*Chemistry of Heterocyclic Compounds* **2023**, *59*(3), 112–117

# [2+1] Cycloaddition reaction of α-atlantone with *m*-CPBA in the light of experimental and MEDT quantum-chemical study

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# SUPPLEMENTARY INFORMATION

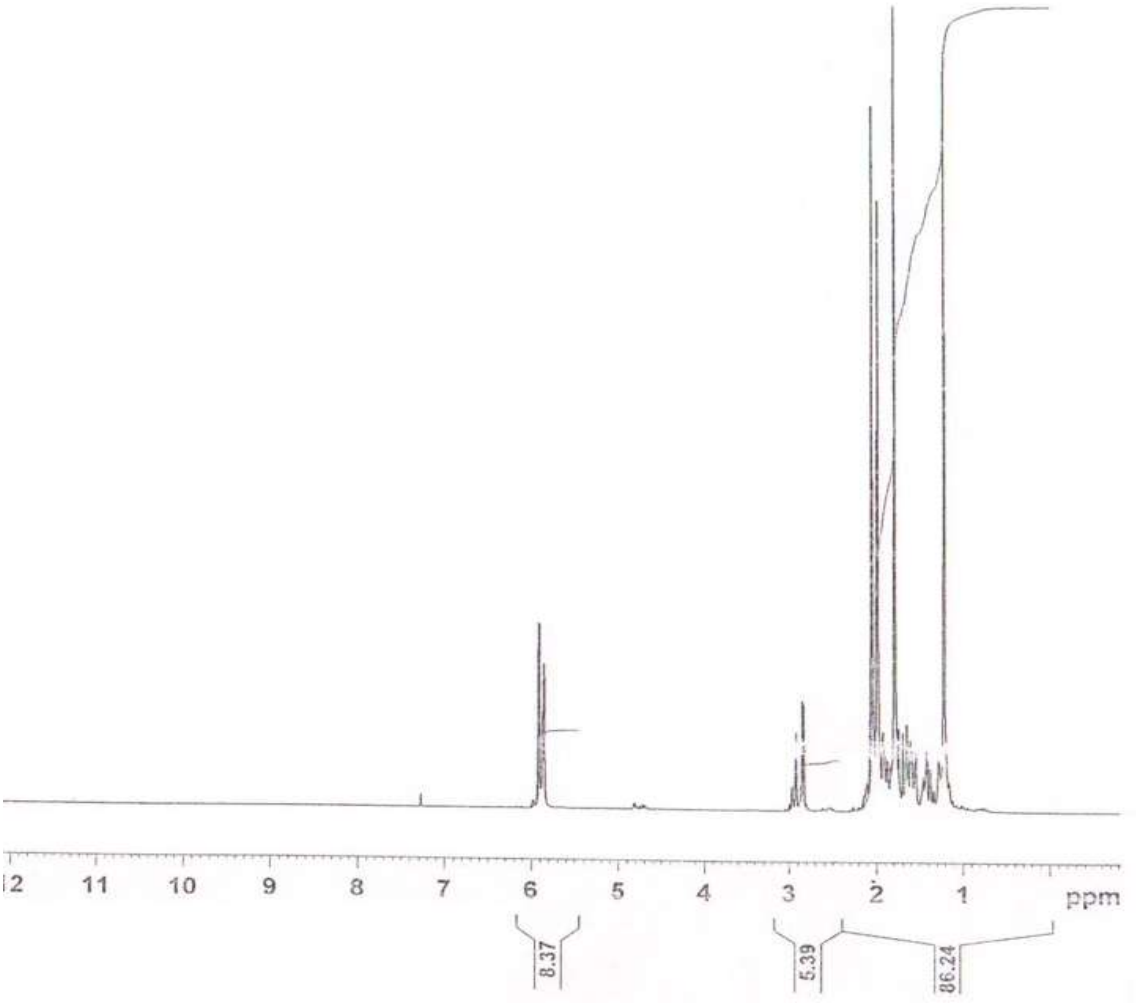


**Figure S1**. $^{1}$H NMR spectrum of monoepoxide α-atlantone (**1**)

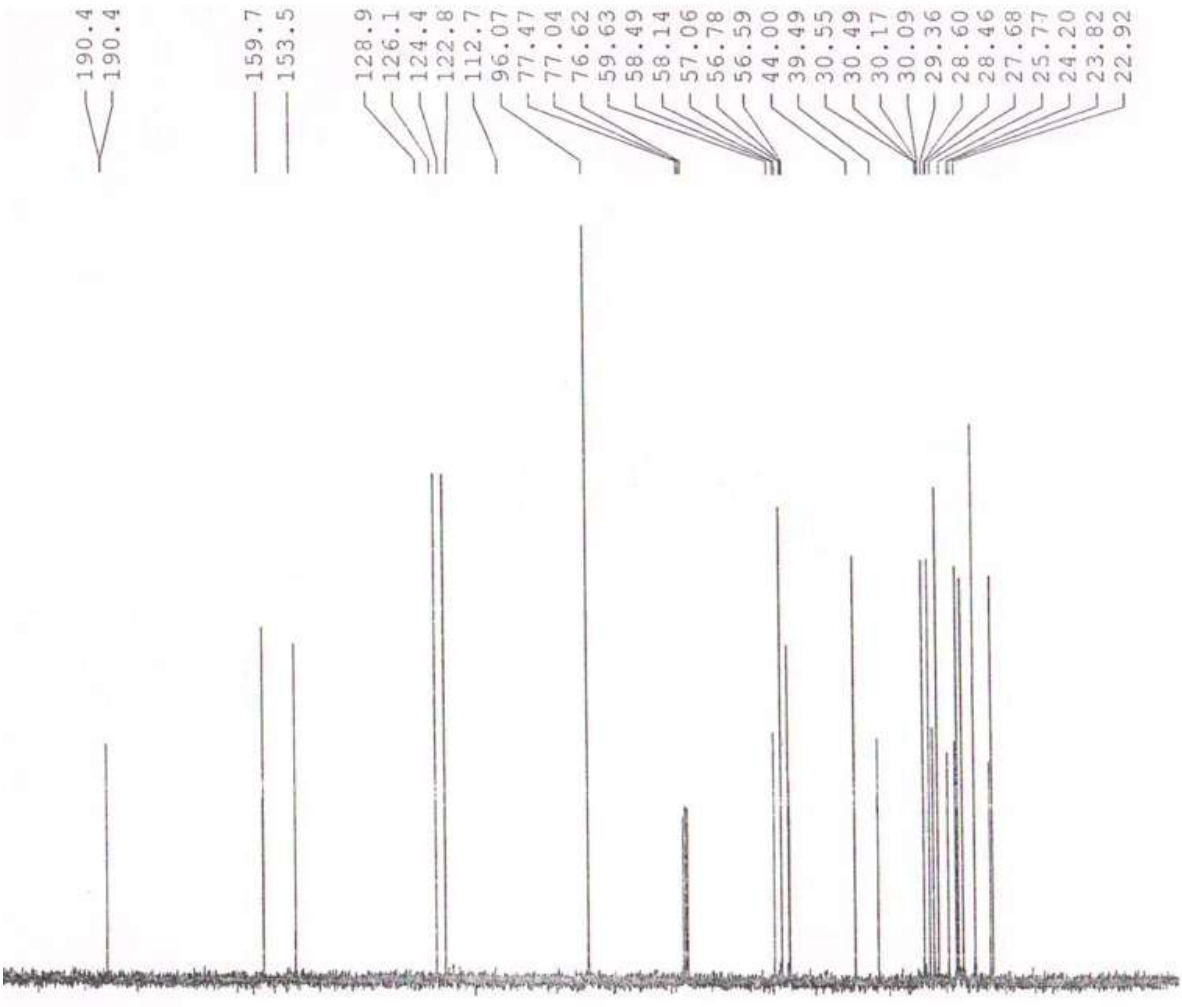


**Figure S2**. $^{13}$C NMR spectrum of monoepoxide α-atlantone (**1**)

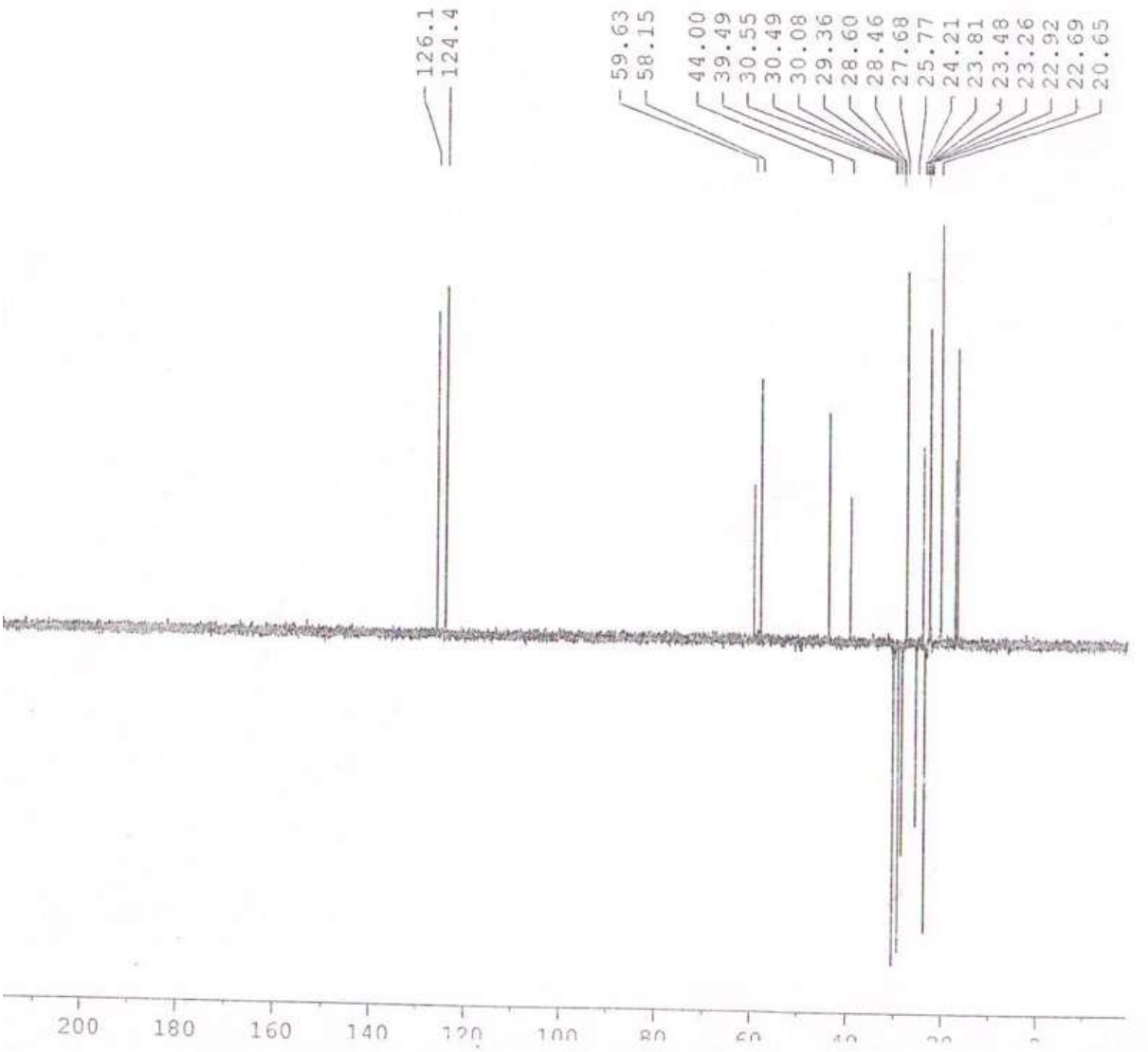


**Figure S3**. Dept NMR spectrum of monoepoxide α-atlantone (**1**)

**Table S1.** B3LYP/6-311G(d,p) total (E, in a.u.) and relative[a] (ΔE, in kcal•mol$^{-1}$) energies, in gas phase and in DCM, for the species involved in the epoxidation reaction of α-atlantone using m-CPBA.

| | **Gas** | | **DCM** | |
|---|---|---|---|---|
| **System** | E | ΔE | E | ΔE |
| **1** | -660.207832109 | -------- | -660.214556977 | -------- |
| **m-CPBA (2)** | -955.703512710 | -------- | -955.709296994 | -------- |
| **m-CBA** | -880.548129055 | -------- | -880.558180800 | -------- |
| **1+2** | -1615.91134481 | -------- | -1615.92385397 | -------- |
| **TS-1** | -1615.89706923 | 8.95 | -1615.91040287 | 8.44 |
| **P-1** | -1.615.97853625 | -42.16 | -1615.99715449 | -45.99 |
| **TS-2** | -1615.89353179 | 11.17 | -1615.90658848 | 10.83 |
| **P-2** | -1615.97581722 | -40.45 | -1615.99456162 | -44.36 |
| **TS-3** | -1615.88680504 | 15.39 | -1615.89952731 | 15.26 |
| **P-3** | -1615.96908262 | -36.23 | -1615.98904202 | -40.90 |
| **TS-4** | -1615.59656921 | 19.75 | -1615.90087844 | 14.41 |
| **P-4** | -1615.96917677 | -36.28 | -1.615.98848543 | -40.55 |
| **TS-5** | -1615.89318406 | 11.39 | -1615.90616570 | 11.09 |
| **P-5** | -1615.980907668 | -43.65 | -1.615.99777305 | -46.38 |
| **TS-6** | -1615.89857459 | 8.01 | -1615.91090739 | 8.12 |
| **P-6** | -1615.979081786 | -42.50 | -1615.99727779 | -46.07 |

**Natural bond orbital (NBO) analysis**

In order to explain the chemoselectivity observed experimentally, the natural bond orbital charges (NBO) have been calculated and are presented in Table. S2**.**

Natural bond orbital (NBO) analysis provides the accurate possible natural Lewis structure. The result of interaction is a loss of occupancy from the concentration of electron NBO of the idealized Lewis structure into an empty non-Lewis orbital. Electron donor orbital, acceptor orbital and the interacting stabilization energy $E^{(2)}$ resulting from the second-order micro disturbance theory [1, 2].

**Table S2-a.** Second order perturbation theory analysis of Fock matrix in NBO basis of α-atlantone (**1**).

| Donor(i) | Acceptor (j) | $E^{(2)a}$ (kcal/mol) | E(j)-E(i)[b] (a.u) | F(i,j)[c] (a.u) |
|---|---|---|---|---|
| $\pi(C_2\text{-}C_3)$ | $\pi^*(C_4\text{-}O)$ | 14.93 | 0.29 | 0.06 |
