

## Electronic Supporting Information

# Damage of amino acids by aliphatic peroxy radicals: A kinetic and computational study

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# 1. General Experimental Procedures

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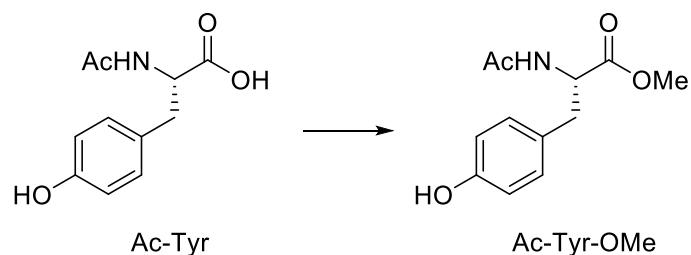
All amino acid and dipeptide derivatives were prepared as enantiomerically pure compounds. Starting materials for the synthesis were purchased from commercial suppliers and used without purification. They are *N*-acetyl-L-tyrosine (98%, AKSci, California, USA), *N*-acetyl-L-tryptophan (99%, Sigma-Aldrich, Castle Hill, Australia), L-methionine (98%, Acros Organics, Geel, Belgium), and L-proline (99.8%, Chem-Impex, Illinois, USA). Thin layer chromatography (TLC) was performed to monitor the reaction progress using aluminium plates coated with silica gel 60 F<sub>254</sub> (Merck, Hindmarsh, Australia) and visualised with UV light at 254 nm or stained with KMnO<sub>4</sub> stain followed by heating. The crude products were purified by recrystallisation from hot solvent. Solvents were removed under reduced pressure and elevated temperature using a rotary evaporator (Büchi, In Vitro Technologies, Melbourne, Australia). The purity was assessed by analytical reversed-phase HPLC on an Alltech Hypersil BDS-C18 5 µm 150 x 4.6 mm (Gradient: 100% water buffered with 0.1% TFA to 100% acetonitrile buffered with 0.1% TFA over 25 minutes, 4% min<sup>-1</sup>, flow rate: 1 mL min<sup>-1</sup>).

<sup>1</sup>H and <sup>13</sup>C spectra were recorded on an Agilent MR 400 MHz NMR spectrometer, an Agilent DD2 500 MHz NMR spectrometer or a Varian Inova 600 MHz NMR spectrometer in deuterated dimethylsulfoxide (DMSO-*d*<sub>6</sub>) at 25.0 °C. Chemical shifts are reported in ppm (δ) using the residual solvent as reference (δ = 2.50 ppm for <sup>1</sup>H NMR and 39.5 ppm for <sup>13</sup>C NMR). <sup>1</sup>H NMR data are reported as follows: chemical shift (δ), multiplicity, coupling constants (in Hz, if any) and relative integral. <sup>13</sup>C NMR data are reported as follows: chemical shift (δ), multiplicity and coupling constants (in Hz, if any). High Resolution Mass Spectrometry (HRMS) was performed by ionising the sample using Electrospray Ionization (ESI) into a Thermo Scientific Exactive Plus Orbitrap mass spectrometer (Thermo Scientific Australia, Scoresby, Australia). Parent ions are commonly denoted by [M + H]<sup>+</sup> or [M + Na]<sup>+</sup>.

Synthetic procedures and spectroscopic details are provided for all isolated intermediates and substrates in the laser flash photolysis and product studies. NMR spectra and HPLC chromatograms are provided for all substrates used in the laser flash photolysis studies. Compounds containing a tertiary amide moiety usually exist as *trans*- and *cis*-isomeric mixtures around the peptide bond. The appearance of these isomeric mixtures in the NMR spectra has been well established in previous works.<sup>1-4</sup> All compounds containing a tertiary amide moiety (i.e., Ac-Pro and Ac-Pro-OMe) show both isomers in their <sup>1</sup>H and <sup>13</sup>C NMR spectra. Only chemical shifts for the major isomer (usually *s-trans*) are assigned.

## 2. Spectroscopic details for the isolated compounds

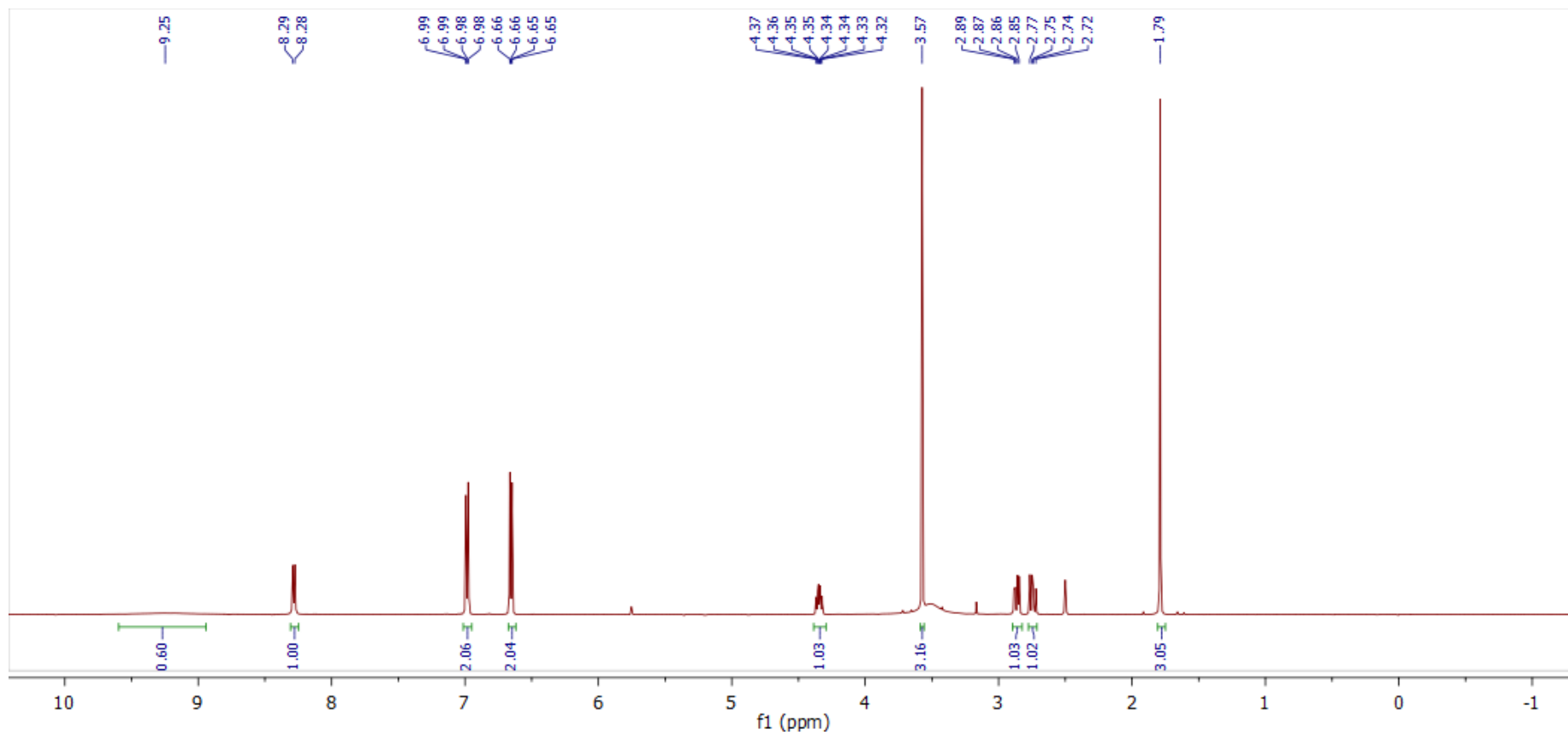
### *N*-Acetyl-L-tyrosine methyl ester (Ac-Tyr-OMe)<sup>5</sup>



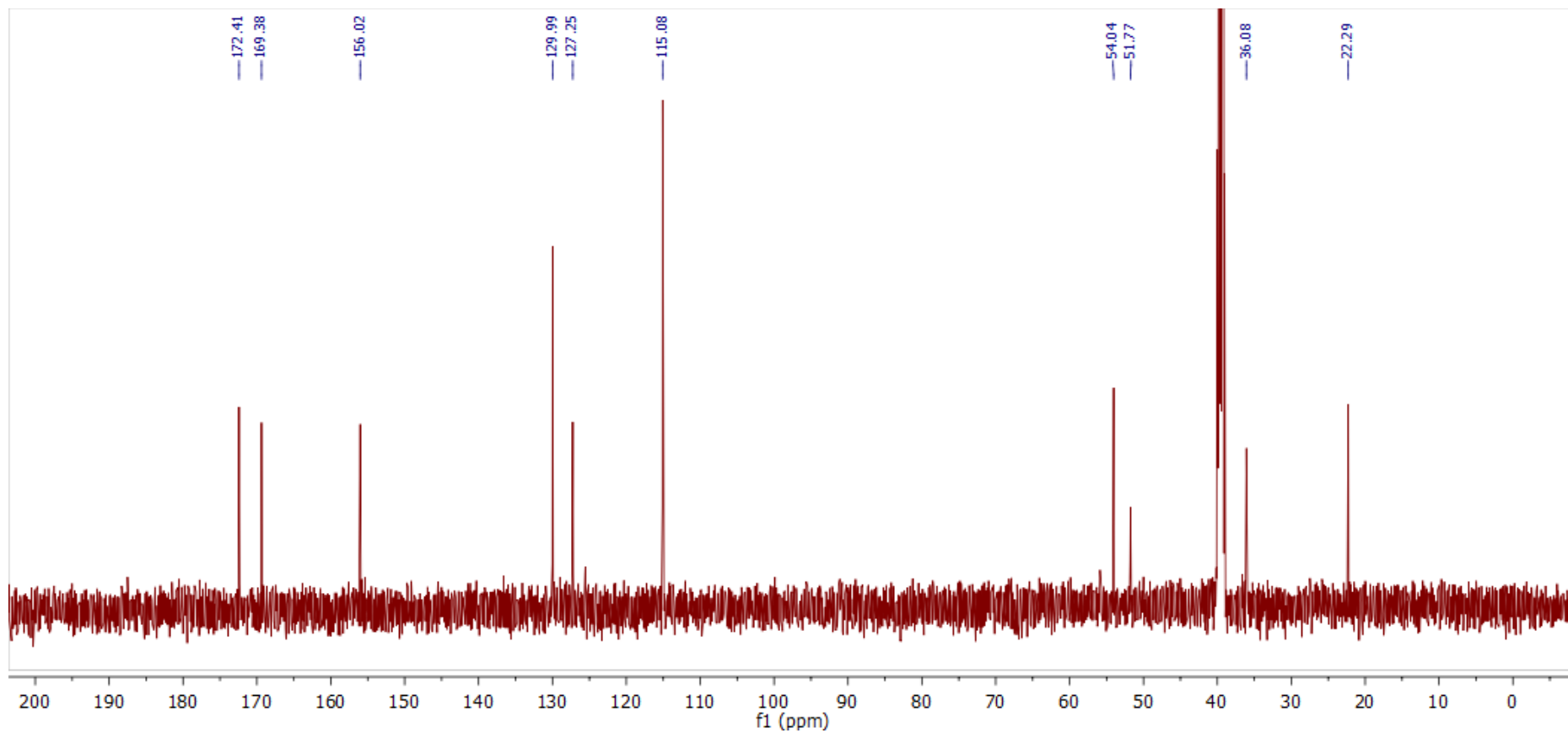
*N*-Acetyl-L-tyrosine (2.63 g, 11.8 mmol) was suspended in methanol (11 mL) at 0 °C. Thionyl chloride (1.0 mL, 13.8 mmol) was added dropwise. The resulting mixture was stirred for 4 hours. The solvent was removed under reduced pressure and the residue was suspended in water (20 mL). The resulting solid was filtered off and washed with dichloromethane to give *N*-acetyl-L-tyrosine methyl ester as a white solid (2.70 g, 96%).

<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 9.25 (s, 1H), 8.28 (d, *J* = 7.7 Hz, 1H), 7.04–6.92 (m, 2H), 6.80–6.60 (m, 2H), 4.35 (ddd, *J* = 9.1, 7.7, 5.7 Hz, 1H), 3.57 (s, 3H), 2.87 (dd, *J* = 13.8, 5.7 Hz, 1H), 2.74 (dd, *J* = 13.8, 9.1 Hz, 1H), 1.79 ppm (s, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (126 MHz, DMSO-*d*<sub>6</sub>): δ 172.4, 169.4, 156.0, 130.0, 127.3, 115.1, 54.0, 51.8, 36.1, 22.3 ppm. HRMS (ESI) *m/z* calcd. for [C<sub>12</sub>H<sub>16</sub>NO<sub>4</sub>]<sup>+</sup>: 238.1074 [M + H]<sup>+</sup>, found 238.1072; HRMS (ESI) *m/z* calcd. for [C<sub>12</sub>H<sub>15</sub>NO<sub>4</sub>Na]<sup>+</sup>: 260.0894 [M + Na]<sup>+</sup>, found 260.0891.

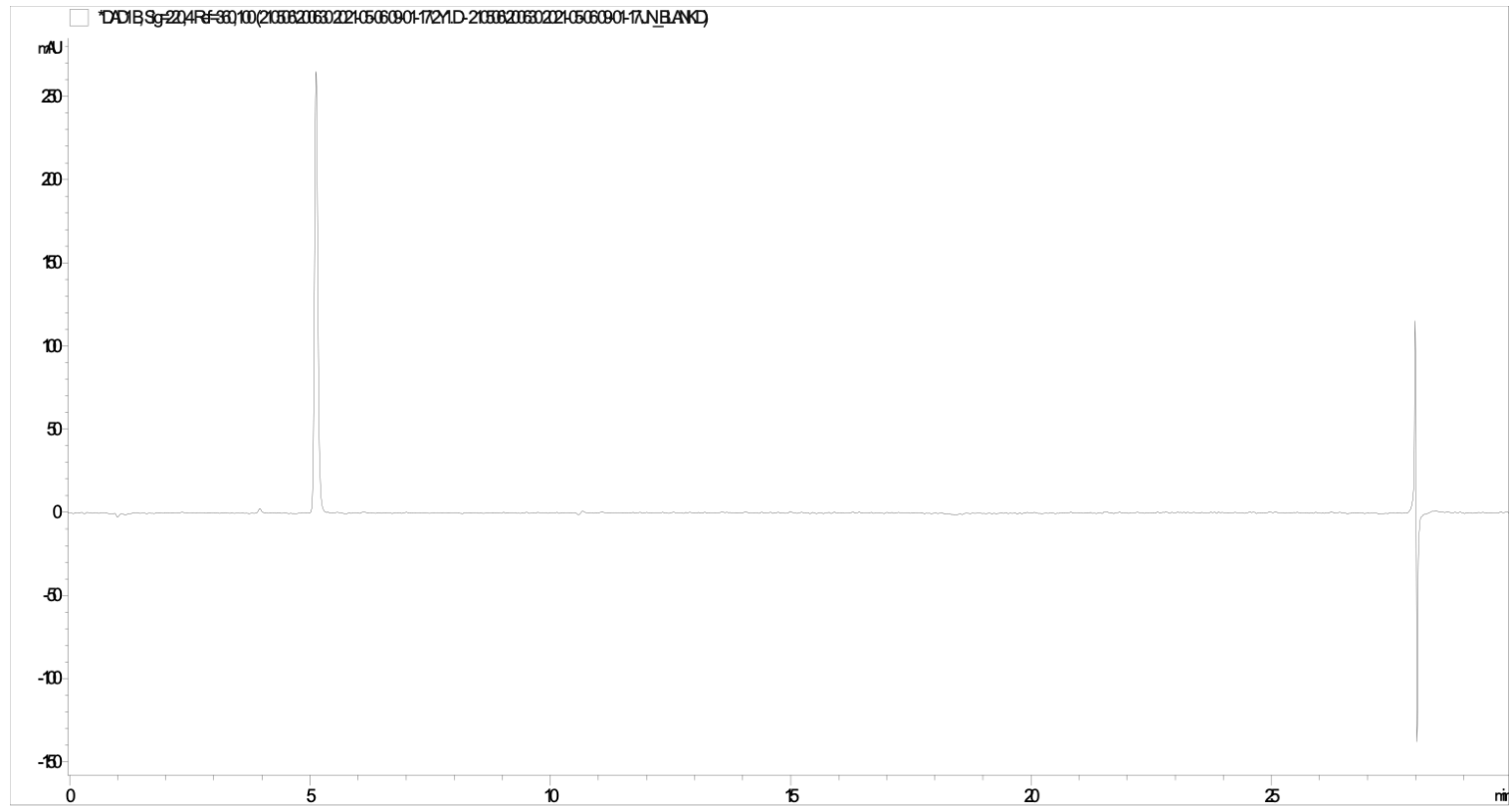
# <sup>1</sup>H NMR spectrum of Ac-Tyr-OMe



