Supporting Information of Pentacycloundecanylidene and Pentcaycloundecanone – Hyperconjugatively Stabilized Carbene and Ketone

Jishnu Sai Gopinath and Pattiyil Parameswaran*

* Department of Chemistry, National Institute of Technology Calicut, Kozhikode, Kerala, India – 673601, Email: param@nitc.ac.in

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Table S1: EDA-NOCV results of **U1-H$^+$**, **U2-H$^+$**, **U1-H$^-$**, **U2-H$^-$** and **U-CO-H$^-$** at the BP86/TZ2P level of theory. Energies are in kcal/mol.

	U1-H$^+$	U2-H$^+$	U1-H$^-$	U2-H$^-$	U-CO-H$^-$
ΔE_{int}	-363.5	-353.5	-200.0	-199.2	-172.7
ΔE_{pauli}	533.3	589.8	677.5	695.7	535.5
ΔE_{ele}	-272.7	-259.1	-395.3	-404.4	-334.2
ΔE_{orb}	-624.1	-684.2	-482.2	-490.5	-374.0
$\Delta E_{\sigma1}$	-315.7	-375.5	-271.7	-276.2	-174.4
$\Delta E_{\sigma2}$	-177.9	-169.6	-157.7	-158.7	-158.7
ΔE_{h1}	-85.0	-84.0	--	--	--
ΔE_{h2}	--	--	-29.1	-32.0	--
ΔE_{rest}	-45.5	-55.1	-55.1	-23.6	-40.2
ΔE_{prep}	70.3	62.5	41.7	40.7	49.3
-De	-293.2	-291.0	-158.3	-158.5	-123.4
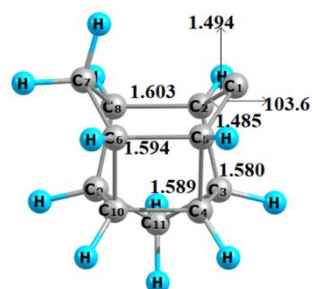
U$_{TS}$
θ$_b$= 7.5°
(1.3)

Figure S1: Equilibrium geometry of transition state (**U$_{TS}$**) between the singlet isomers **U1** and **U2** at the BP86/def2-TZVPP level of theory. θ$_b$ is the bending angle in degrees. The energy barrier based on **U1** in kcal/mol is given in parentheses.

ΔE$_{σ1}$

(-237.2)

ΔE$_{σ2}$

(-186.5)
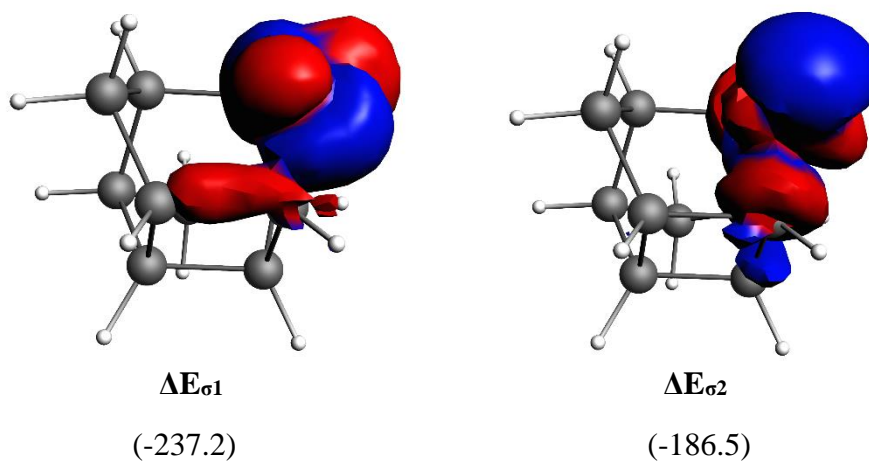
Figure S2: Deformation density plots corresponding to the σ-bonding interactions present in **U1**. Isosurface value is 0.003. The charge flow is from red to blue. Corresponding energies in kcal/mol are given in parentheses.

