On Stereocontrol in Organocatalytic α -Chlorinations of Aldehydes

Sebastian Ponath^{§‡}, Chetan Joshi[‡], Amy T. Merrill[†], Volker Schmidts[×], Kim Greis^{§#}, Maike Lettow^{§#}, Manuela Weber[§], Simon Steinhauer[§], Kevin Page^{‡#*}, Christina Thiele^{×*}, Dean J. Tantillo^{†*}, Mathew J. Vetticatt^{‡*}, Mathias Christmann^{§*}

[§]Institute of Chemistry and Biochemistry, Freie Universität Berlin, 14195 Berlin, Germany

[‡]Department of Chemistry, Binghamton University, Binghamton, New York 13902, United States

[†]Department of Chemistry, University of California – Davis, Davis, California 95616, United States

[×]Clemens Schöpf Institute of Organic Chemistry and Biochemistry, Technische Universität Darmstadt, 64287 Darmstadt, Germany

[#]Fritz Haber Institute of the Max Planck Society, 14195 Berlin, Germany

KEYWORDS: Organocatalysis, Chlorination, Reaction Mechanism, Computational Chemistry, Kinetic Isotope Effect

ABSTRACT: A comprehensive analysis of the organocatalytic α -chlorination of aldehydes with *N*-chloroimides and different catalysts is presented. For this reaction, alternate mechanisms were proposed that differ in the role of resting state intermediates and the rationalization of the observed enantioselectivity. This manuscript aims at resolving these fundamental questions on the basis of rigorous structural characterization of intermediates (configuration and conformation), NMR studies, ion mobility-mass spectrometry, concentration profiles, isotope studies, and DFT calculations.

◆ INTRODUCTION

The development of novel concepts to exert stereochemical control over chemical reactions constitutes a fundamental challenge.¹ Toward this goal, catalytic strategies that avoid expensive catalysts, toxic reagents and byproducts are considered among the most desirable. In order to improve on the selectivity and efficiency of a given transformation,² it is important to align experimental results with consistent models.

Enantioselective organocatalytic reactions³ via enamines commence with a condensation of a carbonyl compound and a chiral amine catalyst. In the selectivity-determining step (Scheme 1), the electrophile reacts preferentially with either of the two diastereotopic faces of the most reactive enamine conformer. The relative rates of formation ($k_{\text{major}}/k_{\text{minor}}$) of the diastereomeric iminium intermediates **I** (d.r.) and the enantiomeric ratio (e.r.) of the hydrolysis products **P** are usually rationalized by the relative energies of the respective transition states of the enamine-electrophile reaction. In a study on enantioselective fluorinations published in 2005, Jørgensen⁴ showed for the first time that processes downstream to the formations of the stereogenic center may result in a product e.r. that is different from the d.r. of the two iminium intermediates (d.r. $\neq$ e.r.).

In 2012, Blackmond, Bures, and Armstrong^{5,6} investigated two reactions catalyzed by Jørgensen-Hayashi diarylprolinol silyl ethers:^{7,8} the addition of aldehydes to nitroolefins, and the α -chlorination of isovaleraldehyde.

They arrived at the conclusion that “selectivity in these examples is rationalized not by comparison of transition states for formation of the stereogenic center but by the relative stability and reactivity of equilibrated downstream intermediates and in the separate branches of a competitive reaction network”.

Scheme 1. Stereopredictive Models

It was further suggested that their concept coined “Curtin-Hammett stereocontrol” may “represent a general phenomenon for amine catalysts lacking an acidic directing proton”. This projection is no exaggeration because if true, the design of enantioselective catalysts in these cases

should be augmenting the relative thermodynamic stability of intermediates rather than relative energies of transition states. In the following study, we will validate both models⁹ against new experimental data for the α -chlorination of aldehydes with different *N*-chloroimides, catalysts and substrates. To facilitate the reading, we will commence by framing the mechanistic discussion in the historical context.

◆ BACKGROUND

Asymmetric Aldehyde Chlorinations

Over the last years, chiral α -haloaldehydes^{10,11} have emerged as important building blocks. The first direct asymmetric α -chlorinations of aldehydes¹² were independently developed by two groups (Scheme 2). In the chlorination of octanal (**1**), MacMillan¹³ and co-workers employed 1.2 equiv of Lectka's chloroketone (**2**)¹⁴ at -30°C in acetone in the presence of 5 mol% of imidazolidinone **3a** ($X=Y=\text{Me}$) to give chloroaldehyde (*S*)-**4** in good yield and high enantiomeric excess.

Scheme 2. α -Chlorination of Aldehydes (2004–2009)

They noted that under these conditions, “product epimerization, formation of 2,2-dichlorooctanal, or octanal aldol dimerization were comprehensively suppressed”. As the byproduct, pentachlorophenol (**5**), is a probable human carcinogen, alternative chlorinating agents were considered. Using *N*-chlorosuccinimide (**6**, NCS) as an alternative Cl^+ source at 4°C , MacMillan observed almost racemic product. By monitoring the chlorination at 23°C , Brown (MacMillan group) noticed an erosion of the product ee over time.¹⁵ Taken together with the concomitant formation of 2,2-dichlorooctanal, this behavior was ascribed to the reversible formation of a chloroenamine intermediate subsequent to the formation of the stereogenic center. Racemization of the chiral chloroaldehyde can be effected by catalysts **3a** and **3b** ($X=\text{tBu}$, $Y=\text{H}$) in or without the presence of a chlorinating reagent.¹⁶ It is suppressed effectively at -30°C . Interestingly, Jørgensen et al. reported that C_2 -

symmetric (*R,R*)-2,5-diphenylpyrrolidine (**7**) (10 mol%) catalyzed the chlorination of aldehydes with NCS (1.3 equiv) at room temperature without noticeable racemization.¹⁷ In order to inhibit chloroenamine formation at room temperature, MacMillan designed imidazolidinone catalyst **3c** with loosely C_2 -like symmetry.¹⁸ This catalyst and Lectka's chloroketone constitute a highly effective combination for chlorinations at elevated temperatures¹⁵ and subsequent follow-up transformations.¹⁹ In 2009, MacMillan demonstrated that **3c** can be used for the SOMO chlorination of aldehydes.¹⁸ We started our own investigations in 2011 by initially using the MacMillan's SOMO protocol²⁰ but later moved to the combination of **3c** (20 mol%) and NCS in acetonitrile²¹ due to side reactions²² of radical intermediates in the SOMO chlorination of terpene aldehydes.

Chlorinations with Jørgensen-Hayashi-type Catalysts

The 2-substituted pyrrolidine scaffold **9** was first employed in enamine chlorinations of isovaleraldehyde **10** by Jørgensen et al. in 2004 (Scheme 3). Using **9a** (20 mol%) in 1,2-dichloroethane afforded (*S*)-2-chloroisovaleraldehyde **12** with moderate enantioselectivity. (e.r. 82:18).¹⁷ The corresponding diarylprolinol silyl ethers **9b** and **9c** ($R=\text{H}$, $X=\text{OTMS}$) had not been disclosed by that time.⁸ In 2012, Blackmond et al. studied the α -chlorination of isovaleraldehyde with NCS in CDCl_3 using these two catalysts achieving enantioselectivities in the same ballpark.⁶ With the aid of reaction calorimetry, they showed that “a rapid initial rate corresponding to ca. one turnover of the catalyst was followed by a slower zero-order regime, demonstrating that the reaction does not depend on the concentration of either of the two reactants.” The observation of two sets of NMR signals at -54°C featuring EXSY cross peaks led the authors to suggest that those correspond to two interconverting diastereomeric amins **11** as resting states of the catalytic system. The two species were proposed to be constitutionally “analogous to a species reported by Jørgensen using pyrrolidine” and diastereomeric at C1. Surprisingly, no attempt was reported to directly determine the structure, yet the major species was assigned to be the *anti*-configured. An inductive reasoning for the structural assignment implies an enamine-NCS reaction occurring with “near perfect facial selectivity” which was derived from the observation of “only two out of four possible diastereomers”. In the mechanistic proposal (Scheme 3), stereoselective enamine (**13**)/NCS reaction followed by reversible addition of succinimide to the iminium carbon of the chloroiminium ion affords two amins **11**, “which equilibrate between one of the two possible *syn* and one of the two possible *anti* diastereomers”.²³ Two separate stereospecific E_2 eliminations proceeding at identical rates ($k_{\text{syn}} \approx k_{\text{anti}}$) would provide an *E*-chloroenamine (*E*-**15**) from the major *anti*-aminal and a *Z*-chloroenamine (*Z*-**15**) from the minor *syn*-aminal. A stereospecific protonation/hydrolysis which, was not further detailed, would lead to the chloroaldehydes in an enantiomeric ratio identical to the ratio of the observed amins.²⁴ The apparent correlation between the ratio of two rapidly equilibrating species (cause) and

the ratio of two product enantiomers (effect) led the authors to formalize a new concept for stereochemical control in organocatalysis entitled the “Curtin-Hammett paradigm”.

Scheme 3. On-Cycle Mechanism for Chlorinations with Monosubstituted Pyrrolidine Catalysts

◆ RESULTS AND DISCUSSION

Chlorinations with Imidazolidinone Catalysts

In 2018, our group reported an investigation of the α -chlorination of aldehyde **16** using catalyst **3c**·TFA (20 mol%) with different *N*-chloroimides in acetonitrile.²⁵ The aim was to improve on the catalytic efficiency and to decrease the catalyst loading. We quickly realized that the main obstacle for good turnover is catalyst accumulation within stable aminals similar to those previously proposed. Grati­fyingly, we were able to isolate aminal intermediates **18** in pure form and to obtain several X-ray crystal structures for the first time (Scheme 4). Each of the isolated species was obtained as a single diastereomer with *syn*-configuration. With *N*-chlorophthalimide (NCP) as the chlorinating reagent, opening of the phthalimide moiety was observed to give **18a** upon reductive quenching/work-up. Merging the absolute configuration of the chloroaldehyde product **19** and the aminal **18**, we concluded that both compounds would be derived from iminium ion precursors possessing identical configurations at the chlorine substituted stereo­genic center (C₂).

Scheme 4. Isolation of Aminal Intermediates Using MacMillan-Type Catalyst **3c**

In our mechanistic proposal (Scheme 5), high facial selectivity for the depicted chloroiminium ion **19** was rationalized by the standard steric shielding model. In contrast to the previously discussed on-cycle model, we placed the aminal species *syn*-**18** and *anti*-**18** off the catalytic cycle. As a major consequence of the model, neither kinetic nor thermodynamic ratios of aminal C1 epimers affect the enantiomeric ratio of the chloroaldehyde. Yet, the accumulation of the catalysts within stable aminals is the major negative influence for diminished catalytic efficiency.

Scheme 5. Chlorination Using MacMillan-Type Catalyst **3c** with Off-Cycle Aminal Intermediates

The problem was overcome by using *N*-chloro-4-nitrophthalimide as NCS surrogate. The on-cycle model proposes the stereochemical outcome to be thermodynamically controlled, i.e. the formation of the major enantiomer must proceed through the most stable aminal. In that sense, the on-cycle mechanism predicts a formal inversion of the initially generated stereogenic center for the (2*S*)-*syn*-aminal to give the (2*R*)-chloroaldehyde product under the premise that chlorination and protonation occur with the same sense of stereocontrol imposed by the catalyst. Importantly, due to the C₂-like symmetry of the catalyst, a 180° rotation along the enamine and the chloroenamine C–N bond axis does not change the facial shielding significantly. Summarizing the stereochemical considerations, only the off-cycle mechanism aligns the configuration of

the most stable aminal with the observed (*S*)-configuration of the product, whereas the on-cycle model predicts the (*R*)-enantiomer as the major product.

In case of the first and second generation MacMillan catalysts **3a** and **3b**, similar aminals were proposed.^{26,27,28} The *syn/anti* ratio of respective aminals had been correlated to the enantiomeric ratio, and the *anti*-diastereomer was suggested to lead to the major product enantiomer. It is somewhat puzzling that to the best of our knowledge not a single aminal structure was established directly either by NMR or by X-ray crystallography. Repeating the experiments described for chlorination of isovaleraldehyde using catalysts **3a** and **3b** and NCS as the chlorinating reagent, we have been able to isolate most of the respective stable aminals which are separable chromatographically with no subsequent equilibration being observed. For each of those aminals, single crystals were grown and analyzed.

Figure 1. ^1H -NMR spectrum of the reaction (in accordance with the literature²⁸) (top). Crystal structure and ^1H -NMR spectrum of the isolated aminal bearing MacMillan-catalyst **3a** (bottom).

The obtained crystal structures reveal two surprising findings: first, the major aminal diastereomers *syn*-**20** and *syn*-**21** for the imidazolidinone catalysts **3a** and **3b** possess the *syn*- and not *anti*-configuration; second, in case of catalyst **3b**, we also isolated a third aminal, clearly visible in the crude NMR data that was previously overlooked (see SI for details). This third aminal also bears *syn*-configuration and is present in higher concentrations than the minor aminal in Blackmond's assignment (Figures 1 and 2).

The conformations of the diastereomeric aminals are reflective of steric and stereoelectronic interactions between the catalyst and the chloroaminal substructures and within the chloroaminal substructure itself. In all crystal structures, both *syn*- and *anti*-aminals adopt an antiperiplanar orientation of C₁-H and C₂-H (Scheme 6). Such an arrangement constitutes the only staggered conformation along the C₁-C₂ axis where each non-hydrogen substituent (N, Cl, R) possesses only one synclinal interaction with another non-hydrogen substituent. A similar conformational preference in solution is indicated by the observation of large $^3J_{\text{C}_1\text{-H}, \text{C}_2\text{-H}}$ coupling constants (10–11 Hz).

Figure 2. ^1H -NMR spectrum of the reaction (in accordance with the literature^{27,28}) (top). Crystal structures and ^1H -NMR spectra of different isolated aminal diastereoisomers bearing MacMillan-catalyst **3b** (bottom).

The stability of the aminals can be rationalized by a synergistic interplay of anomeric stabilization and gauche effects. In the *syn*-diastereomer, the two best $\sigma \rightarrow \sigma^*$ acceptors (C-Cl, C-N-imide) are in a gauche orientation whereas in the *anti*-diastereomer, the succinimide and the chlorine substituent are antiperiplanar. As previously noted by others,²⁹ the catalyst's aminal nitrogen lone pair prefers to be *cis* to the bulkiest substituent (to minimize strain) and *antiperiplanar* to a C-C or a C-X (X = O, N, S) bond (allowing for $n \rightarrow \sigma^*$ stabilization).

Curtin-Hammett conditions refer to situations where each of two rapidly interconverting *conformational isomers* reacts irreversibly to a different product. The Curtin-Hammett principle³⁰ issues a warning not to relate a conformer ratio directly to the product ratio if the rate of product formation is small relative to the rate of interconversion. Diastereomers must not be treated as individual reactive conformers but as an ensemble of conformations. Diastereomer stability is dominated by the lowest energy conformers but not necessarily by reactive conformations relevant to an ensuing transformation (Scheme 6) let alone the standard free energies ($\Delta\Delta G^\ddagger$) of the respective transition states. The “Curtin-Hammett paradigm for stereocontrol” suggests a quantitative relationship between the ratio of two equilibrating diastereomeric aminals and the ratio of their respective E₂ elimination products. However, the rel-

ative stability of amination conformations with C2-H and succinimide in an antiperiplanar orientation (the basis for the stereospecificity of the E2 elimination) is not directly related to the lowest energy conformation. It is also worth noting that the rate of E2 eliminations is expected to be sensitive towards the size of the substituents and other parameters (base, solvent).

Scheme 6. Lowest Energy and Reactive Conformations of *Syn*- and *Anti*-Aminals

Kinetic Isotope Effects and DFT Calculations

In order to evaluate the first irreversible step in the catalytic cycle, we performed the reaction of **16** and **6** using 20 mol% **3c**·TFA for determination of ^{13}C kinetic isotope effects (KIEs) at natural abundance.³¹ By using **6** as a limiting reagent, the reaction was taken to 77% conversion of **16**. The unreacted **16** was re-isolated from the reaction mixture as the corresponding alcohol following a reductive workup (see SI for full experimental details). The ^{13}C isotopic composition of this re-isolated sample was compared to that of a standard sample of reduced **16** (taken from the same batch used for the high conversion reaction) using quantitative NMR methodology. From the relative isotopic composition and the fractional conversion, ^{13}C KIEs for **16** were determined in a standard way.³¹ The resulting ^{13}C KIE measurements, from duplicate runs of this experiment, are shown in Figure 3A. There is a normal KIE of ~ 1.015 on the former carbonyl carbon and unity KIEs on all other carbon atoms of **16**. The qualitative interpretation of the experimental KIEs is that only the carbonyl carbon is involved in the first irreversible step for **16** in the catalytic cycle. There are several steps in the catalytic cycle that involve the carbonyl carbon atom and the exact step that accounts for the experimental KIE is not immediately clear. For the quantitative interpretation of experimental KIEs, we modeled the key steps in the catalytic cycle using B3LYP/6-31+G** with a PCM solvent model for acetonitrile as executed in Gaussian '16.^{32,33,34,35} High-level single point energy calculations that include dispersion corrections were performed for all stationary points using B3LYP-D3(BJ)³⁶/6-311+G**/PCM (acetonitrile). The reported Gibbs free energies were obtained by adding the free energy correction from the optimizations to the high-level single point energy calculations. The free energies were corrected using Grimme's quasi rigid rotor -harmonic oscillator (qRRHO) approach, which raises vibrational frequencies that are below 100 cm^{-1} to

100 cm^{-1} .³⁷ This approach is routinely utilized and is well-established for evaluating reactivity and selectivity in similar catalytic systems.^{38,39} The reaction coordinate diagram for the reaction of **16** and **6** catalyzed by **3c**·TFA leading up to the formation of the chloroiminium ion **Int4** is shown in Figure 3B. The trifluoroacetate counterion of the catalyst salt is included in these calculated structures to either act as a proton shuttle or to stabilize positively charged transition structures/intermediates. The reported free energy barriers ($\Delta G^\ddagger$) are computed with respect to the sum of the energies of neutral **3c**, trifluoroacetic acid, **6**, and **16**. The computed free energy profile reveals that the transition structures (TSs) for initial formation of the carbinol amine intermediate **Int1** (TS1, $\Delta G^\ddagger=10.2\text{ kcal mol}^{-1}$), loss of water to form the iminium ion **Int2** (TS2, $\Delta G^\ddagger=10.1\text{ kcal mol}^{-1}$), and deprotonation of **Int2** to form the enamine **Int3** (TS3, $\Delta G^\ddagger=10.4\text{ kcal mol}^{-1}$) all lie within 0.7 kcal mol^{-1} of each other. The TS for chlorination of **Int3** by **6** (TS4) has a $\Delta G^\ddagger$ of 9.3 kcal mol^{-1} and this step is an exergonic process resulting in a α -chloroiminium ion intermediate **Int4** that is $25.1\text{ kcal mol}^{-1}$ below separated starting materials. The experimental ^{13}C KIE determined for **16** reports on TS for the first irreversible step in the catalytic cycle for **16**. Since the $\Delta G^\ddagger$ for TS1-TS4 lie within 1.1 kcal mol^{-1} of each other, the prediction of ^{13}C KIEs for the interpretation of our experimental KIE values is complicated – each of these TSs contribute to the observed KIE, with the highest energy transition structure (TS3) contributing the most followed by TS1, TS2, and TS4. Figure 4C shows the predicted ^{13}C KIEs for TS1-4 assuming each to be the sole first irreversible step for **16**. The percentage contribution of each TS (based on relative $\Delta G^\ddagger$) to the observed KIEs is also indicated in parentheses. Based on the predicted ^{13}C KIE values for TS1-4, the energy-weighted predicted ^{13}C KIEs for C1 and C2 of **16** are computed (Figure 3C, last row). Comparison of experimental (Figure 3A) and energy-weighted predicted ^{13}C KIEs reveals a good agreement between the two – lending support to the computed reaction coordinate diagram.⁴⁰ Next, we computed the steps from the chloroiminium ion intermediate **Int4a** to the final α -chloroaldehyde product **19** (**Int4a** is a complex between the chloroiminium ion-TFA salt and a molecule of water and differs from **Int4** which is a complex between the chloroiminium ion-TFA salt and a molecule of succinimide). In the resulting reaction coordinate diagram (Figure 4A), the reported free energy barriers ($\Delta G^\ddagger$) are computed with respect to **Int4a** (the global minimum on this reaction coordinate). The hydrolysis of **Int4a** proceeds via two lower barrier steps – TS6 ($\Delta G^\ddagger=8.8\text{ kcal mol}^{-1}$) and TS7 ($\Delta G^\ddagger=8.3\text{ kcal mol}^{-1}$) – to deliver the product aldehyde **19** and regenerate **3c** and trifluoroacetic acid. Based on the observation of *syn*- and *anti*-aminial intermediates in this reaction (Figure 6 and 7), we also computed transition structures for the conversion of **Int4** to *syn*-**18b** (TS5) and *anti*-**18b** (TS5'). The transition structures TS5 and TS5' face a free energy barrier of 11.1 and 8.9 kcal mol^{-1} (relative to **Int4**). The *syn*-aminial *syn*-**18b** was found to be thermodynamically favored over the *anti*-

FIGURE 3. Experimental ^{13}C KIE studies and supporting DFT calculations. (A) Experimental ^{13}C KIEs for the α -chlorination of **16** with the MacMillan Catalyst **3c-TFA**. (B) Reaction coordinate diagram for the reaction of **16** and **6** catalyzed by **3c-TFA** up to the formation of the chloroiminium ion **Int4** calculated at the B3LYP-D3(BJ)/6-311+G** PCM (acetonitrile)//B3LYP/6-31+G** PCM (acetonitrile) level of theory. Some hydrogen atoms have been removed for clarity in the 3D representation of the key transition structures. Key bond-forming and bond-breaking distances are in angstroms (Å). (C) Predicted KIEs at C1 (aldehyde-carbon) and C2 (α -carbon) of **16** for TS1-4 along with energy-weighted predictions for comparison to experimental KIEs.

aminal **anti-18b** by 1.7 kcal mol⁻¹. These computed free energies are consistent with the experimental observation of **anti-18b** in the initial 5 minutes of the reaction (kinetic aminal) and subsequent accumulation of **syn-18b** (thermodynamic aminal) (Figure 7). Our calculations suggest that **syn-18b** is a parasitic off-cycle intermediate that has only one path to product **19** – by re-entering the catalytic cycle via TS5 ($\Delta G^\ddagger=15.3$ kcal mol⁻¹) to form **Int4** followed by the previously described hydrolysis via TS6 and TS7. If this pathway is operational for the conversion of **syn-18b** to **19**, re-entry of the **syn-18b** into the catalytic cycle via TS5 represents the largest change in free energy in the conversion of **syn-18b** to **19** (see Supporting Information for a discussion and supporting calculations for the conversion of **anti-18b** to **19**). Alternatively, **syn-18b** could be an on-cycle intermediate (Curtin-Hammett paradigm⁶) and could undergo an E2-elimination to yield a chloroenamine intermediate. Protonation and subsequent hydrolysis of this chloroenamine intermediate would deliver the product and regenerate the catalyst. In order to evaluate this alternative mechanism, we explored transition state models for the formation of the chloroenamine intermediate utilizing either trifluoroacetate or succinimide anion leaving group as the base that effects the deprotonation with concomitant loss of the succinimide anion. All attempts to locate this TS resulted in an E1-type structure where the succinimide anion is completely dissociated and the base deprotonates a

structure resembling a chloroiminium ion (Figure 4A, TS-E1; $\Delta G^\ddagger=28.2$ kcal mol⁻¹ with respect to **syn-18b**). This is because the incipient carbocation, that forms as the succinimide leaving group departs, is stabilized by the lone pair of electrons on the catalyst nitrogen before deprotonation can occur. Based on this result we hypothesized that disengaging this lone pair from the reaction coordinate by protonation, could result in the identification of an E2-elimination TS.⁴¹ Accordingly, we explored the α -deprotonation of *N*-protonated **syn-18b** (with concomitant loss of the succinimide anion) using trifluoroacetate as the base to generate the protonated chloroenamine intermediate. These explorations resulted in the identification of TS-E2 ($\Delta G^\ddagger=50.3$ kcal mol⁻¹ with respect to **syn-18b**), for the direct conversion of *N*-protonated **syn-18b** to the protonated chloroenamine intermediate. Clearly, the barriers for the E2-elimination and E1-elimination pathways are significantly higher than the pathway involving re-entry of **syn-18b** into the catalytic cycle as **Int4** (Figure 4D, TS5; $\Delta G^\ddagger=14.2$ kcal mol⁻¹ with respect to **syn-18b**). In order to gain experimental evidence on the catalytic role of **syn-18b**, we envisioned that determination of ^{13}C KIEs for the stoichiometric conversion of **syn-18b** to product **19** could probe the first irreversible step in the pathway for this reaction (Figure 4B). If the reaction proceeded via turnover-limiting re-entry into the catalytic cycle, a normal ^{13}C KIE would be expected only on C1. However, if either the E1- or

FIGURE 4. Hydrolysis of chloroiminium ion and investigation of the role of experimentally observed aminal intermediates. (A) Calculated transition state structures for alternative pathways for re-entry of *syn*-18b (as a chloroenamine) into the catalytic cycle. (B) Experimental ^{13}C KIEs determined for the stoichiometric conversion of *syn*-18b to 19. (C) Comparison of experimental ^{13}C KIEs for the conversion of *syn*-18b to 19 with the predicted ^{13}C KIE for the rate-determining step in each pathway that converts *syn*-18b to 19. (D) Reaction coordinate diagram for the conversion of the chloroiminium ion **Int4** to the final product 19 calculated at the B3LYP-D3(BJ)/6-311+G** PCM(acetonitrile)// B3LYP/6-31+G** PCM(acetonitrile) level of theory. Also shown is the calculated pathway for the parasitic off-cycle aminal intermediates *syn*-18b and *anti*-18b. Some hydrogen atoms have been removed for clarity in the 3D representation of the key transition structures. Key bond-forming and bond-breaking distances are in angstroms (Å).

E2-Elimination pathway is operational, a normal ^{13}C KIE would be expected on C2 or both C1 and C2, respectively. The conversion of *syn*-18b to 19 was initiated using 5 equivalents each of trifluoroacetic acid and water (Figure 4B). The ^{13}C KIEs were determined by product analysis⁴² – by comparison of samples of reduced 19 isolated from 24% and 100% conversion reactions. The key result from this experiment was a 1.008 (2) KIE on C1 and a 1.001 (4) KIE on C2 (Figure 4B) – in qualitative agreement with a mechanism involving turnover-limiting re-entry of *syn*-18b into the catalytic cycle. A comparison of this experimental KIE and theoretical KIEs for TS5, TS-E2, and TS-E1 reveals that the experimental values are in excellent agreement with predicted values for TS5 and in poor agreement with those for TS-E2 and TS-E1 (Figure 4C). Thus, evaluation of the reaction energetics and KIEs for the conversion of *syn*-18b to 19 supports the role of *syn*-18b as a parasitic, off-cycle intermediate that can re-enter the catalytic cycle via turnover-limiting formation of **Int4**. Finally, from the computed reaction coordinate diagram shown in Figure 3B, the chlorination of the enamine intermediate (TS4) is irreversible, and the enantioselectivity-determining step of the reaction. Accordingly, we performed a thorough confor-

mational search for the formation of both *R* and *S* chloroiminium ion via chlorination of the *Si*- and *Re*- faces, respectively, of all possible enamine geometries. The $\Delta\Delta G^\ddagger$ between the lowest energy transition structures leading to *R* and *S* chloroiminium ion is 2.9 kcal mol⁻¹ (favoring *S*) – a value that is qualitatively consistent with the >90% ee observed for this reaction. The full details of these explorations are included in the Supporting Information. Thus, our experimental KIE results along with a comprehensive DFT analysis of the entire reaction coordinate supports a scenario where the enantioselectivity-determining step is the initial formation of the chloroiminium ion and not any downstream processes.

Deuterium Incorporation Studies

In a deuterium incorporation study, aldehyde 16 was subjected to a chlorination reaction with the MacMillan catalysts 3b and 3c and the Jørgensen-Hayashi catalyst 9c and NCS at two different temperatures. The obtained chloroaldehyde was reduced to alcohol 22 (to avoid racemization) and submitted to NMR measurements. At -30 °C, all catalysts showed little to no incorporation of deuterium. At 20 °C, the MacMillan catalyst 3b shows significant deuterium incorporation (Figure 5). This observation is in line

with the racemization MacMillan observed for **3b** but not for **3c** (*vide supra*). Our results also rule out the protonation of fleeting chloroenamine intermediates due to the absence of significant deuterium incorporation at low temperature. While the intermediacy of chloroenamine intermediates cannot be studied by these experiments, their presence is not unlikely as chlorination might account for the formation of significant amounts dichloroaldehyde products for catalysts **9c**, **3a**, and **3b**.

Figure 5. Deuterium incorporation of **16** with different catalysts and temperatures with exemplary ¹H-NMR (A) and ¹³C-NMR (B) spectra; C) Quantification of deuterium incorporation under different conditions.

NMR Reaction Progress

We interrogated concentration profiles in order to assess whether the two mechanisms are kinetically distinguishable. Gratifyingly, aldehyde **16** (the substrate), the chloroaldehyde product **19** and the corresponding crystallographically characterized aminal *syn*-**18b** possess separate, non-overlapping NMR resonances (see SI). Monitoring their concentrations over time, it is apparent that the initial rate of chloroaldehyde formation exceeds the build-up of the aminal (Figure 6A). This observation eliminates the possibility of the catalyst being turned over through the thermodynamically most stable aminal. The alternate off-cycle mechanism provides a scenario where the rate of iminium hydrolysis exceeds that of aminal formation. From the iminium ion intermediate, part of the catalyst is diverted

into a stable aminal resting state. To identify these subtleties, it is essential to follow individual concentrations over time (NMR spectroscopy) rather than observing a single value for the whole system, for example, the amount of energy released (reaction calorimetry).

Figure 6. α-Chlorination of aldehyde **16** with catalyst **3c** and NCS (**6**) with concentration/time profile (A) and ¹H-NMR spectra with characteristic aminal signals for the first 15 min of the reaction (B).

Caution is due when arguing based on the presence or absence of intermediates in the NMR spectrum. Fleeting species, e.g. enamines⁴³ and iminium ions,⁴⁴ are difficult to observe and reversibly forming aminal diastereomers are certainly no exception. When reanalyzing our data for this reaction, we noted additional, previously overlooked resonances in the NMR spectrum at t = 5 min (Figure 6B) (quickly disappearing thereafter). The possibility of the corresponding species to be the elusive aminal *anti*-**18b** is supported by comparison of the observed and computed ¹H chemical shifts (Figure 7).

Figure 7. Calculated *syn*-**18b** and *anti*-**18b** lowest energy conformations of the aminal **18b** (top). Key ¹H chemical shifts calculated at PCM(ACN)-mPW1PW91/6-311+G(2d,p)//PCM

(ACN)-B₃LYP-D3(BJ)/6-31G+(d,p) level of theory (bottom) (for additional details see SI).

This hypothesis is in line with the calculated reaction path as the thermodynamically more stable aminal *syn*-**18b** accumulates in favor of *anti*-**18b**. While minor *anti*-**18b** will continue to be formed at an (unknown) kinetic ratio, its concentration quickly becomes too small to be observed by NMR as the amount of available catalyst diminishes rapidly into the *syn*-**18b** aminal reservoir. It is worth noting that under Curtin-Hammett conditions, the equilibrium distribution of the equilibrating species and the product distribution must be time-invariant.⁴⁵

The Role of Chloroamine Intermediates

The DFT calculations for catalyst **3c** demonstrated that chloroamine formation – either by iminium deprotonation or by E2 elimination from the aminal intermediate – is energetically disfavored compared to the alternative hydrolysis pathway. This assessment is supported by the notable lack of evidence of protonation (no deuterium incorporation) and the absence of dichlorination products. For catalyst **3a**, erosion of the ee was shown upon complete turnover of the substrate in a chlorination reaction.¹⁵ In a direct comparison, MacMillan et al.¹⁸ also showed that in the absence of NCS, catalyst **3b** effects rapid racemization of chloroaldehydes. This result suggests that chloroamines are accessible even in the absence of chloroaminals, i.e. from the iminium ions by deprotonation. During our efforts to separate aminals from reaction mixtures, we also have been able to characterize the first dichloroaminal **24a** from catalyst **3a**, which we suspect to be derived from the corresponding dichloroiminium intermediate (Scheme 7). In case of the Jørgensen-Hayashi catalyst or unsubstituted pyrrolidine, it was shown that chloroamine formation is competing⁴⁶ with the hydrolysis thus leading to the observation of significant amounts of dichlorination byproduct in both cases. This problem can be overcome by accelerating the hydrolysis step via intramolecular (proline⁴⁷) or intermolecular assistance (2,6-lutidine and H₂O⁴⁶).

Scheme 7. Chloroamines can competitively lead to racemization and dichlorination

Ion Mobility-Mass Spectrometry Studies

Aminals can be subjected to electrospray ionization followed by collision-induced dissociation. For each aminal,

diastereomeric iminium ions can be formed as *E*- and *Z*-isomers. In a feasibility study, we aimed to find out whether iminium ions derived from two isolated C2-epimeric aminals would be separable due their different ion mobilities in a drift gas (He).

Figure 8. Separate ionization of the diastereomeric aminals *syn*-**25** and *anti*-**25** with arrival time distributions and experimental CCSs of the generated diastereomeric iminium ions (blue and red traces). The trace of the mixture of both diastereomeric ions and their calculated CCSs and relative free energies are shown on the right.

Toward this end, instrument-independent collision cross sections (CCSs) were determined by ion mobility–mass spectrometry experiments on a custom-built instrument.⁴⁸ The arrival time distributions (ATDs) of the selectively dissociated aminals are represented in Figure 8. The conformational space of the iminium ions **26** was sampled using a generic algorithm⁴⁹ and promising candidate structures were reoptimized at the PBEoD3/6-311+G(d,p) level of theory.⁵⁰ Computed CCSs were obtained using the trajectory method.⁵⁰ The combined approach was successfully used to make a prediction whether *E*- or *Z*- iminium ions are formed in the decomposition process of the two diastereomeric aminals *syn*-**25** and *anti*-**25**. The ATD traces of the selectively dissociated aminals suggest that the dissociation of each aminal leads to the corresponding *E*-iminium ion. The comparison of the computed and the experimental CCS value suggests the *E*-iminium to be formed for both epimers (see SI for details). Future research will involve spectroscopic investigation (e.g., IR spectroscopy) of the separate iminium ions and following the iminium ion distribution over the course of the reaction.

Aminals with Jørgensen-Hayashi-Type Catalysts

In light of the observations described above for the MacMillan catalysts, we decided to reinvestigate the Jørgensen-Hayashi system for which we have not been able to obtain crystals of sufficient quality. Toward this end, we prepared a reaction mixture using isovaleraldehyde, catalyst **9b** and *N*-chlorophthalimide (NCP) as previously described.⁶ In order to obtain cleaner spectra than those reported, we removed all volatile constituents by evaporation. In the ¹H-NMR spectrum, **11** showed rather broad resonances at room temperature which split up at around –20 °C and at

–54 °C two sharp signal sets with a 3:1 ratio were observed. The presence of EXSY exchange peaks between the two signal groups indicated two rapidly interconverting species. These observations had been previously interpreted as **11** being a mixture of interconverting diastereomers at the aminal carbon with the *anti*-diastereomer as the major and the *syn*-diastereomer as the minor constituent.⁶ Interestingly, in both species the large $^3J_{\text{H-H}}$ coupling indicates an *antiperiplanar* arrangement of the H-atoms along the C1'–C2' bond. In order to elucidate the structures of the two species from NOE data, we aimed for minimizing exchange contributions to the NOE. This was largely achieved by changing the solvent from CDCl₃ to CD₂Cl₂, which allows cooling to –83 °C. We managed to assign most signals of both species and obtained a rather large body of distance data from the NOE of the major species and far less of the minor (see SI). The challenge now is to find out, why two signal sets are obtained and whether we can assign the two signal sets to possible structures of species. It is conceivable that these are interconverting diastereoisomers (*syn* and *anti*) as proposed previously by Blackmond et al.⁶ (Scheme 9). An alternative explanation would involve interconverting conformational isomers. For the major species, a comparison of distances with calculated structures allowed the assignment of *syn*-configuration (Figure 9). This is in contrast to what has been claimed previously.⁶ The key question now is whether the minor species is a diastereomer or a conformational isomer. For both species, only small difference in the distances were observed indicating a very similar relative orientation of the pyrrolidine ring to the chlorinated substrate; the *antiperiplanar* arrangement of H1' and H2' is conserved (see above). While our recently published pure shift ROE experiment (F1 PSYCHE EASY ROESY⁵¹) afforded additional distance data, still no safe assignment of the minor species was possible. From the $^3J_{\text{H-H}}$ coupling data in the pyrrolidine ring, it is not unlikely that multiple envelope conformations are present. The “averaged” pucker of the pyrrolidine is different for the major and minor species, which we consider unlikely for the *ap* arrangement of H1' and H2' in *syn* vs. *anti*-diastereoisomers. Thus we considered hindered rotation as being a plausible cause. From *J*-coupling analysis (see above and data in the SI) it is quite unlikely, that the pyrrolidine puckers are the reason for the separate signal sets; thus we focused our attention to the orientation of the diarylsilyl ether group. This hypothesis seems plausible as a structure search in the CCDC data base for Jørgensen-Hayashi catalysts with the pyrrolidine nitrogen bound to stereogenic sp³ hybridized carbon reveals striking similarities concerning the catalyst structure (see SI).⁵² Each structure in the database had the pyrrolidine ring in an envelope conformation with the γ -carbon tilted out of plane toward the diarylsilyl ether moiety and the nitrogen lone pair (*down* conformation). For the orientation of the diarylsilyl ether group, two distinct conformational minima are observed. In 7/10 crystal structures, the N- and O-substituent at the exocyclic C–C bond of the catalyst possess an *anti*-*periplanar* (*ap*) relationship whereas in three cases an *exo*-*synclinal* (*exo-sc*) conformation was adopted.

As NOE data was not entirely conclusive on the nature of the minor species and the process of the two interconverting aminal species **14** at –54 °C, a calculation of the NMR shifts for several conformational isomers and stereoisomers was performed (see SI for details). When the predicted conformers for **14** were separated into the *ap* and *exo-sc* classifications the *ap* chemical shifts corresponded to the major product (mean average deviation (MAD): 1.4 ppm ¹³C, 0.10 ppm ¹H) and the *exo-sc* chemical shifts were in excellent agreement with the minor product (MAD: 1.5 ppm ¹³C, 0.13 ppm ¹H) for key chemical shifts (Figure 9).

Figure 9. Calculated *ap* (top left) and *exo-sc* (top right) conformations of the Jørgensen-Hayashi aminal *syn*-**14** (R = C(3,5- CF_3 - C_6H_3)₂OTMS). Bottom: key chemical ¹H and ¹³C shifts. ¹H and ¹³C chemical shifts calculated with the mPW1PW91/6-311+G(2d,p) (GIAO; PCM, CHCl₃, 219.15 K)//B3LYP-D3(BJ)/6-31G+(d,p) (219.15 K) level of theory (indicative atoms are highlighted in bold).

From the integration of the exchange signals in 1D NOE series a barrier of 12.8(4) kcal mol⁻¹ can be determined at –54 °C. Investigation into the rotational barrier from the *ap*

to the *exo-sc* for *syn-14* using DFT calculations (see SI for additional details), revealed the barrier of rotation to be ~ 13.9 kcal mol $^{-1}$, within the error expected for this method to compare to the experimental 12.8 kcal mol $^{-1}$ barrier between the major and minor products at -54 °C. Further separation of the conformers into *concave* and *convex* pyrrolidine ring puckering, led to worse predicted chemical shifts for both the major and minor products, suggesting an averaging of the ring puckering in the NMR solution (barrier of ~ 1 kcal mol $^{-1}$ for the major (*ap*) product). The H5' proton shift appears to be diagnostic of *ap* and *exo-sc* conformations with the shift at -0.01 ppm for the major product and at 1.28 ppm for the minor product. In the lowest energy conformer calculated for the *ap* product, a C-H $\cdots\pi$ interaction can be seen shielding this methyl group proton, which does not occur in the *exo-sc* product (Figure 9).

Additionally, NMR calculations to determine the major and minor products bearing a succinimide (aminal **11**) substituent instead of phthalimide (aminal **14**) found by Blackmond and co workers⁶ at -54 °C were performed. The experimental chemical shifts were compared to the *syn-11 ap* and *exo-sc*, *anti*(C1') *ap* and *exo-sc*, and *anti*(C2')-**11 ap** calculated chemical shifts. The *syn-ap-11* calculated chemical shifts were in good agreement with the major product, while the *syn-exo-sc-11* produced some shifts above the expected deviation (<0.3 ppm for ^1H shifts and ≤ 3.1 ppm for ^{13}C shifts – with the exception of 7.3 ppm for C2'-Cl).⁵³ The *anti* C1' and C2' aminals were found to have greater mean average deviations (MADs) for the ^1H and ^{13}C chemical shifts when compared to the minor product chemical shifts than the *syn-exo-sc-11* aminal. These results, along with the agreement of *syn-exo-sc-14* calculated chemical shifts with the minor product experimental chemical shifts, suggest further analysis of the minor product experimental chemical shifts for **11** at -54 °C may be needed to confirm the chemical shift assignment.

The computationally and NMR spectroscopically derived (2*S*,1'*R*,2'*S*)-configuration and the conformation of the *syn*-aminal **14** share several structural features with the crystallographically determined aminals of the MacMillan catalysts including an *antiperiplanar* orientation of C1'-H and C2'-H and the lone pair of aminal nitrogen from the catalysts being *antiperiplanar* to the imide nitrogen. The stabilization energy of this $n_{\text{N}(\text{cat})} \rightarrow \sigma^*_{\text{C-N}(\text{imide})}$ interaction (Scheme 8) is predicted to be 16.3 kcal mol $^{-1}$ for the *ap* product and 16.0 kcal mol $^{-1}$ for *exo-sc* product. This interaction is even stronger when the succinimide substituent is present 17.5 (*ap*) and 17.2 (*exo-sc*) kcal mol $^{-1}$; and it decreases to ~ 8.0 kcal mol $^{-1}$ in the lowest energy conformer of the *anti*-aminal (see SI for details).⁵⁴

In summary, only the *syn*-diastereomer (2*S*,1'*R*,2'*S*)-**14** allows for an optimal synergistic interplay of stereoelectronic effects and minimized steric interactions.

As additional and independent supporting evidence for the structural assignment, aminal **14** was reduced and the resulting alcohol was converted to the crystalline dinitrobenzoate **15**. After a thorough isolation process only one diastereomer could be isolated. Crystal structure analysis confirmed the *syn*-configuration of aminal **15** (Scheme 8).

Scheme 8. Stereochemical Assignment of Aminal **14**

When substituting isovaleraldehyde with propanal, the analogous aminal could be obtained along with the chloroaldehyde being formed in a 57:43 enantiomeric ratio. NMR spectroscopic analysis of the aminal at -54 °C showed the presence two separate sets of sharp signals in a 68:32 ratio. Decomposition of the aminal into the corresponding chloroaldehyde was promoted by addition of 2 equivalents of water and TFA. Determination of the enantiomeric excess revealed high enantiomeric excess for the chloroaldehyde product (1-120 min: 95-93% ee). Additionally, almost no deuterium incorporation was observed when the decomposition of the propanal-derived aminal or aminal **14** was promoted by D_2O with or without TFA- d_4 . These observations suggest that only one out of four possible aminal diastereomers is present in sufficient concentration to be detected and isolated. Thus, aminal accumulation solely depends on thermodynamic stability.

CONCLUSION

A comparative analysis of the Curtin-Hammett model for stereocontrol and the steric shielding model showed only the latter to be consistent with experimental evidence. Using crystallography, NMR spectroscopy and computational NMR shift prediction, we have elucidated the configuration and conformation of several aminal intermediates of different catalysts in the organocatalytic α -chlorination of aldehydes. Their relative stability was rationalized by minimizing steric interactions and maximizing stabilizing stereoelectronic effects.

In the case of the Jørgensen-Hayashi catalyst **9b**, the underlying assumption of two equilibrating C1-aminal diastereomers **14** with the *anti*-diastereomer being the major and the *syn*-diastereomer being the minor species⁶ was shown to be incorrect. Instead, the two interconverting species, found upon cooling, are proposed to be conformational isomers of the *syn*-diastereomer (Scheme 9). Moreover, the suggested formation of the C2-stereogenic center

by chloroenamine protonation was excluded by the absence of deuterium incorporation under the reaction conditions.

Scheme 9. Structural Revision of Aminoal of 14

In the case of the MacMillan catalyst **3c**, a combination of ^{13}C KIE studies and DFT calculations demonstrated enamine chlorination not to be the first irreversible step. It also provided complementary evidence to rule out decomposition of the aminoal intermediates by an E2 elimination. The calculated transition structures for the enamine chlorination not only correctly predict the stereochemical outcome but also demonstrate that enamine chlorination is faster than (re-)protonation. This is an important finding as it shows that enamine formation in this case is not reversible, i.e. it is not thermodynamically controlled. This observation is supported by the chlorination product lacking significant amounts of deuterium incorporation. With respect to the C1 diastereomeric aminoals, DFT calculations predicted the *anti*-aminoal as the kinetic and the *syn*-aminoal as the thermodynamic intermediate.

Following the concentration/time profile by NMR spectroscopy, we were able to identify the previously overlooked *anti*-aminoal being formed within the first 5 minutes of the reaction. It quickly disappears due to accumulation of the catalyst in the *syn*-aminoal resting state. The structure of the *anti*-aminoal was determined by NMR shift computations and the method was validated against the crystallographically characterized *syn*-aminoal diastereomer. These observations rule out a Curtin-Hammett scenario for two reasons. First, Curtin-Hammett conditions require the ratio of the two interconverting intermediates to be time-invariant. Secondly, the dominant conformational minima of the two diastereomeric aminoals are unrelated to the reactive conformations for an E2 elimination let alone the respective transition states.

Additionally, we were able to isolate and characterize most of the relevant aminoals for the MacMillan catalyst **3a** and **3b** by crystal structure analysis for the first time and to reevaluate the incorrect assignment made in the literature. We also isolated and characterized an intermediate relevant to formation of dihalogenation byproducts. Similar to

the fluorination reaction described by Jørgensen, formation of dichlorinated intermediates also could change the initial stereoisomeric ratio of the monochlorination product.

Regarding the iminium intermediates, we have for the first time been able to separate diastereomeric iminium ions in an organocatalytic reaction by ion mobility-mass spectrometry. Future research will involve spectroscopic characterization of the separated iminium ions.

These results highlight the added value of combined computational work and experimentation. They also demonstrate the importance of a careful characterization of reaction intermediates to the understanding of complex reaction networks. Understanding and countering the stabilizing interactions within stable intermediates may provide clues to the design of more efficient catalytic systems.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures, computational details, characterization data of all compounds, NMR spectra, crystallographic data, HPLC and GC traces. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Accession Codes. 2041073–2041078, 2043370, 2045387 and 2049431 contain supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

Mathias Christmann – Institute of Chemistry and Biochemistry, Freie Universität Berlin, 14195 Berlin, Germany; ORCID: 0000-0001-9313-2392; Email: mathias.christmann@fu-berlin.de

Mathew J. Vetticatt – Department of Chemistry, Binghamton University, Binghamton, New York 13902, United States; ORCID: 0000-0001-5709-0885; Email: vetticatt@binghamton.edu

Dean J. Tantillo – Department of Chemistry, University of California – Davis, Davis, California 95616, United States; ORCID: 0000-0002-2992-8844; Email: djtantillo@ucdavis.edu

Christina Thiele – Clemens Schöpf Institute of Organic Chemistry and Biochemistry, Technische Universität Darmstadt, 64287 Darmstadt, Germany; ORCID: 0000-0001-7876-536X; Email: cthiele@thielelab.de

Kevin Pagel – Institute of Chemistry and Biochemistry, Freie Universität Berlin, 14195 Berlin, Germany; Fritz Haber Institute of the Max Planck Society, 14195 Berlin, Germany; ORCID: 0000-0001-8054-4718; Email: kevin.pagel@fu-berlin.de

Authors

Sebastian Ponath – Institute of Chemistry and Biochemistry, Freie Universität Berlin, 14195 Berlin, Germany; ORCID: 0000-0003-2763-0443;

Chetan Joshi – Department of Chemistry, Binghamton University, Binghamton, New York 13902, United States;

Amy T. Merrill – Department of Chemistry, University of California – Davis, Davis, California 95616, United States; ORCID: 0000-0003-4801-1721;

Volker Schmidts – Clemens Schöpf Institute of Organic Chemistry and Biochemistry, Technische Universität Darmstadt, 64287 Darmstadt, Germany; ORCID: 0000-0002-7195-312X;

Kim Greis – Institute of Chemistry and Biochemistry, Freie Universität Berlin, 14195 Berlin, Germany; Fritz Haber Institute of the Max Planck Society, 14195 Berlin, Germany; ORCID: 0000-0002-9107-2282;

Maike Lettow – Institute of Chemistry and Biochemistry, Freie Universität Berlin, 14195 Berlin, Germany; Fritz Haber Institute of the Max Planck Society, 14195 Berlin, Germany;

Manuela Weber – Institute of Chemistry and Biochemistry, Freie Universität Berlin, 14195 Berlin, Germany

Simon Steinhauer – Institute of Chemistry and Biochemistry, Freie Universität Berlin, 14195 Berlin, Germany; ORCID: 0000-0001-7420-1153;

Author Contributions

‡These authors contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

K.G. thanks the Fonds National de la Recherche (FNR), Luxembourg for funding for the project GlycoCat (13549747). C.M.T. thanks the DFG for funding the project TH115/12-1. D. J. T. is thankful for the support from the US National Science Foundation (CHE-1856416 and the XSEDE program (CHE-030089)). We thank Patrick Voßnacker (FU Berlin) for crystallographic support.

REFERENCES

- (1) Carreira, E. M.; Kvaerno, L. *Classics in Stereoselective Synthesis*; Wiley-VCH, Weinheim, 2009.
- (2) Carlson, R.; Carlson, J. E. *Design and optimization in organic synthesis*, 2nd rev. and enl. ed.; Elsevier, Amsterdam, San Diego, CA, 2005.
- (3) List, B.; Maruoka, K. *Science of Synthesis, Asymmetric Organocatalysis Vol. 1*; Georg Thieme, Stuttgart, New York, 2012.
- (4) Marigo, M.; Fielenbach, D.; Braunton, A.; Kjaersgaard, A.; Jørgensen, K. A. *Angew. Chem. Int. Ed.* **2005**, *44*, 3703–3706.
- (5) Burés, J.; Armstrong, A.; Blackmond, D. G. *Pure Appl. Chem.* **2013**, *85*, 1919–1934.
- (6) a) Burés, J.; Armstrong, A.; Blackmond, D. G. *J. Am. Chem. Soc.* **2012**, *134*, 6741–6750; b) Burés, J.; Armstrong, A.; Blackmond, D. G. *J. Am. Chem. Soc.* **2012**, *134*, 14264.
- (7) a) Reyes-Rodríguez, G. J.; Rezayee, N. M.; Vidal-Albalat, A.; Jørgensen, K. A. *Chem. Rev.* **2019**, *119*, 4221–4260; b) Marigo, M.; Wabnitz, T. C.; Fielenbach, D.; Jørgensen, K. A. *Angew. Chem. Int. Ed.* **2005**, *44*, 794–797.
- (8) Hayashi, Y.; Gotoh, H.; Hayashi, T.; Shoji, M. *Angew. Chem. Int. Ed.* **2005**, *44*, 4212–4215.

- (9) Földes, T.; Madarász, Á.; Révész, Á.; Dobi, Z.; Varga, S.; Hamza, A.; Nagy, P. R.; Pihko, P. M.; Pápai, I. *J. Am. Chem. Soc.* **2017**, *139*, 17052–17063.
- (10) Oestreich, M. *Angew. Chem. Int. Ed.* **2005**, *44*, 2324–2327.
- (11) Britton, R.; Kang, B. *Nat. Prod. Rep.* **2013**, *30*, 227–236.
- (12) Shibatomi, K.; Narayama, A. *Asian J. Org. Chem.* **2013**, *2*, 812–823.
- (13) Brochu, M. P.; Brown, S. P.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2004**, *126*, 4108–4109.
- (14) Wack, H.; Taggi, A. E.; Hafez, A. M.; Drury, W. J.; Lectka, T. *J. Am. Chem. Soc.* **2001**, *123*, 1531–1532.
- (15) Brown, S. P. *Iminium and Enamine Activation: Methods for Enantioselective Organocatalysis*; California Institute of Technology, Pasadena, California, 2005.
- (16) Duan, X.-H.; Mayr, H. *Org. Lett.* **2010**, *12*, 2238–2241.
- (17) Halland, N.; Braunton, A.; Bachmann, S.; Marigo, M.; Jørgensen, K. A. *J. Am. Chem. Soc.* **2004**, *126*, 4790–4791.
- (18) Amatore, M.; Beeson, T. D.; Brown, S. P.; MacMillan, D. W. C. *Angew. Chem. Int. Ed.* **2009**, *48*, 5121–5124.
- (19) a) Bourboulas, A.; Limnios, D.; Kokotou, M. G.; Mountanea, O. G.; Kokotos, G. *Molecules* **2019**, *24*, 2081; b) Mountanea, O. G.; Limnios, D.; Kokotou, M. G.; Bourboulas, A.; Kokotos, G. *Eur. J. Org. Chem.* **2019**, 2010–2019; c) Kaplaneris, N.; Spyropoulos, C.; Kokotou, M. G.; Kokotos, G. *Org. Lett.* **2016**, *18*, 5800–5803.
- (20) Winter, P.; Vaxelaire, C.; Heinz, C.; Christmann, M. *Chem. Commun.* **2011**, *47*, 394–396.
- (21) a) Winter, P.; Swatschek, J.; Willot, M.; Radtke, L.; Olbrisch, T.; Schäfer, A.; Christmann, M. *Chem. Commun.* **2011**, *47*, 12200–12202; b) Winter, P.; Hiller, W.; Christmann, M. *Angew. Chem. Int. Ed.* **2012**, *51*, 3396–3400; c) Swatschek, J.; Grothues, L.; Bauer, J. O.; Strohmman, C.; Christmann, M. *J. Org. Chem.* **2014**, *79*, 976–983.
- (22) Comito, R. J.; Finelli, F. G.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2013**, *135*, 9358–9361.
- (23) The succinimide anion/iminium ion pair must be considered inert toward water as direct hydrolysis of the iminium ion (a.k.a. the “classical” pathway) or proton transfer to the succinimide anion would bypass the amination intermediate.
- (24) A publication on organocatalytic selenylations²⁷ suggested that an exclusive stereospecific reaction of either enamine with water (pKa 14) may “lead selectively and irreversibly” to the two enantiomeric products via iminium ions “being counter-balanced by a hydroxy group [sic]”.
- (25) Ponath, S.; Menger, M.; Grothues, L.; Weber, M.; Lentz, D.; Strohmman, C.; Christmann, M. *Angew. Chem. Int. Ed.* **2018**, *57*, 11683–11687.
- (26) Burés, J.; Armstrong, A.; Blackmond, D. G. *Acc. Chem. Res.* **2016**, *49*, 214–222.
- (27) a) Burés, J.; Dingwall, P.; Armstrong, A.; Blackmond, D. G. *Angew. Chem. Int. Ed.* **2014**, *53*, 8700–8704.
- (28) Wiest, J. *The Role of Charged and Uncharged Intermediates in Organocatalysis*, MS Thesis, 2012, Universität Basel (conducted in the Blackmond group at The Scripps Research Institute).
- (29) a) Alamillo-Ferrer, C.; Nielsen, C. D.-T.; Salzano, A.; Companyó, X.; Di Sanza, R.; Spivey, A. C.; Rzepa, H. S.; Burés, J. *J. Org. Chem.* **2021**, *86*, 4326–4335; b) Seebach, D.; Sun, X.; Ebert, M.-O.; Schweizer, W. B.; Purkayastha, N.; Beck, A. K.; Duschmalé, J.; Wennemers, H.; Mukaiyama, T.; Benohoud, M.; Hayashi, Y.; Reiher, M. *Helv. Chim. Acta* **2013**, *96*, 799–852; c) Seebach, D.; Grošelj, U.; Badine, D. M.; Schweizer, W. B.; Beck, A. K. *Helv. Chim. Acta* **2008**, *91*, 1999–2034.

- (30) a) Seeman, J. I. *Chem. Rev.* **1983**, 83, 83–134; b) Seeman, J. I. *J. Chem. Educ.* **1986**, 63, 42–48; c) Chakraborty, S.; Saha, C. *Reson* **2016**, 21, 151–171.
- (31) Singleton, D. A.; Thomas, A. A. *J. Am. Chem. Soc.* **1995**, 117, 9357–9358.
- (32) a) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648–5652; b) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, 98, 11623–11627; c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785–789.
- (33) Hariharan, P. C.; Pople, J. A. *Theoret. Chim. Acta* **1973**, 28, 213–222.
- (34) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, 105, 2999–3093.
- (35) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16*, Revision C.01; Gaussian, Inc., Wallingford CT, 2016.
- (36) a) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, 132, 154104; b) Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comput. Chem.* **2011**, 32, 1456–1465.
- (37) Grimme, S. *Chem. Eur. J.* **2012**, 18, 9955–9964.
- (38) a) Zhu, H.; Clemente, F. R.; Houk, K. N.; Meyer, M. P. *J. Am. Chem. Soc.* **2009**, 131, 1632–1633; b) Xu, H.; Zuend, S. J.; Woll, M. G.; Tao, Y.; Jacobsen, E. N. *Science* **2010**, 327, 986–990; c) Klausen, R. S.; Kennedy, C. R.; Hyde, A. M.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2017**, 139, 12299–12309; d) Roytman, V. A.; Karugu, R. W.; Hong, Y.; Hirschi, J. S.; Veticatt, M. J. *Chem. Eur. J.* **2018**, 24, 8098–8102.
- (39) Ashley, M. A.; Hirschi, J. S.; Izzo, J. A.; Veticatt, M. J. *J. Am. Chem. Soc.* **2016**, 138, 1756–1759.
- (40) Considering that there are errors (~0.5 kcal mol⁻¹) associated with the computed energetics of the reaction coordinate, the slight discrepancy between experimental and predicted KIEs for the carbonyl carbon is not significant.
- (41) See reference (39) for a similar E2-elimination step in an α -amination reaction catalyzed by L-proline.
- (42) a) Frantz, D. E.; Singleton, D. A.; Snyder, J. P. *J. Am. Chem. Soc.* **1997**, 119, 3383–3384; b) Singleton, D. A.; Schulmeier, B. E. *J. Am. Chem. Soc.* **1999**, 121, 9313–9317; c) Frantz, D. E.; Singleton, D. A. *J. Am. Chem. Soc.* **2000**, 122, 3288–3295; d) Bandar, J. S.; Sauer, G. S.; Wulff, W. D.; Lambert, T. H.; Veticatt, M. J. *J. Am. Chem. Soc.* **2014**, 136, 10700–10707.
- (43) a) Schmid, M. B.; Zeitler, K.; Gschwind, R. M. *Angew. Chem. Int. Ed.* **2010**, 49, 4997–5003; b) Schmid, M. B.; Zeitler, K.; Gschwind, R. M. *Chem. Sci.* **2011**, 2, 1793–1803.
- (44) Mayr, H.; Ofial, A. R.; Würthwein, E.-U.; Aust, N. C. *J. Am. Chem. Soc.* **1997**, 119, 12727–12733.
- (45) Seeman, J. I.; Farone, W. A. *J. Org. Chem.* **1978**, 43, 1854–1864.
- (46) Jimeno, C.; Cao, L.; Renaud, P. *J. Org. Chem.* **2016**, 81, 1251–1255.
- (47) Hayes, M. D.; Rodríguez-Alvarado, M.; Brenner-Moyer, S. E. *Tetrahedron Lett.* **2015**, 56, 4718–4720.
- (48) a) Warnke, S.; Helden, G. von; Pagel, K. *Proteomics* **2015**, 15, 2804–2812; b) Hoffmann, W.; Langenhan, J.; Huhmann, S.; Moschner, J.; Chang, R.; Accorsi, M.; Seo, J.; Rademann, J.; Meijer, G.; Koksche, B.; Bowers, M. T.; Helden, G. von; Pagel, K. *Angew. Chem. Int. Ed.* **2019**, 58, 8216–8220.
- (49) Supady, A.; Blum, V.; Baldauf, C. *J. Chem. Inf. Model.* **2015**, 55, 2338–2348.
- (50) a) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, 110, 6158–6170; b) Mesleh, M. F.; Hunter, J. M.; Shvartsburg; Schatz G. C.; Jarrold, M. F. *J. Phys. Chem.* **1996**, 100, 16082–16086.
- (51) a) Ilgen, J.; Kaltschnee, L.; Thiele, C. M. *Magn. Reson. Chem.* **2018**, 56, 918–933; b) Ilgen, J.; Nowag, J.; Kaltschnee, L.; Schmidts, V.; Thiele, C. M. *J. Magn. Reson.* **2021**, 324, 106900.
- (52) a) Seebach, D.; Sun, X.; Sparr, C.; Ebert, M.-O.; Schweizer, W. B.; Beck, A. K. *Helv. Chim. Acta* **2012**, 95, 1064–1078; b) Seebach, D.; Sun, X.; Ebert, M.-O.; W. Schweizer, W. B.; Purkayastha, N.; Beck, A. K.; Duschmalé, J.; Wennemers, H.; Mukaiyama, T.; Benohoud, M.; Hayashi, Y.; Reiher, M. *Helv. Chim. Acta* **2013**, 96, 799–852; c) Cassani, C.; Melchiorre, P. *Org. Lett.* **2012**, 14, 5590–5593; d) Weber, A. K.; Schachtner, J.; Fichtler, R.; Leermann, T. M.; Neudörfl, J. M.; von Wangelin, A. J. *Org. Biomol. Chem.* **2014**, 12, 5267–5277; e) Gurubrahmanam, R.; Chen, Y. M.; Huang, W.-Y.; Chan, Y.-T.; Chang, H.-K.; Tsai, M.-K.; Chen, K. *Org. Lett.* **2016**, 18, 3046–3049; f) Boeckman Junior, R. K.; Wang, H.; Rugg, K. W.; Genung, N. E.; Chen, K.; Ryder, T. R. *Org. Lett.* **2016**, 18, 6136–6139.
- (53) Lodewyk, M. W.; Siebert, M. R.; Tantillo, D. J. *Chem. Rev.* **2012**, 112, 1839–1862.
- (54) References NBO method: (B3LYP-D3(BJ))/6-31g(d,p), io(3/32=2), 219.15 K, with a Fine grid; a) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, 102, 7211–7218; b) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, 78, 4066–4073; c) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, 83, 735–746; d) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, 83, 1736–1740; e) J. E. Carpenter, Extension of Lewis structure concepts to open-shell and excited-state molecular species, Ph.D. thesis, University of Wisconsin, Madison, WI, 1987; f) Carpenter, J. E.; Weinhold, F. *J. Mol. Struct. (Theochem)*. **1988**, 139, 41–62; g) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, 88, 899–926; h) Weinhold, F. and Carpenter, J. E. in *The Structure of Small Molecules and Ions*, Naaman, E. R.; Vager, Z. Plenum, 1988, 227–236.

Supporting Information

On Stereocontrol in Organocatalytic α -Chlorinations of Aldehydes

Sebastian Ponath^{§‡}, Chetan Joshi^{‡‡}, Amy T. Merrill[†], Volker Schmidts[×], Kim Greis^{§#}, Maïke Lettow^{§#}, Manuela Weber[§], Simon Steinhauer[§], Kevin Pagel^{§#*}, Christina Thiele^{×*}, Dean J. Tantillo^{†*}, Mathew J. Vetticatt^{‡*}, Mathias Christmann^{§*}

[§]Institute of Chemistry and Biochemistry, Freie Universität Berlin, 14195 Berlin, Germany

[‡]Department of Chemistry, Binghamton University, Binghamton, New York 13902, United States

[†]Department of Chemistry, University of California – Davis, Davis, California 95616, United States

[×]Clemens Schöpf Institute of Organic Chemistry and Biochemistry, Technische Universität Darmstadt, 64287 Darmstadt, Germany

[#]Fritz Haber Institute of the Max Planck Society, 14195 Berlin, Germany

TABLE OF CONTENTS

1. GENERAL INFORMATION	1
2. CHLORINATIONS WITH MACMILLAN-TYPE CATALYSTS.....	4
2.1. Amins Derived from 1 st , 2 nd and 3 rd Generation MacMillan Catalysts	4
2.2. NMR Reaction Progress (3 rd Generation MacMillan Catalyst).....	22
2.3. KIEs and DFT Calculations (3 rd Generation MacMillan Catalyst)	28
2.4. Ion Mobility-Mass Spectrometry with Amins (2 nd Generation MacMillan Catalyst)	111
3. CHLORINATIONS WITH THE JØRGENSEN-HAYASHI-TYPE CATALYST	119
3.1. Amins Derived from Isovaleraldehyde	119
3.1.1. Synthesis and Derivatization.....	119
3.1.2. Structural Analysis	131
3.1.3. Decomposition and Deuterium Incorporation Studies	169
3.2. Amins Derived from Propanal	178
3.2.1. Synthesis.....	178
3.2.2. Decomposition and Deuterium Incorporation Studies	184
4. FURTHER RESULTS	188
5. REFERENCES.....	192
6. APPENDIX.....	194
6.1. NMR Spectra.....	194
6.2. HPLC/GC Traces	222
6.3. Crystallographic Data.....	242

1. GENERAL INFORMATION

Anhydrous solvents were provided by purification with MBraun SPS-800 solvent system using solvents of HPLC grade purchased from Fischer Scientific. Solvents for extraction, crystallization and flash column chromatography were purchased in technical grade and distilled under reduced pressure prior to use. Unless otherwise indicated, all starting materials and reagents were purchased from commercial distributors and used without further purification. Products were purified by flash column chromatography on silica gel 60 M (0.040-0.063 mm, 230-400 mesh, Macherey-Nagel). TLC-analysis was performed on silica gel coated aluminum plates ALUGRAM® Xtra SIL G/UV₂₅₄ purchased from Macherey-Nagel. Products were detected by UV light at 254 nm and by using staining reagents based on KMnO₄, anisaldehyde, molybdophosphoric acid and cerium sulfate. ¹H-NMR and ¹³C-NMR spectral data were recorded on Bruker (AC 500, AVIII 700) and JEOL (ECX 400, Eclipse 500, ECZ 600) spectrometers. The chemical shifts (δ) are listed in parts per million (ppm) and are reported relative to the corresponding residual solvent signal (CDCl₃: δ_{H} = 7.26 ppm, δ_{C} = 77.16 ppm, CD₂Cl₂: δ_{H} = 5.32 ppm, δ_{C} = 53.84 ppm, DMSO-d₆: δ_{H} = 2.50 ppm, δ_{C} = 39.52 ppm, CD₃OD: δ_{H} = 3.31 ppm, δ_{C} = 49.00 ppm, CD₃CN: δ_{H} = 1.94 ppm, δ_{C} = 118.26, DMF-d₇: δ_{H} = 8.03 ppm, δ_{C} = 163.15 ppm, C₆D₆: δ_{H} = 7.16 ppm, δ_{C} = 128.06 ppm). Integrals are in accordance with assignments; coupling constants (*J*) are given in Hz. Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), etc. ¹³CNMR spectra are ¹H-broadband decoupled. For detailed peak assignments 2D spectra were measured (COSY, HMQC, HMBC). IR spectra were measured with a Jasco spectrometer (FT/IR-4100) equipped with an ATR unit. High resolution mass spectra were measured with an Agilent 6210 ESI-TOF (10 μ L/min, 1.0 bar, 4 kV) instrument. Melting points were determined by digital melting point apparatus (Stuart SMP30) and are uncorrected. Optical rotations values were determined with a Jasco P-2000 polarimeter at the temperatures given. Diastereomeric ratios were determined by ¹HNMR. Enantiomeric ratios were determined by chiral HPLC (Agilent Series 1200 with DAD) or by GC (Agilent 7890B) on a chiral column. The specific conditions are given in each case.

NMR Methods for NOE and J-Coupling Analysis

NMR spectra for ¹H-¹H NOE and *J*-coupling analysis were recorded on a Bruker AVIII 600 MHz spectrometer equipped with a 5 mm triple-resonance broadband inverse probe (¹H/³¹P-BB-2H) with *z*-gradient (0.494 T·m⁻¹ maximum gradient strength). Sample temperature was regulated between 190 K and 300 K using a liquid nitrogen evaporator. Experiments were recorded and analyzed with TopSpin 3.5pl7. Assignment spectra at 190 K were recorded using the standard library sequences for HSQC,¹ HMBC² and EASY-ROESY³. Selective 1D NOE measurements supplemented with a Thrippleton-Keeler filter⁴ to suppress unwanted zero-quantum contributions of *J*-coupled nuclei were performed using the standard library *selnogpzs* sequence with a spectral width of 12 ppm and 65536 complex points with 32 scans. Sufficient relaxation was ensured by setting the recovery delay to 15 s, which is larger than 5·*T*₁ for every signal as determined by an inversion recovery experiment. The carrier frequency offset was set to 4.7 ppm and the selective pulse offset to the respective signal. The RSnob⁵ shape was used for the selective pulse with bandwidths of 15, 25 or 50 Hz, depending on the required selectivity. A mixing time series of 8 independent time points was acquired between 50 and 400 ms in 50 ms steps for each selected resonance. Spectra were processed by zero-filling once and apodization with exponential broadening with 0.1 Hz. Manual phase correction and automatic baseline correction were applied for each spectrum before integrating the series using the *intser* command. Additionally, a 2D gradient-selected F1-PSYCHE-EASY-ROESY⁶ was acquired with spectral widths of 12 ppm in both dimensions and 4096 and 512 complex points, respectively, with 8 scans. The recovery delay was not sufficient for full relaxation to equilibrium. PSYCHE⁷

homonuclear decoupling in the indirect dimension was applied with a 30 ms element consisting of two low power chirp pulses with 25° flip angle, 10 kHz sweep width and 15 ms durations each. The pair of spinlocks were set to a tilt angle of 45° and an RF field of 6500 Hz. Gradient strengths were set to the values given in the original publication. The spectrum was processed by zero-filling once in the indirect dimension and applying a 90° shifted squared sine bell apodization. While the quantification may show larger deviations due to the insufficient recovery delay, volume integrals were nevertheless collected for all diagonal peaks, where they were sufficiently resolved by the PSYCHE homodecoupling, and all associated cross-peaks. Integrals were normalized using the PANIC⁸ approach: within each spectrum, the cross-peak integrals were divided by the integrals of the selected peak for the 1D spectra or the corresponding diagonal peak at the same chemical shift in F1 for the 2D spectrum. The normalized peak integrals are subjected to a linear fit versus the mixing time. The slope of this fit gives the cross-relaxation rate for NOE cross-peaks or the exchange rate for cross-peaks generated by chemical exchange. The fit usually shows (very) high correlation coefficients (Pearson R > 0.9), with only two exceptions: in some spectra the very last mixing time data point (400 ms) apparently no longer fulfilled the initial rate approximation and had to be excluded from the fitting process to achieve a sufficiently high correlation coefficient. Secondly, for the NOE from the neighboring nuclei 1' and 2' in the aminal part, the fit showed larger deviations resulting in lower apparent cross-relaxation rates, presumably due to insufficient suppression of *J*-coupling contributions and/or strong-coupling effects between these two nuclei.⁹ The individual cross-relaxation rates σ_{IS} were converted to NOE derived distances r_{IS} by internal calibration with the cross-relaxation rate of the diastereotopic proton pair H5a/b (denoted “*ref*”, set to 1.76 Å) using equation (1). For methyl groups, the three internuclear distances to individual protons were averaged using “ r^{-3} averaging” as described in equation (2).^{10,11} Conformational averaging for different conformers was performed using “ r^{-6} averaging” using equation (3),¹⁰ where p_i are the individual conformer populations of the *M* total conformations. Uncertainties were estimated by Gaussian error propagation.¹¹ In cases where both protons could be selected individually by the selective pulse, the NOE derived distances were averaged and the larger value between the deviations of the individual NOE distances to the average distance or the individual estimated uncertainties are used as an error estimate for the NOE distance. While in some cases the error from Gaussian error propagation is as low as 0.01 Å, we assume a reasonable estimate to be at least 0.1 Å in 1D NOE spectra and 0.4 Å in the semiquantitative PSYCHE-EASY ROESY spectra.

$$r_{IS} = r_{ref} (\sigma_{ref} / \sigma_{IS})^{-1/6} \quad (1)$$

$$r_{IS,ave}^{Methyl} = \left(\sum_{i=1}^3 \frac{1}{3} \times r_{IS,i}^{-3} \right)^{-1/3} \quad (2)$$

$$r_{IS,ave} = \left(\sum_{i=1}^M p_i \times r_{IS,i}^{-6} \right)^{-1/6} \quad (3)$$

J-coupling constants were determined either by lineshape analysis in the 1D spectrum or by a 2D (non-pure-shift) version of the PSYCHEDELIC¹² experiment with spectral widths of 7211 Hz and 50 Hz over 16384 and 128 complex points with 16 scans. As for the 1D sel. NOE, the carrier frequency offset was set to 4.7 ppm and the selective pulse offset to the respective signal. The RSnob shape was used for the selective pulse with bandwidths of 15, 25 or 50 Hz, depending on the required selectivity. Spectra were processed by zero-filling to 512 points and apodization with exponential broadening with 1 Hz. Manual phase correction was applied before tilting the spectrum with a shear transformation (45°). Coupling constants were extracted from the peak maxima along the column with the highest sensitivity of the multiplet.

Computational NMR Methods

The NMR chemical shifts for *syn*-**11**, iminium ion derived from *syn*-**11**, *anti*(C1')-**11**, *anti*(C2')-**11**, and *syn*-**14** were calculated using the GIAO method with PCM(chloroform)-mPW1PW91/6-311+G(2d,p)// B3LYP-D3(BJ)/6-31G+(d,p)¹³ at 219.15 K using *Gaussian16*¹⁴ Revision C.01. Conformational searching was performed using Grimme's CREST tool in xTB, using version 2.9 (*syn*-**11**; *anti*(C1')-**11**; *anti*(C2')-**11**; *syn*-**14**) and version 2.10.2 (iminium ion derived from *syn*-**11**) with the gfn-ff method and chloroform as the solvent (force constant of 1.0).^{15,16} Conformers generated from CREST were optimized with B3LYP-D3(BJ)/3-21 and then any conformers within 5 kcal mol⁻¹ from the lowest free energy conformer were reoptimized with B3LYP-D3(BJ)/6-31G+(d,p). If more than 100 conformers were generated from CREST, only the conformers within 5 kcal mol⁻¹ from the conformer search were used for DFT optimization. Any conformers within 3 kcal mol⁻¹ of the lowest energy conformer at this level of theory were reoptimized with the same level of theory at the lower. Unique conformers from this third optimization were used for the NMR calculations. The scaling factors used to convert the isotropics from the NMR calculations to chemical shifts were a slope = -1.0719, intercept = 31.8733 for ¹H shifts and slope = -1.0420, intercept = 186.3567 for ¹³C shifts.^{17,18} The NMR chemical shifts were calculated by averaging the conformer chemical shifts with weights, or percentages, for each conformer determined by minimizing the deviation between the experimental and theoretical shifts using the excel solver function. The barrier of rotation between *syn*-**14** *ap* and *exo-sc* was calculated with optimizing using modredundant and the PCM(chloroform-B3LYP/3-21G (219.15 K) level of theory using *Gaussian16*, Revision C.01 for the 11, 2, 33, 56 atom dihedral angle with 36 steps of 10°. The j-coupling values (Hz) were calculated using the fermi contact (FC) values from reoptimizing relevant conformers from the NMR calculations with B3LYP/6-31G(d) and then calculating coupling using B3LYP/6-31G(d,p) nmr= (FCOnly,Atoms=H,MixedH). The FC values were scaled to j-coupling constants (Hz) values were scaled by 0.9155 as recommended on CHESHIRE.^{17,18} The NMR calculations for **18b** were performed using the GIAO method with PCM(acetonitrile)-mPW1PW91/6-311+G(2d,p) from the lowest energy conformer from the mechanistic calculations (Section #) using *Gaussian16*, Revision C.01. The scaling factors used were slope= -1.0681 and intercept=31.7773 for ¹H shifts and slope= -1.0502 and intercept=186.9263 for ¹³C shifts.^{17,18} The NBO calculations¹⁹ were performed with B3LYP-D3(BJ)/6-31G+(d,p) with the keywords: pop=(full,nbo) int=finegrid, iop(3/32=2), scf=tight, temperature=219.15 with *Gaussian16*, Revision A.03. Molecular images were generated using CylView.²⁰ The optimized geometries for **11** and **14** are deposited in ioChem-BD (doi:10.19061/iochem-bd-6-83; <http://dx.doi.org/10.19061/iochem-bd-6-83>).²¹

2. CHLORINATIONS WITH MACMILLAN-TYPE CATALYSTS

2.1. Aminals Derived from 1st, 2nd and 3rd Generation MacMillan Catalysts

Motivated by the isolation and X-ray crystal structure analysis of several aminals derived from the 3rd generation MacMillan catalyst **3c**,²² we aimed at extending the structure determination to the 1st and 2nd generation MacMillan catalysts **3a** and **3b**. The ¹H-NMR spectra of the isolated and crystallographically characterized aminals were compared to the NMR spectra recorded during the reactions and our stereochemical assignments were compared to those reported in the literature.^{23,24}

Aminals Derived from Isovaleraldehyde, NCS and the 1st Generation MacMillan Catalyst *ent*-**3a** (NMR Experiment)

The TFA-salt of catalyst *ent*-**3a** (6.64 mg, 20.0 μmol, 20 mol%) or catalyst *ent*-**3a** as the free base (4.36 mg, 20.0 μmol, 20 mol% or 21.8 mg, 100 μmol, 100 mol%) and NCS (16.0 mg, 120 μmol, 1.2 equiv) were added successively to an NMR-tube containing a solution of isovaleraldehyde (10.8 μL, 100 μmol, 1.0 equiv) in CDCl₃ (0.70 mL) at 22 °C. ¹H-NMR spectra were recorded after 30 min. The ratio of amina diastereoisomers is 20:1 for the TFA-salt of the catalyst and 2:1 for the free base. The diastereomeric ratios and the ¹H-NMR spectrum for the reaction with the free base of the catalyst is in agreement with the literature.²⁵

Figure SI-1. ^1H -NMR spectra of the α -chlorination reaction (isovaleraldehyde, NCS, catalyst *ent-3a* or *ent-3a*•TFA) after 30 min.

1-((1*S*,2*R*)-1-((*R*)-5-benzyl-2,2,3-trimethyl-4-oxoimidazolidin-1-yl)-2-chloro-3-methylbutyl)-pyrrolidine-2,5-dione (*syn*-20**)**

The TFA-salt of catalyst *ent*-**3a** (0.770 g, 2.32 mmol, 20 mol%) and NCS (1.55 g, 11.6 mmol, 1.0 equiv) were added successively to a solution of isovaleraldehyde (1.25 mL, 11.6 mmol, 1.0 equiv) in CHCl₃ (46 mL). The reaction was stirred for 60 min and quenched with aqueous saturated NaHCO₃ (50 mL). The layers were separated and the aqueous phase was extracted with CH₂Cl₂ (3x50 mL). The combined organic phases were dried over NaSO₄, the solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO₂, pentane/Et₂O/EtOAc, 1:1:1 to 0:1:1 to 0:0:1). Aminoal *syn*-**20** was obtained as a colorless solid (0.664 g, 1.58 mmol, 68%). The absolute configuration was determined by X-ray crystal structure analysis.

The ¹H-NMR-spectrum of the major species is consistent with that reported literature, which was tentatively assigned the *syn*-coniguration.^{23,25}

mp = 107 °C

$[\alpha]_D^{26} = -40.8^\circ$ ($c = 1.00$, dichloromethane)

¹H-NMR (CDCl₃, 600 MHz) δ = 7.26 – 7.13 (m, 5H), 5.29 (d, $J = 11.0$ Hz, 1H), 4.96 (d, $J = 11.2$ Hz, 1H), 4.17 (dd, $J = 7.0, 3.0$ Hz, 1H), 3.46 (dd, $J = 14.8, 2.9$ Hz, 1H), 3.06 (dd, $J = 14.8, 7.1$ Hz, 1H), 2.78 – 2.71 (m, 7H), 2.34 (hept, $J = 6.1$ Hz, 1H), 1.26 (s, 3H), 1.10 (s, 3H), 0.95 (d, $J = 6.8$ Hz, 3H), 0.91 (d, $J = 6.5$ Hz, 3H) ppm.

¹³C-NMR (CDCl₃, 151 MHz) δ = 179.4, 177.6, 170.8, 137.7, 129.8, 128.1, 126.4, 79.9, 67.9, 67.3, 60.7, 39.7, 28.6, 28.4, 27.8, 27.1, 25.4, 23.1, 21.4, 15.1 ppm.

IR (ATR): $\tilde{\nu}$ = 2969, 2930, 1773, 1704, 1364, 1291, 1173, 911, 818, 728 cm⁻¹.

HRMS (ESI, pos. mode): m/z calculated for C₂₂H₃₁ClN₃O₃ [M+H]⁺: 420.2049, found 420.2044; m/z calculated for C₂₂H₃₀ClN₃NaO₃ [M+Na]⁺: 442.1868, found 442.1865; m/z calculated for C₂₂H₃₀ClKN₃O₃ [M+K]⁺: 458.1608, found 458.1598.

1-((S)-1-((R)-5-benzyl-2,2,3-trimethyl-4-oxoimidazolidin-1-yl)-2,2-dichloro-3-methylbutyl)-pyrrolidine-2,5-dione (24a)

Catalyst *ent*-3a (2.23 g, 10.2 mmol, 100 mol%) and NCS (1.64 g, 12.3 mmol, 1.2 equiv) were added successively to a solution of isovaleraldehyde (1.10 mL, 10.2 mmol, 1.0 equiv) in CHCl_3 (20 mL) and the reaction was stirred for 30 min at 22 °C. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO_2 , EtOAc). Aminoal *syn*-20 was obtained as a colorless solid (1.94 g, 4.62 mmol, 45%). The ^1H -NMR spectrum of a mixed fraction showed the existence of the diastereomeric aminoal *minor*-20. After a second chromatographic separation attempt (SiO_2 , Et $_2\text{O}$ then EtOAc), aminoal *minor*-20 was not detectable anymore. Gratifyingly, a previously unknown dichloroaminal 24a (96.0 mg, 0.211 mmol, 2%) could be obtained as a colorless solid. The absolute configuration was confirmed by X-ray crystal structure analysis.

The ^1H -NMR-spectrum of aminoal *syn*-20 is in accordance with the previous experiment.

Aminoal 24a:

mp = 116 °C

$[\alpha]_D^{26} = -53.9^\circ$ ($c = 0.85$, dichloromethane)

^1H -NMR (CDCl_3 , 600 MHz) δ = 7.31 – 7.15 (m, 5H), 6.01 (s, 1H), 5.74 (dd, $J = 8.0, 2.7$ Hz, 1H), 3.54 – 3.45 (m, 1H), 3.05 (dd, $J = 14.4, 7.9$ Hz, 1H), 2.96 (dt, $J = 13.2, 6.4$ Hz, 1H), 2.87 – 2.70 (m, 4H), 2.70 (s, 3H), 1.34 (d, $J = 6.6$ Hz, 3H), 1.31 (s, 3H), 1.22 (d, $J = 6.3$ Hz, 3H), 1.02 (s, 3H) ppm.

^{13}C -NMR (CDCl_3 , 151 MHz) δ = 178.1, 176.8, 172.1, 138.3, 129.7, 128.2, 126.5, 101.0, 80.6, 73.5, 62.2, 41.3, 39.5, 28.6, 28.2, 28.1, 25.4, 24.7, 19.2, 18.7 ppm.

IR (ATR): $\tilde{\nu}$ = 3058, 2978, 1777, 1710, 1431, 1398, 1309, 1266, 1181, 1141, 947, 818, 768, 732 cm^{-1} .

HRMS (ESI, pos. mode): m/z calculated for $\text{C}_{22}\text{H}_{30}\text{Cl}_2\text{N}_3\text{O}_3$ $[\text{M}+\text{H}]^+$: 454.1659, found 454.1666; m/z calculated for $\text{C}_{22}\text{H}_{29}\text{Cl}_2\text{N}_3\text{NaO}_3$ $[\text{M}+\text{Na}]^+$: 476.1478, found 476.1489; m/z calculated for $\text{C}_{22}\text{H}_{29}\text{Cl}_2\text{KN}_3\text{O}_3$ $[\text{M}+\text{K}]^+$: 492.1218, found 492.1231.

Assignment of Amino Diastereoisomers Derived from the 1st Generation MacMillan Catalyst

Figure SI-2. ¹H-NMR spectrum of the reaction with 100 mol% *ent*-3a after 30 min (according to Blackmond et al.^{23,25} (top). ¹H-NMR spectrum of the reaction with 100 mol% *ent*-3a•TFA after 30 min (middle). Crystal structure and ¹H-NMR spectrum of the isolated amino *syn*-20 (bottom).

In their publication “Explaining Anomalies in Enamine Catalysis: “Downstream Species” as a New Paradigm for Stereocontrol”²³ the authors correlated species described as “major” and “minor” for the 1st generation MacMillan catalyst to the major and minor product enantiomer. According to their model, the major diastereoisomer of the corresponding amino was suggested to possess the *anti*-configuration whereas the minor diastereoisomer was suggested to possess the *syn*-configuration. We were able to isolate and characterize the major species by X-ray analysis and determined it to possess the *syn*-configuration. Moreover, the authors correlated the enantiomeric ratio of the product (α -chloroaldehyde) to the diastereomeric ratio of the amino.²³ The e.r.-value of the α -chloroaldehyde (40:60) was cited from the original MacMillan publication²⁶ and the d.r.-value (33:67) of the amino refers to experiments done by the authors²⁵. These two values however are not directly comparable, since MacMillan and co-workers used the TFA-salt and Blackmond and co-workers used the free base of the catalyst to generate a 33:67 ratio of diastereomers. The different diastereomeric ratios of the amino are a consequence of the presence or absence of TFA as apparent in the ¹H-NMR spectra shown above. Therefore, a correlation between enantiomeric ratio of the product and diastereomeric ratio of the amino incorrectly compares two different situations.

Aminals Derived from Isovaleraldehyde, NCS and the 2nd Generation MacMillan Catalyst *ent-3b* (NMR Experiment)

The TFA-salt of catalyst *ent-3b* (7.20 mg, 20.0 μmol , 20 mol%) and NCS (13.3 mg, 100 μmol , 1.0 equiv) were added successively to an NMR-tube containing a solution of isovaleraldehyde (10.8 μL , 100 μmol , 1.0 equiv) in CDCl_3 or CD_3CN (0.70 mL) at 22 °C. ^1H -NMR spectra were recorded after 60 min. The diastereomeric ratio is approximately 9:1:4 in CDCl_3 and 3:2 in CD_3CN . The ^1H -NMR spectrum (CDCl_3) is in accordance with that the literature.^{24,25}

CDCl_3 :

CDCl_3 (zoom):

CD_3CN :

CD_3CN (zoom):

Figure SI-3. ^1H -NMR spectra of the α -chlorination reaction (isovaleraldehyde, NCS, catalyst *ent-3b*•TFA) in different solvents after 60 min.

1-((1*S*,2*R*)-1-((2*R*,5*R*)-5-benzyl-2-(*tert*-butyl)-3-methyl-4-oxoimidazolidin-1-yl)-2-chloro-3-methyl-butyl)pyrrolidine-2,5-dione ((1*S*,2*R*)-*syn*-**21**),

1-((1*S*,2*S*)-1-((2*R*,5*R*)-5-benzyl-2-(*tert*-butyl)-3-methyl-4-oxoimidazolidin-1-yl)-2-chloro-3-methyl-butyl)pyrrolidine-2,5-dione ((1*S*,2*S*)-*anti*-**21**),

1-((1*R*,2*S*)-1-((2*R*,5*R*)-5-benzyl-2-(*tert*-butyl)-3-methyl-4-oxoimidazolidin-1-yl)-2-chloro-3-methyl-butyl)pyrrolidine-2,5-dione ((1*R*,2*S*)-*syn*-**21**)

The TFA-salt of catalyst *ent*-**3b** (1.26 g, 3.48 mmol, 20 mol%) and NCS (2.33 g, 17.4 mmol, 1.0 equiv) were added successively to a solution of isovaleraldehyde (1.88 mL, 17.4 mmol, 1.0 equiv) in CHCl₃ (70 mL). The reaction was stirred for 60 min and quenched with aqueous saturated NaHCO₃ (50 mL). The aqueous phase was extracted with dichloromethane (3x50 mL), the combined organic phases were dried over NaSO₄, the solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO₂, pentane/Et₂O/EtOAc, 1:1:1 to 0:1:1 to 0:0:1). Pure amination (1*S*,2*R*)-*syn*-**21** was obtained as a colorless solid (0.807 g, 1.80 mmol, 52%). Separation of another fraction from the column chromatography by chiral HPLC enabled further separation of amination (1*S*,2*R*)-*syn*-**21** (0.339 g, 0.757 mmol, 22%), (1*S*,2*S*)-*anti*-**21** (93.0 mg, 0.208 mmol, 6%) and (1*R*,2*S*)-*syn*-**21** (0.271 g, 0.605 mmol, 17%). The absolute configuration of the three aminals was confirmed by X-ray crystal structure analysis.

Aminal (1*S*,2*R*)-*syn*-**21**:

The spectroscopic data (¹H- and ¹³C-NMR) are in accordance with the major amination from the literature.^{24,25}

mp = 104 °C

[α]_D²⁶ = −32.1° (*c* = 1.00, CH₂Cl₂)

¹H-NMR (CDCl₃, 600 MHz) δ = 7.37 – 7.31 (m, 4H), 7.24 – 7.20 (m, 1H), 5.08 (d, *J* = 11.1 Hz, 1H), 4.81 (t, 1H), 4.48 (dd, *J* = 11.2, 1.0 Hz, 1H), 4.24 (s, 1H), 3.12 (dd, *J* = 14.9, 6.5 Hz, 1H), 2.88 (s, 3H), 2.85 (dd, *J* = 14.6, 6.9 Hz, 1H), 2.75 – 2.65 (m, 4H), 2.36 (h, *J* = 7.2, 6.6 Hz, 1H), 1.04 (s, 9H), 0.88 (d, *J* = 6.5 Hz, 3H), 0.61 (d, *J* = 6.7 Hz, 3H) ppm.

¹³C-NMR (CDCl₃, 151 MHz) δ = 179.6, 179.2, 173.9, 138.6, 129.3, 128.8, 126.8, 88.5, 76.7, 65.4, 61.8, 41.1, 37.0, 31.7, 29.1, 28.2, 27.9, 26.9, 21.2, 15.8 ppm.

IR (ATR): $\tilde{\nu}$ = 2959, 2924, 2871, 1774, 1702, 1456, 1328, 1172, 1136, 820, 751 cm^{−1}.

HRMS (ESI, pos. mode): *m/z* calculated for C₂₄H₃₅ClN₃O₃ [M+H]⁺: 448.2362, found 448.2373; *m/z* calculated for C₂₄H₃₄ClN₃NaO₃ [M+Na]⁺: 470.2181, found 470.2188; *m/z* calculated for C₂₄H₃₄ClKN₃O₃ [M+K]⁺: 486.1921, found 486.1930.

Aminal (1*S*,2*S*)-anti-21:

The spectroscopic data (¹H- and ¹³C-NMR) are in accordance with the minor amination from the literature.^{24,25}

mp = 86 °C

$[\alpha]_D^{26} = -6.5^\circ$ (*c* = 0.40, dichloromethane)

¹H-NMR (CDCl₃, 500 MHz) δ = 7.43 – 7.40 (m, 2H), 7.33 – 7.29 (m, 2H), 7.23 – 7.19 (m, 1H), 5.23 (d, *J* = 10.8 Hz, 1H), 4.59 (dd, *J* = 7.2, 4.6 Hz, 1H), 4.49 (dd, *J* = 10.8, 2.0 Hz, 1H), 4.11 (s, 1H), 3.23 (dd, *J* = 14.5, 4.5 Hz, 1H), 3.12 (dd, *J* = 14.4, 7.3 Hz, 1H), 2.88 (s, 3H), 2.78 – 2.53 (m, 4H), 1.61 – 1.49 (m, 1H), 1.08 (s, 9H), 0.89 (d, *J* = 6.6 Hz, 3H), 0.76 (d, *J* = 6.6 Hz, 3H) ppm.

¹³C-NMR (CDCl₃, 151 MHz) δ = 179.6, 178.9, 174.1, 139.4, 129.6, 128.4, 126.4, 86.2, 75.4, 66.2, 61.7, 41.2, 38.2, 31.9, 29.8, 28.6, 28.0, 26.3, 21.3, 14.6 ppm.

IR (ATR): $\tilde{\nu}$ = 2964, 2925, 2874, 1772, 1701, 1455, 1364, 1317, 1153, 819, 753, 720 cm⁻¹.

HRMS (ESI, pos. mode): *m/z* calculated for C₂₄H₃₅ClN₃O₃ [M+H]⁺: 448.2362, found 448.2352; *m/z* calculated for C₂₄H₃₄ClN₃NaO₃ [M+Na]⁺: 470.2181, found 470.2163; *m/z* calculated for C₂₄H₃₄ClKN₃O₃ [M+K]⁺: 486.1921, found 486.1904.

Aminal (1*R*,2*S*)-syn-21:

mp = 136 °C

$[\alpha]_D^{26} = -13.1^\circ$ (*c* = 1.00, dichloromethane)

¹H-NMR (CDCl₃, 600 MHz) δ = 7.35 – 7.31 (m, 4H), 7.24 – 7.19 (m, 1H), 5.17 (s, 7H), 4.50 (s, 1H), 4.50 (dd, *J* = 18.0 Hz, 11.4 Hz, 1H), 3.87 (dd, *J* = 11.2, 2.9 Hz, 1H), 3.20 (dd, *J* = 13.9, 3.3 Hz, 1H), 2.90 (s, 3H), 2.81 (dd, *J* = 13.8, 11.6 Hz, 1H), 2.78 – 2.53 (m, 4H), 2.10 (h, *J* = 11.8, 6.5, 6.1 Hz, 1H), 1.04 (s, 9H), 0.88 (d, *J* = 6.8 Hz, 3H), 0.16 (s, 3H) ppm.

¹³C-NMR (CDCl₃, 151 MHz) δ = 179.7, 178.6, 173.9, 138.3, 129.6, 129.1, 127.0, 85.9, 77.4, 67.4, 65.6, 38.6, 37.2, 32.2, 29.7, 28.3, 28.1, 28.0, 20.8, 14.8 ppm.

IR (ATR): $\tilde{\nu}$ = 2964, 2927, 2827, 1776, 1704, 1456, 1329, 1216, 1175, 1091, 908, 750, 735 cm⁻¹.

HRMS (ESI, pos. mode): *m/z* calculated for C₂₄H₃₅ClN₃O₃ [M+H]⁺: 448.2362, found 448.2362; *m/z* calculated for C₂₄H₃₄ClN₃NaO₃ [M+Na]⁺: 470.2181, found 470.2172; *m/z* calculated for C₂₄H₃₄ClKN₃O₃ [M+K]⁺: 486.1921, found 486.1911.

Assignment of Amino Diastereoisomers Derived from the 2nd Generation MacMillan Catalyst (Isovaleraldehyde as the Substrate)

Figure SI-4. ¹H-NMR spectrum of the reaction with 20 mol% *ent*-3b•TFA after 60 min (according to Blackmond et al.^{24,25} (top). Crystal structures and ¹H-NMR spectra of the isolated diastereomeric aminals **21** (below).

In their publication “Rationalization of an Unusual Solvent-Induced Inversion of Enantiomeric Excess in Organocatalytic Selenylation of Aldehydes”^{24,25} the authors discussed two amino diastereomers for the 2nd generation MacMillan catalyst but overlooked a third amino diastereomer (1*R*,2*S*)-*syn*-21 indicated by the green arrows. Their rationale is based on the existence of only two out of four possible amino species. Isolation and subsequent X-ray crystal structure analysis reveals *syn*-configuration for the major amino (1*S*,2*R*)-*syn*-21 and *anti*-configuration for minor amino (1*S*,2*S*)-*anti*-21. The third, previously overlooked amino (1*R*,2*S*)-*syn*-21 also has the *syn*-configuration. It is actually present in higher concentration than the species which was named “minor”.

Figure SI-5. ¹H-NMR spectrum of the reaction with 20 mol% *ent*-**3b**•TFA after 60 min with integrated signals (blue: major aminal (1*S*,2*R*)-*syn*-**21**; red: minor aminal (1*S*,2*S*)-*anti*-**21**; green: previously overlooked aminal (1*R*,2*S*)-*syn*-**21** (according to Blackmond et al.^{24,25}

Since the quality of the crystallographic data for aminal (1*S*,2*R*)-*syn*-**21** was not optimal and to confirm the previous results and conclusions, the same experiments and isolation procedures were repeated using hydrocinnamic aldehyde instead of isovaleraldehyde.

Aminals Derived from Hydrocinnamic Aldehyde, NCS and the 2nd Generation MacMillan Catalyst *ent*-3b** (NMR experiment)**

The TFA-salt of catalyst *ent*-**3b** (7.20 mg, 20.0 μmol , 20 mol%) and NCS (13.3 mg, 100 μmol , 1.0 equiv) were added successively to an NMR-tube containing a solution of hydrocinnamic aldehyde (13.4 μL , 100 μmol , 1.0 equiv) in CDCl_3 (0.70 mL) at 22 °C. The ^1H -NMR spectrum was recorded after 60 min. The diastereomeric ratio is approximately 5:1:3.

Figure SI-6. ^1H -NMR spectra of the α -chlorination reaction (hydrocinnamic aldehyde, NCS, catalyst *ent*-**3b**•TFA) after 60 min.

1-((1*S*,2*R*)-1-((2*R*,5*R*)-5-benzyl-2-(tert-butyl)-3-methyl-4-oxoimidazolidin-1-yl)-2-chloro-3-phenylpropyl)pyrrolidine-2,5-dione ((1*S*,2*R*)-*syn*-25),

1-((1*S*,2*S*)-1-((2*R*,5*R*)-5-benzyl-2-(tert-butyl)-3-methyl-4-oxoimidazolidin-1-yl)-2-chloro-3-phenylpropyl)pyrrolidine-2,5-dione ((1*S*,2*S*)-*anti*-25) ,

1-((1*R*,2*S*)-1-((2*R*,5*R*)-5-benzyl-2-(tert-butyl)-3-methyl-4-oxoimidazolidin-1-yl)-2-chloro-3-phenylpropyl)pyrrolidine-2,5-dione ((1*R*,2*S*)-*syn*-25)

The TFA-salt of catalyst *ent*-3b (0.837 g, 2.32 mmol, 20 mol%) and NCS (1.55 g, 11.6 mmol, 1.0 equiv) were added successively to a solution of hydrocinnamic aldehyde (1.54 mL, 11.6 mmol, 1.0 equiv) in CHCl₃ (46 mL). The reaction was stirred for 60 min and quenched with aqueous saturated NaHCO₃ (50 mL). The aqueous phase was extracted with dichloromethane (3x50 mL), the combined organic phases were dried over NaSO₄, the solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO₂, pentane/Et₂O/EtOAc, 1:1:1 to 0:1:1 to 0:0:1). Aminoal (1*S*,2*R*)-*syn*-25 was obtained as a colorless solid (0.381 g, 0.768 mmol, 33%). Separation of another fraction from the column chromatography by chiral HPLC enabled further separation of aminoal (1*S*,2*S*)-*anti*-25 (57.0 mg, 0.115 mmol, 5%) and aminoal (1*R*,2*S*)-*syn*-25 (0.137 g, 0.272 mmol, 12%). The absolute configuration of the three aminoal was determined by X-ray crystal structure analysis.

