APPLICATION OF KINETIC ISOTOPE EFFECTS AND THEORETICAL CALCULATIONS TO THE STUDY OF INTERESTING REACTION MECHANISMS

A Dissertation

by

JENNIFER SUE HIRSCHI

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

DOCTOR OF PHILOSOPHY

December 2007

Major Subject: Chemistry

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Approved by:

Chair of Committee,	Daniel A. Singleton
Committee Members,	Frank M. Raushel
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ABSTRACT

Application of Kinetic Isotope Effects and Theoretical Calculations to the Study of Interesting Reaction Mechanisms. (December 2007)

Jennifer Sue Hirschi, B.S., Southern Utah University

Chair of Advisory Committee: Dr. Daniel A. Singleton

A variety of biological and organic reaction mechanisms are studied using powerful tools from experimental and theoretical chemistry. These tools include the precise measurement of kinetic isotope effects (KIEs) and the use of theoretical calculations to predict KIEs as well as determine factors that contribute to reaction acceleration and selectivity.

Theoretical analysis of the Swain-Schaad relationship involves the prediction of a large number of isotope effects and establishes the semiclassical boundaries of the relationship. Studies on the mechanism of oxidosqualene cyclase involve the determination of a large number of precise KIEs simultaneously. Transition state models for the Sharpless asymmetric epoxidation have been developed that explain the versatility, high selectivities, and ligand accelerated catalysis of the reaction. Theoretical predictions on the proposed enzymatic mechanism of flavin dependent amine oxidation suggest a hydride transfer mechanism and rules out mechanisms involving covalent intermediates. Finally, a theoretical analysis of Diels-Alder reactions successfully describes the unexpected exo selectivity in some of these reactions.

DEDICATION

To Billy and Katharina

ACKNOWLEDGEMENTS

I would like to thank my committee chair, Dr. Singleton, and my committee members, Dr. Raushel, Dr. Fitzpatrick, and Dr. Watanabe, for their guidance and support throughout the course of this research.

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INTRODUCTION

General Overview

Tools used for mechanistic study have traditionally centered on experimental studies. The traditional physical organic chemist utilized experimental techniques involving linear free energy relationships, kinetics, thermochemistry, photolysis, kinetic isotope effects (KIEs), and spectrometric analysis to probe reaction mechanisms.[1] The arsenal of modern physical organic techniques comprise these experimental tools in combination with advanced theoretical methods to describe the specific details of a reaction mechanism.[2,3] This dissertation describes methods from modern physical organic chemistry used to probe the details of a variety of organic and enzymatic reaction mechanisms including the:

1) measurement of KIEs for the enzymatic reaction of oxidosqualene cyclase (OSC);
2) theoretical studies of the Sharpless Epoxidation (SE) to interpret KIEs, predict stereoselectivity, and explain the observed ligand accelerated catalysis;
3) theoretical evaluation of the kinetic relationship of isotopomers, the Swain-Schaad relationship (SSR), as an experimental probe;

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

4) prediction of KIEs in the enzymatic reaction of *N*-methyl tryptophan oxidase (MTOX) and the mechanistic interpretation of experimental data;
5) explanation of the stereoselectivity in Diels-Alder reactions using theoretical models.

The importance of these studies lies not only within the detailed findings of the experiments, but within the development of the mechanistic methodology used in the analysis. This methodology includes the development of new techniques for measuring product KIEs of an enzymatic reaction (with a large substrate) at natural abundance, calculations using density functional theory (DFT) for the prediction of isotope effects and other experimental variables, as well as for predictions on the limitations of the SSR.

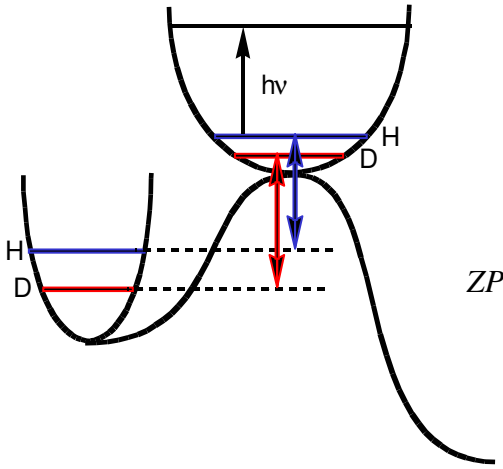
Measurement of KIEs at Natural Abundance

KIEs have been used extensively as a mechanistic probe for a variety of organic, biological, and inorganic reactions.[4-19] KIEs are defined as the difference in rates between two isotopomers and reflect changes in bonding at the transition state of the rate-determining step of a reaction as shown below. The difference in rates is caused by changes in the difference of the zero point energies (ZPE) between the ground state and transition state of a reaction, since the rate of a reaction is dependent upon the activation energy.

The ZPE is the minimum energy in a quantum one dimensional harmonic oscillator model and directly correlates with the vibrational frequency. Since the vibrational frequency (ν) is directly related to the square root of the force constant (*f*) and

inversely proportional to the square root of the reduced mass (μ) as shown in equation 1-1**, t**he differences in the vibrational frequencies of the isotopomers are determined by the differences in masses between the isotopes and the changes in the force constants:

$$k = e^{-Ea/kT}$$



$$ZPE = \frac{1}{2}h\nu$$

between the ground state and transition state of the reaction. Therefore, a change in the rate between isotopes (a KIE) indicates that a bonding change or significant geometric change has occurred at the transition state involving the position of isotopic substitution. Therefore, KIEs are a sensitive probe used to distinguish between several mechanistic possibilities in a reaction.

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

Traditionally KIEs have been determined by measuring the difference in rates between synthetically labeled and unlabeled materials. The measurement of KIEs using synthetically labeled substrates is sometimes difficult or prohibitive since it requires the synthesis of materials labeled in specific positions. Additionally, ^{13}C KIEs have been determined at natural abundance using mass spectrometric analysis of CO_2, however,

this method is limited to labile carbonyls that can easily form CO_2.[20] Consequently, Singleton *et al* have developed a method involving the analysis of ^{13}C, ^{2}H, and ^{17}O KIEs at natural abundance using NMR methodology.[11,16] The advantages of KIE measurements at natural abundance are:

- the material does not require synthetic labeling because of the natural abundance of different isotopomers in chemical materials;
- each peak corresponds to a specific position in the molecule and many isotope effects can be analyzed simultaneously;
- the "unlabeled" material does not interfere with the analysis.

Natural abundance measurements are a reflection of the competition between the isotopomers that occur naturally within the material. Since the lighter isotopomer will not always react faster, the starting material will become enhanced in the heavier isotopomer and the enhancement is measured by comparing reacted and unreacted materials. The enhancement (R/Ro) is related to the KIE by the following equation (1-2) which is dependent upon F, the fractional conversion of the reaction.[5]

$$KIE = \frac{\log(1 - F_1)}{\log\left(1 - F_1\right)\left(\frac{R}{R_0}\right)} \tag{1-2}$$

A similar equation can be derived for measuring the KIEs of the product of a reaction as shown in equation 1-3.

$$KIE = \frac{\log\left(1 - F_1\right)}{\log\left[1 - \left(F_1 \frac{R_p}{R_0}\right)\right]} \tag{1-3}$$

The measurement of KIEs at natural abundance is an excellent method that has been applied in several organic and organometallic reactions, and more recently in an enzymatic reaction.[6-15,21-24] However, this method does have some disadvantages including: the requirements of large amounts of materials (compared to scintillation counting or mass spectrometry), occasionally prohibitive reaction requirements (fractional conversion requirements, no side reactions), and the specific characteristics of the molecule in NMR spectroscopy (inseparable peaks, long relaxation times). Methods for addressing these difficulties will be specifically discussed in the measurement of KIEs for OSC in Chapter III.

Predicting KIEs

The interpretation of experimentally measured KIEs is often aided by the development of theoretical models used to quantitatively predict the experimental KIEs. Theoretical predictions of equilibrium isotope effects (EIEs) and KIEs are based upon the formulation of Bigeleisen and Mayer.[25] The calculation of the KIE is represented by equation 1-4. The KIE is composed of the $(\frac{\nu_1^{\ddagger}}{\nu_2^{\ddagger}})$ term which represents the product of vibrational frequencies for the ground state and transition state. The $[(s_2/s_1)f]$ represent the contributions from the rotational, vibrational and electronic partition functions to the KIE for the different isotopomers.

$$KIE_{TST} = \frac{\nu_1^{\ddagger}}{\nu_2^{\ddagger}} \frac{(s_2/s_1)f_{GS}}{(s_2/s_1)f_{TS}} \qquad (1\text{-}4)$$

At the ground state 3N-6 (for non-linear molecules where N=the number of atoms) vibrational degrees of freedom must be taken into account as shown in equation 1-5, conversely the equation for the transition state requires only 3N-7 because the motion along the reaction coordinate is excluded as shown in equation 1-6.

$$\left(s_2 / s_1\right) f_{GS} = \prod_i^{3N-6} \frac{\nu_{2i}}{\nu_{1i}} \frac{1-e^{-u_{1i}}}{1-e^{-u_{2i}}} \frac{e^{u_{1i}/2}}{e^{u_{2i}/2}} \qquad (1\text{-}5)$$

$$where \rightarrow u_i = \frac{h\nu_i}{kT}$$

$$\left(s_2 / s_1\right) f_{TS} = \prod_i^{3N-7} \frac{\nu_{2i}}{\nu_{1i}} \frac{1-e^{-u_{1i}}}{1-e^{-u_{2i}}} \frac{e^{u_{1i}/2}}{e^{u_{2i}/2}} \qquad (1\text{-}6)$$

These calculated KIEs represent the semi-classical KIE and do not take into account non-statistical effects such as tunneling, barrier recrossing, and variational transition state theory. Singleton as well as others have demonstrated the necessity for including a tunneling correction in the calculation of heavy atom isotope effects.[11,15,26-28] Similar corrections can be used for hydrogen isotope effects, unless a large amount of tunneling is involved (represented by an unusually large KIE); then a more in depth analysis of the KIE is required.[29-33] Several tunneling corrections are available including the Bell, Wigner, and infinite parabola corrections.[34] Other non-statistical effects require a more intense theoretical treatment such as dynamic simulations; however, in most cases these effects are negligible.

The predictions of KIEs are derived from theoretical models of the lowest energy ground state of the molecule and the model of the transition state of the reaction. The FORTRAN program QUIVER developed by Saunders and Wolfsberg, is a useful script for extracting the necessary data from a theoretical frequency calculation in Gaussian used to calculate the theoretical KIE using the Bigeleisen equation.[35]

Theoretical Calculations

Theoretical models also aid in our understanding of the details of a chemical reaction, for example: sources of catalysis; reaction stereo and regioselectivities; and steric and electronic effects of a reaction. Several methodologies are currently available to the theoretical chemist. Some of the calculational methods available include: molecular mechanics, semi-empirical methods, density functional theory, *ab initio* methods, monte carlo simulations, RRKM theory, variational transition state theory, marcus theory, electron valence bond theory, and other more specific methods. An appropriate level of theory is determined depending upon the chemical system to be explored and the desired goal of the study. Density functional theory (DFT) has previously given excellent agreement between experimental and predicted KIEs.[11,14,26,36] Therefore, DFT is the theoretical method used in all of the studies within this dissertation.

The perfect theoretical method would give an exact solution to the non-relativistic Schrodinger equation. However, in systems with many electrons (many being more than H_2) an exact solution is unrealistic. *Ab initio* methods such as Hartree-Fock (HF) and Møller-Plesset (MP) theories include a term for electron exchange which

takes into account the interaction of an electron with other electrons in the system which is displayed in the electron correlation energy. The electronic correlation energy is defined as the difference between the actual energy of the system including relativistic effects and the calculated energy of the system. The more advanced levels of *ab initio* theory include a greater amount of electron correlation and more closely represents reality. An exact quantum mechanical result could theoretically be obtained with an inclusion of all possible electronic excited states (full configuration interaction) and an infinitely large number of orbitals (infinite basis set) placed upon the system. However, this is calculationally prohibitive. Another approach to correctly calculating the energy of a system is DFT.

In DFT, the energy of a molecule is determined as a functional of the electron density of the system rather than the interaction of electronic wave functions as in *ab initio*. Within DFT several functionals have been developed to more correctly describe the energies of specific molecules. Theorists must consider the validity of a particular functional in the calculation of the desired system. The theoretical method that best describes the experimental results of a particular system, or similar systems, should be employed when determining which method and functional to employ. The following chapters employ a series of functionals and methods within DFT to describe a myriad of chemical reactions.

This dissertation includes a wide variety of experimental and theoretical methods to investigate the specific details of chemical reactions from organic, organometallic, and biological chemistry. This includes the largest system to date for the simultaneous

measurement of KIEs at natural abundance. Subsequent chapters involve the theoretical analysis of several reactions. Theory is used to develop models of the transition state and predict KIEs. In addition, theoretical calculations give insight into the specific details of the chemical reaction that determine selectivity and reactivity. Another theoretical analysis is used to predict the relationship between isotopomers for several EIEs and KIEs.

CHAPTER II

THE NORMAL RANGE FOR SECONDARY SWAIN-SCHAAD EXPONENTS WITHOUT TUNNELING OR KINETIC COMPLEXITY*

An analysis is presented of the range of secondary Swain-Schaad exponents to be expected at 25 °C in the absence of tunneling or kinetic complexity. From 15,996 sets of exact harmonic semi-classical equilibrium isotope effects for simple C–H/D/T exchange reactions and 954 sets of exact harmonic semi-classical secondary H/D/T kinetic isotope effects for C–H positions in simple organic reactions, the distribution of Swain-Schaad exponents versus magnitude of the isotope effect is determined. This distribution defines when a secondary Swain-Schaad exponent may be considered to implicate non-semi-classical behavior, revises the expected Swain-Schaad exponent for extrapolation of secondary isotope effects, and serves as a guide to the uncertainty in such extrapolations.

Introduction

Quantum mechanical tunneling affects the rates of barrier crossings in all chemical reactions, and there has been considerable interest in identifying reactions where the impact of tunneling is large. Tunneling is defined as a process where a particle of low molecular weight (such as an electron or proton) penetrates through a potential energy barrier, rather than the classical pathway of surmounting the energy

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barrier. Tunneling is possible because of the wave-particle duality of property of particles as shown in the deBroglie wave equation 2-1.

$$\lambda = \frac{h}{mv} \tag{2-1}$$

Therefore, particles with a small mass are more likely to display wavelike properties and tunnel through a barrier than heavier particles. Since the lighter atom hydrogen (hydrogen) has a higher probability of tunneling through the barrier than larger deuterium atom, the experimental consequence of tunneling is an increase in the H/D KIE. Several examples of large KIEs exist in both organic and enzymatic reactions and have been attributed to a significant amount of tunneling.[37-39]

Large differences in Arrhenius factors for different isotopomers have been attributed to tunneling.[37-45] The Arrhenius equation is defined in equation 2-2.

$$k = Ae^{-\frac{E_a}{RT}} \tag{2-2}$$

A modified form of the Arrhenius equation is shown below and is often used to plot the log of the rates of isotopes versus the inverse of the temperature as shown in equation 2-3.

$$\ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln(A) \tag{2-3}$$

In an Arrhenius plot, the difference in the slopes of isotopomers relates to the difference in the energy of activation for the different isotopes for the reaction and the intercept is related to the pre-exponential Arrhenius factor. Many researchers have assumed that Arrhenius factors that greatly deviate from unity are directly related to the amount of

tunneling that occurs within the reaction, since the pre-exponential factor accounts for effects in the reaction that are not related to the enthalpic barrier. However, the relationship between the Arrhenius pre-exponential factor and tunneling is still unclear since several other factors can affect the factor including entropy, barrier recrossing, and dynamic effects.

Another important probe for tunneling involves the measurement of relative rates for protium versus deuterium versus tritium and comparison of these rates with semi-classical predictions. "Semi-classical" in this context includes the quantum effects on vibrations within conventional transition state theory, but does not include either tunneling or the effects of zero-point energy or barrier recrossing within variational transition state theory. Most often, an approximate treatment first described by Swain and Schaad is used as the measure of semi-classical expectations.[46] For example, experimental KIEs would be expected to fit equation 2-5 with a Swain-Schaad exponent (SSE) of roughly 3.34 in the absence of tunneling.[47] A larger SSE might be taken as evidence for substantial tunneling.[48] Assuming semi-classical behavior, equations 2-4 and 2-5 are often used to extrapolate KIEs to different isotopes (e.g., estimation of k_H/k_T from k_H/k_D).[49-57] SSEs are also often used to assess intrinsic KIEs and kinetic complexity in mechanisms.[58-68]

$$\left(\frac{k_H}{k_T}\right)=\left(\frac{k_D}{k_T}\right)^{SSE} \tag{2-4}$$

$$\left(\frac{k_H}{k_T}\right)=\left(\frac{k_H}{k_D}\right)^{SSE'} \tag{2-5}$$

The determination of SSEs for hydrogen atoms being transferred (1° SSEs) has been carried out for diverse reactions over the last forty years.[69-72] A fair summary is that 1° SSEs are usually close to semi-classical expectations, even for reactions in which other observations suggest extensive tunneling. More recently, SSEs for hydrogen atoms not being transferred (2° SSEs) have become an often-used probe for tunneling, particularly in enzymatic reactions.[73-80] The 2° SSEs vary from the Swain-Schaad expectation much more often than 1° SSEs, so they are considered to be a more sensitive probe for tunneling.

The Swain-Schaad treatment involves greatly simplifying assumptions versus the full semi-classical theory of isotope effects, due to Bigeleisen and Mayer.[81,25,82] A simplified version of the Bigeleisen equation is shown below in equation 2-6. The semi-classical KIE is related to the product of the frequencies and the vibrational and rotational partition functions at the ground state and transition state.

$$KIE_{TST} = \frac{\nu_1^{\ddagger}}{\nu_2^{\ddagger}} \frac{\left(s_2 / s_1\right) f_{GS}}{\left(s_2 / s_1\right) f_{TS}} \tag{2-6}$$

In the derivation of the Swain-Schaad relationship, some over simplifications of this equation ignore the partition function portion of the equation entirely. Additionally, the vibrational frequencies are simplified to a relationship between the masses of the two isotopomers and the force constants are assumed to be equal. The derivation of the Swain-Schaad relationship is shown below and the assumptions of the relationship discussed.

The rate of a reaction is dependent upon the activation energy for the reaction as shown in equation 2-7. The activation energy is related to the difference in zero point energies (equation 2-8) at the ground state and transition state of the reaction. Therefore, the rate of the reaction can be directly related to the frequency by equation 2-9. A KIE is defined as the ratio of rates for two different isotopomers, in this case hydrogen and tritium, and can be related to the differences in vibrational frequencies using equation 2-10). Additionally, the vibrational frequency is proportional to the square root of the force constant and inversely proportional the square root of the reduced mass as shown in equation 2-11. Substituting equation 2-11 into equation 2-10 results in equation 2-12. The Swain-Schaad assumption is that the difference in the force constants between isotopomers is negligible and the reduced mass is approximately equal to the average mass of the isotopes. These assumptions give equation 2-13. The Swain-Schaad relationship assumes that the rates of isotopomers are directly dependent only upon the ratio of the inverse square roots of the masses as shown in equation 2-14.

$$k = e^{-Ea/kT} \tag{2-7}$$

$$ZPE = (n + \frac{1}{2})h\nu \tag{2-8}$$

$$k = e^{\frac{-h(\nu^* - \nu)}{2kT}} \tag{2-9}$$

$$\frac{k_H}{k_T} = e^{\frac{-h(\nu_H^* - \nu_T - \nu_H + \nu_T)}{2kT}} \tag{2-10}$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{f}{\mu}} \tag{2-11}$$

$$\frac{k_H}{k_T} = E^{\left(\frac{1}{\sqrt{m_H}} - \frac{1}{\sqrt{m_T}}\right)} \qquad (2\text{-}12)$$

$$where \longrightarrow E = e^{\frac{-h(f_y^* + f_z^* - f_x - f_y - f_z)}{4\pi kT}}$$

$$\frac{k_D}{k_T} = E^{\left(\frac{1}{\sqrt{m_D}} - \frac{1}{\sqrt{m_T}}\right)} \qquad (2\text{-}13)$$

$$\frac{k_H}{k_T} = \frac{k_D}{k_T}^{\left(\frac{\frac{1}{\sqrt{m_H}} - \frac{1}{\sqrt{m_T}}}{\frac{1}{\sqrt{m_D}} - \frac{1}{\sqrt{m_T}}}\right)} \qquad (2\text{-}14)$$

As previously mentioned Saunders corrected the relationship to include a factor for the reduced masses. Perhaps the most misleading part of the relationship is the ignorance of the well established portion of the Bigeleisen equation including the partition functions for rotation and vibration, this is related to the assumption that force constants are equivalent for isotopomers, and that a reduced mass factor will be similar for the culmination of all reactions.

Over 30 years ago, Stern and Vogel analyzed in detail the range of possible SSEs within the full theory.[83] (See the following references for warnings regarding other aspects of the Swain-Schaad equation).[84,85] They found that for small KIEs, SSEs can in fact vary from negative infinity to positive infinity. Their results also show clearly that there is no reliable expectation for the value of an SSE for a small or inverse isotope effect. Even for "reasonably large" isotope effects (defined as having $k_H/k_D > 2.7$), the

SSEs can fall in a broad range (SSE' = 1.33 to 1.58 for equation 2-5), and it was expected that deviations from this range should not be rare.

Given these conclusions, it may seem rather surprising that the Swain-Schaad relationship is used so commonly, or that it is used at all with small isotope effects, or that the modern literature contains consideration of a "semi-classical limit" for SSEs.[86] However, Stern and Vogel had demonstrated only theoretical possibilities for the range of SSEs and not the likelihood of unusual SSEs. In fact, they emphasize that the Swain-Schaad relationship should work well for large isotope effects. In addition, the expected SSE of about 3.34 for equation 2-4 has been often observed for large KIEs. For real reactions, it is quite uncertain how often the theoretical possibilities for deviation from the Swain-Schaad relationship will materialize.

Results and Discussion

We describe here an analysis of the range of 2° SSEs that may be realistically expected at 25 °C in the absence of tunneling or kinetic complexity. The results define when a 2° SSE may be considered to implicate tunneling or kinetic complexity, revise the SSEs for extrapolation of 2° KIEs, and serve as a guide to the uncertainty in such extrapolations.

To evaluate the range of 2° SSEs to be expected semi-classically, 15,996 sets of exact harmonic semi-classical equilibrium isotope effects (EIEs) were calculated for simple C–H/D/T exchange reactions and 954 sets of exact harmonic semi-classical 2° H/D/T KIEs were calculated for C–H positions in simple organic reactions, shown in Appendix A. EIEs were calculated for all possible C–H/D/T single-position exchange

reactions for methane, ethene, ethyne, ethane, methanimine, ethanol, formaldehyde, HCN, methanol, methylamine, acetone, acetaldehyde, propyne, and 26 additional neutral molecules, H_3CO^-, $H_2C{=}CHO^-$, $H_2C{=}CHCH_2O^-$, $H_2C{=}OH^+$, $H_3CCH{=}OH^+$, allyl cation, 2-propyl cation, $H_3C\bullet$, $ClH_2C\bullet$, $FH_2C\bullet$, $H_2C{=}CHO\bullet$, and 9 additional reactive intermediates, with a total of 127 substitution positions. KIEs were based on single-position isotopic substitutions in 20 ene reactions, 9 diimide reductions, 11 hydride transfer reactions, 24 radical reactions, 5 carbene reactions, 12 electrocyclic reactions, a sigmatropic reaction, a Diels-Alder reaction, 8 S_N2 reactions and the retro-reactions for all non-symmetrical cases. Complete reaction lists are given in Supporting Information. Calculations used the program QUIVER.[35] Frequencies were scaled by 0.9614. This was accomplished by first optimizing diverse ground-state and transition structures in B3LYP/6-31G* calculations, then calculating the isotope effects at 25 °C from the harmonic frequencies. SSEs were then calculated for each set of isotope effects. The results are summarized in Figure 2-1. The B3LYP/6-31G* calculations here have previously led to accurate predictions of experimental KIEs.[26,11,14,36] Limited studies at other theoretical levels (HF/6-31G* and B3LYP/6-311+G**) gave a similar distribution of SSEs.

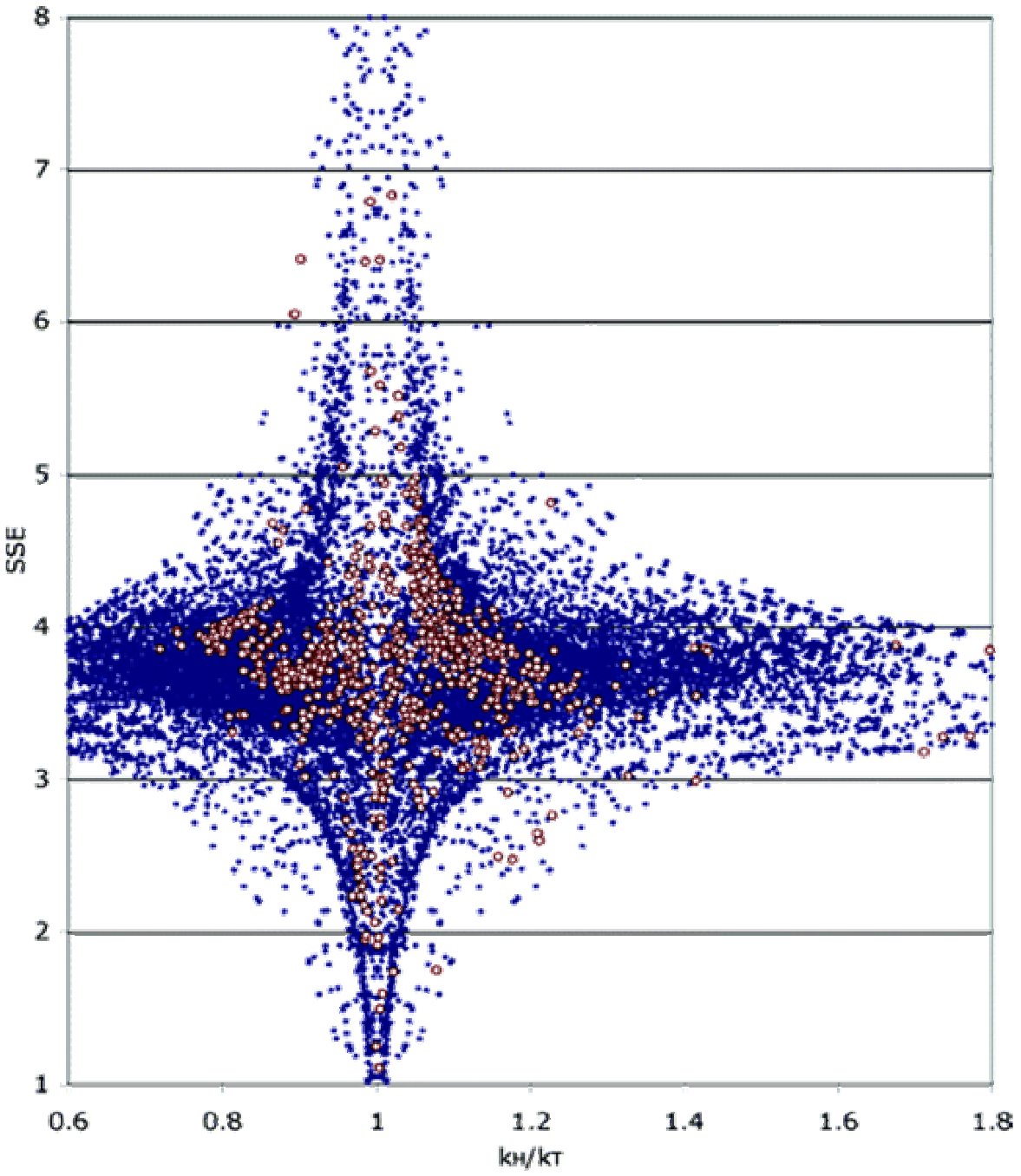


Figure 2-1. Distribution of SSEs for equation 2-4 versus kH/kT based on exact harmonic semi-classical isotope effects. The blue dots are based on 15,996 sets of EIEs, and the red open circles are based on 954 sets of KIEs. The limited domain and range were chosen for clarity – the full distribution is shown in the Appendix.

KIEs are harder to calculate in large numbers than EIEs, so we have far fewer 2° SSEs based on KIEs. Within semi-classical theory, 2° EIEs and 2° KIEs are quite similar: EIEs are derived from the 3N-6 vibrational frequencies while KIEs are derived from 3N-7 vibrations plus a temperature-independent contribution from the imaginary frequency. This imaginary-frequency factor is usually a minor contributor to significant 2° H/D/T KIEs, and its effect on the average of SSEs for $k_H/k_T > 1.1$ and $k_H/k_T < 0.9$ was < 0.01. From this and the similarity of distributions for 2° SSEs based on KIEs versus EIEs, we expect that the distribution of 2° SSEs based on EIEs should adequately represent semi-classical 2° KIEs.

For the purpose of analysis, we will assume that the results of figure 2-1 are statistically representative of the universe of organic reactions. This assumption leads to three conclusions: 1.) In the range $0.9 < k_H/k_T < 1.1$, the Swain-Schaad relationship is of no value. SSEs as low as –296 and as high as 2100 were observed in this range. There is no semi-classical limit for SSEs without the context of the magnitude of the isotope effect. 2.) For $k_H/k_T < 0.9$ and $k_H/k_T > 1.1$, the mean and median 2° SSE is 3.72. This corresponds to 1.368 for SSE' in equation 2-5 [SSE' = SSE/(SSE-1)]. The use of the conventional values for SSE and SSE' to extrapolate 2° KIEs should be discontinued, and conclusions based on these values may need to be reevaluated. The original values came from reduced masses for C-H stretching frequencies,[87] ignoring bending vibrations, and it should not be surprising that they do not apply to 2° KIEs. 3.) For $k_H/k_T > 1.1$, an approximate 95% confidence interval is defined by the lines $\text{Max} = 3.66 + 0.24/(k_H/k_T-1)$ and $\text{Min} = 3.40 – 0.13/(k_H/k_T-1)$. For $k_H/k_T < 0.9$, the approximate 95%

confidence lines are: Max = $3.55 + 0.2/(1-k_H/k_T)$ and Min = $3.52 - 0.12/(1-k_H/k_T)$. Experimental 2° SSEs outside of this range may be sufficiently unusual to be considered as evidence for non-semi-classical behavior or kinetic complexity, but SSEs inside this range are not. Extrapolations of 2° KIEs should take into account the uncertainty.

Conclusions

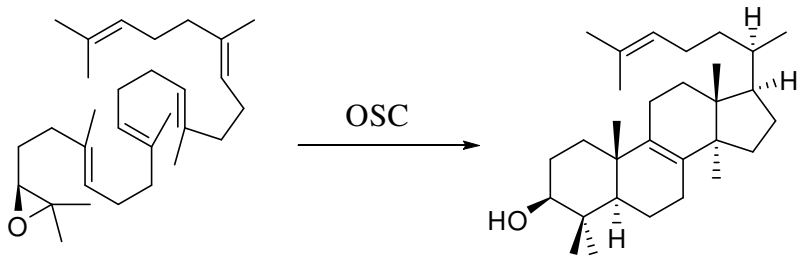
Stern and Vogel warned of the variability of SSEs.[83] The results here amplify that warning, while providing a framework for the interpretation of 2° SSEs and the extrapolation of KIEs with regard to the possible error. Ultimately, however, it should be recognized that the Swain-Schaad treatment is an approximation that should be applied only with proper caution. In many cases, a detailed theoretical analysis of the SSEs to be expected for the particular system of interest would be most appropriate.

CHAPTER III

KINETIC ISOTOPE EFFECT STUDIES ON THE ENZYMATIC CYCLIZATION OF OXIDOSQUALENE

Introduction

We have measured the ^{13}C KIEs for the reaction of oxidosqualene cyclase (OSC), which involves the extraordinary conversion of (3s)-2,3-oxidosqualene **3-1** to lanosterol **3-2**, resulting in the concurrent formation of four rings and six stereocenters. Our goal was to study this system using product KIEs at natural abundance on all 30 carbons of lanosterol simultaneously, to gain insight into the nature of the cyclization.



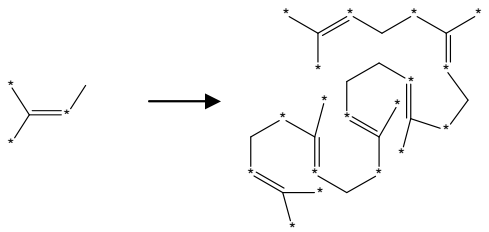
3-1 **3-2**

A fascinating and fundamental question in this reaction is the degree to which the polyclization occurs in a concerted versus stepwise fashion. In order to obtain the samples needed for measurements on this complex enzymatic case, we have optimized reaction conditions by modifying concentrations, solubility, pH, temperature, lysis technique, and reactions times to give 100% conversion of (3S)-2,3-oxidosqualene to lanosterol. In addition, we have developed unique NMR conditions to address the spectral complexity of this molecule by testing several lanosterol derivatives, solvents, temperatures, concentrations, and methods. This is the largest number of isotope effects

ever measured simultaneously for one molecule. From the isotope effects, we discuss the nature of the polycyclization mechanism.

Background. The intricate ring structure of cholesterol (ergosterol in yeast) is formed biosynthetically by a single enzyme, oxidosqualene cyclase. This enzyme is intriguing biologically because it is a regulatory point for steroid synthesis. However, our interest is based upon the unique chemical transformation that has fascinated scientists for decades. The mechanism of oxidosqualene cyclase has engaged the interest of researchers for the last 50 years, and over 500 papers have been published about the cyclization.[88,89] The intriguing chemistry of oxidosqualene cyclase has triggered investigations into every aspect of the enzyme's mechanism using tools from microbiology, synthetic chemistry, crystallography, and computational chemistry.

Early studies began with the research of Woodward and Bloch.[90-92] Labeled isoprene (**3-3**) was fed to yeast, and the labeled lanosterol product **3-4** revealed the fate of the labels from the small molecules, establishing the cyclization structure.

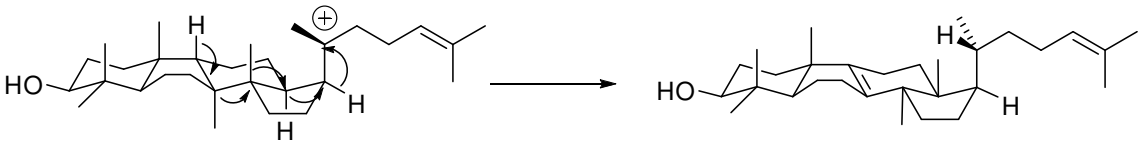


3-3 **3-4**

This study is well accepted and established the basic information about the folding of the squalene. Prestwich and Corey later established that oxidosqualene folds

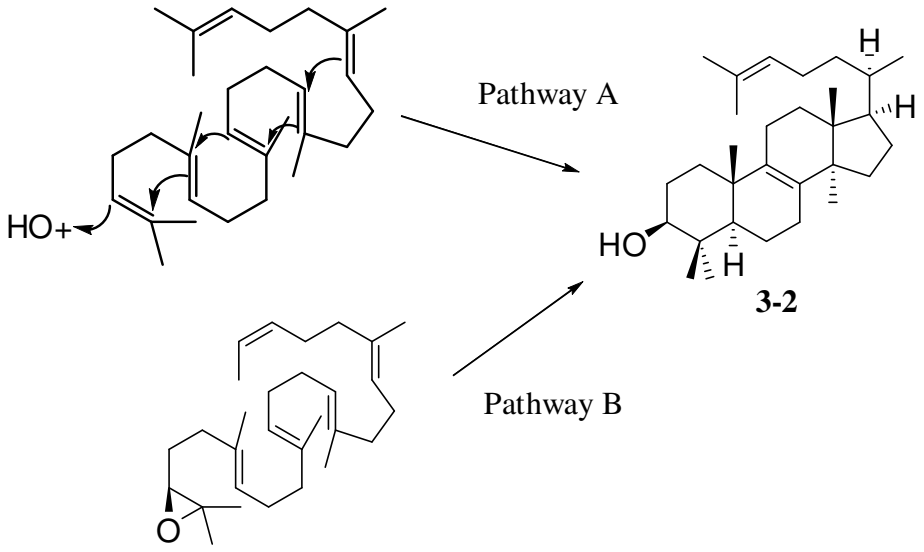
into a chair-boat-chair structure as shown in **3-5**, and that correctly folded substrate is essential for lanosterol formation.[93-95]

Subsequently several researchers identified the subsequent rearrangement which occurs by a deprotonation, several hydride shifts, and a methyl shift of the protosterol cation **3-5** to give lanosterol as shown in structure **3-6**.[91,92,96]



3-5 **3-6**

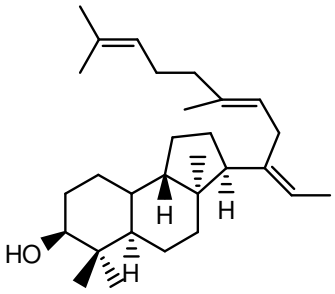
At this point it was unclear whether the water was added to the squalene by the enzyme (**pathway A)** or if an oxygen was present in the precursor to lanosterol (**pathway B**). The Corey and van Tamelen research groups independently established that oxidosqualene is the precursor for lanosterol (**pathway B**). However, the mechanism of the subsequent cyclization is still not well understood.



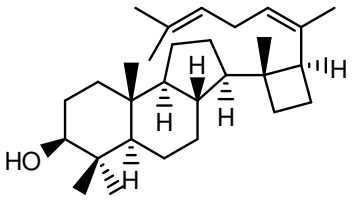
3-2

3-1

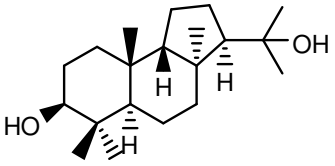
Further studies on the mechanism of cyclization involved the synthesis of substrate mimics that reveal information about the cyclization step.[93-113] The most widely accepted mechanism was provided by Corey and is based on substrate mimics that give the 6-6-5 tricyclic ring structures as products.[95,101,107,113]



trans-syn-trans

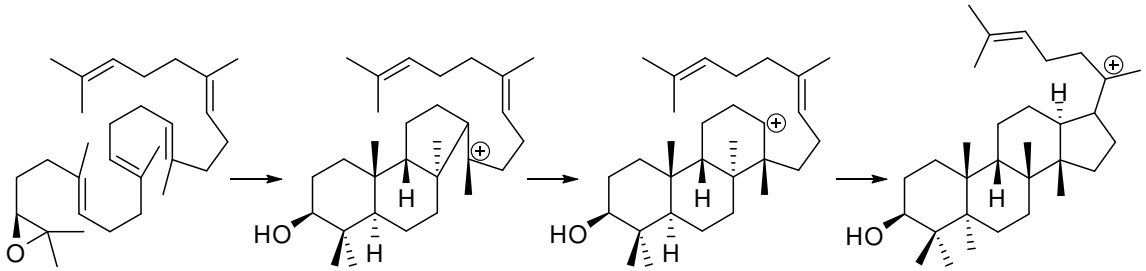


trans-anti-trans



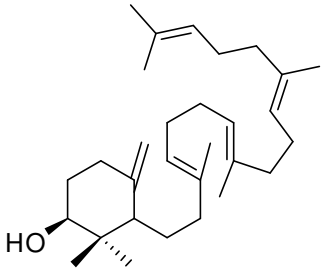
trans-syn-trans

Corey proposed a cationic 6-6-5 intermediate ring structure **3-7** followed by ring expansion **3-8** and subsequent ring closure to give the 6-6-6-5 lanosterol ring system **3-9**.



3-7 **3-8** **3-9**

In addition, nonenzymatic studies have helped chemists develop mechanistic hypotheses for the enzymatic reaction.[110,111] More recently researchers have used site directed mutagenesis on the terpene cyclases and have found several products that allude to a stepwise mechanism.[114,115] Matsuda discovered the monocycle achilleol A **(3-10)** with mutations of oxidosqualene cyclase at V454A or V454G and proposed a cationic stepwise pathway for cyclization.[114]



3-10

Density functional theory calculations by Hess support the mechanism of Corey and suggest concerted ring formation to the 6-6-5 intermediate ring structure, followed by concerted C ring expansion with concurrent D ring formation.[116-118] On the other hand, a recent study by Gao performing a quantum mechanics/molecular mechanics

calculation of the entire enzymatic system of squalene cyclase has shown the ring expansion step proposed by Corey is energetically unfavorable.[119,120]

Finally, the crystal structure of the enzyme has recently been solved by a group of researchers in Switzerland.[121] The structure shows that aromatic residues in the active site lie in close proximity to stabilize the positive charges on intermediate structures and the crystallographers support the Corey stepwise mechanism.

These mechanistic studies are diverse and contradictory to one another. Regardless of the numerous studies, the literature lacks definitive evidence for details of the reaction mechanism.

Plausible Mechanisms for OSC. Shown below in figure 3-1 is a schematic of the possible mechanistic pathways available to OSC. The yellow circles show the positions that KIEs would be expected for each mechanistic pathway. A stepwise ring closure to give the closed A ring carbocation would give KIEs at four possible positions within the A ring. The KIE at the carbocation center and the carbon with the hydroxyl attached may be slightly smaller, theoretical predictions would aid in the interpretation. On the other hand, a concerted mechanism of the simultaneous ring closure of the ABCD rings would KIEs through the entire core of the ring system. The possible mechanisms will be discussed further in the analysis of the measured KIEs.

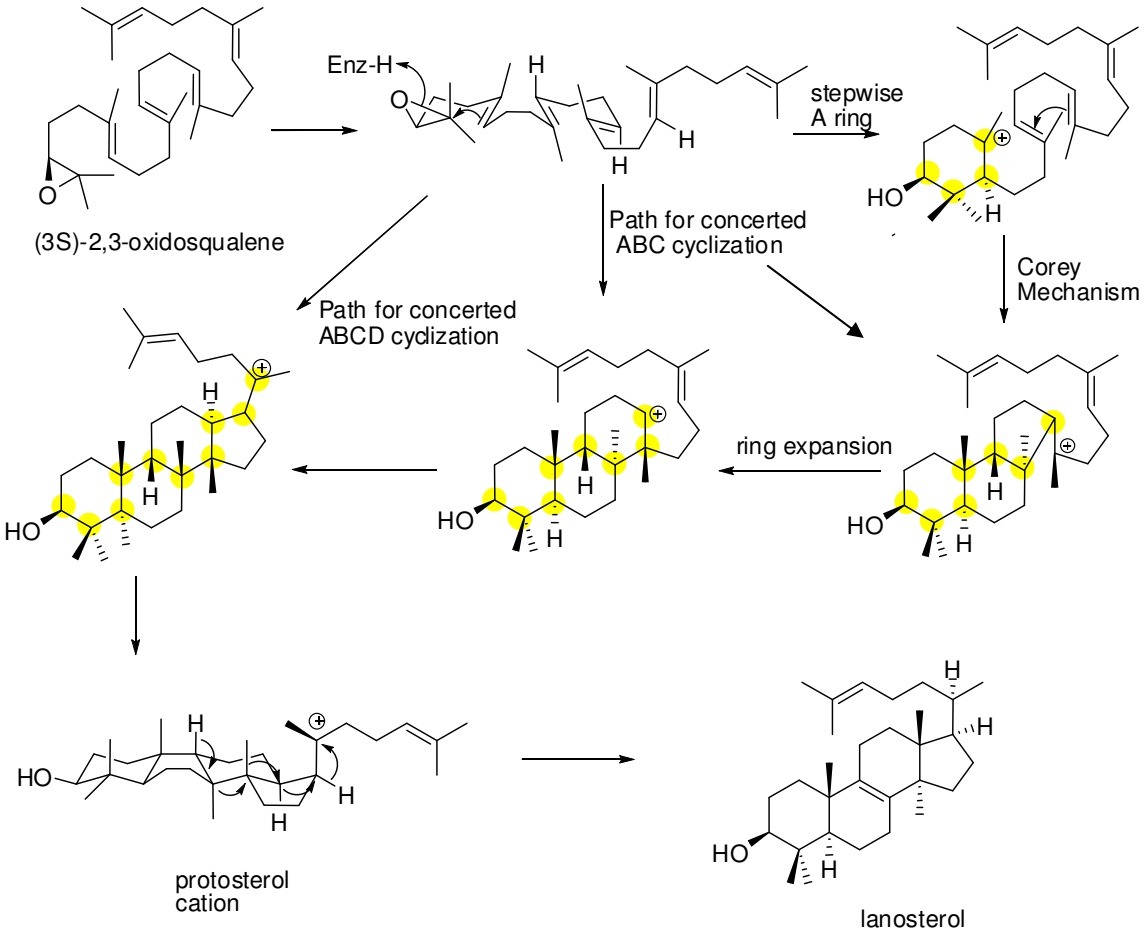


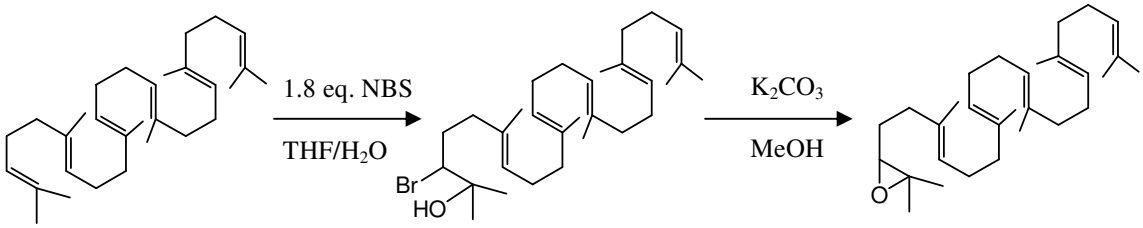
Figure 3-1. Possible mechanisms for the cyclization of oxidosqualene by OSC. The yellow circles show the positions that should display KIEs in each particular mechanism.

Results and Discussion

We have studied the cyclization of oxidosqualene from *Saccharomyces cerviscae* by measuring the product kinetic isotope effects at natural abundance. The product KIEs must be measured in this system, since the measurement of starting material KIEs is not viable because 1) the starting material is racemic and the isolation of pure starting material, (3S)-2,3-oxidosqualene, would be difficult and 2) the ^{13}C peaks of the starting

material overlap in the spectra making isotopic analysis of each individual carbon prohibitive. Therefore, we have developed a new NMR methodology to handle this complicated case, which allows the determination of the isotope effects on all 30 carbons of lanosterone, a derivative of lanosterol, simultaneously.[16] The process for studying the KIEs involved the synthesis of (+)-2,3-oxidosqualene; optimization of reaction conditions; isolation of lanosterol; optimization of NMR conditions and data collection; and KIE analysis.

Optimization of Experimental Conditions. Racemic 2,3-oxidosqualene was synthesized from squalene based on the methodology of Scott.[122] This was accomplished in large scale batches of several 100 gram reactions that were purified and combined into a single batch, resulting in approximately 25-40% yields of isolated ±oxidosqualene. Low yields were due to the insolubility of the squalene and the formation of several side products from the bromohydrin reaction. Therefore, extensive time was needed just in preparation of starting materials.



The measurement of product (rather than starting material) KIEs adds difficulty to the enzymatic experimental procedure, since the measurements require a large amount of starting material to be taken to complete conversion by the enzyme. The initial experimental conditions followed the procedure of Scott *et a.l* and were initially 0.7%

Triton X-100, 100 mM phosphate buffer, pH 6.2, 1 mg/ml oxidosqualene, at 37 °C.[123] The reaction conversion was determined by the amount of (3R)-2,3-oxidosqualene remaining in the reaction mixture determined by NMR chiral shift studies in d_6-benzene using $Eu(hfc)_2$. Initial reactions gave about approximately 60-85% conversion of the oxidosqualene to lanosterol product. The enzymatic reaction was initially optimized by changing the concentration of Triton X-100 (fig 3-2), concentration of ±oxidosqualene (fig 3-3), reaction time (fig 3-4), and temperature (fig 3-5) and leaving all other conditions similar to literature procedure, as shown below**.**

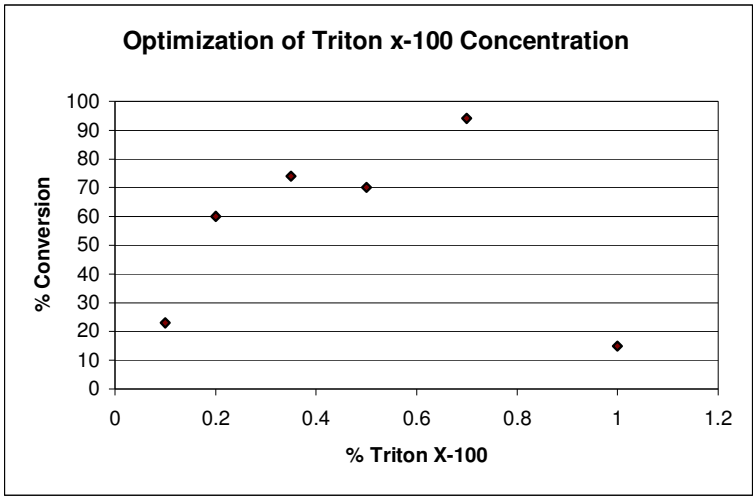


Figure 3-2. Reactions of oxidosqualene cyclase performed with varying amounts of Triton X-100. The % conversion of (3S)-2,3-oxidosqualene to lanosterol is plotted on the y-axis and the % Triton X-100 is plotted on the x-axis.

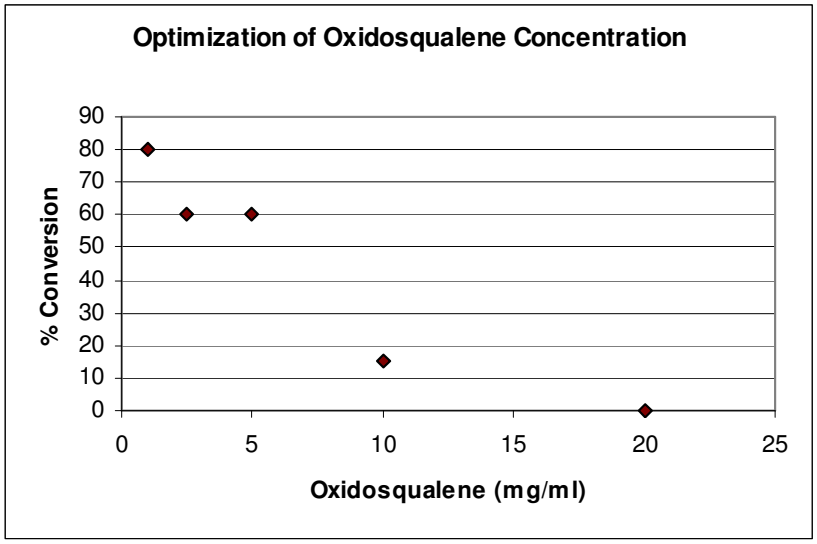


Figure 3-3. Reactions of oxidosqualene cyclase performed with varying amounts of oxidosqualene concentrations. The % conversion of (3S)-2,3-oxidosqualene to lanosterol is plotted on the y-axis and the concentration of oxidosqualene (mg/ml) is plotted on the x-axis.

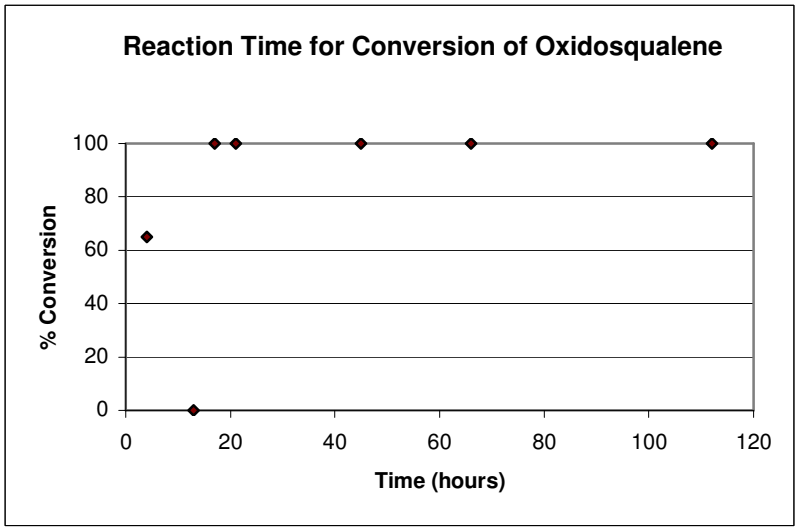


Figure 3-4. Reactions of oxidosqualene cyclase performed with varying reaction times in hours. The % conversion of (3S)-2,3-oxidosqualene to lanosterol is plotted on the y-axis and the reaction times (hours) is plotted on the x-axis.

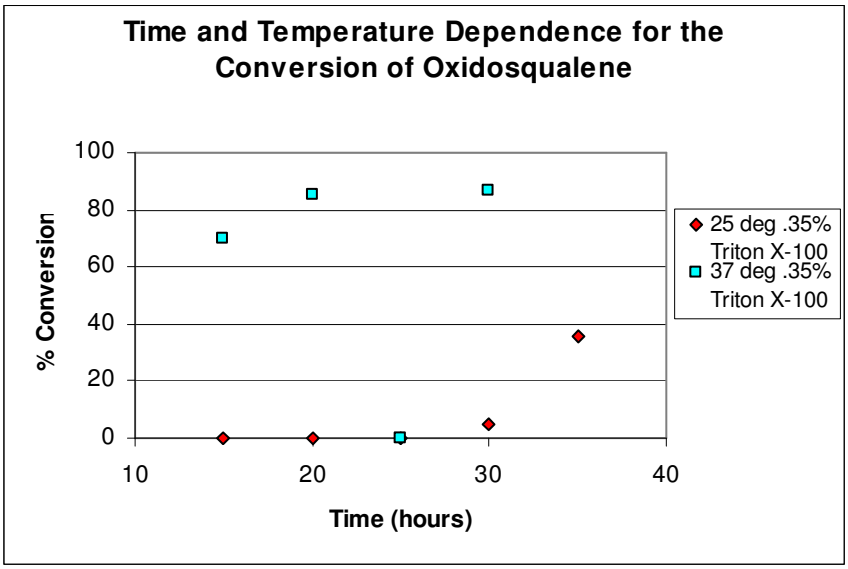


Figure 3-5. Reactions of oxidosqualene cyclase performed with varying reaction times (hours) and temperatures. The % conversion of (3S)-2,3-oxidosqualene to lanosterol is plotted on the y-axis and the reaction times (hours) is plotted on the x-axis.

The best conditions found were 100% reaction completion on 100 mgs of ±oxidosqualene at .7% Triton X-100, 1 mg/ml ±oxidosqualene, 37 °C, 24 hour reaction time, 50 minutes lysis time, and 30 g Fleishman's bakers yeast. Consequently, under these optimized conditions, regardless of the amount of yeast added, the maximum amount of substrate that could undergo complete conversion was 100 mgs of ±oxidosqualene, which is not enough material for ^{13}C NMR isotopic analysis. The inconsistency in the data listed in figures 3-2 to 3-5 for reaction conversions led us to believe that a systematic error existed within the current procedure.

We hypothesized that the solubility of the oxidosqualene may be a problem, since the reaction did not appear homogenous. In addition, we did not have a clear way of measuring the amount of active enzyme that was being added to the reaction since we were adding crude lysate from the cell extracts. A simple NMR experiment in D_2O showed that only 19% of the $\pm$ oxidosqualene was soluble using the current set of conditions (see experimental section for details). To further study the optimization of conditions several attempts were made to increase the solubility of oxidosqualene in the reaction. A Potter-Elvehjem homogenizer was initially used, but did not seem to improve solubility much. A sonicator was then used to homogenize the reaction mixture.

An NMR experiment in D_2O using sonication and increasing the Triton X-100 ten times displayed 100% $\pm$oxidosqualene solubility, even over an extended period of time. These new conditions increased the reactivity greatly, resulting in ~80-85% reaction completion on 2 g of $\pm$oxidosqualene at .7% Triton X-100, 1 mg/ml $\pm$oxidosqualene, 37 °C, 24 hour reaction time, 50 minutes lysis time, and 452 g of Fleishman's bakers yeast (the amount of Triton X-100 was not increased because previous experiments indicate that greater that excess of the surfactant results in enzyme inhibition),[123]

Large scale reactions under these conditions exhibited only ~65% conversion at 3 hours and stopped reacting after approximately 12 hours, extended reaction times for several days did not increase the extent of the reaction. Increasing the amount of yeast above 452 grams did not increase the reaction conversion, but actually decreased the

reactivity (probably due to interference from all of the excess materials in the lysate). Using the new procedure for solubilizing the oxidosqualene, 50 mg test reactions were performed to optimize the temperature of the reaction. Reactions at 37°C gave conversions of 100% in duplicate and 25°C gave 68% and 96%. An increase in the Triton X-100 to 0.1% gave 96% conversion of 2.0 g ±oxidosqualene to lanosterol. However, the reaction was erratic and high conversions were difficult to reproduce. The extent of conversion ranged from ~60-96% using similar conditions each time.

To further optimize the reaction, the type of cell lysis was studied to maximize the amount of active enzyme being added to the reaction. The initial method used to lyse the yeast cells was continuous sonication of the cell lysate.[123] The inability of the sonication method to produce enough enzyme for complete conversion of the oxidosqualene in a consistent manner, is probably due to the heat generated from the long amount of time needed to lyse such a large batch of yeast. This probably causes degradation of the oxidosqualene cyclase enzyme. This is consistent with other studies that show protein degradation increases with long sonication times in yeast lysis.[124] However, sonication is a quick and efficient method for the lysis of small batches of yeast required in the microscale conversion of oxidosqualene to lanosterol.

A series of lysis methods were screened on small scale and included chemical autolysis, freezing, mechanical grinding, french pressing, enzymatic lysis, and vortexing with glass beads (see experimental section for details). Chemical autolysis, freezing, mechanical grinding of the dry yeast before solubilizing, and enzymatic lysis with lyticase (Sigma-Aldrich Chemical Company), gave little or no conversion of the

substrate to lanosterol, despite a series of attempts. The French press method increased the conversion of oxidosqualene to 100% conversion, however, this method was limited by the small amount of yeast that could be lysed in a batch, which was not sufficient for the conversion of the large amount of ±oxidosqualene needed for isotopic analysis. Finally, the mechanical method of beating the yeast with glass beads (.5 mm) in a bead beater (Biospec) gave excellent results on a batch of yeast for a large scale reaction, and the conversion of oxidosqualene increased to >98%.

However, throughout the study of oxidosqualene cyclase the most problematic portion was the lysis of the yeast. The enzyme activity was very sensitive to temperature and the amount of time required for lysis:

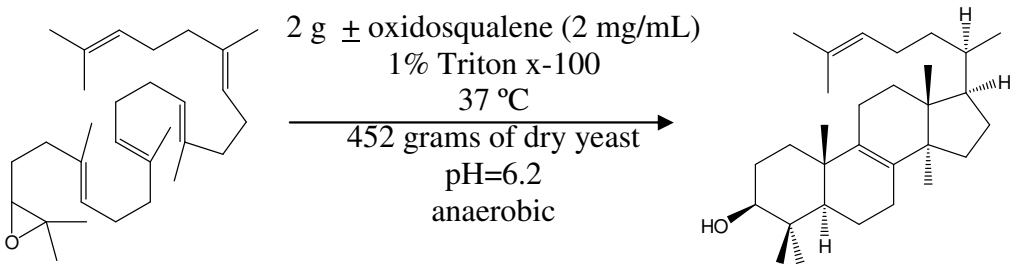


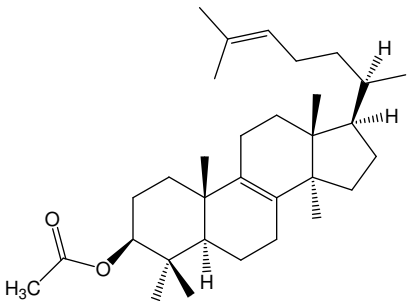
Figure 3-6. The optimal reaction conditions for the reaction of OSC for large scale reaction on a 1 L scale. Conditions are 2 mg/mL ±oxidosqualene, 1% Triton X-100, 452 grams of dry yeast, at 37 ºC, at pH = 6.2, under anaerobic conditions.

Lysates with a pH over 6.1 were not used because these lysates resulted in poor activity, probably resulting from poor lysis exhibited in the lack of acid contributed from the breakage of the yeast cell wall. Additionally, batches that seemed to have a good lysis would sometimes give little or no conversion of the oxidosqualene, destroying valuable

starting material as a result of a "bad batch" of yeast. (This was hypothesized from discussions with Dr. Williams, based upon previous studies in the Scott lab).

The optimal reaction conditions are shown below in figure 3-6**.** (See the experimental section for specific details of the reaction conditions) Further attempts to increase the scale of the reaction failed. Reactions on a 3.0, 3.5, and 4.0 gram scale of ±oxidosqualene never exceeded 90% conversion regardless of the amount of yeast added to the reaction.

Optimization of NMR Conditions. The next step was to optimize the conditions for NMR analysis of the product lanosterol. This involved the synthesis of derivatives to give optimal sample solubility and the best separation of peaks in the ^{13}C spectra. The derivatives of lanosteryl acetate **3-11**, lanosteryl triflouroacetate **3-12**, and lanosterone **3-13** were all synthesized and tested for solubility and NMR properties as described in the experimental section. For each derivative of lanosterol the solubility was tested at various temperatures. The ^{13}C spectra were analyzed for peak separation in a series of solvents including $CDCl_3$, d_6-benzene, d_8-THF, d_8-toluene, CD_2Cl_2, and CD_3OD:



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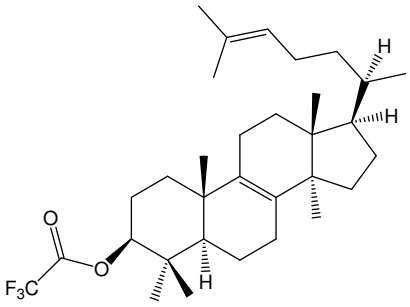

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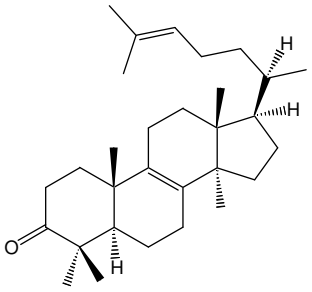
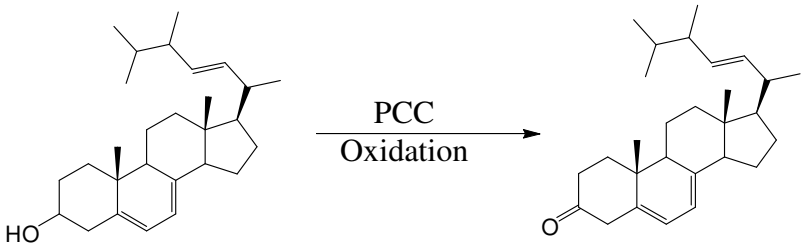


3-13

Ketone **3-13** displayed the best solubility in a series of solvents and each of the 30 carbon peaks resolved in the ^{13}C NMR spectra.

Initially three samples were oxidized with pyridinium chlorochromate (PCC) according to the procedure in the experimental section. NMR samples were prepared using 400 mgs of lanosterone in $CDCl_3$. ^{13}C NMR analysis indicated several small impurity peaks in the spectra. The impurity could be a side product from the oxidation or could result from an impure lanosterol sample from the yeast reaction. An impure sample from the yeast reaction could be a result of side product formation in the enzymatic reaction or impurities from the lysate. Even though the ^{13}C NMR for lanosterol appeared pure, the ketone is much more concentrated and side products would become visible in the NMR spectra. A likely impurity could be ergosterone **3-16**, which is the oxidation product of ergosterol **3-15**, a sterol present in large quantities in yeast lysate.

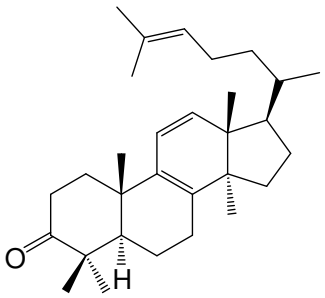


3-15 **3-16**

Attempts to remove the impurity by silica gel chromatography were unsuccessful, this was not surprising since only one spot was visible by TLC in a series of solvent systems. A series of recrystallizations from pentanes, hexanes, methanol, methanol/water, acetone, and acetone/water were also unsuccessful in removing the

impurity. Tandem gas chromatrography/mass spectrometry (GC/MS) indicated a 4.4% impurity (*m/z* [M^+] 422) that was 2 mass units less than lanosterone (*m/z* [M^+] 424). The mass spec data eliminated the possibility of ergosterol (mass 396.7) as the impurity. We suspected that the lanosterone had formed a triene derivative during the PCC oxidation, which was also consistent with ^{13}C NMR data that displayed six peaks in the alkene region of the spectra. We used silver nitrate impregnated and reverse phase TLC plates to see if we could separate the material. Silver nitrate impregnated silica gel is known to separate sterols according to the number of double bonds in the molecule.[125] PCC oxidized lanosterone displays two distinct spots on silver nitrate TLC in 7:3 hexanes/toluene. However, attempts to separate large quantities of the lanosterone on silver impregnated silica gel columns were unsuccessful. Separation of the mixture on reverse phase TLC was unsuccessful in a series of solvent systems. Next, we thought that perhaps the impurity would selectively react and then we could separate the product from lanosterone using chromatography. Tetracyanoethylene would react in a Diels-Alder reaction if the impurity were an s-*cis*-conjugated diene, if the diene was an s-*trans*-diene it could perhaps react in an ene reaction.[126] Unfortunately, even excesses of the reagent did not cause the transformation to occur (as described in the experimental section). In conclusion, initial attempts by recrystallization, chromatographic techniques, and chemical reactivity were unsuccessful in removing the impurity.

Several triene derivatives of lanosterone could exist. Some possibilities are shown below, and represent only some of the possible isomers. Trienes that involve double bond rearrangement or migrations have not been included, but were considered.



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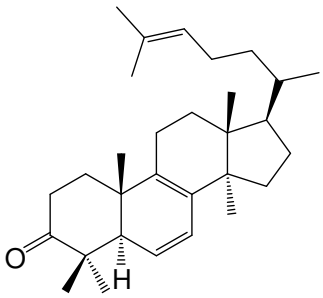

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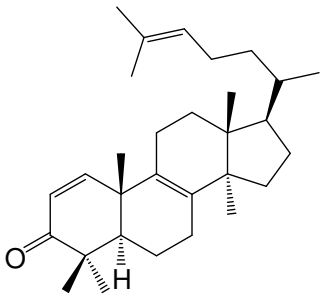

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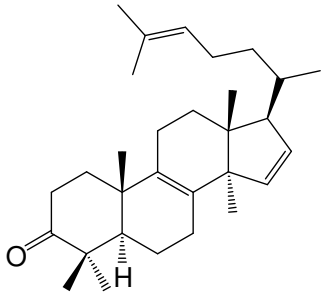
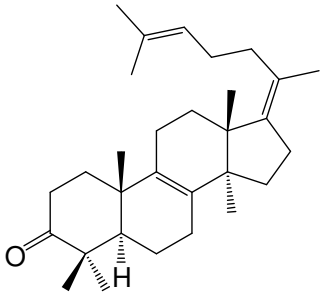
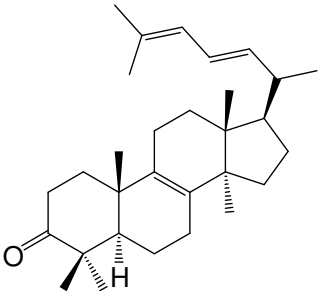


3-20



3-21

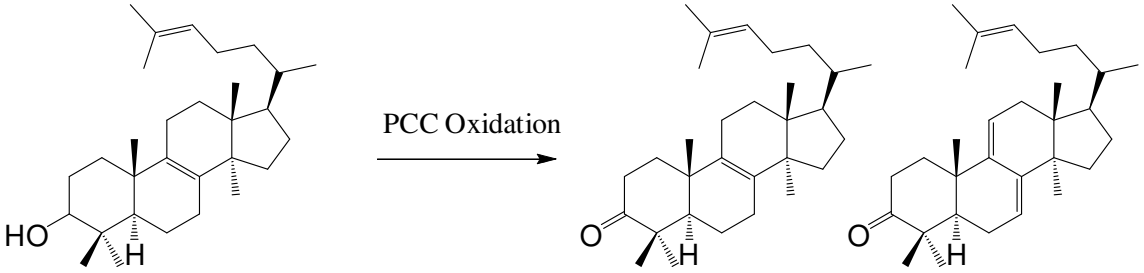


3-22

Most of these isomers could be eliminated based upon the structure or spectroscopic data of the ketones. For example, **3-21** is not a likely possibility because the proton NMR for the impurity displays two doublets for alkene peaks at δ 5.4 (*J*=5.6 Hz) and δ 5.5 (*J*=6.5 Hz). **3-19** is unlikely because the proton NMR of the impurity contains a doublet of triplets at δ2.7 ppm for the diasteriomeric methylene hydrogens α to the ketone. **3-20** is an unlikely chemical transformation, but could not be ruled out. **3-22** is an unattractive possibility because the mass spec pattern for the impurity exhibits an intense peak at 111, representing the side chain with only one double bond. However, compound **A** is quite likely based upon ^{1}H NMR and mass spectral data. We assumed that the structure of the impurity at least resembled compound A, giving similar

spectral properties, and was probably a triene that had a double bond on the side chain and a cyclic conjugated diene system.

In order to remove the impurity, we decided to characterize the compound. However, this is difficult since the impurity could not be isolated and constitutes only a small portion of the reaction mixture. An extensive literature search revealed that a possible side product from oxidation of lanosterol could be agnosterone **3-23**.



3-23
~4% impurity

Analysis by UV spectroscopy of an impure mixture of the PCC oxidation products of lanosterol displays an intense peak at λ=244 nm, characteristic of the diene system of agnosterol.[125] Infrared analysis of the ketone mixture showed the expected peak at 1736 cm^{-1} for the ketone of lanosterone, however the spectrum did not provide information about the nature of the impurity. ^{1}H and ^{13}C NMR analysis of the impure mixture revealed small impurity peaks that were consistent with reported values for agnosterone.[127]

The solubility of the lanosterone was tested in a series of solvents to determine the best solvent system for recrystallization and NMR sample preparation. Solubility tests revealed that lanosterone was soluble in diethyl ether, THF, and pyridine; slightly

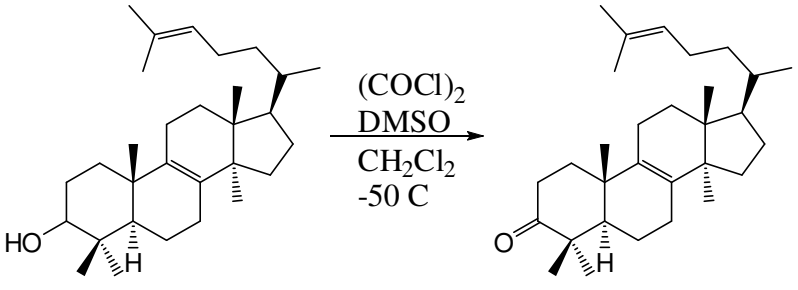
soluble in chloroform, benzene, acetone, cyclohexane, 1,4 dioxane, methylcyclohexane, dimsethyl formamide, and methylene chloride; and insoluble in methanol, ethanol, acetic acid, and diglyme. Several more attempts were made at recrystallization since we now knew the structure of the impurity. Recrystallizations were performed in a series of benzene/methanol mixed solvent systems, chloroform/methanol mixed systems, methanol, heptanes, and cold recrystallizations from ether. These recrystallizations were unsuccessful in removing the impurity. Another attempt was made at selectively reacting the impurity in the mixture and then removing the derivative using chromatography. The reaction mixture was treated with N-phenyl triazoline dione which should give the ene product more readily with the conjugated system than the corresponding lanosterone (see experimental section for details). However, ^{1}H NMR of the products indicated that reaction occured solely with the double bond on the side chain of the sterols and not with the cyclic double bonds within the ring system. Therefore, all attempts to remove the impurity from the lanosterone were unsuccessful.

We then decided to synthesize the agnosterone and dope the samples evenly with impurity to measure the ^{13}C isotope effects. We synthesized agnosterol according to literature procedures and then oxidized with PCC.[128] The impurities of all samples were doped to 5% agnosterone/lanosterone according to ^{1}H NMR integrations of the ketones, on reactions taken to 98, 35, and 27% conversion of the (S)-2,3-oxidosqualene to lanosterol, and measurements were made according to the procedures in the experimental section for runs 1-3.

Our next goal was to obtain data sets on samples that did not contain any impurities in the lanosterone. Another set of reactions gave 99, 100, 15, and 20% conversions, these were run under the same reactions as previously, except an N_2 atmosphere was maintained throughout the reaction to prevent the formation of any side products. Lanosterol from one of the reactions that had been taken to completion was purified and analyzed for any sign of impurity using GC/MS, NMR, and UV. Only a slight impurity at λ=290 was visible in the UV spectra, which was probably ergosterol from the yeast lysate. The sample was purified further with chromatography until analysis indicated pure lanosterol. A test reaction of 20 mgs was oxidized with a minimal amount of PCC. Analysis of the purified lanosterone indicated the presence of 4% agnosterone impurity.

Since reaction of the ketone was prone to impurity, we explored the possibility of acquiring data sets directly on the lanosterol. A series of solvents, temperatures, and concentrations of lanosterol were tested for the desired amount of signal in the ^{13}C spectra to give reproducibility in the integration of the peaks. Regardless of the conditions, the signal was much too low to give reproducibility in the peak integrations.

A test reaction of 20 mgs of lanosterol was submitted to the Swern oxidation conditions, the product lanosterone did not show any signs of the agnosterone impurity by UV or ^{1}H NMR, however, the yield was only 40%:



Several test reactions were performed to optimize the oxidation of lanosterol in the Swern conditions. The main complication of the reaction is the insolubility of lanosterol in the methylene chloride at the temperature (-78 ºC) required for the Swern oxidation. Reactions were tested using different concentrations of materials and at different temperatures. The final conditions are reported in the experimental section and changes from the literature procedure involved a decrease in the concentration of the lanosterol, to improve solubility; an increase in the temperature to -50 ºC; and an increase in the amount of oxalyl chloride and DMSO. Oxidation of two of the samples were successful, however, the oxidation of the other two reaction samples were unsuccessful and destroyed the lanosterol in the process. Data sets were collected on the samples of >99% and 20% conversions according to the procedure in the experimental section for reactions 4 and 5.

Since two of the previous samples had been ruined by the Swern oxidation reaction, we sought another method for oxidation. A series of oxidation methods were tested including PCC on alumina, PCC in sodium acetate, Jones, Collins, and the Parikh-Doering (see experimental section for procedures and reaction details). All of the chromium oxidations gave agnosterone side product, even when buffered. The Parikh-

Doering conditions resulted in very low conversions of the lanosterol to the ketone. Therefore, to date the Swern oxidation is the best method we have found for the oxidation of lanosterol to lanosterone, with no inseparable side product formation, however the reaction is prone to low yields with destruction of the starting material.

In order to acquire a second independent data set on pure lanosterone, the preparation of several other samples have been attempted. Three more samples of lanosterol were successfully run to 100 and 31% conversion of oxidosqualene to product. Unfortunately, the Swern oxidations were too low yielding to provide samples that could be analyzed. Nine other oxidosqualene cyclase reactions resulted in conversions of slightly less than 100% conversion to product (ranged from 92-96%) of the starting material to product, insufficient for KIE study. In these studies starting materials were often wasted by incomplete reactions or poor oxidations. The preparation of samples is very time consuming. This requires large amounts of starting materials that take several months to synthesize and purify. This is magnified by the difficulty to oxidize the lanosterol in high yields without any side product formation and by the random error of poor batches of yeast.

KIE Measurements. Two sets of KIE measurements were collected for independent reactions of OSC. However, one of the sets was contaminated with the agnosterone impurity and must be disregarded. The KIEs predicted from the second set of samples is shown below in figure 3-7, and the details for the analysis are listed in the experimental section of this text.

The measurements display KIEs throughout the core of the ring system, suggesting a concerted type ring ABC closure as demonstrated in figure 3-7. However, this result must be verified by the acquisition of data on a second set of data of independent reactions. KIEs are displayed on a methyl group in the A ring and a methylene carbon in the C ring, an enhancement is not expected in these positions and this is probably an artifact of an impurity within the 100% conversion sample. Also a number of inverse KIEs were apparent in the analysis and the interpretation of these is not well understood from a qualitative analysis.

Measured KIE for the reaction are also slightly lower than might be expected ring closing process, which might be due to partial rate-limiting binding of the substrate. Reaction conditions at a higher pH might cause the chemistry step to become more rate-limiting and unmask the KIE for the cyclization reaction. Also, the importance of extremely clean sample for KIE measurements at natural abundance on large molecules should be emphasized and analytical techniques for purification should be integrated into the sample preparation. Overall, a method was developed for the measurement of 30 simultaneous ^{13}C KIEs with high precision.

Conclusions

The reaction of OSC was optimized for reaction conditions suitable for the measurement of product KIEs using NMR methodology. A method was developed for measuring KIEs on a large 30 carbon system successfully, with excellent precision in the measurement. One set of KIEs was analyzed and suggests a concerted ABC ring closure.

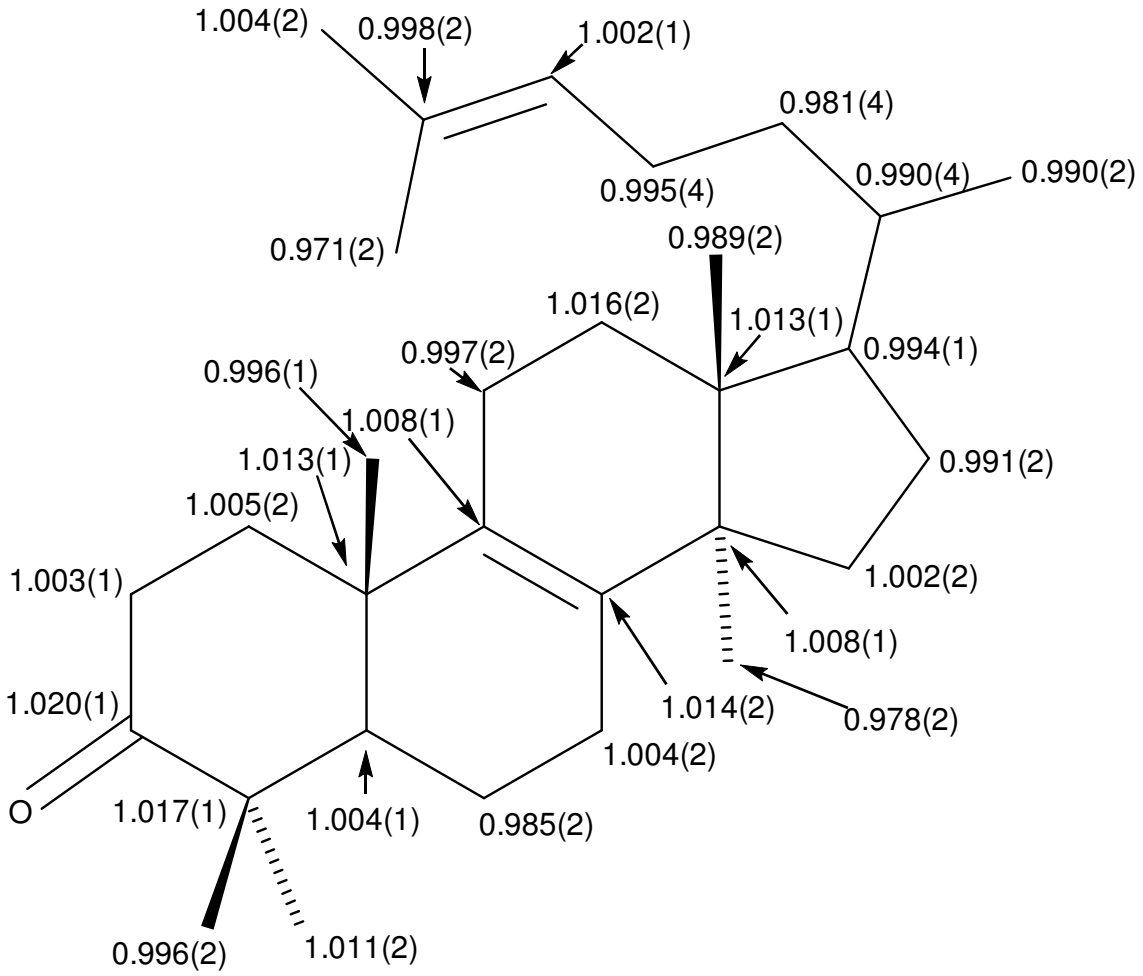


Figure 3-7. KIE measurements for the reaction of oxidosqualene cyclase. The standard deviations are calculated from a set of eight independent measurements for the partial conversion reaction (20%) and ten measurements for the 100% conversion reaction.

CHAPTER IV

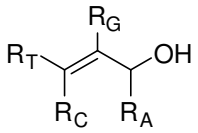
STUDIES ON THE MECHANISM OF THE SHARPLESS EPOXIDATION – ORIGIN OF LIGAND ACCELERATED CATALYSIS

Introduction

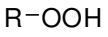
The Sharpless asymmetric epoxidation (AE) was the first general, highly enantioselective, functionalizing reaction in asymmetric catalysis.[129-131] There has been extensive investigation of the AE reaction, and ideas derived from these studies, particularly the concept of ligand-accelerated catalysis (LAC), have been of substantial importance in rational approaches to asymmetric catalysis in general.[132] The idea of ligand-accelerated catalysis is that in asymmetric reactions catalyzed by chiral metal complexes, the overall enantioselectivity obtained depends not only on the enantioselectivity engendered by a chiral ligand but also on the competition between the desired catalysis and that by non-ligated achiral catalysts. The task of achieving high enantioselectivity is thus simplified when the coordination of a ligand increases catalytic activity. The understanding of the nature of the ligand-accelerated catalysis in a reaction depends on a detailed knowledge of the mechanism including the transition state for the selectivity-determining step. In complex catalytic reactions, this knowledge may be elusive – it can be difficult enough to identify the active catalyst. In the AE reaction considerable research has succeeded in establishing the stoichiometry and basic structure of the active catalyst, but proposals for the active transition state are circumstantial.

The necessary components of the AE include an allylic alcohol (**4-1**), alkyl hydroperoxide (**4-2**, usually R=t-butyl), a titanium tetraalkoxide (**4-3**, usually R=iPr),

and a chiral diol (**4-4**, usually R=R'=CO_2alkyl).[129,133,134] Increased selectivities directly correlate with rate enhancements, suggesting rate-limiting C-O bond formation.[135,136] This is supported by the observation of a deuterium isotope effect on the olefinic positions of the allylic alcohol, a dependence of the rate upon olefin concentration, and a lack of a solvent isotope effect.[134]



4-1



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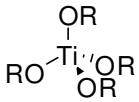

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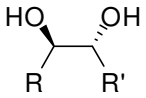


4-4

A variety of observations support a dimeric structure for titanium tartrate ester species in CH_2Cl_2 solution, and support that a dimeric structure is retained in the rate-limiting transition state.[137] The observation of a non-linear effect of the tartrate enantiomeric excess (ee) on product ee and an effect of using racemic tartrate ester on product disastereoselectivity is compelling evidence for the involvement of two tartrates in the rate-limiting transition state.[137] Crystal structures of titanium tartrate complexes exhibit a titanium oxo bridged dimer species, compatible with the experimentally determined molecular weight of the solution structure.[137,138] The rate law (equation 4-1) measured under pseudo-first order conditions is consistent with a rate-limiting step involving two titanium atoms, two molecules of tartrate ester, two isopropanols, one allylic alcohol and one alkyl hydroperoxide.[134,137]

$$\text{rate} = k[\text{allylic alcohol}][\text{Ti-tartrate}][\text{alkyl peroxide}]/[\text{inhibitor alcohol}]^2 \qquad (4\text{-}1)$$

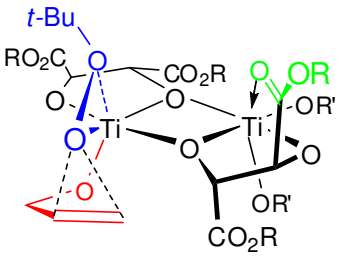
Additional kinetic studies show that the reaction is first order in titanium and tartrate ester (in a 1:1 ratio) over a ten fold concentration supporting a single dimeric aggregation state for the active catalyst. Reaction conditions that deviate from a 1:1 ratio of titanium to tartrate decrease the rate and selectivity.[134]

High enantioselectivities in the AE reaction require specific structural features of the alkyl hydroperoxide oxidant, chiral diol, allylic alcohol substrate, and bystander alcohols. From studies of coordination equilibrium constants the alkyl hydroperoxide coordination is thought to be bidendate.[134] The alkyl group of the hydroperoxide is brought into close proximity of the metal, and steric bulk in the alkyl group is required for high selectivity (**4-2** R=t-butyl is a more selective oxidant than the R=n-butyl). The chiral diol **4-4** must contain two substituents (R' cannot be H), one of which must be an ester or amide (R=CO_2R or $CONR_2$) with the second being ester, amide, or bulky hydrocarbon (R'=CO_2R, $CONR_2$, or alkyl).[135] The detailed steric and electronic characteristics of **4-4** affect selectivities, for example, the selectivity in kinetic resolutions is reduced with decreasing steric bulk of the ester group of tartrates (R and R'=CO_2Me<CO_2Et<CO_2iPr).[139]

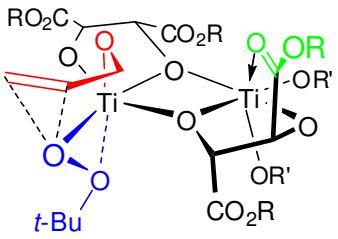
General trends are observed in the steric requirements of the substituents on the substrate **1**. Substitutions in the *trans* position of the olefin **1**, R_T tend to enhance selectivity, alternatively large substituents in the cis position **1**, R_C decrease selectivity. The composition of the titanium tetralkoxide can also affect selectivities. The use of **4-3**, R=t-butyl leads to lower selectivity, and this is thought to result from a decreased ability to form the active dimeric catalyst complex, resulting in an increase of the non-

ligated process.[140] Other reaction conditions that affect the amount of the active dimer complex affect the selectivity. For example, decreased selectivity is observed in non-polar solvents, resulting from the formation of higher aggregate states of the catalyst in the non-polar environment.[134,137]

Several models have been proposed for the transition state geometry of the AE. Experimental evidence has excluded many of these models, such as the 10-membered ring tartrate bridged structure**,** and the alkoxide bridged structure.[135,141,142] From their diverse experimental observations, Sharpless and Finn proposed that a preference for transition state **4-5** is responsible for enantioselectivity.[130] In this model, the dimeric transition state complex consists of two titanium glycolate rings conjoined in a central four-membered ring by bridging alkoxides. One of the titanium glycolates, the "reactive titanocycle," has the titanium coordinated with both the allylic alcohol and the alkyl hydroperoxide. The second titanium glycolate, the "spectator titanocycle," has axially oriented carboxylates with the carboxylate that is distal to the reactive titanocycle serving as the sixth ligand for the spectator titanium. The allylic alcohol on the reactive titanocycle is loaded anti to the ligated carboxylate on the spectator titanocycle and "hooks in", i.e., toward the spectator titanocycle.



4-5



4-6

From a careful analysis based on DFT calculations of monomeric Ti complexes (a necessary limitation at the time), Wu and Dai proposed an alternative model for transition state complex.[143] In the Wu model **4-6**, the allylic alcohol is loaded syn to the ligated carboxylate on the spectator titanocycle and "hooks out", i.e., away from the spectator titanocycle. The Wu model refined some other aspects of the reactive transition state, for example assigning an equatorial orientation of the ester groups in the reactive titanocycle.

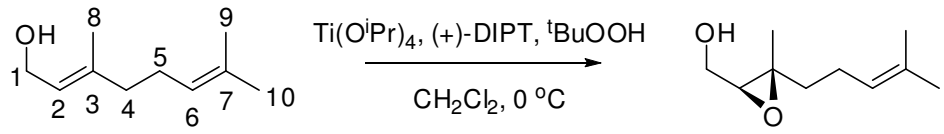
Both the Sharpless and Wu models provide a ready explanation for one aspect of the selectivity in the AE, the differing reactivities of chiral alcohols in kinetic resolutions. In either model, the less reactive of chiral allylic alcohols (**4-1**, R_A= alkyl) would orient an alkyl group into a sterically encumbered position toward the titanocycles. However, the origin of the basic enantioselectivity with achiral allylic alcohols is less clearly defined. Sharpless attributes the enantioselectivity to general steric and electronic effects. In the Wu proposal, a steric interaction of the allylic alcohol with the spectator titanocycle disfavors a key diastereomeric transition state leading to the minor enantiomer, though this steric interaction was not directly

assessable by the calculations on monomeric complexes. Neither model provides a well-defined explanation for the ligand-accelerated catalysis.

We report here that current models of the AE mechanism do not account for its stereoselectivity, and we propose a new model that is supported by high-level theoretical calculations and experimental KIEs. This model provides an explanation for ligand-accelerated catalysis in the AE, and suggests a new principle for the design of catalysts for stereoselective reactions.

Results and Discussion

Experimental Kinetic Isotope Effects. The prototypical epoxidation of geraniol (4-7) to the corresponding epoxide **(4-8)** was chosen for study under standard AE conditions using $Ti(OiPr)_4$, (+)-diisopropyl tartrate, and t-butyl hydroperoxide in CH_2Cl_2 at 0 ºC.[133] The ^{13}C KIEs were measured at natural abundance using NMR methodology.[16] The unreacted starting material was isolated from reactions of geraniol taken to 87.4$\pm$1.0, 87.0$\pm$1.0, and 94.3$\pm$1.0% conversion using fractional vacuum distillation followed by column chromatography. Changes in isotopic composition were determined by ^{13}C NMR analysis of the recovered material against a standard sample of starting material that was not subjected to reaction conditions. The C_5 methylene peak of geraniol was used as an internal standard with the assumption that the KIE in this position is negligible. The KIEs were calculated from the fractional conversion of the reaction and the change in isotopic composition as previously described.[16]



4-7 **4-8**

The resulting KIEs are shown in figure 4-1. Allowing for the uncertainties, the independent sets of ^{13}C KIEs are in good agreement, significant KIEs were observed at the C_2 and C_3 positions of the geraniol, with the C_2 KIE being slightly larger. The measurements indicate that KIEs are present at C_9 and C_{10}, this is an artifact caused by an impurity in the reisolated starting material. The qualitative interpretation of these KIEs is that the epoxidation involves slightly asynchronous C-O bond formation in the rate-limiting step of the reaction, with more advanced bond formation at the C_2 position than the C_3 position. A more quantitative interpretation of these KIEs will be discussed with the assistance of theoretical models.

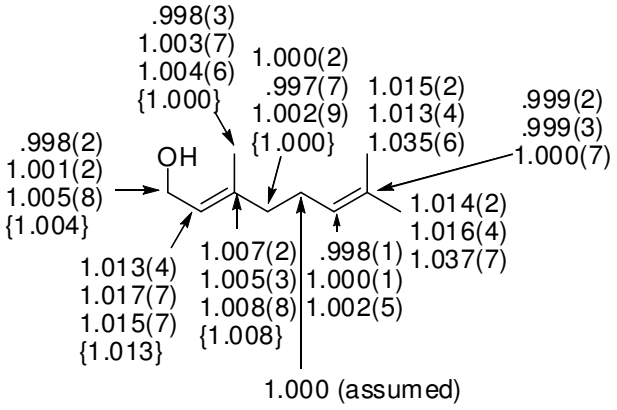


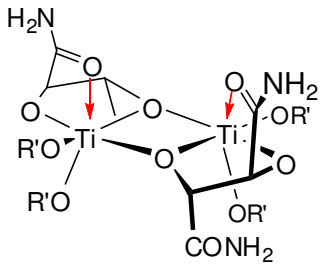
Figure 4-1. Experimental and predicted ^{13}C KIEs $\left(\frac{k_{12_C}}{k_{13_C}}\right)$ for the AE of geraniol using $Ti(OiPr)_4$, (+)-diisopropyl tartrate, and t-butyl hydroperoxide in CH_2Cl_2 at 0 ºC. The three sets of experimental KIEs refer to three independent experiments, and standard deviations in the last digit from six determinations are shown in parentheses. The predicted ^{13}C KIEs are shown in brackets and are based on transition structure **4-16**.

Theoretical Calculations. The choice of method and basis set for the study of the AE is complicated by the balance of calculating a geometrically accurate titanium dimeric complex and an accurate geometry for the epoxidation transition state. B3LYP calculations have been found to perform well with simple epoxidation reactions. However, a substantial issue in applying DFT calculations to the AE is the dative bond between the axial carbonyls and titanium. DFT methods have often performed weakly with such dative bonds. For this study, geometry optimizations were carried out in mPW1K using a SDD basis set with a core potential for titanium and 6-31G* on all other atoms (designated here as SB). Single-point energies were then calculated using an extension of the SDD basis set augmented with three f-functions and a separated d-function (a 3111 contraction instead of the normal 411) for titanium, along with a 6-31+G** basis set on the remaining atoms (designated here as BB). Geometry optimizations of a subset of models in mPW1K/BB gave similar single point energies (less than .01 kcal/mol difference) to corresponding geometries optimized in mPW1K/SB. Therefore, the mPW1K/SB method was found sufficient for geometry optimizations. For the lowest energy structures, geometry optimizations in mPW1K/SB and single point energies in mPW1K/BB were performed using a PCM solvent model in dichloromethane.

We chose to explore the accuracy of a number of DFT functionals and basis sets in reproducing the experimental bond lengths of a truncated model of a crystal structure published by Sharpless and Lippard.[138] Dimeric model **4-9** is shown below and consists

of a bridged titanium dimer complex with two methoxide bystander alcohols and a diamide ethylene glycol as the complexing ligand.

The ability of several theoretical methods to reproduce the experimental geometry of **4-9**, specifically the dative bond of the carbonyl oxygen to the titanium (shown in red), was tested. The mPW1K functional most accurately reproduced the geometry of the published crystal structure and differences in the basis set resulted in negligible geometric effects; the details of this study are included in the appendix.



4-9

To ensure the correctness of the mPW1K/SB in predicting the epoxidation transition state geometry, we analyzed several previously explored epoxidation systems where other theoretical methods have accurately predicted experimentally measured ^{13}C KIEs.[6,144,145] Illustrated below in figure 4-2 are the experimental and theoretical KIEs from the Shi Epoxidation of β-methyl styrene, oxaziridine epoxidation of 2-methyl-2-butene, and mCPBA epoxidation of 1-pentene. Figure 4-2 includes previously measured experimental KIEs (no brackets) and theoretical predictions (square brackets) using the models shown. The KIEs calculated from optimized geometries in mPW1K/SB (curly brackets) for gas phase and PCM solvent models accurately predict experimental

measurements, validating the use of the selected method in modeling transition states for the AE.

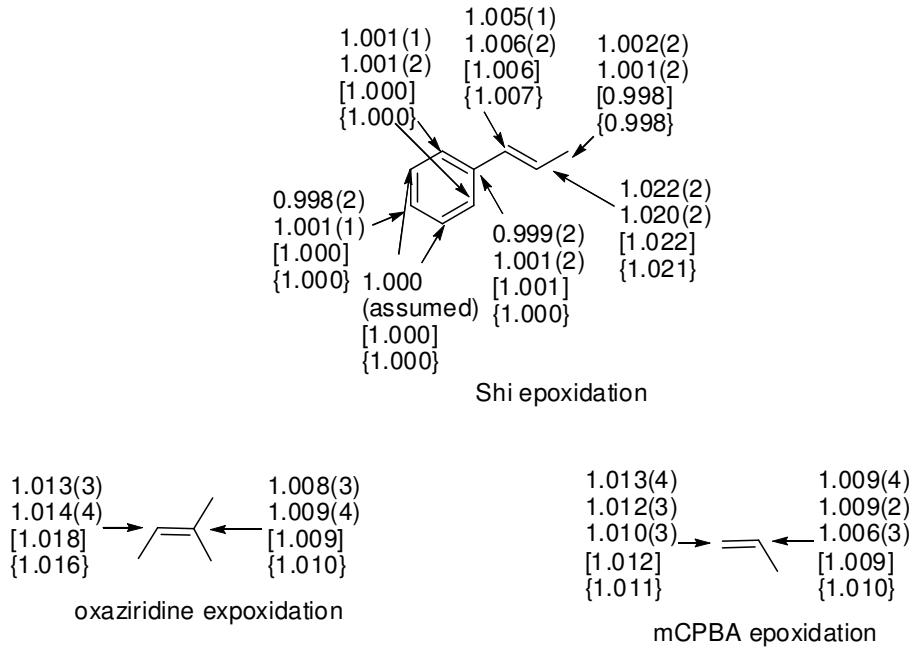


Figure 4-2. Predicted and experimentally determined KIEs for various epoxidations are shown. KIEs are listed for the Shi epoxidation of β-methyl styrene, oxaziridine epoxidation of 2-methyl-2-butene, and mCPBA epoxidation of 1-pentene. ^{13}C KIEs were measured at natural abundance using NMR methodology. Each set of experimental KIEs represent an independent experiment, and standard deviations in the last digit from six independent experiments are shown in parentheses. The previously calculated ^{13}C KIEs are shown in square brackets. Listed are the predicted KIEs from geometries optimized in B3LYP/6-31G* for the Shi and oxaziridine epoxidations, and MP2/6-31G* for the mCPBA epoxidation. KIEs calculated from mPW1K/6-31G* optimized geometries of the same model systems are listed in the curly brackets.

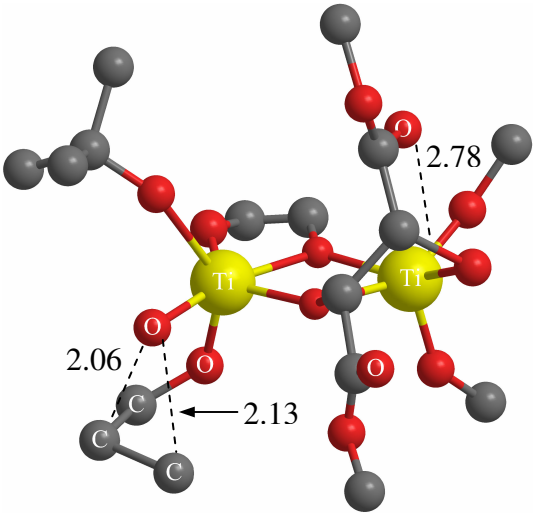
The theoretical model consists of an allyl alcohol as the substrate, t-butyl peroxide as the oxidant, dimethyl tartrate on the spectator titanocycle ring systems, ethylene glycol on the reactive titanocycle, and methoxides as the bystander alcohols.

Methyl groups rather than isopropyl groups were used in the alcohols as well as the tartrates because of the increased conformational complexity added by the inclusion of isopropyls in the system. Several conformations of the titanocycle rings, the esters on the spectator titanocycle, the allylic alcohol, the peroxide, and the bystander alcohols were explored. Initial transition structure searches were performed on a simplified system using tartaric acid as the ligand on the spectator titanocycle and hydroxide groups as the bystander alcohols. The bystander hydroxide groups were modified to methoxides early in the process because of unrealistic hydrogen bonding within the catalytic structure. A variety of functionals and basis sets were sampled in the exploration of the AE transition state geometry and are included within the supporting information. To study the effects of solvent in the stabilization of the transition state, the Onsager and PCM implicit solvent models were utilized in geometry optimization and single point energy calculations for the lowest energy transition state conformations.

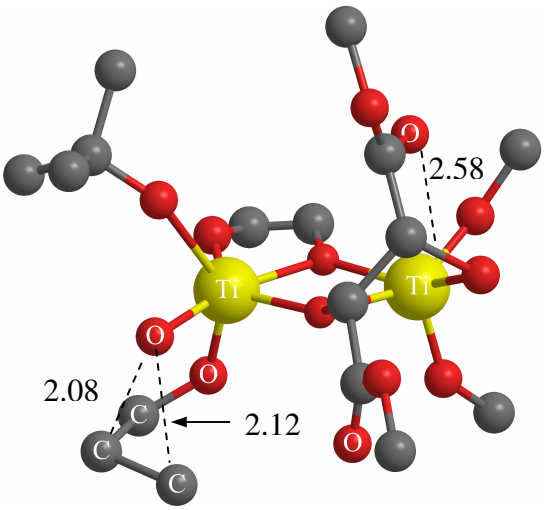
Initial models were based upon the proposed models of Sharpless and Wu. The lowest energy calculational models of structure **4-5** are shown below in figure 4-3, other high energy conformers are included in the supporting information. In all of these structures the allylic alcohol on the reactive titanocycle is loaded anti to the ligated carboxylate on the spectator titanocycle. In structures **4-10** and **4-11** the allylic alcohol "hooks in" toward the spectator titanocycle representing the transition state that would lead to the experimentally favored stereoisomer. Both structures **4-10** and **4-11** resemble the model of **4-5**, and differ only by the conformation of the noncoordinating methyl ester in the reactive titanocycle. In structure **4-10** the carbonyl oxygen of the

noncoordinating ester points away from the catalyst and in **4-11** the carbonyl oxygen points down towards the center of the catalyst. Catalyst **4-11** is favored over **4-10** by 0.1 kcal/mol in the gas phase, however, **4-10** is favored in the solvent calculations by 0.5 kcal/mol. A similar analysis was performed for catalyst structures **4-12** and **4-13** where the allylic alcohol "hooks out" away from the spectator titanocycle representing the experimentally disfavored stereoisomer for the AE. The carbonyl oxygen of the noncoordinating ester points away from the catalyst center in **4-12** and conversely points towards down towards the catalyst center in **4-13**. Structure **4-13** is favored over **4-12** by 1.1 kcal/mol in gas phase and 0.1 kcal/mol in solvent. The conformational preference of the nonligating ester is a delicate balance between steric effects and an electronic interaction of the carbonyl oxygen with the allyl alcohol. In general, the energy difference is often small for the isomers where the allyl alcohol hooks into the spectator titanocycle and larger for the transition states where the allyl alcohols are syn to the nonligating ester and that hook away from the spectator titanocycle. In the remainder of the discussion the transition state with the lowest energy conformation for the nonligating ester will be shown, however, both conformations are listed in the supporting information.

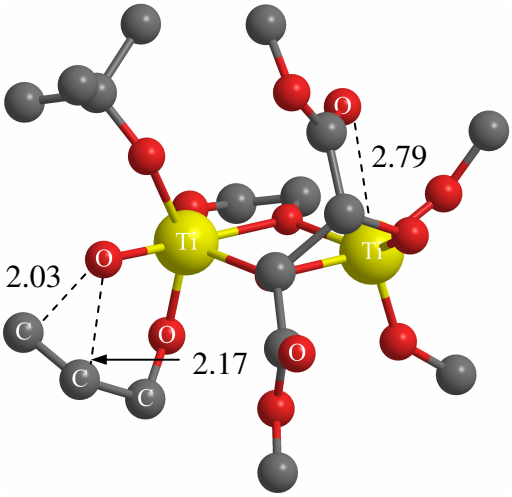
The most important aspect of these calculations is that transition state **4-13** which shows a preference for the experimentally disfavored isomer is the lowest energy conformation in gas phase (relative energies displayed in figure 4-3)!! Though structure **4-10** is slightly favored in solution phase, the difference in energies of the three:



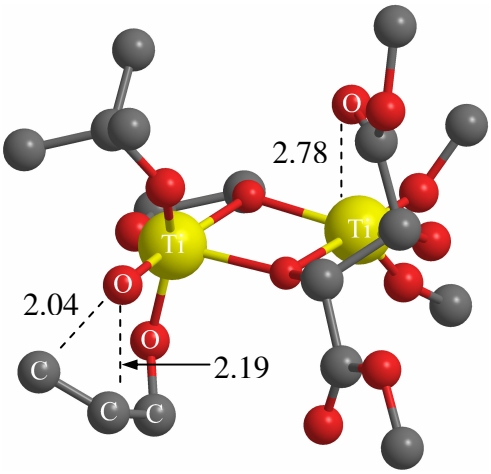
4-10 0.4 (-0.1)



4-11 0.3 (0.4)



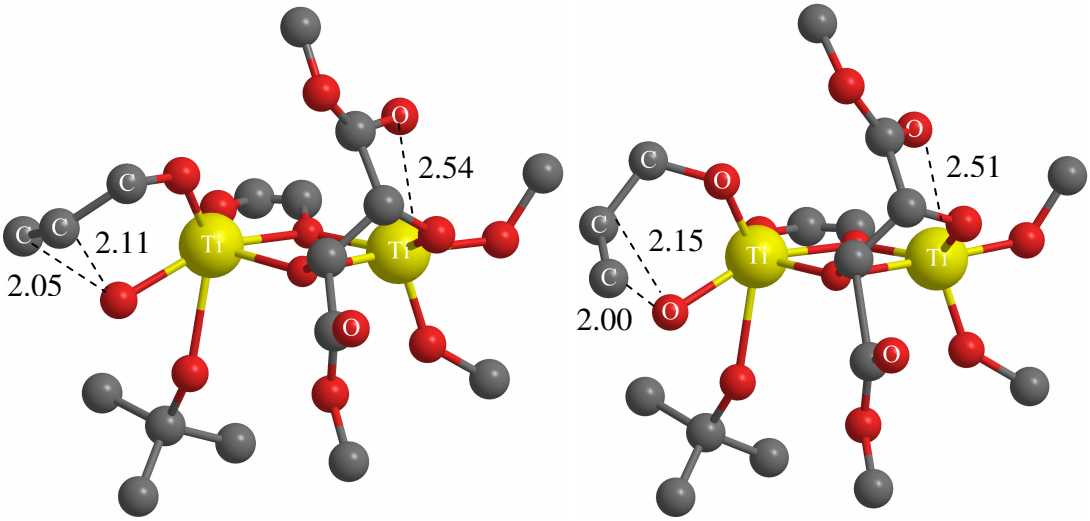
4-12 1.1(0.1)



4-13

Figure 4-3. Calculated structures based upon the Sharpless model for the AE. Transition state **4-10** through **4-13** are based upon model **4-5**. Structures **4-10** and **4-11** represent transition states that lead to the experimentally favored epoxide, **4-12** and **4-13** lead to the disfavored epoxide. Energies in kcal/mol are listed relative to **4-13**, and selected bond lengths are shown in angstroms. Geometry optimizations were performed in mPW1K/SB, and single point energies were calculated in mPW1K/BB for gas phase (outside of parentheses) and in dichloromethane using a PCM model (in parentheses).

lowest conformations are negligible. Models based upon **4-5** cannot account for the high selectivities observed in the AE reaction.



4-14 0.6 (0.0) **4-15** -0.3 (-0.5)

Figure 4-4. Calculated structures based upon the Wu model for the AE. Structures **4-14** and **4-15** represent transition structures based upon model **6** for the SE. Structure **4-14** leads to the favored stereoisomer and **4-15** corresponds to the disfavored isomer. Energies in kcal/mol are listed relative to the lowest energy transition state **4-13**, and selected bond lengths are shown in angstroms. Geometry optimizations were performed in mPW1K/SB, and single point energies were calculated in mPW1K/BB for gas phase (outside of parentheses) and in dichloromethane using a PCM model (in parentheses).

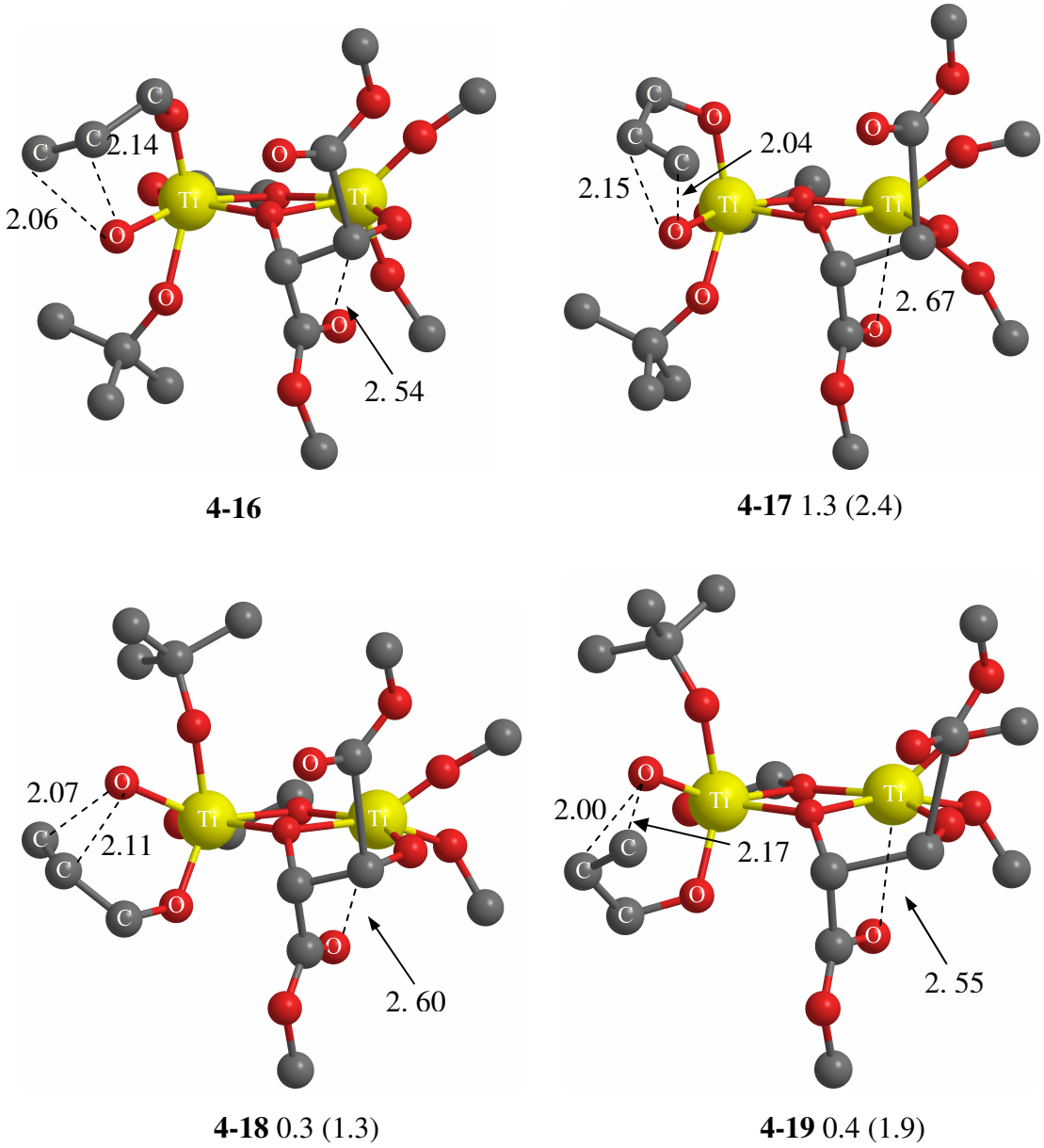
A similar analysis was performed on models of **4-6**. Shown below in figure 4-4 are models that involve the allylic alcohol loaded syn to the ligated carboxylate on the spectator titanocycle. In structure **4-14** the allyl alcohol "hooks out" away from the spectator titanocycle representing the transition state of the experimentally favored epoxide. Conversely, transition state **4-15** depicts the allyl alcohol hooking into the

spectator titanocycle leading to the experimentally disfavored epoxide. The energies are shown below in figure 4-4 relative to the previously discussed lowest energy transition state **4-13**.

Once again transition state **4-15,** which leads to the disfavored stereoisomer, is slightly lower in energy than all of the other calculated structures based upon models **4-5** and **4-6**. Therefore, previously proposed models for catalysis do not explain the selectivity or LAC of the AE system.

To gain some insight on the origin of selectivity and LAC in the SE, we extensively searched a number of possible transition state conformations representing both the favored and disfavored isomers. Structures **4-16** through **4-19** in figure 4-5 are a set of the lowest energy transition state conformations found in the search; other high energy conformations are included within the appendix. The most notable difference among these structures and the previously discussed geometries is that the carbonyl oxygen of the internal ester is forming a dative bond to the titanium and the distal ester on the spectator titanocycle is noncoordinating.

In transition states **4-16** and **4-17,** the allylic alcohol is loaded anti to the ligated carbonyl and hooks out away from the spectator titanocycle. The allylic alcohol in **4-16** hooks out away from the spectator titanocycle and represents a transition state that leads to the favored stereoisomer. Conversely, in **4-17** the allylic alcohol hooks in towards the spectator titanocycle and leads to the disfavored stereoisomer. In both transition states **4-16** and **4-17** the nonligating carbonyl prefers to point towards the allylic alcohol, other conformations of the nonligating ester were explored and found to be slightly higher in:



4-16 **4-17** 1.3 (2.4)

4-18 0.3 (1.3) **4-19** 0.4 (1.9)

Figure 4-5. Structures **4-16** - **4-19** are novel transition state models for the AE. Structures **4-16** and **4-19** lead to the favored stereoisomer, conversely, **4-17** and **4-18** corresponds to the disfavored isomer. Energies in kcal/mol are listed relative to the lowest energy transition state **4-16**, and selected bond lengths are shown in angstroms. Geometry optimizations were performed in mPW1K/SB, and single point energies were calculated in mPW1K/BB for gas phase (outside of parentheses) and in dichloromethane using a PCM model (in parentheses).

energy, these alternative structures will be discussed for the lowest energy transition states later in the discussion.

In the current set of isomers, the lowest energy transition state **4-16** leads to the desired stereoisomer and is favored by 1.3 kcal/mol in the gas phase and 2.4 kcal/mol in the solvent calculation (mPW1K/BB//mPW1K/SB+zpe). A set of transition state structures, **4-18** and **4-19** were located that include the allylic alcohol syn to the ligated carbonyl. The allylic alcohol in **4-18** hooks away from the spectator titanocycle and leads to the disfavored product isomer, conversely, **4-19** hooks in towards the spectator ring and gives the desired product. In this set of isomers **4-18** is 0.1 (0.9) kcal/mol lower in energy than **4-19**. However, **4-18** is higher in energy than transition state **4-16** by 0.3 kcal/mol in the gas phase and 1.27 kcal/mol in solution. Table 4-1 includes a list of the relative energies of all transition states in reference to **4-16** for gas phase and solvent calculations.

Table 4-1. A list of relative energies of the transition states in reference to the lowest energy transition state **4-16**. The gas phase energies are calculated in mPW1K/BB//mPW1K/SB+zpe. Solution energies are a result of a gas phase optimization in mPW1K/SB and single point energy calculations with a PCM model in mPW1K/BB.

	gas phase	solvent	experimentally favored or disfavored
10	1.23	2.48	favored
11	1.2	3.0	favored
12	1.9	2.7	disfavored
13	0.9	2.6	disfavored
14	1.4	2.7	favored
15	0.6	2.1	disfavored
16	0.00	0.00	favored
17	1.3	2.4	disfavored
18	0.3	1.3	disfavored
19	0.4	1.9	favored

The sources of selectivity and LAC are dependent upon several factors that are best described from the lowest energy transition state **4-16**. As depicted in figure 4-5 stabilization of **4-16** is derived from the ability of the transition state to 1) form a strong dative bond from the coordinating ester to the titanium; 2) create a pi bonding network between the ligating carbonyl, titanium, and oxygen of the coordinating t-butoxide (referred to as the "titanium pi bonding network" herein); and 3) hydrogen bond from the nonligated ester carbonyl oxygen to the alpha methylene of the allyl alcohol. Many of the models possess one or more of these attributes; however, only transition state **16** incorporates all three of these stabilizing effects. For example, the closest energy transition state **4-18** displays a relatively strong dative bond to the Ti (2.59 Å), but the coordinating ester lacks the ability to form a titanium pi bonding network because it is placed anti to the t-butoxide, additionally the noncoordinating ester is on the opposite face of the catalyst from the allyl alcohol prohibiting hydrogen bonding interaction. Transition state **4-17** has the ability to generate a titanium pi bonding network; however, steric effects prevent strong dative bonding (2.67 Å), additionally the transition state lacks the hydrogen bonding effect since the allylic alcohol is hooking in towards the spectator titanocycle. From the previous set of structures, **4-13** has a relatively strong interaction between the nonligating ester and the hydrogen on the methylene of the allyl alcohol (2.26 Å), however this transition state exhibits poor dative bonding (2.79 Å) and since the ligating carbonyl is distal the titanium pi bonding network is interrupted. Transition state **4-14** exhibits one of the strongest dative pi bonds (2.54 Å), but is a high energy transition state because the ligating ester is anti to the t-butoxide and cannot

participate in the titanium pi bonding network, additionally the nonligating carbonyl is anti to the allyl alcohol and cannot interact. The general features for catalyst stability include positioning for strong dative bonding to the titanium, the ligating carbonyl must be proximal and syn to the t-butoxide to form the titanium pi bonding network, and the noncoordinating ester must be syn to the allyl alcohol to form the hydrogen bonding interaction.

A conformational search on the two lowest energy transition states (**4-16** and **4-18**) revealed two other low energy transition states that differ in the conformation of the nonligating ester. A conformational isomer of transition state **4-16** with the nonligating carbonyl turned towards the bystander alcohols is 0.5 kcal/mol (0.7 kcal/mol PCM) higher in energy than **4-16**. Similarly a conformational isomer of **4-18** with the nonligating carbonyl turned towards the bystander alcohols is 0.3 kcal/mol (1.6 kcal/mol PCM) higher in energy than **4-16**. Therefore, the two lowest energy conformations of **4-16** lead to the correct stereoisomer and the predicted reaction mixture consists of a ratio of isomers of 88:12 (using solvent energies for all of the four lowest energy transition states), which is a reasonable prediction for allyl alcohol. An increase in selectivity should be seen if the full experimental system was modeled, i.e. isopropyl tartrates and isopropyl bystander alcohols.

To further study the effects of solvent on transition state geometries, optimizations were performed in mPW1K/SB using a PCM solvent model in dichloromethane. Dative bonding was slightly strengthened in the solvent calculation for both isomers, to give a dative bond length of 2.50 Å for **4-16** and 2.52 Å for **4-18.**

The hypothesis is that the solvent increases the interaction of the carbonyl with the titanium stabilizing the transition state of the catalyst.

We were also interested in testing the versatility of the transition state models in predicting experimental trends in selectivity. Transition states **4-16** and **4-18** were modeled with *cis*-2-buten-1-ol (designated as **4-16C** and **4-18C**) and *trans*-2-buten-1-ol (designated as **4-16T** and **4-18T**), the structures are included in the appendix. The difference in energies between **4-16C** and **4-18C** decreases to 0.9 kcal/mol (mPW1K/BB//mPW1K/SB +zpe using dichloromethane PCM), resulting in a decrease in selectivity. A reversal in the asynchronity of the bond formation along the reaction coordinate is clearly visible in the transition states with the cis allyl alcohol substrate (shorter bond distance to the C_2 carbon of the alkene). A larger energy difference of 1.4 kcal/mol (mPW1K/BB//mPW1K/SB +zpe using dichloromethane PCM) was observed between **4-16T** and **4-18T**, increasing the selectivity. Interestingly, a nearly synchronous transition state was observed for **4-16T** and **4-18T** (similar bond distance to C_2 and C_3 of the alkene). Experimental trends in selectivity are nicely reproduced in the models and show greater selectivity between transition states with the trans substituted allyls than the cis congeners. The versatility of the AE for a wide variety of substrates is displayed by the flexibility of the transition state to accommodate several different substrates while maintaining high selectivities.

Sharpless reports a rate enhancement of approximately 10 for the ligand accelerated catalysis of the AE.[132,134] The competence of transition state **4-16** in affecting the rate of LAC was tested by calculating structures for the monomeric titanium catalyst

epoxidation.[146] An energy difference of 25.2 kcal/mol (mPW1K/BB//mPW1K/SB +zpe in gas phase) between the monomeric transition state and the precatalyst monomeric complex was found. The difference in energy between **4-16** and the precatalyst dimeric complex of **4-16** is 22.9 kcal/mol. A rate acceleration of approximately 13 is calculated from the difference in energy between the ligand catalyzed process and the monomeric epoxidation (the number of exchangeable ligand sites must be taken into account for each catalyst). The agreement between experimentally measured rates and the theoretical prediction is striking. The sources of rate acceleration for the dimeric complex are synonymous to those that enhance selectivity. In particular, the dative bonding and pi bonding network enhance the electrophilicity of the alkyl peroxide and increasing the rate for the ligated process.

Predicted Isotope Effects. Theoretical kinetic isotope effects were calculated from the scaled vibrational frequencies using the formulation of Bigeleisen and Mayer using the most stable transition state conformation **4-16** with 3-methyl 2-buten-1-ol as a model for geraniol.[25] Tunneling corrections were applied using a one dimensional infinite parabolic model.[147] The predicted KIEs agree exceptionally well with the experimentally measured values (figure 4-1). In particular, the KIEs at the C_2 and C_3 positions undergoing epoxidation are predicted strikingly well, and support the asynchronous transition state model with more bonding to C_2 (2.01 Å) than C_3 (2.23 Å) at the transition state.

Conclusions

Previously proposed models of the AE failed to explain the high selectivities observed for a variety of substrates in the reaction. We have proposed a novel transition state model that explains the high selectivities and LAC for the AE reaction. The model successfully predicts experimental trends in the AE system. The transition state is labile and flexible towards a variety of substrates while still maintaining high selectivity. A rate acceleration similar to experiment was predicted for LAC from model **4-16**. In addition, experimentally measured KIEs support the theoretical model.

CHAPTER V

THEORETICAL INVESTIGATIONS INTO THE MECHANISM OF FLAVOPROTEIN-CATALYZED AMINE OXIDATION OF N-METHYLTRYPTOPHAN*

The mechanism of *N*-methyltryptophan oxidase, a flavin-dependent amine oxidase from *Escherichia coli*, was studied using theoretical calculations. The $^{15}(k_{cat}/K_m)$ kinetic isotope effect for sarcosine oxidation is pH-dependent with a limiting value of 0.994-0.995 at high pH. Density functional theory (DFT) calculations on model systems were used to interpret these isotope effects. The isotope effects are inconsistent with proposed mechanisms involving covalent amine-flavin adducts but cannot conclusively distinguish between some discrete electron-transfer mechanisms and a direct hydride-transfer mechanism.

Introduction

Flavin-dependent amine oxidases and dehydrogenases catalyze the oxidative deamination of primary amines and the oxidative dealkylation of secondary amines. These enzymes are ubiquitous in nature and are involved in a myriad of biological activities. For example, glycine oxidase is involved in thiamin biosynthesis in microorganisms,[148] while the recently discovered lysine-specific histone demethylase is involved in regulation of transcription in humans.[149] The ubiquity and functional diversity of this family of enzymes underlie its importance and has prompted many

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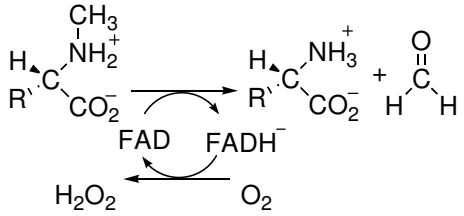
* Reprinted with permission from " Insights into the Mechanism of Flavoprotein-Catalyzed Amine Oxidation from Nitrogen Isotope Effects on the Reaction of *N*-Methyltryptophan Oxidase" by Ralph, E. C.; Hirschi, J. S.; Anderson, M. A.; Cleland, W. W.; Singleton, D. A.; Fitzpatrick, P. F. 2007, *Biochemistry,* 46, 7655-7664, Copyright 2007 by the American Chemical Society.

structural and biochemical studies. To date, flavoenzymes that catalyze amine oxidations have fallen into two structural groups. One class includes D-amino acid oxidase,[150] monomeric sarcosine oxidase (MSOX)[1,151] and glycine oxidase,[148] with monoamine oxidase (MAO) B,[152] polyamine oxidase,[153] lysine-specific demethylase-1,[154] and L-amino acid oxidase[155] forming a separate structural class. While a number of these enzymes have been the subject of kinetic, spectroscopic, and structural studies, only in the case of D-amino acid oxidase have mechanistic[156] and structural studies[150] led to a consensus that the reaction involves hydride transfer. The chemical mechanism of the remaining amine oxidases is still debated.