ΔE$_{σ1}$

(-227.5)

ΔE$_{σ2}$

(-195.1)
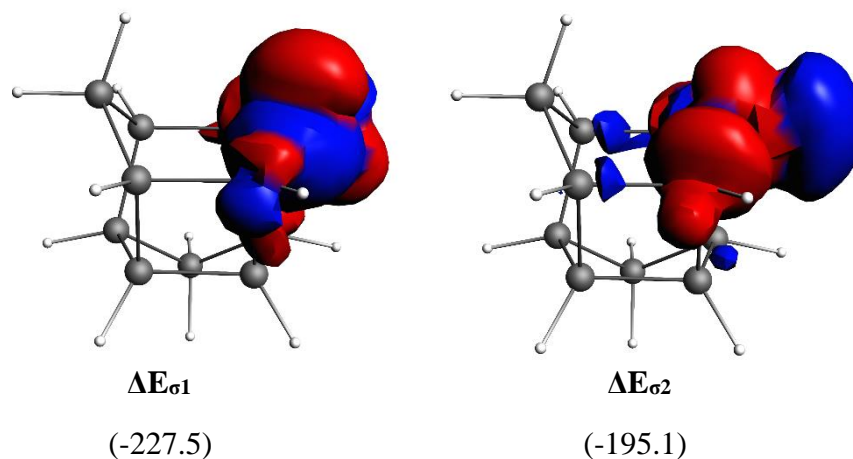
Figure S3: Deformation density plots corresponding to the σ-bonding interactions present in **U2**. Isosurface value is 0.003. The charge flow is from red to blue. Corresponding energies in kcal/mol are given in parentheses.

$\Delta E_{\sigma 1}$ (-157.3) $\Delta E_{\sigma 2}$ (-143.2)
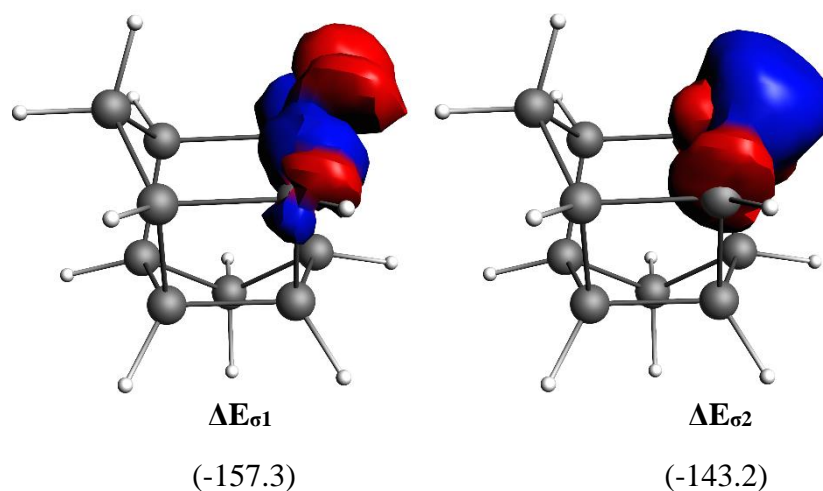
Figure S4: Deformation density plots corresponding to the σ-bonding interactions present in **U3**. Isosurface value is 0.003. The charge flow is from red to blue. Corresponding energies in kcal/mol are given in parentheses.

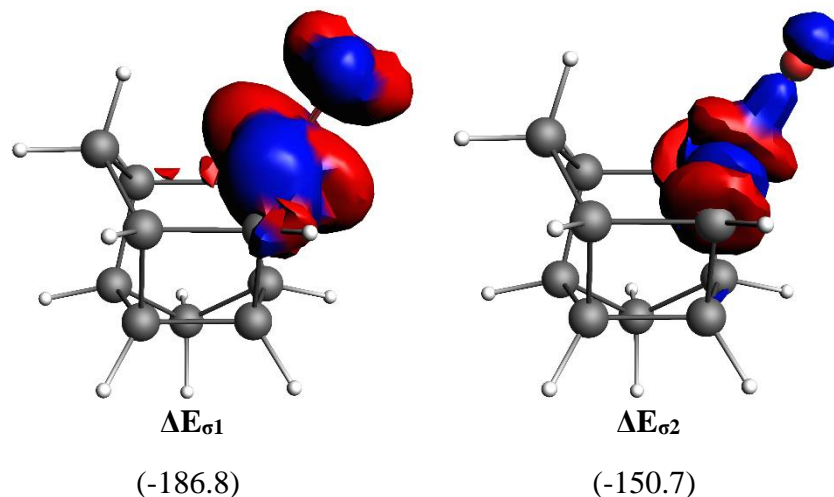$\Delta E_{\sigma 1}$ (-186.8) $\Delta E_{\sigma 2}$ (-150.7)

