AN ABSTRACT OF THE DISSERTATION OF

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Title: Rationalization and Innovative Design of Asymmetric Organocatalysts through Computational Investigation.

Abstract approved:

Paul Ha-Yeon Cheong

My work on computing complex catalyzed organic transformations reveals that only a few subtle chemical factors, *e.g.* non-classical hydrogen bonding, (hyper)conjugation and steric effects, common across different catalyst manifolds are critical for catalysis and selectivity. Rational manipulation and exploitation of these factors has led to improved catalyst designs, which has previously been an oft-promised but rarely delivered endeavor.

Hydrogen bonding is critical to stabilizing structures in both the ground and transition state across many branches of chemistry and life. C–H bonds polarized through either hybridization or proximity to a developing or full positive charge can provide stabilization through interaction with negatively charged atoms in a C–H···O non-classical hydrogen bond (NCHB). In the transition state, where a molecule experiences temporarily amplified polarization, these hydrogen bonds can serve to stabilize the structures and differentiate between diastereomeric TSs

A joint experimental and computational investigation on a diaryl prolinol silyl ether-catalyzed Michael cascade reaction to complex furanyl/pyranyl products uncovered the synergistic relationship between catalyst and substrate beyond the basic enamine activation and steric control. NCHBs were discovered to stabilize the transiently polar transition state. The kinetic resolution of addition products was afforded by virtue of the conformation of the substrate preventing or allowing hyperconjugation.

An *N*-heterocyclic carbene-catalyzed dynamic kinetic resolution of β-ketoesters was discovered to display an unusual resolution mechanism. Rapid substrate epimerization early in the aldol mechanism allowed routing through the lowest energy diastereomeric pathway, which also differs in mechanism from the other diastereomeric TSs. Facial control arises from the presence or absence of a single chiral NCHB donor stabilizing the developing alkoxide. Diastereocontrol is afforded by the configuration of the epimerizable β-stereocenter hydrogen affecting the conjugative ability of the keto aryl group. This same control arises in the rapid and enantioselective retro-[2+2] decarboxylations of the product bicyclic β-lactones to cyclopentenes.

A study on the origins of enantioselectivity of an NHC-catalyzed homoaldol with acylphosphonates uncovered stereodifferentiating pockets of NCHB akin to an oxyanion hole between the catalyst aryl groups and the phosphonyl (P=O) oxygen. Computations predicted an increase of selectivity by blocking the sites stabilizing the minor transition state. Synthesis and test of the catalyst verified computational predictions.

A chiral bifunctional aminothiourea has been developed for the Michael addition of acrylates to α-ketones to generate asymmetric all-carbon quaternary centers. This catalyst both activates the nucleophile via enamine catalysis and employs hydrogen bonding catalysis to activate the carbonyl-bearing electrophile. A joint experimental and computational study reveals the mechanism of this process and seeks to uncover the origins of selectivity. Computations predict that deletion of the catalyst β-phenyl group would increase selectivity; however, experimental synthesis and test led to unforeseen catalyst decomposition.

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Rationalization and Innovative Design of Asymmetric Organocatalysts through Computational Investigation

by

Ryne Connell Johnston

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APPROVED:

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Chair of the Department of Chemistry

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I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

Ryne Connell Johnston, Author

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Dedicated to my
loving parents,
dear friends and
devoted teachers
in my life.

Chapter 1.
Introduction

1.1 Organocatalysis: Biomimicry on the Small Scale

Catalysis is key to creating powerful drugs that conquer disease and materials that improve the quality of life. Enzymes are the reigning champions of catalysis Despite their incredible size, many enzymes perform their tasks with simple chemistry: through acid-base catalysis or covalent catalysis.[1] The structural rigidity afforded by their macromolecularity provides the remarkable rate enhancement and substrate & product selectivity.[2] Toward the goal of reproducing the efficiency and fidelity that Nature has long since optimized, synthetic, often expensive and sometimes toxic transition metal catalysts have been developed in the past century. The discovery of catalytic activity from small organic metal-free molecules offers a cheap, green and bioreminiscent alternative to the metal catalysts dominating the asymmetric catalysis field and the possibilty of a dramatic miniaturization and generalization of Nature's catalysts.[3]

1.1.1 Enamine catalysis

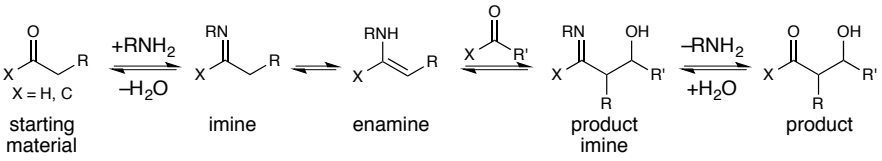


Figure 1.1 Enamine-catalyzed aldol.

Pioneering work on enamine chemistry by Stork in the 1960s discovered the ability of primary and secondary amines react at the α-position of ketones and aldehydes through condensation and enamine tautomerization in conditions far milder than the known enolate chemistry.[4] This method of covalent catalysis is compatible with many electrophiles, including α,β-unsaturated carbonyls (Michael reactivity) and aldehydes (aldol reactivity).[5] Stork discovered reactivity employed by Nature for millions of years. Mammalian aldolase A (ALDOA) is a key enzyme in both glycolysis and gluconeogenesis and catalyzes the reversible aldol reaction of fructose-1,6-bisphosphate (FBP) into glyceraldehyde 3-phosphate (G3P) and dihydroxyacetone phosphate (DHAP).[6] As a class-I aldolase, ALDOA condenses onto the substrate with lysine-229 and severs the bond via enamine chemistry.[7] The reverse gluconeogenesis reaction proceeds stereoselectively.

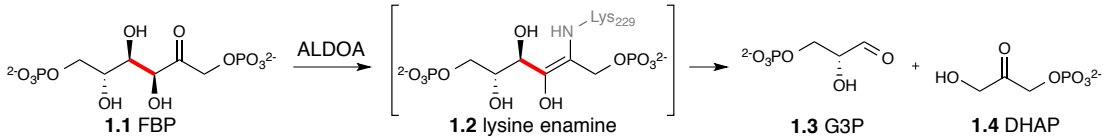


Figure 1.2 ALDOA lyses FBP through an intermediate Lys_{229} enamine.

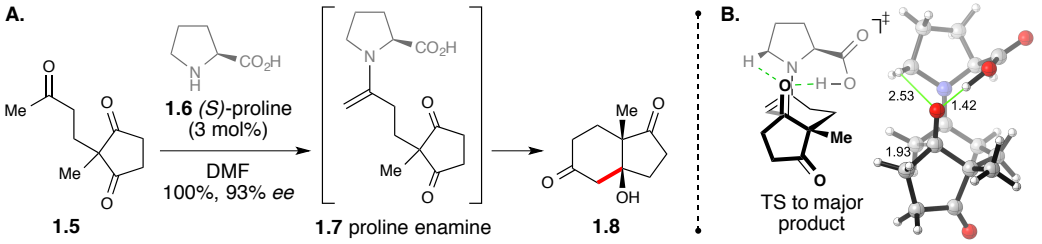


Figure 1.3 A) Proline-catalyzed HPESW reaction with proline enamine. B) TS structure leading to the major product. Green lines indicate stabilizing interactions; distances in Ångstroms.

The amino acid proline, being a secondary amine, stereoselectively catalyzes aldol reactions in much the same way as ALDOA.[8] The reports by Hajos & Parrish and later Eder, Sauer & Wiechert (together HPESW) first described the proline-catalyzed aldol annulation of triketone **1.5** with high stereoselectivity.[9] The bifunctional nature of proline allows both covalent enamine catalysis and hydrogen bonding catalysis. Asymmetric induction was proposed to result from selective hydrogen bonding activation between the proline acid and the electrophilic ketone. Houk later discovered that iminium distortion and non-classical hydrogen bonding were the two main components behind the observed selectivity. [10] These hydrogen bonding motifs stabilize additions to many electrophiles, allowing broad α-reactivity including Michael, aldol/Mannich, halogenation, amination, etc.[11] Subsequent investigations by Barbas, List, MacMillan and others showed proline to be a privileged catalyst: its core structure dominates the enamine catalysis field; of the 48 most common catalysts in List's 2007 seminal review on enamine catalysis[11] only eight were not proline based.

1.1.2 N-Heterocyclic carbene catalysis

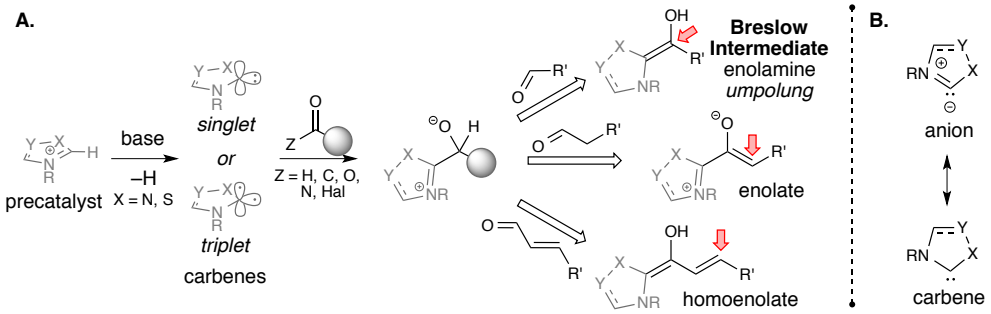


Figure 1.4 A) Deprotonation of the NHC precatalyst yields a free singlet or triplet carbene. Nucleophilic addition to carbonyl-bearing substrates generates a various intermediates. B) Azolium carbenes have an anionic character.

Discovered in 1832 by the father of organic chemistry, Friedrich Wöhler, the cyanide-promoted dimerization of benzaldehyde to benzoin is the ancestral carbene-promoted process.[12] The carbene is a neutral, divalent carbon species capable of electrophilic and nucleophilic additions. C2 deprotonation of *N*-heterocycles in the azolium class generates a paired (singlet) carbene stabilized by the flanking nitrogen lone pair donation into the carbene empty p-orbital.[13] Addition of these *N*-heterocyclic carbenes (NHCs) to carbonyls leads to a stabilized enolamine intermediary species critical for catalysis.[14] The enolamine, termed the Breslow intermediate, behaves functionally

as an acyl anion to access *umpolung* chemistry, whereby the inherent reactivity of the carbonyl is reversed to be nucleophilic at carbon.[12b,15]

Occurring in all organisms as part of the pentose phosphate pathway and the Calvin cycle in photosynthetic organisms, transketolase (TKT) is a ubiquitous enzyme that catalyzes the transfer of a two-carbon segment from xylulose 5-phosphate (**1.9** X5P) to ribose 5-phosphate (**1.11** R5P), generating sedoheptulose-7-phosphate (**1.12** S7P) and G3P.[16] Deprotonation of the thiamine diphosphate (diphosphorylated vitamin B_1) cofactor generates a carbene, which adds to X5P, severs and transfers the two-carbon fragment via a Breslow intermediate to R5P.[14a,17] Because thiamine alone is effective in catalyzing these reactions, although unselectively,[18] a class of asymmetric *N*-heterocyclic carbene (NHC) catalysts have been designed around thiamine's carbene-bearing thiazole group.

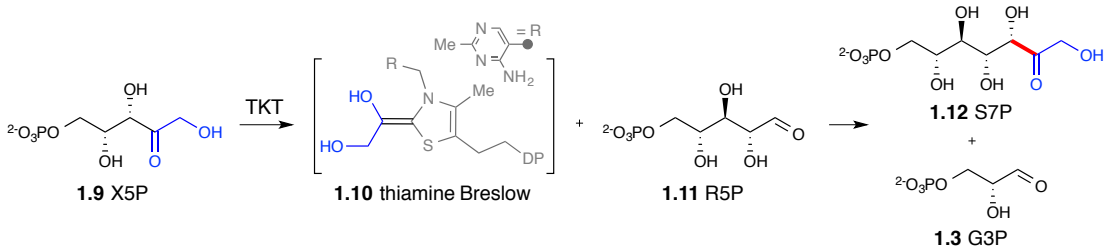


Figure 1.5 TKT transfers 2-hydroxyacetaldehyde from donor X5P to R5P with a thiamine Breslow intermediate.

Synthetic NHC catalysts have been developed to display benzoin-type reactivity (Figure 1.6) with high enantioselectivity.[19] Michael reactivity is common for NHC-catalyzed processes. With the acyl anion, Stetter additions are common and can compete with benzoin reactivity. Enders, Rovis and Scheidt have developed asymmetric variants.[20] More remote reactivity may be unlocked via the "push-pull" azolium nitrogen. α-Reduction of the Breslow or ketene substrates opens reactivity toward aldol reactivity, leading to formal hetero-[4+2]-cycloadduct lactones and lactams with α,β-unsaturated electrophiles.[21] Homoenolate chemistry may be accessed with α,β-unsaturated aldehyde substrates and is a common route to functionalized cyclopentenes and γ-adducts[22] In addition to their organocatalytic properties, NHCs are competent ligands for transition metal catalysts.[23]

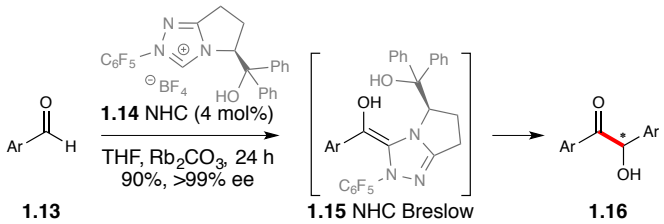


Figure 1.6 NHC-catalyzed asymmetric benzoin condensation.

1.1.3 Hydrogen bonding catalysis

The aromatic amino acids phenylalanine (Phe), tryptophan (Trp) and tyrosine (Tyr) all originate from the shikimate pathway and share chorismate as their last common precursor. [24] This pathway is only found in plants, fungi,

bacteria and some algae and is critical in the biosynthesis of structural lignin in cell walls. Because animals lack the shkimate pathway they must obtain these essential amino acids through their diet. Chorismate mutase (CM) rearranges chorismate **1.17** to prephenic acid **1.18** en route to Tyr and Phe,[25] while anthranilate synthase routes to Trp. Rather than covalent catalysis, a complex hydrogen bonding network within the CM active site stabilizes the dipolar allyl cation/enolate in the chairlike Claisen transition state of chorismate to prephenate.[26] The structure of the active site in the TS was probed with X-ray crystallography of analogue **1.31** in the enzyme.[27]

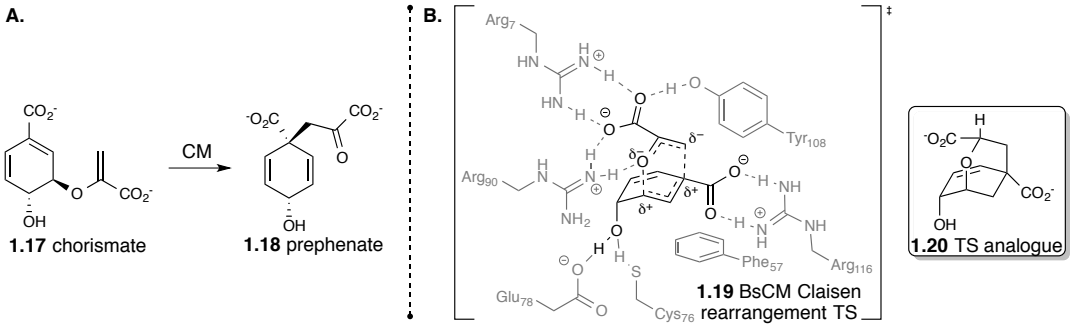


Figure 1.7 A) CM catalyzes the Claisen rearrangement of chorismate. B) Putative Claisen transition state in the *Bacillus subtilis* CM (BsCM) active site probed with a TS analogue.

Drawing direct inspiration from the catalytic arginine in CM, Jacobsen designed a chiral guanidinium hydrogen bonding catalyst (**1.22**) to facilitate selective Claisen rearrangements to yield vicinal stereocenters, of which one is all-carbon quaternary.[28] Experiments and computations show additional cation-π stabilization in the TS; selectivity has a positive correlation with the amount of aryl electron donation. While other hydrogen bonding catalysts like urea and thiourea failed to provide significant Claisen activation, urea and thiourea catalysts have proven effective in catalyzing a [4+2]-cycloaddition between aryl imines and electron-rich dienophiles with high enantioselectivity.[29] Computations indicate 2,4-nitrobenzenesulfonic acid (NBSA) relays the urea **1.27** hydrogen bonds to activate the imine. Direct hydrogen bonding to the iminium proton through the sulfone provides further TS stabilization.

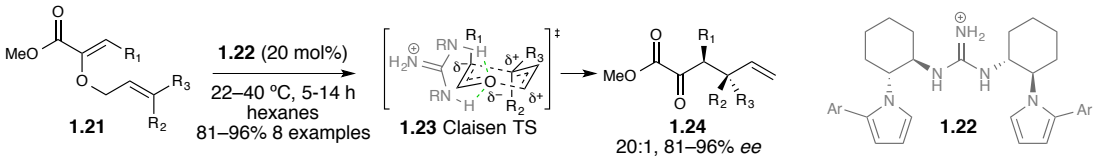


Figure 1.8 Chiral guanidinium catalyzed Claisen rearrangement.

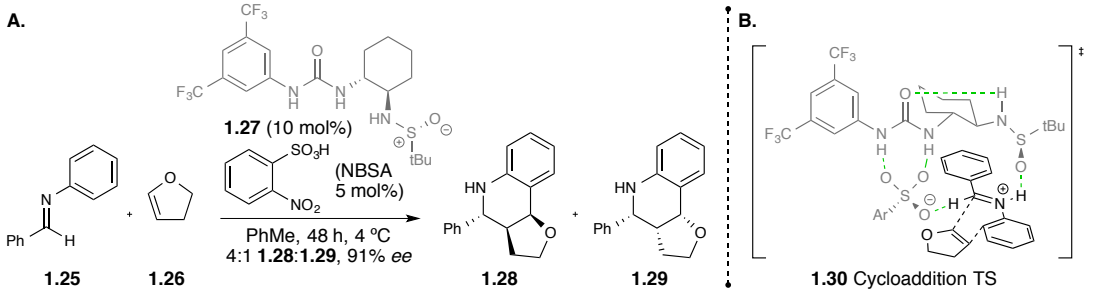


Figure 1.9 Aminosulfoxide urea catalyzed [4+2]-cycloaddition.

Guanidinium, (thio)urea,[30] squaramides,[31] TADDOL[32] and BINOL-derivatives[33] are frequently employed in hydrogen bonding catalysis,[34] and many catalysts that feature hydrogen bond donors often provide good reactivity.[35] In addition to containing stereodirecting fragments, these catalysts also bear electronically modifiable groups to tune hydrogen bonding strength. Thiourea catalysts, for example, perform best with electron-poor *N*-aryl substituents to strengthen the hydrogen bond.[36] The bis-3,5-trifluoromethyl aryl group is both strongly electron-withdrawing and can provide further stabilization through an aryl C–H···X (X = N, O).[37]

1.2 Computational Investigation and Design of Organocatalysts

The advancements of organocatalysts over the past two decades prompted us to consider the process of catalyst discovery. Current methods to find a suitable catalyst are time-consuming and costly brute-force catalyst screening techniques, requiring synthesizing and testing an array of potential catalysts. Even then, obtaining a good hit for a catalyst is often still left up to serendipity. Computational drug design is already a staple in the pharmaceutical industry in the form of QSAR, docking and combinatorial chemistry. Unlike cluster and other heterogeneous catalysts that operate by surface adsorption,[38] small molecule catalysts engage in discrete reactions and rely on turnover, and thus hinge on downstream thermodynamics. Application of computations toward designing solid catalysts maximizing large-scale effects have already found industrial success,[39] but only a handful of reports exist for small molecule catalysts, both transition metal[40] and organic catalysts,[41] because designs require computing reaction coordinates for each proposed catalyst;[42] even fewer have been experimentally verified. The dearth of these reports suggests the formidability of successfully applying computations toward design.

One confounding aspect of computational design is the limitation of the computation itself. In analyzing the reaction profile, care must be taken to choose the appropriate combination of model systems, level of theory and relevant conformations to describe the overall chemical system. Our general routine begins with a mid-level, gas phase geometry optimization of molecular mechanics geometries with either Becke's B3LYP[43] or Truhlar's Minnesota functionals[44] coupled with the double-zeta 6-31G(d) basis set.[45] On these optimized structures are performed high-accuracy single-point energy refinements with Grimme's spin-component scaled second order Møller-Plesset SCS-MP2[46] method and a Dunning ((aug-)cc-pV*n*Z)[47] or Ahlrichs (def2-*n*ZVP)[48] basis set extrapolated to the infinite zeta from the triple- and quadruple-zeta basis sets.[49] To the *in vacuo* single-point calculations is added the energy of solvation from an implicit solvation method, either PCM[50] or SMD,[51] and the geometry optimization method with a larger 6-311+G(d,p) basis set. At the discretion of the researcher, extra calculations may be added to this general scheme to better describe the system.

Simplified model systems often remove or abridge molecular shrubbery unrelated to the chemistry at play to reduce the degrees of freedom (e.g., ethyl groups are commonly modeled as methyl groups) in order to better understand the fundamental elements. Designs often hinge upon modifying the model system to affect the inherent reactivity or selectivity. To have a truly confident design, however, the full chemical system should be computed in order to

account for important secondary interactions. However, the sheer number of conformers in an exhaustive search and the length of computational time for each conformer make this endeavor generally intractable without prior knowledge of the salient interactions and tools to parse out the relevant conformers.

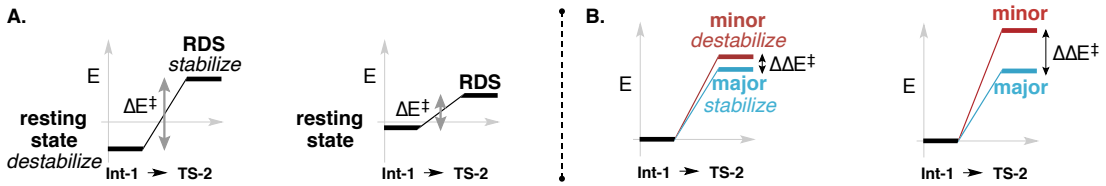


Figure 1.10 A) Designing a more reactive catalyst requires either raising the resting state or lowering the rate-determining TS to lower the overall barrier. B) Designing a more selective catalyst requires increasing the relative barriers by either lowering the RDS barrier of the major TS or raising the barrier of the minor TS.

The chemical factors critical to reactivity and selectivity can be gleaned through quantum mechanical investigation of the reaction mechanism or critical stereodetermining steps. Lowest energy transition state structures (LETS) of the rate- and/or stereodetermining step(s) are the foundation and template upon which the new catalyst is designed. Experimental stereoselectivity results from an energetic difference in transition state (TS) barriers ($\Delta\Delta G^{\ddagger}$) arising from either a stabilizing interaction occurring in the major TS structure, or a destabilizing interaction in the minor TS structure. Preferred TSs maximize stabilizing electronic and/or electrostatic interactions while minimizing destabilizing interactions. Stereoselective catalysts often work by either maximizing the major diastereomeric TS(s) or by maximizing destabilizing interactions in the minor TS(s). Enhancing existing catalysts' selectivity focuses on manipulating chemical moieties to increase these differentiating interactions.

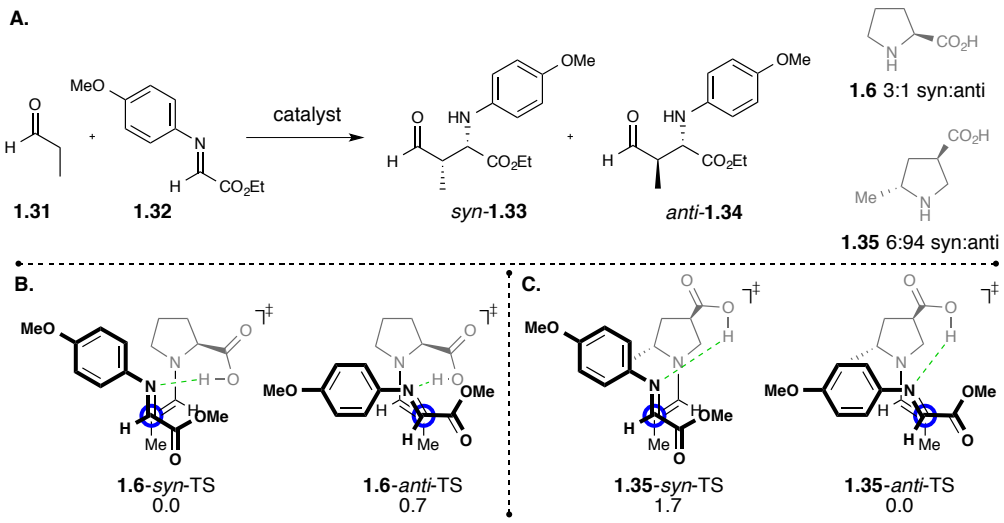


Figure 1.11 A) Proline-catalyzed Mannich reactions typically give *syn* products; a redesigned catalyst **1.44** gives predominately *anti* products. B) Proline TSs favor the *syn* product. C) **1.44** TSs favor the *anti* product. Relative energies given in kcal/mol.

Houk and Barbas's report of a computationally designed catalyst in their 2006 design of an *anti*-selective proline-catalyzed Mannich reaction is an important early example of experimental verification of a computationally

designed catalyst.[52] Quantum mechanical treatment indicated that the typical *syn* Mannich selectivity (*syn*: 3:1 dr, 99% *ee* with proline) arises almost entirely from the *anti*-enamine geometry to avoid steric repulsion with the catalyst substituent. Steric repulsion is a strong controlling element, overriding the more thermodynamically stable *syn*-enamine (4.6:1 *syn:anti*).[10d] Noting this preference, proposed catalyst **1.44** unlocks *anti* selectivity through an α'-methyl group which exploits steric repulsion to fix the enamine geometry *syn* to COOH. Experiments verified the computational predictions to a high degree of agreement. Proline has long been the model for design because of the well-understood transition states and its bifunctionality.[53]

Thiourea catalysts were the second manifolds to be improved through computations. Schreiner's bis-3,5-trifluoromethyl thiourea is generally effective in activating diketones and anhydrides toward nucleophilic addition, but fails at catalyzing additions involving aryl epoxides. When Rozas and Connon modeled the hydrogen bonding motifs of **1.47** with these compounds, they found that both the diketones and anhydrides engaged in additional C–H···O activation with the catalyst aryl groups. [54] The lack of an extra C–H acceptor in **1.45** prompted a modification of the catalyst. Replacement of one catalyst aryl group with a similarly electron-withdrawing tosyl group installs a C–H sulfonyl oxygen acceptor to stabilize the transient benzyl cation during reaction. This simple modification dramatically raised the conversion from <2% to 71% in the parent reaction, above that of other hydrogen bonding catalysts.

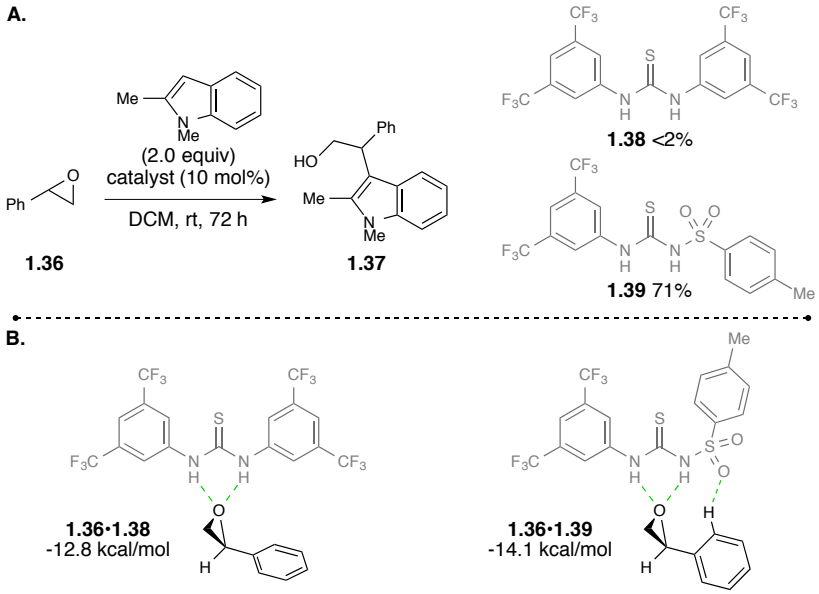


Figure 1.12 A) Styrene oxide opening addition is uncatalyzed by traditional thiourea catalysts but achieved through thiourea sulfonamide catalysts. B) The substrate-catalyst complexes show stronger binding of the thiourea sulfonamide catalyst to styrene oxide.

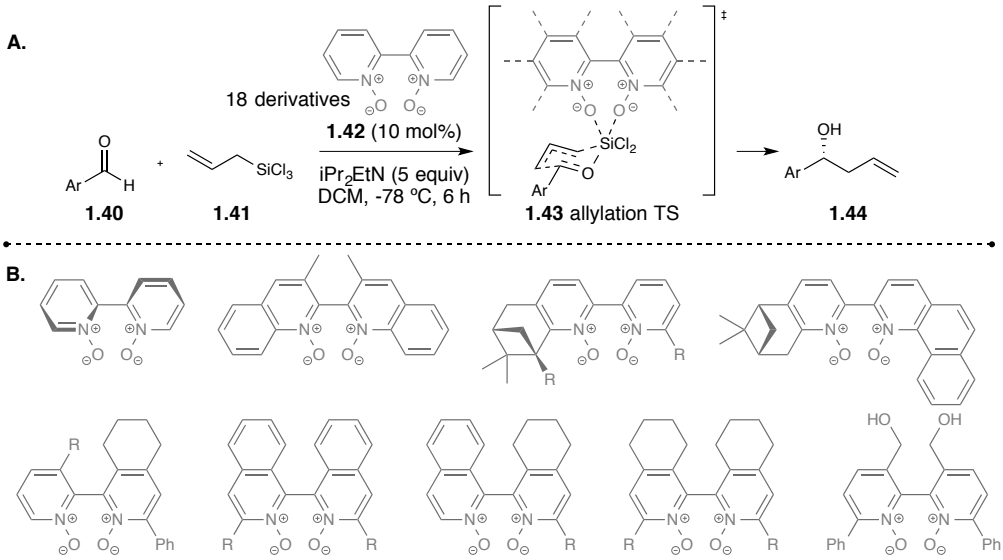


Figure 1.13 A) *N*-oxide bipyridine-catalyzed silylallylation. B) Wheeler has predicted the selectivities of 18 derivatives with automated software.

Wheeler recently disclosed an automated computational design toolkit instrumental in designing a library of axially chiral bipyridine *N*-oxide catalysts for asymmetric allylations and propargylations. [55] Ligation with the allenyl- or allyltrichlorosilane leads to pentavalent silane to which aldehyde is ionically activated toward reaction in a chairlike TS.[56,57,58] This high-throughput method is an automated version of the LETS template design methods. All possible configurations of the stereodetermining TS with the unadorned parent catalyst **1.43** are computed as foundations onto which the other catalysts are templated. Of the 18 computational predictions of enantioselectivity, 16 agree with existing experimental data within 20% of the experimenal value.

1.3 Impetus for Computational Design of Small Molecule Catalysts

Through understanding the chemistry of enzymatic processes we have, over the past almost two centuries, harnessed small organic molecules to mimic and generalize the catalytic processes Nature has honed over hundreds of millions of years. Where in previous decades catalyst discovery and design was relegated to serendipity and toil, the current age of computational power has provided tools to analyze the intimate workings of reaction profiles and develop hypotheses and catalysts to promote reactions and differentiate species. The few reported examples of using computations to design small molecule catalysts stem from the incredible amount of time and insight needed to computationally test a new proposed catalyst. However, hope is found in these reports, for they lay the principles of how to design an improved catalyst.

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Chapter 2.

C–H···O Non-Classical Hydrogen Bonding in the Stereomechanics of Organic Transformations: Theory and Recognition

Ryne C. Johnston, Paul Ha-Yeon Cheong*

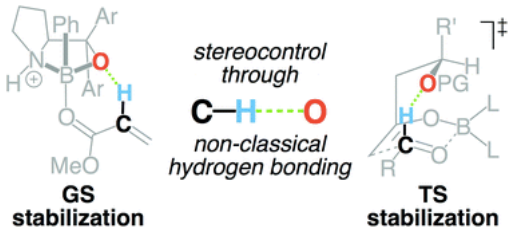
Organic & Biomolecular Chemistry

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2013, *11*, 5057-5064

2.1 Abstract

This manuscript describes the role of non-classical hydrogen bonds (NCHBs), specifically C–H···O interactions, in modern synthetic organic transformations. Our goal is to point out the seminal examples where C–H···O interactions have been invoked as a key stereocontrolling element and to provide predictive value in recognizing future and/or potential C–H···O interactions in modern transformations.



2.2 Introduction

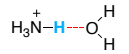
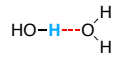
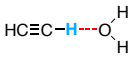
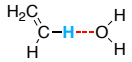
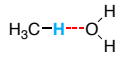
Hydrogen (X–H···A) bonding[1,2] is central to chemistry[3] and biology.[4] Exemplified in water networks[5] and peptide interactions,[6] classical hydrogen bonding involves highly polar donors in the presence of strongly electronegative acceptors (X = A = N, O, F). A number of early reports in the 1930s described anomalous properties of molecules like HCN[7] and acetyl chloride[4] exhibiting hydrogen bonding behavior while having no traditional X–H donor. These studies also showed that less electronegative C-H bonds could be donors as well as other lone-pair bearing atoms and functional groups (sulfur, phosphorous and various π-systems) could be suitable acceptors. Many detailed crystallographic analyses of both inorganic and organic systems in the 1950s and 1960s revealed close C–H···O/N contacts, evidencing the stabilization afforded by NCHB.[8] NCHBs are also found in biological systems; an example being the thiamine-adenine base pair interaction in RNA.[9] These 'non-classical' hydrogen bonds (NCHBs), while weaker ($\Delta G_{interaction}$ = -0.5 to -3.7 kcal/mol)[10] than classical hydrogen bonds ($\Delta G_{interaction}$ = -3.1 to -6.9 kcal/mol),[11] are still found to provide enough stabilization to render complete control of selectivity in chemical reactions.[12]

2.3 General Properties of C–H···O interactions

C–H···O interactions are distinct from van der Waals interactions[13] — H···O distances in C–H···O interactions are often shorter than the sum of the van der Waals radii (2.7 Å for O and H). They also often display directionality (i.e., linear bonds are more stable than bent), indicative of orbital interactions.[14]

Desiraju postulated that NCHBs are a subset of hydrogen bonding.[6c] Indeed, the strength of the H···O interaction, classical or otherwise, is proportional to the polarization of the donor C–H and the charge of the acceptor heteroatom; i.e., more acidic hydrogens and greater anionic characters in acceptors result in stronger hydrogen bonds. As shown in Table 2.1, the trend of proton acidity with respect to hybridization decreases as follows: $sp > sp^2 > sp^3$.[15,16] Direct experimental observation of transition state NCHBs is difficult because of the short lifespan (< 200 fs) of TSs.[17] However, NCHBs in the ground state have been documented via infrared and NMR spectroscopy. C–H···O interactions are characterized in the IR by a strong redshift (-40 $cm^{-1} > \Delta\nu >$ -80 cm^{-1}) for alkynes, little to no redshift (0 $cm^{-1} > \Delta\nu >$ -20 cm^{-1}) for alkenes, and a medium blueshift (+60 $cm^{-1} > \Delta\nu >$ +10 cm^{-1}) for alkanes. Redshifted (lengthened) C–H bonds, typically seen in classical hydrogen bonding, result from lone pair donation of acceptor A into the σ* C–H, the extreme of which is full deprotonation. Conversely, a blueshift (contraction) results when an electron-deficient R_3C–H bond, already lengthened, is compressed by electron density donation from an electron-rich A.[16b,18] ^{1}H-NMR observation is typically marked by an upfield shift of the proton of interest depending on the strength of the hydrogen bond. Alkynes are characterized by a 1.9 ppm shift upfield, alkenes by a 1.5 ppm shift, and alkanes by a 1.2 ppm shift.[13,19]

Table 2.1 Gas-phase distances and energies (ΔH) of salient hydrogen bonding pairs. Distances are in Å, and energies in kcal/mol.[a]

Dimer	H···O Distance	Energy (ΔH)	Reference
	1.74	19	16a
	1.96	4.7	14a
	2.17	2.5	16b
	2.38	0.9	16b
	2.51	0.3	14a

[a] See original literature for computational details.

2.4 C–H···O Interactions in Synthesis

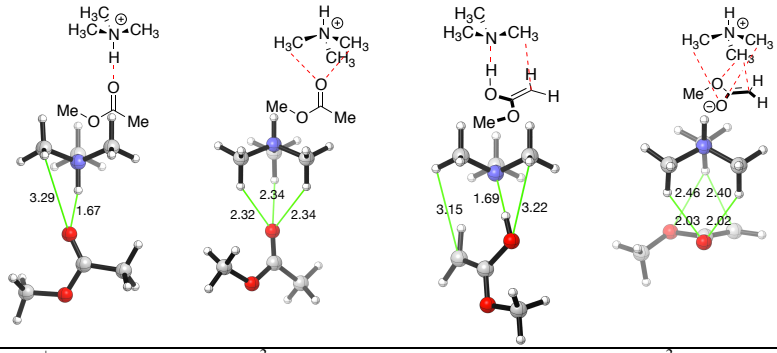
Corey popularized NCHBs in transition states (TSs). He extended the idea of stabilizing C–H···O interactions to TS geometries, recognizing their potential roles in both rigidifying the TS (preorganization) and in overcoming the entropic cost of preorganization.[20] Selectivity by NCHBs arise in two ways: 1) where NCHB stabilization is only possible in the major TS, and 2) where NCHB interactions exist in all TSs, but the resultant preorganization forces the minor TSs to incur destabilizing steric and/or electrostatic interactions.

Various archetypical stereoselective transformations[21] controlled by NCHBs are discussed in the following sections, organized by the type of C–H donors. While C(sp)–H donors are expected to be the strongest, there have been no reports to date implicating the alkynyl proton as a stereocontrolling element.

2.4.1 C(sp^3)–H donors

C(sp^3)–H donors can be subdivided into activated and unactivated donors. Activated donors are α to a full or developing positive charge, and are most commonly seen in Group 15- and metal-bearing molecules. Examples involving unactivated donors are fewer, and mostly involve distal methyl or methylene groups at a critical point. In both cases, proximity to an electron-withdrawing group increases the C–H donating ability.

Table 2.2 Binding energies (ΔZPE) of complexes of trimethylammonium with methyl acetate. Solid green lines show electrostatic interactions. Computations performed at MP2/6-311++G**, with interaction free energies given in kcal/mol.



Solvent	N^+–H···$O_{carbonyl}$	$C(sp^3)$–H···$O_{carbonyl}$	N···H–O_{enol}	$C(sp^3)$–H···$O_{enolate}/\pi$	ε_r
gas	-19.7	-12.9	-10.9	-95.1	1.0
PhMe	-10.3	-5.2	-8.1	-40.9	2.4
$CHCl_3$	-7.5	-3.4	-7.8	-22.2	4.7
THF	-6.2	-2.2	-7.2	-15.2	7.6
MeOH	+0.3	+2.0	-4.3	+0.7	32.7
H_2O	+0.8	+2.4	-3.9	+2.3	80.1

2.4.1.1 Activated $C(sp^3)$–H donors

2.4.1.1.1 Ammonium N+–C(sp3)–H···O interactions

In 2002, Houk reported the magnitude of HB and NCHB stabilizations between trimethylammonium with methyl acetate or the methyl acetate enolate (Table 2.2).[22] In all cases, the magnitudes of classical hydrogen bonding interactions were greater than those of the NCHB interactions. It was also shown that solvent environment had a dramatic effect on the magnitude of stabilization – these interactions are the strongest in the gas phase and non-polar solvents, and decrease as the solvent polarity increases.[23]

The greatest interaction is experienced in the tight ion pair of the trimethylammonium N^+–$C(sp^3)$–H complexing to the negatively charged enolate oxygen and the π-system, resulting in a dramatic 95 kcal/mol of stabilization in the gas phase. The $C(sp^3)$–H···O distances are also remarkably short (2.02 Å). Conversely, the weakest interaction is the post-proton transfer complex of the enol and the deprotonated ammonium (N···H–O), at only 10.9 kcal/mol stabilization.

Comparisons of the neutral acceptor, methyl acetate, illustrate the relative strengths of classical and non-classical hydrogen bonding. The stabilization afforded by three NCHB interactions (N^+–$C(sp^3)$–H···$O_{carbonyl}$) amounts to about two-thirds the stabilization of a single classical hydrogen bond (N^+–H···$O_{carbonyl}$) (-12.9 kcal/mol and -19.7 kcal/mol, respectively).

These specific model systems and interactions are integral to understanding *cinchona* catalysis, and have since been employed to describe the enantiocontrol in a number of reactions.[24]

2.4.1.1.2 Iminium N^+–$C(sp^3)$–H···O interactions

Houk reported the mechanism and origins of stereoselectivity of the Hajos-Parrish reaction[25] (Figure 2.1).[26] C–H···O interactions were seen to be important in controlling the stereoselectivity in the aldol and Mannich reactions. The stereoselectivity in the Hajos-Parrish arises from the addition of the proline-enamine to one of two cyclic ketones. The enantioselectivity originates primarily from the greater iminium planarity distortion in the *syn*-enamine **TS-*(R,R)*** compared to the *anti* **TS-*(S,S)***. A secondary stereocontrolling factor is the ability of a prolinyl $C(sp^3)$–H to stabilize the developing negative charge on the carbonyl oxygen (shown in green lines in Figure 2.1) — the major **TS-*(S,S)*** exhibits a shorter C–H···O interaction and is lower in energy by 3.4 kcal/mol than **TS-*(R,R)***, where this interaction is more distal and presumably weaker.

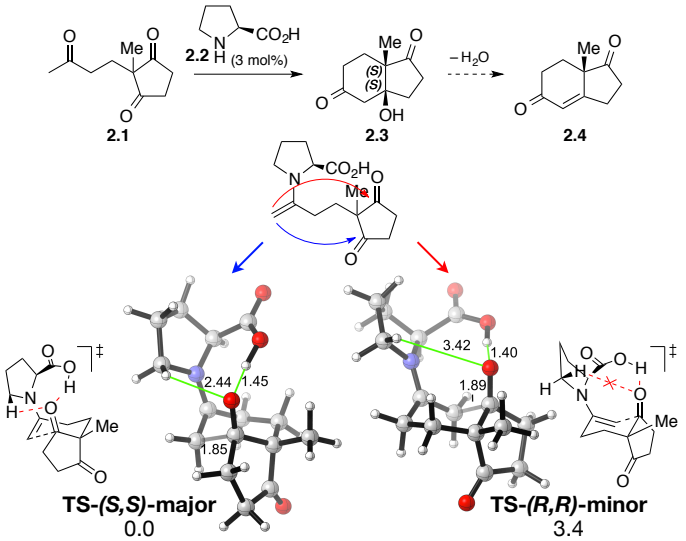


Figure 2.1 Houk model for the enantiocontrol in the Hajos-Parrish reaction. Enamine planarity and NCHB with the proline α-methylene hydrogens control selectivity for **TS-*(S,S)***. Solid green lines show electrostatic interactions, grey lines show forming bonds. Computations performed at B3LYP/6-31G*, with free energies given in kcal/mol.

2.4.1.2 Unactivated $C(sp^3)$–H donors

2.4.1.2.1 Allylic–$C(sp^3)$–H···O interactions

Sordo reported a computational study of the *meta*/*para* selectivity in the hetero [4+2]-cycloaddition between SO_2 and isoprene in 1994. To our knowledge, this is the earliest work citing NCHBs as selectivity controlling elements in the TS (Figure 2.2).[27,28] He showed that regioselectivity is controlled by the $C(sp^3)$–H···O NCHB interaction between the sulfonyl oxygen and the isoprene methyl. **TS-*meta-endo***, with the $C(sp^3)$–H···O interaction, is 1.8 kcal/mol more stable than **TS-*para-endo***, where this interaction is absent. As shown by the *para-endo* and *para-exo*

TSs, the *endo* preference[29] for cycloaddition is minimal (0.2 kcal/mol). To date, there have been no asymmetric additions of SO_2 and dienes, so Sordo's study remains purely theoretical but important nonetheless.

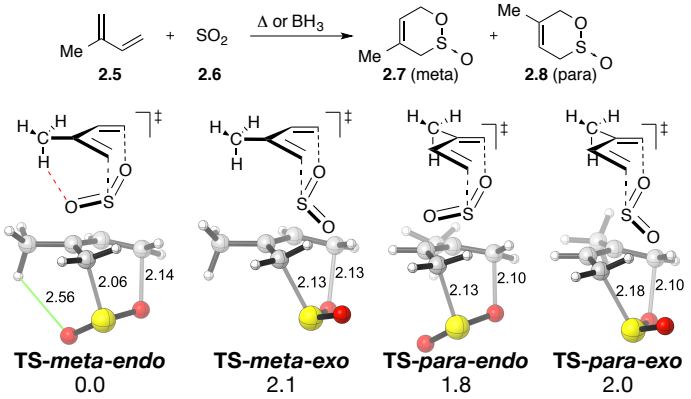
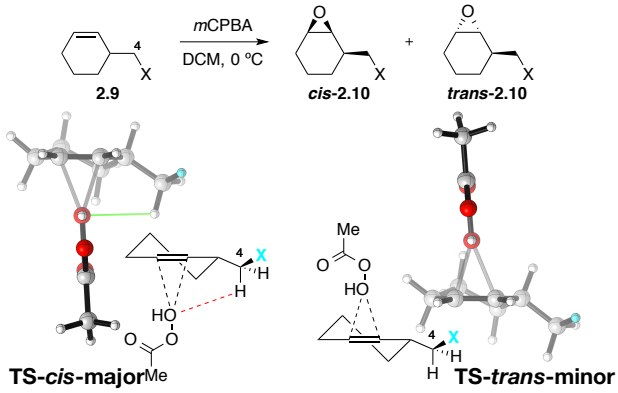


Figure 2.2 SO_2 regioselectively adds to isoprene in the TS-*meta-endo* fashion to engage in NCHB. Solid green lines show electrostatic interactions, while grey lines show forming bonds. Computations performed at MP2/6-31G*//HF/6-31G*, with interaction free energies given in kcal/mol.

Table 2.3 Approach from the π-face where NCHBs are present is preferred. π-Facial selectivity of peracid epoxidation increases with the electron-withdrawing ability of X. Solid green lines show electrostatic interactions, while grey lines show forming bonds. Computations performed at B3LYP/6-31+G**//B3LYP/6-31G*, with interaction free energies given in kcal/mol.



X	*cis:trans* (exp.)	$\Delta\Delta E_{trans\text{-}cis}$ (exp.)	$\Delta\Delta E_{trans\text{-}cis}$ (comp.)
H	1:1	0.0	0.2
Br	2.3:1	0.4	1.7
CN	4:1	0.8	1.5
OMs	13.3:1	1.4	2.3

2.4.1.2.2 Alkyl–C(sp^3)–H···O interactions

In 2001, Houk reported the role of unactivated C(sp^3)–H donors in controlling the stereoselectivity of epoxidations.[30] The origin of π-facial selectivity comes from the propensity of the peracid to approach from the face where an NCHB with the terminal peracid oxygen and the C_4 hydrogens may be realized (Table 2.3). Furthermore,

the selectivity afforded by these NCHBs is enhanced as the electron-withdrawing ability of the C_3 α-substituent increases – the cis preference increases from 0.2 kcal/mol (exp.: 1:1 *cis*:*trans*) in the hydrogen case to 2.3 kcal/mol (exp.: 13:1 *cis*:*trans*) in the mesylate.

2.4.2 C(sp^2)–H donors

NCHB involving C(sp^2)–H are often strong, and can impart preorganization of the TS. By far, the most common of this type are formyl groups. The ubiquity of formyl groups in many highly stereoselective allylboration, aldol and Diels-Alder reactions is conspicuous. The origin of this phenomenon is the presence of NCHB involving the formyl hydrogen that contributes to heightened stereocontrol. Imine C-H donors have similarly been shown to engage in NCHB.[31]

2.4.2.1 Ground and transition state stabilization

In 1997, Corey proposed stereochemical models governing the enantioselectivity of aldol reactions utilizing oxazaborolidine Lewis acids (Figure 2.3).[20a-c,32] He invoked a two-point binding motif in the ground state catalyst-aldehyde complex, which is preserved through the transition state. The primary binding arises from the substrate carbonyl-boron dative bond. The second arises from a NCHB between the formyl hydrogen and the oxazaborolidine oxygen. This two-point binding motif, when coupled with the catalysts' chiral substituents, imparts facial control of addition to the aldehyde. While initial computational studies[33] found this motif to be less favorable, more recent studies[34] have upheld Corey's proposal.

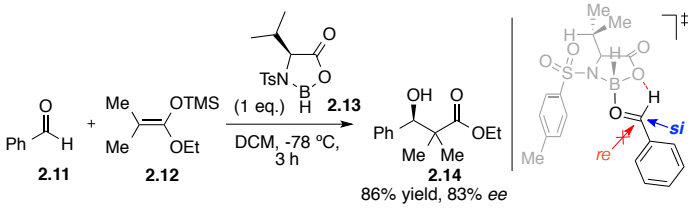


Figure 2.3 Corey's oxazaborolidine-catalyzed Mukaiyama aldol *(left)*. Proposed stereochemical model *(right)* showing two-point binding, with the catalyst tosyl group shielding the *re*-face.

Related oxazaborolidinium catalysts have also been applied to Diels-Alder reactions (Figure 2.4, top left).[35] Like the aldol, the dienophile is bound to the catalyst primarily by the carbonyl oxygen-boron dative bond, and secondarily by NCHB between the formyl proton and the oxazaborolidinium oxygen.

In 2009, Houk verified these models computationally using a slightly simplified catalyst involving a Ph, rather than *o*-Tol on the borane (Figure 2.4, left).[36] The two point binding provided by the dative B–O bond and the C–H···O NCHB interaction restricts dienophile rotation, and allows for the facial discrimination. Steric occlusion by the downward-facing oxazaborolidinium aryl group prevents *si*-addition, which leads to the minor product.

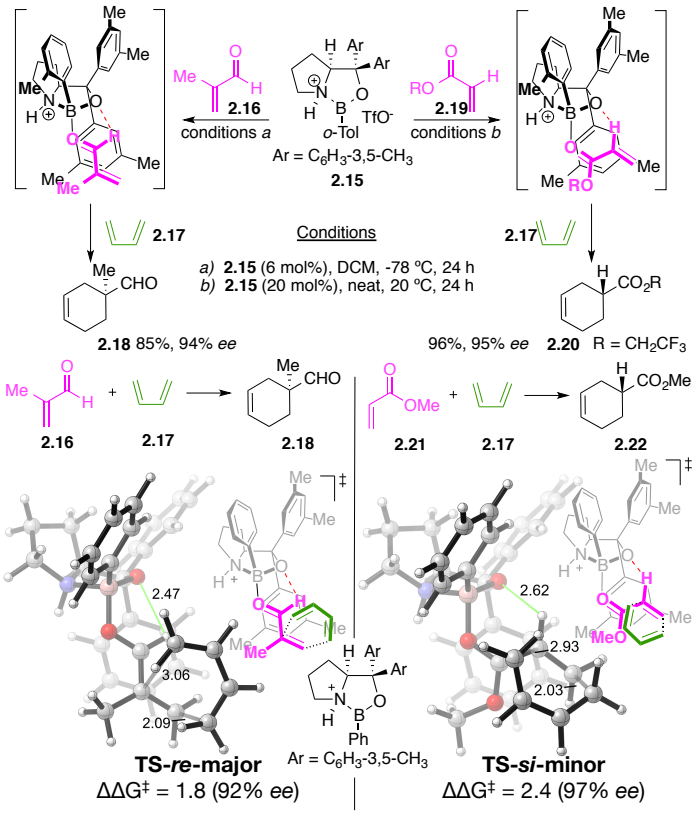


Figure 2.4 Corey's oxazaborolidinium **2.15** catalyzed Diels-Alder cycloaddition of vinylogous aldehydes (left) and esters (right) with 1,3-butadiene, and their respective proposed catalyst-substrate complexes. The catalyst aryl group blocks the concave face of the substrate. Houk's computational investigation on Corey's oxazaborolidinium-catalyzed [4+2]-cycloaddition with methacrylaldehyde (left) and methyl acrylate (right). The catalyst aryl group blocks the concave face of the substrate. Solid green lines show electrostatic interactions, while grey lines show forming bonds. Computations performed at B3LYP/6-31G*/PCM(DCM)//B3LYP/6-31G*, with interaction free energies given in kcal/mol.

In 2002, Corey reported that these oxazaborolidinium catalysts also perform well with acrylates and fumarates (Figure 2.4, right).[35b-d] In the absence of a formyl hydrogen, an NCHB with the vinylogous hydrogen acts as secondary binding, rigidifying the transition state. Houk verified this vinylogous C(sp^2)–H···O interaction in α,β-unsaturated carbonyl compounds, citing the same stereocontrol model as in the formyl cases.[36]

2.4.2.2 Transition state stabilization

Transient NCHBs found only in the transition state can also induce high selectivity. In 1998, Paterson applied the formyl C–H···O NCHB model to explain the 1,4-*syn* stereoinduction in the boron-mediated aldol addition of aldehydes to α-alkoxy ketones **2.23** (Figure 2.5).[37] This featured repeatedly in the synthesis of polyketide ACRL Toxin IIIB to create C_8–C_9 and C_{12}–C_{13} linkages. The chair TS, featuring a C–H···O interaction between a benzoyl carbonyl oxygen and a formyl hydrogen, leads to the major 1,4-*syn* product. In the TS leading to the minor 1,4-*anti* product, the chair flip replaces the stabilizing C–H···O interaction with a repulsive alkyl:alkyl steric repulsion between the β-methyl and the axial boron ligand.

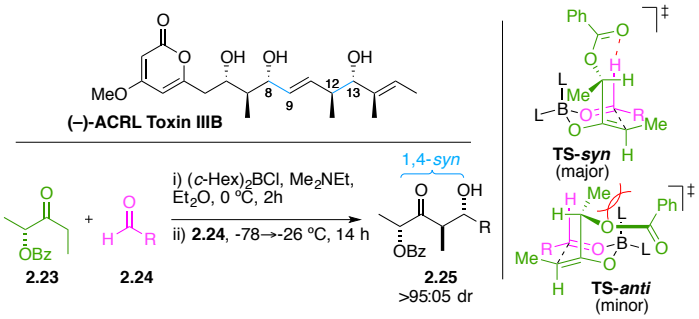


Figure 2.5 ACRL Toxin IIIB *(top)*. 1,4-*syn* selective boron-aldol *(bottom)*. Proposed stereochemical model *(right)* showing critical formyl C(sp^2)–H···O interaction in the favored TS, while steric repulsion destabilizes the disfavored TS.

Goodman later investigated the origins of a related 1,5-stereoinduction in a number of alkoxy and acetal-protected β-alkoxy and β-THP ketones (Figure 2.6).[38] Computations revealed a significant stabilizing C(sp^2)–H···O interaction in a boat conformation.[39] The critical NCHB results from the proximity of the axial alkoxy oxygen to the axial formyl hydrogen, in a seven-membered ring. Like in Paterson's report, Goodman's model derives the selectivity from the chirality of the β-alkoxy center: In order to maintain the NCHB stabilization, the minor **TS-in-*syn*** incurs steric repulsion with the bulky β-R group, amounting to 0.3 kcal/mol selectivity.

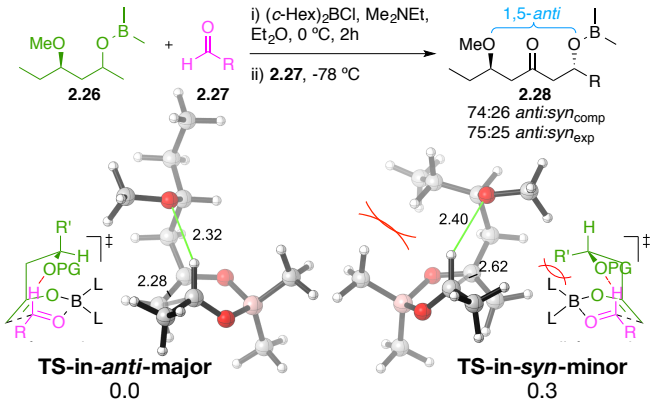


Figure 2.6 Goodman's rationalization for the 1,5-*anti* boron-aldol. Solid green lines show electrostatic interactions, while grey lines show forming bonds. Computations performed at B3LYP/6-31G**/PCM(Et_2O)//B3LYP/6-31G**, with interaction free energies given in kcal/mol.

Antilla reported in 2010 the enantioselective allylboration of aldehydes catalyzed by chiral phosphoric acid (CPA) (Figure 2.7).[40] He proposed a chairlike structure as a likely TS, invoking classical hydrogen bond activation of the equatorial boronate oxygen by the CPA proton.[41]

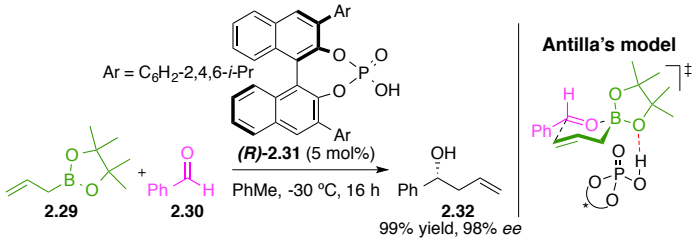


Figure 2.7 Antilla's stereochemical model *(right)* for the enantioselective allylboration catalyzed by chiral phosphoric acid **2.31** *(left)* classically hydrogen bonding to pinacol ligand.

Goodman and coworkers reported a computational study examining the enantiocontrol in this reaction (Figure 2.8).[42] He found that the CPA acts as a bidentate hydrogen bonding ligand, complexing the axial boronate oxygen by classical hydrogen bond (O–H···O) and the aldehyde through NCHB between the formyl hydrogen and the phosphoryl oxygen (C–H···O=P). This two point-binding motif by the CPA conformationally locks the chair transition states and allows for enantiocontrol by the chiral groups on the CPA. The steric clash of the boronate and the CPA aryl group in the minor **TS-*si*** amounts to 6.1 kcal/mol of selectivity. Goodman also found that the Antilla TS is 8.2 kcal/mol higher and results in poorer selectivity ($\Delta\Delta G^{\ddagger}$ = 1.6 kcal/mol). The importance of C–H···O interactions in these reactions have also been shown in recent reports by Houk and Antilla.[43]

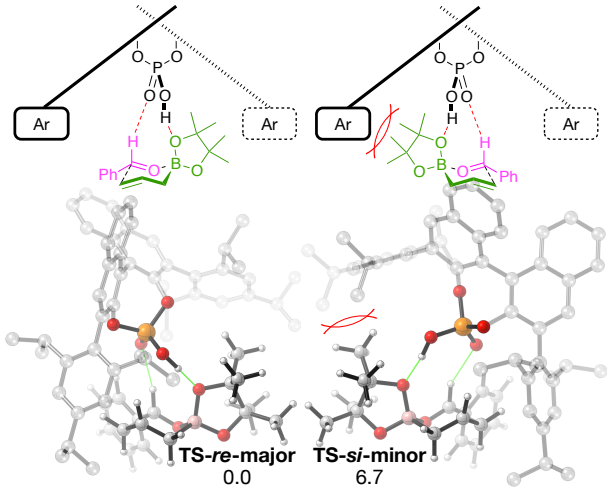


Figure 2.8 Goodman's stereochemical rationalization for the CPA-catalyzed enantioselective allylboration. Selectivity arises from chiral induction by the CPA anchored to the TS through hydrogen bonds. Solid green lines show electrostatic interactions, while grey lines show forming bonds. Computations performed at M06-2X/6-31G**//ONIOM (B3LYP/6-31G**:UFF), with interaction free energies given in kcal/mol.

2.4.3 Cooperative C(sp^2)–H and C(sp^3)–H donors

In complex transition states, mixed hybridizations of C–H···O interactions can and often do occur. We reported in 2010 the mode by which proline sulfonamide catalysts effect stereocontrol in an aldol (Figure 2.9).[44] The sulfonamide oxygens non-classically hydrogen bond with the formyl proton of the electrophile. In addition, another

sulfonamide NCHB with the cyclohexyl methylene group is only possible in the *anti*-enamine approach of the electrophile.

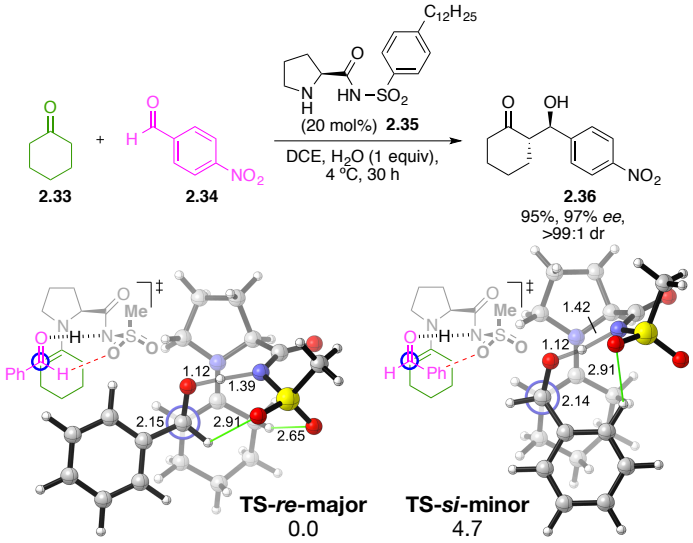


Figure 2.9 Proline sulfonamide-catalyzed aldol reaction. A formyl NCHB selects for the *re* face of the incoming aldehyde. Computations performed at B3LYP/6-31G**/PCM(Et_2O)//B3LYP/6-31G**, with interaction free energies given in kcal/mol.

Planar-chiral DMAP derivative catalyst, PPY* (**2.39**), was known for almost two decades as a general catalyst for ketene additions. Our recent report[45] on the mechanism and stereocontrol behind planar-chiral PPY*-catalyzed pyrrole additions[46] to ketenes uncovered the importance of C(sp^3)–H···O in this catalyst's general mode of ketene activation.[47] Shown in Figure 2.10, following nucleophilic addition of the catalyst to the ketene, the ketene enolate oxygen is sandwiched between the ferrocene rings in a cage of NCHBs formed from the top cyclopentadiene and the bottom permethylated cyclopentadiene. This both stabilizes the alkoxide and, in combination with the planar chirality of the catalyst, imparts selectivity in the subsequent nucleophilic attack by the incoming pyrrole.

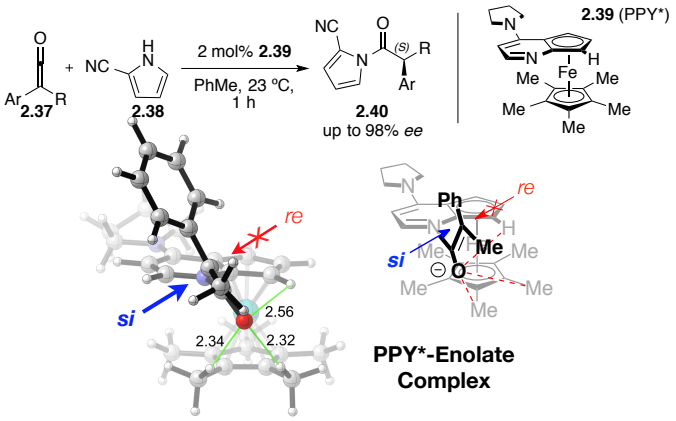


Figure 2.10 Planar-chiral PPY*-ketene enolate is exposed on the *si*-face. Solid green/dotted red lines show electrostatic interactions. Computations performed at B3LYP/6-31G*, with free energies given in kcal/mol.

2.5 Application of C–H···O Model to a New System

Full and developing negative charges in TSs can be stabilized though NCHB interactions. Methylene and methine units α to a full or developing positive charge have increased NCHB donating ability. If a nearby developing negative charge is conformationally able to come into van der Waals proximity, stabilizing C–H···O interactions will occur. These interactions become stereocontrolling when they introduce conformational preference and rigidity in the presence of pre-existing chiral steric environment. Analyzing reactions in these terms suggest that the NCHB contributes to the stereocontrol of a wider variety and range of reactions than presently recognized in the literature.

Lu's 2011 report[48] of an enantioselective phosphinothiourea-catalyzed[49] Morita-Baylis-Hillman reaction displays many of the factors necessary for the existence of stereocontrolling C–H···O interactions (Figure 2.11). In the proposed transition state model, the enolate approach is controlled by classical hydrogen bonds with the thiourea moiety. However, we postulate that there is a developing negative charge on the electrophile carbonyl oxygen that is stabilized by non-classical hydrogen bonds to the hydrogens of the phosphonium α-methylene group (**2.45**, highlighted in blue).[50]

Through classical hydrogen bonding, the thiourea moiety controls the E/Z enolate geometry; this combined with the OTBS group blocking the top face allows approach of the electrophile to the bottom face of the enolate. The geometric constraints imposed by the C(sp^3)–H···O interaction controls the face of the approaching electrophile. The electrophile must approach with the *re* face, orienting the *p*-nitrophenyl group *exo* to avoid steric occlusion with the catalyst.

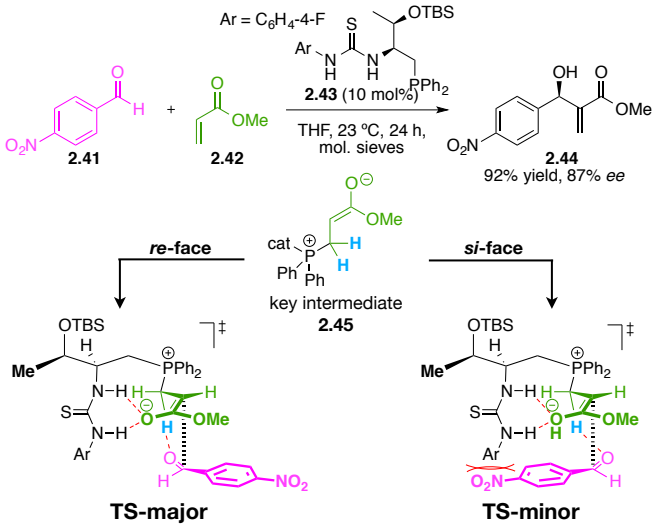


Figure 2.11 We propose that a critical NCHB controls the stereoselectivity of Lu's phoshinothiourea-catalyzed MBH reaction. C(sp^3)–H donors highlighted in blue.

2.6 Conclusions

These studies provide a set of guidelines and scenarios where critical and selective stabilizing non-classical hydrogen bonding C–H···O interactions might be operative so that informed predictions may be made without the use of computations. Although transient and relatively weak, C–H···O interactions are strong enough to render complete control of selectivity in synthetic reactions. These interactions may be much more prevalent, and perhaps more commonplace in stereocontrol than currently acknowledged.

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Chapter 3.

Organocatalytic Kinetic Resolution Cascade Reactions: New Mechanistic and Stereochemical Manifold in Diphenyl Prolinol Silyl Ether Catalysis

Patrick G. McGarraugh, Ryne C. Johnston, Aurora Martínez-Muñoz, Paul Ha-Yeon Cheong, Stacey E. Brenner-Moyer

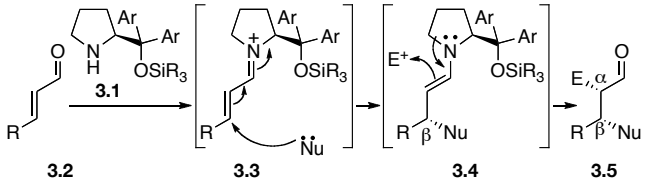
Chemistry – A European Journal
Postfach 10 11 61, 69451 Weinheim, Germany
2012, *18*, 10742–10752

3.1 Abstract

A new cascade reaction involving an iminium-catalyzed intramolecular oxa-Michael addition followed by an enamine-catalyzed intermolecular Michael addition is reported herein. This cascade reaction generates enantiopure, highly functionalized tetrahydropyrans and tetrahydrofurans in a one-pot reaction and in up to 89 % combined yield and up to 99 % *ee*. This cascade reaction is catalyzed by diaryl prolinol silyl ethers, which are a privileged class of catalysts. The stereochemical outcome of these cascade reactions is unprecedented. Computational studies indicate that this stereochemical outcome arises from nonclassical hydrogen-bonding interactions between the electrophile and the substrate, and from entropic considerations of preorganization. The unprecedented configurations of the cascade products, combined with the computational models, reveal for the first time that asymmetric induction by diaryl prolinol silyl ether catalysts is not always exclusively reagent controlled. The stereochemical outcome also arises from a kinetic resolution or dynamic kinetic resolution of the β-stereocenter through an enamine-catalyzed intermolecular reaction. This unprecedented organocascade reaction mechanism may be adaptable to diaryl prolinol silyl ether-catalyzed cascade reactions, in which both the iminium- and enamine-catalyzed steps are intermolecular, an underdeveloped type of cascade reaction.

3.2 Introduction

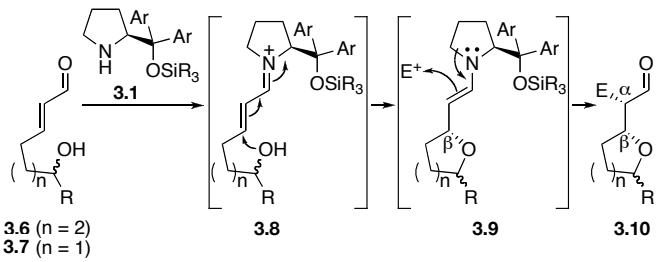
Since they were first reported in 2005, diaryl prolinol silyl ethers (**3.1**, Scheme 3.1) have fast become a privileged class of organocatalysts.[1] While they have proven effective in the production of a diverse array of enantioenriched monofunctionalized saturated aldehydes through enamine or iminium catalysis, arguably their most impressive feat is the catalysis of cascade reactions.[2] Cascade reactions are an efficient green chemical method for rapidly building molecular complexity, in which enamine- and iminium-catalyzed reactions are combined to generate highly functionalized enantiopure aldehydes from simple achiral starting materials in a single flask.



Scheme 3.1 Model for cascade reactions catalyzed by **3.1**.

In the most common class of cascade reactions catalyzed by **3.1**,[3,4,5] an α,β-unsaturated aldehyde **3.2** reacts with **1** to form a conjugated iminium ion, **3.3**. Conjugate addition of a nucleophile (Nu) to **3.3** occurs from the face opposite the bulky groups of the catalyst. The direct product of this conjugate addition is an enamine, **3.4**, which can react with an electrophile (E) that approaches from the face opposite the bulky groups of the catalyst. The vast majority of cascade reactions of this type involve nucleophiles that are tethered to electrophiles, rendering the enamine-catalyzed step intramolecular, generating cyclic products. Subsequent hydrolysis of the catalyst reveals a chiral, vicinally functionalized aldehyde, **3.5**, with the indicated absolute (at the β position) and relative (i.e., α,β-syn) configurations. This simple stereochemical model, in which asymmetric induction in reactions catalyzed by **3.1** is entirely reagent-controlled, rationalizes this stereochemical outcome, which is uniformly observed regardless of the nature of the nucleophile and electrophile, or whether they are tethered or untethered.[3–5]

We recently began investigating the cascade reaction illustrated in Scheme 3.2.[6] We were interested in this cascade reaction for several reasons. First, it would entail a novel oxa-Michael addition (**3.8→3.9**). Second, it would be a rare example of a cascade reaction catalyzed by **3.1** in which the nucleophile (i.e., OH) and electrophile (E) are untethered. Finally, it would generate both 2,5-*cis*- and *trans*-tetrahydrofurans (**3.10**, n=1) and 2,6-*cis*- and trans-tetrahydropyrans (**3.10**, n=2), all of which are prevalent substructures in bioactive complex natural products.



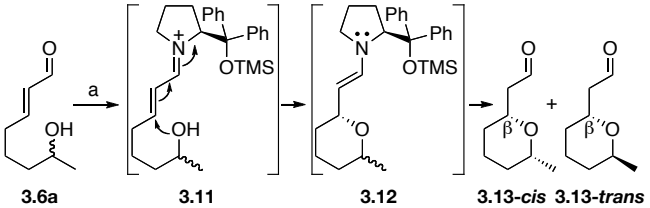
Scheme 3.2 Proposed cascade reaction.

During the course of these investigations, we observed a dramatic difference in the behavior of substrates of type **3.6** and that of substrates of type **3.7** in both steps of this cascade reaction. Additionally, none of the cascade products arising from either **3.6** or **3.7** had the expected absolute (at the β position) and relative (i.e., α,β-*syn*) configurations that are typical of cascade products generated using **3.1** (i.e., those of **3.10**). These results, presented herein, provide new insight into the stereochemical and mechanistic models for cascade reactions employing this popular class of organocatalysts.

3.3 Results and Discussion

3.3.1 Oxa-Michael addition of tetrahydropyran-forming substrates

In the presence of catalyst **3.1**, racemic substrates of type **3.6a** undergo an intramolecular oxa-Michael addition via iminium **3.11** (Scheme 3.3). Conjugate addition of the hydroxyl group from the face opposite the bulky groups of the catalyst directly produces enamine **3.12**, which, upon hydrolysis, yields *cis*- and *trans*-tetrahydropyran products, **3.13-*cis*** and **3.13-*trans***. These products were initially formed in an approximately 1:1 ratio, and in good (in the case of the *cis*-product) to excellent (in the case of the *trans*-product) selectivities. There was, however, a strong thermodynamic preference for the (all-equatorial) *cis*-product. This led to rapid epimerization of **3.13-*trans*** at the β position, thereby generating ***ent*-3.13-*cis***, which increased the cis/trans ratio while decreasing the *ee* of **3.13-*cis***.



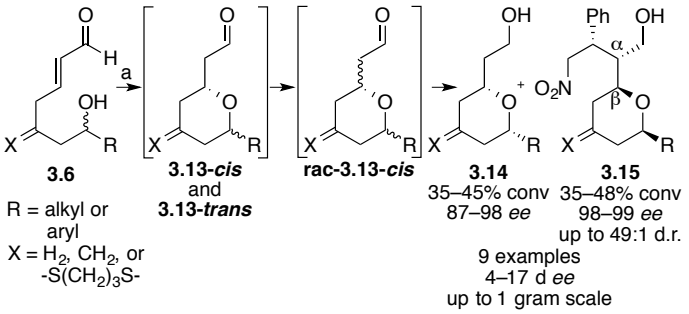
1 min.	*cis* : *trans* = 54/46	68% ee	95% ee
45 min.	*cis* : *trans* = 82/18	17% ee	89% ee

a) **3.6a**, **3.1** (10 mol %), $PhCO_2H$ (10 mol %), toluene, (0.4 M), 0 °C.

Scheme 3.3 Oxa-Michael addition of tetrahydropyran-forming substrates.

3.3.2 Cascade reaction with tetrahydropyran-forming substrates

In the presence of catalyst **3.1** and β-nitrostyrene as an external electrophile, a kinetic resolution of racemic substrates **3.6** resulted (Scheme 3.4). Substrates **3.6** underwent an oxa-Michael addition, initially forming **3.13**-*cis* and -*trans*. The latter rapidly epimerized to **ent-3.13-*cis***, thereby generating a racemic mixture of *cis*-tetrahydropyrans, **rac-3.13-*cis***. One enantiomer, **ent-3.13-*cis***, underwent a subsequent enamine-catalyzed Michael addition to β-nitrostyrene to produce, after reduction, cascade product **3.15**. The rate of this reaction of the other enantiomer, **3.13-*cis***, was substantially diminished, and **3.13-*cis*** was largely recovered (as **3.14**, after reduction).

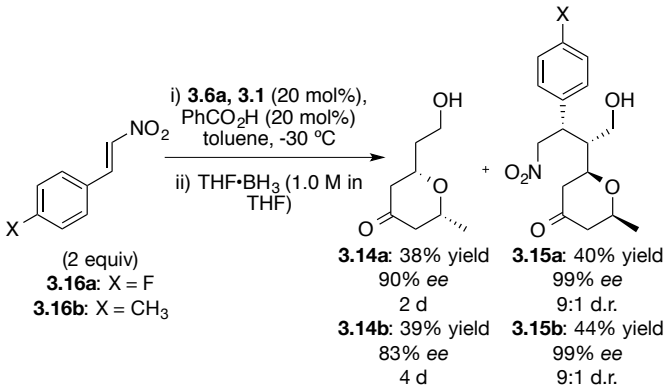


Scheme 3.4 Organocascade kinetic resolution. a) **6** (0.44 mmol), β-nitrostyrene (0.88 mmol), **1** (0.088 mmol), $PhCO_2H$ (0.088 mmol), toluene (1.1 mL), −30 °C, then $THF•BH_3$ (1 M in THF, 0.5 mL) or $NaBH_4$ (2 mmol), MeOH (4.4 mL).

This was, in fact, a rare example of a kinetic resolution by enamine catalysis.[6] Moreover, the resolved intermediates are useful synthons; one was readily transformed in ≤ three steps into known intermediates in the total synthesis of (−)-dactylolide and leucascandrolide A.[6]

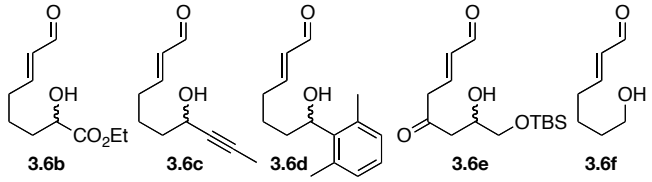
Arguably more notable than the kinetic resolution is the stereochemical outcome of this transformation. The absolute (at the β position) and relative (at the α vs. β positions) configurations of the cascade products **15** were opposite those that normally arise from use of catalyst **3.1** (i.e., **3.15** vs. **3.5**). This unprecedented stereochemical outcome can be accounted for by the proposed stereochemical and mechanistic models for this kinetic resolution, discussed in later sections.

This methodology was also compatible with other β-nitrostyrene substrates, including electron-rich and -poor β-nitrostyrenes (Scheme 3.5). Use of diethylazodicarboxylate or nitrosobenzene as alternative electrophiles in this kinetic resolution, however, was not successful. This may be because these electrophiles lack suitably acidic hydrogens that can participate in nonclassical hydrogen-bonding interactions (see below).



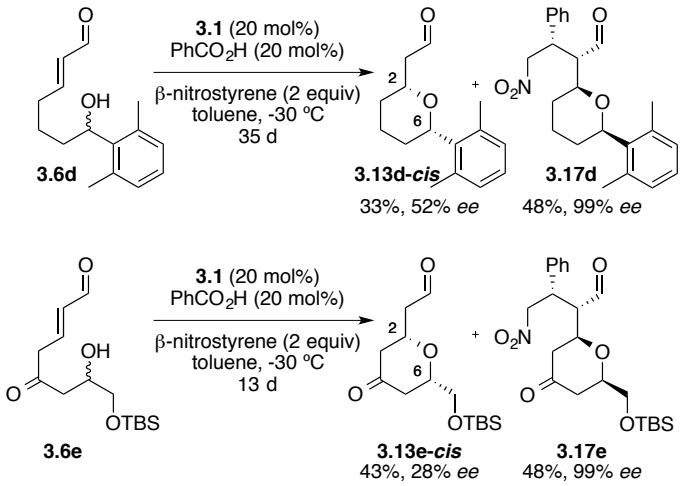
Scheme 3.5 Other β-nitrostyrene substrates.

Although a variety of substrates were tolerated in this kinetic resolution, several substrates were not successfully resolved under these conditions (Scheme 3.6). These included substrates with sterically less demanding R groups, such as **3.6b** and **3.6c**, which contain sp^2- and sp-hybridized carbons, respectively, directly bound to the resulting tetrahydropyran ring. For these substrates, the trans-tetrahydropyran oxa-Michael adduct (**3.13-*trans***) persisted, likely due to the reduced thermodynamic preference for the (all-equatorial) cis-tetrahydropyran. Multiple cascade products were also observed, several of which presumably arose from the trans-tetrahydropyran oxa-Michael adduct.



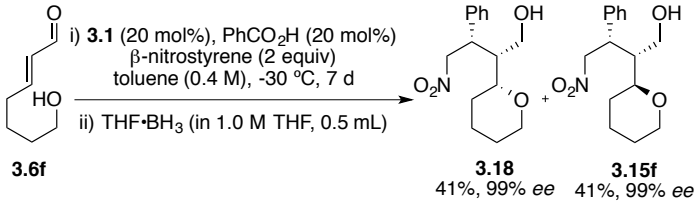
Scheme 3.6 Other substrates for the organocascade kinetic resolution.