<sup>13</sup>C NMR spectrum of Ac-Tyr-OMe

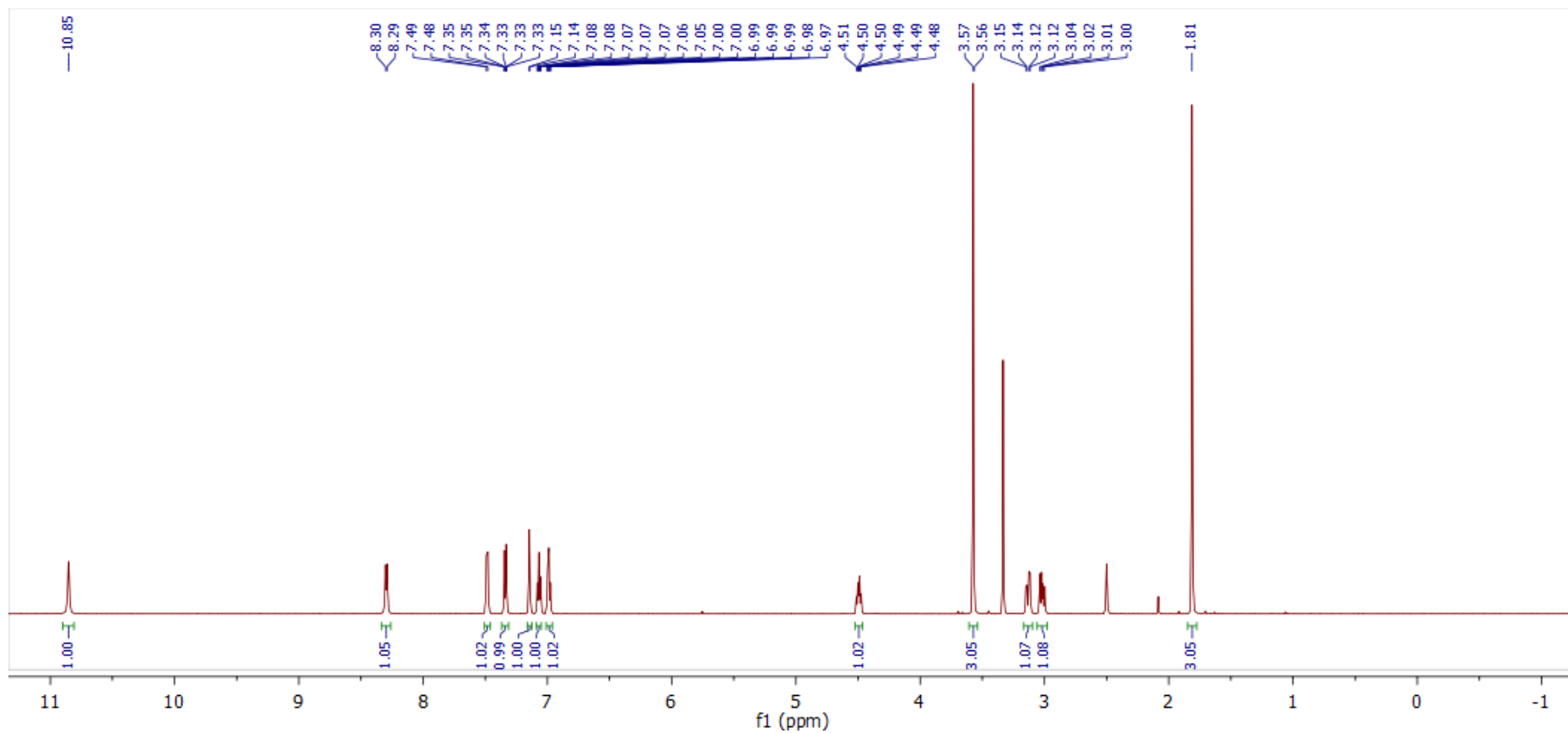


# HPLC chromatogram of Ac-Tyr-OMe



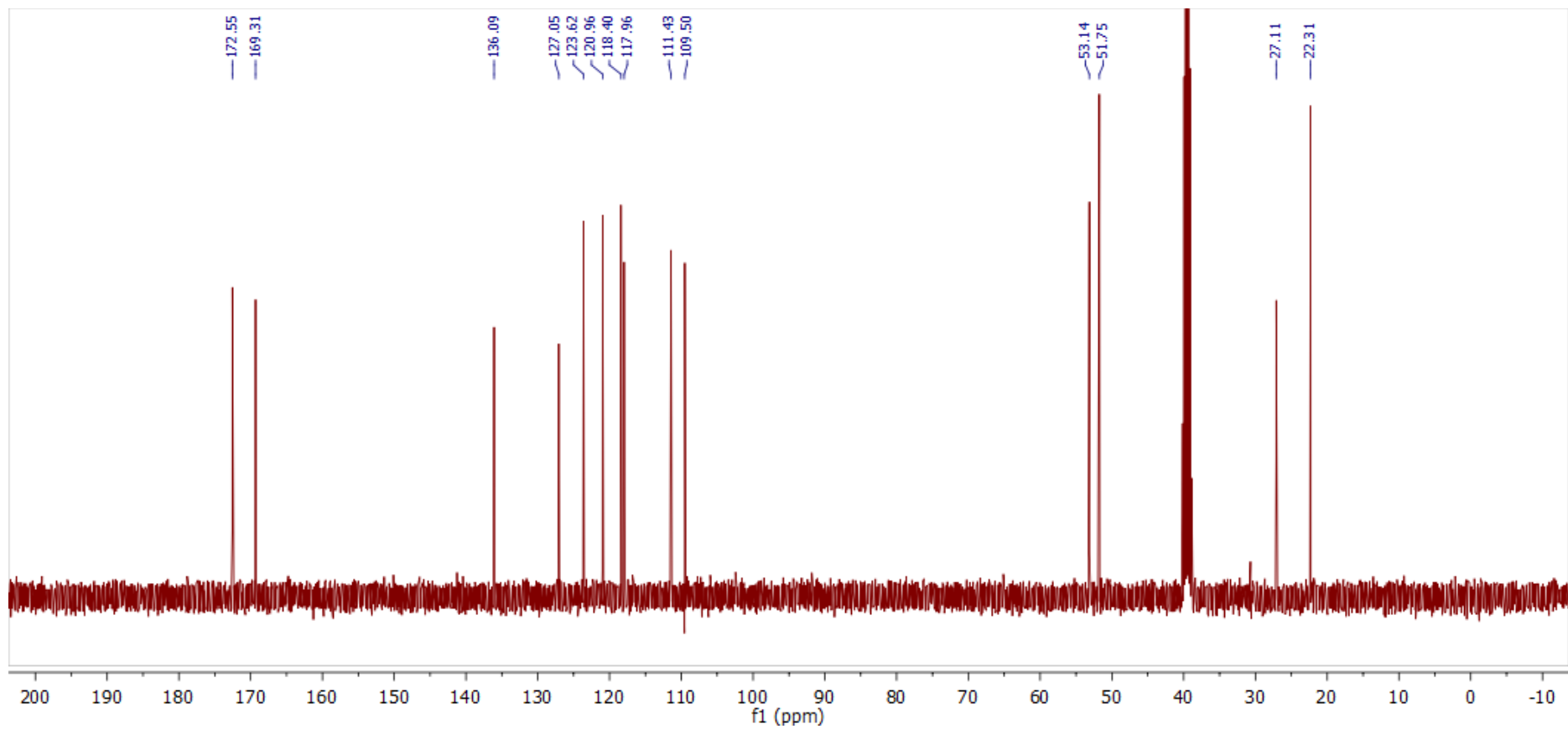


<sup>1</sup>H NMR spectrum of Ac-Trp-OMe

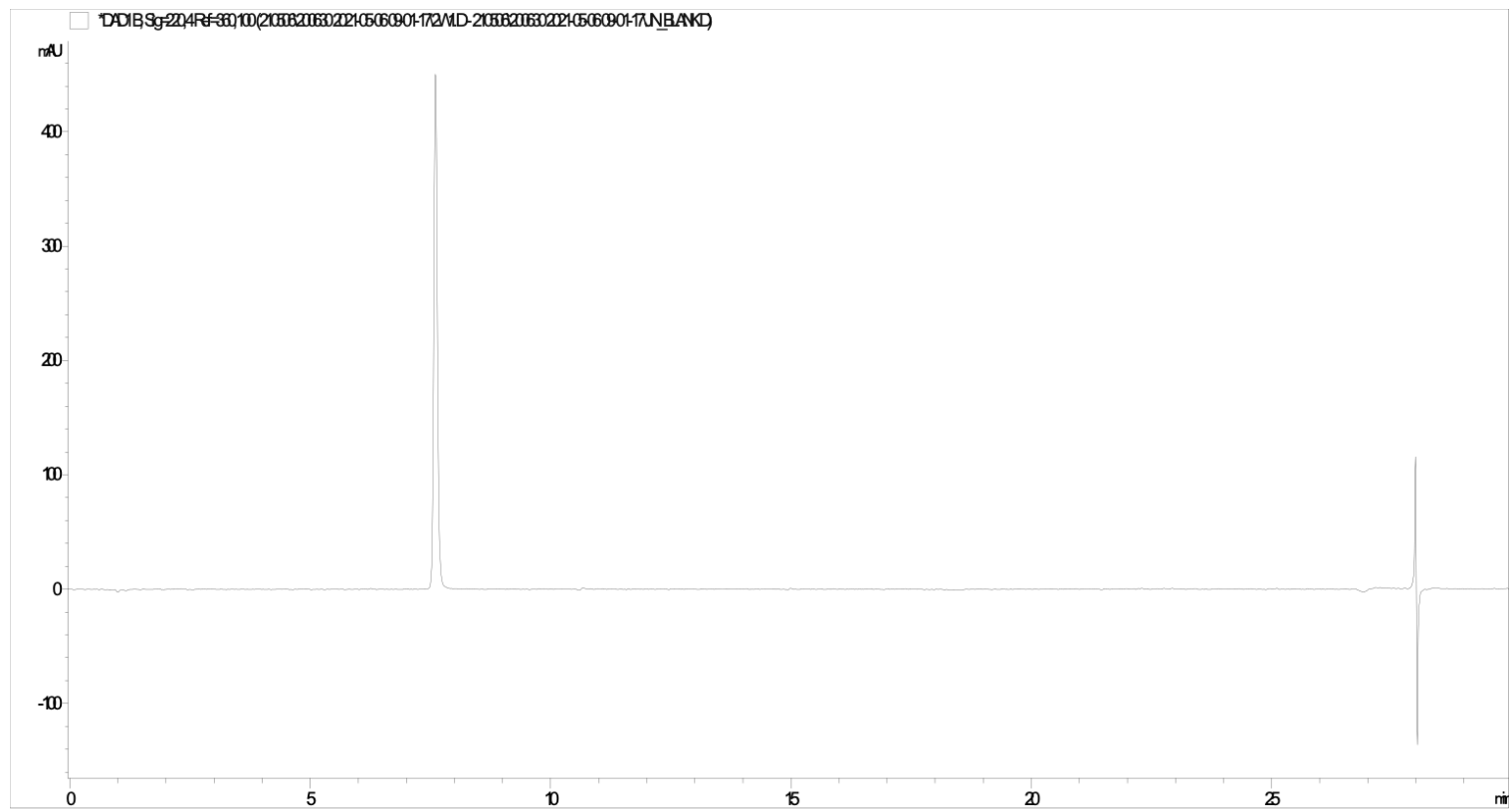




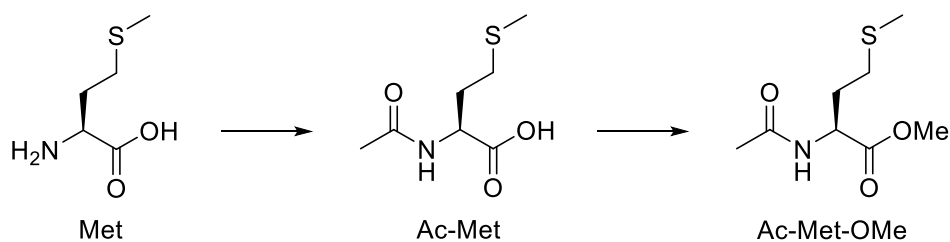
<sup>13</sup>C NMR spectrum of Ac-Trp-OMe



# HPLC chromatogram of Ac-Trp-OMe



### *N*-Acetyl-L-methionine methyl ester (Ac-Met-OMe)



#### (a) *N*-Acetyl-L-methionine (Ac-Met)<sup>6</sup>

L-Methionine (7.96 g, 53.4 mmol) was suspended in 5% aqueous sodium bicarbonate solution (150 mL) at 0 °C. Acetic anhydride (6.2 mL, 65.7 mmol) was added dropwise. The resulting mixture was stirred at room temperature for 6 hours. The reaction mixture was acidified to pH 2 with 6M hydrochloric acid solution. The solvent was removed under reduced pressure. Methanol (75 mL) was added and the solid was removed by filtration. The filtrate was concentrated under reduced pressure to give *N*-acetyl-L-methionine as a white sticky solid (10.2 g, 99%).

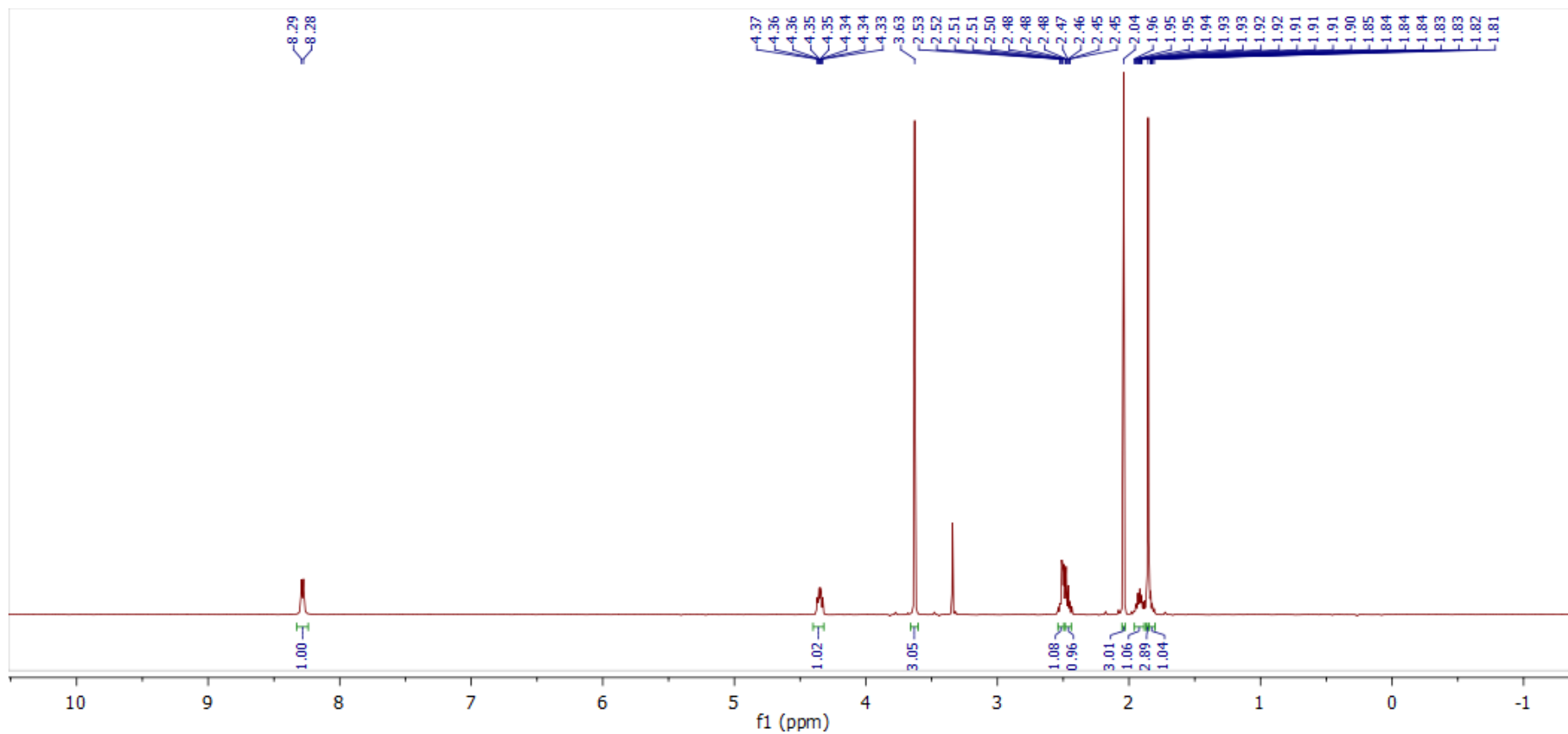
<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 7.64 (d, *J* = 7.5 Hz, 1H), 4.03 (td, *J* = 7.4, 4.9 Hz, 1H), 2.40 (dt, *J* = 9.6, 5.9 Hz, 2H), 2.00 (s, 3H), 1.93–1.85 (m, 1H), 1.82 (s, 3H), 1.80–1.74 ppm (m, 1H). <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, DMSO-*d*<sub>6</sub>): δ 173.8, 168.6, 53.0, 32.3, 29.9, 22.8, 14.7 ppm. HRMS (ESI) *m/z* calcd. for [C<sub>7</sub>H<sub>14</sub>NO<sub>3</sub>S]<sup>+</sup>: 192.0689 [M + H]<sup>+</sup>, found 192.0689, HRMS (ESI) *m/z* calcd. for [C<sub>7</sub>H<sub>13</sub>NO<sub>3</sub>SNa]<sup>+</sup>: 214.0509 [M + Na]<sup>+</sup>, found 214.0508.

#### (b) *N*-Acetyl-L-methionine methyl ester (Ac-Met-OMe)<sup>5</sup>

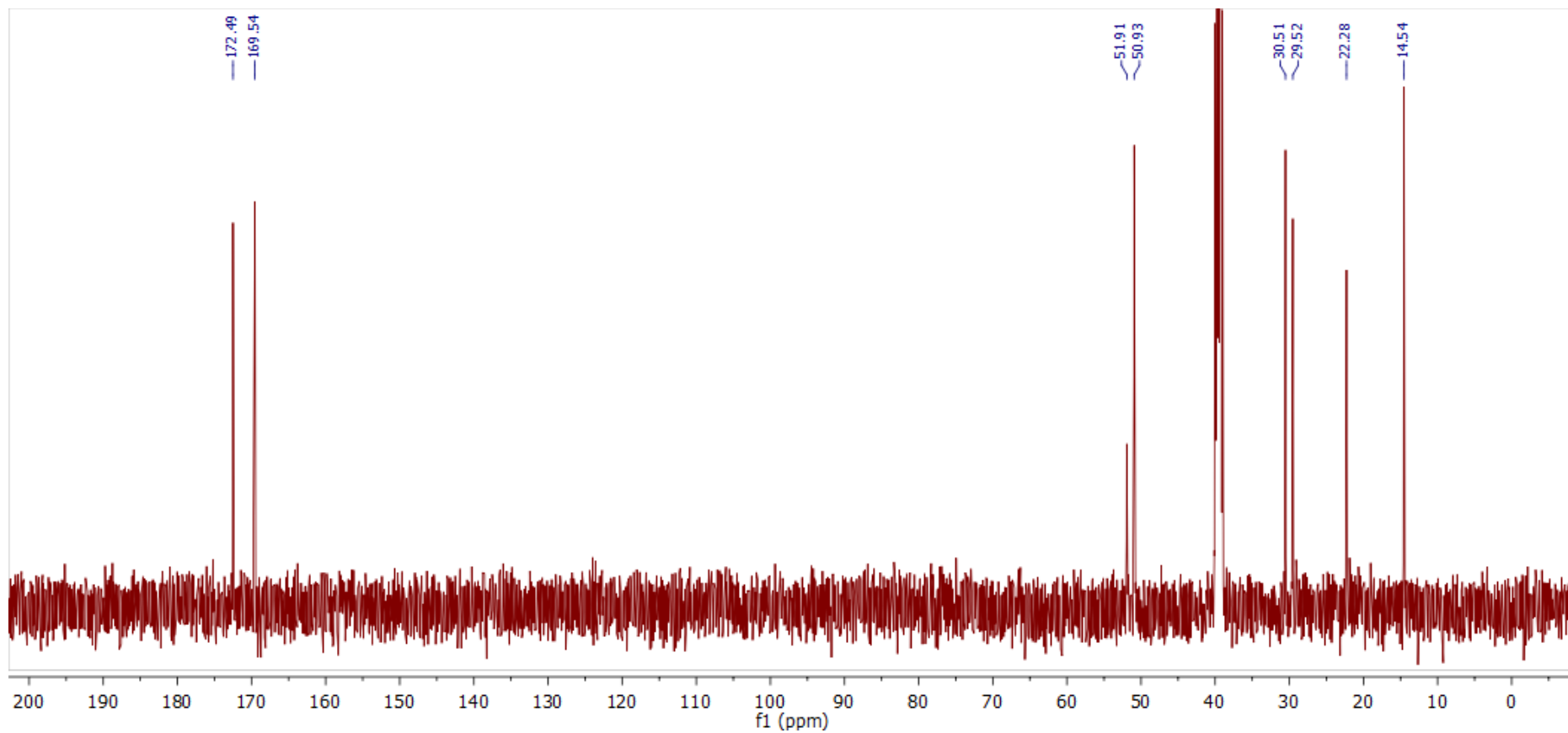
*N*-Acetyl-L-methionine (10.2 g, 53.5 mmol) was suspended in methanol (50 mL) at 0 °C. Thionyl chloride (4.4 mL, 60.6 mmol) was added dropwise. The resulting mixture was stirred for 4 hours until starting material was fully consumed as monitored using TLC (EtOAc, KMnO<sub>4</sub> stain). The solvent was removed under reduced pressure and the residue was suspended in water (30 mL). The aqueous layer was extracted with dichloromethane (3 x 40 mL). The combined organic layers were washed with 5% aqueous sodium bicarbonate (25 mL), dried over anhydrous sodium sulfate and filtered. The solvent was removed under reduced pressure to give *N*-acetyl-L-methionine methyl ester as white crystals (7.82 g, 71%).

