supporting information

for

A New Organocatalytic Desymmetrization Reaction Enables the Enantioselective Total Synthesis of Madangamine E

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1. General information

Proton, carbon and fluorine NMR spectra were recorded on Bruker 400 MHz ($^1$H NMR at 400 MHz and $^{13}$C NMR at 101 MHz unless otherwise specified). Chemical shifts for protons are reported in parts per million downfield from Si(CH$_3$)$_4$ and are referenced to residual protium in the deuterated solvent (CHCl$_3$ at 7.26 ppm, unless otherwise specified). NMR data are presented in the following format: chemical shift (multiplicity [app = apparent, br = broad, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, ddd = doublet of doublet of doublets, m = multiplet], number of equivalent nuclei by integration, coupling constant [in Hz]). High-resolution mass spectra (ESI) were recorded on Bruker μTOF mass spectrometer. Infrared spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer as a thin film. Only selected maximum absorbances are reported (in $\nu_{\text{max}}$ (cm$^{-1}$)). Melting points were obtained on a Leica Galen III Hot-stage melting point apparatus and microscope and on a Kofler hot block and are reported uncorrected. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel 60 F254 plates and visualised with UV light (254 or 365 nm), and/or a vanillin stain or basified aq. KMnO$_4$. Silica gel column chromatography was performed using 60 Å silica gel 40-63 µm purchased from VWR. Chiral HPLC analysis was performed on an Agilent 1200 series instrument using an appropriate chiral stationary phase column, specified in the individual experiment, and by comparing the samples with the appropriate racemic mixtures. All reactions were performed using reagents obtained from Sigma-Aldrich, Acros Organics, Alfa Aesar, STREM or Fluorochem without further purification unless stated. All water used was purified through a Merck Millipore reverse osmosis purification system prior to use. Anhydrous toluene, dichloromethane and diethyl ether were dried by filtration through activated alumina (powder ~150 mesh, pore size 58 Å, basic, Sigma-Aldrich) columns and stored under an atmosphere of N$_2$ prior to use. Anhydrous THF was obtained from Acros Organics Extra dry tetrahydrofuran and stored under AcroSeal® over molecular sieves. Dichloromethane was used as supplied. Deuterated solvents were used as supplied. Reactions were performed under a balloon of N$_2$ if not stated. Temperatures quoted are external. Solvents were removed under reduced pressure using Büchi Rotavapor apparatus.

Catalyst 9f was synthesized according to literature procedures and all analytical data were in agreement with the literature.$^1$

Single crystal X-ray diffraction data were collected at 150 K using either a Nonus Kappa CCD Diffractometer (8; $\lambda_{\text{Mo}} = 0.71073$ Å) or a (Rigaku) Oxford Diffraction Supernova diffractometer (S9; $\lambda_{\text{Cu}} = 1.54184$ Å) fitted with an Oxford CryoSystems 700 Series CryoStream.$^2$ In general, a suitable crystal was
chosen and was mounted on a 200 μm MiTeGen loop using perfluoropolyether oil. Diffraction data were collected and reduced using the instrument manufacturer software, DENZO/SCALEPACK/HKL COLLECT\textsuperscript{3} or CrysAlisPro\textsuperscript{4} as appropriate. This includes indexing reflections in reciprocal space, integration of the raw frames and application of corrections including interframe scaling, Lorentz, flood field and dark current corrections.

Both structures were solved \textit{ab initio} from the integrated intensities using SuperFlip,\textsuperscript{5} and refined using full-matrix least-squares refinement with CRYSTALS.\textsuperscript{6,7} In the case of \textit{8}, on initial refinement, the displacement ellipsoid for C4 was found to be prolate. On closer inspection, this atom was expected to lie out of the plane of the neighbouring atoms in an "envelope-type" configuration, rather than in the same plane. Examination of the difference Fourier map suggested this behaviour was a consequence of disorder. Using a split-site model supported this conclusion and C4 (and its counterpart C104) refined without restraints, suggesting an occupancy ratio of c. 60:40. Only some of the hydrogen atoms were visible in the difference Fourier map. The hydrogen atoms were therefore positioned at geometrically sensible positions and refined using soft restraints prior to inclusion in the refinement using a riding model.\textsuperscript{8} The Flack $x$ parameter\textsuperscript{9–11} was refined\textsuperscript{12,13} by full matrix Least Squares for both structures and determined to be 0.00(4) for \textit{8} and 0.00(2) for \textit{S9}. Determinations by other methods reduced the standard uncertainty further.

For further details see the full crystallographic data (in CIF format) which are available as associated content.
2. Computational Results

All calculations reported in this paper were performed using the Amsterdam Density Functional (ADF) software.\textsuperscript{14–16} Equilibrium structures and transition structure geometries were optimized using the BLYP functional\textsuperscript{17–20} and the DZP basis set.\textsuperscript{21} Solvent effects of dichloromethane were accounted for using the conductor-like screening model (COSMO) of solvation.\textsuperscript{22–25} Dispersion interactions were included using Grimme’s DFT-D3 correction with Becke-Johnson damping.\textsuperscript{26,27} This level is referred to as COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP. All stationary points have been verified, through vibrational analysis, to be minima (zero imaginary frequencies) or transition structures (one imaginary frequency). The character of the normal mode associated with the imaginary frequency has been analyzed to ensure it resembles the reaction under consideration. Optimized structures were illustrated using CYLview.\textsuperscript{28} Potential energies were refined by means of single point calculations using the M06-2X functional.\textsuperscript{29} This level is denoted COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP.

Our computational study began with a conformational analysis on a thiourea-enamine model substrate for the intramolecular Michael addition (Figure S1). The conformation of the model substrate is determined by the s-cis/trans conformations of the enamine moiety, and by the position of the thiourea moiety. The s-cis enamine is more stable than the s-trans enamine, and importantly, benefits from a stabilizing hydrogen bonding between the S atom of the thiourea and the N–H bond of the enamine.

\textbf{Figure S1.} Relative stability ($\Delta G$ [\Delta E]) in kcal mol$^{-1}$ of the thiourea-enamine substrate computed at COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP.
Figure S2. Relative stability ($\Delta \Delta G^\ddagger$ [$\Delta \Delta E^\ddagger$] in kcal mol$^{-1}$) of 16 possible intramolecular Michael addition transition structures computed at COSMO(DCM)-ZORA-M06-2X/TZ2P/COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP that emerge from our DFT conformational search.
A conformational analysis on the key enantioselective intramolecular Michael addition transition structure (TS) was performed (Figure S2). In all, 16 possible TSs leading to every possible enantiomer and diastereomer with different conformations were considered. The lowest-energy transition structure **TS-A1** (TS1 in Figure 3) has an s-cis-down conformation and benefits from two stabilizing H-bonds between the thiourea-nitro and thiourea-enamine groups. TSs with only one type of H-bond have higher energy barriers and those with no H-bonds have the highest energy barriers. **TS-A4** with the s-trans-up and **TS-A3** with s-trans-down conformations have higher energy barriers than the most stable **TS-A1** with the s-cis-down conformation. The relative stability of each H-bond interaction was evaluated using archetypal model systems (Figure S3). **TS-A1** (TS1 in Figure 3) emerged as the most energetically favorable transition structure by ΔΔG‡ = 3.0 kcal mol⁻¹ compared to the second lowest-energy transition structure **TS-C1** (TS1' in Figure 3), amounting to a computed 99% ee that is in excellent agreement with the experimental enantioselectivity (99% ee). These results confirm that H-bonds involving both the thiourea-nitro and thiourea-enamine groups can stabilize the most. **TS-C2** with s-cis-up also benefits from the thiourea-enamine and thiourea-nitro, however steric repulsion between the ³Bu group and the enamine moiety destabilizes the TS.

In order to understand the fundamental hydrogen bonding interactions that feature in our reaction system, the energy changes due to the interactions between model thiourea, enamine and nitro groups were investigated (Figure S3). The hydrogen bond energy associated with the thiourea-enamine complex, thiourea-nitro complex, and enamine-nitro complex are 3.5, 3.2, and 2.6 kcal mol⁻¹, respectively. The lowest-energy transition structure **TS-A1** benefits from hydrogen bond interactions between both the thiourea-enamine and thiourea-nitro groups, the two most stabilizing hydrogen bonding interactions that were studied, consistent with a cooperative push/pull-type mechanism.
Alternative mechanistic pathways originating from the iminium-nitronate species Int4 are depicted in Figure S4. The cyclobutane intermediate IntS1 can be formed through TS-S1 prior to the intermolecular protonation through TS2, however the highly strained species is energetically unstable and immediately cleaves the four-membered ring with a low energy barrier. Intermediate Int4 is in an equilibrium with dihydrooxazine oxide IntS2 that favors Int4 by 2.7 kcal mol$^{-1}$. The energy barrier for intermolecular protonation of IntS2 by benzoic acid through TS-S2 is higher than the one for intramolecular protonation by thiourea through TS2. O-protonation of the nitro group (nitro–aci-nitro tautomerization) first requires the iminium moiety in Int4 to rotate, forming IntS3 in order to facilitate the hydrogen bonding interaction between the iminium and the nitronate. The transition structure TS-S3 for the nitro–aci-nitro tautomerization has a small energy barrier, thus this process is facile. The intermolecular protonation from IntS3 is also considered, however the transition structure TS-S4 has a higher energy barrier than TS2. The transition structure of intermolecular protonation from IntS4 could not be located (TS-S5) and all results converged, instead, to TS-S4. The intramolecular proton transfer from the aci-nitro species IntS4 through the four-membered transition structure TS-S6 can be dismissed, as this step has an exceptionally high energy barrier ($\Delta G^\ddagger = 68.5$ kcal mol$^{-1}$). Therefore, all these calculated alternative protonation pathways are unfavorable compared to the pathway through TS2 shown in Scheme 1.
**Figure S4.** Computed reaction energy profile ($\Delta G$ in kcal mol$^{-1}$) for the alternative pathways from **Int4** computed at COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP. R = SO$_2$Ph.
**Figure S5.** Summary of computed catalytic cycle.
3. Synthetic procedures

3.1 Model substrate synthesis

3.1.1 3-step synthesis of nitroalkene 7

To a solution of 1,4-cyclohexanedione monoethylene acetal (11.5 g, 74 mmol) in 1,2-dichloroethane (260 mL) was added 2-methylallylamine (5.5 g, 77 mmol) at room temperature. Sodium triacetoxyborohydride (23.5 g, 110 mmol) was slowly added to the resulting mixture at 0 °C. The reaction mixture was stirred for 1 h at 23 °C. The resulting mixture was slowly quenched with aqueous NaOH solution (10.2 g / 200 mL of H₂O) at 0 °C. The aqueous layer was extracted three times with CH₂Cl₂. The combined organic layers were dried over MgSO₄, and concentrated under reduced pressure to provide crude amine S1. To a solution of amine S1 (16.2 g) and triethylamine (8.6 g, 84 mmol) in CH₂Cl₂ (80 mL) at 0 °C was slowly added p-toluenesulfonyl chloride (16.1 g, 84 mmol). The reaction mixture was stirred for 14 h at room temperature. The resulting mixture was quenched with water. The aqueous layer was extracted three times with CH₂Cl₂. The combined organic layers were dried over MgSO₄, and concentrated under reduced pressure. The resulting suspension was purified by FCC (CH₂Cl₂) to yield the S2 (24 g, 88% over 2 steps) as a white solid.

mp 138-140 °C.
IR (film) v_max/cm⁻¹ 2943, 2876, 1333, 1153, 1092.

Scheme S1. 3-step synthesis of nitroalkene 7

Compound S2
\textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}) \( \delta \ 7.73 - 7.66 \) (m, 2H), 7.31 - 7.24 (m, 2H), 5.00 - 4.95 (m, 1H), 4.89 (hept, \( J = 1.4 \) Hz, 1H), 3.87 (d, \( J = 2.1 \) Hz, 4H), 3.80 - 3.67 (m, 3H), 2.42 (s, 3H), 1.83 - 1.63 (m, 7H), 1.60 - 1.46 (m, 4H).

\textbf{\textsuperscript{13}C NMR} (101 MHz, CDCl\textsubscript{3}) \( \delta \ 143.1, 142.9, 138.4, 129.8, 127.1, 113.1, 107.5, 64.5, 64.4, 57.1, 49.8, 34.4, 27.8, 21.6, 20.1 \).

\textbf{HRMS} (ES+) exact mass calculated for [M+Na]+ (C\textsubscript{19}H\textsubscript{27}NO\textsubscript{4}SNa) requires m/z 388.1553, found m/z 388.1554.

\textbf{Compounds S3(E/Z)}

To a solution of \textbf{S2} (100 mg, 0.27 mmol) and AgNO\textsubscript{2} (127 mg, 0.80 mmol) in 1,2-dichloroethane (1 mL) was added 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO, 17 mg, 0.10 mmol). The mixture was heated to 70 \( ^\circ \)C and the reaction was stirred for 14 h. The resulting mixture was filtered through celite, washing through EtOAc, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (pentane:EtOAc 10:1 to 2:1) to give \textbf{S3E} (48 mg, 43\%, E isomer) and \textbf{S3Z} (37 mg, 32\%, Z isomer).

**E isomer:**

\textbf{mp} 156-158 \textdegree C.

\textbf{IR} (film) \( v_{\text{max}}/\text{cm}^{-1} \) 2944, 1515, 1337, 1155, 1091.

\textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}) \( \delta \ 7.73 - 7.68 \) (m, 2H), 7.40 - 7.30 (m, 2H), 7.12 (q, \( J = 1.5 \) Hz, 1H), 3.94 - 3.77 (m, 7H), 2.44 (s, 3H), 2.22 (m, 3H), 1.69 (dq, \( J = 6.9, 4.4 \) Hz, 2H), 1.64 - 1.44 (m, 6H).

\textbf{\textsuperscript{13}C NMR} (101 MHz, CDCl\textsubscript{3}) \( \delta \ 149.7, 144.1, 137.3, 136.9, 130.2, 127.2, 107.1, 64.6, 64.4, 56.9, 48.2, 34.1, 27.9, 21.7, 16.6 \).

\textbf{HRMS} (ES+) exact mass calculated for [M+Na]+ (C\textsubscript{19}H\textsubscript{26}N\textsubscript{2}O\textsubscript{5}SNa) requires m/z 433.1404, found m/z 433.1404.

\textbf{Z isomer (isolated with E isomer, double bond isomers and starting material as minor impurities – data for reference):}

\textbf{IR} (film) \( v_{\text{max}}/\text{cm}^{-1} \) 2949, 1555, 1337, 1154, 1103.

\textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}) \( \delta \ 7.72 - 7.68 \) (m, 2H), 7.34 - 7.29 (m, 2H), 7.01 (hept, \( J = 1.5 \) Hz, 1H), 4.50 (d, \( J = 1.9 \) Hz, 2H), 3.91 - 3.72 (m, 7H (5H)), 2.42 (d, \( J = 5.7 \) Hz, 4H (3H)), 2.13 (d, \( J = 1.4 \) Hz, 3H), 1.73 -
1.37 (m, 11H (8H)).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 153.0, 144.0, 136.9, 135.3, 130.1, 127.3, 107.0, 64.6, 64.4, 57.0, 44.1, 34.0, 27.6, 21.7, 20.0.

HRMS (ES+) exact mass calculated for [M+Na]$^+$ (C$_{19}$H$_{26}$N$_2$O$_6$SNa) requires m/z 433.1404, found m/z 433.1404.

**Compound 7**

To a solution of S3E (440 mg, 0.107 mmol) in THF (0.12 mL) was added 1 M aq. HCl (0.47 mL) and the resulting mixture was heated to 70 ºC for 2 hours. The reaction mixture was cooled to 0 ºC. EtOAc was then added, followed by dilute NaHCO$_3$ until the solution had been neutralized. The resulting biphasic mixture was extracted with EtOAc and the combined organics were washed with brine, dried with Na$_2$SO$_4$, filtered and the solvent was removed under reduced pressure to yield 7 as an off-white solid (230 mg, 60%)

mp 159 ºC.

IR (film) $\nu_{\text{max}}$/cm$^{-1}$ 2923, 2845, 1716, 1516, 1339, 1159.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.76 – 7.68 (m, 2H), 7.39 – 7.31 (m, 2H), 7.09 (h, $J$ = 1.5 Hz, 1H), 4.25 (tt, $J$ = 12.1, 3.7 Hz, 1H), 3.87 (d, $J$ = 1.6 Hz, 2H), 2.45 (s, 3H), 2.43 – 2.33 (m, 4H), 2.21 (d, $J$ = 1.4 Hz, 3H), 1.87 (ddt, $J$ = 12.3, 5.9, 2.4 Hz, 2H), 1.70 (qd, $J$ = 12.3, 6.5 Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 207.7, 148.9, 144.6, 137.0, 136.9, 130.3, 127.2, 56.1, 48.5, 39.9, 29.9, 21.7, 16.4.

HRMS (ES+) exact mass calculated for [M+Na]$^+$ (C$_{17}$H$_{22}$N$_2$O$_5$SNa) requires m/z 389.1142, found m/z 389.1139.

**3.1.2 General procedure of enantioselective desymmetrization reaction**

**Compound 8**

To a solution of nitroalkene 7 (10 mg, 0.027 mmol) and benzoic acid (0.16 mg, 0.0014 mmol) in CH$_2$Cl$_2$ (0.6
mL) was added thiourea catalyst 9f (1.4 mg, 0.0054 mmol, 20 mol%). The reaction mixture was heated to 45 °C and stirred for 72 h. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (pentane:EtOAc 8:1 to 1:1) to give a white solid of bicyclic compound 8 (7.0 mg, 70%, 99% ee) as a single diastereomer.

mp 198 °C.

IR (film) v_{max}/cm\(^{-1}\) 2920, 1705, 1551, 1377, 1159.

HPLC (CHIRALPAK® AD-H, hexane:isopropanol [80:20], 1.0 mL/min, λ=220 nm) t_{R}= 24.5 min (major), 31.3 min (minor).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.74 – 7.65 (m, 2H), 7.36 – 7.27 (m, 2H), 4.46 – 4.42 (m, 1H), 4.39 (d, J = 12.0 Hz, 1H), 4.09 (d, J = 12.0 Hz, 1H), 3.71 (d, J = 13.4 Hz, 1H), 3.11 (d, J = 13.5 Hz, 1H), 2.50 (dq, J = 14.5, 4.9 Hz, 1H), 2.44 (s, 3H), 2.37–2.23 (m, 3H), 2.03 – 1.85 (m, 2H), 1.78 (tdd, J = 9.0, 4.6, 2.3 Hz, 1H), 1.24 (s, 3H).

\(^13\)C NMR (101 MHz, CDCl\(_3\)) δ 210.7, 144.0, 136.9, 130.1, 127.2, 82.8, 51.0, 48.4, 46.1, 38.0, 36.6, 27.3, 26.5, 21.7, 20.2.

HRMS (ES+) exact mass calculated for [M+Na]^+ (C\(_{17}\)H\(_{22}\)N\(_2\)O\(_5\)SNa) requires m/z 389.1142, found m/z 389.1142.

[\([\text{a}]\)\(_D\)]\(c (\text{g/100ml}) = 0.91\) -86.0.
Signal 3: DAD1 C, Slg=240,8 Ref=360,100

| # | RetTime | Type | Width | Area  | Height | Area % |
|---|---------|------|-------|-------|--------|--------|
| 1 | 24.824  | BB   | 0.7373| 4048.81445 | 81.82391 | 49.8674 |
| 2 | 31.107  | BB   | 0.7855| 4070.34473 | 78.94825 | 50.1326 |

Totals: 8119.15918 160.77216
3.2 Synthesis of madangamine E

3.2.1 Synthesis of $\beta,\beta'$-disubstituted nitroalkene 17E

Following the failure of the radical nitration on substrates where $R \neq \text{Me}$, a broad survey of alternative oxidation conditions were investigated ($\text{I}_2$, $\text{CAN}$, TCCA, $K_2S_2O_8$, TEMPO, NIS, NBS, PIFA, PIDA) under a range of conditions. Only traces of the desired nitroolefins were observed and as constituents of complex mixtures. Following this set-back, the synthesis of nitro-analogues of Julia-Kocienski reagents was attempted however proved synthetically challenging. Further unsuccessful strategies included the Pd-mediated coupling of vinyl chlorides, oxidation of $\alpha$-bromo-oximes, and the Mitsunobu reaction of $\gamma$-hydroxy-nitroolefins. This led to the following conjugate addition/selenoxide elimination strategy as the most promising route.

**Compound 11**
To a suspension of NaBH₄ (2.4 g, 63 mmol) in DCE (120 mL), cooled to 0 °C, was slowly added AcOH (11 mL). The solution was warmed to room temperature and stirred until gas evolution had ceased (1-2 hrs). To this was added a solution of 1,4-cyclohexanedione monoethylene acetal (7.0 g, 45 mmol) and allyl amine (3.5 mL, 47 mmol) in 1,2-dichloroethane (40 mL) at room temperature under N₂ atmosphere. The reaction mixture was stirred for 2 hours at room temperature. The resulting mixture was slowly quenched with aqueous NaOH solution (10.2 g / 200 mL of H₂O) at 0 °C. The aqueous layer was extracted three times with CH₂Cl₂. The combined organic layers were dried over MgSO₄, and concentrated under reduced pressure. To the crude amine in THF (400 mL), 4-dimethylaminopyridine (DMAP, 0.6 g, 4.5 mmol) was slowly added p-toluenesulfonyl chloride (9.2 g, 48 mmol) and triethylamine (91 mL, 66 mmol) at 0 ºC. The reaction mixture was stirred for 14 h at 23 ºC. The resulting mixture was quenched with water. The aqueous layer was extracted three times with CH₂Cl₂. The combined organic layer was dried over MgSO₄, and concentrated under reduced pressure. The crude product was purified by flash column chromatography with [3:1] as the eluents to give allyl sulfonamide 11 as a white solid (13.6 g, 86% over 2 steps).

mp 118-120 ºC.

IR (film) νmax/cm⁻¹ 2946, 2879, 1333, 1151, 1104, 1090.

¹H NMR (400 MHz, CDCl₃) δ 7.72 – 7.67 (m, 2H), 7.27 (ddd, J = 7.2, 1.4, 0.7 Hz, 2H), 5.80 (ddt, J = 17.1, 10.2, 6.0 Hz, 1H), 5.22 (dq, J = 17.2, 1.6 Hz, 1H), 5.09 (dq, J = 10.2, 1.4 Hz, 1H), 3.89 (d, J = 2.2 Hz, 4H), 3.82 (dt, J = 6.0, 1.6 Hz, 2H), 3.77 (td, J = 8.2, 4.3 Hz, 1H), 2.41 (s, 3H), 1.71 (ddddd, J = 13.4, 11.4, 6.1, 3.4 Hz, 4H), 1.64 – 1.47 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 1423.0, 138.5, 136.3, 129.6, 127.0, 116.9, 107.4, 64.4, 56.6, 46.0, 34.2, 28.3, 21.5.

HRMS (ES+) exact mass calculated for [M+Na]+ (C₁₈H₂₅NO₄SNa ) requires m/z 374.1397, found m/z 374.1397.

**Compound 12**

![Diagram](image)

Adapted from a literature procedure,³¹ to a solution of 11 (2.0 g, 5.69 mmol) and RuCl₃ (0.035 M in 1,2-dichloroethane, 5.7 mL, 0.2 mmol, 3.5 mol%) in CH₃CN (28 mL) and H₂O (4.7 mL) was slowly added NaIO₄ (3.2 g, 14.2 mmol) over a period of 1 h at 0 °C. The reaction mixture was stirred for 1.5 h at room temperature under N₂ atmosphere. The resulting solution was filtered through celite, washing with EtOAc.
The organic layer was quenched with sat. aq. Na$_2$S$_2$O$_3$. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, and concentrated under reduced pressure. To the crude mixture and nitromethane (1.2 mL, 22.8 mmol) in CH$_2$Cl$_2$ (5.7 mL) was added triethylamine (4.0 mL, 28.5 mmol) at room temperature. The reaction mixture was stirred for 2 hours. The resulting mixture was concentrated under reduced pressure and the crude product was purified by flash column chromatography (pentane:EtOAc 2:1) to give 12 as a white solid (1.88 g, 80%).

**mp** 112-114 ºC.

**IR** (film) $v_{\text{max}}$/cm$^{-1}$ 3465, 2946, 1555, 1154, 1104, 1090.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 – 7.67 (m, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 4.65 (dd, $J = 12.9$, 3.2 Hz, 1H), 4.58 (ddd, $J = 9.0$, 7.0, 4.8 Hz, 1H), 4.48 (dd, $J = 12.8$, 8.1 Hz, 1H), 3.96 – 3.82 (m, 4H), 3.74 (ddt, $J = 11.7$, 8.2, 3.5 Hz, 1H), 3.37 – 3.21 (m, 2H), 2.43 (s, 3H), 1.78 – 1.39 (m, 8H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 144.1, 136.6, 130.0, 127.1, 107.0, 78.6, 68.7, 64.5, 64.3, 57.1, 46.5, 34.0, 34.0, 28.2, 27.8, 21.6.

**HRMS** (ES+) exact mass calculated for [M+H]$^+$ (C$_{18}$H$_{27}$N$_2$O$_7$S) requires m/z 415.1532, found m/z 415.1534.

**Compound 13**

To a solution of 12 (31.4 g, 75.8 mmol) and triethylamine (21 mL, 151.6 mmol) in CH$_2$Cl$_2$ (253 mL) was added methanesulfonyl chloride (6.5 mL, 83.3 mmol) at −20 ºC under N$_2$ atmosphere. The reaction mixture was stirred for 10 min at the same temperature and the resulting mixture was quenched with 1 M HCl (151 mL). The aqueous layer was extracted three times with CH$_2$Cl$_2$. The combined organic layer was washed with saturated aqueous NaCl solution, dried over Na$_2$SO$_4$, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (pentane:EtOAc 2:1) to give 13 as a white solid (29.0 g, 97%).

**mp** 118-121 ºC.

**IR** (film) $v_{\text{max}}$/cm$^{-1}$ 2925, 1527, 1342, 1155, 1104.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72 – 7.67 (m, 2H), 7.34 – 7.28 (m, 2H), 7.21 – 7.06 (m, 2H), 4.01 (dd, $J = 4.8$, 1.0 Hz, 2H), 3.95 – 3.81 (m, 4H), 2.43 (s, 3H), 1.71 (dq, $J = 5.7$, 3.0 Hz, 2H), 1.65 – 1.46 (m, 6H).
$^{13}$C NMR (101 MHz, CDCl$_3$) δ 143.9, 141.1, 139.3, 137.4, 130.0, 127.0, 107.0, 64.5, 64.3, 56.4, 40.5, 33.9, 28.0, 21.5.

HRMS (ES+) exact mass calculated for [M+H]$^+$ (C$_{18}$H$_{25}$N$_2$O$_6$S) requires m/z 397.1428, found m/z 397.1427.

**Preparation of but-3-en-1-ylmagnesium bromide**

Following a literature procedure,$^{33}$ a mixture of magnesium (1.1 eq, 4.95 g, 204 mmol) and iodine (71 mg) was heated under a nitrogen atmosphere until the iodine started to sublime and create pink vapours. The mixture was then cooled to room temperature and stirred for 10 min. THF (308 mL) was added and bromobutene (2.0 mL, 20 mmol) was added to the resulting suspension. After the Grignard formation was initiated (by sonication, as indicated by the disappearance of the yellow colour) the reaction mixture was cooled to 10 °C and a further portion of bromobutene (16.8 mL, 165 mmol) was added over 20 min at 10 °C. The mixture was warmed to room temperature and stirred for an additional 30 min yielding a pale-brown solution of the Grignard reagent (0.48 M as determined by a standard titration$^{34}$ using L-menthol, THF and 1,10-phenanthroline).

**Compound 14**

Following a modified literature procedure,$^{35}$ the Grignard reagent (0.48 M in Et$_2$O, 260 mL, 125 mmol) was added to zinc chloride (1.0M solution in Et$_2$O, 62.5 mL, 62.5 mmol) at 0 °C under N$_2$ atmosphere. The reaction mixture was stirred for 2 h at room temperature before addition of dry 1,4-dioxane (26 mL). The resulting suspension was stirred for 45 min providing white cloudy solution of the organozinc reagent.

To a solution of copper cyanide (4.8 g, 53 mmol) and lithium chloride (4.5 g, 106 mmol) in dry THF (144 mL) was rapidly added the organozinc reagent via cannula. The resulting suspension was stirred for 10 min at 0 °C, cooled –78 °C providing dark grey suspension. 13 (17.1 g, 43.1 mmol) in dry THF (60 mL) was added to a suspension of organometallic reagent at the same temperature under N$_2$ atmosphere. The reaction mixture was stirred for 2 h at 0 °C, before being quenched by the addition of acetic acid (7.2 mL) in THF (14.4 mL) at –78 °C. The resulting mixture was poured into water (250 mL), then EtOAc (300 mL) was
added. The resulting suspension was gently stirred overnight, filtered through celite, washing with EtOAc. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (pentane:EtOAc 2:1) to give 14 as a white solid (17.5 g, 90%).

**mp** 103-104 ºC.

**IR** (film) ν_max/cm⁻¹ 2943, 1549, 1336, 1154, 1105.

**¹H NMR** (400 MHz, CDCl₃) δ 7.72 – 7.62 (m, 2H), 7.30 (d, J = 8.1 Hz, 2H), 5.74 (ddt, J = 16.8, 10.2, 6.6 Hz, 1H), 5.11 – 4.98 (m, 2H), 4.66 (dd, J = 12.9, 4.6 Hz, 1H), 3.97 – 3.81 (m, 4H), 3.75 – 3.63 (m, 1H), 3.25 – 3.07 (m, 2H), 2.73 – 2.58 (m, 1H), 2.42 (s, 3H), 2.19 – 2.05 (m, 2H), 1.77 – 1.45 (m, 10H), 1.33 – 1.21 (m, 1H).

**¹³C NMR** (101 MHz, CDCl₃) δ 143.6, 137.1, 137.1, 129.9, 126.9, 115.9, 107.1, 77.7, 64.5, 64.3, 57.2, 45.4, 37.8, 34.3, 34.2, 30.4, 29.4, 29.3, 27.0, 21.5.

**HRMS** (ES⁺) exact mass calculated for [M+H]+ (C₂₂H₃₃N₂O₆S) requires m/z 453.2054, found m/z 453.2054.

**Compound 15**

To a solution of 14 (17.5 g, 38.8 mmol) in dry THF (240 mL) was added n-butyllithium (2.5 M solution in hexanes, 16.3 mL, 40.7 mmol) at –10 ºC. The reaction mixture was stirred for 15 min at the same temperature before addition of phenylselenyl bromide (9.6 g, 40.7 mmol) in dry THF (20 mL). The reaction was stirred for 40 min at 0 ºC. The resulting mixture was quenched with water and the aqueous layer was extracted three times with EtOAc. The combined organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (pentane:EtOAc 4:1 to 3:1) to give 15 as a white solid (18.3 g, 78%).

**mp** 103-104 ºC.

**IR** (film) ν_max/cm⁻¹ 2946, 1546, 1339, 1105.

**¹H NMR** (400 MHz, CDCl₃) δ 7.73 – 7.62 (m, 4H), 7.43 – 7.27 (m, 5H), 5.91 – 5.82 (m, 1H), 5.83 – 5.65 (m, 1H), 5.03 (dddd, J = 14.9, 11.7, 8.5, 1.7 Hz, 2H), 3.89 (d, J = 2.6 Hz, 4H), 3.67 (ddt, J = 11.9, 8.1, 3.7 Hz, 1H), 3.42 (dd, J = 14.8, 7.0, 3.0 Hz, 1H), 3.28 – 3.13 (m, 1H), 2.87 – 2.73 (m, 1H), 2.43 (s, 3H), 2.25 – 2.08
(m, 2H), 1.97 – 1.80 (m, 1H), 1.79 – 1.34 (m, 6H), 1.34 – 1.23 (m, 1H).

^13^C NMR (101 MHz, CDCl\textsubscript{3}) δ 143.8, 143.7, 137.3, 137.2, 137.1, 137.0, 135.6, 135.5, 130.0, 130.0, 129.9, 129.7, 129.6, 127.5, 127.3, 127.1, 116.1, 116.1, 107.2, 89.7, 89.1, 64.6, 64.6, 64.4, 64.4, 57.9, 57.7, 45.4, 45.2, 42.9, 42.5, 34.4, 34.4, 31.4, 31.0, 28.9, 28.2, 28.2, 2.80, 27.8, 21.7.

HRMS (ES+) exact mass calculated for [M+H]^+ (C\textsubscript{28}H\textsubscript{37}N\textsubscript{2}O\textsubscript{6}SSe) requires m/z 609.1533, found m/z 609.1533.

**Compound 17E**

To a solution of 15 (18.3 g, 30.1 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (300 mL) and Et\textsubscript{2}O (602 mL) was added hydrogen peroxide solution (30% in H\textsubscript{2}O, 60 mL) at RT under N\textsubscript{2} atmosphere. The reaction mixture was stirred for 3 h before being quenched by slow addition of sat. aq. Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} solution (600 mL) over a period of 2 hours at 0 °C. The aqueous layer was extracted three times with EtOAc, dried over MgSO\textsubscript{4}, and concentrated under reduced pressure. The crude material was dissolved in THF (600 mL) and 3M aqueous HCl solution (50 mL, 150 mmol) was added. The reaction mixture was stirred for 24 h at 50 °C before addition of H\textsubscript{2}O. The aqueous layer was extracted three times with EtOAc. The combined organic layer was washed with brine, dried over MgSO\textsubscript{4}, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (pentane:EtOAc 4:1 to 3:1) to give 17E as a white solid (5.7 g pure E isolated, 47%; total 8.3 g isolated, 68%, E as major - 3.8:1 by NMR).

IR (film) ν\textsubscript{max}/cm\textsuperscript{-1} 2925, 1716, 1542, 1342, 1162.

^1H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.75 – 7.70 (m, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 1.7 Hz, 1H), 5.82 (ddt, J = 16.9, 10.1, 6.7 Hz, 1H), 5.13 – 5.01 (m, 2H), 4.25 (tt, J = 12.1, 3.7 Hz, 1H), 3.88 (d, J = 1.7 Hz, 2H), 2.67 (t, J = 7.6 Hz, 2H), 2.45 (s, 3H), 2.42 – 2.28 (m, 6H), 1.86 (dtd, J = 12.4, 5.7, 3.0 Hz, 2H), 1.69 (qd, J = 12.4, 6.2 Hz, 2H).

^13^C NMR (101 MHz, CDCl\textsubscript{3}) δ 207.6, 151.9, 144.5, 136.9, 136.8, 136.5, 130.2, 127.1, 116.6, 56.0, 47.2, 39.7, 32.1, 29.8, 29.0, 21.6.

HRMS (ES+) exact mass calculated for [M+Na]^+ (C\textsubscript{20}H\textsubscript{26}N\textsubscript{2}O\textsubscript{5}SSNa) requires m/z 429.1455, found m/z 429.1455.

Z isomer could not be isolated in pure form.
3.2.2 Enantioselective desymmetrization reaction

**Compound 18**

To a solution of **17E** (5.2 g, 12.82 mmol) and benzoic acid (0.3 g, 2.56 mmol, 20 mol%) was added thiourea catalyst **9f** (1.0 g, 2.56 mmol, 20 mol%). The reaction mixture was stirred for 48 hours at room temperature. The resulting mixture was concentrated under reduced pressure. The crude product was purified by flash column chromatography (pentane:EtOAc 3:1 to 2:1) to give **18** as white solid (4.93 g, 95%, 99% ee).

**HPLC** (CHIRALPAK® IA, hexane:isopropanol [70:30], 1.0 mL/min, λ=220 nm) tR= 11.9 min (major), 14.5 min (minor).

**mp** 38-44 °C.

**IR** (film) νmax/cm⁻¹ 2922, 1703, 1544, 1373, 1343.

**1H NMR** (400 MHz, CDCl₃) δ 7.69 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 5.68 (ddt, J = 16.7, 10.1, 6.4 Hz, 1H), 5.07 – 4.91 (m, 2H), 4.55 (d, J = 12.3 Hz, 1H), 4.46 (tt, J = 5.8, 2.3 Hz, 1H), 4.03 (dd, J = 12.3, 1.2 Hz, 1H), 3.71 (d, J = 13.6 Hz, 1H), 3.11 (d, J = 13.6 Hz, 1H), 2.45 (d, J = 17.8 Hz, 5H), 2.38 – 2.20 (m, 2H), 2.20 – 1.64 (m, 7H), 1.35 (ddd, J = 14.7, 11.6, 4.3 Hz, 1H).

**13C NMR** (101 MHz, CDCl₃) δ 211.0, 143.9, 136.7, 136.5, 130.0, 127.0, 115.8, 79.7, 48.7, 46.9, 45.8, 39.1, 38.0, 29.7, 27.0, 26.6, 26.3, 21.6.

**HRMS** (ES+) exact mass calculated for [M+Na]+ (C₂₀H₂₇N₂O₅SNa) requires m/z 429.1455, found m/z 429.1453.

[α]D(c (g/100ml) = 0.64) = -128.8.
3.2.3 Synthesis of tetracyclic ketone 3

Scheme S3. Synthesis of tetracyclic ketone 3

Compound 19
To a solution of 18 (500 mg, 1.23 mmol) in MeOH (12.3 mL) and THF (0.8 mL) was added p-toluenesulfonic acid (23 mg, 0.12 mmol) at room temperature. The reaction mixture was stirred for 22 h before being quenched with sat. aq. NaHCO₃ solution. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography (pentane:EtOAc 4:1) to give 19 as white solid (449.7 mg, 87%).

mp 38 ºC.

IR (film) vₘₐₓ/cm⁻¹ 2931, 1667, 1547, 1157, 710.

¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, J = 8.3 Hz, 2H), 7.34 – 7.26 (m, 2H), 5.74 (ddt, J = 16.5, 10.2, 6.4 Hz, 1H), 5.06 – 4.90 (m, 2H), 4.63 (t, J = 3.6 Hz, 1H), 4.47 (d, J = 12.3 Hz, 1H), 4.33 (dt, J = 6.4, 3.2 Hz, 1H), 3.99 (dd, J = 12.3, 1.0 Hz, 1H), 3.59 – 3.51 (m, 1H), 3.42 (s, 3H), 2.42 (s, 3H), 2.23 (tq, J = 10.0, 3.6 Hz, 2H), 2.18 – 2.07 (m, 2H), 2.04 – 1.89 (m, 2H), 1.77 – 1.70 (m, 1H), 1.63 – 1.55 (m, 1H), 1.46 – 1.35 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 154.3, 143.3, 137.4, 137.3, 129.8, 127.0, 115.3, 95.3, 80.4, 53.8, 47.3, 46.4, 40.5, 35.8, 29.3, 27.9, 27.2, 27.0, 21.5.

HRMS (ES⁺) exact mass calculated for [M+H]+ (C₂₁H₂₉N₂O₅S) requires m/z 421.1792, found m/z 421.1791.

[α]₀ (c (g/100ml) = 1.11) = -41.8.

**Compound 20**

To a solution of 19 (460 mg, 1.05 mmol) in Et₂O (21 mL) was slowly added LiAlH₄ (159 mg, 4.2 mmol) at 0 ºC. The reaction mixture was stirred for 17 h at room temperature under N₂ atmosphere. The reaction mixture was diluted by THF (20 mL) before being quenched with H₂O (0.18 mL) and 15% aqueous NaOH solution (0.18 mL) at 0 ºC. To the resulting mixture was added H₂O (0.36 mL) and vigorously stirred for 2 h at RT.
The resulting suspension was filtered through celite, washing with EtOAc. The collected organic layer was dried over Na$_2$SO$_4$, and concentrated under reduced pressure. To the crude mixture and 4-methoxybenzaldehyde (143 mg, 1.05 mmol) in CH$_2$Cl$_2$ (11 mL) was added NaBH(OAc)$_3$ (344 mg, 1.58 mmol) at room temperature. The reaction mixture was stirred for 1 h before being quenched by aqueous 1M NaOH solution at 0 ºC. The aqueous layer was extracted five times with CH$_2$Cl$_2$. The combined organic layer was washed with brine, dried over Na$_2$SO$_4$, and concentrated under reduced pressure. To the crude mixture in CH$_2$Cl$_2$(11 mL) was added di-tert-butyl dicarbonate (344 mg, 1.58 mmol) and aqueous 1M NaOH solution (5.3 mL) at room temperature. The reaction mixture was stirred for 18 h. The resulting mixture was extracted three times with CH$_2$Cl$_2$ and the combined organic layers were washed with brine, dried over Na$_2$SO$_4$, and concentrated under reduced pressure. The crude mixture was dissolved in acetone (11 mL), H$_2$O (11 mL) and acetic acid (11 mL). The resulting mixture was stirred for 18 h at 65 ºC. The reaction mixture was cooled to room temperature and diluted with EtOAc (20 mL) before being slowly quenched by addition of solid Na$_2$CO$_3$ (20 g, 0.19 mmol). To the resulting suspension was added water and the aqueous layer was extracted three times with EtOAc. The combined organic layers were dried over Na$_2$SO$_4$, and concentrated under reduce pressure. The crude product was purified by flash column chromatography (pentane:EtOAc 4:1 to 3:1) to give 20 as a white solid. (437 mg, 70% over 4 steps).

