-2.815006
1	2.133715	2.948325	-1.873950
1	2.488740	3.074557	0.565900
1	0.738369	2.248740	2.162669

Pi Complex 2 with ClBcat

*B3LYP-D3/6-31+G** PCM(toluene)*

E(RB3LYP) = -1651.99273912

Zero-point correction= 0.261716 (Hartree/Particle)
Thermal correction to Energy= 0.290387

```
Thermal correction to Enthalpy= 0.291520
Thermal correction to Gibbs Free Energy= 0.192916
Sum of electronic and ZPE= -1651.731023
Sum of electronic and thermal Energies= -1651.702353
Sum of electronic and thermal Enthalpies= -1651.701219
Sum of electronic and thermal Free Energies= -1651.799824

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 182.220 87.853 172.836

6 1.596612 2.855711 0.651221
1 2.604244 2.852550 1.071411
1 1.115388 3.808471 0.884207
1 1.663691 2.709069 -0.429512
16 0.740524 1.454581 1.444656
6 -0.862789 1.468938 0.665142
6 -1.753001 0.413186 1.002654
6 -3.031670 0.382818 0.418771
6 -3.435404 1.365727 -0.482298
6 -2.554100 2.397083 -0.813255
6 -1.279095 2.449807 -0.244047
6 -1.352038 -0.612383 1.911063
1 -3.698738 -0.432551 0.679226
1 -4.425327 1.323255 -0.925693
1 -2.853384 3.168887 -1.516557
1 -0.617099 3.260926 -0.520886
6 -0.971947 -1.478003 2.672841
6 -0.494167 -2.523141 3.571947
1 -0.466102 -3.494968 3.065431
1 0.519017 -2.297676 3.922291
1 -1.142500 -2.620314 4.450011
5 2.363951 -0.419515 -0.697679
8 1.801548 -1.598715 -0.252588
8 1.579970 0.231744 -1.633314
17 3.952430 0.146041 -0.211767
6 0.445265 -0.561450 -1.744201
6 -0.680148 -0.355904 -2.521236
6 -1.686349 -1.329285 -2.424883
6 -1.550608 -2.444042 -1.586014
6 -0.402306 -2.636285 -0.802025
6 0.580350 -1.669301 -0.908253
1 -0.781331 0.519523 -3.151670
1 -2.595316 -1.205796 -3.004553
```

1	-2.354935	-3.170651	-1.530689
1	-0.290835	-3.484242	-0.136441

Pi Complex 3 with ClBcat

*B3LYP-D3/6-31+G** PCM(toluene)*

E(RB3LYP) = -1651.99106653

Zero-point correction= 0.261521 (Hartree/Particle)
Thermal correction to Energy= 0.290330
Thermal correction to Enthalpy= 0.291464
Thermal correction to Gibbs Free Energy= 0.191547
Sum of electronic and ZPE= -1651.729546
Sum of electronic and thermal Energies= -1651.700737
Sum of electronic and thermal Enthalpies= -1651.699603
Sum of electronic and thermal Free Energies= -1651.799519

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	182.185	87.877	175.135

6	2.305160	-3.124616	-1.445365
1	1.875848	-4.082357	-1.747818
1	3.330642	-3.289230	-1.104939
1	2.292906	-2.444780	-2.301227
16	1.229622	-2.518009	-0.103343
6	1.927946	-0.927862	0.286293
6	1.226977	-0.127702	1.230125
6	1.747330	1.127108	1.592200
6	2.932128	1.601973	1.034819
6	3.611498	0.818886	0.099058
6	3.115658	-0.434209	-0.271497
6	-0.009042	-0.576255	1.786904
1	1.192741	1.730589	2.303275
1	3.314153	2.577153	1.319580
1	4.534234	1.177417	-0.348223
1	3.669070	-1.020689	-0.994753
6	-1.073397	-0.960963	2.227538
6	-2.370626	-1.407456	2.722726
1	-3.174448	-0.807447	2.281468
1	-2.547574	-2.455025	2.456909

1	-2.432754	-1.315896	3.812624
5	-2.100913	-0.388024	-0.858458
8	-2.595400	0.658944	-0.101892
8	-0.955031	-0.051788	-1.550588
17	-2.883943	-1.950648	-0.967925
6	-0.693773	1.257863	-1.179128
6	0.358910	2.069115	-1.559023
6	0.379746	3.359082	-1.005824
6	-0.614222	3.791851	-0.117430
6	-1.677465	2.953995	0.259730
6	-1.684977	1.687441	-0.295950
1	1.134793	1.712798	-2.226319
1	1.192292	4.030230	-1.264787
1	-0.562340	4.795183	0.293443
1	-2.449573	3.274594	0.950047

Anti Zwitterion with ClBcat

*B3LYP-D3/6-31+G** PCM(toluene)*

E(RB3LYP) = -1651.99130394

Zero-point correction= 0.264494 (Hartree/Particle)
Thermal correction to Energy= 0.288952
Thermal correction to Enthalpy= 0.290086
Thermal correction to Gibbs Free Energy= 0.206621
Sum of electronic and ZPE= -1651.726810
Sum of electronic and thermal Energies= -1651.702352
Sum of electronic and thermal Enthalpies= -1651.701218
Sum of electronic and thermal Free Energies= -1651.784683

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	181.320	81.728	146.298

6	3.746949	-2.034316	0.619948
1	3.629551	-3.118537	0.615270
1	3.280990	-1.584461	1.497065
1	4.802117	-1.772630	0.543727
16	2.910734	-1.393796	-0.865068
6	2.896241	0.351525	-0.555638
6	1.617407	0.737576	-0.133578

6	1.407972	2.087434	0.156689
6	2.465491	2.985477	0.016027
6	3.726892	2.567054	-0.416448
6	3.960107	1.225082	-0.719588
6	0.643768	-0.368569	-0.042572
1	0.428810	2.416807	0.486661
1	2.303808	4.033784	0.244247
1	4.531043	3.286748	-0.524432
1	4.930836	0.887812	-1.068453
6	1.161226	-1.559988	-0.387625
6	0.603078	-2.944179	-0.426818
1	0.686285	-3.379571	-1.427273
1	1.117120	-3.604565	0.280628
1	-0.449619	-2.893083	-0.148636
5	-0.854896	-0.110296	0.499252
8	-1.466394	1.085376	-0.077584
8	-1.803813	-1.197091	0.298686
17	-0.608364	0.173090	2.427465
6	-2.969192	-0.607566	-0.080423
6	-4.206611	-1.194032	-0.261075
6	-5.259250	-0.364322	-0.684672
6	-5.057414	0.994824	-0.911425
6	-3.794766	1.583279	-0.723760
6	-2.765658	0.761020	-0.307328
1	-4.352314	-2.253242	-0.077747
1	-6.245324	-0.792889	-0.832755
1	-5.887857	1.614290	-1.234842
1	-3.626327	2.641147	-0.894644

Syn Zwitterion with ClBcat

*B3LYP-D3/6-31+G** PCM(toluene)*

E(RB3LYP) = -1651.98708514

Zero-point correction= 0.264250 (Hartree/Particle)
Thermal correction to Energy= 0.288922
Thermal correction to Enthalpy= 0.290056
Thermal correction to Gibbs Free Energy= 0.204603
Sum of electronic and ZPE= -1651.722835
Sum of electronic and thermal Energies= -1651.698163
Sum of electronic and thermal Enthalpies= -1651.697030

Sum of electronic and thermal Free Energies= -1651.782482

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	181.301	81.730	149.784

6	-3.153869	-1.440018	-2.102245
1	-3.109522	-2.511573	-2.300094
1	-2.287947	-0.920341	-2.513265
1	-4.089412	-1.028788	-2.480818
16	-3.147224	-1.223522	-0.294518
6	-2.891180	0.523099	-0.133716
6	-1.556069	0.766528	0.213856
6	-1.161386	2.094460	0.390087
6	-2.099337	3.111639	0.216279
6	-3.426277	2.832094	-0.121848
6	-3.847556	1.513338	-0.296710
6	-0.725946	-0.447890	0.339937
1	-0.134005	2.314853	0.658492
1	-1.792250	4.143581	0.350316
1	-4.138168	3.641089	-0.244389
1	-4.877563	1.280494	-0.546993
6	-1.405969	-1.582088	0.100212
6	-1.013821	-3.022375	0.071194
1	-1.610832	-3.612480	0.773157
1	-1.134676	-3.451321	-0.929920
1	0.036940	-3.093218	0.352353
5	0.852102	-0.342461	0.663856
8	1.661654	-1.223442	-0.175665
8	1.440836	0.985185	0.551870
17	0.986203	-0.962536	2.523054
6	2.648734	0.806680	-0.046869
6	3.646725	1.738224	-0.256684
6	4.803478	1.305797	-0.928125
6	4.933471	-0.011048	-1.362235
6	3.913020	-0.952572	-1.143166
6	2.779442	-0.515005	-0.483471
1	3.535374	2.760292	0.089357
1	5.608309	2.011869	-1.106035
1	5.838468	-0.320325	-1.875362
1	4.004237	-1.981487	-1.474332

Cation with ClBcat

E(RB3LYP) = -1191.59089211

Zero-point correction= 0.264776 (Hartree/Particle)
Thermal correction to Energy= 0.288742
Thermal correction to Enthalpy= 0.289876
Thermal correction to Gibbs Free Energy= 0.206059
Sum of electronic and ZPE= -1191.326116
Sum of electronic and thermal Energies= -1191.302150
Sum of electronic and thermal Enthalpies= -1191.301016
Sum of electronic and thermal Free Energies= -1191.384833

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	181.189	79.451	146.916

6	3.623759	-1.963291	1.241938
1	3.537825	-3.050988	1.233976
1	3.026212	-1.514201	2.034751
1	4.672337	-1.670753	1.313029
16	3.018845	-1.361641	-0.385302
6	2.901913	0.404248	-0.181092
6	1.548533	0.784234	-0.091544
6	1.266231	2.150438	0.026555
6	2.320612	3.069437	0.056942
6	3.653810	2.655745	-0.038172
6	3.964521	1.297478	-0.172629
6	0.607184	-0.354091	-0.134009
1	0.240369	2.490016	0.091643
1	2.096636	4.126966	0.151003
1	4.454472	3.387215	-0.018038
1	4.992936	0.964660	-0.265391
6	1.210535	-1.564533	-0.246947
6	0.696031	-2.962929	-0.332887
1	0.953414	-3.415471	-1.297240
1	1.124480	-3.594139	0.454627
1	-0.387533	-2.967769	-0.223256
5	-0.942598	-0.188078	-0.063434
8	-1.576249	1.039057	0.022188
8	-1.850989	-1.232559	-0.083352
6	-3.100660	-0.632271	-0.011459
6	-4.349947	-1.228381	-0.001562

6	-5.447717	-0.357731	0.076540
6	-5.279623	1.034163	0.140467
6	-4.005632	1.622336	0.129650
6	-2.933690	0.749802	0.052375
1	-4.468170	-2.304751	-0.052389
1	-6.450019	-0.773074	0.086826
1	-6.154626	1.673020	0.199209
1	-3.864127	2.696008	0.177579

Chloride Anion

E(RB3LYP) = -460.338866325

Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001701
Thermal correction to Enthalpy= 0.002834
Thermal correction to Gibbs Free Energy= -0.018557
Sum of electronic and ZPE= -460.338866
Sum of electronic and thermal Energies= -460.337166
Sum of electronic and thermal Enthalpies= -460.336032
Sum of electronic and thermal Free Energies= -460.357423

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	1.067	2.981	37.495

17	0.000000	0.000000	0.000000

S_N2 TS with ClBcat

*B3LYP-D3/6-31+G** PCM(toluene)*

E(RB3LYP) = -1651.97480987

Zero-point correction= 0.263472 (Hartree/Particle)
Thermal correction to Energy= 0.290126
Thermal correction to Enthalpy= 0.291260
Thermal correction to Gibbs Free Energy= 0.197920
Sum of electronic and ZPE= -1651.711338
Sum of electronic and thermal Energies= -1651.684683

Sum of electronic and thermal Enthalpies= -1651.683550
Sum of electronic and thermal Free Energies= -1651.776890

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	182.057	84.487	163.608

6	3.492700	-1.278278	0.077590
1	3.482808	-2.253848	-0.388664
1	2.802788	-1.098998	0.890323
1	4.444243	-0.765010	0.107661
16	2.536939	-0.151578	-1.442471
6	2.175671	1.367690	-0.612572
6	0.818147	1.406139	-0.229165
6	0.360006	2.550308	0.442086
6	1.248845	3.592489	0.711835
6	2.593306	3.522417	0.321485
6	3.074232	2.399208	-0.355831
6	0.074343	0.194066	-0.607167
1	-0.675592	2.618794	0.750544
1	0.890377	4.472994	1.235757
1	3.267906	4.342806	0.543465
1	4.111809	2.335427	-0.666210
6	0.848264	-0.727183	-1.251880
6	0.546102	-2.092124	-1.782485
1	-0.510325	-2.325372	-1.660279
1	0.803216	-2.165224	-2.845016
1	1.128985	-2.853008	-1.249012
5	-1.429774	-0.019205	-0.296952
8	-2.216638	0.907122	0.379033
8	-2.172557	-1.141347	-0.648332
17	4.643920	-2.692198	1.961851
6	-3.450870	-0.904420	-0.173505
6	-4.571920	-1.712199	-0.258919
6	-5.746369	-1.207135	0.321606
6	-5.773409	0.046245	0.950912
6	-4.627179	0.853358	1.029059
6	-3.477757	0.341455	0.451653
1	-4.538203	-2.680230	-0.745982
1	-6.652601	-1.802907	0.282457
1	-6.700112	0.401978	1.389576
1	-4.635210	1.822830	1.514398

MeCl

*B3LYP-D3/6-31+G** PCM(toluene)*

```
E(RB3LYP) = -500.118164465

Zero-point correction= 0.037725 (Hartree/Particle)
Thermal correction to Energy= 0.041544
Thermal correction to Enthalpy= 0.042678
Thermal correction to Gibbs Free Energy= 0.008392
Sum of electronic and ZPE= -500.080440
Sum of electronic and thermal Energies= -500.076620
Sum of electronic and thermal Enthalpies= -500.075486
Sum of electronic and thermal Free Energies= -500.109773

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 26.069 8.767 60.098
```

6	-1.146575	0.000099	-0.000102
1	-1.487915	-0.252941	1.003162
1	-1.487362	0.995601	-0.282470
1	-1.488131	-0.742830	-0.720175
17	0.667227	-0.000025	0.000006

Final Product with ClBcat

*B3LYP-D3/6-31+G** PCM(toluene)*

```
E(RB3LYP) = -1151.90508486

Zero-point correction= 0.225500 (Hartree/Particle)
Thermal correction to Energy= 0.246746
Thermal correction to Enthalpy= 0.247880
Thermal correction to Gibbs Free Energy= 0.168808
Sum of electronic and ZPE= -1151.679585
Sum of electronic and thermal Energies= -1151.658339
Sum of electronic and thermal Enthalpies= -1151.657205
Sum of electronic and thermal Free Energies= -1151.736276

     E      CV        S
```

KCal/Mol Cal/Mol-K Cal/Mol-K
Total 154.835 70.770 138.597

16	-3.109568	1.758760	-0.014130
6	-3.146185	0.004068	0.004350
6	-1.832052	-0.526537	-0.001084
6	-1.682233	-1.927967	0.008343
6	-2.809353	-2.744029	0.022837
6	-4.104067	-2.192843	0.027553
6	-4.283050	-0.811603	0.017992
6	-0.807088	0.511361	-0.016610
1	-0.689437	-2.362282	0.004387
1	-2.687626	-3.823245	0.030435
1	-4.971160	-2.846413	0.038679
1	-5.278728	-0.378991	0.021525
6	-1.355370	1.777129	-0.026337
6	-0.659062	3.108536	-0.013314
1	0.247020	3.076870	-0.620991
1	-1.307518	3.903985	-0.390451
1	-0.359660	3.374593	1.007411
5	0.703673	0.242377	-0.011302
8	1.280713	-1.031816	-0.043476
8	1.698916	1.225784	0.030481
6	2.899281	0.544535	0.020299
6	4.186573	1.054105	0.048838
6	5.231703	0.115321	0.030603
6	4.976441	-1.262583	-0.013774
6	3.664442	-1.764291	-0.042021
6	2.645324	-0.827013	-0.023702
1	4.371536	2.122084	0.083440
1	6.258312	0.467219	0.051570
1	5.808797	-1.959149	-0.026779
1	3.454314	-2.827581	-0.076524

Dichlorocatecholborate anion

E(RB3LYP) = -1327.07243711

Zero-point correction= 0.093941 (Hartree/Particle)
Thermal correction to Energy= 0.106582
Thermal correction to Enthalpy= 0.107716
Thermal correction to Gibbs Free Energy= 0.048866

Sum of electronic and ZPE= -1326.978496
Sum of electronic and thermal Energies= -1326.965855
Sum of electronic and thermal Enthalpies= -1326.964721
Sum of electronic and thermal Free Energies= -1327.023571

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	66.881	40.015	103.154

5	-1.197827	-0.011622	0.000051
8	-0.324425	-0.037241	-1.173833
6	0.950246	-0.026083	-0.703335
6	2.133404	-0.015874	-1.425791
6	3.342024	-0.001551	-0.699103
6	3.342212	0.001115	0.698762
6	2.133802	-0.010759	1.425772
6	0.950397	-0.023655	0.703695
1	2.119603	-0.016294	-2.511093
1	4.285437	0.008984	-1.238207
1	4.285701	0.013922	1.237690
1	2.120585	-0.007649	2.511101
8	-0.324283	-0.033610	1.174059
17	-2.370088	-1.518383	0.002362
17	-2.261972	1.582313	-0.002454

298K
all structures below use trichloroborane as the electrophile

BCl$_3$

E(RB3LYP) = -1405.56903690

Zero-point correction= 0.007462 (Hartree/Particle)
Thermal correction to Energy= 0.011858
Thermal correction to Enthalpy= 0.012802
Thermal correction to Gibbs Free Energy= -0.021763
Sum of electronic and ZPE= -1405.561575
Sum of electronic and thermal Energies= -1405.557179
Sum of electronic and thermal Enthalpies= -1405.556235
Sum of electronic and thermal Free Energies= -1405.590800

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

Total 7.441 13.087 72.748

B,0,0.1710741002,0.,-0.0604825075
Cl,0,-0.149884869,0.,1.6652189987
Cl,0,1.8257707271,0.,-0.6455012925
Cl,0,-1.1632259583,0.,-1.2009661987

BCl_4

E(RB3LYP) = -1865.95183699

Zero-point correction= 0.007975 (Hartree/Particle)
Thermal correction to Energy= 0.014099
Thermal correction to Enthalpy= 0.015043
Thermal correction to Gibbs Free Energy= -0.023644
Sum of electronic and ZPE= -1865.943862
Sum of electronic and thermal Energies= -1865.937738
Sum of electronic and thermal Enthalpies= -1865.936794
Sum of electronic and thermal Free Energies= -1865.975481

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 8.847 19.174 81.424

B,0,0.0000542793,0.,-0.0000140657
Cl,0,-0.0009615752,0.,1.8851611551
Cl,0,1.7772132684,0.,-0.6292697617
Cl,0,-0.8881350237,-1.5401200823,-0.6279582298
Cl,0,-0.8881350237,1.5401200823,-0.6279582298

Anti TS with BCl_3

E(RB3LYP) = -2190.82592909

Zero-point correction= 0.174005 (Hartree/Particle)
Thermal correction to Energy= 0.190593
Thermal correction to Enthalpy= 0.191537
Thermal correction to Gibbs Free Energy= 0.128688
Sum of electronic and ZPE= -2190.653926
Sum of electronic and thermal Energies= -2190.637337
Sum of electronic and thermal Enthalpies= -2190.636393

```
Sum of electronic and thermal Free Energies= -2190.699242

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 119.599 58.965 132.277
Zero-point correction= 0.173955 (Hartree/Particle)
Thermal correction to Energy= 0.190822
Thermal correction to Enthalpy= 0.191766
Thermal correction to Gibbs Free Energy= 0.127452
Sum of electronic and ZPE= -2190.651975
Sum of electronic and thermal Energies= -2190.635107
Sum of electronic and thermal Enthalpies= -2190.634163
Sum of electronic and thermal Free Energies= -2190.698477

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 119.743 59.139 135.361

 C,0,3.3370707981,2.1308720586,0.9981845126
 H,0,3.5353654148,3.2046912449,1.0363226352
 H,0,4.1321358827,1.5937967663,1.5187828736
 H,0,2.3744724949,1.9201227887,1.4680140274
 S,0,3.3160906748,1.664056356,-0.7796565335
 C,0,2.9490231949,-0.087194564,-0.6514379932
 C,0,1.6638794573,-0.5751714301,-0.2946169621
 C,0,1.4427846099,-1.9580350388,-0.2365841512
 C,0,2.4633653581,-2.8552411381,-0.5485826202
 C,0,3.7247366669,-2.3802241926,-0.9105530811
 C,0,3.9632487363,-1.0043375398,-0.954583651
 C,0,0.5949338254,0.3781070638,-0.021945885
 H,0,0.4654755765,-2.3269744643,0.0470764288
 H,0,2.2695841721,-3.9223037575,-0.5048768244
 H,0,4.5252777829,-3.0734453389,-1.1501162488
 H,0,4.9459866917,-0.6303548015,-1.2218406788
 C,0,0.1332909643,1.4825057405,-0.3414470139
 C,0,-0.5030590796,2.7397284786,-0.6519189511
 H,0,-0.2407784592,3.5156977678,0.0728981627
 H,0,-0.1582209708,3.0484941772,-1.6467428826
 H,0,-1.590699608,2.6235730902,-0.6892772313
 B,0,-0.6271028092,0.0693410062,1.5676967568
 Cl,0,-1.4528697376,1.5868383988,2.1819871444
 Cl,0,-1.7950645529,-1.1582717677,0.8890043882
 Cl,0,0.6028049156,-0.5671299042,2.7520257785
```

Pi Complex 1 with BCl_3

E(RB3LYP) = -2190.84576931

Zero-point correction= 0.174534 (Hartree/Particle)
Thermal correction to Energy= 0.192656
Thermal correction to Enthalpy= 0.193600
Thermal correction to Gibbs Free Energy= 0.123441
Sum of electronic and ZPE= -2190.671235
Sum of electronic and thermal Energies= -2190.653113
Sum of electronic and thermal Enthalpies= -2190.652169
Sum of electronic and thermal Free Energies= -2190.722328

```
     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 120.893 60.746 147.662
```

```
C,0,3.1661459816,-0.1202933229,-1.9943590803
H,0,3.1405124346,-0.0349310787,-3.0829762959
H,0,4.041094677,-0.7087593621,-1.706817203
H,0,3.2229966096,0.8818123713,-1.5616365534
S,0,1.6081960966,-0.953959468,-1.5414232662
C,0,1.685692523,-1.0197620572,0.2359329807
C,0,0.5552690405,-1.5547716643,0.9123937297
C,0,0.5615823207,-1.6268262824,2.3167354693
C,0,1.6550835497,-1.1775888939,3.0545026873
C,0,2.7618490725,-0.6487993703,2.3857800879
C,0,2.7787504028,-0.5720156864,0.9905368571
C,0,-0.5888109023,-1.9927178724,0.1796208978
H,0,-0.3110286654,-2.0340596687,2.8174929912
H,0,1.6419362934,-1.2369865399,4.1381874017
H,0,3.6211647999,-0.2928455175,2.9466945765
H,0,3.6525566624,-0.1584035219,0.5022660289
C,0,-1.5591316699,-2.3433757495,-0.4618389786
C,0,-2.7245441062,-2.7503166155,-1.238157615
H,0,-2.5986476964,-2.4802372906,-2.2920052475
H,0,-2.8808230485,-3.8330636877,-1.1789490571
H,0,-3.6295252792,-2.2550168045,-0.8686821481
B,0,-2.0897876791,0.9313784083,-0.3999191214
Cl,0,-0.6812638311,1.6310479866,0.3717125162
Cl,0,-2.1554820407,0.7760143378,-2.1493717726
Cl,0,-3.4871385454,0.4774003504,0.5704681149
```

Pi Complex 2 with BCl_3

E(RB3LYP) = -2190.84674597

Zero-point correction= 0.174499 (Hartree/Particle)
Thermal correction to Energy= 0.192648
Thermal correction to Enthalpy= 0.193593
Thermal correction to Gibbs Free Energy= 0.122804
Sum of electronic and ZPE= -2190.672247
Sum of electronic and thermal Energies= -2190.654098
Sum of electronic and thermal Enthalpies= -2190.653153
Sum of electronic and thermal Free Energies= -2190.723942

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 120.889 60.860 148.986
```

```
C,0,1.62951926,2.9013587862,0.7178621254
H,0,2.6278630872,2.9142877368,1.1596761497
H,0,1.0855495776,3.7943672767,1.0341366108
H,0,1.7241323713,2.8750199271,-0.370384532
S,0,0.842405516,1.3868073312,1.3570329487
C,0,-0.786309031,1.4286683874,0.6311322323
C,0,-1.683537325,0.3929589508,1.0068300065
C,0,-2.9719801335,0.3692194822,0.4419828381
C,0,-3.3759574775,1.3415053043,-0.4710374699
C,0,-2.4885072201,2.3576924742,-0.8324891733
C,0,-1.2029093934,2.4002336338,-0.286972263
C,0,-1.2919852551,-0.6119876585,1.9432547278
H,0,-3.649727801,-0.4265594182,0.73405925
H,0,-4.3742433845,1.3058292777,-0.8957569255
H,0,-2.7893558147,3.1211821017,-1.5437538113
H,0,-0.5327679713,3.1947210855,-0.5910214237
C,0,-0.9349701478,-1.4607092652,2.7345682418
C,0,-0.4794882772,-2.4853280322,3.6684584
H,0,0.3626798925,-3.0469700269,3.2478145933
H,0,-0.1467249442,-2.0379871174,4.6117680638
H,0,-1.2808392295,-3.1966362042,3.8956897145
B,0,2.061100645,-0.4281907869,-0.8569934086
Cl,0,1.2353135874,-1.8825885159,-0.3186706146
Cl,0,1.3473986754,0.559934217,-2.133246743
Cl,0,3.7150017933,-0.0987609471,-0.3292305378
```

Pi Complex 3 with BCl_3

E(RB3LYP) = -2190.84576932

Zero-point correction= 0.174534 (Hartree/Particle)
Thermal correction to Energy= 0.192656
Thermal correction to Enthalpy= 0.193600
Thermal correction to Gibbs Free Energy= 0.123438
Sum of electronic and ZPE= -2190.671236
Sum of electronic and thermal Energies= -2190.653113
Sum of electronic and thermal Enthalpies= -2190.652169
Sum of electronic and thermal Free Energies= -2190.722331

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 120.893 60.746 147.668
```

```
 C,0,2.421545238,-3.2445427183,-1.3330302731
 H,0,2.0270494427,-4.2277775164,-1.5988391454
 H,0,3.4306756725,-3.3658078764,-0.9312106917
 H,0,2.4414387986,-2.6170464607,-2.2277641901
 S,0,1.2673998218,-2.5860799315,-0.0833375567
 C,0,1.931691468,-0.9729999744,0.2716806043
 C,0,1.1956267062,-0.1552268248,1.1723015991
 C,0,1.6729748141,1.1299501015,1.4851589633
 C,0,2.8518266601,1.6154008525,0.9225823512
 C,0,3.5695338514,0.8099669789,0.0349309652
 C,0,3.1159146406,-0.4721589445,-0.286406431
 C,0,-0.0305595761,-0.6190517834,1.7370988595
 H,0,1.0967763948,1.7427070831,2.1711401078
 H,0,3.204096621,2.6112918861,1.171942198
 H,0,4.4892605171,1.1746538047,-0.413240959
 H,0,3.6962068528,-1.0721438773,-0.9765516269
 C,0,-1.0806603105,-1.0259990744,2.1927703302
 C,0,-2.3463332826,-1.5166733266,2.7254616885
 H,0,-3.1523080284,-0.7992369155,2.5343617598
 H,0,-2.6207754871,-2.4658801717,2.2531492165
 H,0,-2.2840299866,-1.6784301492,3.8072257347
 B,0,-2.1224903193,-0.0295958691,-0.7955152062
 Cl,0,-3.0244990076,1.1559057607,0.1433037459
 Cl,0,-0.6833094555,0.4588932838,-1.6667730808
 Cl,0,-2.728475046,-1.6732263369,-0.937672963
```

Pi Complex 4 with BCl$_3$

```
E(RB3LYP) = -2190.85401536

Zero-point correction= 0.175417 (Hartree/Particle)
Thermal correction to Energy= 0.192795
Thermal correction to Enthalpy= 0.193739
Thermal correction to Gibbs Free Energy= 0.127359
Sum of electronic and ZPE= -2190.678598
Sum of electronic and thermal Energies= -2190.661220
Sum of electronic and thermal Enthalpies= -2190.660276
Sum of electronic and thermal Free Energies= -2190.726657

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 120.981 60.668 139.710
```

```
C,0,1.8741379834,2.1376555233,-0.079000457
H,0,2.8802641375,2.2310923915,0.3310382221
H,0,1.5593153682,3.0759889842,-0.5363622711
H,0,1.8418271928,1.3131615628,-0.790967345
S,0,0.7878925473,1.8103433064,1.349350076
C,0,-0.8643295786,1.7965491553,0.6376441726
C,0,-1.920886481,2.2593234905,1.4585613447
C,0,-3.2250487328,2.2439188866,0.9241681021
C,0,-3.4641045351,1.7887288411,-0.3697368308
C,0,-2.4071419296,1.3320351611,-1.1626891272
C,0,-1.1069972789,1.3312304122,-0.6565055652
C,0,-1.6973628935,2.7231082255,2.7890323654
H,0,-4.0426518215,2.5956140129,1.5441414754
H,0,-4.4771883581,1.7873589617,-0.7596496045
H,0,-2.5903746503,0.9682713834,-2.1684740305
H,0,-0.2967767843,0.9548677925,-1.2676956891
C,0,-1.5108050287,3.1034702845,3.92617418
C,0,-1.2597153468,3.5354506208,5.2962247244
H,0,-0.5207263229,2.8835229728,5.7749528679
H,0,-0.8736268936,4.5606424543,5.3209794235
H,0,-2.1782082203,3.504933755,5.8918601285
B,0,1.2152571856,-0.1520956094,1.8223371183
Cl,0,-0.0127675694,-0.5864265372,3.1141994497
Cl,0,1.0677534891,-1.1850263511,0.3023530359
Cl,0,2.9544855215,-0.0392136809,2.4414462339
```

Zwitterion with BCl_3

E(RB3LYP) = -2190.86809681

Zero-point correction= 0.178036 (Hartree/Particle)
Thermal correction to Energy= 0.193734
Thermal correction to Enthalpy= 0.194678
Thermal correction to Gibbs Free Energy= 0.134496
Sum of electronic and ZPE= -2190.690061
Sum of electronic and thermal Energies= -2190.674363
Sum of electronic and thermal Enthalpies= -2190.673419
Sum of electronic and thermal Free Energies= -2190.733601

```
      E       CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 121.570 57.910 126.664
```

```
C,0,3.7815524782,-2.0922404762,0.5736147052
H,0,3.6310764213,-3.1726300995,0.5437326427
H,0,3.3760105237,-1.6572647779,1.4873533853
H,0,4.8397968744,-1.8580748514,0.4506664583
S,0,2.887699758,-1.3797580443,-0.8637448323
C,0,2.8774946771,0.3581230475,-0.5106727825
C,0,1.5979826156,0.7426622053,-0.0690392341
C,0,1.4183125089,2.1034011228,0.2181935473
C,0,2.481375981,2.9970207029,0.063077296
C,0,3.7380587206,2.5727223857,-0.3840056554
C,0,3.9487114594,1.2256070587,-0.6903122648
C,0,0.6094744274,-0.3705475257,0.0264601506
H,0,0.4577178203,2.4627763376,0.5583148967
H,0,2.3223776746,4.0461413123,0.2915799141
H,0,4.5475395353,3.2852324744,-0.5035426465
H,0,4.909098008,0.8757998934,-1.0545036251
C,0,1.1330657788,-1.5618412154,-0.3503871547
C,0,0.6404486601,-2.968547465,-0.4761261412
H,0,0.7729035206,-3.3400582356,-1.4987487287
H,0,1.1794780346,-3.6431259311,0.2010579193
H,0,-0.4155086996,-3.0143224371,-0.2240346502
B,0,-0.9010222787,-0.0615501335,0.5644009536
Cl,0,-1.6818873564,1.2075716796,-0.6109170127
Cl,0,-2.0743712155,-1.526316289,0.6802562069
Cl,0,-0.7218109279,0.6629442617,2.3150706521
```

Cation with BCl_3

E(RB3LYP) = -1730.44047038

Zero-point correction= 0.177428 (Hartree/Particle)
Thermal correction to Energy= 0.191572
Thermal correction to Enthalpy= 0.192516
Thermal correction to Gibbs Free Energy= 0.135019
Sum of electronic and ZPE= -1730.263042
Sum of electronic and thermal Energies= -1730.248898
Sum of electronic and thermal Enthalpies= -1730.247954
Sum of electronic and thermal Free Energies= -1730.305452

```
      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 120.213 52.027 121.015
```

C,0,3.8068962673,-2.1255559618,0.5184289813
H,0,3.66066186,-3.2043727323,0.448171903
H,0,3.4235079404,-1.7224677934,1.4555545066
H,0,4.8604435603,-1.8815772733,0.3749252785
S,0,2.8912296656,-1.3658865148,-0.8837786812
C,0,2.8991899637,0.3761261306,-0.5051644581
C,0,1.6199886343,0.7769070656,-0.0752055733
C,0,1.4319066605,2.1258798206,0.2423605174
C,0,2.5045157237,3.0155097767,0.1222120762
C,0,3.7614069973,2.5848274048,-0.3164152378
C,0,3.974449355,1.2415290503,-0.6492618315
C,0,0.6497580353,-0.3327064816,0.0028356612
H,0,0.4644083591,2.4853950874,0.5731154521
H,0,2.3549142661,4.0609080646,0.3704655489
H,0,4.5777551751,3.2928703986,-0.4082411769
H,0,4.9402798586,0.8993745002,-1.0050143528
C,0,1.1531876816,-1.5387060172,-0.3528452808
C,0,0.5550719338,-2.9028280292,-0.4592182854
H,0,0.6213669369,-3.2820725088,-1.4844245543
H,0,1.0662464446,-3.6152909713,0.1982780475
H,0,-0.4959885035,-2.8788584354,-0.1697164319
B,0,-0.8494401135,-0.1307007614,0.4232802598
Cl,0,-1.830958358,1.0404978886,-0.4328859444
Cl,0,-1.5376303441,-1.0525737076,1.744910576

Chloride Anion

```
E(RB3LYP) = -460.338866325

Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001416
Thermal correction to Enthalpy= 0.002360
Thermal correction to Gibbs Free Energy= -0.015023
Sum of electronic and ZPE= -460.338866
Sum of electronic and thermal Energies= -460.337450
Sum of electronic and thermal Enthalpies= -460.336506
Sum of electronic and thermal Free Energies= -460.353889

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 0.889 2.981 36.586

17 0.000000 0.000000 0.000000
```

S_N2 TS with BCl_3

```
E(RB3LYP) = -2190.82731010

Zero-point correction= 0.176540 (Hartree/Particle)
Thermal correction to Energy= 0.192688
Thermal correction to Enthalpy= 0.193632
Thermal correction to Gibbs Free Energy= 0.130207
Sum of electronic and ZPE= -2190.650807
Sum of electronic and thermal Energies= -2190.634659
Sum of electronic and thermal Enthalpies= -2190.633715
Sum of electronic and thermal Free Energies= -2190.697140

     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 120.913 57.022 133.489
Zero-point correction= 0.176569 (Hartree/Particle)
Thermal correction to Energy= 0.192703
Thermal correction to Enthalpy= 0.193648
Thermal correction to Gibbs Free Energy= 0.130222
Sum of electronic and ZPE= -2190.650741
Sum of electronic and thermal Energies= -2190.634607
Sum of electronic and thermal Enthalpies= -2190.633663
```

Sum of electronic and thermal Free Energies= -2190.697089

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 120.923 57.001 133.491

C,0,3.4812670359,-1.2664433038,0.1226424252
H,0,3.4961876623,-2.2535262555,-0.3196553894
H,0,2.7934693793,-1.094384792,0.9393608671
H,0,4.4292985478,-0.74605875,0.1587417679
S,0,2.5351742055,-0.1831803534,-1.4033940827
C,0,2.1685612803,1.3540561957,-0.6105214434
C,0,0.8076586961,1.405268377,-0.24185547
C,0,0.3410959693,2.5744303579,0.3761045702
C,0,1.2265760412,3.6242010095,0.6245847372
C,0,2.5768683455,3.5373330175,0.259210051
C,0,3.064690885,2.3925990519,-0.3756353721
C,0,0.0637269222,0.1897588805,-0.6131647592
H,0,-0.6986827921,2.66566878,0.6663730685
H,0,0.8603339218,4.523338303,1.109534249
H,0,3.249832338,4.3632533358,0.4641728002
H,0,4.1055609419,2.3182953548,-0.6721891011
C,0,0.8405376092,-0.7453282094,-1.2336730574
C,0,0.5449897405,-2.1243082354,-1.7315499013
H,0,-0.4830858958,-2.4090669957,-1.5115043213
H,0,0.695120009,-2.1890808704,-2.8148913507
H,0,1.2056811819,-2.8605240629,-1.2596787914
B,0,-1.4436063845,-0.0314629479,-0.2898402334
Cl,0,-2.0671451873,0.307489958,1.3221040808
Cl,0,-2.5734720167,-0.6086723357,-1.5140059824
Cl,0,4.6690145637,-2.6551135095,2.0298676389

Final Product with BCl_3

E(RB3LYP) = -1690.76120222

Zero-point correction= 0.138838 (Hartree/Particle)
Thermal correction to Energy= 0.150664
Thermal correction to Enthalpy= 0.151609
Thermal correction to Gibbs Free Energy= 0.099550
Sum of electronic and ZPE= -1690.622364
Sum of electronic and thermal Energies= -1690.610538

Sum of electronic and thermal Enthalpies= -1690.609594
Sum of electronic and thermal Free Energies= -1690.661653

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 94.543 44.280 109.567

S,0,2.929615429,-1.4101590584,-0.6671911975
C,0,2.9021006108,0.3293551963,-0.4619573729
C,0,1.6049608985,0.7768462031,-0.1084019402
C,0,1.4205334276,2.1648241634,0.0553924237
C,0,2.4925317388,3.0366734451,-0.1076475502
C,0,3.7725463183,2.5611050626,-0.4426816603
C,0,3.9859466738,1.1985546633,-0.6277429282
C,0,0.6343846901,-0.3210500126,-0.0204032816
H,0,0.4452901227,2.5614041082,0.3053173371
H,0,2.334425553,4.1029399277,0.0234466427
H,0,4.5965606471,3.2573512012,-0.5648033865
H,0,4.9660512255,0.8187316932,-0.8988763573
C,0,1.2250213612,-1.5429105622,-0.3170450299
C,0,0.6346774547,-2.9257613458,-0.356228397
H,0,0.0157768851,-3.053652416,-1.2500288975
H,0,1.4178175881,-3.6879524201,-0.3734476378
H,0,-0.0021396266,-3.1111105249,0.5116952527
B,0,-0.83499996,-0.1818670822,0.4023575812
Cl,0,-1.3881420222,1.0925829309,1.5148980795
Cl,0,-2.1093980155,-1.2897331728,-0.1602946801

358K
all structures below use trichloroborane as the electrophile

BCl_3

E(RB3LYP) = -1405.56903694

Zero-point correction= 0.007462 (Hartree/Particle)
Thermal correction to Energy= 0.013153
Thermal correction to Enthalpy= 0.014286
Thermal correction to Gibbs Free Energy= -0.028840
Sum of electronic and ZPE= -1405.561575
Sum of electronic and thermal Energies= -1405.555884
Sum of electronic and thermal Enthalpies= -1405.554750
Sum of electronic and thermal Free Energies= -1405.597877

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	8.253	14.028	75.593

5	0.000000	0.000181	0.000000
17	-1.516818	-0.883180	0.000000
17	-0.006390	1.755239	0.000000
17	1.523208	-0.872113	0.000000

Anti TS with BCl$_3$

E(RB3LYP) = -2190.82592909

Zero-point correction= 0.173955 (Hartree/Particle)
Thermal correction to Energy= 0.196836
Thermal correction to Enthalpy= 0.197970
Thermal correction to Gibbs Free Energy= 0.113969
Sum of electronic and ZPE= -2190.651975
Sum of electronic and thermal Energies= -2190.629093
Sum of electronic and thermal Enthalpies= -2190.627960
Sum of electronic and thermal Free Energies= -2190.711960

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	123.516	66.850	147.237

6	1.449252	2.318306	1.480944
1	1.399325	3.401962	1.611550
1	2.031723	1.878892	2.292882
1	0.439428	1.903574	1.478982
16	2.283844	2.021910	-0.129859
6	2.245069	0.229474	-0.190916
6	1.052977	-0.501779	-0.438343
6	1.101555	-1.901411	-0.495223
6	2.309990	-2.578258	-0.335637
6	3.485834	-1.863298	-0.103378
6	3.447973	-0.468837	-0.026336
6	-0.192150	0.225465	-0.653999
1	0.189311	-2.456538	-0.672303
1	2.327486	-3.662118	-0.390661
1	4.429464	-2.384351	0.026536

```
1 4.356992 0.090642 0.167909
6 -0.676867 1.259641 -1.134022
6 -1.349267 2.413054 -1.681249
1 -1.579396 3.151700 -0.908123
1 -0.678344 2.867200 -2.421208
1 -2.270263 2.116861 -2.192996
5 -1.892080 -0.433707 0.235611
17 -3.178732 0.856794 0.438523
17 -2.393069 -1.774318 -0.897335
17 -1.191318 -0.958006 1.833875
```

Pi Complex 1 with BCl_3

```
E(RB3LYP) = -2190.84576931

Zero-point correction= 0.174534 (Hartree/Particle)
Thermal correction to Energy= 0.198819
Thermal correction to Enthalpy= 0.199953
Thermal correction to Gibbs Free Energy= 0.108771
Sum of electronic and ZPE= -2190.671236
Sum of electronic and thermal Energies= -2190.646950
Sum of electronic and thermal Enthalpies= -2190.645816
Sum of electronic and thermal Free Energies= -2190.736998

     E      CV       S
  KCal/Mol Cal/Mol-K Cal/Mol-K
Total 124.761 68.392 159.826

6 -2.682099 2.825726 -0.390133
1 -2.362895 3.864671 -0.281810
1 -3.690695 2.721842 0.017850
1 -2.671706 2.560607 -1.450462
16 -1.464089 1.848557 0.552708
6 -2.006223 0.171890 0.299312
6 -1.199626 -0.858744 0.855089
6 -1.579306 -2.201580 0.681768
6 -2.729442 -2.537125 -0.029890
6 -3.516636 -1.521311 -0.577782
6 -3.160527 -0.179982 -0.413742
6 -0.000727 -0.540702 1.561604
1 -0.950149 -2.976040 1.108876
1 -3.005970 -3.578909 -0.157530
```

1	-4.415098	-1.766691	-1.136625
1	-3.792912	0.583772	-0.849392
6	1.024865	-0.249266	2.143996
6	2.260668	0.108213	2.830624
1	2.459307	1.180732	2.732481
1	2.204156	-0.132840	3.897850
1	3.112556	-0.433153	2.403971
5	2.087332	-0.031479	-0.991793
17	0.673009	-0.278068	-1.995675
17	2.572305	1.593213	-0.528960
17	3.086243	-1.406099	-0.530346

Pi Complex 2 with BCl_3

E(RB3LYP) = -2190.84674597

Zero-point correction= 0.174499 (Hartree/Particle)
Thermal correction to Energy= 0.198821
Thermal correction to Enthalpy= 0.199955
Thermal correction to Gibbs Free Energy= 0.108006
Sum of electronic and ZPE= -2190.672247
Sum of electronic and thermal Energies= -2190.647925
Sum of electronic and thermal Enthalpies= -2190.646791
Sum of electronic and thermal Free Energies= -2190.738740

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	124.762	68.480	161.170

6	-0.744325	-1.658433	2.318402
1	-1.570101	-1.336573	2.956020
1	-0.004018	-2.182495	2.927253
1	-1.134824	-2.316448	1.538368
16	-0.055729	-0.124236	1.615527
6	1.299753	-0.701401	0.610069
6	2.094842	0.289632	-0.025973
6	3.160945	-0.116918	-0.849285
6	3.445472	-1.467104	-1.044694
6	2.660548	-2.434568	-0.413220
6	1.594773	-2.054909	0.406624
6	1.823465	1.679194	0.162693
1	3.761729	0.647310	-1.331911

1	4.272351	-1.760567	-1.683745
1	2.869971	-3.490341	-0.557474
1	0.997752	-2.826070	0.877390
6	1.569393	2.854463	0.330482
6	1.233580	4.261183	0.524977
1	0.232627	4.478726	0.134594
1	1.243491	4.524655	1.588539
1	1.947087	4.912384	0.008644
5	-2.095999	-0.039942	-0.732139
17	-1.388897	1.382108	-1.483650
17	-1.613866	-1.647460	-1.278050
17	-3.472242	0.125944	0.363708

Pi Complex 3 with BCl_3

E(RB3LYP) = -2190.84576932

Zero-point correction= 0.174534 (Hartree/Particle)
Thermal correction to Energy= 0.198819
Thermal correction to Enthalpy= 0.199953
Thermal correction to Gibbs Free Energy= 0.108767
Sum of electronic and ZPE= -2190.671236
Sum of electronic and thermal Energies= -2190.646950
Sum of electronic and thermal Enthalpies= -2190.645816
Sum of electronic and thermal Free Energies= -2190.737002

	E KCal/Mol	CV Cal/Mol-K	S Cal/Mol-K
Total	124.761	68.392	159.832

6	-2.682269	2.825540	-0.390607
1	-2.363123	3.864523	-0.282480
1	-3.690931	2.721725	0.017233
1	-2.671688	2.560154	-1.450869
16	-1.464338	1.848640	0.552614
6	-2.006259	0.171878	0.299360
6	-1.199516	-0.858600	0.855184
6	-1.579029	-2.201503	0.681977
6	-2.729129	-2.537248	-0.029636
6	-3.516478	-1.521573	-0.577575
6	-3.160549	-0.180189	-0.413629
6	-0.000630	-0.540364	1.561628

1	-0.949757	-2.975848	1.109124
1	-3.005523	-3.579076	-0.157202
1	-4.414923	-1.767118	-1.136374
1	-3.793059	0.583460	-0.849282
6	1.024949	-0.248742	2.143949
6	2.260789	0.108832	2.830454
1	3.112677	-0.432458	2.403697
1	2.459329	1.181373	2.732321
1	2.204399	-0.132244	3.897676
5	2.087277	-0.031586	-0.991713
17	3.086332	-1.406089	-0.530145
17	0.672830	-0.278486	-1.995374
17	2.572270	1.593222	-0.529407

Pi Complex 4 with BCl_3

E(RB3LYP) = -2190.85401536

Zero-point correction= 0.175417 (Hartree/Particle)
Thermal correction to Energy= 0.198959
Thermal correction to Enthalpy= 0.200093
Thermal correction to Gibbs Free Energy= 0.113444
Sum of electronic and ZPE= -2190.678599
Sum of electronic and thermal Energies= -2190.655056
Sum of electronic and thermal Enthalpies= -2190.653923
Sum of electronic and thermal Free Energies= -2190.740571

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	124.849	68.456	151.879

6	-1.105922	-0.996963	2.337853
1	-1.917638	-0.436008	2.802177
1	-0.336447	-1.234579	3.072842
1	-1.502315	-1.896063	1.866448
16	-0.378078	0.124586	1.097039
6	1.029147	-0.796834	0.458872
6	2.157962	-0.045069	0.052669
6	3.265932	-0.747416	-0.462856
6	3.248994	-2.135687	-0.567510
6	2.122605	-2.859114	-0.164501
6	1.009937	-2.188499	0.344267

6	2.192060	1.378107	0.145515
1	4.136304	-0.181934	-0.777835
1	4.114870	-2.654452	-0.966902
1	2.101998	-3.940465	-0.252568
1	0.132688	-2.753087	0.632939
6	2.216557	2.589659	0.209629
6	2.209847	4.046313	0.278979
1	1.230815	4.440137	-0.015459
1	2.422273	4.392704	1.296615
1	2.964689	4.474442	-0.389049
5	-1.783583	0.126591	-0.413615
17	-0.989637	1.069509	-1.772346
17	-2.179519	-1.614786	-0.871756
17	-3.211008	0.997981	0.376381

Anti Zwitterion with BCl_3

E(RB3LYP) = -2190.86809681

Zero-point correction= 0.178036 (Hartree/Particle)
Thermal correction to Energy= 0.199659
Thermal correction to Enthalpy= 0.200792
Thermal correction to Gibbs Free Energy= 0.121852
Sum of electronic and ZPE= -2190.690061
Sum of electronic and thermal Energies= -2190.668438
Sum of electronic and thermal Enthalpies= -2190.667304
Sum of electronic and thermal Free Energies= -2190.746245

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	125.288	66.200	138.368

6	-2.432421	2.360642	1.173943
1	-2.138619	3.411540	1.182496
1	-1.916283	1.794933	1.949932
1	-3.515958	2.274060	1.264957
16	-1.959562	1.678158	-0.464112
6	-2.125931	-0.072431	-0.234424
6	-0.851649	-0.654440	-0.102021
6	-0.813407	-2.047750	0.051668
6	-2.002185	-2.782053	0.069739
6	-3.249786	-2.163141	-0.070282

6	-3.323853	-0.777612	-0.236828
6	0.284130	0.311681	-0.148095
1	0.134918	-2.555301	0.154851
1	-1.951437	-3.859519	0.190731
1	-4.159854	-2.753810	-0.059979
1	-4.278223	-0.277296	-0.364137
6	-0.129635	1.589280	-0.326642
6	0.522727	2.928308	-0.463510
1	0.240018	3.407081	-1.408059
1	0.234056	3.599421	0.355308
1	1.603369	2.817093	-0.440323
5	1.812489	-0.233767	0.033741
17	2.149640	-1.476185	-1.360720
17	3.181604	1.054405	-0.009246
17	1.890557	-1.089678	1.731732

Cation with BCl_3

E(RB3LYP) = -1730.44047038

Zero-point correction= 0.177428 (Hartree/Particle)
Thermal correction to Energy= 0.196923
Thermal correction to Enthalpy= 0.198056
Thermal correction to Gibbs Free Energy= 0.122967
Sum of electronic and ZPE= -1730.263042
Sum of electronic and thermal Energies= -1730.243548
Sum of electronic and thermal Enthalpies= -1730.242414
Sum of electronic and thermal Free Energies= -1730.317503

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	123.571	60.065	131.617

6	-2.074775	2.527413	0.896791
1	-1.743837	3.557366	0.755927
1	-1.604656	2.063191	1.763485
1	-3.163242	2.490399	0.959642
16	-1.599416	1.597600	-0.616883
6	-1.863924	-0.108035	-0.170937
6	-0.625457	-0.745586	0.032957
6	-0.638467	-2.103714	0.366531
6	-1.862532	-2.770441	0.482748

6	-3.075495	-2.107901	0.264994
6	-3.090490	-0.750613	-0.078763
6	0.533438	0.156500	-0.114973
1	0.288648	-2.641216	0.528558
1	-1.868502	-3.823664	0.742661
1	-4.013018	-2.645716	0.354361
1	-4.023977	-0.230607	-0.264922
6	0.208383	1.434945	-0.422065
6	1.021816	2.657493	-0.693338
1	0.836250	3.036676	-1.703812
1	0.787168	3.458822	0.016602
1	2.084912	2.432887	-0.601174
5	2.019604	-0.328491	0.030858
17	2.583765	-1.671754	-0.941495
17	3.105524	0.450716	1.163897

Chloride Anion

E(RB3LYP) = -460.338866325

Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001701
Thermal correction to Enthalpy= 0.002834
Thermal correction to Gibbs Free Energy= -0.018557
Sum of electronic and ZPE= -460.338866
Sum of electronic and thermal Energies= -460.337166
Sum of electronic and thermal Enthalpies= -460.336032
Sum of electronic and thermal Free Energies= -460.357423

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	1.067	2.981	37.495

17	0.000000	0.000000	0.000000

S_N2 TS with BCl_3

E(RB3LYP) = -2190.82731010

Zero-point correction= 0.176569 (Hartree/Particle)
Thermal correction to Energy= 0.198526