Aminoal (1*S*,2*R*)-*syn*-25:

mp = 158 °C

$[\alpha]_D^{26} = -1.96^\circ$ ($c = 1.00$, dichloromethane)

¹H-NMR (CDCl₃, 600 MHz) δ = 7.39 – 7.36 (m, 2H), 7.33 – 7.28 (m, 2H), 7.26 – 7.18 (m, 4H), 7.00 – 6.97 (m, 2H), 5.18 (d, $J = 10.7$ Hz, 1H), 5.08 (td, $J = 10.8, 1.9$ Hz, 1H), 4.75 (dd, $J = 7.6, 5.7$ Hz, 1H), 4.33 (s, 1H), 3.93 (dd, $J = 14.7, 1.4$ Hz, 1H), 3.18 – 3.09 (m, 2H), 2.88 (s, 3H), 2.77 – 2.70 (m, 5H), 1.09 (s, 9H) ppm.

¹³C-NMR (CDCl₃, 151 MHz) δ = 179.5, 173.4, 138.1, 137.0, 129.4, 129.1, 128.8, 128.5, 127.0, 126.8, 87.8, 79.1, 61.2, 59.6, 42.3, 41.6, 37.7, 31.9, 29.7, 28.1, 26.7 ppm.

IR (ATR): $\tilde{\nu}$ = 2957, 2925, 1774, 1702, 1455, 1328, 1253, 1148, 1061, 749 cm⁻¹.

HRMS (ESI, pos. mode): m/z calculated for C₂₈H₃₅ClN₃O₃ [M+H]⁺: 496.2362, found 496.2350; m/z calculated for C₂₈H₃₄ClN₃NaO₃ [M+Na]⁺: 518.2181, found 518.2160; m/z calculated for C₂₈H₃₄ClKN₃O₃ [M+K]⁺: 534.1921, found 534.1899.

Aminal (1*S*,2*S*)-anti-25:

mp = 150 °C

$[\alpha]_D^{26} = -18.43^\circ$ ($c = 0.45$, dichloromethane)

¹H-NMR (CDCl₃, 700 MHz) δ = 7.41 – 7.38 (m, 2H), 7.32 – 7.24 (m, 5H), 7.24 – 7.19 (m, 1H), 7.03 – 7.01 (m, 2H), 5.29 (d, $J = 10.5$ Hz, 1H), 4.75 (td, $J = 10.2, 3.1$ Hz, 1H), 4.62 (dd, $J = 6.7, 4.8$ Hz, 1H), 4.19 (s, 1H), 3.20 – 3.13 (m, 2H), 2.92 (s, 3H), 2.85 (dd, $J = 14.3, 3.1$ Hz, 1H), 2.76 – 2.66 (m, 4H), 2.64 (dd, $J = 14.3, 10.0$ Hz, 1H), 1.11 (s, 9H) ppm.

¹³C-NMR (CDCl₃, 151 MHz) δ = 179.2, 174.1, 139.3, 136.6, 129.5, 129.1, 128.5, 128.4, 127.1, 126.4, 86.2, 76.9, 61.8, 60.3, 41.2, 41.0, 38.2, 31.9, 29.8, 28.3, 26.3 ppm.

IR (ATR): $\tilde{\nu} = 2955, 2925, 1772, 1702, 1455, 1363, 1255, 1156, 1079, 794, 750$ cm⁻¹.

HRMS (ESI, pos. mode): m/z calculated for C₂₈H₃₅ClN₃O₃ [M+H]⁺: 496.2362, found 496.2381; m/z calculated for C₂₈H₃₄ClN₃NaO₃ [M+Na]⁺: 518.2181, found 518.2191; m/z calculated for C₂₈H₃₄ClKN₃O₃ [M+K]⁺: 534.1921, found 534.1935.

Aminal (1*R*,2*S*)-syn-25:

mp = 178 °C

$[\alpha]_D^{26} = -55.64^\circ$ ($c = 1.45$, dichloromethane)

¹H-NMR (CDCl₃, 700 MHz) δ = 7.45 – 7.39 (m, 4H), 7.33 – 7.19 (m, 4H), 7.06 – 7.03 (m, 2H), 4.98 (s, 1H), 4.85 (t, $J = 11.0$ Hz, 1H), 4.54 (d, $J = 10.0$ Hz, 1H), 4.24 (dd, $J = 11.6, 4.3$ Hz, 1H), 3.35 (dd, $J = 14.1, 4.2$ Hz, 1H), 3.23 (d, $J = 15.9$ Hz, 1H), 2.96 (s, 3H), 2.88 (dd, $J = 14.1, 11.5$ Hz, 1H), 2.85 – 2.58 (m, 4H), 1.72 (s, 1H), 1.10 (s, 9H) ppm.

¹³C-NMR (CDCl₃, 176 MHz) δ = 179.3, 178.2, 173.5, 138.2, 137.2, 129.8, 128.9, 128.7, 128.5, 126.9, 126.8, 86.2, 80.3, 67.2, 58.9, 41.0, 38.6, 37.2, 32.2, 28.1, 28.0, 27.8 ppm.

IR (ATR): $\tilde{\nu} = 3030, 2958, 1705, 1329, 1254, 1161, 1094, 740$ cm⁻¹.

HRMS (ESI, pos. mode): m/z calculated for C₂₈H₃₄ClN₃NaO₃ [M+Na]⁺: 518.2181, found 518.2184; m/z calculated for C₂₈H₃₄ClKN₃O₃ [M+K]⁺: 534.1921, found 534.1920.

Assignment of Amino Acid Diastereoisomers Derived from the 2nd Generation MacMillan Catalyst (Hydrocinnamic Aldehyde as the Substrate)

Figure SI-7. ¹H-NMR spectrum of the reaction with 20 mol% *ent*-**3b**•TFA after 60 min (top). Crystal structures and ¹H-NMR spectra of the isolated diastereomeric aminals **21** (below).

As expected, three diastereomeric species can be detected in the ¹H-NMR spectrum. All of them could be isolated and fully characterized. The absolute configurations of the three aminals were determined by X-ray crystal structure analysis and are in accordance with the previous experiment (isovaleraldehyde as the substrate).

Decomposition of Aminoal *syn*-**18b** (Derived from 3rd Generation MacMillan Catalyst)

Aminoal *syn*-**18b** was synthesized according to the literature procedure.²² H₂O (85.8 μ L, 4.76 mmol, 2.0 equiv) and TFA (364 μ L, 4.76 mmol, 2.0 equiv) were added to a solution of aminoal *syn*-**18b** (1.00 g, 2.38 mmol, 1.0 equiv) in MeCN (30 mL) at 22 $^\circ$ C. Aliquots (6 mL) were taken from the reaction mixture after defined points of time (5 min, 10 min, 60 min) and added to a solution of NaBH₄ (75.1 mg, 1.98 mmol, 5.0 equiv) in EtOH (2.0 mL). After 30 min the reactions were quenched by the addition of aqueous saturated NH₄Cl. The aqueous phase was extracted with EtOAc (3x5 mL), the combined organic phases were dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude products were purified by column chromatography (SiO₂, pentane/EtOAc 10:1 to 5:1) and the enantiomeric excess was determined by chiral HPLC. The absolute configuration was determined by comparison of the optical rotation with the literature.

The ¹H-NMR spectrum is in accordance with the literature.²²

¹H-NMR (CDCl₃, 400 MHz) δ = 7.35 – 7.30 (m, 2H), 7.29 – 7.22 (m, 3H), 4.26 – 4.20 (m, 1H), 3.81 (ddd, J = 12.1, 7.2, 3.6 Hz, 1H), 3.69 (dt, J = 12.1, 6.1 Hz, 1H), 3.14 (dd, J = 14.0, 7.0 Hz, 1H), 3.06 (dd, J = 14.0, 7.4 Hz, 1H), 2.03 (t, J = 6.7 Hz, 1H) ppm.

1. aliquot (5 min): 95% ee
2. aliquot (10 min): 95% ee
3. aliquot (60 min): 94% ee

Sample: $[\alpha]_D^{24} = -11.4^\circ$ (c = 1.00, dichloromethane)

(S)-2-chloro-3-phenylpropan-1-ol (95% ee): $[\alpha]_D^{24} = -13.8^\circ$ (c = 1.00, dichloromethane)

(R)-2-chloro-3-phenylpropan-1-ol (93% ee): $[\alpha]_D^{24} = +14.0^\circ$ (c = 1.00, dichloromethane)

(S)-2-chloro-3-phenylpropan-1-ol (95% ee): $[\alpha]_D = -21.7^\circ$ (c = 1.00, CHCl₃)²⁷

Figure S1-8. Only the off-cycle mechanism (right) can rationalize the observed enantioselectivity (*(S)*-chloroaldehyde) of the α -chlorination reaction and the decomposition pathway. The on-cycle mechanism²⁸ (left) predicts the formation of the wrong enantiomer of the chloroaldehyde (*(R)*-chloroaldehyde).

As observed for most of the aminals derived from the 1st and 2nd generation MacMillan catalyst, aminal **syn-18b** is bench-stable and can be isolated and characterized.²² According to the catalytic cycle of the on-cycle scenario²⁸ aminal **syn-18b** should generate the *(R)*-enantiomer of the chloroaldehyde product. Decomposition under acidic conditions (TFA and water are also present in the catalytic reaction) clearly shows that aminal **syn-18b** was converted almost exclusively (95% ee) to the *(S)*-chloroaldehyde product. This experimental outcome is in accordance with our proposed decomposition pathway via a chloroiminium ion.

(S)-2-chloro-3-phenylpropan-1-ol ((S)-22)

Hydrocinnamic aldehyde (0.266 mL, 2.00 mmol, 1.0 equiv) was dissolved in MeCN (8.0 mL) and cooled to -30 °C. Catalyst **3c** (0.114 g, 0.400 mmol, 20 mol%) and NCS (0.320 g, 2.40 mmol, 1.2 equiv) were added subsequently and the reaction mixture was stirred for 15 h at the same temperature. After the reaction was warmed to 0 °C, MeOH (3.0 mL) and NaBH₄ (0.189 g, 5.00 mmol, 2.5 equiv) were added and the mixture was stirred for 60 min at the same temperature. The reaction was quenched with aqueous saturated NH₄Cl (10 mL), the aqueous phase was extracted with dichloromethane (3x15 mL) and the combined organic phases were dried over NaSO₄. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (Silica, pentane/EtOAc 10:1). Pure chloroalcohol (S)-**22** (0.248 g, 1.45 mmol, 73%, 95% ee) was obtained as a colorless oil.

¹H-NMR is in accordance with the literature.²²

$[\alpha]_D^{24} = -13.8^\circ$ ($c = 1.00$, dichloromethane)

¹H-NMR (CDCl₃, 400 MHz) δ = 7.35 – 7.30 (m, 2H), 7.29 – 7.22 (m, 3H), 4.26 – 4.20 (m, 1H), 3.81 (ddd, J = 12.1, 7.2, 3.6 Hz, 1H), 3.69 (dt, J = 12.1, 6.1 Hz, 1H), 3.14 (dd, J = 14.0, 7.0 Hz, 1H), 3.06 (dd, J = 14.0, 7.4 Hz, 1H), 2.03 (t, J = 6.7 Hz, 1H) ppm.

(R)-2-chloro-3-phenylpropan-1-ol ((R)-22)

Hydrocinnamic aldehyde (0.266 mL, 2.00 mmol, 1.0 equiv) was dissolved in MeCN (8.0 mL) and cooled to -30 °C. Catalyst *ent*-**3c** (0.114 g, 0.400 mmol, 20 mol%) and NCS (0.320 g, 2.40 mmol, 1.2 equiv) were added subsequently and the reaction mixture was stirred for 15 h at the same temperature. After the reaction was warmed to 0 °C, MeOH (3.0 mL) and NaBH₄ (0.189 g, 5.00 mmol, 2.5 equiv) were added and the mixture was stirred for 60 min at the same temperature. The reaction was quenched with aqueous saturated NH₄Cl (10 mL), the aqueous phase was extracted with dichloromethane (3x15 mL) and the combined organic phases were dried over NaSO₄. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (Silica, pentane/EtOAc 10:1). Pure chloroalcohol (R)-**22** (0.229 g, 1.34 mmol, 67%, 93% ee) was obtained as a colorless oil.

¹H-NMR is in accordance with the literature.²²

$[\alpha]_D^{24} = +14.0^\circ$ ($c = 1.00$, dichloromethane)

¹H-NMR (CDCl₃, 400 MHz) δ = 7.35 – 7.30 (m, 2H), 7.29 – 7.22 (m, 3H), 4.26 – 4.20 (m, 1H), 3.81 (ddd, J = 12.1, 7.2, 3.6 Hz, 1H), 3.69 (dt, J = 12.1, 6.1 Hz, 1H), 3.14 (dd, J = 14.0, 7.0 Hz, 1H), 3.06 (dd, J = 14.0, 7.4 Hz, 1H), 2.03 (t, J = 6.7 Hz, 1H) ppm.

2.2. NMR reaction progress (3rd generation MacMillan catalyst)

¹H-NMR reaction progress

Figure SI-9. ¹H-NMR reaction progress of the α-chlorination reaction (hydrocinnamic aldehyde, NCS, catalyst **3c**·TFA) according to our previous publication.²²

Table SI-1. Experimental data of the reaction progress analysis.²²

t [min]	t [h]	aldehyde		Cl-aldehyde		aminal	
0	0	0,7	100,03	0	0	0	0
5	0,08	0,53	75,74	0,13	18,58	0,06	8,57
10	0,17	0,35	50,02	0,25	35,73	0,09	12,86
20	0,33	0,24	34,3	0,36	51,44	0,11	16,15
30	0,5	0,18	25,72	0,39	55,73	0,13	18,58
45	0,75	0,11	15,72	0,43	61,45	0,14	20,01
60	1	0,09	12,86	0,45	64,31	0,14	20,01
90	1,5	0,06	8,57	0,48	68,59	0,14	20,01
150	2,5	0,04	5,72	0,52	74,31	0,13	18,58
210	3,5	0,03	4,29	0,53	75,74	0,12	17,15
375	6,25	0,03	4,29	0,54	77,17	0,11	15,72
1395	23,25	0,03	4,29	0,54	77,17	0,09	12,86

We interrogated concentration profiles in order to assess whether the two mechanisms (steric shielding model and Curtin-Hammett scenario) are kinetically distinguishable. Gratifyingly, aldehyde **16**, the chloroaldehyde product **19** and the corresponding crystallographically characterized aminal *syn*-**18b** possess separate, non-overlapping NMR resonances. By monitoring their concentrations over time²² it is apparent that the initial rate of chloroaldehyde formation exceeds the build-up of the aminal. This observation eliminates the possibility of the catalyst being turned over through the thermodynamically most

stable aminal (Curtin-Hammett scenario). The alternate off-cycle mechanism provides a scenario where the rate of iminium hydrolysis exceeds that of aminal formation. From the iminium ion intermediate, part of the catalyst is diverted into a stable aminal resting state. To further illustrate the absence of an on-cycle-mechanism, the first three ^1H -NMR-spectra of the previously considered reaction are shown below. The aminal concentration at no point exceeds the product concentration, not even in the initial phase (5 min) of the reaction. This observation strongly supports an off-cycle-scenario, in which the product can be formed without going through the aminal intermediate. When reanalyzing our data for this reaction, we noted additional, previously overlooked resonances in the NMR spectrum at $t = 5$ min (quickly disappearing thereafter). The possibility of the corresponding species to be the elusive aminal *anti*-**18b** is supported by comparison of the observed and computed ^1H chemical shifts.

Figure SI-10. ^1H -NMR spectra of the initial phase of the α -chlorination reaction (hydrocinnamic aldehyde, NCS, catalyst **3c**•TFA).

NMR Calculations for *syn*-**18b** and *anti*-**18b**

^1H and ^{13}C NMR calculations were performed to compare to the major and minor species at $t = 5$ min. The key ^1H chemical shifts for *syn*-**18b** and *anti*-**18b** were in good agreement (< 0.3 ppm absolute deviation between experimental and calculated chemical shifts)^{17,18} with the experimental shifts for the major and minor products.

Table SI-2. Calculated ^{13}C NMR δ 's for *syn-18b*.

Exp. #	Comp #	Comp.	Comp.
		Isotropic	δ
C5	1	98.9366	83.8
C2	2	3.6610	174.5
C3	3	123.1277	60.7
C4	7	153.8751	31.5
C1'	11	113.1924	70.2
C2'	13	111.3355	72.0
C3'	14	142.8361	42.0
C4'	17	175.0080	11.3
C5'	22	143.6420	41.2
	26	-4.5320	182.3
	27	-2.1380	180.0
C5''	28	155.0907	30.3
C2''	29	155.6905	29.7
C6	34	158.5958	27.0
	38	156.9911	28.5
	42	163.1739	22.6
	49	41.0137	138.9
	50	50.0409	130.3
	51	53.6789	126.9
	52	52.7727	127.7
	54	52.5161	128.0
	56	54.4196	126.2

Table SI-3. Comparison of calculated and experimental ¹H NMR δ's for *syn*-**18b**.

Exp. C#	Comp. C#	Comp. H#	Comp. Isotropic	Comp. δ	Avg. Comp. δ	Exp. δ	Abs. Dev.
8	7	8	28.57	3.00			
8	7	9	29.26	2.36			
8	7	10	29.12	2.49			
9	11	12	26.64	4.81	4.81	5.01	0.20
11	14	15	29.18	2.43	2.43		
10	13	16	26.22	5.20	5.20	5.10	0.10
6	17	18	30.32	1.37			
6	17	19	30.54	1.16			
6	17	20	29.51	2.13	1.55	1.47	0.08
3	3	21	27.65	3.87			
5	1	23	27.27	4.22			
15	28	30	28.99	2.61			
16	29	31	28.98	2.62			
tBu	34	35	30.82	0.89			
tBu	34	36	30.65	1.05			
tBu	34	37	30.79	0.93			
tBu	38	39	30.29	1.39			
tBu	38	40	30.02	1.64			
tBu	38	41	30.58	1.12			
tBu	42	43	30.76	0.95			
tBu	42	H32	26.54	0.80			
tBu	42	45	30.75	0.96	1.08	1.10	0.02
16	29	46	29.03	2.57			
15	28	47	28.96	2.64			
11	14	48	27.41	4.09	4.09	3.96	0.13
	50	53	24.03	7.25			
	51	55	23.81	7.46			
	52	57	23.95	7.33			
	54	58	23.92	7.36			
	56	59	23.99	7.29			
MAD							0.11

Table SI-4. Calculated ^{13}C NMR δ 's for *anti*-18b

Exp. #	Comp #	Comp.	Comp.
		Isotropic	δ
C5	C	97.8311	84.8
C2	C	2.7976	175.3
C3	C	121.5410	62.3
C4	C	152.4037	32.9
C1'	C	112.1019	71.2
C2'	C	116.7850	66.8
C3'	C	137.7947	46.8
C4'	C	173.1138	13.2
C5'	C	141.3341	43.4
	C	-0.9819	178.9
	C	-3.1036	180.9
C5''	C	155.3086	30.1
C2''	C	156.1731	29.3
C6	C	158.5219	27.0
	C	159.5979	26.0
	C	162.7703	23.0
	C	41.9613	138.0
	C	50.8312	129.6
	C	52.3459	128.1
	C	52.4331	128.1
	C	52.4293	128.1
	C	53.9564	126.6

Table SI-5. Comparison of calculated and experimental ^1H NMR δ 's for *anti*-**18b**.

Exp. C#	Comp. C#	Comp. H#	Comp. Isotropic	Comp. δ	Avg. Comp. δ	Exp. δ	Abs. Dev.
8	7	8	28.48	3.09			
8	7	9	29.02	2.58			
8	7	10	28.98	2.62			
9	11	12	26.27	5.15	5.15	5.27	0.12
11	14	15	28.67	2.91			
11	14	16	28.07	3.47	3.47	3.18	0.29
10	13	17	25.43	5.94	5.94	5.66	0.28
6	18	19	30.11	1.56			
6	18	20	30.13	1.54			
6	18	21	30.26	1.42	1.51	1.50	0.01
3	3	22	27.68	3.83	3.83	3.91	0.08
5	1	24	27.05	4.42	4.42	4.46	0.04
15	29	31	29.62	2.02			
16	30	32	29.70	1.94			
tBu	35	36	30.98	0.75			
tBu	35	37	30.64	1.06			
tBu	35	38	30.79	0.92			
tBu	39	40	30.88	0.84			
tBu	39	41	31.10	0.63			
tBu	39	42	31.21	0.53			
tBu	43	44	26.54	0.86			
tBu	43	45	31.17	0.57			
tBu	43	46	30.97	0.75	0.77	0.91	0.14
16	30	47	30.59	1.11			
15	29	48	29.30	2.32			
	50	53	24.02	7.26			
	51	55	24.26	7.04			
	52	57	23.95	7.33			
	54	58	24.08	7.21			
	56	59	24.07	7.21			
						MAD	0.14

2.3. KIEs and DFT Calculations (3rd Generation MacMillan Catalyst)

KIE-experiment (1)

KIE Sample (KIE1&2): Distilled hydrocinnamic aldehyde (1.61 g, 12.0 mmol, 1.0 equiv) was dissolved in MeCN (40 mL) in a 50 mL graduated flask and cooled to $-30\text{ }^{\circ}\text{C}$. Catalyst **3c** (0.682 g, 2.40 mmol, 20 mol%) and NCS (1.20 g, 9.00 mmol, 0.75 equiv) were added successively, the volume was adjusted to 50 mL by adding MeCN and the solution was stirred for 15 hours at $-30\text{ }^{\circ}\text{C}$. EtOH (15 mL) and NaBH_4 (1.13 g, 30.0 mmol, 2.5 equiv) were added successively and the reaction mixture was stirred for 1 hour at $0\text{ }^{\circ}\text{C}$. The reaction was quenched with aqueous saturated NH_4Cl (30 mL), extracted with EtOAc (6x50 mL) and dried over Na_2SO_4 . The combined organic phases were transferred into a 500 mL graduated flask and the volume was adjusted to 500 mL by adding EtOAc. 10.0 mL were removed from the graduated flask and the solvent was removed under reduced pressure. The crude mixture was taken up with 2 x 0.50 mL MeCNd_3 and transferred into an NMR-tube containing 10.0 mg of the internal standard (1,3,5-trimethoxybenzene). The solvent of the remaining organic phase was removed under reduced pressure and the reduced starting material was purified by column chromatography (Silica, 10:1 to 5:1 pentane/EtOAc).

Standard Sample (STD1&2): NaBH_4 (0.284 g, 7.50 mmol, 2.5 equiv) was added to a solution of distilled hydrocinnamic aldehyde (from the same batch as in the KIE-experiment) (0.403 g, 3.00 mmol, 1.0 equiv) in EtOH (3.5 mL) at $0\text{ }^{\circ}\text{C}$. The reaction mixture was stirred for 60 min at $0\text{ }^{\circ}\text{C}$ and subsequently quenched with aqueous saturated NH_4Cl (5 mL). The aqueous phase was extracted with EtOAc (6x5 mL), the combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (Silica, 10:1 to 5:1 pentane/EtOAc).

This experiment was done in duplicate.

KIE1: m = 0.349 g (2.56 mmol, 21%)

STD1: m = 0.387 g (2.84 mmol, 95%)

KIE2: m = 0.189 g (1.39 mmol, 12%)

STD2: m = 0.378 g (2.78 mmol, 93%)

¹H-NMR spectra are in accordance with the literature.²⁹

¹H-NMR (CDCl_3 , 400 MHz) δ = 7.32 – 7.27 (m, 2H), 7.23 – 7.17 (m, 3H), 3.68 (t, J = 6.4 Hz, 2H), 2.76 – 2.67 (m, 2H), 2.00 – 1.80 (m, 2H), 1.41 – 1.34 (s, 1H) ppm.

Calculation of the conversion:

Mass (internal standard): $m_{is} = 0.010$ g

Amount of substance (internal standard): $n_{is} = 0.060$ mmol

^1H -NMR integration (internal standard): $I_{is} = 3.00$ H

Integration (reduced starting material (3.52 ppm)): $I_{rsm} = 1.85$ H : 2 = 0.93 H

Integration (reduced starting material (1.78 ppm)): $I_{rsm} = 1.85$ H : 2 = 0.93 H

Amount of substance (reduced starting material): $n_{sm} = 0.060$ mmol * 0.93 * 50 = 2.767 mmol

Amount of substance (starting material): $n_{sm} = 12.00$ mmol – (12.00 mmol/50) = 11.76 mmol

(1/50 of the volume was removed before reductive work-up for H-NMR-analysis!)

Conversion: 2.767 mmol / 11.76 mmol – 1) * (-100) = 77%

KIE1 = 77% conversion

KIE2 = 77% conversion

Figure SI-11. Cutout from the ^1H -NMR spectrum of the quenched reaction (for determination of the conversion).

Experimental ^{13}C KIEs for the system were determined from analysis of starting material 3-phenylpropanal using NMR methodology at natural abundance. Two independent reactions of starting aldehyde were taken to 77 ± 2 conversion. The unreacted 3-phenylpropanal was reduced *in situ* to 3-phenylpropanol and reisolated for NMR analysis. The reisolated samples KIE1 and KIE2 were compared to two separate standard samples STD1 and STD2, respectively. The standard samples were prepared by reducing 3-phenylpropanal taken from the same batch used for the KIE experiments. Experimental ^{13}C KIEs were measured from relative isotopic composition of the two samples and fractional conversion in a standard way. The isotope effects were then averaged, and a 95% confidence range (C) was calculated using standard method.

$$C = \frac{t_{p,v}S}{\sqrt{n}}$$

S is the standard deviation, **n** is the number of measurements, and **t_{p,v}** is distribution function corresponding to confidence level **n-1**.

Figure SI-12. ¹³C-NMR spectrum of the reduced and reisolated starting material (3-phenylpropanol).

STD1/KIE1

The sample for determination of ¹³C KIEs was prepared from 160 mg of the reisolated sample KIE1, which was quantitatively transferred to a new 5 mm NMR tube using HPLC grade deuterated chloroform (CDCl₃) to a height of 5 cm. Likewise, 160 mg of standard sample STD1 was also prepared quantitatively in a 5 mm NMR tube using HPLC grade deuterated chloroform (CDCl₃) to a height of 5 cm. For quantitative measurement, ¹³C spectra were recorded at 150 MHz using inverse gated decoupling with an acquisition time of 10 s, delay time 36 s (5 times T₁ of slowest relaxing peak) and 128 transients for acquiring 6 fids for both the samples. A constant integration area was defined for each individual peak which is equal to 10 times the peak-widths at half-height for each peak. The para carbon of 3-phenylpropanol was taken as the standard carbon which was set to an integration value of 1000.0000. All the integrals for STD1 and KIE1 are listed in the tables below.

STD2/KIE2

Similar to the procedure described above, samples for KIE2 and STD2 were each prepared using 268 mg. For quantitative measurement, ¹³C spectra were recorded at 150 MHz using inverse gated decoupling with an acquisition time of 10 s, delay time 30 s (5 times T₁ of slowest relaxing peak) and 128 transients for acquiring 6 fids for both the samples. The spectra were processed as described for the above sample. All the integrals for STD2 and KIE2 are listed in the tables below.

Table SI-6. Standard Sample (STD1 160mg/CDCl₃).

peak	fid1	fid2	fid3	fid4	fid5	fid6	average	stddev	cuts=10 X avg hh
1	1000.9305	1003.0809	1002.0465	1009.6958	996.4917	1006.0323	1003.0463	4.5072	1.5,1.5
2	2025.1360	2035.2550	2018.4216	2036.3256	2025.5118	2036.9713	2029.6036	7.6570	2,2
3	2072.8509	2068.8465	2075.8805	2064.7618	2080.6641	2067.4642	2071.7447	5.8884	2,2
4	1000.0000	1000.0000	1000.0000	1000.0000	1000.0000	1000.0000	1000.0000	0.0000	2,2
5	1025.5784	1026.0890	1024.6846	1025.4123	1027.1945	1023.1769	1025.3560	1.3542	3.5,3.5
6	1041.1890	1042.1708	1038.5628	1038.6082	1040.9270	1040.9304	1040.3980	1.4767	4,4
7	996.7377	999.2351	996.4748	1000.5757	996.1794	1000.3555	998.2597	2.0267	3,3

Table SI-7. Reaction taken to 77% conversion (KIE1 160mg/CDCl₃).

peak	fid1	fid2	fid3	fid4	fid5	fid6	average	stddev	KIE	95% conf
1	1013.6563	1013.2420	1013.8523	1014.0950	1013.5953	1012.7271	1013.5280	0.4839	1.007	0.004
2	2024.8861	2037.0148	2029.6127	2040.8483	2026.1498	2044.3620	2033.8123	8.0881	1.001	0.005
3	2076.6163	2074.6922	2075.3353	2057.5687	2074.9792	2062.1561	2070.2246	8.1830	1.000	0.004
4	1000.0000	1000.0000	1000.0000	1000.0000	1000.0000	1000.0000	1000.0000	0.0000	1.000	0.000
5	1050.1213	1052.8462	1055.0797	1047.5008	1052.0531	1050.8890	1051.4150	2.5751	1.017	0.002
6	1044.5877	1050.5003	1049.9389	1044.8451	1042.4711	1047.6090	1046.6587	3.2104	1.004	0.003
7	992.6145	992.3526	990.7697	985.5134	992.9584	985.9063	990.0192	3.4235	0.994	0.003

Table SI-8. Standard Sample (STD2 268mg/CDCl₃).

peak	fid1	fid2	fid3	fid4	fid5	fid6	average	stddev	cuts=10 X avg hh
1	1013.1913	1015.2475	1017.2836	1012.6850	1014.4221	1016.6279	1014.9096	1.8353	2.5,2.5
2	2057.1301	2050.2951	2057.6368	2052.1572	2051.3216	2060.7208	2054.8769	4.1923	4,4
3	2100.1524	2100.3305	2098.9928	2101.5752	2103.3006	2091.8123	2099.3606	3.9776	4,4
4	1000.0000	1000.0000	1000.0000	1000.0000	1000.0000	1000.0000	1000.0000	0.0000	4,4
5	1015.9678	1014.7441	1015.3965	1015.7316	1014.9892	1014.8254	1015.2758	0.5038	5,5
6	1032.2505	1032.3731	1034.0529	1031.8139	1032.2724	1031.1377	1032.3168	0.9661	6,6
7	988.9633	988.2676	989.7361	987.9015	989.4858	988.0125	988.7278	0.7814	4,4

Table SI-9. Reaction taken to 77% conversion (KIE2 268mg/CDCl₃).

peak	fid1	fid2	fid3	fid4	fid5	fid6	average	stddev	KIE	95% conf
1	1022.9126	1022.9606	1021.5724	1024.8493	1020.9465	1021.8850	1022.5211	1.3821	1.005	0.002
2	2060.4713	2063.4748	2057.1022	2056.2644	2063.5671	2060.5035	2060.2306	3.0759	1.002	0.002
3	2102.8840	2094.4883	2099.5798	2104.5966	2095.5660	2096.5294	2098.9407	4.1225	1.000	0.002
4	1000.0000	1000.0000	1000.0000	1000.0000	1000.0000	1000.0000	1000.0000	0.0000	1.000	0.000
5	1037.2121	1038.4920	1038.6580	1040.5217	1039.7760	1038.1707	1038.8051	1.1789	1.016	0.001
6	1035.0012	1035.9482	1036.6547	1035.4925	1036.0883	1034.6687	1035.6423	0.7347	1.002	0.001
7	991.4310	989.5594	988.8080	992.5506	991.0334	989.8827	990.5442	1.3765	1.001	0.001

KIE-experiment (2)

KIE-Sample: Aminal **syn-18b** was synthesized according to the literature procedure.²² The exact time (20 min) and suitable conditions (equivalents of H₂O and TFA, concentration) for 20-30% conversion were defined by a previously performed kinetic ¹H-NMR-experiment using 1,3,5-trimethoxybenzene as an internal standard. Aminal **syn-18b** (3.36 g, 8.00 mmol, 1.0 equiv) was dissolved in MeCN (200 mL), H₂O (0.722 mL, 40.0 mmol, 5.0 equiv) and TFA (3.06 mL, 40.0 mmol, 5.0 equiv) were added subsequently and the solution was stirred for 20 min at 20 °C. After quenching with saturated aqueous NaHCO₃ (200 mL), the aqueous phase was extracted with EtOAc (3x200 mL) three times. The combined organic phases were dried over NaSO₄ and the exact volume of the organic phase was adjusted to 1200 mL. 12 mL were taken from the solution and added to flask containing 1,3,5-trimethoxybenzene (6.73 mg, 40.0 μmol) as an internal standard. The solvents were removed under reduced pressure and the residue was taken up by 1.0 mL of MeCNd₃. 24% conversion was calculated from the ¹H-NMR spectra. The solvents from the combined organic phases were removed under reduced pressure and the product was obtained after column chromatography (5:1 pentane/EtOAc). The pure α-chloro aldehyde (0.434 g, 2.57 mmol, 1.0 equiv) was dissolved in EtOH (20.0 mL) and cooled to 0 °C. NaBH₄ (0.243 g, 6.43 mmol, 2.5 equiv) was added and the reaction mixture was stirred for 60 min at the same temperature. After quenching with saturated aqueous NH₄Cl, the aqueous phase was extracted with EtOAc (3x20 mL). The combined organic phases were dried over NaSO₄ and the solvents were removed under reduced pressure. The pure β-chloroalcohol (0.350 g, 2.05 mmol, 80%) was obtained after column chromatography (5:1 pentane/EtOAc).

Standard Sample: Aminal **syn-18b** (from the same batch as KIE-experiment) (0.840 mg, 2.00 mmol, 1.0 equiv) was dissolved in MeCN (50 mL), H₂O (0.180 mL) and TFA (0.765 mL) were added subsequently and the solution was stirred at 20 °C until TLC showed complete conversion of the aminal (9 h). After quenching with saturated aqueous NaHCO₃ (40 mL), the aqueous phase was extracted with EtOAc (3x50 mL). The combined organic phases were dried over NaSO₄ and the solvents were removed under reduced pressure. ¹H-NMR of the crude sample confirmed complete conversion of the aminal. The product was obtained after column chromatography (5:1 pentane/EtOAc). The pure α-chloro aldehyde (0.301 g, 1.79 mmol, 1.0 equiv) was dissolved in EtOH (15 mL) and cooled to 0 °C. NaBH₄ (0.169 g, 4.46 mmol, 2.5 equiv) was added and the reaction mixture was stirred for 60 min at the same temperature. After quenching with saturated aqueous NH₄Cl (10 mL), the aqueous phase was extracted with EtOAc

(3x20 mL). The combined organic phases were dried over NaSO₄ and the solvents were removed under reduced pressure. The pure β-chloro alcohol (0.240 g, 1.41 mmol, 79%) was obtained after column chromatography (5:1 pentane/EtOAc).

¹H-NMRs are in accordance with the literature.²²

Product KIEs were performed by isolating the product 2-chloro-3-phenylpropanal from a reaction of *syn*-aminal (*syn*-**18b**) taken to 24% conversion and reduced insitu to 2-chloro-3-phenylpropanol. The standard sample was prepared by isolating the product taken to 100% conversion and reduced in situ Experimental ¹³C KIEs were measured from changes in relative isotopic composition and fractional conversion.

STD/KIE

Similar to the procedure described for determination of ¹³C KIEs for 3-phenylpropanol, low conversion and 100% conversion samples of 2-chloro-3-phenylpropanol were each prepared using 231 mg. For quantitative measurement, ¹³C spectra were recorded at 150 MHz using inverse gated decoupling with an acquisition time of 10 s, delay time 30 s (5 times T₁ of slowest relaxing peak) and 128 transients for acquiring 6 fids for both the samples. The spectra were processed as described for the previous samples. A representative spectrum along with integration for both samples are shown in the table below. This experiment was not performed in duplicate due the challenges associated with synthesizing a larger quantities of *syn*-**18b** required for the experiment.

Figure SI-13. ¹³C-NMR spectrum of the reduced decomposition product of *syn*-**18b** (2-chloro-3-phenylpropanol).

Table SI-10. Standard Sample (STD 231mg/CDCI₃).

peak	fid1	fid2	fid3	fid4	fid5	fid6	average	stddev	cuts=10 X avg hh
1	1026.0648	1026.8439	1026.4918	1024.7271	1028.6749	1025.2016	1026.3340	1.3930	2,2
2	2002.9656	2004.9762	2001.9009	2000.6530	2004.8393	2002.2518	2002.9311	1.7051	2.5,2.5
3	1999.7604	2000.0493	2000.2890	1998.7059	1999.6764	1997.1237	1999.2675	1.1812	2.5,2.5
4	1000.0000	1000.0000	1000.0000	1000.0000	1000.0000	1000.0000	1000.0000	0.0000	3,3
5	994.7805	991.0943	994.3898	995.1336	991.5581	992.6222	993.2631	1.7374	3,3
6	1046.7547	1043.5144	1045.1485	1037.3534	1045.1662	1045.3339	1043.8785	3.3577	10,10
7	997.2385	998.3051	1000.9168	999.3783	998.0785	996.2951	998.3687	1.6234	4,4

Table SI-11. Reaction taken to 24% conversion (KIE 231mg/CDCl₃).

peak	fid1	fid2	fid3	fid4	fid5	fid6	average	stddev	KIE	95% conf
1	1021.2407	1023.3972	1024.4986	1027.7109	1033.4467	1030.6276	1026.8203	4.6355	0.999	0.004
2	1997.0448	2001.1775	2004.2681	2004.6367	2011.8553	2003.1204	2003.6838	4.8723	1.000	0.002
3	1994.1101	1997.2838	1999.9637	1994.5238	2005.8038	1998.4097	1998.3492	4.2877	1.001	0.002
4	1000.0000	1000.0000	1000.0000	1000.0000	1000.0000	1000.0000	1000.0000	0.0000	1.000	0.000
5	984.5027	985.8564	986.8568	986.6361	988.6683	987.7684	986.7148	1.4548	1.008	0.002
6	1043.8129	1042.6836	1040.2764	1043.1687	1045.8196	1043.1081	1043.1449	1.7913	1.001	0.003
7	997.5046	998.9728	1000.1525	999.9749	1002.1993	998.2256	999.5050	1.6626	0.999	0.002

Theoretical Studies

General Information:

All the DFT calculations presented in the manuscript were performed using B3LYP/6-31+G**PCM (solvent = acetonitrile) level of theory as implemented in Gaussian16. All the starting materials and intermediates were verified as true minima (no imaginary frequencies) whereas all the transition states for the system were characterized by one imaginary frequency. Single point energy calculations were performed separately using B3LYP functional with Grimme's dispersion correction with Becke-Johnson damping (D3-BJ) and a triple- ζ basis set (6-311+G**) and a PCM solvent model for acetonitrile was also applied to all single point geometry optimizations. Gibbs free energies were estimated at reaction temperature 243 K and were corrected using Grimme's quasi-RRHO approach. Each intermediate along the reaction coordinate were located by performing Paton's quick reaction coordinate (QRC) procedure from the respective transition states. A thorough conformation search was done for all the optimized transition state and intermediate geometries to identify the lowest energy geometry for each stationary point. Cartesian coordinates of all computed starting materials, intermediates, and transition states are included in the section below. The lowest energy conformation for each transition state reported in the manuscript is highlighted in red. The higher energy conformations for each transition state are also included along with their relative energies.

Exploring the origins of enantioselectivity:

From the computed reaction coordinate diagram shown in Figure 3 of the manuscript, the chlorination of the enamine intermediate (TS4) is irreversible, and the enantioselectivity-determining step of the reaction. Accordingly, we modeled the approach of NCS (**6**) to either face of the two possible (*E*)-enamine intermediates. After a thorough conformational search, the lowest-energy TS for each distinct approach was identified. The approach of **6** from the *Re*-face of enamine that is *syn*-to the *t*-butyl group of the catalyst **3c** was found to be the lowest-energy TS leading to the formation of the (*S*)-enantiomer of **19** (TS4-S1). In contrast, the TS for the approach of **6** to the *Si*-face of the enamine that is *anti* to the *t*-butyl group of **3c** (TS4-R1) was identified as the lowest energy TS for the formation of the (*R*)-enantiomer of **19**. The $\Delta\Delta G^\ddagger$ between these two TSs is 2.9 kcal mol⁻¹ favoring TS4-S1 – a value that is qualitatively consistent with the >90% ee observed for this reaction.

Figure SI-14. Lowest energy transition states for the front and back approach of **6** to the two distinct (*E*)-enamine intermediates calculated at the B3LYP-D3(BJ)/6-311+G** PCM(acetonitrile)// B3LYP/6-31+G** PCM(acetonitrile) level of theory. Some hydrogen atoms have been removed for clarity in the 3D representation of the key transition structures. Key bond-forming and bond-breaking distances are in angstroms (Å).

Computed pathways for the formation of all diastereomers of the amina intermediate:

In the manuscript, we have described the formation of *syn*-**18b** and *anti*-**18b** from the *Z*-chloroiminium ion (**Int4**). We have also computed the formation of diastereomeric amina (*syn*-**18b'** and *anti*-**18b'**) from the *E*-chloroiminium ion with the same *S*-configuration at the α -carbon (**Int4'**). The reaction coordinate diagram for the formation of all four amina diastereomers from the respective enamine intermediates (**Int3** and **Int3'**) is shown in the Figure below. It is important to note that even though **Int4'** is lower in energy than **Int4**, the barrier for its formation from **Int3'** is 1.4 kcal mol⁻¹ higher in energy than the barrier for formation of **Int4** from **Int3** (see Figure below). If **Int4'** forms, then it faces only a 6.2 kcal mol⁻¹ barrier to form *anti*-**18b'** via TS_{*syn*-18b'}. In contrast, formation of *syn*-**18b'** from **Int4'** faces a much higher barrier of 17.2 kcal mol⁻¹ via TS_{*anti*-18b'}.

Figure SI-15. Reaction coordinate diagram for the formation of diastereomeric enamines from the respective enamines calculated at the B3LYP-D3(BJ)/6-311+G** PCM(acetonitrile)// B3LYP/6-31+G** PCM(acetonitrile) level of theory. Some hydrogen atoms have been removed for clarity in the 3D representation of the key transition structures. Key bond-forming and bond-breaking distances are in angstroms (Å).

In the manuscript, we show the pathway that converts **Int4** to *syn*-**18b** and *anti*-**18b** via TS5 and TS5'. These transition structures are TS_{*syn*-18b} and TS_{*anti*-18b} respectively in the Figure above. We implied that *syn*-**18b** and *anti*-**18b** re-entered the catalytic cycle as the *Z*-chloroiminium ion (**Int4**) via these same transition states (principle of microscopic reversibility). However, there is a possibility of a C-N bond-rotation event that converts *syn*-**18b** to *syn*-**18b'** and *anti*-**18b** to *anti*-**18b'** and subsequent re-entry of these intermediates into the catalytic cycle as the *E*-chloroiminium intermediate (**Int4'**) via TS_{*syn*-18b'} and TS_{*anti*-18b'}. This possibility is unlikely for the *syn*-aminal since TS_{*syn*-18b'} is significantly higher in energy than TS_{*syn*-18b}. On the other hand, such a pathway is more than likely for the *anti*-aminal since TS_{*anti*-18b'} is lower in energy than TS_{*anti*-18b}. We computed the reaction coordinate for the conversion of *anti*-**18b'** to the 2-chloroaldehyde product via the three sequential transition states TS_{*anti*-18b'}, TS6', and TS7 corresponding to re-entry into the catalytic cycle as the *E*-chloroiminium, hydrolysis, and catalyst regeneration and product release (Figure below). Incidentally, the highest energy barrier for this reaction pathway is re-entry into the catalytic cycle via TS_{*anti*-18b'}, which is identical to the relative energetics of the corresponding transition states in the conversion of *syn*-**18b** to the product **19** described in Figure 4 of the manuscript.

Figure SI-16. Reaction coordinate diagram for the conversion of *anti-18b'* to **19** calculated at the B3LYP-D3(BJ)/6-311+G** PCM(acetonitrile)// B3LYP/6-31+G** PCM(acetonitrile) level of theory. Some hydrogen atoms have been removed for clarity in the 3D representation of the key transition structures. Key bond-forming and bond-breaking distances are in angstroms (Å).

Table SI-12. Coordinates and energies of computed structures.

Starting Materials

3-Phenylpropanal (sm.log)
Free Energy = -424.09683
Zero-point Energy = -424.07017
Potential Energy = -424.23595
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -424.35584
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -424.21671
Charge = 0 Multiplicity = 1

C	-3.3413160	-0.0005570	0.5403040
H	-3.9288280	-0.0002450	1.4807970
C	-1.8491150	-0.0005340	0.7243600
H	-1.6071760	0.8704580	1.3516390
H	-1.6070840	-0.8719850	1.3509560
C	-1.0313240	0.0000370	-0.5758450
H	-1.3069810	-0.8785130	-1.1687130
H	-1.3071090	0.8790120	-1.1680190
C	0.4615430	0.0000500	-0.3184150
C	1.1687220	1.2054270	-0.1841310
C	1.1688060	-1.2053300	-0.1845390
C	2.5419580	1.2082530	0.0802440
H	0.6406430	2.1499560	-0.2924210
C	2.5420360	-1.2081510	0.0798330
H	0.6407890	-2.1498560	-0.2931560
C	3.2340200	0.0000540	0.2141230
H	3.0706490	2.1524890	0.1765460
H	3.0707990	-2.1523810	0.1758140
H	4.3012090	0.0000500	0.4160980
O	-3.9173610	0.0006900	-0.5356430

Catalyst (cat.log)
Free Energy = -538.35806
Zero-point Energy = -538.32923
Potential Energy = -538.59681
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -538.76234
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -538.52359
Charge = 0 Multiplicity = 1

C	-0.4544180	-0.1166990	-0.6994830
N	0.4266560	1.0008460	-0.2914750
C	1.5852240	0.5777350	0.2652530
O	2.4887570	1.3031530	0.7022350
C	1.5745020	-0.9521890	0.2523210
N	0.4181660	-1.3045010	-0.5947510
H	0.7590160	-1.5344140	-1.5245490
C	2.8849960	-1.5589870	-0.2398010
H	3.7062150	-1.2645140	0.4186440
H	2.8194820	-2.6512640	-0.2414640
H	3.1204180	-1.2213170	-1.2554950
H	1.3979930	-1.2887160	1.2835090
C	0.1807200	2.4085020	-0.5718670
H	-0.2985190	2.9212640	0.2681390
H	-0.4580440	2.4993570	-1.4525720
H	1.1386980	2.8949920	-0.7695520
H	-0.7422380	0.0344340	-1.7475790
C	-1.7730610	-0.2694120	0.1258260
C	-2.6574980	0.9869790	-0.0160930
H	-2.8146340	1.2546050	-1.0678020
H	-3.6416030	0.7942700	0.4248400
H	-2.2356580	1.8533340	0.4996520
C	-2.5421370	-1.4694220	-0.4650670
H	-2.7842300	-1.3035630	-1.5222530
H	-3.4853780	-1.6125740	0.0733430
H	-1.9560190	-2.3888790	-0.3889400
C	-1.4809210	-0.5254740	1.6153320
H	-0.9261150	-1.4578230	1.7573130
H	-2.4212300	-0.6094630	2.1713200
H	-0.9064070	0.2944330	2.0606280

Trifluoroacetic acid (tfa.log)
Free Energy = -526.81566
Zero-point Energy = -526.79175
Potential Energy = -526.83013
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -526.98128
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -526.96680
Charge = 0 Multiplicity = 1

C	0.9502640	-0.1544060	-0.0000050
C	-0.5942250	0.0015770	0.0000060
O	1.4971790	-1.2288920	-0.0000170
O	1.5236480	1.0442750	-0.0000080
H	2.4938330	0.9458880	-0.0000090
F	-1.0055400	0.6793790	1.0919440
F	-1.1885270	-1.1982590	-0.0002140
F	-1.0055640	0.6797710	-1.0917070

Water (h2o.log)
Free Energy = -76.43466
Zero-point Energy = -76.42090
Potential Energy = -76.44210
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -76.46677
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -76.45933
Charge = 0 Multiplicity = 1

O	-0.0000000	-0.0000000	0.1177180
H	-0.0000000	0.7669030	-0.4708720
H	-0.0000000	-0.7669030	-0.4708720

N-chlorosuccinimide (suc.log)
Free Energy = -820.19336
Zero-point Energy = -820.16822
Potential Energy = -820.24947
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -820.38399
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -820.32788
Charge = 0 Multiplicity = 1

C	-0.4323230	1.1871590	0.0000130
C	-1.8907470	0.7700950	0.0001270
C	-1.8907470	-0.7700950	0.0000880
C	-0.4323230	-1.1871590	-0.0000720
N	0.3190470	-0.0000000	-0.0000370
H	-2.3726500	1.1995430	0.8824860
H	-2.3728100	-1.1995470	-0.8821820
H	-2.3726010	-1.1995720	0.8824610
H	-2.3727600	1.1995770	-0.8821560
O	0.0417140	-2.3036950	-0.0001500
O	0.0417140	2.3036950	0.0001580
Cl	2.0274650	-0.0000000	-0.0000790

Succinimide (suc-h.log)
Free Energy = -360.63967
Zero-point Energy = -360.61626
Potential Energy = -360.70798
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -360.81019
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -360.74188
Charge = 0 Multiplicity = 1

C	-1.1670680	0.2088320	-0.0006280
C	-0.7696220	-1.2596600	0.0000790
C	0.7696220	-1.2596600	0.0000120
C	1.1670680	0.2088320	-0.0005610
N	0.0000000	0.9594370	-0.0000830
H	-1.2020090	-1.7408940	0.8816570
H	1.2020600	-1.7415660	-0.8811660
H	1.2020730	-1.7409440	0.8815300
H	-1.2021240	-1.7416150	-0.8810400
O	2.2926660	0.6803470	0.0002360
O	-2.2926660	0.6803470	0.0004760
H	0.0000000	1.9733530	0.0004920

Intermediates

Int1.log
Potential Energy = -1489.67565
Zero-point Energy = -1489.19554
Free Energy = -1489.23816
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.13898
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.70148
Charge = 0 Multiplicity = 1

C	1.9462360	-0.4304000	1.7290860
H	2.3898140	-1.2580300	1.1725630
H	1.5830110	-0.8318660	2.6796860
C	3.0381520	0.6197670	2.0485670
C	0.7674580	0.1622330	0.9633750
O	0.1653840	1.1293300	1.7475260
H	-0.4028390	1.7375180	1.1951310
H	1.0625910	0.5568670	-0.0119310
O	-1.5240140	2.6278790	0.3369240
C	-2.4769980	1.8901530	-0.0099700
C	-3.7216940	2.6623270	-0.5525430
F	-3.3819940	3.4704220	-1.5886500
F	-4.7076170	1.8510100	-0.9891620
F	-4.2547680	3.4549600	0.4131970
O	-2.5666420	0.6405150	0.0248780
H	3.7589450	0.1333660	2.7145960
C	3.7702050	1.1735960	0.8414430
C	4.8448520	0.4704380	0.2722390
C	3.3971740	2.3983560	0.2656780
C	5.5209050	0.9699360	-0.8443490
H	5.1592610	-0.4733240	0.7121220
C	4.0697700	2.9020450	-0.8528430
H	2.5785320	2.9661620	0.7006990
C	5.1334150	2.1882660	-1.4129520
H	6.3523320	0.4120300	-1.2660380
H	3.7655930	3.8529270	-1.2813190
H	5.6596190	2.5796740	-2.2787650
H	2.5813280	1.4368810	2.6134460
N	-0.3493590	-0.8927940	0.6102410
C	-0.6980180	-1.9453390	1.6396240
C	-0.4468280	-1.5868290	-0.7713480
C	-1.6725010	-2.8154890	0.8395450
H	0.2008640	-2.5205480	1.8718850
H	-0.7990720	-0.8075150	-1.4532840
O	-2.4718120	-3.6122840	1.3238100
N	-1.5482370	-2.5083160	-0.4756630
C	-2.5552190	-2.9395790	-1.4468020
H	-2.3812470	-3.9641360	-1.7847900
H	-3.5363920	-2.8905320	-0.9699830
H	-2.5382840	-2.2690890	-2.3056680
C	0.8043460	-2.2703720	-1.4179650
C	0.3191370	-2.8959460	-2.7521310
H	-0.3477650	-3.7452600	-2.5959650
H	-0.1862780	-2.1628410	-3.3899950
H	1.1906660	-3.2640160	-3.3007970
C	1.8810950	-1.2287830	-1.7922360
H	1.4532620	-0.3969480	-2.3629220
H	2.4164870	-0.8211430	-0.9355300
H	2.6304770	-1.7093760	-2.4282470
C	1.4031990	-3.3998650	-0.5580700
H	0.6525450	-4.1562520	-0.3089970
H	2.1948060	-3.8999530	-1.1244980
H	1.8539350	-3.0415460	0.3699470
C	-1.3324190	-1.3964190	2.9124170
H	-0.6244830	-0.8030320	3.4910270
H	-2.2053760	-0.7788260	2.6859920
H	-1.6578290	-2.2470480	3.5158720
H	-1.1988590	-0.2659730	0.5455450

Int2.log
Potential Energy = -1489.67471
Zero-point Energy = -1489.20052
Free Energy = -1489.24669
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.13451

Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.70649
Charge = 0 Multiplicity = 1

C	-0.9076670	-1.4510240	-0.3872190
C	-0.7053740	-2.8638920	1.5019160
C	0.7227300	-2.6529040	0.9841170
N	0.5181550	-1.4692480	0.0906370
N	-1.5554800	-2.1514540	0.7253680
O	-1.0033980	-3.5500940	2.4755070
C	-2.9582150	-1.9579010	1.0920940
H	-3.5989610	-2.7370730	0.6714540
H	-3.0323810	-1.9934810	2.1804440
H	-3.2843840	-0.9790670	0.7399530
C	1.3809230	-0.5192300	-0.0314960
C	1.2192450	0.7867870	-0.7149230
C	2.4250840	1.1515040	-1.6268150
H	2.4994840	0.4246100	-2.4409870
H	2.1759710	2.1138820	-2.0854520
C	1.7463740	-2.4673650	2.0931350
H	1.6535160	-3.3229180	2.7662070
H	2.7672300	-2.4599330	1.7041890
H	1.5515820	-1.5515990	2.6568910
H	0.9956780	-3.5047370	0.3536320
C	-1.1152890	-2.1068240	-1.7988310
H	-1.2533120	-0.4145590	-0.3978180
C	-2.6229500	-2.0259360	-2.1323180
H	-2.7730020	-2.3302500	-3.1725630
H	-3.2195590	-2.6943650	-1.5080200
H	-3.0105980	-1.0074450	-2.0241620
C	-0.3458890	-1.3109870	-2.8717890
H	-0.6860510	-0.2724570	-2.9338690
H	0.7353230	-1.3221330	-2.7055950
H	-0.5233210	-1.7697240	-3.8490820
C	-0.6677540	-3.5802940	-1.8427280
H	-1.1401380	-4.1777900	-1.0567630
H	-0.9632340	-4.0144800	-2.8027090
H	0.4190780	-3.6853190	-1.7664190
H	1.1649890	1.5129720	0.1086330
H	0.2856240	0.8612390	-1.2682000
C	3.7537620	1.2537760	-0.9029550
C	4.0146940	2.3280740	-0.0361460
C	4.7496640	0.2823880	-1.0826630
C	5.2355070	2.4255990	0.6357360
H	3.2608890	3.0982630	0.1094100
C	5.9742900	0.3767590	-0.4120960
H	4.5694440	-0.5514930	-1.7568160
C	6.2199550	1.4481700	0.4506480
H	5.4200860	3.2658580	1.2988600
H	6.7333200	-0.3846850	-0.5667840
H	7.1700720	1.5245520	0.9711210
H	2.3367140	-0.6964060	0.4541960
O	0.2055980	0.6727320	2.5360000
H	-0.5650500	1.0245000	2.0250470
H	0.3612240	1.3062950	3.2479440
O	-1.8272060	1.3783850	0.8585520
C	-2.4962880	2.4448910	0.9188010
C	-3.5454270	2.5697760	-0.2410770
O	-2.4417150	3.3874580	1.7255190
F	-4.3615340	3.6413520	-0.1226540
F	-4.3489880	1.4744090	-0.3167630
F	-2.9249700	2.6827500	-1.4496620

Int3.log
Potential Energy = -2233.46906
Zero-point Energy = -2232.93826
Free Energy = -2232.98928
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.04146
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.56168
Charge = 0 Multiplicity = 1

C	-1.1664720	2.4657730	-0.1544700
C	-0.8513740	2.2752420	2.1757360
C	-2.3119350	1.9105080	1.9023010
N	-2.3392020	1.7958790	0.4289940
N	-0.2484460	2.5334850	0.9948030

O	-0.3144210	2.3101580	3.2878670
C	1.1866930	2.7691910	0.9011040
H	1.6843780	2.1758760	1.6709860
H	1.5438040	2.4572960	-0.0813760
H	1.4423890	3.8218890	1.0576150
C	-2.9811220	0.7477450	-0.2013560
H	-3.7572350	0.3006010	0.4096050
C	-2.7937670	0.2608730	-1.4531300
C	-3.6703920	-0.7961890	-2.1066510
H	-3.0300030	-1.6017840	-2.4904950
H	-2.0634830	0.7088280	-2.1199590
C	-2.7364480	0.6738020	2.6927140
H	-2.5204360	0.8572640	3.7484130
H	-3.8080210	0.4825230	2.5981590
H	-2.1859090	-0.2162640	2.3742630
H	-2.9320000	2.7584290	2.2277080
C	-1.4940740	3.8573210	-0.8060200
H	-0.7157310	1.8236720	-0.9210120
Cl	-0.6328290	-1.4406910	-0.4240500
N	0.6830970	-2.5138660	-0.0345290
C	0.4805070	-3.7822890	0.5498390
C	2.0047690	-2.1910920	-0.2610340
C	1.8549980	-4.3933150	0.7470550
C	2.8523010	-3.3582650	0.1963350
H	1.9936620	-4.5954540	1.8126050
H	3.4239780	-3.7275400	-0.6600470
O	2.3748020	-1.1276540	-0.7528730
O	-0.6062310	-4.2424560	0.8226390
C	-0.2292940	4.4427310	-1.4710590
H	-0.5034150	5.3241060	-2.0605060
H	0.5191650	4.7617330	-0.7420670
H	0.2379380	3.7224030	-2.1528340
C	-2.5584360	3.6566090	-1.9043720
H	-2.1929380	3.0079730	-2.7075700
H	-3.4771210	3.2217720	-1.5022470
H	-2.8069850	4.6255750	-2.3503730
C	-2.0324260	4.8503100	0.2406480
H	-1.3193820	5.0112630	1.0559370
H	-2.2170010	5.8205370	-0.2325960
H	-2.9796260	4.5072470	0.6686220
H	3.5687840	-2.9985350	0.9397540
H	1.8919410	-5.3503410	0.2203270
H	3.8924930	-0.6320820	-0.9117720
O	4.8011550	-0.2227150	-1.0884920
C	5.6235100	-0.4107390	-0.0808380
O	5.4112800	-0.9962000	0.9590350
C	7.0013900	0.2419270	-0.3793350
F	6.8699910	1.5709780	-0.5864840
F	7.5587580	-0.2956490	-1.4872250
F	7.8512910	0.0625310	0.6426210
H	-4.1410040	-0.3493710	-2.9941210
C	-4.7545800	-1.3986480	-1.2351620
C	-6.0382910	-0.8318760	-1.1939430
C	-4.5036130	-2.5347980	-0.4500470
C	-7.0428470	-1.3805660	-0.3904470
H	-6.2535360	0.0446210	-1.8007330
C	-5.5043350	-3.0882180	0.3552080
H	-3.5175480	-2.9913900	-0.4718620
C	-6.7784160	-2.5119950	0.3884050
H	-8.0306510	-0.9282820	-0.3769950
H	-5.2898060	-3.9706590	0.9516830
H	-7.5578880	-2.9427040	1.0103600

Int4.log
Potential Energy = -2233.52559
Zero-point Energy = -2232.99216
Free Energy = -2233.04199
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.09921
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.61562
Charge = 0 Multiplicity = 1

C	0.9402390	2.2301840	0.5755130
C	0.5027330	4.1457900	-0.7397400
C	1.9868650	3.8132210	-0.9631080
N	2.0249080	2.4045230	-0.4527940

N	-0.0284770	3.2119810	0.0836410
O	-0.0837880	5.0894640	-1.2598720
C	-1.4705080	3.1036440	0.3140480
H	-1.9822690	3.4779800	-0.5743480
H	-1.7275290	2.0537610	0.4670710
H	-1.7870090	3.6961130	1.1761920
C	2.7454050	1.4817430	-0.9874700
H	3.4500860	1.8019600	-1.7499830
C	2.6813470	0.0069470	-0.7343940
C	4.0810820	-0.5922070	-0.5054300
H	4.7390100	-0.2847360	-1.3239030
H	4.4684180	-0.1297800	0.4103860
H	1.9639690	-0.2813880	0.0330220
C	2.4441960	4.0079270	-2.3990230
H	2.2023740	5.0366690	-2.6757610
H	3.5239480	3.8811440	-2.5036970
H	1.9227810	3.3364590	-3.0864960
H	2.5907930	4.4261560	-0.2877630
C	1.4341060	2.4492160	2.0519330
H	0.5295620	1.2191770	0.4936670
Cl	1.9440840	-0.5927850	-2.3085880
C	0.2090740	2.2460370	2.9736820
H	0.5486150	2.2349770	4.0137550
H	-0.5172130	3.0558250	2.8760750
H	-0.2924930	1.2945410	2.7735490
C	2.4841840	1.3786940	2.4044470
H	2.0792960	0.3693310	2.2897890
H	3.3947320	1.4774860	1.8050190
H	2.7812480	1.4993960	3.4504460
C	2.0232770	3.8502860	2.2981650
H	1.3376190	4.6469180	1.9929090
H	2.2057970	3.9736950	3.3700080
H	2.9847450	3.9922280	1.7947840
N	-4.6968210	-0.5822140	-0.5044950
C	-5.1131530	-1.1676640	-1.6866090
C	-5.7182360	0.0131040	0.2131920
C	-6.6157670	-0.9585470	-1.8197010
C	-7.0173420	-0.1761770	-0.5586030
H	-7.1030100	-1.9345370	-1.8984060
H	-7.7299820	-0.7113950	0.0752450
H	-7.4467460	0.8059610	-0.7755470
H	-6.8168200	-0.4171750	-2.7484660
O	-5.5737010	0.5869480	1.2843430
O	-4.3766780	-1.7480110	-2.4727230
C	4.0952020	-2.1008840	-0.3592940
C	4.5129340	-2.9137850	-1.4226040
C	3.7082090	-2.7091430	0.8446030
C	4.5360160	-4.3057020	-1.2904990
H	4.8249520	-2.4566540	-2.3575660
C	3.7275560	-4.0998270	0.9784350
H	3.3966170	-2.0960600	1.6859870
C	4.1406900	-4.9026520	-0.0900150
H	4.8642030	-4.9201600	-2.1237840
H	3.4261290	-4.5544150	1.9175990
H	4.1590860	-5.9834430	0.0147770
H	-3.7112260	-0.5937930	-0.1843440
O	0.0996000	-0.9122890	0.9713150
C	-1.1159290	-1.1300350	0.7838390
O	-1.9890280	-0.4009980	0.2577920
C	-1.5906120	-2.5334120	1.2983540
F	-0.9371750	-3.5386520	0.6568490
F	-2.9146170	-2.7571000	1.1266560
F	-1.3378790	-2.6842920	2.6260660

Int4a.log
Potential Energy = -1949.26126
Zero-point Energy = -1948.79604
Free Energy = -1948.84194
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.75917
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.33986
Charge = 0 Multiplicity = 1

C	-2.9040680	-0.4194010	0.2350550
C	-2.6325550	-2.6725610	-0.4206930
C	-1.2574720	-2.0274910	-0.6080670

N	-1.4376240	-0.7549740	0.1673800
N	-3.4767610	-1.7587520	0.1195280
O	-2.8985910	-3.8425840	-0.6762100
C	-4.7923660	-2.1362520	0.6348710
H	-5.5494840	-2.1479020	-0.1532200
H	-4.7169250	-3.1372150	1.0635260
H	-5.0911810	-1.4325230	1.4123930
C	-0.4784210	-0.1969400	0.8226760
C	-0.6089920	0.8921270	1.8509710
C	0.6110340	1.8250560	1.9247100
H	0.5205620	2.3889040	2.8568570
H	1.5157700	1.2140160	1.9877750
C	-0.1269740	-2.9228550	-0.1213980
H	-0.2065090	-3.8660360	-0.6668420
H	0.8500250	-2.4865910	-0.3300750
H	-0.2131470	-3.1336140	0.9484260
H	-1.0885910	-1.7528200	-1.6541730
C	-3.3771390	0.6021360	-0.8629000
H	-3.1201270	-0.0123440	1.2258540
C	-4.8976800	0.8140910	-0.6800610
H	-5.2204640	1.6237170	-1.3413180
H	-5.4755720	-0.0730440	-0.9462230
H	-5.1512320	1.1046410	0.3452410
C	-2.6791020	1.9586820	-0.6596500
H	-2.9102910	2.3953910	0.3175530
H	-1.5939840	1.8966420	-0.7758730
H	-3.0406400	2.6604550	-1.4168920
C	-3.1018020	0.0942390	-2.2904840
H	-3.5533630	-0.8857840	-2.4731620
H	-3.5448580	0.7933110	-3.0060820
H	-2.0316130	0.0402470	-2.5099730
H	-1.5386970	1.4502730	1.7886430
C	0.6941620	2.7826230	0.7489030
C	0.0575970	4.0321350	0.8053310
C	1.4137910	2.4405040	-0.4062140
C	0.1303800	4.9182230	-0.2723730
H	-0.4925490	4.3154130	1.6991690
C	1.4861780	3.3258760	-1.4865580
H	1.9268520	1.4844260	-0.4538080
C	0.8434730	4.5656320	-1.4234280
H	-0.3638680	5.8834290	-0.2113780
H	2.0507550	3.0486270	-2.3720580
H	0.9033330	5.2549600	-2.2605080
Cl	-0.7270040	-0.0834880	3.4123120
H	0.5305050	-0.5953730	0.6739480
O	0.6578420	-0.6755290	-2.7444460
H	1.5411640	-0.7915010	-2.3165700
O	3.1296830	-1.0929550	-1.6112530
C	3.3478300	-1.0444570	-0.3760050
C	4.8433580	-1.3228350	0.0009640
O	2.5720920	-0.8066350	0.5724530
F	5.2605550	-2.5262780	-0.4752800
F	5.6662370	-0.3807570	-0.5359510
F	5.0757760	-1.3294200	1.3330070
H	0.6851830	0.1942080	-3.1631330

syn-18b (syn-aminal).log
Potential Energy = -2233.52383
Zero-point Energy = -2232.98813
Free Energy = -2233.03620
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.10822
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.62060
Charge = 0 Multiplicity = 1

C	-0.4491690	-1.7975970	1.1574570
C	-1.5239110	-3.7805250	0.4830270
C	-2.5342340	-2.6316080	0.3980450
N	-1.6701200	-1.4104740	0.4124130
N	-0.3499070	-3.2517390	0.8952080
O	-1.7378290	-4.9712520	0.2287250
C	0.8717840	-4.0428360	0.9685090
H	0.8645170	-4.7706060	0.1536310
H	1.7374070	-3.3879500	0.8578660
H	0.9563130	-4.5866740	1.9145590
C	-1.5216920	-0.6556080	-0.8301570

H	-2.3139000	-0.9715680	-1.5076500
C	-1.7364110	0.8661820	-0.5967830
C	-3.1391240	1.1523050	-0.0449680
H	-3.8827000	0.7665050	-0.7502160
H	-0.9583350	1.2858360	0.0367750
C	-3.5586120	-2.7996610	-0.7177210
H	-4.1242620	-3.7111330	-0.5079500
H	-4.2673270	-1.9664040	-0.7298210
H	-3.1033820	-2.9052280	-1.7037040
H	-3.0927780	-2.6355340	1.3413190
C	-0.4513420	-1.4065050	2.6785170
H	0.4236440	-1.3086810	0.7267240
Cl	-1.5383760	1.7378200	-2.2092710
N	-0.2798400	-0.9287740	-1.6166500
C	0.9561520	-0.3321510	-1.4665370
C	-0.3161310	-1.7563270	-2.7650000
C	1.8883350	-0.7973030	-2.5603030
C	1.0667240	-1.7992320	-3.3776140
H	2.1970110	0.0771420	-3.1414570
H	1.4467220	-2.8227150	-3.3067670
O	-1.3207750	-2.3135010	-3.1599950
O	1.2308430	0.4576540	-0.5585490
C	0.8860890	-1.8467700	3.3155760
H	0.9605100	-1.4320220	4.3261300
H	0.9654550	-2.9328430	3.4048180
H	1.7485210	-1.4826930	2.7453810
C	-0.5447920	0.1280410	2.7809370
H	0.2601080	0.6199700	2.2235140
H	-1.5031820	0.4900370	2.4026260
H	-0.4622630	0.4359540	3.8284710
C	-1.6105730	-2.0368110	3.4719460
H	-1.6252030	-3.1278980	3.3781310
H	-1.4941480	-1.8017190	4.5355030
H	-2.5804130	-1.6415740	3.1558010
H	0.9936730	-1.5477370	-4.4382980
H	2.7876280	-1.2198940	-2.1045250
H	-3.2356830	0.5615430	0.8719940
C	-3.4281280	2.6117000	0.2486430
C	-4.4150020	3.2993150	-0.4719660
C	-2.7375500	3.3006700	1.2588490
C	-4.7041960	4.6401400	-0.1970360
H	-4.9626210	2.7818060	-1.2553470
C	-3.0199140	4.6410840	1.5344820
H	-1.9755200	2.7890740	1.8406390
C	-4.0054240	5.3167740	0.8065030
H	-5.4734770	5.1529660	-0.7673900
H	-2.4742500	5.1552840	2.3205740
H	-4.2273670	6.3578550	1.0221380
H	2.6555720	1.1278530	-0.3040150
O	3.4957000	1.6485780	-0.0774810
C	4.5546770	0.8726600	-0.0322030
C	5.8198960	1.7052090	0.3140990
F	6.0443260	2.6500860	-0.6263830
F	6.9074390	0.9232660	0.3850580
F	5.6764600	2.3319390	1.5027410
O	4.6161190	-0.3226640	-0.2250980

Int5.log
Potential Energy = -1949.26139
Zero-point Energy = -1948.79334
Free Energy = -1948.83756
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.75481
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.33098
Charge = 0 Multiplicity = 1

C	2.8479570	-0.4198890	0.2974400
C	3.1788680	-2.0851900	-1.3420500
C	1.7708930	-2.2976070	-0.7866200
N	1.5497880	-1.0639370	0.0043330
N	3.7174470	-1.0041560	-0.7385140
O	3.7192410	-2.7693720	-2.2175730
C	4.9482250	-0.3944440	-1.2321830
H	5.8410300	-0.8700730	-0.8165410
H	4.9758230	-0.4998760	-2.3191860
H	4.9574550	0.6650230	-0.9739010

C	0.2907740	-0.4074070	-0.0013390
C	0.2888550	1.1310430	-0.1127780
C	-1.1139280	1.7421000	0.0170570
H	-1.7602340	1.3272430	-0.7631280
H	-1.5075070	1.4056490	0.9815060
C	0.7798260	-2.5898450	-1.9130310
H	1.1464220	-3.4635690	-2.4574550
H	-0.2158730	-2.8261270	-1.5296960
H	0.7045620	-1.7555190	-2.6169870
H	1.7989960	-3.1750510	-0.1239160
C	3.3730440	-0.6330290	1.7646110
H	2.7947160	0.6585110	0.1191560
C	4.8176950	-0.1036950	1.8969710
H	5.1080340	-0.1055460	2.9527070
H	5.5372040	-0.7273040	1.3614860
H	4.9106770	0.9260690	1.5335750
C	2.4938300	0.1870880	2.7312480
H	2.5490060	1.2587960	2.5051630
H	1.4432880	-0.1105950	2.7060870
H	2.8493720	0.0509060	3.7577440
C	3.3463780	-2.1192400	2.1630480
H	3.9600680	-2.7275570	1.4899480
H	3.7492100	-2.2399940	3.1741220
H	2.3292020	-2.5227180	2.1622510
H	0.9591250	1.5815620	0.6189800
C	-1.1448710	3.2569880	-0.0296560
C	-0.6636340	4.0147090	1.0501740
C	-1.6670460	3.9325440	-1.1415380
C	-0.6924050	5.4113320	1.0140520
H	-0.2700580	3.5110630	1.9300370
C	-1.7014550	5.3304200	-1.1804510
H	-2.0501870	3.3611940	-1.9828680
C	-1.2113670	6.0745520	-0.1034320
H	-0.3169830	5.9802880	1.8598650
H	-2.1112780	5.8351730	-2.0506910
H	-1.2378360	7.1599870	-0.1311740
Cl	1.0022510	1.5561170	-1.7515770
H	-0.3244410	-0.8018520	-0.8102060
O	-0.4673670	-0.7159980	1.2419540
H	-2.0000610	-1.1423450	1.1659450
H	0.0218740	-1.4334340	1.6737380
O	-2.9808750	-1.4074570	1.2305400
C	-3.4575800	-1.8027600	0.0724130
C	-4.9484380	-2.2165940	0.2141020
O	-2.8808970	-1.8647910	-0.9923350
F	-5.0818620	-3.2388260	1.0887070
F	-5.6949440	-1.1853330	0.6677750
F	-5.4548690	-2.6094800	-0.9641920

```

product.log (S-(19))
Potential Energy = -883.82667
Zero-point Energy = -883.66972
Free Energy = -883.69775
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -
883.98063
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated
free energy from qRRHO) = -883.85171
Charge = 0 Multiplicity = 1
C      1.5543360   -0.1401000   -0.2522360
C      0.5788650   -0.8150130    0.7258110
H      1.3676790   -0.4306580   -1.2862890
Cl     3.2770780   -0.6606210    0.1189520
H      0.7501140   -1.8944180    0.6703410
C      1.5643120   -1.3750860   -0.1387350
H      1.8473870   1.7745930    0.8535280
O      1.2837260   2.1117370   -1.0628590
H      0.8173130   -0.4989870    1.7465030
C     -0.8671920   -0.4916620    0.3938040
C     -1.5760040   0.4711890    1.1273470
C     -1.5186940   -1.1475590   -0.6630480
C     -2.9044020   0.7751410    0.8117550
H     -1.0912900   0.9815950    1.9557640
C     -2.8451130   -0.8455530   -0.9812380
H     -0.9884110   -1.9045210   -1.2357550
C     -3.5419630   0.1187320   -0.2446900
H     -3.4389460   1.5206960    1.3931920

```

H	-3.3349500	-1.3653710	-1.7995070
H	-4.5739020	0.3521650	-0.4897160
<i>anti-18b.log</i>			
Potential Energy = -2233.51758			
Zero-point Energy = -2232.98167			
Free Energy = -2233.02959			
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -			
2234.10584			
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated			
free energy from qRRHO) = -2233.61785			
Charge = 0 Multiplicity = 1			
C	2.9544110	-1.3243090	-0.1002390
C	2.6737200	-1.0248020	-2.4146860
C	1.2861080	-0.9717320	-1.7662800
N	1.5980950	-0.7775800	-0.3211500
N	3.5820770	-1.2046860	-1.4325050
O	2.9203350	-0.9234620	-3.6224130
C	5.0134190	-1.1134380	-1.6842030
H	5.1836440	-0.3621570	-2.4593090
H	5.5253020	-0.8071010	-0.7707000
H	5.4351900	-2.0639150	-2.0263420
C	1.1601280	0.4374230	0.3404310
H	0.3598170	0.8508330	-0.2698600
C	2.1727410	1.5931060	0.6006320
C	1.5711680	2.8738550	1.2239240
H	2.9882220	1.2656280	1.2385760
C	0.3481590	0.0148920	-2.4544380
H	0.2497460	-0.3008260	-3.4963020
H	-0.6456830	-0.0052230	-2.0011390
H	0.7316020	1.0374070	-2.4508190
H	0.8403080	-1.9676590	-1.8862410
C	2.9920850	-2.7955900	0.4603130
H	3.5033230	-0.6969110	0.6093060
Cl	2.9889070	2.0185560	-0.9878270
N	0.4561460	0.1057430	1.6282660
C	-0.8689050	-0.2899060	1.6061870
C	1.0027610	0.0243020	2.9227410
C	-1.3205100	-0.6577570	3.0003200
C	-0.0875620	-0.4183520	3.8791330
H	-2.1800740	-0.0388340	3.2724590
H	0.2508230	-1.3118100	4.4098930
O	2.1594890	0.2819190	3.2006630
O	-1.5423060	-0.3195560	0.5749050
C	4.4627100	-3.2144140	0.6854470
H	4.4913280	-4.1686520	1.2217670
H	5.0041870	-3.3548050	-0.2529580
H	5.0057940	-2.4792860	1.2909420
C	2.2740340	-2.8443600	1.8201050
H	2.7394210	-2.1719470	2.5471310
H	1.2181620	-2.5809810	1.7167860
H	2.3244460	-3.8599290	2.2264840
C	2.3239680	-3.8080880	-0.4893400
H	2.7638430	-3.7836250	-1.4915270
H	2.4608660	-4.8210290	-0.0954640
H	1.2471240	-3.6338460	-0.5724800
H	-0.2359960	0.3689890	4.6234600
H	-1.6550560	-1.6994000	2.9974680
H	1.2757670	2.6240190	2.2471820
H	2.3980390	3.5847990	1.3163060
C	0.4065630	3.5349510	0.5084340
C	0.6201740	4.4235060	-0.5591730
C	-0.9140560	3.3119760	0.9288940
C	-0.4534840	5.0446110	-1.2028800
H	1.6335620	4.6367890	-0.8838850
C	-1.9919960	3.9311240	0.2883140
H	-1.1052070	2.6642240	1.7796120
C	-1.7651810	4.7961960	-0.7853020
H	-0.2640870	5.7284080	-2.0254310
H	-3.0042010	3.7429140	0.6345360
H	-2.5995260	5.2811400	-1.2835530
H	-3.0867530	-0.7157070	0.4958220
O	-4.0733650	-0.9489840	0.4995030
C	-4.5537260	-1.1134290	-0.7126060
O	-3.9714420	-1.0230510	-1.7711010
C	-6.0670080	-1.4618580	-0.6463300

F -6.2729370 -2.5907890 0.0682100
F -6.5734600 -1.6497260 -1.8741570
F -6.7646690 -0.4665610 -0.0540270

Int3'.log
Potential Energy = -2233.46721
Zero-point Energy = -2232.93678
Free Energy = -2232.98830
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.03863
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.55972
Charge = 0 Multiplicity = 1

C -2.6266560 2.4503800 0.7784270
C -1.5223420 3.9157680 -0.7036390
C -1.4995120 2.5479870 -1.3843830
N -2.3190760 1.7439350 -0.4755820
N -2.2467700 3.8256180 0.4340010
O -1.0229690 4.9494330 -1.1588150
C -2.6800680 5.0203450 1.1497690
H -2.8929100 5.8029220 0.4180380
H -3.5873750 4.7972780 1.7119570
H -1.9141910 5.3914730 1.8372380
C -2.8890640 0.5278930 -0.7748120
H -3.7156960 0.2693140 -0.1181140
C -2.5480320 -0.3347000 -1.7643380
C -3.3463400 -1.5718740 -2.1430910
H -2.6565380 -2.4200540 -2.2465020
H -0.4627090 2.1815710 -1.4321660
C -1.8870200 1.8911850 2.0517060
H -3.7091810 2.4089470 0.9711340
H -1.7300520 -0.0962950 -2.4377340
Cl -0.2363270 -1.6516930 -0.4739190
N 1.1471420 -2.5417150 0.0763850
C 1.0363910 -3.7776350 0.7502140
C 2.4420110 -2.1007200 -0.1074630
C 2.4506000 -4.2249380 1.0669680
C 3.3713980 -3.1349220 0.4890930
H 2.6145650 -5.2083090 0.6189150
H 4.0294480 -3.5060380 -0.3019760
H 4.0006990 -2.6479780 1.2388360
H 2.5447700 -4.3343510 2.1507180
O 2.7320410 -1.0465780 -0.6668220
O -0.0138360 -4.3256460 1.0012080
C -2.0489010 2.7048910 -2.8121990
H -1.9815400 1.7816430 -3.3867170
H -3.0954690 3.0247850 -2.7883540
H -1.4596170 3.4710050 -3.3225100
C -2.2691950 2.7253540 3.2945580
H -1.8821820 2.2333710 4.1930320
H -1.8471390 3.7320160 3.2716330
H -3.3566490 2.8076790 3.4083120
C -0.3611380 1.9234840 1.8549500
H 0.0052410 2.9433680 1.6973150
H 0.1375190 1.5274920 2.7461530
H -0.0552940 1.3089460 1.0025880
C -2.3435480 0.4409220 2.3163490
H -3.4336810 0.3733900 2.4148440
H -2.0249580 -0.2464270 1.5305160
H -1.9061550 0.0909070 3.2574030
H -3.7735670 -1.4198290 -3.1449540
C -4.4630630 -1.9580020 -1.1934430
C -4.2095650 -2.7655950 -0.0733220
C -5.7776370 -1.5172080 -1.4116650
C -5.2380530 -3.1213360 0.8046880
H -3.1989240 -3.1217310 0.1094840
C -6.8105050 -1.8690560 -0.5363640
H -5.9948610 -0.8965530 -2.2779170
C -6.5434660 -2.6727920 0.5765620
H -5.0208980 -3.7518150 1.6625460
H -7.8216360 -1.5197980 -0.7265350
H -7.3442960 -2.9510480 1.2556610
H 4.2053280 -0.4257260 -0.8220110
O 5.0824190 0.0408130 -1.0131430
C 5.8752080 0.0342720 0.0349300
C 7.2094610 0.7594330 -0.2931800

O 5.6676980 -0.4490210 1.1269470
F 8.0263500 0.7706310 0.7706260
F 6.9854230 2.0395260 -0.6632370
F 7.8535440 0.1423900 -1.3090260

syn-18b'.log
Potential Energy = -2233.51380
Zero-point Energy = -2232.97812
Free Energy = -2233.02594
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.10139
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.61352
Charge = 0 Multiplicity = 1

C -1.8564840 1.5162690 0.5390720
C -1.0558940 2.6485280 -1.3582430
C -0.1829640 1.4019620 -1.2095780
N -0.9067160 0.6342080 -0.1733550
N -2.0258090 2.6159430 -0.4207840
O -0.9212940 3.5198530 -2.2252900
C -3.1410830 3.5545640 -0.4437960
H -3.4066970 3.7491130 -1.4854550
H -3.9969730 3.1142900 0.0687400
H -2.8902920 4.5085310 0.0301960
C -1.0612310 -0.7812760 -0.0359600
H -1.8517260 -0.9152110 0.7038930
C -1.5783720 -1.5790380 -1.2979850
C -2.8512570 -2.4065590 -1.0185230
H -3.0719650 -2.9743660 -1.9274720
H -2.6487100 -3.1254320 -0.2211320
H 0.7991750 1.7077950 -0.8262900
C -1.3904810 2.0009280 1.9626020
H -2.8191090 1.0018620 0.6615780
H -1.7776430 -0.8680320 -2.0928030
Cl -0.3275230 -2.7195670 -2.0195620
N 0.0848200 -1.4904980 0.6317360
C 1.4339680 -1.3187860 0.4183320
C -0.1690210 -2.4815330 1.6010800
C 2.2146990 -2.2500960 1.3207470
C 1.1506810 -3.0198380 2.1098960
H 2.8814030 -1.6518450 1.9479080
H 1.2054580 -2.8544120 3.1894060
H 1.1792360 -4.0995380 1.9408560
H 2.8423160 -2.8932250 0.6971150
O -1.2894440 -2.8115390 1.9446560
O 1.9138040 -0.5184570 -0.3868330
C 0.0511510 0.7837330 -2.5922080
H 0.6112370 -0.1475030 -2.5244570
H -0.8787650 0.6189110 -3.1435800
H 0.6483590 1.4966790 -3.1666690
C -2.4786610 2.8953560 2.5975720
H -2.2209090 3.0933550 3.6432880
H -2.5698340 3.8628330 2.0997370
H -3.4604050 2.4073440 2.5879680
C -0.0648890 2.7789510 1.8839380
H -0.1531690 3.6705170 1.2544100
H 0.2311490 3.1102370 2.8851610
H 0.7420380 2.1532840 1.4901630
C -1.2053860 0.7767440 2.8805530
H -2.1085340 0.1571530 2.9235220
H -0.3682180 0.1546080 2.5592900
H -0.9889660 1.1118390 3.9001410
C -4.0529870 -1.5514520 -0.6573110
C -4.5709550 -1.5493350 0.6468020
C -4.6867750 -0.7619670 -1.6317890
C -5.6921380 -0.7773260 0.9717230
H -4.0977860 -2.1612420 1.4099460
C -5.8037200 0.0125290 -1.3099850
H -4.3115380 -0.7612590 -2.6524120
C -6.3102680 0.0075480 -0.0051020
H -6.0808200 -0.7928670 1.9859130
H -6.2821950 0.6137970 -2.0777230
H -7.1812400 0.6063630 0.2446450
H 3.4502220 -0.2769000 -0.6037500
O 4.4160170 -0.0882660 -0.8688960
C 5.1693500 0.1863350 0.1700780

O 4.8473470 0.2370470 1.3382510
C 6.6331210 0.4522780 -0.2786510
F 7.1571450 -0.6422470 -0.8755220
F 7.4107460 0.7653100 0.7688980
F 6.6924280 1.4722900 -1.1630920

anti-18b'.log

Potential Energy = -2233.51605

Zero-point Energy = -2232.98059

Free Energy = -2233.02877

Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.10308

Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.61580

Charge = 0 Multiplicity = 1

C 0.9018130 -1.7271780 -0.9590970
C 2.4756080 -3.2785000 -0.1497600
C 3.0426390 -1.8960290 0.1790040
N 1.9167800 -1.0052690 -0.1549570
N 1.2443790 -3.1291900 -0.6785010
O 3.0338980 -4.3558530 0.0873170
C 0.3585820 -4.2708350 -0.8738650
H 0.4963440 -4.9633590 -0.0401170
H -0.6762420 -3.9277280 -0.8893740
H 0.5722030 -4.8069730 -1.8036170
C 1.5887340 0.2349000 0.4577310
H 0.8024540 0.6880210 -0.1443410
C 2.7428850 1.2705370 0.5925640
C 2.2931770 2.7013300 0.9653110
H 3.8953800 -1.6988840 -0.4877090
C 0.8984730 -1.3844450 -2.4960980
H -0.0999910 -1.5210680 -0.5714640
H 3.4602480 0.9458330 1.3377040
Cl 3.7155140 1.3128120 -0.9603400
N 0.8896240 0.1186550 1.8360340
C -0.4775180 -0.0786710 1.8911410
C 1.4383610 0.2043890 3.1366820
C -0.9379850 -0.2106690 3.3231400
C 0.3393300 -0.0530850 4.1501510
H -1.4254750 -1.1817840 3.4484310
H 0.5984260 -0.9502620 4.7198330
H 0.3062870 0.7840970 4.8517100
H -1.6868140 0.5603480 3.5259430
O 2.5997200 0.4617410 3.3900420
O -1.1957140 -0.1241950 0.8879040
C 3.5652060 -1.9190910 1.6186660
H 4.0298040 -0.9785590 1.9114540
H 2.7745400 -2.1596200 2.3342630
H 4.3238850 -2.7037970 1.6778550
C -0.2001170 -2.2026000 -3.2121960
H -0.3065260 -1.8417970 -4.2407180
H 0.0367120 -3.2670730 -3.2679150
H -1.1747160 -2.0894060 -2.7227090
C 2.2628350 -1.6837230 -3.1419500
H 2.5285200 -2.7427290 -3.0547750
H 2.2294550 -1.4401900 -4.2096240
H 3.0573670 -1.0849130 -2.6881600
C 0.5531480 0.1073580 -2.6889910
H -0.3975130 0.3669720 -2.2088240
H 1.3348850 0.7640070 -2.3033150
H 0.4480280 0.3201950 -3.7583010
H 1.8484580 2.6465940 1.9637900
H 3.2072590 3.2922480 1.0751620
C 1.3379770 3.4111440 0.0244960
C -0.0499260 3.3584040 0.2285570
C 1.8218200 4.1743640 -1.0510960
C -0.9315460 4.0268550 -0.6267690
H -0.4502530 2.8041740 1.0727480
C 0.9452390 4.8453150 -1.9079790
H 2.8926520 4.2496740 -1.2140470
C -0.4362110 4.7700890 -1.7015760
H -2.0013360 3.9721500 -0.4470400
H 1.3418590 5.4314920 -2.7320840
H -1.1181100 5.2937830 -2.3651760
H -2.7786970 -0.3152100 0.9029630
O -3.7789470 -0.4726670 0.9595420

C -4.3987220 -0.1648870 -0.1577250
O -3.9247170 0.2621700 -1.1875490
C -5.9241100 -0.4246520 -0.0130270
F -6.1675200 -1.7218550 0.2795830
F -6.5747430 -0.1260870 -1.1474420
F -6.4488920 0.3273980 0.9804430

Int4'.log

Potential Energy = -2233.52515

Zero-point Energy = -2232.99167

Free Energy = -2233.04178

Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.09953

Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.61616

Charge = 0 Multiplicity = 1

C 0.5057100 2.0118400 -0.5734890
C 0.3276840 3.3585180 1.3565140
C -1.0855050 2.7958810 1.1348800
N -0.8166260 1.7463180 0.1044920
N 1.1647370 2.8349480 0.4340460
O 0.6298980 4.1230640 2.2678620
C 2.6145810 3.0071770 0.5321140
H 2.8852540 3.0151490 1.5896410
H 3.1158550 2.1749730 0.0372260
H 2.9390320 3.9491610 0.0818730
C -1.5083000 0.7082520 -0.2162790
H -1.0354380 0.0051190 -0.9134190
C -2.8825480 0.3440270 0.2850680
C -3.3183950 -1.0261410 -0.2557360
H -1.7141450 3.5636590 0.6713470
C 0.3429650 2.6831150 -1.9874170
H 1.0172930 1.0476930 -0.6744390
H -2.9127650 0.3481070 1.3739920
Cl -4.0387350 1.6686030 -0.2374650
N 4.1818220 -1.1429250 0.8940540
C 5.1854980 -0.2369080 0.6041840
C 4.4671940 -1.9680830 1.9676810
C 6.3226990 -0.4512430 1.5935500
C 5.8474520 -1.6016200 2.4963740
H 6.4992380 0.4816390 2.1363920
H 5.7598100 -1.3191690 3.5492430
H 6.4903840 -2.4849620 2.4477020
H 7.2358910 -0.6838740 1.0385110
O 3.7176470 -2.8341710 2.3972670
O 5.1367910 0.5887320 -0.2980960
C -1.6968020 2.3327890 2.4554620
H -2.7738770 2.1839050 2.3853990
H -1.2109470 1.4286240 2.8312870
H -1.5208150 3.1359420 3.1748650
C 1.7610040 2.8547710 -2.5811740
H 1.6713370 3.1987690 -3.6158120
H 2.3504620 3.5985690 -2.0418160
H 2.3141190 1.9098220 -2.5910260
C -0.3487320 4.0560700 -1.9052010
H 0.1737970 4.7412470 -1.2304970
H -0.3536470 4.5155160 -2.8983030
H -1.3930290 3.9735300 -1.5873380
C -0.4549220 1.7575590 -2.9283600
H -0.0329230 0.7485720 -2.9690800
H -1.5111910 1.6845070 -2.6506810
H -0.4257660 2.1741260 -3.9396110
H -2.5049960 -1.7207440 -0.0113130
H -3.3780880 -0.9798880 -1.3470230
C -4.6195300 -1.5323630 0.3304670
C -5.8015790 -1.5146080 -0.4228450
C -4.6613630 -2.0372810 1.6398420
C -7.0023260 -1.9818210 0.1212780
H -5.7830340 -1.1361010 -1.4412540
C -5.8598210 -2.5017960 2.1875380
H -3.7509370 -2.0771790 2.2333410
C -7.0352610 -2.4738830 1.4291480
H -7.9083690 -1.9622140 -0.4773790
H -5.8739030 -2.8915890 3.2012100
H -7.9665830 -2.8384240 1.8525320
O -0.1177520 -1.6251080 -1.6863120

H	3.2990100	-1.1972780	0.3561010
C	1.0348540	-1.7967120	-1.2376970
O	1.7120970	-1.0605120	-0.4795400
C	1.7065260	-3.1343570	-1.7007020
F	1.0135460	-4.2109070	-1.2423040
F	2.9815280	-3.2776250	-1.2715580
F	1.7351460	-3.2311330	-3.0554200

```

Int4a'.log
Potential Energy = -1949.25759
Zero-point Energy = -1948.79233
Free Energy = -1948.83881
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -
1949.75178
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated
free energy from qRRHO) = -1949.33300
Charge = 0 Multiplicity = 1
C      3.3793040   -0.3438340   -0.6281640
C      3.0655760   -1.7154410    1.2670310
C      2.0713280   -0.5588050    1.4469340
N      2.1267590   0.0767900    0.0955720
N      3.7079030   -1.5715620    0.0841130
O      3.2075540   -2.6371710    2.0632940
C      4.5314220   -2.6463780   -0.4699910
H      4.0957420   -3.5999170   -0.1666090
H      4.5296550   -2.5780160   -1.5581430
H      5.5601560   -2.5981440   -0.1046600
C      1.2463370   0.7983050   -0.5085210
H      1.4831790   1.0792040   -1.5273280
C     -0.0153530   1.3863510    0.0716440
C     -0.8112710   2.1515590   -0.9940500
H     -0.1991810   2.9712710   -1.3824930
H      2.4811850   0.1582300    2.1664910
C      4.4970840   0.7601150   -0.6261380
H      3.0958370   -0.5743460   -1.6597580
H     -0.6306090   0.6118450    0.5263510
Cl     0.4814650   2.4992290    1.4445480
C      0.7142870   -1.0725110    1.9225470
H      0.0921170   -0.2741970    2.3267010
H      0.1770710   -1.6039630    1.1334990
H      0.9171910   -1.7758980    2.7336140
C      5.7146760   0.2024240   -1.3989070
H      6.4513870   1.0019410   -1.5196940
H      6.2062700   -0.6138700   -0.8665150
H      5.4385350   -0.1465920   -2.3998790
C      4.9252890   1.1383090    0.8036840
H      5.2627510   0.2666420    1.3727740
H      5.7620170   1.8415450    0.7547120
H      4.1218280   1.6338760    1.3579490
C      4.0029380   2.0184970   -1.3694640
H      3.6566680   1.7884750   -2.3836170
H      3.2070660   2.5427280   -0.8326210
H      4.8347470   2.7229210   -1.4617320
H     -0.9668460   1.4411140   -1.8146340
C     -2.1478430   2.6722430   -0.5071500
C     -2.3787170   4.0488380   -0.3837030
C     -3.1831380   1.7791330   -0.1860950
C     -3.6168370   4.5283550    0.0572630
H     -1.5877290   4.7508080   -0.6342430
C     -4.4186690   2.2564510    0.2584840
H     -3.0231550   0.7078980   -0.2857540
C     -4.6396370   3.6328990    0.3816820
H     -3.7793100   5.5986310    0.1463910
H     -5.2101650   1.5537520    0.5027270
H     -5.6016240   4.0029630    0.7242030
O      0.1323700   -1.0197810   -1.9114570
H     -0.7084270   -1.3127920   -1.4605150
O     -2.0214000   -1.6607310   -0.4697650
C     -2.8574200   -2.4955140   -0.9143120
O     -2.8958700   -3.0930550   -2.0015370
C     -4.0140370   -2.7960410    0.1011900
F     -4.6918040   -1.6631090    0.4324370
F     -3.5308240   -3.3170380    1.2624030
F     -4.9305710   -3.6737670   -0.3663180
H     -0.0882440   -0.9181980   -2.8470760

```

```

Int5'.log
Potential Energy = -1949.26099
Zero-point Energy = -1948.79335
Free Energy = -1948.83855
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -
1949.75299
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated
free energy from qRRHO) = -1949.33054
Charge = 0 Multiplicity = 1
C      3.1423700   -0.4627680   -0.5876620
C      2.9921210   -1.5649160    1.4859430
C      2.1576970   -0.2863180    1.6051260
N      2.0736570   0.1905140    0.2039530
N      3.4923300   -1.6309230    0.2328640
O      3.1703980   -2.3979020    2.3809440
C      4.2071650   -2.8073760   -0.2464530
H      3.7892620   -3.6889490    0.2444790
H      4.0751140   -2.8992690   -1.3256940
H      5.2768250   -2.7614000   -0.0201730
C      0.8585870   0.4326410   -0.4897690
H      1.1289170   0.7414440   -1.5018270
C     -0.1027130   1.5014070    0.0885170
C     -1.0741420   2.0110830   -0.9896530
H     -0.5034910   2.5569490   -1.7480220
H      2.7526370   0.4336970    2.1851800
C      4.3400090   0.4921030   -0.9247020
H      2.7382860   -0.8231920   -1.5436500
H     -0.6570520   1.0883880    0.9294940
Cl     0.8293510    2.9065140    0.7952750
C      0.8714750   -0.5461420    2.3909940
H      0.3586270   0.3833330    2.6444180
H      0.1875730   -1.2113390    1.8614600
H      1.1583290   -1.0288010    3.3289790
C      5.3866790   -0.2467700   -1.7861810
H      6.1276800   0.4709600   -2.1537010
H      5.9280450   -1.0101580   -1.2225320
H      4.9283600   -0.7234670   -2.6607870
C      5.0109370   1.0273390    0.3528200
H      5.3934650   0.2149320    0.9800920
H      5.8600520   1.6656520    0.0857520
H      4.3166790   1.6300500    0.9455750
C      3.7922260   1.6745430   -1.7507400
H      3.3130630   1.3313720   -2.6761220
H      3.0688460   2.2622880   -1.1800780
H      4.6158060   2.3377890   -2.0356930
H     -1.4886810   1.1219530   -1.4780330
C     -2.2063340   2.8713970   -0.4668650
C     -2.2318620   4.2527590   -0.7052430
C     -3.2628110   2.2970000    0.2587190
C     -3.2803140   5.0446410   -0.2249160
H     -1.4262070   4.7128840   -1.2712090
C     -4.3102960   3.0845900    0.7433830
H     -3.2718190   1.2249810    0.4405740
C     -4.3220010   4.4631320    0.5034780
H     -3.2819480   6.1130930   -0.4210960
H     -5.1194000   2.6215280    1.3010730
H     -5.1375710   5.0758540    0.8764310
O     -0.0120260   -0.7576120   -0.6406340
H     -1.4565980   -1.3224630   -0.1375430
O     -2.3365630   -1.7312320    0.1332700
C     -2.6225620   -2.7602200   -0.6360220
O     -1.9677270   -3.2072360   -1.5521230
C     -3.9846380   -3.3826390   -0.2247640
F     -4.9855390   -2.4886020   -0.3857620
F     -3.9724210   -3.7606370    1.0718730
F     -4.2650080   -4.4608080   -0.9709960
H      0.2688110   -1.2766220   -1.4085040

```


Transition States

Formation of carbinol amine (TS1)

Conformation name	Extrapolated Free energy (kcal/mol)	
TS1-lowest	0.0	
1	0.9	
2	0.1	
3	1.5	
4	2.3	
5	1.4	
6	1.5	
7	0.5	

TS1-lowest.log
Potential Energy = -1489.66362
Zero-point Energy = -1489.18887
Free Energy = -1489.23186
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.12258
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.69083
Nimag = 1 (-162.6618)
Charge = 0 Multiplicity = 1