| LP1(O) | $\sigma^*(C_4\text{-}C_5)$ | 2.11 | 1.14 | 0.04 |
| LP1(O) | $\sigma^*(C_3\text{-}C_4)$ | 1.67 | 1.13 | 0.04 |
| LP2(O | $\pi^*(C_{1'}\text{-}C_6)$ | | | |
| LP2(O) | $\sigma^*(C_4\text{-}C_5)$ | 17.08 | 0.72 | 0.10 |
| LP2(O) | $\sigma^*(C_3\text{-}C_4)$ | 16.67 | 0.71 | 0.10 |
| $\pi(C_4\text{-}O)$ | $\pi^*(C_5\text{-}C_6)$ | 4.26 | 0.42 | 0.04 |
| | $\pi^*(C_2\text{-}C_3)$ | 4.17 | 0.42 | 0.04 |
| $\pi^*(C_4\text{-}O)$ | $\pi^*(C_5\text{-}C_6)$ | 26.64 | 0.04 | 0.07 |
| | $\pi^*(C_2\text{-}C_3)$ | 18.25 | 0.04 | 0.06 |
| $\pi(C_5\text{-}C_6)$ | $\sigma^*(C_{1'}\text{-}C_{6'})$ | 2.62 | 0.63 | 0.04 |
| | $\pi^*(C_5\text{-}C_6)$ | 0.66 | 0.32 | 0.01 |
| | $\pi^*(C_4\text{-}O)$ | 20.99 | 0.29 | 0.07 |
| $\pi(C_{1'}\text{-}C_6)$ | $\sigma^*(C_{5'}\text{-}C_{6'})$ | | | |
| | $\sigma^*(C_{2'}\text{-}C_{3'})$ | | | |
| | $\sigma^*(C_4\text{-}C_5)$ | | | |
| $\pi^*(C_{1'}\text{-}C_6)$ | $\sigma^*(C_4\text{-}C_5)$ | | | |
| $\sigma(C_{3'}\text{-}C_{4'})$ | $\sigma^*(C_{2'}\text{-}C_{3'})$ | 3.06 | 1.16 | 0.05 |
| | $\sigma^*(C_{4'}\text{-}C_{5'})$ | 2.77 | 1.16 | 0.05 |

a. $E^{(2)}$ means energy of hyper conjugative interaction (stabilization energy).

b. Energy difference between donor and acceptor i and j NBO orbitals.

c. F(i,j) is the Fock matrix element between i and j NBO orbitals.

The electron delocalization from filled NBOs (donors) to the empty NBOs (acceptors) describes as a conjugative electron transfer process between them. Higher the stabilization

energy $E^{(2)}$, more intense is the bond interaction. According to the results of the NBO analysis for α-atlantone (1).

The $\pi(C_5\text{-}C_6)$ of (**1**) participates as donor and the anti-bonding orbital for $\pi^*(C_4\text{-}O)$ acts as acceptor resulting in favorable resonance energy $E^{(2)}$. Also $\pi^*(C_4\text{-}O)$ participates as donor and the anti-bonding $\pi^*(C_2\text{-}C_3)$ orbital act as acceptor. This shows the conjugation between the electron donation group and the acceptors, which correspond to the stabilization energy 20.99 kcal/mol and 18.25 kcal/mol, respectively.

The electron delocalization from π(C2 – C3) to antibonding π*(C4 - O) in the (**1**) and (**2**) leads to the stabilization energy 14.93 and 23.26 kcal/mol, respectively, and $\pi^*(C_4\text{-}O)$ NBO conjugates with the anti-bonding orbitals of $\pi^*(C_5\text{-}C_6)$ of (1) and $\pi^*(C_2\text{-}C_3)$ of (2)which lead to strong delocalization of 26.64 And 29.15 kcal/mol, respectively. The various interactions between the filled NBOs and empty NBOs show that the $C_2\text{-}C_3$ and $C_5\text{-}C_6$ double bonds are more stable in the (**1**) and (**2**) molecules. These results were confirmed by NBO analysis which enhance the analysis of intramolecular charge interaction between the localized NBO and empty molecular bonds.