Substrates **3.6d** and **3.6e**[7] formed one predominant cascade product, and the reactions were quenched when a good crude yield of this cascade product **3.17** and of the oxa-Michael adduct **3.13-*cis*** was achieved and when their ratio was approximately 1:1 (Scheme 3.7). For all substrates in Scheme 4, this led to high *ee* values of both the cascade product and of the oxa-Michael adduct. For substrates **3.6d** and **3.6e**, the cascade reaction was exceedingly sluggish (13–35 d) and **3.13-*cis*** was recovered (as its corresponding alcohol) in low *ee*. While all substrates of type **3.13** can epimerize at the 2-, or β position (as in the conversion of **3.13-*trans*** to ***ent*-3.13-*cis***), only **3.13d** and **3.13e** have a mechanism by which they can also epimerize at the 6-position. Substrate **3.13d-*cis*** can form a benzylic cation stabilized through resonance with the electron-rich benzene ring. Substrate **3.13e-*cis*** can undergo a β-alkoxide elimination to form an enone, which could be facilitated by deprotonation of the indicated acidic protons by the secondary amine catalyst. We therefore believe that these two substrates were slowly undergoing a dynamic kinetic resolution; **3.13-*cis*** was slowly converting to ***ent*-3.13-*cis***, which (even more slowly) went on to ultimately produce **3.17**, although it should be noted that we did not allow complete consumption of **3.13-*cis*** to test this hypothesis.



Scheme 3.7 An organocascade dynamic kinetic resolution.

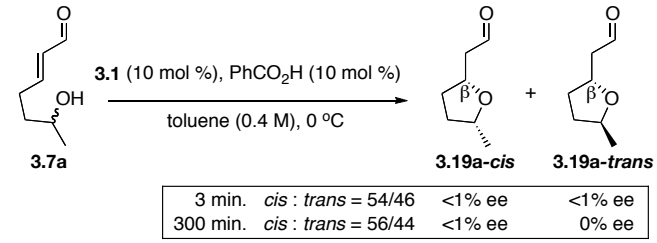
Finally, substrate **3.6f**, without an R group, formed two cascade products, **3.18** and **3.15f**, arising from Michael addition of both enantiomers of **rac-3.13f** to β-nitrostyrene (Scheme 3.8). This result demonstrated that, for the tetrahydropyran-forming substrates, the R group is necessary for the kinetic resolution of oxa-Michael adducts, rac-**3.13**-*cis*.



Scheme 3.8 R group controls outcome of enamine-catalyzed Michael addition.

3.3.3 Oxa-Michael addition of tetrahydrofuran-forming substrates

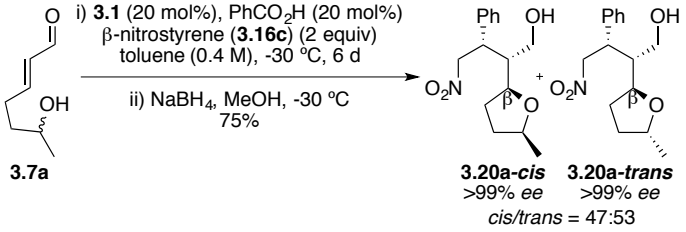
In the presence of catalyst **3.1**, racemic substrates of type **3.7a** also undergo an intramolecular oxa-Michael addition (Scheme 3.9). As in the case of tetrahydropyran-forming substrate **3.6a**, this addition appears to be iminium-catalyzed, as it does not occur on this time scale in the absence of catalyst, nor in the presence of base (Et_3N) or acid ($PhCO_2H$) alone. Also like the tetrahydropyran-forming substrates, *cis*- and *trans*-tetrahydrofuran products, **3.19a**-*cis* and -*trans*, are initially formed in an approximately 1:1 ratio. Unlike the tetrahydropyran-forming substrates, however, both the cis- and trans-tetrahydrofuran products are formed completely nonselectively, in <1 % *ee*. Moreover, the approximately 1:1 *cis/trans* ratio persists over time, possibly due to the reduced thermodynamic preference for a configuration that enables an all-(pseudo)equatorial conformation.



Scheme 3.9 Oxa-Michael addition of tetrahydrofuran-forming substrates.

3.3.4 Cascade reaction with tetrahydrofuran-forming substrates

In the presence of catalyst **3.1** and β-nitrostyrene (**3.16c**) as an external electrophile, cascade products, **3.20a**-*cis* and **3.20a**-*trans*, with *cis*-and *trans*-tetrahydrofuran rings, respectively, were generated (Figure 3.10). This was not entirely surprising in light of the fact that, as discussed in the preceding section, both cis- and trans-tetrahydrofuran rings (i.e., **3.19a**-*cis* and **3.19a**-*trans*) arose from, and persisted in, the iminium-catalyzed oxa-Michael addition. What was surprising, however, was that while racemic cis- and trans-tetrahydrofuran rings arose from the iminium-catalyzed oxa-Michael addition, the subsequent enamine-catalyzed Michael addition to β-nitrostyrene generated cis- and trans-tetrahydrofuran ring-containing cascade products in >99 % *ee*.

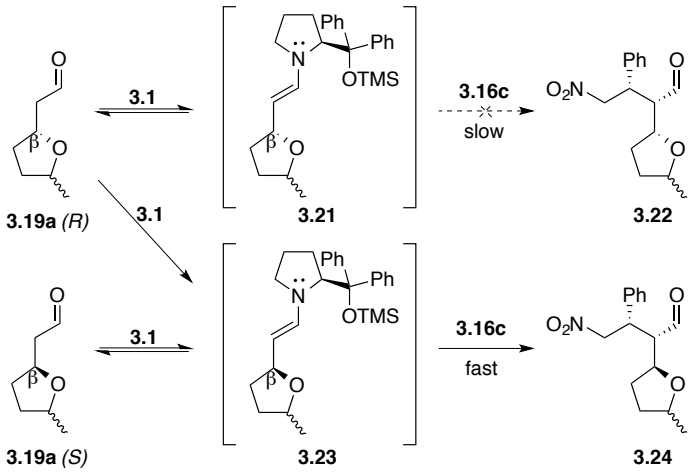


Scheme 3.10 Cascade reaction with tetrahydrofuran-forming substrates.

This is indicative of a dynamic kinetic resolution of the β-stereocenter (Scheme 3.11). Oxa-Michael adducts, **3.19a**-*cis* and -*trans*, with *R* configuration at the β position (i.e., **3.19a** *(R)*), can react with the catalyst to generate enamine **3.21**, which evidently does not react with β-nitrostyrene (**3.16c**). Instead, a retro-oxa-Michael addition followed by a forward oxa-Michael addition, to epimerize the β position of either oxa-Michael adduct **3.19a** *(R)* (to form **3.19a** *(S)*) or of enamine **3.21** (to form **3.23**), occurs. Oxa-Michael adducts **3.19a**-*cis* and -*trans*, with *R* configuration at the β position, would thereby ultimately be converted to enamine **3.23**, with *S* configuration at the β position, which does react with β-nitrostyrene, and which can alternatively form directly from reaction of the catalyst with ent-**3.19a**-*cis* and –*trans* (i.e., **3.19** *(S)*).

As indicated in Scheme 3.11, a variety of substrates afforded similar outcomes to that of **3.7a** in this cascade, including alcohols with adjacent sterically demanding alkyl substituents (**3.7d**), silyl protecting groups (**3.7f**), sp^2-hybridized carbons (**3.7g**, **3.7h**), and stereocenters (**3.7i**, **3.7j**), as well as substrates containing other reactive functional groups (**3.7e**). More specifically, in all cases, cascade products **3.20**-*cis* and **3.20**-*trans*, with *cis*- and *trans*-tetrahydrofuran rings, respectively, were generated in >95 % ee and in an approximately 1:1 ratio.

Interestingly, there was a slight preference for the trans-tetrahydrofuran cascade products in all cases, which contrasts with the initial oxa-Michael addition that slightly favored formation of the *cis*-tetrahydrofuran (Scheme 3.10).

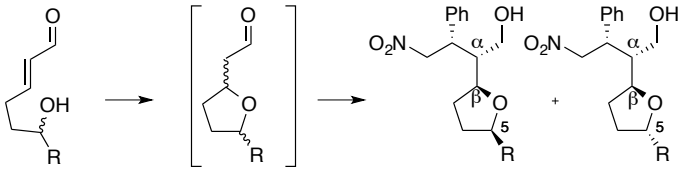


Scheme 3.11 Dynamic kinetic resolution with respect to configuration at β position.

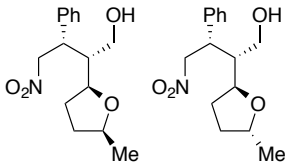
In substrates **3.20i** and **3.20j**, the presence of the additional, adjacent stereocenter did impact the outcome of the cascade reaction. While the cis/trans ratio did not change or changed only modestly, the d.r. of the cis- and trans-products changed dramatically. Compounds **3.20i**-*cis* and **3.20j**-*cis* formed without diastereoselectivity, while **3.20i**-*trans* and **3.20j**-*trans* were formed in outstanding d.r. Additionally, an oxepane-forming substrate readily decomposed under these reaction conditions.

The configuration of cascade products **3.20a**-*cis* and **3.20a**-*trans* at the 5-position was established by running the cascade reaction with the pure R and pure S enantiomers of substrate **3.7a**. The remaining stereocenters in **3.20a**-*cis* and **3.20a**-*trans* were established by X-ray crystallography.[8] The stereochemistry of all other cascade products of type **3.20** was assigned by analogy.

As with the tetrahydropyran-containing cascade products, **3.15**, all tetrahydrofuran-containing cascade products, **3.20**, contain absolute (β position) and relative (α vs. β positions) configurations that are opposite those that normally arise from use of catalyst **3.1** (i.e., **3.20** vs. **3.5**). This unprecedented stereochemical outcome can be accounted for by the proposed stereochemical and mechanistic models for this cascade reaction, discussed in the next two sections.



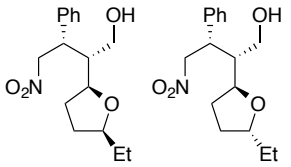
3.7a-j → **rac-3.19-*cis*** and **rac-19-*trans*** → **3.20-*cis*** + **3.20-*trans***



75% yield
47:53

3.20a-*cis* >99% *ee*, 6:1 dr

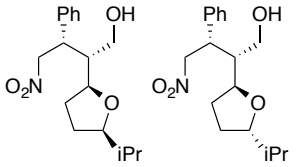
3.20a-*trans* >99% *ee*, 6:1 dr



81% yield
46:54

3.20b-*cis* 98% *ee*, 5:1 dr

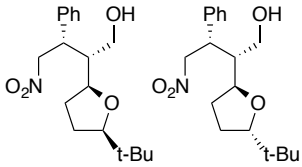
3.20b-*trans* 99% *ee*, 5:1 dr



75% yield
47:53

3.20a-*cis* >99% *ee*, 6:1 dr

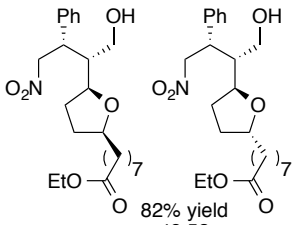
3.20a-*trans* >99% *ee*, 6:1 dr



75% yield
42:58

3.20d-*cis* 97% *ee*, 4:1 dr

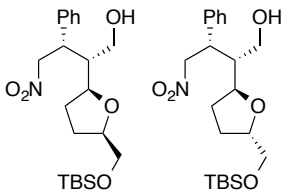
3.20d-*trans* >99% *ee*, 4:1 dr



82% yield
48:52

3.20e-*cis* 98% *ee*, 3:1 dr

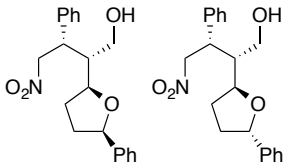
3.20e-*trans* 99% *ee*, 3:1 dr



75% yield
45:55

3.20f-*cis* >99% *ee*, 3:1 dr

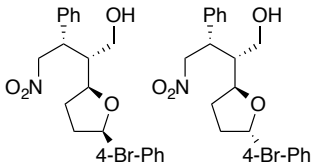
3.20f-*trans* >99% *ee*, 3:1 dr



75% yield
47:53

3.20g-*cis* >99% *ee*, 6:1 dr

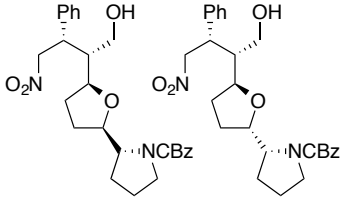
3.20g-*trans* >99% *ee*, 6:1 dr



78% yield
49:51

3.20h-*cis* >99% *ee*, 4:1 dr

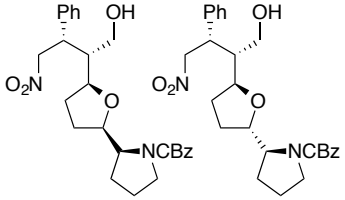
3.20h-*trans* >99% *ee*, 4:1 dr



72% yield
45:55

3.20i-*cis* >99% *ee*, 1:1 dr

3.20i-*trans* >99% *ee*, 18:1 dr



82% yield
35:65

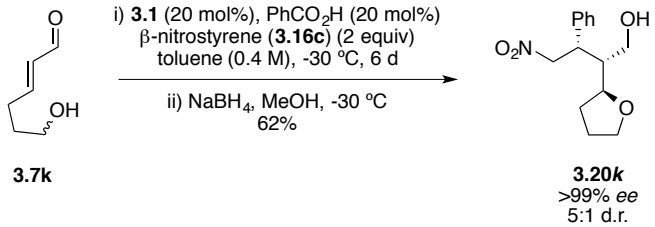
3.20j-*cis* 95% *ee*, 1:1 dr

3.20j-*trans* >99% *ee*, >20:1 dr

Figure 3.1 Scope of cascade reaction with tetrahydrofuran-forming substrates.[a–e]

a) **3.7** (0.44 mmol), **3.16c** (0.88 mmol), **3.1** (0.088 mmol), $PhCO_2H$ (0.088 mmol), toluene (1.1 mL), −30 °C, then $NaBH_4$ (2 mmol), MeOH (4.4 mL), −30 °C. b) Yield = combined isolated yield of **3.20**-*cis* and -*trans*. c) d.r. of the **3.20**-cis and –trans products was determined by ^{1}H NMR spectroscopy and is defined as the ratio of the amount of the major cascade product to the sum of the amounts of the minor cascade products, usually three, arising from the R and S enantiomers, respectively, of **7**. d) *ee* values of alcohol determined by chiral phase HPLC. e) All reaction times were **3.6d**.

Unlike the tetrahydropyran-forming substrates, **3.6**, the R group in the tetrahydrofuran-forming substrates, **3.7**, did not influence the reactivity of the oxa-Michael adducts in the enamine-catalyzed Michael addition to β-nitrostyrene. Evidence in support of this is the formation of cascade products (**3.20a**–**j**) with both R and S configurations at the 5-position. All cascade products do, however, have the same configuration at the β position. This suggests that, in contrast to substrates of type **6**, it is the configuration at the β position that dictates the reactivity of the oxa-Michael adducts arising from substrates **3.7** in the enamine-catalyzed Michael addition to β-nitrostyrene. Further evidence in support of this is that substrate **3.7k**, without an R group, forms a single cascade product (Scheme 3.12).



Scheme 3.12 β-Group, not R group, controls outcome of enamine-catalyzed Michael addition.

3.3.5 Proposed model for stereochemical outcome of cascade reactions

All cascade products generated in these studies (**3.15** and **3.20**) possess *S* configuration at the β position. This configuration effectively arises from the approach of the alcohol from the same face as the bulky groups of the catalyst in the initial iminium-catalyzed oxa-Michael addition. As mentioned, this is not typically observed in reactions catalyzed by **3.1**, and results in cascade products with unprecedented absolute (at the β position) and relative (α vs. β positions) configurations.

With the current understanding of the selectivities of reactions catalyzed by **3.1**, such stereochemical outcomes could only arise if the second step (Michael addition to β-nitrostyrene) was rate- and stereodetermining. The former supposition is supported by experimental data: in all cases, the oxa-Michael addition was observed by ^{1}H NMR to be complete within 12 h, while a further 2–35 d was required for completion of the Michael addition to β-nitrostyrene. Transition states (TSs) of the carbon—carbon bond-forming event involving β-nitrostyrene and the catalyst-enamine of substrates **3.6a** (**TS-IV**), **3.6f** (**TS-II**), **3.7a** (**TS-III**), and **3.7k** (**TS-I**) were, therefore, computed in order to quantify the stereocontrolling elements. Exhaustive DFT conformational searches of the C—C bond-forming transition states were performed. Structures and thermodynamic corrections were computed using B3LYP/6-31G* in

toluene (PCM), as implemented in the Gaussian 09 suite of programs. Energies were refined using SCS-MP2/cc-pVTZ, as implemented in the Q-Chem 4.0.[9] Although the ubiquitous B3LYP/6-31G* often overestimates activation barriers and reaction endergonicity due to poor treatment of dispersion interactions, we at Oregon State have recently discovered that SCS-MP2 single point energies correct for the lack of dispersion in B3LYP/6-31G* results, leading to a remarkable accuracy in barrier heights and stereoselectivities where other methods have failed.[10]

The lowest energy structures of the transition states for the Michael addition to β-nitrostyrene are shown for each stereoisomer in Figure 3.2.[11] The R or S labels refer to the configuration at the β position of the enamine substrate. All transition-state conformations are remarkably similar, with forming C—C bond lengths around 2.1 Å. Although the orientations of the catalyst side chain vary between the different transition states, the energetic differences between these conformations are small, around 0.5 kcal mol^{-1}.[12] The lowest energy conformations have the developing bond between the enamine and β-nitrostyrene occurring from the sterically accessible face of the enamine, opposite the bulky groups of the catalyst side chain. Additionally, the conformation around the β-stereocenters is such that it minimizes the steric and torsional interactions with the approaching β-nitrostyrene electrophile.

There is good agreement between the computed selectivities and experiments. DFT geometry optimizations in solvent (toluene) in conjunction with SCS-MP2 energetics were critical in reproducing the stereoselectivity trends, namely, that the **TS-I**, **TS-III**, and **TS-IV** series are much more selective than **TS-II**. B3LYP gas-phase results erroneously predict that **TS-II** is the most selective (>2 kcal mol^{-1}), and geometry optimizations in solvent erroneously predict the same level of stereoselectivity for **TS-II** and **TS-IV** ($\Delta\Delta G^{\ddagger}$ = 1.2 kcal mol^{-1}), in disagreement with experiments that showed no selectivity for the TS-II series ($\Delta\Delta G^{\ddagger}$ = 0.0 kcal mol^{-1}).

The stereoselectivity of the Michael addition to β-nitrostyrene is controlled by three factors: a) the anti versus syn catalyst-enamine preference; b) the Re or Si facial selectivity of the nitrostyrene electrophile; and c) the effect of the configuration of the β position of the enamine substrate. Prolinol catalysts are known to favor the anti-orientation of the nucleophilic double bond with respect to the catalyst side chain, both in the enamine ground state and the Michael transition states.[12] The nitrostyrene facial selectivity is governed by electrostatic contact between the developing negative charge of the nitro group and the developing positive charge of the enamine in the Michael transition state.[1b] The Si face attack guarantees maximal electrostatic contact and stabilization, and therefore is favored. In all cases, the shortest distance between the nitro group and the enamine nitrogen is >3 Å, indicating nonbonding interaction is in effect, rather than covalent.

While the first two factors are well understood, the effect of the configuration of the β position of the enamine substrate is poorly understood. Initially, in seeking an explanation for this unprecedented stereochemical outcome, we proposed that this might result from differential shielding of enamine faces by the β-stereocenter in the enamine-

catalyzed Michael addition to β-nitrostyrene.[6] However, DFT (B3LYP/6-31G*) modeling of various enamine intermediates revealed no pronounced facial discrimination of the catalyst enamines arising from the β-stereocenter.

The examination of the computed nitrostyrene transition structures reveals that the β-stereocenter of the catalyst–enamine controls the stereoselectivity in two ways: a) enthalpic stabilization from nonclassical hydrogen bonds and b) entropic penalty from preorganization of the reactants in the transition states.

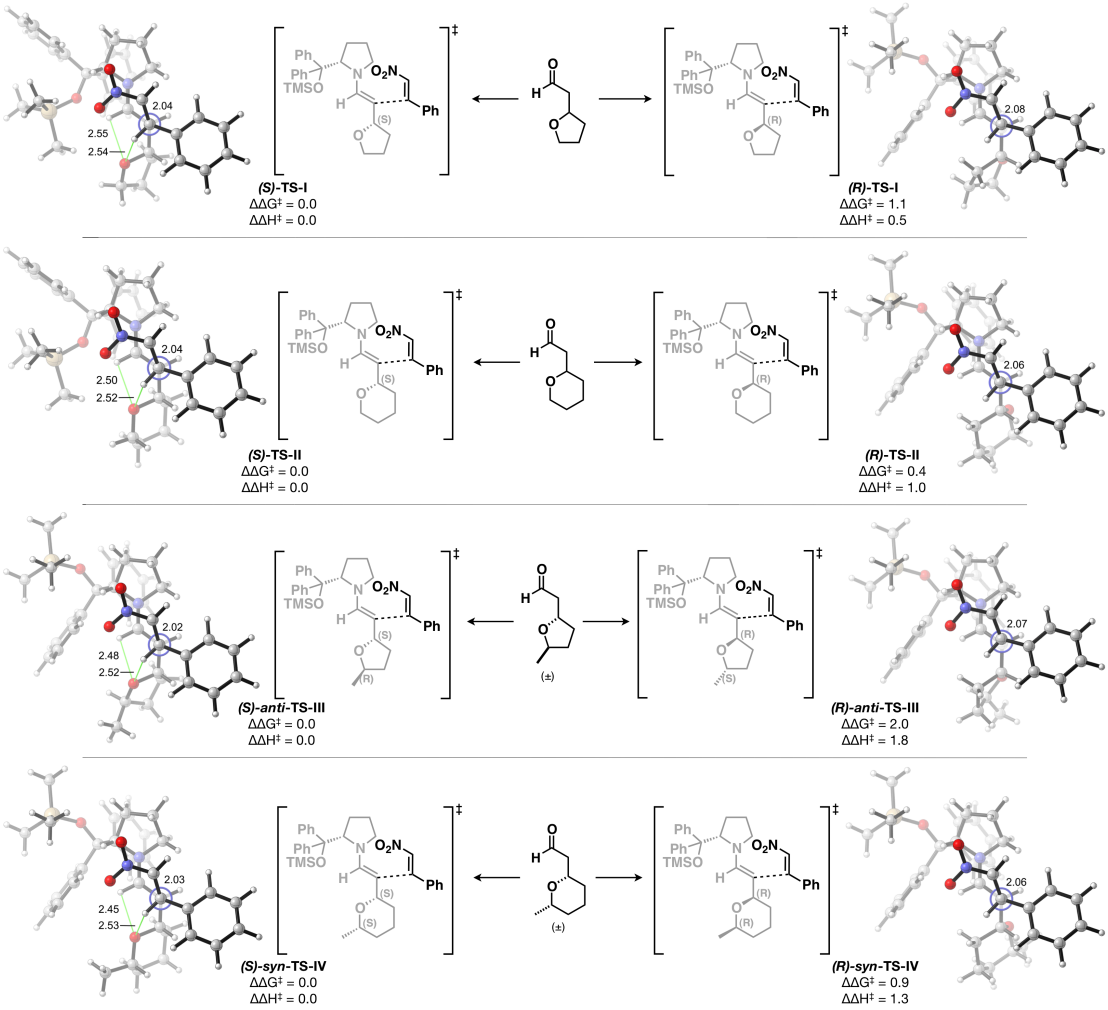


Figure 3.2 C–C Bond-forming transition structures between β-nitrostyrene and the catalyst–enamine of substrates **3.6a** (**TS-IV**), **3.6f** (**TS-II**), **3.7a** (**TS-III**), and **3.7k** (**TS-I**). Experimentally, substrates **3.6a**, **3.7a**, and **3.7k** show greater selectivity than **3.6f**, and the computed results are consistent in that they show that the **TS-I**, **TS-III**, and **TS-IV** are much more selective than the **TS-II** series.

3.3.6 Enthalpic stabilization of (S)-TSs from nonclassical hydrogen bonds

Energetically, at least half of the stereocontrol arises from stabilizing nonclassical hydrogen bonds (electrostatic contacts) between the heterocycle of the catalyst-enamine and the incoming electrophile. Specifically, the *(S)*-TSs are stabilized through nonclassical hydrogen bonds between the approaching β-nitrostyrene benzylic hydrogen and the oxygen of the enamine heterocycle (distances ca. 2.5 Å, indicated by thin lines, Figure 3.2).[13] In the disfavored (R)-TSs, this stabilizing electrostatic contact is replaced by a repulsive electrostatic interaction between a methylene and the β-nitrostyrene benzylic hydrogen. This enthalpic preference is worth 0.5 and 1 kcal mol^{-1} for unsubstituted furan and pyran substrates (**TS-I** and **TS-II**), respectively. However, inclusion of the methyl group (**TS-III** and **TS-IV**) slightly increases the selectivity, possibly through inductive effects that strengthen the basicity of the heterocycle oxygen.

3.3.7 Entropic penalty of preorganization

Entropic penalties accompany preorganization. In this particular study, we have discovered that the entropic considerations play a significant role in determining the stereoselectivity.

In unsubstituted pyrans (**TS-II**), the enthalpic preference ($\Delta\Delta H^{\ddagger}$) for the (S)-TS over the (R) is 1.0 kcal mol^{-1}. However, the conformational preorganization that arises from the nonclassical hydrogen bonds in the (S)-TS is entropically disfavored. Therefore, the free energy preference ($\Delta\Delta G^{\ddagger}$) is smaller in magnitude compared to the enthalpic preference, to the tune of 0.4 kcal mol^{-1}. This entropic penalty is halved in the methyl-substituted case (**TS-IV**) because the equatorial preference of the methyl diminishes the entropic penalty for conformational preorganization of the pyran. This leads to a scenario in which the enthalpic and free energy selectivity are much more similar ($\Delta\Delta H^{\ddagger}$ = 1.3 and $\Delta\Delta G^{\ddagger}$ = 0.9 kcal mol^{-1}).

In unsubstituted (**TS-I**) and methyl-substituted (**TS-III**) furans, the opposite scenario occurs - the free energy preference ($\Delta\Delta G^{\ddagger}$) of (S)-TSs over (R) is greater than the enthalpic preference ($\Delta\Delta H^{\ddagger}$). For an example, in **TS-I**, the $\Delta\Delta H^{\ddagger}$ is 0.5 kcal mol^{-1}, while the free energy preference is 1.1 kcal mol^{-1}. This heightened free energy preference signifies that the (R)-TS is conformationally more rigid (preorganized) than the (S)-TS. This is due to an enthalpic stereoelectronic preference for the furan C—O bond to be anti-periplanar to the forming C—C bond with the incoming electrophile (anti-periplanar atoms circled in Figure 3.3). Only in the (R)-TS, can this anti-periplanar arrangement of a C—O bond with respect to the forming C—C bond be realized, leading to transition state preorganization and thus entropic penalty. In the (S)-TS, the forming C—C bond is anti-periplanar to a ring C—C bond, an arrangement with much weaker electronic bias and therefore weaker entropic penalization. Interestingly, this anti-periplanar arrangement between the forming C—C bond and the heterocycle C—O bond only occurs for the (R)-TS of furans (**TS-I** and **TS-III**), but not the pyrans (**TS-II** and **TS-IV**). In the furan series, this arrangement is clearly anti (~177°), while in the pyran series, it is not (~165°), as shown in Figure 3.3. This explains why the entropic enhancement of selectivity only occurs in the furan series.

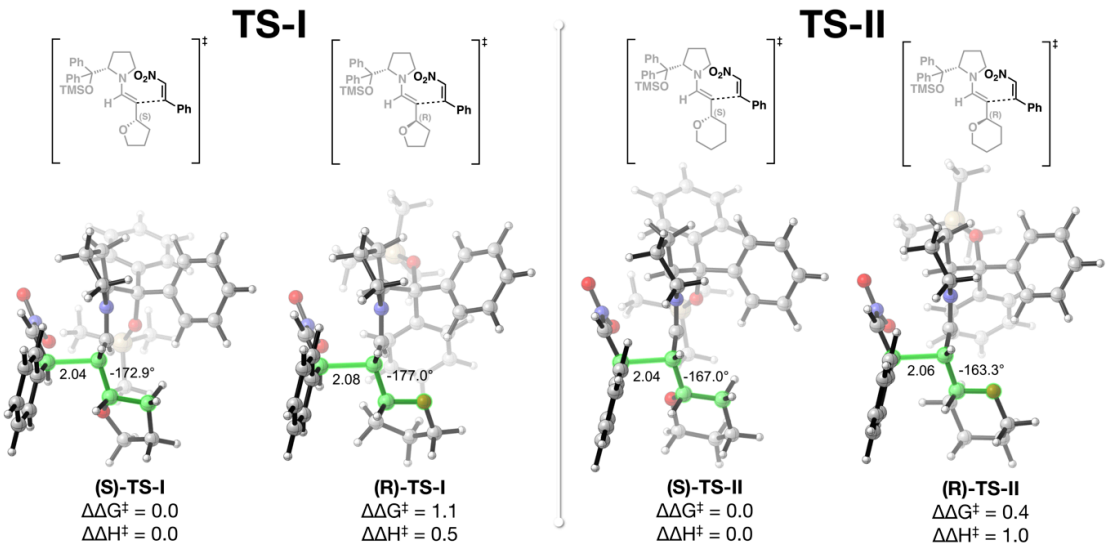


Figure 3.3 Side views of the C—C bond-forming transition structures between β-nitrostyrene and the catalyst–enamine of substrates **3.6f** (**TS-II**) and **3.7k** (**TS-I**) shown in Figure 3.2. In the furan series, for an example the **TS-I** series, the C—O bond of the heterocycle is antiperiplanar to the forming C—C bond, while in the pyran series, for an example the **TS-II** series, it is not. The four atoms involved in this relationship are circled, and the associated dihedral angles reveal that the **TS-I** transition structures are anti (~177°), whereas the analogous angles in **TS-II** transition structures are not (~165°).

Earlier this year, the Blackmond and Armstrong groups published a seminal mechanistic study of **3.1**-catalyzed enamine-mediated conjugate addition of achiral aldehydes to β-nitrostyrene.[14] In this report, they found that the resting state of the catalyst was a cyclobutane intermediate arising from the condensation of the nitroenolate and the catalyst iminium immediately following the Michael addition. Although we cannot rule out a role for analogous cyclobutane species or other stable downstream intermediates in the stereo-determining step, the currently available experimental and computational data are consistent with the hypothesis that the carbon-carbon bond-forming step is stereodetermining.

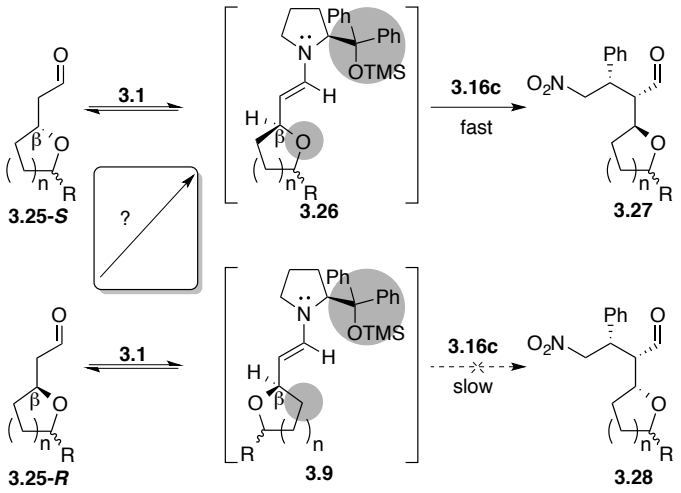
This proposed model accounts for the selectivities of all substrates examined experimentally. Importantly, the unprecedented stereochemical outcome of these **3.1**-catalyzed cascade reactions combined with the proposed enthalpic and entropic stereocontrolling elements that rationalize this outcome together suggest that the accepted stereochemical model for asymmetric induction in reactions catalyzed by **3.1** as being entirely reagent-controlled is an oversimplification. Evidently, there is a more complex relationship between the role of the substrate and that of the catalyst in asymmetric induction in reactions catalyzed by **3.1** than has previously been suggested.

3.3.8 Proposed mechanistic model of cascade reactions

The proposed mechanistic model for these cascade reactions is illustrated in Scheme 3.13. As discussed previously, the initial oxa-Michael addition is reversible and ultimately generates racemic oxa-Michael adducts **3.25** (*cis* only for n=2, *cis* and *trans* for n=1). Oxa-Michael adducts possessing S configuration at the β-carbon react with the

catalyst to form enamine **3.26**, while those possessing R configuration at the β-carbon react with the catalyst to form enamine **3.9**.

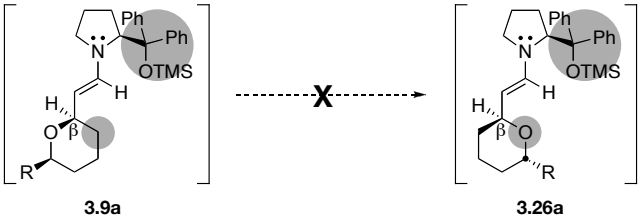
As discussed in the preceding section, synergism between the blocking effects of the catalyst side chain and the directing effects of the nonclassical hydrogen-bond capabilities of the substrate in enamine **3.26**, in conjunction with relatively favorable entropic considerations, result in a relatively rapid reaction with an electrophile that approaches from the back face of the enamine, generating cascade products of type **3.27**. Entropic penalties and/or the absence of this synergism in enamine **3.9**, account for its relative unreactivity and for the observation of, in most cases, only trace formation of cascade products of type **3.28**.



Scheme 3.13 Proposed mechanistic model.

If a retro-oxa-Michael addition/forward oxa-Michael addition to epimerize (R)- **3.25** or **3.9** at the β position can occur, then a dynamic kinetic resolution of the β-stereocenter is possible. This occurs with all tetrahydrofuran-forming substrates (**3.25**, n=1), and both *(S)*- and *(R)*-**3.25** generate cascade products of type **3.27**, with the S configuration at the β position. As mentioned, we also suspect this occurs with tetrahydropyran-forming substrates **3.6d** and **3.6e**.

If a retro-oxa-Michael addition/forward oxa-Michael addition to epimerize *(R)*-**3.25** or **3.9** at the β position is not possible, then a kinetic resolution occurs. This occurs with the tetrahydropyran-forming substrates (**3.25**, n=2), because epimerization of enamine **3.9a** (or its corresponding aldehyde) at the β position would generate a thermodynamically disfavored trans-tetrahydropyran ring, **3.26a**, in which one of the substituents on the ring must occupy an axial position (Figure 3.14). Thus, for tetrahydropyran-forming substrates, enamine **3.26** produces a cascade product, **3.27**, whereas enamine **3.9** cannot readily convert to cascade product **3.28** nor to enamine **3.26**, and so simply reverts back to *(R)*-**3.25**.



3.9a **3.26a**

Scheme 3.14 Epimerization at β position generates the trans-tetrahydropyran ring.

This mechanistic model accounts for the different reactivity of the tetrahydropyran- and -furan-forming substrates. It also presents an interesting possibility. A general strategy to obtain products with high selectivity in cascade reactions initiated by reversible iminium-catalyzed conjugate additions has been to compensate for the reversible conjugate addition to prevent racemization of conjugate addition products at the β position. This has most often been done using an enamine-catalyzed intramolecular reaction. As a result, as mentioned earlier, the vast majority of cascade reactions catalyzed by **3.1** employ nucleophiles tethered to electrophilic centers, forming cyclic products. In so doing, a reversible iminium-catalyzed conjugate addition can be compensated for via: A) an intramolecular enamine-catalyzed reaction that is more rapid than the retro-conjugate addition reaction, or B) a dynamic kinetic resolution of the β-stereocenter of racemic conjugate addition products via an intramolecular enamine-catalyzed reaction. Our data reveals for the first time that the latter scenario is also possible through intermolecular enamine-catalyzed reactions. Thus, using appropriately chosen untethered nucleophiles and electrophiles, it may be possible to develop cascade reactions, in which both steps are intermolecular, and which take advantage of the reversibility of iminium-catalyzed conjugate additions to obtain cascade products with high selectivity through a dynamic kinetic resolution process. Cascade reactions of this type would generate enantiopure, highly functionalized acyclic products, possibly with configurations analogous to those reported herein. Moreover, cascade reactions of this type would lead to an expansion of the limited scope of cascade reactions catalyzed by **3.1** in which both the iminium- and enamine-catalyzed steps are intermolecular.

3.4 Conclusion

In summary, we have developed novel cascade reactions that lead to enantiopure tetrahydropyran and tetrahydrofuran substrates. Notably, all of the cascade products manifest unusual, unprecedented stereochemical configurations opposite of what has been previously reported for diphenyl prolinol silyl ether catalysts. This observation, in conjunction with computational studies, is evidence of a more complex relationship between the role of the substrate and that of the catalyst in asymmetric induction in reactions catalyzed by this privileged class of catalysts than has previously been disclosed. The mechanistic implications of the cascade reactions discussed herein may be amenable to other cascade reactions involving an intermolecular enamine-catalyzed step. This may aid in the development of cascade reactions catalyzed by **3.1** in which both the iminium- and enamine-mediated steps are intermolecular, a class of cascade reactions that has thus far been considerably limited in scope.

3.5 Acknowledgements

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Chapter 4

Catalytic kinetic resolution of a dynamic racemate: highly stereoselective β-lactone formation by *N*-heterocyclic carbene catalysis

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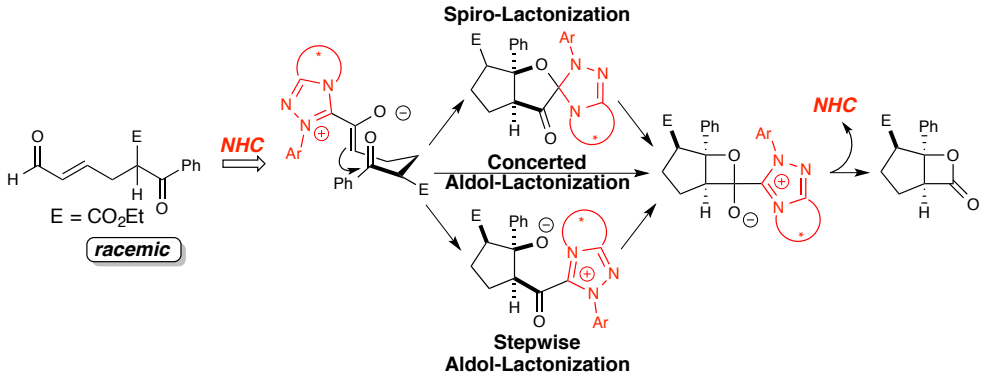
Chemical Science

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4.1 Abstract

This study describes the combined experimental and computational elucidation of the mechanism and origins of stereoselectivities in the NHC-catalyzed dynamic kinetic resolution (DKR) of α-substituted-β-ketoesters. Density functional theory computations reveal that the NHC-catalyzed DKR proceeds by two mechanisms, depending on the stereochemistry around the forming bond: (1) a concerted, asynchronous formal (2 + 2) aldol-lactonization process, or (2) a stepwise spiro-lactonization mechanism where the alkoxide is trapped by the NHC-catalyst. These mechanisms contrast significantly from mechanisms found and postulated in other related transformations. Conjugative stabilization of the electrophile and non-classical hydrogen bonds are key in controlling the stereoselectivity. This reaction constitutes an interesting class of DKRs in which the catalyst is responsible for the kinetic resolution to selectively and irreversibly capture an enantiomer of a substrate undergoing rapid racemization with the help of an exogenous base.



4.2 Introduction

β-Lactones are highly useful building blocks for the synthesis of target compounds, especially in the area of natural product synthesis.[1] Catalytic asymmetric methods have provided new approaches to access this valuable strained ring system, and additional selective routes from different substrate classes open new synthetic possibilities.[2] We recently disclosed the first NHC-catalyzed dynamic kinetic resolution (DKR) reaction that furnishes β-lactones and cyclopentenes in good yields with high stereoselectivities from racemic α-substituted-β-ketoesters (Figure 4.1).[3] Here, we report a collaborative computational study of the origins of stereoselectivities and the reaction mechanism. We have discovered how the degree of conjugation to an electrophile controls the stereoselectivity of this reaction, and how the stereochemical environment around the forming bond leads to a divergence in mechanism. In the process, we have also discovered that this reaction is part of an unusual class of DKRs in which the catalyst is responsible for the kinetic resolution that irreversibly traps an enantiomer of a dynamically racemizing substrate in a stereocontrolled manner.

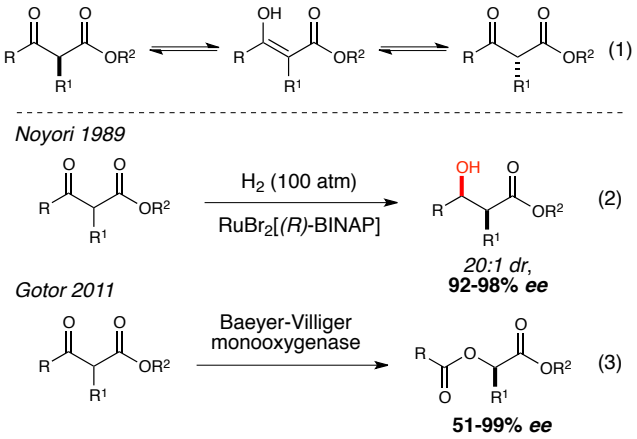


Figure 4.1. DKR of α-substituted-β-ketoesters

The conversion of racemic starting materials to enantioenriched products is an ongoing goal in chemical synthesis with significant impact on the production of high value medicinal compounds.[4] Dynamic kinetic resolutions (DKRs) are one particularly efficient and widely used approach to convert racemic substrates to stereochemically pure products with a theoretical yield of 100%.[5] During the reaction sequence, a catalyst rapidly racemizes the substrate and stereospecifically transforms one enantiomer of the substrate. The ongoing catalyst driven racemization driven by Le Chatelier's principle eventually leads to the accumulation of a stereochemically pure product. Substituted-β-ketoesters are the archetypal substrate for DKR reactions due to their configurational lability at the α-position (Scheme 2 and eqn (1)).[6] Examples of DKRs with α-substituted-β-ketoesters include several asymmetric hydrogenations (eqn (2)),[7] and a Baeyer–Villiger oxidation (eqn (3)).[8] In 2007, we reported the NHC-catalyzed desymmetrization of 1,3-diketones, a kinetic resolution process.[9] In this process, the chiral NHC-generated enol undergoes selective addition to one of the two ketones, to allow for the formation of enantioenriched lactones and

cyclopentenes. Our 2012 report, the title reaction (Figure 4.2), is an expansion of this reaction to a dynamic kinetic resolution process.

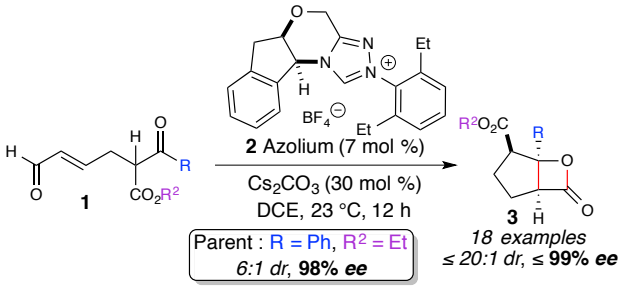


Figure 4.2. The parent transformation. Computational models abbreviated all ethyl groups to methyl.

N-Heterocyclic carbenes (NHCs) have greatly advanced the fields of organic and inorganic chemistry as ligands[10] and as catalysts.[11] These unique Lewis bases have been used to generate acyl anion,[12] homoenolate,[11h,13] and enolate equivalents,[9,14] as well as promote hydroacylation[15] and an exciting variety of non-*umpolung* processes.[16] These carbene-catalyzed processes have been used to access numerous challenging compound classes with high levels of diastereo- and enantioselectivities. With all of the different reaction manifolds accessed through carbene catalysis, it is interesting to note that before our 2012 report, there had been no previous examples in the literature of NHCs facilitating a DKR.[7b]

4.3 Computational methods

The mechanism and origins of stereoselectivity of this reaction were studied using M06-2X[17]/6-31+G**[18]/PCM(DCE)[19]//M06-2X/6-31G* as implemented in the Gaussian 09 suite of programs.[20] This method has previously been shown by Sunoj to reproduce experimentally observed stereoselectivity in a related NHC process.[21] Ethyl groups were modeled as methyl to reduce the degrees of freedom. Manual, exhaustive conformational searches were performed to ensure all relevant intermediates and transition structures were located. Intrinsic reaction coordinates (IRCs) were computed for all transition structures to verify reaction pathways.

4.4 Results and discussion

Previous computational studies of NHC-catalyzed processes have elucidated the mechanisms, reactivities, and stereocontrol in various NHC-organocatalyzed processes.[10g,12e,21-22] This study builds on these earlier reports and reveals not only an unusual method of stereocontrol, but also an unprecedented mechanism. The computed catalytic cycle and the reaction coordinate diagram are shown in Figure 4.3. The attack of the NHC catalyst on the ω-aldehyde, proton transfer, and two tautomerizations lead to the key enolate intermediate **IV**. The subsequent irreversible aldol cyclization diverges to two pathways, depending on the stereochemistry around the forming bond (Figure 4.3): (1) for the major (*R*,*S*,*S*)-product, a concerted asynchronous aldol-lactonization pathway is operative.

This is a formal (2+2) cyclization where the forming alkoxide simultaneously attacks the regenerating adjacent carbonyl, leading directly to the catalyst–lactone adduct **VIII**. (2) For all minor products, a stepwise spiro-lactonization mechanism is operative, where the aldol irreversibly leads to a spiro compound **VIb**, the collapse of which leads to the catalyst–lactone adduct **VIII**. In all cases, the facile dissociation of the NHC catalyst regenerates the catalyst and releases the product lactones **IX**.

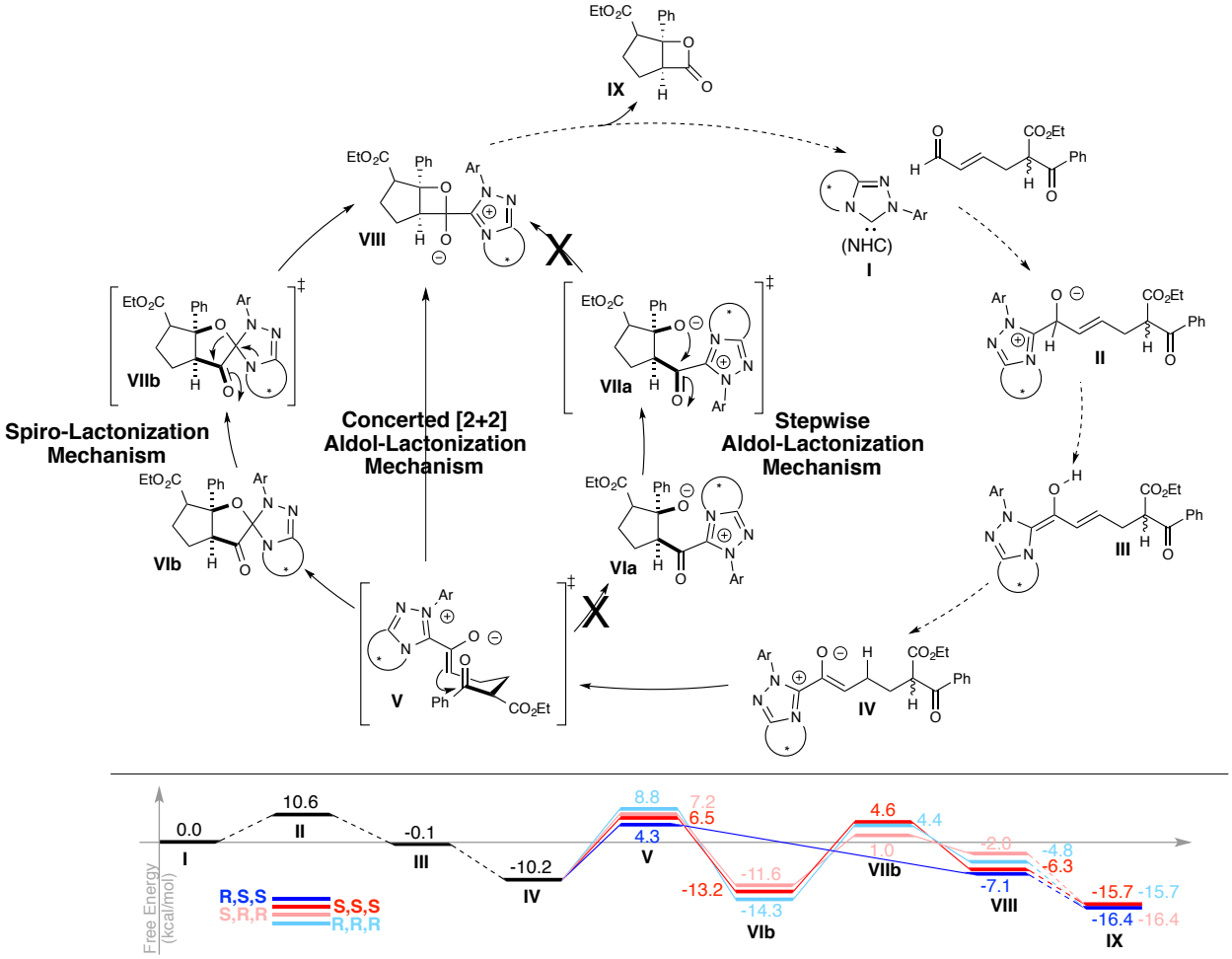


Figure 4.3 The computed catalytic cycle (*top*) and reaction coordinate diagram (*bottom*). The pathway that leads to the major product is a concerted asynchronous (2+2) aldol-lactonization process while all minor products undergo a spiro-lactonization mechanism that traps the forming enolate with the catalyst iminium. Previously postulated pathway, involving the formation of the zwitterionic aldol adduct, does not exist on this potential energy surface.

The discovery of two divergent mechanisms for the aldol-lactonization step contrast to the originally proposed mechanism in two ways: (1) originally, a stepwise mechanism that involves the formation of the zwitterionic aldol adduct **VIa** was postulated (Figure 4.3). This is unusual considering how frequently it is invoked and found in related reactions, most recently in the elegant work by Paddon-Row and Lupton.[22d] Surprisingly, neither this adduct nor the subsequent transition state (**VIIa**) to form the catalyst–lactone adduct **VIII** exist on the potential energy

surface. All our efforts to locate these structures have led to intermediate **VIb** and transition state **VIIb**, respectively. (2) Computations unequivocally reveal that the aldol-cyclization occurs *via* the enolate rather than the enol. In fact, the aldol-lactonization TS involving the enol does not exist. In line with these computational observations, we observed that Lewis acid and thiourea additives either significantly slowed, or completely shut down the reaction.[12d]

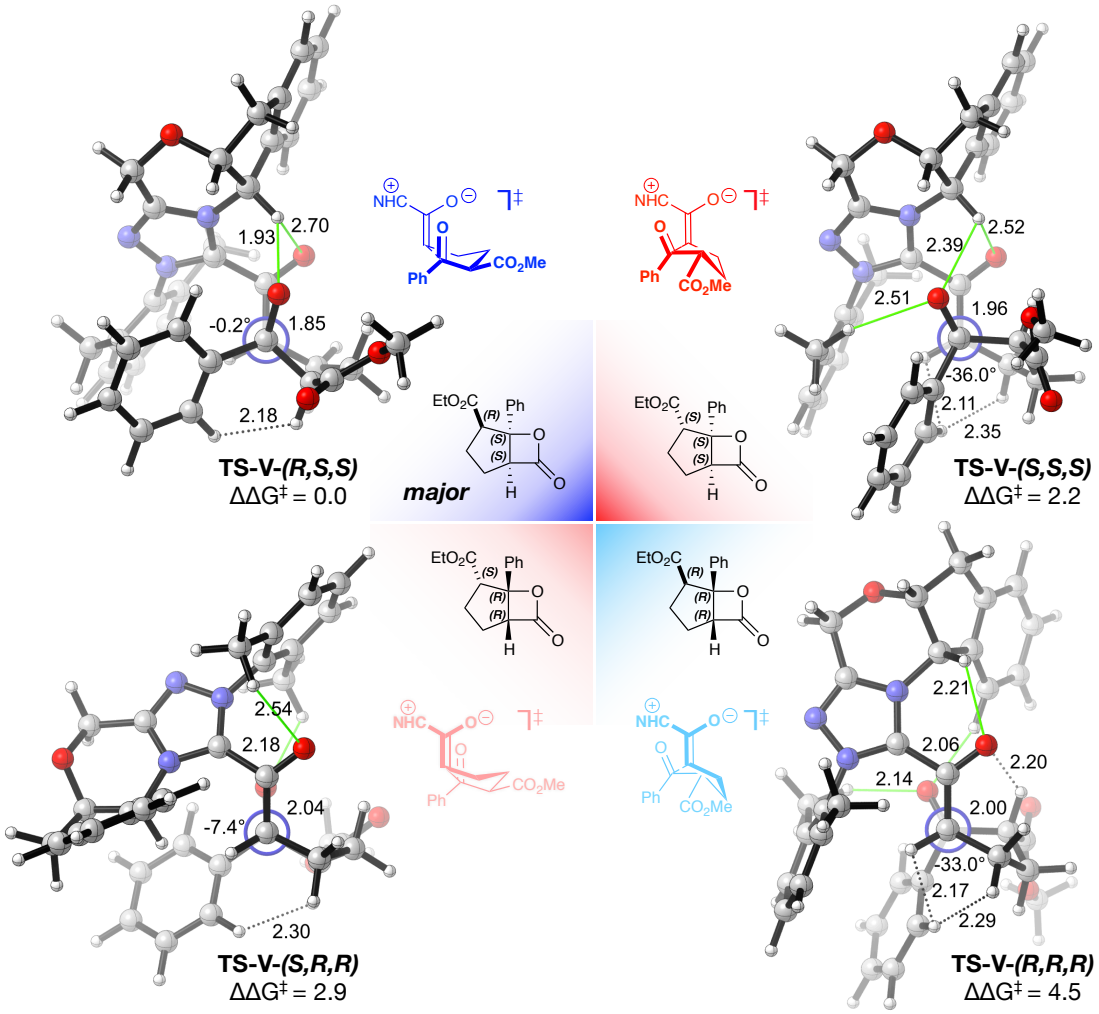
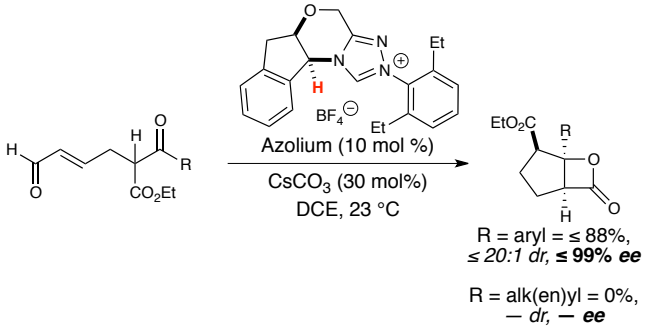


Figure 4.4 Rate- and stereodetermining aldol cyclization transition states. Green lines indicate electrostatic stabilizations, and dotted lines indicate steric repulsions. Dihedral angles describe the planarity of the phenyl group with the electrophilic carbonyl (degree of conjugation). Distances are in Ångströms, dihedrals in degrees and free energies in kcal/mol. Colors correspond to diastereomeric pathways in Figure 4.3.

The aldol transition states (TSs) for all observed products where R_1 = Ph are shown in Figure 4.4. The **TS-V-(*R*,*S*,*S*)**, which leads to the major product, is favored by 2.7 kcal mol^{-1} compared to minor enantiomer **TS-V-(*S*,*R*,*R*)**. This compares favorably with experimental enantioselectivity of 2.9 kcal mol^{-1}. In contrast, the computed diastereoselectivity is overestimated by ~1 kcal mol^{-1} compared to experiments – major **TS-V-(*R*,*S*,*S*)** is favored by 2.2 kcal mol^{-1} compared to the minor diastereomer **TS-V-(*S*,*S*,*S*)**, while the experimental diastereoselectivity is 1.1 kcal mol^{-1}.

The energetic preference for the major **TS-V-(*R*,*S*,*S*)** stems from a double activation of the electrophilic ketone. First, there is significant electrostatic stabilization of the developing negative charge on the ketone undergoing nucleophilic attack by a critical C–H···O non-classical hydrogen bonding interaction[23] from the catalyst pyranyl C–H (indicated by thin green lines, Figure 4.4). Moreover, the phenyl substituent of the electrophilic ketone is in conjugation with the carbonyl (−0.2°), maximizing the reactivity of the ketone.

The origin of diastereocontrol arises from the reduced reactivity of the electrophilic ketone in the minor diastereomer **TS-V-(*S*,*S*,*S*)**. The epimer at the ester stereocenter changes the torsion around the forming C–C bond such that although the stabilizing C–H···O interaction is maintained, it forces the electrophilic ketone to be twisted out of conjugation (−36°) with the phenyl ring to avoid steric interactions with the catalyst.[12f]

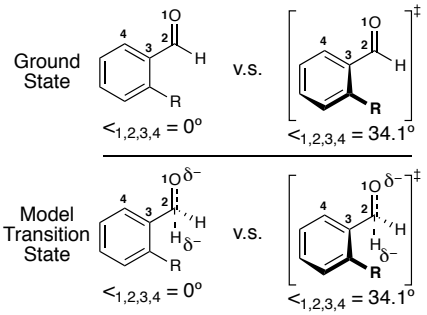


Scheme 4.1. NHC-catalyzed DKR of α-substituted-β-ketoesters to β-lactones is general for aryl substitution, yet ineffective with alkyl and alkenyl substitution.

We have computed a model system to quantify the effect of conjugative electrophilic activation on transition state stabilities. Shown in Table 4.1 are the energetic penalty from the loss of conjugation in various substituted benzaldehydes by comparing the fully conjugated planar (0° dihedral between the carbonyl and the Ph) with the phenyl twisted out of conjugation to the same degree as found in the minor transition state (34° dihedral average, across **TS-V-(*S*,*S*,*S*)** involving substrates where R = H, F, and OMe). In the ground state, the loss of conjugation amounts to ~ 2 kcal mol^{-1} destabilization, regardless of the identity of the phenyl substitution. However, in model transition states of hydride addition to the carbonyl where the hydride approach has been fixed at 2 Å, conjugative stabilization was worth significantly more, ~ 2–7 kcal mol^{-1}, depending on the electronic nature of the aryl substituent (entries 2 and 3, Table 4.1). This highlights a unique conjugative stabilization effect present only in the transition state but absent in the ground state that is strong enough to effect excellent stereocontrol.

The importance of this conjugative stabilization may explain why alkyl ketone substrates are not compatible under these reaction conditions.[12g] This NHC-catalyzed DKR proved to be general for α-substituted-β-ketoesters with aryl ketones. The decreased electron-withdrawing ability of alkyl and alkenyl substrates led to either no reaction or formation of side products (Figure 4.5).

Table 4.1[a] Energetic penalty from loss of conjugation[b] in benzaldehyde: ground state & model transition state[c]



entry	R	ΔG_{GS}	ΔG_{TS}	$\Delta G^{\ddagger}_{exp}$ [d]	$\Delta G^{\ddagger}_{comp}$ [e]
1	H	1.9	2.0	1.1	2.2
2	F	1.6	4.8	>1.7	4.4
3	OMe[g]	1.4	7.6	>1.7	5.3

[a] All energies in kcal/mol, [b] Free energy difference between fully conjugated (0º) and twisted (34º) benzaldehyde, Torsion of twisted geometry corresponds to the average torsion found in **TS-V-(*S,S,S*)**, leading to the minor diastereomeric product. [c] Hydride to carbonyl distance fixed at 2.0 Å, [d] Experimental diastereoselectivity, [e] Computed diastereoselectivity. [g] Experimental ethoxy compound modeled computationally as methoxy.

The minor enantiomeric product is formed *via* **TS-V-(*S,R,R*)**. The pyranyl non-classical hydrogen bonding C–H···O interaction controls the enantioselectivity. In the major TS, the pyranyl C–H is sandwiched between the enolate oxygen and the approaching electrophilic carbonyl, stabilizing the developing negative charges. However, approach to the opposite face of the enolate, as in the minor enantiomer pathway **TS-V-(*S,R,R*)**, precludes stabilization with the pyranyl C–H. Instead, stabilization is realized by weaker alkyl C–H···O interactions. The weakness of these interactions is the cause for the destabilization of this transition state. A related investigation of electrostatic control of stereoselectivity in NHC-catalyzed [4+2] annulation reactions has been recently reported by Bode and Kozlowski.[22i]

After we had computed the reaction coordinate, we questioned whether the NHC catalyst was indeed involved with the epimerization of the α-proton or was simply playing the role of a kinetic resolution catalyst. To test these two possibilities, we carried out a series of deuterium exchange experiments. α-Allylated β-keto ester **4** was dissolved in CD_2Cl_2–CD_3OD mixture (0.07 M).[12i] Addition of cesium carbonate (30 mol%) as the base led to virtually instantaneous and complete deuterium incorporation at 23 °C as seen by ^{1}H NMR spectroscopy (time = 0). The same experiment performed at −10 °C showed significant deuterium exchange after 5 minutes (Figure 4.6), and complete exchange after 30 minutes. These results demonstrate that the optimal basic conditions used in our DKR reaction promote extremely rapid keto/enol tautomerization and epimerization of these α-substituted β-keto esters. An alternative possibility exists where the NHC azolium salts (pK_a ~ 17–25)[24] itself drives the deprotonation.[25] While experiments involving preparation of pre-generated carbene using strong bases (LDA or NaH) led to decomposition of starting materials, this possibility cannot be completely excluded.

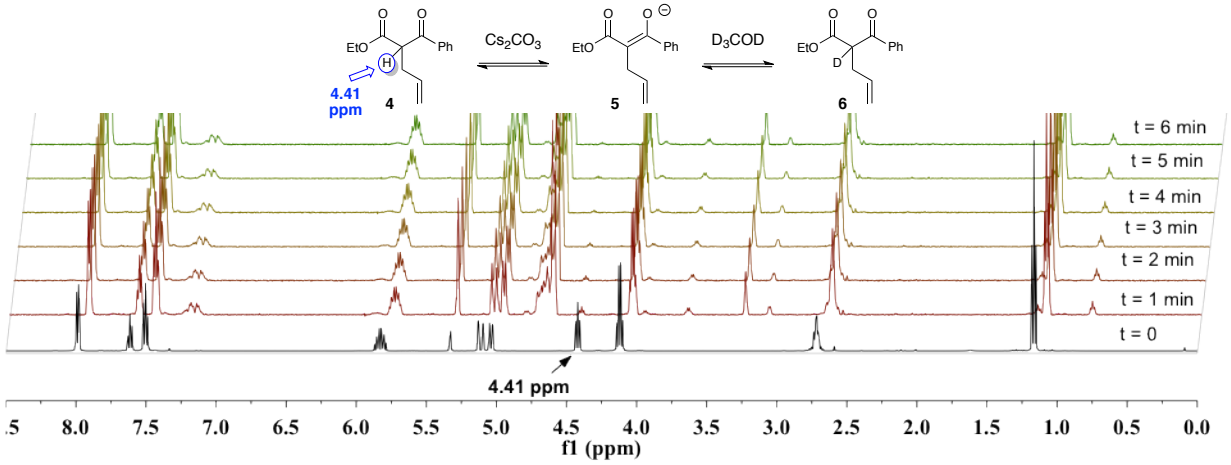
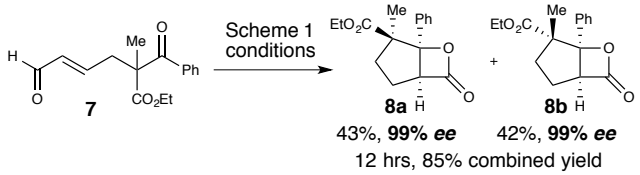


Figure 4.5 ^{1}H NMR (500 MHz) spectroscopic deuterium exchange experiment. The chemical shift at 4.41 ppm represents the α-proton of the α-allylated β-keto ester **30.**



Scheme 4.2. Stereodivergent reaction on a racemic mixture (RRM) study.

We designed a stereodivergent reaction on a racemic mixture (RRM) experiment to verify that the aldol-lactonization process, not the epimerization is rate-limiting. In contrast to a standard kinetic resolution, a divergent RRM converts both enantiomers of a racemic mixture to non-enantiomeric products.[26] We employed racemic α-disubstituted β-ketoester **7**, which is configurationally stable (Scheme 4.2). Complete cyclization to diastereomeric β-lactone products **8a** and **8b** was achieved in excellent yield (50% maximum theoretical yield for each) and enantioselectivity in 12 hours, considerably slower than the exogenous base-mediated epimerization of the substrate.

Together these results suggest that the basic conditions needed to generate the activated catalyst additionally promote substrate racemization at a faster rate than the overall DKR reaction process. We suspect that the NHC catalyst simply plays the role of a kinetic resolution catalyst that captures and irreversibly transforms one enantiomer of the substrate. The current DKR process is different from the classical DKR where the catalyst is involved with both the racemization and kinetic resolution; the racemization occurs tangentially to the kinetic resolution (Figure 4.6). The stark differences in the role of the catalyst prompt us to suggest differentiating these two DKRs. Such processes, in fact, though rarely reported, have been observed by others.[27] We suspect that this unusual DKR is more common than is currently recognized.

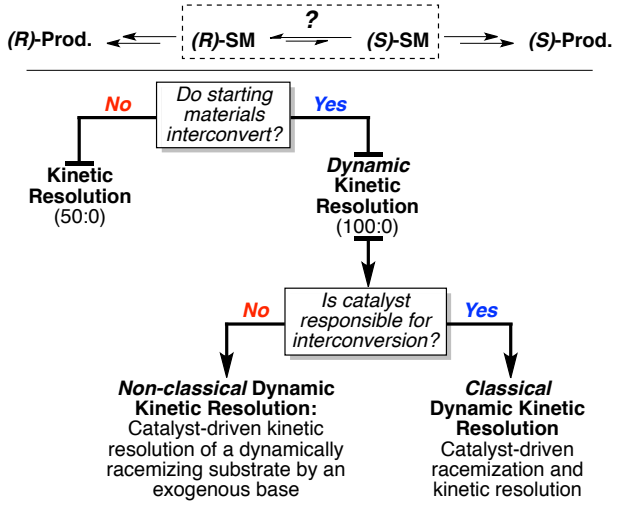


Figure 4.6 Types of kinetic resolution processes. In a kinetic resolution, starting materials do not racemize. Only one enantiomer is transformed to product (maximum 50% yield). Dynamic kinetic resolutions (DKRs) occur when starting materials racemize to the more reactive form, leading to a maximum 100% yield. In a classical DKR, the catalyst is responsible for the racemization and conversion to product. In *non-classical* DKRs, the racemization of starting materials occurs independent of the kinetic resolution catalyst.

4.5 Conclusion

In summary, computations have uncovered the mechanism and origins of stereoselectivity in the first NHC-catalyzed dynamic kinetic resolution of α-substituted-β-ketoesters that provide β-lactones in high yields and selectivity. This study has uncovered two new mechanisms for the aldol-lactonization that challenge the currently accepted mechanism: (1) a concerted, asynchronous formal (2+2) aldol-lactonization process that leads to the major product, or (2) a stepwise spiro-lactonization mechanism that traps the forming enolate with the NHC catalyst iminium for all other products. The previously proposed stepwise mechanism, originally proposed by us, also invoked in other related reactions, is not operative.[3] Additionally, we have uncovered how conjugative stabilization to the electrophile and C–H···O non-classical hydrogen bonds are key to stereocontrol. Finally, we have also discovered that the current reaction exhibits an unusual DKR, one we coined as non-classical due to the atypical role of the catalyst. The combined experimental and theoretical efforts described herein have led to discoveries that refine and further distinguish the current understanding of carbene-catalyzed reactions and DKR processes. These advances will continue to be enhanced and employed towards the discovery and advancement of new processes.

4.6 Acknowledgements

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Chapter 5

Functionalized Cyclopentenes Through a Tandem NHC-Catalyzed Dynamic Kinetic Resolution and Ambient Temperature Decarboxylation: Mechanistic Insight and Synthetic Application

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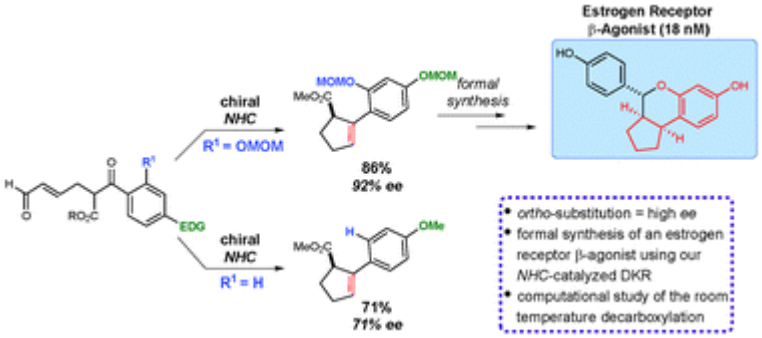
Chemical Communications

Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge CB4 0WF, UK

2015, *51*, 2690-2693.

5.1 Abstract

An unusual room temperature β-lactone decarboxylation facilitated a five-step enantioselective formal synthesis of the cyclopentane core of an estrogen receptor b-agonist. A computational study probed the underlying factors facilitating unprecedented, rapid decarboxylation. Aryl substitution promotes faster reaction in the retro-[2+2] as a result of conjugative stabilization with the forming olefin. Additionally, the configuration of the α-ester in these fused β-lactones leads to differential decarboxylation rates.



5.2 Introduction

Catalytic methods to assemble bioactive molecules and privileged motifs are on-going pursuits in synthesis. Many have sought to achieve this goal by employing organic catalysts, which allows for a greener approach.[1] *N*-Heterocyclic carbenes (NHC) have emerged as powerful class of organic catalysts that can be used to construct important structural motifs, bioactive molecules, and natural products.[2] Our group and others have shown that NHCs react with aldehydes to generate catalytically competent enolate,[3] homoenolate,[4] and acyl anion intermediates,[5] which have been trapped with various electrophiles. In 2012, we reported the first NHC-catalyzed dynamic kinetic resolution (DKR) of α-substituted-β-ketoesters (1) to furnish bicyclic β-lactones (2) and cyclopentenes (3) (Scheme 1 eq. 1).[6] Computational studies[7] shed light on the rare, non-classical nature of this specific organocatalytic DKR and on the origins of stereoselectivity in the β-lactone formation. While examining this NHC-DKR process we determined that aryl ketones with electron-donating substitution or heteroaromatic ketones normally resulted in complete spontaneous decarboxylation to the cyclopentene (3) under the reaction conditions (eq. 2). Unfortunately, this rapid decarboxylation led to cyclopentenes with diminished enantioselectively, due the moderate diastereoselectivity (5-7:1 d.r.) for the lactone forming process. However, substrates possessing an *ortho*-substitution on the aryl ring of the ketone furnished the respective products in 20:1 dr. Therefore, the rapid decarboxylation before the separation of the diastereomer lactones is inconsequential, allowing for the isolation of the desired cyclopentene in high yield while maintaining the high enantioselectivity (*90% ee*). In this communication, we apply this DKR to construct the cyclopentane ring of known bioactive benzopyrans. This report demonstrates that this DKR can be applied to the enantioselective synthesis of different analogues of these bioactive benzopyrans. Additionally, we delve into the mechanism of the rapid decarboxylation for this DKR process using computational methods and explain why certain substrates are more prone to rapid decarboxylation, even under these mild conditions.

5.3 Synthetic Application of a Tandem DKR/Decarboxylation Protocol

In 2006, Eli Lilly disclosed a new class of hydroxylated benzopyrans that were highly potent and selective estrogen receptor β-agonists with nanomolar activity in models of benign prostatic hyperplasia, otherwise known as enlarged prostate (Figure 5.1).[8] A subsequent structure-activity relationship study revealed that the cyclopentane ring was essential to provide nanomolar activity while maintaining the great selectivity.[8e] Previous reported syntheses to these enantioenriched benzopyrans relied on an eight-step linear reaction sequence and a subsequent preparative chiral phase HPLC separation of the final benzopyran to obtain enantiopure products. To the best of our knowledge, a general catalytic asymmetric variant to these compounds has not been reported. The formal synthesis began with the treatment of known[9] acetophenone **4** with dimethyl carbonate and sodium hydride in toluene to afford β-keto ester **5**. A Tsuji-Trost allylation of β-ketoester and with allyl carbonate **6** and subsequent PCC oxidation provided aldehyde **7** in 36% yield over three steps. In the key enantioselective, catalytic DKR step, the exposure of aldehyde **7** to 7 mol % of azolium **8** with 30 mol % of Cs_2CO_3 gave cyclopentene **9** in 86% yield with excellent enantioselectivity (92%

ee). A subsequent hydrogenation (Pd/C) gave cyclopentane **10** in 48% yield as a sole diastereomer based on comparison with reported structures.[10] This cyclopentane (**10**) in racemic form has previously been converted to selective estrogen receptor benzopyran **11** in three steps by scientists at Eli Lilly.[8e] Thus we have been able to employ our NHC-DKR-decarboxylation strategy toward an efficient, asymmetric route to these valuable benzopyrans and related structures. Most notably this synthetic sequence avoids the previously described chiral separation approach and provides a stereocontrolled and efficient method to rapidly assemble a diverse library of these bioactive benzopyrans.

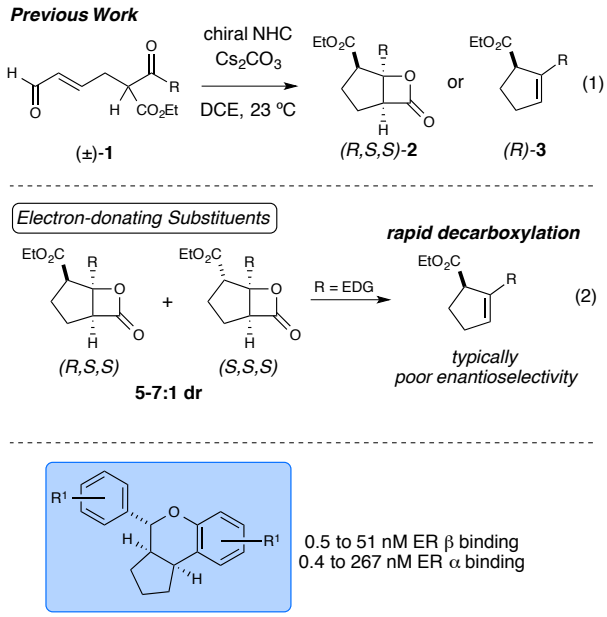
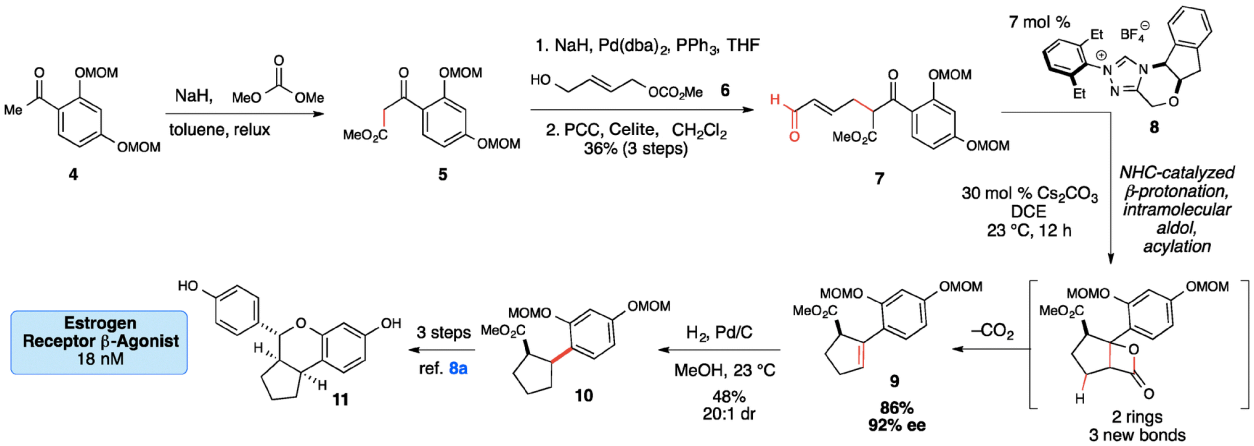


Figure 5.1 NHC-Catalyzed Dynamic Kinetic Resolution



Scheme 5.1 Enantioselective formal synthesis of estrogen receptor β-agonist **11**.

5.4 Computational Insights into Decarboxylation

β-lactones with an electron-rich aryl ring, such as 4-MeOPh (2a, Table 1, entry 1), synthesized under Figure 5.1 conditions undergo unprecedented and rapid decarboxylation to the cyclopentene, often leaving no trace of the lactone.[6] This outcome is in sharp contrast to the thermolytic conditions (>60 ºC) typically required for decarboxylative [2+2]-cycloreversion of β-lactones (Figure 5.3).[11] Reduced temperatures have traditionally only been achieved through radical decarboxylation.[12] Electron-neutral (**2b**) and -poor (**2c**) β-lactones are stable to Scheme 1 conditions; decarboxylation only occurs after heating in SiO_2 (Figure 5.3), as previously observed.

To probe the apparent electronic effects controlling this unusual decarboxylation and the origins of enantioselectivity, we conducted a computational study using quantum mechanical computations (SCS-MP2[13]/def2∞ZVP[14]//B3LYP[15]/6-31G(d)[16] with B3LYP/ 6-31+G(d,p)/PCM(DCE)[17] solvation corrections).[18] The computed retro-[2+2] transition state structures (TSs) are shown in Figure 5.3. The *anti* and *syn* refer to the diastereomeric relationship between the lactone and the loss of CO_2. All transition structures are concerted asynchronous,[19] and our computed barriers match the observed relative rates of decarboxylation. The *anti* configuration reacts faster than the *syn* (Figure 5.2).

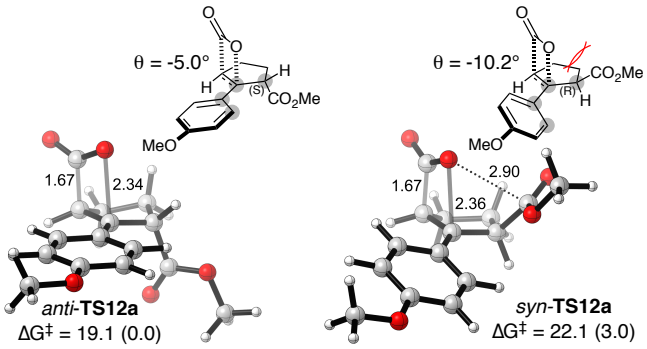


Figure 5.2 Decarboxylation TSs of *syn*- and *anti*-diastereomers of **2a**.

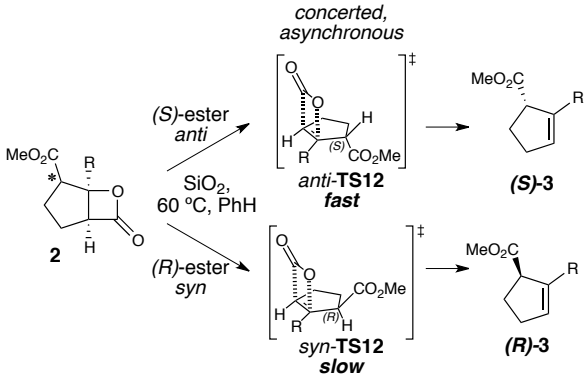


Figure 5.3 β-Lactone decarboxylation to cyclopentene.[20]

Ejection of CO_2 is accelerated by conjugation to the planar aryl group. The configuration of the α-ester affects the conjugation by affecting the degree of planarity of the aryl group with the forming olefin. In the *anti* TS, the aryl groups are planar to the forming olefin, facilitating the ejection. This is in contrast to the *syn* TS, where the aryl group is slightly twisted out of the plane, costing an energetic penalty of 0.3 kcal mol^{-1}.