**mp** 48-52 ºC

**IR (film)** $\nu_{\text{max}}$/cm$^{-1}$ 2933, 1694, 1158, 1248.

**$^1$H NMR** (500 MHz, DMSO, 363K) $\delta$ 7.70 – 7.64 (m, 2H), 7.47 – 7.36 (m, 2H), 7.07 (d, $J = 8.8$ Hz, 2H), 6.96 – 6.85 (m, 2H), 5.86 – 5.70 (m, 1H), 5.07 – 4.92 (m, 2H), 4.48 (d, $J = 15.7$ Hz, 1H), 4.23 (s, 1H), 4.11 (d, $J = 15.8$ Hz, 1H), 3.76 (s, 3H), 3.41 – 3.25 (m, 2H), 3.08 (d, $J = 15.1$ Hz, 1H), 2.99 (d, $J = 15.2$ Hz, 1H), 2.41 (s, 3H), 2.39 – 2.22 (m, 3H), 2.10 – 1.89 (m, 3H), 1.89 – 1.65 (m, 4H), 1.43 (s, 2H), 1.38 (s, 7H), 1.43 – 1.30 (m, 1H).

**$^{13}$C NMR** (126 MHz, DMSO, 363K) $\delta$ 210.8, 210.0, 158.2, 158.2, 155.7, 142.8, 137.9, 137.7, 137.0, 129.8, 129.3, 127.6, 126.2, 114.1, 113.7, 113.7, 79.3, 79.1, 78.6, 54.8, 51.4, 51.2, 50.0, 49.8, 48.6, 48.2, 47.5, 45.63, 37.8, 37.6, 29.4, 27.7, 27.5, 27.5, 27.2, 26.9, 26.4, 26.2.

**HRMS** (ES+) exact mass calculated for [M+Na]$^+$ (C$_{33}$H$_{44}$N$_2$O$_6$SNa) requires m/z 619.2812, found m/z 619.2808.

$[\alpha]_D$ (c (g/100ml) = 0.64) = -41.1.

**Compound 21**
IBX (94 mg, 0.335 mmol) and 4-methylmorpholine N-oxide (41 mg, 0.335 mmol) were dissolved in DMSO (1.7 mL). The resulting mixture was placed in an oil bath and stirred for 20 min at 50 °C. The resulting solution was cooled to room temperature and to this was added 20 (100 mg, 0.168 mmol). The reaction mixture was stirred for 40 h and then cooled to 0 °C and quenched with sat. aq. NaHCO₃ solution. The aqueous layer was extracted eight times with Et₂O. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (pentane:EtOAc 4:1 to 3:1) to give 21 as a white solid (55.1 mg, 55%).

**mp** 52-56 °C.

**IR** (film) νmax/cm⁻¹ 2924, 2853, 1730, 1691, 1248, 1162.

**1H NMR** (500 MHz, d₆-DMSO, 363K) δ 7.70 – 7.64 (m, 2H), 7.41 (d, J = 8.1 Hz, 2H), 7.09 – 7.03 (m, 2H), 6.94 – 6.87 (m, 2H), 6.45 (dd, J = 9.8, 6.0 Hz, 1H), 6.05 (dd, J = 9.9, 1.0 Hz, 1H), 5.79 (ddt, J = 16.5, 10.2, 6.2 Hz, 1H), 5.06 – 4.94 (m, 2H), 4.68 (dt, J = 6.3, 3.1 Hz, 1H), 4.54 (d, J = 15.7 Hz, 1H), 4.07 (d, J = 15.7 Hz, 1H), 3.76 (s, 3H), 3.21 (d, J = 13.1 Hz, 1H), 3.01 (m, 2H), 2.95 (d, J = 13.2 Hz, 1H), 2.42 (s, 3H), 2.23 (d, J = 3.2 Hz, 1H), 2.06 (t, J = 3.2 Hz, 3H), 1.90 – 1.77 (m, 2H), 1.36 (app. s, 10H).

**13C NMR** (126 MHz, d₆-DMSO, 363K) δ 199.2, 158.2, 155.6, 143.1, 140.6, 137.6, 136.3, 132.0, 129.7, 129.4, 127.5, 126.3, 114.2, 113.7, 79.2, 54.8, 51.3, 49.4, 46.7, 45.8, 45.2, 28.2, 28.0, 27.4, 26.0, 20.4.

**HRMS** (ES+) exact mass calculated for [M+Na]+ (C₃₃H₄₂N₂O₆SNa) requires m/z 617.2656, found m/z 617.2652.

[α]D (c (g/100ml) = 0.63) = -174.6.

**Compound 22**

To a solution of 21 (1.65 g, 2.77 mmol) in MeOH (50 mL) was added aqueous 1M NaOH solution (2.9 mL)
and hydrogen peroxide solution (30% in H₂O, 785 mg, 6.93 mmol) with MeOH (5 mL). The reaction mixture was stirred for 30 min at room temperature. To the resulting mixture was added H₂O and extracted three times with Et₂O. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography (pentane:EtOAc 5:1 to 4:1) to give 22 as a white solid (1.54 g, 91%).

**mp** 49-55 °C.

**IR** (film) νmax/cm⁻¹ 2935, 1692, 1512, 1247, 1161.

**¹H NMR** (500 MHz, d₆-DMSO, 363K) δ 7.77 – 7.70 (m, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.10 – 7.04 (m, 2H), 6.95 – 6.87 (m, 2H), 5.75 – 5.63 (m, 1H), 4.98 – 4.90 (m, 2H), 4.68 (q, J = 3.1 Hz, 1H), 4.50 (d, J = 15.7 Hz, 1H), 4.07 (d, J = 15.8 Hz, 1H), 3.76 (s, 3H), 3.34 (d, J = 3.5 Hz, 1H), 3.26 (s, 2H), 3.20 (t, J = 3.3 Hz, 1H), 3.09 (d, J = 15.2 Hz, 1H), 2.99 (d, J = 12.4 Hz, 2H), 2.41 (s, 3H), 2.19 (d, J = 3.1 Hz, 1H), 2.00 (t, J = 13.8 Hz, 1H), 1.88 (dt, J = 14.3, 3.1 Hz, 1H), 1.80 – 1.68 (m, 2H), 1.60 (td, J = 13.6, 5.3 Hz, 1H), 1.37 (s, 9H), 1.31 – 1.19 (m, 1H).

**³C NMR** (126 MHz, d₆-DMSO, 363K) δ 204.0, 158.2, 155.6, 143.1, 137.4, 136.9, 129.7, 129.5, 127.5, 126.2, 114.1, 113.7, 79.3, 54.8, 52.6, 51.4, 49.6, 49.1, 47.2, 46.2, 44.2, 40.2, 28.4, 27.4, 25.8, 20.4, 17.4.

**HRMS** (ES+) exact mass calculated for [M+Na]+ (C₄₅H₄₅N₂O₇SNa) requires m/z 633.2605, found m/z 633.2599.

[α]₀ (c (g/100ml) = 0.63) = -26.9.

**Compound 23**

To a suspension of (methoxymethyl)triphenylphosphonium chloride (1.8 g, 5.29 mmol) in dry THF (25 mL) at −78 °C was added a solution of sodium bis(trimethylsilyl)amide (1 M in THF, 5.0 mL, 5.0 mmol) dropwise over 5 min under N₂ atmosphere. The mixture was stirred for 10 min at the same temperature. The reaction was warmed to 0 °C and stirred for 20 min. The reaction was cooled to −78 °C. A solution of 22 (1.54 g, 2.52 mmol) in dry THF (13 mL) was added to the red solution of the Wittig reagent. The reaction was warmed to 0 °C and stirred 30 min before being quenched with sat. aq. NH₄Cl solution (75 mL). The resulting mixture was heated to 60 °C and stirred for 3 h. The resulting mixture was extracted three times with EtOAc. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure.
The crude product was purified by flash column chromatography (pentane:EtOAc 3:1 to 1:1) to give 23 as a white solid (1.33 g, 86%) and recovered SM (0.2 g, 13%).

mp 60-66 °C.

IR (film) \( \nu_{\text{max}}/\text{cm}^{-1} \): 3460, 2930, 2359, 1692, 1160, 1513.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 9.40 (s, 1H), 7.67 (d, \( J = 7.9 \) Hz, 2H), 7.29 (d, \( J = 8.0 \) Hz, 2H), 7.04 – 6.96 (m, 2H), 6.88 – 6.79 (m, 2H), 6.73 (s, 1H), 5.97 (s, 1H), 5.11 – 4.95 (m, 2H), 4.68 (d, \( J = 15.9 \) Hz, 1H), 4.28 (d, \( J = 3.3 \) Hz, 1H), 3.78 (m, 5H), 3.20 (d, \( J = 13.4 \) Hz, 1H), 2.91 (s, 2H), 2.81 – 2.56 (m, 3H), 2.42 (s, 3H), 2.04 (s, 4H), 1.38 (s, 10H).

\(^13\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \): 192.9, 158.8, 156.7, 150.7, 143.7, 137.6, 137.2, 130.0, 127.8, 126.9, 114.9, 114.0, 80.2, 77.2, 65.9, 60.4, 55.3, 54.2, 52.4, 50.3, 47.5, 42.7, 31.6, 28.2, 27.7 27.2, 22.6, 21.5.

HRMS (ES+) exact mass calculated for [M+Na]+ \((C_{34}H_{44}N_2O_7S)\) requires m/z 647.2761, found m/z 647.2758.

\([\alpha]_D\) (c (g/100ml) = 0.77) = 44.5.

Note: TLC analysis highlighted the complete consumption of starting material however formation of a very polar (baseline) species, proposed to be the implicated betaine or phosphetane species. Following incorporation of the rigorous quench detailed above the yield of the desired product was significantly improved.

**Compound S4**

To a solution of 23 (1.54 g, 2.46 mmol) in THF (49 mL) and H\(_2\)O (4.9 mL) at 0 °C was added sodium borohydride (0.19 g, 4.92 mmol). The reaction mixture was stirred for 1 h at room temperature before being quenched with H\(_2\)O. The aqueous layer was extracted three times with Et\(_2\)O. The combined organic layers were washing with brine, dried over Na\(_2\)SO\(_4\), and concentrated under reduce pressure. The crude mixture was purified by flash column chromatography (pentane:EtOAc 1:2 to 1:5) to give S4 as a white solid (1.52 g, 99%).

IR (film) \( \nu_{\text{max}}/\text{cm}^{-1} \): 3369, 2937, 2160, 1691, 1247, 1159.

\(^1\)H NMR (500 MHz, d\(_6\)-DMSO, 363K) \( \delta \): 7.68 – 7.58 (m, 2H), 7.38 (d, \( J = 8.1 \) Hz, 2H), 7.10 – 7.04 (m, 2H), 6.94 – 6.87 (m, 2H), 5.81 (ddt, \( J = 16.7, 10.2, 6.4 \) Hz, 1H), 5.74 – 5.66 (m, 1H), 5.06 – 4.91 (m, 2H), 4.81 – 4.38 (br m, 2H), 4.50 (d, \( J = 15.8 \) Hz, 1H), 4.09 – 3.99 (m, 2H), 3.78 (dt, \( J = 5.3, 1.7 \) Hz, 2H), 3.76 (s, 3H), 3.75 (s, 3H), 2.81 (s, 3H), 2.04 (s, 4H), 1.38 (s, 10H).
3.42 (s, 1H), 3.12 – 3.07 (m, 3H), 2.79 (d, J = 12.6 Hz, 1H), 2.41 (s, 3H), 2.11 (d, J = 14.0 Hz, 1H), 2.06 (d, J = 3.1 Hz, 1H), 1.94 (qd, J = 11.3, 4.9 Hz, 1H), 1.81 – 1.69 (m, 2H), 1.49 (dt, J = 12.7, 3.2 Hz, 1H), 1.36 (s, 9H), 1.33 – 1.25 (m, 1H).

13C NMR (126 MHz, d6-DMSO, 363K) δ 158.1, 155.5, 142.4, 141.3, 138.1, 137.4, 129.9, 129.2, 127.4, 126.9, 126.1, 113.9, 113.7, 79.0, 64.9, 64.7, 54.8, 53.6, 51.5, 50.3, 47.3, 41.9, 31.3, 28.1, 27.4, 26.3, 22.7, 20.4.

HRMS (ES+) exact mass calculated for [M+Na]+ (C34H46N2O7SNa) requires m/z 649.2918, found m/z 649.2914.

[α]D (c (g/100ml) = 0.62) = 27.3.

**Compound 24**

![Chemical Structure](image)

To a solution of S4 (1.16 g, 1.85 mmol) in CH3CN (18.2 mL) and saturated aqueous NaHCO3 solution (9.1 ml) was added ammonium cerium(IV) nitrate (CAN, 3.04g, 5.55 mmol) at room temperature.37 The reaction mixture was stirred for 2 hours. To the resulting mixture was added brine, and extracted five times with Et2O. The combined organic layers were dried over Na2SO4, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (pentane:EtOAc 1:1 to 1:4) to give 24 as a white solid (742 mg, 79%).

mp 116-120 °C.

IR (film) νmax/cm⁻¹ 3383, 2934, 2886, 2160, 1692, 1160.

1H NMR (600 MHz, CDCl₃) δ 7.69 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 5.82 (dq, J = 2.8, 1.4 Hz, 1H), 5.72 (ddt, J = 16.8, 9.8, 6.5 Hz, 1H), 5.01 – 4.92 (m, 2H), 4.73 – 4.68 (m, 1H), 4.15 – 4.05 (m, 2H), 4.00 (dd, J = 14.2, 6.6 Hz, 1H), 3.59 (s, 1H), 3.24 (d, J = 12.6 Hz, 1H), 2.94 (dd, J = 13.9, 7.4 Hz, 1H), 2.84 (dd, J = 14.5, 5.1 Hz, 1H), 2.53 (d, J = 12.5 Hz, 2H), 2.47 (s, 1H), 2.42 (s, 3H), 2.22 (s, 1H), 2.01 – 1.90 (m, 3H), 1.78 (s, 1H), 1.69 – 1.61 (m, 1H), 1.55 (dt, J = 13.1, 3.2 Hz, 1H), 1.44 (s, 9H).

13C NMR (151 MHz, CDCl₃) δ 156.1, 143.6, 143.2, 138.1, 137.3, 129.9, 127.3, 127.0, 114.9, 79.9, 66.6, 66.0, 54.0, 46.0, 44.2, 40.6, 32.5, 29.5, 28.3, 27.3, 23.4, 21.5.

HRMS (ES+) exact mass calculated for [M+Na]+ (C26H38N2O6SNa) requires m/z 529.2343, found m/z 529.2341

S28
The solution of trifluoroacetic acid (TFA, 10% solution in CH$_2$Cl$_2$, 2.4 mL) was added to 24 (61 mg, 0.12 mmol) at room temperature. The reaction mixture was stirred for 3 hours. The resulting mixture was diluted in CHCl$_3$ before volatiles were removed under a stream of nitrogen gas. To the residue was added aq. 1M NaOH solution and the aqueous layer was extracted five times with CHCl$_3$. The combined organic layer was dried over Na$_2$SO$_4$, and concentrated under reduced pressure to give the crude amine S5. To a solution of crude amine S5 and aldehyde (15 mg, 0.12 mmol) in CH$_2$Cl$_2$ (1.2 mL) was added an acetic acid (17 µL, 0.3 mmol) at room temperature. The mixture was stirred for 1 hour. To the resulting mixture was added NaBH(OAc)$_3$ (38 mg, 0.18 mmol). The reaction mixture was stirred for 14 h. The reaction was cooled to 0 ºC and quenched by addition of aq. 1M NaOH solution (6.0 mL) and brine. The aqueous layer was extracted five times with CH$_2$Cl$_2$. The combined organic layers were dried over Na$_2$SO$_4$, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (pentane:EtOAc 1:2 to EtOAc) as the eluents to give 4 as pale yellow low melting point solid (49 mg, 79%).

**mp** 30-32 ºC.

**IR** (film) $\nu_{max}$/cm$^{-1}$ 3309, 2925, 2855, 2159, 1336, 1160.

**$^1$H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.75 – 7.64 (m, 2H), 7.33 – 7.27 (m, 2H), 5.86 – 5.65 (m, 2H), 5.60 (dt, $J = 3.0$, 1.5 Hz, 1H), 5.06 – 4.87 (m, 4H), 4.13 (dt, $J = 14.5$, 2.4 Hz, 3H), 3.93 (s, 4H), 3.54 (d, $J = 2.9$ Hz, 1H), 3.38 – 3.22 (m, 1H), 2.63 (d, $J = 3.1$ Hz, 1H), 2.54 (t, $J = 7.5$ Hz, 2H), 2.41 (s, 3H), 2.39 – 2.31 (m, 2H), 2.13 (d, $J = 12.1$ Hz, 1H), 2.10 – 1.89 (m, 4H), 1.85 (dq, $J = 12.8$, 6.0 Hz, 1H), 1.62 – 1.41 (m, 2H), 1.41 – 1.21 (m, 9H).

**$^{13}$C NMR** (101 MHz, CDCl$_3$) $\delta$ 145.1, 143.4, 138.9, 137.9, 137.5, 129.9, 127.0, 124.6, 115.2, 114.4, 66.2, 65.8, 54.3, 53.1, 50.1, 44.1, 39.3, 33.7, 33.0, 30.6, 29.1, 28.9, 28.8, 28.0, 27.1, 23.0, 21.5.

**HRMS** (ES+) exact mass calculated for [M+H]$^+$ (C$_{29}$H$_{45}$N$_2$O$_4$S) requires m/z 517.3095, found m/z 517.3094.

$[\alpha]_D^0$ (c (g/100ml) = 0.69) = 8.3.

$[\alpha]_D^0$ (c (g/100ml) = 0.80) = 42.8.
Compound 25

To a mixture of 4 (62 mg, 0.121 mmol), 2-azaadamantane N-oxyl (AZADO, 2.8 mg, 0.018 mmol), CuCl (1.8 mg, 0.018 mmol), 2,2'-bipyridyl (bpy, 2.8 mg, 0.018 mmol) and N,N-dimethyl-4-aminopyridine (4.4 mg, 0.036 mmol) was added CH₃CN at room temperature. The reaction mixture was stirred for 2.5 h, open to air, before being quenched by aq. 20% Na₂S₂O₃ solution (2.4 mL) at 0 ºC. To the resulting mixture was added sat. aq. CuSO₄ solution and extracted three times with EtOAc. The combined organic layers were dried over Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (pentane:EtOAc 2:1 to 1:2) to give 25 as pale yellow oil (43 mg, 70%).

**IR (film)** ν max/cm⁻¹ 2927, 2855, 1687, 1651, 1161.

**1H NMR** (400 MHz, CDCl₃) δ 7.62 (d, J = 8.4 Hz, 2H), 7.28 (t, J = 1.2 Hz, 2H), 6.42 (t, J = 1.0 Hz, 1H), 5.80 (dddt, J = 17.0, 12.1, 10.2, 6.5 Hz, 2H), 5.15 – 4.89 (m, 4H), 4.48 (dt, J = 3.7, 1.9 Hz, 1H), 3.49 (d, J = 12.5 Hz, 1H), 3.42 – 3.19 (m, 3H), 2.87 (dd, J = 13.0, 10.5 Hz, 2H), 2.64 (d, J = 3.1 Hz, 1H), 2.40 (s, 4H), 2.19 – 1.99 (m, 5H), 1.99 – 1.88 (m, 1H), 1.79 (ddd, J = 14.2, 11.4, 5.1 Hz, 1H), 1.53 (p, J = 7.6 Hz, 2H), 1.44 – 1.22 (m, 6H).

**13C NMR** (101 MHz, CDCl₃) δ 191.2, 164.6, 152.6, 143.9, 138.8, 136.7, 135.3, 129.6, 129.4, 127.6, 116.0, 114.4, 55.2, 53.5, 47.0, 46.5, 36.5, 35.1, 33.6, 33.5, 28.7, 27.6, 26.8, 26.7, 24.5, 21.6.

**HRMS** (ES⁺) exact mass calculated for [M+H]+ (C₂⁹H₃₉N₂O₄S) requires m/z 511.2625, found m/z 511.2628.

[α]D (c (g/100ml) = 0.45) = -16.5.

Compound 26(E/Z)

A solution of compound 25 (89 mg, 0.174 mmol) in CH₂Cl₂ (700 mL) was sparged with a flow of N₂ through a needle for 1 h. The solution was heated to reflux and then a solution of 1st generation Grubbs catalyst (14 mg, 0.0174 mmol) in CH₂Cl₂ (6 mL) was added in one portion through the septum. The solution was heated to reflux for 8 h under a flow of argon. DMSO (0.16 mL) was added, and the resulting solution was allowed
to cool to room temperature over 12 h. The solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography (with pentane:EtOAc 4:1 to 1:1) to give 26 as pale brown solid (69 mg, 82%, as a 3:1 mixture of Z/E isomers).

mp 80-90 °C.

IR (film) $\nu_{\text{max}}$/cm$^{-1}$ 2925, 1855, 1711, 1651, 1344, 1161, 729.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.61 (d, $J = 8.3$ Hz, 2H$_{\text{maj}}$), 7.58 (d, $J = 8.4$ Hz, 2H$_{\text{min}}$), 7.28 (d, $J = 8.2$ Hz, 2H$_{\text{maj}}$), 7.25 (d, $J = 9.5$ Hz, 2H$_{\text{min}}$), 6.41 (t, $J = 1.0$ Hz, 1H$_{\text{min}}$), 6.34 (t, $J = 1.1$ Hz, 1H$_{\text{maj}}$), 5.48 – 5.35 (m, 1H$_{\text{maj}}$+1H$_{\text{min}}$), 5.33 – 5.23 (m, 1H$_{\text{maj}}$), 4.51 (dt, $J = 3.9$, 2.1 Hz, 1H$_{\text{min}}$), 4.25 (dt, $J = 4.1$, 1.7 Hz, 1H$_{\text{maj}}$), 4.09 – 3.94 (m, 1H$_{\text{maj}}$+1H$_{\text{min}}$), 3.38 (d, $J = 13.6$ Hz, 1H$_{\text{maj}}$), 3.31 (d, $J = 12.2$ Hz, 1H$_{\text{min}}$), 3.24 (d, $J = 12.5$ Hz, 1H$_{\text{maj}}$), 3.04 (d, $J = 12.5$ Hz, 1H$_{\text{maj}}$), 2.97 (d, $J = 3.1$ Hz, 1H$_{\text{min}}$), 2.77 (d, $J = 12.3$ Hz, 1H$_{\text{min}}$), 2.72 (t, $J = 3.1$ Hz, 1H$_{\text{maj}}$), 2.64 – 2.56 (m, 1H$_{\text{maj}}$), 2.49 (ddd, $J = 13.7$, 10.0, 3.7 Hz, 1H$_{\text{min}}$), 2.40 (s, 3H$_{\text{maj}}$), 2.38 (s, 3H$_{\text{min}}$), 2.36 – 2.28 (m, 1H), 2.28 – 2.21 (m, 1H), 2.21 – 2.11 (m, 4H), 2.06 – 1.96 (m, 1H), 1.88 (tt, $J = 9.9$, 4.7 Hz, 1H), 1.61 – 1.18 (m, 8H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 192.2$_{\text{maj}}$, 191.3$_{\text{min}}$, 166.7$_{\text{maj}}$, 164.6$_{\text{min}}$, 153.2$_{\text{min}}$, 152.9$_{\text{maj}}$, 143.9$_{\text{maj}}$, 143.8$_{\text{min}}$, 134.9$_{\text{maj}}$, 133.1$_{\text{min}}$, 130.8$_{\text{maj}}$, 130.5, 130.1$_{\text{maj}}$, 129.9, 129.7$_{\text{maj}}$, 129.6, 127.6$_{\text{maj}}$, 127.1$_{\text{maj}}$, 56.1$_{\text{maj}}$, 55.9$_{\text{min}}$, 55.0$_{\text{min}}$, 53.7$_{\text{maj}}$, 49.0$_{\text{min}}$, 48.9$_{\text{maj}}$, 47.6$_{\text{min}}$, 44.8$_{\text{maj}}$, 37.9$_{\text{maj}}$, 36.7$_{\text{min}}$, 34.6$_{\text{maj}}$, 34.2$_{\text{maj}}$, 32.7$_{\text{min}}$, 31.5$_{\text{min}}$, 31.1$_{\text{min}}$, 28.1$_{\text{min}}$, 27.9$_{\text{min}}$, 27.6$_{\text{maj}}$, 27.0$_{\text{maj}}$, 26.3$_{\text{min}}$, 25.7$_{\text{maj}}$, 25.4$_{\text{min}}$, 24.7$_{\text{min}}$, 24.5$_{\text{maj}}$, 24.5$_{\text{maj}}$, 23.1$_{\text{maj}}$, 21.6$_{\text{maj}}$, 20.6$_{\text{maj}}$.

HRMS (ES+) exact mass calculated for [M+H]$^+$ (C$_{27}$H$_{35}$N$_2$O$_4$S) requires m/z 483.2312, found m/z 483.2311.

[$\alpha$]$_D$ (c (g/100ml) = 0.47) = 11.4.

**Compound 3**

![Diagram of reaction](image)

To a solution of 26E/Z (67 mg, 0.14 mmol) in EtOH (9.3 mL) was slowly added palladium on carbon (34 mg, 10% loading, 50 w/w% of 26). The atmosphere was replaced by hydrogen (quad-skinned balloon pressure) and the reaction was stirred vigorously for 16 h at 23 °C. The reaction was filtered through celite, washing with EtOAc, and concentrated under reduced pressure. The crude product was purified by flash...
column chromatography (pentane:EtOAc 2:1 to EtOAc to EtOAc:MeOH 9:1) to give 3 as white solid (47 mg, 69%) and alcohol S6 as a white solid (11 mg, 17%).

**mp 118-122 °C.**

**IR (film) v_max/cm⁻¹** 2923, 2853, 1736, 1659, 1162.

**¹H NMR** (400 MHz, CDCl₃) δ 7.70 – 7.63 (m, 2H), 7.38 – 7.30 (m, 2H), 4.27 (ddd, J = 13.5, 9.3, 3.6 Hz, 1H), 3.99 (d, J = 13.9 Hz, 1H), 3.62 (d, J = 5.3 Hz, 1H), 3.34 – 3.19 (m, 3H), 2.83 (ddd, J = 12.7, 6.8, 5.4 Hz, 1H), 2.77 (s, 1H), 2.62 – 2.47 (m, 2H), 2.44 (s, 3H), 2.14 (ddd, J = 14.7, 5.6, 3.0 Hz, 1H), 2.06 – 1.95 (m, 1H), 1.74 (ddd, J = 14.8, 3.4, 1.5 Hz, 1H), 1.70 – 1.53 (m, 2H), 1.51 – 1.15 (m, 16H).

**HRMS (ES+) exact mass calculated for [M+H]+ (C₂₇H₃₉N₂O₄S) requires m/z 487.2625, found m/z 487.2624.**

[α]D (c (g/100ml) = 0.45) = 60.8.

**Alcohol S6 side-product:**

**mp 102-108 °C.**

**IR (film) v_max/cm⁻¹** 3472, 2926, 2858, 1650, 1159, 752.

**¹H NMR** (400 MHz, CDCl₃) δ 7.76 – 7.67 (m, 2H), 7.38 (d, J = 8.1 Hz, 2H), 4.42 (d, J = 7.1 Hz, 1H), 4.23 (ddd, J = 13.5, 9.2, 3.5 Hz, 1H), 3.86 (d, J = 4.8 Hz, 1H), 3.73 (d, J = 13.7 Hz, 1H), 3.55 (dd, J = 10.7, 5.4, 2.9 Hz, 1H), 3.01 (dd, J = 12.8, 3.9 Hz, 2H), 2.55 (d, J = 12.0 Hz, 1H), 2.53 – 2.38 (m, 4H), 2.15 – 2.04 (m, 1H), 1.87 (td, J = 13.4, 11.5 Hz, 1H), 1.74 (ddd, J = 14.7, 5.9, 3.2 Hz, 2H), 1.60 (qt, J = 6.7, 4.0 Hz, 1H), 1.51 – 1.16 (m, 18H), 1.16 – 1.05 (m, 1H).

**¹³C NMR** (101 MHz, CDCl₃) δ 173.2, 144.5, 132.8, 130.1, 128.0, 71.4, 54.4, 51.4, 48.7, 46.4, 42.9, 39.8, 38.4, 32.7, 29.1, 28.2, 26.8, 25.9, 25.7, 24.5, 24.3, 24.1, 23.4, 21.6, 19.4.

**HRMS (ES+) exact mass calculated for [M+H]+ (C₂₇H₄₁N₂O₄S) requires m/z 489.2782, found m/z 489.2782.**

[α]D (c (g/100ml) = 0.73) = 18.1.

**Oxidation of alcohol S6 to ketone 3:**

To a solution of S6 (11.0 mg, 0.022 mmol) in CH₂Cl₂ (0.73 mL) were added AZADO (0.3 mg, 2.2 μL) and PIDA (10.6 mg, 0.033 mmol). The resulting solution was heated to 40 °C for 18 h before addition of CH₂Cl₂ (1 mL), sat. aq. NaHCO₃ (1 mL) and sat. aq. Na₂S₂O₃ (1 mL). The resulting mixture was stirred for 15 minutes before the layers were separated and the aqueous layer was extracted with CH₂Cl₂ (3 x 1.5 mL). The combined organics were dried with Na₂SO₄, filtered and the solvents were removed under reduced pressure.
The crude oil was purified by preparative-TLC (EtOAc) to yield ketone 3 as a white solid (9.8 mg, 91%).

3.2.4 Endgame and synthesis of madangamine E

![Scheme S3. Endgame and synthesis of madangamine E](image)

**Compound 27**

The butenyl Grignard reagent was prepared using literature procedures. To a N₂-purged flask was added Mg (0.348 g, 14.5) and I₂ (~5 mg). The flask was gently heated with a heat-gun until purple vapours were observed at which point the flask was stirred at room temperature for 10 minutes. THF (20 mL) and butenyl bromide (0.22 mL, 2.2 mmol) were then added and the resulting mixture cooled to ~10 °C. The remaining butenyl bromide (0.99 mL, 9.7 mmol) was then added over 25 minutes and the mixture was then stirred at room temperature for 1 h. The concentration was determined via standard 1,10-phenanthroline/L-menthol titration immediately before use (typically 0.42 M was observed).

The trialkyl zincate reagent was prepared according to a modified literature procedure. A flask was charged with ZnCl₂ (129 mg, 0.95 mmol) and evacuated (~0.4 mbar). The flask was gently heated with stirring before raising the temperature to >300 °C until the ZnCl₂ was observed to melt and this was maintained for 5 minutes. The vacuum line was exchanged for a N₂ balloon and the flask was charged with anhydrous LiCl (40 mg, 0.95 mmol). The evacuation/drying procedure was repeated as before and the vacuum line was then
exchanged for a N$_2$ balloon. The flask was allowed to cool to room temperature before addition of THF (0.86 mL) and Grignard reagent (6.8 mL, 0.417 M, 2.8 mmol). The resulting grey-brown solution was stirred for 1 h.

To a solution of trialkylzincate (1.5 mL, theor. 0.12 M, 0.18 mmol), cooled to 0 °C, was added a solution of ketone 3 (9.0 mg, 0.019 mmol) in THF (0.5 mL). The resulting solution was stirred at 0 °C for 2 h before the addition of sat. aq. NH$_4$Cl. The layers were separated and the aqueous layer was extracted with EtOAc (3 x 2 mL). The combined organics were dried with Na$_2$SO$_4$, filtered and the solvent was removed under reduced pressure. The resulting crude oil was purified by prep-TLC (2:1 EtOAc:hexane) to yield 27 as a white solid (7.8 mg, 78%).

**mp** 80 – 86 °C.

**IR** (film) $\nu_{max}$/cm$^{-1}$ 3489, 2925, 2855, 1657, 1334, 1159.

**$^1$H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.80 – 7.75 (m, 2H), 7.39 – 7.34 (m, 2H), 5.84 (ddt, $J$ = 16.8, 10.2, 6.5 Hz, 1H), 5.07 (dq, $J$ = 17.1, 1.6 Hz, 1H), 4.98 (dq, $J$ = 10.2, 1.3 Hz, 1H), 4.35 – 4.15 (m, 2H), 3.86 – 3.80 (m, 1H), 3.55 (d, $J$ = 13.7 Hz, 1H), 2.96 (d, $J$ = 13.6 Hz, 1H), 2.88 (d, $J$ = 12.2 Hz, 1H), 2.69 (d, $J$ = 12.2 Hz, 1H), 2.53 (td, $J$ = 10.1, 5.0 Hz, 1H), 2.46 (s, 3H), 2.38 (dt, $J$ = 13.7, 4.9 Hz, 1H), 2.29 (dddd, $J$ = 13.5, 8.4, 4.6, 1.6 Hz, 1H), 2.23 – 2.10 (m, 1H), 1.89 (d, $J$ = 10.1 Hz, 2H), 1.78 (dd, $J$ = 5.3, 3.0 Hz, 1H), 1.70 – 1.61 (m, 3H), 1.63 – 1.52 (m, 1H), 1.45 – 1.24 (m, 14H), 1.20 – 1.05 (m, 2H).

**$^{13}$C NMR** (101 MHz, CDCl$_3$) $\delta$ 173.1, 144.5, 138.6, 133.5, 129.96, 128.2, 114.8, 71.7, 55.8, 52.1, 49.2, 46.3, 41.7, 40.0, 37.5, 37.0, 32.6, 32.0, 28.0, 27.1, 25.8, 24.5, 24.3, 24.0, 23.8, 23.4, 21.7, 19.3.

**HRMS** (ESI) mass calculated for [M+H]$^+$ (C$_{31}$H$_{47}$O$_4$N$_2$S) requires m/z 543.3251, found m/z 543.3250.

**$[\alpha]_D$ (c (g/100ml) = 0.45) = -3.9.**

**Compound 28(E/Z)**

To a solution of 27 (14.5 mg, 0.027 mmol) in CH$_2$Cl$_2$ (0.53 mL) was added 2,6-dimethyl-4-tert-butylpyridine (DTBMP, 50 mg, 0.24 mmol) and the mixture was cooled to $-78$ °C. SOCl$_2$ (11.6 $\mu$L, 0.16 mmol) was added and the vial was quickly purged with N$_2$ before being sealed by screw-cap. The resulting mixture was slowly allowed to warm to room temperature and stirred for 6 h. A further portion of DTBMP (20 mg, 0.048 mmol)
and SOCl$_2$ (3 µL, 0.04 mmol) were added at –78 °C. Once full conversion was observed by TLC (EtOAc:hexane 2:1), sat. aq. NaHCO$_3$ (1 mL) was slowly added. The layers were separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (3 x 2 mL). The combined organics were dried with Na$_2$SO$_4$, filtered and the solvent was removed under reduced pressure. The crude oil was purified by prep-TLC (EtOAc:hexane 2:1) to yield 28 as a mixture of Z/E isomers (12.6 mg, 90%, 4.3:1). Pure Z product 28Z was obtained by a further prep-TLC.

**Z isomer (major, 28Z)**

mp 70 – 78 °C.

IR (film) $\nu_{\text{max}}$/cm$^{-1}$ 2923, 2852, 1654, 1162, 800.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.65 (d, $J$ = 8.3 Hz, 2H), 7.32 (d, $J$ = 8.0 Hz, 2H), 5.87 (ddt, $J$ = 16.5, 10.1, 6.2 Hz, 1H), 5.32 (td, $J$ = 7.5, 1.7 Hz, 1H), 5.10 – 4.97 (m, 2H), 4.46 (d, $J$ = 4.7 Hz, 1H), 4.23 (ddd, $J$ = 13.4, 9.2, 3.8 Hz, 1H), 3.64 (d, $J$ = 13.6 Hz, 1H), 3.09 (d, $J$ = 12.5 Hz, 1H), 3.04 (d, $J$ = 13.6 Hz, 1H), 2.96 (ddd, $J$ = 7.6, 6.1, 4.8, 1.6 Hz, 2H), 2.73 (d, $J$ = 12.5 Hz, 1H), 2.63 – 2.50 (m, 2H), 2.44 – 2.37 (m, 4H), 2.27 (dd, $J$ = 12.5, 4.9 Hz, 1H), 1.97 – 1.88 (m, 2H), 1.69 – 1.57 (m, 2H), 1.57 – 1.48 (m, 1H), 1.48 – 1.12 (m, 17H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 173.8, 143.7, 137.2, 137.0, 135.3, 129.9, 127.4, 122.5, 115.2, 52.1, 49.3, 47.9, 46.5, 45.4, 39.4, 39.2, 34.2, 31.6, 31.5, 29.3, 28.3, 26.0, 26.0, 24.7, 24.4, 24.3, 23.6, 21.7, 19.6.

HRMS (ESI) mass calculated for [M+H]$^+$ (C$_{31}$H$_{45}$O$_3$N$_2$S) requires m/z 525.3145, found m/z 525.3146.

$[\alpha]_D$ (c (g/100ml) = 0.41) = 6.8.

**E isomer (minor, 28E)**

mp 162 °C.

IR (film) $\nu_{\text{max}}$/cm$^{-1}$ 2927, 2859, 1652, 1346, 1162.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.66 – 7.63 (m, 2H), 7.29 (d, $J$ = 8.0 Hz, 2H), 5.79 (ddt, $J$ = 16.4, 10.1, 6.0 Hz, 1H), 5.46 (td, $J$ = 7.4, 2.0 Hz, 1H), 5.12 – 4.97 (m, 2H), 4.23 (ddd, $J$ = 13.6, 9.2, 4.2 Hz, 1H), 4.10 – 4.06 (m, 1H), 3.56 (d, $J$ = 13.6 Hz, 1H), 3.11 (d, $J$ = 12.6 Hz, 1H), 3.06 (d, $J$ = 13.6 Hz, 1H), 2.81 – 2.73 (m, 3H), 2.63 (ddd, $J$ = 14.9, 6.9 Hz, 1H), 2.49 – 2.38 (m, 5H), 2.15 – 2.07 (m, 1H), 1.99 (ddd, $J$ = 13.8, 4.7, 3.2 Hz, 1H), 1.91 (dt, $J$ = 6.1, 3.3 Hz, 1H), 1.71 – 1.51 (m, 2H), 1.51 – 1.14 (m, app. 19H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 173.7, 143.6, 136.6, 136.5, 135.7, 129.8, 127.5, 123.7, 115.3, 57.2, 52.2, 48.1, 46.4, 44.1, 39.2, 39.1, 33.8, 31.5, 29.6, 28.2, 26.1, 25.9, 24.8, 24.4, 24.2, 24.0, 23.6, 21.7, 19.6.

HRMS (ESI) mass calculated for [M+H]$^+$ (C$_{31}$H$_{45}$O$_3$N$_2$S) requires m/z 525.3145, found m/z 525.3146.

$[\alpha]_D$ (c (g/100ml) = 0.55) = -1.5.

**Compound 29**
To a solution of 28Z (6.0 mg, 0.012 mmol) in THF (1.2 mL), cooled to −78 °C, was added freshly prepared NaNap solution (~350 μL, 0.1 M in THF, vide infra) dropwise until the green colour appeared to linger. At this point starting material consumption was confirmed by TLC (2:1 EtOAc:pentane) and the solution was stirred for a further 10 minutes at −78 °C. Et₃N (4.8 μL, 0.034 mmol) was added followed by freshly prepared acid chloride S7 (120 μL, 0.38 M in THF, assumed 0.046 mmol, vide infra). The solution was warmed to r.t. and stirred for 2 hours. Sat. aq. NaHCO₃ (2 mL) was added and the resulting biphasic mixture was extracted with EtOAc (3 x 2 mL). The combined organics were dried with Na₂SO₄, filtered and concentrated under reduced pressure. The resulting crude oil was purified by FCC (66:33:1 pentane:EtOAc:Et₃N to 50:50:1 pentane:EtOAc:Et₃N) to yield 29 as a colourless oil (4.8 mg, 90%).

IR (film) ν max/cm⁻¹: 2925, 2853, 1647, 1409.

¹H NMR (400 MHz, CDCl₃) δ 5.93 – 5.70 (m, 2H), 5.38 (m, 1H), 5.13 – 4.91 (m, 4H), 4.79 (d, J = 4.4 Hz, 0.3H), 4.58 (d, J = 4.6 Hz, 0.7H), 4.33 – 4.09 (m, 2H), 3.56 – 3.44 (m, 1H), 3.19 – 3.05 (m, 2H), 3.00 – 2.76 (m, 2H), 2.69 (d, J = 14.1 Hz, 1H), 2.58 (dt, J = 11.1, 5.5 Hz, 1H), 2.54 – 2.43 (m, 1H), 2.43 – 2.35 (m, 1H), 2.27 (m, 3H), 2.20 – 2.13 (m, 1H), 2.13 – 2.06 (m, 1H), 2.02 (m, 2H), 1.81 – 1.59 (m, 2H), 1.54 (ddt, J = 10.5, 8.8, 3.2 Hz, 1H), 1.47 – 1.24 (m, 17H).

¹³C NMR (126 MHz, CDCl₃) δ 175.4 maj, 173.8 min, 173.4 maj, 173.2 min, 138.5 maj, 138.4 maj, 138.2 min, 137.5 min, 136.0 min, 135.8 maj, 123.1 min, 122.3 maj, 115.7 maj, 115.4 min, 115.2 maj, 114.6 min, 52.7 min, 52.6 maj, 49.7 maj, 48.2 min, 47.9 min, 46.4 maj, 46.3 min, 45.5 min, 43.6 maj, 40.0 maj, 39.7 min, 39.2 min, 38.9 maj, 34.7 maj, 34.3 min, 33.8 min, 33.5 maj, 33.4 maj, 32.8 maj, 31.6 maj, 31.5 maj, 31.5 maj, 31.3 maj, 30.7 maj, 29.8 min, 28.7 min, 28.3 maj, 28.1 min, 26.1 maj, 26.0 min, 26.0 maj, 24.7 min, 24.6 maj, 24.5 maj, 24.3 maj, 24.3 maj, 24.1 min, 24.0 min, 23.6 maj, 19.7 min, 19.6 maj.