**Table S2-b** Occupancy of natural orbitals (NBOs) and hybrids of α-atlantone (1) calculated by the B3LYP/6-311G(d,p) method.

| σ and π bonding ($C_A\text{-}C_B$) | ED(e) | Energy | Hybrid of atom A | Hybrid of atom B |
|---|---|---|---|---|
| σ ($C_2\text{-}C_3$) | 1.980 | -0.738 | $SP^{1.6}(0.706)$ | $SP^{1.45}(0.708)$ |
| π ($C_2\text{-}C_3$) | 1.876 | -0.271 | $SP^{99.9}(0.674)$ | $SP^{99.9}(0.738)$ |
| σ ($C_4\text{-}O$) | 1.993 | -1.043 | $SP^{2.37}(0.585)$ | $SP^{1.36}(0.811)$ |
| π ($C_4\text{-}O$) | 1.966 | -0.364 | $SP^{1.99}(0.559)$ | $SP^{100}(0.828)$ |
| σ ($C_5\text{-}C_6$) | 1.977 | -0.733 | $SP^{1.5}(0.710)$ | $SP^{1.64}(0.704)$ |
| π ($C_5\text{-}C_6$) | 1.851 | -0.267 | $SP^{99.9}(0.751)$ | $SP^{99.9}(0.660)$ |
| σ ($C_{1'}\text{-}C_6$) | 1.967 | -0.612 | $SP^{2.56}(0.708)$ | $SP^{2.17}(0.706)$ |
| π ($C_{1'}\text{-}C_6$) | ------- | …… | ….. | … |
| σ ($C_{3'}\text{-}C_{4'}$) | 1.979 | -0.725 | $SP^{1.49}(0.705)$ | $SP^{1.6}(0.709)$ |
| π ($C_{3'}\text{-}C_{4'}$) | 1.936 | -0.257 | $SP^{100}(0.717)$ | $SP^{100}(0.697)$ |
| LP1(O) | 1.978 | -0.680 | $SP^{0.74}$ | |
| LP2(O) | 1.900 | -0.257 | $SP^{100}$ | |

Occupancy of natural orbitals (NBOs) and hybrids of (**1**) and (**2**) was calculated by the B3LYP method with 6-311G(d,p) basis set. The π bonding NBO at ($C_2\text{-}C_3$) and ($C_5\text{-}C_6$) of (**1**) and ($C_2\text{-}C_3$) of (**2**) has lowest occupancy, 1.876, 1.851 and 1.849, respectively, indicating that the orbital is extensively involved in charge donation which is evident in table 4, the results

analysis shows that the (**1**) and (**2**) epoxidation will no longer have on ($C_2$-$C_3$) and ($C_5$-$C_6$) double bonds, in agreement with the experimental results.

## References


1. R.P Gangadharana, S.S. Krishnanb, Act. Phys. Polon. A. 125 (2014) 18.
2. B.D. Joshi, P. Tandon, S. Jain. Himalayan. Phys. 3 (2012) 44.

**B3LYP/6-311G(d,p) Cartesian coordinates and electronic energies for TSs structures, together with the single imaginary frequencies.**

**TS-1 GAS**

E(RB3LYP) = -1615.89706923 A.U.

1 imaginary frequency -368.4696 $cm^{-1}$

Zero-point correction= 0.441514 (Hartree/Particle)
Thermal correction to Energy= 0.470077
Thermal correction to Enthalpy= 0.471021
Thermal correction to Gibbs Free Energy= 0.377860
Sum of electronic and zero-point Energies= -1615.455555
Sum of electronic and thermal Energies= -1615.426992
Sum of electronic and thermal Enthalpies= -1615.426048
Sum of electronic and thermal Free Energies= -1615.519209

| | E (Thermal) KCal/Mol | CV Cal/Mol-Kelvin | S Cal/Mol-Kelvin |
|---|---|---|---|
| Total | 294.978 | 105.958 | 196.074 |

| | | | |
|---|---|---|---|
| C | 1.27504300 | 1.36898400 | 1.62913500 |
| C | 1.05965400 | -0.08633700 | 1.31234600 |
| C | 1.20243700 | -0.54853500 | 0.03460500 |
| C | 1.61692400 | 0.30318500 | -1.13251400 |
| C | 2.18770500 | 1.67539500 | -0.73404600 |
| C | 1.29908300 | 2.26907400 | 0.38974800 |
| H | 2.21967500 | 1.44939000 | 2.18466100 |
| H | 1.09642900 | -1.61420900 | -0.14831000 |
| H | 2.32648900 | -0.25244500 | -1.75229100 |
| H | 1.63449800 | 3.27116800 | 0.66363200 |
| C | 0.82001600 | -1.00610300 | 2.47325600 |
| H | 1.69192800 | -0.99604600 | 3.13721800 |
| H | -0.03500200 | -0.67062100 | 3.06682100 |
| H | 0.64605200 | -2.03522900 | 2.15475900 |
| C | 3.65843700 | 1.71292700 | -0.33953800 |
| C | 4.38498800 | 0.59057900 | -0.15135600 |
| H | 3.91092700 | -0.37073400 | -0.30018900 |
| C | 5.79790400 | 0.52398600 | 0.28524600 |
| C | 6.53483500 | -0.76373600 | 0.17729000 |
| H | 7.28256800 | -0.86339000 | 0.96023600 |
| C | 6.48271500 | -1.72149900 | -0.76722300 |
| C | 5.61757200 | -1.70275900 | -2.00010900 |
| H | 4.84040500 | -2.47315300 | -1.93371600 |
| H | 5.13938200 | -0.74254400 | -2.17975600 |
| H | 6.22515100 | -1.95180300 | -2.87603300 |
| C | 7.38214200 | -2.92654400 | -0.66272000 |
| H | 7.96194000 | -2.92820000 | 0.26100000 |
| H | 6.78962300 | -3.84753100 | -0.70428000 |
| H | 8.07533600 | -2.96494300 | -1.51036200 |
| C | 4.22077800 | 3.10360800 | -0.18288600 |
| H | 5.27831900 | 3.14298300 | -0.43539800 |
| H | 3.66460400 | 3.81550400 | -0.79784200 |

| | | | |
|---|---|---|---|
| H | 4.14292000 | 3.43485200 | 0.85819000 |
| O | 6.37810800 | 1.47569600 | 0.81022100 |
| H | 0.28324300 | 2.36644800 | -0.00101400 |
| H | 0.49574000 | 1.70140200 | 2.32200600 |
| H | 0.73798700 | 0.46176800 | -1.76682900 |
| H | 2.09482800 | 2.33892900 | -1.60184300 |
| C | -7.54499200 | -0.90377500 | -0.20590400 |
| C | -6.80917600 | 0.25533100 | -0.43320700 |
| C | -5.42907800 | 0.28365100 | -0.29004200 |
| C | -4.76681800 | -0.88719400 | 0.09270600 |
| C | -5.48971600 | -2.06014700 | 0.32493100 |
| C | -6.87257500 | -2.06363400 | 0.17521500 |
| H | -8.62064300 | -0.89926000 | -0.32455200 |
| H | -4.87193700 | 1.19203300 | -0.47064600 |
| H | -4.95773900 | -2.95496100 | 0.61968400 |
| H | -7.43650100 | -2.97109500 | 0.35456800 |
| Cl | -7.65236800 | 1.72867300 | -0.91619200 |
| C | -3.27401900 | -0.91590200 | 0.26167100 |
| O | -2.67521700 | -1.94119700 | 0.58768300 |
| O | -2.68555700 | 0.22595200 | 0.03290500 |
| O | -0.95659800 | -0.01850000 | 0.28824000 |
| H | -1.13501200 | -0.96467700 | 0.50353200 |

**TS-1 DCM**

E(RB3LYP) = -1615.91040287 A.U.

1 imaginary frequency -405.1810 $cm^{-1}$

Zero-point correction= 0.440774 (Hartree/Particle)
Thermal correction to Energy= 0.469528
Thermal correction to Enthalpy= 0.470472
Thermal correction to Gibbs Free Energy= 0.376420
Sum of electronic and zero-point Energies= -1615.469632
Sum of electronic and thermal Energies= -1615.440879
Sum of electronic and thermal Enthalpies= -1615.439935
Sum of electronic and thermal Free Energies= -1615.533987

| | E (Thermal) KCal/Mol | CV Cal/Mol-Kelvin | S Cal/Mol-Kelvin |
|---|---|---|---|
| Total | 294.633 | 106.460 | 197.949 |

| | | | |
|---|---|---|---|
| C | 1.27504300 | 1.36898400 | 1.62913500 |
| C | 1.05965400 | -0.08633700 | 1.31234600 |
| C | 1.20243700 | -0.54853500 | 0.03460500 |
| C | 1.61692400 | 0.30318500 | -1.13251400 |
| C | 2.18770500 | 1.67539500 | -0.73404600 |
| C | 1.29908300 | 2.26907400 | 0.38974800 |
| H | 2.21967500 | 1.44939000 | 2.18466100 |
| H | 1.09642900 | -1.61420900 | -0.14831000 |
| H | 2.32648900 | -0.25244500 | -1.75229100 |
| H | 1.63449800 | 3.27116800 | 0.66363200 |
| C | 0.82001600 | -1.00610300 | 2.47325600 |