C	1.8517090	-0.8511400	1.6926950
H	2.0070440	-1.7005300	1.0261210
H	1.4013680	-1.2130030	2.6208840
C	3.2250410	-0.2001630	2.0381640
C	0.9361530	0.1470150	1.0546780
O	0.4214710	1.0438850	1.8105020
H	-0.0740900	1.8766850	1.2616730
H	1.0578790	0.3821560	-0.0013810
O	-0.6648440	2.8873570	0.6484180
C	-1.7764790	2.5928830	0.0968280
C	-2.4661420	3.8293810	-0.5562970
F	-1.7045350	4.3270220	-1.5635700
F	-3.6739420	3.5343710	-1.0747810
F	-2.6448290	4.8269570	0.3433280
O	-2.3375590	1.4956530	0.0125340
H	3.7872370	-0.9518640	2.6022390
C	4.0319780	0.2445030	0.8336160
C	4.7148170	-0.6966460	0.0456070
C	4.1130900	1.5989250	0.4760850
C	5.4509620	-0.2970820	-1.0728450
H	4.6757730	-1.7500000	0.3134110
C	4.8487960	2.0035020	-0.6431880
H	3.6020130	2.3446700	1.0800220
C	5.5186850	1.0561710	-1.4225760
H	5.9752980	-1.0401360	-1.6670750
H	4.9001820	3.0573670	-0.9016440
H	6.0926470	1.3683920	-2.2901460
H	3.0559370	0.6454640	2.7114060
N	-0.8125710	-1.0379910	0.5345580
C	-1.2744170	-1.9646060	1.6063180
C	-1.2471790	-1.6343010	-0.7795250
C	-2.4527290	-2.6943130	0.9517430
H	-0.4871050	-2.6962800	1.8190460
H	-1.5765160	-0.8042420	-1.4129600
O	-3.2962320	-3.3773790	1.5380340
N	-2.4280920	-2.4223760	-0.3733750
C	-3.5480770	-2.7692240	-1.2427410
H	-3.4840610	-3.7987480	-1.6069870
H	-4.4743010	-2.6615600	-0.6736720
H	-3.5688350	-2.0892630	-2.0952580
C	-0.1805590	-2.4460100	-1.5841700
C	-0.8325990	-2.9522400	-2.8928420
H	-1.5888910	-3.7185880	-2.7126240

H	-1.2928600	-2.1352340	-3.4600700
H	-0.0615370	-3.4008130	-3.5269190
C	0.9802190	-1.5134500	-1.9876800
H	0.6135150	-0.5892060	-2.4491230
H	1.6204850	-1.2506450	-1.1449520
H	1.6167270	-2.0179160	-2.7214270
C	0.3584270	-3.6590820	-0.8036040
H	-0.4461780	-4.3447160	-0.5187960
H	1.0597230	-4.2178330	-1.4320280
H	0.8974220	-3.3659480	0.1013920
C	-1.6886230	-1.2641990	2.8982030
H	-0.8400980	-0.7734750	3.3776320
H	-2.4619780	-0.5130660	2.7077140
H	-2.0961040	-2.0077730	3.5874050
H	-1.3774290	-0.1821550	0.6063230

1.log
Potential Energy = -1489.66305
Zero-point Energy = -1489.18786
Free Energy = -1489.23113
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.12134
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68941
Nimag = 1 (-133.0078)
Charge = 0 Multiplicity = 1

C	1.3952340	-2.0585190	-0.2956850
H	0.6543910	-2.7384950	-0.7173550
H	1.5549830	-2.3234810	0.7525740
C	2.7223600	-2.2428810	-1.0968820
C	0.8997970	-0.6508130	-0.3909580
O	1.3984420	0.2147100	0.4164610
H	1.1683160	1.2481300	0.1533250
H	0.5363960	-0.2916880	-1.3530400
O	0.9013840	2.5506950	-0.1393410
C	-0.3032820	2.9011140	0.0743550
C	-0.5365840	4.4259900	-0.1568090
F	-0.1999490	4.7857890	-1.4207210
F	-1.8194550	4.7914340	0.0351080
F	0.2243440	5.1668250	0.6875980
O	-1.2666370	2.2105270	0.4283730
H	2.8918930	-3.3241100	-1.1457100
N	-1.1276380	-0.7687640	0.3082940
C	-1.3055380	-1.5724850	1.5509810
C	-2.4312110	-0.8364550	-0.4483670
C	-2.8214460	-1.5322140	1.7740390
H	-1.0095870	-2.6095680	1.3581450
H	-2.5984200	0.1555130	-0.8803050
O	-3.4079200	-1.8478030	2.8120990
N	-3.3967640	-1.0496250	0.6482010
C	-4.8041900	-0.6638800	0.6185940
H	-5.4600800	-1.5120210	0.4016090
H	-5.0726100	-0.2620670	1.5982070
H	-4.9529060	0.1066340	-0.1388470
C	-2.5387860	-1.8794290	-1.6086610
C	-3.9394450	-1.7492500	-2.2536400
H	-4.7378150	-2.0848270	-1.5891580
H	-4.1510560	-0.7185810	-2.5600750
H	-3.9800800	-2.3751560	-3.1504490
C	-1.5046070	-1.5463420	-2.7040070
H	-1.5451900	-0.4889660	-2.9901390
H	-0.4842290	-1.7870390	-2.4039890
H	-1.7176530	-2.1381650	-3.5997510
C	-2.3545080	-3.3304070	-1.1269920
H	-3.0841800	-3.5945350	-0.3548720
H	-2.5005830	-4.0171980	-1.9671150
H	-1.3524710	-3.5143660	-0.7299250
C	-0.5396960	-1.0353980	2.7574440
H	0.5391090	-1.1023900	2.6092910
H	-0.7993970	0.0094530	2.9558850
H	-0.8087180	-1.6271620	3.6357470
H	-1.0704100	0.2198650	0.5867710
H	2.5724970	-1.9048860	-2.1277910
C	3.9415430	-1.5664760	-0.5046010
C	4.5174920	-0.4455590	-1.1196000
C	4.5319200	-2.0612450	0.6699130

C 5.6483880 0.1720030 -0.5743510
H 4.0795290 -0.0518050 -2.0335340
C 5.6601160 -1.4472440 1.2192630
H 4.1094150 -2.9371500 1.1568430
C 6.2224610 -0.3258920 0.5986110
H 6.0789280 1.0392140 -1.0670180
H 6.1030400 -1.8465780 2.1273130
H 7.1009810 0.1509690 1.0234210

2.log
Potential Energy = -1489.66496
Zero-point Energy = -1489.19036
Free Energy = -1489.23392
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.12166
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.69061
Nimag = 1 (-159.5359)
Charge = 0 Multiplicity = 1

C -1.9653850 -0.7125110 0.1104430
H -2.2411440 0.1988790 -0.4212960
H -2.1445120 -0.5648650 1.1787030
C -2.8470350 -1.8908900 -0.4008790
C -0.5229010 -1.0335570 -0.1203970
O 0.0367360 -1.8601330 0.6826190
H 1.0298210 -2.2281050 0.3435010
H -0.1213740 -0.9566050 -1.1303810
O 2.2120980 -2.6975850 -0.0244520
C 3.1570820 -1.8426210 0.0234930
C 4.5447200 -2.4646840 -0.3217580
F 4.5342030 -3.0264980 -1.5560110
F 5.5386610 -1.5555300 -0.3030570
F 4.8723890 -3.4403360 0.5616880
O 3.1057220 -0.6393620 0.2981610
H -2.5724640 -2.7984990 0.1452100
N 0.4916070 0.8218670 0.3783950
C 0.0210830 1.4512440 1.6441730
C 1.0179580 1.9310480 -0.4958790
C 0.8347450 2.7483000 1.7117850
H -1.0395140 1.7097530 1.5494400
H 1.9127700 1.5458770 -0.9956940
O 0.9590800 3.4734240 2.7019940
N 1.4256300 2.9337000 0.5087110
C 2.4563230 3.9488180 0.3158100
H 2.0310410 4.9303660 0.0868400
H 3.0373150 4.0309630 1.2372090
H 3.1154660 3.6457920 -0.4985480
C 0.0622600 2.4852040 -1.6026320
C 0.8123240 3.5825990 -2.3948410
H 0.9933910 4.4785980 -1.7981010
H 1.7723400 3.2206810 -2.7801410
H 0.2043280 3.8831080 -3.2538160
C -0.2800470 1.3605290 -2.6019440
H 0.6199480 0.8382900 -2.9466160
H -0.9699960 0.6257350 -2.1856990
H -0.7691490 1.7898930 -3.4819870
C -1.2290100 3.0931700 -1.0243210
H -1.0129680 3.9051040 -0.3225060
H -1.8332580 3.5114700 -1.8359840
H -1.8458440 2.3506050 -0.5110750
C 0.2293250 0.5859890 2.8846950
H -0.3797080 -0.3185910 2.8485190
H 1.2793060 0.2939310 2.9886820
H -0.0545900 1.1629750 3.7680840
H 1.3318110 0.2729610 0.6003710
H -2.6324740 -2.0687120 -1.4604280
C -4.3223640 -1.6003290 -0.2190490
C -5.0609430 -0.9706910 -1.2326460
C -4.9755740 -1.9366720 0.9767510
C -6.4176120 -0.6818430 -1.0564020
H -4.5726070 -0.7097480 -2.1685520
C -6.3319600 -1.6495970 1.1570440
H -4.4201830 -2.4318310 1.7696800
C -7.0575310 -1.0197750 0.1404570
H -6.9738930 -0.1981590 -1.8543470
H -6.8215800 -1.9217310 2.0878040

H -8.1120450 -0.7989810 0.2778100

3.log
Potential Energy = -1489.66343
Zero-point Energy = -1489.18829
Free Energy = -1489.23175
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.12013
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68845
Nimag = 1 (-134.5445)
Charge = 0 Multiplicity = 1

C 0.1158290 1.5392610 1.6073560
C 1.0535020 1.9694490 -0.5663780
N 0.5247230 0.8806700 0.3344090
H -0.9273680 1.8642190 1.5300780
H 1.9136050 1.5587500 -1.1056700
C 1.0069150 2.7861640 1.6512620
O 1.2218000 3.4885800 2.6418120
N 1.5450560 2.9536430 0.4207820
C 2.6384300 3.8931390 0.1888380
H 3.2476740 3.5395480 -0.6441380
H 2.2774370 4.9002950 -0.0365010
H 3.2526940 3.9387560 1.0909630
C 0.2879640 0.6636660 2.8452930
H 0.1017610 1.2715150 3.7339240
H -0.4207850 -0.1679470 2.8532270
H 1.3043170 0.2629820 2.9109990
C 0.0664120 2.5514000 -1.6273220
C -1.2722050 2.9985010 -1.0113870
H -1.8943810 3.4595720 -1.7854940
H -1.8380170 2.1618160 -0.5955010
H -1.1242470 3.7456830 -0.2244040
C 0.7197470 3.7750080 -2.3101550
H 1.7203950 3.5448820 -2.6925890
H 0.1038910 4.0775210 -3.1630600
H 0.7914970 4.6339780 -1.6390470
C -0.1682280 1.4909240 -2.7222320
H -0.8412390 1.8946020 -3.4857400
H 0.7736790 1.2247730 -3.2161180
H -0.6082060 0.5724040 -2.3362380
C -1.9709030 -0.6179270 -0.0808880
H -2.1935420 0.0568850 0.7484680
H -2.2433430 -0.1318410 -1.0198380
C -2.8099060 -1.9206870 0.0889800
H -2.5064330 -2.4288810 1.0108070
H -2.5875930 -2.5941300 -0.7445000
C -4.2939570 -1.6210990 0.1331700
C -4.9401730 -1.3711560 1.3534460
C -5.0480160 -1.5663330 -1.0492530
C -6.3055840 -1.0725170 1.3926090
H -4.3725720 -1.4163920 2.2798190
C -6.4134370 -1.2679730 -1.0144090
H -4.5646570 -1.7643240 -2.0029570
C -7.0466970 -1.0189630 0.2076770
H -6.7896870 -0.8867430 2.3471900
H -6.9817740 -1.2346870 -1.9396030
H -8.1080450 -0.7902490 0.2366440
C -0.5188640 -0.9695350 -0.0842710
O -0.0044950 -1.4388050 -1.1606430
H 0.9783100 -1.8940480 -1.0063830
H -0.0781410 -1.2928620 0.8601760
O 2.1835600 -2.4978020 -0.8542280
C 3.0198630 -1.9252290 -0.0855850
C 4.3939740 -2.6617440 -0.0366060
F 4.2445780 -3.9552450 0.3411570
F 5.2596090 -2.0903500 0.8234370
F 4.9828430 -2.6652880 -1.2593220
H 1.3577620 0.3139080 0.5441370
O 2.8862970 -0.9005130 0.5951460

4.log
Potential Energy = -1489.66173
Zero-point Energy = -1489.18580
Free Energy = -1489.22874

Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.12018
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68718
Nimag = 1 (-121.2814)
Charge = 0 Multiplicity = 1

C	-1.9362220	-1.2364370	1.6801090
C	-2.1796150	-1.0106530	-0.7029140
N	-1.2733680	-0.6907640	0.4615470
H	-1.6324250	-2.2789660	1.8237220
H	-2.1490240	-0.1541110	-1.3843020
C	-3.4213220	-1.2158550	1.2978550
O	-4.3713680	-1.3083160	2.0782900
N	-3.5012210	-1.0378190	-0.0417000
C	-4.7660950	-0.7094380	-0.6932850
H	-4.5680000	-0.1213330	-1.5905630
H	-5.3329470	-1.6023130	-0.9704380
H	-5.3681280	-0.1172740	-0.0004970
C	-1.6542950	-0.4426060	2.9523350
H	-2.2940510	-0.8231750	3.7521610
H	-0.6155040	-0.5513770	3.2734460
H	-1.8731220	0.6208580	2.8151330
C	-1.8451250	-2.2889170	-1.5360590
C	-1.6683590	-3.5429540	-0.6599880
H	-1.5115150	-4.4163480	-1.3014640
H	-0.8030050	-3.4674180	0.0023290
H	-2.5580740	-3.7405890	-0.0527110
C	-2.9939460	-2.5542530	-2.5363390
H	-3.2299200	-1.6673810	-3.1348620
H	-2.6871920	-3.3450400	-3.2282410
H	-3.9057640	-2.8922280	-2.0386560
C	-0.5713420	-2.0260140	-2.3645790
H	-0.3424100	-2.9062890	-2.9740740
H	-0.7150750	-1.1784090	-3.0448160
H	0.2985450	-1.8079400	-1.7468610
C	1.3528600	-1.8902930	0.9390880
H	0.6522400	-2.3752630	1.6219580
H	1.4412220	-2.4965700	0.0353980
C	2.7329700	-1.8084870	1.6644330
H	2.6439480	-1.1521750	2.5366990
C	0.8550440	-0.5233020	0.5974070
O	1.2402560	0.0186690	-0.5020880
H	1.0395020	1.0786750	-0.5401520
H	0.6412490	0.1473350	1.4312650
O	0.8261190	2.4459400	-0.6095520
C	-0.2825750	2.8814930	-0.1691350
C	-0.4347940	4.4251500	-0.3373100
F	0.5196980	5.0843330	0.3674700
F	-1.6305060	4.8810610	0.0857210
F	-0.3003110	4.7927030	-1.6357530
H	-1.3240700	0.3360380	0.5288940
O	-1.2156550	2.2637620	0.3625670
C	3.8960150	-1.3657270	0.8005320
C	4.4900060	-0.1076740	0.9767820
C	4.4137930	-2.2163540	-0.1900370
C	5.5676450	0.2963630	0.1811120
H	4.1084510	0.5621850	1.7435190
C	5.4885730	-1.8169100	-0.9881540
H	3.9768520	-3.2016240	-0.3354080
C	6.0691910	-0.5565260	-0.8059420
H	6.0133710	1.2750970	0.3344290
H	5.8757580	-2.4902910	-1.7476500
H	6.9061800	-0.2457170	-1.4243980
H	2.9258150	-2.8152190	2.0510700

5.log
Potential Energy = -1489.66220
Zero-point Energy = -1489.18672
Free Energy = -1489.22968
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.12110
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68857
Nimag = 1 (-135.1105)
Charge = 0 Multiplicity = 1

C	-0.9506580	-1.5101310	1.4119860
---	------------	------------	-----------

C	-2.5037390	-0.6472750	-0.2115040
N	-1.0486660	-0.6657880	0.1871530
H	-0.7896810	-2.5542920	1.1223230
H	-2.7331220	0.3635400	-0.5648450
C	-2.3502470	-1.3896660	2.0265770
O	-2.6633830	-1.6939950	3.1799850
N	-3.1685550	-0.8520290	1.0923590
C	-4.4998500	-0.3613880	1.4371840
H	-4.7744930	0.4465040	0.7574600
H	-5.2580780	-1.1471120	1.3809760
H	-4.4727980	0.0218490	2.4597300
C	0.1417270	-1.0743970	2.3850460
H	0.0366650	-1.6482310	3.3090040
H	1.1402380	-1.2643080	1.9844590
H	0.0544960	-0.0114280	2.6306490
C	-2.9442430	-1.6476250	-1.3270330
C	-2.5017090	-3.0936030	-1.0359880
H	-2.8917740	-3.7585470	-1.8136380
H	-1.4147910	-3.2018790	-1.0301350
H	-2.8931870	-3.4492130	-0.0769160
C	-4.4854180	-1.6271670	-1.4479910
H	-4.8741780	-0.6094870	-1.5652340
H	-4.7800730	-2.1954390	-2.3359620
H	-4.9737760	-2.0904220	-0.5876100
C	-2.3756420	-1.1673930	-2.6776960
H	-2.6929920	-1.8494600	-3.4732130
H	-2.7520950	-0.1681500	-2.9262840
H	-1.2876400	-1.1201150	-2.6874470
C	1.1096270	-1.9785120	-1.3281990
H	0.9421260	-2.6234780	-0.4630040
H	0.4780020	-2.3180930	-2.1515030
C	2.6018870	-2.0914680	-1.7694210
C	0.7744810	-0.5620810	-0.9875260
O	0.5354070	0.2544600	-1.9458940
H	0.5373670	1.3037050	-1.6310900
H	1.1943880	-0.1456740	-0.0716440
O	0.5660670	2.6142610	-1.2937820
C	0.0367510	2.9356870	-0.1825340
C	0.0843970	4.4720070	0.0824530
F	1.3567100	4.9382530	0.0371050
F	-0.4232090	4.8080860	1.2844310
F	-0.6245640	5.1462430	-0.8580260
H	-0.8638080	0.3040120	0.4774330
O	-0.4892300	2.2145280	0.6743470
H	2.7407200	-3.1237140	-2.1082340
C	3.6090200	-1.7690440	-0.6823450
C	3.8457250	-2.6765800	0.3633890
C	4.3228660	-0.5612880	-0.6925260
C	4.7644570	-2.3824600	1.3741940
H	3.3122710	-3.6241060	0.3832510
C	5.2436250	-0.2624630	0.3178150
H	4.1617100	0.1498480	-1.4989880
C	5.4658750	-1.1716340	1.3557890
H	4.9362440	-3.0993380	2.1721110
H	5.7868860	0.6778320	0.2904900
H	6.1816290	-0.9427710	2.1399240
H	2.7653780	-1.4457030	-2.6375060

6.log
Potential Energy = -1489.66343
Zero-point Energy = -1489.18829
Free Energy = -1489.23176
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.12013
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68846
Nimag = 1 (-134.5974)
Charge = 0 Multiplicity = 1

C	0.1157540	1.5393690	1.6073830
C	1.0536400	1.9692590	-0.5663350
N	0.5247270	0.8806120	0.3345420
H	-0.9274310	1.8643370	1.5299920
H	1.9137670	1.5584550	-1.1055090
C	1.0068650	2.7862540	1.6512020
O	1.2216510	3.4888220	2.6416660
N	1.5451580	2.9535300	0.4207660

C	2.6385000	3.8930590	0.1887990	H	-1.9199100	0.0267720	-0.7809090
H	3.2474980	3.5396860	-0.6444420	C	-2.2804870	-1.8205580	0.3333950
H	2.2774610	4.9002850	-0.0361610	H	-2.1256540	-1.3865840	1.3251090
H	3.2530230	3.9384170	1.0907630	H	-1.8623840	-2.8310260	0.3590680
C	0.2877830	0.6639120	2.8454320	N	0.5157080	0.8691710	0.3759510
H	0.1015020	1.2718600	3.7339790	C	3.6959380	-1.1549220	0.0828330
H	-0.4209670	-0.1677000	2.8533890	C	5.2039670	-1.5382140	-0.0180230
H	1.3041280	0.2632310	2.9112670	O	3.4047620	0.0100360	0.3679100
C	0.0666680	2.5511730	-1.6274130	H	1.5287650	0.7000970	0.3539300
C	-1.2719390	2.9984770	-1.0116030	O	2.9260650	-2.1445230	-0.1550350
H	-1.8940340	3.4594990	-1.7858040	H	1.6455390	-1.9312690	-0.0082900
H	-1.8378420	2.1618930	-0.5956380	C	0.3494040	2.6362720	-1.5179040
H	-1.1239610	3.7457500	-0.2247090	C	0.3498410	4.1772530	-1.6821340
C	0.7201710	3.7746320	-2.3103540	H	0.6386990	4.4264430	-2.7079490
H	1.7207950	3.5443410	-2.6927540	H	-0.6285710	4.6263820	-1.5042260
H	0.1043660	4.0771370	-3.1632980	H	1.0725610	4.6516440	-1.0092660
H	0.7920230	4.6336610	-1.6393340	C	-0.7491520	2.0362820	-2.4146110
C	-0.1680350	1.4906050	-2.7222190	H	-0.6541690	2.4481880	-3.4245660
H	-0.8408670	1.8943270	-3.4858620	H	-1.7545870	2.2726660	-2.0550440
H	0.7738800	1.2242030	-3.2159540	C	1.7364350	2.1403570	-1.9878610
H	-0.6082510	0.5722240	-2.3361670	H	1.9010690	2.4547000	-3.0229800
C	-1.9709290	-0.6178790	-0.0807230	H	2.5416890	2.5653120	-1.3785330
H	-2.1935190	0.0570010	0.7485900	H	1.8318970	1.0518800	-1.9587410
H	-2.2433960	-0.1318520	-1.0196970	C	0.9692440	1.1336870	2.8657260
C	-2.8099620	-1.9206000	0.0892750	H	0.4784380	1.0320320	3.8375760
H	-2.5065970	-2.4286370	1.0112230	H	1.8476810	0.4834370	2.8502160
H	-2.5875650	-2.5941880	-0.7440670	H	1.3004680	2.1705970	2.7548640
C	-4.2940160	-1.6209920	0.1332460	H	-0.6679660	0.9519230	-2.5058830
C	-4.9404880	-1.3713760	1.3534510	F	5.5025580	-2.0222100	-1.2490470
C	-5.0478240	-1.5658850	-1.0493240	F	6.0194600	-0.4907310	0.2105480
C	-6.3059040	-1.0727200	1.3924020	F	5.5215480	-2.5021540	0.8816280
H	-4.3730880	-1.4168800	2.2799320	C	-3.7668930	-1.8834840	0.0415970
C	-6.4132430	-1.2675090	-1.0146910	C	-4.6391300	-0.9069140	0.5473950
H	-4.5642650	-1.7636250	-2.0029800	C	-4.2991390	-2.9063790	-0.7584330
C	-7.0467620	-1.0188240	0.2073290	C	-6.0067430	-0.9487310	0.2590680
H	-6.7902070	-0.8872000	2.3469320	H	-4.2446260	-0.1122770	1.1762920
H	-6.9813820	-1.2339590	-1.9399980	C	-5.6661800	-2.9519270	-1.0495990
H	-8.1081110	-0.7900970	0.2361310	H	-3.6397390	-3.6765340	-1.1519150
C	-0.5188900	-0.9695120	-0.0841700	C	-6.5249980	-1.9716000	-0.5420200
O	-0.0046290	-1.4388200	-1.1605870	H	-6.6665120	-0.1861660	0.6634840
H	0.9782970	-1.8939170	-1.0065410	H	-6.0595880	-3.7543950	-1.6673160
H	-0.0781190	-1.2928540	0.8602500	H	-7.5876030	-2.0071920	-0.7641970
O	2.1838700	-2.4973260	-0.8549180	H	-1.7303650	-1.4267620	-1.7250610
C	3.0197720	-1.9252860	-0.0854450				
C	4.3940020	-2.6615880	-0.0367050				
F	4.2448790	-3.9542560	0.3441700				
F	5.2607060	-2.0883670	0.8210350				
F	4.9814230	-2.6679720	-1.2600600				
H	1.3576910	0.3138010	0.5444440				
O	2.8856000	-0.9014580	0.5965050				

7.log
Potential Energy = -1489.66169
Zero-point Energy = -1489.18761
Free Energy = -1489.23092
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.12078
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.69002
Nimag = 1 (-225.2892)
Charge = 0 Multiplicity = 1

C	-1.2272110	1.6296880	1.7244310
C	0.2093770	2.2830240	-0.0051090
C	-0.0097490	0.7165340	1.7547960
H	0.9349330	2.9336880	0.5117010
H	-0.3052540	-0.3203680	1.9252010
C	-0.0322600	-0.9759410	-0.6285860
H	0.5214760	-0.6141840	-1.4939590
O	0.5365800	-1.8271480	0.1386550
N	-1.1067290	2.4547060	0.6437900
C	-1.9444290	3.6440330	0.5351690
H	-2.3907120	3.7290280	-0.4566380
H	-2.7414310	3.5444480	1.2724860
H	-1.3688160	4.5495920	0.7535220
O	-2.1363140	1.6398050	2.5557440
C	-1.5343390	-0.9932450	-0.7322160

Formation of iminium ion (TS2)

Conformation name	Extrapolated Free energy (kcal/mol)
TS2-lowest	0.0
1	2.2
2	2.1
3	1.2
4	0.6
5	0.5
6	0.6
7	1.4
8	1.9
9	4.1
10	1.4
11	1.9
12	1.1
13	1.4

14 1.0
15 -0.4
16 -0.1
17 -0.2
18 1.5
19 1.1
20 1.5
21 5.8
22 6.1
23 7.1
24 4.7
25 7.4
26 5.1

TS2-lowest.log (Enamine 2)
Potential Energy = -1489.66107
Zero-point Energy = -1489.18625
Free Energy = -1489.22898
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.12306
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.69097
Nimag = 1 (-269.9625 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-2.1887330	-0.0465630	-0.4475410
C	-2.7481900	-0.1260620	1.8444790
C	-2.5697810	-1.5728380	1.3734760
N	-1.8347970	-1.3904070	0.0881530
N	-2.4932770	0.6877860	0.7939620
O	-3.0679970	0.2296140	2.9811960
C	-2.4508120	2.1389360	0.9339600
H	-3.4414530	2.5905240	0.8241220
H	-2.0710280	2.3770210	1.9296920
H	-1.7767760	2.5548760	0.1848880
C	-0.5887650	-1.9120650	-0.0662850
C	0.0851510	-1.9191980	-1.4268600
C	1.3082870	-2.8621740	-1.5373900
H	1.0196350	-3.8580710	-1.1825680
H	1.5179980	-2.9669310	-2.6075520
C	-1.9418990	-2.4809050	2.4228550
H	-2.5830430	-2.4508140	3.3072180
H	-1.9014060	-3.5178500	2.0782260
H	-0.9425260	-2.1512050	2.7131070
H	-3.5650420	-1.9656920	1.1381160
C	-3.3463480	-0.0415220	-1.5080320
H	-1.3045690	0.4017240	-0.9087200
C	-3.5273770	1.4006170	-2.0344580
H	-4.2194910	1.3912200	-2.8825200
H	-3.9480180	2.0697210	-1.2805420
H	-2.5801040	1.8262400	-2.3846700
C	-2.9527870	-0.9365580	-2.6992030
H	-2.0250170	-0.5983930	-3.1729420
H	-2.8358390	-1.9811100	-2.3962620
H	-3.7413090	-0.8980890	-3.4576200
C	-4.6861930	-0.5387460	-0.9323100
H	-4.9824260	0.0185130	-0.0378730
H	-5.4740820	-0.4007800	-1.6800410
H	-4.6553220	-1.6052750	-0.6898860
H	0.3472340	-0.9044970	-1.7402720
H	-0.6648520	-2.2851630	-2.1325360
C	2.5802210	-2.4220080	-0.8369560
C	3.3477900	-1.3619480	-1.3497680
C	3.0313450	-3.0683030	0.3262110
C	4.5224230	-0.9541730	-0.7148850
H	3.0243870	-0.8554700	-2.2557540
C	4.2083930	-2.6594510	0.9673840
H	2.4677770	-3.9077660	0.7266830
C	4.9562100	-1.6002100	0.4491520
H	5.1016210	-0.1340300	-1.1292890

H	4.5383210	-3.1742420	1.8649700
H	5.8699630	-1.2823890	0.9422360
H	-0.4808910	-2.8478780	0.4729440
O	0.5171030	-0.9860990	0.9686830
H	0.7168780	0.0101890	0.5838690
H	1.3729980	-1.4509040	1.0249260
O	0.8953060	1.2539410	0.0146890
C	1.6225310	2.0897860	0.6466230
C	1.8136060	3.4209040	-0.1497850
O	2.1733030	1.9846670	1.7435760
F	2.5259700	4.3409930	0.5321730
F	0.6211220	3.9909260	-0.4618580
F	2.4663250	3.1983890	-1.3209710

1.log
Potential Energy = -1489.66249
Zero-point Energy = -1489.18824
Free Energy = -1489.23172
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11830
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68753
Nimag = 1 (-309.6177 cm⁻¹)
Charge = 0 Multiplicity = 1

C	2.9163420	-0.0892340	-0.3998050
C	3.0941390	-2.3930880	0.0742480
C	2.4340840	-1.7323080	1.2886810
N	2.0021580	-0.4196300	0.7273880
N	3.3212000	-1.4310090	-0.8507370
O	3.3681970	-3.5895760	-0.0373540
C	3.8155230	-1.7444070	-2.1865760
H	4.9087010	-1.7654930	-2.2261400
H	3.4399180	-2.7298620	-2.4695140
H	3.4464850	-1.0010640	-2.8951280
C	0.6885600	-0.0846140	0.6966300
C	0.2516700	1.3123210	0.3111540
C	-1.2719890	1.5398080	0.4004290
H	-1.7892110	0.9284120	-0.3444370
H	-1.6227930	1.2106010	1.3853150
C	1.3732150	-2.6012100	1.9507580
H	1.8609770	-3.5253290	2.2701570
H	0.9615480	-2.1191500	2.8416240
H	0.5626630	-2.8657380	1.2693160
H	3.2211080	-1.5386160	2.0255120
C	4.1050930	0.8649880	-0.0247340
H	2.3443270	0.3911040	-1.1987510
C	4.8940600	1.2007950	-1.3105310
H	5.6309560	1.9792970	-1.0890220
H	5.4405250	0.3394880	-1.7014760
H	4.2377730	1.5826090	-2.1010160
C	3.5403810	2.1800430	0.5472630
H	2.8848500	2.6874560	-0.1682940
H	2.9855850	2.0104930	1.4744730
H	4.3669960	2.8607140	0.7746210
C	5.0646310	0.2414890	1.0068460
H	5.4427090	-0.7326880	0.6808710
H	5.9285980	0.9006440	1.1403730
H	4.5920740	0.1272190	1.9869770
H	0.6176640	1.5868750	-0.6833930
H	0.7473270	1.9838980	1.0200450
C	-1.6343500	2.9972760	0.1938430
C	-1.6670560	3.8897400	1.2767530
C	-1.9235370	3.4902750	-1.0878270
C	-1.9765150	5.2396480	1.0851320
H	-1.4551670	3.5239490	2.2787680
C	-2.2327660	4.8398060	-1.2847030
H	-1.9127450	2.8116840	-1.9374520
C	-2.2592710	5.7196580	-0.1979470
H	-2.0014380	5.9134190	1.9369710
H	-2.4575730	5.2012740	-2.2841980
H	-2.5031470	6.7673200	-0.3483300
H	0.1435240	-0.4855490	1.5453420
O	-0.1256740	-1.1394490	-0.5045090
H	-0.2425590	-0.6952790	-1.3596100
H	-1.1104150	-1.5302140	-0.1983810
O	-2.2760230	-2.0600690	0.2166960

C -3.2632010 -1.8081300 -0.5529800
O -3.2887880 -1.1654220 -1.6042330
C -4.5957220 -2.4280770 -0.0264160
F -4.5002500 -3.7777020 0.0850540
F -4.9075450 -1.9467770 1.2044070
F -5.6448950 -2.1683600 -0.8325580

2.log
Potential Energy = -1489.65965
Zero-point Energy = -1489.18505
Free Energy = -1489.22863
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11864
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68763
Nimag = 1 (-222.1627 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-2.7695910	-0.1669450	0.3649140
C	-1.8990570	-2.3524920	0.1672370
C	-1.8496940	-1.7152730	-1.2252570
N	-1.9970380	-0.2667750	-0.9043290
N	-2.4034680	-1.4329180	1.0237490
O	-1.5444360	-3.4978390	0.4532300
C	-2.4519230	-1.6621950	2.4629530
H	-3.3818170	-2.1494890	2.7712660
H	-1.6152830	-2.3086270	2.7354160
H	-2.3562610	-0.7096780	2.9868740
C	-1.0130300	0.6208940	-1.1885420
C	-1.2980500	2.1089270	-1.1563150
C	-0.1438890	3.0265960	-1.6216880
H	0.3126100	2.6059020	-2.5241690
H	-0.6074980	3.9714640	-1.9280310
C	-0.6510510	-2.1376540	-2.0620440
H	-0.7053200	-3.2226760	-2.1815740
H	-0.6915760	-1.6925980	-3.0603280
H	0.3064380	-1.9016300	-1.5941070
H	-2.7555600	-2.0250490	-1.7576560
C	-4.3134790	0.0589970	0.1957800
H	-2.3682800	0.6613860	0.9553270
C	-4.9335480	0.2671260	1.5963520
H	-5.9781290	0.5756100	1.4872680
H	-4.9262780	-0.6463810	2.1952730
H	-4.4131240	1.0522860	2.1567470
C	-4.5579460	1.3372450	-0.6295750
H	-4.1190150	2.2202950	-0.1536740
H	-4.1556180	1.2461050	-1.6424990
H	-5.6351200	1.5126960	-0.7146350
C	-5.0186590	-1.1239000	-0.4955230
H	-4.8184070	-2.0741660	0.0093590
H	-6.1012630	-0.9619520	-0.4725170
H	-4.7293430	-1.2146290	-1.5467950
H	-1.6711790	2.4188530	-0.1762330
H	-2.1282030	2.2440450	-1.8566190
C	0.9407990	3.3394800	-0.6035480
C	0.6268950	3.9646150	0.6172480
C	2.2893330	3.0576850	-0.8783500
C	1.6288830	4.2899790	1.5356390
H	-0.4065750	4.2099770	0.8488780
C	3.2946180	3.3851860	0.0375430
H	2.5536510	2.5778210	-1.8170590
C	2.9671930	4.0014750	1.2483160
H	1.3641490	4.7734070	2.4714780
H	4.3303380	3.1566640	-0.1961360
H	3.7459980	4.2548510	1.9613430
H	-0.4100740	0.3146890	-2.0377020
O	0.2498020	0.4462580	0.0892450
H	0.6285480	1.3179610	0.3048790
H	1.0869670	-0.1913560	-0.1366250
O	2.1777580	-1.0070040	-0.4604330
C	2.9763500	-1.3174150	0.4831580
O	2.9531000	-1.0028320	1.6750300
C	4.1438700	-2.2311930	-0.0130220
F	3.6741190	-3.3713620	-0.5819850
F	4.8959010	-1.5990060	-0.9524160
F	4.9800720	-2.6000110	0.9797440

3.log
Potential Energy = -1489.66151
Zero-point Energy = -1489.18751
Free Energy = -1489.23110
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11948
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68907
Nimag = 1 (-324.0648 cm⁻¹)
Charge = 0 Multiplicity = 1

C	3.0112410	-0.4737330	-0.4844450
C	2.6207980	-1.9757880	1.2915410
C	2.0312580	-0.6235450	1.7049870
N	1.9536360	0.0910360	0.3977810
N	3.1374380	-1.8411710	0.0474330
O	2.6222740	-3.0029010	1.9730450
C	3.6489220	-2.9822410	-0.7033290
H	4.7051020	-3.1737100	-0.4916100
H	3.0735890	-3.8660870	-0.4202920
H	3.5261120	-2.8001350	-1.7722060
C	0.7514200	0.4792220	-0.0986660
C	0.6657720	1.3456090	-1.3378940
C	-0.7540190	1.8698410	-1.6509830
H	-0.6964970	2.3740370	-2.6216200
H	-1.4461780	1.0322470	-1.7761580
C	0.7520730	-0.7442590	2.5223790
H	0.9923840	-1.3174110	3.4211090
H	0.3885100	0.2359790	2.8418420
H	-0.0398160	-1.2720120	1.9880260
H	2.7793920	-0.1134720	2.3213340
C	4.3500180	0.3449520	-0.5140560
H	2.6343380	-0.5295950	-1.5098870
C	5.3114770	-0.3167720	-1.5268280
H	6.1850980	0.3271040	-1.6695390
H	5.6766020	-1.2867710	-1.1817280
H	4.8382480	-0.4534000	-2.5058560
C	4.0581100	1.7790190	-0.9973600
H	3.6063460	1.7884280	-1.9951590
H	3.3982810	2.3102380	-0.3054070
H	4.9963450	2.3397690	-1.0570230
C	5.0377360	0.4115470	0.8629530
H	5.2061720	-0.5833960	1.2872790
H	6.0159060	0.8914190	0.7548370
H	4.4629260	1.0084320	1.5773530
H	1.0647980	0.8193970	-2.2111550
H	1.3255260	2.2008780	-1.1661760
C	-1.2977930	2.8358020	-0.6142460
C	-2.2861990	2.4403630	0.3000610
C	-0.8143290	4.1536470	-0.5479490
C	-2.7751350	3.3354720	1.2590260
H	-2.6779170	1.4271490	0.2605910
C	-1.3000650	5.0494080	0.4076540
H	-0.0574450	4.4842950	-1.2556610
C	-2.2832110	4.6419770	1.3169840
H	-3.5416390	3.0100040	1.9567860
H	-0.9166330	6.0654080	0.4389170
H	-2.6637740	5.3381570	2.0587570
H	0.0631210	0.7750910	0.6862780
O	-0.1580410	-0.9898530	-0.5597260
H	-0.0893720	-1.1797920	-1.5090540
H	-1.2276000	-1.0552580	-0.2813260
O	-2.5023720	-1.1546130	0.1139630
C	-3.2453450	-1.8294730	-0.6769120
O	-2.9598880	-2.3687830	-1.7467420
C	-4.7120760	-1.9421230	-0.1535690
F	-4.7555040	-2.5254800	1.0712460
F	-5.2840190	-0.7164070	-0.0326940
F	-5.5003800	-2.6703790	-0.9696810

4.log
Potential Energy = -1489.66303
Zero-point Energy = -1489.18910
Free Energy = -1489.23259
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.12040

Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated
free energy from qRRHO) = -1489.68996
Nimag = 1 (-326.9458 cm⁻¹)
Charge = 0 Multiplicity = 1

C	1.9498940	-0.6852460	0.6724980
C	3.7033260	-0.3305070	-0.8676560
C	2.9514240	-1.5854720	-1.3217480
N	1.6733950	-1.4726930	-0.5610700
N	3.0863740	0.1462170	0.2384880
O	4.6946510	0.1560680	-1.4162020
C	3.4664490	1.4146260	0.8499540
H	4.2667080	1.2922290	1.5859150
H	3.8199250	2.0832420	0.0623780
H	2.5959840	1.8587800	1.3346670
C	0.4915310	-1.3590850	-1.2212330
C	-0.8204140	-1.4594610	-0.4723920
C	-2.0679270	-1.3427020	-1.3729370
H	-2.1503700	-0.3253670	-1.7675130
H	-1.9571730	-2.0170060	-2.2306780
C	2.8615840	-1.7253330	-2.8355860
H	3.8830200	-1.7479590	-3.2230060
H	2.3778890	-2.6635720	-3.1206780
H	2.3396390	-0.8868340	-3.3006720
H	3.4966530	-2.4530430	-0.9340080
C	2.2201560	-1.5479400	1.9550480
H	1.1002040	-0.0287720	0.8800320
C	2.3915150	-0.6000660	3.1636310
H	2.4259030	-1.1912780	4.0842710
H	3.3183670	-0.0241370	3.1137000
H	1.5533230	0.1004770	3.2514750
C	1.0010490	-2.4515790	2.2257070
H	0.0858590	-1.8685330	2.3729280
H	0.8378140	-3.1625740	1.4109210
H	1.1734760	-3.0279490	3.1402830
C	3.4766770	-2.4297430	1.8239170
H	4.3644200	-1.8449620	1.5623190
H	3.6769630	-2.9184760	2.7830100
H	3.3434070	-3.2213810	1.0804460
H	-0.8743300	-0.7274900	0.3377300
H	-0.8170310	-2.4511620	-0.0071680
C	-3.3390300	-1.6853770	-0.6208780
C	-3.7990870	-3.0097650	-0.5543000
C	-4.0698690	-0.6888690	0.0439370
C	-4.9568510	-3.3317150	0.1603620
H	-3.2506110	-3.7945200	-1.0701520
C	-5.2280040	-1.0062500	0.7605160
H	-3.7328940	0.3437730	-0.0035190
C	-5.6751080	-2.3299370	0.8215540
H	-5.2994760	-4.3620190	0.1961250
H	-5.7817580	-0.2199050	1.2656730
H	-6.5765220	-2.5777320	1.3744840
H	0.4935220	-1.9113080	-2.1556880
O	0.4585630	0.2559860	-1.9622620
H	0.1490030	1.0588990	-1.2715310
H	-0.1114070	0.2834180	-2.7479220
O	-0.1404720	1.9824470	-0.3388710
C	-0.8462150	2.9706510	-0.7355600
C	-1.1394870	3.9824360	0.4174190
O	-1.3019890	3.2080180	-1.8544740
F	-1.8582110	5.0462620	0.0058850
F	0.0093440	4.4606090	0.9594990
F	-1.8383140	3.3907220	1.4207500

5.log
Potential Energy = -1489.66201
Zero-point Energy = -1489.18806
Free Energy = -1489.23178
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -
1490.12032
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated
free energy from qRRHO) = -1489.69009
Nimag = 1 (-338.0783 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-0.6678660	2.0195690	0.4497310
C	-0.6493540	2.8554140	-1.7572660
C	0.8029790	2.5509570	-1.3768490

N	0.6328230	1.6693650	-0.1857940
N	-1.4328840	2.5201910	-0.7057340
O	-1.0332190	3.3231880	-2.8315370
C	-2.8888900	2.5535000	-0.7856480
H	-3.2920060	3.5372500	-0.5270820
H	-3.1828790	2.3173560	-1.8104100
H	-3.3072070	1.8058500	-0.1101890
C	1.0733200	0.3840990	-0.2197110
C	1.0737550	-0.4595920	1.0381770
C	1.7316680	-1.8487110	0.8883360
H	1.6081660	-2.3550020	1.8527860
H	1.1824840	-2.4527460	0.1598720
C	1.6373960	2.0202500	-2.5350360
H	1.6280230	2.7798830	-3.3203950
H	2.6778390	1.8645010	-2.2374180
H	1.2324120	1.0964410	-2.9526980
H	1.2565240	3.4883870	-1.0365820
C	-0.5648210	3.0226660	1.6521100
H	-1.1471910	1.1070180	0.8157560
C	-1.9726970	3.2111160	2.2611550
H	-1.8907840	3.7838090	3.1904050
H	-2.6426090	3.7633680	1.5981470
H	-2.4412190	2.2507100	2.5046930
C	0.3498120	2.4227210	2.7379900
H	-0.0271170	1.4613460	3.1028500
H	1.3714210	2.2851260	2.3724480
H	0.3921910	3.1044920	3.5934400
C	-0.0092160	4.3973250	1.2338410
H	-0.5857620	4.8424630	0.4166490
H	-0.0642880	5.0834170	2.0853590
H	1.0414610	4.3385840	0.9343120
H	0.0579940	-0.5823160	1.4230950
H	1.6268180	0.1146490	1.7872030
C	3.2062110	-1.8192050	0.5253400
C	3.6700910	-2.3813670	-0.6734640
C	4.1469920	-1.2428990	1.3965260
C	5.0309630	-2.3617600	-1.0006790
H	2.9643340	-2.8474010	-1.3567630
C	5.5058860	-1.2203430	1.0742960
H	3.8174510	-0.8152050	2.3404280
C	5.9534840	-1.7783740	-0.1288600
H	5.3661560	-2.8038110	-1.9346460
H	6.2155950	-0.7722770	1.7640160
H	7.0100910	-1.7622690	-0.3796240
H	1.9753850	0.2793060	-0.8143100
O	0.0003580	-0.5014050	-1.3285240
H	-0.9032860	-0.9328190	-0.8604480
H	0.4599550	-1.2122210	-1.8032520
O	-2.0262060	-1.3672060	-0.2691220
C	-2.2886720	-2.5991100	-0.4849310
C	-3.5932620	-3.0598410	0.2384820
O	-1.6647700	-3.4237890	-1.1536310
F	-3.4615510	-2.9613780	1.5871270
F	-3.9165290	-4.3392850	-0.0375260
F	-4.6547530	-2.2926230	-0.1157890

6.log
Potential Energy = -1489.66303
Zero-point Energy = -1489.18910
Free Energy = -1489.23259
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -
1490.12040
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated
free energy from qRRHO) = -1489.68996
Nimag = 1 (-327.0302 cm⁻¹)
Charge = 0 Multiplicity = 1

C	1.9497960	-0.6855510	0.6724740
C	3.7032480	-0.3311680	-0.8677400
C	2.9509950	-1.5859030	-1.3218810
N	1.6730390	-1.4728540	-0.5611250
N	3.0864730	0.1456470	0.2384630
O	4.6946800	0.1551780	-1.4162980
C	3.4669310	1.4138960	0.8500180
H	4.2670550	1.2911890	1.5860750
H	3.8207500	2.0824020	0.0625040
H	2.5965680	1.8583490	1.3346420

C	0.4911560	-1.3589270	-1.2212230
C	-0.8207720	-1.4590850	-0.4723180
C	-2.0683000	-1.3420470	-1.3728110
H	-2.1507160	-0.3246080	-1.7671270
H	-1.9575820	-2.0161370	-2.2307270
C	2.8610390	-1.7256130	-2.8357280
H	3.8824490	-1.7484500	-3.2232050
H	2.3771040	-2.6637110	-3.1208790
H	2.3392690	-0.8869490	-3.3007110
H	3.4960260	-2.4536450	-0.9342430
C	2.2198970	-1.5483790	1.9549690
H	1.1002840	-0.0288700	0.8800860
C	2.3914810	-0.6006110	3.1636030
H	2.4257320	-1.1918800	4.0842130
H	3.3184690	-0.0248990	3.1136990
H	1.5534540	0.1001270	3.2514830
C	1.0006030	-2.4517720	2.2256040
H	0.0855480	-1.8685310	2.3728910
H	0.8371860	-3.1626770	1.4107780
H	1.1729320	-3.0282370	3.1401390
C	3.4762280	-2.4304430	1.8237590
H	4.3640890	-1.8458350	1.5621760
H	3.6764310	-2.9192770	2.7828180
H	3.3427750	-3.2220070	1.0802420
H	-0.8745120	-0.7271380	0.3378380
H	-0.8175590	-2.4508040	-0.0071350
C	-3.3394040	-1.6848840	-0.6208270
C	-3.7993220	-3.0093270	-0.5543480
C	-4.0703780	-0.6884940	0.0440130
C	-4.9570830	-3.3314430	0.1602420
H	-3.2507340	-3.7939930	-1.0702170
C	-5.2285120	-1.0060420	0.7605210
H	-3.7335110	0.3441870	-0.0033670
C	-5.6754770	-2.3297800	0.8214600
H	-5.2995990	-4.3617860	0.1959290
H	-5.7823730	-0.2197880	1.2657020
H	-6.5768900	-2.5777040	1.3743350
H	0.4929690	-1.9111120	-2.1557010
O	0.4584900	0.2561280	-1.9621050
H	0.1491980	1.0591180	-1.2712900
H	-0.1115580	0.2837410	-2.7477020
O	-0.1399530	1.9827030	-0.3387040
C	-0.8456320	2.9709460	-0.7354260
C	-1.1386590	3.9828970	0.4174670
O	-1.3015190	3.2082090	-1.8543140
F	-1.8570940	5.0468780	0.0058340
F	0.0102750	4.4608080	0.9595520
F	-1.8376730	3.3914270	1.4208130

7.log
Potential Energy = -1489.66171
Zero-point Energy = -1489.18784
Free Energy = -1489.23117
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11933
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68879
Nimag = 1 (-319.4351 cm⁻¹)
Charge = 0 Multiplicity = 1

C	1.4178620	-1.2262770	0.6745040
C	3.2013550	-1.5723010	-0.8345990
C	2.0640050	-2.5107840	-1.2536040
N	0.8979530	-1.9239230	-0.5341140
N	2.7712060	-0.8499690	0.2258590
O	4.3059410	-1.4900100	-1.3755540
C	3.5648920	0.2322330	0.7976190
H	4.2719440	-0.1307950	1.5495610
H	4.1295870	0.7062580	-0.0077490
H	2.8999670	0.9677010	1.2518420
C	-0.1909630	-1.4704780	-1.2082150
C	-1.4743980	-1.1403080	-0.4750600
C	-2.6317890	-0.7250630	-1.4075760
H	-2.3741560	0.2059880	-1.9178280
H	-2.7571940	-1.4923420	-2.1808990
C	1.9486850	-2.7019800	-2.7599030
H	2.8989160	-3.1115830	-3.1103500

H	1.1628360	-3.4179270	-3.0130320
H	1.7759640	-1.7720760	-3.3080950
H	2.2687700	-3.4920550	-0.8119550
C	1.3804030	-2.0697370	1.9983800
H	0.8397500	-0.3124340	0.8356320
C	1.8397880	-1.1705070	3.1689520
H	1.6739230	-1.6968970	4.1142580
H	2.9032760	-0.9270210	3.1166300
H	1.2719740	-0.2340450	3.2077080
C	-0.0674410	-2.5158510	2.2810980
H	-0.7459950	-1.6620020	2.3781060
H	-0.4450240	-3.1791610	1.4979110
H	-0.0973210	-3.0677840	3.2259900
C	2.2834150	-3.3167630	1.9373110
H	3.3147590	-3.0669500	1.6687210
H	2.3081080	-3.7925580	2.9230800
H	1.9048270	-4.0614110	1.2306500
H	-1.3083760	-0.3714840	0.2852860
H	-1.7585510	-2.0545680	0.0552120
C	-3.9323980	-0.5528230	-0.6488360
C	-4.7996200	-1.6384110	-0.4495570
C	-4.2884410	0.6936340	-0.1105740
C	-5.9891170	-1.4851710	0.2693720
H	-4.5451730	-2.6102790	-0.8661970
C	-5.4764720	0.8519850	0.6098290
H	-3.6331990	1.5482010	-0.2616560
C	-6.3311560	-0.2381670	0.8027820
H	-6.6491730	-2.3368670	0.4081230
H	-5.7356480	1.8261260	1.0150310
H	-7.2563050	-0.1162320	1.3586400
H	-0.3571540	-2.0162580	-2.1316540
O	0.1084320	0.1041850	-1.9885060
H	0.2524590	0.9417600	-1.2896100
H	0.8689460	0.0654900	-2.5881710
O	0.3481200	1.9180930	-0.3629320
C	0.8361630	3.0291990	-0.7619620
C	0.8725280	4.0962700	0.3781170
O	1.2568120	3.3462410	-1.8747470
F	1.4175210	5.2638690	-0.0187690
F	1.5950590	3.6581350	1.4410990
F	-0.3775910	4.3711270	0.8318970

8.log
Potential Energy = -1489.66281
Zero-point Energy = -1489.18914
Free Energy = -1489.23327
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11742
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68788
Nimag = 1 (-301.9079 cm⁻¹)
Charge = 0 Multiplicity = 1

C	2.8651430	-0.4922060	0.2683590
C	3.2823360	-2.0585370	-1.4520040
C	1.7835630	-2.1426610	-1.1535730
N	1.5779300	-0.9171800	-0.3408840
N	3.8234450	-1.0974800	-0.6693640
O	3.8825970	-2.7326000	-2.2912850
C	5.1801200	-0.6066500	-0.8983240
H	5.9303530	-1.2211030	-0.3935500
H	5.3793770	-0.6287680	-1.9719730
H	5.2593130	0.4197160	-0.5386430
C	0.4521800	-0.1676890	-0.4155720
C	0.5144400	1.3280920	-0.1898490
C	-0.8298460	2.0490660	-0.4179590
H	-1.2221620	1.7766390	-1.4046890
H	-1.5589180	1.7113870	0.3237270
C	0.9614520	-2.2432030	-2.4351110
H	1.3283750	-3.1053040	-2.9970900
H	-0.0988210	-2.4087300	-2.2287290
H	1.0752260	-1.3528560	-3.0610170
H	1.6031170	-3.0388050	-0.5461120
C	3.0755840	-0.9145040	1.7668060
H	2.9557420	0.5964730	0.2042090
C	4.5216400	-0.5811040	2.1954280
H	4.6168710	-0.7270460	3.2760740

H	5.2567070	-1.2297720	1.7137370
H	4.7813660	0.4616700	1.9811640
C	2.1249780	-0.0987000	2.6672330
H	2.3331210	0.9750300	2.5946070
H	1.0724450	-0.2644210	2.4284140
H	2.2772320	-0.3904230	3.7113740
C	2.8271640	-2.4191090	1.9783460
H	3.4697290	-3.0321390	1.3378280
H	3.0526770	-2.6837850	3.0163370
H	1.7842710	-2.6943710	1.7936140
H	1.2479060	1.7125240	-0.9103610
H	0.8905830	1.5553510	0.8093320
C	-0.6806880	3.5549060	-0.3288660
C	-0.8714320	4.2250700	0.8893230
C	-0.3241780	4.3092340	-1.4578050
C	-0.7071520	5.6109590	0.9797360
H	-1.1561120	3.6586480	1.7728630
C	-0.1591380	5.6949600	-1.3726600
H	-0.1806690	3.8088910	-2.4127010
C	-0.3491440	6.3508060	-0.1517920
H	-0.8632200	6.1114920	1.9312360
H	0.1123790	6.2613220	-2.2591110
H	-0.2246160	7.4276820	-0.0843650
H	-0.1806830	-0.4535230	-1.2494940
O	-0.6818800	-0.6674930	0.8398350
H	-1.7546010	-0.6605710	0.5400490
H	-0.4843870	-1.5977110	1.0390780
O	-3.0468740	-0.6593970	0.2160810
C	-3.5873260	-1.8065140	0.3768880
O	-3.0775040	-2.8587520	0.7652300
C	-5.1054620	-1.8014020	0.0152990
F	-5.7924510	-0.9317990	0.7993650
F	-5.3032540	-1.4207810	-1.2724430
F	-5.6785560	-3.0122900	0.1657040

9.log
Potential Energy = -1489.65736
Zero-point Energy = -1489.18316
Free Energy = -1489.22653
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11533
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68449
Nimag = 1 (-259.3944 cm⁻¹)
Charge = 0 Multiplicity = 1

C	3.0482640	0.2436420	-0.0441230
C	3.4644160	-1.9819580	-0.7227370
C	1.9581610	-1.8897830	-0.4686920
N	1.7637570	-0.4195740	-0.3912150
N	4.0106260	-0.7612020	-0.5200690
O	4.0670680	-2.9932880	-1.0868310
C	5.3830840	-0.4664820	-0.9244820
H	6.1078560	-0.7529900	-0.1577510
H	5.6030410	-1.0266670	-1.8359390
H	5.4799960	0.6008170	-1.1258950
C	0.6545870	0.1961500	-0.8653320
C	0.7441060	1.6047450	-1.4130420
C	-0.5620650	2.1680300	-2.0237720
H	-0.2627110	2.8253500	-2.8486440
H	-1.1374460	1.3568530	-2.4831300
C	1.1622470	-2.6150730	-1.5496900
H	1.5196910	-3.6468000	-1.5874320
H	0.0942190	-2.6417970	-1.3207940
H	1.3122410	-2.1646520	-2.5355790
H	1.7400970	-2.3533490	0.5019120
C	3.2217230	0.6335620	1.4678860
H	3.1637300	1.1496430	-0.6465170
C	4.6643930	1.1328510	1.7059490
H	4.7353030	1.5542550	2.7136380
H	5.3978000	0.3264100	1.6385020
H	4.9464180	1.9220210	0.9999530
C	2.2699410	1.7978050	1.8117390
H	2.5000130	2.6888600	1.2168060
H	1.2173640	1.5493820	1.6611490
H	2.3932900	2.0675660	2.8653050
C	2.9483320	-0.5590900	2.4026120

H	3.5963100	-1.4113130	2.1734960
H	3.1482290	-0.2650680	3.4378170
H	1.9070620	-0.8933160	2.3579250
H	1.4933000	1.5389680	-2.2124790
H	1.1397260	2.2929000	-0.6649820
C	-1.4565940	2.9656670	-1.0911530
C	-2.7926740	2.5983210	-0.8801170
C	-0.9790790	4.1271470	-0.4616160
C	-3.6279450	3.3597950	-0.0550930
H	-3.1823350	1.7032410	-1.3570420
C	-1.8075600	4.8896910	0.3656200
H	0.0481230	4.4459400	-0.6229630
C	-3.1378290	4.5076540	0.5735390
H	-4.6593140	3.0533660	0.0960450
H	-1.4167570	5.7844800	0.8421830
H	-3.7838090	5.1003250	1.2148030
H	0.0419400	-0.4601420	-1.4746960
O	-0.5507630	0.3432800	0.4279420
H	-1.4788490	-0.1801210	0.1740350
H	-0.1969480	-0.1503970	1.1863850
O	-2.6169520	-0.8721740	-0.1298980
C	-2.7952510	-1.8678820	0.6479280
O	-2.1015080	-2.2544040	1.5918840
C	-4.0937260	-2.6644900	0.3057590
F	-5.1959210	-1.8814690	0.4333880
F	-4.0717520	-3.1167570	-0.9742550
F	-4.2734600	-3.7370440	1.1031990

10.log
Potential Energy = -1489.66178
Zero-point Energy = -1489.18774
Free Energy = -1489.23108
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11946
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68876
Nimag = 1 (-331.0284 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-3.0935230	-0.3488320	-0.4440750
C	-3.4353370	0.0880690	1.8531470
C	-1.9704560	-0.3317880	1.7100630
N	-1.7811600	-0.2371540	0.2412340
N	-3.9986140	0.1052170	0.6237800
O	-3.9926600	0.3907780	2.9102330
C	-5.3130970	0.7003000	0.3972550
H	-6.1237550	-0.0071230	0.5917340
H	-5.4283200	1.5530220	1.0700100
H	-5.3808180	1.0448490	-0.6350980
C	-0.6228760	0.1871470	-0.3245560
C	-0.6483790	0.9181020	-1.6520460
C	0.7003070	1.5548320	-2.0554010
H	1.4760740	0.7859740	-2.1121260
H	0.5737270	1.9419700	-3.0725200
C	-1.0493420	0.5348470	2.5634580
H	-1.4039160	0.4783670	3.5953500
H	-0.0182080	0.1727570	2.5461480
H	-1.0716450	1.5831040	2.2505800
H	-1.8779540	-1.3746650	2.0399930
C	-3.4402470	-1.7683450	-1.0202260
H	-3.1369780	0.3706210	-1.2673680
C	-4.8988700	-1.7726690	-1.5285930
H	-5.0859850	-2.7040550	-2.0723690
H	-5.6227320	-1.7217910	-0.7121630
H	-5.0929250	-0.9445330	-2.2195930
C	-2.5266940	-2.0665370	-2.2269330
H	-2.6745210	-1.3326270	-3.0277950
H	-1.4682490	-2.0788150	-1.9591180
H	-2.7766530	-3.0508580	-2.6358490
C	-3.2769440	-2.8723860	0.0401850
H	-3.8989550	-2.6854640	0.9217490
H	-3.5877900	-3.8336150	-0.3815400
H	-2.2371570	-2.9808300	0.3632940
H	-1.3978530	1.7134800	-1.5602730
H	-0.9837270	0.2467880	-2.4446040
C	1.1532600	2.6808780	-1.1439030
C	0.5076620	3.9287110	-1.1802430

C	2.2177090	2.5064780	-0.2463700
C	0.9096440	4.9702660	-0.3405600
H	-0.3112810	4.0896750	-1.8778230
C	2.6235850	3.5481440	0.5964410
H	2.7342900	1.5508860	-0.2116250
C	1.9702900	4.7825340	0.5535580
H	0.4002300	5.9286980	-0.3877270
H	3.4513710	3.3932430	1.2828920
H	2.2855660	5.5922270	1.2052960
H	0.0522920	0.6268900	0.4021310
O	0.3785640	-1.1959370	-0.7083210
H	1.4916940	-1.0793800	-0.6182840
H	0.1481330	-1.8915130	-0.0700530
O	2.8048640	-0.9987640	-0.5349500
C	3.2963710	-1.9134310	0.2127620
O	2.7142030	-2.7994270	0.8389160
C	4.8523130	-1.8342660	0.2963420
F	5.4162260	-1.9632080	-0.9313160
F	5.2558390	-0.6397620	0.7987060
F	5.3782050	-2.7958360	1.0807000

11.log
Potential Energy = -1489.66281
Zero-point Energy = -1489.18914
Free Energy = -1489.23327
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11742
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68788
Nimag = 1 (-301.8792 cm⁻¹)
Charge = 0 Multiplicity = 1

C	2.8650320	-0.4926000	0.2684990
C	3.2821400	-2.0586630	-1.4521230
C	1.7833850	-2.1428240	-1.1536030
N	1.5777950	-0.9174120	-0.3407940
N	3.8233160	-1.0977640	-0.6693210
O	3.8823220	-2.7325890	-2.2915680
C	5.1799130	-0.6067470	-0.8983450
H	5.9302200	-1.2204870	-0.3928220
H	5.3794230	-0.6298170	-1.9719220
H	5.2587010	0.4199890	-0.5396000
C	0.4521560	-0.1677620	-0.4155270
C	0.5145970	1.3279940	-0.1896900
C	-0.8295090	2.0491880	-0.4181810
H	-1.2215310	1.7768950	-1.4050650
H	-1.5588840	1.7115630	0.3232340
C	0.9611760	-2.2433030	-2.4350770
H	1.3280230	-3.1054070	-2.9970990
H	-0.0990860	-2.4087910	-2.2286130
H	1.0749360	-1.3529530	-3.0609820
H	1.6030060	-3.0390030	-0.5461780
C	3.0754270	-0.9150980	1.7668900
H	2.9557030	0.5960790	0.2045220
C	4.5215120	-0.5818620	2.1955300
H	4.6167130	-0.7277570	3.2761860
H	5.2564980	-1.2306500	1.7138800
H	4.7813620	0.4608710	1.9812040
C	2.1248910	-0.0992850	2.6673860
H	2.3332280	0.9744210	2.5949600
H	1.0723500	-0.2647830	2.4284470
H	2.2770100	-0.3912140	3.7114900
C	2.8268500	-2.4196970	1.9782820
H	3.4693120	-3.0327320	1.3376630
H	3.0523870	-2.6845090	3.0162330
H	1.7839120	-2.6948180	1.7935810
H	1.2483430	1.7123780	-0.9099400
H	0.8904580	1.5551180	0.8096290
C	-0.6801390	3.5549980	-0.3289270
C	-0.8711520	4.2251020	0.8892540
C	-0.3231400	4.3093510	-1.4576940
C	-0.7066580	5.6109550	0.9798260
H	-1.1562120	3.6586610	1.7726600
C	-0.1578840	5.6950420	-1.3723910
H	-0.1794120	3.8090570	-2.4125830
C	-0.3481590	6.3508270	-0.1515310
H	-0.8629380	6.1114420	1.9313150

H	0.1140150	6.2614240	-2.2587120
H	-0.2234620	7.4276750	-0.0839810
H	-0.1806920	-0.4534610	-1.2495050
O	-0.6820350	-0.6674720	0.8397780
H	-1.7547380	-0.6604760	0.5399670
H	-0.4845840	-1.5976860	1.0390900
O	-3.0470200	-0.6591170	0.2160180
C	-3.5876450	-1.8061480	0.3768550
O	-3.0779780	-2.8584560	0.7652060
C	-5.1057700	-1.8008050	0.0152200
F	-5.7925650	-0.9306060	0.7987870
F	-5.3033720	-1.4207960	-1.2727390
F	-5.6792060	-3.0114550	0.1662120

12.log
Potential Energy = -1489.66213
Zero-point Energy = -1489.18799
Free Energy = -1489.23136
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.12005
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68928
Nimag = 1 (-310.6199 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-2.8903140	-0.6469700	-0.5149400
C	-3.5303720	0.2473580	1.5773630
C	-2.0718030	-0.1926140	1.7245390
N	-1.6817550	-0.3732850	0.3048840
N	-3.9211430	0.0116440	0.3036690
O	-4.2180760	0.7582360	2.4634720
C	-5.1774820	0.5445240	-0.2171280
H	-6.0245080	-0.1109680	0.0024070
H	-5.3612260	1.5156180	0.2478380
H	-5.0969960	0.6725620	-1.2970750
C	-0.4325170	-0.1293050	-0.1547310
C	-0.1997140	0.2977170	-1.5904420
C	-0.6051660	1.7687080	-1.8551870
H	-0.5117540	1.9254300	-2.9363410
H	-1.6620160	1.9188220	-1.6124340
C	-1.2482260	0.8113380	2.5244550
H	-1.7419920	0.9525250	3.4888950
H	-0.2376370	0.4435080	2.7200380
H	-1.1889590	1.7810280	2.0224820
H	-2.0564450	-1.1568870	2.2491380
C	-3.1846000	-2.1596560	-0.8249230
H	-2.8121110	-0.1163990	-1.4685130
C	-4.5702860	-2.2803770	-1.4970600
H	-4.7052660	-3.3057640	-1.8554980
H	-5.3875350	-2.0677960	-0.8041190
H	-4.6639980	-1.6155160	-2.3630500
C	-2.1352180	-2.6939350	-1.8215670
H	-2.1670500	-2.1409210	-2.7677910
H	-1.1204760	-2.6470900	-1.4219790
H	-2.3563850	-3.7416490	-2.0504030
C	-3.1719450	-3.0235420	0.4496200
H	-3.8857350	-2.6600320	1.1961920
H	-3.4591800	-4.0492840	0.1967430
H	-2.1780630	-3.0680800	0.9046890
H	-0.7318720	-0.3595860	-2.2795040
H	0.8646090	0.1751370	-1.8034990
C	0.2292100	2.8058820	-1.1247520
C	-0.3592080	3.6865100	-0.2052980
C	1.6071190	2.9256540	-1.3730580
C	0.4042320	4.6560070	0.4550500
H	-1.4261420	3.6183430	-0.0076410
C	2.3739190	3.8903270	-0.7150840
H	2.0856110	2.2651630	-2.0921280
C	1.7747410	4.7594910	0.2039770
H	-0.0734160	5.3276820	1.1627580
H	3.4373650	3.9667740	-0.9233380
H	2.3701370	5.5107410	0.7145550
H	0.1660430	0.4259420	0.5600690
O	0.5238830	-1.5994870	-0.1121890
H	1.6233220	-1.4303830	-0.2344690
H	0.4015280	-2.0097130	0.7597120
O	2.9146110	-1.2328350	-0.4405690

C	3.6602130	-1.6752210	0.4992500
O	3.3420540	-2.2408950	1.5456160
C	5.1745690	-1.4220960	0.2180400
F	5.5551520	-1.9580210	-0.9688460
F	5.4422700	-0.0918030	0.1602850
F	5.9734380	-1.9486950	1.1677840

13.log
 Potential Energy = -1489.66178
 Zero-point Energy = -1489.18774
 Free Energy = -1489.23108
 Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11946
 Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68876
 Nimag = 1 (-330.9669 cm⁻¹)
 Charge = 0 Multiplicity = 1

C	3.0935500	-0.3485140	0.4439820
C	3.4350370	0.0877620	-1.8534080
C	1.9701980	-0.3321370	-1.7100250
N	1.7810920	-0.2371240	-0.2411940
N	3.9984600	0.1053250	-0.6241160
O	3.9922150	0.3901960	-2.9106480
C	5.3129340	0.7005680	-0.3979590
H	6.1236130	-0.0068010	-0.5925510
H	5.4279210	1.5532270	-1.0708370
H	5.3808630	1.0452400	0.6343370
C	0.6228350	0.1871480	0.3246450
C	0.6483910	0.9182950	1.6520230
C	-0.7003040	1.5549860	2.0554170
H	-1.4760150	0.7860850	2.1123190
H	-0.5736450	1.9422630	3.0724730
C	1.0489460	0.5342530	-2.5635230
H	1.4033620	0.4774910	-3.5954540
H	0.0178170	0.1721690	-2.5459580
H	1.0712890	1.5825960	-2.2509380
H	1.8776960	-1.3751040	-2.0396700
C	3.4405120	-1.7678390	1.0204620
H	3.1370350	0.3711650	1.2670760
C	4.8991660	-1.7718040	1.5287470
H	5.0864860	-2.7030730	2.0726530
H	5.6229770	-1.7209130	0.7122740
H	5.0931010	-0.9435290	2.2196150
C	2.5270870	-2.0659030	2.2272980
H	2.6746980	-1.3316710	3.0279030
H	1.4686330	-2.0786520	1.9595300
H	2.7773940	-3.0499960	2.6365520
C	3.2773310	-2.8721640	-0.0396710
H	3.8993130	-2.6853850	-0.9212870
H	3.5883010	-3.8332500	0.3822920
H	2.2375560	-2.9808190	-0.3627420
H	1.3977970	1.7137180	1.5600750
H	0.9838590	0.2471180	2.4446430
C	-1.1534130	2.6808920	1.1438270
C	-0.5079980	3.9288220	1.1800890
C	-2.2178200	2.5062730	0.2462880
C	-0.9101120	4.9702580	0.3403210
H	0.3109050	4.0899520	1.8776790
C	-2.6238290	3.5478180	-0.5966090
H	-2.7342790	1.5506120	0.2116140
C	-1.9707120	4.7823060	-0.5538050
H	-0.4008390	5.9287680	0.3874300
H	-3.4515820	3.3927490	-1.2830610
H	-2.2860930	5.5919050	-1.2056080
H	-0.0524770	0.6266730	-0.4020410
O	-0.3784600	-1.1960140	0.7087670
H	-1.4915860	-1.0794940	0.6188600
H	-0.1481600	-1.8916120	0.0704760
O	-2.8048140	-0.9989940	0.5355310
C	-3.2961330	-1.9135090	-0.2124810
O	-2.7137880	-2.7992780	-0.8387920
C	-4.8520650	-1.8344450	-0.2963200
F	-5.4162050	-1.9631320	0.9312520
F	-5.2555280	-0.6400580	-0.7990310
F	-5.3777820	-2.7962010	-1.0805700

14.log
 Potential Energy = -1489.66326
 Zero-point Energy = -1489.19008
 Free Energy = -1489.23415
 Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11854
 Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68943
 Nimag = 1 (-378.5909 cm⁻¹)
 Charge = 0 Multiplicity = 1

C	-1.2140390	1.6419790	0.4122200
C	-1.1311840	2.7783480	-1.6503700
C	0.2929720	2.2678690	-1.4011770
N	0.0927420	1.3673840	-0.2403640
N	-1.9330390	2.3470900	-0.6518730
O	-1.4855890	3.4448390	-2.6252990
C	-3.3825270	2.5024470	-0.7158030
H	-3.6915490	2.4169630	-1.7595630
H	-3.8571920	1.7118850	-0.1335370
H	-3.7090070	3.4753160	-0.3367380
C	0.7376550	0.1984100	0.0069190
H	0.4142720	-0.2384160	0.9474100
C	2.2390470	0.0932050	-0.2132410
C	2.8822060	-1.0752030	0.5653970
H	2.6429640	-0.9714090	1.6296360
H	0.9133920	3.1225550	-1.1006470
C	-1.0884940	2.4426890	1.7570580
H	-1.7236560	0.6938000	0.6182570
H	2.4660480	-0.0020980	-1.2762420
C	0.8685670	1.6697130	-2.6876890
H	1.9449780	1.5107920	-2.6188410
H	0.3797040	0.7288190	-2.9486030
H	0.6902630	2.3925720	-3.4878940
C	-2.4921340	2.6364900	2.3725230
H	-2.3915260	3.0619660	3.3761700
H	-3.1120180	3.3226610	1.7916210
H	-3.0265510	1.6844590	2.4696650
C	-0.4265150	3.8151050	1.5376880
H	-0.9891470	4.4303260	0.8280660
H	-0.3857640	4.3601270	2.4864780
H	0.6008590	3.7133940	1.1738620
C	-0.2453970	1.6267110	2.7595710
H	-0.6644440	0.6272710	2.9266460
H	0.7943440	1.5238500	2.4363630
H	-0.2340050	2.1408390	3.7259120
O	0.0955260	-1.0241680	-1.0458000
H	-0.9744650	-1.2758530	-0.7932920
H	0.5955700	-1.8531720	-0.9564000
O	-2.2284180	-1.5161810	-0.5095180
C	-2.4620310	-2.7351820	-0.1957170
O	-1.6834850	-3.6860520	-0.1391460
C	-3.9628220	-2.9706050	0.1607560
F	-4.7781470	-2.5962060	-0.8563290
F	-4.2330790	-4.2618780	0.4355540
F	-4.3217100	-2.2436220	1.2503250
H	2.6802960	1.0367060	0.1266030
H	2.4537860	-2.0296920	0.2368740
C	4.3858750	-1.1204550	0.3826400
C	4.9585980	-1.8301260	-0.6841530
C	5.2361810	-0.4321680	1.2617090
C	6.3440140	-1.8489290	-0.8714710
H	4.3158770	-2.3764520	-1.3704340
C	6.6223440	-0.4480250	1.0783210
H	4.8111160	0.1160900	2.0991310
C	7.1809900	-1.1563670	0.0096060
H	6.7684720	-2.4073610	-1.7010110
H	7.2641170	0.0878220	1.7719890
H	8.2576590	-1.1726550	-0.1323980

15.log
 Potential Energy = -1489.66309
 Zero-point Energy = -1489.18922
 Free Energy = -1489.23270
 Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.12199

Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated
free energy from qRRHO) = -1489.69160
Nimag = 1 (-291.0837 cm⁻¹)
Charge = 0 Multiplicity = 1

C	2.1556070	-0.1911370	0.4938210
C	3.1404510	-0.4468800	-1.6319580
C	2.2441500	-1.6756080	-1.4392940
N	1.4850200	-1.3090340	-0.2196250
N	3.0018210	0.3686220	-0.5635870
O	3.8449660	-0.2300750	-2.6205610
C	3.5815790	1.7072980	-0.5446020
H	3.5596060	2.1055200	-1.5610400
H	2.9883340	2.3495780	0.1071690
H	4.6192110	1.7009700	-0.1978920
C	0.1821630	-1.5934850	0.0427450
H	-0.1084380	-1.2286910	1.0238170
C	-0.3686470	-2.9797950	-0.2724990
C	-1.5609040	-3.4003240	0.6178160
H	-1.7700770	-4.4514910	0.3881790
H	2.8899910	-2.5376000	-1.2250280
C	2.9336220	-0.6435150	1.7807420
H	1.4079690	0.5559220	0.7833200
H	-0.6474620	-3.0455780	-1.3258080
C	1.4565020	-1.9588390	-2.7208940
H	0.9747990	-2.9365800	-2.6962580
H	0.7046450	-1.1901640	-2.9109610
H	2.1730190	-1.9617300	-3.5462660
C	3.5393910	0.5954480	2.4769580
H	3.9546150	0.2995010	3.4457290
H	4.3516660	1.0434140	1.9007820
H	2.7817180	1.3651770	2.6637170
C	4.0528090	-1.6446460	1.4418700
H	4.7800220	-1.2213970	0.7414350
H	4.5932980	-1.9155800	2.3547500
H	3.6509130	-2.5679810	1.0128400
C	1.9467430	-1.3007670	2.7682660
H	1.1138310	-0.6328720	3.0181780
H	1.5421390	-2.2401770	2.3813600
H	2.4690450	-1.5332510	3.7018100
O	-0.8246620	-0.5498050	-0.9015100
H	-0.7335280	0.5150370	-0.6010890
H	-1.7567970	-0.8126070	-0.7847880
O	-0.5316870	1.7846920	-0.2357640
C	-1.5216060	2.5751040	-0.4059520
O	-2.6434240	2.3394880	-0.8538430
C	-1.1903730	4.0334840	0.0437590
F	-0.1263620	4.5306420	-0.6368080
F	-2.2190680	4.8832440	-0.1496990
F	-0.8760270	4.0789740	1.3643880
H	0.4454870	-3.6946860	-0.1150570
H	-1.2563340	-3.3679930	1.6692480
C	-2.8336290	-2.5919590	0.4391240
C	-3.3330590	-1.7914240	1.4791070
C	-3.5546830	-2.6414200	-0.7683350
C	-4.5160310	-1.0610930	1.3212500
H	-2.7952390	-1.7449470	2.4226270
C	-4.7355350	-1.9107190	-0.9299330
H	-3.1964880	-3.2649860	-1.5839690
C	-5.2205030	-1.1176740	0.1157390
H	-4.8842240	-0.4497580	2.1400150
H	-5.2779110	-1.9654950	-1.8693120
H	-6.1384190	-0.5511000	-0.0088890

16.log
Potential Energy = -1489.66225
Zero-point Energy = -1489.18884
Free Energy = -1489.23238
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -
1490.12098
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated
free energy from qRRHO) = -1489.69110
Nimag = 1 (-361.3958 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-0.2826440	1.6543360	0.6961040
C	-0.8995090	3.4405790	-0.7097270
C	0.3779920	2.8519770	-1.3213680

N	0.5375240	1.5984350	-0.5428510
N	-1.2536260	2.6999010	0.3629430
O	-1.5150200	4.4133860	-1.1517730
C	-2.5320930	2.8961280	1.0384480
H	-3.2771770	3.1764780	0.2910750
H	-2.8353470	1.9645410	1.5172410
H	-2.4815760	3.6883230	1.7911700
C	0.9706560	0.3964840	-1.0047680
H	1.0047860	-0.3424270	-0.2091530
C	2.1690260	0.3238370	-1.9358550
C	2.7779630	-1.0887970	-2.0978680
H	2.0514140	-1.7699070	-2.5557640
H	1.2085250	3.5322920	-1.0915120
C	0.5568170	1.9322650	1.9928570
H	-0.8126530	0.7034360	0.8231740
H	1.9097380	0.7103170	-2.9219130
C	0.2319540	2.7523980	-2.8422250
H	1.1899460	2.5859480	-3.3353690
H	-0.4670100	1.9646570	-3.1303670
H	-0.1576120	3.7123850	-3.1906610
C	-0.3795190	1.9367010	3.2216290
H	0.2231440	1.9764410	4.1347280
H	-1.0455070	2.8021350	3.2360410
H	-0.9906450	1.0280320	3.2689510
C	1.3011930	3.2770640	1.9084530
H	0.6123110	4.1157380	1.7640280
H	1.8456920	3.4549950	2.8416020
H	2.0340490	3.2819000	1.0955160
C	1.5803310	0.7946270	2.1859410
H	1.0936210	-0.1866020	2.2318720
H	2.3323010	0.7758620	1.3924200
H	2.1105770	0.9406900	3.1324170
O	-0.3083620	-0.3211870	-1.9387240
H	-1.1697440	-0.6460000	-1.2950890
H	-0.0031540	-1.1168810	-2.4058980
O	-2.1835330	-0.9729720	-0.5252020
C	-2.5548070	-2.1913150	-0.6495840
O	-2.1030010	-3.0712750	-1.3814970
C	-3.7525770	-2.5382430	0.2887560
F	-4.8305530	-1.7599440	0.0168340
F	-4.1466900	-3.8216880	0.1719090
F	-3.4296860	-2.3340020	1.5913430
H	2.9272210	0.9963820	-1.5195460
H	3.5935570	-0.9950930	-2.8232270
C	3.3096010	-1.7047970	-0.8180420
C	4.4985100	-1.2287430	-0.2398280
C	2.6357160	-2.7594310	-0.1840040
C	4.9960830	-1.7868410	0.9400590
H	5.0436250	-0.4201970	-0.7214500
C	3.1303720	-3.3214240	0.9986330
H	1.7207400	-3.1519260	-0.6212900
C	4.3117330	-2.8358320	1.5650410
H	5.9196060	-1.4076020	1.3683960
H	2.5937520	-4.1387760	1.4719290
H	4.6994320	-3.2722450	2.4809240

17.log
Potential Energy = -1489.66308
Zero-point Energy = -1489.18914
Free Energy = -1489.23251
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -
1490.12191
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated
free energy from qRRHO) = -1489.69134
Nimag = 1 (-290.5330 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-2.1568900	-0.1633950	-0.4805990
C	-3.1344230	-0.4490860	1.6446970
C	-2.2536260	-1.6841930	1.4232750
N	-1.4958600	-1.3026680	0.2073770
N	-2.9920150	0.3852600	0.5915060
O	-3.8309500	-0.2430910	2.6412660
C	-3.5540640	1.7316490	0.6028710
H	-3.5170670	2.1109870	1.6261150
H	-2.9588080	2.3779870	-0.0430040
H	-4.5949270	1.7454270	0.2662690

C	-0.1963520	-1.5942890	-0.0654330
H	0.0930650	-1.2133900	-1.0406880
C	0.3412410	-2.9928870	0.2172890
C	1.5324410	-3.4025630	-0.6798270
H	1.7325220	-4.4604360	-0.4743360
H	-2.9108150	-2.5339660	1.1950660
C	-2.9454820	-0.5822410	-1.7722720
H	-1.4021940	0.5805900	-0.7595430
H	0.6162480	-3.0880700	1.2694500
C	-1.4637100	-2.0023640	2.6952400
H	-0.9939100	-2.9851090	2.6488020
H	-0.7020370	-1.2464950	2.8971370
H	-2.1764580	-2.0136230	3.5237990
C	-3.5514460	0.6746890	-2.4352620
H	-3.9714040	0.4034670	-3.4092270
H	-4.3604090	1.1095650	-1.8445500
H	-2.7933170	1.4476150	-2.6062990
C	-4.0662500	-1.5868360	-1.4493550
H	-4.7860380	-1.1778990	-0.7328760
H	-4.6152380	-1.8326970	-2.3642580
H	-3.6649370	-2.5221250	-1.0464910
C	-1.9671230	-1.2196790	-2.7811420
H	-1.1345880	-0.5479580	-3.0219900
H	-1.5614850	-2.1681740	-2.4180250
H	-2.4964500	-1.4305930	-3.7158570
O	0.8226500	-0.5778080	0.8921830
H	0.7884350	0.4791440	0.5519370
H	1.7453420	-0.8842340	0.8113060
O	0.6542370	1.7266910	0.0968050
C	1.4967400	2.5857890	0.5283260
O	2.4290960	2.4419420	1.3182590
C	1.2460530	4.0035740	-0.0765760
F	0.0117090	4.4655460	0.2503780
F	2.1396660	4.9170010	0.3530950
F	1.3172730	3.9805180	-1.4323260
H	-0.4792030	-3.6958700	0.0403230
H	1.2311190	-3.3428370	-1.7310130
C	2.8101080	-2.6076760	-0.4775100
C	3.3139570	-1.7782580	-1.4924310
C	3.5284730	-2.6947580	0.7294550
C	4.4979300	-1.0553830	-1.3102130
H	2.7783110	-1.7022530	-2.4352150
C	4.7106180	-1.9716680	0.9153560
H	3.1672140	-3.3415280	1.5254610
C	5.1994190	-1.1488100	-0.1051090
H	4.8694260	-0.4209850	-2.1097280
H	5.2507550	-2.0556760	1.8538470
H	6.1182210	-0.5881470	0.0382890

18.log
Potential Energy = -1489.66019
Zero-point Energy = -1489.18653
Free Energy = -1489.22984
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11899
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68863
Nimag = 1 (-392.7208 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-2.8509660	-0.1189270	0.5924330
C	-2.6438470	-2.2067690	-0.4783960
C	-2.0375180	-1.1791810	-1.4414520
N	-1.9560870	0.0295210	-0.5841970
N	-3.0235780	-1.5726330	0.6533040
O	-2.7410090	-3.4160790	-0.6976450
C	-3.4670080	-2.3088540	1.8319330
H	-2.9247530	-3.2557560	1.8698720
H	-3.2417630	-1.7284480	2.7277280
H	-4.5391600	-2.5247090	1.8030430
C	-0.9581320	0.9485100	-0.5287500
H	-1.2380320	1.7828450	0.1072070
C	-0.2411590	1.3821020	-1.8012260
C	0.2813470	2.8379720	-1.7467280
H	0.6403220	3.0825810	-2.7523730
H	-2.7664470	-0.9980800	-2.2424370
C	-4.1879450	0.6965480	0.4812050

H	-2.3150490	0.2127970	1.4892080
H	0.5802450	0.7007460	-2.0298410
C	-0.7559100	-1.7256030	-2.0692080
H	-0.4122730	-1.1080610	-2.8993880
H	0.0506340	-1.8373430	-1.3422550
H	-0.9942330	-2.7155050	-2.4672690
C	-4.9954720	0.5355290	1.7882740
H	-5.8527880	1.2161530	1.7707930
H	-5.3882320	-0.4755780	1.9148080
H	-4.3931140	0.7855410	2.6692650
C	-5.0404200	0.2283500	-0.7122960
H	-5.2943710	-0.8340920	-0.6402140
H	-5.9795080	0.7908520	-0.7363440
H	-4.5305860	0.4022450	-1.6651410
C	-3.8596250	2.1947980	0.3112590
H	-3.2362160	2.5722230	1.1305520
H	-3.3572470	2.3991400	-0.6385300
H	-4.7894200	2.7724870	0.3178200
O	0.2798580	0.3939260	0.5637880
H	1.0893110	-0.3223170	0.2274600
H	0.7290740	1.1775000	0.9265170
O	2.0134440	-1.1562600	-0.1512960
C	2.9003880	-1.4512960	0.7237960
O	3.0147020	-1.0642580	1.8850630
C	3.9564480	-2.4551270	0.1628790
F	4.5759020	-1.9563490	-0.9368370
F	4.9166570	-2.7512130	1.0613670
F	3.3734420	-3.6255450	-0.2024310
H	-0.9583810	1.3092890	-2.6253360
H	-0.5584990	3.5115010	-1.5427110
C	1.3922950	3.0931200	-0.7464010
C	1.1371610	3.7433820	0.4721430
C	2.7079040	2.6795990	-1.0176280
C	2.1631400	3.9630770	1.4003830
H	0.1324260	4.0961320	0.6921120
C	3.7340510	2.9002250	-0.0963610
H	2.9301420	2.1839760	-1.9595070
C	3.4645330	3.5406980	1.1189860
H	1.9429830	4.4689120	2.3360080
H	4.7444340	2.5749500	-0.3271640
H	4.2626120	3.7122190	1.8351200

19.log
Potential Energy = -1489.66231
Zero-point Energy = -1489.18932
Free Energy = -1489.23334
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11822
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68925
Nimag = 1 (-406.5721 cm⁻¹)
Charge = 0 Multiplicity = 1

C	3.3139270	-0.2198350	-0.5508950
C	3.3116440	-1.3128700	1.5352840
C	2.1613940	-0.3013600	1.5971430
N	2.0808420	0.1560300	0.1884660
N	3.8669720	-1.2717520	0.3039050
O	3.6449860	-2.0640800	2.4538880
C	4.8512580	-2.2608790	-0.1227090
H	4.6121460	-3.2118290	0.3575500
H	4.7990360	-2.3805760	-1.2056180
H	5.8692250	-1.9769150	0.1596130
C	0.9619750	0.4568180	-0.5132440
H	1.2059120	0.7973830	-1.5147950
C	-0.1620720	1.2556710	0.1228170
C	-1.1301690	1.8498940	-0.9215420
H	2.4749730	0.5353030	2.2348190
C	4.2817570	0.9896640	-0.8092750
H	3.0346820	-0.6548400	-1.5182420
H	-0.7217390	0.6504080	0.8366440
C	0.9258030	-0.9570980	2.2179830
H	0.1621150	-0.2265120	2.4841430
H	0.4926190	-1.7153850	1.5619650
H	1.2508300	-1.4471340	3.1392960
C	5.4973880	0.5099840	-1.6329860
H	6.0940670	1.3766850	-1.9349350

H	6.1538380	-0.1511720	-1.0634890
H	5.1877700	-0.0114320	-2.5461010
C	4.7661260	1.6122820	0.5128420
H	5.2935810	0.8840480	1.1372660
H	5.4620020	2.4305250	0.3009270
H	3.9348200	2.0299920	1.0895990
C	3.5484280	2.0658330	-1.6375930
H	3.1631010	1.6628510	-2.5817430
H	2.7219800	2.5203750	-1.0839790
H	4.2494020	2.8681520	-1.8888570
O	0.1943470	-1.0374940	-1.0350620
H	-0.7945880	-1.3560620	-0.5873080
H	0.0921130	-1.0479800	-2.0001180
O	-1.9023870	-1.7625540	-0.0411190
C	-2.7314960	-2.2767180	-0.8699970
O	-2.6267120	-2.4199370	-2.0874350
C	-4.0363550	-2.7645480	-0.1667290
F	-4.6763540	-1.7350090	0.4443360
F	-4.9097870	-3.3230450	-1.0278180
F	-3.7646610	-3.6900080	0.7875730
H	0.3067010	2.0680490	0.6904850
H	-0.5585780	2.4458360	-1.6425130
H	-1.6045850	1.0366880	-1.4807250
C	-2.1969300	2.7160390	-0.2828200
C	-3.3952750	2.1534620	0.1841940
C	-1.9994630	4.0962640	-0.1225070
C	-4.3687880	2.9473430	0.7980620
H	-3.5687960	1.0870530	0.0637760
C	-2.9705470	4.8943780	0.4903760
H	-1.0806230	4.5510750	-0.4851850
C	-4.1592360	4.3215730	0.9539010
H	-5.2910720	2.4934800	1.1497350
H	-2.8002450	5.9616380	0.6010120
H	-4.9162490	4.9400500	1.4273560

20.log
Potential Energy = -1489.66019
Zero-point Energy = -1489.18653
Free Energy = -1489.22984
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11898
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68863
Nimag = 1 (-392.8019 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-2.8507190	-0.1190700	0.5924780
C	-2.6436850	-2.2066600	-0.4788590
C	-2.0374180	-1.1788570	-1.4417230
N	-1.9559650	0.0296610	-0.5842120
N	-3.0232760	-1.5727940	0.6530380
O	-2.7408990	-3.4159140	-0.6983950
C	-3.4666120	-2.3092920	1.8315290
H	-2.9243860	-3.2562240	1.8691720
H	-3.2412480	-1.7291200	2.7274460
H	-4.5387750	-2.5251030	1.8027000
C	-0.9580950	0.9487320	-0.5287180
H	-1.2379930	1.7829440	0.1073980
C	-0.2412510	1.3825630	-1.8011850
C	0.2811030	2.8384800	-1.7465260
H	-2.7663700	-0.9975980	-2.2426490
C	-4.1877460	0.6963760	0.4815780
H	-2.3147160	0.2124730	1.4892670
O	0.5802170	0.7013260	-2.0299240
C	-0.7558170	-1.7251380	-2.0696230
H	-0.4121980	-1.1074150	-2.8996760
H	0.0507380	-1.8370280	-1.3427060
H	-0.9941400	-2.7149550	-2.4678960
C	-4.9950700	0.5351100	1.7887430
H	-5.8524140	1.2157060	1.7715050
H	-5.3877750	-0.4760310	1.9151730
H	-4.3925860	0.7850000	2.6696830
C	-5.0403760	0.2283370	-0.7118730
H	-5.2943020	-0.8341190	-0.6399110
H	-5.9794750	0.7908290	-0.7357140
H	-4.5306740	0.4023750	-1.6647630
C	-3.8595200	2.1946680	0.3118340

H	-3.2359860	2.5719790	1.1310840
H	-3.3573180	2.3991990	-0.6380080
H	-4.7893400	2.7723140	0.3186600
O	0.2800350	0.3940950	0.5636610
H	1.0893790	-0.3223020	0.2273510
H	0.7293540	1.1776420	0.9263190
O	2.0133670	-1.1564140	-0.1513330
C	2.9001330	-1.4517050	0.7238570
O	3.0143760	-1.0647750	1.8851660
C	3.9561000	-2.4556610	0.1629850
F	4.5763040	-1.9565150	-0.9361500
F	4.9157370	-2.7525550	1.0618180
F	3.3728840	-3.6256780	-0.2032470
H	-0.9585070	1.3097720	-2.6252680
H	0.6399120	3.0832940	-2.7521810
H	-0.5587830	3.5118880	-1.5422820
C	1.3921650	3.0935810	-0.7463130
C	1.1371530	3.7437010	0.4723320
C	2.7077650	2.6801690	-1.0177570
C	2.1632440	3.9633750	1.4004530
H	0.1324220	4.0963520	0.6924760
C	3.7340220	2.9007730	-0.0966070
H	2.9299090	2.1846550	-1.9597150
C	3.4646260	3.5411130	1.1188370
H	1.9431800	4.4691010	2.3361600
H	4.7443950	2.5755840	-0.3275770
H	4.2627920	3.7126180	1.8348790

21.log
Potential Energy = -1489.65495
Zero-point Energy = -1489.18085
Free Energy = -1489.22400
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11262
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68166
Nimag = 1 (-330.9198 cm⁻¹)
Charge = 0 Multiplicity = 1

C	2.7836090	-1.4664520	-0.1699070
C	2.8317280	-0.4095240	1.9397200
C	1.5180930	0.0340310	1.2940840
N	1.4377840	-0.8874680	0.1351920
N	3.4491010	-1.2938040	1.1230670
O	3.2286750	-0.0643470	3.0537400
C	4.5380950	-2.1362370	1.6145920
H	4.3367830	-2.3875910	2.6583360
H	4.5798680	-3.0526030	1.0255840
H	5.5060020	-1.6316220	1.5599500
C	0.3589430	-1.1643800	-0.6319060
C	-1.0393860	-1.3671830	-0.0668200
C	-2.0076050	-1.9764890	-1.1038860
H	-2.1126760	-1.2903650	-1.9489430
H	1.6146620	1.0674090	0.9336090
C	3.5715730	-0.8389470	-1.3786910
H	2.6588970	-2.5383010	-0.3656820
H	-0.9366920	-2.0576640	0.7766630
C	0.3978400	-0.0200960	2.3367590
H	-0.5196000	0.4478840	1.9815630
H	0.1861720	-1.0444300	2.6540250
H	0.7446530	0.5423400	3.2073850
C	5.0218340	-1.3756270	-1.3756410
H	5.5233470	-1.0498300	-2.2922130
H	5.6019680	-0.9923310	-0.5341460
H	5.0543380	-2.4703880	-1.3563270
C	3.6211380	0.6971660	-1.2888200
H	4.1283180	1.0246010	-0.3752330
H	4.1822990	1.0995930	-2.1380240
H	2.6303470	1.1612420	-1.2989320
C	2.9446590	-1.2981520	-2.7149060
H	2.9213050	-2.3918080	-2.7841970
H	1.9285150	-0.9381650	-2.8869620
H	3.5519750	-0.9273490	-3.5460430
H	-1.4547220	-0.4369660	0.3238830
H	-1.5736900	-2.9052430	-1.4934650
C	-3.3691640	-2.2678030	-0.5063770
C	-3.6313640	-3.4966490	0.1195550

C	-4.3917060	-1.3070800	-0.5456560
C	-4.8791880	-3.7589440	0.6933070
H	-2.8543300	-4.2569410	0.1527450
C	-5.6412960	-1.5644270	0.0267790
H	-4.2098440	-0.3519110	-1.0324650
C	-5.8890770	-2.7921260	0.6493570
H	-5.0633480	-4.7181660	1.1690310
H	-6.4205880	-0.8087740	-0.0176470
H	-6.8602510	-2.9951380	1.0913610
H	0.6012660	-1.9113420	-1.3836600
O	-0.0150290	0.1494610	-1.7681940
H	-0.5375690	1.0187570	-1.3192900
H	0.8042930	0.4843740	-2.1636460
O	-1.2453960	2.0494480	-0.8454200
C	-0.5612310	3.0081200	-0.3496840
O	0.6580700	3.1025340	-0.2016170
C	-1.4620590	4.1976380	0.1096140
F	-2.1345890	4.7337430	-0.9414170
F	-0.7557170	5.1941050	0.6804630
F	-2.3900360	3.7945780	1.0140680

22.log
Potential Energy = -1489.65593
Zero-point Energy = -1489.18221
Free Energy = -1489.22598
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11120
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68125
Nimag = 1 (-297.0900 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-3.1260970	-0.3858910	-0.7275710
C	-4.2680010	0.9950400	0.8050760
C	-2.8075580	0.9818010	1.2684260
N	-2.1382050	0.3838820	0.0885860
N	-4.3703010	0.2859820	-0.3408020
O	-5.1837310	1.6050900	1.3595050
C	-5.5566060	0.3890970	-1.1884710
H	-5.9312360	1.4138720	-1.1368390
H	-5.2849590	0.1569180	-2.2184910
H	-6.3522220	-0.2881520	-0.8678870
C	-0.8233600	0.3886520	-0.2167930
C	0.0646570	1.6046270	0.0022760
C	1.4234440	1.4957730	-0.7209620
H	1.9845670	0.6404330	-0.3347100
H	-2.7145650	0.3040990	2.1278460
C	-3.1565350	-1.9461630	-0.5310180
H	-2.9258750	-0.1804110	-1.7858330
H	-0.4799500	2.4654140	-0.3994450
C	-2.3971660	2.3896350	1.7060920
H	-1.4305290	2.4016610	2.2088380
H	-2.3825850	3.0896560	0.8668880
H	-3.1498730	2.7316580	2.4208760
C	-4.4183160	-2.5176040	-1.2163860
H	-4.3649410	-3.6106890	-1.2027230
H	-5.3360330	-2.2301250	-0.6987400
H	-4.4942940	-2.2068600	-2.2644310
C	-3.1790660	-2.3329660	0.9588760
H	-4.0447760	-1.9028280	1.4742120
H	-3.2528140	-3.4215220	1.0532110
H	-2.2664890	-2.0163420	1.4701080
C	-1.9350340	-2.5846600	-1.2275560
H	-1.8760850	-2.2882810	-2.2817160
H	-0.9942840	-2.3362720	-0.7379580
H	-2.0330700	-3.6747520	-1.1992640
H	0.2263430	1.8004290	1.0643410
H	1.2454710	1.3072060	-1.7862130
C	2.2478580	2.7572950	-0.5602150
C	2.1234780	3.8188840	-1.4699490
C	3.1360200	2.9011170	0.5170990
C	2.8625180	4.9946460	-1.3067890
H	1.4469770	3.7224740	-2.3160030
C	3.8768710	4.0750420	0.6849160
H	3.2521410	2.0858370	1.2272960
C	3.7416340	5.1269760	-0.2269660
H	2.7550530	5.8031960	-2.0243970

H	4.5617320	4.1652680	1.5234120
H	4.3189860	6.0382010	-0.1002470
H	-0.6450800	-0.0868260	-1.1784200
O	0.0075320	-0.8582640	0.7478410
H	0.8980800	-1.3655960	0.3286360
H	0.2631080	-0.4924740	1.6097470
O	1.9343400	-2.0331700	-0.1933640
C	2.8591220	-2.3056860	0.6449780
O	2.9319900	-2.0320200	1.8437930
C	4.0318870	-3.1007970	-0.0108690
F	4.5716830	-2.4157700	-1.0509880
F	3.6018870	-4.2932170	-0.4980910
F	5.0316740	-3.3617040	0.8553060