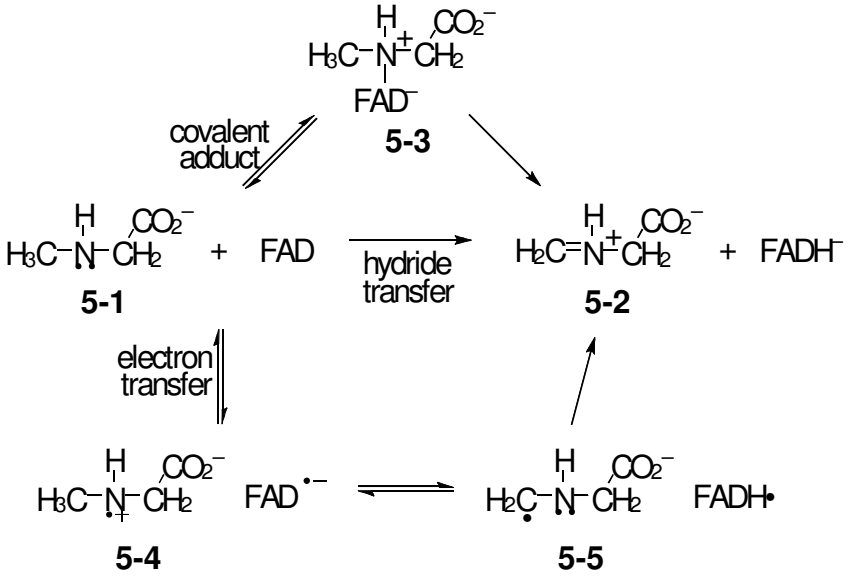
N-Methyltryptophan oxidase (MTOX) catalyzes the oxidative demethylation of *N*-methyl amino acids (Scheme 5-1), with a preference for bulky hydrophobic substrates such as *N*-methyl-L-tryptophan.[157] Although the three dimensional structure of MTOX is unavailable, it shares 41% sequence identity with MSOX and the active site residues are conserved, establishing that it can be assigned to the same structural class. As shown in Scheme 5-2, a variety of mechanisms have been proposed for substrate oxidation by MTOX.[158] Similar mechanisms have been proposed for other flavin-dependent amine demethylases and for flavin-dependent amine oxidation in general.[159,160] Therefore, investigation of the chemical mechanism of MTOX should aid in understanding a number of important flavoenzymes.

Scheme 5-1



The simplest mechanism in Scheme 5-2 is a one-step hydride transfer from the methyl group of the substrate **5-1** to the flavin to form iminium product **5-2** directly. In a second possibility, the substrate nitrogen attacks the flavin cofactor at C^{4a} or N^5 to form a covalently bound flavin adduct **5-3**. This is followed by the loss of a proton from the substrate methyl carbon and elimination to give the final products. In a variation of this mechanism, the addition and elimination occur in a single step.[161] A third possible mechanism involves two separate one-electron transfer steps. The initial transfer of an electron to the flavin from **5-1** forms a flavin semiquinone and aminium cation radical **5-4**, which is then further oxidized by separate proton and electron transfers via **5-5**. In variations of the electron-transfer mechanism, proton and electron transfers are combined into a single hydrogen transfer step, either forming **5-5** directly from **5-1** or forming **5-2** directly from **5-4**.

Scheme 5-2



The deuterium kinetic isotope effects show that CH bond cleavage is fully rate-limiting for sarcosine turnover by MTOX.[162] Moreover, no intermediate flavin species is observable when the reduction of the flavin in MTOX is monitored using a stopped-flow spectrophotometer. These results are fully consistent with the hydride-transfer mechanism and put limitations on the covalent-adduct and electron-transfer mechanisms, each of which involve an intermediate flavin species prior to CH bond cleavage. If an intermediate flavin species is indeed formed, it must be formed reversibly and it must be significantly higher in energy than its precursor, so that less than 5% of the enzyme is in the form of the postulated intermediate species at any time in the reaction.

The observed ^{15}N isotope effects, measured by Ralph and Fitzpatrick, are pH-dependent, starting at a value greater than 1 and then decreasing with increasing pH.[163] The pH dependence of the observed ^{15}N isotope effects is not due to changes in either

the rate-limiting step or the transition state structure, as the observed deuterium kinetic isotope effect is pH-independent.[162] It can therefore be attributed to the ^{15}N equilibrium isotope effect on sarcosine deprotonation. The ^{15}N isotope effect for the *N*-demethylation of sarcosine by MTOX is significantly inverse (less than unity), with a limiting value of 0.994-0.995 at high pH.

Although the previous results are consistent with a hydride-transfer mechanism, they do not by themselves rule out the alternative mechanisms. Mechanistic proposals are difficult to postulate based upon qualitative interpretation of the measured isotope effects. Therefore in the present study, theoretical calculations have been utilized to further probe the mechanism of sarcosine oxidation by MTOX. The results firmly exclude mechanisms involving covalent adducts.

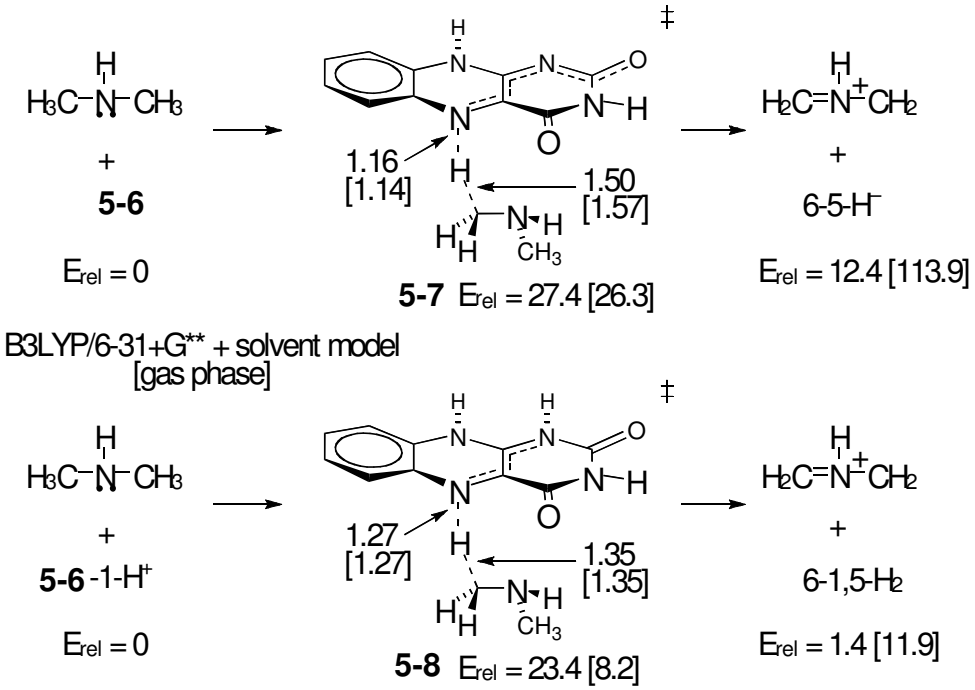
Results and Discussion

Theoretical Mechanisms. No simple theoretical model can adequately represent the energy surface for the enzymatic reaction in solution. Instead, our goal was to calculationally explore a range of mechanistic models for the amine oxidation mechanisms of Scheme 5-2 in order to interpret the experimental ^{15}N kinetic isotope effect. This by itself is complicated due to the involvement of charged intermediates. Gas-phase calculations on mechanistic steps involving charge separation or annihilation are dominated by Coulombic effects, distorting the calculated transition structures for such steps. To mitigate this problem, the calculational models here employ either cationic species (avoiding zwitterionic charge separation), an implicit solvent model, or a combination of the two. The calculational models cannot mimic the specific

interactions employed by the enzyme in promoting the reaction, but should serve as a guide for interpreting the isotope effects.

Scheme 5-3 shows the calculational model reactions for direct hydride transfer. Relative energies (kcal/mol versus starting materials) and selected interatomic distances (in Å) are shown in the Scheme for the structures obtained employing a solvation model (PCM/B3LYP/6-31+G**//Onsager/B3LYP/6-31+G** + zpe), along with corresponding energies and distances in brackets obtained with gas-phase calculations. Transition structure **5-7** was located for the transfer of a hydride from dimethylamine to the neutral FAD model **5-6**, affording a complex of the *N*-methyliminium cation with **5-6**-5-H^- (the model for $FADH^-$). The favored orientation shown minimizes charge separation between the incipient ions and leads to a very tight anion-cation complex. Pulling apart these ions in the gas phase is prohibitively uphill (accounting for most of the ≈114 kcal/mol to form separate gas-phase product ions), but the barrier for hydride transfer to form an ion pair is only 26.3 kcal/mol (B3LYP/6-31+G** + zpe). When an implicit solvent model for water is incorporated, the hydride transfer is predicted to be much less endothermic, with the separate ions only 12.4 kcal/mol uphill from **5-6**/dimethylamine (PCM/B3LYP/6-31+G**//Onsager/B3LYP/6-31+G** + zpe), and the transition structure shifts earlier as expected from Hammond's postulate.

Scheme 5- 3

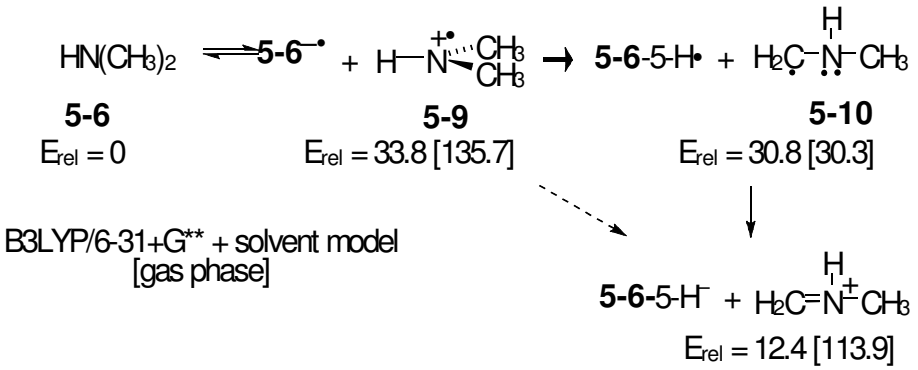


An alternative calculational model for the hydride transfer starts with a 1-protonated FAD model **5-6**-1-H^+, and proceeds to form $FADH_2$ model **5-6**-1,5-H_2 via transition structure **5-8**. The discrete protonation of FAD prior to subsequent steps is probably unrealistic due to its low basicity, but protonation at N^1 could reasonably occur as the reaction coordinate for hydride transfer to N^5 proceeds. Weighing against any concerted hydride transfer / proton transfer mechanism is the lack of a solvent isotope effect on the k_{cat}/K_m value for sarcosine.[162] Because the hydride transfer from dimethylamine to **5-6**-1-H^+ is more nearly thermoneutral than hydride transfer to **5-6**, the transition structure **5-8** is earlier than **5-7**. Interestingly, the barrier for hydride transfer to **5-6**-1-H^+ is increased by about 15 kcal/mol in the PCM solvent model compared to the

gas phase, and this barrier in solution is predicted to be fairly similar to the barrier for hydride transfer to **5-6** in solution. (Similar results were obtained using an IPCM solvent model for water.) The increased barrier with **5-6**-1-H^+ in free solution may be understood by considering that the starting cation **5-6**-1-H^+ is more stabilized by solvent than the more charge-delocalized transition structure **5-8**.

The ion pair that would result from electron transfer between adjacent flavin and amine molecules is an electronic excited state, and is not readily modeled computationally. For this reason, the computational exploration of the electron-transfer mechanism was limited to separate discrete flavin and amine oxidation states as shown in Scheme 5- 4. Electron transfer between dimethylamine and **5-6** to afford separate **5-6**$^{-\bullet}$ and aminium cation radical **5-9** in free solution is predicted to be quite uphill at 33.8 kcal/mol (PCM/UB3LYP/6-31+G**//Onsager/UB3LYP/6-31+G** + zpe). This is in reasonable agreement with an approximate separation of 1.7 V (39 kcal/mol) between the oxidation potential of secondary amines[164] and the reduction potential of FAD.[165] Electron transfer between flavin and amine in the enzyme could of course be much less unfavorable than this calculation suggests, owing to the possibility of flavin distortion or specific solvation by the enzyme, or ion pairing, depending on the distance between resulting ions. However, the active site of MTOX is identical to that of MSOX and the structure of the latter enzyme with dimethylglycine bound[166] shows no negatively charged residue in the active site which could form such an ion pair.

Scheme 5- 4

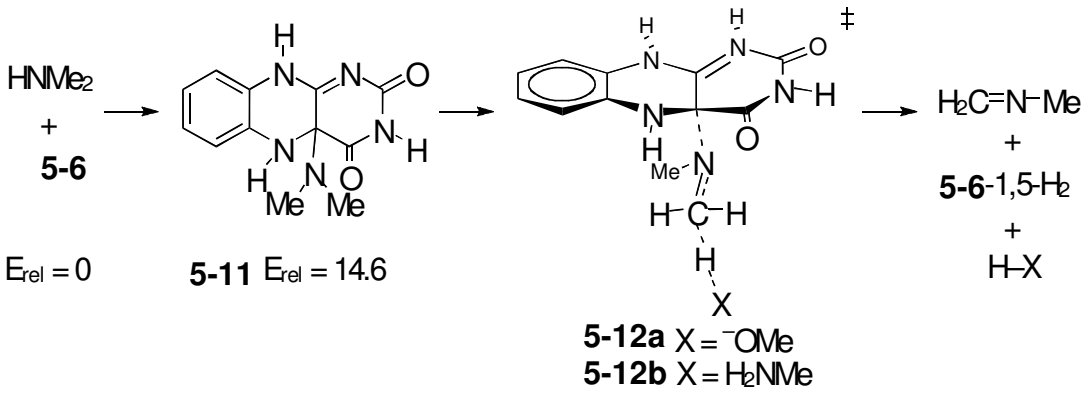


Proton transfer between **5-6**$^{-\bullet}$ and **5-9** affords neutral radicals **5-6**-5-H• and **5-10**. The overall formation of **5-6**-5-H•**/5-10** from **5-6**/dimethylamine is predicted to be uphill by 30.8 kcal/mol, and because the two radicals are neutral, solvation by the enzyme is less likely to be able to avoid this barrier. However, the high-energy radical pair could be avoided by direct hydrogen transfer between **5-6**$^{-\bullet}$ and **5-9** to afford **5-6**-5-H^{-}/*N*-methyliminium cation, which can also result from a notably downhill proton transfer between **5-6**-5-H• and **5-10**.

Mechanisms involving a covalently bound flavin adduct could potentially occur in two ways, either by addition of the amine to C^{4a} or by addition to N^5.[167-171] From our previous observation of a large deuterium kinetic isotope effect of 7.2 ± 1.0 in this reaction,[162] the formation of a discrete adduct would have to be reversible and followed by a rate-limiting elimination step. Alternatively, a concerted addition/elimination process as proposed by Miller and Edmondson[161] could account for the deuterium isotope effect. For the purpose here of interpreting the ^{15}N kinetic isotope effect, the exploration of each of these mechanisms focused on the possible rate-limiting steps.

Scheme 5-5 outlines the model mechanism involving formation of adduct **5-11** by addition of the amine to C^{4a} of **5-6**, followed by an E2 elimination to afford the **5-6**-1,5-H_2 and *N*-methylformaldimine. The adduct **5-11** is predicted to be uphill from **5-6**/dimethylamine, consistent with the failure to observe adducts in simple flavin/secondary amine reactions.[168] The key elimination step was modeled in two ways, using either methoxide anion to model a relatively early, tight transition state (**5-12a**) or methylamine to model a relatively late, loose transition state (**5-12b**). In either case, the elimination requires protonation at N^1 to proceed, as the $FADH^-$ model **5-6**-5-H^- is a poor leaving group. Even after protonating at N^1, the elimination in free solution would be extremely difficult; **5-12b** is uphill by 59.7 kcal/mol from **5-6**/dimethylamine/$MeNH_3^+$ (PCM/B3LYP/6-31+G**//Onsager/B3LYP/6-31+G** + zpe).

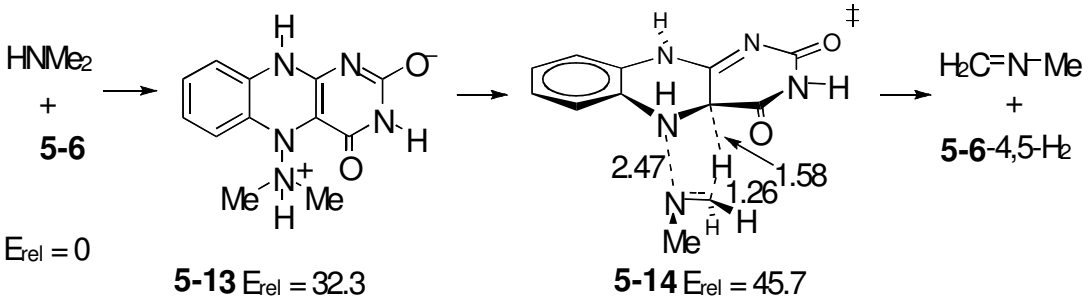
Scheme 5- 5



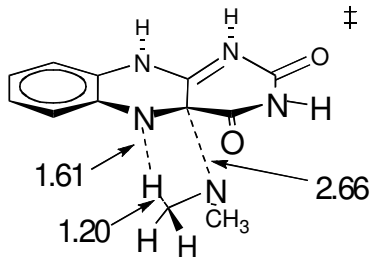
No transition structure could be located for an intramolecular elimination from the C^{4a} adduct. However, an intramolecular elimination process becomes possible if

adduct formation occurs by addition of the amine to N^5 to afford adduct **5-13**, followed by proton transfer from ammonium **5-13** to N^5 (Scheme 5-6). The elimination transition structure **5-14** is predicted to be quite high in energy in free solution at 45.7 kcal/mol, and would initially afford the 4,5-H_2 flavin tautomer.

Scheme 5-6



Finally, transition structure **5-15** was located as a model for the concerted addition/elimination process proposed by Miller and Edmondson,[161] The location of a transition structure of this type requires the combination of protonation at N^1 and deprotonation of the nitrogen of the attacking amine (presumably as the process ensues); otherwise, there is no attraction of the amine to C^{4a}, and the resulting transition structures approach **5-7** or **5-8**. Structure **5-15** is predicted to be 47.0 kcal/mol above **5-6**/dimethylamine in free solution.



5-15 $E_{rel} = 47.0$

Predicted Isotope Effects. The calculated structures in the previous section provide a series of models for the prediction of the ^{15}N isotope effect for various mechanistic possibilities. For the various hydride-transfer and elimination mechanisms, isotope effect predictions were obtained by applying conventional transition state theory to the discrete transition structures **5-7**, **5-8**, **5-12a**, **5-12b**, **5-14**, and **5-15**. The isotope effects associated with possible electron-transfer mediated mechanisms could not be modeled in this way due to the absence of electronically ground-state transition structures. An approach to predicting these isotope effects is described in the Discussion section, but a first step toward a prediction is the calculation of the equilibrium isotope effects for formation of either cation-radical **5-9** or radical **5-10/5-6**-5-H•. These equilibrium isotope effects should be a poor model for the *primary* deuterium isotope effect in this reaction, but may approximate the *secondary* ^{15}N isotope effect. Equilibrium predictions do not include a tunneling correction.

In predicting the isotope effects for the calculational models, a choice must be made of the starting material reference state between neutral dimethylamine and the protonated dimethylammonium ion. For comparison with the limiting pH-independent

^{15}N isotope effect at high pH, dimethylamine was chosen as the reference state. This has the advantage of easing the qualitative understanding of the isotope effect predictions, without their being masked by a normal isotope effect for ammonium deprotonation. However, the choice makes no real difference in how closely predictions match with experiment. This is because the calculated equilibrium isotope effect for deprotonation of the dimethylammonium ion matches the experimental equilibrium ^{15}N isotope effect (1.0226 ± 0.0001)[172-174] used to arrive at the experimental high-pH limiting ^{15}N isotope effect. Dimethylammonium ion was used as the starting material reference state for the prediction of deuterium isotope effects since sarcosine would be predominantly protonated under the conditions used to measure the experimental isotope effect.

The results are summarized in Table 5-1. A key observation in these results is that the mechanisms involving either intramolecular or intermolecular elimination reactions as the rate-limiting step are predicted to result in ^{15}N isotope effects significantly greater than unity. The equilibrium ^{15}N isotope effect associated with possible intermediates in an electron-transfer mechanism are slightly inverse. More substantially inverse ^{15}N kinetic isotope effects are predicted for the hydride transfer transition structures **5-7** and **5-8**.

Table 5-1. Predicted ^{15}N (k_{15N}/k_{14N}, high-pH limit) or deuterium (k_H/k_D) kinetic isotope effects at 25 °C.

Structure	^{15}N isotope effect	^{2}H isotope effect[a]	^{15}N isotope effect/ Wigner correction	^{2}H isotope effect/ Wigner correction
5-7	0.9921	4.00	0.9927	4.77
5-8	0.9932	4.71	0.9942	6.17
5-9	0.9978[b]	1.38[b]	----	----
5-10/6-5-H•	0.9962[b]	1.22[b]	----	----
5-12a	1.0116	6.69	1.0130	9.20
5-12b	1.0223	4.16	1.0250	4.29
5-14	1.0139	4.07	1.0151	4.45
5-15	1.0197	3.24	1.0203	3.34

[a]The ^{2}H isotope effect was calculated for a trideuterated methyl group, in keeping with experimental studies which used a trideuterated methyl group on sarcosine. The predicted ^{2}H isotope effect thus represents the product of a primary and two secondary isotope effects. [b]The isotope effects predicted for **5-9** and **5-10** are equilibrium isotope effects, not kinetic isotope effects.

Discussion

Isotope Effects. Previous analyses of the primary deuterium isotope effect on the MTOX-catalyzed reaction have established that cleavage of the sarcosine CH bond is rate-limiting for turnover.[162] The observation that the intrinsic deuterium isotope effect is expressed in the k_{cat}/K_m value for sarcosine establishes that CH bond cleavage occurs during the first irreversible step in catalysis. While the presence of a primary deuterium isotope effect has thus proven exceedingly useful in identifying rate-limiting hydrogen transfer, the magnitude of a primary deuterium isotope effect is less useful in deciding

among competing mechanisms that all involve rate-limiting hydrogen transfer. A key problem is that primary deuterium isotope effects are not readily predicted accurately due to tunneling and variational transition state effects.[175] The deuterium isotope effects predicted from conventional transition state theory in Table 5-1 are a lower bound, as tunneling will generally increase the deuterium isotope effect. The predictions using a one-dimensional Wigner tunneling correction are also likely to underestimate the isotope effect, as this correction is minimal. Because of this, comparison of the predicted deuterium isotope effects with the experimental deuterium isotope effect of about 7.0 [162] does not distinguish among the various mechanisms. The use of heavy-atom isotope effects in concert with calculational studies has the substantial advantage that tunneling plays a much smaller role. As a result, heavy-atom isotope effects are often accurately predicted when the theoretical mechanism is correct.[144,176-178] Here, such predictions allow a detailed interpretation of the experimental ^{15}N isotope effect.

While the proposed chemical mechanisms in Scheme 5-2 involve substrate with a neutral nitrogen, the zwitterionic form of sarcosine predominates over the pH range accessible for mechanistic study. Deprotonation of the substrate nitrogen is affected by the isotopic content of the nitrogen, such that there is a measurable ^{15}N effect on the equilibrium constant for deprotonation. Because k_{cat}/K_m values reflect the reaction of the free substrate and enzyme, they will include this $^{15}K_{eq}$, and the measured $^{15}(k_{cat}/K_m)$ values must be corrected to obtain the ^{15}N isotope effect on catalysis. The decrease in the measured isotope effects with increasing pH reflects this equilibrium isotope effect, in that the fraction of the substrate in the zwitterionic form decreases with increasing pH.

The accuracy of correction of the measured values to obtain the high-pH isotope effect for the reaction of the anionic substrate is obviously affected by the accuracy of the equilibrium ^{15}N isotope effect for sarcosine protonation which is used. While the ^{15}N isotope effect for sarcosine protonation has not been measured, we have calculated the equilibrium ^{15}N isotope effect for dimethylamine/dimethylammonium ion (Onsager/B3LYP/6-31+G**) as 1.0226. This is identical to literature values for measured equilibrium ^{15}N isotope effects for deprotonation of glycine, alanine, and phenylalanine,[172-174] so that it is likely to be quite reliable. Consequently, this value was used to correct the observed $^{15}(k_{cat}/K_m)$ values, yielding the pH-independent values. As noted above, the $^{15}(k_{cat}/K_m)$ values determined from sarcosine are consistently slightly greater than those determined from glycine, reflecting a systematic but unidentified experimental error. Still, the average ^{15}N effects for oxidation of anionic sarcosine calculated independently from the residual sarcosine and the glycine product are much closer than the isotope effects for several of the different mechanisms under consideration. Even with the caveats above, it is clear that the ^{15}N isotope effect for the *N*-demethylation of sarcosine by MTOX is significantly inverse (less than unity), with a limiting value of 0.994-0.995 at high pH. This value can be used for comparison with values for the isotope effect calculated for the different proposed mechanisms in Scheme 5-2.

Covalent Adducts and Concerted Addition/Elimination. The possibility of a C^{4a} adduct was supported in model reaction studies done by Mariano.[168,169] However, the observable amine adducts in the Mariano work were stabilized by a combination of N^5

alkylation and amine deprotonation. In the absence of such stabilization, formation of a C^{4a} adduct is energetically unfavorable. Thus, calculational model **5-11** is 14.6 kcal/mol above starting materials, and there is no energy minimum in calculations for the zwitterionic adduct that would result from attack of dimethylamine at C^{4a} of **5-6**. Addition at C^{4a} would need to be aided by flavin distortion[179,180] or deprotonation of the amine as it attacks C^{4a}, or a combination of the two. Deprotonation of the amine probably cannot occur by direct transfer from the amine to N^5 during addition — the required four-membered-ring transition state would be expected to be high in energy and was not locatable calculationally. Calculations were also unable to locate a transition state for unimolecular elimination of *N*-methylformaldimine from **5-11**. These observations suggest that both the formation of the C^{4a} adduct and the subsequent elimination step (as in **12**) would require an as yet undefined catalytic base. While the crystal structure of MTOX is not available, a catalytic base in MSOX (sharing 41% sequence identity) has not been identified.[181]

The alternative possibility of an N^5 adduct is favored in calculations by greater electrophilicity at N^5. While zwitterionic adduct **5-13** would be high in energy in free solution, it is at least a local energy minimum, unlike the analogous adduct resulting from attack at C^{4a}. Elimination from an N^5 adduct could also avoid the need for an external base, with imine being formed directly via a transition state resembling model **5-14**. However, the barrier associated with **5-14** in free solution is very high, and the overall neutrality of this cyclic transition structure would make it difficult for an enzyme to electrostatically catalyze the elimination.

In a study of the oxidation of benzylamine analogues by MAO A, Miller and Edmondson made the intriguing observation that the reaction was accelerated by electron-withdrawing groups.[161] From a ρ of ≈2.0, a deuterium isotope effect in a range of 6 to 13, and the lack of observable flavin intermediates, they proposed a concerted addition/elimination mechanism. This unusual process can be modeled as in transition structure **5-15** with the proviso that the amine is deprotonated.

The ^{15}N isotope effect results strongly weigh against any of these mechanisms. For these mechanisms involving elimination reactions as the rate-limiting step, the various calculational models lead to high-pH limit ^{15}N isotope effects of 1.012-1.022. The predictions of normal isotope effects in these cases are readily understandable and expected on a qualitative basis. The mechanisms all involve transition states in which the nitrogen atom is undergoing a σ-bonding change, so that a primary ^{15}N isotope effect should be observed. The observed absence of a primary ^{15}N isotope effect would be conventional qualitative evidence against these mechanisms, and the calculated isotope effects strongly support the conventional interpretation.

One complicating factor in this interpretation is that the ^{15}N isotope effect could be decreased if the amine nitrogen were protonated at the transition state. None of the elimination transition structures **5-12a**, **5-12b**, **5-14**, and **5-15** involve protonated amine nitrogens. However, this is because these elimination steps are not viable when the amine is protonated. This may be understood at an electron-pushing level by considering that any of these eliminations involve pushing electrons away from the amine nitrogen, which is much more difficult when the nitrogen is protonated. As a result, when high-

level calculations search for elimination transition structures in protonated analogs of **5-12a**, **5-12b**, **5-14**, and **5-15**, alternative processes intervene.

It should be noted that the barriers associated with **5-14** and **5-15** in free solution are very high, and the overall neutrality of the transition structures makes it difficult to envision how an enzyme could catalyze these cyclic elimination steps. The calculated energetics thus support the conclusion from the ^{15}N isotope effect that mechanisms of this type are not viable.

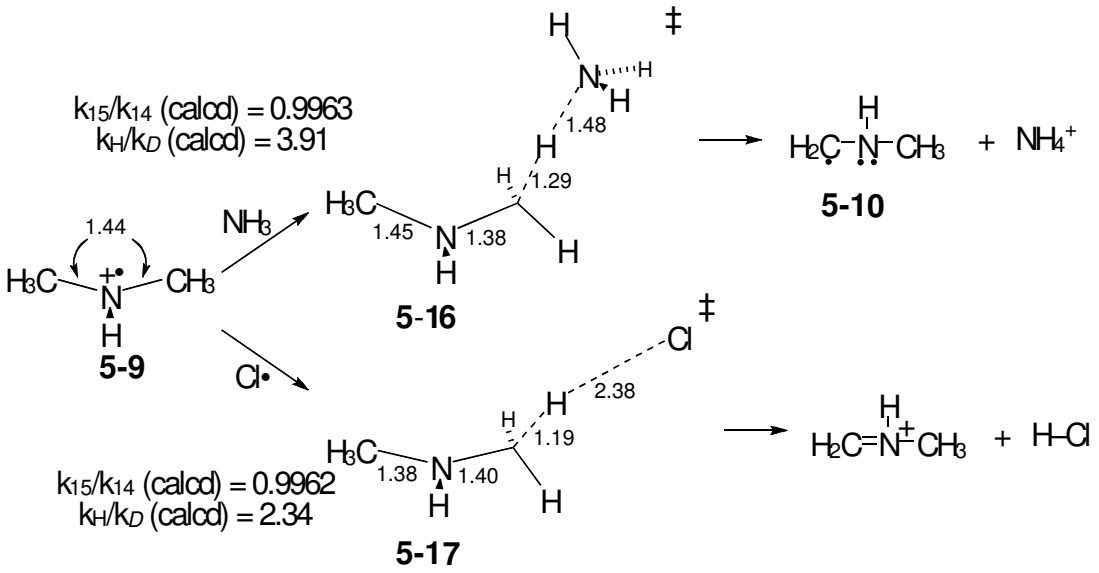
Single Electron Transfer. Electron-transfer mechanisms have been frequently proposed for flavin-dependent amine oxidations.[182] Support for these mechanisms comes primarily from oxidation studies of cyclopropyl or cyclobutyl compounds that act as mechanism based inhibitors for MAO[159] and for MSOX[183,184]. However, it is important to note that a cyclopropyl group blocks hydride transfer, as cyclopropylidene imines are very strained, and facilitates electron transfer, as cyclopropyl groups greatly stabilize adjacent positive charge. Less strained cyclic substrates and inhibitors have failed to give the ring opening products.[185-187] With the latter compounds, the lack of the ring-opening product is consistent with a non-radical mechanism.

To date, monitoring flavin reduction by substrate has failed to show any visible flavin radical spectrum in MTOX[158,162], MSOX[181,188], trimethylamine oxidase[189], lysine-specific histone demethylase-1[190], MAO[161,191], or any of the flavin-dependent amine oxidases. In many of these cases, deuterium isotope effects have shown that CH bond cleavage is partially or completely rate-limiting. Therefore, if an aminium radical is

utilized, its formation must be reversible and energetically unfavorable, but not rate-limiting.

Neither proton nor hydrogen transfer from **5-9** to **5-6**$^{-\bullet}$ can be modeled computationally as these would involve electronic excited states, so theoretical calculations cannot directly calculate a ^{15}k value. To get around this problem, some simpler reactions of **5-9** not complicated by electronic excited states were studied. To model proton transfer from **5-9**, the reaction of **5-9** with ammonia was chosen, and transition structure **5-16** was located (Onsager/UB3LYP/6-31+G**) for the formation of **5-10**/NH_4^+. It is unclear how closely **5-16** would resemble a transition structure for proton transfer from **5-9** to **5-6**$^{-\bullet}$ (or sarcosine cation radical to flavin semiquinone), but **5-16** has the virtue of being a tractable model that could also model proton transfer from **5-9** to an active-site base. Modeling hydrogen transfer from **5-9** is more difficult, and can only be done with a radical that is sufficiently electronegative to maintain radical character in the presence of **5-9**. For this purpose, a chlorine atom was chosen, and transition structure **5-17** was located for the hydrogen transfer affording *N*-methyliminium cation/HCl. This transition state is notably early, as would also be expected for the downhill hydrogen transfer from **5-9** to **5-6**$^{-\bullet}$.

Scheme 5-7



For the calculated transition structures **5-16** and **5-17**, the predicted ^{15}N kinetic isotope effect (including a tunneling correction) was 0.9963 and 0.9962, respectively. These modestly inverse isotope effects may be understood as resulting from a strengthening of bonding to the nitrogen atom as proton or hydrogen transfer proceeds, as evidenced by an overall decrease in the C-N bond distances. Multiplying these kinetic isotope effects by the predicted equilibrium isotope effect for formation of **5-9** from Table 5-1 gives 0.9941 and 0.9940, respectively. Despite the simplicity of the models, both are in remarkable agreement with experiment.

An analogous analysis can be carried out for the deuterium isotope effect. Combining predicted H/D isotope effects for **5-16** and **5-17** of 4.02 and 2.38, respectively (including the Wigner tunneling correction), with the equilibrium isotope effect of 1.38 for formation of **5-9** gives 5.55 and 3.28, respectively. As discussed above,

these predictions with a minimal tunneling correction are likely lower bounds and cannot be considered inconsistent with the experimental H/D isotope effect of about 7.0.

An occasionally proposed mechanism, related to the electron-transfer mediated mechanisms, is rate-limiting abstraction of a hydrogen atom from the substrate, forming a carbon radical.[182,192] This mechanism is not directly calculable because the product is an electronic excited state; in the calculational model, it is downhill from **5-6**-5-H• + **5-10** to **5-6**-5-H$^-$ + *N*-methyliminium cation, and a combined ground-state calculation must give the latter as a hydride transfer instead of a hydrogen transfer. To model this process, a transition structure was located for hydrogen abstraction from dimethylamine by methyl radical (see Appendix). The predicted ^{15}N and H/D isotope effects for this process are 0.9985 and 8.98, respectively. Both isotope effects are somewhat higher than observed experimentally, and the lower-bound nature of the H/D isotope effect prediction adds significance to its being larger than that observed experimentally. While the simplicity of the calculational model in this case makes it difficult to reach a firm conclusion on the direct hydrogen-transfer mechanism, the isotope effects cannot be said to provide support for the mechanism as in the cases above. In addition, considering the energetic preference for **5-6**-5-H$^-$ + *N*-methyliminium cation over **5-6**-5-H• + **5-10**, and a presumed greater difficulty for the enzyme to stabilize the latter neutral molecules over the former charged species, the calculated energetics add weight against a direct hydrogen transfer from starting amine.

Overall, this analysis of the isotope effects and the close correspondence of predicted and experimental ^{15}N kinetic isotope effects appears to support rate-limiting

proton or hydrogen transfer after an initial electron-transfer. However, it will be seen that the results provide equal support for a hydride-transfer mechanism.

Hydride Transfer. A concerted hydride transfer is the simplest proposed mechanism for flavin-dependent amine oxidation, and is frequently accepted as the chemical mechanism for the thoroughly studied D-amino acid oxidase.[160] This mechanism is most consistent with the lack of visible intermediate flavin species during sarcosine oxidation,[162] as it requires no intermediates. The absence of an observable intermediate does not exclude covalent-adduct and electron-transfer mechanisms, as intermediates could be too short-lived to be observed, but it does weigh against such mechanisms, particularly since the mechanisms involve intermediate flavin species prior to the rate-limiting CH bond cleavage.

The evaluation of the hydride-transfer mechanism here is based on the comparison of the experimental ^{15}N isotope effect of 0.994-0.995 versus those predicted for model transition structures **5-7** and **5-8**. The ^{15}N isotope effects predicted for **5-7** and **5-8** are notably inverse at 0.992 and 0.993, respectively. At first glance, these inverse isotope effects may seem surprising, since the nitrogen is undergoing a substantial bonding change in the process. However, heavy-atom isotope effects associated with π-bonding changes depend on the nature of the bonding change. When there is little change in total π-bond order, the isotope effect is very small. For example, the central carbons of a diene in a Diels-Alder reaction do not exhibit a significant ^{13}C isotope effect.[193]

The agreement of the predicted ^{15}N isotope effects for hydride-transfer mechanisms with experiment is striking. Considering the experimental uncertainty discussed above, the agreement must be considered at least as good as that for the electron-transfer mechanisms. It may be argued that the agreement is of greater significance in the case of the hydride-transfer mechanisms, as **5-7** and **5-8** are straight-forward models for hydride transfer while the prediction of isotope effects for electron-transfer mechanisms was necessarily a contrived process. However, the observed ^{15}N isotope effect can clearly be taken as supporting either mechanism.

Although the energetics for the calculational model mechanisms are not directly related to those for possible enzyme-catalyzed mechanisms, some comment can be made on the energetic feasibility of the hydride transfer versus alternative possibilities. The barriers associated with **5-7** and **5-8** in free solution are 10-15 kcal/mol higher than those for the enzymatic reaction, but a direct uncatalyzed hydride transfer should occur at an observable rate at ambient temperature and should be reasonably facile at elevated temperature. The hydride transfer should be readily catalyzed by an enzyme by hydrogen bonding or proton transfer to N^1, and the greatly decreased gas-phase barrier for **5-8** suggests that proton transfer ought to be most effective in a non-polar pocket. Consistent with such a model, many flavoproteins oxidases have a positively charged residue or the positive end of a helix near the flavin N^1.[194,195] The enzyme could also ease the hydride transfer by electrostatically stabilizing the incipient iminium ion. Alternatively, if the flavin is distorted away from planarity by the enzyme, this should facilitate the hydride transfer, just as it facilitates electron transfer. In products **5-6**-5-H^- and **5-6**-1,5-H_2, the

flavin rings are bent approximately 20° from planarity (the C^4–N^5–C^6 angles are approximately 160°) while the starting flavin is planar, so enzymes that pre-bend the flavin will lower the barrier to hydride transfer. Overall, the calculated facility of the reaction in free solution and the expected ease of its catalysis support the viability of the hydride-transfer mechanism.

Electron transfer to form **5-6$^{-\bullet}$/5-9** is predicted to have a higher barrier in free solution than hydride transfer. In the actual mechanism, this electron transfer would necessarily precede a yet higher barrier for rate-limiting proton or hydrogen transfer to account for the observed primary deuterium isotope effect. The combination of the calculated energetics and the primary H/D isotope effect thus adds to an energetic argument against the electron-transfer mechanism. However, it is impossible to dismiss the electron-transfer mechanism on this basis, as MTOX might promote electron transfer either by electrostatic stabilization of the charged intermediates or by flavin distortion.

Conclusions

The computational predictability of heavy-atom kinetic isotope effects has often allowed their detailed interpretation beyond conventional qualitative considerations. In the case of sarcosine oxidation by MTOX, the interpretation of the observed ^{15}N kinetic isotope effect of approximately 0.994 based on calculated isotope effects is not unique. Both a direct hydride-transfer mechanism and reversible electron transfer followed by rate-limiting proton or hydrogen transfer can account for the observed isotope effect. However, the isotope effects predicted for models of mechanisms involving covalent adducts or concerted addition/elimination are significantly different from the

experimental value and thus strongly disfavor these mechanisms. In concert with the absence of observable intermediates and the poor calculated energetics for these mechanisms, consideration of concerted or covalent adduct mechanisms for sarcosine oxidation by MTOX can be discounted. The calculated energetics for model reactions add some support for the hydride-transfer mechanism, as the enzyme need only modestly lower the barrier for the reaction versus that in free solution. The electron-transfer mechanisms in contrast would require somewhat greater energies, and it would be surprising if this left a proton or hydrogen transfer step as rate-limiting.

CHAPTER VI

THEORETICAL ANALYSIS OF EXO SELECTIVE DIELS-ALDER REACTIONS OF VINYLAZEPINES, VINYLPIPERIDEINES, AND VINYLCYCLOALKENES*

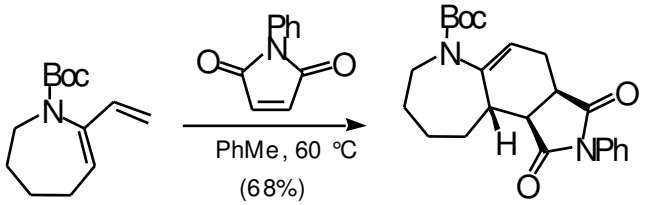
Diels-Alder reactions of vinylazepines with N-phenylmaleimide afforded exclusively the exo cycloadduct, while high endo stereoselectivity was observed, as previously reported, in analogous reactions of vinylpiperideines. This curious contrast was confirmed by x-ray analysis of cycloadducts not susceptible to epimerization. The stereoselectivity of Diels-Alder reactions of vinylazepines, vinylpiperideines, and vinylcycloalkenes exhibits surprising divergence depending on the detailed diene structure, and DFT calculations (Becke3LYP) were undertaken to shed light on these observations. The model calculations correctly predict the major stereoisomers in these reactions, though they tend to significantly underestimate the stereoselectivity. The results suggest some general considerations in predicting or controlling the stereochemistry of this class of Diels-Alder reactions.

Introduction

Diels-Alder reactions employing vinylcycloalkenes and related dienes provide a rapid entry into polycyclic structures. However, to fully take advantage of the power of these reactions, the synthetic chemist must be able to predict or control their stereoselectivity.

Only recently have reports describing Diels-Alder reactions of cyclic 2-(N-acylamino)-1,3-dienes appeared in the literature. Cha studied piperideine-derived enecarbamates and found these dienes react with ethyl acrylate with unusual meta regioselectivity and no endo/exo stereoselectivity.[196] However, N-phenylmaleimide was found to afford exclusively the endo cycloadduct, a result later corroborated by Occhiato.[197] Reactions of pyrollidine-derived 2-(N-acylamino)-1,3-dienes with N-phenylmaleimide also exhibit exclusive endo selectivity.[198,199] No studies on the seven-membered azepine dienes have been reported.

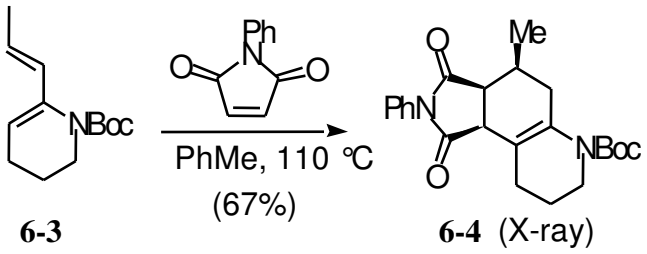
In connection with synthetic studies relating to the synthesis of stenine, Sulikowski and Boren have observed surprising examples of exo selectivity as well as reversals of endo/exo stereoselectivity with changes in diene structures.[200] The Diels-Alder cycloaddition between **6-1** and N-phenylmaleimide gives **6-2** as the only observable cycloadduct, confirmed by single-crystal x-ray analysis.



6-1 **6-2** (X-ray)

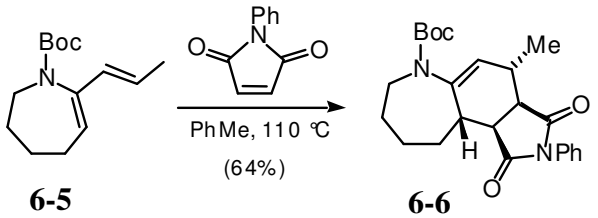
In light of the opposite literature results with smaller rings, this was very surprising. In earlier studies, the stereochemistry of the cycloadducts derived from the Diels-Alder reaction of N-phenylmaleimide and cyclic 2-(N-acylamino)-1,3-dienes were assigned based on NMR analysis. In order to corroborate these structural assignments,

the cycloaddition of diene **6-3** with N-phenylmaleimide was studied. This afforded product **6-4**, resulting from an endo cycloaddition followed by double bond migration, and was confirmed by X-ray analysis.



6-3 **6-4** (X-ray)

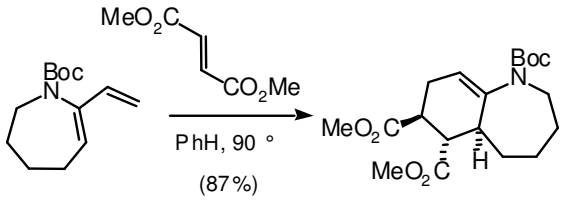
Double bond migration in the product enamides, as observed in **6-4** is presumably catalyzed by adventitious acid. This isomerization raised the concern that **6-2** might be the result of an initial endo cycloaddition followed by epimerization of the ring fusion carbon. This possibility was explored using diene **6-5**. In this case the Diels-Alder cycloadduct includes an additional stereochemical marker center that is not epimerizable. Reaction of **6-5** with N-phenylmaleimide afforded only **6-6**, established as exo by X-ray analysis.



6-5 **6-6**
(X-Ray)

Vinyl azepine **6-5** reacted with ethyl acrylate to provide a mixture of isomers, presumably consisting of regio- and stereoisomers as reported by Cha when utilizing a piperidine derived diene analogous to **6-5**.[196] In contrast the doubly activated dienophile

dimethyl fumarate reacted with vinyl azepine **6-1** to provide a single Diels-Alder adduct **6-7**. In this case the methyl carboxylate group closest to the ring fusion carbon adopts an exo orientation and the second carboxylate group occupies an endo orientation.

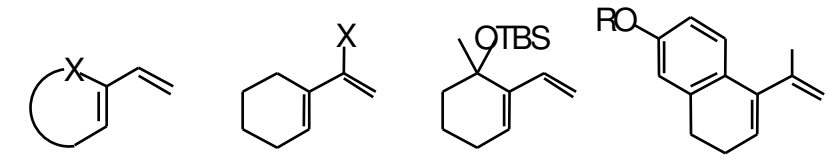


6-1 **6-7**

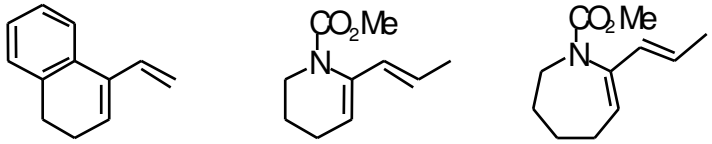
The striking reversal of exo/endo stereoselectivity between azepene-derived 2-(N-acylamino)-1,3-dienes and their smaller-ring congeners is unusual. Quite a few exo-selective Diels-Alder reactions are known, but they tend to involve recognizable structural motifs. For example, exocyclic s-cis dienophiles of all types tend to be exo-selective.[201-205] Preferential exo cycloaddition is often observed in the reaction of cyclopentadiene with α-substituted dienophiles.[206-208] The unique sterics of metal carbene dienophiles also result in exo selectivity.[209-211]

The Diels-Alder reactions of vinylcycloalkenes and cyclic 2-(N-acylamino)-1,3-dienes, as in **6-8**, would appear to compose a motif in which the endo/exo stereoselectivity is highly variable. While 1-vinylcyclohexene **6-9** and the silyloxy derivative **6-10** afford endo cycloadducts,[212,213] Danishefsky obtained the exo cycloadduct from a reaction of the dimethyl derivative 11,[214] and Corey observed exo selectivity in a reaction of **6-12**.[213] Others have reported low endo selectivity of the reaction of diene **6-13** and congeners.[215-217] In these examples and those above,

seemingly minor changes in the structure of the "spectator" ring lead to reversed stereochemistry.



6-8 X=C or N **6-9** X=H **6-10** X=OTBS **6-11** **6-12**



6-15 **6-13** **6-14**

This has led us to a broader study of endo/exo stereoselectivity with vinylcycloalkenes. The theoretical investigation here provides insight into these results as well as observations of exo selectivity in related Diels-Alder reactions.

Results and Discussion

To gain insight into stereoselectivity with this class of dienes, the model reactions of **6-9**, **6-11**, **6-13**, **6-14**, and **6-15** with maleimide were studied in Becke3LYP calculations employing a 6-31G* basis set. Isotope effects have supported the accuracy of transition structure geometries obtained from this level of calculation for simple Diels-Alder reactions.[26] This study was complicated by multiple possible reactive conformations, particularly with **6-15**. Molecular dynamics / simulated annealing was used to identify candidate conformations, and notably found structures for **6-15** corresponding to the chair, boat, and twist-chair conformations of cycloheptane.[218] The

possible reaction pathways were then explored systematically. This process led to a total of 36 transition structures for the five reactions.

Figures 6-1 and 6-2 show selected low-energy transition structures for these reactions, along with relative free-energy barriers at 25 °C (the free energy was estimated as $\Delta E - T\Delta S$ by including zero-point energies and entropies based on the unscaled vibrational frequencies). Complete structures are given in the appendix. In each case, the calculations correctly predict the experimentally observed major isomer. However, they underpredict the degree of selectivity compared to the experimental examples.

Recent work by Paddon-Row and Sherburn suggested the use of MP2 single-point energies on the Becke3LYP structures to more accurately predict endo stereoselectivity in Diels-Alder reactions.[219] When this procedure is applied to the reactions **6-9**, **6-11**, and **6-13**, the MP2/6-31G*//B3LYP/6-31G* free energies correctly predict the endo stereoselectivity with **6-9** (by 1.2 kcal/mol), but they also predict endo stereoselectivity for **6-11** and **6-13** by 0.3 and 1.2 kcal/mol, in contrast to experimental observations with **6-11** and **6-12** and in contrast to the B3LYP/6-31G*//B3LYP/6-31G* results in Figures 6-1 and 6-2. It is best to keep in mind that any feasible theoretical calculation of relative energies for systems this large will have associated with it some "uncertainty." Considering this uncertainty, along with the structural differences between the experimental and theoretical examples, the agreement of experiment and the B3LYP predictions is quite reasonable. The calculations provide a model that may be examined to analyze the factors affecting the stereoselectivity, and the agreement of

predicted major product with experiment suggests that this model adequately represents the major stereochemistry-determining factors.

As a starting point for understanding these reactions, exo transition structures strongly favor "axial attack" on the six-membered ring dienes (Figure 6-1). By axial attack, we mean that the incipient b-b' bond in structures **6-16**, **6-17**, and **6-20** – **6-25** would initially be in an axial position on a chair conformation of the bystander ring. An example is the 1.6 kcal/mol advantage for **6-16** over **6-17**. Similar preferences of 1.6-2.0 kcal/mol are seen with the exo transition structures derived from **6-11**, **6-13**, and **6-14**. This appears analogous to the well-known predilection axial alkylation of cyclohexanone enolates. One generally expects axial attack to be more hindered, but when steric effects are small, axial attack has the advantage of resulting in an initial chair conformation for the bystander ring.[220,221]

The endo transition structures derived from **6-9**, **6-11**, **6-13**, and **6-14** also favor an axial attack, but the preference is decreased compared to the exo. For example, **6-18** is favored over **6-19** by 0.6 kcal/mol. For the endo pathways, axial attack is sterically hindered by an incipient 1,3-diaxial interactions (**6-18**). The equatorial attack remains disfavored in the calculations here for all of the six-membered ring dienes. However, the predicted energy difference is small (0.1 – 0.6 kcal/mol) and within the likely uncertainty in the calculations. Equatorial attack might be expected to be favored for more sterically demanding dienophiles.

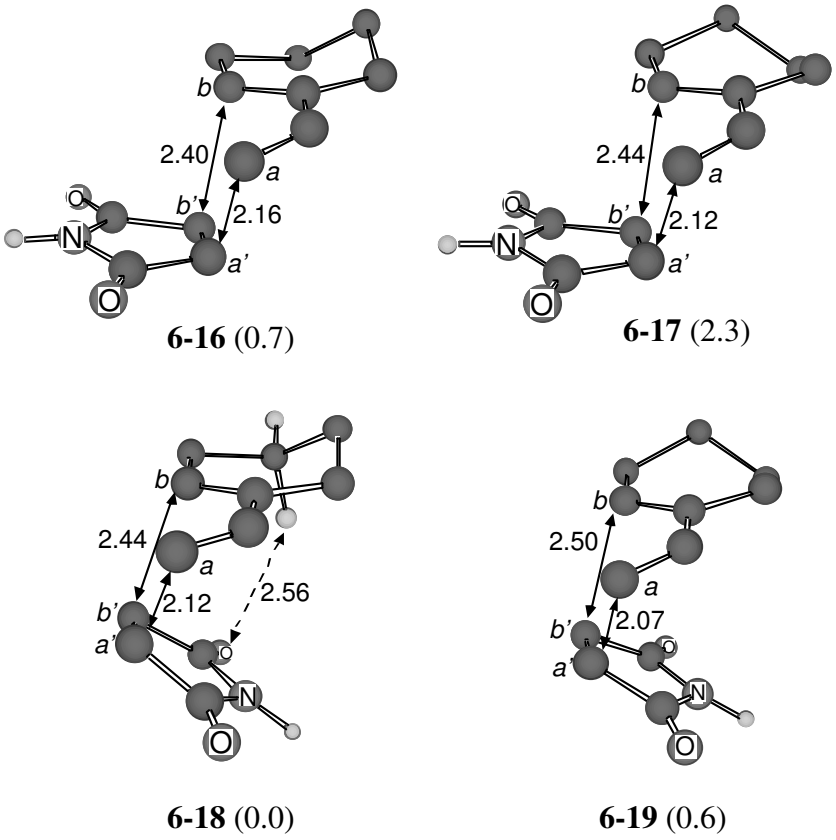


Figure 6-1. Transition structures for the reaction of **6-9** with maleimide. Energies are relative to isomeric transition structures, in kcal/mol. Most hydrogens have been removed for clarity.

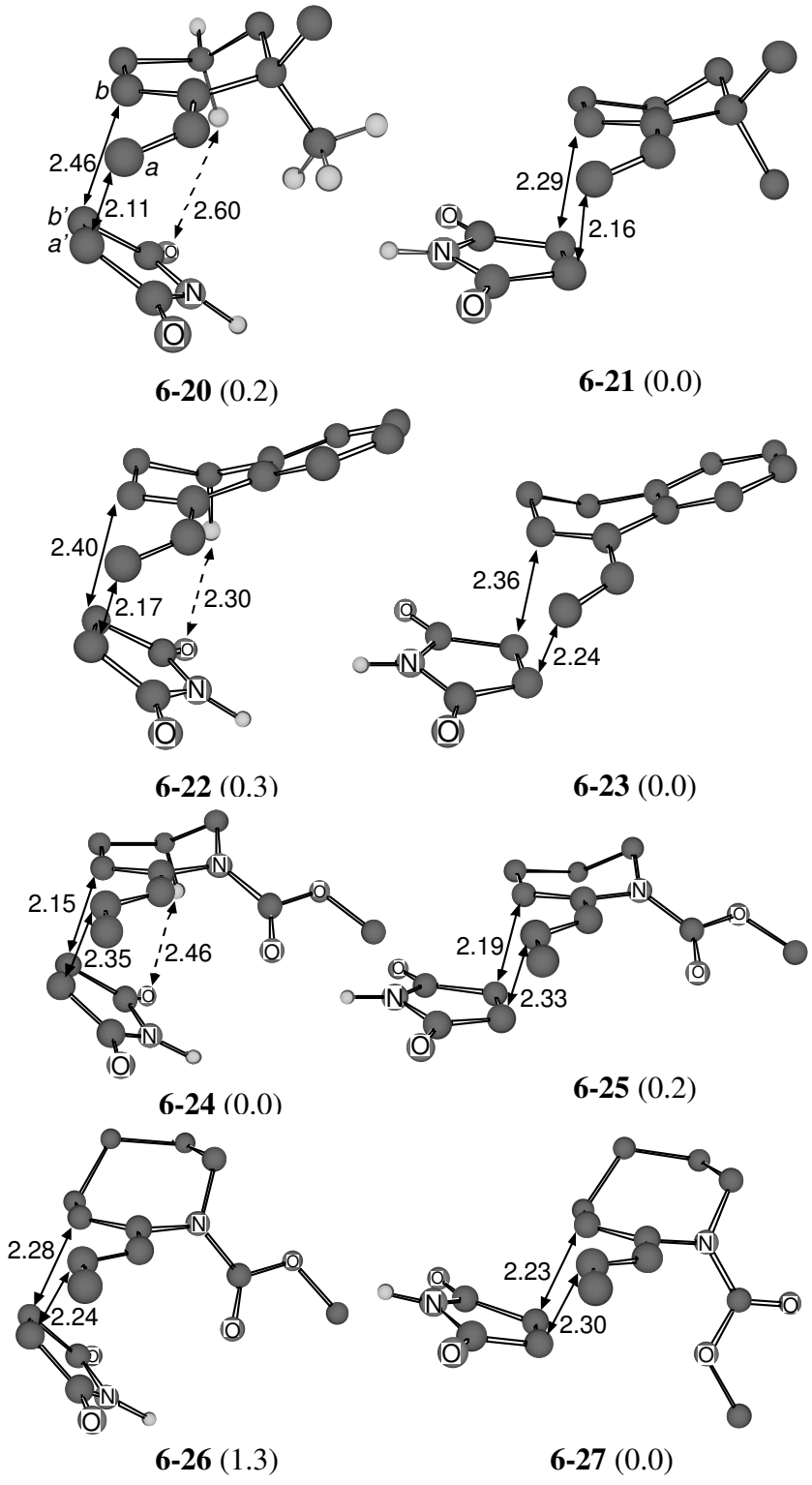


Figure 6-2. Select low-energy transition structures for reaction of several dienes with maleimide. Energies are relative to isomeric transition structures, in kcal/mol.

Exo axial attack also faces an incipient 1,3-diaxial interaction but it has the advantage of placing the imide ring away from the sterics of the spectator ring. When the sterics are increased, as with **6-11**, the endo axial approach is hindered and the exo axial attack unsurprisingly becomes favored (compare **6-20** versus **6-21**). A more surprising example is the reaction of **6-13**. In the endo axial transition structure **6-22**, the cyclohexadiene-like ring is very nonplanar and the axial hydrogen shown has a stronger steric interaction with the dienophile than in any of the analogous structures resulting in a favored exo approach **6-23**.

In the transition structures derived from **6-14**, the piperideine ring and its carbomethoxy substituent have relatively little steric influence on the approaching dienophile, allowing a normal endo stereoselectivity. A surprising observation is that the plane of the carbamate nitrogen in **6-24** is twisted by 38° relative to the plane of the diene. It might have been expected that the carbamate would try to align the nitrogen lone pair with the diene π orbitals in order to maximize donation to the diene. In the predicted conformation, the nitrogen will have a negligible activating effect. This is consistent with the moderate reactivity of the dienes, and explains the meta regioselectivity observed by Cha for these reactions.[196]

The best structures derived from **6-15**, such as **6-26** and **6-27**, all involve a decidedly non-planar chair-like conformation of the azapine ring with the carbomethoxy group twisted well away from the plane of diene. For the seven-membered ring, there is apparently no longer a stereoelectronic effect favoring "axial" attack on the pseudo-chair – in fact the structures analogous to **6-18**, **6-20**, **6-22**, and **6-24** suffer from a severe steric

interaction with the seven-membered ring and are 4 kcal/mol higher in energy. Endo attack on the other face of the diene, as in **6-26**, is better but is still hindered by interaction with the carbomethoxy group. As with the piperideine analogs, the plane of the carbamate nitrogen in **6-26** is twisted relative to the plane of the diene, but now by 56°. This positions the carbomethoxy group to block one face of the diene. With the highly non-planar seven-membered ring blocking the other, the exo pathway becomes favored by a substantial margin.

Conclusions

Diels-Alder reactions of vinylazepines and vinylpiperideines fit in with the reactions of vinylcycloalkenes in that the group, as a whole, exhibits highly variable stereoselectivity. This stereoselectivity depends on the detailed structure of the diene, and will likely depend on the dienophile as well, so that generalizations regarding the selectivity of these reactions are not yet apparent. Nonetheless, the results here suggest some general considerations in predicting or controlling the stereochemistry of this class of Diels-Alder reactions. To counteract the normal endo preference with simple dienes built from five- and six-membered rings, substituents that maximize a 1,3-diaxial interaction with the incoming dienophile should most readily result in exo selectivity. In analogy with the 6,6-dimethyl derivative **6-11**, we would predict that axial substituents in the 4-position of vinylcyclohexene would result in exo product formation. Axial substituents in the 3 or 5 positions would likely exert less effect. The greater non-planarity with seven-membered can readily lead to steric prohibition of the endo

pathway. This presents interesting opportunities for control of stereoselectivity in Diels-Alder reactions involving dienes with bystander ring structures.

CHAPTER VII

EXPERIMENTAL SECTION

Theoretical Methods for the Swain-Schaad Relationship

All structures and energies were obtained using standard procedures in Gaussian98 or Gaussian03.[222] Unless otherwise noted, structures were fully optimized in B3LYP calculations employing a 6-31G* basis set. Unrestricted calculations were employed for open-shell structures. Vibrational frequency analyses were carried out on all stationary points.

Isotope effect calculations made use of a modified version of the program QUIVER. Frequencies for B3LYP/6-31G* calculations were scaled by 0.9614. For each of the reactions given, H/D, H/T, and D/T kinetic isotope effects were calculated for all C-H positions. In addition, for almost all of the reactions, the H/D, H/T, and D/T kinetic isotope effects were also calculated for the reverse reaction. For example, in the Diels-Alder reaction, kinetic isotope effects were calculated for both the forward reaction from 1,3-butadiene and ethylene and the reverse (retro) Diels-Alder reaction for cleavage of cyclohexene.

A series of simple unix shell routines and awk programs were used to ease dealing with the large number of isotope effects. These are listed in Appendix A.

Each of the reactions below is given a title and this title is also used in a later section containing relevant calculated geometries.

Experimental Section for the Reaction of Oxidosqualene Cyclase (OSC)

Bromohydrin of squalene**.** The procedure used for the synthesis of ±oxidosqualene was slightly modified from the procedure of Scott.[122] 6L of THF was added to a 12L 3-neck round bottom flask equipped with a mechanical stirrer in an ice bath, flushed with nitrogen and allowed to cool for 30 minutes. 83g of squalene (Acros) was added to the reaction vessel at once. 1.5L of water was added and the reaction allowed to stir for 10 minutes. 500mls of water was added slowly until the mixture became cloudy, stirring was continued for 15 minutes. 43.4g (1.2 eq) of NBS (Acros, if necessary recrystallized from water) was added to the reaction over a period of 40 minutes. The reaction was allowed to stir at 0°C for 25 minutes. The reaction was checked by TLC in 100:8 hexanes/EtOAc for conversion to the bromohydrin. 2L of water was added to quench the reaction and the reaction mixture was extracted with two 250 ml portions of hexanes. The combined organic layers were dried with Na_2SO_4, filtered, and the solvent removed under reduced pressure . The reaction was repeated two more times and the crude product combined. The reaction gives unreacted squalene due to insolubility in the solvent system, and several other impurities which are assumed to be undesired isomers of the target bromohydrin. The crude product was purified using flash silica gel chromatography (or by MPLC) in a mixed solvent system of pure hexanes to remove unreacted squalene and then followed by 100:4 hexanes/EtOAc. Several columns in 100:4 hexanes/EtOAc were required to give 54.3g of pure bromohydrin.

±Oxidosqualene from the bromohydrin**.** 4L of methanol was added to a 3-neck flask equipped with a stirrer and purged with N_2 at room temperature. 54.3 g of the bromohydrin was added to the flask and allowed to stir for 20 minutes. 20 g of K_2CO_3 was added in one portion and the reaction allowed to stir at room temperature for 12 hours. The reaction progress was monitored by TLC in 100:8 hexanes/EtOAc. The reaction was quenched with 2 L of water. The reaction mixture was extracted with hexanes and the combined organic dried with Na_2SO_4. The solvent was evaporated to give 38.1 g of pure ±oxidosqualene.

Cyclization of oxidosqualene (100% conversion reaction). Four jars of Fleishman's yeast (452 g) is slowly stirred into 500 mls dibasic potassium phosphate buffer, pH=7.4, until completely homogenous. The yeast mixture was cooled on an ice bath to approximately 10°C. The yeast was lysed in ~100 ml aliquots with a bead beater (Biospec Products Inc.) using 0.5mm glass beads. Each batch of yeast was lysed twice for 90 s, and cooled back to 10°C each time. The yeast lysate was centrifuged at 6000 rpm on an SLA3000 rotor for 15 minutes. The lysate (pH=5.8-6.1) was decanted from the pellet into the reaction flask. The reaction flask was prepared by adding 10 mls Triton X-100 to 500 mls of dibasic potassium phosphate buffer, pH=6.4. The mixture was sonicated for 10 minutes, then 2.0 g of ±oxidosqualene was added and the mixture was continuously sonicated for 10 minutes. The oxidosqualene solution is placed in a 3-necked round bottom flask and warmed to 37°C while stirring under N_2 for one hour. The yeast lysate mixture is added. Dibasic potassium phosphate buffer, pH=6.4, is added until the total reaction volume was 1 L. The reaction is stirred at 37°C under N_2

for 24 hours. The reaction progress is checked by TLC in 1:1 hexanes/ether and visualized using iodine or anisaldehyde stains. The reaction is quenched with 1L of ethanol and allowed to sit for several hours. The precipitate is centrifuged at 6,000 r.p.m. for 15 minutes on an SLA3000 rotor. The supernant is combined and stored. The pellets are washed twice with hexanes. The combined organic was dried with Na_2SO_4, filtered, and the solvent removed under reduced pressure to give a crude oil. A silica gel column was ran in dichloromethane/hexanes to purify the oxidosqualene and lanosterol from the reaction mixture. The extent of reaction was determined by measuring the amount of (S)-2,3-oxidosqualene left at the end of the reaction. This was determined by examination of the ^{1}H NMR in d_6-benzene of the diasteriotopic methyl groups at δ1.11 and δ1.16 of the R and S isomers of oxidosqualene using the chiral shift reagent, europium tris[3-heptafluoropropylhydroxymethylene] camphorate as described below. After the reaction was determined to be greater than 99% complete, the lanosterol was further purified by additional silica gel chromatography using the dichloromethane/hexanes solvent system. Approximately 900 mgs of pure lanosterol was recovered from each reaction.

Cyclization of oxidosqualene (partial conversion reaction). The reaction was performed exactly as above with the following changes: 2 jars of Fleishman's yeast (226 g), 10-12 g $\pm$oxidosqualene, oxidosqualene, and Triton X-100 at pH of 6.2. Reactions were taken to 20-40% conversion.

Chiral shift study used to measure percent conversion. A ^{1}H NMR of 30 mgs of reisolated oxidosqualene was measured in d_6-benzene. A minimal amount of the chiral

shift reagent Europium tris[3-heptafluoropropylhydroxymethylene] camphorate was added to the d_6-benzene. The ratio or R and S enantiomers of oxidosqualene was determined by examination of the ^{1}H NMR in d_6-benzene of the diasteriotopic methyl groups at δ1.11 and δ1.16 of the R and S isomers. The ratio of the R and S enantiomers of oxidosqualene was measured using the peak heights for each methyl group which corresponded well with one another. This method of measurement was also verified by analyzing standard oxidosqualene mixtures of known R and S content. The percent conversion could then be determined from equation 7-1, assuming (R)-2,3 oxidosqualene is completely unreactive in the mixture.

%conversion=(S enantiomer peak height/R enantiomer peak height)-100 (7-1)

NMR study to measure the solubility of + oxidosqualene in water. 5 µL $\pm$ oxidosqualene (.011 mmols), 5 µL DMF (.008 mmols), and 35 µL Triton X-100 were placed in 5 mls D_20. The sample was shaken and ^{1}H NMR was taken at 500 MHz. The dimethyl formamide was assumed to be 100% soluble in the D_2O and the aldehyde peak was used as an internal standard to compare to the methine peak on C3 of oxidosqualene. This resulted in 19% solubility of $\pm$ oxidosqualene. A similar mixture was prepared in an identically and sonicated two times for 30 seconds. Comparison of the aldehyde and C3 methine peaks showed 100% solubility of $\pm$ oxidosqualene. The NMR tube containing the sonicated solution was heated at 37 ºC to mimic reaction conditions. NMRs were taken at 1 hour and 24 hours and show 100% oxidosqualene solubility.

Acetylation of lanosterol**.** 3 mls of pyridine were placed in a 3-necked flask equipped with a magnetic stirrer and N_2. 3.008 g of lanosterol was added slowly while stirring. 12 mls of acetic anyhydride was then added and the reaction was slowly heated for 3 hours. The reaction stirred at room temperature for 5 more hours until the reaction was complete by TLC. The reaction was quenched with 30 mls of water and the precipitate filtered. The filtrate was extracted twice with ether, dried the organics with sodium sulfate, and evaporated solvent. 2.0 g of pure material was recovered. The material was recrystallized in 1:1 ethyl acetate methanol. ^{1}H and ^{13}C NMR spectra matched literature values.[223]

Trifluoroacetylation of lanosterol. 1.02 g of lanosterol was added to 10 mls CH_2Cl_2 in a 3-neck round bottom flask equipped with a magnetic stirrer and N_2. 350 µL pyridine and 50 µL trifluoroacetic anhydride were added to the flask. The reaction was stirred at room temperature overnight. The reaction was quenched with 20 mls water. The water layer was extracted two times with CH_2Cl_2. The combined organic layers were washed with water, sodium bisulfate, sodium carbonate, and water. The organic was dried with sodium sulfate and filter. After evaporation of the solvent .8882g of solid was recovered, which was the trifluoroacetyl lanosterol derivative as shown by ^{1}H, ^{13}C, and ^{19}F NMR in $CDCl_3$. (mp=98-100 ºC)

Pyridinium chlorochromate (PCC) oxidation of lanosterol to lanosterone. 510 mgs of lanosterol was placed in 30 mls CH_2Cl_2 in a round bottom flask. 590 mgs of PCC was added at once to the reaction and the solution stirred vigorously at room temperature. After one hour the reaction was incomplete and 50 mgs of PCC was added.

After 3 hours the reaction was complete. The solid was filtered, and the liquid layer was run through silica gel using ether as the eluent. The solvent was evaporated to give 492 mgs of lanosterone as a solid. ^{13}C NMR in d_8-THF. δ 214.73 (C_3), 136.2 (C_8), 134.6 (C_9), 131.32 (C_{25}), 126.19 (C_{24}), 52.25 (C_5), 51.60 (C_{17}), 50.99 (C_{14}), 47.90 (C_4), 45.52 (C_{13}), 37.94 (C_{10}), 37.46 (C_{22}), 37.42 (C_{20}), 37.07 (C_1), 35.09 (C_2), 32.18 (C_{12}), 31.99 (C_{15}), 29.21 (C_{16}), 27.42 (C_7), 26.84 (C_{28}), 26.31 (C_{30}), 25.94 (C_{23}), 24.92 (C_{26}), 22.07 (C_{29}), 21.85 (C_6), 20.47 (C_{11}), 19.43 (C_{19}), 19.24 (C_{21}), 18.13 (C_{27}), 16.62 (C_{18}) d_8-THF referenced to δ 67.57.

Reaction of impure lanosterone sample with tetracyanoethylene (TCNE). 103 mgs of lanosterone sample containing 5% impurity from oxidosqualene cyclase was placed in $CDCl_3$ in a 5mm NMR tube. 5mgs of TCNE was added and the reaction monitored by ^1H and ^{13}C NMR. After 24 hours the impurity still remained. An additional 5 mgs TCNE was added and allowed to react for 24 hours. The impurity was still present by ^1H and ^{13}C NMR analysis. The addition was repeated again. The impurity was still present by ^1H NMR, ^{13}C NMR, and UV after 72 hours.

Reaction of impure lansoterone sample with N-phenyl triazoline dione (PTAD). 100 mgs of lanosterone sample was placed in an NMR tube in $CDCl_3$. PTAD was slowly added (5 mgs, 10mgs, 15 mgs, 18 mgs) until solution remained bright pink. ^1H NMR was taken after every addition. The reaction was allowed to sit overnight at room temperature. The solution color cleared to slightly yellow. ^1H and ^{13}C NMR showed that the cyclic diene peaks of agnosterone remained after the reaction. Only the straight

chain alkene of lanosterone and agnosterone were affected by the reagent. The reaction was also performed in a dry ice/acetone bath with similar results.

PCC on alumina oxidation of lanosterol to lanosterone. 1g of PCC was placed in 3 mls water and slowly heated until dissolved. 4 g of alumina was added to the mixture. The water was evaporated and the solid dried under reduced pressure. 126 mgs of lanosterol was added to 2 mls CH_2Cl_2 and stirred under N_2. .125 g of the PCC-Alumina solid was added to the reaction mixture. The solution was stirred at room temperature for 3 hours until the disappearance of lanosterol by TLC (100:8 hexanes/ethyl acetate). The mixture was ran through a silica gel plug in ether, and the solvent evaporated. 125.5 mgs of solid was recovered and analyzed by ^{1}H NMR, ^{13}C NMR, and UV. The spectral data was consistent with the formation of lanosterone and approximately 4% of the agnosterone side product.

PCC oxidation in sodium acetate of lanosterol to lanosterone. 4 mgs of sodium acetate was placed in a round bottom flask in 2 mls CH_2Cl_2 equipped with 4Å molecular sieves, under N_2. 125 mgs of lanosterol was added, and allowed to stir until soluble. 97 mgs of PCC was added and the reaction stirred at room temperature for 5 hours until disappearance of starting material by TLC (100:8 hexanes/ethyl acetate). The reaction mixture was ran through a silica gel plug in ether, and the solvent evaporated. 129.1 mgs of solid was recovered and analyzed by ^{1}H NMR, ^{13}C NMR, and UV. The spectral data was consistent with the formation of lanosterone and approximately 4% of the agnosterone impurity.

Jones oxidation of lanosterol to lanosterone. 86 mgs of CrO_3 was added to .07 mls of distilled water and stirred at room temperature. .4 mls of sulfuric acid was slowly added dropwise. 125 mgs of lanosterol was added to .8 mls of acetone in a round bottom equipped with N_2. The chromic acid solution was slowly dripped into the reaction. The reaction was stirred at room temperature for one hour and quenched with 5 mls 5% $NaHCO_3$. The reaction mixture was extracted three times with ether. The combined organic layers were washed with water, saturated NaCl, and dried over sodium sulfate. The solvent was evaporated, and the solid dried under reduced pressure. 52 mgs of solid was recovered and analyzed by ^{1}H NMR, ^{13}C NMR, and UV. The spectral data was consistent with the formation of lanosterone and approximately 4% of the agnosterone side product. (Loss of product was probably due to initial insolubility of lanosterol in acetone, however the reaction was not optimized because the final product still contained the agnosterone impurity).

Collins oxidation of lanosterol to lanosterone. 0.3 mls of pyridine was added to 5 mls CH_2Cl_2 in a round bottom flask equipped with 4Å sieves and N_2. 187 mgs CrO_3 was added to the solution and stirred at room temperature for 10 minutes. The reaction was cooled in an ice bath to ~10 ºC. 125.6 mgs of lanosterol in 3 mls of CH_2Cl_2 was slowly added to the reaction. The reaction was allowed to stir overnight and slowly reach room temperature. The reaction mixture was ran through a silica gel plug in ether, and the solvent evaporated. 125 mgs of solid was recovered and analyzed by ^{1}H NMR, ^{13}C NMR, and UV. The spectral data was consistent with the formation of lanosterone (the reaction only went to 10% conversion based upon comparison of the ^{1}H NMR peaks of

the starting alcohol and product ketone peaks) and approximately 3% of the agnosterone side product.

Parikh-Doering oxidation of lanosterol to lanosterone. 0.45 mls pyridine was placed in 2.1 mls CCl_4 and stirred in an ice bath. 250 mgs of chlorosulfonic acid was added slowly dropwise. The reaction was stirred for 5 minutes, 2 mls water added, and the solid filtered. 125 mgs of lanosterol was added to .75 mls DMSO and .7 mls triethyl amine and allowed to stir at room temperature. 56 mgs of the SO_3·pyridine salt in .75 mls DMSO was added to the reaction. After 30 minutes of stirring at room temperature, TLC indicated a significant amount of the starting material was still present. Another batch of salt was made and added to the reaction. The reaction was allowed to stir overnight and quenched with 5% Na_2HCO_3. The solid filtered and the filtrate extracted three times into ether. The combined organics were dried and evaporated. The recovered solid was analyzed by ^{1}H NMR, ^{13}C NMR, and UV. The spectral data was consistent with the formation of lanosterone and approximately 1% of the agnosterone side product. (The impurity may be artificial since the amount of agnosterone is based upon an increase in the diene peaks of the cylic alkene protons in the commercial lanosterol starting material compared to the product lanosterone. Commercial lanosterol contains about 8% agnosterol impurity and the final product had 9.1% based on ^{1}H NMR. However, this method was abandoned due to the poor yield of only 9% conversion of lanosterol to the corresponding ketone.)

Swern oxidation of lanosterol to lanosterone**.** 1.5 mls of CH_2Cl_2 was added to a 3-neck flask equipped with a stir bar and N_2 in a dry ice acetone bath (approximately -60

°C). Freshly distilled oxalyl chloride (.2 mls) was added via syringe and the reaction allowed to stir for 30 minutes. Dried DMSO (.33 mls) was added via syringe dropwise and the reaction allowed to stir for 3 minutes. Lanosterol (831 mgs) was placed in 15 mls CH_2Cl_2 and added at once to the reaction. The reaction was allowed to stir for 20 minutes. 1.36 mls of triethyl amine was slowly added via syringe and the reaction allowed to stir for 20 minutes. The reaction progress was monitored by TLC in 100:8 Hexanes/EtOAc. The reaction was quenched with 10 mls water and extracted with CH_2Cl_2. The combined organic layers were washed 3 times with 1% HCl, 2 times with water, 2 times with Na_2CO_2, and 2 times with NaCl. The methylene chloride was then dried with $MgSO_4$, filtered, and the solvent evaporated. The lanosterone was purified by silica gel chromatography in 1% EtOAc/Hexanes to give 588.5 mgs of pure lanosterone.

Methods for lysing yeast cells**.** For all of the lysis methods dry Fleishman's yeast was mixed with 100 mM dibasic potassium phosphate buffer, pH=7.4, in a ratio of .9 - 1.0g of yeast per ml of buffer unless otherwise indicated. This was homogenized by stirring at 37 °C. After lysis, racemic oxidosqualene was then added and sonicated into solution with 1% by volume of buffer Triton X-100 and allowed to react for 24 hours, unless otherwise indicated in the procedure. The reactions were then checked by TLC in 1:1 hexanes/ether. When possible the lysis was also checked by a Bradford assay for protein content. This was followed by the standard work-up procedure used to isolate the crude oxidosqualene and lanosterol from the reaction solution as described above for the conversion of oxidosqualene to lanosterol. The reactivity was then determined by the ^1H NMR in $CDCl_3$ by comparing the amount of oxidosqualene versus lanosterol.

Duplicate reactions were also performed using dibenzyl ether as a standard to monitor the consumption of oxidosqualene. **Sonication.** The mixture was continuously sonicated for 60 minutes each in a cold water apparatus and the temperature kept below 20 °C. If the temperature increased above 20 °C the sonication was discontinued, the mixture cooled on an ice bath to about 7-10 °C and then sonication continued. The effectiveness of sonication was checked by a Bradford assay and the pH of the solution which was between 5.8 and 6.1 for batches that gave high substrate turnover. **Chemical Autolysis.** 22.5 grams of Fleishman's yeast was placed in 100 mls of toluene and 100 μL ±oxidosqualene was added to the mixture (sonication was not required because of the solubility of oxidosqualene in toluene). The reaction was monitored periodically by TLC in 1:1 hexanes/ether. After 48 hours there was no indication by TLC analysis that lanosterol had been formed. This method resulted in no substrate turnover. **Freezing.** 22.5 g Fleishman's yeast was suspended in a solution of 100 mls of 100 mM dibasic potassium phosphate buffer, pH=7.4. The yeast suspension was frozen with liquid nitrogen for 5 minutes and warmed to a liquid in a warm water bath for 15 minutes. This cycle was repeated 6 times. The cell walls were centrifuged and the protein content measured using the method of Bradford. The lysate was used in the normal reaction conditions and the reaction worked up after 24 hours. This method resulted in no substrate turnover according to TLC and ^{1}H NMR analysis. **Grinding dry yeast.** 22.5 g Fleishman's yeast was ground to a powder with a mortar and pestle. This was placed in a solution of 100 mls of 100 mM dibasic potassium phosphate buffer, pH=7.4, and 100 μL ±oxidosqualene with 1% Triton X-100 that had previously been sonicated. The

reaction percent conversion was monitored by TLC and ^{1}H NMR. This method resulted in no substrate turnover. **French Press.** Fleishman's yeast was suspended in 100 mM dibasic potassium phosphate buffer, pH=7.4. The suspension was cooled on an ice bath to approximately 5-10 °C. The culture was lysed on a French press under 20,000 p.s.i in 35 ml aliquots. The suspension was briefly sonicated for 30 seconds. The suspension was then centrifuged and the lysate subjected to the standard reaction conditions and work-up. This resulted in a yield of 100% conversion to lanosterol. **Enzymatic lysis with lyticase.** 25 g of Fleishman's yeast was suspended in 100 mls of 100 mM dibasic potassium phosphate buffer, pH=7.4. A 20 mM stock of DTT (dithiothreitol) was added to the solution to bring the final DTT concentration to 4mM. The solution was stirred for one hour. The yeast solution was frozen with liquid nitrogen and rapidly warmed in warm water for 15 minutes. 50 µL of a 1mg/250µL stock solution of Lyticase (a total of 500 units) was added to the yeast suspension and incubated for 1 hour. The solution was sonicated 5 times for 10 seconds. The final pH was 5.89. I spun down the cell walls. Aliquots were taken and a Bradford assay performed. 400 µL of Triton X-100 and 50 µL $\pm$oxidosqualene were added, sonicated for 1 minute and let stir at room temperature. After the routine work-up the conversion of lanosterol was very low (less than 5%).

NMR Method for Collection of ^{13}C NMR Data on Lanosterone

Six samples of lanosterone were prepared from oxidosqualene cyclase reactions taken to 98, 35, and 27% conversion of the (S)-2,3-oxidosqualene for runs 1,2, and 3, respectively, and 99 and 20% conversion for runs 4 and 5. Samples for NMR analysis for runs 1,2, and 3 were prepared using 183 mgs of lanosterone/5% agnosterone in d_8-

THF in a 5mm NMR tube. NMR samples for runs 4 and 5 were prepared using 300 mgs of pure lanosterone. Samples were all prepared using the same method of slightly heating lanosterol in 300 μL d_8-THF in a vial until soluble, placing the viscous mixture in the NMR tube, and washing the vial with d_8-THF and adding to the tube until the total sample height is 5 cm. The samples were then centrifuged to collect any dust or paramagnetic impurities at the bottom of the tube. Samples 1-3 were prepared from the same batch of synthesized $\pm$oxidosqualene starting material and 4-5 were made from a different batch.

To eliminate possible integration variations, a T_1 determination was performed using the inversion-recovery method for each of the NMR samples. The ^{13}C spectra were acquired on an Inova 500 NMR and a Unity 500 NMR at 125.896 MHz. Data sets were collected one fid at a time immediately after one another alternating low and high conversion samples. The samples were acquired with inverse gated ^1H decoupling, with an acquisition time of 6 s (number of points=376176), and delays of 34 s which were equal to 5 X T_1 between calibrated $\pi/2$ pulses. The sweep width of 31348 Hz was set to center the peaks on the spectral window and optimize the number of data points collected.

A script was developed to consistently level, phase, and integrate each fid independently. This was necessary to remove any errors from working with a large number of acquired spectra. Integrations were determined using a constant region for each peak in the data set that was five times the peak width at half height on each side of

the peak (the largest half height of the two samples was used for both). A zeroth order baseline correction was applied, but in no case was a first order (tilt) correction applied.

Determination of KIEs for OSC

The product KIEs were determined from the measured enhancements using equation 7-2.

$$KIE = \frac{\log(1 - F_1)}{\log\left[1 - \left(F_1 \frac{R_p}{R_0}\right)\right]} \tag{7-2}$$

The low conversion reaction was used as the fractional conversion F (this assumes the high conversion reaction is complete). R_p/R_0 represent the ratio of integrations for each of the peaks of the low conversion reaction (R_p) /high conversion reaction (R_0).

Theoretical Methods for the Sharpless Asymmetric Epoxidation

Structures for the titanium dimer complex, the monomeric and dimeric precatalyst complexes, various transition states of the titanium dimer complex involving a variety of substrates, and various epoxidations were calculated in mPW1K, B3LYP, BP86, and B3PW91 with a variety of basis sets using Gaussian 03.[222] A vibrational frequency analysis was performed on all stationary points. To allow for solvation effects, structures were also optimized using Onsager and PCM solvent models for dichloromethane. PCM solvent models were also used for single point energies on gas phase and solution phase optimized models. Kinetic isotope effects were calculated based on the Onsager solvent-model structures from the scaled (0.9614) frequencies at 0 ºC using the statistical mechanics/conventional transition state theory formulation of

Bigeleisen and Mayer.[25] Tunneling corrections were applied using the one-dimensional Wigner model.[147]

Theoretical Methods for MTOX

The mechanisms were explored using the parent alloxazine as a model for FAD and using dimethylamine as a model for the *N*-methyl amino acid substrates of MTOX. (The pKa's of the $Me_2NH_2^+$ and $MeNH_2^+CH_2CO_2^-$ are 10.64 and 10.01, respectively, and the calculated methyl-group C-H bond strengths for Me_2NH and sarcosine are 88.6 and 89.2 kcal/mol, respectively.) Ground-state and transition structures were fully optimized in B3LYP/6-31+G** calculations using Gaussian 03.[222] Unrestricted calculations (UB3LYP) were employed for odd-electron species. A vibrational frequency analysis was performed on all stationary points. To allow for solvation effects, structures were also optimized using an Onsager solvent model for water with single-point energies calculated using a PCM solvent model and Bondi atomic radii. Equilibrium and kinetic isotope effects were calculated based on the Onsager solvent-model structures from the scaled (0.9614) frequencies at 25 ºC using the statistical mechanics/conventional transition state theory formulation of Bigeleisen and Mayer.[25] Tunneling corrections were applied using the one-dimensional Wigner model.[147]

Theoretical Methods for Diels-Alder Reactions

Diels-Alder reactions were studied in Becke3LYP calculations employing a 6-31G* basis set were carried out using Gaussian 98. Molecular dynamics / simulated annealing using the program Cerius 2 was used to identify candidate conformations, corresponding to the chair, boat, and twist-chair conformations of cycloheptane. The

possible reaction pathways were then explored systematically. This process led to a total of 36 transition structures for the five reactions.

CHAPTER VIII

CONCLUSIONS

Several physical organic techniques have been applied to a series of reactions in biological and organic chemistry. A new methodology has been developed for the simultaneous measurement of ^{13}C KIEs at natural abundance in large systems containing many isotopically sensitive positions. Theoretical studies have been used to predict experimentally measured KIEs, make predictions on the validity of a widely used experimental probe for relating isotopomers (the Swain-Schaad relationship), and have successfully predicted selectivity and reactivity in the Sharpless epoxidation and Diels-Alder reactions. The techniques developed for experimental and theoretical study will have a wide range of application in the study of reaction mechanisms.

The boundary limits set upon the Swain-Schaad relationship will provide a valuable gauge for the validity of experimentally observed KIE ratios for many researchers. In addition, reaction optimization and NMR techniques have been developed for the measurement of precise KIEs for the mechanism of OSC. The measured KIEs suggest a mechanism for concerted closure of the ABC rings of the terpene system. A model has been developed for the Asymmetric sharpless epoxidation that accounts for the high selectivities of a diverse range of subtrates. The sources for high selectivity and ligand accelerated catalysis have been identified. KIE predictions have aided in the interpretation of KIEs for flavin dependent methyl amine oxidase reaction that discount a mechanism for covalent adduct formation and suggest a hydride transfer mechanism. Studies on the selectivity of Diels-Alder reactions of dienes with

bystander rings explains the surprising exo selectivity observed in some of these reactions.

In conclusion, an ensemble of techniques has been used to probe the fine details of a variety of reaction mechanisms. Novel methodologies have been developed with application in a wide variety of mechanistic studies.

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APPENDIX A

Theoretical calculations: The Normal Range for Secondary Swain-Schaad Exponents Without Tunneling or Kinetic Complexity-Appendix Material

Program progqD

Generates input for quiver from Gaussian output file, using scaling and temperature as command-line parameters. Automatically generates data for each position in a molecule

Requires:

progq1bD (see below)

quivDFTauto.exe (modified version of QUIVER[3], source code available on request)

```
#!/bin/bash
echo $2 > scaling
echo $3 > temperature
awk '/l101/,/Initial/ {print}' $1 > temp19
awk '/Standard orientation/,/Rotational/ {print}' $1 > temp20
awk '/   0    / {print}' temp20 > temp21
awk '/   0    / {k=$1;ar[k]=$0;if (k>i) i=k} END {for (j=1;j<=i;j++) print ar[j]}' temp21 >
temp22
awk -f progq1bD temp22 > $1.q1
awk '/NIm/,/@/ {print}' $1 > temp23
```

```
awk 'BEGIN {i=99999997} /,/ll/0/ {sub(/\\\\/,ORS "XXX" i ORS,$0); i++; print}'
temp23 > temp24
awk '/XXX999999/,/XXX10000/ {print}' temp24 > temp25
awk '! /XXX/ {sub(" ","",$0); gsub(",",ORS,$0); printf("%s",$0)} END {print " "}'
temp25 > $1.q2
cp -f $1.q1 temp.q1
cp -f $1.q2 temp.q2
rm -f temp.qout
./quivDFTauto.exe
cp -f temp.qout $1.qout
awk '/S2/ {print $2}' temp.qout
awk '/FREQ/ && /    -/ {print $3}' temp.qout
echo $1 $2 $3 >> latest
awk '/S2/ {print $2}' temp.qout >> latest
if (test -a killtemps) then
rm -f temp19 temp20 temp21 temp22 temp23 temp24 temp25
fi
```

Program progq1bD

Awk program called by progqD to generate temp.q1, the key input file read by quivDFTauto.exe. Remove comment marks to generate tritium data.

Requires:

File temp22 (generated by progqD)

File temp19 (generated by progqD)

File scaling (generated by progqD, based on parameter supplied when progqD is run)

File temperature (generated by progqD, based on parameter supplied when progqD is run)

```
BEGIN {OFS=",";numatoms=0; numCH=0; numH=0
  getline < "temp19"
  getline < "temp19"
  getline < "temp19"
  str=$0}
/  0  / {
  k=$1
  atn[k]=$2
  ar[k]=$0
  if (k>numatoms) numatoms=k
  if (atn[k]==1) {atw[k]=1;numH++}
  if (atn[k]==3) atw[k]=7;
  if (atn[k]==5) atw[k]=10;
  if (atn[k]==6) atw[k]=12;
  if (atn[k]==8) atw[k]=16;
  if (atn[k]==7) atw[k]=14;
  if (atn[k]==9) atw[k]=19;
```

```
   if (atn[k]==14) atw[k]=28;
   if (atn[k]==16) atw[k]=32;
   if (atn[k]==17) atw[k]=35
   if ((atn[k]==1)||(atn[k]==6)) numCH++
   }
END {
   str="title: " str
   print str
   printf("   ")
   print numH+1
   print "parent"
   str = "   " numatoms
   print str
   for (i=1;i<=numatoms;i++) ar[i]=substr(ar[i],32,45)
   for (i=1;i<=numatoms;i++) print ar[i]
   for (i=1;i<numatoms;i++) {printf(atw[i]);printf(",")}
   print atw[numatoms]
   getline < "scaling"
   if (($1>0.01) && ($1<100.)) {print $1}
     else print " 0.9614"
   print "    1"
   getline < "temperature"
```

```
  if (($1>0.1) && ($1<10000.)) {print $1}
    else print " 298.15"
  for (j=1;j<=numatoms;j++) {
    if (atw[j]==1) {
      print "D"
      atw[j]=2
      for (i=1;i<numatoms;i++) {printf(atw[i]);printf(",")}
      print atw[numatoms]
#      print "T"
#      atw[j]=3
#      for (i=1;i<numatoms;i++) {printf(atw[i]);printf(",")}
#      print atw[numatoms]
      atw[j]=1
      }
    }
  printf(" ")
  print numH
  for (j=1;j<=2*numH;j++) {
    printf("   1  ")
    print j+1
    }
}
```

Program progS2

This awk program takes as input a list of positions/molecules along with the reduced isotopic partition function [(S2/S1)F] that is output from QUIVER, and generates a list of SSEs for all non-degenerate combinations of exchange reactions.

Requires: S2List

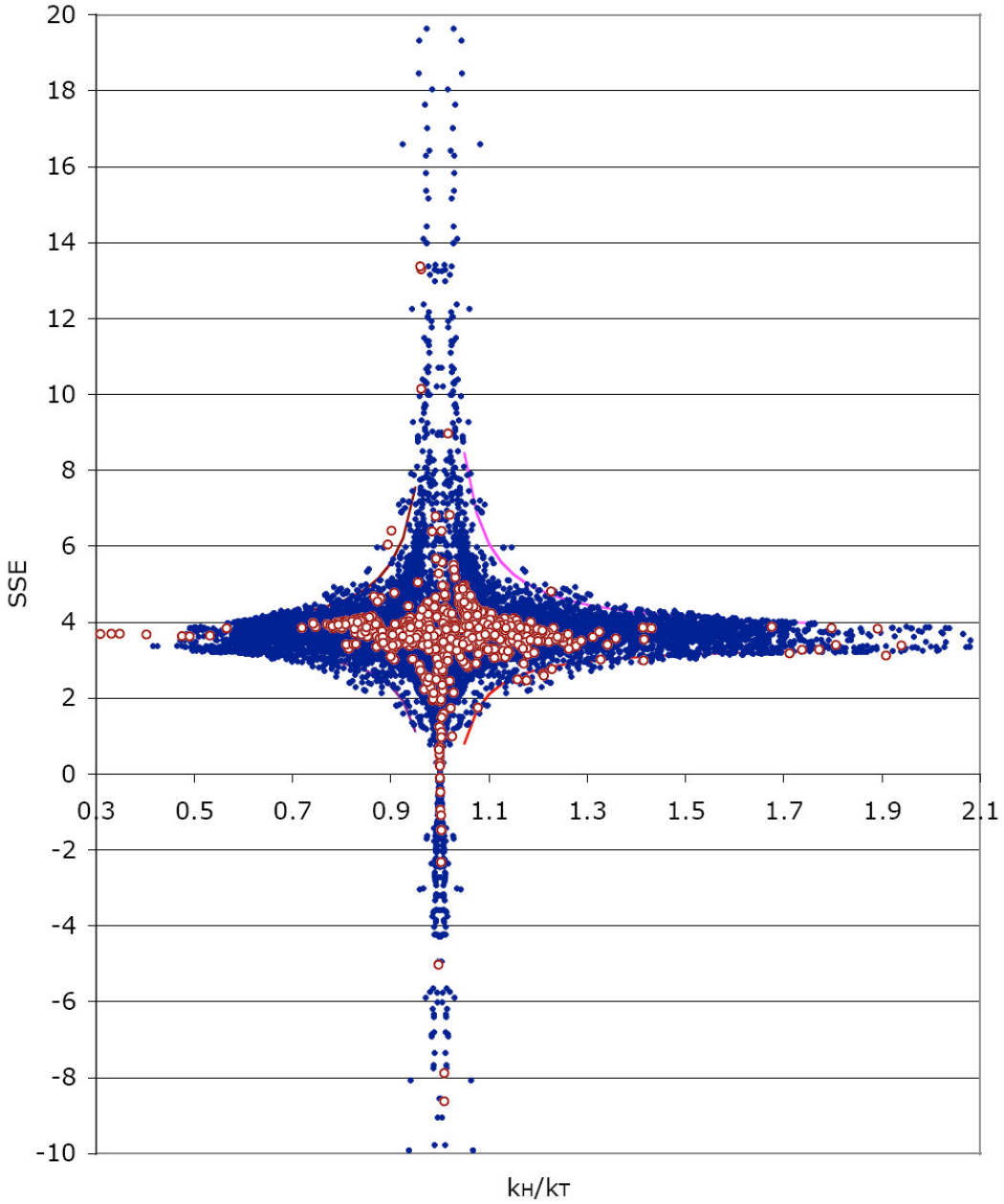
S2List is a text file formatted with the 1st, 4th, 7th, etc lines having a title, the 2nd, 5th, 8th, etc lines containing (S2/S1)F for a D substitution, and the 3rd, 6th, 9th, etc lines containing (S2/S1)F for a T substitution.

```
BEGIN {n=1
do {
  getline < "S2List"
  S[n,1]=$0
  getline < "S2List"
  S[n,2]=$1
  getline < "S2List"
  S[n,3]=$1
  if (oldline==$0) $0=""
  oldline=$0
  n++
  }
while (length($0) > 0)
  n--
```

```
#for (i=1;i<n;i++) {
#   printf(S[i,1])
#  printf("   ")
#  printf(S[i,2])
#  printf("   ")
#  print S[i,3]
#  }
}
END {
for (i=1;i<n;i++) {
   for (j=1;j<n;j++) {
      if (i!=j) {
#        print i,j
#        printf(S[i,2])
#        printf("   ")
#        printf(S[i,3])
#        printf("   ")
#        printf(S[j,2])
#        printf("   ")
#        printf(S[j,3])
#        printf("   ")
```

```
        khkt=S[i,3]/S[j,3]
        khkd=S[i,2]/S[j,2]
        kdkt=khkt/khkd
        if (kdkt!=1) {
          SSE=log(khkt)/log(kdkt)
          if ((SSE>4.5) && (khkt>1.10)) {
            print S[i,1]," to ",S[j,1]
            printf(SSE)
            printf("     ")
            print khkt
            }
          }
        }
#  printf(S[i,2])
#  printf("   ")
#  print S[i,3]
      }
   }
}
```

Expanded view of distribution of Swain-Schaad Exponents



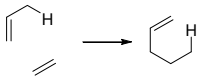
This view still does not include some extreme SSEs for k_H/k_T near unity. The SSEs near unity ranged as high as 2100 and as low as –296.

Reactions Studied for KIEs / Key to Theoretical Structures for KIEs

Each of the reactions below is given a title and this title is also used in a later section containing relevant calculated geometries.

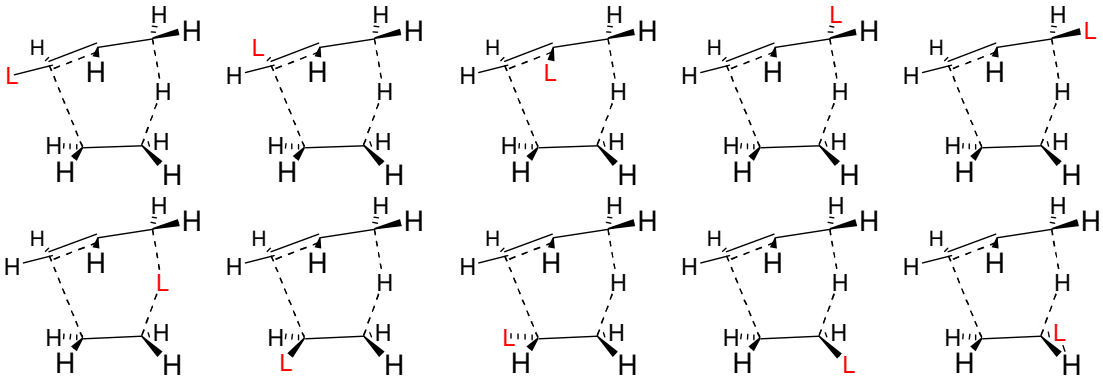
For each of the reactions given, H/D, H/T, and D/T kinetic isotope effects were calculated for all C-H positions. In addition, for almost all of the reactions, the H/D, H/T, and D/T kinetic isotope effects were also calculated for the reverse reaction. For example, in the Diels-Alder reaction, kinetic isotope effects were calculated for both the forward reaction from 1,3-butadiene and ethylene and the reverse (retro) Diels-Alder reaction for cleavage of cyclohexene.

Example of Substitutions for KIEs



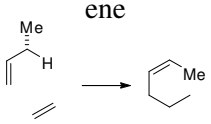
Ene Reaction

L = H, D, or T

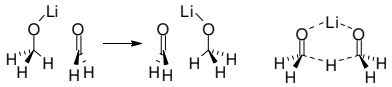


Examples of Reactions for KIEs

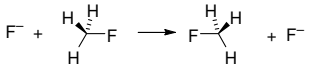
ene



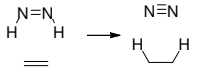
hydride transfer



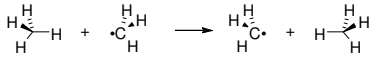
S_N2



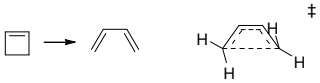
diimide



hydrogen transfer

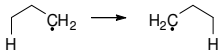


ring opening

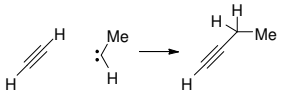


Diels-Alder

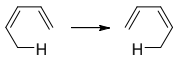
1,3 H transfer



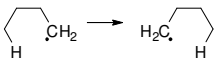
carbene insertion



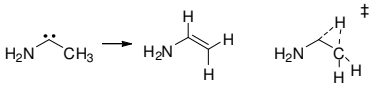
1,5 sigmatropic rearrangement



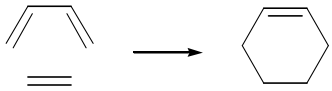
1,4 H transfer



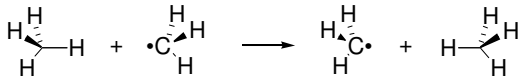
carbene rearrangement



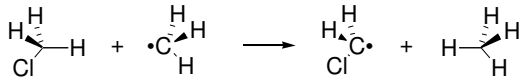
Diels-Alder parent



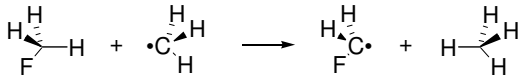
hydrogen transfer parent



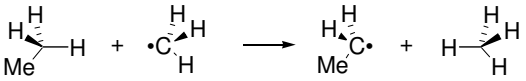
hydrogen transfer Cl



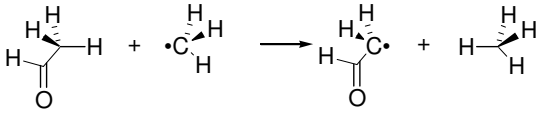
hydrogen transfer F



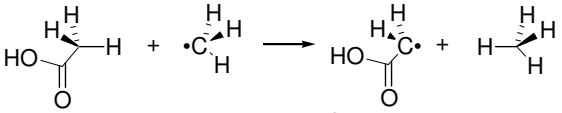
hydrogen transfer methyl



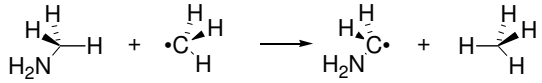
hydrogen transfer CHO



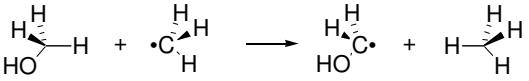
hydrogen transfer COOH



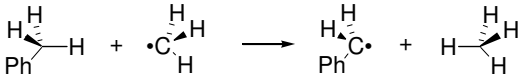
hydrogen transfer NH_2



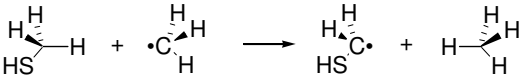
hydrogen transfer OH



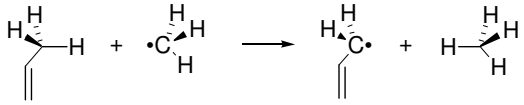
hydrogen transfer phenyl



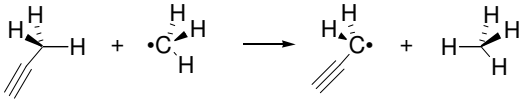
hydrogen transfer SH



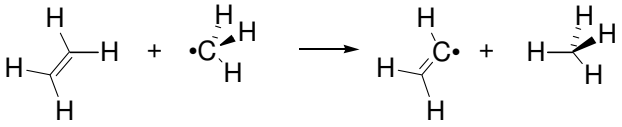
hydrogen transfer vinyl



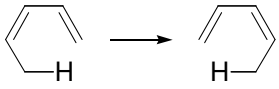
hydrogen transfer ethynyl



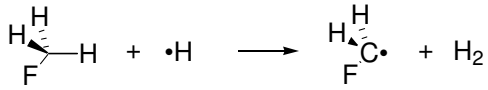
hydrogen transfer ethylene / methyl



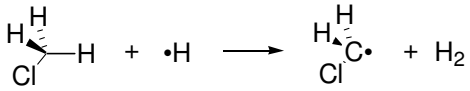
1,5-sigmatropic parent



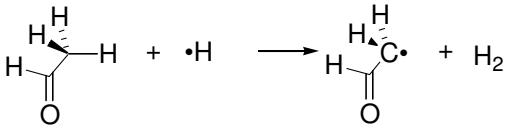
H to H transfer F



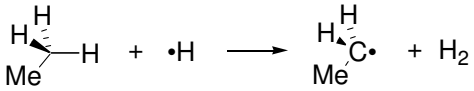
H to H transfer Cl



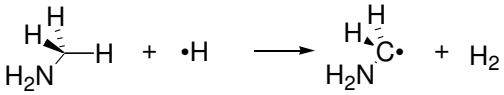
H to H transfer CHO



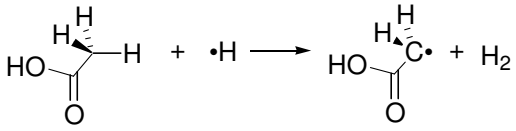
H to H transfer methyl



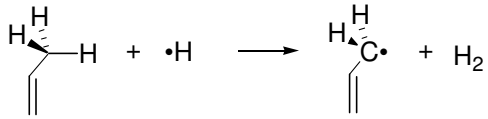
H to H transfer NH_2



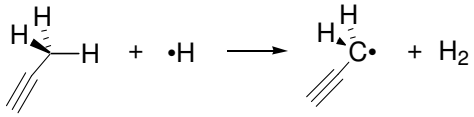
H to H transfer COOH



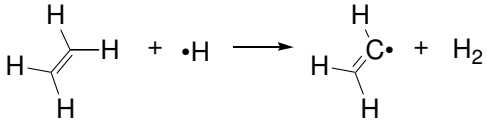
H to H transfer vinyl



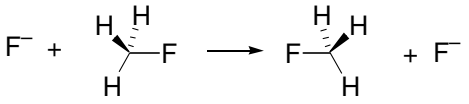
H to H transfer ethynyl



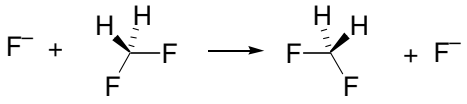
H to H transfer ethylene



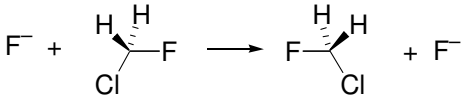
S_N2 parent



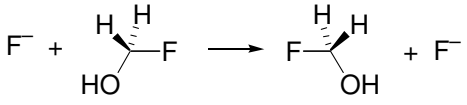
S_N2 F



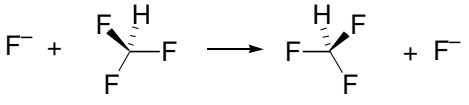
S_N2 Cl



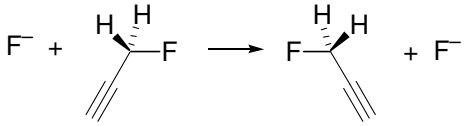
S_N2 OH



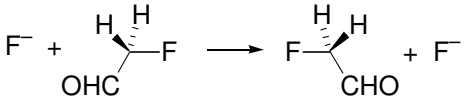
S_N2 F2



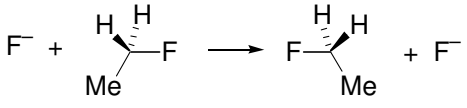
S_N2 CCH



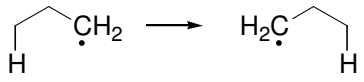
S_N2 CHO



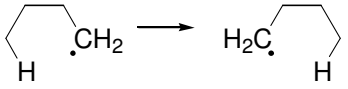
S_N2 Me



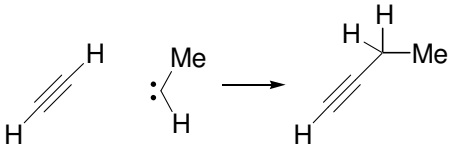
1,3-H transfer



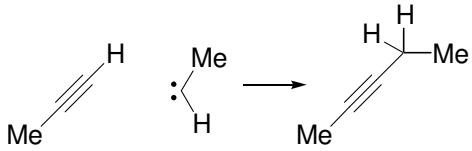
1,4-H transfer



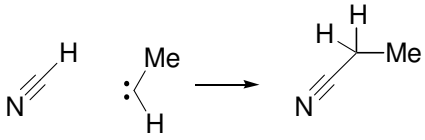
carbene insertion MeCH + HCCH



carbene insertion MeCH + HCCMe



carbene insertion MeCH + HCN



Theoretical Structures for KIEs

The section here includes geometries for all transition structures. The titles for the structures refer back to the drawing in the previous section. Many simple starting structures and product structures have not been included as these can likely be reproduced very rapidly without ambiguity by the computationally proficient. Relatively complex structures were included, particularly to show the conformation calculated. Conformations were generally chosen for convenience, and little effort was made to ensure that the lowest-energy conformations were located.