HRMS (ESI) mass calculated for [M+H]+ (C₃₀H₄₇O₂N₂) requires m/z 467.3632, found m/z 467.3633.

[α]D (c (g/100ml) = 0.41) = 86.4.

Preparation of NaNap (0.1 M in THF) solution

To a fully-purged flask was added naphthalene (321 mg, 2.5 mmol) and anhydrous THF (25 mL). Na metal (61 mg, 2.65 mmol) was added and the flask was quickly put under N₂ atmosphere. The mixture was sonicated for 30 minutes and then stirred and room temperature for a further 1 hour. At this point, the resulting dark green solution was ready to use in the deprotection step.
Preparation of acid chloride S7 THF solution

To a solution of 5-hexenoic acid (77 μL, 0.65 mmol) in pentane (26 mL), were added oxalyl chloride (262 μL, 3.1 mmol) and DMF (50 μL, 0.65 mmol). The resulting mixture was stirred for 1 hour at room temperature and then filtered. The filtrate solvent was evaporated under reduced pressure. THF was added to make up the solution to ~ 0.37 M (based on crude mass) and ready to use in the acylation step.

Compound 2

To a solution of 27 (17.5 mg, 0.032 mmol) in 1,2-dimethoxyethane (3.2 mL), cooled to −78 °C, was added dropwise NaNap solution (~1 mL, 0.1 M in DME) until a dark green colour persisted and starting material consumption was confirmed by TLC. The solution was stirred for a further 10 minutes at this temperature before addition of Et3N (13.4 μL, 0.097 mmol) and acid chloride S7 (0.4 mL, 0.33 M solution in DME). The resulting solution was warmed to room temperature and stirred for 2 hours. Sat. aq. NH4Cl (2 mL) was added and the biphasic mixture was extracted with EtOAc (3 x 2 mL). The combined organics were dried with Na2SO4, filtered and the solvent was removed under reduced pressure. The resulting crude oil was purified by FCC (2:1 to 0:1 pentane:EtOAc) to yield 2 as a colourless oil (11.2 mg, 72%).

IR (thin film) νmax/cm−1 3322, 2926, 2856, 1638, 144, 1425.

1H NMR (500 MHz, CDCl3) δ 5.91 – 5.71 (m, 2H), 5.45 (s, 1H), 5.12 – 4.91 (m, 4H), 4.36 (d, J = 4.3 Hz, 1H), 4.25 (ddd, J = 15.0, 7.4, 3.4 Hz, 1H), 3.61 (d, J = 13.4 Hz, 1H), 3.19 – 3.06 (m, 3H), 2.62 – 2.54 (m, 1H), 2.43 (ddd, J = 15.0, 7.4, 3.4 Hz, 1H), 2.39 – 2.25 (m, 2H), 2.25 – 2.14 (m, 1H), 2.12 (q, J = 7.1 Hz, 2H), 1.93 (d, J = 4.4 Hz, 1H), 1.90 – 1.79 (m, 2H), 1.79 – 1.70 (m, 4H), 1.69 – 1.52 (m, 3H), 1.50 – 1.21 (m, app. 22H).

13C NMR (126 MHz, CDCl3) δ 179.6, 173.4, 138.9, 138.0, 115.6, 114.7, 73.9, 54.9, 53.2, 49.5, 46.2, 42.3, 40.5, 37.9, 37.7, 34.4, 33.0, 32.5, 29.9, 27.9, 27.2, 26.0, 25.9, 24.8, 24.5, 24.1, 23.9, 23.9, 23.6, 19.7.

HRMS (ESI) mass calculated for [M+H]+ (C30H49O3N2S) requires m/z 485.3738, found m/z 485.3737.

[α]D (c (g/100ml) = 0.39) = -32.4.

Compound 30
A solution of 29 (4.2 mg, 0.009 mmol) in PhMe (90 mL, degassed with a stream of argon and 5 subsequent pump/fill cycles, distilled twice) was heated to 110 °C in a N₂ atmosphere in a fully purged flask. To this solution was added a solution of Hoveyda-Grubbs 2nd generation catalyst (0.6 mg, 0.9 μmol, 10 mol%) and para-benzoquinone (0.2 mg, 1.8 μmol) in PhMe (1 mL, degassed and distilled as above) in a dropwise fashion. The reaction mixture was stirred at 110 °C for 1 hour at which point TLC analysis (100% EtOAc) confirmed full starting material consumption. The reaction was cooled to room temperature, air was introduced and the reaction was stirred for 30 minutes. A solution of isonitrile S8 (0.5 mg) in MeOH (1 mL) was introduced and the solution was stirred for a further 30 minutes before removal of the solvents under reduced pressure. The crude oil was purified by FCC (1:2 to 0:1 pentane:EtOAc) to afford 30 as a white amorphous solid (2.8 mg, 71%).

IR (film) νmax/cm⁻¹ 2925, 2855, 1630, 1448.

^1H NMR (500 MHz, CDCl₃) δ 5.55 (q, J = 9.8 Hz, 1H), 5.50 – 5.13 (m, 2.2H), 4.91 (d, J = 4.4 Hz, 1H), 4.22 (ddd, J = 13.4, 9.1, 4.0 Hz, 1H), 3.83 (d, J = 14.0 Hz, 1H), 3.47 (d, J = 13.3 Hz, 0.2H), 3.44 – 3.30 (m, 0.8H), 3.21 (q, J = 11.5 Hz, 1H), 3.11 (d, J = 13.7 Hz, 1H), 3.02 – 2.83 (m, 1.3H), 2.73 – 2.60 (m, 2H), 2.55 (t, J = 12.7 Hz, 1H), 2.46 (ddt, J = 14.2, 10.1, 5.7 Hz, 1H), 2.32 (dt, J = 14.0, 7.1 Hz, 1.4H), 2.27 – 2.17 (m, 1.5H), 2.16 – 1.94 (m, 3.2H), 1.94 – 1.72 (m, 2.2H), 1.70 – 1.18 (m, app. 27H).

^13C NMR (126 MHz, CDCl₃) δ 177.7, 173.1, 137.1, 137.0, 130.0 min, 129.7, 127.3, 127.1 min, 122.7, 52.6, 49.6, 46.28, 44.7, 43.6, 38.8, 38.3, 35.9 min, 33.8, 31.9 min, 31.0, 30.7, 29.8, 29.7, 29.7 min, 27.8, 27.3, 27.2 min, 27.2 min, 26.1, 25.7, 25.5 min, 24.7, 24.6, 24.5, 24.0, 23.5, 22.7 min, 19.6.

HRMS (ESI) mass calculated for [M+H]^+ (C₂₈H₄₂O₂N₂) requires m/z 439.3319, found m/z 439.3319.

[a]D (c g/100ml) = 0.27 = 22.6.

**Madangamine E (1)**

To a solution of 30 (2.4 mg, 0.0054 mmol) in anhydrous Et₂O (0.57 mL), cooled to 0 °C, was added LiAlH₄
(4 M in Et₂O, ~10 μL). The reaction was sealed and stirred at this temperature for 30 minutes before being stirred at room temperature for 2 hours. Et₂O (1 mL) was added and the reaction mixture was cooled to 0 °C. H₂O (3 μL) was added, followed by 15 mol% aq. NaOH (3 μL) and then H₂O (9 μL). The mixture was warmed to r.t. and stirred for 15 minutes. MgSO₄ was added and the mixture was stirred for a further 15 minutes. The resulting suspension was filtered and the solvent was removed under reduced pressure. The resulting crude residue was purified by FCC (9:1 to 7:1 to 3:1 pentane:EtOAc) to yield madangamine E (1) as a colourless oil (1.6 mg, 72%).

**IR** (film) ν<sub>max</sub>/cm<sup>-1</sup> 2925, 2854, 1458, 1351, 1129, 863, 722.

**¹H NMR** (600 MHz, C₆D₆) δ 5.46 (td, J = 10.9, 4.1 Hz, 1H), 5.41 (tdd, J = 10.8, 6.1, 1.5 Hz, 1H), 5.20 (dt, J = 11.6, 3.3 Hz, 1H), 3.71 (t, J = 3.4 Hz, 1H), 3.34 (dt, J = 13.5, 11.3 Hz, 1H), 3.29 (d, J = 11.8 Hz, 1H), 3.02 (ddt, J = 15.6, 11.9, 3.2 Hz, 1H), 2.84 (ddd, J = 13.9, 11.7, 5.6 Hz, 1H), 2.66-2.58 (m, 2H), 2.58 (d, J = 11.4 Hz, 1H), 2.46 (d, J = 11.8 Hz, 1H), 2.38-2.31 (m, 2H), 2.31 – 2.20 (m, 4H), 2.12 (dt, J = 13.1, 4.5 Hz, 1H), 1.91 – 1.76 (m, 5H), 1.70 – 1.61 (m, 1H), 1.59 – 1.25 (m, 19H), 1.23 – 1.10 (m, 2H).

**¹³C NMR** (151 MHz, C₆D₆) δ 139.2, 129.1, 129.0, 122.1, 62.3, 60.2, 57.4, 56.3, 55.4, 51.8, 39.1, 37.1, 36.6, 36.5, 35.5, 32.2, 27.3, 27.1, 26.8, 26.1, 25.7, 25.4, 25.2, 25.1, 24.8, 24.8, 22.8.

**HRMS** (ESI) mass calculated for [M+H]+ (C₂₈H₄₇N₂) requires m/z 411.3734, found m/z 411.3734.

[α]₀<sub>D</sub> (c (g/100ml) = 0.11, EtOAc) = 93.5.

(Chida&Sato: [α]₀<sub>D</sub> (c (g/100mL) = 0.4, 95% ee) +90.9)
**Comparison of NMR spectra of madangamine E**

![Structure of madangamine E]

| Proton | Our synthetic sample | Chida and Sato synthetic sample | Natural sample |
|--------|----------------------|---------------------------------|----------------|
| 18     | 1H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>) | 1H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) | 1H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) |
|        | 5.46 (td, J = 10.9, 4.1 Hz, 1H) | 5.46 (td, J = 10.9, 4.3 Hz, 1H) | 5.48 (1H) |
| 17     | 5.41 (tdd, J = 10.8, 6.1, 1.5 Hz, 1H) | 5.41 (tdd, J = 10.9, 6.3, 1.4 Hz, 1H) | 5.38 (1H) |
| 20     | 5.20 (dt, J = 11.6, 3.3 Hz, 1H) | 5.20 (dt, J = 11.5, 2.6 Hz, 1H) | 5.20 (brt, 1H) |
| 2      | 3.71 (t, J = 3.4 Hz, 1H) | 3.71 (t, J = 2.9 Hz, 1H) | 3.69 (brs, 1H) |
| 19’    | 3.34 (dt, J = 13.5, 11.3 Hz, 1H) | 3.34 (dt, J = 13.5, 11.5 Hz, 1H) | 3.34 (1H) |
| 10’    | 3.29 (d, J = 11.8 Hz, 1H) | 3.30 (d, J = 12.1 Hz, 1H) | 3.25 (1H) |
| 4’     | 3.02 (ddt, J = 15.6, 11.9, 3.2 Hz, 1H) | 3.02 (ddt, J = 15.8, 12.6, 2.6 Hz, 1H) | 3.00 (1H) |
| 13’    | 2.84 (ddd, J = 13.9, 11.7, 5.6 Hz, 1H) | 2.85 (ddd, J = 13.7, 11.7, 5.4 Hz, 1H) | 2.81 (1H) |
| 13”    | 2.66–2.58 (m, 2H) | 2.63 (m, 1H) | 2.61 (1H) |
| 21’    | 2.70–2.56 (m, 1H) | 2.30 (1H) |
| 8’     | 2.58 (d, J = 11.4 Hz, 1H) | 2.58 (d, J = 12.0 Hz, 1H) | 2.55 (1H) |
| 10”    | 2.46 (d, J = 11.8 Hz, 1H) | 2.46 (d, J = 12.1 Hz, 1H) | 2.45 (1H) |
| 11’    | 2.38–2.31 (m, 2H), 2.31–2.20 (m, 4H) | 2.36 (dt, J = 12.0, 2.9 Hz, 1H) | 2.30 (1H) |
| 4”     | 2.25 (m, 1H) | 2.21 (1H) |
| 19’, 6’, 6”, 16’ | 2.39–2.20 (m, 4H) | 2.34 (1H), 2.29 (1H), 2.24 (1H), 2.19 (1H), 2.15 (1H) |
| 21”    | 2.12 (dt, J = 13.1, 4.5 Hz, 1H) | 2.12 (dd, J = 12.9, 4.6, 3.7 Hz, 1H) | 1.85 (1H), 1.8 (1H), 1.80 (m, 1H) |
| 14’, 5, 16”, 30’ | 1.91–1.76 (m, 5H) | 1.95–1.74 (m, 4H) | 30a was not reported |
| Carbon | Our synthetic sample $^{13}$C NMR (176 MHz, C$_6$D$_6$) | Chida and Sato synthetic sample $^{13}$C NMR (125 MHz, C$_6$D$_6$) | Natural sample $^{13}$C NMR (125 MHz, C$_6$D$_6$) |
|--------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| 3      | 139.2                                           | 139.1 (C)                                       | 139.5 (C)                                       |
| 18, 17 | 129.1, 129.0                                    | 129.1 (CH), 129.0 (CH)                         | 129.2 (CH), 129.0 (CH)                         |
| 20     | 122.1                                           | 122.1 (CH)                                     | 122.0 (CH)                                     |
| 8      | 62.3                                            | 62.3 (CH$_2$)                                  | 62.0 (CH$_2$)                                  |
| 6      | 60.2                                            | 60.1 (CH$_2$)                                  | 60.0 (CH$_2$)                                  |
| 21     | 57.4                                            | 57.4 (CH$_2$)                                  | 57.2 (CH$_2$)                                  |
| 13     | 56.3                                            | 56.3 (CH$_2$)                                  | 56.0 (CH$_2$)                                  |
| 10     | 55.4                                            | 55.3 (CH$_2$)                                  | 58.2 (CH$_2$)                                  |
| 2      | 51.8                                            | 51.8 (CH)                                      | 51.8 (CH)                                      |
| 4      | 39.1                                            | 39.0 (CH$_2$)                                  | 39.0 (CH$_2$)                                  |
| 9      | 37.1                                            | 37.0 (C)                                       | 37.0 (C)                                       |
| 5      | 36.6                                            | 36.6 (CH)                                      | 36.5 (CH)                                      |
| 12     | 36.5                                            | 36.5 (CH)                                      | 40.1 (CH)                                      |
| 30     | 35.5                                            | 35.4 (CH$_2$)                                  | not reported                                    |
| 11     | 32.2                                            | 32.2 (CH$_2$)                                  | 32.2 (CH$_2$)                                  |
| 19     | 27.3, 27.1, 26.8, 26.3-25.9, 24.8               | 26.8 (CH$_2$)                                  | 27.1 (CH$_2$)                                  |
| 16     | 25.7, 25.4, 25.2, 25.1, 24.8, 24.8, 22.8       | 26.1 (CH$_2$)                                  | 25.8 (CH$_2$)                                  |
| 15     | 24.8, 22.8                                      | 27.3 (CH$_2$), 27.1 (CH$_2$), 25.7             | 25.2 (CH$_2$)                                  |
| 14     | (CH$_2$), 25.4 (CH$_2$), 25.11 (CH$_2$),        | (CH$_2$), 25.4 (CH$_2$), 25.11 (CH$_2$),       | 23.2 (CH$_2$)                                  |
| 22-29  | 25.09 (CH$_2$), 24.81 (CH$_2$), 24.76           | 25.09 (CH$_2$), 24.81 (CH$_2$), 24.76          | not reported                                    |
(CH₂), 24.2–23.4 (CH₂, br), 22.8 (CH₃)

*broad resonance at 23.4-24.2 not observed

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6. NMR Spectra
Compound S2 \((^1H)\)

Compound S2 \((^{13}C)\)
Compound 7 (\(^1\)H)

Compound 7 (\(^{13}\)C)
Compound 8 (\(^1\)H)

Compound 8 (\(^{13}\)C)
Compound 11 \(^{1}H\)

\[
\begin{align*}
&\text{TsN} \\
&\text{O} \\
&\text{O} \\
&\text{O} \\
&\text{O}
\end{align*}
\]

Compound 11 \(^{13}C\)

\[
\begin{align*}
&\text{TsN} \\
&\text{O} \\
&\text{O} \\
&\text{O} \\
&\text{O}
\end{align*}
\]
Compound 12 (\(^1\)H)

\[
\begin{align*}
\text{TsN} & \quad \text{OH} \\
\text{HO} & \quad \text{NO}_2
\end{align*}
\]

Compound 12 (\(^{13}\)C)

\[
\begin{align*}
\text{TsN} & \quad \text{OH} \\
\text{HO} & \quad \text{NO}_2
\end{align*}
\]
Compound 13 (^1H)

Compound 13 (^13C)
Compound 14 (\(^1\)H)

[Chemical structure image]

Compound 14 (\(^{13}\)C)

[Chemical structure image]
Compound 16E (1H)

Compound 16E (13C)
Compound 18 (\(^1\text{H}\))

Compound 18 (\(^{13}\text{C}\))
Compound 19 (1H)

Compound 19 (1^3C)
Compound 20 ($^1$H, 363K)

![NMR spectrum of Compound 20 ($^1$H, 363K)](image)

Compound 20 ($^{13}$C, 363K)

![NMR spectrum of Compound 20 ($^{13}$C, 363K)](image)
Compound 20 (\textsuperscript{1}H, 273K for reference)

\[
\text{\includegraphics{Compound_20_spectrum.png}}
\]

Compound 21 (\textsuperscript{1}H, 363K)

\[
\text{\includegraphics{Compound_21_spectrum.png}}
\]
Compound 21 (\(^{13}C, 363K\))

Compound 21 (\(^{1}H, 273K\) for reference)
Compound 22 ($^1$H, 363K)

Compound 22 ($^{13}$C, 363K)

S61
Compound 22 (1H, 273K for reference)

Compound 23 (1H)
Compound 23 ($^{13}$C)

Compound S4 ($^1$H, 363K)
Compound S4 ($^{13}$C, 363K)

Compound S4 ($^1$H, 273K for reference)
Compound 24 (\(^1\text{H}\))

Compound 24 (\(^{13}\text{C}\))
Compound 3 ($^1$H)

![NMR spectrum of Compound 3 ($^1$H)](image1)

Compound 3 ($^{13}$C)

![NMR spectrum of Compound 3 ($^{13}$C)](image2)
Compound S6 ($^1$H)

Compound S6 ($^{13}$C)
Compound 27 ($^1$H)

Compound 27 ($^{13}$C)
Compound 28Z (¹H)

Compound 28Z (¹³C)
Compound 28E ('H)
Compound 28E ($^{13}$C)
Compound 29 (\(^{1}H\))

![Compound 29 (\(^{1}H\))](image)

Compound 29 (\(^{13}C\))

![Compound 29 (\(^{13}C\))](image)
Compound 30 (\(^1\text{H}\))

![NMR spectrum of Compound 30 (\(^1\text{H}\))](image)

Compound 30 (\(^{13}\text{C}\))

![NMR spectrum of Compound 30 (\(^{13}\text{C}\))](image)
Compound 2 (\textsuperscript{1}H)

Compound 2 (\textsuperscript{13}C)
Madangamine E (1) (δH)
Madangamine E (1) (\(^{13}\text{C}\))
7. Crystallographic Data

Molecular structures (for compounds 8 and S9) determined through single-crystal X-ray diffraction studies are depicted below. For further details, see the full crystallographic data (in CIF format) which are available as associated content.

**Data for 8**

*Molecular structures of 8 from single-crystal X-ray diffraction studies - displacement ellipsoids are drawn at 50% probability; selected hydrogens have been omitted for clarity.*
Data for S9

Due to more favourable crystallinity, 18 was converted to enone S9 using the following procedure:

\[
\text{IBX, NMO, DMSO, r.t., 20 h}
\]

A solution of IBX (8.6 mg, 0.031 mmol) and NMO (3.6 mg, 0.031 mmol) in DMSO (0.12 mL) was stirred at room temperature for 1 h. This solution was added to a solution of 18 (5 mg, 0.0123 mmol) in CH₂Cl₂ (60 μL) and this mixture was stirred at room temperature for 20 h. Et₂O and 5% aq. NaHCO₃ were added and the layers were separated. The aqueous layer was extracted with Et₂O (6 x 1 mL) and the combined organics were washed with brine, dried with MgSO₄, filtered and the solvent was removed under reduced pressure. The crude residue was purified by FCC (9:1 to 4:1 pentane:EtOAc) to yield the title compound as a white solid (1.6 mg, 32%).

\[
\text{mp 130 °C}
\]

\[
\text{IR (film)/cm}^{-1} \nu_{\text{max}} 2917, 2850, 1673, 1640, 1161, 731
\]

\[
\text{H NMR (600 MHz, CDCl₃) } \delta 7.70 (d, J = 8.3 \text{ Hz}, 2H), 7.33 (d, J = 7.9 \text{ Hz}, 2H), 6.39 (ddd, J = 9.9, 6.1, 1.6 \text{ Hz}, 1H), 6.13 (dd, J = 9.8, 0.9 \text{ Hz}, 1H), 5.72 (ddt, J = 16.7, 10.2, 6.3 \text{ Hz}, 1H), 5.06 – 4.98 (m, 2H), 4.79 (dt, J = 6.2, 3.2 \text{ Hz}, 1H), 4.53 (d, J = 12.3 \text{ Hz}, 1H), 3.97 (dd, J = 12.3, 1.1 \text{ Hz}, 1H), 3.71 (d, J = 13.3 \text{ Hz}, 1H), 2.93 (d, J = 13.3 \text{ Hz}, 1H), 2.47 (d, J = 3.2 \text{ Hz}, 1H), 2.45 (s, 3H), 2.29 (ddt, J = 13.6, 3.9, 1.9 \text{ Hz}, 1H), 2.18 – 2.06 (m, 3H), 1.91 – 1.84 (m, 1H), 1.43 – 1.38 (m, 1H).
\]

\[
\text{C NMR (151 MHz, CDCl₃) } \delta 199.0, 144.4, 141.3, 136.6, 136.5, 133.1, 130.3, 127.2, 116.1, 80.0, 47.1, 46.3, 45.4, 39.3, 29.1, 28.5, 27.0, 21.7.
\]

\[
\text{HRMS (ES+)} \text{ exact mass calculated for } [\text{M+Na}]^+ (C_{20}H_{24}N_{2}O_{5}SNa) \text{ requires m/z 427.1298, found m/z 427.1296.}
\]

\[
[\alpha]_D (c (\text{g/100ml}) = 0.29) = -207.6
\]
Molecular structures of S89 from single-crysal X-ray diffraction studies; displacement ellipsoids are drawn at 50% probability; selected hydrogens have been omitted for clarity.
$^1$H NMR Spectrum for S9

$^{13}$C NMR Spectrum for S9
8. Computational Details

**Table S1.** Cartesian coordinates (in Å), energies (in kcal mol\(^{-1}\)), and number of imaginary frequencies of all stationary points, computed at COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP. Energies (in kcal mol\(^{-1}\)) at COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP are also provided.

**SM**

COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[
\begin{align*}
E &= -8696.53 \\
G &= -8516.52
\end{align*}
\]

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[
\begin{align*}
E &= -5876.20 \\
G &= -5696.19
\end{align*}
\]

\(N_{\text{imag}} = 0\)

|     | x     | y     | z     | \(\text{freq}\) | \(\text{Type}\) |
|-----|-------|-------|-------|-----------------|-----------------|
| C   | 0.74906254 | 1.04678290 | -0.23499446 |                 |                 |
| C   | 1.87004437 | 1.16444391 | -1.29118282 |                 |                 |
| H   | 1.10163547 | 1.46019886 | 0.72451045  |                 |                 |
| H   | 1.49822323 | 0.77396109 | -2.25286322 |                 |                 |
| C   | 3.13234739 | 0.35850102 | -0.92165594 |                 |                 |
| C   | 0.37001557 | -0.40409808 | -0.02248305 |                 |                 |
| C   | 1.52836858 | -1.33900733 | 0.27492272  |                 |                 |
| C   | 2.76163405 | -1.11300163 | -0.63595927 |                 |                 |
| H   | 3.79403446 | 0.35480852 | -1.79665734 |                 |                 |
| H   | 3.62182153 | -1.67300364 | -0.24960779 |                 |                 |
| H   | 2.53068459 | -1.54892618 | -1.61983907 |                 |                 |
| H   | 6.42423922 | 2.82653658 | 2.19344307  |                 |                 |
| H   | -0.14332244 | 1.61208877 | -0.53506257 |                 |                 |
| H   | 2.12690175 | 2.21807439 | -1.45121208 |                 |                 |
| N   | 3.93903413 | 0.99160859 | 0.17499688  |                 |                 |
| C   | 3.81027365 | 0.64201982 | 1.59285054  |                 |                 |
| H   | 4.30184893 | 1.43381364 | 2.17626700  |                 |                 |
| H   | 2.76151644 | 0.66332283 | 1.91155913  |                 |                 |
| C   | 4.46693810 | -0.67270838 | 2.01423252  |                 |                 |
Amine thiourea catalyst

COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -9211.56 \]
\[ G = -8971.07 \]

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -6403.80 \]
\[ G = -6163.31 \]

\[ N_{\text{imag}} = 0 \]
| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| H    | -1.21569178 | 2.58070509 | 1.36238269 |
| C    | -1.06503237 | 4.17890106 | 0.03426255 |
| H    | -0.83106878 | -1.80799501 | 0.41185366 |
| H    | 3.37375705 | 4.74136729 | 0.12962976 |
| H    | 1.16039199 | 6.59243126 | -1.47949984 |
| H    | 0.30692876 | 5.09270811 | -1.92820139 |
| H    | 2.07910445 | 5.14408877 | -1.97829443 |
| C    | -2.08450635 | 5.28981106 | 0.49444019 |
| C    | -1.56203989 | 6.68124207 | 0.07794274 |
| H    | -2.29613550 | 7.44867606 | 0.36317552 |
| H    | -0.61093246 | 6.92317576 | 0.57183523 |
| H    | -1.41638261 | 6.74326032 | -1.00944455 |
| C    | -3.42611691 | 5.01719486 | -0.22131026 |
| H    | -3.30514685 | 5.05816529 | -1.31253721 |
| H    | -4.16648056 | 5.77292896 | 0.07948795 |
| H    | -3.81589385 | 4.02464207 | 0.04046155 |
| C    | -2.30258609 | 5.25521005 | 2.02140927 |
| H    | -1.37015358 | 5.45001762 | 2.56630814 |
| H    | -3.03916071 | 6.02253317 | 2.30160206 |
| O    | 0.54117724 | 3.90247183 | 1.80098048 |
| N    | 1.28428680 | 5.04349765 | -0.04024916 |
| C    | 1.19061024 | 5.49446580 | -1.43424306 |
| C    | 2.57536662 | 5.33219075 | 0.60206880 |
| H    | 2.51118443 | 5.07975590 | 1.66214977 |
| H    | 2.80565315 | 6.39958684 | 0.48186879 |
| S    | -1.96172394 | 2.09197557 | -2.14692845 |
| H    | -2.69313472 | 4.27925413 | 2.34237978 |
| H    | -1.03888192 | 4.18014712 | -1.05670909 |
| C    | 0.33384168 | 4.36347129 | 0.65591975 |
| N    | 0.02940460 | -0.79309250 | -1.21323748 |
| H    | -0.30653140 | -0.23349249 | -2.00833955 |
| C    | -1.11467885 | -1.53281635 | -0.62220607 |
| C    | -1.49212543 | -2.82775715 | -1.37123527 |
| C    | -2.35514065 | -0.61748207 | -0.54245615 |

S86
\begin{verbatim}
C -2.66441887  -3.56182285  -0.69517771
H -1.76314973  -2.56455747  -2.40937895
H -0.60671463  -3.48214827  -1.42156531
C -3.53302178  -1.32823278  0.14810630
H -2.64758460  -0.34259224  -1.56552094
N -2.06241291  0.64478429  0.14063729
C -3.89070736  -2.64011544  -0.57281650
H -2.92312690  -4.46861966  -1.26374127
H -2.35362996  -3.89005068  0.31214513
H -4.39594748  -0.64560137  0.16824440
H -3.25839869  -1.54482481  1.19564798
H -1.92396971  0.58361618  1.15136260
C -1.82660043  1.84190072  -0.45157275
H -4.26816801  -2.40308386  -1.58263828
H -4.70527002  -3.14979189  -0.03529018
N -1.51613496  2.84345116  0.41919356
H  0.69839412  -1.47061571  -1.60005373

Int1
COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP
\[ E = -17920.62 \]
\[ G = -17478.19 \]
COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP
\[ E = -12293.21 \]
\[ G = -11850.78 \]
\[ N_{\text{imag}} = 0 \]
C  1.72262743  0.67326079  -1.39382055
C  3.20823818  0.74657179  -1.76397458
H  1.51339408  1.30498832  -0.52278545
H  3.38448145  0.14607614  -2.66908246
C  4.12089409  0.18766182  -0.65532295
C  1.26639903  -0.76294418  -1.08542049
C  2.15143436  -1.40235191  0.00302986
C  3.66242186  -1.23110570  -0.24677319
\end{verbatim}
H   0.55180607  -5.58793878  -1.84131443
H   -2.10542267  -4.05850736  -4.13614998
H   -1.71131468  -4.33486700  -2.42628110
H   -1.74116679  -1.75030908  -2.00946525
C   -1.40647496  -0.42841894  -3.48543623
H   0.04748747  -5.09665643  -4.83624229
H   -0.84570451  -6.22484566  -3.80111588
N   -2.10305802  0.48328144  -2.74771099
H   -2.38767186  0.18647853  -1.81199200
C   -1.95642657  1.93251387  -2.87115102
H   0.25512766  -3.05404506  -1.38846443
S   5.05385447  2.59235878  0.24843319
O   4.10617526  3.71260744  0.37600744
H   7.67127393  1.46651765  0.66099288
O   5.84042953  2.42784321  -0.98032322
C   -3.35931351  2.63777378  -2.96737727
C   -3.16939466  4.16508599  -3.07577666
H   -4.15071976  4.64874913  -3.18348057
H   -2.68629113  4.57943083  -2.18025882
H   -2.56556949  4.43055542  -3.95431651
C   -4.04526850  2.11697881  -4.24963177
H   -3.45099755  2.36797781  -5.14005745
H   -5.03904927  2.57575549  -4.35381097
H   -4.16626860  1.02614364  -4.21408160
C   -4.23692625  2.31430716  -1.73965014
H   -3.76751222  2.65652743  -0.80834690
H   -5.20968716  2.81613985  -1.84493864
O   -1.29902846  1.84752116  -0.55414504
N   -0.21799561  3.40756332  -1.82486708
C   0.18002773  4.02237087  -3.09867621
C   0.49560650  3.93859651  -0.65058507
H   0.08522342  3.48302548  0.25210949
H   0.36499213  5.02915948  -0.61457249
H   1.56863692  3.71539850  -0.72524974
|   | X            | Y            | Z            |
|---|--------------|--------------|--------------|
| H | -0.19801854  | 5.05184062   | -3.16352112  |
| H | -0.18305525  | 3.44917255   | -3.95101471  |
| H | 1.27742835   | 4.04702412   | -3.14183877  |
| C | 6.17765898   | 2.67359164   | 1.65229409   |
| C | 5.79656683   | 3.35816718   | 2.8074596    |
| C | 6.64035056   | 3.32461847   | 3.92383834   |
| C | 7.85071193   | 2.62622043   | 3.86742261   |
| C | 8.23074937   | 1.96714988   | 2.69142089   |
| C | 7.39340718   | 1.98503551   | 1.57568917   |
| H | 4.85888813   | 3.90757418   | 2.83823683   |
| H | 6.34928080   | 3.84537113   | 4.83493596   |
| H | 8.50251814   | 2.59855613   | 4.73963104   |
| H | 9.17814381   | 1.43195412   | 2.64548861   |
| H | 5.71184101   | -0.12262988  | 2.04614155   |
| H | 5.29619974   | -1.25511676  | 3.37913049   |
| H | 1.91991934   | -2.47600237  | 0.07310805   |
| H | 1.85138680   | -0.97006714  | 0.96057191   |
| O | -0.10039704  | -0.73988958  | -0.51044527  |
| H | -0.44641393  | 0.18655388   | -0.55216535  |

**H$_2$O**

COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

$E = -503.11$

$G = -501.69$

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

$E = -317.57$

$G = -316.15$

$N_{imag} = 0$

|   | X            | Y            | Z            |
|---|--------------|--------------|--------------|
| H | 0.77466463   | 0.00000000   | 1.50030076   |
| O | 0.00000000   | 0.00000000   | 2.10752715   |
| H | -0.77466463  | 0.00000000   | 1.50030076   |

**Int2**

COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP
$E = -17406.22$
$G = -16981.23$
COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP
$E = -11970.88$
$G = -11545.89$
$N_{\text{imag}} = 0$

\begin{tabular}{cccc}
C & 2.29207992 & 0.33542453 & -2.15862393 \\
C & 3.77644948 & -0.03996845 & -1.93236158 \\
H & 2.07739935 & 1.31321907 & -1.70896741 \\
H & 3.97136560 & -0.98513065 & -2.46636647 \\
C & 4.16588966 & -0.27281964 & -0.45003698 \\
C & 1.41490110 & -0.71002065 & -1.50808391 \\
C & 1.62375445 & -0.74516831 & -0.00622603 \\
C & 3.10169556 & -1.10792330 & 0.30013277 \\
H & 5.08753271 & -0.86623060 & -0.45006358 \\
H & 3.28544443 & -1.08644848 & 1.38131681 \\
H & 3.25363506 & -2.15082282 & -0.01878615 \\
H & 4.64084612 & 1.53721322 & 3.78439188 \\
H & 2.07248094 & 0.38992537 & -3.23310905 \\
H & 4.43787824 & 0.71670010 & -2.37377925 \\
N & 4.54202154 & 0.97414242 & 0.29661852 \\
C & 3.55595690 & 1.84137595 & 0.96125601 \\
H & 4.02738095 & 2.82117093 & 1.12476501 \\
H & 2.69747052 & 2.03881753 & 0.31516255 \\
C & 3.09292211 & 1.35166098 & 2.33250238 \\
C & 4.10686555 & 0.73898382 & 3.24347723 \\
C & 1.78776603 & 1.56418306 & 2.59623138 \\
H & 1.10031577 & 1.96969479 & 1.86333121 \\
N & 1.10793209 & 1.21196722 & 3.81332951 \\
O & 1.73804152 & 1.05836795 & 4.88620080 \\
O & -0.14165775 & 1.07843510 & 3.71803598 \\
S & -2.30987800 & 0.67470385 & -3.07288273 \\
H & -1.93533527 & 2.61171046 & 1.84397342 \\
H & -1.95894963 & 2.88558353 & -1.93959733 \\
\end{tabular}
C  -3.75131970  3.44148564  -0.09857792
H  -4.11216787  3.57618517  -1.12877921
H  -4.33294776  4.10063598   0.56183611
H  -3.93620171  2.39999503   0.19749712
C  -1.78601184  3.63480580  1.47218961
H  -0.72579782  3.88915577  1.58602387
H  -2.37867127  4.30877979  2.10842573
O   0.73908954  2.74764377  -0.07184727
N   0.52896767  3.75160886  -2.11076788
C  -0.22131877  4.09163906  -3.33076513
C   1.94329841  4.16172690  -2.10227068
H   2.33521697  4.07797953  -1.08709205
H   2.01502160  5.20226305  -2.44551510
H   2.53117357  3.52297510  -2.77651815
H  -0.62291933  5.11312455  -3.27657255
H  -1.02827813  3.37590409  -3.50330275
H   0.46911683  4.03016365  -4.18060121
C   6.78836429  1.86650641  1.52353295
C   6.69472068  3.07269188  2.22248857
C   7.22095536  3.14802007  3.51575642
C   7.83781096  2.03182223  4.08905494
C   7.94262120  0.83548669  3.36767439
C   7.41630109  0.74559920  2.07873455
H   6.21753309  3.93490274  1.76345927
H   7.14710186  4.08072420  4.07332439
H   8.24198451  2.09324566  5.09871975
H   8.43123075  -0.03062347  3.81201712
H   4.85090006  0.19499518  2.65509366
H   3.65305518  0.08119295  3.98924363
H   0.97594803  -1.46236981  0.50833456

Int3

COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\( E = -17405.86 \)
$G = -16978.14$

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

$E = -11980.62$

$G = -11552.90$

$N_{\text{imag}} = 0$

|     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|
| C   | 2.16316606 | 0.99591676 | -1.22333471 |
| C   | 3.69555718 | 0.86509229 | -1.09590629 |
| H   | 1.7965501  | 1.89455399 | -0.70408389 |
| H   | 4.07982160 | 0.32824828 | -1.97692655 |
| C   | 4.19172165 | 0.06689705 | 0.12772265  |
| C   | 1.37911544 | -0.17416363 | -0.66748859 |
| C   | 1.96435592 | -1.11885285 | 0.14138800  |
| C   | 3.45863065 | -1.28083379 | 0.21167406  |
| H   | 5.25883545 | -0.11766920 | -0.02422592 |
| H   | 3.74673720 | -1.81301306 | 1.12607285  |
| H   | 3.81611276 | -1.90929806 | -0.62569300 |
| H   | 1.35777887 | -1.92201539 | 0.55116996  |
| H   | 1.89704873 | 1.13410436 | -2.28305259 |
| H   | 4.15950449 | 1.86136621 | -1.09661907 |
| N   | 4.11340886 | 0.84229266 | 1.40002305  |
| C   | 2.83817269 | 1.37334465 | 1.91744937  |
| H   | 3.07278771 | 1.91159798 | 2.84713062  |
| H   | 2.45954913 | 2.13026385 | 1.22362661  |
| C   | 1.73248479 | 0.37340857 | 2.24708459  |
| C   | 2.08041187 | -0.79628605 | 3.12396947  |
| C   | 0.47595460 | 0.93596669 | 2.14693015  |
| H   | 0.34144170 | 1.91832393 | 1.70692814  |
| N   | -0.70955312 | 0.36923781 | 2.57821761  |
| O   | -0.81615084 | -0.86105749 | 2.86641415  |
| O   | -1.75397701 | 1.14463007 | 2.62798789  |
| S   | -1.95843046 | 2.19486468 | -2.32910190 |
| H   | -1.71329594 | 3.98612043 | 2.76961443  |
| H   | -1.96326822 | 4.56062362 | -1.00509417 |
| C   | 0.07658436 | 4.17889862 | -0.31139594 |

S94
| Atom | X        | Y        | Z        |
|------|----------|----------|----------|
| N    | 0.04979152 | -0.11429615 | -0.92150629 |
| H    | -0.27539593 | 0.64412706  | -1.53096068 |
| C    | -0.95245825 | -1.11585980 | -0.54762244 |
| C    | -0.81456512 | -2.43235436 | -1.34320275 |
| C    | -2.37303079 | -0.53364894 | -0.77129777 |
| C    | -1.86973001 | -3.45249254 | -0.88282478 |
| H    | -0.94611523 | -2.20435196 | -2.41453297 |
| H    | 0.19930959  | -2.83636500 | -1.21828282 |
| C    | -3.43501328 | -1.53458798 | -0.29133687 |
| H    | -2.50832826 | -0.34407823 | -1.84484024 |
| N    | -2.54402356 | 0.75805750  | -0.09724374 |
| C    | -3.29271960 | -2.88218490 | -1.02235814 |
| H    | -1.77219575 | -4.38079762 | -1.46640058 |
| H    | -1.68249986 | -3.71389739 | 0.17315447  |
| H    | -4.43139811 | -1.10092782 | -0.46228141 |
| H    | -3.32082336 | -1.68555550 | 0.79579803  |
| H    | -2.53318612 | 0.71930193  | 0.93279164  |
| C    | -2.15938335 | 1.95056518  | -0.63513283 |
| H    | -3.51935448 | -2.73453952 | -2.09236332 |
| H    | -4.03282906 | -3.59669596 | -0.63099157 |
| N    | -1.96384365 | 2.94405794  | 0.26857247  |
| H    | -1.83718815 | 2.63906980  | 1.24053000  |
| C    | -1.45151746 | 4.26640599  | -0.08790782 |
| H    | -0.83769378 | -1.33489539 | 0.52786365  |
| S    | 5.49460948  | 1.01794134  | 2.32791289  |
| O    | 5.31727987  | 2.21094830  | 3.16692319  |
| H    | 6.28165723  | -1.73669411 | 1.89869285  |
| O    | 6.64737208  | 0.89923783  | 1.42478545  |
| C    | -1.83115663 | 5.31882103  | 1.01311028  |
| C    | -1.25360474 | 6.69080627  | 0.60146081  |
| H    | -1.56272558 | 7.45433048  | 1.32928780  |
| H    | -0.15542323 | 6.67522585  | 0.57197182  |
| H    | -1.62409704 | 6.99547408  | -0.38748895 |
| C    | -3.37326247 | 5.41263878  | 1.06225990  |
H     -3.77724839    5.71794147    0.08556277
H     -3.67750224    6.15901786    1.81009398
H     -3.82231525    4.44795603    1.33390732
C     -1.28980736    4.93377819    2.40798680
H     -0.19792457    4.83576228    2.39738000
H     -1.57060180    5.71402406    3.13052836
O      0.77424708    3.57448678    0.53243316
N      0.63068712    4.79799895   -1.38486978
C     -0.10242587    5.42862902   -2.49055266
C      2.09651773    4.82257405   -1.51112835
H      2.54449311    4.58923844   -0.54291469
H      2.41042246    5.82217755   -1.83854018
H      2.42908510    4.08324439   -2.25471204
H     -0.16740967    6.51717825   -2.34994848
H     -1.09964606    4.99855058   -2.59103970
H      0.44157735    5.22611206   -3.42205957
C      5.52621826   -0.40647766    3.43028693
C      5.07705907   -0.26903388    4.74683537
C      4.99624027   -1.40415713    5.55783239
C      5.35964517   -2.65681249    5.05332899
C      5.82442896   -2.77787868    3.73744905
C      5.91579337   -1.65094517    2.91892168
H      4.78666578    0.70854887    5.12297536
H      4.64315196   -1.30835344    6.58374727
H      5.28639322   -3.54030543    5.68629675
H      6.11828346   -3.75169000    3.34787524
H      3.09099096   -1.15462153    2.92542302
H      1.36461170   -1.61335770    3.02551222
H      2.06057906   -0.45550202    4.17373980