As a consequence of the conjugation, *the electronic nature of the aryl group has a direct effect on the reactivity*. Initial cleavage of the C–O bond leads to a transient benzylic carbocation character, which is sensitive to the electronics of the aryl group. Electron-donating *para* and/or *ortho* substituted aryl groups dramatically lowers the decarboxylation TS barriers, for example, *p*-OMe aryl substitution (Table 5.1) reacts rapidly *anti* at 19.1 kcal mol^{-1}. This is in contrast to electron-neutral and electron-poor *para*-substituted aryl lactones that have higher barriers of 27.5 and 31.4 kcal mol^{-1}, respectively, in agreement with experimentally observed higher reaction temperatures. In all aryl cases, the *syn* barriers are higher, but still follow the general trend. This trend echoes limited reports on the decarboxylation in a series of related β-lactones at ambient and cryogenic temperatures, with rapid decarboxylation for electron-donating (*p*-OMePh) substituents and none for electron-neutral or -poor substituents.[21] In the absence of conjugating aryl groups, e.g., aliphatic ($\Delta G^{\ddagger} = 33.3$, $\Delta\Delta G^{\ddagger} = 0.1$) and hydro ($\Delta G^{\ddagger} = 38.2$, $\Delta\Delta G^{\ddagger} = -1.0$), barriers are higher and the enantioselectivity is diminished and reversed, respectively (Table 5.2).

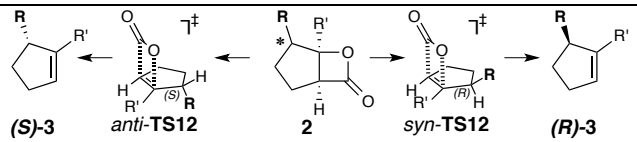
Table 5.1 Electronic effects on decarboxylation rate and selectivity.

Entry		R	Yield (% *ee*)[a]	***anti*-TS12** $\Delta G^{\ddagger}$[b]	***syn*-TS12** $\Delta G^{\ddagger}$ ($\Delta\Delta G^{\ddagger}$)[b]
1	**2a**	4-OMePh	71 (70)	19.1	22.1 (3.0)
2	**2b**	Ph	95 (98)[c,d]	24.7	27.5 (2.8)
3	**2c**	4-CNPh	64 (99)[c]	29.1	31.4 (2.3)
4	**2d**	Me	–[e]	33.3	33.4 (0.1)
5	**2e**	H	–[e]	38.2	37.2 (–1.0)

[a] Figure 5.3 conditions, *(S)*-3 major product. [b] Energies reported in kcal mol^{-1}. [c] No decarboxylation observed under Scheme 1 conditions. [d] Scheme 2 conditions. [e] Theoretical values only. Substrates not accessible through Scheme 1.

Enantioselectivity is inherent to the molecule by virtue of the α-group configuration. We modulated the size and electronics of the α-group to probe whether steric or electronic factors (measured in A values[22] and σ_p^+,[23] respectively) give rise to the different *anti*/*syn* barriers. To test for steric control, the ester ($\sigma_p^+ = 0.49$, A = 1.27) was replaced by the similarly electron-withdrawing but smaller cyano group ($\sigma_p^+ = 0.66$, A = 0.17). CN α-substitution led to a loss of selectivity. Electronic control was investigated by replacement with the equivalently sized, but electron donating methyl group ($\sigma_p^+ = -0.31$, A = 1.7). Retention of selectivity was observed computationally with methyl α-substitution and loss with cyano, indicating that the ester controls selectivity through its steric component. This observed steric effect originates from the strain afforded by decarboxylation *syn* to the α group (Figure 1). The pseudo-equatorial *(R)*-ester in the minor *syn*-TS12 diastereomer leads to a repulsive interaction (2.9 Å) with the departing CO_2. The absence of this repulsion in the favored *anti*-TS12 lowers the barrier by ~2–3 kcal/mol.

Table 5.2 Test for origins of selectivity by α group modulation.



Entry		R	R'	*anti*-TS12 $\Delta G^{\ddagger a}$	*syn*-TS12 $\Delta G^{\ddagger}$ ($\Delta\Delta G^{\ddagger}$)^a
1	**2f**	CN	4-OMePh	33.9	34.3 (0.4)
2	**2g**	CN	H	30.5	29.7 (–0.8)
3	**2h**	Me	4-OMePh	18.4	21.0 (2.6)
4	**2i**	Me	H	35.8	34.6 (–1.2)

[a] Energies reported in kcal mol^{-1}.

5.5 Conclusions

In conclusion, we have demonstrated the NHC-catalyzed DKR/decarboxylation process can be utilized as the key step in the enantioselective formal synthesis of a benzopyran estrogen receptor β-agonist. Using an *ortho*-substituted aryl ketone allowed us to achieve high enantioselectivity (*92% ee*) without prior separation of the diastereomers. This processes alleviates the need for chiral phase HPLC as previously used in a Lilly campaign to separate the enantiomers of the benzopyrans. Utilizing computational studies we uncovered the principles controlling the concerted retro-[2+2] decarboxylation mechanism from this DKR, including the electronic effects on rate. Aryl ketones with electron-rich substitution decarboxylate rapidly through aryl conjugation with the forming olefin. The *anti*-selective decarboxylation observed for aryl ketones is the result of steric interactions between the α group and the carboxylate groups in the *syn*-TSs.

5.6 Acknowledgements

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5.7 References

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Chapter 6.

Asymmetric Homoenolate Additions to Acyl Phosphonates through Rational Design of a Tailored *N*-Heterocyclic Carbene Catalyst

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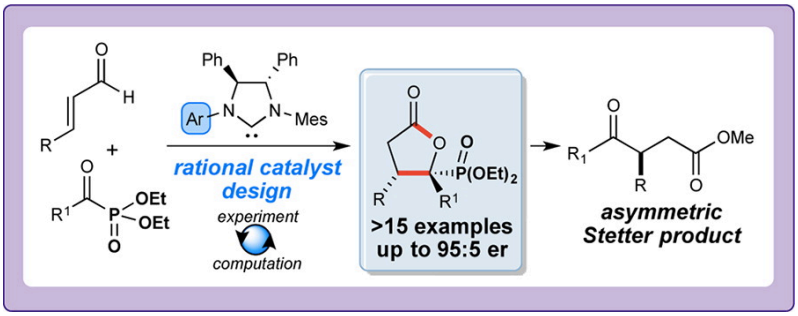
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2014, *136*, 76-79

6.1 Abstract

A highly selective NHC-catalyzed synthesis of γ-butyrolactones from the fusion of enals and α-ketophosphonates has been developed. Computational modeling of competing transition states guided a rational design strategy to achieve enhanced levels of enantioselectivity with a new tailored C_1-symmetric biaryl-saturated imidazolium-derived NHC catalyst.



6.2 Introduction

The ability to forge complex hetero- and carbocyclic systems convergently with high levels of selectivity remains a challenge in organic synthesis. Over the past two decades, *N*-heterocyclic carbenes (NHCs) have been explored intensely for the synthesis of various structural manifolds through Umpolung reactivity.[1] Since the seminal reports of NHC-homoenolate reactions, there have been significant advancements in this area, with a primary focus on additions to various activated π systems.[2,3] While aldehydes and aldimines are productive substrates in a variety of reactions to produce γ-lactones and lactams, respectively,[3a-c,4] more sterically hindered, less reactive ketones and imines impose severe limitations on single NHC catalyst systems.[5,6] To address this challenge, new strategies and/ or new catalyst design approaches are needed. One strategy is cooperative catalysis with NHCs integrating Lewis and Brønsted acids to enhance reactivity, modulate stereocontrol, and access new reactivity with previously inactive electrophiles.[4c,7] However, there are few examples involving the synthesis of γ-butyrolactones with high levels of enantioselectivity.[6,7b] These motifs are highly attractive given the large number of bioactive molecules and natural products with this key architectural feature (Figure 6.1, X = H, C, or heteroatom). *As a complementary strategy, new advances in rational N-heterocyclic carbene structure/reactivity development could provide new solutions for NHC annulations of π electrophiles.*

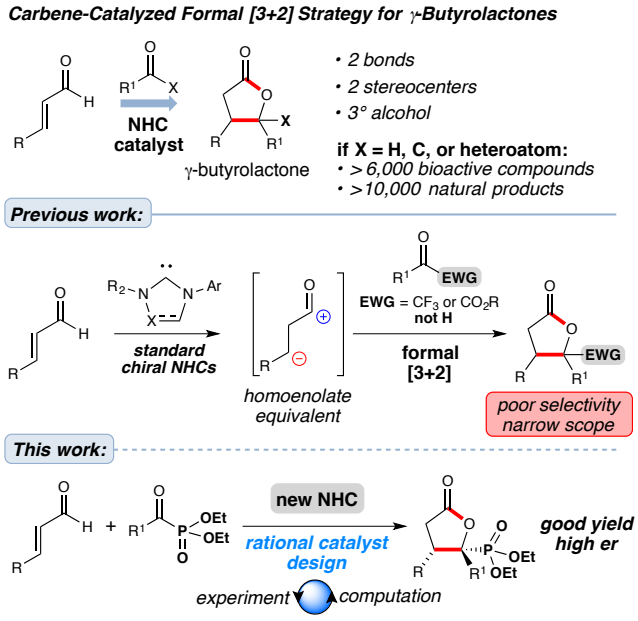


Figure 6.1 NHC annulations of acyl phosphonates.

Acyl phosphonates are potential electrophiles for an NHC-catalyzed [3+2] annulation process, but are particularly challenging given the steric environment around the target carbonyl group. These phosphonates have been employed in a wide range of enantioselective processes.[8] Many methods have been developed to incorporate phosphonate groups due to the prevalence of the phosphinic acid group in naturally occurring and pharmaceutical compounds

with antiviral, antibacterial, and anticancer properties.[9] In particular, the synthesis of phosphonates bearing α-hydroxy[10] and α-amino groups[11] has received significant attention.

Here we report the addition of α,β-unsaturated aldehydes to α-ketophosphonates under carbene catalysis to afford enantioenriched γ-butyrolactones with a previously unreported core structure (Figure 6.1, X = $P(=O)(OR)_2$). The discovery that standard chiral NHC catalysts are ineffective for this transformation resulted in the design of several new C1-symmetric biaryl-saturated imidazolium catalysts. This scaffold was introduced by Hoveyda in an enantioselective, metal-free C−B bond-forming reaction[12] Computationally guided rational catalyst design was employed to improve selectivity for this new formal [3+2] annulation process. This strategy is underutilized in the field of NHC catalysis, but several groups, most prominently Sigman et al., have demonstrated the use of correlative methods to dictate improved catalyst scaffolds for epoxidation, hetero-Diels-Alder, and other catalytic asymmetric reactions.[13] These efforts have resulted in enhanced catalyst performance and relate catalyst structure to the observed enantioselectivity.

6.3 Results and Discussion

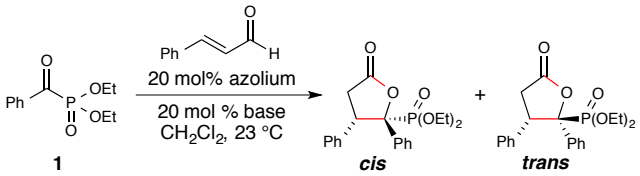
We began our studies by combining α-ketophosphonate **1** with cinnamaldehyde in the presence of imidazolium precatalyst **A** and 20 mol% 1,8-diazabicyclo[5.4.9]undec-7-ene (DBU, Table 6.1, entry 1). Under these conditions, the desired formal [3+2] annulation product was formed in 35% yield with good selectivity for the trans diastereomer. To improve the efficiency, various other NHC precatalysts were examined for this transformation: the use of saturated imidazolium **B** resulted in a decrease in diastereoselectivity but a significant increase in yield (entry 2). Notably, while saturated imidazoliums are frequently employed as ligands for transition metals,[14] there are limited reports on the use of these NHCs as organocatalysts.[7d]

With this backdrop, we turned to rendering this reaction enantioselective. The use of 1,2-aminoindanol-derived triazolium catalyst **C**[4b] resulted in poor conversion to the lactone product with low levels of enantioselectivity (67:33 er, entry 3). Based on the success of achiral saturated imidazolium **B**, we explored the C1-symmetric biaryl-saturated imidazolium precatalyst **D**.[12] Under the previously explored conditions, precatalyst **D** afforded the product in excellent yield and good diastereo- and enantioselectivity (94%, 85:15 er, entry 4). A further increase in enantioselectivity was observed by switching the base from DBU to 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), affording the lactone in 79% yield and 90:10 er (entry 5).

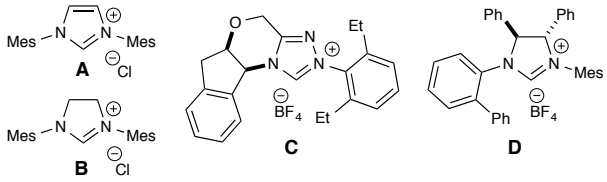
At this stage, a new direction was required to achieve higher levels of selectivity. Faced with the typical arduous empirical approach of evaluating many new analogues of **D**, we initiated a computational investigation of the stereodetermining homoaldol step with density functional theory, B3LYP/6-31G*.[15] The transition structures (TSs) that correspond to the formation of the major *(S,S)* and minor *(R,R)* enantiomer products are shown in Figure 2. In both cases, nucleophilic attack of the homoenol to the acyl phosphonate carbonyl is concomitant with deprotonation

of the enol proton by the forming alkoxide.[16] Stereoselectivity arises from differential stabilization of the phosphonyl oxygen by the catalyst aryl protons through nonclassical hydrogen bonds (NCHBs).[17] The preorganization and anion stabilization present in these TSs are reminiscent of the oxyanion hole stabilization found in enzymes, where an array of backbone amide protons provide stabilization of the developing alkoxide.[18]

Table 6.1 Optimization of Reaction Conditions



entry	azolium	base	% yield[a]	*cis*:*trans*[b]	er[c]
1	A	DBU	35	1:13	-
2	B	DBU	70	1:4.6	-
3	C	DBU	20	1.2:1	67:33
4	D	DBU	94	5.8:1	85:15
5	D	MTBD	79	1.8:1	90:10



[a]NMR yield with internal standard. [b]Diastereomeric ratio determined by ^{1}H NMR spectroscopy (500 MHz). [c] Enantiomeric ratio determined by HPLC analysis using a chiral stationary phase.

It was anticipated that selective destabilization of the minor TS could be achieved because the stabilization sites differ between the major and minor enantiomers (Table 6.2). In the minor TS, the catalyst NCHB sites are only on the terminal biphenyl *meta* positions (shown in pink). This is in contrast to the major TS, where there are multiple stabilizing NCHB interactions, located at the ortho positions of the catalyst backbone phenyl and the internal *N*-biphenyl (shown in cyan). The increased number of strong NCHB interactions is responsible for the computed 1.7 kcal/mol selectivity (95:5 er), which compares favorably with the experimental selectivity of ~1.0 kcal/mol (90:10 er). While both TSs are stabilized by the mesityl methyl C−H, these protons are inferior NCHB donors compared to aryl C−H's.[17] Since the NCHB stabilization motif was clearly different between the major and minor TSs, we envisioned that the installation of methyl groups at the terminal biphenyl meta positions would disrupt the phosphonyl stabilization of the minor TS but leave the major TS unchanged, thus increasing enantioselectivity.

Based on the computational prediction, catalyst **E** was employed in the annulation reaction. Under the previously optimized conditions with the more sterically demanding 3,5-dimethylphenyl substituent we observed an increase in enantioselectivity to 92:8 er (1.5 kcal/mol, Table 2, entry 2). This correlates well with the computationally predicted er of 99:1 (3.0 kcal/mol). Extension of the catalyst to include ethyl groups at the 3- and 5-positions of the aryl ring

was explored to determine if the enantioselectivity could be further enhanced. We were pleased to find that this simple catalyst modification afforded the product in 80% yield and 94:6 er (entry 3).

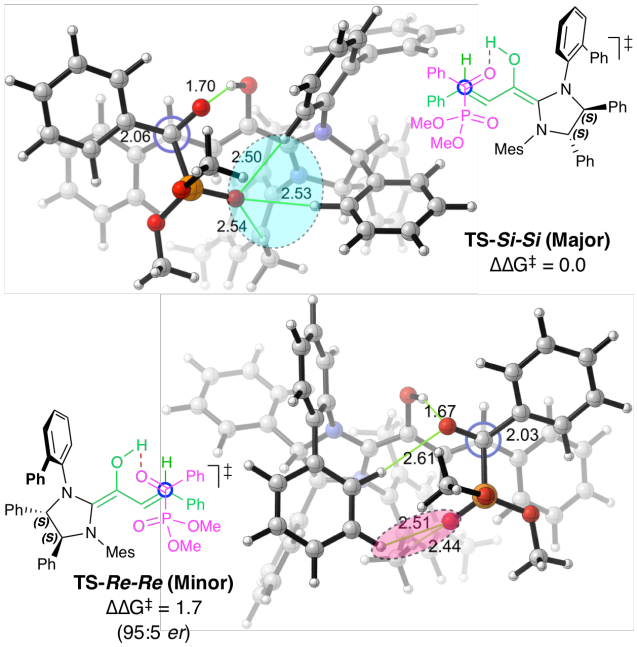
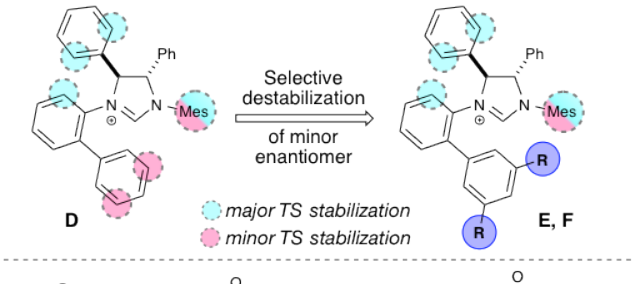


Figure 6.2 Homoaldol transition structures involving catalyst **D**. The first *Re/Si* notation refers to the homoenol face, and the second *Re/Si* refers to the electrophile face. Et groups abbreviated to Me for computational efficiency. Cyan region marks stabilizing non-classical hydrogen bonding (NCHB) interactions in the major TS, while pink marks those found in the minor. Green lines indicate electrostatic interactions. Distances are in Å and energies in kcal/mol.

Table 6.2 Catalyst optimization.



entry	azolium	R	% yield[a]	*cis:trans*[b]	er_{comp}	er_{exp}[c]
1	**D**	H	79	1.8:1	95:5	90:10
2	**E**	Me	82	2.1:1	99:1	92:8
3	**F**	Et	80	2.5:1	N/A	94:6

[a]NMR yield with an internal standard. [b]Diastereomeric ratio was determined by ^{1}H NMR spectroscopy (500 MHz). [c] Enantiomeric ratio was determined by HPLC analysis using a chiral stationary phase.

We surveyed several α,β-unsaturated aldehydes in the reaction with α-ketophosphonate **1** with the optimized reaction conditions (Table 6.3). Both electron-withdrawing and -donating substituents were tolerated, providing the γ-butyrolactones in good to excellent yield and enantioselectivity (3−7, >91:9 er). In addition, enals bearing a pyridine and *N*-Me indole at the β- position were also accommodated. 3-Pyridyl-substituted lactone **11** was formed in slightly diminished yield but with good enantioselectivity. Likewise, the indole-substituted lactones were both produced in >65% yield, with 2-indoyl substrate **12** generated with slightly higher enantioselectivity. Variation of the α-ketophosphonate was also explored. We found that electron-donating groups performed well, with lactones **14** and **15** formed in good yield and 93:7 er. Electron-withdrawing substituents afforded the products in excellent yield and enantioselectivity but with moderate diastereoselectivity (**16**−**18**). Other aromatic groups, such as naphthyl, also performed well in the reaction. Currently, alkyl-substituted substrates (either aldehyde or acyl phosphonate) do not provide practical levels of efficiency.

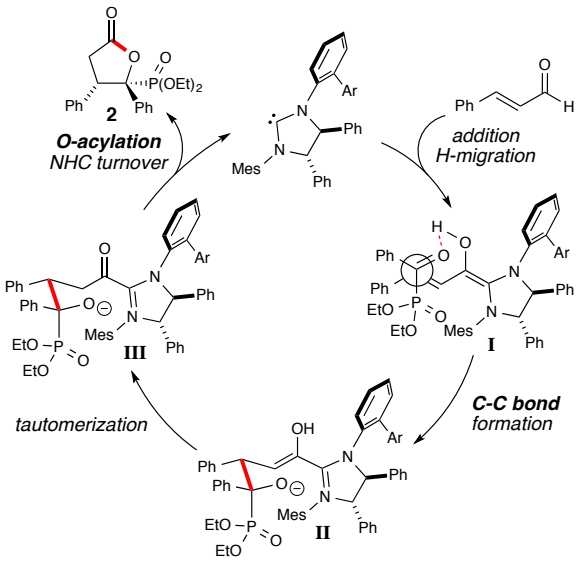
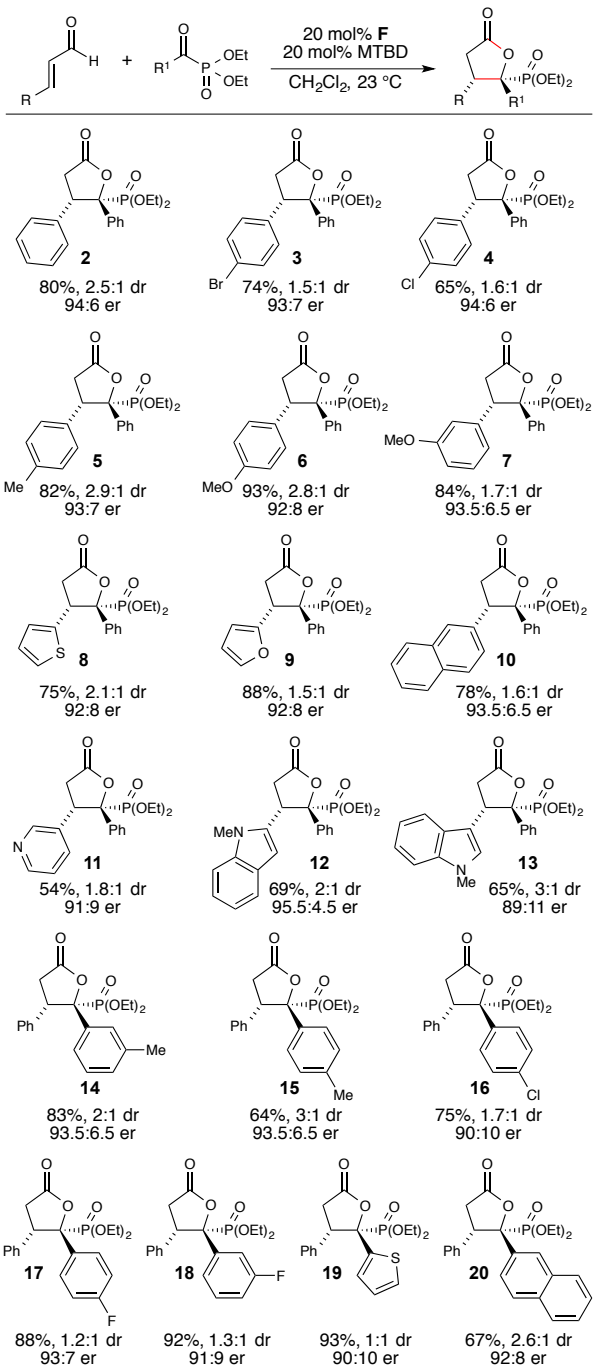


Figure 6.3 Proposed reaction mechanism

Based on our calculations, the proposed mechanism for formation of the lactone products involves initial addition of the catalyst to the aldehyde and subsequent formal 1,2-H migration to generate the extended Breslow intermediate (**I**, Figure 6.3). Based on computational modeling, H-bonding between the ketone of the acyl phosphonate and the enol results in an organized transition state. Following C−C bond formation to generate enol **II**, tautomerization occurs, giving rise to acyl azolium **III**, which then undergoes *O*-acylation to afford lactone **2** and release the NHC catalyst.

Table 6.3 Lactone substrate scope[a]



[a]See Supporting Information for details. Yields are of isolated product after column chromatography. Diastereomeric ratio determined by ^{1}H NMR spectroscopy (500 MHz) of the unpurified reaction. Enantiomeric excess determined by chiral HPLC.

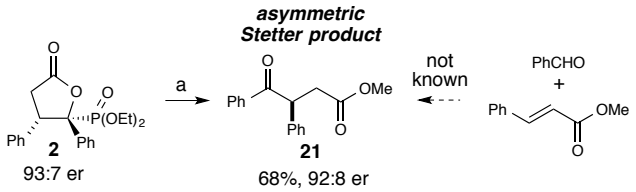


Figure 6.4 Transformation to Stetter products. a) 20 equiv K_2HPO_4, Hexanes/MeOH/H_2O (15:1:1), 23 °C, 42 h

The lactone products can be converted to enantioenriched 1,4-ketoesters in a single, mild operation with almost complete transfer of chirality. Treatment of lactone **2** (93:7 er) with dibasic potassium phosphate afforded ketoester **21** in 68% yield and 92:8 er through initial opening of the lactone and a subsequent retro-phospho aldol reaction (Figure 6.4). Related 1,4-carbonyl systems are often prepared through a Stetter reaction,[19,20] but this particular class is difficult to access through traditional methods due to the diminished reactivity of the ester and the resulting acidity of the α-aryl ketone product.[21] This NHC-catalyzed annulation provides a potential new strategy for accessing this challenging 1,4-carbonyl manifold, which in theory can be accessed through a Stetter reaction. However, to our knowledge, no general, enantioselective intermolecular Stetter reaction of aromatic aldehydes to α,β-unsaturated esters has been reported that provides high levels of enantiocontrol at the β-stereocenter.[21]

6.4 Conclusion

In conclusion, a highly selective NHC-catalyzed formal [3+2] annulation of α,β-unsaturated aldehydes with acyl phosphonates has been developed. The ineffectiveness of known NHC catalysts for this transformation resulted in the creation of new C1-symmetric biaryl-saturated imidazolium catalysts. Computationally guided rational catalyst design resulted in enhanced enantioselectivity, allowing for the synthesis of various γ-butyrolactones with excellent selectivity. These saturated imidazoliums provide a new catalyst scaffold for investigating other NHC-catalyzed transformations. In addition, this new enantioselective platform provides a distinct approach to 1,4-carbonyl compounds that are difficult to access through traditional methods, where various substituents can be incorporated through the appropriate choice of the acyl phosphonate and aldehyde starting materials. Continuing investigations involving the use of these chiral saturated imidazolium catalysts in NHC-catalyzed transformations and the integration of computational methods to enhance selectivity via specific catalyst tailoring are ongoing.

6.5 Acknowledgments

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Chapter 7.

Probing the Mechanism and Origins of Catalysis & Stereocontrol in the Bifunctional Aminothiourea-Catalyzed Michael Reaction

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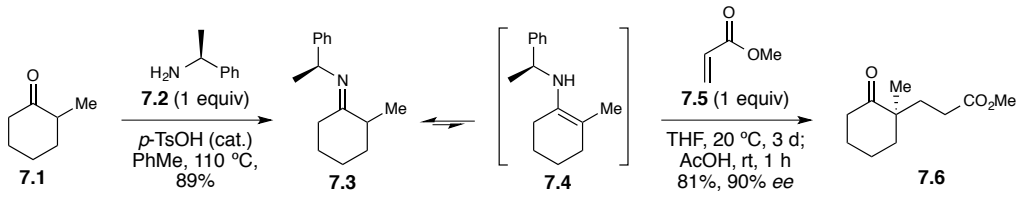
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7.1 Abstract

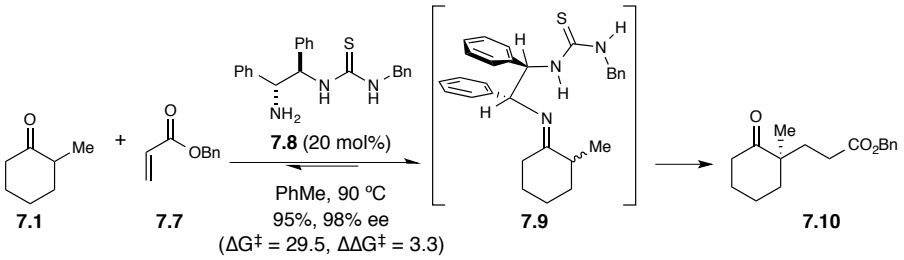
A chiral bifunctional aminothiourea has been developed for the Michael addition of α-ketones to acrylates to generate asymmetric all-carbon quaternary centers. This catalyst both activates the nucleophile via enamine catalysis and employs hydrogen bonding catalysis to activate the carbonyl-bearing electrophile. A joint experimental and computational study reveals the mechanism of this process and seeks to uncover the origins of selectivity. Computations predict that deletion of the catalyst β-phenyl group would increase selectivity; however experimental test led to unforeseen catalyst decomposition.

7.2 Introduction

The controlled synthesis of all carbon-quaternary stereocenters under mild conditions is one of the Holy Grails of organic chemistry. Towards this goal, Pfau and d'Angelo[1] reported the promotion of α-methyl ketones Michael addition to acrylate by stoichiometric 2-methylbenzylamine (Scheme 7.1). Imine **7.3** was preformed with stoichiometric amounts of **7.2** and was subjected to methyl acrylate over three days at room temperature to give good yield and enantioselectivity. This work served as the basis for Wu[2] and Carter[3] to develop a catalytic variant with a bifunctional aminothiourea **7.8**, featuring a primary amine tethered to a thiourea.[4] The bifunctionality serves to dually activate both the nucleophile through covalent catalysis and electrophile via hydrogen bonding catalysis while minimizing the entropic penalty.[5] This method furnished all-carbon quaternary stereocenters in high yield and enantioselectivity (Scheme 7.2). In this combined computational and experimental investigation we report the origins of enantioselectivity and the factors that control reactivity.



Scheme 7.1 Preformed imine with α-methylbenzylamine undergoes an asymmetric Michael addition to acrylates.



Scheme 7.2 This bifunctional aminothiourea catalyst contains functional groups for both nucleophilic and electrophilic activation.

7.3 Results and Discussion

The mechanism (Figure 7.1) was probed with SCS-MP2[6]/def2-∞ZVP[7]//B3LYP[8]/6-31G(d)[9]/SMD[10] (toluene) with energy corrections for solvation.[11] Exhaustive conformational searches ensured all relevant structures were captured. Condensation of aminothiourea **7.8** onto ketone **7.1** leads to the catalyst imine **7.9** (**II**), lying in 12:1 equilibrium with the ketone (ΔG_{exp}= –1.5 kcal mol^{-1}, 15:1). Tautomerization to the desired more substituted enamine proceeds slowly and leads to the optimally planar *trans* conformer (Figure 7.2.A). The acrylate electrophile is captured and activated by thiourea for addition in the rate- and stereodetermining Michael step. Matching experimental and computed secondary kinetic isotope effect (0.82 and 0.84, respectively, Figure 7.2.B) confirms C–C bond formation as rate determining. Facile proton transfer from the subsequent iminium by the enolate is largely exergonic,

furnishing the thermodynamic resting state product imine. The hydrolyzed product and catalyst is about 4 kcal/mol uphill from the product imine. Consequently, this product inhibition raises the **TS-IV** barrier to 28.6 kcal/mol for the subsequent catalytic cycle.

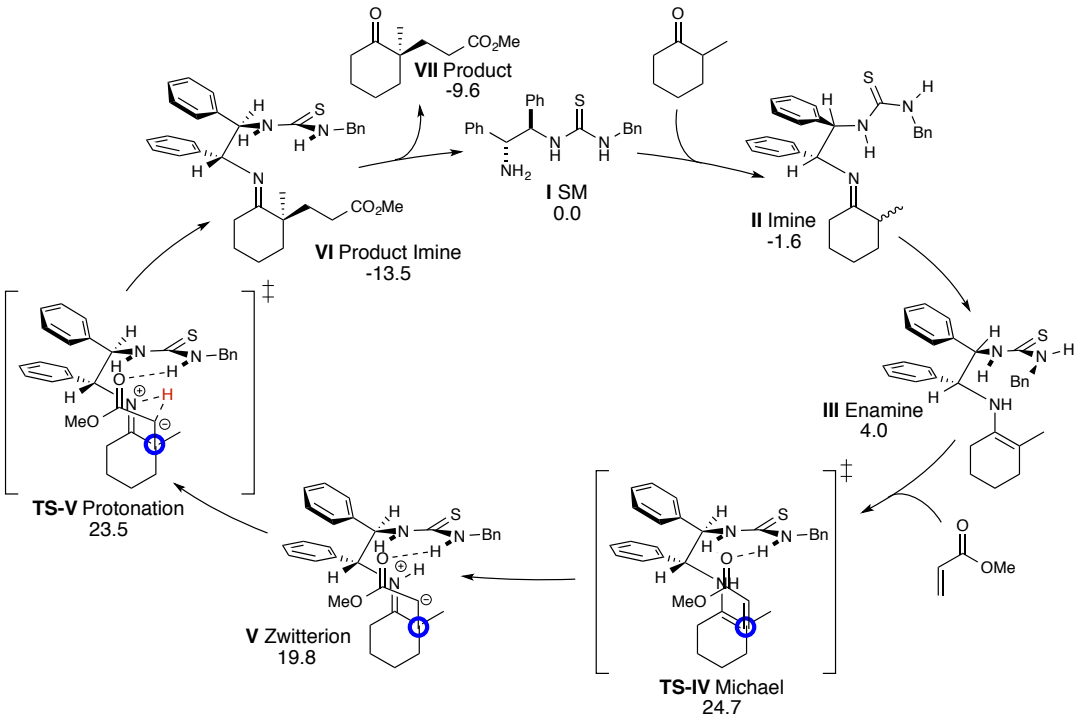


Figure 7.1 The mechanism of the Michael addition.

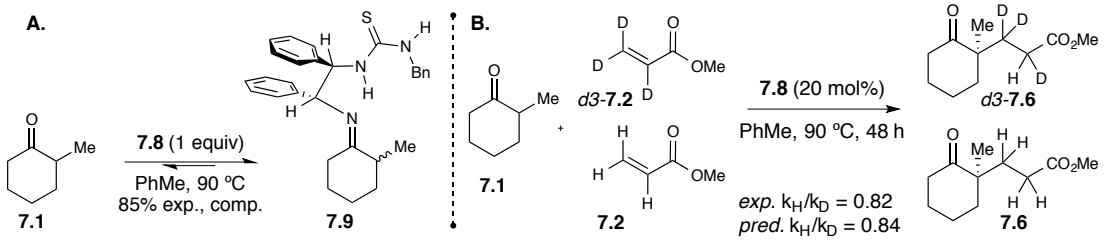


Figure 7.2 A) Computations agree with experiments in the energetics for imine formation; 85% formation of **7.9**. B) The predicted mechanism was probed and verified with a secondary KIE experiment.

The major transition state (TS) for the rate and stereodetermining Michael step, **TS-IV-major** (Figure 7.3), demonstrates the signature thiourea stabilization motif, in which both protons mimic an oxyanion hole and classically hydrogen bond to the developing alkoxide. However, the tether length and substituents frustrates the thiourea from adopting an optimal configuration to stabilize the π-system; instead, thiourea approaches diagonally to the carbonyl plane to stabilize one π system and one lone pair, termed by Goodman *grand jeté* activation.[12] A model system (fig. 7.4) suggests that this configuration is in fact more enthalpically stabilizing by 0.3 kcal/mol than the

traditional dual π-activation, though at an entropic cost (ΔΔG = +0.6 kcal mol^{-1}). The s-*anti* endo electrophile conformation reduces the charge separation of the developing zwitterion in preparation for subsequent proton transfer, bearing a striking resemblance to TSs of other amine-catalyzed processes. An additional enthalpic stabilization is afforded by an electrophile C–H···O interaction with the substrate α-methylene.

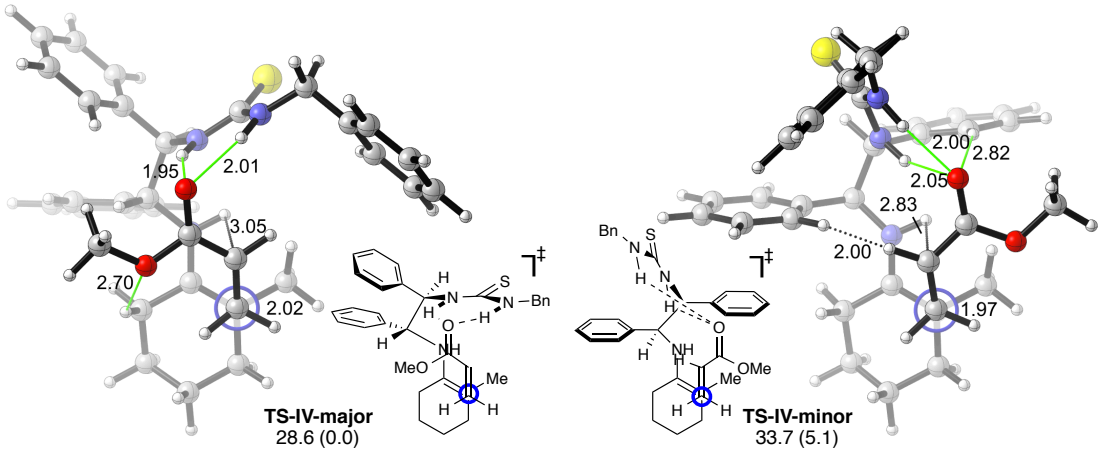


Figure 7.3 Rate-determining Michael TSs leading to the major and minor products. Dotted lines indicate repulsive interactions and green lines indicate stabilizing interactions.

In **TS-IV-minor**, thiourea adopts the dual π-activation motif to hydrogen bond with the s-*anti* electrophile orientation maximizing the electrostatic stabilization of the forming enolate/iminium. The exo approach of the electrophile allows the backbone aryl groups to achieve a favorable antiperiplanar orientation. A C–H···O interaction from the β-phenyl aids in stabilizing the developing alkoxide. Despite these stabilizing effects, a repulsive H···H contact with the α-phenyl group and the electrophile is incurred and overwhelmingly destabilizes the TS, raising the barrier by 5.1 kcal/mol (99.8% ee).

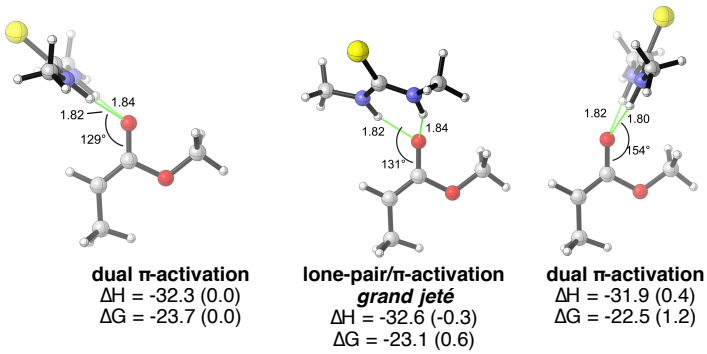
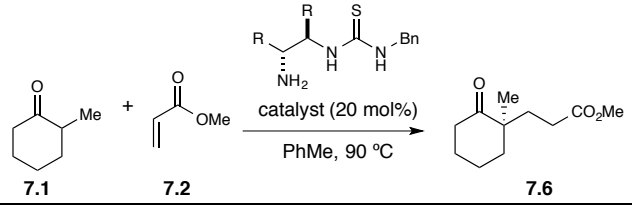


Figure 7.4 Hydrogen bonding motifs of thiourea.

We investigated the origins of selectivity by computing achiral catalyst **7.11**, which necessarily gave no selectivity, and systematically introduced aryl groups. Single phenyl substitution at the α-position, **7.12**, was predicted to yield 6.3 kcal/mol selectivity. The short H···H contact between the α-phenyl and the electrophile is amplified in the

absence of the C–H···O stabilization with the β-phenyl. β-substitution, on the other hand, provided only 3.7 kcal/mol selectivity. Removal of the α-phenyl also eliminates the repulsive interaction and adds the favorable C–H···O interaction with the β-phenyl. These results collectively indicate that steric repulsion between the α-substituent and the electrophile is responsible for the stereoselectivity. Furthermore, an increased selectivity at a lower barrier may be obtained through deletion of the β-substituent.

Table 7.1 Test for origins of selectivity by tether group modulation.



7.1 7.2 7.6

Entry	R_1	R_2	cat.	TS-IV-major $\Delta G^{\ddagger a}$	TS-IV-minor $\Delta G^{\ddagger}$ ($\Delta\Delta G^{\ddagger}$)^a
1	H	H	**7.11**	24.6	–
2	Ph	H	**7.12**	27.5	32.8 (6.3)
3	H	Ph	**7.13**	26.4	30.1 (3.7)
4	Ph	Ph	**7.8**	28.6	33.7 (5.1)

[a] Energies reported in kcal mol^{-1}.

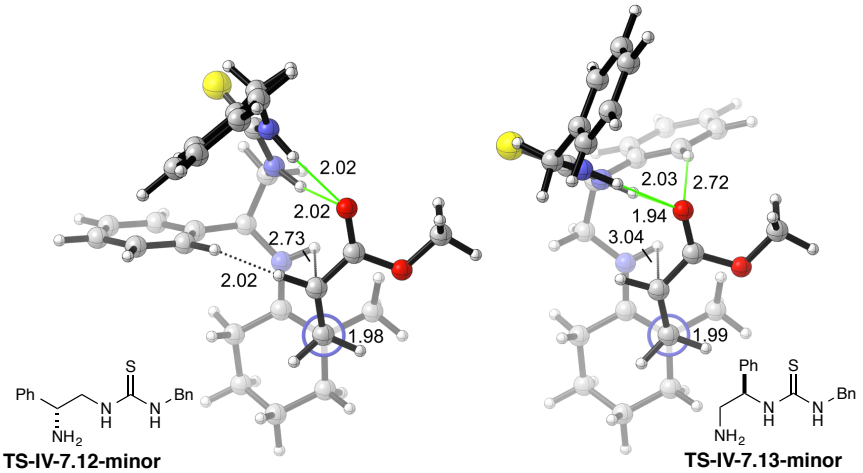
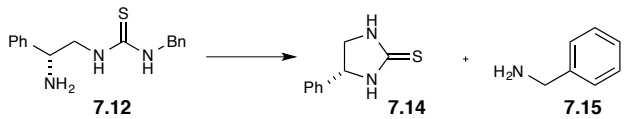


Figure 7.5 Minor TSs for the α-phenyl catalyst (left) and β-phenyl catalyst (right). Selectivities are with respect to the major TSs of each (not shown) and are in kcal/mol. Dotted lines indicate repulsive interactions and green lines indicate stabilizing interactions.

These results prompted experimental synthesis and test of catalyst **7.12**. Unfortunately, performance was surprisingly poor; with *reduced* yield (85%) and selectivity (80%). In reevaluating our computational procedure and conducting further exhaustive conformational searches we found no lower energy structures. We therefore speculated that the disparity between experiments and computations might arise from alternative decomposition pathways. NMR of the reaction mixture confirmed non-isolable, volatile catalyst decomposition products.

Enantioenrichment of only 86% after early termination (3 h) suggests the likelihood of selectivity erosion through unselective decomposition catalysis/racemization. The most likely culprit is benzylamine released from catalyst self-cyclization, as Pfau and d'Angelo have shown the α-methyl variant promotes this transformation. Benzylamine competitively catalyzes this reaction; the barrier of 28.9 kcal/mol lies between the major and minor TS barriers for catalyst **7.12**. These results indicate that the β-phenyl group plays a greater role in catalyst stability than enantioselection.



Scheme 7.6 Proposed decomposition pathway of catalyst **7.12** releasing benzylamine.

7.4 Conclusion

In conclusion, high-accuracy computations have uncovered that the selectivity of a bifunctional aminothiourea catalyst originates from the α-phenyl group, and have shown that deletion of the β-substituent would increase the selectivity. However, experimental test of the proposed catalyst resulted in lowered selectivities, suggesting the possibility of competing nonselective pathways. Through a combination of experimental and computational work, it has been determined that this current catalyst scaffold, while having the potential for further optimization, is not ideal due to its ease of decomposition. Future horizons of this project include increasing the tether length as well as extending this structure to a more stable and acidic squaramide moiety.[13]

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Chapter 8.
Conclusion

Organocatalysts bear resemblance to enzymes in their shared mechanistic paradigms and composition. They also offer a more affordable and environmentally benign alternative to expensive transition metal catalysts. Outside of serendipity, organocatalyst designs draw jointly from bioinspiration and intimate understanding of the chemistry involved. Computational tools add to the experimental toolbox to probe the factors controlling reactivity and selectivity.

Hydrogen bonding is largely responsible for rigidifying structures that impart remarkable reactivity, selectivity and fidelity in enzymatic processes. In organocatalysts, much of the preorganization is already built into the catalyst itself through chiral manifolds. In an environment with fewer overall hydrogen bonds to preorganize and stabilize the transition states, the energetic contribution of each interaction is amplified such that even small energetic differences can have significant results on product distribution. Despite the reduced strength of non-classical hydrogen bonds as compared to classical hydrogen bonds, they are instrumental in the controlling selectivity of many complex organic reactions. Many organocatalysts feature NCHB stabilizing moieties, and when combined with their inherent chirality and other subtle electronic effects, these organocatalysts can be highly selective for the major TS over other enantio-/diastereomeric configurations.

These studies collectively demonstrate the control of seemingly subtle interactions, from NCHB to (hyper)conjugative effects to steric factors. It is further demonstrated that understanding these factors on an atomistic level can aid researchers to make rational modifications to the catalyst to affect selectivity and reactivity. Understanding and exploiting these chemical factors for synthetic gain is a guiding principle of rational, *in silico* catalyst design.

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Appendices

Appendix I:
Computational Data for Chapter 3

Organocatalytic Kinetic Resolution Cascade Reactions: New Mechanistic and Stereochemical Manifold in Diphenyl Prolinol Silyl Ether Catalysis

General Structures and Thermal Corrections for Transition States for TS-I series

***(S)*-TS-I**

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
integral(grid=ultrafine) SCRF=(PCM,SOLVENT=Toluene,SMD)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=20) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C34H42N2O4Si C1[X(C34H42N2O4Si)] #Atoms= 83
Charge = 0 Multiplicity = 1

SCF Energy= -2020.74172779 Predicted Change= -1.101907D-08

==========

Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00291	0.00180	[NO]	0.00291	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	2.392393	1.947118	-1.488020
C	2.853099	1.747814	-0.145121
H	3.952074	1.665605	-0.145324
C	2.286334	0.464801	0.426242
H	2.699460	0.247879	1.407817
C	0.909803	0.193693	0.235892
H	0.396435	0.627638	-0.608826
C	2.470491	3.050441	0.576961
H	3.034283	3.199727	1.503422
H	1.402252	3.036988	0.821353
C	2.780155	4.101755	-0.500388
H	3.832214	4.402815	-0.446930
H	2.171153	5.005592	-0.403022
C	2.499634	3.343416	-1.817253
H	3.304073	3.487317	-2.551027
H	1.556097	3.644761	-2.285168
N	0.202480	-0.669474	0.952547
C	0.687699	-1.336914	2.179846
H	0.418068	-0.719769	3.047955
H	1.769113	-1.453092	2.154547
C	-0.063444	-2.664052	2.173950
H	-0.124892	-3.109933	3.171064
H	0.431632	-3.367570	1.497926
C	-1.436256	-2.276818	1.610537
H	-2.069004	-1.892036	2.412723
H	-1.950854	-3.127043	1.161517
C	-1.147933	-1.179222	0.559468
C	-2.251691	-0.055040	0.399710
O	-1.882476	0.725811	-0.739659

Si	-2.297122	0.827769	-2.380915
C	-2.110041	-0.794662	-3.317142
H	-1.173624	-1.302899	-3.057902
H	-2.089044	-0.583050	-4.395720
H	-2.943058	-1.483716	-3.140517
C	-1.045776	2.086139	-3.011451
H	-0.016175	1.742307	-2.859627
H	-1.161158	3.049775	-2.499276
H	-1.182912	2.267099	-4.085686
C	-4.033589	1.525748	-2.625907
H	-4.175721	1.782260	-3.685024
H	-4.188582	2.443282	-2.044577
H	-4.823310	0.818339	-2.353235
C	-2.233996	0.888973	1.623315
C	-3.647533	-0.678596	0.169483
H	-1.010588	-1.630706	-0.428480
C	-2.819888	0.531444	2.849954
H	-3.372128	-0.397538	2.941337
C	-2.748607	1.377712	3.958333
H	-3.216459	1.074919	4.891542
C	-2.097649	2.608694	3.865650
H	-2.047286	3.270319	4.726365
C	-1.528699	2.985511	2.649138
H	-1.032640	3.948192	2.553955
C	-1.595970	2.134825	1.542991
H	-1.165126	2.443393	0.598737
C	-4.805644	0.048103	0.491497
H	-4.716501	1.021248	0.961707
C	-6.077103	-0.457007	0.217252
H	-6.954107	0.127739	0.482309
C	-6.222198	-1.702460	-0.396211
H	-7.211515	-2.099716	-0.606935
C	-5.082168	-2.428434	-0.741735
H	-5.175609	-3.395040	-1.229537
C	-3.810501	-1.919207	-0.468090
H	-2.947823	-2.501768	-0.770445
C	2.499819	-2.264810	-0.518755
H	2.787713	-3.079125	0.129772
N	1.331811	-2.460522	-1.200979
O	0.687358	-3.541157	-1.066055
O	0.900834	-1.527732	-1.953388
C	3.190824	-1.031413	-0.623010
H	3.036348	-0.512931	-1.564635
C	4.596128	-0.989042	-0.122303
C	5.585949	-0.357878	-0.893893
H	5.308596	0.098565	-1.840628
C	6.916145	-0.326687	-0.470826
H	7.665839	0.160569	-1.088813
C	7.281191	-0.919336	0.738751
H	8.315633	-0.895173	1.070694
C	6.305426	-1.543148	1.521839
H	6.579259	-2.004526	2.467148
C	4.978096	-1.574888	1.097541
H	4.230030	-2.058544	1.720659

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-2020.74172779	Predicted Change= -1.101907D-08
Zero-point correction (ZPE)=	-2020.0433	0.69833
Internal Energy (U)=	-2020.0035	0.73818
Enthalpy (H)=	-2020.0026	0.73912
Gibbs Free Energy (G)=	-2020.1170	0.62472

Frequencies --	-313.2701	14.9879	19.5398

$\Delta G^{\ddagger}_{\text{SCS-MP2/cc-pVTZ}}$ SP = -2009.602196

***(R)*-TS-I**

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
integral(grid=ultrafine) SCRF=(PCM,SOLVENT=Toluene,SMD)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=20) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C34H42N2O4Si C1[X(C34H42N2O4Si)] #Atoms= 83
Charge = 0 Multiplicity = 1

SCF Energy= -2020.74008944 Predicted Change= -3.750748D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00096	0.00180	[YES]	0.00096	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	2.226505	2.870733	0.703211
C	2.836341	1.859881	-0.135112
H	3.923134	1.898903	0.025219
C	2.343224	0.502722	0.324986
H	2.765936	0.204013	1.280074
C	0.975034	0.218819	0.132040
H	0.430952	0.749845	-0.635781
C	2.529170	2.291324	-1.602065
H	1.861428	1.591647	-2.111575
H	3.458161	2.327909	-2.179657
C	1.899274	3.696676	-1.463677
H	0.809916	3.642592	-1.559726
H	2.269514	4.407148	-2.209482
C	2.275161	4.091458	-0.032530
H	1.580898	4.793506	0.438729
H	3.288664	4.526106	0.004929
N	0.284493	-0.718021	0.764942
C	0.799169	-1.519559	1.896962
H	0.567889	-0.994015	2.833255
H	1.877458	-1.643148	1.821509
C	0.022006	-2.826634	1.772801
H	-0.010487	-3.378573	2.716742
H	0.481394	-3.458831	1.006542
C	-1.362823	-2.355812	1.311864
H	-1.956540	-2.034933	2.171783
H	-1.919461	-3.138533	0.794413
C	-1.087898	-1.158526	0.371909
C	-2.238129	-0.069920	0.441319
O	-3.450355	-0.821759	0.341082
Si	-4.415370	-1.462205	-0.888357
C	-5.633104	-2.534625	0.067968
H	-6.355359	-3.005051	-0.612025

H	-6.204374	-1.943453	0.794472
H	-5.127172	-3.336963	0.618784
C	-3.450627	-2.526215	-2.110025
H	-4.154064	-3.003832	-2.806301
H	-2.887851	-3.327757	-1.616908
H	-2.743533	-1.947953	-2.714639
C	-5.375064	-0.130992	-1.816907
H	-5.895617	0.545810	-1.128643
H	-6.139286	-0.605768	-2.447875
H	-4.741756	0.477245	-2.471136
C	-2.222472	0.976271	-0.697953
C	-2.234801	0.609302	1.827155
H	-1.011105	-1.524498	-0.655914
C	-1.650398	0.724267	-1.955396
H	-1.087049	-0.182977	-2.146727
C	-1.763958	1.654736	-2.994270
H	-1.301837	1.436681	-3.953576
C	-2.457993	2.849382	-2.803768
H	-2.543930	3.571099	-3.611803
C	-3.042506	3.106625	-1.561337
H	-3.592444	4.029517	-1.395988
C	-2.927042	2.180471	-0.525624
H	-3.396318	2.395869	0.428513
C	-3.172412	0.243840	2.802448
H	-3.923940	-0.497074	2.558032
C	-3.156722	0.829095	4.071586
H	-3.897915	0.528688	4.807972
C	-2.201029	1.792608	4.391300
H	-2.187903	2.249432	5.377433
C	-1.265881	2.171992	3.425754
H	-0.520139	2.929258	3.653627
C	-1.284743	1.591631	2.156676
H	-0.557365	1.926397	1.424808
C	2.610218	-2.124519	-0.890081
H	2.860387	-3.010931	-0.326071
N	1.444018	-2.208010	-1.603432
O	1.040889	-1.178896	-2.237894
O	0.777105	-3.280082	-1.607711
C	3.326343	-0.908070	-0.842483
H	3.218312	-0.296231	-1.732041
C	4.700172	-0.918910	-0.265357
C	5.728381	-0.215210	-0.914243
H	5.504438	0.333792	-1.825466
C	7.032361	-0.228547	-0.416790
H	7.813560	0.316935	-0.939579
C	7.331820	-0.940898	0.745581
H	8.345678	-0.950244	1.136310
C	6.317142	-1.639469	1.406140
H	6.539762	-2.194094	2.313961
C	5.015832	-1.627215	0.907138
H	4.236137	-2.170301	1.434684

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-2020.74008944	Predicted Change=	-3.750748D-09
Zero-point correction (ZPE)=		-2020.0413	0.69875
Internal Energy (U)=		-2020.0016	0.73843
Enthalpy (H)=		-2020.0007	0.73938
Gibbs Free Energy (G)=		-2020.1142	0.62588
Frequencies --	-315.3444	19.7391	24.4341

$\Delta G^{\ddagger}_{\text{SCS-MP2/cc-pVTZ}}$ SP = -2009.601678

General Structures and Thermal Corrections for Transition States for TS-II series

***(S)*-TS-II**

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
integral(grid=ultrafine) SCRF=(PCM,SOLVENT=Toluene,SMD)
opt=(maxcycle=250,ts,verytight,calcfc,noeigentest,gdiis) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C35H44N2O4Si C1[X(C35H44N2O4Si)] #Atoms= 86
Charge = 0 Multiplicity = 1

SCF Energy= -2060.06294948 Predicted Change= -1.753887D-12

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00000	[YES]	0.00000	0.00000	[YES]
Displ	0.00002	0.00000	[NO]	0.00002	0.00000	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	2.356728	1.980114	-1.089707
C	2.841041	1.540928	0.182783
H	3.933778	1.405819	0.112377
C	2.218013	0.193764	0.502434
H	2.611466	-0.221129	1.426631
C	0.834789	0.020811	0.260586
H	0.345964	0.631781	-0.482735
C	2.571696	2.605574	1.262834
H	2.984325	2.264722	2.221095
H	1.486294	2.706140	1.393188
C	3.180207	3.956766	0.855890
H	2.907833	4.733015	1.581435
H	4.277325	3.880909	0.870673
C	2.716814	4.343682	-0.555371
H	1.641990	4.568538	-0.547550
H	3.236541	5.243233	-0.909503
C	2.972333	3.192900	-1.527457
H	4.057274	3.031264	-1.646652
H	2.552387	3.400101	-2.516308
N	0.086771	-0.941220	0.786727
C	0.528042	-1.862606	1.854919
H	0.251448	-1.433907	2.827766
H	1.607368	-1.998885	1.827516
C	-0.251956	-3.139384	1.557177
H	-0.349355	-3.780087	2.438602
H	0.245199	-3.701062	0.761031
C	-1.601812	-2.609152	1.056603
H	-2.253544	-2.399343	1.906809
H	-2.114826	-3.327365	0.415792

C	-1.270850	-1.311016	0.283573
C	-2.347491	-0.154663	0.382422
O	-1.939513	0.864453	-0.532921
Si	-2.351716	1.417207	-2.080096
C	-2.168107	0.106264	-3.420885
H	-1.250658	-0.479337	-3.286842
H	-2.110579	0.599605	-4.401369
H	-3.017316	-0.585001	-3.455376
C	-1.088652	2.790353	-2.343085
H	-0.061375	2.419776	-2.245081
H	-1.222174	3.600349	-1.614554
H	-1.192389	3.229744	-3.343960
C	-4.083165	2.166957	-2.131051
H	-4.202031	2.737411	-3.062873
H	-4.252043	2.862920	-1.299973
H	-4.877115	1.413542	-2.105554
C	-2.328301	0.470686	1.795624
C	-3.746738	-0.682720	-0.012297
H	-1.135533	-1.527155	-0.780660
C	-2.958542	-0.139565	2.893956
H	-3.549250	-1.038265	2.754114
C	-2.881019	0.416448	4.172514
H	-3.385224	-0.076081	4.999992
C	-2.176409	1.602171	4.384665
H	-2.121039	2.038639	5.378438
C	-1.558327	2.227247	3.301522
H	-1.016723	3.158836	3.445588
C	-1.633924	1.667422	2.024043
H	-1.162801	2.168450	1.187637
C	-4.907800	-0.065071	0.480379
H	-4.824779	0.751062	1.189331
C	-6.177234	-0.479095	0.074169
H	-7.056055	0.016339	0.478661
C	-6.317815	-1.519514	-0.845202
H	-7.305420	-1.846113	-1.159725
C	-5.174717	-2.130806	-1.360999
H	-5.263864	-2.936137	-2.085198
C	-3.905559	-1.714615	-0.952610
H	-3.041361	-2.204018	-1.387229
C	2.317934	-2.303365	-0.976603
H	2.552853	-3.249499	-0.511330
N	1.155954	-2.290162	-1.698284
O	0.456998	-3.339795	-1.799984
O	0.787995	-1.199083	-2.240613
C	3.073068	-1.116390	-0.813486
H	2.969742	-0.403410	-1.626111
C	4.462518	-1.261743	-0.288074
C	5.517935	-0.584428	-0.921046
H	5.303917	0.045206	-1.780900
C	6.833620	-0.728231	-0.476166
H	7.635072	-0.201275	-0.987327
C	7.118416	-1.545673	0.618512
H	8.141391	-1.656825	0.967834
C	6.077078	-2.219038	1.264169

H	6.288318	-2.854774	2.120194
C	4.764578	-2.076867	0.816993
H	3.964256	-2.602641	1.331549

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2060.06294948	Predicted Change= -1.753887D-12	
Zero-point correction (ZPE)=	-2059.3349	0.72803
Internal Energy (U)=	-2059.2943	0.76855
Enthalpy (H)=	-2059.2934	0.76949
Gibbs Free Energy (G)=	-2059.4085	0.65438

Frequencies -- -311.7209 17.2068 20.4453

$\Delta G^{\ddagger}_{\text{SCS-MP2/cc-pVTZ}}$ SP = -2048.654502

***(R)*-TS-II**

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

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#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
integral(grid=ultrafine) SCRF=(PCM,SOLVENT=Toluene,SMD)
opt=(maxcycle=250,ts,verytight,calcfc,noeigentest,gdiis) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C35H44N2O4Si C1[X(C35H44N2O4Si)] #Atoms= 86
Charge = 0 Multiplicity = 1

SCF Energy= -2060.05974607 Predicted Change= -5.374609D-13

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00000	[YES]	0.00000	0.00000	[YES]
Displ	0.00001	0.00000	[NO]	0.00001	0.00000	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	2.564832	2.499736	0.888968
C	2.867912	1.548518	-0.153153
H	3.962546	1.417368	-0.175832
C	2.253334	0.232336	0.291001
H	2.650874	-0.078844	1.253264
C	0.864603	0.048665	0.108628
H	0.357217	0.590889	-0.674772
C	2.430753	2.109148	-1.514925
H	1.343933	2.254481	-1.524705
H	2.669078	1.399174	-2.315567
C	2.882906	4.417788	-0.596074
H	3.466211	5.340221	-0.714778
H	1.823120	4.703487	-0.556215
C	3.119180	3.460375	-1.772763
H	2.753436	3.899281	-2.708787
H	4.199770	3.299514	-1.899560
C	3.258940	3.735754	0.718700
H	4.348102	3.558448	0.755574
H	2.990848	4.351811	1.583622
N	0.113170	-0.824101	0.763708
C	0.570311	-1.633386	1.914959
H	0.365996	-1.076000	2.839008
H	1.639229	-1.825267	1.850544
C	-0.286419	-2.891576	1.811239
H	-0.357965	-3.421574	2.765625
H	0.135823	-3.566138	1.060025
C	-1.637138	-2.344968	1.332912
H	-2.216923	-1.976588	2.183228
H	-2.235355	-3.100993	0.822236
C	-1.285845	-1.180262	0.377006
C	-2.365755	-0.021039	0.430952
O	-3.621604	-0.698374	0.335822

Si	-4.615400	-1.300670	-0.890382
C	-5.862711	-2.337129	0.067321
H	-6.604764	-2.778729	-0.610697
H	-6.408601	-1.732678	0.802412
H	-5.380142	-3.159911	0.608833
C	-3.698304	-2.390652	-2.125404
H	-4.425931	-2.855640	-2.805193
H	-3.143362	-3.202496	-1.640397
H	-2.990872	-1.831128	-2.746767
C	-5.532025	0.071257	-1.802812
H	-6.029470	0.757042	-1.106289
H	-6.311378	-0.369850	-2.439552
H	-4.878236	0.665865	-2.449473
C	-2.284548	1.011052	-0.718283
C	-2.324660	0.674302	1.808065
H	-1.233682	-1.563719	-0.645796
C	-1.714069	0.720365	-1.967955
H	-1.198004	-0.217022	-2.148075
C	-1.770924	1.647321	-3.014791
H	-1.310643	1.398619	-3.967468
C	-2.407076	2.875839	-2.840774
H	-2.448948	3.594476	-3.655050
C	-2.990286	3.171799	-1.606538
H	-3.495890	4.121886	-1.454163
C	-2.929415	2.250524	-0.562087
H	-3.395370	2.497073	0.386109
C	-3.293507	0.391864	2.780197
H	-4.092379	-0.299424	2.540574
C	-3.247823	0.996825	4.039398
H	-4.014780	0.762648	4.773389
C	-2.229869	1.896715	4.352371
H	-2.193337	2.368751	5.330685
C	-1.261987	2.192697	3.389862
H	-0.467216	2.900064	3.612131
C	-1.311718	1.594083	2.130327
H	-0.559583	1.866813	1.397917
C	2.310277	-2.422127	-0.858444
H	2.496833	-3.312786	-0.276722
N	1.143831	-2.435113	-1.573676
O	0.821615	-1.391115	-2.229601
O	0.397939	-3.454683	-1.558305
C	3.114717	-1.258297	-0.834650
H	3.059614	-0.668309	-1.743855
C	4.485835	-1.370194	-0.258877
C	5.567516	-0.765443	-0.920318
H	5.388787	-0.218999	-1.842945
C	6.866635	-0.874849	-0.421368
H	7.689096	-0.404930	-0.954169
C	7.108097	-1.585449	0.755288
H	8.118244	-1.669292	1.146835
C	6.040357	-2.186576	1.428165
H	6.217920	-2.739320	2.347017
C	4.743951	-2.077616	0.928186
H	3.923030	-2.544879	1.465696

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

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SCF Energy=	-2060.05974607	Predicted Change= -5.374609D-13
Zero-point correction (ZPE)=	-2059.3322	0.72751
Internal Energy (U)=	-2059.2915	0.76822
Enthalpy (H)=	-2059.2905	0.76917
Gibbs Free Energy (G)=	-2059.4065	0.65315

Frequencies -- -312.1356 17.7661 20.1892

$\Delta G^{\ddagger}_{\text{SCS-MP2/cc-pVTZ}}$ SP = -2048.652606

General Structures and Thermal Corrections for Transition States for TS-III series

***(S)*-anti-TS-III**

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
integral(grid=ultrafine) SCRF=(PCM,SOLVENT=Toluene,SMD)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=20) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RB3LYP/6-31G(d) Freq

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Pointgroup= C1 Stoichiometry= C35H44N2O4Si C1[X(C35H44N2O4Si)] #Atoms= 86
Charge = 0 Multiplicity = 1

SCF Energy= -2060.06179048 Predicted Change= -5.062771D-10

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00039	0.00180	[YES]	0.00039	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	2.519934	2.114041	-0.694516
C	2.924594	1.467142	0.522420
H	4.015707	1.327656	0.504150
C	2.280010	0.095591	0.627531
H	2.645721	-0.464302	1.484537
C	0.898098	0.001274	0.336029
H	0.476515	0.736591	-0.334468
C	2.585760	2.469680	1.641357
H	3.195736	2.315386	2.537204
H	1.530812	2.380078	1.927303
C	2.843647	3.808926	0.941310
H	3.917210	4.037704	0.934969
H	2.322207	4.651983	1.405559
C	2.352220	3.537436	-0.489883
H	1.276312	3.754695	-0.560687
C	3.087242	4.296511	-1.584003
H	2.718647	4.005245	-2.573717
H	4.163575	4.091548	-1.544411
H	2.935052	5.376904	-1.469906
N	0.093055	-0.983041	0.708783
C	0.468900	-2.063817	1.647650
H	0.171029	-1.765225	2.661808
H	1.543903	-2.231381	1.631920
C	-0.341662	-3.255167	1.146681
H	-0.482007	-4.013017	1.923181
H	0.161354	-3.711430	0.288969
C	-1.659839	-2.609231	0.702860
H	-2.326563	-2.487677	1.560173
H	-2.183035	-3.205796	-0.045744

C	-1.264180	-1.228132	0.127365
C	-2.379102	-0.133173	0.398149
O	-3.602306	-0.757993	0.001617
Si	-4.453735	-1.007549	-1.436842
C	-5.811599	-2.195457	-0.896178
H	-6.479103	-2.436379	-1.733882
H	-6.428248	-1.761214	-0.099242
H	-5.400279	-3.140144	-0.519892
C	-3.406006	-1.801476	-2.787754
H	-4.049641	-2.057714	-3.640939
H	-2.925331	-2.728799	-2.454559
H	-2.618460	-1.140544	-3.165823
C	-5.247523	0.574693	-2.086329
H	-5.830875	1.085410	-1.310609
H	-5.937956	0.325906	-2.904229
H	-4.516115	1.287066	-2.482160
C	-2.220466	1.177993	-0.406240
C	-2.482905	0.144445	1.911462
H	-1.116888	-1.317522	-0.952220
C	-1.541086	1.237383	-1.633308
H	-1.004160	0.377411	-2.019565
C	-1.520868	2.417046	-2.385270
H	-0.977680	2.435609	-3.326340
C	-2.187191	3.556494	-1.935317
H	-2.169580	4.471751	-2.521100
C	-2.880003	3.506134	-0.723334
H	-3.411730	4.381969	-0.360316
C	-2.897302	2.331422	0.027352
H	-3.448871	2.311745	0.961202
C	-3.508924	-0.424005	2.677865
H	-4.257331	-1.032693	2.184669
C	-3.581497	-0.206123	4.056598
H	-4.389185	-0.657212	4.627491
C	-2.628931	0.586047	4.696677
H	-2.685087	0.757011	5.768501
C	-1.607412	1.168152	3.942476
H	-0.865689	1.800884	4.423387
C	-1.538975	0.953004	2.565552
H	-0.755575	1.439698	1.994540
C	2.381839	-2.165236	-1.168929
H	2.626522	-3.159841	-0.825850
N	1.227404	-2.078094	-1.894770
O	0.846175	-0.933676	-2.307658
O	0.547215	-3.117358	-2.134823
C	3.123189	-0.996959	-0.852978
H	3.009112	-0.193337	-1.574751
C	4.522149	-1.190099	-0.366956
C	4.855233	-2.158435	0.596333
H	4.074500	-2.778866	1.029054
C	6.175730	-2.334144	1.006708
H	6.411976	-3.090390	1.750873
C	7.192825	-1.541047	0.467279
H	8.221944	-1.678729	0.788038
C	6.876324	-0.570058	-0.483800

H	7.658580	0.052483	-0.910160
C	5.552927	-0.393562	-0.892617
H	5.312599	0.361479	-1.636774

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2060.06179048	Predicted Change= -5.062771D-10	
Zero-point correction (ZPE)=	-2059.3359	0.72584
Internal Energy (U)=	-2059.2945	0.76721
Enthalpy (H)=	-2059.2936	0.76816
Gibbs Free Energy (G)=	-2059.4112	0.65050

Frequencies -- -313.4045 18.3980 23.2259

$\Delta G^{\ddagger}_{\text{SCS-MP2/cc-pVTZ}}$ SP = -2048.655245

***(R)*-anti-TS-III**

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

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#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
integral(grid=ultrafine) SCRF=(PCM,SOLVENT=Toluene,SMD)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=20) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C35H44N2O4Si C1[X(C35H44N2O4Si)] #Atoms= 86
Charge = 0 Multiplicity = 1

SCF Energy= -2060.05968519 Predicted Change= -7.199951D-10

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00060	0.00180	[YES]	0.00060	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	2.235414	2.671096	0.531269
C	2.849220	1.586769	-0.216622
H	3.926893	1.598413	-0.001212
C	2.293314	0.266548	0.290721
H	2.698812	-0.012499	1.259149
C	0.912836	0.037118	0.109995
H	0.390523	0.562503	-0.675760
C	2.638896	1.953262	-1.695508
H	1.666302	1.606936	-2.061151
H	3.408712	1.520565	-2.341206
C	2.687382	3.484601	-1.652137
H	2.201544	3.959467	-2.510428
H	3.727594	3.833798	-1.616399
C	1.979831	3.805028	-0.328810
H	0.893220	3.860369	-0.498151
C	2.441660	5.079494	0.362092
H	2.222779	5.955698	-0.260887
H	3.521161	5.048544	0.551490
H	1.928972	5.210497	1.321640
N	0.180348	-0.838489	0.781797
C	0.655325	-1.618791	1.945575
H	0.443439	-1.048988	2.860334
H	1.727424	-1.791912	1.880472
C	-0.178189	-2.894647	1.866406
H	-0.239895	-3.407184	2.830963
H	0.257031	-3.575697	1.128610
C	-1.539510	-2.383813	1.377380
H	-2.127876	-2.011918	2.220306
H	-2.121962	-3.160731	0.879861
C	-1.210354	-1.229581	0.401442
C	-2.311066	-0.090272	0.433365
O	-3.551592	-0.792512	0.324603

Si	-4.529749	-1.409131	-0.906394
C	-5.774616	-2.453971	0.045314
H	-6.506391	-2.905343	-0.637425
H	-6.333119	-1.852539	0.773329
H	-5.288369	-3.269968	0.593765
C	-3.593985	-2.497661	-2.129087
H	-4.313597	-2.977106	-2.807381
H	-3.031105	-3.298642	-1.635014
H	-2.891125	-1.935067	-2.752766
C	-5.451888	-0.048355	-1.830096
H	-5.959691	0.634992	-1.138610
H	-6.223411	-0.497666	-2.470620
H	-4.799115	0.550143	-2.474231
C	-2.228350	0.934818	-0.722653
C	-2.302845	0.613493	1.807223
H	-1.149775	-1.629134	-0.614739
C	-1.664803	0.627248	-1.972008
H	-1.158350	-0.316743	-2.143865
C	-1.714091	1.544912	-3.026879
H	-1.260786	1.282028	-3.979121
C	-2.335285	2.782658	-2.861686
H	-2.371555	3.494522	-3.682147
C	-2.911346	3.095744	-1.628594
H	-3.406059	4.052589	-1.483063
C	-2.858941	2.182377	-0.576014
H	-3.319658	2.443262	0.370733
C	-3.295180	0.336817	2.756995
H	-4.087255	-0.356831	2.502407
C	-3.280437	0.948547	4.013679
H	-4.065176	0.717871	4.729781
C	-2.270176	1.849674	4.347047
H	-2.257285	2.326662	5.323561
C	-1.278609	2.139593	3.407050
H	-0.488788	2.847427	3.645140
C	-1.297035	1.534020	2.149886
H	-0.523736	1.800155	1.437451
C	2.428009	-2.424342	-0.797451
H	2.634296	-3.295754	-0.193711
N	1.261250	-2.483188	-1.511633
O	0.909767	-1.463191	-2.189768
O	0.543733	-3.522132	-1.473491
C	3.202950	-1.242432	-0.803144
H	3.126562	-0.671986	-1.722462
C	4.573813	-1.293476	-0.219965
C	4.853896	-1.976112	0.976633
H	4.050014	-2.470870	1.515215
C	6.150494	-2.024182	1.485740
H	6.345098	-2.558858	2.411816
C	7.196241	-1.386580	0.812180
H	8.206376	-1.422985	1.210909
C	6.932478	-0.699997	-0.374160
H	7.737919	-0.201950	-0.907414
C	5.633468	-0.651815	-0.882270
H	5.437494	-0.122753	-1.811520

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-2060.05968519	Predicted Change= -7.199951D-10
Zero-point correction (ZPE)=	-2059.3334	0.72626
Internal Energy (U)=	-2059.2921	0.76751
Enthalpy (H)=	-2059.2912	0.76846
Gibbs Free Energy (G)=	-2059.4084	0.65125

Frequencies -- -314.4515 18.2630 20.7967

$\Delta G^{\ddagger}_{\text{SCS-MP2/cc-pVTZ}}$ SP = -2048.652754

General Structures and Thermal Corrections for Transition States for TS-IV series

***(S)*-syn-TS-IV**

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
integral(grid=ultrafine) SCRF=(PCM,SOLVENT=Toluene,SMD)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=20) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C36H46N2O4Si C1[X(C36H46N2O4Si)] #Atoms= 89
Charge = 0 Multiplicity = 1

SCF Energy= -2099.38197278 Predicted Change= -4.708782D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00108	0.00180	[YES]	0.00108	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	2.450296	1.949430	-0.667844
C	2.896548	1.291443	0.518726
H	3.981712	1.112429	0.437709
C	2.197940	-0.055272	0.611182
H	2.543397	-0.633347	1.464043
C	0.813014	-0.097890	0.326121
H	0.407014	0.659682	-0.328987
C	2.662948	2.183182	1.751512
H	3.045358	1.677677	2.647294
H	1.581777	2.319739	1.888536
C	2.912595	4.173098	0.225951
H	1.847849	4.442508	0.264122
H	3.475857	5.094347	0.029826
C	3.341460	3.547162	1.560367
H	4.433160	3.414545	1.567540
H	3.100059	4.215488	2.395840
C	3.125167	3.189812	-0.930868
H	4.205959	2.979868	-1.018641
C	2.602054	3.700316	-2.264642
H	3.112015	4.628266	-2.547166
H	1.526088	3.899905	-2.206142
H	2.769953	2.959906	-3.054067
N	-0.018177	-1.064628	0.692278
C	0.333075	-2.163847	1.618751
H	0.061013	-1.862493	2.639405
H	1.401182	-2.369252	1.586143
C	-0.524727	-3.323510	1.122220
H	-0.681041	-4.080748	1.896243
H	-0.048876	-3.792045	0.255619

C	-1.825157	-2.629810	0.699365
H	-2.475730	-2.490136	1.566199
H	-2.378902	-3.203449	-0.045184
C	-1.389081	-1.259814	0.126231
C	-2.462969	-0.129544	0.416934
O	-3.712561	-0.713571	0.039151
Si	-4.591514	-0.934278	-1.387054
C	-5.974863	-2.085306	-0.830468
H	-6.655689	-2.311483	-1.661538
H	-6.572824	-1.632833	-0.029440
H	-5.584968	-3.039336	-0.454954
C	-3.586975	-1.754189	-2.755722
H	-4.248543	-1.978027	-3.604309
H	-3.137987	-2.701831	-2.435786
H	-2.779270	-1.119324	-3.135692
C	-5.348642	0.672216	-2.020913
H	-5.912329	1.192776	-1.237182
H	-6.051200	0.446725	-2.835194
H	-4.601745	1.367994	-2.417417
C	-2.275949	1.176575	-0.389384
C	-2.533630	0.148864	1.931891
H	-1.260135	-1.348764	-0.955806
C	-1.619490	1.213826	-1.629574
H	-1.113224	0.338874	-2.023347
C	-1.582956	2.390259	-2.385910
H	-1.060565	2.390788	-3.338876
C	-2.206070	3.549561	-1.925228
H	-2.175265	4.462279	-2.514433
C	-2.873224	3.522523	-0.698313
H	-3.370356	4.414629	-0.326001
C	-2.909013	2.350437	0.055611
H	-3.441983	2.348436	1.000408
C	-3.566099	-0.386531	2.713441
H	-4.342018	-0.968885	2.231040
C	-3.610321	-0.168324	4.093296
H	-4.423910	-0.592832	4.676139
C	-2.622267	0.590928	4.719358
H	-2.656493	0.762379	5.792050
C	-1.593521	1.139604	3.950070
H	-0.823618	1.746445	4.419897
C	-1.553249	0.924503	2.572028
H	-0.762382	1.385628	1.990219
C	2.203524	-2.311225	-1.205348
H	2.401430	-3.318041	-0.867616
N	1.052811	-2.166773	-1.930785
O	0.723625	-1.004855	-2.335435
O	0.328105	-3.173570	-2.176207
C	2.997686	-1.183921	-0.879414
H	2.924510	-0.363919	-1.587978
C	4.380823	-1.453389	-0.384737
C	5.464752	-0.753973	-0.940285
H	5.278726	-0.015116	-1.715623
C	6.773084	-1.009339	-0.524480
H	7.597215	-0.461776	-0.974273

C	7.021375	-1.964507	0.462335
H	8.038602	-2.163290	0.788838
C	5.951356	-2.661760	1.030829
H	6.134185	-3.404578	1.803003
C	4.646156	-2.408040	0.612451
H	3.822910	-2.954286	1.066233

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-2099.38197278	Predicted Change= -4.708782D-09
Zero-point correction (ZPE)=	-2098.6268	0.75508
Internal Energy (U)=	-2098.5846	0.79732
Enthalpy (H)=	-2098.5837	0.79827
Gibbs Free Energy (G)=	-2098.7023	0.67958

Frequencies -- -313.6605 19.6717 22.5898

$\Delta G^{\ddagger}_{\text{SCS-MP2/cc-pVTZ}}$ SP = -2087.706438

***(R)*-syn-TS-IV**

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

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#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
integral(grid=ultrafine) SCRF=(PCM,SOLVENT=Toluene,SMD)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=20) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C36H46N2O4Si C1[X(C36H46N2O4Si)] #Atoms= 89
Charge = 0 Multiplicity = 1

SCF Energy= -2099.37990477 Predicted Change= -2.566915D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00091	0.00180	[YES]	0.00091	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	2.607220	2.340312	0.461233
C	2.848341	1.235464	-0.433967
H	3.934614	1.047271	-0.449618
C	2.179246	0.030041	0.204319
H	2.576765	-0.155742	1.198500
C	0.782729	-0.114939	0.058957
H	0.293241	0.320200	-0.799236
C	2.413504	1.613863	-1.856230
H	1.334236	1.806548	-1.875520
H	2.607823	0.787135	-2.549729
C	2.985519	4.006157	-1.278058
H	3.604905	4.872939	-1.542863
H	1.939476	4.343440	-1.266004
C	3.157159	2.880866	-2.308177
H	2.795307	3.202430	-3.292395
H	4.226663	2.652940	-2.424607
C	3.354900	3.519450	0.128055
H	4.429965	3.264027	0.141226
C	3.070292	4.543030	1.217394
H	3.645731	5.459790	1.045566
H	2.005221	4.802770	1.233504
H	3.341791	4.145172	2.201241
N	-0.002275	-0.838548	0.843913
C	0.424162	-1.480644	2.106618
H	0.258260	-0.775559	2.932183
H	1.480863	-1.737397	2.071432
C	-0.498501	-2.692059	2.202148
H	-0.586320	-3.063849	3.227279
H	-0.120886	-3.495867	1.562677
C	-1.824481	-2.154111	1.650105
H	-2.374417	-1.630637	2.436203
H	-2.467199	-2.946572	1.263844