Ene parent

Transition structure

E(RB+HF-LYP) = -196.442366879

Zero-point correction= 0.131631 (Hartree/Particle)
Thermal correction to Energy= 0.137354
Thermal correction to Enthalpy= 0.138298
Thermal correction to Gibbs Free Energy= 0.103261

Sum of electronic and zero-point Energies= -196.310736
Sum of electronic and thermal Energies= -196.305013
Sum of electronic and thermal Enthalpies= -196.304069
Sum of electronic and thermal Free Energies= -196.339106

E (Thermal)	CV	S
KCAL/MOL	CAL/MOL-KELVIN	CAL/MOL-KELVIN TOTAL
86.191	22.008	73.742

C,0,-0.5852780839,-1.0523817846,-0.935826532
C,0,0.7736717605,-1.3377341093,-0.7095797417
H,0,-1.3350689033,-1.6178847332,-0.3898477575
H,0,-0.9013024189,-0.7501527025,-1.9302263758
H,0,1.0316117204,-2.158183975,-0.0411495589
H,0,1.4871786958,-1.1724047524,-1.5155556557
C,0,-1.0902329631,0.8423876633,-0.1512798443
C,0,-0.3376474896,0.875657077,1.0144210331
C,0,1.0766017385,0.8446903465,0.9165908203

H,0,-2.174895384,0.7767908667,-0.1005071739
H,0,-0.7188615874,1.3783788745,-1.0224234237
H,0,-0.797260592,0.5152426348,1.9353495713
H,0,1.6587575209,0.7751668542,1.836069729
H,0,1.1863054956,-0.2830280307,0.2470467892
H,0,1.540845678,1.5003598068,0.1752894438

Ene M1

Transition structure

E(RB+HF-LYP) = -235.755333052

Zero-point correction= 0.160066 (Hartree/Particle)
Thermal correction to Energy= 0.167284
Thermal correction to Enthalpy= 0.168228
Thermal correction to Gibbs Free Energy= 0.129552

Sum of electronic and zero-point Energies= -235.595267
Sum of electronic and thermal Energies= -235.588049
Sum of electronic and thermal Enthalpies= -235.587105
Sum of electronic and thermal Free Energies= -235.625781

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	104.972	27.359	81.399

C,0,-0.8693300863,-1.4052042827,-0.9146173357
C,0,0.485497422,-1.656947073,-0.6349201625
C,0,-1.456890321,0.5035524887,-0.1134024857
C,0,-0.6666804654,0.5665129266,1.023897444
C,0,0.7521007434,0.5744227752,0.9291890945
H,0,-1.6297276543,-1.976378353,-0.3903633308
H,0,-1.1567429187,-1.0966019221,-1.9153035606
H,0,0.7333262394,-2.4674644884,0.0499081147
H,0,1.2217098488,-1.4939595959,-1.4210319692
H,0,-2.5327136513,0.3778954093,-0.0147828367
H,0,-1.1582589084,1.0404968531,-1.0089577244
H,0,-1.0940958817,0.1864058704,1.952649943
H,0,1.2768788667,0.4701658515,1.8826027723
H,0,0.8431424552,-0.5937482123,0.3049252216
C,0,1.4929964447,1.4831869704,-0.047711943
H,0,2.5302377946,1.1531950645,-0.1750003539
H,0,1.0267385221,1.4899159227,-1.0379041334

H,0,1.5133428628,2.5169347682,0.3186501882

Product structure

E(RB+HF-LYP) = -235.851630630

Zero-point correction= 0.166361 (Hartree/Particle)
Thermal correction to Energy= 0.174262
Thermal correction to Enthalpy= 0.175206
Thermal correction to Gibbs Free Energy= 0.134008

Sum of electronic and zero-point Energies= -235.685270
Sum of electronic and thermal Energies= -235.677368
Sum of electronic and thermal Enthalpies= -235.676424
Sum of electronic and thermal Free Energies= -235.717623

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	109.351	27.514	86.710

C,0,-1.1218612905,-1.3948908679,-0.7047626166
C,0,0.254030209,-2.0308058105,-0.9243237328
C,0,-1.0623523444,0.113205054,-0.3802786822
C,0,-0.4109203404,0.4079993076,0.9455251713
C,0,0.6613951554,1.1699117584,1.1954991857
H,0,-1.6417588531,-1.916518192,0.1113569783
H,0,-1.7399762261,-1.5373376286,-1.6012119236
H,0,0.1660780742,-3.1014853367,-1.141702522
H,0,0.7748749437,-1.56132955,-1.7683954654
H,0,-2.0920133035,0.5017690795,-0.3609530193
H,0,-0.5515800888,0.6389359274,-1.1957936515
H,0,-0.890182151,-0.0758269274,1.7993222562
H,0,0.979384614,1.2603435273,2.2351810966
H,0,0.8893889673,-1.9160145744,-0.0391320918
C,0,1.498169841,1.9419432067,0.2134238155
H,0,2.5488368416,1.6250750337,0.2622615679
H,0,1.1607422549,1.823045685,-0.8197016424
H,0,1.4854375459,3.0151670656,0.448269572

Ene M2

Transition structure

E(RB+HF-LYP) = -235.757484026

Zero-point correction= 0.159697 (Hartree/Particle)
Thermal correction to Energy= 0.167003
Thermal correction to Enthalpy= 0.167947
Thermal correction to Gibbs Free Energy= 0.129095

Sum of electronic and zero-point Energies= -235.597787
Sum of electronic and thermal Energies= -235.590481
Sum of electronic and thermal Enthalpies= -235.589537
Sum of electronic and thermal Free Energies= -235.628389

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	104.796	27.632	81.770

C,0,-0.900380591,-1.1817795293,-1.3757920997
C,0,0.4591634336,-1.4332103208,-1.1294939308
C,0,-1.4572097202,0.7065582743,-0.5099676553
C,0,-0.6946529424,0.7183308617,0.6461660741
C,0,0.7232958808,0.722947631,0.55088166
H,0,-1.6489902476,-1.7701799862,-0.8535428876
H,0,-1.2092167015,-0.8416031667,-2.3597617609
H,0,0.7282110166,-2.2604165668,-0.4731820119
H,0,1.1828444051,-1.2328413366,-1.9185236706
H,0,-2.5382926582,0.6045620355,-0.4522281431
H,0,-1.1065398162,1.2661167805,-1.3743009124
H,0,-1.1388556217,0.3224774941,1.5617647392
C,0,1.5901288627,0.6418476227,1.7969819261
H,0,0.8257566061,-0.3888221988,-0.155633641
H,0,1.1291106784,1.3907421365,-0.2174467654
H,0,2.5991815714,0.2881415518,1.5570682859
H,0,1.6931112792,1.6218799082,2.2799874924
H,0,1.1616099469,-0.0482238891,2.5331434291

Product structure

E(RB+HF-LYP) = -235.853950792

Zero-point correction= 0.166102 (Hartree/Particle)
Thermal correction to Energy= 0.174040
Thermal correction to Enthalpy= 0.174985
Thermal correction to Gibbs Free Energy= 0.134118

Sum of electronic and zero-point Energies= -235.687849

Sum of electronic and thermal Energies= -235.679910
Sum of electronic and thermal Enthalpies= -235.678966
Sum of electronic and thermal Free Energies= -235.719833

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	109.212	27.692	86.011

C,0,-1.1583660969,-1.0879587027,-1.2694664764
C,0,0.199225972,-1.67956658,-1.6596656308
C,0,-1.0670635439,0.3382417319,-0.6853708792
C,0,-0.3504374677,0.4038666118,0.6368387485
C,0,0.7587410818,1.1051612527,0.8876242404
H,0,-1.6493642257,-1.7442748302,-0.5369416775
H,0,-1.8162307086,-1.0659671016,-2.1485217023
H,0,0.0904958104,-2.6953250312,-2.0568252583
H,0,0.6868139937,-1.070245466,-2.4310634252
H,0,-2.0898187043,0.7254517426,-0.5608259575
H,0,-0.5698471787,0.9989851823,-1.4088800191
H,0,-0.7926011665,-0.1843588362,1.4454628005
C,0,1.4655826105,1.1691033648,2.2119366332
H,0,0.8747063298,-1.7225035789,-0.7983772152
H,0,1.2010468442,1.6911659177,0.0792325088
H,0,2.5038449802,0.8198458989,2.1280891862
H,0,1.5125186301,2.1993808331,2.5907599605
H,0,0.9623400604,0.5547591982,2.966510986

Ene M3

Transition structure

E(RB+HF-LYP) = -235.761194536

Zero-point correction= 0.159528 (Hartree/Particle)
Thermal correction to Energy= 0.166910
Thermal correction to Enthalpy= 0.167855
Thermal correction to Gibbs Free Energy= 0.128559

Sum of electronic and zero-point Energies= -235.601666
Sum of electronic and thermal Energies= -235.594284
Sum of electronic and thermal Enthalpies= -235.593340
Sum of electronic and thermal Free Energies= -235.632635

	E (Thermal)	CV	S

	KCAL/MOL	CAL/MOL-KELVIN	CAL/MOL-KELVIN
TOTAL	104.738	27.595	82.704

C,0,-0.4591360334,-1.0545423044,-1.3424194851
C,0,0.8822011566,-1.4262473317,-1.1187433253
C,0,-0.8551858781,0.8284790492,-0.5754997541
C,0,-0.1371102604,0.8178090436,0.6198487912
C,0,1.2788537399,0.7580564171,0.4964579699
H,0,-1.237586418,-1.5882713346,-0.8025314086
H,0,-0.7555383216,-0.7508952127,-2.3429921238
H,0,1.0917507729,-2.2594068584,-0.449815618
H,0,1.6045643498,-1.3026961133,-1.9240637323
H,0,-1.9435510101,0.8271943279,-0.553814507
H,0,-0.4330702204,1.3669952521,-1.4211017245
C,0,-0.7846030361,0.3184827116,1.8891453032
H,0,1.8740008312,0.6721649759,1.407500033
H,0,1.3554410717,-0.3678918952,-0.1626905848
H,0,1.7422338199,1.4125181578,-0.245155232
H,0,-0.4173033967,0.8626436009,2.767134579
H,0,-1.8740423564,0.4216069803,1.8572593206
H,0,-0.5570172526,-0.7461873927,2.0575339997

Product structure

E(RB+HF-LYP) = -235.853126112

Zero-point correction= 0.166305 (Hartree/Particle)
Thermal correction to Energy= 0.174054
Thermal correction to Enthalpy= 0.174998
Thermal correction to Gibbs Free Energy= 0.134605

Sum of electronic and zero-point Energies= -235.686821
Sum of electronic and thermal Energies= -235.679072
Sum of electronic and thermal Enthalpies= -235.678128
Sum of electronic and thermal Free Energies= -235.718521

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	109.220	27.691	85.013

C,0,-0.5746402889,-0.9739050708,-1.1711241081
C,0,0.8258518819,-1.5817059311,-1.2908680739
C,0,-0.5726643243,0.5072184552,-0.7312570527
C,0,-0.0042904265,0.7592966696,0.650650947

C,0,1.1189821225,1.4626285546,0.8311657373
H,0,-1.1764541395,-1.5677749511,-0.4703192525
H,0,-1.0874290714,-1.0414281591,-2.1397168235
H,0,0.776285694,-2.6288668691,-1.6104988824
H,0,1.4299905056,-1.0361555733,-2.0265866613
H,0,-1.6092040797,0.8760581265,-0.7624581675
H,0,-0.0085605991,1.0944070173,-1.4672911774
C,0,-0.7783157144,0.1923894614,1.8171000183
H,0,1.5241103547,1.6520690167,1.8225676871
H,0,1.3607027206,-1.5435027563,-0.3356299814
H,0,1.6735172089,1.8790422651,-0.0064488904
H,0,-0.3175685881,0.4581854484,2.7734376811
H,0,-1.8121791807,0.5650253751,1.8204598478
H,0,-0.8427503276,-0.902591774,1.768479813

Ene M4

Transition structure

E(RB+HF-LYP) = -235.755177739

Zero-point correction= 0.159766 (Hartree/Particle)
Thermal correction to Energy= 0.166974
Thermal correction to Enthalpy= 0.167918
Thermal correction to Gibbs Free Energy= 0.129401

Sum of electronic and zero-point Energies= -235.595411
Sum of electronic and thermal Energies= -235.588204
Sum of electronic and thermal Enthalpies= -235.587260
Sum of electronic and thermal Free Energies= -235.625777

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	104.778	27.539	81.067

C,0,-0.5102275836,-1.3736336111,-0.6338664373
C,0,0.8496662303,-1.6710964874,-0.4216368531
C,0,-0.9658371487,0.6119386794,0.0592253685
C,0,-0.217305465,0.5814967215,1.2331413601
C,0,1.19606768,0.5150162394,1.1980023801
H,0,-1.2592082021,-1.8951627233,-0.0443318908
H,0,-0.8424620909,-1.1009295672,-1.6308495544
H,0,1.1029310959,-2.4848989179,0.25751762

H,0,1.546750364,-1.5512368797,-1.2498671318
H,0,-2.0464893978,0.5211179855,0.1742614682
C,0,-0.5498868878,1.4170629145,-1.1586637398
H,0,-0.7123933757,0.187174683,2.1212027004
H,0,1.7226276564,0.3794761808,2.1429857665
H,0,1.2831203072,-0.6183320575,0.4914609612
H,0,1.7343600969,1.1713345728,0.5126159011
H,0,-1.1419590273,1.1412666045,-2.0380480888
H,0,-0.707258226,2.4896248841,-0.9818552822
H,0,0.5051198484,1.2758584971,-1.41230494

Product structure

E(RB+HF-LYP) = -235.846428757

Zero-point correction= 0.166319 (Hartree/Particle)
Thermal correction to Energy= 0.173983
Thermal correction to Enthalpy= 0.174928
Thermal correction to Gibbs Free Energy= 0.135113

Sum of electronic and zero-point Energies= -235.680110
Sum of electronic and thermal Energies= -235.672445
Sum of electronic and thermal Enthalpies= -235.671501
Sum of electronic and thermal Free Energies= -235.711316

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	109.176	27.739	83.797

C,0,-0.6885960852,-1.2406610462,-0.4847024256
C,0,0.715743547,-1.7814849085,-0.7758328241
C,0,-0.7463117837,0.2510605391,-0.0589828127
C,0,-0.0759825523,0.4484638184,1.2824193588
C,0,0.9034981993,1.3030542629,1.5824037828
H,0,-1.1483665009,-1.8448829052,0.309894512
H,0,-1.3229435671,-1.3714731463,-1.372049521
H,0,0.6780035357,-2.8529840766,-1.0030387813
H,0,1.1743956538,-1.2805451988,-1.6356277371
H,0,-1.8156962203,0.4726054629,0.0946537365
C,0,-0.2402556612,1.1958987953,-1.1560413973
H,0,-0.4587781099,-0.1985024041,2.0750510399
H,0,1.3117978109,1.3631891285,2.5878929932
H,0,1.3815149172,-1.6422387768,0.0832496133

H,0,1.3350047341,1.9777405349,0.84788229
H,0,-0.7731630054,1.0119610368,-2.0961100325
H,0,-0.4004637996,2.2437514362,-0.8794236323
H,0,0.8301205684,1.0633901426,-1.3479565716

Ene M5

Transition structure

E(RB+HF-LYP) = -235.759340710

Zero-point correction= 0.159700 (Hartree/Particle)
Thermal correction to Energy= 0.166910
Thermal correction to Enthalpy= 0.167854
Thermal correction to Gibbs Free Energy= 0.129335

Sum of electronic and zero-point Energies= -235.599641
Sum of electronic and thermal Energies= -235.592431
Sum of electronic and thermal Enthalpies= -235.591486
Sum of electronic and thermal Free Energies= -235.630006

	E (Thermal)	CV	S
	KCAL/MOL	CAL/MOL-KELVIN	CAL/MOL-KELVIN
TOTAL	104.738	27.590	81.071

C,0,-0.0828619959,-1.157795185,-0.9651527441
C,0,1.2797094859,-1.4310029238,-0.7411728408
C,0,-0.6537039939,0.7150789964,-0.0996412351
C,0,0.1206396227,0.6899240047,1.0547823004
C,0,1.532092555,0.6876640338,0.9571644306
H,0,-0.8320664345,-1.7489397347,-0.4454044103
H,0,-0.3988729574,-0.8071730185,-1.9436789604
H,0,1.5425521609,-2.2813328679,-0.1122477008
H,0,1.9908469152,-1.2335841644,-1.5426264341
C,0,-2.1638836998,0.6654344083,-0.0647426021
H,0,-0.239260929,1.2720994647,-0.9408952333
H,0,-0.3331967531,0.2853741809,1.9616165954
H,0,2.1147939486,0.5802509774,1.8721722683
H,0,1.6616917612,-0.4256757542,0.2284914336
H,0,1.9909649363,1.3755183418,0.2427707318
H,0,-2.5741694864,0.2108400932,-0.9742307867
H,0,-2.5224832856,0.0835107726,0.7923308466
H,0,-2.5927517206,1.6732917022,0.0142777962

Product structure

E(RB+HF-LYP) = -235.848888692

Zero-point correction= 0.165952 (Hartree/Particle)
Thermal correction to Energy= 0.173772
Thermal correction to Enthalpy= 0.174716
Thermal correction to Gibbs Free Energy= 0.134448

Sum of electronic and zero-point Energies= -235.682937
Sum of electronic and thermal Energies= -235.675117
Sum of electronic and thermal Enthalpies= -235.674173
Sum of electronic and thermal Free Energies= -235.714441

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	109.043	27.979	84.752

C,0,-0.2415302501,-1.1528352515,-0.7304532202
C,0,1.2132700531,-1.5612914432,-0.9806712925
C,0,-0.4174124969,0.308681615,-0.2581266146
C,0,0.2253802673,0.538365038,1.0874455164
C,0,1.208607453,1.4015442606,1.3458327426
H,0,-0.6915783988,-1.823857539,0.0161242489
H,0,-0.8235039467,-1.2909757652,-1.6521519063
H,0,1.2783188348,-2.6039080501,-1.3121025505
H,0,1.6698962731,-0.9359958166,-1.7580293451
C,0,-1.9106347714,0.6862313319,-0.2078170866
H,0,0.0782166082,0.9639604492,-0.9898491997
H,0,-0.1792288785,-0.0641192323,1.9049316851
H,0,1.617537851,1.5239798087,2.3455331249
H,0,1.8199701736,-1.4550751486,-0.0750419587
H,0,1.6423906979,2.0237675487,0.5652005646
H,0,-2.3843390017,0.5409633566,-1.1861529163
H,0,-2.4492681818,0.0641373731,0.5185893813
H,0,-2.0444935611,1.7329497108,0.0856886013

Ene M6

Transition structure

E(RB+HF-LYP) = -235.757207360

Zero-point correction= 0.159954 (Hartree/Particle)
Thermal correction to Energy= 0.167215
Thermal correction to Enthalpy= 0.168159
Thermal correction to Gibbs Free Energy= 0.129221

Sum of electronic and zero-point Energies= -235.597253
Sum of electronic and thermal Energies= -235.589992
Sum of electronic and thermal Enthalpies= -235.589048
Sum of electronic and thermal Free Energies= -235.627986

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	104.929	27.222	81.952

C,0,-0.9177109317,-0.8398795433,-0.5950220353
C,0,0.4413224073,-1.1614489753,-0.3881925854
C,0,-1.3613149108,1.0452173077,0.124877751
C,0,-0.6678100745,1.0871201187,1.3311313008
C,0,0.7468393058,0.9836722918,1.2898733297
H,0,-1.6681620764,-1.3958990405,-0.0394485133
H,0,-1.2357325767,-0.5678209079,-1.5995521101
H,0,0.6485557246,-1.9856683682,0.296845051
C,0,1.4635458605,-0.9606053282,-1.4903748576
H,0,-2.4495375408,1.0346727309,0.1236967077
H,0,-0.9294196376,1.5637119196,-0.7297880042
H,0,-1.1834307985,0.7679705386,2.2372181434
H,0,1.2879527406,0.9000631035,2.2333004347
H,0,0.8306736389,-0.1381922479,0.637740112
H,0,1.2719852724,1.6129673666,0.5649075048
H,0,2.4834311141,-0.8878481048,-1.0940686643
H,0,1.4533508485,-1.7887950469,-2.2128848998
H,0,1.2611033517,-0.0396171715,-2.0517231809

Product structure

E(RB+HF-LYP) = -235.847096069

Zero-point correction= .166518 (Hartree/Particle)
Thermal correction to Energy= .174241
Thermal correction to Enthalpy= .175185
Thermal correction to Gibbs Free Energy= .134415

Sum of electronic and zero-point Energies= -235.680578

Sum of electronic and thermal Energies= -235.672856
Sum of electronic and thermal Enthalpies= -235.671911
Sum of electronic and thermal Free Energies= -235.712681

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	109.338	27.161	85.806

C,0,0.6802237967,1.1607882848,-0.0700166491
C,0,1.4308604345,-0.0306457611,-0.6865558315
C,0,-0.6295558554,0.80038972,0.6649082029
C,0,-1.6779841199,0.2085484199,-0.2382766438
C,0,-2.2578569529,-0.9822395163,-0.0794459235
H,0,0.4466820644,1.8838305793,-0.8645867932
H,0,1.3440745128,1.6839025907,0.6326966666
H,0,2.2590966293,0.3582735166,-1.2940723565
C,0,1.9897489779,-1.0229393109,0.3398753694
H,0,-1.0267277245,1.7214496356,1.1177886015
H,0,-0.4270791133,0.1124477671,1.4951835517
H,0,-1.9691274988,0.8263452043,-1.0909353198
H,0,-3.0140477665,-1.3492507082,-0.7685722996
H,0,0.7630126321,-0.5599263234,-1.3787492346
H,0,-2.0028827437,-1.63570041,0.7529280495
H,0,2.5636736375,-1.8162609982,-0.1526323417
H,0,2.6580297553,-0.5221501721,1.0520784095
H,0,1.1926779305,-1.5063717003,0.9159419201

Ene M7

Transition structure

E(RB+HF-LYP) = -235.756675440

Zero-point correction= 0.159917 (Hartree/Particle)
Thermal correction to Energy= 0.167157
Thermal correction to Enthalpy= 0.168101
Thermal correction to Gibbs Free Energy= 0.129203

Sum of electronic and zero-point Energies= -235.596759
Sum of electronic and thermal Energies= -235.589519
Sum of electronic and thermal Enthalpies= -235.588575
Sum of electronic and thermal Free Energies= -235.627472

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	104.892	27.237	81.867

C,0,-0.7865994095,-0.5855888911,-1.0030541449
C,0,0.567975808,-0.9055853194,-0.7686053967
C,0,-1.3040470064,1.2551981608,-0.1598980054
C,0,-0.5108392677,1.3042119533,0.981317996
C,0,0.8981585733,1.3030458112,0.814523189
H,0,-1.5454106175,-1.1679633883,-0.4848674882
H,0,-1.0831219473,-0.2725237771,-2.0004327756
C,0,0.9294761547,-2.0529625176,0.1603578541
H,0,1.2628805691,-0.7303112339,-1.5918599437
H,0,-2.3844364006,1.1637577641,-0.0694977147
H,0,-0.9835175454,1.8247823927,-1.0301521496
H,0,-0.9214418789,0.9234808882,1.91687777
H,0,1.5269319432,1.2349868995,1.7029904069
H,0,0.9972543426,0.1989345668,0.121823488
H,0,1.3105589446,1.9815933031,0.0623893654
H,0,1.9846767115,-2.023017161,0.4558821895
H,0,0.3263059594,-2.0139691038,1.0768658336
H,0,0.7445708051,-3.0296663335,-0.3078679336

Product structure

E(RB+HF-LYP) = -235.848308453

Zero-point correction= .166432 (Hartree/Particle)
Thermal correction to Energy= .174192
Thermal correction to Enthalpy= .175136
Thermal correction to Gibbs Free Energy= .134459

Sum of electronic and zero-point Energies= -235.681876
Sum of electronic and thermal Energies= -235.674117
Sum of electronic and thermal Enthalpies= -235.673172
Sum of electronic and thermal Free Energies= -235.713849

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	109.307	27.222	85.611

C,0,-0.768689232,-0.6164526696,-0.450758027
C,0,0.6893230085,-1.0922299386,-0.4593118482

C,0,-0.929262261,0.9159915296,-0.3671992684
C,0,-0.4536992782,1.5016309828,0.9353550673
C,0,0.4955752147,2.4288697739,1.0697504727
H,0,-1.2989384159,-1.0812632261,0.3939100382
H,0,-1.272586974,-0.9742529394,-1.3595785665
C,0,0.8218433443,-2.6163010711,-0.5389625475
H,0,1.2110193469,-0.6336091289,-1.3118007679
H,0,-1.99470252,1.1582215487,-0.4984943916
H,0,-0.3958482141,1.3902149014,-1.2021447471
H,0,-0.9437816131,1.1146318983,1.8316915067
H,0,0.7886897184,2.8137241847,2.0430915464
H,0,1.198164686,-0.7225816849,0.4402438778
H,0,1.0139160341,2.8441496978,0.2074691058
H,0,1.8731391466,-2.9260807159,-0.5494623586
H,0,0.3407869961,-3.1017268315,0.3193640977
H,0,0.3495970314,-3.0104793466,-1.4475324339

Ene M8

Transition structure

E(RB+HF-LYP) = -235.756773132

Zero-point correction= 0.159723 (Hartree/Particle)
Thermal correction to Energy= 0.166864
Thermal correction to Enthalpy= 0.167808
Thermal correction to Gibbs Free Energy= 0.129389

Sum of electronic and zero-point Energies= -235.597050
Sum of electronic and thermal Energies= -235.589909
Sum of electronic and thermal Enthalpies= -235.588965
Sum of electronic and thermal Free Energies= -235.627384

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	104.709	27.476	80.860

C,0,-0.4114832273,-0.945063594,-0.5614092424
C,0,0.9528697337,-1.197925801,-0.3072796442
C,0,-0.9405411082,0.9457447261,0.3796497034
C,0,-0.1115652347,0.9666000695,1.4881890072
C,0,1.2916206964,0.9862295452,1.3004084958
H,0,-1.1299905316,-1.5036104161,0.0348527321

C,0,-0.8796050329,-0.6125469644,-1.9639734821
H,0,1.2101648204,-2.003072709,0.3810608741
H,0,1.6579565167,-1.0749317395,-1.1304974208
H,0,-2.0159080598,0.8313873809,0.4980683315
H,0,-0.644169897,1.501708294,-0.5070987862
H,0,-0.4974656115,0.5768074433,2.4308488025
H,0,1.9383201231,0.9081642721,2.1745391467
H,0,1.3727896759,-0.1471278719,0.5849050655
H,0,1.6894279301,1.6585307161,0.5364337639
H,0,-0.9716910363,-1.5294917367,-2.5629611454
H,0,-1.8557372302,-0.1149443788,-1.9767600501
H,0,-0.1614716615,0.0383528577,-2.4769003404

Product structure

E(RB+HF-LYP) = -235.849104490

Zero-point correction= .165874 (Hartree/Particle)
Thermal correction to Energy= .173665
Thermal correction to Enthalpy= .174609
Thermal correction to Gibbs Free Energy= .134340

Sum of electronic and zero-point Energies= -235.683231
Sum of electronic and thermal Energies= -235.675439
Sum of electronic and thermal Enthalpies= -235.674495
Sum of electronic and thermal Free Energies= -235.714764

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	108.977	27.897	84.753

C,0,-0.4504199646,-0.7349761767,-0.5050764629
C,0,0.9808267268,-1.2746297471,-0.6307105288
C,0,-0.4734265828,0.7014451598,0.0712381823
C,0,0.042346107,0.8049510235,1.4806738436
C,0,1.0684618782,1.5584801543,1.878855488
H,0,-0.9967914414,-1.3818734522,0.1989729673
C,0,-1.1802324915,-0.7867974003,-1.8545910538
H,0,0.9814651002,-2.3091148231,-0.9940876582
H,0,1.5621625038,-0.6720670957,-1.3413000076
H,0,-1.5132203803,1.0628984995,0.0460347895
H,0,0.1042906663,1.3667664417,-0.5858452263
H,0,-0.4867042158,0.2013952456,2.2216082226
H,0,1.3868780979,1.5920978357,2.9175653836

H,0,1.504900282,-1.2501639324,0.3303463872
H,0,1.6279484775,2.1769072224,1.1794128523
H,0,-1.1967667207,-1.8065577791,-2.2569817149
H,0,-2.2180882238,-0.4441923575,-1.763722286
H,0,-0.6814081849,-0.1469338855,-2.59434052

Ene M9

Transition structure

E(RB+HF-LYP) = -235.757131701

Zero-point correction= 0.159508 (Hartree/Particle)
Thermal correction to Energy= 0.166773
Thermal correction to Enthalpy= 0.167717
Thermal correction to Gibbs Free Energy= 0.128944

Sum of electronic and zero-point Energies= -235.597624
Sum of electronic and thermal Energies= -235.590359
Sum of electronic and thermal Enthalpies= -235.589415
Sum of electronic and thermal Free Energies= -235.628188

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	104.651	27.581	81.605

C,0,-0.31860951,-0.7676813729,-0.8912906719
C,0,1.0549966113,-1.0007622929,-0.6722119319
C,0,-0.7566155873,1.2388690482,-0.1816802392
C,0,-0.0365705574,1.2601595813,1.0014383798
C,0,1.3759634483,1.1752954673,0.9503466259
C,0,-1.3501838637,-1.6036218997,-0.1623582772
H,0,-0.6125642677,-0.4372009947,-1.8850011692
H,0,1.3344369542,-1.84318266,-0.0376952116
H,0,1.7528762178,-0.8074720137,-1.486273303
H,0,-1.8437253215,1.225069675,-0.1659026883
H,0,-0.3249312254,1.708562035,-1.0631990447
H,0,-0.5388968957,0.9482774176,1.9176594843
H,0,1.9287960368,1.0861970734,1.8856860562
H,0,1.4467291445,0.0151167931,0.2737952875
H,0,1.8918557821,1.7924946399,0.2107864084
H,0,-1.4112177925,-2.6099340133,-0.6009269961
H,0,-1.0849277071,-1.7270450363,0.8939811951
H,0,-2.3523141732,-1.1644341028,-0.2083733319

Product structure

E(RB+HF-LYP) = -235.847588180

Zero-point correction= .166069 (Hartree/Particle)
Thermal correction to Energy= .173813
Thermal correction to Enthalpy= .174757
Thermal correction to Gibbs Free Energy= .134544

Sum of electronic and zero-point Energies= -235.681519
Sum of electronic and thermal Energies= -235.673775
Sum of electronic and thermal Enthalpies= -235.672831
Sum of electronic and thermal Free Energies= -235.713044

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	109.069	27.798	84.636

C,0,-0.4327771254,-0.6255130616,-0.8582185575
C,0,0.9895713702,-1.1959488121,-0.9416586854
C,0,-0.4354099121,0.8531386078,-0.3858407701
C,0,0.0760215285,1.0825047705,1.0117608167
C,0,1.1565886739,1.7999149483,1.3246192306
C,0,-1.3414648394,-1.5176236414,0.0013014
H,0,-0.8499845819,-0.6173519624,-1.8761100143
H,0,0.9792180205,-2.2190777783,-1.3360232037
H,0,1.6236209509,-0.5893789027,-1.5997374666
H,0,-1.4683524541,1.2280356134,-0.4529833285
H,0,0.1608681718,1.4498605107,-1.0888917027
H,0,-0.4987322144,0.6253470205,1.8183115184
H,0,1.4758308394,1.9390440688,2.3543358947
H,0,1.4657719115,-1.2199235609,0.0454782171
H,0,1.7620185085,2.2827638091,0.5595673
H,0,-1.4077826174,-2.5268568358,-0.4218393427
H,0,-0.9580004319,-1.617597047,1.0238561006
H,0,-2.3596542778,-1.1137018044,0.0622554219

Ene F1

Transition structure

E(RB+HF-LYP) = -295.667825057

Zero-point correction= 0.124327 (Hartree/Particle)
Thermal correction to Energy= 0.130797
Thermal correction to Enthalpy= 0.131741
Thermal correction to Gibbs Free Energy= 0.094366

Sum of electronic and zero-point Energies= -295.543498
Sum of electronic and thermal Energies= -295.537028
Sum of electronic and thermal Enthalpies= -295.536084
Sum of electronic and thermal Free Energies= -295.573459

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	82.076	24.163	78.662

C,0,-1.6756859711,-0.0816196119,-0.6893368649
C,0,-1.6606216478,0.0026518939,0.712717564
C,0,0.324761827,-0.0020176174,-1.4704503305
C,0,0.9610260659,0.8057483382,-0.5420908751
C,0,1.0065066919,0.3728680606,0.8020171204
H,0,-2.0584154718,0.7584704794,-1.2617374369
H,0,-1.8247558086,-1.0487567514,-1.1589406912
H,0,-2.1041256999,0.8774803727,1.1877851588
H,0,-1.7229555942,-0.9138409701,1.296426516
H,0,0.1621015006,0.3582155585,-2.4829880553
H,0,0.4555154229,-1.0759280099,-1.3836818702
H,0,1.013239365,1.8820753351,-0.6992812446
H,0,1.5251049888,0.9659362009,1.5565225318
H,0,-0.2851263952,0.4028534477,1.0251785592
F,0,1.2337217663,-0.9769213381,1.0048418721

Product structure

E(RB+HF-LYP) = -295.766409438

Zero-point correction= 0.130706 (Hartree/Particle)
Thermal correction to Energy= 0.137809
Thermal correction to Enthalpy= 0.138754
Thermal correction to Gibbs Free Energy= 0.099010

Sum of electronic and zero-point Energies= -295.635703
Sum of electronic and thermal Energies= -295.628600
Sum of electronic and thermal Enthalpies= -295.627656
Sum of electronic and thermal Free Energies= -295.667399

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	86.477	24.357	83.646

C,0,-1.6528827612,0.0609491448,-0.84790589
C,0,-2.1033105136,-0.1860065768,0.5946646652
C,0,-0.1449590533,-0.1759164727,-1.0755153229
C,0,0.7322145648,0.7939451295,-0.3321431958
C,0,1.6372057379,0.4727591644,0.5855697062
H,0,-1.9046888776,1.0896287572,-1.1425881189
H,0,-2.2127479566,-0.59672709,-1.5258633287
H,0,-3.1777488894,-0.0036660992,0.7104454374
H,0,-1.904862346,-1.2215067209,0.8973903961
H,0,0.0632316782,-0.0909282366,-2.1519964745
H,0,0.1166665552,-1.1994257421,-0.784355506
H,0,0.6219550648,1.8551730325,-0.5489168793
H,0,2.2714475525,1.1716919946,1.1224580999
H,0,-1.5722591344,0.469081947,1.2941608514
F,0,1.876599834,-0.8075226864,0.9534717497

Ene F2

Transition structure

E(RB+HF-LYP) = -295.667533233

Zero-point correction= 0.123846 (Hartree/Particle)
Thermal correction to Energy= 0.130385
Thermal correction to Enthalpy= 0.131329
Thermal correction to Gibbs Free Energy= 0.093812

Sum of electronic and zero-point Energies= -295.543687
Sum of electronic and thermal Energies= -295.537148
Sum of electronic and thermal Enthalpies= -295.536204
Sum of electronic and thermal Free Energies= -295.573722

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	81.818	24.553	78.963

C,0,-1.7460887672,-0.4175488227,-0.8263470161
C,0,-1.726237808,-0.430056715,0.5774938733

C,0,0.2553826893,-0.4198928974,-1.5607475415
C,0,0.9210620449,0.402552864,-0.6665175084
C,0,0.9797805566,0.0035368361,0.6918856099
H,0,-2.0635562611,0.4853727595,-1.3395086637
H,0,-1.9694168343,-1.3355805486,-1.3619541785
H,0,-2.0885745597,0.4434945066,1.117932029
H,0,-1.8689938998,-1.3749075596,1.100226916
H,0,0.1090028081,-0.0905501951,-2.585894756
H,0,0.3476110764,-1.4979330979,-1.4502380345
H,0,1.0035625263,1.4701255356,-0.8666390447
F,0,1.4893537365,0.9144416338,1.5843940097
H,0,-0.309172033,-0.1576144442,0.8993430451
H,0,1.3319612546,-1.00392925,0.9325820968

Product structure

E(RB+HF-LYP) = -295.765589508

Zero-point correction= 0.130398 (Hartree/Particle)
Thermal correction to Energy= 0.137582
Thermal correction to Enthalpy= 0.138526
Thermal correction to Gibbs Free Energy= 0.098995

Sum of electronic and zero-point Energies= -295.635191
Sum of electronic and thermal Energies= -295.628007
Sum of electronic and thermal Enthalpies= -295.627063
Sum of electronic and thermal Free Energies= -295.666594

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	86.334	24.674	83.200

C,0,-1.7290529407,-0.325012492,-0.9041582928
C,0,-2.1847607325,-0.5972384557,0.5320773558
C,0,-0.2154395433,-0.5334080327,-1.1239399585
C,0,0.642925332,0.451278478,-0.3773560027
C,0,1.5291172061,0.1035256936,0.5482289966
H,0,-1.9937492926,0.7032768239,-1.1873793518
H,0,-2.2737642125,-0.9825721076,-1.5944453014
H,0,-3.2617188192,-0.4288871367,0.6441362321
H,0,-1.9785427735,-1.6357460615,0.8205397116
H,0,-0.0035166737,-0.44946147,-2.1997331659
H,0,0.0565688612,-1.5580517626,-0.8347970465

H,0,0.5270702034,1.5098083762,-0.60715116
F,0,2.2882922859,1.011784623,1.1993459834
H,0,-1.6651023085,0.0530181322,1.2441664431
H,0,1.7413885133,-0.9123175468,0.8714371974

Ene F3

Transition structure

E(RB+HF-LYP) = -295.679317772

Zero-point correction= 0.123665 (Hartree/Particle)
Thermal correction to Energy= 0.130180
Thermal correction to Enthalpy= 0.131125
Thermal correction to Gibbs Free Energy= 0.093702

Sum of electronic and zero-point Energies= -295.555652
Sum of electronic and thermal Energies= -295.549137
Sum of electronic and thermal Enthalpies= -295.548193
Sum of electronic and thermal Free Energies= -295.585616

	E (Thermal)	CV	S
	KCAL/MOL	CAL/MOL-KELVIN	CAL/MOL-KELVIN
TOTAL	81.689	24.652	78.762

C,0,-1.6108277433,-0.550672141,-0.4052218976
C,0,-1.6317276633,-0.5411495247,1.0033133374
C,0,0.3361427213,-0.5600135028,-1.1562461058
C,0,0.9932448778,0.2390886494,-0.2354589139
C,0,1.0850016272,-0.1338983985,1.1245157753
H,0,-1.9233232758,0.3474699743,-0.9314119987
H,0,-1.8515292521,-1.4729847492,-0.9271148859
H,0,-2.0090091286,0.344033728,1.5128147941
H,0,-1.8055572444,-1.4766765591,1.5327462438
H,0,0.1917237563,-0.1895215063,-2.1670185053
H,0,0.5015191844,-1.6294032721,-1.0748937742
F,0,1.015096507,1.5760449951,-0.4904273801
H,0,1.4946497143,0.6040897469,1.8129053104
H,0,-0.197951751,-0.2823696516,1.3551275207
H,0,1.432606516,-1.1491731613,1.3152785438

Product structure

E(RB+HF-LYP) = -295.772897604

Zero-point correction= 0.130239 (Hartree/Particle)
Thermal correction to Energy= 0.137326
Thermal correction to Enthalpy= 0.138270
Thermal correction to Gibbs Free Energy= 0.098904

Sum of electronic and zero-point Energies= -295.642659
Sum of electronic and thermal Energies= -295.635571
Sum of electronic and thermal Enthalpies= -295.634627
Sum of electronic and thermal Free Energies= -295.673993

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	86.174	24.800	82.853

C,0,-1.4194086141,-0.4176080553,-0.5795042481
C,0,-1.8756352009,-0.7023769371,0.8542685091
C,0,0.0874307804,-0.6600607727,-0.8099842753
C,0,0.9644223765,0.280048393,-0.0432818419
C,0,1.8861020482,0.0042298709,0.8739011694
H,0,-1.6514610914,0.6203695054,-0.8462011838
H,0,-1.9785631861,-1.0519359763,-1.278680051
H,0,-2.9503078451,-0.5215339369,0.9675323166
H,0,-1.6820919533,-1.7462935371,1.1313941392
H,0,0.3068378054,-0.540691145,-1.8804418175
H,0,0.35295294,-1.6884580201,-0.5388875091
F,0,0.7281510839,1.5776281174,-0.3788997413
H,0,2.4568824232,0.7931323938,1.350899722
H,0,-1.3505445273,-0.0662406745,1.5752833147
H,0,2.0854673387,-1.0223966589,1.156802862

Ene F4

Transition structure

E(RB+HF-LYP) = -295.672381870

Zero-point correction= 0.124106 (Hartree/Particle)
Thermal correction to Energy= 0.130496
Thermal correction to Enthalpy= 0.131440

Thermal correction to Gibbs Free Energy= 0.094402

Sum of electronic and zero-point Energies= -295.548276
Sum of electronic and thermal Energies= -295.541886
Sum of electronic and thermal Enthalpies= -295.540942
Sum of electronic and thermal Free Energies= -295.577980

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	81.887	24.242	77.953

C,0,-1.523842096,0.1085056953,-0.3423557684
C,0,-1.5328849205,0.0208970374,1.0619187792
C,0,0.4174739028,0.0088071497,-1.0458083656
C,0,1.0754360546,0.8561580412,-0.1699328454
C,0,1.1666700736,0.4734881317,1.1925737099
H,0,-1.8559499885,1.0329621866,-0.8095751215
H,0,-1.7414069252,-0.7863413304,-0.9187778306
H,0,-1.9320800765,0.8529007447,1.639953719
H,0,-1.6521004356,-0.9549386493,1.528048342
H,0,0.2797853414,0.249330399,-2.0974700353
F,0,0.5848840936,-1.3420030555,-0.8668682561
H,0,1.0654721801,1.9118777808,-0.4339162012
H,0,1.5720297262,1.1986821657,1.8979529759
H,0,-0.1095500234,0.3143481702,1.4213439992
H,0,1.4927252713,-0.5479303,1.3958813991

Product structure

E(RB+HF-LYP) = -295.767142231

Zero-point correction= 0.130377 (Hartree/Particle)
Thermal correction to Energy= 0.137411
Thermal correction to Enthalpy= 0.138355
Thermal correction to Gibbs Free Energy= 0.099602

Sum of electronic and zero-point Energies= -295.636765
Sum of electronic and thermal Energies= -295.629731
Sum of electronic and thermal Enthalpies= -295.628787
Sum of electronic and thermal Free Energies= -295.667540

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN

TOTAL	86.227	24.724	81.563

C,0,-1.3683079687,0.1708522924,-0.5659286959
C,0,-1.808033974,-0.0764307353,0.8797126918
C,0,0.1337475353,-0.0376287898,-0.7952884554
C,0,1.0070089676,0.9159090333,-0.0270659665
C,0,1.9323617404,0.5493820413,0.8574284886
H,0,-1.6223776968,1.1931066718,-0.8775162517
H,0,-1.9058315168,-0.5060034011,-1.2415892265
H,0,-2.8915703103,0.0453397303,0.9817488854
H,0,-1.5480316411,-1.0934107879,1.1887537489
H,0,0.3459526951,0.0656626227,-1.8706833205
F,0,0.4525313822,-1.3566949211,-0.4508062962
H,0,0.8367580017,1.9699085374,-0.248336015
H,0,2.5390911278,1.2823214095,1.3811720418
H,0,-1.3200781793,0.6183618233,1.5713482028
H,0,2.1126472759,-0.4975353668,1.0792102248

Ene F5

Transition structure

E(RB+HF-LYP) = -295.672683889

Zero-point correction= 0.124038 (Hartree/Particle)
Thermal correction to Energy= 0.130478
Thermal correction to Enthalpy= 0.131422
Thermal correction to Gibbs Free Energy= 0.094177

Sum of electronic and zero-point Energies= -295.548646
Sum of electronic and thermal Energies= -295.542206
Sum of electronic and thermal Enthalpies= -295.541262
Sum of electronic and thermal Free Energies= -295.578507

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	81.876	24.420	78.388

C,0,-1.4517376985,-0.2882374689,-0.0678816653
C,0,-1.4842247925,-0.2656912571,1.3384165271
C,0,0.4885149558,-0.2615891717,-0.818522607
C,0,1.1456121942,0.5622761717,0.0812391887
C,0,1.2084633423,0.1462512611,1.4355490206

H,0,-1.752175328,0.5982401585,-0.619954596
H,0,-1.6793195172,-1.2179913659,-0.5829261877
H,0,-1.8629722296,0.6234898354,1.8404095718
H,0,-1.6541949071,-1.1951309627,1.8797220584
F,0,0.2911048668,0.1757314108,-2.0942142463
H,0,0.6217171269,-1.3407176255,-0.7901088623
H,0,1.1927348065,1.62245763,-0.1629818923
H,0,1.637470759,0.8428212959,2.1552710327
H,0,-0.0706843109,0.0141012047,1.6857612976
H,0,1.5077117924,-0.8869100776,1.62993301

Product structure

E(RB+HF-LYP) = -295.766239643

Zero-point correction= 0.130116 (Hartree/Particle)
Thermal correction to Energy= 0.137284
Thermal correction to Enthalpy= 0.138228
Thermal correction to Gibbs Free Energy= 0.098963

Sum of electronic and zero-point Energies= -295.636124
Sum of electronic and thermal Energies= -295.628955
Sum of electronic and thermal Enthalpies= -295.628011
Sum of electronic and thermal Free Energies= -295.667277

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	86.147	24.973	82.642

C,0,-1.3430977946,-0.0728708598,-0.2488275369
C,0,-1.7735948506,-0.3678578313,1.1907175471
C,0,0.1488919337,-0.2964293023,-0.5016722718
C,0,1.0405512799,0.6729466216,0.2167565859
C,0,1.9159339304,0.3342362011,1.1625246716
H,0,-1.5878032361,0.9633944554,-0.5166339835
H,0,-1.8904379225,-0.7159633823,-0.949049211
H,0,-2.850196423,-0.2090366498,1.3124105041
H,0,-1.558912842,-1.407826374,1.4661064204
F,0,0.3645958233,-0.1434975172,-1.883729019
H,0,0.4243753764,-1.3276959967,-0.2413648958
H,0,0.9192675919,1.715955747,-0.0772677316
H,0,2.5259848156,1.0751016062,1.6720358954
H,0,-1.2533917135,0.2788064609,1.9053024078

H,0,2.0576449515,-0.7014071883,1.46502779

Ene F6

Transition structure

E(RB+HF-LYP) = -295.667467139

Zero-point correction= 0.124268 (Hartree/Particle)
Thermal correction to Energy= 0.130734
Thermal correction to Enthalpy= 0.131678
Thermal correction to Gibbs Free Energy= 0.094140

Sum of electronic and zero-point Energies= -295.543199
Sum of electronic and thermal Energies= -295.536733
Sum of electronic and thermal Enthalpies= -295.535789
Sum of electronic and thermal Free Energies= -295.573327

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	82.037	24.081	79.007

C,0,-1.1525377233,0.1057111099,-0.7468469426
C,0,-1.173833909,-0.0190731264,0.6475544887
C,0,0.7577394881,-0.0247534093,-1.4389610731
C,0,1.4701730244,0.8306368365,-0.5997099803
C,0,1.5015711995,0.5167345245,0.7867448513
H,0,-1.4609713223,1.0669463795,-1.1472886037
H,0,-1.4708560594,-0.7516530245,-1.3322177803
H,0,-1.6800935646,0.6930811166,1.2952186578
F,0,-1.2010880391,-1.2942705712,1.1559930929
H,0,0.6365046225,0.2277091795,-2.4907772951
H,0,0.8327317909,-1.095168399,-1.2534113473
H,0,1.5978891384,1.8706108896,-0.9002644942
H,0,1.9608926999,1.2335202413,1.468782156
H,0,0.2453733941,0.4668299031,1.0064236391
H,0,1.7296491746,-0.5189767559,1.0569091678

Product structure

E(RB+HF-LYP) = -295.766239643

Zero-point correction= 0.130116 (Hartree/Particle)
Thermal correction to Energy= 0.137284
Thermal correction to Enthalpy= 0.138228
Thermal correction to Gibbs Free Energy= 0.098963

Sum of electronic and zero-point Energies= -295.636124
Sum of electronic and thermal Energies= -295.628955
Sum of electronic and thermal Enthalpies= -295.628011
Sum of electronic and thermal Free Energies= -295.667277

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	86.147	24.973	82.642

C,0,-1.3430977946,-0.0728708598,-0.2488275369
C,0,-1.7735948506,-0.3678578313,1.1907175471
C,0,0.1488919337,-0.2964293023,-0.5016722718
C,0,1.0405512799,0.6729466216,0.2167565859
C,0,1.9159339304,0.3342362011,1.1625246716
H,0,-1.5878032361,0.9633944554,-0.5166339835
H,0,-1.8904379225,-0.7159633823,-0.949049211
H,0,-2.850196423,-0.2090366498,1.3124105041
H,0,-1.558912842,-1.407826374,1.4661064204
F,0,0.3645958233,-0.1434975172,-1.883729019
H,0,0.4243753764,-1.3276959967,-0.2413648958
H,0,0.9192675919,1.715955747,-0.0772677316
H,0,2.5259848156,1.0751016062,1.6720358954
H,0,-1.2533917135,0.2788064609,1.9053024078
H,0,2.0576449515,-0.7014071883,1.46502779

Ene F7

Transition structure

E(RB+HF-LYP) = -295.665358903

Zero-point correction= 0.123929 (Hartree/Particle)
Thermal correction to Energy= 0.130447
Thermal correction to Enthalpy= 0.131391
Thermal correction to Gibbs Free Energy= 0.093706

Sum of electronic and zero-point Energies= -295.541430
Sum of electronic and thermal Energies= -295.534912

Sum of electronic and thermal Enthalpies= -295.533968
Sum of electronic and thermal Free Energies= -295.571653

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	81.856	24.216	79.314

C,0,-1.0888261661,-0.5104894092,-0.734210316
C,0,-1.1122178183,-0.364947862,0.6601205909
C,0,0.8357875846,-0.3386623896,-1.4881155897
C,0,1.4806163034,0.452622313,-0.5407704927
C,0,1.5897251885,-0.0525227041,0.7806566747
H,0,-1.5075421845,0.303013772,-1.3174377498
H,0,-1.2779280144,-1.5042022219,-1.1282826915
F,0,-1.4922926862,0.8697978971,1.1374978061
H,0,-1.41947016,-1.1724768683,1.3220498464
H,0,0.6526273937,0.0527682107,-2.4864376347
H,0,1.0210137685,-1.4112071003,-1.4683403243
H,0,1.4864186155,1.5330763138,-0.6818347995
H,0,1.9895037731,0.6008881712,1.556254428
H,0,0.3295863836,-0.2579934502,1.0104900139
H,0,1.9259140479,-1.0880475902,0.8899734534

Product structure

E(RB+HF-LYP) = -295.760517564

Zero-point correction= 0.130865 (Hartree/Particle)
Thermal correction to Energy= 0.137954
Thermal correction to Enthalpy= 0.138899
Thermal correction to Gibbs Free Energy= 0.099292

Sum of electronic and zero-point Energies= -295.629653
Sum of electronic and thermal Energies= -295.622563
Sum of electronic and thermal Enthalpies= -295.621619
Sum of electronic and thermal Free Energies= -295.661226

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	86.568	24.099	83.360

C,0,-0.7681451754,-0.0707468782,-0.7954169638
C,0,-1.1998816154,-0.3115157692,0.6426079533

C,0,0.7339099221,-0.3294519121,-1.0280648769
C,0,1.6330693628,0.6233817455,-0.2843595499
C,0,2.5716339177,0.2729093808,0.5959902927
H,0,-1.0186615889,0.9631772419,-1.0668361667
H,0,-1.3600963347,-0.7221624117,-1.4497950934
F,0,-2.5680817212,-0.0749016086,0.7636824065
H,0,-1.0043316083,-1.3493553211,0.9446830465
H,0,0.9278049415,-0.2396533499,-2.1065571601
H,0,0.9828337533,-1.3634894733,-0.75351339
H,0,1.4817627858,1.682435218,-0.503734483
H,0,3.1938878577,1.010958139,1.0950138425
H,0,-0.6735779548,0.354255314,1.3364681453
H,0,2.7595951686,-0.7695102798,0.8465884682

Ene F8

Transition structure

E(RB+HF-LYP) = -295.670416425

Zero-point correction= 0.123551 (Hartree/Particle)
Thermal correction to Energy= 0.130041
Thermal correction to Enthalpy= 0.130985
Thermal correction to Gibbs Free Energy= 0.093567

Sum of electronic and zero-point Energies= -295.546865
Sum of electronic and thermal Energies= -295.540376
Sum of electronic and thermal Enthalpies= -295.539431
Sum of electronic and thermal Free Energies= -295.576849

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	81.602	24.604	78.753

C,0,-1.1656997484,-0.0629808816,-0.3253491609
C,0,-1.1351269716,0.087243825,1.0662833934
C,0,0.8347539192,0.1354014425,-1.1050237969
C,0,1.4924551029,0.8888798033,-0.1469119062
C,0,1.5786932347,0.4035645365,1.1804526264
H,0,-1.5700680138,0.695200012,-0.987204648
F,0,-1.3830511441,-1.3208287417,-0.8155203545
H,0,-1.487918086,1.0365653547,1.4654739368
H,0,-1.3819053967,-0.7908025431,1.6593100993

H,0,0.6726840154,0.5369737222,-2.1031172599
H,0,0.8930886092,-0.9491607865,-1.0625116715
H,0,1.592206441,1.9629303257,-0.3077019613
H,0,2.0180377503,1.044700723,1.9446935589
H,0,0.2575646474,0.2907807544,1.396837727
H,0,1.8233171094,-0.6523812417,1.3171964752

Product structure

E(RB+HF-LYP) = -295.768291132

Zero-point correction= 0.130128 (Hartree/Particle)
Thermal correction to Energy= 0.137256
Thermal correction to Enthalpy= 0.138200
Thermal correction to Gibbs Free Energy= 0.098968

Sum of electronic and zero-point Energies= -295.638163
Sum of electronic and thermal Energies= -295.631035
Sum of electronic and thermal Enthalpies= -295.630091
Sum of electronic and thermal Free Energies= -295.669323

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	86.130	24.882	82.572

C,0,-0.9328111518,0.051650396,-0.3821037412
C,0,-1.4116092365,-0.2455562716,1.0283811203
C,0,0.5668186211,-0.1783912072,-0.6043792765
C,0,1.4371517065,0.8144517091,0.1161539914
C,0,2.3487292739,0.5098032634,1.0407363897
H,0,-1.1932061368,1.0823111693,-0.6620125258
F,0,-1.6222609139,-0.7917528516,-1.2665398244
H,0,-2.4929046933,-0.0936848605,1.1035222493
H,0,-1.1891987295,-1.2858031655,1.2915346493
H,0,0.7420028227,-0.111292569,-1.6874197244
H,0,0.8173279649,-1.2020979458,-0.2993773173
H,0,1.2940950518,1.8613060172,-0.1588365439
H,0,2.9539846007,1.2738312613,1.5212222058
H,0,-0.9126144299,0.4079314551,1.7509068294
H,0,2.5311864952,-0.518473036,1.3465876948

Ene F9

Transition structure

E(RB+HF-LYP) = -295.671631139

Zero-point correction= 0.123693 (Hartree/Particle)
Thermal correction to Energy= 0.130155
Thermal correction to Enthalpy= 0.131099
Thermal correction to Gibbs Free Energy= 0.093787

Sum of electronic and zero-point Energies= -295.547939
Sum of electronic and thermal Energies= -295.541476
Sum of electronic and thermal Enthalpies= -295.540532
Sum of electronic and thermal Free Energies= -295.577844

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	81.673	24.448	78.530

C,0,-1.1105731326,-0.3504251013,-0.3288188481
C,0,-1.1128963123,-0.4518407613,1.0661556823
C,0,0.8511874067,-0.4753072915,-1.0442329926
C,0,1.4884612129,0.4034944933,-0.1806869028
C,0,1.584997001,0.0603708395,1.1938335491
F,0,-1.487339754,0.852564595,-0.8579156297
H,0,-1.4041589289,-1.1787044328,-0.9673880284
H,0,-1.5554700984,0.3695330388,1.6245953429
H,0,-1.2336258869,-1.4418756635,1.4987416745
H,0,0.685204251,-0.1982055909,-2.0826724457
H,0,0.9628046636,-1.5459214804,-0.8750796493
H,0,1.5175611258,1.45790744,-0.4537115361
H,0,1.9872442386,0.802102604,1.884464561
H,0,0.3064463811,-0.100704328,1.4223014196
H,0,1.9129949851,-0.9549660153,1.4324864011

Product structure

E(RB+HF-LYP) = -295.768523239

Zero-point correction= 0.130277 (Hartree/Particle)
Thermal correction to Energy= 0.137335
Thermal correction to Enthalpy= 0.138279

Thermal correction to Gibbs Free Energy= 0.099329

Sum of electronic and zero-point Energies= -295.638246
Sum of electronic and thermal Energies= -295.631189
Sum of electronic and thermal Enthalpies= -295.630244
Sum of electronic and thermal Free Energies= -295.669195

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	86.179	24.782	81.977

C,0,-0.9976130844,-0.3497046194,-0.4853122669
C,0,-1.4811987302,-0.5261923909,0.9442515458
C,0,0.5120483137,-0.5357699878,-0.6844829577
C,0,1.3454368641,0.4366287487,0.1058279499
C,0,2.320108429,0.1013783532,0.9516114879
F,0,-1.3260448817,0.9520020052,-0.9033564221
H,0,-1.5352542978,-1.0366710367,-1.1526075036
H,0,-2.5546764714,-0.322106605,1.0063654448
H,0,-1.3031820765,-1.552414707,1.2852232647
H,0,0.7146100672,-0.4036607685,-1.7570675755
H,0,0.7815995525,-1.5690772909,-0.4308942295
H,0,1.1098194899,1.4881229025,-0.0548662557
H,0,2.8976610899,0.8516351041,1.4852566714
H,0,-0.9538392923,0.1558096022,1.6180580497
H,0,2.5849751213,-0.9376958702,1.1393653783

Ene Ac (Acrolein)

Transition structure

E(RB+HF-LYP) = -309.772122832

Zero-point correction= 0.142577 (Hartree/Particle)
Thermal correction to Energy= 0.149977
Thermal correction to Enthalpy= 0.150921
Thermal correction to Gibbs Free Energy= 0.111060

Sum of electronic and zero-point Energies= -309.629546
Sum of electronic and thermal Energies= -309.622146
Sum of electronic and thermal Enthalpies= -309.621201
Sum of electronic and thermal Free Energies= -309.661063

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	94.112	27.501	83.896

C,0,-1.0810370946,-0.2437075804,-0.8311309051
C,0,0.2968419464,-0.6234772736,-0.7749014707
O,0,1.7939457946,-2.3388368068,-0.0592315608
C,0,0.73380554,-1.740108506,0.0528085773
H,0,-1.7429590287,-0.8330104149,-0.1939102223
H,0,-1.4962752513,-0.1320820795,-1.8323979718
H,0,0.9646019298,-0.3479996859,-1.5897369005
H,0,-0.0017098668,-2.0336269174,0.8418628353
C,0,-1.4428229444,1.4967823806,-0.3163469502
C,0,-0.8156011842,1.6496021327,0.9374868042
C,0,0.6096298094,1.5882072129,0.9754729171
H,0,-2.5308307418,1.5433713885,-0.3485418164
H,0,-0.9818980807,2.0303112024,-1.1487539636
H,0,-1.3766976529,1.3879248446,1.8341783219
H,0,1.086930891,1.576422049,1.9561096396
H,0,0.7832562772,0.51557964,0.421465747
H,0,1.1391187315,2.2400142311,0.2732429815

Product structure

E(RB+HF-LYP) = -309.847902399

Zero-point correction= .147240 (Hartree/Particle)
Thermal correction to Energy= .155566
Thermal correction to Enthalpy= .156510
Thermal correction to Gibbs Free Energy= .113390

Sum of electronic and zero-point Energies= -309.700662
Sum of electronic and thermal Energies= -309.692336
Sum of electronic and thermal Enthalpies= -309.691392
Sum of electronic and thermal Free Energies= -309.734513

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	97.619	28.306	90.754

C,0,-0.1046729257,1.020909569,0.1023878427
C,0,-0.8722033506,-0.2789453303,-0.2019827247
O,0,-3.2871718294,-0.422950279,-0.2380137831

C,0,-2.2623499508,-0.2658060203,0.3881406917
H,0,-0.1441941312,1.2271369631,1.1817910045
H,0,-0.6048072368,1.862832129,-0.3923481217
H,0,-0.9520788897,-0.4531963624,-1.2803920992
H,0,-2.2950159599,-0.0887375325,1.4896148762
C,0,1.3703297337,0.9734711575,-0.3510663725
C,0,2.1982396741,-0.0208104252,0.4173698146
C,0,2.8262394148,-1.0744522265,-0.1071349835
H,0,1.7980896203,1.9781067126,-0.2197816783
H,0,1.4192554733,0.7485436788,-1.4243939913
H,0,2.269114476,0.155316308,1.4929448341
H,0,3.412200738,-1.755591677,0.5042665884
H,0,-0.3248068494,-1.1258209144,0.2390738089
H,0,2.7861218215,-1.2911874193,-1.1729505669

Diimide 1

Transition structure

E(RB+HF-LYP) = -189.219728915

Zero-point correction= 0.078051 (Hartree/Particle)
Thermal correction to Energy= 0.082607
Thermal correction to Enthalpy= 0.083551
Thermal correction to Gibbs Free Energy= 0.051195

Sum of electronic and zero-point Energies= -189.141678
Sum of electronic and thermal Energies= -189.137122
Sum of electronic and thermal Enthalpies= -189.136178
Sum of electronic and thermal Free Energies= -189.168534

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	51.836	15.514	68.098

N,0,1.4148863681,0.5993302128,0.2879016053
N,0,1.4148863681,-0.5993302128,0.2879016053
H,0,0.3603824733,-0.988848978,0.073340944
H,0,0.3603824733,0.988848978,0.073340944
C,0,-1.2432414884,-0.6874107666,-0.2529759437
C,0,-1.2432414884,0.6874107666,-0.2529759437
H,0,-1.2188179174,1.2427938233,-1.1884052288
H,0,-1.5863202026,-1.2427957049,0.6176087102

H,0,-1.2188179174,-1.2427938233,-1.1884052288
H,0,-1.5863202026,1.2427957049,0.6176087102

Diimide 2

Transition structure

E(RB+HF-LYP) = -288.442825095

Zero-point correction= 0.069741 (Hartree/Particle)
Thermal correction to Energy= 0.075014
Thermal correction to Enthalpy= 0.075958
Thermal correction to Gibbs Free Energy= 0.041115

Sum of electronic and zero-point Energies= -288.373084
Sum of electronic and thermal Energies= -288.367811
Sum of electronic and thermal Enthalpies= -288.366867
Sum of electronic and thermal Free Energies= -288.401710

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	47.072	17.852	73.335

N,0,1.769500113,0.3144688262,0.0502353909
N,0,1.7410513847,-0.8738856631,0.1645616354
H,0,0.6482472545,-1.2526425825,-0.0260072206
H,0,0.7208207024,0.7075955977,-0.2159105019
C,0,-0.8638428008,-0.9583942844,-0.4229208374
C,0,-0.9013563084,0.4163159531,-0.4202857924
H,0,-0.9458423181,1.0281856657,-1.3186290964
H,0,-1.2944398415,-1.499754968,0.415841449
H,0,-0.8247897202,-1.4741862166,-1.3784388366
F,0,-1.3651846562,1.0732433722,0.6754227557

Product structure

E(RB+HF-LYP) = -177.819641142

Zero-point correction= 0.044283 (Hartree/Particle)
Thermal correction to Energy= 0.047630
Thermal correction to Enthalpy= 0.048574
Thermal correction to Gibbs Free Energy= 0.019927

Sum of electronic and zero-point Energies= -177.775358
Sum of electronic and thermal Energies= -177.772011
Sum of electronic and thermal Enthalpies= -177.771067
Sum of electronic and thermal Free Energies= -177.799714

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	29.888	9.847	60.294

C,0,0.0905696239,-1.1388890953,-0.3665035743
C,0,0.0821350889,0.1859290493,-0.3817179285
H,0,0.2665988478,0.8104029781,-1.2513681873
H,0,-0.1031915798,-1.6978964196,0.5426283515
H,0,0.2947675067,-1.6858915476,-1.2795719778
F,0,-0.1660447835,0.9212383628,0.7197378701

Diimide 3

Transition structure

E(RB+HF-LYP) = -264.427583183

Zero-point correction= 0.081771 (Hartree/Particle)
Thermal correction to Energy= 0.087423
Thermal correction to Enthalpy= 0.088367
Thermal correction to Gibbs Free Energy= 0.052967

Sum of electronic and zero-point Energies= -264.345813
Sum of electronic and thermal Energies= -264.340160
Sum of electronic and thermal Enthalpies= -264.339216
Sum of electronic and thermal Free Energies= -264.374616

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	54.859	19.579	74.506

N,0,1.7852025589,0.2835982442,0.0441393729
N,0,1.7433824169,-0.9038550468,0.160129684
H,0,0.6113857082,-1.2550892252,-0.0607923532
H,0,0.7432755789,0.6868122095,-0.2400606682
C,0,-0.8343008073,-0.9491090242,-0.4535397375
C,0,-0.8983877564,0.4380963888,-0.4180884634
H,0,-0.9007481809,1.0367350346,-1.3257059445

H,0,-1.3160978547,-1.5261751506,0.3365480767
H,0,-0.8123262032,-1.4320874519,-1.4277041334
O,0,-1.3848086958,1.1663989017,0.641389909
H,0,-1.5509829302,0.5664868004,1.386481558

Product structure

E(RB+HF-LYP) = -153.805679859

Zero-point correction= 0.056745 (Hartree/Particle)
Thermal correction to Energy= 0.060349
Thermal correction to Enthalpy= 0.061293
Thermal correction to Gibbs Free Energy= 0.032304

Sum of electronic and zero-point Energies= -153.748935
Sum of electronic and thermal Energies= -153.745331
Sum of electronic and thermal Enthalpies= -153.744386
Sum of electronic and thermal Free Energies= -153.773375

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	37.870	11.341	61.012

C,0,0.0708017736,-1.1415112323,-0.4281588326
C,0,0.1228431933,0.1905834246,-0.3777731373
H,0,0.4091900241,0.7997123359,-1.2305728458
H,0,-0.2168468962,-1.7458561842,0.4295106893
H,0,0.319610864,-1.6623777921,-1.3450454477
O,0,-0.1580580448,0.9865375235,0.6924573076
H,0,-0.4093594346,0.4217882994,1.442040963

Diimide 4

Transition structure

E(RB+HF-LYP) = -244.568270074

Zero-point correction= 0.094738 (Hartree/Particle)
Thermal correction to Energy= 0.100583
Thermal correction to Enthalpy= 0.101528
Thermal correction to Gibbs Free Energy= 0.065799

Sum of electronic and zero-point Energies= -244.473532
Sum of electronic and thermal Energies= -244.467687
Sum of electronic and thermal Enthalpies= -244.466742
Sum of electronic and thermal Free Energies= -244.502471

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	63.117	20.593	75.198

N,0,1.7934136618,0.3020507235,0.0721032075
N,0,1.7753151378,-0.888003961,0.1961559567
H,0,0.650293888,-1.2576418465,-0.0533206055
H,0,0.7512959075,0.6701519778,-0.2400071515
C,0,-0.7945589869,-0.9974075666,-0.4565034451
C,0,-0.9049858155,0.3916714653,-0.4522710079
H,0,-0.8803077684,0.9351506033,-1.3956433779
H,0,-1.2633480682,-1.56446174,0.3484367178
H,0,-0.7711634311,-1.5042681392,-1.4185565146
N,0,-1.5133403468,1.1098182778,0.5922815449
H,0,-1.177348047,2.0604565935,0.702542171
H,0,-1.4998728369,0.6279738766,1.4854105149

Product structure

E(RB+HF-LYP) = -133.942723524

Zero-point correction= 0.069229 (Hartree/Particle)
Thermal correction to Energy= 0.073111
Thermal correction to Enthalpy= 0.074055
Thermal correction to Gibbs Free Energy= 0.044598

Sum of electronic and zero-point Energies= -133.873495
Sum of electronic and thermal Energies= -133.869613
Sum of electronic and thermal Enthalpies= -133.868668
Sum of electronic and thermal Free Energies= -133.898125

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	45.878	12.684	61.998

C,0,0.0468077806,-1.1835049579,-0.4518879544
C,0,0.1106967589,0.1526935086,-0.3924747329
H,0,0.3818604485,0.7275855106,-1.2766745525

H,0,-0.2147669374,-1.7890951614,0.4129363744
H,0,0.2847954446,-1.7064420678,-1.3707682588
N,0,-0.056793169,0.9475208195,0.7444874608
H,0,-0.4911314984,1.8461662112,0.5693686962
H,0,-0.5082325113,0.4740084666,1.5199016384

Diimide 5

Transition structure

E(RB+HF-LYP) = -228.536016371

Zero-point correction= 0.106133 (Hartree/Particle)
Thermal correction to Energy= 0.112150
Thermal correction to Enthalpy= 0.113094
Thermal correction to Gibbs Free Energy= 0.076924

Sum of electronic and zero-point Energies= -228.429883
Sum of electronic and thermal Energies= -228.423867
Sum of electronic and thermal Enthalpies= -228.422923
Sum of electronic and thermal Free Energies= -228.459092

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	70.375	20.752	76.125

N,0,1.77625832,0.3274453283,-0.0436258289
N,0,1.8095085826,-0.8675077082,0.0249892189
H,0,0.7388922,-1.2862694188,-0.1294989237
H,0,0.6977586935,0.6670946228,-0.2440148962
C,0,-0.8397751368,-1.0389786334,-0.4108718115
C,0,-0.905904255,0.3406355521,-0.4196510488
H,0,-0.9286560076,0.8440731743,-1.3877537145
H,0,-1.157680761,-1.5960195278,0.4700366921
H,0,-0.838113351,-1.5973219418,-1.3449630878
C,0,-1.4119439938,1.145841792,0.7584920626
H,0,-1.2418028895,0.6163839082,1.7024910865
H,0,-2.4930017821,1.3191286448,0.6671628131
H,0,-0.9320241066,2.1283749339,0.829181087

Product structure

E(RB+HF-LYP) = -117.907556191

Zero-point correction= 0.080082 (Hartree/Particle)
Thermal correction to Energy= 0.084158
Thermal correction to Enthalpy= 0.085102
Thermal correction to Gibbs Free Energy= 0.055079

Sum of electronic and zero-point Energies= -117.827474
Sum of electronic and thermal Energies= -117.823398
Sum of electronic and thermal Enthalpies= -117.822454
Sum of electronic and thermal Free Energies= -117.852477

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	52.810	12.917	63.189

C,0,0.3107204605,-1.1799937464,-0.4537442385
C,0,-0.009711071,0.1142240499,-0.4607511349
H,0,-0.0988280403,0.6298075884,-1.4182825267
H,0,0.4116097498,-1.7382980281,0.4751803336
H,0,0.4846795988,-1.7325637766,-1.373226035
C,0,-0.2660715304,0.9498334163,0.7607583863
H,0,-0.1577045937,0.3627389383,1.6789308749
H,0,-1.2786324467,1.3754115892,0.7454462255
H,0,0.4292485773,1.79852137,0.8143730499

Diimide 6

Transition structure

E(RB+HF-LYP) = -648.811689592

Zero-point correction= 0.069051 (Hartree/Particle)
Thermal correction to Energy= 0.074531
Thermal correction to Enthalpy= 0.075475
Thermal correction to Gibbs Free Energy= 0.039481

Sum of electronic and zero-point Energies= -648.742638
Sum of electronic and thermal Energies= -648.737158
Sum of electronic and thermal Enthalpies= -648.736214
Sum of electronic and thermal Free Energies= -648.772208

	E (Thermal)	CV	S

	KCAL/MOL	CAL/MOL-KELVIN	CAL/MOL-KELVIN
TOTAL	46.769	18.511	75.756

N,0,2.0496815114,0.0202962666,-0.147847522
N,0,2.0033088207,-1.171697977,-0.0565320106
H,0,0.9256708261,-1.5353966513,-0.257675157
H,0,1.0256796546,0.4346075444,-0.4054058988
C,0,-0.6184754451,-1.2068153268,-0.6529726009
C,0,-0.6168228415,0.1674802578,-0.6423848256
H,0,-0.6217875318,0.7634353346,-1.5499366678
H,0,-1.0305296296,-1.768204144,0.1811141231
H,0,-0.5727285386,-1.7165484201,-1.6132657248
Cl,0,-1.2167910227,1.0657605131,0.7557629772

Product structure

E(RB+HF-LYP) = -538.185384426

Zero-point correction= 0.042848 (Hartree/Particle)
Thermal correction to Energy= 0.046383
Thermal correction to Enthalpy= 0.047327
Thermal correction to Gibbs Free Energy= 0.017392

Sum of electronic and zero-point Energies= -538.142536
Sum of electronic and thermal Energies= -538.139002
Sum of electronic and thermal Enthalpies= -538.138057
Sum of electronic and thermal Free Energies= -538.167992

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	29.106	10.686	63.003

C,0,0.1629950205,-1.4953263903,-0.721891416
C,0,0.2171303129,-0.1690991125,-0.7142263122
H,0,0.5105930862,0.4331714645,-1.5665583503
H,0,-0.1352398235,-2.0723367748,0.1472377474
H,0,0.4242317162,-2.0359874097,-1.6268622211
Cl,0,-0.1811962929,0.8036297492,0.6860523055

Diimide 7

Transition structure

E(RB+HF-LYP) = -187.955071993

Zero-point correction= 0.053358 (Hartree/Particle)
Thermal correction to Energy= 0.057917
Thermal correction to Enthalpy= 0.058861
Thermal correction to Gibbs Free Energy= 0.026743

Sum of electronic and zero-point Energies= -187.901714
Sum of electronic and thermal Energies= -187.897155
Sum of electronic and thermal Enthalpies= -187.896211
Sum of electronic and thermal Free Energies= -187.928329

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	36.343	15.435	67.597

N,0,-1.3713819618,0.5940061932,-0.0062890624
N,0,-1.3649080751,-0.6087443458,-0.0055245499
H,0,-0.307205955,-0.986882211,-0.0008465872
H,0,-0.3178276608,0.9835226373,-0.0021538701
C,0,1.3645017724,-0.6080461566,0.0060787776
C,0,1.3578569247,0.6227085508,0.0057288694
H,0,1.7137073295,1.6340661334,0.0061482863
H,0,1.7312043616,-1.6155138567,0.0087015755

Diimide 8

Transition structure

E(RB+HF-LYP) = -287.162458705

Zero-point correction= 0.047031 (Hartree/Particle)
Thermal correction to Energy= 0.052419
Thermal correction to Enthalpy= 0.053363
Thermal correction to Gibbs Free Energy= 0.018427

Sum of electronic and zero-point Energies= -287.115427
Sum of electronic and thermal Energies= -287.110040
Sum of electronic and thermal Enthalpies= -287.109096

Sum of electronic and thermal Free Energies= -287.144032

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	32.893	17.659	73.529

N,0,-1.7616420347,1.0051727105,-0.0103180457
N,0,-1.7720422296,-0.2006549135,-0.0087480867
H,0,-0.7310044625,-0.5919734015,-0.0027624793
H,0,-0.7242981325,1.3805486953,-0.0053521449
C,0,0.9853678979,-0.2266347454,0.0052481041
C,0,1.0174146309,0.9982131648,0.003697917
H,0,1.3269861169,2.0218185717,0.0034888212
F,0,1.4274901283,-1.4523876624,0.0093791782

Product structure

E(RB+HF-LYP) = -176.536264188

Zero-point correction= 0.019324 (Hartree/Particle)
Thermal correction to Energy= 0.022866
Thermal correction to Enthalpy= 0.023810
Thermal correction to Gibbs Free Energy= 0.000494

Sum of electronic and zero-point Energies= -176.516940
Sum of electronic and thermal Energies= -176.513398
Sum of electronic and thermal Enthalpies= -176.512454
Sum of electronic and thermal Free Energies= -176.535770

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	14.348	9.952	49.073

C,0,-0.0049329975,0.0955344893,-0.0003904296
C,0,-0.0440282613,1.295329315,-0.0032170302
H,0,-0.0769891064,2.3591935156,-0.0055421846
F,0,0.0411951844,-1.1893751491,0.0030207715

Diimide 9

Transition structure

E(RB+HF-LYP) = -227.279567409

Zero-point correction= 0.081933 (Hartree/Particle)
Thermal correction to Energy= 0.088021
Thermal correction to Enthalpy= 0.088966
Thermal correction to Gibbs Free Energy= 0.052632

Sum of electronic and zero-point Energies= -227.197635
Sum of electronic and thermal Energies= -227.191546
Sum of electronic and thermal Enthalpies= -227.190602
Sum of electronic and thermal Free Energies= -227.226935

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	55.234	20.290	76.470

N,0,-1.7182715666,1.1563741855,-0.0411757079
N,0,-1.7823840183,-0.0426454334,-0.0463362579
H,0,-0.7393289411,-0.4710929045,-0.0205933244
H,0,-0.6185138628,1.4687069287,-0.011810181
C,0,0.9530944512,-0.2118617887,0.0239621825
C,0,0.9544323863,1.0247824915,0.0277107125
H,0,1.4109540167,1.9963919164,0.0423414478
C,0,1.4043975005,-1.6162306716,0.0317933874
H,0,2.4999431324,-1.665450164,0.0597252217
H,0,1.062618714,-2.1500932487,-0.8622526619
H,0,1.0173700075,-2.15470398,0.9043755632

Product structure

E(RB+HF-LYP) = -116.653269770

Zero-point correction= 0.055722 (Hartree/Particle)
Thermal correction to Energy= 0.059719
Thermal correction to Enthalpy= 0.060663
Thermal correction to Gibbs Free Energy= 0.031494

Sum of electronic and zero-point Energies= -116.597548
Sum of electronic and thermal Energies= -116.593551
Sum of electronic and thermal Enthalpies= -116.592606
Sum of electronic and thermal Free Energies= -116.621776

	E (Thermal)	CV	S

	KCAL/MOL	CAL/MOL-KELVIN	CAL/MOL-KELVIN
TOTAL	37.474	12.466	61.393

C,0,-0.0204557032,0.2179683241,-0.0020398496
C,0,-0.1286292121,1.4202658811,-0.0132230452
H,0,-0.2211529965,2.4822677165,-0.0230421034
C,0,0.1118797189,-1.2363891747,0.0114999287
H,0,1.160632841,-1.5368643616,0.1206140233
H,0,-0.2664826643,-1.6780599547,-0.9180804169
H,0,-0.449766002,-1.6784135832,0.8430862937

Diels-Alder parent

Transition structure

E(RB+HF-LYP) = -234.543896553

Zero-point correction= 0.140573 (Hartree/Particle)
Thermal correction to Energy= 0.146991
Thermal correction to Enthalpy= 0.147935
Thermal correction to Gibbs Free Energy= 0.111006

Sum of electronic and zero-point Energies= -234.403323
Sum of electronic and thermal Energies= -234.396906
Sum of electronic and thermal Enthalpies= -234.395962
Sum of electronic and thermal Free Energies= -234.432890

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	92.238	24.803	77.723

C,0,-0.07726291,0.9239273262,-1.2826087404
C,0,-0.1864881555,-0.4448718484,-1.4478820505
C,0,-0.7061533279,-1.279144243,-0.4408518614
C,0,-1.1387504839,-0.7801872954,0.7743497153
C,0,0.7218474557,0.262689705,1.5583296433
C,0,1.2336594928,1.0842358004,0.5663421338
H,0,0.1538230668,0.6915283975,2.378973274
H,0,1.0667035099,2.1567323147,0.6098937516
H,0,1.1949480494,-0.688946111,1.7728843685
H,0,2.1077596219,0.7762576795,0.0036931502
H,0,-1.5929273926,0.2020125642,0.8385394893
H,0,-0.8037748387,1.4689754301,-0.6908078051

H,0,0.434649421,1.5232449111,-2.0316114163
H,0,0.3392800057,-0.9145236987,-2.2780130251
H,0,-0.5568642087,-2.3532708935,-0.5412959721
H,0,-1.4247096623,-1.4619072626,1.5716711437

Product structure

E(RB+HF-LYP) = -234.648294877

Zero-point correction= 0.146984 (Hartree/Particle)
Thermal correction to Energy= 0.152474
Thermal correction to Enthalpy= 0.153418
Thermal correction to Gibbs Free Energy= 0.118347

Sum of electronic and zero-point Energies= -234.501311
Sum of electronic and thermal Energies= -234.495821
Sum of electronic and thermal Enthalpies= -234.494877
Sum of electronic and thermal Free Energies= -234.529948

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	95.679	21.315	73.813

C,0,1.4539342258,0.2823307983,0.2601012361
C,0,0.7778967647,0.7133646104,-1.0192310828
C,0,-0.5071286843,0.4678283532,-1.2949165728
C,0,-1.443993221,-0.2389630193,-0.3450502502
C,0,-0.8626994246,-0.3328364416,1.0751290489
C,0,0.6155149913,-0.745482954,1.0374591752
H,0,-0.9491876243,0.6468284288,1.5656859495
H,0,1.0102382363,-0.8646621786,2.0540121336
H,0,-1.4467830712,-1.0398396086,1.67710689
H,0,0.7018876464,-1.7256554554,0.5478842249
H,0,-2.4118308883,0.2812017268,-0.3237010196
H,0,1.6448595667,1.1665292589,0.8895673784
H,0,2.445816756,-0.1329407698,0.033297565
H,0,1.3892658409,1.2488779772,-1.7451495848
H,0,-0.9218399904,0.7901860431,-2.249693662
H,0,-1.663574384,-1.2479735045,-0.7299592013

Hydride transfer parent

Transition structure

E(RB+HF-LYP) = -237.200483851

Zero-point correction= 0.068672 (Hartree/Particle)
Thermal correction to Energy= 0.074596
Thermal correction to Enthalpy= 0.075540
Thermal correction to Gibbs Free Energy= 0.039795

Sum of electronic and zero-point Energies= -237.131812
Sum of electronic and thermal Energies= -237.125888
Sum of electronic and thermal Enthalpies= -237.124944
Sum of electronic and thermal Free Energies= -237.160689

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	46.809	19.133	75.232

O,0,1.373242287,0.5737394626,0.0078377248
C,0,1.3054160549,-0.7081750327,0.0225145476
Li,0,0.0111244279,1.7040016293,-0.0196771946
O,0,-1.3656962177,0.5911638225,-0.0220988572
C,0,-1.3141723991,-0.6918421795,-0.0057531321
H,0,1.600155595,-1.2649355539,-0.8872943865
H,0,1.5812422906,-1.2428835292,0.9513311982
H,0,-1.5973480018,-1.2449100027,-0.921547776
H,0,-0.0075877991,-1.0560439173,0.0132013039
H,0,-1.6176658578,-1.2223548924,0.9168618106

Hydride transfer methyl

Transition structure

E(RB+HF-LYP) = -276.523036362

Zero-point correction= 0.097584 (Hartree/Particle)
Thermal correction to Energy= 0.104769
Thermal correction to Enthalpy= 0.105713
Thermal correction to Gibbs Free Energy= 0.066522

Sum of electronic and zero-point Energies= -276.425452

Sum of electronic and thermal Energies= -276.418268
Sum of electronic and thermal Enthalpies= -276.417324
Sum of electronic and thermal Free Energies= -276.456514

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	65.743	24.125	82.483

O,0,1.7451303901,0.8523576244,-0.0686608323
C,0,1.7109954624,-0.4115802491,-0.1137119653
Li,0,0.3457839745,1.9704074522,-0.2275198731
O,0,-0.9961450074,0.8644125398,-0.3607021521
C,0,-0.9391377932,-0.4412811026,-0.3412475735
H,0,2.0198026409,-0.937256925,-1.0346644211
H,0,1.8565144409,-0.9976144208,0.8112644343
H,0,-1.1863481303,-0.9487815572,-1.2976025678
H,0,0.2765546709,-0.7840465196,-0.2550041607
C,0,-1.5694288796,-1.1509636635,0.8580714428
H,0,-2.6538566223,-0.9863037291,0.8479331034
H,0,-1.1743686282,-0.7371664092,1.7924781738
H,0,-1.3821060947,-2.2312640188,0.834387509

Hydride transfer fluoro

Transition structure

E(RB+HF-LYP) = -336.452674598

Zero-point correction= 0.061889 (Hartree/Particle)
Thermal correction to Energy= 0.068407
Thermal correction to Enthalpy= 0.069352
Thermal correction to Gibbs Free Energy= 0.031106

Sum of electronic and zero-point Energies= -336.390786
Sum of electronic and thermal Energies= -336.384267
Sum of electronic and thermal Enthalpies= -336.383323
Sum of electronic and thermal Free Energies= -336.421569

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	42.926	20.953	80.495

O,0,1.5072750923,0.800915039,0.6963539154

C,0,1.4625462466,-0.4837219446,0.6037642984
Li,0,0.2601874012,1.8944105934,0.1038121395
O,0,-0.7439331815,0.7792503854,-0.9056022209
C,0,-0.7607573051,-0.4610988683,-0.7340084425
H,0,2.2712874718,-0.9950082786,0.0475766912
H,0,1.118654749,-1.0657119623,1.4796421184
H,0,-0.7918734182,-1.1544100766,-1.5878885518
H,0,0.4583793154,-0.8135741033,-0.2018919009
F,0,-1.5727199175,-0.9585473196,0.2673973925

Hydride transfer hydroxy

Transition structure

E(RB+HF-LYP) = -312.430995167

Zero-point correction= 0.074927 (Hartree/Particle)
Thermal correction to Energy= 0.082150
Thermal correction to Enthalpy= 0.083094
Thermal correction to Gibbs Free Energy= 0.043456

Sum of electronic and zero-point Energies= -312.356069
Sum of electronic and thermal Energies= -312.348845
Sum of electronic and thermal Enthalpies= -312.347901
Sum of electronic and thermal Free Energies= -312.387540

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	51.550	23.030	83.427

O,0,1.7348430939,0.8641433254,-0.2111972128
C,0,1.7634525699,-0.3778302632,-0.1772657587
Li,0,0.2187996963,1.8943263051,-0.1100246758
O,0,-1.116397246,0.7965018451,-0.2627499069
C,0,-1.0183222865,-0.5191974492,-0.3005593599
H,0,2.1346103215,-0.9548896603,-1.039106913
H,0,1.6423268811,-0.9277626761,0.768825078
H,0,-1.5906015515,-1.0118378421,-1.1118351029
H,0,0.0911210172,-0.8542709623,-0.5157178484
O,0,-1.3382094197,-1.1738835312,0.9246284675
H,0,-1.6465288832,-0.4461446143,1.489408743

Hydride transfer amino

Starting structure A (H2COLiNH2)

E(RB+HF-LYP) = -178.047613865

Zero-point correction= 0.059650 (Hartree/Particle)
Thermal correction to Energy= 0.064205
Thermal correction to Enthalpy= 0.065149
Thermal correction to Gibbs Free Energy= 0.033259

Sum of electronic and zero-point Energies= -177.987963
Sum of electronic and thermal Energies= -177.983409
Sum of electronic and thermal Enthalpies= -177.982465
Sum of electronic and thermal Free Energies= -178.014355

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	40.289	14.703	67.120

Li,0,0.3667756997,1.3425594764,0.7611101686
O,0,0.4675285684,0.7415367537,-0.8575466268
C,0,-0.0652998516,-0.4520767743,-0.53641906
H,0,-1.0256758256,-0.6789923091,-1.0466039794
H,0,0.6096908777,-1.3177280735,-0.7072235345
N,0,-0.3933164188,-0.4801390657,0.9917549784
H,0,0.1060365383,-1.2366170983,1.4582507897
H,0,-1.3855931953,-0.6532008724,1.148848744

Starting structure B (H2NCH2OH)

E(RB+HF-LYP) = -171.067828272

Zero-point correction= 0.069852 (Hartree/Particle)
Thermal correction to Energy= 0.073848
Thermal correction to Enthalpy= 0.074792
Thermal correction to Gibbs Free Energy= 0.044771

Sum of electronic and zero-point Energies= -170.997976
Sum of electronic and thermal Energies= -170.993980
Sum of electronic and thermal Enthalpies= -170.993036
Sum of electronic and thermal Free Energies= -171.023058

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	46.340	12.502	63.186

H,0,-0.8958721403,-1.1628850967,0.2063741923
H,0,0.7648018411,-0.9794053085,0.822696591
C,0,-0.0308693901,-0.4807096499,0.2489873313
O,0,-0.3159348496,0.6926771173,0.9777143875
N,0,0.3148376915,-0.1442897312,-1.1232141833
H,0,-0.9072620489,1.2125854603,0.4075488722
H,0,0.2946921691,-0.9678072945,-1.7209853025
H,0,1.2524714764,0.2503813187,-1.1687741579

Transition structure

E(RB+HF-LYP) = -292.558472720

Zero-point correction= 0.087065 (Hartree/Particle)
Thermal correction to Energy= 0.094270
Thermal correction to Enthalpy= 0.095214
Thermal correction to Gibbs Free Energy= 0.055818

Sum of electronic and zero-point Energies= -292.471407
Sum of electronic and thermal Energies= -292.464203
Sum of electronic and thermal Enthalpies= -292.463259
Sum of electronic and thermal Free Energies= -292.502655

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	59.155	23.595	82.916

O,0,1.7162279881,0.8607935756,-0.245853446
C,0,1.691327513,-0.3951344253,-0.2347974275
Li,0,0.2336323294,1.8781248269,-0.0082581897
O,0,-1.1112837826,0.8113322283,-0.3425033486
C,0,-0.9875804889,-0.4926694566,-0.2789470933
H,0,2.075238978,-0.9595366426,-1.1017910065
H,0,1.6487218258,-0.9472596102,0.718324204
H,0,-1.4955675894,-1.0584216481,-1.0922089731
H,0,0.1775828265,-0.8021915686,-0.4963673343
N,0,-1.2341193983,-1.0567505661,1.0458464489
H,0,-1.5622836688,-2.0200684776,0.9861240705
H,0,-1.967789361,-0.4998257108,1.4790899475

Product structure (HCONH2)

E(RB+HF-LYP) = -169.888843174

Zero-point correction= 0.045272 (Hartree/Particle)
Thermal correction to Energy= 0.049266
Thermal correction to Enthalpy= 0.050210
Thermal correction to Gibbs Free Energy= 0.020075

Sum of electronic and zero-point Energies= -169.843571
Sum of electronic and thermal Energies= -169.839577
Sum of electronic and thermal Enthalpies= -169.838633
Sum of electronic and thermal Free Energies= -169.868768

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	30.915	10.919	63.424

C,0,-0.3043391394,-0.2897440392,0.
O,0,-0.9999411019,0.7076988558,0.
N,0,1.0578582804,-0.2921650621,0.
H,0,-0.7200849539,-1.317325955,0.
H,0,1.5883878899,-1.1503279515,0.
H,0,1.5522527529,0.5896827297,0.

Hydrogen Transfer Parent

Transition structure

E(UB+HF-LYP) = -80.3337472607

Zero-point correction= 0.074679 (Hartree/Particle)
Thermal correction to Energy= 0.079612
Thermal correction to Enthalpy= 0.080556
Thermal correction to Gibbs Free Energy= 0.048237

Sum of electronic and zero-point Energies= -80.259068
Sum of electronic and thermal Energies= -80.254136
Sum of electronic and thermal Enthalpies= -80.253192
Sum of electronic and thermal Free Energies= -80.285511

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	49.957	14.956	68.021

C,0,1.3423267892,-0.0271114634,0.1263324972
H,0,1.6974035136,0.8863574417,-0.3516338927
H,0,-1.6641410936,0.9343936452,0.3857967578
C,0,-1.3423023996,0.0271167832,-0.1263267894
H,0,-1.6976762776,-0.8853541785,0.3533312131
H,0,1.6641078304,-0.9334186639,-0.3875011128
H,0,1.5329373409,-0.0518256005,1.1996766134
H,0,-1.5327958018,0.0498144209,-1.1997416878
H,0,0.0000181505,0.0000010161,0.0000378619

Hydrogen Transfer Cl

Transition structure

E(UB+HF-LYP) = -539.929040266

Zero-point correction= 0.067196 (Hartree/Particle)
Thermal correction to Energy= 0.072702
Thermal correction to Enthalpy= 0.073647
Thermal correction to Gibbs Free Energy= 0.037360

Sum of electronic and zero-point Energies= -539.861844
Sum of electronic and thermal Energies= -539.856338
Sum of electronic and thermal Enthalpies= -539.855394
Sum of electronic and thermal Free Energies= -539.891681

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	45.621	16.685	76.372

C,0,2.1514727126,-0.0582977772,1.0068177489
C,0,-0.5312135414,-0.0039101271,0.7351435502
H,0,2.4908220845,0.8573368555,0.5232094093
H,0,-0.8690358933,0.9048621693,1.2325552928
H,0,-0.9025537125,-0.9175192711,1.1986461482
H,0,2.4572786708,-0.9671360637,0.4892103893
H,0,2.3296009357,-0.0816057672,2.0819411933
Cl,0,-0.9419847644,0.03575321,-0.9905373883
H,0,0.7860738829,-0.0304950671,0.861805374

Product structure

E(UB+HF-LYP) = -499.438328959

Zero-point correction= 0.022739 (Hartree/Particle)
Thermal correction to Energy= 0.026341
Thermal correction to Enthalpy= 0.027285
Thermal correction to Gibbs Free Energy= -0.001801

Sum of electronic and zero-point Energies= -499.415590
Sum of electronic and thermal Energies= -499.411988
Sum of electronic and thermal Enthalpies= -499.411044
Sum of electronic and thermal Free Energies= -499.440130

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	16.529	8.923	61.217

1	6	0	1.125607	0.000000	-0.018024
2	1	0	1.627936	0.954928	0.041819
3	1	0	1.627954	-0.954919	0.041819
4	17	0	-0.588796	0.000000	0.001442

Hydrogen Transfer F

Transition structure

E(UB+HF-LYP) = -179.554361424

Zero-point correction= 0.068463 (Hartree/Particle)
Thermal correction to Energy= 0.073880
Thermal correction to Enthalpy= 0.074824
Thermal correction to Gibbs Free Energy= 0.039463

Sum of electronic and zero-point Energies= -179.485898
Sum of electronic and thermal Energies= -179.480482
Sum of electronic and thermal Enthalpies= -179.479538
Sum of electronic and thermal Free Energies= -179.514899

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN

TOTAL	46.360	15.980	74.423

C,0,1.8206572415,-0.0444371713,0.5784628515
C,0,-0.8724062221,0.0099821189,0.3210507628
H,0,2.1386972396,0.8708149353,0.0795710973
H,0,-1.2371639557,0.9225092096,0.8034938554
H,0,-1.2708203136,-0.9060877798,0.7689206418
H,0,2.1051426496,-0.9517127632,0.0458748394
H,0,2.0565215159,-0.068467941,1.6426691035
F,0,-1.1018792466,0.0396897771,-1.0268053699
H,0,0.4350299667,-0.0175333407,0.5036371061

Product structure

E(UB+HF-LYP) = -139.064265819

Zero-point correction= 0.024911 (Hartree/Particle)
Thermal correction to Energy= 0.027941
Thermal correction to Enthalpy= 0.028885
Thermal correction to Gibbs Free Energy= 0.002160

Sum of electronic and zero-point Energies= -139.039355
Sum of electronic and thermal Energies= -139.036325
Sum of electronic and thermal Enthalpies= -139.035381
Sum of electronic and thermal Free Energies= -139.062105

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	17.533	7.476	56.246

C,0,0.086609912,-0.013367299,0.6518025741
H,0,-0.0976848041,0.9352586981,1.1457864208
H,0,-0.1333181194,-0.971682273,1.1112668319
F,0,-0.0320729499,0.0129585965,-0.6853187441

Hydrogen Transfer methyl

Transition structure

E(UB+HF-LYP) = -119.649088486

Zero-point correction= 0.104011 (Hartree/Particle)

Thermal correction to Energy= 0.110090
Thermal correction to Enthalpy= 0.111034
Thermal correction to Gibbs Free Energy= 0.074623

Sum of electronic and zero-point Energies= -119.545078
Sum of electronic and thermal Energies= -119.538999
Sum of electronic and thermal Enthalpies= -119.538054
Sum of electronic and thermal Free Energies= -119.574466

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	69.082	19.156	76.634

C,0,1.8526287105,-0.0464446377,0.6740221664
C,0,-0.8389273702,0.0071370935,0.3967254907
H,0,2.2048555531,0.8646166306,0.189702365
H,0,-1.1417532924,0.9023276593,0.9473523033
H,0,-1.1738198425,-0.8978352088,0.9116362002
H,0,2.1709737536,-0.9572962066,0.1664229699
H,0,2.0353574275,-0.063586661,1.7486200415
C,0,-1.1549165481,0.0421005436,-1.0837350458
H,0,0.4760833504,-0.0192198988,0.5427662011
H,0,-2.2392862767,0.0648816581,-1.2650679109
H,0,-0.7268979904,0.9298480084,-1.5642069949
H,0,-0.7582214359,-0.8404939778,-1.5993008436

Product structure

E(UB+HF-LYP) = -79.1578680889

Zero-point correction= 0.059662 (Hartree/Particle)
Thermal correction to Energy= 0.063615
Thermal correction to Enthalpy= 0.064559
Thermal correction to Gibbs Free Energy= 0.035543

Sum of electronic and zero-point Energies= -79.098206
Sum of electronic and thermal Energies= -79.094253
Sum of electronic and thermal Enthalpies= -79.093309
Sum of electronic and thermal Free Energies= -79.122325

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	39.919	11.055	61.068

C,0,0.0660189543,-0.0153756853,0.7926232635
H,0,0.036753617,0.9027792469,1.3708327455
H,0,0.0025216021,-0.9518796296,1.3377096266
C,0,-0.0361956658,0.0130466116,-0.6930796667
H,0,-1.0859917538,0.0386250973,-1.0375791443
H,0,0.4503070802,0.8995766764,-1.1182664823
H,0,0.4174697238,-0.8751269489,-1.1499583265

Hydrogen Transfer CHO

Transition structure

E(UB+HF-LYP) = -193.654991301

Zero-point correction= 0.085329 (Hartree/Particle)
Thermal correction to Energy= 0.091699
Thermal correction to Enthalpy= 0.092643
Thermal correction to Gibbs Free Energy= 0.054321

Sum of electronic and zero-point Energies= -193.569663
Sum of electronic and thermal Energies= -193.563292
Sum of electronic and thermal Enthalpies= -193.562348
Sum of electronic and thermal Free Energies= -193.600670

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	57.542	19.946	80.655

C,0,2.1334763617,0.1928548208,1.0097271611
C,0,-0.5709835794,0.2282428579,0.7059312453
H,0,2.4773893222,1.1221218199,0.5588368163
H,0,-0.8546255579,1.1417203637,1.2346931372
H,0,-0.8652621707,-0.6852427678,1.2256871541
H,0,2.4245971299,-0.7114474528,0.4788154784
H,0,2.232854818,0.1435789256,2.0924294602
C,0,-0.9095370278,0.2192869789,-0.7348582648
H,0,0.7040172317,0.2304527618,0.7974320727
O,0,-1.1414141918,-0.7875559359,-1.3804839407
H,0,-0.9053917653,1.2169558918,-1.2288234425

Product structure

E(UB+HF-LYP) = -153.171536282

Zero-point correction= 0.042712 (Hartree/Particle)
Thermal correction to Energy= 0.046230
Thermal correction to Enthalpy= 0.047174
Thermal correction to Gibbs Free Energy= 0.017795

Sum of electronic and zero-point Energies= -153.128824
Sum of electronic and thermal Energies= -153.125307
Sum of electronic and thermal Enthalpies= -153.124362
Sum of electronic and thermal Free Energies= -153.153741

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	29.010	10.538	61.832

C,0,0.0415418124,0.3232116042,1.1369325436
H,0,0.0775327366,1.2529937362,1.6969090324
H,0,0.0382773586,-0.6205627925,1.6734076971
C,0,-0.0016325719,0.3176527732,-0.2884008558
O,0,-0.0450958289,-0.722926704,-0.9589674003
H,0,0.0055010925,1.305796424,-0.7897676538

Hydrogen Transfer COOH

Transition structure

E(UB+HF-LYP) = -268.904825475

Zero-point correction= 0.091339 (Hartree/Particle)
Thermal correction to Energy= 0.098410
Thermal correction to Enthalpy= 0.099354
Thermal correction to Gibbs Free Energy= 0.058632

Sum of electronic and zero-point Energies= -268.813486
Sum of electronic and thermal Energies= -268.806416
Sum of electronic and thermal Enthalpies= -268.805472
Sum of electronic and thermal Free Energies= -268.846194

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN

TOTAL	61.753	23.073	85.707

C,0,2.2808935492,-0.0486731078,1.2650812469
C,0,-0.4106221981,0.0432552997,0.9991113327
H,0,2.6228068907,0.867166848,0.7855894488
H,0,-0.6940888047,0.9451197367,1.5386048524
H,0,-0.7281284221,-0.8806695949,1.4823256257
H,0,2.5607486352,-0.9644268806,0.7468194574
H,0,2.4245188115,-0.0761886499,2.3441378671
C,0,-0.7236515781,0.1245164134,-0.4461662673
H,0,0.88372931,0.0018939869,1.104199947
O,0,-0.7036934422,-1.1023884369,-1.0404158964
O,0,-0.9294090462,1.1437493704,-1.0752344026
H,0,-0.8844851519,-0.938374546,-1.9846326802

Product structure

E(UB+HF-LYP) = -228.416663658

Zero-point correction= 0.048369 (Hartree/Particle)
Thermal correction to Energy= 0.052589
Thermal correction to Enthalpy= 0.053533
Thermal correction to Gibbs Free Energy= 0.021541

Sum of electronic and zero-point Energies= -228.368294
Sum of electronic and thermal Energies= -228.364075
Sum of electronic and thermal Enthalpies= -228.363131
Sum of electronic and thermal Free Energies= -228.395122

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	33.000	14.157	67.331

C,0,0.0847560212,0.0136725708,1.4039069963
H,0,0.1580829556,0.9319749259,1.9718589017
H,0,0.0742897795,-0.9447033911,1.9088043132
C,0,0.0020785837,0.1038226043,-0.0369263681
O,0,-0.0843492981,-1.1173302993,-0.6377312039
O,0,0.0069865869,1.1480620499,-0.6732610669
H,0,-0.1344786751,-0.9380965902,-1.5946088176

Hydrogen Transfer NH2

Transition structure

E(UB+HF-LYP) = -135.679752216

Zero-point correction= 0.093544 (Hartree/Particle)
Thermal correction to Energy= 0.099481
Thermal correction to Enthalpy= 0.100425
Thermal correction to Gibbs Free Energy= 0.064339

Sum of electronic and zero-point Energies= -135.586209
Sum of electronic and thermal Energies= -135.580271
Sum of electronic and thermal Enthalpies= -135.579327
Sum of electronic and thermal Free Energies= -135.615413

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	62.425	18.685	75.949

C,0,1.9153342326,-0.0459979852,0.5971868104
C,0,-0.8325619921,0.0086178921,0.3644606346
H,0,2.2490228635,0.8701280417,0.1096316723
H,0,-1.1423239976,0.9020988993,0.9157597074
H,0,-1.1753702383,-0.8923502219,0.8830465639
H,0,2.2155033886,-0.9559141306,0.0772886178
H,0,2.1089051682,-0.068538123,1.6693188362
N,0,-1.3132418274,0.0420560228,-0.9864403676
H,0,0.439801027,-0.0167531683,0.4758980864
H,0,-1.0148397968,-0.7753201128,-1.5128312096
H,0,-0.9846390661,0.8665372144,-1.4829143713

Product structure

E(UB+HF-LYP) = -95.1956111322

Zero-point correction= 0.050512 (Hartree/Particle)
Thermal correction to Energy= 0.053878
Thermal correction to Enthalpy= 0.054822
Thermal correction to Gibbs Free Energy= 0.027361

Sum of electronic and zero-point Energies= -95.145099
Sum of electronic and thermal Energies= -95.141733

Sum of electronic and thermal Enthalpies= -95.140789
Sum of electronic and thermal Free Energies= -95.168250

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	33.809	9.685	57.796

C,0,0.1916522651,-0.0162233236,0.71019403
H,0,0.0361251431,0.9048666631,1.2644371327
H,0,0.0018600158,-0.9501397394,1.2313079478
N,0,-0.1943504826,0.0149661884,-0.6369983462
H,0,0.0709442567,-0.8110859229,-1.1637830271
H,0,0.1016103719,0.8489356224,-1.1341378098

Hydrogen Transfer OH

Transition structure

E(UB+HF-LYP) = -155.538214245

Zero-point correction= 0.080625 (Hartree/Particle)
Thermal correction to Energy= 0.086419
Thermal correction to Enthalpy= 0.087363
Thermal correction to Gibbs Free Energy= 0.051476

Sum of electronic and zero-point Energies= -155.457590
Sum of electronic and thermal Energies= -155.451795
Sum of electronic and thermal Enthalpies= -155.450851
Sum of electronic and thermal Free Energies= -155.486738

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	54.229	17.779	75.530

C,0,1.8720018157,-0.0329410566,0.5827556791
C,0,-0.8497092488,0.0040626502,0.3388352975
H,0,2.1794159167,0.8205569017,-0.0208149973
H,0,-1.1815123891,0.9002053956,0.8676490771
H,0,-1.2183941316,-0.9101878996,0.8260428842
H,0,2.1809824572,-0.9948753579,0.1728808504
H,0,2.0867992046,0.0786603508,1.6454936609
O,0,-1.2039748686,0.1261000382,-1.006400834
H,0,0.4373877982,-0.0238367452,0.483775006

H,0,-0.9866353091,-0.7060525126,-1.4533656691

Product structure

E(UB+HF-LYP) = -115.052032509

Zero-point correction= 0.037513 (Hartree/Particle)
Thermal correction to Energy= 0.040788
Thermal correction to Enthalpy= 0.041732
Thermal correction to Gibbs Free Energy= 0.014552

Sum of electronic and zero-point Energies= -115.014520
Sum of electronic and thermal Energies= -115.011244
Sum of electronic and thermal Enthalpies= -115.010300
Sum of electronic and thermal Free Energies= -115.037481

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	25.595	8.882	57.206

C,0,0.1337811195,0.0161968209,0.6776672252
H,0,-0.0106970243,0.9713401067,1.1689759573
H,0,-0.1201347704,-0.903988955,1.2013471778
O,0,-0.0836864587,0.0806492482,-0.6736486303
H,0,-0.0023632523,-0.8097260625,-1.0471374436

Hydrogen Transfer phenyl

Transition structure

HtPh.log
E(UB+HF-LYP) = -311.391722803

Zero-point correction= 0.157473 (Hartree/Particle)
Thermal correction to Energy= 0.166261
Thermal correction to Enthalpy= 0.167205
Thermal correction to Gibbs Free Energy= 0.121305

Sum of electronic and zero-point Energies= -311.234250
Sum of electronic and thermal Energies= -311.225462
Sum of electronic and thermal Enthalpies= -311.224518
Sum of electronic and thermal Free Energies= -311.270418

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	104.330	32.211	96.605

C,0,2.6905719998,-0.0910984524,2.3091339844
C,0,-0.0187858628,-0.0343044436,1.932695896
H,0,3.031459979,0.8274106495,1.8341993287
H,0,-0.3165450295,0.8621356503,2.4830525934
H,0,-0.349769683,-0.9382955252,2.4507759395
H,0,2.9977506421,-1.003451433,1.8005282578
H,0,2.8045381305,-0.1131047172,3.3917808741
C,0,-0.3442129622,-0.0024227834,0.4897292788
H,0,1.2421545408,-0.0604424457,2.0913660341
C,0,-0.5006339545,-1.1924177347,-0.244636778
C,0,-0.7620209434,-1.1640282696,-1.6128823411
C,0,-0.8715807635,0.0570338827,-2.2831098897
C,0,-0.7175404464,1.2484174981,-1.5696132445
C,0,-0.4561895631,1.2180881931,-0.2014022066
H,0,-0.419407673,-2.1474728007,0.2700067563
H,0,-0.8844721821,-2.0967165106,-2.1578462941
H,0,-1.0780130583,0.0799708958,-3.3497342473
H,0,-0.8051771389,2.2039207762,-2.0807108246
H,0,-0.3401635522,2.1504381192,0.3470933867

Product structure

E(UB+HF-LYP) = -270.915143405

Zero-point correction= 0.114949 (Hartree/Particle)
Thermal correction to Energy= 0.120619
Thermal correction to Enthalpy= 0.121563
Thermal correction to Gibbs Free Energy= 0.085280

Sum of electronic and zero-point Energies= -270.800194
Sum of electronic and thermal Energies= -270.794525
Sum of electronic and thermal Enthalpies= -270.793580
Sum of electronic and thermal Free Energies= -270.829864

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	75.689	22.920	76.364

C,0,0.2895567016,-0.0479380233,2.3840475789
H,0,0.3750233208,0.8684543759,2.9590673872
H,0,0.3406753921,-0.9868060124,2.9259340029
C,0,0.1199147672,-0.0198635413,0.9879269677
C,0,0.0079389669,-1.2227617655,0.2283121726
C,0,-0.1591705278,-1.1889170205,-1.1470212729
C,0,-0.2219299024,0.036720002,-1.8260249813
C,0,-0.1143114424,1.234177027,-1.1037466439
C,0,0.0530270884,1.2127014578,0.271807649
H,0,0.0558555738,-2.1759399293,0.7492495783
H,0,-0.2421614158,-2.1196084657,-1.7026094946
H,0,-0.3529413986,0.0583999211,-2.9041502238
H,0,-0.1624412526,2.1865400531,-1.625704974
H,0,0.1358358717,2.144251241,0.8264049031

Hydrogen Transfer SH

Transition structure

E(UB+HF-LYP) = -478.521038103

Zero-point correction= 0.075508 (Hartree/Particle)
Thermal correction to Energy= 0.081644
Thermal correction to Enthalpy= 0.082588
Thermal correction to Gibbs Free Energy= 0.045134

Sum of electronic and zero-point Energies= -478.445531
Sum of electronic and thermal Energies= -478.439394
Sum of electronic and thermal Enthalpies= -478.438450
Sum of electronic and thermal Free Energies= -478.475904

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	51.233	19.152	78.829

C,0,2.2239613494,-0.1378964423,0.9785359283
C,0,-0.4767150066,-0.0659084882,0.7411197267
H,0,2.5644862762,0.6936251349,0.3623301831
H,0,-0.772210409,0.8011633113,1.3350113551
H,0,-0.8360361723,-0.9937815505,1.1915144266
H,0,2.5181330662,-1.1170150716,0.6008405855
H,0,2.4056832327,-0.0041925877,2.0446663147
S,0,-1.033070454,0.1853133083,-0.9528165348

H,0,0.8203145805,-0.1042833706,0.8302906594
H,0,-0.654721366,-1.0176992161,-1.4375228971

Product structure

E(UB+HF-LYP) = -438.034117343

Zero-point correction= 0.031929 (Hartree/Particle)
Thermal correction to Energy= 0.035726
Thermal correction to Enthalpy= 0.036670
Thermal correction to Gibbs Free Energy= 0.007283

Sum of electronic and zero-point Energies= -438.002188
Sum of electronic and thermal Energies= -437.998391
Sum of electronic and thermal Enthalpies= -437.997447
Sum of electronic and thermal Free Energies= -438.026834

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	22.418	10.819	61.851

C,0,0.1372559905,-0.086297984,1.1389109516
H,0,0.1451781566,0.8221121128,1.7273465637
H,0,-0.0550684522,-1.0399502338,1.6133275855
S,0,-0.0596711891,0.1196347293,-0.5774793399
H,0,0.0410933775,-1.1785296432,-0.93447042

Hydrogen Transfer vinyl

Transition structure

E(UB+HF-LYP) = -157.732129875

Zero-point correction= 0.109145 (Hartree/Particle)
Thermal correction to Energy= 0.115851
Thermal correction to Enthalpy= 0.116795
Thermal correction to Gibbs Free Energy= 0.078012

Sum of electronic and zero-point Energies= -157.622984
Sum of electronic and thermal Energies= -157.616279
Sum of electronic and thermal Enthalpies= -157.615335
Sum of electronic and thermal Free Energies= -157.654117

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	72.697	22.035	81.624

C,0,2.1678033725,0.319152886,1.1097774133
C,0,-0.5433715579,0.2449969869,0.7085148116
H,0,2.4810282949,1.2658941357,0.6725904968
H,0,-0.8789835134,1.136879639,1.2461685005
H,0,-0.8320963972,-0.6663801683,1.2399711652
H,0,2.5165389151,-0.5643111066,0.5778887642
H,0,2.2594752467,0.2659533737,2.1933389784
C,0,-0.8715440982,0.236413876,-0.7264419414
H,0,0.7130915538,0.2939558627,0.8630141798
C,0,-1.2109599449,-0.8503840488,-1.4373146607
H,0,-0.792962837,1.1931103507,-1.2450078037
H,0,-1.4135729557,-0.7965215446,-2.5032486045
H,0,-1.3040849355,-1.8296587426,-0.9719294132

Product structure

E(UB+HF-LYP) = -117.260354152

Zero-point correction= 0.066350 (Hartree/Particle)
Thermal correction to Energy= 0.070173
Thermal correction to Enthalpy= 0.071117
Thermal correction to Gibbs Free Energy= 0.041201

Sum of electronic and zero-point Energies= -117.194004
Sum of electronic and thermal Energies= -117.190181
Sum of electronic and thermal Enthalpies= -117.189237
Sum of electronic and thermal Free Energies= -117.219153

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	44.034	12.734	62.964

C,0,0.0821291102,0.4185270224,1.1703074652
H,0,0.1350075437,1.3541983332,1.7169331049
H,0,0.100960722,-0.4992544021,1.7522467662
C,0,-0.0058476703,0.3884479744,-0.2126729888
C,0,-0.0769738103,-0.7623412144,-0.9820403908
H,0,-0.0204017372,1.3449081154,-0.7363768516

H,0,-0.1444944915,-0.7204645142,-2.0640568848
H,0,-0.0669178147,-1.7471902269,-0.5223106486

Hydrogen Transfer ethynyl

Transition structure

E(UB+HF-LYP) = -156.478239557

Zero-point correction= 0.084792 (Hartree/Particle)
Thermal correction to Energy= 0.091299
Thermal correction to Enthalpy= 0.092243
Thermal correction to Gibbs Free Energy= 0.054453

Sum of electronic and zero-point Energies= -156.393447
Sum of electronic and thermal Energies= -156.386941
Sum of electronic and thermal Enthalpies= -156.385997
Sum of electronic and thermal Free Energies= -156.423786

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	57.291	21.577	79.535

C,0,2.0739077939,-0.0579636711,1.0977037981
C,0,-0.6314087836,-0.0020994031,0.7406007819
H,0,2.410626876,0.8608742421,0.6206114586
H,0,-0.9346522901,0.8934588962,1.2913183021
H,0,-0.967438035,-0.9056388528,1.2582608861
H,0,2.3770764006,-0.9711384664,0.5883309996
H,0,2.1905582678,-0.0791741106,2.1801739419
C,0,-0.9634291508,0.029554031,-0.6528926965
H,0,0.6369941239,-0.0279154184,0.8875548442
C,0,-1.1944958328,0.0556192954,-1.8424697183
H,0,-1.4206095034,0.0788721967,-2.8839034237

Product structure

E(UB+HF-LYP) = -116.001281359

Zero-point correction= 0.041011 (Hartree/Particle)
Thermal correction to Energy= 0.045160
Thermal correction to Enthalpy= 0.046105

Thermal correction to Gibbs Free Energy= 0.016472

Sum of electronic and zero-point Energies= -115.960270
Sum of electronic and thermal Energies= -115.956121
Sum of electronic and thermal Enthalpies= -115.955177
Sum of electronic and thermal Free Energies= -115.984810

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	28.339	13.074	62.368

1	6	0	-1.254638	0.000035	-0.000082
2	1	0	-1.815012	0.930075	0.000205
3	1	0	-1.815703	-0.929562	0.000205
4	6	0	0.114911	-0.000222	0.000123
5	6	0	1.343305	0.000119	-0.000255
6	1	0	2.409245	-0.000105	0.000871

Hydrogen Transfer ethylene / methyl

Transition structure

E(UB+HF-LYP) = -118.402067297

Zero-point correction= 0.079744 (Hartree/Particle)
Thermal correction to Energy= 0.085418
Thermal correction to Enthalpy= 0.086362
Thermal correction to Gibbs Free Energy= 0.050742

Sum of electronic and zero-point Energies= -118.322323
Sum of electronic and thermal Energies= -118.316649
Sum of electronic and thermal Enthalpies= -118.315705
Sum of electronic and thermal Free Energies= -118.351325

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	53.601	17.483	74.968

C,0,0.8494122797,0.2919527368,-0.0531029254
C,0,-1.7941454343,0.3811797585,-0.5087732821
H,0,1.4113051623,1.1189619157,-0.4824457999
H,0,-2.1478142064,1.3120879161,-0.0640953543
H,0,-2.1886866892,-0.5051732167,-0.0104047127

C,0,1.3234892918,-0.7225974725,0.6499546738
H,0,-1.9170909765,0.3503870823,-1.5919835767
H,0,-0.4917177927,0.3547261636,-0.2953545343
H,0,0.6750068716,-1.5065163373,1.0394016727
H,0,2.3864608074,-0.8276836603,0.8764115078

Product structure

E(UB+HF-LYP) = -77.9012082789

Zero-point correction= 0.036732 (Hartree/Particle)
Thermal correction to Energy= 0.039827
Thermal correction to Enthalpy= 0.040771
Thermal correction to Gibbs Free Energy= 0.014245

Sum of electronic and zero-point Energies= -77.864477
Sum of electronic and thermal Energies= -77.861381
Sum of electronic and thermal Enthalpies= -77.860437
Sum of electronic and thermal Free Energies= -77.886963

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	24.992	8.279	55.829

C,0,-0.2092902302,0.5142824169,-0.4662045403
H,0,0.2691410402,1.4005556856,-0.8654296187
C,0,0.0895601,-0.4534497004,0.3653101391
H,0,-0.6102665084,-1.2564462048,0.5987228166
H,0,1.0595062494,-0.5091057796,0.8720732094

Carbene rearrangement NH_2

Starting structure

E(RB+HF-LYP) = -133.893986316

Zero-point correction= 0.068058 (Hartree/Particle)
Thermal correction to Energy= 0.072051
Thermal correction to Enthalpy= 0.072995
Thermal correction to Gibbs Free Energy= 0.043147

Sum of electronic and zero-point Energies= -133.825928

Sum of electronic and thermal Energies= -133.821935
Sum of electronic and thermal Enthalpies= -133.820991
Sum of electronic and thermal Free Energies= -133.850839

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	45.213	12.315	62.821

C,0,0.4845971235,-0.4331246447,0.0384070854
C,0,0.5162208002,1.0688770121,0.1168156616
H,0,-0.4598380101,1.589565097,0.0219075345
H,0,1.1896106506,1.4485683162,-0.6627157973
H,0,0.9753399838,1.3626914057,1.0697858816
N,0,-0.7425799116,-0.8686358012,-0.134930846
H,0,-1.5821838908,-0.2715783824,-0.2085912039
H,0,-0.9297768948,-1.8633100326,-0.2072069748

Transition structure

E(RB+HF-LYP) = -133.839596518

Zero-point correction= 0.063779 (Hartree/Particle)
Thermal correction to Energy= 0.067665
Thermal correction to Enthalpy= 0.068609
Thermal correction to Gibbs Free Energy= 0.039137

Sum of electronic and zero-point Energies= -133.775817
Sum of electronic and thermal Energies= -133.771932
Sum of electronic and thermal Enthalpies= -133.770988
Sum of electronic and thermal Free Energies= -133.800460

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	42.460	12.253	62.029

C,0,0.4558930656,-0.2897118584,-0.063608664
C,0,0.4851259425,1.1079380218,-0.0808906985
H,0,-0.4050654775,1.7612928696,-0.1168720582
H,0,1.4370404395,1.6076795118,-0.2440199556
H,0,0.9614194298,0.3340648772,0.9361725929
N,0,-0.7444065526,-0.8984560451,0.0431632881
H,0,-1.6342998232,-0.418641256,-0.0934077618
H,0,-0.7943627485,-1.9045606672,0.0829803412

Product structure

E(RB+HF-LYP) = -133.942723440

Zero-point correction= 0.069228 (Hartree/Particle)
Thermal correction to Energy= 0.073111
Thermal correction to Enthalpy= 0.074055
Thermal correction to Gibbs Free Energy= 0.044596

Sum of electronic and zero-point Energies= -133.873495
Sum of electronic and thermal Energies= -133.869612
Sum of electronic and thermal Enthalpies= -133.868668
Sum of electronic and thermal Free Energies= -133.898127

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	45.878	12.688	62.002

C,0,0.3903036776,-0.1357471293,0.1371050363
C,0,0.4916096292,1.1400274645,-0.2567359953
H,0,-0.360091353,1.6953663214,-0.6430851085
H,0,1.4336178193,1.6693431787,-0.1737883265
H,0,1.2624160893,-0.6596262434,0.5251640061
N,0,-0.7765293444,-0.9026119811,0.1944189688
H,0,-1.5485769483,-0.5256677186,-0.3450703111
H,0,-0.6431400371,-1.8868136811,-0.0063672871

Carbene rearrangement F

Starting structure

E(RB+HF-LYP) = -177.736285554

Zero-point correction= 0.041154 (Hartree/Particle)
Thermal correction to Energy= 0.044392
Thermal correction to Enthalpy= 0.045336
Thermal correction to Gibbs Free Energy= 0.016746

Sum of electronic and zero-point Energies= -177.695132
Sum of electronic and thermal Energies= -177.691894
Sum of electronic and thermal Enthalpies= -177.690949

Sum of electronic and thermal Free Energies= -177.719540

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	27.856	9.074	60.174

C,0,0.4708713532,-0.46436239,0.0352297212
C,0,0.4568623498,1.0340174968,0.1077784591
H,0,-0.5250951033,1.513386435,0.0101033049
H,0,1.1478591898,1.3980734345,-0.6670826194
H,0,0.9344071989,1.3125166896,1.0589933643
F,0,-0.7915081671,-0.8491008,-0.1400070146

Transition structure

E(RB+HF-LYP) = -177.704524714

Zero-point correction= 0.038725 (Hartree/Particle)
Thermal correction to Energy= 0.042023
Thermal correction to Enthalpy= 0.042967
Thermal correction to Gibbs Free Energy= 0.014371

Sum of electronic and zero-point Energies= -177.665800
Sum of electronic and thermal Energies= -177.662502
Sum of electronic and thermal Enthalpies= -177.661558
Sum of electronic and thermal Free Energies= -177.690154

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	26.370	9.406	60.185

C,0,0.4671256809,-0.3571146172,-0.0877023225
C,0,0.4392802556,1.0370179175,-0.0965750812
H,0,-0.477989701,1.6377640908,-0.0759169508
H,0,1.3816334168,1.5562784285,-0.2568171886
H,0,0.8583658159,0.2957554415,0.9571450202
F,0,-0.8000494612,-0.8410241959,0.0534726157

Product structure

E(RB+HF-LYP) = -177.819641296

Zero-point correction= 0.044286 (Hartree/Particle)
Thermal correction to Energy= 0.047633
Thermal correction to Enthalpy= 0.048578
Thermal correction to Gibbs Free Energy= 0.019930

Sum of electronic and zero-point Energies= -177.775355
Sum of electronic and thermal Energies= -177.772008
Sum of electronic and thermal Enthalpies= -177.771064
Sum of electronic and thermal Free Energies= -177.799711

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	29.890	9.847	60.294

C,0,0.3696109054,-0.1730932013,0.1422250672
C,0,0.4369649103,1.0847777894,-0.2680198009
H,0,-0.4359006075,1.6083307394,-0.6426742683
H,0,1.3839664493,1.6106292406,-0.2318718118
H,0,1.1999645268,-0.7579601206,0.5279363547
F,0,-0.7763872514,-0.8812341543,0.1223753475

Ring Opening Cyclobutene

Starting structure

E(RB+HF-LYP) = -155.973264129

Zero-point correction= 0.086940 (Hartree/Particle)
Thermal correction to Energy= 0.090747
Thermal correction to Enthalpy= 0.091691
Thermal correction to Gibbs Free Energy= 0.061984

Sum of electronic and zero-point Energies= -155.886324
Sum of electronic and thermal Energies= -155.882517
Sum of electronic and thermal Enthalpies= -155.881573
Sum of electronic and thermal Free Energies= -155.911280

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	56.944	13.118	62.524

C,0,-0.4963173616,0.1304776409,0.9188563975
C,0,0.9449714671,0.1575242429,0.4415400291

C,0,0.6348452531,-0.1038831795,-0.8360157581
C,0,-0.8601883363,-0.1765364066,-0.5801407939
H,0,1.2248580545,-0.2252808688,-1.7410846358
H,0,1.8817716603,0.3307633082,0.9653680569
H,0,-0.753554974,-0.6664463372,1.6275987429
H,0,-0.8928240121,1.0781159392,1.3040583823
H,0,-1.4704008925,0.5909341869,-1.0722833063
H,0,-1.3297159701,-1.1535800146,-0.749096488

Transition structure

E(RB+HF-LYP) = -155.916553181

Zero-point correction= 0.084220 (Hartree/Particle)
Thermal correction to Energy= 0.087974
Thermal correction to Enthalpy= 0.088918
Thermal correction to Gibbs Free Energy= 0.059215

Sum of electronic and zero-point Energies= -155.832334
Sum of electronic and thermal Energies= -155.828579
Sum of electronic and thermal Enthalpies= -155.827635
Sum of electronic and thermal Free Energies= -155.857338

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	55.204	13.257	62.514

C,0,-0.684113,0.7370775114,-0.012016761
C,0,0.684113,0.7183733853,-0.16543077
H,0,-1.343499,1.5775005413,0.2002538616
H,0,1.343499,1.4831760751,-0.5734093627
C,0,1.063876,-0.6054201694,0.2044798402
C,0,-1.063876,-0.6368152659,-0.0530273856
H,0,1.887022,-1.1422739095,-0.2800861471
H,0,0.860769,-0.9462514395,1.2127907114
H,0,-1.887022,-1.0415175475,0.5463324375
H,0,-0.860769,-1.2099264885,-0.9499110427

Product structure

E(RB+HF-LYP) = -155.986483953

Zero-point correction= 0.085345 (Hartree/Particle)
Thermal correction to Energy= 0.090052
Thermal correction to Enthalpy= 0.090996
Thermal correction to Gibbs Free Energy= 0.059285

Sum of electronic and zero-point Energies= -155.901139
Sum of electronic and thermal Energies= -155.896432
Sum of electronic and thermal Enthalpies= -155.895488
Sum of electronic and thermal Free Energies= -155.927199

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	56.508	15.773	66.742

C,0,-0.8824559391,0.0774471901,1.3583047834
C,0,0.3408592321,-0.114138256,0.8481889359
C,0,0.7298576736,0.0883307413,-0.5551058322
C,0,-0.0706188445,-0.0544752062,-1.6191861743
H,0,1.7732842427,0.3585508061,-0.7209619435
H,0,1.1412410256,-0.428799677,1.5187434176
H,0,-1.0962347894,-0.1135874759,2.4059401067
H,0,-1.7065223427,0.4417369967,0.7497543469
H,0,0.2874468269,0.1330817111,-2.6273264368
H,0,-1.105067696,-0.373969176,-1.5193597676

Ring Opening Oxetane

Starting structure

E(RB+HF-LYP) = -191.864472004

Zero-point correction= 0.062986 (Hartree/Particle)
Thermal correction to Energy= 0.066563
Thermal correction to Enthalpy= 0.067507
Thermal correction to Gibbs Free Energy= 0.037616

Sum of electronic and zero-point Energies= -191.801486
Sum of electronic and thermal Energies= -191.797909
Sum of electronic and thermal Enthalpies= -191.796965
Sum of electronic and thermal Free Energies= -191.826856

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN

TOTAL	41.769	11.753	62.910

C,0,-0.5234589755,0.1126439807,0.8335744246
C,0,0.9380215762,0.1587468967,0.4497576184
C,0,0.5367602783,-0.1056071832,-0.8003056494
O,0,-0.8335446152,-0.1751398783,-0.5844784251
H,0,0.9457028419,-0.2574348593,-1.7936261849
H,0,1.8703891283,0.3293929763,0.9647030931
H,0,-0.8569959528,-0.7151588744,1.4668220351
H,0,-0.9986763695,1.0496176184,1.1397700951

Transition structure

E(RB+HF-LYP) = -191.823277952

Zero-point correction= 0.060525 (Hartree/Particle)
Thermal correction to Energy= 0.064068
Thermal correction to Enthalpy= 0.065012
Thermal correction to Gibbs Free Energy= 0.035025

Sum of electronic and zero-point Energies= -191.762753
Sum of electronic and thermal Energies= -191.759210
Sum of electronic and thermal Enthalpies= -191.758266
Sum of electronic and thermal Free Energies= -191.788253

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	40.203	11.417	63.114

C,0,-0.6918762198,0.6345857066,-0.0591773552
C,0,0.6720674352,0.7336119164,-0.1856064665
H,0,-1.471431852,1.394212314,0.0405288416
H,0,1.331149016,1.4975447065,-0.5748275811
C,0,0.9656141132,-0.6294968006,0.1583456788
O,0,-0.9947218959,-0.6327466035,0.0382958235
H,0,1.6642612867,-1.2540151297,-0.4100995475
H,0,0.758964745,-1.0079739978,1.1566605566

Product structure

E(RB+HF-LYP) = -191.909327451

Zero-point correction= 0.061700 (Hartree/Particle)
Thermal correction to Energy= 0.066051
Thermal correction to Enthalpy= 0.066995
Thermal correction to Gibbs Free Energy= 0.035285

Sum of electronic and zero-point Energies= -191.847627
Sum of electronic and thermal Energies= -191.843277
Sum of electronic and thermal Enthalpies= -191.842333
Sum of electronic and thermal Free Energies= -191.874043

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	41.447	13.664	66.739

C,0,-0.8946317521,-0.0648567381,1.2537094049
C,0,0.3640549794,-0.1495075918,0.8079944051
C,0,0.6887725357,0.0056565649,-0.6322993314
O,0,-0.1326654704,0.2157735356,-1.5045644718
H,0,1.7675433477,-0.0837257375,-0.8846182791
H,0,1.196917867,-0.33510214,1.4837291372
H,0,-1.1450125319,-0.1764604955,2.3044654358
H,0,-1.7072994981,0.1213466787,0.5565126083

Ring Opening Oxetane F1

Starting structure

E(RB+HF-LYP) = -291.100996089

Zero-point correction= 0.055494 (Hartree/Particle)
Thermal correction to Energy= 0.059668
Thermal correction to Enthalpy= 0.060612
Thermal correction to Gibbs Free Energy= 0.028528

Sum of electronic and zero-point Energies= -291.045502
Sum of electronic and thermal Energies= -291.041328
Sum of electronic and thermal Enthalpies= -291.040384
Sum of electronic and thermal Free Energies= -291.072468

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	37.442	14.148	67.527

C,0,-0.2758529318,-0.1587173013,0.5519627718
O,0,-0.6029625447,-0.4036709018,-0.8602839309
C,0,0.7747106427,-0.3856383721,-1.0704610747
C,0,1.1831930291,-0.0887387455,0.1676616908
H,0,1.1819516349,-0.6308109714,-2.04497606
H,0,2.1150965518,0.04395584,0.6933554875
H,0,-0.6034622431,-1.0145252457,1.1490010783
F,0,-0.8846877807,0.9588126783,1.0211011793

Transition structure

E(RB+HF-LYP) = -291.054148995

Zero-point correction= 0.052758 (Hartree/Particle)
Thermal correction to Energy= 0.057034
Thermal correction to Enthalpy= 0.057979
Thermal correction to Gibbs Free Energy= 0.025595

Sum of electronic and zero-point Energies= -291.001391
Sum of electronic and thermal Energies= -290.997114
Sum of electronic and thermal Enthalpies= -290.996170
Sum of electronic and thermal Free Energies= -291.028554

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	35.790	14.061	68.158

C,0,0.8428078614,-0.2449634251,-0.1750415619
C,0,0.3467843527,1.0948484108,-0.1910687961
C,0,-1.0011702956,0.8005430587,-0.2283517953
O,0,-1.1841233713,-0.4635964627,-0.4072343692
H,0,-1.8609032355,1.4717470148,-0.1172855046
H,0,0.9055338218,1.9822730089,-0.4598549581
H,0,1.5558315542,-0.6617856487,-0.8939953432
F,0,0.8602214798,-0.9984478823,0.9217537421

Product structure

E(RB+HF-LYP) = -255.219533173

Zero-point correction= 0.078465 (Hartree/Particle)
Thermal correction to Energy= 0.083725

Thermal correction to Enthalpy= 0.084670
Thermal correction to Gibbs Free Energy= 0.050019

Sum of electronic and zero-point Energies= -255.141068
Sum of electronic and thermal Energies= -255.135808
Sum of electronic and thermal Enthalpies= -255.134863
Sum of electronic and thermal Free Energies= -255.169514

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	52.539	17.656	72.929

C,0,-0.5986753619,-0.0327694964,1.6947340263
C,0,0.6441815977,-0.0222128873,1.1883832853
C,0,1.0331999814,0.0053701573,-0.2222074154
C,0,0.2474511887,0.0252239059,-1.3026367984
H,0,2.0987287785,0.0107204672,-0.4384285027
H,0,1.4818787777,-0.0354019256,1.8844419479
H,0,-0.7560934587,-0.053914962,2.7691234776
H,0,-1.4814663678,-0.0211703245,1.0666156057
H,0,0.5999207736,0.0454868116,-2.3289644534
F,0,-1.0999903265,0.022289984,-1.2336029624

Ring Opening Oxetane F2

Starting structure

E(RB+HF-LYP) = -291.100996089

Zero-point correction= 0.055494 (Hartree/Particle)
Thermal correction to Energy= 0.059668
Thermal correction to Enthalpy= 0.060612
Thermal correction to Gibbs Free Energy= 0.028528

Sum of electronic and zero-point Energies= -291.045502
Sum of electronic and thermal Energies= -291.041328
Sum of electronic and thermal Enthalpies= -291.040384
Sum of electronic and thermal Free Energies= -291.072468

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	37.442	14.148	67.527

C,0,-0.2758529318,-0.1587173013,0.5519627718
O,0,-0.6029625447,-0.4036709018,-0.8602839309
C,0,0.7747106427,-0.3856383721,-1.0704610747
C,0,1.1831930291,-0.0887387455,0.1676616908
H,0,1.1819516349,-0.6308109714,-2.04497606
H,0,2.1150965518,0.04395584,0.6933554875
H,0,-0.6034622431,-1.0145252457,1.1490010783
F,0,-0.8846877807,0.9588126783,1.0211011793

Transition structure

E(RB+HF-LYP) = -291.072597318

Zero-point correction= 0.053633 (Hartree/Particle)
Thermal correction to Energy= 0.057666
Thermal correction to Enthalpy= 0.058610
Thermal correction to Gibbs Free Energy= 0.026627

Sum of electronic and zero-point Energies= -291.018964
Sum of electronic and thermal Energies= -291.014931
Sum of electronic and thermal Enthalpies= -291.013987
Sum of electronic and thermal Free Energies= -291.045970