<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 8.28 (d, *J* = 7.5 Hz, 1H), 4.35 (ddd, *J* = 9.0, 7.4, 4.9 Hz, 1H), 3.63 (s, 3H), 2.53–2.50 (m, 1H), 2.48–2.45 (m, 1H), 2.04 (s, 3H), 1.96–1.90 (m, 1H), 1.85 (s, 3H), 1.84–1.80 ppm (m, 1H). <sup>13</sup>C {<sup>1</sup>H} NMR (126 MHz, DMSO-*d*<sub>6</sub>): δ 172.5, 169.5, 51.9, 50.9, 30.5, 29.5, 22.3, 14.5 ppm. HRMS (ESI) *m/z* calcd. for [C<sub>8</sub>H<sub>16</sub>NO<sub>3</sub>S]<sup>+</sup>: 206.0846 [M + H]<sup>+</sup>, found 206.0851; HRMS (ESI) *m/z* calcd. for [C<sub>8</sub>H<sub>15</sub>NO<sub>3</sub>SNa]<sup>+</sup>: 228.0665 [M + Na]<sup>+</sup>, found 228.0669.

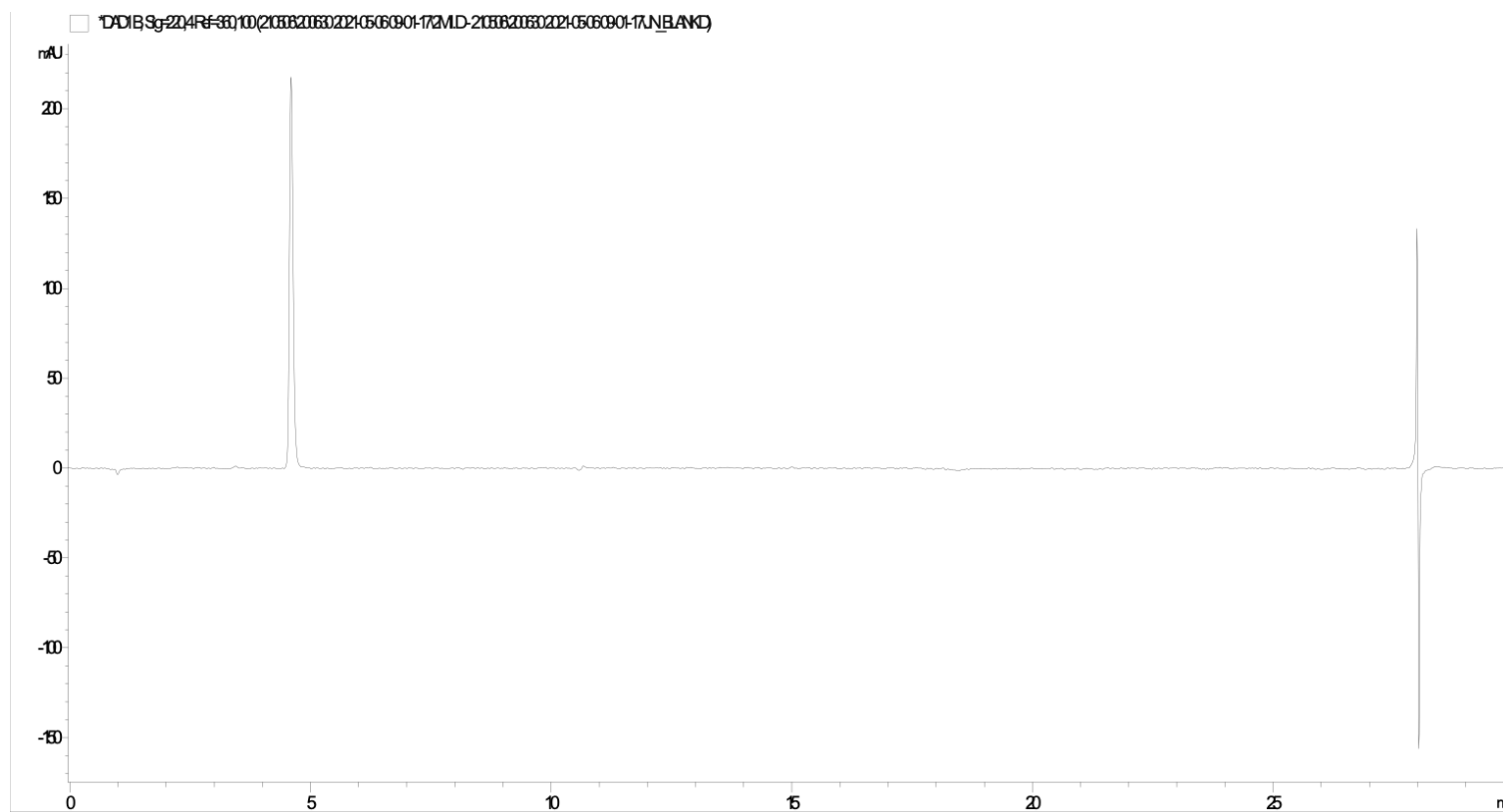
<sup>1</sup>H NMR spectrum of Ac-Met-OMe



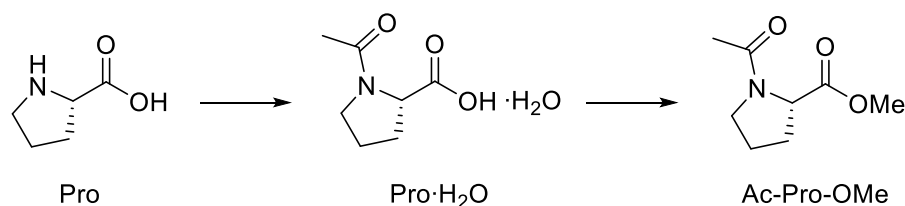
<sup>13</sup>C NMR spectrum of Ac-Met-OMe



# HPLC chromatogram of Ac-Met-OMe



### ***N*-Acetyl-L-proline methyl ester (Ac-Pro-OMe)**



#### (a) *N*-Acetyl-L-proline monohydrate (Ac-Pro·H<sub>2</sub>O)<sup>7</sup>

L-Proline (8.07 g, 70.1 mmol) was dissolved in water (8 mL). The solution was then heated to 55 °C, followed by dropwise addition of acetic anhydride (10 mL, 105 mmol). The resulting mixture was heated to 70 °C and stirred for 1 hour. Half of the solvent was then removed under reduced pressure. The solution was cooled to room temperature and the resulting solid was collected by filtration. The crude product was recrystallised from hot water and washed with cold water and ethanol (2 x 5 mL) to give *N*-acetyl-L-proline monohydrate as white shards (6.99 g, 57%).

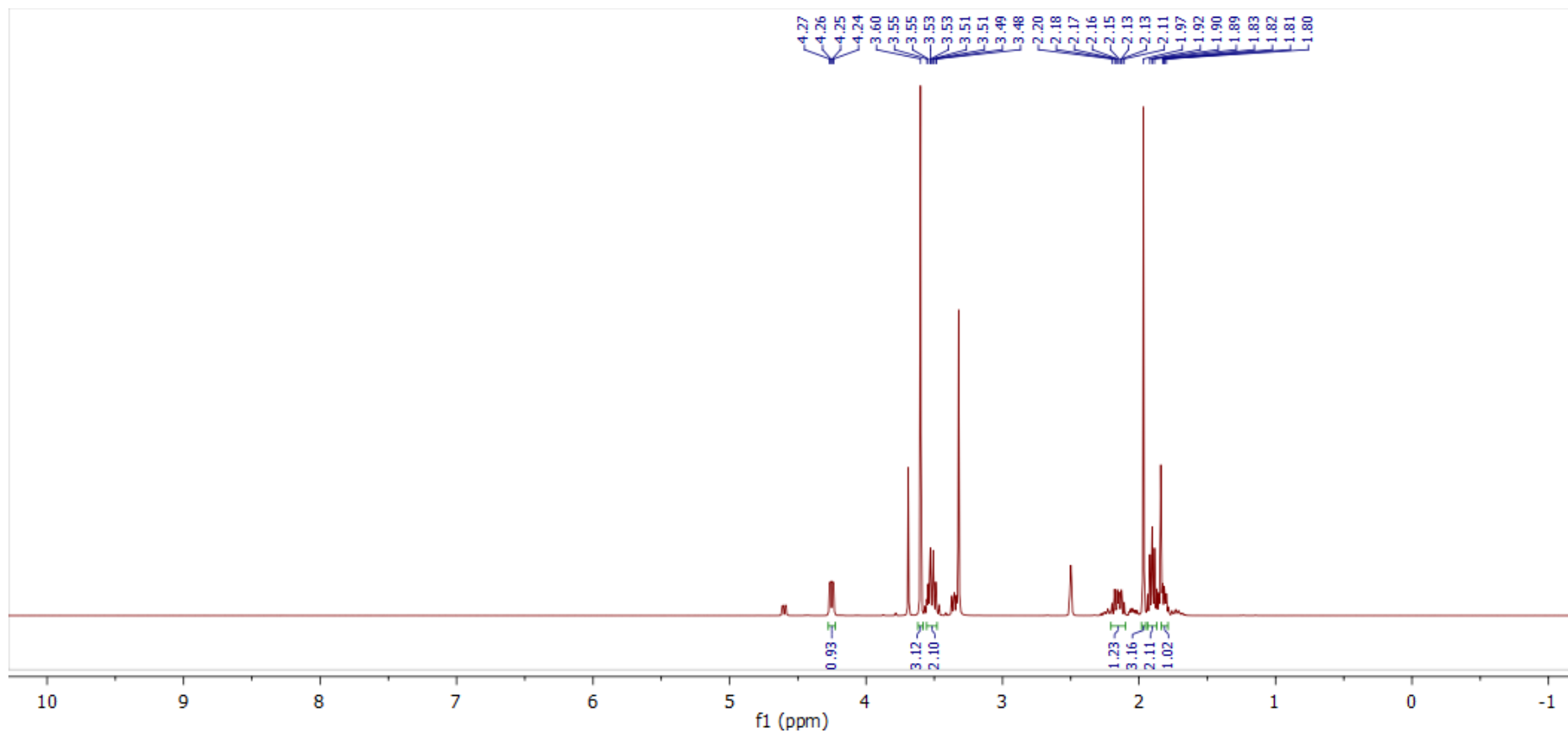
<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) major isomer: δ 12.53 (s, 1H), 4.18 (dd, *J* = 8.8, 3.7 Hz, 1H), 3.57–3.42 (m, 2H), 2.22–1.98 (m, 2H), 1.96 (s, 3H), 1.95–1.85 ppm (m, 2H). <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, DMSO-*d*<sub>6</sub>) major isomer: δ 173.5, 168.2, 58.1, 47.2, 29.1, 24.4, 22.1 ppm. HRMS (ESI) *m/z* calcd. for [C<sub>7</sub>H<sub>12</sub>NO<sub>3</sub>]<sup>+</sup>: 158.0812 [M + H]<sup>+</sup>, found 158.0813, HRMS (ESI) *m/z* calcd. for [C<sub>14</sub>H<sub>23</sub>N<sub>2</sub>O<sub>6</sub>]<sup>+</sup>: 315.1551 [2M + H]<sup>+</sup>, found 315.1550.

#### (b) *N*-Acetyl-L-proline methyl ester (Ac-Pro-OMe)<sup>5</sup>

*N*-Acetyl-L-proline monohydrate (0.99 g, 5.63 mmol) was dissolved in methanol (6 mL) at 0 °C. Thionyl chloride (0.5 mL, 6.88 mmol) was added dropwise. The resulting mixture was stirred for 4 hours until starting material was fully consumed as monitored using TLC (EtOAc, KMnO<sub>4</sub> stain). The solvent was removed under reduced pressure and the residue was suspended in water (10 mL). The product was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried over anhydrous sodium sulfate and filtered. The solvent was removed under reduced pressure to give *N*-acetyl-L-proline methyl ester as a colourless liquid (0.88 g, 91%).

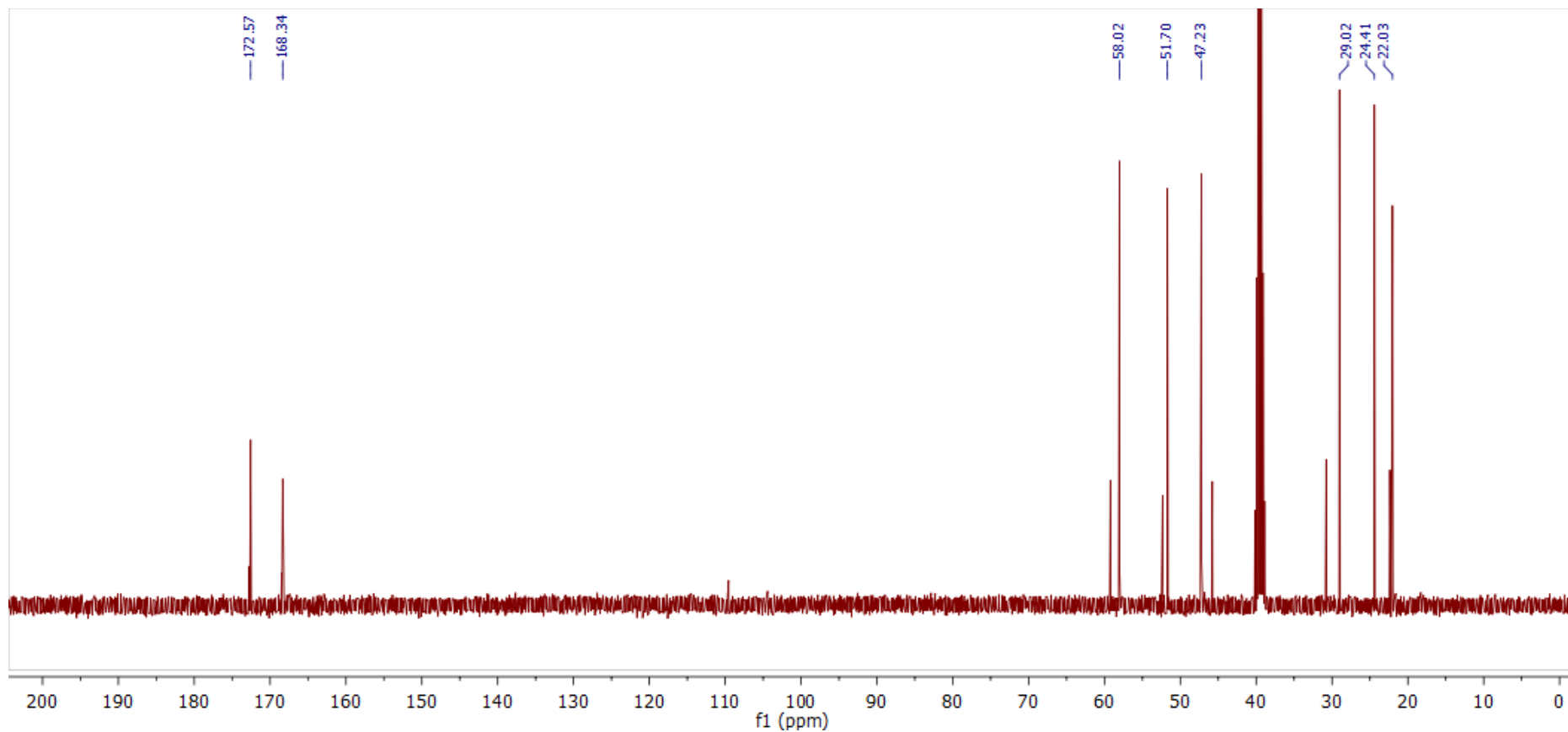
<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) major isomer: δ 4.25 (dd, *J* = 8.8, 4.2 Hz, 1H), 3.60 (s, 3H), 3.58–3.46 (m, 2H), 2.22–2.08 (m, 1H), 1.97 (s, 3H), 1.96–1.86 (m, 2H), 1.85–1.78 ppm (m, 1H). <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, DMSO-*d*<sub>6</sub>) major isomer: δ 172.6, 168.3, 58.0, 51.7, 47.2, 29.0, 24.4, 22.0 ppm. HRMS (ESI) *m/z* calcd. for [C<sub>8</sub>H<sub>14</sub>NO<sub>3</sub>]<sup>+</sup>: 172.0969 [M + H]<sup>+</sup>, found 172.0969, HRMS (ESI) *m/z* calcd. for [C<sub>8</sub>H<sub>13</sub>NO<sub>3</sub>Na]<sup>+</sup>: 194.0788 [M + Na]<sup>+</sup>, found 194.0789.