Figure S5: Deformation density plots corresponding to the σ-bonding interactions present in **U-CO**. Isosurface value is 0.003. The charge flow is from red to blue. Corresponding energies in kcal/mol are given in parentheses.
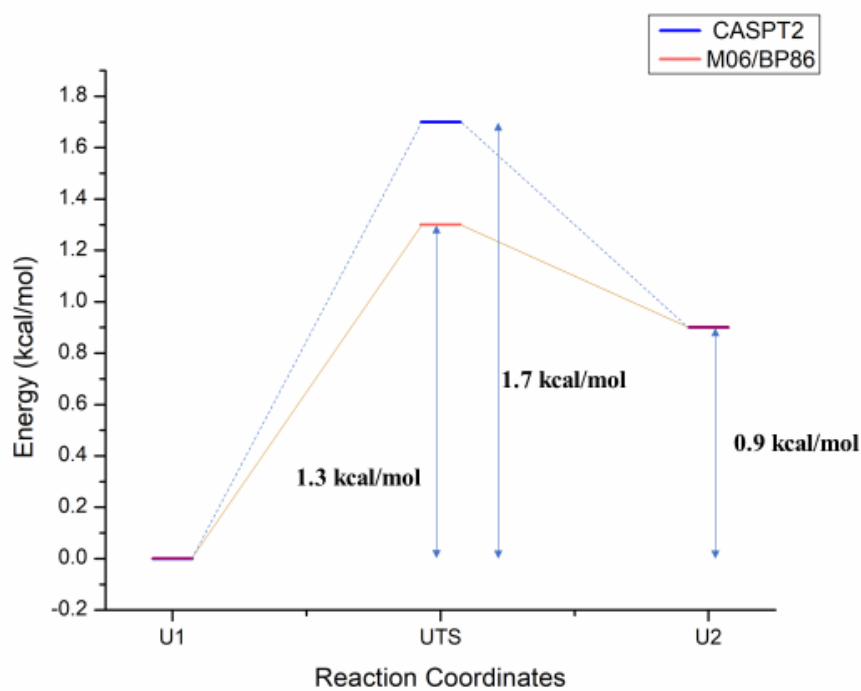
Figure S6: The energy profile diagram of the interconversion between U1 and U2 at M06/def2-TZVPP//BP86/def2-TZVPP level and CASPT2/cc-pVTZ level of theory.
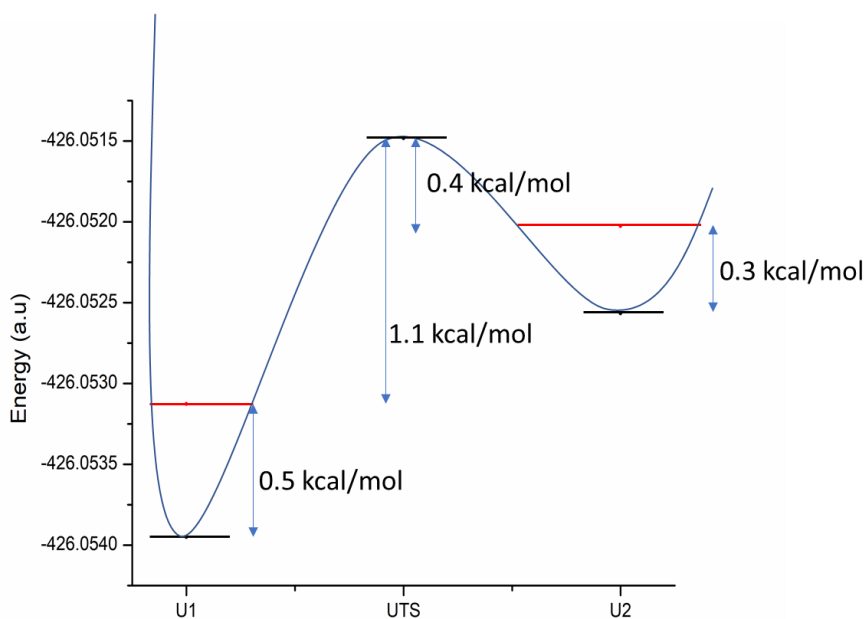
Figure S7: The schematic representation of the potential energy curve for the interconversion of **U1** and **U2** at M06/def2-TZVPP//BP86/def2-TZVPP level. The red line indicates the energy level of the first vibrational state (v = 0).