TS1 (TS-A1)
COSMO(DCM)-ZORA-M06-2X/TZ2P/COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\( E = -17406.24 \)

\( G = -16977.39 \)
COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -11980.56 \]
\[ G = -11551.71 \]

\[ N_{\text{imag}} = 1, 133 i \text{ cm}^{-1} \]

\[
\begin{array}{cccc}
\text{C} & 2.18920497 & 0.95817769 & -1.24194667 \\
\text{C} & 3.71807223 & 0.78681279 & -1.10242441 \\
\text{H} & 1.85078885 & 1.88614103 & -0.75665832 \\
\text{H} & 4.09074741 & 0.20572944 & -1.95975810 \\
\text{C} & 4.18052068 & 0.02640772 & 0.15814502 \\
\text{C} & 1.36597436 & -0.15917546 & -0.64169063 \\
\text{C} & 1.91232970 & -1.03945440 & 0.29037794 \\
\text{C} & 3.40036808 & -1.28803235 & 0.29531325 \\
\text{H} & 5.24375805 & -0.19575616 & 0.03040113 \\
\text{H} & 3.69994618 & -1.81764484 & 1.20637827 \\
\text{H} & 3.67978880 & -1.94530800 & -0.54760931 \\
\text{H} & 1.28316544 & -1.83412946 & 0.68230853 \\
\text{H} & 1.92620774 & 1.06349532 & -2.30547445 \\
\text{H} & 4.20806944 & 1.76942074 & -1.13832345 \\
\text{N} & 4.09082687 & 0.85258154 & 1.39462520 \\
\text{C} & 2.79006372 & 1.34510830 & 1.89194277 \\
\text{H} & 2.98436127 & 1.86470328 & 2.84045786 \\
\text{H} & 2.41769029 & 2.10803073 & 1.20186466 \\
\text{C} & 1.69411847 & 0.30911230 & 2.15784820 \\
\text{C} & 2.03114704 & -0.79118773 & 3.13743236 \\
\text{C} & 0.42627870 & 0.90982174 & 2.10648344 \\
\text{H} & 0.30870053 & 1.90126867 & 1.68381310 \\
\text{N} & -0.74587341 & 0.35338803 & 2.52984562 \\
\text{O} & -0.86292823 & -0.88559881 & 2.81417460 \\
\text{O} & -1.80531709 & 1.12825804 & 2.58308873 \\
\text{S} & -1.89909282 & 2.20743288 & -2.34119352 \\
\text{H} & -1.53129524 & 3.87891785 & 2.78274970 \\
\text{H} & -2.00908215 & 4.60602053 & -0.94972481 \\
\text{C} & 0.06290186 & 4.16481683 & -0.39435493 \\
\text{N} & 0.05933529 & -0.12036098 & -0.93621833 \\
\end{array}
\]
|     | X         | Y         | Z         |
|-----|-----------|-----------|-----------|
| H   | -0.26129167 | 0.62422179 | -1.57110959 |
| C   | -0.95573143 | -1.11385065 | -0.55065271 |
| C   | -0.79418902 | -2.43950355 | -1.32360799 |
| C   | -2.36756903 | -0.52815317 | -0.80588412 |
| C   | -1.86489451 | -3.45155225 | -0.88157619 |
| H   | -0.89222839 | -2.22710210 | -2.40158011 |
| H   | 0.21532831  | -2.84202567 | -1.16059542 |
| C   | -3.44010480 | -1.52708139 | -0.34539400 |
| H   | -2.48141566 | -0.33812228 | -1.88196929 |
| N   | -2.54322879 | 0.76009112  | -0.12863936 |
| C   | -3.28179760 | -2.87840717 | -1.06559459 |
| H   | -1.75297799 | -4.38511806 | -1.45375921 |
| H   | -1.70731133 | -3.70275749 | 0.18150227  |
| H   | -4.43181062 | -1.09287820 | -0.54001469 |
| H   | -3.34953249 | -1.67239224 | 0.74458910  |
| H   | -2.53346864 | 0.71774297  | 0.90443685  |
| C   | -2.14217257 | 1.95297614  | -0.65345886 |
| H   | -3.47793999 | -2.73674294 | -2.14237903 |
| H   | -4.03387816 | -3.58908686 | -0.69090695 |
| N   | -1.96268794 | 2.93863937  | 0.26037605  |
| H   | -1.85756317 | 2.62108601  | 1.23263402  |
| C   | -1.44840577 | 4.26461870  | -0.07790535 |
| H   | -0.85885057 | -1.30886371 | 0.52938687  |
| S   | 5.45470885  | 1.06099878  | 2.33595125  |
| O   | 5.24737760  | 2.26226330  | 3.15531315  |
| H   | 6.27897084  | -1.68876199 | 1.94670766  |
| O   | 6.61799737  | 0.94783895  | 1.44551971  |
| C   | -1.74288750 | 5.27750408  | 1.08510535  |
| C   | -1.17422196 | 6.65841017  | 0.69015386  |
| H   | -1.43502282 | 7.39775527  | 1.46062473  |
| H   | -0.07967930 | 6.63423452  | 0.59950985  |
| H   | -1.59490535 | 7.00166976  | -0.26554670 |
| C   | -3.27725588 | 5.38878314  | 1.23687540  |
| H   | -3.73767180 | 5.73725306  | 0.30041990  |
| Atom | X        | Y        | Z        |
|------|----------|----------|----------|
| H    | -3.52148694 | 6.10950314 | 2.03051629 |
| H    | -3.72441609 | 4.42101807 | 1.50041252 |
| C    | -1.11837357  | 4.83347806  | 2.42716540  |
| H    | -0.03138668  | 4.72101765  | 2.34128298  |
| H    | -1.33814030  | 5.59147909  | 3.19334173  |
| O    | 0.79394346   | 3.50639092   | 0.37731224   |
| N    | 0.57174157   | 4.83875531   | -1.45714027  |
| C    | -0.20148515  | 5.52442556  | -2.49941805  |
| C    | 2.02826008   | 4.83471221   | -1.66391485  |
| H    | 2.52512742   | 4.58691880   | -0.72338234  |
| H    | 2.34271198   | 5.82980942   | -2.00338905  |
| H    | 2.30521208   | 4.09300548   | -2.42820045  |
| H    | -0.18098249  | 6.61344554   | -2.34817707  |
| H    | -1.23092109  | 5.16761371   | -2.52221299  |
| H    | 0.25072284   | 5.29498310   | -3.47350382  |
| C    | 5.49522385   | -0.34913600  | 3.45620453   |
| C    | 5.03349365   | -0.20207805  | 4.76733921   |
| C    | 4.95879756   | -1.32876817  | 5.59061209   |
| C    | 5.33925337   | -2.58315817  | 5.10323274   |
| C    | 5.81541760   | -2.71404042  | 3.79237263   |
| C    | 5.90328431   | -1.59513608  | 2.96266607   |
| H    | 4.72925530   | 0.77641613   | 5.12989280   |
| H    | 4.59619177   | -1.22531699  | 6.61245550   |
| H    | 5.26993317   | -3.46027842  | 5.74541266   |
| H    | 6.12226070   | -3.68901699  | 3.41586246   |
| H    | 3.05077422   | -1.15182887  | 2.99724658   |
| H    | 1.32767642   | -1.62332675  | 3.07910820   |
| H    | 1.97303149   | -0.37031404  | 4.15538145   |

Int4

COSMO(DCM)-ZORA-M06-2X/TZ2P/COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\( E = -17428.96 \)

\( G = -16997.55 \)

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP
\[
E = -11990.05 \\
G = -11558.64 \\
N_{\text{imag}} = 0
\]

|       |       |       |       |
|-------|-------|-------|-------|
| C     | 1.81697693 | 1.15843482 | -1.20818664 |
| C     | 3.33394816  | 0.89289770  | -1.37819361 |
| H     | 1.65381235  | 2.01748400  | -0.54138032 |
| H     | 3.48042049  | 0.28848934  | -2.28568022 |
| C     | 3.95856678  | 0.11836177  | -0.20172167 |
| C     | 1.08314269  | 0.01312147  | -0.57822021 |
| C     | 1.71542233  | -0.71069060 | 0.57337314  |
| C     | 3.13176407  | -1.13543380 | 0.10129981  |
| H     | 4.97725658  | -0.15880218 | -0.48934284 |
| H     | 3.60579460  | -1.74783264 | 0.87554094  |
| H     | 3.05771787  | -1.75296845 | -0.80619236 |
| H     | 1.12310520  | -1.59357823 | 0.82741566  |
| H     | 1.35571936  | 1.42332670  | -2.16710877 |
| H     | 3.86103328  | 1.84425790  | -1.52193713 |
| N     | 4.07184981  | 0.97394431  | 1.01015356  |
| C     | 2.84060366  | 1.32177510  | 1.74939574  |
| H     | 3.11953084  | 1.67737860  | 2.74646757  |
| H     | 2.37008235  | 2.17417393  | 1.25222302  |
| C     | 1.81070954  | 0.16313593  | 1.90265437  |
| C     | 2.24750008  | -0.78329185 | 3.05023012  |
| C     | 0.50419121  | 0.85248013  | 2.20986923  |
| H     | 0.45278736  | 1.93355744  | 2.24182415  |
| N     | -0.62367434 | 0.22829807  | 2.50328833  |
| O     | -0.74307465 | -1.06830760 | 2.53028005  |
| O     | -1.73283727 | 0.96148781  | 2.72597191  |
| S     | -1.80837959 | 2.09061914  | -2.17397447 |
| H     | -2.97069347 | 4.22325599  | 2.32085839  |
| H     | -1.12499160 | 4.16213560  | -0.95647772 |
| C     | 0.26771106  | 4.22931283  | 0.72452222  |
| N     | -0.05965609 | -0.32412302 | -1.08957515 |
| H     | -0.41629665 | 0.27760815  | -1.86635581 |

S100
|    |     |     |     |     |
|----|-----|-----|-----|-----|
| C  | -1.06336661 | -1.28040799 | -0.56728529 |     |
| C  | -1.04307244 | -2.59470407 | -1.36225607 |     |
| C  | -2.45532012 | -0.59510503 | -0.64790531 |     |
| C  | -2.12147970 | -3.54565618 | -0.81023934 |     |
| H  | -1.23230265 | -2.37900905 | -2.42714929 |     |
| H  | -0.04425862 | -3.05017638 | -1.28825248 |     |
| C  | -3.51056700 | -1.54557587 | -0.06361310 |     |
| H  | -2.69162686 | -0.38421073 | -1.70019141 |     |
| N  | -2.44943780 | 0.68106213  | 0.06715214  |     |
| C  | -3.51309185 | -2.88654199 | -0.82025039 |     |
| H  | -2.13159278 | -4.47119495 | -1.40482323 |     |
| H  | -1.85679560 | -3.82495655 | 0.22347530  |     |
| H  | -4.49446860 | -1.05811820 | -0.12609361 |     |
| H  | -3.28547625 | -1.71286178 | 1.00264149  |     |
| H  | -2.39971266 | 0.62633866  | 1.11203836  |     |
| C  | -1.98587931 | 1.84409065  | -0.46274016 |     |
| H  | -3.82504533 | -2.71157214 | -1.86416135 |     |
| H  | -4.25456814 | -3.56383479 | -0.37081953 |     |
| N  | -1.67658604 | 2.79216677  | 0.45303966  |     |
| H  | -1.65613649 | 2.47375569  | 1.43879603  |     |
| C  | -1.14978203 | 4.11625190  | 0.13130872  |     |
| H  | -0.83921849 | -1.45893919 | 0.49225606  |     |
| S  | 5.55328732  | 1.16910738  | 1.75319267  |     |
| O  | 5.46069964  | 2.37553426  | 2.58312856  |     |
| H  | 6.33021122  | -1.57755869 | 1.26882650  |     |
| O  | 6.56955972  | 1.04556187  | 0.69961428  |     |
| C  | -2.09759966 | 5.27358702  | 0.60652763  |     |
| C  | -1.39704560 | 6.61957269  | 0.32088634  |     |
| H  | -2.06983496 | 7.45235669  | 0.57101576  |     |
| H  | -0.48265823 | 6.73215548  | 0.92071614  |     |
| H  | -1.12978137 | 6.70873875  | -0.74239420 |     |
| C  | -3.39202466 | 5.17504004  | -0.2307705  |     |
| H  | -3.17894279 | 5.29899068  | -1.30223588 |     |
| H  | -4.09839049 | 5.95938898  | 0.07758439  |     |
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| H       | -3.87643878 | 4.19914894 | -0.08848535 |
| C       | -2.44645790 | 5.16504515 | 2.10498859 |
| H       | -1.54516269 | 5.20941302 | 2.72688892 |
| H       | -3.11470300 | 5.99296050 | 2.38406758 |
| O       | 0.43786641  | 4.07714155 | 1.95046091 |
| N       | 1.30918564  | 4.47202330 | -0.12935288 |
| C       | 1.19050159  | 4.68852075 | -1.58176201 |
| C       | 2.64346683  | 4.74969450 | 0.43058396 |
| H       | 2.60349734  | 4.63750484 | 1.51542776 |
| H       | 2.94732838  | 5.77464576 | 0.17199317 |
| H       | 3.38042311  | 4.05016983 | 0.01293477 |
| H       | 0.98810354  | 5.74516743 | -1.81192629 |
| H       | 0.41076572  | 4.05750042 | -2.01509032 |
| H       | 2.14542989  | 4.41034295 | -2.04351766 |
| C       | 5.73573460  | -0.23714318 | 2.86195478 |
| C       | 5.43779519  | -0.08786937 | 4.21952954 |
| C       | 5.46299616  | -1.21389383 | 5.04640461 |
| C       | 5.78038895  | -2.46863980 | 4.51696991 |
| C       | 6.09474824  | -2.60113128 | 3.15834720 |
| C       | 6.07907590  | -1.48353625 | 2.32254623 |
| H       | 5.18269966  | 0.89143235 | 4.61602219 |
| H       | 5.22686788  | -1.10950316 | 6.10452799 |
| H       | 5.78943054  | -3.34525148 | 5.16332774 |
| H       | 6.35462633  | -3.57641158 | 2.74882166 |
| H       | 3.22575268  | -1.23423331 | 2.85986391 |
| H       | 1.50014253  | -1.57318945 | 3.18096539 |
| H       | 2.31632015  | -0.20626120 | 3.98156490 |

**PhCO₂H**

COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -3168.54 \]

\[ G = -3119.32 \]

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -2170.63 \]
\[ G = -2121.41 \]
\[ N_{\text{imag}} = 0 \]

|     | X       | Y       | Z       |
|-----|---------|---------|---------|
| O   | -0.00210683 | 0.12479766 | 0.00000000 |
| C   | 0.02202758  | -1.10188738 | 0.00000000 |
| H   | -0.12264488 | -3.85558121 | 0.00000000 |
| O   | 1.92186487  | -1.14174323 | 0.00000000 |
| C   | 1.19098365  | -1.81179849 | 0.00000000 |
| C   | -1.18490189 | -1.97047812 | 0.00000000 |
| C   | -2.44666296 | -1.35205928 | 0.00000000 |
| C   | -3.60610680 | -2.12665900 | 0.00000000 |
| C   | -3.51467733 | -3.52432039 | 0.00000000 |
| C   | -2.25995441 | -4.14483624 | 0.00000000 |
| C   | -1.09657774 | -3.37311805 | 0.00000000 |
| H   | -2.50224871 | -0.26561325 | 0.00000000 |
| H   | -4.58197328 | -1.64275320 | 0.00000000 |
| H   | -4.42077632 | -4.12939160 | 0.00000000 |
| H   | -2.18803807 | -5.23179559 | 0.00000000 |

TS2

COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -20590.91 \]
\[ G = -20097.61 \]

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -14166.95 \]
\[ G = -13673.65 \]

\[ N_{\text{imag}} = 1, 1345i \text{ cm}^{-1} \]

|     | X           | Y           | Z           |
|-----|-------------|-------------|-------------|
| C   | -1.04722105 | 3.02829881  | -0.64585216 |
| C   | 0.26971387  | 2.86489362  | -1.45043350 |
| H   | -0.86471460 | 3.57519423  | 0.29532039  |
| H   | 0.01522791  | 2.71072240  | -2.50983950 |
| C   | 1.13064913  | 1.66284886  | -1.00911195 |
| C   | -1.67537823 | 1.73493838  | -0.23927683 |
| C   | -0.80416391 | 0.59355948  | 0.18691277  |
| C   | 0.25947200  | 0.40468704  | -0.93016256 |

S103
H  -4.56959805  -2.18340917  -0.04572929
H  -6.90780193   0.30329947   1.70115156
H  -5.48123629  -0.71867498   1.97566545
H  -4.37195226   1.34124789   2.77412620
C  -4.38692282   3.18436403   1.91716641
H  -6.98420629  -0.38681191  -0.69296647
H  -6.99986396  -1.82646366   0.34077806
N  -3.74139875   3.63306501   3.01781080
H  -3.36635661   2.91089359   3.64402525
C  -3.25152317   5.00047301   3.18422008
H  -3.28426717  -0.10889342   0.83306049
S   3.43127749   2.05615866   0.46062023
O   3.70382941   3.16971293   1.38052769
H   4.02429067  -0.60025163  -0.51744871
O   3.99956615   2.04623321  -0.89509474
C  -2.84258927   5.24376454   4.68384680
C  -2.32133572   6.69147763   4.82077516
H  -2.09597084   6.90052231   5.87600461
H  -1.40180140   6.84741487   4.24056066
H  -3.07390552   7.41856827   4.48432855
C  -4.11203807   5.08342432   5.55220861
H  -4.89289859   5.79207472   5.23844708
H  -3.86732752   5.28318468   6.60527924
H  -4.52279767   4.06716016   5.48470034
C  -1.75243309   4.26085382   5.16736502
H  -0.84749551   4.32554671   4.55401863
H  -1.49204951   4.50173123   6.20847835
O  -1.16965212   4.38672031   2.14244798
N  -1.99442591   6.42516435   1.54753191
C  -3.06569778   7.42509008   1.44275244
C  -0.78779549   6.70554068   0.75382547
H   0.04138846   6.10338181   1.13209661
H  -0.54562536   7.77187661   0.84076490
H  -0.95966136   6.46379264  -0.30610021

S105
H  -2.90549269  8.25102820  2.15010716
H  -4.04141212  6.96754254  1.61107912
H  -3.05969238  7.82841476  0.42218427
C   3.92141220  0.54762327  1.31313182
C   4.00736639  0.54310326  2.70896662
C   4.24082999 -0.66412391  3.37245785
C   4.39824405 -1.84550630  2.64165316
C   4.33293215 -1.82397478  1.24182000
C   4.08993951 -0.62604290  0.56824890
H   3.88396353  1.46631066  3.26603507
H   4.29302297 -0.67771165  4.45861282
H   4.57537939 -2.78644788  3.16129056
C   4.46577858 -2.74380936  0.67344821
H   4.51765398 -0.64579600  1.31617102
H  -0.02839256 -1.37061847  1.82672123
H   0.97068232 -0.48125080  2.98822755
H  -0.25958812  1.43451212  3.81819584
O  -0.02816183 -0.36452255  5.46826870
O    0.65201591  1.64743194  4.66382985
C   0.80334752  0.55796714  5.38653645
H   1.67056668 -1.45961999  6.92706763
C   2.13250462  0.46694437  6.09879189
C   3.09668306  1.48001068  5.98535501
C   4.34501582  1.33714586  6.59550233
C   4.63769775  0.18261382  7.33202176
C   3.67380436 -0.82555803  7.46112719
C   2.42800597 -0.68235149  6.84712274
H   2.86157047  2.36849449  5.40426806
H   5.09457166  2.12135891  6.49112440
H   5.61368755  0.06798754  7.80336867
H   3.89679996 -1.72369264  8.03680684

Int5
COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

S106
\[ E = -20599.00 \]
\[ G = -20104.96 \]
COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP
\[ E = -14171.09 \]
\[ G = -13677.05 \]
\[ N_{\text{imag}} = 0 \]

\begin{tabular}{ccc}
 & X & Y \\
C & -1.02548005 & 3.00546993 & -0.64988233 \\
C & 0.30821892 & 2.82841485 & -1.42208574 \\
H & -0.87091512 & 3.60202163 & 0.26567535 \\
H & 0.07745568 & 2.60179438 & -2.47383538 \\
C & 1.18860738 & 1.68168490 & -0.88708318 \\
C & -1.63442456 & 1.71945964 & -0.19548298 \\
C & -0.74874629 & 0.61887941 & 0.31259173 \\
C & 0.35309633 & 0.40345075 & -0.76241096 \\
H & 2.01048575 & 1.52629714 & -1.59282665 \\
H & 0.97337843 & -0.45405301 & -0.47999016 \\
H & -0.11110882 & 0.17239960 & -1.73211690 \\
H & -1.32624190 & -0.30287689 & 0.42155053 \\
H & -1.75081521 & 3.56892719 & -1.25178516 \\
H & 0.86799877 & 3.77201524 & -1.39814192 \\
N & 1.80284105 & 2.01630759 & 0.41947178 \\
C & 0.95295253 & 2.08248051 & 1.62354174 \\
H & 1.57848476 & 2.04135760 & 2.52107920 \\
H & 0.44303372 & 3.04998492 & 1.65724212 \\
C & -0.07287910 & 0.90856645 & 1.71629431 \\
C & 0.66131852 & -0.37922951 & 2.16137430 \\
C & -1.05627215 & 1.41363752 & 2.78923514 \\
H & -1.56103083 & 2.34401956 & 2.49862938 \\
N & -2.11552276 & 0.50265477 & 3.25909854 \\
O & -2.20274674 & -0.66840472 & 2.84234151 \\
O & -2.92698981 & 0.98256156 & 4.09892466 \\
S & -4.72527685 & 4.14299445 & 0.48939904 \\
H & -2.19371361 & 3.32952821 & 5.14494479 \\
H & -4.21863886 & 5.72089894 & 2.89896412 \\
\end{tabular}

S107
| Atom | X           | Y           | Z          |
|------|-------------|-------------|------------|
| C    | -2.20595564 | 5.29868888  | 2.14448224 |
| N    | -2.92638427 | 1.59373077  | -0.27883741|
| H    | -3.46002761 | 2.43403678  | -0.58427128|
| C    | -3.78404978 | 0.45492503  | 0.12641179 |
| C    | -4.12467736 | -0.41513569 | -1.09582155|
| C    | -5.06519155 | 1.00862190  | 0.79978381 |
| C    | -5.04093590 | -1.57644443 | -0.67156017|
| H    | -4.62541466 | 0.21196569  | -1.85141401|
| H    | -3.19226331 | -0.79072475 | -1.54219892|
| C    | -5.96118550 | -0.16204198 | 1.23159882 |
| H    | -5.60329480 | 1.63934745  | 0.07881416 |
| N    | -4.73611805 | 1.85198490  | 1.94808454 |
| C    | -6.30877314 | -1.06116229 | 0.03201884 |
| H    | -5.30801359 | -2.17081952 | -1.55753945|
| H    | -4.48673982 | -2.24226502 | 0.01130794 |
| H    | -6.87056155 | 0.24750203  | 1.69409826 |
| H    | -5.43516152 | -0.75326720 | 2.00077707 |
| H    | -4.48649347 | 1.35822024  | 2.81051466 |
| C    | -4.42161191 | 3.17760593  | 1.88086915 |
| H    | -6.91709459 | -0.48593842 | -0.68608666|
| H    | -6.92341538 | -1.90707326 | 0.37286924 |
| N    | -3.85267064 | 3.68455585  | 2.99831821 |
| H    | -3.50894804 | 3.01248454  | 3.68881353 |
| C    | -3.37638866 | 5.06316396  | 3.12573091 |
| H    | -3.23548577 | -0.13970643 | 0.86359821 |
| S    | 3.45219072  | 2.12868256  | 0.60672058 |
| O    | 3.72212428  | 3.17456497  | 1.60153381 |
| H    | 4.00223348  | -0.46078206 | -0.55656035|
| O    | 4.03036156  | 2.20113000  | -0.74287496|
| C    | -2.95328280 | 5.34341257  | 4.61521276 |
| C    | -2.43278687 | 6.79452525  | 4.71396959 |
| H    | -2.20398627 | 7.02805225  | 5.76317709 |
| H    | -1.51552293 | 6.93698633  | 4.12721225 |
| H    | -3.18725457 | 7.51283195  | 4.36361042 |

S108
C  -4.21335744      5.20387991      5.50090690
H   -4.99694323      5.90612863      5.17985320
H  -3.95621693      5.42717406      6.54614546
H  -4.62720348      4.18709095      5.46366306
C  -1.85558738      4.37382535      5.10865438
H  -0.96444944      4.40621106      4.47347816
H  -1.56944821      4.65170982      6.13335930
O  -1.31165748      4.42774679      2.06447721
N  -2.12404032      6.47042857      1.47078635
C  -3.19600993      7.46687106      1.34779436
C  -0.91757795      6.73848153      0.67241778
H  -0.08228209      6.15935386      1.07292638
H  -0.68878881      7.80969663      0.72673722
H  -1.08181658      6.46070469     -0.37988944
H  -3.02156938      8.31817542      2.02075741
H  -4.16920381      7.02023908      1.55408177
H  -3.20941937      7.83178110      0.31272964
C   3.92605346      0.56070335      1.35044444
C   4.01759310      0.46025835      2.74142700
C   4.23808178     -0.79270283      3.31856399
C   4.37009469     -1.92409150      2.50787055
C   4.29360476     -1.80737532      1.11316565
C   4.07002089     -0.56192471      0.52434080
H   3.89825890      1.34179767      3.36292938
H   4.29629417     -0.88110397      4.40007249
H   4.53455912     -2.90106211      2.96114022
H   4.40578130     -2.68880505      0.48279066
H   1.57527357     -0.52431660      1.58117805
H   0.02509095     -1.26209052      2.04058484
H   0.93594763     -0.29784843      3.21677796
H  -0.47151890      1.67556604      3.71096766
O  -0.03073018      0.11636418      5.56217361
O   0.94919920      2.03240271      4.84027373
C   0.95029094      0.90923345      5.45474273

S109
H  1.55215642  -1.46066758  6.62143882
C  2.28353762  0.47712506  6.07004851
C  3.39371570  1.33437302  6.06355127
C  4.61927705  0.91910008  6.59216604
C  4.74897769  -0.36567128  7.13589491
C  3.64453582  -1.22732323  7.15100042
C  2.42081095  -0.80449976  6.62358205
H  3.27973140  2.32417527  5.62518357
H  5.47739309  1.59146079  6.57427282
H  5.70556782  -0.69428165  7.54263789
H  3.74075089  -2.22932296  7.57061115

Int6
COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP
\[ E = -17426.12 \]
\[ G = -16996.71 \]
COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP
\[ E = -11986.23 \]
\[ G = -11556.82 \]
\[ N_{imag} = 0 \]
C  -1.13136318  2.64441339  -1.08633609
C  0.14182319  2.27287650  -1.88040145
H  -0.86314553  3.27122851  -0.22293534
H  -0.14380912  2.03483866  -2.91781009
C  0.87286752  1.03185560  -1.33489989
C  -1.94074552  1.45995623  -0.56612769
C  -1.14957062  0.23811535  -0.06604841
C  -0.11887694  -0.12365051  -1.16151400
H  1.66204334  0.73954029  -2.03705455
H  0.40753887  -1.05163257  -0.90641487
H  -0.63745876  -0.28681493  -2.11732538
H  -1.83707689  -0.60361078  0.06185489
H  -1.80544457  3.25892409  -1.69630209
H  0.82503535  3.13232359  -1.92451494

S110
N   | 1.56063391 | 1.22796944 | -0.01521722
C   | 0.70578012 | 1.52117955 | 1.15655933
H   | 1.33680903 | 1.48325426 | 2.05405788
H   | 0.27299206 | 2.52672815 | 1.10770326
C   | -0.39846176 | 0.43628042 | 1.29902743
C   | 0.28540243 | -0.87255399 | 1.76380482
C   | -1.32531544 | 1.00402488 | 2.38098373
H   | -1.93958556 | 1.81934784 | 1.98114064
N   | -2.34138829 | 0.06344237 | 2.98340466
O   | -2.59831437 | -1.01901959 | 2.44144249
O   | -2.92529574 | 0.48349711 | 4.00943748
S   | -4.29306623 | 4.45445536 | 0.83118711
H   | -3.97893803 | 3.82644207 | 5.85117971
H   | -2.77782776 | 5.31410403 | 2.60946534
C   | -1.18912877 | 4.20400202 | 3.63352592
N   | -3.21306458 | 1.58166888 | 0.64607318
H   | -0.78128957 | 1.40494608 | 3.24331811
C   | -4.16095530 | 0.60772854 | -0.11821438
C   | -4.85028404 | -0.10739383 | -1.30016082
C   | -5.21365387 | 1.37942301 | 0.73256931
C   | -5.97925294 | -1.03690663 | -0.82800203
H   | -5.25165636 | 0.66109720 | -1.98180758
H   | -4.08692753 | -0.67019586 | -1.85938236
C   | -6.34747503 | 0.44889247 | 1.19327564
H   | -5.60981157 | 2.19891566 | 0.11857511
N   | -4.59354916 | 1.99055643 | 1.91513400
C   | -7.01507933 | -0.26338616 | 0.00509191
H   | -6.46238743 | -1.50650139 | -1.69886327
H   | -5.55359261 | -1.85111265 | -0.21623704
H   | -7.08260904 | 1.03988322 | 1.76021915
H   | -5.93156272 | -0.30733037 | 1.88302266
H   | -4.54939096 | 1.39740204 | 2.74528163
C   | -4.11030564 | 3.25882059 | 2.03395179
H   | -7.51046138 | 0.48690771 | -0.63478655

S111
H  -7.79872896  -0.94265666  0.37388302
N  -3.47516201   3.49630055  3.22714265
H  -3.25863158   2.68899353  3.81925005
C  -2.64835200   4.67693382  3.48383221
H  -3.70700647  -0.15859130  0.53246057
S   2.99620842   2.11478168 -0.04450796
O   2.77600874   3.55617936  0.18568962
H  -3.61372555  -0.58374722  0.67838092
O   3.72388706   1.69592525 -1.25283279
C  -3.14127082   5.50537531  4.72087147
C  -2.14768506   6.66395920  4.95538398
H  -2.50925724   7.30876575  5.76922576
H  -1.15284875   6.29010604  5.23702979
H  -2.04368222   7.28423822  4.05306748
C  -4.53076656   6.07774617  4.36336824
H  -4.47078087   6.74029846  3.4883785
H  -4.92870015   6.65230144  5.21250652
H  -5.23550416   5.26824158  4.1281903
C  -3.25676941   4.64313528  5.99448364
H  -2.28984461   4.20718076  6.27077462
H  -3.61722485   5.26753611  6.82542410
O  -0.91766697   3.32393052  4.47854593
N  -0.24060052   4.75261940  2.82166337
C  -0.49071445   5.76751558  1.78398292
C   1.18120520   4.48391970  3.09947150
H   1.25485862   3.64901954  3.79896617
H   1.64924959   5.37671863  3.54336140
H   1.69497251   4.24255828  2.16393633
H  -0.42806308   6.78596620  2.19531332
H  -1.46478180   5.61700436  1.31186655
H   0.28059789   5.65657529  1.01244554
C   3.79599499   1.44369992  1.42276675
C   4.16873743   2.30389079  2.45770891
C   4.76788717   1.76439587  3.60030310

S112
C    4.98245118   0.38582452   3.69512918
C    4.60992366  -0.46272876  2.64385782
C    4.01473738   0.06345491   1.49749259
H    3.98993706   3.37137143   2.36813340
H    5.06150291   2.42281768   4.41656421
H    5.44328795  -0.03103781   4.58974030
H    4.77941066  -1.53576212   2.71992227
H    1.18970070  -1.05317505   1.17461144
H   -0.38123351  -1.73518717   1.66461144
H    0.58723433  -0.78200846   2.81727664

Int7
COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

$E = -17940.33$
$G = -17494.34$

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

$E = -12306.14$
$G = -11860.15$

$N_{\text{imag}} = 0$

C   -1.18542479   3.03935720   0.21454761
C    0.10261001   3.11476460  -0.63159934
H   -0.94921289   3.16151297   1.27350780
H   -0.16422345   3.33446622  -1.67694456
C    0.91699400   1.80478392  -0.65130829
C   -1.98458703   1.72860208   0.04353947
C   -1.06845156   0.45829273   0.07026544
C    0.00942440   0.62830807  -1.02100130
H    1.72651883   1.89905501  -1.38394622
H    0.60160731  -0.28448800  -1.15137751
H   -0.48553076   0.85821762  -1.97096444
H   -1.70560294  -0.39540931  -0.18658062
H   -1.84538632   3.87946517  -0.04934301
H    0.73077409   3.94540246  -0.27731750
N    1.58575983   1.44686157   0.64338003
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | 4.8015  | -1.1800 | 2.0931  |
| C    | 4.1603  | -0.1801 | 1.3619  |
| H    | 3.8731  | 2.1884  | 3.8125  |
| H    | 5.0539  | -2.1237 | 1.6115  |
| H    | 1.2336  | -1.9412 | 0.6223  |
| H    | -0.3207 | -2.0397 | 0.8524  |
| H    | 0.7057  | -1.6352 | 2.2513  |
| O    | -2.9594 | 1.5879  | 1.1311  |
| H    | -2.9861 | 2.4270  | 1.6574  |
| H    | -3.0053 | 2.7291  | -1.4196 |

**pro**

COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -8718.04 \]

\[ G = -8534.08 \]

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -5891.86 \]

\[ G = -5707.90 \]

\[ N_{\text{imag}} = 0 \]

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -1.2349 | 3.0198  | 0.5942  |
| C    | 0.0801  | 3.2315  | -0.1993 |
| H    | -1.0407 | 3.1053  | 1.6768  |
| H    | -0.1741 | 3.6614  | -1.1801 |
| C    | 0.8838  | 1.9448  | -0.5028 |
| C    | -1.9261 | 1.6776  | 0.4135  |
| C    | -1.0614 | 0.4699  | 0.0598  |
| C    | -0.0604 | 0.8662  | -1.0462 |
| H    | 1.6483  | 2.1756  | -1.2528 |
| H    | 0.5057  | -0.0082 | -1.3889 |
| H    | -0.6079 | 1.2697  | -1.9106 |
| H    | -1.7441 | -0.3090 | -0.3016 |
| H    | -1.9666 | 3.8073  | 0.3646  |

S116
TS3
COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

S117
\[ E = -17401.60 \]
\[ G = -16974.18 \]
COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP
\[ E = -11969.25 \]
\[ G = -11541.83 \]
\( N_{\text{imag}} = 1, 1608i \text{ cm}^{-1} \)

| \( \text{atom} \) | \( x \)   | \( y \)   | \( z \)   |
|-----------------|----------|----------|----------|
| C               | -0.26799336 | 2.50835067 | 0.15283642 |
| C               | 0.77442523  | 3.61481746 | -0.14563408 |
| H               | -0.27340496 | 2.28791071 | 1.22812819  |
| H               | 0.54460152  | 4.05781699 | -1.12617338 |
| C               | 2.21830513  | 3.08369678 | -0.20041818 |
| C               | 0.03467790  | 1.21305088 | -0.53273307 |
| C               | 1.45140406  | 0.70976963 | -0.55728380 |
| C               | 2.29307248  | 1.88033469 | -1.14505126 |
| H               | 2.85952706  | 3.89210549 | -0.56441576 |
| H               | 3.32599979  | 1.54830574 | -1.29209450 |
| H               | 1.89658420  | 2.16528948 | -2.13043217 |
| H               | 1.52477505  | -0.15442743 | -1.21983660 |
| H               | -1.28091843 | 2.84377894 | -0.09831817 |
| H               | 0.69321939  | 4.40830605 | 0.60710475  |
| N               | 2.71274465  | 2.71123505 | 1.15119477  |
| C               | 2.19020003  | 1.48662106 | 1.79446650  |
| H               | 2.85730338  | 1.21700742 | 2.61888621  |
| H               | 1.23429657  | 1.71876072 | 2.25833256  |
| C               | 2.04851797  | 0.26760676 | 0.84138593  |
| C               | 3.45419007  | -0.33933141 | 0.59005893  |
| C               | 1.16803888  | -0.73716751 | 1.61438323  |
| H               | 1.46662344  | -0.82294902 | 2.66462356  |
| N               | 1.04008879  | -2.04960476 | 1.08724084  |
| O               | 1.26557109  | -2.29246923 | -0.14134037 |
| O               | 0.55187767  | -2.94615741 | 1.85079865  |
| S               | 4.06492343  | 3.45503625 | 1.78038923  |
| O               | 4.02812554  | 3.26321388 | 3.23411197  |
| H               | 5.37204456  | 3.46008538 | -0.80417724 |

S118
| Element | X        | Y        | Z        |
|---------|----------|----------|----------|
| O       | 4.11919059 | 4.79896504 | 1.18928142 |
| N       | -0.94436769 | 0.61932759  | -1.14766148 |
| H       | -1.88500520 | 1.04686830  | -1.01769019 |
| C       | -0.98570058 | -0.73612597 | -1.73383351 |
| C       | -1.20017113 | -0.68724681 | -3.25279884 |
| C       | -2.13114446 | -1.51834403 | -1.02956508 |
| C       | -1.25777938 | -2.12501663 | -3.80415829 |
| H       | -2.14292260 | -0.15780086 | -3.46946300 |
| H       | -0.38308268 | -0.11955992 | -3.72210968 |
| C       | -2.15042881 | -2.95647065 | -1.56341720 |
| H       | -3.08597900 | -1.02670298 | -1.26359623 |
| N       | -1.97503234 | -1.48652225 | 0.42087544  |
| C       | -2.33531323 | -2.96519279 | -3.09261933 |
| H       | -1.45206058 | -2.09320255 | -4.88649811 |
| H       | -0.27220340 | -2.60078925 | -3.66542885 |
| H       | -2.96540123 | -3.50402040 | -1.06749403 |
| H       | -1.20255128 | -3.45220641 | -1.29430576 |
| H       | -1.29061424 | -2.13420493 | 0.82113789  |
| C       | -2.25689937 | -0.38309299 | 1.20660160  |
| H       | -3.33202696 | -2.55959855 | -3.33608440 |
| H       | -2.3089571  | -4.00097089 | -3.46262167 |
| S       | -3.55249072 | 0.70320732  | 0.74320928  |
| N       | -1.44496390 | -0.25396980 | 2.25262203  |
| H       | -0.14777079 | -0.44862145 | 1.92290881  |
| C       | -1.82982253 | 0.54181862  | 3.42139689  |
| H       | -1.67709614 | 0.98709396  | 6.20244575  |
| H       | -2.69215849 | 1.15383439  | 3.14551162  |
| C       | -0.64775752 | 1.43803153  | 3.83217749  |
| H       | -0.04151004 | -1.23255651 | -1.49329185 |
| H       | 4.16040591  | 0.40687740  | 0.21678316  |
| H       | 3.39946827  | -1.16450982 | -0.12828828 |
| H       | 3.85028888  | -0.72453219 | 1.53909001  |
| C       | 5.46200658  | 2.51607409  | 1.14291653  |
| C       | 6.07189617  | 1.55327462  | 1.95203940  |
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | 7.06767539 | 0.73995602 | 1.40423544 |
| C    | 7.44203912  | 0.89031353 | 0.06536082 |
| C    | 6.83412656  | 1.87024971 | -0.73010122 |
| C    | 5.84233700  | 2.69280522 | -0.19409796 |
| H    | 5.76295587  | 1.43900318 | 2.98779235 |
| H    | 7.54641601  | -0.01608883 | 2.02512890 |
| H    | 8.21298573  | 0.24865288 | -0.35926812 |
| H    | 7.13416947  | 1.99571128 | -1.76960777 |
| C    | -2.32107042 | -0.37381156 | 4.60388301 |
| C    | -3.63936763 | -1.04160363 | 4.15044436 |
| H    | -4.04555331 | -1.65430872 | 4.96888278 |
| H    | -4.39051714 | -0.28955342 | 3.86963725 |
| H    | -3.47109313 | -1.69519524 | 3.28380266 |
| C    | -1.30262039 | -1.47580953 | 4.96141947 |
| H    | -1.04511390 | -2.06183171 | 4.06905879 |
| H    | -1.74244229 | -2.15033608 | 5.71208066 |
| H    | -0.37972925 | -1.04394020 | 5.36252095 |
| C    | -2.60148206 | 0.52692170  | 5.82636790 |
| H    | -3.31042956 | 1.32941479  | 5.56924084 |
| H    | -3.04298855 | -0.06616329 | 6.64076269 |
| O    | 0.37624117  | 0.94633505  | 4.34234704 |
| N    | -0.73948450 | 2.78162729  | 3.55902165 |
| C    | -1.93873241 | 3.47138463  | 3.05106046 |
| C    | 0.34176243  | 3.67593642  | 4.00641332 |
| H    | -0.03023800 | 4.35221618  | 4.79072935 |
| H    | 0.69722899  | 4.27828457  | 3.16035103 |
| H    | 1.16454531  | 3.07441309  | 4.39567549 |
| H    | -2.59893719 | 3.77669973  | 3.87769197 |
| H    | -2.49391494 | 2.84554160  | 2.34771960 |
| H    | -1.61067980 | 4.37356229  | 2.52001992 |