<sup>1</sup>H NMR spectrum of Ac-Pro-OMe

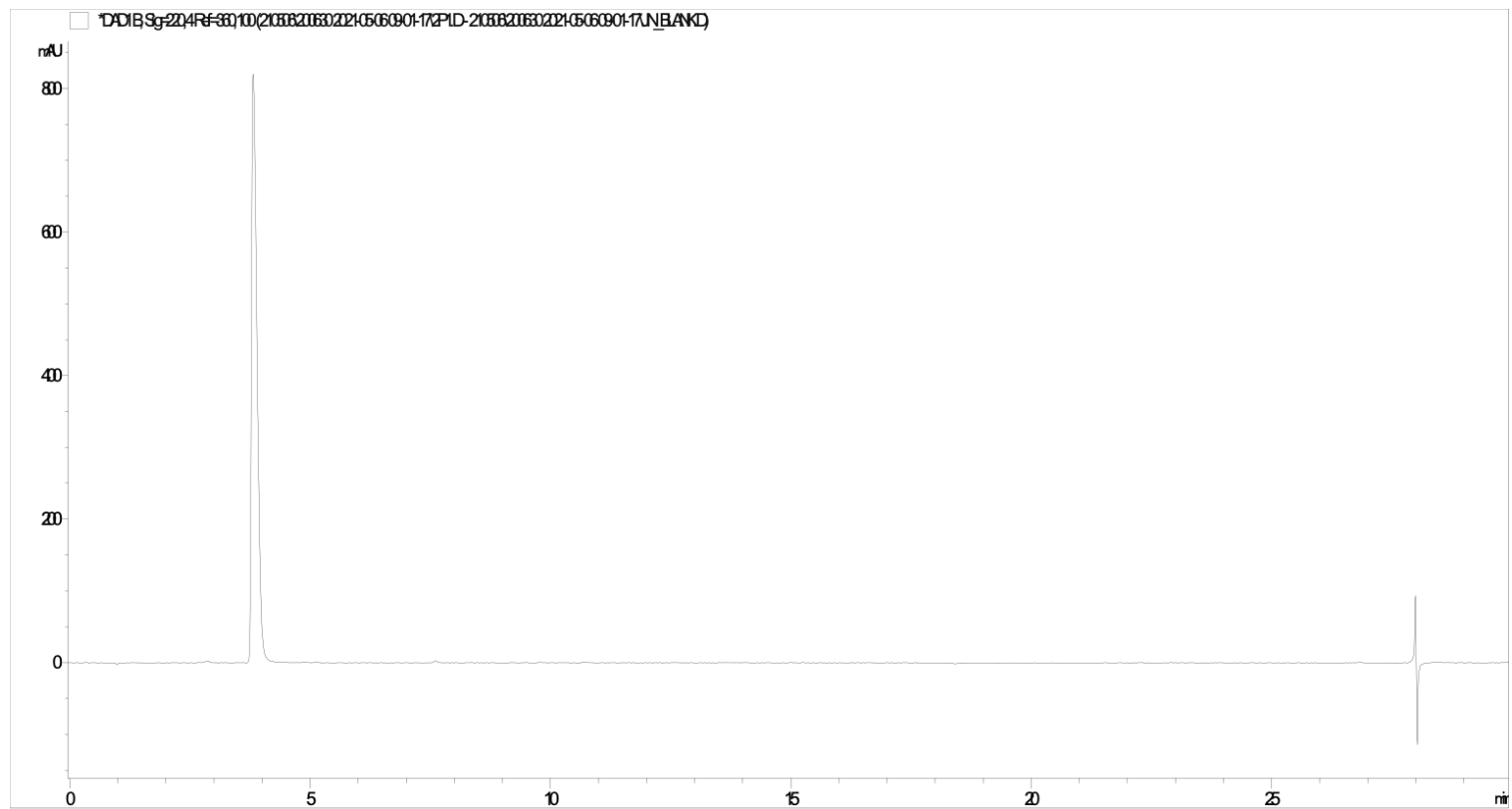




<sup>13</sup>C NMR spectrum of Ac-Pro-OMe



# HPLC chromatogram of Ac-Pro-OMe



### 3. Laser Flash Photolysis Studies

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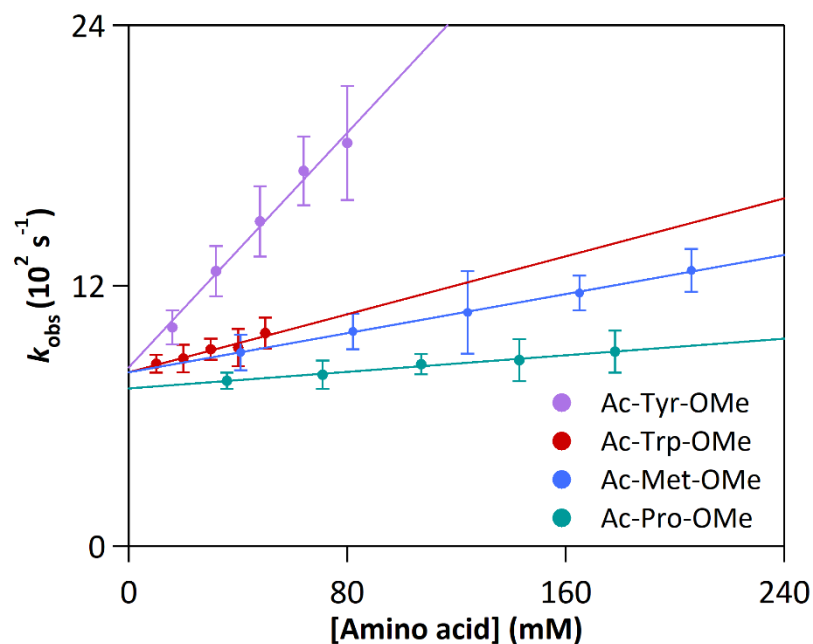
Time-dependent decay plots of TEAOO<sup>•</sup> signals at 365 nm for its reaction with each amino acid are fitted according to the exponential decay fitting available on Curve Fitting Tool on MATLAB R2021a (MathWorks, Inc.; Massachusetts, USA). The fitting used for the calculations follows the equation:  $y = ae^{-bx} + c$ ; where  $y$  is the optical density, OD (proportional to [TEAOO<sup>•</sup>]) and  $x$  is the time (unit in s). The value of  $k_{obs}$  corresponds to the value of  $b$ .

Second-order rate coefficients,  $k$ , for the reactions of TEAOO<sup>•</sup> with amino acids were obtained from the slopes of  $k_{obs}$  vs [amino acid], plotted using Igor Pro 6.03 (WaveMetrics, Inc.; Oregon, USA). The plot is shown in Figure S1 below. The y-intercept is most likely due to the reaction of TEAOO<sup>•</sup> with acetonitrile.

*Error determination:* each result is reported as the average of three different runs. For example, if three different runs produced this set of data:  $(x_1 \pm \sigma_1)$ ,  $(x_2 \pm \sigma_2)$  and  $(x_3 \pm \sigma_3)$ , then the result would be taken as  $\frac{x_1 + x_2 + x_3}{3}$  and  $\sigma$  is the overall standard deviation obtained following the statistical equation below:

$$\sigma = \sqrt{\frac{\sigma_1^2 + \sigma_2^2 + \sigma_3^2}{3} + \frac{2}{9}(x_1^2 + x_2^2 + x_3^2 - x_1 \cdot x_2 - x_2 \cdot x_3 - x_3 \cdot x_1)}, \text{ where}$$

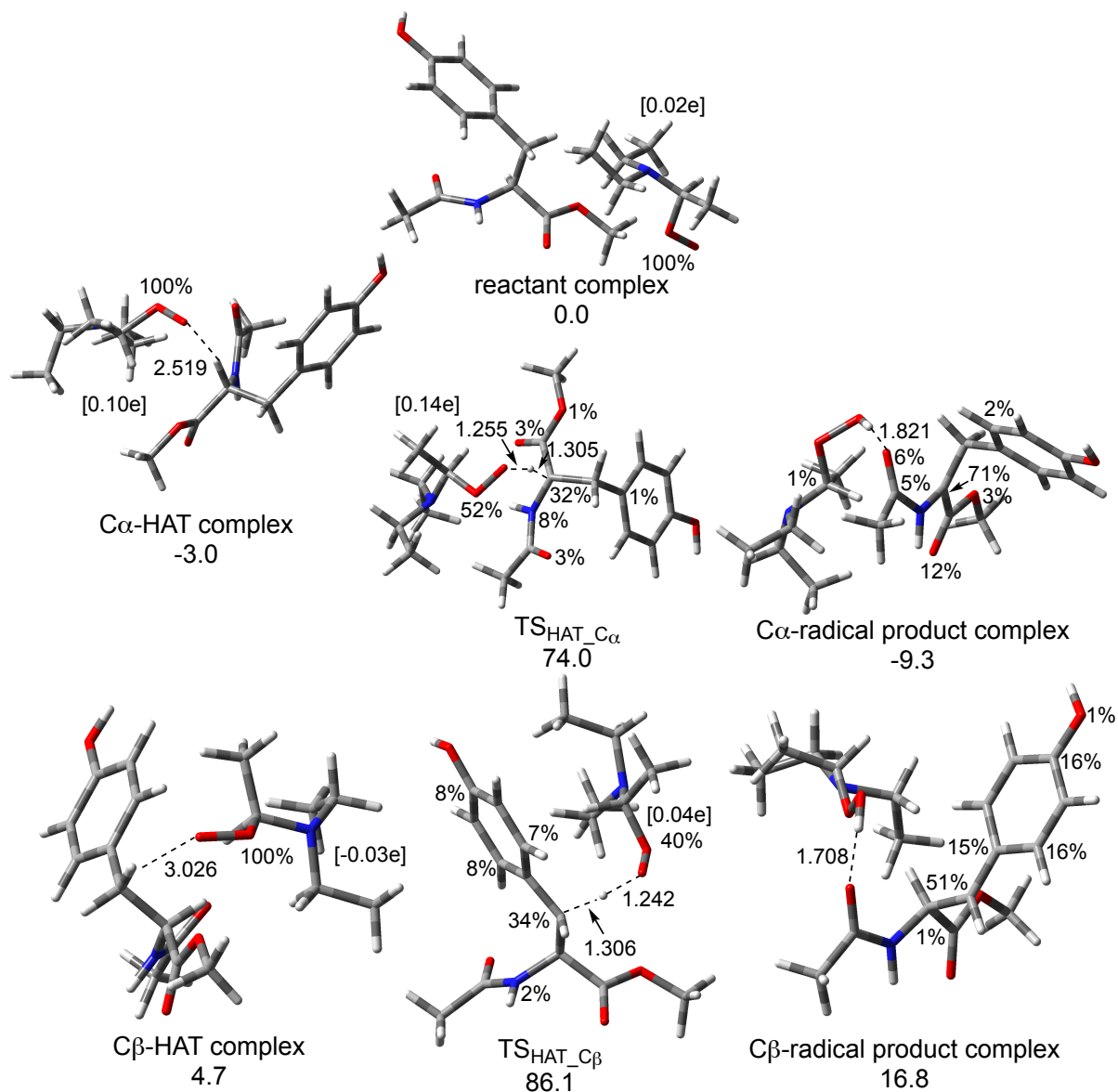
$x_1, x_2, x_3$  are the result from each respective run and  $\sigma_1, \sigma_2, \sigma_3$  are the standard deviation of each result. Overall errors are given as  $2\sigma$  statistical uncertainties.



**Figure S1.** Plot of pseudo-first-order rate coefficient ( $k_{obs}$ ) versus [amino acid] (see Table 1). From the linear regression analysis: Ac-Tyr-OMe: intercept =  $824 \text{ s}^{-1}$ ,  $k = 1.35 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ,  $R^2 = 0.9884$ ; Ac-Trp-OMe: intercept =  $802 \text{ s}^{-1}$ ,  $k = 3.33 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ,  $R^2 = 0.9472$ ; Ac-Met-OMe: intercept =  $801 \text{ s}^{-1}$ ,  $k = 2.25 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ,  $R^2 = 0.9991$ ; Ac-Pro-OMe: intercept =  $727 \text{ s}^{-1}$ ,  $k = 9.49 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ ,  $R^2 = 0.9865$ .

It should be noted that the comparatively large error for the rate coefficient for the reaction involving Ac-Trp-OMe is due to the low solubility of the amino acid in the solvent, which further limited the range of the excess concentration that could be used in these measurements.

## 4. Computational Studies



**Figure S2.** M062X/cc-pVTZ optimized geometries for the stationary points in the reaction of TEA-OO• (*R* configuration) with Ac-Tyr-OMe (using the cpcm solvation model for acetonitrile). Distances in Å, spin densities in % and Mulliken charges on the TEA-OO moiety in square brackets. Free energies in kJ mol<sup>-1</sup> relative to the reactant association complex (figure continues next page).

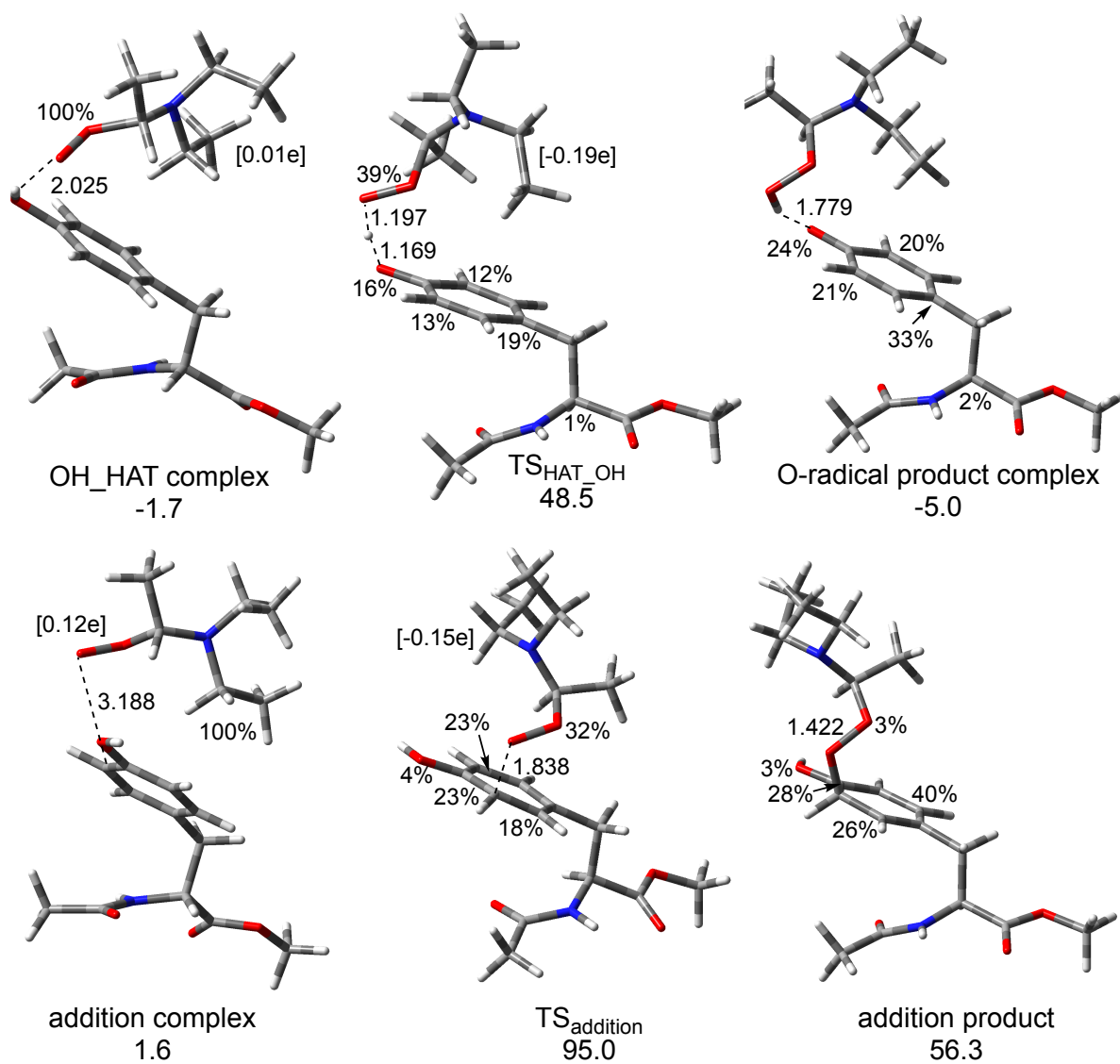
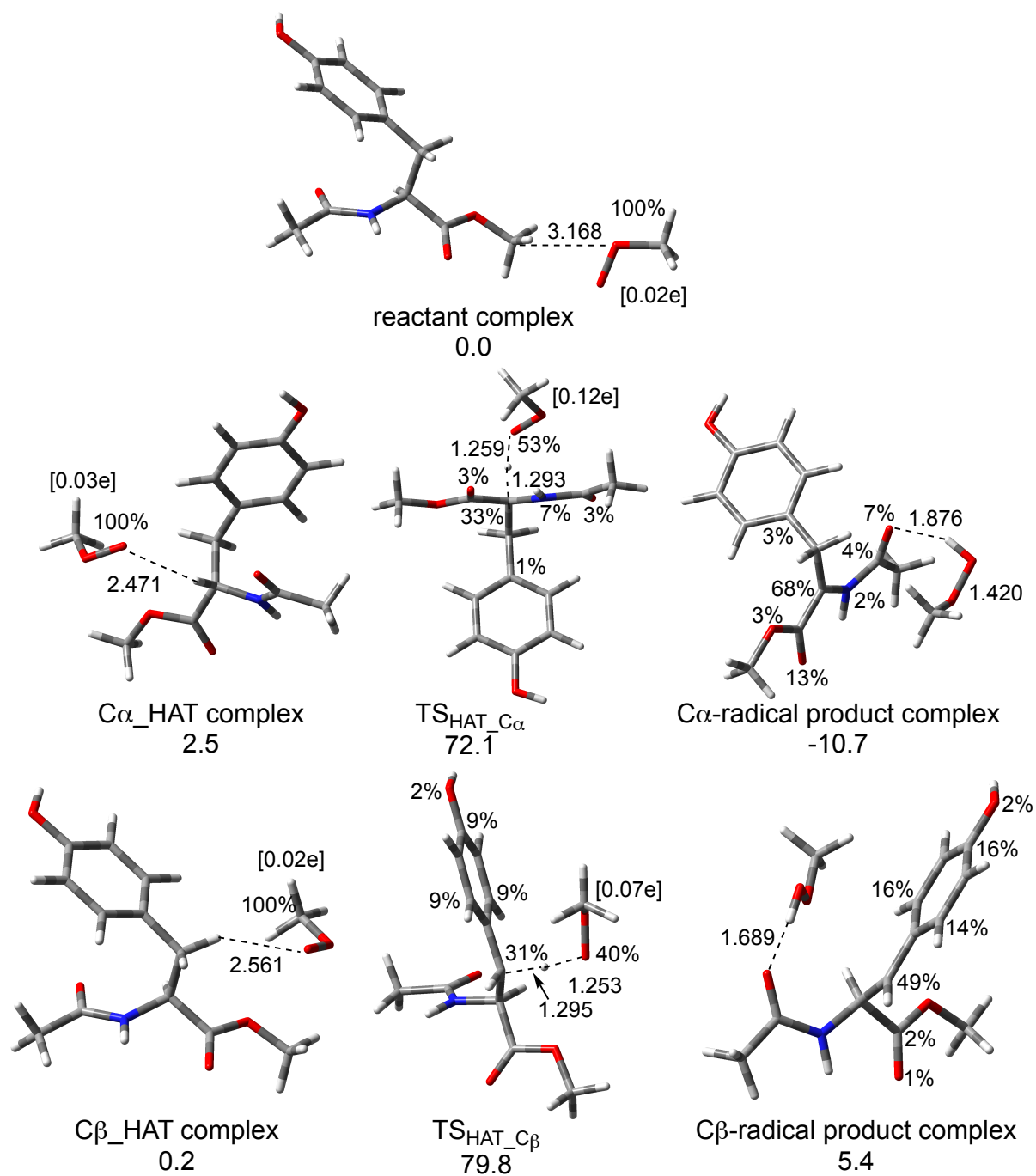


Figure S2. Continued.