Thermal correction to Enthalpy= 0.199660
Thermal correction to Gibbs Free Energy= 0.116936
Sum of electronic and ZPE= -2190.650741
Sum of electronic and thermal Energies= -2190.628784
Sum of electronic and thermal Enthalpies= -2190.627650
Sum of electronic and thermal Free Energies= -2190.710375

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	124.577	64.992	145.000

6	2.723407	-0.743147	-0.209214
1	2.893109	-1.738499	-0.597359
1	2.181232	-0.655032	0.722442
1	3.506528	-0.019664	-0.394042
16	1.272846	-0.054245	-1.557778
6	0.701387	1.427652	-0.780885
6	-0.536683	1.202740	-0.142772
6	-1.147167	2.288515	0.501353
6	-0.511662	3.531038	0.511655
6	0.725562	3.719296	-0.119350
6	1.347182	2.660421	-0.785525
6	-1.020524	-0.179900	-0.294346
1	-2.104092	2.167993	0.994800
1	-0.986395	4.365281	1.018038
1	1.204786	4.692376	-0.097110
1	2.299859	2.797003	-1.286152
6	-0.171908	-0.968476	-1.016046
6	-0.213311	-2.419564	-1.375833
1	-1.081326	-2.908492	-0.935440
1	-0.259127	-2.551502	-2.462505
1	0.682735	-2.937650	-1.015446
5	-2.340564	-0.706470	0.342638
17	-2.711956	-0.366146	2.030329
17	-3.507127	-1.639724	-0.593588
17	4.549806	-1.636659	1.476777

Final Product with BCl_3

E(RB3LYP) = -1690.76120222

Zero-point correction= 0.138838 (Hartree/Particle)

Thermal correction to Energy= 0.155226
Thermal correction to Enthalpy= 0.156359
Thermal correction to Gibbs Free Energy= 0.088663
Sum of electronic and ZPE= -1690.622364
Sum of electronic and thermal Energies= -1690.605977
Sum of electronic and thermal Enthalpies= -1690.604843
Sum of electronic and thermal Free Energies= -1690.672540

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	97.406	51.266	118.660

16	-1.276265	2.199474	0.205289
6	-1.943100	0.589839	0.023098
6	-0.912018	-0.377738	-0.069028
6	-1.298281	-1.720586	-0.255801
6	-2.646604	-2.057704	-0.321071
6	-3.647896	-1.076938	-0.209887
6	-3.301366	0.260143	-0.041179
6	0.427928	0.218100	-0.000764
1	-0.550410	-2.496548	-0.352808
1	-2.927811	-3.096774	-0.463774
1	-4.694663	-1.360093	-0.262565
1	-4.063722	1.029310	0.033507
6	0.360854	1.599563	0.129054
6	1.458886	2.622049	0.234715
1	1.933953	2.777071	-0.739222
1	1.069937	3.583398	0.579779
1	2.236901	2.299748	0.930412
5	1.751913	-0.559220	-0.006162
17	1.885314	-2.215326	0.632156
17	3.271514	0.128741	-0.627095

Calculated Structures for 1,5 Hydrogen Atom Transfer

Starting Material 18

Gaussian calculation: second derivative UM062X/6-31+G**
E(UM062X) = -1024.07893869

Zero-point correction= 0.479484 (Hartree/Particle)
Thermal correction to Energy= 0.505532

```
Thermal correction to Enthalpy= 0.506477
Thermal correction to Gibbs Free Energy= 0.423082
Sum of electronic and ZPE= -1023.599455
Sum of electronic and thermal Energies= -1023.573406
Sum of electronic and thermal Enthalpies= -1023.572462
Sum of electronic and thermal Free Energies= -1023.655857

      E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 317.226 100.200 175.519

C,0,2.918702,-0.549419,0.448437
C,0,2.624237,-1.492457,-0.732154
C,0,2.485132,-1.216370,1.767994
C,0,4.431172,-0.302538,0.502654
C,0,2.124358, 0.736901,0.230639
H,0,2.895846,-0.993224,-1.678851
O,0,3.380005,-2.675055,-0.580282
H,0,1.552956,-1.731233,-0.759754
H,0,2.676237,-0.542837,2.609764
H,0,1.421478,-1.461634,1.751260
H,0,3.058650,-2.135365,1.915126
H,0,4.694559, 0.355751,1.336729
H,0,4.939568,-1.257973,0.644544
H,0,4.804589, 0.141180,-0.426837
C,0,2.744991,1.988604,0.115966
C,0,2.043941,3.186330,-0.075465
C,0,0.638890,3.166163,-0.167992
C,0,-0.008693,1.955414,-0.063207
C,0,0.713494,0.740998,0.136086
H,0,3.825711,2.050033,0.178972
C,0,2.779061,4.497305,-0.174914
H,0,0.089750,4.092919,-0.319695
C,0,-1.415045,1.555105,-0.112891
N,0,-0.126469,-0.344870,0.212881
C,0,-1.401352,0.138228,0.062280
C,0,-2.601959,-0.610661,0.067383
C,0,-3.778918,0.129232,-0.107747
C,0,-3.801986,1.520227,-0.279301
C,0,-2.594419,2.245169,-0.281484
C,0,-2.604050,-2.126901,0.253718
H,0,-4.733046,-0.386181,-0.113619
C,0,-5.107896,2.248562,-0.460197
H,0,-2.607668,3.324776,-0.414519
```

C,0,3.091188,-3.618917,-1.581386
H,0,3.709208,-4.497904,-1.391228
H,0,2.030863,-3.909680,-1.558744
H,0,3.325002,-3.223149,-2.580632
C,0,-4.022390,-2.709138,0.217801
C,0,-1.787179,-2.785197,-0.874942
C,0,-1.975301,-2.476505,1.616195
H,0,-1.997109,-3.562174,1.762590
H,0,-0.939032,-2.137628,1.666984
H,0,-2.537487,-2.009806,2.432028
H,0,-1.809395,-3.874308,-0.756100
H,0,-2.211501,-2.538643,-1.854107
H,0,-0.748047,-2.451735,-0.849724
H,0,-3.965586,-3.793343,0.354841
H,0,-4.649186,-2.305389,1.019921
H,0,-4.516512,-2.520526,-0.741205
H,0,-5.122799,2.793424,-1.409790
H,0,-5.953997,1.558227,-0.451475
H,0,-5.259299,2.982058,0.338619
H,0,2.498787,5.035551,-1.085869
H,0,2.536094,5.144843,0.674392
H,0,3.860744,4.347675,-0.186364

Transition Structure 19

Gaussian calculation: second derivatives
UM062X/6-31+G**
E(UM062X) = -1024.03629029

Zero-point correction= 0.474835 (Hartree/Particle)
Thermal correction to Energy= 0.500277
Thermal correction to Enthalpy= 0.501221
Thermal correction to Gibbs Free Energy= 0.420525
Sum of electronic and ZPE= -1023.561455
Sum of electronic and thermal Energies= -1023.536014
Sum of electronic and thermal Enthalpies= -1023.535070
Sum of electronic and thermal Free Energies= -1023.615766

```
     E      CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 313.928 99.187 169.839
```

C,2.7624035087,-1.0379921492,0.3953564366

C,0,1.813273,-1.785621,-0.562316
C,0,2.586368,-1.576750,1.826169
C,0,4.207504,-1.262174,-0.066022
C,0,2.337543,0.418411,0.309006
H,0,1.876527,-1.426809,-1.602486
O,0,1.906318,-3.146813,-0.450782
H,0,0.635702,-1.313880,-0.135550
H,0,3.248721,-1.031614,2.504992
H,0,1.556518,-1.449868,2.169426
H,0,2.840415,-2.639818,1.862640
H,0,4.910394,-0.782553,0.623171
H,0,4.425490,-2.333785,-0.079756
H,0,4.374827,-0.854843,-1.068570
C,0,3.162691,1.525129,0.128101
C,0,2.642700,2.822620,-0.063203
C,0,1.261136,3.014945,-0.149170
C,0,0.410833,1.919428,0.004859
C,0,0.961662,0.666814,0.309739
H,0,4.242466,1.396044,0.112541
C,0,3.589467,3.990614,-0.195599
H,0,0.866075,4.006009,-0.359494
C,0,-1.017458,1.673433,-0.148471
N,0,-0.010206,-0.317446,0.451962
C,0,-1.216366,0.284228,0.078261
C,0,-2.507372,-0.287925,0.042997
C,0,-3.544668,0.585419,-0.283959
C,0,-3.366651,1.962320,-0.525300
C,0,-2.092060,2.511448,-0.436385
C,0,-2.755794,-1.758607,0.391010
H,0,-4.558601,0.203168,-0.346565
C,0,-4.563123,2.816766,-0.862537
H,0,-1.939718,3.577427,-0.587076
C,0,1.494142,-3.869801,-1.598174
H,0,1.577852,-4.928305,-1.353319
H,0,0.455717,-3.634124,-1.856835
H,0,2.144024,-3.633990,-2.449491
C,0,-4.230195,-2.146973,0.225168
C,0,-1.922306,-2.680518,-0.515868
C,0,-2.357215,-1.996542,1.860099
H,0,-2.513182,-3.049335,2.122203
H,0,-1.306878,-1.746777,2.028275
H,0,-2.970594,-1.381669,2.526639
H,0,-2.203285,-3.725431,-0.341556
H,0,-2.091461,-2.449618,-1.573554

H,0,-0.856171,-2.590189,-0.300894
H,0,-4.354355,-3.201328,0.491254
H,0,-4.881214,-1.561391,0.881714
H,0,-4.570449,-2.018465,-0.808095
H,0,-4.282452,3.868627,-0.955553
H,0,-5.015391,2.503902,-1.809451
H,0,-5.334578,2.739329,-0.089775
H,0,3.090452,4.854025,-0.642767
H,0,3.973461,4.298470,0.783025
H,0,4.450319,3.734963,-0.820452

Product 20

Gaussian calculation: second derivatives
UM062X/6-31+G**
E(UM062X) = -1024.07153770

Zero-point correction= 0.479835 (Hartree/Particle)
Thermal correction to Energy= 0.506125
Thermal correction to Enthalpy= 0.507069
Thermal correction to Gibbs Free Energy= 0.424410
Sum of electronic and ZPE= -1023.591703
Sum of electronic and thermal Energies= -1023.565413
Sum of electronic and thermal Enthalpies= -1023.564469
Sum of electronic and thermal Free Energies= -1023.647128

```
      E       CV        S
   KCal/Mol Cal/Mol-K Cal/Mol-K
Total 317.598 101.507 173.971
```

C,0,-0.090142,-0.082169,0.122572
C,0,-0.583721,-0.782891,1.364896
C,0, 1.299899,0.538790,0.382902
C,0, 0.054840,-1.130708,-0.998385
C,0,-1.079688,1.024234,-0.238274
H,0,-1.651987,-0.990018,1.474786
O,0, 0.261675,-1.721395,1.859966
H,0,-0.660576,1.322268,2.546575
H,0, 1.671388,1.003223,-0.535080
H,0, 1.256314,1.310156,1.157430
H,0, 2.004488,-0.234548,0.700990
H,0, 0.485720,-0.685677,-1.900872
H,0, 0.723462,-1.925079,-0.657489

```
H,0,-0.912084,-1.575652,-1.253754
C,0,-1.594692,1.206890,-1.516819
C,0,-2.463200,2.266094,-1.863707
C,0,-2.839711,3.182607,-0.893332
C,0,-2.356587,3.035251,0.412286
C,0,-1.489377,1.969204,0.722723
H,0,-1.321166,0.507685,-2.301916
C,0,-2.963402,2.377323,-3.283487
H,0,-3.507016,4.003451,-1.144574
C,0,-2.556808,3.779057,1.638325
N,0,-1.149032,2.056949,2.060811
C,0,-1.805891,3.129972,2.642910
C,0,-1.791823,3.580255,3.980535
C,0,-2.559706,4.713557,4.232562
C,0,-3.312185,5.392521,3.248803
C,0,-3.308302,4.918336,1.947058
C,0,-0.990577,2.858712,5.067895
H,0,-2.593194,5.113949,5.241227
C,0,-4.104313,6.617121,3.637131
H,0,-3.884027,5.423743,1.175498
C,0,-0.239836,-2.445199,2.968697
H,0, 0.516863,-3.181278,3.238432
H,0,-0.420322,-1.771886,3.815030
H,0,-1.173635,-2.955843,2.704620
C,0,-1.124503,3.548773,6.431310
C,0,-1.510642,1.416907,5.233230
C,0, 0.506466,2.849080,4.703578
H,0, 1.077363,2.330723,5.481811
H,0, 0.710999,2.352801,3.751477
H,0, 0.883417,3.873554,4.625309
H,0,-0.932591,0.896734,6.005362
H,0,-2.562208,1.425499,5.536606
H,0,-1.443190,0.827721,4.313505
H,0,-0.534319,3.000575,7.172571
H,0,-0.751458,4.577348,6.400449
H,0,-2.163192,3.565347,6.776218
H,0,-4.638971,7.027309,2.776857
H,0,-4.842511,6.383106,4.411181
H,0,-3.451922,7.402539,4.032589
H,0,-3.620822,3.242269,-3.400940
H,0,-2.133583,2.487977,-3.989117
H,0,-3.526538,1.485163,-3.576382
```

Starting Material 21

UM062X/6-31+G**
E(UM062X) = -287.027952252

Zero-point correction= 0.118847 (Hartree/Particle)
Thermal correction to Energy= 0.126106
Thermal correction to Enthalpy= 0.127051
Thermal correction to Gibbs Free Energy= 0.086734
Sum of electronic and ZPE= -286.909106
Sum of electronic and thermal Energies= -286.901846
Sum of electronic and thermal Enthalpies= -286.900902
Sum of electronic and thermal Free Energies= -286.941219

```
    E      CV        S
 KCal/Mol Cal/Mol-K Cal/Mol-K
Total 79.133 24.638 84.854
```

C,0,2.5484892947,-1.0486525478,0.379572518
C,0,2.0095370641,-1.9541208368,-0.7301559432
H,0,2.1275796777,-1.4049762628,1.3256519259
H,0,3.6359675568,-1.1599283938,0.4153765367
C,0,2.1688405272,0.3773417387,0.1596719766
H,0,2.3460844184,-1.5857128076,-1.7103614292
O,0,2.5121083831,-3.2568770685,-0.4847011691
H,0,0.9137641575,-1.9312024617,-0.6996277125
H,0,2.9002414191,1.0737385727,-0.2383393484
C,0,0.8618440867,0.8542561841,0.4178990739
N,0,-0.0627222863,0.0523721173,0.8695594649
H,0,-0.9387736456,0.5604204482,0.9988510044
H,0,0.6716881446,1.9151817057,0.2216291738
H,0,2.0862752018,-3.8807523877,-1.0811390718

Transition Structure 22

UM062X/6-31+G**
E(UM062X) = -286.982962241
Zero-point correction= 0.114050 (Hartree/Particle)
Thermal correction to Energy= 0.120212
Thermal correction to Enthalpy= 0.121156
Thermal correction to Gibbs Free Energy= 0.083907
Sum of electronic and ZPE= -286.868912
Sum of electronic and thermal Energies= -286.862750

Sum of electronic and thermal Enthalpies= -286.861806
Sum of electronic and thermal Free Energies= -286.899055

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 75.434 23.068 78.398

C,0,2.6813334783,-1.01775655,0.3637290048
C,0,1.6943581228,-1.8052149826,-0.4916066278
H,0,2.6012201103,-1.4174352992,1.3841005554
H,0,3.7064048573,-1.1879563846,0.0167473588
C,0,2.3071959597,0.4371053729,0.31223822
H,0,1.6860039826,-1.5020930324,-1.5484527657
O,0,1.8254189535,-3.1672806008,-0.2974148209
H,0,0.6183901541,-1.2892117311,0.0220485537
H,0,3.057986481,1.2016948097,0.1547679646
C,0,0.9973123878,0.7612925583,0.3873026067
N,0,0.0503128482,-0.2211494372,0.6190124759
H,0,-0.8445358906,0.0120051207,0.1850015522
H,0,0.659803021,1.7883861881,0.2514609942
H,0,1.3312615342,-3.6492470318,-0.969164072

Product 23

UM062X/6-31+G**
E(UM062X) = -287.016800365

Zero-point correction= 0.118827 (Hartree/Particle)
Thermal correction to Energy= 0.126186
Thermal correction to Enthalpy= 0.127130
Thermal correction to Gibbs Free Energy= 0.087044
Sum of electronic and ZPE= -286.897973
Sum of electronic and thermal Energies= -286.890614
Sum of electronic and thermal Enthalpies= -286.889670
Sum of electronic and thermal Free Energies= -286.929756

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 79.183 26.068 84.368

C,0,2.6544478721,-1.0838016084,0.3152015487
C,0,2.0510832371,-1.9495843875,-0.7441036346
H,0,2.3629078983,-1.4882316102,1.2971269251

```
H,0,3.7516918698,-1.1623410433,0.276468617
C,0,2.23586665,0.3600098473,0.1903904405
H,0,1.9706013514,-1.5753801639,-1.764015799
O,0,2.318292572,-3.284436976,-0.5901153405
H,0,0.0301553317,-1.0496426183,0.4499274028
H,0,2.9866587671,1.1111030739,-0.0245062556
C,0,0.9661014632,0.7587442931,0.35669412
N,0,-0.0903875106,-0.0762347614,0.7031987793
H,0,-1.0136592696,0.2700684538,0.4915346538
H,0,0.7072068585,1.8118119335,0.2875536077
H,0,1.9936919088,-3.7798844327,-1.3492390652
```

APPENDIX C

SAMPLE INPUT FILES AND PROGRAMS

Sample Input Files for Chapter II

poly.fu5

```
*General

   TITLE
 hydroboration Markovnikov with butene A
 END

  ATOMS
    1  C
    2  C
    3  C
    4  B
    5  C
    6  H
    7  H
    8  H
    9  H
   10  H
   11  H
   12  H
   13  H
   14  H
   15  H
   16  H
  END

  NOSUPERMOL
  DL ispe
  WRITEFU31 ON
  INPUNIT AU

*OPTIMIZATION

  OPTMIN  OHOOK
  OPTTS   OHOOK

*SECOND

  HESSCAL HHOOK

 *REACT1
  SPECIES   NONLINRP
  INITGEO HOOKS
  GEOM
```

```
 1
 2
 3
 4
 5
 6
 7
 8
 9
10
11
12
13
 14
 15
 16
END

*PROD1
INITGEO HOOKS
SPECIES   NONLINRP
GEOM
 1
 2
 3
 4
 5
 6
 7
 8
 9
10
11
12
13
 14
 15
 16
END

*START
 SPECIES NONLINTS
 INITGEO HOOKS
 GEOM
  1
  2
  3
  4
  5
  6
  7
  8
  9
 10
 11
 12
 13
  14
  15
```

```
  16
 END

# end of start section

*PATH

 SCALEMASS  1.00

 RODS ON

 INTMU   3
 SSTEP   0.01
 INH     10

 SRANGE

   SLP   2.01
   SLM  -2.01
 END

 RPM       pagem

 SIGN    PRODUCT

 IDIRECT   1

 COORD  CART

# INTDEF
# 5-6 18-19 5-6-1 9-12-18
# 2-1 3-2 4-3 5-4 6-1 7-3 8-7 9-8 10-9 11-7 12-9 13-4
# 14-5 15-6 16-1 17-2 18-11 19-8 20-8 3-2-1 4-3-2 5-4-3
# 6-1-2 7-3-2 8-7-3 9-8-7 10-9-8 11-7-3 12-9-8 13-4-3
# 14-5-4 15-6-1 16-1-2 17-2-1 18-11-7 19-8-7 20-8-7
# 4-3-2-1 5-4-3-2 6-1-2-3 7-3-2-1 8-7-3-2 9-8-7-3
# 10-9-8-7 11-7-3-2 12-9-8-7 13-4-3-2 14-5-4-3 15-6-1-2
# 16-1-2-3 17-2-1-6 18-11-7-3 19-8-7-3 20-8-7-3
# END

 FREQSCALE 1.00

 PRPATH
   COORD 8 9
   INTERVAL 1
   XMOL
 END

*TUNNEL

QUAD
 NQE   40
 NQTH  40
END

  SCT

*RATE
```

```
  FORWARDK

  SIGMAF       1
  CVT
  PRDELG ON
# PRGIGT ON

  TEMP
    195.15
    273.15
    298.15
    350
  END
```

esp.fu70

```
*GRGENERAL

  GRRESTART
  RSTTOL 0.00001

*GRSTART

  CHARGE       0
  MULTIPLICITY  1

*GRREACT1

  CHARGE       0
  MULTIPLICITY  1

*GRPROD1

  CHARGE       0
  MULTIPLICITY  1

*GRCOMMON

  GRENER
     #p B3LYP/6-31G* FCHK NOSYMM UNITS=AU
     scf=tight
     int(grid=ultrafine)
  END

  GRFIRST
     #p B3LYP/6-31G* FORCE FCHK NOSYMM UNITS=AU
     scf=tight
     int(grid=ultrafine)
  END

  GRSEC
     #p B3LYP/6-31G* FREQ=NORAMAN FCHK NOSYMM UNITS=AU
     scf=tight
     int(grid=ultrafine)
  END

  GRLINK0
```

```
    %chk=g09.chk
    %nproc=20
    %mem=40gb
  END
```

esp.fu71

```
%nproc=20
%mem=40gb
%chk=g09.chk
#p B3LYP/6-31G* opt fchk NOSYMM
scf=tight int(grid=ultrafine)

borane complex with butene A

0 1
 C,0,-0.4238755288,0.3130760765,-1.459316222
 C,0,-0.3048244057,0.3918311965,0.0436234579
 C,0,0.9068370849,0.3809101003,0.7162495166
 B,0,0.1796359643,-1.2762947905,0.8637416931
 C,0,-1.748734541,-0.2517890738,-1.9787513104
 H,0,-0.2984347216,1.3424485951,-1.8290135165
 H,0,-1.1844152206,0.7498958752,0.575588969
 H,0,1.8334837559,0.2928518951,0.1582384213
 H,0,0.9884248208,0.807981692,1.7088719915
 H,0,0.9297413628,-1.9589981541,0.2218029215
 H,0,0.0665391139,-1.3914891293,2.0524787378
 H,0,-0.9407963501,-1.4158010587,0.3993799205
 H,0,0.4226671509,-0.2603793734,-1.8550976714
 H,0,-1.7879536161,-0.1973237558,-3.0717245739
 H,0,-1.8727117131,-1.298651908,-1.6851013448
 H,0,-2.6029621563,0.3129348129,-1.5861999899
```

esp.fu73

```
%nproc=20
%mem=40gb
%chk=g09.chk
#p B3LYP/6-31G* opt fchk NOSYMM
scf=tight int(grid=ultrafine)

product from m with butene A

0 1
 C,0,-0.2310274656,0.1465969499,-1.3961442695
 C,0,-0.3264349594,0.0966749406,0.1390299704
 C,0,1.0053339503,0.5745667248,0.7962104601
 B,0,-0.5429507281,-1.3236843524,0.7609215402
 C,0,-1.5421170727,-0.2325352442,-2.0935844196
 H,0,0.0696740984,1.1557422968,-1.7152039991
 H,0,-1.1088866491,0.795341485,0.4721132253
 H,0,1.2517543942,1.5841341019,0.4443905146
 H,0,0.9400728723,0.6106834632,1.8896205605
 H,0,-0.1244475808,-2.3040027392,0.2090262816
 H,0,1.8464541097,-0.0773304152,0.5290750932
```

```
 H,0,-1.0412702509,-1.4544350061,1.8432160056
 H,0,0.567635157,-0.5313909663,-1.7292101333
 H,0,-1.4482131825,-0.1736669269,-3.1839397134
 H,0,-1.8444093497,-1.2577470149,-1.8433832002
 H,0,-2.3587583434,0.4359997032,-1.7934079165
```

esp.fu75

```
%nproc=20
%mem=40gb
%chk=g09.chk
#p B3LYP/6-31G* opt=(ts,calcfc,noeigentest) fchk NOSYMM
int(grid=ultrafine)

ts for M with butene A

0 1
 C,0,-0.3524889635,0.3614869034,-1.4798311054
 C,0,-0.3528953454,0.3744478104,0.0397807696
 C,0,0.8354805657,0.4121303924,0.79191366
 B,0,-0.0845832688,-1.1706060711,0.8143605506
 C,0,-1.5996827297,-0.2893281835,-2.0854697222
 H,0,-0.2803105874,1.4006302049,-1.8355918196
 H,0,-1.2275564573,0.8330317706,0.4961195438
 H,0,1.7994824255,0.3278793954,0.2967140306
 H,0,0.8607941696,0.8688597126,1.7765256443
 H,0,0.1225614025,-1.9579589028,-0.063202534
 H,0,0.9826846208,-1.1631093501,1.4524099676
 H,0,-0.9297891411,-1.3121644732,1.6493474871
 H,0,0.5477460092,-0.1536653873,-1.8375088923
 H,0,-1.5756208876,-0.239576975,-3.1797917213
 H,0,-1.672868262,-1.3407773446,-1.7898538477
 H,0,-2.5124115506,0.2178614981,-1.7493870111
```

poly.fu51

```
*ISPEGEN           # unit fu51 input using CCSD(T) energies on B3 single points

 MEPTYPER  TWO     # reactant
 MEPTYPEP  TWO     # product

 ENESAD      2.1512
 ENERXN      -18.7710

#+/- 0.1
*POINT
   SMEP -0.6
   VMEP 1.7834
*POINT
   SMEP -0.5
   VMEP 1.9272
*POINT
   SMEP -0.4
   VMEP 2.0553
*POINT
```

```
  SMEP -0.3
  VMEP 2.1559
*POINT
  SMEP -0.2
  VMEP 2.2154
*POINT
  SMEP -0.1
  VMEP 2.2193
*POINT
  SMEP 0.1
  VMEP 1.9966
*POINT
  SMEP 0.2
  VMEP 1.7380
*POINT
  SMEP 0.3
  VMEP 1.3613
*POINT
  SMEP 0.4
  VMEP 0.8545
*POINT
  SMEP 0.5
  VMEP 0.2104
*POINT
  SMEP 0.6
  VMEP -0.5721
```

Sample Input Files for Mesmer

Dodecene, Anti conformation, CCSD(T)/aug-cc-pvtz, full molecule

```
<?xml version="1.0" encoding="utf-8" ?>
<?xml-stylesheet type='text/xsl' href='../../mesmer2.xsl' media='other'?>
<?xml-stylesheet type='text/xsl' href='../../mesmer1.xsl' media='screen'?>
<me:mesmer xmlns="http://www.xml-cml.org/schema"
xmlns:me="http://www.chem.leeds.ac.uk/mesmer">
<title>Hydroboration</title>
<moleculeList>
<molecule id="dodecene" description="C12H24">
<propertyList>
<property dictRef="me:ZPE">
<scalar units="kJ/mol">0.0</scalar>
</property>
<property dictRef="me:rotConsts">
<array units="cm-1">0.219122789      0.005113113 0.005075742</array>
</property>
<property dictRef="me:symmetryNumber">
<scalar>1</scalar>
</property>
<property dictRef="me:frequenciesScaleFactor">
<scalar>0.9854</scalar>
</property>
<property dictRef="me:vibFreqs">
<array units="cm-1">
23.5041 35.7412 44.8815 59.7786 83.8432 94.0883 110.0615
130.7408 135.7867 162.8996 167.1213 192.6601 204.0764 249.7760
738.0284 738.8503 745.8320 766.4055 805.7903 860.7445 904.5081
923.3394 936.1495 940.0673 986.4711 994.4303 1012.5666 1027.5267
1035.0604 1045.7853 1052.0310 1066.6703 1071.4391 1073.0296 1075.8668
1097.5664 1149.5793 1209.0595 1227.7961 1239.6764 1258.6194 1275.7805
```

```
1291.5500 1312.1138 1320.1438 1333.0651 1339.0511 1342.5087 1346.1977
1351.8318 1354.2915 1354.6932 1381.9085 1405.7940 1420.6191 1425.8292
1426.8270 1441.3214 1475.6296 1509.6615 1512.8373 1513.4917 1516.3006
1517.0354 1522.3622 1529.2167 1529.8861 1535.9827 1541.5302 1545.1655
1733.1039 3008.0738 3009.0898 3009.8857 3011.9297 3013.0869 3016.4373
3022.0005 3026.5350 3028.6701 3029.8640 3031.5224 3035.6815 3040.6336
3042.8948 3051.1363 3057.1975 3065.3001 3073.5066 3079.8468 3105.1982
3109.8409 3133.2683 3154.1959 3232.0859
</array>
</property>
<property dictRef="me:MW">
<scalar units="amu">168.319</scalar>
</property>
<property dictRef="me:spinMultiplicity">
<scalar>1</scalar>
</property>
</propertyList>
<me:DOSCMethod>Classical rotors</me:DOSCMethod>
</molecule>

<molecule id="bh3" description="bh3">
<propertyList>
<property dictRef="me:ZPE">
<scalar units="kJ/mol">0.0</scalar>
</property>
<property dictRef="me:rotConsts">
<array units="cm-1">7.824596263      7.824596263 3.912297965</array>
</property>
<property dictRef="me:symmetryNumber">
<scalar>6</scalar>
</property>
<property dictRef="me:frequenciesScaleFactor">
<scalar>0.9854</scalar>
</property>
<property dictRef="me:vibFreqs">
<array units="cm-1">
1160.2127 1213.4739 1213.4744 2593.8604 2726.1153 2726.1166
</array>
S9
</property>
<property dictRef="me:MW">
<scalar units="amu">13.83</scalar>
</property>
<property dictRef="me:spinMultiplicity">
<scalar>1</scalar>
</property>
</propertyList>
<me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
</molecule>

<molecule id="complex3" description="complex3">
<propertyList>
<property dictRef="me:ZPE">
<scalar units="kJ/mol">-42.457</scalar>
</property>
<property dictRef="me:rotConsts">
<array units="cm-1">0.168538205      0.004247915 0.004210544</array>
</property>
<property dictRef="me:symmetryNumber">
```

```
<scalar>1</scalar>
</property>
<property dictRef="me:frequenciesScaleFactor">
<scalar>0.9854</scalar>
</property>
<property dictRef="me:epsilon">
<scalar>272.01</scalar>
</property>
<property dictRef="me:sigma">
<scalar>6.7697</scalar>
</property>
<property dictRef="me:vibFreqs">
<array units="cm-1">
21.0698 31.7876 38.1089 52.1561 76.7525 85.6690 91.8916
119.5449 127.0780 134.0575 162.7833 165.2803 170.8137 191.0036
249.9306 256.0158 280.3986 323.2575 356.8956 412.5383 424.9810
484.0934 500.6757 567.0413 708.1558 737.9541 739.1944 746.6405
767.3003 805.2292 817.6024 857.0909 868.6660 904.8682 924.7710
941.9684 984.5293 991.7264 1008.4904 1014.1664 1024.3885 1038.0670
1049.7925 1063.5014 1066.9047 1073.1518 1073.8921 1081.9925 1096.4566
1116.5043 1149.5331 1171.4746 1183.3677 1213.6796 1229.6065 1240.3765
1259.6838 1276.1546 1290.5863 1303.7212 1315.6165 1324.0562 1338.2075
1342.3447 1346.7538 1352.5892 1355.2723 1355.5623 1382.7208 1405.7826
1420.6822 1426.3776 1427.2211 1441.6392 1471.8852 1512.7692 1513.0042
1515.6433 1516.5391 1518.6102 1523.6915 1529.9741 1530.3247 1536.7517
1541.9020 1545.2562 1609.9873 2481.0479 2557.0594 2643.7082 3009.7424
3010.3695 3013.1656 3014.6174 3018.6578 3023.2525 3027.6480 3030.3082
3030.4653 3032.8847 3037.6916 3040.9590 3045.2447 3053.7540 3057.0048
3062.9856 3071.3403 3077.9371 3102.3547 3105.4282 3110.4577 3179.8993
3182.9846 3268.3122
</array>
</property>
<property dictRef="me:MW">
<scalar units="amu">182.149</scalar>
</property>
<property dictRef="me:spinMultiplicity">
<scalar>1</scalar>
</property>
<property dictRef="me:deltaEDown">
<!--deltaEDown is the average energy transferred upon collision in the
downward direction-->
<scalar>860.1234</scalar>
</property>
</propertyList>
<me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
</molecule>

<molecule id="AMTS" description="AMTS">
<propertyList>
<property dictRef="me:ZPE">
<scalar units="kJ/mol">-42.688</scalar>
</property>
<property dictRef="me:rotConsts">
<array units="cm-1">0.165355355      0.004271939 0.004234902</array>
</property>
<property dictRef="me:symmetryNumber">
<scalar>1</scalar>
</property>
```

```
<property dictRef="me:frequenciesScaleFactor">
<scalar>0.9854</scalar>
</property>
<property dictRef="me:vibFreqs">
<array units="cm-1">
21.4906 32.8223 39.6208 54.5767 81.5338 92.2038 95.1861
126.6999 136.0528 161.1041 163.1062 166.6379 180.2035 233.4436
250.0555 284.7596 346.3512 370.0445 427.6035 444.9497 490.9093
506.3572 635.4032 716.6013 737.9775 739.2514 746.8062 767.5918
803.6578 807.9061 861.0684 896.3989 904.8135 924.1012 939.3775
984.0782 991.8206 1011.2221 1016.3118 1025.3052 1039.5081 1050.0437
1065.0597 1066.7031 1073.0394 1074.1097 1081.8647 1093.0336 1138.6141
1149.9751 1170.0054 1188.7612 1215.3873 1229.6503 1241.0175 1259.4356
1273.5719 1286.1794 1294.5836 1315.3554 1323.1918 1338.1038 1342.3541
1346.6361 1353.0707 1355.1839 1356.1410 1384.1393 1406.9039 1420.9807
1426.2856 1427.1506 1441.5813 1458.9472 1512.7229 1512.9883 1515.5362
1516.5438 1518.4581 1523.5808 1530.0062 1530.2557 1536.7244 1541.8978
1545.2431 1568.5568 2386.9414 2558.4074 2658.4231 3009.7103 3010.3856
3013.1135 3014.5629 3018.5750 3023.2950 3027.6370 3030.1266 3030.4923
3032.9101 3037.7905 3040.9335 3045.3799 3052.6351 3054.6730 3063.3371
3071.4051 3077.8029 3098.7466 3105.4274 3110.4243 3169.9522 3176.1247
3255.2348
</array>
</property>
<property dictRef="me:MW">
<scalar units="amu">182.149</scalar>
</property>
<property dictRef="me:spinMultiplicity">
<scalar>1</scalar>
</property>
<property dictRef="me:imFreqs">
<scalar units="cm-1">337.2266</scalar>
</property>
</propertyList>
<me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
</molecule>

<molecule id="MTS" description="MTS">
<propertyList>
<property dictRef="me:ZPE">
<scalar units="kJ/mol">-33.644</scalar>
</property>
<property dictRef="me:rotConsts">
<array units="cm-1">
0.171014681    0.004253253    0.00421655
</array>
</property>
<property dictRef="me:symmetryNumber">
<scalar>1</scalar>
</property>
<property dictRef="me:frequenciesScaleFactor">
<scalar>0.9854</scalar>
</property>
<property dictRef="me:vibFreqs">
<array units="cm-1">
21.3819 33.6482 38.1231 54.8961 83.0534 91.2539 97.5590
128.6128 137.3051 164.0969 165.3259 171.1004 180.5804 250.3015
255.7835 283.1959 327.1411 359.7441 429.2812 434.3232 490.0040
505.1515 632.5675 737.9585 738.3783 743.2565 747.9672 765.8439
```

```
799.0249 805.5537 858.1430 904.5032 912.7519 928.6027 963.4384
990.0020 998.5021 1012.6040 1028.6545 1035.9554 1051.3515 1057.1956
1060.9848 1067.8084 1073.0420 1074.2663 1088.9764 1101.6510 1136.7832
1150.0787 1170.4541 1196.4960 1217.9783 1230.5519 1240.6890 1259.8527
1275.1692 1287.9725 1295.5357 1315.0062 1323.3623 1337.7705 1342.3659
1346.0830 1352.7005 1354.8413 1355.5385 1383.7697 1406.9828 1421.2708
1426.0841 1427.0787 1441.5305 1458.8487 1511.1602 1512.8258 1513.8121
1516.2442 1517.3534 1522.6668 1529.4046 1530.0401 1536.0483 1541.5307
1545.1699 1554.1247 2331.9922 2573.5304 2676.5607 3009.2819 3009.6339
3011.9618 3013.0588 3015.2519 3019.8539 3025.2349 3028.5043 3030.0727
3031.5454 3035.0312 3040.7364 3040.8870 3042.8409 3049.4248 3058.9350
3067.8747 3075.5445 3085.2311 3105.2551 3110.0758 3161.7617 3170.1155
3247.7746
</array>
</property>
<property dictRef="me:MW">
<scalar units="amu">182.149</scalar>
</property>
S11
<property dictRef="me:spinMultiplicity">
<scalar>1</scalar>
</property>
<property dictRef="me:imFreqs">
<scalar units="cm-1">525.9578</scalar>
</property>
</propertyList>
<me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
</molecule>

<molecule id="THF">
<!--THF collision parameters used in this work; however  this choice is
    arbitrary  since the results are
    reported in terms of collision frequencies-->
<propertyList>
<property dictRef="me:epsilon">
<scalar>68.1</scalar>
</property>
<property dictRef="me:sigma">
<scalar>3.57</scalar>
</property>
<property dictRef="me:MW">
<scalar units="amu">72.11</scalar>
</property>
</propertyList>
</molecule>

<molecule id="antimarkov">
<propertyList>
<property dictRef="me:ZPE">
<scalar units="kJ/mol">-60.0</scalar>
</property>
</propertyList>
</molecule>

<molecule id="markov">
<propertyList>
<property dictRef="me:ZPE">
<scalar units="kJ/mol">-60.0</scalar>
</property>
```

```
</propertyList>
</molecule>

</moleculeList>
<reactionList>
<reaction id="R1">
<reactant>
<molecule ref="dodecene" me:type="deficientReactant" />
</reactant>
<reactant>
<molecule ref="bh3" me:type="excessReactant" />
</reactant>
<product>
<molecule ref="complex3" me:type="modelled" />
</product>
<me:MCRCMethod>Mesmer ILT</me:MCRCMethod>
<me:preExponential>1.75e-11</me:preExponential>
<me:excessReactantConc>2.25E16</me:excessReactantConc>
<me:activationEnergy>0.0</me:activationEnergy>
<me:TInfinity>298.0</me:TInfinity>
<me:nInfinity>-0.01</me:nInfinity>
</reaction>
<reaction id="R2">
<reactant>
<molecule ref="complex3" me:type="modelled" />
</reactant>
<product>
<molecule ref="antimarkov" me:type="sink" />
S12
</product>
<me:transitionState>
<molecule ref="AMTS" me:type="transitionState" />
</me:transitionState>
<me:MCRCMethod>SimpleRRKM</me:MCRCMethod>
</reaction>
<reaction id="R3">
<reactant>
<molecule ref="complex3" me:type="modelled" />
</reactant>
<product>
<molecule ref="markov" me:type="sink" />
</product>
<me:transitionState>
<molecule ref="MTS" me:type="transitionState" />
</me:transitionState>
<me:MCRCMethod>SimpleRRKM</me:MCRCMethod>
</reaction>
</reactionList>
<me:conditions>
<me:bathGas>THF</me:bathGas>
<me:PTs>
<!--the pressure/temp pairs given below are to cover the
entire 368 K range of collision frequencies reported in the paper-->
<me:PTpair me:units="Torr" me:P="209395." me:T="298." />
</me:PTs>
</me:conditions>
<me:modelParameters>
<!--Specify grain size directly...-->
<me:grainSize units="cm-1">25.</me:grainSize>
```

```
<!--...or by the total number of grains
<me:numberOfGrains> 500 </me:numberOfGrains>-->
<!--Specify increased energy range
<me:maxTemperature>6000</me:maxTemperature>-->
<me:energyAboveTheTopHill>25.0</me:energyAboveTheTopHill>
</me:modelParameters>
<me:control>
<me:testDOS />
<me:printSpeciesProfile />
S13
<!--<me:testMicroRates />-->
<me:testRateConstants />
<me:printGrainDOS />
<!--<me:printCellDOS />-->
<!--<me:printReactionOperatorColumnSums />-->
<!--<me:printTunnellingCoefficients />-->
<me:printGrainkfE />
<!--<me:printGrainBoltzmann />-->
<me:printGrainkbE />
<me:eigenvalues>0</me:eigenvalues>
</me:control>
</me:mesmer>
```

Dodecene, Anti conformation, CCSD(T)/aug-cc-pvtz, localized calculation

```
<?xml version="1.0" encoding="utf-8" ?>
<?xml-stylesheet type='text/xsl' href='../../mesmer2.xsl' media='other'?>
<?xml-stylesheet type='text/xsl' href='../../mesmer1.xsl' media='screen'?>
<me:mesmer xmlns="http://www.xml-cml.org/schema"
xmlns:me="http://www.chem.leeds.ac.uk/mesmer">
<title>Hydroboration</title>
<moleculeList>
<molecule id="dodecene" description="C12H24">
<propertyList>
<property dictRef="me:ZPE">
<scalar units="kJ/mol">0.0</scalar>
</property>
<property dictRef="me:rotConsts">
<array units="cm-1">0.219122789      0.005113113 0.005075742</array>
</property>
<property dictRef="me:symmetryNumber">
<scalar>1</scalar>
</property>
<property dictRef="me:frequenciesScaleFactor">
<scalar>0.9854</scalar>
</property>
<property dictRef="me:vibFreqs">
<array units="cm-1">
210.9293 425.3639 589.0547 933.3222 937.1024 956.6329 1036.0412
1081.6911 1203.3971 1339.6015 1434.8730 1474.2160 1509.9348 1524.0905
1739.1122 3032.3826 3079.0754 3116.7134 3144.6133 3156.6634
</array>
</property>
<property dictRef="me:MW">
<scalar units="amu">168.319</scalar>
</property>
<property dictRef="me:spinMultiplicity">
<scalar>1</scalar>
</property>
```

```
</propertyList>
<me:DOSCMethod>Classical rotors</me:DOSCMethod>
</molecule>

<molecule id="bh3" description="bh3">
<propertyList>
<property dictRef="me:ZPE">
<scalar units="kJ/mol">0.0</scalar>
</property>
<property dictRef="me:rotConsts">
<array units="cm-1">7.824596263      7.824596263 3.912297965</array>
</property>
<property dictRef="me:symmetryNumber">
<scalar>6</scalar>
</property>
<property dictRef="me:frequenciesScaleFactor">
<scalar>0.9854</scalar>
</property>
<property dictRef="me:vibFreqs">
<array units="cm-1">
1160.2127 1213.4739 1213.4744 2593.8604 2726.1153 2726.1166
</array>
S9
</property>
<property dictRef="me:MW">
<scalar units="amu">13.83</scalar>
</property>
<property dictRef="me:spinMultiplicity">
<scalar>1</scalar>
</property>
</propertyList>
<me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
</molecule>

<molecule id="complex3" description="complex3">
<propertyList>
<property dictRef="me:ZPE">
<scalar units="kJ/mol">-42.457</scalar>
</property>
<property dictRef="me:rotConsts">
<array units="cm-1">0.168538205      0.004247915 0.004210544</array>
</property>
<property dictRef="me:symmetryNumber">
<scalar>1</scalar>
</property>
<property dictRef="me:frequenciesScaleFactor">
<scalar>0.9854</scalar>
</property>
<property dictRef="me:epsilon">
<scalar>272.01</scalar>
</property>
<property dictRef="me:sigma">
<scalar>6.7697</scalar>
</property>
<property dictRef="me:vibFreqs">
<array units="cm-1">
110.3949 193.9645 276.7160 339.2536 401.5664 494.2255 711.3290
802.5044 851.7722 929.6655 961.5245 1009.7585 1047.6309 1097.8983
1116.0805 1172.2780 1183.1837 1211.5323 1314.3351 1432.6004 1472.3195
```

```
1508.8553 1522.5427 1617.8505 2484.8461 2558.3458 2644.2066 3050.0175
3118.7710 3148.4316 3183.4473 3191.2662 3271.7531
</array>
</property>
<property dictRef="me:MW">
<scalar units="amu">182.149</scalar>
</property>
<property dictRef="me:spinMultiplicity">
<scalar>1</scalar>
</property>
<property dictRef="me:deltaEDown">
<!--deltaEDown is the average energy transferred upon collision in the
downward direction-->
<scalar>134.1234</scalar>
</property>
</propertyList>
<me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
</molecule>

<molecule id="AMTS" description="AMTS">
<propertyList>
<property dictRef="me:ZPE">
<scalar units="kJ/mol">-42.688</scalar>
</property>
<property dictRef="me:rotConsts">
<array units="cm-1">0.165355355      0.004271939 0.004234902</array>
</property>
<property dictRef="me:symmetryNumber">
<scalar>1</scalar>
</property>
S10
<property dictRef="me:frequenciesScaleFactor">
<scalar>0.9854</scalar>
</property>
<property dictRef="me:vibFreqs">
<array units="cm-1">
213.4803 233.4630 388.7657 442.0287 576.9672 716.1992 797.2462
885.6810 929.4999 962.4460 1016.0393 1050.9048 1089.0271 1142.7874
1170.7303 1187.0138 1221.4235 1293.5833 1429.3509 1462.5154 1511.4203
1522.4767 1572.7520 2384.8265 2559.0615 2659.8540 3052.6305 3119.4382
3144.5452 3172.4152 3184.8931 3257.8205
</array>
</property>
<property dictRef="me:MW">
<scalar units="amu">182.149</scalar>
</property>
<property dictRef="me:spinMultiplicity">
<scalar>1</scalar>
</property>
<property dictRef="me:imFreqs">
<scalar units="cm-1">337.2266</scalar>
</property>
</propertyList>
<me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
</molecule>

<molecule id="MTS" description="MTS">
<propertyList>
<property dictRef="me:ZPE">
```

```
<scalar units="kJ/mol">-33.644</scalar>
</property>
<property dictRef="me:rotConsts">
<array units="cm-1">
0.171014681    0.004253253    0.00421655
</array>
</property>
<property dictRef="me:symmetryNumber">
<scalar>1</scalar>
</property>
<property dictRef="me:frequenciesScaleFactor">
<scalar>0.9854</scalar>
</property>
<property dictRef="me:vibFreqs">
<array units="cm-1">
224.9188 268.2195 340.2778 420.6411 604.6537 720.4579 798.1757
890.0871 947.1378 987.8065 1058.3066 1069.1978 1103.5775 1128.5230
1171.6823 1199.2287 1225.1173 1296.3394 1434.8862 1461.8585 1514.2697
1529.1506 1560.8426 2329.9120 2574.5222 2677.6771 3041.0599 3105.7604
3129.5834 3163.5039 3179.7944 3249.6061
</array>
</property>
<property dictRef="me:MW">
<scalar units="amu">182.149</scalar>
</property>
S11
<property dictRef="me:spinMultiplicity">
<scalar>1</scalar>
</property>
<property dictRef="me:imFreqs">
<scalar units="cm-1">525.9578</scalar>
</property>
</propertyList>
<me:DOSCMethod>ClassicalRotors</me:DOSCMethod>
</molecule>

<molecule id="THF">
<!--THF collision parameters used in this work; however  this choice is
    arbitrary  since the results are
    reported in terms of collision frequencies-->
<propertyList>
<property dictRef="me:epsilon">
<scalar>68.1</scalar>
</property>
<property dictRef="me:sigma">
<scalar>3.57</scalar>
</property>
<property dictRef="me:MW">
<scalar units="amu">72.11</scalar>
</property>
</propertyList>
</molecule>

<molecule id="antimarkov">
<propertyList>
<property dictRef="me:ZPE">
<scalar units="kJ/mol">-60.0</scalar>
</property>
</propertyList>
```

```
</molecule>

<molecule id="markov">
<propertyList>
<property dictRef="me:ZPE">
<scalar units="kJ/mol">-60.0</scalar>
</property>
</propertyList>
</molecule>

</moleculeList>
<reactionList>
<reaction id="R1">
<reactant>
<molecule ref="dodecene" me:type="deficientReactant" />
</reactant>
<reactant>
<molecule ref="bh3" me:type="excessReactant" />
</reactant>
<product>
<molecule ref="complex3" me:type="modelled" />
</product>
<me:MCRCMethod>Mesmer ILT</me:MCRCMethod>
<me:preExponential>1.75e-11</me:preExponential>
<me:excessReactantConc>2.25E16</me:excessReactantConc>
<me:activationEnergy>0.0</me:activationEnergy>
<me:TInfinity>298.0</me:TInfinity>
<me:nInfinity>-0.01</me:nInfinity>
</reaction>
<reaction id="R2">
<reactant>
<molecule ref="complex3" me:type="modelled" />
</reactant>
<product>
<molecule ref="antimarkov" me:type="sink" />
S12
</product>
<me:transitionState>
<molecule ref="AMTS" me:type="transitionState" />
</me:transitionState>
<me:MCRCMethod>SimpleRRKM</me:MCRCMethod>
</reaction>
<reaction id="R3">
<reactant>
<molecule ref="complex3" me:type="modelled" />
</reactant>
<product>
<molecule ref="markov" me:type="sink" />
</product>
<me:transitionState>
<molecule ref="MTS" me:type="transitionState" />
</me:transitionState>
<me:MCRCMethod>SimpleRRKM</me:MCRCMethod>
</reaction>
</reactionList>
<me:conditions>
<me:bathGas>THF</me:bathGas>
<me:PTs>
<!--the pressure/temp pairs given below are to cover the
```

```
entire 368 K range of collision frequencies reported in the paper-->
<me:PTpair me:units="Torr" me:P="20939500." me:T="298." />
</me:PTs>
</me:conditions>
<me:modelParameters>
<!--Specify grain size directly...-->
<me:grainSize units="cm-1">25.</me:grainSize>
<!--...or by the total number of grains
<me:numberOfGrains> 500 </me:numberOfGrains>-->
<!--Specify increased energy range
<me:maxTemperature>6000</me:maxTemperature>-->
<me:energyAboveTheTopHill>25.0</me:energyAboveTheTopHill>
</me:modelParameters>
<me:control>
<me:testDOS />
<me:printSpeciesProfile />
S13
<!--<me:testMicroRates />-->
<me:testRateConstants />
<me:printGrainDOS />
<!--<me:printCellDOS />-->
<!--<me:printReactionOperatorColumnSums />-->
<!--<me:printTunnellingCoefficients />-->
<me:printGrainkfE />
<!--<me:printGrainBoltzmann />-->
<me:printGrainkbE />
<me:eigenvalues>0</me:eigenvalues>
</me:control>
</me:mesmer>
```