C	-1.423792	-1.169795	0.525605
C	-2.431919	0.049479	0.412084
O	-3.729244	-0.549846	0.441070
Si	-4.788715	-1.274017	-0.656990
C	-6.097180	-2.010919	0.479499
H	-6.881976	-2.514999	-0.099693
H	-6.583009	-1.235711	1.085107
H	-5.669409	-2.749473	1.168589
C	-3.980815	-2.638850	-1.677308
H	-4.753093	-3.157007	-2.262878
H	-3.486293	-3.393790	-1.054582
H	-3.239713	-2.258108	-2.388725
C	-5.606362	-0.018374	-1.801325
H	-6.041958	0.816686	-1.239245
H	-6.424582	-0.503876	-2.351206
H	-4.916092	0.398348	-2.542328
C	-2.313608	0.881181	-0.886602
C	-2.314349	0.942854	1.664949
H	-1.409489	-1.705697	-0.427658
C	-1.796694	0.357140	-2.082533
H	-1.347729	-0.629952	-2.117597
C	-1.819424	1.108012	-3.263062
H	-1.401587	0.680476	-4.170751
C	-2.369631	2.389210	-3.278273
H	-2.386102	2.970135	-4.196634
C	-2.899901	2.916659	-2.098646
H	-3.338505	3.911152	-2.092571
C	-2.872785	2.170544	-0.921311
H	-3.296593	2.596014	-0.017922
C	-3.257144	0.849217	2.697671
H	-4.093308	0.169493	2.585349
C	-3.138205	1.625066	3.854054
H	-3.885901	1.534288	4.638044
C	-2.072260	2.511878	4.000751
H	-1.978259	3.115923	4.899438
C	-1.130611	2.621780	2.975050
H	-0.298851	3.315461	3.067547
C	-1.252003	1.850373	1.818522
H	-0.514355	1.976223	1.033316
C	2.102139	-2.772502	-0.524748
H	2.270731	-3.565900	0.188364
N	0.917628	-2.853041	-1.206987
O	0.618002	-1.917932	-2.018517
O	0.136562	-3.826579	-1.013206
C	2.948960	-1.654246	-0.703662
H	2.886059	-1.208539	-1.691167
C	4.332514	-1.730555	-0.153177
C	5.415118	-1.312271	-0.944641
H	5.226506	-0.930412	-1.944808
C	6.725851	-1.399851	-0.472598
H	7.548441	-1.077429	-1.105487
C	6.978364	-1.900271	0.805513
H	7.997650	-1.966399	1.176172
C	5.910165	-2.313229	1.607153

H	6.096766	-2.700836	2.605263
C	4.602002	-2.227625	1.133700
H	3.781005	-2.547525	1.770137

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2099.37990477 Predicted Change= -2.566915D-09

Zero-point correction (ZPE)=	-2098.6248	0.75500
Internal Energy (U)=	-2098.5826	0.79729
Enthalpy (H)=	-2098.5816	0.79824
Gibbs Free Energy (G)=	-2098.7010	0.67888

Frequencies -- -309.4759 16.7835 21.1767

$\Delta G^{\ddagger}_{\text{SCS-MP2/cc-pVTZ}}$ SP = -2087.704262

***(S)*-TS-I**

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

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b3lyp/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

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Pointgroup= C1 Stoichiometry= C34H42N2O4Si C1[X(C34H42N2O4Si)] #Atoms= 83
Charge = 0 Multiplicity = 1

SCF Energy= -2020.70698991 Predicted Change= -3.311153D-08

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Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.03917	0.00180	[NO]	0.03917	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	2.473522	1.937056	-1.433198
C	2.873264	1.734242	-0.073722
H	3.972281	1.664740	-0.021135
C	2.298406	0.433891	0.453996
H	2.700351	0.202786	1.438072
C	0.907657	0.200668	0.271179
H	0.393606	0.660533	-0.558474
C	2.433134	3.025127	0.637740
H	2.949982	3.181541	1.590023
H	1.355899	2.987728	0.835498
C	2.767711	4.092627	-0.417719
H	3.801015	4.436816	-0.299243
H	2.119467	4.971718	-0.353300
C	2.597942	3.330266	-1.754707
H	3.459375	3.481129	-2.419223
H	1.693617	3.621333	-2.298619
N	0.194150	-0.662683	0.979226
C	0.678347	-1.359065	2.190366
H	0.412875	-0.757159	3.071217
H	1.759004	-1.481065	2.161183
C	-0.079570	-2.682819	2.159595
H	-0.136418	-3.151602	3.146635
H	0.403557	-3.370918	1.459735
C	-1.452202	-2.270223	1.614583
H	-2.068654	-1.877024	2.425927
H	-1.986148	-3.107876	1.165266
C	-1.152108	-1.172529	0.568932
C	-2.254215	-0.053183	0.390246
O	-1.854428	0.749455	-0.720822
Si	-2.227675	0.886688	-2.372147
C	-2.098308	-0.727935	-3.329982
H	-1.186443	-1.272328	-3.059583
H	-2.048429	-0.498448	-4.403055

H	-2.962261	-1.381645	-3.174354
C	-0.902481	2.089880	-2.963351
H	0.102836	1.688390	-2.792983
H	-0.979679	3.053037	-2.443735
H	-1.009632	2.283486	-4.038028
C	-3.927906	1.673114	-2.616249
H	-4.066480	1.925996	-3.675709
H	-4.026300	2.600418	-2.039225
H	-4.744713	1.005959	-2.323804
C	-2.280801	0.866042	1.631025
C	-3.633234	-0.690616	0.106905
H	-0.993979	-1.627191	-0.414308
C	-2.914072	0.489358	2.827243
H	-3.483054	-0.433070	2.873568
C	-2.870695	1.308474	3.956800
H	-3.375434	0.991973	4.865918
C	-2.200437	2.531223	3.914874
H	-2.170287	3.171955	4.792135
C	-1.586347	2.928458	2.727452
H	-1.076629	3.887156	2.671835
C	-1.628012	2.105911	1.600065
H	-1.167819	2.429396	0.674837
C	-4.810549	0.014680	0.403295
H	-4.747049	0.982749	0.888212
C	-6.064992	-0.503828	0.081514
H	-6.958310	0.064728	0.326565
C	-6.172409	-1.742330	-0.552317
H	-7.148648	-2.150384	-0.799933
C	-5.012322	-2.447595	-0.870636
H	-5.076620	-3.408456	-1.374038
C	-3.757777	-1.925002	-0.550232
H	-2.877298	-2.489365	-0.835677
C	2.460391	-2.239214	-0.526115
H	2.760621	-3.082225	0.078506
N	1.274333	-2.393242	-1.184988
O	0.598888	-3.453543	-1.056750
O	0.848506	-1.421471	-1.892883
C	3.158259	-1.001658	-0.607376
H	3.006418	-0.478122	-1.547414
C	4.575463	-0.992380	-0.131632
C	5.560641	-0.358313	-0.905063
H	5.270981	0.124453	-1.834964
C	6.897346	-0.354238	-0.503602
H	7.644133	0.135340	-1.123236
C	7.273799	-0.977855	0.686362
H	8.313734	-0.975243	1.001507
C	6.302889	-1.604867	1.471579
H	6.585940	-2.091792	2.401239
C	4.969178	-1.609087	1.067680
H	4.224807	-2.100922	1.689422

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

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SCF Energy=	-2020.70698991	Predicted Change=	-3.311153D-08
Zero-point correction (ZPE)=	-2020.0077	0.69920	
Internal Energy (U)=	-2019.9679	0.73899	
Enthalpy (H)=	-2019.9670	0.73994	
Gibbs Free Energy (G)=	-2020.0829	0.62400	

Frequencies --	-301.4236	4.5759	16.7398

$\Delta G^{\ddagger}_{\text{SCS-MP2/cc-pVTZ}}$ SP = -2009.603617

***(R)*-TS-I**

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

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b3lyp/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C34H42N2O4Si C1[X(C34H42N2O4Si)] #Atoms= 83
Charge = 0 Multiplicity = 1

SCF Energy= -2020.70568913 Predicted Change= -5.612587D-09

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Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00773	0.00180	[NO]	0.00773	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	2.151496	2.827767	0.826980
C	2.809726	1.878667	-0.042208
H	3.892720	1.946904	0.134611
C	2.352607	0.486007	0.348276
H	2.780689	0.155347	1.290955
C	0.978301	0.214570	0.157540
H	0.426877	0.797448	-0.565393
C	2.499555	2.355127	-1.496051
H	1.879293	1.641182	-2.044788
H	3.432462	2.468550	-2.058261
C	1.789486	3.715638	-1.308643
H	0.705688	3.601630	-1.415118
H	2.120474	4.473160	-2.026176
C	2.137664	4.075622	0.140038
H	1.404334	4.718958	0.634278
H	3.126532	4.561812	0.199882
N	0.293445	-0.759885	0.733737
C	0.801596	-1.627496	1.816709
H	0.546096	-1.166541	2.780863
H	1.882810	-1.731522	1.751078
C	0.043419	-2.933555	1.592155
H	0.008371	-3.552258	2.493939
H	0.516900	-3.501530	0.785663
C	-1.343163	-2.447071	1.149771
H	-1.954200	-2.196971	2.021076
H	-1.880463	-3.197726	0.568388
C	-1.072123	-1.182543	0.301538
C	-2.226865	-0.109287	0.441097
O	-3.430043	-0.859837	0.268902
Si	-4.365873	-1.405743	-1.027162
C	-5.537742	-2.619760	-0.185955
H	-6.255642	-3.033385	-0.905029
H	-6.110547	-2.130848	0.610747

H	-4.994100	-3.459417	0.262227
C	-3.360204	-2.297941	-2.352289
H	-4.044904	-2.838451	-3.019309
H	-2.660241	-3.032034	-1.937381
H	-2.778844	-1.608312	-2.972481
C	-5.367823	-0.011483	-1.808926
H	-5.936409	0.541439	-1.052185
H	-6.087699	-0.429210	-2.525044
H	-4.739848	0.706007	-2.346658
C	-2.203289	1.020945	-0.613643
C	-2.239966	0.460649	1.874166
H	-0.981609	-1.473287	-0.748826
C	-1.619200	0.868304	-1.881553
H	-1.049355	-0.018682	-2.139288
C	-1.724925	1.878797	-2.843274
H	-1.253600	1.737016	-3.812167
C	-2.424902	3.052472	-2.566072
H	-2.506542	3.834740	-3.316158
C	-3.021549	3.209813	-1.313110
H	-3.575889	4.115554	-1.081226
C	-2.912294	2.205834	-0.352719
H	-3.386401	2.342410	0.613238
C	-3.191926	0.022563	2.803695
H	-3.943030	-0.690301	2.485704
C	-3.188975	0.501606	4.116142
H	-3.941289	0.147725	4.816592
C	-2.231990	1.428763	4.525166
H	-2.228229	1.802256	5.545840
C	-1.283997	1.881400	3.605249
H	-0.537621	2.613301	3.902609
C	-1.290059	1.408445	2.292688
H	-0.553735	1.801860	1.599731
C	2.604315	-2.044796	-0.998709
H	2.866882	-2.973570	-0.514534
N	1.425486	-2.070802	-1.695627
O	1.027305	-0.989710	-2.244508
O	0.738144	-3.124948	-1.751264
C	3.319439	-0.829536	-0.874550
H	3.214732	-0.176877	-1.735782
C	4.698628	-0.877756	-0.309044
C	5.718339	-0.118688	-0.904532
H	5.486187	0.494284	-1.772073
C	7.023599	-0.156070	-0.413427
H	7.797809	0.434196	-0.896364
C	7.333875	-0.950215	0.690920
H	8.349087	-0.979525	1.076892
C	6.328415	-1.706110	1.298880
H	6.559373	-2.326136	2.161069
C	5.025867	-1.667993	0.805561
H	4.254356	-2.259696	1.292154

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

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SCF Energy=	-2020.70568913	Predicted Change=	-5.612587D-09
Zero-point correction (ZPE)=	-2020.0064	0.69920	
Internal Energy (U)=	-2019.9667	0.73895	
Enthalpy (H)=	-2019.9657	0.73989	
Gibbs Free Energy (G)=	-2020.0810	0.62464	

Frequencies --	-301.9834	8.3736	18.2165

$\Delta G^{\ddagger}_{\text{SCS-MP2/cc-pVTZ}}$ SP = -2009.602544

***(S)*-TS-II**

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

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b3lyp/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

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Pointgroup= C1 Stoichiometry= C35H44N2O4Si C1[X(C35H44N2O4Si)] #Atoms= 86
Charge = 0 Multiplicity = 1

SCF Energy= -2060.02739336 Predicted Change= -2.479139D-09

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Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00098	0.00180	[YES]	0.00098	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	2.381371	1.866964	-1.172510
C	2.837329	1.514126	0.134978
H	3.933356	1.389745	0.102561
C	2.220211	0.177693	0.513492
H	2.610034	-0.177385	1.464903
C	0.825506	0.016439	0.300955
H	0.335326	0.589689	-0.470497
C	2.520242	2.636889	1.140697
H	2.914204	2.364715	2.128355
H	1.430147	2.721318	1.239494
C	3.112017	3.973488	0.666186
H	2.809730	4.787162	1.336548
H	4.209862	3.921088	0.709771
C	2.673848	4.263530	-0.776697
H	1.593536	4.457026	-0.807099
H	3.177514	5.155238	-1.171432
C	2.981094	3.061048	-1.669661
H	4.073070	2.919237	-1.749119
H	2.581116	3.195003	-2.678760
N	0.072871	-0.898577	0.896029
C	0.509409	-1.748380	2.023810
H	0.252103	-1.242933	2.965594
H	1.585122	-1.909754	1.994840
C	-0.298757	-3.027947	1.829786
H	-0.391987	-3.604730	2.754976
H	0.170016	-3.650370	1.062089
C	-1.645059	-2.500891	1.317825
H	-2.265029	-2.189516	2.161375
H	-2.197447	-3.257584	0.760272
C	-1.288588	-1.294248	0.419775
C	-2.340627	-0.114370	0.381447
O	-1.902880	0.794921	-0.627768
Si	-2.266990	1.167217	-2.243335

C	-2.190388	-0.311801	-3.404744
H	-1.289423	-0.909766	-3.225262
H	-2.156751	0.050720	-4.441028
H	-3.067626	-0.960091	-3.312805
C	-0.907183	2.399603	-2.673614
H	0.086684	1.955617	-2.551488
H	-0.960643	3.290507	-2.035831
H	-1.004850	2.730999	-3.715181
C	-3.942430	2.030478	-2.380765
H	-4.065001	2.434160	-3.394597
H	-4.018665	2.870273	-1.679794
H	-4.780925	1.353899	-2.188621
C	-2.326937	0.651551	1.722620
C	-3.746045	-0.650571	0.028430
H	-1.143751	-1.623733	-0.614451
C	-2.976412	0.162788	2.868664
H	-3.584930	-0.733247	2.807843
C	-2.898588	0.839596	4.087070
H	-3.417243	0.439488	4.954477
C	-2.176166	2.028764	4.187445
H	-2.119459	2.559182	5.134277
C	-1.544295	2.537016	3.052872
H	-0.992915	3.472304	3.108913
C	-1.620183	1.856434	1.836105
H	-1.144223	2.267016	0.954449
C	-4.890489	0.065602	0.413629
H	-4.783061	0.963642	1.012079
C	-6.166988	-0.353117	0.037969
H	-7.033762	0.220995	0.354857
C	-6.329996	-1.499012	-0.741204
H	-7.323497	-1.829796	-1.031739
C	-5.202691	-2.211963	-1.148370
H	-5.310227	-3.101179	-1.763656
C	-3.925920	-1.789863	-0.772522
H	-3.072078	-2.357094	-1.126065
C	2.291814	-2.377877	-0.766522
H	2.553352	-3.293910	-0.257605
N	1.105575	-2.412750	-1.446024
O	0.392747	-3.455279	-1.439396
O	0.723595	-1.354580	-2.044722
C	3.036735	-1.169572	-0.706472
H	2.906954	-0.532314	-1.577003
C	4.447809	-1.266219	-0.224263
C	5.470342	-0.622319	-0.938970
H	5.215730	-0.059051	-1.833209
C	6.801681	-0.713352	-0.530061
H	7.576814	-0.213011	-1.104662
C	7.136389	-1.445141	0.609616
H	8.171885	-1.515798	0.931303
C	6.129100	-2.085783	1.335686
H	6.379194	-2.657236	2.225832
C	4.800840	-1.994529	0.924113
H	4.028067	-2.497027	1.501097

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-2060.02739336	Predicted Change= -2.479139D-09
Zero-point correction (ZPE)=	-2059.2990	0.72833
Internal Energy (U)=	-2059.2584	0.76895
Enthalpy (H)=	-2059.2574	0.76990
Gibbs Free Energy (G)=	-2059.3739	0.65340

Frequencies -- -297.8217 9.7814 17.3238

$\Delta G^{\ddagger}_{\text{SCS-MP2/cc-pVTZ}}$ SP = -2048.655700

***(R)*-TS-II**

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

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b3lyp/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

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Pointgroup= C1 Stoichiometry= C35H44N2O4Si C1[X(C35H44N2O4Si)] #Atoms= 86
Charge = 0 Multiplicity = 1

SCF Energy= -2060.02423518 Predicted Change= -1.015545D-09

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Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00054	0.00180	[YES]	0.00054	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	2.500112	2.479504	0.925738
C	2.854837	1.546555	-0.114026
H	3.952794	1.437328	-0.108463
C	2.255494	0.213623	0.301792
H	2.650623	-0.097880	1.265580
C	0.861850	0.043757	0.124584
H	0.355485	0.604657	-0.645652
C	2.440328	2.108145	-1.483326
H	1.351210	2.227869	-1.522535
H	2.714044	1.410944	-2.283842
C	2.804958	4.418068	-0.532510
H	3.362670	5.358727	-0.628286
H	1.736480	4.670463	-0.520677
C	3.102163	3.478158	-1.709769
H	2.755418	3.916232	-2.653174
H	4.190255	3.346359	-1.804221
C	3.163925	3.733705	0.787173
H	4.256391	3.584846	0.850154
H	2.855420	4.332755	1.649916
N	0.109365	-0.838394	0.763538
C	0.550186	-1.661775	1.909413
H	0.323496	-1.116739	2.836236
H	1.621606	-1.845870	1.862935
C	-0.297340	-2.924182	1.770484
H	-0.380444	-3.471879	2.714100
H	0.137649	-3.581341	1.011579
C	-1.643936	-2.375202	1.281000
H	-2.242418	-2.027251	2.126776
H	-2.226569	-3.124602	0.743393
C	-1.283438	-1.189475	0.355226
C	-2.360896	-0.031946	0.426553
O	-3.612984	-0.705642	0.289154
Si	-4.569908	-1.275367	-0.981258

C	-5.806916	-2.379139	-0.082792
H	-6.540298	-2.795967	-0.784206
H	-6.358502	-1.816491	0.679445
H	-5.309720	-3.218423	0.416955
C	-3.610750	-2.287734	-2.253859
H	-4.323971	-2.830863	-2.888294
H	-2.943110	-3.030672	-1.802897
H	-3.001109	-1.661618	-2.913315
C	-5.496122	0.125075	-1.842016
H	-6.047869	0.738247	-1.119984
H	-6.225598	-0.291881	-2.548807
H	-4.828132	0.786480	-2.402888
C	-2.257877	1.033527	-0.688441
C	-2.338122	0.616751	1.825681
H	-1.216042	-1.550083	-0.674972
C	-1.681265	0.770737	-1.941531
H	-1.171870	-0.165959	-2.143989
C	-1.717888	1.729564	-2.959515
H	-1.252929	1.502878	-3.915227
C	-2.340890	2.959585	-2.753971
H	-2.368212	3.701885	-3.547372
C	-2.929708	3.226962	-1.516337
H	-3.424228	4.178705	-1.340009
C	-2.888766	2.274852	-0.499539
H	-3.356453	2.495858	0.453914
C	-3.323917	0.304546	2.770584
H	-4.123758	-0.368765	2.487222
C	-3.290305	0.856444	4.053698
H	-4.069634	0.600169	4.766995
C	-2.267681	1.730925	4.417674
H	-2.239934	2.160391	5.415710
C	-1.284216	2.057646	3.481920
H	-0.485934	2.746928	3.744186
C	-1.321325	1.513061	2.198079
H	-0.555324	1.809290	1.489301
C	2.295569	-2.402049	-0.864861
H	2.495319	-3.309985	-0.315507
N	1.115008	-2.392447	-1.558816
O	0.798233	-1.327174	-2.184275
O	0.351373	-3.394845	-1.538473
C	3.097581	-1.233808	-0.831830
H	3.032149	-0.644619	-1.741685
C	4.479370	-1.352377	-0.280860
C	5.551895	-0.755116	-0.961826
H	5.359412	-0.211924	-1.883873
C	6.858555	-0.866837	-0.485212
H	7.673385	-0.402376	-1.034235
C	7.117609	-1.573310	0.689569
H	8.133772	-1.659430	1.064430
C	6.059818	-2.167724	1.382153
H	6.250726	-2.718474	2.299411
C	4.756260	-2.056000	0.902987
H	3.943742	-2.521712	1.455186

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-2060.02423518	Predicted Change= -1.015545D-09
Zero-point correction (ZPE)=	-2059.2959	0.72826
Internal Energy (U)=	-2059.2552	0.76895
Enthalpy (H)=	-2059.2543	0.76990
Gibbs Free Energy (G)=	-2059.3707	0.65347
Frequencies --	-295.0409	17.6682 18.5979

$\Delta G^{\ddagger}_{\text{SCS-MP2/cc-pVTZ}}$ SP = -2048.653504

***(S)*-anti-TS-III**

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

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b3lyp/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

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Pointgroup= C1 Stoichiometry= C35H44N2O4Si C1[X(C35H44N2O4Si)] #Atoms= 86
Charge = 0 Multiplicity = 1

SCF Energy= -2060.02574605 Predicted Change= -3.063158D-10

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Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00074	0.00180	[YES]	0.00074	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	2.593632	2.099468	-0.633221
C	2.937797	1.440897	0.594107
H	4.028577	1.300836	0.627963
C	2.290578	0.064443	0.643047
H	2.641504	-0.512584	1.496180
C	0.897534	0.007357	0.364473
H	0.484878	0.770735	-0.279324
C	2.535380	2.427825	1.706452
H	3.104437	2.273992	2.628910
H	1.469703	2.320533	1.943362
C	2.803059	3.778961	1.032660
H	3.871924	4.024689	1.078331
H	2.248751	4.608698	1.482450
C	2.383355	3.513654	-0.423046
H	1.306910	3.707441	-0.542548
C	3.153587	4.299794	-1.474325
H	2.842163	4.003371	-2.480985
H	4.230137	4.117626	-1.380048
H	2.970914	5.375165	-1.360959
N	0.080838	-0.974518	0.713055
C	0.433034	-2.085149	1.625175
H	0.095991	-1.820331	2.636964
H	1.509193	-2.245473	1.642496
C	-0.350701	-3.265823	1.057794
H	-0.514773	-4.047434	1.805955
H	0.183946	-3.692433	0.204641
C	-1.657598	-2.616084	0.583603
H	-2.369470	-2.545860	1.409643
H	-2.128604	-3.184864	-0.219033
C	-1.261290	-1.203272	0.090742
C	-2.394163	-0.138648	0.383899
O	-3.585622	-0.748371	-0.111684
Si	-4.324016	-0.953193	-1.620331

C	-5.580801	-2.313701	-1.266155
H	-6.189770	-2.524105	-2.154101
H	-6.262172	-2.025301	-0.457087
H	-5.088978	-3.247821	-0.971245
C	-3.142005	-1.503177	-2.984923
H	-3.731570	-1.895294	-3.824654
H	-2.442313	-2.289455	-2.679714
H	-2.540100	-0.674435	-3.371256
C	-5.231370	0.614116	-2.149334
H	-5.924345	0.952902	-1.370361
H	-5.819936	0.418182	-3.055164
H	-4.544711	1.437960	-2.369193
C	-2.213725	1.226085	-0.318746
C	-2.568104	0.036057	1.904960
H	-1.082364	-1.232596	-0.986701
C	-1.494111	1.373683	-1.514987
H	-0.945703	0.543352	-1.947821
C	-1.449418	2.606196	-2.174906
H	-0.874480	2.692517	-3.092891
C	-2.133589	3.709094	-1.665386
H	-2.099042	4.664974	-2.181566
C	-2.869175	3.569382	-0.486485
H	-3.416718	4.415789	-0.079815
C	-2.908192	2.343388	0.175268
H	-3.490243	2.251216	1.086039
C	-3.648720	-0.548953	2.576248
H	-4.385608	-1.096138	2.000952
C	-3.786022	-0.424385	3.961219
H	-4.635670	-0.885644	4.458223
C	-2.844104	0.287410	4.702291
H	-2.950347	0.384876	5.779463
C	-1.767496	0.885032	4.043373
H	-1.033189	1.457083	4.604919
C	-1.634914	0.764630	2.660186
H	-0.809300	1.263272	2.163328
C	2.351787	-2.111664	-1.183497
H	2.601834	-3.123636	-0.901195
N	1.188236	-1.979018	-1.885363
O	0.822976	-0.805518	-2.231355
O	0.477071	-2.989652	-2.147615
C	3.101486	-0.953254	-0.825603
H	2.998792	-0.139177	-1.538415
C	4.506524	-1.178870	-0.364112
C	4.840340	-2.183103	0.559524
H	4.057843	-2.814583	0.973483
C	6.162539	-2.385978	0.950369
H	6.399367	-3.171977	1.662792
C	7.180842	-1.582994	0.430101
H	8.211694	-1.741616	0.734991
C	6.863635	-0.575074	-0.480983
H	7.647647	0.055437	-0.892201
C	5.538541	-0.372880	-0.869971
H	5.294340	0.412161	-1.581196

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-2060.02574605	Predicted Change= -3.063158D-10
Zero-point correction (ZPE)=	-2059.2994	0.72630
Internal Energy (U)=	-2059.2579	0.76779
Enthalpy (H)=	-2059.2570	0.76874
Gibbs Free Energy (G)=	-2059.3762	0.64951
Frequencies --	-304.6776	15.7479 19.0011

$\Delta G^{\ddagger}_{\text{SCS-MP2/cc-pVTZ}}$ SP = -2048.656598

***(R)*-anti-TS-III**

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

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b3lyp/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

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Pointgroup= C1 Stoichiometry= C35H44N2O4Si C1[X(C35H44N2O4Si)] #Atoms= 86
Charge = 0 Multiplicity = 1

SCF Energy= -2060.02423607 Predicted Change= -1.644759D-09

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Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00125	0.00180	[YES]	0.00125	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	2.129838	2.662477	0.582546
C	2.819854	1.618748	-0.153875
H	3.887058	1.678255	0.100686
C	2.303985	0.266228	0.314725
H	2.711385	-0.019243	1.281143
C	0.920548	0.036165	0.136953
H	0.393805	0.583990	-0.629709
C	2.638511	1.985553	-1.638812
H	1.716035	1.559520	-2.048418
H	3.466972	1.624696	-2.255702
C	2.558680	3.515482	-1.585513
H	2.065316	3.955010	-2.458154
H	3.564211	3.950110	-1.511162
C	1.782834	3.762716	-0.285400
H	0.701604	3.708024	-0.489223
C	2.093381	5.074755	0.420736
H	1.798382	5.927396	-0.202716
H	3.165445	5.151239	0.634020
H	1.549808	5.140935	1.368877
N	0.195544	-0.861454	0.784433
C	0.662520	-1.658976	1.937905
H	0.430762	-1.106290	2.859074
H	1.737412	-1.819893	1.884442
C	-0.157728	-2.941973	1.822518
H	-0.224662	-3.476306	2.774996
H	0.289258	-3.601147	1.072344
C	-1.518725	-2.431583	1.329866
H	-2.121383	-2.081527	2.171968
H	-2.087261	-3.202790	0.808215
C	-1.187163	-1.255428	0.382038
C	-2.290548	-0.122199	0.428940
O	-3.524003	-0.826382	0.280337
Si	-4.468154	-1.410817	-0.992461

C	-5.711853	-2.506020	-0.093201
H	-6.436013	-2.934362	-0.797252
H	-6.273631	-1.935050	0.655261
H	-5.217700	-3.337051	0.423041
C	-3.494675	-2.438675	-2.241755
H	-4.200252	-2.993948	-2.874221
H	-2.829991	-3.172618	-1.771958
H	-2.880328	-1.821778	-2.905524
C	-5.387466	-0.022729	-1.880253
H	-5.943478	0.601557	-1.171195
H	-6.112644	-0.449845	-2.585411
H	-4.715336	0.629414	-2.447008
C	-2.192456	0.934710	-0.695470
C	-2.302338	0.538453	1.823101
H	-1.109453	-1.634319	-0.641026
C	-1.621635	0.655723	-1.948237
H	-1.115136	-0.284464	-2.140513
C	-1.655172	1.603306	-2.976167
H	-1.195763	1.363096	-3.931331
C	-2.269403	2.839916	-2.781570
H	-2.295066	3.573891	-3.582747
C	-2.852733	3.123674	-1.545071
H	-3.341738	4.079815	-1.377411
C	-2.815586	2.181310	-0.518141
H	-3.279830	2.415616	0.433655
C	-3.305476	0.224686	2.749157
H	-4.091372	-0.460415	2.455361
C	-3.305416	0.787820	4.027810
H	-4.097529	0.529576	4.726157
C	-2.299681	1.675480	4.406459
H	-2.298122	2.113881	5.400987
C	-1.298612	2.002968	3.489860
H	-0.512541	2.701897	3.763423
C	-1.301626	1.446792	2.210310
H	-0.520217	1.742412	1.518318
C	2.444712	-2.376355	-0.813600
H	2.673217	-3.267706	-0.248432
N	1.263529	-2.417837	-1.506551
O	0.907418	-1.374248	-2.148055
O	0.535863	-3.445932	-1.470745
C	3.206066	-1.182587	-0.801369
H	3.113245	-0.607830	-1.717162
C	4.588694	-1.232614	-0.243696
C	4.892531	-1.915888	0.945629
H	4.100843	-2.419270	1.495017
C	6.196625	-1.959019	1.434466
H	6.408536	-2.495131	2.355791
C	7.227893	-1.315128	0.746337
H	8.244354	-1.347598	1.128760
C	6.941728	-0.628791	-0.434247
H	7.736071	-0.126726	-0.980190
C	5.634862	-0.586131	-0.920650
H	5.422638	-0.058200	-1.847143

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-2060.02423607	Predicted Change= -1.644759D-09
Zero-point correction (ZPE)=	-2059.2977	0.72649
Internal Energy (U)=	-2059.2563	0.76793
Enthalpy (H)=	-2059.2553	0.76888
Gibbs Free Energy (G)=	-2059.3743	0.64984
Frequencies --	-298.1879	15.1202 18.6628

$\Delta G^{\ddagger}_{\text{SCS-MP2/cc-pVTZ}}$ SP = -2048.653605

***(S)*-syn-TS-IV**

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

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b3lyp/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

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Pointgroup= C1 Stoichiometry= C36H46N2O4Si C1[X(C36H46N2O4Si)] #Atoms= 89
Charge = 0 Multiplicity = 1

SCF Energy= -2099.34557937 Predicted Change= -3.095646D-09

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Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00077	0.00180	[YES]	0.00077	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	2.464195	1.942973	-0.641035
C	2.908021	1.277578	0.540342
H	3.994856	1.103241	0.464316
C	2.213283	-0.074475	0.605916
H	2.551821	-0.652657	1.462626
C	0.816913	-0.088834	0.342545
H	0.414952	0.686527	-0.293804
C	2.656954	2.153709	1.780608
H	3.036139	1.643965	2.675625
H	1.573104	2.278290	1.909125
C	2.884935	4.162424	0.280095
H	1.815816	4.412972	0.318099
H	3.432229	5.095836	0.096482
C	3.320346	3.527205	1.608476
H	4.413569	3.407202	1.615822
H	3.071252	4.183044	2.451375
C	3.115798	3.195631	-0.887816
H	4.201280	3.006938	-0.976657
C	2.579301	3.709863	-2.216045
H	3.062527	4.655350	-2.485948
H	1.498415	3.874498	-2.148797
H	2.764817	2.981556	-3.011625
N	-0.019843	-1.050286	0.704075
C	0.316027	-2.161000	1.621590
H	0.014851	-1.872896	2.638462
H	1.385940	-2.359188	1.613580
C	-0.521820	-3.320561	1.089544
H	-0.694402	-4.086698	1.851696
H	-0.023874	-3.776692	0.229370
C	-1.816041	-2.630110	0.639815
H	-2.500012	-2.518914	1.484728
H	-2.331917	-3.193605	-0.138606
C	-1.380708	-1.241709	0.112398

C	-2.469629	-0.132720	0.410301
O	-3.696173	-0.718395	-0.028458
Si	-4.491267	-0.927928	-1.507109
C	-5.777953	-2.239738	-1.082571
H	-6.420581	-2.451514	-1.946139
H	-6.424137	-1.910575	-0.260349
H	-5.306609	-3.181846	-0.779758
C	-3.371599	-1.543381	-2.896639
H	-3.998228	-1.919548	-3.716515
H	-2.699118	-2.355501	-2.597972
H	-2.745111	-0.744925	-3.307132
C	-5.366549	0.655253	-2.042371
H	-6.013916	1.039056	-1.245278
H	-5.999644	0.454893	-2.916715
H	-4.662990	1.448764	-2.314160
C	-2.272225	1.203807	-0.339900
C	-2.586986	0.090767	1.930151
H	-1.227666	-1.297532	-0.968106
C	-1.579457	1.295998	-1.556928
H	-1.055006	0.441983	-1.972884
C	-1.531589	2.503382	-2.261626
H	-0.979785	2.546634	-3.196685
C	-2.182810	3.635717	-1.774904
H	-2.145815	4.571716	-2.326214
C	-2.886873	3.552577	-0.571614
H	-3.406857	4.423422	-0.180679
C	-2.931232	2.351402	0.133426
H	-3.491004	2.301415	1.061332
C	-3.651551	-0.456678	2.656783
H	-4.417381	-1.007870	2.124648
C	-3.736773	-0.289045	4.041371
H	-4.574959	-0.721265	4.582056
C	-2.758086	0.429334	4.726496
H	-2.824242	0.560787	5.803290
C	-1.697028	0.989540	4.011944
H	-0.934345	1.566191	4.529186
C	-1.616046	0.826072	2.629194
H	-0.801494	1.296934	2.088968
C	2.181124	-2.278183	-1.201733
H	2.386799	-3.296379	-0.906058
N	1.018607	-2.102389	-1.899273
O	0.704378	-0.919446	-2.257330
O	0.263681	-3.084580	-2.143629
C	2.981620	-1.153249	-0.857779
H	2.915433	-0.336674	-1.572356
C	4.372513	-1.443706	-0.389552
C	5.453752	-0.743104	-0.946518
H	5.261081	0.007074	-1.709368
C	6.764989	-1.011393	-0.550513
H	7.586897	-0.461877	-1.001934
C	7.019713	-1.981979	0.418737
H	8.039495	-2.191152	0.730170
C	5.953073	-2.682294	0.988020
H	6.141004	-3.439049	1.745246

C	4.644967	-2.413389	0.589539
H	3.824315	-2.964881	1.042371

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

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SCF Energy=	-2099.34557937	Predicted Change= -3.095646D-09
Zero-point correction (ZPE)=	-2098.5898	0.75573
Internal Energy (U)=	-2098.5475	0.79802
Enthalpy (H)=	-2098.5466	0.79896
Gibbs Free Energy (G)=	-2098.6660	0.67950

Frequencies -- -303.8499 19.1302 20.1443

$\Delta G^{\ddagger}_{\text{SCS-MP2/cc-pVTZ}}$ SP = -2087.705248

***(R)*-syn-TS-IV**

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

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b3lyp/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

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Pointgroup= C1 Stoichiometry= C36H46N2O4Si C1[X(C36H46N2O4Si)] #Atoms= 89
Charge = 0 Multiplicity = 1

SCF Energy= -2099.34376564 Predicted Change= -1.123214D-09

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Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00086	0.00180	[YES]	0.00086	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	2.521452	2.346508	0.477050
C	2.832666	1.257780	-0.413624
H	3.925918	1.111201	-0.400442
C	2.193237	0.023688	0.201030
H	2.592258	-0.160463	1.195551
C	0.791435	-0.114880	0.066877
H	0.293354	0.345008	-0.772064
C	2.419537	1.622761	-1.847035
H	1.333823	1.767247	-1.897751
H	2.666162	0.808599	-2.538489
C	2.866740	4.034815	-1.244964
H	3.448936	4.932353	-1.491190
H	1.805699	4.320291	-1.257625
C	3.118357	2.923676	-2.274339
H	2.771856	3.233137	-3.267547
H	4.200387	2.745513	-2.360856
C	3.223024	3.557410	0.168084
H	4.308011	3.348681	0.205752
C	2.866555	4.561237	1.255704
H	3.406842	5.502471	1.105220
H	1.791416	4.773036	1.241323
H	3.125982	4.164212	2.242302
N	0.014756	-0.856625	0.840626
C	0.439883	-1.515280	2.093084
H	0.251457	-0.827557	2.929128
H	1.501429	-1.752066	2.064335
C	-0.462702	-2.745414	2.155361
H	-0.550633	-3.142492	3.171165
H	-0.069757	-3.526358	1.497500
C	-1.793963	-2.215611	1.605998
H	-2.361497	-1.719435	2.397491
H	-2.417564	-3.010268	1.194250
C	-1.400591	-1.199076	0.508061

C	-2.419478	0.009751	0.419990
O	-3.707486	-0.609290	0.409718
Si	-4.733263	-1.287966	-0.749312
C	-6.054827	-2.099702	0.322495
H	-6.831795	-2.566086	-0.295848
H	-6.543950	-1.362893	0.970344
H	-5.629196	-2.878391	0.965790
C	-3.878828	-2.587117	-1.817750
H	-4.633741	-3.132756	-2.399283
H	-3.324626	-3.324744	-1.226443
H	-3.174636	-2.146693	-2.530800
C	-5.535710	0.021164	-1.844529
H	-6.015345	0.803172	-1.244550
H	-6.312332	-0.442648	-2.466962
H	-4.817145	0.505553	-2.512856
C	-2.290211	0.886267	-0.846988
C	-2.328236	0.861960	1.702206
H	-1.370464	-1.712545	-0.457171
C	-1.756837	0.408480	-2.055148
H	-1.298439	-0.573090	-2.123128
C	-1.771768	1.203397	-3.206373
H	-1.341762	0.811322	-4.124143
C	-2.328260	2.481352	-3.179622
H	-2.338419	3.095963	-4.075942
C	-2.872746	2.962372	-1.987174
H	-3.315500	3.954323	-1.948986
C	-2.853867	2.173360	-0.838683
H	-3.287236	2.560111	0.077367
C	-3.300473	0.744458	2.703788
H	-4.137656	0.075921	2.543399
C	-3.207902	1.482482	3.886471
H	-3.978168	1.374644	4.646024
C	-2.138822	2.352934	4.091532
H	-2.065186	2.927504	5.011168
C	-1.168052	2.486616	3.096749
H	-0.332833	3.168491	3.233668
C	-1.263624	1.755215	1.912558
H	-0.504414	1.904236	1.152021
C	2.118942	-2.735932	-0.563164
H	2.297413	-3.557624	0.114525
N	0.925059	-2.785243	-1.232407
O	0.632905	-1.814056	-2.005731
O	0.127597	-3.743629	-1.050453
C	2.961590	-1.606883	-0.716546
H	2.900002	-1.156944	-1.702878
C	4.348257	-1.694029	-0.171889
C	5.427907	-1.239257	-0.945178
H	5.237505	-0.828766	-1.933819
C	6.738236	-1.326873	-0.473636
H	7.558349	-0.975250	-1.093995
C	6.994119	-1.865980	0.787326
H	8.013216	-1.933150	1.158111
C	5.929463	-2.317458	1.571460
H	6.118189	-2.737240	2.556010

C	4.622155	-2.230058	1.097511
H	3.804082	-2.582925	1.720635

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

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SCF Energy= -2099.34376564 Predicted Change= -1.123214D-09

Zero-point correction (ZPE)=	-2098.5877	0.75602
Internal Energy (U)=	-2098.5454	0.79827
Enthalpy (H)=	-2098.5445	0.79921
Gibbs Free Energy (G)=	-2098.6643	0.67941

Frequencies -- -296.3709 15.8912 18.0087

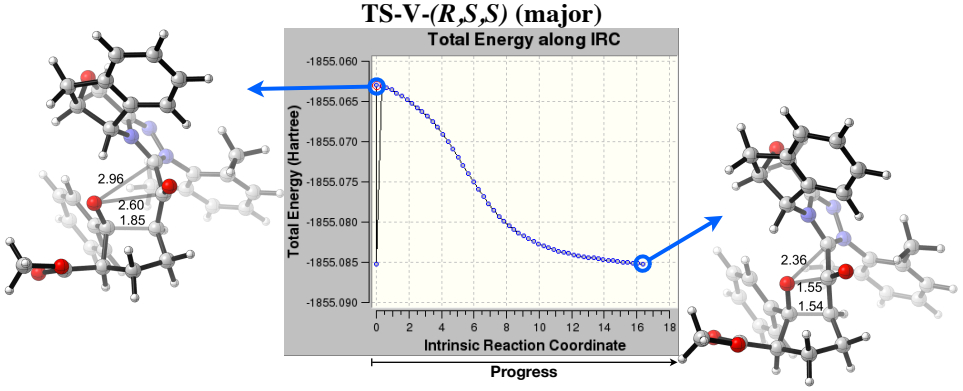
$\Delta G^{\ddagger}_{\text{SCS-MP2/cc-pVTZ}}$ SP = -2087.707727

Appendix II:
Computational Data for Chapter 4

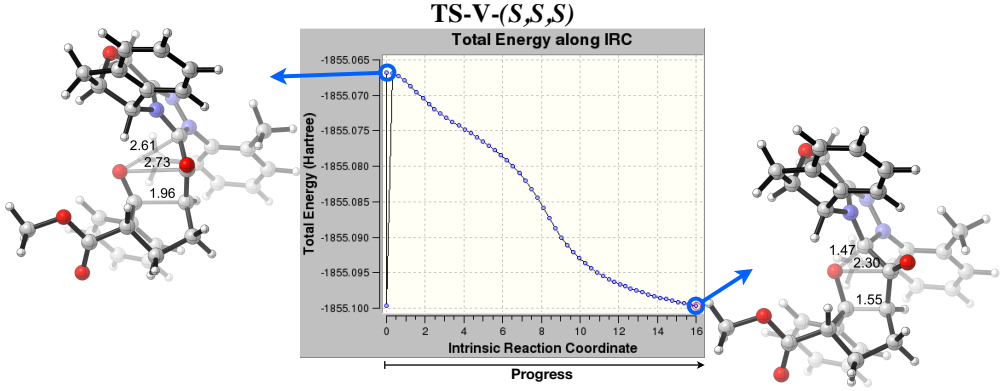
Catalytic kinetic resolution of a dynamic racemate: highly stereoselective β-lactone formation by *N*-heterocyclic carbene catalysis

Intrinsic Reaction Coordinates for TS-V

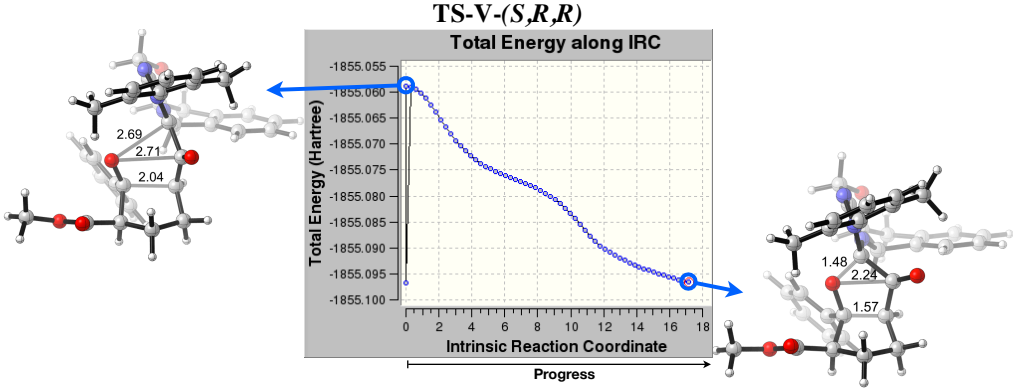
TS-V-*(R,S,S)* (major)



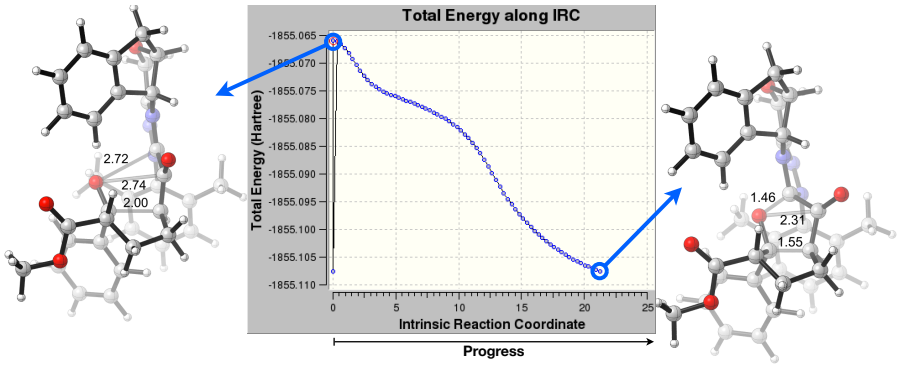
TS-V-*(S,S,S)*



TS-V-*(S,R,R)*



TS-V-*(R,R,R)*



Geometries and Thermodynamic Corrections for All Reported Structures

I-Substrate

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C14H14O4 C1[X(C14H14O4)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -842.443339224 Predicted Change= -1.590531D-08

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00164 ||	0.00180	[YES]	0.00164 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-4.818885	-0.020201	-0.438658
H	-4.886439	0.022643	-1.547590
C	-3.602516	-0.671674	0.080835
H	-3.502958	-0.757426	1.161135
C	-2.660192	-1.113578	-0.758138
H	-2.814194	-0.979795	-1.831337
C	-1.358463	-1.717346	-0.328441
H	-1.111068	-2.599932	-0.925707
H	-1.400343	-2.027528	0.718971
C	-0.216707	-0.693164	-0.472622
H	-0.124576	-0.358833	-1.512218
C	-0.570005	0.500787	0.397471
O	-0.621392	0.457928	1.600089
O	-0.885057	1.581703	-0.330121
C	-1.349684	2.698888	0.433923
H	-0.587162	3.010614	1.150590
H	-2.260270	2.427909	0.973126
H	-1.549452	3.487774	-0.288868

C	1.112741	-1.309720	-0.015738
O	1.144816	-2.451871	0.384470
C	2.353103	-0.477519	-0.096705
O	-5.689315	0.448372	0.256646
C	3.537628	-1.027197	0.404497
H	3.501468	-2.022409	0.835625
C	4.721681	-0.305286	0.345738
H	5.638510	-0.733334	0.738558
C	4.731648	0.970503	-0.217760
H	5.657770	1.535423	-0.263968
C	3.556506	1.521825	-0.720441
H	3.564877	2.514090	-1.160216
C	2.367011	0.801264	-0.660824
H	1.458220	1.246251	-1.055591

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-842.443339224	Predicted Change= -1.590531D-08
Zero-point correction (ZPE)=	-842.1864	0.25693
Internal Energy (U)=	-842.1689	0.27437
Enthalpy (H)=	-842.1680	0.27532
Gibbs Free Energy (G)=	-842.2345	0.20877

Frequencies -- 21.7893 24.2763 42.8717
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -842.5005031

I-NHC

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C20H19N3O C1[X(C20H19N3O)] #Atoms= 43
Charge = 0 Multiplicity = 1

SCF Energy= -1012.58880870 Predicted Change= -1.292471D-08

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00146	0.00180	[YES]	0.00146	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	0.488187	-0.738820	-0.365817
C	-0.562768	-0.011023	-0.864456
N	-1.525512	-0.382301	0.006849
C	-2.879591	0.080751	-0.015513
N	-1.147649	-1.270519	0.997016
C	0.105901	-1.463152	0.734138
C	1.087586	-2.353729	1.428384
O	2.396922	-1.879975	1.202438
C	2.719068	-1.796012	-0.175758
C	1.850334	-0.716499	-0.871603
C	4.146080	-1.241662	-0.260550
C	3.932821	0.255856	-0.260846
C	2.613827	0.560020	-0.594636
C	4.836576	1.275466	0.008751
C	4.396118	2.597443	-0.058507
C	3.073872	2.893162	-0.391924
C	2.165526	1.871181	-0.667514
C	-3.702974	-0.298946	-1.079732
C	-3.183788	-1.177697	-2.186512
C	-5.017947	0.166698	-1.078976
C	-5.488999	0.972758	-0.048629
C	-4.646533	1.332627	0.997628
C	-3.322984	0.893964	1.031498
C	-2.391145	1.290541	2.145753
H	0.983330	-3.387075	1.061717
H	0.915380	-2.347960	2.505737
H	2.600043	-2.784550	-0.642792
H	1.805700	-0.908993	-1.949916
H	4.628267	-1.572986	-1.188430
H	4.742544	-1.604600	0.580918
H	5.864967	1.049919	0.277550
H	5.089190	3.405247	0.156599
H	2.749043	3.928226	-0.434670

H	1.130958	2.079322	-0.926925
H	-2.395336	-0.668319	-2.747692
H	-3.990817	-1.449227	-2.871133
H	-2.748027	-2.097458	-1.782003
H	-5.676574	-0.114383	-1.896034
H	-6.516278	1.324192	-0.062512
H	-5.012098	1.968840	1.799018
H	-2.849856	2.055366	2.776760
H	-1.452332	1.687139	1.744131
H	-2.134539	0.428091	2.767860

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1012.58880870 Predicted Change= -1.292471D-08

Zero-point correction (ZPE)=	-1012.2309	0.35785
Internal Energy (U)=	-1012.2121	0.37668
Enthalpy (H)=	-1012.2111	0.37763
Gibbs Free Energy (G)=	-1012.2788	0.31000

Frequencies -- 21.4932 28.0260 64.7719
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1012.650771

***(R)*-II**

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C34H33N3O5 C1[X(C34H33N3O5)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -1855.05314400 Predicted Change= -3.723794D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00003	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00600	0.00180	[NO]	0.00600	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	1.076587	0.613188	-0.741227
C	2.003138	0.018903	0.029297
N	2.897589	-0.476707	-0.821592
C	4.156549	-1.071540	-0.474931
N	2.549996	-0.267980	-2.130552
C	1.423903	0.379981	-2.044053
C	0.454365	0.693824	-3.143549
H	-0.019952	-0.252511	-3.449125
H	0.973524	1.117311	-4.005712
O	-0.499589	1.624253	-2.715792
C	-1.155882	1.285453	-1.491156
H	-1.653330	0.309504	-1.576499
C	-0.138164	1.332544	-0.330160
H	-0.514882	0.825982	0.556618
C	-2.085078	2.461219	-1.196994
H	-2.861322	2.147133	-0.491410
H	-2.558107	2.815996	-2.116617
C	-1.140854	3.460491	-0.565657
C	-0.000996	2.820306	-0.073932
C	-1.289079	4.832825	-0.420801
H	-2.171487	5.337764	-0.804718
C	-0.278924	5.553264	0.217077
H	-0.375353	6.629479	0.329149
C	0.848270	4.903329	0.718415
H	1.616628	5.476984	1.228156
C	0.995678	3.521300	0.590577
H	1.822694	2.978584	1.039011
C	4.345396	-2.428418	-0.740242
C	3.244487	-3.255518	-1.348134
H	3.008851	-2.915440	-2.360945
H	2.327581	-3.175160	-0.752975
H	3.534494	-4.307451	-1.391456
C	5.581580	-2.975407	-0.398379

H	5.764484	-4.028623	-0.590496
C	6.566711	-2.189821	0.191028
H	7.522398	-2.632785	0.454275
C	6.336851	-0.842147	0.449821
H	7.109830	-0.236192	0.913269
C	5.119256	-0.248111	0.118345
C	4.843749	1.209432	0.390634
H	5.755633	1.708812	0.724981
H	4.074547	1.349292	1.162427
H	4.491141	1.715936	-0.515120
C	1.942073	-0.084311	1.555040
H	2.944168	-0.492073	1.842808
C	0.924553	-1.178477	1.895287
H	0.808566	-1.279191	2.975693
C	0.119726	-1.870308	1.085308
H	0.181169	-1.772853	0.000973
C	-0.996069	-2.746947	1.594137
H	-0.841054	-2.954613	2.656297
H	-1.022083	-3.700626	1.057110
C	-2.381596	-2.075057	1.439630
H	-3.111866	-2.605557	2.063636
C	-2.295458	-0.629273	1.913952
O	-2.577908	0.320770	1.215298
O	-1.827227	-0.539160	3.150474
C	-1.382731	0.774571	3.557112
H	-1.229534	0.700662	4.632820
H	-2.148822	1.515455	3.324745
H	-0.436269	1.008227	3.047916
C	-2.858090	-2.071120	-0.014347
O	-2.073173	-2.310925	-0.911562
C	-4.296432	-1.793326	-0.316380
O	1.613975	1.094251	2.082733
C	-4.719311	-1.940135	-1.640743
H	-3.988564	-2.240940	-2.384614
C	-6.044773	-1.708600	-1.983426
H	-6.368706	-1.827133	-3.012644
C	-6.958067	-1.322739	-1.003374
H	-7.994818	-1.139057	-1.268924
C	-6.542811	-1.168847	0.316824
H	-7.251548	-0.860355	1.078747
C	-5.215841	-1.404495	0.661341
H	-4.902598	-1.266661	1.691609

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1855.05314400 Predicted Change= -3.723794D-08
Zero-point correction (ZPE)= -1854.4342 0.61891
Internal Energy (U)= -1854.3981 0.65501
Enthalpy (H)= -1854.3971 0.65595
Gibbs Free Energy (G)= -1854.5040 0.54906

Frequencies -- 10.9425 17.4096 23.5868
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1855.164611

***(S)*-II**

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C34H33N3O5 C1[X(C34H33N3O5)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -1855.04958441 Predicted Change= -2.790432D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00003	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00363	0.00180	[NO]	0.00363	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	0.915290	1.147845	-0.452581
C	1.674683	0.137919	0.008201
N	2.847643	0.280107	-0.603739
C	4.046792	-0.457021	-0.324120
N	2.856342	1.324860	-1.490671
C	1.656060	1.817899	-1.387863
C	1.006343	2.846191	-2.264460
H	0.828150	2.382997	-3.247821
H	1.665503	3.706081	-2.399980
O	-0.187412	3.304989	-1.695418
C	-1.089695	2.273849	-1.287162
H	-1.346824	1.624291	-2.134961
C	-0.472082	1.490728	-0.107615
H	-0.991242	0.547522	0.059101
C	-2.267379	3.006419	-0.647694
H	-3.137774	2.343013	-0.608146
H	-2.520773	3.902163	-1.221269
C	-1.741421	3.295600	0.740545
C	-0.684869	2.438273	1.058295
C	-2.175587	4.242434	1.657186
H	-2.995226	4.913117	1.413868
C	-1.532931	4.323627	2.892503
H	-1.855368	5.065307	3.617759
C	-0.485361	3.458614	3.205306
H	-0.004804	3.528572	4.176696
C	-0.053880	2.492860	2.293979
H	0.711240	1.760460	2.535667
C	4.537434	-1.323697	-1.301067
C	3.804674	-1.508430	-2.603052
H	3.814533	-0.588151	-3.194881
H	2.756076	-1.771302	-2.422328
H	4.262841	-2.306074	-3.191563
C	5.712748	-2.013736	-1.005239

H	6.123583	-2.698419	-1.741469
C	6.347828	-1.839449	0.220154
H	7.260252	-2.386665	0.436315
C	5.820198	-0.975200	1.174693
H	6.317982	-0.848902	2.131542
C	4.650324	-0.258871	0.922266
C	4.052543	0.678025	1.941258
H	3.081945	0.322272	2.315610
H	3.888354	1.671079	1.507099
H	4.728709	0.788402	2.791845
C	1.238287	-0.913048	1.032679
H	2.178915	-1.483223	1.243794
C	0.300150	-1.904851	0.337531
H	-0.026350	-2.682096	1.030534
C	-0.234353	-1.852871	-0.884861
H	0.038779	-1.068804	-1.592118
C	-1.319291	-2.793049	-1.347580
H	-1.382815	-3.641331	-0.658936
H	-1.097296	-3.188107	-2.345249
C	-2.711422	-2.116031	-1.403940
H	-3.495061	-2.874754	-1.515805
C	-2.830209	-1.138122	-2.553572
O	-1.902741	-0.616670	-3.127431
O	-4.111500	-0.891733	-2.842476
C	-4.326845	0.145661	-3.798252
H	-3.928836	1.089604	-3.417105
H	-5.405701	0.210979	-3.928146
H	-3.835869	-0.095694	-4.743277
C	-2.959671	-1.313933	-0.118094
O	-3.084313	-0.105012	-0.169994
C	-2.905044	-2.038985	1.180056
O	0.673420	-0.309862	2.077685
C	-3.404591	-3.336439	1.330007
H	-3.902053	-3.833167	0.500507
C	-3.281834	-3.987626	2.552115
H	-3.687513	-4.986666	2.677115
C	-2.623675	-3.359622	3.609854
H	-2.505891	-3.880053	4.555794
C	-2.099477	-2.078837	3.450861
H	-1.544890	-1.602666	4.252333
C	-2.255020	-1.406180	2.244373
H	-1.787703	-0.435744	2.103731

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1855.04958441	Predicted Change= -2.790432D-08	
Zero-point correction (ZPE)=	-1854.4307	0.61887
Internal Energy (U)=	-1854.3943	0.65520
Enthalpy (H)=	-1854.3934	0.65614
Gibbs Free Energy (G)=	-1854.4999	0.54967

Frequencies -- 16.8224 22.6388 31.5047
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1855.162748

(R)-III

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C34H33N3O5 C1[X(C34H33N3O5)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -1855.06666709 Predicted Change= -1.701788D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00183	0.00180	[NO]	0.00183	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	3.053538	-1.191853	-0.570643
C	1.681179	-0.935205	-0.641757
N	1.144483	-1.828220	0.283250
C	-0.143659	-1.818597	0.885740
N	2.128875	-2.632383	0.853217
C	3.226085	-2.218597	0.329741
C	4.594939	-2.783131	0.539691
H	4.768345	-3.601700	-0.177229
H	4.687276	-3.177199	1.552462
O	5.562122	-1.773658	0.373408
C	5.499577	-1.169184	-0.907377
H	5.647170	-1.933113	-1.684644
C	4.163903	-0.404684	-1.092199
H	3.986402	-0.228353	-2.156899
C	6.557304	-0.062348	-0.910791
H	6.869557	0.161953	-1.938282
H	7.438738	-0.377560	-0.346039
C	5.818585	1.104782	-0.295958
C	4.439843	0.908036	-0.382770
C	6.330998	2.251741	0.294841
H	7.404136	2.405184	0.369870
C	5.442415	3.197840	0.805706
H	5.826832	4.097032	1.277695
C	4.065267	2.997149	0.718305
H	3.385535	3.743029	1.118603
C	3.549104	1.850208	0.115066
H	2.477145	1.704188	0.027443
C	-0.932914	-2.971831	0.751132
C	-0.416577	-4.157454	-0.018224
H	-0.066229	-3.852388	-1.010200
H	-1.197926	-4.911581	-0.138584
H	0.437436	-4.611535	0.493282
C	-2.197908	-2.978444	1.335951

H	-2.820147	-3.864833	1.241319
C	-2.670533	-1.864426	2.024546
H	-3.667031	-1.875200	2.455980
C	-1.868533	-0.736028	2.153713
H	-2.234570	0.138566	2.685200
C	-0.585187	-0.695284	1.600855
C	0.267424	0.534888	1.759348
H	0.160297	1.198922	0.891044
H	1.327612	0.277390	1.849982
H	-0.035252	1.090587	2.650765
C	1.038586	-0.049380	-1.453914
C	-0.392031	0.124042	-1.520092
H	-1.001341	-0.712975	-1.179691
C	-1.007617	1.230427	-1.972446
H	-0.421824	2.100759	-2.256287
C	-2.507461	1.379154	-1.926613
H	-3.007648	0.535219	-2.416517
H	-2.823761	2.292779	-2.437220
C	-2.990269	1.455009	-0.461497
H	-2.630458	0.577349	0.085983
C	-2.408560	2.674900	0.222121
O	-1.913081	3.623409	-0.328405
O	-2.501896	2.557242	1.559641
C	-2.007914	3.678141	2.290450
H	-0.948069	3.834290	2.074118
H	-2.154483	3.436255	3.342450
H	-2.563106	4.579064	2.021287
C	-4.511326	1.516536	-0.376292
O	-5.077757	2.579343	-0.223859
C	-5.286008	0.242216	-0.524623
O	1.832487	0.859998	-2.153109
H	1.462432	0.919106	-3.048334
C	-6.681835	0.330953	-0.542060
H	-7.134249	1.313951	-0.459576
C	-7.455646	-0.815768	-0.655922
H	-8.538524	-0.740796	-0.669119
C	-6.840273	-2.064417	-0.749206
H	-7.444963	-2.962567	-0.833456
C	-5.451780	-2.160621	-0.732061
H	-4.968427	-3.130381	-0.802255
C	-4.674397	-1.010915	-0.623543
H	-3.592867	-1.107166	-0.604494

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1855.06666709 Predicted Change= -1.701788D-08
Zero-point correction (ZPE)= -1854.4486 0.61800
Internal Energy (U)= -1854.4116 0.65496
Enthalpy (H)= -1854.4107 0.65591
Gibbs Free Energy (G)= -1854.5199 0.54668

Frequencies -- 12.6911 17.1596 22.5587
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1855.179363

***(S)*-III**

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C34H33N3O5 C1[X(C34H33N3O5)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -1855.06813784 Predicted Change= -3.441642D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.01598	0.00180	[NO]	0.01598	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	2.902695	-0.763630	-0.467806
C	1.613374	-0.498717	-0.007551
N	1.374212	-1.549665	0.858437
C	0.171349	-1.809910	1.571654
N	2.471536	-2.384420	0.991796
C	3.349011	-1.886250	0.194592
C	4.706216	-2.429190	-0.119296
H	4.634778	-3.147695	-0.951510
H	5.115282	-2.941021	0.752652
O	5.581609	-1.376859	-0.458154
C	5.111668	-0.622606	-1.561591
H	4.990553	-1.279909	-2.435087
C	3.796705	0.114263	-1.208065
H	3.289328	0.419577	-2.127073
C	6.117070	0.513336	-1.775871
H	6.081347	0.860611	-2.815781
H	7.132603	0.167369	-1.565469
C	5.625956	1.580090	-0.822703
C	4.298592	1.337647	-0.464108
C	6.307522	2.672107	-0.303180
H	7.342981	2.859783	-0.574141
C	5.647411	3.514502	0.591530
H	6.170123	4.366931	1.014680
C	4.327672	3.260837	0.961521
H	3.832791	3.914979	1.672810
C	3.638025	2.168863	0.432644
H	2.619301	1.955151	0.747068
C	-0.934128	-2.296008	0.864245
C	-0.815719	-2.626728	-0.597960
H	-0.008219	-3.347683	-0.766179
H	-0.584314	-1.729267	-1.183169
H	-1.750674	-3.046375	-0.978079
C	-2.137150	-2.427868	1.555415

H	-3.019049	-2.770914	1.022701
C	-2.219468	-2.107337	2.906887
H	-3.170854	-2.196083	3.421793
C	-1.094296	-1.664102	3.595235
H	-1.162030	-1.417552	4.651320
C	0.123205	-1.500324	2.934629
C	1.346060	-0.964994	3.630428
H	2.163292	-1.692361	3.604450
H	1.124817	-0.721548	4.672129
H	1.709777	-0.057979	3.132910
C	0.797632	0.539455	-0.382110
C	-0.435342	0.932873	0.250860
H	-0.716826	0.426580	1.171396
C	-1.227659	1.929008	-0.190813
H	-0.983040	2.435507	-1.124783
C	-2.498337	2.340165	0.491997
H	-2.576425	3.429584	0.575916
H	-2.546303	1.937781	1.510054
C	-3.741305	1.841247	-0.266309
H	-3.662901	2.080966	-1.333111
C	-5.002227	2.517346	0.248698
O	-5.044013	3.394471	1.071473
O	-6.090957	2.017343	-0.360441
C	-7.330304	2.575342	0.073586
H	-8.103317	2.060647	-0.494862
H	-7.355013	3.649048	-0.126049
H	-7.464234	2.409976	1.144731
C	-3.924990	0.330407	-0.075263
O	-4.274513	-0.084703	1.010563
C	-3.726039	-0.605532	-1.223987
O	1.242109	1.312378	-1.457310
H	1.350198	2.224787	-1.135707
C	-2.883183	-0.317022	-2.299349
H	-2.309015	0.604960	-2.310716
C	-2.736278	-1.238122	-3.333612
H	-2.065380	-1.018860	-4.158274
C	-3.446317	-2.435672	-3.309543
H	-3.338899	-3.146431	-4.123449
C	-4.294817	-2.724796	-2.240200
H	-4.852506	-3.656127	-2.223358
C	-4.424216	-1.817594	-1.196235
H	-5.075304	-2.019752	-0.350877

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1855.06813784 Predicted Change= -3.441642D-08
Zero-point correction (ZPE)= -1854.4506 0.61745
Internal Energy (U)= -1854.4133 0.65476
Enthalpy (H)= -1854.4124 0.65570
Gibbs Free Energy (G)= -1854.5231 0.54500

Frequencies -- 10.6442 19.1011 22.6568
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1855.181545

***(R)*-IV**

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

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M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C34H33N3O5 C1[X(C34H33N3O5)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -1855.08800097 Predicted Change= -3.300837D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00004	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00182	0.00180	[NO]	0.00182	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	1.260017	1.625304	-0.518219
C	1.863943	0.446722	-0.267829
C	1.149116	-0.877089	-0.249920
C	1.391732	-1.647632	0.847495
H	2.106131	-1.271497	1.577359
C	0.697700	-2.953470	1.138811
H	0.644977	-3.565698	0.229636
C	-0.733311	-2.770683	1.682971
H	-0.744854	-1.995334	2.456693
H	-1.092362	-3.695053	2.144584
C	-1.678271	-2.366538	0.545719
H	-1.102413	-1.802625	-0.201653
C	-2.161821	-3.604013	-0.191920
O	-1.760391	-4.726404	-0.013497
O	-3.098346	-3.300978	-1.109484
C	-3.580867	-4.409100	-1.865572
H	-2.762327	-4.878463	-2.415808
H	-4.321451	-3.999823	-2.551089
H	-4.034032	-5.151574	-1.204950
C	-2.865003	-1.517512	0.993678
O	-3.313979	-1.629800	2.116641
C	-3.448253	-0.515871	0.034554
H	1.289759	-3.521555	1.863964
O	0.389144	-1.020352	-1.273068
N	3.165079	0.733395	-0.210924
C	4.245900	-0.205465	-0.086993
N	3.416900	2.065585	-0.410104
C	2.235924	2.578750	-0.594462
C	1.864936	3.991782	-0.930005
H	2.063892	4.172307	-1.997768
H	2.462306	4.689876	-0.341118
O	0.512593	4.214273	-0.622162
C	-0.370601	3.304340	-1.268906

H	-0.214188	3.347091	-2.355966
C	-0.172678	1.879244	-0.700567
H	-0.529184	1.100607	-1.385120
C	-1.786401	3.679332	-0.824839
H	-2.517709	3.333005	-1.564951
H	-1.877810	4.764213	-0.723013
C	-1.945178	2.921396	0.472231
C	-0.996993	1.902501	0.568594
C	-2.874750	3.108708	1.485503
H	-3.617974	3.898192	1.413686
C	-2.841650	2.263935	2.594916
H	-3.567472	2.394173	3.391843
C	-1.890936	1.248689	2.687021
H	-1.892315	0.582549	3.544000
C	-0.954566	1.057734	1.669951
H	-0.219948	0.258178	1.733789
C	4.500437	-1.050927	-1.170251
C	3.686239	-0.972652	-2.435814
H	3.689561	0.049113	-2.833120
H	2.640152	-1.260136	-2.276372
H	4.109775	-1.631523	-3.196759
C	5.551724	-1.955797	-1.027131
H	5.778687	-2.631886	-1.846094
C	6.305692	-1.996021	0.141462
H	7.118954	-2.709266	0.232848
C	6.026383	-1.129474	1.192898
H	6.618479	-1.164461	2.102678
C	4.981013	-0.211536	1.098707
C	4.646369	0.734028	2.221427
H	3.585556	0.671031	2.489334
H	4.848239	1.771076	1.935309
H	5.236260	0.498320	3.109520
C	-4.562067	0.212709	0.457877
H	-4.952994	0.019598	1.452082
C	-5.144878	1.160891	-0.376047
H	-6.013288	1.719785	-0.039742
C	-4.613215	1.391626	-1.642826
H	-5.070548	2.126262	-2.300421
C	-3.494045	0.675607	-2.067435
H	-3.078662	0.849598	-3.056726
C	-2.910468	-0.275887	-1.235978
H	-2.036263	-0.819949	-1.583278

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1855.08800097 Predicted Change= -3.300837D-08
Zero-point correction (ZPE)= -1854.4682 0.61970
Internal Energy (U)= -1854.4320 0.65590
Enthalpy (H)= -1854.4311 0.65684
Gibbs Free Energy (G)= -1854.5364 0.55154

Frequencies -- 22.3405 28.7232 35.1065
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1855.200359

***(S)*-IV**

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

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M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C34H33N3O5 C1[X(C34H33N3O5)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -1855.08905003 Predicted Change= -2.839271D-09

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00264	0.00180	[NO]	0.00264	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-1.250019	1.643255	0.255592
C	-1.790649	0.410615	0.173382
C	-1.023328	-0.854843	0.436681
C	-1.330958	-1.949728	-0.316042
H	-2.106088	-1.894151	-1.075213
C	-0.633187	-3.246309	-0.016070
H	-0.471244	-3.311339	1.065938
C	0.733001	-3.414129	-0.704849
H	0.595879	-3.463746	-1.791699
H	1.199040	-4.348945	-0.374196
C	1.693849	-2.251977	-0.409622
H	1.199858	-1.311619	-0.662742
C	2.888808	-2.359056	-1.332336
O	2.919108	-1.951483	-2.470425
O	3.918029	-3.002002	-0.758542
C	5.069840	-3.156620	-1.583604
H	5.802448	-3.683763	-0.974641
H	5.451724	-2.179047	-1.887611
H	4.822094	-3.733415	-2.477387
C	2.107288	-2.191814	1.059278
O	1.938448	-3.131573	1.803605
C	2.758984	-0.928369	1.548637
H	-1.265221	-4.092817	-0.307281
O	-0.164375	-0.715797	1.371012
N	-3.100855	0.624583	0.023661
C	-4.143984	-0.363345	-0.005342
N	-3.415042	1.957612	0.001867
C	-2.265246	2.549202	0.146030
C	-1.971800	4.012362	0.292837
H	-2.223399	4.322971	1.318940
H	-2.577613	4.593312	-0.404618
O	-0.620255	4.265548	0.005455
C	0.281215	3.489496	0.789375

H	0.095741	3.669899	1.857012
C	0.161819	1.998126	0.411704
H	0.562771	1.326349	1.181392
C	1.693647	3.857360	0.328586
H	2.413033	3.620482	1.122905
H	1.759181	4.925025	0.102329
C	1.900290	2.957725	-0.868575
C	0.981233	1.907949	-0.855374
C	2.847170	3.041717	-1.879679
H	3.566862	3.856034	-1.899490
C	2.856145	2.063726	-2.876146
H	3.595816	2.113038	-3.669428
C	1.921338	1.028835	-2.870278
H	1.951573	0.263046	-3.637301
C	0.964958	0.946461	-1.855872
H	0.240830	0.133953	-1.846859
C	-4.446764	-1.030596	1.184197
C	-3.706739	-0.729912	2.461015
H	-3.715336	0.345206	2.672789
H	-2.658671	-1.047806	2.408972
H	-4.178134	-1.243929	3.301265
C	-5.463649	-1.983144	1.128640
H	-5.726649	-2.525571	2.031883
C	-6.136948	-2.240728	-0.061385
H	-6.925570	-2.986657	-0.083353
C	-5.807941	-1.550839	-1.223639
H	-6.334455	-1.758120	-2.150652
C	-4.794952	-0.592896	-1.217813
C	-4.396678	0.157886	-2.460778
H	-4.940845	-0.219750	-3.328876
H	-3.323520	0.050130	-2.656650
H	-4.604167	1.227726	-2.358925
C	3.281138	0.039852	0.688377
H	3.215624	-0.071461	-0.391999
C	3.896642	1.177819	1.209431
H	4.313284	1.916178	0.529629
C	3.972114	1.364223	2.587115
H	4.449083	2.253213	2.990996
C	3.441557	0.402187	3.448315
H	3.497215	0.545744	4.523361
C	2.848371	-0.740974	2.930215
H	2.433133	-1.507425	3.576351

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1855.08905003 Predicted Change= -2.839271D-09
Zero-point correction (ZPE)= -1854.4701 0.61885
Internal Energy (U)= -1854.4337 0.65532
Enthalpy (H)= -1854.4327 0.65626
Gibbs Free Energy (G)= -1854.5405 0.54847

Frequencies -- 9.0908 22.3435 24.5945
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1855.202534

TS-V-*(S,R,R)*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

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M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,calcfc,ts,noeigentest,gdiis) iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C34H33N3O5 C1[X(C34H33N3O5)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -1855.05887507 Predicted Change= -3.140712D-08

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Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00004	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.01051	0.00180	[NO]	0.01051	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-1.084284	-0.613722	-0.734291
C	-0.026007	-1.068438	-0.027975
C	0.476218	-0.716844	1.371815
C	0.156618	0.585795	1.866408
H	-0.881953	0.889986	1.778281
C	0.888670	0.950989	3.140884
H	0.378186	1.785059	3.637993
C	2.298279	1.376838	2.717472
H	2.862422	0.508045	2.364452
H	2.865911	1.836546	3.532532
C	2.101452	2.334896	1.552864
H	1.660400	3.277508	1.899354
C	3.383689	2.651000	0.821704
O	4.443213	2.097006	0.972677
O	3.189048	3.638809	-0.073771
C	4.301159	3.894270	-0.923170
H	3.992812	4.702896	-1.585123
H	4.547026	2.998314	-1.498871
H	5.175522	4.188660	-0.337803
C	1.170979	1.678669	0.480417
O	1.729235	0.934972	-0.379382
C	0.065980	2.591012	-0.049146
H	0.928349	0.113247	3.846252
O	1.283403	-1.511058	1.836416
N	0.634282	-1.877280	-0.855277
C	1.758235	-2.755322	-0.604385
N	0.048454	-1.940668	-2.079495
C	-0.988419	-1.163566	-1.982853
C	-2.011345	-0.860630	-3.032043
H	-2.141426	-1.727112	-3.681981
H	-1.675249	-0.004888	-3.637688
O	-3.242321	-0.584106	-2.411154
C	-3.141515	0.526983	-1.535641

H	-2.760754	1.398571	-2.080403
C	-2.243787	0.191299	-0.316650
H	-1.871703	1.130413	0.098588
C	-4.520349	0.743621	-0.908843
H	-5.308008	0.520331	-1.633159
H	-4.620472	1.791533	-0.599475
C	-4.504319	-0.177861	0.288587
C	-3.192963	-0.517571	0.626390
C	-5.568140	-0.674567	1.028588
H	-6.591209	-0.419536	0.767054
C	-5.302803	-1.521005	2.105167
H	-6.125592	-1.924937	2.686958
C	-3.992011	-1.860196	2.436738
H	-3.800342	-2.522553	3.274781
C	-2.920704	-1.355393	1.699620
H	-1.901562	-1.618521	1.970124
C	3.010520	-2.418121	-1.114953
C	3.279481	-1.115440	-1.814149
H	3.379889	-0.307355	-1.083430
H	2.453974	-0.832856	-2.472606
H	4.193759	-1.193265	-2.407444
C	4.035283	-3.348196	-0.913429
H	5.026813	-3.117654	-1.292115
C	3.804779	-4.543012	-0.246312
H	4.617197	-5.249199	-0.104760
C	2.534285	-4.844988	0.235635
H	2.352626	-5.782286	0.753321
C	1.481494	-3.952519	0.062355
C	0.108661	-4.247477	0.602501
H	0.032132	-5.294549	0.903551
H	-0.674479	-4.049866	-0.138043
H	-0.085266	-3.624028	1.482396
C	-0.113222	2.638285	-1.432570
H	0.564097	2.046060	-2.041234
C	-1.117252	3.427854	-1.992121
H	-1.236607	3.469274	-3.072341
C	-1.970334	4.162976	-1.171799
H	-2.757707	4.772979	-1.605071
C	-1.790905	4.129020	0.212594
H	-2.441657	4.711243	0.858748
C	-0.772306	3.359672	0.765643
H	-0.643315	3.332460	1.846251

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1855.05887507	Predicted Change= -3.140712D-08	
Zero-point correction (ZPE)=	-1854.4403	0.61848
Internal Energy (U)=	-1854.4050	0.65385
Enthalpy (H)=	-1854.4040	0.65479
Gibbs Free Energy (G)=	-1854.5093	0.54949

Frequencies -- -270.7563 7.2320 15.8405
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1855.170435

TS-V-*(R,S,S)*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

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M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C34H33N3O5 C1[X(C34H33N3O5)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -1855.06294493 Predicted Change= -5.451023D-10

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00037	0.00180	[YES]	0.00037	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-1.176830	-0.770375	0.663074
C	-0.198478	-1.065344	-0.203757
C	0.054475	-0.321002	-1.508161
C	1.360086	0.284957	-1.619819
H	2.162251	-0.335821	-1.219959
C	1.627677	0.962048	-2.959254
H	2.700479	0.912886	-3.179226
C	1.194730	2.423424	-2.795361
H	0.103391	2.493335	-2.791442
H	1.583579	3.072449	-3.585702
C	1.706171	2.791490	-1.410933
H	2.801828	2.783647	-1.389826
C	1.265609	4.115270	-0.840180
O	1.761686	4.633126	0.131532
O	0.238412	4.659577	-1.514577
C	-0.283285	5.847448	-0.932467
H	-0.664113	5.639033	0.070354
H	-1.089706	6.173712	-1.588655
H	0.490958	6.615343	-0.861043
C	1.116210	1.696289	-0.451718
O	-0.126277	1.892926	-0.163520
C	2.022074	1.383719	0.747844
H	1.093402	0.469129	-3.777864
O	-0.921567	-0.128085	-2.209949
N	0.517207	-2.032770	0.367062
C	1.575044	-2.796476	-0.235999
N	0.055667	-2.336243	1.612260
C	-0.958299	-1.533400	1.774622
C	-1.740436	-1.271002	3.025866
H	-1.115782	-0.644664	3.682703
H	-1.963018	-2.206574	3.542127
O	-2.954141	-0.641910	2.723405
C	-2.816620	0.539590	1.934745

H	-2.177038	1.269270	2.448610
C	-2.290591	0.186120	0.527874
H	-1.862701	1.060472	0.021228
C	-4.244880	1.013643	1.662565
H	-4.241869	2.072904	1.379902
H	-4.867053	0.892740	2.553146
C	-4.655112	0.135532	0.500720
C	-3.526369	-0.371328	-0.147356
C	-5.927227	-0.192703	0.055231
H	-6.808031	0.196055	0.558709
C	-6.056163	-1.045952	-1.041092
H	-7.044898	-1.321516	-1.395079
C	-4.926984	-1.551013	-1.682883
H	-5.043100	-2.212132	-2.536152
C	-3.646360	-1.210326	-1.245413
H	-2.764683	-1.570537	-1.765695
C	1.302544	-3.482460	-1.426497
C	-0.063530	-3.507149	-2.066793
H	-0.235288	-2.636062	-2.707840
H	-0.862369	-3.531732	-1.318128
H	-0.161039	-4.399891	-2.688584
C	2.358457	-4.188133	-2.004327
H	2.182255	-4.728628	-2.929654
C	3.612937	-4.215477	-1.407711
H	4.421294	-4.767903	-1.876529
C	3.833466	-3.550872	-0.206400
H	4.810990	-3.585091	0.265620
C	2.814146	-2.828567	0.413036
C	3.037899	-2.130561	1.725080
H	4.101356	-1.935407	1.876021
H	2.675380	-2.749175	2.552690
H	2.507457	-1.176517	1.771087
C	1.431154	1.346372	2.011168
H	0.361133	1.528838	2.059204
C	2.200816	1.151195	3.157489
H	1.726474	1.141159	4.135691
C	3.580995	1.002593	3.054739
H	4.186600	0.870400	3.946596
C	4.181313	1.030430	1.795876
H	5.258051	0.915235	1.705015
C	3.406456	1.205852	0.654564
H	3.889050	1.220434	-0.321011