**Figure S3.** M062X/cc-pVTZ optimized geometries for the stationary points in the reaction of MeOO• with Ac-Tyr-OMe (using the cpcm solvation model for acetonitrile). Distances in Å, spin densities in % and Mulliken charges on the MeOO moiety in square brackets. Free energies in  $\text{kJ mol}^{-1}$  relative to the reactant association complex (Figure continues next page).

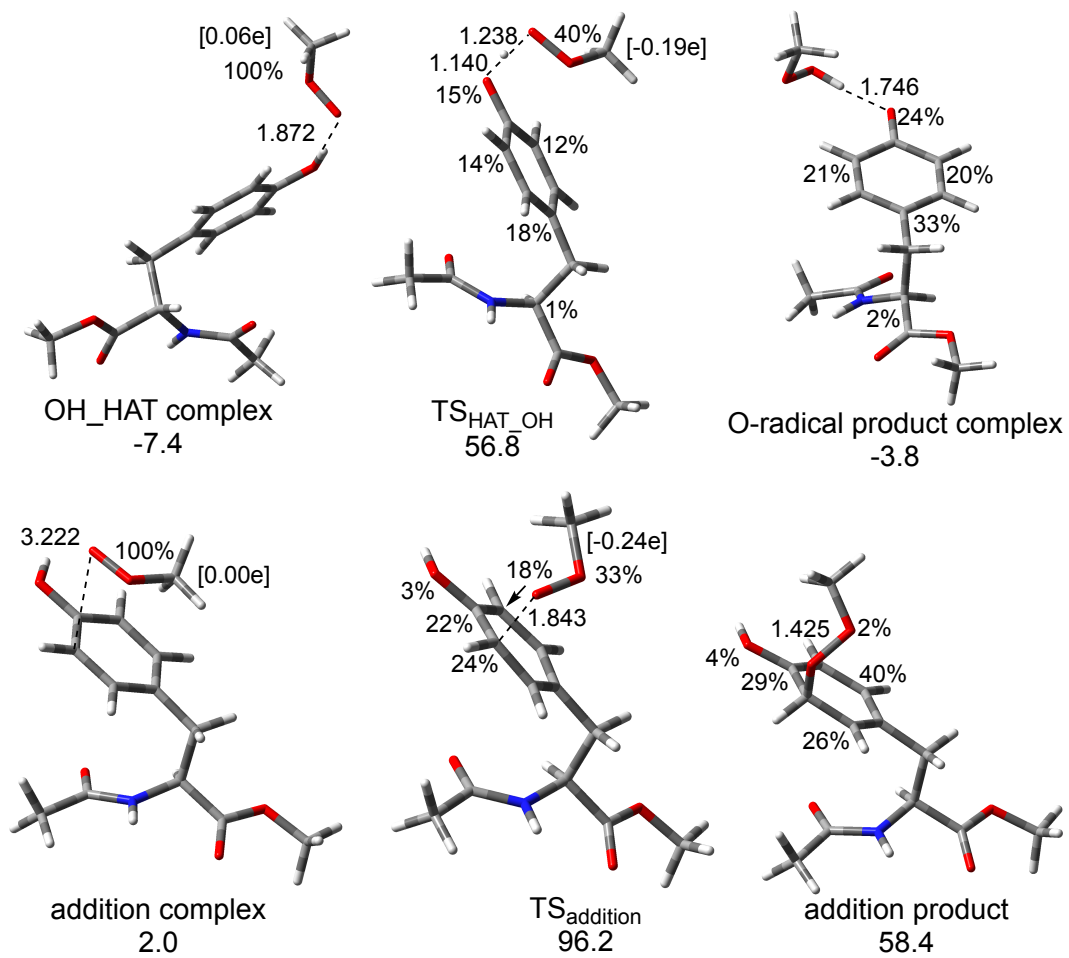
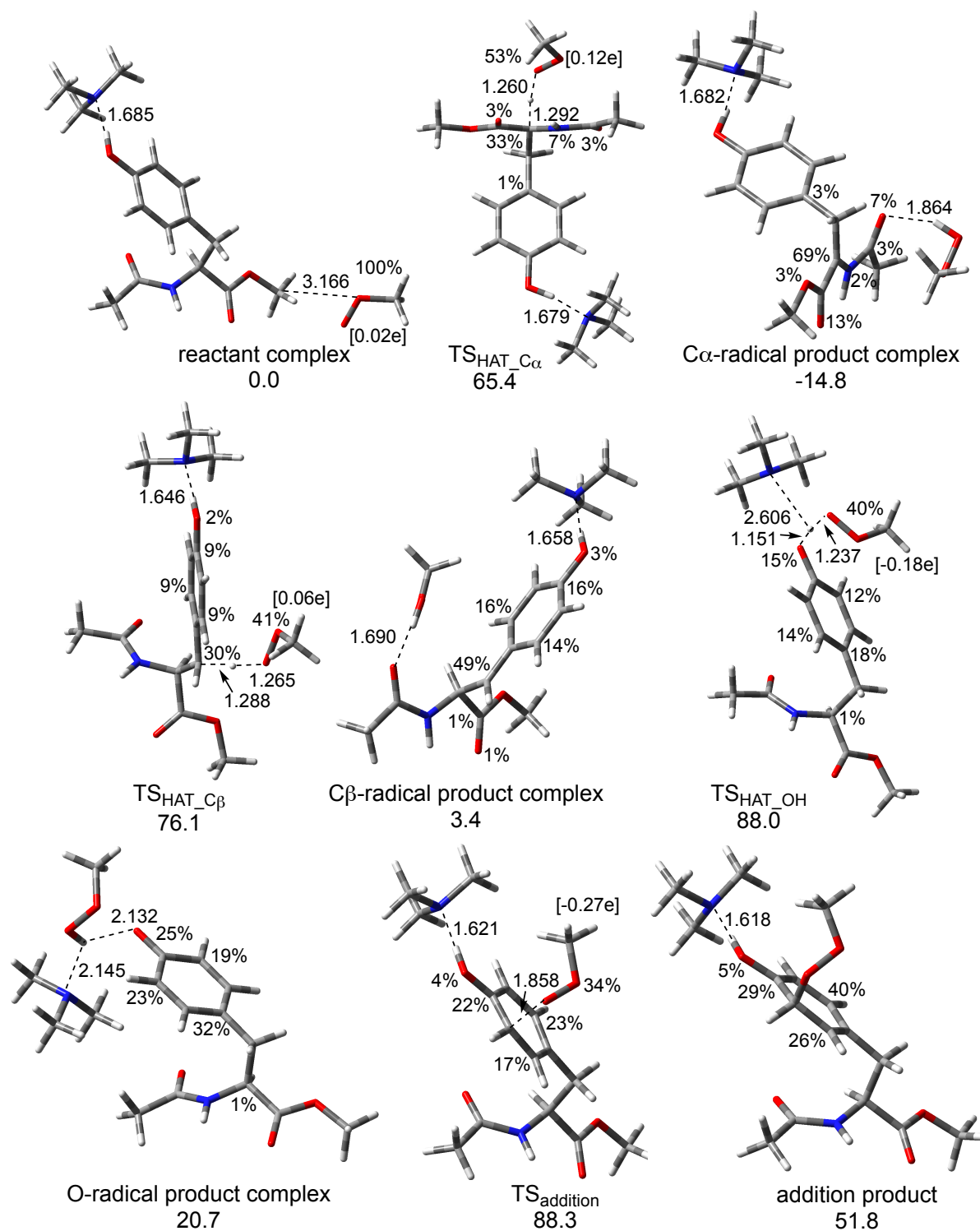
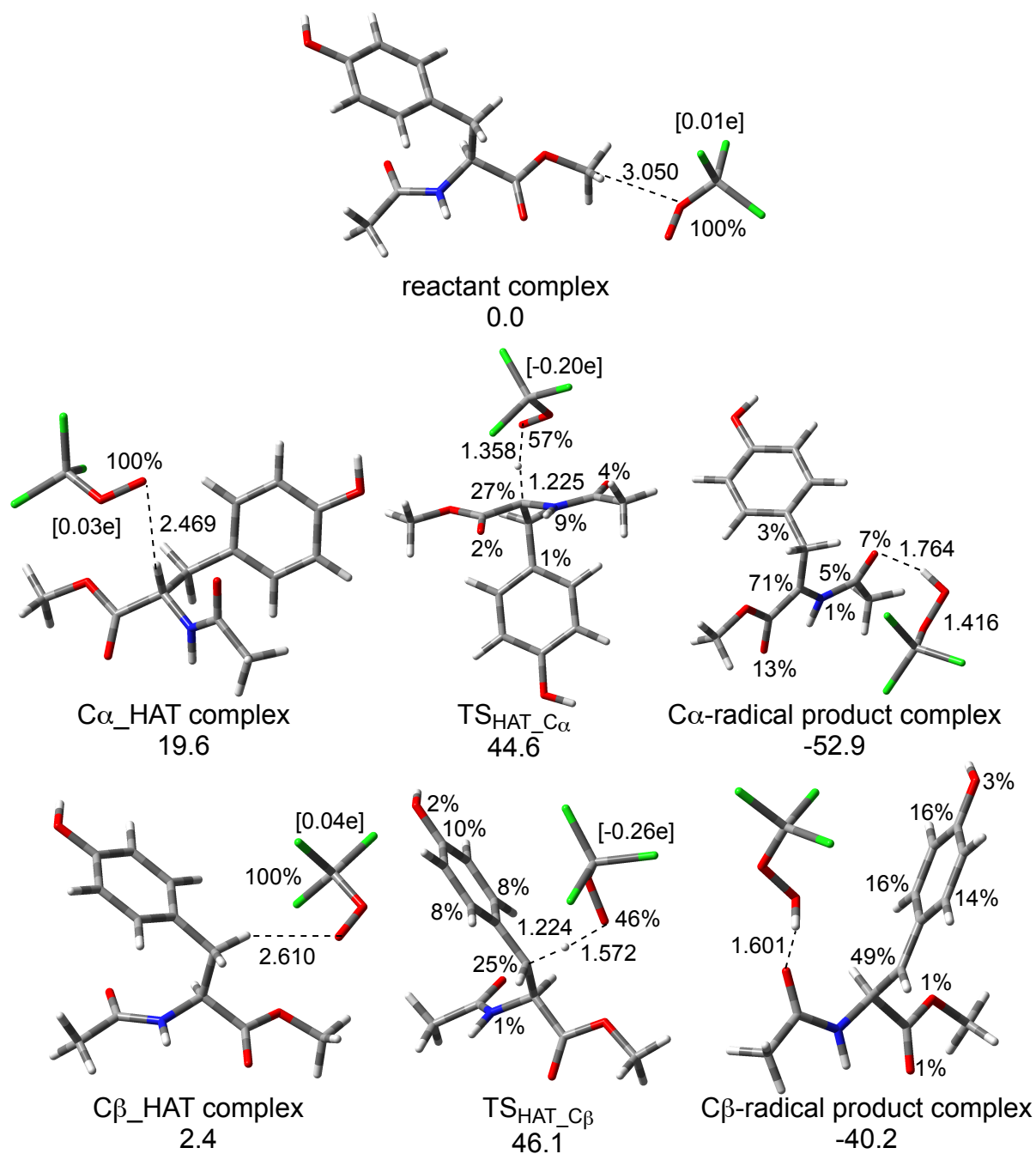


Figure S3. Continued.

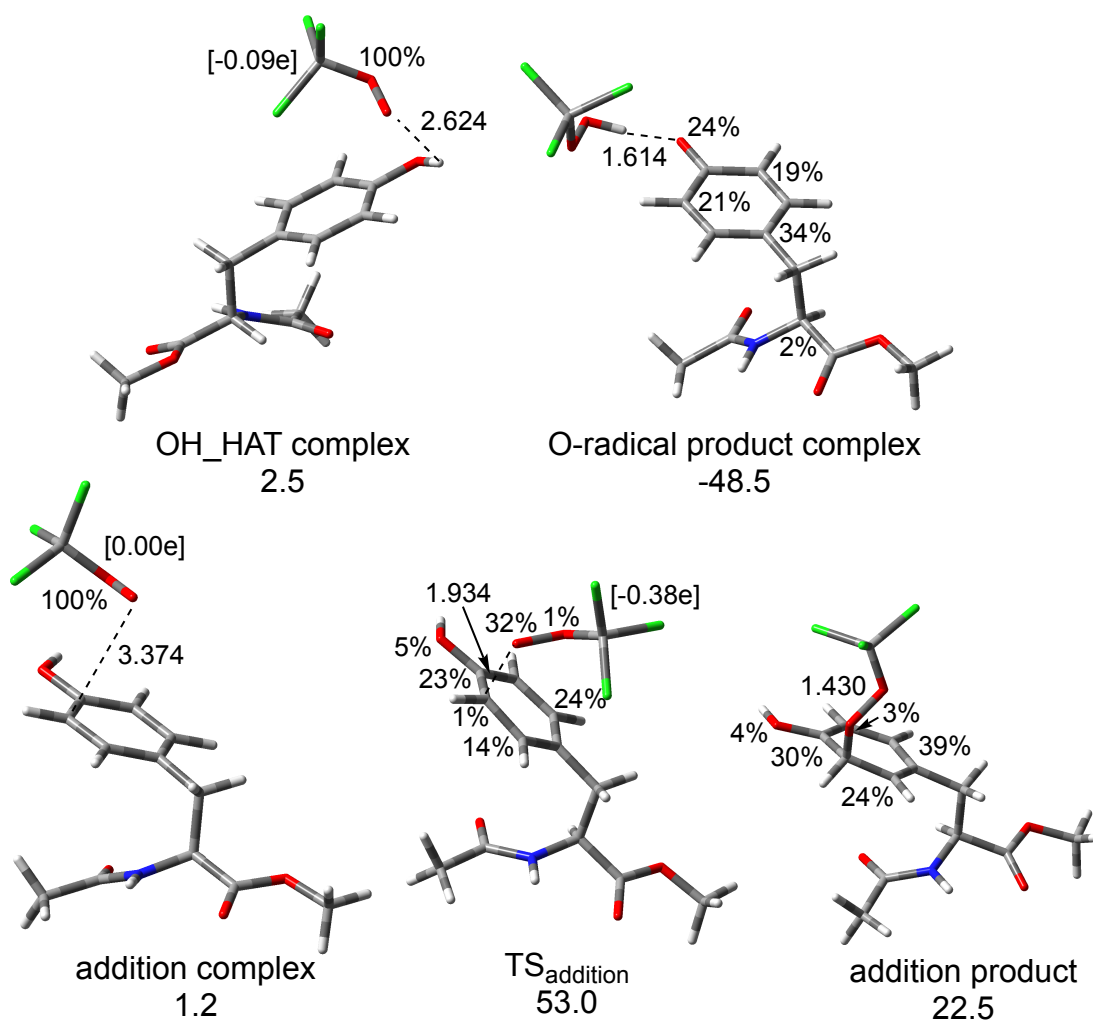


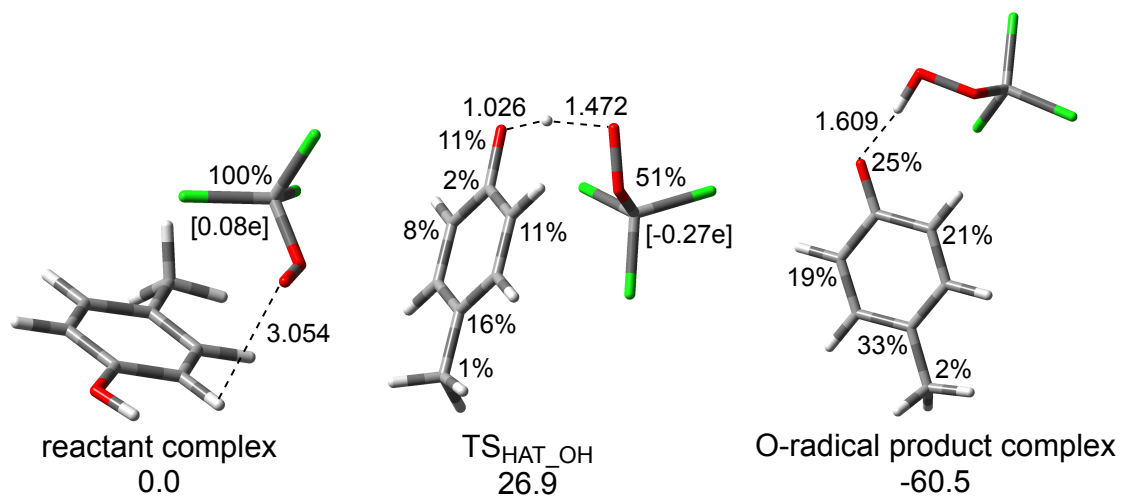


**Figure S4.** M062X/cc-pVTZ optimized geometries for the stationary points in the reaction of MeOO $\cdot$  with Ac-Tyr-OMe in the presence of NMe $_3$  (using the cpcm solvation model for acetonitrile). Distances in Å, spin densities in % and Mulliken charges on the MeOO moiety in square brackets. Free energies in kJ mol $^{-1}$  relative to the reactant association complex.