| | | | |
|---|---|---|---|
| H | 1.69192800 | -0.99604600 | 3.13721800 |
| H | -0.03500200 | -0.67062100 | 3.06682100 |
| H | 0.64605200 | -2.03522900 | 2.15475900 |
| C | 3.65843700 | 1.71292700 | -0.33953800 |
| C | 4.38498800 | 0.59057900 | -0.15135600 |
| H | 3.91092700 | -0.37073400 | -0.30018900 |
| C | 5.79790400 | 0.52398600 | 0.28524600 |
| C | 6.53483500 | -0.76373600 | 0.17729000 |
| H | 7.28256800 | -0.86339000 | 0.96023600 |
| C | 6.48271500 | -1.72149900 | -0.76722300 |
| C | 5.61757200 | -1.70275900 | -2.00010900 |
| H | 4.84040500 | -2.47315300 | -1.93371600 |
| H | 5.13938200 | -0.74254400 | -2.17975600 |
| H | 6.22515100 | -1.95180300 | -2.87603300 |
| C | 7.38214200 | -2.92654400 | -0.66272000 |
| H | 7.96194000 | -2.92820000 | 0.26100000 |
| H | 6.78962300 | -3.84753100 | -0.70428000 |
| H | 8.07533600 | -2.96494300 | -1.51036200 |
| C | 4.22077800 | 3.10360800 | -0.18288600 |
| H | 5.27831900 | 3.14298300 | -0.43539800 |
| H | 3.66460400 | 3.81550400 | -0.79784200 |
| H | 4.14292000 | 3.43485200 | 0.85819000 |
| O | 6.37810800 | 1.47569600 | 0.81022100 |
| H | 0.28324300 | 2.36644800 | -0.00101400 |
| H | 0.49574000 | 1.70140200 | 2.32200600 |
| H | 0.73798700 | 0.46176800 | -1.76682900 |
| H | 2.09482800 | 2.33892900 | -1.60184300 |
| C | -7.54499200 | -0.90377500 | -0.20590400 |
| C | -6.80917600 | 0.25533100 | -0.43320700 |
| C | -5.42907800 | 0.28365100 | -0.29004200 |
| C | -4.76681800 | -0.88719400 | 0.09270600 |
| C | -5.48971600 | -2.06014700 | 0.32493100 |
| C | -6.87257500 | -2.06363400 | 0.17521500 |
| H | -8.62064300 | -0.89926000 | -0.32455200 |
| H | -4.87193700 | 1.19203300 | -0.47064600 |
| H | -4.95773900 | -2.95496100 | 0.61968400 |
| H | -7.43650100 | -2.97109500 | 0.35456800 |
| Cl | -7.65236800 | 1.72867300 | -0.91619200 |
| C | -3.27401900 | -0.91590200 | 0.26167100 |
| O | -2.67521700 | -1.94119700 | 0.58768300 |
| O | -2.68555700 | 0.22595200 | 0.03290500 |
| O | -0.95659800 | -0.01850000 | 0.28824000 |
| H | -1.13501200 | -0.96467700 | 0.50353200 |

**TS-2 GAS**

E(RB3LYP) = -1615.89353179 A.U.

1 imaginary frequency -371.8781 $cm^{-1}$

Zero-point correction= 0.441588 (Hartree/Particle)
Thermal correction to Energy= 0.470143
Thermal correction to Enthalpy= 0.471087
Thermal correction to Gibbs Free Energy= 0.379119

Sum of electronic and zero-point Energies= -1615.451944
Sum of electronic and thermal Energies= -1615.423389
Sum of electronic and thermal Enthalpies= -1615.422445
Sum of electronic and thermal Free Energies= -1615.514413

| | E (Thermal) KCal/Mol | CV Cal/Mol-Kelvin | S Cal/Mol-Kelvin |
|---|---|---|---|
| Total | 295.019 | 105.998 | 193.563 |

| | | | |
|---|---|---|---|
| C | 3.54315700 | -1.81880100 | -1.42211900 |
| C | 2.84071800 | -2.58350300 | -0.33023800 |
| C | 2.86368700 | -2.09996900 | 0.94670400 |
| C | 3.62561400 | -0.88326800 | 1.38649800 |
| C | 4.34998200 | -0.08377000 | 0.27760800 |
| C | 4.74555300 | -1.03456200 | -0.88162000 |
| H | 2.82137300 | -1.14273900 | -1.89553500 |
| H | 2.44215800 | -2.70614600 | 1.74413800 |
| H | 2.97636900 | -0.23607200 | 1.98228700 |
| H | 5.22299700 | -0.47609000 | -1.68903600 |
| C | 2.24392600 | -3.91207800 | -0.68352100 |
| H | 1.57224300 | -3.81824500 | -1.54173500 |
| H | 3.04125700 | -4.60422500 | -0.97789300 |
| H | 1.69337600 | -4.35615300 | 0.14749800 |
| C | 3.66957200 | 1.17091800 | -0.25661200 |
| C | 2.37439200 | 1.46248200 | -0.01645900 |
| H | 1.77817600 | 0.76821100 | 0.55792000 |
| C | 1.65221800 | 2.65211300 | -0.52101700 |
| C | 0.33368400 | 3.01557500 | 0.06154300 |
| H | -0.29008300 | 3.53671600 | -0.66032700 |
| C | -0.13422300 | 2.88906200 | 1.31761500 |
| C | 0.61351900 | 2.30981100 | 2.48999500 |
| H | 0.20976700 | 1.32345400 | 2.74659300 |
| H | 1.68202600 | 2.20850500 | 2.31380700 |
| H | 0.46808800 | 2.94493400 | 3.36930400 |
| C | -1.51662400 | 3.38688800 | 1.65343300 |
| H | -2.04644100 | 3.75306400 | 0.77337000 |
| H | -2.10862400 | 2.58415000 | 2.10730500 |
| H | -1.46696700 | 4.19362700 | 2.39331000 |
| C | 4.58383600 | 2.06038000 | -1.06553400 |
| H | 4.36516900 | 3.11466400 | -0.90293600 |
| H | 5.63152900 | 1.86122600 | -0.82761400 |
| H | 4.44381600 | 1.88669800 | -2.13715600 |
| O | 2.06792000 | 3.33413700 | -1.46038700 |
| H | 5.49121600 | -1.74329500 | -0.50613100 |
| H | 3.86843700 | -2.51423100 | -2.20123300 |
| H | 4.38501200 | -1.24051600 | 2.09483900 |
| H | 5.28905800 | 0.27514100 | 0.71474600 |
| C | -5.72696100 | -0.78442600 | -0.10233800 |
| C | -4.75918900 | 0.04065900 | -0.66752300 |
| C | -3.40352200 | -0.22233100 | -0.52781800 |
| C | -3.00763500 | -1.34932700 | 0.19985700 |
| C | -3.96571500 | -2.18926800 | 0.77325900 |
| C | -5.31844200 | -1.90345200 | 0.62121500 |
| H | -6.77770600 | -0.55677300 | -0.22618700 |

| | | | |
|---|---|---|---|
| H | -2.66362400 | 0.42777000 | -0.97291700 |
| H | -3.63668800 | -3.05646100 | 1.33020400 |
| H | -6.06442800 | -2.55191600 | 1.06468300 |
| Cl | -5.26833200 | 1.45781400 | -1.58763400 |
| C | -1.55472500 | -1.68900400 | 0.37793100 |
| O | -1.19226900 | -2.70600300 | 0.97067500 |
| O | -0.73218900 | -0.82188800 | -0.14460300 |
| O | 0.90620100 | -1.43856800 | 0.11006000 |
| H | 0.51990300 | -2.20433000 | 0.59735600 |

**TS-2 DCM**

E(RB3LYP) = -1615.90658848 A.U.

1 imaginary frequency -403.8446 $cm^{-1}$

Zero-point correction= 0.441052 (Hartree/Particle)
Thermal correction to Energy= 0.469645
Thermal correction to Enthalpy= 0.470589
Thermal correction to Gibbs Free Energy= 0.377637
Sum of electronic and zero-point Energies= -1615.465537
Sum of electronic and thermal Energies= -1615.436943
Sum of electronic and thermal Enthalpies= -1615.435999
Sum of electronic and thermal Free Energies= -1615.528951

| | E (Thermal) KCal/Mol | CV Cal/Mol-Kelvin | S Cal/Mol-Kelvin |
|---|---|---|---|
| Total | 294.707 | 106.323 | 195.634 |

| | | | |
|---|---|---|---|
| C | 3.54315700 | -1.81880100 | -1.42211900 |
| C | 2.84071800 | -2.58350300 | -0.33023800 |
| C | 2.86368700 | -2.09996900 | 0.94670400 |
| C | 3.62561400 | -0.88326800 | 1.38649800 |
| C | 4.34998200 | -0.08377000 | 0.27760800 |
| C | 4.74555300 | -1.03456200 | -0.88162000 |
| H | 2.82137300 | -1.14273900 | -1.89553500 |
| H | 2.44215800 | -2.70614600 | 1.74413800 |
| H | 2.97636900 | -0.23607200 | 1.98228700 |
| H | 5.22299700 | -0.47609000 | -1.68903600 |
| C | 2.24392600 | -3.91207800 | -0.68352100 |
| H | 1.57224300 | -3.81824500 | -1.54173500 |
| H | 3.04125700 | -4.60422500 | -0.97789300 |
| H | 1.69337600 | -4.35615300 | 0.14749800 |
| C | 3.66957200 | 1.17091800 | -0.25661200 |
| C | 2.37439200 | 1.46248200 | -0.01645900 |
| H | 1.77817600 | 0.76821100 | 0.55792000 |
| C | 1.65221800 | 2.65211300 | -0.52101700 |
| C | 0.33368400 | 3.01557500 | 0.06154300 |
| H | -0.29008300 | 3.53671600 | -0.66032700 |
| C | -0.13422300 | 2.88906200 | 1.31761500 |
| C | 0.61351900 | 2.30981100 | 2.48999500 |
| H | 0.20976700 | 1.32345400 | 2.74659300 |
| H | 1.68202600 | 2.20850500 | 2.31380700 |