Sample Input Files for Chapter III

Sample Input Files for Gaussrate

Poly.fu5

```
*General

  TITLE
 blum reaction bimolecular
 END

  ATOMS
    1  C
    2  H
    3  H
    4  H
    5  S
    6  C
    7  C
```

```
   8  C
   9  C
  10  C
  11  C
  12  C
  13  H
  14  H
  15  H
  16  H
  17  C
  18  C
  19  H
  20  H
  21  H
  22  B
  23  O
  24  O
  25  Cl
  26  C
  27  C
  28  C
  29  C
  30  C
  31  C
  32  H
  33  H
  34  H
  35  H
 END

 NOSUPERMOL
 INPUNIT AU

*OPTIMIZATION

 OPTMIN  OHOOK
 OPTTS   OHOOK

*SECOND

 HESSCAL HHOOK

 *REACT1
 SPECIES   NONLINRP
```

```
 INITGEO HOOKS
 GEOM
   1
   2
   3
   4
   5
   6
   7
   8
   9
  10
  11
  12
  13
  14
  15
  16
  17
  18
  19
  20
  21
 END

*REACT2
 SPECIES   NONLINRP
 INITGEO HOOKS
 GEOM
22
23
24
25
26
27
28
29
30
31
32
33
34
35
 END
```

```
 *PROD1
 SPECIES   NONLINRP
 INITGEO HOOKS
 GEOM
  1
  2
  3
  4
  5
  6
  7
  8
  9
 10
 11
 12
 13
 14
 15
 16
 17
 18
 19
 20
 21
 22
 23
 24
 25
 26
 27
 28
 29
 30
 31
 32
 33
 34
 35
 END

*START
 SPECIES NONLINTS
```

```
  INITGEO HOOKS
  GEOM
   1
   2
   3
   4
   5
   6
   7
   8
   9
  10
  11
  12
  13
  14
  15
  16
  17
  18
  19
  20
  21
  22
  23
  24
  25
  26
  27
  28
  29
  30
  31
  32
  33
  34
  35
  END

# end of start section

*PATH

 SCALEMASS  1.00
```

```
 RODS ON

 INTMU   3
 SSTEP   0.01
 INH     10

 SRANGE

   SLP   1.61
   SLM  -1.21
 END

 RPM       pagem

 SIGN    PRODUCT

 IDIRECT   1

 COORD  CART

# INTDEF
# 5-6 18-19 5-6-1 9-12-18
# 2-1 3-2 4-3 5-4 6-1 7-3 8-7 9-8 10-9 11-7 12-9 13-4
# 14-5 15-6 16-1 17-2 18-11 19-8 20-8 3-2-1 4-3-2 5-4-3
# 6-1-2 7-3-2 8-7-3 9-8-7 10-9-8 11-7-3 12-9-8 13-4-3
# 14-5-4 15-6-1 16-1-2 17-2-1 18-11-7 19-8-7 20-8-7
# 4-3-2-1 5-4-3-2 6-1-2-3 7-3-2-1 8-7-3-2 9-8-7-3
# 10-9-8-7 11-7-3-2 12-9-8-7 13-4-3-2 14-5-4-3 15-6-1-2
# 16-1-2-3 17-2-1-6 18-11-7-3 19-8-7-3 20-8-7-3
# END

 FREQSCALE 1.00

 PRPATH
   COORD 8 9
   INTERVAL 1
   XMOL
 END

*TUNNEL

QUAD
 NQE   40
```

```
 NQTH  40
END

  SCT

*RATE

  FORWARDK

  SIGMAF        1
  CVT
  PRDELG ON
# PRGIGT ON

  TEMP
    195.15
    273.15
    298.15
    358.15
  END
```

esp.fu70

```
*GRGENERAL

  GRRESTART
  RSTTOL 0.00001

*GRSTART

  CHARGE       0
  MULTIPLICITY  1

*GRREACT1

  CHARGE       0
  MULTIPLICITY  1

*GRPROD1

  CHARGE       0
  MULTIPLICITY  1

*GRCOMMON
```

```
GRENER
   #p B3LYP/6-31+G** FCHK NOSYMM UNITS=AU
   scf=tight
   int(grid=ultrafine) empiricaldispersion=gd3
   scrf(pcm,solvent=toluene)
END

GRFIRST
   #p B3LYP/6-31+G** FORCE FCHK NOSYMM UNITS=AU
   scf=tight
   int(grid=ultrafine) empiricaldispersion=gd3
   scrf(pcm,solvent=toluene)
END

GRSEC
   #p B3LYP/6-31+G** FREQ=NORAMAN FCHK NOSYMM UNITS=AU
   scf=tight
   int(grid=ultrafine) empiricaldispersion=gd3
   scrf(pcm,solvent=toluene)
END

GRLINK0
  %chk=g09.chk
  %nproc=20
  %mem=40gb
END
```

esp.fu71

```
%nproc=20
%mem=40gb
%chk=g09.chk
#p B3LYP/6-31+G** opt fchk NOSYMM
scf=tight int(grid=ultrafine) empiricaldispersion=gd3
scrf(pcm,solvent=toluene)

MeSPhCCMe

0 1
 C,0,0.1528285835,0.0336116338,0.0625360246
 H,0,-0.1969186933,-0.204561247,1.0696512963
 H,0,1.1507756054,0.4744782708,0.1302901292
```

```
 H,0,0.1845157803,-0.8862831792,-0.5270754443
 S,0,-1.0647758474,1.2189428443,-0.6013718475
 C,0,-0.4434836121,1.5669201469,-2.2348643542
 C,0,-1.1894247594,2.480766189,-3.0300787374
 C,0,-0.7393606942,2.7879430762,-4.3274468818
 C,0,0.420962734,2.2132391462,-4.8433151327
 C,0,1.1493022874,1.31656742,-4.0577746722
 C,0,0.7218949385,0.9962153221,-2.7664398354
 C,0,-2.3821707321,3.0840932257,-2.5258154117
 H,0,-1.3183774401,3.4867552839,-4.9229053915
 H,0,0.7521429043,2.4627051665,-5.8464822667
 H,0,2.0556300356,0.8601045242,-4.4450651848
 H,0,1.3086144331,0.2975869362,-2.1826862753
 C,0,-3.3940637822,3.5876245886,-2.0807612454
 C,0,-4.6088305975,4.1874411472,-1.5365229047
 H,0,-4.7957080249,3.8281812754,-0.5185153805
 H,0,-4.5276988427,5.2797424901,-1.4993597135
 H,0,-5.4822442765,3.9358647389,-2.1488487704
```

esp.fu73

```
%nproc=20
%mem=40gb
%chk=g09.chk
#p B3LYP/6-31+G** opt fchk NOSYMM
scf=tight int(grid=ultrafine) empiricaldispersion=gd3
scrf(pcm,solvent=toluene)

product anti

0 1
 C,0,-3.8917073116,-1.981220484,0.4693219117
 H,0,-3.812163121,-2.788928799,1.1977579935
 H,0,-3.2738875379,-2.1710888859,-0.4087845763
 H,0,-4.9359803005,-1.821005877,0.2019375635
 S,0,-3.2896096989,-0.4643693827,1.2764367086
 C,0,-3.1675777986,0.6568788302,-0.0910470799
 C,0,-1.8249501345,0.7810363281,-0.4712063658
 C,0,-1.5267818092,1.6315749452,-1.537937414
 C,0,-2.5631306613,2.3149263437,-2.173252407
 C,0,-3.8913358962,2.1744683426,-1.7616825709
 C,0,-4.2148010434,1.3362793932,-0.6939842781
 C,0,-0.8862394643,-0.0345217683,0.3247197857
```

```
H,0,-0.4965535562,1.7477847491,-1.8561379727
H,0,-2.3320664845,2.9735653156,-3.0038986748
H,0,-4.6783537674,2.7226145274,-2.2680584692
H,0,-5.2400677577,1.2270421111,-0.3553582265
C,0,-1.4918988441,-0.7551060514,1.2840106708
C,0,-0.9932593871,-1.7309844826,2.2979487089
H,0,-1.2534392987,-1.4185417068,3.3138652299
H,0,-1.4057546062,-2.7319826238,2.128605146
H,0,0.0918897702,-1.7856850052,2.2106167231
B,0,0.6885752166,-0.0665488542,-0.0291259793
O,0,1.2360524024,1.2628668262,-0.2922288941
O,0,1.5557735175,-0.6804258105,0.9673250712
Cl,0,0.7706841295,-1.1229229249,-1.6833402469
C,0,2.6619308985,0.1078768155,1.0334135874
C,0,3.8331918341,-0.1164552757,1.7302666124
C,0,4.8287546106,0.8731290047,1.6562379292
C,0,4.6370288368,2.0319784236,0.9080785986
C,0,3.442106759,2.2511814549,0.2010508972
C,0,2.4688135763,1.273827278,0.2789582659
H,0,3.9722633459,-1.0248178962,2.3067225405
H,0,5.7627016636,0.7263805001,2.1892946124
H,0,5.423060106,2.7791297743,0.8645951567
H,0,3.2826148124,3.1485778645,-0.3870785577
```

esp.fu75

```
%nproc=20
%mem=40gb
%chk=g09.chk
#p B3LYP/6-31+G** opt=(ts,calcfc,noeigentest) fchk NOSYMM
int(grid=ultrafine) empiricaldispersion=gd3
scrf(pcm,solvent=toluene)

TS Anti

0 1
 C,0,-2.3890101531,0.3749515604,2.9888652782
 H,0,-2.2033945879,0.911544352,3.9225141707
 H,0,-3.4642865986,0.3097818732,2.8125722337
 H,0,-1.9023595363,0.8953161361,2.1613412583
 S,0,-1.678065114,-1.3089666984,3.1909369495
 C,0,-1.9709967081,-1.9713780322,1.5526464516
 C,0,-1.0615926038,-1.7184449799,0.4864670714
```

```
C,0,-1.3281346285,-2.2701799176,-0.7748583703
C,0,-2.4593511541,-3.0604050728,-0.982366349
C,0,-3.3443317496,-3.3142584071,0.0663602456
C,0,-3.0972881457,-2.7701448384,1.3301725473
C,0,0.1113904263,-0.8988832566,0.7630469978
H,0,-0.6409335065,-2.0879484202,-1.5898689534
H,0,-2.644065723,-3.4789084104,-1.9668923024
H,0,-4.223884815,-3.9306513432,-0.0926534771
H,0,-3.782158744,-2.9626879537,2.1493786272
C,0,0.6301525678,-0.4029768976,1.7877615072
C,0,1.459233753,0.3312744763,2.7148410729
H,0,0.8798971508,1.0853341685,3.2577004458
H,0,1.9600234713,-0.3311038613,3.4272543471
H,0,2.2214568052,0.8442451758,2.1126480838
B,0,1.2588611161,-0.2651299425,-0.7146391419
O,0,2.4421465218,0.3652995511,-0.2116563319
O,0,1.6231633127,-1.5051405437,-1.330065202
Cl,0,0.1040013596,0.8227852763,-1.6214057389
C,0,2.9325950606,-1.7151848498,-0.9755496782
C,0,3.7211233681,-2.8282308233,-1.2138638898
C,0,5.0497587532,-2.7779503627,-0.7531358281
C,0,5.5447889796,-1.652049078,-0.0851991592
C,0,4.7324482847,-0.5271376318,0.1513205998
C,0,3.4268195424,-0.5892669976,-0.3056383329
H,0,3.3258059524,-3.6939047125,-1.734252956
H,0,5.7002739289,-3.6308945358,-0.920158049
H,0,6.5745629938,-1.6425686944,0.2585145043
H,0,5.1072464198,0.3529696915,0.6631613685
```

Sample Input Files for Chapter IV

Sample Input Files for Gaussrate

The sample input files below are the ones used for UM062X/6-31+G** calculations for the 1,5 HAT of **21** to **23.**

poly.dat

```
*General

  TITLE
rajca c4 OH model
 END
```

```
 ATOMS
   1  C
   2  C
   3  H
   4  H
   5  C
   6  H
   7  O
   8  H
   9  H
  10  C
  11  N
  12  H
  13  H
  14  H
 END

 NOSUPERMOL

 WRITEFU31 ON
 INPUNIT AU

*OPTIMIZATION

 OPTMIN  OHOOK
 OPTTS   OHOOK

*SECOND

 HESSCAL HHOOK

 *REACT1
 SPECIES   NONLINRP
 INITGEO HOOKS
 GEOM
1
2
3
4
5
6
7
8
```

```
9
10
11
12
13
14
 END
 ELEC
   2   0.0
 END


 *PROD1
 INITGEO HOOKS
 SPECIES   NONLINRP
 GEOM
1
2
3
4
5
6
7
8
9
10
11
12
13
14
 END
 ELEC
   2   0.0
 END


*START
 SPECIES NONLINTS
 INITGEO HOOKS
 GEOM
1
2
3
4
```

```
 5
 6
 7
 8
 9
 10
 11
 12
 13
 14
  END
  ELEC
   2   0.0
  END

# end of start section

*PATH

 SCALEMASS  1.00

 RODS ON

 INTMU   3
 SSTEP   0.002
 INH     10

 SRANGE

   SLP   4.01
   SLM  -2.01
 END

 RPM       pagem

 SIGN    PRODUCT

 IDIRECT   1

 COORD  CURV3

 INTDEF
 8-11 2-8-11 2-8-11-10 8-11-10
 2-1 3-1 4-1 5-1 6-2 7-2 8-2 9-5 10-5 11-10 12-11
```

```
 13-10 14-7 3-1-2 4-1-3 5-1-4 6-2-1 7-2-1 8-2-1 9-5-1
 10-5-1 11-10-5 12-11-10 13-10-5 14-7-2 4-1-3-2 5-1-4-3
 6-2-1-5 7-2-1-5 8-2-1-5 9-5-1-2 10-5-1-2 11-10-5-1
 12-11-10-5 13-10-5-1 14-7-2-1
  END

 FREQSCALE 1.00

 PRPATH
   COORD 8 9
   INTERVAL 1
   XMOL
 END

*TUNNEL

QUAD
 NQE   40
 NQTH  40
END

  SCT
 LCTOPT
   ngamp 120
   ngtheta 120
 END

*RATE

  FORWARDK

  SIGMAF        1
  CVT
  PRDELG ON
# PRGIGT ON

  TEMP
    100
    120
    140
    160
    180
    200
    220
```

```
  240
  260
  273.15
  298.15
  323.15
  350
  400
 END
```

esp.fu70

```
*GRGENERAL

 GRRESTART
 RSTTOL 0.00001

*GRSTART

 CHARGE       0
 MULTIPLICITY  2

*GRREACT1

 CHARGE       0
 MULTIPLICITY  2

*GRPROD1

 CHARGE       0
 MULTIPLICITY  2

*GRCOMMON

 GRENER
     #p UM062X/6-31+G** FCHK NOSYMM UNITS=AU
     scf=tight guess=tcheck
     int(grid=ultrafine)
 END

 GRFIRST
     #p UM062X/6-31+G** FORCE FCHK NOSYMM UNITS=AU
     scf=tight guess=tcheck
```

```
    int(grid=ultrafine)
 END

 GRSEC
    #p UM062X/6-31+G** FREQ=NORAMAN FCHK NOSYMM UNITS=AU
    scf=tight
    int(grid=ultrafine)
 END

 GRLINK0
    %chk=g09.chk
    %nproc=20
    %mem=40gb
 END
```

esp.fu71

```
%nproc=20
%mem=40gb
%chk=g09.chk
#p UM062X/6-31+G** opt fchk NOSYMM
scf=tight int(grid=ultrafine)

rajca c4 oh model sm

0 2
 C,0,2.5484892947,-1.0486525478,0.379572518
 C,0,2.0095370641,-1.9541208368,-0.7301559432
 H,0,2.1275796777,-1.4049762628,1.3256519259
 H,0,3.6359675568,-1.1599283938,0.4153765367
 C,0,2.1688405272,0.3773417387,0.1596719766
 H,0,2.3460844184,-1.5857128076,-1.7103614292
 O,0,2.5121083831,-3.2568770685,-0.4847011691
 H,0,0.9137641575,-1.9312024617,-0.6996277125
 H,0,2.9002414191,1.0737385727,-0.2383393484
 C,0,0.8618440867,0.8542561841,0.4178990739
 N,0,-0.0627222863,0.0523721173,0.8695594649
 H,0,-0.9387736456,0.5604204482,0.9988510044
 H,0,0.6716881446,1.9151817057,0.2216291738
 H,0,2.0862752018,-3.8807523877,-1.0811390718
```

esp.fu73

```
%nproc=20
%mem=40gb
%chk=g09.chk
#p UM062X/6-31+G** opt fchk NOSYMM
scf=tight int(grid=ultrafine)

product c4 oh model

0 2
 C,0,2.6544478721,-1.0838016084,0.3152015487
 C,0,2.0510832371,-1.9495843875,-0.7441036346
 H,0,2.3629078983,-1.4882316102,1.2971269251
 H,0,3.7516918698,-1.1623410433,0.276468617
 C,0,2.23586665,0.3600098473,0.1903904405
 H,0,1.9706013514,-1.5753801639,-1.764015799
 O,0,2.318292572,-3.284436976,-0.5901153405
 H,0,0.0301553317,-1.0496426183,0.4499274028
 H,0,2.9866587671,1.1111030739,-0.0245062556
 C,0,0.9661014632,0.7587442931,0.35669412
 N,0,-0.0903875106,-0.0762347614,0.7031987793
 H,0,-1.0136592696,0.2700684538,0.4915346538
 H,0,0.7072068585,1.8118119335,0.2875536077
 H,0,1.9936919088,-3.7798844327,-1.3492390652
```

esp.fu75

```
%nproc=20
%mem=40gb
%chk=g09.chk
#p UM062X/6-31+G** opt=(ts,calcfc,noeigentest) fchk NOSYMM
int(grid=ultrafine)

ts for Rajca c4 oh model

0 2
 C,0,2.6813334783,-1.01775655,0.3637290048
 C,0,1.6943581228,-1.8052149826,-0.4916066278
```

```
 H,0,2.6012201103,-1.4174352992,1.3841005554
 H,0,3.7064048573,-1.1879563846,0.0167473588
 C,0,2.3071959597,0.4371053729,0.31223822
 H,0,1.6860039826,-1.5020930324,-1.5484527657
 O,0,1.8254189535,-3.1672806008,-0.2974148209
 H,0,0.6183901541,-1.2892117311,0.0220485537
 H,0,3.057986481,1.2016948097,0.1547679646
 C,0,0.9973123878,0.7612925583,0.3873026067
 N,0,0.0503128482,-0.2211494372,0.6190124759
 H,0,-0.8445358906,0.0120051207,0.1850015522
 H,0,0.659803021,1.7883861881,0.2514609942
 H,0,1.3312615342,-3.6492470318,-0.969164072
```

esp.fu51 (for H-isotopologue)

```
*ISPEGEN           # unit fu51 input using CCSD(T) energies on the M062X path

 MEPTYPER  TWO     # reactant
 MEPTYPEP  TWO     # product

 ENESAD     28.5797
 ENERXN      8.01315

#+/- 0.1
*POINT
  SMEP -2.00
  VMEP 9.0901
*POINT
  SMEP -1.80
  VMEP 10.2707
*POINT
  SMEP -1.60
  VMEP 11.5799
*POINT
  SMEP -1.40
  VMEP 13.0288
*POINT
  SMEP -1.20
  VMEP 14.6292
*POINT
  SMEP -1.00
  VMEP 16.3893
*POINT
```

```
  SMEP -0.80
  VMEP 18.3121
*POINT
  SMEP -0.60
  VMEP 20.4270
*POINT
  SMEP -0.40
  VMEP 22.9944
*POINT
  SMEP -0.20
  VMEP 26.4488
*POINT
  SMEP -0.08
  VMEP 28.1175
*POINT
  SMEP -0.06
  VMEP 28.2912
*POINT
  SMEP -0.04
  VMEP 28.4272
*POINT
  SMEP -0.02
  VMEP 28.5238
*POINT
  SMEP 0.02
  VMEP 28.5953
*POINT
  SMEP 0.04
  VMEP 28.5693
*POINT
  SMEP 0.06
  VMEP 28.5021
*POINT
  SMEP 0.08
  VMEP 28.3941
*POINT
  SMEP 0.10
  VMEP 28.2459
*POINT
  SMEP 0.12
  VMEP 28.0584
*POINT
  SMEP 0.20
  VMEP 26.9430
```

```
*POINT
  SMEP 0.40
  VMEP 22.4788
*POINT
  SMEP 0.60
  VMEP 18.4198
*POINT
  SMEP 0.80
  VMEP 16.3244
*POINT
  SMEP 1.00
  VMEP 14.8951
*POINT
  SMEP 1.20
  VMEP 13.7770
*POINT
  SMEP 1.40
  VMEP 12.8639
*POINT
  SMEP 1.60
  VMEP 12.1005
*POINT
  SMEP 1.80
  VMEP 11.4538
*POINT
  SMEP 2.00
  VMEP 10.9030
```

esp.fu51 (for D-isotopologue)

```
*ISPEGEN           # unit fu51 input using CCSD(T) energies on the M062X path

 MEPTYPER  TWO     # reactant
 MEPTYPEP  TWO     # product

 ENESAD     28.5797
 ENERXN      8.01315

#+/- 0.1
*POINT
  SMEP -2.00
  VMEP 9.9797
```

```
*POINT
  SMEP -1.80
  VMEP 11.2230
*POINT
  SMEP -1.60
  VMEP 12.5974
*POINT
  SMEP -1.40
  VMEP 14.1151
*POINT
  SMEP -1.20
  VMEP 15.7886
*POINT
  SMEP -1.00
  VMEP 17.6258
*POINT
  SMEP -0.80
  VMEP 19.6373
*POINT
  SMEP -0.60
  VMEP 21.9039
*POINT
  SMEP -0.40
  VMEP 24.6029
*POINT
  SMEP -0.20
  VMEP 27.2687
*POINT
  SMEP -0.08
  VMEP 28.2967
*POINT
  SMEP -0.06
  VMEP 28.4003
*POINT
  SMEP -0.04
  VMEP 28.4823
*POINT
  SMEP -0.02
  VMEP 28.5424
*POINT
  SMEP 0.00
  VMEP 28.5797
*POINT
  SMEP 0.02
```

```
  VMEP 28.5960
*POINT
  SMEP 0.04
  VMEP 28.5893
*POINT
  SMEP 0.06
  VMEP 28.5602
*POINT
  SMEP 0.08
  VMEP 28.5090
*POINT
  SMEP 0.10
  VMEP 28.4356
*POINT
  SMEP 0.12
  VMEP 28.3406
*POINT
  SMEP 0.20
  VMEP 27.7507
*POINT
  SMEP 0.40
  VMEP 25.0514
*POINT
  SMEP 0.60
  VMEP 21.4979
*POINT
  SMEP 0.80
  VMEP 18.4568
*POINT
  SMEP 1.00
  VMEP 16.5445
*POINT
  SMEP 1.20
  VMEP 15.1707
*POINT
  SMEP 1.40
  VMEP 14.0500
*POINT
  SMEP 1.60
  VMEP 13.1130
*POINT
  SMEP 1.80
  VMEP 12.3215
*POINT
```

SMEP 2.00
VMEP 11.6492

Programs

Program Suite PROGDYN

A full listing of the subprograms of PROGDYN is given below. To allow the reader to understand or make use of PROGDYN, we describe here first the overall structure of the program. We also list and describe in this section a number of helper programs that were used to analyze the data from the trajectory calculations.
The newest edition of PROGDYN includes the ability to include additional empirical dispersion using Grimme's D2 model. This was not employed for the 53-THF system but it was employed in the 80-THF system using ProdynONIOM, described in the next section.

The master control program for dynamics, in the form of a Unix Shell Script, is called *progdynstarterHP*. For a user to start to use *progdynstarterHP*, some early lines in it that assign the scratch space and the location of the program files and input files would have to be modified for the local environment. These lines are between lines 45 and 55 and should be apparent. The location of the scratch space is usually passed to *progdynstarterHP* as a parameter.

progdynstarterHP takes as input files:
freqinHP - This is the standard output from a Gaussian 98, 03, or 09 frequency calculation using freq=hpmodes. For isotopically labeled compounds, use freq=(hpmodes,readisotopes).
progdyn.conf – This is a file giving a variety of configuration options, called on by many of the subprograms. progdyn.conf examples are listed below and contains explanations of the program options.
isomernumber - A number in file isomernumber provides a start for numbering runs. The default is 1.
detour – A signal file that, by existing, signals the program to do a side calculations
nogo – A signal file that, by existing, signals the program to stop between points
bypassproggen - A signal file that, by existing, signals the program to use a supplied input file *geoPlusVel* instead of generating one for itself. This pathway for initialization is important here because it is used when the program progdynsam, described later, is used to generate the geoPlusVel file.
methodfile – A file that contains lines to be added to the end of each g09.com input file, such as lines that call for an NMR calculation
ZMAT – An input file for the CFOUR (http://www.cfour.de) suite of programs. When ZMAT is supplied, *progdynstarterHP* will automatically run call CFOUR (which must be set up independently by the user) by making use of the script *progcfour*.

cannontraj – A file containing a vector for each atom, used to fire an initial geometry in a particular direction.

progdynstarterHP calls the following programs:
proggenHP - An awk program that starts a trajectory, giving each mode its zero point energy (if a quasiclassical calculation) plus random additional excitations depending on the temperature.
prog1stpoint – Awk program that creates the first Gaussian input file for each run
prog2ndpoint – Awk program that creates the second Gaussian input file for each run. prog2ndpoint also checks the energy of the first point to see if it fits with the desired energy, and aborts the run if it does not by creating appropriate output in file Echeck
progdynb – Creates subsequent Gaussian input files until run is completed, written in awk
proganal – A program to analyze the latest point and see if a run is done. This program must be redone for each new system. Elaborate changes are sometimes programmed into proganal, such as the automatic changing of configuration variables. proganal creates the output to dynfollowfile and NMRlist or NMRlistdis
randgen – A program that generates random numbers between 0 and 1. These are generated all at once and stored in a file for use by proggenHP.
progcfour – A control script to run CFOUR calculations (not needed for most kinds of runs).

progdynstarterHP has the following output files:
isomernumber – A running tab of the trajectory number
runpointnumber – a running tab of the point in the trajectory
Echeck – output form where prog2ndpoint checks the energy of the trajectory to see if it fits with the desired energy
geoRecord – A record of all of the geoPlusVel files.
geoPlusVel – Created by proggen, this gives the starting positions, velocities, isotopic masses, excitations of the normal modes, and initial displacements of the normal modes for current run.
g09.com – Created by prog1stpoint, prog2ndpoint, and progdynb, this is the latest input file for Gaussian09 for current run and latest point.
olddynrun, *olddynrun2, olddynrun3* – files containing the last three outputs from Gaussian, for creation of the next point
traj, traj1, traj2, traj3, etc. – files containing the geometries and energies for each trajectory, numbered by the isomernumber, in a format suitable for reading by Molden.
dynfollowfile – A short record of the runs and their results. The data desired for *dynfollowfile* must be programed into the script *proganal* as needed for each system studied.
NMRlist or *NMRlistdis* – output of NMR predictions at each point in a trajectory, when desired

skipstart - A signal file that, by existing, tells progdynstarterHP that we are in the middle of a run. For trajectories that are propagated forward and backward in time, skipstart keeps track of whether one is in the forward or reverse part.
diagnostics – optional output that follows which subprograms are running and configuration variables, decided by variable in progdyn.conf
vellist – optional output that lists the velocities of each atom, decided by variable in progdyn.conf, or lists the total kinetic energy in the system and the classical temperature, often also keeps track of the density
A number of files starting with *'temp'* are created then later erased.

The following helper programs were used for the current study.
progdynsam – an awk program that generates a geoPlusVel file based on input from a *traj* file. Typically, the traj file is a trajectory performed with constraints, and the new geoPlusVel will be started without constraints. *progdynsam* must be modified for the desired temperature, and it takes as input the variable pt to decide which points in the traj file are used to define the geoPlusVel. For previously fully fixed atoms, *progdynsam* gives the atoms a Boltzmann-random velocity and direction of motion appropriate for the desired temperature. Usually any prior constraints were harmonic, in which case adjustment was made to the motions of the constrained atoms. The program is invoked with awk –v pt=## –f progdynsam traj where ## is the trajectory point used to start a new geoPlusVel, and traj is the output file from above containing the list of trajectory points.
proglookstart – an awk program used to generate the proper inputs for progdynsam.
progKECM – an awk program that calculates the kinetic energy of the alkene from the traj file while removing the motion of the center of mass. Other versions of the program were implemented to account for different alkenes as well as remove the center of mass calculation. Other kinetic energy programs calculated the energy for different portions of an alkene.
progcomptime – an awk program used to analyze data from the dynfollowfile. It calculated the time from the formation of the pi complex to the formation of the product.

progdynstarterHP

```
#!/bin/bash
#progdynstarterHP, made to use high-precision modes from Gaussian output with
freq=hpmodes
#updated to create a random number file temp811 that is used by proggenHP
#version September 16, 2005, made for workstations
#version August 2007 to allow periodic copying of g09.log to dyn putting it under
control of progdynb
#version Feb 2008 moves variables like the scratch directory and location of randgen to
the beginning
#version March 2008 added proganal reporting to points 1 and 2
#version Jan 2009 fixed bug generator of having proganal run twice in checking for
complete runs
```

```
#version May 2009 Echeck catches bad energies after only one point, other lines written
simpler, triple while loop, revised comments
#version Aug 2010 isomernumber adds words to ease parsing, increased elements up to
bromine, runpointnumber checked for more appropriate restarts
#version Aug 2011 runpointnumber starts better, restart better if died during first few
points, awk bug fix
#version Aug 2012 freqinHP reads with only 3 freqs, goingwell and other temp files
moved to $scratchdir
#version Aug 2013 adds ability to automatically run a CFOUR program if the file
ZMAT exists
#version Nov 2013 adds ability to bypass generation of geoPlusVel using the signal file
bypassproggen
#version Nov 2015 makes using guess=read easier, improves ability to restart after disk
write failures, partially allows for MM runs in Gaussian
#LIMITATIONS - standard version only handles elements up to bromine, must change
program to do higher atomic numbers
#   only handles up to 4000th excited state for modes - this could start to affect the
initialization of classical modes or transition vectors at
#    extremely high temperatures
#   The routine that checks whether the actual energy approximately equals the desired
energy checks for lines containing "SCF Done" or "EUMP2 =" or " Energy="
#   This should handle ordinary calculations HF, DFT, ONIOM, and MP2 calculations
but the routine in prog2ndpoint would have to be changed for other calcs.
#
#                                   OUTLINE
# A. initialize to perform Gaussian jobs, set the scratch, program, and other directories,
remove errant control files
#    start outermost loop L1L1L1L1L1L1L1L1
#    start loop 2 L2L2L2L2L2L2L2L2L2
# B. branch on whether there is a file named "skipstart"
#    if there is, skip B1, B2, B3 entirely
#    if no file named "skipstart" then generate a new isomer.  Instructions: Get rid of
skipstart to start new isomer.
#    the B loop generates geoPlusVel, adds it to geoRecord, generates and runs first and
second points, and sets up for continuous loop
#  B1. generates geoPlusVel, isomernumber, runpointnumber=1, then makes g09.com
for point 1
#  B2. checks for success of B1 or exits, then sets geoRecord then runs g09.com.  Checks
for its success or exits.
#  B3. runpointnumber=2, kills run if XXXX in dynfollowfile due to bad energy
probably, makes g09.com for point 2, runs it
#      checks for its success or exits
#      runpointnumber=3, uses progdynb to make g09.com for point 3
#      sets skipstart=forward
```

```
#  B4. Only runs if skipstart=ireverserestart, performs reverserestart, ends with
runpointnumber=3
#      sets skipstart=reverse
# C. loop over propagation steps
#
#
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
#
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
#
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
#origdir, randdir, scratchdir, g09root, logfile all may need varied from system to system
and assigned here or by program calling this one
export LC_ALL=C
echo $1
scratchdir=$1
export g09root=/software/lms/g09_D01
. $g09root/g09/bsd/g09.profile
origdir=`pwd`
cd $origdir
logfile=docslog
randdir=~/bin
proggramdir=/scratch/user/d-singleton/binall500
freqfile=/scratch/user/d-singleton/binall500/freqinHP
echo
echo ORIGDIR at the beginning of run:
echo $origdir
ls $origdir
echo
echo SCRATCHDIR at the beginning of run:
echo $scratchdir
ls $scratchdir
echo
echo PROGGRAMDIR at the beginning of run::
echo $proggramdir
ls $proggramdir

rm -f nogo    # assume that if someone is starting a job, they want it to go.
```

```
rm -f diagnostics goingwell tempdone # diagnostics contains extra info from previous
runs, other two files are from older versions of progdyn
if (test -s g09.com) then
  sed -i '/guess=tcheck/d' g09.com      # no chk file on first point
fi

#### Triple 'while' loop - will have to break multiple times to get out, but advantage is
ability to control starting over
#L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L
1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L
1L1L1L1L1L1L1L1
while (true)
do
# As long as there is a file "goingwell" the program will not exit entirely by itself
rm -f $scratchdir/goingwell
#L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L
2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L
2L2L2L2L2L2L2L2
while (true)
do
#  BBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBB
  if (test -f skipstart) then
    echo "skipping start and continuing from previous runs"
  else
#
B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1
generate geoPlusVel and first input file
    if [ `cat runpointnumber` = "1" ]; then
      echo "X did not complete first point so new isomer started" >> dynfollowfile
    fi
    if [ `cat runpointnumber` = "2" ]; then
      echo "X did not complete second point so new isomer started" >> dynfollowfile
    fi
    if [ `cat runpointnumber` = "3" ]; then
      echo "X did not complete third point so new isomer started" >> dynfollowfile
    fi
    cd $origdir
    if (test -f bypassproggen) then
      echo "taking starting conditions from pre-generated geoPlusVel"
    else
      $randdir/randgen > temp811
# the next 8 lines would have to be changed to use low-precision modes
      awk '/       1        2/,/Harmonic frequencies/ {print}' $freqfile > temp401
```

```
      awk '/Frequencies --/ {print $3;print $4;print $5;print $6;print $7}' temp401 >
tempfreqs
      awk '/Reduced masses/ {print $4;print $5;print $6;print $7;print $8}' temp401 >
tempredmass
      awk '/Force constants/ {print $4;print $5;print $6;print $7;print $8}' temp401 >
tempfrc
      awk '/0/ && ((length($1) < 2) && ($1 < 4)) {print}' temp401 > tempmodes
      awk '/has atomic number/ {print}' $freqfile > tempmasses
      awk '/Standard orientation:/,/tional const/ {if (($3=="0") || (substr($3,1,2)==10))
print}' $freqfile > tempstangeos
      awk '/Input orientation:/,/Stoichiometry/ {if (($3=="0") || (substr($3,1,2)==10))
print}' $freqfile > tempinputgeos
      awk -f $proggramdir/proggenHP $freqfile > geoPlusVel
    fi
    if (test -f isomernumber) then
      cp isomernumber temp533
      awk 'BEGIN {getline;i=$1+1;print i,"----trajectory isomer number----"}' temp533
> isomernumber
      rm temp533
    else
      echo "1 ----trajectory isomer number----" > isomernumber
    fi
    echo 1 > runpointnumber
    rm g09.com
    awk -f $proggramdir/prog1stpoint isomernumber > g09.com
#
B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B
2B2  if first part successful then clean up and run the first input file, otherwise die
    if (test -s g09.com) then
      rm tempfreqs tempredmass tempfrc tempmodes tempstangeos tempmasses
temp401 temp811 tempinputgeos
      cat isomernumber >> geoRecord
      cat geoPlusVel >> geoRecord
      rm -f $scratchdir/goingwell
      cd $scratchdir
      cp $origdir/g09.com $scratchdir/g09.com
      $g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
      cd $origdir
      grep 'Normal termination' $scratchdir/g09.log > $scratchdir/goingwell
      if (test -s $scratchdir/goingwell) then
        cp $scratchdir/g09.log olddynrun2
      else
        cp $scratchdir/g09.log $origdir/g09.log
        break
```

```
      fi
    else
      break
    fi
#
B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B
3B3 if B2 worked then you are here.  create 2nd point, run it, and set up for propagation
loop
    rm g09.com
    echo 2 > runpointnumber
    awk -f $proggramdir/prog2ndpoint $scratchdir/g09.log > g09.com
# before we decide to run this, check the energy
    awk -f $proggramdir/proganal $scratchdir/g09.log >> dynfollowfile
    rm -f $scratchdir/tempdone
    tail -1 dynfollowfile | awk '/XXXX/ {print}' > $scratchdir/tempdone
    if (test  -s $scratchdir/tempdone) then
      rm -f dyn
      rm -f traj
      echo 0 > runpointnumber
      break
    fi
    if (test -s g09.com) then
      rm -f $scratchdir/goingwell
      cd $scratchdir
      cp $origdir/g09.com $scratchdir/g09.com
      $g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
      cd $origdir
      grep 'Normal termination' $scratchdir/g09.log > $scratchdir/goingwell
      if (test -s $scratchdir/goingwell) then
        cp $scratchdir/g09.log olddynrun
        awk -f $proggramdir/proganal $scratchdir/g09.log >> dynfollowfile
        awk '/Input orientation/,/Distance matrix/ {print};/Matrix
orientation/,/Stoichiometry/ {print}' olddynrun | awk '{if (($2>.5) && ($2<100)) print}'
> old
        awk '/Input orientation/,/Distance matrix/ {print};/Matrix
orientation/,/Stoichiometry/ {print}' olddynrun2 | awk '{if (($2>.5) && ($2<100)) print}'
> older
        echo 3 > runpointnumber
        if (test -f bypassproggen) then
          cat bypassproggen > runpointnumber
          echo 3 > bypassproggen
        fi
        awk -f $proggramdir/progdynb olddynrun > g09.com
        rm -f old older
```

```
         else
            cp $scratchdir/g09.log $origdir/g09.log
            break
         fi
      else
         break
      fi
# we've just completed a start, so lets skipstart until instructed otherwise
      echo "forward" > skipstart
   fi
#
B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B
4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4
B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4
# Reverse trajectories starter routine
   if [ `cat skipstart` = "reverserestart" ]; then
      cd $origdir
      rm g09.com
      echo 1 > runpointnumber
      awk -f $proggramdir/prog1stpoint isomernumber > g09.com
      if (test -s g09.com) then
         rm -f $scratchdir/goingwell
         cd $scratchdir
         cp $origdir/g09.com $scratchdir/g09.com
         $g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
         cd $origdir
         grep 'Normal termination' $scratchdir/g09.log > $scratchdir/goingwell
         if (test -s $scratchdir/goingwell) then
            cp $scratchdir/g09.log olddynrun2
         else
            cp $scratchdir/g09.log $origdir/g09.log
            break
         fi
      else
         break
      fi
      rm g09.com
      echo 2 > runpointnumber
      awk -f $proggramdir/prog2ndpoint $scratchdir/g09.log > g09.com
      awk -f $proggramdir/proganal $scratchdir/g09.log >> dynfollowfile
      rm -f $scratchdir/tempdone
      if (test -s g09.com) then
         rm -f $scratchdir/goingwell
         cd $scratchdir
```

```
      cp $origdir/g09.com $scratchdir/g09.com
      $g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
      cd $origdir
      grep 'Normal termination' $scratchdir/g09.log > $scratchdir/goingwell
      if (test -s $scratchdir/goingwell) then
        cp $scratchdir/g09.log olddynrun
        awk -f $proggramdir/proganal $scratchdir/g09.log >> dynfollowfile
        awk '/Input orientation/,/Distance matrix/ {print};/Matrix
orientation/,/Stoichiometry/ {print}' olddynrun | awk '{if (($2>.5) && ($2<100)) print}'
> old
        awk '/Input orientation/,/Distance matrix/ {print};/Matrix
orientation/,/Stoichiometry/ {print}' olddynrun2 | awk '{if (($2>.5) && ($2<100)) print}'
> older
        echo 3 > runpointnumber
        if (test -f bypassproggen) then
          cat bypassproggen > runpointnumber
        fi
        awk -f $proggramdir/progdynb olddynrun > g09.com
        rm -f old older
      else
        cp $scratchdir/g09.log $origdir/g09.log
        break
      fi
    else
      break
    fi
# we've just completed a reversestart, so lets skipstart until instructed otherwise
    echo "reverse" > skipstart
  fi

#
END_of_B___END_of_B___END_of_B___END_of_B___END_of_B___END_of_B_
__END_of_B___END_of_B___

#
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCC  propagation loop
  while (true)
  do
    rm -f $scratchdir/goingwell
    cd $scratchdir
    cp $origdir/g09.com $scratchdir/g09.com
    $g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
    cd $origdir
```

```
    grep 'Normal termination' $scratchdir/g09.log > $scratchdir/goingwell
    if (test -s $scratchdir/goingwell) then
      awk -f $proggramdir/proganal $scratchdir/g09.log >> $origdir/dynfollowfile
      mv olddynrun2 olddynrun3
      mv olddynrun olddynrun2
      awk '/Input orientation/,/Distance matrix/ {print};/Matrix
orientation/,/Stoichiometry/ {print}' $scratchdir/g09.log | awk '{if (($2>.5) &&
($2<100)) print}' > old
      cp $scratchdir/g09.log olddynrun
      awk '/Input orientation/,/Distance matrix/ {print};/Matrix
orientation/,/Stoichiometry/ {print}' olddynrun2 | awk '{if (($2>.5) && ($2<100)) print}'
> older
      #increment runpointnumber
      cp runpointnumber $scratchdir/temp533
      awk 'BEGIN {getline;i=$1+1;print i}' $scratchdir/temp533 > runpointnumber
      rm $scratchdir/temp533
      awk -f $proggramdir/progdynb $scratchdir/g09.log > g09.com
      rm -f old older
    else
      cp $scratchdir/g09.log $origdir/g09.log
      break
    fi
# kludge to do a side calculation of NMR using progcfour.  If ZMAT is there then it gets
ran and renamed.
# creation of ZMAT is under the control of progdynb, which is controlled by keyword
NMRcc in progdyn.conf
# decisions to be made: erase ZMAT at beginning?  what to do if cfour calc dies?
    if (test  -f ZMAT) then
      cp ZMAT $scratchdir
      cd $scratchdir
      $scratchdir/progcfour $origdir $scratchdir
      cd $origdir
      mv ZMAT temp.ZMAT
      echo "generic one two three" `cat runpointnumber` "runisomer" `cat
isomernumber` >> NMRlistcc
      awk '/Nuclear Magnetic Resonance/,/HF-SCF/ {if ($2=="C") print $1,$2,"Isotropic
=",$3; if ($2=="H") print $1,$2,"Isotropic =",$3}' x.log >> NMRlistcc
    fi

# here is a cool link that lets you interrupt the dynamics with a short job, then
# it automatically goes back to the dynamics  just make the file 'detour' and it
# will delete detour, run run.com, then go back to dynamics
    if (test  -f detour) then
      rm detour
```

```
      date >> $logfile
      cat run.com >> $logfile
      cp run.log temp.log
      cd $scratchdir
      $g09root/g09/g09 $origdir/run.com > $origdir/run.log
      cd $origdir
    fi

#stop it all nicely by creating a nogo file
    if (test  -f nogo) then
      break
    fi

#figure out if this isomer is done - change in April 2013 is to move proganal call up from
here
    rm -f $scratchdir/tempdone
    tail -2 dynfollowfile | awk '/XXXX/ {print}' > $scratchdir/tempdone
    if (test  -s $scratchdir/tempdone) then
      if [ `awk '/reversetraj/ {if ($1=="reversetraj") print $2}' progdyn.conf` = "true" ];
then
        if [ `cat skipstart` = "reverse" ]; then
          rm -f skipstart
          rm -f geoPlusVel
          rm -f olddynrun
          rm -f olddynrun2
          rm -f olddynrun3
          a=`awk '{print $1}' isomernumber`
          mv traj traj$a
        fi
        if [ `cat skipstart` = "forward" ]; then
          echo reverserestart > skipstart
        fi
      else
        rm -f skipstart
        rm -f geoPlusVel
        rm -f olddynrun
        rm -f olddynrun2
        rm -f olddynrun3
        a=`awk '{print $1}' isomernumber`
        mv traj traj$a
      fi
      break
    fi
  done
```

```
#
END_of_C_Loop____END_of_C_Loop____END_of_C_Loop____END_of_C_Loop__
__END_of_C_Loop____END_of_C_Loop____

# We've got to break a second time to get out of this loop
# if we really want to quit.  Otherwise, it will start over
# at the top
  if (test  -f nogo) then
    break
  fi
  if (test  -s $scratchdir/goingwell) then
    echo "starting a new point or a new direction"
  else
    break
  fi
done

  if (test  -f nogo) then
    break
  fi
  if (test  -s $scratchdir/goingwell) then
    echo "starting a new point or a new direction2"
  else
    break
  fi
done
exit 0

proggenHP
BEGIN {
# 2014 - avoids bug with a box on, so that starts without modes use input geometry, not
standard orientation
# aug 2013 summary of changes
#includes molecular rotation, ability to do multiple NMR calculations, ONIOM with link
atoms,
#nonstandard routes, handling of linear molecules using geometry linear, fixed but with
atoms over 99 but
#bug varies with version of Gaussian, randomization based on PROCINFO (solved
many problems), added initialDiss 3 for random
#phase of normal modes
# Aug 2010 changes classicalSpacing to 2 and upped possible excited states to 4000
# Jan 2009 - a number of little changes to improve reporting, precision, etc, specification
of displacement on particular modes
```

```
# Jan 2009 cannonball trajectories.  adds desired energy to initial velocities based on file cannontraj, so one can shoot toward a ts
# updated Nov 2008 to incorporate running DRPs
# updated Nov 2008 to allow for start without an initial freq calc using classical = 2
# updated Aug 2008 added to atom list to handle a large number of atoms without changes needed
# updated June 2008 to incorporate new method for choosing displacements with initialdis 2
# updated Jan 17 2008 - bug fix for > 99 atoms, 300 excitations of low modes possible
# version August 2007 - incorporates classical trajectory calculation option
#also allows listing of number of imaginary frequencies
# version Sept 16, 2005 - incorporates searchdir but not yet rotation
# now reads random numbers from temp811, starting at a random place
# The input files are generated before this and are tempfreqs, tempredmass,
# tempfrc, tempmodes, and tempstangeos.
# It will count the number of atoms.

# default parameters, including quassiclassical, no displacements, transition state, not a DRP
# do not change these - rather, change progdyn.conf to set the parameters
initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
classical=0; numimag=1; DRP=0; cannonball=0
charge=0; multiplicity=1; method="HF/3-21G"; memory=20000000
diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
title3="a"; title4="progdyn.conf"; processors=1; highlevel=999
conver1=4.184E26 #dividing by this converts amu angs^2 /s^2 to kcal/mol
geometry="nonlinear";rotationmode=0

#initialization and constants
for (i=1;i<=10000;i++) {disMode[i]=-1}
i=1;j=1;k=1
c=29979245800; h=6.626075E-34; avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447
numAtoms=0; atomnumber=0; classicalSpacing=2
zpeGauss=0; zpeGaussK=0; zpePlusE=0; potentialE=0

# read progdyn.conf for configuration info
blankLineTester=10
while (blankLineTester>1) {
  getline < "progdyn.conf"
  if ($1=="method") method=$2
  if ($1=="charge") charge=$2
  if ($1=="multiplicity") multiplicity=$2
```

```
  if ($1=="memory") memory=$2
  if ($1=="processors") processors=$2
  if ($1=="checkpoint") checkpoint=$2
  if ($1=="diagnostics") diag=$2
  if ($1=="initialdis") initialDis=$2
  if ($1=="timestep") timestep=$2
  if ($1=="scaling") scaling=$2
  if ($1=="temperature") temp=$2
  if ($1=="searchdir") searchdir=$2
  if ($1=="classical") classical=$2
  if ($1=="numimag") numimag=$2
  if ($1=="geometry") geometry=$2
  if ($1=="highlevel") highlevel=$2
  if ($1=="boxon") boxon=$2
  if ($1=="boxsize") boxsize=$2
  if ($1=="DRP") DRP=$2; if (DRP==1) classical=2 #this lets one start a DRP from a
point that is not a freq calc
  if ($1=="maxAtomMove") maxAtomMove=$2
  if ($1=="cannonball") cannonball=$2
  if ($1=="displacements") disMode[$2]=$3
  if ($1=="controlphase") controlPhase[$2]=$3
  if ($1=="rotationmode") rotationmode=$2
  if ($1=="title") {
    title1=$2
    title2=$3
    title3=$4
    title4=$5
    }
  blankLineTester=length($0)
  }

if (diag>=1) print "****************** starting proggen ******************" >>
"diagnostics"
if (diag>=1) print "method,charge,multiplicity,memory" >> "diagnostics"
if (diag>=1) print method,charge,multiplicity,memory >> "diagnostics"
if (diag>=1) print "processors,checkpoint,title,initialdis,timestep,scaling,temperature" >>
"diagnostics"
if (diag>=1) print
processors,checkpoint,title1,title2,title3,title4,initialDis,timestep,scaling,temp >>
"diagnostics"
if (diag>=1) print
"classical,numimag,highlevel,boxon,boxsize,DRP,maxAtomMove,cannonball" >>
"diagnostics"
```

```
if (diag>=1) print
classical,numimag,highlevel,boxon,boxsize,DRP,maxAtomMove,cannonball >>
"diagnostics"

# put geometries into array, also figure out number of atoms
# note that this picks out the last geometry in a file, assuming
# that if there is an optimization followed by a freq, nothing else follows
# kludgy - repeats last line twice - must be a better way
do {
  getline < "tempstangeos"
  if (oldline==$0) $0=""
  oldline=$0
  atom = $1
  if (atom>numAtoms) numAtoms=atom
  atNum[atom]=$2
  geoArr[atom,1]=$4; geoArr[atom,2]=$5; geoArr[atom,3]=$6
  geoArrOrig[atom,1]=$4; geoArrOrig[atom,2]=$5; geoArrOrig[atom,3]=$6
  velArr[atom,1]=0; velArr[atom,2]=0; velArr[atom,3]=0
  }
while (length($0) > 0)

#output the number of atoms, used in many routines
print numAtoms

# put in atomic symbols and atomic weights - assigns a default mass but then reads it
from tempmasses when possible
for (i=1;i<=numAtoms;i++) {
  getline < "tempmasses"
  if (atNum[i]==1) {atSym[i]="H";atWeight[i]=1.00783}
  if (atNum[i]==2) {atSym[i]="He";atWeight[i]=4.0026}
  if (atNum[i]==3) {atSym[i]="Li";atWeight[i]=6.941}
  if (atNum[i]==4) {atSym[i]="Be";atWeight[i]=9.012}
  if (atNum[i]==5) {atSym[i]="B";atWeight[i]=10.811}
  if (atNum[i]==6) {atSym[i]="C";atWeight[i]=12.}
  if (atNum[i]==7) {atSym[i]="N";atWeight[i]=14.007}
  if (atNum[i]==8) {atSym[i]="O";atWeight[i]=15.9994}
  if (atNum[i]==9) {atSym[i]="F";atWeight[i]=18.9984}
  if (atNum[i]==10) {atSym[i]="Ne";atWeight[i]=20.1797}
  if (atNum[i]==11) {atSym[i]="Na";atWeight[i]=22.989}
  if (atNum[i]==12) {atSym[i]="Mg";atWeight[i]=24.305}
  if (atNum[i]==13) {atSym[i]="Al";atWeight[i]=26.98154}
  if (atNum[i]==14) {atSym[i]="Si";atWeight[i]=28.0855}
  if (atNum[i]==15) {atSym[i]="P";atWeight[i]=30.9738}
  if (atNum[i]==16) {atSym[i]="S";atWeight[i]=32.066}
```

```
  if (atNum[i]==17) {atSym[i]="Cl";atWeight[i]=35.4527}
  if (atNum[i]==18) {atSym[i]="Ar";atWeight[i]=39.948}
  if (atNum[i]==19) {atSym[i]="K";atWeight[i]=39.0983}
  if (atNum[i]==20) {atSym[i]="Ca";atWeight[i]=40.078}
  if (atNum[i]==21) {atSym[i]="Sc";atWeight[i]=44.96}
  if (atNum[i]==22) {atSym[i]="Ti";atWeight[i]=47.867}
  if (atNum[i]==23) {atSym[i]="V";atWeight[i]=50.94}
  if (atNum[i]==24) {atSym[i]="Cr";atWeight[i]=51.9961}
  if (atNum[i]==25) {atSym[i]="Mn";atWeight[i]=54.938}
  if (atNum[i]==26) {atSym[i]="Fe";atWeight[i]=55.845}
  if (atNum[i]==27) {atSym[i]="Co";atWeight[i]=58.933}
  if (atNum[i]==28) {atSym[i]="Ni";atWeight[i]=58.693}
  if (atNum[i]==29) {atSym[i]="Cu";atWeight[i]=63.546}
  if (atNum[i]==30) {atSym[i]="Zn";atWeight[i]=65.38}
  if (atNum[i]==31) {atSym[i]="Ga";atWeight[i]=69.723}
  if (atNum[i]==32) {atSym[i]="Ge";atWeight[i]=72.64}
  if (atNum[i]==33) {atSym[i]="As";atWeight[i]=74.9216}
  if (atNum[i]==34) {atSym[i]="Se";atWeight[i]=78.96}
  if (atNum[i]==35) {atSym[i]="Br";atWeight[i]=79.904}
  if (atNum[i]==46) {atSym[i]="Pd";atWeight[i]=106.42}
  if (atNum[i]==53) {atSym[i]="I";atWeight[i]=126.90447}
# gets actual weight from freqinHP when possible so a prior calc with readisotopes gets
you isotopic substitution
  if ((i<100) && ($9>0)) atWeight[i]=$9
#  if ((i>99) && ($8>0)) atWeight[i]=$8

  if ((diag>1) && (i==1)) print
"atNum[i],atSym[i],atWeight[i],geoArr[i,1],geoArr[i,2],geoArr[i,3]" >> "diagnostics"
  if (diag>1) print atNum[i],atSym[i],atWeight[i],geoArr[i,1],geoArr[i,2],geoArr[i,3] >>
"diagnostics"
  }

# read in frequencies, scale them, read in Reduced masses, read in force
#constants, replace negative frequencies by 2 wavenumbers
numFreq=3*numAtoms-6
if (geometry=="linear") numFreq=3*numAtoms-5
for (i=1;i<=numFreq;i++) {
  $0=""
  getline < "tempfreqs"
  freq[i]=$0*scaling
  if (freq[i]<0) freq[i]=2
  }
for (i=1;i<=numFreq;i++) {
  $0=""
```

```
  getline < "tempredmass"
  redMass[i]=$0
  if (redMass[i]=="") redMass[i]=1.
  }
for (i=1;i<=numFreq;i++) {
  $0=""
  getline < "tempfrc"
  frc[i]=$0
  if (frc[i]=="") frc[i]=0.0001
  if (frc[i]==0) frc[i]=0.0001
  if ((diag>1) && (i==1)) print "freq[i],redMass[i],frc[i]" >> "diagnostics"
  if (diag>1) print freq[i],redMass[i],frc[i] >> "diagnostics"
  }

# read in the modes - note that trajectories always need a freq calc with freq=hpmodes
unless classical=2
if (classical!=2) {
  for (i=1;i<=numFreq;i+=5) {
    for (j=1;j<=(3*numAtoms);j++) {
      getline < "tempmodes"
      mode[i,$2,$1]=$4; mode[i+1,$2,$1]=$5; mode[i+2,$2,$1]=$6;
mode[i+3,$2,$1]=$7; mode[i+4,$2,$1]=$8
      }
    }
  }
if (diag>2) {for (i=1;i<=numFreq;i++) {print mode[i,1,1],mode[i,1,2],mode[i,1,3] >>
"modesread"}}

# if doing a cannonball trajectory, read in the vector
if (cannonball>0) {
  for (i=1;i<=numAtoms;i++) {
    getline < "cannontraj"
    cannonArr[i,1]=$1; cannonArr[i,2]=$2; cannonArr[i,3]=$3
    }
  }

# collect a series of random numbers from file temp811, generated from an outside
random number generator called by prodynstarterHP
# read from temp811, starting at a random place
srand(PROCINFO["pid"]); tester=rand()*1000
for (i=1;i<=tester;i++) getline < "temp811"
for (i=1;i<=numFreq;i++) {
  getline < "temp811"; randArr[i]=$1
  getline < "temp811"; randArrB[i]=$1
```

```
  getline < "temp811"; randArrC[i]=$1
}
if (rotationmode>0) {
  for (i=1;i<=6;i++) {
    getline < "temp811"; randArrR[i]=$1
  }
}

# for a QM distribution for a harmonic oscillator in its ground state, we want to generate
a set of random numbers
#between -1 and 1 weighted such that numbers toward the center are properly more
common
i=1
while (i<=numFreq) {
  if ((initialDis==2) || (disMode[i]==2)) {
    getline < "temp811"
    tempNum=2*($1-.5)
    prob=exp(-(tempNum^2))
    getline < "temp811"
    if ($1<prob) {
      randArrD[i]=tempNum
      i++
      }
    }
  if ((initialDis!=2) && (disMode[i]!=2)) i++
  }

# to start without normal modes or frequencies we need to just pick a random direction
for the motion of each atom, requiring 3N random numbers
for (i=1;i<=numAtoms;i++) {
  for (j=1;j<=3;j++) {
  getline < "temp811"
  if ($1>0.5) randArrE[i,j]=1
  if ($1<.5) randArrE[i,j]=-1
    }
  }

# determine energy in each normal mode
for (i=1;i<=numFreq;i++) {
  zpeJ[i]=0.5*h*c*freq[i]      #units J per molecule
#if classical, treat as modes spaced by classicalSpacing wavenumbers
  if (classical==1) zpeJ[i]=0.5*h*c*classicalSpacing  # the zpe is not used when
classical but the spacing is used to calculate the E in mode
  zpeK[i]=zpeJ[i]*avNum/4184    #units kcal/mol
```

```
  if (temp<10) vibN[i]=0       # avoids working with very small temperatures - if the
temp is too low, it just acts like 0 K
  if (temp>=10) {
    zpeRat[i]=exp((-2*zpeK[i])/(RgasK*temp))
    if (zpeRat[i]==1) zpeRat[i]=.99999999999
    Q[i]=1/(1-zpeRat[i])
    newRand=randArr[i]
    vibN[i]=0
    tester=1/Q[i]
#    get up to 4000 excitations of low modes
    for (j=1;j<=(4000*zpeRat[i]+2);j++) {
      if (newRand>tester) vibN[i]++
      tester=tester+((zpeRat[i]^j)/Q[i])
      }
    }
  }

# figure out mode energies and maximum classical shift and then actual shift
# also calculated total energy desired for molecule
desiredModeEnK=0
for (i=1;i<=numFreq;i++) {
  modeEn[i]=(zpeJ[i]*1E18)*(2*vibN[i]+1) # units here are mDyne Angstroms for
compatibility with Gaussian force constants
  if (classical==1) modeEn[i]=(zpeJ[i]*1E18)*2*vibN[i]   #no zpe when classical
  modeEnK[i]=zpeK[i]*(2*vibN[i]+1)
  if (classical==1) modeEnK[i]=zpeK[i]*2*vibN[i]         #no zpe when classical
  if ((classical==4) && (i>1)) {
    modeEnK[i]=0                        #this lets you turn off the energy in modes outside of
1 for single-trajectory study
    modeEn[i]=0
    }
  desiredModeEnK=desiredModeEnK + modeEnK[i]
# no 1/2 hv for imaginary frequencies
# treating modes with frequencies <10 as translations, ignoring their zero point energies
  if (freq[i]<8) modeEn[i]=(zpeJ[i]*1E18)*(2*vibN[i])
  maxShift[i]=(2*modeEn[i]/frc[i])^0.5
# new 2012 initialDis 3 means random phase of normal mode
  if (initialDis==3) shift[i]=maxShift[i]*sin(randArrC[i]*3.141592*2)
  if (initialDis==2) shift[i]=maxShift[i]*randArrD[i]
  if (initialDis==1) shift[i]=maxShift[i]*(2*(randArrC[i]-0.5))
  if (initialDis==0) shift[i]=0
# lines below allow for setting of displacement mode for individual modes
# It used to be necessary to use disMode 10 to turn off displacements for a mode, but
hopefully that bug is killed and you can use disMode 0
```

```
  if (disMode[i]==3) shift[i]=maxShift[i]*sin(randArrC[i]*3.141592*2)
  if (disMode[i]==2) shift[i]=maxShift[i]*randArrD[i]
  if (disMode[i]==1) shift[i]=maxShift[i]*(2*(randArrC[i]-0.5))
  if (disMode[i]==10) shift[i]=0 #kept for backward compatibility
  if (disMode[i]==0) shift[i]=0
# no displacements along imaginary frequencies and very low ones - it is better to treat
these
# as translations - employing a shift can give you initial weird geometries
  if (freq[i]<10) shift[i]=0
  if (numimag==1) shift[1]=0
  if (numimag==2) shift[2]=0
  }
for (i=1;i<=numFreq;i++) {
  if ((diag>1) && (i==1)) print
"zpeJ[i],zpeK[i],zpeRat[i],Q[i],vibN[i],modeEn[i],maxShift[i],shift[i]" >> "diagnostics"
  if (diag>1) print zpeJ[i],zpeK[i],zpeRat[i],Q[i],vibN[i],modeEn[i],maxShift[i],shift[i]
>> "diagnostics"
  }

# multiply each of the modes by its shift and add them up
# Do not do this if classical=2
if (classical!=2) {
  for (i=1;i<=numFreq;i++) {
    for (j=1;j<=numAtoms;j++) {
      for (k=1;k<=3;k++) {
        shiftMode[i,j,k]=mode[i,j,k]*shift[i]
        geoArr[j,k]=geoArr[j,k]+shiftMode[i,j,k]
        }
      }
    }
  }

#now start toward velocities
for (i=1;i<=numFreq;i++) {
  kinEn[i]=100000*(modeEn[i]-0.5*frc[i]*shift[i]^2)  # the 100000 converts to g
angstrom^2 s^2
  vel[i]=(2*kinEn[i]/(redMass[i]/avNum))^0.5       # in angstrom / s
#use searchdir in progdyn.conf to control the direction for trajectories started from a
saddle point
  if (numimag>1) numimag=1  #only the first freq can be sent in the searchdir direction,
the rest go in a random direction
  if (i>numimag) {
    if (randArrB[i]<0.5) vel[i]=-vel[i]
    }
```

```
  if (i==numimag) {
    if (searchdir=="negative") vel[i]=-vel[i]
    }
  if ((diag>1) && (i==1)) print "vel[i]" >> "diagnostics"
  if (diag>1) print vel[i] >> "diagnostics"
  }

# if controlphase is being used, set the velocity on particular modes as positive or
negative as requested
for (i=1;i<=numFreq;i++) {
  if ((controlPhase[i]=="positive") && (vel[i]<0)) vel[i]=-vel[i]
  if ((controlPhase[i]=="negative") && (vel[i]>0)) vel[i]=-vel[i]
  }

# multiply each of the modes by its velocity and add them up
# Do not do this if classical=2
if (classical!=2) {
  for (i=1;i<=numFreq;i++) {
    for (j=1;j<=numAtoms;j++) {
      for (k=1;k<=3;k++) {
        velMode[i,j,k]=mode[i,j,k]*vel[i]*timestep
        velArr[j,k]=velArr[j,k]+velMode[i,j,k]
        }
      }
    }
  }

# to start without normal modes or frequencies we figure out the energy per atom based
on 1/2RT in degree of freedom
if (classical==2) {
# to avoid a bug with a box on, starts without modes should use the input geometry, not
the standard
  do {
    getline < "tempinputgeos"
    if (oldline==$0) $0=""
    oldline=$0
    atom = $1
    geoArr[atom,1]=$4; geoArr[atom,2]=$5; geoArr[atom,3]=$6
    geoArrOrig[atom,1]=$4; geoArrOrig[atom,2]=$5; geoArrOrig[atom,3]=$6
    }
  while (length($0) > 0)
  degFreedomEnK=temp*RgasK
  degFreedomEnJ=degFreedomEnK/(avNum/4184)
  cartEn=degFreedomEnJ*1E18
```

```
  kinEnCart=100000*cartEn
#print degFreedomEnK, degFreedomEnJ, cartEn, kinEnCart
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
      velArr[i,j]=randArrE[i,j]*timestep*(2*kinEnCart/(atWeight[i]/avNum))^0.5
      if (DRP==1) velArr[i,j]=0
      }
    }
  }

# calculate the KE in the modes at this point
KEinitmodes=0
for (j=1;j<=numAtoms;j++) {
  KEinitmodes=KEinitmodes + 0.5*atWeight[j]*(velArr[j,1]^2 + velArr[j,2]^2 +
velArr[j,3]^2)/((timestep^2)*conver1)
  }

# add molecular rotation if requested
if (rotationmode>0) {
#establish three rotation vectors
  for (j=1;j<=numAtoms;j++) {
    rotateX[j,1]=0
    rotateX[j,2]=-geoArrOrig[j,3]
    rotateX[j,3]=geoArrOrig[j,2]
    rotateY[j,1]=-geoArrOrig[j,3]
    rotateY[j,2]=0
    rotateY[j,3]=geoArrOrig[j,1]
    rotateZ[j,1]=-geoArrOrig[j,2]
    rotateZ[j,2]=geoArrOrig[j,1]
    rotateZ[j,3]=0
    }
#figure out how much energy is in the raw vectors
  eRotX=0;eRotY=0;eRotZ=0
  for (j=1;j<=numAtoms;j++) {
    for (k=1;k<=3;k++) {
      eRotX=eRotX + 0.5*atWeight[j]*(rotateX[j,k]^2)/((timestep^2)*conver1)
      eRotY=eRotY + 0.5*atWeight[j]*(rotateY[j,k]^2)/((timestep^2)*conver1)
      eRotZ=eRotZ + 0.5*atWeight[j]*(rotateZ[j,k]^2)/((timestep^2)*conver1)
      }
    }
#  print "rotation energies if raw vector used",eRotX,eRotY,eRotZ
#now decide how much energy we want in each rotation
  keRx=-0.5*0.001987*temp*log(1-randArrR[1])
  keRy=-0.5*0.001987*temp*log(1-randArrR[2])
```

```
  keRz=-0.5*0.001987*temp*log(1-randArrR[3])
  if (eRotX<1) keRx=0;if (eRotY<1) keRy=0;if (eRotZ<1) keRz=0
  rotEdesired=keRx+keRy+keRz
  signX=1;signY=1;signZ=1
  if (randArrR[4]<.5) signX=-1
  if (randArrR[5]<.5) signY=-1
  if (randArrR[6]<.5) signZ=-1

#  print "desired energies",keRx,keRy,keRz,"and random
numbers",randArrR[1],randArrR[2],randArrR[3]
#protect against zero rotations
  if (eRotX<1) eRotX=1;if (eRotY<1) eRotY=1;if (eRotZ<1) eRotZ=1
#now scale the rotational vectors
  scaleX=(keRx/eRotX)^.5
  scaleY=(keRy/eRotY)^.5
  scaleZ=(keRz/eRotZ)^.5
#  print "scaling factors" scaleX,scaleY,scaleZ
  for (j=1;j<=numAtoms;j++) {
    for (k=1;k<=3;k++) {
      rotateX[j,k]=rotateX[j,k]*scaleX*signX
      rotateY[j,k]=rotateY[j,k]*scaleY*signY
      rotateZ[j,k]=rotateZ[j,k]*scaleZ*signZ
      }
    }
  for (j=1;j<=numAtoms;j++) {
#    print rotateX[j,1],"   ",rotateX[j,2],"   ",rotateX[j,3]
    }
#  print ""
  for (j=1;j<=numAtoms;j++) {
#    print rotateY[j,1],"   ",rotateY[j,2],"   ",rotateY[j,3]
    }
#  print ""
  for (j=1;j<=numAtoms;j++) {
#    print rotateZ[j,1],"   ",rotateZ[j,2],"   ",rotateZ[j,3]
    }
# now add the rotational vectors  to velArr
  for (j=1;j<=numAtoms;j++) {
    for (k=1;k<=3;k++) {
      velArr[j,k]=velArr[j,k]+rotateX[j,k]+rotateY[j,k]+rotateZ[j,k]
      }
    }
  }

# if doing a cannonball, adjust multiplier until extra energy is correct
```

```
if (cannonball>0) {
  multiplier=1; tester=0; tolerance=.1
  while (tester==0) {
    KEinittotal=0
    for (j=1;j<=numAtoms;j++) {
      cannonvelArr[j,1]=velArr[j,1]+multiplier*cannonArr[j,1];
cannonvelArr[j,2]=velArr[j,2]+multiplier*cannonArr[j,2];
cannonvelArr[j,3]=velArr[j,3]+multiplier*cannonArr[j,3]
      KEinittotal=KEinittotal + 0.5*atWeight[j]*(cannonvelArr[j,1]^2 +
cannonvelArr[j,2]^2 + cannonvelArr[j,3]^2)/((timestep^2)*conver1)
      }
    if (KEinittotal>(KEinitmodes+cannonball+tolerance))
multiplier=multiplier*0.98901364
    if (KEinittotal<(KEinitmodes+cannonball-tolerance)) multiplier=multiplier*1.01
    if ((KEinittotal<(KEinitmodes+cannonball+tolerance)) &&
(KEinittotal>(KEinitmodes+cannonball-tolerance))) tester=1
    }
  for (j=1;j<=numAtoms;j++) {
    velArr[j,1]=velArr[j,1]+multiplier*cannonArr[j,1];
velArr[j,2]=velArr[j,2]+multiplier*cannonArr[j,2];
velArr[j,3]=velArr[j,3]+multiplier*cannonArr[j,3]
    }
  }

#output the new geometry.
# ****** this section changed for special experiment for cyclopentadiene.  do not use
this for other cases
# atWeight[4]=140.0001
# ****** line below added for special experiment switching mass from 12 to 140,
keeping momenta the same
#velArr[4,1]=velArr[4,1]/11.66667; velArr[4,2]=velArr[4,2]/11.66667;
velArr[4,3]=velArr[4,3]/11.66667
for (j=1;j<=numAtoms;j++) {
  printf("%2s % .7f % .7f % .7f %9.5f
\n",atSym[j],geoArr[j,1],geoArr[j,2],geoArr[j,3],atWeight[j])
  }

#output the velocities and calculate the total kinetic energy overall
KEinittotal=0
for (j=1;j<=numAtoms;j++) {
  KEinittotal=KEinittotal + 0.5*atWeight[j]*(velArr[j,1]^2 + velArr[j,2]^2 +
velArr[j,3]^2)/((timestep^2)*conver1)
  printf("% .8f % .8f % .8f \n",velArr[j,1],velArr[j,2],velArr[j,3])
  }
```

```
#anything else I add to the file will not affect the trajectories but will keep a record and
be good for analysis
if (classical!=2) {
  for (i=1;i<=numFreq;i++) {
    if (initialDis==0) printf("%.6f   % .6f    %4i    % 1.4e       % .6f %1i\n", randArr[i],
randArrB[i], vibN[i], vel[i], shift[i], disMode[i])
    if (initialDis==1) printf("%.6f   % .6f    %4i    % 1.4e       % .6f %1i\n", randArr[i],
randArrC[i], vibN[i], vel[i], shift[i], disMode[i])
    if (initialDis==2) printf("%.6f   % .6f    %4i    % 1.4e       % .6f %1i\n", randArr[i],
randArrD[i], vibN[i], vel[i], shift[i], disMode[i])
    if (initialDis==3) printf("%.6f   % .6f    %4i    % 1.4e       % .6f %1i % .6f\n",
randArr[i], randArrC[i], vibN[i], vel[i], shift[i], disMode[i],
sin(randArrC[i]*3.141592*2))
    }
  }
print "temp ",temp
print "initialDis",initialDis
print "classical",classical
print "timestep",timestep
print "numimag",numimag
OFMT = "%.3f"
print "Total mode energy desired=",desiredModeEnK
print "KE initial from modes=",KEinitmodes,"   KE initial total=",KEinittotal,"
Rotational Energy desired=",rotEdesired
if (cannonball>0) print "cannonball",cannonball,"  cannon Energy=",KEinittotal-
KEinitmodes
if (boxon>0) print "boxsize",boxsize
if (DRP>0) print "DRP",DRP,"   maxAtomMove",maxAtomMove
if (DRP>0) print maxAtomMove > "maxMove"
}  # End of BEGIN

/Zero-point correction/ {zpeGauss=$3}
/zero-point Energies/ {zpePlusE=$7}
END {
zpeGaussK=zpeGauss*627.509
potentialE=zpePlusE - zpeGauss
OFMT = "%.6f"
print "Gaussian zpe=",zpeGauss,"or",zpeGaussK,"kcal/mol  E + zpe=",zpePlusE,"
potential E=",potentialE
print "" #will use blank line to mark end of geoPlusVel file
}
```