Table S2: Cartesian coordinates of optimized geometries at BP86/def2-TZVPP level of theory, E^{el}_{M06} (the electronic energy obtained at M06/def2-TZVPP level of theory), ZPE_{BP86} (the zero point energy obtained from the geometry optimized at BP86/def2-TZVPP level of theory) and E_{total} (the sum of ZPE_{BP86} and E^{el}_{M06}) of B_2-L and B_2^{2+}-L. Tin parenthesis indicates triplet geometry, rest are singlet geometries. Energies are in a.u.

U1

$E^{el}_{M06} = - 426.0539273$

$ZPE_{BP86} = 0.193064$

$E_{total} = -425.8608633$

C	0.002792000000	0.242371000000	-1.384597000000
C	0.831925000000	1.174582000000	-0.445197000000
C	1.290953000000	-0.901786000000	0.336537000000
C	0.334638000000	-1.188119000000	-0.848954000000
H	0.110228000000	0.436120000000	-2.458494000000
H	0.663260000000	-1.948413000000	-1.567823000000
C	2.074626000000	0.342111000000	-0.104645000000
H	2.680217000000	0.786903000000	0.699573000000
H	2.727552000000	0.159743000000	-0.972106000000
C	-0.051310000000	1.142835000000	0.831992000000
H	0.212356000000	1.888071000000	1.592479000000
C	0.257647000000	-0.361783000000	1.391620000000
H	0.633699000000	-0.303888000000	2.421563000000
H	1.008410000000	2.190782000000	-0.823808000000
H	1.879444000000	-1.762080000000	0.681703000000
C	-1.048796000000	-1.056267000000	1.231556000000
C	-1.445633000000	0.172668000000	-0.794172000000
C	-1.479696000000	1.265494000000	0.277217000000
C	-1.094925000000	-1.317357000000	-0.211944000000
H	-1.788224000000	-2.088381000000	-0.567702000000
H	-2.274577000000	1.155036000000	1.023705000000
H	-1.593274000000	2.246222000000	-0.216733000000
H	-2.292423000000	0.151401000000	-1.488843000000

U2

E^{el}_{M06} = -426.0525657

ZPE_{BP86} = 0.193236

E_{total} = -425.8593297

C	0.150036000000	-0.347785000000	-1.347757000000
C	-0.748644000000	-1.240638000000	-0.448607000000
C	-1.324077000000	0.867429000000	0.205265000000
C	-0.236725000000	1.114052000000	-0.912829000000
H	0.117097000000	-0.564287000000	-2.422253000000
H	-0.481263000000	1.864172000000	-1.671047000000
C	-2.025654000000	-0.418371000000	-0.265890000000
H	-2.709977000000	-0.829814000000	0.490030000000
H	-2.586550000000	-0.257239000000	-1.201242000000
C	-0.003364000000	-1.102733000000	0.913844000000
H	-0.327164000000	-1.833009000000	1.668438000000
C	-0.370364000000	0.370896000000	1.364286000000
H	-0.839407000000	0.426461000000	2.353649000000
H	-0.865799000000	-2.271246000000	-0.810127000000
H	-1.956692000000	1.722791000000	0.453792000000
C	0.547926000000	1.507163000000	1.054198000000
C	1.545148000000	-0.240164000000	-0.651666000000
C	1.483797000000	-1.201431000000	0.539310000000
C	1.221950000000	1.224922000000	-0.211253000000
H	1.878419000000	2.013532000000	-0.596414000000
H	2.159840000000	-0.909786000000	1.358352000000
H	1.739942000000	-2.228485000000	0.234290000000
H	2.431377000000	-0.333137000000	-1.290878000000