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	36.186	13.523	67.314

C,0,0.601088747,-0.297824363,0.2181201279
C,0,0.1432712002,1.0527536274,0.1022618248
C,0,-1.1909499908,0.738963256,0.1969620385
O,0,-1.3205246333,-0.548884348,0.0524528073
H,0,-2.0553257494,1.3588849937,0.4477195111
H,0,0.7149579182,1.9599573533,-0.0299186042
F,0,1.5630782611,-0.7764832915,-0.5621285593
H,0,0.5164008093,-0.9027730619,1.1176697208

Product structure

E(RB+HF-LYP) = -255.217661052

Zero-point correction= 0.077991 (Hartree/Particle)
Thermal correction to Energy= 0.083362

Thermal correction to Enthalpy= 0.084306
Thermal correction to Gibbs Free Energy= 0.049631

Sum of electronic and zero-point Energies= -255.139670
Sum of electronic and thermal Energies= -255.134299
Sum of electronic and thermal Enthalpies= -255.133355
Sum of electronic and thermal Free Energies= -255.168030

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	52.310	18.012	72.980

C,0,-0.9585982298,0.0562328768,1.9580934857
C,0,0.2609418697,-0.1610599204,1.44816771
C,0,0.666979293,0.0724382659,0.0584375438
C,0,-0.1379352071,-0.1148495661,-0.9884396201
H,0,1.6911594761,0.3847249668,-0.13654691
H,0,1.0434198084,-0.537435385,2.1075123939
H,0,-1.1878834915,-0.1794823332,2.9930572085
H,0,-1.7621177107,0.4857594047,1.3649302078
F,0,0.264855823,0.135353349,-2.2489826701
H,0,-1.1566068442,-0.488316732,-0.9456635858

Ring Opening Cyclobutene F in

Starting structure

E(RB+HF-LYP) = -255.204418390

Zero-point correction= 0.079507 (Hartree/Particle)
Thermal correction to Energy= 0.083946
Thermal correction to Enthalpy= 0.084890
Thermal correction to Gibbs Free Energy= 0.052264

Sum of electronic and zero-point Energies= -255.124911
Sum of electronic and thermal Energies= -255.120472
Sum of electronic and thermal Enthalpies= -255.119528
Sum of electronic and thermal Free Energies= -255.152155

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	52.677	15.553	68.668

C,0,-0.1778024719,0.4211677206,1.0959821327
C,0,1.258957148,0.4809827845,0.6019134354
C,0,0.9642745088,0.1379663968,-0.6603629778
C,0,-0.5247855541,0.1297283712,-0.4020789274
H,0,1.5491629347,-0.0219610748,-1.5610225705
H,0,2.1841341482,0.7513388463,1.1040377442
H,0,-0.4117742085,-0.4299611083,1.7437815816
H,0,-0.6026769698,1.3347350332,1.530515984
H,0,-1.0935880816,0.9253613241,-0.8985503016
F,0,-1.194346623,-1.0642871843,-0.6368316017

Transition structure

E(RB+HF-LYP) = -255.133731373

Zero-point correction= 0.076377 (Hartree/Particle)
Thermal correction to Energy= 0.080852
Thermal correction to Enthalpy= 0.081796
Thermal correction to Gibbs Free Energy= 0.049086

Sum of electronic and zero-point Energies= -255.057354
Sum of electronic and thermal Energies= -255.052879
Sum of electronic and thermal Enthalpies= -255.051935
Sum of electronic and thermal Free Energies= -255.084646

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	50.736	15.806	68.846

C,0,1.2948916784,-0.3039343132,0.5147226305
C,0,0.8858970475,0.9883621533,0.08848762
C,0,-0.4839741515,1.0161576463,0.2620860691
C,0,-0.8567179443,-0.3548977202,0.1929612611
H,0,-1.1411782639,1.8435130124,0.5261555862
H,0,1.533950461,1.7466677059,-0.3524847988
H,0,2.1306268581,-0.839722582,0.0559942575
H,0,1.0743224483,-0.6109454454,1.5294002183
H,0,-1.6815244354,-0.7872965289,0.7684475393
F,0,-0.7729752054,-1.0473714177,-0.9863398096

Product structure

E(RB+HF-LYP) = -255.219533173

Zero-point correction= 0.078465 (Hartree/Particle)
Thermal correction to Energy= 0.083725
Thermal correction to Enthalpy= 0.084670
Thermal correction to Gibbs Free Energy= 0.050019

Sum of electronic and zero-point Energies= -255.141068
Sum of electronic and thermal Energies= -255.135808
Sum of electronic and thermal Enthalpies= -255.134863
Sum of electronic and thermal Free Energies= -255.169514

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	52.539	17.656	72.929

C,0,-0.5986753619,-0.0327694964,1.6947340263
C,0,0.6441815977,-0.0222128873,1.1883832853
C,0,1.0331999814,0.0053701573,-0.2222074154
C,0,0.2474511887,0.0252239059,-1.3026367984
H,0,2.0987287785,0.0107204672,-0.4384285027
H,0,1.4818787777,-0.0354019256,1.8844419479
H,0,-0.7560934587,-0.053914962,2.7691234776
H,0,-1.4814663678,-0.0211703245,1.0666156057
H,0,0.5999207736,0.0454868116,-2.3289644534
F,0,-1.0999903265,0.022289984,-1.2336029624

Ring Opening Cyclobutene F out

Starting structure

E(RB+HF-LYP) = -255.204418390

Zero-point correction= 0.079507 (Hartree/Particle)
Thermal correction to Energy= 0.083946
Thermal correction to Enthalpy= 0.084890
Thermal correction to Gibbs Free Energy= 0.052264

Sum of electronic and zero-point Energies= -255.124911
Sum of electronic and thermal Energies= -255.120472
Sum of electronic and thermal Enthalpies= -255.119528
Sum of electronic and thermal Free Energies= -255.152155

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	52.677	15.553	68.668

C,0,-0.1778024719,0.4211677206,1.0959821327
C,0,1.258957148,0.4809827845,0.6019134354
C,0,0.9642745088,0.1379663968,-0.6603629778
C,0,-0.5247855541,0.1297283712,-0.4020789274
H,0,1.5491629347,-0.0219610748,-1.5610225705
H,0,2.1841341482,0.7513388463,1.1040377442
H,0,-0.4117742085,-0.4299611083,1.7437815816
H,0,-0.6026769698,1.3347350332,1.530515984
H,0,-1.0935880816,0.9253613241,-0.8985503016
F,0,-1.194346623,-1.0642871843,-0.6368316017

Transition structure

E(RB+HF-LYP) = -255.158068721

Zero-point correction= 0.077067 (Hartree/Particle)
Thermal correction to Energy= 0.081424
Thermal correction to Enthalpy= 0.082368
Thermal correction to Gibbs Free Energy= 0.049839

Sum of electronic and zero-point Energies= -255.081002
Sum of electronic and thermal Energies= -255.076645
Sum of electronic and thermal Enthalpies= -255.075701
Sum of electronic and thermal Free Energies= -255.108230

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	51.094	15.606	68.462

C,0,1.5075518861,-0.3723919617,0.0677933099
C,0,1.1188093048,0.9446724946,-0.2995086324
C,0,-0.2512607864,0.9832579486,-0.1360120055
C,0,-0.5989092067,-0.3871789152,-0.2144508762
H,0,-0.9297347788,1.8116336661,0.0517847484
H,0,1.759095188,1.696720797,-0.7585546371
H,0,2.336072289,-0.8949974251,-0.4203813582
H,0,1.311621401,-0.712973985,1.0775529535
F,0,-1.6289702363,-0.8826524785,0.5181753284
H,0,-0.473469159,-0.9666681442,-1.1209104368

Product structure

E(RB+HF-LYP) = -255.217661052

Zero-point correction= 0.077991 (Hartree/Particle)
Thermal correction to Energy= 0.083362
Thermal correction to Enthalpy= 0.084306
Thermal correction to Gibbs Free Energy= 0.049631

Sum of electronic and zero-point Energies= -255.139670
Sum of electronic and thermal Energies= -255.134299
Sum of electronic and thermal Enthalpies= -255.133355
Sum of electronic and thermal Free Energies= -255.168030

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	52.310	18.012	72.980

C,0,-0.9585982298,0.0562328768,1.9580934857
C,0,0.2609418697,-0.1610599204,1.44816771
C,0,0.666979293,0.0724382659,0.0584375438
C,0,-0.1379352071,-0.1148495661,-0.9884396201
H,0,1.6911594761,0.3847249668,-0.13654691
H,0,1.0434198084,-0.537435385,2.1075123939
H,0,-1.1878834915,-0.1794823332,2.9930572085
H,0,-1.7621177107,0.4857594047,1.3649302078
F,0,0.264855823,0.135353349,-2.2489826701
H,0,-1.1566068442,-0.488316732,-0.9456635858

Ring Opening Cyclobutene NH_2 in

Starting structure

E(RB+HF-LYP) = -211.317745678

Zero-point correction= 0.104320 (Hartree/Particle)
Thermal correction to Energy= 0.109308
Thermal correction to Enthalpy= 0.110252
Thermal correction to Gibbs Free Energy= 0.076792

Sum of electronic and zero-point Energies= -211.213426

Sum of electronic and thermal Energies= -211.208438
Sum of electronic and thermal Enthalpies= -211.207494
Sum of electronic and thermal Free Energies= -211.240953

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	68.592	18.167	70.421

C,0,-0.1763838443,0.4496782216,1.1043676376
C,0,1.2638947851,0.5397464673,0.6288826589
C,0,0.9817456556,0.231866532,-0.644563762
C,0,-0.5275587685,0.1311569262,-0.3953513041
H,0,1.5877687276,0.1149836941,-1.5409160195
H,0,2.1833880931,0.7920136733,1.1513619933
H,0,-0.4021428814,-0.3809281859,1.7837300597
H,0,-0.6222658429,1.3641885737,1.5162700371
H,0,-1.1005798372,0.9381926382,-0.8689537875
N,0,-1.2577051425,-1.1120156333,-0.614316415
H,0,-1.3978743761,-1.2611354368,-1.613039465
H,0,-0.6945448532,-1.8978944061,-0.2882492957

Transition structure

E(RB+HF-LYP) = -211.247770131

Zero-point correction= 0.100945 (Hartree/Particle)
Thermal correction to Energy= 0.106056
Thermal correction to Enthalpy= 0.107000
Thermal correction to Gibbs Free Energy= 0.073165

Sum of electronic and zero-point Energies= -211.146825
Sum of electronic and thermal Energies= -211.141714
Sum of electronic and thermal Enthalpies= -211.140770
Sum of electronic and thermal Free Energies= -211.174605

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	66.551	18.355	71.212

C,0,1.2780861544,-0.3141019917,0.5664374305
C,0,0.924454999,1.0096632941,0.1912885187
C,0,-0.4480724558,1.053346804,0.2884200295
C,0,-0.8700468793,-0.3074135396,0.1698777807

H,0,-1.0937063723,1.8969617175,0.5333535208
H,0,1.6144960792,1.7713327776,-0.1724120258
H,0,2.1252844949,-0.8465869423,0.1228083282
H,0,0.9995006709,-0.6693816605,1.5512522638
H,0,-1.7243106494,-0.6413805053,0.7854561764
N,0,-0.7219343608,-1.0223617754,-1.090407835
H,0,-0.549077979,-2.0102730929,-0.9115107327
H,0,-1.6251766289,-0.9931072664,-1.5722352422

Product structure

E(RB+HF-LYP) = -211.344427059

Zero-point correction= 0.103759 (Hartree/Particle)
Thermal correction to Energy= 0.109337
Thermal correction to Enthalpy= 0.110281
Thermal correction to Gibbs Free Energy= 0.075508

Sum of electronic and zero-point Energies= -211.240669
Sum of electronic and thermal Energies= -211.235090
Sum of electronic and thermal Enthalpies= -211.234146
Sum of electronic and thermal Free Energies= -211.268919

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	68.610	20.130	73.185

C,0,-0.564560283,0.1046251113,1.7486872063
C,0,0.6597843699,0.0259628296,1.1918666094
C,0,1.0373731933,0.2314568937,-0.2003364431
C,0,0.2548286868,0.0684989025,-1.2933493404
H,0,2.0739730083,0.4980666353,-0.3883485082
H,0,1.491052202,-0.2214990889,1.8549042589
H,0,-0.7080383126,-0.0957816906,2.806576455
H,0,-1.4412482201,0.4362653214,1.1995829168
H,0,0.6796606468,0.2422514909,-2.2795335311
N,0,-1.0878569339,-0.2777727322,-1.3192957169
H,0,-1.3847293865,-0.7571775655,-2.1607999352
H,0,-1.4202272027,-0.7409784003,-0.4785198308

Ring Opening Cyclobutene NH_2 out

Starting structure

E(RB+HF-LYP) = -211.317745678

Zero-point correction= 0.104320 (Hartree/Particle)
Thermal correction to Energy= 0.109308
Thermal correction to Enthalpy= 0.110252
Thermal correction to Gibbs Free Energy= 0.076792

Sum of electronic and zero-point Energies= -211.213426
Sum of electronic and thermal Energies= -211.208438
Sum of electronic and thermal Enthalpies= -211.207494
Sum of electronic and thermal Free Energies= -211.240953

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	68.592	18.167	70.421

C,0,-0.1763838443,0.4496782216,1.1043676376
C,0,1.2638947851,0.5397464673,0.6288826589
C,0,0.9817456556,0.231866532,-0.644563762
C,0,-0.5275587685,0.1311569262,-0.3953513041
H,0,1.5877687276,0.1149836941,-1.5409160195
H,0,2.1833880931,0.7920136733,1.1513619933
H,0,-0.4021428814,-0.3809281859,1.7837300597
H,0,-0.6222658429,1.3641885737,1.5162700371
H,0,-1.1005798372,0.9381926382,-0.8689537875
N,0,-1.2577051425,-1.1120156333,-0.614316415
H,0,-1.3978743761,-1.2611354368,-1.613039465
H,0,-0.6945448532,-1.8978944061,-0.2882492957

Transition structure

E(RB+HF-LYP) = -211.282760449

Zero-point correction= 0.101848 (Hartree/Particle)
Thermal correction to Energy= 0.106755
Thermal correction to Enthalpy= 0.107699
Thermal correction to Gibbs Free Energy= 0.074422

Sum of electronic and zero-point Energies= -211.180913

Sum of electronic and thermal Energies= -211.176005
Sum of electronic and thermal Enthalpies= -211.175061
Sum of electronic and thermal Free Energies= -211.208338

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	66.990	18.605	70.037

C,0,1.5194367661,-0.343053347,-0.0001799519
C,0,1.1218812499,0.9966735978,-0.314059993
C,0,-0.2425587896,1.0098853775,-0.1860465107
C,0,-0.6039998448,-0.3844160714,-0.233374908
H,0,-0.9328942148,1.8334900193,-0.0080530864
H,0,1.7629199048,1.7927214429,-0.6951075401
H,0,2.3585981904,-0.831972899,-0.5065923089
H,0,1.3756687853,-0.6940512689,1.016858747
N,0,-1.626525339,-0.9067844338,0.5455973153
H,0,-0.4664506345,-0.9154586845,-1.1681009307
H,0,-1.8386467454,-1.8887365848,0.4267343448
H,0,-1.6420742014,-0.6230383299,1.5170477486

Product structure

E(RB+HF-LYP) = -211.342271322

Zero-point correction= 0.102799 (Hartree/Particle)
Thermal correction to Energy= 0.108833
Thermal correction to Enthalpy= 0.109777
Thermal correction to Gibbs Free Energy= 0.073887

Sum of electronic and zero-point Energies= -211.239473
Sum of electronic and thermal Energies= -211.233439
Sum of electronic and thermal Enthalpies= -211.232494
Sum of electronic and thermal Free Energies= -211.268385

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	68.294	20.964	75.537

C,0,-0.9485187338,-0.0724190497,2.0162185425
C,0,0.2858468234,-0.116762966,1.4890193519
C,0,0.6735990749,0.0931003314,0.095320972
C,0,-0.1412688137,-0.0645959905,-0.9685738599

H,0,1.7136109155,0.3676105909,-0.0851780315
H,0,1.1156198766,-0.3237575328,2.1666179694
H,0,-1.1191836009,-0.2845382667,3.0673109178
H,0,-1.8263174278,0.1753238433,1.423534942
N,0,0.2198599088,0.0708831805,-2.303521395
H,0,-1.165458726,-0.4027836146,-0.8268861479
H,0,-0.5301665605,0.3174147655,-2.9362149062
H,0,1.0549260572,0.6186139994,-2.4764450181

Ring Opening Cyclobutene CHO in

Starting structure

E(RB+HF-LYP) = -269.290051383

Zero-point correction= 0.096247 (Hartree/Particle)
Thermal correction to Energy= 0.101939
Thermal correction to Enthalpy= 0.102883
Thermal correction to Gibbs Free Energy= 0.066831

Sum of electronic and zero-point Energies= -269.193805
Sum of electronic and thermal Energies= -269.188112
Sum of electronic and thermal Enthalpies= -269.187168
Sum of electronic and thermal Free Energies= -269.223221

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	63.968	19.762	75.879

C,0,0.0907326413,0.7088689799,1.2810212264
C,0,1.5552217252,0.6554465766,0.897944535
C,0,1.3146129993,0.4167620645,-0.3981248141
C,0,-0.2045276056,0.3940077539,-0.2417224904
H,0,1.9432386969,0.271393275,-1.2720583792
H,0,2.4636357225,0.7780272748,1.4813522147
H,0,-0.2581048296,-0.0477209516,1.9955879031
H,0,-0.2897639126,1.6868239407,1.5968224427
H,0,-0.7707334407,1.1587478626,-0.783397087
C,0,-0.8360406083,-0.958402896,-0.4678591403
O,0,-1.7826685354,-1.1700675924,-1.1928357379
H,0,-0.3469188649,-1.7868255355,0.0968229101

Transition structure

E(RB+HF-LYP) = -269.247706000

Zero-point correction= 0.094426 (Hartree/Particle)
Thermal correction to Energy= 0.099762
Thermal correction to Enthalpy= 0.100707
Thermal correction to Gibbs Free Energy= 0.065639

Sum of electronic and zero-point Energies= -269.153280
Sum of electronic and thermal Energies= -269.147944
Sum of electronic and thermal Enthalpies= -269.146999
Sum of electronic and thermal Free Energies= -269.182067

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	62.602	19.206	73.806

C,0,1.4130508858,0.0729651285,0.6534626643
C,0,1.0083334244,1.4015204222,0.2974892267
C,0,-0.3530252436,1.3997190266,0.4374375797
C,0,-0.7243775534,0.0111411413,0.4052764005
H,0,-1.0372254672,2.2345914447,0.5715953948
H,0,1.6646873433,2.1870340177,-0.0717312937
H,0,2.2389078572,-0.446861865,0.160203968
H,0,1.2052480702,-0.2907471663,1.6534681988
H,0,-1.5038707319,-0.4004908416,1.0543433535
C,0,-0.4984404749,-0.8142103555,-0.803307219
O,0,-0.9695866886,-1.9245342403,-0.965867702
H,0,0.1157002075,-0.314063845,-1.5830899177

Product structure

E(RB+HF-LYP) = -269.308544869

Zero-point correction= 0.095652 (Hartree/Particle)
Thermal correction to Energy= 0.101933
Thermal correction to Enthalpy= 0.102877
Thermal correction to Gibbs Free Energy= 0.065661

Sum of electronic and zero-point Energies= -269.212893
Sum of electronic and thermal Energies= -269.206612
Sum of electronic and thermal Enthalpies= -269.205668

Sum of electronic and thermal Free Energies= -269.242884

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	63.964	21.595	78.328

C,0,-0.2133244954,0.3762388075,2.1219449112
C,0,0.9389082492,0.0267032971,1.5320715965
C,0,1.2957212676,0.2649397925,0.1312932199
C,0,0.5096242041,0.1465264184,-0.9621592021
H,0,2.3309055741,0.5690294116,-0.0309296903
H,0,1.7234158228,-0.4203198833,2.1437287399
H,0,-0.3903929055,0.1751516541,3.1746127335
H,0,-0.9978544103,0.9021600961,1.5853696135
H,0,0.9045347607,0.418352047,-1.9387754381
C,0,-0.8519191427,-0.4108796217,-0.9890345308
O,0,-1.5552775943,-0.3969770108,-1.9856595703
H,0,-1.2024485845,-0.8897294013,-0.0534253648

Ring Opening Cyclobutene CHO out

Starting structure

E(RB+HF-LYP) = -269.290051383

Zero-point correction= 0.096247 (Hartree/Particle)
Thermal correction to Energy= 0.101939
Thermal correction to Enthalpy= 0.102883
Thermal correction to Gibbs Free Energy= 0.066831

Sum of electronic and zero-point Energies= -269.193805
Sum of electronic and thermal Energies= -269.188112
Sum of electronic and thermal Enthalpies= -269.187168
Sum of electronic and thermal Free Energies= -269.223221

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	63.968	19.762	75.879

C,0,0.0907326413,0.7088689799,1.2810212264
C,0,1.5552217252,0.6554465766,0.897944535
C,0,1.3146129993,0.4167620645,-0.3981248141
C,0,-0.2045276056,0.3940077539,-0.2417224904

H,0,1.9432386969,0.271393275,-1.2720583792
H,0,2.4636357225,0.7780272748,1.4813522147
H,0,-0.2581048296,-0.0477209516,1.9955879031
H,0,-0.2897639126,1.6868239407,1.5968224427
H,0,-0.7707334407,1.1587478626,-0.783397087
C,0,-0.8360406083,-0.958402896,-0.4678591403
O,0,-1.7826685354,-1.1700675924,-1.1928357379
H,0,-0.3469188649,-1.7868255355,0.0968229101

Transition structure

E(RB+HF-LYP) = -269.241026006

Zero-point correction= 0.093754 (Hartree/Particle)
Thermal correction to Energy= 0.099370
Thermal correction to Enthalpy= 0.100314
Thermal correction to Gibbs Free Energy= 0.064535

Sum of electronic and zero-point Energies= -269.147272
Sum of electronic and thermal Energies= -269.141656
Sum of electronic and thermal Enthalpies= -269.140712
Sum of electronic and thermal Free Energies= -269.176491

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	62.356	19.793	75.304

C,0,1.8138335855,-0.0241049745,-0.0409088388
C,0,1.4412689884,1.3169834391,-0.3798566148
C,0,0.0766676732,1.3332136494,-0.2771223972
C,0,-0.2999323303,-0.0579960466,-0.3376300261
H,0,-0.5975746336,2.1760237819,-0.1366312526
H,0,2.1164907793,2.0910084964,-0.7402469862
H,0,2.6197197576,-0.5609865227,-0.5506589451
H,0,1.6063269225,-0.3953277177,0.9555344139
C,0,-1.377010083,-0.6299480884,0.4921248126
H,0,-0.0745944652,-0.6302453779,-1.2332836344
O,0,-1.7167323367,-1.8003885055,0.4724605893
H,0,-1.8654766695,0.0937475106,1.1859600759

Product structure

E(RB+HF-LYP) = -269.313571604

Zero-point correction= 0.095357 (Hartree/Particle)
Thermal correction to Energy= 0.101879
Thermal correction to Enthalpy= 0.102823
Thermal correction to Gibbs Free Energy= 0.064876

Sum of electronic and zero-point Energies= -269.218214
Sum of electronic and thermal Energies= -269.211693
Sum of electronic and thermal Enthalpies= -269.210748
Sum of electronic and thermal Free Energies= -269.248696

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	63.930	21.773	79.867

C,0,-0.8998947018,-0.0347750315,2.5072945105
C,0,0.3355833243,-0.1309782304,1.9934367401
C,0,0.6913197415,0.0152209693,0.5830201968
C,0,-0.1350907927,-0.065996685,-0.4808588197
H,0,1.7482863449,0.1972249493,0.3808880442
H,0,1.1686426046,-0.3118150138,2.671168054
H,0,-1.0777298861,-0.161282458,3.5708393497
H,0,-1.7680644262,0.1859618605,1.8919034603
C,0,0.3720409605,0.123474775,-1.8433685092
H,0,-1.1963034194,-0.2823265349,-0.382533783
O,0,-0.3156702562,0.0762415962,-2.8476108283
H,0,1.4667796404,0.3206296426,-1.9085232095

Ring Opening Cyclobutene CCH in

Starting structure

E(RB+HF-LYP) = -232.111798845

Zero-point correction= 0.096007 (Hartree/Particle)
Thermal correction to Energy= 0.101729
Thermal correction to Enthalpy= 0.102673
Thermal correction to Gibbs Free Energy= 0.067139

Sum of electronic and zero-point Energies= -232.015792
Sum of electronic and thermal Energies= -232.010070
Sum of electronic and thermal Enthalpies= -232.009126

Sum of electronic and thermal Free Energies= -232.044660

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	63.836	21.063	74.788

C,0,0.0467408834,0.7671381944,1.2008147071
C,0,1.4785423416,0.8367624537,0.7076800565
C,0,1.1800735511,0.5133655393,-0.5556561126
C,0,-0.3263484339,0.4195412306,-0.3013343547
H,0,1.7583595835,0.3630211565,-1.4625351176
H,0,2.4077366876,1.0757261193,1.2175308773
H,0,-0.1768807008,-0.0401397496,1.9058748329
H,0,-0.3927475691,1.7003440473,1.5736729357
H,0,-0.8976082831,1.2277533268,-0.7782272815
C,0,-0.9794716145,-0.8596727306,-0.5486339448
C,0,-1.5182930753,-1.9212787931,-0.7560255456
H,0,-1.9863216327,-2.8618402658,-0.9373850824

Transition structure

Zero-point correction= 0.092957 (Hartree/Particle)
Thermal correction to Energy= 0.098717
Thermal correction to Enthalpy= 0.099661
Thermal correction to Gibbs Free Energy= 0.064070

Sum of electronic and zero-point Energies= -231.961819
Sum of electronic and thermal Energies= -231.956059
Sum of electronic and thermal Enthalpies= -231.955115
Sum of electronic and thermal Free Energies= -231.990705

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	61.946	21.333	74.906

C,0,1.3336626399,0.0054712782,0.8733700939
C,0,0.8993462876,1.3137823471,0.4995201827
C,0,-0.4672837346,1.2576577111,0.5100865137
C,0,-0.8029145778,-0.1458194572,0.411141346
H,0,-1.1916014639,2.0577225246,0.6559330109
H,0,1.5492731949,2.1379746525,0.2078318267
H,0,2.2158872913,-0.4741529626,0.4411065192
H,0,1.0434415628,-0.3892932498,1.8395939354

H,0,-1.6214164345,-0.532707143,1.0333549613
C,0,-0.6263585832,-0.9196635818,-0.7763724262
C,0,-0.5843759341,-1.6115264528,-1.7712199615
H,0,-0.5080407381,-2.1989548898,-2.656974745

Product structure

E(RB+HF-LYP) = -232.133862331

Zero-point correction= 0.095198 (Hartree/Particle)
Thermal correction to Energy= 0.101684
Thermal correction to Enthalpy= 0.102628
Thermal correction to Gibbs Free Energy= 0.064993

Sum of electronic and zero-point Energies= -232.038664
Sum of electronic and thermal Energies= -232.032179
Sum of electronic and thermal Enthalpies= -232.031234
Sum of electronic and thermal Free Energies= -232.068869

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	63.808	22.952	79.210

C,0,-0.1446830128,0.1127691488,1.923935983
C,0,1.041896893,0.28121796,1.3165910382
C,0,1.3435325627,0.2329582471,-0.1115956662
C,0,0.5305158541,0.0109815315,-1.1736385477
H,0,2.3901748879,0.402990667,-0.3574738777
H,0,1.9091987355,0.4811054989,1.945215112
H,0,-0.2210322962,0.1765970137,3.0057823281
H,0,-1.0577103071,-0.0894472766,1.3762079123
H,0,0.9847268824,0.0214183907,-2.1636038385
C,0,-0.8650744254,-0.2381190117,-1.1584054564
C,0,-2.0562848537,-0.4572610096,-1.2218538221
H,0,-3.1047760096,-0.6479454901,-1.2563288101

Ring Opening Cyclobutene CCH out

Starting structure

E(RB+HF-LYP) = -232.111798845

Zero-point correction= 0.096007 (Hartree/Particle)
Thermal correction to Energy= 0.101729
Thermal correction to Enthalpy= 0.102673
Thermal correction to Gibbs Free Energy= 0.067139

Sum of electronic and zero-point Energies= -232.015792
Sum of electronic and thermal Energies= -232.010070
Sum of electronic and thermal Enthalpies= -232.009126
Sum of electronic and thermal Free Energies= -232.044660

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	63.836	21.063	74.788

C,0,0.0467408834,0.7671381944,1.2008147071
C,0,1.4785423416,0.8367624537,0.7076800565
C,0,1.1800735511,0.5133655393,-0.5556561126
C,0,-0.3263484339,0.4195412306,-0.3013343547
H,0,1.7583595835,0.3630211565,-1.4625351176
H,0,2.4077366876,1.0757261193,1.2175308773
H,0,-0.1768807008,-0.0401397496,1.9058748329
H,0,-0.3927475691,1.7003440473,1.5736729357
H,0,-0.8976082831,1.2277533268,-0.7782272815
C,0,-0.9794716145,-0.8596727306,-0.5486339448
C,0,-1.5182930753,-1.9212787931,-0.7560255456
H,0,-1.9863216327,-2.8618402658,-0.9373850824

Transition structure

E(RB+HF-LYP) = -232.066629347

Zero-point correction= 0.093404 (Hartree/Particle)
Thermal correction to Energy= 0.099104
Thermal correction to Enthalpy= 0.100048
Thermal correction to Gibbs Free Energy= 0.064495

Sum of electronic and zero-point Energies= -231.973225
Sum of electronic and thermal Energies= -231.967526
Sum of electronic and thermal Enthalpies= -231.966581
Sum of electronic and thermal Free Energies= -232.002134

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN

TOTAL	62.189	21.148	74.827

C,0,1.8256153689,-0.2023995244,-0.1163938903
C,0,1.4725469829,1.1381164238,-0.4757198483
C,0,0.108602798,1.1810736315,-0.3760541838
C,0,-0.2960318889,-0.2061095117,-0.4167358872
H,0,-0.5574355586,2.0279579585,-0.2260395257
H,0,2.1558636132,1.903895032,-0.8399586017
H,0,2.639049585,-0.7489447205,-0.6044835314
H,0,1.6069447538,-0.5501071395,0.88638941
C,0,-1.3492106174,-0.7431309304,0.377586173
H,0,-0.0814218455,-0.7575844958,-1.3266217892
C,0,-2.2226766174,-1.2111096951,1.0772726467
H,0,-2.9960767048,-1.613858997,1.6909839776

Product structure

E(RB+HF-LYP) = -232.134646228

Zero-point correction= 0.094704 (Hartree/Particle)
Thermal correction to Energy= 0.101370
Thermal correction to Enthalpy= 0.102314
Thermal correction to Gibbs Free Energy= 0.064638

Sum of electronic and zero-point Energies= -232.039942
Sum of electronic and thermal Energies= -232.033276
Sum of electronic and thermal Enthalpies= -232.032332
Sum of electronic and thermal Free Energies= -232.070008

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	63.611	23.311	79.297

C,0,-1.0984400815,-0.0505667168,2.3963569883
C,0,0.1456201806,-0.2056727519,1.918959382
C,0,0.5731233435,-0.0149463179,0.533427426
C,0,-0.22465175,-0.1046904912,-0.5545369171
H,0,1.6293328126,0.1976369527,0.3779264455
H,0,0.9372555213,-0.4789224038,2.6164042995
H,0,-1.32727793,-0.2317216199,3.4422186818
H,0,-1.9234599573,0.2738960219,1.7671733816
C,0,0.2196016058,0.1124329286,-1.8842567794
H,0,-1.2740086689,-0.3708556933,-0.4310500678

C,0,0.5640057249,0.2902448493,-3.0324983552
H,0,0.8826040829,0.4491577417,-4.037383208

Hydride transfer vinyl

Starting structure

E(RB+HF-LYP) = -200.073572989

Zero-point correction= 0.075264 (Hartree/Particle)
Thermal correction to Energy= 0.081222
Thermal correction to Enthalpy= 0.082166
Thermal correction to Gibbs Free Energy= 0.046156

Sum of electronic and zero-point Energies= -199.998309
Sum of electronic and thermal Energies= -199.992351
Sum of electronic and thermal Enthalpies= -199.991407
Sum of electronic and thermal Free Energies= -200.027417

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	50.967	18.826	75.789

Li,0,-2.7716979081,-0.923215899,-0.3773468898
O,0,-1.4950543002,-0.0041473245,-0.073972061
C,0,-0.3255648243,0.6937079746,0.1455571988
C,0,0.8481337924,-0.2296974767,0.3850609217
H,0,-0.0740897885,1.360735384,-0.7023462274
H,0,-0.4190392429,1.3592231545,1.0300588648
C,0,1.9937675222,-0.2204338134,-0.2979463137
H,0,0.6986880119,-0.9572827512,1.1858847061
H,0,2.8055923131,-0.910939642,-0.0803422124
H,0,2.1663578907,0.4896300405,-1.105468814

Transition structure

E(RB+HF-LYP) = -314.597858322

Zero-point correction= 0.103199 (Hartree/Particle)
Thermal correction to Energy= 0.111593
Thermal correction to Enthalpy= 0.112538
Thermal correction to Gibbs Free Energy= 0.069468

Sum of electronic and zero-point Energies= -314.494660
Sum of electronic and thermal Energies= -314.486265
Sum of electronic and thermal Enthalpies= -314.485321
Sum of electronic and thermal Free Energies= -314.528391

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	70.026	27.718	90.648

C,0,2.1033593506,0.0181916217,-0.2377382724
O,0,1.98780623,1.2465933615,-0.2169184296
Li,0,0.4690444635,2.3056470497,-0.14750533
O,0,-0.8135369461,1.2142736814,-0.4098291599
C,0,-0.7977983348,-0.1255230247,-0.5080255561
C,0,-1.4411865021,-0.8534321291,0.6655625181
H,0,2.4284024095,-0.5068859849,-1.1498458673
H,0,2.0403273006,-0.5816126295,0.6836945105
H,0,-1.2268594754,-0.5075230375,-1.4595420376
H,0,0.292802146,-0.5298541982,-0.5585410546
C,0,-1.4472852273,-2.1730636445,0.8605438561
H,0,-1.9321484453,-0.1890461258,1.3772471983
H,0,-1.9387801794,-2.6258337803,1.7177409586
H,0,-0.9675671354,-2.8601586762,0.1636877242

Product structure

E(RB+HF-LYP) = -191.911973361

Zero-point correction= 0.061647 (Hartree/Particle)
Thermal correction to Energy= 0.066003
Thermal correction to Enthalpy= 0.066947
Thermal correction to Gibbs Free Energy= 0.035367

Sum of electronic and zero-point Energies= -191.850326
Sum of electronic and thermal Energies= -191.845970
Sum of electronic and thermal Enthalpies= -191.845026
Sum of electronic and thermal Free Energies= -191.876607

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	41.417	13.707	66.466

O,0,0.2215322774,1.6549749761,-0.6745220176

C,0,0.2084864657,0.4431322996,-0.5848198941
C,0,-0.223096475,-0.2967512055,0.6166744303
H,0,0.5319512923,-0.2015068533,-1.4338177075
C,0,-0.210632507,-1.6343050435,0.6455170947
H,0,-0.5469694518,0.3016723025,1.4651128988
H,0,-0.5234234972,-2.2006340152,1.5177100322
H,0,0.117638535,-2.2117875462,-0.2170588683

Hydride transfer fluoromethyl

Starting Material

E(RB+HF-LYP) = -261.225123623

Zero-point correction= 0.063589 (Hartree/Particle)
Thermal correction to Energy= 0.069374
Thermal correction to Enthalpy= 0.070318
Thermal correction to Gibbs Free Energy= 0.034506

Sum of electronic and zero-point Energies= -261.161535
Sum of electronic and thermal Energies= -261.155750
Sum of electronic and thermal Enthalpies= -261.154805
Sum of electronic and thermal Free Energies= -261.190618

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	43.533	17.541	75.374

Li,0,0.7173818404,2.9890563378,-0.438856923
O,0,0.5257904847,1.398408121,-0.5123502883
C,0,0.3625901845,0.033964459,-0.5753430225
C,0,-0.4717749984,-0.4573506842,0.6068830166
H,0,-0.1466202932,-0.2867939668,-1.5043755757
H,0,1.3264452957,-0.5099951702,-0.5506593835
H,0,-1.4754460078,-0.0132621287,0.5766713593
H,0,0.0120598129,-0.1740184834,1.5509030616
F,0,-0.6021999248,-1.8477829868,0.5726215166

Transition structure

E(RB+HF-LYP) = -375.748308447

Zero-point correction= 0.090368 (Hartree/Particle)
Thermal correction to Energy= 0.098204
Thermal correction to Enthalpy= 0.099149
Thermal correction to Gibbs Free Energy= 0.057637

Sum of electronic and zero-point Energies= -375.657941
Sum of electronic and thermal Energies= -375.650104
Sum of electronic and thermal Enthalpies= -375.649160
Sum of electronic and thermal Free Energies= -375.690672

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	61.624	25.961	87.369

1	6	0	-1.306388	-1.273443	0.163867
2	8	0	-2.205012	-0.454283	-0.276757
3	3	0	-2.054375	1.295088	-0.372282
4	8	0	-0.356867	1.537626	0.132601
5	6	0	0.460435	0.626739	0.499864
6	6	0	1.617157	0.283449	-0.428762
7	1	0	-1.459546	-1.728644	1.161596
8	1	0	-0.862264	-1.993713	-0.550283
9	1	0	0.721870	0.541652	1.571969
10	1	0	-0.223070	-0.597846	0.437419
11	1	0	2.345889	1.105791	-0.426883
12	1	0	1.249355	0.133915	-1.450460
13	9	0	2.250967	-0.870404	0.012992

Product structure

E(RB+HF-LYP) = -253.049209577

Zero-point correction= 0.048711 (Hartree/Particle)
Thermal correction to Energy= 0.053131
Thermal correction to Enthalpy= 0.054076
Thermal correction to Gibbs Free Energy= 0.021639

Sum of electronic and zero-point Energies= -253.000499
Sum of electronic and thermal Energies= -252.996078
Sum of electronic and thermal Enthalpies= -252.995134
Sum of electronic and thermal Free Energies= -253.027570

	E (Thermal)	CV	S

	KCAL/MOL	CAL/MOL-KELVIN	CAL/MOL-KELVIN
TOTAL	33.340	12.899	68.268

O,0,0.197374724,1.6917594735,-0.6624942139
C,0,0.2205259379,0.4860662631,-0.5846175768
C,0,-0.2552406157,-0.2697414517,0.645429058
H,0,0.5918430861,-0.1639118396,-1.4069606793
H,0,-1.3102748111,-0.0349596986,0.8370167146
H,0,0.3337188744,0.0395320303,1.5185888905
F,0,-0.1095552083,-1.6302983498,0.4429377664

Hydride transfer hydroxymethyl

Starting Material

E(RB+HF-LYP) = -237.200600893

Zero-point correction= 0.075278 (Hartree/Particle)
Thermal correction to Energy= 0.081562
Thermal correction to Enthalpy= 0.082507
Thermal correction to Gibbs Free Energy= 0.045900

Sum of electronic and zero-point Energies= -237.125323
Sum of electronic and thermal Energies= -237.119038
Sum of electronic and thermal Enthalpies= -237.118094
Sum of electronic and thermal Free Energies= -237.154701

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	51.181	19.482	77.046

Li,0,0.6005707824,3.0322022378,-0.4925866411
O,0,0.4712991639,1.4368431136,-0.5398225157
C,0,0.3650080387,0.0639748328,-0.5804046869
C,0,-0.4275720324,-0.4655520236,0.6174368975
H,0,-0.1437028221,-0.2886001343,-1.497759684
H,0,1.3540559895,-0.4324356347,-0.5693006837
H,0,-1.4295443675,-0.0046117549,0.6102382146
H,0,0.0796175463,-0.1483422747,1.5440684927
O,0,-0.5060422861,-1.887723424,0.5247829322
H,0,-1.0088097537,-2.2061112866,1.2886369874

Transition structure

E(RB+HF-LYP) = -351.726284404

Zero-point correction= 0.102010 (Hartree/Particle)
Thermal correction to Energy= 0.110363
Thermal correction to Enthalpy= 0.111307
Thermal correction to Gibbs Free Energy= 0.068951

Sum of electronic and zero-point Energies= -351.624274
Sum of electronic and thermal Energies= -351.615922
Sum of electronic and thermal Enthalpies= -351.614977
Sum of electronic and thermal Free Energies= -351.657334

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	69.254	27.937	89.146

C,0,1.8304836562,-0.0582420071,-0.2314008794
O,0,1.9261473463,1.2194754184,-0.1726609571
Li,0,0.580173326,2.3587568209,-0.3690610923
O,0,-0.8139183808,1.2793690243,-0.5163135091
C,0,-0.7643642441,-0.0105139953,-0.4959829659
C,0,-1.3380256544,-0.7225893287,0.7260075391
H,0,2.1928205508,-0.5793237581,-1.1373770135
H,0,1.9844528581,-0.6492241415,0.6905031818
H,0,-0.9802300689,-0.5540619929,-1.4366714436
H,0,0.5115805342,-0.3744290973,-0.3914428826
H,0,-2.4309929916,-0.5747501705,0.719896463
H,0,-0.9381718728,-0.2413850632,1.6321961096
O,0,-0.9931377904,-2.0986864541,0.644530853
H,0,-1.4012709346,-2.5562881605,1.393885605

Product structure

E(RB+HF-LYP) = -229.029276725

Zero-point correction= 0.060492 (Hartree/Particle)
Thermal correction to Energy= 0.065438
Thermal correction to Enthalpy= 0.066382
Thermal correction to Gibbs Free Energy= 0.032974

Sum of electronic and zero-point Energies= -228.968785

Sum of electronic and thermal Energies= -228.963839
Sum of electronic and thermal Enthalpies= -228.962895
Sum of electronic and thermal Free Energies= -228.996303

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	41.063	14.815	70.312

O,0,0.192909406,1.6948728051,-0.7203868824
C,0,0.220372668,0.4916861725,-0.6042021286
C,0,-0.2543568936,-0.2368278485,0.6424271217
H,0,0.5980300286,-0.1779705079,-1.4072983115
H,0,-1.3086641384,0.035529993,0.8147299801
H,0,0.3251020528,0.1431543988,1.4998195328
O,0,-0.0726740784,-1.6237913189,0.4264215187
H,0,-0.37244521,-2.0985157176,1.21512175

Hydride transfer CCH

Starting structure

E(RB+HF-LYP) = -198.818303986

Zero-point correction= 0.050931 (Hartree/Particle)
Thermal correction to Energy= 0.056754
Thermal correction to Enthalpy= 0.057698
Thermal correction to Gibbs Free Energy= 0.022279

Sum of electronic and zero-point Energies= -198.767373
Sum of electronic and thermal Energies= -198.761550
Sum of electronic and thermal Enthalpies= -198.760606
Sum of electronic and thermal Free Energies= -198.796025

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	35.614	18.381	74.547

Li,0,0.8646589695,2.6723733618,-0.4701098013
O,0,0.5682196077,1.1018262617,-0.6100904193
C,0,0.3160598388,-0.244219665,-0.729294866
C,0,-0.4119812116,-0.8083044238,0.43228664
H,0,-0.2825212084,-0.4734839543,-1.6335597884
H,0,1.2498101837,-0.8305434408,-0.8453616077
C,0,-1.0006957945,-1.2592604499,1.3878526187

H,0,-1.5273197417,-1.6569955521,2.2249077981

Transition structure

HydCCH.log
E(RB+HF-LYP) = -313.340920211

Zero-point correction= 0.077796 (Hartree/Particle)
Thermal correction to Energy= 0.085651
Thermal correction to Enthalpy= 0.086595
Thermal correction to Gibbs Free Energy= 0.045486

Sum of electronic and zero-point Energies= -313.263124
Sum of electronic and thermal Energies= -313.255270
Sum of electronic and thermal Enthalpies= -313.254325
Sum of electronic and thermal Free Energies= -313.295434

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	53.747	26.710	86.520

C,0,1.8467367985,-0.275980478,-0.2792113249
O,0,1.9133230452,0.9984029403,-0.2533492156
Li,0,0.5481211845,2.1420632814,-0.3017477426
O,0,-0.8015765451,1.0463612716,-0.6138784064
C,0,-0.7693034815,-0.2480983156,-0.5737035728
C,0,-1.318910356,-0.9324671083,0.6011761439
H,0,2.2458043591,-0.8145586625,-1.1588183404
H,0,1.9468640697,-0.8412335167,0.6658838843
H,0,-0.9956370338,-0.7896863369,-1.511625925
H,0,0.507913573,-0.6112194019,-0.484638368
C,0,-1.7695049939,-1.4989247963,1.5701441567
H,0,-2.1773883249,-1.9947814325,2.4218305357

Product structure

E(RB+HF-LYP) = -190.645525699

Zero-point correction= 0.037218 (Hartree/Particle)
Thermal correction to Energy= 0.041498
Thermal correction to Enthalpy= 0.042442
Thermal correction to Gibbs Free Energy= 0.011294

Sum of electronic and zero-point Energies= -190.608308
Sum of electronic and thermal Energies= -190.604028
Sum of electronic and thermal Enthalpies= -190.603084
Sum of electronic and thermal Free Energies= -190.634232

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	26.040	13.127	65.557

O,0,1.617793823,-0.4040720503,0.
C,0,0.7254509956,0.4203125412,0.
C,0,-0.6840199097,0.085819343,0.
H,0,0.9403267097,1.5070452759,0.
C,0,-1.8697707819,-0.154676674,0.
H,0,-2.9126391177,-0.3832001353,0.

Hydride transfer CHO

Starting structure

E(RB+HF-LYP) = -235.999860619

Zero-point correction= 0.050509 (Hartree/Particle)
Thermal correction to Energy= 0.056415
Thermal correction to Enthalpy= 0.057360
Thermal correction to Gibbs Free Energy= 0.020652

Sum of electronic and zero-point Energies= -235.949351
Sum of electronic and thermal Energies= -235.943445
Sum of electronic and thermal Enthalpies= -235.942501
Sum of electronic and thermal Free Energies= -235.979209

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	35.401	17.218	77.258

Li,0,0.780009203,2.8826809454,-0.3614948178
O,0,0.5558874791,1.2949095074,-0.4745020444
C,0,0.3653861294,-0.0546728643,-0.570556587
C,0,-0.461532332,-0.6172962213,0.586918463
H,0,-0.1564183275,-0.3619003852,-1.4998334404
H,0,1.3140225318,-0.6316919868,-0.5713311861
O,0,-0.8331422102,-1.7660310814,0.6855139086

H,0,-0.7027167484,0.1463366413,1.3693829099

Transition structure

E(RB+HF-LYP) = -350.521245974

Zero-point correction= 0.077786 (Hartree/Particle)
Thermal correction to Energy= 0.085552
Thermal correction to Enthalpy= 0.086496
Thermal correction to Gibbs Free Energy= 0.045351

Sum of electronic and zero-point Energies= -350.443460
Sum of electronic and thermal Energies= -350.435694
Sum of electronic and thermal Enthalpies= -350.434750
Sum of electronic and thermal Free Energies= -350.475895

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	53.684	25.613	86.597

C,0,1.8977636927,-0.1000230298,-0.1555849256
O,0,1.9167310539,1.1835971547,-0.1649071725
Li,0,0.5725049069,2.3168313868,-0.3572846619
O,0,-0.7728787177,1.1564223338,-0.43853936
C,0,-0.718406983,-0.1237203968,-0.4602638507
C,0,-1.2889050404,-0.8821011858,0.7284384158
H,0,2.2722152116,-0.6422943516,-1.0437190112
H,0,2.1249373151,-0.6253570414,0.7906930112
H,0,-0.854193796,-0.6639201775,-1.4153170362
H,0,0.6043472087,-0.4841745304,-0.2609191714
O,0,-1.6229265,-2.0447368945,0.6880065286
H,0,-1.3749373657,-0.2619411374,1.6490983875

Product structure

E(RB+HF-LYP) = -227.818628872

Zero-point correction= 0.037171 (Hartree/Particle)
Thermal correction to Energy= 0.041370
Thermal correction to Enthalpy= 0.042314
Thermal correction to Gibbs Free Energy= 0.010896

Sum of electronic and zero-point Energies= -227.781458
Sum of electronic and thermal Energies= -227.777259
Sum of electronic and thermal Enthalpies= -227.776315
Sum of electronic and thermal Free Energies= -227.807733

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	25.960	12.125	66.125

O,0,0.2784019322,1.5999624886,-0.6101721598
C,0,0.2143606913,0.3922258125,-0.6174880955
C,0,-0.2145937643,-0.3920459447,0.6183244463
H,0,0.4561540455,-0.2327419596,-1.501264359
O,0,-0.2781796422,-1.5999238437,0.6093193142
H,0,-0.4565339272,0.2313535934,1.5030690194

Hydride transfer ethyl

Starting structure

E(RB+HF-LYP) = -201.311181415

Zero-point correction= 0.099115 (Hartree/Particle)
Thermal correction to Energy= 0.105571
Thermal correction to Enthalpy= 0.106515
Thermal correction to Gibbs Free Energy= 0.069599

Sum of electronic and zero-point Energies= -201.212067
Sum of electronic and thermal Energies= -201.205610
Sum of electronic and thermal Enthalpies= -201.204666
Sum of electronic and thermal Free Energies= -201.241583

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	66.247	20.648	77.698

Li,0,0.4351862763,3.1196925426,-0.5237845105
O,0,0.3998221313,1.5198272983,-0.5459046804
C,0,0.3693983831,0.143084802,-0.5649476152
C,0,-0.407224349,-0.4499470902,0.6219032471
H,0,-0.0900286094,-0.2387033048,-1.5006719045
H,0,1.3937296392,-0.2841992924,-0.5426447789
H,0,-1.4235302598,-0.0327559185,0.6085420746

H,0,0.0633262447,-0.0958359232,1.5507316632
C,0,-0.4645271332,-1.9805681543,0.6109626587
H,0,-1.0257686936,-2.3717315827,1.4677376563
H,0,-0.9497185834,-2.3531117471,-0.3004224229
H,0,0.5419729777,-2.4167755913,0.647808944

Transition structure

E(RB+HF-LYP) = -315.836891393

Zero-point correction= 0.126140 (Hartree/Particle)
Thermal correction to Energy= 0.134688
Thermal correction to Enthalpy= 0.135632
Thermal correction to Gibbs Free Energy= 0.092847

Sum of electronic and zero-point Energies= -315.710751
Sum of electronic and thermal Energies= -315.702203
Sum of electronic and thermal Enthalpies= -315.701259
Sum of electronic and thermal Free Energies= -315.744045

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	84.518	29.038	90.051

C,0,1.9223207485,0.041393794,-0.248810848
O,0,1.94666875,1.3052296297,-0.1990373419
Li,0,0.5416295315,2.4147109225,-0.3591595098
O,0,-0.7927887647,1.3006896549,-0.4936711407
C,0,-0.7302605782,-0.0042779925,-0.4705845574
C,0,-1.3585053105,-0.7216002258,0.7314913268
H,0,2.2297131658,-0.4785908101,-1.1732816017
H,0,2.0781141041,-0.546464605,0.6733606674
H,0,-0.9777628495,-0.5168017378,-1.4259412413
H,0,0.4870970865,-0.3441944158,-0.3847878568
H,0,-2.4307249872,-0.4803969573,0.7235271864
H,0,-0.9484295258,-0.2775617724,1.6480216904
C,0,-1.1608549868,-2.2391276089,0.7216410664
H,0,-1.6589396208,-2.710475752,1.5758469558
H,0,-1.5731857212,-2.6877355685,-0.1906499806
H,0,-0.0980093661,-2.5075932255,0.7706286441

Product structure

E(RB+HF-LYP) = -193.143435357

Zero-point correction= 0.084880 (Hartree/Particle)
Thermal correction to Energy= 0.089960
Thermal correction to Enthalpy= 0.090904
Thermal correction to Gibbs Free Energy= 0.057225

Sum of electronic and zero-point Energies= -193.058556
Sum of electronic and thermal Energies= -193.053476
Sum of electronic and thermal Enthalpies= -193.052532
Sum of electronic and thermal Free Energies= -193.086210

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	56.451	15.843	70.882

O,0,0.6773411866,1.6049445555,-0.6094338349
C,0,0.0148927291,0.5921357876,-0.6419156607
C,0,-0.4942170063,-0.153149551,0.5719060908
H,0,-0.2659665794,0.1298615278,-1.618177796
H,0,-1.5921673097,-0.0731439242,0.569258143
H,0,-0.1228647516,0.3520696508,1.4690296068
C,0,-0.0957929001,-1.6379120958,0.54355244
H,0,-0.5350279418,-2.1715156703,1.392105524
H,0,-0.4437617712,-2.1264580607,-0.3743680628
H,0,0.9917619248,-1.7568148117,0.5963660429

1,5-sigmatropic parent

Starting structure

E(RB+HF-LYP) = -195.303982372

Zero-point correction= 0.114123 (Hartree/Particle)
Thermal correction to Energy= 0.120101
Thermal correction to Enthalpy= 0.121045
Thermal correction to Gibbs Free Energy= 0.085203

Sum of electronic and zero-point Energies= -195.189859
Sum of electronic and thermal Energies= -195.183882
Sum of electronic and thermal Enthalpies= -195.182938

Sum of electronic and thermal Free Energies= -195.218780

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	75.364	20.751	75.436

C,0,1.7215745505,-0.7184054766,0.2150221785
C,0,1.2849791163,0.4715798196,-0.2220701224
C,0,-0.0276958641,1.0836243571,0.0179779103
C,0,-1.2306122912,0.485499835,0.0881513581
C,0,-1.5469604282,-0.9703024334,-0.0978189151
H,0,-0.7389268246,-1.501641085,-0.6092377511
H,0,2.7211370929,-1.0715429789,-0.0235636954
H,0,1.1164229708,-1.3635481141,0.8448315327
H,0,1.9800439725,1.0891352481,-0.7939937637
H,0,-0.0104768943,2.1701260176,0.1119198792
H,0,-2.0897668808,1.1297156426,0.2760489392
H,0,-2.4693492318,-1.0918336783,-0.6792478407
H,0,-1.716794704,-1.4723876626,0.8656682433

Transition structure

E(RB+HF-LYP) = -195.248154656

Zero-point correction= 0.110650 (Hartree/Particle)
Thermal correction to Energy= 0.115272
Thermal correction to Enthalpy= 0.116217
Thermal correction to Gibbs Free Energy= 0.083370

Sum of electronic and zero-point Energies= -195.137504
Sum of electronic and thermal Energies= -195.132882
Sum of electronic and thermal Enthalpies= -195.131938
Sum of electronic and thermal Free Energies= -195.164785

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	72.335	17.717	69.132

C,0,1.3094993097,-0.9066451629,-0.0233218711
C,0,1.2116227678,0.5080950078,-0.0116824184
C,0,-0.0001330572,1.1843187667,0.1519350468
C,0,-1.2117427273,0.5078111123,-0.0115899684
C,0,-1.3092883978,-0.9069519077,-0.023222054

H,0,0.0001216371,-1.2018322249,-0.5085693353
H,0,2.1818873826,-1.3291605205,-0.5262895044
H,0,1.0687190157,-1.4589758059,0.8846903842
H,0,2.0459297361,1.0946725711,-0.3966171341
H,0,-0.0002625969,2.2702342252,0.0918861611
H,0,-2.0462166831,1.0941931142,-0.3964607921
H,0,-2.1816156533,-1.3296712028,-0.5261238656
H,0,-1.0683102098,-1.4592270546,0.8847716772

H to H transfer F

Transition structure

E(UB+HF-LYP) = -140.222799622

Zero-point correction= 0.037186 (Hartree/Particle)
Thermal correction to Energy= 0.040694
Thermal correction to Enthalpy= 0.041638
Thermal correction to Gibbs Free Energy= 0.013133

Sum of electronic and zero-point Energies= -140.185613
Sum of electronic and thermal Energies= -140.182106
Sum of electronic and thermal Enthalpies= -140.181162
Sum of electronic and thermal Free Energies= -140.209667

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	25.536	9.829	59.994

H,0,2.2568468587,-0.0589800297,0.8001053963
C,0,-0.028894632,-0.0094315884,0.5579855226
H,0,-0.3482238973,0.9089288311,1.0580383859
H,0,-0.3845998817,-0.9317919572,1.0250349552
F,0,-0.2958004393,0.0196979835,-0.7724928807
H,0,1.3115486661,-0.0388491653,0.7213440531

H to H transfer Cl

Transition structure

E(UB+HF-LYP) = -500.596121394

Zero-point correction= 0.035890 (Hartree/Particle)
Thermal correction to Energy= 0.039474
Thermal correction to Enthalpy= 0.040418
Thermal correction to Gibbs Free Energy= 0.010724

Sum of electronic and zero-point Energies= -500.560231
Sum of electronic and thermal Energies= -500.556648
Sum of electronic and thermal Enthalpies= -500.555704
Sum of electronic and thermal Free Energies= -500.585398

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	24.770	10.489	62.496

H,0,2.3991695353,-0.0710064536,1.3168188219
C,0,0.130493911,-0.0210264586,1.0294651889
H,0,-0.179855968,0.8931371248,1.5330101413
H,0,-0.21606395,-0.9396717873,1.500164726
Cl,0,-0.2503405562,0.017290429,-0.6888274183
H,0,1.4695763718,-0.0502374258,1.1832812879

H to H transfer CHO

Transition structure

E(UB+HF-LYP) = -154.321135999

Zero-point correction= 0.053793 (Hartree/Particle)
Thermal correction to Energy= 0.058211
Thermal correction to Enthalpy= 0.059155
Thermal correction to Gibbs Free Energy= 0.027591

Sum of electronic and zero-point Energies= -154.267343
Sum of electronic and thermal Energies= -154.262925
Sum of electronic and thermal Enthalpies= -154.261981
Sum of electronic and thermal Free Energies= -154.293545

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	36.528	13.814	66.432

H,0,2.4103968766,0.3167224582,1.3542384107
C,0,0.1447986116,0.2713977909,1.0398412329

H,0,-0.1565031373,1.1748659509,1.5756170982
H,0,-0.140232413,-0.6553946591,1.5394960992
C,0,-0.1508962543,0.2800885288,-0.4161225592
H,0,1.4119014183,0.3033685649,1.160072282
O,0,-0.4256589665,-0.7153378821,-1.0578371851
H,0,-0.083705156,1.2742228242,-0.9090384515

H to H transfer methyl

Transition structure

E(UB+HF-LYP) = -80.3188703623

Zero-point correction= 0.072790 (Hartree/Particle)
Thermal correction to Energy= 0.076976
Thermal correction to Enthalpy= 0.077920
Thermal correction to Gibbs Free Energy= 0.048078

Sum of electronic and zero-point Energies= -80.246081
Sum of electronic and thermal Energies= -80.241894
Sum of electronic and thermal Enthalpies= -80.240950
Sum of electronic and thermal Free Energies= -80.270793

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	48.303	13.026	62.809

H,0,2.2626903445,-0.0608594992,0.9381627611
C,0,-0.0215260504,-0.0119324929,0.6867432166
H,0,-0.2950816434,0.8895781975,1.2390379066
H,0,-0.3301696437,-0.9214494886,1.2064575578
C,0,-0.2907315638,0.0199935649,-0.7977218762
H,0,1.3401395972,-0.0412716604,0.8514344145
H,0,-1.3709007417,0.0446484692,-1.0037804911
H,0,0.1506163858,0.906570005,-1.2667789366
H,0,0.1162513866,-0.8655824554,-1.2986612548

H to H transfer NH_2

Transition structure

E(UB+HF-LYP) = -96.3519378151

Zero-point correction= 0.062472 (Hartree/Particle)
Thermal correction to Energy= 0.066436
Thermal correction to Enthalpy= 0.067380
Thermal correction to Gibbs Free Energy= 0.038139

Sum of electronic and zero-point Energies= -96.289466
Sum of electronic and thermal Energies= -96.285502
Sum of electronic and thermal Enthalpies= -96.284557
Sum of electronic and thermal Free Energies= -96.313799

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	41.689	12.331	61.544

H,0,2.3787049241,-0.0610805239,0.81128561
C,0,0.0463065986,-0.0119655078,0.6160978456
H,0,-0.2432766403,0.883079069,1.1741881269
H,0,-0.2784335391,-0.9145363038,1.1417546724
N,0,-0.4459343739,0.0217255233,-0.722229201
H,0,1.2985364373,-0.038183022,0.7143948284
H,0,-0.1723740878,-0.7985498459,-1.2560376543
H,0,-0.1394560687,0.8489850106,-1.2265682495

H to H transfer COOH

Transition structure

E(UB+HF-LYP) = -229.570891738

Zero-point correction= 0.059868 (Hartree/Particle)
Thermal correction to Energy= 0.064921
Thermal correction to Enthalpy= 0.065865
Thermal correction to Gibbs Free Energy= 0.031819

Sum of electronic and zero-point Energies= -229.511024
Sum of electronic and thermal Energies= -229.505971
Sum of electronic and thermal Enthalpies= -229.505027
Sum of electronic and thermal Free Energies= -229.539073

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	40.738	16.931	71.655

H,0,2.4289667664,-0.1354415131,1.5436288518
C,0,0.1694073618,0.0303433111,1.3097766366
H,0,-0.0607655251,0.9478989925,1.8468050745
H,0,-0.1657409782,-0.8818046705,1.8022456047
C,0,-0.1314518794,0.1139913864,-0.1416932398
H,0,1.4695957218,-0.0633896766,1.4145377928
O,0,-0.1139418882,-1.1103000619,-0.7319649459
O,0,-0.337277514,1.1377782252,-0.7602060129
H,0,-0.2900336611,-0.9530966235,-1.6783500342

H to H transfer vinyl

Transition structure

E(UB+HF-LYP) = -118.401334531

Zero-point correction= 0.077958 (Hartree/Particle)
Thermal correction to Energy= 0.082636
Thermal correction to Enthalpy= 0.083580
Thermal correction to Gibbs Free Energy= 0.051632

Sum of electronic and zero-point Energies= -118.323377
Sum of electronic and thermal Energies= -118.318699
Sum of electronic and thermal Enthalpies= -118.317754
Sum of electronic and thermal Free Energies= -118.349702

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	51.855	15.725	67.240

H,0,2.4221288508,0.5484089971,1.5044123148
C,0,0.1561931642,0.3436572834,1.0747779634
H,0,-0.2380095307,1.210024159,1.6136969291
H,0,-0.0897491298,-0.5894102936,1.5885936387
C,0,-0.1254542753,0.3358726207,-0.3714555583
H,0,1.3842112773,0.4631443622,1.2662765946
C,0,-0.4181945946,-0.7591820288,-1.0880231576
H,0,-0.0621439863,1.2970246355,-0.8822911913
H,0,-0.6015341608,-0.7101761211,-2.1576010013
H,0,-0.4901690862,-1.7411029911,-0.6248827696

H to H transfer ethynyl

Transition structure

E(UB+HF-LYP) = -117.146134066

Zero-point correction= 0.053475 (Hartree/Particle)
Thermal correction to Energy= 0.058021
Thermal correction to Enthalpy= 0.058965
Thermal correction to Gibbs Free Energy= 0.027766

Sum of electronic and zero-point Energies= -117.092659
Sum of electronic and thermal Energies= -117.088113
Sum of electronic and thermal Enthalpies= -117.087169
Sum of electronic and thermal Free Energies= -117.118368

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	36.409	15.242	65.664

H,0,2.4145111079,-0.0709805343,1.4729799433
C,0,0.1376554651,-0.0226778401,1.1268833307
H,0,-0.1573992021,0.8748457272,1.677912403
H,0,-0.1907468747,-0.9277802976,1.6457092188
C,0,-0.1848728801,0.0082064445,-0.2679245001
H,0,1.3891810553,-0.0486006092,1.2819518996
C,0,-0.4212169802,0.0337979205,-1.4557239374
H,0,-0.6449397155,0.0565565685,-2.4979628238

H to H transfer ethylene

Transition structure

E(UB+HF-LYP) = -79.0685333289

Zero-point correction= 0.048768 (Hartree/Particle)
Thermal correction to Energy= 0.052649
Thermal correction to Enthalpy= 0.053593
Thermal correction to Gibbs Free Energy= 0.024808

Sum of electronic and zero-point Energies= -79.019765
Sum of electronic and thermal Energies= -79.015884
Sum of electronic and thermal Enthalpies= -79.014940

Sum of electronic and thermal Free Energies= -79.043726

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	33.038	11.774	60.585

C,0,-0.0218945888,0.4712037051,-0.3146541419
H,0,-2.2939166472,0.5338994701,-0.8299665599
H,0,0.5255519158,1.303011974,-0.7473392838
C,0,0.374651393,-0.5387457721,0.4326521991
H,0,-1.4491991536,0.5287788343,-0.650404013
H,0,-0.3175611992,-1.3000668506,0.7890786174
H,0,1.4185842591,-0.6603710262,0.7306428964

S_N2 parent

Transition structure

E(RB+HF-LYP) = -239.522496449

Zero-point correction= 0.038192 (Hartree/Particle)
Thermal correction to Energy= 0.042234
Thermal correction to Enthalpy= 0.043178
Thermal correction to Gibbs Free Energy= 0.013743

Sum of electronic and zero-point Energies= -239.484304
Sum of electronic and thermal Energies= -239.480262
Sum of electronic and thermal Enthalpies= -239.479318
Sum of electronic and thermal Free Energies= -239.508754

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	26.502	11.889	61.952

C,0,0.,0.,-0.000553
F,0,0.,0.,1.80824
F,0,0.,0.,-1.808
H,0,1.078107037,0.,0.000386
H,0,-0.5390535185,-0.9336680821,0.000386
H,0,-0.5390535185,0.9336680821,0.000386

S_N2 F

Transition structure

E(RB+HF-LYP) = -338.766217399

Zero-point correction= 0.031856 (Hartree/Particle)
Thermal correction to Energy= 0.036122
Thermal correction to Enthalpy= 0.037066
Thermal correction to Gibbs Free Energy= 0.004769

Sum of electronic and zero-point Energies= -338.734361
Sum of electronic and thermal Energies= -338.730095
Sum of electronic and thermal Enthalpies= -338.729151
Sum of electronic and thermal Free Energies= -338.761448

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	22.667	13.110	67.975

C,0,0.,-0.2580633299,-0.0000036696
F,0,0.,-0.3793127739,1.758424892
F,0,0.,-0.3792864602,-1.7584352451
F,0,0.,1.0995524715,0.0000169796
H,0,0.953574741,-0.7600995788,-0.0000188104
H,0,-0.953574741,-0.7600995788,-0.0000188104

S_N2 Cl

Transition structure

E(RB+HF-LYP) = -699.128053288

Zero-point correction= 0.029654 (Hartree/Particle)
Thermal correction to Energy= 0.034294
Thermal correction to Enthalpy= 0.035238
Thermal correction to Gibbs Free Energy= 0.001476

Sum of electronic and zero-point Energies= -699.098399
Sum of electronic and thermal Energies= -699.093759
Sum of electronic and thermal Enthalpies= -699.092815

Sum of electronic and thermal Free Energies= -699.126577

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	21.520	14.493	71.058

C,0,0.,-0.6476547133,-0.0000175139
F,0,0.,-0.7669713688,1.7421121126
F,0,0.,-0.7668949068,-1.7421467092
Cl,0,0.,1.173828013,0.0000265443
H,0,0.9606934125,-1.1321757308,-0.0000174007
H,0,-0.9606934125,-1.1321757308,-0.0000174007

S_N2 OH

Transition structure

E(RB+HF-LYP) = -314.747049209

Zero-point correction= 0.043542 (Hartree/Particle)
Thermal correction to Energy= 0.048370
Thermal correction to Enthalpy= 0.049314
Thermal correction to Gibbs Free Energy= 0.016039

Sum of electronic and zero-point Energies= -314.703507
Sum of electronic and thermal Energies= -314.698680
Sum of electronic and thermal Enthalpies= -314.697735
Sum of electronic and thermal Free Energies= -314.731010

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	30.352	15.204	70.032

C,0,-0.0271781278,-0.2403407456,-0.1417203578
F,0,-0.2441710747,-0.6707522089,1.8216096479
F,0,0.109653503,-0.1518204318,-1.7585781304
O,0,0.1660043355,1.1158404822,0.1320898293
H,0,0.7909132826,-0.9121269501,0.0684524839
H,0,-1.0332987042,-0.6243113459,-0.0700352352
H,0,0.2880776495,1.4549126777,-0.7720973932

S_N2 F2

Transition structure

E(RB+HF-LYP) = -438.017759293

Zero-point correction= 0.024203 (Hartree/Particle)
Thermal correction to Energy= 0.028896
Thermal correction to Enthalpy= 0.029840
Thermal correction to Gibbs Free Energy= -0.003850

Sum of electronic and zero-point Energies= -437.993556
Sum of electronic and thermal Energies= -437.988864
Sum of electronic and thermal Enthalpies= -437.987920
Sum of electronic and thermal Free Energies= -438.021610

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	18.132	15.175	70.907

C,0,-0.1938947239,-0.1153921808,0.0000068718
F,0,-0.3101465083,-0.1849071652,1.7131746301
F,0,-0.3101218831,-0.1848925725,-1.713188011
F,0,-0.1422584892,1.2326988798,0.0000057838
F,0,1.0162357291,-0.7118966608,0.000006283
H,0,-1.1200112931,-0.6666692466,-0.0000294047

S_N2 CCH

Transition structure

E(RB+HF-LYP) = -315.675117330

Zero-point correction= 0.047457 (Hartree/Particle)
Thermal correction to Energy= 0.053209
Thermal correction to Enthalpy= 0.054153
Thermal correction to Gibbs Free Energy= 0.018663

Sum of electronic and zero-point Energies= -315.627660
Sum of electronic and thermal Energies= -315.621908
Sum of electronic and thermal Enthalpies= -315.620964
Sum of electronic and thermal Free Energies= -315.656454

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	33.389	19.508	74.696

C,0,0.,-0.669847643,0.0000168932
F,0,0.,-0.730477509,1.7939562602
F,0,0.,-0.7305555973,-1.7939187253
C,0,0.,0.7732811634,-0.0000210621
H,0,0.9306719256,-1.2132583156,0.000024478
H,0,-0.9306719256,-1.2132583156,0.000024478
C,0,0.,1.9844478149,-0.0000473529
H,0,0.,3.0485265763,-0.0000776388

S_N2 CHO

Transition structure

E(RB+HF-LYP) = -352.872760483

Zero-point correction= 0.048665 (Hartree/Particle)
Thermal correction to Energy= 0.054046
Thermal correction to Enthalpy= 0.054990
Thermal correction to Gibbs Free Energy= 0.019950

Sum of electronic and zero-point Energies= -352.824095
Sum of electronic and thermal Energies= -352.818715
Sum of electronic and thermal Enthalpies= -352.817770
Sum of electronic and thermal Free Energies= -352.852811

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	33.914	17.396	73.749

C,0,-0.1333317335,-0.7142463981,0.0000233863
F,0,-0.2240218408,-0.5971963778,1.7915927418
F,0,-0.2239976693,-0.5973048423,-1.7915764123
C,0,-0.1194421,0.7583787702,-0.0000072582
H,0,0.8066461264,-1.2456433119,0.0000234763
H,0,-1.0577569063,-1.2668573631,0.0000162736
O,0,0.8676994638,1.4740003652,-0.0000351963
H,0,-1.1416663372,1.2062145024,-0.0000019128

S_N2 Me

Transition structure

E(RB+HF-LYP) = -278.846168872

Zero-point correction= 0.066905 (Hartree/Particle)
Thermal correction to Energy= 0.072259
Thermal correction to Enthalpy= 0.073204
Thermal correction to Gibbs Free Energy= 0.038082

Sum of electronic and zero-point Energies= -278.779264
Sum of electronic and thermal Energies= -278.773910
Sum of electronic and thermal Enthalpies= -278.772965
Sum of electronic and thermal Free Energies= -278.808087

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	45.343	16.674	73.919

C,0,-0.0001344892,0.3332688649,0.
F,0,1.827799309,0.3469884829,0.
F,0,-1.8182433903,0.5346960804,0.
C,0,-0.0191038852,-1.175368995,0.
H,0,0.0190705031,0.8825023239,0.9264025443
H,0,0.0190705031,0.8825023239,-0.9264025443
H,0,0.5195062474,-1.551881853,0.8771613836
H,0,0.5195062474,-1.551881853,-0.8771613836
H,0,-1.0477265239,-1.5438012312,0.

1,3-H transfer

Transition structure

E(UB+HF-LYP) = -118.402472002

Zero-point correction= 0.084530 (Hartree/Particle)
Thermal correction to Energy= 0.088664
Thermal correction to Enthalpy= 0.089608
Thermal correction to Gibbs Free Energy= 0.058642

Sum of electronic and zero-point Energies= -118.317942
Sum of electronic and thermal Energies= -118.313808

Sum of electronic and thermal Enthalpies= -118.312864
Sum of electronic and thermal Free Energies= -118.343830

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	55.638	13.701	65.174

C,0,0.8351240337,0.7454490644,0.2842363694
H,0,1.1839774842,0.8700874631,1.3092972377
H,0,1.3652721987,1.3415493146,-0.4584597563
C,0,0.3251466279,-0.637546898,-0.1368093198
H,0,-0.5364554792,1.0519088592,0.225599078
H,0,0.6986578895,-0.971933987,-1.1090431447
H,0,0.5244838967,-1.4263379007,0.594375553
C,0,-1.1323083727,-0.1627589502,-0.159207568
H,0,-1.611439997,-0.032390136,-1.1294765925
H,0,-1.7922697264,-0.5037429106,0.6383907351

1,4-H transfer

Transition structure

E(UB+HF-LYP) = -157.743533561

Zero-point correction= 0.114499 (Hartree/Particle)
Thermal correction to Energy= 0.119207
Thermal correction to Enthalpy= 0.120151
Thermal correction to Gibbs Free Energy= 0.087120

Sum of electronic and zero-point Energies= -157.629034
Sum of electronic and thermal Energies= -157.624326
Sum of electronic and thermal Enthalpies= -157.623382
Sum of electronic and thermal Free Energies= -157.656413

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	74.804	17.308	69.520

C,0,-0.6284824022,-1.2707965141,0.1871223783
H,0,-0.6422305316,-1.5544304795,1.2424296685
H,0,0.7020432038,-1.0204189789,-0.0666964341
H,0,-1.0006791343,-2.0623796375,-0.4638644536
C,0,-1.0367704169,0.1664500339,-0.1170509

H,0,-1.2864617941,0.2598813594,-1.1818013476
H,0,-1.9156732725,0.4993641428,0.4493686821
C,0,0.2246621284,1.0139241285,0.1945726251
H,0,0.1958306908,2.0002547166,-0.2854945845
H,0,0.2926235212,1.1851702425,1.2766198074
C,0,1.3978666408,0.1524373255,-0.2605163147
H,0,2.3087605587,0.1619858419,0.3387564383
H,0,1.6021310577,0.1584829505,-1.3340845088

Carbene insertion MeCH + HCCH

Transition structure

E(RB+HF-LYP) = -155.790636814

Zero-point correction= 0.075519 (Hartree/Particle)
Thermal correction to Energy= 0.081343
Thermal correction to Enthalpy= 0.082287
Thermal correction to Gibbs Free Energy= 0.047189

Sum of electronic and zero-point Energies= -155.715118
Sum of electronic and thermal Energies= -155.709294
Sum of electronic and thermal Enthalpies= -155.708349
Sum of electronic and thermal Free Energies= -155.743448

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	51.044	18.559	73.871

C,0,1.0464878972,0.7841499597,0.0301519099
H,0,0.8379994859,1.0583193713,1.0796033107
C,0,1.6722968559,-0.5660840374,-0.0306369387
H,0,-0.22915564,0.9394481901,-0.6315807841
H,0,1.6302816106,-1.0185450502,-1.0265011653
H,0,2.7355547437,-0.3092457912,0.1485916143
H,0,1.3967585336,-1.3054746205,0.7330224131
C,0,-1.1419827927,0.3153156665,-0.2260084488
C,0,-2.134661911,-0.2919337562,0.1112026517
H,0,-3.0242790299,-0.813189095,0.3886095664

Carbene insertion MeCH + HCCMe

Transition structure

E(RB+HF-LYP) = -195.118934874

Zero-point correction= 0.104619 (Hartree/Particle)
Thermal correction to Energy= 0.112104
Thermal correction to Enthalpy= 0.113048
Thermal correction to Gibbs Free Energy= 0.072246

Sum of electronic and zero-point Energies= -195.014316
Sum of electronic and thermal Energies= -195.006831
Sum of electronic and thermal Enthalpies= -195.005887
Sum of electronic and thermal Free Energies= -195.046689

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	70.346	23.368	85.876

C,0,1.7510856453,1.0162470758,-0.2814834183
C,0,2.3431845951,-0.3453876557,-0.4333078969
H,0,1.6537009923,1.2681840602,0.7893034456
H,0,2.1850539115,-0.7745023067,-1.4281590747
H,0,3.42505698,-0.1172267074,-0.3640746142
H,0,2.1306662623,-1.0988823248,0.3372363057
C,0,-0.4357335903,0.5721717776,-0.3071183597
C,0,-1.3681219953,-0.0502840847,0.1587258686
C,0,-2.5119596049,-0.7826453449,0.6927075753
H,0,0.4050582372,1.2043585613,-0.8143027
H,0,-2.3063104979,-1.8587614475,0.7411566404
H,0,-3.3959024466,-0.6420072621,0.0588292075
H,0,-2.7680537373,-0.4417731811,1.7028681752

Carbene insertion MeCH + HCN

Transition structure

E(RB+HF-LYP) = -171.890889205

Zero-point correction= 0.063661 (Hartree/Particle)
Thermal correction to Energy= 0.069416
Thermal correction to Enthalpy= 0.070360

Thermal correction to Gibbs Free Energy= 0.035158

Sum of electronic and zero-point Energies= -171.827228
Sum of electronic and thermal Energies= -171.821473
Sum of electronic and thermal Enthalpies= -171.820529
Sum of electronic and thermal Free Energies= -171.855731

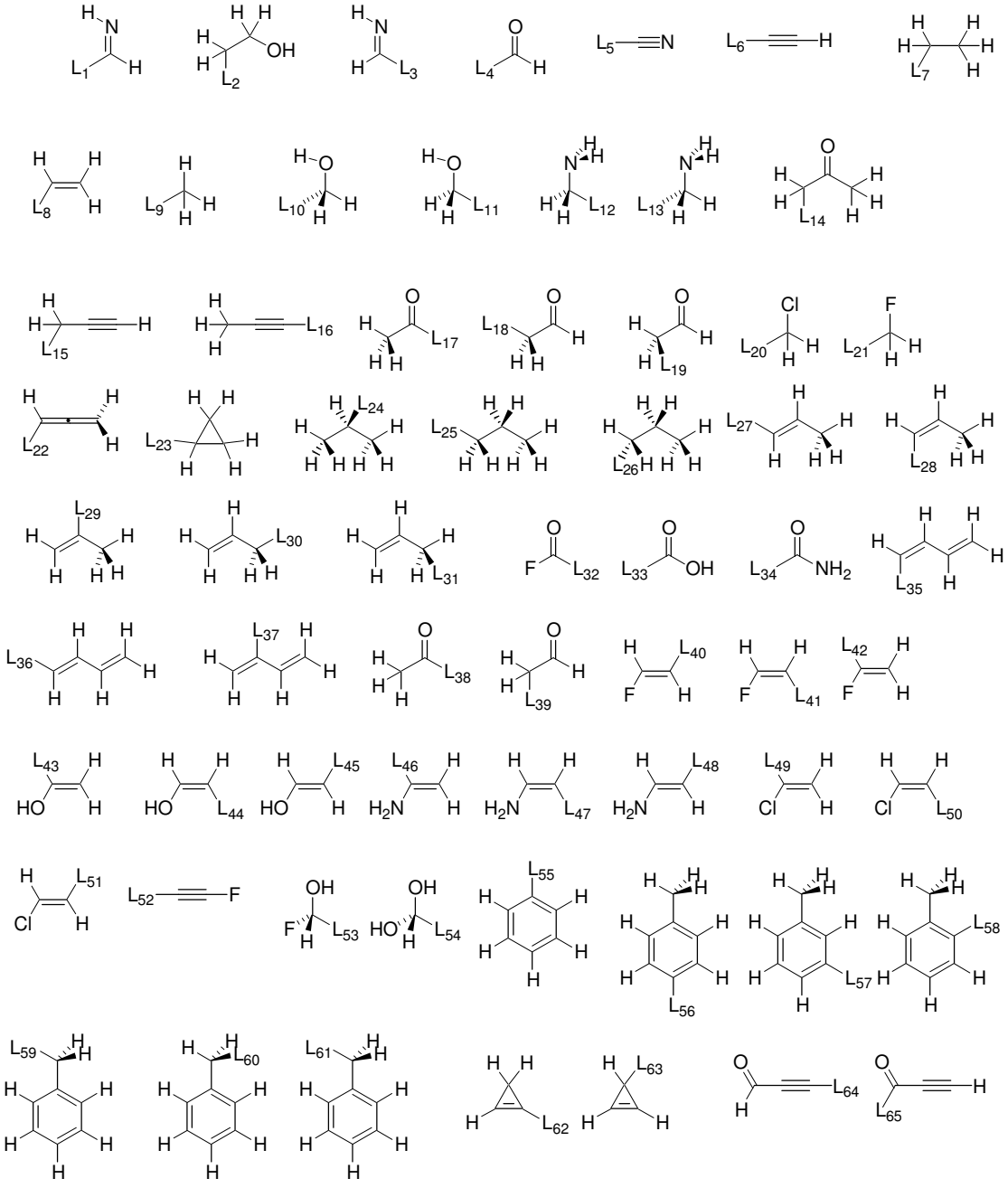
	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	43.559	17.277	74.088

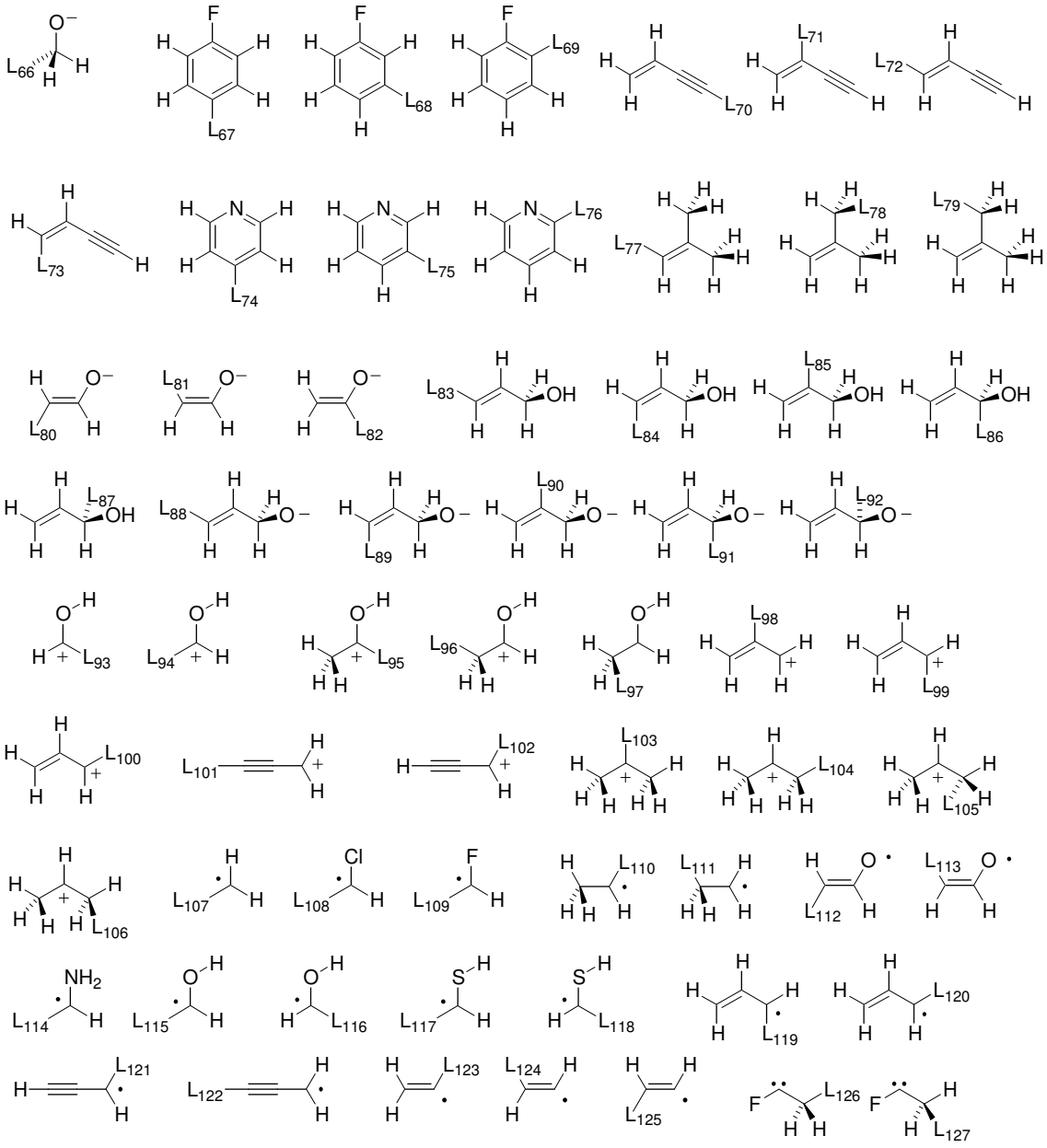
C,0,1.0725088458,0.6910939552,-0.031331066
C,0,1.7434257003,-0.6091791184,-0.2023684959
H,0,1.0923361855,0.9969264856,1.0304988816
H,0,1.5291924992,-1.1006909689,-1.1557773614
H,0,2.7997528968,-0.2636708055,-0.2536606918
H,0,1.7065108185,-1.3245677241,0.630070209
C,0,-1.2992833763,0.3031220743,-0.0710911595
N,0,-2.2787717765,-0.2082365144,0.2929722909
H,0,-0.2762969831,0.8394371471,-0.4731927453

Equilibrium Isotope Effects

H/D, H/T, and D/T EIEs were calculated for all possible exchange reactions for each of the positions marked L in the following section.

Structures and positions for isotopic substitutions





Reduced Isotope Partition Functions

As defined by Bigeleisen. All values refer to 298.15 with a scaling of 0.9614.

CH2NH on C cis to H L1
(S2/S1)F for D: 9.98931380
(S2/S1)F for T: 24.61556800

ethanol on CH3 L2
(S2/S1)F for D: 11.23244600
(S2/S1)F for T: 28.90200100

CH2NH on C trans to H L3
(S2/S1)F for D: 10.86705000
(S2/S1)F for T: 27.70878000

H2CO L4
(S2/S1)F for D: 9.22257340
(S2/S1)F for T: 22.00684600

HCN L5
(S2/S1)F for D: 8.55551670
(S2/S1)F for T: 20.16525800

acetylene L6
(S2/S1)F for D: 8.33861990
(S2/S1)F for T: 19.49756900

ethane L7
(S2/S1)F for D: 11.35717500
(S2/S1)F for T: 29.32040900

ethylene L8
(S2/S1)F for D: 10.48420400
(S2/S1)F for T: 26.39263900

methane L9
(S2/S1)F for D: 10.54520100
(S2/S1)F for T: 26.43556700

methanol on C near OH L10
(S2/S1)F for D: 11.56723400
(S2/S1)F for T: 30.04333400

methanol on C anti OH L11
(S2/S1)F for D: 12.36982500
(S2/S1)F for T: 33.06375600

methylamine on C between NH2 L12
(S2/S1)F for D: 11.10932000
(S2/S1)F for T: 28.37066200

methylamine on C near lp L13
(S2/S1)F for D: 11.89774100
(S2/S1)F for T: 31.29708800

Me2O L14
(S2/S1)F for D: 12.33320000
(S2/S1)F for T: 32.94756600

MeCCH on Me L15
(S2/S1)F for D: 11.12361300
(S2/S1)F for T: 28.49350800

MeCCH on CCH L16
(S2/S1)F for D: 8.09842850
(S2/S1)F for T: 18.75378600

MeCHO on CHO L17
(S2/S1)F for D: 9.72271930
(S2/S1)F for T: 23.70070100

mecho on me in plane L18
(S2/S1)F for D: 11.39375400
(S2/S1)F for T: 29.49934400

meCHO on Me out of plane L19
(S2/S1)F for D: 10.53080400
(S2/S1)F for T: 26.40325200

MeCl L20
(S2/S1)F for D: 11.86430600
(S2/S1)F for T: 31.19814900

MeF L21
(S2/S1)F for D: 12.08409000
(S2/S1)F for T: 31.97354000

allene L22
(S2/S1)F for D: 9.68865810
(S2/S1)F for T: 23.67677600

cyclopropane L23
(S2/S1)F for D: 11.52570800
(S2/S1)F for T: 30.05111400

propane on central L24
(S2/S1)F for D: 12.14925300
(S2/S1)F for T: 32.24141500

propane on methyl anti L25
(S2/S1)F for D: 11.27709100
(S2/S1)F for T: 29.04665700

propane on methyl gauche L26
(S2/S1)F for D: 11.25780600
(S2/S1)F for T: 28.96212700

propene trans L27
(S2/S1)F for D: 10.56399800
(S2/S1)F for T: 26.68980800

propene cis L28
(S2/S1)F for D: 10.43217600
(S2/S1)F for T: 26.20980100

propene gem L29
(S2/S1)F for D: 11.01288700
(S2/S1)F for T: 28.28171300

propene on methyl in plane L30
(S2/S1)F for D: 11.41465800
(S2/S1)F for T: 29.54998800

propene on methyl out of plane L31
(S2/S1)F for D: 10.93246900
(S2/S1)F for T: 27.80095500

FCHO on C L32
(S2/S1)F for D: 11.20391300
(S2/S1)F for T: 29.02885500

HCO2H on C L33
(S2/S1)F for D: 11.34046200
(S2/S1)F for T: 29.49542000

HCONH2 on C L34
(S2/S1)F for D: 10.64988500
(S2/S1)F for T: 26.95325100

butadiene on cis L35
(S2/S1)F for D: 10.38139500
(S2/S1)F for T: 26.04233500

butadiene on trans L36
(S2/S1)F for D: 10.53524500
(S2/S1)F for T: 26.60197300

butadiene on C2 L37
(S2/S1)F for D: 11.17548200
(S2/S1)F for T: 28.87202100

CH3CHO on CHO L38
(S2/S1)F for D: 9.72271930
(S2/S1)F for T: 23.70070100

CH3CHO on CH3 L39
(S2/S1)F for D: 11.39375400
(S2/S1)F for T: 29.49934400

Fluoroethylene on trans L40
(S2/S1)F for D: 10.45169300
(S2/S1)F for T: 26.32860800

Fluoroethylene on cis L41
(S2/S1)F for D: 10.15651100
(S2/S1)F for T: 25.29065200

fluoroethylene gem L42
(S2/S1)F for D: 11.69656200
(S2/S1)F for T: 30.84094300

vinyl alcohol gem L43
(S2/S1)F for D: 12.01520100
(S2/S1)F for T: 32.00788800

vinyl alcohol cis L44
(S2/S1)F for D: 9.85391310
(S2/S1)F for T: 24.24066600

vinyl alcohol trans L45
(S2/S1)F for D: 10.27456400
(S2/S1)F for T: 25.72119900

vinyl amine gem L46
(S2/S1)F for D: 11.63387800
(S2/S1)F for T: 30.56820700

vinyl amine cis L47
(S2/S1)F for D: 9.92335080
(S2/S1)F for T: 24.47700100

vinyl amine trans L48
(S2/S1)F for D: 10.26523800
(S2/S1)F for T: 25.68848500

vinyl chloride gem L49
(S2/S1)F for D: 11.29843600
(S2/S1)F for T: 29.37720700

vinyl chloride cis L50
(S2/S1)F for D: 10.45295100
(S2/S1)F for T: 26.31484300

vinyl chloride trans L51
(S2/S1)F for D: 10.37763500
(S2/S1)F for T: 26.05134700

FCCH L52
(S2/S1)F for D: 8.23273590
(S2/S1)F for T: 19.20120400

FCH2OH L53
(S2/S1)F for D: 13.51755000
(S2/S1)F for T: 37.43580100

HOCH2OH L54
(S2/S1)F for D: 13.70721500
(S2/S1)F for T: 38.19580900

benzene L55
(S2/S1)F for D: 11.34713000
(S2/S1)F for T: 29.54327900

toluene para L56
(S2/S1)F for D: 11.30138300
(S2/S1)F for T: 29.38099000

toluene meta L57
(S2/S1)F for D: 11.31808900
(S2/S1)F for T: 29.43823600

toluene ortho L58
(S2/S1)F for D: 11.34918600
(S2/S1)F for T: 29.54848700

toluene methyl a L59
(S2/S1)F for D: 11.51253900
(S2/S1)F for T: 29.91538700

toluene methyl b L60
(S2/S1)F for D: 10.97890900
(S2/S1)F for T: 27.97188300

toluene methyl c L61
(S2/S1)F for D: 11.07628000
(S2/S1)F for T: 28.32313200

cyclopropene olefinic L62
(S2/S1)F for D: 8.99056380
(S2/S1)F for T: 21.47031300

cyclopropene allylic L63
(S2/S1)F for D: 11.40696700
(S2/S1)F for T: 29.56563200

propynal CCH L64
(S2/S1)F for D: 8.33190520
(S2/S1)F for T: 19.47881000

propynal CHO L65
(S2/S1)F for D: 10.10252400
(S2/S1)F for T: 25.05261800

methoxide L66
(S2/S1)F for D: 7.40414850
(S2/S1)F for T: 15.90746400

PhF para L67
(S2/S1)F for D: 11.37286500
(S2/S1)F for T: 29.64645400

PhF meta L68
(S2/S1)F for D: 11.40118900
(S2/S1)F for T: 29.74390800

PhF ortho L69
(S2/S1)F for D: 11.11037000
(S2/S1)F for T: 28.70990500

butenyne CCH L70
(S2/S1)F for D: 8.12032560
(S2/S1)F for T: 18.82399100

butenyne gem L71
(S2/S1)F for D: 11.00331500
(S2/S1)F for T: 28.27461400

butenyne trans L72
(S2/S1)F for D: 10.63499400
(S2/S1)F for T: 26.95270200

butenyne cis L73
(S2/S1)F for D: 10.55525600
(S2/S1)F for T: 26.66136800

pyridine para L74
(S2/S1)F for D: 11.39688500
(S2/S1)F for T: 29.71975200

pyridine meta L75
(S2/S1)F for D: 11.28530200
(S2/S1)F for T: 29.32463200

pyridine ortho L76
(S2/S1)F for D: 11.89014300
(S2/S1)F for T: 31.53703000

isobutene vinylic L77
(S2/S1)F for D: 10.56533200
(S2/S1)F for T: 26.69773000

isobutene Me out of plane L78
(S2/S1)F for D: 10.93920300
(S2/S1)F for T: 27.82332300

isobutene Me in plane L79
(S2/S1)F for D: 11.51776600
(S2/S1)F for T: 29.93644600

enolate trans L80
(S2/S1)F for D: 8.81703140
(S2/S1)F for T: 20.80308500

enolate cis L81
(S2/S1)F for D: 8.68624110
(S2/S1)F for T: 20.35571200

enolate gem L82
(S2/S1)F for D: 8.27919880
(S2/S1)F for T: 18.81913300

allyl alcohol vinylic trans L83
(S2/S1)F for D: 10.60966700
(S2/S1)F for T: 26.85045900

allyl alcohol vinylic cis L84
(S2/S1)F for D: 10.45682200
(S2/S1)F for T: 26.29683400

allyl alcohol vinylic gem L85
(S2/S1)F for D: 10.97664700
(S2/S1)F for T: 28.16502700

allyl alcohol allylic a L86
(S2/S1)F for D: 12.37261100
(S2/S1)F for T: 33.05222900

allyl alcohol allylic b L87
(S2/S1)F for D: 12.04154200
(S2/S1)F for T: 31.80610500

allyl alcoxide vinylic trans L88
(S2/S1)F for D: 9.51438420
(S2/S1)F for T: 23.04544400

allyl alcoxide vinylic cis L89
(S2/S1)F for D: 9.78487150
(S2/S1)F for T: 23.96727300

allyl alcoxide vinylic gem L90
(S2/S1)F for D: 10.21658800
(S2/S1)F for T: 25.43298300

allyl alcoxide allylic a L91
(S2/S1)F for D: 8.70207620
(S2/S1)F for T: 20.01930600

allyl alcoxide allylic b L92
(S2/S1)F for D: 7.99892980
(S2/S1)F for T: 17.76692000

CH2OH cation cis L93
(S2/S1)F for D: 10.91182900
(S2/S1)F for T: 27.87812400

CH2OH cation trans L94
(S2/S1)F for D: 11.45934400
(S2/S1)F for T: 29.85934900

CH3CHOH cation on carbonyl L95
(S2/S1)F for D: 11.75066400
(S2/S1)F for T: 30.95630000

CH3CHOH cation in plane L96
(S2/S1)F for D: 11.79572200
(S2/S1)F for T: 30.98856500

CH3CHOH cation out of plane L97
(S2/S1)F for D: 9.83754230
(S2/S1)F for T: 24.01934800

allyl cation central L98
(S2/S1)F for D: 12.04119800
(S2/S1)F for T: 32.05848400

allyl cation in L99
(S2/S1)F for D: 10.61918100
(S2/S1)F for T: 26.86754600

allyl cation out L100
(S2/S1)F for D: 10.56078000
(S2/S1)F for T: 26.67770100

HCCCH2plus on CH L101
(S2/S1)F for D: 8.31502530
(S2/S1)F for T: 19.34686900

HCCCH2plus on CH2 L102
(S2/S1)F for D: 9.48370930
(S2/S1)F for T: 22.98520300

isopropyl cation central L103
(S2/S1)F for D: 11.16698000
(S2/S1)F for T: 28.82138700

isopropyl cation me in plane L104
(S2/S1)F for D: 11.89894800
(S2/S1)F for T: 31.36653500

isopropyl cation me out A L105
(S2/S1)F for D: 10.33822500
(S2/S1)F for T: 25.75057500

isopropyl cation me out B L106
(S2/S1)F for D: 8.00188040
(S2/S1)F for T: 18.00015000

methyl radical L107
(S2/S1)F for D: 8.1902535
(S2/S1)F for T: 18.85199

ClCH2 rad L108
(S2/S1)F for D: 8.77216
(S2/S1)F for T: 20.797

FCH2 rad L109
(S2/S1)F for D: 9.38221590
(S2/S1)F for T: 22.75027200

Et rad on CH2 L110
(S2/S1)F for D: 8.6766
(S2/S1)F for T: 20.42639

Et rad methyl CH aligned L111
(S2/S1)F for D: 9.99312130
(S2/S1)F for T: 24.48734600

OHCCH2 rad A L112
(S2/S1)F for D: 9.28982
(S2/S1)F for T: 22.40377

OHCCH2 rad B L113
(S2/S1)F for D: 9.40651710
(S2/S1)F for T: 22.77148700

CH2NH2 rad on CH L114
(S2/S1)F for D: 9.50909700
(S2/S1)F for T: 23.12280100

CH2OH rad A L115
(S2/S1)F for D: 9.8096
(S2/S1)F for T: 24.1808

CH2OH rad B L116
(S2/S1)F for D: 9.200649
(S2/S1)F for T: 22.0907

HSCH2 rad A L117
(S2/S1)F for D: 8.83227
(S2/S1)F for T: 20.94207

HSCH2 rad B L118
(S2/S1)F for D: 8.58325390
(S2/S1)F for T: 20.13665100

allyl rad A L119
(S2/S1)F for D: 9.80262310
(S2/S1)F for T: 24.11804800

allyl rad B L120
(S2/S1)F for D: 9.76251
(S2/S1)F for T: 23.9502

propargyl radical L121
(S2/S1)F for D: 8.881399
(S2/S1)F for T: 21.0764

propargyl radical CCH L122
(S2/S1)F for D: 8.09842850
(S2/S1)F for T: 18.75378600

vinyl radical CH L123
(S2/S1)F for D: 8.07593
(S2/S1)F for T: 18.46506

vinyl radical CH2 A L124
(S2/S1)F for D: 9.36263500
(S2/S1)F for T: 22.57454700

vinyl radical CH2 B L125
(S2/S1)F for D: 8.40980060
(S2/S1)F for T: 19.44304700

FCCH3 carbene in plane L126
(S2/S1)F for D: 10.78732700
(S2/S1)F for T: 27.30948600

FCCH3 out of plane L127
(S2/S1)F for D: 9.90894470
(S2/S1)F for T: 24.26

Studies on the Mechanism of the Sharpless Asymmetric Epoxidation-Origin of Ligand Accelerated Catalysis-Appendix Material

Theoretical Calculations

Calculations on crystal structure derivative

Description: The calculational model is a bridged titanium dimer complex with two methoxide bystander alcohols attached to each titanium, and a diamide ethylene glycol used as the complexing ligand. The model is derived from the published crystal structure by Sharpless and Lippard of a similar titanium dimeric complex. The phenyl amide of the original structure was truncated to the amide in the calculational model, similarly the isopropyl bystander alcohols were changed to methoxides for simplicity.

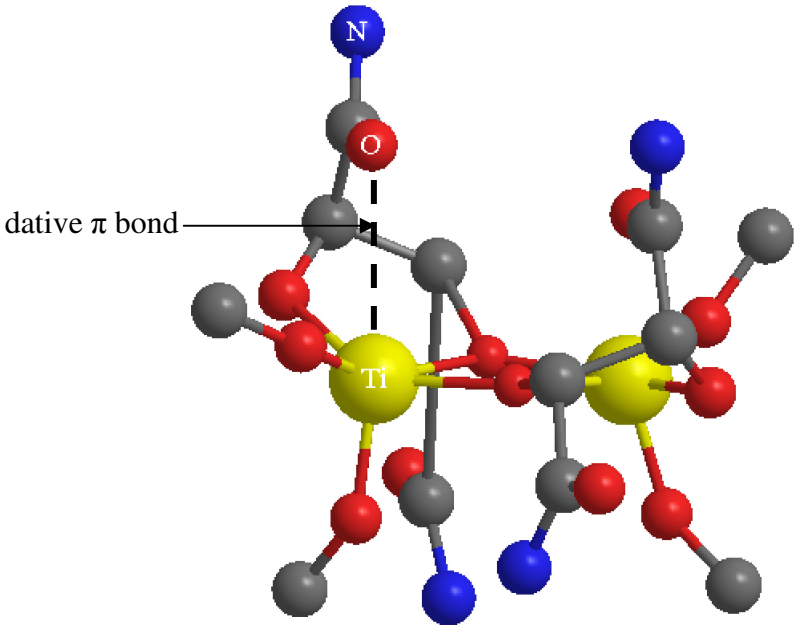


Table of Crystal Structure Bond Lengths

Calculations on crystal structure derivative	dative bond (Å)	Ti-O (Å)

Distances of x-ray structure	2.21	1.91
Optimization B3LYP/SB lanl2dz	2.43	1.89
Optimization B3PW91/SBlanl2dz	2.40	1.88
Optimization B3PW91/SB 6-31G* Ti	2.39	1.88
Optimization B3PW91/SB	2.39	1.88
Optimization mPW1K/SB lanl2dz	2.29	1.87
Optimization mPW1K/SB	2.30	1.87
Optimization mPW1K/6-31G** lanl2dz	2.29	1.87
Optimization mPW1K/SB 6-31G* on Ti	2.31	1.87
Optimization mPW1K/SB diffuse on O	2.31	1.87

*Dative bonding distances could be shorter in crystal structure model because of the steric bulk of the diphenyl amide which was converted to the amide for calculational simplicity.

Optimization B3LYP/SB lanl2dz B3LYP/6-31G* on CHNO and lanl2dz on Ti
File name: (cs2B3LYPTibasissettest.log)

SCF Done: E(RB+HF-LYP) = -1710.59461252 A.U. after 8 cycles

1	1	0	-1.511925	-3.526653	-2.778643
2	6	0	-1.627601	-2.440437	-2.899503
3	8	0	-0.758766	-1.752988	-2.024521
4	22	0	-0.805003	-1.473816	-0.232822
5	8	0	-0.514853	-3.147274	0.365334
6	6	0	-0.816307	-4.028900	1.416332
7	8	0	0.990882	-0.678066	-0.125023
8	22	0	0.804763	1.473824	-0.231743
9	8	0	0.757162	1.754901	-2.023130
10	6	0	1.623133	2.447949	-2.896617
11	8	0	-0.991014	0.678065	-0.123282
12	6	0	-2.292968	1.121347	0.172962
13	6	0	-3.086545	1.631969	-1.044587
14	8	0	-4.282501	1.875495	-0.923862
15	8	0	-2.666691	-1.214957	-0.044401
16	6	0	-2.990444	-0.133475	0.771478
17	6	0	-2.317066	-0.396100	2.121645
18	8	0	-1.254459	-1.035142	2.117404
19	6	0	2.292921	-1.121720	0.170079
20	6	0	3.085804	-1.630980	-1.048519
21	8	0	4.282039	-1.873758	-0.929065
22	6	0	2.990845	0.132315	0.769776
23	8	0	2.666521	1.214897	-0.044424
24	6	0	2.318517	0.393098	2.120790

25	8	0	1.255736	1.031847	2.118270
26	7	0	2.867797	-0.120906	3.237883
27	8	0	0.515727	3.146772	0.368422
28	6	0	0.819830	4.026837	1.420012
29	7	0	-2.865225	0.116657	3.239840
30	7	0	-2.369408	1.805632	-2.178340
31	7	0	2.367732	-1.804376	-2.181718
32	1	0	-1.367543	1.638153	-2.220011
33	1	0	-3.739701	0.620354	3.214859
34	1	0	-2.844383	2.191070	-2.982677
35	1	0	-2.265929	1.947135	0.897424
36	1	0	-4.072796	0.025655	0.844864
37	1	0	-2.380204	0.025837	4.122445
38	1	0	2.266228	-1.948379	0.893576
39	1	0	4.073236	-0.026985	0.842076
40	1	0	1.365821	-1.637006	-2.222536
41	1	0	2.842278	-2.188602	-2.986887
42	1	0	3.742418	-0.624282	3.211516
43	1	0	2.383585	-0.031221	4.121046
44	1	0	1.378006	2.184420	-3.933090
45	1	0	1.506254	3.533391	-2.770123
46	1	0	2.667409	2.175631	-2.697817
47	1	0	0.066322	4.824178	1.461105
48	1	0	0.837229	3.496626	2.379905
49	1	0	1.803339	4.487073	1.252832
50	1	0	-0.060394	-4.823996	1.456960
51	1	0	-0.835383	-3.499407	2.376594
52	1	0	-1.798376	-4.492059	1.248756
53	1	0	-2.671070	-2.167704	-2.697044
54	1	0	-1.384373	-2.172223	-3.935220

Optimization B3PW91/SBlanl2dz: B3PW91/6-31G* on CHNO and lanl2dz on Ti
File name: (cs2BPlanl631G*.log)

SCF Done: E(RB+HF-PW91) = -1710.00598760 A.U. after 10 cycles

1	1	0	-1.498744	-3.374505	-3.011111
2	6	0	-1.646786	-2.288145	-2.936793
3	8	0	-0.744847	-1.735921	-2.012412
4	22	0	-0.789661	-1.473778	-0.225725
5	8	0	-0.472214	-3.142019	0.355267
6	6	0	-0.753883	-4.033315	1.392676
7	8	0	0.994244	-0.664037	-0.113604

8	22	0	0.788069	1.470464	-0.209870
9	8	0	0.723967	1.763847	-1.992501
10	6	0	1.597545	2.397844	-2.890534
11	8	0	-0.995084	0.661908	-0.097764
12	6	0	-2.294791	1.090538	0.195757
13	6	0	-3.084027	1.613731	-1.013160
14	8	0	-4.279610	1.852569	-0.893070
15	8	0	-2.651456	-1.235377	-0.065613
16	6	0	-2.986882	-0.176818	0.763043
17	6	0	-2.310492	-0.450315	2.102339
18	8	0	-1.242576	-1.077539	2.078767
19	6	0	2.296186	-1.097837	0.162187
20	6	0	3.076001	-1.604578	-1.059911
21	8	0	4.273284	-1.841092	-0.952649
22	6	0	2.994128	0.160794	0.741731
23	8	0	2.650924	1.231600	-0.067879
24	6	0	2.331424	0.414193	2.091902
25	8	0	1.263665	1.041921	2.089456
26	7	0	2.884702	-0.093398	3.205193
27	8	0	0.480005	3.130823	0.398035
28	6	0	0.774080	4.005393	1.446519
29	7	0	-2.851787	0.039777	3.229128
30	7	0	-2.361932	1.806793	-2.135051
31	7	0	2.346105	-1.784011	-2.178939
32	1	0	-1.358168	1.645690	-2.171039
33	1	0	-3.732657	0.530818	3.217727
34	1	0	-2.831211	2.202822	-2.936377
35	1	0	-2.279771	1.904210	0.935020
36	1	0	-4.071367	-0.023078	0.835136
37	1	0	-2.354926	-0.048838	4.104204
38	1	0	2.286949	-1.921813	0.890021
39	1	0	4.079189	0.005794	0.800736
40	1	0	1.342860	-1.619987	-2.207627
41	1	0	2.811085	-2.164099	-2.990397
42	1	0	3.765273	-0.584295	3.176727
43	1	0	2.397444	-0.018101	4.086880
44	1	0	1.420180	2.015215	-3.903832
45	1	0	1.426635	3.483544	-2.888467
46	1	0	2.641745	2.200895	-2.616262
47	1	0	0.090478	4.864106	1.412148
48	1	0	0.672298	3.504641	2.417741
49	1	0	1.803532	4.378325	1.352979
50	1	0	-0.058925	-4.882411	1.347335
51	1	0	-0.658591	-3.543921	2.370428

52	1	0	-1.778168	-4.419207	1.294524
53	1	0	-2.681824	-2.087700	-2.633437
54	1	0	-1.475320	-1.841704	-3.925090

Optimization B3PW91/SB 6-31G* Ti: B3PW91/6-31G* on all atoms
File name: (cs2BP631G*allatoms.log)

SCF Done: E(RB+HF-PW91) = -1710.00610799 A.U. after 9 cycles

1	1	0	-1.487877	-3.351021	-3.039787
2	6	0	-1.626866	-2.264049	-2.956646
3	8	0	-0.727523	-1.728087	-2.021423
4	22	0	-0.770848	-1.484851	-0.232118
5	8	0	-0.427163	-3.152306	0.334094
6	6	0	-0.658636	-4.059959	1.369788
7	8	0	1.002172	-0.650642	-0.125159
8	22	0	0.767669	1.481918	-0.204377
9	8	0	0.694868	1.777752	-1.986693
10	6	0	1.554750	2.439028	-2.878669
11	8	0	-1.004304	0.648965	-0.094345
12	6	0	-2.308367	1.058994	0.207072
13	6	0	-3.109089	1.579664	-0.995645
14	8	0	-4.307903	1.798472	-0.870877
15	8	0	-2.635065	-1.269320	-0.065209
16	6	0	-2.980977	-0.219203	0.770203
17	6	0	-2.296950	-0.493436	2.105712
18	8	0	-1.220218	-1.105482	2.075131
19	6	0	2.308546	-1.070370	0.152330
20	6	0	3.094980	-1.564029	-1.070931
21	8	0	4.294027	-1.790589	-0.963058
22	6	0	2.989756	0.192371	0.739466
23	8	0	2.633491	1.264310	-0.063167
24	6	0	2.325467	0.430794	2.091934
25	8	0	1.248176	1.042280	2.094842
26	7	0	2.889992	-0.070699	3.202092
27	8	0	0.443640	3.137100	0.407527
28	6	0	0.704961	4.016362	1.460772
29	7	0	-2.843078	-0.021615	3.237579
30	7	0	-2.392937	1.790925	-2.118158
31	7	0	2.367647	-1.743516	-2.191752
32	1	0	-1.386451	1.648114	-2.155631
33	1	0	-3.729427	0.459646	3.232413
34	1	0	-2.868333	2.192446	-2.913189
35	1	0	-2.300799	1.869608	0.949920

36	1	0	-4.066840	-0.081175	0.847995
37	1	0	-2.348058	-0.120552	4.112697
38	1	0	2.307110	-1.898417	0.875652
39	1	0	4.076485	0.051666	0.798421
40	1	0	1.361739	-1.595718	-2.216361
41	1	0	2.833737	-2.126152	-3.001449
42	1	0	3.775764	-0.551975	3.169572
43	1	0	2.408820	0.003846	4.087279
44	1	0	1.316943	2.135620	-3.906250
45	1	0	1.430942	3.527958	-2.795195
46	1	0	2.600458	2.182605	-2.666402
47	1	0	-0.102114	4.757744	1.532393
48	1	0	0.782650	3.477080	2.413146
49	1	0	1.648340	4.550310	1.281057
50	1	0	0.165243	-4.784669	1.417354
51	1	0	-0.739169	-3.544604	2.335224
52	1	0	-1.591382	-4.611094	1.186380
53	1	0	-2.662337	-2.059025	-2.656953
54	1	0	-1.445938	-1.810022	-3.939365

Optimization B3PW91/SB B3PW91/6-31G* on CHNO SDD on Ti
File name: (cs2BPSDD631G*.log)

SCF Done: E(RB+HF-PW91) = -1710.00610837   A.U. after   9 cycles

1	1	0	-1.485631	-3.352024	-3.039005
2	6	0	-1.626613	-2.265499	-2.953460
3	8	0	-0.726456	-1.729685	-2.018774
4	22	0	-0.772830	-1.484280	-0.229532
5	8	0	-0.431227	-3.151544	0.338749
6	6	0	-0.664191	-4.057334	1.375814
7	8	0	1.000965	-0.652426	-0.120857
8	22	0	0.770385	1.480739	-0.201076
9	8	0	0.698116	1.777411	-1.983516
10	6	0	1.560851	2.437579	-2.873704
11	8	0	-1.002748	0.650103	-0.092998
12	6	0	-2.307301	1.062552	0.202883
13	6	0	-3.103053	1.584161	-1.002723
14	8	0	-4.301651	1.806041	-0.881129
15	8	0	-2.637277	-1.265289	-0.069522
16	6	0	-2.984266	-0.214223	0.764193
17	6	0	-2.305471	-0.488901	2.102282
18	8	0	-1.229445	-1.102409	2.075725
19	6	0	2.307988	-1.073848	0.151302

20	6	0	3.091113	-1.565625	-1.074954
21	8	0	4.290647	-1.791342	-0.970439
22	6	0	2.991843	0.187328	0.738524
23	8	0	2.636020	1.260168	-0.063152
24	6	0	2.329553	0.426303	2.091900
25	8	0	1.253750	1.040429	2.096395
26	7	0	2.894024	-0.077131	3.201169
27	8	0	0.446707	3.135826	0.411457
28	6	0	0.706965	4.013639	1.466276
29	7	0	-2.854881	-0.015999	3.232064
30	7	0	-2.384141	1.789996	-2.124481
31	7	0	2.361278	-1.744086	-2.194224
32	1	0	-1.376980	1.650181	-2.157905
33	1	0	-3.741213	0.465251	3.223869
34	1	0	-2.856317	2.195015	-2.919688
35	1	0	-2.301355	1.873422	0.945460
36	1	0	-4.070163	-0.074253	0.838137
37	1	0	-2.363389	-0.116016	4.109046
38	1	0	2.308098	-1.903304	0.873040
39	1	0	4.078447	0.045145	0.796021
40	1	0	1.354913	-1.598100	-2.216666
41	1	0	2.826035	-2.126057	-3.005020
42	1	0	3.779721	-0.558488	3.167908
43	1	0	2.414487	-0.000804	4.087090
44	1	0	1.329149	2.129433	-3.901258
45	1	0	1.433602	3.526474	-2.795119
46	1	0	2.606119	2.184787	-2.655056
47	1	0	-0.106659	4.746954	1.546413
48	1	0	0.796532	3.471577	2.416009
49	1	0	1.643796	4.557375	1.281795
50	1	0	0.165261	-4.774946	1.433344
51	1	0	-0.757503	-3.539179	2.338581
52	1	0	-1.590562	-4.617004	1.186106
53	1	0	-2.661865	-2.062981	-2.651384
54	1	0	-1.448402	-1.809074	-3.935550

Optimization mPW1K/SB lanl2dz: mPW1K/6-31G* on CHNO lanl2dz on Ti
File name: (cs2MPW1Klanl631G*.log)

SCF Done: E(RmPW+HF-PW91) = -1709.48273454 A.U. after 10 cycles

1	1	0	-0.891656	-3.009940	-3.517271
2	6	0	-1.362313	-2.177698	-3.036901
3	8	0	-0.553859	-1.699069	-1.996071

4	22	0	-0.676526	-1.537252	-0.190220
5	8	0	-0.168800	-3.194492	0.314252
6	6	0	-0.287863	-4.118373	1.359368
7	8	0	1.046719	-0.599615	-0.042423
8	22	0	0.671796	1.532353	-0.232430
9	8	0	0.550991	1.643634	-2.042224
10	6	0	1.359285	2.092309	-3.093580
11	8	0	-1.051613	0.599188	-0.060259
12	6	0	-2.387477	0.881372	0.258142
13	6	0	-3.206211	1.434048	-0.887116
14	8	0	-4.419220	1.511015	-0.789808
15	8	0	-2.586950	-1.434552	-0.115631
16	6	0	-2.972918	-0.443451	0.802408
17	6	0	-2.239996	-0.767354	2.097438
18	8	0	-1.128457	-1.328089	1.961835
19	6	0	2.382248	-0.872772	0.285115
20	6	0	3.202156	-1.457227	-0.843406
21	8	0	4.415061	-1.531427	-0.742734
22	6	0	2.967148	0.466755	0.792744
23	8	0	2.582141	1.431804	-0.153034
24	6	0	2.232898	0.826714	2.077462
25	8	0	1.121509	1.383425	1.925094
26	7	0	2.755595	0.529604	3.225996
27	8	0	0.163575	3.203038	0.225006
28	6	0	0.281576	4.155768	1.244015
29	7	0	-2.763870	-0.438266	3.236681
30	7	0	-2.516564	1.825643	-1.959339
31	7	0	2.513606	-1.878647	-1.904973
32	1	0	-1.553755	1.758700	-2.106922
33	1	0	-3.652161	0.161003	3.109837
34	1	0	-2.971884	2.324916	-2.788983
35	1	0	-2.420754	1.584337	0.897363
36	1	0	-3.911147	-0.388087	0.935165
37	1	0	-2.320571	-0.673088	4.181798
38	1	0	2.414858	-1.557595	0.943767
39	1	0	3.905241	0.415136	0.927962
40	1	0	1.550952	-1.815868	-2.055361
41	1	0	2.969772	-2.400906	-2.719872
42	1	0	3.644006	-0.072965	3.116863
43	1	0	2.311327	0.790741	4.163723
44	1	0	0.837569	1.949942	-4.038814
45	1	0	1.579575	3.149917	-2.956251
46	1	0	2.289447	1.526075	-3.103483
47	1	0	-0.271514	5.052460	0.968413

48	1	0	-0.123640	3.749445	2.169554
49	1	0	1.331669	4.406488	1.386720
50	1	0	0.265497	-5.022410	1.109504
51	1	0	0.116406	-3.686336	2.273606
52	1	0	-1.338105	-4.365024	1.507946
53	1	0	-2.318810	-1.975111	-3.516475
54	1	0	-0.839622	-2.061795	-3.985206

Optimization mPW1K/SB: mPW1K/6-31G* on CHNO SDD on Ti
File name: (cs2MPW1kSDD631G*.log)

SCF Done: E(RmPW+HF-PW91) = -1709.99272373 A.U. after 10 cycles

1	1	0	1.354768	2.929167	-3.452750
2	6	0	1.463929	1.933671	-3.020571
3	8	0	0.551183	1.767802	-1.981898
4	22	0	0.617362	1.541612	-0.208980
5	8	0	0.043242	3.124682	0.361230
6	6	0	0.049235	4.023432	1.414493
7	8	0	-1.054878	0.533398	-0.092668
8	22	0	-0.617262	-1.541158	-0.182612
9	8	0	-0.548738	-1.797130	-1.951841
10	6	0	-1.459971	-2.019805	-2.981222
11	8	0	1.055025	-0.532368	-0.083165
12	6	0	2.383448	-0.818134	0.197067
13	6	0	3.200786	-1.262193	-1.008113
14	8	0	4.406711	-1.358635	-0.903779
15	8	0	2.487713	1.505623	-0.094570
16	6	0	2.938843	0.510102	0.738356
17	6	0	2.239392	0.724614	2.064118
18	8	0	1.117806	1.227261	2.021994
19	6	0	-2.383762	0.823756	0.180727
20	6	0	-3.200395	1.242203	-1.034079
21	8	0	-4.406577	1.339139	-0.933139
22	6	0	-2.938240	-0.493759	0.748133
23	8	0	-2.487029	-1.504921	-0.065775
24	6	0	-2.238020	-0.682429	2.077510
25	8	0	-1.116751	-1.186282	2.045125
26	7	0	-2.812381	-0.254138	3.198143
27	8	0	-0.047055	-3.115680	0.415106
28	6	0	-0.058168	-3.995446	1.484322
29	7	0	2.814042	0.318893	3.192864
30	7	0	2.498687	-1.546261	-2.111391
31	7	0	-2.497163	1.505822	-2.141647

32	1	0	1.489399	-1.528076	-2.129979
33	1	0	3.740796	-0.060301	3.198935
34	1	0	2.996995	-1.925040	-2.894263
35	1	0	2.462307	-1.620361	0.934656
36	1	0	4.025739	0.478027	0.812612
37	1	0	2.313300	0.388566	4.059140
38	1	0	-2.463785	1.640685	0.901867
39	1	0	-4.025117	-0.460950	0.822141
40	1	0	-1.487909	1.486826	-2.158980
41	1	0	-2.994873	1.867139	-2.933087
42	1	0	-3.738953	0.125536	3.196822
43	1	0	-2.311511	-0.306772	4.065536
44	1	0	-1.283281	-1.310943	-3.790479
45	1	0	-1.339443	-3.031896	-3.369740
46	1	0	-2.480306	-1.894446	-2.620703
47	1	0	0.925361	-4.454439	1.595470
48	1	0	-0.317504	-3.482858	2.410929
49	1	0	-0.785690	-4.788760	1.306579
50	1	0	-0.939682	4.471106	1.524200
51	1	0	0.321447	3.531039	2.348347
52	1	0	0.764671	4.823178	1.217649
53	1	0	2.482911	1.811981	-2.655088
54	1	0	1.278185	1.192219	-3.797967

Optimization mPW1K/6-31G** lanl2dz: mPW1K/6-31G** on CHNO lanl2dz on Ti
File name: (cs2MPlanl613G**.log)

SCF Done: E(RmPW+HF-PW91) = -1709.53432199 A.U. after 15 cycles

1	1	0	-1.384845	-2.902443	-3.453604
2	6	0	-1.489969	-1.917398	-2.997433
3	8	0	-0.563184	-1.772930	-1.968254
4	22	0	-0.626689	-1.532730	-0.189429
5	8	0	-0.060843	-3.121042	0.392327
6	6	0	-0.077411	-3.995707	1.465649
7	8	0	1.053983	-0.535512	-0.083583
8	22	0	0.626808	1.533088	-0.187090
9	8	0	0.563696	1.774732	-1.965791
10	6	0	1.490896	1.922437	-2.994165
11	8	0	-1.053795	0.535659	-0.082330
12	6	0	-2.380391	0.833895	0.188516
13	6	0	-3.187521	1.272910	-1.025170
14	8	0	-4.393231	1.380456	-0.926068
15	8	0	-2.497844	-1.488186	-0.094194