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

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SCF Energy= -1855.06294493	Predicted Change= -5.451023D-10	
Zero-point correction (ZPE)=	-1854.4443	0.61856
Internal Energy (U)=	-1854.4093	0.65358
Enthalpy (H)=	-1854.4084	0.65453
Gibbs Free Energy (G)=	-1854.5111	0.55183

Frequencies -- -214.2364 21.6359 21.9340
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1855.177494

TS-V-*(R,R,R)*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest,nofreeze,gdiis) iop(1/8=18)
freq=noraman geom=allcheck guess=read
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C34H33N3O5 C1[X(C34H33N3O5)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -1855.06596657 Predicted Change= -5.484592D-10

Optimization completed. {Found 3 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00078	0.00180	[YES]	0.00078	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	2.213732	1.338826	-0.183190
C	0.915325	1.314927	-0.562908
C	0.392381	0.410106	-1.677865
C	-1.006010	0.211428	-1.810673
H	-1.655376	1.026725	-1.523237
C	-1.431817	-0.699458	-2.948312
H	-2.282271	-0.278193	-3.494943
C	-1.777640	-2.100749	-2.384261
H	-1.527290	-2.890987	-3.098298
H	-2.844607	-2.190314	-2.161407
C	-0.973832	-2.232175	-1.100668
H	0.098482	-2.253285	-1.323093
C	-1.247852	-3.434312	-0.236752
O	-0.430009	-3.978758	0.466692
O	-2.541117	-3.808406	-0.275339
C	-2.892711	-4.839876	0.640433
H	-2.697478	-4.517130	1.666302
H	-2.316104	-5.745775	0.439135
H	-3.956842	-5.019407	0.492394
C	-1.192650	-0.967394	-0.205643
O	-0.329070	-0.745348	0.694093
C	-2.649012	-0.733001	0.229483
H	-0.600922	-0.790717	-3.654463
O	1.284201	-0.209533	-2.263566
N	0.316303	2.245301	0.185095
C	-1.068788	2.649177	0.212425
N	1.183828	2.862357	1.029459
C	2.327317	2.289999	0.788811
C	3.657856	2.652923	1.378532
H	3.558780	2.787536	2.457185
H	3.989109	3.605838	0.936294
O	4.596133	1.637012	1.154534
C	4.684319	1.252860	-0.209914

H	4.930008	2.128529	-0.828427
C	3.378019	0.558710	-0.653554
H	3.305190	0.518281	-1.740907
C	5.716052	0.123477	-0.282429
H	6.542110	0.321274	0.406103
H	6.124623	0.053488	-1.298105
C	4.894431	-1.094974	0.078209
C	3.532011	-0.832901	-0.076024
C	5.318234	-2.337450	0.528080
H	6.376247	-2.548929	0.657790
C	4.356987	-3.303542	0.830824
H	4.674403	-4.278759	1.188247
C	2.997530	-3.022208	0.701465
H	2.248359	-3.766333	0.954460
C	2.566749	-1.775340	0.244578
H	1.504591	-1.544098	0.207021
C	-1.561207	3.383987	-0.870500
C	-0.679692	3.773568	-2.028581
H	-1.163460	4.547909	-2.627834
H	-0.482013	2.916479	-2.683515
H	0.284014	4.162977	-1.684456
C	-2.915428	3.712672	-0.849720
H	-3.336151	4.268863	-1.682514
C	-3.721048	3.333643	0.220397
H	-4.778780	3.578766	0.212345
C	-3.179137	2.656463	1.305379
H	-3.809459	2.368304	2.141171
C	-1.827230	2.309894	1.337455
C	-1.217720	1.624371	2.527965
H	-2.002904	1.327233	3.226863
H	-0.527164	2.300047	3.043586
H	-0.675014	0.729297	2.205791
C	-2.909320	-1.023063	1.575175
H	-2.081461	-1.367302	2.188246
C	-4.180428	-0.858528	2.115350
H	-4.356744	-1.091908	3.161998
C	-5.224004	-0.392342	1.317504
H	-6.217318	-0.257367	1.735801
C	-4.980279	-0.104512	-0.021538
H	-5.783023	0.263095	-0.654688
C	-3.706510	-0.276650	-0.561025
H	-3.549041	-0.027624	-1.605894

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1855.06596657 Predicted Change= -5.484592D-10
Zero-point correction (ZPE)= -1854.4459 0.61997
Internal Energy (U)= -1854.4112 0.65471
Enthalpy (H)= -1854.4103 0.65565
Gibbs Free Energy (G)= -1854.5111 0.55481

Frequencies -- -272.1313 26.4501 35.2386
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1855.173254

TS-V-*(S,S,S)*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

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M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,calcfc,ts,noeigentest,gdiis) iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

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Pointgroup= C1 Stoichiometry= C34H33N3O5 C1[X(C34H33N3O5)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -1855.06679073 Predicted Change= -7.514585D-10

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Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00085	0.00180	[YES]	0.00085	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	1.661874	-0.777219	-0.649049
C	0.635808	-1.209106	0.102553
C	0.262495	-0.592191	1.439432
C	-1.120451	-0.305180	1.625493
H	-1.811058	-1.023092	1.198093
C	-1.480540	0.352349	2.945348
H	-2.349214	-0.130020	3.405568
C	-1.745774	1.853661	2.699009
H	-1.452183	2.464713	3.557326
H	-2.806401	2.051055	2.516326
C	-0.961686	2.226123	1.452265
H	0.119908	2.197494	1.632141
C	-1.334080	3.586735	0.921617
O	-2.338850	4.196726	1.200635
O	-0.421665	4.049447	0.045275
C	-0.768165	5.289847	-0.561430
H	-1.710304	5.196035	-1.107766
H	0.048468	5.528605	-1.242097
H	-0.880194	6.070914	0.194528
C	-1.222626	1.163061	0.330545
O	-0.372945	1.087342	-0.617883
C	-2.690041	1.136273	-0.135342
H	-0.638551	0.238004	3.635539
O	1.215566	-0.191035	2.106777
N	0.012085	-2.125880	-0.629780
C	-1.176671	-2.858211	-0.288936
N	0.577465	-2.269502	-1.858257
C	1.562471	-1.416048	-1.849742
C	2.420114	-1.013003	-3.010995
H	1.776607	-0.498848	-3.740899
H	2.857620	-1.892113	-3.488737
O	3.470357	-0.189430	-2.585351
C	3.044255	0.902628	-1.774938

H	2.274727	1.489970	-2.292292
C	2.543441	0.375842	-0.412644
H	1.914366	1.125587	0.076669
C	4.316130	1.669062	-1.409419
H	4.065748	2.693691	-1.109797
H	4.995757	1.714498	-2.264314
C	4.850018	0.867857	-0.242846
C	3.834689	0.096389	0.326880
C	6.138539	0.824135	0.270535
H	6.931638	1.420027	-0.172624
C	6.401104	-0.013832	1.354013
H	7.406109	-0.068130	1.761481
C	5.385677	-0.786802	1.915160
H	5.606497	-1.433026	2.759078
C	4.086440	-0.733602	1.410073
H	3.284851	-1.305976	1.863553
C	-1.107741	-3.803323	0.737220
C	0.180335	-4.096789	1.462727
H	0.104357	-5.045768	1.997923
H	0.407252	-3.317406	2.200170
H	1.027795	-4.161071	0.773332
C	-2.295981	-4.444096	1.085281
H	-2.282040	-5.185651	1.878818
C	-3.487499	-4.134043	0.436989
H	-4.405021	-4.634582	0.730818
C	-3.513102	-3.185704	-0.579802
H	-4.447754	-2.934533	-1.072722
C	-2.348799	-2.525859	-0.975613
C	-2.363648	-1.489743	-2.066800
H	-2.075464	-1.941813	-3.022544
H	-1.669209	-0.669056	-1.855848
H	-3.365964	-1.063572	-2.165549
C	-2.926717	1.797662	-1.347562
H	-2.077137	2.253662	-1.847650
C	-4.196724	1.836623	-1.910139
H	-4.355815	2.354914	-2.851592
C	-5.262254	1.199158	-1.275642
H	-6.254642	1.217272	-1.716551
C	-5.042568	0.544454	-0.068011
H	-5.864374	0.046943	0.439316
C	-3.770000	0.522475	0.502540
H	-3.634733	0.004269	1.447362

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

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SCF Energy= -1855.06679073	Predicted Change= -7.514585D-10	
Zero-point correction (ZPE)=	-1854.4470	0.61972
Internal Energy (U)=	-1854.4121	0.65462
Enthalpy (H)=	-1854.4112	0.65556
Gibbs Free Energy (G)=	-1854.5132	0.55349

Frequencies -- -267.0310 23.5290 28.7963
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1855.175582

VIb-*(R,R,R)*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

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M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

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Pointgroup= C1 Stoichiometry= C34H33N3O5 C1[X(C34H33N3O5)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -1855.11021853 Predicted Change= -3.634295D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00004	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00408	0.00180	[NO]	0.00408	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	1.352104	1.376452	0.387100
C	0.004093	1.160243	-0.072469
C	-0.107280	0.837683	-1.579417
C	-0.585578	-0.584905	-1.768001
H	0.241752	-1.148949	-2.213320
C	-1.876468	-0.648496	-2.599579
H	-1.863229	0.096379	-3.400811
C	-2.979702	-0.419225	-1.559757
H	-3.956440	-0.763722	-1.906834
H	-3.062006	0.643688	-1.309379
C	-2.503802	-1.194358	-0.324087
H	-2.864213	-0.777090	0.620337
C	-2.915417	-2.648688	-0.399312
O	-3.133617	-3.260084	-1.419275
O	-2.968278	-3.202699	0.818471
C	-3.156736	-4.617317	0.829898
H	-4.094464	-4.882394	0.337016
H	-3.175782	-4.905195	1.879754
H	-2.325841	-5.103990	0.312179
C	-0.935321	-1.057044	-0.335324
O	-0.588413	0.016875	0.549094
C	-0.214253	-2.317020	0.117627
H	-1.987089	-1.641406	-3.043597
O	0.166729	1.616521	-2.452591
N	-0.590087	2.411890	0.328512
C	-2.013407	2.552990	0.358373
N	0.140993	2.957512	1.402760
C	1.260165	2.340588	1.383723
C	2.382154	2.513540	2.370000
H	1.998191	2.286484	3.376455
H	2.746347	3.542975	2.365266
O	3.480371	1.686201	2.059944
C	3.110271	0.348050	1.780491

H	2.523454	-0.067574	2.614085
C	2.333688	0.308747	0.447505
H	1.803123	-0.651850	0.383118
C	4.400055	-0.420371	1.480124
H	4.242333	-1.493419	1.647716
H	5.211827	-0.085268	2.131428
C	4.630204	-0.118409	0.014932
C	3.453606	0.347275	-0.574608
C	5.795176	-0.225468	-0.731498
H	6.716602	-0.577868	-0.275674
C	5.769422	0.150011	-2.075385
H	6.675045	0.081484	-2.670628
C	4.597751	0.634907	-2.654096
H	4.599101	0.943936	-3.694932
C	3.424626	0.740215	-1.904815
H	2.521095	1.148817	-2.347824
C	-2.635352	3.157474	-0.746172
C	-1.857473	3.739208	-1.898680
H	-1.871009	3.070330	-2.766178
H	-0.813359	3.901817	-1.632691
H	-2.309091	4.687216	-2.205846
C	-4.032732	3.230306	-0.768463
H	-4.519563	3.691287	-1.624115
C	-4.790298	2.737295	0.282200
H	-5.874223	2.795702	0.249331
C	-4.154874	2.195997	1.396547
H	-4.744753	1.843983	2.238835
C	-2.765555	2.105149	1.464464
C	-2.120055	1.589335	2.725648
H	-1.361088	0.835046	2.510890
H	-2.876763	1.149533	3.381089
H	-1.628768	2.407443	3.260348
C	0.208788	-2.453430	1.441967
H	0.048733	-1.633110	2.134679
C	0.830548	-3.623969	1.866485
H	1.158160	-3.714836	2.897920
C	1.028794	-4.677063	0.976257
H	1.515923	-5.588958	1.307694
C	0.598155	-4.552849	-0.341639
H	0.746598	-5.366366	-1.045118
C	-0.020856	-3.379969	-0.767968
H	-0.370020	-3.302209	-1.794776

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1855.11021853 Predicted Change= -3.634295D-08
Zero-point correction (ZPE)= -1854.4885 0.62164
Internal Energy (U)= -1854.4540 0.65615
Enthalpy (H)= -1854.4531 0.65709
Gibbs Free Energy (G)= -1854.5547 0.55544

Frequencies -- 15.4073 19.1539 29.8746
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1855.210665

VIb-*(R,S,S)*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C34H33N3O5 C1[X(C34H33N3O5)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -1855.11290152 Predicted Change= -3.668496D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00560	0.00180	[NO]	0.00560	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-1.276898	-1.280914	-0.029714
C	-0.025600	-0.679184	-0.403615
C	0.039943	0.186374	-1.687739
C	1.141373	1.201391	-1.469493
H	2.055792	0.722389	-1.835884
C	0.933123	2.602323	-2.065143
H	1.703438	2.852309	-2.799007
C	0.982184	3.552445	-0.849602
H	0.381805	4.455761	-0.989852
H	2.012323	3.866491	-0.651059
C	0.501030	2.701166	0.343333
H	0.791664	3.114023	1.311080
C	-0.999807	2.581290	0.275156
O	-1.600407	2.149562	-0.684083
O	-1.611093	3.035831	1.373853
C	-3.042465	3.058821	1.303580
H	-3.438831	2.063284	1.091243
H	-3.365646	3.735731	0.509456
H	-3.377849	3.416514	2.275564
C	1.187173	1.328838	0.067768
O	0.438067	0.231600	0.615476
C	2.578571	1.346003	0.680569
H	-0.036791	2.641004	-2.566142
O	-0.612338	0.008282	-2.678818
N	0.781172	-1.880766	-0.588835
C	2.209307	-1.818027	-0.592669
N	0.196253	-2.970769	0.070416
C	-0.987211	-2.588679	0.354652
C	-1.993719	-3.421841	1.097860
H	-1.535345	-3.756967	2.040671
H	-2.262924	-4.305458	0.514663
O	-3.184685	-2.714538	1.344274
C	-2.953917	-1.392090	1.791164

H	-2.304583	-1.397037	2.679821
C	-2.355977	-0.559642	0.633620
H	-1.931679	0.357694	1.059751
C	-4.329822	-0.763870	2.023465
H	-4.244955	0.085702	2.714338
H	-5.018227	-1.491993	2.460700
C	-4.719463	-0.316603	0.631533
C	-3.590646	-0.240522	-0.187360
C	-5.978447	-0.018075	0.127614
H	-6.860005	-0.083302	0.759947
C	-6.093518	0.342196	-1.215066
H	-7.071740	0.567366	-1.629843
C	-4.965332	0.397000	-2.033602
H	-5.073969	0.664993	-3.080189
C	-3.698680	0.107425	-1.525992
H	-2.817301	0.141140	-2.157797
C	2.860514	-1.710977	-1.831737
C	2.105053	-1.759719	-3.137665
H	1.136986	-2.247567	-3.013178
H	2.689424	-2.305743	-3.883630
H	1.913454	-0.760079	-3.546612
C	4.252532	-1.577289	-1.842613
H	4.764438	-1.484078	-2.797279
C	4.977967	-1.591344	-0.659592
H	6.058592	-1.482303	-0.681102
C	4.321369	-1.762323	0.554852
H	4.889106	-1.781654	1.481450
C	2.934644	-1.883524	0.612392
C	2.254506	-2.100694	1.938877
H	1.943802	-3.144617	2.043286
H	1.360004	-1.479629	2.028596
H	2.937380	-1.850944	2.755778
C	2.702318	1.127121	2.056899
H	1.810272	0.911749	2.639072
C	3.948570	1.152680	2.668693
H	4.029483	0.967913	3.735962
C	5.092875	1.416564	1.915232
H	6.067986	1.438383	2.392444
C	4.976093	1.654898	0.551803
H	5.859855	1.860841	-0.044598
C	3.724654	1.619565	-0.062785
H	3.658813	1.799142	-1.132658

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1855.11290152 Predicted Change= -3.668496D-08
Zero-point correction (ZPE)= -1854.4911 0.62178
Internal Energy (U)= -1854.4568 0.65600
Enthalpy (H)= -1854.4559 0.65695
Gibbs Free Energy (G)= -1854.5542 0.55867

Frequencies -- 25.6683 37.9163 47.0323
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1855.212559

VIb-*(S,R,R)*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

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M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C34H33N3O5 C1[X(C34H33N3O5)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -1855.10369860 Predicted Change= -6.528203D-08

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Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00003	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00576	0.00180	[NO]	0.00576	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	0.881110	0.671946	0.817809
C	-0.409914	0.526560	0.206423
C	-0.408273	0.704990	-1.325754
C	-0.315916	-0.658588	-1.978136
H	0.702799	-0.773842	-2.367250
C	-1.401999	-0.823033	-3.055140
H	-1.567337	0.117935	-3.586237
C	-2.608059	-1.306223	-2.248450
H	-3.404159	-1.746080	-2.851859
H	-3.042361	-0.477581	-1.673336
C	-1.973377	-2.311309	-1.287519
H	-1.696979	-3.217881	-1.844638
C	-2.900364	-2.745638	-0.175367
O	-4.097958	-2.601118	-0.196703
O	-2.245839	-3.354235	0.820686
C	-3.064563	-3.780325	1.909315
H	-3.810957	-4.499654	1.565463
H	-3.573681	-2.922927	2.355695
H	-2.385495	-4.240691	2.625377
C	-0.656598	-1.639115	-0.813418
O	-0.954209	-0.815803	0.315590
C	0.433950	-2.642828	-0.474673
H	-1.098599	-1.583484	-3.783669
O	-0.501378	1.757422	-1.899717
N	-1.176695	1.427634	1.004997
C	-2.264131	2.227147	0.542650
N	-0.476013	1.839102	2.146842
C	0.698109	1.349357	2.010179
C	1.769494	1.281987	3.057049
H	1.507785	0.485643	3.772431
H	1.836857	2.226814	3.598786
O	3.033530	1.022765	2.488582
C	3.046878	-0.118998	1.648341

H	2.715619	-1.009199	2.203204
C	2.164530	0.142493	0.405668
H	2.006055	-0.815751	-0.103754
C	4.458778	-0.221656	1.071710
H	4.644331	-1.246058	0.723378
H	5.208672	0.029311	1.826696
C	4.406644	0.756456	-0.081354
C	3.080605	1.017682	-0.440359
C	5.453594	1.385877	-0.738220
H	6.483594	1.190673	-0.451788
C	5.161471	2.293262	-1.757652
H	5.969706	2.801477	-2.274764
C	3.839914	2.566699	-2.101257
H	3.624724	3.288987	-2.882729
C	2.784524	1.929351	-1.444077
H	1.759978	2.167726	-1.710336
C	-3.559165	1.694427	0.543762
C	-3.882467	0.334253	1.107165
H	-2.981881	-0.205241	1.401810
H	-4.429829	-0.277769	0.384393
H	-4.524697	0.447755	1.988076
C	-4.600063	2.490533	0.051068
H	-5.608229	2.083658	0.036816
C	-4.364070	3.783037	-0.390078
H	-5.184073	4.388161	-0.765795
C	-3.075743	4.311132	-0.338843
H	-2.890622	5.328745	-0.672452
C	-2.009646	3.547220	0.125194
C	-0.623724	4.129861	0.201713
H	-0.558205	5.039804	-0.400206
H	0.122987	3.418703	-0.162152
H	-0.366197	4.376672	1.236544
C	1.109675	-3.318924	-1.492273
H	0.844418	-3.137568	-2.532766
C	2.131428	-4.216208	-1.192264
H	2.653309	-4.727162	-1.995491
C	2.486371	-4.449353	0.133571
H	3.286463	-5.144122	0.369671
C	1.804527	-3.789791	1.154574
H	2.069442	-3.974625	2.191850
C	0.781802	-2.894751	0.853841
H	0.249239	-2.368978	1.639668

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1855.10369860 Predicted Change= -6.528203D-08
Zero-point correction (ZPE)= -1854.4827 0.62092
Internal Energy (U)= -1854.4479 0.65575
Enthalpy (H)= -1854.4469 0.65670
Gibbs Free Energy (G)= -1854.5492 0.55441

Frequencies -- 14.3875 22.4667 31.2596
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1855.205426

VIb-*(S,S,S)*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

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Pointgroup= C1 Stoichiometry= C34H33N3O5 C1[X(C34H33N3O5)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -1855.11167315 Predicted Change= -6.695777D-09

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Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00098	0.00180	[YES]	0.00098	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	1.852745	1.102062	0.207702
C	0.525717	0.903264	-0.308416
C	0.414369	0.294427	-1.715597
C	-0.756842	-0.663070	-1.748665
H	-1.590321	-0.154966	-2.245084
C	-0.336365	-1.984704	-2.396750
H	-1.210043	-2.573855	-2.683553
C	0.411502	-2.679712	-1.253157
H	1.403267	-2.224281	-1.123533
H	0.552451	-3.749840	-1.421083
C	-0.456502	-2.392824	-0.019159
H	0.089834	-2.392847	0.927872
C	-1.590640	-3.389667	0.089374
O	-2.131016	-3.935268	-0.843377
O	-1.964410	-3.562119	1.363674
C	-3.189186	-4.275609	1.536976
H	-3.360517	-4.313553	2.611551
H	-3.108660	-5.281256	1.119679
H	-3.999901	-3.738469	1.036763
C	-1.027763	-0.939479	-0.250463
O	-0.203516	-0.023002	0.499981
C	-2.464857	-0.794737	0.219921
H	0.285995	-1.802866	-3.277130
O	1.166714	0.532583	-2.622276
N	0.036666	2.269773	-0.289029
C	-1.372812	2.494669	-0.376329
N	0.779914	3.027608	0.630563
C	1.818916	2.326529	0.874611
C	2.910052	2.694977	1.840516
H	2.452548	2.894882	2.821261
H	3.427399	3.599064	1.511675
O	3.881848	1.679954	1.940761
C	3.319683	0.386493	2.063763

H	2.609270	0.358878	2.903800
C	2.653182	0.000337	0.724166
H	1.976336	-0.847315	0.902969
C	4.486728	-0.594635	2.197388
H	4.151216	-1.516799	2.688501
H	5.288919	-0.159058	2.799292
C	4.874980	-0.842288	0.756424
C	3.843291	-0.454107	-0.101475
C	6.061161	-1.351315	0.247078
H	6.869144	-1.645202	0.911712
C	6.207870	-1.458528	-1.136444
H	7.133055	-1.847833	-1.550618
C	5.184933	-1.049929	-1.989962
H	5.321630	-1.118040	-3.064932
C	3.989661	-0.539970	-1.479026
H	3.207486	-0.188535	-2.144179
C	-2.175018	2.514171	0.780004
C	-1.588159	2.395064	2.162845
H	-2.379492	2.179169	2.886648
H	-1.087452	3.323072	2.453556
H	-0.845451	1.594170	2.208658
C	-3.552534	2.654004	0.624940
H	-4.182460	2.648565	1.510394
C	-4.127778	2.763427	-0.636962
H	-5.205807	2.849591	-0.736972
C	-3.319118	2.778444	-1.764187
H	-3.759490	2.903022	-2.750395
C	-1.929909	2.666556	-1.654044
C	-1.080596	2.774862	-2.897887
H	-1.489602	3.547520	-3.555292
H	-1.062408	1.841902	-3.473714
H	-0.048239	3.027370	-2.651601
C	-3.546085	-0.923456	-0.649377
H	-3.381930	-1.102503	-1.708199
C	-4.853931	-0.839178	-0.169729
H	-5.684505	-0.927956	-0.863231
C	-5.090641	-0.641086	1.185515
H	-6.108261	-0.571246	1.557997
C	-4.012514	-0.541716	2.065654
H	-4.187026	-0.398874	3.128287
C	-2.712076	-0.623352	1.585968
H	-1.871529	-0.552370	2.269060

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

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SCF Energy= -1855.11167315 Predicted Change= -6.695777D-09
Zero-point correction (ZPE)= -1854.4894 0.62223
Internal Energy (U)= -1854.4553 0.65628
Enthalpy (H)= -1854.4544 0.65722
Gibbs Free Energy (G)= -1854.5533 0.55828

Frequencies -- 22.1444 32.4426 38.9729
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1855.211745

TS-VIIb-*(R,S,S)*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest,nofreeze,gdiis) iop(1/8=18)
freq=noraman geom=allcheck guess=read
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C34H33N3O5 C1[X(C34H33N3O5)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -1855.07744994 Predicted Change= -5.140177D-09

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00201	0.00180	[NO]	0.00201	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	1.477326	-0.801093	-0.746255
C	0.385107	-1.022755	0.011437
C	0.149430	-0.343873	1.335175
C	-1.285439	0.027398	1.735999
H	-1.985524	-0.797885	1.571352
C	-1.321713	0.579072	3.159887
H	-2.361277	0.598256	3.509390
C	-0.775146	2.001787	3.011142
H	0.313211	1.975356	2.911472
H	-1.024670	2.649862	3.856036
C	-1.383638	2.491029	1.698454
H	-2.403520	2.864320	1.844099
C	-0.558824	3.558297	1.025439
O	0.580493	3.851372	1.290131
O	-1.255037	4.155694	0.037416
C	-0.508287	5.084926	-0.737550
H	0.331391	4.581960	-1.224956
H	-0.117695	5.887550	-0.107388
H	-1.201147	5.481350	-1.479294
C	-1.420587	1.223430	0.749643
O	-0.249612	1.128604	0.008330
C	-2.668768	1.240916	-0.118598
H	-0.735723	-0.027788	3.855271
O	1.109155	-0.279439	2.089334
N	-0.323243	-1.941969	-0.639209
C	-1.516049	-2.594195	-0.184655
N	0.223861	-2.237014	-1.865206
C	1.301178	-1.511203	-1.901552
C	2.206876	-1.277773	-3.074401
H	1.629034	-0.746368	-3.846013
H	2.551705	-2.225917	-3.491830
O	3.340616	-0.545785	-2.692618
C	3.055883	0.630032	-1.938941

H	2.369273	1.283375	-2.494079
C	2.500464	0.231781	-0.554493
H	1.988951	1.071264	-0.068091
C	4.414589	1.249200	-1.611845
H	4.291931	2.305526	-1.343755
H	5.086703	1.184334	-2.471455
C	4.857117	0.425344	-0.422507
C	3.758487	-0.192957	0.179157
C	6.136771	0.229230	0.076594
H	6.993003	0.706306	-0.392104
C	6.305582	-0.607132	1.179933
H	7.300950	-0.777687	1.578994
C	5.207626	-1.230450	1.770394
H	5.355384	-1.881217	2.626831
C	3.918385	-1.024277	1.278339
H	3.057325	-1.481875	1.752036
C	-1.436349	-3.397365	0.959379
C	-0.132359	-3.630129	1.680153
H	-0.215808	-4.499508	2.336024
H	0.151420	-2.772177	2.300744
H	0.686620	-3.810678	0.976240
C	-2.623879	-3.963964	1.420671
H	-2.599996	-4.588649	2.308760
C	-3.826508	-3.735889	0.758384
H	-4.742339	-4.178819	1.137625
C	-3.862294	-2.946807	-0.385586
H	-4.803181	-2.764679	-0.896923
C	-2.700460	-2.359274	-0.888063
C	-2.722604	-1.513220	-2.130203
H	-3.718711	-1.091870	-2.284451
H	-2.446639	-2.111249	-3.005119
H	-2.016925	-0.683199	-2.053527
C	-3.892626	0.738017	0.326142
H	-3.966044	0.288776	1.315082
C	-5.027537	0.805265	-0.481236
H	-5.970870	0.404454	-0.120518
C	-4.952293	1.388888	-1.743340
H	-5.836410	1.447592	-2.371556
C	-3.732820	1.893225	-2.195383
H	-3.665226	2.345611	-3.180983
C	-2.600614	1.813435	-1.391514
H	-1.637932	2.180576	-1.732691

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1855.07744994 Predicted Change= -5.140177D-09
Zero-point correction (ZPE)= -1854.4565 0.62094
Internal Energy (U)= -1854.4222 0.65518
Enthalpy (H)= -1854.4213 0.65613
Gibbs Free Energy (G)= -1854.5214 0.55603

Frequencies -- -83.7742 23.1236 26.4872
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1855.183955

TS-VIIb-*(R,R,R)*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest,nofreeze,gdiis) iop(1/8=18)
freq=noraman geom=allcheck guess=read
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C34H33N3O5 C1[X(C34H33N3O5)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -1855.07466095 Predicted Change= -1.010715D-09

Optimization completed. {Found 3 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00054	0.00180	[YES]	0.00054	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	0.516295	1.092658	-0.698970
C	1.134214	0.070611	-0.060240
C	0.726677	-0.641914	1.206830
C	-0.777858	-0.837499	1.447468
H	-1.288902	0.118311	1.616947
C	-1.005729	-1.805452	2.614901
H	-0.228222	-1.695664	3.374211
C	-1.000259	-3.197143	1.969388
H	-1.496145	-3.950596	2.587865
H	0.032026	-3.514960	1.795665
C	-1.668769	-3.007626	0.599775
H	-1.337019	-3.736281	-0.142518
C	-3.173561	-3.101708	0.614195
O	-3.841825	-3.626915	-0.240770
O	-3.733239	-2.502119	1.693708
C	-5.158577	-2.508937	1.696906
H	-5.537531	-3.533095	1.686709
H	-5.540161	-1.986107	0.815022
H	-5.458272	-1.996456	2.610505
C	-1.102138	-1.617538	0.126865
O	0.169903	-1.832470	-0.374671
C	-2.009330	-0.903846	-0.872391
H	-1.977089	-1.602753	3.069409
O	1.591827	-0.929327	2.011586
N	2.286858	-0.110171	-0.719435
C	3.376639	-0.995869	-0.409849
N	2.362124	0.679986	-1.837221
C	1.284320	1.393352	-1.800047
C	0.809505	2.428361	-2.767919
H	0.158253	1.953091	-3.518142
H	1.659578	2.891240	-3.270238
O	0.110085	3.433183	-2.070345
C	-1.019184	2.918929	-1.384020

H	-1.702284	2.430172	-2.091299
C	-0.586948	1.947355	-0.256807
H	-1.442331	1.313900	-0.018012
C	-1.644496	4.089327	-0.618532
H	-2.709963	3.893553	-0.445943
H	-1.555007	5.012846	-1.196589
C	-0.875335	4.102854	0.683916
C	-0.243774	2.874828	0.888677
C	-0.744517	5.119139	1.620540
H	-1.224236	6.081414	1.465188
C	0.028649	4.890161	2.759303
H	0.147532	5.678645	3.495951
C	0.657995	3.662362	2.957552
H	1.259369	3.500049	3.846367
C	0.524003	2.636805	2.020460
H	1.020315	1.683368	2.185968
C	4.294156	-0.577407	0.558101
C	4.127667	0.726559	1.290638
H	3.780596	1.523190	0.624177
H	5.076294	1.041000	1.732246
H	3.391539	0.607585	2.092020
C	5.368764	-1.422174	0.829017
H	6.095929	-1.126317	1.579858
C	5.514741	-2.624922	0.146806
H	6.357080	-3.272899	0.370106
C	4.597940	-2.994937	-0.830288
H	4.725110	-3.928137	-1.371416
C	3.505807	-2.181601	-1.138182
C	2.518671	-2.561445	-2.207227
H	2.450748	-1.775662	-2.967504
H	1.522765	-2.692079	-1.770835
H	2.830269	-3.486800	-2.697314
C	-3.216112	-0.303191	-0.494666
H	-3.534602	-0.351541	0.545326
C	-4.000321	0.370572	-1.428698
H	-4.932108	0.834424	-1.116813
C	-3.595016	0.443391	-2.760785
H	-4.210307	0.959320	-3.491983
C	-2.396045	-0.154175	-3.145440
H	-2.075892	-0.108018	-4.183236
C	-1.606577	-0.815419	-2.206014
H	-0.659491	-1.271696	-2.479782

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1855.07466095 Predicted Change= -1.010715D-09
Zero-point correction (ZPE)= -1854.4543 0.62028
Internal Energy (U)= -1854.4198 0.65485
Enthalpy (H)= -1854.4188 0.65579
Gibbs Free Energy (G)= -1854.5205 0.55409

Frequencies -- -91.4280 11.4148 27.9296
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1855.179641

TS-VIIb-*(S,S,S)*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

```
 ======================================================================
 # M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
  opt=(maxcycle=250,calcfc,ts,noeigentest,nofreeze,gdiis) iop(1/8=18)
  freq=noraman geom=allcheck guess=read
  #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
 ----------------------------------------------------------------------
  Pointgroup= C1   Stoichiometry= C34H33N3O5   C1[X(C34H33N3O5)]  #Atoms= 75
  Charge = 0         Multiplicity = 1
 ----------------------------------------------------------------------
  SCF Energy= -1855.07886613       Predicted Change= -2.023844D-08
 ======================================================================
  Optimization completed.          {Found       3       times}
  Item      Max Val.    Criteria    Pass?     RMS Val.    Criteria    Pass?
  Force      0.00003 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
  Displ      0.00137 ||  0.00180   [ YES ]      0.00137 ||  0.00180   [ YES ]
 ----------------------------------------------------------------------
      Atomic             Coordinates (Angstroms)
       Type              X           Y           Z
 ----------------------------------------------------------------------
       N         1.944536    0.491644    0.604424
       C         0.827909    0.685883   -0.136880
       C         0.448176   -0.152896   -1.323767
       C        -1.043772   -0.380455   -1.564783
       H        -1.574630    0.570013   -1.679551
       C        -1.253868   -1.333986   -2.739458
       H        -2.285691   -1.260206   -3.090844
       C        -1.010087   -2.718263   -2.128824
       H         0.065289   -2.883829   -2.012571
       H        -1.424513   -3.525413   -2.738831
       C        -1.659561   -2.636659   -0.744033
       H        -1.225518   -3.312208   -0.003850
       C        -3.145092   -2.882513   -0.814737
       O        -3.863881   -2.613940   -1.751396
       O        -3.613273   -3.396952    0.335092
       C        -5.033326   -3.444685    0.436127
       H        -5.445763   -2.435649    0.347791
       H        -5.246764   -3.859328    1.420617
       H        -5.455306   -4.075799   -0.349584
       C        -1.341750   -1.160882   -0.243809
       O        -0.124863   -1.151055    0.421964
       C        -2.476667   -0.632074    0.621756
       H        -0.574535   -1.115154   -3.567716
       O         1.340950   -0.564982   -2.040450
       N         0.312776    1.843233    0.294469
       C        -0.728302    2.626047   -0.303071
       N         0.976636    2.310215    1.410179
       C         1.936524    1.455783    1.576969
       C         2.870572    1.356887    2.747019
       H         2.272473    1.110890    3.637426
       H         3.374936    2.309581    2.920489
       O         3.859345    0.388566    2.516891
       C         3.351116   -0.864977    2.072232
```

H	2.602890	-1.247721	2.779357
C	2.784124	-0.706309	0.644147
H	2.120739	-1.539049	0.384055
C	4.572606	-1.762564	1.875578
H	4.270786	-2.816976	1.876733
H	5.298284	-1.609729	2.678615
C	5.067820	-1.326718	0.513724
C	4.049684	-0.681862	-0.193247
C	6.330746	-1.470224	-0.043206
H	7.125232	-1.967707	0.506154
C	6.568090	-0.945296	-1.313517
H	7.553136	-1.041892	-1.760035
C	5.554089	-0.288929	-2.008850
H	5.754650	0.121152	-2.993879
C	4.279945	-0.155059	-1.455706
H	3.481450	0.333666	-2.001311
C	-0.566188	3.061437	-1.625641
C	0.678748	2.780939	-2.429895
H	0.813673	3.559287	-3.184606
H	0.620805	1.821421	-2.955695
H	1.574874	2.758830	-1.802081
C	-1.616533	3.781191	-2.196138
H	-1.520771	4.124929	-3.222110
C	-2.765411	4.067701	-1.468024
H	-3.574176	4.623721	-1.932099
C	-2.873887	3.657926	-0.144404
H	-3.766317	3.890871	0.429347
C	-1.852148	2.935598	0.472127
C	-1.957513	2.535705	1.917088
H	-1.420629	3.251651	2.548043
H	-1.523395	1.549437	2.092558
H	-3.004971	2.507026	2.224619
C	-3.586464	0.032368	0.097597
H	-3.641780	0.241017	-0.968382
C	-4.641372	0.415054	0.927297
H	-5.494261	0.939205	0.504550
C	-4.605622	0.117441	2.287035
H	-5.431305	0.406411	2.930984
C	-3.502204	-0.552850	2.816269
H	-3.468216	-0.788669	3.876282
C	-2.444511	-0.916399	1.990164
H	-1.569785	-1.426704	2.382378

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1855.07886613 Predicted Change= -2.023844D-08

Zero-point correction (ZPE)=	-1854.4574	0.62146
Internal Energy (U)=	-1854.4234	0.65542
Enthalpy (H)=	-1854.4224	0.65636
Gibbs Free Energy (G)=	-1854.5209	0.55788

Frequencies -- -107.6158 30.0089 33.2793

M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1855.183069

TS-VIIb-*(S,R,R)*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest,nofreeze,gdiis) iop(1/8=18)
freq=noraman geom=allcheck guess=read
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C34H33N3O5 C1[X(C34H33N3O5)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -1855.07799998 Predicted Change= -5.150604D-09

Optimization completed. {Found 3 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00149	0.00180	[YES]	0.00149	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	1.096772	-0.519687	-0.768894
C	0.008751	-0.965052	-0.098286
C	-0.426889	-0.691970	1.324533
C	-0.097037	0.683825	1.917619
H	0.984274	0.860535	1.968514
C	-0.755173	0.854164	3.292671
H	-0.725369	-0.071512	3.871792
C	-2.178061	1.320358	2.976125
H	-2.681621	1.788718	3.825445
H	-2.788353	0.477831	2.637904
C	-1.975114	2.273844	1.801909
H	-1.573355	3.239871	2.136950
C	-3.234407	2.519407	1.008154
O	-4.323407	2.064835	1.251857
O	-2.994733	3.328904	-0.041473
C	-4.109928	3.538961	-0.899492
H	-4.466644	2.586175	-1.298662
H	-3.750892	4.181537	-1.702931
H	-4.927747	4.021014	-0.358212
C	-0.931307	1.537496	0.903787
O	-1.570428	0.548113	0.177775
C	-0.113065	2.481693	0.033670
H	-0.216073	1.629888	3.849584
O	-0.876363	-1.620800	1.970113
N	-0.595141	-1.819716	-0.932318
C	-1.780801	-2.609853	-0.721815
N	0.022183	-1.860589	-2.153662
C	1.037768	-1.068912	-2.028339
C	2.069259	-0.707201	-3.049238
H	1.731214	0.176180	-3.613440
H	2.217863	-1.537269	-3.741058
O	3.293001	-0.444855	-2.404594
C	3.181361	0.624427	-1.479913

H	2.817645	1.526024	-1.989248
C	2.258801	0.238982	-0.296241
H	1.902932	1.163993	0.163193
C	4.552138	0.792552	-0.817471
H	4.665319	1.822708	-0.457832
H	5.349381	0.590406	-1.537552
C	4.502271	-0.184516	0.335032
C	3.180985	-0.527998	0.626904
C	5.544411	-0.727329	1.073355
H	6.575748	-0.471668	0.846970
C	5.246317	-1.621867	2.101721
H	6.051865	-2.062073	2.681344
C	3.925569	-1.965480	2.385600
H	3.710289	-2.668242	3.184075
C	2.874958	-1.417244	1.648816
H	1.849121	-1.697575	1.877871
C	-2.990386	-2.154833	-1.253753
C	-3.099039	-0.852262	-1.997287
H	-4.079883	-0.772235	-2.472186
H	-2.332444	-0.781022	-2.776309
H	-2.952470	-0.016277	-1.304823
C	-4.107129	-2.970663	-1.063398
H	-5.065402	-2.643277	-1.455829
C	-4.006065	-4.181278	-0.389224
H	-4.888980	-4.798854	-0.253767
C	-2.777480	-4.614157	0.098669
H	-2.696574	-5.569632	0.608904
C	-1.634541	-3.834978	-0.063900
C	-0.295655	-4.292278	0.448471
H	-0.326883	-5.353585	0.705464
H	-0.027610	-3.723464	1.344316
H	0.490578	-4.145619	-0.299765
C	0.771811	3.409057	0.590754
H	0.848983	3.493315	1.674259
C	1.570276	4.210727	-0.222756
H	2.259106	4.921492	0.224806
C	1.478966	4.106581	-1.610137
H	2.094049	4.736179	-2.246311
C	0.584588	3.196169	-2.173109
H	0.497990	3.121217	-3.254462
C	-0.199647	2.384092	-1.356135
H	-0.896348	1.658822	-1.768068

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1855.07799998 Predicted Change= -5.150604D-09
Zero-point correction (ZPE)= -1854.4579 0.62004
Internal Energy (U)= -1854.4232 0.65478
Enthalpy (H)= -1854.4222 0.65572
Gibbs Free Energy (G)= -1854.5245 0.55343

Frequencies -- -71.7826 17.8260 23.4705
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1855.184412

VIII-*(R,R,R)*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C34H33N3O5 C1[X(C34H33N3O5)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -1855.08903078 Predicted Change= -7.223927D-09

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00269	0.00180	[NO]	0.00269	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	1.972386	0.201783	0.657598
C	0.846376	0.442612	-0.038045
C	0.210445	-0.671922	-0.918856
C	-0.535929	-1.728387	-0.013335
H	-0.332908	-1.683087	1.061908
C	-0.463637	-3.121543	-0.628484
H	0.558422	-3.346901	-0.950091
C	-1.416872	-3.049832	-1.833618
H	-1.780648	-4.032291	-2.146249
H	-0.891207	-2.577407	-2.667403
C	-2.554712	-2.119487	-1.388385
H	-3.061698	-1.610768	-2.212701
C	-3.581468	-2.826852	-0.539166
O	-3.350023	-3.723910	0.239261
O	-4.802604	-2.290770	-0.693145
C	-5.788463	-2.773283	0.215905
H	-5.491816	-2.541541	1.242518
H	-5.910649	-3.853865	0.112923
H	-6.709946	-2.253210	-0.041813
C	-1.825990	-1.052820	-0.518714
O	-1.108124	-0.160082	-1.380490
C	-2.732398	-0.324043	0.439469
H	-0.803658	-3.874381	0.086513
O	1.066689	-1.033766	-1.796453
N	0.605540	1.741603	0.147582
C	-0.418663	2.573816	-0.429806
N	1.544475	2.336760	0.959076
C	2.358968	1.369591	1.248891
C	3.519086	1.288159	2.186549
H	3.491735	2.112609	2.899639
H	4.472253	1.310159	1.640481
O	3.352167	0.085737	2.915194
C	3.439028	-1.114696	2.155683

H	2.883287	-1.842655	2.748933
C	2.822041	-0.986923	0.715367
H	2.204877	-1.847669	0.447821
C	4.904128	-1.542021	1.925632
H	5.008048	-2.625757	2.056119
H	5.551855	-1.062178	2.666203
C	5.199866	-1.145474	0.500964
C	4.027850	-0.854006	-0.192943
C	6.429730	-1.068572	-0.145063
H	7.350175	-1.291313	0.387511
C	6.458933	-0.695201	-1.486880
H	7.411782	-0.624140	-2.002991
C	5.276593	-0.414252	-2.176010
H	5.320308	-0.135512	-3.224304
C	4.040836	-0.495170	-1.537730
H	3.099005	-0.317926	-2.052345
C	-1.344389	3.158480	0.435503
C	-1.363123	2.834295	1.905149
H	-1.443553	1.750596	2.056655
H	-2.227840	3.299384	2.383477
H	-0.453618	3.181849	2.403637
C	-2.286648	4.017613	-0.130707
H	-3.023549	4.486226	0.515665
C	-2.303661	4.252453	-1.500525
H	-3.048718	4.918326	-1.925545
C	-1.367667	3.642729	-2.330436
H	-1.380962	3.832561	-3.399634
C	-0.389444	2.796050	-1.809480
C	0.651071	2.159780	-2.690903
H	0.615181	2.599594	-3.690260
H	0.502521	1.077176	-2.779117
H	1.657824	2.319212	-2.286439
C	-2.983819	-0.820761	1.721872
H	-2.484730	-1.728227	2.053099
C	-3.885899	-0.173345	2.563812
H	-4.067979	-0.563819	3.560914
C	-4.551284	0.969812	2.126463
H	-5.256380	1.473661	2.781154
C	-4.305836	1.464782	0.847142
H	-4.816584	2.359308	0.500946
C	-3.398410	0.824195	0.008897
H	-3.182310	1.218634	-0.981243

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1855.08903078 Predicted Change= -7.223927D-09
Zero-point correction (ZPE)= -1854.4675 0.62145
Internal Energy (U)= -1854.4328 0.65616
Enthalpy (H)= -1854.4319 0.65710
Gibbs Free Energy (G)= -1854.5344 0.55456

Frequencies -- 12.4783 28.2943 34.0127
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1855.194782

VIII-*(R,S,S)*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C34H33N3O5 C1[X(C34H33N3O5)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -1855.08730843 Predicted Change= -2.530015D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.03881	0.00180	[NO]	0.03881	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	1.097864	1.231206	0.565775
C	0.004985	1.067475	-0.212677
C	-0.215854	-0.097829	-1.227183
C	-1.682016	-0.655454	-1.236142
H	-2.484831	0.009746	-0.913102
C	-1.971570	-1.395802	-2.542358
H	-3.050499	-1.564239	-2.641608
C	-1.226662	-2.732501	-2.409240
H	-0.170056	-2.579285	-2.647120
H	-1.619741	-3.522165	-3.053139
C	-1.359244	-3.070376	-0.914192
H	-2.369872	-3.453228	-0.708464
C	-0.372415	-4.084942	-0.385267
O	0.158057	-4.049230	0.697434
O	-0.160978	-5.073892	-1.273000
C	0.761455	-6.072844	-0.845556
H	0.411056	-6.548731	0.073378
H	1.742198	-5.628867	-0.660401
H	0.815284	-6.796298	-1.658021
C	-1.178479	-1.709986	-0.227371
O	0.183070	-1.296738	-0.372176
C	-1.703650	-1.585071	1.180432
H	-1.623091	-0.814551	-3.400478
O	0.424717	0.112036	-2.304782
N	-0.741565	2.147410	0.014911
C	-2.026291	2.466977	-0.544983
N	-0.188001	2.984718	0.944678
C	0.924946	2.396739	1.263751
C	1.878217	2.791258	2.350298
H	1.411253	2.559248	3.320650
H	2.077029	3.863729	2.309046
O	3.100605	2.121637	2.204258
C	2.971517	0.711738	2.073739

H	2.443005	0.298790	2.945485
C	2.276304	0.362653	0.737426
H	1.902657	-0.665561	0.728156
C	4.394501	0.185767	1.881620
H	4.441955	-0.879920	2.136671
H	5.091252	0.727181	2.527013
C	4.619908	0.409780	0.403290
C	3.401012	0.539011	-0.266224
C	5.814979	0.485115	-0.297246
H	6.767249	0.391285	0.217558
C	5.769966	0.696752	-1.675786
H	6.696426	0.766624	-2.238210
C	4.548416	0.816810	-2.336115
H	4.531981	0.972191	-3.410524
C	3.341406	0.731180	-1.639344
H	2.378842	0.774298	-2.145384
C	-2.089765	2.880314	-1.877431
C	-0.846451	3.039502	-2.710087
H	-0.123014	3.686979	-2.201668
H	-1.092333	3.494212	-3.672221
H	-0.361646	2.070124	-2.882899
C	-3.361462	3.140022	-2.392622
H	-3.452783	3.457671	-3.427071
C	-4.495918	3.001883	-1.601299
H	-5.475353	3.204642	-2.023928
C	-4.386053	2.611601	-0.269633
H	-5.275322	2.511900	0.346113
C	-3.139865	2.337047	0.290999
C	-2.993157	1.911128	1.727770
H	-3.959886	1.613540	2.139576
H	-2.593907	2.731469	2.333514
H	-2.309089	1.060952	1.831702
C	-3.078915	-1.661684	1.419818
H	-3.757229	-1.843493	0.587786
C	-3.587072	-1.487170	2.702859
H	-4.658113	-1.548197	2.873271
C	-2.724578	-1.222583	3.765514
H	-3.120072	-1.080551	4.766605
C	-1.353183	-1.149677	3.535169
H	-0.674018	-0.958486	4.361506
C	-0.845673	-1.333151	2.250367
H	0.222770	-1.306914	2.061012

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1855.08730843 Predicted Change= -2.530015D-08
Zero-point correction (ZPE)= -1854.4665 0.62075
Internal Energy (U)= -1854.4316 0.65565
Enthalpy (H)= -1854.4307 0.65659
Gibbs Free Energy (G)= -1854.5350 0.55221

Frequencies -- 5.1131 20.5076 22.6603
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1855.195955

VIII-*(S,R,R)*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C34H33N3O5 C1[X(C34H33N3O5)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -1855.08428354 Predicted Change= -5.072045D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00273	0.00180	[NO]	0.00273	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	2.036695	-0.562717	-0.432467
C	0.787829	-0.418523	0.048173
C	0.083377	0.969500	-0.005905
C	-0.452069	1.259657	-1.463536
H	-0.117266	0.576620	-2.251331
C	-0.348463	2.743132	-1.801066
H	0.648763	3.130610	-1.569588
C	-1.418521	3.400410	-0.920321
H	-1.743518	4.380560	-1.275438
H	-1.020836	3.503888	0.093141
C	-2.561787	2.372541	-0.914584
H	-3.110649	2.432419	-1.866363
C	-3.572335	2.562483	0.192731
O	-4.129170	1.690004	0.810423
O	-3.815316	3.871455	0.402528
C	-4.773525	4.143753	1.421314
H	-4.434296	3.742610	2.378980
H	-5.736549	3.691466	1.172171
H	-4.858966	5.228634	1.468054
C	-1.849819	1.005032	-0.856680
O	-1.311675	0.778177	0.455178
C	-2.668074	-0.151999	-1.370120
H	-0.558873	2.908845	-2.864706
O	0.821344	1.819584	0.605103
N	0.489592	-1.606954	0.575445
C	-0.664921	-2.001940	1.340303
N	1.512460	-2.515925	0.429883
C	2.435472	-1.845046	-0.187088
C	3.751018	-2.254594	-0.765146
H	3.792973	-3.336608	-0.892365
H	4.582638	-1.930184	-0.124472
O	3.813477	-1.666907	-2.051414
C	3.864641	-0.245548	-2.072606

H	3.502056	0.016148	-3.067954
C	2.974662	0.426144	-0.964202
H	2.387770	1.265051	-1.344335
C	5.293024	0.281251	-1.814468
H	5.523172	1.105995	-2.499269
H	6.022139	-0.512561	-2.006078
C	5.272908	0.764003	-0.385318
C	3.968205	0.869836	0.090779
C	6.343787	1.106828	0.434958
H	7.365577	1.024835	0.074726
C	6.081039	1.552222	1.728328
H	6.906825	1.817708	2.381687
C	4.768073	1.665373	2.191964
H	4.584633	2.026496	3.199203
C	3.690652	1.329672	1.374912
H	2.655269	1.441696	1.689424
C	-0.875440	-1.384367	2.576336
C	0.043834	-0.310639	3.092857
H	-0.061854	0.621068	2.525598
H	1.092877	-0.622702	3.020723
H	-0.174831	-0.104387	4.143075
C	-1.975521	-1.817302	3.315139
H	-2.178448	-1.351112	4.274632
C	-2.796909	-2.837755	2.845734
H	-3.644375	-3.163763	3.441065
C	-2.539293	-3.440204	1.619748
H	-3.188055	-4.228993	1.249311
C	-1.467739	-3.022613	0.830139
C	-1.220992	-3.606037	-0.535121
H	-1.167373	-2.809538	-1.287686
H	-2.040658	-4.270964	-0.815765
H	-0.282251	-4.166952	-0.566412
C	-3.394558	-0.949877	-0.485730
H	-3.335998	-0.740926	0.578212
C	-4.180032	-1.991209	-0.973239
H	-4.744357	-2.605335	-0.276522
C	-4.242203	-2.251318	-2.340356
H	-4.854951	-3.066558	-2.714104
C	-3.516919	-1.458900	-3.227158
H	-3.557181	-1.654859	-4.294615
C	-2.736190	-0.413615	-2.741321
H	-2.173171	0.209340	-3.434272

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1855.08428354 Predicted Change= -5.072045D-08
Zero-point correction (ZPE)= -1854.4629 0.62133
Internal Energy (U)= -1854.4284 0.65587
Enthalpy (H)= -1854.4274 0.65682
Gibbs Free Energy (G)= -1854.5288 0.55542

Frequencies -- 19.6109 26.0206 31.5618
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1855.191036

VIII-*(S,S,S)*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C34H33N3O5 C1[X(C34H33N3O5)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -1855.08899583 Predicted Change= -1.391529D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00212	0.00180	[NO]	0.00212	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	1.744968	0.436245	0.720256
C	0.694316	1.006484	0.092070
C	-0.088607	0.508109	-1.164363
C	-1.639288	0.471911	-0.919448
H	-2.024145	1.065618	-0.088033
C	-2.402198	0.658837	-2.226163
H	-3.454807	0.867929	-2.023541
C	-2.247989	-0.687844	-2.953878
H	-1.277246	-0.709443	-3.456911
H	-3.036543	-0.867658	-3.689705
C	-2.234028	-1.747525	-1.840824
H	-1.708902	-2.668109	-2.109711
C	-3.615604	-2.093980	-1.344843
O	-4.545905	-1.324998	-1.262230
O	-3.682941	-3.367269	-0.920920
C	-4.902795	-3.717897	-0.272877
H	-5.753130	-3.552097	-0.938011
H	-5.031564	-3.114434	0.630101
H	-4.811563	-4.772590	-0.017057
C	-1.454266	-1.040941	-0.695022
O	-0.063209	-0.998786	-1.034711
C	-1.688854	-1.627653	0.675270
H	-1.965226	1.479331	-2.802389
O	0.419100	1.013848	-2.216422
N	0.567760	2.206697	0.660285
C	-0.441425	3.200552	0.403348
N	1.488788	2.423432	1.646372
C	2.190816	1.331627	1.658696
C	3.292546	0.967002	2.605603
H	2.852085	0.696131	3.578122
H	3.958899	1.819123	2.750901
O	4.051495	-0.090894	2.083986
C	3.262771	-1.221438	1.740576

H	2.693345	-1.559255	2.618644
C	2.344767	-0.895892	0.538651
H	1.511048	-1.597503	0.476978
C	4.231973	-2.264109	1.178600
H	3.805252	-3.269404	1.280967
H	5.177303	-2.236240	1.727085
C	4.347044	-1.860975	-0.274315
C	3.271671	-1.052671	-0.647750
C	5.325512	-2.194630	-1.199716
H	6.170489	-2.815797	-0.915640
C	5.209523	-1.702693	-2.500074
H	5.971264	-1.945272	-3.235265
C	4.128317	-0.900550	-2.863697
H	4.053554	-0.529173	-3.881053
C	3.135021	-0.566989	-1.941382
H	2.279306	0.046122	-2.226835
C	-1.525019	3.248496	1.286806
C	-1.611932	2.305787	2.458131
H	-1.488096	1.260182	2.150137
H	-2.581626	2.397683	2.952606
H	-0.828692	2.524602	3.191638
C	-2.509959	4.200586	1.036481
H	-3.371972	4.256796	1.694613
C	-2.393926	5.070282	-0.044520
H	-3.170921	5.805787	-0.228979
C	-1.286717	5.011604	-0.882049
H	-1.194685	5.704348	-1.713256
C	-0.272393	4.073598	-0.672311
C	0.948579	4.010006	-1.546730
H	1.859422	4.077697	-0.941226
H	0.949023	4.837644	-2.259352
H	0.966550	3.056192	-2.087642
C	-0.880382	-2.675918	1.122274
H	-0.092081	-3.042271	0.469666
C	-1.100614	-3.261507	2.365016
H	-0.467839	-4.079246	2.697976
C	-2.140431	-2.810013	3.175622
H	-2.312643	-3.265039	4.146315
C	-2.962689	-1.778219	2.730475
H	-3.780647	-1.427095	3.353023
C	-2.740117	-1.190996	1.485559
H	-3.395869	-0.399008	1.130529

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1855.08899583 Predicted Change= -1.391529D-08
Zero-point correction (ZPE)= -1854.4676 0.62137
Internal Energy (U)= -1854.4327 0.65628
Enthalpy (H)= -1854.4317 0.65722
Gibbs Free Energy (G)= -1854.5345 0.55442

Frequencies -- 16.3556 25.5806 32.8903
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1855.196951

IX-*(R,S,S) & -(S,R,R)*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C14H14O4 C1[X(C14H14O4)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -842.482413464 Predicted Change= -3.673172D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00046	0.00180	[YES]	0.00046	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.274526	-0.559747	-0.048173
C	1.223551	-0.474421	-0.058708
C	-1.046074	0.384356	-0.989953
H	-0.469626	0.472257	-1.920323
C	-2.388671	-0.314373	-1.243145
H	-2.875261	0.039973	-2.153894
H	-3.064691	-0.095485	-0.409900
C	-2.033685	-1.806845	-1.281433
H	-1.616910	-2.080954	-2.257338
H	-2.889989	-2.457387	-1.085245
C	-0.944180	-1.950084	-0.215457
H	-0.287420	-2.815859	-0.313314
C	-1.428574	-1.679977	1.203265
O	-2.102438	-2.222692	2.018221
O	-0.831059	-0.450633	1.300163
C	-1.208809	1.772583	-0.404665
O	-2.255873	2.360303	-0.310903
O	-0.032446	2.271039	-0.002795
C	-0.096930	3.563229	0.600861
H	-0.737466	3.534473	1.484774
H	-0.497564	4.292832	-0.106136
H	0.927484	3.811512	0.873452
C	1.917540	-0.839679	-1.213943
H	1.367974	-1.182094	-2.089442
C	3.306032	-0.775851	-1.249623
H	3.837920	-1.063389	-2.151282
C	4.011244	-0.347768	-0.126813
H	5.095405	-0.298723	-0.151891
C	3.321299	0.012873	1.027093
H	3.867484	0.343553	1.905313
C	1.930752	-0.049944	1.063973
H	1.383376	0.229039	1.958065

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-842.482413464	Predicted Change= -3.673172D-09
Zero-point correction (ZPE)=	-842.2214	0.26097
Internal Energy (U)=	-842.2061	0.27621
Enthalpy (H)=	-842.2052	0.27716
Gibbs Free Energy (G)=	-842.2649	0.21746

Frequencies -- 41.2683 46.7945 59.8457

M06-2X/6-31+G(d,p)/PCM(DCE) SP: -842.5352615

IX-*(S,S,S) & -(R,R,R)*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C14H14O4 C1[X(C14H14O4)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -842.484864325 Predicted Change= -5.071685D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00110	0.00180	[YES]	0.00110	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.767501	-0.358867	-0.184424
C	0.598675	-0.940424	0.039125
C	-0.822378	1.056341	-0.809639
H	-0.671450	0.972793	-1.889058
C	-2.212065	1.584331	-0.412085
H	-2.951458	1.201994	-1.123258
H	-2.258643	2.675454	-0.429483
C	-2.470633	1.010593	0.992077
H	-3.534953	0.951643	1.235289
H	-1.970076	1.623905	1.744500
C	-1.821819	-0.377263	0.951117
H	-1.530898	-0.798618	1.914319
C	-2.541023	-1.337744	0.014709
O	-1.608292	-1.249168	-0.984393
O	-3.554632	-1.959495	0.002192
C	0.289407	1.899610	-0.224066
O	0.230964	2.481241	0.834594
O	1.377284	1.881615	-0.999803
C	2.528210	2.516963	-0.441386
H	2.314413	3.563396	-0.215097
H	3.306839	2.433203	-1.197324
H	2.825615	2.001357	0.475370
C	1.337409	-0.583020	1.170022
H	0.905656	0.090165	1.907386
C	2.627718	-1.075122	1.345255
H	3.194842	-0.797345	2.228539
C	3.183639	-1.930762	0.396754
H	4.187496	-2.319670	0.536497
C	2.444549	-2.293991	-0.726100
H	2.870834	-2.966966	-1.463649
C	1.155709	-1.800433	-0.906430
H	0.569810	-2.086125	-1.774321

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-842.484864325	Predicted Change= -5.071685D-09
Zero-point correction (ZPE)=	-842.2232	0.26159
Internal Energy (U)=	-842.2081	0.27673
Enthalpy (H)=	-842.2071	0.27767
Gibbs Free Energy (G)=	-842.2663	0.21848

Frequencies -- 41.6851 56.4133 60.6445

M06-2X/6-31+G(d,p)/PCM(DCE) SP: -842.5352903

—2F-Ph Substrate—
***(R)*-IV**
Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

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 ======================================================================
 # M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
 opt=(maxcycle=250) freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
 ----------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C34H32FN3O5   C1[X(C34H32FN3O5)]  #Atoms= 75
 Charge = 0         Multiplicity = 1
 ----------------------------------------------------------------------
 SCF Energy= -1954.29160665       Predicted Change= -9.959896D-09
 ======================================================================
 Optimization completed.          {Found       2       times}
 Item      Max Val.    Criteria    Pass?     RMS Val.    Criteria    Pass?
 Force      0.00001 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
 Displ      0.00112 ||  0.00180   [ YES ]      0.00112 ||  0.00180   [ YES ]
 ----------------------------------------------------------------------
      Atomic             Coordinates (Angstroms)
       Type              X           Y           Z
 ----------------------------------------------------------------------
      N       -1.444138   -1.598403   -0.545335
      C       -2.068241   -0.438640   -0.263482
      C       -1.375662    0.897927   -0.297911
      C       -1.568915    1.692487    0.791333
      H       -2.248216    1.356393    1.572029
      C       -0.834927    2.994562    0.955050
      H       -0.770029    3.505376   -0.011753
      C        0.587418    2.819891    1.520229
      H        0.555854    2.171941    2.403305
      H        0.990208    3.783328    1.848127
      C        1.549502    2.204095    0.497869
      H        1.049985    1.420201   -0.085884
      C        1.951008    3.253365   -0.533433
      O        1.512888    4.374416   -0.588511
      O        2.873744    2.791325   -1.394003
      C        3.260065    3.711473   -2.411621
      H        2.397342    3.978464   -3.025674
      H        4.011740    3.194767   -3.006995
      H        3.675251    4.619691   -1.968979
      C        2.794390    1.623466    1.166610
      O        3.070094    1.943273    2.305448
      C        3.709056    0.652730    0.457598
      H       -1.396483    3.653216    1.626633
      O       -0.652787    1.038646   -1.342737
      N       -3.353628   -0.767594   -0.128380
      C       -4.451422    0.142572    0.046056
      N       -3.573522   -2.109379   -0.311741
      C       -2.388182   -2.584108   -0.563560
      C       -1.983067   -3.981468   -0.929489
      H       -2.249640   -4.167447   -1.981400
      H       -2.507377   -4.706128   -0.304230
      O       -0.603221   -4.152526   -0.720159
      C        0.198035   -3.199961   -1.411623
```

H	-0.026004	-3.238677	-2.486756
C	-0.019568	-1.793866	-0.813310
H	0.267079	-0.987648	-1.497541
C	1.656654	-3.513679	-1.066009
H	2.318854	-3.127561	-1.851202
H	1.808541	-4.593738	-0.989374
C	1.864401	-2.769058	0.233202
C	0.872494	-1.805191	0.409147
C	2.870876	-2.919185	1.178623
H	3.658074	-3.654608	1.037308
C	2.850303	-2.113274	2.316283
H	3.631059	-2.218475	3.063257
C	1.839666	-1.169718	2.501892
H	1.844488	-0.539093	3.385528
C	0.843895	-0.996629	1.539248
H	0.072801	-0.239728	1.665344
C	-4.772573	0.982849	-1.023659
C	-4.016146	0.923707	-2.325742
H	-3.993001	-0.101754	-2.712432
H	-2.976966	1.258043	-2.220015
H	-4.503875	1.554254	-3.072230
C	-5.833564	1.866894	-0.831187
H	-6.111477	2.537951	-1.638468
C	-6.532119	1.893706	0.371576
H	-7.353084	2.592037	0.501404
C	-6.187261	1.033289	1.408490
H	-6.736086	1.058566	2.345384
C	-5.129855	0.135636	1.265117
C	-4.722068	-0.800659	2.371471
H	-3.653642	-0.705161	2.595832
H	-4.903937	-1.843053	2.091631
H	-5.282373	-0.583532	3.283201
C	4.927064	0.369464	1.088230
C	5.844103	-0.520798	0.548049
H	6.781629	-0.712774	1.059316
C	5.557390	-1.158019	-0.658190
H	6.268674	-1.850868	-1.097389
C	4.353204	-0.906561	-1.303302
H	4.094560	-1.378906	-2.245296
C	3.448289	-0.018153	-0.736465
F	2.287668	0.155586	-1.386027
H	5.124863	0.876341	2.026949

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1954.29160665 Predicted Change= -9.959896D-09
Zero-point correction (ZPE)= -1953.6796 0.61198
Internal Energy (U)= -1953.6429 0.64868
Enthalpy (H)= -1953.6419 0.64963
Gibbs Free Energy (G)= -1953.7473 0.54424

Frequencies -- 25.5307 34.7831 36.9097
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1954.408151

***(S)*-IV**

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C34H32FN3O5 C1[X(C34H32FN3O5)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -1954.29551405 Predicted Change= -1.432892D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00003	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00305	0.00180	[NO]	0.00305	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-1.297796	1.649689	0.288436
C	-1.848031	0.419143	0.225306
C	-1.090581	-0.845952	0.515336
C	-1.423125	-1.960631	-0.197178
H	-2.211570	-1.923243	-0.943351
C	-0.721946	-3.251756	0.117834
H	-0.537667	-3.293875	1.197607
C	0.625478	-3.441576	-0.599753
H	0.466317	-3.499909	-1.682295
H	1.083248	-4.381827	-0.271900
C	1.616879	-2.295241	-0.349832
H	1.146129	-1.348512	-0.625737
C	2.793590	-2.449772	-1.290916
O	2.730293	-2.300617	-2.486756
O	3.919691	-2.805392	-0.650974
C	5.076947	-2.882041	-1.478262
H	5.896342	-3.165204	-0.819266
H	5.268188	-1.908989	-1.937756
H	4.937236	-3.627284	-2.264065
C	2.042730	-2.195971	1.109914
O	1.907601	-3.125038	1.873765
C	2.617560	-0.897220	1.617717
H	-1.363678	-4.101876	-0.139659
O	-0.204258	-0.688604	1.420812
N	-3.153505	0.640985	0.043307
C	-4.202539	-0.337909	-0.033589
N	-3.454507	1.975355	-0.020162
C	-2.302842	2.560445	0.132962
C	-1.996587	4.024132	0.233656
H	-2.222408	4.366962	1.255580
H	-2.612955	4.589124	-0.467518
O	-0.649248	4.255312	-0.090138
C	0.260866	3.509597	0.712448

H	0.100893	3.747880	1.773122
C	0.119657	2.000237	0.418564
H	0.519362	1.369118	1.221661
C	1.666782	3.842629	0.202103
H	2.399729	3.665103	0.998457
H	1.723239	4.893152	-0.096064
C	1.850211	2.869473	-0.942521
C	0.919081	1.833962	-0.853269
C	2.761894	2.892652	-1.989465
H	3.490561	3.694721	-2.073805
C	2.716243	1.875694	-2.945281
H	3.426592	1.880312	-3.766375
C	1.763125	0.862195	-2.867243
H	1.745463	0.071389	-3.609471
C	0.845875	0.838069	-1.815842
H	0.101176	0.047256	-1.753704
C	-4.570641	-1.005944	1.136298
C	-3.887896	-0.722666	2.447843
H	-3.869700	0.352285	2.657858
H	-2.850877	-1.078012	2.443729
H	-4.415168	-1.219530	3.264886
C	-5.590421	-1.951047	1.027129
H	-5.900968	-2.494386	1.914673
C	-6.204774	-2.201277	-0.195695
H	-6.995911	-2.941904	-0.260079
C	-5.811380	-1.511651	-1.337939
H	-6.290758	-1.713216	-2.291435
C	-4.792667	-0.561669	-1.278639
C	-4.324089	0.183943	-2.500024
H	-4.816505	-0.199364	-3.396027
H	-3.241170	0.076658	-2.633621
H	-4.538605	1.253934	-2.416026
C	3.244458	0.072349	0.842587
C	3.734020	1.257738	1.376488
H	4.224216	1.960017	0.709582
C	3.583302	1.496745	2.737548
H	3.962941	2.419868	3.166210
C	2.957612	0.545824	3.545734
H	2.836119	0.728291	4.608494
C	2.491938	-0.635561	2.985969
H	1.993333	-1.389245	3.586164
F	3.414499	-0.110983	-0.480502

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1954.29551405 Predicted Change= -1.432892D-08
Zero-point correction (ZPE)= -1953.6847 0.61077
Internal Energy (U)= -1953.6477 0.64781
Enthalpy (H)= -1953.6467 0.64875
Gibbs Free Energy (G)= -1953.7542 0.54125

Frequencies -- 12.4830 27.7049 32.3562
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1954.412102

TS-V-*(S,R,R)*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,calcfc,ts,noeigentest,nofreeze,gdiis) iop(1/8=18) freq=noraman geom=allcheck guess=read

#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C34H32FN3O5 C1[X(C34H32FN3O5)] #Atoms= 75

Charge = 0 Multiplicity = 1

SCF Energy= -1954.26764788 Predicted Change= -2.285562D-08

Optimization completed. {Found 3 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00122	0.00180	[YES]	0.00122	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	1.703823	1.325929	-0.449386
C	0.377551	1.292877	-0.657010
C	-0.280429	0.390128	-1.693345
C	-1.573159	-0.119195	-1.451431
H	-2.260277	0.489622	-0.873230
C	-2.070070	-1.072348	-2.501678
H	-3.126920	-1.296614	-2.344166
C	-1.204944	-2.347484	-2.392447
H	-0.271946	-2.164048	-2.929928
H	-1.704018	-3.204968	-2.850383
C	-0.852223	-2.644501	-0.916918
H	-1.359510	-3.548171	-0.570624
C	0.629201	-2.889833	-0.728100
O	1.528209	-2.299551	-1.282346
O	0.851876	-3.897082	0.130585
C	2.219843	-4.265405	0.293341
H	2.225479	-5.055466	1.043762
H	2.816531	-3.413904	0.624231
H	2.622892	-4.636076	-0.653007
C	-1.274491	-1.501352	0.062679
O	-0.459201	-1.060344	0.913153
C	-2.738431	-1.582574	0.530083
H	-1.965892	-0.659748	-3.512681
O	0.473714	0.152147	-2.645641
N	-0.101305	2.330839	0.032690
C	-1.474669	2.714853	0.210951
N	0.884349	3.050515	0.647585
C	1.972348	2.408606	0.335610
C	3.414793	2.755675	0.526143
H	3.871848	2.140757	1.311108
H	3.509217	3.809928	0.789667
O	4.040843	2.579917	-0.732110
C	4.014572	1.269448	-1.300967

H	3.984689	1.437575	-2.378740
C	2.793940	0.423834	-0.824868
H	2.416199	-0.249681	-1.596883
C	5.234241	0.443562	-0.853044
H	6.087478	1.099863	-0.659624
H	5.522386	-0.258918	-1.644930
C	4.732599	-0.294992	0.365153
C	3.338771	-0.314142	0.383095
C	5.451303	-0.889258	1.396219
H	6.537743	-0.877610	1.393199
C	4.750330	-1.481320	2.446792
H	5.296540	-1.938896	3.266386
C	3.354364	-1.486147	2.458660
H	2.825195	-1.956221	3.282246
C	2.626007	-0.907842	1.417796
H	1.536957	-0.939053	1.397052
C	-2.028759	2.502613	1.476365
C	-1.197395	1.939068	2.598281
H	-0.649830	1.047295	2.268083
H	-1.834799	1.662774	3.441966
H	-0.467045	2.676853	2.945571
C	-3.371191	2.840274	1.640939
H	-3.841050	2.676507	2.606454
C	-4.105160	3.373404	0.586232
H	-5.151132	3.624979	0.731269
C	-3.508064	3.592472	-0.650908
H	-4.083440	4.019849	-1.466919
C	-2.168619	3.268732	-0.866386
C	-1.513992	3.484407	-2.205228
H	-2.103143	4.180844	-2.805880
H	-1.434054	2.543262	-2.761831
H	-0.505127	3.894733	-2.097435
C	-3.077237	-0.831994	1.661345
C	-4.360517	-0.814127	2.190642
H	-4.576420	-0.214340	3.069994
C	-5.363246	-1.581735	1.601894
H	-6.371420	-1.583050	2.004232
C	-5.058107	-2.365627	0.497334
H	-5.795853	-2.998616	0.016129
C	-3.765411	-2.356896	-0.010370
F	-3.545891	-3.166671	-1.069022
H	-2.272356	-0.280193	2.129642

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1954.26764788	Predicted Change= -2.285562D-08	
Zero-point correction (ZPE)=	-1953.6559	0.61169
Internal Energy (U)=	-1953.6203	0.64733
Enthalpy (H)=	-1953.6193	0.64828
Gibbs Free Energy (G)=	-1953.7225	0.54510

Frequencies -- -260.3942 20.9477 30.6210

M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1954.377354

TS-V-*(R,S,S)*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