23.log
Potential Energy = -1489.65068
Zero-point Energy = -1489.17631
Free Energy = -1489.21947
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11087
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.67967
Nimag = 1 (-280.3329 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-2.8367730	-1.0145370	-0.0039030
C	-3.3021610	1.0374540	-1.0736320
C	-1.7779870	0.9659920	-0.9746880
N	-1.5783980	-0.4511600	-0.5862440
N	-3.8291050	-0.1125360	-0.5930170
O	-3.9401320	1.9671540	-1.5695950
C	-5.2206470	-0.4720010	-0.8598700
H	-5.4882090	-0.1036580	-1.8527250
H	-5.3234360	-1.5572230	-0.8386020
H	-5.9066610	-0.0334720	-0.1307890
C	-0.4353250	-1.1697490	-0.6385420
C	0.5255010	-1.1174480	-1.8242490
C	1.3345460	-2.4207190	-2.0296550
H	0.6382300	-3.2664550	-2.0643560
H	-1.4311780	1.6165790	-0.1598950
C	-2.9179120	-1.1123690	1.5637870
H	-2.9820920	-2.0205590	-0.4150130
H	-0.0914990	-0.9795820	-2.7150820
C	-1.1550850	1.4530130	-2.2851570
H	-0.0691710	1.5218720	-2.2244550
H	-1.4353510	0.8203450	-3.1312710
H	-1.5457050	2.4571440	-2.4683730
C	-4.3627840	-1.4799310	1.9740780
H	-4.3851810	-1.6898810	3.0479440
H	-5.0645520	-0.6648010	1.7876950
H	-4.7201640	-2.3771690	1.4569670
C	-2.5428170	0.2194330	2.2385010
H	-3.2194860	1.0239730	1.9324030
H	-2.6234450	0.1182900	3.3253520
H	-1.5223850	0.5441370	2.0134470
C	-2.0175650	-2.2617930	2.0702360
H	-2.2913520	-3.2139710	1.6016670
H	-0.9501490	-2.1078990	1.9013720
H	-2.1496540	-2.3754910	3.1503810
H	1.1948190	-0.2569150	-1.7635830
H	1.7768640	-2.3488710	-3.0303640
C	2.4363380	-2.7125590	-1.0298500
C	3.6025590	-1.9304610	-1.0024660
C	2.3334510	-3.7844290	-0.1318550
C	4.6275340	-2.2006240	-0.0928780
H	3.7113350	-1.1030190	-1.6996630
C	3.3576680	-4.0606340	0.7810860
H	1.4458620	-4.4123830	-0.1464980
C	4.5077950	-3.2672710	0.8057480
H	5.5212510	-1.5828350	-0.0883850
H	3.2562840	-4.8959040	1.4684540
H	5.3053180	-3.4797530	1.5118500
H	-0.6012360	-2.1857820	-0.2903450
O	0.6962800	-0.6996370	0.6644390
H	1.2310040	0.2302480	0.4766850
H	0.2061740	-0.5737040	1.4919320
O	1.9715760	1.3650930	0.2466370

C	1.4605470	2.4463410	0.6897930
O	0.3801050	2.6260340	1.2571550
C	2.3818920	3.6828560	0.4418540
F	3.5915430	3.5235160	1.0373710
F	1.8540730	4.8302940	0.9147650
F	2.6111600	3.8650880	-0.8844740

24.log
Potential Energy = -1489.65446
Zero-point Energy = -1489.18064
Free Energy = -1489.22390
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11397
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68341
Nimag = 1 (-331.0632 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-1.2994360	2.0527380	0.1249970
C	0.1922520	2.8433220	-1.5229660
C	0.6664490	1.4271090	-1.1922750
N	-0.4733880	0.9176870	-0.3920810
N	-0.9388050	3.1039230	-0.8287580
O	0.7219130	3.5980040	-2.3403050
C	-1.7960430	4.2332540	-1.1847940
H	-1.7725200	4.3569070	-2.2698510
H	-2.8182370	4.0249660	-0.8682300
H	-1.4618550	5.1655430	-0.7225060
C	-0.7621490	-0.3661380	-0.0754380
C	-0.6141920	-1.5173730	-1.0583240
C	-1.2642110	-2.8333620	-0.5722210
H	-1.0555090	-3.5879910	-1.3389640
H	1.5637410	1.4775030	-0.5604480
C	-1.0853200	2.4616210	1.6290910
H	-2.3568200	1.7953540	-0.0106120
H	-1.0995030	-1.1962630	-1.9854060
C	1.0215110	0.6983960	-2.4916550
H	1.5259890	-0.2497660	-2.3090410
H	0.1413290	0.5298190	-3.1173900
H	1.7117920	1.3439350	-3.0406620
C	-1.8126650	3.7981080	1.9048970
H	-1.7862490	4.0021310	2.9798610
H	-1.3325900	4.6402150	1.4028240
H	-2.8654400	3.7625450	1.6042230
C	0.4070950	2.6425090	1.9613360
H	0.8552700	3.4354260	1.3534820
H	0.5198080	2.9307150	3.0112210
H	0.9962390	1.7341670	1.8036130
C	-1.7391480	1.4150320	2.5593540
H	-2.8072620	1.3061400	2.3397690
H	-1.2932830	0.4202020	2.5068690
H	-1.6470040	1.7455200	3.5983170
H	0.4339740	-1.7070820	-1.2919060
H	-0.7701410	-3.1682720	0.3436180
C	-2.7616660	-2.7494530	-0.3448290
C	-3.3007540	-2.7797560	0.9503120
C	-3.6462660	-2.6382860	-1.4314000
C	-4.6826160	-2.6969620	1.1580750
H	-2.6346600	-2.8759290	1.8041780
C	-5.0260180	-2.5548330	-1.2293890
H	-3.2525680	-2.6256840	-2.4451390
C	-5.5498420	-2.5823750	0.0685190
H	-5.0780350	-2.7248830	2.1695430
H	-5.6922750	-2.4743300	-2.0837320
H	-6.6226150	-2.5203930	0.2265060
H	-1.6947940	-0.4253770	0.4798020
O	0.2811770	-0.9966660	1.2118330
H	1.3002480	-1.2928230	0.8848590
H	0.3886920	-0.3283220	1.9057670
O	2.5031790	-1.7423490	0.5202240
C	3.4411210	-0.8742810	0.5336810
O	3.3886960	0.3276600	0.7976980
C	4.8231340	-1.4953040	0.1565360
F	5.1943600	-2.4409000	1.0578550
F	5.8100150	-0.5778200	0.1122150
F	4.7803460	-2.0970830	-1.0591070

25.log
Potential Energy = -1489.65026
Zero-point Energy = -1489.17613
Free Energy = -1489.21937
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11007
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.67919
Nimag = 1 (-236.1868 cm⁻¹)
Charge = 0 Multiplicity = 1

C	2.9655790	-0.7450410	0.6106690
C	4.4321080	0.7061370	-0.5284450
C	3.0214750	1.2467400	-0.7881910
N	2.2396610	0.5069990	0.2333050
N	4.3451060	-0.3543190	0.3043430
O	5.4741260	1.1958540	-0.9670610
C	5.5249760	-0.8816780	0.9865860
H	6.2083350	-0.0527500	1.1832920
H	5.2227530	-1.3319140	1.9329440
H	6.0493770	-1.6299140	0.3871820
C	1.0213930	0.8014080	0.7349330
C	0.6384340	2.2166790	1.1385650
C	-0.7581190	2.3781870	1.7796020
H	-0.9990470	1.4958420	2.3824200
H	2.6999500	0.9250300	-1.7875580
C	2.5065830	-2.0757000	-0.0899820
H	2.8711870	-0.8794080	1.6944240
H	1.3939700	2.4908450	1.8840140
C	3.0390790	2.7757330	-0.7580580
H	2.1183460	3.2047510	-1.1544030
H	3.2286320	3.1668860	0.2443520
H	3.8591140	3.0930490	-1.4074760
C	3.5745190	-3.1690130	0.1368200
H	3.1849640	-4.1250250	-0.2269840
H	4.4973810	-2.9632810	-0.4101870
H	3.8161000	-3.2970830	1.1977950
C	2.3024020	-1.8859650	-1.6041390
H	3.2211330	-1.5486300	-2.0963400
H	2.0246950	-2.8432810	-2.0575520
H	1.5021840	-1.1720600	-1.8164090
C	1.2006860	-2.5729550	0.5630510
H	1.3201040	-2.6972810	1.6459840
H	0.3511680	-1.9158500	0.3818990
H	0.9364670	-3.5508610	0.1473550
H	0.7586960	2.9180310	0.3154440
H	-0.6806330	3.2116740	2.4885040
C	-1.9123610	2.6769210	0.8344640
C	-1.8218470	3.6928950	-0.1331350
C	-3.1279210	1.9855930	0.9553580
C	-2.9075200	3.9985270	-0.9601450
H	-0.9043430	4.2661790	-0.2380510
C	-4.2173290	2.2914820	0.1341800
H	-3.2201130	1.1959480	1.6954270
C	-4.1105810	3.2981950	-0.8298360
H	-2.8131800	4.7880780	-1.7002090
H	-5.1463430	1.7396710	0.2458090
H	-4.9543790	3.5348540	-1.4712570
H	0.7140450	0.0686800	1.4776190
O	-0.2215510	0.3850130	-0.4906190
H	-1.0233320	-0.2825890	-0.1737430
H	-0.6430620	1.1944170	-0.8252770
O	-1.9813860	-1.1609470	0.2652910
C	-2.8160470	-1.5887280	-0.5979480
O	-2.9087590	-1.3359580	-1.8008490
C	-3.8506340	-2.5778900	0.0297410
F	-4.5566410	-1.9857090	1.0279140
F	-3.2326250	-3.6610840	0.5688000
F	-4.7458720	-3.0391650	-0.8679560

26.log
Potential Energy = -1489.65542
Zero-point Energy = -1489.18140
Free Energy = -1489.22461
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11360

Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated		
free energy from qRRHO) = -1489.68278		
Nimag = 1 (-305.1265 cm ⁻¹)		
Charge = 0 Multiplicity = 1		
C	-2.6594770	0.3627560
C	-4.2758100	0.6552950
C	-2.9187240	0.7163630
N	-2.0180240	0.2048410
N	-4.0744490	0.3832110
O	-5.3714230	0.7754100
C	-5.1728560	-0.0572890
H	-5.8521990	-0.6717240
H	-4.7727950	-0.6541940
H	-5.7363230	0.7834110
C	-0.7497720	-0.2450180
C	-0.3046190	-1.1100200
C	1.0543550	-1.8112140
H	1.2926120	-2.3376640
H	-2.6781050	1.7664330
C	-2.2165580	1.5991840
H	-2.4633750	-0.5465570
H	-1.0767310	-1.8729200
C	-2.9992220	-0.0479650
H	-2.1170780	0.1050020
H	-3.1557290	-1.1182510
H	-3.8625940	0.3461160
C	-3.1864350	1.7557790
H	-2.7961280	2.5229440
H	-4.1818440	2.0760540
H	-3.2822160	0.8292750
C	-2.2211810	2.9010920
H	-3.2116520	3.1098630
H	-1.9582510	3.7440050
H	-1.4909580	2.8661740
C	-0.8116650	1.3472940
H	-0.7741660	0.4008310
H	-0.0319930	1.3428750
H	-0.5675670	2.1481350
H	-0.2604760	-0.5338740
H	1.8409050	-1.0662890
C	1.0622470	-2.7980890
C	1.7394660	-2.5098690
C	0.3852410	-4.0252420
C	1.7364740	-3.4194550
H	2.2762180	-1.5693480
C	0.3797110	-4.9350850
H	-0.1355890	-4.2746670
C	1.0555220	-4.6340440
H	2.2687020	-3.1777590
H	-0.1460100	-5.8802560
H	1.0541170	-5.3419200
H	-0.3713680	-0.6084600
O	0.3567640	1.1356330
H	1.3936680	1.0421710
H	0.4171990	1.4379030
O	2.6218020	0.9658580
C	3.5103800	1.5887680
O	3.3906440	2.2229370
C	4.9240020	1.4909890
F	5.3135130	0.1986330
F	4.9291690	2.0486450
F	5.8749020	2.1163020

Formation of enamine (TS3)

Conformation name	Extrapolated Free energy (kcal/mol)
TS3-lowest	0.0
1	1.2
2	0.5

3	1.3	
4	0.9	
5	1.6	
6	1.3	
7	3.2	
8	2.3	
9	2.6	
10	2.7	
11	2.2	
12	3.4	
13	3.1	
14	2.7	
15	2.4	
16	2.1	
17	3.2	
18	2.4	
19	2.0	
20	1.8	
21	1.7	
22	2.1	
23	1.6	
24	1.8	
TS3-lowest.log (Enamine 2)		
Potential Energy = -1489.65579		
Zero-point Energy = -1489.18747		
Free Energy = -1489.23284		
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11344		
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.69048		
Nimag = 1 (-1187.7406 cm ⁻¹)		
Charge = 0 Multiplicity = 1		
C	-0.1574210	1.7542590
C	-1.3320550	2.8990120
C	-0.0728660	2.3291580
N	0.3945820	1.3747860
N	-1.3482980	2.5141450
O	-2.1909620	3.5738310
C	-2.5095980	2.7435460
H	-3.4076800	2.6833550
H	-2.5520570	1.9734170
H	-2.4800390	3.7289410
C	0.9173820	0.1811110
C	1.0484730	-0.9477280
C	2.0034900	-2.0666860
C	-0.3612370	1.7340590
H	-0.8513680	2.5040260
H	0.5563790	1.4420260
H	-1.0291510	0.8702780
H	0.6564210	3.1414950
C	0.8500190	2.5471490
H	-0.4803160	0.8499870
C	0.1647760	2.8799520
H	0.9083580	3.2918250
H	-0.6254200	3.6261000
H	-0.2626970	1.9869650
C	2.0777410	1.6630800
H	1.7997300	0.7555850
H	2.6091810	1.3720320
H	2.7778460	2.2222560
C	1.3197570	3.8521460
H	0.4798250	4.4979330

H	1.9483690	4.4130820	1.3346460
H	1.9221090	3.6566850	-0.2570300
H	1.1981000	0.0736060	-2.2594320
H	-0.2430860	-1.5221250	-0.6572260
H	0.9706550	-0.8154030	0.6754280
O	-1.2610430	-2.1561810	-0.8289860
C	-2.1793160	-1.9079390	0.0354620
O	-2.1485280	-1.1296760	0.9854510
C	-3.4663560	-2.7467530	-0.2311360
F	-3.2025320	-4.0721870	-0.1611240
F	-3.9644160	-2.4934630	-1.4633050
F	-4.4354460	-2.4761230	0.6638120
H	2.0067640	-2.1345120	-1.9293480
H	-3.3245770	-0.6518550	2.3728570
O	-3.7938960	-0.2767860	3.1423840
H	-4.6103530	-0.7864980	3.2209610
H	1.6142110	-3.0216520	-0.4643030
C	3.4264910	-1.8885320	-0.3310520
C	3.8032040	-2.3726340	0.9313230
C	4.3901070	-1.2223570	-1.1040280
C	5.1026130	-2.1879600	1.4141390
H	3.0738010	-2.9012680	1.5407440
C	5.6915520	-1.0370630	-0.6271110
H	4.1234540	-0.8496190	-2.0902350
C	6.0522300	-1.5176850	0.6361200
H	5.3737700	-2.5720210	2.3936740
H	6.4236190	-0.5228690	-1.2437360
H	7.0632140	-1.3766510	1.0073250

1.log
Potential Energy = -1489.65425
Zero-point Energy = -1489.18574
Free Energy = -1489.23052
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11230
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68857
Nimag = 1 (-1184.5882 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-2.1995800	-0.6142750	-0.4140810
C	-3.4781750	0.5370270	1.2061690
C	-2.8341940	-0.6468350	1.9347400
N	-1.8205050	-1.0833510	0.9425240
N	-3.0595710	0.5293860	-0.0801630
O	-4.2314890	1.3644400	1.7217140
C	-3.3525130	1.6336070	-0.9893400
H	-3.3871960	2.5567040	-0.4072410
H	-2.5618400	1.7096650	-1.7366250
H	-4.3152640	1.5046960	-1.4922570
C	-0.6069380	-1.5251660	1.2804200
C	0.5526290	-1.6020410	0.5059200
C	1.6791980	-2.5287680	0.9839770
H	1.4273160	-3.5651560	0.7201920
C	-2.2972410	-0.2578130	3.3076120
H	-3.1153710	0.1997900	3.8690340
H	-1.9532280	-1.1292130	3.8696260
H	-1.4818030	0.4673640	3.2303670
H	-3.5932910	-1.4296960	2.0529520
C	-2.8859690	-1.7169040	-1.2967570
H	-1.3077780	-0.2440420	-0.9279140
C	-3.2253200	-1.1160230	-2.6789220
H	-3.5546830	-1.9171600	-3.3483390
H	-4.0339460	-0.3835950	-2.6273720
H	-2.3530190	-0.6383740	-3.1388900
C	-1.9048080	-2.8871840	-1.5153570
H	-1.0018530	-2.5661840	-2.0450560
H	-1.6078170	-3.3580270	-0.5741590
H	-2.3907230	-3.6521010	-2.1296240
C	-4.1729800	-2.2557400	-0.6442030
H	-4.8895580	-1.4569750	-0.4274680
H	-4.6610040	-2.9566130	-1.3290760
H	-3.9619670	-2.8004870	0.2813860
H	-0.5165410	-1.7812550	2.3332640
H	0.9957340	-0.2431380	0.7622300
H	0.4493110	-1.5427120	-0.5756870
O	1.4463780	0.8603840	0.9428050

C	1.1773420	1.6969510	0.0050670
O	0.5343670	1.5143820	-1.0258470
C	1.7812050	3.1046700	0.2954000
F	1.5002420	3.9828990	-0.6860850
F	3.1271700	3.0404060	0.4148750
F	1.2916850	3.6117670	1.4507760
H	1.7401610	-2.4923760	2.0777460
C	3.0371140	-2.1980740	0.3922060
C	3.3270960	-2.5122570	-0.9455620
C	4.0327890	-1.5781210	1.1609950
C	4.5724690	-2.2072000	-1.5021060
H	2.5740990	-3.0056270	-1.5558950
C	5.2824270	-1.2739950	0.6104170
H	3.8293970	-1.3310590	2.2000380
C	5.5559970	-1.5855960	-0.7247450
H	4.7765900	-2.4597910	-2.5389170
H	6.0401870	-0.7957930	1.2248990
H	6.5257800	-1.3512600	-1.1541790
H	0.0036500	2.5699450	-2.4867800
O	-0.3829370	2.9644340	-3.2918480
H	0.0394720	3.8278970	-3.3845810

2.log
Potential Energy = -1489.65426
Zero-point Energy = -1489.18578
Free Energy = -1489.23079
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11317
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68969
Nimag = 1 (-1170.4086 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-1.5988630	-1.4802660	-0.2662370
C	-1.7836370	-1.7350240	2.0758960
C	-0.3720050	-2.2012210	1.7061200
N	-0.2510530	-1.6934900	0.3168800
N	-2.4033040	-1.3087550	0.9516200
O	-2.2573110	-1.7322150	3.2134500
C	-3.6980110	-0.6359000	0.9967630
H	-3.7573780	-0.0682040	1.9275360
H	-3.7817870	0.0489080	0.1521650
H	-4.5293050	-1.3463230	0.9705110
C	0.8802550	-1.1854430	-0.1809500
C	1.0555300	-0.3468300	-1.2815550
C	2.4390800	-0.1990160	-1.9391710
H	2.5383100	-0.9548380	-2.7286760
C	0.6785340	-1.7010260	2.6912290
H	0.3745280	-2.0142270	3.6929540
H	1.6607990	-2.1344970	2.4896790
H	0.7556540	-0.6098940	2.6777190
H	-0.3654850	-3.2981280	1.6988690
C	-2.0743790	-2.6428560	-1.2084850
H	-1.6036170	-0.5396510	-0.8245750
C	-3.4764480	-2.3024900	-1.7605670
H	-3.7427830	-3.0262650	-2.5375250
H	-4.2503870	-2.3528850	-0.9914560
H	-3.5024000	-1.3054150	-2.2142700
C	-1.1088140	-2.7634690	-2.4056260
H	-1.0921020	-1.8485710	-3.0070710
H	-0.0869160	-2.9914860	-2.0901740
H	-1.4445820	-3.5772920	-3.0563730
C	-2.1306790	-3.9934270	-0.4700780
H	-2.7714200	-3.9500120	0.4165280
H	-2.5459530	-4.7552810	-1.1376450
H	-1.1349860	-4.3337370	-0.1689310
H	1.7576570	-1.4101130	0.4187240
H	0.8364150	0.9176020	-0.6076940
H	0.2386470	-0.2719870	-1.9965740
O	0.7219440	2.0371430	-0.1840330
C	-0.4606350	2.5268470	-0.3105380
O	-1.4587960	2.0051850	-0.7997700
C	-0.5494690	3.9742770	0.2619370
F	-1.7831550	4.4943590	0.1182180
F	0.3189740	4.7990000	-0.3669700
F	-0.2483990	3.9912360	1.5809470
H	-3.2350130	2.5415230	-1.1201900

O	-4.1777790	2.6414080	-1.3526460
H	-4.4031180	3.5536130	-1.1296900
H	2.4659490	0.7732520	-2.4452820
C	3.6276570	-0.3076260	-1.0029900
C	4.0272370	0.7830460	-0.2129840
C	4.3564480	-1.5030680	-0.9045150
C	5.1210860	0.6809850	0.6511350
H	3.4792150	1.7193280	-0.2779700
C	5.4518440	-1.6104470	-0.0406480
H	4.0674760	-2.3561010	-1.5140360
C	5.8373280	-0.5176950	0.7413890
H	5.4167070	1.5381540	1.2496550
H	6.0036030	-2.5445160	0.0171640
H	6.6891610	-0.5968570	1.4106160

3.log
Potential Energy = -1489.65556
Zero-point Energy = -1489.18711
Free Energy = -1489.23272
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11126
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68842
Nimag = 1 (-1179.1869 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-1.2013630	-1.7339540	0.7129140
C	-1.1177050	-3.6126720	-0.7172050
C	-1.6616950	-2.4566270	-1.5624440
N	-1.3552170	-1.2910960	-0.6945270
N	-0.8414180	-3.1449970	0.5223580
O	-0.9435410	-4.7650760	-1.1149070
C	-0.1351030	-3.9562770	1.5092570
H	0.5758460	-4.5970220	0.9837740
H	0.4067080	-3.3027000	2.1939280
H	-0.8177720	-4.5904200	2.0819360
C	-0.9329980	-0.1174070	-1.1696340
C	-0.2532820	0.9110000	-0.5113590
C	-0.2219150	2.3048410	-1.1502730
C	-1.0529080	-2.4260030	-2.9596460
H	-1.2217150	-3.4032960	-3.4182280
H	-1.5298130	-1.6738430	-3.5924480
H	0.0247330	-2.2407850	-2.9261350
H	-2.7487850	-2.5748150	-1.6452470
C	-2.4738460	-1.4916820	1.6004530
H	-0.3529830	-1.2099080	1.1640930
C	-2.1918740	-1.9937660	3.0338400
H	-3.0137570	-1.6880500	3.6889990
H	-2.1218890	-3.0824990	3.0879670
H	-1.2690660	-1.5650560	3.4407560
C	-2.7673400	0.0204600	1.6744130
H	-1.9411110	0.5713910	2.1355860
H	-2.9653120	0.4522930	0.6898340
H	-3.6556430	0.1834210	2.2930590
C	-3.7100840	-2.2192170	1.0393240
H	-3.5369620	-3.2939580	0.9237300
H	-4.5485540	-2.0954220	1.7321010
H	-4.0222660	-1.8058470	0.0752090
H	-1.0795080	-0.0068720	-2.2411350
H	1.0767140	0.4409540	-0.7566020
H	-0.2609710	0.9172030	0.5766600
O	2.2264260	0.1224080	-0.9825350
C	3.0862490	0.5276060	-0.1172970
O	2.9027490	1.1998250	0.8937020
C	4.5306140	0.0664240	-0.4823350
F	4.9194450	0.5939970	-1.6669020
F	4.6013680	-1.2800490	-0.5923490
F	5.4288530	0.4466250	0.4465890
H	-0.1868390	2.1993680	-2.2411350
H	4.0005810	1.8736770	2.2649270
O	4.4322160	2.2804310	3.0406110
H	5.3759960	2.1094750	2.9279480
H	0.7070710	2.8039420	-0.8531760
C	-1.3978130	3.1862780	-0.7620130
C	-1.3167730	4.0402370	0.3482670
C	-2.5955710	3.1549750	-1.4933140
C	-2.4043920	4.8351340	0.7251110

H	-0.3934630	4.0857480	0.9210760
C	-3.6849090	3.9487960	-1.1224510
H	-2.6763060	2.5079940	-2.3638220
C	-3.5937260	4.7913580	-0.0090850
H	-2.3200960	5.4908600	1.5873210
H	-4.6013250	3.9133450	-1.7050760
H	-4.4382700	5.4105850	0.2791300

4.log
Potential Energy = -1489.65510
Zero-point Energy = -1489.18668
Free Energy = -1489.23265
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11153
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68908
Nimag = 1 (-1209.0288 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-0.9401270	2.0526560	-0.5268090
C	0.3886130	3.3236300	0.9566900
C	-0.1653610	2.1532730	1.7752950
N	-0.6769740	1.2637380	0.7014760
N	-0.0408920	3.1954900	-0.3204950
O	1.1181890	4.2148540	1.3922600
C	0.4607460	4.0539170	-1.3893150
H	1.5006310	4.3046510	-1.1704420
H	0.4111530	3.5177530	-2.3378700
H	-0.1111640	4.9825910	-1.4708000
C	-0.5576810	-0.0644260	0.7360230
C	-0.6176540	-0.9867070	-0.3126710
C	-0.8340940	-2.4685790	0.0174670
C	0.8810920	1.5455200	2.7018550
H	1.2888760	2.3510730	3.3173300
H	0.4434890	0.8020010	3.3721690
H	1.7001700	1.0868330	2.1405010
H	-1.0062910	2.5233950	2.3739360
C	-2.4505060	2.4295700	-0.7319600
H	-0.5972790	1.4852250	-1.3977260
C	-2.5941270	3.2355070	-2.0418900
H	-3.6570160	3.3640340	-2.2698150
H	-2.1555060	4.2330780	-1.9673410
H	-2.1347720	2.7161540	-2.8905860
C	-3.2877350	1.1416900	-0.8691740
H	-2.9851030	0.5511160	-1.7400470
H	-3.2210720	0.5085460	0.0195050
H	-4.3398170	1.4112360	-1.0063200
C	-2.9965140	3.2634160	0.4424360
H	-2.4052730	4.1687730	0.6133830
H	-4.0205180	3.5784390	0.2177970
H	-3.0314100	2.6843880	1.3704840
H	-0.2922000	-0.4491670	1.7171800
H	0.7609080	-0.9484930	-0.6953280
H	-1.0675190	-0.6669840	-1.2511800
O	1.8543190	-0.9981530	-1.2297570
C	2.8279000	-1.2106700	-0.4182040
O	2.7911430	-1.3840490	0.7972820
C	4.2004500	-1.2363090	-1.1579500
F	4.4275660	-0.0685590	-1.8028250
F	4.2344690	-2.2258170	-2.0808260
F	5.2254450	-1.4375190	-0.3075860
H	-0.3339620	-2.7017070	0.9648200
H	4.0669490	-1.7398580	2.1323530
O	4.5993070	-1.9299470	2.9286040
H	5.5119000	-1.9916970	2.6188180
H	-0.3431410	-3.0744070	-0.7521910
C	-2.2973650	-2.8718430	0.0994090
C	-2.9636860	-3.3814290	-1.0251860
C	-3.0204420	-2.7271390	1.2939810
C	-4.3174380	-3.7288100	-0.9634140
H	-2.4177470	-3.5104260	-1.9569190
C	-4.3726400	-3.0748770	1.3620920
H	-2.5212060	-2.3434240	2.1807630
C	-5.0275300	-3.5753780	0.2312850
H	-4.8139590	-4.1229270	-1.8458230
H	-4.9127270	-2.9597100	2.2978010
H	-6.0777180	-3.8477680	0.2829440

5.log
Potential Energy = -1489.65358
Zero-point Energy = -1489.18548
Free Energy = -1489.23092
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11057
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68791
Nimag = 1 (-1208.5109 cm⁻¹)
Charge = 0 Multiplicity = 1

C	2.6466040	-0.5250640	0.4019880
C	3.3606550	1.6515210	-0.1760490
C	2.7555660	1.0484840	-1.4476990
N	2.0503180	-0.1376920	-0.8993410
N	3.2403340	0.7493020	0.8258790
O	3.8541620	2.7760040	-0.0857880
C	3.5661360	1.0879320	2.2079230
H	3.3127000	2.1366560	2.3757060
H	2.9791580	0.4629220	2.8820140
H	4.6294250	0.9482480	2.4229530
C	0.8606200	-0.5510580	-1.3398560
C	-0.0850030	-1.3609590	-0.7055630
C	-1.1580860	-2.0310920	-1.5761540
C	1.8902880	2.0440840	-2.2113750
H	2.4952720	2.9336360	-2.4031370
H	1.5706340	1.6435820	-3.1763530
H	1.0094930	2.3402460	-1.6345660
H	3.5788240	0.7177540	-2.0923950
C	3.6552830	-1.7248420	0.3069510
H	1.8468100	-0.7924290	1.0997210
C	4.1965910	-2.0394660	1.7190120
H	4.7731760	-2.9692460	1.6841490
H	4.8625570	-1.2585520	2.0929220
H	3.3856460	-2.1803970	2.4424440
C	2.9181730	-2.9767230	-0.2117060
H	2.1142980	-3.2838540	0.4653760
H	2.4948590	-2.8233030	-1.2082370
H	3.6269650	-3.8083510	-0.2773490
C	4.8341910	-1.4082730	-0.6323510
H	5.3660330	-0.4998610	-0.3317860
H	5.5527520	-2.2335250	-0.6024260
H	4.5084720	-1.2992130	-1.6714550
H	0.5769180	-0.1147290	-2.2942460
H	-0.7389700	-0.3002460	0.0276730
H	0.2432760	-1.9630230	0.1400670
O	-1.2720400	0.4581520	0.8094550
C	-1.8548260	1.4630760	0.2602010
O	-1.9631050	1.7302610	-0.9338530
C	-2.4757780	2.4211640	1.3221250
F	-3.0968640	3.4703300	0.7494000
F	-1.5220830	2.9118860	2.1479190
F	-3.3856630	1.7754960	2.0874320
H	-0.7173080	-2.8986870	-2.0854220
H	-2.7476650	3.1240580	-1.9224880
O	-3.0984820	3.7665430	-2.5688070
H	-3.5406980	4.4449160	-2.0426240
H	-1.4736610	-1.3348060	-2.3614100
C	-2.3730850	-2.4961390	-0.7947500
C	-3.5707040	-1.7659690	-0.8116920
C	-2.3223130	-3.6756730	-0.0344230
C	-4.6857870	-2.1961930	-0.0847890
H	-3.6318470	-0.8536740	-1.3996440
C	-3.4325700	-4.1084960	0.6964580
H	-1.4081950	-4.2648400	-0.0195860
C	-4.6199200	-3.3686740	0.6739840
H	-5.6045530	-1.6170080	-0.1143090
H	-3.3727360	-5.0250770	1.2767480
H	-5.4851860	-3.7053970	1.2376660

6.log
Potential Energy = -1489.65300
Zero-point Energy = -1489.18458
Free Energy = -1489.22976
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11164

Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68841
Nimag = 1 (-1198.2314 cm⁻¹)
Charge = 0 Multiplicity = 1

C	2.5755320	-0.0615980	-0.4401340
C	2.5823060	-0.8704600	1.7793790
C	1.8836520	0.4918310	1.8222040
N	1.6324170	0.7357860	0.3795060
N	2.9083000	-1.1449010	0.4943020
O	2.7925320	-1.5954730	2.7524560
C	3.4317050	-2.4473690	0.0951840
H	2.9830380	-3.2097220	0.7351620
H	3.1613740	-2.6436850	-0.9432460
H	4.5191650	-2.5018640	0.1997920
C	0.5132950	1.2980290	-0.0841380
C	-0.0159840	1.2633960	-1.3744860
C	-1.0547490	2.3101680	-1.8198400
C	0.6521150	0.4886020	2.7203270
H	0.9568410	0.1219480	3.7036830
H	0.2475330	1.4953280	2.8504650
H	-0.1271290	-0.1683870	2.3250560
H	2.6029210	1.2302530	2.1969850
C	3.8098330	0.7519600	-0.9716350
H	2.0401580	-0.4841930	-1.2962760
C	4.6903240	-0.1781060	-1.8354380
H	5.4610180	0.4176240	-2.3348740
H	5.2023890	-0.9378730	-1.2407930
H	4.1058620	-0.6815810	-2.6139780
C	3.3202150	1.9096010	-1.8659370
H	2.7811740	1.5435330	-2.7459020
H	2.6719290	2.6035370	-1.3238490
H	4.1859750	2.4753890	-2.2248070
C	4.6540470	1.3291760	0.1801290
H	4.9909690	0.5508800	0.8722520
H	5.5467240	1.8112040	-0.2311200
H	4.1058260	2.0897200	0.7446590
H	-0.0795590	1.7820470	0.6864200
H	-0.7688430	0.0245730	-1.3136820
H	0.6509580	0.9698890	-2.1832680
O	-1.3948820	-0.9665530	-1.5856480
C	-1.7484070	-1.6950090	-0.5863680
O	-1.5497760	-1.5113070	0.6107590
C	-2.5317150	-2.9604770	-1.0529520
F	-1.7830670	-3.7141670	-1.8908920
F	-3.6610960	-2.6144870	-1.7133190
F	-2.8896800	-3.7400040	-0.0146300
H	-1.6203560	1.8835390	-2.6561200
H	-2.1175570	-2.3933680	2.1851710
O	-2.3454370	-2.7237410	3.0750140
H	-2.8619960	-3.5259600	2.9261710
H	-0.5254420	3.1826190	-2.2241360
C	-2.0226710	2.7752800	-0.7491230
C	-1.7779160	3.9511220	-0.0223270
C	-3.1860560	2.0440580	-0.4591550
C	-2.6645170	4.3829570	0.9698560
H	-0.8881120	4.5375090	-0.2396400
C	-4.0754670	2.4711180	0.5310110
H	-3.4010790	1.1376880	-1.0191470
C	-3.8166270	3.6424410	1.2509200
H	-2.4567320	5.2976690	1.5179280
H	-4.9720530	1.8928420	0.7359320
H	-4.5084220	3.9768370	2.0185700

7.log
Potential Energy = -1489.65094
Zero-point Energy = -1489.18265
Free Energy = -1489.22755
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.10884
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68545
Nimag = 1 (-1148.9197 cm⁻¹)
Charge = 0 Multiplicity = 1

C	2.8422840	0.0222060	0.7162370
C	4.7535410	0.4491740	-0.6002260
C	3.5987170	0.2055680	-1.5792960

N	2.4243840	0.3170220	-0.6760040
N	4.2637490	0.3942470	0.6594600
O	5.9212320	0.6778020	-0.9188760
C	5.0768560	0.7372370	1.8211630
H	5.7753310	1.5245400	1.5309220
H	4.4308060	1.1045510	2.6198360
H	5.6510860	-0.1188510	2.1876020
C	1.3234260	1.0017670	-1.0022530
C	0.1863610	1.2912790	-0.2452910
C	-0.6028700	2.5532530	-0.6462910
H	-0.6765920	2.6006750	-1.7389510
C	3.6370330	1.1633880	-2.7637400
H	4.6136580	1.0562370	-3.2415710
H	2.8737240	0.9207550	-3.5068710
H	3.5215230	2.2051120	-2.4497760
H	3.6737870	-0.8230900	-1.9510580
C	2.5748010	-1.4488440	1.1951550
H	2.3147110	0.7086670	1.3866550
C	2.9421890	-1.5591440	2.6920130
H	2.6179500	-2.5335440	3.0710170
H	4.0180340	-1.4858640	2.8658610
H	2.4413090	-0.7889960	3.2895160
C	1.0763340	-1.7679250	1.0437300
H	0.4503260	-1.0903650	1.6318300
H	0.7566220	-1.7199660	-0.0002470
H	0.8849280	-2.7841750	1.4026040
C	3.3919460	-2.4793760	0.3927300
H	4.4660740	-2.2723040	0.4274220
H	3.2358050	-3.4750160	0.8202500
H	3.0761540	-2.5252290	-0.6540480
H	1.3092880	1.3237100	-2.0404650
H	-0.6742560	0.2125650	-0.7324520
H	-0.0357570	3.4409800	-0.3354630
C	-1.9917630	2.6410960	-0.0428930
C	-3.1391380	2.4397270	-0.8237520
C	-2.1571980	2.9447590	1.3182950
C	-4.4172890	2.5311090	-0.2618940
H	-3.0328730	2.2112770	-1.8812810
C	-3.4312060	3.0343810	1.8855480
H	-1.2812450	3.1194040	1.9388850
C	-4.5677730	2.8266600	1.0960940
H	-5.2927390	2.3734770	-0.8857830
H	-3.5367240	3.2712400	2.9406080
H	-5.5590060	2.8989660	1.5342720
H	0.2242210	1.0976300	0.8266450
O	-1.4139080	-0.5805730	-1.2306070
C	-2.2596010	-1.1566930	-0.4496740
O	-2.4032180	-1.0307770	0.7612160
C	-3.1801650	-2.1393420	-1.2363710
F	-2.4529820	-3.1242980	-1.8146040
F	-4.0905400	-2.7237740	-0.4341880
F	-3.8529650	-1.4981810	-2.2193480
H	-3.5178250	-1.8093330	2.0648750
O	-4.0032980	-2.1377200	2.8457500
H	-4.7222410	-2.6771930	2.4926620

8.log
Potential Energy = -1489.65382
Zero-point Energy = -1489.18543
Free Energy = -1489.23089
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.10971
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68677
Nimag = 1 (-1155.2441 cm⁻¹)
Charge = 0 Multiplicity = 1

C	2.0155920	-1.1994680	0.7191720
C	3.9205020	-1.5198830	-0.6376280
C	2.7184950	-1.4563950	-1.5873390
N	1.6721310	-0.8987490	-0.6924380
N	3.4781120	-1.3184850	0.6248120
O	5.0899840	-1.7008210	-0.9792260
C	4.3965730	-1.1458380	1.7456710
H	5.2838310	-0.6201650	1.3869230
H	3.9132600	-0.5492520	2.5203160
H	4.7083920	-2.1040890	2.1711670

C	0.8281670	0.0637500	-1.0752860
C	-0.1395070	0.7476050	-0.3367150
C	-0.5812380	2.1346820	-0.8285620
H	-1.6087310	2.3129490	-0.4933410
C	3.0231210	-0.6614760	-2.8511080
H	3.8985240	-1.1150490	-3.3218030
H	2.1989430	-0.7061030	-3.5670860
H	3.2561200	0.3840090	-2.6291640
H	2.4473790	-2.4809550	-1.8678260
C	1.2989120	-2.4590000	1.3228660
H	1.7632380	-0.3266120	1.3303650
C	1.7131220	-2.6074920	2.8039190
H	1.1006830	-3.3850410	3.2713580
H	2.7576210	-2.9058080	2.9180610
H	1.5534070	-1.6798060	3.3650630
C	-0.2270850	-2.2535660	1.2714460
H	-0.5393840	-1.3734680	1.8430290
H	-0.5916600	-2.1525950	0.2464170
H	-0.7226360	-3.1236040	1.7138420
C	1.6579480	-3.7499180	0.5627120
H	2.7386800	-3.9198530	0.5266680
H	1.2084430	-4.6069790	1.0743330
H	1.2673450	-3.7427690	-0.4595490
H	0.8769210	0.2825280	-2.1387240
H	-1.3099290	-0.0159080	-0.7043150
H	-0.6000400	2.1404930	-1.9247410
C	0.3041390	3.2640330	-0.3282580
C	0.0548430	3.8708200	0.9125790
C	1.4006310	3.7122480	-1.0810850
C	0.8826100	4.8901480	1.3938500
H	-0.7962310	3.5446270	1.5059090
C	2.2301240	4.7326210	-0.6056040
H	1.6054480	3.2636160	-2.0503440
C	1.9751450	5.3243380	0.6361130
H	0.6708970	5.3477120	2.3563010
H	3.0708760	5.0679430	-1.2066140
H	2.6172200	6.1183730	1.0061990
H	-0.1246400	0.6369480	0.7472690
O	-2.3198040	-0.5629090	-1.0544830
C	-3.3533630	-0.3299340	-0.3242540
O	-3.4474100	0.3880210	0.6664760
C	-4.6035270	-1.1086410	-0.8346910
F	-4.3978880	-2.4452180	-0.7653970
F	-5.7004560	-0.8263920	-0.1086870
F	-4.8755300	-0.8041130	-2.1246060
H	-4.8319060	0.8289030	1.8819560
O	-5.4731140	1.1096570	2.5622250
H	-4.9873710	1.7187150	3.1331980

9.log
Potential Energy = -1489.65129
Zero-point Energy = -1489.18284
Free Energy = -1489.22819
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.10949
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68639
Nimag = 1 (-1151.9620 cm⁻¹)
Charge = 0 Multiplicity = 1

C	2.4854800	-1.1826820	0.4863830
C	4.3367050	-0.0291300	-0.4153150
C	3.0962660	0.5068580	-1.1393590
N	2.0078240	0.0067150	-0.2605160
N	3.9336460	-0.9257030	0.5139370
O	5.4975780	0.3203630	-0.6344670
C	4.8588640	-1.4953200	1.4881700
H	5.5984990	-0.7348560	1.7468600
H	4.3090470	-1.7823280	2.3854100
H	5.3835930	-2.3698690	1.0925990
C	0.9766440	0.7711920	0.1179670
C	-0.0654470	0.4835860	0.9985280
C	-0.8098080	1.6321840	1.7121070
H	-0.3292650	1.8005460	2.6837060
C	3.1592200	2.0142460	-1.3526810
H	4.0825690	2.2311410	-1.8949660
H	2.3239710	2.3730850	-1.9588770

H	3.1818440	2.5603510	-0.4051120
H	3.0290650	0.0129700	-2.1159190
C	2.0848770	-2.5666320	-0.1362290
H	2.0904780	-1.1313600	1.5065390
C	2.5967460	-3.6964470	0.7849830
H	2.1857650	-4.6518030	0.4435840
H	3.6850160	-3.7878800	0.7694050
H	2.2753600	-3.5509690	1.8226100
C	0.5498850	-2.6679440	-0.2099230
H	0.0885030	-2.5918480	0.7801310
H	0.1212700	-1.8985820	-0.8563270
H	0.2720460	-3.6417370	-0.6257170
C	2.6689790	-2.7586720	-1.5488580
H	3.7576030	-2.6451500	-1.5636850
H	2.4403180	-3.7701230	-1.8996940
H	2.2314310	-2.0605560	-2.2691840
H	0.9318610	1.7242390	-0.4001670
H	-1.0747930	0.0294610	0.0625280
H	-1.8277070	1.2895270	1.9323850
C	-0.8723130	2.9519740	0.9665600
C	0.0084740	3.9965150	1.2891820
C	-1.8113900	3.1661440	-0.0558050
C	-0.0430110	5.2189640	0.6112940
H	0.7381970	3.8531990	2.0826680
C	-1.8668480	4.3860070	-0.7364650
H	-2.5061740	2.3735610	-0.3190860
C	-0.9817190	5.4175230	-0.4056710
H	0.6460360	6.0145210	0.8806630
H	-2.6045660	4.5318410	-1.5205800
H	-1.0265490	6.3667510	-0.9316820
H	0.0295870	-0.4082780	1.6179600
O	-1.9742050	-0.2999010	-0.6577600
C	-2.9233130	-0.9549510	-0.0854320
O	-3.0418730	-1.2569540	1.0977330
C	-4.0249200	-1.3754920	-1.1045700
F	-5.0171130	-2.0648450	-0.5129250
F	-4.5754650	-0.2896970	-1.6963250
F	-3.5085960	-2.1557010	-2.0823600
H	-4.3186440	-2.1996040	2.1345320
O	-4.9114780	-2.6681500	2.7522020
H	-4.4944810	-2.5815630	3.6191120

10.log
Potential Energy = -1489.65071
Zero-point Energy = -1489.18202
Free Energy = -1489.22688
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.10994
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68610
Nimag = 1 (-1179.5848 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-2.7589840	-0.3587960	-0.6907580
C	-3.8148220	0.7923480	1.0785090
C	-2.3273100	0.7110010	1.4399430
N	-1.7320350	0.3222720	0.1355180
N	-3.9887320	0.2309490	-0.1399210
O	-4.6921740	1.3035980	1.7761100
C	-5.2662060	0.2923320	-0.8420980
H	-5.7482810	1.2407210	-0.5964490
H	-5.0916720	0.2447170	-1.9178960
H	-5.9347380	-0.5227240	-0.5496270
C	-0.6312020	0.9005670	-0.3575370
C	-0.0070480	0.7113550	-1.5894580
C	0.8679780	1.8313230	-2.1939570
H	0.2273250	2.4699930	-2.8150730
C	-1.8127000	2.0021810	2.0638380
H	-2.4382510	2.2197170	2.9327800
H	-0.7816990	1.9011880	2.4110460
H	-1.8821280	2.8460500	1.3713080
H	-2.1931240	-0.1073940	2.1569460
C	-2.7184160	-1.9275920	-0.6502060
H	-2.6366330	-0.0334930	-1.7292190
C	-3.7805410	-2.4804460	-1.6265860
H	-3.6527180	-3.5635190	-1.7206380
H	-4.8009250	-2.3038980	-1.2793800

H	-3.6751440	-2.0474620	-2.6278150
C	-1.3350210	-2.4138930	-1.1209570
H	-1.1144950	-2.0921290	-2.1438900
H	-0.5397770	-2.0609760	-0.4608550
H	-1.3137030	-3.5083200	-1.1100990
C	-2.9893270	-2.4790760	0.7626590
H	-3.9409500	-2.1223530	1.1692460
H	-3.0400170	-3.5718320	0.7201580
H	-2.1881950	-2.2202670	1.4616340
H	-0.1351210	1.5590380	0.3485940
H	1.0108490	-0.2724590	-1.2412030
H	1.5874750	1.3654770	-2.8767210
C	1.6142800	2.7053130	-1.2041690
C	1.0547400	3.9099280	-0.7483710
C	2.8833730	2.3396570	-0.7275730
C	1.7371930	4.7224720	0.1625190
H	0.0782000	4.2175630	-1.1153160
C	3.5700830	3.1483780	0.1831250
H	3.3407130	1.4190240	-1.0795430
C	2.9980760	4.3426690	0.6332800
H	1.2866120	5.6519350	0.4991610
H	4.5530950	2.8484220	0.5353010
H	3.5317340	4.9734400	1.3382860
H	-0.5530880	0.1499450	-2.3480810
O	1.9359010	-1.0332650	-1.2343550
C	2.2550580	-1.4810050	-0.0708910
O	1.7196790	-1.2568950	1.0103110
C	3.4910510	-2.4285550	-0.1400090
F	3.8324900	-2.8941330	1.0765410
F	3.2378720	-3.4967520	-0.9310370
F	4.5671260	-1.7870760	-0.6503830
H	2.0375450	-1.7874030	2.7911810
O	2.0736810	-1.9703710	3.7493960
H	2.8368770	-2.5493950	3.8713870

11.log
Potential Energy = -1489.65354
Zero-point Energy = -1489.18515
Free Energy = -1489.23091
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.10954
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68691
Nimag = 1 (-1180.7665 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-1.9986950	-1.4229600	-0.5600410
C	-2.9907190	-1.9988850	1.5034270
C	-1.5235830	-1.6723660	1.8053490
N	-1.1155190	-0.9892290	0.5506270
N	-3.2109190	-1.7951420	0.1843860
O	-3.8255450	-2.3630350	2.3326280
C	-4.5515340	-1.8510430	-0.3898370
H	-5.2587920	-1.4629030	0.3460060
H	-4.5873120	-1.2309390	-1.2861550
H	-4.8439630	-2.8729440	-0.6479760
C	-0.3808400	0.1262000	0.5392600
C	0.0110900	0.9264010	-0.5355630
C	0.3609330	2.3966680	-0.2576890
H	1.0847410	2.7338360	-1.0079470
C	-1.3618610	-0.8754080	3.0939770
H	-1.8366910	-1.4460860	3.8955930
H	-0.3104390	-0.7404870	3.3587130
H	-1.8497430	0.1017300	3.0326730
H	-0.9743410	-2.6164650	1.8991720
C	-1.4161310	-2.5653590	-1.4652340
H	-2.2142410	-0.5532980	-1.1897520
C	-2.4284820	-2.8758640	-2.5903300
H	-1.9633190	-3.5517900	-3.3148350
H	-3.3283200	-3.3701570	-2.2174650
H	-2.7277240	-1.9696360	-3.1292480
C	-0.1071530	-2.0833310	-2.1190510
H	-0.2650940	-1.1972040	-2.7425660
H	0.6617720	-1.8548820	-1.3774810
H	0.2841040	-2.8740270	-2.7671430
C	-1.1345830	-3.8516980	-0.6658170
H	-2.0241580	-4.2132160	-0.1403020

H -0.8169860 -4.6419980 -1.3535430
H -0.3276490 -3.7115790 0.0600480
H 0.0193970 0.3909400 1.5139290
H 1.3427960 0.4085420 -0.7573400
H 0.8593640 2.4699380 0.7156010
C -0.8442260 3.3220970 -0.2869700
C -1.2564990 3.9198040 -1.4879320
C -1.5834430 3.5856930 0.8768730
C -2.3805130 4.7511550 -1.5291190
H -0.6905990 3.7358270 -2.3983020
C -2.7063880 4.4179660 0.8418210
H -1.2760680 3.1412540 1.8206310
C -3.1108820 5.0024570 -0.3632280
H -2.6812470 5.2054550 -2.4691580
H -3.2613830 4.6132620 1.7552400
H -3.9818360 5.6508160 -0.3917710
H -0.4611820 0.7500280 -1.5018810
O 2.4597270 0.1193330 -1.1005300
C 3.3036730 0.0773210 -0.1305810
O 3.1156770 0.3106820 1.0600200
C 4.7245460 -0.3363490 -0.6210950
F 5.6135470 -0.3677410 0.3899550
F 4.7029600 -1.5658520 -1.1859170
F 5.1899690 0.5315540 -1.5487610
H 4.1783810 0.2740210 2.6138850
O 4.5877200 0.2900150 3.5001150
H 5.5284430 0.1299500 3.3516050

12.log
Potential Energy = -1489.65137
Zero-point Energy = -1489.18299
Free Energy = -1489.22808
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.10840
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68511
Nimag = 1 (-1166.0594 cm⁻¹)
Charge = 0 Multiplicity = 1
C -2.9115690 -0.6317250 0.3494180
C -4.3509180 0.5274750 -1.1199090
C -2.9918330 1.2327820 -1.1976470
N -2.1067990 0.2275280 -0.5543430
N -4.2352880 -0.5303100 -0.2843120
O -5.3639510 0.8609110 -1.7361660
C -5.3015500 -1.5164980 -0.1384630
H -5.8053890 -1.6238900 -1.1012210
H -4.8708180 -2.4757370 0.1517000
H -6.0407480 -1.2139810 0.6086870
C -0.9156210 -0.1136550 -1.0555320
C -0.0069710 -1.0788470 -0.6198500
C 0.9657450 -1.6566590 -1.6635130
H 1.3420290 -0.8448860 -2.2958210
C -2.6329830 1.6416840 -2.6207510
H -3.4462910 2.2661130 -2.9978850
H -1.7149760 2.2334420 -2.6532510
H -2.5311830 0.7755820 -3.2812790
H -3.0342260 2.1304740 -0.5700120
C -2.8828860 -0.2179230 1.8628610
H -2.5470610 -1.6606430 0.2615100
C -3.7530750 -1.2077460 2.6689900
H -3.6080600 -1.0236710 3.7382090
H -4.8190950 -1.0907110 2.4618330
H -3.4725890 -2.2488400 2.4728700
C -1.4387390 -0.3115960 2.3905150
H -1.0379240 -1.3269490 2.3020420
H -0.7659730 0.3746430 1.8716430
H -1.4252990 -0.0464620 3.4525950
C -3.4073250 1.2137750 2.0822960
H -4.4162130 1.3486690 1.6794230
H -3.4533350 1.4211310 3.1562150
H -2.7452560 1.9626110 1.6366580
H -0.5968480 0.5151310 -1.8824950
H 0.8530900 -0.1932880 0.1615880
H 0.4157490 -2.3390650 -2.3257060
C 2.1356530 -2.4125160 -1.0610830
C 3.4415020 -1.9057940 -1.1302570

C 1.9348210 -3.6509960 -0.4292470
C 4.5175750 -2.6097510 -0.5784630
H 3.6190050 -0.9527230 -1.6220200
C 3.0052690 -4.3567300 0.1266590
H 0.9329860 -4.0710440 -0.3773250
C 4.3027370 -3.8371720 0.0547560
H 5.5212090 -2.1990080 -0.6453050
H 2.8278300 -5.3135720 0.6098170
H 5.1363860 -4.3859070 0.4833670
H -0.3441190 -1.7908280 0.1331640
O 1.6059750 0.4143070 0.8691060
C 2.1943510 1.3948080 0.2802730
O 2.1139580 1.7435190 -0.8943030
C 3.1006330 2.1963690 1.2630770
F 3.7558630 3.1939200 0.6389200
F 2.3632140 2.7488510 2.2548090
F 4.0259960 1.3959550 1.8389250
H 2.8809260 3.1120330 -1.9350250
O 3.1853600 3.7640610 -2.5948840
H 3.8755110 4.2742460 -2.1521010

13.log
Potential Energy = -1489.65086
Zero-point Energy = -1489.18293
Free Energy = -1489.22874
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.10774
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68561
Nimag = 1 (-1175.9065 cm⁻¹)
Charge = 0 Multiplicity = 1

C 3.1581390 0.1724770 0.5004580
C 3.5154660 0.2860960 -1.8270180
C 2.2784190 -0.6004070 -1.6528610
N 2.0049990 -0.4450310 -0.2086340
N 3.8882160 0.7665370 -0.6187210
O 4.0362650 0.5664360 -2.9068380
C 4.8688790 1.8417140 -0.4988340
H 4.7315320 2.5272330 -1.3375850
H 4.7037810 2.3783530 0.4357680
H 5.8955290 1.4658310 -0.5227510
C 0.8881240 -0.7751150 0.4431770
C -0.2731740 -1.3896950 -0.0270410
C -1.1851510 -2.0624460 1.0145110
H -1.2872280 -1.4066490 1.8860450
C 1.1787180 -0.1133400 -2.6040410
H 1.6179480 -0.0394500 -3.6018600
H 0.3368370 -0.8020330 -2.6560120
H 0.8128600 0.8738770 -2.3097760
H 2.5342680 -1.6433430 -1.8802860
C 4.0056060 -0.8463920 1.3508500
H 2.7876950 0.9630440 1.1634930
C 5.1660180 -0.0862630 2.0323680
H 5.6730430 -0.7580290 2.7319410
H 5.9150540 0.2608740 1.3182650
H 4.8054210 0.7755950 2.6054340
C 3.1384750 -1.4649640 2.4679050
H 2.6686790 -0.6984620 3.0951850
H 2.3596010 -2.1264210 2.0782020
H 3.7763410 -2.0722660 3.1175780
C 4.5732480 -1.9728130 0.4679170
H 5.2126350 -1.5834100 -0.3305720
H 5.1831360 -2.6452560 1.0795920
H 3.7773240 -2.5742570 0.0167630
H 0.8859250 -0.4469210 1.4800640
H -0.2079830 -1.9186370 -0.9769720
O -1.7001040 0.6919240 -0.8465450
C -2.0014860 1.5818530 0.0315960
O -1.7059610 1.6152910 1.2228240
C -2.8508900 2.7346980 -0.5848550
F -3.1895910 3.6552730 0.3382010
F -3.9948660 2.2600870 -1.1284240
F -2.1653690 3.3698150 -1.5638460
H -0.7058630 -2.9849950 1.3699630
C -2.5627730 -2.4132600 0.4836910
C -3.7035170 -1.7110910 0.8990480

C	-2.7252570	-3.4635030	-0.4349340
C	-4.9712510	-2.0412720	0.4073260
H	-3.5999560	-0.8998180	1.6152010
C	-3.9885510	-3.7955610	-0.9318570
H	-1.8563660	-4.0312910	-0.7598600
C	-5.1180130	-3.0837440	-0.5122480
H	-5.8416070	-1.4851390	0.7444670
H	-4.0919040	-4.6124420	-1.6407170
H	-6.1011390	-3.3424780	-0.8947770
H	-1.0171690	-0.1940660	-0.4210170
H	-2.0238650	2.8047190	2.6442980
O	-2.0921160	3.3226880	3.4691490
H	-2.6994580	4.0461860	3.2683520

14.log
Potential Energy = -1489.65001
Zero-point Energy = -1489.18150
Free Energy = -1489.22641
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.10979
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68619
Nimag = 1 (-1181.5008 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-2.5365300	-0.2219870	0.5204660
C	-2.7903430	-2.2793990	-0.5991670
C	-1.8958920	-1.4328110	-1.5102460
N	-1.6189180	-0.2630750	-0.6498550
N	-3.0134180	-1.6041490	0.5510910
O	-3.1779470	-3.4202880	-0.8531750
C	-3.6127270	-2.2568250	1.7114510
H	-3.2481560	-3.2852330	1.7539450
H	-3.3118830	-1.7303320	2.6174470
H	-4.7045430	-2.2785830	1.6524870
C	-0.6701210	0.6620720	-0.8177660
C	0.2527520	0.8052780	-1.8527310
C	0.9477330	2.1634850	-2.0881440
C	-0.6823000	-2.2739100	-1.9242820
H	-1.0605860	-3.2165720	-2.3269990
H	-0.0833720	-1.7939930	-2.6965740
H	-0.0489940	-2.4947150	-1.0612800
H	-2.4580340	-1.1243430	-2.4010120
C	-3.6864450	0.8470010	0.3991310
H	-1.9517060	-0.0101240	1.4232960
C	-4.5518410	0.8002460	1.6789450
H	-5.2600640	1.6345140	1.6638200
H	-5.1370340	-0.1180220	1.7551850
H	-3.9429220	0.9012130	2.5846880
C	-3.0883670	2.2650360	0.2954620
H	-2.4065530	2.8452740	1.1247910
H	-2.5578770	2.4269500	-0.6467190
H	-3.9000000	2.9982100	0.3356200
C	-4.5705430	0.5795320	-0.8327950
H	-5.0350620	-0.4108190	-0.7960450
H	-5.3762200	1.3195910	-0.8724480
H	-4.0033880	0.6651800	-1.7654330
H	-0.5908840	1.3505630	0.0198940
H	0.0320640	0.2837130	-2.7837320
O	2.3857980	-0.6233270	-1.2537900
C	2.5273830	-1.2151880	-0.1193870
O	1.7372680	-1.2786640	0.8171780
C	3.9149150	-1.9174490	-0.0096120
F	4.0629130	-2.5501850	1.1682760
F	4.9211740	-1.0194210	-0.1232540
F	4.0732890	-2.8348180	-0.9917210
H	0.3177690	2.7681300	-2.7528230
H	1.3580620	-0.0278140	-1.3872180
H	1.7881650	-2.0258960	2.5606280
O	1.7228000	-2.3694170	3.4717770
H	0.8725030	-2.0525560	3.8025590
H	1.8743710	1.9706590	-2.6410320
C	1.2702530	2.9761800	-0.8486670
C	0.4357430	4.0298190	-0.4441030
C	2.4173290	2.7065150	-0.0836510
C	0.7296530	4.7868150	0.6952190
H	-0.4485600	4.2658870	-1.0310320

C	2.7154330	3.4590390	1.0556660
H	3.0868860	1.9073110	-0.3891920
C	1.8703550	4.5016920	1.4511420
H	0.0707420	5.5997530	0.9871190
H	3.6103550	3.2357670	1.6297530
H	2.1028990	5.0893900	2.3344470

15.log
Potential Energy = -1489.65263
Zero-point Energy = -1489.18455
Free Energy = -1489.23051
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.10882
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68670
Nimag = 1 (-1202.9716 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-1.6477470	-1.9980930	0.6194240
C	-1.5440690	-2.9808100	-1.5207660
C	-1.1989170	-1.5043720	-1.7393170
N	-1.0784370	-1.0195600	-0.3473450
N	-1.6758590	-3.2122820	-0.1948260
O	-1.6167740	-3.8274110	-2.4116610
C	-1.7362100	-4.5714110	0.3360410
H	-1.0787190	-5.2042590	-0.2636530
H	-1.3906640	-4.5707290	1.3700960
H	-2.7479080	-4.9841570	0.2940910
C	-0.5088200	0.1132940	0.0675460
C	0.0591230	1.1499880	-0.6763660
C	0.2753980	2.5085160	0.0076170
C	0.0675770	-1.4136910	-2.5995180
H	-0.0864130	-2.0499220	-3.4744350
H	0.2640120	-0.4014730	-2.9494860
H	0.9414500	-1.7787600	-2.0531320
H	-2.0321000	-1.0000220	-2.2450000
C	-3.0497850	-1.5806580	1.1995300
H	-0.9461080	-2.1266870	1.4519030
C	-3.5427320	-2.6834720	2.1635280
H	-4.4432040	-2.3335580	2.6777880
H	-3.8061300	-3.6060790	1.6428630
H	-2.7952810	-2.9170850	2.9303050
C	-2.9207840	-0.2763970	2.0134990
H	-2.1557190	-0.3553940	2.7948500
H	-2.6946130	0.5898970	1.3862130
H	-3.8743550	-0.0698900	2.5093940
C	-4.0819640	-1.3785300	0.0751310
H	-4.2182560	-2.2858750	-0.5217900
H	-5.0529010	-1.1229480	0.5113230
H	-3.7986880	-0.5588090	-0.5930630
H	-0.4252090	0.1794490	1.1498550
H	-0.2109090	1.2156640	-1.7294310
O	2.5863500	0.4708880	-1.0042180
C	3.2817210	0.2139730	0.0464920
O	2.9166190	0.1741690	1.2180810
C	4.7730010	-0.0736520	-0.3067530
F	5.5043800	-0.3453040	0.7910350
F	5.3390590	0.9899850	-0.9226320
F	4.8785840	-1.1333300	-1.1415330
H	1.4213470	0.6886840	-0.7775840
H	3.7448250	-0.2009390	2.8652140
O	4.0202790	-0.3792480	3.7848260
H	4.9764060	-0.5094480	3.7460940
H	1.1353630	3.0013500	-0.4610710
H	0.5439410	2.3465540	1.0573820
C	-0.9251220	3.4363380	-0.0748040
C	-1.7871760	3.6057020	1.0190760
C	-1.2042340	4.1392230	-1.2582050
C	-2.9024720	4.4461650	0.9329610
H	-1.5810690	3.0816780	1.9492740
C	-2.3181840	4.9783410	-1.3502850
H	-0.5414010	4.0319190	-2.1138170
C	-3.1736740	5.1337950	-0.2537940
H	-3.5546970	4.5659850	1.7936350
H	-2.5147010	5.5146270	-2.2745610
H	-4.0377890	5.7882730	-0.3223260

16.log
Potential Energy = -1489.65301
Zero-point Energy = -1489.18503
Free Energy = -1489.23095
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.10925
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68719
Nimag = 1 (-1172.7140 cm⁻¹)
Charge = 0 Multiplicity = 1

C	2.7467140	-1.4089580	-0.5812360
C	2.2282760	-2.6018590	1.3847600
C	1.3111580	-1.3749960	1.4057380
N	1.5485490	-0.8050750	0.0623380
N	2.9130310	-2.6217610	0.2184620
O	2.2728250	-3.4640330	2.2624080
C	3.6603010	-3.8033780	-0.2030700
H	3.1141790	-4.6900790	0.1253740
H	3.7399670	-3.8113470	-1.2904720
H	4.6628910	-3.8327530	0.2325360
C	0.8014310	0.0994820	-0.5742460
C	-0.3325000	0.7844350	-0.1323790
C	-0.7647770	2.0513040	-0.8857710
C	-0.1221780	-1.8347780	1.7008640
H	-0.0848900	-2.4682010	2.5903910
H	-0.7938440	-1.0032030	1.9081480
H	-0.5245570	-2.4230830	0.8716640
H	1.6462040	-0.6739300	2.1806860
C	4.0088790	-0.4688450	-0.5926550
H	2.4983420	-1.6776940	-1.6147750
C	5.1774240	-1.2060590	-1.2852130
H	6.0106220	-0.5095100	-1.4206910
H	5.5513650	-2.0450740	-0.6955870
H	4.8929620	-1.5762240	-2.2768980
C	3.7156450	0.8058630	-1.4108110
H	3.3641380	0.5712940	-2.4224200
H	2.9835220	1.4572400	-0.9261970
H	4.6390560	1.3846600	-1.5120210
C	4.4217750	-0.0712890	0.8362470
H	4.6590340	-0.9451870	1.4511770
H	5.3176530	0.5565050	0.7969020
H	3.6396790	0.5078590	1.3378110
H	1.1041490	0.2539710	-1.6078820
H	-0.5065050	0.8205400	0.9418460
O	-2.2573070	-0.8261510	-0.9604750
C	-3.3787680	-0.6749780	-0.3487510
O	-3.6511320	0.0798590	0.5797690
C	-4.4804890	-1.6124700	-0.9299230
F	-5.6542160	-1.4649790	-0.2864090
F	-4.1172150	-2.9116420	-0.8265820
F	-4.6965110	-1.3512420	-2.2400250
H	-1.3590980	-0.1347660	-0.5563110
H	-5.1986510	0.4475830	1.5903740
O	-5.9097640	0.7447770	2.1896000
H	-6.6845520	0.2217600	1.9470980
H	-1.8535210	2.1503630	-0.8049120
H	-0.5397480	1.9350180	-1.9520050
C	-0.1185730	3.3242110	-0.3649290
C	0.9631540	3.9155410	-1.0346590
C	-0.5872910	3.9321410	0.8110600
C	1.5673730	5.0767970	-0.5406400
H	1.3327340	3.4684010	-1.9543300
C	0.0140080	5.0910450	1.3099190
H	-1.4328640	3.4967700	1.3385220
C	1.0962700	5.6675950	0.6357120
H	2.4014730	5.5204150	-1.0773130
H	-0.3656890	5.5466030	2.2202990
H	1.5624070	6.5702450	1.0200060

17.log
Potential Energy = -1489.65085
Zero-point Energy = -1489.18269
Free Energy = -1489.22774
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.10845

Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68534
Nimag = 1 (-1147.5580 cm⁻¹)
Charge = 0 Multiplicity = 1

C	3.5330880	-0.0058360	-0.6121920
C	3.4042920	-1.5510720	1.1651460
C	2.1670000	-0.6633110	1.3167540
N	2.2241460	0.1414470	0.0799990
N	4.0498390	-1.2170440	0.0238690
O	3.7104130	-2.4712070	1.9238290
C	5.1040350	-2.0645950	-0.5259480
H	4.8407930	-3.1070850	-0.3355250
H	5.1746210	-1.9016020	-1.6015570
H	6.0753850	-1.8629230	-0.0657820
C	1.2585060	0.9189690	-0.4153500
C	0.0040750	1.2295390	0.1121410
C	-0.6801900	2.5016600	-0.4236840
C	0.9332060	-1.5621560	1.4679520
H	1.1250150	-2.2492410	2.2956640
H	0.0286770	-1.0010850	1.6963530
H	0.7676990	-2.1500800	0.5604580
H	2.2724200	-0.0173880	2.1977250
C	4.4785010	1.2459160	-0.4658250
H	3.3556690	-0.1930250	-1.6780840
C	5.7923350	0.9737280	-1.2332010
H	6.3946020	1.8873520	-1.2489600
H	6.3982160	0.1964190	-0.7642530
H	5.6017480	0.6868780	-2.2737480
C	3.8264460	2.4937150	-1.0988310
H	3.5283040	2.3192670	-2.1392990
H	2.9560810	2.8446560	-0.5375970
H	4.5539830	3.3113290	-1.1007910
C	4.7922550	1.5349320	1.0136060
H	5.2878460	0.6886500	1.4994620
H	5.4654890	2.3952220	1.0838360
H	3.8877510	1.7816020	1.5793250
H	1.4895410	1.3101230	-1.4036240
H	-0.1485480	1.0481110	1.1755110
O	-1.4300380	-0.6631700	-1.0719940
C	-2.3365110	-1.2559980	-0.3768570
O	-2.5887900	-1.1418700	0.8178750
C	-3.1760540	-2.2354290	-1.2525860
F	-4.1224150	-2.8660820	-0.5312930
F	-2.3887130	-3.1834410	-1.8120140
F	-3.7984220	-1.5765010	-2.2571310
H	-0.7708910	0.1444240	-0.4946570
H	-3.8375050	-1.9224240	1.9959970
O	-4.4098770	-2.2485250	2.7164970
H	-5.0593930	-2.8207520	2.2883490
H	-0.5701560	2.5419800	-1.5134300
H	-0.1608390	3.3833920	-0.0241830
C	-2.1495040	2.6107280	-0.0619800
C	-2.5352880	2.9603150	1.2423960
C	-3.1538180	2.3761690	-1.0123710
C	-3.8849800	3.0631050	1.5902130
H	-1.7723600	3.1599900	1.9914110
C	-4.5065700	2.4805500	-0.6706840
H	-2.8759570	2.1113390	-2.0294260
C	-4.8770540	2.8222580	0.6332900
H	-4.1615510	3.3356670	2.6049140
H	-5.2682750	2.2969790	-1.4234110
H	-5.9266050	2.9046680	0.9005920

18.log
Potential Energy = -1489.65101
Zero-point Energy = -1489.18265
Free Energy = -1489.22799
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.10962
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68661
Nimag = 1 (-1145.3557 cm⁻¹)
Charge = 0 Multiplicity = 1

C	2.9284020	-0.6227170	-0.5075450
C	2.4269210	-2.8838830	-0.0762700
C	1.4389360	-2.0810820	0.7765820

H	-2.3851920	2.0941950	1.5574330
H	-1.3018420	-0.7425730	2.0681240
C	-2.5118000	-2.3701720	-0.9836760
H	-3.3021370	-0.3742730	-1.3968320
C	-3.7506360	-3.0942270	-1.5570030
H	-3.4355740	-4.0418430	-2.0047750
H	-4.4895200	-3.3300600	-0.7887960
H	-4.2389510	-2.5059420	-2.3423540
C	-1.4622180	-2.2827610	-2.1120950
H	-1.8097850	-1.6586580	-2.9439480
H	-0.4991990	-1.9019940	-1.7642480
H	-1.2818520	-3.2865630	-2.5095410
C	-1.9371650	-3.1824440	0.1911070
H	-2.6570050	-3.2782410	1.0104040
H	-1.6885620	-4.1930240	-0.1484080
H	-1.0185440	-2.7343450	0.5830640
H	-1.0822350	0.4077290	-1.7179480
H	1.1427890	-0.2591250	-0.4392820
H	2.1729430	1.8193630	-1.0182480
C	0.7059620	3.3767720	-0.9065650
C	-0.3606050	3.9742820	-1.5960260
C	1.3971160	4.1422870	0.0451230
C	-0.7316270	5.2975220	-1.3381580
H	-0.9028560	3.4024160	-2.3455920
C	1.0285380	5.4654770	0.3087290
H	2.2328640	3.6998310	0.5821570
C	-0.0390110	6.0479650	-0.3819260
H	-1.5570160	5.7428600	-1.8867350
H	1.5779320	6.0411900	1.0484570
H	-0.3245970	7.0765910	-0.1816080
H	0.5478320	1.0719170	0.8089590
O	1.8602080	-1.2264300	-0.5984020
C	2.9891400	-1.1721880	0.0142410
O	3.4442570	-0.2686480	0.7096940
C	3.8280130	-2.4672480	-0.2107690
F	5.0138130	-2.4137880	0.4258370
F	3.1684760	-3.5577910	0.2439940
F	4.0788560	-2.6606880	-1.5264190
H	5.0382740	-0.0077060	1.6766790
O	5.8013080	0.2679330	2.2199670
H	6.4462000	-0.4461300	2.1370100

21.log
Potential Energy = -1489.65274
Zero-point Energy = -1489.18458
Free Energy = -1489.23013
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11031
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68769
Nimag = 1 (-1176.9071 cm⁻¹)
Charge = 0 Multiplicity = 1

C	2.9590250	-0.0971970	0.3830970
C	3.5438430	-1.8075490	-1.1324680
C	2.0946440	-1.4478880	-1.4719530
N	1.8828100	-0.2504280	-0.6316800
N	3.9952780	-0.9666350	-0.1740900
O	4.2045710	-2.6805620	-1.6961160
C	5.4146110	-0.8931800	0.1613460
H	5.9918900	-1.0551800	-0.7512780
H	5.6412440	0.0958690	0.5603480
H	5.7035140	-1.6523640	0.8933840
C	0.9180770	0.6629160	-0.7678990
C	-0.2995430	0.5486050	-1.4396420
C	-1.0670050	1.8013290	-1.8956300
H	-2.1244650	1.5275160	-1.9879860
C	1.9764400	-1.2259490	-2.9855080
H	2.4280340	-2.0884910	-3.4812960
H	0.9433390	-1.1477070	-3.3209930
H	2.5178140	-0.3251350	-3.2888870
H	1.4320640	-2.2640920	-1.1575740
C	2.5201100	-0.4686920	1.8468030
H	3.3056950	0.9436330	0.3757360
C	3.7240520	-0.2880950	2.7986440
H	3.3838880	-0.4050440	3.8323720
H	4.5056590	-1.0313400	2.6300990

H	4.1674440	0.7103810	2.7092390
C	1.4066020	0.4895840	2.3194520
H	1.7067860	1.5399750	2.2290220
H	0.4685380	0.3443380	1.7789650
H	1.1981610	0.2992980	3.3770270
C	2.0141890	-1.9205420	1.9239130
H	2.7816650	-2.6360660	1.6117190
H	1.7414320	-2.1598290	2.9567420
H	1.1226420	-2.0723450	1.3071390
H	1.0962770	1.5741250	-0.2011910
H	-1.0838020	0.0137790	-0.3639200
H	-0.7333170	2.0703260	-2.9057760
C	-0.9388130	3.0158560	-0.9958160
C	-1.7187110	3.1407010	0.1656970
C	-0.0375510	4.0464190	-1.3056870
C	-1.5999930	4.2604740	0.9938270
H	-2.4274210	2.3573990	0.4209550
C	0.0858470	5.1687710	-0.4796390
H	0.5686840	3.9724480	-2.2055300
C	-0.6954920	5.2789950	0.6744450
H	-2.2171140	4.3396780	1.8844640
H	0.7874070	5.9561340	-0.7406880
H	-0.6049750	6.1510170	1.3156390
H	-0.4232870	-0.2970180	-2.1127070
O	-1.8046220	-0.4504170	0.4903130
C	-2.8346120	-1.0800060	0.0466230
O	-3.1973540	-1.2392030	-1.1151350
C	-3.6800730	-1.6875380	1.2073340
F	-4.7648510	-2.3408200	0.7484330
F	-2.9493890	-2.5661320	1.9318880
F	-4.1112940	-0.7210830	2.0505600
H	-4.6252940	-2.1398300	-1.9507730
O	-5.2978760	-2.5613080	-2.5192880
H	-5.9209500	-2.9798680	-1.9116150

22.log
Potential Energy = -1489.65177
Zero-point Energy = -1489.18389
Free Energy = -1489.22932
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.10954
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68709
Nimag = 1 (-1199.7506 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-3.2328400	0.0939410	0.8033320
C	-4.1367980	-1.3447230	-0.8332130
C	-2.6256020	-1.5903040	-0.8726920
N	-2.1704560	-0.8228460	0.3066430
N	-4.4185080	-0.4799010	0.1677420
O	-4.9613830	-1.9039320	-1.5564820
C	-5.7897330	-0.2816580	0.6315090
H	-6.3169310	-1.2358700	0.5671330
H	-5.7754100	0.0526190	1.6690380
H	-6.3257380	0.4526260	0.0244110
C	-0.9962430	-0.9366710	0.9302350
C	0.1895020	-1.5169620	0.4733690
C	1.2250000	-1.9657100	1.5160260
H	0.8453880	-2.8518640	2.0423140
C	-2.3633260	-3.1012640	-0.8276880
H	-2.9989080	-3.5670860	-1.5845460
H	-1.3293160	-3.3570420	-1.0537430
H	-2.6261410	-3.5127660	0.1511070
H	-2.2091040	-1.1626350	-1.7933930
C	-2.9816880	1.6080110	0.4629230
H	-3.3107240	-0.0115790	1.8923280
C	-4.2024920	2.4413900	0.9124630
H	-3.9645620	3.5050930	0.8134910
H	-5.0857370	2.2491270	0.3001570
H	-4.4577990	2.2581530	1.9623160
C	-1.7576950	2.1208450	1.2496160
H	-1.8720470	1.9566020	2.3276560
H	-0.8203120	1.6625240	0.9276800
H	-1.6552200	3.1988920	1.0907820
C	-2.7521460	1.8084010	-1.0461170
H	-3.6049710	1.4569010	-1.6361000

H	-2.6231140	2.8743770	-1.2590640
H	-1.8504320	1.2938130	-1.3926350
H	-0.9670120	-0.4371920	1.8971960
H	0.7494440	-0.3636470	-0.1957210
H	1.3456240	-1.1811680	2.2715680
C	2.5775170	-2.3082450	0.9188360
C	2.7514540	-3.4980970	0.1927180
C	3.6826140	-1.4601490	1.0811370
C	3.9906800	-3.8267770	-0.3635130
H	1.9112720	-4.1773320	0.0674550
C	4.9264360	-1.7860830	0.5290280
H	3.5685050	-0.5369730	1.6427610
C	5.0844850	-2.9698550	-0.1974130
H	4.1037690	-4.7530320	-0.9200340
H	5.7700660	-1.1158190	0.6689550
H	6.0494960	-3.2251110	-0.6257140
H	0.1312060	-2.1503850	-0.4094110
O	1.2672250	0.4377030	-0.9368700
C	1.8656010	1.4175680	-0.3583950
O	1.9489950	1.6670710	0.8407940
C	2.5403330	2.3697870	-1.3920500
F	3.1817980	3.3895770	-0.7895560
F	3.4454170	1.7065500	-2.1473460
F	1.6208760	2.9033250	-2.2298550
H	2.7540260	3.0254720	1.8655230
O	3.1079470	3.6511020	2.5263520
H	3.5819860	4.3212370	2.0175850

23.log
Potential Energy = -1489.65395
Zero-point Energy = -1489.18594
Free Energy = -1489.23165
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11023
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68794
Nimag = 1 (-1207.5758 cm⁻¹)
Charge = 0 Multiplicity = 1

C	1.8357380	-2.0017510	0.8069500
C	3.2612390	-2.0519450	-1.0725350
C	2.2607000	-0.9287750	-1.3583270
N	1.5467820	-0.8322580	-0.0669380
N	3.0381570	-2.5376380	0.1700720
O	4.1659360	-2.4004230	-1.8313980
C	4.0096400	-3.4084200	0.8274000
H	5.0120070	-3.0892190	0.5342750
H	3.9036990	-3.3161270	1.9085440
H	3.8814260	-4.4557790	0.5413710
C	0.7797000	0.1768180	0.3472300
C	0.1721890	1.1854340	-0.4060800
C	-0.2569870	2.4800870	0.2935070
H	-0.5978740	2.2447300	1.3079380
C	3.0304950	0.3285560	-1.7830760
H	3.7138460	0.0413340	-2.5857520
H	2.3781730	1.1146490	-2.1601280
H	3.6168730	0.7242930	-0.9488370
H	1.5749790	-1.2407980	-2.1559810
C	0.6485920	-3.0269580	0.9167230
H	2.0809830	-1.6398470	1.8128040
C	1.0963080	-4.2328330	1.7727860
H	0.2301740	-4.8719230	1.9704280
H	1.8431550	-4.8478760	1.2670460
H	1.5007870	-3.9180670	2.7415800
C	-0.5478230	-2.3681120	1.6347250
H	-0.2621040	-1.9583780	2.6106780
H	-1.0091300	-1.5727170	1.0450830
H	-1.3204850	-3.1233410	1.8092100
C	0.2088970	-3.5183310	-0.4743260
H	1.0307040	-4.0013540	-1.0127850
H	-0.5923850	-4.2563180	-0.3665310
H	-0.1799250	-2.7005760	-1.0894290
H	0.5450150	0.1393070	1.4095230
H	-1.0702970	0.5419070	-0.6942430
H	-1.1198020	2.8973920	-0.2373520
C	0.8403300	3.5303950	0.3516550
C	1.7404400	3.5764970	1.4277690

C	0.9900860	4.4666540	-0.6829350
C	2.7656900	4.5262920	1.4669640
H	1.6363380	2.8672810	2.2457060
C	2.0155690	5.4172760	-0.6501140
H	0.2960660	4.4535340	-1.5201680
C	2.9086120	5.4497000	0.4256110
H	3.4486110	4.5480270	2.3117550
H	2.1127730	6.1340650	-1.4608280
H	3.7034340	6.1893830	0.4553360
H	0.5011930	1.3137340	-1.4357250
O	-2.1161300	0.1271370	-1.1587260
C	-3.1228480	0.1635420	-0.3599430
O	-3.1623690	0.5298190	0.8112390
C	-4.4234860	-0.3493360	-1.0504420
F	-5.4862640	-0.2910900	-0.2250280
F	-4.7162360	0.3880460	-2.1463440
F	-4.2846830	-1.6355170	-1.4483620
H	-4.4922510	0.6113850	2.1394900
O	-5.0632820	0.7021580	2.9263090
H	-5.9476390	0.4493480	2.6320100

24.log
Potential Energy = -1489.65274
Zero-point Energy = -1489.18457
Free Energy = -1489.23008
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1490.11033
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1489.68767
Nimag = 1 (-1177.1316 cm⁻¹)
Charge = 0 Multiplicity = 1

C	2.9618060	-0.0865770	0.3642210
C	3.5449600	-1.7715100	-1.1802500
C	2.0928870	-1.4117810	-1.5070080
N	1.8814780	-0.2275070	-0.6481950
N	3.9980810	-0.9442650	-0.2108650
O	4.2059500	-2.6331860	-1.7607690
C	5.4188520	-0.8710010	0.1186110
H	5.9921740	-1.0148280	-0.7995470
H	5.6436580	0.1118480	0.5335870
H	5.7143450	-1.6416300	0.8358910
C	0.9113860	0.6828860	-0.7642310
C	-0.3093480	0.5737050	-1.4313550
C	-1.0876200	1.8297760	-1.8583990
H	-2.1435150	1.5499780	-1.9493270
C	1.9657300	-1.1686240	-3.0165530
H	2.4194020	-2.0215190	-3.5269350
H	0.9305020	-1.0912490	-3.3456550
H	2.5007360	-0.2606640	-3.3097000
H	1.4346260	-2.2346490	-1.2009180
C	2.5303060	-0.4820040	1.8238860
H	3.3055510	0.9552160	0.3713500
C	3.7388810	-0.3174100	2.7727180
H	3.4037430	-0.4525860	3.8058660
H	4.5199460	-1.0572290	2.5874240
H	4.1813320	0.6827240	2.6987670
C	1.4195950	0.4687400	2.3178670
H	1.7197490	1.5203380	2.2425140
H	0.4785630	0.3324030	1.7802980
H	1.2167910	0.2615880	3.3733670
C	2.0243950	-1.9348380	1.8796590
H	2.7898190	-2.6452050	1.5510070
H	1.7577890	-2.1912940	2.9099760
H	1.1291080	-2.0760200	1.2658340
H	1.0875040	1.5852070	-0.1828920
H	-1.0797110	0.0076730	-0.3615410
H	-0.7617680	2.1204570	-2.8651090
C	-0.9618600	3.0275200	-0.9361170
C	-1.7374220	3.1261560	0.2308040
C	-0.0672400	4.0685930	-1.2298300
C	-1.6211380	4.2305440	1.0796890
H	-2.4416990	2.3349760	0.4738190
C	0.0537570	5.1756310	-0.3830470
H	0.5355870	4.0150360	-2.1334130
C	-0.7232930	5.2597220	0.7761290
H	-2.2350250	4.2895290	1.9741130

H	0.7500840	5.9715370	-0.6319190
H	-0.6346890	6.1198750	1.4334130
H	-0.4309980	-0.2590190	-2.1208050
O	-1.7743690	-0.5028890	0.4879370
C	-2.8387380	-1.0749220	0.0475940
O	-3.2737010	-1.1113690	-1.0996330
C	-3.6117900	-1.8066920	1.1868750
F	-4.7825030	-2.3121880	0.7532730
F	-2.8787870	-2.8345850	1.6769500
F	-3.8828750	-0.9718060	2.2152340
H	-4.7583180	-1.9102490	-1.9397790
O	-5.4641260	-2.2646170	-2.5137660
H	-6.0593720	-2.7436240	-1.9230980

Chlorination of enamine (TS4)

(S)-TS-front

Conformation name	Extrapolated Free energy (kcal/mol)	
TS4-Sf-lowest	0.0	
1	0.5	
2	1.0	
3	0.2	
4	1.4	
5	0.6	
6	0.6	
7	0.9	

TS-Sf-lowest.log
Potential Energy = -2233.46980
Zero-point Energy = -2232.93920
Free Energy = -2232.98976
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.04089
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.56086
Nimag = 1 (-171.2674 cm⁻¹)
Charge = 0 Multiplicity = 1

C	1.4362000	-2.0260730	0.1852510
C	0.6589640	-2.5454550	2.3535050
C	1.9872400	-1.8056210	2.5386940
N	2.2158010	-1.2590210	1.1802660
N	0.3820540	-2.6041080	1.0309380
O	-0.0429360	-2.9908790	3.2634590
C	-0.9020110	-3.0898600	0.5364720
H	-1.6744240	-2.8186980	1.2590040
H	-1.1237620	-2.6181050	-0.4216270
H	-0.9089440	-4.1766620	0.4121940
C	2.6962700	-0.0165110	0.9672230
H	3.1743400	0.4192710	1.8393750
C	2.6298390	0.7631100	-0.1734300
C	3.4840250	2.0109890	-0.3095340
H	3.7139220	2.4055100	0.6867900
H	2.9099480	2.7835200	-0.8322730
H	2.2665530	0.3375310	-1.1023570
C	1.9217000	-0.7861010	3.6715830
H	1.5900990	-1.3082500	4.5724590
H	2.9013980	-0.3496510	3.8798890
H	1.2096700	0.0145820	3.4518760
H	2.7596910	-2.5493130	2.7731390
C	2.2850320	-3.0774390	-0.6150130
H	0.9755380	-1.3327920	-0.5265310
Cl	0.4689130	1.7273330	0.4829900

N	-1.2008020	2.5821520	0.7876870
C	-1.3399020	3.7131330	1.5954140
C	-2.3732320	2.1463290	0.2431010
C	-2.8144340	4.0976710	1.6004990
C	-3.4990880	3.0598870	0.6961410
H	-3.1780470	4.0783990	2.6314920
H	-3.9716900	3.5004970	-0.1866800
O	-2.4718490	1.1604460	-0.4986300
O	-0.4271040	4.2681930	2.1794700
C	1.3752820	-3.8038310	-1.6299300
H	1.9936850	-4.4149550	-2.2952100
H	0.6614060	-4.4734930	-1.1450620
H	0.8183980	-3.0962140	-2.2546980
C	3.3899880	-2.3456000	-1.4034120
H	2.9707990	-1.6475540	-2.1357420
H	4.0669580	-1.7934900	-0.7462370
H	3.9855440	-3.0805060	-1.9546820
C	2.9351940	-4.1129440	0.3214480
H	2.1929360	-4.6324590	0.9360870
H	3.4537290	-4.8694300	-0.2764430
H	3.6781470	-3.6526550	0.9803000
H	-4.2550230	2.4590660	1.2094640
H	-2.9121420	5.1228650	1.2333920
C	4.7781290	1.7606790	-1.0718350
C	4.8343980	1.9359080	-2.4627700
C	5.9369270	1.3332880	-0.4050200
C	6.0135370	1.6837950	-3.1717770
H	3.9493190	2.2762250	-2.9952770
C	7.1187870	1.0828490	-1.1084250
H	5.9164780	1.1995340	0.6740020
C	7.1605770	1.2552410	-2.4963600
H	6.0367420	1.8274260	-4.2484800
H	8.0066210	0.7579240	-0.5730110
H	8.0785510	1.0629090	-3.0441750
H	-3.7921740	0.5960690	-1.0643750
O	-4.5875760	0.1596840	-1.5413600
C	-5.5791260	-0.0979560	-0.7233580
O	-5.6488720	0.1226780	0.4677200
C	-6.7532220	-0.7683980	-1.4897840
F	-6.3628880	-1.9411010	-2.0385400
F	-7.1952980	0.0269540	-2.4897950
F	-7.7868040	-1.0179020	-0.6713350

1.log
Potential Energy = -2233.46971
Zero-point Energy = -2232.93890
Free Energy = -2232.98921
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.04053
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.56003
Nimag = 1 (-171.7683 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-3.6684520	-1.2846770	0.0439140
C	-3.1339440	-2.8612820	-1.6305480
C	-2.9388380	-1.4799660	-2.2628740
N	-2.9850500	-0.5982410	-1.0729360
N	-3.4985410	-2.6935340	-0.3390530
O	-2.9658140	-3.9391640	-2.2042870
C	-3.5938430	-3.8190540	0.5844800
H	-2.8382370	-4.5570070	0.3076520
H	-3.4027260	-3.4714640	1.6004680
H	-4.5767530	-4.2978240	0.5472560
C	-2.1605030	0.4586480	-0.9178040
H	-1.6905320	0.7812090	-1.8419910
C	-1.8223210	1.1420680	0.2357150
C	-1.1164920	2.4843520	0.1620650
H	-0.5429530	2.5430960	-0.7700860
H	-0.3958140	2.5566160	0.9835840
H	-2.3425670	0.9332850	1.1640620
C	-1.6676740	-1.4089620	-3.1034460
H	-1.7067390	-2.2170420	-3.8380570
H	-1.5959210	-0.4648870	-3.6487410
H	-0.7717180	-1.5398480	-2.4898910
H	-3.8036920	-1.2774690	-2.9078000
C	-5.1603820	-0.8375750	0.2497230

H	-3.1164690	-1.1035410	0.9725750
Cl	0.0755730	-0.3545370	0.6944540
N	1.5740650	-1.3810250	1.2446500
C	2.8640780	-0.9720530	1.0693310
C	1.4567550	-2.6250500	1.8692570
C	3.7991320	-2.0318770	1.6256780
C	2.8650860	-3.1361220	2.1468190
H	4.4705540	-2.3625960	0.8284330
H	2.9681890	-3.3202260	3.2195200
O	0.4034320	-3.1768090	2.1303680
O	3.1889180	0.0976490	0.5386820
C	-5.7570470	-1.5887310	1.4602600
H	-6.7360890	-1.1625780	1.7019930
H	-5.9074070	-2.6518710	1.2595060
H	-5.1250830	-1.4892690	2.3501780
C	-5.2029910	0.6726930	0.5585660
H	-4.6681250	0.9126690	1.4833470
H	-4.7788860	1.2703530	-0.2525180
H	-6.2443400	0.9830880	0.6925900
C	-6.0149210	-1.1202460	-1.0000870
H	-5.9872710	-2.1767110	-1.2857080
H	-7.0588290	-0.8634470	-0.7928520
H	-5.6943830	-0.5164430	-1.8548300
H	2.9983050	-4.0915050	1.6318550
H	4.4150930	-1.5815920	2.4096780
C	-2.0765920	3.6631450	0.2459770
C	-2.3922390	4.2428020	1.4840310
C	-2.6791270	4.1853430	-0.9091200
C	-3.2919500	5.3105240	1.5690170
H	-1.9269620	3.8583670	2.3887120
C	-3.5765370	5.2542600	-0.8301860
H	-2.4407000	3.7553670	-1.8790830
C	-3.8883170	5.8197040	0.4111580
H	-3.5216100	5.7466870	2.5372550
H	-4.0280650	5.6476450	-1.7367530
H	-4.5839200	6.6515250	0.4742240
H	4.6400180	0.5562630	0.2808210
O	5.5511380	0.9935370	0.1096450
C	6.3794550	0.1925400	-0.5153900
O	6.1896900	-0.9479880	-0.8835480
C	7.7403280	0.9030150	-0.7578160
F	8.2996620	1.2878020	0.4115320
F	8.6064930	0.0914900	-1.3837460
F	7.5783660	2.0081600	-1.5198910

2.log

Potential Energy = -2233.46737

Zero-point Energy = -2232.93698

Free Energy = -2232.98725

Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.03933

Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.55921

Nimag = 1 (-167.5942 cm⁻¹)

Charge = 0 Multiplicity = 1

C	-3.7582770	-1.2903020	0.0612160
C	-2.6282090	-3.3491590	-0.1830060
C	-2.4951300	-2.6227220	-1.5246840
N	-2.9446640	-1.2565110	-1.1712110
N	-3.3054780	-2.5488370	0.6713530
O	-2.1764780	-4.4674510	0.0727590
C	-3.4510990	-2.8829010	2.0839360
H	-2.5559740	-3.4194740	2.4049950
H	-3.5495660	-1.9654210	2.6655410
H	-4.3215950	-3.5197630	2.2672320
C	-2.3370910	-0.1428660	-1.6402840
H	-1.7237270	-0.3211680	-2.5186430
C	-2.3848910	1.1471720	-1.1532920
C	-1.9172930	2.3062050	-2.0198820
H	-1.0772150	1.9837600	-2.6448560
H	-3.0629580	1.4002420	-0.3459600
C	-1.0892480	-2.7408880	-2.1053500
H	-0.8380130	-3.8029610	-2.1613090
H	-1.0345800	-2.3312140	-3.1168600
H	-0.3491290	-2.2411590	-1.4740110
H	-3.2074580	-3.0775090	-2.2256660

C	-5.3056810	-1.2061500	-0.1958200
H	-3.4660920	-0.4595990	0.7127990
Cl	-0.4588620	0.6652590	0.3627440
N	0.9475810	0.4923970	1.6026870
C	2.2560700	0.3560530	1.2366210
C	0.7472150	0.5238770	2.9855990
C	3.1122930	0.2815920	2.4885040
C	2.1095970	0.3747720	3.6503370
H	3.6829460	-0.6508850	2.4712050
H	2.2796910	1.2358750	4.3020250
O	-0.3349360	0.6474210	3.5288400
O	2.6484770	0.3065740	0.0646700
C	-6.0507950	-1.2070520	1.1569640
H	-7.1097410	-0.9876390	0.9863340
H	-5.9976320	-2.1741710	1.6619650
H	-5.6596430	-0.4399380	1.8350970
C	-5.6311700	0.1173390	-0.9181900
H	-5.3589230	0.9877870	-0.3121200
H	-5.1226210	0.1933590	-1.8831280
H	-6.7089750	0.1708090	-1.1031470
C	-5.8019640	-2.3836980	-1.0555470
H	-5.5617200	-3.3511810	-0.6030570
H	-6.8909000	-2.3288760	-1.1554380
H	-5.3799250	-2.3536320	-2.0649510
H	2.0959750	-0.5195130	4.2794210
H	3.8300110	1.1073040	2.4710170
H	4.1144480	0.0888980	-0.3798640
O	5.0452210	0.0058580	-0.7987800
C	5.7380100	-0.9802450	-0.2824840
O	5.4095180	-1.7524050	0.5938620
C	7.1364070	-1.0694720	-0.9546840
F	7.8324010	0.0756200	-0.7733370
F	7.8575600	-2.0780460	-0.4416560
F	7.0203220	-1.2743060	-2.2859970
H	-2.7323200	2.5690050	-2.7113840
C	-1.5332080	3.5590400	-1.2531360
C	-2.5125380	4.3185530	-0.5928070
C	-0.2029150	3.9987030	-1.2017000
C	-2.1704710	5.4771020	0.1103750
H	-3.5533530	4.0055340	-0.6331790
C	0.1445290	5.1604160	-0.5036630
H	0.5685970	3.4268470	-1.7107320
C	-0.8382740	5.9026070	0.1578690
H	-2.9437210	6.0502890	0.6143400
H	1.1815390	5.4836250	-0.4778760
H	-0.5709840	6.8047820	0.7005110

3.log

Potential Energy = -2233.46751

Zero-point Energy = -2232.93690

Free Energy = -2232.98708

Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.04096

Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.56052

Nimag = 1 (-185.2852 cm⁻¹)

Charge = 0 Multiplicity = 1

C	4.1883060	-0.5942920	-0.1173580
C	3.8784760	-1.1507810	2.1561150
C	3.5007990	0.3270880	2.0199240
N	3.4264230	0.4820260	0.5489490
N	4.2126800	-1.6218250	0.9332250
O	3.8595620	-1.7994760	3.2042620
C	4.4555190	-3.0407760	0.6963100
H	3.8036710	-3.6175260	1.3556340
H	4.2203530	-3.2799180	-0.3415020
H	5.4930890	-3.3193510	0.9031320
C	2.4785970	1.2282170	-0.0587720
H	1.9863450	1.9304810	0.6053870
C	2.0566760	1.1885710	-1.3731780
C	1.2203700	2.2940210	-2.0057160
H	0.4867730	1.8314010	-2.6764420
H	2.5954070	0.5796870	-2.0904700
C	2.2315120	0.6678470	2.7949610
H	2.3769340	0.3546660	3.8317380
H	2.0346480	1.7424710	2.7949010

H	1.3612070	0.1425800	2.3912820
H	4.3312890	0.9264020	2.4154520
C	5.6058360	-0.1469850	-0.6275030
H	3.6122030	-0.9752390	-0.9676110
Cl	0.4071210	-0.5897190	-0.9327190
N	-0.9070010	-1.9556400	-0.8533110
C	-2.2433120	-1.6950980	-0.7623890
C	-0.6000060	-3.3169400	-0.9140380
C	-3.0036540	-3.0101370	-0.7489200
C	-1.9118680	-4.0888190	-0.8398800
H	-3.5998200	-3.0634710	0.1662620
H	-1.9996480	-4.7199460	-1.7282390
O	0.5243860	-3.7740500	-1.0084380
O	-2.7276790	-0.5578660	-0.7031980
C	6.2962370	-1.3349560	-1.3328370
H	7.2102860	-0.9823460	-1.8215390
H	6.5858410	-2.1234850	-0.6346910
H	5.6569620	-1.7745910	-2.1069850
C	5.4443760	0.9896650	-1.6577550
H	4.8757600	0.6644600	-2.5353570
H	4.9501010	1.8653290	-1.2285500
H	6.4341220	1.3023110	-2.0062140
C	6.4934980	0.3465150	0.5305170
H	6.6114410	-0.4136630	1.3094850
H	7.4919800	0.5832970	0.1489380
H	6.0942190	1.2578310	0.9865380
H	-1.8823840	-4.7468080	0.0329320
H	-3.6966200	-3.0244700	-1.5953440
H	-4.2322830	-0.2478210	-0.5574580
O	-5.2041920	0.0770120	-0.5262050
C	-5.8759540	-0.4537370	0.4665300
O	-5.4869730	-1.2437450	1.3013030
C	-7.3421750	0.0618870	0.4648040
F	-7.9755770	-0.2992870	-0.6745780
F	-8.0339860	-0.4394450	1.4995160
F	-7.3840980	1.4102930	0.5488230
H	1.8847310	2.8838230	-2.6526390
C	0.5110260	3.2357420	-1.0511320
C	-0.7552280	2.9240800	-0.5300640
C	1.1077490	4.4489580	-0.6731060
C	-1.4041060	3.7996080	0.3463260
H	-1.2357390	1.9911900	-0.8111460
C	0.4626350	5.3270830	0.2037950
H	2.0842520	4.7111390	-1.0737000
C	-0.7972250	5.0041030	0.7174190
H	-2.3855250	3.5424920	0.7351010
H	0.9412330	6.2624820	0.4799900
H	-1.3029920	5.6856610	1.3953180