| | | | |
|---|---|---|---|
| H | 0.46808800 | 2.94493400 | 3.36930400 |
| C | -1.51662400 | 3.38688800 | 1.65343300 |
| H | -2.04644100 | 3.75306400 | 0.77337000 |
| H | -2.10862400 | 2.58415000 | 2.10730500 |
| H | -1.46696700 | 4.19362700 | 2.39331000 |
| C | 4.58383600 | 2.06038000 | -1.06553400 |
| H | 4.36516900 | 3.11466400 | -0.90293600 |
| H | 5.63152900 | 1.86122600 | -0.82761400 |
| H | 4.44381600 | 1.88669800 | -2.13715600 |
| O | 2.06792000 | 3.33413700 | -1.46038700 |
| H | 5.49121600 | -1.74329500 | -0.50613100 |
| H | 3.86843700 | -2.51423100 | -2.20123300 |
| H | 4.38501200 | -1.24051600 | 2.09483900 |
| H | 5.28905800 | 0.27514100 | 0.71474600 |
| C | -5.72696100 | -0.78442600 | -0.10233800 |
| C | -4.75918900 | 0.04065900 | -0.66752300 |
| C | -3.40352200 | -0.22233100 | -0.52781800 |
| C | -3.00763500 | -1.34932700 | 0.19985700 |
| C | -3.96571500 | -2.18926800 | 0.77325900 |
| C | -5.31844200 | -1.90345200 | 0.62121500 |
| H | -6.77770600 | -0.55677300 | -0.22618700 |
| H | -2.66362400 | 0.42777000 | -0.97291700 |
| H | -3.63668800 | -3.05646100 | 1.33020400 |
| H | -6.06442800 | -2.55191600 | 1.06468300 |
| Cl | -5.26833200 | 1.45781400 | -1.58763400 |
| C | -1.55472500 | -1.68900400 | 0.37793100 |
| O | -1.19226900 | -2.70600300 | 0.97067500 |
| O | -0.73218900 | -0.82188800 | -0.14460300 |
| O | 0.90620100 | -1.43856800 | 0.11006000 |
| H | 0.51990300 | -2.20433000 | 0.59735600 |

**TS-3 Gas**

E(RB3LYP) = -1615.88680504 A.U.

1 imaginary frequency -401.9194 $cm^{-1}$

Zero-point correction= 0.440704 (Hartree/Particle)
Thermal correction to Energy= 0.469417
Thermal correction to Enthalpy= 0.470361
Thermal correction to Gibbs Free Energy= 0.377632
Sum of electronic and zero-point Energies= -1615.446101
Sum of electronic and thermal Energies= -1615.417388
Sum of electronic and thermal Enthalpies= -1615.416444
Sum of electronic and thermal Free Energies= -1615.509173

| | E (Thermal) KCal/Mol | CV Cal/Mol-Kelvin | S Cal/Mol-Kelvin |
|---|---|---|---|
| Total | 294.563 | 106.304 | 195.165 |

| | | | |
|---|---|---|---|
| C | -1.52242300 | -3.01139700 | 0.04529600 |
| C | -2.00663100 | -2.60801700 | -1.32901400 |
| C | -3.19087200 | -2.01327100 | -1.50540400 |
| C | -4.16189300 | -1.69228900 | -0.39784800 |
| C | -3.54340100 | -1.74038800 | 1.01077200 |
| C | -2.61391900 | -2.98228900 | 1.12025100 |
| H | -0.68886600 | -2.36424800 | 0.33376900 |
| H | -3.50614600 | -1.75219500 | -2.51307100 |
| H | -4.62990000 | -0.71747300 | -0.57359900 |
| H | -2.16547100 | -3.04200600 | 2.11468900 |
| C | -1.06640900 | -2.88706400 | -2.46898100 |
| H | -0.12615100 | -2.34702500 | -2.32013700 |
| H | -0.82800300 | -3.95539800 | -2.52790900 |
| H | -1.49166900 | -2.57728500 | -3.42605200 |
| C | -2.91396500 | -0.46432800 | 1.52387200 |
| C | -2.56986000 | 0.59434900 | 0.69335700 |
| C | -2.33448800 | 2.00704000 | 1.14826400 |
| C | -1.91205800 | 3.01066100 | 0.13209900 |
| H | -1.11252800 | 3.64279600 | 0.50719600 |
| C | -2.43119000 | 3.27948700 | -1.07536000 |
| C | -3.62534800 | 2.59205500 | -1.68834400 |
| H | -3.32367200 | 1.98098500 | -2.54708700 |
| H | -4.17052500 | 1.96202600 | -0.98717600 |
| H | -4.32554100 | 3.34196900 | -2.07044300 |
| C | -1.84708800 | 4.38052200 | -1.92281300 |
| H | -0.96851700 | 4.83049600 | -1.45931100 |
| H | -1.55659800 | 3.99114000 | -2.90533200 |
| H | -2.58679400 | 5.16875700 | -2.10330200 |
| C | -2.74592200 | -0.37973600 | 3.00675900 |
| H | -3.44422600 | 0.35973000 | 3.41213700 |
| H | -2.92410600 | -1.34450300 | 3.48338600 |
| H | -1.75155000 | -0.01223100 | 3.26188600 |
| O | -2.40375600 | 2.32928400 | 2.32048600 |
| H | -3.25652200 | -3.86153200 | 1.00945300 |
| H | -1.10434500 | -4.02398200 | -0.00580600 |
| H | -4.99217200 | -2.41115800 | -0.42411400 |
| H | -4.35783900 | -1.91440700 | 1.72831600 |
| H | -2.71572000 | 0.45898400 | -0.37015400 |
| O | -0.67909600 | 0.08227600 | 0.89763000 |
| H | -0.56052500 | -0.12702800 | -0.06725400 |
| O | 1.19293000 | 0.03874900 | 0.94944300 |
| C | 1.56159900 | -0.13674500 | -0.27428600 |
| C | 3.05206100 | -0.12366900 | -0.49693400 |
| C | 3.93519000 | 0.05144200 | 0.57209100 |
| C | 3.54159600 | -0.28608100 | -1.79465600 |
| C | 5.30037700 | 0.05766100 | 0.32114500 |
| H | 3.55197700 | 0.17939600 | 1.57483400 |
| C | 4.91345700 | -0.27486300 | -2.02320400 |
| H | 2.83491300 | -0.41493500 | -2.60387500 |
| C | 5.80472200 | -0.10370500 | -0.96587600 |
| H | 5.29817100 | -0.39938800 | -3.02890100 |
| H | 6.87403500 | -0.09411400 | -1.13361300 |
| Cl | 6.42214600 | 0.27607400 | 1.66239200 |
| O | 0.77874700 | -0.30866700 | -1.21834800 |

**TS-3 DCM**

E(RB3LYP) = -1615.89952731 A.U.

1 imaginary frequency -432.9754 $cm^{-1}$

Zero-point correction= 0.440063 (Hartree/Particle)
Thermal correction to Energy= 0.468890
Thermal correction to Enthalpy= 0.469835
Thermal correction to Gibbs Free Energy= 0.376746
Sum of electronic and zero-point Energies= -1615.459465
Sum of electronic and thermal Energies= -1615.430637
Sum of electronic and thermal Enthalpies= -1615.429693
Sum of electronic and thermal Free Energies= -1615.522781

| | E (Thermal) KCal/Mol | CV Cal/Mol-Kelvin | S Cal/Mol-Kelvin |
|---|---|---|---|
| Total | 294.233 | 106.707 | 195.921 |

| | | | |
|---|---|---|---|
| C | -1.43163500 | -3.07824400 | 0.06772000 |
| C | -1.86200800 | -2.67412000 | -1.32442900 |
| C | -3.04188300 | -2.08593500 | -1.54811200 |
| C | -4.06142100 | -1.77857700 | -0.48070500 |
| C | -3.50178900 | -1.82951100 | 0.95116500 |
| C | -2.57089900 | -3.06808900 | 1.09227700 |
| H | -0.62084300 | -2.41926100 | 0.39537700 |
| H | -3.31779800 | -1.82356900 | -2.56696600 |
| H | -4.53506200 | -0.81111800 | -0.67485500 |
| H | -2.16967500 | -3.13980400 | 2.10535400 |
| C | -0.87938000 | -2.95505700 | -2.42905700 |
| H | 0.06117000 | -2.42535600 | -2.24572700 |
| H | -0.64475000 | -4.02446000 | -2.48199200 |
| H | -1.26472200 | -2.63883700 | -3.40088600 |
| C | -2.89754900 | -0.55861900 | 1.50212300 |
| C | -2.58878900 | 0.53282300 | 0.70303400 |
| C | -2.34554800 | 1.92795600 | 1.19008000 |
| C | -2.11899100 | 2.99807100 | 0.18449800 |
| H | -1.34689100 | 3.69124400 | 0.50726400 |
| C | -2.77800900 | 3.26789000 | -0.95604200 |
| C | -3.96775100 | 2.51146200 | -1.48771400 |
| H | -3.69551000 | 1.94794000 | -2.38745400 |
| H | -4.40862100 | 1.82615300 | -0.76604600 |
| H | -4.74474500 | 3.22054500 | -1.78953300 |
| C | -2.37049600 | 4.45042100 | -1.79605300 |
| H | -1.48195100 | 4.94564900 | -1.40325700 |
| H | -2.16587000 | 4.13099800 | -2.82405100 |
| H | -3.18382500 | 5.18216100 | -1.85249500 |
| C | -2.72176700 | -0.52330900 | 2.98611800 |
| H | -3.36437900 | 0.25230400 | 3.41328600 |
| H | -2.96254700 | -1.48347800 | 3.44139600 |
| H | -1.70233400 | -0.23351300 | 3.24542900 |
| O | -2.25058700 | 2.19681100 | 2.37975400 |
| H | -3.20294400 | -3.94810300 | 0.94074800 |

| | | | |
|---|---|---|---|
| H | -0.99826600 | -4.08479000 | 0.03158600 |
| H | -4.87971900 | -2.50787400 | -0.54391800 |
| H | -4.34281300 | -2.01117200 | 1.63510000 |
| H | -2.75753600 | 0.43279100 | -0.36014800 |
| O | -0.61542600 | 0.06233100 | 0.82703200 |
| H | -0.54937500 | -0.09342500 | -0.14750900 |
| O | 1.22223700 | 0.02319700 | 0.85882800 |
| C | 1.61574400 | -0.03847400 | -0.37506300 |
| C | 3.11043300 | 0.00049400 | -0.55826600 |
| C | 3.96840300 | 0.10945200 | 0.54065900 |
| C | 3.63206000 | -0.06928200 | -1.85243200 |
| C | 5.33808300 | 0.14419100 | 0.31944000 |
| H | 3.56657000 | 0.16561200 | 1.54254900 |
| C | 5.00873100 | -0.03203100 | -2.04906200 |
| H | 2.95026100 | -0.14954400 | -2.68852900 |
| C | 5.87509300 | 0.07471700 | -0.96245800 |
| H | 5.41639600 | -0.08565000 | -3.05141900 |
| H | 6.94720500 | 0.10431000 | -1.10738900 |
| Cl | 6.42762900 | 0.28154000 | 1.70182400 |
| O | 0.85191300 | -0.12775200 | -1.34102100 |

**TS-4 Gas**

E(RB3LYP) = -1615.59656837 A.U.