U3

E^{el}_{M06} = -426.0454726

ZPE$_{BP86}$ = 0.19356

E$_{total}$ = -425.8519126

C	0.052516000000	-0.314119000000	-1.376539000000
C	-0.832154000000	-1.187625000000	-0.436724000000
C	-1.276236000000	0.924512000000	0.264977000000
C	-0.256244000000	1.143836000000	-0.896123000000
H	-0.038148000000	-0.530637000000	-2.447942000000
H	-0.539386000000	1.898501000000	-1.639574000000
C	-2.069153000000	-0.311456000000	-0.181537000000
H	-2.729753000000	-0.709348000000	0.603795000000
H	-2.669126000000	-0.135631000000	-1.087850000000
C	-0.011120000000	-1.114560000000	0.883173000000
H	-0.309991000000	-1.857951000000	1.634683000000
C	-0.317192000000	0.385898000000	1.396107000000
H	-0.753643000000	0.396461000000	2.402334000000
H	-1.019856000000	-2.209839000000	-0.792580000000
H	-1.845336000000	1.814105000000	0.560378000000
C	0.884771000000	1.223756000000	1.183670000000
C	1.486139000000	-0.256277000000	-0.750392000000
C	1.450105000000	-1.243626000000	0.420064000000
C	1.196233000000	1.240604000000	-0.250400000000
H	1.882854000000	2.005993000000	-0.629495000000
H	2.175855000000	-0.991947000000	1.208643000000
H	1.655482000000	-2.270207000000	0.075767000000
H	2.345053000000	-0.355158000000	-1.425825000000

U-CO

E$^{el}_{M06}$ = -501.4079901

ZPE$_{BP86}$ = 0.200079

E$_{total}$ = -501.2079111

C	-1.103935000000	0.854708000000	0.890797000000
C	-1.686381000000	0.377047000000	-0.469418000000
C	-0.594229000000	-1.463490000000	0.280512000000
C	-0.347530000000	-0.413062000000	1.415418000000
H	-1.813329000000	1.353359000000	1.561673000000
H	-0.558105000000	-0.769048000000	2.430409000000
C	-1.999965000000	-1.107244000000	-0.228155000000
H	-2.282284000000	-1.647995000000	-1.143841000000
H	-2.781645000000	-1.268429000000	0.530435000000
C	-0.397665000000	0.368558000000	-1.347105000000
H	-0.595534000000	0.298849000000	-2.424656000000
C	0.362543000000	-0.935950000000	-0.828121000000
H	0.595346000000	-1.645132000000	-1.630063000000
H	-2.498376000000	0.994625000000	-0.875604000000
H	-0.417259000000	-2.506551000000	0.572085000000
C	1.594707000000	-0.505322000000	-0.040325000000
C	0.270630000000	1.552187000000	0.596621000000
C	0.342465000000	1.653231000000	-0.931182000000
C	1.033149000000	0.270044000000	1.139995000000
H	1.742962000000	0.426570000000	1.958158000000
H	1.371843000000	1.713838000000	-1.316494000000
H	-0.203645000000	2.540501000000	-1.288663000000
H	0.500842000000	2.476265000000	1.139770000000
O	2.762055000000	-0.733887000000	-0.298430000000

U1-H$^+$

E^{el}_{M06} = -426.4853801

ZPE_{BP86} = 0.206102

E_{total} = -426.2792781

| C | -0.081965000000 | 0.107529000000 | 1.369620000000 |

C	-0.979842000000	1.078020000000	0.521275000000
C	-1.193697000000	-0.924182000000	-0.515644000000
C	-0.343019000000	-1.299327000000	0.732914000000
H	-0.177824000000	0.169272000000	2.459708000000
H	-0.750950000000	-2.077803000000	1.383548000000
C	-2.113192000000	0.183139000000	0.004344000000
H	-2.708818000000	0.667404000000	-0.781256000000
H	-2.795271000000	-0.164294000000	0.792369000000
C	-0.057080000000	1.292343000000	-0.708631000000
H	-0.384813000000	2.081202000000	-1.393959000000
C	-0.108743000000	-0.176711000000	-1.377938000000
H	-0.296842000000	-0.124654000000	-2.456097000000
H	-1.276577000000	2.005186000000	1.025211000000
H	-1.662158000000	-1.780969000000	-1.014599000000
C	1.170520000000	-0.867521000000	-1.025088000000
C	1.363418000000	0.312090000000	0.850251000000
C	1.332064000000	1.483851000000	-0.094261000000
C	1.069851000000	-1.508402000000	0.195498000000
H	1.838123000000	-2.144447000000	0.636220000000
H	2.177758000000	1.573278000000	-0.786138000000
H	1.342939000000	2.383827000000	0.551056000000
H	2.246098000000	0.119087000000	1.465844000000
H	2.098435000000	-0.792061000000	-1.595945000000