4.log
Potential Energy = -2233.46733
Zero-point Energy = -2232.93678
Free Energy = -2232.98692
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.03906
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.55865
Nimag = 1 (-169.1557 cm⁻¹)
Charge = 0 Multiplicity = 1

C	2.3315200	-2.1027860	-0.5619230
C	2.2387070	-3.1470730	1.5532530
C	3.4184580	-2.1721090	1.6073580
N	3.2012690	-1.3704900	0.3811250
N	1.6461990	-3.0365800	0.3426470
O	1.8832200	-3.8897320	2.4709260
C	0.3886080	-3.7106670	0.0388320
H	-0.2096270	-3.7521820	0.9513070
H	-0.1521440	-3.1446890	-0.7206940
H	0.5468520	-4.7322810	-0.3192110
C	3.3978360	-0.0330410	0.3386070
H	4.0277540	0.3384410	1.1416030
C	2.9031380	0.8916660	-0.5581840
C	3.5209430	2.2783460	-0.6446620
H	3.8577810	2.5942750	0.3488150
H	2.3507570	0.5614480	-1.4309200

C	3.4557230	-1.3954720	2.9205180
H	3.4479790	-2.1198850	3.7387680
H	4.3660680	-0.7982920	3.0116430
H	2.5848790	-0.7421020	3.0251070
H	4.3438680	-2.7552940	1.5121720
C	3.1112390	-2.7874540	-1.7416700
H	1.5905280	-1.4153090	-0.9841910
Cl	0.8819810	1.1958520	0.8787330
N	-0.7154320	1.5425790	1.8148560
C	-0.7413320	2.1682860	3.0645770
C	-1.9517230	1.2320780	1.3259730
C	-2.2000130	2.2936200	3.4854020
C	-3.0026220	1.6687260	2.3322340
H	-2.3370770	1.7745770	4.4378270
H	-3.6857230	2.3722520	1.8477680
O	-2.1506510	0.6838830	0.2353700
O	0.2428160	2.5350500	3.6794220
C	2.1056600	-3.4793470	-2.6880620
H	2.6293470	-3.8139260	-3.5894260
H	1.6448130	-4.3602730	-2.2355380
H	1.3095770	-2.7950880	-3.0034620
C	3.8631590	-1.7103630	-2.5503470
H	3.1758280	-0.9850530	-2.9982170
H	4.5877260	-1.1685180	-1.9364530
H	4.4106430	-2.1912080	-3.3675700
C	4.1241330	-3.8249230	-1.2222470
H	3.6443560	-4.5946060	-0.6090940
H	4.5980510	-4.3287180	-2.0709270
H	4.9198960	-3.3549130	-0.6359400
H	-3.5867580	0.7948250	2.6344040
H	-2.4289170	3.3504560	3.6472890
H	-3.5447110	0.3194480	-0.3362230
O	-4.4265390	0.1355780	-0.8220400
C	-5.0199380	-0.9518760	-0.3915060
O	-4.6506440	-1.7218310	0.4697350
C	-6.3572960	-1.1735390	-1.1521000
F	-6.1470400	-1.2793560	-2.4833810
F	-7.2027030	-0.1372190	-0.9503450
F	-6.9699500	-2.2937630	-0.7392860
H	4.4248440	2.2131120	-1.2693980
C	2.6165400	3.3422430	-1.2410680
C	2.2649410	3.2989250	-2.5999490
C	2.1291660	4.4002870	-0.4608750
C	1.4388470	4.2773500	-3.1602500
H	2.6449680	2.4969470	-3.2286620
C	1.3061900	5.3853520	-1.0176290
H	2.3941980	4.4540990	0.5918820
C	0.9551470	5.3255670	-2.3694860
H	1.1789060	4.2250070	-4.2138720
H	0.9407340	6.1971300	-0.3947480
H	0.3161190	6.0889550	-2.8038810

5.log
Potential Energy = -2233.46755
Zero-point Energy = -2232.93690
Free Energy = -2232.98702
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.04042
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.55989
Nimag = 1 (-182.4978 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-1.8954910	2.4654130	-0.1473520
C	-2.4465080	2.5194600	2.1477600
C	-3.5036680	1.6414560	1.4713940
N	-2.8977740	1.4181920	0.1383960
N	-1.5567540	2.9171320	1.2097250
O	-2.4091360	2.7967130	3.3483490
C	-0.3303870	3.6235060	1.5637370
H	0.0054000	3.2645020	2.5387600
H	0.4374120	3.4127050	0.8181500
H	-0.4830430	4.7050210	1.6259610
C	-2.9475610	0.2264450	-0.4958300
H	-3.7074990	-0.4422300	-0.1061660
C	-2.1558650	-0.2368410	-1.5282260
C	-2.5159530	-1.4591580	-2.3634370

H	-1.5925380	-2.0026160	-2.5950300
H	-1.4638300	0.4394710	-2.0172750
C	-3.8159240	0.3894130	2.2849650
H	-4.1003920	0.7056680	3.2915570
H	-4.6538630	-0.1688090	1.8609110
H	-2.9457300	-0.2687580	2.3598130
H	-4.4206340	2.2361940	1.3673570
C	-2.4134340	3.5981870	-1.1048680
H	-1.0081520	2.0064930	-0.5963350
Cl	-0.4156240	-1.0628910	0.0157620
N	1.0554580	-1.7356210	1.0069190
C	0.9047710	-2.4619160	2.1912860
C	2.3545090	-1.5605350	0.6291690
C	2.2983210	-2.8256120	2.6888120
C	3.2602340	-2.2352950	1.6447800
H	2.4348770	-2.4029780	3.6879930
H	3.8599570	-2.9935780	1.1326680
O	2.7085210	-0.9459070	-0.3851650
O	-0.1622890	-2.7376270	2.7079140
C	-1.2736110	4.6067590	-1.3674340
H	-1.5810860	5.3021900	-2.1550980
H	-1.0328160	5.2032460	-0.4845970
H	-0.3600180	4.1056060	-1.7073690
C	-2.8213270	2.9776600	-2.4569360
H	-1.9720750	2.5003080	-2.9570790
H	-3.6188800	2.2382250	-2.3448110
H	-3.1892620	3.7681420	-3.1191300
C	-3.6238630	4.3378370	-0.5049710
H	-3.3967220	4.7663760	0.4765180
H	-3.9106920	5.1626800	-1.1652690
H	-4.4932370	3.6800270	-0.4084250
H	3.9490090	-1.4902400	2.0525720
H	2.3683420	-3.9130990	2.7764500
H	4.1768120	-0.6857380	-0.7844390
O	5.1050350	-0.4999680	-1.1778690
C	5.9092430	0.0666600	-0.3113950
O	5.6811260	0.3675700	0.8417500
C	7.2980440	0.3338390	-0.9557670
F	7.1839570	1.1411450	-2.0342400
F	7.8691810	-0.8215910	-1.3651070
F	8.1319770	0.9220430	-0.0844920
C	-3.5280870	-2.4156830	-1.7628530
C	-3.1215700	-3.4830520	-0.9467190
C	-4.8995220	-2.2577460	-2.0189570
C	-4.0581870	-4.3641850	-0.3974220
H	-2.0641620	-3.6262680	-0.7429340
C	-5.8404060	-3.1354730	-1.4711020
H	-5.2329840	-1.4433750	-2.6579670
C	-5.4218870	-4.1923870	-0.6564740
H	-3.7220210	-5.1863310	0.2281730
H	-6.8964730	-2.9966370	-1.6849340
H	-6.1499360	-4.8781210	-0.2328000
H	-2.8999740	-1.0999900	-3.3287060

6.log

Potential Energy = -2233.46970

Zero-point Energy = -2232.93905

Free Energy = -2232.98951

Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.04006

Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.55987

Nimag = 1 (-169.4774 cm⁻¹)

Charge = 0 Multiplicity = 1

C	1.3950860	-2.0067280	0.4283510
C	0.9290820	-2.3898500	2.7111870
C	2.2618500	-1.6362050	2.6642300
N	2.2935500	-1.1746490	1.2565240
N	0.4738700	-2.5331540	1.4457330
O	0.3645460	-2.7796200	3.7352760
C	-0.8556250	-3.0632200	1.1627250
H	-1.5286490	-2.7526120	1.9644640
H	-1.2129920	-2.6583030	0.2151990
H	-0.8587130	-4.1559960	1.1107260
C	2.7184810	0.0565190	0.9028700
H	3.3063360	0.5501230	1.6708350

C	2.4816200	0.7604280	-0.2634450
C	3.2844710	2.0057710	-0.5947880
H	3.6370040	2.4697750	0.3334060
H	2.6297400	2.7341880	-1.0850930
H	1.9986110	0.2738240	-1.1036760
C	2.3453660	-0.5498460	3.7317600
H	2.1455110	-1.0165650	4.6994110
H	3.3410920	-0.1023330	3.7762970
H	1.6036240	0.2366230	3.5655830
H	3.0670280	-2.3628690	2.8329900
C	2.1387220	-3.1044010	-0.4137870
H	0.8332100	-1.3619450	-0.2558050
Cl	0.4146430	1.7537730	0.6256440
N	-1.2047800	2.6239330	1.0939920
C	-1.2435580	3.8560640	1.7510980
C	-2.4366310	2.1137700	0.8043730
C	-2.7082240	4.2312820	1.9409610
C	-3.5001310	3.0757400	1.3068350
H	-2.9037780	4.3526370	3.0098740
H	-4.1211890	3.3884170	0.4624850
O	-2.6252310	1.0372570	0.2243800
O	-0.2647480	4.4910920	2.0984270
C	1.1094350	-3.8821040	-1.2631480
H	1.6400410	-4.5327380	-1.9657880
H	0.4632980	-4.5199400	-0.6558920
H	0.4769630	-3.2073350	-1.8513050
C	3.1315550	-2.4217270	-1.3763380
H	2.6199090	-1.7647560	-2.0874490
H	3.8843410	-1.8356920	-0.8425800
H	3.6547810	-3.1885730	-1.9567520
C	2.9066870	-4.0884670	0.4883160
H	2.2508190	-4.5732620	1.2187170
H	3.3508370	-4.8766900	-0.1281520
H	3.7235670	-3.5940070	1.0231170
H	-4.1462300	2.5512260	2.0165030
H	-2.8897900	5.1955210	1.4586970
C	4.4703020	1.7196880	-1.5059130
C	4.3315710	1.7802630	-2.9008330
C	5.7218490	1.3730790	-0.9735710
C	5.4108830	1.4944170	-3.7433460
H	3.3720330	2.0573410	-3.3312680
C	6.8046510	1.0893940	-1.8111300
H	5.8522220	1.3289230	0.1051290
C	6.6520820	1.1468460	-3.2007470
H	5.2832590	1.5488650	-4.8209370
H	7.7668150	0.8283910	-1.3791320
H	7.4927940	0.9287080	-3.8529590
H	-4.0145400	0.4493170	-0.1154240
O	-4.9256270	0.0070650	-0.2683420
C	-5.1716100	-0.2196350	-1.5363600
O	-4.4712630	0.0226760	-2.4963950
C	-6.5656130	-0.8870050	-1.7031680
F	-7.5419330	-0.1027060	-1.1933220
F	-6.6121780	-2.0742710	-1.0571920
F	-6.8459540	-1.1085250	-2.9966490

7.log

Potential Energy = -2233.46969

Zero-point Energy = -2232.93889

Free Energy = -2232.98902

Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.04007

Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.55940

Nimag = 1 (-169.2657 cm⁻¹)

Charge = 0 Multiplicity = 1

C	1.2996140	-1.9352750	0.6324310
C	0.8454910	-2.0783730	2.9448770
C	2.1951360	-1.3657420	2.8145450
N	2.2263070	-1.0484250	1.3674750
N	0.3752800	-2.3351570	1.7031670
O	0.2806820	-2.3493760	4.0065110
C	-0.9729830	-2.8479740	1.4832690
H	-1.6266920	-2.4412530	2.2575250
H	-1.3292360	-2.5240510	0.5046630

H	-1.0101160	-3.9399670	1.5361330
C	2.6817160	0.1287730	0.8893260
H	3.2897080	0.6797960	1.6005110
C	2.4539930	0.7190740	-0.3400200
C	3.2881840	1.9015090	-0.7995490
H	3.6639790	2.4444070	0.0752150
H	2.6492810	2.5969230	-1.3544130
H	1.9490470	0.1656530	-1.1241720
C	2.3095850	-0.1794730	3.7667990
H	2.1062350	-0.5418190	4.7775200
H	3.3147540	0.2486050	3.7613670
H	1.5837030	0.6021890	3.5251810
H	2.9850590	-2.0900320	3.0515190
C	2.0088670	-3.1294120	-0.1008830
H	0.7466410	-1.3475560	-0.1080210
Cl	0.4247100	1.8592730	0.4627130
N	-1.1594390	2.8222390	0.8609130
C	-1.1525850	4.0630080	1.5028280
C	-2.4072310	2.3762320	0.5347240
C	-2.5999400	4.5201990	1.6374720
C	-3.4327780	3.3983590	0.9952590
H	-2.8236110	4.6718210	2.6969080
H	-4.0150400	3.7306980	0.1310360
O	-2.6347940	1.3061260	-0.0427680
O	-0.1526790	4.6483240	1.8763170
C	0.9518150	-3.9728350	-0.8468940
H	1.4590750	-4.7034140	-1.4852420
H	0.3066790	-4.5312040	-0.1648020
H	0.3197410	-3.3527620	-1.4927350
C	2.9967670	-2.5706830	-1.1449180
H	2.4847250	-1.9812690	-1.9127470
H	3.7692450	-1.9471250	-0.6872610
H	3.4959230	-3.4038300	-1.6502810
C	2.7747850	-4.0279130	0.8882630
H	2.1229010	-4.4179840	1.6766380
H	3.1918250	-4.8867090	0.3523590
H	3.6109430	-3.4969420	1.3539240
H	-4.1229800	2.9165870	1.6937480
H	-2.7122330	5.4838230	1.1332820
C	4.4554320	1.4921780	-1.6874360
C	4.3067090	1.4296120	-3.0812210
C	5.6990190	1.1523810	-1.1324390
C	5.3682110	1.0303350	-3.8999550
H	3.3535240	1.6993330	-3.5300540
C	6.7641040	0.7556540	-1.9464270
H	5.8370820	1.2029250	-0.0549470
C	6.6014540	0.6909150	-3.3346370
H	5.2330320	0.9902140	-4.9772560
H	7.7205390	0.5019090	-1.4977070
H	7.4284850	0.3846710	-3.9686760
H	-4.0399810	0.7948480	-0.4477000
O	-4.9815630	0.4899030	-0.7087540
C	-4.9855200	-0.6646490	-1.3309880
O	-4.0435450	-1.3763150	-1.6081920
C	-6.4377840	-1.0627520	-1.7173610
F	-6.9727660	-0.1576790	-2.5685470
F	-7.2336880	-1.1210980	-0.6262270
F	-6.4684960	-2.2628790	-2.3169850

(R)-TS-front

Conformation name	Extrapolated Free energy (kcal/mol)
TS4-Rf-lowest	0.0
1	0.9
2	0.7
3	0.5
4	1.7
5	1.0

60.3

TS4-Rf-lowest.log		
Potential Energy = -2233.46593		
Zero-point Energy = -2232.93534		
Free Energy = -2232.98602		
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.03614		
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.55623		
Nimag = 1 (-187.5221 cm ⁻¹)		
Charge = 0 Multiplicity = 1		
C	4.4000250	-1.2425990 -0.3594760
C	4.2129450	-2.0664110 1.8393300
C	3.2823380	-0.8511910 1.7804990
N	3.2966190	-0.5371380 0.3392030
N	4.7121860	-2.2984330 0.6045560
O	4.4118610	-2.7583960 2.8391880
C	5.4119630	-3.5398940 0.2888250
H	4.9318380	-4.3547750 0.8348710
H	5.3395200	-3.7323540 -0.7818300
H	6.4660880	-3.5032030 0.5781510
C	2.4552490	0.2707560 -0.3356960
H	2.6290590	0.2687660 -1.4081080
C	1.4126760	1.0519050 0.1282470
C	0.8313370	2.1594600 -0.7365040
H	-0.2476540	2.2259870 -0.5591040
H	1.2584990	1.1601240 1.1962360
Cl	-0.2804220	-0.6748720 -0.3578210
N	-1.7415300	-1.8426890 -0.6698720
C	-3.0299030	-1.5339690 -0.3440030
C	-1.5948840	-3.0997180 -1.2613000
C	-3.9305470	-2.6928160 -0.7353360
C	-2.9787460	-3.7310010 -1.3516370
H	-4.4456250	-3.0559920 0.1588480
H	-2.9678620	-4.6819150 -0.8121960
H	-3.1972920	-3.9473700 -2.4009530
H	-4.6932290	-2.3277820 -1.4288260
O	-0.5371680	-3.5770760 -1.6297210
O	-3.3781910	-0.4715290 0.1866930
C	1.9305190	-1.2417980 2.3917860
H	2.1311490	-1.6632810 3.3799310
H	1.2650980	-0.3889660 2.5171320
H	1.4268290	-1.9971680 1.7839970
H	3.7189960	-0.0231740 2.3553590
C	5.6337740	-0.3312190 -0.7216980
H	4.0126390	-1.6900540 -1.2831520
C	6.7020710	-1.1901250 -1.4357510
H	7.4936410	-0.5365650 -1.8155420
H	7.1738590	-1.9127300 -0.7673170
H	6.2822170	-1.7306060 -2.2919510
C	5.2093590	0.7844970 -1.6996710
H	4.7142980	0.3819690 -2.5912450
H	4.5491620	1.5202220 -1.2336770
H	6.1016010	1.3219240 -2.0363850
C	6.2432420	0.3078930 0.5393680
H	6.5846220	-0.4464230 1.2553320
H	7.1115210	0.9137530 0.2606720
H	5.5305390	0.9698650 1.0418080
H	-4.8350680	-0.0901000 0.5245130
O	-5.7464270	0.2488840 0.8492910
C	-6.6711790	0.1597230 -0.0754620
O	-6.5650670	-0.2636830 -1.2076310
C	-8.0293330	0.6888240 0.4640650
F	-7.9277010	1.9818730 0.8455330
F	-8.9878780	0.6069150 -0.4714170
F	-8.4328190	-0.0265920 1.5383770
H	0.9639280	1.9087710 -1.7946990
C	1.4610620	3.5154190 -0.4492710
C	1.0409270	4.2777710 0.6524450
C	2.4806960	4.0282750 -1.2652020
C	1.6300410	5.5129400 0.9379380
H	0.2432920	3.9033180 1.2899060
C	3.0712420	5.2651350 -0.9857490
H	2.8120050	3.4587940 -2.1300990
C	2.6496010	6.0110580 0.1193690

H 1.2893030 6.0881620 1.7943710
H 3.8561480 5.6461990 -1.6331910
H 3.1057850 6.9723950 0.3371990

1.log
Potential Energy = -2233.46286
Zero-point Energy = -2232.93195
Free Energy = -2232.98172
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.03590
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.55476
Nimag = 1 (-208.1776 cm⁻¹)
Charge = 0 Multiplicity = 1
C -2.5843210 2.0334160 -0.0069720
C -2.5821120 2.5607910 2.2868460
C -2.9226860 1.0687680 2.2118540
N -2.6792770 0.7813400 0.7849360
N -2.2926970 3.0084830 1.0447690
O -2.5153950 3.2209110 3.3252550
C -1.6792330 4.3152890 0.8303970
H -0.9761600 4.5035220 1.6446230
H -1.1397020 4.3095740 -0.1170140
H -2.4189970 5.1208750 0.8192480
C -2.5630360 -0.4230960 0.1879840
H -2.3267310 -0.3555180 -0.8693490
C -2.6692240 -1.6897150 0.7303460
C -2.8922710 -2.9393700 -0.1178430
H -3.9416150 -3.2358450 0.0160930
H -2.2973280 -3.7579180 0.3039740
H -2.9952970 -1.7976610 1.7587640
Cl -0.2520810 -1.8798750 1.1905940
N 1.5513880 -2.2587060 1.6481990
C 2.6188000 -1.6692550 1.0362110
C 1.9049880 -3.1703490 2.6453420
C 3.9000400 -2.2080000 1.6505560
C 3.4264490 -3.2051660 2.7207260
H 4.5025060 -2.6702330 0.8633460
H 3.7642430 -4.2286750 2.5370690
H 3.7345250 -2.9305870 3.7332170
H 4.4748000 -1.3725400 2.0602810
O 1.1153750 -3.8083350 3.3175690
O 2.5275850 -0.8339820 0.1278520
C -2.0603430 0.3214770 3.2367250
H -2.2023060 0.8174120 4.2002270
H -2.3512480 -0.7220030 3.3484030
H -1.0018550 0.3678790 2.9713090
H -3.9842900 0.9200160 2.4527850
C -3.8714370 2.3799110 -0.8479500
H -1.7298120 1.9615550 -0.6907740
C -3.6289030 3.6975600 -1.6186960
H -4.4587680 3.8663240 -2.3122130
H -3.5782470 4.5658450 -0.9591060
H -2.7076790 3.6564890 -2.2112410
C -4.1427160 1.2779420 -1.8923940
H -3.2698630 1.0921420 -2.5288510
H -4.4473190 0.3336240 -1.4346820
H -4.9611960 1.5982860 -2.5449750
C -5.1071610 2.5315110 0.0578000
H -4.9729910 3.3200200 0.8050030
H -5.9768250 2.7998270 -0.5507730
H -5.3463260 1.5966220 0.5748700
C -2.6136960 -2.8280040 -1.6052570
C -1.3214530 -3.0148390 -2.1226900
C -3.6573260 -2.5612420 -2.5055500
C -1.0783870 -2.9285620 -3.4968680
H -0.5017090 -3.2334570 -1.4449150
C -3.4197890 -2.4745670 -3.8810220
H -4.6676110 -2.4273490 -2.1262930
C -2.1270880 -2.6566040 -4.3816850
H -0.0715910 -3.0803170 -3.8759670
H -4.2439610 -2.2709350 -4.5589300
H -1.9397790 -2.5938870 -5.4497600
H 3.7252460 -0.1400000 -0.5623340
O 4.4610530 0.2905460 -1.1300920
C 4.9584850 1.3695140 -0.5751840

O 4.6588170 1.8799650 0.4834820
C 6.0608560 1.9834860 -1.4829980
F 5.5526130 2.3384090 -2.6849450
F 6.5979500 3.0775880 -0.9214390
F 7.0569140 1.0960850 -1.7034010

2.log
Potential Energy = -2233.46590
Zero-point Energy = -2232.93524
Free Energy = -2232.98560
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.03546
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.55515
Nimag = 1 (-185.9689 cm⁻¹)
Charge = 0 Multiplicity = 1
C 1.1550040 2.5438430 -0.1961330
C 1.1257300 2.5353320 -2.5514090
C 1.9157310 1.2859100 -2.1508830
N 1.7031090 1.2563890 -0.6916680
N 0.6377590 3.1238870 -1.4363430
O 0.9132840 2.8975160 -3.7098390
C -0.3733170 4.1740460 -1.5130640
H -1.0466950 3.9435480 -2.3413940
H -0.9418950 4.1971180 -0.5830920
H 0.0685050 5.1587110 -1.6903890
C 1.9468610 0.2363010 0.1548110
H 1.6268760 0.4394610 1.1728580
C 2.5004900 -1.0065790 -0.0910560
C 3.0186490 -1.8631180 1.0535660
H 2.8174920 -2.9175410 0.8346830
H 2.9203470 -1.2230150 -1.0672810
Cl 0.2988060 -2.0946630 -0.3529930
N -1.2685800 -3.1352170 -0.5747340
C -2.5225670 -2.6556310 -0.3303050
C -1.2456090 -4.4630630 -1.0074390
C -3.5346300 -3.7533900 -0.6130270
C -2.6868230 -4.9547350 -1.0628520
H -4.1110470 -3.9457640 0.2964570
H -2.7872550 -5.8237760 -0.4070710
H -2.9076240 -5.2813390 -2.0826450
H -4.2324250 -3.4033420 -1.3791750
O -0.2380800 -5.0880710 -1.2836680
O -2.7642770 -1.5065780 0.0593500
C 1.3813730 0.0923370 -2.9532330
H 1.4027480 0.3750300 -4.0086370
H 1.9912110 -0.8015520 -2.8306620
H 0.3513360 -0.1408250 -2.6730860
H 2.9803720 1.4331080 -2.3783190
C 2.2033630 3.4598250 0.5424720
H 0.3246230 2.3398660 0.4909430
C 1.5043010 4.7616870 0.9956500
H 2.1871170 5.3332990 1.6321030
H 1.2313800 5.4045040 0.1567530
H 0.6025130 4.5544300 1.5832880
C 2.7321820 2.7561120 1.8098590
H 1.9175180 2.4371210 2.4706860
H 3.3560720 1.8893740 1.5779840
H 3.3547070 3.4580500 2.3737410
C 3.3889610 3.8027930 -0.3777710
H 3.0654450 4.3278510 -1.2821160
H 4.0869710 4.4592030 0.1518880
H 3.9434930 2.9063340 -0.6734900
H -4.1784070 -0.9384690 0.3313930
O -5.1271040 -0.5877290 0.4899330
C -5.1431090 0.6237500 0.9918000
O -4.2037510 1.3355620 1.2774030
C -6.6082680 1.1002110 1.1996930
F -7.2758880 0.2675640 2.0297900
F -6.6469250 2.3322560 1.7303120
F -7.2760790 1.1316240 0.0240190
H 2.4726570 -1.6196800 1.9716140
C 4.5128930 -1.6862680 1.2851020
C 5.4439310 -2.3632170 0.4811630
C 4.9946960 -0.8372640 2.2928140
C 6.8179160 -2.1887530 0.6707070

H	5.0904430	-3.0355870	-0.2971710
C	6.3685420	-0.6616950	2.4887330
H	4.2900800	-0.3135260	2.9341820
C	7.2856690	-1.3350670	1.6757450
H	7.5218790	-2.7231750	0.0388150
H	6.7206250	-0.0031010	3.2778920
H	8.3528570	-1.2012630	1.8271800

3.log
Potential Energy = -2233.46576
Zero-point Energy = -2232.93514
Free Energy = -2232.98568
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.03546
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.55538
Nimag = 1 (-187.8362 cm⁻¹)
Charge = 0 Multiplicity = 1

C	4.4464930	-1.0152420	-0.1966280
C	4.1597430	-1.7940070	2.0074730
C	3.1261750	-0.6768850	1.8335430
N	3.2267720	-0.4036630	0.3875120
N	4.7781540	-2.0094900	0.8247140
O	4.3411700	-2.4359480	3.0433880
C	5.6182820	-3.1836730	0.6097270
H	5.1745910	-4.0273070	1.1427910
H	5.6557330	-3.4108060	-0.4559130
H	6.6357560	-3.0353770	0.9825940
C	2.3687880	0.2953190	-0.3815640
H	2.6300630	0.2784630	-1.4358770
C	1.2201730	0.9818870	-0.0329070
C	0.6052800	1.9941870	-0.9867860
H	-0.4863310	1.9471690	-0.9079840
H	0.9682880	1.1096700	1.0141720
Cl	-0.2551720	-0.9209390	-0.5682280
N	-1.5698980	-2.2390650	-0.9273380
C	-2.9075660	-2.0258560	-0.7632520
C	-1.2532330	-3.5244110	-1.3728410
C	-3.6586610	-3.2952840	-1.1285110
C	-2.5601990	-4.2901470	-1.5383050
H	-4.2395920	-3.6241490	-0.2620530
H	-2.5275460	-5.1819940	-0.9068170
H	-2.6437960	-4.6217270	-2.5768330
H	-4.3638460	-3.0717510	-1.9340400
O	-0.1249520	-3.9303670	-1.5837000
O	-3.3998050	-0.9587480	-0.3762060
C	1.7725230	-1.1780960	2.3527030
H	1.9323270	-1.5507290	3.3675630
H	1.0228890	-0.3894310	2.3967100
H	1.3914470	-1.9946330	1.7349610
H	3.4353170	0.2053850	2.4103920
C	5.6126400	0.0032540	-0.4905470
H	4.1805260	-1.5217010	-1.1326220
C	6.8136650	-0.7654060	-1.0868190
H	7.5669710	-0.0478140	-1.4267920
H	7.2965910	-1.4187340	-0.3577940
H	6.5189470	-1.3688500	-1.9532210
C	5.1654380	1.0444200	-1.5379240
H	4.7891360	0.5703400	-2.4521180
H	4.3997230	1.7224300	-1.1529360
H	6.0262130	1.6593060	-1.8194140
C	6.0506070	0.7332320	0.7922340
H	6.3995240	0.0358240	1.5604050
H	6.8785530	1.4121700	0.5637490
H	5.2387360	1.3368740	1.2107390
H	-4.9137670	-0.7098520	-0.1767190
O	-5.9234920	-0.5798290	-0.0655270
C	-6.2302190	0.5680890	0.4895910
O	-5.4857500	1.4496420	0.8627270
C	-7.7722620	0.6986960	0.6370740
F	-8.2683760	-0.2919220	1.4127230
F	-8.1085570	1.8707090	1.1975300
F	-8.3820570	0.6222920	-0.5674100
H	0.8607640	1.7293050	-2.0187010
C	1.0569840	3.4189250	-0.6979660
C	0.4505920	4.1655720	0.3248260

C	2.0927220	4.0139740	-1.4338960
C	0.8739670	5.4665080	0.6121500
H	-0.3626610	3.7266330	0.8981920
C	2.5179640	5.3165050	-1.1525170
H	2.5666810	3.4566290	-2.2381800
C	1.9113590	6.0468850	-0.1257880
H	0.3901700	6.0281840	1.4064410
H	3.3185940	5.7604550	-1.7376660
H	2.2387390	7.0591250	0.0931640

4.log
Potential Energy = -2233.46324
Zero-point Energy = -2232.93284
Free Energy = -2232.98280
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.03401
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.55357
Nimag = 1 (-191.0590 cm⁻¹)
Charge = 0 Multiplicity = 1

C	2.7482410	-2.6180430	-0.2848630
C	3.7041980	-2.3771060	1.8540380
C	3.7316070	-0.9763590	1.2348760
N	2.9300200	-1.1777050	0.0152660
N	3.0525600	-3.2153350	1.0165620
O	4.1449640	-2.6691520	2.9672500
C	2.6345370	-4.5460280	1.4466470
H	2.3305730	-4.4904010	2.4941710
H	1.7867580	-4.8711580	0.8430460
H	3.4412020	-5.2794570	1.3591740
C	2.4100290	-0.2314630	-0.7964080
H	1.7922580	-0.6451400	-1.5884270
C	2.5333960	1.1415800	-0.7538350
C	2.1981110	1.9686980	-1.9878030
H	3.0459210	1.8987310	-2.6865470
H	3.2059760	1.6008030	-0.0377060
Cl	0.3671970	1.3204150	0.5078240
N	-1.2326160	1.6623610	1.4310920
C	-2.4430780	1.1719230	1.0322090
C	-1.2949690	2.4619560	2.5765930
C	-3.5121470	1.6578560	1.9954380
C	-2.7514410	2.5169520	3.0188700
H	-4.2661930	2.2172640	1.4343950
H	-3.0748880	3.5612930	3.0304010
H	-2.8231710	2.1359260	4.0410930
H	-4.0070280	0.7899370	2.4404450
O	-0.3391140	3.0027020	3.1003010
O	-2.6087930	0.4504630	0.0416160
C	3.1886800	0.0258350	2.2613620
H	3.7609780	-0.1083300	3.1826870
H	3.3054960	1.0593670	1.9382250
H	2.1331620	-0.1602640	2.4733150
H	4.7653330	-0.7080560	0.9753490
C	3.6506520	-3.1628360	-1.4573100
H	1.6972870	-2.8034440	-0.5397170
C	3.3711660	-4.6705940	-1.6502170
H	3.8823500	-5.0190010	-2.5532010
H	3.7395720	-5.2737390	-0.8182510
H	2.3013870	-4.8718410	-1.7787070
C	3.2974500	-2.4549470	-2.7828370
H	2.2276710	-2.5249990	-3.0125440
H	3.5882100	-1.4011290	-2.7852250
H	3.8397140	-2.9396470	-3.6009230
C	5.1450860	-2.9500670	-1.1548410
H	5.4510650	-3.4549120	-0.2330110
H	5.7471990	-3.3621590	-1.9711520
H	5.3926390	-1.8870210	-1.0699430
H	-3.9702520	-0.1166810	-0.4368190
O	-4.8293780	-0.4536870	-0.8790290
C	-5.3609860	-1.4665390	-0.2375030
O	-4.9623690	-2.0147840	0.7682570
C	-6.6590940	-1.9359790	-0.9519220
F	-6.3930190	-2.3483900	-2.2120680
F	-7.2323130	-2.9558890	-0.2947760
F	-7.5600310	-0.9308570	-1.0296960
H	1.3387970	1.5301490	-2.5064820

C	1.9380230	3.4407040	-1.7215850
C	2.9676750	4.2724910	-1.2521120
C	0.6805980	4.0116760	-1.9638870
C	2.7439520	5.6322270	-1.0187430
H	3.9560760	3.8557740	-1.0726900
C	0.4522790	5.3734220	-1.7372730
H	-0.1284130	3.3859240	-2.3317980
C	1.4829300	6.1885990	-1.2605400
H	3.5546800	6.2574440	-0.6550540
H	-0.5299680	5.7947640	-1.9327560
H	1.3079480	7.2458350	-1.0832060

5.log

Potential Energy = -2233.46325

Zero-point Energy = -2232.93305

Free Energy = -2232.98350

Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.03446

Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.55471

Nimag = 1 (-192.4734 cm⁻¹)

Charge = 0 Multiplicity = 1

C	3.0240340	-2.4589160	-0.3299190
C	3.9688390	-2.1618410	1.8070340
C	3.8716210	-0.7566610	1.2051170
N	3.0819700	-1.0117790	-0.0125360
N	3.3886730	-3.0434540	0.9616540
O	4.4378100	-2.4280400	2.9151470
C	3.0843850	-4.4085310	1.3793450
H	2.7845240	-4.3890550	2.4293380
H	2.2616990	-4.7952890	0.7773280
H	3.9476070	-5.0724950	1.2785430
C	2.4749780	-0.1047690	-0.8081680
H	1.8917740	-0.5611110	-1.6028200
C	2.4751760	1.2733500	-0.7468860
C	2.0627920	2.0837810	-1.9684920
H	3.1079820	1.7807880	-0.0271300
Cl	0.3100390	1.2414760	0.5219470
N	-1.3102800	1.4304960	1.4563660
C	-2.4990500	0.9403130	0.9970680
C	-1.4094610	2.1007770	2.6795350
C	-3.5938470	1.2956010	1.9873310
C	-2.8673000	2.0434650	3.1172000
H	-4.3412350	1.9096840	1.4759300
H	-3.2317010	3.0630980	3.2672990
H	-2.9223560	1.5263820	4.0792770
H	-4.0891490	0.3765510	2.3120920
O	-0.4782150	2.6218460	3.2642610
O	-2.6306750	0.3131540	-0.0610720
C	3.2513650	0.1824790	2.2472200
H	3.8399840	0.0880160	3.1631390
H	3.2754840	1.2260390	1.9363830
H	2.2177050	-0.0972000	2.4638250
H	4.8765570	-0.3972630	0.9426370
C	3.9615610	-2.9077970	-1.5151870
H	1.9913670	-2.7324860	-0.5800500
C	3.8229110	-4.4335460	-1.7191010
H	4.3586330	-4.7251110	-2.6279600
H	4.2519770	-5.0057860	-0.8943960
H	2.7761220	-4.7339270	-1.8434920
C	3.5299760	-2.2253750	-2.8308700
H	2.4686220	-2.3922540	-3.0496840
H	3.7220630	-1.1491910	-2.8272930
H	4.1053450	-2.6515100	-3.6588790
C	5.4325400	-2.5588480	-1.2243060
H	5.7923800	-3.0389380	-0.3087280
H	6.0628250	-2.9082650	-2.0485600
H	5.5810580	-1.4779210	-1.1341860
H	-3.9517100	-0.3173870	-0.5603260
O	-4.7675720	-0.7318900	-1.0204680
C	-5.4597600	-1.4981270	-0.2126430
O	-5.2480540	-1.7443010	0.9564440
C	-6.6793690	-2.1083080	-0.9580010
F	-6.2781240	-2.8496300	-2.0150780
F	-7.3975520	-2.8991350	-0.1461040

F	-7.4959960	-1.1361550	-1.4232820
H	1.2478990	1.5743570	-2.4940640
H	2.9129550	2.1037150	-2.6676370
C	1.6651750	3.5207770	-1.6813560
C	2.6091430	4.4380000	-1.1913860
C	0.3612160	3.9749810	-1.9247590
C	2.2568990	5.7667840	-0.9388730
H	3.6313940	4.1136210	-1.0108790
C	0.0042170	5.3053420	-1.6788510
H	-0.3827560	3.2817060	-2.3085700
C	0.9505990	6.2059530	-1.1815580
H	3.0028770	6.4595910	-0.5594380
H	-1.0121270	5.6354840	-1.8753660
H	0.6758430	7.2390510	-0.9891160

6.log

Potential Energy = -2233.46284

Zero-point Energy = -2232.93211

Free Energy = -2232.98229

Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.03622

Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.55567

Nimag = 1 (-207.1104 cm⁻¹)

Charge = 0 Multiplicity = 1

C	-4.5370210	0.5806250	-0.2161190
C	-4.3850850	2.6059480	0.9738200
C	-3.3864980	1.6602270	1.6496020
N	-3.3821360	0.5179380	0.7148350
N	-4.9022520	1.9941700	-0.1147890
O	-4.6202250	3.7614740	1.3316000
C	-5.6803100	2.7323980	-1.1046720
H	-5.2479700	3.7299140	-1.2087040
H	-5.6281780	2.2158300	-2.0633490
H	-6.7279420	2.8388700	-0.8087330
C	-2.4974600	-0.4981730	0.6474160
H	-2.6917500	-1.1810390	-0.1737470
C	-1.3936440	-0.7614400	1.4366790
C	-0.7187530	-2.1300910	1.4877250
H	-1.0037260	-2.5934410	2.4421410
H	-1.2208210	-0.1577910	2.3205380
Cl	0.1589790	0.4505080	-0.0441080
N	1.5399860	1.3187960	-1.0215580
C	2.8553220	1.2623780	-0.6647980
C	1.3013350	2.0630690	-2.1789610
C	3.6748750	2.0596600	-1.6648930
C	2.6437190	2.5857550	-2.6765170
H	4.2026970	2.8559760	-1.1317700
H	2.6011800	3.6772480	-2.7231760
H	2.8086910	2.2163120	-3.6923490
H	4.4291990	1.4021720	-2.1059600
O	0.2055080	2.2428460	-2.6785280
O	3.2823120	0.6514370	0.3234370
C	-2.0637210	2.4100310	1.8511180
H	-2.2981080	3.3438340	2.3683290
H	-1.3561540	1.8540120	2.4645940
H	-1.5934290	2.6476090	0.8944320
H	-3.7792060	1.3481860	2.6271320
C	-5.7183460	-0.4026530	0.1332750
H	-4.1895410	0.3620570	-1.2331750
C	-6.8369400	-0.2393130	-0.9208270
H	-7.5930240	-1.0154690	-0.7657680
H	-7.3447550	0.7242160	-0.8484630
H	-6.4516150	-0.3538390	-1.9405890
C	-5.2360490	-1.8662740	0.0698540
H	-4.7749690	-2.1051210	-0.8954000
H	-4.5259800	-2.1077260	0.8645410
H	-6.0967780	-2.5311650	0.1941410
C	-6.2851580	-0.1192610	1.5364320
H	-6.6611270	0.9046980	1.6271940
H	-7.1221630	-0.7959530	1.7369040
H	-5.5356850	-0.2870820	2.3166990
H	4.7672430	0.5084410	0.7098470
O	5.7070170	0.3854460	1.1014800
C	6.5692750	-0.0352380	0.2084280
O	6.3812850	-0.2711270	-0.9669480

C	7.9720400	-0.2146700	0.8532430
F	7.9277630	-1.1092020	1.8660250
F	8.8673960	-0.6510230	-0.0459710
F	8.4241260	0.9558330	1.3575830
H	0.3660390	-1.9820140	1.5428060
C	-1.0388870	-3.1045560	0.3694880
C	-2.0358450	-4.0781700	0.5397390
C	-0.3353370	-3.0796600	-0.8458530
C	-2.3301070	-4.9953520	-0.4741680
H	-2.5823290	-4.1233130	1.4787520
C	-0.6262090	-3.9937440	-1.8630840
H	0.4484200	-2.3428250	-0.9938370
C	-1.6263670	-4.9546880	-1.6816110
H	-3.1032110	-5.7424730	-0.3179390
H	-0.0668930	-3.9590550	-2.7938550
H	-1.8496500	-5.6679510	-2.4697800

(S)-TS-back

Conformation name	Extrapolated Free energy (kcal/mol)	
TS4-Sb-lowest	0.0	
1	1.9	
2	2.4	
3	1.5	
TS4-Sb-lowest.log		
Potential Energy = -2233.46543		
Zero-point Energy = -2232.93478		
Free Energy = -2232.98492		
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.03911		
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.55860		
Nimag = 1 (-192.3533 cm ⁻¹)		
Charge = 0 Multiplicity = 1		
C	-2.3955980	2.4865830
C	-1.3161090	3.9298080
C	-1.2860590	2.5499090
N	-2.1288780	1.7612910
N	-2.0238940	3.8527700
O	-0.8334860	4.9563420
C	-2.4697650	5.0583040
H	-2.7242770	5.8123630
H	-3.3540380	4.8277010
H	-1.6940600	5.4670470
C	-2.6982290	0.5677980
H	-3.4593230	0.2822410
C	-2.4136100	-0.3207910
C	-3.3688660	-1.4401540
H	-2.7750740	-2.3116890
H	-0.2561020	2.1688400
C	-1.6181800	1.9288640
H	-3.4712880	2.4454240
H	-1.7252400	-0.0240820
Cl	-0.5771380	-1.4955010
N	0.8929820	-2.5142660
C	0.7425780	-3.7398220
C	2.1919690	-2.1242340
C	2.1351470	-4.2464640
C	3.0981290	-3.1802700
H	2.2779830	-5.2318660
H	3.7653410	-3.5609750
H	3.7209060	-2.7119440
H	2.1967860	-4.3666180
O	2.5456680	-1.0728230
O	-0.3237020	-4.2799460
C	-1.8059920	2.6823530
H	-1.6431490	1.7826820
H	-2.8734920	2.9219470
H	-1.2611350	3.5017680
C	-1.9164000	2.8175840

H	-1.5008290	2.3426200
H	-1.4632770	3.8076220
H	-2.9936040	2.9385930
C	-0.1014040	1.9016520
H	0.2899430	2.9004980
H	0.4181270	1.5335870
H	0.1539060	1.2348940
C	-2.1151350	0.5056540
H	-3.2025610	0.4795630
H	-1.8424520	-0.2235510
H	-1.6569250	0.1761380
H	-3.9018680	-1.1174210
C	-4.3904750	-1.8564790
C	-4.0747600	-2.8023100
C	-5.6822120	-1.3067430
C	-5.0226080	-3.1852910
H	-3.0818570	-3.2424330
C	-6.6331480	-1.6858910
H	-5.9475790	-0.5794590
C	-6.3053450	-2.6274690
H	-4.7601950	-3.9226330
H	-7.6281580	-1.2505360
H	-7.0428310	-2.9275640
H	3.9990760	-0.5681260
O	4.9180340	-0.1483500
C	5.6569310	-0.0982780
C	7.0254430	0.5709370
O	5.3852560	-0.4903180
F	7.8150200	0.5823730
F	6.8529280	1.8500810
F	7.6781810	-0.0869450

1.log		
Potential Energy = -2233.46774		
Zero-point Energy = -2232.93705		
Free Energy = -2232.98699		
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.03861		
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.55785		
Nimag = 1 (-170.9527 cm ⁻¹)		
Charge = 0 Multiplicity = 1		
C	-1.8852200	2.5765870
C	-1.6050980	3.4927530
C	-1.7219820	1.9825740
N	-2.0737010	1.5139850
N	-1.8021620	3.7677550
O	-1.4330760	4.3241830
C	-2.0397650	5.1348930
H	-2.6154150	5.6576070
H	-2.6116760	5.1133230
H	-1.1071300	5.6813010
C	-2.5947170	0.3140520
H	-2.9837310	0.2655960
C	-2.6634770	-0.8381500
C	-3.5960680	-1.9682770
H	-3.1347190	-2.9264490
H	-3.7266590	-1.9634870
H	-0.7490840	1.5789840
C	-0.6397750	2.3701280
H	-2.7852940	2.6346200
H	-2.3684890	-0.8105830
Cl	-0.4914990	-1.7713120
N	1.1433030	-2.6604090
C	1.2343040	-3.7956370
C	2.3398460	-2.2527310
C	2.6986370	-4.2143880
C	3.4309800	-3.1925460
H	2.7816030	-5.2413450
H	3.9168140	-3.6434890
H	4.1864690	-2.6093790
H	3.0356890	-4.2044890
O	2.4807750	-1.2711490
O	0.2938900	-4.3296240
C	-2.7691030	1.7212200
H	-2.7769410	0.6859380

H	-3.7704130	1.9870800	-1.9020550
H	-2.5189640	2.3535250	-3.1087340
C	-0.5152300	3.5760430	3.1088980
H	0.2554950	3.3609310	3.8557500
H	-0.2184550	4.4914940	2.5936030
H	-1.4506650	3.7656820	3.6478240
C	0.6539950	2.2288520	1.3294870
H	0.8418580	3.1151560	0.7145770
H	1.5077400	2.1098680	2.0045940
H	0.6250290	1.3502440	0.6780460
C	-0.8430240	1.1121050	3.0219520
H	-1.7850350	1.1552800	3.5817080
H	-0.8234560	0.1894140	2.4390320
H	-0.0306970	1.0488280	3.7532240
C	-4.9566250	-1.8776400	-0.5279670
C	-5.9989950	-1.1307930	0.0428020
C	-5.1909250	-2.5242280	-1.7509510
C	-7.2401440	-1.0282070	-0.5922030
H	-5.8401480	-0.6286430	0.9943030
C	-6.4299140	-2.4222110	-2.3922330
H	-4.3982050	-3.1155290	-2.2033820
C	-7.4594630	-1.6724840	-1.8148050
H	-8.0358860	-0.4496980	-0.1310780
H	-6.5913500	-2.9319140	-3.3380830
H	-8.4236650	-1.5950280	-2.3088320
H	3.8312090	-0.7171300	-1.0224150
O	4.6511420	-0.2855950	-1.4591250
C	5.6108760	-0.0562610	-0.5959110
O	5.6263960	-0.2971460	0.5932020
C	6.8261200	0.6091770	-1.3000530
F	6.4792470	1.8029400	-1.8322250
F	7.8319400	0.8172670	-0.4364790
F	7.2913840	-0.1689930	-2.3028370

2.log
Potential Energy = -2233.46485
Zero-point Energy = -2232.93457
Free Energy = -2232.98474
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.03723
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.55711
Nimag = 1 (-171.8028 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-2.7058680	3.0154530	0.6276940
C	-1.8811130	3.7965180	-1.4413000
C	-1.9170200	2.2731130	-1.5712490
N	-2.5903330	1.8808380	-0.3214810
N	-2.4226090	4.1501540	-0.2540050
O	-1.4918530	4.5736960	-2.3151280
C	-2.8014910	5.5340440	0.0175810
H	-3.1744500	5.9778370	-0.9081480
H	-3.5909720	5.5517160	0.7690210
H	-1.9556600	6.1303670	0.3706090
C	-3.1477100	0.6794350	-0.0599520
H	-3.7954200	0.6824560	0.8139220
C	-2.9881560	-0.5168990	-0.7311370
C	-3.9937280	-1.6392060	-0.5170510
H	-4.3015620	-1.6611780	0.5344890
H	-4.9005250	-1.4058200	-1.0957840
H	-0.8917990	1.8807690	-1.6040410
C	-1.7561670	2.9254220	1.8793070
H	-3.7422300	3.0792560	0.9854010
H	-2.4203300	-0.5450690	-1.6532300
Cl	-0.9680190	-1.2229210	0.5375410
N	0.5877030	-1.8890280	1.3528590
C	0.5680300	-2.6744550	2.5094870
C	1.8414160	-1.6568590	0.8628440
C	2.0112280	-3.0218040	2.8517570
C	2.8541230	-2.3588540	1.7498760
H	2.1140180	-4.1098580	2.8798160
H	3.4118360	-3.0776490	1.1421560
H	3.5678170	-1.6198360	2.1241040
H	2.2346870	-2.6415540	3.8523500
O	2.0785310	-0.9803870	-0.1447560
O	-0.4373480	-3.0010550	3.1121990

C	-2.6569520	1.9112220	-2.8685320
H	-2.5856000	0.8525200	-3.1133250
H	-3.7133950	2.1878530	-2.8005930
H	-2.1985990	2.4779830	-3.6825020
C	-1.9106450	4.2021860	2.7358800
H	-1.3662340	4.0694240	3.6762110
H	-1.4985940	5.0869160	2.2468490
H	-2.9589220	4.3991320	2.9887990
C	-0.2872460	2.7711010	1.4466650
H	0.0463530	3.6185750	0.8386330
H	0.3554040	2.7285790	2.3322150
H	-0.1288030	1.8492440	0.8791010
C	-2.1694420	1.7293900	2.7631340
H	-3.2287440	1.7814810	3.0421000
H	-1.9799080	0.7671060	2.2844990
H	-1.5855070	1.7499860	3.6890280
C	-3.5179310	-3.0181110	-0.9373960
C	-3.2595130	-3.3032360	-2.2880760
C	-3.3525920	-4.0450890	0.0025000
C	-2.8352680	-4.5740310	-2.6861440
H	-3.3964510	-2.5271430	-3.0375770
C	-2.9330340	-5.3206520	-0.3908330
H	-3.5509050	-3.8454600	1.0524250
C	-2.6698580	-5.5891850	-1.7371680
H	-2.6405460	-4.7731820	-3.7363370
H	-2.8118150	-6.1015390	0.3548520
H	-2.3435480	-6.5784020	-2.0450910
H	3.4846340	-0.5998850	-0.6684180
O	4.3475510	-0.3149500	-1.1398130
C	5.2296730	0.1802760	-0.3057800
O	5.1357230	0.3139860	0.8964810
C	6.5119960	0.6143270	-1.0691440
F	6.2277470	1.5668820	-1.9857080
F	7.4326260	1.1102860	-0.2282180
F	7.0642440	-0.4331310	-1.7217370

3.log
Potential Energy = -2233.46543
Zero-point Energy = -2232.93491
Free Energy = -2232.98531
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.03863
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.55852
Nimag = 1 (-190.9753 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-3.7783670	-0.3556430	1.4307710
C	-5.5319040	0.9399670	0.5300570
C	-4.5051520	0.8098680	-0.5974540
N	-3.5493990	-0.1532610	-0.0213310
N	-5.1249230	0.1984310	1.5845880
O	-6.5926070	1.5624790	0.4534660
C	-6.0338280	-0.1106920	2.6850990
H	-7.0376160	-0.2451630	2.2761610
H	-5.7147660	-1.0342610	3.1686120
H	-6.0673800	0.6908200	3.4281010
C	-2.6275470	-0.8701160	-0.6939810
H	-2.2022530	-1.6857150	-0.1159730
C	-2.1528860	-0.6753540	-1.9787980
C	-1.4118530	-1.7614940	-2.7501900
H	-0.6387170	-1.2846260	-3.3636260
H	-4.0239930	1.7817560	-0.7703030
C	-2.6997920	0.3124040	2.3611140
H	-3.7988860	-1.4326750	1.6424910
H	-2.6187670	0.0754620	-2.6051770
Cl	-0.4011950	0.9407510	-1.4227980
N	0.9772170	2.2364860	-1.2374980
C	0.8642230	3.5373580	-1.7327390
C	2.1701300	1.9802970	-0.6268790
C	2.1590610	4.2706300	-1.4038050
C	3.0278930	3.2339150	-0.6726880
H	1.9214550	5.1439270	-0.7902370
H	3.2836630	3.5254180	0.3499950
H	3.9611830	3.0048060	-1.1949460
H	2.6063740	4.6305030	-2.3342530
O	2.4761440	0.8917700	-0.1247690

O	-0.1084200	3.9782560	-2.3174940
C	-5.2299520	0.3521020	-1.8721190
H	-4.6024440	0.4139090	-2.7601200
H	-5.5919560	-0.6746850	-1.7645910
H	-6.0885930	1.0116550	-2.0192300
C	-3.1023040	0.1129540	3.8393230
H	-2.2786010	0.4406840	4.4814040
H	-3.9804640	0.6996030	4.1160260
H	-3.2992310	-0.9403820	4.0697430
C	-2.5681550	1.8168630	2.0633320
H	-3.5159530	2.3440500	2.2147610
H	-1.8323550	2.2628540	2.7405690
H	-2.2260370	1.9974810	1.0397390
C	-1.3360180	-0.3805600	2.1575160
H	-1.4063050	-1.4636370	2.3134640
H	-0.9142000	-0.1963460	1.1678360
H	-0.6227200	0.0103330	2.8903460
H	-2.1220120	-2.2089050	-3.4596270
C	-0.7897640	-2.8703940	-1.9232950
C	0.5001350	-2.7376310	-1.3852320
C	-1.4921620	-4.0621650	-1.6839380
C	1.0703550	-3.7643510	-0.6263500
H	1.0619400	-1.8253880	-1.5642640
C	-0.9266890	-5.0917320	-0.9247800
H	-2.4887120	-4.1871040	-2.1011280
C	0.3581460	-4.9453350	-0.3924520
H	2.0718800	-3.6435580	-0.2230510
H	-1.4865550	-6.0071890	-0.7550620
H	0.8019860	-5.7448710	0.1936970
H	3.8284510	0.5742090	0.5543120
O	4.6564440	0.3192020	1.1008010
C	5.6489640	-0.0924380	0.3491570
C	6.8745280	-0.4633750	1.2304460
O	5.6885440	-0.1951230	-0.8587350
F	7.8968810	-0.9020480	0.4800070
F	6.5590760	-1.4359020	2.1151410
F	7.3038690	0.6090100	1.9340450

(R)-TS-back

Conformation name	Extrapolated Free energy (kcal/mol)
TS4-Rb-lowest	0.0
1	0.6
2	0.9
3	1.7

TS4-Rb-lowest.log
Potential Energy = -2233.46612
Zero-point Energy = -2232.93524
Free Energy = -2232.98573
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.03577
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.55538
Nimag = 1 (-203.2629 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-3.3008510	-1.1285990	-1.2914060
C	-5.2086170	-2.0593700	-0.2577480
C	-4.1217700	-1.9819430	0.8201900
N	-3.1343610	-1.0759070	0.1821480
N	-4.7156180	-1.5244490	-1.3974470
O	-6.3450400	-2.5092930	-0.0981590
C	-5.5671230	-1.2645690	-2.5540690
H	-6.5544980	-0.9647180	-2.1962530
H	-5.1374910	-0.4550950	-3.1452800
H	-5.6812330	-2.1493110	-3.1868930
C	-2.6007950	-0.0235120	0.8367350
H	-2.8642470	0.0193710	1.8887950
C	-1.7481330	0.9609320	0.3653790
C	-1.6451990	2.2967620	1.0842670

H	-0.6224410	2.6771120
H	-1.8405000	2.1532950
H	-1.4573530	0.9631370
C	-4.6837830	-1.5467210
H	-5.4704360	-2.2546630
H	-3.9230020	-1.5757000
H	-5.1247410	-0.5465510
H	-3.6774990	-2.9784400
C	-2.3083690	-2.0806760
H	-3.1822950	-0.1150950
Cl	0.2191250	-0.0853760
N	1.8748670	-0.6814830
C	3.0460280	-0.6931600
C	2.0030770	-1.1167490
C	4.1566500	-1.2059950
C	3.4657930	-1.4796240
H	4.9438360	-0.4489110
H	3.8555830	-0.8668030
O	1.0907140	-1.1834540
O	3.1564830	-0.3373420
C	-2.6353330	-2.0632550
H	-1.8480350	-2.5959910
H	-3.5803090	-2.5611870
H	-2.6748620	-1.0421860
C	-2.3905470	-3.5283320
H	-1.7435840	-4.1691420
H	-2.0463880	-3.6075500
H	-3.4062130	-3.9316970
C	-0.8708420	-1.5589130
H	-0.7525780	-0.5501000
H	-0.5699240	-1.5440250
H	-0.1769230	-2.2137130
H	3.5248150	-2.5256460
H	4.5919550	-2.1019600
C	-2.6092740	3.3330440
C	-3.9029410	3.4755300
C	-2.2282040	4.1570940
C	-4.7945890	4.4117340
H	-4.2143040	2.8530440
C	-3.1173850	5.0930340
H	-1.2261690	4.0680600
C	-4.4052800	5.2228960
H	-5.7899050	4.5103920
H	-2.8022950	5.7228770
H	-5.0961730	5.9518630
H	4.4803670	-0.2698870
O	5.2819090	-0.2286310
C	6.2986220	0.4182710
O	6.3866630	0.9320900
C	7.4785950	0.4672500
F	7.1144790	1.1043420
F	8.5339270	1.1146620
F	7.8786260	-0.7794740

1.log		
Potential Energy = -2233.46607		
Zero-point Energy = -2232.93504		
Free Energy = -2232.98523		
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.03525		
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.55440		
Nimag = 1 (-203.4857 cm ⁻¹)		
Charge = 0 Multiplicity = 1		
C	-3.2966830	-0.8747570
C	-5.2671500	-1.8516490
C	-4.2042890	-1.9768120
N	-3.1623870	-1.0383910
N	-4.7250260	-1.1838230
O	-6.4252730	-2.2672610
C	-5.5380460	-0.7245360
H	-6.5199940	-0.4353080
H	-5.0623340	0.1411190
H	-5.6745530	-1.5043010
C	-2.5964370	-0.1163530
H	-2.8817150	-0.2110850
		1.8787430

C	-1.6902180	0.8834270	0.5241440
C	-1.5427480	2.0964180	1.4286310
H	-0.4999200	2.4297500	1.4201340
H	-1.7802110	1.8144610	2.4606280
H	-1.3757580	1.0211110	-0.5059020
C	-4.7808620	-1.7061380	1.9009100
H	-5.6070470	-2.4043450	2.0542780
H	-4.0438440	-1.8818010	2.6883500
H	-5.1730670	-0.6889330	1.9904080
H	-3.8075620	-2.9990700	0.4955700
C	-2.3309450	-1.7569920	-2.3051800
H	-3.1223800	0.1777640	-1.6879310
Cl	0.2107420	-0.3895880	1.3914400
N	1.8272150	-1.1668340	2.0423010
C	3.0253380	-1.0405600	1.4036480
C	1.8928980	-1.9135590	3.2202550
C	4.0916980	-1.7750780	2.1995480
C	3.3384310	-2.3597840	3.4054900
H	4.8749340	-1.0651570	2.4807630
H	3.7022210	-1.9841410	4.3656750
O	0.9467860	-2.1509110	3.9492890
O	3.1887520	-0.4207110	0.3446390
C	-2.6253090	-1.5140430	-3.8020210
H	-1.8485390	-1.9980100	-4.4026560
H	-3.5843130	-1.9345840	-4.1126260
H	-2.6161710	-0.4466820	-4.0507910
C	-2.4859500	-3.2576960	-1.9952190
H	-1.8530390	-3.8360900	-2.6761310
H	-2.1690720	-3.4958380	-0.9751580
H	-3.5159770	-3.6015750	-2.1352250
C	-0.8764960	-1.3311820	-2.0320760
H	-0.7070500	-0.2810140	-2.2953210
H	-0.5965620	-1.4771390	-0.9871390
H	-0.2005620	-1.9347580	-2.6464640
H	3.3667690	-3.4521250	3.4440750
H	4.5488310	-2.5370340	1.5618090
C	-2.4337560	3.2529350	0.9959330
C	-3.7549830	3.3593370	1.4577440
C	-1.9556970	4.2293570	0.1089420
C	-4.5782580	4.4096580	1.0416160
H	-4.1424020	2.6175570	2.1522320
C	-2.7764010	5.2806150	-0.3129460
H	-0.9315970	4.1687790	-0.2519420
C	-4.0919720	5.3738660	0.1517850
H	-5.5963000	4.4773530	1.4150740
H	-2.3863410	6.0274770	-0.9988570
H	-4.7299250	6.1914670	-0.1711260
H	4.5374210	-0.2996810	-0.3961310
O	5.3771070	-0.2739740	-0.9838440
C	6.1586870	0.7410680	-0.7049120
O	5.9988500	1.6111220	0.1249910
C	7.4204920	0.7148700	-1.6125220
F	7.0802630	0.7407870	-2.9205090
F	8.2148870	1.7690000	-1.3704050
F	8.1422950	-0.4089450	-1.3974070

2.log
Potential Energy = -2233.46318
Zero-point Energy = -2232.93256
Free Energy = -2232.98266
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.03449
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.55397
Nimag = 1 (-210.8518 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-3.9907910	-1.0164820	-0.9464790
C	-5.9962170	-0.9961520	0.2988210
C	-4.8967050	-0.4768100	1.2316440
N	-3.8000060	-0.1938080	0.2728710
N	-5.4481600	-1.2314190	-0.9144640
O	-7.1820660	-1.1446750	0.6016960
C	-6.2710620	-1.5317320	-2.0820460
H	-7.2012990	-0.9645640	-2.0049490
H	-5.7406850	-1.2308210	-2.9862270
H	-6.5178450	-2.5950880	-2.1486560

C	-3.1225930	0.9763750	0.2865730
H	-3.3782970	1.6223050	1.1205470
C	-2.1483350	1.4337220	-0.5812480
C	-1.8804550	2.9282130	-0.6977060
H	-1.9665750	3.3972020	0.2886820
H	-2.6767860	3.3692440	-1.3159290
H	-1.8572040	0.8248880	-1.4314950
C	-5.3813240	0.6884370	2.0873380
H	-6.2562310	0.3446970	2.6441410
H	-4.6252320	1.0013240	2.8115670
H	-5.6800120	1.5477860	1.4797850
H	-4.5943370	-1.2954310	1.8962330
C	-3.1484230	-2.3382090	-1.0034560
H	-3.7386020	-0.4059480	-1.8205200
Cl	-0.3945840	0.8091800	1.0480730
N	1.0963940	0.4412040	2.1667260
C	2.2361870	-0.1587690	1.7168030
C	1.1354130	0.7803270	3.5209200
C	3.2160670	-0.2890720	2.8699630
C	2.4931070	0.3526750	4.0651710
H	4.1500890	0.2099730	2.5978950
H	3.0069650	1.2356330	4.4553080
O	0.2308090	1.3221250	4.1300980
O	2.4128690	-0.5295290	0.5493110
C	-3.5113930	-3.1202040	-2.2850770
H	-2.8103160	-3.9519850	-2.4074430
H	-4.5162650	-3.5464730	-2.2432580
H	-3.4362230	-2.4924450	-3.1803990
C	-3.3982150	-3.2338310	0.2244330
H	-2.8537900	-4.1760450	0.1036970
H	-3.0394480	-2.7657290	1.1462440
H	-4.4580950	-3.4819180	0.3428780
C	-1.6520550	-1.9807570	-1.0733950
H	-1.4195240	-1.3900360	-1.9667260
H	-1.3223450	-1.4251060	-0.1936990
H	-1.0612600	-2.9009830	-1.1279260
H	2.3380320	-0.3365170	4.8994850
H	3.4407840	-1.3492340	3.0206210
C	-0.5472160	3.2917590	-1.3263400
C	-0.2878870	2.9876050	-2.6727010
C	0.4422450	3.9620320	-0.5933380
C	0.9301090	3.3313990	-3.2657070
H	-1.0468480	2.4831980	-3.2663330
C	1.6614970	4.3129870	-1.1831730
H	0.2587530	4.2103610	0.4487220
C	1.9112960	3.9958640	-2.5214870
H	1.1102180	3.0864770	-4.3087700
H	2.4140640	4.8323390	-0.5963060
H	2.8573500	4.2665490	-2.9813900
H	3.7121550	-1.1494270	-0.0000130
O	4.4927890	-1.6179090	-0.4722120
C	5.6426100	-1.0348500	-0.2361470
O	5.8655410	-0.0605940	0.4520500
C	6.7877000	-1.7725740	-0.9845790
F	6.5838100	-1.7475440	-2.3211420
F	7.9762220	-1.2011600	-0.7363460
F	6.8597750	-3.0678710	-0.6035340

3.log
Potential Energy = -2233.46277
Zero-point Energy = -2232.93196
Free Energy = -2232.98065
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.03485
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.55273
Nimag = 1 (-221.9132 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-3.1584530	-2.2484970	-0.4667830
C	-5.2630690	-1.9280350	0.5547800
C	-4.3275320	-0.8621820	1.1349350
N	-3.1880880	-0.9150100	0.1850450
N	-4.5767060	-2.6375010	-0.3690790
O	-6.4464170	-2.0874420	0.8615140
C	-5.2418430	-3.5903310	-1.2524250
H	-6.2349070	-3.2043230	-1.4928770

H	-4.6645720	-3.6958980	-2.1715000
H	-5.3555390	-4.5729650	-0.7858910
C	-2.6773370	0.2028990	-0.3766570
H	-3.1008660	1.1234910	0.0083110
C	-1.6766090	0.3180890	-1.3254730
C	-1.5293870	1.5430730	-2.2238310
H	-1.8807260	1.2486410	-3.2224600
H	-0.4638230	1.7714490	-2.3382760
H	-1.2251020	-0.5828600	-1.7292440
C	-5.0273120	0.4822110	1.2992050
H	-5.8959000	0.3224580	1.9423680
H	-4.3815450	1.2179960	1.7846090
H	-5.3796140	0.8824430	0.3441760
H	-3.9891020	-1.2013830	2.1215450
C	-2.1647990	-3.2869250	0.1615200
H	-2.8972720	-2.1117940	-1.5219750
Cl	0.0097550	0.8107780	0.3758520
N	1.4984790	1.2249670	1.5067340
C	2.7564720	0.7480430	1.2873610
C	1.3965270	2.0466720	2.6305190
C	3.6859910	1.2822890	2.3648960
C	2.7809120	2.1426100	3.2617760
H	4.4899080	1.8502890	1.8878110
H	3.0798050	3.1937480	3.2959630
O	0.3706550	2.5779810	3.0160790
C	3.0641840	-0.0004890	0.3503580
C	-2.3038080	-4.6361870	-0.5777280
H	-1.5031270	-5.3073130	-0.2508840
H	-3.2519570	-5.1342290	-0.3632460
H	-2.2101900	-4.5174710	-1.6633030
C	-2.4291710	-3.5027560	1.6634520
H	-1.7672890	-4.2896840	2.0393980
H	-2.2233800	-2.5987180	2.2447270
H	-3.4584740	-3.8217330	1.8574710
C	-0.7211550	-2.7874760	-0.0316820
H	-0.4717600	-2.6742790	-1.0929130
H	-0.5476010	-1.8340640	0.4702870
H	-0.0243450	-3.5188970	0.3906360
H	2.7234570	1.7801760	4.2917380
H	4.1432450	0.4390180	2.8903300
C	-2.2765520	2.7941960	-1.8016890
C	-1.6607010	3.7816580	-1.0175820
C	-3.6059770	2.9980930	-2.2064230
C	-2.3545550	4.9368080	-0.6420560
H	-0.6304040	3.6466580	-0.7015280
C	-4.3041870	4.1500770	-1.8329200
H	-4.0962450	2.2498570	-2.8249730
C	-3.6796720	5.1243430	-1.0469960
H	-1.8577600	5.6907440	-0.0378680
H	-5.3308330	4.2888080	-2.1600430
H	-4.2183090	6.0223960	-0.7586340
H	4.4771560	-0.5550870	0.0883270
O	5.3606920	-1.0414950	-0.0983450
C	6.2184790	-0.2964520	-0.7523380
O	6.0850070	0.8453300	-1.1397110
C	7.5368390	-1.0820150	-0.9993610
F	7.3024910	-2.2200340	-1.6903770
F	8.4162630	-0.3473280	-1.6977570
F	8.1183410	-1.4248810	0.1729530

Formation of syn-aminal syn-18b (TS5)

Conformation name	Extrapolated Free energy (kcal/mol)
TS5-int-lowest	0.0
1	6.0
2	0.4
3	2.5
4	2.9

TS5-int-lowest.log
Potential Energy = -2233.49662

Zero-point Energy = -2232.96689		
Free Energy = -2233.01536		
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.07919		
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.59792		
Nimag = 1 (-242.8971 cm ⁻¹)		
Charge = 0 Multiplicity = 1		
C	-0.0676900	2.1356700 -0.6441190
C	0.9788090	3.1016740 1.2401920
C	-0.5069930	2.9616280 1.5893770
N	-0.9509820	1.9741380 0.5565620
N	1.1690310	2.5910120 0.0026550
O	1.8373290	3.5880490 1.9750120
C	2.4970760	2.4401650 -0.5832410
H	3.2135170	2.3313810 0.2325880
H	2.5237350	1.5438740 -1.2048540
H	2.7799400	3.3122370 -1.1802000
C	-1.6942840	0.9372200 0.8608640
H	-2.1639830	0.9970090 1.8353970
C	-2.4458780	0.0269650 -0.0963270
C	-3.3817480	-0.9441160 0.6443950
H	-2.7845330	-1.6901020 1.1700190
H	-3.9068770	-0.3570510 1.4072770
H	-3.0491590	0.6961920 -0.7150180
C	-0.7655650	2.6180150 3.0469230
H	-0.2965590	3.4011620 3.6471960
H	-1.8332430	2.6174410 3.2788630
H	-0.3272610	1.6609880 3.3316340
H	-0.9998720	3.9116160 1.3569160
C	-0.6157420	3.1043120 -1.7578170
H	0.0974660	1.1490490 -1.0755460
Cl	-1.4136870	-0.8828310 -1.2879210
C	0.2834820	2.9306420 -3.0045730
H	-0.1396280	3.5043420 -3.8349190
H	1.2995430	3.2964250 -2.8415670
H	0.3395630	1.8825890 -3.3176700
C	-2.0544100	2.7154100 -2.1509580
H	-2.1112020	1.6905540 -2.5296750
H	-2.7515780	2.8350020 -1.3156950
H	-2.3965060	3.3763980 -2.9532310
C	-0.6004470	4.5850190 -1.3291630
H	0.3842370	4.9041600 -0.9752460
H	-0.8561500	5.2076520 -2.1922510
H	-1.3401610	4.8007420 -0.5522300
N	-0.3978570	-0.6315820 1.8649200
C	-0.7766850	-1.1686660 3.0935660
C	0.8306060	-1.0403030 1.5649360
C	0.3165750	-2.0852860 3.6416530
C	1.4286050	-1.9865420 2.5908720
H	-0.0848200	-3.0963210 3.7555430
H	1.6711590	-2.9410090 2.1140590
H	2.3630620	-1.5690780 2.9778770
H	0.6206480	-1.7372640 4.6326570
O	1.4394860	-0.6535150 0.5116560
O	-1.8443010	-0.9175730 3.6424710
H	2.4918950	-1.0858790 0.3430170
O	3.6545720	-1.5644430 0.1757170
C	4.1898400	-1.3628880 -0.9718070
C	5.6122050	-1.9990250 -1.0639670
O	3.7456330	-0.7647180 -1.9484080
F	6.4442030	-1.4802660 -0.1254900
F	5.5650180	-3.3399090 -0.8600690
F	6.1895210	-1.7974740 -2.2649060
C	-4.3991650	-1.6148080 -0.2566480
C	-4.2834460	-2.9728860 -0.5841800
C	-5.4881580	-0.8905870 -0.7674960
C	-5.2268660	-3.5932020 -1.4097180
H	-3.4509800	-3.5495840 -0.1901910
C	-6.4311560	-1.5055800 -1.5950360
H	-5.6072120	0.1594780 -0.5103080
C	-6.3020670	-2.8603420 -1.9201860
H	-5.1209280	-4.6468120 -1.6516680
H	-7.2683870	-0.9299920 -1.9792050
H	-7.0362030	-3.3405350 -2.5605070

1.log
Potential Energy = -2233.48496
Zero-point Energy = -2232.95406
Free Energy = -2233.00229
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.07105
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.58838
Nimag = 1 (-101.8706 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-0.0106870	2.4907310	-0.4376370
C	0.2278160	2.9209930	1.8731100
C	-1.2757390	2.9052890	1.5746230
N	-1.2982800	2.1796660	0.2681380
N	0.8815700	2.6473780	0.7203170
O	0.7354740	3.1427780	2.9716370
C	2.3304100	2.4804990	0.6638020
H	2.6648120	2.1164680	1.6368010
H	2.5872920	1.7457870	-0.1006790
H	2.8398480	3.4258870	0.4535010
C	-2.0723070	1.1379720	0.0490340
H	-2.8608890	1.0032940	0.7807140
C	-2.4184770	0.5864320	-1.3307070
C	-3.7019110	-0.2802240	-1.4140390
H	-4.4454720	0.2145910	-0.7783600
H	-4.0542820	-0.1513040	-2.4427020
H	-2.6536750	1.4886440	-1.8984220
C	-2.1385950	2.3733380	2.7040690
H	-1.9397210	2.9993540	3.5772540
H	-3.2024320	2.4597560	2.4686050
H	-1.9108740	1.3404560	2.9632030
H	-1.5808930	3.9353060	1.3617420
C	-0.0410040	3.7264970	-1.4126750
H	0.2870370	1.6048200	-0.9971630
Cl	-1.0450820	-0.1541010	-2.2584830
C	1.2661130	3.6896900	-2.2400150
H	1.2264660	4.4672850	-3.0090340
H	2.1524350	3.8799850	-1.6308330
H	1.3954150	2.7264540	-2.7449950
C	-1.2262820	3.6129790	-2.3913350
H	-1.1699180	2.7030320	-2.9965030
H	-2.1887250	3.6480110	-1.8707510
H	-1.2022700	4.4615950	-3.0819850
C	-0.1316300	5.0793390	-0.6790390
H	0.6424320	5.1894560	0.0860750
H	0.0075460	5.8868170	-1.4047110
H	-1.1098010	5.2357390	-0.2145750
N	-1.1139780	-0.6278450	1.0797740
C	-1.7910530	-1.2411960	2.1367090
C	0.1167650	-1.1198340	1.0117440
C	-0.9380270	-2.3467230	2.7543530
C	0.3922140	-2.2354450	2.0023130
H	-1.4392100	-3.3075140	2.6039190
H	0.6757970	-3.1443340	1.4634900
H	1.2355540	-1.9600270	2.6427460
H	-0.8488910	-2.1842280	3.8315430
O	0.9893500	-0.6705680	0.1905560
O	-2.9060750	-0.9031140	2.5134950
H	1.9902380	-1.1695170	0.2266670
O	3.1535260	-1.7760390	0.2709330
C	4.1032370	-1.2430160	-0.3996990
C	5.4309260	-2.0554690	-0.2715260
O	4.1011350	-0.2270230	-1.0936050
F	5.8339460	-2.1392190	1.0223750
F	5.2755800	-3.3260430	-0.7243680
F	6.4453920	-1.5058180	-0.9691460
C	-3.6811230	-1.7670060	-1.1067940
C	-4.2671320	-2.2631730	0.0661790
C	-3.1858400	-2.6900760	-2.0444480
C	-4.3257870	-3.6380280	0.3166990
H	-4.6750240	-1.5708210	0.7947880
C	-3.2369220	-4.0638180	-1.7956780
H	-2.7678240	-2.3347750	-2.9806610
C	-3.8041910	-4.5439470	-0.6103770
H	-4.7837150	-3.9976820	1.2338120
H	-2.8456240	-4.7583930	-2.5336240

H -3.8506140 -5.6121940 -0.4191220

2.log
Potential Energy = -2233.49716
Zero-point Energy = -2232.96578
Free Energy = -2233.01358
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.08080
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.59722
Nimag = 1 (-41.5476 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-0.2079630	2.0054930	0.0927230
C	0.2336690	1.6796300	2.3910850
C	-1.2249670	1.2658580	2.1687090
N	-1.2420470	1.0896830	0.6819630
N	0.7512260	2.0605390	1.2012560
O	0.8200500	1.6530350	3.4715570
C	2.1754370	2.3338310	1.0310920
H	2.7229610	1.7397450	1.7644590
H	2.4855200	2.0373530	0.0285540
H	2.4084040	3.3900490	1.1919530
C	-1.8114260	0.0648760	0.1111190
H	-2.4566640	-0.5140270	0.7589900
C	-2.0629700	-0.1502940	-1.3692320
C	-3.0049530	-1.3410270	-1.6331140
H	-3.0293390	-1.4901980	-2.7159990
H	-2.5888080	-2.2407270	-1.1767560
H	-2.5363160	0.7594890	-1.7395210
C	-1.6667590	0.0829670	3.0141540
H	-1.4802460	0.3492260	4.0572100
H	-2.7366170	-0.1110050	2.9072590
H	-1.1032980	-0.8209730	2.7804590
H	-1.8605040	2.1276850	2.3968520
C	-0.7439880	3.4084070	-0.3733680
H	0.2493010	1.4936390	-0.7546610
Cl	-0.5614480	-0.3093210	-2.3907240
C	0.4313480	4.1504000	-1.0519320
H	0.0558580	5.0732780	-1.5043210
H	1.2118260	4.4311920	-0.3418930
H	0.8849040	3.5506130	-1.8483690
C	-1.8634140	3.2365380	-1.4183050
H	-1.5253300	2.6644420	-2.2884000
H	-2.7526590	2.7630160	-0.9909670
H	-2.1698940	4.2231180	-1.7789880
C	-1.2760370	4.2663930	0.7906410
H	-0.5454950	4.3652660	1.5992110
H	-1.4928330	5.2734050	0.4209180
H	-2.2098390	3.8708160	1.2017360
N	-0.3852940	-1.8578010	0.4756280
C	-0.8543680	-3.0948900	0.8726380
C	0.9553810	-1.8789870	0.4420200
C	0.2968100	-4.0774160	1.1038010
C	1.5429090	-3.2397990	0.8027220
H	0.1760400	-4.9380370	0.4392860
H	2.1335090	-3.6178540	-0.0377040
H	2.2197850	-3.1354290	1.6562660
H	0.2568890	-4.4483060	2.1321790
O	1.6585160	-0.8705390	0.1495960
O	-2.0475620	-3.3668060	1.0228970
H	2.9908630	-0.9936730	0.0928700
O	4.0898510	-1.1087500	0.0847470
C	4.7145330	-0.3105810	-0.7252880
C	6.2504860	-0.5618770	-0.6743310
O	4.2597940	0.5474750	-1.4631090
F	6.7351370	-0.3715400	0.5760140
F	6.5478190	-1.8329230	-1.0362130
F	6.9179330	0.2634070	-1.4997520
C	-4.4122270	-1.0819270	-1.1209010
C	-5.2650740	-0.1997290	-1.8054900
C	-4.8887090	-1.7204870	0.0342090
C	-6.5609250	0.0432280	-1.3444490
H	-4.9183150	0.2921150	-2.7114300
C	-6.1876820	-1.4791690	0.4962020
H	-4.2376830	-2.4099610	0.5645290
C	-7.0260750	-0.5961730	-0.1894670

H -7.2083420 0.7247450 -1.8887040
H -6.5429990 -1.9844700 1.3898350
H -8.0346600 -0.4104220 0.1681380

3.log
Potential Energy = -2233.49340
Zero-point Energy = -2232.96070
Free Energy = -2233.00849
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.07881
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.59390
Nimag = 1 (-57.5343 cm⁻¹)
Charge = 0 Multiplicity = 1
C -2.9809140 0.1760540 -0.7843200
C -3.2989800 -2.1426870 -0.4827470
C -1.8699800 -1.9682390 -1.0069420
N -1.6479400 -0.5092420 -0.7503780
N -3.8573470 -0.9199850 -0.3590240
O -3.8275400 -3.2214260 -0.2130040
C -5.1434840 -0.7206130 0.2996650
H -5.9760910 -0.7768430 -0.4076050
H -5.2682080 -1.5029260 1.0501380
H -5.1479590 0.2519350 0.7921500
C -0.5216150 -0.0552300 -0.2599430
H 0.3050640 -0.7521950 -0.3210400
C -0.0713320 1.3920670 -0.1578110
C 1.3899750 1.5074310 0.3068300
H 1.4623290 1.1963390 1.3496520
H 1.9583230 0.7841620 -0.2888760
H -0.1485410 1.7952440 -1.1698570
C -0.8794700 -2.9434100 -0.3907870
H -1.2629120 -3.9488480 -0.5803230
H 0.1049620 -2.8633470 -0.8552610
H -0.7879960 -2.8032900 0.6871560
H -1.8850300 -2.1090050 -2.0930120
C -3.3769310 0.8029190 -2.1736920
H -2.9789870 0.9491390 -0.0170180
Cl -1.1382720 2.4835280 0.8376360
C -4.6811680 1.6073020 -1.9614660
H -4.9174350 2.1550960 -2.8789220
H -5.5358030 0.9651340 -1.7380580
H -4.5774220 2.3399010 -1.1536000
C -2.2918980 1.7804250 -2.6652510
H -2.1121260 2.5873320 -1.9484200
H -1.3503460 1.2671030 -2.8837390
H -2.6265730 2.2438700 -3.5984620
C -3.6136590 -0.2591650 -3.2653480
H -4.3386570 -1.0174520 -2.9552440
H -4.0132230 0.2309100 -4.1588330
H -2.6865920 -0.7580930 -3.5639300
N -0.4299630 -0.5585310 2.0319830
C -1.5746620 -0.4464490 2.8024210
C 0.5817410 -1.0257320 2.7925970
C -1.3034760 -0.8398770 4.2578970
C 0.1735090 -1.2351470 4.2487710
H -1.9754690 -1.6545110 4.5437740
H 0.3555520 -2.2778450 4.5267570
H 0.8034610 -0.6119770 4.8911750
H -1.5273090 0.0126010 4.9064390
O 1.7499330 -1.2709540 2.4055770
O -2.6709330 -0.0850540 2.3761520
H 2.6082350 -1.6864800 1.2727640
O 3.3933050 -2.0690860 0.7136350
C 3.2188310 -2.0144780 -0.5766370
C 4.4425440 -2.6184870 -1.3209350
O 2.2691860 -1.5718540 -1.1957940
F 4.6269260 -3.9120560 -0.9738300
F 4.2770510 -2.5665270 -2.6518330
F 5.5736170 -1.9441730 -1.0147920
C 1.9857420 2.8875180 0.1156510
C 2.2391460 3.7196440 1.2149850
C 2.3117060 3.3537670 -1.1681600
C 2.7961020 4.9904970 1.0386130
H 2.0001380 3.3710030 2.2160900
C 2.8648710 4.6240520 -1.3494130

H 2.1407110 2.7176290 -2.0337330
C 3.1077510 5.4479360 -0.2449210
H 2.9859560 5.6201490 1.9031640
H 3.1122110 4.9666940 -2.3500950
H 3.5410510 6.4341100 -0.3838930

4.log
Potential Energy = -2233.49469
Zero-point Energy = -2232.96320
Free Energy = -2233.01182
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.07622
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.59335
Nimag = 1 (-78.2152 cm⁻¹)
Charge = 0 Multiplicity = 1
C 2.3706890 2.0188620 0.0951800
C 0.6256560 3.3962350 -0.7103440
C 0.8831690 2.3336090 -1.7881450
N 1.5994580 1.2984390 -0.9784650
N 1.4503170 3.1413770 0.3324070
O -0.1945290 4.3080640 -0.7912610
C 1.3869530 3.8940940 1.5809500
H 0.3570050 4.2249200 1.7255840
H 1.6762370 3.2438970 2.4070350
H 2.0360420 4.7748400 1.5585560
C 1.1375770 0.0810020 -0.8797500
H 0.3705870 -0.1890720 -1.5964970
C 1.8168330 -1.0857280 -0.2045950
C 2.8152490 -1.7367740 -1.1991160
H 2.2626690 -2.0503620 -2.0895390
H 2.2895350 -0.8019810 0.7343670
C -0.3564400 1.8927540 -2.5459530
H -0.7793650 2.7870270 -3.0102610
H -0.1019480 1.1926440 -3.3464990
H -1.1147270 1.4530210 -1.8947970
H 1.6125680 2.7367350 -2.4972620
C 3.8405550 2.4612300 -0.2484910
H 2.3721040 1.3769430 0.9791850
Cl 0.5697870 -2.3397740 0.2310160
N -0.5894940 0.4465120 0.8170910
C -1.9213530 0.3539430 0.7114470
C -0.2397960 0.5121820 2.1491370
C -2.6362800 0.3916360 2.0576720
C -1.4758850 0.5033840 3.0513820
H -3.3242250 1.2424070 2.0872100
H -1.4120040 -0.3389140 3.7465230
O 0.9246270 0.5651810 2.5576620
O -2.5211560 0.2413200 -0.3971940
C 4.5116610 2.8644510 1.0871130
H 5.5671190 3.0883630 0.9049010
H 4.0621880 3.7558950 1.5298790
H 4.4638700 2.0532470 1.8214720
C 4.6388140 1.2909290 -0.8458470
H 4.6724730 0.4314740 -0.1699930
H 4.2353030 0.9773960 -1.8129800
H 5.6728600 1.6081920 -1.0115580
C 3.9084720 3.6556150 -1.2216790
H 3.3117820 4.5056110 -0.8790300
H 4.9470500 3.9924840 -1.2956780
H 3.5897860 3.3885940 -2.2335090
H -1.4966610 1.4204740 3.6475720
H -3.2335150 -0.5173000 2.1792010
H 3.5190090 -0.9654680 -1.5180200
C 3.5768330 -2.9165840 -0.6248940
C 3.4357690 -4.1903850 -1.1923610
C 4.4555960 -2.7563360 0.4577940
C 4.1540900 -5.2808880 -0.6915740
H 2.7597720 -4.3311500 -2.0314180
C 5.1716810 -3.8440850 0.9634570
H 4.5890230 -1.7786760 0.9134650
C 5.0230670 -5.1113450 0.3896970
H 4.0314930 -6.2600230 -1.1453770
H 5.8470810 -3.7005300 1.8018030
H 5.5805960 -5.9569640 0.7814420
H -3.8704250 0.1329330 -0.4348510

O	-4.9587500	0.1233960	-0.5683730
C	-5.5384690	-0.9701480	-0.1750460
C	-7.0767990	-0.8933330	-0.4008290
F	-7.6175240	0.1415650	0.2853010
F	-7.6949860	-2.0170480	0.0019000
F	-7.3687020	-0.7101810	-1.7103760
O	-5.0397640	-1.9679260	0.3169070

Formation of anti-aminal *anti*-18b (TS5')

Conformation name	Extrapolated Free energy (kcal/mol)	
TS-lowest	0.0	
1	3.2	
2	0.0	
TS5'-lowest.log		
Potential Energy = -2233.50047		
Zero-point Energy = -2232.96722		
Free Energy = -2233.01545		
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.08648		
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.60146		
Nimag = 1 (-94.9987)		
Charge = 0 Multiplicity = 1		
C	2.9618650	-1.5642330
C	1.9922820	-2.1236090
C	0.9290250	-1.3190890
N	1.7342770	-0.7355930
N	3.1171150	-2.1622620
O	1.8550800	-2.6041590
C	4.3976650	-2.5832650
H	4.4278680	-2.2777080
H	5.2085030	-2.0941960
H	4.5352060	-3.6659710
C	1.4269200	0.4300670
H	0.6002530	0.9299270
C	2.4364540	1.3628500
C	1.8746620	2.7225910
H	2.7314510	3.2909240
H	2.9514930	0.8885630
C	0.2614040	-0.3061880
H	-0.1302860	-0.8552580
H	-0.5738430	0.1925060
H	0.9779180	0.4362040
H	0.1713550	-1.9931910
C	2.8688980	-2.6071120
H	3.8084330	-0.9000150
Cl	3.7578040	1.6704260
N	0.1311670	0.1736090
C	-1.1200310	-0.2409550
C	0.2566440	0.3419070
C	-1.9896290	-0.4076160
C	-1.0521050	-0.0122430
H	-2.8715850	0.2330960
H	-0.8664710	-0.8203380
O	1.2792640	0.7235780
O	-1.5075170	-0.4593300
C	4.0194670	-3.6286020
H	4.0383040	-4.2560540
H	3.8857250	-4.2898350
H	4.9973250	-3.1416100
C	3.0538370	-1.8693820
H	4.0280560	-1.3682800
H	2.2768980	-1.1286960
H	3.0176200	-2.5901400
C	1.5296000	-3.3659840
H	1.3683380	-3.8975460
H	1.5326400	-4.1156480
H	0.6819370	-2.6985830
H	-1.3972550	0.8560160
H	-2.3408810	-1.4424970

H	-2.8788490	-0.8574420
O	-3.8022470	-1.2140170
C	-4.8026960	-0.4295210
O	-4.7862480	0.6192520
C	-6.1364630	-1.0142400
F	-6.0933630	-1.1462850
F	-7.1779900	-0.2228900
F	-6.3786850	-2.2378710
H	1.2427280	2.5180100
C	1.1132750	3.5486910
C	-0.2815680	3.4344780
C	1.7762660	4.4776060
C	-0.9918290	4.2063230
H	-0.8207070	2.7476510
C	1.0701840	5.2523220
H	2.8511330	4.6010890
C	-0.3167810	5.1158630
H	-2.0705320	4.1018340
H	1.6026380	5.9666000
H	-0.8664000	5.7199450

1.log
Potential Energy = -2233.49345
Zero-point Energy = -2232.96020
Free Energy = -2233.00817
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.08163
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.59635
Nimag = 1 (-107.7322)
Charge = 0 Multiplicity = 1

C	3.3205930	-1.2017400
C	2.4327860	-2.9175490
C	1.2917090	-1.9249120
N	2.0242210	-0.7422980
N	3.5452170	-2.4323800
O	2.3546530	-3.9578160
C	4.8675570	-2.9845730
H	4.8799230	-3.3257100
H	5.6190400	-2.2051840
H	5.1121070	-3.8293630
C	1.5094600	0.4760500
H	0.6113970	0.4761210
C	2.2589560	1.8136230
C	1.5625820	2.8073060
H	1.5540310	2.3514190
H	2.2197340	3.6793160
H	2.4000360	2.2434650
C	0.5334220	-1.6788290
H	0.2324680	-2.6523390
H	-0.3695110	-1.0909650
H	1.1663980	-1.1862230
H	0.5996180	-2.3078710
C	3.3139700	-1.4000550
H	4.1006470	-0.4844200
Cl	3.9598750	1.6151750
N	0.2659280	0.9410490
C	-0.9402640	0.3315930
C	0.3380440	1.8862920
C	-1.8226930	0.8315280
C	-0.9563370	1.8987930
H	-2.7588900	1.2159730
H	-0.7262230	1.6805600
O	1.3117720	2.6035410
O	-1.2761550	-0.5495660
C	4.5395620	-2.2451060
H	4.6124560	-2.2471680
H	4.4513270	-3.2847570
H	5.4766430	-1.8329760
C	3.4569240	-0.0188090
H	4.3992650	0.4604100
H	2.6409810	0.6584650
H	3.4656490	-0.1353980
C	2.0407600	-2.1091650
H	1.9201440	-3.0946380
H	2.1081480	-2.2651920

H	1.1433700	-1.5164880	1.9665010
H	-1.3900200	2.9019000	2.7858190
H	-2.0744340	-0.0071490	2.8092560
C	0.1620810	3.2695220	-1.2853190
C	-0.0358470	4.2963680	-0.3484940
C	-0.9577620	2.7359200	-1.9404330
C	-1.3205300	4.7604590	-0.0571770
H	0.8208450	4.7365200	0.1539810
C	-2.2462960	3.1965130	-1.6503740
H	-0.8244970	1.9657150	-2.6961030
C	-2.4316370	4.2086220	-0.7049690
H	-1.4536070	5.5571260	0.6691790
H	-3.1001470	2.7705000	-2.1689850
H	-3.4305420	4.5715810	-0.4813640
H	-2.5894480	-1.2027000	0.1962010
O	-3.4533530	-1.7934380	0.1488990
C	-4.5486990	-1.0980270	-0.0026280
O	-4.6762920	0.1076170	-0.0868010
C	-5.7860980	-2.0376070	-0.0710760
F	-5.6939740	-2.8821210	-1.1242240
F	-6.9246690	-1.3379870	-0.2025550
F	-5.8881130	-2.7891260	1.0491910

2.log
 Potential Energy = -2233.50217
 Zero-point Energy = -2232.96933
 Free Energy = -2233.01848
 Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.08509
 Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.60140
 Nimag = 1 (-86.7932)
 Charge = 0 Multiplicity = 1

C	-1.7531000	2.5492890	0.2229870
C	-0.2696500	3.6869190	-1.2227940
C	0.3534760	2.3092670	-0.9936490
N	-0.7866820	1.5731760	-0.3732690
N	-1.4651000	3.7343240	-0.5918680
O	0.2185850	4.5779720	-1.9173640
C	-2.4355150	4.7907220	-0.8742090
H	-2.3424510	5.0715390	-1.9253260
H	-3.4418870	4.4132860	-0.6898860
H	-2.2684160	5.6781550	-0.2591230
C	-0.9253970	0.2682310	-0.5093920
H	-0.1868970	-0.1840050	-1.1574790
C	-2.2540690	-0.4740520	-0.4555020
C	-2.1089420	-1.9590650	-0.8194550
H	-2.7695420	-0.3400940	0.4921190
C	0.8749770	1.7230060	-2.3025140
H	1.5646280	2.4510920	-2.7363560
H	1.4240190	0.7965130	-2.1320100
H	0.0628060	1.5516990	-3.0152830
H	1.1734650	2.3834140	-0.2718320
C	-1.6081390	2.7752630	1.7702480
H	-2.7702960	2.2128760	0.0098600
Cl	-3.3442240	0.3237000	-1.7222850
N	0.0802780	-0.7760010	1.0758870
C	1.4289140	-0.7764700	1.0010440
C	-0.3354700	-1.5472280	2.1526210
C	2.0717140	-1.5916880	2.1135900
C	0.8690410	-2.1035140	2.9114400
H	2.6783430	-2.3874210	1.6709350
H	0.8416020	-1.7376210	3.9420280
O	-1.5106270	-1.7510880	2.4470670
O	2.0685060	-0.1686570	0.1088180
C	-2.3792820	4.0514230	2.1726960
H	-2.4005090	4.1187520	3.2648620
H	-1.8998250	4.9587710	1.7982320
H	-3.4179740	4.0329470	1.8255530
C	-2.2525720	1.5878220	2.5093860
H	-3.3159600	1.4960650	2.2582350
H	-1.7629070	0.6392860	2.2929180
H	-2.1838070	1.7495750	3.5900360
C	-0.1365920	2.9288620	2.1953700
H	0.3510580	3.7633970	1.6803750
H	-0.0889880	3.1383110	3.2687180

H	0.4371600	2.0162180	2.0116470
H	0.7977470	-3.1942250	2.9474270
H	2.7437650	-0.9506880	2.6922750
H	3.5214700	-0.2174080	0.0043700
O	4.5606300	-0.1250710	-0.1207960
C	5.1531930	-1.2628860	-0.3647370
O	4.6611580	-2.3711290	-0.4512790
C	6.6827310	-1.0533480	-0.5524100
F	6.9327330	-0.2432540	-1.6071630
F	7.3133950	-2.2187690	-0.7699150
F	7.2338110	-0.4817020	0.5428010
H	-1.3897980	-2.3886370	-0.1189740
H	-1.6715780	-2.0317040	-1.8201040
C	-3.4036870	-2.7458750	-0.7619280
C	-3.9852200	-3.2526140	-1.9324060
C	-4.0328480	-2.9990150	0.4679490
C	-5.1728930	-3.9901040	-1.8810080
H	-3.5066700	-3.0700950	-2.8910650
C	-5.2218830	-3.7312940	0.5214840
H	-3.5807200	-2.6276560	1.3834310
C	-5.7967970	-4.2291170	-0.6532520
H	-5.6080870	-4.3755430	-2.7986780
H	-5.6956230	-3.9189770	1.4810140
H	-6.7191920	-4.8011120	-0.6107420

Formation of syn-18b' (TS_{syn-18b'})

Conformation name	Extrapolated Free energy (kcal/mol)		
TS-lowest	0.0		
1	1.4		
TS-lowest.log			
Potential Energy = -2233.49084			
Zero-point Energy = -2232.95906			
Free Energy = -2233.00727			
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.07235			
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.58878			
Nimag = 1 (-58.6095)			
Charge = 0 Multiplicity = 1			
C	3.3758330	-1.2079090	-0.6598080
C	2.2233830	-1.2548260	-2.7199250
C	1.1945980	-0.7703580	-1.6951220
N	2.0766130	-0.4323860	-0.5336930
N	3.4199070	-1.4046260	-2.1065300
O	1.9987620	-1.4196840	-3.9164320
C	4.6561960	-1.5404920	-2.8776180
H	4.5565080	-0.9521490	-3.7918840
H	5.4905030	-1.1564650	-2.2899860
H	4.8567750	-2.5793350	-3.1491310
C	1.8576010	0.3433720	0.4912330
H	2.6334280	0.3328340	1.2500660
C	0.9705990	1.5679850	0.5216520
C	1.6926170	2.7073230	-0.2538520
H	2.6649340	2.8820700	0.2163040
H	0.5671310	-1.6032150	-1.3595520
C	3.4792960	-2.5207660	0.1901660
H	4.1831310	-0.5308780	-0.3647720
H	-0.0266880	1.3763210	0.1380870
Cl	0.7416250	2.1101380	2.2421080
N	0.3458150	-0.9495720	1.9479720
C	-0.8834150	-1.2372330	1.5052380
C	0.4088030	-1.1919290	3.3102950
C	-1.8158260	-1.7580470	2.5916780
C	-0.9242390	-1.7354600	3.8361900
H	-2.1734200	-2.7571470	2.3232850
H	-0.7641300	-2.7236810	4.2774500
H	-1.2949130	-1.0781100	4.6281690
H	-2.6915140	-1.1056370	2.6652910
O	1.4046430	-1.0000090	4.0070730
O	-1.2336810	-1.0847430	0.2966370

C	0.2864820	0.2898610	-2.3072060
H	-0.5374900	0.5448310	-1.6436340
H	0.8288170	1.1827370	-2.6211600
H	-0.1413610	-0.1638080	-3.2047130
C	4.7223430	-3.3090410	-0.2819260
H	4.8827140	-4.1474640	0.4025230
H	4.5925920	-3.7250990	-1.2833100
H	5.6308640	-2.6971490	-0.2686770
C	2.2335450	-3.4108810	0.0324270
H	2.0530900	-3.6769900	-1.0146220
H	2.3863960	-4.3450310	0.5821430
H	1.3408200	-2.9308570	0.4409640
C	3.6936990	-2.1587390	1.6742370
H	4.5764080	-1.5210300	1.8041810
H	2.8324110	-1.6663490	2.1260570
H	3.8697450	-3.0778310	2.2425990
H	1.8936980	2.3439270	-1.2653200
C	0.9121700	4.0056700	-0.3178440
C	1.3882170	5.1506510	0.3358320
C	-0.2812630	4.0965470	-1.0514140
C	0.6884660	6.3592960	0.2631730
H	2.3122390	5.0975380	0.9051180
C	-0.9848560	5.3013390	-1.1229720
H	-0.6656380	3.2271210	-1.5776620
C	-0.5021280	6.4374370	-0.4645900
H	1.0738070	7.2360210	0.7755570
H	-1.9058990	5.3530210	-1.6961870
H	-1.0477760	7.3746630	-0.5217350
H	-2.5066280	-1.3861940	-0.1142360
O	-3.4572070	-1.6772830	-0.5552050
C	-4.4428740	-0.8758100	-0.2794600
O	-4.4425340	0.1304530	0.4074990
C	-5.7523160	-1.3528970	-0.9726190
F	-6.0649080	-2.6194650	-0.6119930
F	-5.6187140	-1.3340360	-2.3204680
F	-6.7959300	-0.5679840	-0.6547000

l.log
 Potential Energy = -2233.49102
 Zero-point Energy = -2232.95979
 Free Energy = -2233.00858
 Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.07121
 Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.58877
 Nimag = 1 (-61.9068)
 Charge = 0 Multiplicity = 1