Int8
COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -17412.45 \]
\[ G = -16984.08 \]

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -11976.66 \]

\[ G = -11548.29 \]

\[ N_{\text{imag}} = 0 \]

\[
\begin{array}{ccc}
\text{atom} & \text{X} & \text{Y} & \text{Z} \\
\hline
C & -0.23200261 & 2.45481402 & 0.26420244 \\
C & 0.76114520 & 3.59450947 & -0.06486977 \\
H & -0.17511979 & 2.21450260 & 1.33465482 \\
H & 0.47479979 & 4.04776737 & -1.02582991 \\
C & 2.21226015 & 3.10114874 & -0.19410915 \\
C & 0.06211062 & 1.18317036 & -0.47111502 \\
C & 1.49228460 & 0.72445529 & -0.60845116 \\
C & 2.27819080 & 1.93483682 & -1.18539354 \\
H & 2.82318310 & 3.93531958 & -0.55164120 \\
H & 3.31237095 & 1.63751500 & -1.38870474 \\
H & 1.83180267 & 2.24537126 & -2.14090458 \\
H & 1.54528258 & -0.10595750 & -1.31623008 \\
H & -1.26647776 & 2.76438230 & 0.07888864 \\
H & 0.69571045 & 4.37324925 & 0.70482885 \\
N & 2.76589491 & 2.69451218 & 1.12618151 \\
C & 2.33319546 & 1.42113264 & 1.73894162 \\
H & 3.06861347 & 1.13501807 & 2.49831763 \\
H & 1.40218521 & 1.57957864 & 2.28457182 \\
C & 2.18141469 & 0.24304280 & 0.72927064 \\
C & 3.58346668 & -0.31816825 & 0.39190950 \\
C & 1.35543966 & -0.79890615 & 1.51308855 \\
H & 1.77825553 & -0.95278683 & 2.51198416 \\
N & 1.26162895 & -2.17750707 & 0.92592829 \\
O & 1.48746638 & -2.36191859 & -0.28893926 \\
O & 0.87968348 & -3.07712799 & 1.70104015 \\
S & 4.11058027 & 3.46845468 & 1.74168636 \\
O & 4.10972366 & 3.24795866 & 3.19160920 \\
H & 5.36007367 & 3.54955746 & -0.87104147 \\
O & 4.10994212 & 4.82328330 & 1.17517477 \\
\end{array}
\]
| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| N       | -0.93891204 | 0.55831598 | -1.00849446 |
| H       | -1.90473814 | 0.92317716  | -0.76208041 |
| C       | -0.96149503 | -0.77830081 | -1.63605606 |
| C       | -1.10590100 | -0.67309850 | -3.16272811 |
| C       | -2.13803621 | -1.58347817 | -1.01183262 |
| C       | -1.13249448 | -2.08799808 | -3.77048276 |
| H       | -2.03857255 | -0.13543838 | -3.40049923 |
| H       | -0.27009714 | -0.08604734 | -3.57206918 |
| C       | -2.12847708 | -2.99904457 | -1.60712013 |
| H       | -3.07668125 | -1.08101201 | -1.28534633 |
| N       | -2.08892252 | -1.62732123 | 0.44736593 |
| C       | -2.24118748 | -2.95285850 | -3.14252029 |
| H       | -1.27315532 | -2.01664860 | -4.85929016 |
| H       | -0.15373711 | -2.56834378 | -3.60949222 |
| H       | -2.96309371 | -3.56685875 | -1.17048891 |
| H       | -1.19351923 | -3.50841583 | -1.31528799 |
| H       | -1.38273742 | -2.25071035 | 0.84898177 |
| C       | -2.33666003 | -0.51585002 | 1.27389952 |
| H       | -3.22527208 | -2.53644720 | -3.41685949 |
| H       | -2.19766131 | -3.97424046 | -3.54954832 |
| S       | -3.52808187 | 0.68592266  | 0.68372925 |
| N       | -1.65641796 | -0.50352927 | 2.38416472 |
| H       | 0.29335857  | -0.52709721 | 1.70269473 |
| C       | -1.99342050 | 0.45858713  | 3.42754973 |
| H       | -1.86591105 | 1.23295006  | 6.13867370 |
| H       | -2.77857711 | 1.13241512  | 3.07329469 |
| C       | -0.72657997 | 1.25781503  | 3.78310154 |
| H       | -0.02536914 | -1.28609810 | -1.38867229 |
| H       | 4.26686413  | 0.47835367  | 0.08862832 |
| H       | 3.53418709  | -1.06046070 | -0.41274770 |
| H       | 4.00939335  | -0.79550295 | 1.28403949 |
| C       | 5.51836400  | 2.57887564  | 1.05874042 |
| C       | 6.17134167  | 1.62079587  | 1.83960949 |
| C       | 7.17452429  | 0.84130000  | 1.25700837 |
| Element | X        | Y        | Z        |
|---------|----------|----------|----------|
| C       | 7.51413399 | 1.02125652 | -0.08731704 |
| C       | 6.86390488 | 1.99726011 | -0.85384224 |
| C       | 5.86408932 | 2.78611850 | -0.28337022 |
| H       | 5.89109196 | 1.48511567 | 2.88095868  |
| H       | 7.68655763 | 0.08900310 | 1.85542689  |
| H       | 8.29054372 | 0.40545631 | -0.53935415 |
| H       | 7.13719847 | 2.14569411 | -1.89770455 |
| C       | -2.59430448 | -0.25642422 | 4.69652476  |
| C       | -3.95476009 | -0.85518909 | 4.27577380  |
| H       | -4.42738507 | -1.35733552 | 5.13343719  |
| H       | -4.63373599 | -0.07114078 | 3.91037491  |
| H       | -3.82044663 | -1.59084250 | 3.47113832  |
| C       | -1.68275393 | -1.38696611 | 5.21375243  |
| H       | -1.47734000 | -2.10152575 | 4.40586155  |
| H       | -2.18090481 | -1.91332838 | 6.04267780  |
| H       | -0.72371149 | -0.98887936 | 5.56432310  |
| C       | -2.81825694 | 0.79862778 | 5.80137560  |
| H       | -3.46293283 | 1.61511647 | 5.44215574  |
| H       | -3.30773888 | 0.33856101 | 6.67288703  |
| O       | 0.30504816  | 0.68338853 | 4.18210692  |
| N       | -0.75622807 | 2.62285633 | 3.60702078  |
| C       | -1.92717025 | 3.40380919 | 3.17302564  |
| C       | 0.38356980  | 3.43047995 | 4.07150772  |
| H       | 0.05820679  | 4.10916461 | 4.87440158  |
| H       | 0.78267615  | 4.03191806 | 3.24362184  |
| H       | 1.16334192  | 2.76398979 | 4.44382096  |
| H       | -2.56215781 | 3.68154022 | 4.02848064  |
| H       | -2.51967847 | 2.85386116 | 2.43726835  |
| H       | -1.56285225 | 4.32471185 | 2.70024701  |

**TE1**

COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -11782.94 \]

\[ G = -11467.79 \]
COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

$E = -8244.99$

$G = -7929.84$

$N_{\text{imag}} = 0$

|   |   |   |   |
|---|---|---|---|
| C | 1.48522540 | 1.04786766 | -1.66441363 |
| C | 2.92999694 | 1.37868394 | -1.25869748 |
| H | 0.81694758 | 1.88028906 | -1.39611972 |
| H | 3.62139918 | 0.68669519 | -1.77036073 |
| C | 3.10279128 | 1.23902952 | 0.26090736 |
| C | 0.95933750 | -0.21671078 | -1.00826804 |
| C | 1.57904495 | -0.78016015 | 0.05238379 |
| C | 2.82831131 | -0.21247825 | 0.69225368 |
| H | 4.11555167 | 1.54324332 | 0.56872713 |
| H | 2.73661619 | -0.25916642 | 1.79115464 |
| H | 3.70485923 | -0.84125828 | 0.43876408 |
| H | 1.19680535 | -1.70807217 | 0.47988440 |
| C | 3.18325801 | -0.8346641 | 2.75914965 |
| H | -3.76585172 | 5.77576748 | 0.36556457 |
| H | -3.57247438 | 4.00720089 | 0.24799172 |
| C | -1.81392861 | -0.8346641 | 1.3246199 |
| H | -0.83305240 | 5.15628803 | 2.60963287 |
| H | -2.47337603 | 5.84832988 | 2.48540961 |
| O | 0.87078529 | 3.55809555 | 1.6845730 |
| N | 1.58961327 | 4.57940897 | -0.2340930 |
| C | 1.43229294 | 5.01881844 | -1.62532112 |
| C | 2.92533347 | 4.82158014 | 0.33161536 |
| H | 2.92345176 | 4.53121915 | 1.38348151 |
| H | 3.17212980 | 5.88868531 | 0.23396704 |
| S | 2.23609711 | -2.06525409 | -2.08217640 |
| H | 2.4660845 | 4.08496022 | 2.45668637 |
| H | -0.88164511 | 3.98047127 | -1.06517415 |
| C | -0.63032513 | 4.01034310 | 0.54427155 |
| N | -0.18553080 | -0.72971913 | -1.64905977 |
H  -0.64241254  -0.01761563  -2.22753161
C  -1.16993856  -1.54605507  -0.92196598
C  -1.53979225  -2.82582859  -1.69483046
C  -2.45070433  -0.73076472  -0.60314461
C  -2.55813135  -3.67779945  -0.91673933
H  -1.96216799  -2.53717485  -2.67300157
H  -0.61903350  -3.39515416  -1.89342789
C  -3.46162701  -1.57428323  0.19088889
H  -2.90902802  -0.4083037  -1.54811861
N  -2.11981420  0.49635657  0.12755521
C  -3.81801860  -2.86337651  -0.57148108
H  -2.82995093  -4.56977032  -1.50234320
H  -2.09075488  -4.03582438  0.01748610
H  -4.36153645  -0.97032406  0.38237186
H  -3.02354530  -1.83419171  1.17084195
H  -1.75718981  0.35069410  1.07289637
C  -1.86182348  1.70540176  -0.44306902
H  -4.34357856  -2.59490803  -1.50424531
H  -4.51483810  -3.46885679  0.02828896
N  -1.31986254  2.61861981  0.40535814
H  -0.93517885  2.28891396  1.29568529
C  -0.81847218  3.93735020  0.02340847
H  -0.72273000  -1.84142484  0.03747224
H  3.67653207  4.23306222  -0.21133389
H  1.40154345  6.11645448  -1.68601903
H  0.52889484  4.60852251  -2.07630307
H  2.29516834  4.66038506  -2.20299969
C  -1.70874974  5.10749791  0.59486389
C  -1.09812654  6.46010484  0.17046304
H  -1.73996946  7.28072700  0.52202324
H  -0.09737146  6.60654794  0.59971803
H  -1.02319433  6.53624901  -0.92344137
C  -3.11996750  4.97190092  -0.01712492
H  -3.08359755  5.03985322  -1.11261575

S125
TE2
COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\( E = -11779.25 \)
\( G = -11464.31 \)

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\( E = -8241.36 \)
\( G = -7926.42 \)

\( N_{\text{imag}} = 0 \)

\[
\begin{array}{ccc}
C & -3.13637077 & 1.36351142 \\
C & -1.69807630 & 0.90873511 \\
H & -3.49955021 & 0.21605888 \\
H & -1.60072788 & 0.15988148 \\
C & -1.20725220 & 0.28594623 \\
C & -4.00738463 & 0.94921831 \\
C & -3.58357438 & 0.02596445 \\
C & -2.25921130 & -0.69723759 \\
H & -0.24392087 & -0.22452576 \\
H & -1.90158230 & -1.20417685 \\
H & -2.43993483 & -1.46438422 \\
H & -1.04163352 & 1.08305713 \\
H & -4.37359943 & -0.72146619 \\
H & -1.05037872 & 1.75621004 \\
H & -6.52110315 & -6.60901185 \\
H & -5.89511803 & -5.57723676 \\
C & -3.78585258 & -6.44615747 \\
H & -2.87523214 & -6.30890803 \\
H & -4.19273861 & -7.44169972 \\
O & -4.72308634 & -3.34191805 \\
N & -2.57150933 & -3.99815788 \\
C & -1.42756075 & -4.23879254 \\
C & -2.22055270 & -3.89805439 \\
H & -3.13591235 & -3.86771392 \\
\end{array}
\]

\( S126 \)
C  -5.19543605   -5.45260630    2.16537385
H  -5.61857862   -6.44185392    2.39388135
H  -4.30281861   -5.30016513    2.78776524
H  -5.93416009   -4.68693194    2.43684401
C  -6.11125663   -5.61654748   -0.17749513
H  -6.88464179   -4.86828617    0.04646990
H  -3.47309693    2.01928035    1.92233816

TE3
COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\( E = -11778.91 \)
\( G = -11463.71 \)

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\( E = -8240.94 \)
\( G = -7925.74 \)
\( N_{\text{imag}} = 0 \)

C  -3.07752615    1.63398070    1.04828266
C  -1.70370457    0.95929548    1.21721484
H  -2.96905316    2.64454083    0.61410985
H  -1.81441000    0.11724385    1.91895587
C  -1.18392799    0.41746084   -0.12224540
C  -4.01867216    0.83463949    0.16956329
C  -3.59078683   -0.19763205   -0.58212938
C  -2.15437630   -0.65111905   -0.65317343
H  -0.17538142   -0.00886338   -0.00485735
H  -1.89328421   -0.92801651   -1.68745852
H  -2.03969710   -1.56708028   -0.04878773
H  -4.31714922   -0.77286177   -1.16101421
H  -3.52108339    1.78108332    2.04093290
H  -0.99424440    1.67579102    1.65949936
H  -6.55443271   -6.65752561    0.05322430
H  -5.96329662   -5.58201295   -1.24171134
C  -3.82095208   -6.48738825    0.27982377
H  -2.90069344   -6.36704924    0.86804698

S128
| Element | X-coordinate | Y-coordinate | Z-coordinate |
|---------|--------------|--------------|--------------|
| H       | -4.22331537  | -7.48966506  | 0.48705263   |
| O       | -4.77699173  | -3.35268734  | -1.85711552  |
| N       | -2.60835281  | -3.95584723  | -1.44484108  |
| C       | -1.47466048  | -4.2677437   | -0.56828524  |
| C       | -2.24599611  | -3.79449552  | -2.85935576  |
| H       | -3.15443527  | -3.64703105  | -3.44612744  |
| H       | -1.71423533  | -4.69250012  | -3.20349311  |
| S       | -3.78788422  | -1.99357346  | 2.80628461   |
| H       | -3.56230064  | -6.44117397  | -0.78696844  |
| H       | -3.45457821  | -3.82897694  | 1.09726116   |
| C       | -3.89278842  | -3.73045677  | -1.05804237  |
| N       | -5.36453683  | 1.29956609   | 0.08862151   |
| H       | -5.86330490  | 0.75040551   | -0.61704649  |
| C       | -6.20999104  | 1.39982602   | 1.31449149   |
| C       | -6.13983857  | 2.78682453   | 1.98493053   |
| C       | -5.96247748  | 0.27608308   | 2.35493995   |
| C       | -7.12269743  | 2.88778043   | 3.16521089   |
| H       | -5.11949298  | 2.97592954   | 2.34786293   |
| H       | -6.35776912  | 3.54912221   | 1.22229810   |
| C       | -6.94010380  | 0.38590920   | 3.53911481   |
| H       | -4.93698034  | 0.34468487   | 2.73604651   |
| N       | -6.05783279  | -1.03177252  | 1.70123654   |
| C       | -6.86445789  | 1.77444035   | 4.19658413   |
| H       | -7.03686879  | 3.87782911   | 3.63940786   |
| H       | -8.15685688  | 2.79882046   | 2.78814690   |
| H       | -6.70408787  | -0.40918212  | 4.26278346   |
| H       | -7.96525273  | 0.20419890   | 3.17179302   |
| H       | -6.80138781  | -1.12723666  | 1.00662501   |
| C       | -5.08383810  | -1.98107678  | 1.69156081   |
| H       | -5.86177093  | 1.91262535   | 4.63769785   |
| H       | -7.59542202  | 1.83794359   | 5.02196689   |
| N       | -5.27024122  | -2.94733040  | 0.74608041   |
| H       | -5.85593597  | -2.70432881  | -0.05848598  |
| C       | -4.29151077  | -3.97928746  | 0.41238030   |

S129
H  -7.24451463  1.27973700  0.94735692
H  -1.58442339 -2.92417184 -2.97855665
H  -0.66702505 -3.54844369 -0.76545518
H  -1.10134428 -5.28141912 -0.77382184
H  -1.74741586 -4.19684657  0.48361646
C  -4.87221412 -5.42317567  0.65829113
C  -5.19494676 -5.54111106  2.16431528
H  -5.61582590 -6.53439544  2.37868085
H  -4.28865176 -5.40582016  2.77116725
H  -5.92529422 -4.77975040  2.46873475
C  -6.15744078 -5.65499045 -0.16378479
H  -6.93180813 -4.92035022  0.09809757
H  -1.11119878  1.24426434 -0.85031151

TE4
COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

$E = -11782.04$

$G = -11467.19$

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

$E = -8243.46$

$G = -7928.61$

$N_{imag} = 0$

C  1.45517700  0.78688835 -1.71337234
C  2.64841047  1.55576729 -1.19876414
C  -3.08642838  4.87055668 -0.13025920
H  3.53683428  1.35490283 -1.83088845
C  2.97645213  1.21212661  0.26514538
C  0.94758761 -0.31236004 -1.11842076
C  1.51342328 -0.85143615  0.18129142
C  2.92503211 -0.30875645  0.47369676
H  3.96702873  1.60881977  0.53797017
H  3.21612397 -0.57553726  1.50150466
H  3.64502042 -0.79445069 -0.20753753
H  -3.01766044  4.93364614 -1.22443011

S130
\[
\begin{align*}
\text{C} & : -1.65225832, 1.67200984, -0.50181822 \\
\text{H} & : -4.43081102, -2.40933837, -1.40089019 \\
\text{H} & : -4.65516408, -3.21973330, 0.15999335 \\
\text{N} & : -1.19445398, 2.61891753, 0.36169186 \\
\text{H} & : -0.80969720, 2.30990509, 1.25941701 \\
\text{C} & : -0.73453671, 3.95464176, -0.00774169 \\
\text{H} & : -0.68679744, 2.04825237, 0.02316318 \\
\text{H} & : 3.71944684, 4.35879344, -0.04636820 \\
\text{H} & : 1.52579548, 6.36003018, -1.49229714 \\
\text{H} & : 0.61419962, 4.90501607, -1.97480247 \\
\text{H} & : 2.38465348, 4.90782819, -2.07614360 \\
\text{C} & : -1.70420540, 5.08024729, 0.52530851 \\
\text{C} & : -1.16006247, 6.46733649, 0.12253563 \\
\text{H} & : -1.85658716, 7.24737552, 0.46257429 \\
\text{H} & : -0.18040286, 6.66790159, 0.57757872 \\
\text{H} & : -1.06320527, 6.55577555, -0.96846029 \\
\text{H} & : 0.99140928, 1.14478418, -2.63525601 \\
\text{H} & : 1.53601389, -1.95221384, 0.14299168 \\
\text{H} & : 0.84167660, -0.58277354, 1.01505663
\end{align*}
\]

**TS-A2**

COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[E = -17398.38\]

\[G = -16969.49\]

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[E = -11965.96\]

\[G = -11537.07\]

\[N_{\text{imag}} = 1, 397\text{i cm}^{-1}\]

\[
\begin{align*}
\text{C} & : 2.07014260, 1.62731605, -0.19376629 \\
\text{C} & : 3.03227511, 2.01643379, 0.94539108 \\
\text{C} & : 1.02431922, 1.80791791, 0.10495276 \\
\text{H} & : 4.00897632, 2.24741964, 0.50075403 \\
\text{C} & : 3.29133955, 0.89973253, 1.97748986 \\
\text{C} & : 2.17767431, 0.18765022, -0.63252185
\end{align*}
\]

S132
| Atoms | X          | Y          | Z          |
|-------|------------|------------|------------|
| C     | 2.62714243 | -0.81301212| 0.28340297 |
| C     | 3.71902814 | -0.37778134| 1.25328610 |
| H     | 4.09883882 | 1.21963365 | 2.64489275 |
| H     | 3.9305986  | -1.17179787| 1.97633178 |
| H     | 4.64130044 | -0.17814432| 0.69049384 |
| H     | 2.7993279  | -1.79653463| -0.15086803|
| H     | 2.3975036  | 2.27645840 | -1.06243546|
| H     | 2.66505453 | 2.92283592 | 1.43641219 |
| N     | 2.13741242 | 0.55812140 | 2.86502898 |
| C     | 0.88730132 | 0.06327349 | 2.24322790 |
| H     | 0.21071959 | -0.21339759| 3.05955451 |
| H     | 0.39013838 | 0.84863188 | 1.65915195 |
| C     | 1.09096827 | -1.20496363| 1.38811986 |
| C     | 1.60534741 | -2.36488901| 2.24939619 |
| C     | -0.08029836| -1.41656730| 0.57453774 |
| H     | -0.67067604| -0.57218150| 0.23471522 |
| N     | -0.55479447| -2.61019946| 0.12902996 |
| O     | -1.66006308| -2.61528264| -0.55810288|
| O     | 0.06173322 | -3.71738897| 0.35187537 |
| S     | 5.51360393 | 0.72017866 | -1.63920193|
| H     | 4.36730247 | 3.94835976 | -5.53671232|
| H     | 5.44258242 | 3.22742526 | -1.97388447|
| C     | 3.49807918 | 4.23822871 | -2.14271945|
| N     | 1.61308044 | -0.08745274| -1.80875089|
| H     | 1.19810328 | 0.72206447 | -2.27612101|
| C     | 1.90314512 | -1.20664795| -2.75858206|
| C     | 1.38251561 | -2.58456411| -2.33630044|
| C     | 3.41350470 | -1.20072330| -3.11655600|
| C     | 1.72461052 | -3.63509772| -3.40692612|
| H     | 1.81851917 | -2.89564572 | -1.38081114|
| H     | 0.29731244 | -2.52300466 | -2.18816367|
| C     | 3.73754994 | -2.29181936 | -4.14942185|
| H     | 4.01085300 | -1.35836462 | -2.21027993|
| N     | 3.77714138 | 0.12824850 | -3.62465786|

S133
C  3.23595715  -3.67049347  -3.68817407
H  1.36888503  -4.61947798  -3.0681991
H  1.18541940  -3.39969390  -4.34093391
H  4.82455112  -2.29614753  -4.31874121
H  3.25707659  -2.02878382  -5.10771098
H  3.22547869   0.44991494  -4.42427171
C  4.46293596   1.08516003  -2.93475455
H  3.77289629  -3.96763246  -2.77075443
H  3.46814711  -4.42361040  -4.45613704
N  4.27174965   2.34766913  -3.41087302
H  3.40985215   2.51226677  -3.93903257
C  4.74939170   3.56320620  -2.74754898
H  1.35280590  -0.91629098  -3.66715470
S  1.99973504   1.40699154   4.30423397
O  3.34254631   1.48669492   4.89109532
H  0.51810802   2.49524745  3.37529029
O  0.88738526   0.80394137   5.04871233
C  5.35646398   4.47917471  -3.75414182
C  5.98883040   5.77104044  -3.04340533
H  6.56496862   6.39156915  -3.74490887
H  5.13145354   6.36451741  -2.69608146
H  6.63457667   5.55023842  -2.18294347
C  6.77977574   3.68760033  -4.21627986
H  7.43007667   3.44794327  -3.36252308
H  7.35771817   4.28503277  -4.93593320
H  6.48761569   2.74640645  -4.70086145
C  4.66749151   4.84489285  -4.97624175
H  3.76093121   5.38643319  -4.67637558
H  5.24736014   5.48539804  -5.65643349
O  2.42606271   4.17692034  -2.78621604
N  3.58266864   4.84718124  -0.92941552
C  4.77097666   4.93127972  -0.07175444
C  2.39851925   5.53051696  -0.38670174
H  2.09886410   5.05744579   0.55591894
TS-A3
COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP
E = -17401.14
G = -16972.55
COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP
E = -11976.11
G = -11547.52
N_{imag} = 1, 166i \text{ cm}^{-1}

C  1.45430843  1.37579955  0.13530378
C  2.33274308  1.94405780  1.27509578
H  0.38937811  1.50213592  0.38831278
H  3.26837625  2.32808740  0.84111185
C  2.77496475  0.93515489  2.36092245
C  1.66635571  -0.08373605  -0.16804250
C  2.37941476  -0.89806869  0.71220725
C  3.37167757  -0.30044411  1.67724817
H  3.55260913  1.40809081  2.97018605
H  3.67467358 -1.03713170  2.43013049
H  4.28850738  0.00318272  1.14302674
H  2.54578213 -1.93080713  0.40224124
H  1.60881297  1.97972306 -0.76816050
H  1.81844125  2.80384593  1.71742309
N  1.73281409  0.48150267  3.34206334
C  0.47157100 -0.09176592  2.83045495
H  -0.17264698 -0.30688770  3.69179909
H  -0.06365074  0.63333329  2.20308992
C  0.64195562 -1.40133189  2.06109454
C  1.32744684 -2.5287975  2.79683166
C  -0.45984004 -1.60025017  1.22009904
H  -1.20488935 -0.83004553  1.16508316
N  -0.70766120 -2.64507276  0.38497859
O  0.13671759 -3.59011901  0.20125485
O  -1.83700644 -2.63375769 -0.28049765
S  -2.34875951  2.50295009  0.25811983
H  -4.89940287 -2.16930024  0.86500798
H  -4.29278288  1.50154495  1.67314346
C  -3.28449814  0.19960683  3.11395565
N  0.95204158 -0.68015808 -1.14576293
H  1.12743848 -1.68399716 -1.23952462
C  0.25589530 -0.10235874 -2.31822690
C  1.24231471  0.56173571 -3.30374817
C  -0.91713274  0.84479806 -1.98570129
C  0.52603814  1.01104293 -4.58896352
H  1.70904624  1.43267107 -2.81895813
H  2.04462897 -0.15545206 -3.53114119
C  -1.63144643  1.26208512 -3.28857934
H  -0.55453111  1.75477861 -1.49685678
N  -1.84092250  0.19608338 -1.05924557
C  -0.65866289  1.93805747 -4.26801766
H   -3.57811428   0.99084166  6.12945415
H   -4.88538213   2.54733746  4.27554251
H   -3.80669316   2.86231096  2.87276383
H   -3.25758197   3.22910322  4.51443602
C   0.97903590   3.00728968  4.17621583
C   1.83904284   4.11037148  4.18058772
C   1.40650733   5.30990330  3.60905208
C   0.13535909   5.39481745  3.03049255
C   -0.71607605  4.28405970  3.03616399
C   -0.30307628  3.08422160  3.61569085
H   2.83288370   4.02051120  4.61169918
H   2.06928142   6.17424709  3.60591531
H  -0.19165684   6.32655403  2.57051447
H  -1.69878676   4.34278056  2.57541766
H   2.19872379  -2.17053054  3.35263805
H   1.60932169  -3.34109962  2.12255199
H   0.60832245  -2.92970088  3.53153367

**TS-A4**

COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -17401.14 \]
\[ G = -16972.69 \]

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -11972.03 \]
\[ G = -11543.58 \]

\( N_{\text{imag}} = 1, \ 186 \ i \ \text{cm}^{-1} \)

C   2.03199191  0.98389975  -1.49723126
C   3.52640425  0.61834661  -1.33194888
H   1.83921187  1.99946863  -1.10961544
H   3.81062524  -0.05529214  -2.15237269
C   3.88484648  -0.13144970  -0.03513163
C   1.07080185   0.06852899  -0.78326365
C   1.51444169  -0.84023456   0.20207283
C   2.94198443  -1.32642047   0.14030271
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| H       | 4.91469372| -0.48049204| -0.15250678|
| H       | 3.20223047| -1.89487827| 1.04017800 |
| H       | 3.06698468| -2.00769474| -0.71087245|
| H       | 0.76705637| -1.55687142| 0.54478227 |
| H       | 1.79165737| 1.03153830  | -2.56672017|
| H       | 4.13849435| 1.52566124  | -1.42107804|
| N       | 3.87970887| 0.72570792  | 1.18580991 |
| C       | 2.63016550| 1.34197535  | 1.67896835 |
| H       | 2.86564729| 1.82379836  | 2.63579942 |
| H       | 2.36202923| 2.14598170  | 0.98047163 |
| C       | 1.42383827| 0.40969390  | 1.87163715 |
| C       | 0.21014112| 1.15871345  | 1.84083646 |
| H       | 0.21052593| 2.2246540   | 1.64616960 |
| N       | 1.04617033| 0.64106069  | 1.99268159 |
| O       | -1.24533027| -0.63645787| 1.91314215 |
| O       | -2.04225016| 1.44255269  | 2.15451596 |
| S       | 0.67996849 | -2.75872472 | -2.31369886|
| H       | 2.21718464 | -2.38494831 | -6.40506943|
| H       | 1.54292419| -3.79513177 | -2.96257666|
| C       | 3.50650956 | -2.83139319 | -3.20583730|
| N       | -0.23825711| 0.30350391 | -0.85932364|
| H       | -0.83295335| -0.33132858 | -0.31090183|
| C       | -0.94438372| 1.13417404 | -1.83664131|
| C       | -2.14447349| 1.82996585 | -1.17714660|
| C       | -1.41066886| 0.25170371 | -3.03229123|
| C       | -2.91201407| 2.67666540 | -2.20611980|
| H       | -2.81057226| 1.06247640 | -0.74887263|
| H       | -1.79099818| 2.44403051 | -0.33810186|
| C       | -2.16194852| 1.10735638 | -4.06340067|
| H       | -2.07532054| -0.52967592| -2.63916499|
| N       | -0.28208221| -0.43641253 | -3.65281986|
| C       | -3.35542908| 1.82978372 | -3.41248165|
| H       | -3.78592644| 3.13862322 | -1.72285244|

S139
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| H       | -2.26381143| 3.49905255 | -2.55487956|
| H       | -2.49745043| 0.45786833 | -4.88541467|
| H       | -1.46664974| 1.85111056 | -4.49118552|
| H       | 0.26476532 | 0.10766709 | -4.32238657|
| C       | 0.17751429 | -1.68041085| -3.32613569|
| H       | -4.09083799| 1.07825433 | -3.07866763|
| H       | -3.85625139| 2.46239188 | -4.16059618|
| N       | 1.37082002 | -1.98789755| -3.90249207|
| H       | 1.93592787 | -1.23478015| -4.30149475|
| C       | 2.10747608 | -3.23392051| -3.70973156|
| H       | -0.24679281| 1.89562023 | -2.20829107|
| S       | 5.25343619 | 0.68126921 | 2.13863934 |
| O       | 5.01679208 | 1.56463469 | 3.28737404 |
| H       | 6.52759709 | -1.6822010 | 1.03705740 |
| O       | 6.40837802 | 0.88951699 | 1.25326667 |
| C       | 2.15949880 | -4.09348635| -5.02984517|
| C       | 2.97903589 | -5.37633364| -4.77661970|
| H       | 2.98492365 | -5.99348745| -5.68641004|
| H       | 4.02261794 | -5.14731051| -4.51896818|
| H       | 2.54193511 | -5.97662518| -3.96699382|
| C       | 0.70944151 | -4.47874829| -5.39589699|
| H       | 0.24051201 | -5.05912040| -4.58956190|
| H       | 0.70830093 | -5.08606479| -6.31261597|
| H       | 0.09668858 | -3.58467483| -5.57255013|
| C       | 2.78877506 | -3.29961039| -6.19360698|
| H       | 3.82604945 | -3.01656963| -5.97459506|
| H       | 2.77911464 | -3.91888354| -7.10225139|
| O       | 4.05917301 | -1.83268260| -3.71619057|
| N       | 4.09159323 | -3.55666983| -2.21231849|
| C       | 3.51710723 | -4.71624475| -1.51863237|
| C       | 5.45497869 | -3.21021231| -1.78267891|
| H       | 5.72634966 | -2.23765875| -2.19732471|
| H       | 6.16915845 | -3.97169079| -2.12997688|
| H       | 5.48328087 | -3.17623062| -0.68707749|

S140
|     | X     | Y     | Z     |
|-----|-------|-------|-------|
| H   | 4.06004585 | -5.63219402 | -1.79160007 |
| H   | 2.46199523  | -4.84434689  | -1.75536985  |
| H   | 3.61138701  | -4.56100095  | -0.43480004  |
| C   | 5.37545166  | -1.01485290  | 2.73861076   |
| C   | 4.76257136  | -1.36029018  | 3.94735935   |
| C   | 4.76628833  | -2.69674605  | 4.35307515   |
| C   | 5.37437628  | -3.67330802  | 3.55614919   |
| C   | 6.00569533  | -3.31163241  | 2.36053491   |
| C   | 6.01825568  | -1.97718333  | 1.94996467   |
| H   | 4.29021264  | -0.59461680  | 4.55648656   |
| H   | 4.28956303  | -2.97496659  | 5.29192867   |
| H   | 5.36488372  | -4.71567392  | 3.87201281   |
| H   | 6.49919339  | -4.06809604  | 1.75194091   |
| H   | 2.45378095  | -1.29890548  | 2.76416258   |
| H   | 0.69271015  | -1.26539289  | 3.03462675   |
| H   | 1.76862646  | -0.14083866  | 3.90988794   |

**TS-B1**

COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -17402.15 \]

\[ G = -16974.21 \]

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -11971.99 \]

\[ G = -11544.05 \]

\( N_{\text{imag}} = 1, 369 \text{ cm}^{-1} \)

|     | X     | Y     | Z     |
|-----|-------|-------|-------|
| C   | 1.85333379  | 0.96934828  | -1.46700174 |
| C   | 3.39208633  | 0.85361739  | -1.46440176 |
| H   | 1.53818239  | 1.87559080  | -0.92742654 |
| H   | 3.70433958  | 0.26042017  | -2.33731308 |
| C   | 3.97117047  | 0.15225931  | -0.22058162 |
| C   | 1.13180186  | -0.19332823  | -0.81705542 |
| C   | 1.77450841  | -1.00313664  | 0.15512182 |
| C   | 3.27269825  | -1.19601837  | -0.00980658 |
| H   | 5.03762850  | -0.00658066  | -0.40373937 |
H  0.54154233  4.17733483  -1.89238636
H  2.29103874  4.41757192  -1.77549914
C  5.63528097  0.08242935  2.92844427
C  5.36878988  0.23834355  4.29227499
C  5.52172607 -0.86068254  5.14248453
C  5.92932954 -2.09505361  4.62921211
C  6.20972148 -2.23286011  3.26429375
C  6.06908011 -1.14260027  2.40523074
H  5.03414755  1.19973918  4.67336217
H  5.30902133 -0.75193985  6.20504501
H  6.02896988 -2.95316077  5.29223877
H  6.53503808 -3.19311880  2.86642397
H  0.23489636  1.14793926  2.93752389
H  -0.36028940 -0.44354271  2.38383368
H  -0.10566600  0.90262517  1.22548671

TS-B2
COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP
E = -17395.48
G  = -16965.96
COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP
E = -11965.44
G  = -11535.92
Nimag = 1, 433 \text{ \textit{i} cm}^{-1}
C  1.99013386  0.37463373  -1.68729410
C  3.50411258  0.08300925  -1.68302032
H  1.79864485  1.39920427  -1.33095950
H  3.69471279 -0.74650564  -2.37656423
C  4.04544720 -0.35665993  -0.31290048
C  1.18402795 -0.58385079  -0.83440718
C  1.77307944 -1.22539959  0.28981418
C  3.25105901 -1.56642045  0.18333083
H  5.09624055 -0.63013710  -0.4490310
H  3.61525150 -1.89668725  1.16455708
| Atom | X-Coord | Y-Coord | Z-Coord |
|------|---------|---------|---------|
| H    | 3.38710362 | -2.39341842 | -0.52729231 |
| H    | 1.17183960  | -1.99063597  | 0.77514298  |
| H    | 1.61184642  | 0.34113648   | -2.71863034 |
| H    | 4.05292633  | 0.96490295   | -2.03538072 |
| N    | 4.02550041   | 0.76074826   | 0.67819198  |
| C    | 2.74853389  | 1.19428314   | 1.29137505  |
| H    | 2.98768659  | 1.85395285   | 2.13463067  |
| H    | 2.20588617  | 1.81358309   | 0.56798425  |
| C    | 1.81477863  | 0.08102826   | 1.79602410  |
| C    | 0.39904179   | 0.61802524   | 1.94714604  |
| C    | 2.38159926   | -0.66807977  | 2.88033154  |
| H    | 3.41237402   | -0.54405991  | 3.17715537  |
| N    | 1.77186170   | -1.70681926  | 3.52229156  |
| O    | 0.62144071   | -2.15339845  | 3.13329464  |
| O    | 2.37941800   | -2.26054473  | 4.51902476  |
| S    | 2.32243649   | -3.55007218  | -2.67787024 |
| H    | -0.06128228  | -2.01760315  | -7.06097607 |
| H    | 2.99288167   | -2.46172660  | -4.85864329 |
| C    | 2.41548954   | -0.37226119  | -5.21697124 |
| N    | -0.11193808  | -0.66732714  | -1.16723483 |
| H    | -0.39098572  | -0.06401020  | -1.94249537 |
| C    | -1.10223889  | -1.73758440  | -0.86796309 |
| C    | -1.55964114  | -1.82826844  | 0.59647636  |
| C    | -0.60017531  | -3.09494989  | -1.43216584 |
| C    | -2.61105583  | -2.94020349  | 0.75915888  |
| H    | -0.71441567  | -2.03806777  | 1.25932258  |
| H    | -1.97488788  | -0.85551453  | 0.89428030  |
| C    | -1.64516628  | -4.20010306  | -1.21232563 |
| H    | 0.34319894   | -3.37436122  | -0.94835886 |
| N    | -0.30144840  | -2.93228268  | -2.85981843 |
| C    | -2.06717629  | -4.29063948  | 0.26330183  |
| H    | -2.90144909  | -3.00813252  | 1.81823859  |
| H    | -3.52032498  | -2.68101028  | 0.18923196  |
| H    | -1.22319380  | -5.15164968  | -1.56825043 |
|   | x        | y        | z        |
|---|----------|----------|----------|
| H | -2.53043049 | -3.98056307 | -1.83426957 |
| H | -1.06713178 | -2.54640238 | -3.41850424 |
| C | 0.94736105  | -2.84813873 | -3.40492172 |
| H | -1.19733692 | -4.58139814 | 0.87688858  |
| H | -2.82571342 | -5.07867504 | 0.38333238  |
| N | 0.97670853  | -2.20728281 | -4.60767127 |
| H | 0.22432369  | -1.53839220 | -4.79155273 |
| C | 2.19872259  | -1.89489951 | -5.34727813 |
| H | -1.98037491 | -1.44680572 | -1.46606054 |
| S | 5.46405127  | 1.28099343  | 1.34390351  |
| O | 5.23983127  | 2.63396919  | 1.87034444  |
| H | 6.34311633  | -1.47365886 | 1.50182810  |
| O | 6.51055244  | 1.02414230  | 0.3445598   |
| C | 2.09334238  | -2.38410381 | -6.83888076 |
| C | 3.38641732  | -2.02451321 | -7.59971597 |
| H | 3.32148064  | -2.40219673 | -8.63021964 |
| H | 3.53991585  | -0.93772305 | -7.64817329 |
| H | 4.26707345  | -2.48240267 | -7.12915047 |
| C | 1.93215307  | -3.92025017 | -6.80590990 |
| H | 2.80022013  | -4.39412676 | -6.32505520 |
| H | 1.84785759  | -4.30948697 | -7.83074361 |
| H | 1.03040139  | -4.20864451 | -6.24924348 |
| C | 0.88294869  | -1.74926908 | -7.55542358 |
| H | 0.96137186  | -0.65471347 | -7.58216989 |
| H | 0.83530858  | -2.12122075 | -8.58920613 |
| O | 1.40909530  | 0.37220304  | -5.22765539 |
| N | 3.68005940  | 0.11291715  | -5.09942551 |
| C | 4.90850826  | -0.67826493 | -4.95981819 |
| C | 3.89553347  | 1.56762826  | -5.10040604 |
| H | 2.94090967  | 2.06937650  | -5.26720781 |
| H | 4.60502645  | 1.83004000  | -5.89784328 |
| H | 4.31746068  | 1.88390635  | -4.13666939 |
| H | 5.51431058  | -0.61461441 | -5.87483290 |
| H | 4.69057973  | -1.72423815 | -4.74622450 |