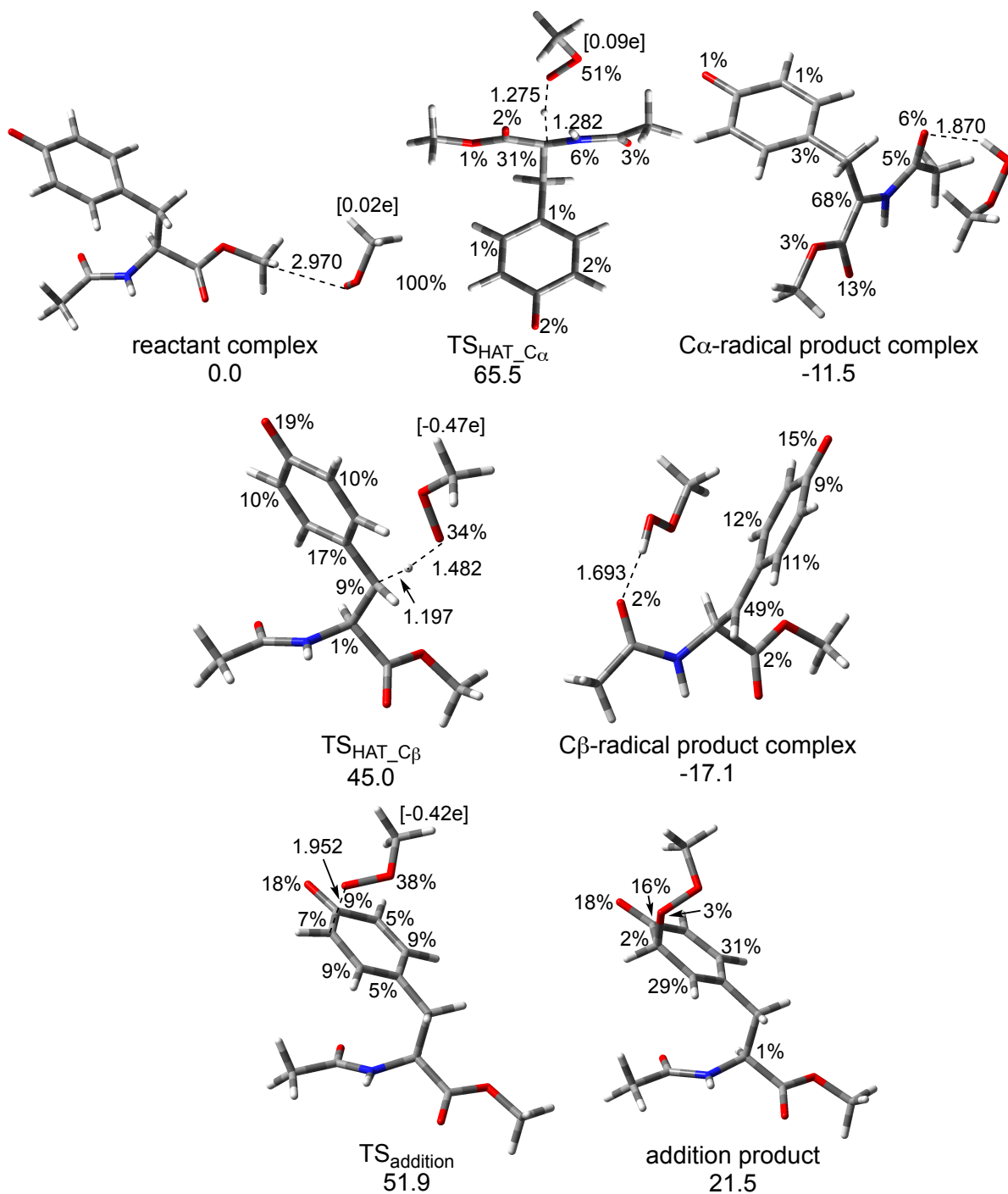


**Figure S5.** M062X/cc-pVTZ optimized geometries for the stationary points in the reaction of  $CCl_3OO^\bullet$  with Ac-Met-OMe (using the cpcm solvation model for acetonitrile). Distances in Å, spin densities in % and Mulliken charges on the  $CCl_3OO$  moiety in square brackets. Free energies in  $\text{kJ mol}^{-1}$  relative to the reactant association complex. The transition state for HAT from OH ( $TS_{HAT\_OH}$ ) could not be located for the reaction with Ac-Tyr-OMe. The geometries for the simplified model system involving 4-hydroxy toluene are shown in Figure S5 (figure continues next page).

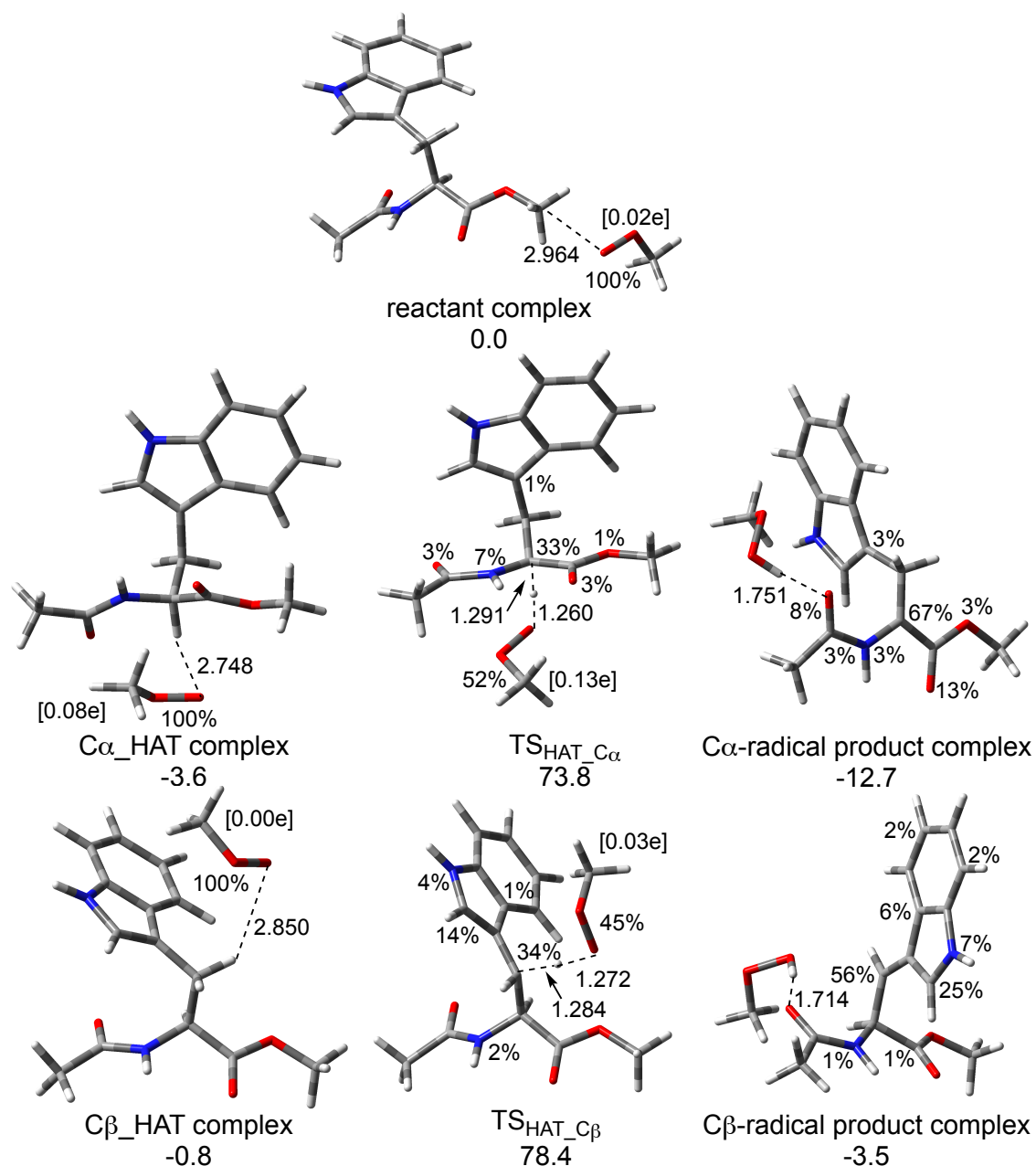




**Figure S6.** M062X/cc-pVTZ optimized geometries for the stationary points in the reaction of  $\text{CCl}_3\text{OO}^\bullet$  with 4-methyl phenol as model system for Ac-Tyr-OMe (using the cpcm solvation model for acetonitrile). Distances in Å, spin densities in % and Mulliken charges on the  $\text{CCl}_3\text{OO}$  moiety in square brackets. Free energies in  $\text{kJ mol}^{-1}$  relative to the reactant association complex.



**Figure S7.** M062X/cc-pVTZ optimized geometries for the stationary points in the reaction of MeOO<sup>•</sup> with the phenolate anion of Ac-Tyr-OMe (using the cpcm solvation model for acetonitrile). Distances in Å, spin densities in % and Mulliken charges on the MeOO moiety in square brackets. Free energies in kJ mol<sup>-1</sup> relative to the reactant association complex.



**Figure S8.** M062X/cc-pVTZ optimized geometries for the stationary points in the reaction of MeOO $\cdot$  with Ac-Trp-OMe (using the cpcm solvation model for acetonitrile). Distances in Å, spin densities in % and Mulliken charges on the MeOO moiety in square brackets. Free energies in kJ mol $^{-1}$  relative to the reactant association complex. The transition state for HAT from NH (TS<sub>HAT\_NH</sub>) could not be located (figure continues next page).

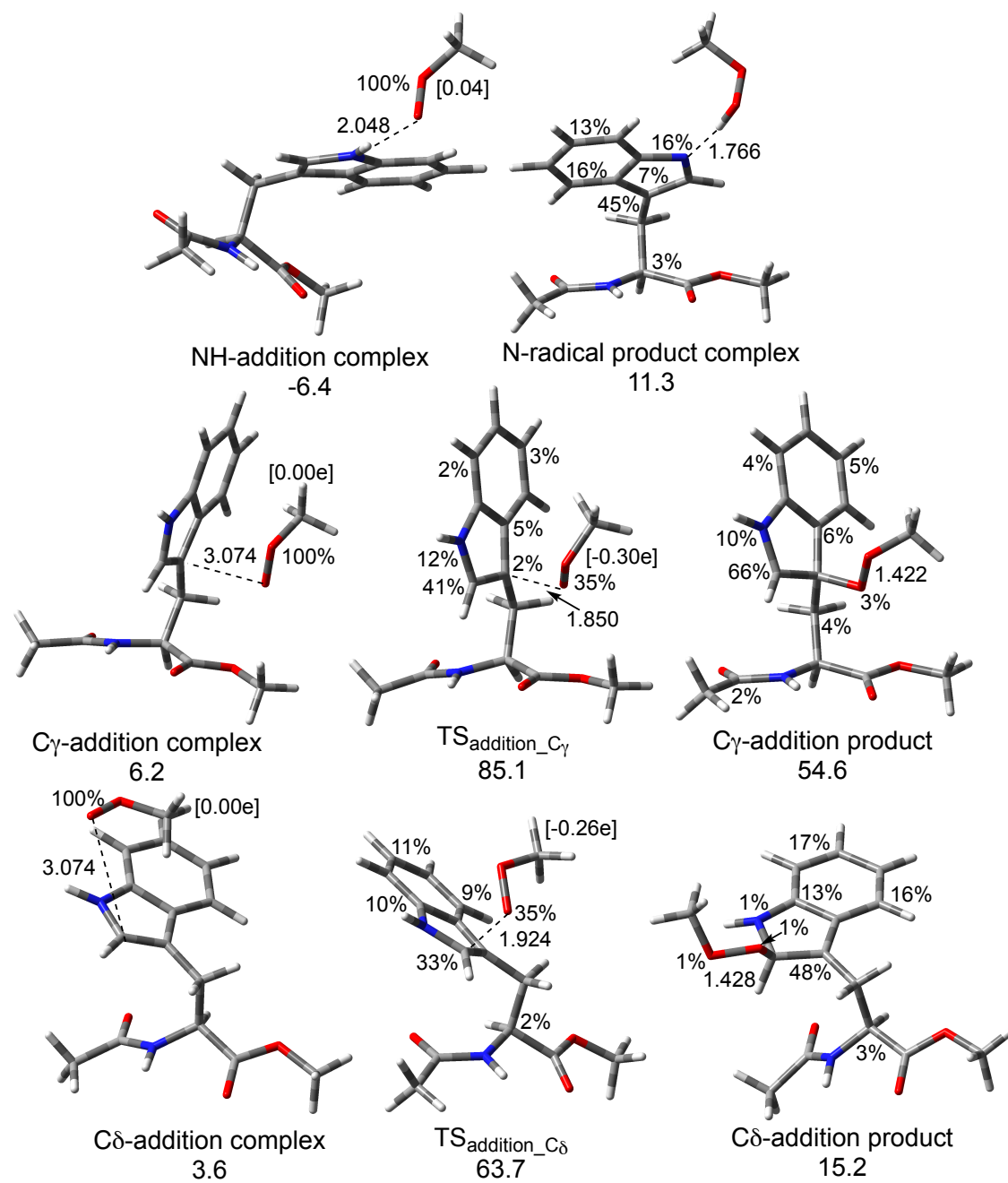
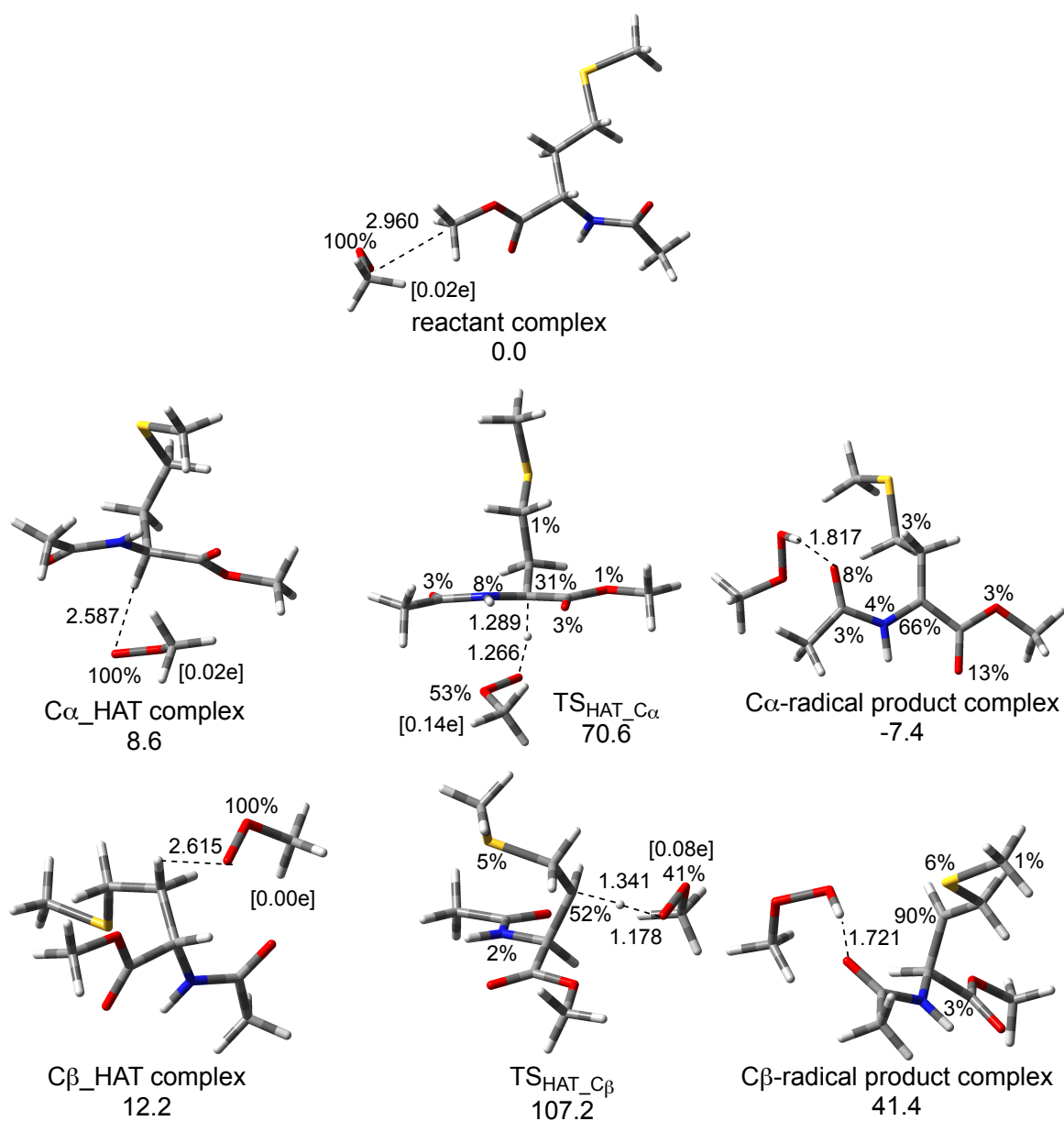


Figure S8. Continued.



**Figure S9.** M062X/cc-pVTZ optimized geometries for the stationary points in the reaction of MeOO $\cdot$  with Ac-Met-OMe (using the cpcm solvation model for acetonitrile). Distances in Å, spin densities in % and Mulliken charges on the MeOO moiety in square brackets. Free energies in kJ mol $^{-1}$  relative to the reactant association complex. Different pre-HAT complexes for abstraction from C $\gamma$  and C $\delta$  could not be located (figure continues next page).



