Supporting Information for

Tuning Through-Space Interactions via the Secondary Coordination Sphere of an Artificial Metalloenzyme leads to Enhanced Rh(III)-Catalysis

Isra S. Hassan, 1,‡ Jack T. Fuller, 2,‡ Vanessa N. Dippon, 1 Angeline N. Ta, 3 Michael W. Danneman, 1 Brian R. McNaughton, 3✉ Anastassia Alexandrova, 2,✉ Tomislav Rovis 1,✉

1Department of Chemistry, Columbia University, New York, NY 10025, USA
2Department of Chemistry & Biochemistry, University of California Los Angeles, Los Angeles, CA, 90095, USA.
3Department of Chemistry, Colorado State University, Fort Collins, CO, 80523, USA.

Corresponding author: Email: tr2504@columbia.edu; ana@chem.ucla.edu

†Current Address: Delaware Institute for Science & Technology, Delaware State University, Dover, DE 19901.

Table of Contents

1. General methods .............................................................................................................2
2. Preparation of starting materials .................................................................................2
3. Copies of NMR spectra .................................................................................................4
4. General procedures for asymmetric dihydropyridone synthesis ...............................6
5. Extended mutant yield and enantioselectivity data ...................................................7
6. Analytical data for enantioenriched dihydropyridones (NMR/HPLC) .....................7
7. Preparation of artificial metalloenzymes ....................................................................23
8. Protein sequences .......................................................................................................24
1. General methods

Flash column chromatography was performed on SiliCycle Inc.® silica gel 60 (230-400 mesh). Thin layer chromatography was performed on SiliCycle Inc.® 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light (254 nm) or KMnO$_4$ staining.

$^1$H-NMR and $^{13}$C-NMR spectra were recorded on Bruker 300, 400 or 500 MHz spectrometers at ambient temperature. $^1$H-NMR data are reported as the following: chemical shift in parts per million (δ, ppm) from chloroform (CDCl$_3$) taken as 7.26 ppm, integration, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, dd=doublet of doublets) and coupling constant (J in Hz unit). $^{13}$C-NMR is reported as the following: chemical shifts are reported in ppm from CDCl$_3$ taken as 77.0 ppm.

Low-resolution mass spectra (LSMS) were obtained on ACQUITY Waters UPLC/mass spectrometer equipped with electrospray ionization.

Infrared spectra (IR) were recorded on a Perkin Elmer Paragon 1000 FT-IR spectrometer.
2. Preparation of starting materials

N-(pivaloyloxy) α-substituted acrylamides

\[
\begin{align*}
\text{R} & \quad \text{CO}_2\text{H} \\
\rightarrow & \\
\text{R} & \quad \Rightarrow \quad \text{CO}_2\text{H} \\
\text{NH}_2\text{OPiv} \cdot \text{TfOH}, & \quad \text{K}_2\text{CO}_3 \\
\text{EtOAc/H}_2\text{O}, & \quad 0 \degree \text{C}
\end{align*}
\]

i. \((\text{COCl})_2\), cat. DMF, \text{CH}_2\text{Cl}_2, 0 \degree \text{C}

ii. \text{NH}_2\text{OPiv} \cdot \text{TfOH}, \text{K}_2\text{CO}_3, \text{EtOAc/H}_2\text{O}, 0 \degree \text{C}

To the solution of \(\text{NH}_2\text{OPiv} \cdot \text{TfOH}\) (1.1 equiv), \(\text{K}_2\text{CO}_3\) (2.0 equiv) and EtOAc/H\(_2\)O (2/1 by v/v, 0.1M) at 0 \degree C (ice bath), the crude acid chloride was added dropwise (while a small amount of EtOAc can be used as a solvent). The mixture was stirred at the same temperature for 0.75 - 1 h (prolonged reaction time led to the decomposition of the N-pivaloyloxy acrylamide). Upon the completion (monitored by TLC), saturated NaHCO\(_3\) was added. The aqueous layer was extracted with EtOAc (×3), washed with brine, dried with MgSO\(_4\), and filtered. The solvent was removed under reduced pressure to give a crude N-(pivaloyloxy) α-substituted acrylamide, which was purified by a flash column chromatography (10% EtOAc/hexane).

N-(Pivaloyloxy)methacrylamide (1)

\[
\begin{align*}
\text{Me} & \quad \text{O} \quad \text{OPiv} \\
\text{2a} & \quad \text{NH}
\end{align*}
\]

**\(^1\text{H NMR}\)** (500 MHz, CDCl\(_3\)) \(\delta\) 9.22 (s, NH), 5.84 (s, 1H), 5.50 – 5.47 (m, 1H), 1.99 (t, \(J = 1.3\) Hz, 3H), 1.34 (s, 9H).

**\(^{13}\text{C NMR}\)** (126 MHz, CDCl\(_3\)) \(\delta\) 176.90, 167.26, 136.91, 121.97, 38.39, 26.98, 18.29

**IR** (neat, cm\(^{-1}\)) 3225, 2977, 1782, 1671, 1629, 1481, 1055, 1033, 1015.

**LRMS** (ESI) m/z calcd for C\(_9\)H\(_{15}\)NO\(_3\) [M+H]\(^+\): 186.1, found: 186.2.
3. Copies of NMR spectra
4. General procedures for asymmetric dihydropyridone synthesis

**General procedure A for asymmetric dihydropyridone synthesis**

To a 750 µL clear glass shell vial (8 x 30mm) equipped with a parylene coated stir bar (1.67 x 2.01 x 4.80mm) was added a solution of the acrylamide in MeOH (3.0 µL, 1.0 M, 0.0030 mmol). The alkene (0.0015 mmol) was added followed by 125 µL of acetate buffer (100 mM NaOAc, 100 mM NaCl, pH 7.4). 75 µL of the monomeric streptavidin wild-type metalloenzyme (600 µM, 3 mol%, 0.000045 mmol) in salt water (100 mM NaCl, pH 7.4) was added to the vial achieving the desired reaction mixture (225 µM enzyme, 62.5 mM NaOAc, 100 mM NaCl, pH 7.4). The vial was placed in a 24-well high-throughput experimentation block and the reaction mixture was allowed to stir at 200 rpm at 25 °C. After 72 h the reaction is diluted with ethyl acetate and filtered through a Celite plug into a 20 mL scintillation vial. The reaction vial was washed twice more with ethyl acetate and filtered through the Celite plug into the scintillation vial. The Celite plug was washed an additional three times with ethyl acetate, collecting the filtrate into the scintillation vial. The contents of the scintillation vial were carefully removed via concentration under vacuum. The crude residue of the scintillation vial was dissolved in 600 µL of MeOD. A trimethyl(phenyl)silane internal standard (0.258 µL, 0.0015 mmol) was added to the solution, and mixed thoroughly. The sample was then analyzed by NMR (400 MHz or 500 MHz, MeOD, minimum of 400 scans), and the yield was determined relative to the trimethyl(phenyl)silane internal standard. Enantioselectivity was determined by chiral HPLC.

**Chiral HPLC Analysis** - The crude residue of the scintillation vial was rediluted with 120 µL of HPLC grade isopropanol and 300 µL of HPLC grade hexanes. 1.5 µL of a 1,3,5-trimethoxybenzene solution (1.0 M in MeOH) was added to the scintillation vial. The contents of the scintillation vial were thoroughly mixed via pipette to ensure uniformity of the solution. 180 µL of the uniform solution were incorporated into at 200 µL vial insert, and the sample was submitted for analysis. Enantioselectivity was also determined by chiral HPLC.
NMR Analysis - The crude residue of the scintillation vial was dissolved in 600 µL of MeOD. A trimethyl(phenyl)silane internal standard (0.258 µL, 0.0015 mmol) was added to the solution, and mixed thoroughly. The sample was then analyzed by NMR (400 MHz or 500 MHz, MeOD, minimum of 400 scans), and the yield was determined relative to the trimethyl(phenyl)silane internal standard. Enantioselectivity was determined by chiral HPLC.

5. Extended mutant yield and enantioselectivity data

| Mutant | TON | ee (%) |
|--------|-----|--------|
| G49A   | 97  | 91     |
| WT     | 33  | 91     |
| T111E  | 32  | 92     |
| E113A  | 22  | 94     |
| H87E   | 20  | 92     |
| T32R   | 14  | 92     |
| T111A  | 10  | 93     |

6. Analytical data for enantioenriched dihydropyridones (NMR/HPLC)

6-(4-Methoxyphenyl)-3-methyl-5,6-dihydropyridin-2(1H)-one (3)

Product synthesized according to general procedure A. Product yield was determined to be 99% by ¹H NMR analysis (400 MHz, MeOD) relative to a trimethyl(phenyl)silane internal standard. The product was determined to be 91% ee by chiral HPLC analysis. (Chiralpak IE, 20% iPrOH/hexanes, 1 mL/min, \( t_r(e_1, \text{minor}) = 30.8 \text{ min}, t_r(e_2, \text{major}) = 34.1 \text{ min} \).
WT

NMR Yield Data

HPLC Racemic Assay (Full)

| # | Time | Area | Height | Width  | Area% | Symmetry |
|---|------|------|--------|--------|-------|----------|
| 1 | 26.815 | 1999.6 | 50.4 | 0.607 | 50.038 | 0.76 |
| 2 | 29.325 | 1996.6 | 40.7 | 0.679 | 49.901 | 0.76 |
HPLC Enantioselective Assay (Full)

HPLC Racemic Assay (Product)

HPLC Enantioselective Assay (Product)
NMR Yield Data

HPLC Enantioselective Assay (Full)
HPLC Enantioselective Assay (Product)

| Time | Area | Height | Width | Area% | Symmetry |
|------|------|--------|-------|-------|----------|
| 1    | 38.125 | 56.3   | 2.4   | 46.655 | 0.700    |
| 1    | 35.725 | 220.4  | 4.6   | 0.768  | 0.998    |
NMR Yield Data

HPLC Enantioselective Assay (Full)

HPLC Enantioselective Assay (Product)
G49A

NMR Yield Data

HPLC Enantioselective Assay (Full)
Signal 5: DAD1 E, Sig=220,16 Ref=360,100

| # | RetTime | Type | Width | Area     | Height   | Area % |
|---|---------|------|-------|----------|----------|--------|
| 1 | 21.289  | MM T | 0.4537| 1579.55676 | 58.01941 | 5.8578 |
| 2 | 23.095  | MM T | 0.5867| 2.53856e4  | 721.11731| 94.1422|

Totals: 2.69651e4 779.13672

HPLC Enantioselective Assay (Product)
T32R

NMR Yield Data
HPLC Enantioselective Assay (Product)

T111A

NMR Yield Data
HPLC Enantioselective Assay (Full)
HPLC Enantioselective Assay (Product)

H87E

NMR Yield Data
HPLC Enantioselective Assay (Product)
7. Preparation of artificial metalloenzyme

Protein production and purification:

MBP-mSav was expressed from plasmid pET-MBP-mSav purchased from addgene (plasmid #52319). Plasmid was transformed into BL21 (DE3) E.coli for protein production. An overnight culture was grown in LB containing kanamycin at 37 °C shaking at 200 RPM and used to inoculate 1 L (x8) of LB containing kanamycin at 37 °C shaking at 200 RPM for 3.5 hrs to an OD$_{600}$ of 0.6-0.9. Culture was then induced with IPTG (final concentration of 1 mM) and brought to 20 °C shaking at 200 RPM overnight. Cells were harvested by centrifugation (5000 RPM for 10 min at 4 °C) and resuspended in acetate glycerol lysis buffer (10 mL, 25 mM sodium acetate, 100 mM sodium chloride, 10% glycerol, 0.2% Triton-X-100, pH 7.4) with a protease inhibitor tablet (1/2 tablet, Roche cOmplete ULTRA Tables, Mini, EDTA free, EASYpack). Cell suspension was subject to one freeze-thaw cycle at -20 °C followed by sonication (6 min cycle, 50% amplitude, over ice). Cell lysate was cleared by centrifugation (9500 RPM for 20 min at 4 °C) and the supernatant was incubated with Ni-NTA agarose resin (2 mL) rotating overnight at 4 °C. The resin was collected by centrifugation (4750 RPM for 10 min at 4 °C) and washed with acetate wash buffer (50 mL, 25 mM sodium acetate, 100 mM sodium chloride, 50 mM imidazole, pH 7.4). Protein was then eluted with acetate elution buffer (12 mL, 25 mM sodium acetate, 100 mM sodium chloride, 400 mM imidazole, pH 7.4) and dialyzed in acetate buffer (2 L, 25 mM sodium acetate, 100 mM sodium chloride, pH 7.4) overnight. Purified protein was then observed by SDS-PAGE.

Protein cleavage and re-purification:

Purified MBP-mSav was then subjected to a TEV protease cleavage. TEV protease was expressed from plasmid pRK793 purchased from addgene (plasmid #8827). An overnight culture was grown in LB containing chloramphenicol and carbenicillin at 37 °C shaking at 200 RPM and used to inoculate 1 L (x2) of LB containing chloramphenicol and carbenicillin at 37 °C shaking at 200 RPM for 3 hrs to an OD$_{600}$ of ~0.5. Culture was then induced with IPTG (final concentration of 1 mM) and brought to 30 °C shaking at 200 RPM overnight. Cells were harvested by centrifugation (5000 RPM for 10 min at 4 °C) and resuspended in acetate glycerol lysis buffer (10 mL, 25 mM sodium acetate, 100 mM sodium chloride, 10% glycerol, 0.2% Triton-X-100, pH 7.4) with a protease inhibitor tablet (1/2 tablet, Roche cOmplete ULTRA Tables, Mini, EDTA free, EASYpack). Cell suspension was subject to one freeze-thaw cycle at -20 °C followed by sonication (2 min cycle, 50% amplitude, over ice). Cell lysate was cleared by centrifugation (9500 RPM for 20 min at 4 °C) and the supernatant was incubated with Ni-NTA agarose
resin (1 mL) rotating for 30 min at 4 °C. The resin was collected by centrifugation (4750 RPM for 10 min at 4 °C) and washed with acetate wash buffer (50 mL, 25 mM sodium acetate, 100 mM sodium chloride, 50 mM imidazole, pH 7.4). Protein was then eluted with acetate elution buffer (12 mL, 25 mM sodium acetate, 100 mM sodium chloride, 400 mM imidazole, pH 7.4) and dialyzed in acetate buffer (2 L, 25 mM sodium acetate, 100 mM sodium chloride, pH 7.4) overnight. Purified protein was then observed by SDS-PAGE.

Purified TEV protease was then added to purified MBP-mSav (100 mg protein to 1 mg protease) and rotated for 48 hrs at 4 °C. Ni-NTA resin was then added to cleavage mixture and rotated for ~12 hrs at 4 °C. Supernatant was separated from the resin. Cleaved and re-purified protein was observed by SDS-PAGE.

**Metalloenzyme preparation:**

The metalloenzyme was prepared by incubating purified mSav with Cp*biotinRh (30uM protein:60uM biotin) in acetate buffer at RT rotating overnight. Mixtures were then centrifuged to eliminate any precipitation (14000 RPM, 10 min) and transferred to a 10 kDa MWCO ultracentrifugal filter unit for several washes with acetate buffer. Protein solution will now have a yellowish tint due to binding of Rh.

8. **Protein sequences**

mSav –
GAEAGITGTWYNQHGSTFTVTAGADGNLTGQYENRAQGTGCQNSPYTLTGTYNGTKLEWRVEWNNSTENCHSRTEWRGQYQGGAEARINTQWNLTYEGGSGPATEQGQDTFTKVKPASAASGSDYKDDDDK

mSav T32R–
GAEAGITGTWYNQHGSTFTVRAGADGNLTGQYENRAQGTGCQNSPYLTGTYNGTKLEWRVEWNNSTENCHSRTEWRGQYQGGAEARINTQWNLTYEGGSGPATEQGQDTFTKVKPASAASGSDYKDDDDK

mSav H87E –
GAEAGITGTWYNQHGSTFTVTAGADGNLTGQYENRAQGTGCQNSPYLTGTYNGTKLEWRVEWNNSTENCHSRTEWRGQYQGGAEARINTQWNLTYEGGSGPATEQGQDTFTKVKPASAASGSDYKDDDDK

mSav T111E –
GAEAGITGTWYNQHGSTFTVTAGADGNLTGQYENRAQGTGCQNSPYLTGTYNGTKLEWRVEWNNSTENCHSRTEWRGQYQGGAEARINTQWNLTYEGGSGPATEQGQDTFTKVKPASAASGSDYKDDDDK
mSav T111A –

GAEAGITGWYNNQHGSTFTVAGADGNLTGQYENRAQGTCQNSPYLTGRTYNGTKLEWRVE
WNNSTENCSRTIEWRGQYQGGAEARINTQWNLTYEGGGSPATEQGQDTFTKVPSAAAGSDY
KDDDDK

mSav E113A –

GAEAGITGWYNNQHGSTFTVAGADGNLTGQYENRAQGTCQNSPYLTGRTYNGTKLEWRVE
WNNSTENCSRTIEWRGQYQGGAEARINTQWNLTYEGGGSPATEQGQDTFTKVPSAAAGSDY
KDDDDK

mSav G49A –

GAEAGITGWYNNQHGSTFTVAGADGNLTGQYENRAQGTACQNSPYLTGRTYNGTKLEWRVE
WNNSTENCSRTIEWRGQYQGGAEARINTQWNLTYEGGGSPATEQGQDTFTKVPSAAAGSDY
KDDDDK

9. Protein data bank

mSav – 4JNJ
11. Computational methods

All quantum-mechanical calculations were performed in Turbomole (1-13) with the M06 density functional (14). Geometries were optimized with the def2-SVP basis set, and final electronic energies were calculated with the def2-TZVP basis set (15). The conductor-like screening model (COSMO) was used as an implicit solvent model with a dielectric of 80 to simulate water (16) for the mechanistic calculations. For the scan represented in Figure 5a of the text, the calculations were performed in vacuum with the following atoms frozen: the methyl group of acetate, the methyl group of 4-methylphenol, and the 11 atoms corresponding to the linker between Cp* and biotin.