U2-H$^+$

$E^{el}_{M06} = $ **-426.4852523**

$ZPE_{BP86} = $ **0.206985**

$E_{total} = $ **-426.2782673**

C	0.150226000000	-0.322639000000	-1.296964000000
C	-0.790921000000	-1.220523000000	-0.446603000000

C	-1.426375000000	0.861825000000	0.205872000000
C	-0.278600000000	1.133638000000	-0.841244000000
H	0.110788000000	-0.448287000000	-2.383961000000
H	-0.335761000000	1.960847000000	-1.551790000000
C	-2.083268000000	-0.412227000000	-0.323550000000
H	-2.786784000000	-0.833556000000	0.407680000000
H	-2.612085000000	-0.261880000000	-1.275552000000
C	-0.084455000000	-1.078829000000	0.932892000000
H	-0.471130000000	-1.757560000000	1.702150000000
C	-0.410563000000	0.417682000000	1.310415000000
H	-0.697411000000	0.583226000000	2.352358000000
H	-0.876014000000	-2.248245000000	-0.817183000000
H	-2.041401000000	1.735236000000	0.439308000000
C	0.598565000000	1.413826000000	0.763525000000
C	1.570043000000	-0.391534000000	-0.636846000000
C	1.398814000000	-1.293601000000	0.601538000000
C	1.521988000000	1.054940000000	-0.218477000000
H	2.119060000000	1.831291000000	-0.704100000000
H	2.086094000000	-1.020048000000	1.415827000000
H	1.586960000000	-2.344220000000	0.342903000000
H	2.406253000000	-0.633030000000	-1.297782000000
H	0.518719000000	2.460887000000	1.066787000000

U1-H⁻

E^{el}_{M06} = -426.7207567

ZPE_{BP86} = 0.200746

E_{total} = -426.5200107

C	-0.172068000000	0.725982000000	1.250128000000
C	-1.046552000000	1.160268000000	0.033950000000
C	-1.136814000000	-1.102085000000	-0.039664000000

C	-0.243581000000	-0.841560000000	1.194217000000
H	-0.410837000000	1.232875000000	2.198879000000
H	-0.519046000000	-1.388203000000	2.111682000000
C	-2.132076000000	0.069465000000	-0.044747000000
H	-2.730096000000	0.123435000000	-0.973188000000
H	-2.825064000000	0.093690000000	0.815376000000
C	-0.074388000000	0.834901000000	-1.137795000000
H	-0.382407000000	1.292702000000	-2.093407000000
C	-0.089169000000	-0.773379000000	-1.202599000000
H	-0.461039000000	-1.113397000000	-2.185600000000
H	-1.401193000000	2.203791000000	0.063929000000
H	-1.555578000000	-2.116372000000	-0.115929000000
C	1.257873000000	-1.346005000000	-0.793093000000
C	1.313490000000	0.697794000000	0.760656000000
C	1.295955000000	1.322131000000	-0.637696000000
C	1.274838000000	-0.898730000000	0.646241000000
H	1.997849000000	-1.410718000000	1.303206000000
H	2.105655000000	0.901443000000	-1.256381000000
H	1.352944000000	2.427028000000	-0.607056000000
H	2.072866000000	1.111649000000	1.444952000000
H	1.270887000000	-2.450615000000	-0.884048000000

U2-H$^-$

E^{el}_{M06} = -426.7215657

ZPE_{BP86} = 0.200674

E_{total} = -426.5208917

C	-0.166321000000	-0.725926000000	-1.249501000000
C	-1.039341000000	-1.173830000000	-0.040087000000
C	-1.143350000000	1.095639000000	0.064017000000
C	-0.239664000000	0.845069000000	-1.176037000000