S146
| Atom | X    | Y    | Z    |
|------|------|------|------|
| H    | 5.49353749 | -0.27098325 | -4.12395983 |
| C    | 5.77388912  | 0.20196290  | 2.75100380 |
| C    | 5.53649317  | 0.67033888  | 4.04719200 |
| C    | 5.65724963  | -0.21670636 | 5.12073893 |
| C    | 6.00475357  | -1.55132302 | 4.89488599 |
| C    | 6.25533929  | -2.00344916 | 3.59375421 |
| C    | 6.14638246  | -1.12759810 | 2.51337553 |
| H    | 5.25064805  | 1.70694798  | 4.20610831 |
| H    | 5.46721889  | 0.13635532  | 6.13337389 |
| H    | 6.08012606  | -2.24248006 | 5.73296410 |
| H    | 6.53378360  | -3.04174167 | 3.41880993 |
| H    | 0.34190177  | 1.52065139  | 2.57864550 |
| H    | -0.24814388 | -0.11428510 | 2.43164695 |
| H    | -0.03497426 | 0.90721030  | 0.98253431 |

**TS-B3**

COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -17396.58 \]

\[ G = -16968.24 \]

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -11968.29 \]

\[ G = -11539.95 \]

\[ N_{\text{imag}} = 1, 369i \text{ cm}^{-1} \]

| Atom | X    | Y    | Z    |
|------|------|------|------|
| C    | 1.63379431  | 3.89338557  | -1.31105280 |
| C    | 1.53646352  | 5.26126941  | -0.60227614 |
| H    | 0.88098336  | 3.20902551  | -0.88411759 |
| H    | 1.88483393  | 6.05073338  | -1.28555841 |
| C    | 2.39100106  | 5.36229931  | 0.67149695  |
| C    | 2.97245082  | 3.21442840  | -1.20615295 |
| C    | 3.90735201  | 3.58468951  | -0.19983948 |
| C    | 3.84204430  | 5.00434434  | 0.32686838 |
| H    | 2.34084165  | 6.39251321  | 1.03481985 |
| H    | 4.48650577  | 5.09358541  | 1.21129867 |
| H    | 4.21021666  | 5.72138112  | -0.42410035 |
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| H       | 1.71753884| -0.62714455| -1.51426743|
| C       | 0.23386517| 0.24780112 | -0.41720716|
| H       | -0.30203893| 1.94909764 | -4.94929349|
| H       | -0.07317754| 0.49083401 | -5.93003296|
| N       | 0.38948235 | -0.74955799 | 0.49587029 |
| H       | 1.24594816 | -1.30905704 | 0.44850877 |
| C       | -0.21715202| -0.75209916 | 1.83109941 |
| H       | 3.06348463 | 0.61383826 | -3.30741606|
| S       | 1.16231085 | 5.22120845 | 3.11161427 |
| O       | 0.05466758 | 4.36742215 | 3.56362576 |
| H       | 3.54939528 | 6.79334644 | 3.53788284 |
| O       | 0.93051530 | 6.63380992 | 2.78139217 |
| C       | -1.11241022| -2.02029156 | 2.06265163 |
| C       | -1.64753612| -2.00133501 | 3.51038970 |
| H       | -2.30540382| -2.86724186 | 3.67209379 |
| H       | -0.83057487| -2.05607568 | 4.24386363 |
| H       | -2.23289096| -1.09271006 | 3.70846275 |
| C       | -2.29613352| -1.93989900 | 1.07410941 |
| H       | -2.90901314| -1.04802318 | 1.26701529 |
| H       | -2.93248963| -2.83069172 | 1.1783082 |
| H       | -1.93654726| -1.88976836 | 0.03733150 |
| C       | -0.32442874| -3.32467788 | 1.81925473 |
| H       | 0.54444168 | -3.39753575 | 2.48490973 |
| H       | -0.98242355| -4.18667440 | 2.00220179 |
| O       | 1.96922772 | -1.33498195 | 2.64852009 |
| N       | 0.86607933 | 0.25206449 | 3.85820038 |
| C       | -0.28925269| 1.09675760 | 4.19426428 |
| C       | 2.02230992 | 0.36285910 | 4.76913471 |
| H       | 2.77853437 | 1.04864113 | 4.35911127 |
| H       | 2.48218442 | -0.62072658 | 4.90493910 |
| H       | 1.67319162 | 0.74913051 | 5.73175210 |
| H       | -0.71670156| 0.77761044 | 5.15540501 |
| H       | -1.06121495| 1.03814507 | 3.42868342 |
| H       | 0.02481965 | 2.14305422 | 4.26909302 |

S149
\begin{verbatim}
C  2.44113810  5.13257059  4.37453924
C  2.39631175  4.11733132  5.3393723
C  3.47740444  3.95752191  6.20541938
C  4.58142064  4.80963980  6.1165550
C  4.60347482  5.8385633  5.16706257
C  3.53319159  6.00649756  4.2875111
H  1.53161519  3.46477466  5.39323359
H  3.45787053  3.16095260  6.94795381
H  5.42914851  4.67222363  6.78614308
H  5.46238086  6.50446808  5.10219638
H  3.20870983  0.43856242  1.84629086
H  4.48137506  0.82517515  0.67455796
H  2.75814281  0.93157821  0.21069165

TS-B4
COSMO(DCM)-ZORA-M06-2X/TZ2P/COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP
\[ E = -17398.20 \]
\[ G = -16971.95 \]
COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP
\[ E = -11969.55 \]
\[ G = -11543.30 \]
\( N_{imag} = 1, 279i \text{ cm}^{-1} \)
\begin{verbatim}
C  1.56765281  0.47348188  0.40120588
C  1.84586461  0.77111668  1.89284757
H  1.29971735 -0.58745495  0.26305168
H  1.58599751  1.81932507  2.09602923
C  3.31196371  0.60446111  2.32451815
C  2.71805918  0.77758534 -0.52701217
C  4.04146759  0.90505336 -0.04309919
C  4.22523277  1.39283925  1.37777110
H  3.39232901  1.01024080  3.33642812
H  5.27670586  1.27956052  1.67453801
H  3.97302983  2.45761776  1.44624066
H  4.77024501  1.27397641 -0.76962106
\end{verbatim}
S150
\end{verbatim}
| Atomic Symbol | X-coordinate  | Y-coordinate | Z-coordinate  |
|---------------|--------------|--------------|---------------|
| H             | 0.68228225   | 1.04003465   | 0.08868748    |
| H             | 1.20095981   | 0.14078271   | 2.51927588    |
| N             | 3.73722033   | -0.82174185  | 2.41258418    |
| C             | 3.91374219   | -1.62682406  | 1.18577793    |
| H             | 4.33691085   | -2.59421060  | 1.48273223    |
| H             | 2.92247643   | -1.83696474  | 0.76558631    |
| C             | 4.79674735   | -1.00112694  | 0.09706268    |
| C             | 4.51581934   | -1.60790028  | -1.26578099   |
| C             | 6.13941670   | -0.77418590  | 0.51766622    |
| H             | 6.43060314   | -0.87588297  | 1.55274150    |
| N             | 7.12666692   | -0.22252454  | -0.25253953   |
| O             | 6.88787579   | 0.19250842   | -1.45088475   |
| O             | 8.30813726   | -0.09962805  | 0.25669081    |
| S             | 3.18903492   | 4.06735715   | -2.18628115   |
| H             | -0.25617154  | 6.22609076   | 0.82638543    |
| H             | 3.31919889   | 5.28242745   | 0.02390053    |
| C             | 2.59985876   | 4.62696991   | 1.99614825    |
| N             | 2.50326782   | 0.80369198   | -1.84781442   |
| H             | 3.29283087   | 1.11826043   | -2.41880024   |
| C             | 1.22371423   | 0.74036443   | -2.55457569   |
| C             | 1.33316293   | -0.14898111  | -3.80480804   |
| C             | 0.76886800   | 2.17573582   | -2.94950678   |
| C             | -0.01328372  | -0.19686935  | -4.54895999   |
| H             | 2.11459286   | 0.26158726   | -4.46682031   |
| H             | 1.65146770   | -1.15764127  | -3.50443674   |
| C             | -0.58747979  | 2.12264517   | -3.66797506   |
| H             | 1.52731947   | 2.60013733   | -3.62184510   |
| N             | 0.71023344   | 3.05207047   | -1.78305439   |
| C             | -0.50947617  | 1.21490846   | -4.90941346   |
| H             | 0.08960236   | -0.80829199  | -5.45774418   |
| H             | -0.76071959  | -0.69458859  | -3.90760326   |
| H             | -0.88112832  | 3.14476535   | -3.94923613   |
| H             | -1.35256259  | 1.73642758   | -2.97170416   |
| H             | -0.15836290  | 3.03984443   | -1.24597857   |

S151
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | 1.73251859| 3.82914820| -1.31921914|
| H       | 0.18089658| 1.66782510| -5.64109622|
| H       | -1.49811005| 1.15964033| -5.38908945|
| N       | 1.47509657| 4.41477881| -0.11899177|
| H       | 0.71091991| 4.04939020| 0.45419368|
| C       | 2.40073167| 5.27574747| 0.61330709|
| H       | 0.47962162| 0.30615797| -1.87619388|
| S       | 4.21390623| -1.39370484| 3.90421234|
| O       | 4.43356983| -2.83904968| 3.76643294|
| H       | 4.91773517| 1.17026298| 5.06768739|
| O       | 3.27289850| -0.86145703| 4.90005288|
| C       | 1.86973622| 6.75661894| 0.70531695|
| C       | 2.87413359| 7.61409310| 1.50381565|
| H       | 2.52132032| 8.65478839| 1.53835092|
| H       | 2.97810294| 7.25924359| 2.53858692|
| H       | 3.86616248| 7.6118766| 1.03156907|
| C       | 1.76178308| 7.30422416| -0.73482992|
| H       | 2.73853854| 7.28498960| -1.23755625|
| H       | 1.40016364| 8.34241083| -0.71001787|
| H       | 1.05878565| 6.70796074| -1.33179244|
| C       | 0.48510987| 6.81627044| 1.38348526|
| H       | 0.52387828| 6.43931413| 2.41325748|
| H       | 0.13592797| 7.85888398| 1.40524999|
| O       | 1.60888965| 4.11726821| 2.56304123|
| N       | 3.84300116| 4.61831046| 2.55194943|
| C       | 5.08293400| 5.10745259| 1.93593307|
| C       | 4.02642119| 4.05476718| 3.89707587|
| H       | 4.78184774| 3.25972757| 3.85340869|
| H       | 3.07576739| 3.65057170| 4.24936892|
| H       | 4.37967152| 4.83588029| 4.58573186|
| H       | 5.45234647| 5.99125133| 2.47476794|
| H       | 4.93943350| 5.36400171| 0.88766562|
| H       | 5.84302795| 4.31560782| 1.99638835|
| C       | 5.80518955| -0.61251294| 4.22854042|

S152
TS1' (TS-C1)
COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP
\[ E = -17403.47 \]
\[ G = -16974.37 \]
COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP
\[ E = -11972.85 \]
\[ G = -11543.75 \]
\[ N_{\text{imag}} = 1, 359 \text{ cm}^{-1} \]
S -1.31016113  2.33403666  1.47198664
N -1.14160369  2.25526800 -1.25776330
C -2.41925546  2.68690793 -1.87682827
H -2.17014798  3.38805112 -2.68293403
H -2.98370957  3.26501171 -1.13450975
C -3.31102356  1.57960932 -2.46743393
C -2.68576503  0.87679004 -3.67354101
C -4.65916535  2.05407278 -2.58270527
H -4.97210713  2.97483336 -2.10138966
N -5.67044227  1.41591537 -3.23344921
O -5.53166135  0.20405738 -3.66060605
O -6.80125491  2.03005750 -3.38898012
S -4.69866727 -1.15635996  3.06904715
H  0.44002065 -3.39654494  4.14420073
H -2.25708127 -1.78106101  3.47935369
C -0.59023457 -2.02929599  2.05867850
N -5.26402326  0.53855347  0.08617251
H -5.68701406  1.01600452  0.88759446
C -6.12932481 -0.46765128 -0.54384972
C -7.55098487  0.08592645 -0.72176175
C -6.16489228 -1.75511347  0.33066830
C -8.44657199 -0.96995876 -1.39260264
H -7.95925628  0.35259845  0.26914235
H -7.50986302  0.99453452 -1.33594637
C -7.03624305 -2.82029040 -0.35596625
H -6.59781899 -1.49259043  1.30538643
N -4.82795268 -2.27350762  0.60480662
C -8.46102345 -2.28794628 -0.59808955
H -9.46886298 -0.57569573 -1.49406593
H -8.06634879 -1.15231961 -2.41136222
H -7.05731357 -3.72083209  0.27549807
H -6.57383596 -3.09923287 -1.31891450
H -4.40711547 -2.84967916 -0.12620338
C -4.10792677 -2.06776278  1.74440110

S154
|   |       |       |       |
|---|-------|-------|-------|
| C | 0.54883282 | 1.39850172 | -5.6475974 |
| C | 1.04826458 | 0.10903393 | -5.43920727 |
| C | 1.38802205 | -0.31461660 | -4.14792115 |
| C | 1.21490196 | 0.54311497 | -3.06074420 |
| H | -0.03507430 | 3.26485650 | -4.71354764 |
| H | 0.29393770 | 1.73122780 | -6.65291209 |
| H | 1.18017751 | -0.56606225 | -6.28371036 |
| H | 1.79002107 | -1.31408654 | -3.98723932 |
| H | -1.63742895 | 0.63166750 | -3.49914506 |
| H | -3.24027235 | -0.02478217 | -3.94185428 |
| H | -2.72283466 | 1.57052240 | -4.52731519 |

**TS-C2**

COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -17390.22 \]

\[ G = -16963.33 \]

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -11963.16 \]

\[ G = -11536.27 \]

\[ N_{imag} = 1, 115i \text{ cm}^{-1} \]

|   |       |       |       |
|---|-------|-------|-------|
| C | -4.64671863 | 1.62656614 | 1.10500226 |
| C | -3.15447564 | 1.76807234 | 1.46555854 |
| H | -4.96514599 | 2.46738641 | 0.47186189 |
| H | -2.95832257 | 1.20232239 | 2.38932898 |
| C | -2.20185231 | 1.20792946 | 0.39516936 |
| C | -4.99491643 | 0.34060874 | 0.37614538 |
| C | -4.02083935 | -0.34788456 | -0.35683572 |
| C | -2.57481293 | -0.24675733 | 0.0821456 |
| H | -1.18784967 | 1.24258998 | 0.80333209 |
| H | -1.90646561 | -0.66244529 | -0.67903467 |
| H | -2.41333509 | -0.84484877 | 0.99588207 |
| H | -4.31525877 | -1.26656970 | -0.85360389 |
| H | -5.25350143 | 1.69388161 | 2.01942046 |
| H | -2.91659404 | 2.82134899 | 1.66528775 |

S156
|  | X        | Y        | Z        |
|---|----------|----------|----------|
| N | -2.17188361 | 2.05187526 | -0.8333861 |
| C | -3.32075186 | 2.14382334 | -1.75432331 |
| H | -2.98513259 | 2.71337615 | -2.63195336 |
| H | -4.11035246 | 2.74950731 | -1.29336282 |
| C | -3.90203451 | -0.08065494 | -2.27702679 |
| C | -2.92144565 | 1.00549560 | -2.75289019 |
| H | -5.80291281 | 1.86212457 | -2.45661973 |
| N | -5.86726641 | 0.18456046 | -3.62790106 |
| O | -5.39433996 | -0.94018487 | -4.00001205 |
| O | -7.03670026 | 0.57990107 | -4.06643194 |
| S | -9.49636243 | 0.84533103 | 0.61292505 |
| H | -9.52699621 | 6.10867650 | -1.62859032 |
| H | -9.97354953 | 3.18677888 | -0.35531228 |
| C | -10.83686498 | 3.81656837 | -2.27768072 |
| N | -6.30105955 | 0.03787423 | 0.39586729 |
| H | -6.92334691 | 0.73087537 | 0.83084317 |
| C | -7.03437220 | -1.22625111 | 0.18038133 |
| C | -6.26332075 | -2.52447275 | 0.45518078 |
| C | -7.74099016 | -1.31266120 | -1.19693866 |
| C | -7.27066519 | -3.69136064 | 0.51121815 |
| H | -5.52932414 | -2.72956696 | -0.33639108 |
| H | -5.71428336 | -2.43010953 | 1.40372258 |
| C | -8.76666599 | -2.46287422 | -1.15705509 |
| H | -6.97682064 | -1.55947807 | -1.94858439 |
| N | -8.30698057 | -0.04858745 | -1.68043478 |
| C | -8.07754611 | -3.79322512 | -0.79722040 |
| H | -6.73309624 | -4.63311613 | 0.69885331 |
| H | -7.55879434 | -3.53440696 | 1.35882967 |
| H | -9.25596017 | -2.53499664 | -2.13955607 |
| H | -9.54131783 | -2.21254027 | -0.41501444 |
| H | -7.98854315 | 0.19958134 | -2.63492980 |
| C | -9.03304378 | 0.89515133 | -1.04751034 |
| H | -7.39492410 | -4.07384834 | -1.61807433 |

S157
H  -8.83002645  -4.59256015  -0.71879883
N  -9.38899621  1.93492595  -1.85977524
H  -9.16574112  1.86083570  -2.85394130
C  -9.68496007  3.28867334  -1.40225401
H  -7.83611718  -1.15859418  0.92706572
S  -0.74223360  2.80385826  -1.27186331
O  -1.08843957  3.97958719  -2.08066883
H  0.80828042  0.42634793  -0.70998016
O  0.06709138  2.93528979  -0.05385464
C  -8.40836008  4.22177862  -1.46706266
C  -7.33065002  3.63399876  -0.52836039
H  -6.43160914  4.26658840  -0.56031388
H  -7.68550164  3.58327006  0.50988066
H  -7.04679669  2.62181374  -0.83803279
C  -7.83548380  4.30429785  -2.89849376
H  -7.52501346  3.31749538  -3.26975402
H  -6.94795530  4.95386789  -2.89664383
H  -8.56940613  4.71637604  -3.60205553
C  -8.78082639  5.63664316  -0.97524998
H  -9.17970506  5.60951299  0.04831355
H  -7.88367471  6.27233766  -0.97110003
O  -10.82114139  3.56236844  -3.50116558
N  -11.80987392  4.57499763  -1.70032203
C  -11.98964156  4.82426642  -0.26474588
C  -12.84072972  5.18731537  -2.55157570
H  -12.55337277  5.07248857  -3.59842629
H  -12.92888385  6.25293823  -2.29932173
H  -13.18125039  4.70038703  -2.38027105
H  -13.03442786  4.61127176  0.00207159
H  -11.77399903  5.87622895  -0.02873825
H  -11.34721912  4.18458923  0.33943585
C  0.07974469  1.62728661  -2.35751284
C  -0.03209074  1.77432490  -3.74332511
C  0.48566802  0.77664356  -4.57381684
|      |          |          |          |
|------|----------|----------|----------|
| C    | 1.10470415 | -0.34850907 | -4.02059206 |
| C    | 1.22623295 | -0.47402778 | -2.63063274 |
| C    | 0.71695193  | 0.51644269  | -1.78957587 |
| H    | -0.52581479 | 2.64834372  | -4.16024980 |
| H    | 0.39839092  | 0.87791830  | -5.65462499 |
| H    | 1.49793353  | -1.12802548 | -4.67187457 |
| H    | 1.71925147  | -1.34477187 | -2.20038845 |
| H    | -1.91055426 | 0.06599492  | -2.60831165 |
| H    | -3.19573940 | -1.13538003 | -2.91115607 |
| H    | -2.92146766 | 0.17630270  | -4.05843616 |

**TS-C3**

COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -17398.11 \]

\[ G = -16969.06 \]

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -11970.47 \]

\[ G = -11541.42 \]

\[ N_{\text{imag}} = 1, 122 i \text{ cm}^{-1} \]

|      |          |          |          |
|------|----------|----------|----------|
| C    | -3.03382072 | 1.28056387 | 1.32309852 |
| C    | -1.51942960 | 0.97484066 | 1.30753025 |
| H    | -3.20970300 | 2.32746615 | 1.02694702 |
| H    | -1.32143578 | 0.18650939 | 2.04820420 |
| C    | -0.95951427  | 0.44343827  | -0.02655439 |
| C    | -3.85965300  | 0.44909439  | 0.37857655 |
| C    | -3.25534909  | -0.24790756 | -0.68399939 |
| C    | -1.83313553  | -0.71266443 | -0.51843758 |
| H    | 0.05520145   | 0.08822526  | 0.17651777 |
| H    | -1.44303742  | -1.11175687 | -1.45862452 |
| H    | -1.79646816  | -1.52543583 | 0.22410053 |
| H    | -3.91908155  | -0.89014798 | -1.26184948 |
| H    | -3.40781095  | 1.18867293  | 2.34829384 |
| H    | -0.96249344  | 1.86908506  | 1.61766311 |
| N    | -0.82097554  | 1.48668520  | -1.08611964 |

S159
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| C       | -2.00576968 | 2.19468315 | -1.61718842 |
| H       | -1.65995195 | 2.81733455 | -2.45158300 |
| H       | -2.35074352 | 2.88424282 | -0.83578279 |
| C       | -3.18346287 | 1.33375070 | -2.09853696 |
| C       | -2.90135162 | 0.46979877 | -3.31814448 |
| C       | -4.39787949 | 2.07207424 | -2.03088427 |
| H       | -4.42449775 | 3.07123233 | -1.60806979 |
| N       | -5.64014981 | 1.60142519 | -2.35713055 |
| O       | -5.82721000 | 0.33972678 | -2.58680205 |
| O       | -6.63878285 | 2.41670000 | -2.36811846 |
| S       | -3.61642718 | -1.87884757 | 2.77728374 |
| H       | -3.66074058 | -6.27550679 | -0.94929256 |
| H       | -3.40138844 | -3.73665017 | 1.03888212 |
| C       | -4.07607251 | -3.56893579 | -1.04878805 |
| N       | -5.18748904 | 0.60314276 | 0.32187749 |
| H       | -5.63009313 | 0.10824573 | -0.46275713 |
| C       | -6.13143582 | 1.07927899 | 1.35021406 |
| C       | -6.01389134 | 2.56549407 | 1.72659950 |
| C       | -6.10172581 | 0.15944443 | 2.60414345 |
| C       | -7.16320597 | 2.93918127 | 2.68249410 |
| H       | -5.05606347 | 2.76331049 | 2.22469269 |
| H       | -6.04790367 | 3.16932903 | 0.80800939 |
| C       | -7.24299257 | 0.54393192 | 3.55605993 |
| H       | -5.14255395 | 0.26521204 | 3.12348678 |
| N       | -6.18821900 | -1.24965454 | 2.19213192 |
| C       | -7.16527995 | 2.03652465 | 3.93082576 |
| H       | -7.06800243 | 3.99511120 | 2.97633438 |
| H       | -8.12562496 | 2.83548350 | 2.15307887 |
| H       | -7.18771913 | -0.09086676 | 4.45266627 |
| H       | -8.20815488 | 0.33548818 | 3.06263840 |
| H       | -7.02449532 | -1.47167542 | 1.64297074 |
| C       | -5.08252599 | -2.01908837 | 1.91109060 |
| H       | -6.24223656 | 2.21482950 | 4.50900642 |
| H       | -8.01014451 | 2.29637768 | 4.58613319 |
| Atom | C    | C    | H    | H    | H    | H    | H    | N    | C    | H    | C    | C    |
|------|------|------|------|------|------|------|------|------|------|------|------|------|
|      | 1.25556819 | -2.33658408 | -2.94124510 | 1.23937570 | -1.13888095 | -2.22360019 | 0.00277983 | 0.92555787 | -4.65289578 | 0.04272504 | -1.21451160 | -5.92771257 |
|      | 1.23937570 | -1.13888095 | -2.22360019 | 0.82906606 | -3.30453426 | -4.82471347 | 1.61513888 | -3.24592155 | -2.46181521 | -2.05575262 | -0.20096920 | -3.15902470 |
|      | -2.98822512 | 0.88328656 | 1.30532664 | -3.33126547 | 1.93095729 | 1.35426945 | -1.10260078 | -0.10431611 | 1.67614196 | -0.87948008 | 0.75895950 | -0.25394584 |
|      | -1.44378645 | 0.81583724 | 1.17972887 | -3.73896423 | 0.22822587 | 0.18541643 | -3.10232757 | 0.00297909 | -1.07496329 | -1.62209332 | -0.31185929 | -1.06342604 |
|      | -1.23293362 | -0.35505673 | -2.08386938 | -1.44478792 | -1.30072688 | -0.60942742 | -3.70069184 | -0.56189476 | -1.79454383 | -3.28732838 | 0.43074313 | 2.25690299 |
|      | -0.99861530 | 1.66127769 | 1.71970653 | -0.93394361 | 2.07680180 | -0.94337851 | -2.24441081 | 2.69451775 | -1.22676530 |              |              |              |

**TS-C4**

COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -17396.47 \]

\[ G = -16966.65 \]

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -11967.82 \]

\[ G = -11538.00 \]

\( \text{N_{imag} = 1, 396 \text{ cm}^{-1}} \)
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| H    | -2.06885452 | 3.57741165 | -1.85353856 |
| H    | -2.64714175 | 3.07099055 | -0.27773767 |
| C    | -3.29473246 | 1.81215507 | -1.93114466 |
| C    | -2.93860832 | 1.45331727 | -3.36816032 |
| C    | -4.61037914 | 2.31903731 | -1.62553575 |
| H    | -4.75914843 | 2.93125115 | -0.74213992 |
| N    | -5.77412403 | 1.97420385 | -2.21420045 |
| O    | -5.81282498 | 1.21313690 | -3.2665722 |
| O    | -6.89898104 | 2.38147423 | -1.68837992 |
| S    | -7.31204264 | -3.02931227 | -0.73402071 |
| H    | -6.32410581 | -3.05178013 | -6.46828638 |
| H    | -6.46809077 | -3.23223230 | -3.20457123 |
| C    | -5.14148695 | -1.89914897 | -4.3235101 |
| N    | -5.05188101 | 0.04309750 | 0.22595979 |
| H    | -5.41993500 | -0.39373967 | -0.62213403 |
| C    | -6.15918741 | 0.59551008 | 1.05155295 |
| C    | -5.95874933 | 0.57819127 | 2.57339826 |
| C    | -7.43846001 | -0.21493817 | 0.67987890 |
| C    | -7.20449046 | 1.16606487 | 3.26960010 |
| H    | -5.78555082 | -0.45937551 | 2.90186141 |
| H    | -5.08616985 | 1.17341845 | 2.86031798 |
| C    | -8.67118568 | 0.41390568 | 1.33974462 |
| H    | -7.31322432 | -1.24005739 | 1.0530615 |
| N    | -7.57816104 | -0.33046442 | -0.77490139 |
| C    | -8.49831194 | 0.43899606 | 2.86849426 |
| H    | -7.05912171 | 1.11959984 | 4.35912902 |
| H    | -7.28815807 | 2.23294696 | 3.00103748 |
| H    | -9.55550987 | -0.17303188 | 1.05220367 |
| H    | -8.81173408 | 1.43773738 | 0.95420803 |
| H    | -7.55223257 | 0.57135386 | -1.28367386 |
| C    | -7.25910879 | -1.47950982 | -1.46774805 |
| H    | -8.46540657 | -0.59876641 | 3.24223664 |
| H    | -9.36692306 | 0.92457500 | 3.33807665 |
| N    | -6.88868554 | -1.26156760 | -2.75166923 |

S163
|    |       |       |       |       |
|----|-------|-------|-------|-------|
| H  | -6.68012710 | -0.27882929 | -3.02357782 |
| C  | -6.53587182 | -2.28217220 | -3.74235853 |
| H  | -6.30538179 | 1.63345179  | 0.70462224  |
| S  | 0.44031743  | 2.65399419  | -1.70874383 |
| O  | 0.22428952  | 4.08460197  | -1.95531951 |
| H  | 1.27697116  | -0.01455807 | -2.47818706 |
| O  | 1.58655079  | 2.18172383  | -0.92124465 |
| C  | -7.65539619 | -2.46732784 | -4.82392624 |
| C  | -8.88917807 | -3.06748440 | -4.10951644 |
| H  | -9.70419810 | -3.20392164 | -4.83554788 |
| H  | -8.65362904 | -4.04228963 | -3.66007027 |
| H  | -9.24701534 | -2.40321840 | -3.31156223 |
| C  | -8.06812449 | -1.13340467 | -5.48259794 |
| H  | -8.45905178 | -0.43295841 | -4.73062291 |
| H  | -8.86764322 | -1.32103299 | -6.21483252 |
| H  | -7.21801244 | -0.66488392 | -5.98818982 |
| C  | -7.15497321 | -3.46976319 | -5.88688375 |
| H  | -6.81706086 | -4.40495720 | -5.41339139 |
| H  | -7.97298326 | -3.71931821 | -6.57824597 |
| O  | -5.03848261 | -1.19105881 | -5.33915555 |
| N  | -4.03151301 | -2.33979962 | -3.64496393 |
| C  | -4.04036385 | -3.29402421 | -2.52556196 |
| C  | -2.71072851 | -2.11255258 | -4.25470498 |
| H  | -2.76038825 | -1.24453861 | -4.91380526 |
| H  | -2.39801881 | -2.99379985 | -4.83800959 |
| H  | -1.97440329 | -1.93953948 | -3.46342524 |
| H  | -3.18012188 | -3.07772019 | -1.87985319 |
| H  | -3.94726160 | -4.33090521 | -2.88758632 |
| H  | -4.94714107 | -3.20302430 | -1.92309601 |
| C  | 0.51280572  | 1.83301485  | -3.31058548 |
| C  | 0.07584046  | 2.51135065  | -4.45201327 |
| C  | 0.00269831  | 1.82116985  | -5.66460423 |
| C  | 0.35764994  | 0.47005220  | -5.72806999 |
| C  | 0.81974410  | -0.19078976 | -4.58311336 |
|     |     |     |     |     |
|-----|-----|-----|-----|-----|
| C   | 0.90905364 | 0.49014042 | -3.36805896 |
| H   | -0.21792580 | 3.55556024  | -4.38401353 |
| H   | -0.34338228 | 2.33907558  | -6.55798202 |
| H   | 0.28434819  | -0.06757185 | -6.67246425 |
| H   | 1.11361146  | -1.23819607 | -4.63585713 |
| H   | -1.94021714 | 1.01949541  | -3.43194573 |
| H   | -3.67147752 | 0.77320133  | -3.80298039 |
| H   | -2.93638934 | 2.37857690  | -3.96510391 |

**TS-D1**

COSMO(DCM)-ZORA-M06-2X/TZ2P/COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -17401.71 \]

\[ G = -16972.26 \]

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -11971.82 \]

\[ G = -11542.37 \]

\[ \text{\( N_{\text{imag}} = 1, 361 \) cm}^{-1} \]

|     |     |     |     |     |
|-----|-----|-----|-----|-----|
| C   | -2.47575453 | -1.04048245 | -3.40070693 |
| C   | -1.16558868 | -1.85369437 | -3.38830070 |
| H   | -3.20392254 | -1.46983220 | -2.69376696 |
| H   | -0.67536803 | -1.72747587 | -4.36081755 |
| C   | -0.14603852 | -1.39824391 | -2.32843912 |
| C   | -2.30449326 | 0.41980403  | -3.05299139 |
| C   | -1.18159688 | 0.87586777  | -2.32307283 |
| C   | 0.11278065  | 0.10299088  | -2.47212873 |
| H   | 0.77921343  | -1.95165288 | -2.50400248 |
| H   | 0.82453975  | 0.44634489  | -1.70934767 |
| H   | 0.57698907  | 0.29201747  | -3.44895969 |
| H   | -1.05747625 | 1.95302646  | -2.23582126 |
| H   | -2.93817055 | -1.10184270 | -4.39738147 |
| H   | -1.38887407 | -2.92128298 | -3.26204505 |
| N   | -0.57495926 | -1.74648020 | -0.94226598 |
| C   | -1.66941145 | -0.99676685 | -0.28045608 |
| H   | -1.68551904 | -1.29301587 | 0.77614724 |

S165
|   | X          | Y          | Z          |
|---|------------|------------|------------|
| H | -2.62195125 | -1.33530066 | -0.70543192 |
| C | -1.60976427 | 0.53705896  | -0.36554735 |
| C | -2.98843476 | 1.14069666  | -0.14539063 |
| C | -0.48161743 | 1.11849758  | 0.29411770  |
| H | 0.32436806  | 0.51574060  | 0.68605266  |
| N | -0.20508798 | 2.45634701  | 0.32197955  |
| O | -0.94850020 | 3.30879091  | -0.30992520 |
| O | 0.83695794  | 2.86095926  | 0.96967356  |
| S | -2.68501372 | 0.76872385  | -6.67860218 |
| H | 1.94136429  | 2.58997492  | -7.35901117 |
| H | -0.44817927 | -0.34059330 | -7.18309080 |
| C | 1.35191415  | -0.52835392 | -5.92937724 |
| N | -3.33850067 | 1.20422162  | -3.37155249 |
| H | -4.08214674 | 0.77268326  | -3.92592258 |
| C | -3.36951929 | 2.66932884  | -3.32816784 |
| C | -4.76404961 | 3.17592220  | -2.93039473 |
| C | -2.95481926 | 3.24299419  | -4.71426355 |
| C | -4.78529302 | 4.71435511  | -2.89749948 |
| H | -5.50287512 | 2.80589362  | -3.66196489 |
| H | -5.03339687 | 2.76022753  | -1.94922019 |
| C | -2.95734109 | 4.77949378  | -4.66814256 |
| H | -3.67882318 | 2.89071723  | -5.46148383 |
| N | -1.64974292 | 2.73984749  | -5.13285627 |
| C | -4.33814284 | 5.31190225  | -4.24350745 |
| H | -5.79665855 | 5.06390665  | -2.64189939 |
| H | -4.11065618 | 5.06627341  | -2.09854184 |
| H | -2.67712490 | 5.16460162  | -5.65960048 |
| H | -2.19060615 | 5.12068774  | -3.95073716 |
| H | -0.83588195 | 3.21882561  | -4.74312642 |
| C | -1.42361078 | 1.66180417  | -5.93688300 |
| H | -5.07698647 | 5.05270092  | -5.02083587 |
| H | -4.30647295 | 6.40987189  | -4.18075534 |
| N | -0.10822007 | 1.37034626  | -6.11379782 |
| H | 0.58653714  | 1.83602732  | -5.52577243 |
| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| C       | 0.42157981 | 0.24609001 | -6.88296985 |
| H       | -2.64626171 | 3.00103877 | -2.57406424 |
| S       | 0.39395684 | -2.75573776 | -0.03334807 |
| O       | -0.43810587 | -3.31635025 | 1.03918045 |
| H       | 2.74522651 | -1.43916501 | -1.09456605 |
| O       | 1.09970493 | -3.63081474 | -0.98009760 |
| C       | 1.15492661 | 0.71944272 | -8.19441670 |
| C       | 1.70776660 | -0.51602909 | -8.93558484 |
| H       | 2.18896967 | -0.19910424 | -9.87185838 |
| H       | 2.45905511 | -1.04681934 | -8.3341213 |
| H       | 0.90325406 | -1.2193850 | -9.19169990 |
| C       | 0.11408105 | 1.42875226 | -9.08765285 |
| H       | -0.71053533 | 0.75109618 | -9.34720818 |
| H       | 0.59544204 | 1.76912011 | -10.01595612 |
| H       | -0.31160570 | 2.30362845 | -8.57841270 |
| C       | 2.30848516 | 1.69461118 | -7.88053752 |
| H       | 3.07763142 | 1.22266254 | -7.25706524 |
| H       | 2.77167397 | 2.02209406 | -8.82264765 |
| O       | 2.11915866 | 0.12301964 | -5.18853658 |
| N       | 1.28879226 | -1.88836334 | -5.89960822 |
| C       | 0.41187662 | -2.73618852 | -6.71931680 |
| C       | 2.21618244 | -2.62933786 | -5.03048138 |
| H       | 2.85042461 | -1.91674603 | -4.50062871 |
| H       | 2.83669680 | -3.30371457 | -5.63791519 |
| H       | 1.64541914 | -3.23267408 | -4.31101761 |
| H       | 0.95539771 | -3.14029480 | -7.58493995 |
| H       | -0.46486899 | -2.18854635 | -7.06785575 |
| H       | 0.06686448 | -3.57391752 | -6.09960724 |
| C       | 1.61749938 | -1.68396678 | 0.73784243 |
| C       | 1.47259277 | -1.32511198 | 2.08171845 |
| C       | 2.34901342 | -0.38451738 | 2.63050627 |
| C       | 3.34926841 | 0.18916999 | 1.84093365 |
| C       | 3.49563559 | -0.19275668 | 0.50179365 |
| C       | 2.63302296 | -1.13617880 | -0.05687770 |

S167
TS-D2

COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -17390.08 \]
\[ G = -16962.46 \]

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -11959.29 \]
\[ G = -11531.67 \]

\[ N_{\text{imag}} = 1, 417i \text{ cm}^{-1} \]

|       |       |       |       |
|-------|-------|-------|-------|
| C     | -2.26109754 | -0.48886382 | -2.50324586 |
| C     | -1.12740203 | -1.52101585 | -2.30336375 |
| H     | -3.01155227 | -0.59021068 | -1.70364153 |
| H     | -0.63960262 | -1.69599538 | -3.27451035 |
| C     | -0.02557347 | -1.06772069 | -1.32716969 |
| C     | -1.78576965 | 0.94940333  | -2.51561573 |
| C     | -0.64363963 | 1.32614414  | -1.76657186 |
| C     | 0.49467406  | 0.31523862  | -1.73504984 |
| H     | 0.78402056  | -1.80122375 | -1.38324845 |
| H     | 1.26241157  | 0.66377187  | -1.03202795 |
| H     | 0.96644917  | 0.23985782  | -2.72783425 |
| H     | -0.33455311 | 2.36424924  | -1.85101975 |
| H     | -2.78949309 | -0.70520728 | -3.44313116 |
| H     | -1.55282158 | -2.47594470 | -1.96768989 |
| N     | -0.49593780 | -1.07963593 | 0.08745413  |
| C     | -1.44617089 | -0.04916955 | 0.55966644  |
| H     | -1.50456443 | -0.12181957 | 1.65291301  |
| H     | -2.44689363 | -0.29971735 | 0.18872420  |
| Element | Xcoordinate | Ycoordinate | Zcoordinate |
|---------|-------------|-------------|-------------|
| C       | -1.12161590 | 1.40396317  | 0.18149778  |
| C       | -2.36987820 | 2.26097247  | 0.24932024  |
| C       | 0.08327700  | 1.89267071  | 0.77811299  |
| H       | 0.75741087  | 1.24606624  | 1.31997852  |
| N       | 0.59897665  | 3.14489613  | 0.57898651  |
| O       | 0.05196762  | 3.97008884  | -0.24972435 |
| O       | 1.67053074  | 3.47740024  | 1.21844716  |
| S       | -3.56476996 | 5.68896127  | -0.02061232 |
| H       | -8.21020828 | 3.50472524  | -0.93088488 |
| H       | -5.42448264 | 4.67210946  | 1.33813907  |
| C       | -5.67787146 | 2.49060210  | 1.29733428  |
| N       | -2.56706190 | 1.79764948  | -3.20107021 |
| H       | -3.38050032 | 1.36172071  | -3.63835798 |
| C       | -2.29346322 | 3.17071133  | -3.71204890 |
| C       | -0.89064392 | 3.32672458  | -4.33174793 |
| C       | -2.59941726 | 4.30783004  | -2.70781878 |
| C       | -0.76904352 | 4.68919881  | -5.03672797 |
| H       | -0.11902539 | 3.26348560  | -3.55504083 |
| H       | -0.72448775 | 2.49769358  | -5.03523745 |
| C       | -2.47199851 | 5.66306858  | -3.43370285 |
| H       | -1.88627326 | 4.27503250  | -1.87324076 |
| N       | -3.94797873 | 4.09978408  | -2.16388991 |
| C       | -1.07932461 | 5.83632177  | -4.06011661 |
| H       | 0.24568205  | 4.79438537  | -5.44917992 |
| H       | -1.47196376 | 4.72843981  | -5.88647555 |
| H       | -2.68173949 | 6.45885734  | -2.70736016 |
| H       | -3.24775222 | 5.71005607  | -4.21707561 |
| H       | -4.53178793 | 3.42057470  | -2.65240179 |
| C       | -4.39977164 | 4.53757277  | -0.95900676 |
| H       | -0.31954772 | 5.85038240  | -3.26002770 |
| H       | -1.02229042 | 6.80622174  | -4.57686042 |
| N       | -5.60127854 | 3.98319400  | -0.58711048 |
| H       | -5.84893767 | 3.11506259  | -1.07378638 |
| C       | -6.01849595 | 3.91903899  | 0.81943861  |
S  -3.02165941  3.27324564  -4.53255875
H   0.28387247 -2.04452814  1.20469178
O  -0.64751493 -2.25720284  2.32034307
H   2.82458982 -1.30638775  0.02694444
O   0.85072545 -3.17985616  0.46424920
H   -7.52756145  4.29951099  0.99646556
C  -7.91153143  4.15974869  2.48476010
H  -8.96133807  4.45418841  2.62657728
H  -7.80145890  3.12357905  2.83513187
H  -7.29048422  4.80974216  3.11689888
C  -7.68103925  5.77410910  0.56258562
H  -7.05857384  6.43203795  1.18638756
H  -8.72975681  6.08902745  0.66328505
H  -7.37523235  5.90459373 -0.48431730
C  -8.45005689  3.40923746  0.13768562
H  -8.36214713  2.35263754  0.41947180
H  -9.49439516  3.72517046  0.27678673
O  -5.96099031  1.52887751  0.54863484
N  -5.04845052  2.32692006  2.49244036
C  -4.65719949  3.41169738  3.40605699
C  -4.77087068  0.96374112  2.97001294
H  -4.94458697  0.26138757  2.15246804
H  -5.42591161  0.71327115  3.81806676
H  -3.72684700  0.90191451  3.30321435
H  -3.76948388  3.08485469  3.96039861
H  -5.45528447  3.63680015  4.12736942
H  -4.39436528  4.31663019  2.85347968
C  1.65325998 -1.05858319  1.83195193
C  1.55319106 -0.46003462  3.09181161
C  2.56380665  0.41014511  3.51057468
C  3.65309488  0.67566812  2.67649312
C  3.75071730  0.05457101  1.42554776
C  2.75240069 -0.82033800  0.99665673
H  0.69211748 -0.66371719  3.72312533