1 imaginary frequency - -416.8667 $cm^{-1}$

Zero-point correction= 0.443755 (Hartree/Particle)
Thermal correction to Energy= 0.472183
Thermal correction to Enthalpy= 0.473127
Thermal correction to Gibbs Free Energy= 0.381497
Sum of electronic and zero-point Energies= -1615.152813
Sum of electronic and thermal Energies= -1615.124385
Sum of electronic and thermal Enthalpies= -1615.123441
Sum of electronic and thermal Free Energies= -1615.215071

| | E (Thermal) KCal/Mol | CV Cal/Mol-Kelvin | S Cal/Mol-Kelvin |
|---|---|---|---|
| Total | 296.299 | 105.748 | 192.852 |

| | | | |
|---|---|---|---|
| C | 1.30244700 | 3.00263800 | 0.11053200 |
| C | 1.44700500 | 2.66857200 | -1.35828400 |
| C | 2.59087700 | 2.17690400 | -1.85563200 |
| C | 3.83819100 | 1.92335000 | -1.04659000 |
| C | 3.59636800 | 1.87288100 | 0.47456100 |
| C | 2.63062600 | 3.02293600 | 0.87776400 |
| H | 0.60362100 | 2.29550500 | 0.57185100 |
| H | 2.65512200 | 1.96573800 | -2.92234000 |
| H | 4.33345600 | 1.00413700 | -1.38322800 |
| H | 2.44348200 | 3.01016800 | 1.95591500 |
| C | 0.23091300 | 2.90137900 | -2.21410800 |
| H | -0.60794200 | 2.29519700 | -1.85392800 |
| H | -0.08352900 | 3.95243400 | -2.17237000 |

| | | | |
|---|---|---|---|
| H | 0.41788300 | 2.64327600 | -3.26041300 |
| C | 3.24238700 | 0.51956200 | 1.06444700 |
| C | 2.83039700 | -0.55544600 | 0.28393000 |
| H | 2.69818500 | -0.36847300 | -0.77473200 |
| C | 2.95859100 | -1.99461400 | 0.68873300 |
| C | 2.71086000 | -3.08298800 | -0.28658600 |
| H | 3.16617200 | -4.00462000 | 0.06948800 |
| C | 2.02073500 | -3.13949800 | -1.44666500 |
| C | 1.23612200 | -2.02181400 | -2.09145500 |
| H | 0.73883800 | -1.37202500 | -1.37223700 |
| H | 1.88088700 | -1.40091900 | -2.72779800 |
| H | 0.46256400 | -2.43437400 | -2.74591100 |
| C | 1.98227000 | -4.44129800 | -2.20830600 |
| H | 2.60190700 | -5.21349200 | -1.74716500 |
| H | 0.95280200 | -4.81543600 | -2.27678100 |
| H | 2.32456500 | -4.29033900 | -3.24047200 |
| C | 3.49639900 | 0.38267200 | 2.53519200 |
| H | 3.63442500 | 1.35996500 | 3.00400900 |
| H | 2.68831500 | -0.15978300 | 3.02563700 |
| H | 4.39875100 | -0.21988600 | 2.69155700 |
| O | 3.36894200 | -2.30042800 | 1.80605400 |
| H | 3.15796800 | 3.95941700 | 0.66126300 |
| H | 0.82292100 | 3.98614800 | 0.20865900 |
| H | 4.56659500 | 2.72438700 | -1.24327800 |
| H | 4.55247900 | 2.10204000 | 0.97000400 |
| C | -3.77007200 | 0.09871800 | -0.25723800 |
| C | -5.14527600 | -0.00422000 | -0.07829100 |
| C | -5.69314900 | -0.37033300 | 1.15162000 |
| C | -4.83702800 | -0.63873900 | 2.22097700 |
| C | -3.45580300 | -0.54241800 | 2.06401300 |
| C | -2.92302400 | -0.17276800 | 0.82346700 |
| H | -3.34254500 | 0.38074800 | -1.21145800 |
| H | -6.76901000 | -0.44340600 | 1.26568600 |
| H | -5.25621300 | -0.92521600 | 3.18060700 |
| H | -2.78405500 | -0.75061500 | 2.88852100 |
| Cl | -6.21929500 | 0.33386900 | -1.43217500 |
| C | -1.43947400 | -0.05706800 | 0.60885500 |
| O | -0.97219400 | 0.27027100 | -0.49928000 |
| O | -0.71239000 | -0.31636200 | 1.64887400 |
| O | 1.03150300 | -0.20168600 | 1.06962200 |
| H | 0.64130800 | 0.13886700 | 0.21812500 |

**TS-4 DCM**

E(RB3LYP) = -1615.89952731 A.U.

1 imaginary frequency -432.9754 $cm^{-1}$

Zero-point correction= 0.440063 (Hartree/Particle)
Thermal correction to Energy= 0.468890
Thermal correction to Enthalpy= 0.469835
Thermal correction to Gibbs Free Energy= 0.376746
Sum of electronic and zero-point Energies= -1615.459465

Sum of electronic and thermal Energies= -1615.430637
Sum of electronic and thermal Enthalpies= -1615.429693
Sum of electronic and thermal Free Energies= -1615.522781

| | E (Thermal) KCal/Mol | CV Cal/Mol-Kelvin | S Cal/Mol-Kelvin |
|---|---|---|---|
| Total | 294.233 | 106.707 | 195.921 |

| | | | |
|---|---|---|---|
| C | -1.46055400 | -3.12509000 | 0.09868400 |
| C | -1.41343600 | -2.71207400 | -1.35582200 |
| C | -2.45128900 | -2.10657200 | -1.94333800 |
| C | -3.76120700 | -1.79841500 | -1.26195700 |
| C | -3.69022600 | -1.85118700 | 0.27321900 |
| C | -2.87044000 | -3.10100600 | 0.69890200 |
| H | -0.78815800 | -2.48056000 | 0.67664800 |
| H | -2.38052500 | -1.83778200 | -2.99482600 |
| H | -4.15149300 | -0.83421200 | -1.60154200 |
| H | -2.81919500 | -3.18485900 | 1.78619700 |
| C | -0.13335000 | -3.01124400 | -2.08823800 |
| H | 0.71092700 | -2.51058800 | -1.60369800 |
| H | 0.07853900 | -4.08669700 | -2.08018700 |
| H | -0.17654400 | -2.67717300 | -3.12723800 |
| C | -3.29519000 | -0.58198200 | 0.99799700 |
| C | -2.85131900 | 0.54843000 | 0.32829200 |
| H | -2.76604100 | 0.47608800 | -0.74600600 |
| C | -2.89870800 | 1.93980400 | 0.87521100 |
| C | -2.84836000 | 3.09701900 | -0.04860300 |
| H | -3.34873900 | 3.95354300 | 0.39565600 |
| C | -2.25993800 | 3.27887300 | -1.24816600 |
| C | -1.41636400 | 2.28283500 | -2.00023400 |
| H | -0.95067500 | 1.53529700 | -1.36334900 |
| H | -2.01521100 | 1.77180800 | -2.76338700 |
| H | -0.61842500 | 2.80609000 | -2.53355700 |
| C | -2.40363900 | 4.60910500 | -1.94056100 |
| H | -3.07242200 | 5.28404900 | -1.40571700 |
| H | -1.42628700 | 5.09286000 | -2.04581600 |
| H | -2.78878400 | 4.46468600 | -2.95630500 |
| C | -3.52832700 | -0.59274700 | 2.47581300 |
| H | -3.91501700 | -1.55336500 | 2.81361900 |
| H | -2.60369100 | -0.36229800 | 3.00806400 |
| H | -4.22898000 | 0.20126600 | 2.74629400 |
| O | -3.08542200 | 2.15702800 | 2.06801900 |
| H | -3.42781400 | -3.97268900 | 0.34330600 |
| H | -1.05090900 | -4.13728100 | 0.19808400 |
| H | -4.51216700 | -2.53191400 | -1.58377400 |
| H | -4.70963300 | -2.02234000 | 0.64936500 |
| C | 3.87131900 | 0.00229500 | -0.32268700 |
| C | 5.23713500 | 0.08797900 | -0.09646500 |
| C | 5.75579500 | 0.28250300 | 1.18031700 |
| C | 4.87452400 | 0.39378400 | 2.25425400 |
| C | 3.50010400 | 0.31136200 | 2.05250800 |
| C | 2.99771500 | 0.11444800 | 0.76302600 |
| H | 3.47376200 | -0.14542500 | -1.31712300 |
| H | 6.82555100 | 0.34618300 | 1.33127400 |

| | | | |
|---|---|---|---|
| H | 5.26861700 | 0.54633300 | 3.25171500 |
| H | 2.81586700 | 0.39894300 | 2.88566800 |
| Cl | 6.34533500 | -0.05262100 | -1.46343600 |
| C | 1.52001900 | 0.02165800 | 0.49100800 |
| O | 1.08077700 | -0.14414900 | -0.64989400 |
| O | 0.77409400 | 0.12428300 | 1.54916400 |
| O | -0.95659800 | 0.11001100 | 0.99696900 |
| H | -0.64163100 | -0.16145100 | 0.10203000 |

**TS-5 Gas**

E(RB3LYP) = -1615.89318406 A.U.