prog1stpoint

```
BEGIN {
# Nov 2016 organized by functions
# 2014 added ONIOMcharge, more reliable convergence commands
# 2013 added multiple NMR calculations, molecular rotations
# 2012 added NMR calculations
# 2011 added linkatoms in ONIOM
# aug 2010 changed so that it is more careful in reading in from geoPlusVel
#     removed some default parameters that should always be defined
# Jan 2009 - a number of little changes to improve reporting, precision, etc
# aug 2008 added to atom list so handles H to Cl without change needed
# version Feb 2008 incorporates methodfile, boxon and boxsize, though this point
unaffected by box
# version Jan 2008 - allows for ONIOM jobs, fixed atoms
# version Sept 2005 - incorporates meth3, meth4, meth5, meth6, but not yet rotation
# this program creates the first input file for g09
# the title should be changed as appropriate
# the isomer number comes from a file isomernumber

initializeparameters()
initializeconstants()
readprogdynconf()

getline < "isomernumber"
isomernum = $1
getline < "runpointnumber"
runpointnum = $1

if (diag>=1) diagnosticsA()
readgeoPlusVel() #this is different from prog2ndpoint and progdynb because we are just
getting the geometry, no velocities or old geos

writecomfile()
}

END {
}

################################################## FUNCTIONS
#########################################
function Distance(Atom1,Atom2) {
  return sqrt((oldarr[Atom1,1]-oldarr[Atom2,1])^2+(oldarr[Atom1,2]-
oldarr[Atom2,2])^2+(oldarr[Atom1,3]-oldarr[Atom2,3])^2)
  }
```

```
# default parameters, including quassiclassical, no displacements, transition state, not a DRP
# do not change these - rather, change progdyn.conf to set the parameters
function initializeparameters() {
  initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
  classical=0; numimag=1; DRP=0; cannonball=0
  memory=20000000
  diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
  boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
  title3="a"; title4="progdyn.conf"; processors=1; highlevel=99999; linkatoms=0
  damping=1;nonstandard=0;geometry="nonlinear";nonstandard=0
  nmrtype=0;nmrevery=9999999;nmrcc=0;nmrrand=0;nmrdo=0
  thermostat=0;thermostatemult=1.00
  oniomcharge=0; oniommult=0
  applyforce=0; applyforceB=0; applyforceC=0; zeroatomon=0
  sphereon=0; spheresize=999; sphereforceK=0.01
  empiricaldispersion=0; radiusmultiplier=1.25
  }

function initializeconstants() {
  srand(PROCINFO["pid"])
  i=1;j=1;k=1
  c=29979245800; h=6.626075E-34; avNum=6.0221415E23
  RgasK=0.00198588; RgasJ=8.31447; pi=3.14159265359
  numAtoms=0; atomnumber=0
  conver1=4.184E26 #dividing by this converts amu angs^2 /s^2 to kcal/mol
  OFS="   "
  }

# read progdyn.conf for configuration info
function readprogdynconf() {
  blankLineTester=10
  while (blankLineTester>1) {
    getline < "progdyn.conf"
    if ($1=="method") method=$2
    if ($1=="method2") meth2=$2
    if ($1=="charge") charge=$2
    if ($1=="multiplicity") multiplicity=$2
    if ($1=="oniomchargemult") {
      oniomcharge=$2
      oniommult=$3
      }
    if ($1=="memory") memory=$2
    if ($1=="processors") processors=$2
```

```
if ($1=="checkpoint") checkpoint=$2
if ($1=="timestep") timestep=$2
if ($1=="diagnostics") diag=$2
if ($1=="temperature") temp=$2
if ($1=="thermostat") thermostat=$2
if ($1=="thermostatmult") thermostatmult=$2
if (thermostatmult>1) thermostatmult=1/thermostatmult
if ($1=="method3") meth3=$2
if ($1=="method4") meth4=$2
if ($1=="method5") meth5=$2
if ($1=="method6") meth6=$2
if ($1=="method7") meth7=$2
if ($1=="highlevel") highlevel=$2
if ($1=="linkatoms") linkatoms=$2
if ($1=="fixedatom1") fixedatom1=$2
if ($1=="fixedatom2") fixedatom2=$2
if ($1=="fixedatom3") fixedatom3=$2
if ($1=="fixedatom4") fixedatom4=$2
if ($1=="boxon") boxon=$2
if ($1=="boxsize") boxsize=$2
if ($1=="sphereon") sphereon=$2
if ($1=="spheresize") spheresize=$2
if ($1=="sphereforce") sphereforceK=$2
if ($1=="DRP") DRP=$2
if ($1=="maxAtomMove") maxAtomMove=$2
if ($1=="methodfile") methodfilelines=$2
if ($1=="killcheck") killcheck=$2
if ($1=="empiricaldispersion") empiricaldispersion=$2
if ($1=="radiusmultiplier") radiusmultiplier=$2
if ($1=="damping") damping=$2
if ($1=="NMRmethod") nmrmethod=$2
if ($1=="NMRmethod2") nmrmethod2=$2
if ($1=="NMRmethod3") nmrmethod3=$2
if ($1=="NMRtype") nmrtype=$2
if ($1=="NMRevery") nmrevery=$2
if ($1=="NMRrand") nmrrand=$2
if ($1=="loadlimit") loadlimit=$2
if ($1=="NMRcc") nmrcc=$2
if ($1=="nonstandard") nonstandard=$2
if ($1=="applyforce") {
  applyforce=$2; apforce=$3; apforceX0=$4; apforce2=$5; apforce3=$6
  }
if ($1=="applyforceB") {
  applyforceB=$2; apforceB=$3; apforceX0B=$4; apforce2B=$5; apforce3B=$6
```

```
      }
    if ($1=="applyforceC") {
      applyforceC=$2; apforceC=$3; apforceX0C=$4; apforce2C=$5; apforce3C=$6
      }
    if ($1=="afatoms") {
      for (i=1;i<8;i++) {
        if ($(i+1)>0) afatom[i]=$(i+1)
        }
      }
    if ($1=="afatomsB") {
      for (i=1;i<8;i++) {
        if ($(i+1)>0) afatomB[i]=$(i+1)
        }
      }
    if ($1=="afatomsC") {
      for (i=1;i<8;i++) {
        if ($(i+1)>0) afatomC[i]=$(i+1)
        }
      }
    if ($1=="applyforceplane") {
      applyforceplane=$2; apforceplane=$3; apforceplaneX0=$4
      }
    if ($1=="afplaneatoms") {
      for (i=1;i<8;i++) {
        if ($(i+1)>0) afplaneatoms[i]=$(i+1)
        }
      }
    if ($1=="zeroatom") {
      zeroatomon=1
      zeroatom=$2
      }
    if ($1=="title") {
      title1=$2
      title2=$3
      title3=$4
      title4=$5
      }
    blankLineTester=length($0)
    }
  }

function diagnosticsA() {
  print "**************** starting progdynb ****************" >> "diagnostics"
  print "method,charge,multiplicity,memory" >> "diagnostics"
```

```
  print method,charge,multiplicity,memory >> "diagnostics"
  print "processors,checkpoint,title" >> "diagnostics"
  print processors,checkpoint,title1,title2,title3,title4 >> "diagnostics"
  }

function readgeoPlusVel() {
#this is different from prog2ndpoint and progdynb because we are just getting the
geometry, no velocities or old geos
#read in number of atoms, geometry, masses from geoPlusVel
  getline < "geoPlusVel"
  numAtoms=$1
# geometry
  for (i=1;i<=numAtoms;i++) {
    getline < "geoPlusVel"
    weight[i]=$5
    atSym[i]=$1
    for (j=1;j<=3;j++) {
      geoArr[i,j]=$(1+j)
      }
    }
  blankLineTester=10
  while (blankLineTester>1) {
    getline < "geoPlusVel"
    if ($11=="potential") potentialE=$13
    blankLineTester=length($0)
    }
  }

function writecomfile () {
  print "%nproc=" processors
  print "%mem=" memory
  if (killcheck!=1) print "%chk=" checkpoint
  if (nonstandard==0) {
    print "#p " method " force scf=(xqc,maxconven=155,fulllinear,nosym) "
    if (meth2=="unrestricted") print "guess=mix" #for unrestricted calculations
    if (length(meth3)>2) print meth3
    if (length(meth4)>2) print meth4
    }
  if (nonstandard==1) {
    print "# "
    print "nonstd"
    system("cat nonstandard")
    }
  print ""
```

```
  print  title1,title2,title3,title4
  print "runpoint ",runpointnum
  print "runisomer ",isomernum
  if (DRP==1) {
    print "maxForce and forceMult and
maxAtomMove",maxForce,forceMult,maxAtomMove
    print "maxForce and forceMult and
maxAtomMove",maxForce,forceMult,maxAtomMove >> "movelist"
    }
  print ""
  if (oniommult==0) print charge,multiplicity
  if (oniommult>0) print charge,multiplicity,oniomcharge,oniommult
  for (i=1;i<=numAtoms;i++) {
    printf("%s %.7f %.7f %.7f",atSym[i],geoArr[i,1],geoArr[i,2],geoArr[i,3])
    if ((i>highlevel) && (i<=highlevel+linkatoms)) printf(" %s","M H")
    if (i>(highlevel+linkatoms)) printf(" %s","M")
    print ""
    }
  print ""
  if (length(meth5)>2) print meth5
  if (length(meth6)>2) print meth6
  if (methodfilelines>=1) {
    for (i=1;i<=methodfilelines;i++) {
      getline < "methodfile"
      print $0
      }
    }
  print ""
  if ((nmrtype>0) && ((runpointnum % nmrevery)==0)) {
    print "--link1--"
    print "%nproc=" processors
    print "%mem=" memory
    print "%chk=" checkpoint
    print "# " nmrmethod " nmr=giao geom=check"
    if (nmrmethod==method) print "guess=tcheck"
    if (length(meth7)>2) print meth7
    print ""
    print title1,title2,title3,title4
    print "runpoint ",runpointnum
    print "runisomer ",isomernum
    print ""
    print charge,multiplicity
    }
  print ""
```

```
  if ((nmrtype>1) && ((runpointnum % nmrevery)==0)) {
    print "--link1--"
    print "%nproc=" processors
    print "%mem=" memory
    print "%chk=" checkpoint
    print "# " nmrmethod2 " nmr=giao geom=check"
    if (length(meth7)>2) print meth7
    print ""
    print title1,title2,title3,title4
    print "runpoint ",runpointnum
    print "runisomer ",isomernum
    print ""
    print charge,multiplicity
    }
  print ""
  if ((nmrtype>2) && ((runpointnum % nmrevery)==0)) {
    print "--link1--"
    print "%nproc=" processors
    print "%mem=" memory
    print "%chk=" checkpoint
    print "# " nmrmethod3 " nmr=giao geom=check"
    if (length(meth7)>2) print meth7
    print ""
    print title1,title2,title3,title4
    print "runpoint ",runpointnum
    print "runisomer ",isomernum
    print ""
    print charge,multiplicity
    }
  print ""
  }
```

prog2ndpoint

```
BEGIN {
# Nov 2016 organized into functions
# 2014 added ONIOMcharge, more reliable convergence commands
# aug 2013 includes molecular rotation, ability to do multiple NMR calculations,
ONIOM with link atoms,
#nonstandard routes, checks more kinds of energies at point 2
#Aug 2010 added etolerance to make it controllable from progdyn.conf, made it so that
DRP does not check energy
# aug 2008 added to atom list so handles 1 to 17 without change needed
# version Feb 2008 incorporates methodfile, boxon and boxsize, though this point
unaffected by box
```

```
# version Jan 2008 - allows for ONIOM jobs, fixed atoms
# version Sept 9, 2005 - incorportates meth3, meth4, meth5, meth6, but not yet rotation
# read progdyn.conf for configuration info

initializeparameters()
initializeconstants()
readprogdynconf()

getline < "isomernumber"
isomernum = $1
getline < "runpointnumber"
runpointnum = $1

if (diag>=1) diagnosticsA()

#get forward or reverse from skipstart if it exists
getline < "skipstart"
trajdirection = $1

readgeoPlusVel()
putPoint1Traj()
addVelocities()
} # end of BEGIN

#pull out the potential energy
/SCF Done/ || /EUMP2 =/ || / Energy=/ || /ONIOM:/ {
if (($1=="Energy=") && ($3=="NIter="))  newPotentialE=$2
if ($1=="SCF") newPotentialE=$5  #This was subject to a bug at one time - grep Samae
in old files
if ($2=="extrapolated")  newPotentialE=$5
if ($1=="E2") {
  tempstring=$6
  split(tempstring, arr10, "D")
  newPotentialE=arr10[1]*(10^arr10[2])
  }
newPotEK=(newPotentialE-potentialE)*627.509
newPotentialEK=(newPotentialE-potentialE)*627.509
}

# now we go ahead and collect the forces from the point 1 file
(/      1    / || /      2    / || /      3    / || /      4    / || /      5    / || /      6    / || /      7    / || /
8    / || /      9    / || /     10    / || /     11    / || /     12    / || /     13    / || /     14    / || /
15    / || /     16    / || /     17    / || /     18    / || /     19    / || /     20    / || /     21    / || /
22    / || /     23    / || /     24    / || /     25    / || /     26    / || /     27    / || /     28    / || /
```

```
29    / || /      30    / || /      31    / || /      32    / || /      33    / || /      34    / || /      35    /) &&
length($3) > 9 {
i=$1
for (j=1;j<=3;j++) {
  forceArr[i,j]=$(2+j)    #the raw units of the forces are Hartree/Bohr
  }
if ((diag>1) && (i==1)) print "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]" >>
"diagnostics"
if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >> "diagnostics"
}

END {
if (DRP==0) doEcheck()
addForceEffect()
writecomfile()
writetraj()
}

################################################################ FUNCTIONS
####################################################
function Distance(Atom1,Atom2) {
  return sqrt((oldarr[Atom1,1]-oldarr[Atom2,1])^2+(oldarr[Atom1,2]-
oldarr[Atom2,2])^2+(oldarr[Atom1,3]-oldarr[Atom2,3])^2)
  }

# default parameters, including quassiclassical, no displacements, transition state, not a
DRP
# do not change these - rather, change progdyn.conf to set the parameters
function initializeparameters() {
  initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
  classical=0; numimag=1; DRP=0; cannonball=0
  memory=20000000
  diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
  boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
  title3="a"; title4="progdyn.conf"; processors=1; highlevel=99999; linkatoms=0
  damping=1;nonstandard=0;geometry="nonlinear";nonstandard=0
  nmrtype=0;nmrevery=9999999;nmrcc=0;nmrrand=0;nmrdo=0
  thermostat=0;thermostatemult=1.00
  oniomcharge=0; oniommult=0
  applyforce=0; applyforceB=0; applyforceC=0; zeroatomon=0
  sphereon=0; spheresize=999; sphereforceK=0.01
  empiricaldispersion=0; radiusmultiplier=1.25
  etolerance=1
  }
```

```
function initializeconstants() {
  srand(PROCINFO["pid"])
  i=1;j=1;k=1
  c=29979245800; h=6.626075E-34; avNum=6.0221415E23
  RgasK=0.00198588; RgasJ=8.31447; pi=3.14159265359
  numAtoms=0; atomnumber=0
  conver1=4.184E26 #dividing by this converts amu angs^2 /s^2 to kcal/mol
  OFS="   "
  }

# read progdyn.conf for configuration info
function readprogdynconf() {
  blankLineTester=10
  while (blankLineTester>1) {
    getline < "progdyn.conf"
    if ($1=="method") method=$2
    if ($1=="method2") meth2=$2
    if ($1=="charge") charge=$2
    if ($1=="multiplicity") multiplicity=$2
    if ($1=="oniomchargemult") {
      oniomcharge=$2
      oniommult=$3
      }
    if ($1=="memory") memory=$2
    if ($1=="processors") processors=$2
    if ($1=="checkpoint") checkpoint=$2
    if ($1=="timestep") timestep=$2
    if ($1=="diagnostics") diag=$2
    if ($1=="temperature") temp=$2
    if ($1=="thermostat") thermostat=$2
    if ($1=="thermostatmult") thermostatmult=$2
    if (thermostatmult>1) thermostatmult=1/thermostatmult
    if ($1=="method3") meth3=$2
    if ($1=="method4") meth4=$2
    if ($1=="method5") meth5=$2
    if ($1=="method6") meth6=$2
    if ($1=="method7") meth7=$2
    if ($1=="highlevel") highlevel=$2
    if ($1=="linkatoms") linkatoms=$2
    if ($1=="fixedatom1") fixedatom1=$2
    if ($1=="fixedatom2") fixedatom2=$2
    if ($1=="fixedatom3") fixedatom3=$2
    if ($1=="fixedatom4") fixedatom4=$2
```

```
if ($1=="boxon") boxon=$2
if ($1=="boxsize") boxsize=$2
if ($1=="sphereon") sphereon=$2
if ($1=="spheresize") spheresize=$2
if ($1=="sphereforce") sphereforceK=$2
if ($1=="DRP") DRP=$2
if ($1=="maxAtomMove") maxAtomMove=$2
if ($1=="methodfile") methodfilelines=$2
if ($1=="killcheck") killcheck=$2
if ($1=="etolerance") etolerance=$2
if ($1=="reversetraj") reversetraj=$2
if ($1=="empiricaldispersion") empiricaldispersion=$2
if ($1=="radiusmultiplier") radiusmultiplier=$2
if ($1=="damping") damping=$2
if ($1=="NMRmethod") nmrmethod=$2
if ($1=="NMRmethod2") nmrmethod2=$2
if ($1=="NMRmethod3") nmrmethod3=$2
if ($1=="NMRtype") nmrtype=$2
if ($1=="NMRevery") nmrevery=$2
if ($1=="NMRrand") nmrrand=$2
if ($1=="loadlimit") loadlimit=$2
if ($1=="NMRcc") nmrcc=$2
if ($1=="nonstandard") nonstandard=$2
if ($1=="applyforce") {
  applyforce=$2; apforce=$3; apforceX0=$4; apforce2=$5; apforce3=$6
  }
if ($1=="applyforceB") {
  applyforceB=$2; apforceB=$3; apforceX0B=$4; apforce2B=$5; apforce3B=$6
  }
if ($1=="applyforceC") {
  applyforceC=$2; apforceC=$3; apforceX0C=$4; apforce2C=$5; apforce3C=$6
  }
if ($1=="afatoms") {
  for (i=1;i<8;i++) {
    if ($(i+1)>0) afatom[i]=$(i+1)
    }
  }
if ($1=="afatomsB") {
  for (i=1;i<8;i++) {
    if ($(i+1)>0) afatomB[i]=$(i+1)
    }
  }
if ($1=="afatomsC") {
  for (i=1;i<8;i++) {
```

```
          if ($(i+1)>0) afatomC[i]=$(i+1)
          }
        }
      if ($1=="applyforceplane") {
        applyforceplane=$2; apforceplane=$3; apforceplaneX0=$4
        }
      if ($1=="afplaneatoms") {
        for (i=1;i<8;i++) {
          if ($(i+1)>0) afplaneatoms[i]=$(i+1)
          }
        }
      if ($1=="zeroatom") {
        zeroatomon=1
        zeroatom=$2
        }
      if ($1=="title") {
        title1=$2
        title2=$3
        title3=$4
        title4=$5
        }
      blankLineTester=length($0)
      }
  }

function diagnosticsA() {
  print "***************** starting progdynb *****************" >> "diagnostics"
  print "method,charge,multiplicity,memory" >> "diagnostics"
  print method,charge,multiplicity,memory >> "diagnostics"
  print "processors,checkpoint,title" >> "diagnostics"
  print processors,checkpoint,title1,title2,title3,title4 >> "diagnostics"
  }

function readgeoPlusVel() {
#this is different from prog1stpoint and progdynb because we are just getting velocities
#read in number of atoms, geometry, masses from geoPlusVel
  getline < "geoPlusVel"
  numAtoms=$1
# geometry
  for (i=1;i<=numAtoms;i++) {
    getline < "geoPlusVel"
    weight[i]=$5
    atSym[i]=$1
    for (j=1;j<=3;j++) {
```

```
        geoArr[i,j]=$(1+j)
        }
      }
#velocities
  for (i=1;i<=numAtoms;i++) {
    getline < "geoPlusVel"
    for (j=1;j<=3;j++) {
      velArr[i,j]=$j
      }
    }
#pull out other information useful for testing whether total energy is right or bad
  blankLineTester=10
  while (blankLineTester>1) {
    getline < "geoPlusVel"
    if ($4=="desired=") desiredModeEnK=$5
    if ($4=="modes=") {
      KEinitmodes=$5
      KEinittotal=$9
      }
    if ($11=="potential") potentialE=$13
    blankLineTester=length($0)
    }
  }

function addVelocities() {
# ok, now we have to figure the second point.  this should be
# x(t) = x + v*t + 1/2*F*t^2/m
#now we go ahead and add the velocities
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
      arr[i,j]=velArr[i,j]+geoArr[i,j]
      if (trajdirection=="reverserestart") arr[i,j]=geoArr[i,j]-velArr[i,j]
      }
    if ((diag>1) && (i==1)) print "geometry after adding velocities" >> "diagnostics"
    if (diag>1) print arr[i,1],arr[i,2],arr[i,3] >> "diagnostics"
    }
  }

function putPoint1Traj() {
#get initial geometry into file traj
  print numAtoms >> "traj"
  print potentialE,title1,title2,title3,title4,"runpoint 1 ","runisomer ",isomernum >> "traj"
  for (i=1;i<=numAtoms;i++) {
    print atSym[i],geoArr[i,1],geoArr[i,2],geoArr[i,3] >> "traj"
```

```
    }
  }

function doEcheck() {
  print "trajectory #",isomernum >> "Echeck"
  print "point 1 potential E=",newPotentialEK,"   point 1 kinetic E=",KEinitmodes,"
Total=",newPotentialEK+KEinitmodes >> "Echeck"
  print "desired total energy=", desiredModeEnK >> "Echeck"
  if ((newPotentialEK+KEinitmodes)>(desiredModeEnK+etolerance)) print "XXXX bad
total Energy" >> "Echeck"
  if ((newPotentialEK+KEinitmodes)<(desiredModeEnK-etolerance)) print "XXXX bad
total Energy" >> "Echeck"
  }

function addForceEffect() {
# x(t) = x + v*t + 1/2*F*t^2/m
# turn the forces into motion
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
# conversions here take force to J/angstrom, 1E20 converts to kg angstroms / s^2, then
mult time (s^s) and divide by weight in kg to get angstroms

forceArr[i,j]=0.5*1E20*forceArr[i,j]*627.509*(4184/(0.529177*avNum))*(timestep^2)/
(weight[i]/(avNum*1000))
# for simplicity, DRPs will throw away the forces at the second pont.  This means that if
we are not at a saddlepoint, point 2 = point 1 but this is a minor waste
      if (DRP==1) forceArr[i,j]=0
      arr[i,j]=arr[i,j]+forceArr[i,j]
# if atoms are fixed, replace calcd new position by original position
      if ((i==fixedatom1) || (i==fixedatom2) || (i==fixedatom3) || (i==fixedatom4))
arr[i,j]=geoArr[i,j]
      }
    if ((diag>1) && (i==1)) print "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]"
>> "diagnostics"
    if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >> "diagnostics"
    }
  }

function writecomfile() {
  print "%nproc=" processors
  print "%mem=" memory
  if (killcheck!=1) print "%chk=" checkpoint
  if (nonstandard==0) {
    print "# " method " force scf=(xqc,maxconven=55,fulllinear,nosym) "
```

```
    if (meth2=="unrestricted") print "guess=mix" #for unrestricted calculations
    if (meth2=="read") print "guess=tcheck" #for reading orbitals from check, sometimes faster, sometimes not
    if (length(meth3)>2) print meth3
    if (length(meth4)>2) print meth4
    }
  if (nonstandard==1) {
    print "# "
    print "nonstd"
    system("cat nonstandard")
    }
  print ""
  print title1,title2,title3,title4
  print "runpoint ",runpointnum
  print "runisomer ", isomernum
  print ""
  if (oniommult==0) print charge,multiplicity
  if (oniommult>0) print charge,multiplicity,oniomcharge,oniommult
  for (i=1;i<=numAtoms;i++) {
    printf("%s %.7f %.7f %.7f",atSym[i],arr[i,1],arr[i,2],arr[i,3])
    if ((i>highlevel) && (i<=highlevel+linkatoms)) printf(" %s","M H")
    if (i>(highlevel+linkatoms)) printf(" %s","M")
    print ""
    }
  print ""
  if (length(meth5)>2) print meth5
  if (length(meth6)>2) print meth6
  if (methodfilelines>=1) {
    for (i=1;i<=methodfilelines;i++) {
      getline < "methodfile"
      print $0
      }
    }
  if ((nmrtype>0) && ((runpointnum % nmrevery)==0)) {
    print "--link1--"
    print "%nproc=" processors
    print "%mem=" memory
    print "%chk=" checkpoint
    print "# " nmrmethod " nmr=giao geom=check"
    if (nmrmethod==method) print "guess=tcheck"
    if (length(meth7)>2) print meth7
    print ""
    print title1,title2,title3,title4
    print "runpoint ",runpointnum
```

```
    print "runisomer ",isomernum
    print ""
    print charge,multiplicity
    }
  print ""
  if ((nmrtype>1) && ((runpointnum % nmrevery)==0)) {
    print "--link1--"
    print "%nproc=" processors
    print "%mem=" memory
    print "%chk=" checkpoint
    print "# " nmrmethod2 " nmr=giao geom=check"
    if (length(meth7)>2) print meth7
    print ""
    print title1,title2,title3,title4
    print "runpoint ",runpointnum
    print "runisomer ",isomernum
    print ""
    print charge,multiplicity
    }
  print ""
  if ((nmrtype>2) && ((runpointnum % nmrevery)==0)) {
    print "--link1--"
    print "%nproc=" processors
    print "%mem=" memory
    print "%chk=" checkpoint
    print "# " nmrmethod3 " nmr=giao geom=check"
    if (length(meth7)>2) print meth7
    print ""
    print title1,title2,title3,title4
    print "runpoint ",runpointnum
    print "runisomer ",isomernum
    print ""
    print charge,multiplicity
    }
  print ""
  }

function writetraj() {
#get second geometry into file traj
  print numAtoms >> "traj"
  print newPotentialE,title1,title2,title3,title4,"runpoint ",runpointnum,"runisomer
",isomernum >> "traj"
  for (i=1;i<=numAtoms;i++) {
    print atSym[i],arr[i,1],arr[i,2],arr[i,3] >> "traj"
```

```
    }
  }
```