16	6	0	-2.948064	-0.487300	0.733678
17	6	0	-2.252111	-0.703770	2.060458
18	8	0	-1.130030	-1.204788	2.017542
19	6	0	2.380384	-0.834085	0.187734
20	6	0	3.188274	-1.270846	-1.026256
21	8	0	4.393992	-1.378006	-0.926880
22	6	0	2.947503	0.486118	0.735824
23	8	0	2.497841	1.488585	-0.090457
24	6	0	2.250342	0.699929	2.062412
25	8	0	1.128215	1.200858	2.019398
26	7	0	2.824453	0.297044	3.191771
27	8	0	0.061539	3.121042	0.396233
28	6	0	0.078644	3.993972	1.470989
29	7	0	-2.827275	-0.303016	3.190053
30	7	0	-2.478129	1.538987	-2.126706
31	7	0	2.479344	-1.535604	-2.128412
32	1	0	-1.470521	1.503942	-2.140700
33	1	0	-3.753842	0.071655	3.195448
34	1	0	-2.973367	1.905724	-2.914780
35	1	0	-2.460541	1.642257	0.919493
36	1	0	-4.035325	-0.444328	0.802360
37	1	0	-2.325018	-0.380896	4.052503
38	1	0	2.460101	-1.643811	0.917261
39	1	0	4.034708	0.443148	0.805312
40	1	0	1.471733	-1.500834	-2.142583
41	1	0	2.974923	-1.900956	-2.916911
42	1	0	3.751012	-0.077645	3.197327
43	1	0	2.321258	0.373006	4.053847
44	1	0	1.318766	1.166104	-3.760236
45	1	0	1.386373	2.909119	-3.446929
46	1	0	2.504833	1.809287	-2.611839
47	1	0	-0.899240	4.464722	1.581173
48	1	0	0.328401	3.473265	2.395784
49	1	0	0.816337	4.779489	1.301332
50	1	0	0.901725	-4.463550	1.577171
51	1	0	-0.330748	-3.477263	2.390739
52	1	0	-0.812222	-4.783307	1.293166
53	1	0	-2.504076	-1.806009	-2.615026
54	1	0	-1.317968	-1.158296	-3.760798

Optimization mPW1K/SB 6-31G* on Ti: mPW1K/6-31G* on all atoms
File name: (cs2MPW1K631G*allatoms.log)

SCF Done: E(RmPW+HF-PW91) = -3292.22953431 A.U. after 9 cycles

1	1	0	-1.504986	-3.066902	-3.253128
2	6	0	-1.576935	-2.019153	-2.957382
3	8	0	-0.646460	-1.739855	-1.960039
4	22	0	-0.703128	-1.505183	-0.190065
5	8	0	-0.250899	-3.117044	0.394663
6	6	0	-0.371689	-4.017604	1.439021
7	8	0	1.027050	-0.597256	-0.082795
8	22	0	0.702975	1.504902	-0.185738
9	8	0	0.645049	1.745171	-1.955060
10	6	0	1.574595	2.036220	-2.949933
11	8	0	-1.027186	0.596947	-0.080708
12	6	0	-2.341854	0.951784	0.181258
13	6	0	-3.125341	1.412447	-1.040810
14	8	0	-4.325503	1.573159	-0.950217
15	8	0	-2.568273	-1.367153	-0.084157
16	6	0	-2.968385	-0.338517	0.735151
17	6	0	-2.287846	-0.575967	2.066834
18	8	0	-1.192365	-1.132694	2.037832
19	6	0	2.341868	-0.952934	0.177285
20	6	0	3.124781	-1.409413	-1.046723
21	8	0	4.324994	-1.570384	-0.957222
22	6	0	2.968596	0.335546	0.735128
23	8	0	2.568116	1.366798	-0.080704
24	6	0	2.288626	0.568682	2.067879
25	8	0	1.193174	1.125559	2.041250
26	7	0	2.851639	0.121263	3.186846
27	8	0	0.251816	3.115242	0.404092
28	6	0	0.374113	4.012455	1.451171
29	7	0	-2.850300	-0.132248	3.187535
30	7	0	-2.398907	1.636363	-2.141078
31	7	0	2.397851	-1.629698	-2.147383
32	1	0	-1.392870	1.553244	-2.151969
33	1	0	-3.755444	0.295588	3.182751
34	1	0	-2.870464	2.009975	-2.942336
35	1	0	-2.390796	1.768333	0.905569
36	1	0	-4.052388	-0.247570	0.803459
37	1	0	-2.359399	-0.216463	4.057945
38	1	0	2.391223	-1.771894	0.898838
39	1	0	4.052630	0.244423	0.802678
40	1	0	1.391841	-1.546354	-2.157612
41	1	0	2.869054	-2.000440	-2.950179
42	1	0	3.756711	-0.306698	3.180172

43	1	0	2.361161	0.202581	4.057768
44	1	0	1.377835	1.421938	-3.828821
45	1	0	1.500550	3.086690	-3.235376
46	1	0	2.585248	1.833372	-2.597490
47	1	0	-0.540051	4.600745	1.542245
48	1	0	0.556658	3.494147	2.392840
49	1	0	1.201942	4.697711	1.263289
50	1	0	0.543644	-4.604303	1.528657
51	1	0	-0.555588	-3.502490	2.382184
52	1	0	-1.198038	-4.704000	1.248806
53	1	0	-2.587029	-1.817771	-2.602528
54	1	0	-1.379341	-1.396636	-3.830271

Optimization mPW1K/SB diffuse on O: mPW1K/6-31G* on CHN 6-31+G* on O and SDD on Ti
File name: (cs2MPdiffuse.log)

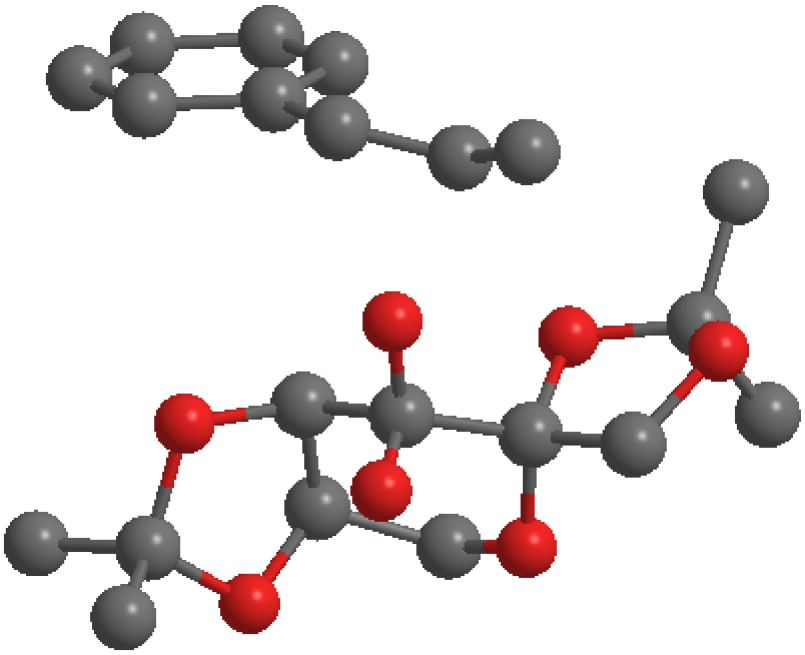
SCF Done: E(RmPW+HF-PW91) = -1710.01789671 A.U. after 10 cycles

1	1	0	-1.290859	-3.014930	-3.407200
2	6	0	-1.441359	-2.006401	-3.019447
3	8	0	-0.541552	-1.759159	-1.984679
4	22	0	-0.616735	-1.541053	-0.209858
5	8	0	-0.043867	-3.123247	0.360644
6	6	0	-0.062604	-4.045263	1.394417
7	8	0	1.057218	-0.533546	-0.089182
8	22	0	0.616215	1.539541	-0.184772
9	8	0	0.536460	1.788988	-1.955860
10	6	0	1.431035	2.099303	-2.978177
11	8	0	-1.057537	0.531542	-0.079079
12	6	0	-2.385419	0.817369	0.204846
13	6	0	-3.199573	1.278578	-0.995356
14	8	0	-4.404253	1.413605	-0.877915
15	8	0	-2.487529	-1.507031	-0.100006
16	6	0	-2.942022	-0.515644	0.735935
17	6	0	-2.247729	-0.736338	2.064450
18	8	0	-1.124702	-1.236302	2.024451
19	6	0	2.385941	-0.823893	0.186610
20	6	0	3.198025	-1.261717	-1.023767
21	8	0	4.403317	-1.396136	-0.911773
22	6	0	2.942638	0.499196	0.741420
23	8	0	2.486723	1.505422	-0.075920
24	6	0	2.250170	0.695683	2.074725

25	8	0	1.127358	1.196681	2.045936
26	7	0	2.833250	0.275916	3.193469
27	8	0	0.047597	3.113033	0.413770
28	6	0	0.072453	4.018430	1.462003
29	7	0	-2.828930	-0.337709	3.191762
30	7	0	-2.506225	1.532298	-2.107892
31	7	0	2.502390	-1.496645	-2.138832
32	1	0	-1.496899	1.497453	-2.130668
33	1	0	-3.757755	0.037025	3.194778
34	1	0	-3.000854	1.923665	-2.887293
35	1	0	-2.463018	1.612851	0.950096
36	1	0	-4.029359	-0.488692	0.808576
37	1	0	-2.334730	-0.416116	4.061151
38	1	0	2.465600	-1.633319	0.916443
39	1	0	4.030080	0.471482	0.812031
40	1	0	1.493173	-1.459746	-2.159504
41	1	0	2.995857	-1.870178	-2.927624
42	1	0	3.762031	-0.098889	3.187909
43	1	0	2.340737	0.338620	4.065075
44	1	0	1.283459	1.415788	-3.814798
45	1	0	1.258461	3.119432	-3.324323
46	1	0	2.458531	2.009617	-2.626404
47	1	0	-0.877887	4.552122	1.507929
48	1	0	0.243713	3.511714	2.412485
49	1	0	0.868234	4.748280	1.305377
50	1	0	0.891099	-4.573612	1.431644
51	1	0	-0.236713	-3.554791	2.352882
52	1	0	-0.853766	-4.777573	1.226350
53	1	0	-2.466941	-1.908160	-2.664542
54	1	0	-1.277352	-1.292431	-3.827088

Predicted KIEs for Various Epoxidations

Optimization of the Shi Epoxidation in mPW1K/SB



E(RmPW+HF-PW91) = -1343.10030047

Zero-point correction=	0.481971 (Hartree/Particle)
Thermal correction to Energy=	0.507939
Thermal correction to Enthalpy=	0.508884
Thermal correction to Gibbs Free Energy=	0.425263
Sum of electronic and zero-point Energies=	-1342.618329
Sum of electronic and thermal Energies=	-1342.592361
Sum of electronic and thermal Enthalpies=	-1342.591417
Sum of electronic and thermal Free Energies=	-1342.675038

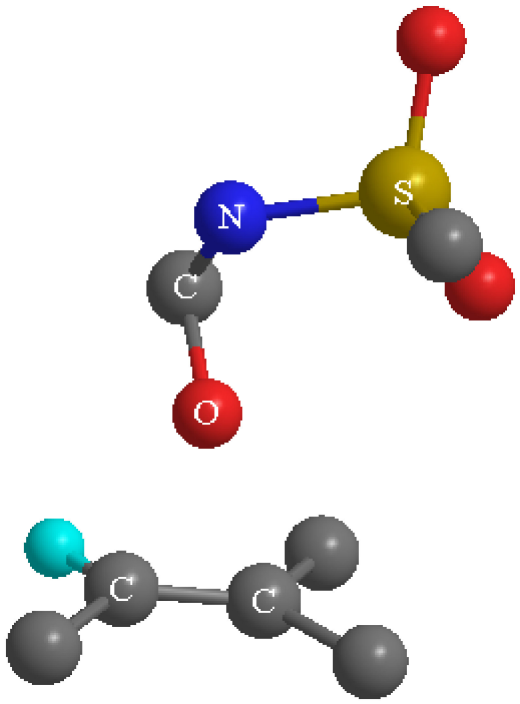
	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	318.737	101.442	175.995

C,0,1.0852579557,-2.8208055362,-0.9245015584
C,0,1.5728885254,-2.4122334223,0.3215335188
C,0,2.9392181113,-2.1520299654,0.4518278461
C,0,3.7897917057,-2.2800703828,-0.6295807678
C,0,3.2917185615,-2.6793823262,-1.8599731274
C,0,1.9377410504,-2.9501031418,-2.0033482081
C,0,0.71846576,-2.2695964306,1.481289154

C,0,-0.6464984133,-2.1422181493,1.482822678
C,0,-1.4891160353,-2.3703850119,2.6876905521
O,0,-1.8409447643,-0.2837862477,-0.8536943635
C,0,-1.6822389881,0.7806937826,0.0445751467
C,0,-2.8966429636,0.6774422294,0.9639766384
O,0,-3.6150584782,-0.4337054615,0.4775143735
C,0,-3.2238779853,-0.6208851342,-0.8525128442
C,0,-0.3391186824,0.7394783684,0.7813243522
C,0,0.8323816701,0.8303342674,-0.1922290828
C,0,0.632508831,1.9576675105,-1.1943249276
C,0,-0.796061559,2.1813093679,-1.6273415458
O,0,-1.7376373903,2.0224643678,-0.5965004427
O,0,2.0183060807,1.1919245822,0.4498101884
C,0,2.2384442696,2.5846649843,0.2639396332
O,0,1.1436895475,3.0546350831,-0.4885690324
C,0,2.2559893824,3.3025985294,1.589281902
C,0,3.5304938273,2.7541592453,-0.5123594672
O,0,-0.3471589098,1.5274164736,1.8319125047
O,0,-0.1958970989,-0.2929785491,1.7582134072
C,0,-3.3830195823,-2.0740214804,-1.2195993816
C,0,-4.0016628274,0.2823592453,-1.7940680413
H,0,-4.4380898727,-2.3357594699,-1.2313481508
H,0,-2.9683467264,-2.2581443933,-2.2077245173
H,0,-2.8838036414,-2.7106798487,-0.4950752373
H,0,-5.0599154115,0.034948722,-1.7463946207
H,0,-3.8692598706,1.3259469576,-1.5255077211
H,0,-3.6559058111,0.1447144657,-2.8167254667
H,0,3.0948815477,2.9540520146,2.1879918453
H,0,2.3607337179,4.3738645501,1.4296892233
H,0,1.3295486862,3.0936417397,2.1129964178
H,0,4.3558951268,2.30679459,0.037075118
H,0,3.4616607512,2.262988914,-1.4808537551
H,0,3.7422491199,3.8098445711,-0.6677651102
H,0,-3.4783309133,1.5950247908,0.901258091
H,0,-2.6089925784,0.497998631,1.9928103494
H,0,0.9653097994,-0.1294115859,-0.6850168219
H,0,1.2348058407,1.7687211117,-2.0899983332
H,0,-1.0241286567,1.4938427402,-2.4431652573
H,0,-0.9113912025,3.1992347363,-1.987798711
H,0,-2.4031844565,-1.7871415196,2.6272442746
H,0,-1.7713982204,-3.4230218696,2.7489053155
H,0,-0.9554291491,-2.1051403969,3.5969321256
H,0,3.3233255605,-1.8226128785,1.4059457317
H,0,4.8413801334,-2.0642094815,-0.5142170536

H,0,3.9561140708,-2.7842036987,-2.7050192507
H,0,1.5485504839,-3.2709387376,-2.9583086696
H,0,0.0368988083,-3.0480042303,-1.0440057122
H,0,-1.1557436533,-2.1147319558,0.5325887588
H,0,1.2164649169,-2.2595252664,2.4417280334

Optimization of the Epoxidation by Oxaziridine in mPW1K/SB



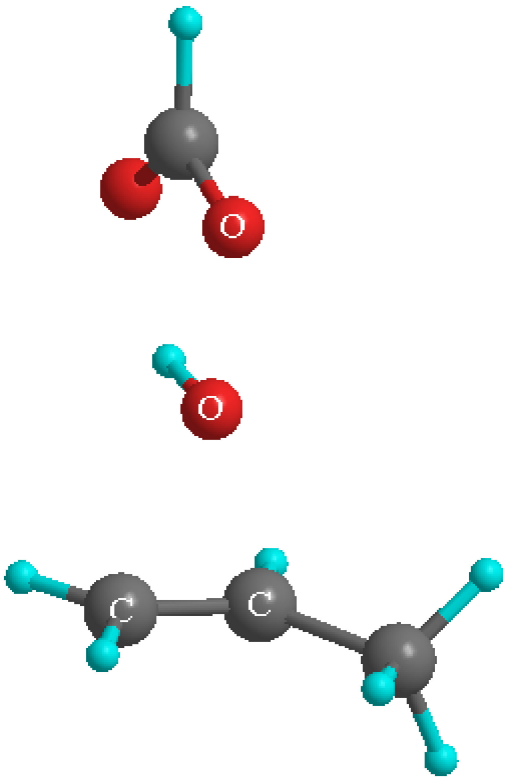
E(RmPW+HF-PW91) = -953.999074076

Zero-point correction=	0.228679 (Hartree/Particle)
Thermal correction to Energy=	0.243350
Thermal correction to Enthalpy=	0.244294
Thermal correction to Gibbs Free Energy=	0.186598
Sum of electronic and zero-point Energies=	-953.770395
Sum of electronic and thermal Energies=	-953.755724
Sum of electronic and thermal Enthalpies=	-953.754780
Sum of electronic and thermal Free Energies=	-953.812476

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	152.704	51.936	121.432

C,0,0.5898483158,-2.1423987205,-1.5353422369
C,0,0.7631139847,-2.1917015959,-0.1739072467
O,0,-0.0386782871,-0.3729729647,-0.885761886
C,0,0.8246971973,0.7145525554,-1.1121447909
N,0,-0.2769585682,1.5152696168,-0.8065800749
S,0,-0.4023016729,1.8638448227,0.8066953287
O,0,-0.1713599744,3.2842005736,0.9770500671
O,0,0.3661008206,0.9410471367,1.6335818018
C,0,-0.5773921694,-2.6227670277,-2.320231211
C,0,-0.2967464718,-2.5985997096,0.7859715877
C,0,2.0691776353,-1.837657638,0.4467344373
C,0,-2.1197596079,1.5543298545,1.0821865277
H,0,1.4631187291,-1.8769815314,-2.1190795248
H,0,1.1260437944,0.8051412713,-2.1532944145
H,0,1.6752977084,0.7208926463,-0.4334747113
H,0,-0.7780615388,-1.9402038329,-3.142936062
H,0,-1.480248548,-2.7020940108,-1.7237744211
H,0,-0.3645478655,-3.6031835346,-2.7501329296
H,0,0.0077257971,-3.5044541931,1.3127401292
H,0,-1.2568272722,-2.7816561859,0.3164022487
H,0,-0.412177069,-1.8106266755,1.5301367845
H,0,1.9285632237,-1.0087150539,1.1421225147
H,0,2.8218852655,-1.5670068448,-0.289821366
H,0,2.4455154225,-2.6837146758,1.0242161806
H,0,-2.3381900733,1.8325217071,2.1089482364
H,0,-2.3190366291,0.5013687448,0.9171562072
H,0,-2.6941321469,2.1654152659,0.3944898242

Optimization of MCPBA Epoxidation in mPW1K/SB



E(RmPW+HF-PW91) = -382.612246132

Zero-point correction=	0.121958 (Hartree/Particle)
Thermal correction to Energy=	0.130302
Thermal correction to Enthalpy=	0.131246
Thermal correction to Gibbs Free Energy=	0.088426
Sum of electronic and zero-point Energies=	-382.490288
Sum of electronic and thermal Energies=	-382.481944
Sum of electronic and thermal Enthalpies=	-382.481000
Sum of electronic and thermal Free Energies=	-382.523820

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	81.766	27.880	90.124

C,0,-1.812045772,0.41058385,-0.4440962856
C,0,-1.5258361455,1.0869359064,0.6989237104
H,0,-1.8440799508,0.7156947076,1.6600942605
H,0,-1.0723680904,2.0658324741,0.6757718831
C,0,2.3643688503,-0.1782042998,-0.1433544882

O,0,2.0244258426,0.8658674463,-0.691305424
H,0,3.409462502,-0.5119589296,-0.1726704752
O,0,1.5894777274,-0.9605602737,0.4915053943
O,0,-0.0125856944,-0.1462628756,0.3641251417
H,0,0.503677399,0.5317038828,-0.1570778251
H,0,-1.5333540647,0.8581720036,-1.3896852138
C,0,-2.5601200748,-0.8683744588,-0.500894922
H,0,-2.7149650373,-1.281799338,0.4919830915
H,0,-3.5324952601,-0.7121808484,-0.9705153431
H,0,-2.0189882313,-1.5976252471,-1.0999965044

Table of Energies

	opt	opt+zpe	Single point+zpe	pcm+zpe
RevIs1	-1761.3424	-1760.8177	-1760.8903	-1760.9055
Revis1d	-1761.3415	-1760.8169	-1760.8895	-1760.9043
RevIs2	-1761.3401	-1760.8155	-1760.8882	-1760.9016
RevIs3	-1761.3411	-1760.8164	-1760.8899	-1760.9035
Revis3b	-1761.3411	-1760.8168	-1760.8898	-1760.9029
Is1	-1761.3388	-1760.8142	-1760.8880	-1760.9013
Is3	-1761.3383	-1760.8134	-1760.8872	-1760.9012
Is3b	-1761.3402	-1760.8156	-1760.8889	-1760.9013
Is4	-1761.3401	-1760.8155	-1760.8882	-1760.9016
Is4b	-1761.3398	-1760.8150	-1760.8884	-1760.9007
revis1trans	-1800.6554	-1800.1020	-1800.1773	-1800.1927
revis1dtrans	-1800.6545	-1800.1010	-1800.1763	-1800.1912
revis3trans	-1800.6547	-1800.1014	-1800.1774	-1800.1907

is3btrans	-1800.6528	-1800.0994	-1800.1754	-1800.1879
revis1cis	-1800.6531	-1800.0996	-1800.1750	-1800.1890
revis3cis	-1800.6519	-1800.0983	-1800.1747	-1800.1880
is3bcis	-1800.6517	-1800.0981	-1800.1742	-1800.1859
revis1meooh	-1643.4145	-1642.9764	-1643.0401	-1643.0573
revis1meoohc	-1643.4035	-1642.9656	-1643.0293	-1643.0471
revis3meooh	-1643.4119	-1642.9736	-1643.0377	-1643.0532
revis3meoohb	-1643.4125	-1642.9742	-1643.0379	-1643.0548
is3bmeooh	-1643.4139	-1642.9758	-1643.0399	-1643.0549

Table of Relative Energies

	opt	opt+zpe	single point	pcm
RevIs1	0.00	0.00	0.00	0.00
RevIs2	1.43	1.33	1.29	2.43
RevIs3	0.81	0.76	0.25	1.27
Is1	2.23	2.16	1.44	2.65
Is3	2.57	2.67	1.92	2.70
Is3b	1.35	1.31	0.86	2.62
Is4	1.43	1.33	1.29	2.43
Is4b	1.62	1.68	1.18	3.03
is3btrans	1.65	1.59	1.17	3.00
is3bcis	0.92	0.95	0.49	1.92
is3bmeooh	0.39	0.37	0.14	1.53
revis1dtrans	0.61	0.57	0.60	0.93
revis1meoohc	6.92	6.74	6.78	6.40
revis3trans	0.43	0.35	-0.05	1.25
revis3cis	0.74	0.82	0.16	0.58
revis3meooh	1.64	1.76	1.53	2.57
revis3meoohb	1.22	1.36	1.38	1.58
revis3b	0.78	0.53	0.29	1.64
is3c	2.57	2.67	1.92	2.72

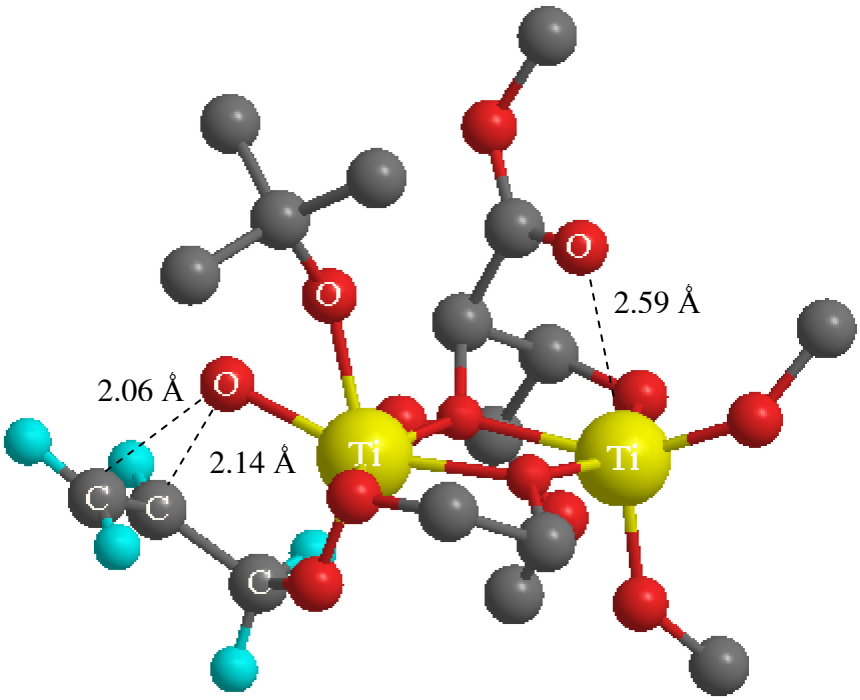
Table of Bond Lengths

	bond lengths alpha carbon	beta carbon	co-Ti
Revls1	2.14	2.06	2.59
Revls2	2.15	2.04	2.67
Revls3	2.11	2.07	2.60
ls1	2.11	2.05	2.54
ls3	2.17	2.03	2.79
ls3b	2.19	2.04	2.78
ls4	2.15	2.04	2.68
ls4b	2.12	2.08	2.58
revis1d	2.14	2.06	2.65
is3btrans	2.18	2.09	2.83
is3bcis	2.12	2.13	2.83
is3bmeooh	2.17	2.04	2.58
revis1dtrans	2.14	2.11	2.67
revis1trans	2.14	2.12	2.61
revis1cis	2.09	2.15	2.60
revis1meooh	2.14	2.06	2.59
revis1meoohb			
revis1meoohc	2.18	2.05	2.73
revis3trans	2.10	2.13	2.58
revis3cis	2.06	2.13	2.55
revis3meooh	2.12	2.04	2.57
revis3meoohb	2.14	2.03	2.56
revis3b	2.11	2.06	2.63

Theoretical Structures with propenol as allyl alcohol

Revls1

Description: Gives correct enantiomer using propenol as substrate. Coordinating carbonyl *cis* to t-butoxide, closest to butoxide. Bystander carbonyl closest to bystander alcohols, carbonyl points towards allyl alkoxide.



Optimization: MPW1K/6-31G* on CHO and SDD on Ti
File name: (revis1optfreq)

E(RmPW+HF-PW91) = -1761.34236086

Zero-point correction=	0.524707 (Hartree/Particle)
Thermal correction to Energy=	0.563280
Thermal correction to Enthalpy=	0.564224
Thermal correction to Gibbs Free Energy=	0.452092
Sum of electronic and zero-point Energies=	-1760.817654
Sum of electronic and thermal Energies=	-1760.779081
Sum of electronic and thermal Enthalpies=	-1760.778136
Sum of electronic and thermal Free Energies=	-1760.890269

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	353.464	136.073	236.003

C,0,-3.2348429649,2.6471095045,-1.3348854216
C,0,-2.0485746258,3.1609314221,-0.9510256651
C,0,-0.7638797998,2.7918032721,-1.6270667161
O,0,-0.8142586147,1.477571641,-2.0725409205
Ti,0,-1.16969768,0.094657531,-0.9535688115
O,0,-2.437061494,1.2566597853,-0.0448921848

O,0,0.4298231847,0.5492885683,0.1896437427
Ti,0,1.9055925113,-0.7927566849,-0.3151143659
O,0,0.5904517619,-1.5213467261,1.7917816724
C,0,0.3311472584,-0.4545026718,2.2981730132
O,0,-0.0349947109,-0.2955807751,3.5508477846
O,0,-2.0055963811,-1.0313244367,-2.1018392938
C,0,-1.4515159116,-2.2431771409,-2.5139089337
C,0,0.0566750195,-2.1021464274,-2.3958912321
O,0,0.2471681213,-1.3232705153,-1.2424285611
O,0,-2.1065332993,-0.3021166319,0.7109964215
C,0,-3.3079686379,-0.9394435358,1.1263909841
C,0,-2.9491909423,-2.4082579122,1.3065243373
C,0,0.5375491645,0.8325315278,1.541488092
C,0,2.0265315286,1.1786648957,1.7073850824
C,0,2.2551158709,2.5827781715,1.1681144036
O,0,1.5077934747,3.4988550526,1.39278035
O,0,2.7084254472,-2.3541448736,-0.0591372965
C,0,3.0119074344,-3.2801512239,0.9270117357
O,0,2.7235311593,0.1936523009,1.0523903036
O,0,2.7314152641,-0.1585410204,-1.74627715
C,0,4.0665859267,0.0733237419,-2.0632495525
C,0,-4.421677178,-0.7955948912,0.1040458528
C,0,-3.7097117009,-0.3073507158,2.4478116847
O,0,3.3712551268,2.6968306409,0.4737379566
H,0,-1.8083996385,-3.0504462656,-1.8688606267
H,0,-1.7549456479,-2.46719733,-3.537560121
H,0,0.4692940222,-1.5729490053,-3.2559135314
H,0,0.5620120751,-3.062749334,-2.2965995574
H,0,-0.5856624677,3.4534815897,-2.4804147899
H,0,0.0628748632,2.930568088,-0.9282091929
H,0,-2.0050214157,3.8587558733,-0.1264755482
H,0,-4.1492336961,2.9254638222,-0.835671057
H,0,-3.3137700377,2.0083562425,-2.2011012747
H,0,2.297252366,1.2165861906,2.7687854453
H,0,-0.134272358,1.6198183688,1.8697312375
H,0,3.666352746,-4.0487330884,0.514712564
H,0,2.1057034841,-3.7537012131,1.3041117953
H,0,3.5244426111,-2.7951533959,1.7592912266
H,0,4.1251201947,0.5302394561,-3.0509451824
H,0,4.6258052258,-0.8638395218,-2.0767696944
H,0,4.5193848345,0.7441362496,-1.3329930068
C,0,3.6415690023,3.9938775697,-0.0260814897
C,0,-0.0784452618,-1.4710588039,4.3462546525
H,0,-4.6094228579,-0.7770767224,2.8437487272

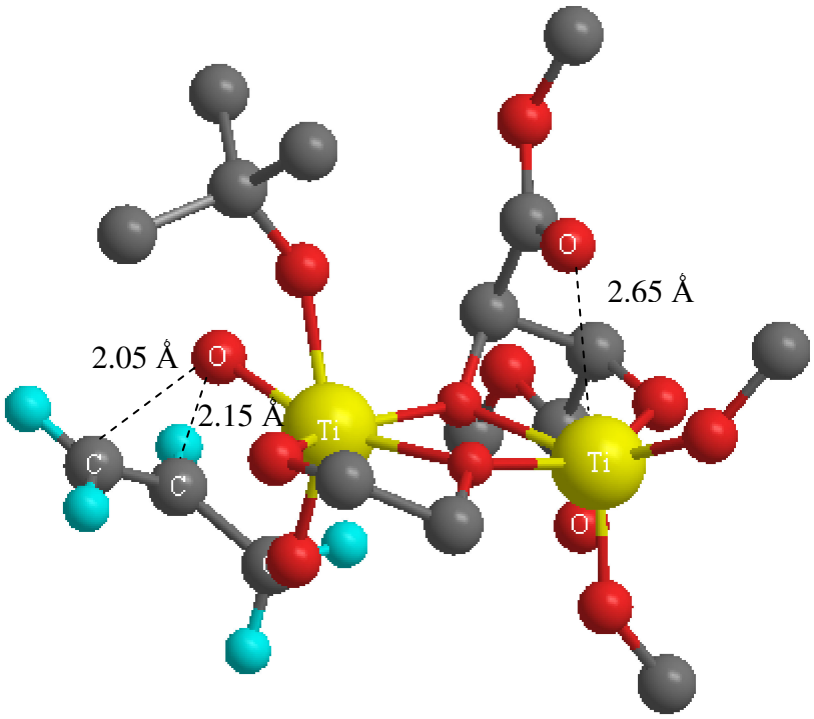
H,0,-3.9030896308,0.7535536596,2.3047468334
H,0,-2.9108946621,-0.4111403238,3.1798637046
H,0,-3.7926217326,-2.9528440294,1.7300871598
H,0,-2.0931392891,-2.5187117552,1.9678178289
H,0,-2.694724019,-2.8577992964,0.3489318771
H,0,-5.2871648505,-1.3722536064,0.4291756621
H,0,-4.1025586715,-1.162117588,-0.8684519504
H,0,-4.7185097565,0.2447694215,0.0025796268
H,0,-0.3346808393,-1.1393724581,5.3446893736
H,0,-0.8323218961,-2.1554411249,3.9700570726
H,0,0.8888354215,-1.9645353858,4.3430572348
H,0,4.5954284046,3.920664154,-0.5340070292
H,0,2.8655251974,4.3016568113,-0.7211558906
H,0,3.6950409671,4.7133358793,0.7860776085

Single point energy: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1760.890285300
File: revis1energy

PCM solvent calculation in dichloromethane: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti=-1760.905502680
File: revis1PCM

RevIs1d

Description: Gives correct enantiomer using propenol as substrate. Coordinating carbonyl *cis* to t-butoxide, closest to butoxide. Bystander carbonyl closest to bystander alcohols, carbonyl points towards bystander alcohols.



Optimization: MPW1K/6-31G* on CHO and SDD on Ti
File name: (revis1doptfreq)

E(RmPW+HF-PW91) = -1761.34145204

Zero-point correction=	0.524525 (Hartree/Particle)
Thermal correction to Energy=	0.563246
Thermal correction to Enthalpy=	0.564190
Thermal correction to Gibbs Free Energy=	0.451450
Sum of electronic and zero-point Energies=	-1760.816928
Sum of electronic and thermal Energies=	-1760.778206
Sum of electronic and thermal Enthalpies=	-1760.777262
Sum of electronic and thermal Free Energies=	-1760.890002

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	353.442	136.242	237.282

C,0,-2.6244436038,3.1766905868,-1.4712682543
C,0,-1.3243872799,3.3865246694,-1.1821350581
C,0,-0.2214909451,2.6817571002,-1.9126220521
O,0,-0.6267229386,1.4055690991,-2.2737675369

Ti,0,-1.2257211578,0.2018435927,-1.0550968019
O,0,-2.1401846658,0.1200271206,0.6673119611
C,0,-3.4379364271,-0.2050423996,1.1513466022
C,0,-3.6022143593,0.5108270544,2.4809592387
O,0,-2.1180916943,1.6825476803,-0.1502711201
O,0,0.482752994,0.3292322689,0.0079919071
C,0,0.7050535207,0.5427543253,1.3560473035
C,0,2.2455696008,0.5652240739,1.4684601662
O,0,2.6940615911,-0.5030365868,0.7401981245
Ti,0,1.6510515976,-1.2619599624,-0.6136779556
O,0,2.4815784283,-0.7606038591,-2.0784262622
C,0,3.7477467641,-0.361624204,-2.499922906
O,0,-2.3679882181,-0.754948173,-2.0864461741
C,0,-2.0853738464,-2.0504153595,-2.5226061549
C,0,-0.5725787169,-2.1924775467,-2.5302449475
O,0,-0.1479999549,-1.4649586754,-1.405777091
O,0,2.1209765701,-2.9642928286,-0.4186773557
C,0,2.2481103386,-3.9466921325,0.5507894605
C,0,-3.438602796,-1.7162125609,1.3357141948
C,0,-4.5347603206,0.2033465415,0.1836383507
C,0,0.2698633632,-0.6897665418,2.108807412
O,0,0.0062338679,-0.4769526324,3.3809501901
C,0,-0.2419468076,-1.6311412348,4.1698897823
O,0,0.2736321849,-1.7769851951,1.5839908408
C,0,2.7743486041,1.8877539257,0.9428651663
O,0,3.4284594874,2.045183265,-0.0455401098
H,0,-2.5316742292,-2.7755541056,-1.8370211431
H,0,-2.5094813297,-2.2140585324,-3.514217957
H,0,-0.1428618537,-1.7462023561,-3.4280869192
H,0,-0.2457186926,-3.2296550695,-2.4595112778
H,0,0.0492479565,3.24155276,-2.8131307974
H,0,0.6703793391,2.6334365092,-1.2840587609
H,0,-1.0571081675,4.0838541953,-0.4001006065
H,0,-3.4044420096,3.696406286,-0.9381888087
H,0,-2.9184214164,2.5467218587,-2.2964738717
H,0,2.5477797083,0.4966019209,2.5180684927
H,0,0.2170846804,1.436690584,1.7352444195
H,0,2.7460915935,-4.8170278043,0.1219981787
H,0,1.2708441682,-4.2495794667,0.9269458257
H,0,2.8450492392,-3.5818114055,1.3883556885
H,0,3.6607267864,0.1255891674,-3.4705803793
H,0,4.4004490376,-1.2297999988,-2.6010321566
H,0,4.1767122688,0.3376469672,-1.7852279442
H,0,-4.5656329274,0.2755046966,2.9318604052

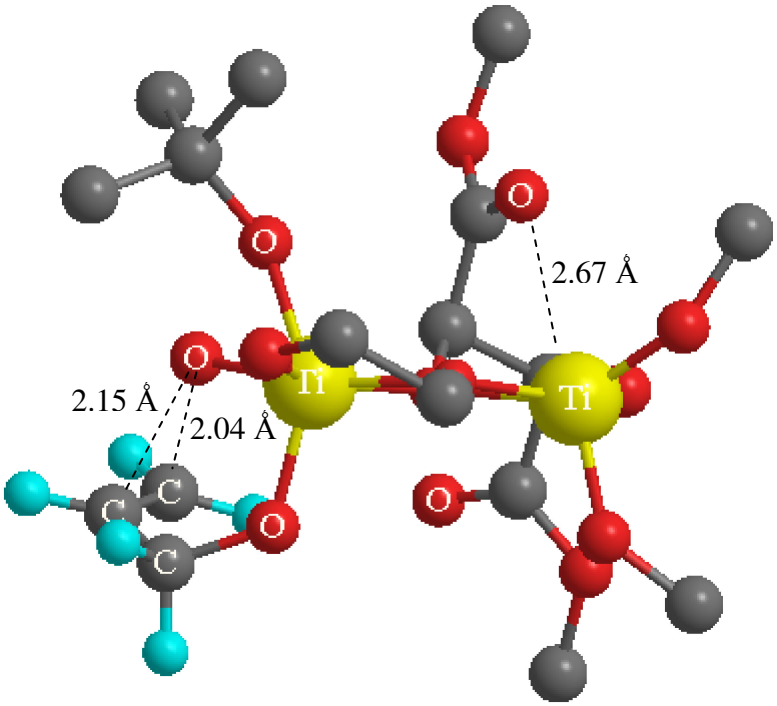
H,0,-3.5414968189,1.5866251445,2.3300273415
H,0,-2.8128857803,0.2190280202,3.1713952543
H,0,-4.3662196016,-2.0378788524,1.8083201638
H,0,-2.6028826504,-2.0303521894,1.956490456
H,0,-3.3501838793,-2.2153546833,0.3730976427
H,0,-5.4964080269,-0.141522583,0.5625549877
H,0,-4.3678085216,-0.236746369,-0.7964235081
H,0,-4.5722628845,1.2843342287,0.07921611
H,0,-0.380738776,-1.2701087065,5.1813273007
H,0,-1.1353950634,-2.1418735062,3.82468692
H,0,0.6026460207,-2.3118045978,4.1189392492
O,0,2.4089112745,2.8824492827,1.7538257959
C,0,2.8586125866,4.1704421221,1.375872698
H,0,2.4887130011,4.8490824737,2.1352272476
H,0,3.9439031097,4.1988542512,1.3372341176
H,0,2.4663565814,4.4424246515,0.3996576212

Single point energy: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti -1760.889537020
File: revis1denergyPCM

PCM solvent calculation in dichloromethane: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1760.904329040
File: revis1denergyPCM

RevIs2

Description: Gives incorrect enantiomer using propenol as substrate. Coordinating carbonyl *cis* to t-butoxide, closest to butoxide. Bystander carbonyl closest to bystander alcohols, carbonyl points towards allyl alkoxide.



Optimization: MPW1K/6-31G* on CHO and SDD on Ti
File name: (revis2optfreq)

E(RmPW+HF-PW91) = -1761.34007531

Zero-point correction=	0.524547 (Hartree/Particle)
Thermal correction to Energy=	0.563304
Thermal correction to Enthalpy=	0.564248
Thermal correction to Gibbs Free Energy=	0.451133
Sum of electronic and zero-point Energies=	-1760.815528
Sum of electronic and thermal Energies=	-1760.776772
Sum of electronic and thermal Enthalpies=	-1760.775827
Sum of electronic and thermal Free Energies=	-1760.888942

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	353.478	136.116	238.070

C,0,1.342628362,3.2939283443,-1.2171972594
C,0,2.1092609413,3.5776711728,-0.1444090367
C,0,1.6061626785,3.4220222073,1.2597660427
O,0,0.7455048687,2.3389610216,1.3457122242
Ti,0,1.1907107779,0.6647208739,0.8092034627
O,0,2.255068995,-0.2549748582,-0.5346327544

C,0,3.5833757699,-0.7280246814,-0.7141898781
C,0,3.84243423,-0.75756144,-2.210710876
O,0,2.1430746886,1.4937682899,-0.6788846747
O,0,-0.4524037882,0.2817846034,-0.2636071258
C,0,-0.5923790882,-0.1192318006,-1.5834214601
C,0,-0.1518713566,-1.5587756009,-1.6741589909
O,0,0.1804988832,-1.9405482421,-2.8887568029
Ti,0,-1.7165187965,-0.8194723689,0.9260043585
O,0,-2.6436295145,-0.76973686,-0.6980005004
C,0,-2.1147200163,-0.1135396075,-1.7829195651
C,0,-2.5595049067,1.3347811632,-1.9307033183
O,0,-3.6451645064,1.6208258785,-1.2392324448
O,0,2.2679512134,0.2246345062,2.2165703504
C,0,1.8711754342,-0.6683730748,3.2098779279
C,0,0.3516423973,-0.6663686885,3.233992184
O,0,-0.0179228413,-0.5375815323,1.8846647154
O,0,-2.6969263141,0.2691235037,1.916688298
C,0,-4.0660699948,0.4060932867,2.1278652013
O,0,-2.2021936254,-2.4299699534,1.4852393854
C,0,-2.3212026856,-3.7438475943,1.0564475002
C,0,3.5962907903,-2.1316197364,-0.1254231569
C,0,4.6043435382,0.1494470512,-0.0119024803
O,0,-1.9851654688,2.1207380027,-2.6379047679
O,0,-0.198911658,-2.291800242,-0.7157334992
H,0,2.2414328041,-1.6710342439,2.9775162332
H,0,2.2853214884,-0.3706783415,4.1749542094
H,0,-0.031295898,0.1910319133,3.7887018107
H,0,-0.0654763968,-1.5790171671,3.659213181
H,0,2.4532665538,3.2926232263,1.9398957246
H,0,1.0781814156,4.3271666882,1.5752757361
H,0,3.1233973168,3.9251168351,-0.287003928
H,0,1.7230906304,3.4155514226,-2.2186149456
H,0,0.3043264696,3.0192055091,-1.11589436
H,0,-2.3856110075,-0.6132381229,-2.7191559224
H,0,-0.0595646962,0.5195412804,-2.2811398546
H,0,-2.8710539955,-4.3196400436,1.8013563441
H,0,-1.338853279,-4.1937392468,0.9160260935
H,0,-2.8631477525,-3.7868219414,0.110602324
H,0,-4.2470051031,1.3016838911,2.7218446713
H,0,-4.4580551214,-0.4574477139,2.6678659235
H,0,-4.5899706064,0.497123677,1.1765174958
C,0,-4.0958068378,2.9591451094,-1.3497032031
C,0,0.4698549558,-3.320673688,-3.0518654256
H,0,4.835006286,-1.1530159138,-2.4237642579

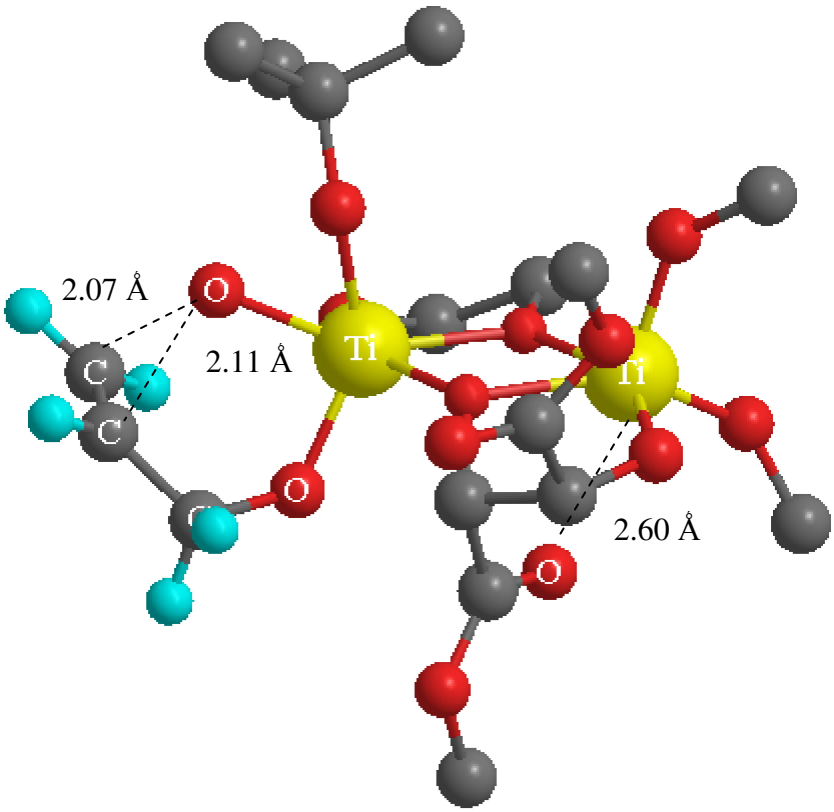
H,0,3.7732913868,0.2492170129,-2.6171052565
H,0,3.1042313041,-1.3792545393,-2.7142523093
H,0,4.5583571023,-2.6094835172,-0.3087669296
H,0,2.8130050598,-2.7424106733,-0.5695962158
H,0,3.4292565513,-2.0894295439,0.9484200084
H,0,5.5956142615,-0.2890840768,-0.1232624644
H,0,4.3746199704,0.2315114905,1.047220897
H,0,4.6159573967,1.1449636494,-0.4477565695
H,0,-4.9917825742,3.0186664714,-0.7440360165
H,0,-3.3398945772,3.6441898525,-0.976798436
H,0,-4.3170680059,3.2035508577,-2.3848035551
H,0,0.6828811404,-3.4530122765,-4.1052911403
H,0,1.331049894,-3.599819581,-2.4526873737
H,0,-0.3838612032,-3.9231053866,-2.7558783078

Single point energy: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1760.888227590
File: revis2energy

PCM solvent calculation in dichloromethane: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1760.901629560
File: revis2PCM

RevIs3

Description: Gives incorrect enantiomer using propenol as substrate. Coordinating carbonyl *cis* to alkoxide, closest to alkoxide. Bystander carbonyl closest to bystander alcohols, carbonyl points towards t-butoxide.



Optimization: MPW1K/6-31G* on CHO and SDD on Ti
File name: (revis3optfreq)

E(RmPW+HF-PW91) = -1761.34107234

Zero-point correction=	0.524625 (Hartree/Particle)
Thermal correction to Energy=	0.563347
Thermal correction to Enthalpy=	0.564291
Thermal correction to Gibbs Free Energy=	0.451384
Sum of electronic and zero-point Energies=	-1760.816448
Sum of electronic and thermal Energies=	-1760.777726
Sum of electronic and thermal Enthalpies=	-1760.776782
Sum of electronic and thermal Free Energies=	-1760.889688

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	353.505	136.135	237.631

C,0,-4.01887952,1.9489502209,-1.1046873274
C,0,-3.1099734611,2.0559660239,-2.0956250873
C,0,-1.7169647683,2.5596634173,-1.8739931084

O,0,-1.2291207863,2.1873976662,-0.6303430297
Ti,0,-1.4351594578,0.5537752548,0.1864943582
O,0,-2.0522462422,-1.1690018149,-0.377786196
C,0,-2.9534362452,-2.2102103866,-0.0335528601
C,0,-3.5423345813,-2.7422401776,-1.3283770609
O,0,-2.8731875958,0.2311571153,-1.0635970045
O,0,0.4203631519,0.0724952413,-0.4976874622
C,0,1.2227656886,0.866925073,-1.3052724268
C,0,1.5240121688,2.1266649255,-0.5332048617
O,0,1.6203080327,2.0969532592,0.6726764034
Ti,0,1.5347891935,-0.4507153657,1.1679448278
O,0,2.8500136352,-0.3410277758,-0.1476067172
C,0,2.5376555292,0.0788318708,-1.4150139694
C,0,2.3328376044,-1.031020545,-2.4342627366
O,0,2.6607442637,-2.229300379,-1.9906818143
O,0,-2.4593427134,1.0329937202,1.612839831
C,0,-1.9568137029,1.1168525822,2.909102426
C,0,-0.8754063621,0.0576475769,3.0252470022
O,0,-0.2671428894,0.0496553298,1.7628434848
O,0,1.3875172377,-2.202678222,1.3904142045
C,0,2.321045241,-3.2299221723,1.4934941944
O,0,2.5034262441,0.0418006843,2.5735331011
C,0,3.4312385368,1.0035781338,2.9462897125
C,0,-2.0893943612,-3.2667701291,0.6407816057
C,0,-4.0450458909,-1.7232255603,0.8998756151
O,0,1.932010869,-0.8087782371,-3.5457824381
O,0,1.743573787,3.1898153838,-1.2709167222
H,0,-1.5332277169,2.1105977767,3.0763624434
H,0,-2.7573407917,0.96107201,3.6347352105
H,0,-1.3054443005,-0.9255682901,3.2248010697
H,0,-0.1431179823,0.2820619204,3.7999765115
H,0,-1.700663355,3.6513216965,-1.9527146236
H,0,-1.0762315815,2.1806058095,-2.6749144562
H,0,-3.385606577,1.7783975661,-3.1036027456
H,0,-5.0135201933,1.5845825455,-1.30768964
H,0,-3.8039196878,2.2690950138,-0.0964747567
H,0,3.3267589885,0.7160060368,-1.8288584215
H,0,0.7883743849,1.0726067,-2.2789514303
H,0,3.8868529375,0.7198129546,3.8954715168
H,0,2.9540241301,1.9766941727,3.0607879489
H,0,4.2156646474,1.0874719161,2.1925406196
C,0,2.0702283559,4.3772508152,-0.5630429347
H,0,1.8025933014,-4.1885581297,1.4678105504
H,0,2.8694324077,-3.1551994618,2.4342293801

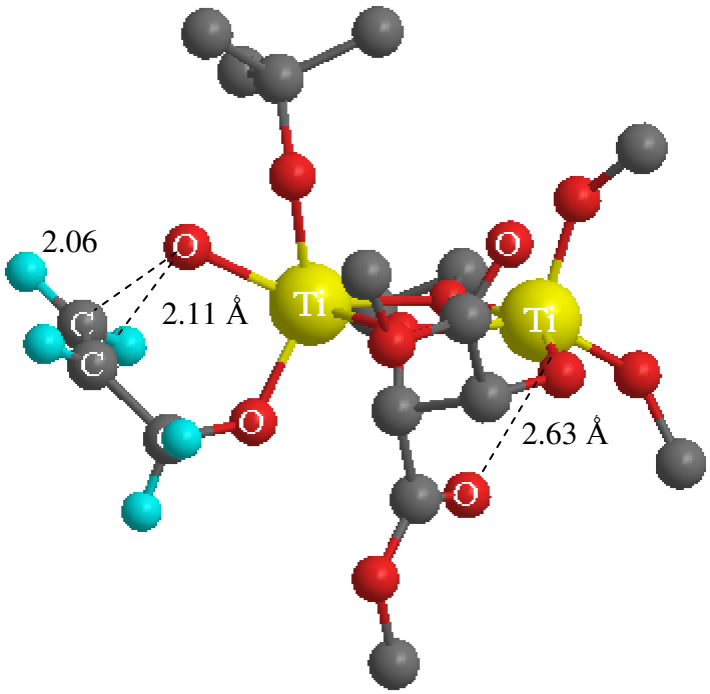
H,0,3.0293978659,-3.1865151059,0.6662688559
C,0,2.4763706571,-3.2824929525,-2.9192761344
H,0,-4.1857561966,-3.5993355992,-1.1331809756
H,0,-2.7457491387,-3.0503455798,-2.0027467317
H,0,-4.1264024108,-1.9673247832,-1.8189633848
H,0,-2.7003943404,-4.125522495,0.9182884995
H,0,-1.6178588519,-2.8674440131,1.5358741689
H,0,-1.3012939017,-3.5989620492,-0.0309702982
H,0,-4.7252510333,-2.5430262014,1.1282315899
H,0,-4.6099801318,-0.9182999993,0.4366678676
H,0,-3.6275664443,-1.3492140637,1.831379702
H,0,2.2170291041,5.1383070186,-1.3192063815
H,0,1.2554897246,4.6487996903,0.101152073
H,0,2.9774954406,4.234895282,0.0163732598
H,0,2.7899006228,-4.184309901,-2.4076332826
H,0,1.4319364092,-3.3525647421,-3.2092378259
H,0,3.0797551981,-3.1180033232,-3.8076058172

Single point energy: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1760.889892540
File: revis3energy

PCM solvent calculation in dichloromethane: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= - 1760.903478790
File: revis3PCM

RevIs3b

Description: Gives incorrect enantiomer using propenol as substrate. Coordinating carbonyl *cis* to alkoxide, closest to alkoxide. Bystander carbonyl closest to bystander alcohols, carbonyl points towards bystander alcohols.



Optimization: MPW1K/6-31G* on CHO and SDD on Ti
File name: (revis3boptfreqenergyPCM)

E(RmPW+HF-PW91) = -1761.42719890

Zero-point correction=	0.524305 (Hartree/Particle)
Thermal correction to Energy=	0.563208
Thermal correction to Enthalpy=	0.564152
Thermal correction to Gibbs Free Energy=	0.450034
Sum of electronic and zero-point Energies=	-1760.816806
Sum of electronic and thermal Energies=	-1760.777904
Sum of electronic and thermal Enthalpies=	-1760.776960
Sum of electronic and thermal Free Energies=	-1760.891078

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	353.418	136.301	240.182

C,0,-4.0102970674,1.9007056776,-1.1164761924
C,0,-3.0953949399,2.0073495997,-2.1019621532
C,0,-1.7105252704,2.5331165429,-1.8763186211
O,0,-1.2191883617,2.1732339495,-0.6312420174
Ti,0,-1.4216705416,0.551299697,0.2114785936

O,0,-0.2644634441,0.1049604377,1.8071270501
C,0,-0.8875733133,0.1208378535,3.0620991749
C,0,-1.9878869596,1.1561671764,2.9150502041
O,0,-2.4734770435,1.038561351,1.6146184715
O,0,-2.0154861648,-1.182951544,-0.3408155665
C,0,-2.9023779652,-2.2346554426,0.0091921804
C,0,-4.0025520574,-1.7551013859,0.936170246
O,0,-2.847201514,0.1998209913,-1.0501985225
O,0,0.4391593141,0.0611942073,-0.4467652161
Ti,0,1.5397136354,-0.4384496843,1.2413008783
O,0,2.4835409962,0.0983165162,2.6491514901
C,0,3.3744303883,1.0961186506,3.0157989135
C,0,-3.4808436137,-2.7842925532,-1.2831467235
C,0,-2.0250653604,-3.2751146258,0.6913283
C,0,1.2499654922,0.8255470395,-1.2698064791
C,0,2.5635335979,0.0252405596,-1.344815023
C,0,2.37614692,-1.1823908911,-2.2487672556
O,0,2.0877422203,-0.789440192,-3.490291525
C,0,1.5549775945,2.1098231599,-0.5376777111
O,0,1.7898259425,3.1421784851,-1.3163959907
C,0,2.1153685085,4.3543634521,-0.6512869705
O,0,1.6348554088,2.1281714637,0.6678327489
O,0,2.8682961957,-0.3369427378,-0.0606555899
O,0,1.3627382735,-2.1739725336,1.4874254343
C,0,2.1518721819,-3.3164115682,1.3655600298
O,0,2.485072339,-2.3268479283,-1.9225033179
H,0,-1.5858096553,2.161085359,3.0679486148
H,0,-2.7936897755,0.9979361929,3.6342184836
H,0,-1.3008315786,-0.8672143438,3.2731178745
H,0,-0.1688149565,0.3719450818,3.8412686749
H,0,-1.711460467,3.6247417135,-1.9589241612
H,0,-1.0609217766,2.162912238,-2.6749864082
H,0,-3.3611401208,1.7148606128,-3.1084100593
H,0,-4.9987338841,1.5213150623,-1.3221418275
H,0,-3.8067542528,2.2352099605,-0.110526738
H,0,3.3545374658,0.6373330913,-1.7909627069
H,0,0.8153913215,1.0145147639,-2.2476071422
H,0,3.8410244934,0.8344256485,3.9661069347
H,0,2.8618275749,2.0518717799,3.1258934371
H,0,4.1553043941,1.2064620538,2.2617028921
H,0,1.508473107,-4.195828162,1.3913040414
H,0,2.8578324683,-3.3771763562,2.1952090764
H,0,2.6955897094,-3.2988940223,0.4231202719
H,0,-4.1152694436,-3.6468870599,-1.0829482367

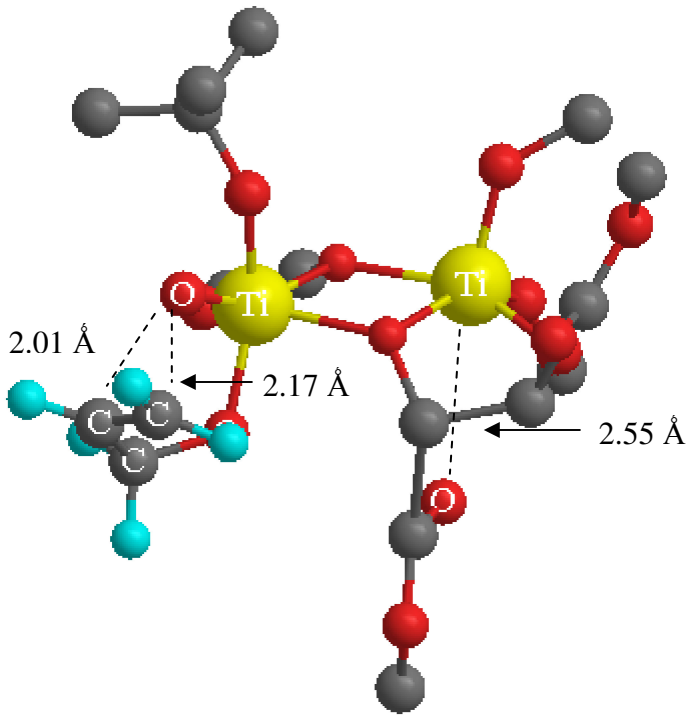
H,0,-2.6781287687,-3.0902201825,-1.9512866413
H,0,-4.0722240301,-2.0203665251,-1.7824177721
H,0,-2.623447789,-4.1452287514,0.9609685739
H,0,-1.5703277037,-2.8694190497,1.5921251843
H,0,-1.2244036968,-3.5909178324,0.0265766426
H,0,-4.6693054823,-2.5830765075,1.1744848858
H,0,-4.5806320104,-0.9650451502,0.4633922612
H,0,-3.5911973613,-1.363109602,1.8630928192
H,0,2.272326462,5.0858120515,-1.4342579834
H,0,1.2961796528,4.6542407334,-0.0049688564
H,0,3.0167052,4.2307648897,-0.058475072
C,0,1.8893081975,-1.8350149408,-4.424722851
H,0,1.678615402,-1.3514432416,-5.3712207361
H,0,2.7812122657,-2.4502661126,-4.5027416142
H,0,1.0536686466,-2.4600681165,-4.1229187015

Single point energy: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1760.889827740
File: revis3bfreqenergyPCM

PCM solvent calculation in dichloromethane: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1760.902893900
File: revis3bfreqenergyPCM

RevIs4

Description: Gives correct enantiomer using propenol as substrate. Coordinating carbonyl *cis* to alkoxide, closest to alkoxide. Bystander carbonyl closest to bystander alcohols, carbonyl points towards t-butoxide.



Optimization: MPW1K/6-31G* on CHO and SDD on Ti
File name: (revis4optfreq)

E(RmPW+HF-PW91) = -1761.34047987

Zero-point correction=	0.524277 (Hartree/Particle)
Thermal correction to Energy=	0.563108
Thermal correction to Enthalpy=	0.564052
Thermal correction to Gibbs Free Energy=	0.450195
Sum of electronic and zero-point Energies=	-1760.816203
Sum of electronic and thermal Energies=	-1760.777372
Sum of electronic and thermal Enthalpies=	-1760.776428
Sum of electronic and thermal Free Energies=	-1760.890285

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	353.356	136.262	239.634

C,0,2.8110945962,2.6976160918,1.2679479051
C,0,3.2654362922,2.6800332663,-0.0026601232
C,0,2.3420724178,2.7739107505,-1.1821133615
O,0,1.1589704153,2.0879512361,-0.9300363397
Ti,0,1.2496545804,0.2991980403,-0.4931921391

O,0,1.9987366476,-0.8934540691,0.8127234771
C,0,3.0130185993,-1.8499008621,1.0624167273
C,0,3.4201837092,-1.708287753,2.5188028098
O,0,2.6331352743,0.7613806784,0.7775456058
O,0,-0.4974954666,0.4971293622,0.4614948746
C,0,-1.1893430931,1.6697809916,0.7368835883
C,0,-1.6105823257,2.2570341402,-0.5860733112
O,0,-1.7531556191,3.5600866736,-0.596184845
Ti,0,-1.8290924135,-0.7952645925,-0.4834249553
O,0,-2.9497076277,0.1389694442,0.6807653424
C,0,-2.4667226242,1.1767825732,1.4363515009
C,0,-2.0959511005,0.8200504469,2.8675861262
O,0,-2.4469849188,-0.4013124081,3.2196919251
O,0,2.1672191218,-0.2315787863,-1.9729663663
C,0,1.5193927611,-0.8075100051,-3.0645670881
C,0,0.3695572609,-1.6291603275,-2.5070881696
O,0,-0.1080866494,-0.8679845824,-1.4309110343
O,0,-1.7069652878,-2.3629704877,0.3318571951
C,0,-2.6448901873,-3.1865307562,0.9476596414
O,0,-2.982076446,-1.1349228402,-1.7902547742
C,0,-3.946773751,-0.5046762946,-2.5625210579
C,0,2.3536843759,-3.2005128273,0.8161763223
C,0,4.2033284659,-1.6550074797,0.1416831546
O,0,-1.5518218105,1.6045477046,3.5984335266
O,0,-1.8639300024,1.5313294141,-1.5211936394
H,0,1.1352898597,-0.0234056689,-3.722596565
H,0,2.2166219179,-1.4222410186,-3.6369880607
H,0,0.7169645881,-2.5956351767,-2.1392606301
H,0,-0.422002733,-1.7967520428,-3.2368298743
H,0,2.8400082622,2.3593337829,-2.0623406125
H,0,2.1142677004,3.8230160323,-1.3965204875
H,0,4.3246322706,2.5713700139,-0.1904995147
H,0,3.4871908223,2.6323102088,2.1047569508
H,0,1.7728727987,2.8852434873,1.4888899545
H,0,-3.197131665,1.9892981148,1.5113047139
H,0,-0.6248357773,2.373834274,1.3398445703
H,0,-4.4969056467,-1.2510262756,-3.1363417318
H,0,-3.4874198105,0.2030683151,-3.2523215312
H,0,-4.6498779684,0.0353308703,-1.9264781209
H,0,-3.2084663476,-2.6287745286,1.6954283949
H,0,-2.1295504786,-4.0147361507,1.4342886012
H,0,-3.3392687559,-3.5929793126,0.2100654588
C,0,-2.1023471911,-0.7653312342,4.5442835464
C,0,-2.1950853228,4.1257355643,-1.8216999958

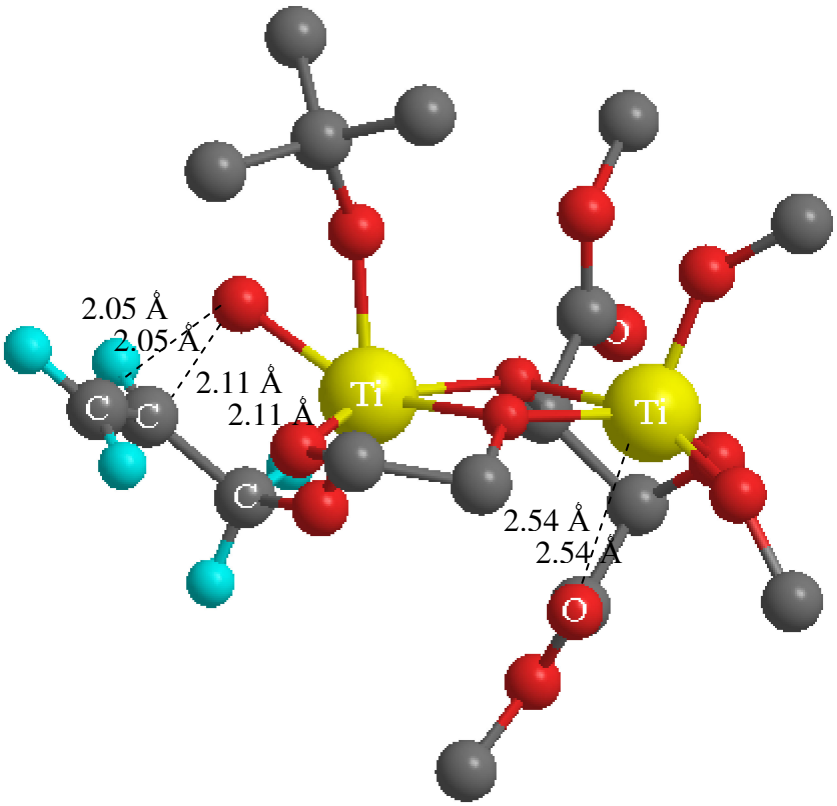
H,0,4.1737305595,-2.4497493783,2.7820919319
H,0,2.555959295,-1.8433107096,3.1665772911
H,0,3.8285601222,-0.7155948599,2.6935685333
H,0,3.0380231715,-4.0048389845,1.0849367378
H,0,2.0871035235,-3.3113286351,-0.2329290268
H,0,1.4476249188,-3.2957803656,1.4105507133
H,0,4.9331825323,-2.4458959853,0.3117890739
H,0,4.6780887344,-0.6958434386,0.3326924182
H,0,3.8916784986,-1.6777899241,-0.8992599775
H,0,-2.4636953812,-1.7781132806,4.6747285367
H,0,-1.0252679337,-0.7252677432,4.6788299409
H,0,-2.5737824552,-0.0964726702,5.2588513072
H,0,-2.248233921,5.1933577212,-1.649178828
H,0,-1.4854221055,3.8998488882,-2.6115654239
H,0,-3.1715762764,3.7332143683,-2.0892988119

Single point energy: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1761.41392185
File: revis4energy

PCM solvent calculation in dichloromethane: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1761.42669638
File: revis4PCMsp

ls1

Description: Gives correct enantiomer using propenol as substrate. Coordinating carbonyl *cis* to alkoxide, closest to bystander alcohols. Bystander carbonyl closest to t-butoxide, carbonyl points away from catalyst.



Optimization: MPW1K/6-31G* on CHO and SDD on Ti
File name: (is1optfreq)

E(RmPW+HF-PW91) = -1761.33880038

Zero-point correction=	0.524581 (Hartree/Particle)
Thermal correction to Energy=	0.563347
Thermal correction to Enthalpy=	0.564292
Thermal correction to Gibbs Free Energy=	0.450905
Sum of electronic and zero-point Energies=	-1760.814219
Sum of electronic and thermal Energies=	-1760.775453
Sum of electronic and thermal Enthalpies=	-1760.774509
Sum of electronic and thermal Free Energies=	-1760.887895

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	353.506	136.231	238.642

C,0,-3.6515451072,2.6029876934,0.0745204568
C,0,-2.9147265661,2.7973917332,1.1875731378
C,0,-1.4402123065,3.0564342399,1.1483617203

O,0,-0.8150576745,2.3334020459,0.1429749575
Ti,0,-1.1672675363,0.6186274666,-0.41588156
O,0,0.3912262184,-0.0420651633,0.6704147598
C,0,1.0373146458,0.5507585226,1.741747026
C,0,1.0875920461,-0.2987539064,2.9955621214
O,0,0.437290898,-1.4392408313,2.8958618754
O,0,-1.8135978672,0.9884768397,-2.0798578517
C,0,-1.3988751942,0.3402478217,-3.2394242281
C,0,0.0343881285,-0.098476483,-3.0143372136
O,0,0.0937611825,-0.4452895616,-1.6536224058
Ti,0,1.6881067153,-1.0001411454,-0.6604573389
O,0,1.4134369326,-2.7104337939,-0.3210801711
C,0,1.9702974939,-3.9373727976,-0.6551905883
O,0,-2.2249098445,-0.8279692106,0.2427739782
C,0,-3.2316739845,-1.7509431678,-0.1421778405
C,0,-4.236713764,-1.1233174347,-1.0901193971
O,0,-2.8393353932,0.7879281682,0.5602004264
O,0,2.8682757368,-0.4059579803,0.6645923429
C,0,2.4769398342,0.7771685337,1.2448114375
C,0,2.3604599263,1.8075085028,0.1458968845
O,0,2.4534386317,3.0571322152,0.5239911184
O,0,2.8245811055,-1.1463625807,-2.0233796825
C,0,3.9476819257,-0.5119314235,-2.5341689166
O,0,2.1348784902,1.4500635694,-0.9905952488
O,0,1.6666393784,0.071395492,3.9820240292
C,0,-3.9093472782,-2.2164017727,1.1347516146
C,0,-2.4875279362,-2.896432561,-0.8143203096
H,0,-2.0395103831,-0.5261439033,-3.4284261767
H,0,-1.4811455475,1.0098501385,-4.0975099286
H,0,0.7270706733,0.7220714758,-3.2044349939
H,0,0.3155609326,-0.9458628326,-3.638545037
H,0,-1.2543453775,4.1238179304,0.9898106558
H,0,-1.017814541,2.8122843827,2.1275916317
H,0,-3.3949072139,2.7759711994,2.1559240106
H,0,-4.7130148614,2.4238585647,0.1413805109
H,0,-3.2235490925,2.6772399841,-0.9138394823
H,0,3.1376886285,1.1033997414,2.0462388971
H,0,0.5718656804,1.494480054,2.0235446083
H,0,1.1778062549,-4.6458624407,-0.8985527113
H,0,2.5406618988,-4.3311211192,0.1868189042
H,0,2.6339224275,-3.8391161558,-1.5160897144
H,0,4.4742370611,-1.1874285582,-3.2091798493
H,0,4.6229097826,-0.2234644582,-1.7270833797
H,0,3.6655380832,0.3845840781,-3.087082971

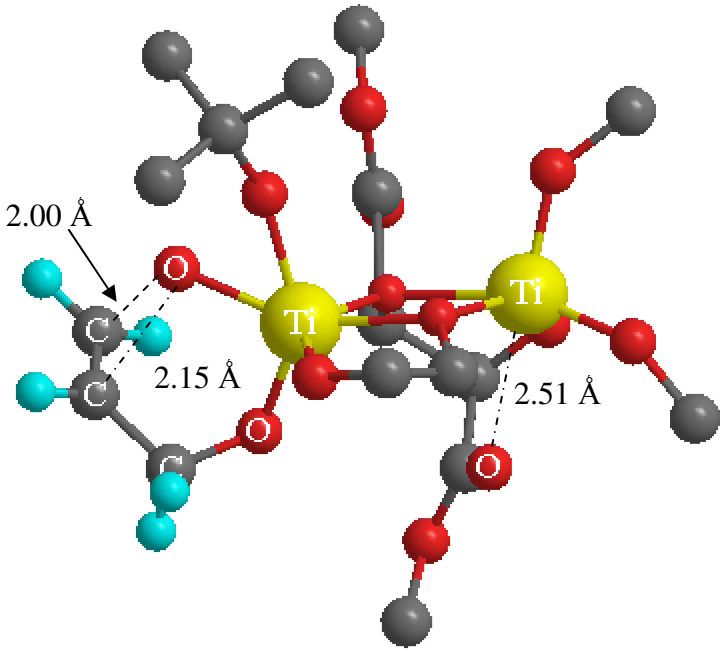
C,0,2.1767842983,4.0245581899,-0.482475599
C,0,0.4880499133,-2.2534209703,4.0527140819
H,0,-4.6838910144,-2.9503942739,0.9148990073
H,0,-4.3645266362,-1.3685083093,1.6423513894
H,0,-3.1796140284,-2.6672973719,1.8043655639
H,0,-3.180129935,-3.7028199721,-1.0546959337
H,0,-1.7113870135,-3.280414269,-0.156257341
H,0,-2.0119804502,-2.5582061661,-1.7325943843
H,0,-4.9394037333,-1.8820044231,-1.4329457466
H,0,-3.7381095273,-0.6912276417,-1.9537545118
H,0,-4.7917240092,-0.3332555894,-0.5912248834
H,0,-0.0832594031,-3.1416042773,3.8128022346
H,0,1.5165625602,-2.5127849013,4.2869355067
H,0,0.051771817,-1.7354036445,4.9023039957
H,0,2.2907709034,4.98787362,-0.0010982963
H,0,2.8816693621,3.9238515884,-1.3022723056
H,0,1.1634759548,3.8882764905,-0.8466548434

Single point energy: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1760.887992720
File: is1energy

PCM solvent calculation in dichloromethane: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= - 1760.901282910
File: is1PCM

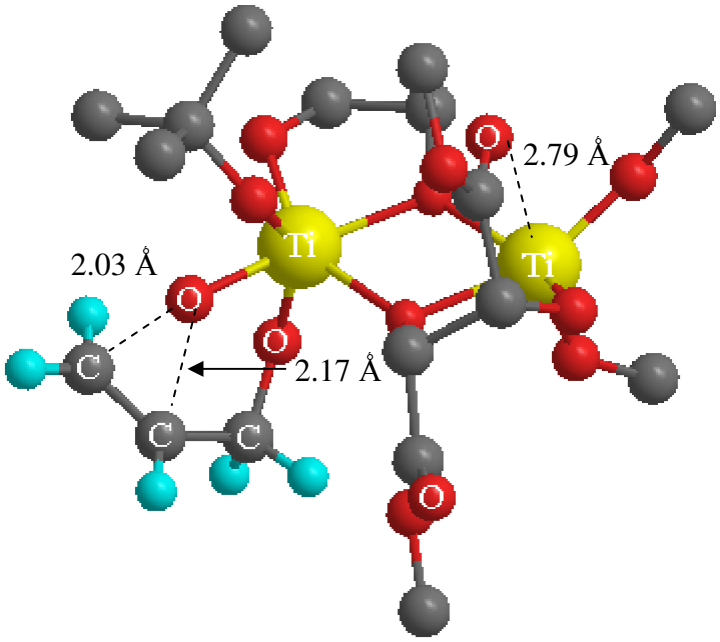
Is2

Description: Gives correct enantiomer using propenol as substrate. Coordinating carbonyl *cis* to alkoxide, closest to bystander alcohols. Bystander carbonyl closest to t-butoxide, carbonyl points away from catalyst.



Is3

Description: Gives incorrect enantiomer using propenol as substrate. Coordinating carbonyl *cis* to t-butoxide, closest to bystander alcohols. Bystander carbonyl closest to allyl alkoxide, carbonyl points directly away from catalyst in between allyl alkoxide and bystander alcohols (not towards either).



Optimization: MPW1K/6-31G* on CHO and SDD on Ti
File name: (is3optfreqenergyPCMesters)

E(RmPW+HF-PW91) = -1761.33826056

Zero-point correction=	0.524863 (Hartree/Particle)
Thermal correction to Energy=	0.563572
Thermal correction to Enthalpy=	0.564516
Thermal correction to Gibbs Free Energy=	0.451576
Sum of electronic and zero-point Energies=	-1760.813398
Sum of electronic and thermal Energies=	-1760.774688
Sum of electronic and thermal Enthalpies=	-1760.773744
Sum of electronic and thermal Free Energies=	-1760.886685

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	353.647	136.192	237.704

C,0,3.6604592026,2.4072103593,-0.7270514614
C,0,2.6272937845,3.0642860999,-0.1620795421
C,0,1.3033569635,3.2059761215,-0.8500803031
O,0,1.0010164678,2.05353525,-1.562962779
Ti,0,1.0678060277,0.3685745389,-0.904773986
O,0,-0.372380662,0.6348636857,0.4779796203
C,0,-0.3259803619,0.5904284276,1.861572946
C,0,-0.6019063148,1.9110418692,2.5529025468
O,0,-0.6229092935,2.0003009866,3.7507665093
O,0,1.6376387574,-0.5176841229,-2.387951505
C,0,0.739883195,-0.7912178377,-3.420917361
C,0,-0.5665860888,-1.2098945961,-2.770708032
O,0,-0.6752162946,-0.3970215081,-1.6300767014
Ti,0,-2.1339885349,-0.0661001709,-0.3738934149
O,0,-2.937137203,1.3796827254,-0.9822169907
C,0,-4.1061564534,1.7302206051,-1.6441894503
O,0,1.9942722507,-0.7221646241,0.4154461999
C,0,3.0296547531,-1.701532478,0.3815194817
C,0,4.1988351443,-1.277900999,-0.4905298448
O,0,2.5991312283,0.9150710981,0.1589701382
O,0,-2.5147284268,-0.1360355068,1.4478298256
C,0,-1.445950229,-0.3879632319,2.2766006622
C,0,-0.980438554,-1.8008379545,2.0086349319
O,0,-0.5349596497,-2.4277856611,3.0785368913

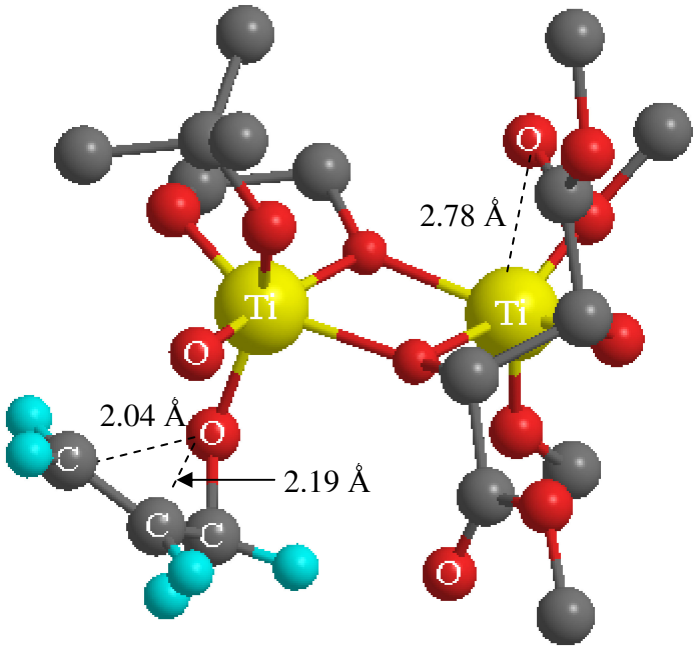
O,0,-3.2305983856,-1.3368192999,-0.9540349771
C,0,-3.7860769948,-2.5494163768,-0.5732711304
O,0,-1.0386451989,-2.2854043521,0.904509659
O,0,-0.8205053579,2.9249492144,1.7343920055
C,0,3.4787877866,-1.8951689532,1.8198316977
C,0,2.3978071608,-2.9667554792,-0.182648669
H,0,0.5923106561,0.1086657939,-4.0232938893
H,0,1.1352397327,-1.5762222155,-4.06808218
H,0,-0.534750946,-2.2540616663,-2.4577033201
H,0,-1.4214060929,-1.0691955954,-3.4311451881
H,0,1.3335303402,4.0549678658,-1.5406086418
H,0,0.5242981559,3.4045297591,-0.1157538774
H,0,2.7434473453,3.4968566805,0.8221060852
H,0,4.6090470557,2.3191351549,-0.2221999297
H,0,3.5998147906,2.0350405838,-1.7383204632
H,0,-1.6962135577,-0.2671981969,3.3290120298
H,0,0.6512175084,0.2526610858,2.2098879666
H,0,-3.8658640767,2.342594119,-2.5135328759
H,0,-4.7502212736,2.307306199,-0.9801939828
H,0,-4.646215386,0.8413284088,-1.9743612018
C,0,-1.1405088651,4.1502249984,2.369535722
H,0,-4.6860304491,-2.7390159718,-1.1590895025
H,0,-4.0515788236,-2.5308648336,0.4845654137
H,0,-3.0805558335,-3.3630777913,-0.7399770664
C,0,-0.1581997614,-3.7854324953,2.9127188131
H,0,4.2548592835,-2.6568779188,1.8856059557
H,0,2.640787079,-2.1983549104,2.4456053958
H,0,3.8750659324,-0.9611316868,2.2136241558
H,0,3.0877744986,-3.8054770343,-0.0906396447
H,0,2.1586204955,-2.8252356493,-1.2339461803
H,0,1.4771647189,-3.2067307385,0.3435359816
H,0,4.918001828,-2.0949518007,-0.5434096191
H,0,4.6963525341,-0.4055742603,-0.0758888423
H,0,3.8603730808,-1.0495206558,-1.4980470094
H,0,0.0210288544,-4.16357679,3.9116744707
H,0,-0.9563567204,-4.3418994966,2.4306412786
H,0,0.7447158053,-3.8615189031,2.3159454156
H,0,-1.3016067809,4.8625681522,1.5694494711
H,0,-2.0405658992,4.0408998098,2.9670732555
H,0,-0.3264809478,4.4719851703,3.013204037

Single point energy: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1760.887220320
File: is3optfreqenergyPCMesters

PCM solvent calculation in dichloromethane: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1760.901201950
File: is3optfreqenergyPCMesters

Is3b

Description: Gives incorrect enantiomer using propenol as substrate. Coordinating carbonyl *cis* to t-butoxide, closest to bystander alcohols. Bystander carbonyl closest to alkoxide, carbonyl points down directly down from catalyst in between alkoxide and bystander alcohols (not towards either).



Optimization: MPW1K/6-31G* on CHO and SDD on Ti
File name: (is3bfreq)
E(RmPW+HF-PW91) = -1761.34021144

Zero-point correction=	0.524653 (Hartree/Particle)
Thermal correction to Energy=	0.563534
Thermal correction to Enthalpy=	0.564479
Thermal correction to Gibbs Free Energy=	0.450663
Sum of electronic and zero-point Energies=	-1760.815559
Sum of electronic and thermal Energies=	-1760.776677
Sum of electronic and thermal Enthalpies=	-1760.775733
Sum of electronic and thermal Free Energies=	-1760.889549

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

Total	353.623	136.288	239.546

C,0,3.5267839197,2.3804019383,-1.0030238714
C,0,2.4049576828,3.0242987801,-0.6214363912
C,0,1.1428806658,2.9739499274,-1.4273561776
O,0,0.9726042697,1.7045324528,-1.9749865511
Ti,0,1.0410536774,0.1720305359,-1.0245097323
O,0,-0.3749243065,0.6780206952,0.3104636727
C,0,-0.3021764133,0.846886038,1.679568549
C,0,-0.4396595301,2.3028496898,2.077662598
O,0,-0.4822717536,3.2421760445,1.3367034987
O,0,1.5915062276,-0.9715001658,-2.3306130662
C,0,0.6760137874,-1.4312108188,-3.278209991
C,0,-0.6169069976,-1.7210363603,-2.5386655009
O,0,-0.7197227444,-0.6952433152,-1.5837896683
Ti,0,-2.1603367457,-0.1058915608,-0.4069008966
O,0,-2.8988667868,1.2509709168,-1.2465459758
C,0,-4.0594391745,1.5901865839,-1.9266623028
O,0,1.9845160978,-0.6950425299,0.449494111
C,0,3.0823409946,-1.5907346694,0.5754976106
C,0,4.2150116207,-1.2552502227,-0.3799631138
O,0,2.5080508258,0.9282949786,-0.0005546494
O,0,-2.5321704459,0.1573610588,1.4029428194
C,0,-1.464981822,0.0073548165,2.2548297519
C,0,-1.0505744501,-1.4467681177,2.2173411522
O,0,-0.5991069065,-1.9069782224,3.3665789383
O,0,-3.3168327802,-1.406416617,-0.7592850645
C,0,-3.9336387328,-2.5089115783,-0.1886753285
O,0,-1.145188357,-2.100791364,1.2071294704
O,0,-0.4777457962,2.4113671011,3.4038847458
C,0,3.5528062872,-1.5002506993,2.017111504
C,0,2.5326600506,-2.9742593133,0.2541577207
H,0,0.514083837,-0.6584981336,-4.0339193555
H,0,1.0609585317,-2.3233144708,-3.7759370543
H,0,-0.5659733379,-2.6797821681,-2.0208693851
H,0,-1.4826109683,-1.7243638274,-3.1998606854
H,0,1.1923122536,3.7058920863,-2.2394065958
H,0,0.295319464,3.226399659,-0.7936263739
H,0,2.39367284,3.5879923953,0.300780537
H,0,4.4294679976,2.4326739671,-0.415532603
H,0,3.5837207677,1.8772027784,-1.9561933004
H,0,-1.7020056121,0.3015423377,3.2755128429
H,0,0.6604569432,0.5019816374,2.0640353423
H,0,-3.8038164681,2.036763172,-2.8875834826

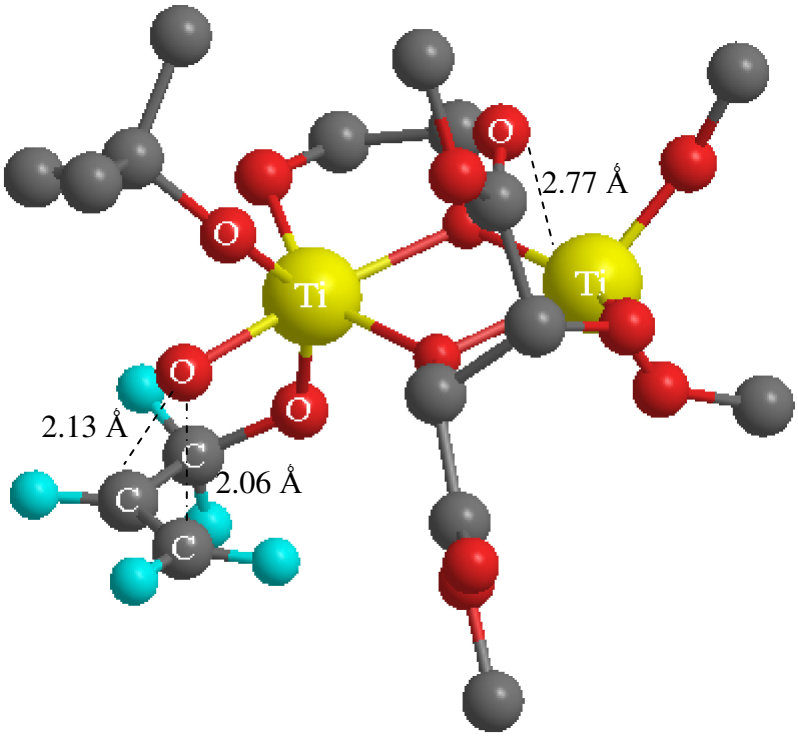
H,0,-4.6305791808,2.3155248397,-1.3469766322
H,0,-4.678786476,0.7081288243,-2.0985376203
C,0,-0.5895492691,3.7313486397,3.9046989325
H,0,-4.8385112586,-2.7519688886,-0.7467042622
H,0,-4.205558493,-2.3005820454,0.8472519329
H,0,-3.268668222,-3.3722811526,-0.2060127634
C,0,-0.2421317607,-3.2800812551,3.403206771
H,0,4.386551158,-2.1778467629,2.1974669609
H,0,2.7440968184,-1.7565965976,2.7003016785
H,0,3.8765241888,-0.4847865401,2.2377759591
H,0,3.2799387453,-3.7375203171,0.4696205214
H,0,2.2641365528,-3.0318053645,-0.7981127743
H,0,1.6418521463,-3.1793602718,0.8424654338
H,0,4.9850051207,-2.0227141096,-0.3052098605
H,0,4.6589589836,-0.2943112725,-0.1347086428
H,0,3.8544711712,-1.228396593,-1.4054526114
H,0,-0.6087562692,3.637417932,4.9837879299
H,0,0.2601952157,4.3313404465,3.5912256722
H,0,-1.5031300863,4.1975696233,3.5470491756
H,0,0.0147128706,-3.4884500006,4.4345084498
H,0,-1.0787682954,-3.8957826602,3.0866597815
H,0,0.608004728,-3.4707259098,2.7574612203

Single point energy: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1760.888913520
File: is3benergy

PCM solvent calculation in dichloromethane: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1760.901328890
File: is3bPCM

Is4

Description: Gives correct enantiomer using propenol as substrate. Coordinating carbonyl *cis* to t-butoxide, closest to bystander alcohols. Bystander carbonyl closest to alkoxide, nonligating carbonyl points points away from catalyst.



Optimization: MPW1K/6-31G* on CHO and SDD on Ti
File name: (is4optfreq)

E(RmPW+HF-PW91) = -1761.33920844

Zero-point correction=	0.524731 (Hartree/Particle)
Thermal correction to Energy=	0.563451
Thermal correction to Enthalpy=	0.564395
Thermal correction to Gibbs Free Energy=	0.451454
Sum of electronic and zero-point Energies=	-1760.814477
Sum of electronic and thermal Energies=	-1760.775757
Sum of electronic and thermal Enthalpies=	-1760.774813
Sum of electronic and thermal Free Energies=	-1760.887755

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	353.571	136.137	237.706

C,0,-2.4091430262,-1.7758446272,2.4907159645
C,0,-3.0775679743,-2.3863079992,1.491325563
C,0,-2.3688353963,-3.1065519361,0.3842953405
O,0,-1.1611668931,-2.4889662392,0.1000001616
Ti,0,-1.0550280832,-0.7321540506,-0.3495553354
O,0,0.4346084641,-0.0917038001,0.8089795954

C,0,0.4607864106,0.8041049494,1.8651450083
C,0,0.8016968858,0.1770530548,3.2030950334
O,0,0.8845386913,-1.1408835969,3.1702873677
O,0,-1.6876139089,-0.9301135262,-2.060458983
C,0,-0.8505288408,-1.5611300526,-2.9804262716
C,0,0.5269137869,-0.9475950479,-2.812888494
O,0,0.6692303092,-0.7667248033,-1.4249590202
Ti,0,2.1749410276,-0.1681228404,-0.3313189414
O,0,2.9903658467,-1.6590791032,0.1292924044
C,0,4.1667935435,-2.3463691118,-0.1366955924
O,0,-2.0219061133,0.9255491274,-0.0983729309
C,0,-3.1510037871,1.5825233538,-0.6659725149
C,0,-4.2859899451,0.6183779316,-0.964570009
O,0,-2.4735759552,-0.4132559147,0.9515514357
C,0,-3.591044284,2.6309781313,0.3411688127
C,0,-2.6570480177,2.2213670805,-1.9562465272
O,0,2.6189580643,1.0545315989,1.0028802174
C,0,1.5806772023,1.8011994519,1.5101753946
C,0,1.0760761862,2.6992854192,0.4037775346
O,0,0.6394244491,3.8696029491,0.820820266
O,0,3.2172661425,0.408807355,-1.6464286561
C,0,3.7579035328,1.5712872498,-2.1767276676
O,0,1.0888004074,2.3431505895,-0.7497644514
O,0,0.9675107427,0.8395264138,4.1909890793
H,0,-0.8083779647,-2.6337674984,-2.7705024687
H,0,-1.2293370057,-1.4226271817,-3.9949019818
H,0,0.5883730391,0.0247480786,-3.3022131753
H,0,1.3175947753,-1.588060511,-3.2022295648
H,0,-3.009128665,-3.1248485389,-0.5028641708
H,0,-2.1846410521,-4.1472661786,0.6684699879
H,0,-4.1587012601,-2.3647248415,1.474275977
H,0,-2.9381099921,-1.2626337196,3.2780516409
H,0,-1.335333415,-1.8461038218,2.5675581728
H,0,1.8718811882,2.3874161193,2.3796709857
H,0,-0.5039204395,1.3015323474,1.9818541685
H,0,3.939681976,-3.3905140879,-0.3521441647
H,0,4.8258046176,-2.3057721145,0.7309478
H,0,4.6843547318,-1.9114298315,-0.993274029
H,0,3.0239980939,2.0874859791,-2.7949961795
H,0,4.6237815396,1.3233522407,-2.7912574682
H,0,4.0736035818,2.2431775755,-1.3776103501
C,0,0.1931062928,4.7730231104,-0.1777577238
C,0,1.2489443599,-1.7531049502,4.3949381251
H,0,-4.4395561183,3.1998496558,-0.037275395

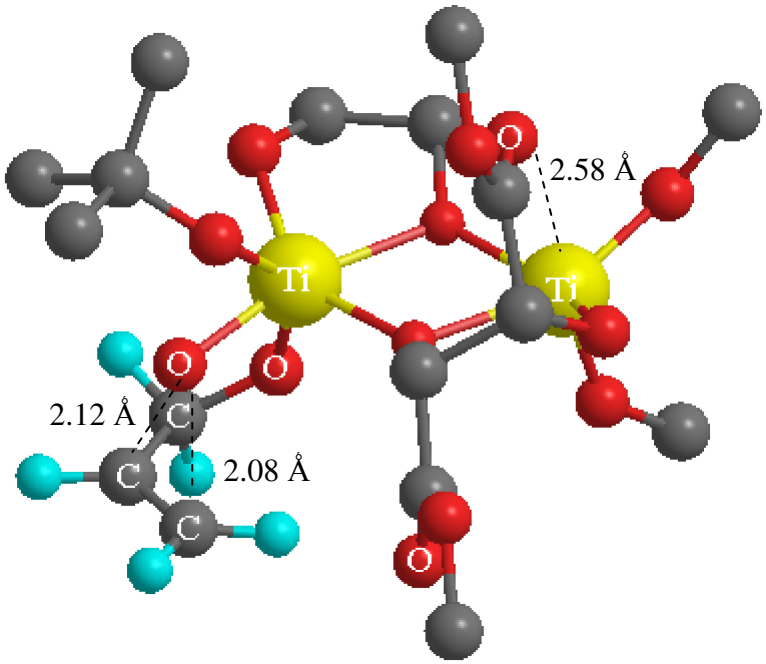
H,0,-2.7775124794,3.3229744036,0.553761881
H,0,-3.8823481225,2.1511215871,1.2734368752
H,0,-3.4416150337,2.8388540182,-2.3931724511
H,0,-2.3758002191,1.4489899063,-2.6671303765
H,0,-1.7860797731,2.8450865664,-1.7687042614
H,0,-5.0954569931,1.1593578313,-1.453874718
H,0,-4.6680746519,0.1769722972,-0.0481937426
H,0,-3.948050291,-0.1734058906,-1.6281317031
H,0,1.28777852,-2.8158311746,4.1902995933
H,0,2.2196287899,-1.3920514274,4.7213369731
H,0,0.513710684,-1.5358363907,5.1649394415
H,0,-0.0027928999,5.7055778614,0.3369428827
H,0,0.9601363551,4.9078263927,-0.9344850163
H,0,-0.7131646363,4.4040751813,-0.646359348

Single point energy: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1761.41305795
File: is4energy

PCM solvent calculation in dichloromethane: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= --1761.42628262
File: is4PCMsp

Is4b

Description: Gives correct enantiomer using propenol as substrate. Coordinating carbonyl *cis* to t-butoxide, closest to bystander alcohols. Bystander carbonyl closest to alkoxide, carbonyl points points down directly down from catalyst in between alkoxide and bystander alcohols (not towards either).



Optimization: MPW1K/6-31G* on CHO and SDD on Ti
File name: (is4boptfreq)

E(RmPW+HF-PW91) = -1761.33978389

Zero-point correction=	0.524810 (Hartree/Particle)
Thermal correction to Energy=	0.563433
Thermal correction to Enthalpy=	0.564377
Thermal correction to Gibbs Free Energy=	0.451487
Sum of electronic and zero-point Energies=	-1760.814974
Sum of electronic and thermal Energies=	-1760.776351
Sum of electronic and thermal Enthalpies=	-1760.775406
Sum of electronic and thermal Free Energies=	-1760.888297

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	353.560	136.041	237.599

C,0,2.3169188543,2.5959556573,-1.7145348539
C,0,3.1445832739,1.6884034417,-2.2699358373
C,0,2.6304700858,0.5338595829,-3.0761543368
O,0,1.4243962855,0.0819113833,-2.5617058443
Ti,0,1.2127488098,-0.4113913531,-0.8325624229
O,0,2.4324123039,1.0295038856,-0.3622430947
O,0,-0.4461877093,0.5435555127,-0.2876812576

Ti,0,-2.0404446681,-0.7514698869,-0.6185430361
O,0,-3.0153303021,-2.1736915631,-0.1997228124
C,0,-3.6171322267,-2.8069853983,0.8780565013
O,0,2.0482249195,-2.0400839273,-0.9872101777
C,0,1.3835413027,-3.0223558825,-1.7226671682
C,0,-0.0580774567,-3.0282104396,-1.2483408469
O,0,-0.3717743844,-1.67189542,-1.0494353888
O,0,1.9899379728,-0.094908613,0.9170487745
C,0,3.1177810576,-0.5327618017,1.6671665309
C,0,2.7366317217,-1.890412284,2.239786066
C,0,-0.671342631,1.5480856009,0.6341528918
C,0,-1.8625741778,1.0445276553,1.4749166255
C,0,-1.3506713054,-0.0457011142,2.3905166458
O,0,-1.2201757124,-1.1832387121,2.0123354304
C,0,-1.0074397995,2.8580227691,-0.0508424478
O,0,-0.9226031017,3.077090331,-1.2240940139
O,0,-1.3783769686,3.7689438273,0.846291155
O,0,-2.7145756211,-0.3066883655,-2.17797456
C,0,-3.8256832676,-0.5347827858,-2.9780240412
O,0,-2.7519806734,0.4784835913,0.594262335
C,0,4.3635156398,-0.6627746453,0.8080289285
C,0,3.3265834443,0.4915042971,2.7693425094
O,0,-1.0620810919,0.3758493751,3.6067680015
H,0,1.4221842036,-2.7792951838,-2.788446607
H,0,1.8582510703,-3.9939929931,-1.5723062581
H,0,-0.1575866014,-3.5547139168,-0.2986458181
H,0,-0.734007899,-3.4788735669,-1.9742973265
H,0,3.3718624568,-0.2706736228,-3.0734082015
H,0,2.4854717488,0.835524822,-4.1177808098
H,0,4.2146027815,1.7840860649,-2.1446137699
H,0,2.7108849691,3.4199671776,-1.14047505
H,0,1.2512041397,2.5690718458,-1.8856496891
H,0,-2.3068742865,1.8472685574,2.0602959927
H,0,0.2123185617,1.7205642578,1.2532520735
H,0,-3.5080817894,-0.6671146101,-4.0120135393
H,0,-4.5013813618,0.3191736205,-2.9278542259
H,0,-4.3593880989,-1.4291586206,-2.6522068005
H,0,-2.8720322061,-3.3097313917,1.4938254376
H,0,-4.3308364865,-3.5463896523,0.513548481
H,0,-4.1469615681,-2.0819434119,1.4976333557
C,0,-0.5760895741,-0.6030197079,4.5110992403
C,0,-1.696694724,5.0438084298,0.3172290979
H,0,4.1685433805,0.2143036211,3.4028286198
H,0,2.4358800542,0.5674089694,3.3923506212

H,0,3.5251892326,1.4695127956,2.3352589607
H,0,3.5177371454,-2.2479340276,2.9105035129
H,0,2.6038239036,-2.6075753482,1.4343125586
H,0,1.8049057412,-1.8236117953,2.7966833375
H,0,5.1749822701,-1.0679949989,1.4119846986
H,0,4.6685846695,0.30542492,0.4208345875
H,0,4.1807237168,-1.3376663984,-0.0244769828
H,0,-0.4865046398,-0.1020027204,5.4671739696
H,0,-1.2721303269,-1.4337440406,4.5789299338
H,0,0.391399614,-0.9716703769,4.1862031304
H,0,-1.974211633,5.6563926076,1.1665956658
H,0,-0.8374889533,5.4691587722,-0.1938071474
H,0,-2.5227635648,4.9675452309,-0.3837940199

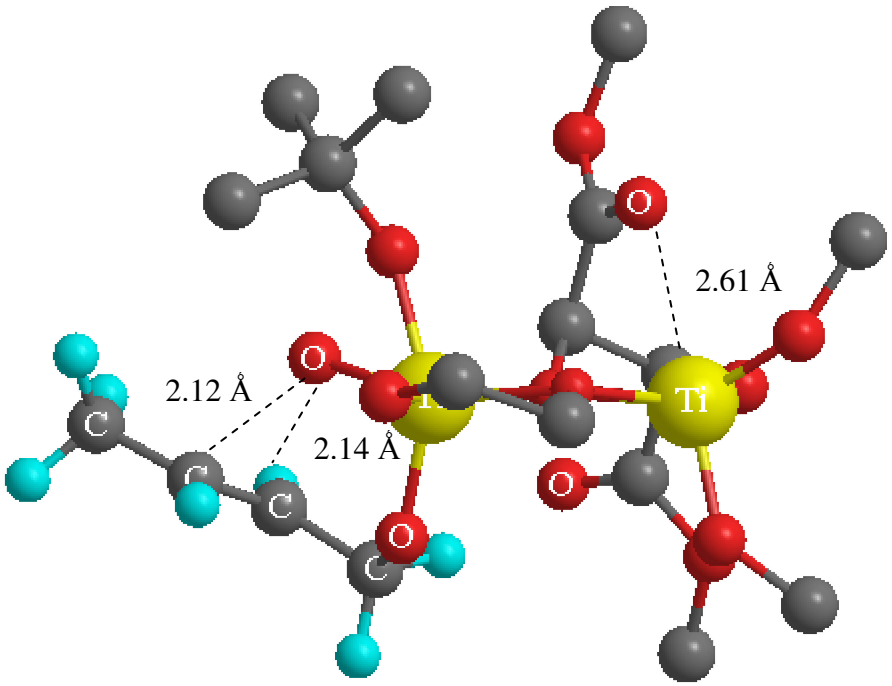
Single point energy: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1760.888406440
File: is4benergyPCM

PCM solvent calculation in dichloromethane: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1760.900673540
File: is4benergyPCM

Theoretical Structures with *trans* butenol as allyl alcohol

RevIs1trans

Description: Gives correct enantiomer using *trans* butenol as substrate. Coordinating carbonyl *cis* to t-butoxide, closest to butoxide. Bystander carbonyl closest to bystander alcohols, carbonyl points towards allyl alkoxide.



Optimization: MPW1K/6-31G* on CHO and SDD on Ti
File name: (revis1*trans*butfreqenergyPCM)
E(RmPW+HF-PW91) = -1800.74613352

Zero-point correction=	0.553470 (Hartree/Particle)
Thermal correction to Energy=	0.593777
Thermal correction to Enthalpy=	0.594721
Thermal correction to Gibbs Free Energy=	0.478554
Sum of electronic and zero-point Energies=	-1800.101963
Sum of electronic and thermal Energies=	-1800.061656
Sum of electronic and thermal Enthalpies=	-1800.060712
Sum of electronic and thermal Free Energies=	-1800.176879

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	372.601	141.634	244.493

C,0,-2.6552750908,3.6198692452,-0.0099614865
C,0,-1.3850251977,3.5900065519,0.4472180723
C,0,-0.2096650609,3.2857971804,-0.4308401099
O,0,-0.5393800318,2.3223491744,-1.3759042899
Ti,0,-1.1983434212,0.7049174724,-0.8942225289
O,0,-2.2401405248,-0.1467457657,0.518339844
C,0,-3.5510443666,-0.6585714391,0.713990303

C,0,-3.8811957347,-0.4826135425,2.1861610695
O,0,-2.2012605772,1.6166048408,0.4965609851
O,0,0.439099407,0.3243681414,0.2262883839
C,0,0.5844990651,0.0403367175,1.5742758946
C,0,2.1107886603,-0.0203158485,1.7555444607
O,0,2.5867133859,-0.7974915542,0.7292653051
Ti,0,1.6003994723,-0.9829289618,-0.8529847817
O,0,2.5788621842,-0.0382366513,-1.9866087113
C,0,3.9408154341,-0.0007370818,-2.2715984255
O,0,-2.2136299014,0.3431700193,-2.3518631701
C,0,-1.9253064968,-0.6922167937,-3.2402177508
C,0,-0.4288627972,-0.9427046291,-3.1582472507
O,0,-0.1110455967,-0.7445110252,-1.8042459465
O,0,2.0257082484,-2.6548812425,-1.2673105192
C,0,2.0839687041,-3.9345624399,-0.7370907917
C,0,-3.4682106601,-2.1330696057,0.3429334226
C,0,-4.5780624832,0.0420347186,-0.1566808438
C,0,0.0905640134,-1.3645781419,1.8071176097
O,0,-0.2562748369,-1.6157319768,3.050837138
C,0,-0.5642657439,-2.9673774574,3.3568104148
O,0,0.1230089003,-2.1911539919,0.9259863742
C,0,2.6469045968,1.4031944573,1.7755431523
O,0,3.7446548869,1.5562100472,1.0602484719
C,0,4.2938719951,2.8613874159,1.0675935134
O,0,2.132518372,2.2842290324,2.413933603
H,0,-2.4783990221,-1.5905501107,-2.9525175115
H,0,-2.2300687274,-0.416825718,-4.2509668101
H,0,0.1223059446,-0.2215546638,-3.7632599915
H,0,-0.1537769313,-1.9495989667,-3.4722764146
H,0,0.1174242723,4.1932128756,-0.9477504903
H,0,0.6218154155,2.9462104107,0.1887454546
H,0,-1.1885420109,3.826790225,1.4847842213
C,0,-3.828349224,4.0002681198,0.8192864017
H,0,-2.8272042251,3.4404058784,-1.0631990702
H,0,2.3660159552,-0.4505389973,2.7306177181
H,0,0.0966997259,0.7636323708,2.2209046654
H,0,2.560333797,-4.6035920895,-1.4544170376
H,0,1.0837876671,-4.30719243,-0.5172850752
H,0,2.667831536,-3.9380978093,0.1846381909
H,0,4.1346557901,0.8012221719,-2.9836731661
H,0,4.2663008197,-0.9455263365,-2.7104977899
H,0,4.5145063724,0.1831869041,-1.3631351107
H,0,-4.8624781977,-0.8961014377,2.4163803763
H,0,-3.8778829858,0.574823078,2.4408606502

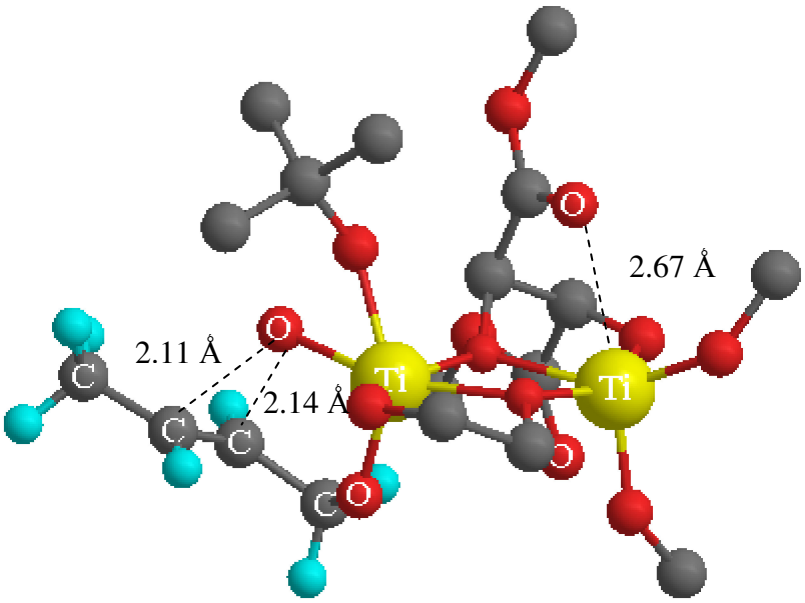
H,0,-3.1373734568,-0.9822364309,2.8042699494
H,0,-4.4145916795,-2.6286906039,0.5581066621
H,0,-2.6773013923,-2.6280925893,0.9007961608
H,0,-3.2516426288,-2.2477527014,-0.7171840975
H,0,-5.5514331382,-0.4289872143,-0.0232850043
H,0,-4.2989133597,-0.0148082514,-1.2054836854
H,0,-4.6614216607,1.0890799774,0.1187547443
H,0,-0.7542771771,-2.9901145362,4.4226427256
H,0,-1.4446967329,-3.2888854776,2.8093929183
H,0,0.2719809163,-3.6120426181,3.1031282057
H,0,5.1935317196,2.8054039354,0.4670481839
H,0,3.5935687862,3.5699334134,0.6344944953
H,0,4.5297410488,3.171391798,2.0816971182
H,0,-4.6351616582,3.2777955091,0.7124011097
H,0,-3.5666665736,4.0719041491,1.8724763849
H,0,-4.2197557888,4.9664742999,0.4953045063

Single point energy: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1800.177299210
File: revis1*trans*butfreqenergyPCM

PCM solvent calculation in dichloromethane: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1800.192663520
File: revis1*trans*butfreqenergyPCM

RevIs1dtrans

Description: Gives correct enantiomer using *trans* butenol as substrate. Coordinating carbonyl *cis* to t-butoxide, closest to butoxide. Bystander carbonyl closest to bystander alcohols, carbonyl points towards bystander alcohols.



Optimization: MPW1K/6-31G* on CHO and SDD on Ti
File name: (revis1d*trans*butfreqenergyPCM)

E(RmPW+HF-PW91) = -1800.65446342

Zero-point correction=	0.553415 (Hartree/Particle)
Thermal correction to Energy=	0.593787
Thermal correction to Enthalpy=	0.594731
Thermal correction to Gibbs Free Energy=	0.478449
Sum of electronic and zero-point Energies=	-1800.101048
Sum of electronic and thermal Energies=	-1800.060677
Sum of electronic and thermal Enthalpies=	-1800.059732
Sum of electronic and thermal Free Energies=	-1800.176014

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	372.607	141.725	244.735

C,0,-2.5941897943,3.2400526248,-1.3688250951
C,0,-1.2743524121,3.3896821161,-1.1144547495
C,0,-0.2110491708,2.6818130733,-1.8969979967
O,0,-0.6415619998,1.417113228,-2.2682364285
Ti,0,-1.2353919999,0.2008182214,-1.0591294759
O,0,-0.147069432,-1.4581409832,-1.4238693945
C,0,-0.5584355284,-2.170619888,-2.5627148864

C,0,-2.0718809881,-2.0349369309,-2.5674124607
O,0,-2.3653455704,-0.748895773,-2.1117623833
O,0,-2.1584645536,0.0940333281,0.6493859474
C,0,-3.4492723741,-0.2666193114,1.1235303531
C,0,-4.5456486953,0.086636955,0.1344534255
O,0,-2.1136777351,1.6765950112,-0.1307107293
O,0,0.4746155706,0.3191931184,0.0048720907
Ti,0,1.6472677422,-1.2576445093,-0.6217078859
O,0,2.1055922952,-2.961287679,-0.4173862538
C,0,2.2205939943,-3.9452835847,0.5519175559
C,0,-3.6550306418,0.4649797898,2.4390496787
C,0,-3.4055301581,-1.7738609808,1.3339577516
C,0,0.6970319222,0.5466850723,1.3502381655
C,0,0.2589755045,-0.6753478186,2.1189197077
O,0,0.2564573976,-1.7703901979,1.6123374899
C,0,2.2374093364,0.5688536199,1.4623944096
C,0,2.7703677386,1.8876397946,0.9317749992
O,0,2.4056806443,2.8875234326,1.7368812056
C,0,2.8634141963,4.171584773,1.355519587
O,0,2.6842342808,-0.5030861669,0.7385271576
O,0,2.4892726927,-0.7598888111,-2.0821608548
C,0,3.7727487545,-0.4064471689,-2.4919278168
O,0,0.0006364505,-0.4401230398,3.3892226337
C,0,-0.2463805861,-1.5804213025,4.1978298434
O,0,3.4278368242,2.0384997195,-0.0554691823
H,0,-2.5219876103,-2.7741566797,-1.8993661096
H,0,-2.4851193877,-2.1833980124,-3.5660697769
H,0,-0.1220995179,-1.7093110969,-3.449715148
H,0,-0.2279123923,-3.2074468068,-2.5042638104
H,0,0.035832603,3.2544172144,-2.7966804433
H,0,0.7027163121,2.611988579,-1.3028594001
H,0,-0.9644859909,4.0562176761,-0.3196316306
C,0,-3.6627434692,3.9997339348,-0.6676451835
H,0,-2.8882962053,2.6329311434,-2.2144835808
H,0,2.5399086646,0.5039029427,2.5121338614
H,0,0.2095170724,1.4458294207,1.717768623
H,0,2.720147644,-4.8165701261,0.1268556646
H,0,1.238606845,-4.2452423281,0.9177318302
H,0,2.8100279812,-3.583130564,1.3958553017
H,0,3.7136720439,0.0691224248,-3.4704259202
H,0,4.4002271823,-1.2952567729,-2.5718220277
H,0,4.2143294466,0.2897786739,-1.7817721405
H,0,-4.6150823984,0.2039792696,2.8831495795
H,0,-3.6286034845,1.5396704848,2.2717834049

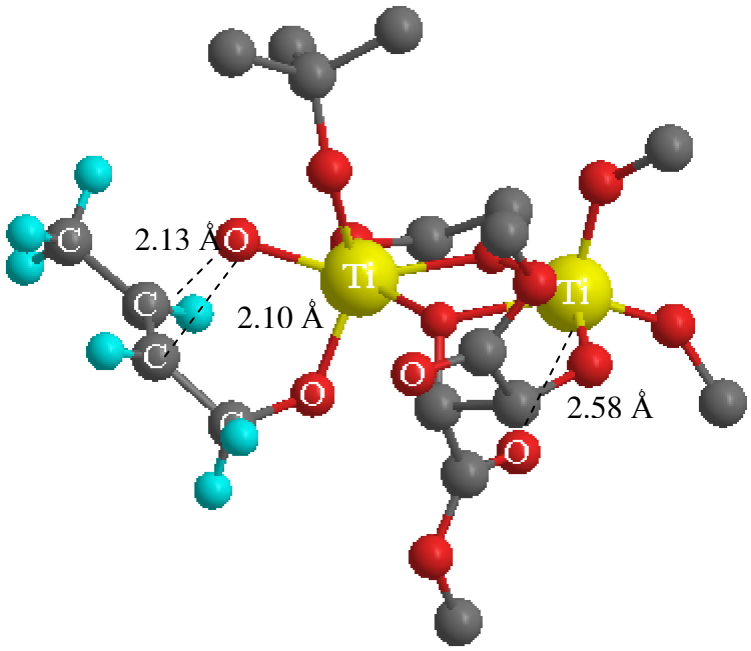
H,0,-2.8644927071,0.2116965217,3.1432695379
H,0,-4.3326591761,-2.1173450166,1.7923126687
H,0,-2.573507711,-2.0517439141,1.9762750932
H,0,-3.2810874397,-2.2857739255,0.3820066643
H,0,-5.5039379746,-0.2687501494,0.5119621449
H,0,-4.3560288042,-0.3740463569,-0.8315863576
H,0,-4.6072584695,1.1622054038,-0.0007290292
H,0,-0.3780795998,-1.2030936497,5.2043117415
H,0,-1.1433534051,-2.0941200608,3.8664421731
H,0,0.5957893415,-2.2645687557,4.1527381871
H,0,2.4946729709,4.8551157,2.1110858636
H,0,3.9489959872,4.1941048251,1.3205339943
H,0,2.4760717607,4.4419634027,0.3769030283
H,0,-4.4798504289,3.3453351972,-0.3729485465
H,0,-3.2808195677,4.4960803473,0.2215995314
H,0,-4.0811198208,4.7580733219,-1.3320761978

Single point energy: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1800.176349210
File: revis1d*trans*butfreqenergyPCM

PCM solvent calculation in dichloromethane: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1800.191188150
File: revis1d*trans*butfreqenergyPCM

RevIs3trans

Description: Gives incorrect enantiomer using *trans* butenol as substrate. Coordinating carbonyl *cis* to allyl alkoxide, closest to allyl alkoxide. Bystander carbonyl closest to bystander alcohols, carbonyl points towards t-butoxide.



Optimization: MPW1K/6-31G* on CHO and SDD on Ti
File name: (revis3*trans*butoptfreqenergyPCM)

E(RmPW+HF-PW91) = -1800.74401052

Zero-point correction=	0.553336 (Hartree/Particle)
Thermal correction to Energy=	0.593779
Thermal correction to Enthalpy=	0.594723
Thermal correction to Gibbs Free Energy=	0.477749
Sum of electronic and zero-point Energies=	-1800.101405
Sum of electronic and thermal Energies=	-1800.060962
Sum of electronic and thermal Enthalpies=	-1800.060018
Sum of electronic and thermal Free Energies=	-1800.176992

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	372.602	141.612	246.194

C,0,-4.0395344116,1.984810594,-1.1432406887
C,0,-3.1039408689,2.0374252298,-2.1157893422
C,0,-1.7096951951,2.5386655138,-1.8943960485
O,0,-1.2233417136,2.1814781533,-0.6435661595
Ti,0,-1.4334073793,0.550788128,0.1711486328
O,0,-0.2722931743,0.0768566466,1.7651771192
C,0,-0.8955509797,0.0771904656,3.0198732648

C,0,-1.9991978453,1.1113160101,2.8860554741
O,0,-2.4858304706,1.0125155521,1.5849573434
O,0,-2.0296328466,-1.1773849191,-0.414740185
C,0,-2.9131464457,-2.2320703626,-0.0669983299
C,0,-3.9352314285,-1.7923304257,0.9634007514
O,0,-2.8477537869,0.2231200077,-1.0938219477
O,0,0.4309940691,0.0675550472,-0.4913106417
Ti,0,1.5367899979,-0.4220596771,1.1900774085
O,0,2.5033485081,0.0895280386,2.5910883959
C,0,3.4381713025,1.050850756,2.9465324569
C,0,-3.5916275751,-2.6990426032,-1.3430734615
C,0,-2.0100039406,-3.3226321174,0.492528871
C,0,1.2362859016,0.8523607011,-1.3042246756
C,0,2.5517900087,0.0622570545,-1.3967835561
C,0,2.3472276465,-1.0634848314,-2.3984451113
O,0,1.9616597742,-0.8572113273,-3.5183839325
C,0,1.5311587371,2.1206117955,-0.5440336164
O,0,1.7519833266,3.1775754538,-1.2895375397
C,0,2.0691163261,4.372723843,-0.5903692305
O,0,1.6201489775,2.1018478136,0.6629063073
O,0,2.8584516633,-0.3382532364,-0.1216651305
O,0,1.3796632087,-2.1688460416,1.443639366
C,0,2.2930026704,-3.2126669078,1.5540594427
O,0,2.6548099553,-2.2575070504,-1.9291197933
C,0,2.4658564079,-3.3253401083,-2.8396969576
H,0,-1.5993613626,2.1147773662,3.0546121977
H,0,-2.8038123805,0.9403161472,3.6038500441
H,0,-1.3049727951,-0.9149081411,3.2195031922
H,0,-0.1780543825,0.3219426061,3.8024033711
H,0,-1.6851880247,3.6290411586,-1.9849967819
H,0,-1.0681196759,2.1461914247,-2.6883009053
H,0,-3.3722839721,1.7436883274,-3.1223204741
C,0,-5.4432903342,1.5506541773,-1.3607153262
H,0,-3.777925386,2.3206175007,-0.1481900472
H,0,3.3432358896,0.6916766634,-1.817642757
H,0,0.806276875,1.0473865455,-2.2821580971
H,0,3.8874993245,0.7840194415,3.9036395499
H,0,2.9695816967,2.0306339305,3.0378002337
H,0,4.2265498336,1.1111205521,2.1945092067
H,0,1.7541537691,-4.1604117721,1.5634404138
H,0,2.8623817038,-3.1267581372,2.4813434129
H,0,2.9845993232,-3.2057862795,0.7116739814
H,0,-4.2111753334,-3.5736117517,-1.1480604852
H,0,-2.8435728258,-2.9603353051,-2.0888887913

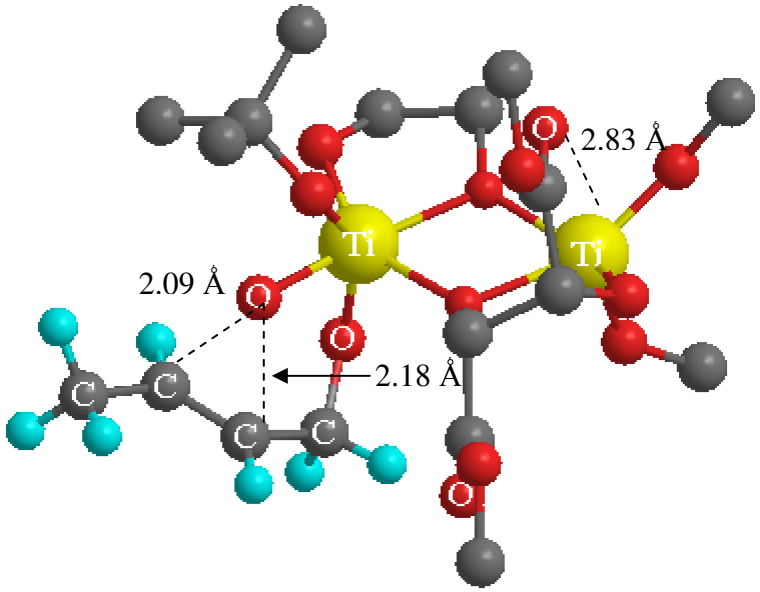
H,0,-4.2163886054,-1.906956195,-1.7481971361
H,0,-2.6077068722,-4.1853120717,0.786890016
H,0,-1.4597394583,-2.9623614943,1.3588172648
H,0,-1.2862559181,-3.6367807564,-0.2561837865
H,0,-4.6235813951,-2.6104154386,1.1728760372
H,0,-4.5028758618,-0.9418893725,0.5958570347
H,0,-3.4542993389,-1.4986543482,1.8932505125
H,0,2.2154645853,5.127961695,-1.3524357
H,0,1.2498075951,4.6454852996,0.0676441779
H,0,2.9744804571,4.2402357529,-0.00568233
H,0,2.7606285347,-4.2216750691,-2.3076164334
H,0,1.4238429228,-3.3861625208,-3.1403370032
H,0,3.0814558592,-3.1864912778,-3.7240402801
H,0,-5.7245979191,0.7869332049,-0.6376803824
H,0,-6.1246040688,2.3915882535,-1.2185737876
H,0,-5.5921398794,1.1524686883,-2.3618866277

Single point energy: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1800.177381210
File: revis3*trans*butoptfreqenergyPCM

PCM solvent calculation in dichloromethane: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1800.190674520
File: revis3*trans*butoptfreqenergyPCM

ls3btrans

Description: Gives incorrect enantiomer using *trans* butenol as substrate. Coordinating carbonyl *cis* to t-butoxide, closest to bystander alcohols. Bystander carbonyl closest to alkoxide, carbonyl points down directly down from catalyst in between alkoxide and bystander alcohols (not towards either).