Full enzymes were modeled with QM/DMD (17). QM/DMD is a hybrid quantum mechanics/molecular mechanics (QM/MM) method that simulates proteins piecewise. Discrete molecular dynamics (DMD) equilibrates the entire system except for the metal and part of the substrate (18). After a trajectory of ~0.5 ns, quantum mechanics (QM) is used to optimize the metal region plus sidechains and residues immediately surrounding it. This process is repeated, providing efficient sampling of the entire protein scaffold while treating the metal environment quantum-mechanically. For this study, the migratory insertion transition state was modeled in WT by freezing the coordinates of the rhodium atom and the two carbon atoms forming a bond. For each system, five replicate simulations were run for ~20 ns each. The QM region consisted of the side chains of C86, S88, Y112, and E113; the segment from the T48 carbonyl to the C50 sidechain; the segment from the G115 alpha-carbon to the S119 sidechain; and the Rh complex up to the amide of the linker, inclusive.
12. Calculated free energy surface
13. M06/def2-TZVP//M06/def2-SVP COSMO(\(\varepsilon = 80\))-solvated energies (Ha) and XYZ coordinates (Å)

N-(Pivaloyloxy)Methacrylamide
Electronic Energy:     -632.228828814
Free Energy Correction:     0.191609217
N     31.628965779  -15.411817810  -20.50952136
C     31.488722522  -15.456453766  -23.327741245
C     32.783078821  -15.626367942  -21.23050674
O     33.806856961  -16.029080785  -20.711063742
C     32.664181335  -15.355339699  -22.692941488
H     31.41805104  -15.274678032  -24.404930042
C     33.958892297  -15.040522549  -23.366041232
H     34.41068792  -14.158765942  -22.911541032
H     34.664897169  -15.87931740  -23.242519521
H     33.814102559  -14.851353285  -24.438707353
O     31.735873218  -15.563590929  -19.149959925
C     32.366534149  -14.524135954  -18.51321854
O     32.60257404  -13.509677687  -19.085305255
C     32.680269732  -14.882227171  -17.078040026
C     32.942642651  -13.601004407  -16.297431458
H     32.044190214  -12.963002812  -16.261212392
H     33.22641826  -13.852282227  -15.262599187
H     33.759083154  -13.015536694  -16.747119031
C     31.549625527  -16.76679359  -16.428663114
H     30.604697092  -15.108529412  -16.431979878
H     31.376634868  -16.38762529  -16.933549829
H     31.814198496  -15.886013646  -15.379198911
C     33.956936306  -15.731591183  -17.143243887
H     34.251483441  -16.02850178  -16.122867080
H     33.802724950  -16.639426308  -17.747495109
H     34.787388412  -15.160851890  -17.591306457
H     30.56835956  -15.744589586  -22.811046267
H     30.98218482  -14.673677957  -20.786958914

p-Methoxystyrene
Electronic Energy:     -424.020085596
Free Energy Correction:     0.132211007
C     29.433871156  -16.596918597  -21.662090608
H     29.970178901  -17.406638165  -21.153970136
C     29.471035357  -16.432478912  -22.906262221
H     28.905906306  -15.97880155  -23.428523007
C     30.194457190  -17.253032466  -23.96403363
C     30.112408671  -16.937409707  -25.32757956
C     30.982490374  -18.362514169  -23.604240922
C     30.776890522  -17.680781788  -26.302757182
C     31.648912586  -19.111049932  -24.557898437
C     31.553551537  -18.778729052  -25.919791163
H     29.506960009  -16.078670901  -25.637994666
H     31.075921019  -18.646641069  -22.551156258
Acetic Acid
Electronic Energy:  \(-229.068686332\)
Free Energy Correction:  \(0.035604647\)

H  \(x=30.679987538, y=-17.392690377, z=-27.352042313\)
H  \(x=32.260468953, y=-19.973422898, z=-24.276368144\)
O  \(x=32.236118481, y=-19.565840066, z=-26.775061527\)
C  \(x=32.177139518, y=-19.277037456, z=-28.151123968\)
H  \(x=31.143575230, y=-19.335726343, z=-28.535573656\)
H  \(x=32.582773926, y=-18.274316759, z=-28.374353228\)
H  \(x=32.788988992, y=-20.029335458, z=-28.665027179\)
H  \(x=28.856493395, y=-15.918876308, z=-21.027201722\)

Acetate
Electronic Energy:  \(-228.600302349\)
Free Energy Correction:  \(0.022647115\)

O  \(x=16.339292155, y=-22.443641029, z=1.028748919\)
O  \(x=16.340164348, y=-20.371850229, z=1.871944869\)
C  \(x=16.339757834, y=-21.618776273, z=1.971827063\)
C  \(x=16.339849836, y=-22.217234868, z=3.383217152\)
H  \(x=17.222029874, y=-22.866510094, z=3.512412450\)
H  \(x=16.339676565, y=-21.444795664, z=4.167075368\)
H  \(x=15.455542261, y=-22.86584522, z=3.484355785\)

Pivalic Acid
Electronic Energy:  \(-346.955994067\)
Free Energy Correction:  \(0.115082841\)

H  \(x=16.337871809, y=-21.976582986, z=0.192700340\)
O  \(x=16.336478016, y=-22.466117402, z=1.039497505\)
O  \(x=16.341954208, y=-20.386770217, z=1.38095369\)
C  \(x=16.339485813, y=-21.579433033, z=2.036487281\)
C  \(x=16.339835806, y=-22.24450394, z=3.402173970\)
C  \(x=17.593109514, y=-21.14648549, z=3.525120545\)
H  \(x=16.339836209, y=-21.457361057, z=4.25729376\)
H  \(x=16.339676565, y=-22.866510094, z=3.512412450\)
H  \(x=15.457978754, y=-22.866937297, z=3.512352795\)

C  \(x=16.339577728, y=-21.173575970, z=4.483042824\)
H  \(x=15.448294275, y=-20.530311643, z=4.410623351\)
H  \(x=16.341273124, y=-21.649236058, z=5.477680738\)
H  \(x=17.228854519, y=-20.52781358, z=4.408630756\)
C  \(x=15.087840413, y=-23.116264793, z=3.526121820\)
| Atom | X    | Y    | Z    |
|------|------|------|------|
| H    | 15.074283726 | -23.917181377 | 2.771174994 |
| H    | 15.06411659 | -23.584512250 | 4.524180893 |
| H    | 14.168719988 | -22.517211826 | 3.412269602 |

Catalyst

Electronic Energy: -1165.500944705
Free Energy Correction: 0.322871834

| Atom | X    | Y    | Z    |
|------|------|------|------|
| N    | 0.107839724  | -1.496735432 | -4.757575786 |
| C    | 2.072230979  | 2.583752877  | -0.741879811 |
| C    | 1.879757718  | 2.197250380  | -2.116052349 |
| C    | 1.748581741  | 0.766656136  | -2.174243469 |
| C    | 1.841783326  | 0.270782793  | -0.826828541 |
| C    | 2.062293643  | 1.382261379  | 0.058294866 |
| C    | 1.610628652  | -0.069030353 | -3.406397732 |
| C    | 0.174511327  | -0.472459316 | -3.741789984 |
| C    | 0.314680642  | -2.790294564 | -4.450053198 |
| C    | 1.674130106  | -1.142057400 | -0.406645949 |
| C    | 1.772142998  | 3.104918330  | -3.28326216 |
| C    | 2.308288478  | 1.300180177  | 1.518502503 |
| C    | 2.251331046  | 3.962597662  | -0.22402404 |
| O    | 0.555378694  | -3.206125375 | -3.327742512 |
| Rh   | 0.195224542  | 1.624044642  | -0.949923722 |
| H    | -0.404373280 | 0.404431449  | -0.074026573 |
| H    | -0.320222689 | -0.853072715 | -2.832613515 |
| H    | 2.206290948  | -0.987576894 | -3.268443012 |
| H    | 2.057407875  | 0.461889236  | -4.263876999 |
| H    | -0.049963732 | -1.448434095 | -5.728738012 |
| H    | 3.323460411  | 4.198227182  | -0.114008955 |
| H    | 1.778661510  | 4.078239789  | 0.762781449 |
| H    | 1.811475904  | 4.709770826  | -0.900741004 |
| H    | 2.754368455  | 3.20606247   | -3.774887190 |
| H    | 1.441043159  | 4.110560013  | -2.985411054 |
| H    | 1.062698083  | 2.711642780  | -4.026291067 |
| H    | 3.388892658  | 1.169096821  | 1.702508011 |
| H    | 1.769762915  | 0.457927407  | 1.971919343 |
| H    | 1.990865969  | 2.217862288  | 2.035235912 |
| H    | 2.640840369  | -1.558640966 | -0.076365903 |
| H    | 1.289082315  | -1.772432513 | -1.223501494 |
| H    | 0.978167080  | -1.205948544 | 0.445257357 |
| H    | 0.236898016  | -3.461128267 | -5.33741018 |
| O    | -0.918813892 | 2.700175320  | 0.448736446 |
| C    | -1.152244057 | 2.13483751   | 1.584430535 |
| O    | -0.751859368 | 1.022856791  | 1.919226733 |
| C    | -2.008979239 | 2.970685437  | 2.508327475 |
| H    | -3.035096520 | 3.016893766  | 2.110053678 |
| H    | -1.635934608 | 4.004645153  | 2.554397548 |
| H    | -2.036450145 | 2.535570217  | 3.516389704 |
| O    | -1.594309604 | 0.322796139  | -1.06060163 |
| C    | -2.140103906 | 1.108503270  | -1.884566553 |
Substrate Association TS
Electronic Energy: -1797.742016249
Free Energy Correction: 0.542902304

O      -1.491191994      2.118503024     -2.285396986
C      -3.497986414      0.815275400     -2.430214565
H      -4.091317301      0.229022393     -1.716039394
H      -3.377770907      0.212550159     -3.346253872
H      -4.023251094      1.740415257     -2.702873319

N      -0.218084983     -3.043123270     -3.345724757
C       1.692276140      2.402533429     -1.560088528
C       1.186621069      1.584970722     -2.661954428
C       1.438325946      0.220559350     -2.345736634
C       2.056760220     0.176749870     -1.038319222
C       2.245216183      1.528780946     -0.572790313
C       1.145052578     -0.976275970     -3.189644146
C       0.110497690     -1.730277755     -2.756063089
C       0.444796271     -4.094348475     -2.832153781
C       2.480843070     -1.049484912     -0.324232338
C       0.501929523      2.094481207     -3.873099770
C       2.842527334      1.906518451      0.730132014
C       1.569814229      3.874843798     -1.474505561
O       1.189211520     -4.040399481     -2.156211852
N      -0.464730925     -1.184151419      1.224263922
C      -2.397681521     -2.573058970     -0.316863836
Rh      0.163331430      1.149681977     -0.864224872
H      -1.012711549     -1.145916858     -2.986172756
H      -0.108779940     -1.849814293     -1.659671223
H       2.010304432     -1.658563305     -3.121155003
H       1.066235515     -0.678764186     -4.248173736
H      -0.804941372     -3.188746086     -4.161635969
H       2.363511155      4.359997852     -2.067903031
H       1.652875556      4.225016617     -0.436323423
H       0.599758842      4.206779338     -1.875488537
H       1.238984031      2.351959098     -4.652928432
H      -0.084192517      2.995981750     -3.643448986
H      -0.184877514      1.341169729     -4.288018037
H       3.939561768      1.983406166      0.651142431
H       2.611103574      1.142853939      1.488436090
H       2.454876636      2.870229800      1.090895800
H       3.576239772     -1.154670333     -0.420788465
H       2.012953636     -1.957885580     -0.732647881
H       2.245670122     -0.994988314      0.750456302
C      -0.393532477     -2.555150431      1.162200147
O       0.499499325     -3.173259732      1.717756313
C      -1.448951500     -3.241178024      0.354622402
H      -3.151370880     -3.125350286     -0.889352359
C      -1.340007688     -4.731077565      0.359121973
H      -0.361852272     -5.036332183     -0.047692770
N-H Activation Association Complex
Electronic Energy:  -1797.745438401
Free Energy Correction:  0.543824034

N  0.039546499  -1.422541576  -5.013919893
C  2.100598759  1.860064194  -0.318627768
C  1.537126230  1.895780460  -1.656967074
C  1.656573165  0.571567106  -2.214561166
C  2.201460119  -0.286640946  -1.211953984
C  2.489480521  0.519607834  -0.039449661
C  1.348264872  0.147737980  -3.613519631
C  0.045800259  -0.636015783  -3.801868046
C  0.564655645  -2.658960142  -5.055628210
C  2.575309419  -1.713448414  -1.377222140
C   1.035745429  3.103796669  -2.353686250
C   3.125539799  0.005743381  1.198344933
C   2.182835886  3.019745348  0.599859989
O   1.078203276  -3.232803516  -4.106982102
N  -0.350732699  -0.847143740  1.165016172
C  -2.411653460  -2.560370127  0.144476845
Rh  0.372698526  0.604197383  -0.448580963
H  -0.801781987  0.062786037  -3.820179657
H  -0.115950556  -1.314724031  -2.948580963
H   2.186542532  -0.489233054  -3.948496713
H   1.349136767  1.030472100  -0.427368450
H  -0.339473410  -1.029606850  -5.870533038
H   3.075806810  3.62517524     0.370591219
H   2.247869692  2.698696170  1.649612038
H   1.295925071  3.661200888  0.496288699
H   1.863236687  3.629264054  -2.861400490
H   0.577234789  3.801294269  -1.636360998
H   0.263763557  2.836231803  -3.087429196
H   4.207566107  -0.130412335  1.029794460
H   2.702433466  -0.967540938  1.492981489
H   3.000951564  0.703584273  2.039323084
H   3.659898809  -1.779178183  -1.577412546
H   2.051336865  -2.194153615  -2.218303859
H   2.384955812  -2.293876728  -0.461158673
C  -0.107714711  -2.208108027  0.87463707
C   0.888385514  -2.762563753  1.293992360
C  -1.139198877  -2.862452601  0.005961198
H  -3.171718349  -3.089632220  -0.438720738
O  -0.589308178  -3.915805089  -0.914907099
C   0.013083035  -3.475817459  -1.730861320
C   0.666373770  -4.617687425  -0.375770397
H  -1.413086801  -4.480729198  -1.373685614
O   0.256227913  -0.404461880  2.336488420
C  -0.394723871  -0.799785136  3.471070226
O  -1.276752664  -1.612699149  3.446108703
C   0.144043367  -0.049432965  4.669204841
C  -0.630698638  -0.484679999  5.904616696
H  -0.521001216  -1.565640449  6.086741291
H  -0.249441723  0.054405721  6.786377881
H  -1.705326235  -0.264394332  5.803028389
C   1.639914301  -0.367397376  4.837009039
H   1.794793741  -1.447554251  4.986869003
H   2.216640445  -0.047491387  3.962258258
H   2.019272796  0.161829929  5.722393054
C  -0.061560288  1.446912874  4.410976173
H   0.229046661  2.020307049  5.306238612
H   0.542326387  1.798796421  3.557857180
H  -1.121056139  1.664357621  4.188569182
H   0.478761669  -3.128316589  -6.063508070
### N-H Activation TS

| Atom | x     | y     | z     |
|------|-------|-------|-------|
| N    | -0.297912031 | -0.878260974 | -5.097150230 |
| C    | 2.289416354 | 1.527576993 | -0.133764153 |
| C    | 1.747243776 | 1.792459617 | -1.456348789 |
| C    | 1.617899654 | 0.531010718 | -2.132681506 |
| C    | 1.987283605 | -0.506374675 | -1.216955513 |
| C    | 2.435256121 | 0.119564114 | 0.012201437 |
| C    | 1.248892087 | 0.300961429 | -3.562072277 |
| C    | -0.169625550 | -0.216562543 | -3.818596282 |
| C    | -0.006625339 | -2.181503632 | -5.250606553 |
| C    | 2.081781563 | -1.958146925 | -1.510547600 |
| C    | 1.476860771 | 3.135370523 | -2.022802090 |
| C    | 2.994340116 | -0.621853576 | 1.168594338 |
| C    | 2.581869745 | 2.564346137 | 0.884206591 |
| O    | 0.381994876 | -2.920500626 | -4.358794978 |
| N    | -0.579567408 | -0.731754299 | 1.200789750 |
| C    | -2.896791849 | -1.994023438 | 0.057719877 |
| Rh   | 0.361846169 | 0.624516591 | -0.346479010 |
| H    | -0.876723845 | 0.622879977 | -3.776749307 |
| H    | -0.464122324 | 0.926828371 | -3.029537975 |
| H    | 1.963368250 | -0.443457498 | -3.958322065 |
| H    | 1.416733302 | 1.225926021 | -4.137332985 |
| H    | -0.590081594 | -0.349477456 | -5.913745681 |
| H    | 3.559212455 | 3.033834516 | 0.681266394 |
| H    | 2.611407191 | 2.138517046 | 1.897843043 |
| H    | 1.814607207 | 3.352720373 | 0.870255345 |
| H    | 2.399772019 | 3.572926699 | -2.441743252 |
| H    | 1.102235752 | 3.814566173 | -1.241428881 |
| H    | 0.706170001 | 3.083003118 | -2.803338314 |
| H    | 4.013975528 | -0.965266640 | 0.922411358 |

Electronic Energy: -1797.740372434
Free Energy Correction: 0.537924205
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| H       | 2.384932650 | -1.508026273 | 1.407367760 |
| H       | 3.057136444  | 0.006010902  | 2.068712272  |
| H       | 3.142818091  | -2.228284034 | -1.658533889 |
| H       | 1.533112114  | -2.241371848 | -2.422685946 |
| H       | 1.712146737  | -2.567832307 | -0.670218294 |
| C       | -0.571664912 | -2.075152710 | 0.811893581  |
| O       | 0.282452499   | -2.854865113 | 1.199423270  |
| C       | -1.661442862  | -2.479349568 | -0.116679992 |
| H       | -3.727391406  | -2.348933838 | -0.562012019 |
| C       | -1.307385135  | -3.519855622 | -1.128736999 |
| H       | -0.658011490  | 3.108518473  | -1.923704518 |
| H       | -0.753077705  | -4.348947268 | -0.660607785 |
| H       | -2.208771723  | -3.921737731 | -1.613120164 |
| O       | 0.188847342   | -0.526621677 | 2.360007033  |
| C       | -0.412658661  | -0.966348238 | 3.493816237  |
| O       | -1.477826209  | -1.523601832 | 3.483751796  |
| C       | 0.462532829   | -0.706448292 | 4.703071638  |
| C       | -0.391679401  | -0.840847378 | 5.956628119  |
| H       | -0.854169551  | 1.837599974  | 6.019628844  |
| C       | -2.316074060  | -0.692056346 | 6.850042115  |
| C       | -1.198705525  | -0.089348676 | 5.974041255  |
| C       | 1.548947095   | -1.788216052 | 4.689762385  |
| H       | 1.103371611   | -2.797199751 | 4.698627525  |
| H       | 2.190613644   | -1.705234312 | 3.798491906  |
| H       | 2.184510220   | -1.684029065 | 5.584630925  |
| C       | 1.092577439   | 0.683350655  | 4.636814880  |
| H       | 1.671897942   | 0.868200845  | 5.556229638  |
| H       | 1.774815682   | 0.783616988  | 3.778469747  |
| H       | 0.324963274   | 1.471239632  | 4.552846180  |
| H       | -0.164112450  | -2.536397503 | -6.296013451 |
| H       | -3.128510149  | -1.250130024 | 0.825072364  |
| O       | -0.562141282  | 2.172341490  | 0.840719539  |
| C       | -1.658304210  | 2.086697536  | 1.452580014  |
| O       | -2.253200786  | 1.004897762  | 1.725962550  |
| C       | -2.316565077  | 3.372903897  | 1.854684311  |
| H       | -2.820439246  | 3.789708943  | 0.967051296  |
| H       | -1.564306518  | 4.106725175  | 2.177041107  |
| H       | -3.064799272  | 3.209707998  | 2.640056146  |
| H       | -1.526560618  | -0.006888392 | 1.352861253  |
| O       | -1.563502861  | 0.467996006  | -1.119886315 |
| C       | -2.147870775  | 1.402072655  | -1.778263756 |
| O       | -1.600056014  | 2.363627478  | -2.315244702 |
| C       | -3.645571552  | 1.204155235  | -1.855982326 |
| H       | -4.058201119  | 1.143183857  | -0.835675091 |
| H       | -3.866307108  | 0.241769600  | -2.344714924 |
| H       | -4.128394181  | 2.021005663  | -2.409391965 |