progdynb

```
BEGIN { #this is the main routine for generating new .com files by the Verlet
algorithym
# Nov 2016 organized into functions, added empirical dispersion
# Oct 2015 added sanity check, eliminated dyn files and keepevery
# May 2015 added ability to force solvent into a sphere
# Feb 2015 added zeroatom ability to make solute centered in solvent
# Jan 2015 added applyforce to apply forces on motion of atoms and allow PMF
calculations
# Dec 2014 added oniom charge specifications
# 2013 added multiple NMR calculations, molecular rotations, thermostat commands
# 2012 added NMR calculations
# 2011 added linkatoms in ONIOM
# Aug 2010 increased elements handled automatically but only up to bromine!
# Jan 2009 - a number of little changes to improve reporting, precision, etc
# Nov 2008 added ability to handle DRPs
# Aug 2008 added long list of atoms to handle 1-17 without change
# May 2008 added option to put out velocities in vellist - make diag=3
# version Feb 2008 incorporates methodfile, boxon and boxsize
# version Jan 2008 incorporates fixed atoms, oniom, and velocity damping
# version August 2007 incorporates keepevery to decrease size of dyn file
# version Sept 11, 2005 - incorportates meth3, meth4, meth5, meth6, but not yet rotation

initializeparameters()
initializeconstants()
readprogdynconf()

getline < "isomernumber"
isomernum = $1
getline < "runpointnumber"
runpointnum = $1

if (diag>=1) diagnosticsA()
readgeoPlusVelAndoldAndolder() #readgeoPlusVelAndoldAndolder sets numAtoms,
weight[i], atSym[i], potentialE, oldarr[at,1to3], olderarr[at,1to3]
        # also sets apparentTemp,  KEold, does sanitycheck
if (DRP==1) readoldAdjForcesAndmaxMove() #for DRPs read in oldForce[at,123] and
maxAtomMove
nmrstuffA() # sets nmrdo to 0 or 1, controls where NMR calcs are done
}
```

```
######################## END OF BEGIN
####################################

#pull out the potential energy
/SCF Done/ || /EUMP2 =/ || / Energy=/ || /ONIOM:/ {
if (($1=="Energy=") && ($3=="NIter="))  newPotentialE=$2
if ($1=="SCF") newPotentialE=$5
if ($2=="extrapolated")  newPotentialE=$5
if ($1=="E2") {
   tempstring=$6
   split(tempstring, arr10, "D")
   newPotentialE=arr10[1]*(10^arr10[2])
   }
newPotEK=(newPotentialE-potentialE)*627.509
}

#must adjust next line for weird atoms
(/      1    / || /      2    / || /      3    / || /      4    / || /      5    / || /      6    / || /      7    / || /
8    / || /      9    / || /     10    / || /     11    / || /     12    / || /     13    / || /     14    / || /
15    / || /     16    / || /     17    / || /     18    / || /     19    / || /     20    / || /     21    / || /
22    / || /     23    / || /     24    / || /     25    / || /     26    / || /     27    / || /     28    / || /
29    / || /     30    / || /     31    / || /     32    / || /     33    / || /     34    / || /     35    /) &&
length($3) > 9 {
i=$1
for (j=1;j<=3;j++) {
   forceArr[i,j]=$(2+j)    #the raw units of the forces are Hartree/Bohr
   }
#if ((diag>1) && (i==1)) print "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]" >>
"diagnostics"
#if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >> "diagnostics"
}

END {
if (sphereon==1) applysphereforce() # apply a force to bring atoms within a sphere.
This also figures out the density at 0.9*spheresize
# routines to apply forces between atoms, used for umbrella sampling
if (applyforceplane>0) doapplyforceplane() #used to apply a force on an atom versus its
distance from a plane
setinterlockingsphereatom() #apply force to one of a series of atoms, whichever is
closest to afatom[1]
if (applyforce>0) doapplyforce()
if (applyforceB>0) doapplyforceB()
if (applyforceC>0) doapplyforceC()
if (empiricaldispersion>0) doempiricaldispersion()
```

```
if (zeroatomon==1) dozeroatom() #routine to slowly move an atom toward the origin
if (thermostat==1) dothermostat()
if (DRP==1) doDRP() #routine for steepest descent path in mass weighted coordinates
if (DRP==0) doVerlet() #normal routine for Verlet
writetraj()
writecomfile()
}

############################################################## FUNCTIONS
##################################################
function Distance(Atom1,Atom2) {
  return sqrt((oldarr[Atom1,1]-oldarr[Atom2,1])^2+(oldarr[Atom1,2]-
oldarr[Atom2,2])^2+(oldarr[Atom1,3]-oldarr[Atom2,3])^2)
  }

# default parameters, including quassiclassical, no displacements, transition state, not a
DRP
# do not change these - rather, change progdyn.conf to set the parameters
function initializeparameters() {
  initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
  classical=0; numimag=1; DRP=0; cannonball=0
  memory=20000000
  diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
  boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
  title3="a"; title4="progdyn.conf"; processors=1; highlevel=99999; linkatoms=0
  damping=1;nonstandard=0;geometry="nonlinear";nonstandard=0
  nmrtype=0;nmrevery=9999999;nmrcc=0;nmrrand=0;nmrdo=0
  thermostat=0;thermostatemult=1.00
  oniomcharge=0; oniommult=0
  applyforce=0; applyforceB=0; applyforceC=0; zeroatomon=0
  sphereon=0; spheresize=999; sphereforceK=0.01
  empiricaldispersion=0; radiusmultiplier=1.25
  }

function initializeconstants() {
  srand(PROCINFO["pid"])
  i=1;j=1;k=1
  c=29979245800; h=6.626075E-34; avNum=6.0221415E23
  RgasK=0.00198588; RgasJ=8.31447; pi=3.14159265359
  numAtoms=0; atomnumber=0
  conver1=4.184E26 #dividing by this converts amu angs^2 /s^2 to kcal/mol
  OFS="   "
  }
```

```
# read progdyn.conf for configuration info
function readprogdynconf() {
  blankLineTester=10
  while (blankLineTester>1) {
    getline < "progdyn.conf"
    if ($1=="method") method=$2
    if ($1=="method2") meth2=$2
    if ($1=="charge") charge=$2
    if ($1=="multiplicity") multiplicity=$2
    if ($1=="oniomchargemult") {
      oniomcharge=$2
      oniommult=$3
      }
    if ($1=="memory") memory=$2
    if ($1=="processors") processors=$2
    if ($1=="checkpoint") checkpoint=$2
    if ($1=="timestep") timestep=$2
    if ($1=="diagnostics") diag=$2
    if ($1=="temperature") temp=$2
    if ($1=="thermostat") thermostat=$2
    if ($1=="thermostatmult") thermostatmult=$2
    if (thermostatmult>1) thermostatmult=1/thermostatmult
    if ($1=="method3") meth3=$2
    if ($1=="method4") meth4=$2
    if ($1=="method5") meth5=$2
    if ($1=="method6") meth6=$2
    if ($1=="method7") meth7=$2
    if ($1=="highlevel") highlevel=$2
    if ($1=="linkatoms") linkatoms=$2
    if ($1=="fixedatom1") fixedatom1=$2
    if ($1=="fixedatom2") fixedatom2=$2
    if ($1=="fixedatom3") fixedatom3=$2
    if ($1=="fixedatom4") fixedatom4=$2
    if ($1=="boxon") boxon=$2
    if ($1=="boxsize") boxsize=$2
    if ($1=="sphereon") sphereon=$2
    if ($1=="spheresize") spheresize=$2
    if ($1=="sphereforce") sphereforceK=$2
    if ($1=="DRP") DRP=$2
    if ($1=="maxAtomMove") maxAtomMove=$2
    if ($1=="methodfile") methodfilelines=$2
    if ($1=="killcheck") killcheck=$2
    if ($1=="empiricaldispersion") empiricaldispersion=$2
    if ($1=="radiusmultiplier") radiusmultiplier=$2
```

```
if ($1=="damping") damping=$2
if ($1=="NMRmethod") nmrmethod=$2
if ($1=="NMRmethod2") nmrmethod2=$2
if ($1=="NMRmethod3") nmrmethod3=$2
if ($1=="NMRtype") nmrtype=$2
if ($1=="NMRevery") nmrevery=$2
if ($1=="NMRrand") nmrrand=$2
if ($1=="loadlimit") loadlimit=$2
if ($1=="NMRcc") nmrcc=$2
if ($1=="nonstandard") nonstandard=$2
if ($1=="applyforce") {
  applyforce=$2; apforce=$3; apforceX0=$4; apforce2=$5; apforce3=$6
  }
if ($1=="applyforceB") {
  applyforceB=$2; apforceB=$3; apforceX0B=$4; apforce2B=$5; apforce3B=$6
  }
if ($1=="applyforceC") {
  applyforceC=$2; apforceC=$3; apforceX0C=$4; apforce2C=$5; apforce3C=$6
  }
if ($1=="afatoms") {
  for (i=1;i<8;i++) {
    if ($(i+1)>0) afatom[i]=$(i+1)
    }
  }
if ($1=="afatomsB") {
  for (i=1;i<8;i++) {
    if ($(i+1)>0) afatomB[i]=$(i+1)
    }
  }
if ($1=="afatomsC") {
  for (i=1;i<8;i++) {
    if ($(i+1)>0) afatomC[i]=$(i+1)
    }
  }
if ($1=="applyforceplane") {
  applyforceplane=$2; apforceplane=$3; apforceplaneX0=$4
  }
if ($1=="afplaneatoms") {
  for (i=1;i<8;i++) {
    if ($(i+1)>0) afplaneatoms[i]=$(i+1)
    }
  }
if ($1=="zeroatom") {
  zeroatomon=1
```

```
      zeroatom=$2
      }
    if ($1=="title") {
      title1=$2
      title2=$3
      title3=$4
      title4=$5
      }
    blankLineTester=length($0)
    }
  }

function diagnosticsA() {
  print "***************** starting progdynb *****************" >> "diagnostics"
  print "method,charge,multiplicity,memory" >> "diagnostics"
  print method,charge,multiplicity,memory >> "diagnostics"
  print "processors,checkpoint,title" >> "diagnostics"
  print processors,checkpoint,title1,title2,title3,title4 >> "diagnostics"
  }

function readgeoPlusVelAndoldAndolder() {
# get number of atoms and weights from geoPlusVel, and previous geometries from old
and older
  getline < "geoPlusVel"
  numAtoms=$1
  for (i=1;i<=numAtoms;i++) {
    getline < "geoPlusVel"
    weight[i]=$5; atSym[i]=$1
    }
  blankLineTester=10
  while (blankLineTester>1) {
    getline < "geoPlusVel"
    if ($11=="potential") potentialE=$13
    blankLineTester=length($0)
    }

  for (at=1;at<=numAtoms;at++) {
    getline < "old"
    oldarr[at,1]=$4; oldarr[at,2]=$5; oldarr[at,3]=$6
    }

  for (at=1;at<=numAtoms;at++) {
    getline < "older"
    olderarr[at,1]=$4; olderarr[at,2]=$5; olderarr[at,3]=$6
```

```
    atomVel=((oldarr[at,1]-olderarr[at,1])^2 + (oldarr[at,2]-olderarr[at,2])^2
+(oldarr[at,3]-olderarr[at,3])^2)^.5
    KEold=KEold+0.5*weight[at]*(atomVel^2)/((timestep^2)*conver1)
# sanity check - avoids trajectory blow up
    if (atomVel>1) exit
    }
  apparentTemp=KEold*2/(3*RgasK*numAtoms) # this is not the temperature at the
previous point but rather 1.5 points back.
# sanity check - avoids trajectory blow up
  for (at=1;at<=numAtoms;at++) {
    if (((oldarr[at,1]-olderarr[at,1])^2)>1) exit
    }
  }

function readoldAdjForcesAndmaxMove() {
#for DRPs read in oldAdjForces and maxAtomMove
  for (at=1;at<=numAtoms;at++) {
    getline < "oldAdjForces"
    oldForce[at,1]=$1; oldForce[at,2]=$2; oldForce[at,3]=$3
    }
  getline < "maxMove"
  if (($1<maxAtomMove) && ($1>0)) maxAtomMove=$1
  if (maxAtomMove<0.000001) maxAtomMove=0.000001
  }

function nmrstuffA() {
# sets nmrdo to 0 or 1, controls where NMR calcs are done
  if ((nmrrand==0) && ((runpointnum % nmrevery)==0)) nmrdo=1
  if ((nmrrand==1) && (rand()<(1/nmrevery))) nmrdo=1
  getline < "uptimelist"
  x=1.0001*substr($10,1,3);if (x<8) x=8
# turn of nmrs if load is too high - this is under control of loadlimit parameter in
progdyn.conf and requires proganal to make uptimelist
  if ((nmrrand==1) && (x>loadlimit)) nmrdo=0
  }

function applysphereforce() {
# apply a force to bring atoms within a sphere.  This also figures out the density at
0.9*spheresize
# We are going through the loop twice, the first time figure outs the total pressure, then
scales the forces to limit the pressure to maxpressure
# the second time actually applies the pressure
  maxpressure=1000 #atmospheres.  Later we may parameterize this.
  sphereforcetotal=0
```

```
  for (i=1;i<=numAtoms;i++) {
    distToOrig=((oldarr[i,1]^2+oldarr[i,2]^2+oldarr[i,3]^2)^.5)
    if (distToOrig>spheresize) {
      sphereforce=sphereforceK*(distToOrig-spheresize)
      if (sphereforce>0.01) sphereforce=0.01 #important limit on force for atoms far
outside of the sphere, not sure if value chosen is best
      sphereforcetotal=sphereforcetotal+sphereforce
      }
    }
  sphereforcetotalNewtons=sphereforcetotal*627.509*4184*1E10/(0.529177*avNum)
  surfaceareaSqMeters=4*pi*spheresize^2/1E20
  pressurePascal=sphereforcetotalNewtons/surfaceareaSqMeters
  pressureAtm=pressurePascal/101325
  if (pressureAtm>maxpressure) sphereforceK=sphereforceK*maxpressure/pressureAtm
# go through the loop again
  sphereforcetotal=0; totalweight=0
  for (i=1;i<=numAtoms;i++) {
    distToOrig=((oldarr[i,1]^2+oldarr[i,2]^2+oldarr[i,3]^2)^.5)
    if (distToOrig>spheresize) {
      sphereforce=sphereforceK*(distToOrig-spheresize)
      if (sphereforce>0.01) sphereforce=0.01 #important limit on force for atoms far
outside of the sphere, not sure if value chosen is best
      sphereforcetotal=sphereforcetotal+sphereforce

unitX=sphereforce*oldarr[i,1]/distToOrig;unitY=sphereforce*oldarr[i,2]/distToOrig;unit
Z=sphereforce*oldarr[i,3]/distToOrig
      forceArr[i,1]=forceArr[i,1]-unitX;forceArr[i,2]=forceArr[i,2]-
unitY;forceArr[i,3]=forceArr[i,3]-unitZ
      }
# calculate the density at 0.9*spheresize
    if (distToOrig<0.9*spheresize) {
      totalweight=totalweight+weight[i]
      }
    }
#recalculate pressure
  sphereforcetotalNewtons=sphereforcetotal*627.509*4184*1E10/(0.529177*avNum)
  surfaceareaSqMeters=4*pi*spheresize^2/1E20
  pressurePascal=sphereforcetotalNewtons/surfaceareaSqMeters
  pressureAtm=pressurePascal/101325
  density=(totalweight/avNum)/((4/3)*pi*(0.9*spheresize*1E-8)^3)
  }

function doapplyforceplane() {
#used to apply a force on an atom versus its distance from a plane
```

```
  if (afplaneatoms[4]<.5) {
    print "you need more atoms to define a plane"
    exit
    }
  for (i=2;i<8;i++) {
    if (afplaneatoms[i]>.5) {
      k=afplaneatoms[i]

A[1,1]=A[1,1]+oldarr[k,1]^2;A[1,2]=A[1,2]+oldarr[k,1]*oldarr[k,2];A[1,3]=A[1,3]+old
arr[k,1]

A[2,1]=A[2,1]+oldarr[k,1]*oldarr[k,2];A[2,2]=A[2,2]+oldarr[k,2]^2;A[2,3]=A[2,3]+old
arr[k,2]
      A[3,1]=A[3,1]+oldarr[k,1];A[3,2]=A[3,2]+oldarr[k,2];A[3,3]++

b[1]=b[1]+oldarr[k,1]*oldarr[k,3];b[2]=b[2]+oldarr[k,2]*oldarr[k,3];b[3]=b[3]+oldarr[k,
3]
# find center of mass assuming all atoms same weight

cmass[1]=cmass[1]+oldarr[k,1];cmass[2]=cmass[2]+oldarr[k,2];cmass[3]=cmass[3]+old
arr[k,3];
      }
    }
  numplaneatoms=A[3,3]
  cmass[1]=cmass[1]/A[3,3];cmass[2]=cmass[2]/A[3,3];cmass[3]=cmass[3]/A[3,3]
#   print "matrix A"
#   for (i=1;i<=3;i++) {
#     print A[i,1],A[i,2],A[i,3]
#     }
#   print "matrix b"
#   print b[1],b[2],b[3]
  Det=A[1,1]*A[2,2]*A[3,3]+A[1,2]*A[2,3]*A[3,1]+A[1,3]*A[2,1]*A[3,2]-
A[1,3]*A[2,2]*A[3,1]-A[1,2]*A[2,1]*A[3,3]-A[1,1]*A[2,3]*A[3,2]
  E=(b[1]*A[2,2]*A[3,3]+A[1,2]*A[2,3]*b[3]+A[1,3]*b[2]*A[3,2]-
A[1,3]*A[2,2]*b[3]-A[1,2]*b[2]*A[3,3]-b[1]*A[2,3]*A[3,2])/Det
  F=(A[1,1]*b[2]*A[3,3]+b[1]*A[2,3]*A[3,1]+A[1,3]*A[2,1]*b[3]-
A[1,3]*b[2]*A[3,1]-b[1]*A[2,1]*A[3,3]-A[1,1]*A[2,3]*b[3])/Det
  G=(A[1,1]*A[2,2]*b[3]+A[1,2]*b[2]*A[3,1]+b[1]*A[2,1]*A[3,2]-
b[1]*A[2,2]*A[3,1]-A[1,2]*A[2,1]*b[3]-A[1,1]*b[2]*A[3,2])/Det
#  E, F, and G are the coefficients in the plane z=Ex+Fy+G"
# make a function that tests the fit
  for (i=2;i<8;i++) {
    if (afplaneatoms[i]>.5) {
      k=afplaneatoms[i]
```

```
      distplane=(-oldarr[k,1]*E-oldarr[k,2]*F+oldarr[k,3]-G)/(E^2+F^2+1)^.5;if
(distplane<0) distplane=-distplane
      aberror=aberror+distplane
      }
    }
# if the fit is bad, as can happen, decrease to 3 atoms in plane, using only the first three
atoms in list after the conatom
  if (aberror>2) {
    print "original aberror",aberror >> "diagnostics"

A[1,1]=0;A[1,2]=0;A[1,3]=0;A[2,1]=0;A[2,2]=0;A[2,3]=0;A[3,1]=0;A[3,2]=0;A[3,3]=0
    for (i=2;i<5;i++) {
      k=afplaneatoms[i]

A[1,1]=A[1,1]+oldarr[k,1]^2;A[1,2]=A[1,2]+oldarr[k,1]*oldarr[k,2];A[1,3]=A[1,3]+old
arr[k,1]

A[2,1]=A[2,1]+oldarr[k,1]*oldarr[k,2];A[2,2]=A[2,2]+oldarr[k,2]^2;A[2,3]=A[2,3]+old
arr[k,2]
      A[3,1]=A[3,1]+oldarr[k,1];A[3,2]=A[3,2]+oldarr[k,2];A[3,3]++

b[1]=b[1]+oldarr[k,1]*oldarr[k,3];b[2]=b[2]+oldarr[k,2]*oldarr[k,3];b[3]=b[3]+oldarr[k,
3]
      }
    Det=A[1,1]*A[2,2]*A[3,3]+A[1,2]*A[2,3]*A[3,1]+A[1,3]*A[2,1]*A[3,2]-
A[1,3]*A[2,2]*A[3,1]-A[1,2]*A[2,1]*A[3,3]-A[1,1]*A[2,3]*A[3,2]
    E=(b[1]*A[2,2]*A[3,3]+A[1,2]*A[2,3]*b[3]+A[1,3]*b[2]*A[3,2]-
A[1,3]*A[2,2]*b[3]-A[1,2]*b[2]*A[3,3]-b[1]*A[2,3]*A[3,2])/Det
    F=(A[1,1]*b[2]*A[3,3]+b[1]*A[2,3]*A[3,1]+A[1,3]*A[2,1]*b[3]-
A[1,3]*b[2]*A[3,1]-b[1]*A[2,1]*A[3,3]-A[1,1]*A[2,3]*b[3])/Det
    G=(A[1,1]*A[2,2]*b[3]+A[1,2]*b[2]*A[3,1]+b[1]*A[2,1]*A[3,2]-
b[1]*A[2,2]*A[3,1]-A[1,2]*A[2,1]*b[3]-A[1,1]*b[2]*A[3,2])/Det
    aberror=0
    for (i=2;i<5;i++) {
      k=afplaneatoms[i]
      distplane=(-oldarr[k,1]*E-oldarr[k,2]*F+oldarr[k,3]-G)/(E^2+F^2+1)^.5;if
(distplane<0) distplane=-distplane
      aberror=aberror+distplane
      }
    }
  conatom=afplaneatoms[1]
  distplane=(-oldarr[conatom,1]*E-oldarr[conatom,2]*F+oldarr[conatom,3]-
G)/(E^2+F^2+1)^.5
  if (distplane<0) distplane=-distplane
```

```
  t=(oldarr[conatom,1]*E+oldarr[conatom,2]*F-oldarr[conatom,3]+G)/(E^2+F^2+1)
  planepoint[1]=oldarr[conatom,1]-t*E;planepoint[2]=oldarr[conatom,2]-t*F;planepoint[3]=oldarr[conatom,3]+t
  distcmass=((planepoint[1]-cmass[1])^2+(planepoint[2]-cmass[2])^2+(planepoint[3]-cmass[3])^2)^.5
  print "distplane",distplane,"t",t,"planepoint",planepoint[1],planepoint[2],planepoint[3],"distcmass",distcmass,"aberror",aberror >> "diagnostics"
  if (distcmass>1.4) {
    vector[1]=planepoint[1]-cmass[1];vector[2]=planepoint[2]-cmass[2];vector[3]=planepoint[3]-cmass[3]
    vector[1]=vector[1]*1.4/distcmass;vector[2]=vector[2]*1.4/distcmass;vector[3]=vector[3]*1.4/distcmass
    planepoint[1]=cmass[1]+vector[1];planepoint[2]=cmass[2]+vector[2];planepoint[3]=cmass[3]+vector[3];
    distcmass=((planepoint[1]-cmass[1])^2+(planepoint[2]-cmass[2])^2+(planepoint[3]-cmass[3])^2)^.5
    distplane=((planepoint[1]-oldarr[conatom,1])^2+(planepoint[2]-oldarr[conatom,2])^2+(planepoint[3]-oldarr[conatom,3])^2)^.5
    print "new distplane",distplane,"newplanepoint",planepoint[1],planepoint[2],planepoint[3],"newdistcmass",distcmass >> "diagnostics"
    }
  delX=oldarr[conatom,1]-planepoint[1];delY=oldarr[conatom,2]-planepoint[2];delZ=oldarr[conatom,3]-planepoint[3]
  if (applyforceplane==2) apforceplane=apforceplane*(distplane-apforceplaneX0)
  unitX=apforceplane*delX/distplane;unitY=apforceplane*delY/distplane;unitZ=apforceplane*delZ/distplane
  forceArr[conatom,1]=forceArr[conatom,1]-unitX;forceArr[conatom,2]=forceArr[conatom,2]-unitY;forceArr[conatom,3]=forceArr[conatom,3]-unitZ
  for (i=2;i<8;i++) {
    if (afplaneatoms[i]>.5) {
      platom=afplaneatoms[i]
      forceArr[platom,1]=forceArr[platom,1]+unitX/numplaneatoms;forceArr[platom,2]=forceArr[platom,2]+unitY/numplaneatoms;forceArr[platom,3]=forceArr[platom,3]+unitZ/numplaneatoms
      }
    }
  }
```

```
function setinterlockingsphereatom() {
#apply force to one of a series of atoms, whichever is closest to afatom[1]
  for (i=3;i<8;i++) {
    if (afatom[i]>0) {
      if(Distance(afatom[1],afatom[i])<Distance(afatom[1],afatom[2]))
afatom[2]=afatom[i]
      }
    if (afatomB[i]>0) {
      if(Distance(afatomB[1],afatomB[i])<Distance(afatomB[1],afatomB[2]))
afatomB[2]=afatomB[i]
      }
    if (afatomC[i]>0) {
      if(Distance(afatomC[1],afatomC[i])<Distance(afatomC[1],afatomC[2]))
afatomC[2]=afatomC[i]
      }
    }
  }

function doapplyforce() {
# applyforce 1 puts a linear constant force.
# applyforce 2 puts on a harmonic restoring force to apforceX0
  delX=oldarr[afatom[1],1]-oldarr[afatom[2],1];delY=oldarr[afatom[1],2]-
oldarr[afatom[2],2];delZ=oldarr[afatom[1],3]-oldarr[afatom[2],3];
  distatoms=(delX^2+delY^2+delZ^2)^.5
  if (applyforce==2) apforce=apforce*(distatoms-apforceX0)
  if (applyforce==3) apforce=apforce*(distatoms-apforceX0) + apforce2*(distatoms-
apforceX0)^2
  if (applyforce==4) apforce=apforce*(distatoms-apforceX0) + apforce2*(distatoms-
apforceX0)^2 + apforce3*(distatoms-apforceX0)^3

unitX=apforce*delX/distatoms;unitY=apforce*delY/distatoms;;unitZ=apforce*delZ/dist
atoms;
  forceArr[afatom[1],1]=forceArr[afatom[1],1]-
unitX;forceArr[afatom[1],2]=forceArr[afatom[1],2]-
unitY;forceArr[afatom[1],3]=forceArr[afatom[1],3]-unitZ

forceArr[afatom[2],1]=forceArr[afatom[2],1]+unitX;forceArr[afatom[2],2]=forceArr[afa
tom[2],2]+unitY;forceArr[afatom[2],3]=forceArr[afatom[2],3]+unitZ
  }

function doapplyforceB() {
  delX=oldarr[afatomB[1],1]-oldarr[afatomB[2],1];delY=oldarr[afatomB[1],2]-
oldarr[afatomB[2],2];delZ=oldarr[afatomB[1],3]-oldarr[afatomB[2],3];
```

```
  distatoms=(delX^2+delY^2+delZ^2)^.5
  if (applyforceB==2) apforceB=apforceB*(distatoms-apforceX0B)
  if (applyforceB==3) apforceB=apforceB*(distatoms-apforceX0B) +
apforce2B*(distatoms-apforceX0B)^2
  if (applyforceB==4) apforceB=apforceB*(distatoms-apforceX0B) +
apforce2B*(distatoms-apforceX0B)^2 + apforce3B*(distatoms-apforceX0B)^3

unitX=apforceB*delX/distatoms;unitY=apforceB*delY/distatoms;;unitZ=apforceB*delZ
/distatoms;
  forceArr[afatomB[1],1]=forceArr[afatomB[1],1]-
unitX;forceArr[afatomB[1],2]=forceArr[afatomB[1],2]-
unitY;forceArr[afatomB[1],3]=forceArr[afatomB[1],3]-unitZ

forceArr[afatomB[2],1]=forceArr[afatomB[2],1]+unitX;forceArr[afatomB[2],2]=forceA
rr[afatomB[2],2]+unitY;forceArr[afatomB[2],3]=forceArr[afatomB[2],3]+unitZ
  }

function doapplyforceC() {
  delX=oldarr[afatomC[1],1]-oldarr[afatomC[2],1];delY=oldarr[afatomC[1],2]-
oldarr[afatomC[2],2];delZ=oldarr[afatomC[1],3]-oldarr[afatomC[2],3];
  distatoms=(delX^2+delY^2+delZ^2)^.5
  if (applyforceC==2) apforceC=apforceC*(distatoms-apforceX0C)
  if (applyforceC==3) apforceC=apforceC*(distatoms-apforceX0C) +
apforce2C*(distatoms-apforceX0C)^2
  if (applyforceC==4) apforceC=apforceC*(distatoms-apforceX0C) +
apforce2C*(distatoms-apforceX0C)^2 + apforce3C*(distatoms-apforceX0C)^3

unitX=apforceC*delX/distatoms;unitY=apforceC*delY/distatoms;;unitZ=apforceC*delZ
/distatoms;
  forceArr[afatomC[1],1]=forceArr[afatomC[1],1]-
unitX;forceArr[afatomC[1],2]=forceArr[afatomC[1],2]-
unitY;forceArr[afatomC[1],3]=forceArr[afatomC[1],3]-unitZ

forceArr[afatomC[2],1]=forceArr[afatomC[2],1]+unitX;forceArr[afatomC[2],2]=forceA
rr[afatomC[2],2]+unitY;forceArr[afatomC[2],3]=forceArr[afatomC[2],3]+unitZ
  }

function doempiricaldispersion() {
  EdispHtotal=0
  s6=empiricaldispersion
  for (i=1;i<=numAtoms;i++) {
    if (atSym[i]=="H") {c6[i]=0.14;r0[i]=1.001}
#    if (atSym[i]=="H") {c6[i]=0.16;r0[i]=1.11}
    if (atSym[i]=="He") {c6[i]=0.08;r0[i]=1.012}
```

```
    if (atSym[i]=="Li") {c6[i]=1.61;r0[i]=0.825}
    if (atSym[i]=="Be") {c6[i]=1.61;r0[i]=1.408}
    if (atSym[i]=="B") {c6[i]=3.13;r0[i]=1.485}
    if (atSym[i]=="C") {c6[i]=1.75;r0[i]=1.452}
#    if (atSym[i]=="C") {c6[i]=1.65;r0[i]=1.61}
    if (atSym[i]=="N") {c6[i]=1.23;r0[i]=1.397}
#    if (atSym[i]=="N") {c6[i]=1.11;r0[i]=1.55}
    if (atSym[i]=="O") {c6[i]=0.70;r0[i]=1.342}
#    if (atSym[i]=="O") {c6[i]=0.70;r0[i]=1.49}
    if (atSym[i]=="F") {c6[i]=0.75;r0[i]=1.287}
    if (atSym[i]=="Ne") {c6[i]=0.63;r0[i]=1.243}
    if (atSym[i]=="Na") {c6[i]=5.71;r0[i]=1.144}
    if (atSym[i]=="Mg") {c6[i]=5.71;r0[i]=1.364}
    if (atSym[i]=="Al") {c6[i]=10.79;r0[i]=1.639}
    if (atSym[i]=="Si") {c6[i]=9.23;r0[i]=1.716}
    if (atSym[i]=="P") {c6[i]=7.84;r0[i]=1.705}
    if (atSym[i]=="S") {c6[i]=5.57;r0[i]=1.683}
    if (atSym[i]=="Cl") {c6[i]=5.07;r0[i]=1.639}
#    if (atSym[i]=="Cl") {c6[i]=8.00;r0[i]=1.82}
    if (atSym[i]=="Ar") {c6[i]=4.61;r0[i]=1.595}
    if (atSym[i]=="K") {c6[i]=10.8;r0[i]=1.485}
    if (atSym[i]=="Ca") {c6[i]=10.8;r0[i]=1.474}
    if (atSym[i]=="Sc") {c6[i]=10.8;r0[i]=1.562}
    if (atSym[i]=="Ti") {c6[i]=10.8;r0[i]=1.562}
    if (atSym[i]=="V") {c6[i]=10.8;r0[i]=1.562}
    if (atSym[i]=="Cr") {c6[i]=10.8;r0[i]=1.562}
    if (atSym[i]=="Mn") {c6[i]=10.8;r0[i]=1.562}
    if (atSym[i]=="Fe") {c6[i]=10.8;r0[i]=1.562}
    if (atSym[i]=="Co") {c6[i]=10.8;r0[i]=1.562}
    if (atSym[i]=="Ni") {c6[i]=10.8;r0[i]=1.562}
    if (atSym[i]=="Cu") {c6[i]=10.8;r0[i]=1.562}
    if (atSym[i]=="Zn") {c6[i]=10.8;r0[i]=1.562}
    if (atSym[i]=="Ga") {c6[i]=16.99;r0[i]=1.65}
    if (atSym[i]=="Ge") {c6[i]=17.10;r0[i]=1.727}
    if (atSym[i]=="As") {c6[i]=16.37;r0[i]=1.76}
    if (atSym[i]=="Se") {c6[i]=12.64;r0[i]=1.771}
    if (atSym[i]=="Br") {c6[i]=12.47;r0[i]=1.749}
    if (atSym[i]=="Pd") {c6[i]=24.67;r0[i]=1.639}
    if (atSym[i]=="I") {c6[i]=31.5;r0[i]=1.892}
    r0[i]=r0[i]*radiusmultiplier
    }
  for (i=1;i<numAtoms;i++) {
    for (j=i+1;j<=numAtoms;j++) {
      Rij=Distance(i,j)
```

```
      if (Rij<8) { #cutoff of 8 angstroms to save time - later this can be parameterized
#need to get units of force to Hartrees/Bohr, since that is the units of forceArr
        EdispK=Edisp(c6[i],c6[j],Rij,r0[i],r0[j])*1E6/4184 #in kcal/mol
        FdispK=Fdisp(c6[i],c6[j],Rij,r0[i],r0[j])*1E6/4184 #in kcal/mol per angstrom
        EdispH=EdispK/627.509
        EdispHtotal=EdispHtotal+EdispH
        FdispHB=FdispK*0.52917725/627.509
#        print i,j,Cij,Rij,r0[i],r0[j],fdmp,"     ",EdispK,FdispK,"
",EdispH,FdispHB,EdispHtotal
        delX=oldarr[i,1]-oldarr[j,1];delY=oldarr[i,2]-oldarr[j,2];delZ=oldarr[i,3]-
oldarr[j,3];
        unitX=FdispHB*delX/Rij;unitY=FdispHB*delY/Rij;;unitZ=FdispHB*delZ/Rij;

forceArr[i,1]=forceArr[i,1]+unitX;forceArr[i,2]=forceArr[i,2]+unitY;forceArr[i,3]=force
Arr[i,3]+unitZ
        forceArr[j,1]=forceArr[j,1]-unitX;forceArr[j,2]=forceArr[j,2]-
unitY;forceArr[j,3]=forceArr[j,3]-unitZ
        }
      }
    }
  newPotentialE=newPotentialE+EdispHtotal
  }

function Edisp(c6i,c6j,rij,r0i,r0j) {
  cij=(c6i*c6j)^.5
  fdmp=1/(1+exp(-20*((rij/(r0i+r0j)-1))))
  return -s6*cij*fdmp/(rij^6)
  }

function Fdisp(c6i,c6j,rij,r0i,r0j) {
  delta=0.001
  return (Edisp(c6i,c6j,rij-delta,r0i,r0j)-Edisp(c6i,c6j,rij+delta,r0i,r0j))/(2*delta)
  }

function dozeroatom() {
#routine to slowly move an atom toward the origin as set by a harmonic potential
  multiple=0.99996
  oldarr[zeroatom,1]=multiple*oldarr[zeroatom,1]
  oldarr[zeroatom,2]=multiple*oldarr[zeroatom,2]
  oldarr[zeroatom,3]=multiple*oldarr[zeroatom,3]
  }

function dothermostat() {
#print out some things to vellist and do thermostat
```

```
# the damping in the thermostat is based on temperature based on old geo vs older geo
  if (diag<4) print "KEold",KEold,"desired temperature",temp,"apparent
Temperature",apparentTemp >> "vellist"
  if (apparentTemp>temp) damping=thermostatmult
  if (apparentTemp<temp) damping=1/thermostatmult
  }

function doDRP() {
#routine for DRPs
  maxForce=0;oscillTest=0
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
# conversions here take force to J/angstrom, 1E20 converts to kg angstroms / s^2, then
mult time (s^s) and divide by weight in kg to get angstroms

forceArr[i,j]=1E20*forceArr[i,j]*627.509*(4184/(0.529177*avNum))*(timestep^2)/(wei
ght[i]/(avNum*1000))
      oscillTest=oscillTest+forceArr[i,j]*oldForce[i,j]
      if (forceArr[i,j]>maxForce) maxForce=forceArr[i,j]
      if ((0-forceArr[i,j])>maxForce) maxForce=-forceArr[i,j]
      }
    if (i==1) printf("% .8f % .8f % .8f \n",forceArr[1,1],forceArr[1,2],forceArr[1,3])  >
"oldAdjForces"
    if (i>1) printf("% .8f % .8f % .8f \n",forceArr[i,1],forceArr[i,2],forceArr[i,3])  >>
"oldAdjForces"
    }
  print "oscillTest ",oscillTest >> "oldAdjForces"
  if (oscillTest<0) {
    maxAtomMove = maxAtomMove*0.5
    print maxAtomMove > "maxMove"
    }
  if (oscillTest>0) {
    maxAtomMove = maxAtomMove*1.2
    print maxAtomMove > "maxMove"
    }
  print "maxAtomMove ",maxAtomMove >> "oldAdjForces"
  forceMult=maxAtomMove/maxForce
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
      newarr[i,j]=oldarr[i,j]+forceMult*forceArr[i,j]
      }
    }
  }
```

```
function doVerlet() {
#normal routine for Verlet
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
# conversions here take force to J/angstrom, 1E20 converts to kg angstroms / s^2, then mult time (s^s) and divide by weight in kg to get angstroms

forceArr[i,j]=1E20*forceArr[i,j]*627.509*(4184/(0.529177*avNum))*(timestep^2)/(weight[i]/(avNum*1000))
#       if ((diag>1) && (i==1)) print "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]" >> "diagnostics"
#       if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >> "diagnostics"
      newarr[i,j]=oldarr[i,j]+damping*(oldarr[i,j]-olderarr[i,j])+forceArr[i,j]
      if ((i==fixedatom1) || (i==fixedatom2) || (i==fixedatom3) || (i==fixedatom4)) newarr[i,j]=oldarr[i,j]
#turn around atoms outside the box
      if (boxon==1) {
        if (newarr[i,j]>boxsize) if (oldarr[i,j]>olderarr[i,j]) newarr[i,j]=oldarr[i,j]+damping*(olderarr[i,j]-oldarr[i,j])+forceArr[i,j]
        if (newarr[i,j]<-1*boxsize) if (oldarr[i,j]<olderarr[i,j]) newarr[i,j]=oldarr[i,j]+damping*(olderarr[i,j]-oldarr[i,j])+forceArr[i,j]
        }
      }
    }
#calculate the kinetic energy.  This is for the point prior to the current point.  Corrected calculation
  for (at=1;at<=numAtoms;at++) {
    atomVel=(((olderarr[at,1]-newarr[at,1])^2 + (olderarr[at,2]-newarr[at,2])^2 +(olderarr[at,3]-newarr[at,3])^2)^.5)/2
    KEnew=KEnew+0.5*weight[at]*(atomVel^2)/((timestep^2)*conver1)
    }
    KEave=KEnew # we used to average with KEold but that is incorrect.  This is better.
    Etotal=newPotEK+KEave
#still basing apparent Temperature on velocities from old vs older, even though the KE now represents an average of old and new
    if (diag==4) print runpointnum,"KEave",KEave,"apparent Temperature",apparentTemp,"newPotEK",newPotEK,"Etotal",Etotal,"pressure in Atm",pressureAtm,"density in 0.9r",density >> "vellist"
  }

function writetraj() {
  print numAtoms >> "traj"
```

```
  print newPotentialE,title1,title2,title3,title4,"runpoint ",runpointnum,"runisomer
",isomernum >> "traj"
  for (i=1;i<=numAtoms;i++) {
    printf("%s %.7f %.7f %.7f",atSym[i],newarr[i,1],newarr[i,2],newarr[i,3]) >> "traj"
    print "" >> "traj"
    }
  }

function writecomfile() {
  print "%nproc=" processors
  print "%mem=" memory
  if (killcheck!=1) print "%chk=" checkpoint
  if (nonstandard==0) {
    print "#p " method " force scf=(xqc,maxconven=155,fulllinear,nosym) "
    if (meth2=="unrestricted") print "guess=mix" #for unrestricted calculations
    if (meth2=="read") print "guess=tcheck" #for reading orbitals from check,
sometimes faster, sometimes not
    if (length(meth3)>2) print meth3
    if (length(meth4)>2) print meth4
    }
  if (nonstandard==1) {
    print "# "
    print "nonstd"
    system("cat nonstandard")
    }
  print ""
  print  title1,title2,title3,title4
  print "runpoint ",runpointnum
  print "runisomer ",isomernum
  if (DRP==1) {
    print "maxForce and forceMult and
maxAtomMove",maxForce,forceMult,maxAtomMove
    print "maxForce and forceMult and
maxAtomMove",maxForce,forceMult,maxAtomMove >> "movelist"
    }
  print ""
  if (oniommult==0) print charge,multiplicity
  if (oniommult>0) print charge,multiplicity,oniomcharge,oniommult
  for (i=1;i<=numAtoms;i++) {
    printf("%s %.7f %.7f %.7f",atSym[i],newarr[i,1],newarr[i,2],newarr[i,3])
    if ((i>highlevel) && (i<=highlevel+linkatoms)) printf(" %s","M H")
    if (i>(highlevel+linkatoms)) printf(" %s","M")
    print ""
    }
```

```
print ""
if (length(meth5)>2) print meth5
if (length(meth6)>2) print meth6
if (methodfilelines>=1) {
  for (i=1;i<=methodfilelines;i++) {
    getline < "methodfile"
    print $0
    }
  }
if ((nmrtype>0) && (nmrdo==1)) {
  print "--link1--"
  print "%nproc=" processors
  print "%mem=" memory
  print "%chk=" checkpoint
  print "# " nmrmethod " nmr=giao geom=check"
  if (nmrmethod==method) print "guess=tcheck"
  if (length(meth7)>2) print meth7
  print ""
  print title1,title2,title3,title4
  print "runpoint ",runpointnum
  print "runisomer ",isomernum
  print ""
  print charge,multiplicity
  }
print ""
if ((nmrtype>1) && (nmrdo==1)) {
  print "--link1--"
  print "%nproc=" processors
  print "%mem=" memory
  print "%chk=" checkpoint
  print "# " nmrmethod2 " nmr=giao geom=check"
  if (length(meth7)>2) print meth7
  print ""
  print title1,title2,title3,title4
  print "runpoint ",runpointnum
  print "runisomer ",isomernum
  print ""
  print charge,multiplicity
  }
print ""
if ((nmrtype>2) && (nmrdo==1)) {
  print "--link1--"
  print "%nproc=" processors
  print "%mem=" memory
```

```
    print "%chk=" checkpoint
    print "# " nmrmethod3 " nmr=giao geom=check"
    if (length(meth7)>2) print meth7
    print ""
    print title1,title2,title3,title4
    print "runpoint ",runpointnum
    print "runisomer ",isomernum
    print ""
    print charge,multiplicity
    }
  print ""
  if ((nmrcc==1) && (nmrdo==1)) {
    print "CCSD(T) NMR calculation" > "ZMAT"
    for (i=1;i<=numAtoms;i++) {
      printf("%s %.7f %.7f %.7f",atSym[i],newarr[i,1],newarr[i,2],newarr[i,3]) >>
"ZMAT"
      print "" >> "ZMAT"
      }
    print "" >> "ZMAT"
    print "*ACES2(CALC=CCSD[T],PROP=NMR,BASIS=dzp" >> "ZMAT"
    print "ABCDTYPE=AOBASIS,TREAT_PERT=SEQUENTIAL,CC_PROG=ECC"
>> "ZMAT"
    print "COORD=CARTESIAN" >> "ZMAT"
    print "MEM_UNIT=GB,MEMORY=2)" >> "ZMAT"
    print "" >> "ZMAT"
    }
  }
```

Program progcfour
This module calls an outside calculation with CFOUR but was not used for the current paper and its presence is not needed to reproduce the current work. Its listing was published in the SI for a previous paper: Biswas, B.; Singleton, D. A. *J. Am. Chem. Soc.* **2015**, *137*, 14244-14247.

Program randgen.c
This is compiled before use to give the service program *randgen*

```
#include <stdio.h>
#include <stdlib.h>

int a,b,c;
double d;

int product(int x, int y);
```

```
int main(void)
{
  int count=1;
  srand48(time (0));
  while (count<=100000)
  {
    d = drand48();
    printf ("%.20f\n", d);
    count++;
  }
  return 0;
}
```

Program proganal used for 53-THF product-forming trajectories (using PROGDYN)

```
BEGIN {
firsttitle=1
getline < "isomernumber"
isomer=$1
}
/ hydroboration/ {
  if (firsttitle==1) {
    printf("%s %s %s %s %s %s %s  ",$1,$2,$3,$4,$6,$7,$8)
    runpoint=$6
    }
  firsttitle++
  }
/Standard orientation/,/Rotational constants/ {
  if (($1>.5) && ($1<99)) {
    A[$1]=$4;B[$1]=$5;C[$1]=$6
    }
  }
#/before annihilation/ {
#   printf("%s %.5f ",$1,$6)
#   }

END {
BC1=Distance(1,2)
BC2=Distance(1,3)
HC1=Distance(14,2)
if (Distance(15,2)<HC1) HC1=Distance(15,2)
if (Distance(16,2)<HC1) HC1=Distance(16,2)
HC2=Distance(14,3)
if (Distance(15,3)<HC2) HC2=Distance(15,3)
if (Distance(16,3)<HC2) HC2=Distance(16,3)
```

```
  printf("%s %.3f %s %.3f %s %.3f %s %.3f
","BC1",BC1,"BC2",BC2,"HC1",HC1,"HC2",HC2)
  if (runpoint>500000) {
    print "Too many points.  XXXXN"
#     system("date > nogo")
    }
  if ((HC1<1.1) && (BC2<1.6)) {
    print "Mark product formed XXXX"
    }
  if ((HC2<1.1) && (BC1<1.6)) {
    print "Antimark product formed XXXX"
    }
  if ((HC1>4.5) && (HC2>4.5)) {
    print "Returning to separate SMs XXXX"
    }

  system("date '+%b:%d:%Y %T'")
  system("tail -1 Echeck | grep XXXX")
  }

function Distance(Atom1,Atom2) {
 return sqrt((A[Atom1]-A[Atom2])^2 + (B[Atom1]-B[Atom2])^2 + (C[Atom1]-
C[Atom2])^2)
}

function Angle(Atom1,Atom2,Atom3) {
  value=((-
Distance(Atom1,Atom3)^2+Distance(Atom1,Atom2)^2+Distance(Atom2,Atom3)^2)/(2
*Distance(Atom1,Atom2)*Distance(Atom2,Atom3)))
  return acos(value)
}

function asin(x) { return (180/3.141592)*atan2(x, sqrt(1-x*x)) }

function acos(x) { return (180/3.141592)*atan2(sqrt(1-x*x), x) }

function atan(x) { return (180/3.141592)*atan2(x,1) }

function Dihedral(Atom1,Atom2,Atom3,Atom4) {
  B1x=A[Atom2]-A[Atom1]
  B1y=B[Atom2]-B[Atom1]
  B1z=C[Atom2]-C[Atom1]
  B2x=A[Atom3]-A[Atom2]
  B2y=B[Atom3]-B[Atom2]
```

```
   B2z=C[Atom3]-C[Atom2]
   B3x=A[Atom4]-A[Atom3]
   B3y=B[Atom4]-B[Atom3]
   B3z=C[Atom4]-C[Atom3]
   modB2=sqrt((B2x^2)+(B2y^2)+(B2z^2))
# yAx is x-coord. etc of modulus of B2 times B1
   yAx=modB2*(B1x)
   yAy=modB2*(B1y)
   yAz=modB2*(B1z)
# CP2 is the crossproduct of B2 and B3
   CP2x=(B2y*B3z)-(B2z*B3y)
   CP2y=(B2z*B3x)-(B2x*B3z)
   CP2z=(B2x*B3y)-(B2y*B3x)
   termY=((yAx*CP2x)+(yAy*CP2y)+(yAz*CP2z))
# CP is the crossproduct of B1 and B2
   CPx=(B1y*B2z)-(B1z*B2y)
   CPy=(B1z*B2x)-(B1x*B2z)
   CPz=(B1x*B2y)-(B1y*B2x)
   termX=((CPx*CP2x)+(CPy*CP2y)+(CPz*CP2z))
  dihed4=(180/3.141592)*atan2(termY,termX)
  return dihed4
}

function killdyn(isomer) {
   system("rm -f dyn")
}

Program progdynsam
BEGIN {
temp=298.15
if (pt<1) startpoint=6363
if (pt>1) startpoint=pt
line=0
printon=0
pointline=0
secondpoint=0
}

{
line++
if (line==1) numAtoms=$1
pointline++
if (printon==1) {
   if ($1=="H") atWeight[pointline]=1.00783
```

```
  if ($1=="C") atWeight[pointline]=12.0000
  if ($1=="B") atWeight[pointline]=10.81
  if ($1=="O") atWeight[pointline]=15.99940
  if ($1=="F") atWeight[pointline]=18.9984
  if ($1=="P") atWeight[pointline]=30.9738
  if ($1=="S") atWeight[pointline]=31.972
  if ($1=="N") atWeight[pointline]=14.0030740
  if ($1=="Al") atWeight[pointline]=26.981
  if ($1=="Cl") atWeight[pointline]=35.4527
  if (($1=="C") || ($1=="H") || ($1=="O") || ($1=="P") || ($1=="N") || ($1=="Cl")  ||
($1=="B") || ($1=="F") || ($1=="S") || ($1=="Al")) {
    Arr0[pointline,0]=$1
    Arr0[pointline,1]=$2
    Arr0[pointline,2]=$3
    Arr0[pointline,3]=$4
    Arr1[pointline,0]=$1
    Arr1[pointline,1]=$2
    Arr1[pointline,2]=$3
    Arr1[pointline,3]=$4
    }
  }
if (secondpoint==1) {
  if (($1=="C") || ($1=="H") || ($1=="O") || ($1=="P") || ($1=="N") || ($1=="Cl")  ||
($1=="B") || ($1=="F") || ($1=="S") || ($1=="Al")) {
    Arr1[pointline,1]=$2-Arr1[pointline,1]
    Arr1[pointline,2]=$3-Arr1[pointline,2]
    Arr1[pointline,3]=$4-Arr1[pointline,3]
    }
  }
if ($8=="runisomer") {
  pointline=0
  }
if ($7==startpoint) {
  pointline=0
  printon=1
  }
if ($7==startpoint+1) {
  secondpoint=1
  pointline=0
  printon=0
  }
if ($7>startpoint+1) {
  secondpoint=0
  printon=0
```

```
  }

}

END {
print numAtoms
for (i=1;i<=numAtoms;i++) {
  print Arr0[i,0],Arr0[i,1],Arr0[i,2],Arr0[i,3],atWeight[i]
  }
conver1=4.184E26
srand()
timestep=1E-15
for (i=1;i<=100;i++) {
  newRand=rand()
  newRand2=rand()
  randArr[i]=newRand
  sign[i]=1
  if (newRand2<0.5) sign[i]=-1
}
for (i=1;i<=numAtoms;i++) {
  if ((Arr1[i,1]==0) && (Arr1[i,2]==0) && (Arr1[i,3]==0)) {
    for (j=1;j<=3;j++) {
      KE=-0.001987*temp*log(1-randArr[3*i+j])
      Vel=sign[3*i+j]*timestep*(2*KE*conver1/atWeight[i])^0.5
      Arr1[i,j]=Vel
      }
    }
  print Arr1[i,1],Arr1[i,2],Arr1[i,3]
  }
printf("%s %i %i %s ","generated from points",startpoint,startpoint+1,"in a trajectory, so
no modes to print out")
system("pwd")
print "Total mode energy desired=",0
for (i=1;i<=700;i++) {
  velsq= Arr1[i,1]^2+Arr1[i,2]^2+Arr1[i,3]^2
  KE=1E30*0.5*atWeight[i]*velsq/conver1
  KE=2.388E3*0.5*atWeight[i]*velsq
  #print i,KE
  }
print ""
}
```

Program proglookstart

```
BEGIN {
```

```
dirnum=666
}
{
if (($5 % 250)==0) {
        print "cd /scratch/user/johnathanbailey13/"substr(FILENAME,1,4)
        print "mkdir /scratch/user/johnathanbailey13/n"dirnum
        print "cp /scratch/user/johnathanbailey13/progdyn.conf
/scratch/user/johnathanbailey13/n"dirnum
        print "echo 3 > /scratch/user/johnathanbailey13/n"dirnum"/bypassproggen"
        print "awk -v pt="$5,"-f ~/progdynsam traj >
/scratch/user/johnathanbailey13/n"dirnum"/geoPlusVel"
        dirnum++
  }
}
```

Program progKECM

```
BEGIN {
structure=0
point=0
}
/runpoint/ {
  oldpoint=point
  point=$7
  if ((point<2) || (point>99999999)) point=1
  linenumber=-1
# array A is three points back, B is two points back, and C is latest point
# calculation is done at the beginning of the new point, and once at the end
# D is the array of distances traveled by each atom between points A and B
  KE1=0;
  for (i=1;i<=22;i++) {
    D[i]=.5*((C[i,1]-A[i,1])^2+(C[i,2]-A[i,2])^2+(C[i,3]-A[i,3])^2)^.5
    KE1=KE1+.5*atWeight[i]*D[i]^2
    }
  KE1=KE1/6.02E26
  KE1=KE1/1E20
  KE1=KE1*1E30
  KE1=KE1*6.02E23
  KE1=KE1/4184
  if (point==2) print "                    "
  if (point>=4) print oldpoint-1,"       ",KE1
  if (point<oldpoint) {
    print oldpoint-1,"  ",KE1
    print "                              "
    }
```

```
  for (i=1;i<=22;i++) {
    for (j=1;j<=3;j++) {
      A[i,j]=B[i,j]
      B[i,j]=C[i,j]
      }
    }
  }
{
linenumber++
if ((linenumber>0) && (linenumber < 23)) {
  i=linenumber
  if ($1=="H") atWeight[i]=1.00783
  if ($1=="B") atWeight[i]=10.811
  if ($1=="C") atWeight[i]=12.
  if ($1=="O") atWeight[i]=15.9994
  C[i,1]=$2;C[i,2]=$3;C[i,3]=$4
  }
molmass=0
CMtot[1]=0;CMtot[2]=0;CMtot[3]=0
if (linenumber==23) {
  for (i=1;i<=23;i++) {
    for (j=1;j<=3;j++) {
      CM[i,j]=C[i,j]*atWeight[i]
      CMtot[j]=CM[i,j]+CMtot[j]
      }
    molmass=molmass+atWeight[i]
    }
  for (j=1;j<=3;j++) {
    CMtot[j]=CMtot[j]/molmass
    }
  for (i=1;i<=23;i++) {
    for (j=1;j<=3;j++) {
      C[i,j]=C[i,j]-CMtot[j]
      }
    }
  }
}
END {
  KE1=0;
  for (i=1;i<=23;i++) {
    D[i]=.5*((C[i,1]-A[i,1])^2+(C[i,2]-A[i,2])^2+(C[i,3]-A[i,3])^2)^.5
    KE1=KE1+.5*atWeight[i]*D[i]^2
    }
  KE1=KE1/6.02E26
```

```
  KE1=KE1/1E20
  KE1=KE1*1E30
  KE1=KE1*6.02E23
  KE1=KE1/4184
  if (point>=4) print point-1," ",KE1

}
```

progEchangelocal example

```
awk 'BEGIN {
section=0
}
/XXX/ {
section++
}
/product/ {
sectionchoice=section;finalpt=$5
}
END {
print sectionchoice,2,21,finalpt-40,finalpt-21
}' dynfollowfile > tempptlist
pwd >> tempptlist
#
awk 'BEGIN {
getline < "tempptlist";goodsection=$1;ptA=$2;ptB=$3;ptC=$4;ptD=$5
getline < "tempptlist";dir=$1
point=0;oldpoint=0;section=1
}
/runpoint/ {
linenumber=-1
if ($5=="runpoint") point=$6
if ($6=="runpoint") point=$7
if (point<oldpoint) section++
oldpoint=point
if (section==goodsection) {
  if (((point>=ptA) && (point<=ptB)) || ((point>=ptC) && (point<=ptD))) {
    if (point>ptA) print ""
    print "--link1--"
    print "%chk=g09.chk"
    print "#p SP B3LYP/6-31G*"
    print "  "
    print dir,"energy point",point
    print ""
```

```
    print "0 1"
    }
  }
}
{
linenumber++
if (section==goodsection) {
  if (((point>=ptA) && (point<=ptB)) || ((point>=ptC) && (point<=ptD))) {
    if ((linenumber>=1) && (linenumber<=4)) print
    if ((linenumber>=9) && (linenumber<=16)) print
    if (linenumber==4) {
      X1=$2;Y1=$3;Z1=$4
      }
    if (linenumber==5) {
      X2=$2;Y2=$3;Z2=$4
      CCdist=((X2-X1)^2+(Y2-Y1)^2+(Z2-Z1)^2)^.5
      ratio=1.09/CCdist
      X3=ratio*(X2-X1)+X1;Y3=ratio*(Y2-Y1)+Y1;Z3=ratio*(Z2-Z1)+Z1;
      print "H",X3,Y3,Z3
      }
    }
  }
}
END {
print ""
#print goodsection,ptA,ptB,ptC,ptD
}' traj?
```

ProgEchangetail example

```
awk 'BEGIN {
getline < "tempptlist";goodsection=$1;ptA=$2;ptB=$3;ptC=$4;ptD=$5
getline < "tempptlist";dir=$1
point=0;oldpoint=0;section=1
}
/runpoint/ {
linenumber=-1
if ($5=="runpoint") point=$6
if ($6=="runpoint") point=$7
if (point<oldpoint) section++
oldpoint=point
if (section==goodsection) {
  if (((point>=ptA) && (point<=ptB)) || ((point>=ptC) && (point<=ptD))) {
```

```
    if (point>ptA) print ""
    print "--link1--"
    print "%chk=g09.chk"
    print "#p SP B3LYP/6-31G*"
    print "  "
    print dir,"energy point",point
    print ""
    print "0 1"
    }
  }
}
{
linenumber++
if (section==goodsection) {
  if (((point>=ptA) && (point<=ptB)) || ((point>=ptC) && (point<=ptD))) {
    if ((linenumber>=5) && (linenumber<=8)) print
    if ((linenumber>=17) && (linenumber<=22)) print
    if (linenumber==4) {
      X2=$2;Y2=$3;Z2=$4
      }
    if (linenumber==5) {
      X1=$2;Y1=$3;Z1=$4
      CCdist=((X2-X1)^2+(Y2-Y1)^2+(Z2-Z1)^2)^.5
      ratio=1.09/CCdist
      X3=ratio*(X2-X1)+X1;Y3=ratio*(Y2-Y1)+Y1;Z3=ratio*(Z2-Z1)+Z1;
      print "H",X3,Y3,Z3
      }
    }
  }
}
END {
print ""
#print goodsection,ptA,ptB,ptC,ptD
}' traj?
```

```
 Program progcomptime
BEGIN {
compformed=0
}
{
if ($5<5) compformed=0
if ((compformed==0) && (($9<2) && ($11<2))) {
    compformed=1
```

```
    formedat=$5
    }
}
/Antimark/ {
print "Antimark:   complex formed at  ",formedat,"   and finished at  ",$5,"   difference:
",$5-formedat
compformed=0
formedat=0
}
/Mark/ {
print "Mark:       complex formed at  ",formedat,"   and finished at  ",$5,"   difference:
",$5-formedat
compformed=0
formedat=0
}
```

Program Suite ProgdynONIOM

ProgdynONIOM is a new program adapted from PROGDYN but designed to combine forces from Gaussian09 and MOPAC2016 in ONIOM calculations. Its ONIOM capabilities are currently limited to systems where there is no covalent bond between the model (small) system and the real (full) system. The combination of the two programs extends the practical size of the QM/QM calculation, aside from allowing the extended semi-empirical methods in MOPAC2016.

PROGDYN and ProgdynONIOM are similar, and some of the description below is identical to that above, but there are differences to note. In particular, ProgdynONIOM runs three separate QM calculations for each trajectory point, with a separate input and output file for each.

ProgdynONIOM includes the ability to include additional empirical dispersion using Grimme's D2 model (reference 22 in the main text). The progdyn.conf employed for the 80-THF model includes additional empirical dispersion by the use of the parameters empiricaldispersion .7 and radiusmultiplier 1.6. The PM6-D3H4 method already includes dispersion, but this additional small corrections was added to bring the solution to an accurate density at pressures less than 1000 atm.