Optimization: MPW1K/6-31G* on CHO and SDD on Ti
File name: (is3b*trans*butoptfreqenergyPCM)

E(RmPW+HF-PW91) = -1800.65279643

Zero-point correction=	0.553372 (Hartree/Particle)
Thermal correction to Energy=	0.593967
Thermal correction to Enthalpy=	0.594911
Thermal correction to Gibbs Free Energy=	0.477205
Sum of electronic and zero-point Energies=	-1800.099425
Sum of electronic and thermal Energies=	-1800.058829
Sum of electronic and thermal Enthalpies=	-1800.057885
Sum of electronic and thermal Free Energies=	-1800.175591

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	372.720	141.883	247.734

C,0,3.7021277737,1.8881888597,-1.6514881256
C,0,2.4851696844,2.4697063456,-1.7230725772
C,0,1.3875869931,1.9733135386,-2.6165869826
O,0,1.2839667872,0.5857040064,-2.5467530879
Ti,0,1.2165060975,-0.3615072326,-1.0172560889
O,0,2.5291545015,0.8559792654,-0.2653672624
O,0,-0.3711519424,0.6020579365,-0.2332164731
Ti,0,-2.0413122314,-0.5221247327,-0.7194456535
O,0,-3.128859505,-1.9149918365,-0.5402884731

C,0,-3.788366526,-2.6601440305,0.4255533188
O,0,1.9256869175,-1.9316966904,-1.6118249419
C,0,1.1396799866,-2.7796138042,-2.3939808217
C,0,-0.2446254726,-2.8019941536,-1.7703899814
O,0,-0.458183845,-1.4876005196,-1.3229227264
O,0,1.9461234099,-0.4357529916,0.7890262095
C,0,2.9779512999,-1.1749115688,1.4326100024
C,0,2.3832704013,-2.5469495267,1.7191705984
C,0,-0.4778605348,1.3898212798,0.8962450675
C,0,-1.7017354812,0.8368972008,1.6622320935
C,0,-1.2708563427,-0.4239412127,2.3784996556
O,0,-1.2194108497,-1.4896176835,1.8170901377
C,0,-0.6840882475,2.8512484389,0.5523811433
O,0,-0.8527726006,3.5604536884,1.6670593244
C,0,-1.0457158901,4.9507843252,1.4810122866
O,0,-0.6753214623,3.3353565153,-0.5423028076
O,0,-2.6909350924,0.2452750456,-2.1637096724
C,0,-3.8307977151,0.2217043889,-2.9556168046
O,0,-2.6439750174,0.4946780891,0.7239690775
C,0,4.2145181785,-1.3215272904,0.5637147332
C,0,3.3077235789,-0.4315855002,2.7158278125
O,0,-0.9683479162,-0.2318735832,3.6487570984
C,0,-0.6011622737,-1.3822773182,4.3926929946
H,0,1.0878481625,-2.3917032383,-3.4144159683
H,0,1.5791212021,-3.778295427,-2.4285042516
H,0,-0.2811020323,-3.4746541109,-0.9126076894
H,0,-1.014508538,-3.0998676474,-2.481349342
H,0,1.596684492,2.2568534765,-3.6524862819
H,0,0.4453908907,2.4305217195,-2.3230777403
H,0,2.286945305,3.3550192595,-1.1332107874
C,0,4.8343375256,2.4284796649,-0.8539887424
H,0,3.907293286,1.0413184349,-2.2936654981
H,0,-2.0790823109,1.559596014,2.3834208206
H,0,0.4289947793,1.3289326932,1.5017760329
H,0,-3.5442418001,0.242580818,-4.0069558556
H,0,-4.4484177316,1.0952861093,-2.7461186003
H,0,-4.4159096685,-0.679557679,-2.764964005
H,0,-4.6277327018,-3.1871007269,-0.0294117662
H,0,-4.1669494061,-2.0096835428,1.2153377368
H,0,-3.1146600002,-3.3913573447,0.8716301257
H,0,4.0748886619,-0.9563804686,3.2841432072
H,0,2.4200263144,-0.3344349507,3.3392839249
H,0,3.670064275,0.5677400415,2.4826187946
H,0,3.0638634712,-3.1324599932,2.3372831498

H,0,2.2128313282,-3.0779276132,0.7855266425
H,0,1.4299164929,-2.453578982,2.2334518173
H,0,4.9410939157,-1.9515958712,1.075988829
H,0,4.6699372854,-0.3543447792,0.374980445
H,0,3.9612912523,-1.7845420897,-0.3865226206
H,0,-1.166584612,5.3684067949,2.4733358949
H,0,-0.1853278379,5.3923365908,0.9858701526
H,0,-1.9317155065,5.1347416834,0.8801173575
H,0,-0.5164802207,-1.0523625527,5.4209082795
H,0,-1.3627696722,-2.1507437567,4.2996762945
H,0,0.3487990226,-1.7747708434,4.0449573317
H,0,5.3096390438,1.6473546325,-0.2647941086
H,0,5.5971485993,2.8404902727,-1.5173395723
H,0,4.5047960685,3.2156171629,-0.1797600807

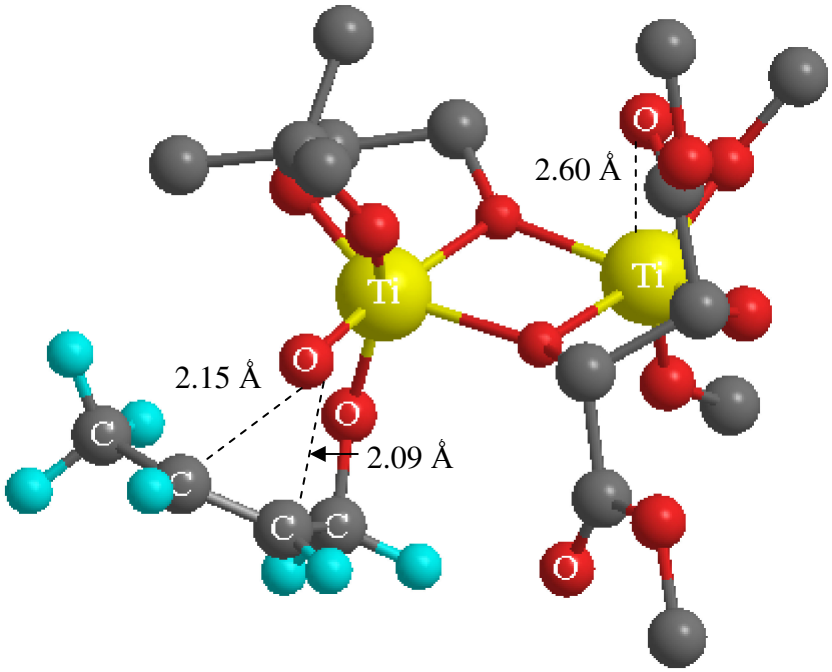
Single point energy: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1800.175434550
File: is3b*trans*butenergyPCM

PCM solvent calculation in dichloromethane: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1800.187883020
File: is3b*trans*butenergyPCM

Theoretical Structures with *cis* butenol as allyl alcohol

RevIs1cis

Description: Gives correct enantiomer using *cis* butenol as substrate. Coordinating carbonyl *cis* to t-butoxide, closest to butoxide. Bystander carbonyl closest to bystander alcohols, carbonyl points towards allyl alkoxide.



Optimization: MPW1K/6-31G* on CHO and SDD on Ti
File name: (revis1*cis*butfreqenergyPCM)

E(RmPW+HF-PW91) = -1800.65166028

Zero-point correction=	0.553581 (Hartree/Particle)
Thermal correction to Energy=	0.594094
Thermal correction to Enthalpy=	0.595038
Thermal correction to Gibbs Free Energy=	0.477698
Sum of electronic and zero-point Energies=	-1800.098079
Sum of electronic and thermal Energies=	-1800.057566
Sum of electronic and thermal Enthalpies=	-1800.056622
Sum of electronic and thermal Free Energies=	-1800.173962

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	372.800	141.695	246.963

C,0,3.7352302792,1.8698136302,-1.7065003662
C,0,2.4887172211,2.39624777,-1.7320789269
C,0,1.4186456913,1.9474309839,-2.6871709911
O,0,1.1600932373,0.5853938878,-2.5312572991
Ti,0,1.1540569626,-0.3654323737,-1.0067137682
O,0,2.5226372706,0.8233510192,-0.3093097038

O,0,-0.4175026001,0.5761980912,-0.1741738093
Ti,0,-2.0974802127,-0.5277358469,-0.6522698541
O,0,-3.1798746726,-1.9233403337,-0.4649619503
C,0,-3.8313920078,-2.6749294298,0.5012408802
O,0,1.8565248097,-1.9383029131,-1.6108674326
C,0,1.057669863,-2.7708474308,-2.3960608162
C,0,-0.3168474399,-2.8036143751,-1.7515550874
O,0,-0.5239700307,-1.4962114495,-1.2825848169
O,0,1.926565014,-0.4349422468,0.7776126877
C,0,2.9598153846,-1.1632336944,1.4296543605
C,0,2.3850072782,-2.5464912564,1.7030944984
C,0,-0.5104214732,1.3799620816,0.9436603654
C,0,-1.7368573029,0.8476590747,1.7179065845
C,0,-1.3094065047,-0.4124832662,2.4378715685
O,0,-1.2806818591,-1.4834246191,1.884928464
C,0,-0.6832355154,2.838969014,0.5713350519
O,0,-0.9283568985,3.5672756726,1.6585603013
C,0,-1.0816917451,4.9575725599,1.4380249896
O,0,-0.5785071216,3.3051222516,-0.5262853095
O,0,-2.760003608,0.2401194773,-2.0902897346
C,0,-3.8627097354,0.1569166017,-2.9288049002
O,0,-2.6854921626,0.5066048887,0.7858398226
C,0,4.2102386518,-1.2803693494,0.5769345789
C,0,3.2617271837,-0.4226671467,2.7215744251
O,0,-0.9756939308,-0.2142181099,3.6995202055
C,0,-0.5999059885,-1.3641117724,4.440125013
H,0,0.9880512661,-2.3638978141,-3.4084037268
H,0,1.4956840464,-3.7689465411,-2.4566650917
H,0,-0.338543621,-3.4896714425,-0.9039075803
H,0,-1.0969412207,-3.0928181394,-2.455091963
H,0,1.7341565979,2.1261048743,-3.7190984124
H,0,0.5076574767,2.5112504932,-2.5044822315
H,0,2.2437804568,3.1976645861,-1.0515255969
H,0,4.4313946941,2.2665652111,-0.9796863425
C,0,4.2828819618,0.8761281586,-2.667871184
H,0,-2.1038757571,1.5788152049,2.4356131347
H,0,0.3976865814,1.3129688977,1.547891628
H,0,-3.5325681039,0.1546731272,-3.9676409157
H,0,-4.5138033529,1.0173638116,-2.7732087134
H,0,-4.4295761671,-0.7552256769,-2.7345522255
H,0,-4.6694289691,-3.2054047797,0.0478713324
H,0,-4.2107169737,-2.028959979,1.2942098783
H,0,-3.1519726366,-3.4035336018,0.9429262443
H,0,4.0290937027,-0.9393976635,3.2969976578

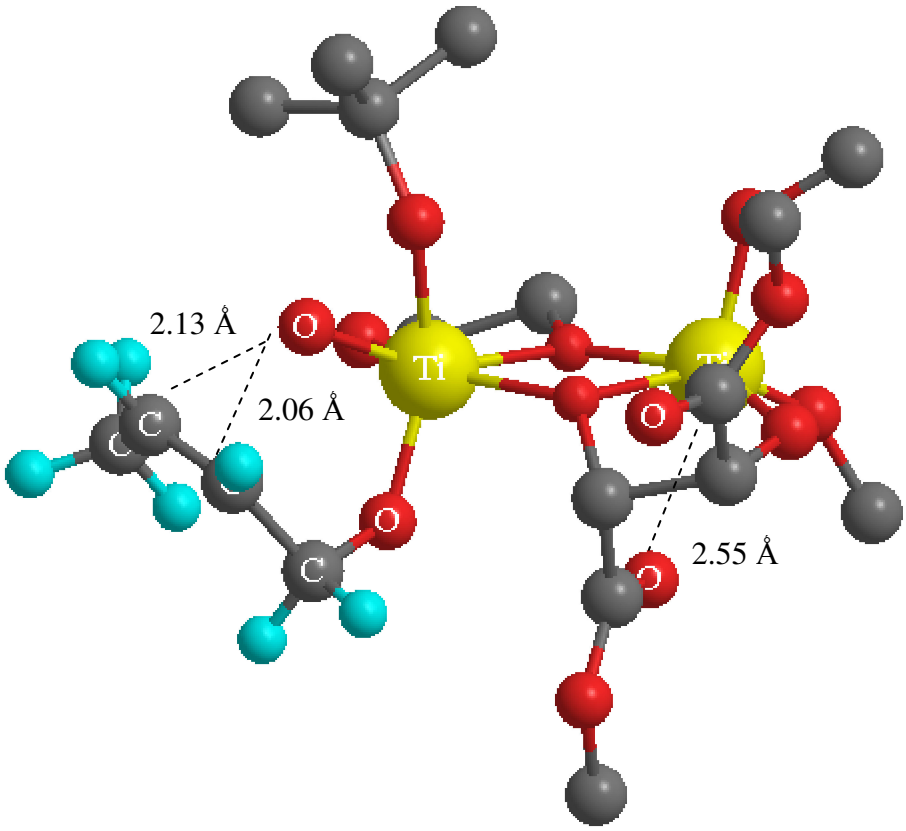
H,0,2.3647614747,-0.3424314478,3.3340191659
H,0,3.612754489,0.5832395036,2.4990961195
H,0,3.072737069,-3.1267807702,2.3182237151
H,0,2.2234752889,-3.0722781766,0.7650878434
H,0,1.4300000549,-2.4711870843,2.2180757894
H,0,4.9355760196,-1.9124317472,1.0886463073
H,0,4.6577002007,-0.303723361,0.4128373555
H,0,3.9743931422,-1.730928969,-0.384071879
H,0,-1.2770959957,5.3920356999,2.4110474781
H,0,-0.1759995398,5.3778306064,1.0096941166
H,0,-1.9120359145,5.1456520583,0.7635327971
H,0,-0.4601941736,-1.0244821276,5.4591049307
H,0,-1.3823163491,-2.1157541242,4.3925640564
H,0,0.3231998185,-1.7830667263,4.052975736
H,0,4.7780882232,0.0629821474,-2.1407502943
H,0,3.5115427677,0.4507601422,-3.301557853
H,0,5.035555405,1.3570632593,-3.2966343072

Single point energy: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1800.174222290
File: revis1*cis*butfreqenergyPCM

PCM solvent calculation in dichloromethane: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1800.185808550
File: revis1*cis*butfreqenergyPCM

RevIs3cis

Description: Gives incorrect enantiomer using *cis* butenol as substrate. Coordinating carbonyl *cis* to alkoxide, closest to butoxide. Bystander carbonyl closest to bystander alcohols, carbonyl points towards bystander alcohols.



Optimization: MPW1K/6-31G* on CHO and SDD on Ti
File name: (revis3*cis*butoptfreqenergyPCM)

E(RmPW+HF-PW91) = -1800.65194556

Zero-point correction=	0.553656 (Hartree/Particle)
Thermal correction to Energy=	0.593975
Thermal correction to Enthalpy=	0.594919
Thermal correction to Gibbs Free Energy=	0.478563
Sum of electronic and zero-point Energies=	-1800.098289
Sum of electronic and thermal Energies=	-1800.057970
Sum of electronic and thermal Enthalpies=	-1800.057026
Sum of electronic and thermal Free Energies=	-1800.173383

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	372.725	141.456	244.893

C,0,4.2231967571,1.3641494418,0.9054233114

C,0,3.1614769882,1.9000025689,1.8480552919
C,0,2.0376920013,2.5710009643,1.0700912249
O,0,3.6720466277,2.9083771088,2.7032046883
Ti,0,4.9868172112,4.2871470949,2.8462044308
Ti,0,2.850633658,6.7573960021,3.1839775977
O,0,1.353824775,6.0944139409,2.5036267983
C,0,0.0212607142,6.489476334,2.5676574384
O,0,6.4257342142,4.7154126257,3.8861571134
C,0,7.1199947825,3.9649070905,4.8311715884
C,0,6.854471103,2.4924313229,4.6836922488
C,0,7.234971907,1.7753692963,3.5992731098
H,0,7.0040623139,0.7186608679,3.595553828
O,0,4.1015431573,5.8781108332,1.9486365503
C,0,4.2886489073,6.0022540441,0.5654939264
C,0,5.6365098569,5.3505049786,0.3111233446
O,0,5.7323985687,4.2694658494,1.1839936097
O,0,5.2261440551,2.4547650505,3.4224532992
O,0,3.786515553,5.2138290825,4.1945708295
C,0,4.1669196979,5.7025194194,5.4351630518
C,0,5.1595171726,6.8107018332,5.1890412617
O,0,5.0537263328,7.5183970903,4.2132340612
C,0,2.617895871,0.7961388927,2.7386133224
O,0,2.8396440929,8.4219581143,2.5604391243
C,0,3.2888862849,9.6907298798,2.8948379374
O,0,2.3624319773,7.1036407517,4.9524946479
C,0,2.8852656563,6.3590124526,5.9776808111
C,0,1.98479142,5.2498234428,6.4989411145
O,0,0.7670083225,5.2695478958,5.992635326
C,0,-0.0894058201,4.2404420947,6.4533461737
O,0,2.3639732325,4.4530165785,7.3157656582
O,0,6.057903366,6.9755056644,6.1321073062
C,0,6.9742380236,8.0431080548,5.9340515687
H,0,6.4433084037,6.0598856939,0.5144541542
H,0,5.7334165222,5.012815433,-0.7226325045
H,0,3.4891263628,5.474265787,0.0433356425
H,0,4.2643712661,7.0508915196,0.2700464886
H,0,8.1897772026,4.1643359002,4.7196805927
H,0,6.8442541117,4.2866922848,5.8371081829
H,0,6.3799259053,1.9779251014,5.5054841305
C,0,8.0231450646,2.2781239876,2.4452456344
H,0,3.1170596179,6.9841645325,6.8468682237
H,0,4.5540172585,4.9372939729,6.1022212656
H,0,2.8391720488,10.4240193189,2.2245569771
H,0,4.3735912643,9.7522667425,2.8075713732

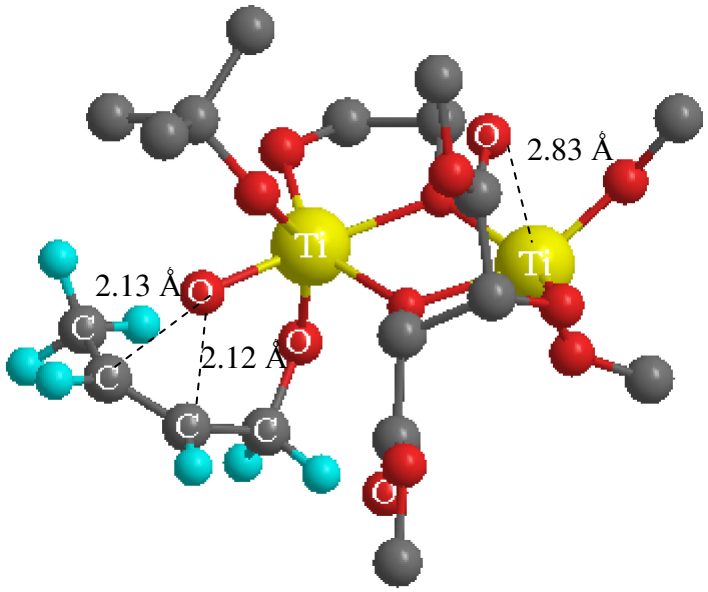
H,0,3.0080768056,9.9359582384,3.9204143563
H,0,-0.5940947342,5.7637296192,2.0354287605
H,0,-0.1120602426,7.4676347665,2.1017756051
H,0,-0.3109957403,6.5439554633,3.6044937754
H,0,2.1783889955,-0.0010795773,2.1400432154
H,0,1.8557205392,1.1924034042,3.406852675
H,0,3.4206060916,0.3797580885,3.3431216667
H,0,1.5055964642,1.8330104278,0.4701435969
H,0,2.435407694,3.334912514,0.405293128
H,0,1.3356504959,3.0473403021,1.7503818507
H,0,3.7705882562,0.6611129144,0.2069136183
H,0,5.0012329176,0.8472077536,1.4616143565
H,0,4.6837041345,2.1733481285,0.3443380013
H,0,7.6340016085,8.0260375007,6.7925333382
H,0,7.5332245283,7.8864889543,5.0166697308
H,0,6.4451739075,8.9896791548,5.878346959
H,0,-1.0363631071,4.3989178452,5.9517810271
H,0,0.3184183376,3.2665863884,6.1980014505
H,0,-0.213393544,4.300504603,7.5310114135
H,0,8.967642841,1.7332717222,2.3874576571
H,0,7.4880044675,2.1055449743,1.5133022795
H,0,8.2289454729,3.3414728769,2.5128057825

Single point energy: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1800.174741740
File: revis3*cis*butoptfreqenergyPCM

PCM solvent calculation in dichloromethane: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1800.188027030
File: revis3*cis*butoptfreqenergyPCM

ls3bcis

Description: Gives incorrect enantiomer using *cis* butenol as substrate. Coordinating carbonyl *cis* to t-butoxide, closest to bystander alcohols. Bystander carbonyl closest to alkoxide, carbonyl points down directly down from catalyst in between alkoxide and bystander alcohols (not towards either).



Optimization: MPW1K/6-31G* on CHO and SDD on Ti
File name: (is3b*cis*butoptfreqenergyPCM)

E(RmPW+HF-PW91) = -1800.65166006

Zero-point correction=	0.553579 (Hartree/Particle)
Thermal correction to Energy=	0.594093
Thermal correction to Enthalpy=	0.595038
Thermal correction to Gibbs Free Energy=	0.477695
Sum of electronic and zero-point Energies=	-1800.098081
Sum of electronic and thermal Energies=	-1800.057567
Sum of electronic and thermal Enthalpies=	-1800.056622
Sum of electronic and thermal Free Energies=	-1800.173965

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	372.799	141.695	246.969

C,0,-4.0257963493,-1.7932611411,0.2614093946
C,0,-2.8505657497,-2.4499007722,0.4001168717
C,0,-1.9700881496,-2.8274810343,-0.7578453916
O,0,-1.5910670642,-1.6940277348,-1.4775197652
Ti,0,-1.2070891704,-0.0606877461,-0.8347829634
O,0,-2.4831323349,-0.3700360614,0.5965102247
O,0,0.4323193121,-0.6153955419,0.1919429285
Ti,0,2.0513976421,-0.3033798637,-1.0534012089
O,0,3.2435236577,0.7289147224,-1.8704621214
C,0,4.1294428297,1.7688361449,-1.6325244663

O,0,-1.9073888867,0.9761540779,-2.1640399892
C,0,-1.2303618978,1.050926538,-3.3821813869
C,0,0.2458806089,1.2030820529,-3.06073613
O,0,0.4533149809,0.3890742474,-1.935350434
O,0,-1.5912491054,1.1541118998,0.6356296763
C,0,-2.4160509971,2.2934153303,0.8474384444
C,0,-1.7028511468,3.4552908205,0.1692271768
C,0,0.6960432291,-0.6344274848,1.5463084975
C,0,2.0889590664,0.0179955687,1.6915200448
C,0,1.906564263,1.5145760775,1.5650577054
O,0,1.8396823008,2.0596522041,0.4917838801
C,0,0.6872075554,-2.045836623,2.0986115716
O,0,1.0984226971,-2.0489633125,3.3648946934
C,0,1.106421542,-3.3149587884,3.9991348679
O,0,0.3279601208,-3.0292893126,1.518267469
O,0,2.3504371053,-1.8591256032,-1.8193420515
C,0,3.2612760748,-2.468342222,-2.6709395647
O,0,2.8480565471,-0.4112272102,0.6310894848
C,0,-3.8033263907,2.1199253769,0.2560192521
C,0,-2.4978017098,2.4944429644,2.3512855421
O,0,1.8253382402,2.1380896535,2.7256799742
C,0,1.6899895727,3.5491432555,2.6748595718
H,0,-1.3979047215,0.1328573858,-3.9517178701
H,0,-1.6011131147,1.8924022995,-3.9705638307
H,0,0.4882705573,2.2339487536,-2.7995601799
H,0,0.8835668647,0.8931339037,-3.888043671
H,0,-2.5017616021,-3.5058813731,-1.4312271469
H,0,-1.0824271991,-3.3352852311,-0.3899274312
H,0,-2.52781196,-2.7446549484,1.3872172048
H,0,-4.5842826873,-1.5710675572,1.1608754703
C,0,-4.6882785035,-1.4519280347,-1.025512255
H,0,2.5434212089,-0.2207391374,2.6511368031
H,0,-0.0622380576,-0.0737641981,2.0984959827
H,0,2.7264961195,-3.0037146898,-3.4555187443
H,0,3.8692633423,-3.1826862919,-2.115451047
H,0,3.9176614051,-1.727512502,-3.1307284016
H,0,4.8911740482,1.7856253089,-2.4127409263
H,0,4.617963111,1.6390236541,-0.665846994
H,0,3.6068035544,2.7250818179,-1.631150646
H,0,-3.0934041735,3.3734616494,2.5953318076
H,0,-1.5022532834,2.6224026944,2.7738784529
H,0,-2.9558747127,1.6241280802,2.8174263201
H,0,-2.2081209805,4.3938339144,0.3971110734
H,0,-1.7006803269,3.310075628,-0.9084136015

H,0,-0.6702222355,3.5210314909,0.5042948358
H,0,-4.3629252816,3.0472900494,0.3756467
H,0,-4.3415663281,1.3235143905,0.7629841075
H,0,-3.7384910015,1.8881810251,-0.8042887998
H,0,1.466149055,-3.1396061483,5.0058929264
H,0,0.105282765,-3.736347123,4.021846427
H,0,1.7660475423,-3.9989775078,3.4730197302
H,0,1.7387362093,3.8861088789,3.7030936356
H,0,2.4963230944,3.9846955918,2.0921811794
H,0,0.7385154058,3.8260041364,2.2326183836
H,0,-5.0074371994,-0.411538698,-1.0300914209
H,0,-4.0353334893,-1.6111192118,-1.8774388282
H,0,-5.58524409,-2.0638109302,-1.144721246

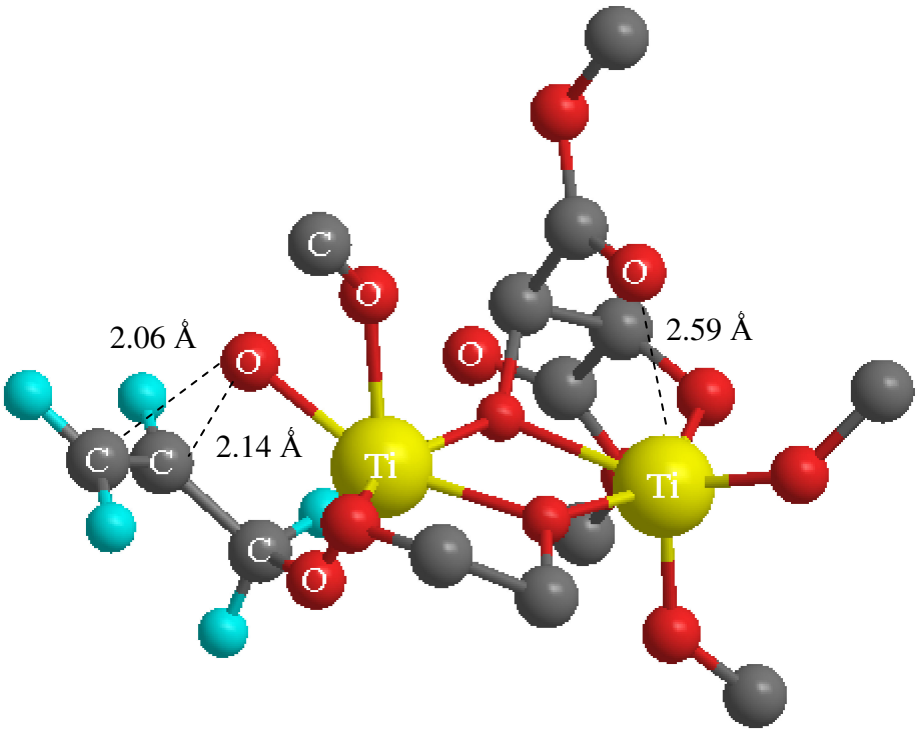
Single point energy: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1800.175434550
File: is3b*cis*butenergyPCM

PCM solvent calculation in dichloromethane: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1800.187883020
File: is3b*cis*butenergyPCM

Theoretical Structures with methyl peroxide and propenol

RevIs1meooh

Description: Gives correct enantiomer using propenol as substrate. Coordinating carbonyl *cis* to t-butoxide, closest to butoxide. Bystander carbonyl closest to bystander alcohols, carbonyl points towards allyl alkoxide. Methyl peroxide points toward bystander ring system.



Optimization: MPW1K/6-31G* on CHO and SDD on Ti
File name: (revis1meoohoptfreqenergyPCM)

E(RmPW+HF-PW91) = -1643.49545068

Zero-point correction=	0.438113 (Hartree/Particle)
Thermal correction to Energy=	0.472823
Thermal correction to Enthalpy=	0.473767
Thermal correction to Gibbs Free Energy=	0.369429
Sum of electronic and zero-point Energies=	-1642.976381
Sum of electronic and thermal Energies=	-1642.941671
Sum of electronic and thermal Enthalpies=	-1642.940727
Sum of electronic and thermal Free Energies=	-1643.045065

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	296.701	120.082	219.597

C,0,-2.8010500262,3.4849302615,-0.1305419039
C,0,-1.5548411572,3.6568403164,0.3557630817
C,0,-0.3308259019,3.3946507424,-0.4673072745
O,0,-0.5723701781,2.3714439984,-1.3754649022

Ti,0,-1.1403049384,0.7368666232,-0.8400412986
O,0,-2.084402113,-0.1231619415,0.6535135923
C,0,-3.3907301487,-0.6195398533,0.6248218085
H,0,-3.9055309193,-0.3492402572,1.5447902692
O,0,-2.2017419508,1.6256676755,0.5217202386
O,0,0.5236964031,0.4035109275,0.2345315044
C,0,0.6606255737,0.0715210419,1.5753679082
C,0,2.1829864524,-0.0261096802,1.7564104198
O,0,2.6492353752,-0.7864849248,0.712764812
Ti,0,1.6491610795,-0.951805373,-0.8601139687
O,0,2.6274232566,-0.0073400634,-1.992223934
C,0,3.9859046237,0.0358094775,-2.2900258198
O,0,-2.2719682619,0.263273779,-2.1754985274
C,0,-2.0370377282,-0.844081347,-2.9910901507
C,0,-0.5296250084,-1.0191633866,-3.0685134293
O,0,-0.0768497059,-0.6968164972,-1.7792327765
O,0,2.0641122439,-2.6204805962,-1.3006573606
C,0,2.1356277507,-3.8973176509,-0.7646902435
H,0,-3.3311674573,-1.7068328566,0.5524367957
H,0,-3.9423595682,-0.2374679958,-0.2316350818
C,0,0.1213581044,-1.3248971048,1.7520184986
O,0,-0.3045269466,-1.6029969049,2.9610418017
C,0,-0.7347161712,-2.9382646784,3.1785538064
O,0,0.17836252,-2.1258031131,0.845539031
C,0,2.7450877967,1.3872850487,1.8098878674
O,0,3.8696342496,1.5244550872,1.1338240024
C,0,4.444846252,2.8176926425,1.1758621878
O,0,2.2281288447,2.2718423662,2.4406824598
H,0,-2.4980671776,-1.7319955875,-2.5497869118
H,0,-2.4760340198,-0.6859548736,-3.9771664011
H,0,-0.0914637723,-0.3239330835,-3.7858385454
H,0,-0.2365258063,-2.0343377257,-3.3348906004
H,0,-0.0437530853,4.2989779863,-1.0122736704
H,0,0.4992732302,3.1348507655,0.1932357877
H,0,-1.41726514,3.986275518,1.3762106035
H,0,-3.6674227263,3.6725669029,0.4831243189
H,0,-2.968496955,3.2275402792,-1.1649737679
H,0,2.4280175547,-0.4852933378,2.721105585
H,0,0.1880012468,0.7852279244,2.243097788
H,0,2.5997477714,-4.5691600038,-1.4873404179
H,0,1.1406946555,-4.2711344509,-0.523561879
H,0,2.7368279172,-3.8943713453,0.1458413752
H,0,4.170319087,0.8387422195,-3.0034787004
H,0,4.3103374907,-0.9076542494,-2.7325697035

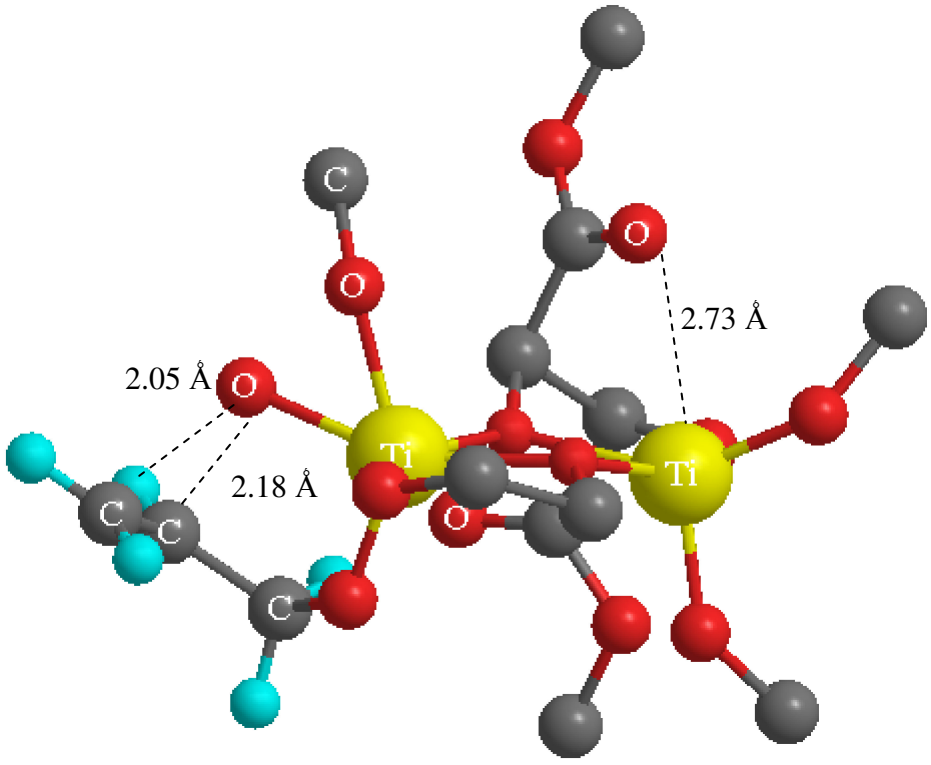
H,0,4.5679670646,0.2208664905,-1.3870579864
H,0,-1.0481460138,-2.9802350253,4.2140823413
H,0,-1.5636732203,-3.1770623544,2.5194031154
H,0,0.0804144176,-3.6326218978,2.9973861616
H,0,5.3585009722,2.7523638411,0.5977796741
H,0,3.7702632271,3.5473110341,0.7370216326
H,0,4.6608369371,3.1069212104,2.2005347872

Single point energy: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1643.040146270
File: revis1meoohfreqenergyPCM

PCM solvent calculation in dichloromethane: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1643.057337680
File: revis1meoohtfreqenergyPCM

RevIs1meoohc

Description: Gives correct enantiomer using propenol as substrate. Coordinating carbonyl *cis* to t-butoxide, closest to butoxide. Bystander carbonyl closest to bystander alcohols, carbonyl points towards allyl alkoxide. Methyl peroxide points toward coordinating carbonyl.



Optimization: MPW1K/6-31G* on CHO and SDD on Ti
File name: (revis1meoohcoptfreqenergyPCM)

E(RmPW+HF-PW91) = -1643.40346554

Zero-point correction=	0.437826 (Hartree/Particle)
Thermal correction to Energy=	0.472824
Thermal correction to Enthalpy=	0.473768
Thermal correction to Gibbs Free Energy=	0.367125
Sum of electronic and zero-point Energies=	-1642.965639
Sum of electronic and thermal Energies=	-1642.930642
Sum of electronic and thermal Enthalpies=	-1642.929698
Sum of electronic and thermal Free Energies=	-1643.036341

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	296.701	120.291	224.449

C,0,-4.3583327523,1.923417356,-0.2209161091
C,0,-3.2556346382,2.5946680118,0.1648999369
C,0,-2.0266268116,2.6343331093,-0.6774457215
O,0,-1.9324757237,1.4373244702,-1.370770397
Ti,0,-1.8831463301,-0.1569928452,-0.5260634453
O,0,-0.4088848701,-1.2272147263,-1.431293359
C,0,-0.8269624735,-1.8931087126,-2.598204066
C,0,-2.2689496494,-2.27273112,-2.3203632253
O,0,-2.8295174059,-1.2026697833,-1.6268924203
O,0,-2.5018633546,-1.0309067879,1.1691299371
O,0,-3.1702173307,0.5333578022,0.7264954107
O,0,0.0216438566,0.3305696674,0.3408074745
Ti,0,1.404293441,-0.7073179397,-0.9027950178
O,0,0.7689543377,-2.010914439,1.4162270984
C,0,0.6274838061,-1.0857419046,2.1778583012
O,0,0.4762041325,-1.2504248254,3.4734212936
C,0,0.5974421615,-2.5895117148,3.9366972001
C,0,-2.2273828284,-0.7528795958,2.5081037715
C,0,0.5548658766,0.3648790477,1.6211959977
C,0,2.0302740608,0.8014176953,1.3846205292
C,0,1.9905786363,2.297911124,1.1209761344
O,0,1.2913925283,3.04327774,1.7588140528
O,0,2.5618974383,0.0799948432,0.347720387
O,0,1.7016607661,0.3435729752,-2.3086038802
C,0,2.8449983152,0.8383449855,-2.9275456999

O,0,2.374087835,-2.1385139963,-1.3447105781
C,0,3.066540283,-3.2040651652,-0.7967205073
O,0,2.8095395056,2.6876095763,0.1671915009
C,0,2.812055265,4.0796520734,-0.0972622866
H,0,-1.7894609607,-1.6372019522,3.0018452073
H,0,-3.0706277632,-0.3316694756,3.0350365573
H,0,-1.3594717752,-0.0994751601,2.5119191367
H,0,-2.3241265284,-3.1781993017,-1.7118571126
H,0,-2.8196282444,-2.445917328,-3.2462446836
H,0,-0.7615257335,-1.2082639604,-3.4445527716
H,0,-0.1892199947,-2.7554130927,-2.791630704
H,0,-2.0751894861,3.464715916,-1.3879914404
H,0,-1.1479210287,2.795342227,-0.0483514823
H,0,-3.2392443181,3.1151717696,1.1127068734
H,0,-5.232828038,1.882238698,0.4081303908
H,0,-4.4227089907,1.4564152824,-1.1914001413
H,0,2.6063412474,0.6738259495,2.3098461994
H,0,0.1360887272,1.1317767348,2.2589336538
H,0,3.6098608442,-3.7270897532,-1.584092064
H,0,2.3843505622,-3.9061931443,-0.3168799635
H,0,3.785083445,-2.8498681083,-0.0550663704
H,0,2.5581819229,1.5288337467,-3.7207953668
H,0,3.4240750344,0.0234558521,-3.3659427367
H,0,3.4694317942,1.3650497894,-2.2054903099
H,0,0.4562536081,-2.5319987653,5.0084325965
H,0,-0.1652476219,-3.2149531101,3.481753892
H,0,1.5799260298,-2.9834224467,3.6976714832
H,0,3.5454291218,4.2284433721,-0.8800900679
H,0,1.8300580553,4.4023110281,-0.4309070874
H,0,3.0854144239,4.6369112319,0.794244805

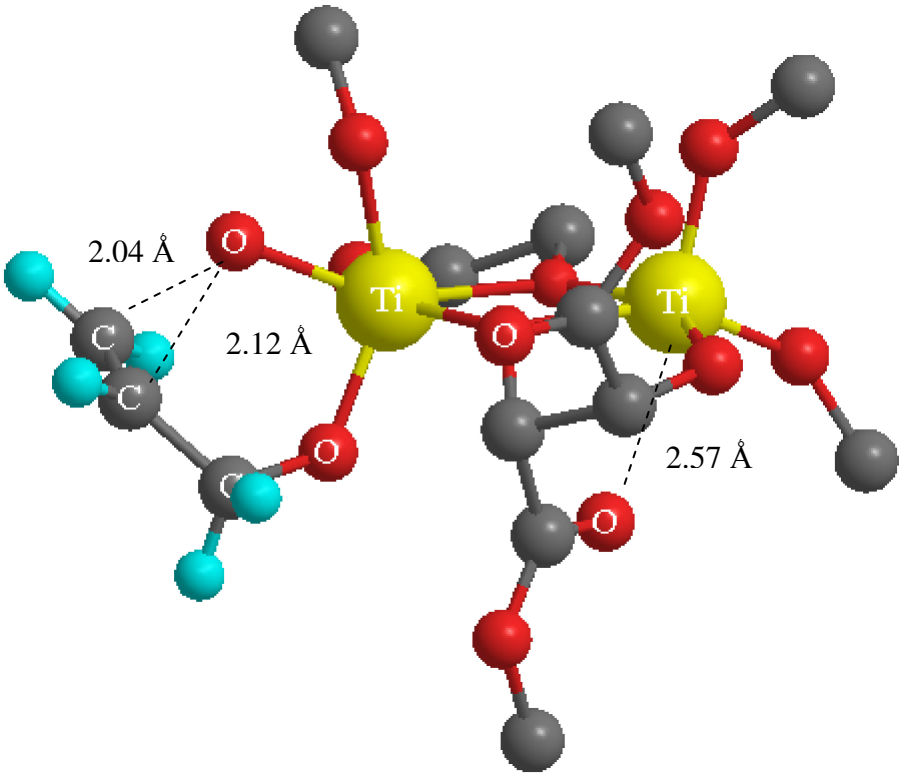
Single point energy: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1643.029344400
File: revis1meoohcfreqenergyPCM

PCM solvent calculation in dichloromethane: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1643.047135660
File: revis1meoohcfreqenergyPCM

Revis3meooh

Description: Gives incorrect enantiomer using propenol as substrate. Coordinating carbonyl *cis* to alkoxide, closest to butoxide. Bystander carbonyl closest to bystander

alcohols, carbonyl points towards bystander alcohols. Methyl peroxide points toward bystander ring system.



Optimization: MPW1K/6-31G* on CHO and SDD on Ti
File name: (revis3meoohoptfreqenergyPCM)

E(RmPW+HF-PW91) = -1643.49154376

Zero-point correction=	0.438306 (Hartree/Particle)
Thermal correction to Energy=	0.473001
Thermal correction to Enthalpy=	0.473945
Thermal correction to Gibbs Free Energy=	0.369736
Sum of electronic and zero-point Energies=	-1642.973577
Sum of electronic and thermal Energies=	-1642.938881
Sum of electronic and thermal Enthalpies=	-1642.937937
Sum of electronic and thermal Free Energies=	-1643.042146

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	296.813	120.039	219.326

C,0,-3.9966284599,1.7908976021,-1.2419928954
C,0,-3.0331295958,2.0146428644,-2.1596085725

C,0,-1.7122047745,2.6321020229,-1.8142067256
O,0,-1.2609812365,2.2153606143,-0.5693973548
Ti,0,-1.3993611373,0.5420794109,0.1622705598
O,0,-0.2279579514,0.1260856705,1.7544263684
C,0,-0.8790472892,-0.0239288379,2.9878543802
C,0,-2.0858656452,0.8909323543,2.8833892218
O,0,-2.5327151921,0.8162975978,1.565546677
O,0,-1.9549042323,-1.2131959732,-0.4186798663
C,0,-2.9461040678,-2.0191542053,0.1496451307
H,0,-3.6115349086,-1.4397441037,0.7865780476
O,0,-2.7581913195,0.168544849,-1.1554298746
O,0,0.4540063782,0.1110198892,-0.5152966699
Ti,0,1.5706465049,-0.4008980843,1.158999745
O,0,2.5591483299,0.0708657329,2.5568506142
C,0,3.5010787494,1.0182110883,2.9305430711
H,0,-3.5171594457,-2.5014110175,-0.6408331362
H,0,-2.4448927373,-2.7826004803,0.7455692018
C,0,1.2586329663,0.901362549,-1.3237495528
C,0,2.5669327959,0.1001475058,-1.433826704
C,0,2.3376317488,-1.0134909556,-2.4438758847
O,0,1.9598886568,-0.7874487741,-3.5626691462
C,0,1.5676403874,2.1569721043,-0.5483544532
O,0,1.7651625401,3.228054219,-1.280070791
C,0,2.096625618,4.4121984982,-0.5679307015
O,0,1.6807220313,2.1181520921,0.6557462559
O,0,2.87945937,-0.3154029829,-0.1651615317
O,0,1.3778151548,-2.1457676419,1.392517119
C,0,2.2731290319,-3.2083812785,1.4742756534
O,0,2.6097136858,-2.217707198,-1.9810968119
C,0,2.3822925445,-3.2758373898,-2.8949669171
H,0,-1.802372731,1.9203145509,3.1181354343
H,0,-2.8801174745,0.5921383521,3.5697437398
H,0,-1.1809026868,-1.065273605,3.1116784844
H,0,-0.2120521559,0.2465810849,3.8057941102
H,0,-1.8025950793,3.7228764656,-1.814177747
H,0,-0.9883803032,2.3802512597,-2.5932835892
H,0,-3.2073532452,1.7448268039,-3.1917167677
H,0,-4.9366860061,1.3460559787,-1.5264774876
H,0,-3.8867714215,2.0997755852,-0.2134502461
H,0,3.3610031988,0.7250765688,-1.8559576496
H,0,0.8236800714,1.1098269816,-2.2969065358
H,0,3.9337530051,0.740331745,3.8920890466
H,0,3.0434705941,2.0031881197,3.0210707478
H,0,4.3003879902,1.0720831268,2.1896979849

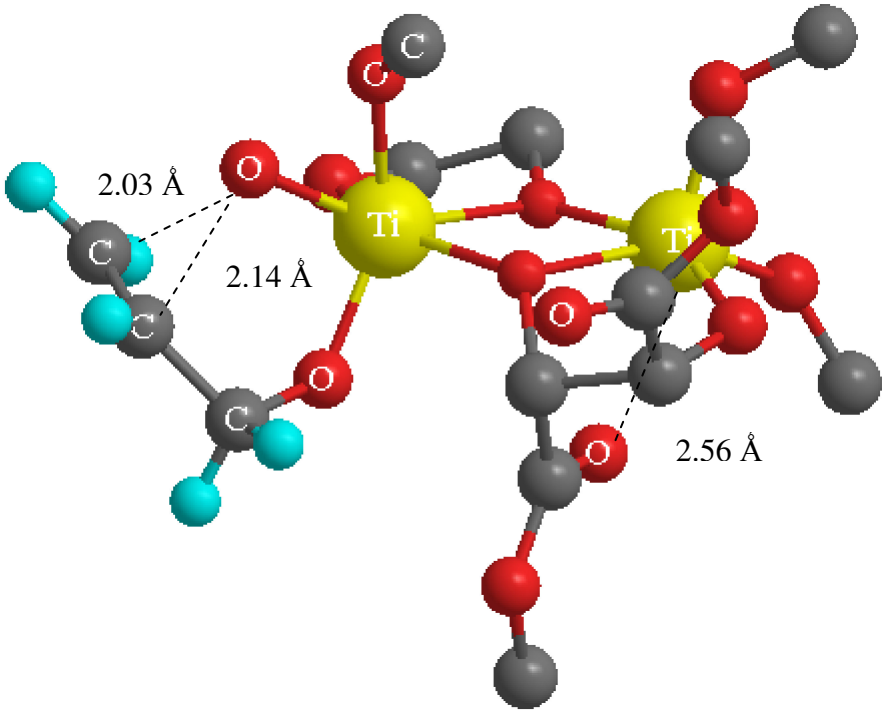
H,0,1.716721792,-4.1456505388,1.4793192066
H,0,2.8587895736,-3.1448847215,2.3931097039
H,0,2.950516104,-3.2013781632,0.6205935615
H,0,2.2155165563,5.1823742278,-1.3196757604
H,0,1.296463287,4.6672490342,0.1199736655
H,0,3.0201822119,4.2738770791,-0.0138993487
H,0,2.6541527999,-4.1826933457,-2.3686520985
H,0,1.3364054507,-3.3038268104,-3.1863802305
H,0,2.9952869672,-3.1511955214,-3.7831566806

Single point energy: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1643.037709010
File: revis3meoohoptfreqenergyPCM

PCM solvent calculation in dichloromethane: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1643.053237760
File: revis3meoohoptfreqenergyPCM

Revis3meoohb

Description: Gives incorrect enantiomer using propenol as substrate. Coordinating carbonyl *cis* to alkoxide, closest to butoxide. Bystander carbonyl closest to bystander alcohols, carbonyl points towards bystander alcohols. Methyl peroxide points toward bystander carbonyl.



Optimization: MPW1K/6-31G* on CHO and SDD on Ti
File name: (revis3meoohboptfreqenergyPCM)

E(RmPW+HF-PW91) = -1643.41254935

Zero-point correction=	0.438329 (Hartree/Particle)
Thermal correction to Energy=	0.473019
Thermal correction to Enthalpy=	0.473963
Thermal correction to Gibbs Free Energy=	0.369714
Sum of electronic and zero-point Energies=	-1642.974221
Sum of electronic and thermal Energies=	-1642.939531
Sum of electronic and thermal Enthalpies=	-1642.938587
Sum of electronic and thermal Free Energies=	-1643.042836

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	296.824	120.032	219.411

C,0,4.5787353589,-0.9461945576,-0.7440060279
C,0,3.7613055263,-2.0120208334,-0.6165376246
C,0,2.801332388,-2.1743663637,0.5243029309
O,0,2.2242185417,-0.9655749992,0.8872908293
Ti,0,1.7107213019,0.3937147846,-0.2299762288
Ti,0,-1.4232691986,1.1217377658,0.3750050201
O,0,-1.9135804895,1.9863423127,-1.0938923571
C,0,-3.150196195,2.355262481,-1.6166321073
O,0,0.4167705565,1.7832229289,0.4651155246
C,0,0.9443589907,3.0767445961,0.6093293446
C,0,2.3923268737,2.8435360684,1.0009175965
O,0,2.82582797,1.7305616527,0.2851227254
O,0,1.5547936569,0.7246931052,-2.1237305722
O,0,2.807716701,-0.3947324405,-1.5999446983
O,0,-0.1617046471,-0.3991350818,-0.2747673546
C,0,-0.5841398207,-1.5696426049,0.3420687463
C,0,-0.3996341547,-1.3787633628,1.8260443669
O,0,-0.5447478738,-0.283641636,2.3209844458
C,0,0.7582057943,0.077676079,-3.0724524917
O,0,-2.2017215377,2.0563086337,1.6654970861
C,0,-2.7210546171,1.9094786371,2.9434165684
O,0,-2.5746856781,-0.3499603767,0.3548047546
C,0,-2.0962792212,-1.6035446976,0.0752907352
C,0,-2.3114936318,-2.0656362177,-1.3584348518
O,0,-3.2151467426,-1.3568887892,-2.0080045734

C,0,-3.4739195953,-1.7817142889,-3.3341797509
O,0,-1.7335214907,-3.0106561851,-1.8273049349
O,0,-0.1539623754,-2.4747846364,2.5026907176
C,0,-0.0118984877,-2.3169287367,3.9081087637
H,0,0.4704596579,-0.9193593375,-2.7469637408
H,0,-0.1403523527,0.6797225277,-3.2065338886
H,0,1.3023683809,0.015372017,-4.0126129906
H,0,2.4684258683,2.6439230914,2.0732288565
H,0,3.0162593045,3.7079303114,0.7683734725
H,0,0.8742982008,3.5988828017,-0.3457014004
H,0,0.3852448176,3.6337659411,1.3604823603
H,0,3.324205783,-2.5936251611,1.3896936706
H,0,2.0365929361,-2.9032023751,0.2428559202
H,0,3.8001052806,-2.8008264533,-1.3548751788
H,0,5.2607699364,-0.8687941153,-1.5752661666
H,0,4.6178847046,-0.1647888529,0.000079951
H,0,-2.576824995,-2.3613519721,0.7052287446
H,0,-0.0831561608,-2.4588144084,-0.028349044
H,0,-3.2280213573,2.828776388,3.2375592787
H,0,-1.9270696682,1.6995127479,3.6598685823
H,0,-3.4402970392,1.0894192995,2.9683797211
H,0,-3.0031022261,2.8158096028,-2.5935670278
H,0,-3.6434797782,3.0760278203,-0.9622657559
H,0,-3.7928793487,1.4816937813,-1.7276813029
H,0,0.1845657644,-3.3086763248,4.2956105505
H,0,0.8167215744,-1.649502561,4.1234604091
H,0,-0.923975298,-1.912910993,4.3368162882
H,0,-4.2358766272,-1.1123002914,-3.7142900208
H,0,-2.5733673209,-1.714969287,-3.9379174002
H,0,-3.8286969402,-2.8084684339,-3.3432854707

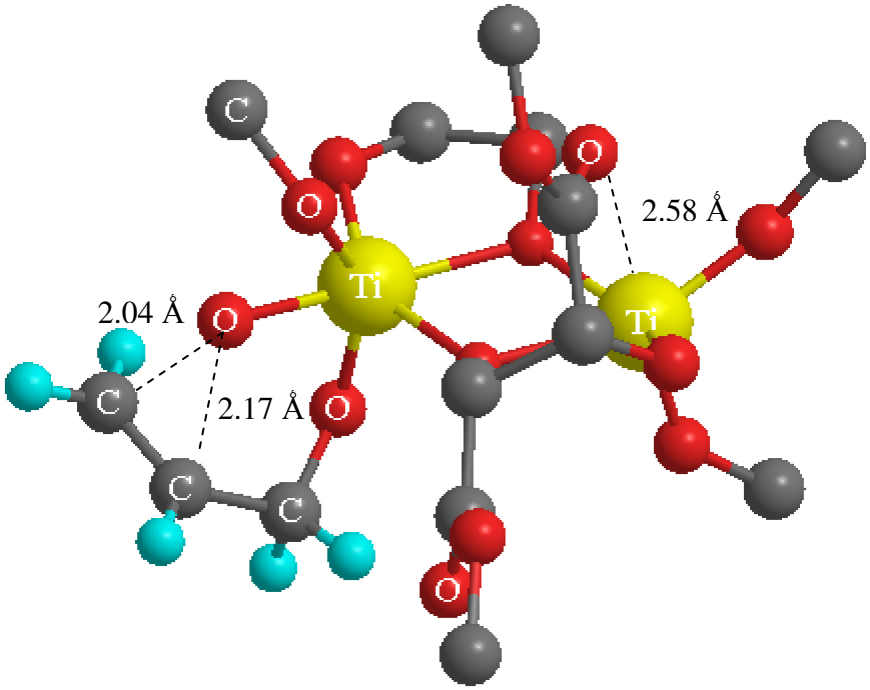
Single point energy: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1643.037941380
File: revis3meoohboptfreqenergyPCM

PCM solvent calculation in dichloromethane: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1643.054818770
File: revis3meoohboptfreqenergyPCM

ls3bmeooh

Description: Gives incorrect enantiomer using propenol as substrate. Coordinating carbonyl *cis* to t-butoxide, closest to bystander alcohols. Bystander carbonyl closest to

alkoxide, carbonyl points down directly down from catalyst in between alkoxide and bystander alcohols (not towards either).



Optimization: MPW1K/6-31G* on CHO and SDD on Ti
File name: (is3bmeoohoptfreqenergyPCM)

E(RmPW+HF-PW91) = -1643.49298357

Zero-point correction=	0.438088 (Hartree/Particle)
Thermal correction to Energy=	0.472959
Thermal correction to Enthalpy=	0.473903
Thermal correction to Gibbs Free Energy=	0.369102
Sum of electronic and zero-point Energies=	-1642.975791
Sum of electronic and thermal Energies=	-1642.940920
Sum of electronic and thermal Enthalpies=	-1642.939976
Sum of electronic and thermal Free Energies=	-1643.044776

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	296.786	120.297	220.571

C,0,3.8058988375,1.5503833228,-1.6497551847
C,0,2.7398333558,2.3727815585,-1.7345709548
C,0,1.5234867532,2.0255337098,-2.536787271

O,0,1.2885115145,0.6539886829,-2.4792818862
Ti,0,1.1495319771,-0.270933932,-0.9378508886
O,0,2.5529476853,0.8474230619,-0.202379456
O,0,-0.4170386803,0.721633591,-0.2040700228
Ti,0,-2.0994835482,-0.4455341853,-0.6599117857
O,0,-3.2117313828,-1.8275468577,-0.5419648758
C,0,-3.8703258336,-2.6114956196,0.3923966448
O,0,1.8826317962,-1.8737351787,-1.3887958222
C,0,1.1353632151,-2.8095746718,-2.1051464148
C,0,-0.2804157477,-2.7543865768,-1.5609193104
O,0,-0.5144140441,-1.3927631771,-1.3056180887
O,0,1.8217268792,-0.2983951125,0.9198458767
C,0,2.8759902166,-1.0984370599,1.3713464381
H,0,2.4486812002,-1.9360809912,1.9244529892
C,0,-0.54491965,1.5027663783,0.9296148882
C,0,-1.727304822,0.8813355856,1.7010324541
C,0,-1.2310693184,-0.4352616543,2.2513934772
O,0,-1.2503145279,-1.4309086834,1.5635757909
C,0,-0.8173331373,2.951504721,0.5772972141
O,0,-1.1438676913,3.6398294833,1.6683384276
C,0,-1.387984129,5.0201361613,1.465574742
O,0,-0.7144684948,3.4425327999,-0.5093115585
O,0,-2.7366686171,0.347765192,-2.0932180488
C,0,-3.8020278966,0.2629594437,-2.9774539116
O,0,-2.7007224531,0.5989147992,0.7742907771
H,0,3.4588576578,-1.4960575375,0.5437790117
H,0,3.5179516423,-0.5205835729,2.0338360887
O,0,-0.7755179866,-0.3909537105,3.481684415
C,0,-0.2655521651,-1.6082112316,4.0052905655
H,0,1.1432277802,-2.5476352423,-3.1661844201
H,0,1.5675985125,-3.8055730836,-1.9943241616
H,0,-0.3620631954,-3.3100369119,-0.6256772338
H,0,-1.012199601,-3.1458577073,-2.2666084756
H,0,1.6711367607,2.3169739436,-3.5811315146
H,0,0.6608650519,2.5701822004,-2.155095833
H,0,2.742464866,3.3111363406,-1.1975537923
H,0,4.6713590982,1.8166192902,-1.064596912
H,0,3.8609444826,0.6460484775,-2.2359479831
H,0,-2.0783321137,1.5302317237,2.5010379226
H,0,0.3704314663,1.4840049391,1.5261733947
H,0,-3.4273657267,0.2095057889,-3.9997158895
H,0,-4.4321572568,1.1475993863,-2.884097806
H,0,-4.4035410725,-0.6243010514,-2.7721287182
H,0,-4.6713327067,-3.1679640769,-0.0953467867

H,0,-4.3039493631,-1.9887228909,1.1765647707
H,0,-3.1823248309,-3.3205469254,0.8534569668
H,0,-1.6399076007,5.4223489324,2.4394527303
H,0,-0.5022500133,5.5092974308,1.0699634841
H,0,-2.2106595605,5.1614471059,0.7707330374
H,0,0.0731361993,-1.377601588,5.0075539708
H,0,-1.0470491039,-2.3619321679,4.03128078
H,0,0.5582083221,-1.9640946524,3.3956321486

Single point energy: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1643.039927720
File: is3bmeoohenergyPCM

PCM solvent calculation in dichloromethane: MPW1K/6-31+G** on CHO, Ti SDD (split valence qz)//MPW1K/6-31G* on CHO SDD on Ti= -1643.054895570
File: is3bmeoohenergyPCM

titButRevIs1

Frequency
B3LYP/gen (titButRevIs1)
E(RB+HF-LYP) = -1682.63625650

Zero-point correction= 0.450616 (Hartree/Particle)
Thermal correction to Energy= 0.486938
Thermal correction to Enthalpy= 0.487882
Thermal correction to Gibbs Free Energy= 0.381154
Sum of electronic and zero-point Energies= -1682.185640
Sum of electronic and thermal Energies= -1682.149319
Sum of electronic and thermal Enthalpies= -1682.148375
Sum of electronic and thermal Free Energies= -1682.255103

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	305.558	129.918	224.628

1	6	0	-3.170501	2.739015	-1.409490
2	6	0	-1.956509	3.226179	-1.033524
3	6	0	-0.674192	2.815966	-1.713506

4	8	0	-0.758653	1.456964	-2.142559
5	22	0	-1.175691	0.090240	-0.983544
6	8	0	-2.418156	1.317892	-0.096154
7	8	0	0.483743	0.480371	0.171437
8	22	0	1.934673	-0.879744	-0.356299
9	8	0	0.337446	-1.403301	2.211143
10	6	0	0.218932	-0.217513	2.461392
11	8	0	-0.189928	0.249576	3.674208
12	8	0	-2.037919	-1.031906	-2.152044
13	6	0	-1.518242	-2.320056	-2.507881
14	6	0	0.008756	-2.229069	-2.398184
15	8	0	0.230477	-1.399888	-1.241098
16	8	0	-2.132076	-0.272852	0.720659
17	6	0	-3.394814	-0.862747	1.166468
18	6	0	-3.036874	-2.322621	1.514563
19	6	0	0.603431	0.912320	1.515094
20	6	0	2.132085	1.161148	1.666406
21	6	0	2.490932	2.511622	1.032974
22	8	0	1.785619	3.504720	1.096665
23	8	0	2.637565	-2.483764	0.058955
24	6	0	2.931785	-3.207468	1.255039
25	8	0	2.770430	0.064431	1.058434
26	8	0	2.849937	-0.338377	-1.807687
27	6	0	4.262611	-0.271451	-2.043173
28	6	0	-4.474739	-0.805752	0.076819
29	6	0	-3.821179	-0.075075	2.415655
30	8	0	3.706254	2.511204	0.429505
31	1	0	-1.910810	-3.074343	-1.811445
32	1	0	-1.841302	-2.578355	-3.524085
33	1	0	0.442382	-1.737930	-3.278138
34	1	0	0.482547	-3.208046	-2.258689
35	1	0	-0.481796	3.447165	-2.595392
36	1	0	0.168602	2.943595	-1.022011
37	1	0	-1.887120	3.929745	-0.207008
38	1	0	-4.077796	3.050870	-0.904099
39	1	0	-3.276638	2.101048	-2.280000
40	1	0	2.413294	1.227615	2.730252
41	1	0	0.009662	1.806946	1.711561
42	1	0	3.622670	-4.023738	1.014631
43	1	0	2.012172	-3.621047	1.683110
44	1	0	3.396833	-2.536290	1.987600
45	1	0	4.427524	0.066787	-3.072200
46	1	0	4.718629	-1.260455	-1.909214
47	1	0	4.723152	0.437799	-1.346026

48	1	0	3.829098	3.417962	0.085636
49	1	0	-0.345366	-0.535960	4.234296
50	1	0	-4.734047	-0.498520	2.850114
51	1	0	-4.006883	0.969031	2.147824
52	1	0	-3.027121	-0.098113	3.168689
53	1	0	-3.904963	-2.824388	1.957980
54	1	0	-2.204536	-2.357891	2.222527
55	1	0	-2.741661	-2.869327	0.613419
56	1	0	-5.381787	-1.308614	0.431747
57	1	0	-4.130071	-1.296490	-0.836807
58	1	0	-4.719079	0.232478	-0.161357

B3LYP/gen solvent=CH_2Cl_2 (RevIs1PCMND)
PCM= -1682.65344272

B3PW91/gen solvent=CH_2Cl_2 (RevIs1PCMNDBP)
PCM= -1682.08458334

B3LYP/gen solvent= CH_2Cl_2 (titButRevIs1IPCMLanl2dz)
IPCM= -1672.67727922

B3PW91/6-31G* solvent=CH_2Cl_2 (RevIs1PCMBPND631G)
PCM= -3264.81538608

TitButRevIs1 Onsager (solRevIs1)

- optimized from titButRevIs1/gen (geom above)

B3LYP/gen solvent=CH_2Cl_2 a0=6.09
SCF Done: E(RB+HF-LYP) = -1682.63643712 A.U. after 9 cycles

1	6	0	-3.172853	2.754208	-1.376836
2	6	0	-1.955743	3.234077	-1.001543
3	6	0	-0.677994	2.829934	-1.693988
4	8	0	-0.763899	1.474194	-2.133458
5	22	0	-1.177604	0.098224	-0.983233
6	8	0	-2.414310	1.320149	-0.081706
7	8	0	0.483794	0.478506	0.170537
8	22	0	1.931870	-0.880504	-0.364163
9	8	0	0.346034	-1.422266	2.187865

10	6	0	0.224688	-0.239862	2.453403
11	8	0	-0.182696	0.213019	3.670841
12	8	0	-2.041698	-1.015317	-2.159718
13	6	0	-1.524756	-2.302501	-2.521794
14	6	0	0.002708	-2.214505	-2.414838
15	8	0	0.228416	-1.391311	-1.254882
16	8	0	-2.128075	-0.279002	0.719004
17	6	0	-3.391098	-0.869943	1.165321
18	6	0	-3.034110	-2.332969	1.500708
19	6	0	0.605128	0.900199	1.517661
20	6	0	2.133428	1.150475	1.667949
21	6	0	2.489876	2.505440	1.043386
22	8	0	1.781818	3.496274	1.108744
23	8	0	2.635340	-2.486924	0.042363
24	6	0	2.926251	-3.213052	1.238242
25	8	0	2.772770	0.059088	1.050064
26	8	0	2.849286	-0.332755	-1.814086
27	6	0	4.264308	-0.249793	-2.027486
28	6	0	-4.473761	-0.802552	0.079159
29	6	0	-3.811541	-0.091085	2.421697
30	8	0	3.708340	2.512672	0.445051
31	1	0	-1.916928	-3.059583	-1.828192
32	1	0	-1.850007	-2.556246	-3.538589
33	1	0	0.435098	-1.720007	-3.293644
34	1	0	0.475231	-3.194978	-2.281142
35	1	0	-0.492636	3.468470	-2.572199
36	1	0	0.169632	2.953103	-1.007684
37	1	0	-1.880538	3.927445	-0.167024
38	1	0	-4.076739	3.061353	-0.862563
39	1	0	-3.284987	2.126362	-2.253965
40	1	0	2.416806	1.209050	2.731593
41	1	0	0.009391	1.791552	1.722627
42	1	0	3.626072	-4.022351	1.000031
43	1	0	2.006862	-3.636064	1.657236
44	1	0	3.379424	-2.540805	1.977120
45	1	0	4.441490	0.114438	-3.045780
46	1	0	4.726113	-1.238552	-1.911281
47	1	0	4.710438	0.445284	-1.307034
48	1	0	3.829365	3.422775	0.109552
49	1	0	-0.336434	-0.577333	4.224709
50	1	0	-4.723171	-0.516657	2.856433
51	1	0	-3.997184	0.955237	2.162747
52	1	0	-3.014957	-0.120965	3.171715
53	1	0	-3.902852	-2.837813	1.939098

54	1	0	-2.202727	-2.375308	2.209369
55	1	0	-2.738522	-2.871788	0.594912
56	1	0	-5.381166	-1.305135	0.433361
57	1	0	-4.133042	-1.288301	-0.838656
58	1	0	-4.716022	0.237948	-0.151260

B3LYP/gen solvent=CH_2Cl_2 (RevIs1PCMbND)
PCM=-1682.65268803

B3PW91/gen solvent=CH_2Cl_2 (RevIs1PCMbBPNODIS)
PCM=-1682.08381029

titButRevIs1 B3LYP/6-31G* (RevIs1631G) (from RevIs1geom)
E(RB+HF-LYP) = -3265.53321734

Zero-point correction= 0.450558 (Hartree/Particle)
Thermal correction to Energy= 0.486864
Thermal correction to Enthalpy= 0.487808
Thermal correction to Gibbs Free Energy= 0.381408
Sum of electronic and zero-point Energies= -3265.082659
Sum of electronic and thermal Energies= -3265.046353
Sum of electronic and thermal Enthalpies= -3265.045409
Sum of electronic and thermal Free Energies= -3265.151809

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	305.512	129.926	223.937

1	6	0	-3.180253	2.824402	-1.252826
2	6	0	-1.969177	3.293605	-0.850087
3	6	0	-0.681107	2.908519	-1.534629
4	8	0	-0.761082	1.594357	-2.031957
5	22	0	-1.182499	0.161708	-0.965436
6	8	0	-2.429616	1.321303	-0.003426
7	8	0	0.478997	0.490185	0.210095
8	22	0	1.924282	-0.862412	-0.401916
9	8	0	0.414200	-1.549737	2.042112
10	6	0	0.266496	-0.403648	2.415475
11	8	0	-0.141916	-0.075198	3.657381
12	8	0	-2.055968	-0.881844	-2.191020
13	6	0	-1.561820	-2.138862	-2.610752
14	6	0	-0.035074	-2.084489	-2.492852
15	8	0	0.207989	-1.338211	-1.307010

16	8	0	-2.138402	-0.311199	0.719680
17	6	0	-3.370624	-0.931073	1.140198
18	6	0	-3.006327	-2.407891	1.379552
19	6	0	0.621329	0.810900	1.566848
20	6	0	2.149297	1.045412	1.721394
21	6	0	2.493942	2.443403	1.184878
22	8	0	1.802817	3.426058	1.360570
23	8	0	2.641282	-2.474106	-0.097702
24	6	0	3.020553	-3.262700	1.004373
25	8	0	2.780387	0.006478	1.046921
26	8	0	2.798596	-0.222465	-1.825084
27	6	0	4.164121	-0.067229	-2.144205
28	6	0	-4.470098	-0.813597	0.079644
29	6	0	-3.790001	-0.246974	2.447256
30	8	0	3.670746	2.484079	0.532425
31	1	0	-1.968346	-2.930103	-1.962856
32	1	0	-1.880179	-2.344087	-3.641505
33	1	0	0.407086	-1.559533	-3.350507
34	1	0	0.414125	-3.083204	-2.419595
35	1	0	-0.478743	3.596394	-2.371699
36	1	0	0.152268	3.005817	-0.825549
37	1	0	-1.906899	3.967286	0.001444
38	1	0	-4.091285	3.118187	-0.743176
39	1	0	-3.283688	2.222846	-2.149071
40	1	0	2.433099	1.053824	2.787231
41	1	0	0.029628	1.682340	1.856252
42	1	0	3.811713	-3.959447	0.699653
43	1	0	2.164992	-3.838431	1.377885
44	1	0	3.396753	-2.622556	1.813090
45	1	0	4.249657	0.401210	-3.132459
46	1	0	4.669411	-1.042339	-2.171208
47	1	0	4.657631	0.571111	-1.401000
48	1	0	3.790335	3.414328	0.260800
49	1	0	-0.271897	-0.913477	4.140926
50	1	0	-4.684751	-0.720910	2.867145
51	1	0	-4.006002	0.809347	2.262578
52	1	0	-2.982360	-0.305011	3.184137
53	1	0	-3.867535	-2.941225	1.798699
54	1	0	-2.164600	-2.496132	2.071950
55	1	0	-2.724558	-2.892915	0.439487
56	1	0	-5.362453	-1.356262	0.411790
57	1	0	-4.136011	-1.231817	-0.873050
58	1	0	-4.738405	0.233962	-0.079146

B3LYP/6-31G* solvent=CH_2Cl_2 (RevIs1631GPCMND)
PCM= -3265.54623420

titButRevIs1 B3PW91/gen (BPfreqRevIs1)

BPfreqRevIs1.log
E(RB+HF-PW91) = -1682.06795861

Zero-point correction=	0.452324 (Hartree/Particle)
Thermal correction to Energy=	0.488586
Thermal correction to Enthalpy=	0.489530
Thermal correction to Gibbs Free Energy=	0.382342
Sum of electronic and zero-point Energies=	-1681.615635
Sum of electronic and thermal Energies=	-1681.579373
Sum of electronic and thermal Enthalpies=	-1681.578429
Sum of electronic and thermal Free Energies=	-1681.685617

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	306.592	129.416	225.596

1	6	0	-3.203528	2.639268	-1.450213
2	6	0	-1.996647	3.155471	-1.097153
3	6	0	-0.719650	2.739832	-1.773738
4	8	0	-0.800105	1.378452	-2.172199
5	22	0	-1.180028	0.050546	-0.968094
6	8	0	-2.416559	1.283630	-0.099633
7	8	0	0.474792	0.518700	0.145079
8	22	0	1.923428	-0.855467	-0.326429
9	8	0	0.431478	-1.376896	2.107420
10	6	0	0.269084	-0.207991	2.408034
11	8	0	-0.119716	0.196052	3.641086
12	8	0	-2.032551	-1.117692	-2.089243
13	6	0	-1.492975	-2.393474	-2.428272
14	6	0	0.027245	-2.273184	-2.314705
15	8	0	0.225959	-1.429828	-1.172597
16	8	0	-2.112827	-0.246474	0.758624
17	6	0	-3.367270	-0.839400	1.203847
18	6	0	-2.999839	-2.286289	1.570338
19	6	0	0.590379	0.949853	1.482431
20	6	0	2.108761	1.238266	1.625243
21	6	0	2.427924	2.588501	0.983263

22	8	0	1.712108	3.570337	1.076387
23	8	0	2.691084	-2.418756	0.109348
24	6	0	3.056765	-3.093726	1.304055
25	8	0	2.767768	0.155278	1.031278
26	8	0	2.793979	-0.361043	-1.815120
27	6	0	4.191558	-0.350339	-2.097204
28	6	0	-4.440156	-0.808340	0.113676
29	6	0	-3.806875	-0.042334	2.436084
30	8	0	3.617749	2.605304	0.343218
31	1	0	-1.874250	-3.148667	-1.726629
32	1	0	-1.807308	-2.668899	-3.442846
33	1	0	0.454446	-1.783594	-3.198783
34	1	0	0.520767	-3.240424	-2.162640
35	1	0	-0.534641	3.355403	-2.668260
36	1	0	0.126097	2.885144	-1.089139
37	1	0	-1.931826	3.886548	-0.294045
38	1	0	-3.302629	1.971468	-2.299923
39	1	0	2.388356	1.325072	2.688762
40	1	0	-0.032842	1.821561	1.693488
41	1	0	3.830600	-3.834767	1.072498
42	1	0	2.186340	-3.601089	1.734387
43	1	0	3.446966	-2.373184	2.033226
44	1	0	4.333954	-0.066794	-3.145872
45	1	0	4.623216	-1.344858	-1.928664
46	1	0	4.698198	0.376088	-1.451732
47	1	0	3.716427	3.513824	0.001156
48	1	0	-0.225758	-0.613087	4.175491
49	1	0	-4.721810	-0.465106	2.866203
50	1	0	-3.995171	0.997391	2.153608
51	1	0	-3.020155	-0.053522	3.196580
52	1	0	-3.869577	-2.794584	2.002105
53	1	0	-2.181091	-2.306213	2.294498
54	1	0	-2.680422	-2.835043	0.679321
55	1	0	-5.340650	-1.320647	0.471199
56	1	0	-4.084584	-1.303633	-0.793638
57	1	0	-4.698368	0.223955	-0.135309
58	1	0	-4.113036	2.952714	-0.948835

B3PW91/6-31G* solvent=CH_2Cl_2 (RevIs1PCMNDBPBP631G)
PCM= -3264.81791034

titButRevIs1 Onsager (BPsolRevIs1)

B3PW91/gen solvent=CH_2Cl_2 a0=5.78
SCF Done: E(RB+HF-PW91) = -1682.06823348 A.U. after 7 cycles

1	6	0	-3.226316	2.661530	-1.368752
2	6	0	-2.019235	3.175558	-1.012628
3	6	0	-0.745542	2.784423	-1.709908
4	8	0	-0.822121	1.434123	-2.144788
5	22	0	-1.184339	0.075262	-0.968143
6	8	0	-2.420218	1.278779	-0.060854
7	8	0	0.475660	0.536615	0.140374
8	22	0	1.916970	-0.847460	-0.339251
9	8	0	0.490744	-1.425695	2.008319
10	6	0	0.295861	-0.277381	2.368309
11	8	0	-0.103712	0.055822	3.615781
12	8	0	-2.035513	-1.068952	-2.115464
13	6	0	-1.504163	-2.345753	-2.462528
14	6	0	0.016577	-2.237494	-2.343766
15	8	0	0.218788	-1.404621	-1.195121
16	8	0	-2.100687	-0.272065	0.756791
17	6	0	-3.350708	-0.873871	1.205388
18	6	0	-2.974107	-2.320730	1.562502
19	6	0	0.593058	0.923503	1.491668
20	6	0	2.109741	1.221294	1.636676
21	6	0	2.415605	2.588337	1.025559
22	8	0	1.691427	3.561692	1.139388
23	8	0	2.704321	-2.412326	0.056874
24	6	0	3.070497	-3.120050	1.232385
25	8	0	2.775444	0.158124	1.014431
26	8	0	2.778987	-0.332446	-1.829405
27	6	0	4.181034	-0.300953	-2.084362
28	6	0	-4.426967	-0.842682	0.118855
29	6	0	-3.789653	-0.086817	2.443894
30	8	0	3.606223	2.631515	0.386797
31	1	0	-1.892796	-3.103663	-1.767949
32	1	0	-1.817541	-2.611612	-3.480090
33	1	0	0.450071	-1.744399	-3.222951
34	1	0	0.502436	-3.209616	-2.197914
35	1	0	-0.570242	3.425587	-2.588484
36	1	0	0.104309	2.914965	-1.027466
37	1	0	-1.951634	3.885571	-0.191078
38	1	0	-3.328533	2.014770	-2.234269
39	1	0	2.392296	1.285031	2.701117
40	1	0	-0.040458	1.778018	1.738319

41	1	0	3.840584	-3.857954	0.979212
42	1	0	2.199627	-3.635047	1.652362
43	1	0	3.466222	-2.421044	1.979283
44	1	0	4.340613	-0.001919	-3.126570
45	1	0	4.621840	-1.292471	-1.920262
46	1	0	4.667340	0.422350	-1.419705
47	1	0	3.695428	3.549614	0.068790
48	1	0	-0.192159	-0.778609	4.113609
49	1	0	-4.699131	-0.518715	2.876163
50	1	0	-3.987093	0.953022	2.168525
51	1	0	-2.999332	-0.096885	3.200548
52	1	0	-3.841306	-2.836704	1.989901
53	1	0	-2.157404	-2.341020	2.288916
54	1	0	-2.649497	-2.862754	0.669264
55	1	0	-5.325105	-1.357915	0.477728
56	1	0	-4.073487	-1.334196	-0.791290
57	1	0	-4.688512	0.189758	-0.126134
58	1	0	-4.133268	2.956184	-0.851628

titButRevIs1 B3PW91/6-31G* (BPRevIs1631G)

E(RB+HF-PW91) = -3264.80663946

Zero-point correction= 0.451808 (Hartree/Particle)
Thermal correction to Energy= 0.488115
Thermal correction to Enthalpy= 0.489059
Thermal correction to Gibbs Free Energy= 0.382118
Sum of electronic and zero-point Energies= -3264.354832
Sum of electronic and thermal Energies= -3264.318525
Sum of electronic and thermal Enthalpies= -3264.317580
Sum of electronic and thermal Free Energies= -3264.424521

			E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL			306.297	129.603	225.076
1	6	0	-3.233714	2.700531	-1.307806
2	6	0	-2.033846	3.215097	-0.933001
3	6	0	-0.749069	2.834171	-1.615466
4	8	0	-0.812648	1.512256	-2.074613
5	22	0	-1.184857	0.118576	-0.956730
6	8	0	-2.435549	1.273413	-0.017089
7	8	0	0.469848	0.547266	0.178390
8	22	0	1.918068	-0.836207	-0.359777
9	8	0	0.558359	-1.509120	1.904573

10	6	0	0.333920	-0.396607	2.340968
11	8	0	-0.071998	-0.163332	3.595421
12	8	0	-2.041913	-0.980331	-2.133902
13	6	0	-1.532776	-2.236391	-2.511811
14	6	0	-0.012620	-2.158444	-2.383328
15	8	0	0.207319	-1.378546	-1.222843
16	8	0	-2.115414	-0.298135	0.757040
17	6	0	-3.339521	-0.909129	1.192307
18	6	0	-2.964388	-2.364213	1.500793
19	6	0	0.606623	0.856329	1.531758
20	6	0	2.123036	1.140673	1.683520
21	6	0	2.416540	2.544697	1.147104
22	8	0	1.707608	3.506742	1.353856
23	8	0	2.721792	-2.399140	-0.049985
24	6	0	3.161814	-3.166878	1.033246
25	8	0	2.783284	0.123360	1.019538
26	8	0	2.730611	-0.235558	-1.827714
27	6	0	4.076332	-0.126254	-2.209812
28	6	0	-4.427667	-0.855329	0.122630
29	6	0	-3.780348	-0.176019	2.459194
30	8	0	3.567644	2.617538	0.464108
31	1	0	-1.934928	-3.015374	-1.846226
32	1	0	-1.839717	-2.476049	-3.539019
33	1	0	0.429217	-1.652239	-3.252526
34	1	0	0.450803	-3.148051	-2.278959
35	1	0	-0.563610	3.503850	-2.471445
36	1	0	0.088517	2.962809	-0.916088
37	1	0	-1.981189	3.920551	-0.106526
38	1	0	-4.148510	2.988874	-0.800858
39	1	0	-3.326804	2.064960	-2.182308
40	1	0	2.403348	1.167258	2.751080
41	1	0	-0.021595	1.693922	1.845623
42	1	0	3.962407	-3.842061	0.704202
43	1	0	2.339530	-3.768051	1.440971
44	1	0	3.549594	-2.515429	1.827789
45	1	0	4.130245	0.292761	-3.222459
46	1	0	4.562416	-1.111636	-2.209495
47	1	0	4.616824	0.535848	-1.521712
48	1	0	3.656221	3.550912	0.198242
49	1	0	-0.134208	-1.029981	4.036964
50	1	0	-4.678401	-0.637663	2.885436
51	1	0	-3.999907	0.869873	2.225935
52	1	0	-2.983274	-0.198532	3.209144
53	1	0	-3.830445	-2.892395	1.915971

54	1	0	-2.144860	-2.413495	2.223298
55	1	0	-2.645859	-2.882040	0.590911
56	1	0	-5.314093	-1.397292	0.471206
57	1	0	-4.078961	-1.308340	-0.808971
58	1	0	-4.710849	0.180185	-0.083022

B3PW91/6-31G* solvent=CH_2Cl_2 (BPRevIs1631GPCMND)
PCM= - -3264.81988195

titButRevIs1methyl

(titButRevIs1 with trans-2-buten-1-ol as substrate)

B3LYP/gen

SCF Done: E(RB+HF-LYP) = -1721.94893753 A.U. after 33 cycles

Zero-point correction= 0.478809 (Hartree/Particle)
Thermal correction to Energy= 0.516812
Thermal correction to Enthalpy= 0.517756
Thermal correction to Gibbs Free Energy= 0.407192
Sum of electronic and zero-point Energies= -1721.470129
Sum of electronic and thermal Energies= -1721.432125
Sum of electronic and thermal Enthalpies= -1721.431181
Sum of electronic and thermal Free Energies= -1721.541746

	E (Thermal)	CV	S
	KCAL/MOL	CAL/MOL-KELVIN	CAL/MOL-KELVIN
TOTAL	324.305	135.439	232.702

C,2.710 045,-1.4200470657,-3.0399789964
C,3.105901,-1.0176710657,-1.7999009964
C,2.676868,-1.7120200657,-0.5307279964
O,1.316775,-2.1384310657,-0.62 88099964
Ti,-0.033154,-0.9631440657,-1.0439929964
O,1.208923,-0.086197 0657,-2.2682689964
O,0.377855,0.1926629343,0.6111310036
Ti,-0.971772,- 0.3253280657,2.0726310036
O,-1.486226,2.2521919343,0.4854570036
C,-0.2 99172,2.4882999343,0.3510210036
O,0.175463,3.6927229343,-0.0742189964
O,-1.177181,-2.1181110657,-1.8980179964
C,-2.462561,-2.4632440657,-1.3 652489964
C,-2.358371,-2.3475080657,0.1602840036

O,-1.524205,-1.191820 0657,0.3709330036
O,-0.378428,0.7440509343,-2.0052349964
C,-0.976434,1 .1878039343,-3.2641759964
C,-2.414177,1.5979079343,-2.8821289964
C,0.8 24403,1.5314709343,0.7278130036
C,1.087162,1.6807859343,2.2550580036
C ,2.438772,1.0440759343,2.6023160036
O,3.427924,1.1112559343,1.89192900 36
O,-2.55993,0.0941649343,2.8089410036
C,-3.279127,1.2848079343,3.131 8260036
O,-0.00576,1.0773659343,2.9039510036
O,-0.419967,-1.7893460657 ,2.9611730036
C,-0.292578,-2.0332370657,4.3680410036
C,-0.986837,0.075 7819343,-4.3222669964
C,-0.154618,2.3999889343,-3.7319679964
O,2.44620 5,0.4345239343,3.8150420036
H,-3.216722,-1.7645140657,-1.7547049964
H, -2.730144,-3.4795470657,-1.6808219964
H,-1.865629,-3.2271910657,0.5928 650036
H,-3.332888,-2.2039820657,0.6421690036
H,3.301476,-2.5989750657 ,-0.3410069964
H,2.797452,-1.0313430657,0.3213010036
H,3.791627,-0.177 5590657,-1.7044109964
H,2.073951,-2.2990840657,-3.1190189964
H,1.16088 6,2.7445149343,2.5353890036
H,1.716109,1.7192719343,0.1269170036
H,-4. 083524,1.0342709343,3.8331290036
H,-3.709653,1.7254129343,2.2257750036
H,-2.601521,2.0120759343,3.5960490036
H,0.07962,-3.0538360657,4.51122 00036
H,-1.267001,-1.9308390657,4.8621860036
H,0.414486,-1.3201500657, 4.8069340036
H,3.354146,0.0911139343,3.9301430036
H,-0.606383,4.259724 9343,-0.2231829964
H,-0.584877,2.8330659343,-4.6423139964
H,0.875026,2 .0934859343,-3.9363309964
H,-0.133386,3.1665889343,-2.9509389964
H,-2. 920593,2.0337899343,-3.7514669964
H,-2.404774,2.3307109343,-2.07089999 64
H,-2.985122,0.7264139343,-2.5468039964
H,-1.47818,0.4380909343,-5.2 326489964
H,-1.519056,-0.8048240657,-3.9549099964
H,0.034364,-0.222707 0657,-4.5700529964
C,3.183868,-0.7988950657,-4.3183349964

H,2.339136,- 0.5553370657,-4.9720229964
H,3.752986,0.1176259343,-4.1344569964
H,3.8 26112,-1.4999610657,-4.8699299964

B3LYP/gen solvent=CH_2Cl_2
PCM= -1721.96307723

Onsager

B3LYP/gen solvent=CH_2Cl_2 a0=6.00
SCF Done: E(RB+HF-LYP) = -1721.94917928 A.U. after 8 cycles

C,2.7142356303,-1.4101804169,-3.0471566329
C,3.1077771469,-1.0112884871,-1.805152807
C,2.6830437441,-1.71 33376184,-0.5386532133
O,1.3230102405,-2.1416244721,-0.6340422865
Ti,- 0.0295245046,-0.9672430042,-1.0444498173
O,1.2075618716,-0.0850811142, -2.2662758953
O,0.3850610678,0.1847028708,0.6140180843
Ti,-0.973656562 6,-0.321595152,2.0700638849
O,-1.4877976069,2.2281503619,0.502549203
C ,-0.303749674,2.4752487974,0.3573847685
O,0.1584040204,3.6807106893,-0 .0734813884
O,-1.1739099671,-2.1247128453,-1.8957986169
C,-2.464080170 2,-2.4576449799,-1.368334165
C,-2.3661978198,-2.3400316941,0.157577784 9
O,-1.5242282465,-1.1911329314,0.3708026542
O,-0.3823573484,0.7394905 898,-2.000452209
C,-0.9782619774,1.1882547592,-3.2598508437
C,-2.41477 08823,1.6015370715,-2.8768592702
C,0.8275265289,1.5254317646,0.7290551 3
C,1.0930924354,1.6756476378,2.2554240852
C,2.4443802064,1.0384883978 ,2.601609592
O,3.4314103154,1.0978250509,1.8880729981
O,-2.5620266334, 0.0992530031,2.8081817393
C,-3.2833664163,1.2930983665,3.1143371595
O, 0.0005813006,1.0719606134,2.9062206137
O,-0.4308211488,-1.7889987617,2 .9631620194
C,-0.2944226173,-2.0092477365,4.3724893608
C,-0.9916835038 ,0.077708672,-4.3192196373
C,-0.153026338,2.3987434427,-3.7250612646
O ,2.4556170383,0.4372629505,3.8193706038
H,-3.2110541217,-1.7536838113, -1.7622569995
H,-2.7391669324,-3.4723629743,-1.6830859408

H,-1.8826878 437,-3.223177694,0.5938439175
H,-3.3420529867,-2.1882202703,0.63445745 04
H,3.3095904761,-2.600402164,-0.3555867984
H,2.8049336919,-1.0370423 873,0.3166386167
H,3.7892401589,-0.1681698886,-1.706152365
H,2.0817696 855,-2.2915607851,-3.1301481629
H,1.1668415054,2.7393835144,2.53547703 95
H,1.7159710397,1.7170096598,0.1247131644
H,-4.0964197726,1.04839367 37,3.8079022234
H,-3.7024839019,1.7286955728,2.2007086758
H,-2.6106982 486,2.022917142,3.5817751664
H,0.0772425108,-3.0280996263,4.5308807638
H,-1.2654852333,-1.8971780169,4.8717372231
H,0.4162626144,-1.29023308 12,4.7958086976
H,3.3643354565,0.0952113011,3.9321462373
H,-0.62697105 01,4.2432814076,-0.2211961291
H,-0.5823679246,2.834860742,-4.634216605 8
H,0.875666942,2.0902415427,-3.9308168461
H,-0.1293651427,3.163959356 ,-2.9428299765
H,-2.9196961399,2.0400963005,-3.745580119
H,-2.40355719 31,2.3335846307,-2.0649741127
H,-2.9882664575,0.7311753685,-2.54277282 2
H,-1.4788207617,0.4439521492,-5.2301623212
H,-1.5294185606,-0.800848 8465,-3.9548863871
H,0.0285163346,-0.2253734484,-4.5653882012
C,3.1841 441094,-0.7805053588,-4.3226240377
H,2.3379369671,-0.5372067252,-4.974 4456789
H,3.7497037148,0.1373486636,-4.1350155342
H,3.8286030122,-1.47 60956156,-4.8784998734

B3LYP/gen solvent=CH_2Cl_2
PCM=-1721.96311489

B3PW91/gen (BPfreqRevIs1methyl)

SCF Done: E(RB+HF-PW91) = -1721.36713565 A.U. after 32 cycles

Zero-point correction= 0.480751 (Hartree/Particle)
Thermal correction to Energy= 0.518632
Thermal correction to Enthalpy= 0.519576
Thermal correction to Gibbs Free Energy= 0.409031
Sum of electronic and zero-point Energies= -1720.886384
Sum of electronic and thermal Energies= -1720.848504
Sum of electronic and thermal Enthalpies= -1720.847559

Sum of electronic and thermal Free Energies= -1720.958105

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	325.447	134.873	232.662

C,-3.4612579124,2.2671 070365,-1.1379408942
C,-2.2890269124,2.8293270365,-0.7351098942
C,-0.9 961539124,2.6490490365,-1.4821058942
O,-0.9126019124,1.3354840365,-2.0 192558942
Ti,-1.0565399124,-0.1281289635,-0.9299738942
O,-2.4171759124 ,0.8354820365,0.0697111058
O,0.5429180876,0.4985380365,0.1927151058
Ti ,2.1653100876,-0.5992379635,-0.4186938942
O,0.8705080876,-1.5511309635 ,1.9615511058
C,0.5233560876,-0.4592599635,2.3757121058
O,0.0975290876 ,-0.2465589635,3.6434761058
O,-1.7531669124,-1.3144289635,-2.137388894 2
C,-1.0393129124,-2.4646979635,-2.5848868942
C,0.4487840876,-2.131163 9635,-2.4756818942
O,0.5479530876,-1.3662639635,-1.2670508942
O,-1.886 3199124,-0.7113039635,0.7783791058
C,-3.0212809124,-1.5260759635,1.188 8411058
C,-2.4112279124,-2.9028499635,1.4983931058
C,0.6321400876,0.81 67130365,1.5631701058
C,2.0933140876,1.3216320365,1.7092351058
C,2.183 7120876,2.7581010365,1.1949481058
O,1.3361850876,3.6080830365,1.405215 1058
O,3.1941330876,-2.0489639635,-0.1634858942
C,3.6983920876,-2.7942 439635,0.9341501058
O,2.8909130876,0.4118340365,1.0057381058
O,2.87632 30876,0.1654310365,-1.8771748942
C,4.2348450876,0.4654450365,-2.188022 8942
C,-4.0803009124,-1.6363069635,0.0908011058
C,-3.5924709124,-0.872 6149635,2.4515581058
O,3.3298290876,3.0143010365,0.5263571058
H,-1.290 9879124,-3.3223319635,-1.9446748942
H,-1.3307659124,-2.7016709635,-3.6 159958942
H,0.7796900876,-1.5115939635,-3.3186908942
H,1.0822090876,-3 .0240489635,-2.4124368942
H,-0.9225289124,3.3680890365,-2.3131418942
H ,-0.1512079124,2.8328480365,-0.8065298942
H,-2.2765639124,3.4700780365 ,0.1454601058
H,-3.4620509124,1.6802760365,-2.0549768942

H,2.387210087 6,1.3538290365,2.7721081058
H,-0.1105869124,1.5568910365,1.8683361058
H,4.5177970876,-3.4335799635,0.5854311058
H,2.9086190876,-3.4200739635 ,1.3641941058
H,4.0730720876,-2.1118889635,1.7071461058
H,4.2749080876 ,0.9024930365,-3.1919548942
H,4.8423830876,-0.4480499635,-2.1664098942
H,4.6355700876,1.1824480365,-1.4625448942
H,3.2782300876,3.9554200365 ,0.2738841058
H,0.1381810876,-1.1097869635,4.0960001058
H,-4.417722912 4,-1.4687129635,2.8570321058
H,-3.9599869124,0.1297420365,2.2153671058
H,-2.8136739124,-0.7799769635,3.2147401058
H,-3.1840099124,-3.5720149 635,1.8940241058
H,-1.6079549124,-2.8142809635,2.2345681058
H,-1.99268 79124,-3.3486059635,0.5911431058
H,-4.8991869124,-2.2794429635,0.43243 11058
H,-3.6515929124,-2.0562139635,-0.8223368942
H,-4.4835329124,-0.6 494119635,-0.1462038942
C,-4.7755309124,2.4975680365,-0.4659288942
H,- 5.2877999124,1.5505160365,-0.2660278942
H,-4.6553889124,3.0311550365,0 .4816681058
H,-5.4366829124,3.0895820365,-1.1139978942

B3PW91/gen solvent=CH_2Cl_2
PCM= -1721.38065588

B3PW91/6-31G* solvent=CH_2Cl_2
PCM= -3304.12568103

Onsager

solvent=CH_2Cl_2 a0=6.09
SCF Done: E(RB+HF-PW91) = -1721.36739682 A.U. after 8 cycles

C,-3.4719808388,2.2669472256,- 1.1282563655
C,-2.2997588205,2.8307955808,-0.7272883178
C,-1.008738366 7,2.657797724,-1.4794351082
O,-0.920840437,1.3463545339,-2.0213031514
Ti,-1.0575604732,-0.1207264828,-0.9344584315
O,-2.4162867234,0.8364165 122,0.0707363525
O,0.5448053335,0.5114347702,0.1832738025
Ti,2.1619626 758,-0.6044736755,-0.4119259434
O,0.893989363,-1.545710743,1.920433478 5

C,0.5330564294,-0.4648266065,2.3536348288
O,0.102739276,-0.276590689 7,3.6215017158
O,-1.7521770194,-1.3047651249,-2.1454018376
C,-1.044717 2347,-2.4635418285,-2.5797155879
C,0.4453619599,-2.1398138328,-2.46690 43811
O,0.5454195712,-1.364777558,-1.2653094622
O,-1.8793007086,-0.711 5356927,0.7736235419
C,-3.0139898415,-1.5249000405,1.1912502988
C,-2.4 016188962,-2.8980221899,1.5117833623
C,0.6334951383,0.8209916665,1.556 0800348
C,2.0937390975,1.3280184821,1.7045291216
C,2.1830101235,2.7645 343746,1.1912459947
O,1.3333748967,3.6132816206,1.3967327167
O,3.19345 07206,-2.0537539285,-0.1575234471
C,3.6816186528,-2.8097207264,0.94009 82897
O,2.8934001251,0.4198277042,1.0005060514
O,2.8794726121,0.150472 5822,-1.8755151682
C,4.2419459686,0.459354521,-2.1562190786
C,-4.07169 98877,-1.6457179113,0.0932762851
C,-3.5867552115,-0.862915795,2.448481 1085
O,3.3326069296,3.0245619979,0.5284938284
H,-1.3051537075,-3.31418 31726,-1.9337349369
H,-1.3333005394,-2.7075149905,-3.6101229459
H,0.78 45388947,-1.5305068806,-3.3142338532
H,1.0718450333,-3.0368529919,-2.3 929490945
H,-0.9409114751,3.3800082064,-2.3083798969
H,-0.1623780281,2 .8429023405,-0.8059398635
H,-2.2862287893,3.4677873337,0.1559571779
H, -3.4741437184,1.6830604631,-2.0472212967
H,2.3865141775,1.3594260432,2 .7677438895
H,-0.1122201962,1.5550685658,1.8681529961
H,4.4952538982,- 3.4578447993,0.5937753189
H,2.8820065001,-3.4274750958,1.363300163
H,4 .0603100333,-2.135651197,1.7184152407
H,4.3016903315,0.8982396605,-3.1 587146405
H,4.8549417763,-0.4504755877,-2.1228128722
H,4.6233992287,1. 1775317036,-1.4213364106
H,3.2781997526,3.9661448378,0.2785482828
H,0. 1474115711,-1.1454244983,4.0630416675
H,-4.4094951783,-1.458697401,2.8 59105761
H,-3.9583596048,0.1360602289,2.2048434548
H,-2.8083632097,-0. 76144636,3.2108647898
H,-3.1746827733,-3.5662998961,1.9080212527
H,-1. 6027048113,-2.8035519959,2.2519233277

H,-1.9776084746,-3.3486722405,0. 6094908855
H,-4.8931743774,-2.2812799424,0.4424302544
H,-3.6442518501, -2.0793187876,-0.8140084906
H,-4.4715238072,-0.6606897716,-0.156823677 8
C,-4.784310399,2.4895928933,-0.4500751094
H,-5.2914680815,1.53974625 21,-0.2505451639
H,-4.6630318856,3.0210854484,0.4984702669
H,-5.451137 9036,3.0800589102,-1.0937049644

B3PW91/gen solvent=CH_2Cl_2
PCM= -1721.38069749

B3PW91/6-31G* solvent=CH_2Cl_2
PCM= -3304.12297058

titButIs3b

B3LYP/gen

B3LYP/gen solvent=CH_2Cl_2
PCM= -1682.65255947

B3PW91/6-31G* solvent=CH_2Cl_2
PCM= -3264.81382852

Onsager

B3LYP/gen solvent=CH_2Cl_2 a0=6.20
SCF Done: E(RB+HF-LYP) = -1682.63662677 A.U. after 11 cycles

C,3.6516992216,2.4693021845,-0.1855743377
C,2.5399607537,3.0711362626,0.3192296407
C,1.3010189396,3.3121183411,-0.5056817217
O,1.0998551744,2.2313606426,-1.4220184962
Ti,1.0919277763,0.4652800006,-0.9345846495
O,-0.4508066471,0.6558914711,0.4119972119
C,-0.4065393882,0.5022542692,1.8154365512
C,-0.6991508967,1.8220589528,2.5263476682
O,-0.8071379909,2.9215065017,2.0231674261
O,1.6985677906,-0.2703038144,-2.5104923086
C,0.8000344568,-0.4445729717,-3.6132242947
C,-0.5305434411,-0.9412993501,-3.0359299291
O,-0.6732831826,-0.2326914813,-1.7887099473
Ti,-2.1809421806,0.0002313487,-0.550886547

O,-3.0730042683,1.4920617149,-1.0010987067
C,-4.4423075658,1.8125098654,-1.2481709583
O,1.8753251344,-0.8563465616,0.3336700445
C,2.9586156864,-1.8449720289,0.280692247
C,4.1144237892,-1.3967109536,-0.6266574491
O,2.5187803715,0.8402644157,0.3402049148
O,-2.5475519043,-0.4179486325,1.2448637413
C,-1.4935564727,-0.5790027158,2.1563260442
C,-0.8822451994,-1.973125311,2.0176718392
O,-0.1679744483,-2.3125966315,3.1298922145
O,-3.2425260247,-1.2952990736,-1.2214281907
C,-3.7312907113,-2.5709989404,-0.8063537186
O,-0.9894936835,-2.7019081259,1.0497506069
O,-0.792408576,1.6229644341,3.8784472092
C,3.4331089923,-2.0298526358,1.730561864
C,2.2944335726,-3.1214302463,-0.2747810414
H,0.6640471637,0.5212918211,-4.119060118
H,1.2254670622,-1.1603314283,-4.3284131182
H,-0.4996666369,-2.0170593681,-2.824330979
H,-1.3784179836,-0.7310692529,-3.6973378228
H,1.3996490452,4.242795819,-1.0868512254
H,0.4260935558,3.4043043645,0.1462104487
H,2.5165639281,3.3715520639,1.3646191037
H,3.7373022047,2.2419856529,-1.2426058465
H,-1.8412467484,-0.4575058719,3.1879991259
H,0.5873256617,0.1652864317,2.1364234531
H,-4.4877635201,2.6358123977,-1.9705169617
H,-4.9250922885,2.129495564,-0.3154246619
H,-4.9746997758,0.9425322265,-1.6533189738
H,-0.9586181569,2.5018139287,4.270688599
H,-4.7120500549,-2.7445719546,-1.2651504889
H,-3.8197042385,-2.5937186344,0.2856909915
H,-3.0400107229,-3.3607031691,-1.1215284112
H,0.2222602699,-3.190659028,2.9537210191
H,4.2094308759,-2.8009198886,1.7910307757
H,2.5956067598,-2.3213601559,2.3725478681
H,3.8420448928,-1.088379495,2.1101353973
H,3.0051988282,-3.9555554808,-0.2427058528
H,1.9885214822,-2.9618733381,-1.3131635726
H,1.4075575348,-3.3865931674,0.3075701588
H,4.8668260697,-2.192434785,-0.6738482658
H,4.5849932391,-0.4941673069,-0.2295749703
H,3.7537776114,-1.1920602418,-1.6375949707
H,4.5302164512,2.3107154068,0.4298354432

B3LYP/gen solvent=CH2Cl2
PCM= -1682.65197655

B3PW91/gen

SCF Done: E(RB+HF-PW91) = -1682.06734612 A.U. after 31 cycles

Zero-point correction= 0.452299 (Hartree/Particle)
Thermal correction to Energy= 0.488661
Thermal correction to Enthalpy= 0.489605
Thermal correction to Gibbs Free Energy= 0.382168
Sum of electronic and zero-point Energies= -1681.615047
Sum of electronic and thermal Energies= -1681.578685
Sum of electronic and thermal Enthalpies= -1681.577741
Sum of electronic and thermal Free Energies= -1681.685178

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	306.639	129.658	226.121

C,3.8788619662,1.8661010188,-0.7734190301
C,2.881732966 2,2.6910370188,-0.3574250301
C,1.6310639662,2.9075500188,-1.1616940301
O,1.2816279662,1.7114700188,-1.8517920301
Ti,1.0844629662,0.103676018 8,-1.0124140301
O,-0.3280570338,0.7640180188,0.3084089699
C,-0.2354470 338,0.8592980188,1.7077179699
C,-0.3121040338,2.3070680188,2.173251969 9
O,-0.3134380338,3.3030280188,1.4821419699
O,1.4998999662,-1.00434598 12,-2.4169720301
C,0.5327039662,-1.2353519812,-3.4402340301
C,-0.81660 10338,-1.4200939812,-2.7459370301
O,-0.7871990338,-0.4927349812,-1.652 4160301
Ti,-2.1781230338,0.2060780188,-0.4654290301
O,-2.8401040338,1. 7001540188,-1.1886000301
C,-4.1376000338,2.1676180188,-1.5316760301
O, 1.7954499662,-1.0112819812,0.4760269699
C,2.7558009662,-2.1072789812,0 .5596999699
C,3.8897219662,-1.9689999812,-0.4596220301
O,2.6059129662, 0.5354320188,0.1170019699
O,-2.5130950338,0.2260120188,1.3814379699
C, -1.4446420338,0.0340220188,2.2595569699
C,-1.0594480338,-1.4388759812, 2.2952839699

O,-0.3845500338,-1.7570309812,3.4309869699
O,-3.465458033 8,-0.9871169812,-0.8512910301
C,-4.1516900338,-2.0438499812,-0.1977170 301
O,-1.3024210338,-2.2453969812,1.4188479699
O,-0.3454570338,2.36390 90188,3.5367889699
C,3.2979979662,-2.0860919812,1.9924429699
C,1.92975 99662,-3.3719699812,0.2776359699
H,0.5050959662,-0.3636659812,-4.10852 90301
H,0.8150339662,-2.1194649812,-4.0262290301
H,-0.9256130338,-2.43 33099812,-2.3403970301
H,-1.6622160338,-1.2081609812,-3.4095680301
H,1 .7829789662,3.7057080188,-1.9056420301
H,0.8063329662,3.2044700188,-0. 5040390301
H,2.9624179662,3.1983000188,0.6019859699
H,3.8631219662,1.4 231070188,-1.7640860301
H,-1.6985790338,0.3561870188,3.2760049699
H,0. 7168139662,0.4428760188,2.0640259699
H,-4.0586860338,2.8191480188,-2.4 092540301
H,-4.5576860338,2.7425050188,-0.6976630301
H,-4.8027540338,1 .3259300188,-1.7614610301
H,-0.3830880338,3.3113870188,3.7635199699
H, -5.1634070338,-2.1262369812,-0.6121070301
H,-4.2069380338,-1.839447981 2,0.8778839699
H,-3.6211100338,-2.9900949812,-0.3507940301
H,-0.142625 0338,-2.6983929812,3.3525889699
H,3.9953039662,-2.9152199812,2.1569059 699
H,2.4777789662,-2.1669119812,2.7128189699
H,3.8225059662,-1.143217 9812,2.1751559699
H,2.5487319662,-4.2640019812,0.4281369699
H,1.573863 9662,-3.3605049812,-0.7566310301
H,1.0597989662,-3.4267219812,0.937951 9699
H,4.5413109662,-2.8481739812,-0.3972350301
H,4.4845539662,-1.0765 609812,-0.2517110301
H,3.4880099662,-1.8993269812,-1.4737940301
H,4.77 40079662,1.7251990188,-0.1770500301

B3PW91/gen solvent=CH2Cl2
PCM= -1682.08305821

B3PW91/6-31G* solvent=CH2Cl2
PCM= -3264.81527330

Onsager

B3PW91/solvent=CH2Cl2 a0=6.09
SCF Done: E(RB+HF-PW91) = -1682.06772284 A.U. after 7 cycles

C,3.6098725103,2.4528568461,-0.349302439
C,2.5007620907,3.0723475459,0 .1345190737
C,1.2511490878,3.2364613594,-0.6839779857
O,1.0794847806,2 .1148595497,-1.5449335033
Ti,1.0857848378,0.3911702164,-0.9431387873
O ,-0.4407567374,0.6644916233,0.3896540442
C,-0.3944412405,0.5765494194, 1.792124426
C,-0.6782337639,1.922538778,2.4448157309
O,-0.807310769,2. 9952477656,1.8944705485
O,1.6832964142,-0.4405264353,-2.4677010514
C,0 .7831109425,-0.6529923768,-3.553255962
C,-0.5439797886,-1.1135850173,- 2.9502737467
O,-0.671410136,-0.3529427449,-1.741392686
Ti,-2.172484750 6,-0.02773512,-0.52945708
O,-3.0289982714,1.4452111618,-1.0776882731
C ,-4.3839666744,1.7589017755,-1.3658959333
O,1.9028573625,-0.8150851724 ,0.4083973989
C,3.0025950078,-1.7770570833,0.3892779984
C,4.1330363695 ,-1.3510539009,-0.5509268573
O,2.5043191266,0.8595459907,0.2982238815
O,-2.5545313594,-0.3033865198,1.2858625312
C,-1.4922182912,-0.46941250 15,2.1777506121
C,-0.9100495628,-1.8694157949,2.0349042443
O,-0.231341 2364,-2.2488273458,3.1477058035
O,-3.2681353466,-1.3231204729,-1.12571 05425
C,-3.8022938192,-2.5479960829,-0.6464453884
O,-1.016495079,-2.56 99577953,1.046982631
O,-0.7412820017,1.7842788528,3.8009263867
C,3.498 111602,-1.8816162947,1.834848002
C,2.3640930353,-3.0880522315,-0.09504 37912
H,0.6500632427,0.2926132283,-4.0970601282
H,1.1999009829,-1.3994 933219,-4.241642222
H,-0.5205508955,-2.1791164318,-2.6915678121
H,-1.3 942581267,-0.9265226831,-3.6156520392
H,1.3125088304,4.1444515727,-1.3 050283805
H,0.3793368775,3.3293508397,-0.0264707454
H,2.4901069285,3.4 430446214,1.1575983034
H,3.6771596025,2.1560063996,-1.3910947481
H,-1. 8144097996,-0.3256056781,3.2153640706
H,0.5971424355,0.2433898734,2.12 81293617

H,-4.4109847747,2.5488621688,-2.1253579938
H,-4.8848909694,2. 1199360151,-0.4592881665
H,-4.9137519087,0.874529563,-1.7420181985
H,- 0.9094985855,2.6771760006,4.1542788904
H,-4.7764999995,-2.7243164902,- 1.1178700602
H,-3.9205797504,-2.4994283986,0.4422977955
H,-3.128098267 ,-3.376066491,-0.8910771626
H,0.140140251,-3.1307808366,2.9600321318
H ,4.2985387948,-2.6250277016,1.9185256593
H,2.6787438136,-2.1703047582, 2.5007710951
H,3.8828852528,-0.9120335263,2.1653903257
H,3.0942760882, -3.9032034623,-0.0348111797
H,2.0393357862,-2.982656887,-1.1343098396
H,1.491857329,-3.3466109164,0.5116708043
H,4.8962356882,-2.1371188001, -0.5768970557
H,4.5954928597,-0.4259295543,-0.1992387771
H,3.752882591 8,-1.1955418079,-1.5638895586
H,4.5014547947,2.345671037,0.2592394562

B3PW91/gen solvent=CH2Cl2
PCM=-1682.08248988

titButIs3bmethyl

(titButIs3b with trans-methyl-2-buten-1-ol as substrate)

B3LYP/gen

SCF Done: E(RB+HF-LYP) = -1721.94893754 A.U. after 32 cycles

Zero-point correction= 0.478822 (Hartree/Particle)
Thermal correction to Energy= 0.516958
Thermal correction to Enthalpy= 0.517902
Thermal correction to Gibbs Free Energy= 0.406492
Sum of electronic and zero-point Energies= -1721.470116
Sum of electronic and thermal Energies= -1721.431980
Sum of electronic and thermal Enthalpies= -1721.431036
Sum of electronic and thermal Free Energies= -1721.542445

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	324.396	135.651	234.481

C,3.8279399745,1.8845890073,-0.6691849526
C ,2.7565589745,2.6238590073,-0.2652749526

C,1.5514579745,2.8853720073,- 1.1346449526
O,1.1792169745,1.7004990073,-1.8480919526
Ti,0.9423489745 ,0.0744820073,-1.0457039526
O,-0.4925110255,0.7237210073,0.2817530474
C,-0.3983010255,0.8330180073,1.6862830474
C,-0.4884860255,2.2901110073 ,2.1358110474
O,-0.4878330255,3.2794400073,1.4327710474
O,1.3594999745 ,-1.0174879927,-2.4712199526
C,0.3906699745,-1.2382689927,-3.504600952 6
C,-0.9682470255,-1.4186589927,-2.8183899526
O,-0.9449240255,-0.49087 49927,-1.7152009526
Ti,-2.3432610255,0.1589410073,-0.4954209526
O,-3.0 568060255,1.6535710073,-1.1827519526
C,-4.3730540255,2.1084220073,-1.5 004899526
O,1.5965769745,-1.1022999927,0.4258890474
C,2.5195889745,-2. 2358489927,0.5307370474
C,3.6524699745,-2.1678859927,-0.5044959526
O,2 .4524739745,0.4696210073,0.1196800474
O,-2.6655060255,0.1218400073,1.3 583460474
C,-1.5963950255,-0.0081169927,2.2556680474
C,-1.1777060255,- 1.4730069927,2.3773950474
O,-0.4365490255,-1.6832169927,3.5061540474
O ,-3.5889000255,-1.0848239927,-0.8832329526
C,-4.2279820255,-2.17894199 27,-0.2252349526
O,-1.4431460255,-2.3586119927,1.5875370474
O,-0.53310 80255,2.3647740073,3.5037660474
C,3.0727919745,-2.2003779927,1.9645260 474
C,1.6390399745,-3.4784719927,0.2863530474
H,0.3728869745,-0.364190 9927,-4.1699669526
H,0.6701399745,-2.1226079927,-4.0917399526
H,-1.085 5300255,-2.4332509927,-2.4183929526
H,-1.8071030255,-1.1995149927,-3.4 882779526
H,1.7725069745,3.6717010073,-1.8732999526
H,0.7090409745,3.2 167110073,-0.5197419526
H,2.7668319745,3.0758040073,0.7253950474
H,3.8 321579745,1.4936420073,-1.6845899526
H,-1.8721960255,0.3509990073,3.25 35070474
H,0.5604269745,0.4346890073,2.0418070474
H,-4.3166960255,2.77 35160073,-2.3697799526
H,-4.7879820255,2.6651270073,-0.6513649526
H,-5 .0286220255,1.2597050073,-1.7324859526
H,-0.5762890255,3.3163150073,3. 7197050474
H,-5.2396170255,-2.2978679927,-0.6309119526
H,-4.2773370255 ,-1.9825159927,0.8517930474

H,-3.6604820255,-3.1015919927,-0.390967952 6
H,-0.1789050255,-2.6252469927,3.4954770474
H,3.7306789745,-3.0569539 927,2.1510420474
H,2.2522519745,-2.2201449927,2.6892010474
H,3.6409959 745,-1.2783019927,2.1203740474
H,2.2279339745,-4.3896799927,0.44596304 74
H,1.2687409745,-3.4770919927,-0.7432779526
H,0.7771889745,-3.488070 9927,0.9590050474
H,4.2818389745,-3.0608199927,-0.4131209526
H,4.27279 69745,-1.2854039927,-0.3356749526
H,3.2462659745,-2.1230309927,-1.5176 559526
C,5.0755479745,1.6992660073,0.1404890474
H,5.3721959745,0.64572 00073,0.1724750474
H,5.9087879745,2.2561300073,-0.3109759526
H,4.94391 09745,2.0513720073,1.1683660474

B3LYP/gen solvent=CH2Cl2
PCM= -1721.96208805

Onsager

B3LYP/gen solvent=CH2Cl2 a0=6.22
SCF Done: E(RB+HF-LYP) = -1721.94933645 A.U. after 8 cycles

C,3.8452691622,1.8723618269,-0.6498247747
C,2.7735052358,2.6125792701,-0.2482850604
C,1.5777440282,2.8893865627,-1.1262960026
O,1.1925448339,1.7096266122,-1.8416731615
Ti,0.9475345291,0.0791669727,-1.0507115776
O,-0.4984223089,0.7257757443,0.2698510733
C,-0.4056721984,0.8450226056,1.6738840762
C,-0.4979574196,2.304551162,2.1144661175
O,-0.5163638603,3.2893891917,1.4051499699
O,1.3680790907,-1.0037137234,-2.4822058287
C,0.4015695571,-1.2304732682,-3.5150049255
C,-0.9573756518,-1.4164806179,-2.8302036976
O,-0.9412612052,-0.4852929576,-1.7302327182
Ti,-2.3406475724,0.1529447827,-0.5082565542
O,-3.0724065302,1.6385920384,-1.2038148334
C,-4.4075353602,2.0883751893,-1.433752552
O,1.5831207075,-1.1058036463,0.4195111243
C,2.5048839809,-2.2413524588,0.5322316142
C,3.6391367514,-2.18039057,-0.5016714785
O,2.4489290234,0.4633513168,0.1242472099

O,-2.6692725647,0.1215946959,1.34289718
C,-1.6041728458,0.0072900596,2.2483144536
C,-1.1814038987,-1.4543798072,2.3923907721
O,-0.4442367725,-1.6436976482,3.5259547914
O,-3.5786164744,-1.1037253899,-0.8905294654
C,-4.1866606834,-2.2093657011,-0.22241935
O,-1.441124494,-2.3511116004,1.6131584495
O,-0.5233772644,2.3861336345,3.4820345229
C,3.0550973667,-2.2009867308,1.9666382608
C,1.6209278448,-3.4822696217,0.2917346894
H,0.3796266975,-0.3575959564,-4.1820985503
H,0.6854749057,-2.1145179345,-4.1006400578
H,-1.0691258642,-2.4307142118,-2.4276662451
H,-1.796634504,-1.2042447005,-3.5021039297
H,1.8150107052,3.6714667187,-1.8644955723
H,0.7353669278,3.2335660685,-0.5183549393
H,2.7788385175,3.0566681646,0.7459413348
H,3.8552023128,1.4886759023,-1.6681153483
H,-1.8871525519,0.3788895732,3.2394734316
H,0.55256349,0.449082229,2.0329804789
H,-4.401572583,2.7996585681,-2.267898651
H,-4.7920308385,2.592611539,-0.5383451645
H,-5.0621896629,1.2427815516,-1.6810009801
H,-0.5649443733,3.3382894074,3.6954112381
H,-5.1874651969,-2.372493096,-0.6401260865
H,-4.2588693645,-1.9969678232,0.8503323939
H,-3.5837511675,-3.1135900832,-0.3621093895
H,-0.1783868539,-2.5835845946,3.5320939989
H,3.7132966596,-3.0563596688,2.156381177
H,2.233753008,-2.2201056489,2.6904218675
H,3.6224688489,-1.2784132989,2.1217447624
H,2.2067228237,-4.3939636785,0.4588429004
H,1.2544912603,-3.4862252033,-0.7394044741
H,0.7573735544,-3.4851709734,0.9621738567
H,4.2659587777,-3.0743441692,-0.4051760484
H,4.2620254494,-1.2991246014,-0.336246554
H,3.2347070431,-2.1389213785,-1.5157046915
C,5.084412498,1.672436619,0.1686682013
H,5.3762565244,0.6174038159,0.1920249011
H,5.9242117216,2.2295988464,-0.2699632774
H,4.9459130358,2.0144127563,1.1989179447

B3PW91/6-31G* solvent=CH2Cl2
PCM= -3304.12122286

B3PW91/gen

SCF Done: E(RB+HF-PW91) = -1721.36623720 A.U. after 31 cycles

Zero-point correction= 0.480557 (Hartree/Particle)
Thermal correction to Energy= 0.518661
Thermal correction to Enthalpy= 0.519605
Thermal correction to Gibbs Free Energy= 0.407737
Sum of electronic and zero-point Energies= -1720.885681
Sum of electronic and thermal Energies= -1720.847576
Sum of electronic and thermal Enthalpies= -1720.846632
Sum of electronic and thermal Free Energies= -1720.958500

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	325.465	135.172	235.446

C,3.7662940584,1.9109021423,-0.7087829891
C,2.6903950584,2 .6331921423,-0.2915529891
C,1.4649120584,2.8503241423,-1.1351169891
O, 1.1382750584,1.6636661423,-1.8536589891
Ti,0.9349570584,0.0520961423,- 1.0286709891
O,-0.4835689416,0.7113691423,0.2948850109
C,-0.3894839416 ,0.8078691423,1.6936570109
C,-0.4771609416,2.2548211423,2.1601090109
O ,-0.5051919416,3.2510241423,1.4699140109
O,1.3480870584,-1.0447118577, -2.4436839891
C,0.3756120584,-1.2815968577,-3.4599869891
C,-0.96829594 16,-1.4748978577,-2.7579709891
O,-0.9401119416,-0.5452788577,-1.666516 9891
Ti,-2.3302999416,0.1515771423,-0.4780359891
O,-2.9964999416,1.646 9371423,-1.1950729891
C,-4.2915359416,2.1111681423,-1.5503999891
O,1.6 346210584,-1.0760008577,0.4545370109
C,2.5850080584,-2.1787138577,0.54 60460109
C,3.6847090584,-2.0936568577,-0.5149159891
O,2.4373410584,0.4 841791423,0.1194980109
O,-2.6630499416,0.1589521423,1.3692560109
C,-1. 5942089416,-0.0225688577,2.2485900109
C,-1.2037689416,-1.4936778577,2. 3014540109
O,-0.5028059416,-1.7865118577,3.4292220109
O,-3.6164349416, -1.0429778577,-0.8623579891
C,-4.3125409416,-2.0923158577,-0.207322989 1