N-H Activation Product

Electronic Energy: -1797.744192824
Free Energy Correction: 0.542296705

N  0.287006879  -0.945317166  -5.052829232
C  1.063584482  2.542176172  -0.125325106
C  0.481929043  2.483046821  -1.455082812
C  1.048319407  1.346840632  -2.118982571
C  1.931958931  0.680970358  -1.198099829
C  1.95893067  1.445546235  0.028233548
C  0.854364318  0.937025457  -3.541886391
C  0.033873153  -0.337407644  -3.766502424
C  1.327590165  -1.771191654  -5.255186907
C  2.837845268  -0.458237640  -1.486577249
C  -0.448324376  3.488285176  -2.024008368
C  2.832614869  1.140992250  1.187559690
C  0.744008163  3.561681996  0.901035313
O  2.147378944  -2.082588739  -4.404568771
N  -0.044148922  -0.941639746  1.102060530
C  -1.168572002  -3.141959373  -0.328400270
Rh  -0.042026629  0.721271180  -0.339570113
H  -1.033360185  -0.91591433  -3.698460475
H  0.246521351  -1.080667684  -2.979137119
H  1.862593066  0.780289778  -3.966589880
H  0.404373211  1.769548433  -4.106995478
H  -0.324307084  -0.738246883  -5.837129438
H  1.441032886  4.412955723  0.817384286
H  0.835776138  3.148925930  1.916698665
H  -0.277545155  3.946320904  0.777110613
H  0.102593288  4.397976364  -2.319445747
H  -1.207045509  3.77862930  -1.280022869
H  -0.985064876  3.086246745  -2.891807236
H  3.873668695  1.416267811  0.945027180
H  2.808232641  0.067141085  1.432957966
H  2.534148654  1.706031974  2.082828537
H  3.869095191  -0.071724986  -1.573348157
H  2.594310947  -0.974810713  -2.427308255
H  2.846374726  -1.191156389  -0.662394227
C  0.736544057  -2.024538355  0.750499112
O  0.454570101  -0.366976760  2.303865115
C  0.096932904  -1.009214992  5.886261113
H  0.266677377  -2.096268892  5.926623971
Acetic Acid Dissociation TS
Electronic Energy: -1797.737242545
Free Energy Correction: 0.544281089
| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| H    | 0.651186589| -0.934018442| -3.014105877|
| H    | 1.255910087| 1.319040197 | -4.247529613|
| H    | -0.478457357| 1.687297441 | -4.157906877|
| H    | -0.538384472| -1.006427714| -3.697025830|
| H    | 0.225347495 | 4.445731600 | 0.883821946 |
| H    | 0.070050780 | 2.970440190 | 1.879170403 |
| H    | -1.291506812| 3.496174161 | 0.868742914 |
| H    | -1.344687878| 4.229078918 | -2.146656180|
| H    | -2.286291756| 3.116244620 | -1.126463284|
| H    | -1.972010132| 2.687522352 | -2.819360767|
| H    | 3.516140979 | 2.351471960 | 0.560332208 |
| H    | 2.851146223 | 0.792533868 | 1.120442638 |
| H    | 2.238592078 | 2.32371231 | 1.798718652 |
| H    | 3.706666086 | 1.172392477 | -2.121399448|
| H    | 2.701426414 | -0.13030811 | -2.796786753|
| H    | 3.238706843 | -0.177731704 | -1.078597752|
| C    | 1.299297602 | -1.756033311 | 0.569871419 |
| O    | 2.989047508 | -1.842932978 | 1.109987467 |
| C    | 0.943466317 | -2.618192278 | -0.606283481|
| H    | -0.596514125 | 3.666644109 | -1.657301663|
| C    | 2.093936748 | -3.098401446 | -1.431381316|
| H    | 2.590072999 | -2.26756850 | -1.960834534 |
| H    | 2.859792351 | -3.565894905 | -0.792351676|
| H    | 1.763467484 | -3.824682306 | -2.188345485|
| O    | 0.681853949 | -0.212239001 | 2.144574922 |
| C    | 0.575159149 | -0.948032617 | 3.265738056 |
| O    | 0.259158787 | -2.109726984 | 3.275015444 |
| C    | 0.959091537 | -0.138679066 | 4.492794809 |
| C    | 0.299941392 | -0.775938407 | 5.709534826 |
| H    | 0.596037050 | -1.830605293 | 5.819941375 |
| H    | 0.594070874 | -0.232752609 | 6.622389567 |
| H    | -0.800084268 | -0.740436943 | 5.628566050 |
| C    | 2.484192574 | -0.239333380 | 4.602501380 |
| H    | 2.806631712 | -1.292318086 | 4.663578484 |
| H    | 2.975892719 | 0.219524597 | 3.729053229 |
| H    | 2.830093122 | 0.282171290 | 5.510712219 |
| C    | 0.535530857 | 1.322198078 | 4.375002586 |
| H    | 0.755962922 | 1.845304348 | 5.318342515 |
| H    | 1.077011374 | 1.837543050 | 3.567402871 |
| H    | -0.544583151 | 1.420930570 | 4.170248617 |
| H    | 1.428156787 | -1.828208673 | -6.455401210|
| H    | -1.142152154 | -2.656818023 | -0.187465283|
| O    | -2.266722653 | 1.356474270 | 1.824044607 |
| C    | -2.768113647 | 0.378609565 | 2.338596655 |
| O    | -2.348070735 | -0.860290705 | 2.122755453 |
| C    | -3.925566762 | 0.422914698 | 3.284043216 |
| H    | -4.200196839 | 1.460884760 | 3.506098667 |
| H    | -3.677936514 | 0.112952654 | 4.212865513 |
| H    | -4.784497098 | -0.100759989 | 2.384915673 |
Intermediate I
Electronic Energy: \(-1568.662002778\)
Free Energy Correction: \(0.478472672\)

H  -1.618851191  -0.849987204  1.453546302
O  -1.900008505  -0.351060143  -0.649157987
C  -2.907604293  -0.039821783  -1.402492982
O  -2.827350754  0.452366750  -2.521880594
C  -4.237202285  -0.326398230  -0.751941385
H  -4.399724158  0.429611461  0.035349082
H  -4.229374820  -1.310147725  -0.259574756
H  -5.059948459  -0.262891108  -1.476404834

N  29.641434519  -12.735117717  -26.208954231
C  30.172479933  -12.835472703  -20.116537198
C  29.276475722  -13.015067370  -21.225954805
C  29.930716711  -12.554049231  -22.420884377
C  31.216313369  -12.035066478  -22.031786092
C  31.382088451  -12.224067630  -20.622262600
C  29.320033217  -12.424877498  -23.777139726
C  30.056894937  -13.164425962  -24.892214127
C  30.139894778  -11.623791465  -26.777266930
C  32.173033303  -11.305651279  -22.90473149
C  27.908353152  -13.578034703  -21.141229222
C  32.544653712  -11.777631004  -19.813837741
C  29.892507569  -13.208368841  -18.706494987
O  30.985426891  -10.901125253  -26.271631792
N  32.259821263  -15.336844406  -20.227170421
C  32.436479364  -15.315084502  -23.062010004
Rh 31.082824400  -14.179758936  -21.502015173
H  29.876544654  -14.242127387  -24.773687801
H  31.143742546  -12.993818324  -24.812627710
H  29.284565614  -11.347125489  -24.025523203
H  28.274453969  -12.771738738  -23.747443761
H  28.916988822  -13.246985364  -26.703706180
H  29.172662521  -12.508205002  -18.250531848
H  30.811507023  -13.192425248  -18.102017028
H  29.455379344  -14.219504111  -18.649883731
H  27.184329227  -12.759531807  -20.987754524
H  27.808594450  -14.272849509  -20.294494633
H  27.637952040  -14.107182802  -22.066298059
H  32.289911724  -10.855883380  -19.262975619
H  33.411286796  -11.549386731  -20.451816597
H  32.845161874  -12.543393419  -19.081789111
H  32.265463949  -10.269625452  -22.536286823
H  31.842035049  -11.256929755  -23.952140493
H  33.185649527  -11.736106594  -22.872192893
C  33.419848494  -15.662971435  -20.793070842
O  34.349400033  -16.344135071  -20.385543317
C  33.381400510  -14.953036915  -22.134914507
H      32.450679973    -14.858631646    -24.057876269
C      34.490015708    -13.998284214    -22.393131662
H      34.602850572    -13.262379849    -21.579483675
H      35.430333382    -14.576352431    -22.40814074
H      34.388582313    -13.485405698    -23.360503433
O      31.914803991    -15.959616757    -19.039522556
C      32.442858614    -15.423946583    -17.918124199
O      33.146753451    -14.46667776    -17.912484074
C      32.073084428    -16.250227970    -16.99373926
C      32.28399657    -15.40613902    -15.452612466
H      31.62714356    -15.514195247    -15.458835622
H      32.046728286    -15.992751024    -14.53644398
H      33.323503390    -15.049630223    -15.373729920
C      30.627944786    -16.738107579    -16.764091943
H      29.920034875    -15.893115620    -16.808254685
H      30.447688818    -13.780123428    -17.638929083
H      30.398574421    -17.318882600    -15.855256029
C      33.036438203    -17.443393331    -16.696402461
H      32.846755070    -18.072324553    -15.810634113
H      32.907782965    -18.062724130    -17.598959294
H      34.085038279    -17.103295551    -16.659106167
H      29.703696902    -14.22138181    -27.73675449
H      31.845231719    -16.225560926    -22.933293155
O      29.971066352    -15.990348405    -21.506511029
C      29.127857937    -16.318352335    -22.471408696
O      28.943958004    -15.730338946    -23.483665386
C      28.284344930    -17.521030778    -22.054219684
H      27.449082085    -17.176841293    -21.421279275
H      28.85600661    -18.255411371    -21.470211668
H      27.863141844    -17.987488585    -22.955768871

C-H Activation TS
Electronic Energy:      -1568.642131565
Free Energy Correction:     0.481504475
N       0.140089464     -2.403241224     -4.338427536
C     -2.215234535     1.263610264     -0.184029097
C     -2.344575387     0.065010623    -0.947849530
C     -1.537044862     0.192735063    -2.140675369
C     -0.929295870     1.489775870    -2.118206251
C     -1.302320180     2.143162872     -0.891619409
C     -1.412976078     -0.793939412    -3.258813770
C     -0.251158222     -1.778728634    -3.096149122
C     0.950143955     -1.769453788    -5.205988590
C    -0.072684581     2.051313648    -3.192226369
C     -3.148172783     -1.130574399    -0.592740359
C     -0.918720009     3.513207614    -0.464093144
C     -2.881123589     1.585997902    1.105277538
O     1.423011242     -0.657449891    -5.029694491
N     0.622528444     0.917263779     1.403329283
| atom | x           | y           | z           |
|------|-------------|-------------|-------------|
| C    | 0.841419739 | 0.802961849 | -0.89053337 |
| Rh   | -0.255022037| 0.35788694  | -0.387080671|
| H    | -0.503740380| -2.563798012| 2.365824389  |
| H    | 0.623195907 | 0.2140155216| -2.693514518 |
| H    | -1.263573242| 0.35657103  | -4.19871667  |
| H    | -2.360029701| 0.347554244 | -3.37838659  |
| H    | -2.25331264  | -3.31654480  | 4.59018498   |
| H    | -3.610700329 | 4.01489221   | 0.96593468   |
| H    | -2.151734059 | 1.915396749  | 1.862950529  |
| H    | -3.424456924 | 0.719657260  | 1.509771918  |
| H    | -4.170508970 | -1.037517080 | -0.997526562 |
| H    | -3.227251017 | -1.26035308  | 0.496813461  |
| H    | -2.706957186 | -2.04796188  | -1.010013297 |
| H    | -1.665177421 | 4.252020806  | -0.80308546  |
| H    | 0.054015583  | 3.807293485  | -0.88613826  |
| H    | -0.851876416 | 3.586458817  | 0.632127286  |
| H    | -0.707002806 | 2.586600038  | -3.920032253 |
| H    | 0.467394148  | 1.262442932  | -3.741973843 |
| H    | 0.659500012  | 2.773478810  | -2.800554455 |
| C    | 1.830673943  | 1.505271980  | 1.450844031  |
| O    | 2.444412795  | 1.885215847  | 2.447139813  |
| C    | 2.346284782  | 1.649124897  | 0.04401425   |
| H    | 2.177077172  | 0.921674115  | -1.933502762 |
| C    | 3.364238101  | 2.706455555  | -0.818434987 |
| H    | 2.953162448  | 3.699937700  | 0.074464966  |
| H    | 4.224932274  | 2.55803910   | 0.492452410  |
| H    | 3.71576471   | 2.724603386  | -1.223038842 |
| O    | 0.020010575  | 0.613155187  | 2.617057061  |
| C    | 0.450171309  | -0.520789301 | 3.220158608  |
| O    | 1.455124143  | -1.101798424 | 2.907109492  |
| C    | -0.549887410 | -0.968417744 | 4.27066187   |
| C    | 0.050905810  | -2.118249296 | 5.065450175  |
| H    | 0.966225057  | 2.086784131  | 5.59469903   |
| H    | 0.65318972   | -2.474169856 | 5.84362970   |
| H    | 0.311932012  | 2.962419235  | 4.407553932  |
| C    | -0.926453465 | 0.184778156  | 5.198648831  |
| H    | -0.042549851 | 0.585847924  | 5.721724549  |
| H    | 1.406750463  | 1.009287532  | 4.649078601  |
| H    | -1.636374800 | -0.175535638 | 5.961837267  |
| C    | -1.787295181 | -1.451481827 | 3.505051803  |
| H    | -2.525091930 | -1.865962390 | 4.212019771  |
| H    | -2.258529057 | -0.624389023 | 2.950591870  |
| H    | -1.524933912 | -2.237094456 | 2.775370528  |
| H    | 1.158833567  | -2.373611107 | 6.119695633  |
| H    | 1.827822993  | -0.458797695 | 0.535824171  |
| C    | -0.046351624 | -1.652851170 | 0.341232986  |
| O    | 1.80055338   | -2.214831574 | 0.338215024  |
| O    | 2.118281917  | -1.703961545 | -0.162763948 |
| C    | 1.172536909  | -3.593180162 | 0.918221959  |
Intermediate II (Acetic Acid Associated)
Electronic Energy:  -1568.657342496
Free Energy Correction:  0.485286612

H       0.870950776     -4.322832000      0.149334021
H       0.485718292     -3.696316817      1.770161201
H  2.201147830     -3.819229987      1.227709802

N      29.614869160    -13.253550462    -25.710579858
C      30.277163454    -12.597832475    -19.745397118
C      29.422752903    -12.769396277    -20.850938933
C      30.127432164    -12.333209279    -22.054701659
C      31.409204340    -11.851852903    -21.66495156
C      31.555256570    -12.099350668    -20.249433191
C      29.557256182    -12.264443728    -23.437409754
C      29.86352242     -13.485572757    -24.306169147
C      30.59705729     -12.607493908    -26.479871149
C      32.41699302     -11.216107606    -22.584644990
C      28.05078678     -13.337861777    -20.865301308
C      32.72591864     -11.734400490    -19.408980355
C      29.998643769    -12.899820494    -18.316096604
O      31.584666526    -12.180391121    -26.089122953
N      32.328790135    -15.240942742    -19.933144545
C      33.064421575    -14.345048330    -22.178714498
Rh     31.306618324    -13.962591052    -21.192687695
H      29.277517365    -14.356083709    -23.977139221
H      30.927976240    -13.756734698    -24.185447778
H      29.964214447    -11.372203601    -23.943044194
H      28.464493878    -12.115396947    -23.84314230
H      28.73549205     -13.543489774    -26.127621446
H      29.919413890    -11.969337397    -17.727925894
H      30.83055165    -13.506698939    -17.870456888
H      29.056965840    -13.454647190    -18.193563518
H      27.304766223    -12.557781798    -21.095182886
H      27.780533406    -13.788011628    -19.899397525
H      27.957534928    -14.118184919    -21.637908875
H      32.618074874    -10.713687825    -19.002193763
H      33.660202089    -11.767073826    -19.990223939
H      32.835454702    -12.423547474    -18.557700176
H      32.326801292    -10.117258594    -22.502337560
H      32.271110382    -11.50942856     -23.611087450
H      33.441759051    -11.479384413    -22.265689700
C      33.560296066    -15.700148415    -20.243215909
O      34.230210692    -16.500593119    -19.587921578
C      33.989516898    -15.098616708    -21.546643782
H      33.309363808    -13.864922622    -23.142563778
C      35.374660623    -15.404890589    -22.00984421
H      36.121903068    -15.049389884    -21.278924651
H      35.530959439    -16.493798903    -22.099183672
H      35.587760503    -14.936947891    -22.982511775
| Atom | X        | Y        | Z        |
|------|----------|----------|----------|
| O    | 31.793548269 | -15.766277706 | -18.759004451 |
| C    | 31.354429967  | -17.040430921  | -18.827030219  |
| O    | 30.977588491  | -17.550724042  | -17.447050822  |
| C    | 32.296841362  | -18.823146301  | -16.716276837  |
| H    | 32.881275442  | -16.898621592  | -16.590030756  |
| C    | 32.089886423  | -18.251203162  | -15.721032190  |
| H    | 32.078889992  | -18.251203162  | -15.721032190  |
| H    | 32.881275442  | -16.898621592  | -16.590030756  |
| C    | 30.151065397  | -16.518747077  | -16.683199177  |
| H    | 30.712914381  | -15.587440420  | -16.512305988  |
| H    | 29.24994230   | -16.265159059  | -17.22995345   |
| H    | 29.864124771  | -16.931228077  | -15.701760447  |
| C    | 30.189288499  | -18.843361644  | -17.599556007  |
| H    | 29.928018711  | -19.240888580  | -16.604882836  |
| H    | 29.254876984  | -18.680832258  | -18.161566928  |
| H    | 30.774623149  | -19.608401819  | -18.133846763  |
| H    | 30.170197660  | -12.504122963  | -27.537429637  |
| C    | 32.313174202  | -16.157951756  | -22.630126071  |
| O    | 30.160223943  | -15.738039895  | -21.877801063  |
| C    | 30.549983023  | -16.788670377  | -22.377891309  |
| O    | 31.766358561  | -16.959262630  | -22.834569777  |
| C    | 29.668850766  | -17.975173146  | -22.519409264  |
| H    | 29.888261649  | -18.524362682  | -23.444737184  |
| C    | 28.614894156  | -17.67011035   | -22.477887344  |
| H    | 29.884584074  | -18.636582697  | -21.665576368  |