A full listing of the subprograms of ProgdynONIOM is given below. To allow the reader to understand or make use of ProgdynONIOM , we first describe the overall structure of the program.

The master control program for dynamics, in the form of a Unix Shell Script, is called progdynONIOM. For a user to start to use progdynONIOM, some early lines in it that assign the scratch space and the location of the program files and input files would have to be modified for the local environment. These lines are between lines 45 and 55 and should be apparent. The location of the scratch space is usually passed to progdynONIOM as a parameter.

progdynONIOM takes as input files:

freqinHP - This is the standard output from a Gaussian 98, 03, or 09 frequency calculation using freq=hpmodes. For isotopically labeled compounds, use freq=(hpmodes,readisotopes).

progdyn.conf – This is a file giving a variety of configuration options, called on by many of the subprograms. progdyn.conf examples are listed below and contains explanations of the program options.

isomernumber - A number in file isomernumber provides a start for numbering runs. The default is 1.

detour – A signal file that, by existing, signals the program to do a side calculations

nogo – A signal file that, by existing, signals the program to stop between points

bypassproggen - A signal file that, by existing, signals the program to use a supplied input file *geoPlusVel* instead of generating one for itself. This pathway for initialization is important here because it is used when the program progdynsam, described later, is used to generate the geoPlusVel file.

methodfile – A file that contains lines to be added to the end of each g09.com input file, such as lines that call for an NMR calculation

cannontraj – A file containing a vector for each atom, used to fire an initial geometry in a particular direction.

progdynONIOM calls the following programs:

proggenHP - An awk program that starts a trajectory, giving each mode its zero point energy (if a quasiclassical calculation) plus random additional excitations depending on the temperature.

prog1stpoint – Awk program that creates the first Gaussian input file for each run

prog2ndpoint – Awk program that creates the second Gaussian input file for each run. prog2ndpoint also checks the energy of the first point to see if it fits with the desired energy, and aborts the run if it does not by creating appropriate output in file Echeck

progdynb – Creates subsequent Gaussian input files until run is completed, written in awk

proganal – A program to analyze the latest point and see if a run is done. This program must be redone for each new system. Elaborate changes are sometimes programmed into proganal, such as the automatic changing of configuration variables. proganal creates the output to dynfollowfile and NMRlist or NMRlistdis

randgen – A program that generates random numbers between 0 and 1. These are generated all at once and stored in a file for use by proggenHP.

progdynONIOM has the following output files:

isomernumber – A running tab of the trajectory number

runpointnumber – a running tab of the point in the trajectory
Echeck – output form where prog2ndpoint checks the energy of the trajectory to see if it fits with the desired energy
geoRecord – A record of all of the geoPlusVel files.
geoPlusVel – Created by proggen, this gives the starting positions, velocities, isotopic masses, excitations of the normal modes, and initial displacements of the normal modes for current run.
g09.com – Created by prog1stpoint, prog2ndpoint, and progdynb, this is the latest input file for Gaussian09 for current run and latest point.
model.mop - Created by prog1stpoint, prog2ndpoint, and progdynb, this is the latest input file for the model system for MOPAC2016, for current run and latest point.
real.mop - Created by prog1stpoint, prog2ndpoint, and progdynb, this is the latest input file for the real (full) system for MOPAC2016, for current run and latest point.
g09.log, real.out, model.out – These are the output files for the latest Gaussian09 and MOPAC 2016 calculations, used for extracting forces in the creation of the next point.
olddynrun, *olddynrun2, olddynrun3* – files containing the last three outputs from MOPAC2016, for creation of the next point
traj, traj1, traj2, traj3, etc. – files containing the geometries and energies for each trajectory, numbered by the isomernumber, in a format suitable for reading by Molden.
dynfollowfile – A short record of the runs and their results. The data desired for *dynfollowfile* must be programed into the script *proganal* as needed for each system studied.
skipstart - A signal file that, by existing, tells progdynstarterHP that we are in the middle of a run. For trajectories that are propagated forward and backward in time, skipstart keeps track of whether one is in the forward or reverse part.
diagnostics – optional output that follows which subprograms are running and configuration variables, decided by variable in progdyn.conf
vellist – optional output that lists the velocities of each atom, decided by variable in progdyn.conf, or lists the total kinetic energy in the system and the classical temperature, often also keeps track of the density
A number of files starting with *'temp'* are created then later erased.

The helper programs *progdynsam*, *proglookstart*, *progKECM*, and *progcomptime* listed above for PROGDYN were also employed with ProgdynONIOM.

progdynONIOM

```
#!/bin/bash
#progdynMOPAC started November 6, 2016
#LIMITATIONS -
#
#                         OUTLINE
# A. initialize
#    start outermost loop L1L1L1L1L1L1L1L1
#    start loop 2 L2L2L2L2L2L2L2L2L2
```

```
# B. branch on whether there is a file named "skipstart"
#    if there is, skip B1, B2, B3 entirely
#    if no file named "skipstart" then generate a new isomer.
#  B1. generates geoPlusVel, isomernumber, runpointnumber=1, then makes real.mop,
model.mop, g09.com for point 1
#  B2. checks for success of B1 or exits, then sets geoRecord then runs real.mop,
model.mop, g09.com.  Checks for their success or exits.
#  B3. runpointnumber=2, kills run if XXXX in dynfollowfile due to bad energy
probably, makes real.mop, model.mop, g09.com for point 2, runs them
#      checks for their success or exits
#      runpointnumber=3, uses progdynb to make real.mop, model.mop, g09.com for
point 3
#      sets skipstart=forward
#  B4. Only runs if skipstart=reverserestart, performs reverserestart, ends with
runpointnumber=3
#      sets skipstart=reverse
# C. loop over propagation steps
#
#
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
#
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
#
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
#origdir, randdir, scratchdir, g09root, logfile all may need varied from system to system
and assigned here or by program calling this one
export LC_ALL=C
export MOPAC_LICENSE='/home/d-singleton/mopac'
export LD_LIBRARY_PATH='/home/d-singleton/mopac'
echo $1
scratchdir=$1
export g09root=/software/lms/g09_D01
. $g09root/g09/bsd/g09.profile
cp /home/d-singleton/mopac/MOPAC2016.exe $scratchdir
cp /home/d-singleton/mopac/lib* $scratchdir
export LD_LIBRARY_PATH=$scratchdir
origdir=`pwd`
cd $origdir
```

```
logfile=docslog
randdir=~/bin
proggramdir=/scratch/user/d-singleton/binoniom1100
freqfile=/scratch/user/d-singleton/binoniom1100/freqinHP
echo
echo ORIGDIR at the beginning of run:
echo $origdir
ls $origdir
echo
echo SCRATCHDIR at the beginning of run:
echo $scratchdir
ls $scratchdir
echo
echo PROGGRAMDIR at the beginning of run::
echo $proggramdir
ls $proggramdir

rm -f nogo    # assume that if someone is starting a job, they want it to go.
rm -f diagnostics goingwell tempdone # diagnostics contains extra info from previous
runs, other two files are from older versions of progdyn
if (test -s g09.com) then
   sed -i '/guess=tcheck/d' g09.com      # no chk file on first point
fi

##### Triple 'while' loop - will have to break multiple times to get out, but advantage is
ability to control starting over
#L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L
1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L1L
1L1L1L1L1L1L1L1L1
while (true)
do
# As long as there is a file "goingwell" the program will not exit entirely by itself
rm -f $scratchdir/goingwell
#L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L
2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L2L
2L2L2L2L2L2L2L2L2
while (true)
do
#  BBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBB
   if (test -f skipstart) then
      echo "skipping start and continuing from previous runs"
   else
```

```
#
B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1
generate geoPlusVel and first input file
    if [ `cat runpointnumber` = "1" ]; then
      echo "X did not complete first point so new isomer started" >> dynfollowfile
    fi
    if [ `cat runpointnumber` = "2" ]; then
      echo "X did not complete second point so new isomer started" >> dynfollowfile
    fi
    if [ `cat runpointnumber` = "3" ]; then
      echo "X did not complete third point so new isomer started" >> dynfollowfile
    fi
    cd $origdir
    if (test -f bypassproggen) then
      echo "taking starting conditions from pre-generated geoPlusVel"
    else
      $randdir/randgen > temp811
# the next 8 lines would have to be changed to use low-precision modes
      awk '/        1         2/,/Harmonic frequencies/ {print}' $freqfile > temp401
      awk '/Frequencies --/ {print $3;print $4;print $5;print $6;print $7}' temp401 >
tempfreqs
      awk '/Reduced masses/ {print $4;print $5;print $6;print $7;print $8}' temp401 >
tempredmass
      awk '/Force constants/ {print $4;print $5;print $6;print $7;print $8}' temp401 >
tempfrc
      awk '/0/ && ((length($1) < 2) && ($1 < 4)) {print}' temp401 > tempmodes
      awk '/has atomic number/ {print}' $freqfile > tempmasses
      awk '/Standard orientation:/,/tional const/ {if (($3=="0") || (substr($3,1,2)==10))
print}' $freqfile > tempstangeos
      awk '/Input orientation:/,/Stoichiometry/ {if (($3=="0") || (substr($3,1,2)==10))
print}' $freqfile > tempinputgeos
      awk -f $proggramdir/proggenHP $freqfile > geoPlusVel
    fi
    if ! (test -s geoPlusVel) then
      echo "XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX No geoPlusVel
XXXXXXXXXXXXXXXXXXXXXXXXXX"
      exit 0
    fi
    if (test -f isomernumber) then
      cp isomernumber temp533
      awk 'BEGIN {getline;i=$1+1;print i,"----trajectory isomer number----"}' temp533
> isomernumber
      rm temp533
    else
```

```
      echo "1 ----trajectory isomer number----" > isomernumber
    fi
    echo 1 > runpointnumber
    rm real.mop model.mop g09.com
    awk -f $proggramdir/prog1stpoint isomernumber > real.mop     #prog1stpoint now
also makes model.mop and g09.com
#
B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B
2B2  if first part successful then clean up and run the first input file, otherwise die
    if ((test -s real.mop) && (test -s model.mop) && (test -s g09.com)) then
      rm tempfreqs tempredmass tempfrc tempmodes tempstangeos tempmasses
temp401 temp811 tempinputgeos
      cat isomernumber >> geoRecord
      cat geoPlusVel >> geoRecord
      rm -f $scratchdir/goingwell
      cd $scratchdir
      cp $origdir/real.mop $scratchdir/real.mop
      cp $origdir/model.mop $scratchdir/model.mop
      cp $origdir/g09.com $scratchdir/g09.com
      $g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
      grep 'Normal termination' $scratchdir/g09.log > $scratchdir/goingwell
      if ! (test -s $scratchdir/goingwell) then
        cp $scratchdir/g09.log $origdir/g09.log
        break
      fi
      $scratchdir/MOPAC2016.exe $scratchdir/model.mop
      grep 'JOB ENDED NORMALLY' $scratchdir/model.out > $scratchdir/goingwell
      if ! (test -s $scratchdir/goingwell) then
        cp $scratchdir/real.out $origdir/real.out
        break
      fi
      $scratchdir/MOPAC2016.exe $scratchdir/real.mop
      cd $origdir
      grep 'JOB ENDED NORMALLY' $scratchdir/real.out > $scratchdir/goingwell
      if (test -s $scratchdir/goingwell) then
        cp $scratchdir/real.out olddynrun2
      else
        cp $scratchdir/real.out $origdir/real.out
        break
      fi
    else
      break
    fi
```

```
#
B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B
3B3 if B2 worked then you are here.  create 2nd point, run it, and set up for propagation
loop
    rm real.mop model.mop g09.com
    echo 2 > runpointnumber
    awk -f $proggramdir/prog2ndpoint $scratchdir/real.out $scratchdir/model.out
$scratchdir/g09.log > real.mop #prot2ndpoint now also makes model.mop and g09.com
# before we decide to run this, check the energy
    awk -f $proggramdir/proganal $scratchdir/real.out >> dynfollowfile
    rm -f $scratchdir/tempdone
    tail -1 dynfollowfile | awk '/XXXX/ {print}' > $scratchdir/tempdone
    if (test  -s $scratchdir/tempdone) then
      rm -f traj
      echo 0 > runpointnumber
      break
    fi
    if ((test -s real.mop) && (test -s model.mop) && (test -s g09.com)) then
      rm -f $scratchdir/goingwell
      cd $scratchdir
      cp $origdir/real.mop $scratchdir/real.mop
      cp $origdir/model.mop $scratchdir/model.mop
      cp $origdir/g09.com $scratchdir/g09.com
      $g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
      grep 'Normal termination' $scratchdir/g09.log > $scratchdir/goingwell
      if ! (test -s $scratchdir/goingwell) then
        cp $scratchdir/g09.log $origdir/g09.log
        break
      fi
      $scratchdir/MOPAC2016.exe $scratchdir/model.mop
      grep 'JOB ENDED NORMALLY' $scratchdir/model.out > $scratchdir/goingwell
      if ! (test -s $scratchdir/goingwell) then
        cp $scratchdir/real.out $origdir/real.out
        break
      fi
      $scratchdir/MOPAC2016.exe $scratchdir/real.mop
      cd $origdir
      grep 'JOB ENDED NORMALLY' $scratchdir/real.out > $scratchdir/goingwell
      if (test -s $scratchdir/goingwell) then
        cp $scratchdir/real.out olddynrun
        awk -f $proggramdir/proganal $scratchdir/real.out >> dynfollowfile
        awk '/ATOM   CHEMICAL          X/,/CARTESIAN COORDINATES/ {print}'
olddynrun | awk '{if (($1>.5) && ($1<10000)) print}' > old
```

```
        awk '/ATOM   CHEMICAL          X/,/CARTESIAN COORDINATES/ {print}'
olddynrun2 | awk '{if (($1>.5) && ($1<10000)) print}' > older
        echo 3 > runpointnumber
        if (test -f bypassproggen) then
          cat bypassproggen > runpointnumber
          echo 3 > bypassproggen
        fi
        awk -f $proggramdir/progdynb $scratchdir/real.out $scratchdir/model.out
$scratchdir/g09.log > real.mop
        rm -f old older
      else
        cp $scratchdir/real.out $origdir/real.out
        break
      fi
    else
      break
    fi
# we've just completed a start, so lets skipstart until instructed otherwise
    echo "forward" > skipstart
  fi
#
B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B
4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4
B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4B4
# Reverse trajectories starter routine
  if [ `cat skipstart` = "reverserestart" ]; then
    cd $origdir
    rm real.mop model.mop g09.com
    echo 1 > runpointnumber
    awk -f $proggramdir/prog1stpoint isomernumber > real.mop     #prog1stpoint now
also makes model.mop and g09.com
    if ((test -s real.mop) && (test -s model.mop) && (test -s g09.com)) then
      rm -f $scratchdir/goingwell
      cd $scratchdir
      cp $origdir/real.mop $scratchdir/real.mop
      cp $origdir/model.mop $scratchdir/model.mop
      cp $origdir/g09.com $scratchdir/g09.com
      $g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
      grep 'Normal termination' $scratchdir/g09.log > $scratchdir/goingwell
      if ! (test -s $scratchdir/goingwell) then
        cp $scratchdir/g09.log $origdir/g09.log
        break
      fi
      $scratchdir/MOPAC2016.exe $scratchdir/model.mop
```

```
      grep 'JOB ENDED NORMALLY' $scratchdir/model.out > $scratchdir/goingwell
      if ! (test -s $scratchdir/goingwell) then
        cp $scratchdir/real.out $origdir/real.out
        break
      fi
      $scratchdir/MOPAC2016.exe $scratchdir/real.mop
      cd $origdir
      grep 'JOB ENDED NORMALLY' $scratchdir/real.out > $scratchdir/goingwell
      if (test -s $scratchdir/goingwell) then
        cp $scratchdir/real.out olddynrun2
      else
        cp $scratchdir/real.out $origdir/real.out
        break
      fi
    else
      break
    fi
    rm real.mop model.mop g09.com
    echo 2 > runpointnumber
    awk -f $proggramdir/prog2ndpoint $scratchdir/real.out $scratchdir/model.out
$scratchdir/g09.log > real.mop #prot2ndpoint now also makes model.mop and g09.com
    awk -f $proggramdir/proganal $scratchdir/real.out >> dynfollowfile
    rm -f $scratchdir/tempdone
    if ((test -s real.mop) && (test -s model.mop) && (test -s g09.com)) then
      rm -f $scratchdir/goingwell
      cd $scratchdir
      cp $origdir/real.mop $scratchdir/real.mop
      cp $origdir/model.mop $scratchdir/model.mop
      cp $origdir/g09.com $scratchdir/g09.com
      $g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
      grep 'Normal termination' $scratchdir/g09.log > $scratchdir/goingwell
      if ! (test -s $scratchdir/goingwell) then
        cp $scratchdir/g09.log $origdir/g09.log
        break
      fi
      $scratchdir/MOPAC2016.exe $scratchdir/model.mop
      grep 'JOB ENDED NORMALLY' $scratchdir/model.out > $scratchdir/goingwell
      if ! (test -s $scratchdir/goingwell) then
        cp $scratchdir/real.out $origdir/real.out
        break
      fi
      $scratchdir/MOPAC2016.exe $scratchdir/real.mop
      cd $origdir
      grep 'JOB ENDED NORMALLY' $scratchdir/real.out > $scratchdir/goingwell
```

```
      if (test -s $scratchdir/goingwell) then
        cp $scratchdir/real.out olddynrun
        awk -f $proggramdir/proganal $scratchdir/real.out >> dynfollowfile
        awk '/ATOM   CHEMICAL         X/,/CARTESIAN COORDINATES/ {print}'
olddynrun | awk '{if (($1>.5) && ($1<10000)) print}' > old
        awk '/ATOM   CHEMICAL         X/,/CARTESIAN COORDINATES/ {print}'
olddynrun2 | awk '{if (($1>.5) && ($1<10000)) print}' > older
        echo 3 > runpointnumber
        if (test -f bypassproggen) then
          cat bypassproggen > runpointnumber
          echo 3 > bypassproggen
        fi
        awk -f $proggramdir/progdynb $scratchdir/real.out $scratchdir/model.out
$scratchdir/g09.log > real.mop
        rm -f old older
      else
        cp $scratchdir/real.out $origdir/real.out
        break
      fi
    else
      break
    fi
# we've just completed a reversestart, so lets skipstart until instructed otherwise
    echo "reverse" > skipstart
  fi

#
END_of_B___END_of_B___END_of_B___END_of_B___END_of_B___END_of_B_
__END_of_B___END_of_B___

#
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCC  propagation loop
  while (true)
  do
    rm -f $scratchdir/goingwell
    cd $scratchdir
    cp $origdir/real.mop $scratchdir/real.mop
    cp $origdir/model.mop $scratchdir/model.mop
    cp $origdir/g09.com $scratchdir/g09.com
    $g09root/g09/g09 $scratchdir/g09.com > $scratchdir/g09.log
cp $scratchdir/g09.log $origdir/g09.log
    grep 'Normal termination' $scratchdir/g09.log > $scratchdir/goingwell
    if ! (test -s $scratchdir/goingwell) then
```

```
      cp $scratchdir/g09.log $origdir/g09.log
      break
    fi
    $scratchdir/MOPAC2016.exe $scratchdir/model.mop
    grep 'JOB ENDED NORMALLY' $scratchdir/model.out > $scratchdir/goingwell
cp $scratchdir/model.out $origdir/model.out
    if ! (test -s $scratchdir/goingwell) then
      cp $scratchdir/model.out $origdir/model.out
      break
    fi
    $scratchdir/MOPAC2016.exe $scratchdir/real.mop
    cd $origdir
    grep 'JOB ENDED NORMALLY' $scratchdir/real.out > $scratchdir/goingwell
cp $scratchdir/real.out $origdir/real.out
    if (test -s $scratchdir/goingwell) then
      awk -f $proggramdir/proganal $scratchdir/real.out >> $origdir/dynfollowfile
      mv olddynrun2 olddynrun3
      mv olddynrun olddynrun2
      cp $scratchdir/real.out olddynrun
      awk '/ATOM   CHEMICAL          X/,/CARTESIAN COORDINATES/ {print}'
olddynrun | awk '{if (($1>.5) && ($1<10000)) print}' > old
      awk '/ATOM   CHEMICAL          X/,/CARTESIAN COORDINATES/ {print}'
olddynrun2 | awk '{if (($1>.5) && ($1<10000)) print}' > older
      #increment runpointnumber
      cp runpointnumber $scratchdir/temp533
      awk 'BEGIN {getline;i=$1+1;print i}' $scratchdir/temp533 > runpointnumber
      rm $scratchdir/temp533
      awk -f $proggramdir/progdynb $scratchdir/real.out $scratchdir/model.out
$scratchdir/g09.log > real.mop
      rm -f old older
    else
      cp $scratchdir/real.out $origdir/real.out
      break
    fi

# here is a cool link that lets you interrupt the dynamics with a short job, then
# it automatically goes back to the dynamics  just make the file 'detour' and it
# will delete detour, run run.com, then go back to dynamics
    if (test  -f detour) then
      rm detour
      date >> $logfile
      cat run.com >> $logfile
      cp run.log temp.log
      export g09root=/software/lms/g09_D01
```

```
      . $g09root/g09/bsd/g09.profile
      cd $scratchdir
      $g09root/g09/g09 $origdir/run.com > $origdir/run.log
      cd $origdir
    fi

#stop it all nicely by creating a nogo file
    if (test  -f nogo) then
      break
    fi

#figure out if this isomer is done - change in April 2013 is to move proganal call up from
here
    rm -f $scratchdir/tempdone
    tail -2 dynfollowfile | awk '/XXXX/ {print}' > $scratchdir/tempdone
    if (test  -s $scratchdir/tempdone) then
      if [ `awk '/reversetraj/ {if ($1=="reversetraj") print $2}' progdyn.conf` = "true" ];
then
        if [ `cat skipstart` = "reverse" ]; then
          rm -f skipstart
          rm -f geoPlusVel
          rm -f olddynrun
          rm -f olddynrun2
          rm -f olddynrun3
          a=`awk '{print $1}' isomernumber`
          mv traj traj$a
        fi
        if [ `cat skipstart` = "forward" ]; then
          echo reverserestart > skipstart
        fi
      else
        rm -f skipstart
        rm -f geoPlusVel
        rm -f olddynrun
        rm -f olddynrun2
        rm -f olddynrun3
        a=`awk '{print $1}' isomernumber`
        mv traj traj$a
      fi
      break
    fi
  done
```

```
#
END_of_C_Loop____END_of_C_Loop____END_of_C_Loop____END_of_C_Loop__
__END_of_C_Loop____END_of_C_Loop____

# We've got to break a second time to get out of this loop
# if we really want to quit.  Otherwise, it will start over
# at the top
  if (test  -f nogo) then
    break
  fi
  if (test  -s $scratchdir/goingwell) then
    echo "starting a new point or a new direction"
  else
    break
  fi
done

  if (test  -f nogo) then
    break
  fi
  if (test  -s $scratchdir/goingwell) then
    echo "starting a new point or a new direction2"
  else
    break
  fi
done
exit 0
```

```
proggenHP
BEGIN {
# 2014 - avoids bug with a box on, so that starts without modes use input geometry, not
standard orientation
# aug 2013 summary of changes
#includes molecular rotation, ability to do multiple NMR calculations, ONIOM with link
atoms,
#nonstandard routes, handling of linear molecules using geometry linear, fixed but with
atoms over 99 but
#bug varies with version of Gaussian, randomization based on PROCINFO (solved
many problems), added initialDiss 3 for random
#phase of normal modes
# Aug 2010 changes classicalSpacing to 2 and upped possible excited states to 4000
# Jan 2009 - a number of little changes to improve reporting, precision, etc, specification
of displacement on particular modes
```

```
# Jan 2009 cannonball trajectories.  adds desired energy to initial velocities based on file
cannontraj, so one can shoot toward a ts
# updated Nov 2008 to incorporate running DRPs
# updated Nov 2008 to allow for start without an initial freq calc using classical = 2
# updated Aug 2008 added to atom list to handle a large number of atoms without
changes needed
# updated June 2008 to incorportates new method for choosing displacements with
initialdis 2
# updated Jan 17 2008 - bug fix for > 99 atoms, 300 excitations of low modes possible
# version August 2007 - incorporates classical trajectory calculation option
#also allows listing of number of imaginary frequencies
# version Sept 16, 2005 - incorportates searchdir but not yet rotation
# now reads random numbers from temp811, starting at a random place
# The input files are generated before this and are tempfreqs, tempredmass,
# tempfrc, tempmodes, and tempstangeos.
# It will count the number of atoms.

# default parameters, including quassiclassical, no displacements, transition state, not a
DRP
# do not change these - rather, change progdyn.conf to set the parameters
initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
classical=0; numimag=1; DRP=0; cannonball=0
charge=0; multiplicity=1; method="HF/3-21G"; memory=20000000
diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
title3="a"; title4="progdyn.conf"; processors=1; highlevel=999
conver1=4.184E26 #dividing by this converts amu angs^2 /s^2 to kcal/mol
geometry="nonlinear";rotationmode=0

#initialization and constants
for (i=1;i<=10000;i++) {disMode[i]=-1}
i=1;j=1;k=1
c=29979245800; h=6.626075E-34; avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447
numAtoms=0; atomnumber=0; classicalSpacing=2
zpeGauss=0; zpeGaussK=0; zpePlusE=0; potentialE=0

# read progdyn.conf for configuration info
blankLineTester=10
while (blankLineTester>1) {
  getline < "progdyn.conf"
  if ($1=="method") method=$2
  if ($1=="charge") charge=$2
  if ($1=="multiplicity") multiplicity=$2
```

```
  if ($1=="memory") memory=$2
  if ($1=="processors") processors=$2
  if ($1=="checkpoint") checkpoint=$2
  if ($1=="diagnostics") diag=$2
  if ($1=="initialdis") initialDis=$2
  if ($1=="timestep") timestep=$2
  if ($1=="scaling") scaling=$2
  if ($1=="temperature") temp=$2
  if ($1=="searchdir") searchdir=$2
  if ($1=="classical") classical=$2
  if ($1=="numimag") numimag=$2
  if ($1=="geometry") geometry=$2
  if ($1=="highlevel") highlevel=$2
  if ($1=="boxon") boxon=$2
  if ($1=="boxsize") boxsize=$2
  if ($1=="DRP") DRP=$2; if (DRP==1) classical=2 #this lets one start a DRP from a
point that is not a freq calc
  if ($1=="maxAtomMove") maxAtomMove=$2
  if ($1=="cannonball") cannonball=$2
  if ($1=="displacements") disMode[$2]=$3
  if ($1=="controlphase") controlPhase[$2]=$3
  if ($1=="rotationmode") rotationmode=$2
  if ($1=="title") {
    title1=$2
    title2=$3
    title3=$4
    title4=$5
    }
  blankLineTester=length($0)
  }

if (diag>=1) print "***************** starting proggen *****************" >>
"diagnostics"
if (diag>=1) print "method,charge,multiplicity,memory" >> "diagnostics"
if (diag>=1) print method,charge,multiplicity,memory >> "diagnostics"
if (diag>=1) print "processors,checkpoint,title,initialdis,timestep,scaling,temperature" >>
"diagnostics"
if (diag>=1) print
processors,checkpoint,title1,title2,title3,title4,initialDis,timestep,scaling,temp >>
"diagnostics"
if (diag>=1) print
"classical,numimag,highlevel,boxon,boxsize,DRP,maxAtomMove,cannonball" >>
"diagnostics"
```

```
if (diag>=1) print
classical,numimag,highlevel,boxon,boxsize,DRP,maxAtomMove,cannonball >>
"diagnostics"

# put geometries into array, also figure out number of atoms
# note that this picks out the last geometry in a file, assuming
# that if there is an optimization followed by a freq, nothing else follows
# kludgy - repeats last line twice - must be a better way
do {
  getline < "tempstangeos"
  if (oldline==$0) $0=""
  oldline=$0
  atom = $1
  if (atom>numAtoms) numAtoms=atom
  atNum[atom]=$2
  geoArr[atom,1]=$4; geoArr[atom,2]=$5; geoArr[atom,3]=$6
  geoArrOrig[atom,1]=$4; geoArrOrig[atom,2]=$5; geoArrOrig[atom,3]=$6
  velArr[atom,1]=0; velArr[atom,2]=0; velArr[atom,3]=0
  }
while (length($0) > 0)

#output the number of atoms, used in many routines
print numAtoms

# put in atomic symbols and atomic weights - assigns a default mass but then reads it
from tempmasses when possible
for (i=1;i<=numAtoms;i++) {
  getline < "tempmasses"
  if (atNum[i]==1) {atSym[i]="H";atWeight[i]=1.00783}
  if (atNum[i]==2) {atSym[i]="He";atWeight[i]=4.0026}
  if (atNum[i]==3) {atSym[i]="Li";atWeight[i]=6.941}
  if (atNum[i]==4) {atSym[i]="Be";atWeight[i]=9.012}
  if (atNum[i]==5) {atSym[i]="B";atWeight[i]=10.811}
  if (atNum[i]==6) {atSym[i]="C";atWeight[i]=12.}
  if (atNum[i]==7) {atSym[i]="N";atWeight[i]=14.007}
  if (atNum[i]==8) {atSym[i]="O";atWeight[i]=15.9994}
  if (atNum[i]==9) {atSym[i]="F";atWeight[i]=18.9984}
  if (atNum[i]==10) {atSym[i]="Ne";atWeight[i]=20.1797}
  if (atNum[i]==11) {atSym[i]="Na";atWeight[i]=22.989}
  if (atNum[i]==12) {atSym[i]="Mg";atWeight[i]=24.305}
  if (atNum[i]==13) {atSym[i]="Al";atWeight[i]=26.98154}
  if (atNum[i]==14) {atSym[i]="Si";atWeight[i]=28.0855}
  if (atNum[i]==15) {atSym[i]="P";atWeight[i]=30.9738}
  if (atNum[i]==16) {atSym[i]="S";atWeight[i]=32.066}
```

```
  if (atNum[i]==17) {atSym[i]="Cl";atWeight[i]=35.4527}
  if (atNum[i]==18) {atSym[i]="Ar";atWeight[i]=39.948}
  if (atNum[i]==19) {atSym[i]="K";atWeight[i]=39.0983}
  if (atNum[i]==20) {atSym[i]="Ca";atWeight[i]=40.078}
  if (atNum[i]==21) {atSym[i]="Sc";atWeight[i]=44.96}
  if (atNum[i]==22) {atSym[i]="Ti";atWeight[i]=47.867}
  if (atNum[i]==23) {atSym[i]="V";atWeight[i]=50.94}
  if (atNum[i]==24) {atSym[i]="Cr";atWeight[i]=51.9961}
  if (atNum[i]==25) {atSym[i]="Mn";atWeight[i]=54.938}
  if (atNum[i]==26) {atSym[i]="Fe";atWeight[i]=55.845}
  if (atNum[i]==27) {atSym[i]="Co";atWeight[i]=58.933}
  if (atNum[i]==28) {atSym[i]="Ni";atWeight[i]=58.693}
  if (atNum[i]==29) {atSym[i]="Cu";atWeight[i]=63.546}
  if (atNum[i]==30) {atSym[i]="Zn";atWeight[i]=65.38}
  if (atNum[i]==31) {atSym[i]="Ga";atWeight[i]=69.723}
  if (atNum[i]==32) {atSym[i]="Ge";atWeight[i]=72.64}
  if (atNum[i]==33) {atSym[i]="As";atWeight[i]=74.9216}
  if (atNum[i]==34) {atSym[i]="Se";atWeight[i]=78.96}
  if (atNum[i]==35) {atSym[i]="Br";atWeight[i]=79.904}
  if (atNum[i]==46) {atSym[i]="Pd";atWeight[i]=106.42}
  if (atNum[i]==53) {atSym[i]="I";atWeight[i]=126.90447}
# gets actual weight from freqinHP when possible so a prior calc with readisotopes gets
you isotopic substitution
  if ((i<100) && ($9>0)) atWeight[i]=$9
#  if ((i>99) && ($8>0)) atWeight[i]=$8

  if ((diag>1) && (i==1)) print
"atNum[i],atSym[i],atWeight[i],geoArr[i,1],geoArr[i,2],geoArr[i,3]" >> "diagnostics"
  if (diag>1) print atNum[i],atSym[i],atWeight[i],geoArr[i,1],geoArr[i,2],geoArr[i,3] >>
"diagnostics"
  }

# read in frequencies, scale them, read in Reduced masses, read in force
#constants, replace negative frequencies by 2 wavenumbers
numFreq=3*numAtoms-6
if (geometry=="linear") numFreq=3*numAtoms-5
for (i=1;i<=numFreq;i++) {
  $0=""
  getline < "tempfreqs"
  freq[i]=$0*scaling
  if (freq[i]<0) freq[i]=2
  }
for (i=1;i<=numFreq;i++) {
  $0=""
```

```
  getline < "tempredmass"
  redMass[i]=$0
  if (redMass[i]=="") redMass[i]=1.
  }
for (i=1;i<=numFreq;i++) {
  $0=""
  getline < "tempfrc"
  frc[i]=$0
  if (frc[i]=="") frc[i]=0.0001
  if (frc[i]==0) frc[i]=0.0001
  if ((diag>1) && (i==1)) print "freq[i],redMass[i],frc[i]" >> "diagnostics"
  if (diag>1) print freq[i],redMass[i],frc[i] >> "diagnostics"
  }

# read in the modes - note that trajectories always need a freq calc with freq=hpmodes
unless classical=2
if (classical!=2) {
  for (i=1;i<=numFreq;i+=5) {
    for (j=1;j<=(3*numAtoms);j++) {
      getline < "tempmodes"
      mode[i,$2,$1]=$4; mode[i+1,$2,$1]=$5; mode[i+2,$2,$1]=$6;
mode[i+3,$2,$1]=$7; mode[i+4,$2,$1]=$8
      }
    }
  }
if (diag>2) {for (i=1;i<=numFreq;i++) {print mode[i,1,1],mode[i,1,2],mode[i,1,3] >>
"modesread"}}

# if doing a cannonball trajectory, read in the vector
if (cannonball>0) {
  for (i=1;i<=numAtoms;i++) {
    getline < "cannontraj"
    cannonArr[i,1]=$1; cannonArr[i,2]=$2; cannonArr[i,3]=$3
    }
  }

# collect a series of random numbers from file temp811, generated from an outside
random number generator called by prodynstarterHP
# read from temp811, starting at a random place
srand(PROCINFO["pid"]); tester=rand()*1000
for (i=1;i<=tester;i++) getline < "temp811"
for (i=1;i<=numFreq;i++) {
  getline < "temp811"; randArr[i]=$1
  getline < "temp811"; randArrB[i]=$1
```

```
  getline < "temp811"; randArrC[i]=$1
}
if (rotationmode>0) {
  for (i=1;i<=6;i++) {
    getline < "temp811"; randArrR[i]=$1
  }
}

# for a QM distribution for a harmonic oscillator in its ground state, we want to generate
a set of random numbers
#between -1 and 1 weighted such that numbers toward the center are properly more
common
i=1
while (i<=numFreq) {
  if ((initialDis==2) || (disMode[i]==2)) {
    getline < "temp811"
    tempNum=2*($1-.5)
    prob=exp(-(tempNum^2))
    getline < "temp811"
    if ($1<prob) {
      randArrD[i]=tempNum
      i++
      }
    }
  if ((initialDis!=2) && (disMode[i]!=2)) i++
  }

# to start without normal modes or frequencies we need to just pick a random direction
for the motion of each atom, requiring 3N random numbers
for (i=1;i<=numAtoms;i++) {
  for (j=1;j<=3;j++) {
  getline < "temp811"
  if ($1>0.5) randArrE[i,j]=1
  if ($1<.5) randArrE[i,j]=-1
    }
  }

# determine energy in each normal mode
for (i=1;i<=numFreq;i++) {
  zpeJ[i]=0.5*h*c*freq[i]      #units J per molecule
#if classical, treat as modes spaced by classicalSpacing wavenumbers
  if (classical==1) zpeJ[i]=0.5*h*c*classicalSpacing  # the zpe is not used when
classical but the spacing is used to calculate the E in mode
  zpeK[i]=zpeJ[i]*avNum/4184    #units kcal/mol
```

```
  if (temp<10) vibN[i]=0       # avoids working with very small temperatures - if the
temp is too low, it just acts like 0 K
  if (temp>=10) {
    zpeRat[i]=exp((-2*zpeK[i])/(RgasK*temp))
    if (zpeRat[i]==1) zpeRat[i]=.99999999999
    Q[i]=1/(1-zpeRat[i])
    newRand=randArr[i]
    vibN[i]=0
    tester=1/Q[i]
#    get up to 4000 excitations of low modes
    for (j=1;j<=(4000*zpeRat[i]+2);j++) {
      if (newRand>tester) vibN[i]++
      tester=tester+((zpeRat[i]^j)/Q[i])
      }
    }
  }

# figure out mode energies and maximum classical shift and then actual shift
# also calculated total energy desired for molecule
desiredModeEnK=0
for (i=1;i<=numFreq;i++) {
  modeEn[i]=(zpeJ[i]*1E18)*(2*vibN[i]+1) # units here are mDyne Ansgroms for
compatibility with Gaussian force constants
  if (classical==1) modeEn[i]=(zpeJ[i]*1E18)*2*vibN[i]   #no zpe when classical
  modeEnK[i]=zpeK[i]*(2*vibN[i]+1)
  if (classical==1) modeEnK[i]=zpeK[i]*2*vibN[i]        #no zpe when classical
  desiredModeEnK=desiredModeEnK + modeEnK[i]
# no 1/2 hv for imaginary frequencies
# treating modes with frequencies <10 as translations, ignoring their zero point energies
  if (freq[i]<10) modeEn[i]=(zpeJ[i]*1E18)*(2*vibN[i])
  maxShift[i]=(2*modeEn[i]/frc[i])^0.5
# new 2012 initialDis 3 means random phase of normal mode
  if (initialDis==3) shift[i]=maxShift[i]*sin(randArrC[i]*3.141592*2)
  if (initialDis==2) shift[i]=maxShift[i]*randArrD[i]
  if (initialDis==1) shift[i]=maxShift[i]*(2*(randArrC[i]-0.5))
  if (initialDis==0) shift[i]=0
# lines below allow for setting of displacement mode for individual modes
# It used to be necessary to use disMode 10 to turn off displacements for a mode, but
hopefully that bug is killed and you can use disMode 0
  if (disMode[i]==3) shift[i]=maxShift[i]*sin(randArrC[i]*3.141592*2)
  if (disMode[i]==2) shift[i]=maxShift[i]*randArrD[i]
  if (disMode[i]==1) shift[i]=maxShift[i]*(2*(randArrC[i]-0.5))
  if (disMode[i]==10) shift[i]=0 #kept for backward compatibility
  if (disMode[i]==0) shift[i]=0
```

```
# no displacements along imaginary frequencies and very low ones - it is better to treat
these
# as translations - employing a shift can give you initial weird geometries
  if (freq[i]<10) shift[i]=0
  if (numimag==1) shift[1]=0
  if (numimag==2) shift[2]=0
  }
for (i=1;i<=numFreq;i++) {
  if ((diag>1) && (i==1)) print
"zpeJ[i],zpeK[i],zpeRat[i],Q[i],vibN[i],modeEn[i],maxShift[i],shift[i]" >> "diagnostics"
  if (diag>1) print zpeJ[i],zpeK[i],zpeRat[i],Q[i],vibN[i],modeEn[i],maxShift[i],shift[i]
>> "diagnostics"
  }

# multiply each of the modes by its shift and add them up
# Do not do this if classical=2
if (classical!=2) {
  for (i=1;i<=numFreq;i++) {
    for (j=1;j<=numAtoms;j++) {
      for (k=1;k<=3;k++) {
        shiftMode[i,j,k]=mode[i,j,k]*shift[i]
        geoArr[j,k]=geoArr[j,k]+shiftMode[i,j,k]
        }
      }
    }
  }

#now start toward velocities
for (i=1;i<=numFreq;i++) {
  kinEn[i]=100000*(modeEn[i]-0.5*frc[i]*shift[i]^2)  # the 100000 converts to g
angstrom^2 s^2
  vel[i]=(2*kinEn[i]/(redMass[i]/avNum))^0.5       # in angstrom / s
#use searchdir in progdyn.conf to control the direction for trajectories started from a
saddle point
  if (numimag>1) numimag=1  #only the first freq can be sent in the searchdir direction,
the rest go in a random direction
  if (i>numimag) {
    if (randArrB[i]<0.5) vel[i]=-vel[i]
    }
  if (i==numimag) {
    if (searchdir=="negative") vel[i]=-vel[i]
    }
  if ((diag>1) && (i==1)) print "vel[i]" >> "diagnostics"
  if (diag>1) print vel[i] >> "diagnostics"
```

```
  }

# if controlphase is being used, set the velocity on particular modes as positive or
negative as requested
for (i=1;i<=numFreq;i++) {
  if ((controlPhase[i]=="positive") && (vel[i]<0)) vel[i]=-vel[i]
  if ((controlPhase[i]=="negative") && (vel[i]>0)) vel[i]=-vel[i]
  }

# multiply each of the modes by its velocity and add them up
# Do not do this if classical=2
if (classical!=2) {
  for (i=1;i<=numFreq;i++) {
    for (j=1;j<=numAtoms;j++) {
      for (k=1;k<=3;k++) {
        velMode[i,j,k]=mode[i,j,k]*vel[i]*timestep
        velArr[j,k]=velArr[j,k]+velMode[i,j,k]
        }
      }
    }
  }

# to start without normal modes or frequencies we figure out the energy per atom based
on 1/2RT in degree of freedom
if (classical==2) {
# to avoid a bug with a box on, starts without modes should use the input geometry, not
the standard
  do {
    getline < "tempinputgeos"
    if (oldline==$0) $0=""
    oldline=$0
    atom = $1
    geoArr[atom,1]=$4; geoArr[atom,2]=$5; geoArr[atom,3]=$6
    geoArrOrig[atom,1]=$4; geoArrOrig[atom,2]=$5; geoArrOrig[atom,3]=$6
    }
  while (length($0) > 0)
  degFreedomEnK=temp*RgasK
  degFreedomEnJ=degFreedomEnK/(avNum/4184)
  cartEn=degFreedomEnJ*1E18
  kinEnCart=100000*cartEn
#print degFreedomEnK, degFreedomEnJ, cartEn, kinEnCart
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
      velArr[i,j]=randArrE[i,j]*timestep*(2*kinEnCart/(atWeight[i]/avNum))^0.5
```

```
        if (DRP==1) velArr[i,j]=0
        }
      }
   }

# calculate the KE in the modes at this point
KEinitmodes=0
for (j=1;j<=numAtoms;j++) {
   KEinitmodes=KEinitmodes + 0.5*atWeight[j]*(velArr[j,1]^2 + velArr[j,2]^2 +
velArr[j,3]^2)/((timestep^2)*conver1)
   }

# add molecular rotation if requested
if (rotationmode>0) {
#establish three rotation vectors
   for (j=1;j<=numAtoms;j++) {
      rotateX[j,1]=0
      rotateX[j,2]=-geoArrOrig[j,3]
      rotateX[j,3]=geoArrOrig[j,2]
      rotateY[j,1]=-geoArrOrig[j,3]
      rotateY[j,2]=0
      rotateY[j,3]=geoArrOrig[j,1]
      rotateZ[j,1]=-geoArrOrig[j,2]
      rotateZ[j,2]=geoArrOrig[j,1]
      rotateZ[j,3]=0
      }
#figure out how much energy is in the raw vectors
   eRotX=0;eRotY=0;eRotZ=0
   for (j=1;j<=numAtoms;j++) {
      for (k=1;k<=3;k++) {
         eRotX=eRotX + 0.5*atWeight[j]*(rotateX[j,k]^2)/((timestep^2)*conver1)
         eRotY=eRotY + 0.5*atWeight[j]*(rotateY[j,k]^2)/((timestep^2)*conver1)
         eRotZ=eRotZ + 0.5*atWeight[j]*(rotateZ[j,k]^2)/((timestep^2)*conver1)
         }
      }
#  print "rotation energies if raw vector used",eRotX,eRotY,eRotZ
#now decide how much energy we want in each rotation
   keRx=-0.5*0.001987*temp*log(1-randArrR[1])
   keRy=-0.5*0.001987*temp*log(1-randArrR[2])
   keRz=-0.5*0.001987*temp*log(1-randArrR[3])
   if (eRotX<1) keRx=0;if (eRotY<1) keRy=0;if (eRotZ<1) keRz=0
   rotEdesired=keRx+keRy+keRz
   signX=1;signY=1;signZ=1
   if (randArrR[4]<.5) signX=-1
```

```
  if (randArrR[5]<.5) signY=-1
  if (randArrR[6]<.5) signZ=-1

#  print "desired energies",keRx,keRy,keRz,"and random
numbers",randArrR[1],randArrR[2],randArrR[3]
#protect against zero rotations
  if (eRotX<1) eRotX=1;if (eRotY<1) eRotY=1;if (eRotZ<1) eRotZ=1
#now scale the rotational vectors
  scaleX=(keRx/eRotX)^.5
  scaleY=(keRy/eRotY)^.5
  scaleZ=(keRz/eRotZ)^.5
#  print "scaling factors" scaleX,scaleY,scaleZ
  for (j=1;j<=numAtoms;j++) {
    for (k=1;k<=3;k++) {
      rotateX[j,k]=rotateX[j,k]*scaleX*signX
      rotateY[j,k]=rotateY[j,k]*scaleY*signY
      rotateZ[j,k]=rotateZ[j,k]*scaleZ*signZ
      }
    }
  for (j=1;j<=numAtoms;j++) {
#    print rotateX[j,1],"   ",rotateX[j,2],"   ",rotateX[j,3]
    }
#  print ""
  for (j=1;j<=numAtoms;j++) {
#    print rotateY[j,1],"   ",rotateY[j,2],"   ",rotateY[j,3]
    }
#  print ""
  for (j=1;j<=numAtoms;j++) {
#    print rotateZ[j,1],"   ",rotateZ[j,2],"   ",rotateZ[j,3]
    }
# now add the rotational vectors  to velArr
  for (j=1;j<=numAtoms;j++) {
    for (k=1;k<=3;k++) {
      velArr[j,k]=velArr[j,k]+rotateX[j,k]+rotateY[j,k]+rotateZ[j,k]
      }
    }
  }

# if doing a cannonball, adjust multiplier until extra energy is correct
if (cannonball>0) {
  multiplier=1; tester=0; tolerance=.1
  while (tester==0) {
    KEinittotal=0
    for (j=1;j<=numAtoms;j++) {
```

```
      cannonvelArr[j,1]=velArr[j,1]+multiplier*cannonArr[j,1];
cannonvelArr[j,2]=velArr[j,2]+multiplier*cannonArr[j,2];
cannonvelArr[j,3]=velArr[j,3]+multiplier*cannonArr[j,3]
      KEinittotal=KEinittotal + 0.5*atWeight[j]*(cannonvelArr[j,1]^2 +
cannonvelArr[j,2]^2 + cannonvelArr[j,3]^2)/((timestep^2)*conver1)
      }
    if (KEinittotal>(KEinitmodes+cannonball+tolerance))
multiplier=multiplier*0.98901364
    if (KEinittotal<(KEinitmodes+cannonball-tolerance)) multiplier=multiplier*1.01
    if ((KEinittotal<(KEinitmodes+cannonball+tolerance)) &&
(KEinittotal>(KEinitmodes+cannonball-tolerance))) tester=1
    }
  for (j=1;j<=numAtoms;j++) {
    velArr[j,1]=velArr[j,1]+multiplier*cannonArr[j,1];
velArr[j,2]=velArr[j,2]+multiplier*cannonArr[j,2];
velArr[j,3]=velArr[j,3]+multiplier*cannonArr[j,3]
    }
  }

#output the new geometry.
# ****** this section changed for special experiment for cyclopentadiene.  do not use
this for other cases
# atWeight[4]=140.0001
# ****** line below added for special experiment switching mass from 12 to 140,
keeping momenta the same
#velArr[4,1]=velArr[4,1]/11.66667; velArr[4,2]=velArr[4,2]/11.66667;
velArr[4,3]=velArr[4,3]/11.66667
for (j=1;j<=numAtoms;j++) {
  printf("%2s % .7f % .7f % .7f %9.5f
\n",atSym[j],geoArr[j,1],geoArr[j,2],geoArr[j,3],atWeight[j])
  }

#output the velocities and calculate the total kinetic energy overall
KEinittotal=0
for (j=1;j<=numAtoms;j++) {
  KEinittotal=KEinittotal + 0.5*atWeight[j]*(velArr[j,1]^2 + velArr[j,2]^2 +
velArr[j,3]^2)/((timestep^2)*conver1)
  printf("% .8f % .8f % .8f \n",velArr[j,1],velArr[j,2],velArr[j,3])
  }

#anything else I add to the file will not affect the trajectories but will keep a record and
be good for analysis
if (classical!=2) {
  for (i=1;i<=numFreq;i++) {
```

```
    if (initialDis==0) printf("%.6f  % .6f   %4i   % 1.4e      % .6f %1i\n", randArr[i],
randArrB[i], vibN[i], vel[i], shift[i], disMode[i])
    if (initialDis==1) printf("%.6f  % .6f   %4i   % 1.4e      % .6f %1i\n", randArr[i],
randArrC[i], vibN[i], vel[i], shift[i], disMode[i])
    if (initialDis==2) printf("%.6f  % .6f   %4i   % 1.4e      % .6f %1i\n", randArr[i],
randArrD[i], vibN[i], vel[i], shift[i], disMode[i])
    if (initialDis==3) printf("%.6f  % .6f   %4i   % 1.4e      % .6f %1i % .6f\n",
randArr[i], randArrC[i], vibN[i], vel[i], shift[i], disMode[i],
sin(randArrC[i]*3.141592*2))
    }
  }
print "temp ",temp
print "initialDis",initialDis
print "classical",classical
print "timestep",timestep
print "numimag",numimag
OFMT = "%.3f"
print "Total mode energy desired=",desiredModeEnK
print "KE initial from modes=",KEinitmodes,"   KE initial total=",KEinittotal,"
Rotational Energy desired=",rotEdesired
if (cannonball>0) print "cannonball",cannonball,"  cannon Energy=",KEinittotal-
KEinitmodes
if (boxon>0) print "boxsize",boxsize
if (DRP>0) print "DRP",DRP,"   maxAtomMove",maxAtomMove
if (DRP>0) print maxAtomMove > "maxMove"
}  # End of BEGIN

/Zero-point correction/ {zpeGauss=$3}
/zero-point Energies/ {zpePlusE=$7}
END {
zpeGaussK=zpeGauss*627.509
potentialE=zpePlusE - zpeGauss
OFMT = "%.6f"
print "Gaussian zpe=",zpeGauss,"or",zpeGaussK,"kcal/mol  E + zpe=",zpePlusE,"
potential E=",potentialE
print "" #will use blank line to mark end of geoPlusVel file
}

prog1stpoint
BEGIN {
# Nov 2016 Created
# this program creates the first input files for our homegrown ONIOM's first point

initializeparameters()
```

```
initializeconstants()
readprogdynconf()

getline < "isomernumber"
isomernum = $1
getline < "runpointnumber"
runpointnum = $1

if (diag>=1) diagnosticsA()
readgeoPlusVel() #this is different from prog2ndpoint and progdynb because we are just
getting the geometry, no velocities or old geos

writereal()
writemodel()
writeg09()
}

END {
}

################################################################# FUNCTIONS
######################################################
function Distance(Atom1,Atom2) {
  return sqrt((oldarr[Atom1,1]-oldarr[Atom2,1])^2+(oldarr[Atom1,2]-
oldarr[Atom2,2])^2+(oldarr[Atom1,3]-oldarr[Atom2,3])^2)
  }

# default parameters, including quassiclassical, no displacements, transition state, not a
DRP
# do not change these - rather, change progdyn.conf to set the parameters
function initializeparameters() {
  initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
  classical=0; numimag=1; DRP=0; cannonball=0
  memory=20000000
  diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
  boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
  title3="a"; title4="progdyn.conf"; processors=1; highlevel=99999; linkatoms=0
  damping=1;nonstandard=0;geometry="nonlinear";nonstandard=0
  nmrtype=0;nmrevery=9999999;nmrcc=0;nmrrand=0;nmrdo=0
  thermostat=0;thermostatemult=1.00
  oniomcharge=0; oniommult=1
  applyforce=0; applyforceB=0; applyforceC=0; zeroatomon=0
  sphereon=0; spheresize=999; sphereforceK=0.01
  empiricaldispersion=0; radiusmultiplier=1.25
```

```
  lowmethod="PM3";method="HF/3-21G"
  }

function initializeconstants() {
  srand(PROCINFO["pid"])
  i=1;j=1;k=1
  c=29979245800; h=6.626075E-34; avNum=6.0221415E23
  RgasK=0.00198588; RgasJ=8.31447; pi=3.14159265359
  numAtoms=0; atomnumber=0
  conver1=4.184E26 #dividing by this converts amu angs^2 /s^2 to kcal/mol
  OFS="   "
  }

# read progdyn.conf for configuration info
function readprogdynconf() {
  blankLineTester=10
  while (blankLineTester>1) {
    getline < "progdyn.conf"
    if ($1=="method") method=$2
    if ($1=="lowmethod") lowmethod=$2
    if ($1=="method2") meth2=$2
    if ($1=="charge") charge=$2
    if ($1=="multiplicity") multiplicity=$2
    if ($1=="oniomchargemult") { #this will be the charge and multiplicity for the small
model system - or else it will be 0 and 1
      oniomcharge=$2
      oniommult=$3
      }
    if ($1=="memory") memory=$2
    if ($1=="processors") processors=$2
    if ($1=="checkpoint") checkpoint=$2
    if ($1=="timestep") timestep=$2
    if ($1=="diagnostics") diag=$2
    if ($1=="temperature") temp=$2
    if ($1=="thermostat") thermostat=$2
    if ($1=="thermostatmult") thermostatmult=$2
    if (thermostatmult>1) thermostatmult=1/thermostatmult
    if ($1=="method3") meth3=$2
    if ($1=="method4") meth4=$2
    if ($1=="method5") meth5=$2
    if ($1=="method6") meth6=$2
    if ($1=="method7") meth7=$2
    if ($1=="highlevel") highlevel=$2
    if ($1=="linkatoms") linkatoms=$2
```

```
if ($1=="fixedatom1") fixedatom1=$2
if ($1=="fixedatom2") fixedatom2=$2
if ($1=="fixedatom3") fixedatom3=$2
if ($1=="fixedatom4") fixedatom4=$2
if ($1=="boxon") boxon=$2
if ($1=="boxsize") boxsize=$2
if ($1=="sphereon") sphereon=$2
if ($1=="spheresize") spheresize=$2
if ($1=="sphereforce") sphereforceK=$2
if ($1=="DRP") DRP=$2
if ($1=="maxAtomMove") maxAtomMove=$2
if ($1=="methodfile") methodfilelines=$2
if ($1=="killcheck") killcheck=$2
if ($1=="empiricaldispersion") empiricaldispersion=$2
if ($1=="radiusmultiplier") radiusmultiplier=$2
if ($1=="damping") damping=$2
if ($1=="NMRmethod") nmrmethod=$2
if ($1=="NMRmethod2") nmrmethod2=$2
if ($1=="NMRmethod3") nmrmethod3=$2
if ($1=="NMRtype") nmrtype=$2
if ($1=="NMRevery") nmrevery=$2
if ($1=="NMRrand") nmrrand=$2
if ($1=="loadlimit") loadlimit=$2
if ($1=="NMRcc") nmrcc=$2
if ($1=="nonstandard") nonstandard=$2
if ($1=="applyforce") {
  applyforce=$2; apforce=$3; apforceX0=$4; apforce2=$5; apforce3=$6
  }
if ($1=="applyforceB") {
  applyforceB=$2; apforceB=$3; apforceX0B=$4; apforce2B=$5; apforce3B=$6
  }
if ($1=="applyforceC") {
  applyforceC=$2; apforceC=$3; apforceX0C=$4; apforce2C=$5; apforce3C=$6
  }
if ($1=="afatoms") {
  for (i=1;i<8;i++) {
    if ($(i+1)>0) afatom[i]=$(i+1)
    }
  }
if ($1=="afatomsB") {
  for (i=1;i<8;i++) {
    if ($(i+1)>0) afatomB[i]=$(i+1)
    }
  }
```

```
    if ($1=="afatomsC") {
      for (i=1;i<8;i++) {
        if ($(i+1)>0) afatomC[i]=$(i+1)
        }
      }
    if ($1=="applyforceplane") {
      applyforceplane=$2; apforceplane=$3; apforceplaneX0=$4
      }
    if ($1=="afplaneatoms") {
      for (i=1;i<8;i++) {
        if ($(i+1)>0) afplaneatoms[i]=$(i+1)
        }
      }
    if ($1=="zeroatom") {
      zeroatomon=1
      zeroatom=$2
      }
    if ($1=="title") {
      title1=$2
      title2=$3
      title3=$4
      title4=$5
      }
    blankLineTester=length($0)
    }
  }

function diagnosticsA() {
  print "**************** starting progdynb ****************" >> "diagnostics"
  print "method,charge,multiplicity,memory" >> "diagnostics"
  print method,charge,multiplicity,memory >> "diagnostics"
  print "processors,checkpoint,title" >> "diagnostics"
  print processors,checkpoint,title1,title2,title3,title4 >> "diagnostics"
  }

function readgeoPlusVel() {
#this is different from prog2ndpoint and progdynb because we are just getting the geometry, no velocities or old geos
#read in number of atoms, geometry, masses from geoPlusVel
  getline < "geoPlusVel"
  numAtoms=$1
# geometry
  for (i=1;i<=numAtoms;i++) {
    getline < "geoPlusVel"
```

```
    weight[i]=$5
    atSym[i]=$1
    for (j=1;j<=3;j++) {
      geoArr[i,j]=$(1+j)
      }
    }
  blankLineTester=10
  while (blankLineTester>1) {
    getline < "geoPlusVel"
    if ($11=="potential") potentialE=$13
    blankLineTester=length($0)
    }
  }

function writereal() {
  print "XYZ GRADIENTS 1SCF PRTXYZ",lowmethod,"THREADS="
processors,"CHARGE=" charge
  print title1,title2,title3,title4,"runpoint ",runpointnum,"runisomer ",isomernum
  print ""
  for (i=1;i<=numAtoms;i++) {
    printf("%s %.7f %s %.7f %s %.7f %s
",atSym[i],geoArr[i,1],"1",geoArr[i,2],"1",geoArr[i,3],"1")
    print ""
    }
  print ""
  }

function writemodel() {
  print "XYZ GRADIENTS 1SCF PRTXYZ",method,"THREADS="
processors,"CHARGE=" oniomcharge > "model.mop"
  print title1,title2,title3,title4,"runpoint ",runpointnum,"runisomer ",isomernum >>
"model.mop"
  print "" >> "model.mop"
  if (highlevel>numAtoms) highlevel=numAtoms
  for (i=1;i<=highlevel;i++) {
    printf("%s %.7f %s %.7f %s %.7f %s
",atSym[i],geoArr[i,1],"1",geoArr[i,2],"1",geoArr[i,3],"1") >> "model.mop"
    print "" >> "model.mop"
    }
  print "" >> "model.mop"
  }

function writeg09() {
  print "%nproc=" processors > "g09.com"
```

```
  print "%mem=" memory >> "g09.com"
  if (killcheck!=1) print "%chk=" checkpoint >> "g09.com"
  if (nonstandard==0) {
    print "#p " method " force scf=(xqc,maxconven=155,fulllinear,nosym) " >>
"g09.com"
    if (meth2=="unrestricted") print "guess=mix" >> "g09.com" #for unrestricted
calculations
    if (length(meth3)>2) print meth3 >> "g09.com"
    if (length(meth4)>2) print meth4 >> "g09.com"
    }
  if (nonstandard==1) {
    print "# " >> "g09.com"
    print "nonstd"  >> "g09.com"
    system("cat nonstandard >> g09.com")
    }
  print "" >> "g09.com"
  print  title1,title2,title3,title4 >> "g09.com"
  print "runpoint ",runpointnum >> "g09.com"
  print "runisomer ",isomernum >> "g09.com"
  if (DRP==1) {
    print "maxForce and forceMult and
maxAtomMove",maxForce,forceMult,maxAtomMove >> "g09.com"
    print "maxForce and forceMult and
maxAtomMove",maxForce,forceMult,maxAtomMove >> "movelist"
    }
  print "" >> "g09.com"
  print oniomcharge,oniommult >> "g09.com"
  if (highlevel>numAtoms) highlevel=numAtoms
  for (i=1;i<=highlevel;i++) {
    printf("%s %.7f %.7f %.7f",atSym[i],geoArr[i,1],geoArr[i,2],geoArr[i,3]) >>
"g09.com"
    print "" >> "g09.com"
    }
  print "" >> "g09.com"
  if (length(meth5)>2) print meth5 >> "g09.com"
  if (length(meth6)>2) print meth6 >> "g09.com"
  if (methodfilelines>=1) {
    for (i=1;i<=methodfilelines;i++) {
      getline < "methodfile"
      print $0 >> "g09.com"
      }
    }
  print "" >> "g09.com"
  }
```