C	-1.8130170	-2.4931970	-1.1402690
C	-3.8246230	-2.7245180	0.0727710
C	-3.0569120	-1.6039910	0.7782400
N	-2.0022920	-1.2892390	-0.2360220
N	-3.1279240	-3.1172680	-1.0187790
O	-4.9254770	-3.1473700	0.4179770
C	-3.7491450	-3.9274280	-2.0669600
H	-4.8054300	-3.6580460	-2.1271030
H	-3.2664680	-3.7124190	-3.0210900
H	-3.6714160	-4.9968830	-1.8588220
C	-1.2660640	-0.2217790	-0.3820060
H	-0.4972460	-0.2971870	-1.1440820
C	-1.6536880	1.1972650	-0.0267710
C	-2.7005070	1.6923450	-1.0645390
H	-2.2633010	1.6063350	-2.0637200
H	-2.5227240	-1.9908450	1.6530020
C	-0.6024710	-3.4291430	-0.7987290
H	-1.6886300	-2.1133340	-2.1586160
H	-2.0067920	1.2936300	0.9955180
Cl	-0.1893940	2.2705920	-0.1457840
N	0.3949080	-0.3482360	1.3969580
C	-0.0490660	-0.2869960	2.7011350
C	1.7258500	-0.1716540	1.3714040
C	1.1111470	-0.0766010	3.6769500
C	2.3343000	0.0029300	2.7590160
H	1.1464170	-0.9117540	4.3827990
H	3.0729720	-0.7840240	2.9403270
H	2.8596970	0.9618190	2.8097700
H	0.9373890	0.8353620	4.2556860

O	2.4012120	-0.1538000	0.3052730
O	-1.2334650	-0.3869600	3.0343500
C	-4.0141380	-0.5180310	1.2549270
H	-3.5054780	0.2183840	1.8738090
H	-4.5554090	-0.0409260	0.4367680
H	-4.7521090	-1.0230550	1.8832440
C	-0.7446210	-4.7294210	-1.6221700
H	0.1681660	-5.3202900	-1.4998680
H	-1.5800690	-5.3449890	-1.2818670
H	-0.8650420	-4.5304850	-2.6926380
C	-0.5534600	-3.7882710	0.6970860
H	-1.4770350	-4.2744720	1.0291170
H	0.2647320	-4.4942600	0.8713890
H	-0.3673120	-2.9082600	1.3176850
C	0.7125190	-2.7477950	-1.2299550
H	0.6913490	-2.4803750	-2.2932380
H	0.9458030	-1.8571090	-0.6471910
H	1.5410920	-3.4489100	-1.0866880
H	-3.5495590	1.0042980	-1.0329590
C	-3.1794360	3.1126060	-0.8350750
C	-2.8914600	4.1155150	-1.7711090
C	-3.9398020	3.4467890	0.2966450
C	-3.3489700	5.4235270	-1.5827210
H	-2.3058790	3.8722950	-2.6535510
C	-4.3948410	4.7534250	0.4903200
H	-4.1864030	2.6863200	1.0325170
C	-4.1002580	5.7470050	-0.4494780
H	-3.1166170	6.1864660	-2.3200240
H	-4.9827210	4.9932890	1.3715000
H	-4.4558900	6.7622370	-0.3003350
H	3.7538890	0.0246360	0.3358730
O	4.8380730	0.1351660	0.3763710
C	5.3811670	0.4974920	-0.7473270
C	6.9262320	0.6188720	-0.5995170
O	4.8478370	0.7308190	-1.8176920
F	7.5060890	1.0015960	-1.7503050
F	7.4742910	-0.5654650	-0.2371360
F	7.2561790	1.5271120	0.3490590

Formation of anti-anti18b' (TS_{anti-18b'})

TS-lowest.log
 Potential Energy = -2233.50709
 Zero-point Energy = -2232.97791
 Free Energy = -2233.02678
 Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.08656
 Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.60624
 Nimag = 1 (-494.2657)
 Charge = 0 Multiplicity = 1

C	0.7553950	2.0075520	-0.1593370
C	0.2995140	2.8729210	1.9872940
C	-1.0680540	2.4503560	1.4277240
N	-0.6532540	1.6570390	0.2335520
N	1.2637350	2.5507530	1.0957680
O	0.4695730	3.3815280	3.0920910
C	2.6837520	2.6033130	1.4462810
H	2.7816970	2.3576760	2.5055510
H	3.2295660	1.8696990	0.8514970
H	3.1043600	3.5983810	1.2792520
C	-1.2604740	0.6747920	-0.3513370
H	-0.7053660	0.1912140	-1.1459570
C	-2.7142960	0.2818740	-0.2167870
C	-3.0654790	-0.8567410	-1.1849440
H	-1.6004830	3.3397430	1.0742580
C	0.8302640	2.9761920	-1.3923690
H	1.2719540	1.0727950	-0.3981280
H	-2.9483800	0.0030550	0.8081800
Cl	-3.7337960	1.7689450	-0.5820500
N	-0.4735560	-1.4067320	0.8263090
C	0.7597970	-1.8201470	0.5668020
C	-0.9996430	-2.1714740	1.8588800
C	1.2274440	-2.9758000	1.4358890
C	0.0053300	-3.2274680	2.3275200

H	2.1242030	-2.6839770	1.9911980
H	0.2069320	-3.0922170	3.3939080
H	-0.4286110	-4.2232040	2.1982200
H	1.4977250	-3.8292530	0.8066020
O	-2.1255430	-2.0065410	2.3245710
O	1.4776180	-1.2734230	-0.3415940
C	-1.8926690	1.7263430	2.4888510
H	-2.9451290	1.6599210	2.2139220
H	-1.4994630	0.7293090	2.6978530
H	-1.8233980	2.3236400	3.4010400
C	2.3214220	3.2690830	-1.6760050
H	2.4017200	3.8195800	-2.6180780
H	2.7760740	3.8863470	-0.8986310
H	2.9057750	2.3484020	-1.7769920
C	0.0879850	4.2999610	-1.1340690
H	0.4625840	4.8109670	-0.2414560
H	0.2410070	4.9719670	-1.9840850
H	-0.9915810	4.1524690	-1.0304690
C	0.2381520	2.2841240	-2.6378060
H	0.7211940	1.3211860	-2.8387200
H	-0.8423220	2.1299950	-2.5625300
H	0.4048610	2.9218760	-3.5110210
H	-2.3519090	-1.6596160	-0.9676150
H	-2.8820800	-0.5251930	-2.2115970
C	-4.4822070	-1.3758820	-1.0485500
C	-5.4078690	-1.2068570	-2.0871710
C	-4.8855820	-2.0543560	0.1133120
C	-6.7122220	-1.6990960	-1.9701700
H	-5.1080000	-0.6881560	-2.9940340
C	-6.1890880	-2.5430530	0.2336870
H	-4.1749090	-2.2010720	0.9231240
C	-7.1071300	-2.3673020	-0.8079500
H	-7.4158670	-1.5597180	-2.7858850
H	-6.4862490	-3.0664100	1.1381300
H	-8.1191260	-2.7505810	-0.7147530
H	2.6018430	-1.6573800	-0.4675820
O	3.7335270	-2.0611650	-0.6549070
C	4.6670350	-1.1894870	-0.5031280
C	6.0746670	-1.8103610	-0.7591650
O	4.5837530	-0.0031650	-0.2038500
F	6.1826360	-2.2617720	-2.0340160
F	6.3051030	-2.8645830	0.0617720
F	7.0677870	-0.9225030	-0.5616410

l.log
 Potential Energy = -2233.50099
 Zero-point Energy = -2232.97161
 Free Energy = -2233.02034
 Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.08469
 Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.60403
 Nimag = 1 (-389.2397)
 Charge = 0 Multiplicity = 1

C	-1.1561550	1.4775340	-1.2816290
C	-2.7760180	2.9260920	-0.3623500
C	-3.1981720	1.5178010	0.0829510
N	-1.9823030	0.7295480	-0.2737740
N	-1.6173240	2.8439240	-1.0544130
O	-3.3867600	3.9558020	-0.0876860
C	-0.8588390	4.0399240	-1.4172450
H	0.1940090	3.7797770	-1.5269370
H	-1.2213630	4.4824740	-2.3488290
H	-0.9692440	4.7730640	-0.6159710
C	-1.5144300	-0.3538880	0.2667590
H	-0.5661160	-0.6950600	-0.1273800
C	-2.2664960	-1.3156440	1.1566980
C	-1.4431560	-2.5427760	1.5937880
H	-2.1162160	-3.1687290	2.1863620
H	-0.6842880	-2.1566050	2.2798250
N	-0.0491940	0.3793210	2.0910860
C	1.1522630	0.8726510	1.7977880
C	-0.2696240	0.4893950	3.4558820
C	1.9168260	1.3861640	3.0089610
C	0.9317430	1.1303760	4.1556190
H	2.8593000	0.8391060	3.1097970

H	1.3162690	0.4458430	4.9171570
H	0.6108510	2.0431950	4.6658400
H	2.1668220	2.4422680	2.8695210
O	-1.3006160	0.1173000	4.0145120
O	1.6027450	0.9048410	0.6060810
C	-3.6319310	1.5169140	1.5468160
H	-4.2944960	2.3759140	1.6768140
H	-4.1960600	0.6209250	1.8054400
H	-2.7829050	1.6292050	2.2239110
H	-4.0212260	1.1749050	-0.5533780
C	-1.3308770	0.9480280	-2.7492960
H	-0.1075350	1.3812960	-0.9811850
Cl	-3.7820070	-1.8347810	0.2468940
H	-2.6225610	-0.8107010	2.0511680
C	-0.8657360	-0.5201380	-2.8361930
H	0.1588000	-0.6472740	-2.4693360
H	-1.5235940	-1.2040940	-2.2925600
H	-0.8786020	-0.8352290	-3.8838910
C	-0.4182100	1.7885860	-3.6717190
H	-0.7646140	2.8189860	-3.7728600
H	0.6180570	1.8011540	-3.3168370
H	-0.4199180	1.3453900	-4.6720040
C	-2.7884920	1.0570540	-3.2328530
H	-3.1661260	2.0822700	-3.1668380
H	-2.8445530	0.7544890	-4.2830490
H	-3.4576410	0.3975190	-2.6715550
C	-0.7798090	-3.3664270	0.5076590
C	0.5610970	-3.1364440	0.1589370
C	-1.4726610	-4.3979320	-0.1473800
C	1.1875140	-3.8988460	-0.8320700
H	1.1266130	-2.3649470	0.6754580
C	-0.8493880	-5.1624790	-1.1371830
H	-2.5022760	-4.6097840	0.1247920
C	0.4821490	-4.9126170	-1.4859810
H	2.2258620	-3.7049100	-1.0846910
H	-1.4013610	-5.9575810	-1.6301480
H	0.9674970	-5.5094220	-2.2526650
H	2.7458930	1.4011750	0.4130400
O	3.7336280	1.9633310	0.2171470
C	4.7854380	1.3795160	-0.2556840
C	4.6232730	-0.1441130	-0.5601680
F	3.6437630	-0.3552530	-1.4737500
F	5.7529090	-0.6859170	-1.0440570
F	4.2870850	-0.8311490	0.5599900
O	5.8648710	1.9056760	-0.4799020

E2-Mechanism (TS-E2)

Conformation name	Extrapolated Free energy (kcal/mol)	
TS-E2	0.0	
1	0.9	
TS-E2.log		
Potential Energy = -2233.42985		
Zero-point Energy = -2232.89629		
Free Energy = -2232.94300		
Single-Point Energy B3LYP-D3(BJ)/6-311+G** 2234.02725		
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (e free energy from qRRHO) = -2233.54041		
Nimag = 1 (-338.6068 cm ⁻¹)		
Charge = 0 Multiplicity = 1		
C	-2.2726820	-0.9271960 -0.7481570
C	-3.1142270	-1.2022830 1.4434540
C	-1.6178270	-1.4975780 1.5356850
N	-1.0817470	-0.8216420 0.2523880
N	-3.4090540	-0.8714840 0.1665630
O	-3.9001980	-1.2481600 2.3867650
C	-4.7162290	-0.3178230 -0.1867410
H	-5.0405680	0.3502890 0.6140570
H	-4.6305640	0.2445990 -1.1154850
H	-5.4634790	-1.1059000 -0.3093810

C	-0.4888800	0.5420700	0.4951520	H	-3.4642540	-2.9428840	-0.1133960
H	-0.4783400	0.7825330	1.5482030	H	-3.2547290	-3.9143110	1.3623180
C	0.6685680	0.9533080	-0.1725320	C	-0.4393850	0.3142990	-0.1668660
C	1.2007610	2.3320760	0.2112530	H	-0.6478580	1.0227210	0.6218580
H	0.6130110	3.0947730	-0.3191040	C	0.2701650	0.8605970	-1.2360620
H	1.8647630	-0.2221270	0.3789040	C	-0.0476120	2.2698960	-1.7346830
C	-0.9881730	-1.1159980	2.8668330	H	0.7686350	2.5695480	-2.4024650
H	-1.4143400	-1.7937190	3.6111600	H	1.9137280	0.9895550	-0.6359380
H	0.0936260	-1.2666010	2.8631620	C	0.1655660	0.1761880	2.7071130
H	-1.2262470	-0.0953020	3.1691910	H	0.2582210	-0.1134280	3.7570900
H	-1.4609540	-2.5640220	1.3665690	H	1.0959430	0.6677640	2.4149840
C	-2.2450480	-2.1968370	-1.6700770	H	-0.6737250	0.8670630	2.6229150
H	-2.2403510	-0.0303830	-1.3699270	H	0.7409650	-1.8109210	2.1713760
Cl	0.8090770	0.6159590	-1.9388910	C	-0.0535120	-3.5770610	-0.3184400
N	-2.0358710	1.7908020	0.3421700	H	-1.4034650	-1.9871710	-0.9724210
C	-2.5292130	2.4522740	-0.7622140	Cl	0.6898770	-0.2082340	-2.6288440
C	-2.2567880	2.5230590	1.4880050	N	-2.4218580	0.1529340	-0.4051890
C	-3.1928190	3.7657990	-0.3470270	C	-3.1311150	-0.1712350	-1.5400340
C	-3.0390260	3.7962760	1.1766840	C	-3.1797360	0.9272400	0.4442170
H	-2.6849810	4.5931490	-0.8520690	C	-4.5245200	0.4590920	-1.4975550
H	-3.9935210	3.7665700	1.7110230	C	-4.5697120	1.1703790	-0.1411620
O	-1.8664190	2.1888550	2.6107570	H	-4.6301790	1.1392340	-2.3485170
O	-2.4671140	2.0358290	-1.9209940	H	-5.3205920	0.7597570	0.5406520
C	-3.5459110	-2.1541910	-2.5095850	O	-2.7837080	1.3557890	1.5309980
H	-3.4937160	-2.9353800	-3.2734280	O	-2.7149820	-0.8932980	-2.4485210
H	-4.4351700	-2.3466970	-1.9057710	C	-1.0788010	-4.6821220	-0.6747450
H	-3.6698140	-1.1959010	-3.0246730	H	-0.5337260	-5.5660970	-1.0182210
C	-1.0587800	-2.1344200	-2.6532160	H	-1.6798330	-4.9836770	0.1854410
H	-1.0862160	-1.2231250	-3.2565110	H	-1.7495410	-4.3729150	-1.4831150
H	-0.0884820	-2.1877220	-2.1552460	C	0.8763820	-3.4017580	-1.5356530
H	-1.1221990	-2.9909290	-3.3317260	H	0.3174500	-3.1151450	-2.4302660
C	-2.2061980	-3.5351400	-0.9050420	H	1.6623820	-2.6621520	-1.3693880
H	-3.0082540	-3.6123060	-0.1642640	H	1.3697090	-4.3576840	-1.7373180
H	-2.3478390	-4.3517440	-1.6195900	C	0.7752130	-4.0567500	0.8904120
H	-1.2433310	-3.7113590	-0.4157050	H	0.1685230	-4.1598620	1.7954040
H	-2.4824810	4.6611420	1.5492080	H	1.1852050	-5.0455430	0.6632180
H	-4.2321450	3.7640100	-0.6874780	H	1.6290120	-3.4050090	1.0995250
H	0.9942020	2.4671940	1.2792650	H	-4.7470330	2.2476460	-0.2110190
C	2.6774590	2.5838060	-0.0375620	H	-5.2774960	-0.3258020	-1.6114860
C	3.1145450	3.1916480	-1.2238080	H	-0.9508390	2.2287600	-2.3588900
C	3.6345840	2.2424070	0.9302760	C	-0.2337290	3.3376430	-0.6688680
C	4.4732970	3.4370180	-1.4462210	C	0.8354710	3.7614010	0.1383650
H	2.3859310	3.4785840	-1.9771280	C	-1.4745840	3.9723210	-0.5153810
C	4.9935410	2.4871090	0.7140550	C	0.6626880	4.7784550	1.0805470
H	3.3142480	1.7859200	1.8635970	H	1.8145630	3.3055870	0.0253010
C	5.4180660	3.0832520	-0.4780510	C	-1.6509090	4.9951240	0.4223590
H	4.7914240	3.9086710	-2.3717270	H	-2.3099170	3.6689680	-1.1408800
H	5.7181140	2.2180010	1.4774640	C	-0.5827580	5.3992660	1.2270030
H	6.4734040	3.2770320	-0.6468880	H	1.5030520	5.0917500	1.6935320
H	-0.2941070	-1.4078670	-0.0853860	H	-2.6212980	5.4729630	0.5220490
O	1.2065520	-2.5374070	-0.0206420	H	-0.7158720	6.1925150	1.9568080
C	2.3055770	-2.1190380	0.3109540	H	0.9413660	-1.1742460	0.0954950
O	2.6543340	-0.8886610	0.5511390	O	2.8404570	-1.0719010	0.2444320
C	3.4997560	-3.0943460	0.4978530	C	3.4415600	-0.0449040	-0.0284180
F	3.9810410	-3.0183410	1.7567560	O	2.9456650	1.0719020	-0.4808280
F	4.5020160	-2.7846810	-0.3510950	C	4.9820090	0.0451330	0.1440610
F	3.1299900	-4.3615970	0.2662250	F	5.3101470	1.0562670	0.9751630
				F	5.5761940	0.2736870	-1.0462160
				F	5.4783190	-1.0922890	0.6495350

l.log
 Potential Energy = -2233.43162
 Zero-point Energy = -2232.89817
 Free Energy = -2232.94495
 Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.02560
 Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.53893
 Nimag = 1 (-323.8199 cm⁻¹)
 Charge = 0 Multiplicity = 1

C	-0.8868030	-2.2718910	-0.0544120
C	-1.4009180	-1.7870380	2.2002150
C	-0.0587240	-1.1098600	1.9276830
N	-0.0445590	-1.0360190	0.3834360
N	-1.8257100	-2.3735510	1.0575630
O	-1.9851120	-1.7831920	3.2806250
C	-3.1807220	-2.9097540	0.9381560
H	-3.8650170	-2.2519030	1.4779420

E1-Mechanism (TS-E1)

Conformation name	Extrapolated Free energy (kcal/mol)
TS-E1	0.0
1	2.8
2	1.9
3	1.1
TS-E1.log	
Potential Energy = -2233.47717	
Zero-point Energy = -2232.94991	

Free Energy = -2232.99863
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.05418
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.57563
Nimag = 1 (-1285.1321 cm⁻¹)
Charge = 0 Multiplicity = 1

C	1.3689690	-2.0491260	-0.7237330
C	0.2940610	-3.3944340	0.8866180
C	1.7298810	-3.1901280	1.3841540
N	2.1691450	-2.0459990	0.5295190
N	0.1338850	-2.6826180	-0.2520010
O	-0.5550960	-4.0831730	1.4509940
C	-1.1408350	-2.5872250	-0.9523900
H	-1.9280990	-2.8401450	-0.2412560
H	-1.2896690	-1.5642440	-1.3034300
H	-1.1961960	-3.2836280	-1.7947210
C	2.9679790	-1.1028390	0.9976430
H	3.4076700	-1.3738900	1.9513660
C	3.2284560	0.2503300	0.6268280
C	3.2459730	0.8283380	-0.7930200
H	4.1085340	0.4142400	-1.3252960
H	2.1888830	0.8220090	1.3634110
C	1.8005340	-2.9720910	2.8892500
H	1.2788340	-3.8063340	3.3643820
H	2.8293400	-2.9722260	3.2563250
H	1.3064450	-2.0425920	3.1863610
H	2.3164230	-4.0765110	1.1159810
C	2.0504700	-2.7997610	-1.9409670
H	1.1454130	-1.0175760	-0.9971440
Cl	4.6860040	0.8378580	1.5750640
N	-0.2254080	0.8900300	0.5289000
C	0.1632540	1.3678640	1.7152120
C	-1.5733250	1.0696170	0.4316080
C	-0.9562680	1.9254890	2.5727250
C	-2.1792970	1.7175390	1.6731320
H	-1.0049260	1.3787940	3.5192580
H	-2.6806470	2.6498410	1.3962690
O	-2.2267910	0.7360390	-0.5810730
O	1.3718970	1.3753500	2.1200210
C	1.3838910	-2.2876840	-3.2387590
H	1.8557690	-2.7644920	-4.1036080
H	0.3160900	-2.5163670	-3.2805230
H	1.5038430	-1.2045840	-3.3493950
C	3.5585040	-2.4895170	-2.0172610
H	3.7553220	-1.4258320	-2.1634850
H	4.0954050	-2.8256200	-1.1254870
H	3.9839250	-3.0156030	-2.8775160
C	1.8765220	-4.3299780	-1.8482440
H	0.8268810	-4.6314920	-1.8011190
H	2.3110070	-4.7903090	-2.7409590
H	2.3970820	-4.7553420	-0.9848690
H	-2.9353200	1.0530800	2.1014620
H	-0.7544860	2.9742630	2.8100480
H	2.3465750	0.4842140	-1.3074080
C	3.3025620	2.3444030	-0.8993940
C	2.1335940	3.1181160	-0.8448390
C	4.5271610	2.9951650	-1.1112790
C	2.1897600	4.5088590	-0.9763820
H	1.1755760	2.6264670	-0.7058750
C	4.5876810	4.3856470	-1.2435030
H	5.4407550	2.4103080	-1.1739670
C	3.4178190	5.1483580	-1.1728800
H	1.2733060	5.0907430	-0.9331470
H	5.5462390	4.8701520	-1.4062560
H	3.4616830	6.2285110	-1.2784510
H	-3.6659990	0.8996880	-0.6801070
O	-4.6886710	1.0347100	-0.8914340
C	-5.4755860	0.4245080	-0.0474010
C	-6.9665160	0.6578860	-0.4234770
O	-5.1755860	-0.2460590	0.9214110
F	-7.2290440	0.2096930	-1.6725800
F	-7.2728440	1.9756860	-0.3883260
F	-7.7912890	0.0212940	0.4239030

1.log

Potential Energy = -2233.47575
Zero-point Energy = -2232.94890
Free Energy = -2232.99826
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.04871
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.57122
Nimag = 1 (-1295.0076 cm⁻¹)
Charge = 0 Multiplicity = 1

C	2.9849450	2.0380300	0.3581050
C	1.0843850	3.4271840	0.4489930
C	1.1370300	2.8444990	-0.9701130
N	2.0778810	1.7007670	-0.7689890
N	2.1058080	2.8931610	1.1611230
O	0.2491830	4.2326480	0.8546230
C	2.3191630	3.1715970	2.5751710
H	1.3661850	3.4870400	3.0015500
H	2.6597170	2.2647160	3.0799680
H	3.0524280	3.9692090	2.7301560
C	1.8723700	0.5214660	-1.3295430
H	1.0939470	0.5508840	-2.0835690
C	2.3221410	-0.7985250	-1.0265770
C	3.7060190	-1.1857200	-0.4870360
H	4.4365310	-1.0610340	-1.2939470
H	1.3645590	-1.1144050	-0.0623030
C	-0.2354590	2.5050250	-1.5299010
H	-0.8563000	3.3989880	-1.4313600
H	-0.1863080	2.2499890	-2.5915130
H	-0.7079870	1.6849930	-0.9828250
H	1.6229840	3.5805750	-1.6205290
C	4.3513130	2.7177300	-0.0657190
H	3.1967710	1.1307240	0.9235510
Cl	1.8623020	-1.9095260	-2.4091090
N	-1.1868470	-0.8494400	-0.3862090
C	-0.6202230	-1.3798330	0.7014370
C	-2.5372430	-0.9004080	-0.2159170
C	-1.5988880	-1.8475150	1.7629530
C	-2.9487630	-1.5247310	1.1146080
H	-1.4465710	-2.9117360	1.9651650
H	-3.5553180	-0.8138680	1.6829020
O	-3.3426740	-0.4740160	-1.0733930
O	0.6370460	-1.5008050	0.8723940
C	5.3550630	2.5054060	1.0909660
H	6.3217570	2.9410740	0.8203490
H	5.0293330	2.9818150	2.0195010
H	5.5159890	1.4408600	1.2930640
C	4.9238930	2.0614100	-1.3379810
H	5.1282960	0.9974930	-1.2009150
H	4.2573420	2.1794560	-2.1971200
H	5.8748730	2.5424270	-1.5868230
C	4.1943650	4.2306370	-0.3248420
H	3.7907840	4.7638430	0.5399310
H	5.1794120	4.6549100	-0.5422380
H	3.5583380	4.4434790	-1.1889970
H	-3.5654720	-2.4098430	0.9307000
H	-1.4176160	-1.3069370	2.6969210
H	3.9792590	-0.4822290	0.3010170
C	3.8400890	-2.5912310	0.0768730
C	4.3698600	-3.6257050	-0.7081860
C	3.4935500	-2.8703920	1.4073900
C	4.5319200	-4.9124370	-0.1854090
H	4.6596230	-3.4232720	-1.7355810
C	3.6550470	-4.1544420	1.9348460
H	3.0924930	-2.0801010	2.0353270
C	4.1722450	-5.1815480	1.1385350
H	4.9432530	-5.7000390	-0.8102900
H	3.3820720	-4.3504800	2.9678910
H	4.3007230	-6.1791630	1.5484130
H	-4.7732380	-0.5065760	-0.8896170
O	-5.8286780	-0.5484920	-0.8972330
C	-6.3819040	0.0987880	0.0911780
C	-7.9319930	-0.0013930	0.0105390
O	-5.8445390	0.7172260	0.9900350
F	-8.3380330	-1.2916890	0.0438180
F	-8.3928150	0.5429590	-1.1395120
F	-8.5192780	0.6407180	1.0335780

2.log
Potential Energy = -2233.47519
Zero-point Energy = -2232.94829
Free Energy = -2232.99732
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.05049
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.57262
Nimag = 1 (-1259.1695 cm⁻¹)
Charge = 0 Multiplicity = 1

C	2.0498260	1.8758320	0.4238910
C	0.0898470	2.7268940	-0.5656430
C	0.8114320	1.9101900	-1.6486550
N	1.7480020	1.1008190	-0.8094870
N	0.7880520	2.6055080	0.5892540
O	-0.9474910	3.3645870	-0.7321720
C	0.3496220	3.1930280	1.8484260
H	-0.7335960	3.3119600	1.8036720
H	0.6069940	2.5242600	2.6727260
H	0.8018440	4.1743190	2.0233420
C	1.8763960	-0.2040580	-0.9813270
H	1.4159670	-0.5521190	-1.8990550
C	2.3209290	-1.2435930	-0.1108110
C	3.5172410	-1.2388880	0.8371880
H	3.5758340	-0.2560830	1.3164360
H	1.2678590	-1.3163430	0.7554230
C	-0.1448790	1.1362520	-2.5425030
H	-0.8460440	1.8587240	-2.9672670
H	0.3779460	0.6546450	-3.3728120
H	-0.7121350	0.3914160	-1.9776500
H	1.4055250	2.5981900	-2.2597040
C	3.3291090	2.8029110	0.3525920
H	2.1631080	1.1746830	1.2524840
Cl	2.1894250	-2.8589800	-0.9594130
N	-1.2182530	-1.2356040	0.1639400
C	-0.7657930	-1.4451750	1.4038700
C	-2.5793740	-1.2549920	0.2115160
C	-1.8472490	-1.6338310	2.4514440
C	-3.1244870	-1.5012090	1.6158950
H	-1.7315600	-2.6102200	2.9313360
H	-3.7623090	-0.6640850	1.9141150
O	-3.2939820	-1.0860100	-0.8015390
O	0.4689340	-1.4876430	1.7174500
C	3.7780970	3.0867240	1.8047530
H	4.6862080	3.6972180	1.7931150
H	3.0235260	3.6326600	2.3770220
H	4.0078530	2.1601060	2.3421790
C	4.4782070	2.0918710	-0.3855850
H	4.7763940	1.1614260	0.1015070
H	4.2204150	1.8698280	-1.4251490
H	5.3557850	2.7458250	-0.3933170
C	3.0454220	4.1433240	-0.3569430
H	2.2347530	4.7045810	0.1151190
H	3.9454870	4.7639750	-0.3090640
H	2.8046110	4.0133090	-1.4160480
H	-3.7432990	-2.4035470	1.6188660
H	-1.7465020	-0.8718270	3.2300600
H	3.2983220	-1.9387400	1.6499940
C	4.8820340	-1.5938300	0.2572290
C	5.8415780	-2.1572390	1.1130100
C	5.2379270	-1.3529710	-1.0762240
C	7.1262940	-2.4595460	0.6537150
H	5.5807170	-2.3614580	2.1486140
C	6.5207500	-1.6577430	-1.5418490
H	4.5133680	-0.9327910	-1.7672410
C	7.4711140	-2.2101930	-0.6784170
H	7.8526650	-2.8948380	1.3340110
H	6.7735390	-1.4661550	-2.5807220
H	8.4664980	-2.4495280	-1.0409000
H	-4.7354010	-1.0677030	-0.7406680
O	-5.7880650	-1.1082210	-0.8207020
C	-6.3969050	-0.2008100	-0.1078870
C	-7.9392760	-0.3233670	-0.2666330
O	-5.9120320	0.6510470	0.6120710
F	-8.3746760	-1.5244730	0.1811780

F	-8.3078930	-0.2120650	-1.5631600
F	-8.5813520	0.6308000	0.4271480

3.log
Potential Energy = -2233.47279
Zero-point Energy = -2232.94589
Free Energy = -2232.99537
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -2234.05134
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -2233.57392
Nimag = 1 (-1303.8422 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-3.6113070	1.2122550	0.1742270
C	-2.4974060	2.5515250	-1.4138140
C	-1.4539120	2.2071300	-0.3462540
N	-2.1440510	1.1051440	0.3846140
N	-3.6542310	1.9193400	-1.1078660
O	-2.2928160	3.2599570	-2.3986260
C	-4.7942750	1.9124360	-2.0199670
H	-4.4148550	1.8880300	-3.0432730
H	-5.3970870	1.0222020	-1.8384180
H	-5.4176640	2.8032340	-1.9009070
C	-1.4780230	0.1811510	1.0580480
H	-0.4598440	0.4672810	1.3133660
C	-1.7722930	-1.1811050	1.3571830
C	-3.0548830	-1.9764760	1.1340950
H	-2.8220540	-2.9968470	1.4635910
H	-0.7495980	-1.7895450	0.5933580
C	-0.1118010	1.8275950	-0.9616940
H	0.2202980	2.6617790	-1.5844860
H	0.6472090	1.6455580	-0.1992440
H	-0.2042490	0.9373690	-1.5902760
H	-1.3300190	3.0696080	0.3184460
C	-4.3502390	1.9520030	1.3550200
H	-4.0441800	0.2193210	0.0550350
Cl	-1.0783390	-1.5991500	2.9993370
N	1.6605580	-0.9517030	0.6751260
C	1.2855760	-2.0942030	0.0968160
C	3.0132320	-0.8445620	0.5401860
C	2.4142910	-2.8980960	-0.5183470
C	3.6332980	-2.0255890	-0.2011780
H	2.4511140	-3.8932430	-0.0653540
H	4.1631430	-1.6658200	-1.0878040
O	3.6601560	0.1287310	0.9842660
O	0.0791500	-2.5101670	0.0425230
C	-5.8661420	1.9443530	1.0506060
H	-6.4082290	2.3186720	1.9245070
H	-6.1241720	2.5894660	0.2080940
H	-6.2339120	0.9341360	0.8403400
C	-4.1258830	1.1939620	2.6778110
H	-4.5183980	0.1737170	2.6364570
H	-3.0711090	1.1538750	2.9643490
H	-4.6596910	1.7122290	3.4803980
C	-3.8748850	3.4074710	1.5255330
H	-3.9587270	3.9818470	0.5977760
H	-4.5013780	3.9034320	2.2735320
H	-2.8426540	3.4635160	1.8845320
H	4.3674070	-2.5200690	0.4422190
H	2.2332700	-3.0319470	-1.5890970
H	-3.8469440	-1.6359880	1.8107060
C	-3.6161960	-2.0743910	-0.2816020
C	-4.9904930	-2.3338250	-0.4266730
C	-2.8310390	-1.9917020	-1.4414610
C	-5.5640920	-2.5074540	-1.6880920
H	-5.6173290	-2.4003680	0.4591290
C	-3.4053160	-2.1581620	-2.7069680
H	-1.7655090	-1.8051000	-1.3724070
C	-4.7715980	-2.4180150	-2.8371270
H	-6.6283620	-2.7077850	-1.7719370
H	-2.7779990	-2.0859530	-3.5908490
H	-5.2142220	-2.5474250	-3.8202870
H	5.0942590	0.2672730	0.8143140
O	6.1335020	0.4388930	0.8125370
C	6.6477480	0.4860620	-0.3860950
C	8.1788560	0.7499210	-0.3142150

O	6.0891410	0.3512460	-1.4577040
F	8.8076550	-0.2336760	0.3703100
F	8.4414450	1.9186180	0.3145690
F	8.7236720	0.8106880	-1.5401960

Hydrolysis of chloroiminium ion (TS6)

Conformation name	Extrapolated Free energy (kcal/mol)		
TS6-lowest	0.0		
1	3.7		
2	5.6		
3	4.5		
4	4.0		
5	2.6		
6	2.0		
7	1.6		
8	1.1		
9	2.2		
10	2.6		
TS6-lowest.log			
Potential Energy = -1949.25117			
Zero-point Energy = -1948.78680			
Free Energy = -1948.83082			
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.74621			
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.32585			
Nimag = 1 (-334.7303 cm ⁻¹)			
Charge = 0 Multiplicity = 1			
C	2.8955910	-0.0482040	0.1680960
C	3.3827080	-1.9184980	-1.1956040
C	1.9931950	-2.1754130	-0.6106640
N	1.6500630	-0.8319040	-0.0725290
N	3.8134410	-0.7085280	-0.7701720
O	3.9865730	-2.6754010	-1.9565940
C	4.9835810	-0.0681420	-1.3674970
H	5.9142360	-0.3904180	-0.8932950
H	5.0215260	-0.3365020	-2.4254350
H	4.8913790	1.0142570	-1.2740780
C	0.3887410	-0.3649380	-0.0606740
C	0.1073720	1.1334310	-0.1578130
C	-1.3636050	1.5186740	0.0527000
H	-1.9841560	0.9700550	-0.6619880
H	-1.6355370	1.1772550	1.0552300
C	1.0347960	-2.7372850	-1.6557870
H	1.4825630	-3.6488260	-2.0586000
H	0.0663930	-2.9980050	-1.2235440
H	0.8823480	-2.0347010	-2.4804220
H	2.0900890	-2.8953500	0.2117130
C	3.4022340	-0.0169090	1.6545150
H	2.7442570	0.9815200	-0.1670940
C	4.8005240	0.6392610	1.7010610
H	5.0824460	0.8027360	2.7458240
H	5.5691920	0.0069530	1.2516840
H	4.8125070	1.6144620	1.2017180
C	2.4570170	0.8579320	2.5045900
H	2.4396960	1.8923230	2.1418340
H	1.4316250	0.4833980	2.5301740
H	2.8194450	0.8834030	3.5370200
C	3.4983560	-1.4298860	2.2579750
H	4.1547930	-2.0786350	1.6690970
H	3.9174040	-1.3691500	3.2671700
H	2.5206820	-1.9141480	2.3442290
H	0.7495260	1.7083960	0.5061280
C	-1.6284650	3.0082380	-0.0467960
C	-1.2175730	3.8732190	0.9799540

C	-2.3010370	3.5493270	-1.1511980
C	-1.4610340	5.2467510	0.8984580
H	-0.7111170	3.4708650	1.8542360
C	-2.5508290	4.9230530	-1.2345340
H	-2.6327820	2.8924230	-1.9507320
C	-2.1285540	5.7765510	-0.2111940
H	-1.1371220	5.9003740	1.7033080
H	-3.0750960	5.3236820	-2.0974100
H	-2.3223280	6.8433720	-0.2739470
Cl	0.6329890	1.6004930	-1.8595830
H	-0.3149590	-0.9651320	-0.6304690
O	-0.3816310	-0.7214830	1.5286200
H	-1.4001990	-1.1730380	1.4189980
H	0.1793360	-1.3944580	1.9462030
O	-2.6177710	-1.6904950	1.3615540
C	-3.0128880	-2.0296770	0.1949010
C	-4.4366550	-2.6675900	0.2143890
O	-2.4311580	-1.9202830	-0.8863440
F	-4.4504550	-3.8032910	0.9579780
F	-5.3480060	-1.8221440	0.7573920
F	-4.8760320	-2.9912920	-1.0179130

l.log
Potential Energy = -1949.24688
Zero-point Energy = -1948.78171
Free Energy = -1948.82596
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.74093
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.32002
Nimag = 1 (-222.3064 cm⁻¹)
Charge = 0 Multiplicity = 1

C	3.0208430	-0.1564760	-0.3326480
C	3.1710770	-2.4505080	0.1991190
C	2.3387470	-1.7907600	1.3046420
N	1.9540580	-0.4993170	0.6548990
N	3.4969950	-1.4971020	-0.7045160
O	3.4782950	-3.6414590	0.1470840
C	4.1596550	-1.8173120	-1.9646690
H	5.2488800	-1.8254910	-1.8643290
H	3.8326560	-2.8093020	-2.2825050
H	3.8746640	-1.0841330	-2.7208260
C	0.6660350	-0.1588130	0.5356160
C	0.1764590	1.2384760	0.1499530
C	-1.2988920	1.4475700	0.5316560
H	-1.9314590	0.7816770	-0.0621500
H	-1.3911670	1.1348680	1.5795980
C	1.2203870	-2.6786750	1.8308400
H	1.6858710	-3.5930820	2.2063740
H	0.6935940	-2.2100730	2.6663900
H	0.5058540	-2.9577900	1.0545510
H	3.0121430	-1.5551160	2.1350460
C	4.1332430	0.8105020	0.2084680
H	2.5605610	0.3109390	-1.2034170
C	5.0865100	1.1468360	-0.9614250
H	5.7781930	1.9344450	-0.6468720
H	5.6897250	0.2882190	-1.2650900
H	4.5414120	1.5148480	-1.8378080
C	3.4841760	2.1226040	0.6912930
H	2.9192600	2.6158190	-0.1067560
H	2.8267270	1.9556680	1.5500300
H	4.2667610	2.8169710	1.0124960
C	4.9527010	0.2031550	1.3631570
H	5.3777320	-0.7702360	1.0990350
H	5.7870630	0.8708500	1.6006720
H	4.3591150	0.0950540	2.2758340
H	0.8025100	1.9552700	0.6811980
C	-1.7722000	2.8813410	0.3998400
C	-1.3470770	3.8606940	1.3116490
C	-2.6546460	3.2536400	-0.6237390
C	-1.7839230	5.1827580	1.1956740
H	-0.6768810	3.5889210	2.1239640
C	-3.0964840	4.5755080	-0.7413250
H	-2.9998130	2.5051310	-1.3315270
C	-2.6602420	5.5445530	0.1666020
H	-1.4464960	5.9268450	1.9114150

H	-3.7813710	4.8451910	-1.5400890
H	-3.0035870	6.5710800	0.0776080
H	0.0547610	-0.5798070	1.3258100
O	-0.1160670	-1.2443160	-0.7628840
H	-0.2406990	-0.7564940	-1.5941480
H	-1.0555830	-1.6722160	-0.4765930
O	-2.2140850	-2.3383180	-0.0336620
C	-3.3264630	-1.8800520	-0.4501430
O	-3.5552820	-0.9059090	-1.1729060
C	-4.5429530	-2.7096330	0.0738980
F	-4.4369140	-4.0189620	-0.2694920
F	-4.6195250	-2.6590390	1.4301720
F	-5.7248240	-2.2692010	-0.4055400
Cl	0.4281750	1.6405450	-1.6216870

2.log
Potential Energy = -1949.24102
Zero-point Energy = -1948.77561
Free Energy = -1948.81978
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.73822
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.31697
Nimag = 1 (-192.4248 cm⁻¹)
Charge = 0 Multiplicity = 1

C	2.8894970	0.4179300	0.3334400
C	1.9558430	2.4592440	-0.3999840
C	1.7478320	1.4390170	-1.5255110
N	1.9463970	0.1504670	-0.7949480
N	2.5694180	1.8239840	0.6266920
O	1.6198690	3.6430760	-0.4302890
C	2.7918360	2.4695610	1.9160210
H	3.7414650	3.0121030	1.9444520
H	1.9807310	3.1797810	2.0874890
H	2.7844320	1.7167250	2.7058150
C	0.9881180	-0.7810200	-0.7533630
C	1.2649510	-2.2372670	-0.3661630
C	0.2700700	-3.2468120	-0.9773750
H	0.3833770	-3.1507590	-2.0636930
H	0.6469790	-4.2403780	-0.7169870
C	0.4550880	1.6231910	-2.3043350
H	0.4854960	2.6240780	-2.7422440
H	0.3830250	0.9072500	-3.1277170
H	-0.4374990	1.5607890	-1.6797890
H	2.5841280	1.5426380	-2.2243130
C	4.4055310	0.1416630	0.0270390
H	2.5936490	-0.1983500	1.1833380
C	5.1935200	0.3079790	1.3473810
H	6.2282490	-0.0129210	1.1920110
H	5.2235470	1.3459740	1.6862210
H	4.7725200	-0.3062330	2.1510700
C	4.5844710	-1.3108130	-0.4568240
H	4.2292000	-2.0344590	0.2842180
H	4.0734040	-1.4852690	-1.4088790
H	5.6485190	-1.5091650	-0.6190590
C	4.9952690	1.0951550	-1.0304710
H	4.8283590	2.1467100	-0.7775010
H	6.0774120	0.9402260	-1.0881030
H	4.5916740	0.9035200	-2.0291240
H	2.2465620	-2.4731730	-0.7744000
C	-1.1977920	-3.1367630	-0.6131450
C	-1.6901780	-3.6668010	0.5920030
C	-2.1074970	-2.5447310	-1.5034050
C	-3.0496080	-3.5831160	0.9068390
H	-1.0111460	-4.1593760	1.2810550
C	-3.4681320	-2.4641760	-1.1930640
H	-1.7536540	-2.1532530	-2.4538320
C	-3.9428200	-2.9790660	0.0163960
H	-3.4107550	-3.9992230	1.8428030
H	-4.1543180	-2.0031770	-1.8973560
H	-4.9996240	-2.9190220	0.2590010
H	0.3030960	-0.7143960	-1.5913040
O	-0.2605370	-0.2465070	0.5422210
H	-0.6111020	-0.9975070	1.0487370
H	-1.0955650	0.3295850	0.2269110
O	-2.1910560	1.1610540	-0.1716250

C	-3.0805160	1.3804530	0.7112190
O	-3.1585750	0.9743680	1.8743230
C	-4.2183640	2.3154250	0.1853990
F	-3.7302810	3.5353450	-0.1625320
F	-4.8156700	1.7974860	-0.9195600
F	-5.1910690	2.5251690	1.0974720
Cl	1.4641170	-2.5203600	1.4324080

3.log
Potential Energy = -1949.24357
Zero-point Energy = -1948.77902
Free Energy = -1948.82349
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.73882
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.31874
Nimag = 1 (-270.5133 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-1.0258770	-1.7574150	-0.5882850
C	-2.5649860	-2.3536380	1.1003070
C	-1.1685940	-2.6872120	1.6360520
N	-0.2976520	-1.9019590	0.7074530
N	-2.4216590	-1.8005640	-0.1259950
O	-3.6259040	-2.5546840	1.6927850
C	-3.5519460	-1.2590890	-0.8716840
H	-4.0326460	-2.0191450	-1.4949580
H	-4.2838410	-0.8824680	-0.1551640
H	-3.2093260	-0.4357180	-1.4991950
C	0.5927710	-1.0273360	1.1904650
C	1.7553820	-0.4376040	0.3920710
C	2.8097950	0.2101550	1.3102420
H	2.4040620	1.1214370	1.7583460
H	2.9964970	-0.4990320	2.1259030
C	-1.0157840	-2.4335390	3.1292590
H	-1.7885120	-3.0167270	3.6359260
H	-0.0464630	-2.7799600	3.4978110
H	-1.1534250	-1.3813000	3.3851330
H	-0.9830910	-3.7495530	1.4444520
C	-0.6641210	-2.8335330	-1.6760540
H	-0.8191030	-0.7689580	-0.9999490
C	-1.3379500	-2.4165650	-3.0040180
H	-0.9894480	-3.0733930	-3.8071530
H	-2.4261660	-2.5016850	-2.9651640
H	-1.0816740	-1.3879640	-3.2810550
C	0.8605180	-2.8579410	-1.9019750
H	1.2405750	-1.8840450	-2.2257070
H	1.3964690	-3.1740110	-1.0018810
H	1.0963460	-3.5787670	-2.6911660
C	-1.1329990	-4.2516540	-1.2965740
H	-2.2003500	-4.2845640	-1.0574080
H	-0.9661320	-4.9233450	-2.1447860
H	-0.5700270	-4.6585360	-0.4511880
H	2.2119870	-1.2757470	-0.1375880
C	4.1206840	0.5205640	0.6156410
C	5.0060650	-0.5147710	0.2764800
C	4.4806480	1.8406750	0.3121540
C	6.2172150	-0.2379420	-0.3625780
H	4.7526000	-1.5438700	0.5202600
C	5.6939210	2.1219210	-0.3244250
H	3.8098290	2.6539250	0.5754930
C	6.5644660	1.0830850	-0.6659500
H	6.8913260	-1.0510600	-0.6158380
H	5.9570950	3.1510770	-0.5509040
H	7.5075280	1.3000350	-1.1589600
H	0.9192290	-1.2943370	2.1892300
O	-0.3467970	0.4513560	1.8041540
H	-1.0017590	0.9784800	1.1236980
O	-1.9211670	1.6449010	0.3228360
C	-1.8718290	2.9096320	0.4609950
O	-1.1483910	3.5917820	1.1927050
C	-2.8964960	3.6489300	-0.4579750
F	-2.6502070	3.3956360	-1.7701490
F	-4.1684320	3.2443360	-0.2071050
F	-2.8691780	4.9887960	-0.3016830
Cl	1.2651020	0.7311390	-0.9157250
H	0.1999970	1.1214450	2.2446370

4.log
Potential Energy = -1949.24205
Zero-point Energy = -1948.77664
Free Energy = -1948.82065
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.74090
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.31950
Nimag = 1 (-226.1030 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-2.1799620	-0.6944740	-0.3179740
C	-2.5365210	-0.4004970	1.9976650
C	-1.7824220	-1.7241620	1.8336030
N	-1.2595600	-1.5969300	0.4384980
N	-2.6916310	0.1501390	0.7717890
O	-2.9246590	0.0731650	3.0661610
C	-3.2666740	1.4778340	0.5873060
H	-4.3567080	1.4420440	0.5000260
H	-3.0063060	2.0846810	1.4559160
H	-2.8420720	1.9345710	-0.3068840
C	0.0427710	-1.7568460	0.1799630
C	0.6106880	-1.9775460	-1.2232280
C	1.9645790	-2.7226070	-1.2262990
H	1.7540690	-3.7192350	-0.8207040
H	2.2324720	-2.8685850	-2.2768030
C	-0.7716530	-1.9837110	2.9421950
H	-1.3144500	-1.9404370	3.8895360
H	-0.3316500	-2.9810220	2.8592980
H	0.0203850	-1.2328760	2.9613130
H	-2.5213550	-2.5326060	1.8394900
C	-3.2971000	-1.4262030	-1.1489710
H	-1.5880560	-0.0798430	-0.9986840
C	-4.0350890	-0.3656330	-1.9990490
H	-4.7220800	-0.8700230	-2.6857140
H	-4.6300380	0.3185530	-1.3905490
H	-3.3375500	0.2258420	-2.6022630
C	-2.6576400	-2.4435440	-2.1139820
H	-1.9538970	-1.9651610	-2.8032430
H	-2.1500020	-3.2492310	-1.5746600
H	-3.4419810	-2.9051150	-2.7219140
C	-4.3197010	-2.1607290	-0.2605380
H	-4.7681310	-1.4999480	0.4875970
H	-5.1309950	-2.5425520	-0.8885100
H	-3.8776180	-3.0218100	0.2495580
H	-0.0993260	-2.6187570	-1.7431020
C	3.1313380	-2.1151880	-0.4709920
C	3.9040900	-1.0804490	-1.0276980
C	3.4904780	-2.6104200	0.7943260
C	4.9901790	-0.5448970	-0.3291480
H	3.6603590	-0.6985030	-2.0140380
C	4.5778110	-2.0772280	1.4933770
H	2.9246100	-3.4290910	1.2319000
C	5.3290210	-1.0398070	0.9342990
H	5.5742850	0.2540050	-0.7760850
H	4.8383330	-2.4765860	2.4689980
H	6.1750980	-0.6252430	1.4739980
H	0.5262590	-2.3999200	0.9056910
O	0.9643160	-0.2601940	0.8207230
H	0.6103050	0.7067270	0.5360940
O	0.1151090	2.0083910	0.2583510
C	1.0082980	2.9068060	0.1521450
O	2.2356470	2.8181320	0.2591870
C	0.4007380	4.3131030	-0.1614240
F	-0.3109920	4.2967090	-1.3192720
F	-0.4489270	4.7140430	0.8205070
F	1.3379890	5.2760880	-0.2891350
Cl	0.6801800	-0.4717460	-2.2509480
H	1.9059950	-0.3029650	0.5801070

5.log
Potential Energy = -1949.24618
Zero-point Energy = -1948.78104
Free Energy = -1948.82472
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.74322

Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.32175
Nimag = 1 (-261.7286 cm⁻¹)
Charge = 0 Multiplicity = 1

C	2.9130930	-0.0045410	-0.0920550
C	3.3528360	2.3167710	0.0171920
C	1.8725980	2.1869440	-0.3446230
N	1.6263550	0.7482990	-0.0568310
N	3.8649320	1.0768240	0.1937540
O	3.9603010	3.3781240	0.1616750
C	5.1741910	0.8773790	0.8121020
H	5.9855310	0.9279140	0.0815060
H	5.3272350	1.6613040	1.5568300
H	5.1966090	-0.0955330	1.3039560
C	0.4398440	0.3006290	0.3898440
C	0.3506340	-0.9335190	1.2841040
C	-1.0789220	-1.4551230	1.5609090
H	-1.1249700	-1.7122400	2.6226890
H	-1.8014300	-0.6489030	1.4104100
C	1.0145490	3.1766990	0.4371680
H	1.3990460	4.1788810	0.2336520
H	-0.0321160	3.1456320	0.1275200
H	1.0752710	2.9964620	1.5145210
H	1.7561740	2.3802580	-1.4183320
C	3.2042930	-0.7875680	-1.4225410
H	2.9403480	-0.7143830	0.7397360
C	4.6610840	-1.3023960	-1.4017620
H	4.8111240	-1.9806740	-2.2474530
H	5.3863890	-0.4919740	-1.5012500
H	4.8851950	-1.8630110	-0.4876340
C	2.2824660	-2.0218270	-1.5058310
H	2.4637610	-2.7092110	-0.6715170
H	1.2207910	-1.7672840	-1.5166500
H	2.4932970	-2.5696860	-2.4294300
C	3.0131610	0.0998790	-2.6659650
H	3.6448250	0.9932310	-2.6282170
H	3.2938820	-0.4617060	-3.5623170
H	1.9740190	0.4174260	-2.7991630
H	0.9896640	-1.7379410	0.9288470
C	-1.4712070	-2.6872470	0.7607090
C	-2.5808210	-2.6721500	-0.0951540
C	-0.7622570	-3.8893330	0.9177100
C	-2.9690720	-3.8255940	-0.7848010
H	-3.1415990	-1.7518920	-0.2297660
C	-1.1430430	-5.0419480	0.2257180
H	0.0884920	-3.9334050	1.5939550
C	-2.2495100	-5.0137030	-0.6300660
H	-3.8321780	-3.7925870	-1.4436540
H	-0.5814350	-5.9618350	0.3613150
H	-2.5491100	-5.9094480	-1.1662420
Cl	1.1214350	-0.3854150	2.8696480
H	-0.2478580	1.0856020	0.6917810
O	-0.5755970	-0.2415570	-0.9932330
H	-1.5668580	0.2344320	-0.9924020
H	-0.1198490	0.0683590	-1.7921080
O	-2.8076090	0.7835340	-1.0505970
C	-3.0748940	1.6554160	-0.1587290
C	-4.4958080	2.2745060	-0.3404560
O	-2.3806380	2.0434650	0.7848240
F	-4.6188110	2.8718620	-1.5529300
F	-5.4578980	1.3198830	-0.2651350
F	-4.7820250	3.2038370	0.5930370

6.log
Potential Energy = -1949.24682
Zero-point Energy = -1948.78252
Free Energy = -1948.82707
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.74236
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.32261
Nimag = 1 (-303.8552 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-2.9405970	0.4737770	0.2440760
C	-2.8819030	0.9851190	-2.0648600
C	-1.4254360	0.9857490	-1.5957550

N	-1.5491580	0.3158870	-0.2733930
N	-3.6717200	0.6514360	-1.0177150
O	-3.2600850	1.2129770	-3.2138920
C	-5.0774910	0.2991690	-1.2102990
H	-5.7249970	1.1795660	-1.2077020
H	-5.1781350	-0.2040870	-2.1742520
H	-5.3925340	-0.3782380	-0.4161100
C	-0.5742100	-0.4546230	0.2289240
C	-0.8674160	-1.5843140	1.2128260
C	0.3627620	-2.3397080	1.7580610
H	0.9676050	-1.5992500	2.2889220
H	-0.0200850	-3.0316920	2.5136000
C	-0.5054750	0.3051960	-2.6035740
H	-0.6446610	0.8041970	-3.5654110
H	0.5470140	0.4054010	-2.3282680
H	-0.7523290	-0.7532820	-2.7267160
H	-1.0999440	2.0241290	-1.4574770
C	-3.1550860	1.6315330	1.2849350
H	-3.2615610	-0.4656410	0.7011370
C	-4.6705490	1.8369850	1.5075120
H	-4.8163350	2.5326570	2.3395840
H	-5.1606000	2.2685560	0.6322180
H	-5.1775210	0.9019580	1.7689590
C	-2.5486170	1.2230880	2.6441360
H	-3.0248730	0.3157780	3.0333130
H	-1.4705930	1.0531990	2.6074490
H	-2.7213780	2.0205290	3.3731920
C	-2.5458800	2.9619800	0.8069530
H	-2.9685190	3.2786060	-0.1519560
H	-2.7652420	3.7475590	1.5364070
H	-1.4571490	2.9156740	0.7026590
H	-1.4478900	-1.2163930	2.0561320
C	1.2161230	-3.1035780	0.7618300
C	0.9597080	-4.4603290	0.5037550
C	2.2972220	-2.4934280	0.1056830
C	1.7448200	-5.1815540	-0.3993050
H	0.1425850	-4.9573620	1.0184440
C	3.0834560	-3.2121020	-0.8014060
H	2.5473840	-1.4572380	0.3112530
C	2.8078370	-4.5573710	-1.0602520
H	1.5295440	-6.2305130	-0.5817590
H	3.9160800	-2.7204000	-1.2963160
H	3.4208790	-5.1169240	-1.7607500
Cl	-1.9853350	-2.7594940	0.3438450
H	0.1990080	-0.6979050	-0.4906090
O	0.5248390	0.5406790	1.2881700
H	1.5629640	0.6852280	0.9160610
H	0.1557160	1.4394350	1.2851160
O	2.8104600	0.9215060	0.5067550
C	3.0177190	2.1739100	0.3503520
C	4.4692900	2.4793060	-0.1331610
O	2.2419550	3.1146800	0.5252570
F	5.3907580	1.9894600	0.7336870
F	4.7106760	1.9067380	-1.3402620
F	4.7049420	3.7999160	-0.2631600

7.log
Potential Energy = -1949.24800
Zero-point Energy = -1948.78443
Free Energy = -1948.82873
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.74262
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.32334
Nimag = 1 (-448.0910 cm⁻¹)
Charge = 0 Multiplicity = 1

C	2.9079170	-0.0286740	0.1623210
C	3.3687160	-1.9005530	-1.2049060
C	1.9605740	-2.1174130	-0.6485620
N	1.6475950	-0.7660510	-0.1228810
N	3.8233570	-0.7026090	-0.7696180
O	3.9663290	-2.6700060	-1.9588610
C	5.0104370	-0.0825980	-1.3544190
H	5.9320870	-0.4294580	-0.8800600
H	5.0477990	-0.3393980	-2.4153630
H	4.9415650	1.0005520	-1.2489830

C	0.3890350	-0.3032600	-0.0596060
C	0.0963090	1.1970090	-0.1365290
C	-1.3923660	1.5545160	-0.0024100
H	-1.9542800	1.0247860	-0.7770780
H	-1.7395460	1.1681400	0.9602490
C	1.0114650	-2.6471080	-1.7197060
H	1.4448690	-3.5658120	-2.1221630
H	0.0274360	-2.8872250	-1.3117190
H	0.8946040	-1.9323700	-2.5399460
H	2.0109550	-2.8390500	0.1763870
C	3.3937610	-0.0476440	1.6584360
H	2.7976700	1.0128120	-0.1543490
C	4.8425050	0.4841860	1.7301580
H	5.1257640	0.6063630	2.7802100
H	5.5565040	-0.2077990	1.2785590
H	4.9468800	1.4615210	1.2462040
C	2.5185520	0.9010700	2.5011440
H	2.5288260	1.9229800	2.1054120
H	1.4846640	0.5600320	2.5722860
H	2.9047510	0.9426080	3.5240590
C	3.3483450	-1.4642510	2.2594310
H	3.9659480	-2.1658700	1.6890880
H	3.7427710	-1.4403870	3.2804280
H	2.3260380	-1.8503080	2.3077100
H	0.6960140	1.7668180	0.5718530
C	-1.6765610	3.0426860	-0.0620890
C	-1.3082810	3.8813120	1.0018030
C	-2.3275110	3.6067870	-1.1677540
C	-1.5735050	5.2523810	0.9563390
H	-0.8173510	3.4608110	1.8763840
C	-2.5989850	4.9781270	-1.2151830
H	-2.6249200	2.9701040	-1.9966220
C	-2.2199510	5.8056510	-0.1543780
H	-1.2824920	5.8856990	1.7894470
H	-3.1058840	5.3970480	-2.0797100
H	-2.4304160	6.8705560	-0.1893160
Cl	0.6923570	1.7302100	-1.7946690
H	-0.3206270	-0.8911660	-0.6348510
O	-0.3374150	-0.8133460	1.4866310
H	-1.3709470	-1.2809390	1.3952960
H	-0.3429530	-0.1420810	2.1864500
O	-2.5296390	-1.8511860	1.3516070
C	-2.9676010	-2.1039460	0.1762180
C	-4.3733550	-2.7790850	0.2050100
O	-2.4373600	-1.8859350	-0.9134890
F	-4.3432900	-3.9443670	0.8988200
F	-5.2876460	-1.9769450	0.8065240
F	-4.8362640	-3.0590540	-1.0289010

8.log
Potential Energy = -1949.24828
Zero-point Energy = -1948.78306
Free Energy = -1948.82687
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.74551
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.32411
Nimag = 1 (-221.1495 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-2.7520840	0.0407560	0.3317730
C	-2.9423950	2.2811700	-0.3972320
C	-1.4443950	1.9729000	-0.3778850
N	-1.4544570	0.4930800	-0.2443250
N	-3.6196960	1.1606140	-0.0575620
O	-3.4430200	3.3602300	-0.7171940
C	-5.0618980	1.0528570	-0.2684670
H	-5.6321140	1.4602920	0.5702050
H	-5.3217270	1.6122140	-1.1698030
H	-5.3300520	0.0048340	-0.4058150
C	-0.4720850	-0.2775020	-0.7309370
C	-0.7578620	-1.6950240	-1.2367380
C	0.4531090	-2.4765850	-1.7917240
H	0.0428870	-3.2423630	-2.4561450
H	1.0544420	-1.8089630	-2.4161450
C	-0.7551050	2.5157850	-1.6273950
H	-0.9575430	3.5883630	-1.6775630

H	0.3275260	2.3783790	-1.5911680
H	-1.1503060	2.0475530	-2.5339390
H	-0.9969290	2.4292640	0.5137080
C	-2.7456920	-0.2620930	1.8744650
H	-3.0883120	-0.8563390	-0.1961120
C	-4.2010170	-0.4210900	2.3676120
H	-4.1873680	-0.7766740	3.4026310
H	-4.7476110	0.5244970	2.3553730
H	-4.7582880	-1.1561430	1.7763100
C	-2.0200030	-1.5982810	2.1338040
H	-2.4996190	-2.4236640	1.5936160
H	-0.9654180	-1.5541270	1.8595070
H	-2.0726690	-1.8367890	3.2010590
C	-2.0666010	0.8640110	2.6750150
H	-2.5543730	1.8305890	2.5096810
H	-2.1369080	0.6438640	3.7451400
H	-1.0056180	0.9555210	2.4266350
H	-1.2996630	-2.2840890	-0.4990710
C	1.3315240	-3.1674400	-0.7607330
C	2.6907980	-2.8338140	-0.6410010
C	0.8166880	-4.1916750	0.0536830
C	3.5134090	-3.4975110	0.2777680
H	3.1107070	-2.0575950	-1.2754600
C	1.6352660	-4.8520130	0.9711460
H	-0.2266410	-4.4827500	-0.0364080
C	2.9867260	-4.5052530	1.0876980
H	4.5617920	-3.2254820	0.3538620
H	1.2204940	-5.6409720	1.5913840
H	3.6221890	-5.0209210	1.8012160
Cl	-1.9373770	-1.4656400	-2.6332270
H	0.2284320	0.2620050	-1.3607740
O	0.6984830	-0.5791320	0.6048750
H	1.3553260	0.2774960	0.7299370
H	1.2797140	-1.3447370	0.4289420
O	2.2248110	1.3233300	0.9756600
C	2.8150090	1.7834240	-0.0560900
C	3.8855480	2.8628690	0.3018100
O	2.6474090	1.4987070	-1.2453620
F	3.3212480	3.9195310	0.9417010
F	4.8367240	2.3577130	1.1285530
F	4.5205880	3.3492800	-0.7842530

9.log
Potential Energy = -1949.24741
Zero-point Energy = -1948.78399
Free Energy = -1948.82843
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.74140
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.32242
Nimag = 1 (-442.2547 cm⁻¹)
Charge = 0 Multiplicity = 1

C	2.7191600	-0.2041100	0.7638350
C	4.5393150	-0.4094500	-0.7304020
C	3.2870380	-0.7790120	-1.5292260
N	2.2186010	-0.2645920	-0.6368800
N	4.1609790	-0.0529110	0.5187420
O	5.6902090	-0.4035680	-1.1688430
C	5.0897000	0.6031930	1.4366960
H	5.6944710	-0.1171470	1.9936510
H	5.7578550	1.2418880	0.8548840
H	4.5282460	1.2174800	2.1412870
C	1.0497860	0.1802760	-1.1105650
C	0.2225040	1.2251810	-0.3623110
C	-1.0819220	1.6098090	-1.0771300
H	-0.8377930	2.0020550	-2.0691950
H	-1.6548270	0.6911020	-1.2229420
C	3.3176910	-0.1930320	-2.9368540
H	4.2447510	-0.5220110	-3.4121450
H	2.4869260	-0.5555120	-3.5472160
H	3.3087010	0.9007960	-2.9208440
H	3.2213820	-1.8718660	-1.5968500
C	2.3445550	-1.4249090	1.6782770
H	2.3495210	0.7092380	1.2379090
C	3.1501070	-1.3364480	2.9932920
H	2.7791680	-2.0952670	3.6893110

H	4.2142740	-1.5282020	2.8390160
H	3.0365970	-0.3612300	3.4798250
C	0.8489760	-1.3486350	2.0427710
H	0.6065240	-0.4077350	2.5507890
H	0.2035610	-1.4609390	1.1715990
H	0.6011230	-2.1622770	2.7317340
C	2.6415290	-2.7723860	0.9956000
H	3.6954250	-2.8610240	0.7113130
H	2.4233130	-3.5885240	1.6919460
H	2.0195340	-2.9207890	0.1081810
H	0.0328310	0.9272360	0.6675390
C	-1.9341110	2.6037630	-0.3125270
C	-2.6262310	2.2044080	0.8420910
C	-2.0637910	3.9292710	-0.7492050
C	-3.4185540	3.1122510	1.5495010
H	-2.5550530	1.1745880	1.1833240
C	-2.8597340	4.8396890	-0.0461910
H	-1.5403700	4.2519990	-1.6451920
C	-3.5370750	4.4345100	1.1074780
H	-3.9487220	2.7853240	2.4394210
H	-2.9493680	5.8625250	-0.4007170
H	-4.1561360	5.1398330	1.6542000
Cl	1.2926670	2.7199000	-0.2376770
H	1.0602780	0.3494780	-2.1816800
O	-0.0940980	-1.2212090	-1.2173520
H	-1.0842360	-1.3713070	-0.6763750
H	-0.2685590	-1.4000370	-2.1554150
O	-2.1971090	-1.5884870	-0.0599540
C	-3.0439210	-2.2483560	-0.7601000
C	-4.3666850	-2.5177610	0.0216830
O	-2.9413380	-2.6622300	-1.9133620
F	-4.1281640	-3.1660360	1.1887880
F	-4.9941230	-1.3541380	0.3297630
F	-5.2369520	-3.2677160	-0.6823350

10.log
Potential Energy = -1949.24591
Zero-point Energy = -1948.78201
Free Energy = -1948.82618
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.74144
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.32170
Nimag = 1 (-480.8318 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-2.7588980	-0.9998410	-0.4688040
C	-4.0750940	-0.1463160	1.3005930
C	-2.6173310	0.0506980	1.7218570
N	-1.9155980	-0.1633540	0.4306890
N	-4.0944050	-0.6870590	0.0607950
O	-5.0595890	0.1724430	1.9684750
C	-5.3263020	-0.7439100	-0.7235560
H	-5.9172790	-1.6347300	-0.4958340
H	-5.9250670	0.1395320	-0.4916000
H	-5.0789990	-0.7420730	-1.7854880
C	-0.7534060	0.4303280	0.1428800
C	-0.3340510	0.7367420	-1.2920280
C	1.0309720	1.4347470	-1.4615320
H	1.8008310	0.7012580	-1.2102090
H	1.1360220	1.6355690	-2.5315880
C	-2.3968440	1.4096950	2.3784540
H	-3.1045950	1.4961120	3.2062730
H	-1.3902680	1.5062580	2.7925700
H	-2.5824350	2.2299890	1.6789670
H	-2.3461140	-0.7414290	2.4307560
C	-2.4185860	-2.5334610	-0.4988370
H	-2.6899590	-0.6104470	-1.4880270
C	-3.5427690	-3.2837490	-1.2469370
H	-3.2338690	-4.3221150	-1.4024100
H	-4.4758340	-3.3026860	-0.6793140
H	-3.7410070	-2.8493240	-2.2330470
C	-1.1094210	-2.7527310	-1.2842360
H	-1.1871640	-2.3644030	-2.3069480
H	-0.2531070	-2.2940500	-0.7885340
H	-0.9086340	-3.8262950	-1.3597700
C	-2.2787080	-3.1220070	0.9166820

H	-3.1879310	-2.9757700	1.5094400
H	-2.1066150	-4.2009600	0.8469300
H	-1.4303620	-2.6873880	1.4528750
H	-0.3497050	-0.1607460	-1.9075220
C	1.2595780	2.7116390	-0.6742950
C	0.9303120	3.9625380	-1.2214220
C	1.8394010	2.6762270	0.6045850
C	1.1538880	5.1411760	-0.5044240
H	0.5029750	4.0149090	-2.2183490
C	2.0635900	3.8533130	1.3256700
H	2.1336010	1.7237870	1.0362520
C	1.7172220	5.0902570	0.7746930
H	0.8937810	6.0981570	-0.9476660
H	2.5156070	3.8019530	2.3120030
H	1.8942790	6.0059040	1.3312770
Cl	-1.6559370	1.8111550	-1.9963600
H	-0.4911890	1.2201740	0.8369330
O	0.5996500	-0.6804320	0.6471830
H	1.6280550	-0.9291430	0.2162200
H	0.6982530	-0.6068590	1.6091220
O	2.7653220	-1.2725730	-0.2645030
C	3.6354640	-1.5504090	0.6354870
C	5.0010960	-1.9778990	0.0144600
O	3.5215070	-1.5211930	1.8589030
F	4.8612370	-3.0838800	-0.7590820
F	5.5096920	-0.9981260	-0.7740550
F	5.9270600	-2.2591190	0.9518270

Hydrolysis of chloroiminium ion (TS6')

Conformation name	Extrapolated Free energy (kcal/mol)		
TS6'-lowest	0.0		
1	0.3		
2	0.4		
3	1.3		
4	1.4		
5	7.8		
TS6'-lowest.log			
Potential Energy = -1949.24993			
Zero-point Energy = -1948.78615			
Free Energy = -1948.83066			
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.74410			
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.32483			
Nimag = 1 (-394.5465 cm ⁻¹)			
Charge = 0 Multiplicity = 1			
C	3.3143630	-0.3728650	-0.6322180
C	3.2125240	-1.5659510	1.3980330
C	2.1441210	-0.4717540	1.5097160
N	2.0901440	0.0360690	0.1147710
N	3.7866740	-1.4968120	0.1760890
O	3.4749480	-2.3887490	2.2755060
C	4.6968430	-2.5351590	-0.2987110
H	4.3712660	-3.4922370	0.1136690
H	4.6585420	-2.5796420	-1.3876470
H	5.7273660	-2.3525940	0.0185900
C	1.0189370	0.4459970	-0.5736820
H	1.2718860	0.7991990	-1.5674850
C	-0.1277950	1.2342110	0.0631440
C	-1.0601490	1.8436440	-0.9957120
H	-0.4865610	2.5379880	-1.6176840
H	2.5302590	0.3220860	2.1602310
C	4.3516930	0.7887180	-0.8216370
H	3.0173970	-0.7425430	-1.6204870
H	-0.6905590	0.6171060	0.7587660
Cl	0.5938430	2.5687080	1.0954060
C	0.8632590	-1.0367110	2.1229130
H	0.1755740	-0.2500000	2.4352360

H	0.3536080	-1.7290030
H	1.1564220	-1.5885800
C	5.5659580	0.2606790
H	6.2166290	1.1010970
H	6.1665320	-0.4462110
H	5.2607990	-0.2232420
C	4.8261780	1.3480660
H	5.2812280	0.5723990
H	5.5830090	2.1208340
H	4.0048160	1.8103470
C	3.7060300	1.9234310
H	3.3310080	1.5645590
H	2.8895930	2.4124660
H	4.4590870	2.6897270
H	-1.3835220	1.0220180
C	-2.2810110	2.5367470
C	-2.4289480	3.9267900
C	-3.2947930	1.7937010
C	-3.5604550	4.5649000
H	-1.6555240	4.5148890
C	-4.4239530	2.4285480
H	-3.2042640	0.7128080
C	-4.5603050	3.8175490
H	-3.6583100	5.6431720
H	-5.1991690	1.8385410
H	-5.4396750	4.3108730
O	0.1195270	-1.0138210
H	-0.8530080	-1.3550020
O	-1.9392930	-1.7639340
C	-2.7419960	-2.4054470
O	-2.6442510	-2.6474990
C	-3.9949680	-2.9254450
F	-4.6747740	-1.9043110
F	-3.6378220	-3.7824230
F	-4.8601210	-3.5780190
H	-0.0036890	-0.9769930

l.log
Potential Energy = -1949.24780
Zero-point Energy = -1948.78402
Free Energy = -1948.82865
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.74365
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.32449
Nimag = 1 (-416.3740 cm⁻¹)
Charge = 0 Multiplicity = 1

C	2.4085910	-1.2682910
C	1.8237410	-3.2259470
C	1.2459380	-2.0655920
N	1.4125200	-0.9247690
N	2.4051040	-2.7299470
O	1.7384640	-4.4161160
C	2.8645740	-3.6046480
H	2.1963810	-4.4666190
H	2.8290250	-3.0639740
H	3.8830810	-3.9640470
C	0.5769410	0.1005620
H	0.9545620	0.8094490
C	-0.2127310	0.7610050
C	-0.9287320	2.0704680
H	1.8917130	-1.9038330
C	3.8117260	-0.6019720
H	2.0172360	-0.9492180
H	-0.9588090	0.0779200
Cl	0.9299800	1.0520030
C	-0.1633820	-2.4072350
H	-0.5072360	-1.7259000
H	-0.8850210	-2.4303240
H	-0.1146250	-3.4070020
C	4.7518600	-1.0109970
H	5.6766170	-0.4293010
H	5.0296730	-2.0662390
H	4.3042430	-0.8080960
C	4.4340590	-1.0219860
H	4.5459410	-2.1085090

H	5.4315960	-0.5811980	0.8813120
H	3.8387140	-0.6700930	1.6345050
C	3.6599670	0.9330980	-0.5938750
H	3.1972880	1.2756090	-1.5270450
H	3.0769270	1.3115530	0.2497090
H	4.6508060	1.3942090	-0.5342400
H	-1.7321960	1.7871540	0.1223100
O	-0.7977950	-0.4820210	-0.9598230
H	-1.8548720	-0.5849260	-0.5641110
O	-3.0320940	-0.7513090	-0.0518260
C	-4.0045460	-0.5508810	-0.8613790
O	-3.9757840	-0.2134940	-2.0432090
C	-5.3884060	-0.7935710	-0.1824690
F	-5.5467530	-0.0064180	0.9110420
F	-5.5093480	-2.0812240	0.2295730
F	-6.4206280	-0.5399710	-1.0108070
H	-0.8313520	-0.0053840	-1.8040330
H	-1.4169280	2.4377180	1.7162530
C	-0.0911210	3.1701530	0.1854960
C	0.6317820	4.0736720	0.9823320
C	-0.0507990	3.3328760	-1.2086140
C	1.3907520	5.0926430	0.4009740
H	0.5936090	3.9848550	2.0635570
C	0.7083190	4.3509880	-1.7945860
H	-0.6349420	2.6733620	-1.8454350
C	1.4362050	5.2317290	-0.9902930
H	1.9402540	5.7822620	1.0352860
H	0.7217940	4.4588310	-2.8752310
H	2.0232990	6.0262750	-1.4413900

2.log
Potential Energy = -1949.24751
Zero-point Energy = -1948.78376
Free Energy = -1948.82843
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.74337
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.32429
Nimag = 1 (-381.0451 cm⁻¹)
Charge = 0 Multiplicity = 1

C	2.1176430	0.9731310	0.9323700
C	3.4741420	2.0704710	-0.6512730
C	2.9562280	0.8109220	-1.3558230
N	1.9210180	0.3366280	-0.4023190
N	2.9276180	2.1399490	0.5825520
O	4.2364400	2.8965920	-1.1538200
C	3.0703450	3.3316330	1.4140100
H	3.0879320	4.2058710	0.7602430
H	2.2190100	3.4043340	2.0916260
H	3.9953030	3.3154590	1.9972570
C	0.7416970	-0.2323160	-0.6831590
H	0.1823960	-0.4968330	0.2072320
C	0.5574570	-1.2317880	-1.8265640
C	-0.8068230	-1.9555910	-1.8325960
H	3.7680970	0.0749140	-1.3947380
C	2.7642150	0.0179260	1.9960390
H	1.1456450	1.3114200	1.3091390
H	0.6866500	-0.7441760	-2.7898130
Cl	1.9304330	-2.4460640	-1.7602710
C	2.5255170	1.1497470	-2.7833510
H	2.3578600	0.2582720	-3.3884890
H	1.6393100	1.7885790	-2.8021460
H	3.3488950	1.7037600	-3.2407800
C	2.8857650	0.7670830	3.3416990
H	3.1938830	0.0610490	4.1192120
H	3.6341220	1.5616770	3.3117140
H	1.9288480	1.2024210	3.6514610
C	4.1547340	-0.4674320	1.5473760
H	4.8409920	0.3671710	1.3711880
H	4.5932000	-1.0945110	2.3302940
H	4.0970220	-1.0729800	0.6376220
C	1.8448630	-1.2012690	2.2172750
H	0.8329100	-0.9017060	2.5138630
H	1.7800110	-1.8371080	1.3305330
H	2.2515150	-1.8160040	3.0263570
O	-0.4240640	1.0640550	-1.1678400

H	-1.3944220	1.1637050	-0.6054160
O	-2.4852520	1.3041200	0.0985040
C	-3.4636540	1.8039220	-0.5592290
O	-3.5125610	2.1476670	-1.7392100
C	-4.7409190	1.9649360	0.3227800
F	-4.4989300	2.7514960	1.4015840
F	-5.1652690	0.7632210	0.7903610
F	-5.7687720	2.5168910	-0.3517550
H	-0.6113200	1.1205340	-2.1184720
H	-0.8072130	-2.5990920	-2.7167870
H	-1.5667080	-1.1875120	-2.0094260
C	-1.1782820	-2.7640980	-0.6040710
C	-0.8047380	-4.1135170	-0.4930050
C	-1.9363070	-2.1921560	0.4308100
C	-1.1599170	-4.8648680	0.6303010
H	-0.2399070	-4.5810580	-1.2939400
C	-2.2918850	-2.9421510	1.5568060
H	-2.2669770	-1.1596110	0.3535120
C	-1.9016110	-4.2798590	1.6620490
H	-0.8636500	-5.9078640	0.6957260
H	-2.8805280	-2.4814500	2.3449550
H	-2.1812770	-4.8644930	2.5336140

3.log
Potential Energy = -1949.249631
Zero-point Energy = -1948.78593
Free Energy = -1948.83085
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.74168
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.32290
Nimag = 1 (-355.7261 cm⁻¹)
Charge = 0 Multiplicity = 1

C	2.8627180	0.7576730	0.3601370
C	3.8037000	0.0081630	-1.6670530
C	2.7100560	-1.0092370	-1.3209250
N	2.0088240	-0.3272390	-0.2044480
N	3.8004560	0.9902260	-0.7381290
O	4.5361930	-0.0533380	-2.6546330
C	4.5912050	2.2056460	-0.9097940
H	4.6401110	2.4349030	-1.9760520
H	4.1066910	3.0299970	-0.3852160
H	5.6108690	2.0876690	-0.5326430
C	0.7004050	-0.3313200	0.0729530
H	0.4616890	0.2365400	0.9654660
C	-0.1886180	-1.5667240	-0.0999830
C	-1.5379380	-1.4018820	0.6188140
H	-1.3566120	-1.3227040	1.6950990
H	3.1884440	-1.9183920	-0.9377380
C	3.5293970	0.3842840	1.7306160
H	2.2464590	1.6527940	0.5023330
H	-0.3403050	-1.8010320	-1.1514950
Cl	0.6995020	-3.0251330	0.5694680
C	1.9031250	-1.3628170	-2.5700510
H	1.2499090	-2.2215080	-2.4123140
H	1.3230290	-0.5128180	-2.9379180
H	2.6213360	-1.6373650	-3.3464710
C	4.3518600	1.5902680	2.2369190
H	4.6934270	1.3895980	3.2572090
H	5.2399470	1.7751040	1.6291370
H	3.7522360	2.5072980	2.2639070
C	4.4444030	-0.8464710	1.5957800
H	5.2366540	-0.6865240	0.8573910
H	4.9266770	-1.0509980	2.5569970
H	3.8794650	-1.7412670	1.3166680
C	2.4311140	0.0924170	2.7750980
H	1.7368080	0.9340000	2.8839650
H	1.8610780	-0.8094060	2.5362400
H	2.8980780	-0.0711340	3.7513340
H	-1.9589970	-0.4443490	0.2944510
C	-2.5315700	-2.5088740	0.3309370
C	-2.8320240	-3.4774470	1.2985700
C	-3.1798050	-2.5759020	-0.9126460
C	-3.7518720	-4.4961720	1.0292500
H	-2.3452260	-3.4346460	2.2691480
C	-4.0964180	-3.5941250	-1.1868480

H	-2.9739220	-1.8228230	-1.6697920
C	-4.3846090	-4.5591210	-0.2155260
H	-3.9730550	-5.2373160	1.7918800
H	-4.5899390	-3.6293290	-2.1537930
H	-5.0997860	-5.3489190	-0.4259280
O	-0.1375420	0.8610760	-1.0069230
H	-0.8752150	1.5495950	-0.5174920
O	-1.6760590	2.3684370	0.1231140
C	-2.6199060	2.8650380	-0.5837380
O	-2.8859150	2.6809300	-1.7707570
C	-3.5270410	3.8269470	0.2462300
F	-2.8055420	4.8386050	0.7916730
F	-4.1287280	3.1676830	1.2695740
F	-4.5028620	4.3877000	-0.4954100
H	-0.5446520	0.4745950	-1.7986640

4.log
Potential Energy = -1949.247187
Zero-point Energy = -1948.78263
Free Energy = -1948.82673
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.74308
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.32262
Nimag = 1 (-310.9690 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-2.6986250	0.4657670	-0.8877210
C	-2.3567930	2.3382520	0.5025160
C	-1.9179440	1.1233180	1.3285200
N	-1.8854940	0.0566510	0.2936240
N	-2.7302300	1.9200200	-0.7280910
O	-2.3435540	3.5045270	0.8973940
C	-3.0111670	2.8663030	-1.8036490
H	-2.3672810	3.7377620	-1.6700490
H	-2.7911020	2.3991840	-2.7643800
H	-4.0527940	3.1994440	-1.7950520
C	-1.0165880	-0.9531120	0.1518680
H	-1.2934790	-1.6204180	-0.6568350
C	-0.3934530	-1.6937070	1.3412590
C	0.1620690	-3.0917230	0.9846510
H	-2.7164440	0.8886570	2.0424190
C	-4.1054930	-0.2248560	-0.9574270
H	-2.1412680	0.2183090	-1.7980030
H	0.3652930	-1.0850420	1.8282190
Cl	-1.6958140	-1.9515560	2.6134520
C	-0.6400660	1.4293320	2.1056200
H	-0.4217640	0.6610240	2.8482080
H	0.2235440	1.5722240	1.4542250
H	-0.8154470	2.3643390	2.6439920
C	-4.8367240	0.2469510	-2.2338950
H	-5.7522400	-0.3392810	-2.3614890
H	-5.1299580	1.2975840	-2.1819800
H	-4.2237180	0.1011380	-3.1306690
C	-4.9624010	0.1039090	0.2786890
H	-5.1086150	1.1822290	0.3983170
H	-5.9517270	-0.3520770	0.1698240
H	-4.5182570	-0.2946700	1.1959600
C	-3.9206450	-1.7540110	-1.0571620
H	-3.2945270	-2.0348170	-1.9126130
H	-3.4882100	-2.1780730	-0.1466490
H	-4.8973400	-2.2265950	-1.2007150
O	0.4309350	-0.3485620	-0.7378910
H	1.2179940	0.3012090	-0.2936140
O	2.1562380	1.0911600	0.2196490
C	3.0262320	1.5476110	-0.5988100
O	3.1461220	1.3530810	-1.8077530
C	4.0566810	2.4835630	0.1095810
F	3.4408090	3.5552600	0.6715820
F	4.9918920	2.9606690	-0.7365390
F	4.7115850	1.8323100	1.1046640
H	0.8826560	-1.0953540	-1.1693810
H	0.3844720	-3.5827400	1.9360120
H	-0.6347650	-3.6703770	0.5071440
C	1.4110940	-3.1102730	0.1225150
C	1.3509910	-3.4956290	-1.2267300
C	2.6605230	-2.7755120	0.6706840

C	2.5090760	-3.5321820	-2.0136230
H	0.3982110	-3.7857520	-1.6625820
C	3.8161080	-2.8123630	-0.1120960
H	2.7304780	-2.4903420	1.7173200
C	3.7437330	-3.1882240	-1.4585270
H	2.4423780	-3.8348650	-3.0543210
H	4.7735190	-2.5515570	0.3291730
H	4.6431540	-3.2176770	-2.0660220

5.log
Potential Energy = -1949.23941
Zero-point Energy = -1948.77437
Free Energy = -1948.81900
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.73291
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.31249
Nimag = 1 (-186.9810 cm⁻¹)
Charge = 0 Multiplicity = 1

C	3.1181100	0.5354530	-0.8234870
C	4.3992260	-0.8366830	0.6059300
C	2.9543720	-1.0417580	1.0668240
N	2.1941190	-0.3111330	0.0165670
N	4.4048120	-0.0854250	-0.5166800
O	5.3819840	-1.3696430	1.1200890
C	5.5626730	-0.0867920	-1.4112300
H	5.9905320	-1.0916980	-1.4185320
H	5.2380640	0.1737550	-2.4185060
H	6.3335550	0.6171530	-1.0898670
C	0.8743770	-0.2896400	-0.1859570
C	-0.0494010	-1.4899800	0.0760330
C	-1.3163060	-1.4094250	-0.7931530
H	-1.8953630	-0.5245470	-0.5159560
H	2.7905050	-0.5683310	2.0415960
C	3.0905050	2.0882560	-0.5626190
H	2.8709100	0.3548470	-1.8761930
H	0.5065240	-2.3946070	-0.1675040
Cl	-0.5043900	-1.6974070	1.8415520
C	2.7336070	-2.5584810	1.1697460
H	1.7889200	-2.8167410	1.6422850
H	2.8050570	-3.0347130	0.1874920
H	3.5367650	-2.9532980	1.7965040
C	4.3162510	2.7349400	-1.2494700
H	4.2180430	3.8228320	-1.1852220
H	5.2551630	2.4649230	-0.7624950
H	4.3811060	2.4757380	-2.3119040
C	3.1442450	2.4075990	0.9423250
H	4.0432050	1.9888800	1.4079520
H	3.1818600	3.4927590	1.0836440
H	2.2630820	2.0339960	1.4678440
C	1.8400570	2.7166820	-1.2158340
H	1.7784070	2.4597640	-2.2800030
H	0.9109700	2.4288540	-0.7287550
H	1.9097270	3.8068810	-1.1463480
H	-0.9679460	-1.2561510	-1.8226710
C	-2.1835550	-2.6506700	-0.7443110
C	-3.4143510	-2.6407240	-0.0734770
C	-1.7749140	-3.8312320	-1.3847630
C	-4.2168030	-3.7856200	-0.0350460
H	-3.7481260	-1.7323880	0.4206310
C	-2.5722810	-4.9778990	-1.3458280
H	-0.8312320	-3.8540450	-1.9249910
C	-3.7967520	-4.9583730	-0.6690570
H	-5.1682380	-3.7589660	0.4882400
H	-2.2415790	-5.8820340	-1.8487940
H	-4.4193510	-5.8478220	-0.6414460
H	0.6121250	0.2142600	-1.1111280
O	0.0749520	1.0253110	0.8481290
H	-0.8164190	1.4617730	0.4348660
H	-0.1720190	0.6380890	1.7055100
O	-1.9303770	2.0646620	-0.1663760
C	-2.8245870	2.4913420	0.6348910
C	-4.0053950	3.1889250	-0.1142660
O	-2.8748540	2.4261550	1.8656720
F	-4.6102350	2.3366770	-0.9824610
F	-3.5695330	4.2517870	-0.8393840

F -4.9602590 3.6454570 0.7223510

Catalyst regeneration and product release (TS7)

Conformation name	Extrapolated Free energy (kcal/mol)
TS7-lowest	0.0
1	3.6
2	3.6
3	4.5
4	2.3
5	5.3
6	3.8
7	5.6
8	1.1
9	0.7
10	1.6

TS7-lowest.log
Potential Energy = -1949.25101
Zero-point Energy = -1948.78659
Free Energy = -1948.83046
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.74709
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.32653
Nimag = 1 (-492.3687 cm⁻¹)
Charge = 0 Multiplicity = 1

C	1.0639590	1.7565980	-1.7950990
C	-0.2708930	2.3394820	0.0328890
C	-0.1808220	0.8788080	-1.8252270
H	-0.9995880	3.0098360	-0.4502400
H	0.0659700	-0.1538370	-2.0768710
C	-0.1489250	-0.8124890	0.4540330
H	-0.6715330	-0.5341840	1.3706490
O	-0.6908270	-1.6602060	-0.3341430
N	1.0289200	2.5007140	-0.6487910
C	1.9203040	3.6473820	-0.4984670
H	2.3730770	3.6700700	0.4930590
H	2.7081110	3.5396320	-1.2441460
H	1.3868740	4.5863310	-0.6790740
O	1.9286660	1.7983340	-2.6690720
C	1.3778500	-0.8602110	0.5916570
H	1.7864850	0.1287560	0.7839120
C	2.1135610	-1.5683490	-0.5498780
H	1.8706510	-1.0305140	-1.4725620
H	1.7078280	-2.5763580	-0.6604390
N	-0.6271330	0.9464870	-0.4067470
C	-3.8247910	-1.0629700	-0.2117750
C	-5.3295320	-1.4568300	-0.1564260
O	-3.5182530	0.1205400	-0.3345990
H	-1.6437700	0.8025400	-0.3472500
O	-3.0553030	-2.0889970	-0.1176320
H	-1.9104120	-1.8428750	-0.2039220
C	-0.3851580	2.6589670	1.5545680
C	-0.3428680	4.1973580	1.7431830
H	-0.6213520	4.4353270	2.7742350
H	0.6471800	4.6218070	1.5700880
H	-1.0544310	4.7031880	1.0816820
C	0.7004860	2.0169540	2.4374130
H	0.6293040	2.4311810	3.4481500
H	1.7109970	2.2210180	2.0719910
C	-1.7832970	2.1937080	2.0250640
H	-1.9293570	2.4928870	3.0671670
H	-2.5810110	2.6541600	1.4320100
H	-1.9110970	1.1090200	1.9795190
C	-1.2108860	1.3949030	-2.8426400
H	-0.7744940	1.3495420	-3.8439080

H	-2.1022840	0.7631120	-2.8231080
H	-1.5090980	2.4285260	-2.6452470
H	0.5802510	0.9365340	2.5342450
Cl	1.6440390	-1.7747320	2.1772690
F	-5.6133560	-2.1331630	0.9811550
F	-6.1342890	-0.3805610	-0.2026320
F	-5.6549450	-2.2581010	-1.1988180
C	3.6209790	-1.6130600	-0.3902230
C	4.3981510	-0.4602750	-0.5857570
C	4.2701170	-2.8116730	-0.0623630
C	5.7876570	-0.5018580	-0.4426900
H	3.9181180	0.4742910	-0.8648520
C	5.6608930	-2.8581950	0.0785730
H	3.6842230	-3.7152580	0.0830470
C	6.4240590	-1.7019910	-0.1081280
H	6.3725040	0.3998660	-0.6003930
H	6.1453790	-3.7968230	0.3320110
H	7.5042880	-1.7362130	-0.0005890

1.log
Potential Energy = -1949.24594
Zero-point Energy = -1948.78197
Free Energy = -1948.82590
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.74085
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.32081
Nimag = 1 (-506.0454 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-0.4872840	2.5446190	1.7234570
C	1.0762730	2.2660040	0.0038530
C	0.1217160	1.1589380	1.8817700
H	2.0289420	2.5006800	0.5057360
H	-0.6537840	0.4297950	2.1172460
C	-0.3080020	-0.6205850	-0.3207610
H	0.0157800	-0.3655960	-1.3310290
O	0.2235360	-1.6211500	0.2839970
N	0.0248150	3.1081160	0.5952660
C	-0.1561850	4.5334570	0.3445280
H	-0.5049350	4.7192850	-0.6718900
H	-0.9123850	4.8860940	1.0460720
H	0.7734970	5.0846920	0.5186860
O	-1.2706190	3.0666710	2.5170300
C	-1.8077000	-0.5146900	-0.0544560
H	-1.9958980	-0.5702960	1.0177990
C	-2.5096700	-1.7012040	-0.7606600
H	-1.9825670	-2.6038020	-0.4352370
H	-2.3657290	-1.6077240	-1.8417360
N	0.6829530	0.8962630	0.5233480
C	3.3518350	-1.7996570	0.1976880
C	4.7337570	-2.4920670	0.0195940
O	3.2919670	-0.7046010	0.7510930
H	1.5453660	0.3433990	0.6139270
O	2.3902640	-2.5034540	-0.2885910
H	1.3345030	-2.0376040	-0.0569430
C	1.3892290	2.3986890	-1.5201030
C	2.1495840	3.7304700	-1.7535410
H	2.5334120	3.7429820	-2.7782020
H	1.5172560	4.6112730	-1.6358790
H	3.0057910	3.8286690	-1.0772270
C	0.1587540	2.3583410	-2.4432950
H	0.4815200	2.5520000	-3.4716370
H	-0.5838910	3.1148360	-2.1785410
C	2.3704160	1.2675120	-1.9059270
H	2.7017290	1.4180130	-2.9375620
H	3.2588010	1.2674330	-1.2662390
H	1.9177530	0.2743840	-1.8586530
C	1.1699940	1.1363750	3.0050450
H	0.6849770	1.3973950	3.9492260
H	1.5986200	0.1356160	3.0988020
H	1.9797150	1.8497220	2.8256400
H	-0.3442650	1.3908570	-2.4340150
Cl	-2.5273120	1.0581990	-0.6082370
F	4.9879130	-2.7377960	-1.2873290
F	5.7401080	-1.7382280	0.4961600
F	4.7655200	-3.6790310	0.6708520

C	-3.9838620	-1.8268520	-0.4351590
C	-4.9621170	-1.5094110	-1.3875890
C	-4.3968780	-2.2813720	0.8275070
C	-6.3222590	-1.6359250	-1.0863690
H	-4.6588070	-1.1625290	-2.3717580
C	-5.7544120	-2.4055210	1.1335800
H	-3.6531530	-2.5471540	1.5751160
C	-6.7225150	-2.0817910	0.1764440
H	-7.0658010	-1.3867800	-1.8380340
H	-6.0555300	-2.7606740	2.1149610
H	-7.7780640	-2.1811940	0.4120840

2.log
Potential Energy = -1949.24440
Zero-point Energy = -1948.77977
Free Energy = -1948.82337
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.74179
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.32076
Nimag = 1 (-500.3399 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-0.8663320	-3.3403780	-1.0437420
C	0.1349870	-2.2737740	0.7848040
C	0.0726130	-2.2784330	-1.5966060
H	1.1083300	-2.7843610	0.8642510
H	-0.4068830	-1.7442420	-2.4170640
C	-0.5309800	0.4263900	-0.8299190
H	-0.6076720	0.7018920	0.2214320
O	0.3927900	0.9424720	-1.5579610
N	-0.8614910	-3.2485480	0.3141580
C	-1.4395300	-4.3188200	1.1191670
H	-2.1163530	-3.9268540	1.8792780
H	-2.0048500	-4.9573890	0.4401760
H	-0.6572060	-4.9156670	1.5988190
O	-1.4793790	-4.1637100	-1.7236550
C	-1.8457870	0.2817290	-1.5893160
H	-1.6606870	-0.2223320	-2.5377240
C	-2.4340900	1.6802750	-1.9203900
H	-1.7038590	2.1616400	-2.5782890
N	0.2591420	-1.3694190	-0.4270920
C	3.2919530	0.9235950	-0.3629900
C	4.6795040	1.5161040	0.0172690
O	3.1314240	-0.2941950	-0.3527040
H	1.2187860	-0.9997250	-0.4347920
O	2.4357760	1.8405000	-0.6506470
H	1.4179440	1.3968250	-1.0379920
C	-0.0714030	-1.5933200	2.1748960
C	0.2341610	-2.6327520	3.2851260
H	0.2761220	-2.1169310	4.2492800
H	-0.5282130	-3.4081260	3.3681820
H	1.2032110	-3.1182130	3.1259630
C	-1.4775050	-1.0136570	2.4092600
H	-1.5420420	-0.6454520	3.4385090
H	-2.2614450	-1.7625930	2.2731410
C	0.9907020	-0.4793760	2.3255830
H	0.9377040	-0.0696060	3.3384800
H	2.0035710	-0.8662160	2.1744670
H	0.8402230	0.3548980	1.6367140
C	1.3762340	-2.9035110	-2.1170710
H	1.1393990	-3.5907750	-2.9334300
H	2.0399660	-2.1242610	-2.4995920
H	1.9030450	-3.4628020	-1.3383970
H	-1.7070370	-0.1784240	1.7470680
Cl	-3.0731040	-0.7399810	-0.7219070
F	4.5757030	2.3354400	1.0905160
F	5.5710690	0.5565600	0.3212620
F	5.1912580	2.2443810	-1.0029040
C	-2.7517330	2.5878710	-0.7477990
C	-1.7878690	3.4787270	-0.2477660
C	-4.0240040	2.5784060	-0.1546740
C	-2.0800710	4.3225810	0.8279310
H	-0.8046500	3.5205300	-0.7088580
C	-4.3202500	3.4215570	0.9204500
H	-4.7893930	1.9112540	-0.5404580
C	-3.3473510	4.2939930	1.4182720

H	-1.3209400	5.0057370	1.1980010
H	-5.3116830	3.4004510	1.3638640
H	-3.5775460	4.9518970	2.2512240
H	-3.3352780	1.5030900	-2.5143420

3.log
Potential Energy = -1949.24375
Zero-point Energy = -1948.77976
Free Energy = -1948.82349
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.73962
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.31936
Nimag = 1 (-491.2565 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-2.9135440	-1.3243350	1.6240160
C	-2.7165180	0.3464560	-0.0061310
C	-1.5584750	-0.6610650	1.8181770
H	-3.0123460	1.2622580	0.5311450
H	-0.7946290	-1.4194170	1.9938590
C	0.3072860	-0.8350170	-0.3847590
H	0.0295450	-0.4679820	-1.3725930
O	1.2410800	-0.2502170	0.2727870
N	-3.5042300	-0.7755950	0.5279240
C	-4.9217240	-1.0039940	0.2715990
H	-5.0955640	-1.3314330	-0.7543060
H	-5.2455610	-1.7918750	0.9518780
H	-5.5064080	-0.1002540	0.4707210
O	-3.3963840	-2.1761480	2.3710240
C	0.3229550	-2.3443950	-0.2038150
H	0.4770870	-2.5887190	0.8472130
C	1.4623590	-2.9673970	-1.0634920
H	1.3414410	-2.6386670	-2.1004660
N	-1.3308390	0.0080390	0.5041160
C	1.1362100	2.8807350	0.3133440
C	1.7070240	4.3254860	0.2055460
O	0.0590520	2.7050300	0.8843280
H	-0.8367290	0.8977750	0.6546250
O	1.9006950	2.0111520	-0.2358670
H	1.5293940	0.8459250	-0.0214940
C	-2.8524760	0.7074530	-1.5194080
C	-4.2254630	1.3917940	-1.7485770
H	-4.2442720	1.8166920	-2.7568770
H	-5.0664190	0.7013110	-1.6748990
H	-4.3899070	2.2113220	-1.0403820
C	-2.7252820	-0.4890280	-2.4784950
H	-2.9249660	-0.1488720	-3.5000450
H	-3.4390000	-1.2831040	-2.2452890
C	-1.7807510	1.7696260	-1.8571260
H	-1.9345630	2.1196520	-2.8821190
H	-1.8501170	2.6373220	-1.1932740
H	-0.7605240	1.3831940	-1.8021930
C	-1.5784650	0.3017130	3.0157010
H	-1.8072840	-0.2628600	3.9234000
H	-0.5998020	0.7727300	3.1358970
H	-2.3328990	1.0852880	2.8982320
H	-1.7293500	-0.9334010	-2.4695590
Cl	-1.2391730	-3.1337400	-0.6890370
F	1.9087570	4.6735640	-1.0881790
F	0.8836570	5.2413600	0.7479860
F	2.8998330	4.4217190	0.8417020
H	1.2858470	-4.0470800	-1.0490460
C	2.8696280	-2.6839530	-0.5774840
C	3.7244290	-1.8391360	-1.2988820
C	3.3560990	-3.2970990	0.5879760
C	5.0322920	-1.6031090	-0.8635670
H	3.3662940	-1.3622310	-2.2076680
C	4.6602230	-3.0600070	1.0291120
H	2.7145450	-3.9703430	1.1517030
C	5.5030420	-2.2099880	0.3043560
H	5.6805030	-0.9464180	-1.4366750
H	5.0199460	-3.5433250	1.9329340
H	6.5183240	-2.0277820	0.6443020