Intermediate II
Electronic Energy:  -1339.575801430
Free Energy Correction:  0.425667492

N    32.614063053 | -11.263209481 | -24.733429855
C    28.602225340 | -13.536734605 | -20.926702542
C    28.803136801 | -12.939074100 | -22.214987200
C    30.009814056 | -12.183704573 | -22.125729702
C    30.489469846 | -12.211174173 | -20.739474591
C    29.615614691 | -13.022176612 | -20.002263784
C    30.659448604 | -11.402497902 | -22.20042302
C    31.825421290 | -12.132334541 | -23.891258437
C    33.554427280 | -10.451703629 | -24.215926525
C    31.707173047 | -11.517489690 | -20.243103638
C    27.954052593 | -13.106636797 | -23.424659139
C    29.686940908 | -13.348762525 | -18.555259154
C    27.511027986 | -14.460212450 | -20.536134736
O    33.835575484 | -10.381619753 | -23.030114605
N    31.948019254 | -15.458723920 | -21.160663833
C    30.434010179 | -15.586430398 | -23.222067817
Rh   30.462417072 | -14.233406358 | -21.679771168
H    31.455962762 | -12.976714268 | -24.494458481
H    32.488014160 | -12.562332334 | -23.120029969
H    31.039392856 | -10.458164894 | -22.792251555
Intermediate III (Major Stereoisomer)

Electronic Energy: -1763.621753239
Free Energy Correction: 0.587362407

N  31.262758492  -11.343202456  -25.662394248
C  28.913559538  -13.619751722  -20.472938491
C  28.780220222  -13.287282990  -21.879468625
C  29.951310231  -12.578415293  -22.82124087
C  30.880984384  -12.615210542  -21.190345273
C  30.198572499  -13.214677895  -20.053447940
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
|      | C     | 30.10608496 | -11.757303586 | -23.524726652 |
|      | C     | 30.961595038 | -12.328767063 | -24.648485137 |
|      | C     | 32.269565735 | -10.464286756 | -25.508338369 |
|      | C     | 32.228462655 | -11.982217454 | -21.154900403 |
|      | C     | 27.548953890 | -13.466851446 | -22.694576123 |
|      | C     | 30.721699119 | -13.321560703 | -18.666157751 |
|      | C     | 32.234827510 | -15.486760919 | -20.867045469 |
|      | C     | 31.708551771 | -15.135245612 | -23.302971423 |
|      | Rh    | 30.499452697 | -14.712036757 | -21.696937839 |
|      | H     | 30.452855029 | -13.180536916 | -25.12657501 |
|      | H     | 31.914056980 | -12.705468033 | -24.241551608 |
|      | H     | 30.551069759 | -10.793571560 | -23.218531150 |
|      | H     | 29.106257037 | -11.513398777 | -23.92311310 |
|      | H     | 30.681283874 | -11.273760463 | -26.492227179 |
|      | H     | 27.321751394 | -13.391415572 | -19.064509347 |
|      | H     | 28.275486749 | -14.870809481 | -18.836017215 |
|      | H     | 27.099608424 | -14.752997183 | -20.173651601 |
|      | H     | 26.865800875 | -12.609037382 | -22.567064263 |
|      | H     | 26.99048551 | -14.368599116 | -22.397740843 |
|      | H     | 27.780485051 | -13.550922514 | -23.768550862 |
|      | H     | 30.192146852 | -12.616181697 | -18.003109334 |
|      | H     | 31.795173351 | -13.088371451 | -18.615718609 |
|      | H     | 30.573090657 | -14.334380719 | -18.255940296 |
|      | H     | 32.224539004 | -11.090978605 | -20.503128607 |
|      | H     | 32.552541523 | -11.660202166 | -22.157272149 |
|      | H     | 32.975126979 | -12.685949861 | -20.751347126 |
|      | C     | 33.22695196 | -15.973427434 | -21.648897399 |
|      | C     | 34.228459180 | -16.571176601 | -21.253046347 |
|      | C     | 32.910415227 | -15.685315528 | -23.070818518 |
|      | H     | 31.355042289 | -14.970624330 | -24.329511959 |
|      | C     | 33.917820949 | -16.092306543 | -24.095110037 |
|      | H     | 34.884140420 | -15.583644010 | -23.932427981 |
|      | H     | 34.127705723 | -17.17457622 | -24.027563934 |
|      | H     | 33.573196234 | -15.866370210 | -25.115561887 |
|      | O     | 32.350931622 | -15.860998041 | -19.532154652 |
|      | C     | 33.344245826 | -15.271949727 | -18.839899620 |
|      | O     | 33.971189797 | -14.316524886 | -19.22542003 |
|      | C     | 33.583220160 | -15.999744891 | -17.524926759 |
|      | C     | 34.535104722 | -15.174718308 | -16.671084940 |
|      | H     | 34.101825266 | -14.190528406 | -16.425857940 |
|      | H     | 34.741461638 | -15.703734786 | -15.725779873 |
|      | H     | 35.492522418 | -15.001796895 | -17.187165459 |
|      | C     | 32.273259252 | -16.226084747 | -16.773057964 |
|      | H     | 31.794441785 | -15.269880801 | -16.501273433 |
|      | H     | 31.561951677 | -16.818289982 | -17.368346395 |
|      | H     | 32.479288667 | -16.772791432 | -15.837419319 |
|      | C     | 34.220923270 | -17.346604208 | -17.879533427 |
Intermediate III (Minor Stereoisomer)
Electronic Energy: -1763.625386457
Free Energy Correction: 0.584102076

N  30.684196642 -11.335925907 -25.647799137
C  29.344397628 -13.754823520 -20.162704454
C  28.833845414 -13.493353240 -21.488747183
C  29.830561649 -12.719243580 -22.193739494
C  30.960609472 -12.581136256 -21.322442566
C  30.655364742 -13.227936118 -20.066433747
C  29.657153536 -12.040341211 -23.515421011
C  30.768023492 -12.262134524 -24.540656492
C  31.20146942 -10.097106033 -25.565695439
C  32.180713097 -11.755068566 -21.563798792
C  27.466356614 -13.857638224 -21.949224076
C  31.522973379 -13.273031835 -18.857432077
C  28.594677217 -14.402956308 -19.058874297
O  31.798987046 -9.655990085 -24.596351839
Rh 30.585072795 -14.747329630 -21.77395622
H  30.739369024 -13.286344781 -24.939702063
H  31.757033818 -12.131346816 -24.074291892
H  29.585143592 -10.952226593 -23.324742297
H  28.691332257 -12.329853020 -23.962218635
H  30.173170489 -11.594281938 -26.486809050
H  28.116405719 -13.629854159 -18.432747986
Migratory Insertion TS (Major Stereoisomer)
Electronic Energy: -1763.603513857
Free Energy Correction: 0.585244715

N  1.194077404  5.574984609  -1.017636534
C  -2.235570661  1.248351633  1.665157594
C  -2.213801564  2.403117163  0.802878024
C  -0.883543428  2.972671786  0.852488375
C  -0.066596031  2.103912261  1.610861973
C  -0.897051027  1.005522845  2.093137651
C  -0.464971323  4.299487326  0.300160905
C  0.602280854  4.274571435  -0.793525205
C  2.183188733  6.046423346  -0.238492565
C  1.370855727  2.286270534  1.952857935
C  -3.384434207  3.011405718  0.112199925
C  -0.416770259  -0.087068680  2.982444103
C  -3.440485125  0.472458067  2.058228371
O  2.685674672  5.439849383  0.694603529
N  0.751734081  -0.301917644  -0.481232032
C  -0.381757753  1.393012509  -2.076010478
Rh -0.910613683  0.876161113  -0.071388282
H  0.177158217  3.920349287  -1.742771968
H  1.406862125  3.568105807  -0.527355829
H  -0.067883823  4.893611028  1.144253730
H  -1.347646178  4.850469306  -0.064582137
H  0.828966140  6.176207124  -1.750356217
H  -3.186306879  -0.556902183  2.354135735
H  -4.192711273  0.427801681  1.254534329
H  -3.928840536  0.948434057  2.926047962
H  -3.834210071  3.824397164  0.708385544
H  -4.173782716  2.266798251  -0.075325335
H  -3.093252724  3.439761574  -0.861579201
H  -0.514984441  0.188400984  4.047338848
H  0.648621735  -0.301130086  2.797327077
H  -0.977892652  -1.021205384  2.822081123
H  1.513667716  2.215713127  3.044853233
H  1.754101055  3.265244391  1.625268146
H  1.992861868  1.499030896  1.493454353
C  1.416045709  -0.178182489  -1.649456239
O  2.337911966  -0.896640940  -2.048082183
C   0.866888951  0.980458425  -2.403166975
H  -0.818596333  2.257965397  -2.593869765
C   1.728701965  1.597681437  -3.449069880
H   2.669993460  1.982184692  -3.015802218
C   1.728701965  1.597681437  -3.449069880
H   2.669993460  1.982184692  -3.015802218
H   2.025352123  0.845935736  -4.201664417
H   1.218354848  2.426259226  -3.967346742
O   1.064351846  -1.470406238   0.211331024
C   2.235872206  -1.481134238   0.866113744
O   2.942727000  -2.810370583   2.364604910
H   3.382308754  -2.236269248   3.254396723
H   3.968077111  -3.826112804   2.692010946
H   4.585441044  -3.234801650   1.943864886
C   1.347956723  -3.574264522   1.949687817
H   0.977108857  -3.027683246   2.833778002
H   0.522759570  -3.654771805   1.22652198
C   1.623743139  -4.592380419   2.74611493
C   3.03354607   -3.652013211   0.098355145
H   3.323041566  -4.678921785   0.380605279
H   2.230357064  -3.699626061  -0.655342697
H   3.904979411  -3.16921298   -0.366177297
C  -1.861951990   0.208496547  -2.047882981
H   0.557349654   -0.305732528  -2.929200632
C   2.173651367  -0.636788467  -0.92034893
C   -3.125819386  -0.419558946  -0.418338915
C  -1.794454982  -2.053557473  -0.82967318
C   0.886751803  -2.682407578  -1.690632020
C  -2.075460549  -2.842788570   0.179739185
O  -0.542031739  -4.023499777   1.541123677
C  -2.047275424  -4.178907344   0.340735266
C  -1.109317959  -4.779234554  -0.508942313
C  -0.405601570  -2.118801632  -2.496874549
H  -3.106075243  -2.386609179   0.857528530
H   0.181806013  -4.463653389  -2.231892240
H  -2.493899841  -4.783677482  1.135574520
O  -0.808532964  -6.071944415  -0.254081566
C   0.220505025  -6.683068899  -0.991050230
C  -0.022541355  -6.747173933  -2.066462139
H   1.176814906  -6.140157476  -0.87103766
H   0.341699192  -7.700113253  -0.596314184
H  -2.639542384   0.933976148  -2.315526436
H   2.514973955   7.067994618  -0.538913530

Migratory Insertion TS (Minor Stereoisomer)
Electronic Energy:  -1763.602096630
Free Energy Correction:  0.585378023
N  -1.249327192   5.762721731  -1.083570983
C   1.539898533  1.417635333  1.984479209

49
| Element | x       | y       | z       |
|---------|---------|---------|---------|
| C       | 1.376212924 | 2.634790998 | 1.232946918 |
| C       | -0.030976942 | 2.961659232 | 1.219887606 |
| C       | -0.738831661 | 1.885317131 | 1.801478893 |
| C       | 0.240608495 | 0.913071713 | 2.280843924 |
| C       | -0.612145391 | 4.264625326 | 0.770971439 |
| C       | -0.843599604 | 4.422271498 | -0.726736406 |
| C       | -0.348500061 | 1.885317131 | 1.801478893 |
| C       | 2.214773655 | 1.770461498 | 1.941099013 |
| C       | 2.473626833 | 3.523849760 | 0.756642141 |
| C       | -0.063497754 | -0.316565560 | 3.062177086 |
| C       | 2.830761480 | 0.819767089 | 2.414644997 |
| O       | 0.859510944 | 6.613521768 | -1.132704538 |
| N       | -0.894179289 | -0.559513648 | -0.383837352 |
| C       | -0.220355844 | 1.456914141 | -1.871025278 |
| Rh      | 0.417377383 | 0.978660535 | 0.124124256 |
| H       | 0.088104921 | 4.194268344 | -1.270883566 |
| H       | -1.606860297 | 3.709613518 | -1.07851533 |
| H       | -1.565604244 | 4.436710076 | 1.299162803 |
| H       | 0.067783648 | 5.072391995 | 1.096740334 |
| H       | -2.236394421 | 5.989030969 | -1.161867483 |
| H       | 2.753166826 | -0.271088403 | 2.54494456 |
| H       | 3.647820206 | 1.02641356 | 1.705411903 |
| H       | 3.139067710 | 1.241849849 | 3.386894028 |
| H       | 2.912922526 | 4.093801423 | 1.594439111 |
| H       | 3.294386166 | 2.951060029 | 0.294105825 |
| H       | 2.115047385 | 4.257285078 | 0.016576611 |
| H       | 0.057049509 | -0.136116136 | 4.144413236 |
| H       | -1.098697902 | -0.651640682 | 2.895501316 |
| H       | 0.607587853 | -1.144843636 | 2.781539813 |
| H       | -2.539143521 | 1.976407913 | 2.97637949 |
| H       | -2.730117033 | 2.482387600 | 1.277347888 |
| H       | -2.557429485 | 0.758441039 | 1.671189458 |
| C       | -1.567682029 | -0.538512723 | -1.553202135 |
| O       | -2.286132582 | -1.439085755 | -1.998135445 |
| C       | -1.320163047 | 0.754800856 | -2.238124966 |
| H       | -0.028014523 | 2.419248682 | -2.35932385 |
| C       | -2.288662618 | 1.176204523 | -3.288265360 |
| H       | -3.317635396 | 1.220849452 | -2.889839076 |
| H       | -2.314341286 | 0.439179529 | -4.11005278 |
| H       | -2.032298705 | 2.160107943 | -3.709416445 |
| O       | -0.907379650 | -1.815928251 | 0.223039761 |
| C       | -2.052313209 | -2.164152740 | 0.832782612 |
| O       | -2.961432207 | -1.403926753 | 1.060969447 |
| C       | -2.061072516 | -3.649596199 | 1.158929220 |
| C       | -3.204173610 | -3.935052398 | 2.122611645 |
| H       | -3.075326754 | -3.384471232 | 3.069641366 |
| H       | -3.235823220 | -5.012505667 | 2.354304092 |
| H       | -4.175333789 | -3.644533417 | 1.693024039 |
| C       | -0.736542876 | -4.097996940 | 1.770908505 |
Intermediate IV
Electronic Energy: -1763.628721931
Free Energy Correction: 0.589144925

| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| H       | -0.543828445 | -3.59170815 | 2.732265329 |
| H       | 0.112097687  | -3.89735779 | 1.099826882 |
| H       | -0.772635975  | -5.183673694 | 1.965665414 |
| C       | -2.295533890  | -4.379016287 | -0.168091319 |
| H       | -2.377284431  | -5.464078079 | 0.015569957  |
| H       | -1.464942763  | -4.195754351 | -0.868773581 |
| H       | -3.224497597  | -0.034601830 | -0.652153367 |
| C       | 1.534665276  | 0.751037474  | -1.863582468 |
| H       | 1.321469657  | 0.254905841  | -2.816704621 |
| C       | 2.022076368  | -0.100354480 | -0.805133591 |
| H       | 2.880835856  | 0.288246011  | -0.241764376 |
| C       | 1.977437827  | -1.567564636 | -0.855402102 |
| C       | 1.264380091  | -2.292721845 | -1.817416574 |
| C       | 2.673982867  | -2.303658864 | 0.119992751  |
| C       | 1.210188542  | -3.683748134 | -1.797384121 |
| C       | 2.633503731  | -3.87720802  | 0.153339224  |
| C       | 1.880609877  | -4.392817119 | -0.794669067 |
| C       | 0.707111782  | -1.771137238 | -2.602669307 |
| H       | 3.258493371  | -1.767261838 | 0.876488603  |
| H       | 0.627179333  | -4.201121160 | -2.563491208 |
| C       | 3.165102431  | -4.254796626 | 0.923491464  |
| O       | 1.847012887  | -5.736831331 | -0.655910211 |
| C       | 1.010016179  | -6.480646225 | -1.505421142 |
| H       | 1.331085088  | -6.417153504 | -2.560562546 |
| H       | -0.040998605  | -6.143065301 | -1.435799892 |
| H       | 1.067067148  | -7.527911880 | -1.181820296 |
| H       | 2.099565676  | 1.679304156  | -2.01122187 |
| H       | -0.824664236  | 7.726353528  | -1.494201473 |