```
 ============================================================================
 # M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
  opt=(maxcycle=250,calcfc,ts,noeigentest,nofreeze,gdiis) iop(1/8=18)
  freq=noraman geom=allcheck guess=read
  #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq
 ----------------------------------------------------------------------------
  Pointgroup= C1   Stoichiometry= C34H32FN3O5   C1[X(C34H32FN3O5)]  #Atoms= 75
  Charge = 0         Multiplicity = 1
 ----------------------------------------------------------------------------
  SCF Energy= -1954.27256639       Predicted Change= -6.301316D-09
 ============================================================================
  Optimization completed.           {Found       3       times}
  Item      Max Val.    Criteria    Pass?     RMS Val.    Criteria    Pass?
  Force      0.00001 ||  0.00045   [ YES ]      0.00000 ||  0.00030   [ YES ]
  Displ      0.00159 ||  0.00180   [ YES ]      0.00159 ||  0.00180   [ YES ]
 ----------------------------------------------------------------------------
      Atomic             Coordinates (Angstroms)
       Type              X           Y           Z
 ----------------------------------------------------------------------------
      N         1.342784    0.750431    0.667329
      C         0.367911    1.075139   -0.193518
      C         0.082992    0.318974   -1.483746
      C        -1.252707   -0.187223   -1.608116
      H        -2.023501    0.475328   -1.218421
      C        -1.552923   -0.894553   -2.920460
      H        -2.627904   -0.830851   -3.119057
      C        -1.143773   -2.359307   -2.732006
      H        -0.053654   -2.447992   -2.720839
      H        -1.536654   -3.011756   -3.517680
      C        -1.678825   -2.710887   -1.351853
      H        -2.772041   -2.682364   -1.346670
      C        -1.268341   -4.040164   -0.770328
      O        -1.784575   -4.542048    0.199603
      O        -0.246658   -4.610661   -1.431018
      C         0.233231   -5.814604   -0.845646
      H         0.598148   -5.622492    0.166271
      H         1.044240   -6.157279   -1.487615
      H        -0.561583   -6.562973   -0.795494
      C        -1.097483   -1.631990   -0.374746
      O         0.112305   -1.850169   -0.010910
      C        -2.053686   -1.256554    0.761229
      H        -1.021931   -0.433466   -3.760267
      O         1.064767    0.031307   -2.150838
      N        -0.302453    2.076427    0.375206
      C        -1.338744    2.875676   -0.219166
      N         0.186913    2.375685    1.611436
      C         1.170007    1.535089    1.771365
      C         1.954609    1.256766    3.017853
      H         1.309018    0.674070    3.694341
      H         2.229329    2.189297    3.514288
      O         3.132732    0.563728    2.714595
      C         2.933506   -0.617392    1.938965
```

H	2.263506	-1.311677	2.462913
C	2.413820	-0.252719	0.533120
H	1.951713	-1.111684	0.035686
C	4.336810	-1.158181	1.660911
H	4.284000	-2.218317	1.386293
H	4.970554	-1.059670	2.546033
C	4.777671	-0.308141	0.489042
C	3.668026	0.242737	-0.155900
C	6.059791	-0.041034	0.031456
H	6.926115	-0.464719	0.531839
C	6.217912	0.795146	-1.074091
H	7.215227	1.022285	-1.438401
C	5.107351	1.343179	-1.713416
H	5.246783	1.989174	-2.574765
C	3.816304	1.063756	-1.263830
H	2.946872	1.455445	-1.781887
C	-2.559667	2.976579	0.457537
C	-2.788779	2.310216	1.785871
H	-2.342319	2.901002	2.592098
H	-2.340208	1.313711	1.823538
H	-3.858514	2.208664	1.978868
C	-3.558059	3.737175	-0.149464
H	-4.521639	3.824616	0.343667
C	-3.335556	4.372587	-1.366109
H	-4.127973	4.955886	-1.824549
C	-2.099123	4.274827	-1.991959
H	-1.920768	4.790281	-2.931018
C	-1.064447	3.527619	-1.428202
C	0.281591	3.469914	-2.106955
H	0.405987	4.343234	-2.751167
H	0.387955	2.578002	-2.733630
H	1.103226	3.467929	-1.383113
C	-1.564835	-1.294947	2.067911
C	-2.390069	-1.063892	3.166756
H	-1.984434	-1.116377	4.172741
C	-3.743609	-0.799171	2.974482
H	-4.400700	-0.635954	3.823178
C	-4.259850	-0.743338	1.681392
H	-5.306236	-0.533896	1.485179
C	-3.407223	-0.959160	0.611283
F	-3.929873	-0.871026	-0.632921
H	-0.516041	-1.556026	2.176698

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-1954.27256639	Predicted Change= -6.301316D-09
Zero-point correction (ZPE)=	-1953.6617	0.61081
Internal Energy (U)=	-1953.6258	0.64670
Enthalpy (H)=	-1953.6249	0.64765
Gibbs Free Energy (G)=	-1953.7295	0.54297

Frequencies -- -235.8270 15.2149 24.7379
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1954.389875

TS-V-*(R,R,R)*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,calcfc,ts,noeigentest,nofreeze,gdiis) iop(1/8=18) freq=noraman geom=allcheck guess=read

#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C34H32FN3O5 C1[X(C34H32FN3O5)] #Atoms= 75

Charge = 0 Multiplicity = 1

SCF Energy= -1954.27230702 Predicted Change= -2.599199D-10

Optimization completed. {Found 3 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00038	0.00180	[YES]	0.00038	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	2.345361	-1.306017	0.198958
C	1.039841	-1.292753	0.558128
C	0.493904	-0.379372	1.653721
C	-0.902718	-0.229188	1.813244
H	-1.549309	-1.047623	1.532052
C	-1.331485	0.694493	2.936915
H	-2.134946	0.249037	3.527319
C	-1.778006	2.051532	2.343765
H	-1.595764	2.874178	3.041943
H	-2.846827	2.050924	2.116003
C	-0.974696	2.224498	1.065109
H	0.095044	2.290864	1.292390
C	-1.302173	3.419128	0.206102
O	-0.512512	3.995455	-0.503276
O	-2.609113	3.742686	0.257016
C	-3.006432	4.765738	-0.649930
H	-2.818336	4.450926	-1.679747
H	-2.454001	5.687947	-0.455647
H	-4.072942	4.913023	-0.484423
C	-1.125144	0.969643	0.155667
O	-0.235921	0.769868	-0.715369
C	-2.559794	0.696190	-0.347519
H	-0.475250	0.859533	3.597616
O	1.377171	0.285290	2.208824
N	0.464385	-2.237902	-0.190690
C	-0.916167	-2.653216	-0.248111
N	1.353397	-2.855817	-1.012590
C	2.485932	-2.268454	-0.758527
C	3.829284	-2.623171	-1.323150
H	3.746373	-2.781284	-2.399958
H	4.169728	-3.561375	-0.856954
O	4.747691	-1.587842	-1.107288
C	4.815232	-1.184320	0.252826

H	5.067943	-2.048234	0.884889
C	3.493803	-0.505150	0.675955
H	3.408443	-0.456138	1.761894
C	5.829565	-0.039371	0.320452
H	6.664495	-0.233511	-0.358340
H	6.228158	0.049357	1.338577
C	4.993727	1.162607	-0.061169
C	3.634201	0.884247	0.088739
C	5.404844	2.405839	-0.521099
H	6.460958	2.629131	-0.646264
C	4.433863	3.356794	-0.838928
H	4.740857	4.332182	-1.204868
C	3.077447	3.060413	-0.710864
H	2.322191	3.794632	-0.974614
C	2.659688	1.813946	-0.241865
H	1.600688	1.574168	-0.195125
C	-1.431135	-3.386485	0.825154
C	-0.578808	-3.759187	2.010077
H	-1.071631	-4.534033	2.601130
H	-0.408786	-2.894179	2.661867
H	0.397628	-4.141336	1.694743
C	-2.780157	-3.731849	0.766340
H	-3.219743	-4.283746	1.591979
C	-3.557506	-3.374582	-0.331625
H	-4.611331	-3.635342	-0.353462
C	-2.991347	-2.700110	-1.406586
H	-3.598872	-2.429301	-2.264975
C	-1.644297	-2.334207	-1.398542
C	-1.008733	-1.646444	-2.574539
H	-1.777002	-1.359974	-3.296357
H	-0.296981	-2.315850	-3.068670
H	-0.484166	-0.744525	-2.242374
C	-2.745256	0.984522	-1.708951
C	-3.964515	0.809767	-2.352540
H	-4.058824	1.053214	-3.406486
C	-5.058957	0.322328	-1.641095
H	-6.018552	0.175876	-2.127409
C	-4.913402	0.025537	-0.292838
H	-5.731315	-0.361386	0.305853
C	-3.684245	0.222528	0.324695
F	-3.633116	-0.102271	1.633108
H	-1.878569	1.346428	-2.253629

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1954.27230702 Predicted Change= -2.599199D-10
Zero-point correction (ZPE)= -1953.6598 0.61240
Internal Energy (U)= -1953.6245 0.64773
Enthalpy (H)= -1953.6236 0.64867
Gibbs Free Energy (G)= -1953.7253 0.54693

Frequencies -- -250.0376 22.2972 35.1885
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1954.382604

TS-V-*(S,S,S)*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,calcfc,ts,noeigentest,gdiis) iop(1/8=18) freq=noraman #N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C34H32FN3O5 C1[X(C34H32FN3O5)] #Atoms= 75
Charge = 0 Multiplicity = 1

SCF Energy= -1954.27285391 Predicted Change= -3.511477D-11

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00006	0.00180	[YES]	0.00006	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-1.809513	-0.725489	0.653592
C	-0.782873	-1.176293	-0.087422
C	-0.388088	-0.560612	-1.418442
C	0.999766	-0.349061	-1.627770
H	1.675828	-1.081831	-1.206784
C	1.370559	0.305675	-2.943664
H	2.168445	-0.244304	-3.447803
C	1.793413	1.762474	-2.673296
H	1.596610	2.412542	-3.530942
H	2.863732	1.834081	-2.460095
C	1.014171	2.211896	-1.449722
H	-0.062134	2.263764	-1.654292
C	1.482810	3.547711	-0.927082
O	2.528317	4.082008	-1.210341
O	0.609020	4.077835	-0.049918
C	1.043654	5.293356	0.550668
H	1.980475	5.136176	1.091688
H	0.249254	5.589221	1.235188
H	1.203589	6.062881	-0.208372
C	1.156540	1.161199	-0.303629
O	0.265389	1.137623	0.600422
C	2.595810	1.068174	0.255851
H	0.491054	0.299331	-3.595158
O	-1.333850	-0.098414	-2.061009
N	-0.192073	-2.112716	0.648821
C	0.993858	-2.858888	0.329328
N	-0.782456	-2.254680	1.866107
C	-1.747807	-1.379487	1.848639
C	-2.617463	-0.970029	2.998738
H	-1.977784	-0.472458	3.743572
H	-3.076951	-1.845269	3.462739
O	-3.646684	-0.125713	2.563316
C	-3.191174	0.964250	1.766318
H	-2.424063	1.538787	2.301691

C	-2.675028	0.438787	0.409187
H	-2.032657	1.180902	-0.073799
C	-4.446647	1.749469	1.384319
H	-4.177992	2.771365	1.091213
H	-5.138431	1.802154	2.228993
C	-4.973186	0.958154	0.207753
C	-3.958961	0.176582	-0.349833
C	-6.254683	0.931640	-0.323957
H	-7.046721	1.535859	0.109731
C	-6.511569	0.100519	-1.413981
H	-7.511242	0.059490	-1.835924
C	-5.497189	-0.682177	-1.963511
H	-5.713435	-1.322352	-2.813210
C	-4.204734	-0.645940	-1.440033
H	-3.402857	-1.224458	-1.885034
C	0.943174	-3.784020	-0.715329
C	-0.323535	-4.043079	-1.488896
H	-0.252267	-4.992951	-2.023220
H	-0.497856	-3.255927	-2.232223
H	-1.198882	-4.084838	-0.833654
C	2.133262	-4.433710	-1.040611
H	2.133544	-5.158565	-1.849469
C	3.309394	-4.151141	-0.353680
H	4.228948	-4.656513	-0.632039
C	3.317010	-3.223326	0.682408
H	4.239757	-2.995027	1.208010
C	2.149807	-2.556975	1.056679
C	2.143823	-1.548163	2.173748
H	1.809791	-2.015047	3.106817
H	1.475100	-0.708663	1.955752
H	3.150000	-1.146281	2.322419
C	2.762656	1.704160	1.496713
C	3.975089	1.717375	2.173395
H	4.057336	2.226705	3.128517
C	5.078627	1.062360	1.629090
H	6.031384	1.052391	2.149366
C	4.951619	0.422498	0.403552
H	5.780375	-0.095264	-0.067800
C	3.731978	0.453454	-0.263790
F	3.707162	-0.174652	-1.457906
H	1.879853	2.168436	1.925465

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1954.27285391 Predicted Change= -3.511477D-11

Zero-point correction (ZPE)=	-1953.6609	0.61187
Internal Energy (U)=	-1953.6254	0.64744
Enthalpy (H)=	-1953.6244	0.64839
Gibbs Free Energy (G)=	-1953.7279	0.54487

Frequencies -- -262.7897 21.7884 27.2544
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1954.384783

—2-OMePh Substrate—
***(R)*-IV**

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C35H35N3O6 C1[X(C35H35N3O6)] #Atoms= 79
Charge = 0 Multiplicity = 1

SCF Energy= -1969.56513087 Predicted Change= -1.952173D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00196	0.00180	[NO]	0.00196	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-1.512232	-1.594728	-0.500977
C	-2.131657	-0.426604	-0.248231
C	-1.428258	0.906475	-0.283301
C	-1.608468	1.684273	0.819568
H	-2.281833	1.328270	1.597235
C	-0.865456	2.973850	1.031353
H	-0.752048	3.497082	0.075683
C	0.528570	2.760091	1.653539
H	0.450681	2.074230	2.504136
H	0.928925	3.702494	2.039074
C	1.510998	2.168628	0.637661
H	1.004678	1.437633	-0.004192
C	1.984328	3.263293	-0.310657
O	1.586865	4.401311	-0.308847
O	2.922323	2.833084	-1.177722
C	3.396577	3.826358	-2.083255
H	2.584312	4.174046	-2.726159
H	4.175138	3.341882	-2.672457
H	3.804116	4.679833	-1.536965
C	2.710138	1.492763	1.312755
O	2.941236	1.739292	2.480732
C	3.632878	0.547805	0.579476
H	-1.447026	3.631270	1.686996
O	-0.720336	1.053546	-1.340228
N	-3.422435	-0.744483	-0.138586
C	-4.514681	0.174315	0.024925
N	-3.649464	-2.086117	-0.316317
C	-2.462364	-2.572923	-0.536714
C	-2.058839	-3.972571	-0.899756
H	-2.322120	-4.154982	-1.953189
H	-2.589682	-4.696313	-0.278890
O	-0.680891	-4.153804	-0.684781

C	0.134787	-3.194956	-1.351596
H	-0.076284	-3.214299	-2.430312
C	-0.084685	-1.801991	-0.729305
H	0.227677	-0.983380	-1.385192
C	1.588197	-3.516938	-0.991581
H	2.263239	-3.103906	-1.753059
H	1.743508	-4.598267	-0.945329
C	1.772570	-2.807974	0.331266
C	0.779379	-1.846000	0.511715
C	2.759069	-2.985091	1.291898
H	3.546600	-3.719737	1.149038
C	2.719048	-2.204132	2.446955
H	3.485861	-2.327848	3.205387
C	1.710551	-1.259489	2.633595
H	1.706279	-0.642364	3.526474
C	0.733660	-1.060907	1.656086
H	-0.033465	-0.299806	1.780565
C	-4.819237	1.018682	-1.046265
C	-4.053185	0.952679	-2.342308
H	-4.048714	-0.070723	-2.735189
H	-3.008183	1.264350	-2.225224
H	-4.521619	1.598249	-3.088368
C	-5.873166	1.912833	-0.861587
H	-6.137719	2.587620	-1.670259
C	-6.581281	1.945249	0.335431
H	-7.396270	2.651557	0.459524
C	-6.253104	1.080567	1.374147
H	-6.808993	1.110335	2.306726
C	-5.203031	0.173097	1.238600
C	-4.813651	-0.767412	2.347996
H	-3.745529	-0.685517	2.579254
H	-5.006865	-1.807661	2.067838
H	-5.376757	-0.542524	3.256091
C	4.831019	0.239280	1.229904
C	5.788495	-0.583669	0.652214
H	6.714469	-0.797149	1.175899
C	5.554648	-1.114058	-0.613559
H	6.298285	-1.747465	-1.088821
C	4.363502	-0.842362	-1.277317
H	4.175867	-1.266676	-2.258614
C	3.393283	-0.035218	-0.677533
H	4.990808	0.680814	2.208148
O	2.185252	0.170305	-1.255856
C	2.104448	0.293619	-2.662704
H	2.168231	-0.686159	-3.156645
H	1.125105	0.739614	-2.846582
H	2.902166	0.943548	-3.038326

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1969.56513087 Predicted Change= -1.952173D-08
Zero-point correction (ZPE)= -1968.9121 0.65300
Internal Energy (U)= -1968.8736 0.69149

Enthalpy (H)=	-1968.8726	0.69243
Gibbs Free Energy (G)=	-1968.9818	0.58330

Frequencies -- 26.2079 32.9433 33.7113

M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1969.682038

***(S)*-IV**

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

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M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

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Pointgroup= C1 Stoichiometry= C35H35N3O6 C1[X(C35H35N3O6)] #Atoms= 79
Charge = 0 Multiplicity = 1

SCF Energy= -1969.56629281 Predicted Change= -6.492674D-09

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Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00305	0.00180	[NO]	0.00305	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-1.439610	1.628422	0.251870
C	-1.974923	0.393809	0.154844
C	-1.217855	-0.867843	0.455112
C	-1.479912	-1.973247	-0.297143
H	-2.212016	-1.935219	-1.099033
C	-0.781218	-3.254751	0.058513
H	-0.658707	-3.290765	1.146962
C	0.608201	-3.429561	-0.577676
H	0.507427	-3.517965	-1.665996
H	1.064071	-4.353050	-0.203040
C	1.573022	-2.262672	-0.304306
H	1.133501	-1.326660	-0.653043
C	2.804949	-2.483066	-1.157469
O	2.883058	-2.232804	-2.337054
O	3.793290	-3.081539	-0.468752
C	4.958789	-3.387148	-1.225328
H	5.630270	-3.906101	-0.542531
H	5.425847	-2.470957	-1.596907
H	4.706585	-4.022076	-2.077644
C	1.903344	-2.117577	1.181328
O	1.735061	-3.039656	1.948524
C	2.419966	-0.801308	1.709309
H	-1.395208	-4.114595	-0.233039
O	-0.410390	-0.714309	1.432500
N	-3.280939	0.602622	-0.029924
C	-4.315891	-0.391742	-0.097430
N	-3.600032	1.934039	-0.058716
C	-2.456602	2.529277	0.116559
C	-2.172573	3.992448	0.265500
H	-2.415873	4.300353	1.294488
H	-2.787193	4.571328	-0.425832
O	-0.824885	4.249183	-0.033626
C	0.087880	3.492563	0.756000

H	-0.082623	3.697753	1.821705
C	-0.027087	1.987681	0.420007
H	0.361883	1.340247	1.216572
C	1.487740	3.865659	0.261281
H	2.224258	3.656153	1.046464
H	1.532579	4.928598	0.009389
C	1.680153	2.941814	-0.919882
C	0.793213	1.865783	-0.845416
C	2.558757	3.046003	-1.988963
H	3.237349	3.891656	-2.068700
C	2.550955	2.048096	-2.967036
H	3.240375	2.112264	-3.804023
C	1.673426	0.969434	-2.879350
H	1.697884	0.183618	-3.627164
C	0.767554	0.880583	-1.820616
H	0.067676	0.049745	-1.764623
C	-4.662191	-1.057154	1.080921
C	-3.977567	-0.744365	2.385407
H	-4.017380	0.330029	2.597622
H	-2.921700	-1.039290	2.372996
H	-4.469588	-1.269905	3.206475
C	-5.668377	-2.018165	0.987253
H	-5.963182	-2.560236	1.880879
C	-6.290288	-2.284846	-0.228469
H	-7.071074	-3.037412	-0.280716
C	-5.919312	-1.595995	-1.378651
H	-6.406033	-1.809765	-2.325756
C	-4.914463	-0.630473	-1.334789
C	-4.470484	0.119052	-2.562906
H	-4.978898	-0.262445	-3.450754
H	-3.390083	0.014586	-2.716635
H	-4.685478	1.188446	-2.471831
C	3.171267	0.120949	0.965953
C	3.632123	1.299642	1.560906
H	4.228298	1.999511	0.984708
C	3.321952	1.573045	2.889759
H	3.683835	2.493016	3.341331
C	2.565258	0.672059	3.636005
H	2.323418	0.884554	4.672312
C	2.132921	-0.507341	3.042973
O	3.420313	-0.179762	-0.335923
C	4.585533	0.338197	-0.943475
H	4.629460	-0.134837	-1.926945
H	4.526121	1.422718	-1.076313
H	5.474678	0.082431	-0.353444
H	1.542448	-1.233243	3.591746

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1969.56629281 Predicted Change= -6.492674D-09
Zero-point correction (ZPE)= -1968.9138 0.65241
Internal Energy (U)= -1968.8751 0.69117
Enthalpy (H)= -1968.8741 0.69211

Gibbs Free Energy (G)= -1968.9858 0.58043

Frequencies -- 8.9581 25.6388 26.8358

M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1969.685099

TS-V-*(S,R,R)*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

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M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,calcfc,ts,noeigentest,gdiis) iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

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Pointgroup= C1 Stoichiometry= C35H35N3O6 C1[X(C35H35N3O6)] #Atoms= 79
Charge = 0 Multiplicity = 1

SCF Energy= -1969.53737937 Predicted Change= -2.642704D-10

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Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00031	0.00180	[YES]	0.00031	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-1.058229	-0.881811	-0.737129
C	0.006381	-1.248403	0.012783
C	0.484008	-0.751483	1.380790
C	0.144643	0.591195	1.732206
H	-0.875438	0.902899	1.539455
C	0.760498	1.086908	3.025991
H	0.158709	1.917403	3.411475
C	2.172189	1.579227	2.690910
H	2.829772	0.729816	2.480967
H	2.621551	2.163545	3.499354
C	2.017014	2.391504	1.413757
H	1.436352	3.300128	1.600729
C	3.341027	2.789334	0.809114
O	4.432798	2.519954	1.241824
O	3.156713	3.522359	-0.309606
C	4.354315	3.866345	-0.994248
H	4.045526	4.428428	-1.875377
H	4.897474	2.963932	-1.285220
H	5.001700	4.475713	-0.358484
C	1.301174	1.485503	0.368214
O	2.049715	0.635440	-0.205240
C	0.272713	2.174840	-0.536183
H	0.790050	0.301347	3.789393
O	1.294381	-1.478660	1.934606
N	0.674413	-2.130232	-0.733057
C	1.827293	-2.945926	-0.417505
N	0.086808	-2.323695	-1.943383
C	-0.958458	-1.553760	-1.923954
C	-1.974456	-1.352673	-3.002591
H	-2.088138	-2.270937	-3.580388
H	-1.639382	-0.542955	-3.669182
O	-3.214640	-1.040343	-2.417758
C	-3.137046	0.144660	-1.643448

H	-2.773144	0.973896	-2.262026
C	-2.234550	-0.067042	-0.399098
H	-1.880606	0.910634	-0.069599
C	-4.522587	0.382207	-1.038296
H	-5.301226	0.069692	-1.739190
H	-4.656584	1.450920	-0.829433
C	-4.487728	-0.423349	0.240137
C	-3.170203	-0.704319	0.605890
C	-5.541683	-0.869723	1.025508
H	-6.569708	-0.660177	0.743654
C	-5.259210	-1.605766	2.176290
H	-6.073765	-1.968387	2.795609
C	-3.941887	-1.886847	2.535304
H	-3.736621	-2.462926	3.431768
C	-2.880637	-1.432535	1.752265
H	-1.856487	-1.649677	2.043794
C	3.023480	-2.683604	-1.087511
C	3.158237	-1.548709	-2.065163
H	2.925497	-0.597105	-1.576396
H	2.472045	-1.684115	-2.908297
H	4.177081	-1.514374	-2.457843
C	4.094302	-3.535350	-0.809311
H	5.045853	-3.353333	-1.299888
C	3.957342	-4.598634	0.074020
H	4.805243	-5.245901	0.276555
C	2.735816	-4.846414	0.690581
H	2.625384	-5.686595	1.369983
C	1.637860	-4.023978	0.450352
C	0.316602	-4.284228	1.121960
H	0.273478	-5.311135	1.491869
H	-0.526816	-4.137686	0.437886
H	0.193197	-3.604435	1.971274
C	-0.718595	3.085812	-0.115500
C	-1.594352	3.663475	-1.039087
H	-2.352418	4.367301	-0.715265
C	-1.484465	3.353353	-2.395941
H	-2.159578	3.824737	-3.104649
C	-0.520660	2.451175	-2.828391
H	-0.423440	2.214665	-3.884366
C	0.340653	1.873518	-1.894556
H	1.120331	1.176056	-2.189368
O	-0.803004	3.324687	1.224391
C	-1.790700	4.219727	1.684727
H	-2.799128	3.855219	1.450462
H	-1.667395	4.271272	2.766582
H	-1.657983	5.218574	1.253315

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

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SCF Energy= -1969.53737937 Predicted Change= -2.642704D-10
Zero-point correction (ZPE)= -1968.8853 0.65203
Internal Energy (U)= -1968.8475 0.68979
Enthalpy (H)= -1968.8466 0.69073

Gibbs Free Energy (G)=	-1968.9554	0.58191

Frequencies --	-286.5602	16.4568	21.3561

M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1969.657747

TS-V-*(R,S,S)*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

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M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,calcfc,ts,noeigentest,gdiis) iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

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Pointgroup= C1 Stoichiometry= C35H35N3O6 C1[X(C35H35N3O6)] #Atoms= 79
Charge = 0 Multiplicity = 1

SCF Energy= -1969.54226807 Predicted Change= -5.784934D-09

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Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00186	0.00180	[NO]	0.00186	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-1.497691	-0.762816	0.646686
C	-0.505868	-1.086233	-0.194461
C	-0.196528	-0.330743	-1.480284
C	1.142683	0.172059	-1.573040
H	1.902914	-0.493525	-1.170022
C	1.476764	0.882590	-2.874824
H	2.556639	0.814377	-3.045922
C	1.070080	2.348360	-2.689049
H	-0.019876	2.439152	-2.701147
H	1.480835	3.002314	-3.464599
C	1.575804	2.693956	-1.295948
H	2.667989	2.672861	-1.266808
C	1.140570	4.015550	-0.716550
O	1.633186	4.520035	0.264462
O	0.126885	4.581817	-1.395251
C	-0.377805	5.775021	-0.810497
H	-0.768151	5.569220	0.189285
H	-1.174481	6.118583	-1.469948
H	0.408595	6.529726	-0.730567
C	0.977237	1.603669	-0.339713
O	-0.245041	1.827786	-0.010951
C	1.898056	1.221767	0.828141
H	0.964243	0.428185	-3.729929
O	-1.164532	-0.047921	-2.169244
N	0.154750	-2.086087	0.388774
C	1.214719	-2.873039	-0.178447
N	-0.358438	-2.385093	1.615509
C	-1.345256	-1.545342	1.755210
C	-2.151383	-1.262752	2.986918
H	-1.514582	-0.682823	3.674020
H	-2.440070	-2.193380	3.479030
O	-3.320414	-0.563788	2.661954
C	-3.100312	0.615846	1.889159

H	-2.434435	1.305572	2.424096
C	-2.559279	0.246733	0.492926
H	-2.080727	1.101910	0.003963
C	-4.494848	1.166301	1.587103
H	-4.429584	2.226105	1.313778
H	-5.144874	1.072207	2.460831
C	-4.921483	0.320054	0.407191
C	-3.804699	-0.239381	-0.217871
C	-6.197176	0.063482	-0.073843
H	-7.069073	0.493974	0.410828
C	-6.341935	-0.770866	-1.182653
H	-7.334249	-0.989218	-1.565641
C	-5.224350	-1.327791	-1.801791
H	-5.353079	-1.972285	-2.665966
C	-3.939509	-1.059001	-1.328511
H	-3.063550	-1.457271	-1.830143
C	0.987519	-3.513214	-1.403389
C	-0.335459	-3.464838	-2.126799
H	-0.424744	-2.574839	-2.758603
H	-1.181389	-3.465434	-1.431932
H	-0.432377	-4.340518	-2.772573
C	2.049006	-4.240077	-1.943988
H	1.906066	-4.745359	-2.894600
C	3.266628	-4.330635	-1.281783
H	4.079809	-4.899141	-1.722338
C	3.441956	-3.709231	-0.050017
H	4.388974	-3.794705	0.475181
C	2.415116	-2.969430	0.535555
C	2.593854	-2.324341	1.881844
H	3.655662	-2.210130	2.109389
H	2.132648	-2.937969	2.662354
H	2.129909	-1.335344	1.924345
C	1.341286	1.269317	2.103123
C	2.097364	1.038482	3.252642
H	1.636964	1.098916	4.234338
C	3.453307	0.770503	3.128074
H	4.068067	0.609514	4.008974
C	4.041562	0.703070	1.864749
H	5.100513	0.485875	1.784509
C	3.268763	0.909480	0.721544
O	3.781116	0.818566	-0.541525
C	5.126076	0.424916	-0.685284
H	5.298451	-0.563511	-0.239962
H	5.312627	0.376694	-1.758584
H	5.809336	1.151302	-0.229766
H	0.290279	1.539507	2.149151

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1969.54226807 Predicted Change= -5.784934D-09

Zero-point correction (ZPE)=	-1968.8894	0.65280
Internal Energy (U)=	-1968.8521	0.69010
Enthalpy (H)=	-1968.8512	0.69104

Gibbs Free Energy (G)=	-1968.9582	0.58400

Frequencies --	-249.5503	21.5826	22.9568

M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1969.662038

TS-V-*(R,R,R)*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest,nofreeze,gdiis) iop(1/8=18)
freq=noraman geom=allcheck guess=read
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C35H35N3O6 C1[X(C35H35N3O6)] #Atoms= 79
Charge = 0 Multiplicity = 1

SCF Energy= -1969.53936259 Predicted Change= -7.796367D-10

==========

Optimization completed. {Found 3 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00090	0.00180	[YES]	0.00090	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	2.449868	-1.330289	0.197894
C	1.136643	-1.301109	0.524722
C	0.581173	-0.406406	1.632179
C	-0.817010	-0.237487	1.750145
H	-1.465578	-1.039321	1.432869
C	-1.271960	0.663532	2.880763
H	-2.098421	0.209986	3.433771
C	-1.692854	2.035212	2.304513
H	-1.523784	2.843448	3.022942
H	-2.754581	2.042957	2.045814
C	-0.856807	2.224748	1.050030
H	0.207952	2.282547	1.302370
C	-1.162181	3.426293	0.193752
O	-0.369739	3.964366	-0.543053
O	-2.454787	3.799219	0.272021
C	-2.843292	4.798400	-0.663983
H	-2.728491	4.420023	-1.683527
H	-2.232363	5.696375	-0.547079
H	-3.890460	5.013153	-0.454151
C	-0.990678	0.980955	0.115845
O	-0.063471	0.784999	-0.719507
C	-2.409228	0.772533	-0.476086
H	-0.436822	0.805958	3.573536
O	1.461521	0.222595	2.230945
N	0.562061	-2.211883	-0.266771
C	-0.823851	-2.598316	-0.376495
N	1.460281	-2.822821	-1.084680
C	2.596773	-2.266049	-0.784582
C	3.947729	-2.630431	-1.324295
H	3.890444	-2.757185	-2.406855
H	4.258502	-3.587540	-0.876065
O	4.880051	-1.619857	-1.055938

C	4.918905	-1.252538	0.315447
H	5.141944	-2.136507	0.930869
C	3.598725	-0.562563	0.723824
H	3.487723	-0.540406	1.808293
C	5.949133	-0.126251	0.439090
H	6.798739	-0.316133	-0.222506
H	6.321899	-0.070795	1.469363
C	5.142220	1.098712	0.067986
C	3.775175	0.838724	0.176431
C	5.584256	2.346181	-0.349847
H	6.646545	2.555989	-0.441865
C	4.636201	3.319313	-0.669873
H	4.966903	4.297986	-1.005080
C	3.272550	3.040805	-0.585155
H	2.536025	3.791992	-0.854085
C	2.823055	1.790705	-0.156714
H	1.759170	1.566071	-0.144081
C	-1.384788	-3.349622	0.660975
C	-0.576205	-3.767963	1.861122
H	-1.100545	-4.548174	2.417184
H	-0.408981	-2.922479	2.538583
H	0.401874	-4.161271	1.565113
C	-2.736440	-3.671550	0.550994
H	-3.209600	-4.239698	1.347102
C	-3.471470	-3.278770	-0.564459
H	-4.526720	-3.528432	-0.630966
C	-2.860310	-2.587991	-1.603613
H	-3.435839	-2.286998	-2.474003
C	-1.509648	-2.240607	-1.541487
C	-0.830688	-1.527164	-2.677347
H	-1.573660	-1.210093	-3.412608
H	-0.111298	-2.190364	-3.168853
H	-0.308149	-0.640852	-2.301248
C	-2.487404	1.183358	-1.812239
C	-3.659189	1.109645	-2.559696
H	-3.669170	1.447002	-3.591565
C	-4.806611	0.601986	-1.966329
H	-5.736406	0.530898	-2.523447
C	-4.770211	0.180956	-0.641218
H	-5.670428	-0.219832	-0.191325
C	-3.589572	0.265718	0.104530
H	-1.574321	1.564030	-2.259759
O	-3.540130	-0.164291	1.396811
C	-4.687400	-0.753117	1.959587
H	-5.002029	-1.636270	1.389551
H	-4.401810	-1.055467	2.968443
H	-5.519751	-0.040932	2.016817

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1969.53936259 Predicted Change= -7.796367D-10
Zero-point correction (ZPE)= -1968.8859 0.65341
Internal Energy (U)= -1968.8488 0.69052

Enthalpy (H)=	-1968.8478	0.69147
Gibbs Free Energy (G)=	-1968.9538	0.58555

Frequencies --	-278.1862	19.8730	33.1533

M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1969.651892

TS-V-*(S,S,S)*

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,calcfc,ts,noeigentest,gdiis) iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C35H35N3O6 C1[X(C35H35N3O6)] #Atoms= 79
Charge = 0 Multiplicity = 1

SCF Energy= -1969.54093721 Predicted Change= -4.659666D-10

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00043	0.00180	[YES]	0.00043	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-1.977492	-0.743319	0.639006
C	-0.915041	-1.177646	-0.060167
C	-0.505968	-0.588496	-1.401037
C	0.881244	-0.358142	-1.584285
H	1.561763	-1.065965	-1.133330
C	1.278971	0.266857	-2.905387
H	2.076278	-0.305562	-3.388125
C	1.724308	1.718653	-2.653273
H	1.563424	2.357906	-3.526760
H	2.788946	1.767870	-2.408828
C	0.925572	2.205909	-1.457433
H	-0.144083	2.281933	-1.689091
C	1.416747	3.541282	-0.953750
O	2.456821	4.068703	-1.268309
O	0.570563	4.082722	-0.055798
C	1.042710	5.283682	0.544794
H	1.985438	5.100065	1.067642
H	0.267963	5.591628	1.246505
H	1.206044	6.055788	-0.210887
C	1.007831	1.172424	-0.285913
O	0.063953	1.170070	0.566744
C	2.416425	1.110901	0.367766
H	0.409768	0.261836	-3.571201
O	-1.450176	-0.172902	-2.076514
N	-0.320554	-2.081880	0.713715
C	0.919893	-2.764762	0.465356
N	-0.945954	-2.217453	1.914786
C	-1.935007	-1.372072	1.848977
C	-2.847515	-0.962714	2.965762
H	-2.238367	-0.450537	3.726127
H	-3.311812	-1.838794	3.423563
O	-3.871815	-0.135227	2.488988
C	-3.404208	0.947278	1.688606

H	-2.654422	1.534787	2.234531
C	-2.851602	0.405751	0.352630
H	-2.204224	1.146133	-0.127003
C	-4.655230	1.717448	1.265032
H	-4.385996	2.735816	0.960326
H	-5.367207	1.780448	2.092043
C	-5.148721	0.901890	0.090380
C	-4.115615	0.119124	-0.430212
C	-6.417653	0.855183	-0.469246
H	-7.224084	1.460369	-0.064334
C	-6.643281	0.002541	-1.549577
H	-7.633002	-0.054995	-1.992594
C	-5.610416	-0.780872	-2.062188
H	-5.802231	-1.438602	-2.904358
C	-4.330240	-0.724181	-1.510963
H	-3.513588	-1.303155	-1.927253
C	0.979317	-3.700525	-0.569100
C	-0.230539	-4.047971	-1.397075
H	-0.075588	-4.997802	-1.913523
H	-0.417810	-3.280689	-2.157887
H	-1.131112	-4.135802	-0.781871
C	2.224274	-4.269992	-0.834875
H	2.309862	-5.002166	-1.632474
C	3.346652	-3.901423	-0.099752
H	4.310124	-4.347571	-0.328938
C	3.243967	-2.968024	0.926843
H	4.123831	-2.670982	1.491412
C	2.018311	-2.381059	1.242707
C	1.893042	-1.373943	2.353895
H	1.506751	-1.854283	3.259481
H	1.213521	-0.559705	2.080761
H	2.870256	-0.935652	2.574678
C	2.471871	1.825742	1.570056
C	3.621485	1.909582	2.347937
H	3.617530	2.483629	3.269124
C	4.763927	1.236369	1.936551
H	5.673435	1.269507	2.529213
C	4.750323	0.514234	0.747384
H	5.649916	-0.002076	0.434467
C	3.598217	0.466019	-0.047872
H	1.551094	2.300800	1.893745
O	3.583479	-0.214082	-1.229382
C	4.769483	-0.827901	-1.673053
H	5.103771	-1.607416	-0.976927
H	4.525772	-1.285832	-2.632934
H	5.572220	-0.093540	-1.810786

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1969.54093721 Predicted Change= -4.659666D-10

Zero-point correction (ZPE)=	-1968.8875	0.65335
Internal Energy (U)=	-1968.8504	0.69048
Enthalpy (H)=	-1968.8495	0.69143

Gibbs Free Energy (G)=	-1968.9555	0.58541

Frequencies --	-280.3552	22.5330	28.8409

M06-2X/6-31+G(d,p)/PCM(DCE) SP: -1969.655002

Energetic Penalty from Loss of Conjugation (see Table 4)

—Benzaldehyde—
GS-0°

```
---------------------------------------------------------------------
 Using  Gaussian 09:  AM64L-G09RevC.01 23-Sep-2011
=====================================================================
 # M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
 opt=(maxcycle=250) freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
---------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C7H6O   C1[X(C7H6O)]  #Atoms= 14
 Charge = 0         Multiplicity = 1
---------------------------------------------------------------------
 SCF Energy= -345.419894063       Predicted Change= -1.791021D-07
=====================================================================
 Optimization completed.           {Found       2       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00013 ||  0.00045   [ YES ]      0.00004 ||  0.00030   [ YES ]
 Displ      0.00058 ||  0.00180   [ YES ]      0.00058 ||  0.00180   [ YES ]
---------------------------------------------------------------------
     Atomic              Coordinates (Angstroms)
      Type              X              Y          Z
---------------------------------------------------------------------
      C       -0.360987       1.290505       0.000007
      C       -1.732612       1.056242       0.000021
      C       -2.208097      -0.253119       0.000021
      C       -1.318287      -1.329032      -0.000013
      C        0.050244      -1.096007      -0.000041
      C        0.528812       0.216815      -0.000022
      H        0.024685       2.307790       0.000021
      H       -2.428388       1.889205       0.000043
      H       -3.278162      -0.437996       0.000044
      H       -1.697529      -2.346147      -0.000016
      H        0.768276      -1.910737      -0.000061
      C        1.989680       0.470533      -0.000050
      O        2.829951      -0.397579       0.000083
      H        2.278994       1.542893      -0.000229
---------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin       Pressure= 1.00000 Atm
=====================================================================
 SCF Energy=     -345.419894063   Predicted Change= -1.791021D-07
 Zero-point correction (ZPE)=              -345.3085       0.11132
 Internal Energy (U)=                      -345.3023       0.11758
 Enthalpy (H)=                             -345.3013       0.11853
 Gibbs Free Energy (G)=                    -345.3390       0.08082
---------------------------------------------------------------------
 Frequencies --   122.6338             223.2633             246.2309
M06-2X/6-31+G(d,p)/PCM(DCE) SP:  -345.445236
```

GS-34°

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,modredundant) freq=noraman
Modredundant Input: D 5 6 13 12 F
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C7H6O C1[X(C7H6O)] #Atoms= 14
Charge = 0 Multiplicity = 1

SCF Energy= -345.415883146 Predicted Change= -2.012823D-08

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00004	0.00045	[YES]	0.00001	0.00030	[YES]
Displ	0.00041	0.00180	[YES]	0.00041	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.336621	1.286007	-0.000916
C	1.709244	1.073947	-0.080712
C	2.211232	-0.225798	-0.056651
C	1.345615	-1.315490	0.040992
C	-0.026974	-1.106541	0.095914
C	-0.530734	0.195424	0.051701
H	-0.065824	2.296479	0.007444
H	2.388015	1.918306	-0.147267
H	3.283448	-0.390668	-0.103506
H	1.744724	-2.324290	0.078206
H	-0.725247	-1.935520	0.162201
C	-1.996448	0.407193	0.181333
O	-2.827541	-0.351660	-0.256608
H	-2.296128	1.360522	0.665824

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -345.415883146 Predicted Change= -2.012823D-08

Zero-point correction (ZPE)=	-345.3047	0.11113
Internal Energy (U)=	-345.2983	0.11751
Enthalpy (H)=	-345.2974	0.11845
Gibbs Free Energy (G)=	-345.3354	0.08041

Frequencies -- 108.1004 186.9145 243.2398

M06-2X/6-31+G(d,p)/PCM(DCE) SP: -345.441798

TS-0°

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,modredundant) freq=noraman
Modredundant Input: D 5 6 13 12 F
Modredundant Input: B 12 15 F
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C7H7O(1-) C1[X(C7H7O)] #Atoms= 15
Charge = -1 Multiplicity = 1

SCF Energy= -345.946931958 Predicted Change= -5.220313D-08

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00003	0.00045	[YES]	0.00001	0.00030	[YES]
Displ	0.00108	0.00180	[YES]	0.00108	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.406585	1.280617	-0.037114
C	1.770114	1.040985	-0.069863
C	2.260523	-0.271889	-0.020476
C	1.355989	-1.326266	0.049036
C	-0.017770	-1.082607	0.060045
C	-0.512683	0.224067	0.035838
H	0.015317	2.296582	-0.020225
H	2.466349	1.876078	-0.123000
H	3.331422	-0.460043	-0.033442
H	1.723418	-2.350854	0.082140
H	-0.746590	-1.887565	0.084105
C	-1.994845	0.438685	-0.056635
O	-2.779586	-0.523667	-0.111872
H	-2.252093	1.417038	-0.510408
H	-1.908615	1.476554	1.650817

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-345.946931958	Predicted Change= -5.220313D-08
Zero-point correction (ZPE)=	-345.8339	0.11301
Internal Energy (U)=	-345.8274	0.11945
Enthalpy (H)=	-345.8265	0.12040
Gibbs Free Energy (G)=	-345.8643	0.08258

Frequencies -- -540.7046 163.1241 223.3664
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -346.073882

TS-34°

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,modredundant) freq=noraman
Modredundant Input: D 5 6 13 12 F
Modredundant Input: B 12 15 F
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C7H7O(1-) C1[X(C7H7O)] #Atoms= 15
Charge = -1 Multiplicity = 1

SCF Energy= -345.942834096 Predicted Change= -4.870032D-07

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00024	0.00045	[YES]	0.00005	0.00030	[YES]
Displ	0.00179	0.00180	[YES]	0.00179	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.395907	1.282381	0.013175
C	1.766294	1.052364	0.025561
C	2.267961	-0.252932	0.022974
C	1.375863	-1.321173	-0.007629
C	0.002068	-1.085082	-0.042181
C	-0.509809	0.216794	-0.014334
H	-0.034760	2.279859	0.073903
H	2.455232	1.894450	0.057602
H	3.340648	-0.430498	0.056036
H	1.752471	-2.342580	-0.013926
H	-0.714211	-1.901855	-0.075004
C	-2.003463	0.360136	-0.218915
O	-2.778050	-0.512788	0.212150
H	-2.236950	0.937953	-1.135071
H	-2.106950	2.150054	0.667362

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -345.942834096 Predicted Change= -4.870032D-07

Zero-point correction (ZPE)=	-345.8294	0.11338
Internal Energy (U)=	-345.8230	0.11979
Enthalpy (H)=	-345.8220	0.12073
Gibbs Free Energy (G)=	-345.8599	0.08290

Frequencies -- -618.6265 146.9034 215.4274
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -346.070968

—2-fluorobenzaldehyde—

GS-0°
Supporting Information: GS-benzaldehyde-2F.log