1 imaginary frequency -393.5528 $cm^{-1}$

Zero-point correction= 0.440715 (Hartree/Particle)
Thermal correction to Energy= 0.469488
Thermal correction to Enthalpy= 0.470432
Thermal correction to Gibbs Free Energy= 0.376932
Sum of electronic and zero-point Energies= -1615.452469
Sum of electronic and thermal Energies= -1615.423696
Sum of electronic and thermal Enthalpies= -1615.422752
Sum of electronic and thermal Free Energies= -1615.516252

| | E (Thermal) KCal/Mol | CV Cal/Mol-Kelvin | S Cal/Mol-Kelvin |
|---|---|---|---|
| Total | 294.608 | 106.216 | 196.788 |

| | | | |
|---|---|---|---|
| C | 2.80039600 | -2.97347500 | -1.08415400 |
| C | 1.74667200 | -2.84609200 | -0.00727800 |
| C | 2.04177600 | -2.34616400 | 1.19540800 |
| C | 3.40698100 | -1.85406900 | 1.60728400 |
| C | 4.37816000 | -1.65341600 | 0.43010100 |
| C | 4.22992500 | -2.85186000 | -0.54503300 |
| H | 2.61557500 | -2.21011300 | -1.85264600 |
| H | 1.25471800 | -2.26725900 | 1.94122600 |
| H | 3.30979000 | -0.92465700 | 2.17897100 |
| H | 4.94262800 | -2.77136900 | -1.37002300 |
| C | 0.35501600 | -3.27564200 | -0.38334200 |
| H | -0.00436100 | -2.70907000 | -1.25018600 |
| H | 0.32909200 | -4.33523300 | -0.66454200 |
| H | -0.35027400 | -3.11665600 | 0.43393800 |
| C | 4.26784800 | -0.33811500 | -0.32498600 |
| C | 3.20182800 | 0.48220500 | -0.18512200 |
| H | 2.38827600 | 0.19963300 | 0.46812200 |
| C | 3.00892400 | 1.73765900 | -0.92042000 |
| C | 1.85429300 | 2.63969500 | -0.57286000 |
| H | 1.37992300 | 3.05301000 | -1.45837800 |
| C | 1.54214900 | 3.20276300 | 0.64383100 |
| C | 2.25901900 | 2.88758600 | 1.92324300 |
| H | 1.53484500 | 2.59979900 | 2.68954500 |
| H | 2.99325600 | 2.09233600 | 1.81684300 |
| H | 2.77129000 | 3.78808200 | 2.28030800 |

| | | | |
|---|---|---|---|
| C | 0.55881100 | 4.33855000 | 0.71726100 |
| H | -0.01971700 | 4.44557800 | -0.20068100 |
| H | -0.13156200 | 4.19632900 | 1.55218000 |
| H | 1.09730800 | 5.27644200 | 0.89689800 |
| C | 5.42449300 | -0.03920700 | -1.24573700 |
| H | 5.75537300 | 0.99530200 | -1.14650500 |
| H | 6.26339500 | -0.71127600 | -1.05296400 |
| H | 5.12629800 | -0.14658200 | -2.29299100 |
| O | 3.71138500 | 2.12492500 | -1.84707600 |
| H | 4.48729800 | -3.76190500 | 0.00715200 |
| H | 2.68499200 | -3.93681000 | -1.59532000 |
| H | 3.85712900 | -2.57360100 | 2.30488200 |
| H | 5.40204400 | -1.68319300 | 0.82401700 |
| C | -4.42437400 | 0.32514600 | -0.46547600 |
| C | -5.60841500 | -0.37770400 | -0.29555800 |
| C | -5.70747400 | -1.42350700 | 0.61777200 |
| C | -4.58960000 | -1.76721700 | 1.37500900 |
| C | -3.39136700 | -1.07763400 | 1.21912400 |
| C | -3.30935000 | -0.03104800 | 0.29729400 |
| H | -4.34627400 | 1.14004600 | -1.17192200 |
| H | -6.64301200 | -1.95574300 | 0.73222700 |
| H | -4.66017200 | -2.57919900 | 2.08941400 |
| H | -2.51955100 | -1.33688300 | 1.80488300 |
| Cl | -7.01829000 | 0.06311500 | -1.25453800 |
| C | -2.03996700 | 0.74827700 | 0.09548200 |
| O | -1.99743700 | 1.72028800 | -0.66630400 |
| O | -1.02000800 | 0.32003000 | 0.77439100 |
| O | 0.31893500 | 1.48632400 | 0.37073400 |
| H | -0.34481100 | 1.90713400 | -0.24231800 |

**TS-5 DCM**

E(RB3LYP) = -1615.89952731 A.U.

1 imaginary frequency -432.9754 $cm^{-1}$

Zero-point correction= 0.440063 (Hartree/Particle)
Thermal correction to Energy= 0.468890
Thermal correction to Enthalpy= 0.469835
Thermal correction to Gibbs Free Energy= 0.376746
Sum of electronic and zero-point Energies= -1615.459465
Sum of electronic and thermal Energies= -1615.430637
Sum of electronic and thermal Enthalpies= -1615.429693
Sum of electronic and thermal Free Energies= -1615.522781

| | E (Thermal) KCal/Mol | CV Cal/Mol-Kelvin | S Cal/Mol-Kelvin |
|---|---|---|---|
| Total | 294.233 | 106.707 | 195.921 |

| | | | |
|---|---|---|---|
| C | 2.83002100 | -3.02329200 | -1.01694400 |
| C | 1.80170300 | -2.88468400 | 0.08377400 |
| C | 2.11372200 | -2.32469700 | 1.25679300 |
| C | 3.47405000 | -1.77351400 | 1.60830900 |

| | | | |
|---|---|---|---|
| C | 4.40566100 | -1.59291900 | 0.39665400 |
| C | 4.26852100 | -2.83615800 | -0.52213400 |
| H | 2.60086100 | -2.30047800 | -1.81234300 |
| H | 1.34953700 | -2.25183500 | 2.02774100 |
| H | 3.36489100 | -0.82886300 | 2.15130200 |
| H | 4.95700800 | -2.77299300 | -1.36813700 |
| C | 0.41775500 | -3.38672500 | -0.22989100 |
| H | 0.00674700 | -2.87189000 | -1.10648500 |
| H | 0.43083100 | -4.45574000 | -0.47263000 |
| H | -0.26780800 | -3.23160200 | 0.60562200 |
| C | 4.23976800 | -0.31373100 | -0.40867600 |
| C | 3.18372600 | 0.51309300 | -0.23279900 |
| H | 2.42934000 | 0.25923400 | 0.49750100 |
| C | 2.92691000 | 1.74440200 | -0.98813900 |
| C | 1.85587800 | 2.69286800 | -0.52850200 |
| H | 1.36331500 | 3.17803200 | -1.36630100 |
| C | 1.64672700 | 3.22487600 | 0.72329400 |
| C | 2.39306300 | 2.82131100 | 1.95724100 |
| H | 1.68841100 | 2.46164600 | 2.71250100 |
| H | 3.14431500 | 2.05638000 | 1.77994000 |
| H | 2.88456500 | 3.70451300 | 2.37865100 |
| C | 0.70530700 | 4.38226500 | 0.89276300 |
| H | 0.10701200 | 4.56721500 | 0.00058000 |
| H | 0.04013200 | 4.21427500 | 1.74360600 |
| H | 1.28317000 | 5.28660400 | 1.11461400 |
| C | 5.33932200 | -0.05577200 | -1.40691900 |
| H | 5.57712000 | 1.00477700 | -1.47838500 |
| H | 6.23834900 | -0.61918700 | -1.14855700 |
| H | 5.02705300 | -0.36398100 | -2.41029300 |
| O | 3.51060300 | 2.06497200 | -2.02184700 |
| H | 4.56711400 | -3.71225000 | 0.06268500 |
| H | 2.73100000 | -4.01048400 | -1.48348900 |
| H | 3.96597200 | -2.45295000 | 2.31711400 |
| H | 5.43950300 | -1.57660100 | 0.76283800 |
| C | -4.47964800 | 0.34921000 | -0.45024900 |
| C | -5.64436200 | -0.38454200 | -0.28059100 |
| C | -5.69862000 | -1.48129700 | 0.57465100 |
| C | -4.55004500 | -1.84607300 | 1.27472800 |
| C | -3.36864600 | -1.12722800 | 1.11868900 |
| C | -3.33338000 | -0.02873200 | 0.25513100 |
| H | -4.44303900 | 1.20242100 | -1.11318600 |
| H | -6.61954700 | -2.03756200 | 0.69148100 |
| H | -4.58334000 | -2.69701100 | 1.94427800 |
| H | -2.47763000 | -1.40895600 | 1.66339300 |
| Cl | -7.09397600 | 0.08611300 | -1.17056600 |
| C | -2.08638400 | 0.78516900 | 0.05466900 |
| O | -2.08148800 | 1.80470700 | -0.63970900 |
| O | -1.03363600 | 0.32545400 | 0.66759700 |
| O | 0.29211300 | 1.48948000 | 0.32474900 |
| H | -0.35431000 | 1.99348200 | -0.23186600 |

**TS-6 Gas**

E(RB3LYP) = -1615.89857459 A.U.