H	-0.412720000000	-1.217262000000	-2.204482000000
H	-0.523875000000	1.392108000000	-2.088916000000
C	-2.127207000000	-0.089606000000	0.048614000000
H	-2.735409000000	-0.156649000000	0.968142000000
H	-2.808125000000	-0.092485000000	-0.821804000000
C	-0.072464000000	-0.846411000000	1.134868000000
H	-0.376436000000	-1.307423000000	2.091957000000
C	-0.110979000000	0.792182000000	1.199283000000
H	-0.470457000000	1.100917000000	2.198118000000
H	-1.390672000000	-2.219067000000	-0.090516000000
H	-1.577974000000	2.100748000000	0.135542000000
C	1.134330000000	1.506997000000	0.712634000000
C	1.316969000000	-0.707223000000	-0.772306000000
C	1.310964000000	-1.297518000000	0.638925000000
C	1.249798000000	0.929128000000	-0.667648000000
H	1.976338000000	1.406048000000	-1.350246000000
H	2.115195000000	-0.848283000000	1.253696000000
H	1.422999000000	-2.397974000000	0.651838000000
H	2.074696000000	-1.127733000000	-1.456694000000
H	2.030023000000	1.396049000000	1.356792000000

U-CO-H⁻

E^{el}_{M06} = -502.0006927

ZPE_{BP86} = 0.206749

E_{total} = -501.7939437

C	-1.048208000000	0.931828000000	0.895085000000
C	-1.587034000000	0.655272000000	-0.537523000000
C	-0.888576000000	-1.392041000000	0.140398000000
C	-0.564996000000	-0.482175000000	1.376033000000
H	-1.723430000000	1.503631000000	1.549695000000

H	-0.949639000000	-0.856886000000	2.337987000000
C	-2.172316000000	-0.762845000000	-0.431187000000
H	-2.465120000000	-1.187510000000	-1.406504000000
H	-3.038568000000	-0.823098000000	0.254588000000
C	-0.243443000000	0.466018000000	-1.312162000000
H	-0.369423000000	0.514339000000	-2.405569000000
C	0.237494000000	-0.963094000000	-0.832646000000
H	0.385838000000	-1.652624000000	-1.677828000000
H	-2.246582000000	1.438488000000	-0.945518000000
H	-0.924499000000	-2.469421000000	0.355511000000
C	1.548541000000	-0.886709000000	0.078604000000
C	0.447449000000	1.393512000000	0.752529000000
C	0.669442000000	1.577700000000	-0.756510000000
C	0.920499000000	-0.020690000000	1.245222000000
H	1.546055000000	-0.022260000000	2.149534000000
H	1.721562000000	1.405483000000	-1.028471000000
H	0.317065000000	2.572445000000	-1.091356000000
H	0.762950000000	2.249056000000	1.369250000000
H	1.583650000000	-1.942805000000	0.540854000000
O	2.685879000000	-0.478686000000	-0.463654000000

U_{TS}

$E^{el}_{M06} = -426.0514582$

$ZPE_{BP86} = 0.192688$

$E_{total} = -425.8587702$

C	-0.046103000000	0.439105000000	-1.351787000000
C	0.842468000000	1.220617000000	-0.340560000000
C	1.257762000000	-0.950511000000	0.186192000000
C	0.240948000000	-1.054946000000	-0.993443000000
H	0.045014000000	0.749022000000	-2.399230000000

H	0.501628000000	-1.752471000000	-1.797348000000
C	2.064879000000	0.316121000000	-0.139498000000
H	2.717194000000	0.644141000000	0.682726000000
H	2.678754000000	0.192916000000	-1.046155000000
C	0.011823000000	1.042094000000	0.961145000000
H	0.325045000000	1.694511000000	1.786528000000
C	0.285376000000	-0.490556000000	1.342958000000
H	0.732018000000	-0.580174000000	2.341508000000
H	1.037837000000	2.267089000000	-0.610251000000
H	1.826735000000	-1.862809000000	0.397593000000
C	-0.854749000000	-1.423870000000	1.098124000000
C	-1.474518000000	0.326687000000	-0.718970000000
C	-1.440192000000	1.241583000000	0.505864000000
C	-1.195297000000	-1.193089000000	-0.328679000000
H	-1.894397000000	-1.912915000000	-0.770304000000
H	-2.188035000000	0.986070000000	1.270115000000
H	-1.600040000000	2.289225000000	0.202344000000
H	-2.336135000000	0.445991000000	-1.385601000000