prog2ndpoint

```
BEGIN {
# Nov 2016 Created
# this program creates the input files for our homegrown ONIOM's second point

initializeparameters()
initializeconstants()
readprogdynconf()

getline < "isomernumber"
isomernum = $1
getline < "runpointnumber"
runpointnum = $1

if (diag>=1) diagnosticsA()

#get forward or reverse from skipstart if it exists
getline < "skipstart"
trajdirection = $1

readgeoPlusVel()
putPoint1Traj()
addVelocities()
} # end of BEGIN

#pull out the potential energy
/FINAL HEAT OF FORMATION/ {
if (basename(FILENAME)=="real.out") {
  newPotEK=newPotEK+$6
  newPotentialE=newPotEK/627.509
  }
if (basename(FILENAME)=="model.out") {
  newPotEK=newPotEK-$6
  newPotentialE=newPotEK/627.509
  }
}

/KCAL/ {
if (basename(FILENAME)=="real.out") {
  if ($5=="X") forceArr[$2,1]=forceArr[$2,1]-$7*0.52917725/627.509 #must translate
into Hartree/Bohr for other calcs to work
  if ($5=="Y") forceArr[$2,2]=forceArr[$2,2]-$7*0.52917725/627.509
  if ($5=="Z") forceArr[$2,3]=forceArr[$2,3]-$7*0.52917725/627.509
```

```
  }
if (basename(FILENAME)=="model.out") {
  if ($5=="X") forceArr[$2,1]=forceArr[$2,1]+$7*0.52917725/627.509 #must translate
into Hartree/Bohr for other calcs to work
  if ($5=="Y") forceArr[$2,2]=forceArr[$2,2]+$7*0.52917725/627.509
  if ($5=="Z") forceArr[$2,3]=forceArr[$2,3]+$7*0.52917725/627.509
  }
}

/SCF Done/ || /EUMP2 =/ || / Energy=/ || /ONIOM:/ {
if (basename(FILENAME)=="g09.log") {
  if (($1=="Energy=") && ($3=="NIter="))  newPotentialE=newPotentialE+$2
  if ($1=="SCF") newPotentialE=newPotentialE+$5  #This was subject to a bug at one
time - grep Samae in old files
  if ($2=="extrapolated")  newPotentialE=newPotentialE+$5
  if ($1=="E2") {
    tempstring=$6
    split(tempstring, arr10, "D")
    newPotentialE=newPotentialE+arr10[1]*(10^arr10[2])
    }
  newPotEK=(newPotentialE-potentialE)*627.509
  newPotentialEK=(newPotentialE-potentialE)*627.509
  }
}

# now we go ahead and collect the forces from the point 1 file
(/      1    / || /      2    / || /      3    / || /      4    / || /      5    / || /      6    / || /      7    / || /
8    / || /      9    / || /     10    / || /     11    / || /     12    / || /     13    / || /     14    / || /
15    / || /     16    / || /     17    / || /     18    / || /     19    / || /     20    / || /     21    / || /
22    / || /     23    / || /     24    / || /     25    / || /     26    / || /     27    / || /     28    / || /
29    / || /     30    / || /     31    / || /     32    / || /     33    / || /     34    / || /     35    /) &&
length($3) > 9 {
if (basename(FILENAME)=="g09.log") {
  i=$1
  for (j=1;j<=3;j++) {
    forceArr[i,j]=forceArr[i,j]+$(2+j)    #the raw units of the forces are Hartree/Bohr
    }
  if ((diag>1) && (i==1)) print "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]" >>
"diagnostics"
  if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >> "diagnostics"
  }
}

END {
```

```
if (DRP==0) doEcheck()
addForceEffect()
writereal()
writemodel()
writeg09()
writetraj()
}

######################################################################## FUNCTIONS
############################################################
function Distance(Atom1,Atom2) {
  return sqrt((oldarr[Atom1,1]-oldarr[Atom2,1])^2+(oldarr[Atom1,2]-
oldarr[Atom2,2])^2+(oldarr[Atom1,3]-oldarr[Atom2,3])^2)
  }

function basename(file) {
  sub(".*/", "", file)
  return file
}

# default parameters, including quassiclassical, no displacements, transition state, not a
DRP
# do not change these - rather, change progdyn.conf to set the parameters
function initializeparameters() {
  initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
  classical=0; numimag=1; DRP=0; cannonball=0
  memory=20000000
  diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
  boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
  title3="a"; title4="progdyn.conf"; processors=1; highlevel=99999; linkatoms=0
  damping=1;nonstandard=0;geometry="nonlinear";nonstandard=0
  nmrtype=0;nmrevery=9999999;nmrcc=0;nmrrand=0;nmrdo=0
  thermostat=0;thermostatemult=1.00
  oniomcharge=0; oniommult=0
  applyforce=0; applyforceB=0; applyforceC=0; zeroatomon=0
  sphereon=0; spheresize=999; sphereforceK=0.01
  empiricaldispersion=0; radiusmultiplier=1.25
  etolerance=1
  includeacceleration=1
  getline < "bypassproggen"
  if (($1>2) && ($1<999999999)) includeacceleration=0
  }

function initializeconstants() {
```

```
  srand(PROCINFO["pid"])
  i=1;j=1;k=1
  c=29979245800; h=6.626075E-34; avNum=6.0221415E23
  RgasK=0.00198588; RgasJ=8.31447; pi=3.14159265359
  numAtoms=0; atomnumber=0
  conver1=4.184E26 #dividing by this converts amu angs^2 /s^2 to kcal/mol
  OFS="   "
  }

# read progdyn.conf for configuration info
function readprogdynconf() {
  blankLineTester=10
  while (blankLineTester>1) {
    getline < "progdyn.conf"
    if ($1=="method") method=$2
    if ($1=="lowmethod") lowmethod=$2
    if ($1=="method2") meth2=$2
    if ($1=="charge") charge=$2
    if ($1=="multiplicity") multiplicity=$2
    if ($1=="oniomchargemult") {
      oniomcharge=$2
      oniommult=$3
      }
    if ($1=="memory") memory=$2
    if ($1=="processors") processors=$2
    if ($1=="checkpoint") checkpoint=$2
    if ($1=="timestep") timestep=$2
    if ($1=="diagnostics") diag=$2
    if ($1=="temperature") temp=$2
    if ($1=="thermostat") thermostat=$2
    if ($1=="thermostatmult") thermostatmult=$2
    if (thermostatmult>1) thermostatmult=1/thermostatmult
    if ($1=="method3") meth3=$2
    if ($1=="method4") meth4=$2
    if ($1=="method5") meth5=$2
    if ($1=="method6") meth6=$2
    if ($1=="method7") meth7=$2
    if ($1=="highlevel") highlevel=$2
    if ($1=="linkatoms") linkatoms=$2
    if ($1=="fixedatom1") fixedatom1=$2
    if ($1=="fixedatom2") fixedatom2=$2
    if ($1=="fixedatom3") fixedatom3=$2
    if ($1=="fixedatom4") fixedatom4=$2
    if ($1=="boxon") boxon=$2
```

```
if ($1=="boxsize") boxsize=$2
if ($1=="sphereon") sphereon=$2
if ($1=="spheresize") spheresize=$2
if ($1=="sphereforce") sphereforceK=$2
if ($1=="DRP") DRP=$2
if ($1=="maxAtomMove") maxAtomMove=$2
if ($1=="methodfile") methodfilelines=$2
if ($1=="killcheck") killcheck=$2
if ($1=="etolerance") etolerance=$2
if ($1=="reversetraj") reversetraj=$2
if ($1=="empiricaldispersion") empiricaldispersion=$2
if ($1=="radiusmultiplier") radiusmultiplier=$2
if ($1=="includeacceleration") includeacceleration=$2
if ($1=="damping") damping=$2
if ($1=="NMRmethod") nmrmethod=$2
if ($1=="NMRmethod2") nmrmethod2=$2
if ($1=="NMRmethod3") nmrmethod3=$2
if ($1=="NMRtype") nmrtype=$2
if ($1=="NMRevery") nmrevery=$2
if ($1=="NMRrand") nmrrand=$2
if ($1=="loadlimit") loadlimit=$2
if ($1=="NMRcc") nmrcc=$2
if ($1=="nonstandard") nonstandard=$2
if ($1=="applyforce") {
  applyforce=$2; apforce=$3; apforceX0=$4; apforce2=$5; apforce3=$6
  }
if ($1=="applyforceB") {
  applyforceB=$2; apforceB=$3; apforceX0B=$4; apforce2B=$5; apforce3B=$6
  }
if ($1=="applyforceC") {
  applyforceC=$2; apforceC=$3; apforceX0C=$4; apforce2C=$5; apforce3C=$6
  }
if ($1=="afatoms") {
  for (i=1;i<8;i++) {
    if ($(i+1)>0) afatom[i]=$(i+1)
    }
  }
if ($1=="afatomsB") {
  for (i=1;i<8;i++) {
    if ($(i+1)>0) afatomB[i]=$(i+1)
    }
  }
if ($1=="afatomsC") {
  for (i=1;i<8;i++) {
```

```
        if ($(i+1)>0) afatomC[i]=$(i+1)
        }
      }
    if ($1=="applyforceplane") {
      applyforceplane=$2; apforceplane=$3; apforceplaneX0=$4
      }
    if ($1=="afplaneatoms") {
      for (i=1;i<8;i++) {
        if ($(i+1)>0) afplaneatoms[i]=$(i+1)
        }
      }
    if ($1=="zeroatom") {
      zeroatomon=1
      zeroatom=$2
      }
    if ($1=="title") {
      title1=$2
      title2=$3
      title3=$4
      title4=$5
      }
    blankLineTester=length($0)
    }
  }

function diagnosticsA() {
  print "**************** starting progdynb ****************" >> "diagnostics"
  print "method,charge,multiplicity,memory" >> "diagnostics"
  print method,charge,multiplicity,memory >> "diagnostics"
  print "processors,checkpoint,title" >> "diagnostics"
  print processors,checkpoint,title1,title2,title3,title4 >> "diagnostics"
  }

function readgeoPlusVel() {
#this is different from prog1stpoint and progdynb because we are just getting velocities
#read in number of atoms, geometry, masses from geoPlusVel
  getline < "geoPlusVel"
  numAtoms=$1
# geometry
  for (i=1;i<=numAtoms;i++) {
    getline < "geoPlusVel"
    weight[i]=$5
    atSym[i]=$1
    for (j=1;j<=3;j++) {
```

```
        geoArr[i,j]=$(1+j)
        }
      }
#velocities
  for (i=1;i<=numAtoms;i++) {
    getline < "geoPlusVel"
    for (j=1;j<=3;j++) {
      velArr[i,j]=$j
      }
    }
#pull out other information useful for testing whether total energy is right or bad
  blankLineTester=10
  while (blankLineTester>1) {
    getline < "geoPlusVel"
    if ($4=="desired=") desiredModeEnK=$5
    if ($4=="modes=") {
      KEinitmodes=$5
      KEinittotal=$9
      }
    if ($11=="potential") potentialE=$13
    blankLineTester=length($0)
    }
  }

function addVelocities() {
# ok, now we have to figure the second point.  this should be
# x(t) = x + v*t + 1/2*F*t^2/m
#now we go ahead and add the velocities
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
      arr[i,j]=velArr[i,j]+geoArr[i,j]
      if (trajdirection=="reverserestart") arr[i,j]=geoArr[i,j]-velArr[i,j]
      }
    if ((diag>1) && (i==1)) print "geometry after adding velocities" >> "diagnostics"
    if (diag>1) print arr[i,1],arr[i,2],arr[i,3] >> "diagnostics"
    }
  }

function putPoint1Traj() {
#get initial geometry into file traj
  print numAtoms >> "traj"
  print potentialE,title1,title2,title3,title4,"runpoint 1 ","runisomer ",isomernum >> "traj"
  for (i=1;i<=numAtoms;i++) {
    print atSym[i],geoArr[i,1],geoArr[i,2],geoArr[i,3] >> "traj"
```

```
    }
  }

function doEcheck() {
  print "trajectory #",isomernum >> "Echeck"
  print "point 1 potential E=",newPotentialEK,"   point 1 kinetic E=",KEinitmodes,"
Total=",newPotentialEK+KEinitmodes >> "Echeck"
  print "desired total energy=", desiredModeEnK >> "Echeck"
  if ((newPotentialEK+KEinitmodes)>(desiredModeEnK+etolerance)) print "XXXX bad
total Energy" >> "Echeck"
  if ((newPotentialEK+KEinitmodes)<(desiredModeEnK-etolerance)) print "XXXX bad
total Energy" >> "Echeck"
  }

function addForceEffect() {
# x(t) = x + v*t + 1/2*F*t^2/m
# turn the forces into motion
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
# conversions here take force to J/angstrom, 1E20 converts to kg angstroms / s^2, then
mult time (s^s) and divide by weight in kg to get angstroms

forceArr[i,j]=0.5*1E20*forceArr[i,j]*627.509*(4184/(0.529177*avNum))*(timestep^2)/
(weight[i]/(avNum*1000))
# for simplicity, DRPs will throw away the forces at the second pont.  This means that if
we are not at a saddlepoint, point 2 = point 1 but this is a minor waste
# restarts using bypassproggen should also normally use no acceleration so that the
second point is exactly what it was in the starting structure
# but if this is a rerun then it should - set this by putting in parameter includeacceleration
      if (DRP==1) forceArr[i,j]=0
      arr[i,j]=arr[i,j]+includeacceleration*forceArr[i,j]
# if atoms are fixed, replace calcd new position by original position
      if ((i==fixedatom1) || (i==fixedatom2) || (i==fixedatom3) || (i==fixedatom4))
arr[i,j]=geoArr[i,j]
      }
    if ((diag>1) && (i==1)) print "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]"
>> "diagnostics"
    if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >> "diagnostics"
    }
  }

function writereal() {
  print "XYZ GRADIENTS 1SCF PRTXYZ",lowmethod,"THREADS="
processors,"CHARGE=" charge
```

```
  print title1,title2,title3,title4,"runpoint ",runpointnum,"runisomer ",isomernum
  print ""
  for (i=1;i<=numAtoms;i++) {
    printf("%s %.7f %s %.7f %s %.7f %s ",atSym[i],arr[i,1],"1",arr[i,2],"1",arr[i,3],"1")
    print ""
    }
  print ""
  }

function writemodel() {
  print "XYZ GRADIENTS 1SCF PRTXYZ",method,"THREADS="
processors,"CHARGE=" oniomcharge > "model.mop"
  print title1,title2,title3,title4,"runpoint ",runpointnum,"runisomer ",isomernum >>
"model.mop"
  print "" >> "model.mop"
  if (highlevel>numAtoms) highlevel=numAtoms
  for (i=1;i<=highlevel;i++) {
    printf("%s %.7f %s %.7f %s %.7f %s ",atSym[i],arr[i,1],"1",arr[i,2],"1",arr[i,3],"1")
>> "model.mop"
    print "" >> "model.mop"
    }
  print "" >> "model.mop"
  }

function writeg09() {
  print "%nproc=" processors > "g09.com"
  print "%mem=" memory >> "g09.com"
  if (killcheck!=1) print "%chk=" checkpoint >> "g09.com"
  if (nonstandard==0) {
    print "#p " method " force scf=(xqc,maxconven=155,fulllinear,nosym) " >>
"g09.com"
    if (meth2=="unrestricted") print "guess=mix" >> "g09.com" #for unrestricted
calculations
    if (length(meth3)>2) print meth3 >> "g09.com"
    if (length(meth4)>2) print meth4 >> "g09.com"
    }
  if (nonstandard==1) {
    print "# " >> "g09.com"
    print "nonstd"  >> "g09.com"
    system("cat nonstandard >> g09.com")
    }
  print "" >> "g09.com"
  print  title1,title2,title3,title4 >> "g09.com"
  print "runpoint ",runpointnum >> "g09.com"
```

```
  print "runisomer ",isomernum >> "g09.com"
  if (DRP==1) {
    print "maxForce and forceMult and
maxAtomMove",maxForce,forceMult,maxAtomMove >> "g09.com"
    print "maxForce and forceMult and
maxAtomMove",maxForce,forceMult,maxAtomMove >> "movelist"
    }
  print "" >> "g09.com"
  print oniomcharge,oniommult >> "g09.com"
  if (highlevel>numAtoms) highlevel=numAtoms
  for (i=1;i<=highlevel;i++) {
    printf("%s %.7f %.7f %.7f",atSym[i],arr[i,1],arr[i,2],arr[i,3]) >> "g09.com"
    print "" >> "g09.com"
    }
  print "" >> "g09.com"
  if (length(meth5)>2) print meth5 >> "g09.com"
  if (length(meth6)>2) print meth6 >> "g09.com"
  if (methodfilelines>=1) {
    for (i=1;i<=methodfilelines;i++) {
      getline < "methodfile"
      print $0 >> "g09.com"
      }
    }
  print "" >> "g09.com"
  }

function writetraj() {
#get second geometry into file traj
  print numAtoms >> "traj"
  print newPotentialE,title1,title2,title3,title4,"runpoint ",runpointnum,"runisomer
",isomernum >> "traj"
  for (i=1;i<=numAtoms;i++) {
    print atSym[i],arr[i,1],arr[i,2],arr[i,3] >> "traj"
    }
  }

progdynb
BEGIN { #this is the main routine for generating new .com files by the Verlet
algorithym
# Nov 2016 created for progdynONIOM

initializeparameters()
initializeconstants()
readprogdynconf()
```

```
getline < "isomernumber"
isomernum = $1
getline < "runpointnumber"
runpointnum = $1

if (diag>=1) diagnosticsA()
readgeoPlusVelAndoldAndolder() #readgeoPlusVelAndoldAndolder sets numAtoms,
weight[i], atSym[i], potentialE, oldarr[at,1to3], olderarr[at,1to3]
        # also sets apparentTemp,  KEold, does sanitycheck
if (DRP==1) readoldAdjForcesAndmaxMove() #for DRPs read in oldForce[at,123] and
maxAtomMove
nmrstuffA() # sets nmrdo to 0 or 1, controls where NMR calcs are done
}
########################  END OF BEGIN
####################################

#pull out the potential energy
/FINAL HEAT OF FORMATION/ {
if (basename(FILENAME)=="real.out") {
  newPotEK=newPotEK+$6
  newPotentialE=newPotEK/627.509
  }
if (basename(FILENAME)=="model.out") {
  newPotEK=newPotEK-$6
  newPotentialE=newPotEK/627.509
  }
}

/KCAL/ {
if (basename(FILENAME)=="real.out") {
#  if (($2==2) && ($5=="X")) print
FILENAME,$0,forceArr[$2,1],forceArr[$2,2],forceArr[$2,1] >> "forcelist"
  if ($5=="X") forceArr[$2,1]=forceArr[$2,1]-$7*0.52917725/627.509 #must translate
into Hartree/Bohr for other calcs to work
  if ($5=="Y") forceArr[$2,2]=forceArr[$2,2]-$7*0.52917725/627.509
  if ($5=="Z") forceArr[$2,3]=forceArr[$2,3]-$7*0.52917725/627.509
#  if (($2==2) && ($5=="Z")) print
FILENAME,$0,forceArr[$2,1],forceArr[$2,2],forceArr[$2,1] >> "forcelist"
  }
if (basename(FILENAME)=="model.out") {
#  if (($2==2) && ($5=="X")) print
FILENAME,$0,forceArr[$2,1],forceArr[$2,2],forceArr[$2,1] >> "forcelist"
```

```
  if ($5=="X") forceArr[$2,1]=forceArr[$2,1]+$7*0.52917725/627.509 #must translate
into Hartree/Bohr for other calcs to work
  if ($5=="Y") forceArr[$2,2]=forceArr[$2,2]+$7*0.52917725/627.509
  if ($5=="Z") forceArr[$2,3]=forceArr[$2,3]+$7*0.52917725/627.509
#  if (($2==2) && ($5=="Z")) print
FILENAME,$0,forceArr[$2,1],forceArr[$2,2],forceArr[$2,1] >> "forcelist"
  }
}

/SCF Done/ || /EUMP2 =/ || / Energy=/ || /ONIOM:/ {
if (basename(FILENAME)=="g09.log") {
  if (($1=="Energy=") && ($3=="NIter="))  newPotentialE=newPotentialE+$2
  if ($1=="SCF") newPotentialE=newPotentialE+$5  #This was subject to a bug at one
time - grep Samae in old files
  if ($2=="extrapolated")  newPotentialE=newPotentialE+$5
  if ($1=="E2") {
    tempstring=$6
    split(tempstring, arr10, "D")
    newPotentialE=newPotentialE+arr10[1]*(10^arr10[2])
    }
  newPotEK=(newPotentialE-potentialE)*627.509
  newPotentialEK=(newPotentialE-potentialE)*627.509
  }
}

(/      1    / || /      2    / || /      3    / || /      4    / || /      5    / || /      6    / || /      7    / || /
8    / || /      9    / || /     10    / || /     11    / || /     12    / || /     13    / || /     14    / || /
15    / || /     16    / || /     17    / || /     18    / || /     19    / || /     20    / || /     21    / || /
22    / || /     23    / || /     24    / || /     25    / || /     26    / || /     27    / || /     28    / || /
29    / || /     30    / || /     31    / || /     32    / || /     33    / || /     34    / || /     35    /) &&
length($3) > 9 {
if (basename(FILENAME)=="g09.log") {
  i=$1
  for (j=1;j<=3;j++) {
    forceArr[i,j]=forceArr[i,j]+$(2+j)    #the raw units of the forces are Hartree/Bohr
    }
  if ((diag>1) && (i==1)) print "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]" >>
"diagnostics"
  if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >> "diagnostics"
  }
}

END {
```

```
if (sphereon==1) applysphereforce() # apply a force to bring atoms within a sphere.
This also figures out the density at 0.9*spheresize
# routines to apply forces between atoms, used for umbrella sampling
if (applyforceplane>0) doapplyforceplane() #used to apply a force on an atom versus its
distance from a plane
setinterlockingsphereatom() #apply force to one of a series of atoms, whichever is
closest to afatom[1]
if (applyforce>0) doapplyforce()
if (applyforceB>0) doapplyforceB()
if (applyforceC>0) doapplyforceC()
if (s6!=0) doempiricaldispersion()
if (s6b!=0) {
  s6=s6b; radiusmultiplier=radiusmultiplierb; EdispHtotal=0
  doempiricaldispersion()
  }
if (zeroatomon==1) dozeroatom() #routine to slowly move an atom toward the origin
if (specialforce>0) dospecialforce()
if (thermostat==1) dothermostat()
if (DRP==1) doDRP() #routine for steepest descent path in mass weighted coordinates
if (DRP==0) doVerlet() #normal routine for Verlet
writereal()
writemodel()
writeg09()
writetraj()
}

################################################################ FUNCTIONS
####################################################
function Distance(Atom1,Atom2) {
  return sqrt((oldarr[Atom1,1]-oldarr[Atom2,1])^2+(oldarr[Atom1,2]-
oldarr[Atom2,2])^2+(oldarr[Atom1,3]-oldarr[Atom2,3])^2)
  }

function basename(file) {
  sub(".*/", "", file)
  return file
}

# default parameters, including quassiclassical, no displacements, transition state, not a
DRP
# do not change these - rather, change progdyn.conf to set the parameters
function initializeparameters() {
  initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
  classical=0; numimag=1; DRP=0; cannonball=0
```

```
  memory=20000000
  diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
  boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
  title3="a"; title4="progdyn.conf"; processors=1; highlevel=99999; linkatoms=0
  damping=1;nonstandard=0
  nmrtype=0;nmrevery=9999999;nmrcc=0;nmrrand=0;nmrdo=0
  thermostat=0;thermostatemult=1.00
  oniomcharge=0; oniommult=0
  applyforce=0; applyforceB=0; applyforceC=0; zeroatomon=0
  sphereon=0; spheresize=999; sphereforceK=0.01
  s6=0; radiusmultiplier=1.0; s6b=0; radiusmultiplierb=1.0
  EdispHtotal=0; specialforce=0
  }

function initializeconstants() {
  srand(PROCINFO["pid"])
  i=1;j=1;k=1
  c=29979245800; h=6.626075E-34; avNum=6.0221415E23
  RgasK=0.00198588; RgasJ=8.31447; pi=3.14159265359
  numAtoms=0; atomnumber=0
  conver1=4.184E26 #dividing by this converts amu angs^2 /s^2 to kcal/mol
  OFS="   "
  }

# read progdyn.conf for configuration info
function readprogdynconf() {
  blankLineTester=10
  while (blankLineTester>1) {
    getline < "progdyn.conf"
    if ($1=="method") method=$2
    if ($1=="lowmethod") lowmethod=$2
    if ($1=="method2") meth2=$2
    if ($1=="charge") charge=$2
    if ($1=="multiplicity") multiplicity=$2
    if ($1=="oniomchargemult") {
      oniomcharge=$2
      oniommult=$3
      }
    if ($1=="memory") memory=$2
    if ($1=="processors") processors=$2
    if ($1=="checkpoint") checkpoint=$2
    if ($1=="timestep") timestep=$2
    if ($1=="diagnostics") diag=$2
    if ($1=="temperature") temp=$2
```

```
if ($1=="thermostat") thermostat=$2
if ($1=="thermostatmult") thermostatmult=$2
if (thermostatmult>1) thermostatmult=1/thermostatmult
if ($1=="method3") meth3=$2
if ($1=="method4") meth4=$2
if ($1=="method5") meth5=$2
if ($1=="method6") meth6=$2
if ($1=="method7") meth7=$2
if ($1=="highlevel") highlevel=$2
if ($1=="linkatoms") linkatoms=$2
if ($1=="fixedatom1") fixedatom1=$2
if ($1=="fixedatom2") fixedatom2=$2
if ($1=="fixedatom3") fixedatom3=$2
if ($1=="fixedatom4") fixedatom4=$2
if ($1=="boxon") boxon=$2
if ($1=="boxsize") boxsize=$2
if ($1=="sphereon") sphereon=$2
if ($1=="spheresize") spheresize=$2
if ($1=="sphereforce") sphereforceK=$2
if ($1=="DRP") DRP=$2
if ($1=="maxAtomMove") maxAtomMove=$2
if ($1=="methodfile") methodfilelines=$2
if ($1=="killcheck") killcheck=$2
if ($1=="empiricaldispersion") s6=$2
if ($1=="radiusmultiplier") radiusmultiplier=$2
if ($1=="empiricaldispersionb") s6b=$2
if ($1=="radiusmultiplierb") radiusmultiplierb=$2
if ($1=="damping") damping=$2
if ($1=="NMRmethod") nmrmethod=$2
if ($1=="NMRmethod2") nmrmethod2=$2
if ($1=="NMRmethod3") nmrmethod3=$2
if ($1=="NMRtype") nmrtype=$2
if ($1=="NMRevery") nmrevery=$2
if ($1=="NMRrand") nmrrand=$2
if ($1=="loadlimit") loadlimit=$2
if ($1=="NMRcc") nmrcc=$2
if ($1=="nonstandard") nonstandard=$2
if ($1=="specialforce") specialforce=$2
if ($1=="applyforce") {
  applyforce=$2; apforce=$3; apforceX0=$4; apforce2=$5; apforce3=$6
  }
if ($1=="applyforceB") {
  applyforceB=$2; apforceB=$3; apforceX0B=$4; apforce2B=$5; apforce3B=$6
  }
```

```
    if ($1=="applyforceC") {
      applyforceC=$2; apforceC=$3; apforceX0C=$4; apforce2C=$5; apforce3C=$6
      }
    if ($1=="afatoms") {
      for (i=1;i<8;i++) {
        if ($(i+1)>0) afatom[i]=$(i+1)
        }
      }
    if ($1=="afatomsB") {
      for (i=1;i<8;i++) {
        if ($(i+1)>0) afatomB[i]=$(i+1)
        }
      }
    if ($1=="afatomsC") {
      for (i=1;i<8;i++) {
        if ($(i+1)>0) afatomC[i]=$(i+1)
        }
      }
    if ($1=="applyforceplane") {
      applyforceplane=$2; apforceplane=$3; apforceplaneX0=$4
      }
    if ($1=="afplaneatoms") {
      for (i=1;i<8;i++) {
        if ($(i+1)>0) afplaneatoms[i]=$(i+1)
        }
      }
    if ($1=="zeroatom") {
      zeroatomon=1
      zeroatom=$2
      }
    if ($1=="title") {
      title1=$2
      title2=$3
      title3=$4
      title4=$5
      }
    blankLineTester=length($0)
    }
  }

function diagnosticsA() {
  print "**************** starting progdynb ****************" >> "diagnostics"
  print "method,charge,multiplicity,memory" >> "diagnostics"
  print method,charge,multiplicity,memory >> "diagnostics"
```

```
  print "processors,checkpoint,title" >> "diagnostics"
  print processors,checkpoint,title1,title2,title3,title4 >> "diagnostics"
  }

function readgeoPlusVelAndoldAndolder() {
# get number of atoms and weights from geoPlusVel, and previous geometries from old
and older
  getline < "geoPlusVel"
  numAtoms=$1
  for (i=1;i<=numAtoms;i++) {
    getline < "geoPlusVel"
    weight[i]=$5; atSym[i]=$1
    }
  blankLineTester=10
  while (blankLineTester>1) {
    getline < "geoPlusVel"
    if ($11=="potential") potentialE=$13
    blankLineTester=length($0)
    }

  for (at=1;at<=numAtoms;at++) {
    getline < "old"
    oldarr[at,1]=$3; oldarr[at,2]=$5; oldarr[at,3]=$7
    }

  for (at=1;at<=numAtoms;at++) {
    getline < "older"
    olderarr[at,1]=$3; olderarr[at,2]=$5; olderarr[at,3]=$7
    atomVel=((oldarr[at,1]-olderarr[at,1])^2 + (oldarr[at,2]-olderarr[at,2])^2
+(oldarr[at,3]-olderarr[at,3])^2)^.5
    KEold=KEold+0.5*weight[at]*(atomVel^2)/((timestep^2)*conver1)
# sanity check - avoids trajectory blow up
    if (atomVel>0.5) exit
    }
  apparentTemp=KEold*2/(3*RgasK*numAtoms) # this is not the temperature at the
previous point but rather 1.5 points back.
# sanity check - avoids trajectory blow up
  for (at=1;at<=numAtoms;at++) {
    if (((oldarr[at,1]-olderarr[at,1])^2)>1) exit
    }
  }

function readoldAdjForcesAndmaxMove() {
#for DRPs read in oldAdjForces and maxAtomMove
```

```
  for (at=1;at<=numAtoms;at++) {
    getline < "oldAdjForces"
    oldForce[at,1]=$1; oldForce[at,2]=$2; oldForce[at,3]=$3
    }
  getline < "maxMove"
  if (($1<maxAtomMove) && ($1>0)) maxAtomMove=$1
  if (maxAtomMove<0.000001) maxAtomMove=0.000001
  }

function nmrstuffA() {
# sets nmrdo to 0 or 1, controls where NMR calcs are done
  if ((nmrrand==0) && ((runpointnum % nmrevery)==0)) nmrdo=1
  if ((nmrrand==1) && (rand()<(1/nmrevery))) nmrdo=1
  getline < "uptimelist"
  x=1.0001*substr($10,1,3);if (x<8) x=8
# turn of nmrs if load is too high - this is under control of loadlimit parameter in
progdyn.conf and requires proganal to make uptimelist
  if ((nmrrand==1) && (x>loadlimit)) nmrdo=0
  }

function applysphereforce() {
# apply a force to bring atoms within a sphere.   This also figures out the density at
0.9*spheresize
# We are going through the loop twice, the first time figure outs the total pressure, then
scales the forces to limit the pressure to maxpressure
# the second time actually applies the pressure
  maxpressure=100000 #atmospheres.  Later we may parameterize this. Setting this
really high eliminates the first scaling
  sphereforcetotal=0
  for (i=1;i<=numAtoms;i++) {
    distToOrig=((oldarr[i,1]^2+oldarr[i,2]^2+oldarr[i,3]^2)^.5)
    if (distToOrig>spheresize) {
      sphereforce=sphereforceK*(distToOrig-spheresize)
      if (sphereforce>0.01) sphereforce=0.01 #important limit on force for atoms far
outside of the sphere, not sure if value chosen is best
      sphereforcetotal=sphereforcetotal+sphereforce
      }
    }
  sphereforcetotalNewtons=sphereforcetotal*627.509*4184*1E10/(0.529177*avNum)
  surfaceareaSqMeters=4*pi*spheresize^2/1E20
  pressurePascal=sphereforcetotalNewtons/surfaceareaSqMeters
  pressureAtm=pressurePascal/101325
  if (pressureAtm>maxpressure) sphereforceK=sphereforceK*maxpressure/pressureAtm
# go through the loop again
```

```
  sphereforcetotal=0; totalweight=0
  for (i=1;i<=numAtoms;i++) {
    distToOrig=((oldarr[i,1]^2+oldarr[i,2]^2+oldarr[i,3]^2)^.5)
    if (distToOrig>spheresize) {
      sphereforce=sphereforceK*(distToOrig-spheresize)
      if (sphereforce>0.01) sphereforce=0.01 #important limit on force for atoms far
outside of the sphere, not sure if value chosen is best
      sphereforcetotal=sphereforcetotal+sphereforce

unitX=sphereforce*oldarr[i,1]/distToOrig;unitY=sphereforce*oldarr[i,2]/distToOrig;unit
Z=sphereforce*oldarr[i,3]/distToOrig
      forceArr[i,1]=forceArr[i,1]-unitX;forceArr[i,2]=forceArr[i,2]-
unitY;forceArr[i,3]=forceArr[i,3]-unitZ
      }
# calculate the density at 0.9*spheresize
    if (distToOrig<0.9*spheresize) {
      totalweight=totalweight+weight[i]
      }
    }
#recalculate pressure
  sphereforcetotalNewtons=sphereforcetotal*627.509*4184*1E10/(0.529177*avNum)
  surfaceareaSqMeters=4*pi*spheresize^2/1E20
  pressurePascal=sphereforcetotalNewtons/surfaceareaSqMeters
  pressureAtm=pressurePascal/101325
  density=(totalweight/avNum)/((4/3)*pi*(0.9*spheresize*1E-8)^3)
  }

function doapplyforceplane() {
#used to apply a force on an atom versus its distance from a plane
  if (afplaneatoms[4]<.5) {
    print "you need more atoms to define a plane"
    exit
    }
  for (i=2;i<8;i++) {
    if (afplaneatoms[i]>.5) {
      k=afplaneatoms[i]

A[1,1]=A[1,1]+oldarr[k,1]^2;A[1,2]=A[1,2]+oldarr[k,1]*oldarr[k,2];A[1,3]=A[1,3]+old
arr[k,1]

A[2,1]=A[2,1]+oldarr[k,1]*oldarr[k,2];A[2,2]=A[2,2]+oldarr[k,2]^2;A[2,3]=A[2,3]+old
arr[k,2]
      A[3,1]=A[3,1]+oldarr[k,1];A[3,2]=A[3,2]+oldarr[k,2];A[3,3]++
```

```
b[1]=b[1]+oldarr[k,1]*oldarr[k,3];b[2]=b[2]+oldarr[k,2]*oldarr[k,3];b[3]=b[3]+oldarr[k,
3]
# find center of mass assuming all atoms same weight

cmass[1]=cmass[1]+oldarr[k,1];cmass[2]=cmass[2]+oldarr[k,2];cmass[3]=cmass[3]+old
arr[k,3];
      }
    }
  numplaneatoms=A[3,3]
  cmass[1]=cmass[1]/A[3,3];cmass[2]=cmass[2]/A[3,3];cmass[3]=cmass[3]/A[3,3]
#   print "matrix A"
#   for (i=1;i<=3;i++) {
#     print A[i,1],A[i,2],A[i,3]
#     }
#   print "matrix b"
#   print b[1],b[2],b[3]
  Det=A[1,1]*A[2,2]*A[3,3]+A[1,2]*A[2,3]*A[3,1]+A[1,3]*A[2,1]*A[3,2]-
A[1,3]*A[2,2]*A[3,1]-A[1,2]*A[2,1]*A[3,3]-A[1,1]*A[2,3]*A[3,2]
  E=(b[1]*A[2,2]*A[3,3]+A[1,2]*A[2,3]*b[3]+A[1,3]*b[2]*A[3,2]-
A[1,3]*A[2,2]*b[3]-A[1,2]*b[2]*A[3,3]-b[1]*A[2,3]*A[3,2])/Det
  F=(A[1,1]*b[2]*A[3,3]+b[1]*A[2,3]*A[3,1]+A[1,3]*A[2,1]*b[3]-
A[1,3]*b[2]*A[3,1]-b[1]*A[2,1]*A[3,3]-A[1,1]*A[2,3]*b[3])/Det
  G=(A[1,1]*A[2,2]*b[3]+A[1,2]*b[2]*A[3,1]+b[1]*A[2,1]*A[3,2]-
b[1]*A[2,2]*A[3,1]-A[1,2]*A[2,1]*b[3]-A[1,1]*b[2]*A[3,2])/Det
#  E, F, and G are the coefficients in the plane z=Ex+Fy+G"
# make a function that tests the fit
  for (i=2;i<8;i++) {
    if (afplaneatoms[i]>.5) {
      k=afplaneatoms[i]
      distplane=(-oldarr[k,1]*E-oldarr[k,2]*F+oldarr[k,3]-G)/(E^2+F^2+1)^.5;if
(distplane<0) distplane=-distplane
      aberror=aberror+distplane
      }
    }
# if the fit is bad, as can happen, decrease to 3 atoms in plane, using only the first three
atoms in list after the conatom
  if (aberror>2) {
    print "original aberror",aberror >> "diagnostics"

A[1,1]=0;A[1,2]=0;A[1,3]=0;A[2,1]=0;A[2,2]=0;A[2,3]=0;A[3,1]=0;A[3,2]=0;A[3,3]=0
    for (i=2;i<5;i++) {
      k=afplaneatoms[i]
```

```
A[1,1]=A[1,1]+oldarr[k,1]^2;A[1,2]=A[1,2]+oldarr[k,1]*oldarr[k,2];A[1,3]=A[1,3]+old
arr[k,1]

A[2,1]=A[2,1]+oldarr[k,1]*oldarr[k,2];A[2,2]=A[2,2]+oldarr[k,2]^2;A[2,3]=A[2,3]+old
arr[k,2]
      A[3,1]=A[3,1]+oldarr[k,1];A[3,2]=A[3,2]+oldarr[k,2];A[3,3]++

b[1]=b[1]+oldarr[k,1]*oldarr[k,3];b[2]=b[2]+oldarr[k,2]*oldarr[k,3];b[3]=b[3]+oldarr[k,
3]
      }
    Det=A[1,1]*A[2,2]*A[3,3]+A[1,2]*A[2,3]*A[3,1]+A[1,3]*A[2,1]*A[3,2]-
A[1,3]*A[2,2]*A[3,1]-A[1,2]*A[2,1]*A[3,3]-A[1,1]*A[2,3]*A[3,2]
    E=(b[1]*A[2,2]*A[3,3]+A[1,2]*A[2,3]*b[3]+A[1,3]*b[2]*A[3,2]-
A[1,3]*A[2,2]*b[3]-A[1,2]*b[2]*A[3,3]-b[1]*A[2,3]*A[3,2])/Det
    F=(A[1,1]*b[2]*A[3,3]+b[1]*A[2,3]*A[3,1]+A[1,3]*A[2,1]*b[3]-
A[1,3]*b[2]*A[3,1]-b[1]*A[2,1]*A[3,3]-A[1,1]*A[2,3]*b[3])/Det
    G=(A[1,1]*A[2,2]*b[3]+A[1,2]*b[2]*A[3,1]+b[1]*A[2,1]*A[3,2]-
b[1]*A[2,2]*A[3,1]-A[1,2]*A[2,1]*b[3]-A[1,1]*b[2]*A[3,2])/Det
    aberror=0
    for (i=2;i<5;i++) {
      k=afplaneatoms[i]
      distplane=(-oldarr[k,1]*E-oldarr[k,2]*F+oldarr[k,3]-G)/(E^2+F^2+1)^.5;if
(distplane<0) distplane=-distplane
      aberror=aberror+distplane
      }
    }
  conatom=afplaneatoms[1]
  distplane=(-oldarr[conatom,1]*E-oldarr[conatom,2]*F+oldarr[conatom,3]-
G)/(E^2+F^2+1)^.5
  if (distplane<0) distplane=-distplane
  t=(oldarr[conatom,1]*E+oldarr[conatom,2]*F-oldarr[conatom,3]+G)/(E^2+F^2+1)
  planepoint[1]=oldarr[conatom,1]-t*E;planepoint[2]=oldarr[conatom,2]-
t*F;planepoint[3]=oldarr[conatom,3]+t
  distcmass=((planepoint[1]-cmass[1])^2+(planepoint[2]-cmass[2])^2+(planepoint[3]-
cmass[3])^2)^.5
  print
"distplane",distplane,"t",t,"planepoint",planepoint[1],planepoint[2],planepoint[3],"distcm
ass",distcmass,"aberror",aberror >> "diagnostics"
  if (distcmass>1.4) {
    vector[1]=planepoint[1]-cmass[1];vector[2]=planepoint[2]-
cmass[2];vector[3]=planepoint[3]-cmass[3]
```

```
vector[1]=vector[1]*1.4/distcmass;vector[2]=vector[2]*1.4/distcmass;vector[3]=vector[
3]*1.4/distcmass

planepoint[1]=cmass[1]+vector[1];planepoint[2]=cmass[2]+vector[2];planepoint[3]=cm
ass[3]+vector[3];
    distcmass=((planepoint[1]-cmass[1])^2+(planepoint[2]-cmass[2])^2+(planepoint[3]-
cmass[3])^2)^.5
    distplane=((planepoint[1]-oldarr[conatom,1])^2+(planepoint[2]-
oldarr[conatom,2])^2+(planepoint[3]-oldarr[conatom,3])^2)^.5
    print "new
distplane",distplane,"newplanepoint",planepoint[1],planepoint[2],planepoint[3],"newdist
cmass",distcmass >> "diagnostics"
    }
  delX=oldarr[conatom,1]-planepoint[1];delY=oldarr[conatom,2]-
planepoint[2];delZ=oldarr[conatom,3]-planepoint[3]
  if (applyforceplane==2) apforceplane=apforceplane*(distplane-apforceplaneX0)

unitX=apforceplane*delX/distplane;unitY=apforceplane*delY/distplane;unitZ=apforcep
lane*delZ/distplane
  forceArr[conatom,1]=forceArr[conatom,1]-
unitX;forceArr[conatom,2]=forceArr[conatom,2]-
unitY;forceArr[conatom,3]=forceArr[conatom,3]-unitZ
  for (i=2;i<8;i++) {
    if (afplaneatoms[i]>.5) {
      platom=afplaneatoms[i]

forceArr[platom,1]=forceArr[platom,1]+unitX/numplaneatoms;forceArr[platom,2]=forc
eArr[platom,2]+unitY/numplaneatoms;forceArr[platom,3]=forceArr[platom,3]+unitZ/nu
mplaneatoms
      }
    }
  }

function setinterlockingsphereatom() {
#apply force to one of a series of atoms, whichever is closest to afatom[1]
  for (i=3;i<8;i++) {
    if (afatom[i]>0) {
      if(Distance(afatom[1],afatom[i])<Distance(afatom[1],afatom[2]))
afatom[2]=afatom[i]
      }
    if (afatomB[i]>0) {
      if(Distance(afatomB[1],afatomB[i])<Distance(afatomB[1],afatomB[2]))
afatomB[2]=afatomB[i]
```

```
      }
    if (afatomC[i]>0) {
      if(Distance(afatomC[1],afatomC[i])<Distance(afatomC[1],afatomC[2]))
afatomC[2]=afatomC[i]
      }
    }
  }

function doapplyforce() {
# applyforce 1 puts a linear constant force.
# applyforce 2 puts on a harmonic restoring force to apforceX0
  delX=oldarr[afatom[1],1]-oldarr[afatom[2],1];delY=oldarr[afatom[1],2]-
oldarr[afatom[2],2];delZ=oldarr[afatom[1],3]-oldarr[afatom[2],3];
  distatoms=(delX^2+delY^2+delZ^2)^.5
  if (applyforce==2) apforce=apforce*(distatoms-apforceX0)
  if (applyforce==3) apforce=apforce*(distatoms-apforceX0) + apforce2*(distatoms-
apforceX0)^2
  if (applyforce==4) apforce=apforce*(distatoms-apforceX0) + apforce2*(distatoms-
apforceX0)^2 + apforce3*(distatoms-apforceX0)^3

unitX=apforce*delX/distatoms;unitY=apforce*delY/distatoms;;unitZ=apforce*delZ/dist
atoms;
  forceArr[afatom[1],1]=forceArr[afatom[1],1]-
unitX;forceArr[afatom[1],2]=forceArr[afatom[1],2]-
unitY;forceArr[afatom[1],3]=forceArr[afatom[1],3]-unitZ

forceArr[afatom[2],1]=forceArr[afatom[2],1]+unitX;forceArr[afatom[2],2]=forceArr[afa
tom[2],2]+unitY;forceArr[afatom[2],3]=forceArr[afatom[2],3]+unitZ
  }

function doapplyforceB() {
  delX=oldarr[afatomB[1],1]-oldarr[afatomB[2],1];delY=oldarr[afatomB[1],2]-
oldarr[afatomB[2],2];delZ=oldarr[afatomB[1],3]-oldarr[afatomB[2],3];
  distatoms=(delX^2+delY^2+delZ^2)^.5
  if (applyforceB==2) apforceB=apforceB*(distatoms-apforceX0B)
  if (applyforceB==3) apforceB=apforceB*(distatoms-apforceX0B) +
apforce2B*(distatoms-apforceX0B)^2
  if (applyforceB==4) apforceB=apforceB*(distatoms-apforceX0B) +
apforce2B*(distatoms-apforceX0B)^2 + apforce3B*(distatoms-apforceX0B)^3

unitX=apforceB*delX/distatoms;unitY=apforceB*delY/distatoms;;unitZ=apforceB*delZ
/distatoms;
```

```
  forceArr[afatomB[1],1]=forceArr[afatomB[1],1]-
unitX;forceArr[afatomB[1],2]=forceArr[afatomB[1],2]-
unitY;forceArr[afatomB[1],3]=forceArr[afatomB[1],3]-unitZ

forceArr[afatomB[2],1]=forceArr[afatomB[2],1]+unitX;forceArr[afatomB[2],2]=forceA
rr[afatomB[2],2]+unitY;forceArr[afatomB[2],3]=forceArr[afatomB[2],3]+unitZ
  }

function doapplyforceC() {
  delX=oldarr[afatomC[1],1]-oldarr[afatomC[2],1];delY=oldarr[afatomC[1],2]-
oldarr[afatomC[2],2];delZ=oldarr[afatomC[1],3]-oldarr[afatomC[2],3];
  distatoms=(delX^2+delY^2+delZ^2)^.5
  if (applyforceC==2) apforceC=apforceC*(distatoms-apforceX0C)
  if (applyforceC==3) apforceC=apforceC*(distatoms-apforceX0C) +
apforce2C*(distatoms-apforceX0C)^2
  if (applyforceC==4) apforceC=apforceC*(distatoms-apforceX0C) +
apforce2C*(distatoms-apforceX0C)^2 + apforce3C*(distatoms-apforceX0C)^3

unitX=apforceC*delX/distatoms;unitY=apforceC*delY/distatoms;;unitZ=apforceC*delZ
/distatoms;
  forceArr[afatomC[1],1]=forceArr[afatomC[1],1]-
unitX;forceArr[afatomC[1],2]=forceArr[afatomC[1],2]-
unitY;forceArr[afatomC[1],3]=forceArr[afatomC[1],3]-unitZ

forceArr[afatomC[2],1]=forceArr[afatomC[2],1]+unitX;forceArr[afatomC[2],2]=forceA
rr[afatomC[2],2]+unitY;forceArr[afatomC[2],3]=forceArr[afatomC[2],3]+unitZ
  }

function doempiricaldispersion() {
  for (i=1;i<=numAtoms;i++) {
    if (atSym[i]=="H") {c6[i]=0.14;r0[i]=1.001}
#    if (atSym[i]=="H") {c6[i]=0.16;r0[i]=1.11}
    if (atSym[i]=="He") {c6[i]=0.08;r0[i]=1.012}
    if (atSym[i]=="Li") {c6[i]=1.61;r0[i]=0.825}
    if (atSym[i]=="Be") {c6[i]=1.61;r0[i]=1.408}
    if (atSym[i]=="B") {c6[i]=3.13;r0[i]=1.485}
    if (atSym[i]=="C") {c6[i]=1.75;r0[i]=1.452}
#    if (atSym[i]=="C") {c6[i]=1.65;r0[i]=1.61}
    if (atSym[i]=="N") {c6[i]=1.23;r0[i]=1.397}
#    if (atSym[i]=="N") {c6[i]=1.11;r0[i]=1.55}
    if (atSym[i]=="O") {c6[i]=0.70;r0[i]=1.342}
#    if (atSym[i]=="O") {c6[i]=0.70;r0[i]=1.49}
    if (atSym[i]=="F") {c6[i]=0.75;r0[i]=1.287}
    if (atSym[i]=="Ne") {c6[i]=0.63;r0[i]=1.243}
```

```
    if (atSym[i]=="Na") {c6[i]=5.71;r0[i]=1.144}
    if (atSym[i]=="Mg") {c6[i]=5.71;r0[i]=1.364}
    if (atSym[i]=="Al") {c6[i]=10.79;r0[i]=1.639}
    if (atSym[i]=="Si") {c6[i]=9.23;r0[i]=1.716}
    if (atSym[i]=="P") {c6[i]=7.84;r0[i]=1.705}
    if (atSym[i]=="S") {c6[i]=5.57;r0[i]=1.683}
    if (atSym[i]=="Cl") {c6[i]=5.07;r0[i]=1.639}
#    if (atSym[i]=="Cl") {c6[i]=8.00;r0[i]=1.82}
    if (atSym[i]=="Ar") {c6[i]=4.61;r0[i]=1.595}
    if (atSym[i]=="K") {c6[i]=10.8;r0[i]=1.485}
    if (atSym[i]=="Ca") {c6[i]=10.8;r0[i]=1.474}
    if (atSym[i]=="Sc") {c6[i]=10.8;r0[i]=1.562}
    if (atSym[i]=="Ti") {c6[i]=10.8;r0[i]=1.562}
    if (atSym[i]=="V") {c6[i]=10.8;r0[i]=1.562}
    if (atSym[i]=="Cr") {c6[i]=10.8;r0[i]=1.562}
    if (atSym[i]=="Mn") {c6[i]=10.8;r0[i]=1.562}
    if (atSym[i]=="Fe") {c6[i]=10.8;r0[i]=1.562}
    if (atSym[i]=="Co") {c6[i]=10.8;r0[i]=1.562}
    if (atSym[i]=="Ni") {c6[i]=10.8;r0[i]=1.562}
    if (atSym[i]=="Cu") {c6[i]=10.8;r0[i]=1.562}
    if (atSym[i]=="Zn") {c6[i]=10.8;r0[i]=1.562}
    if (atSym[i]=="Ga") {c6[i]=16.99;r0[i]=1.65}
    if (atSym[i]=="Ge") {c6[i]=17.10;r0[i]=1.727}
    if (atSym[i]=="As") {c6[i]=16.37;r0[i]=1.76}
    if (atSym[i]=="Se") {c6[i]=12.64;r0[i]=1.771}
    if (atSym[i]=="Br") {c6[i]=12.47;r0[i]=1.749}
    if (atSym[i]=="Pd") {c6[i]=24.67;r0[i]=1.639}
    if (atSym[i]=="I") {c6[i]=31.5;r0[i]=1.892}
    r0[i]=r0[i]*radiusmultiplier
    }
  for (i=1;i<numAtoms;i++) {
#the line below turns off empirical dispersion for within the solute, since this is best
handled with the high-level method
    jstart=i+1;if (jstart<highlevel+1) jstart=highlevel+1
    for (j=jstart;j<=numAtoms;j++) {
      Rij=Distance(i,j)
      if (Rij<8) { #cutoff of 8 angstroms to save time - later this can be parameterized
#need to get units of force to Hartrees/Bohr, since that is the units of forceArr
        EdispK=Edisp(c6[i],c6[j],Rij,r0[i],r0[j])*1E6/4184 #in kcal/mol
        FdispK=Fdisp(c6[i],c6[j],Rij,r0[i],r0[j])*1E6/4184 #in kcal/mol per angstrom
        EdispH=EdispK/627.509
        EdispHtotal=EdispHtotal+EdispH
        FdispHB=FdispK*0.52917725/627.509
```

```
#          print i,j,Cij,Rij,r0[i],r0[j],fdmp,"     ",EdispK,FdispK,"
",EdispH,FdispHB,EdispHtotal
        delX=oldarr[i,1]-oldarr[j,1];delY=oldarr[i,2]-oldarr[j,2];delZ=oldarr[i,3]-
oldarr[j,3];
        unitX=FdispHB*delX/Rij;unitY=FdispHB*delY/Rij;;unitZ=FdispHB*delZ/Rij;

forceArr[i,1]=forceArr[i,1]+unitX;forceArr[i,2]=forceArr[i,2]+unitY;forceArr[i,3]=force
Arr[i,3]+unitZ
        forceArr[j,1]=forceArr[j,1]-unitX;forceArr[j,2]=forceArr[j,2]-
unitY;forceArr[j,3]=forceArr[j,3]-unitZ
        }
      }
    }
  print "Total empirical Dispersion Energy in Hartrees",EdispHtotal,"  in
kcal/mol",EdispHtotal*627.509 >> "diagnostics"
  newPotentialE=newPotentialE+EdispHtotal
  }

function Edisp(c6i,c6j,rij,r0i,r0j) {
  cij=(c6i*c6j)^.5
  fdmp=1/(1+exp(-20*((rij/(r0i+r0j)-1))))
  return -s6*cij*fdmp/(rij^6)
  }

function Fdisp(c6i,c6j,rij,r0i,r0j) {
  delta=0.001
  return (Edisp(c6i,c6j,rij-delta,r0i,r0j)-Edisp(c6i,c6j,rij+delta,r0i,r0j))/(2*delta)
  }

function dozeroatom() {
#routine to slowly move an atom toward the origin as set by a harmonic potential
  multiple=0.99996
  oldarr[zeroatom,1]=multiple*oldarr[zeroatom,1]
  oldarr[zeroatom,2]=multiple*oldarr[zeroatom,2]
  oldarr[zeroatom,3]=multiple*oldarr[zeroatom,3]
  }

#reprogram as needed, but take care
function dospecialforce() {
  for (i=45;i<numAtoms;i++) {
    if (atSym[i]=="H") {
      j=9
      Rij=Distance(i,j)
      if (Rij<2.1) {
```

```
          delX=oldarr[i,1]-oldarr[j,1];delY=oldarr[i,2]-oldarr[j,2];delZ=oldarr[i,3]-
oldarr[j,3];
          FdispHB=specialforce*(2.1-Rij)
          unitX=FdispHB*delX/Rij;unitY=FdispHB*delY/Rij;;unitZ=FdispHB*delZ/Rij;

forceArr[i,1]=forceArr[i,1]+unitX;forceArr[i,2]=forceArr[i,2]+unitY;forceArr[i,3]=force
Arr[i,3]+unitZ
          forceArr[j,1]=forceArr[j,1]-unitX;forceArr[j,2]=forceArr[j,2]-
unitY;forceArr[j,3]=forceArr[j,3]-unitZ
#          print "unitX",unitX,"unitY",unitY,"unitZ",unitZ >> "diagnostics"
          }
        }
      }
  }

function dothermostat() {
#print out some things to vellist and do thermostat
# the damping in the thermostat is based on temperature based on old geo vs older geo
  if (diag<4) print "KEold",KEold,"desired temperature",temp,"apparent
Temperature",apparentTemp >> "vellist"
  if (apparentTemp>temp) damping=thermostatmult
  if (apparentTemp<temp) damping=1/thermostatmult
  }

function doDRP() {
#routine for DRPs
  maxForce=0;oscillTest=0
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
# conversions here take force to J/angstrom, 1E20 converts to kg angstroms / s^2, then
mult time (s^s) and divide by weight in kg to get angstroms

forceArr[i,j]=1E20*forceArr[i,j]*627.509*(4184/(0.529177*avNum))*(timestep^2)/(wei
ght[i]/(avNum*1000))
      oscillTest=oscillTest+forceArr[i,j]*oldForce[i,j]
      if (forceArr[i,j]>maxForce) maxForce=forceArr[i,j]
      if ((0-forceArr[i,j])>maxForce) maxForce=-forceArr[i,j]
      }
    if (i==1) printf("% .8f % .8f % .8f \n",forceArr[1,1],forceArr[1,2],forceArr[1,3])  >
"oldAdjForces"
    if (i>1) printf("% .8f % .8f % .8f \n",forceArr[i,1],forceArr[i,2],forceArr[i,3])  >>
"oldAdjForces"
    }
  print "oscillTest ",oscillTest >> "oldAdjForces"
```

```
  if (oscillTest<0) {
    maxAtomMove = maxAtomMove*0.5
    print maxAtomMove > "maxMove"
    }
  if (oscillTest>0) {
    maxAtomMove = maxAtomMove*1.2
    print maxAtomMove > "maxMove"
    }
  print "maxAtomMove ",maxAtomMove >> "oldAdjForces"
  forceMult=maxAtomMove/maxForce
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
      newarr[i,j]=oldarr[i,j]+forceMult*forceArr[i,j]
      }
    }
  }

function doVerlet() {
#normal routine for Verlet
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
# conversions here take force to J/angstrom, 1E20 converts to kg angstroms / s^2, then
mult time (s^s) and divide by weight in kg to get angstroms

forceArr[i,j]=1E20*forceArr[i,j]*627.509*(4184/(0.529177*avNum))*(timestep^2)/(wei
ght[i]/(avNum*1000))
#       if ((diag>1) && (i==1)) print "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]"
>> "diagnostics"
#       if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >>
"diagnostics"
# examine old motion.  If an atom is moving in a crazy way then say so in diagnostics
      oldmotion=damping*(oldarr[i,j]-olderarr[i,j])
      motionlimit=0.04
      if ((oldmotion>motionlimit) || (oldmotion<-1*motionlimit)) {
        print "Atom",i,"is moving",oldmotion,"in dimension",j,"in old motion" >>
"diagnostics"
#          oldmotion=oldmotion/2; print "**** Non-production motion" >> "diagnostics"
# only uncomment for non-production to move atoms while limiting massive disruptions
        }
      newarr[i,j]=oldarr[i,j]+oldmotion+forceArr[i,j]
      if ((i==fixedatom1) || (i==fixedatom2) || (i==fixedatom3) || (i==fixedatom4))
newarr[i,j]=oldarr[i,j]
#turn around atoms outside the box
      if (boxon==1) {
```

```
          if (newarr[i,j]>boxsize) if (oldarr[i,j]>olderarr[i,j])
newarr[i,j]=oldarr[i,j]+damping*(olderarr[i,j]-oldarr[i,j])+forceArr[i,j]
          if (newarr[i,j]<-1*boxsize) if (oldarr[i,j]<olderarr[i,j])
newarr[i,j]=oldarr[i,j]+damping*(olderarr[i,j]-oldarr[i,j])+forceArr[i,j]
          }
        }
      }
#calculate the kinetic energy.  This is for the point prior to the current point.  Corrected
calculation
   for (at=1;at<=numAtoms;at++) {
     atomVel=(((olderarr[at,1]-newarr[at,1])^2 + (olderarr[at,2]-newarr[at,2])^2
+(olderarr[at,3]-newarr[at,3])^2)^.5)/2
     KEnew=KEnew+0.5*weight[at]*(atomVel^2)/((timestep^2)*conver1)
     }
     KEave=KEnew # we used to average with KEold but that is incorrect.  This is better.
     Etotal=newPotEK+KEave
#still basing apparent Temperature on velocities from old vs older, even though the KE
now represents an average of old and new
     if (diag==4) print runpointnum,"KEave",KEave,"apparent
Temperature",apparentTemp,"newPotEK",newPotEK,"Etotal",Etotal,"pressure in
Atm",pressureAtm,"density in 0.9r",density >> "vellist"
   }

function writetraj() {
   print numAtoms >> "traj"
   print newPotentialE,title1,title2,title3,title4,"runpoint ",runpointnum,"runisomer
",isomernum >> "traj"
   for (i=1;i<=numAtoms;i++) {
     printf("%s %.7f %.7f %.7f",atSym[i],newarr[i,1],newarr[i,2],newarr[i,3]) >> "traj"
     print "" >> "traj"
     }
   }

function writereal() {
   print "XYZ GRADIENTS 1SCF PRTXYZ",lowmethod,"THREADS="
processors,"CHARGE=" charge
   print title1,title2,title3,title4,"runpoint ",runpointnum,"runisomer ",isomernum
   print ""
   for (i=1;i<=numAtoms;i++) {
     printf("%s %.7f %s %.7f %s %.7f %s
",atSym[i],newarr[i,1],"1",newarr[i,2],"1",newarr[i,3],"1")
     print ""
     }
   print ""
```

```
  }

function writemodel() {
  print "XYZ GRADIENTS 1SCF PRTXYZ",lowmethod,"THREADS="
processors,"CHARGE=" oniomcharge > "model.mop"
  print title1,title2,title3,title4,"runpoint ",runpointnum,"runisomer ",isomernum >>
"model.mop"
  print "" >> "model.mop"
  if (highlevel>numAtoms) highlevel=numAtoms
  for (i=1;i<=highlevel;i++) {
    printf("%s %.7f %s %.7f %s %.7f %s
",atSym[i],newarr[i,1],"1",newarr[i,2],"1",newarr[i,3],"1") >> "model.mop"
    print "" >> "model.mop"
    }
  print "" >> "model.mop"
  }

function writeg09() {
  print "%nproc=" processors > "g09.com"
  print "%mem=" memory >> "g09.com"
  if (killcheck!=1) print "%chk=" checkpoint >> "g09.com"
  if (nonstandard==0) {
    print "#p " method " force scf=(xqc,maxconven=155,fulllinear,nosym) " >>
"g09.com"
    if (meth2=="unrestricted") print "guess=mix" >> "g09.com" #for unrestricted
calculations
    if (length(meth3)>2) print meth3 >> "g09.com"
    if (length(meth4)>2) print meth4 >> "g09.com"
    if (length(meth5)>2) print meth5 >> "g09.com"
    }
  if (nonstandard==1) {
    print "# " >> "g09.com"
    print "nonstd"  >> "g09.com"
    system("cat nonstandard >> g09.com")
    }
  print "" >> "g09.com"
  print  title1,title2,title3,title4 >> "g09.com"
  print "runpoint ",runpointnum >> "g09.com"
  print "runisomer ",isomernum >> "g09.com"
  if (DRP==1) {
    print "maxForce and forceMult and
maxAtomMove",maxForce,forceMult,maxAtomMove >> "g09.com"
    print "maxForce and forceMult and
maxAtomMove",maxForce,forceMult,maxAtomMove >> "movelist"
```

```
      }
   print "" >> "g09.com"
   print oniomcharge,oniommult >> "g09.com"
   if (highlevel>numAtoms) highlevel=numAtoms
   for (i=1;i<=highlevel;i++) {
      printf("%s %.7f %.7f %.7f",atSym[i],newarr[i,1],newarr[i,2],newarr[i,3]) >>
"g09.com"
      print "" >> "g09.com"
      }
   print "" >> "g09.com"
   if (length(meth6)>2) print meth6 >> "g09.com"
   if (length(meth7)>2) print meth7 >> "g09.com"
   if (methodfilelines>=1) {
      for (i=1;i<=methodfilelines;i++) {
         getline < "methodfile"
         print $0 >> "g09.com"
         }
      }
   print "" >> "g09.com"
   }
```