Intermediate IV
Electronic Energy: -1763.628721931
Free Energy Correction: 0.589144925

| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| N       | 31.049492974 | -11.277571939 | -25.854014999 |
| C       | 29.076453766 | -13.998482776 | -20.870677565 |
| C       | 29.007606433 | -13.574686680 | -22.33763327 |
| C       | 29.986403446 | -12.520554432 | -22.412372458 |
| C       | 30.746515122 | -12.393266973 | -21.230047017 |
| C       | 30.204949435 | -13.344374888 | -20.272549723 |
| C       | 30.072333937 | -11.635192101 | -23.611210550 |
| C       | 30.697818524 | -12.258888431 | -24.852810698 |
| C       | 32.143284063 | -10.505755568 | -25.712333214 |
| C       | 31.908479026 | -11.488934967 | -21.00403425 |
| C       | 27.939158088 | -13.939221037 | -23.206113483 |
| C       | 30.655174177 | -13.511911131 | -18.863564584 |
| C       | 28.073562813 | -14.84397298 | -20.173688814 |
| O       | 32.924261164 | -10.572745793 | -24.776692034 |
| N       | 32.775182892 | -15.12381344 | -21.037455449 |
| C       | 31.789252898 | -15.643886418 | -23.792064584 |
| Rh      | 30.956246069 | -14.577202044 | -21.876969171 |
| Atom | x          | y          | z          |
|------|------------|------------|------------|
| H    | 30.035129981 | -13.008742547 | -25.312736398 |
| H    | 31.615034688 | -12.776826031 | -24.547222013 |
| H    | 30.664149229 | -10.744086083 | -23.347776363 |
| H    | 29.05503345 | -11.273235436 | -25.312736398 |
| H    | 29.05503345 | -11.273235436 | -25.312736398 |
| H    | 29.05503345 | -11.273235436 | -25.312736398 |
| H    | 29.05503345 | -11.273235436 | -25.312736398 |
| H    | 29.05503345 | -11.273235436 | -25.312736398 |
| H    | 29.05503345 | -11.273235436 | -25.312736398 |
| H    | 29.05503345 | -11.273235436 | -25.312736398 |
| H    | 29.05503345 | -11.273235436 | -25.312736398 |
| H    | 29.05503345 | -11.273235436 | -25.312736398 |
| H    | 29.05503345 | -11.273235436 | -25.312736398 |
| H    | 29.05503345 | -11.273235436 | -25.312736398 |
| H    | 29.05503345 | -11.273235436 | -25.312736398 |
| C    | 33.59674929 | -14.982333034 | -23.07586615 |
| C    | 32.273351535 | -11.071384950 | -21.957117434 |
| H    | 32.74672234 | -12.037447357 | -20.541080858 |
| C    | 33.96460461 | -15.516363182 | -19.748272694 |
| C    | 33.647403204 | -13.919701635 | -23.98300928 |
| O    | 32.85387617 | -15.010124663 | -23.267239455 |
| C    | 33.46460461 | -14.715487565 | -19.10691522 |
| O    | 34.362210582 | -13.655708389 | -19.534457828 |
| C    | 34.446730386 | -15.378884046 | -17.823200757 |
| C    | 35.260459662 | -14.379678473 | -17.014116140 |
| H    | 34.656635271 | -13.499767611 | -16.736706837 |
| C    | 35.617936587 | -14.857017741 | -16.087214007 |
| H    | 36.136084233 | -14.024202760 | -17.579436462 |
| C    | 33.259077717 | -15.835956177 | -17.004402701 |
| H    | 32.621636998 | -15.048053241 | -16.668723807 |
| H    | 32.635765668 | -16.586053275 | -17.578285397 |
| H    | 33.629125115 | -16.404124982 | -16.104219414 |
| C    | 35.333603884 | -16.554479893 | -18.255055455 |
| H    | 35.773174012 | -17.036325078 | -17.366046754 |
| H    | 34.745342017 | -17.301084545 | -18.841264617 |
| H    | 36.154183004 | -16.213437860 | -18.906780034 |
| C    | 31.219363341 | -16.957495920 | -23.305495774 |
| H    | 32.006794835 | -17.731139323 | -23.264320727 |
| C    | 30.558793693 | -16.695069844 | -21.96488862 |
| H    | 29.459748879 | -16.688698615 | -22.048321751 |
| C    | 30.981638004 | -17.499872112 | -20.795369628 |
| C    | 32.213408117 | -18.16262189 | -20.705912817 |
| C    | 30.125014845 | -17.624065915 | -19.683965401 |
| C    | 32.595328336 | -18.877309432 | -19.570528061 |
Intermediate IV (Conformation 2)
Electronic Energy: -1763.627452235
Free Energy Correction: 0.587922301

N  31.044876972 -12.298579081 -25.202683165
C  28.890762291 -13.775863353 -19.668115725
C  28.642683424 -13.864172391 -21.068286038
C  29.677497211 -13.113798830 -21.733815193
C  30.460598734 -12.417523527 -20.710094147
C  29.981849965 -12.81961262 -19.457220567
C  29.688930591 -12.759314977 -23.185680101
C  30.111498194 -12.961074889 -23.91655398
C  31.316203411 -10.986621666 -25.317607006
C  31.591238104 -11.479920917 -20.969726134
C  27.506691717 -14.570717874 -21.716783956
C  30.494995374 -12.431088725 -18.118474549
C  28.116474548 -14.412937195 -18.569709432
O  31.577016980 -10.243677367 -24.384376626
N  32.623095798 -15.075020077 -21.070527841
C  31.459038901 -16.422478784 -23.586877079
Rh  30.59192159 -14.687759223 -20.579120109
H  31.19657731 -14.03072570 -24.064923090
H  31.852827740 -12.582594349 -23.31670577
H  29.41298391 -11.688967750 -23.255086672
H  28.894842793 -13.311230854 -23.716590702
H  30.806173201 -12.815776451 -26.043676409
H  27.40638657 -13.698313507 -18.120026804
H  28.784244263 -14.760766388 -17.764825377
H  27.538830891 -15.278743496 -18.926981072
H  26.658066447 -13.879591900 -21.857725127
H  27.143050802 -15.409886677 -21.104090940
H  27.772666222 -14.965756519 -22.709112941
H  29.719544135 -11.900867489 -17.539414757
H  31.373402359 -11.772887646 -18.191789954
H  30.783885923 -13.317148285 -17.527160496
H  31.724318467 -10.775423308 -20.135392703

53
|     | X      | Y      | Z      |
|-----|--------|--------|--------|
| H   | 31.431079243 | -10.894633106 | -21.890562827 |
| H   | 32.544298828 | -12.023372379 | -21.098367718 |
| C   | 33.328311595 | -15.777014513 | -21.137890417 |
| O   | 34.461911139 | -16.234767873 | -21.811049747 |
| C   | 32.683201769 | -15.936610697 | -23.321922868 |
| H   | 31.248279709 | -16.59628550 | -24.662843657 |
| O   | 34.556664606 | -16.16309166 | -24.36428450 |
| C   | 33.167251435 | -15.760447955 | -25.424762029 |
| O   | 33.403986996 | -15.047827354 | -19.860893535 |
| C   | 32.751726822 | -15.39194936 | -18.769185735 |
| O   | 31.529724744 | -15.46613438 | -18.734969398 |
| C   | 33.648999437 | -15.528242774 | -17.562291082 |
| H   | 32.820860622 | -16.06230365 | -16.378265502 |
| C   | 32.37769003 | -16.72836800 | -16.597476115 |
| H   | 33.476753676 | -16.13435996 | -15.50211264 |
| H   | 32.030784150 | -15.238478884 | -16.117510267 |
| C   | 34.734103187 | -16.55096552 | -17.896784771 |
| H   | 34.285128266 | -17.540064232 | -18.109376131 |
| H   | 35.317616642 | -16.253578850 | -18.780302039 |
| H   | 35.416653150 | -16.663138594 | -17.037682652 |
| C   | 34.275386387 | -14.163921105 | -17.259382910 |
| C   | 34.886562475 | -14.235527183 | -16.344870240 |
| H   | 34.922200341 | -13.823915852 | -18.082892897 |
| H   | 33.499018864 | -13.398320624 | -17.087837828 |
| C   | 30.268887513 | -16.822058727 | -22.773706110 |
| H   | 30.051581397 | -17.882460937 | -23.037862402 |
| C   | 30.147351235 | -16.660920586 | -21.269220070 |
| H   | 30.068843936 | -16.694723016 | -21.032598587 |
| C   | 30.819488771 | -17.67699900 | -20.415961463 |
| C   | 32.013656715 | -18.314986265 | -20.758682302 |
| C   | 30.27911686 | -17.974462651 | -19.150943456 |
| C   | 32.684259112 | -19.15909611 | -19.869860606 |
| C   | 31.91747637 | -18.816766758 | -18.260471242 |
| C   | 32.149822957 | -19.398008238 | -18.601630158 |
| H   | 32.45041712 | -18.144376726 | -21.740549376 |
| H   | 30.341051714 | -17.488307571 | -18.851397952 |
| H   | 33.629988355 | -19.610735315 | -20.180839814 |
| H   | 30.500527138 | -19.027363691 | -17.271392386 |
| O   | 32.743731287 | -20.153428299 | -17.645302185 |
| C   | 33.980756502 | -20.751952137 | -17.935583043 |
| H   | 33.907236683 | -21.458984455 | -18.781580415 |
| H   | 34.754322869 | -19.99016967 | -18.173868367 |
| H   | 34.293093985 | -21.304120050 | -17.039493374 |
| H   | 29.423024094 | -16.274043621 | -23.235155307 |
| H   | 31.287101931 | -10.634742766 | -26.375804435 |

N-O Bond Cleavage TS
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| N       | 0.139944636| 5.014184812| -2.098825707|
| C       | -1.529091652| 1.159360566| 2.329349415|
| C       | -2.009691134| 1.990879305| 1.278156102|
| C       | -0.898056562| 2.776087993| 0.804808539|
| C       | 0.235891828 | 2.531761836| 1.682545824|
| C       | -0.140564162| 1.529229946| 2.596257554|
| C       | -0.968901729 | 3.891211963| -0.189494918|
| C       | -0.004649193 | 3.774444669| -1.367660707|
| C       | 0.958172528  | 5.996775698| -1.683418324|
| C       | 1.574448610  | 3.181627033| 1.589838151|
| C       | -3.406610758 | 2.066082758| 0.775733726|
| C       | 0.714479851  | 0.913115294| 3.644747788|
| C       | -2.288719249 | 0.150783053| 3.116794239|
| O       | 1.664138450  | 5.945408891| -0.68651437|
| N       | 1.132904630  | 0.493736355| -0.674158236|
| C       | -0.618605503 | 0.750687326| -3.051331804|
| Rh      | -0.394524213 | 0.656059508| 0.538063561|
| H       | -0.348457496 | 2.998117761| -2.066370748|
| H       | 0.991676763  | 3.541491768| -1.019318080|
| H       | -0.745019539 | 4.830623158| 0.351036379|
| H       | -1.999275679 | 3.997430701| -0.568355283|
| H       | -0.427277083 | 5.179610100| -2.925153359|
| H       | -2.519457824 | 0.527445740| 4.128350211|
| H       | -1.702524423 | -0.776346830| 3.235738800|
| H       | -3.241796377 | -0.112421700| 2.634085948|
| H       | -3.937029599 | 2.908296167| 1.251973083|
| H       | -3.976893095 | 1.153164885| 1.004259324|
| H       | -3.450791637 | 2.229502596| -0.312598468|
| H       | 0.447877278  | 1.289512336| 4.647434514|
| H       | 1.780845118  | 1.125213286| 3.474596064|
| H       | 0.587584112  | -0.181885884| 3.667846712|
| H       | 1.988527776  | 3.375912562| 2.591378321|
| H       | 1.532984208  | 4.138229378| 1.045938883|
| H       | 2.294346037  | 2.535305626| 1.056077576|
| C       | 1.378199046  | -0.195042394| -1.790509828|
| O       | 2.089193503  | -1.155726314| -2.039659726|
| C       | 0.706042009  | 0.589407868| -2.903803517|
| H       | -0.920314506 | 1.271850617| -3.97219741|
| C       | 1.703228116  | 1.144423944| -3.871182871|
| H       | 2.349649915  | 1.888696439| -3.370730595|
| H       | 2.367186674  | 0.352057622| -4.253252353|
| H       | 1.205839765  | 1.638065959| -4.719836210|
| O       | 2.273623870  | -0.602044754| 0.584252934|
| C       | 1.488343412  | -1.393575403| 1.158751195|
| O       | 0.240579552  | -1.227559544| 1.246401459|
| C       | 2.070835895  | -2.681765429| 1.744669989|
| C       | 1.092344705  | -3.328917496| 2.714678438|
Nitrene Intermediate
Electronic Energy: -1763.615138347
Free Energy Correction: 0.584182061

H  0.144618085  -3.582173852  2.214390032
H  1.532759652  -4.25492559  3.122732029
H  0.860247741  -2.659376409  3.560868849
C  2.299279651  -3.598884513  0.539006803
H  1.349333587  -3.92625413  0.011020232
H  2.992326564  -3.16944261  -0.181574008
H  2.718008697  -4.56302854  0.875743898
C  3.392514219  -2.38450918  2.443826137
H  3.823532235  -3.319074953  2.840864731
H  4.119388473  -1.933578265  1.751229269
H  3.250403285  -1.671204698  3.291041695
C  -1.786362793  0.413406211  -2.184718876
H  -2.51947556  -0.109994135  -2.837349284
C  -1.676734171  -0.347683553  -0.879276913
H  -2.625492091  -0.199379335  -0.336554131
C  -1.44630348  -1.811939921  -0.965132760
C  -0.793434556  -2.44649999  -2.027730744
C  -1.926876281  -2.643831283  0.066483830
C  -0.585889312  -3.828279301  -2.055281484
C  -1.740526423  -4.013799422  0.05401244
C  -1.045129503  -4.620710713  -1.002796545
H  -0.418893524  -1.858046640  -2.868911966
H  -2.451013486  -2.184070886  0.912267972
H  -0.054816888  -4.26588288  -2.904195066
H  -2.111263367  -4.647131907  0.866317799
O  -0.86442376  -5.959507418  -0.913672576
C  -0.666887747  -6.593719687  -1.880316072
H  -0.505548603  -6.521220486  -2.891760969
H  0.952553078  -6.16856516  -1.908532828
H  -0.000019296  -7.653556272  -1.601711392
H  -2.282085592  1.385171021  -1.980880983
H  0.934670362  6.885152815  -2.357675865

Nitrene Intermediate
Electronic Energy: -1763.615138347
Free Energy Correction: 0.584182061

N  30.783796096  -12.08795903  -25.112017135
C  28.85366941  -13.92667044  -19.635341240
C  28.599325967  -13.914571132  -21.034949203
C  29.460917508  -12.918727946  -21.639724109
C  30.188143869  -12.263945378  -20.595197725
C  29.84494475  -12.909306099  -19.367578222
C  29.44329776  -12.505967767  -23.075944142
C  30.736468851  -12.780052203  -23.844695011
C  31.144633074  -10.794628597  -25.191779901
C  31.14877307  -11.137509535  -20.736206363
C  27.554977277  -14.68955162  -21.753727034
C  30.316702043  -12.526564368  -18.013973803
C  28.196669575  -14.751432957  -18.584951260
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| O    | 31.471908429 | -10.103825907 | -24.239714638 |
| N    | 32.319070675 | -14.489830260 | -21.651546314 |
| C    | 31.805906320 | -16.654777715 | -23.498684142 |
| Rh   | 30.743220178 | -14.499000590 | -20.676423483 |
| H    | 30.859867988 | -13.859417068 | -24.024799148 |
| H    | 31.56884402 | -15.46485359 | -19.015527642 |
| H    | 29.250654607 | -11.417957227 | -23.107354015 |
| H    | 28.596131612 | -12.982038497 | -23.596863991 |
| H    | 31.605893947 | -12.470423699 | -23.241715703 |
| H    | 29.250654607 | -11.417957227 | -23.107354015 |
| H    | 28.596131612 | -12.982038497 | -23.596863991 |
| H    | 30.497343367 | -12.565132978 | -25.961646324 |
| H    | 27.547756949 | -14.132336543 | -19.742145883 |
| H    | 28.948424734 | -15.22910474 | -17.932458071 |
| H    | 27.56884402 | -15.46485359 | -19.015527642 |
| H    | 26.68475239 | -14.039516634 | -21.956333390 |
| H    | 27.18384575 | -15.54309632 | -21.16256154 |
| H    | 27.904377369 | -15.072158171 | -22.725639305 |
| H    | 29.577454382 | -11.857395655 | -17.538946479 |
| H    | 31.286772835 | -12.013679273 | -18.049354361 |
| H    | 30.420868364 | -13.407944672 | -17.361860359 |
| H    | 30.829822207 | -10.280624100 | -20.119354510 |
| H    | 31.238027289 | -10.792555455 | -21.777831076 |
| H    | 32.149272509 | -11.437133532 | -20.382611051 |
| C    | 33.239937604 | -15.449539166 | -21.811630604 |
| O    | 34.235229331 | -16.738660111 | -21.130328620 |
| C    | 32.990368978 | -16.132304004 | -23.131558301 |
| H    | 31.784143570 | -17.115307194 | -24.496876458 |
| C    | 34.197181063 | -16.170048388 | -24.014310481 |
| H    | 34.534699636 | -15.149046980 | -24.264955263 |
| H    | 35.037260755 | -16.657647301 | -23.493499949 |
| H    | 33.993658127 | -16.707357033 | -24.952548496 |
| O    | 33.090020672 | -13.658207081 | -18.863465834 |
| C    | 32.638308755 | -14.733324656 | -18.484906737 |
| O    | 31.658794639 | -15.376121213 | -19.027856768 |
| C    | 33.263583833 | -15.467375145 | -17.283386642 |
| C    | 32.209615318 | -16.203269336 | -16.465602544 |
| H    | 31.685250438 | -16.955732978 | -17.073838500 |
| H    | 32.687159207 | -16.715134879 | -15.611389522 |
| H    | 31.452833509 | -15.507925458 | -16.059551020 |
| C    | 34.256669187 | -16.472366112 | -17.868665164 |
| H    | 33.734641893 | -17.210730233 | -18.499677538 |
| H    | 35.004365781 | -15.965502482 | -18.501041662 |
| H    | 34.780653688 | -17.00851160 | -17.056920305 |
| C    | 33.993899999 | -14.463632431 | -16.402170666 |
| H    | 34.464289171 | -14.980105179 | -15.547771905 |
| H    | 34.777457434 | -13.933602153 | -16.964889973 |
| H    | 33.299839822 | -13.704238565 | -16.000578428 |
| C    | 30.474489708 | -16.701952318 | -22.819404341 |
| H    | 30.019178549 | -17.677230523 | -23.091912690 |
| C    | 30.253615651 | -16.544177769 | -21.331497554 |
| H    | 29.169039660 | -16.474132564 | -21.172478986 |
C  30.779686452  -17.568820315  -20.414516894
C  31.990461089  -18.252136695  -20.591128230
C  30.010913828  -17.911680588  -19.284346948
C  32.432005361  -19.211185434  -19.681280713
C  30.430082491  -18.863648377  -18.375266010
C  31.663714104  -19.507743832  -18.552161388
H  32.621582547  -18.035588544  -21.456000342
H  29.055029164  -17.401731472  -19.120789860
H  33.389154678  -20.703264994  -19.85908227
H  29.830578274  -19.11741702  -17.49593574
O  32.027499553  -21.382358471  -18.530534743
C  33.319934886  -20.935238903  -17.640661696
H  33.462531240  -21.572542670  -18.530534743
H  34.094379799  -20.146748199  -17.640661696
H  33.44184985  -21.55408584  -16.741802112
H  29.826948668  -15.974339394  -23.353164455
H  31.122022392  -10.406182252  -26.236751423

Reductive Elimination TS
Electronic Energy:  -1763.607729221
Free Energy Correction:  0.583462198

N  -0.922325572  5.291752437  -1.441366653
C  -0.543939535  0.844393436  2.717864455
C  -1.368582146  1.787518248  2.021303542
C  -0.516552432  2.741713385  1.361135236
C   0.843196760  2.383603435  1.655557411
C   0.820155042  1.203668517  2.475586377
C  -0.951838718  3.988615135  0.658547436
C  -0.751645328  3.98070551  -0.854859247
C   0.070819905  6.198426131  -1.434593972
C   2.069746428  3.089333094  1.202514531
C  -2.853509041  1.847762409  2.036836419
C   1.991645521  0.515915492  3.075113902
C  -0.964839048  0.240657814  3.645354891
O   1.181791742  6.012243297  -0.963171472
N  -0.049619428  0.974964306  -1.321813234
C  -2.01143822  -0.292108230  -2.994796112
Rh  -0.094479749  0.743995574  0.523216928
H  -1.444590802  3.274210192  -1.336453678
H   0.260159542  3.617096243  -1.095702252
H  -0.373775858  4.832031162  1.077921594
H  -2.009530664  4.201514899  0.887920291
H  -1.820066725  5.559893654  -1.833451929
H  -0.693587777  0.019961126  4.684491780
H  -0.462612842  -1.194660780  3.411138225
H  -2.051618157  -0.411491278  3.625130197
H  -3.193410967  2.604296856  2.765055864
H  -3.309126833  0.889965512  2.331661136
H  -3.263040596  2.137284531  1.055139899
### Intermediate V