S170
|     |        |        |        |
|-----|--------|--------|--------|
| H   | 2.49061835 | 0.88901533 | 4.48594842 |
| H   | 4.42905887 | 1.36787728 | 2.99985801 |
| H   | 4.60425814 | 0.25548231 | 0.77963591 |
| H   | -2.75660963 | 2.23144590 | 1.27808275 |
| H   | -2.15140374 | 3.30094103 | 0.01181123 |
| H   | -3.16196538 | 1.88525922 | -0.40813316 |

**TS-D3**

COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -17397.02 \]

\[ G = -16967.70 \]

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -11968.79 \]

\[ G = -11539.47 \]

\( N_{\text{imag}} = 1, 351 i \text{ cm}^{-1} \)

|     |        |        |        |
|-----|--------|--------|--------|
| C   | -1.97442071 | -0.93571664 | -3.70415383 |
| C   | -0.64330681 | -1.66723953 | -3.41348019 |
| H   | -2.79206440 | -1.38366668 | -3.11729310 |
| H   | -0.02729168 | -1.60892149 | -4.32164227 |
| C   | 0.21315992  | -1.07635060 | -2.27930002 |
| C   | -1.97156953 | 0.53767180  | -3.39200533 |
| C   | -1.03529862 | 1.07995278  | -2.47690167 |
| C   | 0.33640645  | 0.44057345  | -2.44706702 |
| H   | 1.20034244  | -1.54090337 | -2.35805152 |
| H   | 0.91689439  | 0.86598043  | -1.62046574 |
| H   | 0.86513222  | 0.65181646  | -3.38699113 |
| H   | -1.04634373 | 2.17031698  | -2.39726460 |
| H   | -2.23605084 | -1.09503764 | -4.75458930 |
| H   | -0.84371773 | -2.72790214 | -3.21211275 |
| N   | -0.29744443 | -1.41059883 | -0.92036211 |
| C   | -1.58589784 | -0.83870469 | -0.48066328 |
| H   | -1.74070662 | -1.12959273 | 0.56537164  |
| H   | -2.37570203 | -1.33071614 | -1.06100229 |
| C   | -1.74597505 | 0.68588047  | -0.60944788 |
C  -3.21233255  1.07957944  -0.67659663
C  -0.86023164  1.41488652   0.23926863
H   -0.05352506  0.92419654   0.75923140
N   -0.83689105  2.77214694   0.39240194
O   -1.57793798  3.54056031  -0.32930613
O   -0.02446097  3.27776860   1.26136079
S   -0.09273797  0.56943859  -6.31692045
H   -0.14314485  5.65358252  -6.56508434
H   1.43003121  2.41316960  -5.38101133
C   0.84082945  3.79084963  -3.76536174
N  -2.95178285  1.33323374  -3.84643830
H  -2.86997170  2.30687454  -3.54778387
C  -3.95072346  1.19698076  -4.91609639
C  -4.94772569  -0.02767562  -4.67743593
C  -3.27124093  1.01192371  -6.31237574
C  -6.01681208  -0.01358610  -5.78719054
H  -4.43270751  -0.99648434  -4.69170217
H  -5.40706763  0.09260509  -3.68538413
C  -4.34357448  1.01416844  -7.41142930
H  -2.68566935  0.08800924  -6.37588455
N  -2.31372726  2.11185356  -6.48746245
C  -5.37185522  -0.10950170  -7.18236202
H  -6.71560040  -0.84905891  -5.63182606
H  -6.60396457  0.91795562  -5.71693288
H  -3.84920576  0.90330197  -8.38759729
H  -4.85644188  1.99171187  -7.41044209
H  -2.72452518  3.04519757  -6.38828427
C  -0.98675568  2.01278902  -6.13465203
H  -4.86800123  -1.08612559  -7.28284037
H  -6.14615840  -0.06548451  -7.96289825
N  -0.45492069  3.17197006  -5.68090434
H  -1.09054850  3.87608804  -5.29558796
C  0.92911823  3.37503839  -5.25244416
H  -4.52921515  2.05661174  -4.91484385

S172
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| S       | 0.78579861| -2.08658237| 0.15810136|
| O       | 0.06232519| -2.29672424| 1.41872961|
| H       | 3.21367340| -1.41729091| -1.30580738|
| O       | 1.44203084| -3.20583125| -0.53320134|
| C       | 1.64401669| 4.43999400  | -6.16696477|
| C       | 3.08486982| 4.68210251  | -5.67244063|
| H       | 3.58054384| 5.40580557  | -6.33537750|
| H       | 3.09968453| 5.09423640  | -4.65397358|
| H       | 3.67518953| 3.75642239  | -5.68597142|
| C       | 1.68719993| 3.86425910  | -7.59966531|
| H       | 2.26902107| 2.93204429  | -7.63021709|
| H       | 2.15692485| 4.59032311  | -8.27893925|
| H       | 0.67577854| 3.64983909  | -7.96999332|
| C       | 0.87447940| 5.77829695  | -6.16936160|
| H       | 0.80359363| 6.20275667  | -5.15971707|
| H       | 1.39900433| 6.49737774  | -6.81496055|
| O       | -0.12077711| 4.50891650  | -3.41430173|
| N       | 1.78163080| 3.35006553  | -2.88836032|
| C       | 2.95326135| 2.52880587  | -3.20939191|
| C       | 1.69781756| 3.76801504  | -1.47878269|
| H       | 0.72680129| 4.23022487  | -1.29772981|
| H       | 2.50585030| 4.47819420  | -1.24596189|
| H       | 1.80812664| 2.88950421  | -0.83213367|
| H       | 3.86937256| 3.13689211  | -3.19029118|
| H       | 2.86102910| 2.05864222  | -4.18827769|
| H       | 3.04400619| 1.74030917  | -2.45371042|
| C       | 2.07068556| -0.84803261 | 0.44181270|
| C       | 1.96136704| 0.01660380  | 1.53585645|
| C       | 2.88219839| 1.05655464  | 1.67902209|
| C       | 3.91087830| 1.21753101  | 0.74583172|
| C       | 4.03494751| 0.32296553  | -0.32307071|
| C       | 3.11615810| -0.71660906 | -0.48134480|
| H       | 1.16368675| -0.12107191 | 2.26132772|
| H       | 2.78628916| 1.74544968  | 2.51618007|

S173
|    |     X          |     Y          |     Z          |
|----|----------------|----------------|----------------|
| H  | 4.62030844     | 2.03672207     | 0.85435101     |
| H  | 4.84850001     | 0.43376603     | -1.03846791    |
| H  | -3.66871305    | 0.89782866     | 0.30997333     |
| H  | -3.32825737    | 2.14058532     | -0.91284839    |
| H  | -3.75589174    | 0.47646960     | -1.41259764    |

**TS-D4**

COSMO(DCM)-ZORA-M06-2X/TZ2P/COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -17401.71 \]

\[ G = -16972.76 \]

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -11970.66 \]

\[ G = -11541.71 \]

\[ N_{\text{imag}} = 1, \: 287i \: \text{cm}^{-1} \]

|    |     X          |     Y          |     Z          |
|----|----------------|----------------|----------------|
| C  | -4.86812132    | -1.08056192    | -2.19343599    |
| C  | -4.13965385    | -2.15787927    | -3.03055755    |
| H  | -4.68601358    | -1.24424359    | -1.11810574    |
| H  | -4.68986148    | -2.29502476    | -3.97397615    |
| C  | -2.68995905    | -1.81132457    | -3.41685052    |
| C  | -4.46224830    | 0.34006261     | -2.50799402    |
| C  | -3.21899738    | 0.61701719     | -3.13116274    |
| C  | -2.64882643    | -0.42490123    | -4.07294313    |
| H  | -2.35069077    | -2.56978407    | -4.12801526    |
| H  | -1.61678710    | -0.15130982    | -4.33070410    |
| H  | -3.22414608    | -0.46089863    | -5.01250463    |
| H  | -3.05818601    | 1.65965855     | -3.41686940    |
| H  | -5.94979937    | -1.20094071    | -2.32558879    |
| H  | -4.16284466    | -3.11565283    | -2.49419038    |
| N  | -1.76322698    | -1.89856017    | -2.25156484    |
| C  | -1.81245242    | -0.87690957    | -1.18126754    |
| H  | -0.95466526    | -1.04332662    | -0.51702101    |
| H  | -2.70614058    | -1.05533785    | -0.57110856    |
| C  | -1.80738905    | 0.58526246     | -1.64501142    |
| C  | -2.38460138    | 1.49961421     | -0.58673487    |

S174
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| C    | -0.60821162 | 0.97578866 | -2.31567234 |
| H    | 0.17187099    | 0.26978931    | -2.5565593  |
| N    | -0.38493847    | 2.21714350    | -2.84285638 |
| O    | -1.32121793    | 3.10146002    | -2.87979845 |
| O    | 0.78401441     | 2.48310089    | -3.32715188 |
| S    | -4.60840856    | 4.62115503    | -1.49420002 |
| H    | -3.56515699    | 5.35600058    | 3.39193717  |
| H    | -2.46672521    | 5.24015033    | -0.23169232 |
| C    | -1.29969374    | 4.00550182    | 1.16408792  |
| N    | -5.23421119    | 1.34177405    | -2.07017646 |
| H    | -4.92176984    | 2.31134466    | -2.25096036 |
| C    | -6.44613960    | 1.21302651    | -1.24091045 |
| C    | -7.70512432    | 0.94757899    | -2.09589452 |
| C    | -6.65753001    | 2.50647419    | -0.41619933 |
| C    | -8.94700387    | 0.79379237    | -1.20184505 |
| H    | -7.83441937    | 1.79557637    | -2.78886740 |
| H    | -7.55813868    | 0.04947929    | -2.71071788 |
| C    | -7.88476998    | 2.35520103    | 0.49896107  |
| H    | -6.82635126    | 3.33436475    | -1.11855861 |
| N    | -5.47774186    | 2.87195320    | 0.36941053  |
| C    | -9.15010212    | 2.03509012    | -0.31646778 |
| H    | -9.83485671    | 0.62144306    | -1.82854895 |
| H    | -8.82398333    | -0.09778165   | -0.56297982 |
| H    | -8.01374912    | 3.28826624    | 1.06709181  |
| H    | -7.69490352    | 1.54657266    | 1.22632127  |
| H    | -5.40825355    | 2.46030616    | 1.30195992  |
| C    | -4.58934203    | 3.85238437    | 0.03934653  |
| H    | -9.39244752    | 2.90096273    | -0.95560444 |
| H    | -10.00159914   | 1.88655728    | 0.36427663  |
| N    | -3.69252444    | 4.15295333    | 1.01252008  |
| H    | -3.60164425    | 3.49948958    | 1.79773834  |
| C    | -2.47498190    | 4.94772116    | 0.82018321  |
| H    | -6.29274983    | 0.37798269    | -0.54029819 |
| S    | -0.49449966    | -2.97953830   | -2.28539875 |

S175
O  -0.12855104  -3.27471963  -0.89331359
H   0.05276002  -2.19319778  -5.01570873
O  -0.87596492  -4.05790364  -3.20832290
C  -2.50292819   6.25510667   1.69540360
C  -1.20434552   7.05627945   1.46624431
H  -1.24089460   7.98827769   2.04854875
H  -0.31887609   6.49104048   1.78830053
H  -1.08205169   7.32401328   0.40798958
C  -3.71105990   7.10270841   1.24077859
H  -3.62636603   7.36890737   0.17808035
H  -3.75770645   8.02889289   1.83196144
H  -4.65186944   6.55379314   1.38071068
C  -2.64290287   5.92093879   3.19561933
H  -1.79236164   5.32870707   3.55637827
H  -2.69014488   6.85519711   3.74035822
O  -1.44600711   3.19857634   2.11191366
N  -0.16457427   4.05795913   0.42604984
C   0.09004488   4.92001542  -0.73805002
C   0.92380699   3.11711744   0.74100088
H   0.86203054   2.82348675   1.79143267
H   1.88383834   3.60803473   0.54314923
H   0.84153649   2.22364625   0.10319160
H   0.78058149   5.73029641  -0.46367043
H  -0.83342897   5.34487422  -1.12814047
H   0.53546380   4.31238604  -1.53401134
C   0.88778091  -2.09086991  -3.02031067
C   1.91526487  -1.61153166  -2.20199598
C   2.91415996  -0.81305525  -2.76647950
C   2.87719533  -0.49861664  -4.12756322
C   1.85192944  -0.99954117  -4.93908251
C   0.85179769  -1.80240450  -4.39055092
H   1.92106668  -1.85069090  -1.14158910
H   3.71405461  -0.42714909  -2.13614724
H   3.64813439   0.13767483  -4.55949581
\[ \begin{align*}
H & \quad 1.82834280 \quad -0.76044063 \quad -6.00145725 \\
H & \quad -1.73268718 \quad 1.47948182 \quad 0.29799580 \\
H & \quad -2.43881839 \quad 2.52416898 \quad -0.95743296 \\
H & \quad -3.38110293 \quad 1.17684755 \quad -0.26741476 \\
\end{align*} \]

\[ \text{\textit{N,N\textsuperscript{\prime}-dimethylthiourea}} \]

COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -2494.50 \]
\[ G = -2445.34 \]

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -1693.14 \]
\[ G = -1643.98 \]

\[ N_{\text{imag}} = 0 \]

\[ \begin{align*}
H & \quad -1.29840416 \quad 2.60553986 \quad 1.38386617 \\
C & \quad -1.00440510 \quad 4.16360933 \quad -0.03417530 \\
N & \quad -1.28990718 \quad 2.79141034 \quad 0.38021423 \\
H & \quad -0.23957514 \quad 4.17614788 \quad -0.82000229 \\
H & \quad -1.83056821 \quad 0.52147254 \quad 1.13152415 \\
C & \quad -1.74322331 \quad 1.81747963 \quad -0.45214533 \\
S & \quad -1.92360906 \quad 2.06693813 \quad -2.13902144 \\
H & \quad -3.39130091 \quad -0.36945765 \quad -1.14190619 \\
N & \quad -2.04134382 \quad 0.63106215 \quad 0.13886860 \\
C & \quad -2.46777898 \quad -0.56586660 \quad -0.58371388 \\
H & \quad -1.90656254 \quad 4.66247370 \quad -0.41460500 \\
H & \quad -0.63226094 \quad 4.70276901 \quad 0.84323888 \\
H & \quad -1.69594077 \quad -0.90079995 \quad -1.29008631 \\
H & \quad -2.65092509 \quad -1.35117231 \quad 0.15698618 \\
\end{align*} \]

\[ \text{\textit{N-methylprop-1-en-2-amine}} \]

COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -2414.85 \]
\[ G = -2357.29 \]

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -1700.75 \]
\[ G = -1643.19 \]

\[ N_{\text{imag}} = 0 \]

C       0.45869183       0.64532042       0.61146429
C       0.18397641       -0.70820309       1.22699344
C       -0.25796532       -1.75900443       0.49384032
N       0.38414484       -0.74664208       2.60320976
C       0.39326492       -2.01958742       3.32164940
H       1.51338360       0.92855619       0.75548732
H       -0.16052635       1.42012134       1.08828912
H       0.24696788       0.63779032       -0.46358073
H       -0.45448832       -1.63157542       -0.56799432
H       -0.44827074       -2.73818729       0.92702894
H       1.04971144       -0.05636863       2.95201914
H       1.11956678       -2.73582162       2.89770231
H       -0.60405870       -2.48058187       3.28406945
H       0.64615661       -1.83035995       4.37079453

Nitromethane

COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -1383.14 \]

\[ G = -1369.87 \]

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -862.37 \]

\[ G = -849.10 \]

\[ N_{\text{imag}} = 0 \]

N       -0.02712591       -0.77332776       1.57667624
O       -0.20698283       0.41947012       1.88903879
O       -0.55345990       -1.74019476       2.16019806
C       0.91218697       -1.07422538       0.44756776
H       1.02873626       -0.17174506       -0.15201661
H       0.49558042       -1.90821424       -0.11948209
H       1.86107334       -1.36722744       0.90786592

thiourea-enamine complex
COSMO(DF)-ZORA-M06-2X/TZ2P//COSMO(DF)-ZORA-BLYP-D3(BJ)/DZP

$E = -4912.82$

$G = -4793.73$

COSMO(DF)-ZORA-BLYP-D3(BJ)/DZP

$E = -3401.12$

$G = -3282.03$

$N_{\text{imag}} = 0$

| Atom | X         | Y         | Z         | E1         |
|------|-----------|-----------|-----------|------------|
| C    | 4.36071095| 1.18833588| 2.99649657|
| C    | 3.92241991| 0.22518470| 1.91390845|
| C    | 4.80445107| -0.32335065| 1.03804071|
| N    | 2.56076377| 0.00091610| 1.89255335|
| C    | 1.96123574| -1.02561574| 1.05207686|
| H    | 4.10080803| 0.79471153| 3.99129580|
| H    | 3.85149148| 2.15717637| 2.88571222|
| H    | 5.44327911| 1.35434309| 2.95828430|
| H    | 5.85648649| -0.05286542| 1.08979724|
| H    | 4.50039900| -1.02250294| 0.26197314|
| H    | 2.04534415| 0.22944050| 2.74788208|
| H    | 2.40450289| -2.02286258| 1.22668037|
| H    | 2.09186471| -0.77780044| -0.01276968|
| H    | 0.88880793| -1.07149287| 1.26770337|
| H    | -0.89905493| 1.62434080| 0.87346927|
| C    | 0.52158960| 2.82123388| 1.90583569|
| N    | -0.45972613| 1.74244994| 1.78759599|
| H    | 0.41922993| 3.31601710| 2.87753971|
| H    | -2.03910934| -0.10514477| 1.48600912|
| C    | -0.64877436| 0.76511417| 2.70922252|
| S    | 0.17130483| 0.75386091| 4.21908857|
| H    | -1.04098168| -1.87710286| 3.56832149|
| N    | -1.51795710| -0.21648863| 2.35695982|
| C    | -1.92083961| -1.31678024| 3.23066891|
| H    | 1.54329705| 2.43206734| 1.80507776|
| H    | 0.32126437| 3.54083300| 1.10477461|
| H    | -2.46263680| -0.94987060| 4.11345114|

S179
thiourea-nitromethane complex
COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP
\[ E = -3880.87 \]
\[ G = -3806.41 \]
COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP
\[ E = -2561.39 \]
\[ G = -2486.93 \]
\[ N_{\text{imag}} = 0 \]

enamine-nitromethane complex
COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

H  -2.57315126  -1.97748750  2.65030556

O  -1.97748750  2.65030556
\[ E = -3800.58 \]
\[ G = -3718.15 \]
COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP
\[ E = -2567.99 \]
\[ G = -2485.56 \]
\[ N_{\text{imag}} = 0 \]

\[
\begin{array}{cccc}
\text{C} & 2.91911475 & 1.52304041 & 0.79245291 \\
\text{C} & 3.25837975 & 0.04861071 & 0.81836397 \\
\text{C} & 4.31011542 & -0.43674982 & 1.52282202 \\
\text{N} & 2.43168762 & -0.73305386 & 0.02005100 \\
\text{C} & 2.54078880 & -2.18883515 & 0.02325678 \\
\text{H} & 1.87171948 & 1.70096575 & 1.07529759 \\
\text{H} & 3.05298718 & 1.92660760 & -0.22270611 \\
\text{H} & 3.56089096 & 2.08229577 & 1.48205307 \\
\text{H} & 4.95137465 & 0.24609723 & 2.07482233 \\
\text{H} & 4.56704783 & -1.49328024 & 1.53993360 \\
\text{H} & 1.48517879 & -0.37300332 & -0.09812341 \\
\text{H} & 2.46097155 & -2.1950953 & 1.03712340 \\
\text{H} & 3.50979085 & -2.49544268 & -0.39691118 \\
\text{H} & 1.74309627 & -2.60319512 & -0.60293091 \\
\text{N} & 0.08838723 & 0.21598094 & 2.42039051 \\
\text{O} & -0.39794282 & 0.19229789 & 1.27175396 \\
\text{O} & 0.11792502 & 1.22704776 & 3.14551289 \\
\text{C} & 0.72286820 & -1.03228536 & 2.94905053 \\
\text{H} & 0.38203124 & -1.87298248 & 2.34573561 \\
\text{H} & 0.44314922 & -1.12789465 & 4.00061946 \\
\text{H} & 1.80558124 & -0.88734440 & 2.85681295
\end{array}
\]

**TS-S1**

COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP
\[ E = -17409.13 \]
\[ G = -16979.26 \]
COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP
\[ E = -11967.08 \]
\( G = -11537.21 \)

\( N_{\text{imag}} = 1, \ 152 \ i \ \text{cm}^{-1} \)

|   |   |   |   |   |
|---|---|---|---|---|
| C | 2.78917925 | 0.49138083 | 0.07559651 |
| C | 3.67859764 | -0.29333689 | 1.05549336 |
| H | 2.92694882 | 1.55300976 | 0.29064614 |
| H | 3.80247741 | -1.33735274 | 0.73082386 |
| C | 3.03842583 | -0.29391092 | 2.45325065 |
| C | 1.28578140 | 0.11762896 | 0.16510783 |
| C | 0.74381596 | -0.46161498 | 1.51159148 |
| C | 1.77146689 | -1.15844216 | 2.39961056 |
| H | 3.73363081 | -0.70066942 | 3.19947531 |
| H | 1.34297355 | -1.31637749 | 3.40040589 |
| H | 2.04831280 | -2.14541449 | 2.00478334 |
| H | -0.11415857 | 11.1437902 | 1.32308639 |
| H | 3.13050952 | 0.32507528 | 0.95467386 |
| H | 4.67109501 | 0.17348612 | 1.08629351 |
| N | 2.66332815 | 1.12897230 | 2.82136212 |
| C | 1.24671909 | 1.39144477 | 3.18317822 |
| H | 0.99082271 | 0.88919858 | 4.13058837 |
| H | 1.12994459 | 2.47080904 | 3.32364674 |
| C | 0.26139640 | 0.89662594 | 2.09481194 |
| C | -1.13667417 | 0.87423652 | 2.72238028 |
| C | 0.46657751 | 1.68075184 | 0.77425894 |
| H | 1.19091569 | 2.49084079 | 0.80750308 |
| N | -0.61819415 | 2.09994595 | -0.03936143 |
| O | -1.69308211 | 1.42831312 | -0.08376623 |
| O | -0.42240363 | 3.08215570 | -0.81739280 |
| S | 1.38483670 | 0.49541451 | -4.22309440 |
| H | -1.88075854 | 3.86393685 | -5.47929946 |
| H | 1.62838340 | 3.06885906 | -4.42022958 |
| C | 0.82593553 | 4.67218652 | -3.16619396 |
| N | 0.88445724 | -0.52939015 | -0.98443284 |
| H | 1.37174543 | -0.2709179 | -1.85137501 |
| C | -0.41825827 | -1.17893389 | -1.20113610 |

S182
C  -0.34029412  -2.71172193  -1.05998063
C  -0.96057112  -0.82622799  -2.60944950
C  -1.73220697  -3.34180702  -1.24996054
H   0.36519325  -3.10186439  -1.81352590
H   0.06997619  -2.96634095  -0.07166596
C  -2.37001627  -1.41434435  -2.79127470
H  -0.28619580  -1.26587786  -3.35642690
N  -0.95600254   0.61411326  -2.86801212
C  -2.34823740  -2.94342057  -2.60381591
H  -1.66442571  -4.43756087  -1.17022061
H  -2.39379075  -2.99989813  -0.43480142
H  -2.74013253  -1.15077670  -3.79324592
H  -3.05177069  -0.95474813  -2.0547904
H  -1.59820484  1.17114274  -2.29618861
C  -0.01006119  1.27562801  -3.58763749
H  -1.75402936  -3.39299717  -3.41782094
H  -3.36993851  -3.34328001  -2.69151017
N  -0.26407706  2.59934302  -3.77276875
H  -1.06389690  2.98407305  -3.26515678
C   0.68534865  3.60055559  -4.27670449
H  -1.12747419  -0.78802198  -0.46341056
S   3.80859679  1.97538730  3.71402748
O   3.33636169  3.36167303  3.81232633
H   5.37515697  -0.11996770  4.96670775
O   5.11745325  1.66320648  3.12952506
C   0.27796335  4.17075053  -5.67762141
C   1.25558311  5.31149954  -6.03606027
H   1.07738678  5.64677614  -7.06804505
H   1.12637115  6.17143832  -5.36616549
H   2.29969470  4.96832170  -5.96757238
C   0.43082924  3.02939015  -6.70863546
H   1.46806611  2.66903057  -6.75149830
H   0.14324122  3.39240432  -7.70651554
H  -0.21158569  2.17687373  -6.45002235
|     | X   | Y   | Z   |
|-----|-----|-----|-----|
| C   | -1.17971415 | 4.67785482 | -5.71527787 |
| H   | -1.33209878 | 5.49287250 | -5.00050041 |
| H   | -1.41355833 | 5.03724915 | -6.72864208 |
| O   | -0.00054599 | 5.59907982 | -3.06491406 |
| N   | 1.87515326  | 4.53376420 | -2.30157037 |
| C   | 2.64514543  | 3.28473547 | -2.17217663 |
| C   | 1.92931685  | 5.43787063 | -1.14134819 |
| H   | 1.49707986  | 6.40260798 | -1.41720833 |
| H   | 2.97530592  | 5.56732605 | -0.84239900 |
| H   | 1.35404989  | 5.01612233 | -0.30288383 |
| H   | 3.44823397  | 3.45435108 | -1.44861205 |
| H   | 3.1013304   | 2.98803603 | -3.12149932 |
| H   | 2.00609411  | 2.47037339 | -1.81458077 |
| C   | 3.73636396  | 1.23490895 | 5.35182359  |
| C   | 2.74618761  | 1.65907094 | 6.24773751  |
| C   | 2.61745190  | 1.00408272 | 7.47481321  |
| C   | 4.45882027  | -0.46795448 | 6.89825241 |
| C   | 4.59895442  | 0.17753409 | 5.66694479  |
| H   | 2.09959197  | 2.49533281 | 5.99504283  |
| H   | 1.85415708  | 1.32891571 | 8.18056222  |
| H   | 3.36247206  | -0.56689814 | 8.75616523 |
| H   | 5.12823810  | -1.28778288 | 7.15509798  |
| H   | -1.12486537 | 0.21160554 | 3.59954871  |
| H   | -1.88421834 | 0.51003027 | 2.01353302  |
| H   | -1.43397345 | 1.88033266 | 3.05336591  |

IntS1
COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -17409.53 \]
\[ G = -16980.34 \]

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -11966.93 \]
\[ G = -11537.74 \]
$N_{\text{imag}} = 0$

C  2.81092479  0.46070285  0.11164401
C  3.68572732 -0.33542139  1.09422622
H  2.96965808  1.52089568  0.32327310
H  3.79822197 -1.38020922  0.76745880
C  3.03967832 -0.33548699  2.49019776
C  1.29527310  0.11794497  0.19979873
C  0.75260650 -0.49098455  1.53763584
C  1.76957475 -1.19380207  2.43073119
H  3.73142632 -0.74600952  3.23736732
H  1.33567096 -1.34927980  3.42982351
H  2.04312743 -2.18218552  2.03726373
H -0.10704639 -1.13782858  1.33795704
H  3.14836042  0.28575797 -0.91862712
H  4.68443920  0.11781360  1.13211223
N  2.66811825  1.08794903  2.86262313
C  1.24901799  1.35912352  3.21330098
H  0.98149683  0.85733955  4.15766545
H  1.13885870  2.43928436  3.3592357
C  0.27139184  0.87038117  2.11580466
C -1.13887437  0.86844792  2.71433494
C  0.51813689  1.62818283  0.78462511
H  1.24407265  2.43665362  0.83529392
N -0.55322867  2.08819502 -0.0502354
O -1.65675441  1.47254476 -0.08243908
O -0.29933121  3.04484277 -0.83486198
S  1.41401212  0.51655197 -4.19507047
H -1.92276356  3.84303883 -5.55958613
H  1.58076286  3.07062559 -4.46889487
C  0.74709192  4.64837636 -3.19949790
N  0.90354520 -0.54387752 -0.96249998
H  1.35848215 -0.22783957 -1.82795655
C -0.41130974 -1.17395396 -1.17863625
C -0.35111446 -2.70570462 -1.01164232
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| C       | -0.93858353| -0.84077505| -2.59634356|
| C       | -1.74227329| -3.33309757| -1.2089206 |
| H       | 0.36158729 | -3.11117328| -1.75037773|
| H       | 0.04764718 | -2.94796719| -0.01574842|
| C       | -2.34378405| -1.43513039| -2.79511600|
| H       | -0.25075610| -1.28065249| -3.33094006|
| N       | -0.94596039| 0.59864838 | -2.86780948|
| C       | -2.33003046| -2.96018286| -2.58184650|
| H       | -1.68274650| -4.42723659| -1.10337417|
| H       | -2.41664894| -2.96923795| -0.41379574|
| H       | -2.69490623| -1.18667102| -3.80781083|
| H       | -3.03911922| -0.96321090| -2.07914299|
| H       | -1.61380337| 1.15330549 | -2.32423997|
| C       | -0.01747886| 1.26663437 | -3.60074108|
| H       | -1.71981225| -3.42586132| -3.37475911|
| H       | -3.35089025| -3.35878704| -2.68431074|
| N       | -0.31428071| 2.57127438 | -3.84257138|
| H       | -1.13687207| 2.94916158 | -3.36661989|
| C       | 0.63246643 | 3.58771291 | -4.31775186|
| H       | -1.12634740| -0.76517834| -0.45500493|
| S       | 3.81063139 | 1.92143728 | 3.77005108 |
| O       | 3.34824481 | 3.31102522 | 3.87139461 |
| H       | 5.34962334 | -0.19134703| 5.02859489 |
| O       | 5.12277651 | 1.60247333 | 3.19659102 |
| C       | 0.23603394 | 4.17732650 | -5.71526774|
| C       | 1.20253413 | 5.33751693 | -6.03753130|
| H       | 1.02890495 | 5.69641713 | -7.06225835|
| H       | 1.05557204 | 6.17992843 | -5.34844381|
| H       | 2.25022417 | 5.00693960 | -5.96639771|
| C       | 0.42019688 | 3.05248651 | -6.75944770|
| H       | 1.46463832 | 2.71231240 | -6.79612255|
| H       | 0.13590993 | 3.42109362 | -7.75671250|
| H       | -0.20907012| 2.18550008 | -6.51638401|
| C       | -1.22634392| 4.66845602 | -5.76766350|

S186
|   | X          | Y          | Z          |
|---|------------|------------|------------|
| H | -1.40037797 | 5.46779247 | -5.04005510 |
| H | -1.44668015 | 5.04481260 | -6.77787513 |
| O | -0.15399495 | 5.49714564 | -3.04766405 |
| N | 1.85769985  | 4.62707667 | -2.40733370 |
| C | 2.77751056  | 3.49361107 | -2.24704933 |
| C | 1.94252411  | 5.61934816 | -1.32546375 |
| H | 1.47468155  | 6.55338777 | -1.64590449 |
| H | 2.99947915  | 5.78936702 | -1.08947968 |
| H | 1.42359862  | 5.24748628 | -0.42793903 |
| H | 3.81679626  | 3.83896754 | -2.33758731 |
| H | 2.59061506  | 2.70512558 | -2.97633251 |
| H | 2.63348576  | 3.06033468 | -1.24831963 |
| C | 3.71722300  | 1.17384143 |  5.40379098 |
| C | 2.72146280  | 1.60128685 |  6.29199411 |
| C | 2.57530542  | 0.94140588 |  7.51449277 |
| C | 3.41450070  | -0.13038518|  7.84099779 |
| C | 4.41155801  | -0.54144339|  6.94937155 |
| C | 4.56862313  |  0.10854150|  5.72242772 |
| H | 2.08420517  |  2.44411791|  6.03742892 |
| H | 1.80763328  |  1.26885758|  8.21424326 |
| H | 3.29608532  | -0.64089013|  8.79588142 |
| H | 5.07253058  | -1.36720064|  7.20905794 |
| H | -1.14458101 |  0.24252615|  3.61805808 |
| H | -1.87032882 |  0.47131783|  2.00580315 |
| H | -1.44833755 |  1.88564117|  2.99627810 |

**IntS2**

COSMO(DCM)-ZORA-M06-2X/TZ2P/COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -17426.00 \]

\[ G = -16994.81 \]

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -11979.40 \]

\[ G = -11548.21 \]

\[ N_{imag} = 0 \]
C        1.25252520       1.33794826       -0.54195907
C        2.74386788       1.31322369       -0.93833524
H        1.06625501       2.04405444        0.26871955
H        2.84494780       0.85583593       -1.93448159
C        3.62742310       0.49340935        0.02379185
C        0.71954889       -0.03753980       -0.10962740
C        1.64950478       -0.78599746        0.86215822
C        3.04011447       -0.90968021        0.21717074
H        4.63333983       0.43487829       -0.40234951
H        3.70193452       -1.52638329        0.83622883
H        2.94054418       -1.39725841       -0.76127507
H        1.22402820       -1.78772007        1.01923261
H        0.64817477       1.68854535       -1.38890349
H        3.13188177       2.33934681       -1.00476815
N        3.76629176        1.18010933        1.34378823
C        2.59202950       1.21351958        2.24377132
H        2.93558088       1.42608512        3.26147804
H        1.95486873       2.05505048        1.95156856
C        1.74741458       -0.11286075        2.26159743
C        2.37904778       -1.11968754        3.25632674
C        0.38341230       0.24145860        2.78331738
H        0.21945996       0.40665301        3.84560257
N       -0.68624686       0.38107033        2.05154785
O       -0.61899278       0.19267383        0.60159629
O       -1.86961151       0.63785520        2.40725852
S       -1.73082023       0.94337344       -3.50838138
H       -4.46157987       2.88920854        0.37732446
H       -1.94707515       3.16650329       -2.41691067
C       -1.11197815       3.66604352       -0.45007159
N        0.41211268       -0.81281973       -1.26741232
H        0.11626472       -0.21496984       -2.04513460
C       -0.47215289       -1.98949182       -1.13553412
C        0.17906869       -3.26434401       -1.70113495
C       -1.84335139       -1.74599027       -1.83345215

S188
|   |   |   |   |
|---|---|---|---|
| H | -5.09936455 | 4.53752203 | 0.17749805 |
| O | -1.16589106 | 3.40583342 | 0.76793910 |
| N | -0.08498473 | 4.37498975 | -1.00224528 |
| C | 0.12807894 | 4.63404673 | -2.43190085 |
| H | 0.65161673 | 4.77707033 | 0.91844796 |
| H | 1.05495510 | 6.01307807 | -0.31892635 |
| H | 1.91350668 | 4.44823393 | -0.30982051 |
| H | -0.15152561 | 5.66628495 | -2.69003474 |
| H | -0.43497234 | 3.93764487 | -3.05434285 |
| H | 1.19530461 | 4.49642264 | -2.65349719 |
| C | 5.75334461 | 0.05001835 | 2.83680441 |
| C | 5.60222386 | -0.13508621 | 4.22413868 |
| C | 5.86288488 | -1.35099095 | 4.86215005 |
| C | 6.26689523 | -2.46363311 | 4.11749288 |
| C | 6.43067223 | -2.36051462 | 2.72997220 |
| C | 6.17938646 | -1.15039617 | 2.08161307 |
| H | 5.28049340 | 0.73552375 | 4.78980721 |
| H | 5.74487410 | -1.42814703 | 5.94213472 |
| H | 6.46126339 | -3.41155403 | 4.61772470 |
| H | 6.75766571 | -3.22368448 | 2.15157059 |
| H | 3.40567309 | -1.36538889 | 2.97020103 |
| H | 1.79054249 | -2.04693001 | 3.28202770 |
| H | 2.40516673 | -0.69289517 | 4.26784684 |

**TS-S2**

COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -20584.81 \]

\[ G = -20094.20 \]

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -14160.87 \]

\[ G = -13670.26 \]

\[ N_{\text{imag}} = 1, 1414i \text{ cm}^{-1} \]

| C | 2.39622631 | -1.48832843 | -1.30837674 |

S190
| Attrib  | X-coordinate  | Y-coordinate  | Z-coordinate  |
|--------|---------------|---------------|---------------|
| C      | 3.78815221    | -2.15571839   | -1.41143695   |
| H      | 2.47901121    | -0.49179599   | -0.85907996   |
| H      | 3.74884265    | -2.95528667   | -2.16647116   |
| C      | 4.22808252    | -2.78719270   | -0.08119438   |
| C      | 1.43349596    | -2.26769944   | -0.45833943   |
| C      | 1.88061379    | -2.86346345   | 0.85836371    |
| C      | 3.12158898    | -3.71709624   | 0.43586482    |
| H      | 5.14032662    | -3.36248672   | -0.26529833   |
| H      | 3.45760914    | -4.32188464   | 1.28286581    |
| H      | 2.84154892    | -4.41306973   | -0.36818800   |
| H      | 1.10411972    | -3.52992784   | 1.24825287    |
| H      | 1.96477406    | -1.33524782   | -2.30658088   |
| H      | 4.52960119    | -1.41685799   | -1.73829732   |
| N      | 4.57200251    | -1.73805801   | 0.92132329    |
| C      | 3.48669434    | -1.00664093   | 1.62691291    |
| H      | 3.91241856    | -0.54437978   | 2.52344877    |
| H      | 3.13330157    | -0.18802352   | 0.98777792    |
| C      | 2.30326723    | -1.91945834   | 2.04617955    |
| C      | 2.72919823    | -2.82465620   | 3.23557721    |
| C      | 1.17583020    | -1.05794104   | 2.62976960    |
| H      | 1.42300973    | -0.63673201   | 3.60804582    |
| N      | 0.57196230    | -0.06176778   | 1.85567397    |
| O      | 0.48633447    | -0.23955938   | 0.58757129    |
| O      | 0.00018010    | 0.92546464    | 2.40403370    |
| S      | -1.23573720   | -1.03501539   | -3.55641362   |
| H      | -1.02621085   | 3.26213050    | -0.55205494   |
| H      | -0.23731263   | 1.26514032    | -3.65615088   |
| C      | 1.51978731    | 1.59498127    | -2.39362434   |
| N      | 0.32406608    | -2.65159544   | -1.02944228   |
| H      | 0.16886413    | -2.35001247   | -2.00849262   |
| C      | -0.88211578   | -3.18066136   | -0.36401210   |
| C      | -1.09328886   | -4.68174220   | -0.60502371   |
| C      | -2.11389691   | -2.39170459   | -0.88401449   |
| C      | -2.34785774   | -5.15014949   | 0.15633984    |
|    |          |          |          |
|----|----------|----------|----------|
| H  | -1.19946146 | -4.85301735 | -1.68882202 |
| H  | -0.21002943 | -5.24046667 | -0.26267916 |
| C  | -3.32217068 | -2.77125824 | -0.02065320 |
| H  | -2.30306316 | -2.68502910 | -1.92411699 |
| N  | -1.86383296 | -0.94494891 | -0.91629294 |
| C  | -3.59361586 | -4.28753365 | -0.13565491 |
| H  | -2.55664276 | -6.20177123 | -0.09194880 |
| H  | -2.12419405 | -5.11765890 | 1.22725625  |
| H  | -4.19869613 | -2.19782814 | -0.35610665 |
| H  | -3.12540751 | -2.49467856 | 1.02571391  |
| H  | -1.64972932 | -0.52522604 | -0.00529080 |
| C  | -1.26385850 | -0.32541325 | -1.98408845 |
| H  | -3.95330342 | -4.49894932 | -1.15678337 |
| H  | -4.39997284 | -4.56710115 | 0.5585035   |
| N  | -0.69032982 | 0.86798700  | -1.69870671 |
| H  | -0.37196007 | 0.98785355  | -0.72691695 |
| C  | 0.00927895 | 1.69304952  | -2.68611883 |
| H  | -0.76599388 | -2.98062107 | 0.70557069  |
| S  | 6.13079029 | -1.64731627 | 1.50419941  |
| O  | 6.30759269 | -0.30289933 | 2.06622531  |
| H  | 6.41023288 | -4.53029391 | 1.56502572  |
| O  | 7.01213660 | -2.15031477 | 0.44174295  |
| C  | -0.51909882 | 3.16972151  | -2.68445681 |
| C  | 0.31181819 | 3.98626508  | -3.69748418 |
| H  | -0.07327095 | 5.01461286  | -3.75212108 |
| H  | 1.36958947 | 4.03685604  | -3.40245574 |
| H  | 0.25196876 | 3.54808346  | -4.70413303 |
| C  | -1.99444462 | 3.12793304 | -3.14093207 |
| H  | -2.08172999 | 2.69657056  | -4.14899988 |
| H  | -2.41006476 | 4.14576513  | -3.16243904 |
| H  | -2.59947925 | 2.52152159  | -2.45291377 |
| C  | -0.42880509 | 3.81860013  | -1.28788223 |
| H  | 0.60736491 | 3.85493447  | -0.93157568 |
| H  | -0.82556631 | 4.84339215  | -1.33661846 |
|   | X         | Y         | Z         |
|---|-----------|-----------|-----------|
| O | 1.92284037| 1.78862985| -1.22908588|
| N | 2.36512201| 1.27368871| -3.41623814|
| C | 1.98258015| 1.03014057| -4.81449009|
| C | 3.81546858| 1.30207523| -3.17504257|
| H | 3.99540104| 1.48194316| -2.11366758|
| H | 4.27911230| 2.10328818| -3.77021770|
| H | 4.25783551| 0.34270333| -3.47463072|
| H | 2.09905318| 1.94136926| -5.41981975|
| H | 0.95819311| 0.66256789| -4.8830121 |
| H | 2.64622194| 0.25575005| -5.2206798 |
| C | 6.19617866| -2.81648725| 2.87140909|
| C | 6.05136570| -2.35259685| 4.18215577|
| C | 5.96317159| -3.27960690| 5.22402704|
| C | 6.01817321| -4.65028096| 4.95288438|
| C | 6.18126666| -5.10155612| 3.63685598|
| C | 6.27712307| -4.18622438| 2.58764592|
| H | 5.99888992| -1.28473078| 4.37828857|
| H | 5.84522396| -2.92811893| 6.24816400|
| H | 5.93944135| -5.36950053| 5.76711457|
| H | 6.23629450| -6.16900950| 3.42693518|
| H | 3.63565191| -3.39284147| 3.02189650|
| H | 1.91682672| -3.51298159| 3.48210101|
| H | 2.93926595| -2.19856660| 4.11205264|
| H | -0.00805773| -1.88184734| 2.94410135|
| O | -0.32558604| -4.32126381| 3.01682097|
| O | -1.13985757| -2.20692560| 3.21667697|
| C | -1.24892358| -3.52010047| 3.25236808|
| H | -2.03193146| -6.06893382| 3.60599480|
| C | -2.64713169| -4.00995267| 3.53559430|
| C | -3.73345140| -3.12277559| 3.58942489|
| C | -5.03467667| -3.60905848| 3.73389699|
| C | -5.26057234| -4.98636727| 3.83798571|
| C | -4.17854111| -5.87517564| 3.80720912|
| C | -2.87961641| -5.38869212| 3.65678451|
H  -3.55168047    -2.05480209    3.49759199
H  -5.87397589    -2.91449125    3.75808562
H  -6.27674972    -5.36679111    3.94043388
H  -4.35141400    -6.94793512    3.88993078