O,-1.4651099416,-2.3202678577,1.4497660109
O,-0.4885519416,2.3112451 423,3.5244060109
C,3.1715160584,-2.1179478577,1.9601810109
C,1.7344710 584,-3.4410148577,0.3340220109
H,0.3382140584,-0.4103258577,-4.1284189 891
H,0.6592160584,-2.1640768577,-4.0480759891
H,-1.0670429416,-2.4879 958577,-2.3492499891
H,-1.8191399416,-1.2715738577,-3.4176659891
H,1.6 379370584,3.6565551423,-1.8653619891
H,0.6182930584,3.1369201423,-0.50 20559891
H,2.7146270584,3.1044771423,0.6902910109
H,3.7528960584,1.502 4121423,-1.7179449891
H,-1.8511069416,0.3055851423,3.2627090109
H,0.56 64330584,0.3990531423,2.0482510109
H,-4.2092729416,2.7444561423,-2.441 0329891
H,-4.7110399416,2.7046561423,-0.7291719891
H,-4.9593699416,1.2 673771423,-1.7641979891
H,-0.5381889416,3.2581221423,3.7513110109
H,-5 .3251119416,-2.1652618577,-0.6214639891
H,-4.3656219416,-1.8863058577, 0.8680790109
H,-3.7913769416,-3.0439518577,-0.3595369891
H,-0.26354794 16,-2.7295748577,3.3665340109
H,3.8600740584,-2.9526188577,2.133298010 9
H,2.3710820584,-2.1596088577,2.7058460109
H,3.7148100584,-1.17797685 77,2.0951460109
H,2.3495550584,-4.3352708577,0.4882790109
H,1.33926805 84,-3.4576618577,-0.6858779891
H,0.8889120584,-3.4662828577,1.02651401 09
H,4.3406500584,-2.9676198577,-0.4294599891
H,4.2834160584,-1.192091 8577,-0.3724399891
H,3.2511160584,-2.0726368577,-1.5178729891
C,5.0336 120584,1.7732571423,0.0716640109
H,5.3683900584,0.7316981423,0.1067880 109
H,5.8365080584,2.3536661423,-0.4039029891
H,4.9137720584,2.1311941 423,1.0986550109

B3PW91/gen solvent=CH2Cl2
PCM= -1721.37890681

B3PW91/6-31G* solvent=CH2Cl2
PCM= -3304.12351023

Onsager

B3PW91 solvent=CH2Cl2 a0=5.87

SCF Done: E(RB+HF-PW91) = -1721.36673090 A.U. after 8 cycles

C,3.7721822081,1.8606777365,-0.8357304929
C ,2.692170689,2.6035642663,-0.4679628013
C,1.466716234,2.7602900112,-1. 3253552899
O,1.1406506602,1.5271139674,-1.9611220621
Ti,0.9408378425,- 0.0233964025,-1.0229665523
O,-0.4799169525,0.739528574,0.2437126882
C, -0.3878445559,0.9316064886,1.6330621729
C,-0.4689389046,2.4061701753,2 .0030039316
O,-0.5061993013,3.3554684229,1.2496897718
O,1.3529500933,- 1.2133934566,-2.3604849394
C,0.3755632801,-1.5467157228,-3.3429286201
C,-0.9597976583,-1.6988859399,-2.6148434125
O,-0.936350645,-0.68154904 52,-1.6053407324
Ti,-2.3251429317,0.1156234201,-0.4834338156
O,-2.9784 959309,1.5475473874,-1.3377483075
C,-4.2853548049,1.9880029684,-1.6744 330979
O,1.6378468709,-1.0402998488,0.5361780398
C,2.5908729497,-2.132 7819814,0.7107272473
C,3.695510325,-2.1186195378,-0.3482419892
O,2.439 5987158,0.4922481607,0.0903296346
O,-2.6714378378,0.305542707,1.351944 5869
C,-1.6008080558,0.1493965952,2.2365837979
C,-1.2313173767,-1.3239 626746,2.3362795952
O,-0.5687784978,-1.6069889158,3.4853754283
O,-3.63 2366492,-1.0858030089,-0.77886247
C,-4.3250004625,-2.0840674912,-0.045 9029903
O,-1.4803082313,-2.156004808,1.4846790544
O,-0.464945223,2.549 6995778,3.3604196613
C,3.1677601128,-1.9723952658,2.1204488341
C,1.744 7893217,-3.4089942951,0.5809208265
H,0.31966709,-0.734525222,-4.081158 3662
H,0.6662772356,-2.4712710245,-3.8586233651
H,-1.0404150603,-2.675 4841376,-2.1220124117
H,-1.8190909269,-1.5629913788,-3.2812504583
H,1. 639437562,3.5146859397,-2.1093501063
H,0.6196872166,3.089129462,-0.713 6509674
H,2.7136773021,3.139255467,0.4803414864
H,3.7605918782,1.38484 24734,-1.8150887176
H,-1.8467058908,0.5244514358,3.2364824646
H,0.5636 6031,0.5404960002,2.0181123222
H,-4.2346619305,2.5775335664,-2.5974014 005
H,-4.685681938,2.6192568241,-0.8714189935

H,-4.9547047886,1.131493 2185,-1.826367095
H,-0.506066304,3.5090027429,3.5289486224
H,-5.312430 0888,-2.2415804457,-0.4964517807
H,-4.4422325118,-1.7654597532,0.99690 47009
H,-3.764983638,-3.0253313237,-0.0650304953
H,-0.3340249318,-2.55 2754736,3.447844386
H,3.8609025931,-2.7883621486,2.3529246034
H,2.3636 434731,-1.970583348,2.8633935949
H,3.7043684091,-1.0220275282,2.195638 3951
H,2.3608776797,-4.2879116965,0.8028809521
H,1.3573012471,-3.49889 09475,-0.4381187757
H,0.8946131477,-3.3884152126,1.267773332
H,4.35126 62528,-2.9840118899,-0.2001686178
H,4.2936702424,-1.2094622615,-0.2648 682298
H,3.2667260085,-2.1667830247,-1.3523812658
C,5.038200033,1.7781 909436,-0.046043498
H,5.3795052281,0.7430231321,0.0529258725
H,5.83900 97979,2.3328148007,-0.554715018
H,4.9146294619,2.1971312613,0.95702531 57

B3PW91/gen solvent=CH2Cl2
PCM= -1721.37895026

titButRevIs2methyl

B3LYP/gen

B3PW91/6-31G* solvent=CH2Cl2
PCM= -3264.81171686

B3PW91/gen

SCF Done: E(RB+HF-PW91) = -1721.36405313 A.U. after 32 cycles

Zero-point correction= 0.479645 (Hartree/Particle)
Thermal correction to Energy= 0.517367
Thermal correction to Enthalpy= 0.518311
Thermal correction to Gibbs Free Energy= 0.410227
Sum of electronic and zero-point Energies= -1720.884409
Sum of electronic and thermal Energies= -1720.846686
Sum of electronic and thermal Enthalpies= -1720.845742
Sum of electronic and thermal Free Energies= -1720.953826

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	324.653	135.442	227.482

C,3.0667969854,-0.290277073,-2.0782590474
C,2. 5875829854,-1.364791073,-2.7660930474
C,1.9876919854,-2.573955073,-2.0 884070474
O,1.1933559854,-2.181044073,-0.9713990474
Ti,-0.1485320146,- 0.930469073,-1.0801790474
O,0.9804859854,0.034316927,-2.3533960474
O,0 .3603839854,0.179483927,0.5460459526
Ti,-0.7218480146,-0.496268073,2.1 617209526
O,0.0291399854,-1.908480073,2.9833099526
C,0.3413129854,-2.1 23349073,4.3660699526
O,-1.4291060146,-1.989892073,-1.8924270474
C,-2. 5821980146,-2.463594073,-1.1880930474
C,-2.2037150146,-2.548915073,0.2 967889526
O,-1.3732080146,-1.392323073,0.5124669526
O,-0.6335580146,0. 754369927,-2.0159810474
C,-1.3104550146,1.174827927,-3.2429480474
C,-2 .7743820146,1.400495927,-2.8133290474
C,0.7419379854,1.538861927,0.648 8559526
C,1.1919049854,1.658552927,2.1314139526
C,2.6116439854,1.08919 6927,2.2634009526
O,3.4872859854,1.246605927,1.4294059526
C,-0.4692700 146,2.437158927,0.4303339526
O,-1.6247740146,2.120426927,0.6431969526
O,-0.1013730146,3.690489927,0.0387359526
O,-2.2515820146,-0.187558073, 3.0566049526
C,-3.0112620146,0.961286927,3.4381869526
O,0.2280469854,0 .970738927,2.8932959526
C,-1.2123500146,0.115384927,-4.3497430474
C,-0 .6409150146,2.490980927,-3.6711900474
O,2.8185679854,0.431210927,3.431 4919526
H,-3.4128530146,-1.756687073,-1.3285670474
H,-2.8838870146,-3. 440938073,-1.5870670474
H,-1.6170740146,-3.451676073,0.5074449526
H,-3 .0760750146,-2.518642073,0.9603589526
H,1.3702059854,-3.133732073,-2.8 065000474
H,2.6558549854,-1.376779073,-3.8528260474
H,3.0474699854,-0. 314909073,-0.9908760474
H,1.2439129854,2.714482927,2.4423299526
H,1.54 07319854,1.791186927,-0.0506330474

H,-3.7266790146,0.669967927,4.21568 49526
H,-3.5523360146,1.361677927,2.5740219526
H,-2.3390200146,1.73528 1927,3.8285649526
H,0.7681199854,-3.126753073,4.4731669526
H,-0.566924 0146,-2.049075073,4.9772789526
H,1.0690289854,-1.376642073,4.702921952 6
H,3.7475539854,0.128535927,3.4016149526
H,-0.9246510146,4.214004927, -0.0161160474
H,-1.1401400146,2.912625927,-4.5512510474
H,0.4099819854 ,2.309096927,-3.9142030474
H,-0.6828690146,3.221904927,-2.8571230474
H ,-3.3487670146,1.824138927,-3.6456290474
H,-2.8234040146,2.086329927,- 1.9624110474
H,-3.2343800146,0.452581927,-2.5185100474
H,-1.7613040146 ,0.458311927,-5.2345530474
H,-1.6353300146,-0.833699073,-4.0124720474
H,-0.1671110146,-0.046691073,-4.6249710474
C,3.7196719854,0.898567927, -2.7121570474
H,4.7768679854,0.955898927,-2.4192520474
H,3.6620169854, 0.860535927,-3.8045860474
H,3.2419719854,1.824009927,-2.3714470474
H,2 .7741399854,-3.255504073,-1.7281150474

titButIs2b

B3LYP/gen
SCF Done: E(RB+HF-LYP) = -1682.63009029 A.U. after 11 cycles

titButIs3

B3LYP/gen

SCF Done: E(RB+HF-LYP) = -1682.63472965 A.U. after 1 cycles

Zero-point correction= 0.450880 (Hartree/Particle)
Thermal correction to Energy= 0.487235
Thermal correction to Enthalpy= 0.488180
Thermal correction to Gibbs Free Energy= 0.380579
Sum of electronic and zero-point Energies= -1682.183849
Sum of electronic and thermal Energies= -1682.147494

Sum of electronic and thermal Enthalpies= -1682.146550
Sum of electronic and thermal Free Energies= -1682.254151

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	305.745	129.961	226.465

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-1.106969	-0.628355	-0.777052
2	8	0	-1.739660	-0.182311	-2.449270
3	8	0	0.642904	-0.143501	-1.785725
4	6	0	-0.868939	-0.278925	-3.584135
5	6	0	0.491499	0.282665	-3.154789
6	8	0	-1.875226	0.897865	0.240237
7	8	0	-1.145004	-2.456130	-0.931284
8	8	0	-2.562668	-0.754441	0.521008
9	6	0	-1.439690	-3.365569	0.130476
10	6	0	-2.687511	-2.935756	0.860760
11	6	0	-3.757236	-2.391198	0.219301
12	22	0	2.174752	-0.091066	-0.553907
13	8	0	2.556955	0.687160	1.111902
14	8	0	0.465057	-0.571207	0.551565
15	6	0	1.518265	0.997173	2.004151
16	6	0	0.465419	-0.160374	1.906376
17	8	0	3.178502	1.070004	-1.497915
18	8	0	3.098717	-1.622801	-0.708313
19	6	0	0.878238	2.330452	1.625945
20	8	0	0.960259	2.875805	0.541450
21	6	0	0.873986	-1.260449	2.886380
22	6	0	4.453593	-1.967658	-1.003054
23	8	0	0.961424	-2.504082	2.341892
24	6	0	-2.935479	1.886367	-0.000094
25	6	0	3.666355	2.404177	-1.348485
26	8	0	0.176165	2.858703	2.671133
27	8	0	1.090650	-1.044649	4.065080
28	6	0	-3.384201	2.360050	1.391421
29	6	0	-2.254350	3.014545	-0.801001
30	6	0	-4.114868	1.300124	-0.791059
31	1	0	-0.775523	-1.334789	-3.873152
32	1	0	-1.294478	0.281670	-4.426142

33	1	0	0.504326	1.378750	-3.184063
34	1	0	1.313671	-0.100330	-3.769410
35	1	0	-1.573238	-4.369514	-0.303181
36	1	0	-0.591908	-3.403577	0.821984
37	1	0	-2.709912	-3.051110	1.942273
38	1	0	-4.646290	-2.096170	0.765271
39	1	0	-3.800496	-2.344160	-0.863438
40	1	0	1.886095	1.069359	3.034088
41	1	0	-0.531468	0.188299	2.203895
42	1	0	4.466671	-2.924240	-1.538039
43	1	0	5.021782	-2.072079	-0.070489
44	1	0	4.921621	-1.195417	-1.626246
45	1	0	1.245432	-3.086148	3.074270
46	1	0	4.634023	2.489112	-1.856775
47	1	0	3.780452	2.636548	-0.283700
48	1	0	2.960408	3.114779	-1.792822
49	1	0	-0.221565	3.689274	2.345793
50	1	0	-4.139324	3.150289	1.310050
51	1	0	-2.529454	2.743953	1.957181
52	1	0	-3.811346	1.521051	1.949515
53	1	0	-2.952471	3.849854	-0.932069
54	1	0	-1.960364	2.646797	-1.788597
55	1	0	-1.358806	3.375541	-0.288383
56	1	0	-4.841015	2.095235	-0.997169
57	1	0	-4.611314	0.514876	-0.216289
58	1	0	-3.771806	0.882353	-1.740511

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titButIs4

B3LYP/gen

SCF Done: E(RB+HF-LYP) = -1682.63492063 A.U. after 1 cycles

Zero-point correction= 0.450543 (Hartree/Particle)
Thermal correction to Energy= 0.487034
Thermal correction to Enthalpy= 0.487978
Thermal correction to Gibbs Free Energy= 0.379972
Sum of electronic and zero-point Energies= -1682.184378
Sum of electronic and thermal Energies= -1682.147887
Sum of electronic and thermal Enthalpies= -1682.146943
Sum of electronic and thermal Free Energies= -1682.254948

	E (Thermal)	CV	S

	KCAL/MOL	CAL/MOL-KELVIN	CAL/MOL-KELVIN
TOTAL	305.618	129.992	227.317

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	22	0	-1.083739	-0.833242	-0.401056
2	8	0	-1.729452	-0.977889	-2.136805
3	8	0	0.672670	-1.078912	-1.482676
4	6	0	-0.947196	-1.756311	-3.051600
5	6	0	0.504711	-1.291025	-2.902004
6	8	0	-1.879177	0.959835	-0.164904
7	8	0	-1.343065	-2.591088	0.075777
8	8	0	-2.457653	-0.357407	0.922073
9	6	0	-2.995374	1.733087	-0.721980
10	6	0	-2.623794	-3.111220	0.425384
11	6	0	-3.258069	-2.274684	1.510759
12	6	0	-2.533492	-1.702936	2.510373
13	22	0	2.213794	-0.386517	-0.466669
14	8	0	2.617908	1.068041	0.651155
15	8	0	0.502150	-0.250461	0.723329
16	6	0	1.606792	1.751590	1.346497
17	6	0	0.551750	0.686186	1.784838
18	8	0	3.164423	0.221333	-1.869722
19	8	0	3.171812	-1.792324	0.105839
20	6	0	0.947907	2.788551	0.439042
21	8	0	0.989424	2.799891	-0.776375
22	8	0	1.368199	0.718945	4.064078
23	6	0	0.985096	0.063950	3.112483
24	6	0	4.555352	-2.149271	0.059793
25	6	0	3.622345	1.479241	-2.370143
26	8	0	0.270527	3.724002	1.168229
27	8	0	0.862178	-1.290334	3.148955
28	6	0	-3.403488	2.729426	0.374679
29	6	0	-2.398834	2.444302	-1.953051
30	6	0	-4.174990	0.835853	-1.124049
31	1	0	-1.033038	-2.821109	-2.792207
32	1	0	-1.317670	-1.607528	-4.074094
33	1	0	0.679724	-0.342605	-3.422785
34	1	0	1.222975	-2.036452	-3.261757
35	1	0	-3.276318	-3.124076	-0.460126
36	1	0	-2.497037	-4.153098	0.758628

37	1	0	-4.336785	-2.137765	1.476742
38	1	0	-3.019618	-1.110499	3.278028
39	1	0	-1.469608	-1.885456	2.613956
40	1	0	2.005883	2.259038	2.232015
41	1	0	-0.435851	1.140182	1.938590
42	1	0	4.637986	-3.241732	0.084314
43	1	0	5.077971	-1.730378	0.928535
44	1	0	5.020191	-1.769058	-0.858295
45	1	0	2.894661	1.888903	-3.079621
46	1	0	4.581365	1.330969	-2.880042
47	1	0	3.743382	2.183454	-1.539676
48	1	0	-0.149277	4.325811	0.523581
49	1	0	1.168874	-1.557420	4.037907
50	1	0	-4.195501	3.397602	0.017683
51	1	0	-2.543309	3.333837	0.680455
52	1	0	-3.768444	2.187258	1.252412
53	1	0	-3.136466	3.135816	-2.377373
54	1	0	-2.126719	1.706825	-2.712966
55	1	0	-1.500530	3.005754	-1.680447
56	1	0	-4.965290	1.452896	-1.567325
57	1	0	-4.579409	0.323210	-0.247872
58	1	0	-3.855205	0.090801	-1.856074

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titButIs4b

B3LYP/gen

SCF Done: E(RB+HF-LYP) = -1682.63506859 A.U. after 19 cycles
Zero-point correction= 0.450680 (Hartree/Particle)
Thermal correction to Energy= 0.487061
Thermal correction to Enthalpy= 0.488005
Thermal correction to Gibbs Free Energy= 0.380703
Sum of electronic and zero-point Energies= -1682.184389
Sum of electronic and thermal Energies= -1682.148008
Sum of electronic and thermal Enthalpies= -1682.147063
Sum of electronic and thermal Free Energies= -1682.254366

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	305.635	129.969	225.836

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.398223	-0.786363	2.964059
2	6	0	-3.160928	-1.663566	2.257817
3	6	0	-2.566443	-2.815737	1.484597
4	8	0	-1.318324	-2.441753	0.905116
5	22	0	-1.078342	-0.933935	-0.115358
6	8	0	0.487258	0.033864	0.737617
7	6	0	0.518944	1.283195	1.397717
8	6	0	0.865559	1.097935	2.873884
9	8	0	1.144542	2.302425	3.463407
10	8	0	-1.701647	-1.635191	-1.720137
11	6	0	-0.917214	-2.689124	-2.294850
12	6	0	0.541799	-2.218847	-2.284824
13	8	0	0.691528	-1.523402	-1.027376
14	22	0	2.220045	-0.526831	-0.282074
15	8	0	3.139149	-1.650958	0.766757
16	6	0	4.502952	-2.056055	0.895171
17	8	0	-1.908897	0.823790	-0.481016
18	6	0	-3.042869	1.337495	-1.256561
19	6	0	-4.207682	0.337767	-1.306543
20	8	0	-2.433045	-0.053840	1.000670
21	6	0	-3.461957	2.646641	-0.569047
22	6	0	-2.466355	1.585682	-2.664838
23	8	0	2.626792	1.227984	0.268440
24	6	0	1.603589	2.114893	0.634631
25	6	0	0.964688	2.733908	-0.609483
26	8	0	0.281944	3.875900	-0.299001
27	8	0	3.212157	-0.454192	-1.783161
28	6	0	3.703887	0.544647	-2.678108
29	8	0	1.018690	2.281498	-1.736775
30	8	0	0.856392	0.053616	3.490815
31	1	0	-1.025382	-3.598493	-1.687001
32	1	0	-1.268888	-2.896995	-3.313736
33	1	0	0.746869	-1.518027	-3.102263
34	1	0	1.249546	-3.053745	-2.342461
35	1	0	-3.264616	-3.132292	0.695807
36	1	0	-2.395968	-3.681625	2.143024
37	1	0	-4.243148	-1.552182	2.242689
38	1	0	-2.860068	0.027353	3.513280
39	1	0	-1.325381	-0.913408	3.065268
40	1	0	1.985852	2.921755	1.269053
41	1	0	-0.462054	1.773084	1.342809

42	1	0	4.531293	-3.065017	1.321580
43	1	0	5.033762	-1.369023	1.565496
44	1	0	4.997531	-2.059909	-0.084287
45	1	0	2.983576	0.713516	-3.486262
46	1	0	4.654302	0.203357	-3.104812
47	1	0	3.853603	1.484409	-2.134508
48	1	0	-0.132076	4.183707	-1.128491
49	1	0	1.327823	2.105960	4.402524
50	1	0	-4.273101	3.133686	-1.122192
51	1	0	-2.611969	3.334577	-0.510319
52	1	0	-3.804330	2.438187	0.449289
53	1	0	-3.223987	2.058845	-3.300803
54	1	0	-2.165283	0.635898	-3.114498
55	1	0	-1.588046	2.236259	-2.615197
56	1	0	-5.019180	0.755062	-1.913955
57	1	0	-4.586269	0.144795	-0.299688
58	1	0	-3.882689	-0.605636	-1.751392

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titButRevIs3

freq not done

TitButRevIs1withmethylbutenol (structure for KIE's for geraniol)

B3LYP/gen

SCF Done: E(RB+HF-LYP) = -1761.25883156 A.U. after 32 cycles

Zero-point correction= 0.506844 (Hartree/Particle)
Thermal correction to Energy= 0.546530
Thermal correction to Enthalpy= 0.547474
Thermal correction to Gibbs Free Energy= 0.433032
Sum of electronic and zero-point Energies= -1760.751988
Sum of electronic and thermal Energies= -1760.712302
Sum of electronic and thermal Enthalpies= -1760.711358
Sum of electronic and thermal Free Energies= -1760.825799

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	342.953	141.113	240.863

C,2.788395307,-1.3578843 078,-3.0311078188
C,2.9805383617,-0.9150098506,-1.7484952438
C,2.62114 92329,-1.6906399649,-0.5008173684
O,1.238188695,-2.0673583226,-0.50834 28149
Ti,-0.1091819311,-0.8980568399,-0.9286907737
O,1.1282975845,-0.0 397137351,-2.1611753398
O,0.2962923315,0.2760541765,0.7162001348
Ti,-1 .0422580876,-0.2278548379,2.1854767999
O,-1.5156842896,2.3864920858,0. 5602716119
C,-0.3213122041,2.5880144013,0.4387109464
O,0.1916773985,3. 7786248832,0.0162418364
O,-1.2669229597,-2.0527539578,-1.7745501444
C, -2.5563191212,-2.3743403832,-1.2380224921
C,-2.4501302013,-2.254006258 7,0.2871397709
O,-1.6018715645,-1.108463052,0.4928629653
O,-0.45863835 09,0.7995172523,-1.9029301674
C,-1.0566589852,1.2346989134,-3.16373748 57
C,-2.5058145877,1.6080376654,-2.7875982794
C,0.7746149957,1.6033201 581,0.8255806512
C,1.0428596033,1.7521983509,2.3513558002
C,2.38122641 32,1.0852448881,2.6948610561
O,3.3665051499,1.1204916456,1.9766244106
O,-2.6276925161,0.2287936201,2.9059031654
C,-3.3168296339,1.4448171483 ,3.2006882185
O,-0.0605196229,1.1724969427,3.0042460002
O,-0.517713008 7,-1.6876318817,3.0984307245
C,-0.4203911585,-1.9188269876,4.509651747 1
C,-1.0326831981,0.1298674327,-4.2292327904
C,-0.2586822464,2.4668685 634,-3.6203591381
O,2.3817871063,0.4862020955,3.9126706748
H,-3.300637 7268,-1.6654030407,-1.628416564
H,-2.8417321968,-3.3875912619,-1.54853 73664
H,-1.9695669336,-3.1388373694,0.7233169636
H,-3.4232851597,-2.09 66130378,0.7676841256
H,3.2195657131,-2.6106164447,-0.4187642814
H,2.8 277780105,-1.073603161,0.3816960775
H,3.5251276897,0.0140450797,-1.602 4943316
H,1.1392082333,2.8144817805,2.6297874744
H,1.6720262374,1.7645 53916,0.225441564
H,-4.1423394754,1.2268895618,3.888172806
H,-3.714452 7869,1.8875130672,2.2809172437
H,-2.6260838981,2.1562998198,3.67003315 6
H,-0.0853896424,-2.9496656647,4.6705843013
H,-1.397886934,-1.7771595 173,4.9878701687

H,0.303775578,-1.2251647577,4.951865385
H,3.280707121 1,0.1186079464,4.0235603065
H,-0.5728244926,4.3664280889,-0.1416046644
H,-0.6874849965,2.8915051066,-4.5353959472
H,0.7799367145,2.183563702 6,-3.8129796519
H,-0.2629829241,3.2335842159,-2.8391750582
H,-3.015629 542,2.0470568301,-3.6534797645
H,-2.5173531564,2.3262254196,-1.9632903 582
H,-3.0581128967,0.7173692555,-2.4717868939
H,-1.5381032767,0.48224 6244,-5.135915361
H,-1.5358017105,-0.769831158,-3.8667301929
H,-0.0019 261209,-0.1300055712,-4.4809626567
C,2.1911173525,-2.6973611603,-3.370 5488308
H,2.89314472,-3.268104689,-3.9950091077
H,1.935158684,-3.28083 7558,-2.486003448
H,1.2729216091,-2.5678601555,-3.9569269694
C,3.24711 73727,-0.5231697483,-4.1969880325
H,3.6045446396,0.460082036,-3.880346 5388
H,4.0591476329,-1.033560402,-4.7348815529
H,2.4314002568,-0.37852 85513,-4.9156301617

TitButRevIs1withmethylbutenolBP (structure for KIE's for geraniol)

B3PW91/gen

SCF Done: E(RB+HF-PW91) = -1760.66346368 A.U. after 33 cycles

Zero-point correction= 0.508868 (Hartree/Particle)
Thermal correction to Energy= 0.548354
Thermal correction to Enthalpy= 0.549299
Thermal correction to Gibbs Free Energy= 0.435287
Sum of electronic and zero-point Energies= -1760.154596
Sum of electronic and thermal Energies= -1760.115109
Sum of electronic and thermal Enthalpies= -1760.114165
Sum of electronic and thermal Free Energies= -1760.228177

	E (Thermal)	CV	S
	KCAL/MOL	CAL/MOL-KELVIN	CAL/MOL-KELVIN
TOTAL	344.098	140.546	239.958

C,2.7781048004,-1.3776 281001,-3.0157823509
C,2.9620465043,-0.9275052696,-1.7361664879
C,2.58 91667794,-1.6929033002,-0.4916443072
O,1.2161318901,-2.0775565012,-0.5 182783103

Ti,-0.1092753355,-0.8917699087,-0.9274637821
O,1.1296891909, -0.0392261624,-2.1497900566
O,0.3516095483,0.2541746244,0.7133784893
T i,-1.0258326011,-0.1975997258,2.1628570265
O,-1.5825001237,2.166192266 6,0.6707064949
C,-0.4239321843,2.4934827795,0.4821264571
O,-0.06008325 96,3.7280715298,0.0612995859
O,-1.2821713801,-2.0267535198,-1.76586906 54
C,-2.5659007519,-2.3339852877,-1.2279909114
C,-2.456142766,-2.19393 89531,0.2904818239
O,-1.6064655738,-1.0546278882,0.4750016504
O,-0.416 5230631,0.8138551577,-1.8964214362
C,-1.0019681518,1.2352165297,-3.160 7236774
C,-2.44380731,1.6293786334,-2.8011647259
C,0.7581158431,1.6000 373199,0.8050970535
C,1.0537102693,1.7708630428,2.3195232391
C,2.41493 99967,1.1517834866,2.6366676143
O,3.3908825795,1.2527160162,1.91384715 96
O,-2.5842469449,0.2290367627,2.9486276794
C,-3.2698502905,1.4182457 202,3.3091381547
O,-0.0168787572,1.1725753183,2.9939401601
O,-0.519287 9865,-1.6795233489,3.0385998755
C,-0.4861995505,-1.9520472967,4.437079 7501
C,-0.9878695913,0.1185797616,-4.2059122893
C,-0.1915623334,2.4473 247634,-3.631688957
O,2.4492203389,0.5234126676,3.8325016651
H,-3.3081 142259,-1.6271498351,-1.6259824383
H,-2.8576503293,-3.3496014686,-1.52 48572938
H,-1.9769216438,-3.0741581454,0.7375481043
H,-3.4265039994,-2 .0263297362,0.7731601688
H,3.1951296735,-2.6063502534,-0.3909929195
H, 2.7748916856,-1.0653524283,0.388199991
H,3.514608635,-0.0021567639,-1. 5919019131
H,1.1287389942,2.8397034517,2.5822805936
H,1.6201891446,1.8 196469811,0.1718297204
H,-3.9763402278,1.1927761784,4.1166226134
H,-3. 8198736458,1.8150383937,2.4484497252
H,-2.5516926912,2.17287347,3.6528 037791
H,-0.1863847676,-2.9958186367,4.5829238542
H,-1.4773545841,-1.7 945000707,4.8808849187
H,0.2378367074,-1.2933286272,4.9300635266
H,3.3 630937631,0.1947947793,3.9269340642
H,-0.8853929988,4.2380127627,-0.04 090112
H,-0.6061530599,2.8553203136,-4.5603973656

H,0.8463323935,2.150 5135791,-3.8057956142
H,-0.1995950583,3.229723774,-2.8665741005
H,-2.9 454612748,2.0502892456,-3.6802767191
H,-2.4538376131,2.3704460361,-1.9 974803497
H,-3.0051970976,0.7532483223,-2.4633232576
H,-1.4836692201,0 .4648351365,-5.1199176124
H,-1.5045667095,-0.7690609613,-3.8322141716
H,0.0407514765,-0.1585509221,-4.4467893097
C,2.1742668902,-2.710232306 8,-3.3494000123
H,2.8881720741,-3.3018156798,-3.9400621967
H,1.8823668 862,-3.2724558526,-2.4619094117
H,1.2780892203,-2.5801137973,-3.968404 4266
C,3.2576361474,-0.5586975436,-4.1789269634
H,3.6223895804,0.42277 73831,-3.8655470615
H,4.0709360362,-1.0823433653,-4.7015362817
H,2.454 0200044,-0.4114005645,-4.9101204675

titButRevIs3methylcalcfc
(titButRevIs3 with trans-2-buten-1-ol as substrate)

B3LYP/gen
SCF Done: E(RB+HF-LYP) = -1721.94604294 A.U. after 6 cycles

Nitrogen Isotope Effects on Flavoprotein Catalyzed *N*-Demethylation Reactions: Sarcosine Oxidation by *N*-Methyltryptophan Oxidase-Appendix Material

Theoretical Structures

All structures were fully optimized in B3LYP/6-31+G** calculations using default procedures and parameters in Gaussian 03. (*1*) Optimizations were carrier out either in the gas phase or employing an Onsager (dipole) solvent model using an a0 radius derived from a volume calculation on the gas phase structure. Vibrational frequency analyses were carried out on all stationary points.

1. Gaussian 03, Revision B.04, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.

Gas-Phase Structures

dimethylamine

E(RB+HF-LYP) = -135.181274470

Zero-point correction=	0.092339 (Hartree/Particle)
Thermal correction to Energy=	0.096742
Thermal correction to Enthalpy=	0.097687
Thermal correction to Gibbs Free Energy=	0.066876
Sum of electronic and zero-point Energies=	-135.088935
Sum of electronic and thermal Energies=	-135.084532
Sum of electronic and thermal Enthalpies=	-135.083588
Sum of electronic and thermal Free Energies=	-135.114399

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	60.707	13.913	64.846

N,0,-0.2524541214,0.4359469667,0.2875782358
H,0,-0.3063004494,0.5280079417,1.2976324969
C,0,1.1416377674,0.4600970976,-0.1405059379
C,0,-0.967593225,-0.7605619182,-0.1416933076
H,0,-1.0336581663,-0.769374814,-1.235788817
H,0,-0.4898371035,-1.7078220855,0.1720790802
H,0,-1.9881163149,-0.7412888921,0.2527008463

H,0,1.1831164846,0.5135220972,-1.2345408939
H,0,1.6330367406,1.3543531135,0.2547393486
H,0,1.7246704008,-0.4262372061,0.1733257616

Alloxazine Model for FAD (6)

fadNeutralSMfreq
E(RB+HF-LYP) = -754.210014565

Zero-point correction=	0.156272 (Hartree/Particle)
Thermal correction to Energy=	0.167457
Thermal correction to Enthalpy=	0.168401
Thermal correction to Gibbs Free Energy=	0.118663
Sum of electronic and zero-point Energies=	-754.053742
Sum of electronic and thermal Energies=	-754.042558
Sum of electronic and thermal Enthalpies=	-754.041614
Sum of electronic and thermal Free Energies=	-754.091352

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	105.081	45.067	104.683

1	6	0	-2.866381	1.342617	-0.000638
2	6	0	-1.648856	0.630120	-0.000332
3	6	0	-1.677961	-0.791073	0.000270
4	6	0	-2.902371	-1.476866	0.000714
5	6	0	-4.084341	-0.747569	0.000364
6	6	0	-4.072453	0.661823	-0.000384
7	7	0	-0.465250	-1.444931	0.000324
8	6	0	0.744775	-0.802116	-0.000153
9	6	0	0.657152	0.661015	-0.000255
10	7	0	-0.460558	1.322410	-0.000532
11	6	0	1.962098	1.401472	0.000189
12	7	0	3.050024	0.548707	-0.000998
13	6	0	3.054775	-0.870428	-0.000363
14	7	0	1.831716	-1.522104	-0.000342
15	8	0	2.068136	2.614994	0.001536
16	8	0	4.124846	-1.452771	0.000155
17	1	0	-2.917730	-2.563112	0.001241
18	1	0	-0.425602	-2.459443	0.000229
19	1	0	3.966918	0.983228	0.000480
20	1	0	-5.032340	-1.276667	0.000743
21	1	0	-5.008938	1.209353	-0.000628
22	1	0	-2.816315	2.426293	-0.001234

Hydride Transfer Transition Structure (7)

fadhydrideneutral
E(RB+HF-LYP) = -889.346959236

Zero-point correction=	0.246238 (Hartree/Particle)
Thermal correction to Energy=	0.262579
Thermal correction to Enthalpy=	0.263523
Thermal correction to Gibbs Free Energy=	0.202248
Sum of electronic and zero-point Energies=	-889.100721
Sum of electronic and thermal Energies=	-889.084380
Sum of electronic and thermal Enthalpies=	-889.083436
Sum of electronic and thermal Free Energies=	-889.144711

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	164.771	63.519	128.965

C,0,-2.4625969713,-0.4190239012,-2.0745807466
C,0,-1.4309887502,0.0383763432,-1.2447982434
C,0,-0.6624805231,1.1518899706,-1.6472208776
C,0,-0.9382083544,1.7886311584,-2.8657232597
C,0,-1.9600451716,1.3135151835,-3.6836064021
C,0,-2.723878881,0.2052407548,-3.2916680746
N,0,0.3590203416,1.5875570994,-0.8107162169
C,0,0.5598431457,1.0741321798,0.4512378192
C,0,-0.2435797422,-0.0506122463,0.8182965156
N,0,-1.1869359995,-0.6058185373,-0.0097083675
C,0,-0.068341483,-0.5903530644,2.1560190854
N,0,0.8711691027,0.1014627812,2.9059241304
C,0,1.6544907789,1.2072025563,2.4878042709
N,0,1.4518707188,1.6779702067,1.2083665606
O,0,-0.6303028937,-1.6064387238,2.5851032326
O,0,2.4685291472,1.6796687194,3.2712581197
C,0,0.1238943844,-2.8292046069,-0.3539119313
N,0,1.2260932655,-2.2985137879,0.2265074911
C,0,2.374369522,-1.7955946606,-0.5157651006
H,0,2.9280509852,-1.0860900373,0.1017619957
H,0,1.3418734437,-2.4580500595,1.220065366
H,0,0.1442296801,-2.9460309397,-1.4346259687
H,0,-0.439982752,-3.5494898668,0.2317181384
H,0,-0.9537941093,-1.7066751584,-0.1641689549
H,0,-0.3435648484,2.6469389454,-3.1669016721

H,0,0.8741448087,2.4325341026,-1.0262830627
H,0,1.0341760975,-0.2232213965,3.8521677912
H,0,-2.1645152742,1.8108944147,-4.6265163602
H,0,-3.5255042856,-0.158253064,-3.9262467681
H,0,-3.0584353664,-1.2637164958,-1.7412719379
H,0,3.0442577495,-2.612258579,-0.8161873562
H,0,2.029864114,-1.2762241684,-1.4135155452

FADH⁻ Model (6-5H⁻)

FADHanion
E(RB+HF-LYP) = -754.899901275

Zero-point correction=	0.165890 (Hartree/Particle)
Thermal correction to Energy=	0.177628
Thermal correction to Enthalpy=	0.178572
Thermal correction to Gibbs Free Energy=	0.127942
Sum of electronic and zero-point Energies=	-754.734011
Sum of electronic and thermal Energies=	-754.722273
Sum of electronic and thermal Enthalpies=	-754.721329
Sum of electronic and thermal Free Energies=	-754.771959

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	111.463	47.718	106.560

C,0,-2.1006447046,-0.9953941469,-2.1644954979
C,0,-1.0206606083,-0.6070391693,-1.3618750731
C,0,-0.2670128756,0.5415758866,-1.7390151716
C,0,-0.6187013036,1.2497688415,-2.8867004461
C,0,-1.6916415649,0.8356798926,-3.6956436014
C,0,-2.4292887729,-0.287956603,-3.330825591
N,0,0.8409969115,0.8981386755,-0.9510779025
C,0,0.9143961063,0.4811506483,0.3910276018
C,0,0.164022379,-0.6288042863,0.7418472914
N,0,-0.6093514097,-1.3161708175,-0.2425667582
C,0,0.1876761705,-1.0788082523,2.0832576439
N,0,1.0367678951,-0.314581569,2.8900630365
C,0,1.801851213,0.806086214,2.4979480824
N,0,1.7051956536,1.2010873768,1.1934936078
O,0,-0.4607960118,-2.0485121017,2.5453340665
O,0,2.5062049596,1.3661660692,3.3550209174
H,0,-0.0384664019,2.1291905031,-3.1584240573
H,0,1.2581438869,1.8068232722,-1.1069500193
H,0,1.108205261,-0.5855863394,3.8618445372
H,0,-1.9393069359,1.3963447368,-4.5925601216
H,0,-3.2654924927,-0.620389003,-3.940489834
H,0,-2.679907417,-1.8688160224,-1.8735193501
H,0,-1.2616870697,-1.9756686991,0.1647236586

FADH$^+$ Model (6-1-H$^+$)

fadhydrideSMfreq
E(RB+HF-LYP) = -754.572674508

Zero-point correction=	0.169109 (Hartree/Particle)
Thermal correction to Energy=	0.180545
Thermal correction to Enthalpy=	0.181489
Thermal correction to Gibbs Free Energy=	0.131382
Sum of electronic and zero-point Energies=	-754.403566
Sum of electronic and thermal Energies=	-754.392130
Sum of electronic and thermal Enthalpies=	-754.391186
Sum of electronic and thermal Free Energies=	-754.441293

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	113.293	46.420	105.459

1	7	0	-1.867152	-1.418983	-0.000646
2	6	0	-0.682086	-0.775296	-0.000095
3	6	0	-0.629631	0.658769	-0.000050
4	6	0	-1.921787	1.427867	0.000213
5	7	0	-3.064909	0.612670	0.001123
6	6	0	-3.137660	-0.764652	-0.000009
7	7	0	0.503612	1.313344	-0.000266
8	6	0	1.679082	0.635549	-0.000230
9	6	0	1.711967	-0.793366	0.000124
10	7	0	0.483512	-1.441016	0.000172
11	6	0	2.922686	-1.491966	0.000479
12	6	0	4.102893	-0.759118	0.000288
13	6	0	4.096542	0.655552	-0.000186
14	6	0	2.903093	1.349320	-0.000418
15	8	0	-1.990566	2.631217	-0.000045
16	8	0	-4.150771	-1.416634	-0.000459
17	1	0	2.941717	-2.578024	0.000877
18	1	0	0.484002	-2.458547	-0.000010
19	1	0	-3.960076	1.096084	0.000963
20	1	0	5.050893	-1.287453	0.000531
21	1	0	5.038762	1.192627	-0.000334
22	1	0	2.859980	2.433083	-0.000683
23	1	0	-1.940613	-2.432486	-0.000688

Hydride Transfer Transition Structure (8)

fadhydride.log
E(RB+HF-LYP) = -889.737479702

Zero-point correction=	0.258069 (Hartree/Particle)
Thermal correction to Energy=	0.274934
Thermal correction to Enthalpy=	0.275878
Thermal correction to Gibbs Free Energy=	0.212894
Sum of electronic and zero-point Energies=	-889.479411
Sum of electronic and thermal Energies=	-889.462546
Sum of electronic and thermal Enthalpies=	-889.461602
Sum of electronic and thermal Free Energies=	-889.524586

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	172.523	65.024	132.561

C,0,1.5806451346,1.1960833902,2.5566024586
C,0,0.6784471288,0.5996209165,1.6597453812
C,0,-0.1019574571,-0.4913302858,2.1026947857
C,0,0.0212981159,-0.9829603924,3.405632853
C,0,0.9327508216,-0.3868499193,4.2714569958
C,0,1.7114549167,0.7036207776,3.8484548295
N,0,-1.035249559,-1.0358210088,1.2070393825
C,0,-1.2250226357,-0.4930461436,-0.0148146124
C,0,-0.4144496496,0.5710536062,-0.4367065169
N,0,0.5675345226,1.1074898358,0.3546654992
C,0,-0.6425482332,1.1646353562,-1.761437706
N,0,-1.729255343,0.6216413502,-2.4654196507
C,0,-2.5666670751,-0.4027483281,-2.067916431
N,0,-2.2403850023,-0.9448623113,-0.8042131916
O,0,-3.4967465302,-0.8317463523,-2.7112511741
O,0,0.0589556106,2.0324065625,-2.2558965574
C,0,2.6189671011,0.4769494631,-1.0920044008
N,0,2.0500730525,-0.3834776482,-1.9853703882
C,0,2.2635956933,-1.8274777337,-1.9690949783
H,0,1.6979384713,0.0233907887,-2.8444319372
H,0,3.3315267676,0.0276251909,-0.3987482162
H,0,2.8856044219,1.4590572642,-1.484539025
H,0,1.6600325834,0.9388075011,-0.261725385
H,0,-0.5890119503,-1.8191289071,3.7357646338
H,0,-1.6466351424,-1.7723123865,1.5397757322
H,0,-1.9368393831,1.0351711468,-3.3697834643

H,0,1.0327307604,-0.765035365,5.2833124916
H,0,2.409156291,1.1688774687,4.536340772
H,0,2.1603935796,2.0490736357,2.2184169438
H,0,1.4412478935,-2.3293875605,-2.4824410182
H,0,3.2039057671,-2.0938126433,-2.4680997767
H,0,2.3063279248,-2.1818258101,-0.9364217577
H,0,-2.8821574926,-1.6658777689,-0.4928256491

$FADH_2$ Model (6-1,5-H_2)

FADH2
E(RB+HF-LYP) = -755.425419671

Zero-point correction=	0.179059 (Hartree/Particle)
Thermal correction to Energy=	0.191351
Thermal correction to Enthalpy=	0.192295
Thermal correction to Gibbs Free Energy=	0.140513
Sum of electronic and zero-point Energies=	-755.246360
Sum of electronic and thermal Energies=	-755.234069
Sum of electronic and thermal Enthalpies=	-755.233125
Sum of electronic and thermal Free Energies=	-755.284907

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	120.074	49.579	108.985

C,0,-2.1099876859,-1.0235015662,-2.1854201806
C,0,-1.04551102,-0.6075768197,-1.3823543113
C,0,-0.3107546198,0.5343228234,-1.7702301008
C,0,-0.6411588397,1.2255616688,-2.9295971987
C,0,-1.7022661057,0.791274503,-3.7363788686
C,0,-2.4327228474,-0.333174226,-3.359850211
N,0,0.7936013113,0.9485871413,-0.9584001841
C,0,0.836093844,0.4889096483,0.3464930459
C,0,0.1213533071,-0.6088227536,0.7209369623
N,0,-0.6509376815,-1.306192324,-0.233308294
C,0,0.1779254672,-1.0882777682,2.0750978958
N,0,1.042532358,-0.3554006513,2.9150508591
C,0,1.8083801123,0.7421607775,2.5785080265
N,0,1.642399354,1.1468502787,1.2549606428
O,0,-0.4594380762,-2.0496704536,2.5056429959
O,0,2.5593046155,1.3241820152,3.3474918321
H,0,-0.063493664,2.1023913521,-3.2126373976
H,0,1.1144664653,1.8941920131,-1.1217627031

H,0,1.1203903042,-0.6763688558,3.8729439994
H,0,-1.9459098547,1.3327980253,-4.6442803877
H,0,-3.2580722904,-0.6813344464,-3.9728835681
H,0,-2.6816081812,-1.8992288895,-1.8904973792
H,0,2.2267901856,1.9227780463,0.9747395224
H,0,-1.3127723439,-1.9534885751,0.1779477665

FAD Radical Anion Model ($6^{-\bullet}$)

FADHanion
E(RB+HF-LYP) = -754.899901275

Zero-point correction=	0.165890 (Hartree/Particle)
Thermal correction to Energy=	0.177628
Thermal correction to Enthalpy=	0.178572
Thermal correction to Gibbs Free Energy=	0.127942
Sum of electronic and zero-point Energies=	-754.734011
Sum of electronic and thermal Energies=	-754.722273
Sum of electronic and thermal Enthalpies=	-754.721329
Sum of electronic and thermal Free Energies=	-754.771959

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	111.463	47.718	106.560

C,0,-2.1006447046,-0.9953941469,-2.1644954979
C,0,-1.0206606083,-0.6070391693,-1.3618750731
C,0,-0.2670128756,0.5415758866,-1.7390151716
C,0,-0.6187013036,1.2497688415,-2.8867004461
C,0,-1.6916415649,0.8356798926,-3.6956436014
C,0,-2.4292887729,-0.287956603,-3.330825591
N,0,0.8409969115,0.8981386755,-0.9510779025
C,0,0.9143961063,0.4811506483,0.3910276018
C,0,0.164022379,-0.6288042863,0.7418472914
N,0,-0.6093514097,-1.3161708175,-0.2425667582
C,0,0.1876761705,-1.0788082523,2.0832576439
N,0,1.0367678951,-0.314581569,2.8900630365
C,0,1.801851213,0.806086214,2.4979480824
N,0,1.7051956536,1.2010873768,1.1934936078
O,0,-0.4607960118,-2.0485121017,2.5453340665
O,0,2.5062049596,1.3661660692,3.3550209174
H,0,-0.0384664019,2.1291905031,-3.1584240573
H,0,1.2581438869,1.8068232722,-1.1069500193

H,0,1.108205261,-0.5855863394,3.8618445372
H,0,-1.9393069359,1.3963447368,-4.5925601216
H,0,-3.2654924927,-0.620389003,-3.940489834
H,0,-2.679907417,-1.8688160224,-1.8735193501
H,0,-1.2616870697,-1.9756686991,0.1647236586

Dimethylamine cation radical (9)

catradMe2NHBB.log
E(UB+HF-LYP) = -134.881527902

Zero-point correction= 0.090195 (Hartree/Particle)
Thermal correction to Energy= 0.095366
Thermal correction to Enthalpy= 0.096310
Thermal correction to Gibbs Free Energy= 0.061776
Sum of electronic and zero-point Energies= -134.791333
Sum of electronic and thermal Energies= -134.786162
Sum of electronic and thermal Enthalpies= -134.785218
Sum of electronic and thermal Free Energies= -134.819752

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	59.843	14.926	72.683

C,0,-0.0540337838,0.1969409484,1.2794181655
N,0,0.0985455112,-0.4385787099,-0.0010231804
C,0,-0.0389972887,0.2074378457,-1.2778707858
H,0,-0.5331370498,1.1696791095,1.1695419224
H,0,0.9489269902,0.3298883334,1.7247765844
H,0,-0.615402575,-0.4614931962,1.9529114432
H,0,0.3312132732,-1.4352978557,-0.0043425884
H,0,0.7919385246,-0.0897507984,-1.9303454639
H,0,-0.9645874651,-0.1582654989,-1.7574902689
H,0,-0.0905838411,1.2890181111,-1.1571736435

FADH radical model (6-5-H˙)

fadhRad
E(UB+HF-LYP) = -754.814268013

Zero-point correction= 0.167424 (Hartree/Particle)
Thermal correction to Energy= 0.179053
Thermal correction to Enthalpy= 0.179997
Thermal correction to Gibbs Free Energy= 0.128964

Sum of electronic and zero-point Energies= -754.646844
Sum of electronic and thermal Energies= -754.635215
Sum of electronic and thermal Enthalpies= -754.634271
Sum of electronic and thermal Free Energies= -754.685304

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	112.358	47.208	107.409

C,0,-2.0938048185,-1.0122534887,-2.1798290893
C,0,-1.1410113745,-0.4749973482,-1.3048990236
C,0,-0.3839867253,0.6609606816,-1.6890787307
C,0,-0.6006344958,1.2339768678,-2.94628678
C,0,-1.5516820439,0.6914454157,-3.8100980367
C,0,-2.2982860328,-0.4307510744,-3.4283324298
N,0,0.5564819772,1.1733085169,-0.7979773468
C,0,0.8009443643,0.6389795781,0.4506802896
C,0,0.0265632616,-0.4985182123,0.8056120762
N,0,-0.8999750509,-1.0173468096,-0.051036912
C,0,0.2229605498,-1.1191337848,2.0993147216
N,0,1.1904344113,-0.4813841824,2.8468232763
C,0,1.9493975771,0.6597579607,2.4609147567
N,0,1.7102624399,1.2009240353,1.2113072229
O,0,-0.4138112137,-2.1093006215,2.4752359319
O,0,2.7713477112,1.1040199242,3.2477382108
H,0,-0.0212290134,2.1040928274,-3.2413909159
H,0,1.1094091035,1.9838053221,-1.0492159027
H,0,1.3909160045,-0.8520987288,3.7687527777
H,0,-1.7097870778,1.1457508383,-4.7826138154
H,0,-3.03743574,-0.8507000665,-4.1021422699
H,0,-2.6665085036,-1.8825822561,-1.8724253158
H,0,-1.4088447676,-1.8313328515,0.2834420939

Methylaminomethyl radical (10)

CH2NHMeRad
E(UB+HF-LYP) = -134.523651710

Zero-point correction= 0.076124 (Hartree/Particle)
Thermal correction to Energy= 0.080454
Thermal correction to Enthalpy= 0.081398
Thermal correction to Gibbs Free Energy= 0.050063
Sum of electronic and zero-point Energies= -134.447528
Sum of electronic and thermal Energies= -134.443198

Sum of electronic and thermal Enthalpies= -134.442254
Sum of electronic and thermal Free Energies= -134.473589

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	50.486	12.680	65.950

C,0,0.4771563034,-0.8264594675,0.7511798402
H,0,0.4699836932,-0.8140368428,1.8436469712
H,0,1.5247053313,-0.8606420365,0.4162426054
H,0,-0.0170150817,-1.7507547264,0.4162420493
N,0,-0.1995682627,0.3456622097,0.2474457901
C,0,-0.3445632031,0.5968017548,-1.1000212942
H,0,-0.5791865231,1.0031796434,0.908117794
H,0,-0.8607546894,1.4908717542,-1.4157636766
H,0,0.0636865366,-0.1103069663,-1.8075575495

N-Methyl iminium cation

dimethyliminiumcationBB
E(RB+HF-LYP) = -134.312028036

E(RB+HF-LYP) = -134.311962252

Zero-point correction= 0.082747 (Hartree/Particle)
Thermal correction to Energy= 0.086793
Thermal correction to Enthalpy= 0.087737
Thermal correction to Gibbs Free Energy= 0.057682
Sum of electronic and zero-point Energies= -134.229281
Sum of electronic and thermal Energies= -134.225235
Sum of electronic and thermal Enthalpies= -134.224291
Sum of electronic and thermal Free Energies= -134.254346

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	54.463	12.464	63.256

N,0,-0.2156722128,0.,0.3755577341
H,0,-0.4671624946,0.,1.3665735719
C,0,1.2305582032,0.,0.0833396765
C,0,-1.1664018712,0.,-0.4802927984
H,0,-2.1985419416,0.,-0.1396609073
H,0,-0.9358577313,0.,-1.542969319
H,0,1.3816977047,0.,-0.9956578048

H,0,1.67231598,0.8927782156,0.5322645261
H,0,1.67231598,-0.8927782156,0.5322645261

FAD-4a adduct model (11)

fad-5H-4aNMe2Rot2B3BB

E(RB+HF-LYP) = -889.390539936

Zero-point correction=	0.252420 (Hartree/Particle)
Thermal correction to Energy=	0.268204
Thermal correction to Enthalpy=	0.269149
Thermal correction to Gibbs Free Energy=	0.210039
Sum of electronic and zero-point Energies=	-889.138120
Sum of electronic and thermal Energies=	-889.122336
Sum of electronic and thermal Enthalpies=	-889.121391
Sum of electronic and thermal Free Energies=	-889.180501

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	168.301	63.043	124.408

C,0,1.7808999315,0.9940914809,2.5693775565
C,0,0.8489644481,0.4627707723,1.6715316028
C,0,0.3626315996,-0.8431294705,1.8842166958
C,0,0.8184185635,-1.6076912187,2.9580696931
C,0,1.7500787731,-1.0684783601,3.8472737279
C,0,2.2232001652,0.2332986403,3.6536514463
N,0,-0.6429303989,-1.3081486455,1.0163600999
C,0,-1.0206393976,-0.6761374606,-0.1163900047
C,0,-0.0602423599,0.4220379578,-0.5786147412
N,0,0.3100767258,1.1684407509,0.5987836554
C,0,-0.7805272934,1.391438277,-1.5324198904
N,0,-1.8620168725,0.8570510701,-2.174655914
C,0,-2.5316296479,-0.3592642752,-1.8463583167
N,0,-2.1120131124,-1.0441264307,-0.7228330096
N,0,1.1128126218,-0.2150793101,-1.2330710395
C,0,0.8233528917,-1.1659272627,-2.3100556391
O,0,-0.341091612,2.5125324379,-1.7557561094
O,0,-3.4676043796,-0.7062408566,-2.5434256797
C,0,2.1819217816,0.7115932659,-1.6148327722
H,0,2.4384797717,1.3653696442,-0.7797127561
H,0,3.0690104096,0.1179693082,-1.8548844532
H,0,1.9306606718,1.339542671,-2.48379836

H,0,0.4358612658,-2.614903678,3.1008806487
H,0,-1.2444880823,-2.0674871788,1.3161065453
H,0,-2.2993695776,1.4117748067,-2.9036424869
H,0,2.1018085208,-1.6617384663,4.6847461475
H,0,2.9465855468,0.6574334571,4.3429578685
H,0,2.1534572095,2.0032940733,2.4162996998
H,0,0.4411689469,-0.6890779396,-3.2286566837
H,0,1.7530012532,-1.6834753997,-2.5633359841
H,0,0.1048449884,-1.9207643691,-1.9847134301
H,0,0.6184675273,2.1171542984,0.4264248621

Elimination Transition Structure with Methoxide Base (12a)

fadnubasetsBB
E(RB+HF-LYP) = -1005.00387434

Zero-point correction= 0.297243 (Hartree/Particle)
Thermal correction to Energy= 0.317464
Thermal correction to Enthalpy= 0.318408
Thermal correction to Gibbs Free Energy= 0.246798
Sum of electronic and zero-point Energies= -1004.706631
Sum of electronic and thermal Energies= -1004.686410
Sum of electronic and thermal Enthalpies= -1004.685466
Sum of electronic and thermal Free Energies= -1004.757076

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	199.212	76.507	150.716

C,0,3.0473026071,1.228247757,1.1585602044
C,0,2.0993817905,0.3273763728,0.653699305
C,0,2.4353389131,-0.4134302113,-0.4975349071
C,0,3.6668925482,-0.2582467711,-1.1341646933
C,0,4.5987607098,0.6412637675,-0.6184394258
C,0,4.2823340649,1.3789952452,0.5288527078
N,0,1.4805441658,-1.3441248993,-0.9608915279
C,0,0.2332192096,-1.4101306979,-0.4734953922
C,0,-0.2527909752,-0.4018932748,0.4927681276
N,0,0.8821178818,0.0741062226,1.2673824775
C,0,-1.2616212523,-1.0418654073,1.4567474529
N,0,-2.0418389126,-2.0551203958,0.9100193686
C,0,-1.84802872,-2.6861064681,-0.3025588987
N,0,-0.6508730197,-2.3327311087,-0.9461401375
N,0,-1.1044645351,0.6631275447,-0.2274547892

C,0,-0.6541479247,1.0054427653,-1.5859137706
O,0,-1.4223117108,-0.648264415,2.5943480264
O,0,-2.5959887021,-3.5210587869,-0.7742989304
C,0,-1.2708070542,1.8628340981,0.5707612495
O,0,-2.6902365115,3.4236814855,-0.9729287218
H,0,-1.9779025926,2.6153623805,-0.1003460529
H,0,-1.7741707041,1.6576923933,1.5194840635
H,0,-0.3322811633,2.4191933673,0.7431940035
H,0,3.8909260334,-0.8361469379,-2.0274880945
H,0,1.7675760014,-1.9887523335,-1.6877615258
H,0,-2.8442283848,-2.3648680943,1.4476973851
H,0,5.5569074744,0.7692696441,-1.1098373718
H,0,5.0000288981,2.0859578643,0.9326428002
H,0,2.8056418536,1.8103038725,2.0428958754
H,0,-0.6748292985,0.1253337039,-2.2367535816
H,0,-1.367531032,1.7385391868,-1.9713985828
H,0,0.3514960679,1.4565481185,-1.6156082822
H,0,-0.4748008511,-2.8642551149,-1.7917239518
H,0,0.6127702553,0.6593885851,2.0494233456
C,0,-4.0073707627,3.5694850142,-0.5651338031
H,0,-4.6562591361,3.80296941,-1.4316246158
H,0,-4.4288589602,2.6448299896,-0.1158411732
H,0,-4.1553670515,4.3851330144,0.1707860873

Elimination Transition Structure with Methylamine Base (12b)

E(RB+HF-LYP) = -985.593595068

Zero-point correction= 0.323371 (Hartree/Particle)
Thermal correction to Energy= 0.344788
Thermal correction to Enthalpy= 0.345733
Thermal correction to Gibbs Free Energy= 0.271039
Sum of electronic and zero-point Energies= -985.270224
Sum of electronic and thermal Energies= -985.248807
Sum of electronic and thermal Enthalpies= -985.247862
Sum of electronic and thermal Free Energies= -985.322556

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	216.358	79.680	157.205

N,0,-0.5504235623,-2.4467003652,-0.6451749824
C,0,0.3690584156,-1.5109332692,-0.271509303
C,0,0.0300930786,-0.5753877313,0.7036352531

C,0,-1.2067183495,-0.7215844629,1.4547446929
N,0,-2.035308551,-1.7609971351,1.0316082426
C,0,-1.8062409923,-2.6235697192,-0.0208873543
N,0,0.9823280427,0.3124045628,1.1683110885
C,0,2.2889021037,0.296775682,0.6679004983
C,0,2.6043485934,-0.5927126677,-0.3793849363
N,0,1.5873447702,-1.4677180792,-0.8555298434
C,0,3.8850052358,-0.625747633,-0.9243176046
C,0,4.8736568579,0.2249537834,-0.4242123736
C,0,4.5720861743,1.1000662192,0.6223093582
C,0,3.2868269683,1.1380112186,1.1661596344
N,0,-1.3963257751,0.8210068866,-0.7652952505
C,0,-1.1436321642,2.0094872088,-0.146643832
O,0,-1.4971634883,0.0137081608,2.3917394959
O,0,-2.5750026177,-3.4811769178,-0.3973645469
C,0,-0.8613185773,0.7131933651,-2.1073498993
N,0,-3.2536018176,3.7117173507,-0.7831326529
C,0,-4.5126438381,3.0141580192,-0.4399132342
H,0,-2.087185397,2.7703000367,-0.5055178004
H,0,-1.3404185686,1.9908941979,0.9323465835
H,0,-0.2321457288,2.56378625,-0.4275440712
H,0,4.1127444354,-1.3170965117,-1.7313165942
H,0,1.8472383859,-2.1627404402,-1.5437391415
H,0,-2.9222897865,-1.870857804,1.5118127057
H,0,5.8712246809,0.1975045942,-0.8481071936
H,0,5.337729408,1.7579172269,1.0195006862
H,0,3.0526051554,1.8206097644,1.9777774251
H,0,-0.8399076233,-0.3310212887,-2.4296563773
H,0,-1.5559875925,1.2244996241,-2.7928130896
H,0,0.1301612079,1.1736535885,-2.2362432025
H,0,-0.356481091,-3.1274342946,-1.3705950052
H,0,0.7769896967,0.7572057947,2.0555841231
H,0,-5.3946007623,3.6324082585,-0.6344093426
H,0,-4.5821051872,2.0967829503,-1.028170316
H,0,-4.4918671012,2.7459242391,0.6181788184
H,0,-3.1252522417,4.5512342549,-0.2198257586
H,0,-3.2377558273,3.9979269925,-1.7609536528

Concerted addition / elimination transition structure (15)

fadnubBB
E(RB+HF-LYP) = -889.315160596

Zero-point correction= 0.244922 (Hartree/Particle)

Thermal correction to Energy= 0.261228
Thermal correction to Enthalpy= 0.262173
Thermal correction to Gibbs Free Energy= 0.201517
Sum of electronic and zero-point Energies= -889.070239
Sum of electronic and thermal Energies= -889.053932
Sum of electronic and thermal Enthalpies= -889.052988
Sum of electronic and thermal Free Energies= -889.113643

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	163.923	63.639	127.659

N,0,1.7072280492,-1.636041443,-0.1183362087
C,0,0.5373686925,-0.9284611736,-0.1864200526
C,0,0.4997882054,0.3799041857,-0.6782650714
C,0,1.7765563081,1.0085905545,-1.07008432
N,0,2.9044893038,0.1646496095,-0.9669794991
C,0,2.9618557526,-1.106791996,-0.455374899
N,0,-0.6408680731,1.1106396503,-0.7613506451
C,0,-1.8284013311,0.4208041711,-0.5197616564
C,0,-1.8572655466,-0.9094293731,-0.0386958391
N,0,-0.6159439725,-1.5414692054,0.1750348772
C,0,-3.0583030739,-1.5726010881,0.2134362538
C,0,-4.2663273052,-0.909791531,-0.0065656423
C,0,-4.2634092566,0.4079554845,-0.4838963245
C,0,-3.0609917926,1.0611045697,-0.7401593819
N,0,1.176156263,1.1338038443,1.7533247091
C,0,0.274285935,2.1637908623,1.5865006597
O,0,1.9048609207,2.1467249412,-1.4795666852
O,0,3.9793601338,-1.7650408164,-0.320359168
C,0,0.7631187503,0.1321162431,2.7116517555
H,0,-0.5043850145,2.2805726283,2.3594368476
H,0,0.7546673743,3.1140598579,1.3266671388
H,0,-0.3471214561,1.9557121466,0.5805736202
H,0,-3.0489770241,-2.5946969361,0.585361513
H,0,-0.6074414823,-2.498272798,0.5011971439
H,0,3.7960730812,0.593476184,-1.1869231025
H,0,-5.2031083452,-1.4204701737,0.19145852
H,0,-5.2034044078,0.9221294387,-0.6583272279
H,0,-3.0387760364,2.0798797016,-1.1133712405
H,0,1.3539246946,-0.783447456,2.5924552505
H,0,0.9585322421,0.4981990321,3.7336153773
H,0,-0.3114248394,-0.1267968997,2.6714498636
H,0,1.7405897571,-2.5780403687,0.2497675968

Methyl Amine

MeNH2B3BB
E(RB+HF-LYP) = -95.8718478880

Zero-point correction=	0.064040 (Hartree/Particle)
Thermal correction to Energy=	0.067473
Thermal correction to Enthalpy=	0.068418
Thermal correction to Gibbs Free Energy=	0.041109
Sum of electronic and zero-point Energies=	-95.807808
Sum of electronic and thermal Energies=	-95.804374
Sum of electronic and thermal Enthalpies=	-95.803430
Sum of electronic and thermal Free Energies=	-95.830739

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	42.340	9.602	57.475

C,0,-0.0105459784,-0.0196992013,-0.0074570607
H,0,0.0098560045,-0.0093250496,1.0867355191
H,0,1.0278692014,-0.0093250622,-0.3529531639
H,0,-0.4657882924,-0.9707472029,-0.3293618426
N,0,-0.6858054955,1.1912891398,-0.4849374515
H,0,-0.7015824407,1.2279536831,-1.4993528968
H,0,-1.6474644009,1.2279536948,-0.1616732304

Dimethylammonium cation

dimethylammoniumBB
E(RB+HF-LYP) = -135.548840373

Zero-point correction=	0.108075 (Hartree/Particle)
Thermal correction to Energy=	0.112581
Thermal correction to Enthalpy=	0.113525
Thermal correction to Gibbs Free Energy=	0.082328
Sum of electronic and zero-point Energies=	-135.440766
Sum of electronic and thermal Energies=	-135.436259
Sum of electronic and thermal Enthalpies=	-135.435315
Sum of electronic and thermal Free Energies=	-135.466513

	E (Thermal)	CV	S

	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	70.646	14.342	65.661

C,0,0.0216412827,-0.0374834372,-0.1078065733
N,0,-0.0158630221,0.0274752804,1.3998950969
H,0,0.9437129202,0.0002100215,1.7603037218
C,0,-0.7176009469,1.2429206025,1.9559985295
H,0,-0.4720386072,-0.8171746274,1.7603033781
H,0,-1.0037854197,-0.0516889677,-0.477156064
H,0,0.5466570035,0.8434595179,-0.4771556876
H,0,0.5459266706,-0.9455721038,-0.4069022686
H,0,-0.6905937935,1.1961423897,3.0450594421
H,0,-0.1977565984,2.1328263344,1.601108647
H,0,-1.748203962,1.2376749965,1.6011082706

Structures Using Onsager Solvent Model

dimethylamine

Onsager/B3LYP/6-31+G**
dimethylamineOnsgr
E(RB+HF-LYP) = -135.181685500

Zero-point correction= 0.092337 (Hartree/Particle)
Thermal correction to Energy= 0.096743
Thermal correction to Enthalpy= 0.097687
Thermal correction to Gibbs Free Energy= 0.066868
Sum of electronic and zero-point Energies= -135.089349
Sum of electronic and thermal Energies= -135.084942
Sum of electronic and thermal Enthalpies= -135.083998
Sum of electronic and thermal Free Energies= -135.114818

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	60.707	13.916	64.865

N,0,-0.2546458931,0.4397370623,0.2857115686
H,0,-0.3037410074,0.5235891374,1.2971520533
C,0,1.1416431946,0.4589733501,-0.1400850858
C,0,-0.9666223277,-0.7611270345,-0.1412686012
H,0,-1.0338265441,-0.7722486851,-1.2355205193
H,0,-0.4851027304,-1.7050843122,0.1734831921

H,0,-1.9864609076,-0.7455456905,0.2552733592
H,0,1.1856886155,0.5122366331,-1.2342744715
H,0,1.6359017893,1.3507950307,0.2573084977
H,0,1.7199368348,-0.428979443,0.17471903

PCM/B3LYP/6-31+G**//Onsager/B3LYP/6-31+G= -135.189498748

Alloxazine Model for FAD (6)

fadSMNeuOnsgr

Onsager/B3LYP/6-31+G**
E(RB+HF-LYP) = -754.223336827

Zero-point correction= 0.156236 (Hartree/Particle)
Thermal correction to Energy= 0.167331
Thermal correction to Enthalpy= 0.168276
Thermal correction to Gibbs Free Energy= 0.118849
Sum of electronic and zero-point Energies= -754.067101
Sum of electronic and thermal Energies= -754.056005
Sum of electronic and thermal Enthalpies= -754.055061
Sum of electronic and thermal Free Energies= -754.104487

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	105.002	44.890	104.026

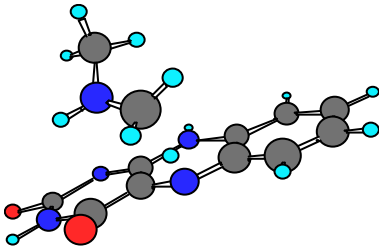
C,0,-2.8802120529,1.3466455782,0.
C,0,-1.6529846992,0.6380629057,0.
C,0,-1.6786206664,-0.7903413381,0.
C,0,-2.8966279582,-1.4838956779,0.
C,0,-4.0802828443,-0.7577342764,0.
C,0,-4.0764159202,0.6569900216,0.
N,0,-0.4588812648,-1.4357190895,0.
C,0,0.7433060241,-0.794316704,0.
C,0,0.6546476606,0.659927072,0.
N,0,-0.4734540428,1.3221749209,0.
C,0,1.9494822131,1.3981283353,0.
N,0,3.0387198815,0.5421047758,0.
C,0,3.0473644631,-0.8775216604,0.
N,0,1.8431306282,-1.5254201878,0.
O,0,2.0875113822,2.6135175349,0.
O,0,4.1439731926,-1.4375593317,0.
H,0,-2.9132308446,-2.5699681629,0.
H,0,-0.4247100906,-2.4515671434,0.

H,0,3.9512120737,0.9807308337,0.
H,0,-5.0279452124,-1.2873745698,0.
H,0,-5.0198259461,1.1922816675,0.
H,0,-2.8419203115,2.4305832775,0.

PCM/B3LYP/6-31+G**//Onsager/B3LYP/6-31+G=-754.261223663

Hydride Transfer Transition Structure (7)

fadHydrideNeuOnsgr



Onsager/B3LYP/6-31+G**
E(RB+HF-LYP) = -889.356443368

Zero-point correction=	0.245574 (Hartree/Particle)
Thermal correction to Energy=	0.262078
Thermal correction to Enthalpy=	0.263022
Thermal correction to Gibbs Free Energy=	0.200939
Sum of electronic and zero-point Energies=	-889.110870
Sum of electronic and thermal Energies=	-889.094365
Sum of electronic and thermal Enthalpies=	-889.093421
Sum of electronic and thermal Free Energies=	-889.155504

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	164.457	63.627	130.666

C,0,1.5363019479,1.2046320592,2.5608675541
C,0,0.6572502644,0.6137601936,1.6418522669
C,0,-0.0740648211,-0.5303713251,2.0241830739
C,0,0.0835151284,-1.0682639867,3.3089192879
C,0,0.9726301247,-0.4782759925,4.2028019247
C,0,1.7022278085,0.6608935381,3.8305747752
N,0,-0.9520555396,-1.0937031447,1.0996218317
C,0,-1.2082225872,-0.5291422142,-0.1226887966

C,0,-0.4157466852,0.6036075347,-0.4828629704
N,0,0.5231429645,1.1691739162,0.3473374564
C,0,-0.6649888529,1.2025116042,-1.7802581775
N,0,-1.7063707444,0.5945047847,-2.4734906277
C,0,-2.4941800435,-0.5004693446,-2.0480658047
N,0,-2.1932812405,-1.0601653446,-0.8360212483
O,0,-3.4006432354,-0.8875088483,-2.7904698409
O,0,-0.0109325126,2.1254610037,-2.285113234
C,0,2.5876246239,0.5308659958,-1.0671163706
N,0,1.9035424828,-0.3448748722,-1.8429520074
C,0,1.9262182189,-1.7896848936,-1.6486835662
H,0,1.5174813991,0.0113251168,-2.7078776136
H,0,3.2635749056,0.1047488641,-0.328394717
H,0,2.8734906686,1.4719834869,-1.5303139903
H,0,1.5509542871,1.1641352271,-0.1900226614
H,0,-0.4770852378,-1.9548991375,3.5930165692
H,0,-1.5501970033,-1.8652414826,1.3680292554
H,0,-1.9283357392,0.9765328905,-3.3843462715
H,0,1.1030056131,-0.9073077601,5.190952757
H,0,2.3943384699,1.1167624296,4.5304299526
H,0,2.0859325299,2.0912833068,2.258938893
H,0,1.0187470113,-2.2309030931,-2.065452855
H,0,2.8030725823,-2.2427942079,-2.1287011046
H,0,1.9613902768,-2.0141692716,-0.5802006277

PCM/B3LYP/6-31+G**//Onsager/B3LYP/6-31+G**= -889.404088608

FADH⁻ Model (6-5H⁻)

FADHanionPCMonOnsgr

Onsager/B3LYP/6-31+G**
E(RB+HF-LYP) = -754.915956018

Zero-point correction= 0.165867 (Hartree/Particle)
Thermal correction to Energy= 0.177612
Thermal correction to Enthalpy= 0.178557
Thermal correction to Gibbs Free Energy= 0.127993
Sum of electronic and zero-point Energies= -754.750089
Sum of electronic and thermal Energies= -754.738344
Sum of electronic and thermal Enthalpies= -754.737399
Sum of electronic and thermal Free Energies= -754.787963

E (Thermal) CV S

	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	111.454	47.733	106.420

C,0,-2.1024404572,-0.9989414919,-2.1855455741
C,0,-1.0418715563,-0.5908219322,-1.3716168961
C,0,-0.2988128542,0.5519807151,-1.741566069
C,0,-0.6246977945,1.249378876,-2.9034034365
C,0,-1.6796268524,0.8221775268,-3.7225994324
C,0,-2.4174897361,-0.3027773721,-3.3600291112
N,0,0.7926557332,0.938050416,-0.9195431104
C,0,0.8763672448,0.5064988864,0.3980011295
C,0,0.1221837449,-0.6102596942,0.7527222432
N,0,-0.6359655741,-1.3085317557,-0.2314565686
C,0,0.1881462388,-1.0740894373,2.0847399374
N,0,1.0602741255,-0.3159124264,2.8861044896
C,0,1.8303640176,0.787106623,2.4898116654
N,0,1.7043783758,1.2038014881,1.2108648342
O,0,-0.4251975548,-2.0542850336,2.5828294964
O,0,2.5832937361,1.3138057491,3.356166707
H,0,-0.0435699585,2.126919081,-3.1785803047
H,0,1.2171479943,1.8388619641,-1.0934902141
H,0,1.1497320336,-0.6136624696,3.8470544699
H,0,-1.9144195307,1.3656846588,-4.6317351313
H,0,-3.23541234,-0.6459264937,-3.9854256546
H,0,-2.6751833629,-1.8801100044,-1.9064692112
H,0,-1.3251948816,-1.9313027111,0.1718021685

PCM/B3LYP/6-31+G**//Onsager/B3LYP/6-31+G**= -755.005678873

FADH^{+} Model (6-1-H^{+})

fadhydrideSMPCMonOnsgr

PCM/B3LYP/6-31+G**//Onsager/B3LYP/6-31+G**
E(RB+HF-LYP) = -754.708146579

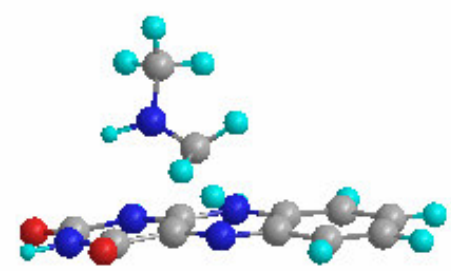
1	7	0	-1.871374	-1.424591	-0.000102
2	6	0	-0.682254	-0.769794	-0.000035
3	6	0	-0.629220	0.659374	-0.000052
4	6	0	-1.915107	1.424639	0.000109
5	7	0	-3.054115	0.606077	0.000242
6	6	0	-3.129234	-0.774961	-0.000233

7	7	0	0.509567	1.317411	-0.000037
8	6	0	1.679724	0.642656	-0.000014
9	6	0	1.711176	-0.793556	0.000008
10	7	0	0.481775	-1.436353	0.000006
11	6	0	2.918447	-1.495382	0.000027
12	6	0	4.100656	-0.764159	0.000037
13	6	0	4.098096	0.654149	0.000022
14	6	0	2.909147	1.352118	-0.000003
15	8	0	-2.006756	2.631367	-0.000123
16	8	0	-4.160651	-1.404168	0.000086
17	1	0	2.940195	-2.581654	0.000040
18	1	0	0.485713	-2.455404	0.000026
19	1	0	-3.948419	1.085856	0.000307
20	1	0	5.048122	-1.294758	0.000060
21	1	0	5.044937	1.183498	0.000032
22	1	0	2.872286	2.435841	-0.000013
23	1	0	-1.933131	-2.439289	-0.000111

PCM/B3LYP/6-31+G**//Onsager/B3LYP/6-31+G**= -754.708146579

Hydride Transfer Transition Structure (8)

fadhydrideCatOnsgr



E(RB+HF-LYP) = -889.742198383

Zero-point correction= 0.258017 (Hartree/Particle)
Thermal correction to Energy= 0.274901
Thermal correction to Enthalpy= 0.275845
Thermal correction to Gibbs Free Energy= 0.212691
Sum of electronic and zero-point Energies= -889.484181
Sum of electronic and thermal Energies= -889.467298
Sum of electronic and thermal Enthalpies= -889.466354
Sum of electronic and thermal Free Energies= -889.529507

E (Thermal) CV S

	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	172.503	65.023	132.918

C,0,1.5736323168,1.2065311811,2.5492247163
C,0,0.6769466772,0.6113329106,1.6458366328
C,0,-0.0730000708,-0.509406207,2.0688416606
C,0,0.0733322993,-1.0312013059,3.3571202141
C,0,0.9800523286,-0.4359431648,4.2288396272
C,0,1.7281666528,0.6843947171,3.8266456602
N,0,-1.0011163196,-1.0547255996,1.1662515654
C,0,-1.2114661305,-0.4916692797,-0.0398907439
C,0,-0.4264960484,0.5981105514,-0.4454431529
N,0,0.5543163308,1.1374216951,0.3487333922
C,0,-0.6720258908,1.2074117481,-1.7557723326
N,0,-1.7569474223,0.6568427821,-2.4599890704
C,0,-2.5794697573,-0.3829058595,-2.0715385964
N,0,-2.2294292237,-0.9481034044,-0.8310855137
O,0,-3.5194879225,-0.7959117931,-2.7160928818
O,0,0.0016044526,2.1005067493,-2.2476589571
C,0,2.6068295574,0.4770346252,-1.079135855
N,0,2.0511571577,-0.4306757926,-1.932632038
C,0,2.2523738358,-1.8747116697,-1.821668155
H,0,1.7296138453,-0.0788943841,-2.8264478109
H,0,3.3099250354,0.0674992691,-0.3519514264
H,0,2.8782293955,1.4368149852,-1.5198416115
H,0,1.6445223171,0.9698933489,-0.2722546078
H,0,-0.5082093257,-1.8936174628,3.6713616093
H,0,-1.5747410365,-1.8295393323,1.4803854469
H,0,-1.9712871937,1.0751678052,-3.3590457192
H,0,1.1053159145,-0.8419125151,5.2270864307
H,0,2.4267461669,1.142171947,4.5186859389
H,0,2.1367035849,2.076165782,2.2255405068
H,0,1.4262197916,-2.4032115987,-2.3011792569
H,0,3.1910223411,-2.1789888547,-2.300686004
H,0,2.2938370666,-2.1604707398,-0.7684610424
H,0,-2.8439484248,-1.6970251462,-0.5304841429

PCM/B3LYP/6-31+G**//Onsager/B3LYP/6-31+G**= -889.856939442

$FADH_2$ Model (6-1,5-H_2)

FADH2PCMonOnsgr

PCM/B3LYP/6-31+G**//Onsager/B3LYP/6-31+G**

E(RB+HF-LYP) = -755.428943518

Zero-point correction=	0.178946 (Hartree/Particle)
Thermal correction to Energy=	0.191255
Thermal correction to Enthalpy=	0.192200
Thermal correction to Gibbs Free Energy=	0.140447
Sum of electronic and zero-point Energies=	-755.249997
Sum of electronic and thermal Energies=	-755.237688
Sum of electronic and thermal Enthalpies=	-755.236744
Sum of electronic and thermal Free Energies=	-755.288496

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	120.015	49.641	108.922

C,0,-2.110473447,-1.0234700309,-2.1903197814
C,0,-1.0500459648,-0.6050948046,-1.3857037145
C,0,-0.3182497191,0.5360585748,-1.7706809243
C,0,-0.6426229796,1.2287296572,-2.9309740734
C,0,-1.7000065913,0.7922237896,-3.7399869624
C,0,-2.4310139993,-0.3325433505,-3.365470154
N,0,0.7762710546,0.9540599225,-0.9467088672
C,0,0.8278329582,0.4946900456,0.3482983463
C,0,0.1116981083,-0.6085714883,0.7253907164
N,0,-0.6520630364,-1.3112459992,-0.2333777919
C,0,0.180209904,-1.0893157341,2.072715233
N,0,1.0517029519,-0.3567945589,2.9094663212
C,0,1.8136465004,0.742100603,2.5741457015

PCM/B3LYP/6-31+G**//Onsager/B3LYP/6-31+G** = -755.470453917

FAD Radical Anion Model ($6^{-\bullet}$)

fadRadAnionPCMonOnsgr

Onsager/B3LYP/6-31+G**
E(UB+HF-LYP) = -754.300146470

Zero-point correction=	0.153264 (Hartree/Particle)
Thermal correction to Energy=	0.164664
Thermal correction to Enthalpy=	0.165608
Thermal correction to Gibbs Free Energy=	0.114976
Sum of electronic and zero-point Energies=	-754.146883
Sum of electronic and thermal Energies=	-754.135482

Sum of electronic and thermal Enthalpies= -754.134538
Sum of electronic and thermal Free Energies= -754.185170

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	103.328	46.149	106.564

C,0,-2.1070029886,-1.0067268869,-2.1909100408
C,0,-1.1508144293,-0.4980585924,-1.2762596887
C,0,-0.3955500525,0.642124216,-1.6937771769
C,0,-0.5926253291,1.226447865,-2.9462723401
C,0,-1.5452883021,0.6966965669,-3.8221074199
C,0,-2.3008097248,-0.4222795597,-3.4377747791
N,0,0.5437580254,1.1369672906,-0.7879133798
C,0,0.7567008953,0.5804577749,0.4497290388
C,0,-0.0432659313,-0.5529252202,0.7775946715
N,0,-0.9814681243,-1.0922462501,-0.0578422561
C,0,0.1892922812,-1.1326495365,2.0864938463
N,0,1.1844490575,-0.4601927585,2.8154079139
C,0,1.9399943343,0.6589326323,2.4306222786
N,0,1.6982437894,1.1761204734,1.2032281671
O,0,-0.3688101753,-2.115490104,2.6084996408
O,0,2.7834053117,1.0998532545,3.2470248021
H,0,-0.0030826314,2.09343985,-3.2367038965
H,0,1.1103158256,1.941275764,-1.0225371125
H,0,1.3769934425,-0.8346872586,3.7341559008
H,0,-1.6965639151,1.1527254192,-4.7951214677
H,0,-3.0400387679,-0.8319795059,-4.1195148855
H,0,-2.6830488002,-1.8723363162,-1.8786675349

PCM/B3LYP/6-31+G**//Onsager/B3LYP/6-31+G**= -754.396111232

Dimethylamine cation radical (9)

catradMe2NHOnsgr

Onsager/B3LYP/6-31+G**
E(UB+HF-LYP) = -134.881818979

Zero-point correction= 0.090218 (Hartree/Particle)
Thermal correction to Energy= 0.095366
Thermal correction to Enthalpy= 0.096310

Thermal correction to Gibbs Free Energy= 0.061937
Sum of electronic and zero-point Energies= -134.791601
Sum of electronic and thermal Energies= -134.786453
Sum of electronic and thermal Enthalpies= -134.785509
Sum of electronic and thermal Free Energies= -134.819882

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	59.843	14.896	72.344

C,0,-0.0436337216,0.2003014433,1.280174069
N,0,0.1072734138,-0.4335567792,-0.0009756587
C,0,-0.0564290691,0.2029969324,-1.2792184427
H,0,-0.4585692766,1.2009423726,1.1670038884
H,0,0.9474524998,0.2548765037,1.7641472472
H,0,-0.6714821535,-0.4280223474,1.9261041744
H,0,0.3543311448,-1.42741396,-0.0032959872
H,0,0.7952581678,-0.051146716,-1.9245760195
H,0,-0.9545207124,-0.2145481583,-1.7674387001
H,0,-0.1630068221,1.2804195056,-1.1608487499

PCM/B3LYP/6-31+G**//Onsager/B3LYP/6-31+G**= -134.995699532

FADH radical model (6-5-H˙)

fadhRadPCMonOnsgr

Onsager/B3LYP/6-31+G**
E(UB+HF-LYP) = -754.828689553

Zero-point correction= 0.167439 (Hartree/Particle)
Thermal correction to Energy= 0.178977
Thermal correction to Enthalpy= 0.179921
Thermal correction to Gibbs Free Energy= 0.129194
Sum of electronic and zero-point Energies= -754.661251
Sum of electronic and thermal Energies= -754.649713
Sum of electronic and thermal Enthalpies= -754.648768
Sum of electronic and thermal Free Energies= -754.699495

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	112.310	47.036	106.764

C,0,-2.1029033613,-1.0163471194,-2.1900712962
C,0,-1.1485365198,-0.4794137163,-1.311405279
C,0,-0.3895109703,0.6568975549,-1.6922793793
C,0,-0.5992843669,1.2367383428,-2.94774025
C,0,-1.5484511609,0.6961806414,-3.8116547846
C,0,-2.3002874514,-0.4300928906,-3.4332733024
N,0,0.551536477,1.1635237765,-0.7911439635
C,0,0.7923274858,0.6297382273,0.449348964
C,0,0.0199500212,-0.5049301085,0.8039297278
N,0,-0.908580753,-1.0217866983,-0.0593230394
C,0,0.2225550152,-1.1156527778,2.0936257838
N,0,1.1967106828,-0.4671270483,2.8375039634
C,0,1.9523835407,0.6691182027,2.4514439995
N,0,1.7144991626,1.2021877169,1.2169755788
O,0,-0.3923536753,-2.1068069233,2.509966905
O,0,2.780864323,1.1050349306,3.2604745742
H,0,-0.0204448505,2.1068904881,-3.2436709674
H,0,1.1023556166,1.9745256136,-1.0466652414
H,0,1.3925769523,-0.8417594219,3.7564244087
H,0,-1.7085189423,1.1484646873,-4.7846007186
H,0,-3.0368269101,-0.8424965853,-4.1143968533
H,0,-2.6800647813,-1.8865424027,-1.8910841993
H,0,-1.4257746462,-1.8359088043,0.260828861

PCM/B3LYP/6-31+G**//Onsager/B3LYP/6-31+G**= -754.865306675

Methylaminomethyl radical (10)

CH2NHMeRadPCMonOnsgr

Onsager/B3LYP/6-31+G**
E(UB+HF-LYP) = -134.524516376

Zero-point correction=	0.076163 (Hartree/Particle)
Thermal correction to Energy=	0.080480
Thermal correction to Enthalpy=	0.081424
Thermal correction to Gibbs Free Energy=	0.050115
Sum of electronic and zero-point Energies=	-134.448353
Sum of electronic and thermal Energies=	-134.444037
Sum of electronic and thermal Enthalpies=	-134.443092
Sum of electronic and thermal Free Energies=	-134.474401

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

Total	50.502	12.657	65.894

C,0,0.4773733738,-0.8268354451,0.7517585966
H,0,0.4697200888,-0.8135802736,1.8436232482
H,0,1.5248781096,-0.8601420504,0.4177377898
H,0,-0.0175344784,-1.7506543607,0.4177372335
N,0,-0.1994392299,0.3454387219,0.2459092564
C,0,-0.3447680609,0.5971565795,-1.099553336
H,0,-0.5788306185,1.0025631854,0.9075851783
H,0,-0.8612641112,1.4917540866,-1.4140076702
H,0,0.0634737655,-0.1099384331,-1.8072721381

PCM/B3LYP/6-31+G**//Onsager/B3LYP/6-31+G**= -134.531335624

N-Methyl iminium cation

MeNCH2cationOnsgr

Onsager/B3LYP/6-31+G**
E(RB+HF-LYP) = -134.310357811

Zero-point correction=	0.082363 (Hartree/Particle)
Thermal correction to Energy=	0.085833
Thermal correction to Enthalpy=	0.086777
Thermal correction to Gibbs Free Energy=	0.057792
Sum of electronic and zero-point Energies=	-134.227995
Sum of electronic and thermal Energies=	-134.224525
Sum of electronic and thermal Enthalpies=	-134.223581
Sum of electronic and thermal Free Energies=	-134.252565

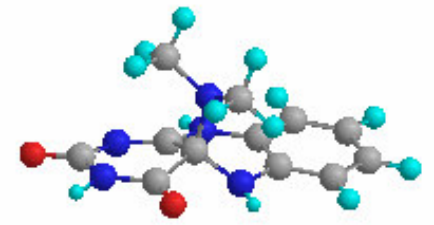
	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	53.861	10.639	61.003

N,0,-0.2149525227,0.,0.3754656262
H,0,-0.4683041496,0.,1.366302555
C,0,1.2302499555,0.,0.0837423589
C,0,-1.1663892375,0.,-0.4804249512
H,0,-2.1991759429,0.,-0.1398465621
H,0,-0.9365147235,0.,-1.5432214014
H,0,1.3805528623,0.,-0.9954058228
H,0,1.672472652,0.8928286716,0.5320037008
H,0,1.672472652,-0.8928286716,0.5320037008

PCM/B3LYP/6-31+G**//Onsager/B3LYP/6-31+G**= -134.412124784

FAD-4a adduct model (11)

fad-5H-4aNMe2Rot2PCMonOnsgr



Onsager/B3LYP/6-31+G**
E(RB+HF-LYP) = -889.394470385

Zero-point correction=	0.252323 (Hartree/Particle)
Thermal correction to Energy=	0.268129
Thermal correction to Enthalpy=	0.269073
Thermal correction to Gibbs Free Energy=	0.209849
Sum of electronic and zero-point Energies=	-889.142148
Sum of electronic and thermal Energies=	-889.126342
Sum of electronic and thermal Enthalpies=	-889.125398
Sum of electronic and thermal Free Energies=	-889.184621

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	168.253	63.011	124.647

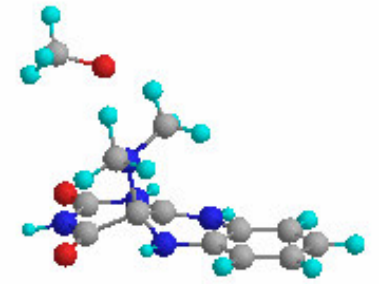
C,0,-3.0236270803,0.9383264556,-0.8438527489
C,0,-1.8189836554,0.2782961232,-0.5814875852
C,0,-1.8512827765,-0.9717573995,0.0640298856
C,0,-3.0610006981,-1.5425604115,0.461085826
C,0,-4.257167003,-0.8746600412,0.1978776848
C,0,-4.2347992687,0.3606028104,-0.4592025812
N,0,-0.6225667473,-1.645280689,0.2261343557
C,0,0.5821297605,-1.0864605059,0.0144336531
C,0,0.5556399823,0.439952234,-0.1219095577
N,0,-0.5645640335,0.7524991393,-0.9741989754
C,0,1.8304652515,0.9323681382,-0.8268153956
N,0,2.8975422288,0.0797348155,-0.7325964003
C,0,2.8661454795,-1.2860118499,-0.3261875972
N,0,1.6464918059,-1.8467951444,-0.0357661298
N,0,0.4248720367,1.035210025,1.2323925066

C,0,1.4040462813,0.6115515042,2.233912326
O,0,1.9017081138,2.0430100229,-1.3376831708
O,0,3.9264203911,-1.8962277162,-0.3040237471
C,0,0.2221078515,2.4861913487,1.2568348164
H,0,-0.5732197294,2.7742345515,0.5682178151
H,0,-0.1016707208,2.7621338146,2.2643248462
H,0,1.1279049835,3.0602304462,1.0052171597
H,0,-3.0641819767,-2.5040328426,0.9677885061
H,0,-0.6258907186,-2.6497970409,0.3657843062
H,0,3.7917300561,0.4113816411,-1.0775477109
H,0,-5.1999989005,-1.3131516498,0.5061669724
H,0,-5.1637363733,0.8833529847,-0.6624082648
H,0,-3.0094154954,1.9019598415,-1.3455847766
H,0,2.4178806712,1.0126503893,2.0574501592
H,0,1.0673117845,0.9705643909,3.2105055778
H,0,1.4649207744,-0.4775033449,2.2873688961
H,0,-0.5111341764,1.6511109024,-1.4376979989

PCM/B3LYP/6-31+G**//Onsager/B3LYP/6-31+G**= -889.431167990

Elimination Transition Structure with Methoxide Base (12a)

FadnuadductOMePCMonOnsgrTS



Onsager/B3LYP/6-31+G**
E(RB+HF-LYP) = -1005.02265242

Zero-point correction= 0.295844 (Hartree/Particle)
Thermal correction to Energy= 0.316457
Thermal correction to Enthalpy= 0.317401
Thermal correction to Gibbs Free Energy= 0.245636
Sum of electronic and zero-point Energies= -1004.726808
Sum of electronic and thermal Energies= -1004.706196
Sum of electronic and thermal Enthalpies= -1004.705251
Sum of electronic and thermal Free Energies= -1004.777016

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	198.580	77.634	151.042

C,0,3.0642849522,1.0043934144,1.5647818984
C,0,2.141890837,0.2907853573,0.7891072965
C,0,2.6004479768,-0.3052348651,-0.3990937009
C,0,3.9276338268,-0.1977799297,-0.8179676051
C,0,4.8327829419,0.5146134733,-0.0353887196
C,0,4.3937298484,1.1087432877,1.1545153263
N,0,1.6660542735,-1.0823730384,-1.127936012
C,0,0.3799619689,-1.1709217539,-0.8036914282
C,0,-0.2017558008,-0.3474273237,0.2708855167
N,0,0.8241856591,0.083643618,1.1748200027
C,0,-1.2715929526,-1.1305599908,1.027658234
N,0,-1.999574362,-2.0202645158,0.2508878202
C,0,-1.7207313254,-2.3967626773,-1.0500526113
N,0,-0.4660063036,-1.970532333,-1.5145425565
N,0,-1.1233878608,0.8251966191,-0.3853252174
C,0,-0.4783545011,1.4218437647,-1.5632612587
O,0,-1.5314473407,-0.9358419975,2.1994978615
O,0,-2.4538034692,-3.0850493284,-1.7309479539
C,0,-1.4252084153,1.8505551377,0.5787565466
O,0,-3.2636085592,3.4832761846,-0.2988532372
H,0,-2.367010543,2.7121294901,0.0701648449
H,0,-1.8945676651,1.4394039788,1.4774046517
H,0,-0.5586458932,2.4813307504,0.8520490357
H,0,4.2531871082,-0.681502568,-1.7353759797
H,0,2.0323140161,-1.6522895777,-1.8845948352
H,0,-2.82408822,-2.438966278,0.6648809649
H,0,5.8699196377,0.5912379629,-0.3411737155
H,0,5.0992861573,1.6526875666,1.774125872
H,0,2.7379189711,1.4598336228,2.4951773874
H,0,-0.307561706,0.673505237,-2.3432501687
H,0,-1.1686536645,2.1713338039,-1.957457972
H,0,0.4745971309,1.9271519495,-1.3344954283
H,0,-0.1877276158,-2.3983356368,-2.39205924
H,0,0.4899050172,0.4935271669,2.035926802
C,0,-4.4517348301,2.771773515,-0.3753623572
H,0,-4.8985201344,2.7950846338,-1.3922187068
H,0,-4.3217578405,1.6995999589,-0.1216995125
H,0,-5.2324673197,3.1617133208,0.3178041552

PCM/B3LYP/6-31+G**//Onsager/B3LYP/6-31+G**= -1005.02263231

Elimination Transition Structure with Methylamine Base (12b)

nuAdductElimTSMeNH2PCMOnonsgr

Onsager/B3LYP/6-31+G**
E(RB+HF-LYP) = -985.598013430

Zero-point correction=	0.323808 (Hartree/Particle)
Thermal correction to Energy=	0.345157
Thermal correction to Enthalpy=	0.346101
Thermal correction to Gibbs Free Energy=	0.272058
Sum of electronic and zero-point Energies=	-985.274206
Sum of electronic and thermal Energies=	-985.252856
Sum of electronic and thermal Enthalpies=	-985.251912
Sum of electronic and thermal Free Energies=	-985.325956

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	216.589	79.588	155.837

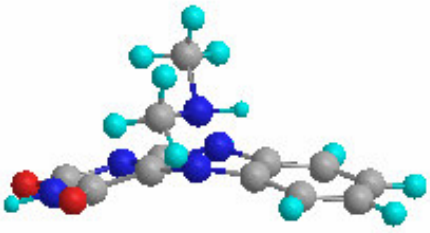
N,0,-0.5016647524,-2.5077148836,-0.6569610924
C,0,0.376868501,-1.5309977076,-0.2835678661
C,0,0.0216084954,-0.6485548549,0.7394931215
C,0,-1.1656218563,-0.9099660381,1.5414765935
N,0,-1.9524482827,-1.9764456407,1.0993043625
C,0,-1.7097854826,-2.7903292942,0.013395805
N,0,0.9558556015,0.2466526171,1.2196807675
C,0,2.2364652367,0.3357948379,0.6629169143
C,0,2.5544219285,-0.4872140175,-0.4355856058
N,0,1.5666024486,-1.4012399333,-0.9030832898
C,0,3.8062787627,-0.4197101753,-1.0409195317
C,0,4.763770941,0.4706852477,-0.5501890042
C,0,4.4602404385,1.2819077124,0.546685867
C,0,3.203828024,1.2165588568,1.1522119166
N,0,-1.4708203158,0.702238727,-0.6244325012

C,0,-1.2133064073,1.8999028886,-0.0004720444
O,0,-1.451538048,-0.255617151,2.5361901545
O,0,-2.4321617406,-3.6956234987,-0.3498869091
C,0,-0.9820314919,0.6319983226,-1.98637595
N,0,-3.0540568139,3.8618492666,-0.9010237587
C,0,-4.4489476956,3.4284835991,-0.6815056606
H,0,-2.0295994065,2.698667756,-0.4440754586
H,0,-1.4458918509,1.8874783649,1.0697181526
H,0,-0.2557282859,2.3984096809,-0.2323651164
H,0,4.0334942963,-1.0551952669,-1.8927943808
H,0,1.8191952227,-2.020421177,-1.663175282
H,0,-2.8173311812,-2.1477742006,1.6001696694
H,0,5.7358123735,0.5320678862,-1.0264325187
H,0,5.1998755143,1.9772937004,0.9288384785
H,0,2.9663766227,1.8567153477,1.9968514503
H,0,-0.9926690132,-0.3986396047,-2.3498179673
H,0,-1.6935757933,1.1816692657,-2.6231913091
H,0,0.0094499355,1.0844910827,-2.1398618507
H,0,-0.3048693382,-3.133280032,-1.4295750036
H,0,0.7414285512,0.6917509899,2.1038655102
H,0,-5.1748595478,4.1975412815,-0.966315624
H,0,-4.6410498064,2.5279642736,-1.2693079848
H,0,-4.5853931861,3.1879780617,0.3752623507
H,0,-2.8324987611,4.69053382,-0.3508099632
H,0,-2.8895795991,4.1039366312,-1.8771878608

PCM/B3LYP/6-31+G**//Onsager/B3LYP/6-31+G** = -985.708625232

N5 Adduct Structure (13)

NNadductPCMonOnsgr



Onsager/B3LYP/6-31+G**
E(RB+HF-LYP) = -889.356736098

Zero-point correction= 0.253205 (Hartree/Particle)

Thermal correction to Energy= 0.269035
Thermal correction to Enthalpy= 0.269979
Thermal correction to Gibbs Free Energy= 0.210107
Sum of electronic and zero-point Energies= -889.103531
Sum of electronic and thermal Energies= -889.087701
Sum of electronic and thermal Enthalpies= -889.086757
Sum of electronic and thermal Free Energies= -889.146629

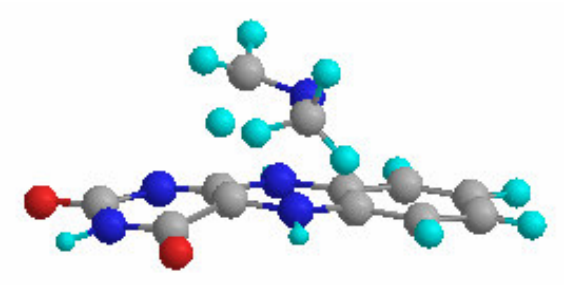
	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	168.822	62.612	126.012

C,0,-2.8048761325,0.5096887101,-0.9814224523
C,0,-1.6140106598,0.0551630963,-0.3998677522
C,0,-1.5601451118,-1.2211505146,0.1898078858
C,0,-2.7191598662,-2.0088435896,0.2329077313
C,0,-3.9106684331,-1.5270697891,-0.3072391487
C,0,-3.9584312613,-0.2720811006,-0.9271280305
N,0,-0.3344403098,-1.6691879117,0.6932916103
C,0,0.8525671822,-1.0763715612,0.2967503633
C,0,0.7858700068,0.2327684027,-0.2228807529
N,0,-0.4625960929,0.9246755755,-0.3431360836
C,0,1.9996180405,0.8023316437,-0.7441668702
N,0,3.0996257025,-0.0526384081,-0.606287199
C,0,3.1255517035,-1.3406104699,-0.0412160764
N,0,1.9444795364,-1.8444115919,0.4077059562
N,0,-0.7187077656,1.9430260046,0.7376185837
C,0,-0.1589222716,3.2747343238,0.331915682
O,0,2.1631717655,1.9286425665,-1.2418804217
O,0,4.2158946465,-1.9420123339,-0.003112287
C,0,-0.3233958595,1.5361918276,2.1263656417
H,0,-0.6456687556,2.3164529665,2.8175775379
H,0,-0.8151610308,0.5939657008,2.3663585511
H,0,0.7590723888,1.4201166149,2.1543325659
H,0,-2.6869520081,-2.9871199738,0.705419279
H,0,-0.2471716379,-2.6396622041,0.9670950034
H,0,3.9831574763,0.3161896176,-0.9322731816
H,0,-4.8089480134,-2.1331229203,-0.2470977238
H,0,-4.8856364118,0.0935769873,-1.3547416016
H,0,-2.8191035995,1.4797883276,-1.471695604
H,0,-0.6107134429,3.5461942547,-0.6206983452
H,0,-0.4125039869,4.0026829464,1.104555023
H,0,0.9156528619,3.1706208176,0.1939927099
H,0,-1.7410666521,2.02852345,0.7298100579

PCM/B3LYP/6-31+G**//Onsager/B3LYP/6-31+G**= -889.403859870

N5 Adduct Elimination Transition Structure (14)

NNelimTSPCMonOnsgr



PCM/B3LYP/6-31+G**//Onsager/B3LYP/6-31+G**
E(RB+HF-LYP) = -889.374434337

E(RB+HF-LYP) = -985.598013430

Zero-point correction=	0.323808 (Hartree/Particle)
Thermal correction to Energy=	0.345157
Thermal correction to Enthalpy=	0.346101
Thermal correction to Gibbs Free Energy=	0.272058
Sum of electronic and zero-point Energies=	-985.274206
Sum of electronic and thermal Energies=	-985.252856
Sum of electronic and thermal Enthalpies=	-985.251912
Sum of electronic and thermal Free Energies=	-985.325956

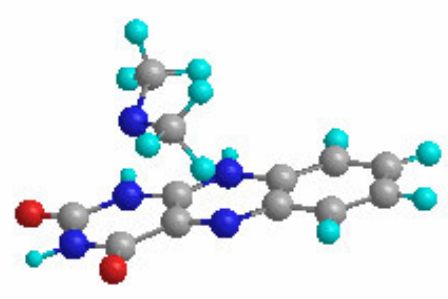
	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	216.589	79.588	155.837

N,0,-0.5016647524,-2.5077148836,-0.6569610924
C,0,0.376868501,-1.5309977076,-0.2835678661
C,0,0.0216084954,-0.6485548549,0.7394931215
C,0,-1.1656218563,-0.9099660381,1.5414765935
N,0,-1.9524482827,-1.9764456407,1.0993043625
C,0,-1.7097854826,-2.7903292942,0.013395805
N,0,0.9558556015,0.2466526171,1.2196807675
C,0,2.2364652367,0.3357948379,0.6629169143
C,0,2.5544219285,-0.4872140175,-0.4355856058
N,0,1.5666024486,-1.4012399333,-0.9030832898

C,0,3.8062787627,-0.4197101753,-1.0409195317
C,0,4.763770941,0.4706852477,-0.5501890042
C,0,4.4602404385,1.2819077124,0.546685867
C,0,3.203828024,1.2165588568,1.1522119166
N,0,-1.4708203158,0.702238727,-0.6244325012
C,0,-1.2133064073,1.8999028886,-0.0004720444
O,0,-1.451538048,-0.255617151,2.5361901545
O,0,-2.4321617406,-3.6956234987,-0.3498869091
C,0,-0.9820314919,0.6319983226,-1.98637595
N,0,-3.0540568139,3.8618492666,-0.9010237587
C,0,-4.4489476956,3.4284835991,-0.6815056606
H,0,-2.0295994065,2.698667756,-0.4440754586
H,0,-1.4458918509,1.8874783649,1.0697181526
H,0,-0.2557282859,2.3984096809,-0.2323651164
H,0,4.0334942963,-1.0551952669,-1.8927943808
H,0,1.8191952227,-2.020421177,-1.663175282
H,0,-2.8173311812,-2.1477742006,1.6001696694
H,0,5.7358123735,0.5320678862,-1.0264325187
H,0,5.1998755143,1.9772937004,0.9288384785
H,0,2.9663766227,1.8567153477,1.9968514503
H,0,-0.9926690132,-0.3986396047,-2.3498179673
H,0,-1.6935757933,1.1816692657,-2.6231913091
H,0,0.0094499355,1.0844910827,-2.1398618507
H,0,-0.3048693382,-3.133280032,-1.4295750036
H,0,0.7414285512,0.6917509899,2.1038655102
H,0,-5.1748595478,4.1975412815,-0.966315624
H,0,-4.6410498064,2.5279642736,-1.2693079848
H,0,-4.5853931861,3.1879780617,0.3752623507
H,0,-2.8324987611,4.69053382,-0.3508099632
H,0,-2.8895795991,4.1039366312,-1.8771878608

PCM/B3LYP/6-31+G**//Onsager/B3LYP/6-31+G**= -889.374434337

Concerted addition / elimination transition structure (15)



Onsager/B3LYP/6-31+G**
E(RB+HF-LYP) = -889.323140728

Zero-point correction=	0.244968 (Hartree/Particle)
Thermal correction to Energy=	0.261258
Thermal correction to Enthalpy=	0.262203
Thermal correction to Gibbs Free Energy=	0.201442
Sum of electronic and zero-point Energies=	-889.078173
Sum of electronic and thermal Energies=	-889.061882
Sum of electronic and thermal Enthalpies=	-889.060938
Sum of electronic and thermal Free Energies=	-889.121699

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	163.942	63.488	127.881

N,0,1.687686364,-1.6636540008,-0.1218151605
C,0,0.5172909904,-0.9505518665,-0.1959627861
C,0,0.4898509071,0.3718220592,-0.664424906
C,0,1.7670802148,0.9972796317,-1.0359810637
N,0,2.8889643495,0.144613301,-0.9358409634
C,0,2.9406744624,-1.1329928522,-0.43721708
N,0,-0.6499928568,1.1060166876,-0.7417389974
C,0,-1.8429920345,0.4179385115,-0.5145106881
C,0,-1.8768402725,-0.9185345113,-0.0543973478
N,0,-0.6359644296,-1.5572370332,0.1508113095
C,0,-3.0785185777,-1.5870917579,0.1831421068
C,0,-4.2824686658,-0.9190502351,-0.0327295896
C,0,-4.2759092668,0.407412752,-0.4894903413
C,0,-3.0733603541,1.0645814761,-0.7294467642
N,0,1.2255783127,1.2060151445,1.7544917388
C,0,0.2722083263,2.1908318434,1.5917794841
O,0,1.9198798627,2.1387232108,-1.4429685891
O,0,3.9672524877,-1.7817012481,-0.3018462943
C,0,0.8513547696,0.1768192145,2.7036802487

H,0,-0.5022168895,2.2759451839,2.3734496656
H,0,0.702992455,3.1638077875,1.3256458482
H,0,-0.3548855215,1.9503803514,0.5978554467
H,0,-3.0754790272,-2.6154704643,0.5359566157
H,0,-0.6383136358,-2.5193822721,0.4660395783
H,0,3.7835040194,0.5750651387,-1.131452529
H,0,-5.2207282893,-1.4313572318,0.1512003745
H,0,-5.2165516798,0.9212019182,-0.659662903
H,0,-3.0505748624,2.0892579996,-1.0862052907
H,0,1.5123550434,-0.6918321882,2.609703408
H,0,0.9695470946,0.5536065362,3.733967271
H,0,-0.1968236419,-0.16428838,2.6215602573
H,0,1.7081068521,-2.6154128595,0.2239021038

PCM/B3LYP/6-31+G**//Onsager/B3LYP/6-31+G**= -889.372291214

Methyl Amine

MeNH2PCMOnOnsgr

Onsager/B3LYP/6-31+G**
E(RB+HF-LYP) = -95.8728272351

Zero-point correction=	0.064091 (Hartree/Particle)
Thermal correction to Energy=	0.067517
Thermal correction to Enthalpy=	0.068462
Thermal correction to Gibbs Free Energy=	0.041160
Sum of electronic and zero-point Energies=	-95.808736
Sum of electronic and thermal Energies=	-95.805310
Sum of electronic and thermal Enthalpies=	-95.804366
Sum of electronic and thermal Free Energies=	-95.831667

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	42.368	9.549	57.460

C,0,-0.0096240992,-0.0166616027,-0.006805194
H,0,0.0108728194,-0.0118649523,1.0877658484
H,0,1.0291795437,-0.0118649648,-0.3523379453
H,0,-0.4701735501,-0.9619932286,-0.3324626869
N,0,-0.680674157,1.2000730704,-0.4813090488
H,0,-0.7060361797,1.220205834,-1.4972918182
H,0,-1.647005779,1.2202058456,-0.1665592821

PCM/B3LYP/6-31+G**//Onsager/B3LYP/6-31+G**= -95.8823274193

Dimethylammonium cation

Onsager/B3LYP/6-31+G**
E(RB+HF-LYP) = -135.549595166

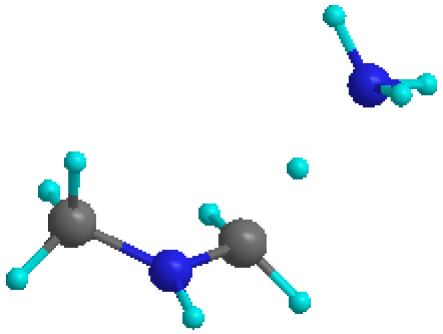
Zero-point correction=	0.108061 (Hartree/Particle)
Thermal correction to Energy=	0.112566
Thermal correction to Enthalpy=	0.113510
Thermal correction to Gibbs Free Energy=	0.082314
Sum of electronic and zero-point Energies=	-135.441534
Sum of electronic and thermal Energies=	-135.437029
Sum of electronic and thermal Enthalpies=	-135.436085
Sum of electronic and thermal Free Energies=	-135.467281

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	70.636	14.329	65.659

C,0,0.0211684799,-0.0366645191,-0.107075741
N,0,-0.0158153932,0.0273927847,1.4000044362
H,0,0.9439689237,-0.001270279,1.7615748547
C,0,-0.717369227,1.2425192524,1.9548973112
H,0,-0.4708846315,-0.8181364833,1.7615745112
H,0,-1.0046138458,-0.0504684373,-0.4754315739
H,0,0.5460142055,0.8447872206,-0.4754311975
H,0,0.5452629488,-0.9444225038,-0.4075622374
H,0,-0.6910070035,1.1968580906,3.0440334951
H,0,-0.1969844105,2.1317345237,1.5990865052
H,0,-1.7476445193,1.2364603573,1.5990861287

PCM/B3LYP/6-31+G**//Onsager/B3LYP/6-31+G**= -135.549595166

Proton transfer from N-methyliminium cation (16)



Onsager/B3LYP/6-31+G**
E(UB+HF-LYP) = -191.476490584

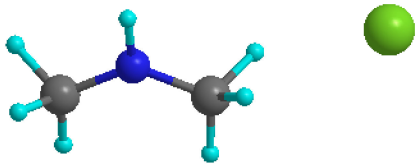
Zero-point correction=	0.125721 (Hartree/Particle)
Thermal correction to Energy=	0.132926
Thermal correction to Enthalpy=	0.133870
Thermal correction to Gibbs Free Energy=	0.093525
Sum of electronic and zero-point Energies=	-191.350769
Sum of electronic and thermal Energies=	-191.343565
Sum of electronic and thermal Enthalpies=	-191.342621
Sum of electronic and thermal Free Energies=	-191.382966

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	83.412	22.980	84.914

C,0,-1.8401033217,-0.7285420883,0.0149993847
N,0,-0.9859006688,0.39048659,-0.3466630977
C,0,0.1071983001,0.8141203189,0.3901223458
H,0,-1.8251720871,-0.8625637148,1.0979377865
H,0,-1.5006393283,-1.6546164381,-0.4675730731
H,0,-2.8624785302,-0.524446902,-0.313658981
H,0,-1.0888222505,0.7566936828,-1.2884686574
H,0,1.1757746694,0.1455648055,0.1139447108
H,0,0.4150588911,1.8329260629,0.1413350132
H,0,-0.0110351306,0.6422292824,1.4630436739
N,0,2.492082644,-0.4984039264,-0.1048922577
H,0,2.7098706398,-0.5517061598,-1.1006654464
H,0,3.2209564474,0.0528387942,0.3503136398

H,0,2.5166587254,-1.4420293074,0.2822729586

Hydrogen transfer from N-methyliminium cation (17)



Onsager/B3LYP/6-31+G**
E(UB+HF-LYP) = -595.016267136

Zero-point correction=	0.085071 (Hartree/Particle)
Thermal correction to Energy=	0.090719
Thermal correction to Enthalpy=	0.091663
Thermal correction to Gibbs Free Energy=	0.055639
Sum of electronic and zero-point Energies=	-594.931196
Sum of electronic and thermal Energies=	-594.925548
Sum of electronic and thermal Enthalpies=	-594.924604
Sum of electronic and thermal Free Energies=	-594.960628

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	56.927	18.951	75.820

C,0,-1.9803291504,-0.6618518578,0.0843745462
N,0,-0.9321582569,0.1020906104,-0.3808102588
C,0,0.1818677836,0.5607522214,0.3255901137
H,0,-1.9080573744,-1.0217310411,1.1100648786
H,0,-2.3592364662,-1.402619369,-0.6890633329
H,0,-2.9738081081,-0.0715788929,-0.0787548547
H,0,-1.0298910415,0.4251299495,-1.3581977406
H,0,1.2244145522,0.1178000503,-0.0208859093
H,0,0.3633589966,1.6132843956,0.0539539017
H,0,0.096870123,0.3666161242,1.3947445225
Cl,0,3.586927942,0.1906488095,0.2268591335

Table of Energies

*Gas Phase Energies B3LYP/6-31+G***

STRUCTURE	Energy	ZPE	Energy+ZPE
Dimethylamine	-135.1813	0.092352	-135.088924
Alloxazine Model for FAD (6)	-754.21	0.156272	-754.053742
$FADH^+$ Model (6-1-H^+)	-754.5727	0.169109	-754.403566
Hydride Transfer Transition Structure (7)	-889.347	0.246238	-889.100721
Hydride Transfer Transition Structure (8)	-889.7375	0.258069	-889.479411
complex FADH-MeNCH2+	-889.3713	0.253563	-889.117691
N-Methyl iminium cation	-134.3096	0.082373	-134.227206
$FADH^-$ Model (6-5H^-)	-754.8999	0.16589	-754.734011
$FADH_2$ Model (6-1,5-H_2)	-755.4254	0.179059	-755.24636
Dimethylamine cation radical (9)	-134.8815	0.090195	-134.791333
FAD Radical Anion Model ($6^{-\bullet}$)	-754.2883	0.153184	-754.135105
FADH radical model (6-5-$H^\bullet$)	-754.8143	0.167424	-754.646844
Methylaminomethyl radical (10)	-134.5237	0.076124	-134.447528
FAD-4a adduct model (11)	-889.3905	0.25241994	-889.13812

Energies of Structures using Onsager Solvent Model

PCM/B3LYP/6-31+G**//Onsager/B3LYP/6-31+G**

STRUCTURE	Energy	ZPE	Energy+ZPE
Dimethylamine	-135.1895	0.092337	-135.0971617
Alloxazine Model for FAD (6)	-754.2612	0.156236	-754.1049877
$FADH^+$ Model (6-1-H^+)	-754.7081	0.169054	-754.5390926
Hydride Transfer Transition Structure (7)	-889.4041	0.245574	-889.1585146
Hydride Transfer Transition Structure (8)	-889.8569	0.258017	-889.5989224
N-Methyl iminium cation	-134.4249	0.082363	-134.3425661
$FADH^-$ Model (6-5H^-)	-755.0057	0.165867	-754.8398119
$FADH_2$ Model (6-1,5-H_2)	-755.4705	0.178946	-755.2915079
Dimethylamine cation radical (9)	-134.9957	0.090218	-134.9054815
FAD Radical Anion Model ($6^{-\bullet}$)	-754.3961	0.153264	-754.2428472
FADH radical model (6-5-$H^\bullet$)	-754.8653	0.167439	-754.6978677
Methylaminomethyl radical (10)	-134.5313	0.076163	-134.4551726
N-N adduct zwitterion	-889.4039	0.253205	-889.1506549
FAD-4a adduct model higher energy conformer	-889.4281	0.252351	-889.1757613
FAD-4a adduct model (11)	-889.4312	0.252323	-889.178845

N5 Adduct Structure (13)	-889.4039	0.253205	-889.1506549
N5 Adduct Elimination Transition Structure (14)	-889.3744	0.245137	-889.1292973
Methyl ammonium	-96.35716	0.079363	-96.27779299
Elimination Transition Structure with Methylamine Base (12b)	-985.7086	0.323808	-985.3848172
Concerted addition / elimination transition structure (15)	-889.3723	0.244968	-889.1273232
Elimination Transition Structure with Methoxide Base (12a)	-1005.023	0.295844	-1004.726788
Methanol	-115.7452	0.051228	-115.6939812

Theoretical calculations: Exo Selective Diels-Alder Reactions of Vinylazepines. Origin of Divergent Stereoselectivity in Diels-Alder Reactions of Vinylazepines, Vinylpiperideines, and Vinylcycloalkenes-Appendix Material

Theoretical Structures

A. Endo, Azapene in chair, dienophile coming in from face opposite carbamate, OMe away from diene, file sevdatsaendofreq.log

B3LYP/6-31G*

SCF Done: E(RB+HF-LYP) = -993.996197909 A.U. after 1 cycles

Zero-point correction= 0.340532 (Hartree/Particle)
Thermal correction to Energy= 0.360568
Thermal correction to Enthalpy= 0.361512
Thermal correction to Gibbs Free Energy= 0.292111
Sum of electronic and zero-point Energies= -993.655666
Sum of electronic and thermal Energies= -993.635630
Sum of electronic and thermal Enthalpies= -993.634686
Sum of electronic and thermal Free Energies= -993.704087

E (Thermal) CV S

	KCAL/MOL	CAL/MOL-KELVIN	CAL/MOL-KELVIN
TOTAL	226.260	76.230	146.067

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.668658	1.860265	1.928827
2	6	0	-0.111717	0.635187	1.499330
3	6	0	0.331927	-0.351492	0.612472
4	7	0	1.502740	-0.149114	-0.189516
5	6	0	1.679201	1.100711	-0.952271
6	1	0	0.046108	2.417112	2.639860
7	1	0	1.529464	1.493112	2.513704
8	1	0	-0.767438	0.269534	2.279160
9	1	0	2.366797	0.882456	-1.768698
10	6	0	-0.433740	-1.507727	0.398537
11	6	0	-1.614997	-1.788969	1.086185
12	6	0	-2.402284	-3.043135	0.803357
13	1	0	0.712870	1.361056	-1.391854
14	1	0	-0.159123	-2.142204	-0.439591
15	1	0	-1.697468	-1.428397	2.108801
16	1	0	-1.971634	-3.884782	1.363076
17	1	0	-3.447672	-2.942363	1.110627
18	1	0	-2.395105	-3.295340	-0.259945
19	6	0	2.488814	-1.111925	-0.122084
20	8	0	2.417466	-2.154521	0.503863
21	8	0	3.580422	-0.754384	-0.852255
22	6	0	4.638620	-1.721769	-0.846512
23	1	0	4.299908	-2.670438	-1.271364
24	1	0	5.428453	-1.287960	-1.461338
25	6	0	1.173238	2.845231	0.861065
26	6	0	2.204544	2.274218	-0.117390
27	1	0	0.317682	3.230956	0.297684
28	1	0	1.621068	3.697538	1.388464
29	1	0	3.111209	1.952604	0.413216
30	1	0	2.510019	3.069472	-0.810360
31	6	0	-2.897152	-0.087150	0.559975
32	6	0	-2.195589	1.130841	0.649869
33	6	0	-1.917205	1.597396	-0.736891
34	7	0	-2.329766	0.554836	-1.573789
35	6	0	-3.088476	-0.404208	-0.885854
36	8	0	-3.747469	-1.281432	-1.408544

37	8	0	-1.446111	2.651726	-1.130049
38	1	0	-2.331639	0.632901	-2.582485
39	1	0	-3.645699	-0.417089	1.269697
40	1	0	-2.313268	1.863570	1.437773
41	1	0	4.997133	-1.897757	0.170917

B. Exo, Azapene in chair, dienophile coming in from face opposite carbamate, OMe away from diene, file sevdatsaexofreq.log

B3LYP/6-31G*

SCF Done: E(RB+HF-LYP) = -993.996921444 A.U. after 1 cycles

Zero-point correction= 0.340071 (Hartree/Particle)
Thermal correction to Energy= 0.360184
Thermal correction to Enthalpy= 0.361128
Thermal correction to Gibbs Free Energy= 0.291379
Sum of electronic and zero-point Energies= -993.656850
Sum of electronic and thermal Energies= -993.636738
Sum of electronic and thermal Enthalpies= -993.635794
Sum of electronic and thermal Free Energies= -993.705543