**Electronic Energy:** \(-1763.722758437\)

**Free Energy Correction:** \(0.587438583\)

| Element | X Coordinate | Y Coordinate | Z Coordinate |
|---------|--------------|--------------|--------------|
| H       | -2.732462624 | 1.164374402  | -1.593043104 |
| H       | -0.222556987 | 7.159346372  | -1.919283429 |

| Element | X Coordinate | Y Coordinate | Z Coordinate |
|---------|--------------|--------------|--------------|
| N       | -1.338726275 | 5.075912518  | -1.479672001 |
| C       | -0.090452254 | 1.022015586  | 2.821024657  |
| C       | -1.048034358 | 1.900316148  | 2.201479217  |
| C       | -0.328414819 | 2.915129056  | 1.482909268  |
| C       | 1.082852304  | 2.662690402  | 1.672895386  |
| C       | 1.23504314   | 1.515261710  | 2.511000959  |
| C       | -0.916973303 | 4.075991251  | 0.746281253  |
| C       | -1.041761309 | 3.857499055  | -0.761115047 |
| C       | -0.371821228 | 5.963341193  | -1.773542382 |
| C       | 2.191525373  | 3.422160364  | 1.039525069  |
| C       | -2.525884751 | 1.786279792  | 2.272358111  |
| C       | 2.504554081  | 0.944741887  | 3.024694891  |
| C       | -0.369767222 | -0.171663341 | 3.660961558  |
| O       | 0.807044438  | 5.829164560  | -1.485524859 |
| N       | -1.144351382 | 0.402222508  | -0.848847537 |
| C       | -1.569562139 | -0.496622768 | -3.461628319 |
| Rh      | 0.178525377  | 0.973759849  | 0.712112011  |
| H       | -1.822842162 | 3.111499494  | -0.978655557 |
| H       | -0.096065078 | 3.443258625  | -1.150613645 |
| H       | -0.279185001 | 4.960403484  | 0.918477158  |
| H       | -1.905159175 | 4.322387473  | 1.170484514  |
| H       | -2.296539843 | 5.299654815  | -1.732520708 |
| H       | -0.087505321 | 0.019404285  | 4.710196605  |
| H       | 0.211155936  | -1.041331036 | 3.309627711  |
| H       | -1.434230436 | -0.447684923 | 3.638352082  |
| H       | -2.912439934 | 2.400697132  | 3.103819573  |
| H       | -2.847526118 | 0.747045891  | 2.440246817  |
| H       | -3.002276395 | 2.138993400  | 1.344283996  |
| H       | 2.696124037  | 1.316499639  | 4.046649909  |
| H       | 3.356892550  | 1.217432294  | 2.388263125  |
| H       | 2.464123850  | -0.154043967 | 3.067834156  |
| H       | 2.718763909  | 4.035849941  | 1.789545622  |
| H       | 1.829305283  | 4.091627168  | 0.242984807  |
| H       | 2.925503624  | 2.726660690  | 0.601502997  |
| C       | -0.264908954 | 0.632302213  | -1.793024415 |
| O       | 0.835890433  | 1.154577926  | -1.404787195 |
| C       | -0.529790856 | 0.318680765  | -3.212352065 |
| H       | -1.782922800 | -0.805705000 | -4.492486829 |
| C       | 0.394653242  | 0.878558738  | -4.238154120 |
| H       | 0.422611523  | 1.980878705  | -4.193280389 |
| H       | 1.428327184  | 0.537786774  | -4.058145737 |
| H       | 0.097100994  | 0.576982868  | -5.253312535 |
| O       | 2.991317658  | -0.463945544 | 0.301128206 |
Intermediate V (Acetic Acid Associated)
Electronic Energy: -1992.789857375
Free Energy Correction: 0.642163397

N  -2.798457800  -3.375284271  -1.915723327
C   1.582428960  -2.277920686   2.142972250
C   1.245802650  -3.018964767   0.971061492
C  -0.192199485  -2.983972455   0.817292440
C  -0.744240038  -2.322103424   1.976819539
C   0.339761470  -1.835363447   2.758372726
C  -1.002158089  -3.676990154  -0.226792031
C  -1.807504825  -2.714626723  -1.097313978
C  -4.047394723  -3.601810196  -1.472841901

O  0.827039406  -0.999351043   0.504744928
C  2.285568793  -2.756811546  -0.033073446
C  1.702109761  -3.598527789   1.100807235
H  0.616645340  -3.435945157   1.201706674
H  1.877311064  -4.673019540   0.915395732
H  2.172488678  -3.342257297   2.067371284
C  1.550353728  -3.058020074  -1.339598439
H  0.473042312  -2.842534618  -1.244240641
H  1.942826991  -2.437766019  -2.165383951
H  1.674977057  -4.118096223  -1.622718472
C  3.768791630  -3.052524872  -0.427939936
H  3.924016543  -4.119316897  -0.098808476
H  4.211171109  -2.449635407  -0.998808476
C  4.321243956  -2.820944370   0.735829099
C  -2.395978688  -1.065450737  -2.352007430
C  -1.957548883  -2.037368840  -2.039831204
C  -2.456886120  -0.136401399  -1.136999808
C  -3.135376681   0.709807398  -1.396537606
C  -3.047752297  -0.842551842   0.054852258
C  -2.262841797  -1.688212908   0.840576767
C  -4.400599980  -0.698596019   0.380894346
C  -2.799564132  -2.360878325   1.938237648
C  -4.950367894  -1.362437481  -1.470210124
C  -4.149764962  -2.193008524   2.265316701
C  -1.195129829  -1.796922724   0.610306349
C  -5.034515348  -0.037379218  -0.221970926
C  -2.147204321  -3.003377848   2.536209576
C  -6.004660417  -1.244045744   1.738046275
O  -4.758708190  -2.784827705   3.318110043
C  -3.981595892  -3.551383582   4.204149609
C  -3.530619470  -4.427445754   3.705163576
C  -3.173803321  -2.950338402   4.659688970
C  -4.651195289  -3.904894935   4.998855098
H  -3.420587208  -1.296593875  -2.688453952
H  -0.758716255   6.853384941  -2.323566717

Intermediate V (Acetic Acid Associated)
Electronic Energy: -1992.789857375
Free Energy Correction: 0.642163397

N  -2.798457800  -3.375284271  -1.915723327
C   1.582428960  -2.277920686   2.142972250
C   1.245802650  -3.018964767   0.971061492
C  -0.192199485  -2.983972455   0.817292440
C  -0.744240038  -2.322103424   1.976819539
C   0.339761470  -1.835363447   2.758372726
C  -1.002158089  -3.676990154  -0.226792031
C  -1.807504825  -2.714626723  -1.097313978
C  -4.047394723  -3.601810196  -1.472841901

61
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| C       | -2.168724120 | -2.333863424 | 2.382806596 |
| C       | 2.198440913  | -3.706841340 | 0.067495349 |
| C       | 0.206072069  | -1.064854074 | 4.020466592 |
| C       | 2.955610390  | -1.995574246 | 2.630187676 |
| O       | -4.471093287  | -3.279980803 | -0.373048711 |
| N       | -0.740554739  | 0.550735791  | -0.060486400 |
| C       | -2.279465864  | 0.819629988  | -2.435908800 |
| Rh      | 0.574815466   | -0.990420671 | 0.787995288 |
| H       | -1.109018152  | -2.151625570 | -1.732714906 |
| H       | -2.342028794  | -1.995033033 | -0.458807749 |
| H       | -1.698149543  | -4.368333302 | 0.284718188 |
| H       | -0.346592252  | -2.925963335 | -0.864538113 |
| H       | -2.549621546  | -3.709666820 | -2.841829506 |
| H       | 3.327182992   | -2.818588123 | 3.263871468 |
| H       | 2.987478648   | -1.069832057 | 3.222322277 |
| H       | 3.652540790   | -1.873637686 | 1.786401744 |
| H       | 2.293909543   | -4.761732771 | 0.377438727 |
| H       | 3.200312150   | -3.255431111 | 0.113734297 |
| H       | 1.848941395   | -3.679907811 | -0.973914988 |
| H       | -0.060191864  | -1.739899522 | 4.851956421 |
| H       | -0.588452203  | -0.306986335 | 3.940459377 |
| H       | 1.142601557   | -0.558929111 | 4.295148971 |
| H       | -2.324829672  | -3.248070337 | 2.986078228 |
| H       | -2.861591318  | -2.374387236 | 1.530797014 |
| H       | -2.432304493  | -1.468381475 | 3.003320592 |
| C       | -2.097592799  | 0.383934501  | -0.023887952 |
| O       | -2.682312549  | 0.073838432  | 1.017085083 |
| C       | -2.901064986  | 0.560384965  | -1.274186385 |
| H       | -2.866327949  | 0.872069604  | -3.362261306 |
| C       | -4.373122494  | 0.355716514  | -1.143185138 |
| H       | -4.597148311  | -0.652141871 | -0.752024293 |
| H       | -4.811229441  | 1.066977783  | -0.422075957 |
| H       | -4.880684204  | 0.482000037  | -2.111517858 |
| O       | -0.181313971  | 1.926231359  | 2.109281824 |
| C       | 1.103115934   | 1.748251900  | 2.192786534 |
| O       | 1.688706120   | 0.824740135  | 1.619367977 |
| C       | -0.804534390  | 0.995055804  | -2.514920556 |
| H       | -0.356614520  | 1.763117118  | -3.262736841 |
| C       | -0.191850768  | 1.358089197  | -1.163700797 |
| H       | 0.875774716   | 1.113815016  | -1.223003649 |
| C       | -0.234705599  | 2.843735609  | -0.850583735 |
| C       | -1.393886133  | 3.537348974  | -0.492637504 |
| C       | 0.965855647   | 3.567400529  | -0.868007675 |
| C       | -1.369541446  | 4.893573659  | -0.167111128 |
| C       | 1.013030335   | 4.917992585  | -0.548535328 |
| C       | -0.159105537  | 5.594703233  | -0.191459819 |
| H       | -2.356285125  | 3.017023740  | -0.447599588 |
| H       | 1.897230158   | 3.047928414  | -1.124630442 |
| H       | -2.303138947  | 5.389116554  | 0.110153987 |
Protodemetallation TS

Electronic Energy: -1992.789790150
Free Energy Correction: 0.643633594

N  -2.803874381  -3.370792561  -1.919115325
C   1.582262293  -2.287323136   2.138804969
C   1.242428996   -3.025713171   0.965719502
C  -0.195399490  -2.986624424   0.813259102
C  -0.744515897  -2.324574719   1.974241476
C   0.341337220  -1.842763749   2.756281313
C  -1.006319686  -3.676117173  -0.232372845
C  -1.813965208  -2.711646983  -1.098317496
C  -4.049311831  -3.609514853  -1.472776184
C  -2.168893974  -2.331059731   2.380756627
C   2.192166300  -3.712405815   0.058177226
C   0.210755914  -1.073479982   4.019360640
C   2.956165800  -2.008911958   2.625896496
O  -4.469362506  -3.300538378  -0.367949597
N  -0.738781000   0.559740530  -0.048421188
C  -2.273694679   0.811193224  -2.429131363
| Atom | X        | Y        | Z        |
|------|----------|----------|----------|
| Rh   | 0.577237748 | -0.995244967 | 0.787216071 |
| H    | -1.116381373 | -2.14598549 | -1.732123303 |
| H    | -2.349543323 | -1.994735717 | -0.457289585 |
| H    | -1.700565345 | -4.370733489 | 0.277125640 |
| H    | -0.350978037 | -4.28150918 | -0.873709589 |
| H    | -2.556499764 | -3.695874602 | -2.849022853 |
| H    | 3.322437447 | -2.829898753 | 3.265282431 |
| H    | 2.991538134 | -1.079583059 | 3.212174662 |
| H    | 3.654902513 | -1.895719577 | 1.782502664 |
| H    | 2.285570785 | -4.768728825 | 0.363798354 |
| H    | 3.195106699 | -3.263502742 | 0.104156070 |
| H    | 1.841060319 | -3.680725935 | -0.982641730 |
| H    | -0.059248161 | -1.748242486 | 4.849844797 |
| H    | -0.579986320 | -0.311538238 | 3.93962762 |
| H    | 1.149756239 | -0.572560042 | 4.294869168 |
| H    | -2.328601539 | -3.245404138 | 2.982800860 |
| H    | -2.862354976 | -2.368358300 | 1.529092610 |
| H    | -2.428627792 | -1.465422941 | 3.002699451 |
| C    | -0.97673380 | 0.387878786 | -0.015373304 |
| O    | -2.682021827 | 0.085946744 | 1.027154128 |
| C    | 0.550723825 | -1.268665657 |
| H    | 0.856617291 | -3.357207554 |
| C    | 0.332722623 | -1.141609589 |
| H    | -0.676457553 | -0.748669429 |
| H    | 1.041278998 | -0.423533224 |
| H    | 0.451665668 | -2.111820578 |
| O    | 1.915149168 | 2.096353105 |
| C    | 1.736836924 | 2.192045631 |
| O    | 0.815550551 | 1.618602481 |
| C    | 0.995279412 | -2.50852683 |
| H    | 1.763813710 | -3.254496686 |
| C    | 1.363575828 | -1.155140349 |
| H    | 1.118670139 | -1.211791907 |
| C    | 2.849984595 | -0.848300385 |
| C    | 3.544882700 | -0.502652065 |
| C    | 3.573214995 | -0.860994113 |
| C    | 4.902952845 | -0.184776361 |
| C    | 4.925636948 | -0.549351641 |
| C    | 5.604066490 | -0.208450104 |
| H    | 3.024266983 | -0.462254912 |
| H    | 3.052180150 | -1.10808831 |
| H    | 5.400116408 | 0.082721095 |
| H    | 5.481264097 | -0.555093889 |
| O    | 6.916376034 | 0.094034892 |
| C    | 7.636872388 | 0.472228597 |
| H    | 7.663924855 | -0.336387431 |
| H    | 7.211056538 | 1.376984967 |
| H    | 8.663521298 | 0.690425071 |
| H    | 0.051481949 | -2.873213680 |
Intermediate V (Protonated)
Electronic Energy:      -1992.805570582
Free Energy Correction:     0.646726338

N     -2.933828136     -3.099028027     -2.039603159
C      1.464894973     -2.515403617      2.105358699
C      1.079461327     -3.168547104      0.881795194
C     -0.342594194     -3.038311874      0.734189778
C     -0.847055431     -2.375344384     1.916440221
C      0.256207112     -2.032352125     2.749114148
C     -1.187694043     -3.624733399    -0.348309567
C     -1.886508550     -2.567622740     -1.198237936
C     -4.170238462     -3.329000286     -1.565496068
C     -2.271612882     -2.197094299     2.284013774
C     -1.996560312     -3.851936230     -0.059816889
C      0.152865425     -1.343026438     4.059928301
C      2.853348305     -2.373786615     2.606355575
O     -4.527495800     -3.108595808    -0.417704738
N     -0.711040924      0.763417038      0.151063939
C     -2.011314553      0.938954846     -2.334355048
Rh     0.589792262     -1.083161582      0.850142421
H     -1.131138274     -2.061150333     -1.817077821
H     -2.343620671     -1.815034830     -0.536180573
H     -1.949777325     -4.270521238      0.125459298
H     -0.574107374     -4.273568026     -0.994673459
H     -2.736494941     -3.334363075     -3.007596788
H      3.167122982     -3.281621349      3.148860317
| Element | x       | y       | z       |
|---------|---------|---------|---------|
| H       | 2.949912477 | -1.516056842 | 3.287180307  |
| H       | 3.554396394 | -2.217361746 | 1.771338861  |
| H       | 2.073240559 | -4.917908862 | 0.215655035  |
| H       | 3.009132959 | -3.423911145 | -0.020870496 |
| H       | 1.631135039 | -3.776293668 | -1.092755366 |
| H       | -0.256972049 | -2.028782034 | 4.820987889  |
| H       | -0.513508752 | -0.469435098 | 3.991513833  |
| H       | 1.132023293 | -0.992270346 | 4.416238052  |
| H       | -2.527081430 | -2.967808841 | 3.033841164  |
| H       | -2.955953630 | -2.320389953 | 1.430978326  |
| H       | -2.456732330 | -1.212506479 | 2.735306247  |
| C       | -2.106831814 | 0.623726648 | 0.081938969  |
| O       | -2.753032305 | 0.473759129 | 1.104861557  |
| C       | -2.750952966 | 0.654548686 | -1.248309794 |
| H       | -2.492514505 | 0.940922647 | -3.320377278 |
| C       | -4.217603916 | 0.382191377 | -1.270849315 |
| H       | -4.453271097 | -0.576892358 | -0.777557058 |
| H       | -4.771075665 | 1.157244108 | -0.713952137 |
| H       | -4.598443343 | 0.354649490 | -2.302122626 |
| O       | 0.150067190  | 1.704713767 | 2.622033790  |
| C       | 1.347209677  | 1.427738801 | 2.445098645  |
| O       | 1.782361386  | 0.514142148 | 1.665870874  |
| C       | -0.551657573 | 1.210740966 | -2.276267674 |
| H       | -0.278438690 | 2.004437722 | -2.993572460 |
| C       | -0.040831458 | 1.586203576 | -0.887947042 |
| H       | 1.021759459  | 1.308645629 | -0.839579160 |
| C       | -0.120319489 | 3.054900200 | -0.539277007 |
| C       | -1.312298820 | 3.783534268 | -0.527988299 |
| C       | 1.052204698  | 3.720353236 | -0.156723017 |
| C       | -1.346477731 | 5.126789184 | -0.153608889 |
| C       | 1.039422911  | 5.055351274 | 0.219745748  |
| C       | -0.164012438 | 5.772292948 | 0.226196244  |
| H       | -2.254292858 | 3.304402377 | -0.815652046 |
| H       | 1.999907937  | 3.16761322 | -0.147160364 |
| H       | -2.302693710 | 5.655027668 | -0.15964809  |
| H       | 1.956642452  | 5.571078742 | 0.519521845  |
| O       | -0.090679665 | 7.064198746 | 0.608696137  |
| C       | -1.267073055 | 7.835949341 | 0.624263780  |
| H       | -1.726517750 | 7.899611572 | -0.377935192 |
| H       | -2.012401480 | 7.429864255 | 1.331040021  |
| H       | -0.985339955 | 8.845868567 | 0.948592655  |
| H       | -0.032211548 | 0.298884047 | -2.634471542 |
| H       | -4.859169704 | -3.741006720 | -2.339664521 |
| C       | 2.418041148  | 2.188777167 | 3.187569241  |
| H       | 3.228455534  | 2.480505819 | 2.503162627  |
| H       | 1.999361047  | 3.077247838 | 3.679123195  |
| H       | 2.864162563  | 1.530402954 | 3.951444411  |
| H       | -0.502327376 | 1.141975570 | 1.103488459  |
| O       | 1.888832210  | -0.676541638 | -0.753364244 |
C 1.842126614 -1.152982626 -1.939340709
O 0.980018189 -1.916197802 -2.381841943
C 3.022728944 -0.706099342 -2.824102742
C 4.220095792 -1.566531083 -2.415981578
H 4.472956226 -1.412559813 -1.353342505
H 4.009635674 -2.639524295 -2.571542974
H 5.105344552 -1.305231593 -3.021552742
C 2.693012716 -0.938858068 -4.291397399
H 3.546255165 -0.644259819 -4.926511218
H 2.462109207 -1.997912515 -4.482993659
H 1.815777139 -0.345277867 -4.603259741
C 3.345883898 0.766948596 -2.587015003
H 3.593215309 0.956310101 -1.530719193
H 4.205061040 1.073008553 -3.209448989
H 2.494473163 1.417266652 -2.855815525