IntS3
COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -17426.76 \]
\[ G = -16997.18 \]

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -11988.04 \]
\[ G = -11558.46 \]

\[ N_{\text{imag}} = 0 \]

C  2.46011432    -0.24154383    -2.36313466
C  3.93494781    -0.08962819    -1.91926645
H  2.00943855    0.76345088    -2.49602579
H  4.50213530    -0.96419387    -2.27087916
C  4.13793088    -0.01243474    -0.39580515
C  1.56295794    -0.96189529    -1.41290071
C  1.88593590    -0.99207950    0.07060194
C  3.40108789    -1.17464114    0.27135403
H  5.21215056    -0.07112879    -0.19875939
H  3.63419068    -1.23547264    1.33977399
H  3.72396535    -2.12016594    -0.18846587
H  1.34239999    -1.82973161    0.51832065
H  2.41417444    -0.69917454    -3.35649488
H  4.36382953    0.79855419    -2.40076595
N  3.67247688    1.28781528    0.16624535
C  2.21998411    1.54082617    0.28091882
H  2.06480961    2.38755498    0.95512701
H  1.84593019    1.86237141    -0.70089659
C  1.38311666    0.32037746    0.78909542
C  1.52487134    0.13453424    2.32217191
C  -0.04379611    0.70316307    0.46712763
| Element | X-Coordinate | Y-Coordinate | Z-Coordinate |
|---------|--------------|--------------|--------------|
| H       | -0.28732379  | 1.75581803   | 0.45215585   |
| N       | -1.07896648  | -0.08295221  | 0.27125461   |
| O       | -2.23696482  | 0.41942460   | -0.14571106  |
| O       | -1.00581787  | -1.41413119  | 0.39657151   |
| S       | 0.71655960   | 2.74593825   | -3.56569799  |
| H       | -3.71883755  | 3.66225448   | -1.13336811  |
| H       | -0.16416000  | 4.50916047   | -2.05354048  |
| C       | -0.39918445  | 4.26513588   | 0.10461854   |
| N       | 0.44362611   | -1.51928054  | -1.75754519  |
| H       | -0.18644641  | -1.76101403  | -0.91613616  |
| C       | -0.25571454  | -1.54867495  | -3.06284573  |
| C       | 0.38182570   | -2.52836118  | -4.06707245  |
| C       | -0.44889330  | -0.14960441  | -3.69601264  |
| C       | -0.50659557  | -2.64211138  | -5.31999598  |
| H       | 1.38149115   | -2.17189045  | -4.35591395  |
| H       | 0.50556117   | -3.50693367  | -3.58170665  |
| C       | -1.36731464  | -0.28219407  | -4.92697556  |
| H       | 0.51196696   | 0.24647798   | -4.03933900  |
| N       | -0.96553719  | 0.80074107   | -2.71744760  |
| C       | -0.76886643  | -1.26273971  | -5.95130940  |
| H       | -0.02554643  | -3.31295402  | -6.04732489  |
| H       | -1.46768099  | -3.10428867  | -5.03770913  |
| H       | -1.49089297  | 0.71857054   | -5.36592731  |
| H       | -2.36192362  | -0.62871573  | -4.59954477  |
| H       | -1.67353297  | 0.48175580   | -2.03275507  |
| C       | -0.56086939  | 2.09139968   | -2.60824671  |
| H       | 0.18081083   | -0.84925627  | -6.3243910   |
| H       | -1.44548649  | -1.36242898  | -6.81324121  |
| N       | -1.22954622  | 2.81287419   | -1.67216578  |
| H       | -1.81777132  | 2.27700584   | -1.01523155  |
| C       | -0.92658538  | 4.20214806   | -1.33947679  |
| H       | -1.25224727  | -1.93736925  | -2.80129074  |
| S       | 4.73488672   | 2.25035840   | 1.01589509   |
| O       | 4.21248426   | 3.62181086   | 0.97309147   |

S195
S196
H  2.56109721  -0.02641298  2.63342239
H  0.91859931  -0.72334234  2.64243833
H  1.15377813  1.03285172  2.83154317

TS-S3
COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP
\[ E = -17424.09 \]
\[ G = -16996.88 \]
COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP
\[ E = -11985.11 \]
\[ G = -11557.90 \]
\[ N_{imag} = 1, \ 700 \text{ i cm}^{-1} \]

|   |   |   |
|---|---|---|
| C | 2.46387647 | -0.28022707 | -2.36595629 |
| C | 3.93749214 | -0.16555289 | -1.91052704 |
| H | 2.04327648 | 0.73365235  | -2.49071090 |
| H | 4.48569986 | -1.06234082 | -2.23710155 |
| C | 1.53215232 | -1.00616946 | -1.43031261 |
| C | 3.37136473 | -1.21777741 | 0.28424958  |
| H | 5.19301963 | -0.12532765 | -0.17203082 |
| H | 6.0025631 | -1.27326430 | 1.35431073  |
| H | 3.69205048 | -2.16812380 | -0.16740516 |
| H | 1.32249219 | -1.87450540 | 0.51204102  |
| H | 2.42361065 | -0.72865505 | -3.3632698 |
| H | 4.4005023 | 0.70128821  | -2.40066565 |
| N | 3.65133602 | 1.24324530  | 0.15053609  |
| C | 2.19975187 | 1.49988577  | 0.26535675  |
| H | 2.04741634 | 2.35071364  | 0.93576677  |
| H | 1.82283936 | 1.81485375  | -0.71737216 |
| C | 1.36552364 | 0.27851623  | 0.78409814  |
| C | 1.50792075 | 0.11161797  | 2.32045038  |
| C | -0.06309685 | 0.68816835  | 0.49694888  |
| H | -0.28989852 | 1.74774499  | 0.55203555  |

S197
| N  | -1.12260763 | -0.03590410 | 0.26203957 |
| O  | -2.28056545 | 0.45707042  | -0.06719509 |
| O  | -1.04761874 | -1.43755293 | 0.28028714  |
| S  | 0.72890521  | 2.76398717  | -3.56211925 |
| H  | -3.68430183 | 3.63140670  | -1.00242858 |
| H  | -0.17026516 | 4.51206324  | -2.05966858 |
| C  | -0.33904439 | 4.25104417  | 0.10177120  |
| N  | 0.40553438  | -1.54178276 | -1.75269145 |
| H  | -0.42072885 | -1.65358623 | -0.67162080 |
| C  | -0.25081073 | -1.54643578 | -3.07506869 |
| C  | 0.38822463  | -2.53345322 | -4.07467708 |
| C  | -0.41678053 | -0.14632144 | -3.71761784 |
| C  | -0.47246326 | -2.63198505 | -5.34763960 |
| H  | 1.40079830  | -2.19579674 | -4.34048487 |
| H  | 0.48538545  | -3.51526028 | -3.58881083 |
| C  | -1.30681632 | -0.25981504 | -4.97015674 |
| H  | 0.55411420  | 0.24770814  | -4.03062803 |
| N  | -0.95255555 | 0.80782731  | -2.74676297 |
| C  | -0.69798198 | -1.24728724 | -5.98191233 |
| H  | 0.01175794  | -3.30934322 | -6.06735941 |
| H  | -1.44803265 | -3.07772755 | -5.08848149 |
| H  | -1.40802191 | 0.74291678  | -5.41081670 |
| H  | -2.31338895 | -0.59544139 | -4.66821528 |
| H  | -1.70685384 | 0.49185453  | -2.12316372 |
| C  | -0.54466624 | 2.09506659  | -2.61405529 |
| H  | 0.26769737  | -0.84752920 | -6.33708343 |
| H  | -1.35353902 | -1.33358442 | -6.86174329 |
| N  | -1.20864978 | 2.80518301  | -1.66339707 |
| H  | -1.81090474 | 2.27639510  | -1.01727774 |
| C  | -0.90908659 | 4.19415429  | -1.32568656 |
| H  | -1.26581717 | -1.92152517 | -2.85984742 |
| S  | 4.71067345  | 2.22786401  | 0.97798413  |
| O  | 4.18954095  | 3.59824070  | 0.89784599  |
| H  | 5.86748879  | -0.01098373 | 2.39474694  |

S198
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| O    | 6.05916434| 1.90234910| 0.49659996|
| C    | -2.16011812| 5.12622536| -1.50849252|
| C    | -1.77347227| 6.55616798| -1.07313531|
| H    | -2.61154328| 7.24270344| -1.26140014|
| H    | -1.53424268| 6.60037168| -0.00120794|
| H    | -0.90349139| 6.92042130| -1.63844710|
| C    | -2.51658987| 5.12291328| -3.01173694|
| H    | -1.67835110| 5.49983211| -3.61526870|
| H    | -3.39170055| 5.76430021| -3.19087286|
| H    | -2.75567632| 4.10688002| -3.35438360|
| C    | -3.37418787| 4.63911800| -0.69109154|
| H    | -3.14868972| 4.61474219| 0.38154377|
| H    | -4.22361680| 5.31699151| -0.86162946|
| O    | -0.96575636| 3.68742780| 1.02675859|
| N    | 0.82917888 | 4.91574923 | 0.31527897 |
| C    | 1.68035788 | 5.52825431 | -0.71629611|
| C    | 1.28291432 | 5.13933067 | 1.69716655|
| H    | 1.27670090 | 6.21760233 | 1.91812363|
| H    | 2.30594169 | 4.76358507 | 1.80622980|
| H    | 0.60880735 | 4.61854065 | 2.38008996|
| H    | 2.72586393 | 5.37194632 | -0.42512608|
| H    | 1.48756499 | 6.60844413 | -0.79515090|
| H    | 1.53040908 | 5.05165668 | -1.68656517|
| C    | 4.59610604 | 1.71428563 | 2.69978363|
| C    | 3.79676356 | 2.43876607 | 3.58837237|
| C    | 3.61591609 | 1.95679883 | 4.88761296|
| C    | 4.22975925 | 0.76585529 | 5.28693071|
| C    | 5.04357455 | 0.05856978 | 4.39239208|
| C    | 5.23409986 | 0.53068577 | 3.09311473|
| H    | 3.32399174 | 3.36157101 | 3.26713943|
| H    | 2.99091416 | 2.51244182 | 5.58550415|
| H    | 4.08052154 | 0.38959762 | 6.29811961|
| H    | 5.53144736 | -0.86281393| 4.70748634|
| H    | 2.54801444 | -0.03451196| 2.62432973|

S199
IntS4

COSMO(DCM)-ZORA-M06-2X/TZ2P/COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -17424.04 \]

\[ G = -16995.45 \]

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -11985.23 \]

\[ G = -11556.64 \]

\[ N_{\text{imag}} = 0 \]

\[
\begin{array}{ccc}
\text{C} & 2.45693649 & -0.27696960 \\
\text{C} & 3.93172019 & -0.17182570 \\
\text{H} & 2.04284790 & 0.73893337 \\
\text{H} & 4.47474698 & -1.07154584 \\
\text{C} & 4.11815500 & -0.07624186 \\
\text{C} & 1.52092925 & -1.00775623 \\
\text{C} & 1.85175339 & -1.03227563 \\
\text{C} & 3.36258223 & -1.22269084 \\
\text{H} & 5.18866812 & -0.13750247 \\
\text{H} & 3.59221060 & -1.27922871 \\
\text{H} & 3.67956163 & -2.17414179 \\
\text{H} & 1.31299800 & -1.87300704 \\
\text{H} & 2.41676380 & -0.72276774 \\
\text{H} & 4.40019693 & 0.69273717 \\
\text{N} & 3.65203945 & 1.23718768 \\
\text{C} & 2.20201959 & 1.49931986 \\
\text{H} & 2.05161345 & 2.35225444 \\
\text{H} & 1.82707038 & 1.81248583 \\
\text{C} & 1.36405187 & 0.28130613 \\
\text{C} & 1.50742194 & 0.11747577 \\
\text{C} & -0.06260363 & 0.69963289 \\
\text{H} & -0.28061254 & 1.76213050 \\
\text{N} & -1.13118097 & -0.01194797 \\
\end{array}
\]

\[ E = -17424.04 \]

\[ G = -16995.45 \]

\[ E = -11985.23 \]

\[ G = -11556.64 \]

\[ N_{\text{imag}} = 0 \]
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| O       | -2.28743719 | 0.47281518 | -0.04090319 |
| O       | -1.06309954 | -1.42921396 | 0.32563019 |
| S       | 0.72693202 | 2.76778707 | -3.56305893 |
| H       | -3.69796601 | 3.62552452 | -1.03676479 |
| H       | -0.17772918 | 4.52008708 | -2.06188747 |
| C       | -0.33990167 | 4.25305176 | 0.09923608 |
| N       | 0.39770504 | -1.54898466 | -1.74776803 |
| H       | -0.47942675 | -1.65242829 | -0.58492890 |
| C       | -0.25037689 | -1.54674183 | -3.07406662 |
| C       | 0.39027768 | -2.53092485 | -4.07599698 |
| C       | -0.41442183 | -0.14603144 | -3.71626824 |
| C       | -0.46868425 | -2.62794235 | -5.35040125 |
| H       | 1.40312392 | -2.19243966 | -4.33979950 |
| H       | 0.48754826 | -3.51387238 | -3.59225998 |
| C       | -1.30498513 | -0.25655340 | -4.96861068 |
| H       | 0.55644333 | -0.24762920 | -4.02915377 |
| N       | -0.94841237 | 0.80865646 | -2.74406922 |
| C       | -0.69592900 | -1.24223071 | -5.98221373 |
| H       | 0.01687878 | -3.30288044 | -6.07159675 |
| H       | -1.44397747 | -3.07555818 | -5.09326699 |
| H       | -1.40665750 | 0.74672159 | -5.40803904 |
| H       | -2.31144729 | -0.59328079 | -4.66737231 |
| H       | -1.71266356 | 0.49547472 | -2.13290875 |
| C       | -0.54479632 | 2.09745370 | -2.61455709 |
| H       | 0.26916641 | -0.84090893 | -6.33724658 |
| H       | -1.35184999 | -1.32771555 | -6.86191956 |
| N       | -1.21102127 | 2.80856414 | -1.66551456 |
| H       | -1.81624292 | 2.28266761 | -1.02082025 |
| C       | -0.91396936 | 4.19812498 | -1.32687139 |
| H       | -1.26770229 | -1.92212659 | -2.86872424 |
| S       | 4.71405278 | 2.22178605 | 0.97763609 |
| O       | 4.19486270 | 3.59279257 | 0.89519288 |
| H       | 5.86667783 | -0.01759847 | 2.39738966 |
| O       | 6.06130321 | 1.89322362 | 0.49492863 |
C  -2.16816905  5.12705962  -1.50378563  
C  -1.79034248  6.55280133  -1.04753938  
H  -2.62942471  7.23839837  -1.23385844  
H  -1.55982800  6.58441170  0.02676925  
H  -0.91749419  6.92738609  -1.60150382  
C  -2.51671055  5.14172055  -3.00868801  
H  -1.68299076  5.54525667  -3.60114941  
H  -3.40353996  5.76837135  -3.18248098  
H  -2.73378086  4.12682934  -3.36908554  
C  -3.38421172  4.62371216  -0.69923903  
H  -3.15865012  4.57130405  0.37235927  
H  -4.23113957  5.30872494  -0.85260630  
O  -0.96772180  3.69497788  1.02720034  
N  0.83589770  4.90563704  0.30617679  
C  1.68099057  5.51233814  -0.73470377  
C  1.29507871  5.13289505  1.68578600  
H  1.28226991  6.21104298  1.90734224  
H  2.32102550  4.76389495  1.78948338  
H  0.62794759  4.60748144  2.37193215  
H  2.72609840  5.40030695  -0.42399291  
H  1.45509199  6.58218804  -0.85449961  
H  1.56076752  4.99598926  -1.68934587  
C  4.60125518  1.71234832  2.70081210  
C  3.80512484  2.44086127  3.58899845  
C  3.62468967  1.96206463  4.88949510  
C  4.23505151  0.76979016  5.29016681  
C  5.04536873  0.05820437  4.39585163  
C  5.23602983  0.52746987  3.09557473  
H  3.33429864  3.36424466  3.26645799  
H  3.00212499  2.52085569  5.58705469  
H  4.08570376  0.39573334  6.30215535  
H  5.53036764  -0.86437316  4.71189623  
H  2.54888285  -0.02267074  2.62593425  
H  0.91989541  -0.74812210  2.65818909  

S202
TS-S4

COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -20581.89 \]
\[ G = -20090.25 \]

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -14154.72 \]
\[ G = -13663.08 \]

\[ N_{\text{imag}} = 1, \ 1033 \text{i cm}^{-1} \]

\[
\begin{align*}
\text{C} & : -2.11545934 \quad -3.38097199 \quad -0.35228796 \\
\text{C} & : -2.22338540 \quad -4.91891891 \quad -0.24642095 \\
\text{H} & : -1.18950909 \quad -6.51195867 \quad 0.80787110 \\
\text{H} & : -3.21591010 \quad -5.19301796 \quad 0.12592277 \\
\text{H} & : -2.11054509 \quad -5.36793447 \quad -1.24441090 \\
\text{H} & : -2.91906859 \quad -2.99791733 \quad -0.99028044 \\
\text{H} & : 1.22639733 \quad -3.67722892 \quad -1.25012721 \\
\text{H} & : 1.05317582 \quad -5.32900822 \quad 0.79217275 \\
\text{N} & : -1.27387680 \quad -4.82797567 \quad 2.02981139 \\
\text{C} & : -1.36003334 \quad -3.35704705 \quad 2.12347346 \\
\text{H} & : -1.70200154 \quad -3.08164194 \quad 3.12574853 \\
\text{H} & : -0.34587443 \quad -2.95415747 \quad 2.05179294 \\
\text{C} & : -2.28891666 \quad -2.68772451 \quad 1.06378555 \\
\text{C} & : -3.78062915 \quad -2.82609857 \quad 1.45127795 \\
\text{C} & : -1.85157654 \quad -1.20846616 \quad 1.07988358 \\
\text{H} & : -0.82394199 \quad -1.03242492 \quad 1.40121482 \\
\text{N} & : -2.16843404 \quad -0.35919262 \quad 0.01879445 \\
\text{O} & : -1.49763069 \quad 0.73397103 \quad -0.11303615
\end{align*}
\]

\text{S203}
|   | O     | S     | H    | H    | C     | N     | H    | H    | H    | C     |
|---|-------|-------|------|------|-------|-------|------|------|------|-------|
| X | -3.12080714 | -3.27627649 | -0.80884672 | 2.91696022 | 1.62215799 | -0.83168909 | -1.76174545 | 0.24196413 | 0.63568605 | 1.48651836 |
| Y | -0.62216311 | -0.62216311 | 1.89666751 | 0.93386532 | -0.60754716 | -2.17021019 | -1.76392280 | -1.59926342 | -2.57124987 | -1.10177320 |
| Z | -0.78323728 | -3.12080714 | 2.32804267 | 2.41672121 | 3.27445073 | -1.95909908 | -2.13937437 | -2.82199006 | -3.95076908 | -2.06094928 |
|   |       |       |       |       |       |       |       |       |       |       |
|   | S     | S     | O    | H    | C     | N     | H    | H    | C     | S     |
| X | 1.22155799 | 1.33686809 | 2.91696022 | 1.62215799 | 1.48651836 | 1.59006876 | 1.12628085 | 0.24196413 | -0.7293217 |
| Y | -0.60754716 | -0.60754716 | 0.93386532 | -2.17021019 | -1.10177320 | -1.76392280 | -1.59926342 | -2.57124987 | -2.53828103 |
| Z | 3.27445073 | 3.27445073 | 2.41672121 | 3.27445073 | 2.06094928 | 1.76392280 | 1.59926342 | 3.95076908 | 3.05642389 |
|   |       |       |       |       |       |       |       |       |       |       |
|   | O     | S     | H    | H    | C     | N     | H    | H    | H    | C     |
| X | -2.17021019 | -1.95909908 | -2.13937437 | -2.82199006 | -3.95076908 | -2.06094928 | -4.46611244 | -3.5642389 | -3.05642389 |
| Y | -2.17021019 | -2.17021019 | -2.13937437 | -2.82199006 | -3.95076908 | -2.06094928 | -4.46611244 | -3.5642389 | -3.05642389 |
| Z | -1.95909908 | -1.95909908 | -2.13937437 | -2.82199006 | -3.95076908 | -2.06094928 | -4.46611244 | -3.5642389 | -3.05642389 |
|   |       |       |       |       |       |       |       |       |       |       |
|   | O     | S     | H    | H    | C     | N     | H    | H    | H    | C     |
| X | -1.90780671 | -1.27103711 | -1.03936666 | 3.26404298 | 2.38817521 | 0.633282103 | 2.06978431 | 1.48651836 | 0.633282103 |
| Y | -2.57965883 | -2.57965883 | -1.05690386 | 0.02333605 | -0.34328103 | -3.05642389 | -1.94557008 | -1.10177320 | -3.05642389 |
| Z | -5.4076026 | -5.4076026 | -5.4076026 | -5.4076026 | -3.05642389 | -3.05642389 | -1.67618724 | -2.06094928 | -3.05642389 |
|   |       |       |       |       |       |       |       |       |       |       |
|   | O     | S     | H    | H    | C     | N     | H    | H    | H    | C     |
| X | 1.03936666 | 1.03936666 | 1.03936666 | 1.03936666 | 1.03936666 | 1.03936666 | 1.03936666 | 1.03936666 | 1.03936666 |
| Y | 1.03936666 | 1.03936666 | 1.03936666 | 1.03936666 | 1.03936666 | 1.03936666 | 1.03936666 | 1.03936666 | 1.03936666 |
| Z | 1.03936666 | 1.03936666 | 1.03936666 | 1.03936666 | 1.03936666 | 1.03936666 | 1.03936666 | 1.03936666 | 1.03936666 |
|   |       |       |       |       |       |       |       |       |       |       |
|   | O     | S     | H    | H    | C     | N     | H    | H    | H    | C     |
| X | 1.19484377 | 1.30255687 | 1.84149923 | 1.84149923 | 1.82620607 | 1.82620607 | 1.82620607 | 1.82620607 | 1.82620607 |
| Y | 1.96152155 | 1.96152155 | 1.96152155 | 1.96152155 | 1.96152155 | 1.96152155 | 1.96152155 | 1.96152155 | 1.96152155 |
| Z | 3.2607607 | 3.2607607 | 3.2607607 | 3.2607607 | 3.2607607 | 3.2607607 | 3.2607607 | 3.2607607 | 3.2607607 |
| S204 |
H  -2.45824563  -0.67993415  2.15384673
O  -4.02831451  1.20101533  1.95806031
O  -2.89873670  -0.25320637  3.28897756
C  -3.57890419   0.84612299  3.06535478
H  -2.63385037   0.44575325  5.60285533
C  -3.75776055  1.72205920  4.28617775
C  -4.46318596   2.92907194  4.16909340
C  -4.59500026   3.78237730  5.26728913
C  -4.02151743   3.43409480  6.49712865
C  -3.32015629   2.22828554  6.62168234
C  -3.18909967   1.37699559  5.52169774
H  -4.89498124   3.18783657  3.20392111
H  -5.14145942   4.72013073  5.16589823
H  -4.11991928   4.10052052  7.35406425
H  -2.87005159   1.95609647  7.57644263

**TS-S6**

COSMO(DCM)-ZORA-M06-2X/TZ2P/COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -17352.11 \]

\[ G = -16926.89 \]

COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP

\[ E = -11922.62 \]

\[ G = -11497.40 \]

\[ N_{\text{imag}} = 1, 1908i \text{ cm}^{-1} \]

C  2.27706739  -0.57836644  -2.30016491
C  3.73297526  -0.79133654  -1.80591984
H  2.04192193   0.49726715  -2.30513794
H  4.12539138  -1.71608331  -2.25763038
C  3.89798222  -0.96266252  -0.28344518
C  1.19445540  -1.28585784  -1.49284913
C  1.46663913  -1.46506787   0.00327240
C  2.89400850  -2.00033801   0.22683661
H  4.92049697  -1.29406126  -0.07088009
H  3.07634302  -2.23025277   1.28323372

S206
| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| H    | 3.02837059 | -2.93174819 | -0.34390759 |
| H    | 0.71969299  | -2.18094134 | 0.37253359  |
| H    | 2.22163620  | -0.88750499 | -3.34808226 |
| H    | 4.36308655  | 0.03243198  | -2.16888887 |
| N    | 3.69887146  | 0.28195931  | 0.53458185  |
| C    | 2.35888323  | 0.91105774  | 0.45462599  |
| H    | 2.31819723  | 1.72107339  | 1.18792098  |
| H    | 2.18184479  | 1.36006246  | -0.53056566 |
| C    | 1.25583127  | -0.12039520 | 0.81634644  |
| C    | 1.30082806  | -0.41920022 | 2.32571280  |
| C    | -0.04556517 | 0.57089526  | 0.34709245  |
| H    | -0.00978502 | 0.77088355  | -0.71840938 |
| N    | -1.30294415 | 0.06245479  | 0.69721117  |
| O    | -2.19318466 | -0.41395455 | -0.01032005 |
| O    | -1.54582265 | 0.41975985  | 1.99878912  |
| S    | 0.83284891  | 2.75537281  | -3.38734006 |
| H    | -3.66786816 | 4.05429432  | -1.24655999 |
| H    | 0.07596419  | 4.34844771  | -1.64647391 |
| C    | -0.46583273 | 3.75379530  | 0.38756705  |
| N    | 0.04418241  | -1.68940718 | -1.89109644 |
| H    | -0.56546709 | 1.24345168  | 1.62393051  |
| C    | -0.47559602 | -1.51817257 | -3.26163945 |
| C    | 0.14823141  | -2.50873759 | -4.27188564 |
| C    | -0.45094938 | -0.07724878 | -3.83702211 |
| C    | -0.58119234 | -2.44947513 | -5.62556236 |
| H    | 1.21280814  | -2.27180587 | -4.41746531 |
| H    | 0.09658751  | -3.52024985 | -3.84191719 |
| C    | -1.21013668 | -0.02978056 | -5.17679024 |
| H    | 0.57480746  | 0.25554691  | -4.01300182 |
| N    | -1.02318458 | 0.86740000  | -2.86674348 |
| C    | -0.59890011 | -1.01621556 | -6.18766182 |
| H    | -0.09756210 | -3.13473506 | -6.33885905 |
| H    | -1.61921693 | -2.80000838 | -5.49223778 |
| H    | -1.17430988 | 1.00087468  | -5.56034657 |
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| H    | -2.26928331 | -0.28209933 | -4.99734378 |
| H    | -1.83831919 | 0.53862736  | -2.34388165 |
| C    | -0.56867161 | 2.12352845  | -2.62852390 |
| H    | 0.43389579  | -0.70196101 | -6.41846353 |
| H    | -1.16414271 | -0.98182462 | -7.13161009 |
| N    | -1.29522329 | 2.83897250  | -1.71640094 |
| H    | -2.02234425 | 2.34809446  | -1.19201485 |
| C    | -0.81106423 | 4.06734977  | -1.08068715 |
| H    | -1.54408451 | -1.79089395 | -3.18115300 |
| S    | 4.96284639  | 1.39890892  | 0.50660533  |
| O    | 4.80516259  | 2.41320330  | -0.55294416 |
| H    | 4.26438804  | 0.42085753  | 3.16045927  |
| O    | 6.21502201  | 0.62569354  | 0.56256632  |
| C    | -1.83032363 | 5.25112155  | -1.22318143 |
| C    | -1.26907638 | 6.46938560  | -0.45865540 |
| H    | -1.91773033 | 7.34224756  | -0.62019899 |
| H    | -1.22060618 | 6.27911832  | 0.62298634  |
| H    | -0.26023213 | 6.72762776  | -0.81195071 |
| C    | -1.93247804 | 5.58645508  | -2.72773387 |
| H    | -0.96218093 | 5.92003869  | -3.12272770 |
| H    | -2.66770825 | 6.38907509  | -2.88383981 |
| H    | -2.25123246 | 4.70591440  | -3.30219516 |
| C    | -3.22814333 | 4.88855523  | -0.68085785 |
| H    | -3.18425525 | 4.60650592  | 0.37765695  |
| H    | -3.89735728 | 5.75451913  | -0.79130287 |
| O    | -1.33333650 | 3.21645555  | 1.11232123  |
| N    | 0.77381847  | 4.07617851  | 0.84616610  |
| C    | 1.87140183  | 4.62408209  | 0.03198782  |
| C    | 1.05544111 | 3.99548942  | 2.28718459  |
| H    | 0.15749968  | 3.64580648  | 2.80674422  |
| H    | 1.35554599  | 4.97417445  | 2.66346889  |
| H    | 1.87972033  | 3.28643417  | 2.47523583  |
| H    | 1.87048095  | 5.72394790  | 0.05084884  |
| H    | 1.81808547  | 4.26469298  | -0.99802068 |
H  2.81563815  4.26783151  0.45413162  
C  4.68704763  2.24145485  2.08105281  
C  4.82236873  3.63206149  2.12657662  
C  4.61370270  4.293534  3.33961684  
C  4.26559592  3.56855901  4.48328724  
C  4.14378300  2.17448309  4.42487968  
C  4.36464051  1.50033156  3.22263939  
H  5.07571636  4.18321801  1.22487248  
H  4.70986239  5.37735518  3.38507617  
H  4.08628696  4.08933200  5.42308164  
H  3.87208352  1.61067523  5.31623290  
H  2.28027095 -0.81835209  2.60482511  
H  0.53225286 -1.14947264  2.60752756  
H  1.13645005  0.49812537  2.90604843  

IntS5
COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP
E = -17428.37
G = -16999.42
COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP
E = -11988.81
G = -11559.86
N_{imag} = 0
C  3.14727685  0.46907650 -2.02115856  
C  4.02553312  1.63269169 -2.54284385  
H  2.09984380  0.64706022 -2.31137744  
H  5.05451804  1.26862416 -2.68843615  
C  4.12121014  2.83557689 -1.59034761  
C  3.17273671  0.23683911 -0.51518031  
C  3.44200440  1.45508163  0.37733828  
C  4.55135011  2.34804444 -0.20397013  
H  4.85214411  3.53859022 -2.00087943  
H  4.76623093  3.18968537  0.46477490  
H  5.47942788  1.76573318 -0.30550236  

S209
| Atom | X       | Y       | Z        |
|------|---------|---------|----------|
| H    | 3.74334578 | 1.06583397 | 1.35709205 |
| H    | 3.43720743  | -0.44753549 | -2.54387641 |
| H    | 3.65216216  | 1.96291783  | -3.52210947 |
| N    | 2.82365113  | 3.57609675  | -1.50561065 |
| C    | 1.70465782  | 2.97617930  | -0.74935721 |
| H    | 0.97097073  | 3.75767089  | -0.54147426 |
| H    | 1.20279898  | 2.24838739  | -1.40080834 |
| C    | 2.13786320  | 2.30510385  | 0.59417228  |
| C    | 2.35888147  | 3.38367295  | 1.67584753  |
| C    | 0.93297571   | 1.41458530  | 0.93957826  |
| H    | 2.70435006  | 2.92877907  | 2.61053632  |
| N    | 1.06718026  | 0.43159921  | 2.07605840  |
| O    | 0.28150063  | -0.54401655 | 2.04138090  |
| O    | 1.86399953  | 0.64412977  | 2.99856797  |
| S    | -0.37278510 | -0.05577337 | -3.25517274 |
| H    | -3.91878527 | -0.62245005 | 0.40443471  |
| H    | -2.18705879 | 1.34041275  | -2.30971548 |
| C    | -2.08878365 | 2.36253866  | -0.37766903 |
| N    | 2.90410999  | -0.84629774 | 0.11783574  |
| H    | 1.41679187  | 3.91407107  | 1.87322336  |
| C    | 2.51911846  | -2.11922597 | -0.52207329 |
| C    | 3.72629277  | -2.86461071 | -1.13581173 |
| C    | 1.34547426  | -2.06713319 | -1.53581854 |
| C    | 3.32878767  | -4.28245129 | -1.58290860 |
| H    | 4.11162340  | -2.30032764 | -1.99851484 |
| H    | 4.53007838  | -2.90040921 | -0.38530792 |
| C    | 0.94079389  | -3.49645313 | -1.94576366 |
| H    | 1.62874578  | -1.52151636 | -2.43888389 |
| N    | 0.21319373  | -1.33842868 | -0.95097551 |
| C    | 2.13670048  | -4.24802572 | -2.55650812 |
| H    | 4.19189285  | -4.77987318 | -2.05176746 |
| H    | 3.05497935  | -4.87744723 | -0.69458601 |
| H    | 0.10883683  | -3.43000418 | -2.66274862 |
| H    | 0.57176833  | -4.03381917 | -1.05552655 |
| Atom | X             | Y             | Z             |
|------|---------------|---------------|---------------|
| H    | 0.04176365    | -1.48861385   | 0.04712581    |
| C    | -0.60781561   | -0.48519270   | -1.61099203   |
| H    | 2.44196810    | -3.74205913   | -3.48904137   |
| H    | 1.83559618    | -5.27105476   | -2.82949522   |
| N    | -1.62675486   | 0.02561384    | -0.85477279   |
| H    | -1.59919422   | -0.13940076   | 0.15469770    |
| C    | -2.45240021   | 1.16172919    | -1.26887955   |
| H    | 2.16230813    | -2.74505043   | 0.31685910    |
| S    | 2.75587421    | 5.19180221    | -1.89857199   |
| O    | 1.34932418    | 5.51471408    | -2.17583484   |
| H    | 5.32309471    | 5.64908181    | -0.63701433   |
| O    | 3.80181877    | 5.43194079    | -2.90078376   |
| C    | -3.98489965   | 0.82559260    | -1.24122277   |
| C    | -4.77207501   | 2.10185455    | -1.60885677   |
| H    | -5.84612975   | 1.87384691    | -1.66515033   |
| H    | -4.63330133   | 2.89187579    | -0.85713696   |
| H    | -4.45782724   | 2.49312865    | -2.58702126   |
| C    | -4.23233221   | -0.26135812   | -2.31039960   |
| H    | -3.96488767   | 0.10516059    | -3.31174943   |
| H    | -5.29388968   | -0.54813526   | -2.31520730   |
| H    | -3.63083963   | -1.15673288   | -2.10210713   |
| C    | -4.44279067   | 0.30655221    | 0.13728193    |
| H    | -4.25940906   | 1.04781338    | 0.92416232    |
| H    | -5.51946892   | 0.08396695    | 0.10313247    |
| O    | -2.09475269   | 2.21697213    | 0.86557034    |
| N    | -1.75291749   | 3.53929865    | -0.97439501   |
| C    | -1.67809492   | 3.77920953    | -2.42606144   |
| C    | -1.57452515   | 4.74018085    | -0.14239639   |
| H    | -2.39402860   | 5.45033314    | -0.33095743   |
| H    | -0.62886037   | 5.22736794    | -0.40620416   |
| H    | -1.57422697   | 4.44992838    | 0.90998448    |
| H    | -0.89027105   | 4.51957821    | -2.60307729   |
| H    | -2.63148963   | 4.16908402    | -2.81133400   |
| H    | -1.40537441   | 2.86832244    | -2.96276490   |
| Element | X | Y | Z | Energy 1 | Energy 2 |
|---------|---|---|---|---------|---------|
| C       | 3.21421037 | 6.07977010 | -0.39937348 |
| C       | 2.21890851 | 6.65693937 | 0.39414267 |
| C       | 2.57189622 | 7.22716070 | 1.62026442 |
| C       | 3.90496687 | 7.21631193 | 2.04218131 |
| C       | 4.89652199 | 6.65284612 | 1.22855826 |
| C       | 4.55727309 | 6.08493130 | -0.00019082 |
| H       | 1.18691617 | 6.65636746 | 0.05622859 |
| H       | 1.80207591 | 7.67506518 | 2.24730310 |
| H       | 4.17491370 | 7.65272109 | 3.00297565 |
| H       | 5.93661417 | 6.65527741 | 1.55211630 |
| H       | 3.09378560 | 4.12579578 | 1.35594545 |
| H       | 0.65964367 | 4.12579578 | 1.35594545 |
| IntS6   |    |    |    |         |         |
| COSMO(DCM)-ZORA-M06-2X/TZ2P//COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP |
| $E = -17427.76$ |
| $G = -16997.89$ |
| COSMO(DCM)-ZORA-BLYP-D3(BJ)/DZP |
| $E = -11988.33$ |
| $G = -11558.46$ |
| $N_{imag} = 0$ |

S212
| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| H    | -0.80682984 | 1.34560671 | 2.97814506 |
| H    | 0.52422960  | 3.01851188  | -2.13135550 |
| N    | 1.41388008  | 1.20996390  | -0.37262767 |
| C    | 0.54195958  | 1.54596902  | 0.77757617  |
| H    | 1.17739820  | 1.66294221  | 1.66378234  |
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| C    | -0.45259605 | 0.38055050  | 1.02438019  |
| C    | 0.34393352  | -0.86374632 | 1.48339158  |
| C    | -1.36341197 | 0.89288123  | 2.14977631  |
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| O    | -2.81469792 | 0.25477978  | 3.87539747  |
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| H    | -3.62770878 | 3.28668847  | 6.11156363  |
| H    | -2.87654287 | 5.17622215  | 2.94297270  |
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| H    | -3.52400204 | 2.64437175  | -0.38783844 |
| C    | -4.26890968 | 0.75425241  | 0.05805476  |
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| H    | -5.27877992 | 1.13197377  | -1.81724342 |
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| C    | -6.48803419 | 0.37796456  | 1.22810390  |
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| C    | -7.09391810 | -0.15720419 | -0.08274001 |
| H    | -6.46045579 | -1.07849035 | -1.95508800 |
| H    | -5.58498293 | -1.65258815 | -0.52541640 |
| H    | -7.25989269 | 0.85920372  | 1.84687663  |
| H    | -6.07197202 | -0.46143303 | 1.81298724  |
| H    | -4.57697607 | 1.21623481  | 2.90117428  |
C  -4.24787164  3.14861713  2.33845588
H   -7.59950182  0.67173630 -0.60736249
H   -7.86275799 -0.91099918  0.14566676
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H   -3.15037630  2.41363359  3.90606876
C   -2.61892424  4.45048141  3.71328608
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H    3.62944634 -0.52356303  0.33630202
O    3.54704604  1.69482920 -1.65529386
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|   | X       | Y       | Z       |
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| C | 4.02738826 | 2.42205072 | 2.03024721 |
| C | 4.65557379 | 1.93091559 | 3.17913802 |
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| H | 4.93939637 | 2.61918898 | 3.97397427 |
| H | 5.39212055 | 0.18238328 | 4.20847285 |
| H | 4.75078020 | -1.38975316 | 2.38662605 |
| H | 1.23245597 | -0.99843351 | 0.86064771 |
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| H | -2.01142717 | 3.10633238 | -2.00513294 |