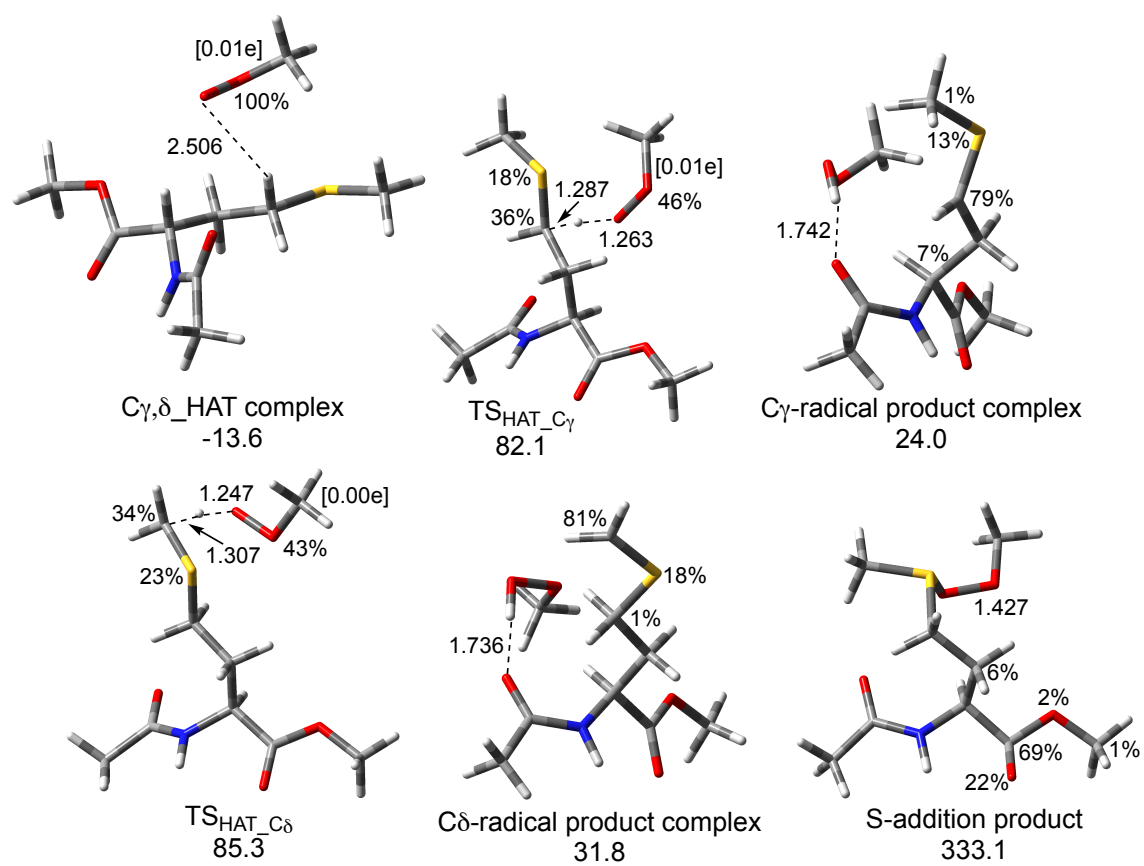
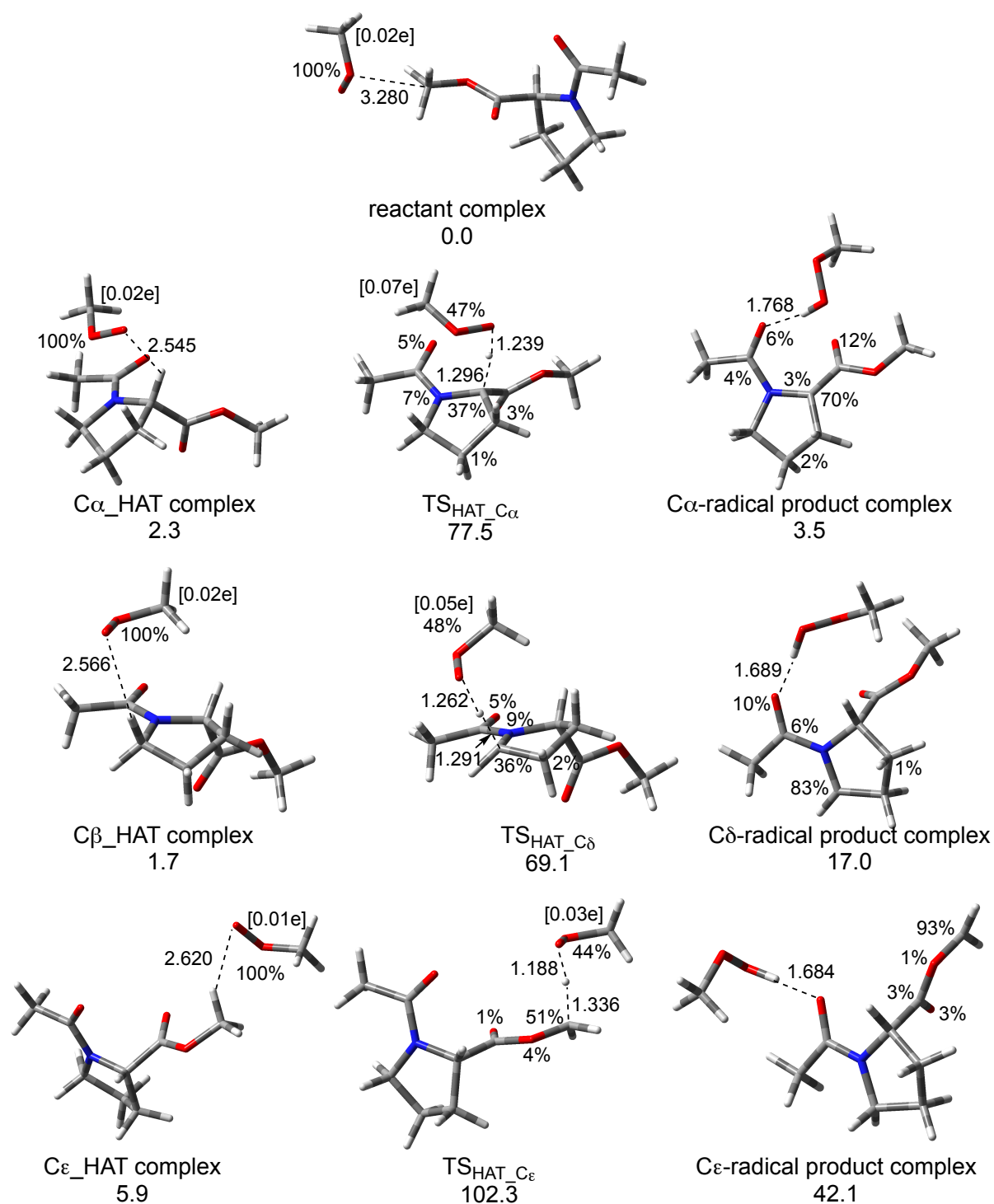


Figure S9. Continued.



**Figure S10.** M062X/cc-pVTZ optimized geometries for the stationary points in the reaction of MeOO• with Ac-Pro-OMe (using the cpcm solvation model for acetonitrile). Distances in Å, spin densities in % and Mulliken charges on the MeOO moiety in square brackets. Free energies in kJ mol<sup>-1</sup> relative to the reactant association complex.

## 5. Gaussian Archive Entries for Computational Data

Energies are given in Hartrees; imaginary frequencies (TS) are in  $\text{cm}^{-1}$ .

### 1. Table 2 - Reaction of ROO<sup>\*</sup> with Ac-Tyr-OMe

#### a) Entry 1 - Reaction of TEAOO<sup>\*</sup>

##### Reactant complex

```
1\1\GINC-SPARTAN-BM116\FOpt\UM062X\CC-pVTZ\C18H29N2O6(2)\UWILLE\14-Apr
-2022\0\#p scf=(qc,direct) opt=(readfc,maxcycle=500) freq=noraman M06
2X/cc-pVTZ geom=checkpoint guess=check scrf=(cpcm,solvent=acetonitrile
) nosymm\geom&freq\0,2\C,0.137167287,4.2574751278,-2.4268268394\H,-0
.1882249182,4.8266216686,-3.2956275312\C,0.1268266652,2.7802694813,-2.
761121989\H,-0.8194663507,3.8354982689,-0.6018613985\C,-1.5920977377,5
.595353087,-1.3137528979\C,-2.4128696994,5.7453041919,-0.0588811985\H,
-3.3884009879,6.1458220106,-0.3205406502\H,-1.9103297377,6.4661046104,
0.587232848\H,-2.5282037369,4.8106873038,0.4844175103\O,-0.2736357014,
1.9201463256,-2.0180478179\O,0.6632034633,2.5444083357,-3.9529037441\C
,0.7165659961,1.1668269261,-4.351308163\H,1.2899376168,0.5880408612,-3
.6304506078\H,1.2005263925,1.158688129,-5.3214331786\H,-0.2915596647,0
.764910595,-4.4220065715\O,-1.6339018759,6.4175706485,-2.2172681748\N,
-0.7908703792,4.5051550093,-1.3545423277\C,1.5804028459,4.6732103573,-
2.0561888812\H,1.8946226554,4.0701741728,-1.2012610734\H,2.2319378272,
4.4319437331,-2.8969312426\C,1.6656237813,6.1350601319,-1.7221388573\C
,1.8856309599,7.0812978156,-2.7174625029\C,1.4604592315,6.5848068978,-
0.4201947286\C,1.8936012444,8.4379254913,-2.4316203543\H,2.0482442767,
6.7554559569,-3.737877446\C,1.4616918011,7.9370634723,-0.1173308221\H,
1.2930562107,5.8651047676,0.3719425249\C,1.6765498086,8.8680238041,-1.
127217367\H,2.0673740932,9.1631570375,-3.2168313084\H,1.3032458562,8.2
850144107,0.8942298444\O,1.6716169633,10.1852672575,-0.7834247804\H,1.
8324376757,10.7273043303,-1.5627003269\O,3.0512849142,-0.8390541001,-2
.5262415236\O,2.9346078264,-1.5559646535,-3.5974184137\C,4.4739278156,
-0.3860950293,-2.3024192332\N,4.4510905784,0.8544640941,-1.6340401911\
C,5.1780136806,-1.5249729656,-1.6022370572\H,6.1833659672,-1.216309735
9,-1.3213527126\H,4.6387398855,-1.8451521352,-0.7138413788\H,5.2443940
371,-2.367505606,-2.2868319557\C,4.0941626819,0.8099307712,-0.21193992
11\H,3.0386450809,0.5325227354,-0.0850780328\H,4.6941826749,0.03609196
28,0.2593176723\C,3.7394385757,1.9175855337,-2.3530754146\H,4.04326621
8,2.8657866319,-1.913250634\H,2.6559028392,1.8222727271,-2.1829268222\
C,4.3661966969,2.1239704684,0.5043865127\H,3.6609418643,2.9048639736,0
.2255702406\H,4.2792846697,1.972964471,1.5792158954\H,5.3754549354,2.4
737110961,0.2853595677\C,4.0237115167,1.9691766391,-3.8445143664\H,5.0
964165814,2.017646057,-4.0331500881\H,3.6161353408,1.1113323275,-4.378
7020114\H,3.5621727618,2.8628720741,-4.2630430907\H,4.8535609955,-0.26
65955548,-3.3128919871\Version=ES64L-G16RevC.01\HF=-1264.0894218\S2=0
.755359\S2-1=0.\S2A=0.750016\RMSD=9.747e-10\RMSF=1.098e-06\Dipole=1.75
35984,-0.2431896,0.593838\Quadrupole=9.7750168,-13.2233567,3.4483399,1
2.1058754,-9.7655667,-3.4052686\PG=C01 [X(C18H29N2O6)]\@\
Sum of electronic and thermal Free Energies= -1263.690186
```

### C $\alpha$ \_HAT complex\_

```
1\1\GINC-SPARTAN-BM088\FOpt\UM062X\CC-pVTZ\C18H29N2O6(2)\UWILLE\22-Jan-2022\0\#p scf=(qc,direct) opt=(calcfc,maxcycle=500) freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,-0.4436107833,-0.3889153483,0.8780896613\H,-1.1007150331,0.1120331767,1.5880578119\C,0.3113600319,-1.4916709713,1.5893016784\H,-0.8352333163,-1.6927436041,-0.7250062119\C,-2.5270406252,-0.5817921293,-0.4123887404\C,-3.1789284072,-1.230317498,-1.6060723967\H,-4.2151215259,-1.4511924971,-1.3629667065\H,-3.1678761574,-0.5124504758,-2.4268631629\H,-2.6713271177,-2.1369534504,-1.9259607383\O,0.5267837307,-2.5802810903,1.1204412218\O,0.7373391666,-1.0974164454,2.7841226968\C,1.47980378,-2.0669875359,3.5361126555\H,2.3760597742,-2.3555332011,2.9925943159\H,1.7362556294,-1.5822063425,4.4710657388\H,0.8626318876,-2.9453493952,3.7163056185\O,-3.1083548239,0.2518266668,0.2677436573\N,-1.2569278468,-0.974311334,-0.1573742369\C,0.5621263435,0.6456850251,0.3232955236\H,1.2185031341,0.1409143005,-0.3881391069\H,1.1732635183,1.0025106787,1.1525406023\C,-0.1555717329,1.7887079664,-0.3361941196\C,-0.5906642097,2.8775987751,0.4122922112\C,-0.4704500325,1.7537299088,-1.6919367709\C,-1.3228270755,3.9024840678,-0.1668685106\H,-0.3612670012,2.923752002,1.4703055029\C,-1.2047916945,2.7677552993,-2.2863765633\H,-0.1394619043,0.9164546326,-2.2943190139\C,-1.6348885972,3.8454908998,-1.5209665326\H,-1.652984314,4.7448491704,0.4282816714\H,-1.4483164928,2.7398890254,-3.339638789\O,-2.3516387189,4.8187334211,-2.1478650773\H,-2.5952382051,5.5040429483,-1.5170650955\N,-3.17288874,-1.8648611642,4.096054361\C,-3.445676551,-2.9778021656,5.0064576217\H,-3.820292352,-2.5703456907,5.9422764523\H,-4.2672047523,-3.5526750899,4.5809219533\C,-2.2566157179,-3.8984159653,5.2705188218\H,-1.4009584696,-3.3414947946,5.6566769773\H,-2.526100883,-4.6560046586,6.0055121145\H,-1.9409172629,-4.4125612904,4.3624584275\C,-2.7366459356,-2.2698295765,2.7568750533\H,-2.6372413113,-1.3563395083,2.171393526\H,-1.7464119375,-2.7475236266,2.7954288655\C,-3.7184726325,-3.1850696922,2.0487784339\H,-4.7193707834,-2.7530727005,2.0612560033\H,-3.4084599393,-3.3100625176,1.0110633717\H,-3.761884622,-4.1748241155,2.5021071898\C,-2.3435848208,-0.820016642,4.5973148308\H,-1.2869173998,-0.9188333795,4.3213702466\C,-2.494613376,-0.4862548161,6.0611605407\H,-1.9406317351,0.4283303502,6.2622196908\H,-3.5432073115,-0.3330407282,6.3123390497\H,-2.0857807431,-1.2782237911,6.6851510235\O,-2.7775432976,0.3857399987,3.8405474387\O,-1.8247588066,1.2507299184,3.7155762121\Version=ES64L-G16RevC.01\HF=-1264.0904998\S2=0.755354\S2-1=0.\S2A=0.750015\RMSD=2.108e-09\RMSF=1.974e-06\Dipole=1.3595464,-1.8068247,1.1015165\Quadrupole=-16.4742529,1.9276776,14.5465753,6.971695,3.5429119,-7.949661\PG=C01 [X(C18H29N2O6)]\@\nSum of electronic and thermal Free Energies= -1263.691313
```

### TS<sub>HAT\_C $\alpha$</sub>

```
1\1\GINC-SPARTAN-BM095\FTS\UM062X\CC-pVTZ\C18H29N2O6(2)\UWILLE\14-Apr-2022\0\#p opt=(ts,noeigentest,readfc,maxcycle=500) freq=noraman M062X/cc-pVTZ geom=checkpoint guess=check scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,-0.7804481507,0.3395454725,-1.8154903488\H,-0.8675952156,0.0687182348,-3.0892962611\C,0.2949913419,-0.607431695,-1.3708622368\H,-2.0041618003,-1.0081556208,-0.8665062902\C,-3.2373744998,0.4456083844,-1.5988503252\C,-4.3931704956,-0.2906063569,-0.979011939
```

4\H,-4.3514843048,-0.1881513327,0.1060583352\H,-4.3268764084,-1.350259  
734,-1.2276478135\H,-5.3244044127,0.1267864992,-1.3478966115\O,0.07075  
98728,-1.6574024943,-0.8123281818\O,1.5068555521,-0.1922303861,-1.7072  
974263\C,2.5878914538,-1.066099283,-1.354783703\H,2.6177470687,-1.2006  
818271,-0.2761326381\H,3.4883124565,-0.5753013788,-1.7049351998\H,2.46  
01426217,-2.0299799433,-1.8413629771\O,-3.3631922567,1.4429733439,-2.2  
844012001\N,-2.0124650375,-0.0875501054,-1.2890213489\C,-0.439672381,1  
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1.2083351028,2.379631947,-2.2663113489\C,-0.3461772125,2.2921323779,-0  
.3038974914\C,-1.4865947809,2.7018416342,0.3815679483\C,0.8686229028,2  
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6683375\H,1.7694559209,1.9840080343,-0.1363701386\C,-0.2014677731,3.09  
76199652,2.3717578296\H,-2.3176364399,3.4246176742,2.2263836197\H,1.89  
30851484,2.7013283773,2.229662778\O,-0.0744037345,3.4841617237,3.67074  
28251\H,-0.9319431739,3.7500686385,4.018505098\O,-2.3328563075,-1.1060  
522851,-3.8933873453\O,-1.2355985587,-0.3637012364,-4.2088040819\C,-1.  
9254490782,-2.4714799549,-3.6011898444\H,-0.9950351945,-2.3858008322,-  
3.0415916552\C,-1.6665624669,-3.2067939075,-4.9041149816\H,-0.86432529  
38,-2.7085080841,-5.4450188879\H,-1.3587041208,-4.2309824065,-4.690081  
3516\H,-2.5521599481,-3.2306087717,-5.5356015505\N,-2.916717964,-3.019  
2392433,-2.7119739696\C,-2.3538508985,-4.0044445059,-1.7800896985\H,-1  
.309589513,-3.7495727359,-1.6032158514\H,-2.3697923659,-5.0087561941,-  
2.2253986855\C,-4.1336419755,-3.5243098158,-3.3521845238\H,-3.90187041  
39,-4.3676058545,-4.0178003349\H,-4.7626305912,-3.9254770409,-2.558616  
296\C,-4.9219597956,-2.4645133429,-4.1057495779\H,-5.1543213454,-1.622  
2699983,-3.4548548002\H,-4.3751397319,-2.0784387436,-4.9635256196\H,-5  
.8564923624,-2.8945530094,-4.4646849261\C,-3.0776082356,-4.0203433087,  
-0.4422249641\H,-4.1406102959,-4.2309228214,-0.5521868692\H,-2.6516289  
875,-4.7878811774,0.2034564758\H,-2.9724502002,-3.0579493472,0.0602056  
527\Version=ES64L-G16RevC.01\HF=-1264.0602046\S2=0.759894\S2-1=0.\S2A  
=0.750054\RMSD=5.328e-09\RMSF=3.028e-06\Dipole=0.4211064,-2.0051313,1.  
163058\Quadrupole=7.9172309,3.6795797,-11.5968105,6.4056828,-14.401724  
6,16.1164513\PG=C01 [X(C18H29N2O6)]\@\@  
Frequencies -2054.6651  
Sum of electronic and thermal Free Energies= -1263.662019

### **C $\alpha$ -radical product complex**

1\1\GINC-SPARTAN-BM118\FOpt\UM062X\CC-pVTZ\C18H29N2O6(2)\UWILLE\28-Jan  
-2022\0\#p scf=(qc,direct) opt=(calcf, maxcycle=500) freq=noraman M06  
2X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,-  
0.568659893,0.1058193663,-1.4432053088\H,-2.7393533315,1.1291887086,-3  
.063664971\C,0.4101046057,-0.8716040719,-1.8863857392\H,-1.5077252232,  
-1.4258319312,-0.5129919609\C,-2.9141750141,0.044952389,-0.7090401577\  
C,-3.8447366928,-0.6955034773,0.2045964419\H,-4.8309052952,-0.73415373  
27,-0.2513030899\H,-3.920803151,-0.1290655656,1.1338647314\H,-3.497498  
2804,-1.6985226576,0.4382320353\O,0.2361884263,-2.074813668,-1.7841272  
763\O,1.5072990128,-0.3279808034,-2.4199065909\C,2.4825015589,-1.25685  
94794,-2.9015316008\H,2.8346745549,-1.8876060917,-2.0885300545\H,3.293  
1943961,-0.6552049775,-3.2963315606\H,2.0523189014,-1.8789910915,-3.68  
36481877\O,-3.2593291968,1.0479085026,-1.3201012164\N,-1.6469690464,-0