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	226.019	76.442	146.799

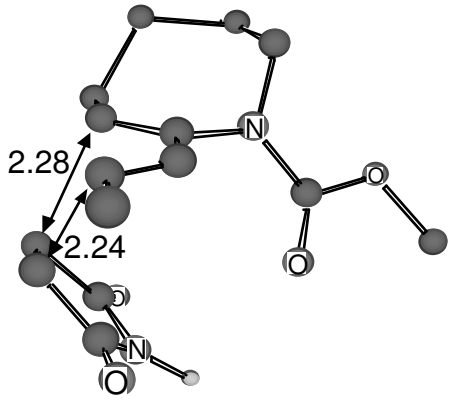
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.304402	2.003414	-1.140465
2	6	0	0.192653	0.618448	-0.778896
3	6	0	-0.593063	-0.395740	-0.220337
4	7	0	-1.898149	-0.093698	0.294084
5	6	0	-2.063763	0.999429	1.265067
6	1	0	0.528908	2.545820	-1.595665
7	1	0	-1.065332	1.882624	-1.929115
8	1	0	0.985456	0.265509	-1.429882
9	1	0	-2.955691	0.782373	1.853182
10	6	0	-0.068147	-1.673996	0.022712
11	6	0	1.227944	-2.055064	-0.303028
12	6	0	1.781332	-3.406308	0.056727

13	1	0	-1.205774	0.962593	1.947136
14	1	0	-0.664276	-2.345443	0.636153
15	1	0	1.704128	-1.582477	-1.158891
16	1	0	1.640047	-4.107251	-0.777761
17	1	0	2.857008	-3.346408	0.251727
18	1	0	1.281454	-3.826673	0.936016
19	6	0	-2.965895	-0.807507	-0.205992
20	8	0	-2.888944	-1.716205	-1.012422
21	8	0	-4.142989	-0.365912	0.317244
22	6	0	-5.299636	-1.075953	-0.146266
23	1	0	-5.240008	-2.133552	0.124028
24	1	0	-6.147166	-0.601633	0.350435
25	1	0	-5.395194	-0.992948	-1.231876
26	6	0	-0.881481	2.887752	-0.021311
27	6	0	-2.177569	2.386744	0.624691
28	1	0	-0.113697	3.034394	0.749288
29	1	0	-1.064507	3.881377	-0.449141
30	1	0	-2.988017	2.357925	-0.115535
31	1	0	-2.488360	3.097884	1.402287
32	6	0	2.357415	-0.536389	0.970584
33	6	0	1.835791	0.748243	0.748491
34	6	0	2.812630	1.503197	-0.094343
35	7	0	3.794545	0.571611	-0.452122
36	6	0	3.664150	-0.631363	0.260942
37	8	0	4.478934	-1.535804	0.255670
38	8	0	2.793863	2.671689	-0.434104
39	1	0	4.611571	0.806096	-1.000055
40	1	0	2.186861	-1.140416	1.850617
41	1	0	1.223140	1.295234	1.450762

C. Endo, Azapene in chair, dienophile coming in from face toward carbamate, OMe away from diene, file sevdatsbendofreq.log

B3LYP/6-31G*



33 (1.3)

SCF Done: E(RB+HF-LYP) = -994.002206198 A.U. after 1 cycles

Zero-point correction= 0.340302 (Hartree/Particle)
Thermal correction to Energy= 0.360258
Thermal correction to Enthalpy= 0.361202
Thermal correction to Gibbs Free Energy= 0.292422
Sum of electronic and zero-point Energies= -993.661905
Sum of electronic and thermal Energies= -993.641949
Sum of electronic and thermal Enthalpies= -993.641004
Sum of electronic and thermal Free Energies= -993.709784

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	226.065	76.354	144.759

Standard orientation:

Center Number	Atomic Number	Atomic Type		Coordinates (Angstroms) X	Y	Z
1	6	0	C	-1.120918	-2.272914	0.908113
2	6	0	C	-0.059999	-1.772963	-0.048194
3	6	0	C	-0.213725	-0.622101	-0.858684
4	7	0	N	-1.442954	0.110707	-0.783980
5	6	0	C	-2.661339	-0.585857	-1.241640
6	1	0	H	-0.713318	-3.144794	1.433541
7	1	0	H	-1.303183	-1.510963	1.675120
8	1	0	H	0.580608	-2.547395	-0.462030

9	1	0	H	-3.366765	0.171624	-1.583233
10	6	0	C	0.840783	-0.136986	-1.627194
11	6	0	C	2.101032	-0.756327	-1.675411
12	6	0	C	3.226582	-0.159558	-2.481450
13	1	0	H	-2.373340	-1.187138	-2.112560
14	1	0	H	0.731726	0.850508	-2.067803
15	1	0	H	2.123207	-1.840726	-1.593891
16	1	0	H	3.311912	0.916793	-2.311157
17	1	0	H	4.187504	-0.613425	-2.220907
18	1	0	H	3.059754	-0.332385	-3.554043
19	6	0	C	-1.461696	1.421638	-0.359559
20	8	0	O	-0.485049	2.087743	-0.062383
21	8	0	O	-2.732069	1.902677	-0.306566
22	6	0	C	-2.834896	3.265683	0.128890
23	1	0	H	-2.286134	3.930280	-0.543442
24	1	0	H	-3.901167	3.494561	0.107501
25	1	0	H	-2.439593	3.377131	1.141710
26	6	0	C	-2.462085	-2.670269	0.254278
27	6	0	C	-3.318456	-1.476254	-0.182946
28	1	0	H	-2.280175	-3.331501	-0.605471
29	1	0	H	-3.032113	-3.261369	0.982309
30	1	0	H	-3.568988	-0.857363	0.688234
31	1	0	H	-4.268583	-1.842457	-0.595489
32	6	0	C	2.720809	-0.758627	0.435482
33	6	0	C	1.650172	-1.232978	1.230211
34	6	0	C	1.063864	-0.057159	1.947554
35	7	0	N	1.783297	1.051108	1.503873
36	6	0	C	2.831153	0.717802	0.642680
37	8	0	O	3.643436	1.499735	0.184845
38	8	0	O	0.154615	-0.026284	2.758507
39	1	0	H	1.449302	1.998205	1.625312
40	1	0	H	3.616580	-1.328103	0.218072
41	1	0	H	1.635212	-2.203946	1.710978

D. Exo, Azapene in chair, dienophile coming in from face toward carbamate, OMe away from diene, file sevdatsbexofreq.log

B3LYP/6-31G*

SCF Done: E(RB+HF-LYP) = -994.002849254 A.U. after 16 cycles

Zero-point correction= 0.340139 (Hartree/Particle)
Thermal correction to Energy= 0.360227

Thermal correction to Enthalpy= 0.361171
Thermal correction to Gibbs Free Energy= 0.291429
Sum of electronic and zero-point Energies= -993.662710
Sum of electronic and thermal Energies= -993.642623
Sum of electronic and thermal Enthalpies= -993.641679
Sum of electronic and thermal Free Energies= -993.711420

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	226.046	76.373	146.784

Standard orientation:

Center Number	Atomic Number	Atomic Type		Coordinates (Angstroms) X	Y	Z
1	6	0	C	-0.712080	2.220176	0.077396
2	6	0	C	0.064651	1.039197	0.618396
3	6	0	C	-0.533551	-0.195092	0.886729
4	7	0	N	-1.924964	-0.361010	0.574492
5	6	0	C	-2.901229	0.378375	1.391228
6	1	0	H	-0.006978	3.032294	-0.117361
7	1	0	H	-1.150708	1.957466	-0.895034
8	1	0	H	0.949219	1.289150	1.198869
9	1	0	H	-3.847863	-0.163054	1.354788
10	6	0	C	0.195600	-1.328532	1.271186
11	6	0	C	1.577542	-1.345897	1.410964
12	6	0	C	2.337258	-2.601497	1.737894
13	1	0	H	-2.537912	0.341984	2.424606
14	1	0	H	-0.337397	-2.276961	1.277731
15	1	0	H	2.077578	-0.420584	1.686825
16	1	0	H	3.308376	-2.609050	1.231740
17	1	0	H	2.534212	-2.660658	2.817660
18	1	0	H	1.777599	-3.496623	1.446504
19	6	0	C	-2.256931	-1.049941	-0.567385
20	8	0	O	-1.455809	-1.569780	-1.327687
21	8	0	O	-3.602522	-1.083216	-0.756947
22	6	0	C	-4.021830	-1.796686	-1.928806
23	1	0	H	-3.721786	-2.846270	-1.871095
24	1	0	H	-5.109098	-1.710667	-1.945095
25	1	0	H	-3.587903	-1.352735	-2.828370
26	6	0	C	-1.850412	2.711630	1.000862
27	6	0	C	-3.110122	1.834052	0.953483
28	1	0	H	-1.484623	2.790938	2.034237

29	1	0	H	-2.127146	3.728117	0.693741
30	1	0	H	-3.516086	1.833655	-0.067031
31	1	0	H	-3.884669	2.271104	1.598452
32	6	0	C	2.102825	-0.760155	-0.735079
33	6	0	C	1.408359	0.412478	-1.059396
34	6	0	C	2.378350	1.551573	-0.996268
35	7	0	N	3.574098	0.999468	-0.519336
36	6	0	C	3.524352	-0.401922	-0.467820
37	8	0	O	4.477087	-1.124322	-0.237287
38	8	0	O	2.214640	2.725195	-1.273294
39	1	0	H	4.427031	1.531033	-0.408143
40	1	0	H	1.845241	-1.749886	-1.083659
41	1	0	H	0.565120	0.451945	-1.734033

E. Endo, Azapene in boat, dienophile coming in from face toward carbamate, OMe away from diene, file sevdtsaendofreq.log

B3LYP/6-31G*

SCF Done: E(RB+HF-LYP) = -993.998930180 A.U. after 1 cycles

Zero-point correction= 0.340287 (Hartree/Particle)
Thermal correction to Energy= 0.360260
Thermal correction to Enthalpy= 0.361204
Thermal correction to Gibbs Free Energy= 0.292577
Sum of electronic and zero-point Energies= -993.658643
Sum of electronic and thermal Energies= -993.638670
Sum of electronic and thermal Enthalpies= -993.637726
Sum of electronic and thermal Free Energies= -993.706353

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	226.067	76.379	144.438

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.190641	-2.161641	-1.163871
2	6	0	0.099419	-1.743927	-0.206265
3	6	0	0.310242	-0.678331	0.698574
4	7	0	1.489481	0.116143	0.560337

5	6	0	2.841940	-0.504309	0.629453
6	1	0	0.790607	-2.866593	-1.902011
7	1	0	1.518541	-1.281015	-1.725048
8	1	0	-0.512317	-2.559209	0.173245
9	1	0	3.396533	-0.243610	-0.278178
10	6	0	-0.697531	-0.286033	1.599996
11	6	0	-1.922937	-0.918092	1.715701
12	6	0	-3.025238	-0.377037	2.581226
13	1	0	3.374450	-0.044269	1.468664
14	1	0	-0.558455	0.652883	2.126676
15	1	0	-2.013795	-1.956927	1.418036
16	1	0	-2.672809	0.461916	3.190188
17	1	0	-3.850894	0.002859	1.965725
18	1	0	-3.425796	-1.150322	3.248020
19	6	0	1.397639	1.487803	0.414997
20	8	0	0.370829	2.143878	0.384021
21	8	0	2.633727	2.038762	0.310964
22	6	0	2.638989	3.459340	0.110447
23	1	0	3.692166	3.739018	0.063134
24	1	0	2.142140	3.969121	0.939747
25	6	0	2.388492	-2.805847	-0.434456
26	6	0	2.818627	-2.021811	0.817650
27	1	0	2.147463	-3.836430	-0.144161
28	1	0	3.228038	-2.869741	-1.138659
29	1	0	3.830644	-2.327453	1.109593
30	1	0	2.170313	-2.269940	1.666138
31	6	0	-1.500753	-1.101196	-1.390093
32	6	0	-2.652355	-0.843509	-0.634698
33	6	0	-2.892769	0.610331	-0.597297
34	7	0	-1.838724	1.181936	-1.334480
35	6	0	-0.986006	0.232890	-1.878382
36	8	0	-0.022301	0.460440	-2.588351
37	8	0	-3.803802	1.236528	-0.081529
38	1	0	-1.592038	2.160975	-1.274794
39	1	0	-1.384132	-1.969196	-2.029789
40	1	0	-3.446173	-1.544300	-0.413240
41	1	0	2.132189	3.717030	-0.823025

F. Exo, Azapene in boat, dienophile coming in from face toward carbamate, OMe away from diene, file sevdtsaexofreq.log

B3LYP/6-31G*

SCF Done: E(RB+HF-LYP) = -993.999726704 A.U. after 1 cycles

Zero-point correction= 0.339957 (Hartree/Particle)
Thermal correction to Energy= 0.360106
Thermal correction to Enthalpy= 0.361050
Thermal correction to Gibbs Free Energy= 0.291244
Sum of electronic and zero-point Energies= -993.659769
Sum of electronic and thermal Energies= -993.639621
Sum of electronic and thermal Enthalpies= -993.638676
Sum of electronic and thermal Free Energies= -993.708483

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	225.970	76.487	146.920

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.600097	2.303756	-0.244426
2	6	0	0.111075	1.148942	0.414129
3	6	0	-0.609703	0.007070	0.788938
4	7	0	-1.975591	-0.089305	0.368722
5	6	0	-2.992886	0.876028	0.856193
6	1	0	0.130022	3.004317	-0.658780
7	1	0	-1.187644	1.920595	-1.088086
8	1	0	0.975436	1.405554	1.021809
9	1	0	-3.575432	1.226495	-0.001675
10	6	0	0.008051	-1.122936	1.348796
11	6	0	1.374659	-1.222554	1.553927
12	6	0	2.032747	-2.478042	2.049420
13	1	0	-3.689008	0.346636	1.518488
14	1	0	-0.592908	-2.023188	1.447752
15	1	0	1.947215	-0.311353	1.704084
16	1	0	1.402918	-3.357303	1.878606
17	1	0	2.997594	-2.629735	1.552447
18	1	0	2.234719	-2.407325	3.127787
19	6	0	-2.317529	-1.082359	-0.522332
20	8	0	-1.539775	-1.857628	-1.053953

21	8	0	-3.656706	-1.087647	-0.752018
22	6	0	-4.095091	-2.070967	-1.700277
23	1	0	-5.174837	-1.936625	-1.776784
24	1	0	-3.618848	-1.912366	-2.671336
25	1	0	-3.857713	-3.078541	-1.349377
26	6	0	-1.554854	3.027743	0.734152
27	6	0	-2.388054	2.067445	1.605255
28	1	0	-0.982976	3.692038	1.393996
29	1	0	-2.222734	3.673199	0.149021
30	1	0	-3.221007	2.618519	2.058757
31	1	0	-1.782893	1.695044	2.439869
32	6	0	1.996578	-0.910328	-0.693446
33	6	0	1.410612	0.285848	-1.125516
34	6	0	2.481820	1.338778	-1.132089
35	7	0	3.610138	0.727470	-0.579058
36	6	0	3.430301	-0.657887	-0.407481
37	8	0	4.309756	-1.434620	-0.080007
38	8	0	2.424097	2.494284	-1.510058
39	1	0	4.504777	1.188953	-0.484766
40	1	0	1.641649	-1.903146	-0.927458
41	1	0	0.605087	0.342740	-1.845188

G. Endo, Azapene in twist, dienophile coming in from face toward carbamate, OMe away from diene, file sevdtsbendofreq.log

B3LYP/6-31G*

SCF Done: E(RB+HF-LYP) = -993.997848671 A.U. after 1 cycles

Zero-point correction= 0.340081 (Hartree/Particle)
Thermal correction to Energy= 0.360194
Thermal correction to Enthalpy= 0.361138
Thermal correction to Gibbs Free Energy= 0.291434
Sum of electronic and zero-point Energies= -993.657768
Sum of electronic and thermal Energies= -993.637655
Sum of electronic and thermal Enthalpies= -993.636711
Sum of electronic and thermal Free Energies= -993.706415

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	226.025	76.460	146.705

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.009617	-2.691505	-0.107611
2	6	0	-0.042539	-1.754526	-0.675211
3	6	0	0.139155	-0.427304	-1.092109
4	7	0	1.409526	0.205878	-0.907268
5	6	0	2.593748	-0.536255	-1.378169
6	1	0	0.498018	-3.377376	0.579100
7	1	0	1.366423	-3.331589	-0.932906
8	1	0	-0.832456	-2.291126	-1.191331
9	1	0	2.241528	-1.164651	-2.201270
10	6	0	-0.934494	0.320289	-1.604047
11	6	0	-2.226357	-0.186465	-1.740250
12	6	0	-3.349786	0.670719	-2.266025
13	1	0	3.309279	0.174654	-1.796252
14	1	0	-0.783441	1.387817	-1.731483
15	1	0	-2.334378	-1.249085	-1.941912
16	1	0	-3.303991	0.723227	-3.362885
17	1	0	-4.327450	0.257820	-1.998879
18	1	0	-3.300329	1.686235	-1.865610
19	6	0	1.525994	1.394770	-0.221965
20	8	0	0.608825	2.049250	0.243974
21	8	0	2.829780	1.769476	-0.128443
22	6	0	3.046888	3.002647	0.571580
23	1	0	4.126251	3.158380	0.551895
24	1	0	2.530848	3.827424	0.073367
25	1	0	2.689593	2.929236	1.601914
26	6	0	2.213697	-2.076040	0.626378
27	6	0	3.245939	-1.402149	-0.290714
28	1	0	1.844791	-1.367329	1.371569
29	1	0	2.712827	-2.872937	1.191491
30	1	0	3.869675	-2.155610	-0.791668
31	1	0	3.919905	-0.787345	0.316209
32	6	0	-1.688030	-1.483013	0.893729
33	6	0	-2.738749	-0.746141	0.328536
34	6	0	-2.721109	0.624572	0.927825
35	7	0	-1.607191	0.642680	1.769909
36	6	0	-0.975987	-0.597509	1.863648
37	8	0	-0.052501	-0.858834	2.614704
38	8	0	-3.493005	1.548627	0.756506
39	1	0	-1.208564	1.493480	2.143965
40	1	0	-1.689032	-2.554808	1.045773

41	1	0	-3.678541	-1.167022	-0.007071

H. Exo, Azapene in boat, dienophile coming in from face opposite carbamate, OMe away from diene, file sevdtsbexofreq.log

B3LYP/6-31G*

SCF Done: E(RB+HF-LYP) = -993.989360530 A.U. after 1 cycles

Zero-point correction= 0.339977 (Hartree/Particle)
Thermal correction to Energy= 0.360155
Thermal correction to Enthalpy= 0.361099
Thermal correction to Gibbs Free Energy= 0.291365
Sum of electronic and zero-point Energies= -993.649384
Sum of electronic and thermal Energies= -993.629206
Sum of electronic and thermal Enthalpies= -993.628262
Sum of electronic and thermal Free Energies= -993.697996

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	226.000	76.610	146.767

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.201358	-2.091083	-1.119885
2	6	0	-0.209250	-0.680320	-0.775472
3	6	0	0.683528	0.236653	-0.203539
4	7	0	2.022610	-0.146356	0.149809
5	6	0	2.392976	-1.423945	0.814218
6	1	0	-0.568089	-2.556317	-1.740795
7	1	0	1.113351	-2.031646	-1.733724
8	1	0	-0.966274	-0.242643	-1.415049
9	1	0	3.047567	-1.995736	0.146216
10	6	0	0.258666	1.538811	0.117456
11	6	0	-0.991860	2.050492	-0.200209
12	6	0	-1.418624	3.430628	0.219594
13	1	0	2.992104	-1.170039	1.694095
14	1	0	0.905353	2.134601	0.755014
15	1	0	-1.494243	1.668867	-1.085980
16	1	0	-0.897899	3.755017	1.126979

17	1	0	-1.191118	4.154827	-0.574987
18	1	0	-2.498705	3.468326	0.394165
19	6	0	3.041701	0.711584	-0.227554
20	8	0	2.911995	1.774776	-0.805907
21	8	0	4.251477	0.204432	0.133751
22	6	0	5.370195	1.026867	-0.225951
23	1	0	6.249312	0.489212	0.131788
24	1	0	5.418039	1.163039	-1.309387
25	1	0	5.299042	2.007631	0.251359
26	6	0	0.468717	-2.991673	0.103034
27	6	0	1.210789	-2.285188	1.249013
28	1	0	-0.486223	-3.381661	0.471991
29	1	0	1.051758	-3.861028	-0.226260
30	1	0	1.604263	-3.041168	1.939680
31	1	0	0.527507	-1.669797	1.844720
32	6	0	-2.317553	0.604499	0.971931
33	6	0	-1.918628	-0.711751	0.697649
34	6	0	-2.928077	-1.319679	-0.221476
35	7	0	-3.796240	-0.276760	-0.562035
36	6	0	-3.577581	0.868262	0.224815
37	8	0	-4.300999	1.847305	0.241344
38	8	0	-3.008306	-2.465376	-0.625851
39	1	0	-4.612294	-0.398832	-1.146777
40	1	0	-2.113310	1.148190	1.883441
41	1	0	-1.396192	-1.353057	1.390651

I. Endo, Azapene in chair, dienophile coming in from face opposite carbamate, OMe toward diene, file seveatsaendofreq.log

B3LYP/6-31G*

SCF Done: E(RB+HF-LYP) = -993.996921254 A.U. after 1 cycles

Zero-point correction= 0.340268 (Hartree/Particle)
Thermal correction to Energy= 0.360358
Thermal correction to Enthalpy= 0.361302
Thermal correction to Gibbs Free Energy= 0.291637
Sum of electronic and zero-point Energies= -993.656653
Sum of electronic and thermal Energies= -993.636564
Sum of electronic and thermal Enthalpies= -993.635619
Sum of electronic and thermal Free Energies= -993.705284

E (Thermal) CV S

	KCAL/MOL	CAL/MOL-KELVIN	CAL/MOL-KELVIN
TOTAL	226.128	76.298	146.622

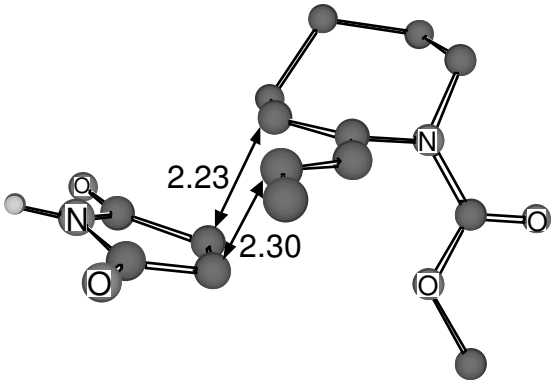
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.781630	-1.801342	1.918746
2	6	0	-0.054023	-0.554616	1.459627
3	6	0	-0.475394	0.301368	0.435525
4	7	0	-1.534687	-0.084546	-0.448318
5	6	0	-1.516712	-1.396401	-1.119126
6	1	0	-0.210612	-2.231042	2.750939
7	1	0	-1.736377	-1.463596	2.357443
8	1	0	0.484491	-0.065425	2.261844
9	1	0	-0.494888	-1.591559	-1.453428
10	6	0	0.225511	1.488228	0.169360
11	6	0	1.300608	1.939952	0.935167
12	6	0	2.020038	3.220637	0.594996
13	1	0	-2.154028	-1.296423	-1.998811
14	1	0	0.000643	2.001191	-0.762598
15	1	0	1.300033	1.692077	1.993978
16	1	0	1.481698	4.075964	1.026331
17	1	0	3.036461	3.232902	0.999604
18	1	0	2.095897	3.368013	-0.485196
19	6	0	-2.683328	0.666117	-0.588409
20	8	0	-3.628828	0.352697	-1.291342
21	8	0	-2.647732	1.802468	0.154445
22	6	0	-3.818211	2.622540	0.038903
23	1	0	-3.631746	3.482139	0.684234
24	1	0	-3.967248	2.944974	-0.994984
25	1	0	-4.706936	2.079566	0.371396
26	6	0	-1.066907	-2.921707	0.903492
27	6	0	-2.017841	-2.546055	-0.238906
28	1	0	-0.119152	-3.273729	0.484344
29	1	0	-1.502054	-3.761489	1.460770
30	1	0	-2.158652	-3.424846	-0.882006
31	1	0	-3.010277	-2.280603	0.150112
32	6	0	2.141294	-0.947923	0.873279
33	6	0	2.756862	0.310424	0.730139
34	6	0	3.083999	0.505020	-0.713312
35	7	0	2.479152	-0.573997	-1.373454
36	6	0	2.058458	-1.566292	-0.480790

37	8	0	1.723813	-2.691484	-0.809364
38	8	0	3.730669	1.382570	-1.250782
39	1	0	2.600019	-0.747277	-2.362971
40	1	0	2.227591	-1.590535	1.739968
41	1	0	3.394168	0.769783	1.475642

J. Exo, Azapene in chair, dienophile coming in from face toward carbamate, OMe toward diene, file seveatsbexofreq.log

B3LYP/6-31G*



34 (0.0)

SCF Done: E(RB+HF-LYP) = -994.003022199 A.U. after 1 cycles

Zero-point correction= 0.339982 (Hartree/Particle)
Thermal correction to Energy= 0.360090
Thermal correction to Enthalpy= 0.361034
Thermal correction to Gibbs Free Energy= 0.291336
Sum of electronic and zero-point Energies= -993.663040
Sum of electronic and thermal Energies= -993.642932
Sum of electronic and thermal Enthalpies= -993.641988
Sum of electronic and thermal Free Energies= -993.711687

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	225.960	76.442	146.693

Standard orientation:

Center Number	Atomic Number	Atomic Type		Coordinates (Angstroms) X	Y	Z
1	6	0	C	-0.901185	2.227742	-0.154172

2	6	0	C	-0.119578	1.115864	0.509839
3	6	0	C	-0.698644	-0.112941	0.847878
4	7	0	N	-2.074881	-0.332079	0.516991
5	6	0	C	-3.088146	0.448786	1.244838
6	1	0	H	-0.207440	3.037441	-0.394673
7	1	0	H	-1.304515	1.872862	-1.112535
8	1	0	H	0.723501	1.436862	1.116753
9	1	0	H	-2.764828	0.501892	2.290830
10	6	0	C	0.047484	-1.180306	1.369204
11	6	0	C	1.418441	-1.131194	1.584011
12	6	0	C	2.203489	-2.319738	2.063918
13	1	0	H	-4.017749	-0.122111	1.203214
14	1	0	H	-0.453677	-2.143204	1.443960
15	1	0	H	1.870120	-0.165848	1.798148
16	1	0	H	3.201235	-2.332433	1.612300
17	1	0	H	2.342844	-2.272364	3.153139
18	1	0	H	1.694550	-3.260723	1.829467
19	6	0	C	-2.500531	-1.166367	-0.490187
20	8	0	O	-3.666843	-1.377054	-0.772538
21	8	0	O	-1.451857	-1.726662	-1.154322
22	6	0	C	-1.831312	-2.633738	-2.200014
23	1	0	H	-0.893168	-2.988365	-2.628971
24	1	0	H	-2.408210	-3.470414	-1.797274
25	1	0	H	-2.430460	-2.122781	-2.957999
26	6	0	C	-2.078046	2.767449	0.691045
27	6	0	C	-3.314497	1.857131	0.681092
28	1	0	H	-1.745177	2.942527	1.723928
29	1	0	H	-2.366282	3.747479	0.290482
30	1	0	H	-4.118593	2.326178	1.264226
31	1	0	H	-3.689217	1.760914	-0.346669
32	6	0	C	1.336619	0.422586	-1.030603
33	6	0	C	2.053752	-0.694192	-0.581210
34	6	0	C	3.442362	-0.262684	-0.262081
35	7	0	N	3.446786	1.131958	-0.418587
36	6	0	C	2.264095	1.599862	-1.004096
37	8	0	O	2.076928	2.740028	-1.384542
38	8	0	O	4.403055	-0.929653	0.076944
39	1	0	H	4.273320	1.702857	-0.302492
40	1	0	H	0.537253	0.387025	-1.757486
41	1	0	H	1.857079	-1.719800	-0.858285

K. Endo, Azapene in boat, dienophile coming in from face toward carbamate, OMe toward diene, file sevetsaendofreq.log

B3LYP/6-31G*

SCF Done: E(RB+HF-LYP) = -993.996668846 A.U. after 1 cycles

Zero-point correction= 0.339918 (Hartree/Particle)
Thermal correction to Energy= 0.360126
Thermal correction to Enthalpy= 0.361070
Thermal correction to Gibbs Free Energy= 0.291310
Sum of electronic and zero-point Energies= -993.656751
Sum of electronic and thermal Energies= -993.636543
Sum of electronic and thermal Enthalpies= -993.635599
Sum of electronic and thermal Free Energies= -993.705359

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	225.982	76.571	146.822

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.769193	-1.839427	-1.084385
2	6	0	0.644932	-1.616219	-0.100770
3	6	0	0.619892	-0.457042	0.707324
4	7	0	1.598569	0.554462	0.480451
5	6	0	3.054737	0.246602	0.560216
6	1	0	1.515453	-2.662164	-1.762701
7	1	0	1.873126	-0.946496	-1.708829
8	1	0	0.264266	-2.518855	0.371459
9	1	0	3.471764	0.864697	1.362189
10	6	0	-0.425086	-0.245426	1.631291
11	6	0	-1.453885	-1.138165	1.864103
12	6	0	-2.625638	-0.803688	2.742859
13	1	0	3.528559	0.583675	-0.367890
14	1	0	-0.494340	0.736176	2.089815
15	1	0	-1.298615	-2.190025	1.652389
16	1	0	-2.484166	0.161466	3.240465
17	1	0	-3.546597	-0.726049	2.150590
18	1	0	-2.781859	-1.572083	3.509970
19	6	0	1.342202	1.900066	0.288167
20	8	0	2.222467	2.736140	0.186601

21	8	0	0.021614	2.190132	0.214474
22	6	0	-0.266809	3.574884	-0.029526
23	1	0	-1.355048	3.651080	-0.001305
24	1	0	0.179619	4.207020	0.741802
25	1	0	0.116605	3.880894	-1.006540
26	6	0	3.103870	-2.151415	-0.374388
27	6	0	3.372086	-1.224133	0.823625
28	1	0	3.114984	-3.193274	-0.029514
29	1	0	3.915765	-2.057655	-1.106933
30	1	0	2.812296	-1.565338	1.702683
31	1	0	4.431932	-1.281613	1.099274
32	6	0	-1.120132	-1.531172	-1.240064
33	6	0	-2.270266	-1.500604	-0.442830
34	6	0	-2.904306	-0.175848	-0.554017
35	7	0	-2.067337	0.563298	-1.411763
36	6	0	-1.013007	-0.185736	-1.917900
37	8	0	-0.194861	0.194316	-2.734493
38	8	0	-3.938532	0.243080	-0.060893
39	1	0	-2.211205	1.539406	-1.627935
40	1	0	-0.790727	-2.406574	-1.788391
41	1	0	-2.832625	-2.354011	-0.089156

L. Exo, Azapene in boat, dienophile coming in from face toward carbamate, OMe toward diene, file sevetsaexofreq.log

B3LYP/6-31G*

SCF Done: E(RB+HF-LYP) = -993.999567679 A.U. after 1 cycles

Zero-point correction= 0.339846 (Hartree/Particle)
Thermal correction to Energy= 0.360037
Thermal correction to Enthalpy= 0.360982
Thermal correction to Gibbs Free Energy= 0.291124
Sum of electronic and zero-point Energies= -993.659721
Sum of electronic and thermal Energies= -993.639530
Sum of electronic and thermal Enthalpies= -993.638586
Sum of electronic and thermal Free Energies= -993.708443

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	225.927	76.550	147.027

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.851644	2.253418	-0.423899
2	6	0	-0.099581	1.187196	0.331183
3	6	0	-0.769125	0.027000	0.748597
4	7	0	-2.118329	-0.155123	0.311177
5	6	0	-3.191010	0.772016	0.750430
6	1	0	-0.148203	2.965368	-0.864075
7	1	0	-1.391646	1.781657	-1.253997
8	1	0	0.719614	1.533482	0.956841
9	1	0	-3.843347	0.238695	1.453092
10	6	0	-0.110202	-1.023290	1.410207
11	6	0	1.247562	-1.021871	1.684072
12	6	0	1.960183	-2.196484	2.289733
13	1	0	-3.803818	1.011341	-0.124380
14	1	0	-0.664006	-1.948114	1.553813
15	1	0	1.753721	-0.067399	1.797755
16	1	0	1.396647	-3.125607	2.154056
17	1	0	2.954838	-2.314233	1.844807
18	1	0	2.108127	-2.042899	3.368117
19	6	0	-2.522375	-1.171901	-0.523533
20	8	0	-3.683169	-1.383100	-0.827347
21	8	0	-1.473401	-1.895792	-1.001782
22	6	0	-1.847482	-2.966743	-1.881121
23	1	0	-0.910894	-3.450094	-2.162370
24	1	0	-2.506585	-3.675295	-1.372687
25	1	0	-2.359269	-2.579789	-2.766095
26	6	0	-1.874764	2.987713	0.476466
27	6	0	-2.662655	2.048232	1.409805
28	1	0	-1.361974	3.739834	1.088876
29	1	0	-2.569460	3.537028	-0.171742
30	1	0	-2.046236	1.776968	2.275172
31	1	0	-3.530291	2.583047	1.814867
32	6	0	1.976956	-0.791603	-0.553367
33	6	0	1.327022	0.327943	-1.087185
34	6	0	2.320984	1.455516	-1.111312
35	7	0	3.456266	0.967475	-0.458749
36	6	0	3.368719	-0.414078	-0.208109
37	8	0	4.280585	-1.102435	0.214738
38	8	0	2.203233	2.574989	-1.572590
39	1	0	4.309120	1.500092	-0.351971
40	1	0	1.717377	-1.823610	-0.737004

41	1	0	0.557210	0.285389	-1.846017

M. Endo, Azapene in boat, dienophile coming in from face opposite carbamate, OMe toward diene, file sevetsbendofreq.log

B3LYP/6-31G*

SCF Done: E(RB+HF-LYP) = -993.984911557 A.U. after 1 cycles

Zero-point correction= 0.339849 (Hartree/Particle)
Thermal correction to Energy= 0.360059
Thermal correction to Enthalpy= 0.361004
Thermal correction to Gibbs Free Energy= 0.291249
Sum of electronic and zero-point Energies= -993.645062
Sum of electronic and thermal Energies= -993.624852
Sum of electronic and thermal Enthalpies= -993.623908
Sum of electronic and thermal Free Energies= -993.693663

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	225.941	76.681	146.811

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.470122	-2.106214	1.768498
2	6	0	-0.062130	-0.690159	1.472039
3	6	0	-0.649124	0.054084	0.455670
4	7	0	-1.706273	-0.510385	-0.338792
5	6	0	-1.650230	-1.839517	-1.001868
6	1	0	-0.025059	-2.433715	2.713683
7	1	0	-1.560741	-2.099746	1.925056
8	1	0	0.467434	-0.149894	2.241472
9	1	0	-1.795009	-1.677061	-2.075676
10	6	0	-0.207860	1.355535	0.157965
11	6	0	0.755477	2.050397	0.912232
12	6	0	1.022808	3.509510	0.596423
13	1	0	-2.513301	-2.422329	-0.661033
14	1	0	-0.553459	1.802016	-0.770581
15	1	0	0.764609	1.830662	1.979406
16	1	0	0.162238	4.120981	0.895194

17	1	0	1.897075	3.882778	1.139750
18	1	0	1.207387	3.659010	-0.470298
19	6	0	-2.923176	0.123873	-0.479317
20	8	0	-3.839319	-0.322600	-1.148420
21	8	0	-3.003516	1.285735	0.219574
22	6	0	-4.260239	1.965170	0.094022
23	1	0	-4.157645	2.871776	0.692080
24	1	0	-4.464738	2.215602	-0.950254
25	1	0	-5.076241	1.345538	0.475269
26	6	0	-0.132327	-3.128092	0.658088
27	6	0	-0.353303	-2.603257	-0.769873
28	1	0	0.915528	-3.428499	0.746241
29	1	0	-0.743491	-4.024081	0.825733
30	1	0	0.491434	-1.983348	-1.076996
31	1	0	-0.356030	-3.455823	-1.459949
32	6	0	2.481228	-0.265558	1.002813
33	6	0	2.487015	1.099182	0.641547
34	6	0	2.707815	1.150700	-0.856981
35	7	0	2.661039	-0.171830	-1.281447
36	6	0	2.688829	-1.082518	-0.198386
37	8	0	2.888479	-2.279481	-0.320446
38	8	0	2.888712	2.121062	-1.566426
39	1	0	2.860297	-0.450476	-2.233432
40	1	0	2.701421	-0.668614	1.982073
41	1	0	3.012119	1.844180	1.232447

N. Exo, Azapene in twist, dienophile coming in from face opposite carbamate, OMe toward diene, file sevetsbexofreq.log

B3LYP/6-31G*

SCF Done: E(RB+HF-LYP) = -993.990039733 A.U. after 1 cycles

Zero-point correction= 0.339940 (Hartree/Particle)
Thermal correction to Energy= 0.360142
Thermal correction to Enthalpy= 0.361086
Thermal correction to Gibbs Free Energy= 0.291223
Sum of electronic and zero-point Energies= -993.650100
Sum of electronic and thermal Energies= -993.629898
Sum of electronic and thermal Enthalpies= -993.628954
Sum of electronic and thermal Free Energies= -993.698816

E (Thermal) CV S

	KCAL/MOL	CAL/MOL-KELVIN	CAL/MOL-KELVIN
TOTAL	225.992	76.601	147.038

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.236392	-2.107554	-1.152843
2	6	0	-0.125917	-0.699144	-0.750060
3	6	0	0.782669	0.120932	-0.066145
4	7	0	2.075555	-0.376623	0.311449
5	6	0	2.322965	-1.670272	0.996956
6	1	0	-0.516642	-2.498261	-1.841641
7	1	0	1.184584	-2.058039	-1.709801
8	1	0	-0.821878	-0.181538	-1.400004
9	1	0	2.833886	-1.449387	1.940643
10	6	0	0.415227	1.414499	0.347362
11	6	0	-0.781925	2.030667	0.011197
12	6	0	-1.153089	3.394668	0.525715
13	1	0	3.032860	-2.245653	0.392514
14	1	0	1.059032	1.906222	1.072970
15	1	0	-1.254659	1.751812	-0.927640
16	1	0	-0.666333	3.610765	1.482981
17	1	0	-0.844355	4.168419	-0.191193
18	1	0	-2.237328	3.482667	0.648979
19	6	0	3.235949	0.308895	0.009144
20	8	0	4.344690	-0.073816	0.342825
21	8	0	3.017284	1.434257	-0.714992
22	6	0	4.206578	2.161413	-1.052676
23	1	0	3.861601	3.030183	-1.614860
24	1	0	4.740370	2.474693	-0.151501
25	1	0	4.874538	1.549492	-1.664594
26	6	0	0.392128	-3.090826	0.028295
27	6	0	1.069909	-2.492575	1.273130
28	1	0	-0.597950	-3.470888	0.304072
29	1	0	0.969649	-3.956976	-0.317965
30	1	0	0.366060	-1.881795	1.849617
31	1	0	1.366122	-3.308853	1.943353
32	6	0	-1.924652	-0.733590	0.612924
33	6	0	-2.258263	0.576269	0.983623
34	6	0	-3.453878	0.987168	0.196995
35	7	0	-3.694463	-0.066881	-0.701429
36	6	0	-2.911452	-1.190472	-0.413024

37	8	0	-3.034420	-2.287151	-0.926204
38	8	0	-4.114559	2.007488	0.264372
39	1	0	-4.480517	-0.083485	-1.337618
40	1	0	-1.484094	-1.466472	1.270772
41	1	0	-2.072385	1.024915	1.949206

O. Exo, Azapene in chair, dienophile coming in from face opposite carbamate, OMe toward diene, file sevexocsfreq.log

B3LYP/6-31G*

SCF Done: E(RB+HF-LYP) = -993.998488912 A.U. after 1 cycles

Zero-point correction= 0.340014 (Hartree/Particle)
Thermal correction to Energy= 0.360128
Thermal correction to Enthalpy= 0.361072
Thermal correction to Gibbs Free Energy= 0.291290
Sum of electronic and zero-point Energies= -993.658475
Sum of electronic and thermal Energies= -993.638361
Sum of electronic and thermal Enthalpies= -993.637417
Sum of electronic and thermal Free Energies= -993.707199

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	225.984	76.421	146.868

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	4.345042	-1.656525	0.226398
2	8	0	2.805993	2.549451	-0.751129
3	8	0	-4.237911	-0.130267	0.570254
4	8	0	-2.980387	-1.461698	-0.776161
5	7	0	3.710334	0.409781	-0.632136
6	7	0	-1.951537	0.092543	0.511480
7	1	0	4.501416	0.554364	-1.245423
8	6	0	3.573339	-0.715580	0.195688
9	6	0	2.319051	-0.492702	0.969598
10	1	0	2.176898	-1.007662	1.909310
11	6	0	1.048929	-2.055613	-0.094670
12	1	0	1.490971	-1.682131	-1.015447

13	6	0	-0.206153	-1.585289	0.271644
14	1	0	-0.786268	-2.167257	0.984928
15	6	0	-0.697027	-0.311253	-0.054950
16	6	0	-2.010994	1.241896	1.425682
17	1	0	-1.126898	1.198072	2.072548
18	1	0	-2.894610	1.098286	2.050139
19	6	0	-2.093565	2.591450	0.705898
20	1	0	-2.309583	3.365880	1.454385
21	1	0	-2.957569	2.563250	0.029241
22	6	0	-0.825127	2.980163	-0.061705
23	1	0	-0.991713	3.952833	-0.541348
24	1	0	0.003109	3.136820	0.641295
25	6	0	-0.370530	2.000725	-1.159695
26	1	0	0.450364	2.472932	-1.706403
27	1	0	-1.192146	1.868189	-1.882839
28	6	0	0.091335	0.619412	-0.741683
29	1	0	0.824002	0.185314	-1.414405
30	6	0	1.842173	0.791355	0.662937
31	1	0	1.298815	1.426901	1.347072
32	6	0	2.794820	1.417659	-0.304788
33	6	0	-3.150527	-0.473230	0.137675
34	6	0	-4.195585	-2.091725	-1.203820
35	1	0	-4.867580	-1.364373	-1.666975
36	1	0	-4.708746	-2.560575	-0.359966
37	1	0	-3.888334	-2.845048	-1.930452
38	6	0	1.564398	-3.396323	0.352010
39	1	0	1.094291	-3.718085	1.287519
40	1	0	2.650257	-3.369164	0.488851
41	1	0	1.352625	-4.158178	-0.411259

P. Endo, Azapene in chair, dienophile coming in from face toward carbamate, OMe toward diene, file seveatsbendofreq.log

B3LYP/6-31G*

SCF Done: E(RB+HF-LYP) = -994.000282476 A.U. after 1 cycles

Zero-point correction= 0.340043 (Hartree/Particle)
Thermal correction to Energy= 0.360210
Thermal correction to Enthalpy= 0.361155
Thermal correction to Gibbs Free Energy= 0.291164
Sum of electronic and zero-point Energies= -993.660240
Sum of electronic and thermal Energies= -993.640072

Sum of electronic and thermal Enthalpies= -993.639128
Sum of electronic and thermal Free Energies= -993.709118

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	226.035	76.454	147.308

Standard orientation:

Center Number	Atomic Number	Atomic Type		Coordinates (Angstroms) X	Y	Z
1	6	0	C	1.645936	-2.032797	-0.847036
2	6	0	C	0.563942	-1.677966	0.146827
3	6	0	C	0.515949	-0.470617	0.859515
4	7	0	N	1.596847	0.454866	0.708171
5	6	0	C	2.931416	0.000696	1.145718
6	1	0	H	1.375617	-2.987896	-1.313057
7	1	0	H	1.651491	-1.288974	-1.652910
8	1	0	H	0.065621	-2.522030	0.614057
9	1	0	H	2.790398	-0.597919	2.053776
10	6	0	C	-0.591600	-0.138978	1.660729
11	6	0	C	-1.691008	-0.969191	1.845191
12	6	0	C	-2.876721	-0.537949	2.667260
13	1	0	H	3.492701	0.897590	1.410742
14	1	0	H	-0.653143	0.882631	2.025788
15	1	0	H	-1.532086	-2.042553	1.791107
16	1	0	H	-3.060047	0.535777	2.574338
17	1	0	H	-3.790122	-1.054639	2.357206
18	1	0	H	-2.711061	-0.772158	3.728449
19	6	0	C	1.493286	1.772774	0.309852
20	8	0	O	2.435056	2.543441	0.243290
21	8	0	O	0.221420	2.119443	-0.003871
22	6	0	C	0.069272	3.475312	-0.448191
23	1	0	H	-1.005187	3.618144	-0.575452
24	1	0	H	0.459830	4.174229	0.295092
25	1	0	H	0.593845	3.631892	-1.394667
26	6	0	C	3.068105	-2.152171	-0.257795
27	6	0	C	3.702757	-0.802801	0.095419
28	1	0	H	3.051809	-2.801272	0.629673
29	1	0	H	3.701278	-2.656835	-0.998458
30	1	0	H	4.718697	-0.967466	0.479204
31	1	0	H	3.802865	-0.188804	-0.808928
32	6	0	C	-1.329825	-1.606550	-1.092953

33	6	0	C	-2.426076	-1.307685	-0.278616
34	6	0	C	-2.877661	0.080656	-0.587054
35	7	0	N	-1.968265	0.557444	-1.536695
36	6	0	C	-1.044612	-0.408245	-1.941344
37	8	0	O	-0.213847	-0.261367	-2.819049
38	8	0	O	-3.828238	0.701305	-0.149272
39	1	0	H	-1.974276	1.502554	-1.893160
40	1	0	H	-1.074192	-2.591327	-1.462184
41	1	0	H	-3.138204	-2.026620	0.105132

Piperidine transition structures

Table S2. Summary of Piperidine Transition Structures.[a]

Label	Endo	Exo	Axial Attack	Equatorial Attack	OMe Away	OMe Twrd	Energy + zpe (Hartrees)	Erel kcal/ mol	S(298)
A	√		√		√		-954.379800	0.4	142.307
B		√		√	√		-954.376286	2.6	142.389
C	√			√	√		-954.380509	0.0	139.151
D	√			√		√	-954.378522	1.2	140.825
E		√	√		√		-954.379719	0.5	141.822
F		√	√			√	-954.379102	0.9	141.813
G		√		√		√	-954.376107	2.8	141.921
H	√		√			√	-954.378303	1.4	142.252

A. Endo, axial attack of dienophile, OMe away from diene, file sixendocsfreq.log

B3LYP/6-31G*

SCF Done: E(RB+HF-LYP) = -954.691200947 A.U. after 1 cycles

Zero-point correction= 0.311401 (Hartree/Particle)
Thermal correction to Energy= 0.330344
Thermal correction to Enthalpy= 0.331288
Thermal correction to Gibbs Free Energy= 0.263673

Sum of electronic and zero-point Energies= -954.379800
Sum of electronic and thermal Energies= -954.360857
Sum of electronic and thermal Enthalpies= -954.359913
Sum of electronic and thermal Free Energies= -954.427528

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	207.294	71.609	142.307

Standard orientation:

Center Number	Atomic Number	Atomic Type		Coordinates (Angstroms) X	Y	Z
1	6	0	C	-2.545407	1.171961	-0.891170
2	7	0	N	-1.517515	0.111561	-0.850950
3	6	0	C	-0.183065	0.548054	-1.086283
4	6	0	C	0.178707	1.843495	-0.658186
5	6	0	C	-0.842803	2.865158	-0.193157
6	6	0	C	-2.210791	2.253228	0.134611
7	6	0	C	-1.795618	-1.147232	-0.345840
8	8	0	O	-3.129445	-1.324444	-0.166036
9	6	0	C	-3.493722	-2.604324	0.370126
10	6	0	C	0.795823	-0.331591	-1.585341
11	6	0	C	2.134159	0.013099	-1.706424
12	6	0	C	3.171904	-0.983380	-2.143667
13	8	0	O	-0.976674	-2.015180	-0.097684
14	6	0	C	1.528879	1.407871	0.952005
15	6	0	C	2.613365	0.636039	0.508008
16	6	0	C	2.476555	-0.736580	1.045329
17	7	0	N	1.250943	-0.738671	1.737276
18	6	0	C	0.661181	0.515763	1.799343
19	8	0	O	3.228379	-1.689408	0.956847
20	8	0	O	-0.355348	0.793177	2.412698
21	1	0	H	0.523928	-1.373343	-1.706400
22	1	0	H	1.016797	2.286437	-1.185749
23	1	0	H	2.401585	1.053987	-1.859864
24	1	0	H	3.583323	1.015797	0.214846
25	1	0	H	1.591640	2.462489	1.193062
26	1	0	H	-0.956012	3.604333	-1.001150
27	1	0	H	-0.460528	3.421914	0.670138
28	1	0	H	-2.189934	1.804806	1.131652
29	1	0	H	-2.984963	3.030037	0.127210
30	1	0	H	-3.514384	0.719161	-0.701384

31	1	0	H	-2.557611	1.589032	-1.906814
32	1	0	H	-3.048962	-2.749781	1.357871
33	1	0	H	-4.581935	-2.585955	0.440427
34	1	0	H	-3.164091	-3.408744	-0.292103
35	1	0	H	0.796589	-1.583058	2.058588
36	1	0	H	3.336857	-0.910115	-3.228374
37	1	0	H	2.870434	-2.006838	-1.906347
38	1	0	H	4.132968	-0.802904	-1.652615

B. Exo, equatorial attack of dienophile, OMe away from diene, file sixexocsfreq.log

B3LYP/6-31G*

SCF Done: E(RB+HF-LYP) = -954.687737448 A.U. after 1 cycles

Zero-point correction= 0.311451 (Hartree/Particle)
Thermal correction to Energy= 0.330424
Thermal correction to Enthalpy= 0.331368
Thermal correction to Gibbs Free Energy= 0.263715
Sum of electronic and zero-point Energies= -954.376286
Sum of electronic and thermal Energies= -954.357313
Sum of electronic and thermal Enthalpies= -954.356369
Sum of electronic and thermal Free Energies= -954.424023

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	207.344	71.652	142.389

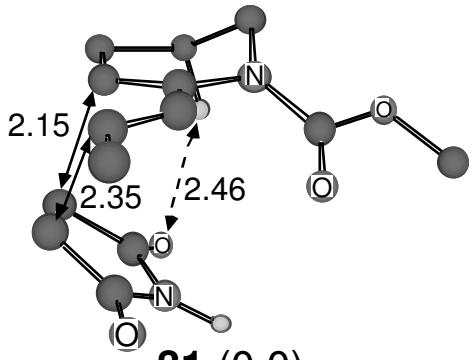
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.073981	-1.673701	-0.521955
2	7	0	1.950352	-0.272641	-0.077341
3	6	0	0.675836	0.124137	0.426745
4	6	0	-0.253744	-0.881238	0.757633
5	6	0	0.113810	-2.345169	0.900100
6	6	0	1.590244	-2.616367	0.578365
7	6	0	3.042896	0.572839	-0.019402
8	8	0	4.150988	-0.009645	-0.550587
9	6	0	5.328247	0.809864	-0.511188
10	6	0	0.259273	1.467555	0.357463

11	6	0	-1.035898	1.877093	0.645512
12	6	0	-1.479842	3.302366	0.463416
13	8	0	3.047894	1.700948	0.439318
14	6	0	-2.127034	0.670033	-0.963930
15	6	0	-3.490296	0.734453	-0.380494
16	7	0	-3.752209	-0.557760	0.114573
17	6	0	-2.789865	-1.479843	-0.305643
18	6	0	-1.681285	-0.662720	-0.893020
19	8	0	-4.261194	1.674352	-0.302921
20	8	0	-2.870654	-2.689146	-0.186080
21	1	0	0.930036	2.186080	-0.096818
22	1	0	-1.054577	-0.557062	1.410453
23	1	0	-1.830615	1.394442	-1.708973
24	1	0	-1.024663	-1.131016	-1.614372
25	1	0	-0.543885	-2.947152	0.261492
26	1	0	-0.113523	-2.666668	1.924362
27	1	0	2.215456	-2.458388	1.465641
28	1	0	1.733143	-3.656054	0.262961
29	1	0	3.112776	-1.859130	-0.778751
30	1	0	1.473619	-1.807128	-1.431911
31	1	0	5.588912	1.064127	0.519305
32	1	0	6.113123	0.205377	-0.967372
33	1	0	5.175611	1.732214	-1.077180
34	1	0	-4.641157	-0.826112	0.515094
35	1	0	-0.870881	3.822707	-0.283331
36	1	0	-1.391529	3.851129	1.411520
37	1	0	-2.531362	3.344153	0.160774
38	1	0	-1.621686	1.313413	1.367035

C. Endo, equatorial attack of dienophile, OMe away from diene, file Sul6njEn

B3LYP/6-31G*



31 (0.0)

SCF Done: E(RB+HF-LYP) = -954.691958379 A.U. after 1 cycles

Zero-point correction= 0.311449 (Hartree/Particle)
Thermal correction to Energy= 0.330240
Thermal correction to Enthalpy= 0.331184
Thermal correction to Gibbs Free Energy= 0.265069
Sum of electronic and zero-point Energies= -954.380509
Sum of electronic and thermal Energies= -954.361719
Sum of electronic and thermal Enthalpies= -954.360774
Sum of electronic and thermal Free Energies= -954.426890

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	207.229	71.671	139.151

Standard orientation:

Center Number	Atomic Number	Atomic Type		Coordinates (Angstroms) X	Y	Z
1	6	0	C	0.685614	0.316993	-1.823545
2	6	0	C	1.514371	1.348161	-1.083422
3	6	0	C	2.662198	0.684835	-0.618837
4	6	0	C	2.582692	-0.732817	-0.963858
5	7	0	N	1.345070	-0.882188	-1.639715
6	8	0	O	3.374524	-1.642702	-0.770829
7	8	0	O	-0.363270	0.479673	-2.426788
8	6	0	C	0.224364	1.853828	0.396582
9	6	0	C	-0.207404	0.613818	0.933557
10	7	0	N	-1.518769	0.182158	0.628006

11	6	0	C	-2.612492	1.179189	0.461202
12	6	0	C	-2.111912	2.611282	0.614008
13	6	0	C	-0.820215	2.779715	-0.196473
14	6	0	C	-1.798511	-1.142212	0.318002
15	8	0	O	-0.993861	-2.051969	0.232128
16	6	0	C	0.705467	-0.231004	1.605172
17	6	0	C	2.028284	0.089041	1.820245
18	6	0	C	3.015982	-0.901421	2.360023
19	8	0	O	-3.128338	-1.305455	0.114576
20	6	0	C	-3.516692	-2.634664	-0.263117
21	1	0	H	0.385254	-1.239896	1.834650
22	1	0	H	0.994416	2.352802	0.977389
23	1	0	H	2.351761	1.122635	1.785306
24	1	0	H	3.588609	1.139179	-0.294854
25	1	0	H	1.532295	2.363526	-1.467524
26	1	0	H	-1.015702	2.508981	-1.240681
27	1	0	H	-0.466289	3.816045	-0.178924
28	1	0	H	-1.927768	2.850816	1.668773
29	1	0	H	-2.900237	3.286432	0.261054
30	1	0	H	-3.399946	0.956730	1.188204
31	1	0	H	-3.037244	1.045678	-0.537167
32	1	0	H	-3.238689	-3.352415	0.512642
33	1	0	H	-4.600155	-2.594520	-0.380066
34	1	0	H	-3.039783	-2.921503	-1.203658
35	1	0	H	0.936888	-1.781410	-1.857310
36	1	0	H	3.663703	-1.267082	1.550309
37	1	0	H	2.510201	-1.775539	2.783435
38	1	0	H	3.655671	-0.455079	3.130446

D. Endo, equatorial attack of dienophile, OMe toward diene, file Sul6njEnOrot

B3LYP/6-31G*

SCF Done: E(RB+HF-LYP) = -954.689699049 A.U. after 17 cycles

Zero-point correction= 0.311177 (Hartree/Particle)
Thermal correction to Energy= 0.330138
Thermal correction to Enthalpy= 0.331082
Thermal correction to Gibbs Free Energy= 0.264172
Sum of electronic and zero-point Energies= -954.378522
Sum of electronic and thermal Energies= -954.359561
Sum of electronic and thermal Enthalpies= -954.358617
Sum of electronic and thermal Free Energies= -954.425527

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	207.165	71.831	140.825

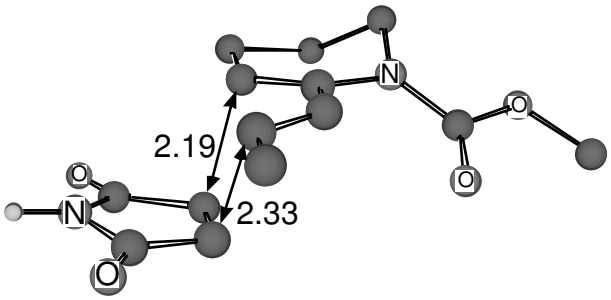
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.423787	-2.586746	-0.099925
2	6	0	0.269917	-1.820200	0.511065
3	6	0	0.504142	-0.483523	0.920281
4	7	0	1.716604	0.117734	0.517296
5	6	0	2.961700	-0.696643	0.428777
6	6	0	2.698013	-2.181073	0.655177
7	6	0	-0.501556	0.239823	1.605281
8	6	0	-1.730976	-0.280872	1.940807
9	6	0	-2.842308	0.566037	2.485664
10	6	0	1.917760	1.438511	0.136214
11	8	0	0.774982	2.147955	0.000599
12	6	0	0.968701	3.510203	-0.415127
13	8	0	3.024295	1.896070	-0.081810
14	6	0	-1.223152	-1.711145	-0.885532
15	6	0	-0.661223	-0.665395	-1.824413
16	7	0	-1.488859	0.434037	-1.678129
17	6	0	-2.622959	0.164983	-0.872683
18	6	0	-2.424150	-1.195661	-0.375524
19	8	0	0.318703	-0.738471	-2.545723
20	8	0	-3.541796	0.950702	-0.696598
21	1	0	-0.346833	1.300658	1.760538
22	1	0	-0.355497	-2.398098	1.185029
23	1	0	-1.867874	-1.353740	2.002077
24	1	0	-3.227751	-1.751883	0.087031
25	1	0	-1.085882	-2.755633	-1.146805
26	1	0	1.531404	-2.325560	-1.159649
27	1	0	1.243721	-3.665142	-0.037272
28	1	0	2.582642	-2.400677	1.723985
29	1	0	3.571394	-2.741778	0.302655
30	1	0	3.683891	-0.300750	1.149927
31	1	0	3.382567	-0.538020	-0.567715
32	1	0	1.442048	3.547026	-1.399452
33	1	0	-0.031887	3.942693	-0.451177
34	1	0	1.595062	4.047810	0.300968

35	1	0	-1.333535	1.317069	-2.143743
36	1	0	-3.600596	0.739291	1.708630
37	1	0	-2.475837	1.548915	2.800664
38	1	0	-3.336888	0.085579	3.338015

E. Exo, axial attack of dienophile, OMe away from diene, file Sul6njEx

B3LYP/6-31G*



32 (0.2)

SCF Done: E(RB+HF-LYP) = -954.691178879 A.U. after 17 cycles

Zero-point correction= 0.311460 (Hartree/Particle)
Thermal correction to Energy= 0.330328
Thermal correction to Enthalpy= 0.331273
Thermal correction to Gibbs Free Energy= 0.263888
Sum of electronic and zero-point Energies= -954.379719
Sum of electronic and thermal Energies= -954.360851
Sum of electronic and thermal Enthalpies= -954.359906
Sum of electronic and thermal Free Energies= -954.427291

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	207.284	71.523	141.822

Standard orientation:

Center Number	Atomic Number	Atomic Type		Coordinates (Angstroms) X	Y	Z
1	6	0	C	-1.371337	0.603427	-0.921278
2	6	0	C	-1.854974	-0.715400	-0.904729
3	6	0	C	-3.307365	-0.679360	-0.611650
4	7	0	N	-3.607447	0.672808	-0.353252
5	6	0	C	-2.536784	1.512376	-0.666227

6	8	0	O	-4.118867	-1.587092	-0.572023
7	8	0	O	-2.582166	2.729346	-0.699025
8	6	0	C	-0.223738	1.036340	0.888376
9	6	0	C	0.651177	-0.066729	0.874638
10	7	0	N	2.020619	0.164050	0.550263
11	6	0	C	2.550977	1.491671	0.918657
12	6	0	C	1.689789	2.582792	0.281981
13	6	0	C	0.254317	2.468921	0.804832
14	6	0	C	2.731599	-0.697369	-0.269684
15	8	0	O	2.303505	-1.715797	-0.782132
16	6	0	C	0.151890	-1.374999	1.014705
17	6	0	C	-1.201637	-1.661512	1.120999
18	6	0	C	-1.722590	-3.070458	1.156465
19	8	0	O	4.011736	-0.273617	-0.440160
20	6	0	C	4.811354	-1.120127	-1.278823
21	1	0	H	0.830736	-2.199473	0.837126
22	1	0	H	-1.120174	0.910192	1.486460
23	1	0	H	-1.426334	-1.553289	-1.435118
24	1	0	H	-0.569798	0.955124	-1.558266
25	1	0	H	0.205793	2.895580	1.818541
26	1	0	H	-0.445885	3.058134	0.202059
27	1	0	H	1.720982	2.464678	-0.808840
28	1	0	H	2.102246	3.572577	0.510353
29	1	0	H	3.587116	1.550784	0.598288
30	1	0	H	2.527128	1.577605	2.012852
31	1	0	H	4.379756	-1.192926	-2.280259
32	1	0	H	5.790880	-0.642020	-1.317143
33	1	0	H	4.889728	-2.123046	-0.851700
34	1	0	H	-4.543876	1.008649	-0.172647
35	1	0	H	-1.009830	-3.775294	0.716240
36	1	0	H	-2.674411	-3.142359	0.618553
37	1	0	H	-1.914584	-3.382237	2.193074
38	1	0	H	-1.871415	-0.920841	1.548498

F. Exo, axial attack of dienophile, OMe toward diene, file Sul6njExOrot

B3LYP/6-31G*

SCF Done: E(RB+HF-LYP) = -954.690402930 A.U. after 1 cycles

Zero-point correction= 0.311300 (Hartree/Particle)
Thermal correction to Energy= 0.330179
Thermal correction to Enthalpy= 0.331123

Thermal correction to Gibbs Free Energy= 0.263743
Sum of electronic and zero-point Energies= -954.379102
Sum of electronic and thermal Energies= -954.360224
Sum of electronic and thermal Enthalpies= -954.359280
Sum of electronic and thermal Free Energies= -954.426660

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	207.190	71.528	141.813

Standard orientation:

Center Number	Atomic Number	Atomic Type		Coordinates (Angstroms) X	Y	Z
1	6	0	C	0.404122	2.601111	0.627329
2	6	0	C	-0.093744	1.186424	0.840340
3	6	0	C	0.776690	0.083747	0.947775
4	7	0	N	2.143224	0.275187	0.596906
5	6	0	C	2.692244	1.615207	0.875725
6	6	0	C	1.857286	2.663419	0.138994
7	6	0	C	0.279272	-1.197751	1.242586
8	6	0	C	-1.073767	-1.475989	1.362803
9	6	0	C	-1.602476	-2.869369	1.546358
10	6	0	C	2.881769	-0.514618	-0.273545
11	8	0	O	2.181097	-1.568689	-0.756862
12	6	0	C	2.922731	-2.415054	-1.650071
13	8	0	O	4.036195	-0.283837	-0.586032
14	6	0	C	-1.206262	0.579653	-0.910284
15	6	0	C	-1.691720	-0.733268	-0.781546
16	6	0	C	-3.146910	-0.677095	-0.519795
17	7	0	N	-3.456661	0.692661	-0.399300
18	6	0	C	-2.382953	1.504051	-0.768360
19	8	0	O	-3.955430	-1.581691	-0.405858
20	8	0	O	-2.429855	2.711307	-0.919043
21	1	0	H	0.966634	-2.034559	1.187767
22	1	0	H	-0.990153	1.132873	1.450096
23	1	0	H	-1.247691	-1.618289	-1.213061
24	1	0	H	-0.401206	0.870471	-1.573661
25	1	0	H	0.328288	3.120788	1.594641
26	1	0	H	-0.274416	3.134791	-0.047447
27	1	0	H	1.918475	2.464153	-0.938648
28	1	0	H	2.269495	3.666015	0.302455
29	1	0	H	3.733412	1.613012	0.558413

30	1	0	H	2.656998	1.782243	1.959305
31	1	0	H	3.808158	-2.819894	-1.153948
32	1	0	H	2.234645	-3.216158	-1.922623
33	1	0	H	3.235127	-1.858626	-2.537253
34	1	0	H	-4.397239	1.039838	-0.268116
35	1	0	H	-0.879084	-3.624266	1.220914
36	1	0	H	-2.533560	-3.001404	0.983558
37	1	0	H	-1.837530	-3.056127	2.603818
38	1	0	H	-1.750038	-0.689328	1.683058

G. Exo, equatorial attack of dienophile, OMe toward diene, file SuljenExOrot

B3LYP/6-31G*

SCF Done: E(RB+HF-LYP) = -954.687505873 A.U. after 16 cycles

Zero-point correction= 0.311399 (Hartree/Particle)
Thermal correction to Energy= 0.330361
Thermal correction to Enthalpy= 0.331306
Thermal correction to Gibbs Free Energy= 0.263875
Sum of electronic and zero-point Energies= -954.376107
Sum of electronic and thermal Energies= -954.357144
Sum of electronic and thermal Enthalpies= -954.356200
Sum of electronic and thermal Free Energies= -954.423631

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	207.305	71.585	141.921

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.752788	-0.674129	0.827200
2	6	0	2.100078	0.684042	0.951145
3	6	0	3.400626	0.893147	0.262285
4	7	0	3.711658	-0.338425	-0.341756
5	6	0	2.859990	-1.360003	0.090541
6	8	0	4.088400	1.895532	0.187756
7	8	0	3.018838	-2.547975	-0.123849
8	6	0	0.192076	-0.906471	-0.713972
9	6	0	-0.767244	0.009034	-0.240579

10	7	0	-1.961878	-0.513997	0.337753
11	6	0	-1.912063	-1.916991	0.779161
12	6	0	-1.476188	-2.808464	-0.382737
13	6	0	-0.090100	-2.384288	-0.900704
14	6	0	-3.213181	0.075456	0.282390
15	8	0	-4.225736	-0.430047	0.735032
16	6	0	-0.436619	1.367846	-0.093650
17	6	0	0.795281	1.899859	-0.452595
18	6	0	1.148601	3.339165	-0.193085
19	8	0	-3.197377	1.276951	-0.340734
20	6	0	-4.478664	1.918583	-0.431234
21	1	0	-1.105021	1.989628	0.492121
22	1	0	0.918996	-0.496143	-1.404519
23	1	0	1.824645	1.328296	1.774054
24	1	0	1.198669	-1.238004	1.565600
25	1	0	0.705970	-2.960314	-0.413732
26	1	0	0.000931	-2.623706	-1.968280
27	1	0	-2.227588	-2.722347	-1.176825
28	1	0	-1.463997	-3.857067	-0.064933
29	1	0	-2.905229	-2.174366	1.142795
30	1	0	-1.207977	-1.995813	1.617191
31	1	0	-4.895255	2.094391	0.563730
32	1	0	-4.289489	2.863684	-0.941577
33	1	0	-5.177017	1.305155	-1.006041
34	1	0	4.577603	-0.508931	-0.835572
35	1	0	0.582394	3.748195	0.650704
36	1	0	0.924501	3.951429	-1.077835
37	1	0	2.218975	3.444278	0.011787
38	1	0	1.345136	1.442195	-1.271297

H. Endo, axial attack of dienophile, OMe toward diene, file SulnjEnOrot

B3LYP/6-31G*

E(RB+HF-LYP) = -954.689546581

Zero-point correction= 0.311244 (Hartree/Particle)
Thermal correction to Energy= 0.330276
Thermal correction to Enthalpy= 0.331221
Thermal correction to Gibbs Free Energy= 0.263632
Sum of electronic and zero-point Energies= -954.378303
Sum of electronic and thermal Energies= -954.359270
Sum of electronic and thermal Enthalpies= -954.358326

Sum of electronic and thermal Free Energies= -954.425914

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	207.252	71.708	142.252

Standard orientation:

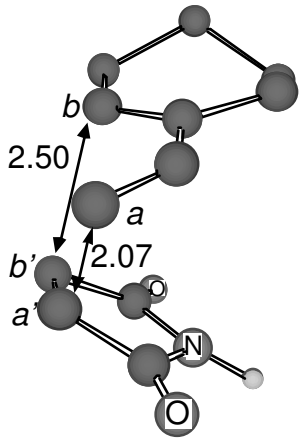
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.606419	-1.122337	1.721702
2	6	0	-1.324258	-1.827344	0.617835
3	6	0	-2.399170	-1.024660	0.214885
4	6	0	-2.371581	0.228925	1.018797
5	7	0	-1.221877	0.126989	1.815732
6	8	0	-3.147458	1.166471	1.028089
7	8	0	0.315399	-1.510791	2.416912
8	6	0	0.316508	-1.737094	-0.903053
9	6	0	0.456393	-0.350730	-1.103346
10	7	0	1.690815	0.257162	-0.738732
11	6	0	2.879661	-0.612156	-0.832740
12	6	0	2.676106	-1.845646	0.043924
13	6	0	1.450610	-2.629764	-0.445050
14	6	0	1.888078	1.494766	-0.144320
15	8	0	2.986141	1.956636	0.111387
16	6	0	-0.638347	0.405052	-1.567826
17	6	0	-1.892851	-0.141105	-1.810357
18	6	0	-3.057722	0.723631	-2.216109
19	8	0	0.733567	2.143398	0.136632
20	6	0	0.905196	3.441017	0.728698
21	1	0	-0.551953	1.484454	-1.561476
22	1	0	-0.400396	-2.230477	-1.549273
23	1	0	-1.960390	-1.178632	-2.123258
24	1	0	-3.335828	-1.383105	-0.191513
25	1	0	-1.303812	-2.908862	0.575462
26	1	0	1.733908	-3.265914	-1.297604
27	1	0	1.105549	-3.311342	0.340948
28	1	0	2.526848	-1.526346	1.079939
29	1	0	3.568869	-2.481655	0.016419
30	1	0	3.737994	-0.020339	-0.521413
31	1	0	3.017154	-0.896927	-1.884281
32	1	0	1.464995	4.100081	0.060304
33	1	0	-0.106362	3.818539	0.883082

34	1	0	1.439428	3.363633	1.678915
35	1	0	-0.923580	0.849144	2.456721
36	1	0	-2.997407	0.971167	-3.285332
37	1	0	-3.080949	1.655586	-1.644791
38	1	0	-4.011043	0.210889	-2.054269

Vinylcyclohexene transition structures

	B3LYP	+zpe	E(rel)	S	E+zpe-TdelS(298)
Endo eq	-671.45587	-671.20424	0.27	111.298	0.60
Endo ax	-671.45591	-671.20467	0.00	112.412	0.00
Exo ax	-671.45472	-671.20347	0.75	112.506	0.72
Exo eq	-671.45183	-671.20053	2.59	113.245	2.35

Endo Equatorial, File Cor1stEnB3



26 (0.6)

E(RB+HF-LYP) = -671.455874489

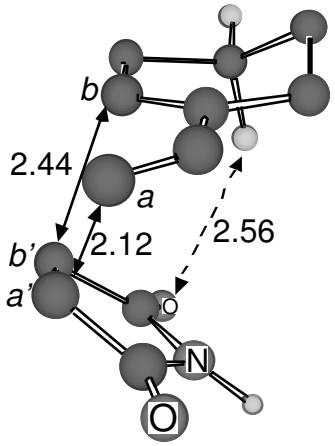
Zero-point correction= 0.251639 (Hartree/Particle)
Thermal correction to Energy= 0.264525
Thermal correction to Enthalpy= 0.265469
Thermal correction to Gibbs Free Energy= 0.212588
Sum of electronic and zero-point Energies= -671.204236
Sum of electronic and thermal Energies= -671.191349
Sum of electronic and thermal Enthalpies= -671.190405
Sum of electronic and thermal Free Energies= -671.243287

E (Thermal)	CV	S
KCAL/MOL	CAL/MOL-KELVIN	CAL/MOL-KELVIN

TOTAL	165.992	51.696	111.298

C,0,-1.3135375692,2.2709202177,0.2289756968
C,0,-0.2592217294,1.38679845,0.847989214
C,0,-0.5239304984,0.1227221881,1.3605033224
C,0,-1.9389117278,-0.4415083448,1.3411169581
C,0,-2.8800358064,0.3069766788,0.3870196375
C,0,-2.7431293706,1.8219041658,0.5729038155
C,0,0.5314024886,-0.7094895584,1.7871774214
C,0,1.881467381,-0.3741892665,1.6719482534
H,0,2.6219170509,-1.1175219453,1.9553269697
H,0,-1.9082529495,-1.5084947574,1.0882045133
C,0,1.3508737433,0.7234039986,-0.949450454
C,0,0.3148846806,-0.0078615619,-1.6943645522
N,0,0.5816517281,-1.3737337303,-1.4577650192
C,0,1.8010059512,-1.5711810889,-0.8104131072
C,0,2.2307107062,-0.1961494697,-0.3651377928
O,0,-0.5961980214,0.4090969356,-2.3927544856
O,0,2.3605408124,-2.6361228936,-0.6453784326
H,0,0.2865196606,-1.746726632,2.0109605087
H,0,0.6762223802,1.8658794379,1.1135101917
H,0,2.2001210925,0.6523817344,1.8282859704
H,0,3.2882317435,-0.0137483082,-0.2106789782
H,0,1.5321899253,1.7741854426,-1.1276421209
H,0,-1.1927426355,2.2416972242,-0.8639617642
H,0,-1.1456732704,3.312231005,0.5336753279
H,0,-2.9776880175,2.0884303166,1.6132371708
H,0,-3.4591022702,2.356623115,-0.0619292497
H,0,-3.913515405,-0.0148874597,0.5629501591
H,0,-2.634058907,0.0521186931,-0.651487481
H,0,0.0718077848,-2.1181795728,-1.9148018916
H,0,-2.3417501026,-0.385722971,2.364158676

Endo Axial, file Cor1stEnJB3



25 (0.0)

E(RB+HF-LYP) = -671.455911393

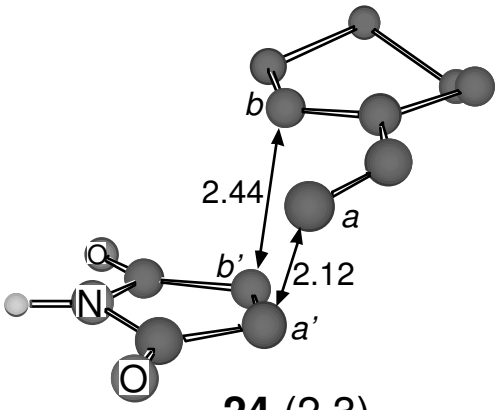
Zero-point correction= 0.251247 (Hartree/Particle)
Thermal correction to Energy= 0.264255
Thermal correction to Enthalpy= 0.265199
Thermal correction to Gibbs Free Energy= 0.211788
Sum of electronic and zero-point Energies= -671.204665
Sum of electronic and thermal Energies= -671.191657
Sum of electronic and thermal Enthalpies= -671.190713
Sum of electronic and thermal Free Energies= -671.244123

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	165.822	51.848	112.412

C,0,0.3548078275,0.0389565582,1.7079254611
C,0,1.3115016558,0.7849544586,0.8621054638
C,0,2.2283039529,-0.1179136283,0.3126251733
C,0,1.8969851545,-1.4835609276,0.848560823
N,0,0.692545852,-1.3180862361,1.5368300104
O,0,2.5098705588,-2.524352991,0.724925832
O,0,-0.5374080097,0.4461058405,2.4313253427
C,0,-0.2957322432,1.3185751425,-0.8912174704
C,0,-0.5798229577,0.0317649753,-1.3339449224
C,0,-1.9839134228,-0.5379714269,-1.1874398
C,0,-3.0568822964,0.5519461041,-1.0691757936
C,0,-2.6662368347,1.5634882831,0.0140847147
C,0,-1.3410731573,2.256253302,-0.3390185083
H,0,-2.023155746,-1.1797927873,-0.2952394892

C,0,0.4593297092,-0.8195153878,-1.7613655368
C,0,1.8061911843,-0.466880712,-1.7311446991
H,0,2.5491095002,-1.2171712686,-1.9876517803
H,0,0.2103375608,-1.8683264038,-1.9185159175
H,0,0.61267522,1.7951576014,-1.2449996074
H,0,2.1060567562,0.5533744023,-1.9501386165
H,0,3.2634148382,0.1142656248,0.0912285217
H,0,1.4560275816,1.8478512836,0.9987449905
H,0,-1.5153180672,3.0394002864,-1.0955518099
H,0,-0.9444734506,2.7775650605,0.5412962379
H,0,-2.5547190479,1.047673007,0.9743632723
H,0,-3.4505228031,2.3187526232,0.1437222637
H,0,-4.0264178634,0.0942925011,-0.839622525
H,0,-3.1692645379,1.0658452202,-2.0347565843
H,0,0.2499627748,-2.0624589269,2.0595055394
H,0,-2.1919855054,-1.1944278141,-2.0421733966

Exo Equatorial, file Cor1stExJB3



24 (2.3)

E(RB+HF-LYP) = -671.451830213

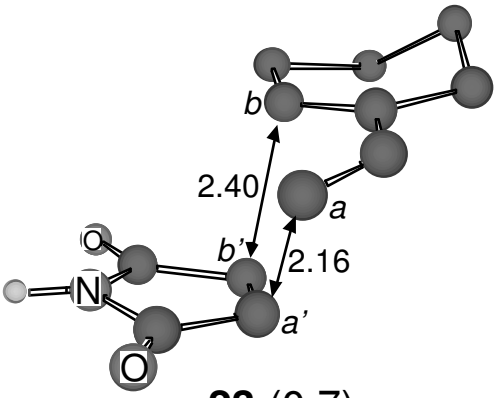
Zero-point correction= 0.251298 (Hartree/Particle)
Thermal correction to Energy= 0.264391
Thermal correction to Enthalpy= 0.265335
Thermal correction to Gibbs Free Energy= 0.211529
Sum of electronic and zero-point Energies= -671.200532
Sum of electronic and thermal Energies= -671.187439
Sum of electronic and thermal Enthalpies= -671.186495
Sum of electronic and thermal Free Energies= -671.240302

E (Thermal)	CV	S
KCAL/MOL	CAL/MOL-KELVIN	CAL/MOL-KELVIN

TOTAL	165.908	51.863	113.245

C,0,-0.7984027561,-0.1580688532,-0.9821458078
C,0,-1.187295406,1.1877665682,-0.966454972
C,0,-2.5544453845,1.2510143172,-0.3341270169
N,0,-2.8090734849,-0.043108407,0.1268489051
C,0,-1.8522730756,-0.968674583,-0.3354963513
O,0,-3.2915637307,2.2079118326,-0.2119526714
O,0,-1.9289778596,-2.1768878575,-0.1972689714
C,0,0.8193513131,-0.4412353469,0.8180403974
C,0,1.6753964184,0.5719638388,0.3991635353
C,0,3.0658136019,0.2279867493,-0.1147413061
C,0,3.1840367553,-1.2384561032,-0.5537841423
C,0,2.6800484064,-2.1689497145,0.5551470661
C,0,1.2020123658,-1.8992390863,0.8914375962
H,0,3.7997324183,0.4212705402,0.6825818325
C,0,1.2029984683,1.8950236004,0.2845241789
C,0,-0.1210670582,2.2580148283,0.5177337133
H,0,-0.4371014451,3.2800217512,0.3283262605
H,0,1.8492518549,2.6129778426,-0.2199616992
H,0,-0.056162608,-0.1671912945,1.3964009579
H,0,-0.9481891661,1.9030291462,-1.7426174424
H,0,-0.0927072136,-0.6171891405,-1.6586233874
H,0,0.5355510799,-2.4693387523,0.228879261
H,0,0.9718788392,-2.2720084423,1.8989532833
H,0,3.2946301197,-2.0084898623,1.4518528222
H,0,2.8106913722,-3.2195978149,0.2713550061
H,0,4.2266766676,-1.4680389271,-0.8039335119
H,0,2.5977006463,-1.3993276639,-1.4693935719
H,0,-3.6721064222,-0.3144603775,0.5784969045
H,0,-0.6841650184,1.7699242178,1.307770326
H,0,3.3351241001,0.8991085349,-0.9400375804

Exo Axial, File Cor1stExB3



23 (0.7)

E(RB+HF-LYP) = -671.454715687

Zero-point correction= 0.251247 (Hartree/Particle)
Thermal correction to Energy= 0.264271
Thermal correction to Enthalpy= 0.265215
Thermal correction to Gibbs Free Energy= 0.211760
Sum of electronic and zero-point Energies= -671.203469
Sum of electronic and thermal Energies= -671.190445
Sum of electronic and thermal Enthalpies= -671.189501
Sum of electronic and thermal Free Energies= -671.242956

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	165.832	51.857	112.506

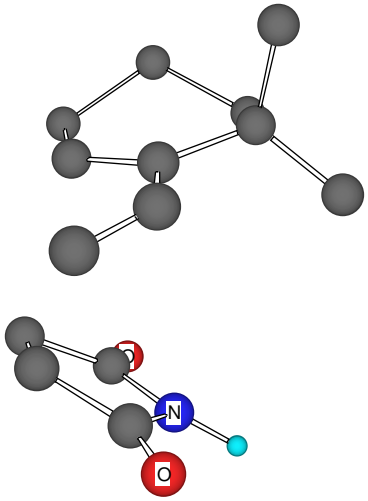
C,0,-1.8558606173,1.3876715505,-0.6532203895
C,0,-0.9843498842,0.1604641042,-0.7034396658
C,0,-1.4013438941,-1.0946281608,-0.2727319924
C,0,-2.755607145,-1.2649259583,0.4016841168
C,0,-3.7316848128,-0.1213868432,0.0940380357
C,0,-3.0497448571,1.2367864603,0.2990282297
C,0,-0.5018119475,-2.1801037741,-0.2641266372
C,0,0.8388458416,-2.0663087503,-0.6097426796
H,0,1.5024272811,-2.9179921088,-0.4897811074
H,0,-2.6094723911,-1.3296306102,1.4913477273
C,0,0.7771183518,0.4596910333,0.9063483316
C,0,1.5878869907,-0.6800426494,0.8686615104
C,0,2.8539445168,-0.3139557717,0.1438781502
N,0,2.6383632792,0.9788613514,-0.3442222925
C,0,1.4622703918,1.5514731649,0.1733163151
O,0,3.8572893372,-0.9771974274,-0.0217286944

O,0,1.1250303208,2.7113655482,0.0136018841
H,0,-0.8254512282,-3.0900680925,0.2418365378
H,0,-0.1541974345,0.2152848231,-1.4010208817
H,0,1.631965549,-1.4356055754,1.6415153127
H,0,0.0241605694,0.6888398099,1.6466280337
H,0,-2.2218084714,1.5828272829,-1.6748753373
H,0,-1.2398654677,2.2576293045,-0.3926938992
H,0,-2.7059600454,1.3162539227,1.3404148518
H,0,-3.7581663099,2.0582113954,0.1407341821
H,0,-4.6211844144,-0.212296796,0.7285956757
H,0,-4.0754979488,-0.2002714934,-0.9469733464
H,0,3.331847231,1.5038093042,-0.8598763018
H,0,1.1420492217,-1.3814541616,-1.3955419937
H,0,-3.1859239676,-2.2293178643,0.1021011253

6,6-Dimethyl-1-vinylcyclohexene transition structures

	B3LYP	+zpe	E(rel)	S	E+zpe-TdelS(298)
Endo eq	-750.07929	-749.77151	0.38	123.489	0.34
Endo ax	-750.07978	-749.77212	0.00	122.834	0.15
Exo eq	-750.07554	-749.76818	2.47	125.579	1.81
Exo ax	-750.0788	-749.77158	0.34	124.49	0.00

Endo Equatorial, File CorDanEnEqB3



E(RB+HF-LYP) = -750.079290639

Zero-point correction= 0.307781 (Hartree/Particle)
Thermal correction to Energy= 0.323495

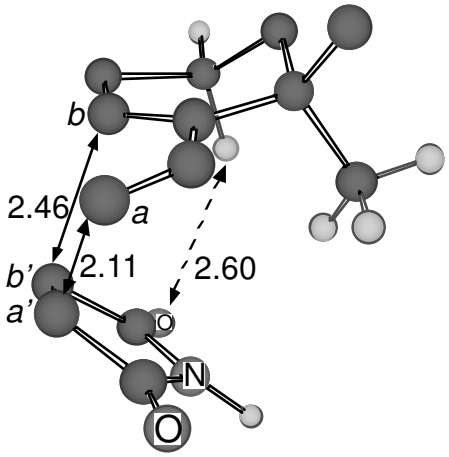
Thermal correction to Enthalpy= 0.324439
Thermal correction to Gibbs Free Energy= 0.265765
Sum of electronic and zero-point Energies= -749.771509
Sum of electronic and thermal Energies= -749.755796
Sum of electronic and thermal Enthalpies= -749.754851
Sum of electronic and thermal Free Energies= -749.813525

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	202.996	63.173	123.489

C,0,2.5412827191,0.0325593202,-0.5771591849
C,0,1.6372524222,0.927467453,-1.158645122
C,0,0.6621858544,0.1723729314,-1.9629938226
N,0,0.998333173,-1.1852829006,-1.7755999345
C,0,2.1957994648,-1.3456723902,-1.0778395988
O,0,-0.25158086,0.5696315778,-2.6684929744
O,0,2.7979301784,-2.3883423772,-0.920880838
C,0,2.1289597751,-0.215510454,1.4610342177
C,0,0.7877318384,-0.5906905398,1.5353903679
C,0,-0.2892502133,0.2155419062,1.101713242
C,0,-0.0177366596,1.490490238,0.6138271553
C,0,-1.0428439024,2.4005072851,-0.0109866708
C,0,-2.4761620915,1.9997189932,0.3618616915
C,0,-2.6480567516,0.4886835099,0.1927947846
C,0,-1.7258298592,-0.3492809669,1.1149034206
H,0,2.8824913722,-0.9442130988,1.747722056
C,0,-1.7985879868,-1.8150080653,0.6358271893
H,0,0.5844240063,-1.6358455463,1.7518103171
H,0,0.9107478588,1.9601489744,0.9170722209
H,0,2.4184421651,0.8162893787,1.6375508417
H,0,3.5812215933,0.2585317166,-0.3714263785
H,0,1.7744128838,1.9901160977,-1.3020360273
H,0,-0.9384436319,2.3435901633,-1.1046953551
H,0,-0.834427603,3.4408986978,0.2697112657
H,0,-2.6940910139,2.2987265562,1.395229653
H,0,-3.1892709151,2.5346626044,-0.2763519804
H,0,-3.6888123929,0.1956304507,0.3824647902
H,0,-2.4315326299,0.2311500168,-0.8528069403
H,0,0.5427440897,-1.9385997398,-2.2733192367
C,0,-2.2353390484,-0.2922042762,2.5769824422
H,0,-2.8472289792,-2.1318257825,0.5863080016
H,0,-1.3632058524,-1.9283885701,-0.3616050001
H,0,-1.2863681349,-2.5072264346,1.3124819487

H,0,-3.2533679849,-0.6960220494,2.641553426
H,0,-1.5940071445,-0.8860538107,3.2383256865
H,0,-2.2492878131,0.731247407,2.9659400798

Endo Axial, file CorDanEnAxB3



27 (0.2)

E(RB+HF-LYP) = -750.079779291

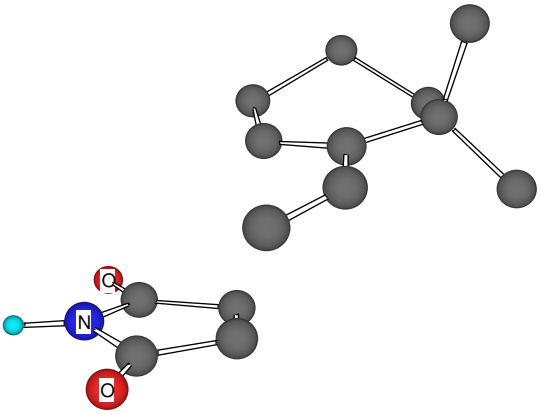
Zero-point correction= 0.307658 (Hartree/Particle)
Thermal correction to Energy= 0.323316
Thermal correction to Enthalpy= 0.324260
Thermal correction to Gibbs Free Energy= 0.265898
Sum of electronic and zero-point Energies= -749.772122
Sum of electronic and thermal Energies= -749.756463
Sum of electronic and thermal Enthalpies= -749.755519
Sum of electronic and thermal Free Energies= -749.813881

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	202.884	63.162	122.834

C,0,-1.0743615667,2.4217660506,-0.2981515308
C,0,-0.0670243346,1.4281319835,-0.8120532811
C,0,-0.3700527804,0.1160847539,-1.1634640196
C,0,-1.8055939408,-0.4413877934,-1.0485437526
C,0,-2.8184023449,0.7196363318,-0.8775640674
C,0,-2.3790919667,1.7598110955,0.1552501089
C,0,0.6861835439,-0.7515781851,-1.5251892262
C,0,2.027040049,-0.3753665014,-1.5656577995
C,0,2.5415061151,0.1554404649,0.4087504866

C,0,1.6165011156,1.0603838445,0.9398172519
C,0,0.7392263411,0.3426971192,1.8884895883
N,0,1.1509957212,-1.0023575383,1.8282119009
C,0,2.309747103,-1.1752903204,1.0714475084
O,0,-0.1528941586,0.7608639867,2.6071595952
O,0,2.9595510383,-2.1974024298,0.9835603649
C,0,-1.9320810713,-1.422450909,0.1407427303
H,0,2.7733510614,-1.1352123729,-1.7805703451
H,0,0.4674061819,-1.8150015887,-1.5879628959
H,0,0.84802652,1.860238211,-1.2021605708
H,0,2.2990658144,0.6238340812,-1.8923868088
H,0,3.550755004,0.4134295517,0.109653876
H,0,1.7175341092,2.1357386525,0.9854815864
H,0,-1.2788534001,3.1437234058,-1.1066822583
H,0,-0.6351302038,3.0067752486,0.5194372849
H,0,-2.2257595815,1.2953669007,1.1344007262
H,0,-3.1571517274,2.5217244035,0.2833794687
H,0,-3.7945985252,0.2955445785,-0.6099215255
H,0,-2.9542955684,1.2204189509,-1.8477613375
H,0,0.7532549339,-1.7276125806,2.4098856089
C,0,-2.1661321152,-1.1947743777,-2.3496863215
H,0,-2.9393416509,-1.8567790569,0.1613180767
H,0,-1.2156164096,-2.2465838263,0.0544340552
H,0,-1.756882852,-0.9255474023,1.0994723533
H,0,-3.2147554411,-1.5143077511,-2.3151602195
H,0,-2.0368114687,-0.5533690231,-3.228827353
H,0,-1.555206765,-2.092191411,-2.4943987625

Exo Equatorial, file CorDanExEqB3



E(RB+HF-LYP) = -750.075543396

Zero-point correction= 0.307361 (Hartree/Particle)

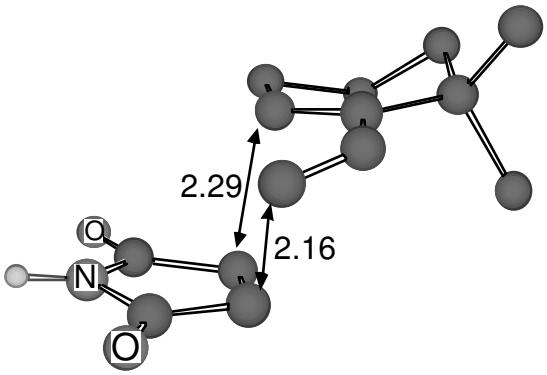
Thermal correction to Energy= 0.323264
Thermal correction to Enthalpy= 0.324208
Thermal correction to Gibbs Free Energy= 0.264542
Sum of electronic and zero-point Energies= -749.768182
Sum of electronic and thermal Energies= -749.752279
Sum of electronic and thermal Enthalpies= -749.751335
Sum of electronic and thermal Free Energies= -749.811001

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	202.851	63.350	125.579

C,0,0.669209049,-2.053400626,0.8192223317
C,0,0.3188830141,-0.5872085935,0.7822162812
C,0,1.1916533681,0.4330433428,0.4132921152
C,0,2.6107149841,0.1240181174,-0.1053186972
C,0,2.750084272,-1.3859528583,-0.4290405909
C,0,2.1739239208,-2.3016387261,0.652046081
C,0,0.7110893449,1.7617025908,0.4019210949
C,0,-0.6127815818,2.1056772436,0.6631947285
C,0,-1.6841290083,1.1330724853,-0.8920292797
C,0,-1.2940617009,-0.2081223308,-0.9942355093
C,0,-2.3464225834,-1.0599029223,-0.3984806919
N,0,-3.3016236427,-0.1662927618,0.1258578887
C,0,-3.0491690327,1.1548687263,-0.2530491814
O,0,-3.7870448583,2.1011872517,-0.0687231645
O,0,-2.4229003828,-2.27429979,-0.3403144846
C,0,3.6316839518,0.5356992354,0.9825493996
H,0,-0.9257838498,3.1395906543,0.5464472658
H,0,1.3443951814,2.5290813435,-0.0363009046
H,0,-0.550898539,-0.3139800145,1.3687239854
H,0,-1.4455673463,1.8990745041,-1.6182242418
H,0,-0.5904472068,-0.6236679827,-1.7004760083
H,0,0.0970029889,-2.5811697296,0.0431238396
H,0,0.3110953568,-2.4792834183,1.765471829
H,0,2.68613183,-2.1214589744,1.6057805403
H,0,2.3554194993,-3.3522205286,0.3966265218
H,0,3.8112909342,-1.609531166,-0.5987511303
H,0,2.2357591224,-1.5943859052,-1.3787309701
H,0,-4.1642814763,-0.4666243169,0.5595267353
H,0,-1.1817229193,1.5661246282,1.4143621889
C,0,2.935677946,0.9040840112,-1.3992531781
H,0,4.6565800627,0.3609342095,0.6319945219
H,0,3.5351703237,1.6000828568,1.2252875579

H,0,3.4886790361,-0.0262359404,1.9112721738
H,0,3.9022615824,0.5728418983,-1.7978001031
H,0,2.1776996418,0.7304450297,-2.1719288093
H,0,3.0100075413,1.983694316,-1.2333184421

Exo Axial, File CorDanExAxB3



28 (0.0)

E(RB+HF-LYP) = -750.078803662

Zero-point correction= 0.307221 (Hartree/Particle)
Thermal correction to Energy= 0.323070
Thermal correction to Enthalpy= 0.324014
Thermal correction to Gibbs Free Energy= 0.264865
Sum of electronic and zero-point Energies= -749.771582
Sum of electronic and thermal Energies= -749.755734
Sum of electronic and thermal Enthalpies= -749.754789
Sum of electronic and thermal Free Energies= -749.813939

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	202.730	63.402	124.490

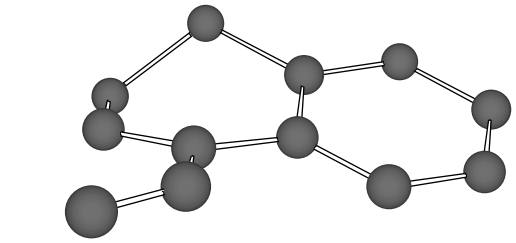
C,0,1.7869978957,1.8199883169,-0.0823412775
C,0,1.0933425536,0.776769617,0.7224698701
C,0,1.9115715158,-0.3308650759,0.7888502824
C,0,3.1826428005,-0.0224319208,0.0551970271
N,0,2.9718570195,1.2287531484,-0.5150976417
O,0,4.1771812112,-0.6938659013,-0.0607402997
O,0,1.4361592877,2.947550451,-0.3465140683
C,0,1.2570547244,-1.7577996856,-0.6961319649
C,0,-0.055664007,-1.9022535816,-0.3316011607

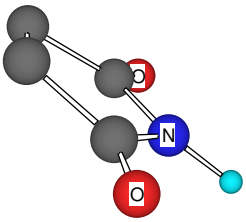
C,0,-0.9794162299,-0.8483719403,-0.3567982252
C,0,-0.563321919,0.3844676941,-0.8045238787
C,0,-1.4306201424,1.622729285,-0.7887036904
C,0,-2.5609634997,1.5082929107,0.2406147179
C,0,-3.2740279915,0.1637762721,0.0444547949
C,0,-2.3485545714,-1.0452913835,0.316641898
H,0,1.948342462,-2.5663677916,-0.5526791381
C,0,-2.1671612964,-1.2286934248,1.8416231822
H,0,-0.3314383426,-2.8062503253,0.1764363978
H,0,0.2416343527,0.4180233968,-1.5114846462
H,0,1.9175308191,-1.0552614455,1.569506984
H,0,0.3432915193,1.0503647795,1.4251675518
H,0,-1.8646569368,1.7445577659,-1.7797308201
H,0,-0.807870603,2.4884757546,-0.6078387028
H,0,-2.1613851844,1.5844345998,1.2453415632
H,0,-3.2609442689,2.3257504053,0.1093651349
H,0,-4.1413558871,0.0864785339,0.6916144053
H,0,-3.6279948864,0.1122942501,-0.9814114021
H,0,3.6439115387,1.6976709881,-1.0826840829
H,0,1.5425426591,-1.0621333036,-1.4591936277
C,0,-3.038315794,-2.3038299598,-0.2578286499
H,0,-3.1317559519,-1.3877459713,2.3128471821
H,0,-1.5425164256,-2.087770635,2.0559053378
H,0,-1.7078001146,-0.3580306499,2.2924034655
H,0,-4.0314976926,-2.4012281533,0.169066909
H,0,-3.1320891134,-2.226417148,-1.3347221086
H,0,-2.4870553032,-3.2065162276,-0.0257295199

4-vinyl-1,2-dihydronaphthalene transition structures

	B3LYP	+zpe	E(rel)	S	E+zpe-TdelS(298)
Endo eq	-823.8863	-823.61137	0.26	122.314	0.84
Endo ax	-823.88664	-823.61177	0.00	123.352	0.28
Exo ax	-823.88678	-823.61214	-0.23	123.519	0.00
Exo eq	-823.88313	-823.60866	1.95	124.635	1.85

Endo Equatorial, File Cor1stPhEnB3





E(RB+HF-LYP) = -823.886301994

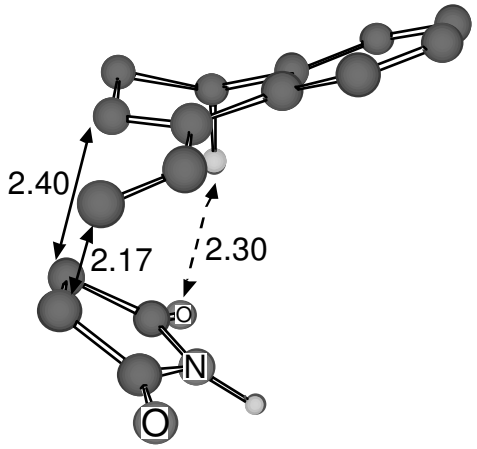
Zero-point correction= 0.274937 (Hartree/Particle)
Thermal correction to Energy= 0.289986
Thermal correction to Enthalpy= 0.290931
Thermal correction to Gibbs Free Energy= 0.232815
Sum of electronic and zero-point Energies= -823.611365
Sum of electronic and thermal Energies= -823.596316
Sum of electronic and thermal Enthalpies= -823.595371
Sum of electronic and thermal Free Energies= -823.653487

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	181.969	61.591	122.314

C,0,2.9792029192,0.2799987684,-0.1058985131
C,0,2.0900006699,1.1649333366,-0.7199506283
C,0,1.2855362423,0.4116877078,-1.7128643253
N,0,1.6677907542,-0.930658252,-1.5541725674
C,0,2.7774271265,-1.0751611227,-0.7153397488
O,0,0.468229895,0.8169070182,-2.5202598425
O,0,3.4102635672,-2.0976737712,-0.5435706136
C,0,2.24498791,-0.1934785485,1.9072156074
C,0,0.9362222837,-0.5972091973,1.6902262223
C,0,-0.0464130334,0.2337279004,1.1042645359
C,0,0.2814387001,1.5491034909,0.7653062629
C,0,-0.7203983131,2.4300172008,0.0618758435
C,0,-2.1381451644,2.1097996206,0.5618898444
C,0,-2.420194285,0.6272709035,0.4455798756

H,0,2.9705653715,-0.9211903774,2.2591220856
H,0,0.7140433583,-1.653740869,1.8083021254
H,0,1.0810601273,2.0378157474,1.3087142438
H,0,2.4767091914,0.8360798546,2.1586330013
H,0,3.9505943677,0.5421822304,0.2942811671
H,0,2.208883265,2.236329238,-0.8099853607
H,0,-0.6724021648,2.2420153803,-1.020345461
H,0,-0.481066225,3.4870010502,0.221223775
H,0,-2.23685792,2.424739354,1.6123460141
H,0,-2.8790294572,2.6811807809,-0.0083902869
H,0,1.3084499544,-1.676866452,-2.1344835073
C,0,-3.688722151,0.1550326766,0.104109377
C,0,-3.9444179359,-1.2122383234,-0.0018808092
C,0,-2.9136298467,-2.1243603442,0.2247766367
C,0,-1.6429533987,-1.6660188007,0.5654241159
C,0,-1.376677724,-0.2935985533,0.6960379348
H,0,-4.4850339181,0.870679795,-0.0878862804
H,0,-4.9371671129,-1.5611138518,-0.2729663168
H,0,-3.0938252871,-3.1914779741,0.1273181404
H,0,-0.8469905238,-2.3899324124,0.7093348912

Endo Axial, file Cor1stPhEnJB3



29 (0.3)

E(RB+HF-LYP) = -823.886641911

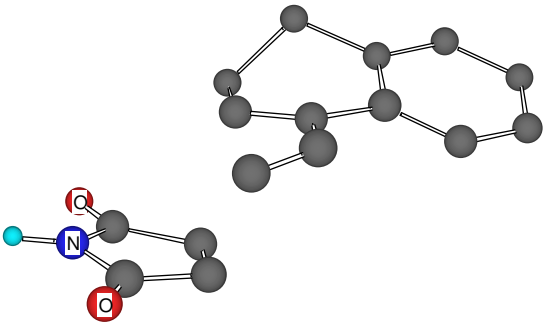
Zero-point correction= 0.274870 (Hartree/Particle)
Thermal correction to Energy= 0.290005
Thermal correction to Enthalpy= 0.290949
Thermal correction to Gibbs Free Energy= 0.232340
Sum of electronic and zero-point Energies= -823.611772

Sum of electronic and thermal Energies= -823.596637
Sum of electronic and thermal Enthalpies= -823.595693
Sum of electronic and thermal Free Energies= -823.654301

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	181.981	61.604	123.352

C,0,-0.8370076492,2.1226372946,-1.2727831913
C,0,0.1336340197,0.9853943881,-1.4429443343
C,0,-0.2136211469,-0.3178584478,-1.0844377494
C,0,-1.5434558383,-0.5659287106,-0.467824321
C,0,-2.3147458105,0.5216654639,0.0010780501
C,0,-1.7503599734,1.9240751664,-0.0560961512
C,0,0.7438052301,-1.3522942612,-1.2167016044
C,0,2.0122049382,-1.1556818631,-1.7421080876
C,0,2.0927011662,1.3105727671,-0.0901844079
C,0,1.528014902,1.1059097611,1.2703040561
N,0,1.9888449879,-0.1548554069,1.6783396076
C,0,2.9641501852,-0.6692339058,0.8196248514
C,0,2.9493131027,0.2423883738,-0.3716075791
O,0,0.839746147,1.8455123188,1.950265382
O,0,3.6513046547,-1.6483088431,1.0288567248
H,0,2.7286380463,-1.9712281141,-1.714243865
H,0,0.5566491854,-2.2868933172,-0.6947579294
H,0,0.9053894992,1.1278593597,-2.1902516039
H,0,2.1743476741,-0.4346036464,-2.5369365927
H,0,3.8287763768,0.2982663707,-1.0013535813
H,0,2.1526713065,2.3063966049,-0.5081579941
H,0,-1.4393425458,2.1893979932,-2.1952458899
H,0,-0.301079187,3.0754298647,-1.1920151696
H,0,-1.1657460538,2.1182913986,0.8508584646
H,0,-2.5650817964,2.6569264837,-0.0732469378
H,0,1.7961609267,-0.5399512689,2.5935496139
C,0,-3.5781264571,0.2795588239,0.5459227105
C,0,-2.0834569815,-1.8607147657,-0.3940409882
C,0,-4.0947365888,-1.0129883124,0.6324810883
H,0,-4.1644483275,1.121439939,0.9075866469
H,0,-5.081011622,-1.1780189367,1.0578153595
C,0,-3.3434338807,-2.0870634644,0.1546102519
H,0,-1.5256295183,-2.7017581541,-0.7947288864
H,0,-3.7398905988,-3.0978243818,0.1980186953

Exo Equatorial, file Cor1stPhExJB3



E(RB+HF-LYP) = -823.883134682

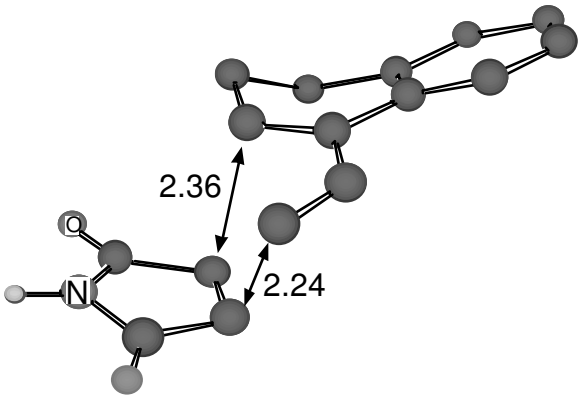
Zero-point correction= 0.274473 (Hartree/Particle)
Thermal correction to Energy= 0.289791
Thermal correction to Enthalpy= 0.290735
Thermal correction to Gibbs Free Energy= 0.231517
Sum of electronic and zero-point Energies= -823.608661
Sum of electronic and thermal Energies= -823.593344
Sum of electronic and thermal Enthalpies= -823.592400
Sum of electronic and thermal Free Energies= -823.651618

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	181.846	61.893	124.635

C,0,-0.5350595345,1.9611671503,0.4117000516
C,0,0.1477570511,0.6359541115,0.714275286
C,0,-0.5694242187,-0.5407232781,0.67883724
C,0,-1.9738381623,-0.4913949653,0.1797220144
C,0,-2.6846062268,0.7059148306,0.3175789547
C,0,-1.9824793917,1.9028104065,0.9323742266
C,0,0.0862464688,-1.7588251584,0.9150817694
C,0,1.4317557845,-1.8314608462,1.1377749937
C,0,1.5280837503,0.2212207615,-0.9790287752
C,0,2.1697915477,-0.9803493001,-0.7826203234
C,0,3.5420508621,-0.7046230057,-0.2564725038
N,0,3.59123242,0.6778167841,-0.0861147636
C,0,2.4667448567,1.3208814141,-0.5942738936
O,0,4.4319978202,-1.4765841143,0.0003283129
O,0,2.31407403,2.5163871395,-0.6683124675
H,0,1.9227098909,-2.7840842943,1.1923734322
H,0,-0.4483235638,-2.6726871125,0.7474052635
H,0,1.0220681603,0.6859332447,1.3297384264
H,0,1.9650577412,-1.8930616862,-1.2903702093

H,0,0.7356540831,0.4034420747,-1.666660863
H,0,-0.5498780287,2.1447424833,-0.6564579902
H,0,0.0136349752,2.7720034275,0.8673316379
H,0,-1.9761170393,1.8061145411,2.0145883476
H,0,-2.509531058,2.8138651083,0.677378836
H,0,4.3908113889,1.1612764738,0.2613594424
H,0,1.9604321888,-1.0309294251,1.6124124723
C,0,-3.997212791,0.7775415485,-0.1117289785
C,0,-2.6016403302,-1.5805239728,-0.4134452033
C,0,-4.616547967,-0.3189829927,-0.6862707376
H,0,-4.537599938,1.6974890136,-0.0002237701
H,0,-5.6337745604,-0.2483836583,-1.0166241175
C,0,-3.9142342394,-1.4977207833,-0.8413253259
H,0,-2.0668929856,-2.4963340805,-0.5597916612
H,0,-4.3797777534,-2.347843321,-1.2988554357

Exo Axial, File Cor1stPhExNJAxB3



30 (0.0)

E(RB+HF-LYP) = -823.886781624

Zero-point correction= 0.274647 (Hartree/Particle)
Thermal correction to Energy= 0.289849
Thermal correction to Enthalpy= 0.290793
Thermal correction to Gibbs Free Energy= 0.232106
Sum of electronic and zero-point Energies= -823.612135
Sum of electronic and thermal Energies= -823.596932
Sum of electronic and thermal Enthalpies= -823.595988
Sum of electronic and thermal Free Energies= -823.654676

E (Thermal)	CV	S
KCAL/MOL	CAL/MOL-KELVIN	CAL/MOL-KELVIN

TOTAL 181.883 61.742 123.519

C,0,-2.2259577877,-0.8189690088,-0.9531047246
C,0,-1.6573407815,0.4540831263,-0.8891256552
C,0,-2.6345170304,1.3706356658,-0.2385451697
N,0,-3.7129353684,0.5589015491,0.1447733683
C,0,-3.6002868749,-0.7439608465,-0.3602357675
O,0,-2.5594658731,2.5706096037,-0.0457869219
O,0,-4.4562430892,-1.60273717,-0.2960414447
C,0,-1.3452983595,-2.0892847282,0.6630202682
C,0,0.007840304,-1.9049653454,0.4481963653
H,0,0.5562972706,-2.712007561,-0.0320184547
C,0,0.6519225564,-0.6483386481,0.5560326724
C,0,2.0838582704,-0.4864611345,0.194802629
C,0,2.5806951231,0.7925323413,-0.1445204172
C,0,1.6283215008,1.9676867848,-0.1889133225
C,0,0.5384425957,1.8531294289,0.8836859889
C,0,-0.093200194,0.4890688129,0.8769492242
C,0,3.9333992807,0.9435150259,-0.456403818
C,0,4.8060001762,-0.1449414293,-0.434498634
C,0,4.3233939547,-1.4060235906,-0.0835594402
C,0,2.9763687781,-1.570531218,0.2314916597
H,0,-1.8030096876,-3.0524652613,0.4588682342
H,0,-0.9826358159,0.3696557583,1.4865168461
H,0,-2.0102564332,-1.5686457881,-1.7013347245
H,0,-0.9051478575,0.8481824997,-1.5566410869
H,0,0.9749190061,2.0286064018,1.8812764915
H,0,-0.2311035273,2.6187421322,0.7395302656
H,0,1.14905614,2.0128593005,-1.1787038884
H,0,2.179023954,2.9079759125,-0.0755485863
H,0,-4.5501057387,0.9165223904,0.5849101151
H,0,-1.882657861,-1.4829831272,1.3847009665
H,0,2.621667959,-2.550339721,0.5373268887
H,0,4.9949732127,-2.2593284967,-0.0441971986
H,0,4.307288958,1.9310437902,-0.7181226072
H,0,5.8560606262,-0.0061599623,-0.6769810587

transition structures from reaction of trimethylsiloxy hydroxy analog of 4-vinyl-1,2-dihydronaphthalene (4-(1-trimethylsiloxyvinyl)-7-hydroxy-1,2-dihydronaphthalene) with N-phenylmaleimide

Exo equatorial, file TMSaexo

B3LYP/6-31G*

SCF Done: E(RB+HF-LYP) = -1614.08212796 A.U. after 1 cycles

Zero-point correction= 0.465474 (Hartree/Particle)
Thermal correction to Energy= 0.495754
Thermal correction to Enthalpy= 0.496698
Thermal correction to Gibbs Free Energy= 0.401492
Sum of electronic and zero-point Energies= -1613.616654
Sum of electronic and thermal Energies= -1613.586374
Sum of electronic and thermal Enthalpies= -1613.585430
Sum of electronic and thermal Free Energies= -1613.680636

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	311.090	116.636	200.379

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.915309	-2.626979	-0.276457
2	6	0	4.746479	-1.384385	-0.890668
3	6	0	2.700794	-2.441758	0.702439
4	6	0	3.885018	-3.150896	0.509726
5	6	0	3.569152	-0.671479	-0.694454
6	6	0	2.527733	-1.163291	0.116115
7	8	0	6.090531	-3.289991	-0.489329
8	6	0	1.574481	-3.036932	1.517390
9	6	0	0.231580	-2.713972	0.848524
11	6	0	1.243337	-0.449881	0.366426
12	6	0	1.053013	0.961457	0.200876
13	6	0	-0.221073	1.530945	0.216111
14	8	0	2.113297	1.710558	-0.214988
15	14	0	2.618981	3.261575	0.278598
16	6	0	4.446638	3.286914	-0.154078
17	6	0	1.705271	4.596086	-0.689605
18	6	0	2.339681	3.443005	2.131878

19	1	0	5.538907	-0.993988	-1.521360
20	1	0	4.000721	-4.132664	0.968159
21	1	0	3.451960	0.283122	-1.186595
22	1	0	6.066944	-4.134295	-0.012339
23	1	0	1.705321	-4.119995	1.619224
24	1	0	1.583654	-2.617865	2.535261
25	1	0	0.175442	-3.229056	-0.120350
26	1	0	-0.609890	-3.082806	1.441253
27	1	0	-0.749656	-0.751668	1.091624
28	1	0	-0.328915	2.584968	-0.015597
29	1	0	-0.978593	1.145239	0.885558
30	1	0	4.986744	2.485242	0.361491
31	1	0	4.602747	3.155893	-1.231204
32	1	0	4.904399	4.241496	0.132656
33	1	0	0.647595	4.674924	-0.414654
34	1	0	2.164158	5.576066	-0.505899
35	1	0	1.756958	4.406292	-1.768130
36	1	0	2.700447	4.418783	2.479857
37	1	0	2.880050	2.669302	2.689377
38	1	0	1.279613	3.368385	2.397745
39	6	0	-1.205748	0.599639	-1.479864
40	6	0	-1.120466	-0.787311	-1.384048
41	6	0	-2.600578	0.996808	-1.102731
42	7	0	-3.248396	-0.180084	-0.665341
43	6	0	-2.408521	-1.312522	-0.898799
44	8	0	-3.088964	2.109079	-1.133937
45	8	0	-2.733841	-2.471149	-0.711226
46	1	0	-0.666032	1.214511	-2.188198
47	1	0	-0.422262	-1.434254	-1.894865
48	6	0	-4.568841	-0.230370	-0.131400
49	6	0	-5.423023	-1.292286	-0.456069
50	6	0	-6.708536	-1.333358	0.082756
51	6	0	-7.158572	-0.319119	0.928709
52	6	0	-6.306899	0.741721	1.240754
53	6	0	-5.014181	0.787905	0.722106
54	1	0	-5.074898	-2.081961	-1.108635
55	1	0	-7.362440	-2.163978	-0.169188
56	1	0	-8.163819	-0.353765	1.339682
57	1	0	-6.645460	1.539717	1.896189
58	1	0	-4.358624	1.616164	0.960897

Exo axial, file TMSbexo

B3LYP/6-31G*

SCF Done: E(RB+HF-LYP) = -1614.08526930 A.U. after 1 cycles

Zero-point correction= 0.465439 (Hartree/Particle)
Thermal correction to Energy= 0.495662
Thermal correction to Enthalpy= 0.496606
Thermal correction to Gibbs Free Energy= 0.402508
Sum of electronic and zero-point Energies= -1613.619830
Sum of electronic and thermal Energies= -1613.589608
Sum of electronic and thermal Enthalpies= -1613.588664
Sum of electronic and thermal Free Energies= -1613.682761

	E (Thermal)	CV	S
	KCAL/MOL	CAL/MOL-KELVIN	CAL/MOL-KELVIN
TOTAL	311.032	116.662	198.045

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.170727	-2.437519	0.143868
2	6	0	-5.097428	-1.118261	0.596206
3	6	0	-2.749076	-2.507414	-0.035854
4	6	0	-3.993333	-3.124940	-0.161464
5	6	0	-3.858923	-0.499136	0.715405
6	6	0	-2.660793	-1.161377	0.389318
7	8	0	-6.408702	-3.006217	0.033418
8	6	0	-1.481640	-3.267832	-0.353986
9	6	0	-0.360789	-2.883062	0.616520
10	6	0	-0.223194	-1.392587	0.702919
11	6	0	-1.315333	-0.546306	0.569594
12	6	0	-1.068683	0.866956	0.484695
13	6	0	0.227303	1.384363	0.555864
14	8	0	-2.098662	1.647478	0.071467
15	14	0	-2.306121	3.332892	-0.081664
16	6	0	-4.135258	3.497660	-0.472101
17	6	0	-1.884459	4.188687	1.543355
18	6	0	-1.265848	3.990806	-1.508719
19	1	0	-6.012923	-0.595582	0.854501
20	1	0	-4.042273	-4.161333	-0.494503
21	1	0	-3.822061	0.518020	1.080142

22	1	0	-6.309264	-3.916823	-0.285557
23	1	0	-1.664093	-4.347611	-0.326277
24	1	0	-1.156525	-3.033460	-1.378619
25	1	0	-0.578284	-3.282707	1.621669
26	1	0	0.594694	-3.317939	0.303562
27	1	0	0.702501	-1.023970	1.123180
28	1	0	0.382070	2.452372	0.456374
29	1	0	0.945423	0.904030	1.208399
30	1	0	-4.399634	2.929708	-1.370929
31	1	0	-4.755682	3.125506	0.351027
32	1	0	-4.406130	4.546230	-0.645534
33	1	0	-0.826423	4.100275	1.810952
34	1	0	-2.118416	5.258446	1.473942
35	1	0	-2.473929	3.775284	2.370040
36	1	0	-1.504284	5.046086	-1.693124
37	1	0	-1.482157	3.441139	-2.432526
38	1	0	-0.187681	3.928176	-1.324216
39	6	0	1.159203	0.701925	-1.223536
40	6	0	1.088674	-0.684278	-1.346816
41	6	0	2.560443	1.044560	-0.803841
42	7	0	3.208526	-0.177684	-0.537914
43	6	0	2.361337	-1.269861	-0.920547
44	8	0	3.042081	2.154565	-0.684760
45	8	0	2.685376	-2.445219	-0.871521
46	1	0	0.628159	1.406354	-1.851683
47	1	0	0.380926	-1.254814	-1.928726
48	6	0	4.532129	-0.302644	-0.024852
49	6	0	5.378994	-1.315558	-0.493655
50	6	0	6.669068	-1.430969	0.022821
51	6	0	7.131373	-0.537885	0.990078
52	6	0	6.286880	0.475220	1.446584
53	6	0	4.989674	0.593078	0.950833
54	1	0	5.021836	-2.012280	-1.240454
55	1	0	7.316867	-2.223515	-0.342209
56	1	0	8.140147	-0.629177	1.383306
57	1	0	6.634465	1.179284	2.197928
58	1	0	4.340371	1.385002	1.303064

Endo axial, file TMSbendo

B3LYP/6-31G*

SCF Done: E(RB+HF-LYP) = -1614.08673957 A.U. after 1 cycles

Zero-point correction= 0.466237 (Hartree/Particle)
Thermal correction to Energy= 0.496001
Thermal correction to Enthalpy= 0.496945
Thermal correction to Gibbs Free Energy= 0.405681
Sum of electronic and zero-point Energies= -1613.620503
Sum of electronic and thermal Energies= -1613.590738
Sum of electronic and thermal Enthalpies= -1613.589794
Sum of electronic and thermal Free Energies= -1613.681059

	E (Thermal) KCAL/MOL	CV CAL/MOL-KELVIN	S CAL/MOL-KELVIN
TOTAL	311.245	116.375	192.083

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.161162	0.316846	-1.583901
2	6	0	-3.310601	1.423946	-1.611534
3	6	0	-3.052824	-0.484500	0.425499
4	6	0	-4.032181	-0.623268	-0.558594
5	6	0	-2.327879	1.559741	-0.638047
6	6	0	-2.155205	0.608534	0.383939
7	8	0	-5.106915	0.213483	-2.565548
8	6	0	-2.946939	-1.494420	1.545469
9	6	0	-2.562960	-0.799779	2.856803
10	6	0	-1.367817	0.087508	2.660969
11	6	0	-1.145937	0.755528	1.472421
12	6	0	0.094470	1.480205	1.319096
13	6	0	1.037140	1.542468	2.360205
14	8	0	0.416854	1.882560	0.080337
15	14	0	1.535650	2.864282	-0.764573
16	6	0	0.541095	4.371565	-1.307403
17	6	0	3.014588	3.415238	0.262335
18	6	0	2.072441	1.819935	-2.223338
19	1	0	-3.432963	2.167198	-2.392973
20	1	0	-4.712922	-1.473083	-0.515880
21	1	0	-1.690495	2.432380	-0.666438

22	1	0	-5.619121	-0.597799	-2.423179
23	1	0	-3.893496	-2.034179	1.660891
24	1	0	-2.178408	-2.242547	1.313802
25	1	0	-3.404027	-0.187068	3.225716
26	1	0	-2.355110	-1.541941	3.635183
27	1	0	-0.800201	0.339043	3.544444
28	1	0	1.937463	2.116184	2.181483
29	1	0	0.670492	1.602767	3.377730
30	1	0	-0.310916	4.090724	-1.936877
31	1	0	0.154398	4.931813	-0.447751
32	1	0	1.170269	5.055860	-1.890559
33	1	0	3.589090	2.554198	0.617678
34	1	0	3.674407	4.017296	-0.376461
35	1	0	2.735287	4.040811	1.117963
36	1	0	2.710446	2.396051	-2.905224
37	1	0	1.208695	1.458281	-2.791914
38	1	0	2.638034	0.949573	-1.875068
39	6	0	1.840671	-0.329034	2.595871
40	6	0	0.905857	-1.331351	2.872805
41	6	0	2.341282	-0.567150	1.193069
42	7	0	1.553062	-1.584260	0.661817
43	6	0	0.702109	-2.145568	1.684490
44	8	0	3.241839	0.025825	0.619661
45	8	0	0.009388	-3.134071	1.510224
46	1	0	2.555189	0.045150	3.321916
47	1	0	0.557153	-1.656676	3.842797
48	6	0	1.646331	-2.089132	-0.665969
49	6	0	2.898533	-2.321802	-1.247519
50	6	0	2.973962	-2.814535	-2.550092
51	6	0	1.810889	-3.090752	-3.270422
52	6	0	0.565339	-2.861651	-2.682956
53	6	0	0.476985	-2.355562	-1.387306
54	1	0	3.799907	-2.108956	-0.685618
55	1	0	3.948498	-2.989216	-2.998118
56	1	0	1.874450	-3.480379	-4.282799
57	1	0	-0.345992	-3.070261	-3.236817
58	1	0	-0.489109	-2.165777	-0.935360

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