Product Dissociation TS
Electronic Energy: -1992.804144486
Free Energy Correction: 0.645880785
N -3.348126789 -2.232363579 -2.052467800
C 1.311247768 -3.131982523 1.603376069
C 0.565779336 -3.575107544 0.434284703
C -0.779672707 -3.138510832 0.587558108
C -0.886993358 -2.456090201 1.863362331
C 0.389606122 -2.468210089 2.499578429
C -1.902452845 -3.353122723 -0.373131926
C -2.105205846 -2.169901119 -1.320104576
C -4.519844264 -1.963521632 -1.447832236
C -2.124406165 -1.854631672 2.405949085
C 1.106562448 -4.33127674 -0.717780743
C 0.696785668 -1.923919424 3.845780765
C 2.762914580 -3.35461309 1.808885743
O -4.638023432 -1.677050087 -0.266524570
N -1.054051703 0.980726229 0.389720739
C -2.708241436 1.497239157 -1.783654847
Rh 0.566060014 -1.453923145 0.608722661
H -1.265782520 -2.100281605 -2.031392295
H -2.095295151 -1.233723873 -0.735356151
H -2.829613127 -3.508145223 0.202711201
H -1.729696812 -4.275058557 -0.952548541
H -3.352620016 -2.489558081 -3.034753618
H 2.971091340 -4.393088600 2.045229269
H 3.146527687 -2.716994369 2.632749233
H 3.305338863 -3.067914684 0.888476931
H 0.947874773 -5.413298215 -0.555914823
H 2.179405082 -4.145549863 -0.851148942
H 0.596889199 -4.053222711 -1.652232724
H 0.481302795 -2.681559655 4.618375471
H 0.095974492 -1.028932470 4.059175243
H  1.756833081  -1.645846186  3.939521280
H  -2.502569892  -2.480908665  3.232913735
H  -2.913678067  -1.775388302  1.640660716
H  -1.943140748  -0.843113132  2.800539706
C  -2.400874653   1.139687393  0.615382999
O  -2.872077290   1.044062365  1.743393811
C  -3.266244445   1.401235322 -0.564372275
H  -3.551571888   1.654929829 -2.656263692
C  -4.724846422   1.549532864 -0.293553350
H  -5.122614617   0.637993328  0.179460332
H  -4.913396118   2.384913834  0.401719472
H  -5.281372685   1.735472279 -1.224293471
O  0.703479254   1.053731434  2.649761912
C  1.785277285   0.836294033  2.088930674
H  1.948751033   0.050414176  1.089416205
C  -1.243521415   1.368599927 -2.017072010
H  -0.916726663  2.048656428 -2.823005743
C  -0.401108606   1.608204474 -0.771355442
H  0.545342815   1.066598188 -0.913749865
C  -0.032801267   3.047274596 -0.487881003
C  -0.939742707   4.107794172 -0.547136390
C  1.282965338   3.35688524  -0.098259473
C  -0.562638372   5.411908176 -0.224826682
C  1.676776901   4.625016038  0.229640372
C  0.752956530   5.67716867  0.172544959
H  -1.975457954   3.925794853 -0.852948656
H  2.010452858   2.514861753 -0.053488703
H  -1.305978398   6.21047933 -0.287663805
H  2.703957605   4.847981387  0.534907130
O  1.215036148   6.899862921  0.510230956
C  0.330770270   7.993134022  0.473317767
H  -0.066435131  8.163191792 -0.543051616
H  -0.518104401   7.855652499  1.166609545
H  0.900387372   8.878952791  0.783087909
H  -1.031029714   0.345929487 -2.38879368
H  -5.389648622  -2.029388595 -2.142535688
C  3.044759065   1.504959148  2.577145740
H  3.724435979   1.732964724  1.743524666
H  2.810212929   2.414924339  3.146560998
H  3.574237491   0.803919099  3.244582704
H  -0.514643625  1.026832681  1.271745166
O  1.015850923  -1.002406356 -1.370391038
C  2.187447849  -1.279671520 -1.830170851
O  3.056954775  -1.898592175 -1.222085841
C  2.436101496  -0.746069423 -3.250393519
C  2.539626467   0.777637558 -3.162155269
H  1.588908259   1.231932374 -2.838788028
H  3.322297302   1.081521678 -2.444920781
H  2.798585094   1.201826659 -4.14778371
Product (Dissociated from Catalyst with Acetate Dissociated)
Electronic Energy: -709.403313992
Free Energy Correction: 0.217013902

Intermediate with 4-Methylphenol and Acetate
Electronic Energy: -2338.934331686
Free Energy Correction: 0.753605028

N 30.575528094 -11.083172302 -24.975060610
C 29.531293876 -13.950722181 -19.647966954
| Atoms | X         | Y         | Z         |
|-------|-----------|-----------|-----------|
| C     | 28.971275725 | -13.595924793 | -20.930308156 |
| C     | 29.940815650 | -12.769212320 | -21.613038937 |
| C     | 31.101874883 | -12.692480253 | -20.775040593 |
| C     | 30.848073359 | -13.443726977 | -19.568821344 |
| C     | 29.705497774 | -12.000617098 | -22.871215512 |
| C     | 30.76509144  | -12.098418296 | -23.961225312 |
| C     | 30.960526761 | -9.810692539  | -24.769897422 |
| C     | 32.305777731 | -11.831867206 | -20.963852903 |
| C     | 27.587075400 | -13.925736727 | -21.364848788 |
| C     | 31.760235084 | -13.58722921  | -18.403170686 |
| C     | 28.819809301 | -14.637049415 | -18.544121500 |
| O     | 31.540485510 | -9.411129120  | -23.772692597 |
| Rh    | 30.703349262 | -14.81772498  | -21.390537900 |
| H     | 30.759511721 | -13.08422376  | -24.448747589 |
| H     | 31.774658759 | -11.963916566 | -23.535884684 |
| H     | 29.623445952 | -10.937070327 | -22.583950042 |
| H     | 28.724280202 | -12.272876267 | -23.298597360 |
| H     | 30.065411186 | -11.305349117 | -25.824803731 |
| H     | 28.442778784 | -13.866132672 | -17.847373767 |
| H     | 29.495909667 | -15.290714134 | -17.968936606 |
| H     | 27.973815899 | -15.24201081  | -18.895903261 |
| H     | 26.846353095 | -13.285452879 | -20.854356933 |
| H     | 27.350700624 | -14.975759586 | -21.129023979 |
| H     | 27.457732197 | -13.793166065 | -22.449071092 |
| H     | 31.526274573 | -12.837503574 | -17.628209321 |
| H     | 32.811547011 | -13.418401088 | -18.683945337 |
| H     | 31.681079053 | -14.592564054 | -17.957034267 |
| H     | 32.512010514 | -11.313732711 | -20.009825902 |
| H     | 32.145615187 | -11.068686974 | -21.741201989 |
| H     | 33.213272478 | -12.404600796 | -21.229426105 |
| H     | 30.70047083  | -9.141288653 | -25.623709884 |
| N     | 30.105793331 | -16.753332863 | -21.017854523 |
| C     | 29.955151987 | -15.495080247 | -23.185815339 |
| C     | 29.685779060 | -17.571094378 | -22.009434905 |
| O     | 29.439959820 | -18.773690473 | -21.905757470 |
| C     | 29.548791867 | -16.772557203 | -23.258555479 |
| H     | 29.895145551 | -14.836661511 | -24.065707338 |
| C     | 28.979655546 | -17.466155931 | -24.452196070 |
| H     | 27.964531209 | -17.848778055 | -24.246425965 |
| H     | 29.587175754 | -18.347656464 | -24.723201355 |
| H     | 28.928418398 | -16.797166303 | -25.324919235 |
| O     | 30.316878881 | -17.377400176 | -19.794879527 |
| C     | 29.210868949 | -17.808368812 | -19.160181803 |
| O     | 28.083883006 | -17.592856846 | -19.529285221 |
| C     | 29.587633580 | -18.640320745 | -17.943953747 |
| C     | 28.351385109 | -18.820413755 | -17.074531362 |
| H     | 27.973715161 | -17.848529698 | -16.713340245 |
| H     | 28.598928807 | -19.439685826 | -16.196759818 |
| H     | 27.537075714 | -19.311853247 | -17.629150709 |
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | 30.702264869 | -17.978464274 | -17.136920599 |
| H       | 30.398492276  | -16.983325181  | -16.766688378  |
| H       | 31.619391572  | -17.862505491  | -17.733903201  |
| H       | 30.938021099  | -18.600755947  | -16.257124864  |
| C       | 30.066300066  | -19.994736249  | -18.47986613   |
| H       | 30.398492276  | -16.983325181  | -16.766688378  |
| H       | 31.619391572  | -17.862505491  | -17.733903201  |
| H       | 30.938021099  | -18.600755947  | -16.257124864  |
| C       | 30.066300066  | -19.994736249  | -18.47986613   |
| H       | 30.398492276  | -16.983325181  | -16.766688378  |
| H       | 31.619391572  | -17.862505491  | -17.733903201  |
| H       | 30.938021099  | -18.600755947  | -16.257124864  |
| C       | 30.066300066  | -19.994736249  | -18.47986613   |
| H       | 30.398492276  | -16.983325181  | -16.766688378  |
| H       | 31.619391572  | -17.862505491  | -17.733903201  |
| H       | 30.938021099  | -18.600755947  | -16.257124864  |
| C       | 30.066300066  | -19.994736249  | -18.47986613   |
| H       | 30.398492276  | -16.983325181  | -16.766688378  |
| H       | 31.619391572  | -17.862505491  | -17.733903201  |
| H       | 30.938021099  | -18.600755947  | -16.257124864  |
| C       | 30.066300066  | -19.994736249  | -18.47986613   |
| H       | 30.398492276  | -16.983325181  | -16.766688378  |
| H       | 31.619391572  | -17.862505491  | -17.733903201  |
| H       | 30.938021099  | -18.600755947  | -16.257124864  |
| C       | 30.066300066  | -19.994736249  | -18.47986613   |
| H       | 30.398492276  | -16.983325181  | -16.766688378  |
| H       | 31.619391572  | -17.862505491  | -17.733903201  |
| H       | 30.938021099  | -18.600755947  | -16.257124864  |
| C       | 30.066300066  | -19.994736249  | -18.47986613   |
| H       | 30.398492276  | -16.983325181  | -16.766688378  |
| H       | 31.619391572  | -17.862505491  | -17.733903201  |
| H       | 30.938021099  | -18.600755947  | -16.257124864  |
| C       | 30.066300066  | -19.994736249  | -18.47986613   |
| H       | 30.398492276  | -16.983325181  | -16.766688378  |
| H       | 31.619391572  | -17.862505491  | -17.733903201  |
| H       | 30.938021099  | -18.600755947  | -16.257124864  |
| C       | 30.066300066  | -19.994736249  | -18.47986613   |
| H       | 30.398492276  | -16.983325181  | -16.766688378  |
| H       | 31.619391572  | -17.862505491  | -17.733903201  |
| H       | 30.938021099  | -18.600755947  | -16.257124864  |
| C       | 30.066300066  | -19.994736249  | -18.47986613   |
| H       | 30.398492276  | -16.983325181  | -16.766688378  |
| H       | 31.619391572  | -17.862505491  | -17.733903201  |
| H       | 30.938021099  | -18.600755947  | -16.257124864  |
| C       | 30.066300066  | -19.994736249  | -18.47986613   |
Migratory Insertion TS with 4-Methylphenol and Acetate
Electronic Energy: -2338.912525491
Free Energy Correction: 0.749316321

N  1.277848121  3.110900776 -4.402585917
C  -1.711691672  1.017513472  0.534462029
C  -1.829839192  1.615414448 -0.769681374
C  -0.497072491  1.927909181 -1.240757031
C   0.427113844  1.419102059 -0.300453590
C  -0.325108921  0.813468805  0.790743400
C  -0.157714524  2.754146486 -2.437780267
C   0.733566389  2.117216662 -3.499359954
C   2.274424259  3.934223532 -4.034464720
C   1.911453305  1.527061345 -0.338612029
C  -3.094516973  2.011508964 -1.446178030
C   0.284829989  0.215088023  2.007463765
C  -2.824666676  0.707592133  1.467705638
O   2.839456737  3.908493150 -2.951561917
N   0.646529775 -1.779908941 -1.059744660
C  -0.711104197 -0.857880505 -3.066477929
Rh -0.824162607 -0.305840829 -1.001275777
H   0.178943829  1.380037699 -4.095388005
H   1.566800061  1.569198972 -3.025530591
H   0.374894538  3.642152958 -2.056139127
H  -1.079842378  3.133687891 -2.911363462
H   0.861565152  3.239540288 -5.319958786
H  -2.602905006 -0.175645825  2.087581506
H  -3.780539145  0.535443147  0.948348866
H  -2.959241429  1.561480507  2.154723064
H  -3.33816492  3.071687585 -1.245032024
H  -3.947420645  1.407087124 -1.099872316
H  -3.022224906  1.891265848 -2.540235721
H   0.430058613  0.970839893  2.802699384
H   1.273371445 -0.215516773  1.775613001
H  -0.343255167 -0.594166656  2.415557421
H   2.290943228  1.837923668  0.649744884
H   2.247501215  2.271187155 -1.078214573
H   2.379014922  0.554323032 -0.569437334
C   1.044136722 -2.312484385 -2.23391236
O   1.815635662 -3.266475802 -2.383972581
C   0.411616516 -1.562409763 -3.351133844
H  -1.193954463 -0.270598862 -3.860539120
C   1.060456868 -1.642037392 -4.689415600
H   2.091123046 -1.244275213 -4.660129295
H   1.149736228 -2.693552027 -5.015244044
H   0.494440074 -1.085852808 -5.452480592
O   1.036841223 -2.531437613  0.047934581
C    2.314538845 -2.404297850  0.435560027
O    3.091575727 -1.601517908 -0.019599284
C    2.652590342 -3.446260621  1.491440064
C    3.978700883 -3.079061206  2.141396837
H    3.915415536 -2.103751603  2.652955684
H    4.251102263 -3.841844450  2.889433230
H    4.788049553 -3.017688665  1.397286204
C    1.557066048 -3.541542347  2.550296221
H    1.437680718 -2.588448900  3.093293411
H    0.585342620 -3.807791429  2.108291306
H    1.825972261 -4.317548146  3.287711634
C    2.777036658 -4.78095805  0.749612086
H    2.917623311 -5.58230012  1.464705042
H    1.557066048 -4.317548146  2.550296221
H    3.030987901 -5.58230012  1.464705042
C    1.557066048 -3.541542347  2.550296221
H    1.437680718 -2.588448900  3.093293411
H    0.585342620 -3.807791429  2.108291306
H    1.825972261 -4.317548146  3.287711634
C    2.777036658 -4.78095805  0.749612086
H    2.917623311 -5.58230012  1.464705042
H    1.557066048 -4.317548146  2.550296221
H    3.030987901 -5.58230012  1.464705042
C    1.557066048 -3.541542347  2.550296221
H    1.437680718 -2.588448900  3.093293411
H    0.585342620 -3.807791429  2.108291306
H    1.825972261 -4.317548146  3.287711634
C    2.777036658 -4.78095805  0.749612086
H    2.917623311 -5.58230012  1.464705042
H    1.557066048 -4.317548146  2.550296221
H    3.030987901 -5.58230012  1.464705042
C    1.557066048 -3.541542347  2.550296221
H    1.437680718 -2.588448900  3.093293411
H    0.585342620 -3.807791429  2.108291306
H    1.825972261 -4.317548146  3.287711634
C    2.777036658 -4.78095805  0.749612086
H    2.917623311 -5.58230012  1.464705042
H    1.557066048 -4.317548146  2.550296221
H    3.030987901 -5.58230012  1.464705042
C    1.557066048 -3.541542347  2.550296221
H    1.437680718 -2.588448900  3.093293411
H    0.585342620 -3.807791429  2.108291306
H    1.825972261 -4.317548146  3.287711634
C    2.777036658 -4.78095805  0.749612086
H    2.917623311 -5.58230012  1.464705042
Intermediate with 4-Methylphenol, Acetate, and Methanol

Electronic Energy: -2454.652711206

Free Energy Correction: 0.799683870

N 30.446786730 -11.07027234 -24.865351030
C 29.459649847 -14.046293815 -19.581802789
C 28.89256368 -13.679720112 -20.858898128
C 29.843667458 -12.821759100 -21.528154711
C 31.003707858 -12.736661443 -20.691564473
C 30.762599879 -13.504354656 -19.492701622
C 29.594683136 -12.031043123 -22.770875040
C 30.647968104 -12.105216039 -23.872233560
C 30.891723435 -9.816568249 -24.671595998
C 32.191150888 -11.852919301 -20.879602791
C 27.509585479 -14.017676455 -21.288764576
C 31.669889442 -13.615644978 -18.319753415
C 28.764770795 -14.793992609 -18.506610262
O 31.543299557 -9.448462240 -23.707748452
Rh 30.648633818 -14.858265439 -21.33774960
H 30.638860177 -13.082024860 -24.377108882
H 31.658006982 -11.974522132 -23.453678721
H 29.508637884 -10.971378917 -22.466509617
H 28.610519870 -12.299360480 -23.194359496
H 29.878851114 -11.263274703 -25.685591513
H 28.338658044 -14.077466964 -17.780991042
H 29.462772977 -15.442576688 -17.951624656
H 27.953027230 -15.422477005 -18.896263599
H 26.769102136 -13.391249739 -20.760076348
H 27.285063558 -15.073442773 -21.065595958
H 27.369067427 -13.869307029 -22.369547532
H 31.39968419 -12.873694049 -17.548074327
H 32.717667991 -13.412050384 -18.590771932
H 31.622847513 -14.620438063 -17.867878946
H 32.395153723 -11.326005741 -19.930016838
H 32.014849335 -11.091622030 -21.655018290
H 33.107052308 -12.409564168 -21.150015690
H 30.609289723 -9.129986581 -25.504721582
N 30.100469757 -16.818965296 -21.010782961
C 29.915252247 -15.514395929 -23.147581500
| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| C       | 27.779682429 | -10.727068629 | -19.674438114 |
| C       | 29.734852249 | -9.360429799 | -20.038517556 |
| C       | 29.070231543 | -10.339910660 | -19.287493136 |
| O       | 29.630971131 | -10.923568500 | -18.219539136 |
| H       | 30.627666463 | -10.651486516 | -18.090700231 |
| H       | 27.648568819 | -9.249625420 | -23.723695166 |
| H       | 26.164014775 | -8.787672557 | -22.872151513 |
| H       | 26.18915581 | -10.496989820 | -21.098978335 |
| O       | 29.670933092 | -8.064040981 | -21.751587567 |
| H       | 27.268815074 | -11.491965744 | -19.077465300 |
| H       | 30.746706004 | -9.064725398 | -19.741435148 |
| O       | 32.046276889 | -10.325758038 | -17.926803140 |
| C       | 32.362114830 | -9.401385962 | -17.103440152 |
| C       | 31.197542358 | -8.723816111 | -16.395338120 |
| C       | 30.557472531 | -9.480285984 | -15.908030258 |
| H       | 31.547516979 | -8.001550803 | -15.648265450 |
| H       | 30.56238952 | -8.207090945 | -17.132504427 |
| C       | 27.146090914 | -11.065556776 | -16.113249599 |
| H       | 26.273418780 | -11.400576541 | -15.529491124 |
| H       | 27.791723738 | -10.480231850 | -15.429608819 |
| H       | 26.772468043 | -10.371257749 | -16.893348496 |
| O       | 27.791423148 | -12.182541956 | -16.651354070 |
| H       | 28.539730814 | -11.851259080 | -17.189749808 |