4.log
Potential Energy = -1949.24967

Zero-point Energy = -1948.78455
Free Energy = -1948.82828
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.74430
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.32292
Nimag = 1 (-353.0256 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-0.2350390	-0.9723700	-0.4731210
H	0.2935820	-0.8131030	-1.4123540
O	0.2216980	-1.8435150	0.3476350
C	-1.7506830	-0.8167670	-0.5376460
H	-2.0272890	0.1872770	-0.8486700
C	3.3816840	-1.6531910	0.1521120
C	4.8358420	-2.1969680	0.0250670
O	3.2168810	-0.4504010	0.3742200
O	2.5021340	-2.5672250	-0.0025820
H	1.3090400	-2.1661570	0.1625800
Cl	-2.2184270	-1.8774470	-1.9747610
F	5.0444000	-2.7332470	-1.2023480
F	5.7603500	-1.2361920	0.2088820
F	5.0728320	-3.1701410	0.9373090
N	0.5324180	0.7975310	0.2406800
C	0.0159300	1.3490050	1.5325950
C	1.0426340	1.9752410	-0.5712650
C	0.7963720	2.6615130	1.6762370
H	-1.0495820	1.5780350	1.4350350
H	1.9510520	1.6344390	-1.0782280
H	1.4031120	0.2953860	0.4699680
O	0.8855720	3.3338550	2.7043540
N	1.4170040	2.9151410	0.5002810
C	2.4701980	3.9234210	0.4010910
H	2.0662880	4.9260310	0.2369350
H	3.0346960	3.9261560	1.3361890
H	3.1387930	3.6675780	-0.4214420
C	0.2577120	0.4368700	2.7342540
H	-0.2783420	-0.5081200	2.6415730
H	1.3237060	0.2183860	2.8500810
H	-0.0867590	0.9486180	3.6358290
C	0.0963690	2.5869260	-1.6552420
C	0.8102440	3.8055770	-2.2890420
H	0.2223310	4.1564840	-3.1425820
H	0.9019770	4.6417260	-1.5935280
H	1.8079910	3.5470000	-2.6602580
C	-0.1310850	1.5674030	-2.7909960
H	0.8187070	1.1775740	-3.1745990
H	-0.7545250	0.7230620	-2.4974360
H	-0.6447510	2.0592970	-3.6226550
C	-1.2472690	3.0649950	-1.0753030
H	-1.1027240	3.8107250	-0.2871030
H	-1.8414810	3.5334950	-1.8661660
H	-1.8463880	2.2479260	-0.6653510
C	-2.5054800	-1.2508130	0.7213050
H	-2.2202970	-2.2755280	0.9692800
H	-2.1439760	-0.6165010	1.5376080
C	-4.0137050	-1.1259060	0.6260050
C	-4.8151100	-2.2661800	0.4722390
C	-4.6394830	0.1278300	0.7092090
C	-6.2070920	-2.1580260	0.3921580
H	-4.3477990	-3.2455750	0.4160790
C	-6.0300020	0.2406550	0.6265370
H	-4.0406690	1.0240090	0.8503240
C	-6.8189220	-0.9032910	0.4661150
H	-6.8107490	-3.0533350	0.2744080
H	-6.4959470	1.2194250	0.6952560
H	-7.8999140	-0.8174260	0.4059730

5.log
Potential Energy = -1949.24583
Zero-point Energy = -1948.77984
Free Energy = -1948.82356
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.74041
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.31813
Nimag = 1 (-182.7738 cm⁻¹)

Charge = 0 Multiplicity = 1

C	-0.4263140	-0.7666210	-0.3001490
H	-0.1255300	-1.2251390	0.6439450
O	0.1220020	-1.2109160	-1.3699740
C	-1.8984960	-0.3937960	-0.3160830
C	-2.7102910	-1.6160730	0.1901840
H	-2.5565940	-2.4493500	-0.5016470
H	-2.2782530	-1.9106530	1.1541600
C	2.8965280	-2.1112280	0.0191990
C	4.2033880	-2.9515910	0.1476470
O	2.6878930	-1.2268180	0.8598960
O	2.1852890	-2.4569360	-0.9776660
H	1.0624870	-1.7597240	-1.1754870
F	3.9265770	-4.2750010	0.2407800
F	4.9308560	-2.6154520	1.2301380
F	4.9942070	-2.7804980	-0.9410210
C	-4.1893320	-1.3418860	0.3715860
C	-4.6460630	-0.5921910	1.4669770
C	-5.1286550	-1.8428010	-0.5404020
C	-6.0092050	-0.3388760	1.6398060
H	-3.9350620	-0.2105470	2.1958700
C	-6.4942100	-1.5944760	-0.3682010
H	-4.7913190	-2.4317410	-1.3888610
C	-6.9381580	-0.8390000	0.7208460
H	-6.3454120	0.2411870	2.4943420
H	-7.2080740	-1.9921320	-1.0837600
H	-7.9982860	-0.6460270	0.8564180
H	-2.0835440	0.4603930	0.3344050
Cl	-2.4707480	0.1024800	-1.9629800
N	0.6753100	0.8485570	0.3522160
C	0.1436060	1.5363480	1.5679230
C	1.5201210	1.8712290	-0.3914650
C	1.2012360	2.6162770	1.8311170
H	-0.8032990	2.0281410	1.3229480
H	2.3824010	1.3345900	-0.8001050
O	1.3406770	3.2448820	2.8810260
C	3.2489280	3.4391950	0.7564580
H	3.1224210	4.5014770	0.5328920
H	3.6800150	3.3421340	1.7551900
H	3.9300390	3.0003910	0.0262380
N	1.9803960	2.7143930	0.7292800
H	1.3849230	0.1774860	0.6825000
C	-0.0396580	0.6226470	2.7770100
H	-0.2687100	1.2430330	3.6466330
H	-0.8660220	-0.0787480	2.6432760
H	0.8726410	0.0578670	2.9922280
C	0.8503490	2.6557080	-1.5622020
C	1.7749790	3.8222520	-1.9818640
H	1.8091280	4.6145370	-1.2304290
H	2.7974890	3.4853980	-2.1843380
H	1.3869270	4.2632560	-2.9053790
C	-0.5182660	3.2450140	-1.1753870
H	-0.9087330	3.8363640	-2.0100240
H	-1.2574830	2.4715340	-0.9579620
H	-0.4388520	3.9145330	-0.3122080
C	0.7257160	1.7159240	-2.7785460
H	0.1230170	0.8337230	-2.5719470
H	0.2615610	2.2544860	-3.6112950
H	1.7160200	1.3812530	-3.1094650

6.log
Potential Energy = -1949.24520
Zero-point Energy = -1948.77947
Free Energy = -1948.82349
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.74218
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.32047
Nimag = 1 (-184.3497 cm⁻¹)
Charge = 0 Multiplicity = 1

C	0.7139820	-0.3444080	-1.0328300
H	1.1607050	0.2641110	-0.2446750
O	0.1745010	0.2686700	-2.0208860
C	1.4989440	-1.6141770	-1.2925640
C	2.9902150	-1.2552330	-1.5667990
H	3.0289940	-0.5430540	-2.3963320

C	-0.6336890	2.9344980	-0.3845530
C	-0.9798820	4.4469490	-0.2338760
O	-0.6765710	2.2228750	0.6273310
O	-0.3415570	2.6140260	-1.5810210
H	-0.0640200	1.3257380	-1.7972240
F	0.0446560	5.2271940	-0.6564210
F	-1.2498430	4.7920110	1.0396640
F	-2.0661670	4.7687800	-0.9797120
H	1.4341980	-2.2911070	-0.4413460
Cl	0.8724320	-2.5388000	-2.7241510
N	-0.7753960	-0.7079250	0.3613030
C	-0.3565940	-1.4767910	1.5731260
C	-2.2759000	-0.9105740	0.2128410
C	-1.6422120	-1.5178300	2.4088140
H	-0.0907440	-2.4984460	1.2829840
H	-2.6930430	0.0426090	-0.1274340
O	-1.7137200	-1.8106420	3.6032280
C	-3.9657770	-0.7583660	2.1843450
H	-4.6202530	-1.6258140	2.3016600
H	-3.8033360	-0.3091940	3.1666070
H	-4.4518140	-0.0317080	1.5320780
N	-2.6666820	-1.1186880	1.6205320
H	-0.7146040	0.2892960	0.6143910
C	0.7886630	-0.8343910	2.3516020
H	0.9252720	-1.3859120	3.2847560
H	1.7311070	-0.8691160	1.8017790
H	0.5613410	0.2066040	2.6014610
C	-2.7668450	-2.0239320	-0.7639550
C	-4.2795100	-2.2596000	-0.5445260
H	-4.4880200	-2.7492250	0.4095530
H	-4.8540150	-1.3283180	-0.5947840
H	-4.6509950	-2.9161530	-1.3375730
C	-2.0387140	-3.3626440	-0.5453170
H	-2.4605280	-4.1201490	-1.2140120
H	-0.9721060	-3.2962140	-0.7673530
H	-2.1670220	-3.7266290	0.4797440
C	-2.5925200	-1.5232120	-2.2121600
H	-1.5607420	-1.2760240	-2.4537310
H	-2.9271890	-2.2972810	-2.9106310
H	-3.2055440	-0.6308350	-2.3860990
H	3.4633260	-2.1792750	-1.9095500
C	3.7394860	-0.7181530	-0.3622390
C	3.9569610	0.6583600	-0.1975490
C	4.2510010	-1.6005490	0.6031610
C	4.6575450	1.1436880	0.9112190
H	3.5867250	1.3561650	-0.9444200
C	4.9516490	-1.1186370	1.7118450
H	4.1078470	-2.6716250	0.4827900
C	5.1543470	0.2563400	1.8703780
H	4.8183770	2.2121130	1.0208060
H	5.3425990	-1.8158260	2.4470770
H	5.7007660	0.6318370	2.7304190

7.log
Potential Energy = -1949.24378
Zero-point Energy = -1948.77757
Free Energy = -1948.82128
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.74017
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.31767
Nimag = 1 (-166.7933 cm⁻¹)
Charge = 0 Multiplicity = 1

C	0.6752510	-0.6500430	0.1739330
H	0.7524660	0.0164450	1.0346350
O	0.9418270	-0.1531300	-0.9781810
C	1.1078590	-2.0690590	0.4975860
C	2.3932850	-2.0672730	1.3750050
C	0.0470380	2.8675910	-0.2387100
C	0.0695870	4.4207630	-0.3729760
O	-0.7258530	2.3668250	0.5899550
O	0.8548910	2.2926090	-1.0342230
H	0.8842690	0.9437210	-0.9913280
F	1.3206460	4.9104360	-0.1958450
F	-0.7312860	5.0307070	0.5219870
F	-0.3409940	4.8012930	-1.6089070

H	0.3316210	-2.5759320	1.0695100
Cl	1.3425340	-3.0769260	-0.9922950
N	-1.3491250	-0.4953750	0.4685840
C	-1.8539370	-1.0804500	1.7477600
C	-2.5180530	-0.5038380	-0.5044690
C	-3.3533010	-0.7598440	1.6943160
H	-1.7295270	-2.1680070	1.7252370
H	-2.4501200	0.4170960	-1.0922010
O	-4.1298460	-0.7960150	2.6492880
C	-4.9220910	0.2719630	0.1123960
H	-5.7045770	-0.4461960	-0.1447110
H	-5.2440850	0.8398520	0.9877850
H	-4.7758300	0.9545830	-0.7260550
N	-3.6538350	-0.3809090	0.4302040
H	-1.2112200	0.5124210	0.6410390
C	-1.1978270	-0.5060550	3.0005800
H	-1.7371390	-0.8768600	3.8752000
H	-0.1550470	-0.8163270	3.0967720
H	-1.2433390	0.5872650	3.0089200
C	-2.6246200	-1.6975640	-1.5042260
C	-4.0150670	-1.6651450	-2.1803630
H	-4.8168420	-1.9379010	-1.4901590
H	-4.2406760	-0.6838090	-2.6114720
H	-4.0253310	-2.3922660	-2.9983330
C	-2.4588090	-3.0654050	-0.8176430
H	-2.6088240	-3.8622280	-1.5533240
H	-1.4600760	-3.2017980	-0.3981150
H	-3.2006050	-3.2115760	-0.0252960
C	-1.5739780	-1.5058000	-2.6169670
H	-0.5546100	-1.4746180	-2.2369860
H	-1.6426040	-2.3325370	-3.3316150
H	-1.7602350	-0.5751660	-3.1660400
H	2.6130250	-3.1168820	1.5899040
H	2.1166040	-1.6063460	2.3302920
C	3.6184810	-1.3754110	0.8116440
C	4.5142710	-2.0620070	-0.0234000
C	3.8999310	-0.0398910	1.1401470
C	5.6476800	-1.4238870	-0.5347400
H	4.3274120	-3.1027050	-0.2701960
C	5.0325510	0.6017180	0.6302610
H	3.2379930	0.5029280	1.8104190
C	5.9082880	-0.0879690	-0.2131530
H	6.3293840	-1.9723900	-1.1783560
H	5.2322290	1.6351730	0.8980480
H	6.7906450	0.4071950	-0.6077890

8.log
Potential Energy = -1949.25022
Zero-point Energy = -1948.785715
Free Energy = -1948.82956
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.74546
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.32480
Nimag = 1 (-381.4409 cm⁻¹)
Charge = 0 Multiplicity = 1

C	0.5113790	2.3894900	-1.8330060
C	-0.4357110	2.3747420	0.3008610
C	-0.6177670	1.3674950	-1.8331020
H	-1.3019540	3.0344680	0.1323670
H	-0.3165630	0.4604450	-2.3572620
C	0.0135680	-0.7607400	-0.0582360
H	-0.2790290	-0.7283410	0.9957960
O	-0.6626630	-1.4858070	-0.8595100
N	0.6742930	2.8427850	-0.5521700
C	1.4759140	4.0371800	-0.3040440
H	2.1263050	3.9047380	0.5610270
H	2.0932140	4.1968150	-1.1882330
H	0.8404300	4.9161070	-0.1525930
O	1.1352120	2.7640380	-2.8243990
C	1.5321930	-0.6995040	-0.2302080
C	2.1565290	-1.8598560	0.5839970
H	1.7599960	-2.8040380	0.1989230
H	1.7952040	-1.7565330	1.6146950
N	-0.7604260	1.0723340	-0.3779680
C	-3.7217120	-1.2779530	0.0419550

C	-5.1433020	-1.8425490	0.3269950
O	-3.5313730	-0.0668710	0.0939920
H	-1.7289560	0.8000970	-0.1671330
O	-2.8798140	-2.2149840	-0.2291290
H	-1.8270460	-1.8326380	-0.4976910
C	-0.2551260	2.3478960	1.8483900
C	-0.2880900	3.8034570	2.3814370
H	-0.3667560	3.7788920	3.4725630
H	0.6112580	4.3697100	2.1353440
H	-1.1552770	4.3519990	1.9982040
C	1.0352580	1.6651210	2.3352760
H	1.1591830	1.8498380	3.4069570
H	1.9266570	2.0474040	1.8300860
C	-1.4854310	1.6292560	2.4498420
H	-1.4337880	1.6793220	3.5414850
H	-2.4207920	2.1067920	2.1382750
H	-1.5390050	0.5723350	2.1762990
C	-1.8877010	1.9295770	-2.4907840
H	-1.6726950	2.1645640	-3.5366070
H	-2.6853540	1.1829690	-2.4606870
H	-2.2425030	2.8415650	-2.0013210
H	1.0019670	0.5816810	2.2071570
F	-5.1180430	-2.7243360	1.3535200
F	-6.0148630	-0.8697530	0.6450270
F	-5.6288670	-2.4922470	-0.7571310
C	3.6720180	-1.8899080	0.5857330
C	4.4092590	-1.0116910	1.3957050
C	4.3679640	-2.8097270	-0.2119970
C	5.8065070	-1.0424910	1.3971830
H	3.8929710	-0.3038610	2.0388660
C	5.7659000	-2.8458850	-0.2108090
H	3.8126000	-3.5032080	-0.8373770
C	6.4900080	-1.9595810	0.5918470
H	6.3594900	-0.3564130	2.0323220
H	6.2863720	-3.5667080	-0.8348330
H	7.5757400	-1.9867970	0.5952690
H	1.9227920	0.2586540	0.1060780
Cl	2.0213880	-0.8309190	-1.9799760

9.log
Potential Energy = -1949.24902
Zero-point Energy = -1948.78464
Free Energy = -1948.82845
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.74601
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.32543
Nimag = 1 (-453.2927 cm⁻¹)
Charge = 0 Multiplicity = 1

C	-1.5214730	-3.1195530	-0.6560270
C	-0.9135380	-1.9030380	1.2401530
C	-0.1401490	-2.5299160	-0.9057060
H	-0.2814690	-2.6478690	1.7503390
H	-0.0684390	-2.1323290	-1.9177700
C	-0.2336920	0.3209230	-0.9920280
H	-0.0678050	0.9114280	-0.0871150
O	0.7256320	0.1814740	-1.8224700
N	-1.9887090	-2.6209230	0.5286920
C	-3.1491770	-3.2365470	1.1645650
H	-3.8366170	-2.4826820	1.5493730
H	-3.6593330	-3.8219990	0.3994970
H	-2.8466500	-3.9045870	1.9778390
O	-2.0903700	-3.9353910	-1.3798080
C	-1.6428670	0.5025530	-1.5429140
C	-1.8489010	1.9765280	-1.9908940
H	-1.0795060	2.2187940	-2.7299450
N	-0.1069820	-1.4030850	0.0718620
C	3.4071860	0.0397090	-0.0875220
C	4.8992390	0.3590610	0.2179620
O	2.8002070	-0.7472720	0.6335900
H	0.8606840	-1.2303830	0.3725520
O	2.9812490	0.6778560	-1.1208000
H	1.8798750	0.4297330	-1.4135200
C	-1.2841830	-0.8729790	2.3479150
C	-1.7747320	-1.6417540	3.6019530
H	-1.8411050	-0.9429930	4.4414470

H	-2.7629850	-2.0851370	3.4726690
H	-1.0759220	-2.4362570	3.8855230
C	-2.3525200	0.1539910	1.9361310
H	-2.6803740	0.7086260	2.8211590
H	-3.2370520	-0.3158910	1.4963470
C	0.0130740	-0.1390610	2.7604700
H	-0.2015190	0.5235850	3.6041690
H	0.7894230	-0.8430810	3.0791410
H	0.4262610	0.4804700	1.9602840
C	0.9654620	-3.5774620	-0.7004850
H	0.8229600	-4.3892160	-1.4188470
H	1.9450190	-3.1264290	-0.8775440
H	0.9543080	-4.0056420	0.3062650
H	-1.9680260	0.8924480	1.2312620
F	5.0901550	1.6891950	0.3787820
F	5.3261610	-0.2526700	1.3365710
F	5.6939620	-0.0465170	-0.8012280
H	-2.3895060	0.2158170	-0.8063690
Cl	-1.9580920	-0.5586410	-2.9935230
H	-2.8147910	2.0092790	-2.5023940
C	-1.8410400	2.9932100	-0.8638980
C	-0.6785860	3.7114480	-0.5435760
C	-3.0125590	3.2529960	-0.1351290
C	-0.6817280	4.6549510	0.4884900
H	0.2330870	3.5407570	-1.1105550
C	-3.0199280	4.1959990	0.8960860
H	-3.9269210	2.7183010	-0.3806250
C	-1.8524550	4.8981170	1.2131800
H	0.2270990	5.2027360	0.7201450
H	-3.9367790	4.3856130	1.4467150
H	-1.8573700	5.6334180	2.0124100

10.log
Potential Energy = -1949.24828
Zero-point Energy = -1948.78385
Free Energy = -1948.82750
Single-Point Energy B3LYP-D3(BJ)/6-311+G** PCM = -1949.74475
Free Energy B3LYP-D3(BJ)/6-311+G** PCM (extrapolated free energy from qRRHO) = -1949.32397
Nimag = 1 (-533.9049 cm⁻¹)
Charge = 0 Multiplicity = 1

C	3.1105990	-0.5891380	-1.5764200
C	2.7654150	0.5519640	0.4332690
C	1.8510890	0.2519050	-1.7318080
H	3.2081330	1.5316230	0.1907390
H	1.0685650	-0.3165230	-2.2351290
C	-0.1719290	-0.6699280	0.0412660
H	-0.2702150	-0.2611160	1.0504640
O	-0.9765110	-0.2706630	-0.8637940
N	3.5296740	-0.4917140	-0.2777750
C	4.8716910	-0.9379430	0.0842810
H	4.8628760	-1.5075260	1.0139780
H	5.2222060	-1.5831640	-0.7214070
H	5.5569860	-0.0893320	0.1824370
O	3.6680490	-1.2123160	-2.4783790
C	0.2732070	-2.1292750	0.0491580
C	-0.5983710	-2.9795080	1.0136650
N	1.4601320	0.4828650	-0.3113630
C	-1.5114290	2.8287570	-0.3068340
C	-2.3983320	4.1040390	-0.2070370
O	-0.2932690	2.9341030	-0.1821090
H	0.9598380	1.3768130	-0.2222830
O	-2.2112050	1.7714220	-0.5165380
H	-1.5742250	0.7824280	-0.6540990
C	2.6998910	0.5178630	1.9902780
C	4.0708280	0.9658520	2.5595340
H	3.9677790	1.1392610	3.6350500
H	4.8542960	0.2183640	2.4270180
H	4.4084910	1.9024080	2.1028020
C	2.3334040	-0.8523000	2.5883890
H	2.4828780	-0.8241270	3.6723240
H	2.9519870	-1.6622170	2.1916370
C	1.6677230	1.5777290	2.4403850
H	1.6666220	1.6379900	3.5327380
H	1.9171260	2.5710430	2.0519490

H	0.6475580	1.3407670	2.1277560
C	2.1282840	1.5362320	-2.5289570
H	2.4625090	1.2662080	-3.5342340
H	1.2130440	2.1272610	-2.6151630
H	2.9024710	2.1550150	-2.0655210
H	1.2852660	-1.1081850	2.4251080
F	-3.2878190	3.9949990	0.8085400
F	-1.6677240	5.2123430	0.0088790
F	-3.1036250	4.2935450	-1.3472090
H	1.3058380	-2.2023560	0.3833770
Cl	0.2691760	-2.8510260	-1.6231840
H	-0.1841790	-3.9916060	0.9862640
H	-0.4090340	-2.5950440	2.0225660
C	-2.0920220	-3.0177510	0.7597090
C	-2.9518120	-2.1143220	1.4040930
C	-2.6522870	-3.9769510	-0.0984570
C	-4.3313490	-2.1522970	1.1819960
H	-2.5437270	-1.3789350	2.0931600
C	-4.0313360	-4.0183000	-0.3234290
H	-2.0066350	-4.6990220	-0.5893570
C	-4.8755280	-3.1031200	0.3132650
H	-4.9786820	-1.4443730	1.6915200
H	-4.4453950	-4.7689110	-0.9905780
H	-5.9474310	-3.1367670	0.1415870

2.4. Ion Mobility-Mass Spectrometry with Aminals (2nd Generation MacMillan Catalyst)

Diastereomeric amins were dissolved in acetonitrile to yield pure and 1:1 mixed solutions. Arrival time distributions (ATDs) and mass spectra of iminium ions were recorded on a home-built drift-tube ion mobility instrument which is described in detail elsewhere.^{30,31} Briefly, iminium ions in the gas phase were generated by nanoelectrospray ionization followed by in-source fragmentation of intact amina precursors. Subsequently, the ions are injected to the drift tube (161.2 cm) using helium at ca. 4.00 mbar as drift gas. Drift times were recorded at 14 different drift voltages from 2300 to 1000 V in 100 V steps. After transfer of the ions for mbar pressure to high vacuum, the ions are selected by their mass-to-charge ratio in a quadrupole mass filter. The ATDs are recorded using an electron multiplier detector which is on axis to the drift tube. For mass spectral analysis, the ions are pulsed off-axis to a Wiley-McLaren time-of-flight mass analyser. From the drift times, the instrument-independent collision cross sections (CCSs) can be derived using the Mason-Schamp equation.^{32,33} Arrival time distributions (ATDs) of iminium ions generated from both diastereomeric amins and their mixture are shown below.

Figure SI-17. Ionization of amins *syn*-25 and *anti*-25 and arrival time distributions of diastereomeric *E*-(*R*)- (blue trace) and *E*-(*S*)-iminium ions (red trace). The trace of the mixture of both diastereomers is depicted in light grey.

Figure SI-18. Mass spectra of iminium ions ($m/z = 399$) generated from amination precursor ions $[M+H]^+$ ($m/z = 496$) and $[M+Na]^+$ ($m/z = 518$).

Computational Methods

For each iminium ion (E -(R), E -(S), Z -(R) and Z -(S)) the conformational space was sampled by using a genetic algorithm (GA) FAFOOM.³⁴ In this case, all rotatable bonds were sampled, generating a pool of starting structures, which are automatically optimized with FHI-aims³⁵ (version 171221) at the dispersion corrected density functional PBE+vdW^{TS 36,37} level of theory using *light* basis set settings. For each type of isomers, ten GA runs were performed that yielded ca. 120 structures for each candidate. From that pool of structures, a certain number of distinct low-energy structures for each isomer were reoptimized, frequencies and Merz-Singh-Kollman³⁸ charges calculated at the hybrid-DFT level PBE0+D3/6-311+G(d,p)³⁹ using default settings in Gaussian 16, Revision A.03.¹⁴ The reoptimized structures and computed Merz-Singh-Kollman were used as input to compute theoretical CCS values using the trajectory method using the software hpccs.⁴⁰ The calculation was carried out in helium as drift gas at 298.15 K. Default settings were used except for the number of points in velocity integration (60) and the number of points in Monte Carlo integrations of impact parameters and orientation (750). Computed energies plus zero-point vibrational energy, free energies at 298.15 K and computed CCSs are shown in Table SI-13. 3D-structures of each lowest-energy isomer are shown below and their xyz-coordinates can be found at the end of this chapter.

Table SI-13. List of conformations reoptimized at PBE0+D3/6-311+G(d,p) level of theory. Energies (ΔE , including zero-point-vibrational energy), free energies (ΔF) at 298.15 K and collision cross sections calculated with the trajectory method (CCSTM) in He are assigned to each structure. The lowest-energy conformers for each isomer are labelled with an asterisk (*).

ID	$\Delta E(\text{PBE0+D3})$ [kcal mol ⁻¹]	$\Delta F(\text{PBE0+D3})$	CCS TM [Å ²]
		[kcal mol ⁻¹]	
trans_S/conf_00*	0.0	0.0	123
trans_S/conf_01	1.4	0.5	124
trans_S/conf_02	3.6	3.8	125
trans_S/conf_03	3.7	2.8	127
trans_S/conf_04	5.9	4.5	129
trans_S/conf_05	6.6	5.1	129
trans_R/conf_00*	2.4	1.8	128
trans_R/conf_01	2.4	2.1	125
trans_R/conf_02	4.4	5.3	123
trans_R/conf_03	5.3	4.4	131
trans_R/conf_04	5.5	5.1	127
cis_S/conf_00*	4.5	4.1	126
cis_S/conf_01	5.7	5.2	128
cis_S/conf_02	6.2	4.9	133
cis_S/conf_03	7.9	8.3	123
cis_S/conf_04	7.1	7.1	123
cis_R/conf_00*	1.4	0.8	123
cis_R/conf_01	5.0	4.2	124
cis_R/conf_02	6.0	6.0	123
cis_R/conf_03	7.9	6.6	133

Figure SI-19. Computed lowest-energy structures for four distinct iminium ions: (a) *E*-(*R*), (b) *E*-(*S*), (c) *Z*-(*R*) and (d) *Z*-(*S*). Hydrogens are omitted for clarity.

Table SI-14. xyz-Coordinates of reoptimized structures

MacMillan_Catalyst/trans_R/conf_00

Charge=+1,

Multiplicity=+1

C	1.84003	0.99505	0.73778
C	1.87689	-1.39314	0.16100
C	3.20941	0.38309	0.98485
C	0.57872	2.65319	-0.74446
H	1.49436	-2.20115	0.79753
N	1.02636	-0.19435	0.46042
N	3.15318	-0.93582	0.65539
O	4.16256	0.98874	1.40093
C	4.27626	-1.81150	0.92437
H	4.90108	-1.31845	1.66978
H	3.91977	-2.76549	1.31794
H	4.88011	-1.98828	0.03147
C	1.83570	-1.89411	-1.30880
C	2.49158	-3.28176	-1.33395
H	2.35714	-3.72038	-2.32549
H	3.56365	-3.24543	-1.14025
H	2.03039	-3.96123	-0.61011
C	0.38475	-2.05627	-1.76311
H	0.37340	-2.48931	-2.76622
H	-0.18391	-2.73604	-1.11920
H	-0.14883	-1.10394	-1.82123
C	2.57569	-0.96109	-2.26105
H	3.58578	-0.73216	-1.91160
H	2.66458	-1.43742	-3.24034
H	2.03820	-0.02259	-2.41211
C	-0.22548	-0.31614	0.71021
C	-1.10207	0.71089	1.32873
H	-0.65278	1.69874	1.36399
C	-2.50843	0.78235	0.73921
H	-2.44310	1.46510	-0.11296
H	-3.14719	1.26456	1.48379
C	-3.06516	-0.54151	0.29415
C	-3.00226	-0.89306	-1.05507
C	-3.60588	-1.45076	1.20434
C	-3.45602	-2.13359	-1.48830
H	-2.61068	-0.17809	-1.77407
C	-4.05726	-2.69272	0.77274
H	-3.68457	-1.18389	2.25304
C	-3.97868	-3.03872	-0.57213
H	-3.41420	-2.38775	-2.54213
H	-4.48313	-3.38799	1.48800
H	-4.34081	-4.00463	-0.90682
Cl	-1.08994	0.08438	3.03342
C	-0.14099	2.19010	-1.84663
C	-1.35629	2.77053	-2.19751
H	0.26865	1.39488	-2.46276
C	0.05139	3.70581	0.00806

C	-1.87497	3.81130	-1.43714
H	-1.89064	2.41892	-3.07390
C	-1.16902	4.27651	-0.33069
H	0.61337	4.09914	0.85154
H	-1.55961	5.10148	0.25517
H	-2.81795	4.27042	-1.71287
H	-0.67395	-1.29503	0.55978
C	1.90178	2.04431	-0.38138
H	2.59058	2.80653	-0.00499
H	2.37666	1.60581	-1.25992
H	1.48721	1.44767	1.66739

MacMillan_Catalyst/trans_S/conf_00

Charge=+1,

Multiplicity=+1

C	0.41962	0.36877	-0.95798
C	2.26889	-0.46636	0.43457
C	1.75472	0.95658	-1.38065
C	-1.58113	-0.95126	-1.78399
H	2.54054	-0.09008	1.42983
N	0.78370	-0.30263	0.30796
N	2.72979	0.44849	-0.57849
O	1.89818	1.74227	-2.28135
C	4.07297	0.99252	-0.62465
H	4.00882	1.98443	-1.07374
H	4.47731	1.07097	0.38653
H	4.74258	0.38337	-1.23482
C	2.75948	-1.93583	0.33659
C	4.26519	-1.93514	0.63010
H	4.60753	-2.96758	0.73142
H	4.84539	-1.48000	-0.17267
H	4.50010	-1.41973	1.56710
C	2.07124	-2.78487	1.40757
H	2.49767	-3.79052	1.39031
H	2.23377	-2.38976	2.41690
H	0.99628	-2.89864	1.23752
C	2.50604	-2.53977	-1.03969
H	2.87715	-1.89740	-1.84304
H	3.02445	-3.49834	-1.11770
H	1.44427	-2.73809	-1.20398
C	0.03497	-0.48273	1.33093
C	-1.42521	-0.23976	1.45397
Cl	-2.05801	-1.67239	2.32485
C	-1.67126	1.05380	2.24405
H	-1.20116	0.98452	3.22939
H	-2.75031	1.13186	2.39888
C	-1.13248	2.21497	1.45425
C	0.16780	2.67500	1.66643
C	-1.88680	2.77205	0.42037
C	0.71763	3.64794	0.83910
H	0.75041	2.27996	2.49572
C	-1.34045	3.74922	-0.40351

H	-2.90621	2.43351	0.25816
C	-0.03189	4.17713	-0.20557
H	1.72786	4.00178	1.01519
H	-1.93580	4.17772	-1.20245
H	0.39883	4.92880	-0.85710
H	-1.92421	-0.20674	0.48701
C	-2.65040	-0.06158	-1.91293
C	-3.93919	-0.45584	-1.57791
H	-2.46984	0.94368	-2.28394
C	-1.83037	-2.24765	-1.33786
C	-4.17575	-1.74859	-1.11739
H	-4.76423	0.23956	-1.69048
C	-3.12159	-2.64579	-1.00697
H	-1.01228	-2.95798	-1.25564
H	-3.30273	-3.65772	-0.66190
H	-5.18254	-2.05794	-0.85962
H	0.53429	-0.81742	2.23759
C	-0.18458	-0.48871	-2.07474
H	-0.17113	0.17170	-2.94792
H	0.47112	-1.32801	-2.30641
H	-0.25628	1.19090	-0.71267

MacMillan_Catalyst/cis_R/conf_00

Charge=+1,

Multiplicity=+1

C	-0.34914	-1.21055	-1.23991
C	1.11752	-0.83267	0.69123
C	0.93105	-2.01645	-1.34987
C	-2.82433	-1.11879	-0.96727
H	1.76623	0.03044	0.87372
N	-0.06297	-0.34109	-0.08195
N	1.72474	-1.69737	-0.29445
O	1.19576	-2.76155	-2.25902
C	3.10152	-2.14299	-0.24262
H	3.43423	-2.30245	-1.26897
H	3.71710	-1.37308	0.22477
H	3.20982	-3.08369	0.30241
C	0.77712	-1.51543	2.05075
C	2.10648	-1.73471	2.78532
H	1.89847	-2.06654	3.80540
H	2.72409	-2.50062	2.31632
H	2.68989	-0.81060	2.85272
C	-0.09652	-0.61756	2.92789
H	-0.35338	-1.16520	3.83791
H	0.42715	0.28720	3.25018
H	-1.04017	-0.33622	2.45209
C	0.07471	-2.85627	1.85754
H	0.59086	-3.49816	1.13934
H	0.04556	-3.38732	2.81195
H	-0.96092	-2.72838	1.53568
C	-0.63263	0.80074	0.03160
C	-0.23846	1.91779	0.92622

Cl	-1.73447	2.52456	1.68834
C	0.45283	2.99433	0.07400
H	-0.22503	3.33234	-0.71488
H	0.64435	3.84757	0.72992
C	1.72832	2.43297	-0.49593
C	2.88929	2.39682	0.27825
C	1.74938	1.86739	-1.77134
C	4.04439	1.79708	-0.21002
H	2.89522	2.85834	1.26239
C	2.90079	1.25969	-2.25898
H	0.86418	1.92465	-2.40077
C	4.04882	1.21951	-1.47571
H	4.94623	1.79319	0.39295
H	2.90654	0.83126	-3.25550
H	4.95200	0.75798	-1.85993
H	0.42086	1.59985	1.72827
C	-3.38150	-0.93287	0.29765
C	-3.31429	-0.36597	-2.03715
C	-4.40352	-0.00920	0.49455
H	-3.02461	-1.52475	1.13584
C	-4.87400	0.74421	-0.57268
H	-4.83216	0.11883	1.48248
C	-4.33170	0.55958	-1.84172
H	-2.90648	-0.51564	-3.03379
H	-5.67011	1.46473	-0.42179
H	-4.71125	1.12989	-2.68268
H	-1.43727	1.00664	-0.67398
C	-1.64331	-2.02644	-1.15713
H	-0.40159	-0.56442	-2.11959
H	-1.69932	-2.57349	-2.10282
H	-1.58009	-2.76935	-0.36249

MacMillan_Catalyst/cis_S/conf_00

Charge=+1,

Multiplicity=+1

C	1.65003	1.56613	0.30206
C	2.05068	-0.80711	-0.09756
C	3.12435	1.28632	0.03486
C	-0.46934	2.75200	-0.42391
H	2.09183	-1.63748	0.61480
N	1.10968	0.20172	0.45798
N	3.28487	-0.06258	-0.04360
O	3.97689	2.13246	-0.03395
C	4.58765	-0.68646	-0.10740
H	5.32400	0.07464	0.15167
H	4.64246	-1.50711	0.61275
H	4.81662	-1.06621	-1.10607
C	1.66566	-1.36577	-1.51148
C	2.21408	-2.79569	-1.57549
H	2.00231	-3.23023	-2.55523
H	3.29639	-2.83265	-1.42703
H	1.74550	-3.43717	-0.82166

C	0.15098	-1.40508	-1.70647
H	-0.06810	-1.84675	-2.68126
H	-0.36403	-2.02089	-0.96558
H	-0.29958	-0.40930	-1.69125
C	2.28422	-0.53333	-2.63445
H	3.37386	-0.50438	-2.59051
H	2.00620	-0.97594	-3.59393
H	1.92347	0.49698	-2.64169
C	0.11389	-0.04810	1.22494
C	-0.27294	-1.37833	1.77425
H	0.10325	-2.21290	1.18635
C	-1.76381	-1.51922	2.03905
H	-1.90885	-2.40227	2.66538
H	-2.11789	-0.65394	2.60766
C	-2.49464	-1.66161	0.73224
C	-2.92618	-0.53673	0.03142
C	-2.68352	-2.92686	0.17552
C	-3.52849	-0.67704	-1.21363
H	-2.81286	0.45570	0.46037
C	-3.28785	-3.06649	-1.06687
H	-2.36762	-3.81008	0.72431
C	-3.70636	-1.93919	-1.76645
H	-3.87035	0.20274	-1.74667
H	-3.44123	-4.05519	-1.48542
H	-4.18490	-2.04696	-2.73370
Cl	0.67223	-1.36424	3.31884
C	-0.83474	3.30457	0.80724
C	-1.46090	2.52739	-1.37630
C	-2.16157	3.61141	1.08146
H	-0.07663	3.53330	1.55265
C	-3.14247	3.38945	0.11886
H	-2.42739	4.04767	2.03831
C	-2.78617	2.85855	-1.11368
H	-1.19158	2.11277	-2.34349
H	-4.17578	3.64511	0.32570
H	-3.54109	2.70762	-1.87794
H	-0.42278	0.81888	1.60795
C	0.96808	2.43933	-0.74439
H	1.58953	2.05194	1.27860
H	1.56995	3.35430	-0.78664
H	1.03645	1.97745	-1.73064

The combined approach (comparison of experimental and calculated CCSs) was successfully used to make a prediction whether *E*- or *Z*-iminium ions are formed in the decomposition process of the two diastereomeric amins (1*S*,2*R*)-*syn*-**25** and (1*S*,2*S*)-*anti*-**25**. The ATD traces of the selectively dissociated amins suggest that the dissociation of each amine leads to the corresponding *E*-iminium ion. The comparison of the computed and the experimental CCS value suggests the *E*-iminium to be formed for both epimers.

3. CHLORINATIONS WITH THE JØRGENSEN-HAYASHI-TYPE CATALYST

3.1. Aminals Derived from Isovaleraldehyde

3.1.1. Synthesis and Derivatization

2-(1-((*S*)-2-(bis(3,5-bis(trifluoromethyl)phenyl)((trimethylsilyl)oxy)methyl)pyrrolidin-1-yl)-2-chloro-3-methylbutyl)isoindoline-1,3-dione (**14**)

Catalysts **9b** (0.896 g, 1.50 mmol, 50 mol%) and NCP (0.272 g, 1.50 mmol, 0.5 equiv) were added successively to a solution of isovaleraldehyde (0.323 mL, 3.00 mmol, 1.0 equiv) in CHCl_3 (14 mL) at $22\text{ }^{\circ}\text{C}$. After 60 min the solvent and unreacted isovaleraldehyde were removed under reduced pressure. The crude product was dissolved in pentane (5 mL) and the precipitating solids were filtered off. Pentane was removed under reduced pressure and the product was obtained as a foamy off-white solid (1.04 g, 1.23 mmol, 82%). Attempts to further purify the product by column chromatography (Silica, Alox) resulted in decomposition. $^1\text{H-NMR}$ -spectra were recorded at $22\text{ }^{\circ}\text{C}$ and $-54\text{ }^{\circ}\text{C}$. Both spectra and the ratio of the two signal sets at $-54\text{ }^{\circ}\text{C}$ (80:20) are in accordance with the spectra from the literature.²⁸ (The aromatic signals were left out)

mp = $56\text{ }^{\circ}\text{C}$

IR (ATR): $\tilde{\nu} = 3017, 2970, 1738, 1366, 1278, 1217, 1135, 907, 842, 733\text{ cm}^{-1}$.

HRMS (ESI, pos. mode): m/z calculated for $\text{C}_{37}\text{H}_{35}\text{ClF}_{12}\text{N}_2\text{NaO}_3\text{Si}$ $[\text{M}+\text{Na}]^+$: 869.1806, found 869.1766.

major species:

$^1\text{H-NMR}$ (CDCl_3 , 600 MHz, $-54\text{ }^{\circ}\text{C}$) $\delta = 5.16$ (d, $J = 10.3\text{ Hz}$, 1H), 4.99 (d, $J = 10.5\text{ Hz}$, 1H), 4.60 (dd, $J = 7.3, 4.8\text{ Hz}$, 1H), 3.29 (dt, $J = 11.7, 7.9\text{ Hz}$, 1H), $2.16 - 2.10$ (m, 1H), 1.97 (dt, $J = 11.3, 7.3\text{ Hz}$, 1H), $1.73 - 1.68$ (m, 2H), 1.19 (dq, $J = 13.1, 6.6\text{ Hz}$, 1H), 0.95 (d, $J = 6.7\text{ Hz}$, 3H), $0.14 - 0.05$ (m, 1H), -0.07 (d, $J = 6.5\text{ Hz}$, 3H), -0.22 (s, 9H) ppm.

¹³C-NMR (CDCl₃, 151 MHz, −54 °C) δ = 171.2, 170.3, 84.0, 76.1, 68.5, 65.4, 48.6, 29.1, 27.5, 24.0, 21.2, 12.0, 1.6 ppm.

minor species:

¹H-NMR (CDCl₃, 600 MHz, −54 °C) δ = 5.81 (d, J = 10.7 Hz, 1H), 5.05 (d, J = 10.8 Hz, 1H), 4.14 (dd, J = 9.9, 4.0 Hz, 1H), 3.27 – 3.22 (m, 1H), 2.39 – 2.32 (m, 1H), 2.19 – 2.16 (m, 1H), 1.87 – 1.80 (m, 2H), 1.42 – 1.35 (m, 1H), 1.28 (d, J = 6.6 Hz, 3H), 1.06 (d, J = 6.9 Hz, 3H), 0.62 (dp, J = 14.7, 7.5 Hz, 1H), - 0.21 (s, 9H) ppm.

¹³C-NMR (CDCl₃, 151 MHz, −54 °C) δ = 170.7, 170.8, 82.2, 75.9, 68.7, 66.5, 48.2, 29.2, 28.8, 23.9, 21.3, 15.5, 1.8 ppm.

The combination of aldehyde, Jørgensen-Hayashi-type catalyst **9b**, and NCP generates the corresponding aminor species almost quantitatively. The conversion of the aldehyde to the α -chloroaldehyde is always below 5%. The low conversion in combination with the high volatility of chloroaldehyde **12** and alcohol **SI5** makes the isolation and purification difficult. To overcome these problems, *in-situ* reduced chloroaldehyde **12** was directly converted into the non-volatile 3,5-dinitrobenzylester **SI2**.

Enantiomeric Excess (Isovaleraldehyde, catalyst **9b** and NCS)

Isovaleraldehyde (0.215 mL, 2.00 mmol, 1.0 equiv) was dissolved in CHCl_3 (4.0 mL) at 22 °C. Catalyst **9b** (0.120 g, 0.200 mmol, 10 mol%) and NCS (0.293 g, 2.20 mmol, 1.1 equiv) were added subsequently and the reaction mixture was stirred for 60 min at the same temperature. After the reaction was cooled to 0 °C, MeOH (1.3 mL) and NaBH_4 (0.189 g, 5.00 mmol, 2.5 equiv) were added and the mixture was stirred for 60 min at the same temperature. The reaction was quenched with aqueous saturated NH_4Cl (5 mL), the aqueous phase was extracted with dichloromethane (3x5 mL) and the combined organic phases were dried over NaSO_4 . The solvent was removed under reduced pressure (product is volatile!) and the crude product was redissolved in dichloromethane (4 mL). The solution was cooled to 0 °C and DMAP (12.2 mg, 0.100 mmol, 0.05 equiv) and 3,5-dinitrobenzoylchloride (0.300 g, 1.30 mmol, 0.7 equiv) were added subsequently. Et_3N (0.236 mL, 1.70 mmol, 0.9 equiv) was added dropwise and the reaction mixture was stirred for 10 min at 0 °C. The reaction was quenched with aqueous saturated NaHCO_3 (5 mL), the aqueous phase was extracted with dichloromethane (3x5 mL) and the combined organic phases were dried over NaSO_4 . The solvent was removed under reduced pressure and the crude product was purified by column chromatography (Silica, pentane/EtOAc 10:1). Ester **SI2** (0.013 g, 41.0 μmol , 2%, 49% ee for the (S)-enantiomer) was obtained as a colorless solid.

$^1\text{H-NMR}$ (CDCl_3 , 600 MHz) δ = 9.24 (t, J = 2.2 Hz, 1H), 9.16 (d, J = 2.1 Hz, 2H), 4.66 (dd, J = 11.7, 4.7 Hz, 1H), 4.61 (dd, J = 11.7, 7.9 Hz, 1H), 4.18 (dt, J = 7.9, 4.6 Hz, 1H), 2.17 (heptd, J = 6.8, 4.7 Hz, 1H), 1.13 (d, J = 6.8 Hz, 3H), 1.09 (d, J = 6.7 Hz, 3H) ppm.

$^{13}\text{C-NMR}$ (CDCl_3 , 151 MHz) δ = 162.3, 148.9, 133.5, 129.7, 122.8, 68.5, 65.0, 31.7, 20.0, 17.5 ppm.

(S)-2-chloro-3-methylbutyl-3,5-dinitrobenzoate ((S)-SI2)

Isovaleraldehyde (0.108 mL, 1.00 mmol, 1.0 equiv) was dissolved in MeCN (4.0 mL) and cooled to -30 °C. Catalyst **3c** (56.9 mg, 0.200 mmol, 20 mol%) and NCS (0.147 g, 1.10 mmol, 1.1 equiv) were added subsequently and the reaction mixture was stirred for 15 h at the same temperature. After the reaction was warmed to 0 °C, MeOH (1.3 mL) and NaBH₄ (94.6 mg, 2.50 mmol, 2.5 equiv) were added and the mixture was stirred for 60 min at the same temperature. The reaction was quenched with aqueous saturated NH₄Cl (10 mL), the aqueous phase was extracted with dichloromethane (3x10 mL) and the combined organic phases were dried over NaSO₄. The solvent was removed under reduced pressure (product is volatile!) and the crude product was redissolved in dichloromethane (4 mL). The solution was cooled to 0 °C and DMAP (12.2 mg, 0.100 mmol, 0.1 equiv) and 3,5-dinitrobenzoylchloride (0.300 g, 1.30 mmol, 1.3 equiv) were added subsequently. Et₃N (0.237 mL, 1.70 mmol, 1.7 equiv) was added dropwise and the reaction mixture was stirred for 10 min at 0 °C. The reaction was quenched with aqueous saturated NaHCO₃ (10 mL), the aqueous phase was extracted with dichloromethane (3x10 mL) and the combined organic phases were dried over NaSO₄. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (Silica, pentane/EtOAc 10:1). Ester (S)-**SI2** (0.108 g, 0.341 mmol, 34%, 96% ee) was obtained as colorless solid.

The ¹H-NMR spectrum is in accordance with the previous experiment.

(*R*)-2-chloro-3-methylbutyl-3,5-dinitrobenzoate ((*R*)-SI2)

Isovaleraldehyde (0.108 mL, 1.00 mmol, 1.0 equiv) was dissolved in MeCN (4.0 mL) and cooled to $-30\text{ }^{\circ}\text{C}$. Catalyst *ent*-**3c** (56.9 mg, 0.200 mmol, 20 mol%) and NCS (0.147 g, 1.10 mmol, 1.1 equiv) were added subsequently and the reaction mixture was stirred for 15 h at the same temperature. After the reaction was warmed to $0\text{ }^{\circ}\text{C}$, MeOH (1.3 mL) and NaBH_4 (94.6 mg, 2.50 mmol, 2.5 equiv) were added and the mixture was stirred for 60 min at the same temperature. The reaction was quenched with aqueous saturated NH_4Cl (10 mL), the aqueous phase was extracted with dichloromethane (3x10 mL) and the combined organic phases were dried over NaSO_4 . The solvent was removed under reduced pressure (product is volatile!) and the crude product was redissolved in dichloromethane (4 mL). The solution was cooled to $0\text{ }^{\circ}\text{C}$ and DMAP (12.2 mg, 0.100 mmol, 0.1 equiv) and 3,5-dinitrobenzoylchloride (0.300 g, 1.30 mmol, 1.3 equiv) were added subsequently. Et_3N (0.237 mL, 1.70 mmol, 1.7 equiv) was added dropwise and the reaction mixture was stirred for 10 min at $0\text{ }^{\circ}\text{C}$. The reaction was quenched with aqueous saturated NaHCO_3 (10 mL), the aqueous phase was extracted with dichloromethane (3x10 mL) and the combined organic phases were dried over NaSO_4 . The solvent was removed under reduced pressure and the crude product was purified by column chromatography (Silica, pentane/EtOAc 10:1). Ester (*R*)-**SI2** (97.0 mg, 0.306 mmol, 31%, 95% ee) was obtained as colorless solid.

Spectroscopic data are in accordance with the previous experiment.

In contrast to most of the amins derived from the MacMillan-type catalysts, all attempts to purify or crystallize amina **14** failed and led to decomposition. The reduction of *N*-alkylphthalimides to amides is literature known^{22,41} and was anticipated to increase the stability of amina **14** and enabled subsequent purification and crystallization.

***N*-((1*S*,2*S*)-1-((*S*)-2-(bis(3,5-bis(trifluoromethyl)phenyl)((trimethylsilyl)oxy)methyl)pyrrolidin-1-yl)-2-chloro-3-methylbutyl)-2-(hydroxymethyl)benzamide (**SI3**),
2-((1*R*,2*S*)-1-((*S*)-2-(bis(3,5-bis(trifluoromethyl)phenyl)((trimethylsilyl)oxy)methyl)pyrrolidin-1-yl)-2-chloro-3-methylbutyl)-3-hydroxyisoindolin-1-one (**SI4**)**

NaBH₄ (67.0 mg, 1.77 mmol, 3.0 equiv) was added to a solution of amina **14** (0.500 g, 0.590 mmol, 1.0 equiv) in dry MeOH (7.0 mL) at 0 °C. After 4 h at 0 °C the reaction was quenched by the addition of aqueous saturated NaHCO₃ (5 mL). The aqueous phase was extracted with dichloromethane (3x5 mL), the combined organic phases were dried over Na₂SO₄ and the solvent was removed under reduced pressure. After purification by column chromatography (SiO₂, pentane/EtOAc 20:1 to 5:1) amide **SI3** (0.122 g, 0.143 mmol, 24%) was obtained as an off-white foamy solid. The absolute configuration was determined by x-ray crystal structure analysis of the 3,5-dinitrobenzoyl-derivative. Hemiaminal **SI4** (94.0 mg, 0.111 mmol, 19%) was obtained as a pale yellow oil. The substance appears as a defined spot on the TLC. ¹H-NMR of the hemiaminal **SI4** shows extremely broadened signals for every hydrogen atom. A tentative structure proposal is based on the molecular mass and was supported by a further reduction process.

Amide **SI3**:

mp = 76 °C

[α]_D²⁶ = -99.8° (c = 3.00, dichloromethane)

¹H-NMR (CDCl₃, 400 MHz) δ = 8.31 (s, 2H), 8.06 (s, 2H), 7.94 (s, 2H), 7.62 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.54 – 7.38 (m, 3H), 7.03 (d, *J* = 8.9 Hz, 1H), 5.29 (s, 1H), 4.95 – 4.86 (m, 1H), 4.72 (dd, *J* = 12.1, 5.9 Hz, 1H), 4.63 (dd, *J* = 12.2, 6.2 Hz, 1H), 4.24 (t, *J* = 6.1 Hz, 1H), 3.76 (d, *J* = 7.4 Hz, 1H), 2.61 (dd, *J* =

9.8, 7.8 Hz, 1H), 2.31 (t, $J = 8.6$ Hz, 1H), 2.09 – 1.98 (m, 1H), 1.86 – 1.73 (m, 2H), 1.35 (s, 1H), 0.91 (d, $J = 6.6$ Hz, 3H), 0.30 (s, 3H), 0.07 – -0.10 (m, 1H), -0.12 (s, 9H) ppm.

^{13}C -NMR (CDCl_3 , 176 MHz) $\delta = 171.3, 145.6, 144.4, 140.4, 135.6, 132.5 - 131.9$ (m), 131.9, 131.3, 131.2 – 130.7 (m), 130.5, 129.5, 128.5, 127.9, 123.4 (2xq, $J = 273.0, 47.6$ Hz), 122.3, 121.7, 83.1, 71.6, 70.5, 68.9, 64.9, 47.2, 31.2, 28.1, 24.2, 20.5, 14.4, 1.7 ppm.

IR (ATR): $\tilde{\nu} = 3276, 2968, 2924, 1734, 1636, 1541, 1372, 1278, 1173, 1136, 910, 844, 712\text{ cm}^{-1}$.

HRMS (ESI, pos. mode): m/z calculated for $\text{C}_{37}\text{H}_{40}\text{ClF}_{12}\text{N}_2\text{O}_3\text{Si}$ $[\text{M}+\text{H}]^+$: 851.2300, found 851.2320; m/z calculated for $\text{C}_{37}\text{H}_{39}\text{ClF}_{12}\text{N}_2\text{NaO}_3\text{Si}$ $[\text{M}+\text{Na}]^+$: 873.2119, found 873.2157; m/z calculated for $\text{C}_{37}\text{H}_{39}\text{ClF}_{12}\text{KN}_2\text{O}_3\text{Si}$ $[\text{M}+\text{K}]^+$: 889.1859, found 889.1889.

Figure SI-20. ^1H -NMR spectra of amide **SI3** at 23 °C (red spectrum) and -60 °C (blue spectrum). We noted the absence of a second set of signals at -60 °C.

Hemiaminal **SI4**:

HRMS (ESI, pos. mode): m/z calculated for $\text{C}_{37}\text{H}_{37}\text{ClF}_{12}\text{N}_2\text{NaO}_3\text{Si}$ $[\text{M}+\text{Na}]^+$: 871.1962, found 871.2005; m/z calculated for $\text{C}_{37}\text{H}_{37}\text{ClF}_{12}\text{KN}_2\text{O}_3\text{Si}$ $[\text{M}+\text{K}]^+$: 887.1702, found 887.1733.

Chemical reaction scheme showing the reduction of compound **SI4** to compound **SI3** using NaBH_4 in MeOH at 22°C for 30 min.

Compound **SI4** (left) is a complex molecule featuring a central carbon atom bonded to a 2,4,6-trifluorophenyl group, a 3,5-bis(trifluoromethyl)phenyl group, a trimethylsilyloxy (OTMS) group, and a pyrrolidine ring. The pyrrolidine ring is further substituted with a 1-chloro-3-methylbutyl chain and a 1-hydroxy-2-phenylisoindolin-1-one group.

Compound **SI3** (right) is the reduced product, where the hydroxyl group in the isoindolinone moiety has been reduced to a hydrogen atom, forming a secondary amine.

The spectroscopic data are in accordance with the previously isolated amide **S13**.

After the reduction of amina **14** isolation and purification without notable decomposition was possible. Unfortunately, all attempts to isolate single crystals for X-ray crystal structure analysis failed. The esterification of the primary alcohol in amide **SI3** with 3,5-dinitrobenzoyl chloride was anticipated to positively impact the crystallization behavior.

2-(((1*S*,2*S*)-1-((*S*)-2-(bis(3,5-bis(trifluoromethyl)phenyl)((trimethylsilyl)oxy)methyl)pyrrolidin-1-yl)-2-chloro-3-methylbutyl)carbamoyl)benzyl 3,5-dinitrobenzoate (15**)**

3,5-Dinitrobenzoylchlorid (16.5 mg, 71.5 μmol , 1.3 equiv) and DMAP (1.00 mg, 8.25 μmol , 0.15 equiv) were added to an ice-cold solution of alcohol **SI3** (46.8 mg, 55.0 μmol , 1.0 equiv) in dichloromethane (0.30 mL). Et_3N (13.0 μL , 93.5 μmol , 1.7 equiv) was added slowly and the solution was warmed to 22 °C over 10 min. The reaction was quenched with aqueous saturated NaHCO_3 (0.5 mL), the aqueous phase was extracted with dichloromethane (3x0.5 mL) and the combined organic phases were dried over Na_2SO_4 . The solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO_2 , pentane/ EtOAc 6:1). Ester **15** (39.0 mg, 37.3 μmol , 68%) was obtained as an off-white foamy solid. The absolute configuration was determined by X-ray crystal structure analysis.

mp = 151 °C

$[\alpha]_D^{26} = -53.9^\circ$ ($c = 2.00$, dichloromethane)

$^1\text{H-NMR}$ (CDCl_3 , 700 MHz) δ = 9.22 (t, $J = 2.1$ Hz, 1H), 9.17 (d, $J = 2.2$ Hz, 2H), 8.30 (s, 2H), 8.07 (s, 2H), 7.93 (d, $J = 6.8$ Hz, 2H), 7.61 (ddd, $J = 7.7, 6.4, 1.3$ Hz, 2H), 7.53 (td, $J = 7.6, 1.4$ Hz, 1H), 7.47 (td, $J = 7.5, 1.3$ Hz, 1H), 6.94 (d, $J = 9.0$ Hz, 1H), 5.85 (d, $J = 12.8$ Hz, 1H), 5.75 (d, $J = 13.1$ Hz, 1H), 5.33 (s, 1H), 4.98 (d, $J = 9.4$ Hz, 1H), 3.79 (s, 1H), 2.67 (td, $J = 9.6, 7.3$ Hz, 1H), 2.33 (ddd, $J = 9.9, 7.9, 2.7$ Hz, 1H), 2.08 (s, 1H), 1.93 – 1.86 (m, 1H), 1.85 – 1.79 (m, 1H), 1.40 (dddd, $J = 12.5, 10.1, 7.0, 2.7$ Hz, 1H), 0.91 (d, $J = 6.6$ Hz, 3H), 0.32 (s, 3H), 0.02 (s, 1H), -0.12 (s, 9H) ppm.

¹³C-NMR (CDCl₃, 176 MHz) δ = 169.9, 162.8, 148.8, 145.6, 144.5, 136.1, 133.9, 133.7, 132.0 (q, J = 33.5, 33.0 Hz), 131.2, 131.1 – 130.7 (m), 130.6, 130.2, 129.7, 129.6, 129.3, 127.5, 123.4 (qd, J = 273.0, 40.2 Hz), 122.7, 122.2, 121.7, 83.2, 71.7, 70.8, 68.8, 66.2, 47.1, 31.0, 28.2, 24.2, 20.7, 1.7 ppm.

IR (ATR): $\tilde{\nu}$ = 3353, 3106, 2964, 1736, 1666, 1629, 1548, 1463, 1371, 1345, 1276, 1171, 1133, 910, 843, 722 cm⁻¹.

HRMS (ESI, pos. mode): m/z calculated for C₄₄H₄₁ClF₁₂N₄NaO₈Si [M+Na]⁺: 1067.2083, found 1067.2087; m/z calculated for C₄₄H₄₁ClF₁₂KN₄O₈Si [M+K]⁺: 1083.1823, found 1083.1816.

To avoid the oversight and potential loss of possible additional stereoisomers during the numerous purifications, an optimized synthesis protocol with a subsequent thorough isolation and purification process was developed.

2-(((1*S*,2*S*)-1-((*S*)-2-(bis(3,5-bis(trifluoromethyl)phenyl)((trimethylsilyl)oxy)methyl)pyrrolidin-1-yl)-2-chloro-3-methylbutyl)carbamoyl)benzyl 3,5-dinitrobenzoate (15**) (optimized procedure)**

Catalyst **9b** (2.39 g, 4.00 mmol, 50 mol%) and NCP (0.726 g, 4.00 mmol, 0.5 equiv) were added successively to a solution of isovaleraldehyde (0.861 mL, 8.00 mmol, 1.0 equiv) in CHCl_3 (36 mL) at $22\text{ }^\circ\text{C}$. After 45 min the solvent and unreacted isovaleraldehyde were removed under reduced pressure. The crude product was dissolved in dry MeOH (40 mL) and cooled to $0\text{ }^\circ\text{C}$. NaBH_4 (1.34 g, 35.4 mmol, 10.0 equiv) was added in portions and the reaction was stirred for 2 h at $22\text{ }^\circ\text{C}$. The reaction was quenched with aqueous saturated NaHCO_3 (20 mL), the aqueous phase was extracted with dichloromethane (3x20 mL) and the combined organic phases were dried over Na_2SO_4 . The solvent was removed under reduced pressure and the crude product was dissolved again in dichloromethane (14 mL). The reaction mixture was cooled to $0\text{ }^\circ\text{C}$ and 3,5-dinitrobenzoyl chloride (1.02 g, 4.41 mmol, 1.3 equiv) and DMAP (41.5 mg, 0.340 mmol, 10 mol%) were added successively. Et_3N (0.804 mL, 5.77 mmol, 1.7 equiv) was added dropwise and the reaction mixture was stirred for 10 min at $22\text{ }^\circ\text{C}$. The reaction was quenched with aqueous saturated NaHCO_3 (15 mL), the aqueous phase was extracted with dichloromethane (3x20 mL) and the combined organic phases were dried over Na_2SO_4 . The solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO_2 , pentane/EtOAc 10:1 to 0:1). Ester **15** (1.96 g, 1.87 mmol, 47% over 3 steps, single diastereomer) was obtained as an off-white foamy solid. The spectroscopic data are in accordance with the previously isolated ester **15**.

After a thorough analysis of all fractions from the column chromatographic, only a single diastereomer could be detected and isolated. This of course does not exclude the presence of additional, labile diastereomers, but it is the best we could do.

***N*-((1*S*,2*S*)-1-((*S*)-2-(bis(3,5-bis(trifluoromethyl)phenyl)((trimethylsilyl)oxy)methyl)pyrrolidin-1-yl)-2-chloro-3-methylbutyl)-2-(hydroxymethyl)benzamide (**SI3**) (ester hydrolysis)**

Three drops of aqueous NaOH (1 M) were added to a solution of ester **15** (0.140 g, 0.134 mmol, 1.0 equiv) in MeOH (0.5 mL) at 22 °C and the reaction was stirred for 60 min at the same temperature. H₂O (1 mL) was added, the aqueous phase was extracted with dichloromethane (3x1 mL), the combined organic phases were dried over Na₂SO₄ and the solvent was removed under reduced pressure. After column chromatography (SiO₂, pentane/EtOAc 10:1 to 5:1) pure alcohol **SI3** (62.0 mg, 72.8 μmol, 54%) was obtained as an off-white foamy solid.

The spectroscopic data are in accordance with the previously synthesized alcohol **SI3**.

3.1.2. Structural Analysis

NOE and J-Coupling Analysis of Aminoal 14

To extend the characterization data above, a full assignment of all NMR resonances of the aminoal **14** was attempted in CDCl₃ at 219 K (see Table SI-15). At this temperature there is still severe overlap of the two species in the NMR spectra, particularly in the aromatic region, where most of the signals are additionally split by the ¹⁹F J-couplings (see Figures SI-21 to SI-22). Subsequently, aminoal **14** was dissolved in CD₂Cl₂, showing almost the exact same chemical shifts and coupling patterns (see Table SI-16), indicating that no major structural change is observed in this solvent. The solvent change however allows to further cool down to 190 K, at which most resonances for the major species could be assigned. For the minor species, however, some aromatic signals (particularly quaternary carbons) remain unassigned as they could not be resolved.

Table SI-15. Assignment of aminoal **14** in CDCl₃ at 219 K, shifts relative to CHCl₃ at 7.26 ppm.

Position	Major (80%)		Minor (20%)	
	$\delta^{13}\text{C}$ (ppm)	$\delta^1\text{H}$ (ppm)	$\delta^{13}\text{C}$ (ppm)	$\delta^1\text{H}$ (ppm)
2	68.6	4.60	68.6	4.15
3a	27.7	1.71 ¹	29.0	1.82
3b	27.7	1.71 ¹	29.0	1.38
4a	24.3	1.20	24.1	1.28
4b	24.3	0.09	24.1	0.63
5a	48.8	3.29	48.5	3.27
5b	48.8	1.97	48.5	2.16
6	82.4		84.2	
OTMS	1.7	-0.16	1.9	-0.15
1'	76.3	5.16	76.1	5.81
2'	65.6	4.98	66.8	5.05
3'	29.3	2.13	29.0	2.35
4'	21.3	0.95	21.4	1.06
5'	12.2	-0.01	15.7	1.28
Phth-1 ²	170.5/171.4		170.8/170.9	

¹ diastereotopic protons strongly coupled

² hindered rotation around C1'-N-bond, no assignment Phth-1 vs Phth-1' etc.

Table SI-16. Assignment of aminoral **14** in CD₂Cl₂ at 190 K, shifts relative to CHDCl₂ @ 5.35 ppm.

Position	Major (78%)			Minor (22%)		
	$\delta^{13}\text{C}$ (ppm)	$\delta^1\text{H}$ (ppm)	J (Hz)	$\delta^{13}\text{C}$ (ppm)	$\delta^1\text{H}$ (ppm)	J (Hz)
2	68.3	4.56	$^3J_{2,3a/b} = 7.6, 4.7$	67.5	4.13	$^3J_{2,3a/b} = 9.8, 2.4$
3a	27.5	1.68 ¹	¹	28.7	1.82	?
3b	27.5	1.68 ¹	¹	28.7	1.38	?
4a	24.1	1.15	$^3J_{4a,5a} = 8.0$	23.6	1.24	$^2J_{4a,4b} = 11.8$
4b	24.1	0.05	$^3J_{4b,5a} = 6.7$	23.6	0.36	$^2J_{4a,4b} = 11.8,$ $^3J_{4b,5a} = 9.3,$ $^3J_{4b,5b} = 6.7$
5a	48.8	3.24	$^2J_{5a,5b} = 11.1, 48.2$ $^3J_{4b,5a} = 6.7,$ $^3J_{4a,5a} = 8.0$	48.2	3.12	$^2J_{5a,5b} = 9.8,$ $^3J_{4b,5a} = 9.3$
5b	48.8	1.94	$^2J_{5a,5b} = 11.1$	48.2	2.29	$^2J_{5a,5b} = 9.8,$ $^3J_{4b,5b} = 6.7$
6	82.2			84.3		
7A ²	145.6			145.5		
7B ²	143.9			?		
8A ²	130.4/131.4	9.37/7.36		?	?	
8B ²	128.5/130.0	8.20/7.68		129.2/132.1	8.02/7.49	
10A ²	122.7	8.02		?	?	
10B ²	122.1	7.98		?	?	
11A ²	123.9/124.4			?		
11B ²	124.4/124.6			?		
OTMS	1.3	-0.24		1.7	-0.21	
1'	75.9	5.15	$^3J_{1',2'} = 10.3$	75.4	5.81	$^3J_{1',2'} = 10.9$
2'	65.8	5.02	$^3J_{1',2'} = 10.3, 67.0$ $^3J_{2',3'} < 1.0$	5.07		$^3J_{1',2'} = 10.9,$ $^3J_{2',3'} < 1.0$
3'	29.3	2.14	$^3J_{2',3'} < 1.0$	29.3	2.38	$^3J_{2',3'} < 1.0$
4'	21.2	0.93		21.3	1.03	
5'	12.0	-0.08		15.7	1.27	
Phth-1 ³	170.2/171.7			170.9/171.0		
Phth-2 ³	131.5/?			?		

¹ diastereotopic protons strongly coupled

² hindered rotation around C2-C6-bond, no assignment of diastereotopic aromatic rings A vs B, NOE contacts hint at ring B being atop the pyrrolidine

³ hindered rotation around C1'-N-bond, no assignment Pth-1 vs Pth-1' etc.

[?] obfuscated by overlap / not determined

Figure SI-21. ¹H Spectrum of aminal **14** in CDCl₃ at 219 K.

Figure SI-22. ¹H/¹³C Spectrum of aminal **14** in CDCl₃ at 219 K.

Figure SI-23. ¹H Spectrum of aminal **14** in CD₂Cl₂ at 190 K.

Figure SI-25. ^1H - ^{13}C HSQC Spectrum of aminal **14** in CD_2Cl_2 at 190 K.

Figure SI-26. ^1H - ^{13}C HMBC Spectrum of aminal **14** in CD_2Cl_2 at 190 K.

The experimental ^{13}C chemical shifts of major and minor species are fairly similar, while the observed ^1H chemical shifts as well as some – but notably not all – J -couplings show more marked differences between the two signal sets. The aminal proton H1' as well as the pyrrolidine proton H2 show the largest deviations in chemical shift between the major and the minor species, accompanied by a large difference for the resonance of the methyl group 5'. The J -couplings in the aminal part indicate an *anti-periplanar* arrangement of the protons H1' and H2' for both major and minor species. While not all J -couplings along the pyrrolidine ring could be determined experimentally, the observed values apparently differ between the major and minor species, possibly indicating a difference in the (average) ring pucker.

From the EASY-ROESY spectra, the interconversion between the major and minor species is evident (see Figure SI-27). While the NOE/ROE contacts have the opposite phase to the diagonal, the cross-peaks generated by chemical exchange have the same phase. These exchange peaks become even more prevalent at higher temperatures (219 K and 240 K, not shown here). Based on the exchange rate determined by the PANIC analysis, we estimate an energy difference for interconversion at 190 K of $\Delta G^\ddagger \approx 12.4 \text{ kcal mol}^{-1}$. The distinction between chemical exchange and NOE is not immediately obvious in the 1D NOE spectra, as the compound is in the slow motion regime, i.e. both effects show signals with the same phase as the selected (diagonal) signal. A representative mixing time series of selective 1D NOE spectra showing this behavior is given in Figure SI-28.

Figure SI-27. EASY-ROESY of aminal **14** in CD_2Cl_2 at 190 K. Diagonal peaks and signals generated by chemical exchange are colored green, while NOE/ROE cross-peaks are colored blue. a) full spectrum. b) zoom into the spectral region between 6 and 4 ppm. The highlighted signals show the interconversion of the major and minor species (negative phase, green cross-peaks) vs. the positive, blue cross-peaks for the NOE/ROE contacts.

Figure SI-28. a) Example of a selective 1D NOE mixing time series of aminal **14** in CD_2Cl_2 at 190 K, with the signal H2'-major selected. The mixing time is indicated with each spectrum. The NOE spectra are scaled to match the intensity of the selected signal for display purposes. The blue spectrum at the very top shows the corresponding part of the 1D ^1H NMR spectrum. Note the distorted line shape of the H1'-major signal at 5.15 ppm which never reaches the expected doublet lineshape due to insufficient zero-quantum suppression. This leads to a larger error on the distance extracted from this peak (see below). All other signals show the expected undistorted linear build-up of the NOE cross-peak intensities with increasing mixing time. b) Selected PANIC plots for the normalized NOE integrals for the NOEs H2'-major $\rightarrow$ H1'-major (top panel) and H2'-major $\rightarrow$ H5a-major. As expected from the lineshapes, the linear fit of the normalized integrals is fairly bad for the first NOE (H2'-major $\rightarrow$ H1'-major) due to the J -coupling contributions, while the latter example shows the high-confidence linear fit ($R^2 > 0.99$) observed for all other NOE contacts. The slope of the linear fit to the PANIC plot is used as cross-relaxation rate σ . Note that some "relayed" cross peaks are visible, which originate from magnetization transfer between the two species caused by chemical exchange and subsequent NOE (or vice versa).

The NOE derived distances calculated from the cross-relaxation rates by internal calibration with the cross-relaxation rate of the diastereotopic proton pair H5a/b are collected in Table SI-17. In cases where both signals could be selected with the selective pulse in the 1D NOE spectra, the distances corresponding to the individual cross-relaxation rates are averaged. While the set of distances for the minor species is smaller, the observed distances show very similar values for both species. Particularly the close distances from the protons H1' and H2' of the aminal to the pyrrolidine protons H2 and H5b indicate a similar geometry of both major and minor species with respect to the relative arrangement of the Cl and phthalimide substituents with respect to the pyrrolidine ring. The particularly interesting distance between the protons H1' and H2' in the aminal is difficult to address with these measurements. We used a variant of the 1D NOE pulse sequence already including a Thrippleton-Keeler element⁴ to suppress unwanted contributions by J -coupling of the two neighboring nuclei, however, the applied filter element was apparently not able to fully suppress these effects in the case of these two protons. Over

the course of the mixing time series, the shape of the multiplet of the H2' signal changes over time (see Figure SI-28, the mixing time series for the H1'-minor -> H2'-minor NOE shows the same effect but to a lesser extent), indicating *J*-coupling evolution alongside the desired NOE build-up. This effect results in an apparent oscillation in the normalized intensities of the PANIC plot (noted already by Kolmer *et al.*⁹ for such cases) and finally gives a reduced apparent NOE derived distance (see Table SI-17). Correcting for these effects would require extensive numerical simulations, which we did not undertake. We estimate the true experimental value for the H1'-H2' NOE distance to be around 2.9 Å, consistent with the *anti*-periplanar arrangement derived from the large (>10 Hz) $^3J_{HH}$ couplings.

Table SI-17. Experimental NOE derived distances for aminor **14** in CDCl₃ at 219 K and CD₂Cl₂ at 190 K.

Nucleus 1	Nucleus 2	Quantitative 1D selective NOE				Semi-quantitative 2D F1-PSYCHE- EASY-ROESY CD ₂ Cl ₂ @ 190K	
		CDCl ₃ @ 219K		CD ₂ Cl ₂ @ 190K		Major (Å)	Minor (Å)
		Major (Å)	Minor (Å)	Major (Å)	Minor (Å)		
1'	2	2.30	2.44	2.21 (2)	2.30 (3)	2.38	2.14
1'	5a	3.10		3.08 (6)		2.29	
1'	2'	2.58 ¹	2.67 ¹	2.39 (27) ¹	2.79 (5) ¹		
1'	3'			2.79 (4)		2.44	
1'	5'					2.43	2.47
2'	2			3.56 (9)			
2'	5a	2.16	2.16	2.15 (6)	2.21 (3)	1.98	1.98
2'	5b	2.22		2.53 (7)			
2'	3'			2.22 (6)		2.22	2.01
2'	4'			3.03 (3)		2.72	2.74
3'	5a			2.72 (5)			
3'	5b			2.41 (3)		2.28	
3'	4'			2.90 (3)		2.61	2.35
3'	5'					2.50	2.47
4'	5'					3.05	
5'	5a			3.47 (5)			
5'	5b			3.28 (4)			
2	5a			3.17 (10)			
4a	4b					1.85	1.85
4a	5a					2.46	
4b	5b					2.31	
5a	5b	1.76 ²	1.77	1.76 ²	1.83 (1)	1.76 ²	1.83

¹ insufficient zero-quantum suppression. Oscillation observed in PANIC fit.

² fixed reference distance.

Using the optimized geometries from the DFT calculations of chemical shifts enables the comparison of experimental distances to expected ones for different relative configurations of C1' and C2' as well as different conformations of the pyrrolidine ring and the bulky ligand. The *syn* geometries use the phthalimide substituent, while the *anti* geometries are taken from the corresponding succinimide calculations below. The values in Table SI-18 show an overall better agreement of experimental and calculated values for the *syn* arrangement of Cl and imide substituents at C2' and C1', respectively. Applying ensemble averaging with the populations used below in the calculation of chemical shifts improves the agreement with the experimental data slightly (see Table SI-19). From the geometry optimizations, particularly short distances are expected for H1'-H2, H2'-H5a and H3'-H5b for the *syn* diastereoisomers, while the latter distance is expected to be much larger in the *anti* diastereoisomers. Distances expected to be larger than 3 Å from the DFT calculations are apparently underestimated by the experimental methods, which might be taken as indication for conformational flexibility (see below). Also distances involving the methyl groups 4' and 5' are underestimated. Interestingly, the experimental value for the H2'-H2 NOE distance is much shorter as compared to the expected value from the calculated ensembles. While this one particular value is well reproduced in the *anti*(S,S)/*sc-exo* geometry, several others (notably the short H3'-H5b distance) show much larger deviations from the experimental values. The observed deviations of NOEs involving methyl groups are a notorious issue in NOE analysis. The internal averaging of the internuclear interactions of the three methyl protons and another proton of interest are coupled to the overall tumbling of the molecule as well as any internal averaging related to conformational flexibility of the entire molecule. Furthermore the averaging depends on the angle the bond vectors (C-Me axis for the methyl group) of the two interacting partner take with respect to each other.^{10,42} The approximations taken herein, namely equal weighting of the three methyl proton distances (usually called "slow tumbling" or " r^{-3} averaging", equation (2)) without considering corrections to angular contributions in addition to the " r^{-6} averaging" of several geometries to form a conformer ensemble may not be applicable to the case here. Ignoring the methyl groups in the distance comparisons improves the agreement of experimental and calculated distances significantly, to ~0.4 Å RMSD for the favored *syn* models vs up to 1.0 Å for the disfavored *anti* models of the major species. Thus the NOE data indicate that the major species is the *syn*-configured aminor. As the RMSD values are the root mean squared deviations normalized to the number of observations, they are expected to be larger for the major species, where four times the number of NOEs are experimentally observed than for the minor species. Thus the smaller value of the RMSD for the minor species does not indicate a better fit to any of the structures and no discrimination between structures is possible as all RMSD values for the minor species are (almost) within experimental error (at least 0.1 Å). The experimental NOE data therefore suggests that the major species is the *syn* diastereoisomer and not any of the *anti* models. With the reduced dataset for the minor species, however, no discrimination between the two configurations is possible based on NOEs alone. The NOEs indicate that the conformation of the pyrrolidine ring with respect to the rest of the compound (rotation around N-C1' bond) is unchanged. Thus this can be excluded as a reason for the second signal set.⁴³ As the large 3J coupling between H1'

and H2' indicates that the antiperiplanar arrangement prevails, and the average ring-pucker is different in the two signal sets, we consider it unlikely that the minor signal set would be due to the *anti*-diastereoisomer but consider a different conformation (*sc-exo*, see below and main text) more likely. Furthermore, quite distinct chemical shifts are observed. Thus we conducted calculations of the chemical shifts (see below).

Table SI-18. Comparison of experimentally derived NOE distances from quantitative 1D selective NOE spectra (CD₂Cl₂, 190 K) with the internuclear distances of different structure models of aminoral **14**. For the calculated geometries, the first row specifies the arrangement of the Cl and imide substituents at C2' and C1', while the second row specifies the orientation of the bulky ligand at C2. The last column shows a potential geometry where the pyrrolidine ring is rotated 180° relative to the aminoral.

Nucleus 1	Nucleus 2	Experimental		Calculated					
		Major (Å)	Minor (Å)	<i>syn</i> (R,S)	<i>syn</i> (R,S)	<i>anti</i> (R,R)	<i>anti</i> (S,S)	<i>anti</i> (S,S)	<i>syn</i> (R,S)
				<i>ap</i>	<i>sc-exo</i>	<i>ap</i>	<i>ap</i>	<i>sc-exo</i>	<i>sc-exo</i>
				(Å)	(Å)	(Å)	(Å)	(Å)	(Å)
H1'	H2	2.21 (2)	2.30 (3)	2.40	2.51	2.38	2.47	2.45	3.62
H1'	H5a	3.08 (6)		3.62	3.71	3.67	3.70	3.71	2.60
H1'	H2'	2.39 (27) ¹	2.79 (5) ¹	3.04	3.06	3.05	3.06	3.07	3.04
H1'	H3'	2.79 (4)		3.18	3.09	3.17	3.12	3.11	3.08
H2'	H2	3.56 (9)		4.55	4.43	4.57	3.89	3.80	2.89
H2'	H5a	2.15 (6)	2.21 (3)	2.42	2.57	2.64	2.16	2.20	4.48
H2'	H5b	2.53 (7)		2.78	2.54	2.52	3.12	3.08	4.67
H2'	H3'	2.22 (6)		2.45	2.49	2.44	2.43	2.44	2.49
H2'	H4'	3.03 (3)		2.89	2.87	3.97	2.92	2.91	2.92
H3'	H5a	2.72 (5)		3.34	3.51	4.18	4.39	4.46	3.15
H3'	H5b	2.41 (3)		2.26	2.21	4.76	4.69	4.70	4.27
H3'	H4'	2.90 (3)		2.61	2.63	2.64	2.61	2.61	2.62
H5'	H5a	3.47 (5)		5.32	5.50	5.51	5.61	5.61	3.20
H5'	H5b	3.28 (4)		4.64	4.64	5.34	6.11	6.12	4.19
H2	H5a	3.17 (10)		3.65	3.38	3.61	3.44	3.32	2.99
H5a	H5b	1.76 ²	1.83 (1)	1.76	1.77	1.76	1.77	1.77	1.79
RMSD vs major (Å)				0.71	0.74	1.10	1.18	1.18	1.06
RMSD vs major (Å) /without 5'				0.45	0.45	0.89	0.83	0.84	1.10
RMSD vs minor (Å)				0.18	0.25	0.26	0.17	0.16	1.32

¹ insufficient zero-quantum suppression. Oscillation observed in PANIC fit.

² fixed reference distance.

Table SI-19. Comparison of experimentally derived NOE distances from quantitative 1D selective NOE spectra (CD₂Cl₂, 190 K) with the internuclear distances of different averaged ensemble structure models of aminal **14**. For the calculated ensembles, the first row specifies the arrangement of the Cl and imide substituents at C2' and C1', while the second row specifies the orientation of the bulky ligand at C2.

		Experimental		Calculated averaged ensemble				
				<i>syn</i> (R,S)	<i>syn</i> (R,S)	<i>anti</i> (R,R)	<i>anti</i> (S,S)	<i>anti</i> (S,S)
				<i>ap</i>	<i>sc-exo</i>	<i>ap</i>	<i>ap</i>	<i>sc-exo</i>
Nucleus 1	Nucleus 2	Major (Å)	Minor (Å)	(Å)	(Å)	(Å)	(Å)	(Å)
H1'	H2	2.21 (2)	2.30 (3)	2.38	2.48	2.33	2.47	2.45
H1'	H5a	3.08 (6)		3.62	3.68	3.64	3.58	3.71
H1'	H2'	2.39 (27) ¹	2.79 (5) ¹	3.04	3.06	3.04	3.06	3.07
H1'	H3'	2.79 (4)		3.19	3.12	3.21	3.17	3.11
H2'	H2	3.56 (9)		4.54	4.43	4.56	3.79	3.80
H2'	H5a	2.15 (6)	2.21 (3)	2.29	2.27	2.35	2.16	2.20
H2'	H5b	2.53 (7)		2.96	2.79	2.73	3.32	3.08
H2'	H3'	2.22 (6)		2.44	2.48	2.44	2.43	2.44
H2'	H4'	3.03 (3)		2.89	2.88	3.98	2.94	2.91
H3'	H5a	2.72 (5)		3.04	2.99	3.99	4.20	4.46
H3'	H5b	2.41 (3)		2.38	2.35	4.97	4.88	4.70
H3'	H4'	2.90 (3)		2.61	2.62	2.64	2.61	2.61
H5'	H5a	3.47 (5)		5.15	5.17	5.23	5.58	5.61
H5'	H5b	3.28 (4)		4.73	4.72	5.63	6.20	6.12
H2	H5a	3.17 (10)		3.74	3.55	3.76	3.58	3.32
H5a	H5b	1.76 ²	1.83 (1)	1.77	1.77	1.76	1.77	1.77
RMSD vs major (Å)				0.69	0.67	1.12	1.20	1.18
RMSD vs major (Å) /without 5'				0.43	0.40	0.91	0.85	0.84
RMSD vs minor (Å)				0.14	0.17	0.15	0.16	0.16

¹ insufficient zero-quantum suppression. Oscillation observed in PANIC fit.

² fixed reference distance.

Computational NMR Analysis of Aminals **11** (Succinimide Substituent) and **14** (Phthalimide Substituent)

The calculated ^1H and ^{13}C chemical shifts for the *syn*, *anti*(C1'), and *anti*(C2') isomers of **11** were compared to Blackmond and coworkers experimental shifts (*)²⁸ (Tables SI-20–SI-29). The weights, or percentages, for the conformers used in the calculations can be found in Table SI-40. The *syn*-**11** diastereomer resulted in the lowest MAD of the ^1H and ^{13}C chemical shifts compared to their major product at -54°C . The calculated chemical shifts for the *anti*(C1') and *anti*(C2') isomers were compared to the minor product at -54°C , but did not result in good agreement with the experimental shifts. Continuation of the search for the minor product at -54°C , led to the separation of the calculated *ap* and *exo-sc* rotational conformer chemical shifts for *syn*-**14**. When the calculated chemical shifts were separated by this rotational classification, the *ap* and *exo-sc* weighted chemical shifts were in good agreement with major and minor chemical shifts respectively at -54°C (Tables SI-30–SI-33). Using the same classification of the *ap* and *exo-sc* conformers for the succinimide version of the aminal (*syn*-**11**) the weighted *ap* conformers were in good agreement with major product chemical shifts (mean average deviations (MADs): 1.7 ppm for ^{13}C ; 0.16 ppm for ^1H), while not all the *exo-sc* conformer chemical shifts were in good agreement with the minor product chemical shifts, such as the C(5')H shift predicted to be 1.51 ppm, but which was reported to occur at -0.13 ppm. Given the similarities between the calculated lowest energy conformers between the phthalimide (*syn*-**14**) and succinimide (*syn*-**11**) substituent aminals, and the good agreement between the *exo-sc* chemical shifts, further investigation may be needed to confirm all of the experimental minor product chemical shifts.

For NMR calculations with this level of theory: PCM(chloroform)-mPW1PW91/6-311+G(2d,p)//B3LYP-D3(BJ)/6-31G+(d,p) expected absolute deviation for the ^1H chemical shifts is < 0.3 ppm and $< 7\text{--}8$ ppm for ^{13}C chemical shifts^{17,18} and are highlighted in red in the tables below. The C2' ^{13}C shift deviations for both major and minor products when compared to the *ap* and *exo-sc* calculated chemical shifts are around this upper limit of deviation. This is expected for carbons bonded to halogens due to relativistic effects.⁴⁴ The ^1H shifts for the H2' carbon also had deviations ~ 0.3 ppm as well, suggesting minor variations in conformers or solvent interactions may be affecting this chemical shift.⁴⁵ Chemical shifts that differ in the major and minor products are indicated (*). Chemical shift assignments which could be switched are assigned to minimize the mean average deviation (MAD and indicated (**).

The *J*-couplings for the *syn*-**14** *ap* and *exo-sc* rotamers were also calculated for the pyrrolidine ring and compared to the calculated experimental *J*-couplings which were generally within ~ 0.5 Hz of the experimental values (Tables SI-34–SI-37). Additionally, the theoretical chemical shifts for the iminium ion that forms from *syn*-**11** were calculated to compare to unassigned peaks in the *syn*-**11** spectra; however, no iminium ion peaks were able to be determined with this comparison (Tables SI-38 & SI-39). The barrier of rotation for the *syn*-**14** *ap* and *exo-sc* rotamers was also calculated and found to be $13.9\text{ kcal mol}^{-1}$ at -54°C with implicit chloroform when rotating the -OTMS group from the *ap* orientation towards the *exo-sc* orientation, similar to the experimental value of $12.8\text{ kcal mol}^{-1}$ (Figure SI-29).

Table SI-20. Comparison of calculated and experiment major ^{13}C NMR δ 's for *syn-11* (*ap*) at -54°C

Exp. C#	Comp. C#	Comp. Isotropic	Comp. δ	Avg. Comp. δ	Syn. $\delta^\dagger$	Abs. Dev.
C5	C1	135.6845	48.6		48.4	0.2
C2	C2	116.4527	67.1		67.8	0.7
C3	C3	156.9831	28.2		27.3	0.9
C4	C4	159.9259	25.4		23.8	1.6
*C1'	C12	107.0240	76.1		76.5	0.4
*C2'	C14	111.0191	72.3		64.3	8.0
C3'	C16	152.8208	32.2		28.7	3.5
*C4'	C18	165.6695	19.9		20.8	0.9
*C5'	C22	173.5483	12.3		11.7	0.6
	C27	154.8925	30.2			
	C28	155.4406	29.7			
**C5''	C34	-2.2923	181.0		179.5	1.5
**C2''	C36	-3.8047	182.5		180.9	1.6
*C6	C38	100.1433	82.7		81.9	0.8
	C39	34.6347	145.6			
	C40	50.0127	130.8			
	C41	48.8364	132.0			
	C42	50.6022	130.3			
	C44	51.8776	129.1			
	C46	59.7108	121.5			
	C48	33.1497	147.0			
	C49	48.2190	132.6			
	C50	46.7355	134.0			
	C51	48.3657	132.4			
	C53	49.2026	131.6			
	C55	58.2757	122.9			
	C57	52.3549	128.6			
	C58	52.4529	128.5			
	C59	51.8145	129.1			
	C60	51.9597	129.0			
	C62	184.8693	1.4			
	C66	186.5223	-0.2			
*OTMS	C70	185.8696	0.5	0.6	1.3	0.7
MAD:						1.7

Table SI-21. Comparison of calculated and experimental major ^1H NMR δ 's for *syn*-**11** (*ap*) at -54°C .

Exp. #	Comp. C#	Comp. H#	Comp. Isotropic	Comp. δ	Avg. Comp. δ	Exp. $\delta^\dagger$	Abs. Dev.
C(5)H	1	H5	28.22	3.41	3.41	3.20	0.21
C(5)H	1	H6	29.88	1.86	1.86	1.85	0.01
*C(2)H	2	H7	26.77	4.76	4.76	4.48	0.28
C(3)H	3	H8	29.94	1.80			
C(4)H	4	H9	31.64	0.21	0.21	0.13	0.08
C(4)H	4	H10	30.57	1.21	1.21	1.15	0.06
*C(1')H	12	H13	26.35	5.16	5.16	5.00	0.16
*C(2')H	14	H15	26.29	5.21	5.21	4.90	0.31
C(3')H	16	H17	29.39	2.32	2.32	2.05	0.27
	18	H19	30.65	1.14			
	18	H20	30.74	1.06			
**C(4')H	18	H21	30.86	0.95	1.05	0.91	0.14
	22	H23	31.39	0.45			
	22	H24	31.83	0.04			
**C(5')H	22	H25	32.15	-0.26	0.08	-0.13	0.21
	27	H29	29.07	2.62			
**C(3"/C4")H	27	H30	28.98	2.70	2.66	2.77	0.11
	28	H31	28.89	2.78			
**C(3"/C4")H	28	H32	28.89	2.79	2.79	2.94	0.15
	40	H43	22.84	8.43			
	41	H32	26.54	7.74			
	46	H47	23.36	7.94			
	49	H52	21.22	9.94			
	50	H54	46.39	-13.55			
	55	H56	23.35	7.95			
	62	H63	31.37	0.47			
	62	H64	31.43	0.41			
	62	H65	31.66	0.20			
	66	H67	32.17	-0.28			
	66	H68	32.39	-0.48			
	66	H69	32.83	-0.90			
	70	H71	31.85	0.02			
	70	H72	31.80	0.07			
*OTMS	70	H73	32.03	-0.14	-0.07	-0.26	0.19
C(3)H	3	H87	29.86	1.88	1.84	1.72	0.12
MAD							0.16

Table SI-22. Comparison of calculated and experimental minor ^{13}C NMR δ 's for *syn-11* (*exo-sc*) at -54°C .

Exp. C#	Comp. C#	Comp. Isotropic	Comp. δ	Avg. Comp. δ	Syn. $\delta^\dagger$	Abs. Dev.
C5	C1	136.4713	47.9		48.4	0.5
C2	C2	117.7784	65.8		70.7	4.9
C3	C3	156.1918	28.9		27.3	1.6
C4	C4	160.7078	24.6		23.8	0.8
*C1'	C12	107.8337	75.4		76.5	1.1
*C2'	C14	109.9297	73.3		65.4	7.9
C3'	C16	153.0082	32.0		28.7	3.3
*C4'	C18	165.8347	19.7		20.8	1.1
*C5'	C22	169.4198	16.3		11.7	4.6
	C27	155.0574	30.0			
	C28	155.2203	29.9			
**C5''	C34	-2.7958	181.5		179	2.5
**C2''	C36	-2.1768	180.9		180.1	0.8
*C6	C38	98.5761	84.2		83.7	0.5
	C39	34.5114	145.7			
	C40	46.9006	133.8			
	C41	49.8154	131.0			
	C42	49.4106	131.4			
	C44	49.4941	131.3			
	C46	57.4787	123.7			
	C48	33.6336	146.6			
	C49	51.1595	129.7			
	C50	47.3518	133.4			
	C51	51.6159	129.3			
	C53	51.1792	129.7			
	C55	59.7931	121.5			
	C57	52.2149	128.7			
	C58	51.6628	129.3			
	C59	52.2399	128.7			
	C60	52.5823	128.4			
	C62	185.8896	0.4			
	C66	184.4579	1.8			
*OTMS	C70	184.2350	2.0	1.4	1.5	0.1
MAD:						2.3

Table SI-23. Comparison of calculated and experimental minor ^1H NMR δ 's for *syn*-**11** (*exo-sc*) at -54°C .

Exp. C#	Comp. C#	Comp. H#	Comp. Isotropic	Comp. δ	Avg. Comp. δ	Exp. $\delta^\ddagger$	Abs. Dev.
C(5)H	1	H5	28.34	3.29	3.29	3.2	0.09
C(5)H	1	H6	29.45	2.26	2.26	1.85	0.41
*C(2)H	2	H7	27.34	4.23	4.23	4.08	0.15
C(3)H	3	H8	29.88	1.86			
C(4)H	4	H9	31.73	0.13	0.13	0.13	0.00
C(4)H	4	H10	30.61	1.18	1.18	1.15	0.03
*C(1')H	12	H13	25.50	5.95	5.95	5.66	0.29
*C(2')H	14	H15	26.24	5.25	5.25	4.95	0.30
C(3')H	16	H17	29.06	2.62	2.62	2.05	0.57
	18	H19	30.56	1.23			
	18	H20	30.75	1.05			
**C(4')H	18	H21	30.52	1.26	1.18	0.91	0.27
	22	H23	30.28	1.49			
	22	H24	30.50	1.28			
**C(5')H	22	H25	29.97	1.77	1.51	-0.13	1.64
	27	H29	29.02	2.66			
**C(3"/C4")H	27	H30	28.98	2.70	2.68	2.77	0.09
	28	H31	28.85	2.82			
**C(3"/C4")H	28	H32	28.94	2.74	2.78	2.94	0.16
	40	H43	23.70	7.63			
	41	H32	26.54	8.05			
	46	H47	23.33	7.97			
	49	H52	24.19	7.17			
	50	H54	44.85	-12.10			
	55	H56	23.36	7.94			
	62	H63	31.59	0.27			
	62	H64	33.66	-1.67			
	62	H65	32.31	-0.40			
	66	H67	31.11	0.71			
	66	H68	31.89	-0.02			
	66	H69	31.69	0.17			
	70	H71	31.64	0.22			
	70	H72	31.75	0.12			
*OTMS	70	H73	31.85	0.02	-0.06	-0.29	0.23
C(3)H	3	H87	30.40	1.38	1.62	1.72	0.10
						MAD	0.31

Table SI-24. Comparison of calculated and experimental minor ^{13}C NMR δ 's for *anti*(C1')-11 (*ap*) at -54°C .

Exp. C#	Comp. C#	Comp. Isotropic	Comp. δ	Avg. Comp. δ	Syn. $\delta^\dagger$	Abs. Dev.
C5	C1	135.9947	48.3		48.4	0.1
C2	C2	115.7302	67.8		70.7	2.9
C3	C3	157.0734	28.1		27.3	0.8
C4	C4	160.2338	25.1		23.8	1.3
*C1'	C12	114.5331	68.9		76.5	7.6
*C2'	C14	108.4440	74.8		65.4	9.4
C3'	C16	151.6796	33.3		28.7	4.6
*C4'	C18	165.9822	19.6		20.8	1.2
*C5'	C22	171.6763	14.1		11.7	2.4
	C27	155.5999	29.5			
	C28	155.5434	29.6			
**C5''	C34	-1.1724	180.0		179	1.0
**C2''	C36	0.6840	178.2		180.1	1.9
*C6	C38	100.5030	82.4		83.7	1.3
	C39	36.4178	143.9			
	C40	48.3516	132.4			
	C41	49.8264	131.0			
	C42	54.0621	127.0			
	C44	51.5846	129.3			
	C46	60.4671	120.8			
	C48	34.4201	145.8			
	C49	50.9172	130.0			
	C50	46.9404	133.8			
	C51	49.8517	131.0			
	C53	48.0804	132.7			
	C55	56.4885	124.6			
	C57	51.7504	129.2			
	C58	52.3672	128.6			
	C59	51.8414	129.1			
	C60	51.3528	129.6			
	C62	185.8755	0.5			
	C66	184.8698	1.4			
*OTMS	C70	186.2035	0.1	0.7	1.5	0.8
MAD:						2.7

Table SI-25. Comparison of calculated and experimental minor ^1H NMR δ 's for *anti*(C1')-11 (*ap*) at -54°C .

Exp. #	Comp. C#	Comp. H#	Comp. Isotropic	Comp. δ	Avg. Comp. δ	Exp. $\delta^\dagger$	Abs. Dev.
C(5)H	1	H5	28.45	3.19	3.19	3.2	0.01
C(5)H	1	H6	29.84	1.90	1.90	1.85	0.05
*C(2)H	2	H7	26.12	5.37	5.37	4.08	1.29
C(3)H	3	H8	29.64	2.09			
C(4)H	4	H9	31.73	0.13	0.13	0.13	0.00
C(4)H	4	H10	30.34	1.43	1.43	1.15	0.28
*C(1')H	12	H13	26.40	5.10	5.10	5.66	0.56
*C(2')H	14	H15	25.93	5.54	5.54	4.95	0.59
C(3')H	16	H17	30.19	1.57	1.57	2.05	0.48
	18	H19	30.78	1.02			
	18	H20	30.64	1.15			
**C(4')H	18	H21	30.86	0.94	1.04	0.91	0.13
	22	H23	31.16	0.67			
	22	H24	31.15	0.67			
**C(5')H	22	H25	30.59	1.19	0.85	-0.13	0.98
	27	H29	29.28	2.42			
**C(3"/C4")H	27	H30	29.05	2.63	2.52	2.77	0.25
	28	H31	29.31	2.39			
**C(3"/C4")H	28	H32	28.94	2.74	2.57	2.94	0.37
	40	H43	23.98	7.36			
	41	H32	26.54	8.40			
	46	H47	23.40	7.91			
	49	H52	22.52	8.73			
	50	H54	24.02	7.32			
	55	H56	23.34	7.96			
	62	H63	32.02	-0.13			
	62	H64	31.85	0.02			
	62	H65	32.28	-0.38			
	66	H67	31.80	0.07			
	66	H68	31.33	0.51			
	66	H69	31.44	0.41			
	70	H71	32.57	-0.65			
	70	H72	31.91	-0.04			
*OTMS	70	H73	32.21	-0.31	-0.06	-0.29	0.23
C(3)H	3	H87	29.91	1.83	1.96	1.72	0.24
MAD							0.39

Table SI-26. Comparison of calculated and experimental minor ^{13}C NMR δ 's for *anti*(C1')-11 (*exo-sc*) at -54°C .