Program proganal used for 80-THF product-forming trajectories (using ProgdynONIOM)

```
BEGIN {
firsttitle=1
getline < "isomernumber"
isomer=$1
}
/ hydroboration/ {
   if (firsttitle==1) {
      printf("%s %s %s %s %s %s %s  ",$1,$2,$3,$4,$6,$7,$8)
      runpoint=$6
      }
   firsttitle++
   }
/ATOM   CHEMICAL          X  /,/CARTESIAN COORDINATES/ {
   if (($1>.5) && ($1<99)) {
      A[$1]=$3;B[$1]=$5;C[$1]=$7
```

```
    }
  }

END {
BC1=Distance(1,2)
BC2=Distance(1,3)
HC1=Distance(14,2)
if (Distance(15,2)<HC1) HC1=Distance(15,2)
if (Distance(16,2)<HC1) HC1=Distance(16,2)
HC2=Distance(14,3)
if (Distance(15,3)<HC2) HC2=Distance(15,3)
if (Distance(16,3)<HC2) HC2=Distance(16,3)
  printf("%s %.3f %s %.3f %s %.3f %s %.3f
","BC1",BC1,"BC2",BC2,"HC1",HC1,"HC2",HC2)
  if (runpoint>500000) {
    print "Too many points.  XXXXN"
#    system("date > nogo")
    }
  if ((HC1<1.1) && (BC2<1.6)) {
    print "Mark product formed XXXX"
    }
  if ((HC2<1.1) && (BC1<1.6)) {
    print "Antimark product formed XXXX"
    }
  if ((HC1>4.5) && (HC2>4.5)) {
    print "Returning to separate SMs XXXX"
    }

  system("date '+%b:%d:%Y %T'")
  system("tail -1 Echeck | grep XXXX")
  }

function Distance(Atom1,Atom2) {
 return sqrt((A[Atom1]-A[Atom2])^2 + (B[Atom1]-B[Atom2])^2 + (C[Atom1]-
C[Atom2])^2)
}

function Angle(Atom1,Atom2,Atom3) {
  value=((-
Distance(Atom1,Atom3)^2+Distance(Atom1,Atom2)^2+Distance(Atom2,Atom3)^2)/(2
*Distance(Atom1,Atom2)*Distance(Atom2,Atom3)))
  return acos(value)
}
```

```
function asin(x) { return (180/3.141592)*atan2(x, sqrt(1-x*x)) }

function acos(x) { return (180/3.141592)*atan2(sqrt(1-x*x), x) }

function atan(x) { return (180/3.141592)*atan2(x,1) }

function Dihedral(Atom1,Atom2,Atom3,Atom4) {
  B1x=A[Atom2]-A[Atom1]
  B1y=B[Atom2]-B[Atom1]
  B1z=C[Atom2]-C[Atom1]
  B2x=A[Atom3]-A[Atom2]
  B2y=B[Atom3]-B[Atom2]
  B2z=C[Atom3]-C[Atom2]
  B3x=A[Atom4]-A[Atom3]
  B3y=B[Atom4]-B[Atom3]
  B3z=C[Atom4]-C[Atom3]
  modB2=sqrt((B2x^2)+(B2y^2)+(B2z^2))
# yAx is x-coord. etc of modulus of B2 times B1
  yAx=modB2*(B1x)
  yAy=modB2*(B1y)
  yAz=modB2*(B1z)
# CP2 is the crossproduct of B2 and B3
  CP2x=(B2y*B3z)-(B2z*B3y)
  CP2y=(B2z*B3x)-(B2x*B3z)
  CP2z=(B2x*B3y)-(B2y*B3x)
  termY=((yAx*CP2x)+(yAy*CP2y)+(yAz*CP2z))
# CP is the crossproduct of B1 and B2
  CPx=(B1y*B2z)-(B1z*B2y)
  CPy=(B1z*B2x)-(B1x*B2z)
  CPz=(B1x*B2y)-(B1y*B2x)
  termX=((CPx*CP2x)+(CPy*CP2y)+(CPz*CP2z))
 dihed4=(180/3.141592)*atan2(termY,termX)
 return dihed4
}

function killdyn(isomer) {
  system("rm -f dyn")
}
```

progdyn.conf used for 80-THF product-forming trajectories (using ProgdynONIOM)

```
#This is the configuration file for ProgdynONIOM.  This file is read by progdynONIOM
and
# the awk programs proggenHP, prog1stpoint, prog2ndpoint, and progdynb.
#The programs won't read anything past the first blank line,
```

```
#and this file must end with a blank line.
#The program has a number of default values but they are unlikely to be what you want.
#Do not delete lines - rather, comment out lines for unwanted options.
#The values here are read repeatedly and most can be changed in the middle of running jobs
#***The keywords are case sensitive.  The following keywords should always be defined:***
#***method, charge, multiplicity, memory, processors, title
#*** method --The following word is copied exactly to the gaussian input file.
method B3LYP/6-31G*
lowmethod PM6-D3H4
#To do a nonstandard route, make nonstandard 1.  For normal calcs, use nonstandard 0 or else leave it out.
#Then make a file called "nonstandard" containing the nonstandard route with no extra lines.
nonstandard 0
# NMRoptions As is NMRtype=1 will add a section for an NMR calc at every NMRevery intervals.  If you want to combine the two use nonstandard
#NMRtype 1
#NMRmethod2 B97D/6-31G*
#NMRmethod LC-wPBE/6-31G*
#NMRmethod3 B3LYP/cc-pvtz
#NMRevery 4
#NMRrand 1
#NMRcc 1
#loadlimit 10.0
#geometry linear
rotationmode 0
#*** method2 --The options here are restricted, unrestricted, and read. restricted is the default
#If the method is U..., put unrestricted here and the .com files will have in them guess=mix.
#If you put read here, the .com files will contain guess=tcheck, which sometimes makes things faster, sometimes not.
#The use of read requires a specifically defined checkpoint file name using the keyword checkpoint.
method2 read
charge 0
multiplicity 1
oniomchargemult 0 1
processors 3
#*** memory --The following "word" is copied exactly to the gaussian input file after %mem=.
memory 7gb
```

```
#*** killcheck and checkpoint -- You can use a specifically defined checkpoint file
name by putting
#the name after the keyword checkpoint.  This is necessary if you use the read option
with method2.
#Defined checkpoint names are an unnecessary modest hassle and if you do not want to
bother, use killcheck 1
killcheck 0
checkpoint g09.chk
#*** diagnostics -- 0 prints out nothing extra, 1 (default) prints out extra stuff to a
#file "diagnostics", 2 adds more stuff, 3 adds velocities to a file "vellist"
#4 adds the apparent temperature to vellist, but this is meaningless with quasiclassical
calculations
diagnostics 4
#*** title -- the title keyword must be followed by exactly four words
title hydroboration dodeceneVTS80THF ONIOM traj
#*** initialdis -- 0 (default) turns off displacement of the normal modes, so that all
trajectories start from the same place
# and only the energies and signs of the motion in the modes are randomized
# 1 gives a flat distribution of displacements where all of the possible values are equally
likely
# 2 (recommended) gives a QM-like gaussian distribution of displacements, so that
displacements in the middle are more likely that
# those at the end by 1/e
initialdis 0
#*** timestep -- this is the time between points in the trajectory.  Typical values would
be 1E-15 or 0.5E-15 or 0.25E-15
timestep 1E-15
#*** scaling -- this lets you scale the gaussian frequencies by a constant
scaling 1.0
temperature 298.15
#*** thermostat 1 puts in a damping factor so as to bring the classical temperature
toward the desired temperature.
#*** use a thermostatmult between 0.95 and 1, typically 0.995, so the damping happens
slowly - otherwise there will be
#*** over adjustment in response to random variation
#*** the thermostat is not exact.  The second traj point ignores this, so it only applies to
later points handled by progdynb.
thermostat 1
thermostatmult 0.999
#*** method3, method4, method5, and method6 -- These keywords let you add extra
lines to the gaussian input file.
#method3 and method4 add lines at the top of the input after the lines defining the
method, and
#this is useful to implement things like the iop for mPW1k
```

```
#method5 and method6 add lines after the geometry, after a blank line of course
#only a single term with no spaces can be added, one per method line.  Here are some examples to uncomment if needed
#method3 IOp(3/76=0572004280)
method3 scf=(conver=5)
#method3 scrf=(pcm,Solvent=dichloromethane)
#add the line below with big structures to get it to put out the distance matrix and the input orientation
method4 iop(2/9=2000)
#method4 iop(3/124=3)
#method4 scrf=(pcm,solvent=dmso,read)
#method5 radii=bondi
#method6
#*** methodfile -- This keyword lets you add more complicated endings to gaussian input files
#such as a gen basis set.  Put after the keyword the number of lines in a file you create called
#methodfile that contains the test you want to add to the end of the gaussian input
methodfile 0
#*** numimag --This tells the program the number of imaginary frequencies in the starting structure.
#if 0, treats as ground state and direction of all modes is random
#if 1, motion along the reaction coordinate will start out in the direction defined by searchdir
#if 2, only lowest freq will go direction of searchdir and other imag mode will go in random direction
numimag 0
#*** searchdir -- This keyword says what direction to follow the mode associated with the imaginary frequency.
#The choices are "negative" and "positive".  Positive moves in the direction defined in the gaussian frequency calculation
#for the imaginary frequency, while negative moves in the opposite direction.  The correct choice can be made either
#by a careful inspection of the normal modes and standard orientation geometry, or by trial and error.
searchdir positive
#*** classical --  for quassiclassical dynamics, the default, use 0.  for classical dynamics, use 1
#if there are no normal modes and the velocities are to be generated from scratch, use classical 2
classical 2
#*** DRP, saddlepoint, and maxAtomMove --to run a DRP use 'DRP 1' in the line below, otherwise leave it at 0 or comment it out
#the treatment of starting saddlepoints is not yet implemented so use saddlepoint no
```

```
#if DRP shows oscillations then decrease maxAtomMove
#DRP 1
#saddlepoint no
#maxAtomMove 0.01
#*** cannonball -- The program can "fire" a trajectory from a starting position toward a particular target, such as toward
#a ts.  To use this, make a file cannontraj with numAtom lines and three numbers per line that defines the vector
#for firing the trajectory, relative to the starting geometry's standard orientation.  The number following cannonball sets
#the extra energy being put into the structure in kcal/mol
#cannonball 10
#*** keepevery --This tells the program how often to write the gaussian output file to file dyn, after the first two points.
#Use 1 for most dynamics to start with, but use a higher number to save on disk space or molden loading time.
keepevery 999999
#*** highlevel --For ONIOM jobs, the following line states the number of highlevel atoms,
#which must come before the medium level atoms.  Use some high value such as 999 if not using ONIOM
highlevel 40
#*** fixedatom1, fixedatom2, fixedatom3, and fixedatom4 - These fix atoms in space.
#Fixing one atom serves no useful purpose and messes things up, while fixing two atoms
#fixes one distance and fixing three has the effect of fixing three distances, not just two
#in current form fixed atoms only are meant to work with no displacements, that is, initialdis=0
#fixedatom1 16
#fixedatom2 1
#fixedatom3 4
#fixedatom4 20
#applyforce 1 lets one push atoms together or apart - a positive force pushes them together
#format is applyforce force    - with the units on force the same as in the Gaussian output file
#applyforce 2 or 3 or 4 applies a polynomial force centered at dist0.  2 is just harmonic, 3 is second order, 4 is third order
#format is applyforce 4 forcecoefficient dist0 forcecoefficient2 forcecoefficient3
#then use afatoms to chose the atoms with format afatoms firstatom secondatom [additional atoms]
#applyforce 2 0.1 3.4
#afatoms 1 2
#applyforceB 2 0.1 3.8
#afatomsB 1 3
```

```
#applyforceC 2 0.01 5.2
#afatomsC 8 15
#zeroatom pushes the numbered atom toward the origin with a small harmonic potential
- good with boxon when you want to keep the reaction in the center
#zeroatom 3
#*** boxon and boxsize - With boxon 1, a cubic box is set such that atoms that reach the
edge
#are reflected back toward the middle.  Useful for dynamics with solvent molecules.
This is a crude
#implementation that is ok for a few thousand femtoseconds but will not conserve
energy long term.
#Set the box size so as to fit the entire initial molecule but not have too much extra
room.
#The dimensions of the box are two times the boxsize, e.g. boxsize 7.5 leads to a box
that is 15 x 15 x 15 angstroms
#boxon 1
#boxsize 11.2
#*** sphereon and spheresize and sphereforce - uses a force to push atoms within a
sphere.  notice that if the atom is far outside of
#the sphere then the force is large unless sphereforce is set small
sphereon 1
spheresize 14.5
sphereforce .1
#setting a value for empiricaldispersion sets its s6 value with the Grimme 2006
algorithm.  Default is 0, with no empiricaldispersion
#setting a radiusmultiplier sets the size of atoms relative to the standard in 2006.
empiricaldispersion .7
radiusmultiplier 1.6
#*** displacements -- This keyword lets you set the initialdis of particular modes by
using a series of lines of the format
# displacements NumberOfMode InitialDisForThatMode, as in the example below. You
should be able to do as many of these as you like
# you might consider this for rotations where a straight-line displacement goes wrong at
large displacements
# The choices for InitialDisForThatMode are 0, 1, 2, and 10, where 10 does the same
thing as 0 but is maintained for now because
# a previous version of the program had a bug that made 0 not work.
#displacements 2 0
#displacements 3 0
#displacements 4 0
#displacements 5 0
#displacements 6 0
#displacements 7 0
#displacements 8 0
```

```
#displacements 9 0
#displacements 10 0
#*** etolerance --This sets the allowable difference between the desired energy in a trajectory and the actual
#energy, known after point 1 from the potential energy + the kinetic energy in the initial velocities.
#The unit is kcal/mol and 1 is a normal value for mid-sized organic systems.  For very large and floppy molecules, a larger value
#may be needed, but the value must stay way below the average thermal energy in the molecule (not counting zpe).
#If initialdis is not 0 and few trajectories are being rejected, decrease the value.
etolerance 9999999
#*** controlphase --It is sometimes useful to set the phase of particular modes in the initialization of trajectories.
#The format is controlphase numberOfModeToControl positive or controlphase numberOfModeToControl negative.
#controlphase 2 positive
#*** damping -- The damping keyword lets you add or subtract energy from the system at each point, by multiplying the velocities
#by the damping factor.  A damping of 1 has no effect, and since you mostly want to change the energy slowly, normal values range
#from 0.95 to 1.05.  The use of damping lets one do simulated annealing - you add energy until the structure is moving enough
#to sample the kinds of possibilities you are interested in, then you take away the energy slowly.
damping 1.000
#at a damping of .9995, the energy is cut in half in 693 points
#*** reversetraj --This keyword sets the trajectories so that both directions from a transition state are explored.
reversetraj true
```

progdyn.conf used for 80-THF feeder trajectories (using ProgdynONIOM)

```
#This is the configuration file for ProgdynONIOM.  This file is read by progdynONIOM and
# the awk programs proggenHP, prog1stpoint, prog2ndpoint, and progdynb.
#The programs won't read anything past the first blank line,
#and this file must end with a blank line.
#The program has a number of default values but they are unlikely to be what you want.
#Do not delete lines - rather, comment out lines for unwanted options.
#The values here are read repeatedly and most can be changed in the middle of running jobs
#***The keywords are case sensitive.  The following keywords should always be defined:***
#***method, charge, multiplicity, memory, processors, title
```

```
#*** method --The following word is copied exactly to the gaussian input file.
method B3LYP/6-31G*
lowmethod PM6-D3H4
#To do a nonstandard route, make nonstandard 1.  For normal calcs, use nonstandard 0 or else leave it out.
#Then make a file called "nonstandard" containing the nonstandard route with no extra lines.
nonstandard 0
# NMRoptions As is NMRtype=1 will add a section for an NMR calc at every NMRevery intervals.  If you want to combine the two use nonstandard
#NMRtype 1
#NMRmethod2 B97D/6-31G*
#NMRmethod LC-wPBE/6-31G*
#NMRmethod3 B3LYP/cc-pvtz
#NMRevery 4
#NMRrand 1
#NMRcc 1
#loadlimit 10.0
#geometry linear
rotationmode 0
#*** method2 --The options here are restricted, unrestricted, and read. restricted is the default
#If the method is U..., put unrestricted here and the .com files will have in them guess=mix.
#If you put read here, the .com files will contain guess=tcheck, which sometimes makes things faster, sometimes not.
#The use of read requires a specifically defined checkpoint file name using the keyword checkpoint.
method2 read
charge 0
multiplicity 1
oniomchargemult 0 1
processors 3
#*** memory --The following "word" is copied exactly to the gaussian input file after %mem=.
memory 7gb
#*** killcheck and checkpoint -- You can use a specifically defined checkpoint file name by putting
#the name after the keyword checkpoint.  This is necessary if you use the read option with method2.
#Defined checkpoint names are an unnecessary modest hassle and if you do not want to bother, use killcheck 1
killcheck 0
checkpoint g09.chk
```

```
#*** diagnostics -- 0 prints out nothing extra, 1 (default) prints out extra stuff to a
#file "diagnostics", 2 adds more stuff, 3 adds velocities to a file "vellist"
#4 adds the apparent temperature to vellist, but this is meaningless with quasiclassical
calculations
diagnostics 4
#*** title -- the title keyword must be followed by exactly four words
title hydroboration dodeceneVTS80THF ONIOM traj
#*** initialdis -- 0 (default) turns off displacement of the normal modes, so that all
trajectories start from the same place
# and only the energies and signs of the motion in the modes are randomized
# 1 gives a flat distribution of displacements where all of the possible values are equally
likely
# 2 (recommended) gives a QM-like gaussian distribution of displacements, so that
displacements in the middle are more likely that
# those at the end by 1/e
initialdis 0
#*** timestep -- this is the time between points in the trajectory.  Typical values would
be 1E-15 or 0.5E-15 or 0.25E-15
timestep 1E-15
#*** scaling -- this lets you scale the gaussian frequencies by a constant
scaling 1.0
temperature 298.15
#*** thermostat 1 puts in a damping factor so as to bring the classical temperature
toward the desired temperature.
#*** use a thermostatmult between 0.95 and 1, typically 0.995, so the damping happens
slowly - otherwise there will be
#*** over adjustment in response to random variation
#*** the thermostat is not exact.  The second traj point ignores this, so it only applies to
later points handled by progdynb.
thermostat 1
thermostatmult 0.999
#*** method3, method4, method5, and method6 -- These keywords let you add extra
lines to the gaussian input file.
#method3 and method4 add lines at the top of the input after the lines defining the
method, and
#this is useful to implement things like the iop for mPW1k
#method5 and method6 add lines after the geometry, after a blank line of course
#only a single term with no spaces can be added, one per method line.  Here are some
examples to uncomment if needed
#method3 IOp(3/76=0572004280)
method3 scf=(conver=5)
#method3 scrf=(pcm,Solvent=dichloromethane)
#add the line below with big structures to get it to put out the distance matrix and the
input orientation
```

```
method4 iop(2/9=2000)
#method4 iop(3/124=3)
#method4 scrf=(pcm,solvent=dmso,read)
#method5 radii=bondi
#method6
#*** methodfile -- This keyword lets you add more complicated endings to gaussian
input files
#such as a gen basis set.  Put after the keyword the number of lines in a file you create
called
#methodfile that contains the test you want to add to the end of the gaussian input
methodfile 0
#*** numimag --This tells the program the number of imaginary frequencies in the
starting structure.
#if 0, treats as ground state and direction of all modes is random
#if 1, motion along the reaction coordinate will start out in the direction defined by
searchdir
#if 2, only lowest freq will go direction of searchdir and other imag mode will go in
random direction
numimag 0
#*** searchdir -- This keyword says what direction to follow the mode associated with
the imaginary frequency.
#The choices are "negative" and "positive".  Positive moves in the direction defined in
the gaussian frequency calculation
#for the imaginary frequency, while negative moves in the opposite direction.  The
correct choice can be made either
#by a careful inspection of the normal modes and standard orientation geometry, or by
trial and error.
searchdir positive
#*** classical --  for quassiclassical dynamics, the default, use 0.  for classical dynamics,
use 1
#if there are no normal modes and the velocities are to be generated from scratch, use
classical 2
classical 2
#*** DRP, saddlepoint, and maxAtomMove --to run a DRP use 'DRP 1' in the line
below, otherwise leave it at 0 or comment it out
#the treatment of starting saddlepoints is not yet implemented so use saddlepoint no
#if DRP shows oscillations then decrease maxAtomMove
#DRP 1
#saddlepoint no
#maxAtomMove 0.01
#*** cannonball -- The program can "fire" a trajectory from a starting position toward a
particular target, such as toward
#a ts.  To use this, make a file cannontraj with numAtom lines and three numbers per
line that defines the vector
```

```
#for firing the trajectory, relative to the starting geometry's standard orientation.  The
number following cannonball sets
#the extra energy being put into the structure in kcal/mol
#cannonball 10
#*** keepevery --This tells the program how often to write the gaussian output file to
file dyn, after the first two points.
#Use 1 for most dynamics to start with, but use a higher number to save on disk space or
molden loading time.
keepevery 999999
#*** highlevel --For ONIOM jobs, the following line states the number of highlevel
atoms,
#which must come before the medium level atoms.  Use some high value such as 999 if
not using ONIOM
highlevel 40
#*** fixedatom1, fixedatom2, fixedatom3, and fixedatom4 - These fix atoms in space.
#Fixing one atom serves no useful purpose and messes things up, while fixing two atoms
#fixes one distance and fixing three has the effect of fixing three distances, not just two
#in current form fixed atoms only are meant to work with no displacements, that is,
initialdis=0
#fixedatom1 16
#fixedatom2 1
#fixedatom3 4
#fixedatom4 20
#applyforce 1 lets one push atoms together or apart - a positive force pushes them
together
#format is applyforce force    - with the units on force the same as in the Gaussian output
file
#applyforce 2 or 3 or 4 applies a polynomial force centered at dist0.  2 is just harmonic,
3 is second order, 4 is third order
#format is applyforce 4 forcecoefficient dist0 forcecoefficient2 forcecoefficient3
#then use afatoms to chose the atoms with format afatoms firstatom secondatom
[additional atoms]
applyforce 2 0.1 3.4
afatoms 1 2
applyforceB 2 0.1 3.8
afatomsB 1 3
#applyforceC 2 0.01 5.2
#afatomsC 8 15
#zeroatom pushes the numbered atom toward the origin with a small harmonic potential
- good with boxon when you want to keep the reaction in the center
zeroatom 6
#*** boxon and boxsize - With boxon 1, a cubic box is set such that atoms that reach the
edge
```

```
#are reflected back toward the middle.  Useful for dynamics with solvent molecules.  This is a crude
#implementation that is ok for a few thousand femtoseconds but will not conserve energy long term.
#Set the box size so as to fit the entire initial molecule but not have too much extra room.
#The dimensions of the box are two times the boxsize, e.g. boxsize 7.5 leads to a box that is 15 x 15 x 15 angstroms
#boxon 1
#boxsize 11.2
#*** sphereon and spheresize and sphereforce - uses a force to push atoms within a sphere.  notice that if the atom is far outside of
#the sphere then the force is large unless sphereforce is set small
sphereon 1
spheresize 15
sphereforce .1
#setting a value for empiricaldispersion sets its s6 value with the Grimme 2006 algorithm.  Default is 0, with no empiricaldispersion
#setting a radiusmultiplier sets the size of atoms relative to the standard in 2006.
empiricaldispersion .7
radiusmultiplier 1.6
#*** displacements -- This keyword lets you set the initialdis of particular modes by using a series of lines of the format
# displacements NumberOfMode InitialDisForThatMode, as in the example below. You should be able to do as many of these as you like
# you might consider this for rotations where a straight-line displacement goes wrong at large displacements
# The choices for InitialDisForThatMode are 0, 1, 2, and 10, where 10 does the same thing as 0 but is maintained for now because
# a previous version of the program had a bug that made 0 not work.
#displacements 2 0
#displacements 3 0
#displacements 4 0
#displacements 5 0
#displacements 6 0
#displacements 7 0
#displacements 8 0
#displacements 9 0
#displacements 10 0
#*** etolerance --This sets the allowable difference between the desired energy in a trajectory and the actual
#energy, known after point 1 from the potential energy + the kinetic energy in the initial velocities.
```

```
#The unit is kcal/mol and 1 is a normal value for mid-sized organic systems.  For very large and floppy molecules, a larger value
#may be needed, but the value must stay way below the average thermal energy in the molecule (not counting zpe).
#If initialdis is not 0 and few trajectories are being rejected, decrease the value.
etolerance 9999999
#*** controlphase --It is sometimes useful to set the phase of particular modes in the initialization of trajectories.
#The format is controlphase numberOfModeToControl positive or controlphase numberOfModeToControl negative.
#controlphase 2 positive
#*** damping -- The damping keyword lets you add or subtract energy from the system at each point, by multiplying the velocities
#by the damping factor.  A damping of 1 has no effect, and since you mostly want to change the energy slowly, normal values range
#from 0.95 to 1.05.  The use of damping lets one do simulated annealing - you add energy until the structure is moving enough
#to sample the kinds of possibilities you are interested in, then you take away the energy slowly.
damping 1.000
#at a damping of .9995, the energy is cut in half in 693 points
#*** reversetraj --This keyword sets the trajectories so that both directions from a transition state are explored.
reversetraj false
```

NMR Integration Macro

The listing below is the macro used to calculate and output the NMR integrations for the standard **1a.** The spectra were first carefully phased, and those phases were recorded for use in the macro. The integration points used were the same ones used in all samples, so the only difference is the for the standard or either sample was the phase and baseline lvl.

Macro “blum1”

```
shell('rm /home/singleton/jbailey/vnmrsys/maclib/tempblum1')
$filename='/nmrdata/singleton/johnathan/2017-01-15-blum-standard-6spectra.fid'
rt($filename)

rp=-73.6
lp=-20.5
lvl=0
"peaks at "
$cut[1]=9.0
```

```
$cut[2]=7.5
$cut[3]=11.0
$cut[4]=10.0
$cut[5]=10.0
$cut[6]=9.0
$cut[7]=9.0
$cut[8]=9.0
$cut[9]=10.0

setlimit('fn',2097152,8,2)
fn=2097152
wft('all')
wc=550
axis='p'

"For this program the argument is the number of spectra to be worked up in the array"
" changed 6 to 1 below for test"
if ($#<1) then $numspec=6 else $numspec=$1 endif
$multiplier=1

$spectrum=1
repeat
ds($spectrum)
echo('new spectrum')

"spectrum-specific phases"
if (1>2) then
   if ($spectrum=2) then rp=184.5 endif
   if ($spectrum=3) then rp=184 endif
   if ($spectrum=5) then lp=3  endif
   if ($spectrum=6) then rp=184.5 lp=2  endif
endif

"First, I want to get the full spectrum, set some basics and set the shifts"
$totalwidth=0
$sp=sp $wp=wp
vp=12 f intmod='partial' cz vs=160 th=3 nm

"count lines in case something is going wrong and exit if so"
nll('pos',10):$count
echo('here1')
if ($count<4 or $count>35) then
   text
   echo('Problem with wrong number of peaks.')
```

```
  return
endif

"---------------------------Setting shifts-------------------------"
"get carbonyl set to 190p then find chlororm and set it at 77.00"
getll(1):$ht,$freq
cr=$freq
rl(140.92p)
sp=75.0p wp=2.5p
echo('here2')
repeat
  nll('pos',10):$count
  if ($count<3) then th=th-1 endif
  if ($count>3) then th=th+1 endif
  nll('pos',10):$count
until ($count=3)
getll(2):$ht,$freq
cr=$freq rl(77.00p) f
echo('here3')
"-------------------------------------------------------------"

"--------------------------Setting the level---------------------"
"to turn off this section make the next line false"
if (1>2) then
  f cz intmod='partial'
  z(80p,110p)
  repeat
    integ(79p,111p):$intmid
    echo($intmid)
    if ($intmid>0) then lvl=lvl-1 endif
    integ(69p,111p):$intmid
  until ($intmid<0)
  repeat
    integ(69p,111p):$intmid
    echo($intmid)
    if ($intmid<0) then lvl=lvl+.1 endif
    integ(69p,111p):$intmid
  until ($intmid>0)
  repeat
    integ(69p,111p):$intmid
    echo($intmid)
    if ($intmid>0) then lvl=lvl-.01 endif
    integ(69p,111p):$intmid
  until ($intmid<0)
```

```
  cz
  sp=$sp wp=$wp
endif
"--------------------------------------------------------------"

"----------------------------Cutting integrations---------------"
"to turn off this section make the next line false, to turn it on make the line true"
if (2>1) then

cz
$i=1
"1st peak from left"
sp=140.0p wp=2p
repeat
  nll('pos',4):$count
  if ($count<1) then th=th-1 endif
  if ($count>1) then th=th+1 endif
  nll('pos',4):$count
until ($count=1)
getll($i):$ht,$freq
dres($freq):$lw
$totalwidth=$totalwidth+$lw
z($freq+$cut[$i]*$multiplier,$freq-$cut[$i]*$multiplier)
$i=$i+1

"2nd peak from left"
sp=130p wp=2p
repeat
  nll('pos',10):$count
  if ($count<1) then th=th-1 endif
  if ($count>1) then th=th+1 endif
  nll('pos',10):$count
until ($count=1)
getll(1):$ht,$freq
dres($freq):$lw
$totalwidth=$totalwidth+$lw
z($freq+$cut[$i]*$multiplier,$freq-$cut[$i]*$multiplier)
$i=$i+1

"3rd from the left"
sp=126.5p wp=2p
repeat
  nll('pos',10):$count
  if ($count<1) then th=th-1 endif
```

```
   if ($count>1) then th=th+1 endif
   nll('pos',10):$count
until ($count=1)
getll(1):$ht,$freq
dres($freq):$lw
$totalwidth=$totalwidth+$lw
z($freq+$cut[$i]*$multiplier,$freq-$cut[$i]*$multiplier)
$i=$i+1

"4th and 5th from the left"
sp=122.5p wp=2p
repeat
   nll('pos',10):$count
   if ($count<2) then th=th-1 endif
   if ($count>2) then th=th+1 endif
   nll('pos',10):$count
until ($count=2)
getll(1):$ht,$freq
dres($freq):$lw
$totalwidth=$totalwidth+$lw
z($freq+$cut[$i]*$multiplier,$freq-$cut[$i]*$multiplier)
$i=$i+1
getll(2):$ht,$freq
dres($freq):$lw
$totalwidth=$totalwidth+$lw
z($freq+$cut[$i]*$multiplier,$freq-$cut[$i]*$multiplier)
$i=$i+1

"6th from the left"
sp=120.5p wp=2p
repeat
   nll('pos',10):$count
   if ($count<1) then th=th-1 endif
   if ($count>1) then th=th+1 endif
   nll('pos',10):$count
until ($count=1)
getll(1):$ht,$freq
dres($freq):$lw
$totalwidth=$totalwidth+$lw
z($freq+$cut[$i]*$multiplier,$freq-$cut[$i]*$multiplier)
$i=$i+1

"7th from the left"
sp=96p wp=2p
```

```
repeat
  nll('pos',10):$count
  if ($count<1) then th=th-1 endif
  if ($count>1) then th=th+1 endif
  nll('pos',10):$count
until ($count=1)
getll(1):$ht,$freq
dres($freq):$lw
$totalwidth=$totalwidth+$lw
z($freq+$cut[$i]*$multiplier,$freq-$cut[$i]*$multiplier)
$i=$i+1

"8th from the left"
"********************** special unsym cut ***************"
sp=77.5p wp=2p
repeat
  nll('pos',10):$count
  if ($count<1) then th=th-1 endif
  if ($count>1) then th=th+1 endif
  nll('pos',10):$count
until ($count=1)
getll(1):$ht,$freq
dres($freq):$lw
$totalwidth=$totalwidth+$lw
z($freq+$cut[$i]*$multiplier,$freq-4.8)
$i=$i+1

"11th from the left"
sp=18.0p wp=2p
repeat
  nll('pos',10):$count
  if ($count<1) then th=th-1 endif
  if ($count>1) then th=th+1 endif
  nll('pos',10):$count
until ($count=1)
getll(1):$ht,$freq
dres($freq):$lw
$totalwidth=$totalwidth+$lw
z($freq+$cut[$i]*$multiplier,$freq-$cut[$i]*$multiplier)
$i=$i+1
```

```
endif
"----------------------------------------------------------------"

echo('The average line width is ',$totalwidth/6)

"--------------------------Output integrals-----------------------"
"to turn off this section make the next line false, to turn it on make the line true"
if (2>1) then
  intmod='partial'
  f
  nll('pos',20):$count
  printon
  shell('date')
  text(file)
  echo('The average line width is ',$totalwidth/6)
  nli
  setint(3,1000)
  printoff('/home/singleton/jbailey/vnmrsys/maclib/temp1')
  shell('cat /home/singleton/jbailey/vnmrsys/maclib/temp1 >>
/home/singleton/jbailey/vnmrsys/maclib/tempblum1')
  shell('rm -f /home/singleton/jbailey/vnmrsys/maclib/temp1')

endif
"----------------------------------------------------------------"

$spectrum=$spectrum+1
until ($spectrum>$numspec)

sp=$sp wp=$wp
sp=96.2p wp=1.1p intmod='full'
is=8000000
nm
vs=1900
```