Migratory Insertion TS with 4-Methylphenol, Acetate, and Methanol

Electronic Energy: -2454.632298212
Free Energy Correction: 0.799082080
| Atoms | X    | Y    | Z    |
|-------|------|------|------|
| H     | -0.110814615 | 2.306746004 | -5.900969686 |
| H     | -1.972140998  | 0.191102742  | 2.530397990  |
| H     | -3.380338164  | 0.527784120  | 1.482477368  |
| H     | -2.487155877  | 1.862864494  | 2.235759173  |
| H     | -3.371063310  | 2.891804878  | -1.051941647 |
| H     | -3.969117155  | 1.284448419  | -0.583119756 |
| H     | -3.355034132  | 1.559707518  | -2.230562275 |
| C     | 1.163154228   | 1.039205211  | 2.339271198  |
| H     | 1.642672897   | -0.345634820 | 1.325605594  |
| H     | 0.203798802   | -0.468437271 | 2.361282919  |
| H     | 2.496283586   | 1.588368686  | -0.236142495 |
| H     | 2.110305081   | 1.724390477  | -1.970222761 |
| H     | 2.292135846   | 0.113252616  | -1.199645978 |
| C     | 0.509735812   | -2.826175347 | -2.228079047 |
| O     | 1.195823837   | -3.837389847 | -2.413178234 |
| C     | -0.329748712  | -2.179296755 | -3.276813388 |
| H     | -1.964500597  | -0.861666268 | -3.586781581 |
| C     | 0.002973905   | -2.460320666 | -4.695951172 |
| C     | 1.022605526   | -2.115081791 | -4.946576010 |
| H     | 0.004646072   | -3.547842172 | -4.888495926 |
| H     | 0.706433872   | -1.977366442 | -5.385346537 |
| O     | 0.993418827   | -2.766641508 | 0.012526240  |
| C     | 2.328340386   | -2.682744786 | 0.104538780  |
| O     | 3.022388065   | -1.993365482 | -0.602126616 |
| C     | 2.844385776   | -3.619041066 | 1.187567775  |
| C     | 4.287642207   | -3.25842589 | 1.508114003  |
| H     | 4.363880147   | -2.231188307 | 1.902672446  |
| H     | 4.683660640   | -3.948303582 | 2.271712050  |
| H     | 4.927696145   | -3.324472436 | 0.614807201  |
| C     | 1.990935369   | -3.538762662 | 2.450461672  |
| H     | 2.022267635   | -2.529478724 | 2.895535191  |
| H     | 0.939576025   | -3.791637447 | 2.248621645  |
| H     | 2.379354506   | -4.248570471 | 3.201185132  |
| C     | 2.768479905   | -5.030515162 | 0.596146959  |
| C     | 3.148729862   | -5.762795845 | 1.329114393  |
| H     | 1.729342615   | -5.287093880 | 0.334309699  |
| H     | 3.376543754   | -5.108556826 | -0.32047855  |
| C     | -2.641468736  | -1.971950052 | -1.611444068 |
| H     | -2.640564048  | -2.962629895 | -2.078733891 |
| C     | -2.440089480  | -1.960592317 | -0.180413088 |
| H     | -3.100922858  | -1.288318875 | 0.383108438  |
| C     | -2.033156644  | -3.139403066 | 0.597461087  |
| C     | -1.551357294  | -4.327645861 | 0.034973812  |
| C     | -2.128733733  | -3.086281469 | 2.000222275  |
| C     | -1.149875979  | -5.404070189 | 0.823115113  |
| C     | -1.738806895  | -4.148416812 | 2.799133594  |
| C     | -1.225619702  | -5.314575053 | 2.217167173  |
| H     | -1.456887615  | -4.427370524 | -1.051372399 |
| H     | -2.519126581  | -2.177402567 | 2.472263003  |
| Atom | X-Coordinate | Y-Coordinate | Z-Coordinate |
|------|--------------|--------------|--------------|
| H    | -0.767812376 | -6.303763707 | 0.334247731  |
| H    | -1.804847704 | -4.095125374 | 3.890048006  |
| O    | -0.822604491 | -6.283975800 | 3.069857979  |
| C    | -0.188463244 | -7.422717099 | 2.545624768  |
| H    | -0.860403271 | -8.007227203 | 1.892018386  |
| H    | 0.716208750  | -7.154109752 | 1.969925537  |
| H    | 0.107452640  | -8.049648161 | 3.396826059  |
| H    | -3.478574260 | -1.358730433 | -1.967188658 |
| H    | 1.744177311  | 3.590952578  | -5.984886863 |
| H    | 0.460139133  | 6.893189030  | -2.425790172 |
| C    | 0.335718452  | 5.797330109  | -2.484823777 |
| C    | 0.145596411  | 5.176126014  | -1.132687377 |
| O    | -0.412776506 | 3.451920729  | 2.631082513  |
| H    | 0.478464597  | 3.177380520  | 3.090914437  |
| H    | 1.231255413  | 5.394082989  | -2.984535094 |
| H    | -0.513150666 | 5.610369026  | -3.141095244 |
| C    | -0.981929164 | 5.537875685  | -1.053190416 |
| H    | 2.216440894  | 4.621617021  | -0.891229990 |
| H    | -2.285507729 | 4.522017600  | 1.206048171  |
| H    | 1.904740598  | 3.593364894  | 1.355711194  |
| O    | 1.737028474  | 2.770796668  | 3.723619359  |
| O    | 3.518658381  | 3.412785729  | 4.890582973  |
| C    | 2.443391159  | 3.646014947  | 4.329268042  |
| C    | 1.889855636  | 5.061743413  | 4.317115174  |
| H    | 0.839494903  | 5.068721039  | 4.649995921  |
| H    | 2.485761317  | 5.731189952  | 4.952783539  |
| H    | 1.893400851  | 5.451053354  | 3.284212051  |
| C    | -2.463692233 | 5.636922010  | 3.956865686  |
| H    | -3.388269492 | 6.201271387  | 4.160506451  |
| H    | -1.810981788 | 5.746924380  | 4.845875067  |
| H    | -1.951464359 | 6.138959753  | 3.110362955  |
| O    | -2.789937016 | 4.306564060  | 3.678759464  |
| H    | -1.960515567 | 3.871198152  | 3.397060418  |

Intermediate with 3-Methylindole and Acetate
Electronic Energy: -2395.238646352
Free Energy Correction: 0.778708817
| Atom | X            | Y            | Z            |
|------|--------------|--------------|--------------|
| H    | 30.433450246 | -20.712804694 | -17.565092508 |
| H    | 31.040397260 | -19.908394990 | -19.050153435 |
| H    | 29.375293427 | -20.535968147 | -18.99843274 |
| C    | 32.539468154 | -15.048179566 | -22.46983653 |
| H    | 32.442614611 | -15.760367596 | -23.29519922 |
| C    | 32.877817669 | -15.493871404 | -21.90527865 |
| H    | 33.288210942 | -14.757459334 | -20.48577122 |
| C    | 33.129503529 | -16.883105434 | -20.79990138 |
| C    | 32.819798455 | -17.975295574 | -21.61935266 |
| C    | 33.692728186 | -17.151708374 | -19.54227844 |
| C    | 33.016246314 | -19.284310083 | -21.96526858 |
| C    | 33.918724516 | -18.450790657 | -19.11380826 |
| C    | 33.56049071 | -19.531814801 | -19.93015861 |
| H    | 32.385749524 | -17.811084529 | -22.61065919 |
| H    | 33.952543519 | -16.315470730 | -18.88297027 |
| H    | 32.720682613 | -20.102371555 | -21.85744075 |
| H    | 34.352425488 | -18.660394273 | -18.13134675 |
| O    | 33.765244125 | -20.765408763 | -19.41868376 |
| C    | 33.88402486 | -21.885297714 | -20.18100194 |
| H    | 33.950834982 | -21.943506794 | -21.12980678 |
| H    | 32.307696835 | -21.877026013 | -20.41211298 |
| H    | 33.614396696 | -22.775813019 | -19.58040665 |
| H    | 32.793364879 | -14.027821117 | -22.77556832 |
| O    | 32.271446167 | -10.351184171 | -18.08943626 |
| O    | 33.537647884 | -10.192637257 | -16.25963074 |
| C    | 32.441605832 | -10.220071277 | -16.84076522 |
| C    | 31.166729783 | -10.114863947 | -16.00945607 |
| H    | 30.643867408 | -11.087782723 | -16.01343615 |
| H    | 31.379302186 | -9.841566452 | -14.96545134 |
| C    | 30.472898444 | -9.379292007 | -16.44986148 |
| C    | 26.600747394 | -10.111238932 | -20.57719797 |
| C    | 27.960750541 | -9.771200562 | -20.48253685 |
| C    | 28.734421193 | -10.297299498 | -19.40972757 |
| C    | 28.173016652 | -11.134371876 | -18.43915364 |
| C    | 26.823549917 | -11.445261394 | -18.55042506 |
| C    | 26.043102402 | -10.938859507 | -19.61076176 |
| C    | 28.846058876 | -8.967790269 | -21.27924297 |
| C    | 30.076424834 | -9.051558706 | -20.66556087 |
| N    | 30.015798653 | -9.841397680 | -19.54493282 |
| H    | 25.987954220 | -9.724360868 | -21.39985321 |
| H    | 28.787551669 | -11.523104555 | -17.61873018 |
| H    | 26.358326884 | -12.098943391 | -17.80501505 |
| H    | 24.983750031 | -11.208662720 | -19.67160773 |
| H    | 31.023474111 | -8.609372700 | -20.98174188 |
| H    | 30.820796312 | -10.071146292 | -18.92407018 |
| C    | 28.515302617 | -8.273482915 | -22.55404225 |
| H    | 29.416059345 | -7.825535817 | -23.00343034 |
| H    | 28.094574735 | -8.978524852 | -23.29612583 |
| H    | 27.764503937 | -7.474441571 | -22.42298882 |
Migratory Insertion TS with 3-Methylindole and Acetate

Electronic Energy:   -2395.21602255
Free Energy Correction: 0.775897924

N   -0.133457839   2.981193380   -4.684436986
C   -0.871918764   1.088729542   1.104892322
C   -1.454623266   1.756128806   -0.028551998
C   -0.419663430   1.918185391   -1.027702332
C    0.734940810   1.237469095   -0.577582117
C    0.444126197   0.686197203   0.740642661
C   -0.521571268   2.760230138   -2.258517877
C   -0.358628285   2.049270212   -3.59708861
C    1.075404096   3.520617838   -4.914931664
C    2.051257815   1.138768774   -1.264809550
C   -2.827529663   2.323664038   -0.121234736
C    1.392378352  -0.058444550   1.615496617
C   -1.481199317   0.880520363   2.443078060
O    2.089053727   3.257962449   -4.285186843
N    0.197031980  -1.921198193   -1.257257400
C   -1.742768948  -0.778610517   -2.552268840
Rh   -0.916676884  -0.272178691   -0.641754000
H   -1.249377134   1.452058299  -3.839536530
H    0.489075777   1.344385442  -3.562126016
H    0.267650289   3.530874969  -2.182289313
H   -1.475898119   3.314268423  -2.251241585
H   -0.916935344   3.296133149  -5.248899129
H   -1.235084090  -0.113385908   2.851442236
H   -2.575729171   1.000815425   2.436709381
H   -1.046148152   1.610698986   3.148941809
H   -2.830519306   3.400274295   0.125046371
H   -3.520425906   1.821398768   0.572469380
H   -3.236137723   2.213373776  -1.140212053
H    1.664786080   0.548338039   2.498694727
H    2.307670913  -0.334201536   1.070702706
H    0.930732070  -0.987334766   1.992805353
H    2.855208564   1.493057356  -0.595221823
H    2.087682400   1.753185106  -2.177810357
H    2.285605695   0.093194269  -1.527670881
C    0.008345300  -2.464059092  -2.477437778
O    0.530889080  -3.497941082  -2.907925647
C   -0.932895903  -1.610975686  -3.252637243
H   -2.430982030  -0.118192139  -3.098223961
C   -0.902588701  -1.725275513  -4.737680722
H    0.090145372  -1.452822399  -5.139830759
H   -1.081894924  -2.768552155  -5.052621325
H   -1.657397420  -1.080015382  -5.212917243
O    0.902888381  -2.756436720  -0.391850881
C    2.229905877  -2.819467328  -0.571742462
O    2.859655143  -2.086816431  -1.294260247
14. **Protein Gel**

15. **Biochemical and technical replicate data**

Mutant R46A was used to assess quality of data via biochemical and technical replicates. To assess technical replicates the following reaction was repeated in triplicate:
NMR and HPLC data

Trial 1

| A     | B       | C  | D    | E    |
|-------|---------|----|------|------|
|       | Technical Replicate Analysis                  |    |      |      |
|       | Yield   | ee |      |      |
| 4     | 1       | 23 | 89.072 |      |
| 5     | 2       | 26 | 88.502 |      |
| 6     | 3       | 24 | 88.794 |      |

Yield Analysis

|      | Mean   |    |
|------|--------|----|
| 9    | 24.3   |

Sample Standard Deviation 1.5275252
Sample Size 3
Standard Uncertainty 0.8819171
Degrees of freedom 2

| t-value | 4.3026527 |
|---------|-----------|

95% Confidence deviation 3.794583

| 16     | Maximum | Minimum |
|--------|---------|---------|
| 17     | 28.1    | 20.5    |

ee Analysis

|      | Mean   |    |
|------|--------|----|
| 19    | 88.8   |

Sample Standard Deviation 0.2850287
Sample Size 3
Standard Uncertainty 0.1645614
Degrees of freedom 2

| t-value | 4.3026527 |
|---------|-----------|

95% Confidence deviation 0.7080504

| 26     | Maximum | Minimum |
|--------|---------|---------|
| 27     | 89.5    | 88.1    |

| 28     | 95% Confidence interval | 89.5 | 88.1 |
|--------|-------------------------|------|------|
Trial 2
Trial 3
To assess biochemical replicates the following reaction was setup in duplicate using different batches of protein:

\[
\text{MeO} \quad \text{N} \quad \text{OPiv} + \quad \text{NH} \quad \text{O} \quad \text{Me} \\
\text{R46A-mSav:Cp}* \quad \text{biotin} \quad \text{RhX}_2 (3 \text{ mol%}) \quad \text{H}_2\text{O; MeOH} \quad \text{NaOAc, NaCl, pH 7.4} \quad 25 \degree \text{C, 15.5 h}
\]
# Biochemical Replicate Analysis

|   | A      | B    | C    | D    | E    |
|---|--------|------|------|------|------|
| 1 | Trial  | Yield| ee   |      |      |
| 2 | 1      | 19.0 | 88.03|      |      |
| 3 | 2      | 21.0 | 88.07|      |      |

**Yield Analysis**

|   |   |      |      |      |      |
|---|---|------|------|------|------|
| 9 | Mean | 20.0 |      |      |      |
| 10| Sample Standard Deviation | 1.4142135 |      |      |      |
| 11| Sample Size | 2 |      |      |      |
| 12| Standard Uncertainty | 1 |      |      |      |
| 13| Degrees of freedom | 1 |      |      |      |
| 14| t-value | 12.706205 |      |      |      |
| 15| 95% Confidence deviation | 12.706205 |      |      |      |
| 16|   | Maximum | Minimum |      |      |
| 17| 95% Confidence interval | 32.7 | 7.3 |      |      |
| 18| ee Analysis |      |      |      |      |
| 19| Mean | 88.0 |      |      |      |
| 20| Sample Standard Deviation | 0.0268701 |      |      |      |
| 21| Sample Size | 2 |      |      |      |
| 22| Standard Uncertainty | 0.019 |      |      |      |
| 23| Degrees of freedom | 1 |      |      |      |
| 24| t-value | 12.706205 |      |      |      |
| 25| 95% Confidence deviation | 0.2414179 |      |      |      |
| 26|   | Maximum | Minimum |      |      |
| 27| 95% Confidence interval | 88.3 | 87.8 |      |      |

NMR and HPLC data

Trial 1
Trial 2
References

1. R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, 162, 165.
2. M. Häser, R. Ahlrichs, *J. Comput. Chem.* **1989**, 10, 104.
3. O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, 102, 346.
4. K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, 97, 119.
5. K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, 242, 652.
6. F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, 8, 1057.
7. M. Sierka, A. Hogekamp, R. Ahlrichs, *J. Chem. Phys.* **2003**, 118, 9136.
8. P. Deglmann, K. May, F. Furche, R. Ahlrichs, *Chem. Phys. Lett.* **2004**, 384, 103.
9. P. Deglmann, F. Furche, R. Ahlrichs, *Chem. Phys. Lett.* **2002**, 362, 511.
10. P. Deglmann, F. Furche, *J. Chem. Phys.* **2002**, 117, 9535.
11. M. v. Arnim, R. Ahlrichs, *J. Comp. Chem.* **1998**, 19, 1746.
12. M. v. Arnim, R. Ahlrichs, *J. Chem. Phys.* **1999**, 111, 9183.
13. R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2004**, 6, 5119.
14. Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, 120, 215.
15. F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, 7, 3297.
16. A. Klamt, G. Schüürmann, *J. Chem. Soc., Perkin Trans. 2* **1993**, 5, 799.
17. M. Sparta, D. Shirvanyants, F. Ding, N. V. Dokholyan, A. N. Alexandrova, *Biophys. J.* **2012**, 103, 767.
18. F. Ding, D. Tsao, H. Nie, N. V. Dokholyan, *Structure (Oxford, U. K.)* **2008**, 16, 1010.