Exp. C#	Comp. C#	Comp. Isotropic	Comp. δ	Avg. Comp. δ	Syn. $\delta^\dagger$	Abs. Dev.
C5	C1	135.4575	48.8		48.4	0.4
C2	C2	110.9980	72.3		70.7	1.6
C3	C3	156.3759	28.8		27.3	1.5
C4	C4	160.0842	25.2		23.8	1.4
*C1'	C12	113.3557	70.1		76.5	6.4
*C2'	C14	109.9617	73.3		65.4	7.9 [‡]
C3'	C16	151.9450	33.0		28.7	4.3
*C4'	C18	165.7677	19.8		20.8	1.0
*C5'	C22	171.3154	14.4		11.7	2.7
	C27	155.0763	30.0			
	C28	154.6013	30.5			
**C5''	C34	-2.1163	180.9		179	1.9
**C2''	C36	-0.3893	179.2		180.1	0.9
*C6	C38	96.1129	86.6		83.7	2.9
	C39	33.8334	146.4			
	C40	48.5481	132.3			
	C41	48.0533	132.7			
	C42	49.9668	130.9			
	C44	48.8141	132.0			
	C46	58.6709	122.5			
	C48	34.4047	145.8			
	C49	51.4280	129.5			
	C50	46.5023	134.2			
	C51	51.3556	129.6			
	C53	52.2943	128.7			
	C55	59.7534	121.5			
	C57	52.1849	128.8			
	C58	51.1248	129.8			
	C59	52.2953	128.7			
	C60	52.5062	128.5			
	C62	185.1263	1.2			
	C66	185.3374	1.0			
*OTMS	C70	186.3819	0.0	0.7	1.5	0.8
MAD:						2.6

Table SI-27. Comparison of calculated and experimental minor ^1H NMR δ 's for *anti*(C1')-11 (*exo-sc*) at -54°C .

Exp. #	Comp. C#	Comp. H#	Comp. Isotropic	Comp. δ	Avg. Comp. δ	Exp. $\delta^\ddagger$	Abs. Dev.
C(5)H	1	H5	28.55	3.10	3.10	3.2	0.10
C(5)H	1	H6	29.35	2.35	2.35	1.85	0.50
*C(2)H	2	H7	26.17	5.32	5.32	4.08	1.24
C(3)H	3	H8	29.54	2.17			
C(4)H	4	H9	31.20	0.63	0.63	0.13	0.50
C(4)H	4	H10	30.44	1.33	1.33	1.15	0.18
*C(1')H	12	H13	25.27	6.16	6.16	5.66	0.50
*C(2')H	14	H15	25.69	5.77	5.77	4.95	0.82
C(3')H	16	H17	30.11	1.64	1.64	2.05	0.41
	18	H19	30.82	0.99			
	18	H20	30.90	0.91			
**C(4')H	18	H21	30.49	1.29	1.06	0.91	0.15
	22	H23	30.62	1.17			
	22	H24	30.63	1.16			
**C(5')H	22	H25	31.08	0.74	1.03	-0.13	1.16
	27	H29	29.21	2.48			
**C(3"/C4")H	27	H30	29.12	2.57	2.52	2.77	0.25
	28	H31	29.04	2.64			
**C(3"/C4")H	28	H32	28.60	3.05	2.85	2.94	0.09
	40	H43	23.64	7.68			
	41	H32	26.54	8.23			
	46	H47	23.34	7.96			
	49	H52	23.93	7.41			
	50	H54	22.55	8.70			
	55	H56	23.42	7.89			
	62	H63	30.13	1.63			
	62	H64	31.48	0.37			
	62	H65	32.00	-0.12			
	66	H67	31.55	0.31			
	66	H68	32.05	-0.17			
	66	H69	32.11	-0.22			
	70	H71	32.58	-0.66			
	70	H72	32.48	-0.56			
*OTMS	70	H73	33.84	-1.84	-0.14	-0.29	0.15
C(3)H	3	H87	30.32	1.45	1.81	1.72	0.09
						MAD	0.44

Table SI-28. Comparison of calculated and experimental minor ^{13}C NMR δ 's for *anti*(C2')-11 (*ap*) at -54°C .

Exp. C#	Comp. C#	Comp. Isotropic	Comp. δ	Avg. Comp. δ	Syn. $\delta^\ddagger$	Abs. Dev.
C5	C1	136.9004	47.5		48.4	0.9
C2	C2	115.5457	68.0		70.7	2.7
C3	C3	156.5798	28.6		27.3	1.3
C4	C4	160.0619	25.2		23.8	1.4
C1'	C12	108.9728	74.3		76.5	2.2
C2'	C14	108.1558	75.0		65.4	9.6 [†]
C3'	C16	152.3606	32.6		28.7	3.9
C4'	C18	171.9968	13.8		20.8	7.0
C5'	C22	165.6509	19.9		11.7	8.2
	C27	155.1158	30.0			
	C28	154.7914	30.3			
C5''	C34	-2.7252	181.5		179	2.5
C2''	C36	-2.8807	181.6		180.1	1.5
C6	C38	100.0367	82.8		83.7	0.9
	C39	35.3661	144.9			
	C40	49.8824	131.0			
	C41	46.8657	133.9			
	C42	51.2183	129.7			
	C44	51.2936	129.6			
	C46	60.2623	121.0			
	C48	33.8848	146.3			
	C49	47.5167	133.2			
	C50	48.6472	132.2			
	C51	49.5448	131.3			
	C53	49.3588	131.5			
	C55	57.4194	123.7			
	C57	52.2395	128.7			
	C58	52.1519	128.8			
	C59	51.9835	129.0			
	C60	51.7189	129.2			
	C62	185.5768	0.7			
	C66	185.4877	0.8			
	C70	185.4005	0.9	0.8	1.5	0.7
MAD:						3.3

Table SI-29. Comparison of calculated and experimental minor ^1H NMR δ 's for *anti*(C2')-11 (*ap*) at -54°C .

Exp. #	Comp. C#	Comp. H#	Comp. Isotropic	Comp. δ	Avg. Comp. δ	Exp. $\delta^\ddagger$	Abs. Dev.
C(5)H	1	H5	28.44	3.21	3.21	3.2	0.01
C(5)H	1	H6	29.52	2.20	2.20	1.85	0.35
*C(2)H	2	H7	26.72	4.80	4.80	4.08	0.72
C(3)H	3	H8	29.93	1.81			
C(4)H	4	H9	31.73	0.13	0.13	0.13	0.00
C(4)H	4	H10	30.66	1.14	1.14	1.15	0.01
*C(1')H	12	H13	26.37	5.13	5.13	5.66	0.53
*C(2')H	14	H15	26.69	4.83	4.83	4.95	0.12
C(3')H	16	H17	30.02	1.73	1.73	2.05	0.32
	18	H19	31.16	0.66			
	18	H20	31.07	0.75			
**C(4')H	18	H21	31.18	0.64	0.68	0.91	0.23
	22	H23	30.82	0.98			
	22	H24	30.79	1.01			
**C(5')H	22	H25	30.91	0.90	0.97	-0.13	1.10
	27	H29	29.06	2.63			
**C(3"/C4")H	27	H30	29.11	2.58	2.60	2.77	0.17
	28	H31	28.87	2.80			
**C(3"/C4")H	28	H32	28.93	2.75	2.78	2.94	0.16
	40	H43	22.83	8.43			
	41	H32	26.54	8.77			
	46	H47	23.36	7.94			
	49	H52	23.34	7.96			
	50	H54	22.36	8.87			
	55	H56	23.38	7.92			
	62	H63	31.97	-0.09			
	62	H64	32.08	-0.19			
	62	H65	32.12	-0.23			
	66	H67	31.50	0.34			
	66	H68	31.47	0.37			
	66	H69	31.42	0.43			
	70	H71	32.37	-0.47			
	70	H72	32.35	-0.44			
*OTMS	70	H73	32.07	-0.18	-0.05	-0.29	0.24
C(3)H	3	H87	30.06	1.69	1.75	1.72	0.03
						MAD	0.28

Table SI-30. Comparison of calculated and experimental major ^{13}C NMR δ 's for *syn-14* (*ap*) at -54°C .

Exp. C#	Comp. C#	Comp. Isotropic	Comp. δ	Avg. Comp. δ	Syn. δ	Abs. Dev.
C5	C1	135.9388	48.4		48.8	0.4
C1'	C12	107.9988	75.2		76.3	1.1
C2'	C14	110.3959	72.9		65.6	7.3 [†]
C3'	C16	152.7793	32.2		29.3	2.9
C4'	C18	165.6499	19.9		21.3	1.4
C2	C2	115.6540	67.9		68.6	0.7
C5'	C22	173.5018	12.3		12.2	0.1
	C27	49.2818	131.5			
C2"/C5"	C29	6.8274	172.3		171.4	0.9
C3	C3	156.9539	28.2		27.7	0.5
C2"/C5"	C31	8.1297	171.0		170.5	0.5
C6	C33	100.1346	82.7		82.4	0.3
	C34	35.4051	144.9			
	C35	49.7620	131.1			
	C36	48.7174	132.1			
	C37	50.5989	130.3			
	C39	51.8300	129.1			
C4	C4	160.0826	25.2		24.3	0.9
	C41	59.6637	121.6			
	C43	33.8341	146.4			
	C44	46.4848	134.2			
	C45	48.1872	132.6			
	C46	48.4947	132.3			
	C48	49.1247	131.7			
	C50	58.0782	123.1			
	C52	52.3296	128.6			
	C53	52.3279	128.6			
	C54	51.7803	129.2			
	C55	51.8710	129.1			
OTMS	C57	185.6073	0.7			
OTMS	C61	185.5508	0.8			
OTMS	C65	185.6881	0.6	0.7	1.7	1.0
	C83	49.9831	130.9			
	C84	57.2058	123.9			
	C85	57.5833	123.6			
	C86	45.7889	134.9			
	C88	45.6369	135.0			
MAD:						1.4

Table SI-31. Comparison of calculated and experimental major ^1H NMR δ 's for *syn-14* (*ap*) at -54°C .

Exp. C#	Comp. C#	Comp. H#	Comp. Isotropic	Comp. δ	Avg. Comp. δ	Exp. δ	Abs. Dev.
C4a	C4	H10	30.61	1.18	1.18	1.20	0.02
C1'	C12	H13	26.26	5.24	5.24	5.16	0.08
C2'	C14	H15	26.24	5.25	5.25	4.98	0.27
C3'	C16	H17	29.31	2.39	2.39	2.13	0.26
C4'	C18	H19	30.70	1.09			
C4'	C18	H20	30.75	1.05			
C4'	C18	H21	30.74	1.06	1.07	0.95	0.12
C5'	C22	H23	31.34	0.50			
C5'	C22	H24	32.43	-0.52			
C5'	C22	H25	31.69	0.17	0.05	-0.01	0.06
	C35	H38	22.87	8.40			
	C36	H40	23.44	7.87			
	C41	H42	23.34	7.97			
	C44	H47	22.28	8.95			
	C45	H49	22.75	8.52			
C5a	C1	H5	28.26	3.37	3.37	3.29	0.08
	C50	H51	23.30	8.00			
OTMS	C57	H58	31.77	0.10			
OTMS	C57	H59	31.98	-0.10			
C5b	C1	H6	29.76	1.97	1.97	1.97	0.00
OTMS	C57	H32	26.54	-0.05			
OTMS	C61	H62	31.54	0.31			
OTMS	C61	H63	31.20	0.63			
OTMS	C61	H64	31.83	0.04			
OTMS	C65	H66	32.09	-0.20			
OTMS	C65	H67	32.15	-0.26			
OTMS	C65	H68	33.17	-1.21	-0.08	-0.16	0.08
C2	C2	H7	26.73	4.80	4.80	4.60	0.20
C3a	C3	H8	29.99	1.76	1.76	1.71	0.05
C3b	C3	H82	29.94	1.80	1.80	1.71	0.09
	C84	H87	23.36	7.94			
	C85	H89	23.50	7.81			
C4b	C4	H9	31.79	0.08	0.08	0.09	0.01
	C86	H90	23.53	7.79			
	C88	H91	23.55	7.76			
						MAD	0.10

Table SI-32. Comparison of calculated and experimental minor ^{13}C NMR δ 's for *syn-14* (*exo-sc*) at -54°C .

Exp. C#	Comp. C#	Comp. Isotropic	Comp. δ	Avg. Comp. δ	Syn. δ	Abs. Dev.
C5	C1	136.4232	47.9		48.5	0.6
C1'	C12	108.6580	74.6		76.1	1.5
C2'	C14	109.1710	74.1		66.8	7.3
C3'	C16	152.8625	32.1		29.0	3.1
C4'	C18	165.8239	19.7		21.4	1.7
C2	C2	116.4201	67.1		68.6	1.5
C5'	C22	169.4610	16.2		15.7	0.5
	C27	48.8475	132.0			
C2"/C5"	C29	8.3013	170.9		170.8	0.1
C3	C3	155.8692	29.3		29.0	0.3
C2"/C5"	C31	7.8370	171.3		170.9	0.4
C6	C33	98.5273	84.3		84.2	0.1
	C34	34.5708	145.7			
	C35	47.0622	133.7			
	C36	49.5313	131.3			
	C37	49.5707	131.3			
	C39	49.6703	131.2			
C4	C4	159.8652	25.4		24.1	1.3
	C41	57.9075	123.3			
	C43	34.3743	145.9			
	C44	50.9557	129.9			
	C45	46.9211	133.8			
	C46	51.8629	129.1			
	C48	50.8591	130.0			
	C50	59.5760	121.7			
	C52	52.2178	128.7			
	C53	51.6846	129.2			
	C54	52.3688	128.6			
	C55	52.5147	128.4			
OTMS	C57	184.1522	2.1			
OTMS	C61	184.4262	1.9			
OTMS	C65	185.9906	0.4	1.4	1.9	0.5
	C83	49.5982	131.2			
	C84	57.5751	123.6			
	C85	57.9324	123.2			
	C86	46.5484	134.2			
	C88	46.3394	134.4			
MAD:						1.5

Table SI-33. Comparison of calculated and experimental minor ^1H NMR δ 's for *syn*-**14** (*exo-sc*) at -54°C .

Exp. C#	Comp. C#	Comp. H#	Comp. Isotropic	Comp. δ	Avg. Comp. δ	Exp. δ	Abs. Dev.
C4a	C4	H10	30.53	1.25	1.25	1.28	0.03
C1'	C12	H13	25.39	6.04	6.04	5.81	0.23
C2'	C14	H15	26.21	5.28	5.28	5.05	0.23
C3'	C16	H17	29.01	2.67	2.67	2.35	0.32
C4'	C18	H19	30.54	1.25			
C4'	C18	H20	30.64	1.15			
C4'	C18	H21	30.59	1.20	1.20	1.06	0.14
C5'	C22	H23	30.41	1.37			
C5'	C22	H24	30.21	1.55			
C5'	C22	H25	30.17	1.59	1.50	1.28	0.22
	C35	H38	23.52	7.80			
	C36	H40	23.29	8.00			
	C41	H42	23.37	7.94			
	C44	H47	24.09	7.27			
	C45	H49	22.31	8.92			
C5a	C1	H5	28.18	3.44	3.44	3.27	0.17
	C50	H51	23.33	7.97			
OTMS	C57	H58	31.59	0.26			
OTMS	C57	H59	31.09	0.73			
C5b	C1	H6	29.56	2.16	2.16	2.16	0.00
OTMS	C57	H60	26.54	0.43			
OTMS	C61	H62	31.71	0.15			
OTMS	C61	H63	31.76	0.10			
OTMS	C61	H64	31.73	0.13			
OTMS	C65	H66	31.56	0.30			
OTMS	C65	H67	33.86	-1.85			
OTMS	C65	H68	32.27	-0.37	-0.01	-0.15	0.14
C2	C2	H7	27.33	4.24	4.24	4.15	0.09
C3a	C3	H8	29.94	1.81	1.81	1.82	0.01
C3b	C3	H82	30.46	1.32	1.32	1.38	0.06
	C84	H87	23.43	7.88			
	C85	H89	23.46	7.85			
C4b	C4	H9	31.20	0.63	0.63	0.63	0.00
	C86	H90	23.52	7.80			
	C88	H91	23.53	7.79			
MAD							0.13

Table SI-34. Comparison of the experimental J -couplings for the *syn*-**14** major product to the calculated *ap* conformers averaged according to Table SI-31.

		Scaling Factor: 0.9155			
		Comp. FC	Comp. FC	Syn.	
Exp. H#	Comp. H#	J (Hz)	J (Hz) Scaled	J -coupling	Abs. Dev.
5a-5b	5-6	-11.93	-10.92		
5a-4b	5-9	6.87	6.29		
5a-4a	5-10	8.95	8.19		
5b-4a	6-10	8.67	7.94		
5b-4b	6-9	6.27	5.74		
4a-4b	9-10	-13.68	-12.52		
4a-3b	10-82	5.56	5.09		
2-3a	8-7	9.56	8.75	7.6	1.15
3a-3b	8-82	-14.93	-13.67		
2-3b	82-7	3.49	3.19	4.7	1.51
1'-2'	13-15	10.72	9.81	10.3	0.49
2'-3'	15-17	1.89	1.73	1.0	0.73

Table SI-35. Calculated J -couplings for the relevant *syn*-**14** *ap* conformers.

		Weight of Conformer:				
		0.1393	0.3362	0.0028	0.4677	0.0540
Exp. H#	Comp. H#	4	58	8	17	46
5a-5b	5-6	-11.03	-13.22	-11.06	-11.13	-13.19
5a-4b	5-9	10.93	0.58	10.96	10.89	0.56
5a-4a	5-10	9.34	8.31	9.30	9.36	8.22
5b-4a	6-10	10.47	5.87	10.43	10.46	5.78
5b-4b	6-9	1.42	13.84	1.40	1.43	13.85
4a-4b	9-10	-13.94	-13.26	-13.93	-13.95	-13.22
4a-3b	10-82	0.58	13.35	0.58	0.57	13.41
2-3a	8-7	9.70	9.41	9.73	9.67	9.18
3a-3b	8-82	-14.32	-15.15	-14.48	-14.92	-15.34
2'-3b	82-7	0.69	7.80	0.70	0.73	7.90
1'-2'	13-15	10.79	10.51	10.82	10.87	10.55
2'-3'	15-17	1.94	1.84	1.96	1.92	1.84

Table SI-36. Comparison of the experimental J -couplings for the *syn*-**14** minor product to the calculated *exo*-*sc* conformers averaged according to Table SI-33.

Scaling Factor:		0.9155			
		Comp. FC	Comp. FC	Syn.	
Exp. H#	Comp. H#	J (Hz)	J (Hz) Scaled	J-coupling	Abs. Dev.
5a-5b	5-6	-11.31	-10.35		
5a-4b	5-9	6.45	5.90		
5a-4a	5-10	7.99	7.32		
5b-4a	6-10	7.19	6.59		
5b-4b	6-9	7.24	6.63		
4a-4b	9-10	-13.41	-12.28		
4a-3b	10-82	7.24	6.63		
2-3a	7-8	9.84	9.00	9.8	0.80
3a-3b	8-82	-14.55	-13.32		
2-3b	82-7	5.73	5.25	2.4	2.85
1'-2'	13-15	11.40	10.44	10.9	0.46
2'-3'	15-17	1.37	1.25	1	0.25

Table SI-37. Calculated J -couplings for the relevant *syn*-**14** *exo*-*sc* conformers.

		Weight of Conformer:		
		0.4860	0.4150	0.0990
Exp. H#	Comp. H#	33	62	21
5a-5b	5-6	-10.08	-12.57	-12.06
5a-4b	5-9	12.68	0.56	0.53
5a-4a	5-10	7.57	8.31	8.74
5b-4a	6-10	8.93	5.53	5.68
5b-4b	6-9	0.64	13.53	13.32
4a-4b	9-10	-13.67	-13.18	-13.07
4a-3b	10-82	0.57	13.38	14.29
2-3a	8-7	11.19	8.94	6.96
3a-3b	8-82	-14.75	-14.53	-13.62
2'-3b	82-7	1.12	9.64	12.02
1'-2'	13-15	11.63	11.29	10.79
2'-3'	15-17	1.27	1.32	2.03

Table SI-38. Calculated ^{13}C NMR δ 's for the *syn*-**11** iminium ion.

Exp. #	Comp #	Comp. Isotropic	Comp. δ	Avg. Comp. δ
C5	C1	127.0736	56.9	19.2
C2	C2	100.6921	82.2	
C3	C3	154.3676	30.7	
C4	C4	157.6886	27.5	
C1'	C12	4.3992	174.6	
C2'	C14	114.4977	69.0	
C3'	C16	146.7122	38.0	
C4'	C18	161.9306	23.4	
C5'	C22	165.5088	20.0	
	C27	98.2156	84.6	
	C28	39.8560	140.6	
C5''	C34	22.8471	156.9	
C2''	C36	22.5460	157.2	
C6	C38	48.7216	132.1	
	C39	49.0893	131.7	
	C40	46.4822	134.2	
	C41	22.8941	156.9	
	C42	46.4378	134.3	
	C44	55.6195	125.5	
	C46	51.8209	129.1	
	C48	52.1416	128.8	
	C49	52.1917	128.8	
	C50	205.2978	-18.2	
	C51	181.5245	4.6	
	C53	31.8869	148.2	
	C55	180.5291	5.6	
	C57	30.8771	149.2	
	C58	30.7102	149.4	
	C59	181.3023	4.9	
	C60	31.8039	148.3	
	C62	31.1726	148.9	
	C66	240.5816	-52.0	
	C70	227.3965	-39.4	

Table SI-39. Calculated ^1H NMR δ 's for the *syn*-11 iminium ion.

Exp. #	Comp. C #	Comp #	Comp. Isotropic	Comp. δ	Avg. Comp. δ
C(5)H	1	H5	27.1258	4.43	4.43
C(5)H	1	H6	28.2451	3.38	3.38
C(2)H	2	H7	25.7323	5.73	5.73
C(3)H	3	H8	28.3500	3.29	
C(4)H	4	H9	29.8048	1.93	1.93
C(4)H	4	H10	29.0370	2.65	2.65
C(1')H	12	H13	22.0869	9.13	9.13
C(2')H	14	H15	26.5460	4.97	4.97
C(3')H	16	H17	28.5227	3.13	3.13
	18	H19	29.6889	2.04	
	18	H20	29.6119	2.11	
C(4' or 5')H	18	H21	29.6133	2.11	2.09
	22	H23	29.9158	1.83	
	22	H24	29.5853	2.13	
C(4' or 5')H	22	H25	29.7018	2.03	2.00
	27	H29	47.6406	-14.71	
C(3"/C4")H	27	H30	48.4402	-15.46	-15.08
	28	H31	45.5225	-12.73	
C(3"/C4")H	28	H32	22.8399	8.43	-2.15
	40	H43	22.7776	8.49	
	41	H32	26.5383	8.70	
	46	H47	51.9737	-18.75	
	49	H52	31.0776	0.74	
	50	H54	30.9380	0.87	
	55	H56	30.7511	1.05	
	62	H52	31.0776	0.74	
	62	H53	31.8869	-0.01	
	62	H54	30.9380	0.87	
	66	H56	30.7511	1.05	
	66	H57	30.8771	0.93	
	66	H58	30.7102	1.09	
	70	H60	31.8039	0.06	
	70	H61	31.2639	0.57	
OTMS	70	H62	31.1726	0.65	0.66
C(3)H	3	H76	28.8069	2.86	3.07

Table SI-40. Weighted Averaging for the Calculated NMR and NBO calculations for *syn*-11, *anti*(C1')-11, *anti*(C2')-11, and *syn*-14

syn-11 (*ap*) at –54°C

Filename	Computed Energy (H)	Conformer Weight
crest_confs_1_h_2_nmr_2.log	-3561.5159	0.4707
crest_confs_8_h_2_nmr_2.log	-3561.5156	0.1656
crest_confs_5_h_2_nmr_2.log	-3561.5153	0.0668
crest_confs_7_h_2_nmr.log	-3561.5153	0.1344
crest_confs_21_h_7_nmr_2.log	-3561.5145	0.1625

syn-11 (*exo-sc*) at –54°C

Filename	Computed Energy (H)	Conformer Weight
crest_confs_11_h_2_nmr_2.log	-3561.5131	0.8337
crest_confs_12_h_6_nmr_8.log	-3561.5130	0.1663

anti(C1')-11 (*ap*) at –54°C

Filename	Computed Energy (H)	Conformer Weight
crest_confs_2_h_5_nmr_2.log	-3561.5137	0.0994
crest_confs_3_h_3_nmr_2.log	-3561.5133	0.4934
crest_confs_39_h_2_nmr.log	-3561.5114	0.1949
crest_confs_7_h_4_nmr_2.log	-3561.5113	0.1826
crest_confs_10_h_5_nmr.log	-3561.5101	0.0105
crest_confs_18_h_2_nmr.log	-3561.5101	0.0099
crest_confs_12_h_5_nmr.log	-3561.5094	0.0093

anti(C1')-11 (*exo-sc*) at –54°C

Filename	Computed Energy (H)	Conformer Weight
crest_confs_44_h_4_nmr.log	-3561.5098	1

anti(C2')-11 (*ap*) at –54°C

Filename	Computed Energy (H)	Conformer Weight
crest_confs_55_h_3_low.log	-3561.5143	0.2927
crest_confs_23_h_2_low.log	-3561.5134	0.1472
crest_confs_6_h_3_low.log	-3561.5133	0.0620
crest_confs_7_h_3_low.log	-3561.5129	0.3022
crest_confs_9_h_3_low.log	-3561.5128	0.1959

syn-**14** (*ap*) at -54°C

Filename	Computed Energy (H)	Conformer Weight
crest_confs_8_h_2_low.log	-3713.9415	0.0028
crest_confs_4_h_2_low.log	-3713.9408	0.1393
crest_confs_58_h_2_low.log	-3713.9398	0.3362
crest_confs_17_h_3_low.log	-3713.9389	0.4677
crest_confs_46_h_4_low.log	-3713.9379	0.0540

syn-**14** (*exo-sc*) at -54°C

Filename	Computed Energy (H)	Conformer Weight
crest_confs_33_h_2_low.log	-3713.9381	0.4860
crest_confs_21_h_2_low.log	-3713.9380	0.0990
crest_confs_62_h_3_low.log	-3713.9375	0.4150

DFT NBO Analysis for 11 and 14

NBO analysis was performed to assess the $n_{N(\text{cat})}-\sigma^*_{C-N(\text{imide})}$ interaction differences between the *ap* and *exo-sc* conformers for **11** and **14**, and between the *syn* and *anti* (C1')-**11** diastereomers. The *syn* interactions were higher in energy when compared to the *anti*-conformers for **11**, with a minor difference in the weighted energies between the *ap* and *exo-sc* products (0.31 kcal mol⁻¹). The phthalimide aminal had a similar difference in energies between the two rotational isomers (0.30 kcal mol⁻¹).

Table SI-41. DFT NBO Analysis

<i>syn</i>-11 (<i>ap</i>) Interaction: LP(1)N11-BD*(1)C12-N33		
Conformer	E2 Stabilization Energy (kcal mol ⁻¹)	Conformer Weight
1	17.91	0.4707
5	17.09	0.0668
7	17.74	0.1344
8	17.08	0.1656
21	16.92	0.1625
Weighted Energy:	17.53	
<i>syn</i>-11 (<i>exo-sc</i>) Interaction: LP(1)N11-BD*(1)C12-N33		
Conformer	E2 Stabilization Energy (kcal mol ⁻¹)	Conformer Weight
11	17.19	0.8337
12	17.36	0.1663
Weighted Energy:	17.22	

<i>anti</i>(C1')-11 Interaction: LP(1)N11-BD*(1)C12-N33		
Conformer	E2 Stabilization Energy (kcal mol ⁻¹)	Orientation of OTMS
crest_confs_2_h_5_nmr_2.log	7.95	Ap
crest_confs_3_h_3_nmr_2.log	7.68	Ap
crest_confs_39_h_2_nmr.log	7.84	Ap
crest_confs_7_h_4_nmr_2.log	7.51	Ap
crest_confs_10_h_5_nmr.log	8.51	Ap
crest_confs_18_h_2_nmr.log	8.42	Ap
crest_confs_44_h_4_nmr.log	7.48	Exo-sc
crest_confs_12_h_5_nmr.log	15.91	Ap

<i>syn</i>-14 (<i>ap</i>) Interaction: LP(1)N11-BD*(1)C12-N28		
Conformer	E2 Stabilization Energy (kcal mol ⁻¹)	Conformer Weight
crest_confs_8_h_2_low.log	16.65	0.0028
crest_confs_4_h_2_low.log	16.65	0.1393
crest_confs_58_h_2_low.log	15.99	0.3362
crest_confs_17_h_3_low.log	16.48	0.4677
crest_confs_46_h_4_low.log	15.86	0.0540
Weighted Energy:	16.31	

<i>syn</i>-14 (<i>exo-sc</i>) Interaction: LP(1)N11-BD*(1)C12-N28		
Conformer	E2 Stabilization Energy (kcal mol ⁻¹)	Conformer Weight
crest_confs_33_h_2_low.log	15.97	0.4860
crest_confs_21_h_2_low.log	15.52	0.0990
crest_confs_62_h_3_low.log	16.17	0.4150
Weighted Energy:	16.01

Frame	Dihedral Angle	Relative Energy (kcal mol ⁻¹)
1	-180	1.24
2	-170	0.00
3	-160	1.02
4	-150	2.57
5	-140	5.03
6	-130	7.38
7	-120	8.88
8	-110	8.98
9	-100	8.58
10	-90	7.75
11	-80	7.52
12	-70	8.65
13	-60	10.12
14	-50	6.68
15	-40	9.28
16	-30	10.73
17	-20	13.31
18	-10	16.54
19	0	20.66
20	10	25.84
21	20	24.55
22	30	18.48
23	40	17.73
24	50	18.40

25	60	20.71
26	70	24.51
27	80	29.97
28	90	4.55
29	100	6.92
30	110	10.18
31	120	13.73
32	130	13.70
33	140	13.90
34	150	13.30
35	160	13.09
36	170	13.19
37	180	13.16

Figure SI-29. Dihedral angle scan to calculate the *ap* to *exo-sc* rotational barrier for *syn-14*.

Structure Search in the CCDC Data Base

A structure search in the CCDC data base for Jørgensen-Hayashi catalysts **9b** and **9c** with the pyrrolidine nitrogen bound to a stereogenic sp^3 hybridized carbon reveals striking similarities concerning the catalyst structure. Each structure in the database had the pyrrolidine ring in an envelope conformation with the γ -carbon tilted out of plane toward the diarylsilylether moiety and the nitrogen lone pair (down conformation). For the orientation of the diarylsilylether group, two distinct conformational minima can be observed. In 7/10 crystal structures, the N- and O-substituent at the exocyclic C-C bond of the catalyst possess an antiperiplanar (*ap*) relationship whereas in three cases an *exo-synclinal* (*exo-sc*) conformation was adopted.

Figure SI-30. 883666^{46,47} (*ap*)

Figure SI-31. 883667^{46,47} (*ap*)

Figure SI-32. 883668^{46,47} (*sc-exo*)

Figure SI-33. 885695⁴⁸ (*ap*)

Figure SI-34. 919662⁴⁷ (*sc-exo*)

Figure SI-35. 919664⁴⁷ (*ap*)

Figure SI-36. 973119⁴⁹ (*ap*)

Figure SI-37. 1434063⁵⁰ (*sc-exo*)

Figure SI-38. 1521504⁵¹ (*ap*)

Figure SI-39. 2045387 (*ap*)

(This work)

3.1.3. Decomposition and Deuterium Incorporation Studies

Decomposition and deuterium incorporation experiments were envisioned to shed more light on the decomposition mechanism of aminal **14** and should allow the distinction between E2-elimination (via chloroenamine)²⁸ and hydrolysis via chloroiminium ion.

Decomposition of Aminal **14** (1)

D₂O (36.1 μ L, 2.00 mmol, 2.0 equiv) and TFAAd₁ (154 μ L, 2.00 mmol, 2.0 equiv) were added subsequently to a solution of aminal **14** (0.847 g, 1.00 mmol, 1.0 equiv) in CHCl₃ (50 mL) at 22 °C. Aliquots (5 mL) were taken from the reaction mixture after defined points of time (10 min, 30 min, 60 min, 2 h, 4 h, 22 h, 70 h) and added to a solution of NaBH₄ (18.9 mg, 500 μ mol, 5.0 equiv) in EtOH (2.0 mL). After 30 min the reactions were quenched with aqueous saturated NH₄Cl. The aqueous phase was extracted with EtOAc (3x5 mL), the combined organic phases were dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude products were purified by column chromatography (SiO₂, pentane/EtOAc 10:1). Deuterium incorporation was quantified by ¹H-NMR spectra analysis and the enantiomeric excess was determined by chiral GC.

Figure SI-40. Monitoring of the decomposition of aminal **14** with deuterium incorporation and ee over time.

Figure SI-41. Exemplary ^1H -NMR spectrum of a reduced sample (70 h).

When synthesizing aminal **14** it was not possible to remove all chloroaldehyde residues under reduced pressure. At the beginning of the decomposition experiment, these residues are present in higher concentrations than the chloroaldehydes formed by the decomposition of the aminal. As a consequence, the ee of the first sample ($t = 10$ min; ee = 46%) corresponds roughly with the ee of the products formed from the α -chlorination reaction (ee = 49% with NCS). Over time, the proportion of chloroaldehyde originating from the decomposition of the aminal increases compared to the chloroaldehyde originating from the α -chlorination reaction. Since the aminal decomposes exclusively to the (S)-chloroaldehyde (see decomposition with the aminal **SI6** derived from propanal), the ee increases over time. The acid-catalyzed (TFA-d_1) racemization of the chloroaldehydes subsequently leads to a continuous decrease of the ee over time. A comparison with the decomposition experiment of the propanal-derived aminal (aminal could be obtained without chloroaldehyde impurities) helps to rationalize this experiment.

Decomposition of Aminoal 14 (2)

0.60 mL of a stock solution (CDCl₃ (6.0 mL), D₂O (4.73 μ L) and TFA_d (9.11 μ L)) was added to a NMR-tube containing aminal **14** (10.0 mg, 11.8 μ mol, 1.0 equiv). The NMR-tube was tightly sealed and ¹H-NMR spectra were recorded every 5 min over a period of 10 h. Two additional spectra were recorded after 24 h and 43 h. Conversion was quantified by ¹H-NMR spectra analysis with CDCl₃ as the internal standard. Deuterium incorporation was qualitatively evaluated by ¹H-NMR spectroscopy.

Figure SI-42. Monitoring of the decomposition of a mineral 14.

Figure SI-43. ^1H -NMR spectra of the ongoing decomposition reaction (2 equiv of D_2O , 1 equiv of TFAd_1) of amination **14** allows a qualitative evaluation of the deuterium incorporation into the α -chloroaldehydes.

The analysis of the aldehyde-H signals in the ^1H -NMR spectra allows a qualitative evaluation of the deuterium incorporation into the α -chloroaldehydes. Almost no deuterium incorporation was observed during the first hours. Downstream incorporation of deuterium into the chloroaldehyde can be explained by acid-catalyzed enolization or enamine formation (doublet at 9.52 ppm (α -H-chloroaldehyde) $\rightarrow$ singlet at 9.52 ppm (α -D-chloroaldehyde)).

14

D₂O (2 equiv), TFA-d₁ (20 mol%)

CDCl₃, 22 °C, 4 d

H-12 + D-12

Chemical structures:
H-12: CC(C)C(Cl)C=O
D-12: CC(C)C(D)C=O

Compound 14: CC(C)C(Cl)C(=O)N1C(=O)c2ccccc2C1=O

Annotations:
 - **0 min:** Initial spectrum showing broad peaks.
 - **1 h:** First time point showing emerging structure.
 - **3 h:** Intermediate time point.
 - **7 h:** Intermediate time point.
 - **4 d:** Final time point showing well-resolved peaks.

Lowering the amount of TFA-d₁ (from to 2 equiv to 20 mol%) leads to a slower decomposition of aminoral **14**. Deuterium incorporation into the α-position of the aldehyde can be almost completely suppressed when using 20 mol% TFA-d₁ (clean doublet for the aldehyde-proton).

Chemical reaction scheme showing the conversion of compound **14** to H-12 and D-12.

Compound **14** is a complex molecule featuring a central carbon atom bonded to a trifluoromethylphenyl group, a trimethylsilyloxyphenyl group, a pyrrolidine ring, and a 1-(2-chloro-3-methylbutyl)-2-oxo-1,2,3,4-tetrahydrobenzoxazin-5(1H)-one moiety.

The reaction conditions are D_2O (5 equiv) in CDCl_3 at $22\text{ }^\circ\text{C}$ for 8 d.

The products are H-12 and D-12, which are 2-chloro-3-methylbutanal and its deuterated form, respectively.

174

Omitting acidic conditions further decreases the rate of amination hydrolysis. Nevertheless, only D₂O can mediate the decomposition effectively. As shown in the figure above, amination hydrolysis under non acidic conditions takes place without any detectable incorporation of deuterium in the α -position of the aldehyde over long term (8 days). The sharp doublet of the aldehyde proton (red) and the 1:1 ratio between the aldehyde proton (red) and the α -proton of the aldehyde (orange) prove this issue. E2-elimination of the amination with generation of chloroamines, as proposed for the Curtin-Hammett-scenario cannot explain the complete absence of deuterium incorporation. Whereas the "classical" hydrolysis pathway via chloroiminium ion with an intact α -position is in line with the absence of deuterium incorporation.

(S)-2-chloro-3-methylbutan-1-ol ((S)-SI5)

Isovaleraldehyde (0.215 mL, 2.00 mmol, 1.0 equiv) was dissolved in MeCN (8.0 mL) and cooled to -30 °C. Catalyst **3c** (0.114 g, 0.400 mmol, 20 mol%) and NCS (0.320 g, 2.40 mmol, 1.2 equiv) were added subsequently and the reaction mixture was stirred for 15 h at the same temperature. After the reaction was warmed to 0 °C, MeOH (3.0 mL) and NaBH₄ (0.189 g, 5.00 mmol, 2.5 equiv) were added and the mixture was stirred for 60 min at the same temperature. The reaction was quenched with aqueous saturated NH₄Cl (10 mL), the aqueous phase was extracted with dichloromethane (3x15 mL) and the combined organic phases were dried over NaSO₄. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (Silica, pentane/EtOAc 10:1). Pure chloroalcohol (S)-**SI5** (0.111 g, 0.905 mmol, 45%, 89% ee) was obtained as a colorless oil.

¹H-NMR (CDCl₃, 400 MHz) δ = 3.92 (ddd, J = 7.8, 5.2, 3.8 Hz, 1H), 3.81 (dd, J = 12.0, 3.8 Hz, 1H), 3.73 (dd, J = 12.0, 7.8 Hz, 1H), 2.12 – 2.03 (m, 1H), 2.02 (s, 1H), 1.03 (d, J = 6.8 Hz, 3H), 1.01 (d, J = 6.7 Hz, 3H) ppm.

(*R*)-2-chloro-3-methylbutan-1-ol ((*R*)-SI5)

Isovaleraldehyde (0.215 mL, 2.00 mmol, 1.0 equiv) was dissolved in MeCN (8.0 mL) and cooled to -30 °C. Catalyst *ent*-**3c** (0.114 g, 0.400 mmol, 20 mol%) and NCS (0.320 g, 2.40 mmol, 1.2 equiv) were added subsequently and the reaction mixture was stirred for 15 h at the same temperature. After the reaction was warmed to 0 °C, MeOH (3.0 mL) and NaBH₄ (0.189 g, 5.00 mmol, 2.5 equiv) were added and the mixture was stirred for 60 min at the same temperature. The reaction was quenched with aqueous saturated NH₄Cl (10 mL), the aqueous phase was extracted with dichloromethane (3x15 mL) and the combined organic phases were dried over NaSO₄. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (Silica, pentane/EtOAc 10:1). Pure chloroalcohol (*R*)-**SI5** (0.102 g, 0.832 mmol, 42%, 95% ee) was obtained as a colorless oil.

Spectroscopic data are in accordance with the previous experiment.

3.2. Aminals Derived from Propanal

3.2.1. Synthesis

When synthesizing amina **14**, it was not possible to remove all impurities of isovaleraldehyde (**10**) and 2-chloro-3-methylbutanal (**12**) under reduced pressure. Due to the fact, that a pure and aldehyde-free amina is crucial for some follow-up experiments we changed from isovaleraldehyde to the more volatile propanal. As a result, all aldehyde-impurities could be removed under reduced pressure.

2-(1-((S)-2-(bis(3,5-bis(trifluoromethyl)phenyl)((trimethylsilyl)oxy)methyl)pyrrolidin-1-yl)-2-chloropropyl)isoindoline-1,3-dione (**SI6**)

Catalysts **9b** (2.91 g, 4.87 mmol, 50 mol%) and NCP (0.884 g, 4.87 mmol, 0.5 equiv) were added successively to a solution of propanal (0.698 mL, 9.74 mmol, 1.0 equiv) in CHCl_3 (44 mL) at 22 °C. After 60 min the solvent and aldehydes were removed under reduced pressure. The crude product was dissolved in pentane (20 mL) and the precipitating solids were filtered off. Pentane was removed under reduced pressure and the amina **SI6** was obtained as a foamy off-white solid (3.54 g, 4.32 mmol, 89%). $^1\text{H-NMR}$ spectroscopy at $-54\text{ }^\circ\text{C}$ shows two signal sets with a ratio of 68:32.

mp = 65 °C

IR (ATR): $\tilde{\nu}$ = 3055, 2988, 2307, 1713, 1280, 1264, 1176, 1139, 844, 733, 704 cm^{-1} .

HRMS (ESI, pos. mode): m/z calculated for $\text{C}_{35}\text{H}_{31}\text{ClF}_{12}\text{N}_2\text{NaO}_3\text{Si}$ $[\text{M}+\text{Na}]^+$: 841.1493, found 841.1487; m/z calculated for $\text{C}_{35}\text{H}_{31}\text{ClF}_{12}\text{KN}_2\text{O}_3\text{Si}$ $[\text{M}+\text{K}]^+$: 857.1233, found 857.1207.

major stereoisomer:

$^1\text{H-NMR}$ (CDCl_3 , 600 MHz, $-54\text{ }^\circ\text{C}$) δ = 5.88 (d, J = 10.5 Hz, 1H), 5.19 (dq, J = 13.1, 6.7 Hz, 1H), 4.18 (dd, J = 10.2, 3.2 Hz, 1H), 3.00 (td, J = 9.5, 6.5 Hz, 1H), 2.46 (ddd, J = 9.9, 6.8, 3.4 Hz, 1H), 1.86 – 1.81 (m, 1H), 1.79 (d, J = 6.8 Hz, 3H), 1.40 – 1.34 (m, 1H), 1.32 – 1.26 (m, 1H), 0.41 – 0.31 (m, 1H), -0.18 (s, 9H) ppm.

^{13}C -NMR (CDCl_3 , 151 MHz, $-54\text{ }^\circ\text{C}$) δ = 171.0, 170.9, 83.7, 77.9, 66.8, 55.0, 47.6, 27.9, 23.8, 23.3, 1.5 ppm.

minor stereoisomer:

^1H -NMR (CDCl_3 , 600 MHz, $-54\text{ }^\circ\text{C}$) δ = 5.01 – 4.92 (m, 1H), 4.91 – 4.87 (m, 1H), 4.58 (d, J = 8.1 Hz, 1H), 3.12 (q, J = 8.3 Hz, 1H), 2.28 – 2.23 (m, 1H), 1.73 – 1.67 (m, 1H), 1.64 – 1.58 (m, 1H), 1.24 – 1.20 (m, 1H), 0.99 (d, J = 6.3 Hz, 3H), -0.15 (s, 9H) ppm.

^{13}C -NMR (CDCl_3 , 151 MHz, $-54\text{ }^\circ\text{C}$) δ = 171.1, 170.2, 78.5, 70.0, 53.8, 48.0, 27.4, 24.1, 22.3, 1.7 ppm.

Figure SI-47. ^1H -NMR spectra of aminal **SI6** at different temperatures shows the emergence of two signal sets at low temperatures.

Figure SI-48. The isomeric ratio (68:32) was assigned at $-54\text{ }^\circ\text{C}$.

The combination of aldehyde, Jørgensen-Hayashi-type catalyst **9b**, and NCP generates almost quantitatively the corresponding aminor species. As a consequence, the conversion of the aldehyde to the α -chloroaldehyde is always below 5%. The low conversion in combination with the high volatility of aldehyde **SI8** and alcohol **SI9** makes the isolation and purification difficult. To overcome these problems, the *in-situ* reduced chloroaldehyde **SI8** was directly transformed into the non-volatile 3,5-dinitrobenzylester **SI10**.

Enantiomeric Excess (Propanal, Catalyst **9b** and NCS/NCP)

Propanal (0.359 mL, 5.00 mmol, 1.0 equiv) was dissolved in CHCl_3 (10.0 mL) at $22\text{ }^\circ\text{C}$. Catalyst **9b** (0.299 g, 0.500 mmol, 10 mol%) and A: NCS (0.734 g, 5.50 mmol, 1.1 equiv) or B: NCP (0.999 g, 5.50 mmol, 1.1 equiv) were added subsequently and the reaction mixture was stirred for 60 min at the same temperature. After the reaction was cooled to $0\text{ }^\circ\text{C}$, MeOH (3.3 mL) and NaBH_4 (0.473 g, 12.5 mmol, 2.5 equiv) were added and the mixture was stirred for 60 min at the same temperature. The reaction was quenched with aqueous saturated NH_4Cl (10 mL), the aqueous phase was extracted with dichloromethane (3x15 mL) and the combined organic phases were dried over NaSO_4 . The solvent was removed under reduced pressure (product is volatile!) and the crude product was dissolved in dichloromethane (10 mL). The solution was cooled to $0\text{ }^\circ\text{C}$ and DMAP (30.5 mg, 0.250 mmol, 0.1 equiv) and 3,5-dinitrobenzoylchloride (0.749 g, 3.25 mmol, 1.3 equiv) were added subsequently. Et_3N (0.589 mL, 4.25 mmol, 1.7 equiv) was added dropwise and the reaction mixture was stirred for 10 min at $0\text{ }^\circ\text{C}$. The reaction was quenched with aqueous saturated NaHCO_3 (10 mL), the aqueous phase was extracted with dichloromethane (3x15 mL) and the combined organic phases were dried over NaSO_4 . The solvent was removed under reduced pressure and the crude product was purified by column chromatography (Silica, pentane/EtOAc 10:1).

A: Ester **SI10** (0.073 g, 0.253 mmol, 5%, 5% ee for the (*R*)-enantiomer) was obtained as a yellow oil.

B: Ester **SI10** (0.050 g, 0.173 mmol, 3%, 14% ee for the (*R*)-enantiomer) was obtained as a yellow oil.

$^1\text{H-NMR}$ (CDCl_3 , 600 MHz) δ = 9.23 (t, J = 2.1 Hz, 1H), 9.16 (d, J = 2.1 Hz, 2H), 4.57 (dd, J = 11.6, 5.1 Hz, 1H), 4.53 (dd, J = 11.6, 7.0 Hz, 1H), 4.44 – 4.31 (m, 1H), 1.64 (d, J = 6.7 Hz, 3) ppm.

$^{13}\text{C-NMR}$ (CDCl_3 , 151 MHz) δ = 162.2, 148.8, 133.4, 129.6, 122.8, 70.5, 53.6, 21.5.ppm.

HRMS (EI): m/z calculated for $\text{C}_{10}\text{H}_{10}\text{ClN}_2\text{O}_6$ [$\text{M}+\text{H}$] $^+$: 289.0222, found 289.0219.

The low ee and the inverted absolute configuration (compared to isovaleraldehyde) for propanal as a substrate may be due to the lower energy barrier for the rotation around the C-N-bond of the enamine compared to other substrates carrying more bulky alkyl-substituents (isovaleraldehyde).⁵²

Figure SI-49. Relative free energies (ΔG) of isovaleraldehyde- and propanal-derived enamines according to Jørgensen et al.⁵²

By simply replacing the substrate (isovaleraldehyde $\rightarrow$ propanal) we demonstrated that the correlation between the ratio of interconverting amins (68:32; 36% excess) and the enantiomeric ratio of the chloroaldehyde product (57:43; 14% excess) is no longer present.

(S)-2-chloropropyl-3,5-dinitrobenzoate ((S)-SI10)

Propanal (0.143 mL, 2.00 mmol, 1.0 equiv) was dissolved in MeCN (8.0 mL) and cooled to $-30\text{ }^{\circ}\text{C}$. Catalyst **3c**•TFA (0.114 g, 0.400 mmol, 20 mol%) and NCS (0.320 g, 2.40 mmol, 1.2 equiv) were added subsequently and the reaction mixture was stirred for 15 h at the same temperature. After the reaction was warmed to $0\text{ }^{\circ}\text{C}$, MeOH (3.0 mL) and NaBH_4 (0.189 g, 5.00 mmol, 2.5 equiv) were added and the mixture was stirred for 60 min at the same temperature. The reaction was quenched with aqueous saturated NH_4Cl (10 mL), the aqueous phase was extracted with dichloromethane (3x15 mL) and the combined organic phases were dried over NaSO_4 . The solvent was removed under reduced pressure (product is volatile!) and the crude product was dissolved in dichloromethane (8 mL). The solution was cooled to $0\text{ }^{\circ}\text{C}$ and DMAP (24.4 mg, 0.200 mmol, 0.1 equiv) and 3,5-dinitrobenzoylchloride (0.599 g, 2.60 mmol, 1.3 equiv) were added subsequently. Et_3N (0.474 mL, 3.40 mmol, 1.7 equiv) was added dropwise and the reaction mixture was stirred for 10 min at $0\text{ }^{\circ}\text{C}$. The reaction was quenched with aqueous saturated NaHCO_3 (10 mL), the aqueous phase was extracted with dichloromethane (3x10 mL) and the combined organic phases were dried over NaSO_4 . The solvent was removed under reduced pressure and the crude product was purified by column chromatography (Silica, pentane/EtOAc 10:1). Ester (S)-**SI10** (0.108 g, 0.374 mmol, 19%, 94% ee) was obtained as a yellowish oil.

The ^1H -NMR spectrum is in accordance with the previous experiment.

(*R*)-2-chloropropyl-3,5-dinitrobenzoate ((*R*)-SI10**)**

Propanal (0.143 mL, 2.00 mmol, 1.0 equiv) was dissolved in MeCN (8.0 mL) and cooled to -30 °C. Catalyst *ent*-**3c**•TFA (0.114 g, 0.400 mmol, 20 mol%) and NCS (0.320 g, 2.40 mmol, 1.2 equiv) were added subsequently and the reaction mixture was stirred for 15 h at the same temperature. After the reaction was warmed to 0 °C, MeOH (3.0 mL) and NaBH₄ (0.189 g, 5.00 mmol, 2.5 equiv) were added and the mixture was stirred for 60 min at the same temperature. The reaction was quenched with aqueous saturated NH₄Cl (10 mL), the aqueous phase was extracted with dichloromethane (3x15 mL) and the combined organic phases were dried over NaSO₄. The solvent was removed under reduced pressure (product is volatile!) and the crude product was redissolved in dichloromethane (8 mL). The solution was cooled to 0 °C and DMAP (24.4 mg, 0.200 mmol, 0.1 equiv) and 3,5-dinitrobenzoylchloride (0.599 g, 2.60 mmol, 1.3 equiv) were added subsequently. Et₃N (0.474 mL, 3.40 mmol, 1.7 equiv) was added dropwise and the reaction mixture was stirred for 10 min at 0 °C. The reaction was quenched with aqueous saturated NaHCO₃ (10 mL), the aqueous phase was extracted with dichloromethane (3x10 mL) and the combined organic phases were dried over NaSO₄. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (Silica, pentane/EtOAc 10:1). Ester (*R*)-**SI10** (0.109 g, 0.378 mmol, 19%, 94% ee) was obtained as a yellowish oil.

The ¹H-NMR spectrum is in accordance with the previous experiment.

3.2.2. Decomposition and Deuterium Incorporation Studies

Decomposition of Aminoal SL6 (1)

H₂O (72.1 μ L, 4.00 mmol, 2.0 equiv) and TFA (308 μ L, 4.00 mmol, 2.0 equiv) were added subsequently to a solution of amina **516** (1.64 g, 2.00 mmol, 1.0 equiv) in CHCl₃ (100 mL) at 22 °C. Aliquots (10 mL) were taken from the reaction mixture after defined points of time (1 min, 5 min, 10 min, 20 min, 30 min, 60 min, 2 h, 98 h) and added to a solution of NaBH₄ (75.7 mg, 2.00 mmol, 10.0 equiv) in MeOH (4.0 mL). After 60 min the reactions were quenched with aqueous saturated NH₄Cl. The aqueous phase was extracted with dichloromethane (3x5 mL), the combined organic phases were dried over Na₂SO₄ and the solvent was partially removed under reduced pressure (product is volatile!). The enantiomeric excess of the crude products was determined by chiral GC.

1 min:	94% ee for the (S)-enantiomer	10
5 min:	94% ee	8
10 min:	94% ee	6
20 min:	95% ee	4
30 min:	94% ee	2
60 min:	93% ee	
120 min:	93% ee	
(98 h:	58% ee)

Figure SI-50. The acid-catalyzed decomposition of aminoral **SI6** generates almost enantiopure (S)-chloroaldehyde product.

As mentioned before (decomposition of aminor **14**, synthesis of aminor **S16**) it was possible to obtain aminor **S16** without any detectable aldehyde or chloroaldehyde impurities. The decomposition experiment shows that aminor **S16** decomposes to almost enantiopure chloroaldehyde (S)-**S18**. In contrast, the mechanism of the Curtin-Hammett scenario predicts the existence of both enantiomers in the same ratio as the interconverting species (ratio of signal sets at -54°C = 68:32 $\rightarrow$ 36% ee).

2-Chloropropan-1-ol (*rac*-**SI9**)

Racemic proline (**SI11**) (0.104 g, 0.900 mmol, 0.3 equiv) and NCS (0.401 g, 3.00 mmol, 1.0 equiv) were added successively to an ice-cold solution of propanal (0.215 mL, 3.00 mmol, 1.0 equiv) in dichloromethane (8.1 mL). After stirring for 2 h at 0 °C, MeOH (4.1 mL) and NaBH₄ (0.284 g, 7.50 mmol, 2.5 equiv) were added and the solution was stirred for another 2 h at 0 °C. The reaction was quenched with aqueous saturated NH₄Cl (5 mL), the aqueous phase was extracted with dichloromethane (3x10 mL) and the combined organic phases were dried over NaSO₄. The solvent was removed under reduced pressure (product is volatile!) and the crude product was purified by column chromatography (Silica, pentane/Et₂O 3:1). Alcohol *rac*-**SI9** (35.0 mg, 0.370 mmol, 12%; product is volatile!) was obtained as a colorless oil.

The ¹H-NMR spectrum is in accordance with the literature.⁵³

¹H-NMR (CD₂Cl₂, 400 MHz) δ = 4.13 (pdd, *J* = 6.8, 4.2, 1.0 Hz, 1H), 3.71 (dd, *J* = 11.9, 4.0 Hz, 1H), 3.60 (dd, *J* = 12.0, 7.0 Hz, 1H), 2.29 (s, 1H), 1.48 (d, *J* = 6.7 Hz, 3H) ppm.

(S)-2-chloropropan-1-ol ((S)-SI9)

Propanal (0.143 mL, 2.00 mmol, 1.0 equiv) was dissolved in MeCN (8.0 mL) and cooled to -30 °C. Catalyst **3c**•TFA (0.114 g, 0.400 mmol, 20 mol%) and NCS (0.320 g, 2.40 mmol, 1.2 equiv) were added subsequently and the reaction mixture was stirred for 15 h at the same temperature. After the reaction was warmed to 0 °C, MeOH (3.0 mL) and NaBH₄ (0.189 g, 5.00 mmol, 2.5 equiv) were added and the mixture was stirred for 60 min at the same temperature. The reaction was quenched with aqueous saturated NH₄Cl (10 mL), the aqueous phase was extracted with dichloromethane (3x15 mL) and the combined organic phases were dried over NaSO₄. The solvent was removed under reduced pressure (product is volatile!) and the crude product (99% ee; determined by chiral GC) was used without further purification.

(R)-2-chloropropan-1-ol ((R)-SI9)

Propanal (0.143 mL, 2.00 mmol, 1.0 equiv) was dissolved in MeCN (8.0 mL) and cooled to -30 °C. Catalyst *ent*-**3c**•TFA (0.114 g, 0.400 mmol, 20 mol%) and NCS (0.320 g, 2.40 mmol, 1.2 equiv) were added subsequently and the reaction mixture was stirred for 15 h at the same temperature. After the reaction was warmed to 0 °C, MeOH (3.0 mL) and NaBH₄ (0.189 g, 5.00 mmol, 2.5 equiv) were added and the mixture was stirred for 60 min at the same temperature. The reaction was quenched with aqueous saturated NH₄Cl (10 mL), the aqueous phase was extracted with dichloromethane (3x15 mL) and the combined organic phases were dried over NaSO₄. The solvent was removed under reduced pressure (product is volatile!) and the crude product (>99% ee; determined by chiral GC) was used without further purification.

Chemical reaction scheme showing the conversion of compound **SI6** to **H-SI8** and **D-SI8**.

SI6 (Starting material) is a complex molecule featuring a central carbon atom bonded to a 2,4,6-trifluorophenyl group, a 3,5-bis(trifluoromethyl)phenyl group, a trimethylsilyloxy (OTMS) group, and a 1-(2-chloropropan-2-yl)pyrrolidine-2-carboxamide group.

Reaction conditions: D_2O (5 equiv), CHCl_3 , 22 °C, 8 d.

The reaction yields two products:

- H-SI8**: The product where the central carbon is bonded to a 2,4,6-trifluorophenyl group, a 3,5-bis(trifluoromethyl)phenyl group, a trimethylsilyloxy (OTMS) group, and a 1-(2-chloropropan-2-yl)pyrrolidine-2-carboxamide group.
- D-SI8**: The product where the central carbon is bonded to a 2,4,6-trifluorophenyl group, a 3,5-bis(trifluoromethyl)phenyl group, a trimethylsilyloxy (OTMS) group, and a 1-(2-chloropropan-2-yl)pyrrolidine-2-carboxamide group, with the deuterium atom at the 2-position of the propan-2-yl group.

The figure displays five stacked ¹H NMR spectra recorded at 0 h, 16 h, 2 d, 5 d, and 8 d. The x-axis represents the chemical shift in ppm (f1), ranging from 9.55 to 4.20, with a scale break between 4.20 and 5.00. Three regions are highlighted with colored boxes: a red box for the aliphatic region (9.55–9.45 ppm), a green box for the methine region (5.15–5.00 ppm), and a blue box for the aliphatic region (4.30–4.20 ppm). The spectra show the evolution of these signals over time. To the left, the chemical structure of the starting material is shown: a chiral amide with a deuterium atom (D) and a chlorine atom (Cl) on the α-carbon, and a hydrogen atom (H) on the β-carbon. The β-hydrogen is labeled as a doublet (dublett) in red. To the right, the chemical structure of the product is shown: a chiral amide with a trifluoromethyl group (CF₃) and a trifluoromethyl group (CF₃) on the α-carbon, and a hydrogen atom (H) on the β-carbon. The β-hydrogen is labeled as a doublet (dublett) in green.

In accordance to the previous D₂O-mediated hydrolysis experiment of aminor **14**, significant deuterium incorporation cannot be detected.

4. FURTHER RESULTS

Deuterium incorporation experiment

D₂O (98.0 μ L, 6.02 mmol, 2 equiv), TFAAd₁ (464 μ L, 6.02 mmol, 2.0 equiv), the catalyst (0.602 mmol, 20 mol%) and NCS (0.442 g, 3.31 mmol, 1.1 equiv) were added subsequently to a solution of distilled hydrocinnamic aldehyde (0.400 mL, 3.01 mmol, 1.0 equiv) in MeCN (catalyst **3c** and *ent*-**3b**) or dichloromethane (catalyst **9c**) (12 mL) at 20 °C or –30 °C. After 18 h the reaction was adjusted to 0 °C. EtOH (4.00 mL) and NaBH₄ (0.569 g, 15.0 mmol, 5.0 equiv) were added and the reaction mixture was stirred for 60 min at the same temperature. The reaction was quenched with aqueous saturated NH₄Cl, extracted with EtOAc (3x10 mL) and the combined organic phases were dried over Na₂SO₄. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (Silica, 10:1 to 5:1 pentane/EtOAc). Deuterium incorporation was qualitatively evaluated by comparison of the ¹³C-NMR spectra and quantified by ¹H-NMR spectroscopy

Example:

Figure SI-52. Exemplary ¹H- (top) and ¹³C-NMR (bottom) spectrum for the evaluation of deuterium incorporation.

Table SI-41. Quantification of deuterium incorporation under various conditions

catalyst	solvent	T [°C]	H : D	t
3c	MeCN	20	90 : 10	18 h
	MeCN	−30	100 : 0	18 h
ent-3b	MeCN	20	57 : 43	18 h
	MeCN	−30	95 : 5	18 h
9c	dichloromethane	20	83 : 17	18 h
	dichloromethane	−30	89 : 11	18 h
	dichloromethane	20	97 : 3	5 min ^[a]

^[a] no TFA-d₁, 12% conversion, 59% ee

Comparison of Different Catalysts

The catalyst (0.150 mmol, 20 mol%) and NCS (0.111 g, 0.828 mmol, 1.1 equiv) were added successively to a tempered (22 °C or 0 °C) solution of hydrocinnamic aldehyde (0.100 mL, 0.752 mmol, 1.0 equiv) and MeCN (3.0 mL). The reaction was stirred for 60 min at the indicated temperature and then cooled to 0 °C. EtOH (1.0 mL) and NaBH₄ (71.2 mg, 1.88 mmol, 2.5 equiv) were added and the reaction mixture was stirred for further 60 min at 0 °C. The reaction was quenched with aqueous saturated NH₄Cl, the aqueous phase was extracted with EtOAc (3x5 mL), the combined organic phases were dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO₂, pentane/EtOAc 10:1 to 5:1) and the pure alcohols **23**, **22** and **SI12** were obtained as colorless oils. The enantiomeric excesses of the chloroalcohols **22** were determined by chiral HPLC.

Table SI-42. Comparison of different pyrrolidine- and imidazolidinone-based organocatalysts in the α-chlorination of **16**

	temperature	23 [%]	22 [%]	SI12 [%]	sum [%]	ee (22) [%]
pyrrolidine (SI13)	22 °C	26	17	19	62	0
	0 °C	42	16	10	68	0
L-proline ((S)- SI11)	22 °C	26	32	0	58	1
	0 °C	49	14	0	63	9
L-prolinamide (SI14)	22 °C	37	20	0	57	29
	0 °C	46	8	0	54	44
Jørgensen-Hayashi catalyst (9c) in dichloromethane	22 °C	0	3	43	46	11
	0 °C	0	17	25	42	16
	0 °C	0	33	13	46	69
diphenylpyrrolidine catalyst (SI15)	22 °C	0	18	22	40	97
	0 °C	0	24	8	32	98
1 st gen. MacMillan catalyst (3a)	22 °C	0	51	23	74	36
	0 °C	17	48	18	83	70
2 nd gen. MacMillan catalyst (<i>ent</i> - 3b)	22 °C	39	26	9	74	28
	0 °C	53	27	2	82	48
3 rd gen. MacMillan catalyst (3c)	22 °C	2	64	0	66	91
	0 °C	24	54	0	78	96

Figure SI-53. Comparison of the catalytic performance between numerous pyrrolidine- and imidazolidinone-based organocatalysts.

The comparison of different pyrrolidine- and imidazolidinone-based organocatalysts reveals some major differences in the catalytic performance. Dichlorination can be completely suppressed when catalysts (**(S)-SI11**, **SI14** and **3c**) were used. Raising the temperature enhances the amount of dichlorinated byproduct for all other catalysts. Excellent enantioselectivities under these conditions were exclusively achieved with catalyst **SI15** and **3c**. The C2 or C2-like symmetry of both catalysts might play a role here. The sum of **23**, **22** and **SI12** can be considered as a parameter for the selectivity of the catalytic system. Low values are indicative for ongoing side-reactions, whereas high values reflect a “clean” reaction with less side products. Concerning the formation of side products, imidazolidinone-based catalysts perform better than pyrrolidine-based catalysts under these conditions.

5. REFERENCES

- (1) Bodenhausen, G.; Ruben, D. J. *Chem. Phys. Lett.* **1980**, *69*, 185–189.
- (2) Bax, A.; Summers, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 2093–2094.
- (3) Thiele, C. M.; Petzold, K.; Schleucher, J. *Chem. Eur. J.* **2009**, *15*, 585–588.
- (4) Thrippleton, M. J.; Keeler, J. *Angew. Chem. Int. Ed.* **2003**, *42*, 3938–3941.
- (5) Kupče, E.; Boyd, J.; Campbell, I. D. *J. Magn. Reson. B* **1995**, *106*, 300–303.
- (6) Ilgen, J.; Nowag, J.; Kaltschnee, L.; Schmidts, V.; Thiele, C. M. *J. Magn. Reson.* **2021**, *324*, 106900.
- (7) Foroozandeh, M.; Adams, R. W.; Meharry, N. J.; Jeannerat, D.; Nilsson, M.; Morris, G. A. *Angew. Chem. Int. Ed.* **2014**, *53*, 6990–6992.
- (8) Hu, H.; Krishnamurthy, K. *J. Magn. Reson.* **2006**, *182*, 173–177.
- (9) Kolmer, A.; Edwards, L. J.; Kuprov, I.; Thiele, C. M. *J. Magn. Reson.* **2015**, *261*, 101–109.
- (10) Neuhaus, D.; Williamson, M. P. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*, 2nd Ed., Wiley, Chichester, 2000.
- (11) Kolmer, A.; Edwards, L. J.; Kuprov, I.; Thiele, C. M. *J. Magn. Reson.* **2015**, *261*, 101–109.
- (12) Sinnaeve, D.; Foroozandeh, M.; Nilsson, M.; Morris, G. A. *Angew. Chem. Int. Ed.* **2016**, *55*, 1090–1093.
- (13) a) <https://gaussian.com/scrf/>; b) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999–3093; c) London, F. *J. Phys. Radium*, **1937**, *8*, 397–409; d) McWeeny, R. *Phys. Rev.* **1962**, *126*, 1028–1034; e) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789–807; f) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251–8260; g) Cheeseman, J. R.; Trucks, G. W.; Keith, T. A.; Frisch, M. J. *J. Chem. Phys.* **1996**, *104*, 5497–5509; h) Towns, J.; Cockerill, T.; Dahan, M.; Foster, I.; Gaither, K.; Grimshaw, A.; Hazlewood, V.; Lathrop, S.; Lifka, D.; Peterson, G. D.; Roskies, R.; Scott, J. R.; Wilkins-Diehr, N. *Comput. Sci. Eng.* **2014**, *16*, 62–74; i) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104; j) Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comput. Chem.* **2011**, *32*, 1456–1465.
- (14) Gaussian 16, Revision C.01: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.
- (15) Pracht, P.; Bohle, F.; Grimme, S. *Phys. Chem. Chem. Phys.* **2020**, *22*, 7169–7192.
- (16) Grimme, S. *J. Chem. Theory Comput.* **2019**, *15*, 2847–2862.
- (17) Lodewyk, M. W.; Siebert, M. R.; Tantillo, D. J. *Chem. Rev.* **2012**, *112*, 1839–1862.
- (18) CHESHIRE, Chemical Shift Repository with Coupling Constants Added Too. <http://cheshirenmr.info>
- (19) a) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211–7218; b) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 4066–4073; c) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735–746; d) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736–1740; e) J. E. Carpenter, *Extension of Lewis structure concepts to open-shell and excited-state molecular species*, Ph.D. thesis, University of Wisconsin, Madison, WI, 1987; f) Carpenter, J. E.; Weinhold, F. *J. Mol. Struct. (Theochem)* **1988**, *139*, 41–62; g) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899–926; h) Weinhold, F. and Carpenter, J. E. in *The Structure of Small Molecules and Ions*, Naaman, E. R.; Vager, Z. Plenum, 1988, 227–236.
- (20) Legault, C. Y. CYLview, 1.0b. Université de Sherbrooke. 2009.
- (21) Álvarez-Moreno, M.; de Graaf, C.; López, N.; Maseras, F.; Poblet, J. M.; Bo, C. *J. Chem. Inf. Model.* **2015**, *55*, 95–103.

- (22) Ponath, S.; Menger, M.; Grothues, L.; Weber, M.; Lentz, D.; Strohmam, C.; Christmann, M. *Angew. Chem. Int. Ed.* **2018**, *57*, 11683–11687.
- (23) Burés, J.; Armstrong, A.; Blackmond, D. G. *Acc. Chem. Res.* **2016**, *49*, 214–222.
- (24) Burés, J.; Dingwall, P.; Armstrong, A.; Blackmond, D. G. *Angew. Chem. Int. Ed.* **2014**, *53*, 8700–8704.
- (25) Wiest, J. The Role of Charged and Uncharged Intermediates in Organocatalysis, MS Thesis, 2012, Universität Basel (conducted in the Blackmond group at The Scripps Research Institute)
- (26) Brochu, M. P.; Brown, S. P.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2004**, *126*, 4108–4109.
- (27) Amatore, M.; Beeson, T. D.; Brown, S. P.; MacMillan, D. W. C. *Angew. Chem. Int. Ed.* **2009**, *48*, 5121–5124.
- (28) Burés, J.; Armstrong, A.; Blackmond, D. G. *J. Am. Chem. Soc.* **2012**, *134*, 6741–6750.
- (29) Chen, G.; Fu, C.; Ma, S. *Tetrahedron* **2006**, *62*, 4444–4452.
- (30) Warnke, S.; von Helden, G.; Pagel, K. *Proteomics* **2015**, *15*, 2804–2812.
- (31) Hoffmann, W.; Langenhan, J.; Huhmann, S.; Moschner, J.; Chang, R.; Accorsi, M.; Seo, J.; Rademann, J.; Meijer, G.; Koks, B.; Bowers, M. T.; von Helden, G.; Pagel, K. *Angew. Chem. Int. Ed.* **2019**, *58*, 8216–8220.
- (32) Revercomb, H. E.; Mason, E. A. *Anal. Chem.* **1975**, *47*, 970–983.
- (33) Gabelica, V.; Shvartsburg, A. A.; Afonso, C.; Barran, P.; Benesch, J. L. P.; Bleiholder, C.; Bowers, M. T.; Bilbao, A.; Bush, M. F.; Campbell, J. L.; Campuzano, I. D. G.; Causon, T.; Clowers, B. H.; Creaser, C. S.; De Pauw, E.; Far, J.; Fernandez-Lima, F.; Fjeldsted, J. C.; Giles, K.; Groessl, M.; Hogan, C. J., Jr.; Hann, S.; Kim, H. I.; Kurulugama, R. T.; May, J. C.; McLean, J. A.; Pagel, K.; Richardson, K.; Ridgeway, M. E.; Rosu, F.; Sobott, F.; Thalassinou, K.; Valentine, S. J.; Wyttenbach, T. *Mass Spectrom. Rev.* **2019**, *38*, 291–320.
- (34) Supady, A.; Blum, V.; Baldauf, C. *J. Chem. Inf. Model.* **2015**, *55*, 2338–2348.
- (35) Blum, V.; Gehrke, R.; Hanke, F.; Havu, P.; Havu, V.; Ren, X.; Reuter, K.; Scheffler, M. *Comput. Phys. Commun.* **2009**, *180*, 2175–2196.
- (36) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (37) Tkatchenko, A.; Scheffler, M. *Phys. Rev. Lett.* **2009**, *102*, 073005.
- (38) Singh, U. C.; Kollman, P. A. *J. Comput. Chem.* **1984**, *5*, 129–145.
- (39) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158–6170.
- (40) Zanotto, L.; Heerdt, G.; Souza, P. C. T.; Araujo, G.; Skaf, M. S. *J. Comput. Chem.* **2018**, *39*, 1675–1681.
- (41) Horii, Z.-I.; Iwata, C.; Tamura, Y. *J. Org. Chem.* **1961**, *26*, 2273–2276.
- (42) Thiele, C. M.; Kolmer, A. *J. Magn. Reson.* **2016**, *266*, 69–72.
- (43) a) Schmid, M. B.; Zeitler, K.; Gschwind, R. M. *Angew. Chemie. Int. Ed.* **2010**, *49*, 4997–5003; b) Schmid, M. B.; Zeitler, K.; Gschwind, R. M. *Chem. Sci.* **2011**, *2*, 1793–1803; c) Renzi, P.; Hioe, J.; Gschwind, R. M. *Acc. Chem. Res.* **2017**, *50*, 2936–2948.
- (44) Iron, M. A. *J. Chem. Theory Comput.* **2017**, *13*, 5798–5819.
- (45) Merrill, A.T.; Tantillo, D. J. *Magn. Reson. Chem.* **2020**, *58*, 576–583.
- (46) Seebach, D.; Sun, X.; Sparr, C.; Ebert, M.-O.; Schweizer, W. B.; Beck, A. K. *Helv. Chim. Acta* **2012**, *95*, 1064–1078.
- (47) Seebach, D.; Sun, X.; Ebert, M.-O.; W. Schweizer, W. B.; Purkayastha, N.; Beck, A. K.; Duschmalé, J.; Wennemers, H.; Mukaiyama, T.; Benohoud, M.; Hayashi, Y.; Reiher, M. *Helv. Chim. Acta* **2013**, *96*, 799–852.
- (48) Cassani, C.; Melchiorre, P. *Org. Lett.* **2012**, *14*, 5590–5593.
- (49) Weber, A. K.; Schachtner, J.; Fichtler, R.; Leermann, T. M.; Neudörfl, J. M.; von Wangelin, A. *J. Org. Biomol. Chem.* **2014**, *12*, 5267–5277.
- (50) Gurubrahmam, R.; Chen, Y. M.; Huang, W.-Y.; Chan, Y.-T.; Chang, H.-K.; Tsai, M.-K.; Chen, K. *Org. Lett.* **2016**, *18*, 3046–3049.
- (51) Boeckman Junior, R. K.; Wang, H.; Rugg, K. W.; Genung, N. E.; Chen, K.; Ryder, T. R. *Org. Lett.* **2016**, *18*, 6136–6139.
- (52) Dinér, P.; Kjærsgaard, A.; Lie, M.; Jørgensen, K. *Chem. Eur. J.* **2008**, *14*, 122–127.
- (53) Marathias, V. M.; Goljer, I.; Bach II, A. C. *Magn. Reson. Chem.* **2005**, *43*, 512–519.

6. APPENDIX

6.1. NMR-Spectra

1-((1*S*,2*R*)-1-((*R*)-5-benzyl-2,2,3-trimethyl-4-oxoimidazolidin-1-yl)-2-chloro-3-methylbutyl)pyrrolidine-2,5-dione (*syn*-20)

1-((S)-1-((R)-5-benzyl-2,2,3-trimethyl-4-oxoimidazolidin-1-yl)-2,2-dichloro-3-methylbutyl)pyrrolidine-2,5-dione (24a)

1-((1*S*,2*R*)-1-((2*R*,5*R*)-5-benzyl-2-(tert-butyl)-3-methyl-4-oxoimidazolidin-1-yl)-2-chloro-3-methylbutyl)pyrrolidine-2,5-dione ((1*S*,2*R*)-*syn*-21)

1-((1*S*,2*S*)-1-((2*R*,5*R*)-5-benzyl-2-(tert-butyl)-3-methyl-4-oxoimidazolidin-1-yl)-2-chloro-3-methylbutyl)pyrrolidine-2,5-dione ((1*S*,2*S*)-*anti*-21)

1-((1*R*,2*S*)-1-((2*R*,5*R*)-5-benzyl-2-(tert-butyl)-3-methyl-4-oxoimidazolidin-1-yl)-2-chloro-3-methylbutyl)pyrrolidine-2,5-dione ((1*R*,2*S*)-*syn*-21)

1-((1*S*,2*R*)-1-((2*R*,5*R*)-5-benzyl-2-(tert-butyl)-3-methyl-4-oxoimidazolidin-1-yl)-2-chloro-3-phenylpropyl)pyrrolidine-2,5-dione ((1*S*,2*R*)-*syn*-25)

1-((1*S*,2*S*)-1-((2*R*,5*R*)-5-benzyl-2-(tert-butyl)-3-methyl-4-oxoimidazolidin-1-yl)-2-chloro-3-phenylpropyl)pyrrolidine-2,5-dione ((1*S*,2*S*)-*anti*-25)

(1*S*,2*S*)-*anti*-25

1-((1*R*,2*S*)-1-((2*R*,5*R*)-5-benzyl-2-(tert-butyl)-3-methyl-4-oxoimidazolidin-1-yl)-2-chloro-3-phenylpropyl)pyrrolidine-2,5-dione ((1*R*,2*S*)-*syn*-25)

Decomposition of Aminal *syn*-18b

KIE-experiment (1)

¹H-NMR (crude) after reductive work-up:

2-(1-((S)-2-(bis(3,5-bis(trifluoromethyl)phenyl)((trimethylsilyl)oxy)methyl)pyrrolidin-1-yl)-2-chloro-3-methylbutyl)isoindoline-1,3-dione (14)

(S)-2-chloro-3-methylbutyl 3,5-dinitrobenzoate ((S)-SI2)

***N*-((1*S*,2*S*)-1-((*S*)-2-(bis(3,5-bis(trifluoromethyl)phenyl)((trimethylsilyl)oxy)methyl)pyrrolidin-1-yl)-2-chloro-3-methylbutyl)-2-(hydroxymethyl)benzamide (SI3)**

2-(((1*S*,2*S*)-1-((*S*)-2-(bis(3,5-bis(trifluoromethyl)phenyl)((trimethylsilyl)oxy)methyl)pyrrolidin-1-yl)-2-chloro-3-methylbutyl)carbamoyl)benzyl 3,5-dinitrobenzoate (15**)**

Figure 1 displays the ^1H and ^{13}C NMR spectra of H-SI5 and D-SI5. The top panel shows the ^1H NMR spectrum (4.0-3.75 ppm) with peaks for H-SI5 (1.00 integration) and D-SI5 (2.50 integration). The bottom panel shows the ^{13}C NMR spectrum (72.1-71.2 ppm) with peaks for H-SI5 (71.87 ppm) and D-SI5 (71.58 ppm).

(S)-2-chloro-3-methylbutan-1-ol ((S)-SI5)

2-(1-((S)-2-(bis(3,5-bis(trifluoromethyl)phenyl)((trimethylsilyl)oxy)methyl)pyrrolidin-1-yl)-2-chloropropyl)isoindoline-1,3-dione (SI6)

2-(1-((S)-2-(bis(3,5-bis(trifluoromethyl)phenyl)((trimethylsilyl)oxy)methyl)pyrrolidin-1-yl)-2-chloropropyl)isoindoline-1,3-dione (SI6)

(S)-2-chloropropyl 3,5-dinitrobenzoate ((S)-SI10)

2-chloropropan-1-ol (rac-SI9)

Deuterium incorporation experiment

2,2-dichloro-3-phenylpropan-1-ol (SI12)

3-phenylpropanal-2,2-d₂ (D₂-16)

Isotopic competition experiment

6.2. HPLC /GC Traces

1-((1*S*,2*R*)-1-((2*R*,5*R*)-5-benzyl-2-(tert-butyl)-3-methyl-4-oxoimidazolidin-1-yl)-2-chloro-3-methylbutyl)pyrrolidine-2,5-dione ((1*S*,2*R*)-*syn*-21), 1-((1*S*,2*S*)-1-((2*R*,5*R*)-5-benzyl-2-(tert-butyl)-3-methyl-4-oxoimidazolidin-1-yl)-2-chloro-3-methylbutyl)pyrrolidine-2,5-dione ((1*S*,2*S*)-*anti*-21), 1-((1*R*,2*S*)-1-((2*R*,5*R*)-5-benzyl-2-(tert-butyl)-3-methyl-4-oxoimidazolidin-1-yl)-2-chloro-3-methylbutyl)pyrrolidine-2,5-dione ((1*R*,2*S*)-*syn*-21)

HPLC: 1.0 ml/min, 25% iPrOH/hexane, Nucleosil 50-5 (0.4 x 25 cm)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.025	BV	0.4153	3.49800e4	1294.37756	57.9933
2	11.328	VB	0.3489	1.59431e4	681.62506	26.4321
3	14.962	VB	0.4726	9394.18164	294.14526	15.5746

(1*S*,2*R*)-*syn*-21

(1*S*,2*S*)-*anti*-21

(1*R*,2*S*)-*syn*-21

1-((1*S*,2*R*)-1-((2*R*,5*R*)-5-benzyl-2-(tert-butyl)-3-methyl-4-oxoimidazolidin-1-yl)-2-chloro-3-phenylpropyl)pyrrolidine-2,5-dione ((1*S*,2*R*)-*syn*-25), 1-((1*S*,2*S*)-1-((2*R*,5*R*)-5-benzyl-2-(tert-butyl)-3-methyl-4-oxoimidazolidin-1-yl)-2-chloro-3-phenylpropyl)pyrrolidine-2,5-dione ((1*S*,2*S*)-*anti*-25), 1-((1*R*,2*S*)-1-((2*R*,5*R*)-5-benzyl-2-(tert-butyl)-3-methyl-4-oxoimidazolidin-1-yl)-2-chloro-3-phenylpropyl)pyrrolidine-2,5-dione ((1*R*,2*S*)-*syn*-25)

HPLC: 1.0 ml/min, 20% iPrOH/hexane, Nucleosil 50-5 (0.4 x 25 cm)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.402	BB	0.3199	1263.66797	57.60223	80.3618
2	11.269	BB	0.3338	308.80560	13.97331	19.6382

HPLC: 20.0 ml/min, 5% EtOH/hexane, Nucleosil 50-5 (1.6 x 25 cm)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.620	BV	0.2665	54.80790	3.12625	22.2573
2	15.104	VB	0.3160	191.43855	9.15442	77.7427

(1*S*,2*R*)-*syn*-25

(1*S*,2*S*)-*anti*-25
223

(1*R*,2*S*)-*syn*-25

Decomposition of Aminal *syn*-18b

HPLC: 0.8 ml/min, 5% EtOH/hexane, Chiralpak IA (0.46 x 25 cm)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.567	MM	0.2986	16.36597	9.13470e-1	2.4270
2	15.409	BB	0.5419	657.95312	17.69229	97.5730

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.079	BB	0.5355	2435.25098	66.45875	96.2897
2	15.434	BB	0.3249	93.83700	3.63817	3.7103

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.417	VV	0.3072	427.34329	20.00624	2.2579
2	15.318	VB	0.4600	1.84990e4	570.97870	97.7421

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.366	VV	0.2906	681.08905	33.29926	2.3432
2	15.212	VB	0.5104	2.83855e4	807.01697	97.6568

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.341	VV	0.2942	1034.41980	50.65568	2.8259
2	15.146	VB	0.5620	3.55711e4	938.95190	97.1741

Enantiomeric excess (Isovaleraldehyde, Catalyst 9b and NCS)

HPLC: 0.8 ml/min, 10% EtOH/hexane, Chiralpak IA (0.46 x 25 cm)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.820	MM	0.8110	1025.23926	21.07000	25.7159
2	30.070	MM	1.1454	2961.54541	43.09299	74.2841

Enantiomeric Excess (Propanal, Catalyst 9b and NCP or NCS)

HPLC: 1.0 ml/min, 20% EtOH/hexane, Chiralpak IA (0.46 x 25 cm)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.798	BV	0.7513	5542.09766	106.82458	3.0138
2	29.551	VB	1.8062	1.78352e5	1161.00269	96.9862

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.392	BB	1.4621	9.27877e4	923.58813	96.9844
2	30.724	BB	1.0172	2885.07446	39.63746	3.0156

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.190	BV	0.1254	659.03363	71.59568	2.0853
2	3.342	VV	0.1079	514.15607	69.82114	1.6269
3	3.466	VV	0.0726	163.46495	33.66722	0.5172
4	26.573	BB	0.8810	1.58659e4	258.16086	50.2025
5	30.678	BB	0.9658	1.44013e4	209.03409	45.5681

corrected: t=26.573 area: 52.4195%; t=30.678 area: 47.5805%

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.797	BB	0.7625	3951.39868	74.05814	57.1695
2	30.958	BB	0.8495	2960.32642	49.37291	42.8305

Decomposition of amina 14 (1)

GC: Lipodex-E, 70°C, 1,1 ml/min He ; FID 300°C, Split 50:1

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	26.833	MM	1.5808	4400.40869	46.39410	94.59394
2	32.194	MM	1.2375	251.48433	3.38700	5.40606

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	29.091	MM	0.3463	46.89983	2.25745	2.34659
2	30.844	MM	1.3296	1951.74133	24.46551	97.65341

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	29.088	MM	0.5721	295.00470	8.59443	70.11639
2	32.595	MM	0.5154	114.01585	3.68689	27.09916
3	35.711	MM	1.0918	11.71514	1.78837e-1	2.78444

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	29.497	MM	0.4188	73.28048	2.91662	83.82590
2	32.914	MM	0.4191	14.13937	5.62286e-1	16.17410

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	28.762	MM	0.7094	571.47546	13.42658	84.96886
2	32.617	MM	0.5011	101.09499	3.36233	15.03114

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	29.153	MM	0.5473	265.36035	8.08067	85.44559
2	32.816	MM	0.4243	45.20028	1.77552	14.55441

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	28.954	MM	0.6382	419.13995	10.94524	83.26438
2	32.710	MM	0.4847	84.24448	2.89672	16.73562

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	27.369	MM	0.8590	9.63606	1.86967e-1	6.59252
2	29.451	MM	0.4386	101.87379	3.87100	69.69704
3	32.909	MM	0.4375	34.65674	1.32032	23.71044

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	28.961	MM	0.5849	341.99069	9.74476	68.19890
2	32.464	MM	0.5527	159.47005	4.80860	31.80110

Decomposition of amina1 SI6 (1)

GC: Lipodex-E, 40 – 70°C (1.5 °C / min), 1,1 ml/min He ; FID 300°C, Split 50:1

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	19.093	MM	0.0767	5.56108	1.20808	0.67186
2	19.249	BB	0.3803	822.15637	26.68312	99.32814

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	18.941	BB	0.4068	886.03485	26.61722	1.000e2

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	19.019	MF	0.1061	14.99774	2.35689	2.94455
2	19.196	FM R	0.3587	492.78448	22.89794	96.74974
3	20.130	MM T	0.1128	1.55711	2.30102e-1	0.30571

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	19.032	MF	0.1098	13.22100	2.00708	2.83256
2	19.216	FM	0.3513	453.52966	21.51792	97.16744

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	18.784	MF	0.0695	41.12918	9.85845	2.30791
2	18.901	FM	0.5504	1740.96619	52.72257	97.69209

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	19.000	MF	0.1030	18.28292	2.95949	2.98231
2	19.160	FM	0.3671	594.76196	27.00425	97.01769

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	19.031	MF	0.1137	19.96338	2.92755	3.45421
2	19.214	FM	0.3861	557.98065	24.08886	96.54579

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	18.915	BV	0.1388	152.47072	14.96760	21.03967
2	19.191	VB	0.2948	572.21130	24.29045	78.96033

Deuterium incorporation experiment

HPLC: 0.8 ml/min, 5% EtOH/hexane, Chiralpak IA (0.46 x 25 cm)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.120	BV	0.3020	78.58987	3.78948	20.7408
2	14.916	VB	0.4263	300.32538	10.06108	79.2592

6.3. Crystallographic Data

1-((1*S*,2*R*)-1-((*R*)-5-benzyl-2,2,3-trimethyl-4-oxoimidazolidin-1-yl)-2-chloro-3-methylbutyl)pyrrolidine-2,5-dione (*syn*-20)

Deposition number: 2041073

Bond precision: C-C = 0.0022 Å

Wavelength = 1.54178

Cell: *a* = 10.1851(2) Å, *b* = 12.6098(2) Å, *c* = 16.6551(3) Å

α = 90°, β = 90°, γ = 90°

Temperature: 100 K

Volume: 2139.05(7) Å³

Space group: P 21 21 21

Hall group: P 2ac 2ab

*D*_x, g cm⁻³: 1.304

Z: 4

μ (mm⁻¹): 1.808

*F*₀₀₀: 896.0

*F*₀₀₀[']: 899.88

h, *k*, *l*_{max}: 12, 15, 20

*N*_{ref}: 3871

*T*_{min}, *T*_{max}: 0.588, 0.753

*T*_{min}[']: 0.384

Reported *T* Limits: *T*_{min} = 0.588, *T*_{max} = 0.753

AbsCorr = MULTI-SCAN

Data completeness = 1.73/0.99

Theta(max) = 68.353

R(reflections) = 0.0214 (3831)

*wR*₂(reflections) = 0.0556 (3871)

S = 1.045

*N*_{par} = 268

1-((*S*)-1-((*R*)-5-benzyl-2,2,3-trimethyl-4-oxoimidazolidin-1-yl)-2,2-dichloro-3-methylbutyl)pyrrolidine-2,5-dione (24a)

Deposition number: 2049431

Bond precision: C-C = 0.0032 Å

Wavelength = 1.54178

Cell: a = 10.72160(7) Å, b = 9.17122(6) Å, c = 22.72408(14) Å

alpha = 90°, beta = 91.1666(3)°, gamma = 90°

Temperature: 100 K

Volume: 2234.00(2) Å³

Space group: P 21

Hall group: P 2yb

Dx, g cm⁻³: 1.351

Z: 4

Mu (mm⁻¹): 2.848

F₀₀₀: 960.0

F₀₀₀[']: 965.35

h,k,lmax: 12, 11, 27

Nref: 8056

Tmin, Tmax: 0.540, 0.693

Tmin[']: 0.417

Reported T Limits: Tmin = 0.540, Tmax = 0.693

AbsCorr = MULTI-SCAN

Data completeness = 1.85/0.99

Theta(max) = 68.262

R(reflections) = 0.0231 (7929)

wR2(reflections) = 0.0615 (8056)

S = 1.040

Npar = 551

1-((1*S*,2*R*)-1-((2*R*,5*R*)-5-benzyl-2-(tert-butyl)-3-methyl-4-oxoimidazolidin-1-yl)-2-chloro-3-methylbutyl)pyrrolidine-2,5-dione ((1*S*,2*R*)-*syn*-21)

Deposition number: 2041074

Bond precision: C-C = 0.0075 Å

Wavelength = 1.54178

Cell: a = 10.4883(4) Å, b = 25.9417(10) Å, c = 13.7281(5) Å

Alpha = 90°, beta = 96.445(1)°, gamma = 90°

Temperature: 101 K

Volume: 3711.6(2) Å³

Space group: P 21 P 1 21 1

Hall group: P 2yb P 2yb

Dx,g cm-3 = 1.203

Z: 6

Mu (mm-1): 1.592

F000: 1440.0

F000': 1446.02

h,k,lmax: 12, 31, 16

Nref: 13347

Tmin,Tmax: 0.638,0.728

Tmin': 0.548

Reported T Limits: Tmin = 0.638, Tmax = 0.728

AbsCorr = MULTI-SCAN

Data completeness = 1.89/0.97

Theta(max) = 68.874

R(reflections) = 0.0548 (13035)

wR2(reflections) = 0.1294 (13347)

S = 1.024

Npar = 857

1-((1*S*,2*S*)-1-((2*R*,5*R*)-5-benzyl-2-(tert-butyl)-3-methyl-4-oxoimidazolidin-1-yl)-2-chloro-3-methylbutyl)pyrrolidine-2,5-dione ((1*S*,2*S*)-*anti*-21)

Deposition number: 2041075

Bond precision: C-C = 0.0029 Å

Wavelength = 1.54178

Cell: *a* = 24.00236(15) Å, *b* = 9.35451(6) Å, *c* = 10.74110(7) Å

α = 90°, β = 93.6494(1)°, γ = 90°

Temperature: 100 K

Volume: 2406.81(3) Å³

Space group: C 2 C 2

Hall group: C 2y C 2y

*D*_x, g cm⁻³: 1.236

Z: 4

μ (mm⁻¹): 1.637

*F*₀₀₀: 960.0

*F*₀₀₀[']: 964.01

h, *k*, *l*_{max}: 28, 11, 12

*N*_{ref}: 4089

*T*_{min}, *T*_{max}: 0.464, 0.563

*T*_{min}[']: 0.365

Reported *T* Limits: *T*_{min} = 0.464, *T*_{max} = 0.563

AbsCorr = MULTI-SCAN

Data completeness = 1.74/0.93

Theta(max) = 68.276

R(reflections) = 0.0236 (4085)

*wR*²(reflections) = 0.0581 (4089)

S = 1.079

*N*_{par} = 287

1-((1*R*,2*S*)-1-((2*R*,5*R*)-5-benzyl-2-(tert-butyl)-3-methyl-4-oxoimidazolidin-1-yl)-2-chloro-3-methylbutyl)pyrrolidine-2,5-dione ((1*R*,2*S*)-*syn*-21)

Deposition number: 2041077

Bond precision: C-C = 0.0320 Å

Wavelength = 1.54178

Cell: a = 10.2163(4) Å, b = 25.1458(11) Å, c = 14.4592(6) Å

alpha = 90°, beta = 94.880(2)°, gamma = 90°

Temperature: 100 K

Volume: 3701.1(3) Å³

Space group: P 21 P 1 21 1

Hall group: P 2yb P 2yb

Moiety formula

Dx, g cm⁻³: 1.207

Z: 6

Mu (mm⁻¹): 1.597

F000: 1442.0

F000': 1448.02

h,k,lmax: 12, 30, 17

Nref: 11279

Tmin,Tmax: 0.557, 0.753

Tmin': 0.270

Reported T Limits: Tmin = 0.557, Tmax = 0.753

AbsCorr = MULTI-SCAN

Data completeness= 1.62/0.83

Theta(max) = 68.367

R(reflections) = 0.1344 (10576)

wR2(reflections) = 0.3992 (11279)

S = 1.382

Npar = 392

1-((1*S*,2*R*)-1-((2*R*,5*R*)-5-benzyl-2-(tert-butyl)-3-methyl-4-oxoimidazolidin-1-yl)-2-chloro-3-phenylpropyl)pyrrolidine-2,5-dione ((1*S*,2*R*)-*syn*-25)

Deposition number: 2041078

Bond precision: C-C = 0.0024 Å

Wavelength = 1.54178

Cell: a = 10.52726(7) Å, b = 13.34540(9) Å, c = 18.82390(12) Å

alpha = 90°, beta = 90°, gamma = 90°

Temperature: 100 K

Volume: 2644.58(3) Å³

Space group: P 21 21 21

Hall group: P 2ac 2ab

Dx, g cm⁻³: 1.246

Z: 4

Mu (mm⁻¹): 1.544

F₀₀₀: 1056.0

F₀₀₀[′]: 1060.29

h,k,l_{max}: 12, 16, 22

N_{ref}: 4815

T_{min}, T_{max}: 0.480, 0.714

T_{min}[′]: 0.420

Reported T Limits: T_{min} = 0.480, T_{max} = 0.714

AbsCorr = MULTI-SCAN

Data completeness = 1.75/0.99

Theta (max) = 68.453

R (reflections) = 0.0227 (4763)

wR2 (reflections) = 0.0586 (4815)

S = 1.046

N_{par} = 320

1-((1*S*,2*S*)-1-((2*R*,5*R*)-5-benzyl-2-(tert-butyl)-3-methyl-4-oxoimidazolidin-1-yl)-2-chloro-3-phenylpropyl)pyrrolidine-2,5-dione ((1*S*,2*S*)-*anti*-25)

Deposition number: 2041076

Bond precision: C-C = 0.0030 Å

Wavelength = 1.54178

Cell: *a* = 9.0086(4) Å, *b* = 10.9058(6) Å, *c* = 13.4651(6) Å

α = 90°, β = 97.426(2)°, γ = 90°

Temperature: 100 K

Volume: 1311.80(11) Å³

Space group: P 1 21 1

Hall group: P 2yb

*D*_x, g cm⁻³: 1.256

Z: 2

μ (mm⁻¹): 1.557

*F*₀₀₀: 528.0

*F*₀₀₀[']: 530.14

h, *k*, *l*_{max}: 10, 13, 16

*N*_{ref}: 4722

*T*_{min}, *T*_{max}: 0.583, 0.753

*T*_{min}[']: 0.388

Reported *T* Limits: *T*_{min} = 0.583, *T*_{max} = 0.753

AbsCorr = MULTI-SCAN

Data completeness = 1.85/0.98

Theta(max) = 68.467

R(reflections) = 0.0250 (4685)

*wR*²(reflections) = 0.0624 (4722)

S = 1.032

*N*_{par} = 321

1-((1*R*,2*S*)-1-((2*R*,5*R*)-5-benzyl-2-(tert-butyl)-3-methyl-4-oxoimidazolidin-1-yl)-2-chloro-3-phenylpropyl)pyrrolidine-2,5-dione ((1*R*,2*S*)-*syn*-25)

Deposition number: 2043370

Bond precision: C-C = 0.0028 Å

Wavelength = 0.71073

Cell: *a* = 8.9226(2) Å, *b* = 15.9789(3) Å, *c* = 17.9095(3) Å

α = 90°, β = 90°, γ = 90°

Temperature: 100 K

Volume: 2553.42(9) Å³

Space group: P 21 21 21

Hall group: P 2ac 2ab

*D*_x, g cm⁻³: 1.290

Z: 4

μ (mm⁻¹): 0.184

*F*₀₀₀: 1056.0

*F*₀₀₀[']: 1057.00

h, *k*, *l*_{max}: 10, 19, 21

*N*_{ref}: 4853

*T*_{min}, *T*_{max}: 0.780, 0.836

*T*_{min}[']: 0.941

Reported *T* Limits: *T*_{min} = 0.780, *T*_{max} = 0.836

AbsCorr = MULTI-SCAN

Data completeness = 1.76/1.00

Theta(max) = 25.702

R(reflections) = 0.0247 (4738)

*wR*₂(reflections) = 0.0603 (4853)

S = 1.075

*N*_{par} = 320

2-(((1*S*,2*S*)-1-((*S*)-2-(bis(3,5-bis(trifluoromethyl)phenyl)((trimethylsilyl)oxy)methyl)pyrrolidin-1-yl)-2-chloro-3-methylbutyl)carbamoyl)benzyl 3,5-dinitrobenzoate (15)

Deposition number: 2045387

Bond precision: C-C = 0.0060 Å

Wavelength = 1.54178

Cell: $a = 9.87405(7)$ Å, $b = 19.31855(13)$ Å, $c = 25.10775(17)$ Å

$\alpha = 90^\circ$, $\beta = 96.9297(3)^\circ$, $\gamma = 90^\circ$

Temperature: 100 K

Volume: $4754.37(6)$ Å³

Space group: P 21

Hall group: P 2yb

D_x , g cm⁻³: 1.460

Z: 4

μ (mm⁻¹): 1.876

F₀₀₀: 2144.0

F₀₀₀[']: 2154.95

h, k, l max: 11, 23, 30

Nref: 16869

T_{min}, T_{max}: 0.502, 0.705

T_{min}[']: 0.394

Reported T Limits: T_{min} = 0.502, T_{max} = 0.705

AbsCorr = MULTI-SCAN

Data completeness = 1.88/0.97

Theta(max) = 68.297

R(reflections) = 0.0435 (16690)

wR2(reflections) = 0.1138 (16869)

S = 1.111

Npar = 1272