```
 Using  Gaussian 09:  AM64L-G09RevC.01 23-Sep-2011
 ======================================================================
 # M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
 opt=(maxcycle=250) freq=noraman
 #N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq
 ----------------------------------------------------------------------
 Pointgroup= C1   Stoichiometry= C7H5FO   C1[X(C7H5FO)]  #Atoms= 14
 Charge = 0         Multiplicity = 1
 ----------------------------------------------------------------------
 SCF Energy= -444.624760642       Predicted Change= -5.877905D-08
 ======================================================================
 Optimization completed.           {Found       2       times}
 Item      Max Val.    Criteria    Pass?      RMS Val.    Criteria    Pass?
 Force      0.00009 ||  0.00045   [ YES ]      0.00002 ||  0.00030   [ YES ]
 Displ      0.00056 ||  0.00180   [ YES ]      0.00056 ||  0.00180   [ YES ]
 ----------------------------------------------------------------------
     Atomic              Coordinates (Angstroms)
      Type             X             Y         Z
 ----------------------------------------------------------------------
      C       -0.369974       0.958548      -0.000029
      C       -1.743204       0.769216      -0.000068
      C       -2.229973      -0.533878      -0.000032
      C       -1.355138      -1.623304       0.000025
      C        0.014913      -1.405968       0.000077
      C        0.527975      -0.104964       0.000064
      F        0.109364       2.211472       0.000009
      H       -2.398826       1.632519      -0.000114
      H       -3.302622      -0.700389      -0.000063
      H       -1.747679      -2.634462       0.000047
      H        0.725038      -2.227494       0.000152
      C        1.994233       0.122789       0.000124
      O        2.798164      -0.780694      -0.000187
      H        2.321492       1.177494       0.000422
 ----------------------------------------------------------------------
 Statistical Thermodynamic Analysis
 Temperature= 298.150 Kelvin       Pressure= 1.00000 Atm
 ======================================================================
 SCF Energy=     -444.624760642   Predicted Change= -5.877905D-08
 Zero-point correction (ZPE)=              -444.5213       0.10341
 Internal Energy (U)=                      -444.5142       0.11048
 Enthalpy (H)=                             -444.5133       0.11142
 Gibbs Free Energy (G)=                    -444.5530       0.07167
 ----------------------------------------------------------------------
 Frequencies --   122.1716             197.3278             205.6357
M06-2X/6-31+G(d,p)/PCM(DCE) SP:  -444.654146
```

GS-34°

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,modredundant) freq=noraman
Modredundant Input: D 5 6 13 12 F
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C7H5FO C1[X(C7H5FO)] #Atoms= 14
Charge = 0 Multiplicity = 1

SCF Energy= -444.620981071 Predicted Change= -1.020215D-07

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00010	0.00045	[YES]	0.00002	0.00030	[YES]
Displ	0.00057	0.00180	[YES]	0.00057	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.336523	0.958232	-0.008146
C	1.713326	0.818759	-0.069935
C	2.249454	-0.465685	-0.044160
C	1.418675	-1.584482	0.037987
C	0.040619	-1.417426	0.082051
C	-0.518832	-0.137499	0.036638
F	-0.196493	2.189464	-0.007841
H	2.336437	1.704136	-0.126480
H	3.326750	-0.592494	-0.083025
H	1.848913	-2.579566	0.073955
H	-0.633701	-2.266307	0.143123
C	-1.988809	0.030490	0.186507
O	-2.786826	-0.767917	-0.243902
H	-2.321094	0.958052	0.688556

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -444.620981071 Predicted Change= -1.020215D-07
Zero-point correction (ZPE)= -444.5177 0.10322
Internal Energy (U)= -444.5105 0.11038
Enthalpy (H)= -444.5096 0.11132
Gibbs Free Energy (G)= -444.5497 0.07124

Frequencies -- 103.3907 159.6882 217.3730
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -444.651215

TS-0°

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,modredundant) freq=noraman
Modredundant Input: D 5 6 13 12 F
Modredundant Input: B 12 15 F
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C7H6FO(1-) C1[X(C7H6FO)] #Atoms= 15
Charge = -1 Multiplicity = 1

SCF Energy= -445.156273357 Predicted Change= -1.745023D-08

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00003	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00069	0.00180	[YES]	0.00069	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.419406	0.946561	-0.016427
C	1.781473	0.729547	-0.035901
C	2.267375	-0.584541	-0.010316
C	1.359234	-1.637872	0.023560
C	-0.012660	-1.388309	0.033954
C	-0.525278	-0.085400	0.054282
F	-0.020422	2.221981	-0.054442
H	2.445209	1.588531	-0.073161
H	3.338036	-0.768740	-0.027206
H	1.721330	-2.663934	0.026439
H	-0.744851	-2.190283	0.040187
C	-2.001161	0.125787	-0.032097
O	-2.779387	-0.838768	-0.122156
H	-2.287161	1.137438	-0.367110
H	-1.784009	0.974665	1.765749

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -445.156273357 Predicted Change= -1.745023D-08

Zero-point correction (ZPE)=	-445.0511	0.10508
Internal Energy (U)=	-445.0440	0.11227
Enthalpy (H)=	-445.0430	0.11321
Gibbs Free Energy (G)=	-445.0827	0.07352

Frequencies -- -499.8950 155.5629 200.2193

M06-2X/6-31+G(d,p)/PCM(DCE) SP: -445.286703

TS-34°

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc) opt=(maxcycle=250,modredundant) freq=noraman
Modredundant Input: D 5 6 13 12 F
Modredundant Input: B 12 15 F
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C7H6FO(1-) C1[X(C7H6FO)] #Atoms= 15
Charge = -1 Multiplicity = 1

SCF Energy= -445.145357953 Predicted Change= -4.113030D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00257	0.00180	[NO]	0.00257	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.433771	0.948684	0.014779
C	1.794363	0.692133	0.062277
C	2.255097	-0.626453	0.044882
C	1.328890	-1.662611	-0.031144
C	-0.033594	-1.373961	-0.063056
C	-0.532602	-0.065004	0.047617
F	0.064361	2.235541	-0.072845
H	2.475422	1.537942	0.084522
H	3.322464	-0.829509	0.070369
H	1.669219	-2.694247	-0.089823
H	-0.779936	-2.161255	-0.121670
C	-2.009247	0.090562	-0.186441
O	-2.800146	-0.807046	0.151711
H	-2.254316	0.853185	-0.948496
H	-2.031003	1.610296	1.113535

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-445.145357953	Predicted Change= -4.113030D-08
Zero-point correction (ZPE)=	-445.0401	0.10521
Internal Energy (U)=	-445.0329	0.11237
Enthalpy (H)=	-445.0320	0.11331
Gibbs Free Energy (G)=	-445.0717	0.07361

Frequencies -- -581.8833 145.8275 204.6362

M06-2X/6-31+G(d,p)/PCM(DCE) SP: -445.279217

—2-methoxybenzaldehyde—

GS-0°

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,modredundant) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C8H8O2 C1[X(C8H8O2)] #Atoms= 18
Charge = 0 Multiplicity = 1

SCF Energy= -459.897779330 Predicted Change= -2.873977D-08

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00004	0.00045	[YES]	0.00001	0.00030	[YES]
Displ	0.00069	0.00180	[YES]	0.00069	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.652601	-0.084151	0.000120
C	-1.202965	1.199641	0.000006
C	-0.358579	2.307489	-0.000083
C	1.026380	2.160709	-0.000037
C	1.567652	0.882138	0.000057
C	0.744943	-0.243823	0.000199
H	-2.276120	1.346747	0.000186
H	-0.798094	3.300699	-0.000143
H	1.670564	3.033178	-0.000116
H	2.640832	0.715490	0.000094
C	1.366226	-1.590820	0.000197
O	2.565457	-1.762567	-0.000268
H	0.670082	-2.447244	0.000458
O	-1.389496	-1.222601	-0.000025
C	-2.796537	-1.099060	-0.000092
H	-3.147370	-0.572004	-0.894909
H	-3.187399	-2.116100	-0.000296
H	-3.147313	-0.572163	0.894861

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -459.897779330 Predicted Change= -2.873977D-08

Zero-point correction (ZPE)=	-459.7525	0.14520
Internal Energy (U)=	-459.7438	0.15393
Enthalpy (H)=	-459.7429	0.15487
Gibbs Free Energy (G)=	-459.7864	0.11128

Frequencies -- 82.2810 122.1542 168.1714

M06-2X/6-31+G(d,p)/PCM(DCE) SP: -459.929073

GS-34°

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,modredundant) freq=noraman
Modredundant Input: D 5 6 11 12 F
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C8H8O2 C1[X(C8H8O2)] #Atoms= 18
Charge = 0 Multiplicity = 1

SCF Energy= -459.894522491 Predicted Change= -3.580185D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00044	0.00180	[YES]	0.00044	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.639927	-0.073586	0.000705
C	-1.197696	1.204526	0.052063
C	-0.359233	2.318231	0.036231
C	1.023617	2.179202	-0.028103
C	1.572615	0.902394	-0.068271
C	0.756741	-0.226378	-0.036499
H	-2.270920	1.344120	0.100727
H	-0.803307	3.308676	0.071337
H	1.663162	3.054752	-0.051562
H	2.646780	0.748992	-0.118673
C	1.371148	-1.570777	-0.186888
O	2.471303	-1.843109	0.236663
H	0.750301	-2.332531	-0.692513
O	-1.361998	-1.222376	0.001041
C	-2.770123	-1.114222	0.017828
H	-3.135951	-0.565252	-0.857818
H	-3.150858	-2.134774	-0.006501
H	-3.116501	-0.616450	0.930976

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -459.894522491 Predicted Change= -3.580185D-09

Zero-point correction (ZPE)=	-459.7495	0.14498
Internal Energy (U)=	-459.7407	0.15378
Enthalpy (H)=	-459.7397	0.15472
Gibbs Free Energy (G)=	-459.7836	0.11090

Frequencies -- 80.0372 106.8365 144.9286

M06-2X/6-31+G(d,p)/PCM(DCE) SP: -459.926539

TS-0°

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,modredundant) freq=noraman
Modredundant Input: B 11 14 F
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C8H9O2(1-) C1[X(C8H9O2)] #Atoms= 19
Charge = -1 Multiplicity = 1

SCF Energy= -460.420861330 Predicted Change= -2.252962D-08

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00098	0.00180	[YES]	0.00098	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.662216	-0.099900	-0.042036
C	-1.297507	1.134566	-0.053600
C	-0.541124	2.316248	-0.009373
C	0.843669	2.239298	0.034366
C	1.471823	0.993641	0.040680
C	0.745858	-0.198811	0.040809
H	-2.380087	1.198425	-0.102546
H	-1.048514	3.277602	-0.021215
H	1.439564	3.149610	0.053898
H	2.552863	0.892739	0.061210
C	1.491908	-1.494045	-0.005422
O	2.728609	-1.511937	-0.141364
H	0.869838	-2.360618	-0.282479
H	0.740525	-1.766009	1.828010
O	-1.333912	-1.292185	-0.097147
C	-2.724500	-1.253390	0.026307
H	-3.203134	-0.747747	-0.826364
H	-3.061503	-2.291929	0.057454
H	-3.034601	-0.744728	0.949735

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -460.420861330 Predicted Change= -2.252962D-08

Zero-point correction (ZPE)=	-460.2740	0.14676
Internal Energy (U)=	-460.2653	0.15555
Enthalpy (H)=	-460.2643	0.15650
Gibbs Free Energy (G)=	-460.3077	0.11314

Frequencies -- -511.1198 83.9317 147.6450
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -460.556958

TS-34°

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

M062X/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,modredundant) freq=noraman
Modredundant Input: D 5 6 11 12 F
Modredundant Input: B 11 14 F
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RM062X/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C8H9O2(1-) C1[X(C8H9O2)] #Atoms= 19
Charge = -1 Multiplicity = 1

SCF Energy= -460.413822765 Predicted Change= -2.826828D-08

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00127	0.00180	[YES]	0.00127	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.707329	0.115605	-0.221212
C	-1.064306	1.459273	-0.134944
C	-0.100979	2.448822	0.059242
C	1.236124	2.073912	0.145361
C	1.579581	0.727325	0.070220
C	0.623880	-0.298160	-0.014285
H	-2.112143	1.717632	-0.271732
H	-0.393444	3.494885	0.109632
H	2.012100	2.829808	0.246524
H	2.616017	0.406552	0.134833
C	1.168356	-1.680707	-0.270146
O	2.267633	-2.017648	0.197949
H	0.696428	-2.186883	-1.130849
H	-0.280664	-2.530065	0.815644
O	-1.689129	-0.782140	-0.574102
C	-2.545135	-1.122030	0.504241
H	-3.107677	-0.240072	0.848695
H	-3.249684	-1.864723	0.119467
H	-1.950122	-1.573077	1.306136

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -460.413822765 Predicted Change= -2.826828D-08
Zero-point correction (ZPE)= -460.2673 0.14647
Internal Energy (U)= -460.2585 0.15531
Enthalpy (H)= -460.2575 0.15625
Gibbs Free Energy (G)= -460.3008 0.11293

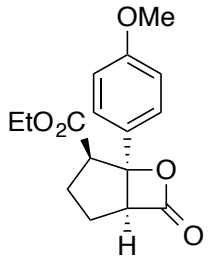
Frequencies -- -579.5891 128.5224 162.5795
M06-2X/6-31+G(d,p)/PCM(DCE) SP: -460.544673

Appendix III:

Computational Data for Chapter 5

Functionalized Cyclopentenes Through a Tandem NHC-Catalyzed Dynamic Kinetic Resolution and Ambient Temperature Decarboxylation: Mechanistic Insight and Synthetic Application

Molecular Geometries and Energies of Compounds Reported



***(syn)*-2a**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.899665	-0.576294	-0.047802
C	0.593395	-0.417915	0.057276
C	-1.663699	0.403040	-0.982804
H	-1.023674	0.566008	-1.858909
C	-2.951822	-0.341509	-1.385121
H	-3.370908	0.036858	-2.321860
H	-3.709949	-0.186876	-0.611256
C	-2.537372	-1.822708	-1.466006
H	-2.060327	-2.042692	-2.429297
H	-3.381741	-2.509962	-1.352578
C	-1.501843	-1.985901	-0.343409
H	-0.801034	-2.813607	-0.471592
C	-2.064943	-1.855682	1.069965
O	-2.732963	-2.504861	1.818691
O	-1.545925	-0.597351	1.286731
C	-1.933446	1.760768	-0.348881
O	-3.031469	2.204357	-0.096760
O	-0.783013	2.421714	-0.108440
C	-0.928468	3.704504	0.525351
H	-1.432682	3.599103	1.489262
H	-1.508563	4.380882	-0.108115
H	0.086499	4.078734	0.660211
C	2.793201	-0.520314	-0.988084
H	3.389463	-0.716398	-1.871766
C	3.391509	-0.139309	0.219222
C	2.586642	0.097403	1.342417
H	3.066451	0.388204	2.271706
C	1.207205	-0.041340	1.260199
H	0.593259	0.139114	2.135671
O	4.733283	0.024345	0.403840
C	5.597042	-0.204481	-0.698125
H	5.381816	0.480039	-1.529422
H	6.607380	-0.017210	-0.330130
H	5.528726	-1.240059	-1.056970
C	1.405161	-0.655403	-1.055304
H	0.958605	-0.956930	-2.000813

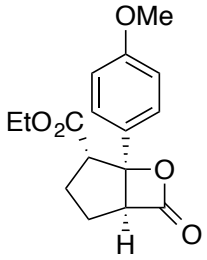
SCF Energy= -957.342074647 Predicted Change= -8.564827D-09

Zero-point correction (ZPE)=	-957.0519	0.29013
Internal Energy (U)=	-957.0336	0.30839
Enthalpy (H)=	-957.0327	0.30933
Gibbs Free Energy (G)=	-957.1003	0.24169

Frequencies -- 21.3288 30.3948 39.8145

E_{solv} = -0.014900792

$E_{SCS\text{-}MP2/\infty}$ = -956.059353



***(anti)*-2a**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.125563	-0.571296	-0.184794
C	0.366731	-0.519853	0.010878
C	-1.839582	0.701232	-0.732796
H	-1.717434	0.732463	-1.818345
C	-3.315947	0.521001	-0.294775
H	-3.830869	-0.098230	-1.037151
H	-3.848627	1.473891	-0.232549
C	-3.250495	-0.203979	1.065709
H	-4.171882	-0.745508	1.302742
H	-3.056935	0.517772	1.863463
C	-2.044300	-1.148193	0.934490
H	-1.580087	-1.444180	1.877140
C	-2.261670	-2.284755	-0.059593
O	-2.860753	-3.318586	-0.107412
O	-1.505265	-1.711903	-1.058729
C	-1.238943	1.966552	-0.144531
O	-1.434314	2.371713	0.984823
O	-0.444684	2.592611	-1.032505
C	0.226258	3.767944	-0.543162
H	0.791436	4.154221	-1.391454
H	0.897091	3.504226	0.278387
H	-0.499528	4.505932	-0.192688
C	0.923803	0.057681	1.164803
C	2.300228	0.121454	1.336372
H	2.735247	0.560746	2.228615
C	3.159319	-0.399488	0.356872
C	2.617537	-0.983097	-0.793893
H	3.256670	-1.400928	-1.563160
C	1.231350	-1.037750	-0.955959
H	0.818290	-1.507242	-1.842757
H	0.275648	0.468715	1.933344
O	4.492906	-0.293711	0.621794
C	5.410106	-0.819608	-0.325293
H	5.320907	-0.315463	-1.296616
H	6.403772	-0.634995	0.086728
H	5.270197	-1.899488	-0.465422

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

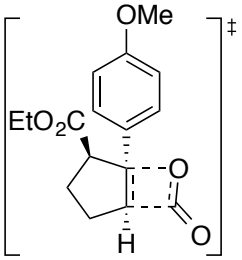
SCF Energy= -957.343130117 Predicted Change= -3.410116D-09

Zero-point correction (ZPE)=	-957.0524	0.29068
Internal Energy (U)=	-957.0343	0.30875
Enthalpy (H)=	-957.0334	0.30970
Gibbs Free Energy (G)=	-957.0998	0.24325

Frequencies -- 28.5676 37.7136 52.7896

E_{solv} = -0.012402154

$E_{SCS\text{-}MP2/\infty}$ = -956.0617947



***(syn)*-TS3a**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.731230	-0.541743	-0.573881
C	0.671848	-0.284050	-0.428886
C	-1.759785	0.445614	-1.100623
H	-1.346517	0.924799	-1.999936
C	-3.014918	-0.402670	-1.439974
H	-3.436597	-0.124386	-2.409792
H	-3.778709	-0.205092	-0.685179
C	-2.554041	-1.873159	-1.383220
H	-2.237086	-2.232878	-2.370643
H	-3.332472	-2.545619	-1.011020
C	-1.367054	-1.839997	-0.416755
H	-0.714432	-2.712758	-0.454565
C	-1.898776	-1.668391	1.155274
O	-2.611766	-2.570081	1.563351
O	-1.469212	-0.603954	1.667499
C	-2.099424	1.587825	-0.120414
O	-3.221592	1.861386	0.230943
O	-1.007335	2.280044	0.242485
C	-1.228931	3.289499	1.245784
H	-1.616986	2.825102	2.154998
H	-1.938257	4.038790	0.885689
H	-0.251399	3.736735	1.427389
C	1.293274	0.873082	-0.966088
H	0.694122	1.625702	-1.462091
C	2.657446	1.060412	-0.879233
H	3.135511	1.935842	-1.306164
C	3.462416	0.112654	-0.219065
C	2.870686	-1.033228	0.343541
H	3.467275	-1.766555	0.872792
C	1.504361	-1.223276	0.225887
H	1.059724	-2.096872	0.688344
O	4.781317	0.392676	-0.177411
C	5.662824	-0.516277	0.479560
H	5.643273	-1.502849	0.001789
H	6.658479	-0.082766	0.380240
H	5.410594	-0.615517	1.541785

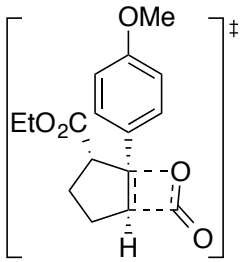
Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
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SCF Energy= -957.296640488	Predicted Change=	-2.905245D-09
Zero-point correction (ZPE)=	-957.0093	0.28725
Internal Energy (U)=	-956.9907	0.30589
Enthalpy (H)=	-956.9897	0.30684
Gibbs Free Energy (G)=	-957.0577	0.23884

Frequencies -- -549.4244	31.2267	42.4267

E_{solv} = -0.025875457

$E_{SCS\text{-}MP2/\infty}$ = -955.9993388



***(anti)*-TS3a**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.830381	-0.504426	0.069497
C	0.574812	-0.238102	0.003389
C	-1.890739	0.413474	-0.521523
H	-1.720364	0.596993	-1.583508
C	-3.232748	-0.328049	-0.246903
H	-3.459131	-0.951471	-1.115373
H	-4.065015	0.365332	-0.095832
C	-2.938988	-1.202219	0.986854
H	-3.583299	-2.084142	1.046275
H	-3.053819	-0.621597	1.908450
C	-1.470508	-1.601188	0.777203
H	-0.959561	-2.011454	1.647314
C	-1.414635	-2.722988	-0.462438
O	-1.049448	-2.189796	-1.540151
O	-1.757813	-3.853025	-0.158558
C	-1.883657	1.748759	0.223141
O	-1.991799	1.878561	1.422947
O	-1.773455	2.786330	-0.635796
C	-1.805429	4.092881	-0.029356
H	-2.744513	4.239007	0.509817
H	-1.721321	4.798325	-0.856023
H	-0.971617	4.210782	0.667342
C	1.504537	-1.078820	0.659191
H	1.150222	-1.947060	1.203319
C	2.867059	-0.836322	0.612990
H	3.546301	-1.507377	1.124806
C	3.349863	0.274435	-0.103103
C	2.445159	1.124588	-0.768836
H	2.842428	1.970272	-1.320294
C	1.090882	0.868516	-0.721250
H	0.414881	1.532490	-1.248378
O	4.651741	0.607641	-0.212535
C	5.633737	-0.212056	0.419355
H	5.612650	-1.233239	0.021505
H	6.594002	0.249905	0.188017
H	5.490555	-0.235361	1.506043

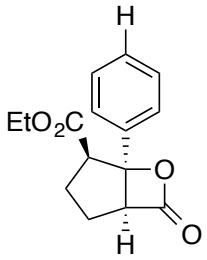
Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -957.298763099 Predicted Change= -4.597832D-09

Zero-point correction (ZPE)=	-957.0110	0.28767
Internal Energy (U)=	-956.9924	0.30630
Enthalpy (H)=	-956.9915	0.30724
Gibbs Free Energy (G)=	-957.0597	0.23897
Frequencies --	-592.0414	27.2230	35.3647

E_{solv} = -0.024944837

$E_{SCS\text{-}MP2/\infty}$ = -956.0019535



***(syn)*-2b**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.284516	-0.568349	-0.066455
C	1.219854	-0.491644	-0.070018
C	-1.058301	0.461092	-0.934944
H	-0.474163	0.605606	-1.852588
C	-2.407529	-0.211864	-1.256366
H	-2.867866	0.200235	-2.158731
H	-3.104121	-0.029819	-0.432176
C	-2.075480	-1.710411	-1.381235
H	-1.675981	-1.939936	-2.376953
H	-2.943904	-2.356441	-1.218194
C	-0.975905	-1.942108	-0.333855
H	-0.329400	-2.802515	-0.519268
C	-1.433199	-1.802921	1.116463
O	-2.080527	-2.426997	1.903336
O	-0.836156	-0.574881	1.309060
C	-1.213248	1.822776	-0.271008
O	-2.269703	2.335074	0.024160
O	-0.013107	2.400340	-0.062728
C	-0.048750	3.684007	0.585196
H	-0.521956	3.603053	1.567023
H	-0.606067	4.403007	-0.021084
H	0.993252	3.988822	0.683366
C	1.924167	-0.725689	-1.259484
H	1.384232	-0.957085	-2.175444
C	3.316782	-0.672242	-1.281434
H	3.848534	-0.859111	-2.210544
C	4.024791	-0.384371	-0.112448
H	5.110491	-0.343598	-0.128028
C	3.329478	-0.153325	1.074511
H	3.872171	0.069001	1.989447
C	1.934735	-0.207782	1.097989
H	1.393464	-0.032517	2.021072

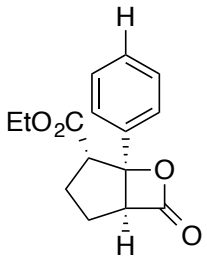
Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-842.819466143	Predicted Change= -1.618595D-08
Zero-point correction (ZPE)=	-842.5619	0.25749
Internal Energy (U)=	-842.5463	0.27311
Enthalpy (H)=	-842.5454	0.27405
Gibbs Free Energy (G)=	-842.6068	0.21258

Frequencies -- 23.7926 31.8948 49.7944

E_{solv} = -0.013076256

$E_{SCS\text{-}MP2/\infty}$ = -841.6686078



***(anti)*-2b**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.747820	-0.343477	-0.180216
C	0.597921	-0.992003	0.022018
C	-0.773451	1.115284	-0.726332
H	-0.641334	1.087570	-1.810726
C	-2.165194	1.650138	-0.300488
H	-2.904024	1.348738	-1.050775
H	-2.186954	2.741409	-0.235528
C	-2.462172	0.976525	1.055708
H	-3.532507	0.928840	1.280196
H	-1.962820	1.522018	1.860726
C	-1.838284	-0.423302	0.929561
H	-1.575964	-0.902683	1.874581
C	-2.554742	-1.325050	-0.071208
O	-1.607985	-1.173525	-1.061549
O	-3.568386	-1.956299	-0.128493
C	0.346054	1.949507	-0.126262
O	0.358348	2.388624	1.007082
O	1.342277	2.140927	-1.010169
C	2.482036	2.865637	-0.513270
H	2.183513	3.857222	-0.164018
H	3.167215	2.943346	-1.357406
H	2.946583	2.318427	0.310895
C	1.332821	-0.759353	1.193444
H	0.927115	-0.116683	1.969409
C	2.590005	-1.340606	1.363798
H	3.147261	-1.156358	2.278402
C	3.124029	-2.163162	0.370404
H	4.100759	-2.619599	0.506541
C	2.393751	-2.402555	-0.794752
H	2.799241	-3.047253	-1.569866
C	1.137608	-1.821322	-0.969072
H	0.562512	-2.020371	-1.867401

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

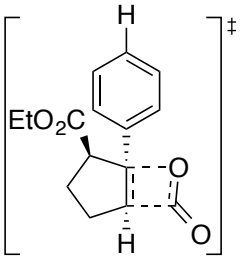
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SCF Energy=	-842.820071910	Predicted Change= -1.289883D-07
Zero-point correction (ZPE)=	-842.5620	0.25804
Internal Energy (U)=	-842.5466	0.27346
Enthalpy (H)=	-842.5456	0.27440
Gibbs Free Energy (G)=	-842.6057	0.21433

Frequencies -- 35.8631 49.5705 54.5701

E_{solv} = -0.01087943

$E_{SCS\text{-}MP2/\infty}$ = -841.6705523



***(syn)*-TS3b**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.122112	-0.555630	0.536604
C	-1.302079	-0.421720	0.310999
C	1.034349	0.520156	1.097204
H	0.550683	0.927192	1.997914
C	2.357556	-0.205287	1.456395
H	2.759343	0.140259	2.412695
H	3.098597	0.030177	0.689617
C	2.018610	-1.708726	1.448941
H	1.708290	-2.056744	2.442628
H	2.856807	-2.329378	1.119296
C	0.853235	-1.801491	0.461493
H	0.270743	-2.722094	0.488690
C	1.425026	-1.599256	-1.116884
O	2.208134	-2.451046	-1.489265
O	0.935670	-0.567327	-1.638846
C	1.277065	1.717361	0.157081
O	2.374502	2.107000	-0.161416
O	0.129616	2.306193	-0.214329
C	0.269826	3.375736	-1.169682
H	0.737963	2.998550	-2.081509
H	0.878227	4.182631	-0.753692
H	-0.745143	3.719079	-1.370139
C	-2.048670	0.624078	0.895593
H	-1.546487	1.392378	1.469863
C	-3.431312	0.674233	0.752663
H	-3.991782	1.476498	1.223673
C	-4.094641	-0.296828	-0.000339
H	-5.173599	-0.249332	-0.119243
C	-3.368398	-1.327719	-0.606979
H	-3.879175	-2.074478	-1.207575
C	-1.991996	-1.396974	-0.446186
H	-1.431937	-2.180911	-0.942798

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

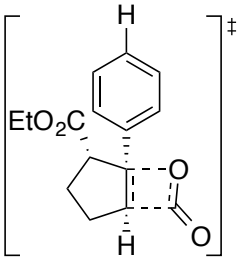
SCF Energy= -842.768810382 Predicted Change= -9.121044D-09

Zero-point correction (ZPE)=	-842.5146	0.25411
Internal Energy (U)=	-842.4985	0.27022
Enthalpy (H)=	-842.4976	0.27116
Gibbs Free Energy (G)=	-842.5598	0.20900

Frequencies -- -637.2643 35.2215 42.0718

E_{solv} = -0.021359966

$E_{SCS\text{-}MP2/\infty}$ = -841.6046034



***(anti)*-TS3b**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.343571	-0.405414	0.083301
C	0.798866	0.966160	0.072688
C	-0.955719	-0.862753	-0.560269
H	-1.010284	-0.583526	-1.613409
C	-0.965656	-2.405180	-0.341374
H	-0.503756	-2.875349	-1.213279
H	-1.979812	-2.801179	-0.237540
C	-0.099382	-2.616706	0.914779
H	0.365213	-3.606314	0.948616
H	-0.692996	-2.477128	1.824404
C	0.956951	-1.510559	0.785758
H	1.549582	-1.295146	1.672985
C	2.007173	-1.948971	-0.466951
O	1.749107	-1.302152	-1.511869
O	2.805931	-2.821110	-0.185854
C	-2.135972	-0.237496	0.186339
O	-2.309411	-0.294650	1.384089
O	-2.989876	0.363694	-0.669137
C	-4.163436	0.940852	-0.062844
H	-4.742756	0.170758	0.452117
H	-4.735099	1.367353	-0.886979
H	-3.879875	1.714779	0.654700
C	1.961909	1.345903	0.781257
H	2.534019	0.598207	1.318912
C	2.392710	2.665271	0.782017
H	3.290691	2.939506	1.327490
C	1.674014	3.637959	0.078797
H	2.013304	4.670114	0.080693
C	0.523314	3.282414	-0.629646
H	-0.032264	4.035537	-1.180582
C	0.091297	1.961444	-0.638576
H	-0.799814	1.698589	-1.197630

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

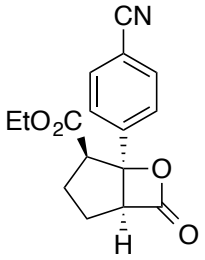
SCF Energy= -842.770601903 Predicted Change= -1.100520D-08

Zero-point correction (ZPE)=	-842.5160	0.25460
Internal Energy (U)=	-842.4999	0.27066
Enthalpy (H)=	-842.4989	0.27160
Gibbs Free Energy (G)=	-842.5614	0.20914

Frequencies -- -668.3250 27.0736 37.7094

E_{solv} = -0.020522123

$E_{SCS\text{-}MP2/\infty}$ = -841.6067542



***(syn)*-2c**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.790511	-0.569240	-0.064040
C	0.710339	-0.445777	-0.053113
C	-1.583713	0.432847	-0.944703
H	-0.999285	0.590113	-1.860444
C	-2.909984	-0.281268	-1.273765
H	-3.374726	0.114879	-2.180592
H	-3.618507	-0.117761	-0.455885
C	-2.532106	-1.769447	-1.391243
H	-2.117619	-1.990802	-2.382552
H	-3.381548	-2.441032	-1.232665
C	-1.435324	-1.966091	-0.333092
H	-0.762964	-2.808431	-0.509971
C	-1.909439	-1.836049	1.113019
O	-2.543613	-2.474504	1.897111
O	-1.349677	-0.587161	1.304844
C	-1.782750	1.795038	-0.291549
O	-2.857592	2.301315	-0.062655
O	-0.599249	2.377442	-0.014814
C	-0.677037	3.668482	0.618126
H	-1.205754	3.593707	1.571526
H	-1.201192	4.378066	-0.027105
H	0.356338	3.978761	0.772699
C	2.821405	-0.549535	-1.248961
H	3.376616	-0.709760	-2.167409
C	3.510444	-0.243978	-0.063070
C	2.790554	-0.044680	1.125263
H	3.322389	0.189186	2.041858
C	1.402639	-0.147448	1.125940
H	0.846219	0.004398	2.043490
C	1.435374	-0.648302	-1.236774
H	0.915854	-0.890659	-2.160557
C	4.940391	-0.138524	-0.068831
N	6.100503	-0.051937	-0.075361

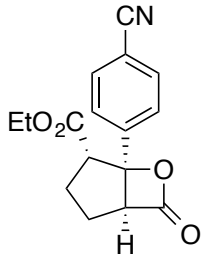
Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -935.062014156 Predicted Change= -1.485578D-08
Zero-point correction (ZPE)= -934.8060 0.25599
Internal Energy (U)= -934.7885 0.27343
Enthalpy (H)= -934.7876 0.27438

Gibbs Free Energy (G)=		-934.8533	0.20866
Frequencies --	27.7741	34.9776	39.6901

E_{solv} = -0.017854208

$E_{SCS\text{-}MP2/\infty}$ = -933.7957567



***(anti)*-2c**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.040313	-0.553747	-0.190801
C	0.462053	-0.600601	-0.069394
C	-1.686421	0.777391	-0.676814
H	-1.614102	0.828570	-1.765878
C	-3.151700	0.680684	-0.173452
H	-3.737815	0.112702	-0.903663
H	-3.618469	1.663921	-0.069440
C	-3.071922	-0.076490	1.168165
H	-4.014675	-0.563140	1.437146
H	-2.795105	0.611920	1.970679
C	-1.938284	-1.095012	0.962450
H	-1.452105	-1.440952	1.876684
C	-2.276025	-2.193873	-0.041289
O	-2.941712	-3.184383	-0.082628
O	-1.528051	-1.645287	-1.065473
C	-0.983636	1.989371	-0.086875
O	-1.052244	2.334018	1.077057
O	-0.262525	2.640377	-1.016045
C	0.471630	3.786877	-0.544207
H	0.970093	4.193837	-1.423673
H	1.203490	3.483385	0.208423
H	-0.208669	4.522338	-0.108192
C	1.103657	-0.084004	1.066507
C	2.490726	-0.110539	1.169368
H	2.982668	0.286649	2.051305
C	3.260395	-0.661950	0.131976
C	2.622514	-1.187418	-1.003283
H	3.216899	-1.619803	-1.801583
C	1.234950	-1.156159	-1.097679
H	0.741692	-1.578299	-1.966297
H	0.517940	0.350593	1.870153
C	4.690573	-0.689902	0.234571
N	5.850748	-0.708183	0.317941

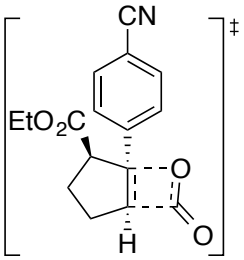
Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -935.062366287 Predicted Change= -2.217380D-08
Zero-point correction (ZPE)= -934.8059 0.25642
Internal Energy (U)= -934.7886 0.27375
Enthalpy (H)= -934.7876 0.27469

Gibbs Free Energy (G)=		-934.8528	0.20951
Frequencies --	21.7873	41.4729	53.4631

E_{solv} = -0.015335828

$E_{SCS\text{-}MP2/\infty}$ = -933.7973863



***(syn)*-TS3c**

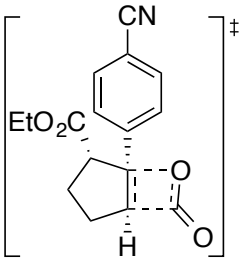
Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.668371	-0.547238	0.542673
C	-0.763357	-0.387738	0.339990
C	1.611050	0.522482	1.058335
H	1.162719	0.934306	1.975701
C	2.936294	-0.216781	1.375425
H	3.394382	0.154484	2.295799
H	3.640386	-0.025102	0.562608
C	2.566018	-1.711200	1.440664
H	2.286766	-2.014037	2.457895
H	3.377427	-2.362836	1.104308
C	1.360668	-1.812475	0.504301
H	0.758037	-2.717864	0.572278
C	1.880417	-1.659758	-1.111759
O	2.643354	-2.525085	-1.483947
O	1.374346	-0.638058	-1.638079
C	1.827854	1.715143	0.106997
O	2.913393	2.075944	-0.277206
O	0.673670	2.330342	-0.194737
C	0.782216	3.413499	-1.141323
H	1.192824	3.043527	-2.083188
H	1.428132	4.200925	-0.745601
H	-0.235151	3.779022	-1.279856
C	-1.481282	0.652360	0.965396
H	-0.958737	1.400542	1.547276
C	-2.862947	0.731095	0.855481
H	-3.407747	1.526251	1.353228
C	-3.560406	-0.216591	0.089274
C	-2.855920	-1.247124	-0.560720
H	-3.394934	-1.967681	-1.166460
C	-1.480209	-1.333190	-0.427158
H	-0.942549	-2.110107	-0.957274
C	-4.985581	-0.130454	-0.033455
N	-6.142683	-0.059822	-0.129954

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -935.008185308 Predicted Change= -1.447063D-10
Zero-point correction (ZPE)= -934.7558 0.25236
Internal Energy (U)= -934.7378 0.27034
Enthalpy (H)= -934.7368 0.27129

Gibbs Free Energy (G)=	-934.8036	0.20456
Frequencies --	-690.8340	33.8678	41.2570

E_{solv} = -0.023688736
$E_{SCS\text{-}MP2/\infty}$ = -933.730019



***(anti)*-TS3c**

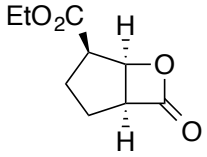
Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.762869	-0.488657	0.081247
C	0.682543	-0.363401	0.058313
C	-1.701068	0.520348	-0.559078
H	-1.474803	0.679807	-1.614453
C	-3.118811	-0.082519	-0.326159
H	-3.374531	-0.697208	-1.193498
H	-3.883980	0.691429	-0.221195
C	-2.960303	-0.955907	0.933369
H	-3.679502	-1.778887	0.972137
H	-3.067279	-0.353922	1.841694
C	-1.524942	-1.478804	0.800510
H	-1.083212	-1.943577	1.680164
C	-1.505041	-2.619306	-0.467573
O	-0.964573	-2.132648	-1.490866
O	-2.029558	-3.680738	-0.204862
C	-1.585579	1.853652	0.186066
O	-1.702763	1.988827	1.384119
O	-1.365088	2.871562	-0.670542
C	-1.291158	4.180495	-0.067666
H	-2.227037	4.414612	0.444953
H	-1.120223	4.869853	-0.894130
H	-0.468656	4.222135	0.650454
C	1.497633	-1.281939	0.756488
H	1.045698	-2.107528	1.293932
C	2.877133	-1.157398	0.753796
H	3.494706	-1.869650	1.290294
C	3.483629	-0.101123	0.049188
C	2.688961	0.819344	-0.654626
H	3.160867	1.628633	-1.201483
C	1.308354	0.684128	-0.651799
H	0.711463	1.401556	-1.203107
C	4.909968	0.036965	0.049469
N	6.067379	0.153064	0.051740

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -935.009456865 Predicted Change= -1.148036D-09
Zero-point correction (ZPE)= -934.7565 0.25286
Internal Energy (U)= -934.7386 0.27081
Enthalpy (H)= -934.7376 0.27175

Gibbs Free Energy (G)=	-934.8048	0.20464
Frequencies --	-717.6194	25.3047	36.6871

E_{solv} = -0.02264074
$E_{SCS\text{-}MP2/\infty}$ = -933.7315975



***(syn)*-2d**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.527658	-0.313113	-0.963550
C	0.337244	0.848158	-0.453900
H	0.608335	1.444573	-1.337262
C	-0.597953	1.656757	0.466314
H	-0.264723	2.689910	0.594742
H	-0.610046	1.198562	1.460357
C	-1.979352	1.549613	-0.212393
H	-2.069784	2.284552	-1.021535
H	-2.811108	1.716134	0.478973
C	-2.001896	0.132737	-0.818933
H	-2.676174	0.006410	-1.668905
C	-2.061933	-1.001162	0.208761
O	-2.871587	-1.496831	0.933922
O	-0.733884	-1.346892	0.066822
C	1.631366	0.400465	0.205297
O	1.975284	0.675429	1.331996
O	2.364470	-0.348133	-0.647394
C	3.602566	-0.853842	-0.116248
H	3.413122	-1.483540	0.756514
H	4.259817	-0.029654	0.173111
H	4.049076	-1.437004	-0.921909
H	-0.187077	-0.776206	-1.888939

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

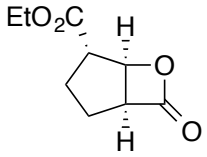
SCF Energy= -611.766157398 Predicted Change= -1.318925D-06

Zero-point correction (ZPE)=	-611.5889	0.17716
Internal Energy (U)=	-611.5781	0.18799
Enthalpy (H)=	-611.5772	0.18894
Gibbs Free Energy (G)=	-611.6267	0.13941

Frequencies -- 38.4476 62.1701 112.8694

E_{solv} = -0.012654385

$E_{SCS\text{-}MP2/\infty}$ = -611.3703829



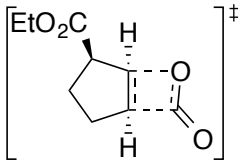
***(anti)*-2d**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.519774	-0.800470	-0.153132
C	-0.342738	0.061773	0.783821
H	-0.464115	-0.453713	1.743135
C	0.434586	1.390834	0.899189
H	1.204064	1.290947	1.672278
H	-0.218390	2.221718	1.174271
C	1.082235	1.588156	-0.488863
H	1.964158	2.235379	-0.461864
H	0.356472	2.032405	-1.177668
C	1.423266	0.162217	-0.961627
H	1.486724	0.038520	-2.045053
C	2.549538	-0.518667	-0.180453
O	3.740806	-0.459294	-0.107341
O	1.702934	-1.334023	0.543048
C	-1.734715	0.262038	0.192070
O	-2.193975	1.313400	-0.198393
O	-2.408377	-0.907675	0.151511
C	-3.740319	-0.838541	-0.389930
H	-4.124740	-1.857704	-0.348768
H	-3.716842	-0.475606	-1.420684
H	-4.360971	-0.167707	0.209467
H	-0.007239	-1.607543	-0.662158

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -611.766435478	Predicted Change= -1.467407D-08	
Zero-point correction (ZPE)=	-611.5892	0.17723
Internal Energy (U)=	-611.5783	0.18804
Enthalpy (H)=	-611.5774	0.18898
Gibbs Free Energy (G)=	-611.6269	0.13945

Frequencies -- 34.1564 72.9554 100.7333
E_{solv} = -0.011271013
$E_{SCS\text{-}MP2/\infty}$ = -611.370721



***(syn)*-TS3d**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.504556	0.020062	1.184839
C	-0.300769	1.009526	0.406653
H	-0.637459	1.745249	1.160406
C	0.710826	1.650813	-0.572015
H	0.479043	2.698999	-0.775157
H	0.658526	1.114375	-1.523486
C	2.087063	1.446424	0.104753
H	2.336337	2.289024	0.763319
H	2.899781	1.339200	-0.619834
C	1.886189	0.168608	0.922110
H	2.621073	-0.126150	1.668714
C	1.765678	-1.218913	-0.202482
O	2.782389	-1.456086	-0.794777
O	0.594624	-1.665431	-0.152989
C	-1.565463	0.445866	-0.238373
O	-1.856567	0.578285	-1.402496
O	-2.321859	-0.187677	0.676266
C	-3.517753	-0.807956	0.164151
H	-3.258295	-1.565358	-0.579048
H	-4.169172	-0.059137	-0.293200
H	-4.000933	-1.264510	1.027881
H	0.060448	-0.610987	1.944564

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

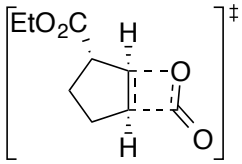
SCF Energy= -611.706032962 Predicted Change= -6.202190D-10

Zero-point correction (ZPE)=	-611.5333	0.17268
Internal Energy (U)=	-611.5219	0.18411
Enthalpy (H)=	-611.5209	0.18506
Gibbs Free Energy (G)=	-611.5718	0.13418

Frequencies -- -793.3788 49.3912 52.7238

E_{solv} = -0.01570163

$E_{SCS\text{-}MP2/\infty}$ = -611.2997325



***(anti)*-TS3d**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.379662	-0.719376	0.325348
C	0.345423	0.098211	-0.701156
H	0.383731	-0.423008	-1.665329
C	-0.426425	1.437793	-0.737219
H	-1.177045	1.392273	-1.531945
H	0.243495	2.274694	-0.941835
C	-1.114877	1.532675	0.645885
H	-2.062918	2.077095	0.607331
H	-0.467567	2.037045	1.374568
C	-1.321735	0.065870	1.030393
H	-1.604176	-0.200936	2.047210
C	-2.598774	-0.624013	-0.015670
O	-2.072375	-1.476747	-0.769230
O	-3.687537	-0.150621	0.165072
C	1.812683	0.272501	-0.256082
O	2.398870	1.326323	-0.194882
O	2.366029	-0.922430	0.029490
C	3.757521	-0.889609	0.407937
H	4.362169	-0.489195	-0.409289
H	4.025889	-1.925391	0.614254
H	3.895285	-0.267833	1.295730
H	-0.083693	-1.731267	0.569102

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

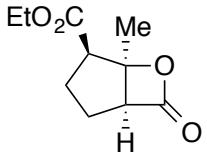
SCF Energy= -611.704906181 Predicted Change= -1.438706D-08

Zero-point correction (ZPE)=	-611.5320	0.17290
Internal Energy (U)=	-611.5205	0.18437
Enthalpy (H)=	-611.5195	0.18532
Gibbs Free Energy (G)=	-611.5711	0.13380

Frequencies -- -810.5918 30.5916 53.5322

E_{solv} = -0.015481563

$E_{SCS\text{-}MP2/\infty}$ = -611.298722



***(syn)*-2e**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.550774	-0.658112	-0.535872
C	-0.155083	-1.930890	-1.251173
C	0.345525	0.588784	-0.745154
H	0.644977	0.588333	-1.801852
C	-0.567344	1.795409	-0.447194
H	-0.212380	2.710955	-0.928802
H	-0.569728	1.982283	0.631136
C	-1.960884	1.358547	-0.937343
H	-2.056018	1.503468	-2.020635
H	-2.775063	1.911195	-0.458176
C	-2.015099	-0.145037	-0.624232
H	-2.718798	-0.718115	-1.233443
C	-2.050998	-0.489738	0.864867
O	-2.840958	-0.445384	1.761675
O	-0.742524	-0.911214	0.917891
C	1.615255	0.583113	0.093514
O	1.862605	1.355113	0.991465
O	2.457452	-0.399542	-0.300437
C	3.677275	-0.502846	0.457145
H	3.457219	-0.705252	1.508245
H	4.250941	0.424616	0.384624
H	4.227958	-1.331760	0.011878
H	-0.135628	-1.766708	-2.334639
H	0.839423	-2.257848	-0.937021
H	-0.872738	-2.728329	-1.033409

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

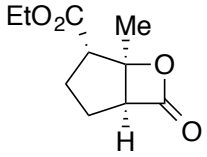
SCF Energy= -651.086734965 Predicted Change= -1.340264D-08

Zero-point correction (ZPE)=	-650.8819	0.20475
Internal Energy (U)=	-650.8696	0.21711
Enthalpy (H)=	-650.8686	0.21806
Gibbs Free Energy (G)=	-650.9211	0.16563

Frequencies -- 36.3778 59.0412 109.3810

E_{solv} = -0.012646663

$E_{SCS\text{-}MP2/\infty}$ = -650.6610849



***(anti)*-2e**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.596170	-0.688377	0.096712
C	-0.003816	-1.905160	0.775193
C	0.357003	0.210733	-0.734369
H	0.504711	-0.237565	-1.720154
C	-0.374142	1.577311	-0.798640
H	-1.086403	1.555660	-1.630536
H	0.313222	2.409250	-0.974755
C	-1.116150	1.702371	0.548722
H	-1.970331	2.385221	0.501026
H	-0.428619	2.058666	1.320326
C	-1.542557	0.263045	0.880635
H	-1.708148	0.065922	1.942436
C	-2.612965	-0.300575	-0.051312
O	-3.789857	-0.176660	-0.226846
O	-1.738908	-1.088409	-0.766771
C	1.710048	0.338984	-0.055119
O	1.941503	1.016272	0.926086
O	2.641935	-0.419229	-0.670525
C	3.955889	-0.382830	-0.084016
H	4.569420	-1.036863	-0.703690
H	3.925811	-0.744540	0.947134
H	4.349010	0.636876	-0.091339
H	0.492706	-2.554943	0.046942
H	0.729841	-1.604546	1.530602
H	-0.791441	-2.481933	1.269618

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

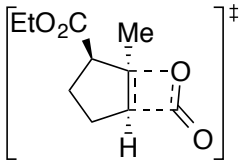
SCF Energy= -651.086446805 Predicted Change= -1.710189D-08

Zero-point correction (ZPE)=	-650.8813	0.20507
Internal Energy (U)=	-650.8690	0.21738
Enthalpy (H)=	-650.8681	0.21832
Gibbs Free Energy (G)=	-650.9206	0.16583

Frequencies -- 27.7645 67.5595 99.2661

E_{solv} = -0.010970117

$E_{SCS\text{-}MP2/\infty}$ = -650.6616946



***(syn)*-TS3e**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.756844	1.061852	0.205284
C	-0.603269	2.369139	-0.474208
C	0.335403	0.410495	1.022009
H	0.518956	1.125122	1.844039
C	-0.301763	-0.884531	1.579903
H	0.095181	-1.143939	2.564858
H	-0.077203	-1.712400	0.903817
C	-1.818171	-0.591448	1.585697
H	-2.127983	-0.101412	2.518543
H	-2.422614	-1.494940	1.463999
C	-1.980508	0.354860	0.395432
H	-2.919184	0.892307	0.263286
C	-1.724503	-0.574059	-1.068036
O	-2.579235	-1.398577	-1.281951
O	-0.653061	-0.214373	-1.611249
C	1.667242	0.314657	0.276140
O	2.264851	1.282740	-0.144155
O	2.096740	-0.947250	0.163282
C	3.312809	-1.121777	-0.589859
H	4.127593	-0.553056	-0.135338
H	3.164389	-0.786061	-1.618633
H	3.520124	-2.191119	-0.559050
H	0.366271	2.452898	-0.967825
H	-1.416552	2.546164	-1.180838
H	-0.645721	3.150990	0.301565

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

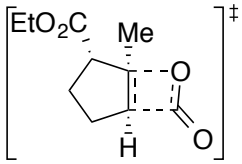
SCF Energy= -651.032937939 Predicted Change= -5.390633D-09

Zero-point correction (ZPE)=	-650.8320	0.20091
Internal Energy (U)=	-650.8191	0.21380
Enthalpy (H)=	-650.8181	0.21474
Gibbs Free Energy (G)=	-650.8719	0.16095

Frequencies -- -705.9702 34.4721 61.6065

E_{solv} = -0.016714969

$E_{SCS\text{-}MP2/\infty}$ = -650.5950795



***(anti)*-TS3e**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.596755	0.777852	0.179344
C	0.518085	2.255737	0.232505
C	-0.412310	-0.075986	-0.556679
H	-0.461015	0.175087	-1.619704
C	0.073644	-1.539570	-0.307319
H	0.728026	-1.831660	-1.133486
H	-0.756488	-2.249546	-0.272283
C	0.874663	-1.454853	1.010590
H	1.657165	-2.216465	1.075077
H	0.217528	-1.564384	1.882521
C	1.466350	-0.045727	0.951384
H	1.936654	0.375796	1.839137
C	2.677412	-0.032776	-0.312112
O	2.269544	0.659846	-1.274857
O	3.653084	-0.699733	-0.067956
C	-1.800097	0.130637	0.049642
O	-2.032711	0.628522	1.131923
O	-2.745315	-0.359010	-0.771978
C	-4.097427	-0.282493	-0.279177
H	-4.197196	-0.848114	0.650538
H	-4.715703	-0.717741	-1.063977
H	-4.378132	0.757856	-0.097724
H	1.455122	2.693936	0.581506
H	0.252401	2.684913	-0.737241
H	-0.277618	2.506405	0.949512

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

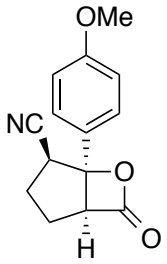
SCF Energy= -651.031310175 Predicted Change= -1.820783D-09

Zero-point correction (ZPE)=	-650.8303	0.20091
Internal Energy (U)=	-650.8173	0.21393
Enthalpy (H)=	-650.8164	0.21487
Gibbs Free Energy (G)=	-650.8708	0.16050

Frequencies -- -728.3993 35.2388 52.0656

E_{solv} = -0.015665419

$E_{SCS\text{-}MP2/\infty}$ = -650.593945



Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.175451	-0.066535	0.053038
C	-0.325675	0.050372	0.079366
C	1.770257	-1.440257	0.434832
H	1.165846	-2.185841	-0.102629
C	3.181959	-1.430892	-0.193093
H	3.579579	-2.441252	-0.333689
H	3.878545	-0.897817	0.466348
C	3.011665	-0.665774	-1.521140
H	2.606107	-1.327501	-2.296591
H	3.946887	-0.244381	-1.903558
C	1.975753	0.424028	-1.193224
H	1.414125	0.808387	-2.047266
C	2.489450	1.495492	-0.236210
O	3.227419	2.436581	-0.276618
O	1.812921	1.012172	0.858774
C	-2.499017	-0.601858	-0.815641
H	-3.067439	-1.178639	-1.536140
C	-3.139324	0.220774	0.119467
C	-2.369068	0.957384	1.029773
H	-2.880178	1.593055	1.746081
C	-0.982374	0.872712	1.007159
H	-0.395052	1.453291	1.710201
O	-4.491330	0.373717	0.222964
C	-5.320625	-0.346959	-0.674360
H	-5.188838	-1.431607	-0.563835
H	-6.346402	-0.080581	-0.413330
H	-5.128158	-0.065270	-1.718198
C	-1.104984	-0.678644	-0.824655
H	-0.625213	-1.319572	-1.561325
C	1.722347	-1.751198	1.930834
H	0.691271	-1.753236	2.301231
H	2.155909	-2.736472	2.136008
H	2.286042	-1.004189	2.498859

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

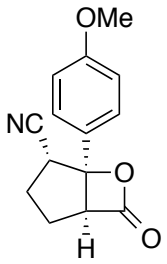
SCF Energy= -768.787817231 Predicted Change= -3.454760D-08

Zero-point correction (ZPE)=	-768.5122	0.27560
Internal Energy (U)=	-768.4971	0.29065
Enthalpy (H)=	-768.4962	0.29159
Gibbs Free Energy (G)=	-768.5549	0.23283

Frequencies -- 28.6658 50.9944 69.2970

E_{solv} = -0.015515356

$E_{SCS\text{-}MP2/\infty}$ = -821.1142395



Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.201714	0.012560	-0.201981
C	-0.290999	0.001417	-0.010224
C	1.854762	-1.176477	-0.952286
H	1.736696	-1.007732	-2.029410
C	3.345991	-1.090003	-0.534273
H	3.867150	-0.351738	-1.153866
H	3.867409	-2.044536	-0.660057
C	3.322691	-0.617952	0.935633
H	4.261069	-0.149574	1.249434
H	3.132466	-1.457626	1.614367
C	2.140890	0.364867	0.992198
H	1.699894	0.512696	1.979971
C	2.391995	1.647903	0.204378
O	3.027011	2.653977	0.337724
O	1.622776	1.281926	-0.871211
C	-0.881142	-0.604038	1.110538
C	-2.260981	-0.639705	1.264732
H	-2.718940	-1.103431	2.132750
C	-3.093110	-0.061007	0.295327
C	-2.520526	0.552580	-0.825091
H	-3.138450	1.016904	-1.585126
C	-1.131572	0.577504	-0.966793
H	-0.695258	1.072855	-1.828561
H	-0.255224	-1.053689	1.877368
O	-4.432844	-0.143146	0.538089
C	-5.322876	0.432529	-0.405740
H	-5.226158	-0.040316	-1.391981
H	-6.327058	0.253813	-0.017259
H	-5.160105	1.513620	-0.506806
C	1.237326	-2.537753	-0.601422
H	0.176770	-2.579871	-0.865194
H	1.757202	-3.330920	-1.150053
H	1.322013	-2.767057	0.467646

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

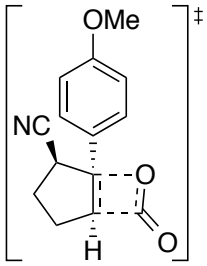
SCF Energy= -768.783907129 Predicted Change= -7.189245D-09

Zero-point correction (ZPE)=	-768.5081	0.27577
Internal Energy (U)=	-768.4931	0.29073
Enthalpy (H)=	-768.4922	0.29167
Gibbs Free Energy (G)=	-768.5505	0.23331

Frequencies -- 34.0681 52.6720 77.6812

E_{solv} = -0.012842371

$E_{SCS\text{-}MP2/\infty}$ = -821.1150703



***(syn)*-TS3d**

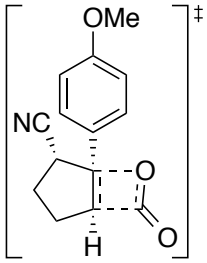
Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.036407	0.044206	-0.472554
C	0.382876	0.114537	-0.320245
C	-1.960461	1.255114	-0.566320
H	-1.699839	1.738794	-1.524145
C	-3.391688	0.660717	-0.703780
H	-4.046155	1.326965	-1.271293
H	-3.815383	0.524553	0.293780
C	-3.142165	-0.698073	-1.379973
H	-3.053274	-0.585229	-2.468891
H	-3.935760	-1.423136	-1.179472
C	-1.810212	-1.150325	-0.763703
H	-1.302061	-1.967046	-1.274362
C	-2.115094	-1.601247	0.829572
O	-2.647013	-2.688660	0.961918
O	-1.757734	-0.696497	1.620961
C	1.077407	1.351262	-0.241001
H	0.530243	2.286508	-0.259188
C	2.451684	1.393638	-0.139317
H	2.984469	2.337018	-0.085834
C	3.195906	0.198550	-0.085166
C	2.531747	-1.041862	-0.141576
H	3.083500	-1.972426	-0.085456
C	1.153908	-1.072450	-0.261481
H	0.655554	-2.035256	-0.281443
O	4.529474	0.346409	0.023363
C	5.355571	-0.814775	0.110104
H	5.266151	-1.432111	-0.791334
H	6.376202	-0.441399	0.197014
H	5.106240	-1.411624	0.994830
C	-1.835706	2.275114	0.476735
N	-1.755986	3.125422	1.262582

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -821.660325603 Predicted Change= -1.618803D-10

Zero-point correction (ZPE)=	-821.4175	0.24278
Internal Energy (U)=	-821.4016	0.25864
Enthalpy (H)=	-821.4007	0.25959
Gibbs Free Energy (G)=	-821.4618	0.19849

Frequencies -- -618.0876 39.4848 46.5785
E_{solv} = -0.017766138
$E_{SCS\text{-}MP2/\infty}$ = -821.0519291



***(anti)*-TS3d**

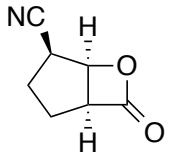
Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.077609	0.125524	-0.094822
C	-0.346906	0.147507	-0.023253
C	1.977257	1.204396	0.519753
H	1.782380	1.320225	1.590573
C	3.428009	0.710803	0.232967
H	3.752039	0.110049	1.085537
H	4.123564	1.543708	0.106937
C	3.279334	-0.166499	-1.023216
H	4.068177	-0.918764	-1.110087
H	3.291369	0.446327	-1.933645
C	1.904169	-0.823608	-0.823519
H	1.472779	-1.300998	-1.702228
C	2.055604	-1.956277	0.399453
O	1.635820	-1.492854	1.490190
O	2.562943	-3.015000	0.074341
C	-1.118219	-0.853030	-0.663898
H	-0.619123	-1.651382	-1.201746
C	-2.500244	-0.857603	-0.602844
H	-3.054165	-1.645343	-1.098870
C	-3.166702	0.158201	0.109483
C	-2.422095	1.165339	0.756858
H	-2.958716	1.936115	1.299515
C	-1.046047	1.153729	0.696909
H	-0.496801	1.938800	1.203983
O	-4.502878	0.253982	0.231946
C	-5.334117	-0.731350	-0.382530
H	-5.129584	-1.728785	0.022927
H	-6.357084	-0.441508	-0.141538
H	-5.200768	-0.737653	-1.470402
C	1.720546	2.491236	-0.147891
N	1.529952	3.507139	-0.677640

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -821.662031198 Predicted Change= -6.133344D-09

Zero-point correction (ZPE)=	-821.4190	0.24296
Internal Energy (U)=	-821.4032	0.25883
Enthalpy (H)=	-821.4022	0.25977
Gibbs Free Energy (G)=	-821.4636	0.19839

Frequencies -- -599.1291 32.2311 49.7146
E_{solv} = -0.014264308
$E_{SCS\text{-}MP2/\infty}$ = -821.0539874



***(syn)*-2d**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.036644	-0.269081	1.008732
C	-1.200217	0.511023	0.371330
H	-1.578167	1.197951	1.142395
C	-0.528098	1.345752	-0.753694
H	-1.144338	2.195974	-1.056373
H	-0.376204	0.715042	-1.635596
C	0.821440	1.759916	-0.133030
H	0.692228	2.631169	0.520019
H	1.572106	2.018175	-0.885757
C	1.245802	0.545858	0.716086
H	1.924143	0.774220	1.540586
C	1.628808	-0.691402	-0.102607
O	2.546692	-1.059862	-0.770128
O	0.447611	-1.359260	0.156026
H	-0.230250	-0.637472	2.016796
C	-2.318134	-0.323822	-0.069335
N	-3.213097	-0.973079	-0.422021

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

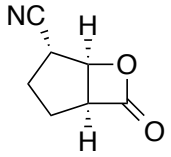
SCF Energy= -476.128578212 Predicted Change= -1.729369D-08

Zero-point correction (ZPE)=	-475.9958	0.13277
Internal Energy (U)=	-475.9877	0.14080
Enthalpy (H)=	-475.9868	0.14174
Gibbs Free Energy (G)=	-476.0290	0.09952

Frequencies -- 79.4877 132.3824 153.6379

E_{solv} = -0.016765537

$E_{SCS\text{-}MP2/\infty}$ = -475.8020758



***(anti)*-2d**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.012381	-0.904209	-0.299692
C	-1.082355	-0.352740	0.665875
H	-1.151724	-0.978791	1.562374
C	-0.582877	1.087344	0.986035
H	0.169910	1.020709	1.778521
H	-1.385826	1.736917	1.342310
C	0.054085	1.573263	-0.331943
H	0.776925	2.380240	-0.179985
H	-0.718820	1.939376	-1.016955
C	0.705051	0.312816	-0.931759
H	0.842667	0.337036	-2.014459
C	1.909321	-0.214287	-0.145690
O	3.054955	0.073854	0.022936
O	1.210957	-1.263752	0.425251
H	-0.339192	-1.729581	-0.932620
C	-2.391637	-0.335808	0.002521
N	-3.416640	-0.312142	-0.542395

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

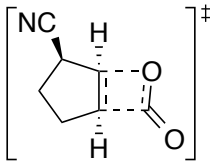
SCF Energy= -476.130057133 Predicted Change= -1.720813D-07

Zero-point correction (ZPE)=	-475.9973	0.13273
Internal Energy (U)=	-475.9892	0.14077
Enthalpy (H)=	-475.9883	0.14172
Gibbs Free Energy (G)=	-476.0305	0.09946

Frequencies -- 82.0971 109.2521 163.8843

E_{solv} = -0.014381199

$E_{SCS\text{-}MP2/\infty}$ = -475.8042826



***(syn)*-TS3d**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.099193	0.029770	1.162964
C	-1.205760	0.615442	0.327317
H	-1.651460	1.386269	0.983852
C	-0.455695	1.335946	-0.832651
H	-1.026965	2.184375	-1.215748
H	-0.309606	0.626731	-1.652582
C	0.897411	1.728843	-0.198294
H	0.832869	2.705589	0.299415
H	1.701877	1.784902	-0.937542
C	1.138591	0.613853	0.820683
H	1.934487	0.697849	1.556816
C	1.479851	-0.917705	-0.102593
O	2.528235	-0.912073	-0.678174
O	0.488373	-1.667960	0.050992
H	-0.299254	-0.590008	2.028586
C	-2.283709	-0.291565	-0.067920
N	-3.163398	-0.977564	-0.386052

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

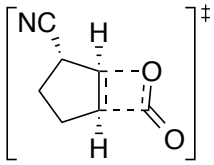
SCF Energy= -476.064168003 Predicted Change= -7.058537D-09

Zero-point correction (ZPE)=	-475.9359	0.12818
Internal Energy (U)=	-475.9273	0.13685
Enthalpy (H)=	-475.9263	0.13779
Gibbs Free Energy (G)=	-475.9702	0.09390

Frequencies -- -843.7129 59.6547 93.4813

E_{solv} = -0.027249056

$E_{SCS\text{-}MP2/\infty}$ = -475.7281364



***(anti)*-TS3d**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.174944	-0.748287	-0.585769
C	-1.084953	-0.389294	0.571061
H	-1.047782	-1.137282	1.369602
C	-0.572244	1.017199	1.014758
H	0.164741	0.870311	1.809817
H	-1.377179	1.640392	1.409785
C	0.102073	1.604570	-0.246679
H	0.923199	2.283134	0.002397
H	-0.617520	2.159913	-0.861230
C	0.595780	0.361733	-0.987357
H	0.965885	0.436579	-2.007172
C	1.950397	-0.371052	-0.027051
O	1.529465	-1.450767	0.453081
O	2.946600	0.291150	-0.008226
H	-0.271981	-1.688326	-1.115351
C	-2.455872	-0.342439	0.036358
N	-3.529900	-0.297482	-0.402659

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

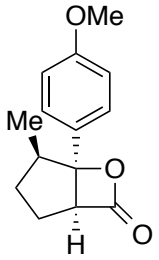
SCF Energy= -476.065091637 Predicted Change= -6.191872D-09

Zero-point correction (ZPE)=	-475.9366	0.12844
Internal Energy (U)=	-475.9279	0.13715
Enthalpy (H)=	-475.9269	0.13810
Gibbs Free Energy (G)=	-475.9710	0.09402

Frequencies -- -846.7863 60.3044 85.5107

E_{solv} = -0.024887874

$E_{SCS\text{-}MP2/\infty}$ = -475.7292272



***(syn)*-2d**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.175451	-0.066535	0.053038
C	-0.325675	0.050372	0.079366
C	1.770257	-1.440257	0.434832
H	1.165846	-2.185841	-0.102629
C	3.181959	-1.430892	-0.193093
H	3.579579	-2.441252	-0.333689
H	3.878545	-0.897817	0.466348
C	3.011665	-0.665774	-1.521140
H	2.606107	-1.327501	-2.296591
H	3.946887	-0.244381	-1.903558
C	1.975753	0.424028	-1.193224
H	1.414125	0.808387	-2.047266
C	2.489450	1.495492	-0.236210
O	3.227419	2.436581	-0.276618
O	1.812921	1.012172	0.858774
C	-2.499017	-0.601858	-0.815641
H	-3.067439	-1.178639	-1.536140
C	-3.139324	0.220774	0.119467
C	-2.369068	0.957384	1.029773
H	-2.880178	1.593055	1.746081
C	-0.982374	0.872712	1.007159
H	-0.395052	1.453291	1.710201
O	-4.491330	0.373717	0.222964
C	-5.320625	-0.346959	-0.674360
H	-5.188838	-1.431607	-0.563835
H	-6.346402	-0.080581	-0.413330
H	-5.128158	-0.065270	-1.718198
C	-1.104984	-0.678644	-0.824655
H	-0.625213	-1.319572	-1.561325
C	1.722347	-1.751198	1.930834
H	0.691271	-1.753236	2.301231
H	2.155909	-2.736472	2.136008
H	2.286042	-1.004189	2.498859

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -768.787817231 Predicted Change= -3.454760D-08

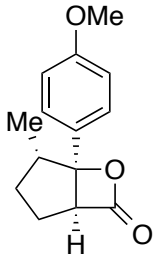
Zero-point correction (ZPE)=	-768.5122	0.27560
Internal Energy (U)=	-768.4971	0.29065
Enthalpy (H)=	-768.4962	0.29159

Gibbs Free Energy (G)=		-768.5549	0.23283

Frequencies --	28.6658	50.9944	69.2970

E_{solv} = -0.010359111

$E_{SCS\text{-}MP2/\infty}$ = -768.2309019



***(anti)*-2d**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.201714	0.012560	-0.201981
C	-0.290999	0.001417	-0.010224
C	1.854762	-1.176477	-0.952286
H	1.736696	-1.007732	-2.029410
C	3.345991	-1.090003	-0.534273
H	3.867150	-0.351738	-1.153866
H	3.867409	-2.044536	-0.660057
C	3.322691	-0.617952	0.935633
H	4.261069	-0.149574	1.249434
H	3.132466	-1.457626	1.614367
C	2.140890	0.364867	0.992198
H	1.699894	0.512696	1.979971
C	2.391995	1.647903	0.204378
O	3.027011	2.653977	0.337724
O	1.622776	1.281926	-0.871211
C	-0.881142	-0.604038	1.110538
C	-2.260981	-0.639705	1.264732
H	-2.718940	-1.103431	2.132750
C	-3.093110	-0.061007	0.295327
C	-2.520526	0.552580	-0.825091
H	-3.138450	1.016904	-1.585126
C	-1.131572	0.577504	-0.966793
H	-0.695258	1.072855	-1.828561
H	-0.255224	-1.053689	1.877368
O	-4.432844	-0.143146	0.538089
C	-5.322876	0.432529	-0.405740
H	-5.226158	-0.040316	-1.391981
H	-6.327058	0.253813	-0.017259
H	-5.160105	1.513620	-0.506806
C	1.237326	-2.537753	-0.601422
H	0.176770	-2.579871	-0.865194
H	1.757202	-3.330920	-1.150053
H	1.322013	-2.767057	0.467646

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -768.783907129 Predicted Change= -7.189245D-09

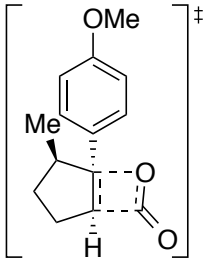
Zero-point correction (ZPE)=	-768.5081	0.27577
Internal Energy (U)=	-768.4931	0.29073
Enthalpy (H)=	-768.4922	0.29167

Gibbs Free Energy (G)=		-768.5505	0.23331

Frequencies --	34.0681	52.6720	77.6812

E_{solv} = -0.010632435

$E_{SCS\text{-}MP2/\infty}$ = -768.2285162



***(syn)*-TS3d**

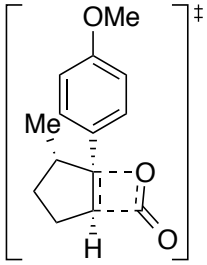
Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.080735	0.293877	-0.343191
C	0.351603	0.275493	-0.226008
C	-1.943052	1.517784	-0.111734
H	-1.594960	2.261416	-0.850518
C	-3.372470	1.063897	-0.510467
H	-3.946173	1.876710	-0.966417
H	-3.909168	0.746398	0.390646
C	-3.163359	-0.140693	-1.444770
H	-3.003147	0.183767	-2.481739
H	-3.997134	-0.848412	-1.431444
C	-1.896242	-0.790234	-0.871507
H	-1.397278	-1.514825	-1.516779
C	-2.282117	-1.542877	0.562969
O	-3.099563	-2.444975	0.476840
O	-1.667765	-1.024394	1.530159
C	1.110264	1.470116	-0.141197
H	0.608309	2.430945	-0.157014
C	2.489507	1.442894	-0.081586
H	3.072033	2.357138	-0.036695
C	3.171554	0.211807	-0.072727
C	2.442750	-0.989238	-0.141997
H	2.946330	-1.948287	-0.120134
C	1.060508	-0.947498	-0.227472
H	0.508174	-1.879961	-0.244605
O	4.517322	0.289523	0.004419
C	5.279449	-0.915385	0.029823
H	5.130681	-1.498818	-0.886518
H	6.321844	-0.602035	0.096996
H	5.024143	-1.527994	0.902476
C	-1.866730	2.139108	1.293105
H	-2.155721	1.385413	2.029643
H	-0.862109	2.490722	1.544453
H	-2.551350	2.992302	1.356878

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -768.743835760 Predicted Change= -4.631974D-09
Zero-point correction (ZPE)= -768.4711 0.27266
Internal Energy (U)= -768.4557 0.28808
Enthalpy (H)= -768.4548 0.28903

Gibbs Free Energy (G)=	-768.5141	0.22969
Frequencies --	-526.9860	45.9245 54.8248

E_{solv} = -0.022030259
$E_{SCS\text{-}MP2/\infty}$ = -768.1709828



***(anti)*-TS3d**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.130725	0.289910	-0.137412
C	-0.303386	0.249715	-0.047723
C	1.976031	1.456011	0.331261
H	1.768424	1.705493	1.376607
C	3.433084	0.970079	0.126615
H	3.774848	0.456898	1.029642
H	4.116508	1.802206	-0.070533
C	3.337229	-0.029843	-1.043122
H	4.141142	-0.771265	-1.043531
H	3.357789	0.486292	-2.012321
C	1.973920	-0.694675	-0.799371
H	1.556499	-1.262946	-1.629871
C	2.148294	-1.728290	0.510328
O	1.661878	-1.224137	1.552573
O	2.736692	-2.769621	0.273249
C	-1.055911	-0.710272	-0.760039
H	-0.546076	-1.437606	-1.381866
C	-2.440036	-0.755638	-0.688403
H	-2.978819	-1.507775	-1.252094
C	-3.123158	0.170536	0.118615
C	-2.395873	1.131971	0.847326
H	-2.943622	1.826952	1.475136
C	-1.019604	1.166234	0.764649
H	-0.477171	1.897165	1.353872
O	-4.464177	0.220308	0.263355
C	-5.270399	-0.736074	-0.421155
H	-5.030563	-1.757501	-0.103254
H	-6.299765	-0.501559	-0.147936
H	-5.151631	-0.650401	-1.507895
C	1.675900	2.697041	-0.549928
H	1.882039	2.496043	-1.607028
H	0.634323	3.020898	-0.468165
H	2.320040	3.524479	-0.234034

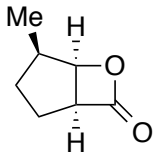
Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -768.741636490 Predicted Change= -3.424605D-08

Zero-point correction (ZPE)=	-768.4688	0.27283
Internal Energy (U)=	-768.4533	0.28829
Enthalpy (H)=	-768.4524	0.28923

Gibbs Free Energy (G)=	-768.5122	0.22943
Frequencies --	-581.8261	32.3986	52.4538

E_{solv} = -0.023065949
$E_{SCS\text{-}MP2/\infty}$ = -768.1704906



***(syn)*-2d**

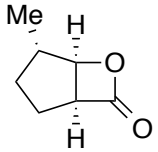
Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.231770	-0.458354	0.923166
C	-1.495273	0.092625	0.259589
H	-2.045232	0.615566	1.057983
C	-0.953998	1.159296	-0.721671
H	-1.716657	1.892908	-1.001490
H	-0.616555	0.673542	-1.646078
C	0.243456	1.793592	0.016466
H	-0.103129	2.551999	0.729100
H	0.962368	2.274976	-0.653992
C	0.870294	0.619717	0.794961
H	1.440932	0.905533	1.681491
C	1.554543	-0.429464	-0.084868
O	2.569765	-0.534862	-0.708403
O	0.539271	-1.351728	0.028809
H	-0.383077	-0.955253	1.883786
C	-2.404118	-0.968517	-0.362304
H	-2.774807	-1.669593	0.394593
H	-3.273329	-0.505055	-0.842404
H	-1.861609	-1.545267	-1.118272

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -423.210405045 Predicted Change= -3.369239D-08

Zero-point correction (ZPE)=	-423.0480	0.16236
Internal Energy (U)=	-423.0402	0.17011
Enthalpy (H)=	-423.0393	0.17105
Gibbs Free Energy (G)=	-423.0803	0.13010

Frequencies -- 100.6444 156.0922 228.1187E_{solv} =
E_{solv} = -0.008377591
$E_{SCS\text{-}MP2/\infty}$ = -422.9192498



***(anti)*-2d**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.183552	-0.901218	0.385480
C	1.349948	-0.431346	-0.485780
H	1.449446	-1.089686	-1.356739
C	0.926249	0.999297	-0.909834
H	0.250791	0.944370	-1.771181
H	1.780363	1.616521	-1.207221
C	0.173092	1.573694	0.311586
H	-0.522183	2.376392	0.046491
H	0.875076	1.979071	1.049365
C	-0.552294	0.355296	0.914435
H	-0.775824	0.431632	1.980880
C	-1.707768	-0.176054	0.062558
O	-2.831947	0.138768	-0.197775
O	-1.007494	-1.261193	-0.412173
H	0.414338	-1.711803	1.080399
C	2.664614	-0.452055	0.308936
H	2.918472	-1.469257	0.629373
H	3.491210	-0.077313	-0.304200
H	2.609487	0.173787	1.208125

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

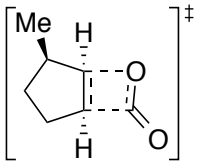
SCF Energy= -423.208799237 Predicted Change= -1.728368D-07

Zero-point correction (ZPE)=	-423.0465	0.16228
Internal Energy (U)=	-423.0387	0.17006
Enthalpy (H)=	-423.0377	0.17101
Gibbs Free Energy (G)=	-423.0788	0.12994

Frequencies -- 98.3277 142.9239 209.1589

E_{solv} = -0.008509072

$E_{SCS\text{-}MP2/\infty}$ = -422.9184377



***(anti)*-TS3d**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.384767	-0.199142	1.108738
C	-1.531796	0.146035	0.219627
H	-2.204227	0.703503	0.903770
C	-0.918384	1.157029	-0.785279
H	-1.650985	1.892351	-1.130064
H	-0.562459	0.607331	-1.664671
C	0.276127	1.787393	-0.033118
H	-0.039170	2.664510	0.548054
H	1.083246	2.101495	-0.701541
C	0.722803	0.655868	0.896297
H	1.428703	0.854347	1.700882
C	1.475778	-0.619463	-0.098547
O	2.483739	-0.269152	-0.652390
O	0.763986	-1.649588	-0.040607
H	-0.468767	-0.926960	1.908548
C	-2.313955	-1.025635	-0.379460
H	-2.717055	-1.678179	0.402844
H	-3.152732	-0.657991	-0.979929
H	-1.653188	-1.622996	-1.013469

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

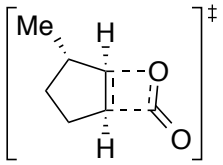
SCF Energy= -423.151954418 Predicted Change= -1.914241D-09

Zero-point correction (ZPE)=	-422.9941	0.15785
Internal Energy (U)=	-422.9857	0.16621
Enthalpy (H)=	-422.9847	0.16715
Gibbs Free Energy (G)=	-423.0273	0.12456

Frequencies -- -759.2363 59.5962 132.2421

E_{solv} = -0.012615218

$E_{SCS\text{-}MP2/\infty}$ = -422.8501678



***(anti)*-TS3d**

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.361312	-0.774603	0.625955
C	1.353196	-0.452232	-0.445220
H	1.340952	-1.206882	-1.238213
C	0.905182	0.951169	-0.936874
H	0.222227	0.835792	-1.784996
H	1.750787	1.558229	-1.274489
C	0.151379	1.575524	0.263043
H	-0.636883	2.267316	-0.048561
H	0.832926	2.126444	0.924520
C	-0.423696	0.350075	0.975484
H	-0.840217	0.442772	1.976898
C	-1.742546	-0.320469	-0.028345
O	-1.389439	-1.447621	-0.446415
O	-2.688901	0.411870	-0.139900
H	0.377904	-1.716276	1.163414
C	2.763548	-0.445694	0.199496
H	3.023707	-1.427186	0.610758
H	3.505643	-0.190916	-0.564321
H	2.839418	0.294089	1.004279

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -423.148965457 Predicted Change= -7.821573D-08
Zero-point correction (ZPE)= -422.9908 0.15814
Internal Energy (U)= -422.9824 0.16655
Enthalpy (H)= -422.9814 0.16750
Gibbs Free Energy (G)= -423.0242 0.12470

Frequencies -- -788.3104 59.5144 119.8466
E_{solv} = -0.012677933
$E_{SCS\text{-}MP2/\infty}$ = -422.8478843

Appendix IV:

Computational Data for Chapter 6

Asymmetric Homoenolate Additions to Acyl Phosphonates through Rational Design of a Tailored *N*-Heterocyclic Carbene Catalyst

Molecular Geometries for Aldol TSs with Catalyst D (3,5-H)

TS-Major

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

b3lyp/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C54H51N2O5P C1[X(C54H51N2O5P)] #Atoms= 113
Charge = 0 Multiplicity = 1

SCF Energy= -2915.44004613 Predicted Change= -3.452388D-09

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00189	0.00180	[NO]	0.00189	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.233810	-0.049880	-1.021420
C	1.011530	0.064330	-0.310860
O	-0.265550	-1.033030	-1.986210
H	-1.015870	-1.629600	-1.725470
C	-1.338020	0.684780	-0.671190
H	-1.211720	1.421770	0.109850
C	-2.665850	0.466171	-1.171320
H	-2.688730	-0.027929	-2.141400
C	-3.657330	1.564271	-1.063600
C	-3.691409	2.476721	0.009090
H	-2.976639	2.386431	0.820900
C	-4.638839	3.497121	0.058650
H	-4.638459	4.186511	0.900140
C	-5.586009	3.638331	-0.958750
H	-6.323239	4.436041	-0.918270
C	-5.572439	2.739661	-2.026420
H	-6.302069	2.831701	-2.827320
C	-4.623760	1.719561	-2.075260
H	-4.624230	1.026521	-2.912740
N	1.493910	1.174910	0.308630
C	0.921091	2.494830	0.324850
C	2.786020	0.906010	0.997750
H	2.633300	1.037370	2.071740
C	3.917080	1.831740	0.579640
C	3.024040	-0.606630	0.706400
C	3.098070	-1.436450	1.977730
H	3.954150	-0.746210	0.149210
N	1.888370	-0.960520	-0.180770
C	1.710490	-2.340170	-0.555240
C	2.604860	-2.921370	-1.473950

C	2.520430	-4.305610	-1.687810
H	3.199600	-4.764230	-2.401210
H	1.503799	-6.147300	-1.237680
C	1.557400	-5.079450	-1.043740
C	0.649850	-4.474440	-0.174320
H	-0.121960	-5.063850	0.311850
C	0.733830	-3.107910	0.082550
C	3.577360	-2.118800	-2.267910
H	0.033670	-2.622930	0.753470
C	4.948730	-2.417530	-2.246650
H	5.308810	-3.214681	-1.601050
C	5.847590	-1.701261	-3.039430
H	6.906600	-1.943931	-3.007720
C	5.386960	-0.680341	-3.872570
H	6.084400	-0.128821	-4.497700
C	4.021930	-0.380120	-3.907860
H	3.653480	0.401180	-4.567760
C	3.122470	-1.089760	-3.111020
H	2.057930	-0.878130	-3.156860
C	0.366481	2.977700	1.528460
C	0.244351	2.115280	2.764870
H	-0.157910	1.123040	2.531050
H	-0.428699	2.588990	3.486220
H	1.205521	1.972240	3.275690
C	-0.135159	4.283510	1.549210
H	-0.565979	4.659950	2.474700
C	-0.120029	5.104070	0.419470
C	-0.716359	6.491050	0.454520
H	-0.168539	7.180170	-0.197220
H	-0.712309	6.905100	1.468160
H	-1.758569	6.476360	0.109420
C	0.425681	4.587740	-0.758490
H	0.442731	5.207950	-1.652010
C	0.951611	3.295290	-0.835690
C	1.481001	2.789480	-2.154830
H	1.615341	3.619450	-2.854750
H	0.781341	2.077340	-2.608690
H	2.441801	2.280650	-2.043920
C	4.311751	2.859510	1.444090
H	3.800021	2.985530	2.395260
C	5.354841	3.721659	1.101960
H	5.647651	4.512879	1.786720
C	6.020161	3.562869	-0.113740
H	6.835141	4.229889	-0.381640
C	5.636741	2.538669	-0.982450
H	6.151331	2.401469	-1.929530
C	4.594170	1.678840	-0.638530
H	4.313990	0.886790	-1.327110
C	4.325280	-1.986720	2.360690
H	5.193970	-1.858871	1.718500
C	4.446200	-2.693570	3.559050
H	5.407160	-3.113671	3.843830
C	3.333340	-2.862560	4.382190
H	3.422240	-3.415740	5.313430

C	2.101790	-2.323240	4.000780
H	1.227510	-2.458990	4.631630
C	1.980340	-1.611590	2.807850
H	1.007550	-1.218270	2.521860
C	-6.096100	-2.607559	-2.369640
H	-6.239180	-3.308019	-3.189210
C	-4.818340	-2.393949	-1.857760
H	-3.958430	-2.922919	-2.254080
C	-4.608680	-1.497839	-0.796510
C	-3.181920	-1.339409	-0.316940
O	-2.308520	-2.176860	-0.759530
P	-2.876430	-1.161329	1.521210
O	-3.559260	-2.496029	2.168830
C	-2.906040	-3.766559	2.021560
H	-2.809080	-4.022869	0.962580
H	-3.536890	-4.498929	2.530640
H	-1.915820	-3.744080	2.488890
O	-1.443390	-0.986990	1.927050
O	-3.873570	-0.024249	2.108300
C	-3.898660	0.228541	3.523160
H	-2.885420	0.389251	3.904180
H	-4.362600	-0.611329	4.048970
H	-4.496250	1.131081	3.665120
C	-5.713930	-0.818989	-0.260310
H	-5.576150	-0.118329	0.553890
C	-6.993800	-1.042699	-0.769030
H	-7.839090	-0.510849	-0.339410
C	-7.192140	-1.934129	-1.824320
H	-8.191470	-2.103879	-2.217640

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

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SCF Energy= -2915.44004613 Predicted Change= -3.452388D-09

Zero-point correction (ZPE)=	-2914.5161	0.92392
Internal Energy (U)=	-2914.4592	0.98083
Enthalpy (H)=	-2914.4582	0.98178
Gibbs Free Energy (G)=	-2914.6132	0.82677

Frequencies -- -290.8654 12.9779 15.0218

TS-Minor

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

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b3lyp/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

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Pointgroup= C1 Stoichiometry= C54H51N2O5P C1[X(C54H51N2O5P)] #Atoms= 113
Charge = 0 Multiplicity = 1

SCF Energy= -2915.43895520 Predicted Change= -4.861316D-10

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Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00066	0.00180	[YES]	0.00066	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.244726	-0.271756	-1.100954
C	-1.125292	-0.009159	-0.761588
O	0.443500	-1.419560	-1.833188
H	1.132778	-1.923767	-1.317249
C	1.295685	0.544372	-0.753359
H	1.090787	1.409882	-0.142689
C	2.662165	0.275654	-1.109125
H	2.741169	-0.323640	-2.015737
C	3.609243	1.423243	-1.096825
C	4.568801	1.544401	-2.118263
H	4.606144	0.788776	-2.898547
C	5.463560	2.613956	-2.150548
H	6.191286	2.680290	-2.955823
C	5.422157	3.596784	-1.160706
H	6.116311	4.432925	-1.185216
C	4.476792	3.491466	-0.136817
H	4.435657	4.246856	0.644834
C	3.586975	2.419925	-0.102227
H	2.874801	2.348182	0.714616
N	-1.656503	1.173514	-0.324466
C	-1.047614	2.478485	-0.472578
C	-3.146937	1.105454	-0.310964
H	-3.503151	1.633118	-1.202959
C	-3.830429	1.735590	0.888486
C	-3.424142	-0.409690	-0.479424
C	-4.563515	-0.714162	-1.433493
H	-3.661418	-0.851964	0.493033
N	-2.109096	-0.939875	-0.907024
C	-1.986049	-2.379529	-0.990660
C	-1.986671	-3.173213	0.173445
C	-2.041890	-4.568993	0.012883
H	-2.030576	-5.190413	0.903858
H	-2.116946	-6.241353	-1.336385

C	-2.084181	-5.159011	-1.246464
C	-2.075296	-4.356125	-2.388402
H	-2.101227	-4.803212	-3.377938
C	-2.035839	-2.972674	-2.255113
C	-1.941796	-2.612911	1.555713
H	-2.026920	-2.332935	-3.129458
C	-2.981023	-2.899213	2.458637
H	-3.824147	-3.500121	2.126183
C	-2.941045	-2.417394	3.767890
H	-3.753372	-2.648726	4.452446
C	-1.859066	-1.642932	4.194809
H	-1.825288	-1.269988	5.215525
C	-0.816457	-1.360228	3.308656
H	0.042784	-0.770511	3.613818
C	-0.852713	-1.845279	1.998695
H	-0.007451	-1.657106	1.343251
C	-1.007299	3.086730	-1.744532
C	-1.489068	2.388464	-2.996417
H	-1.247421	2.987394	-3.879040
H	-2.574628	2.230216	-3.001755
H	-1.012175	1.409996	-3.121834
C	-0.461410	4.369199	-1.849942
H	-0.420359	4.839000	-2.830250
C	0.043349	5.053891	-0.742204
C	0.671184	6.419195	-0.891103
H	0.263387	6.958138	-1.752592
H	1.755443	6.333281	-1.041134
H	0.513058	7.033339	0.001839
C	-0.006642	4.418194	0.500091
H	0.392222	4.929241	1.373598
C	-0.535179	3.132910	0.665624
C	-0.459332	2.472121	2.021712
H	0.285091	1.665340	2.035943
H	-1.414235	2.040101	2.324792
H	-0.165342	3.205344	2.779260
C	-3.757037	1.167573	2.169002
H	-3.162642	0.274740	2.339843
C	-4.431195	1.751887	3.240291
H	-4.361771	1.299241	4.225576
C	-5.189570	2.909629	3.049049
H	-5.716302	3.361450	3.885301
C	-5.267590	3.481923	1.779743
H	-5.854544	4.382276	1.620167
C	-4.591624	2.895566	0.707976
H	-4.658722	3.343159	-0.280809
C	-4.454328	-0.466456	-2.808743
H	-3.518978	-0.091303	-3.215338
C	-5.529861	-0.713096	-3.660383
H	-5.429176	-0.522612	-4.725542
C	-6.732629	-1.205627	-3.147252
H	-7.570887	-1.397385	-3.811489
C	-6.850231	-1.454036	-1.779946
H	-7.780577	-1.840508	-1.372814
C	-5.768978	-1.212738	-0.929973

H	-5.862668	-1.411494	0.134895
C	6.806363	-1.606688	-1.258940
H	7.753543	-1.079361	-1.175508
C	5.687226	-1.113692	-0.586094
H	5.776460	-0.219032	0.015785
C	4.454671	-1.780438	-0.674360
C	3.179692	-1.329490	0.013344
O	2.169115	-2.139378	-0.023420
P	3.267255	-0.706556	1.770034
O	4.608139	0.186192	1.941937
C	4.845065	0.866207	3.184483
H	5.176873	0.153318	3.946076
H	3.938221	1.375091	3.524329
H	5.632197	1.597784	2.992191
O	2.020574	-0.036265	2.259188
O	3.700297	-2.013756	2.639540
C	2.768513	-3.076184	2.902186
H	1.883055	-2.694775	3.419470
H	3.292429	-3.788288	3.544557
H	2.469243	-3.553117	1.966041
C	4.377538	-2.949376	-1.449036
H	3.428806	-3.472946	-1.491165
C	5.494790	-3.435048	-2.124616
H	5.414722	-4.344469	-2.715678
C	6.716755	-2.764370	-2.033039
H	7.591884	-3.144316	-2.554567

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

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SCF Energy=	-2915.43895520	Predicted Change= -4.861316D-10
Zero-point correction (ZPE)=	-2914.5147	0.92422
Internal Energy (U)=	-2914.4580	0.98088
Enthalpy (H)=	-2914.4571	0.98182
Gibbs Free Energy (G)=	-2914.6105	0.82844

Frequencies --	-304.0075	14.6040	16.4500

Molecular Geometries for Aldol TSs with Catalyst E (3,5-Me)

TS-Major

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

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b3lyp/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,modredundant)
Modredundant Input: B 7 90 F
b3lyp/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest,gdiis) iop(1/8=18) freq=noraman
geom=allcheck guess=read
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RB3LYP/6-31G(d) Freq

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Pointgroup= C1 Stoichiometry= C56H55N2O5P C1[X(C56H55N2O5P)] #Atoms= 119
Charge = 0 Multiplicity = 1

SCF Energy= -2994.07608244 Predicted Change= 7.405757D-10

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Optimization completed on the basis of negligible forces. {Found 3 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00187	0.00180	[NO]	0.00187	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.359402	-0.045609	-0.903114
C	0.824886	0.118644	-0.109932
O	-0.283721	-1.032671	-1.865179
H	-1.014484	-1.665351	-1.654859
C	-1.515298	0.655125	-0.650570
H	-1.475357	1.401338	0.131241
C	-2.784975	0.394063	-1.251327
H	-2.725775	-0.131466	-2.202214
C	-3.827160	1.445131	-1.231859
C	-3.981179	2.370111	-0.179869
H	-3.325189	2.322611	0.683545
C	-4.973591	3.347065	-0.217839
H	-5.065638	4.047418	0.609499
C	-5.848532	3.431619	-1.304189
H	-6.620831	4.195988	-1.331361
C	-5.717006	2.519165	-2.351930
H	-6.389217	2.566637	-3.205288
C	-4.723640	1.542351	-2.313549
H	-4.632757	0.837620	-3.136203
N	1.221733	1.248549	0.539879
C	0.593233	2.542873	0.529282
C	2.493400	1.040523	1.285081
H	2.296465	1.195259	2.348761
C	3.610674	1.992383	0.885236
C	2.792261	-0.468902	1.041042
C	2.794322	-1.278459	2.328024

H	3.765610	-0.590155	0.558980
N	1.738449	-0.867578	0.076345
C	1.632208	-2.257707	-0.284313
C	2.613885	-2.823892	-1.118913
C	2.589337	-4.213216	-1.314731
H	3.338615	-4.659565	-1.962671
H	1.596415	-6.079828	-0.916075
C	1.601778	-5.008027	-0.736877
C	0.609782	-4.419186	0.047436
H	-0.180146	-5.025383	0.481170
C	0.631670	-3.047212	0.287157
C	3.623242	-2.003521	-1.847319
H	-0.135058	-2.576072	0.892179
C	4.993515	-2.242755	-1.688494
H	5.320655	-3.003872	-0.983075
C	5.946294	-1.521987	-2.422207
C	5.497116	-0.564114	-3.335589
H	6.226768	-0.012637	-3.926935
C	4.130242	-0.306693	-3.523631
C	3.201881	-1.028496	-2.767949
H	2.136480	-0.868396	-2.912388
C	-0.054877	2.988380	1.700320
C	-0.222323	2.103875	2.915297
H	-0.605682	1.113442	2.644699
H	-0.929877	2.559470	3.615089
H	0.716371	1.956274	3.464535
C	-0.607841	4.273630	1.703979
H	-1.108955	4.621242	2.605021
C	-0.555565	5.108590	0.585928
C	-1.204879	6.472054	0.599135
H	-0.642989	7.190067	-0.007934
H	-1.280536	6.871496	1.615825
H	-2.221821	6.424616	0.187880
C	0.079913	4.627959	-0.561811
H	0.126230	5.259061	-1.446644
C	0.661095	3.358247	-0.619386
C	1.291182	2.890518	-1.907884
H	1.396939	3.726612	-2.605390
H	0.671698	2.125517	-2.390703
H	2.281226	2.456808	-1.745256
C	3.919959	3.070844	1.722205
H	3.352336	3.217710	2.638007
C	4.948552	3.957235	1.398063
H	5.173917	4.788101	2.061078
C	5.686404	3.771219	0.229003
H	6.491072	4.456357	-0.024043
C	5.389078	2.696117	-0.611642
H	5.961743	2.536912	-1.521311
C	4.359613	1.813051	-0.286873
H	4.145547	0.982642	-0.953895
C	4.006305	-1.784011	2.809138
H	4.915505	-1.637240	2.230156
C	4.060918	-2.470594	4.023967
C	2.896266	-2.664128	4.766025

H	2.933254	-3.201662	5.709876
C	1.680208	-2.169846	4.286765
C	1.624644	-1.478865	3.076799
H	0.663431	-1.122922	2.714071
C	-6.022777	-2.804021	-2.655777
H	-6.085530	-3.509094	-3.481395
C	-4.793075	-2.555126	-2.051345
H	-3.892541	-3.061071	-2.382196
C	-4.687704	-1.652348	-0.979658
C	-3.310000	-1.460115	-0.391992
O	-2.379069	-2.257195	-0.766226
P	-3.137390	-1.232305	1.458209
O	-3.831854	-2.571892	2.083870
C	-3.135527	-3.826055	2.012942
H	-2.970781	-4.111207	0.969582
H	-3.773872	-4.562113	2.506988
H	-2.174676	-3.760716	2.534047
O	-1.740182	-1.016798	1.955934
O	-4.200171	-0.110792	1.948524
C	-4.338717	0.162323	3.353510
H	-3.361003	0.348330	3.808497
H	-4.826528	-0.678741	3.855077
H	-4.961609	1.055194	3.433979
C	-5.847511	-1.002437	-0.529626
H	-5.789149	-0.295630	0.288785
C	-7.079224	-1.261541	-1.131570
H	-7.968074	-0.751683	-0.768541
C	-7.174215	-2.159952	-2.195253
H	-8.136521	-2.357455	-2.661140
C	3.675858	0.729323	-4.527291
H	2.604397	0.642552	-4.731224
H	3.860822	1.748593	-4.162988
H	4.211256	0.626243	-5.478347
C	7.423362	-1.769775	-2.216339
H	7.637633	-2.837256	-2.092563
H	8.012660	-1.402824	-3.062972
H	7.791500	-1.260673	-1.315543
H	0.766356	-2.325359	4.853815
H	5.010871	-2.856140	4.384560

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -2994.07608244 Predicted Change= 7.405757D-10
Zero-point correction (ZPE)= -2993.0969 0.97918
Internal Energy (U)= -2993.0362 1.03982
Enthalpy (H)= -2993.0353 1.04076
Gibbs Free Energy (G)= -2993.1988 0.87723

Frequencies -- -262.4672 14.6579 16.2928

TS-Minor

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

b3lyp/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250,calcfc,ts,noeigentest,gdiis) iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C56H55N2O5P C1[X(C56H55N2O5P)] #Atoms= 119
Charge = 0 Multiplicity = 1

SCF Energy= -2994.07262511 Predicted Change= -7.178404D-09

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00300	0.00180	[NO]	0.00300	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.436422	-0.103627	-1.172898
C	-0.935400	0.215825	-0.897425
O	0.623211	-1.171591	-2.019389
H	1.255598	-1.769102	-1.529826
C	1.512597	0.604390	-0.687686
H	1.331316	1.399476	0.018276
C	2.874006	0.301383	-1.032543
H	2.951517	-0.192844	-2.000678
C	3.878883	1.383325	-0.855702
C	4.864966	1.584413	-1.838638
H	4.880155	0.935752	-2.710598
C	5.812249	2.601149	-1.719446
H	6.558894	2.732801	-2.498992
C	5.799437	3.448786	-0.610825
H	6.534850	4.243727	-0.516609
C	4.829810	3.260745	0.377945
H	4.811448	3.908814	1.251438
C	3.886671	2.241682	0.260667
H	3.156657	2.099535	1.052057
N	-1.418731	1.384199	-0.371109
C	-0.711895	2.645757	-0.321219
C	-2.905624	1.433720	-0.483293
H	-3.143296	2.072839	-1.341451
C	-3.638012	2.007859	0.716160
C	-3.275055	-0.029347	-0.832427
C	-4.342480	-0.143224	-1.904323
H	-3.631043	-0.547478	0.062512
N	-1.968684	-0.616754	-1.207898
C	-1.930820	-2.035228	-1.487829
C	-2.165576	-2.982652	-0.472623
C	-2.245645	-4.336267	-0.850562
H	-2.413064	-5.076416	-0.073487
H	-2.157509	-5.793606	-2.428027

C	-2.099206	-4.738915	-2.173303
C	-1.876360	-3.783548	-3.166542
H	-1.760523	-4.081719	-4.204522
C	-1.802550	-2.440020	-2.820456
C	-2.389337	-2.646474	0.966021
H	-1.621883	-1.684919	-3.575620
C	-3.606561	-3.026303	1.551487
H	-4.359656	-3.512113	0.934699
C	-3.872014	-2.788009	2.905385
C	-2.886146	-2.159125	3.669113
H	-3.073297	-1.969969	4.725399
C	-1.652746	-1.775431	3.120282
C	-1.413442	-2.019247	1.760329
H	-0.450338	-1.754404	1.329587
C	-0.522056	3.387889	-1.505852
C	-0.934108	2.869054	-2.865100
H	-0.584312	3.545941	-3.649752
H	-2.022193	2.783415	-2.974605
H	-0.503122	1.881571	-3.064914
C	0.114581	4.628920	-1.415552
H	0.272615	5.200865	-2.327314
C	0.565783	5.145155	-0.198507
C	1.294832	6.466057	-0.136525
H	1.003463	7.126003	-0.960261
H	2.379860	6.313413	-0.206814
H	1.099433	6.989274	0.805688
C	0.366528	4.380357	0.952606
H	0.721431	4.757735	1.909154
C	-0.257488	3.128277	0.921874
C	-0.337748	2.310120	2.188601
H	0.400435	1.497341	2.181808
H	-1.321252	1.858646	2.327515
H	-0.127159	2.940469	3.058308
C	-3.776585	1.299455	1.918819
H	-3.324877	0.318412	2.033800
C	-4.482368	1.851887	2.987038
H	-4.579851	1.288561	3.911061
C	-5.059770	3.118735	2.871212
H	-5.611204	3.545681	3.704602
C	-4.925388	3.831706	1.680298