1 imaginary frequency -395.4896 $cm^{-1}$

| | |
|---|---|
| Zero-point correction= | 0.440903 (Hartree/Particle) |
| Thermal correction to Energy= | 0.469659 |
| Thermal correction to Enthalpy= | 0.470603 |
| Thermal correction to Gibbs Free Energy= | 0.377353 |
| Sum of electronic and zero-point Energies= | -1615.457672 |
| Sum of electronic and thermal Energies= | -1615.428916 |
| Sum of electronic and thermal Enthalpies= | -1615.427972 |
| Sum of electronic and thermal Free Energies= | -1615.521222 |

| | E (Thermal) KCal/Mol | CV Cal/Mol-Kelvin | S Cal/Mol-Kelvin |
|---|---|---|---|
| Total | 294.715 | 106.064 | 196.261 |

| | | | |
|---|---|---|---|
| C | 1.09245900 | 2.60417000 | 0.53279800 |
| C | 1.07913100 | 2.78407900 | -0.96873900 |
| C | 2.21409100 | 2.96979100 | -1.64963400 |
| C | 3.59248300 | 3.00770100 | -1.03873800 |
| C | 3.65223800 | 2.56773600 | 0.44011300 |
| C | 2.39269300 | 3.09291000 | 1.18071800 |
| H | 0.91847800 | 1.54618600 | 0.77015700 |
| H | 2.16600000 | 3.11008900 | -2.72768800 |
| H | 4.27851800 | 2.39393900 | -1.63405600 |
| H | 2.42073700 | 2.80590200 | 2.23573400 |
| C | -0.26425000 | 2.70911500 | -1.64314500 |
| H | -0.72780300 | 1.72906000 | -1.48175600 |
| H | -0.95301100 | 3.45801600 | -1.23541100 |
| H | -0.18318900 | 2.87063100 | -2.72038100 |
| C | 3.82722100 | 1.07727200 | 0.68768400 |
| C | 3.35606100 | 0.15898500 | -0.18307400 |
| H | 2.84291900 | 0.51601500 | -1.06859800 |
| C | 3.36487000 | -1.30265000 | -0.00798300 |
| C | 2.44306400 | -2.02134500 | -0.94652300 |
| H | 2.17356100 | -1.47765700 | -1.84692300 |
| C | 2.00042900 | -3.32538100 | -0.83826200 |
| C | 2.36003500 | -4.24176500 | 0.28857400 |
| H | 3.25025800 | -4.81619900 | 0.00351900 |
| H | 2.60546000 | -3.69924800 | 1.19572300 |
| H | 1.54967400 | -4.95088700 | 0.47044300 |
| C | 1.20702500 | -3.93749900 | -1.95655700 |
| H | 0.95407100 | -3.21921900 | -2.73710800 |
| H | 1.78909700 | -4.75083700 | -2.40615400 |
| H | 0.28552800 | -4.38160300 | -1.57176700 |
| C | 4.51990100 | 0.73644100 | 1.97871100 |
| H | 5.60573300 | 0.76304600 | 1.82215800 |
| H | 4.29188000 | 1.48084700 | 2.74653400 |
| H | 4.27570500 | -0.26128700 | 2.33400500 |
| O | 4.03485700 | -1.91077900 | 0.81741800 |
| H | 2.42141100 | 4.18748000 | 1.15023500 |
| H | 0.24504400 | 3.14560600 | 0.96936900 |
| H | 3.98548900 | 4.03096100 | -1.11024200 |
| H | 4.52167200 | 3.05352500 | 0.89812600 |

| | | | |
|---|---|---|---|
| C | -3.94822200 | -0.13992300 | -0.35578400 |
| C | -5.19659600 | 0.28363200 | 0.07661900 |
| C | -5.52760800 | 0.30696400 | 1.42837600 |
| C | -4.58062400 | -0.10664100 | 2.36301300 |
| C | -3.32295300 | -0.53654800 | 1.95211500 |
| C | -3.00663800 | -0.55064900 | 0.59140500 |
| H | -3.69040600 | -0.15972700 | -1.40569300 |
| H | -6.50849900 | 0.64223800 | 1.73983400 |
| H | -4.83169100 | -0.09170700 | 3.41722800 |
| H | -2.58230700 | -0.86091800 | 2.67099900 |
| Cl | -6.39010500 | 0.80341400 | -1.11030100 |
| C | -1.66066600 | -1.00697400 | 0.10011200 |
| O | -1.37066000 | -0.97238100 | -1.10353700 |
| O | -0.85456700 | -1.42309300 | 1.02290800 |
| O | 0.66449900 | -1.92693300 | 0.12499600 |
| H | 0.16957200 | -1.63331800 | -0.68826800 |

**TS-6 DCM**

E(RB3LYP) = -1615.91090739 A.U.

1 imaginary frequency -431.4749 $cm^{-1}$

Zero-point correction= 0.439999 (Hartree/Particle)
Thermal correction to Energy= 0.468929
Thermal correction to Enthalpy= 0.469874
Thermal correction to Gibbs Free Energy= 0.375788
Sum of electronic and zero-point Energies= -1615.470908
Sum of electronic and thermal Energies= -1615.441978
Sum of electronic and thermal Enthalpies= -1615.441034
Sum of electronic and thermal Free Energies= -1615.535120

| | E (Thermal) KCal/Mol | CV Cal/Mol-Kelvin | S Cal/Mol-Kelvin |
|---|---|---|---|
| Total | 294.258 | 106.585 | 198.021 |

| | | | |
|---|---|---|---|
| C | -1.17512170 | -2.72937375 | 0.49173767 |
| C | -1.19676519 | -2.84328447 | -1.01632027 |
| C | -2.35182572 | -2.92900597 | -1.68394239 |
| C | -3.71954325 | -2.91271081 | -1.04846716 |
| C | -3.72834817 | -2.52797575 | 0.44600323 |
| C | -2.49357146 | -3.16118751 | 1.14280451 |
| H | -0.93066409 | -1.69489174 | 0.76897781 |
| H | -2.33033739 | -3.02103812 | -2.76813737 |
| H | -4.37930670 | -2.24149904 | -1.60982747 |
| H | -2.48623222 | -2.91991103 | 2.20904019 |
| C | 0.13899190 | -2.82299007 | -1.71051643 |
| H | 0.67433038 | -1.89025995 | -1.49674880 |
| H | 0.77914193 | -3.64068843 | -1.35957683 |
| H | 0.03200965 | -2.91144987 | -2.79397621 |
| C | -3.81054863 | -1.04161821 | 0.75418998 |
| C | -3.35236303 | -0.11278119 | -0.11480802 |
| H | -2.91094118 | -0.45843501 | -1.04190713 |

| | | | |
|---|---|---|---|
| C | -3.31074467 | 1.34332777 | 0.09080837 |
| C | -2.45898292 | 2.06226270 | -0.90858969 |
| H | -2.24263217 | 1.50656824 | -1.81517273 |
| C | -2.04562184 | 3.37845376 | -0.86482045 |
| C | -2.33595334 | 4.31728127 | 0.26160707 |
| H | -3.23057806 | 4.89870693 | 0.00478881 |
| H | -2.54016688 | 3.79717893 | 1.19156118 |
| H | -1.51441371 | 5.02626794 | 0.38399665 |
| C | -1.32887327 | 3.97064404 | -2.04060247 |
| H | -1.15149728 | 3.24738233 | -2.83649765 |
| H | -1.92891170 | 4.79484346 | -2.44312654 |
| H | -0.37499247 | 4.40402079 | -1.72762005 |
| C | -4.41440817 | -0.71810131 | 2.09358737 |
| H | -5.50377227 | -0.64071287 | 1.98734864 |
| H | -4.22245179 | -1.52141412 | 2.80882163 |
| H | -4.06508044 | 0.23154191 | 2.49104071 |
| O | -3.90141204 | 1.94211783 | 0.98679510 |
| H | -2.59380004 | -4.24899650 | 1.06664960 |
| H | -0.35705768 | -3.34067463 | 0.89016293 |
| H | -4.17079535 | -3.90877244 | -1.14852570 |
| H | -4.61831085 | -2.97635165 | 0.90191913 |
| C | 4.01290492 | 0.12063160 | -0.36524653 |
| C | 5.25280594 | -0.30082924 | 0.09195248 |
| C | 5.56416479 | -0.31828613 | 1.44835720 |
| C | 4.60156796 | 0.10057049 | 2.36507540 |
| C | 3.35094271 | 0.52918729 | 1.93059629 |
| C | 3.05564253 | 0.53758830 | 0.56444765 |
| H | 3.77658868 | 0.13334647 | -1.42014845 |
| H | 6.53861453 | -0.65191485 | 1.78049203 |
| H | 4.83465916 | 0.09047604 | 3.42294080 |
| H | 2.60359670 | 0.85523874 | 2.64139218 |
| Cl | 6.46601829 | -0.82853648 | -1.07647013 |
| C | 1.71988727 | 0.99196973 | 0.04561357 |
| O | 1.44070914 | 0.94722945 | -1.15670305 |
| O | 0.90413424 | 1.42527949 | 0.95976388 |
| O | -0.60497637 | 1.92557461 | 0.09911901 |
| H | -0.16236929 | 1.64231220 | -0.74047905 |