H	-5.370158	4.817911	1.579250
C	-4.219980	3.276232	0.611387
H	-4.120452	3.834994	-0.316115
C	-4.090546	0.223956	-3.233180
H	-3.096032	0.554700	-3.520625
C	-5.100597	0.153405	-4.191154
H	-4.889589	0.435361	-5.219233
C	-6.379397	-0.280150	-3.831825
H	-7.166655	-0.334471	-4.578786
C	-6.638884	-0.647055	-2.511540
H	-7.629466	-0.988995	-2.224204
C	-5.623393	-0.582365	-1.555344
H	-5.826912	-0.874011	-0.527885
C	6.933792	-1.737763	-1.267239

H	7.897042	-1.265824	-1.089485
C	5.810088	-1.280898	-0.576876
H	5.911410	-0.469981	0.132392
C	4.556733	-1.878078	-0.786869
C	3.275773	-1.456689	-0.094777
O	2.233398	-2.205093	-0.258604
P	3.299794	-1.036671	1.719658
O	4.696835	-0.297909	2.077658
C	4.918029	0.172268	3.416825
H	5.132872	-0.670940	4.080833
H	4.043436	0.718055	3.783403
H	5.780961	0.839548	3.372887
O	2.083027	-0.310800	2.205756
O	3.552912	-2.464923	2.459464
C	2.518898	-3.459980	2.530402
H	1.597407	-3.031734	2.935789
H	2.889627	-4.238871	3.201559
H	2.324477	-3.867946	1.536229
C	4.463167	-2.941498	-1.699633
H	3.496560	-3.413791	-1.836885
C	5.585589	-3.390909	-2.391467
H	5.492908	-4.218653	-3.090808
C	6.828320	-2.789255	-2.178875
H	7.707197	-3.141371	-2.713494
C	-0.609415	-1.127548	4.002153
H	0.295690	-0.868211	3.446804
H	-1.001289	-0.211689	4.463725
H	-0.327886	-1.797361	4.825572
C	-5.178344	-3.230238	3.524532
H	-5.156631	-4.298921	3.776305
H	-5.390215	-2.682527	4.448684
H	-6.020732	-3.078489	2.840259

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

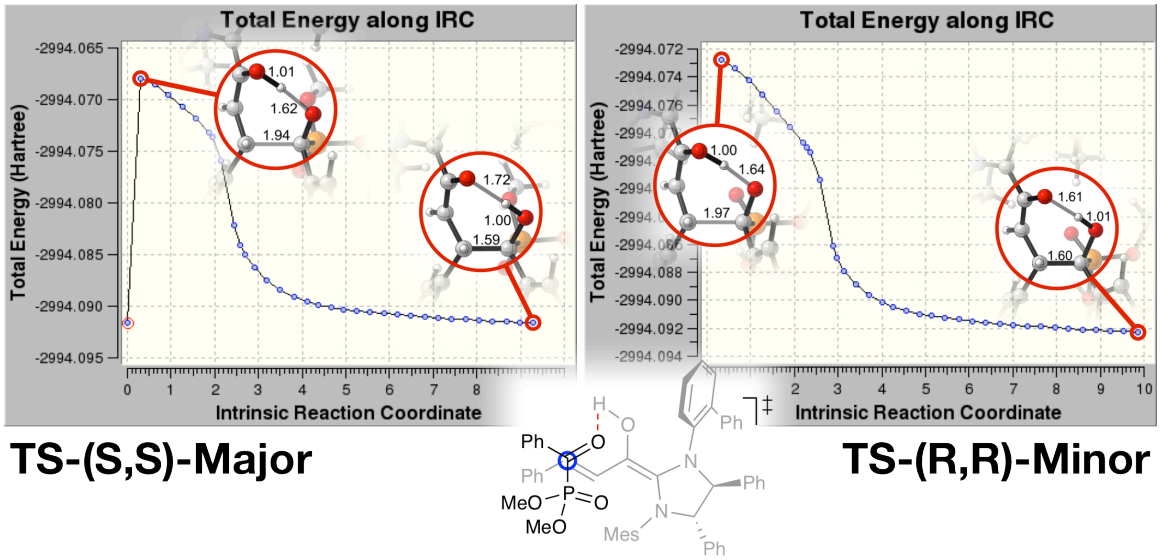
SCF Energy= -2994.07262511 Predicted Change= -7.178404D-09

Zero-point correction (ZPE)=	-2993.0931	0.97949
Internal Energy (U)=	-2993.0328	1.03976
Enthalpy (H)=	-2993.0319	1.04070
Gibbs Free Energy (G)=	-2993.1941	0.87850

Frequencies -- -304.8507 13.2592 13.3127

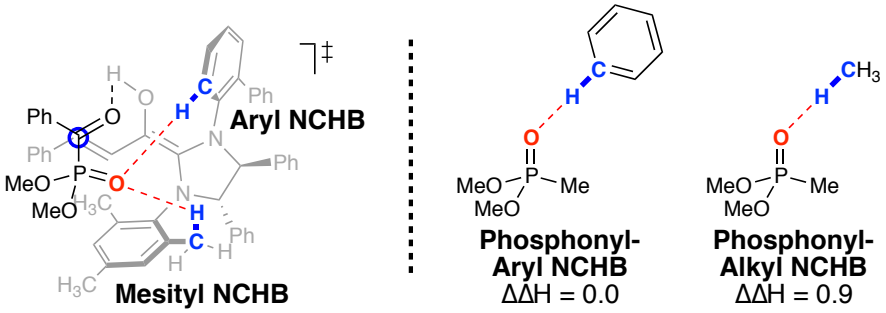
Intrinsic Reaction Coordinates (IRC) Computations for Major and Minor TSs with E

Concerted, asynchronous proton transfer occurs with stereodetermining aldol C–C bond formation.



Aryl and Mesityl Non-Classical Hydrogen Bonding (NCHB) Magnitudes

Enthalpic stabilization of the phosphonyl oxygen can be achieved by non-classical hydrogen bonding. Aryl C–H groups (modeled as benzene) is a better NCHB donor than alkyl (from mesityl) C–H groups (modeled as methyl) by 0.7 kcal/mol.



Phosphonate

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

b3lyp/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C3H9O3P C1[X(C3H9O3P)] #Atoms= 16
Charge = 0 Multiplicity = 1

SCF Energy= -686.820019942 Predicted Change= -1.067129D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00286	0.00180	[NO]	0.00286	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
P	-0.001123	0.375482	0.178526
C	0.343049	2.023732	-0.485828
O	-1.470170	0.116144	-0.441705
C	-2.149467	-1.110936	-0.123707
O	0.904118	-0.650121	-0.706836
O	0.155946	0.203395	1.646440
C	2.106879	-1.207941	-0.153001
H	1.373409	2.299174	-0.243271
H	-0.332149	2.750793	-0.026996
H	0.209213	2.035395	-1.570294
H	-2.192761	-1.257093	0.959588
H	-1.639751	-1.958016	-0.593752
H	-3.159199	-1.018252	-0.527132
H	2.306544	-2.130769	-0.702062
H	1.983534	-1.421228	0.911615
H	2.946100	-0.516712	-0.293570

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -686.820019942 Predicted Change= -1.067129D-08
Zero-point correction (ZPE)= -686.6906 0.12938
Internal Energy (U)= -686.6807 0.13926
Enthalpy (H)= -686.6798 0.14020
Gibbs Free Energy (G)= -686.7261 0.09387

Frequencies -- 54.8149 78.4385 94.1897

Benzene

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

b3lyp/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C6H6 C1[X(C6H6)] #Atoms= 12
Charge = 0 Multiplicity = 1

SCF Energy= -232.248657353 Predicted Change= -7.177522D-08

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00008	0.00045	[YES]	0.00002	0.00030	[YES]
Displ	0.00038	0.00180	[YES]	0.00038	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.038957	1.395972	0.000002
C	-1.228673	0.664209	0.000003
C	-1.189631	-0.731764	-0.000037
C	0.039045	-1.395979	-0.000027
C	1.228601	-0.664306	-0.000009
C	1.189603	0.731847	-0.000006
H	-0.069306	2.482561	0.000155
H	-2.184677	1.181568	-0.000036
H	-2.115337	-1.301553	0.000087
H	0.069245	-2.482590	0.000251
H	2.184761	-1.181383	0.000008
H	2.115387	1.301519	-0.000021

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -232.248657353 Predicted Change= -7.177522D-08

Zero-point correction (ZPE)=	-232.1479	0.10074
Internal Energy (U)=	-232.1435	0.10513
Enthalpy (H)=	-232.1425	0.10607
Gibbs Free Energy (G)=	-232.1753	0.07328

Frequencies -- 414.7043 415.5416 621.9032

Methane

Supporting Information: Methyl.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

b3lyp/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= TD Stoichiometry= CH4 TD[O(C),4C3(H)] #Atoms= 5
Charge = 0 Multiplicity = 1

SCF Energy= -40.5183890143 Predicted Change= -1.533072D-07

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00016	0.00045	[YES]	0.00008	0.00030	[YES]
Displ	0.00045	0.00180	[YES]	0.00045	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.000000	0.000000	0.000000
H	0.631339	0.631339	0.631339
H	-0.631339	-0.631339	0.631339
H	-0.631339	0.631339	-0.631339
H	0.631339	-0.631339	-0.631339

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-40.5183890143	Predicted Change= -1.533072D-07
Zero-point correction (ZPE)=	-40.4731	0.04521
Internal Energy (U)=	-40.4703	0.04807
Enthalpy (H)=	-40.4693	0.04902
Gibbs Free Energy (G)=	-40.4904	0.02789

Frequencies -- 1373.9889 1373.9889 1373.9889

Phosphonate-Benzene-NCHB
Supporting Information: Phosphonate-Benzene-NCHB.log

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

b3lyp/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C9H15O3P C1[X(C9H15O3P)] #Atoms= 28
Charge = 0 Multiplicity = 1

SCF Energy= -919.072381975 Predicted Change= -4.641557D-07

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.01982	0.00180	[NO]	0.01982	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.558059	-0.002616	-0.046219
C	-3.240204	1.217103	-0.036904
C	-4.636582	1.244663	-0.016364
C	-5.358463	0.048991	-0.005043
C	-4.681306	-1.172541	-0.014248
C	-3.284834	-1.196239	-0.034848
H	-1.471451	-0.022089	-0.061034
H	-2.679213	2.148494	-0.045126
H	-5.162579	2.196395	-0.009014
H	-6.445472	0.069120	0.011042
H	-5.242004	-2.104248	-0.005249
H	-2.759022	-2.148061	-0.041643
P	2.293183	0.007660	0.361700
C	2.674195	-0.351376	2.093230
O	3.051958	1.419674	0.181303
C	2.972732	2.097727	-1.085610
O	3.238788	-0.983975	-0.515671
O	0.856799	-0.040734	-0.022574
C	2.679374	-2.154169	-1.135512
H	2.311075	-1.353205	2.339638
H	2.167832	0.373618	2.735889
H	3.752019	-0.302118	2.266279
H	1.929700	2.218158	-1.392459
H	3.524034	1.538981	-1.848381
H	3.433017	3.076255	-0.940171
H	3.355512	-2.430686	-1.947145
H	1.681495	-1.946628	-1.529187
H	2.625835	-2.977875	-0.414308

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-919.072381975	Predicted Change=	-4.641557D-07
Zero-point correction (ZPE)=		-918.8415	0.23084
Internal Energy (U)=		-918.8249	0.24747
Enthalpy (H)=		-918.8239	0.24841
Gibbs Free Energy (G)=		-918.8933	0.17902

Frequencies --	9.3889	12.7302	15.4288

Phosphonate-Methane-NCHB

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

b3lyp/6-31G* gfprint gfinput scf=(direct,tight,maxcycle=300,xqc)
opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C4H13O3P C1[X(C4H13O3P)] #Atoms= 21
Charge = 0 Multiplicity = 1

SCF Energy= -727.340670034 Predicted Change= -1.691383D-07

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.04592	0.00180	[NO]	0.04592	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	4.491392	-0.350285	0.022259
H	4.887141	-0.971751	0.831075
H	4.789411	-0.779353	-0.939193
H	3.401168	-0.310333	0.087990
P	-0.519471	0.015766	0.374855
C	-1.122023	0.517055	2.005803
O	-1.450300	-1.274965	0.105455
C	-1.260864	-2.028551	-1.105518
O	-1.145225	1.090043	-0.675963
O	0.949558	-0.170393	0.240028
C	-0.318891	2.132432	-1.220578
H	-0.654136	1.465521	2.284626
H	-0.848071	-0.240673	2.744599
H	-2.208081	0.637261	1.992325
H	-0.210887	-2.312769	-1.221212
H	-1.586133	-1.441904	-1.970521
H	-1.879940	-2.922269	-1.012227
H	-0.780161	2.438362	-2.162017
H	0.697128	1.771564	-1.397774
H	-0.290639	2.989558	-0.537855
H	4.905327	0.658909	0.109418

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -727.340670034 Predicted Change= -1.691383D-07

Zero-point correction (ZPE)=	-727.1649	0.17571
Internal Energy (U)=	-727.1502	0.19038
Enthalpy (H)=	-727.1493	0.19133
Gibbs Free Energy (G)=	-727.2113	0.12932

Frequencies -- 13.6305 14.0363 18.3904

Appendix V:

Computational Data for Chapter 7

Probing the Mechanism and Origins of Catalysis & Stereocontrol in the Bifunctional Aminothiourea-Catalyzed Michael Reaction

Molecular Geometries and Energies of Compounds Reported

Ia 2-methylketone

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

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#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene,SMD) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C7H12O C1[X(C7H12O)] #Atoms= 20
Charge = 0 Multiplicity = 1

SCF Energy= -349.217644037 Predicted Change= -8.837405D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00008	0.00045	[YES]	0.00001	0.00030	[YES]
Displ	0.00181	0.00180	[NO]	0.00181	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-0.838769	-0.501788	0.390644
C	-2.289619	-0.804771	0.019826
H	-2.549515	-1.832809	0.298008
H	-2.454340	-0.691682	-1.057680
H	-2.981417	-0.127077	0.529815
H	-0.713057	-0.616377	1.480004
C	-0.444573	0.942777	0.080006
O	-1.230487	1.753984	-0.380344
C	1.005147	1.300221	0.375004
H	1.143877	1.268649	1.466139
H	1.186564	2.327247	0.043579
C	1.979738	0.301400	-0.283355
H	3.007248	0.537023	0.019243
H	1.936326	0.424722	-1.374353
C	1.624577	-1.146130	0.079339
H	1.778027	-1.301638	1.157229
H	2.300228	-1.839522	-0.437251
C	0.168401	-1.469848	-0.281287
H	-0.079549	-2.498593	0.009088
H	0.040094	-1.412980	-1.372141

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -349.217644037 Predicted Change= -8.837405D-08

Zero-point correction (ZPE)=	-349.0378	0.17981
Internal Energy (U)=	-349.0299	0.18768
Enthalpy (H)=	-349.0290	0.18863
Gibbs Free Energy (G)=	-349.0698	0.14779

Frequencies -- 93.2898 163.5872 191.3996
$E_{SCS\text{-}MP2/def2\text{-}\infty}$ SP = -348.952186
$E_{solvation}$ = -.010583

Ib catalyst 7.8

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene,SMD) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C22H23N3S C1[X(C22H23N3S)] #Atoms= 49
Charge = 0 Multiplicity = 1

SCF Energy= -1414.68375761 Predicted Change= -1.737734D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.01313	0.00180	[NO]	0.01313	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.297484	-0.690287	1.111219
N	1.608484	-0.880360	0.820052
S	-0.249412	-0.851495	2.719493
N	-0.506477	-0.378540	0.069396
H	2.179327	-1.189180	1.595047
C	2.238236	-0.783441	-0.498459
C	3.745512	-0.850276	-0.375660
H	1.950197	0.171967	-0.957967
H	1.881027	-1.586185	-1.158693
H	-0.120837	-0.292282	-0.865945
C	-1.911431	-0.011437	0.156925
C	-2.868132	-1.188558	-0.031403
C	-1.488051	2.413743	-0.550134
C	-2.185135	1.106658	-0.905758
H	-2.083526	0.412222	1.148911
N	-1.743833	0.609526	-2.216552
H	-1.874471	1.333680	-2.921392
H	-2.335730	-0.173011	-2.493389
H	-3.269794	1.290107	-0.865038
C	-0.289212	2.812019	-1.155520
H	0.159057	2.182544	-1.917664
C	0.326542	4.014377	-0.796872
H	1.254795	4.307481	-1.280783
C	-0.245984	4.835537	0.174816
H	0.232303	5.770816	0.453086
C	-1.443021	4.448821	0.783565
H	-1.901650	5.083413	1.537344
C	-2.057786	3.251162	0.420186
H	-2.993905	2.962270	0.893622
C	-2.522533	-2.328936	-0.767226
H	-1.519125	-2.422231	-1.172983
C	-3.447600	-3.358070	-0.962489
H	-3.160609	-4.238126	-1.532363

C	-4.731387	-3.261903	-0.423788
H	-5.448894	-4.064541	-0.571613
C	-5.084264	-2.130647	0.316584
H	-6.076747	-2.051367	0.752578
C	-4.159222	-1.104763	0.509479
H	-4.436331	-0.232363	1.097495
C	4.461215	-1.927758	-0.909250
H	3.927146	-2.727330	-1.417230
C	5.852557	-1.982994	-0.794180
H	6.395549	-2.825094	-1.214896
C	6.540808	-0.961978	-0.137515
H	7.622829	-1.004282	-0.046014
C	5.833348	0.115832	0.402756
H	6.363602	0.914713	0.914216
C	4.445064	0.171828	0.282739
H	3.897116	1.012744	0.701426

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-1414.68375761	Predicted Change= -1.737734D-08
Zero-point correction (ZPE)=	-1414.2751	0.40856
Internal Energy (U)=	-1414.2517	0.43197
Enthalpy (H)=	-1414.2508	0.43291
Gibbs Free Energy (G)=	-1414.3340	0.34975

Frequencies -- 2.5397 23.5694 29.2711

$E_{SCS\text{-}MP2/def2\text{-}\infty}$ SP = -1413.677676

$E_{solvation}$ = -.037101

Ic methyl acrylate

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene,SMD) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C4H6O2 C1[X(C4H6O2)] #Atoms= 12
Charge = 0 Multiplicity = 1

SCF Energy= -306.473326898 Predicted Change= -2.238747D-08

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00005	0.00045	[YES]	0.00001	0.00030	[YES]
Displ	0.00065	0.00180	[YES]	0.00065	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.493947	-0.016016	0.000087
H	2.544999	1.069621	0.000203
H	3.431522	-0.564542	0.000070
C	1.316517	-0.644995	-0.000031
H	1.240118	-1.728416	-0.000147
C	0.043515	0.118109	0.000001
O	-0.058784	1.330490	0.000122
O	-1.015419	-0.721266	-0.000107
C	-2.307336	-0.091038	-0.000069
H	-2.435014	0.529654	-0.891503
H	-2.435078	0.529398	0.891536
H	-3.032772	-0.905874	-0.000206

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-306.473326898	Predicted Change= -2.238747D-08
Zero-point correction (ZPE)=	-306.3772	0.09602
Internal Energy (U)=	-306.3707	0.10254
Enthalpy (H)=	-306.3698	0.10349
Gibbs Free Energy (G)=	-306.4074	0.06587

Frequencies -- 102.2219 167.2717 206.7190

$E_{SCS\text{-}MP2/def2\text{-}\infty}$ SP = -306.264201
$E_{solvation}$ = -.005608

II Imine

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene,SMD) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C29H33N3S C1[X(C29H33N3S)] #Atoms= 66
Charge = 0 Multiplicity = 1

SCF Energy= -1687.46744833 Predicted Change= -1.892481D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00087	0.00180	[YES]	0.00087	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.389321	0.785200	1.626560
N	-2.516667	0.726421	0.882492
S	-1.372722	1.292648	3.255577
N	-0.235916	0.407585	1.020903
H	-2.450699	0.429072	-0.082598
C	-3.837080	1.176190	1.320070
H	-3.962419	0.868158	2.363204
C	-4.922733	0.587410	0.443552
H	-3.891725	2.272183	1.305320
H	0.587886	0.372927	1.610234
C	-0.041961	-0.051891	-0.346101
C	-0.420337	-1.514508	-0.574075
C	1.690195	1.714264	-0.991332
C	1.454350	0.225850	-0.745158
H	-0.646194	0.566032	-1.021607
N	2.306077	-0.287582	0.321952
H	1.596783	-0.296047	-1.698568
C	4.066082	-1.149257	-1.251126
C	5.480339	-0.529801	-1.306939
H	5.392533	0.564793	-1.274541
H	5.946773	-0.781457	-2.267187
C	5.661880	-0.752674	1.206660
H	6.268251	-1.154388	2.028220
H	5.578582	0.330548	1.377214
C	6.348219	-1.011556	-0.139463
H	7.325771	-0.513489	-0.165477
H	6.540369	-2.088885	-0.249138
H	3.462559	-0.774236	-2.080311
H	4.152591	-2.238015	-1.379391
C	3.413986	-0.886085	0.096664
C	1.471145	2.231639	-2.275971
H	1.168601	1.561752	-3.078478
C	1.640913	3.591444	-2.540439

H	1.470583	3.971229	-3.544630
C	2.037354	4.457333	-1.519129
H	2.173333	5.516337	-1.721811
C	2.262269	3.951596	-0.237338
H	2.572379	4.617079	0.564131
C	2.090506	2.590919	0.026110
H	2.275184	2.209115	1.024645
C	-0.904077	-1.909304	-1.829203
H	-1.043349	-1.163387	-2.609588
C	-1.213000	-3.245610	-2.088610
H	-1.591682	-3.532889	-3.066146
C	-1.044293	-4.207748	-1.090498
H	-1.289312	-5.248124	-1.287172
C	-0.567268	-3.822998	0.164577
H	-0.438949	-4.564573	0.948839
C	-0.255976	-2.486172	0.421141
H	0.104039	-2.192782	1.402345
C	4.244449	-1.378405	1.279063
H	4.371471	-2.463226	1.127847
C	3.598005	-1.154244	2.645893
H	2.615494	-1.632031	2.712203
H	3.462913	-0.088092	2.857705
H	4.233744	-1.576831	3.433004
C	-5.858858	1.418731	-0.182652
H	-5.789625	2.496105	-0.051112
C	-6.877465	0.878519	-0.971607
H	-7.596767	1.538192	-1.449978
C	-6.965962	-0.502731	-1.150441
H	-7.755596	-0.924463	-1.766740
C	-6.033283	-1.341247	-0.533285
H	-6.096779	-2.418146	-0.666174
C	-5.021115	-0.800391	0.259571
H	-4.299425	-1.456640	0.740120

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1687.46744833 Predicted Change= -1.892481D-09
Zero-point correction (ZPE)= -1686.9037 0.56369
Internal Energy (U)= -1686.8733 0.59412
Enthalpy (H)= -1686.8723 0.59506
Gibbs Free Energy (G)= -1686.9704 0.49699

Frequencies -- 11.5420 21.2013 22.8380E

$_{\text{SCS-MP2/def2-}\infty}$ SP = -1686.230838
$E_{solvation}$ = -.042709

III Enamine

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene,SMD) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C29H33N3S C1[X(C29H33N3S)] #Atoms= 66
Charge = 0 Multiplicity = 1

SCF Energy= -1687.45620546 Predicted Change= -1.677646D-08

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00141	0.00180	[YES]	0.00141	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.249979	-2.156472	0.092089
N	2.378430	-1.535293	-0.310406
S	1.132792	-3.847011	0.278797
N	0.172086	-1.365966	0.368364
H	2.383479	-0.524187	-0.373687
C	3.639603	-2.209430	-0.618398
H	3.760165	-3.029459	0.097588
C	4.807682	-1.248439	-0.544946
H	3.589831	-2.666844	-1.614262
H	-0.699571	-1.882854	0.452417
C	-0.033464	0.015889	-0.075802
C	0.865259	1.015111	0.649163
C	-1.924046	1.711132	-0.424277
C	-1.545807	0.352047	0.159315
H	0.170085	0.091173	-1.155389
N	-2.357952	-0.768893	-0.338265
H	-2.224309	-0.898505	-1.336267
H	-1.682989	0.397049	1.241767
C	-3.714615	-0.952404	0.042393
C	-3.982277	-0.871435	1.533273
C	-5.471671	-0.973187	1.888272
C	-6.146045	-2.080269	1.078777
C	-6.042985	-1.768592	-0.417299
C	-4.662808	-1.311514	-0.852490
H	-3.590794	0.069708	1.939469
H	-3.415633	-1.669973	2.036873
H	-5.967018	-0.015857	1.673403
H	-5.578119	-1.148617	2.965640
H	-7.197471	-2.194244	1.370673
H	-5.650446	-3.038098	1.290988
H	-6.786885	-1.000899	-0.689319
H	-6.321749	-2.657903	-1.002562
C	-4.430845	-1.366425	-2.345117

H	-4.127718	-2.368791	-2.684848
H	-5.358214	-1.124648	-2.880485
H	-3.671964	-0.657352	-2.696560
C	-1.906197	1.940010	-1.808629
H	-1.604096	1.145033	-2.487230
C	-2.276747	3.178429	-2.333013
H	-2.256777	3.336671	-3.408144
C	-2.674163	4.211789	-1.480103
H	-2.965874	5.175656	-1.888480
C	-2.695990	3.996593	-0.101775
H	-3.004183	4.792944	0.570654
C	-2.322831	2.755202	0.419185
H	-2.337787	2.596053	1.494900
C	1.050030	0.938292	2.037498
H	0.577207	0.134788	2.595712
C	1.850097	1.870517	2.697926
H	1.985796	1.797392	3.773804
C	2.479814	2.892096	1.980465
H	3.105813	3.615305	2.496216
C	2.305660	2.973684	0.598681
H	2.795020	3.760505	0.031021
C	1.503207	2.039650	-0.061792
H	1.368699	2.109478	-1.138522
C	5.053037	-0.500989	0.617065
H	4.381594	-0.593600	1.467196
C	6.147823	0.360345	0.688746
H	6.323890	0.933653	1.595247
C	7.020680	0.480208	-0.396303
H	7.875184	1.149279	-0.338342
C	6.786906	-0.261624	-1.555038
H	7.458588	-0.173177	-2.404997
C	5.685556	-1.117866	-1.627646
H	5.504586	-1.690522	-2.534386

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1687.45620546 Predicted Change= -1.677646D-08
Zero-point correction (ZPE)= -1686.8920 0.56415
Internal Energy (U)= -1686.8615 0.59463
Enthalpy (H)= -1686.8606 0.59557
Gibbs Free Energy (G)= -1686.9575 0.49861

Frequencies -- 15.4229 20.1607 27.7014

$E_{SCS\text{-}MP2/def2\text{-}\infty}$ SP = -1686.223553
$E_{solvation}$ = -.042709

TS-IV-7.8-major

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene,SMD) opt=(maxcycle=250,ts,calcfc,noeigentest)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C33H39N3O2S C1[X(C33H39N3O2S)] #Atoms= 78
Charge = 0 Multiplicity = 1

SCF Energy= -1993.91345572 Predicted Change= -2.120799D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00212	0.00180	[NO]	0.00212	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.221899	-2.020577	-0.542777
N	-2.382064	-1.975024	0.152750
S	-1.054442	-2.738279	-2.083161
N	-0.193988	-1.398882	0.105905
H	-2.361436	-1.461289	1.038945
C	-3.648777	-2.583310	-0.234567
H	-3.957226	-3.279784	0.554694
H	-3.459022	-3.163811	-1.140756
H	-0.394258	-1.092707	1.060323
C	1.186930	-1.330436	-0.345004
C	-4.748646	-1.563359	-0.469949
C	2.054082	-2.436630	0.253112
C	3.139996	0.252553	-0.705530
C	1.777477	0.090260	-0.033062
H	1.164645	-1.457419	-1.430318
N	0.802552	1.103915	-0.470811
H	0.013666	0.733799	-0.987133
H	1.905788	0.178784	1.051803
C	0.812080	2.427622	-0.245875
C	1.900391	3.011796	0.623592
C	2.184931	4.486756	0.307385
C	0.889576	5.299321	0.290130
C	-0.093932	4.728540	-0.737740
C	-0.293007	3.211947	-0.665579
H	2.816501	2.424874	0.528903
H	1.571856	2.910184	1.668245
H	2.681176	4.558992	-0.670186
H	2.887402	4.884151	1.049511
H	1.097561	6.350266	0.054738
H	0.440066	5.286222	1.291804
H	0.255550	4.986303	-1.750175
H	-1.072644	5.216360	-0.631536

C	-1.158674	2.682045	-1.802851
H	-1.631249	1.719038	-1.575893
H	-1.972730	3.385890	-2.009460
H	-0.583950	2.566255	-2.732555
C	3.238239	0.524904	-2.076908
H	2.335136	0.663479	-2.665389
C	4.486755	0.627969	-2.691200
H	4.546816	0.840684	-3.755302
C	5.654740	0.458549	-1.943416
H	6.626531	0.539344	-2.422950
C	5.565943	0.188174	-0.576945
H	6.468327	0.056728	0.014148
C	4.315842	0.087516	0.037119
H	4.252642	-0.126700	1.101098
C	2.041557	-2.697880	1.630641
H	1.395881	-2.120491	2.288220
C	2.835078	-3.710886	2.170015
H	2.810425	-3.903145	3.239540
C	3.653115	-4.479664	1.338189
H	4.268747	-5.270962	1.757727
C	3.668222	-4.230538	-0.034917
H	4.294047	-4.828726	-0.691907
C	2.872454	-3.216445	-0.572242
H	2.882711	-3.031817	-1.643037
C	-5.882341	-1.534724	0.349558
H	-5.969677	-2.248900	1.165462
C	-6.898489	-0.599798	0.132683
H	-7.771474	-0.590547	0.780275
C	-6.789080	0.320529	-0.909972
H	-7.576876	1.049680	-1.080442
C	-5.661019	0.299143	-1.736492
H	-5.573420	1.008921	-2.555239
C	-4.649849	-0.636572	-1.519526
H	-3.778271	-0.658350	-2.169378
O	-1.504887	-0.341793	2.473126
O	-0.342786	1.537035	2.988165
C	0.190969	0.823699	4.106145
H	0.730660	-0.077088	3.797469
H	-0.599108	0.534470	4.806530
H	0.881035	1.515959	4.594101
C	-1.272531	0.866405	2.227158
C	-1.889641	1.647845	1.219483
H	-2.655077	1.138714	0.643184
C	-1.533550	2.972194	0.907214
H	-2.290026	3.575241	0.406102
H	-0.975415	3.526160	1.656918

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1993.91345572 Predicted Change= -2.120799D-08

Zero-point correction (ZPE)=	-1993.2509	0.66253
Internal Energy (U)=	-1993.2140	0.69939
Enthalpy (H)=	-1993.2131	0.70033

Gibbs Free Energy (G)=	-1993.3235	0.58991
Frequencies --	-326.7816	16.6186	20.1941

$E_{SCS\text{-}MP2/def2\text{-}\infty}$ SP = -1992.485607
$E_{solvation}$ = -.042827

TS-IV-7.8-minor

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

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#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
iop(1/8=18) SCRF=(PCM,SOLVENT=Toluene,SMD)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C33H39N3O2S C1[X(C33H39N3O2S)] #Atoms= 78
Charge = 0 Multiplicity = 1

SCF Energy= -1993.90579328 Predicted Change= -4.049463D-10

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00083	0.00180	[YES]	0.00083	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.851152	-0.762634	-1.509553
N	-2.748848	-0.931913	-0.510739
S	-2.266665	-0.650065	-3.158985
N	-0.566137	-0.666227	-1.051655
H	-2.368588	-1.065021	0.428444
C	-4.182078	-1.122882	-0.670962
H	-4.423058	-0.865839	-1.706637
C	-4.989817	-0.276770	0.295497
H	-4.434965	-2.182851	-0.533363
H	-0.448607	-0.838014	-0.052185
C	0.619427	-0.586831	-1.880654
C	1.396419	-1.905338	-1.964243
C	0.853477	1.943210	-1.621423
C	1.550303	0.601404	-1.443748
H	0.271107	-0.333321	-2.884950
N	2.073084	0.304376	-0.093194
H	1.959777	-0.666296	0.170574
H	2.398827	0.581400	-2.138251
C	3.208301	2.439246	0.364477
C	4.481126	2.965716	1.038911
C	4.474996	2.626581	2.528527
C	4.424364	1.107877	2.719242
H	5.398585	0.682838	2.431441
H	4.296763	0.862720	3.782551
H	2.348999	3.052834	0.674817
H	3.274610	2.558103	-0.721284
C	2.910642	0.997498	0.696509
H	4.547301	4.047990	0.878183
H	5.365146	2.518736	0.563684
H	3.607211	3.101175	3.007041
H	5.366571	3.030801	3.023099
C	1.109230	2.670922	-2.791971

H	1.828184	2.289682	-3.514119
C	0.453336	3.876616	-3.044045
H	0.665318	4.424918	-3.958050
C	-0.468192	4.376423	-2.122455
H	-0.979376	5.316025	-2.314025
C	-0.729454	3.659932	-0.952799
H	-1.445376	4.040018	-0.228766
C	-0.075983	2.451209	-0.705756
H	-0.288241	1.902645	0.203534
C	1.195813	-2.956089	-1.059739
H	0.440714	-2.869248	-0.283654
C	1.941828	-4.134795	-1.161514
H	1.769279	-4.939692	-0.451835
C	2.892271	-4.282606	-2.170831
H	3.466719	-5.201344	-2.252782
C	3.090205	-3.244806	-3.086370
H	3.816370	-3.355161	-3.887505
C	2.349891	-2.068585	-2.981571
H	2.502015	-1.273038	-3.707898
C	3.326089	0.394918	1.922477
C	3.525635	-1.121130	1.932726
H	2.616502	-1.689203	1.715975
H	3.855462	-1.443686	2.926284
H	4.297436	-1.425004	1.212738
C	-6.032453	-0.848492	1.033732
H	-6.237762	-1.912079	0.933479
C	-6.808954	-0.070500	1.896188
H	-7.613438	-0.532742	2.462635
C	-6.545941	1.292778	2.035880
H	-7.145390	1.899648	2.709452
C	-5.503573	1.872248	1.306494
H	-5.292078	2.933681	1.409419
C	-4.732890	1.094179	0.442727
H	-3.923315	1.550155	-0.121390
C	1.704459	0.581444	3.033321
H	2.111369	-0.028847	3.838020
H	1.777783	1.647794	3.242840
C	0.494633	0.142905	2.450884
H	-0.108416	0.842079	1.883689
C	-0.024244	-1.179396	2.468958
O	-0.986008	-1.590197	1.778798
O	0.599370	-2.037933	3.334757
C	0.087269	-3.372202	3.379170
H	0.660039	-3.880394	4.158275
H	0.226554	-3.889310	2.423668
H	-0.976871	-3.382005	3.632761

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1993.90579328 Predicted Change= -4.049463D-10

Zero-point correction (ZPE)=	-1993.2432	0.66252
Internal Energy (U)=	-1993.2063	0.69942
Enthalpy (H)=	-1993.2054	0.70037

Gibbs Free Energy (G)=	-1993.3163	0.58944
Frequencies --	-329.0277	9.8354	16.5927

$E_{SCS\text{-}MP2/def2\text{-}\infty}$ SP = -1992.475507
$E_{solvation}$ = -.04431

V Zwitterion

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

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#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene,SMD) opt=(maxcycle=250) freq=noraman iop(1/8=18)
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C33H39N3O2S C1[X(C33H39N3O2S)] #Atoms= 78
Charge = 0 Multiplicity = 1

SCF Energy= -1993.91824351 Predicted Change= -2.335213D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00263	0.00180	[NO]	0.00263	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.224905	-2.054907	-0.345883
N	-2.339831	-2.021202	0.414792
S	-1.119694	-2.805857	-1.876975
N	-0.176158	-1.394483	0.235930
H	-2.280276	-1.458537	1.275201
C	-3.625470	-2.633216	0.092862
H	-3.973825	-3.151617	0.993623
H	-3.448944	-3.378615	-0.684565
H	-0.337194	-1.098518	1.207865
C	1.175458	-1.321305	-0.291103
C	-4.678213	-1.631715	-0.355387
C	2.099377	-2.395753	0.278037
C	3.056279	0.310218	-0.820094
C	1.762947	0.110924	-0.039596
H	1.095358	-1.472553	-1.370567
N	0.724680	1.106851	-0.405038
H	-0.133139	0.693821	-0.764201
H	1.957090	0.228455	1.031649
C	0.706443	2.398591	-0.181036
C	1.844304	3.062678	0.541424
C	2.056789	4.529823	0.137369
C	0.739939	5.305194	0.188101
C	-0.301700	4.645510	-0.720798
C	-0.555632	3.139443	-0.450907
H	2.765199	2.490241	0.417893
H	1.578406	3.008978	1.608046
H	2.474897	4.572228	-0.877302
H	2.803053	4.972814	0.806562
H	0.896358	6.342844	-0.130949
H	0.376120	5.346669	1.222906
H	0.018731	4.762928	-1.765881
H	-1.265309	5.163013	-0.634912
C	-1.379945	2.563008	-1.616689

H	-1.788957	1.569382	-1.406318
H	-2.237732	3.218980	-1.802339
H	-0.793855	2.510916	-2.542052
C	3.036017	0.489235	-2.210427
H	2.086885	0.518770	-2.739670
C	4.227318	0.632027	-2.921989
H	4.196846	0.770961	-3.999293
C	5.453958	0.594035	-2.254005
H	6.381263	0.705861	-2.809223
C	5.482212	0.411931	-0.870576
H	6.431386	0.380229	-0.342610
C	4.289501	0.272079	-0.157948
H	4.316699	0.127796	0.919173
C	2.239079	-2.568873	1.662508
H	1.678299	-1.938901	2.349405
C	3.079256	-3.558642	2.173579
H	3.173618	-3.682490	3.249270
C	3.791249	-4.391494	1.306479
H	4.442814	-5.164917	1.704455
C	3.654876	-4.229236	-0.072880
H	4.197496	-4.877510	-0.755872
C	2.813461	-3.237793	-0.582267
H	2.704100	-3.121212	-1.657084
C	-5.520410	-1.019933	0.582952
H	-5.426012	-1.278521	1.635583
C	-6.478931	-0.086806	0.181800
H	-7.125052	0.377278	0.922660
C	-6.610599	0.243282	-1.168668
H	-7.359516	0.965349	-1.483959
C	-5.779299	-0.364285	-2.113136
H	-5.880813	-0.117297	-3.167058
C	-4.820077	-1.294553	-1.709225
H	-4.174417	-1.767420	-2.444244
O	-1.393666	-0.357589	2.581132
O	-0.066401	1.484663	2.847735
C	0.431889	0.867939	4.031474
H	0.765838	-0.159754	3.857343
H	-0.325011	0.852982	4.825338
H	1.279898	1.478425	4.355373
C	-1.164953	0.847147	2.245910
C	-1.842298	1.616613	1.316351
H	-2.687890	1.141853	0.829606
C	-1.457308	2.984636	0.920451
H	-2.336036	3.593516	0.667943
H	-0.915260	3.497739	1.718990

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1993.91824351 Predicted Change= -2.335213D-08

Zero-point correction (ZPE)=	-1993.2539	0.66429
Internal Energy (U)=	-1993.2172	0.70094
Enthalpy (H)=	-1993.2163	0.70189
Gibbs Free Energy (G)=	-1993.3265	0.59174

Frequencies -- 11.9003 18.2198 20.0487

$E_{SCS\text{-}MP2/def2\text{-}\infty}$ SP = -1992.492664

$E_{solvation}$ = -.045444

VI Product Imine

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

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#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene,SMD) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C33H39N3O2S C1[X(C33H39N3O2S)] #Atoms= 78
Charge = 0 Multiplicity = 1

SCF Energy= -1993.96530243 Predicted Change= -3.660397D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00168	0.00180	[YES]	0.00168	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.982703	0.893291	0.889760
N	-3.676818	-0.145633	0.360719
S	-3.766588	1.997841	1.927195
N	-1.681816	0.985831	0.530906
H	-4.622437	-0.243227	0.704966
C	-3.140326	-1.220024	-0.476822
H	-2.612167	-0.772865	-1.330742
C	-4.254443	-2.111403	-0.982606
H	-2.408943	-1.818698	0.083667
H	-1.261371	0.266934	-0.048585
C	-0.740323	1.994163	0.990077
C	-0.602906	3.186745	0.045141
C	0.606080	0.376790	2.446505
C	0.649468	1.303065	1.232562
H	-1.100315	2.362006	1.953954
N	1.005113	0.579672	0.016566
H	1.337298	2.121720	1.470326
C	2.146006	0.678420	-0.556610
C	3.328782	1.518100	-0.097365
C	3.753224	2.528035	-1.184643
C	4.033683	1.824622	-2.516031
C	2.844140	0.954414	-2.942573
C	2.377689	-0.086379	-1.874918
H	4.170328	0.843973	0.110858
H	3.115994	2.039894	0.837250
H	4.637589	3.078959	-0.841986
H	2.951153	3.266569	-1.317566
H	4.941521	1.214175	-2.425441
H	4.238873	2.566404	-3.298252
H	3.078873	0.418119	-3.871646
H	1.991220	1.610425	-3.166741
C	1.092474	-0.751680	-2.391456
H	0.677522	-1.472205	-1.681526

H	0.315843	-0.006573	-2.592416
H	1.301456	-1.281146	-3.329388
C	0.448445	-1.010456	2.335713
H	0.378441	-1.463439	1.352513
C	0.396828	-1.815310	3.477064
H	0.277047	-2.890575	3.370649
C	0.499539	-1.245557	4.746693
H	0.459829	-1.871869	5.633898
C	0.658360	0.137101	4.868154
H	0.744159	0.593162	5.850976
C	0.712305	0.937820	3.727416
H	0.839487	2.013340	3.831996
C	-0.942473	3.120258	-1.310583
H	-1.372106	2.207983	-1.712820
C	-0.755453	4.223193	-2.148133
H	-1.030779	4.153542	-3.197471
C	-0.224793	5.410288	-1.641098
H	-0.082501	6.269158	-2.291611
C	0.111473	5.489602	-0.287101
H	0.511980	6.413194	0.122898
C	-0.079243	4.387276	0.546417
H	0.172970	4.461771	1.602296
O	5.541795	-2.884885	-0.678689
O	4.014205	-4.286923	0.213848
C	5.081024	-5.188826	0.559568
H	5.788136	-4.709112	1.242029
H	5.613462	-5.520560	-0.336153
H	4.600694	-6.037130	1.049395
C	4.388426	-3.145290	-0.401242
C	3.192031	-2.249770	-0.657132
H	2.916651	-1.806374	0.310163
H	2.346184	-2.881419	-0.946123
C	3.489173	-1.163407	-1.697217
H	4.442157	-0.697659	-1.435640
H	3.647549	-1.638712	-2.673958
C	-4.313690	-3.459877	-0.614097
H	-3.553201	-3.868520	0.047057
C	-5.339390	-4.281767	-1.087801
H	-5.372085	-5.327651	-0.794427
C	-6.320718	-3.758839	-1.930921
H	-7.120359	-4.396172	-2.298888
C	-6.272286	-2.411404	-2.299901
H	-7.033360	-1.998831	-2.956847
C	-5.244836	-1.593630	-1.830226
H	-5.208126	-0.546056	-2.119951

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1993.96530243 Predicted Change= -3.660397D-09

Zero-point correction (ZPE)=	-1993.3011	0.66418
Internal Energy (U)=	-1993.2637	0.70157
Enthalpy (H)=	-1993.2627	0.70251
Gibbs Free Energy (G)=	-1993.3769	0.58837

Frequencies -- 15.4833 16.2622 20.5700

$E_{SCS\text{-}MP2/def2\text{-}\infty}$ SP = -1992.5357719

$E_{solvation}$ = -.0477654

VII Product

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

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#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene,SMD) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C11H18O3 C1[X(C11H18O3)] #Atoms= 32
Charge = 0 Multiplicity = 1

SCF Energy= -655.717420991 Predicted Change= -4.598532D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00099	0.00180	[YES]	0.00099	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	-1.545387	1.756397	1.483812
C	-1.603251	0.697402	0.879728
C	-2.036081	-0.584769	1.580012
C	-3.131748	-1.331548	0.795024
C	-2.704172	-1.566410	-0.658029
C	-2.332556	-0.243987	-1.343243
C	-1.235864	0.589623	-0.613446
H	-2.362248	-0.322291	2.591096
H	-1.155650	-1.237105	1.675664
H	-4.055686	-0.736649	0.813341
H	-3.359168	-2.281110	1.294191
H	-3.518003	-2.045913	-1.216687
H	-1.858431	-2.266049	-0.685272
H	-3.237854	0.375778	-1.414999
H	-2.000891	-0.426999	-2.373989
C	-1.167561	1.988730	-1.243841
H	-0.870060	1.914683	-2.297107
H	-2.144596	2.482572	-1.202478
H	-0.457142	2.639969	-0.728609
O	2.667382	-1.422642	-0.514573
O	3.635763	0.418319	0.363448
C	4.892328	-0.282068	0.386163
H	4.822574	-1.184632	0.999769
H	5.609101	0.416455	0.820536
H	5.201001	-0.558180	-0.626120
C	2.582615	-0.281039	-0.109197
C	1.312827	0.543597	-0.039639
H	1.528795	1.531124	-0.460892
H	1.097244	0.718489	1.023112
C	0.136304	-0.138156	-0.746629
H	0.361135	-0.220397	-1.817767
H	0.060765	-1.164583	-0.376701

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

SCF Energy=	-655.717420991	Predicted Change= -4.598532D-09
Zero-point correction (ZPE)=	-655.4374	0.27999
Internal Energy (U)=	-655.4224	0.29496
Enthalpy (H)=	-655.4215	0.29590
Gibbs Free Energy (G)=	-655.4808	0.23657

Frequencies -- 17.8323 41.8181 61.8872

$E_{SCS\text{-}MP2/def2\text{-}\infty}$ SP = -655.2557987

$E_{solvation}$ = -.01500899

Geometries and Energy Refinements for Catalysts in Table 7.1.

VII-Product Imine-7.11

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene,SMD) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C20H29N3O2S C1[X(C20H29N3O2S)] #Atoms= 55
Charge = 0 Multiplicity = 1

SCF Energy= -1492.54474845 Predicted Change= -1.271530D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00222	0.00180	[NO]	0.00222	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.018960	-1.662631	0.266752
N	2.618671	-0.433551	0.144507
S	2.852810	-3.144540	0.290879
N	0.672957	-1.569333	0.384861
H	2.010173	0.365055	0.312544
C	3.972969	-0.080820	-0.055159
H	0.247996	-0.643524	0.416698
C	-0.246502	-2.666532	0.636199
C	4.416680	1.108413	0.546988
C	5.718868	1.562397	0.344691
H	6.043294	2.483612	0.821730
C	6.602611	0.832885	-0.453127
C	6.160401	-0.347092	-1.054993
H	6.833894	-0.919919	-1.687349
C	4.855217	-0.804088	-0.871087
H	3.735930	1.668286	1.183789
H	7.620966	1.179587	-0.605509
H	4.520395	-1.712951	-1.352045
C	-1.552677	-2.461199	-0.137227
H	-0.465229	-2.734271	1.711819
H	0.234897	-3.597850	0.334972
N	-2.104004	-1.151471	0.194144
H	-1.339189	-2.500829	-1.214653
H	-2.226718	-3.295512	0.099477
C	-3.339319	-0.857344	0.059417
C	-4.425558	-1.782835	-0.473509
C	-5.341027	-1.093113	-1.504546
C	-5.904800	0.224390	-0.965207
C	-4.768654	1.158934	-0.531122
C	-3.804004	0.541267	0.519254

H	-5.038465	-2.120293	0.375022
H	-3.982554	-2.680024	-0.913172
H	-6.150207	-1.778748	-1.784561
H	-4.766537	-0.894637	-2.420440
H	-6.580418	0.021721	-0.123701
H	-6.510053	0.718876	-1.735464
H	-5.175036	2.095002	-0.124697
H	-4.195766	1.431719	-1.427256
C	-4.537669	0.365950	1.874691
H	-3.855900	-0.038901	2.631694
H	-4.905317	1.335065	2.233904
H	-5.396001	-0.308877	1.806756
O	0.439625	1.589441	0.447650
O	-0.140350	3.603747	-0.370564
C	1.173373	4.099959	-0.037401
H	1.940874	3.563182	-0.601086
H	1.362880	3.994280	1.033817
H	1.163849	5.153160	-0.319482
C	-0.387116	2.321681	-0.080697
C	-1.779881	1.885557	-0.464317
H	-1.656486	1.015230	-1.115717
H	-2.266428	2.680742	-1.032948
C	-2.604392	1.484005	0.781157
H	-1.938702	0.994089	1.495709
H	-2.983549	2.395660	1.260290

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1492.54474845	Predicted Change= -1.271530D-08	
Zero-point correction (ZPE)=	-1492.0703	0.47435
Internal Energy (U)=	-1492.0440	0.50065
Enthalpy (H)=	-1492.0431	0.50160
Gibbs Free Energy (G)=	-1492.1291	0.41559

Frequencies -- 14.7082 24.2197 32.6645

$E_{SCS\text{-}MP2/def2\text{-}\infty}$ SP = -1491.548685
$E_{solvation}$ = -.0304724

VII-TS-IV-7.11

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
iop(1/8=18) SCRF=(PCM,SOLVENT=Toluene,SMD)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C20H29N3O2S C1[X(C20H29N3O2S)] #Atoms= 55
Charge = 0 Multiplicity = 1

SCF Energy= -1492.49095355 Predicted Change= -2.495742D-08

==========

Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.04586	0.00180	[NO]	0.04586	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.011305	1.395210	0.445934
N	-2.597521	0.158461	0.419926
S	-2.600230	2.807959	-0.290619
N	-0.834595	1.367213	1.131842
H	-1.994073	-0.593140	0.773267
C	-3.824896	-0.304042	-0.099436
H	-0.609543	0.493329	1.610239
C	0.112289	2.456442	1.273107
C	-4.948939	0.498112	-0.348717
C	-6.120624	-0.084933	-0.834432
H	-6.980897	0.551644	-1.025413
C	-6.204044	-1.458174	-1.067808
C	-5.090508	-2.258818	-0.802085
H	-5.133163	-3.331914	-0.969577
C	-3.913211	-1.690678	-0.324152
H	-4.902890	1.562626	-0.168200
H	-7.121959	-1.898668	-1.446918
H	-3.050004	-2.319376	-0.119535
C	1.550218	1.931982	1.236388
H	-0.034233	2.994792	2.219566
H	-0.060980	3.169471	0.463481
N	1.813308	1.255930	-0.034228
H	1.015783	1.176655	-0.652783
H	2.228984	2.783561	1.361063
H	1.730072	1.241509	2.070323
C	2.952484	0.669503	-0.428782
C	4.124545	0.688431	0.525252
C	5.472814	0.475531	-0.175865
C	5.410382	-0.727911	-1.117501
C	4.323694	-0.522141	-2.178403
C	2.966721	-0.089767	-1.623718
H	3.961594	-0.102232	1.272292

H	4.135643	1.632932	1.079881
H	6.255173	0.344053	0.580733
H	5.733088	1.376171	-0.748534
H	5.203792	-1.635694	-0.534921
H	6.378828	-0.883611	-1.608005
H	4.187178	-1.444266	-2.760181
H	4.667164	0.234880	-2.901386
C	1.966523	0.259302	-2.718989
H	2.068719	-0.443235	-3.553846
H	0.921669	0.204170	-2.392167
H	2.140639	1.268507	-3.116933
O	-0.464330	-1.458421	1.631837
O	1.777089	-1.706806	1.845650
C	1.566479	-1.783511	3.259237
H	1.043054	-0.902679	3.642370
H	2.563289	-1.844368	3.701606
H	0.990802	-2.676071	3.525428
C	0.647125	-1.606594	1.070075
C	0.874708	-1.694386	-0.327052
H	-0.016296	-1.626006	-0.943506
C	2.141641	-1.822403	-0.919738
H	2.958848	-2.155616	-0.286640
H	2.176412	-2.241099	-1.924379

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1492.49095355	Predicted Change= -2.495742D-08	
Zero-point correction (ZPE)=	-1492.0191	0.47184
Internal Energy (U)=	-1491.9927	0.49816
Enthalpy (H)=	-1491.9918	0.49910
Gibbs Free Energy (G)=	-1492.0792	0.41166

Frequencies -- -332.6645 2.5771 16.7236

$E_{SCS\text{-}MP2/def2\text{-}\infty}$ SP = -1491.4914991

$E_{solvation}$ = -.0313496

VII-Product Imine-7.12-major

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene,SMD) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C26H33N3O2S C1[X(C26H33N3O2S)] #Atoms= 65
Charge = 0 Multiplicity = 1

SCF Energy= -1723.60078085 Predicted Change= -9.990317D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00128	0.00180	[YES]	0.00128	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.629039	-1.764574	-0.441916
N	-2.746760	-0.970195	-0.381124
S	-1.451125	-3.305493	0.250650
N	-0.632504	-1.168701	-1.146743
H	-2.642763	-0.081934	-0.870012
C	-4.036049	-1.129597	0.166846
H	-0.785871	-0.213444	-1.459337
C	0.711058	-1.681778	-1.344408
C	-4.471082	-2.211341	0.948323
C	-5.779332	-2.229093	1.436794
H	-6.097112	-3.076267	2.039450
C	-6.671547	-1.191379	1.168808
C	-6.238280	-0.113624	0.392056
H	-6.913378	0.707875	0.166600
C	-4.939001	-0.081559	-0.103014
H	-3.793437	-3.024214	1.164593
H	-7.686219	-1.220136	1.555751
H	-4.612493	0.760111	-0.709991
C	3.103006	-1.723925	-0.585143
C	1.705246	-1.219075	-0.249242
H	1.056284	-1.313073	-2.316012
H	0.675057	-2.771687	-1.376041
N	1.622677	0.245951	-0.177065
H	1.384619	-1.681616	0.692457
C	2.027432	0.903715	0.842367
C	2.695115	0.316955	2.079081
C	2.223687	0.952417	3.398950
C	2.324427	2.478590	3.350392
C	1.512196	3.023109	2.169728
C	1.924671	2.446382	0.786792
H	3.778385	0.479097	1.973616
H	2.555547	-0.766047	2.110785

H	2.817445	0.546348	4.226969
H	1.180439	0.662684	3.588168
H	3.377315	2.780266	3.269054
H	1.947493	2.914043	4.284436
H	1.583876	4.118284	2.123029
H	0.456588	2.788851	2.358195
C	3.321953	2.986818	0.387745
H	3.599077	2.640193	-0.614354
H	3.315747	4.083704	0.378408
H	4.108160	2.665513	1.077674
C	3.905381	-1.063086	-1.527383
H	3.541354	-0.152430	-1.994565
C	5.166211	-1.559274	-1.861478
H	5.776062	-1.032255	-2.591021
C	5.643620	-2.728294	-1.263796
H	6.625828	-3.113796	-1.524434
C	4.850645	-3.396876	-0.329127
H	5.212926	-4.306864	0.142387
C	3.590574	-2.897126	0.006726
H	2.977305	-3.423124	0.735054
O	-1.862195	1.595754	-1.823787
O	-1.525618	3.815865	-1.783329
C	-2.277080	3.928361	-3.010758
H	-1.783677	3.374323	-3.813248
H	-2.296571	4.993966	-3.240528
H	-3.292406	3.547821	-2.874540
C	-1.380877	2.585915	-1.281304
C	-0.556257	2.570506	-0.019748
H	-0.648777	1.573536	0.413192
H	-0.984940	3.294625	0.680886
C	0.928786	2.907789	-0.305885
H	1.225536	2.439593	-1.248568
H	1.026421	3.991870	-0.435427

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-1723.60078085	Predicted Change= -9.990317D-09
Zero-point correction (ZPE)=	-1723.0452	0.55557
Internal Energy (U)=	-1723.0143	0.58645
Enthalpy (H)=	-1723.0133	0.58739
Gibbs Free Energy (G)=	-1723.1097	0.49101

Frequencies -- 15.6471 23.3708 29.5182

$E_{SCS\text{-}MP2/def2\text{-}\infty}$ SP = -1722.4053531
$E_{solvation}$ = -.0370648

VII-Product Imine-7.12-minor

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene,SMD) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C26H33N3O2S C1[X(C26H33N3O2S)] #Atoms= 65
Charge = 0 Multiplicity = 1

SCF Energy= -1723.59415795 Predicted Change= -1.599050D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00313	0.00180	[NO]	0.00313	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	3.417316	0.326282	-1.469146
N	3.455782	1.692538	-1.346770
S	4.703111	-0.459218	-2.260132
N	2.350304	-0.314930	-0.957489
H	4.201869	2.110754	-1.888475
C	2.598211	2.593004	-0.671220
H	1.521860	0.220127	-0.711887
C	2.107195	-1.742614	-1.103856
C	2.020986	2.303966	0.575425
C	1.218532	3.256828	1.205906
H	0.780185	3.020541	2.171880
C	1.000526	4.506890	0.624401
C	1.596280	4.802019	-0.604786
H	1.442312	5.772766	-1.068186
C	2.383144	3.853134	-1.252868
H	2.219329	1.356988	1.065217
H	0.382867	5.246319	1.126046
H	2.835377	4.079183	-2.215221
C	1.448686	-2.148262	1.327881
C	0.996641	-2.206445	-0.132369
H	3.034669	-2.284182	-0.910055
H	1.797448	-1.972818	-2.132622
N	-0.167653	-1.360794	-0.378350
H	0.827741	-3.262478	-0.380253
C	-1.350223	-1.810519	-0.565916
C	-1.788106	-3.268186	-0.511745
C	-2.551023	-3.691306	-1.782489
C	-3.721992	-2.746444	-2.067468
C	-3.242512	-1.291731	-2.137044
C	-2.473644	-0.792765	-0.876060
H	-2.448426	-3.393107	0.357546
H	-0.939748	-3.935014	-0.344488
H	-2.900132	-4.725073	-1.669206

H	-1.858522	-3.682676	-2.635618
H	-4.486516	-2.861868	-1.287036
H	-4.205068	-3.017376	-3.014738
H	-4.086980	-0.620330	-2.332831
H	-2.568950	-1.186936	-2.999722
C	-1.894488	0.596027	-1.187761
H	-2.686948	1.271993	-1.525782
H	-1.408190	1.045594	-0.317444
H	-1.148382	0.536471	-1.986760
C	0.981170	-1.181670	2.226376
H	0.258106	-0.445974	1.890498
C	1.430468	-1.162224	3.550260
H	1.054118	-0.404825	4.233413
C	2.351943	-2.109746	3.996215
H	2.698727	-2.095707	5.026044
C	2.820629	-3.081908	3.108481
H	3.533410	-3.830326	3.445001
C	2.370661	-3.099953	1.788701
H	2.737624	-3.865343	1.107929
O	-4.726036	2.604649	-0.211028
O	-3.533849	1.949833	1.590367
C	-3.224152	3.329156	1.857150
H	-4.138968	3.913125	1.988860
H	-2.635850	3.758202	1.041216
H	-2.642367	3.325863	2.780161
C	-4.298451	1.718811	0.501320
C	-4.597996	0.241736	0.331439
H	-5.170715	0.136032	-0.592772
H	-5.272789	-0.025621	1.156084
C	-3.396526	-0.727219	0.384302
H	-2.780386	-0.469904	1.253191
H	-3.806093	-1.721618	0.584904

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-1723.59415795	Predicted Change= -1.599050D-08
Zero-point correction (ZPE)=	-1723.0387	0.55539
Internal Energy (U)=	-1723.0079	0.58623
Enthalpy (H)=	-1723.0069	0.58717
Gibbs Free Energy (G)=	-1723.1044	0.48974

Frequencies -- 15.4363 22.6934 25.5994

$E_{SCS\text{-}MP2/def2\text{-}\infty}$ SP = -1722.3964294

$E_{solvation}$ = -0.0304419

TS-IV-7.12-major

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene,SMD)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C27H35N3O2S C1[X(C27H35N3O2S)] #Atoms= 68
Charge = 0 Multiplicity = 1

SCF Energy= -1762.86076231 Predicted Change= -2.611113D-10

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00037	0.00180	[YES]	0.00037	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.522000	-1.616959	-0.616433
N	-2.644510	-0.903210	-0.368052
S	-1.268505	-2.500579	-2.056862
N	-0.606667	-1.547629	0.392401
H	-2.596531	-0.243986	0.416279
C	-3.770986	-0.765570	-1.283521
C	-5.054279	-0.460871	-0.535984
H	-3.858077	-1.703984	-1.839550
H	-3.575752	0.021897	-2.024809
H	-0.859089	-0.952212	1.182361
C	0.723116	-2.114260	0.381083
C	3.196561	-1.772664	0.445775
C	1.850261	-1.059835	0.545748
H	0.848015	-2.649596	-0.562650
N	1.662610	0.002107	-0.454143
H	0.953801	-0.189146	-1.152612
H	1.763892	-0.606774	1.540074
C	2.273052	1.195492	-0.517976
C	3.309132	1.541758	0.526318
C	4.344738	2.555779	0.019585
C	3.656250	3.769528	-0.604701
C	2.741993	3.340631	-1.757689
C	1.806215	2.171286	-1.436885
H	3.811158	0.636723	0.875296
H	2.774764	1.957063	1.393057
H	4.993640	2.072804	-0.723750
H	4.989208	2.857191	0.853900
H	4.399694	4.487133	-0.972965
H	3.073390	4.291044	0.165692
H	3.363157	3.061433	-2.623597
H	2.135336	4.193036	-2.092643
C	1.025180	1.697209	-2.655913

H	0.101817	1.166369	-2.398100
H	0.730409	2.557623	-3.267170
H	1.627303	1.035295	-3.293767
C	3.735704	-2.133009	-0.796638
H	3.213991	-1.860183	-1.710219
C	4.940447	-2.832858	-0.868274
H	5.348320	-3.103745	-1.838510
C	5.619870	-3.186383	0.300488
H	6.559340	-3.729343	0.242461
C	5.086304	-2.837369	1.542186
H	5.608580	-3.105426	2.456720
C	3.881369	-2.134627	1.612670
H	3.472454	-1.858485	2.582387
O	-1.641835	0.783188	1.800552
O	0.265278	1.924176	2.249212
C	0.129963	1.480934	3.601872
H	0.087254	0.389715	3.672294
H	-0.770470	1.895360	4.067149
H	1.016595	1.850223	4.122543
C	-0.753403	1.567822	1.392373
C	-0.680291	2.158506	0.106754
H	-1.487190	1.892311	-0.568231
C	0.353827	3.009485	-0.330550
H	0.110036	3.684485	-1.150789
H	0.963468	3.478367	0.437112
H	0.838639	-2.841139	1.193936
C	-5.494861	-1.296463	0.501127
H	-4.894440	-2.157274	0.784902
C	-6.689410	-1.030180	1.169255
H	-7.017483	-1.687034	1.970881
C	-7.465027	0.075794	0.808736
H	-8.395817	0.283116	1.330312
C	-7.035932	0.912346	-0.222125
H	-7.629869	1.777233	-0.506474
C	-5.835964	0.645640	-0.886644
H	-5.502017	1.304406	-1.685096

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1762.86076231	Predicted Change= -2.611113D-10	
Zero-point correction (ZPE)=	-1762.2790	0.58174
Internal Energy (U)=	-1762.2468	0.61390
Enthalpy (H)=	-1762.2459	0.61485
Gibbs Free Energy (G)=	-1762.3458	0.51494

Frequencies -- -309.3516 14.4814 17.4417

$E_{SCS\text{-}MP2/def2\text{-}\infty}$ SP = -1761.63048544

$E_{solvation}$ = -.03704431

TS-IV-7.12-minor

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene,SMD)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C27H35N3O2S C1[X(C27H35N3O2S)] #Atoms= 68
Charge = 0 Multiplicity = 1

SCF Energy= -1762.85014962 Predicted Change= -1.143806D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00410	0.00180	[NO]	0.00410	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.876526	0.628366	-1.812674
N	-2.674353	-0.258878	-1.171469
S	-2.446822	2.040324	-2.581238
N	-0.557243	0.278680	-1.762094
H	-2.217658	-1.085157	-0.780662
C	-4.128181	-0.228455	-1.122774
H	-4.438239	0.740952	-1.523251
C	-4.664534	-0.426607	0.282731
H	-4.538261	-1.002000	-1.785861
H	-0.374702	-0.658659	-1.399908
C	0.538138	0.998012	-2.373472
C	1.140373	2.409562	-0.334439
C	1.652506	1.431209	-1.382042
H	0.128307	1.890858	-2.847773
N	2.292538	0.197875	-0.871684
H	2.018385	-0.635388	-1.375409
H	2.396988	1.960029	-1.992281
C	3.782800	1.176277	0.822777
C	5.185313	0.971371	1.408292
C	5.293630	-0.406007	2.061840
C	5.050660	-1.500657	1.018832
H	5.917105	-1.539881	0.340255
H	5.008900	-2.485616	1.503899
H	3.061628	1.320245	1.641534
H	3.743151	2.098185	0.233981
C	3.315588	0.016280	-0.021716
H	5.390977	1.770775	2.129471
H	5.936710	1.060282	0.611576
H	4.558673	-0.483097	2.874928
H	6.281711	-0.543587	2.517630
C	1.372609	3.777981	-0.529759
H	1.952243	4.106558	-1.389853

C	0.868297	4.724858	0.362831
H	1.058892	5.781088	0.192474
C	0.125136	4.314442	1.470830
H	-0.267337	5.048708	2.169090
C	-0.109604	2.953291	1.675942
H	-0.687304	2.622837	2.535184
C	0.392217	2.008041	0.779192
H	0.200743	0.954709	0.945371
C	3.779949	-1.318567	0.181726
C	3.765471	-2.259806	-1.023990
H	2.765944	-2.449488	-1.426370
H	4.163187	-3.238098	-0.733493
H	4.396170	-1.874314	-1.836581
C	2.337341	-2.087429	1.290750
H	2.581581	-1.593411	2.230052
H	2.747440	-3.094409	1.231607
C	1.016929	-1.909084	0.819956
H	0.448312	-1.042394	1.136470
C	0.323163	-2.750718	-0.091643
O	-0.774797	-2.489364	-0.632849
O	0.942365	-3.942188	-0.366929
C	0.273579	-4.796933	-1.297737
H	0.906734	-5.682122	-1.391934
H	0.161259	-4.316566	-2.275447
H	-0.716416	-5.087342	-0.932946
H	0.998904	0.380266	-3.158964
C	-4.216882	0.375069	1.343396
H	-3.454278	1.127773	1.159838
C	-4.739262	0.211493	2.626050
H	-4.383985	0.841511	3.437747
C	-5.719397	-0.755663	2.869440
H	-6.125420	-0.882438	3.869663
C	-6.169901	-1.558718	1.821219
H	-6.927846	-2.317081	2.000368
C	-5.642323	-1.394823	0.537696
H	-5.993036	-2.026962	-0.275181

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1762.85014962 Predicted Change= -1.143806D-08

Zero-point correction (ZPE)=	-1762.2688	0.58130
Internal Energy (U)=	-1762.2365	0.61357
Enthalpy (H)=	-1762.2356	0.61451
Gibbs Free Energy (G)=	-1762.3356	0.51451

Frequencies -- -329.7761 12.3536 13.4893

$E_{SCS\text{-}MP2/def2\text{-}\infty}$ SP = -1761.61804884

$E_{solvation}$ = -.03941266

VII-Product Imine 7.13-major

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene,SMD) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C26H33N3O2S C1[X(C26H33N3O2S)] #Atoms= 65
Charge = 0 Multiplicity = 1

SCF Energy= -1723.60078085 Predicted Change= -9.990317D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00128	0.00180	[YES]	0.00128	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-1.629039	-1.764574	-0.441916
N	-2.746760	-0.970195	-0.381124
S	-1.451125	-3.305493	0.250650
N	-0.632504	-1.168701	-1.146743
H	-2.642763	-0.081934	-0.870012
C	-4.036049	-1.129597	0.166846
H	-0.785871	-0.213444	-1.459337
C	0.711058	-1.681778	-1.344408
C	-4.471082	-2.211341	0.948323
C	-5.779332	-2.229093	1.436794
H	-6.097112	-3.076267	2.039450
C	-6.671547	-1.191379	1.168808
C	-6.238280	-0.113624	0.392056
H	-6.913378	0.707875	0.166600
C	-4.939001	-0.081559	-0.103014
H	-3.793437	-3.024214	1.164593
H	-7.686219	-1.220136	1.555751
H	-4.612493	0.760111	-0.709991
C	3.103006	-1.723925	-0.585143
C	1.705246	-1.219075	-0.249242
H	1.056284	-1.313073	-2.316012
H	0.675057	-2.771687	-1.376041
N	1.622677	0.245951	-0.177065
H	1.384619	-1.681616	0.692457
C	2.027432	0.903715	0.842367
C	2.695115	0.316955	2.079081
C	2.223687	0.952417	3.398950
C	2.324427	2.478590	3.350392
C	1.512196	3.023109	2.169728
C	1.924671	2.446382	0.786792
H	3.778385	0.479097	1.973616

H	2.555547	-0.766047	2.110785
H	2.817445	0.546348	4.226969
H	1.180439	0.662684	3.588168
H	3.377315	2.780266	3.269054
H	1.947493	2.914043	4.284436
H	1.583876	4.118284	2.123029
H	0.456588	2.788851	2.358195
C	3.321953	2.986818	0.387745
H	3.599077	2.640193	-0.614354
H	3.315747	4.083704	0.378408
H	4.108160	2.665513	1.077674
C	3.905381	-1.063086	-1.527383
H	3.541354	-0.152430	-1.994565
C	5.166211	-1.559274	-1.861478
H	5.776062	-1.032255	-2.591021
C	5.643620	-2.728294	-1.263796
H	6.625828	-3.113796	-1.524434
C	4.850645	-3.396876	-0.329127
H	5.212926	-4.306864	0.142387
C	3.590574	-2.897126	0.006726
H	2.977305	-3.423124	0.735054
O	-1.862195	1.595754	-1.823787
O	-1.525618	3.815865	-1.783329
C	-2.277080	3.928361	-3.010758
H	-1.783677	3.374323	-3.813248
H	-2.296571	4.993966	-3.240528
H	-3.292406	3.547821	-2.874540
C	-1.380877	2.585915	-1.281304
C	-0.556257	2.570506	-0.019748
H	-0.648777	1.573536	0.413192
H	-0.984940	3.294625	0.680886
C	0.928786	2.907789	-0.305885
H	1.225536	2.439593	-1.248568
H	1.026421	3.991870	-0.435427

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1723.60078085 Predicted Change= -9.990317D-09
Zero-point correction (ZPE)= -1723.0452 0.55557
Internal Energy (U)= -1723.0143 0.58645
Enthalpy (H)= -1723.0133 0.58739
Gibbs Free Energy (G)= -1723.1097 0.49101

Frequencies -- 15.6471 23.3708 29.5182

$E_{SCS\text{-}MP2/def2\text{-}\infty}$ SP = -1723.597534
$E_{solvation}$ = -0.0415076

VII Product Imine 7.13-minor

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene,SMD) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C26H33N3O2S C1[X(C26H33N3O2S)] #Atoms= 65
Charge = 0 Multiplicity = 1

SCF Energy= -1723.59415795 Predicted Change= -1.599050D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00313	0.00180	[NO]	0.00313	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	3.417316	0.326282	-1.469146
N	3.455782	1.692538	-1.346770
S	4.703111	-0.459218	-2.260132
N	2.350304	-0.314930	-0.957489
H	4.201869	2.110754	-1.888475
C	2.598211	2.593004	-0.671220
H	1.521860	0.220127	-0.711887
C	2.107195	-1.742614	-1.103856
C	2.020986	2.303966	0.575425
C	1.218532	3.256828	1.205906
H	0.780185	3.020541	2.171880
C	1.000526	4.506890	0.624401
C	1.596280	4.802019	-0.604786
H	1.442312	5.772766	-1.068186
C	2.383144	3.853134	-1.252868
H	2.219329	1.356988	1.065217
H	0.382867	5.246319	1.126046
H	2.835377	4.079183	-2.215221
C	1.448686	-2.148262	1.327881
C	0.996641	-2.206445	-0.132369
H	3.034669	-2.284182	-0.910055
H	1.797448	-1.972818	-2.132622
N	-0.167653	-1.360794	-0.378350
H	0.827741	-3.262478	-0.380253
C	-1.350223	-1.810519	-0.565916
C	-1.788106	-3.268186	-0.511745
C	-2.551023	-3.691306	-1.782489
C	-3.721992	-2.746444	-2.067468
C	-3.242512	-1.291731	-2.137044
C	-2.473644	-0.792765	-0.876060
H	-2.448426	-3.393107	0.357546
H	-0.939748	-3.935014	-0.344488
H	-2.900132	-4.725073	-1.669206

H	-1.858522	-3.682676	-2.635618
H	-4.486516	-2.861868	-1.287036
H	-4.205068	-3.017376	-3.014738
H	-4.086980	-0.620330	-2.332831
H	-2.568950	-1.186936	-2.999722
C	-1.894488	0.596027	-1.187761
H	-2.686948	1.271993	-1.525782
H	-1.408190	1.045594	-0.317444
H	-1.148382	0.536471	-1.986760
C	0.981170	-1.181670	2.226376
H	0.258106	-0.445974	1.890498
C	1.430468	-1.162224	3.550260
H	1.054118	-0.404825	4.233413
C	2.351943	-2.109746	3.996215
H	2.698727	-2.095707	5.026044
C	2.820629	-3.081908	3.108481
H	3.533410	-3.830326	3.445001
C	2.370661	-3.099953	1.788701
H	2.737624	-3.865343	1.107929
O	-4.726036	2.604649	-0.211028
O	-3.533849	1.949833	1.590367
C	-3.224152	3.329156	1.857150
H	-4.138968	3.913125	1.988860
H	-2.635850	3.758202	1.041216
H	-2.642367	3.325863	2.780161
C	-4.298451	1.718811	0.501320
C	-4.597996	0.241736	0.331439
H	-5.170715	0.136032	-0.592772
H	-5.272789	-0.025621	1.156084
C	-3.396526	-0.727219	0.384302
H	-2.780386	-0.469904	1.253191
H	-3.806093	-1.721618	0.584904

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-1723.59415795	Predicted Change= -1.599050D-08
Zero-point correction (ZPE)=	-1723.0387	0.55539
Internal Energy (U)=	-1723.0079	0.58623
Enthalpy (H)=	-1723.0069	0.58717
Gibbs Free Energy (G)=	-1723.1044	0.48974

Frequencies -- 15.4363 22.6934 25.5994

$E_{SCS\text{-}MP2/def2\text{-}\infty}$ SP = -1722.404716

$E_{solvation}$ = -0.0455295

TS-IV-7.13-major

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene,SMD)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C27H35N3O2S C1[X(C27H35N3O2S)] #Atoms= 68
Charge = 0 Multiplicity = 1

SCF Energy= -1762.86206791 Predicted Change= -1.883867D-09

==========

Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00205	0.00180	[NO]	0.00205	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.444369	0.384890	-1.258537
N	2.180066	-0.623142	-0.730196
S	1.670361	1.022292	-2.824330
N	0.484226	0.839230	-0.403769
H	1.855072	-0.999320	0.164457
C	3.234086	-1.364439	-1.411502
C	4.447433	-1.567748	-0.524526
H	3.493886	-0.794854	-2.307330
H	2.849939	-2.338728	-1.742588
H	0.453853	0.389293	0.513631
C	-0.504055	1.867136	-0.677283
C	-0.149220	3.245869	-0.121032
C	-1.865169	1.407622	-0.110368
H	-0.587146	1.946300	-1.765398
N	-2.255350	0.129456	-0.705649
H	-1.557819	-0.294912	-1.305232
H	-1.803931	1.312467	0.981431
C	-3.371637	-0.572897	-0.469443
C	-4.370323	-0.005257	0.512449
C	-5.784044	-0.569889	0.322144
C	-5.749809	-2.096176	0.232270
C	-4.868944	-2.546930	-0.938748
C	-3.491983	-1.884518	-0.992042
H	-4.387389	1.087070	0.435437
H	-4.009432	-0.234692	1.525654
H	-6.222704	-0.157140	-0.596707
H	-6.418753	-0.238856	1.152508
H	-6.762991	-2.496611	0.105976
H	-5.366245	-2.507584	1.175621
H	-5.396838	-2.340905	-1.883709
H	-4.733394	-3.636958	-0.908605
C	-2.717494	-2.227576	-2.258859

H	-1.634093	-2.095270	-2.155077
H	-2.880090	-3.278387	-2.524190
H	-3.048847	-1.618988	-3.111462
C	0.682903	3.401698	0.993295
H	1.134685	2.528973	1.456635
C	0.956831	4.673609	1.501347
H	1.610614	4.778619	2.363268
C	0.399388	5.805331	0.903841
H	0.616997	6.794757	1.297226
C	-0.431136	5.659083	-0.209834
H	-0.860668	6.534557	-0.689828
C	-0.701049	4.387843	-0.717337
H	-1.335908	4.280680	-1.594516
O	0.534825	-1.125736	1.710636
O	-1.602258	-1.188057	2.463125
C	-1.155466	-0.433496	3.594198
H	-0.695309	0.513706	3.297627
H	-0.433877	-1.003136	4.188604
H	-2.050633	-0.239054	4.189427
C	-0.628943	-1.568403	1.568508
C	-1.070298	-2.456515	0.554395
H	-0.302096	-2.770890	-0.145460
C	-2.398025	-2.891203	0.394879
H	-2.548783	-3.819150	-0.155189
H	-3.062959	-2.787000	1.247550
H	-2.613677	2.174344	-0.334347
C	4.825236	-2.850079	-0.111574
H	4.233501	-3.707942	-0.423546
C	5.951131	-3.038957	0.694858
H	6.230157	-4.042193	1.006764
C	6.712083	-1.941738	1.098898
H	7.588755	-2.085307	1.725173
C	6.341300	-0.655399	0.693745
H	6.931683	0.203486	1.002751
C	5.218156	-0.470581	-0.111193
H	4.933597	0.530822	-0.425371

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1762.86206791 Predicted Change= -1.883867D-09
Zero-point correction (ZPE)= -1762.2806 0.58143
Internal Energy (U)= -1762.2483 0.61375
Enthalpy (H)= -1762.2473 0.61470
Gibbs Free Energy (G)= -1762.3476 0.51445

Frequencies -- -326.0360 9.6223 18.7889

$E_{SCS\text{-}MP2/def2\text{-}\infty}$ SP = -1761.628855
$E_{solvation}$ = -0.03900204

TS-IV-7.13-minor

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene,SMD)
opt=(maxcycle=250,ts,calcfc,noeigentest,gdiis) iop(1/8=18) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C27H35N3O2S C1[X(C27H35N3O2S)] #Atoms= 68
Charge = 0 Multiplicity = 1

SCF Energy= -1762.85992568 Predicted Change= -3.116418D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00168	0.00180	[YES]	0.00168	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.608253	0.590538	-1.572161
N	2.423511	-0.325892	-0.996845
S	1.886928	1.283403	-3.109291
N	0.536029	0.905096	-0.792822
H	2.120211	-0.696861	-0.093393
C	3.600714	-0.933816	-1.599884
C	4.800807	-0.923589	-0.670862
H	3.812682	-0.374173	-2.515066
H	3.373857	-1.967445	-1.893985
H	0.455808	0.372617	0.075990
C	-0.530255	1.818138	-1.153260
C	-0.876044	2.804492	-0.036150
C	-1.783318	1.060529	-1.662910
H	-0.167275	2.382178	-2.017284
N	-2.439075	0.306494	-0.592262
H	-2.280868	0.663340	0.342773
H	-2.485050	1.786882	-2.093167
C	-3.647712	-1.175801	-2.111960
C	-4.998652	-1.901261	-2.186263
C	-5.103185	-2.970073	-1.098254
C	-4.936313	-2.347329	0.292977
H	-5.850463	-1.788179	0.547269
H	-4.852081	-3.138302	1.050758
H	-2.843613	-1.854231	-2.442166
H	-3.635902	-0.332496	-2.809833
C	-3.318518	-0.694966	-0.720138
H	-5.115510	-2.342377	-3.182976
H	-5.809455	-1.169976	-2.065438
H	-4.333195	-3.734599	-1.266972
H	-6.070128	-3.484348	-1.156922
C	-0.471490	2.627769	1.293977
H	0.147240	1.780437	1.573621

C	-0.838289	3.552768	2.277373
H	-0.511840	3.399115	3.302622
C	-1.608305	4.666969	1.947500
H	-1.888820	5.385867	2.712541
C	-2.009820	4.856692	0.622048
H	-2.599137	5.728333	0.349674
C	-1.646327	3.934339	-0.357231
H	-1.953204	4.098088	-1.387926
C	-3.733932	-1.409900	0.436795
C	-3.731659	-0.668929	1.770143
H	-2.740573	-0.308811	2.063646
H	-4.062202	-1.340856	2.569659
H	-4.420925	0.186815	1.756071
C	-2.177000	-2.634346	0.651367
H	-2.435255	-3.335044	-0.140643
H	-2.500453	-2.974199	1.633871
C	-0.900360	-2.040874	0.566630
H	-0.426505	-1.934834	-0.404067
C	-0.162754	-1.481919	1.639839
O	0.907558	-0.834045	1.524209
O	-0.682420	-1.702779	2.887140
C	0.066934	-1.178319	3.986646
H	-0.454815	-1.516950	4.884693
H	0.094586	-0.083507	3.968770
H	1.093167	-1.557182	3.986470
H	-1.469253	0.379550	-2.456284
C	5.476929	-2.112223	-0.373160
H	5.117468	-3.050173	-0.790831
C	6.602921	-2.107691	0.454592
H	7.114487	-3.041163	0.675259
C	7.065234	-0.908929	0.998315
H	7.939184	-0.901773	1.644533
C	6.394613	0.283751	0.709936
H	6.749439	1.222214	1.128462
C	5.273429	0.276462	-0.119018
H	4.757788	1.207420	-0.339670

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-1762.85992568	Predicted Change= -3.116418D-09
Zero-point correction (ZPE)=	-1762.2777	0.58214
Internal Energy (U)=	-1762.2457	0.61416
Enthalpy (H)=	-1762.2448	0.61511
Gibbs Free Energy (G)=	-1762.3436	0.51622

Frequencies -- -304.7096 11.8765 19.9045

$E_{SCS\text{-}MP2/def2\text{-}\infty}$ SP = -1761.630485
$E_{solvation}$ = -0.038677550

Benzylamine-catalyzed Michael

I Benzylamine

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene,SMD) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C7H9N C1[X(C7H9N)] #Atoms= 17
Charge = 0 Multiplicity = 1

SCF Energy= -326.916890744 Predicted Change= -8.131607D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00081	0.00180	[YES]	0.00081	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	2.754667	-0.478752	-0.321261
C	1.909983	0.549474	0.300339
H	2.103650	1.570957	-0.069561
H	2.158401	0.562573	1.371213
C	0.430858	0.247628	0.137361
C	-0.492475	1.289705	-0.018992
H	-0.136937	2.317603	-0.056737
C	-1.859716	1.026560	-0.129061
H	-2.559980	1.849248	-0.250802
C	-2.324123	-0.289643	-0.092758
H	-3.387122	-0.498031	-0.182815
C	-1.411056	-1.336897	0.055226
H	-1.762846	-2.365408	0.081614
C	-0.045853	-1.070193	0.170264
H	0.666029	-1.882917	0.278117
H	2.657590	-0.428129	-1.335170
H	3.732842	-0.274438	-0.121312

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-326.916890744	Predicted Change= -8.131607D-09
Zero-point correction (ZPE)=	-326.7703	0.14650
Internal Energy (U)=	-326.7632	0.15365
Enthalpy (H)=	-326.7622	0.15460
Gibbs Free Energy (G)=	-326.8021	0.11469

Frequencies -- 51.8440 158.9819 252.1436

$E_{SCS\text{-}MP2/def2\text{-}\infty}$ SP = -326.649083983
$E_{solvation}$ = .010712586

II Benzylamine Imine

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene,SMD) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C14H19N C1[X(C14H19N)] #Atoms= 34
Charge = 0 Multiplicity = 1

SCF Energy= -599.700825215 Predicted Change= -3.371404D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.01214	0.00180	[NO]	0.01214	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	0.238010	0.203705	0.286370
C	-0.735610	-0.876311	0.435883
H	-0.703289	-1.268272	1.465128
H	-0.497897	-1.727737	-0.217577
C	-2.154243	-0.416284	0.140708
C	1.486948	-0.016938	0.435623
C	2.148884	-1.347043	0.763392
C	3.236127	-1.704984	-0.272499
C	4.251875	-0.567999	-0.432155
C	3.555057	0.755365	-0.771752
C	2.471391	1.137962	0.267485
H	2.989018	1.241789	1.236166
H	1.415588	-2.153820	0.839175
H	2.622995	-1.252866	1.751966
H	2.756516	-1.905095	-1.240809
H	3.737058	-2.633002	0.029753
H	4.982094	-0.821036	-1.211422
H	4.818374	-0.452124	0.503610
H	3.084042	0.679346	-1.762732
H	4.290062	1.567877	-0.835181
C	1.809893	2.473946	-0.070755
H	1.267186	2.420063	-1.020841
H	1.092311	2.772986	0.699464
H	2.569690	3.260615	-0.153572
C	-2.552386	0.911178	0.339239
H	-1.814336	1.638029	0.662369
C	-3.873869	1.300101	0.109491
H	-4.164528	2.336219	0.265869
C	-4.819163	0.366951	-0.321579
H	-5.847126	0.670743	-0.502213
C	-4.431476	-0.959567	-0.524194
H	-5.156328	-1.693995	-0.866650
C	-3.109083	-1.344223	-0.296308

H -2.813569 -2.378576 -0.462563

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-599.700825215	Predicted Change= -3.371404D-08
Zero-point correction (ZPE)=	-599.3993	0.30149
Internal Energy (U)=	-599.3854	0.31538
Enthalpy (H)=	-599.3844	0.31632
Gibbs Free Energy (G)=	-599.4415	0.25929

Frequencies -- 16.3170 41.4040 67.6897

$E_{SCS\text{-}MP2/def2\text{-}\infty}$ SP = -599.196678655
$E_{solvation}$ = .017320230

TS-IV-benzylamine

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene,SMD) opt=(maxcycle=250,ts,calcfc,noeigentest)
freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C18H25NO2 C1[X(C18H25NO2)] #Atoms= 46
Charge = 0 Multiplicity = 1

SCF Energy= -906.144832138 Predicted Change= -1.022399D-08

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00003	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00095	0.00180	[YES]	0.00095	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	-0.116442	-0.887105	0.046186
H	0.239873	-0.713776	0.977814
C	0.893505	-0.824775	-1.021804
H	0.776812	0.135178	-1.544070
H	0.707039	-1.626552	-1.741753
C	2.284481	-0.976354	-0.443102
C	-1.445571	-0.905664	-0.102622
C	-2.016476	-1.039683	-1.493119
C	-3.433616	-1.629543	-1.501174
C	-4.335838	-0.895965	-0.507790
C	-3.754665	-0.971330	0.909104
C	-2.272910	-0.598277	1.014120
H	-1.354060	-1.651819	-2.113537
H	-2.016852	-0.036097	-1.943073
H	-3.387337	-2.695799	-1.238773
H	-3.841643	-1.571059	-2.517234
H	-5.345067	-1.326046	-0.514579
H	-4.439437	0.152049	-0.817770
H	-3.889729	-1.992935	1.298235
H	-4.326644	-0.319239	1.583459
C	-1.711768	-0.847872	2.409478
H	-0.815397	-0.252759	2.621687
H	-2.455523	-0.569100	3.164917
H	-1.464314	-1.906638	2.568069
C	2.855513	0.054231	0.319605
H	2.303732	0.977747	0.481479
C	4.131240	-0.095679	0.866482
H	4.563013	0.710426	1.453902
C	4.854969	-1.271267	0.652473
H	5.850150	-1.383934	1.074565
C	4.296166	-2.299005	-0.109336
H	4.853482	-3.215993	-0.282187

C	3.016864	-2.152042	-0.649357
H	2.583386	-2.956646	-1.238969
O	-0.497362	2.105279	-1.318032
O	0.927430	3.049295	0.189576
C	1.654669	3.571530	-0.920954
H	2.017068	2.780627	-1.585736
H	2.505622	4.108783	-0.493932
H	1.041624	4.263709	-1.508988
C	-0.225610	2.343853	-0.131189
C	-0.974279	1.984697	1.024069
H	-0.569627	2.245558	1.996836
C	-2.235322	1.361374	0.905079
H	-2.910383	1.473494	1.754525
H	-2.739345	1.494588	-0.050312

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -906.144832138	Predicted Change= -1.022399D-08	
Zero-point correction (ZPE)=	-905.7448	0.39995
Internal Energy (U)=	-905.7241	0.42071
Enthalpy (H)=	-905.7231	0.42165
Gibbs Free Energy (G)=	-905.7943	0.35044

Frequencies --	-307.4379	38.9860	43.3807

$E_{SCS\text{-}MP2/def2\text{-}\infty}$ SP = -905.443763948
$E_{solvation}$ = 0.021136372

VII-Product Imine Benzylamine

Using Gaussian 09: AM64L-G09RevC.01 23-Sep-2011

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene,SMD) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C18H25NO2 C1[X(C18H25NO2)] #Atoms= 46
Charge = 0 Multiplicity = 1

SCF Energy= -906.199649786 Predicted Change= -6.470737D-09

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00251	0.00180	[NO]	0.00251	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	3.246895	0.204808	-0.412232
C	2.063483	-0.619324	-0.889192
N	1.003146	-0.682784	0.118789
C	-0.089801	-1.304319	-0.113133
C	-0.446285	-2.033124	-1.402261
C	-0.911700	-3.479809	-1.140901
C	-2.053286	-3.519431	-0.120943
C	-1.650191	-2.803889	1.174094
C	-1.165249	-1.333571	0.989944
C	-0.608948	-0.847762	2.338196
C	4.551686	-0.167334	-0.758313
C	5.645808	0.611599	-0.373938
C	5.447795	1.777240	0.368116
C	4.149946	2.155099	0.722521
C	3.059555	1.375213	0.334698
O	-4.125318	1.320265	-0.880487
O	-3.082999	3.132378	-0.029445
C	-4.087316	3.964085	-0.636640
C	-3.213590	1.805100	-0.240758
C	-2.068231	1.041979	0.393390
C	-2.377707	-0.449362	0.566396
H	2.414995	-1.625977	-1.155053
H	1.680914	-0.174825	-1.821586
H	0.397369	-2.030686	-2.096621
H	-1.260026	-1.485059	-1.898825
H	-0.063159	-4.066840	-0.762095
H	-1.217295	-3.941081	-2.088252
H	-2.321194	-4.559446	0.105461
H	-2.950372	-3.057298	-0.553993
H	-0.835046	-3.371530	1.645685
H	-2.484195	-2.808889	1.888602
H	-0.219069	0.171152	2.287753
H	-1.399850	-0.878175	3.098572

H	0.212746	-1.487791	2.676663
H	4.714122	-1.078324	-1.331098
H	6.651493	0.303544	-0.648998
H	6.296948	2.383947	0.672042
H	3.986250	3.059349	1.303714
H	2.052564	1.663710	0.621309
H	-3.825662	4.987508	-0.363741
H	-5.081189	3.713353	-0.255632
H	-4.080408	3.849266	-1.724316
H	-1.818103	1.524100	1.343251
H	-1.191572	1.187430	-0.253418
H	-3.158355	-0.564754	1.330019
H	-2.814577	-0.817522	-0.365770

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy=	-906.199649786	Predicted Change= -6.470737D-09
Zero-point correction (ZPE)=	-905.7974	0.40217
Internal Energy (U)=	-905.7765	0.42308
Enthalpy (H)=	-905.7756	0.42402
Gibbs Free Energy (G)=	-905.8501	0.34946

Frequencies -- 18.9441 19.3048 29.2555

$E_{SCS\text{-}MP2/def2\text{-}\infty}$ SP = -944.788632363
$E_{solvation}$ = .021795088

Hydrogen Bonding Motifs

***N,N'*-methylthiourea**

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010
==========
opt=(tight,maxcycle=250) freq=noraman b3lyp/6-31g(d) gfinput gfprint
scf=(direct,tight,maxcycle=300,xqc)
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq
---
Pointgroup= C1 Stoichiometry= C3H8N2S C1[X(C3H8N2S)] #Atoms= 14
Charge = 0 Multiplicity = 1

SCF Energy= -626.833384847 Predicted Change= -1.880234D-11
==========
Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00001	[YES]	0.00000	0.00001	[YES]
Displ	0.00003	0.00006	[YES]	0.00003	0.00006	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
H	-1.069755	1.910171	0.230239
H	1.069760	1.910168	-0.230248
N	-1.143585	0.941633	-0.056298
N	1.143588	0.941632	0.056296
C	-2.475746	0.360496	0.007268
H	-2.589933	-0.388906	-0.778526
H	-3.201944	1.163105	-0.149300
H	-2.669029	-0.127407	0.970699
C	0.000000	0.194149	0.000000
S	-0.000003	-1.486725	-0.000001
C	2.475747	0.360493	-0.007264
H	2.589929	-0.388911	0.778528
H	3.201947	1.163099	0.149309
H	2.669037	-0.127409	-0.970695

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm
==========
SCF Energy= -626.833384847 Predicted Change= -1.880234D-11
Zero-point correction (ZPE)= -626.7154 0.11793
Internal Energy (U)= -626.7075 0.12588
Enthalpy (H)= -626.7065 0.12682
Gibbs Free Energy (G)= -626.7476 0.08570

Frequencies -- 115.3418 123.3901 139.9199

Methacrylate enolate

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene,SMD) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C4H7O2(1-) C1[X(C4H7O2)] #Atoms= 13
Charge = -1 Multiplicity = 1

SCF Energy= -307.126608699 Predicted Change= -1.253812D-07

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00015	0.00045	[YES]	0.00003	0.00030	[YES]
Displ	0.00161	0.00180	[YES]	0.00161	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.197188	-0.684946	0.000072
C	-1.354066	0.563028	0.000071
C	0.028677	0.580722	-0.000087
O	0.841426	1.536061	-0.000015
O	0.576387	-0.758584	-0.000362
C	1.980783	-0.809429	0.000193
H	-1.850202	1.531014	0.000233
H	-2.042386	-1.343013	-0.876871
H	-3.267452	-0.427619	0.000145
H	-2.042286	-1.343080	0.876952
H	2.427043	-0.330751	0.884942
H	2.427792	-0.329470	-0.883461
H	2.255748	-1.873141	-0.000416

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -307.126608699 Predicted Change= -1.253812D-07

Zero-point correction (ZPE)=	-307.0236	0.10292
Internal Energy (U)=	-307.0167	0.10982
Enthalpy (H)=	-307.0158	0.11076
Gibbs Free Energy (G)=	-307.0552	0.07137

Frequencies -- -81.7308 37.8541 117.1526

Dual π-activation 1

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene,SMD) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C7H15N2O2S(1-) C1[X(C7H15N2O2S)] #Atoms= 27
Charge = -1 Multiplicity = 1

SCF Energy= -934.016361554 Predicted Change= -2.464691D-07

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.02528	0.00180	[NO]	0.02528	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-3.370459	-0.614629	2.192590
C	-2.153209	-0.332591	1.357410
C	-2.156233	0.034587	0.039842
O	-1.151306	0.274790	-0.731037
O	-3.433174	0.163463	-0.550266
C	-3.442425	0.522917	-1.916500
H	-1.174163	-0.431716	1.822589
H	-4.285275	-0.470618	1.608198
H	-3.452888	0.037802	3.081319
H	-3.401930	-1.647974	2.585308
H	-2.913390	-0.203366	-2.547436
H	-2.994822	1.509493	-2.097511
H	-4.497701	0.551328	-2.213134
C	2.060112	0.003745	-0.059331
N	1.377501	1.162510	0.084156
C	1.971468	2.433392	0.429033
S	3.751901	-0.126327	0.202462
N	1.287634	-1.041583	-0.429093
C	1.766337	-2.388299	-0.638563
H	0.367937	1.109385	-0.126167
H	2.723383	2.749628	-0.305350
H	2.459545	2.404022	1.410881
H	1.170764	3.178562	0.456840
H	0.290153	-0.820104	-0.587942
H	0.908018	-3.006780	-0.917577
H	2.221169	-2.806172	0.267949
H	2.515151	-2.439501	-1.439267

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -934.016361554 Predicted Change= -2.464691D-07
Zero-point correction (ZPE)= -933.7925 0.22382

Internal Energy (U)=	-933.7758	0.24053
Enthalpy (H)=	-933.7748	0.24147
Gibbs Free Energy (G)=	-933.8406	0.17566

Frequencies --	13.0122	24.9423	32.3751

***Grand jeté* activation**

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene,SMD) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C7H15N2O2S(1-) C1[X(C7H15N2O2S)] #Atoms= 27
Charge = -1 Multiplicity = 1

SCF Energy= -934.017009307 Predicted Change= -1.843100D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00281	0.00180	[NO]	0.00281	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.049977	0.003256	-0.019320
N	1.299062	1.115513	0.152165
S	3.717525	-0.067973	0.387233
N	1.370445	-1.042095	-0.538109
H	0.307368	1.031378	-0.119988
H	0.368139	-0.870957	-0.732398
O	-1.132663	0.144515	-0.844016
O	-3.190835	0.819703	-0.081822
C	-2.927444	2.032493	-0.754455
H	-2.715421	1.887078	-1.821319
H	-2.083496	2.586084	-0.317955
H	-3.834558	2.639066	-0.647615
C	-2.191166	-0.174270	-0.183963
C	-2.485440	-1.362525	0.426916
H	-1.717867	-2.132163	0.368370
C	1.784340	2.360353	0.701578
H	2.603023	2.780391	0.104314
H	0.951643	3.070378	0.705599
H	2.150962	2.242052	1.729092
C	1.938664	-2.342572	-0.808232
H	2.338228	-2.812247	0.099121
H	1.142728	-2.976173	-1.210836
H	2.753491	-2.290718	-1.541423
C	-3.754052	-1.681236	1.167055
H	-4.278559	-2.567996	0.766735
H	-3.595449	-1.894789	2.240566
H	-4.458471	-0.844480	1.112837

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -934.017009307 Predicted Change= -1.843100D-08
Zero-point correction (ZPE)= -933.7927 0.22421

Internal Energy (U)=	-933.7763	0.24069
Enthalpy (H)=	-933.7753	0.24163
Gibbs Free Energy (G)=	-933.8398	0.17719

Frequencies --	12.7944	30.1323	50.4690

Dual π-activation 2

Using Gaussian 09: AM64L-G09RevB.01 12-Aug-2010

==========

#b3lyp/6-31G(d) scf=(maxcycle=300,direct,tight) density=current
SCRF=(PCM,SOLVENT=Toluene,SMD) opt=(maxcycle=250) freq=noraman
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RB3LYP/6-31G(d) Freq

---

Pointgroup= C1 Stoichiometry= C7H15N2O2S(1-) C1[X(C7H15N2O2S)] #Atoms= 27
Charge = -1 Multiplicity = 1

SCF Energy= -934.015679682 Predicted Change= -7.673179D-09

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00162	0.00180	[YES]	0.00162	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-4.913694	0.146551	-0.569412
C	-3.488492	0.131059	-1.045941
C	-2.381784	-0.030969	-0.258572
O	-1.152908	-0.037151	-0.632992
O	-2.648825	-0.211941	1.120692
C	-1.521897	-0.255143	1.969885
H	-3.296192	0.243220	-2.110931
H	-5.506214	-0.727614	-0.900863
H	-5.472666	1.030582	-0.924591
H	-4.958468	0.158567	0.524794
H	-0.929584	0.670292	1.941425
H	-0.848829	-1.092597	1.743617
H	-1.914533	-0.386298	2.985134
C	2.073510	0.032190	-0.143351
N	1.299147	1.140530	-0.134374
C	1.800892	2.493331	-0.047144
S	3.781467	0.082537	0.022146
N	1.381911	-1.121390	-0.289106
C	1.977711	-2.436720	-0.351116
H	0.289918	0.984513	-0.289868
H	2.443610	2.753514	-0.898497
H	2.383414	2.651572	0.867856
H	0.939566	3.168021	-0.038375
H	0.362783	-1.022090	-0.412680
H	1.167741	-3.163391	-0.465227
H	2.539120	-2.673642	0.560538
H	2.665841	-2.538290	-1.199985

Statistical Thermodynamic Analysis
Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -934.015679682 Predicted Change= -7.673179D-09
Zero-point correction (ZPE)= -933.7918 0.22382

Internal Energy (U)=	-933.7751	0.24049
Enthalpy (H)=	-933.7742	0.24143
Gibbs Free Energy (G)=	-933.8388	0.17685

Frequencies --	23.6557	30.7257	46.9305