.4661056037,-0.8067555034\C,-0.3500089368,1.5837876797,-1.4645882894\H  
,0.5750128735,1.7708650023,-2.0041245581\H,-1.1515045832,2.0933314116,  
-1.9950137958\C,-0.2565443481,2.1309530794,-0.0537590955\C,-1.27194002  
35,2.9051262548,0.49221385\C,0.8545937377,1.8393789783,0.7361687271\C,  
-1.185196699,3.3852766086,1.7928438274\H,-2.1452427044,3.1362033645,-0  
.1039897831\C,0.9553483527,2.3100442108,2.0330684588\H,1.6564104853,1.  
2364959189,0.3254215739\C,-0.0707132727,3.0860273197,2.565506829\H,-1.  
981073258,3.9926652902,2.2056679018\H,1.8192118216,2.0890063328,2.6447  
286165\O,0.073248991,3.5253633954,3.8453082797\H,-0.695005297,4.046109  
5076,4.1016294204\N,-3.4581522814,-2.323014462,-4.2732164593\C,-2.9733  
412752,-3.6511726537,-4.6530558414\H,-2.450135931,-3.5622399549,-5.602  
0325397\H,-3.8447670098,-4.2747320144,-4.8507152075\C,-2.0756510891,-4  
.3357801174,-3.6227089488\H,-1.2393601948,-3.6962891393,-3.3337837335\  
H,-1.6720560116,-5.2598195568,-4.0359281452\H,-2.6283432277,-4.5915075  
674,-2.7182430238\C,-4.231223262,-2.3182809465,-3.0277294097\H,-4.5564  
229853,-1.2916564821,-2.8611301676\H,-3.592320172,-2.5939630816,-2.174  
3785461\C,-5.4456590478,-3.228624877,-3.0692038221\H,-6.04503409,-3.02  
28829677,-3.9562685002\H,-6.0627883089,-3.0573800003,-2.1880206676\H,-  
5.1678926164,-4.2821013074,-3.0785735195\C,-2.4579890221,-1.2859853941  
, -4.2319639307\H,-1.9988700696,-1.209461468,-3.2372347443\C,-1.3733708  
759,-1.3739672433,-5.2817962085\H,-0.7981612288,-0.450374175,-5.244802  
1719\H,-1.810392222,-1.4802979435,-6.2744886896\H,-0.695523228,-2.2050  
36552,-5.0928775878\O,-3.2150428575,-0.0748747077,-4.4269421784\O,-2.4  
255164637,1.0190684425,-3.983171911\Version=ES64L-G16RevC.01\HF=-1264.  
0954775\S2=0.756722\S2-1=0.\S2A=0.750037\RMSD=3.666e-10\RMSF=1.040e-06  
\Dipole=0.6741802,-1.0534456,2.0772183\Quadrupole=4.4302969,7.7930393,  
-12.2233362,2.2957987,-26.4460383,12.4835127\PG=C01 [X(C18H29N2O6)]\@  
Sum of electronic and thermal Free Energies= -1263.693710

### C $\beta$ \_HAT complex

1\1\GINC-SPARTAN-BM012\FOpt\UM062X\CC-pVTZ\C18H29N2O6(2)\UWILLE\29-Jan  
-2022\0\#p scf=(qc,direct) opt=(calcfc,maxcycle=500) freq=noraman M06  
2X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,1  
.5858577277,-0.3176924791,-0.658146087\H,1.7073281286,-0.2386610533,-1  
.7385083163\C,2.4678787254,-1.4379861412,-0.1466643016\H,-0.026115081,  
-1.0204667769,0.4990345491\C,-0.773931562,-0.413054799,-1.3090175076\C  
, -2.1738510656,-0.6932392346,-0.8283037627\H,-2.7496330129,-1.11907548  
11,-1.6453498572\H,-2.6293714753,0.2576973685,-0.5491099508\H,-2.19940  
55033,-1.3580349006,0.0314751892\O,2.111076666,-2.3010899696,0.6130616  
925\O,3.704090852,-1.3142522921,-0.6140266608\C,4.6591689955,-2.281409  
3811,-0.161963421\H,4.7359599319,-2.2511654612,0.9223179605\H,5.600177  
8506,-1.9974824367,-0.6204122114\H,4.358287149,-3.2770893711,-0.480415  
8792\O,-0.5483093271,0.0080740296,-2.4346837657\N,0.2059877364,-0.6306  
937078,-0.4008534716\C,2.0253042306,1.0153454768,-0.0063500617\H,1.901  
7174879,0.9225344951,1.0746127854\H,3.0871389189,1.1606146349,-0.21141  
8185\C,1.2212193237,2.1685021523,-0.534592116\C,1.6563412204,2.8869601  
706,-1.6425671109\C,-0.010409359,2.5049296947,0.022703577\C,0.88753302  
86,3.8997799426,-2.1965551131\H,2.6201504272,2.6570773647,-2.081504350  
4\C,-0.7929606922,3.5123085314,-0.5175501784\H,-0.3665181802,1.9671177  
162,0.8927849108\C,-0.345737604,4.2097761977,-1.6345710475\H,1.2436297  
742,4.4500644,-3.0589081361\H,-1.7485526555,3.7728358362,-0.0834917893

\O,-1.1497828942,5.1904302531,-2.1289362343\H,-0.732111124,5.603161996  
3,-2.8918515119\N,4.3817331547,-0.3279570861,-4.3619775572\C,3.8625665  
119,-1.6153544327,-3.8864689328\H,2.8573418284,-1.4994731823,-3.456701  
5489\C,3.6756433218,0.2050557807,-5.5302914183\H,3.7972976107,-0.51254  
88284,-6.3398200031\H,4.185220988,1.1085436279,-5.85551362\C,2.1911516  
724,0.4860742169,-5.3087351365\H,2.0333120659,1.1738002592,-4.47446313  
51\H,1.6388281463,-0.4292349892,-5.0950410649\H,1.7579490575,0.9367252  
295,-6.2009257443\C,4.5544021069,0.5874192461,-3.2813731502\H,3.754050  
5848,0.5441433213,-2.5305719251\C,4.8654578086,2.0133550464,-3.6687392  
349\H,5.1532916643,2.5583535895,-2.7719889853\H,3.9949215963,2.5012367  
8,-4.1033593077\H,5.6856188914,2.0407001326,-4.3849645748\O,5.73184518  
33,0.069090672,-2.5441559778\O,5.8261419277,0.5907476117,-1.3648906249  
\C,3.8417220764,-2.6829534989,-4.9657406241\H,4.8093271022,-2.73988023  
55,-5.4647098986\H,3.0763818509,-2.4928032498,-5.7171972852\H,3.628522  
3154,-3.6510702985,-4.5153180233\H,4.5104288961,-1.9400404876,-3.07360  
28636\\Version=ES64L-G16RevC.01\HF=-1264.0892499\S2=0.755058\S2-1=0.\S  
2A=0.750015\RMSD=1.467e-09\RMSF=2.331e-06\Dipole=-0.1419338,0.1541475,  
-0.272049\Quadrupole=-10.9333143,3.2338348,7.6994795,2.7563883,-8.2997  
828,-7.6106959\PG=C01 [X(C18H29N2O6)]\@\@  
Sum of electronic and thermal Free Energies= -1263.688382

#### TS<sub>HAT\_CB</sub>

1\1\GINC-SPARTAN-BM006\FTS\UM062X\CC-pVTZ\C18H29N2O6(2)\UWILLE\22-Jan-  
2022\0\#p scf=(qc,direct) opt=(ts,noeigentest,calcf, maxcycle=500) fr  
eq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom  
&freq\0,2\C,1.4064167994,-0.9511025569,0.2041029333\H,1.4239388631,-1  
.3186294923,1.227196999\C,2.3332237543,-1.8086899273,-0.6414002908\H,-  
0.1255985719,-0.8308161507,-1.2412448586\C,-0.9586374127,-1.5820291803  
,0.4715172575\C,-2.303395727,-1.6598037235,-0.2021805932\H,-2.65495706  
52,-2.6881847095,-0.1476610663\H,-3.0009105306,-1.0385467251,0.3571769  
846\H,-2.283686466,-1.3360843876,-1.2391165564\O,2.2137984591,-1.94349  
16736,-1.8321473488\O,3.3047649618,-2.3432884823,0.0829057946\C,4.3052  
464828,-3.0664212718,-0.6458719669\H,4.7858915997,-2.4078282383,-1.365  
6709005\H,5.0186794796,-3.4104588885,0.093795707\H,3.8530409479,-3.908  
2333519,-1.1645065814\O,-0.7974214458,-1.9445117413,1.6288925732\N,0.0  
475912348,-1.0729990956,-0.2783832643\C,1.8953558733,0.4860719754,0.13  
25444997\H,2.0263269787,0.8337331583,-0.8931597044\H,3.148675479,0.472  
2925183,0.4993887859\C,1.297998742,1.4797221904,1.0282012614\C,0.53729  
46589,1.1343315733,2.1486930784\C,1.6241957028,2.832527385,0.845051328  
7\C,0.1507155714,2.0926904556,3.0707471415\H,0.2484130279,0.1051016042  
,2.3194071079\C,1.2542436197,3.7923987117,1.7619721296\H,2.2093170971,  
3.1204960658,-0.0195972644\C,0.5250411641,3.4203873184,2.8925321467\H,  
-0.4309555231,1.8103635497,3.9396532588\H,1.5234037711,4.8309447136,1.  
6286794192\O,0.2093498593,4.393042541,3.780782912\H,-0.2773657643,4.01  
88475296,4.5233658249\N,4.0960563816,0.4856610645,4.3231596575\C,2.895  
5977051,-0.3586540593,4.3782928506\H,1.984114189,0.2512399801,4.343850  
5129\C,4.2283139162,1.3671041227,5.4869823215\H,4.2871331712,0.7345383  
612,6.3710927159\H,5.1865543835,1.8774398211,5.422275516\C,3.104839358  
3,2.3898234115,5.6618576994\H,3.0009600526,3.0262678344,4.7806200701\H  
,2.1435112165,1.905787524,5.8376448293\H,3.3163146985,3.0313460844,6.5  
168519591\C,4.1896999361,1.1727965818,3.0587819422\H,3.2393593157,1.63

21167669,2.7558758686\C,5.3103386513,2.1849505328,2.9749769716\H,5.434  
4282915,2.4701020198,1.9326820308\H,5.080667762,3.0818188523,3.5470845  
435\H,6.2397355332,1.7493692151,3.3417180216\O,4.4443197637,0.10621421  
36,2.1044577202\O,4.3413146267,0.5818257824,0.8268088394\C,2.864066012  
5,-1.2642883164,5.5980454866\H,3.8101601711,-1.7960067515,5.7034578745  
\H,2.6761083586,-0.7111439169,6.517573064\H,2.0668515947,-1.9981847473  
,5.4877431389\H,2.8948692895,-0.9722110709,3.4788086181\\Version=ES64L  
-G16RevC.01\HF=-1264.0523818\S2=0.764679\S2-1=0.\S2A=0.750153\RMSE=1.8  
11e-09\RMSF=8.834e-07\Dipole=-1.1362875,1.1744402,0.3115463\Quadrupole  
=-8.0147776,-1.0018372,9.0166148,0.947881,-0.2912053,11.1360613\PG=C01  
[X(C18H29N2O6)]\@\@  
Frequencies -2202.9212  
Sum of electronic and thermal Free Energies= -1263.657409

### C $\beta$ -radical product complex

1\1\GINC-SPARTAN-BM109\FOpt\UM062X\CC-pVTZ\C18H29N2O6(2)\UWILLE\24-Feb  
-2022\0\#\#p opt=(calcf, maxcycle=500) freq=noraman M062X/cc-pVTZ scrf=  
(cp, solvent=acetonitrile) nosymm\geom&freq\0,2\C,2.8539578813,-2.0  
97044346,1.6793619377\H,2.7881677394,-1.5113318412,0.7624199132\C,3.92  
31249852,-3.1610957875,1.4698271374\H,1.6600074792,-3.7666383951,2.151  
0063365\C,0.4124215271,-2.1736715231,1.8564944928\C,-0.7939427989,-3.0  
107422071,2.1779376691\H,-1.4850729323,-2.9542044909,1.3393261342\H,-1  
.2870977727,-2.5785740333,3.0470610327\H,-0.5481219872,-4.0492900083,2  
.380218235\O,3.7937796678,-4.319485975,1.7744919774\O,5.0236238487,-2.  
639487605,0.9479526274\C,6.1341416661,-3.5367996017,0.8076701711\H,6.4  
189367181,-3.9274132667,1.7817640681\H,6.9375344399,-2.9465304389,0.38  
20238046\H,5.8678791394,-4.3574814139,0.1457850892\O,0.2956600701,-0.9  
805122785,1.5685553623\N,1.6008955452,-2.7893976278,1.906009566\C,3.24  
08465277,-1.2395488035,2.8483087566\H,2.9761721038,-1.6312190451,3.822  
3694099\C,3.965874743,-0.0354120734,2.7712196876\C,4.38023036,0.552085  
892,1.552291086\C,4.3142706241,0.6481739873,3.9641655171\C,5.087255463  
7,1.7350938396,1.5303906903\H,4.1298453143,0.0803087142,0.6131789146\C  
,5.0207832515,1.8264046639,3.9436383551\H,4.0124808145,0.2236765206,4.  
9131812379\C,5.4159291039,2.3795296863,2.723025586\H,5.3911381596,2.16  
90204804,0.5854766198\H,5.2821864471,2.3387241475,4.8593317591\O,6.114  
8458882,3.5412783249,2.7581042018\H,6.3394202619,3.819953082,1.8638944  
031\O,1.9862095073,-0.5719154825,-1.0461296029\C,2.3702239711,-0.01718  
39969,-2.3083173032\O,1.6381915787,0.5305160448,-0.2027543283\H,1.1485  
143156,0.0425801066,0.4986083491\C,1.1301201705,0.4499881686,-3.040306  
3253\H,1.3663933667,0.9049289602,-4.0000574016\H,0.4542910469,-0.39016  
45935,-3.1920245162\H,0.6321421088,1.193154323,-2.4219828122\H,3.02584  
4723,0.8419549576,-2.0889654501\N,3.0928359723,-1.0917326976,-2.947730  
4268\C,4.3841030076,-1.3279097369,-2.2898498837\H,4.2731983474,-1.1033  
169361,-1.2312436695\H,5.1467174044,-0.6449168857,-2.689652588\C,3.251  
8635884,-0.9501040019,-4.401888004\H,3.2910766063,0.1066903831,-4.6905  
412717\H,4.2277788336,-1.360538627,-4.6581492634\C,4.8343026573,-2.771  
4913737,-2.4322977557\H,4.8839665288,-3.0764677829,-3.4780479159\H,5.8  
24682404,-2.9065569695,-1.9980752725\H,4.1353478297,-3.433152933,-1.91  
901123\C,2.2027850097,-1.6928409425,-5.2156273635\H,1.2031809306,-1.29  
32702385,-5.0628959854\H,2.4358338202,-1.6218742326,-6.2785741607\H,2.  
1952679912,-2.7456650898,-4.9331005983\\Version=ES64L-G16RevC.01\HF=-1



264.0839574\S2=0.777574\S2-1=0.\S2A=0.75044\RMSD=8.594e-09\RMSF=1.047e-06\Dipole=1.3659224,-0.853016,-0.6313212\Quadrupole=11.7179463,-8.1327651,-3.5851812,0.7945639,-11.1295638,-8.701315\PG=C01 [X(C18H29N2O6)]\@\Sum of electronic and thermal Free Energies= -1263.683785

### **OH\_HAT complex**

1\1\GINC-SPARTAN-BM006\FOpt\UM062X\CC-pVTZ\C18H29N2O6(2)\UWILLE\21-Jan-2022\0\#\#p scf=(qc,direct) opt=(calcfc,maxcycle=500) freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,0.199922885,-0.3561141962,0.6910014056\H,-0.7516475055,-0.2772435513,1.2138089087\C,0.8548959739,-1.6769561309,1.0372459501\H,0.6466476614,-0.688560373,-1.3369854112\C,-1.1868535807,0.2215159403,-1.2490499851\C,-1.2293718322,0.2855840076,-2.7541311749\H,-2.2422610018,0.0781185765,-3.088272207\H,-0.9729407032,1.3023443744,-3.0541763108\H,-0.5334148109,-0.4035266774,-3.226177176\O,1.3817783518,-2.4050064391,0.23490878\O,0.8232657563,-1.9060739316,2.3444028426\C,1.486670019,-3.0971512806,2.787737879\H,2.5400868212,-3.0576723059,2.521004491\H,1.3652940521,-3.11982938,3.8644529167\H,1.0271624517,-3.9707132212,2.331696846\O,-2.0997998936,0.6483882167,-0.5569941101\N,-0.0606126663,-0.314564848,-0.7241768875\C,1.1272218217,0.7952929029,1.1494561691\H,2.090681874,0.6751169903,0.6491565042\H,1.2907284353,0.6946334022,2.2221518767\C,0.5368594057,2.1380654338,0.8265058264\C,-0.3253229363,2.770228656,1.7175309979\C,0.788568668,2.7558156686,-0.3952257245\C,-0.9180597604,3.9839400594,1.4073162958\H,-0.5393311348,2.3056282764,2.6727709413\C,0.2062469986,3.9717089164,-0.7204849949\H,1.4595832895,2.2831742736,-1.1024869757\C,-0.6452017003,4.5940725927,0.1853564944\H,-1.5806255497,4.4693541098,2.1123507295\H,0.4167075551,4.4586512715,-1.6629984739\O,-1.18548438,5.7937312995,-0.1623524528\H,-1.4046634276,6.2848865106,0.6430549481\N,2.7312718132,6.1865450299,2.5294149533\C,2.6400348387,4.7863713993,2.1017115533\H,2.5972911345,4.1145625923,2.9708346382\C,4.0014530613,6.5602370045,3.1508714516\H,4.7819390503,6.4315541467,2.4018326971\H,3.9767966144,7.6235397223,3.3743549319\C,4.3589576186,5.7661019466,4.4045633933\H,3.5761408025,5.8444141383,5.1606216708\H,4.5020784518,4.7095200704,4.1779429254\H,5.2857433593,6.1435615106,4.8353240111\C,1.5366573064,6.6154218796,3.1602591129\H,1.0226623562,5.8246023566,3.7201746845\C,1.6038153853,7.8939296768,3.9581008292\H,0.594107541,8.1667663803,4.2556392774\H,2.2022668215,7.7562350842,4.8560983724\H,2.0300106015,8.697366644,3.359466286\O,0.5931298472,6.8709099431,2.0222877198\O,-0.6377550877,6.9008368493,2.4130868665\C,3.7672102248,4.3675879796,1.1760876034\H,3.8524157027,5.0633806871,0.340591625\H,4.7287083157,4.3211951195,1.6868672687\H,3.5522852855,3.376603682,0.7770396189\H,1.6940118181,4.6736180128,1.5736286815\Version=ES64L-G16RevC.01\HF=-1264.0923518\S2=0.755267\S2-1=0.\S2A=0.750016\RMSD=3.927e-09\RMSF=1.760e-06\Dipole=2.9564384,-0.6260786,1.9026429\Quadrupole=-7.131505,-8.3377142,15.4692192,18.0990871,10.1276191,14.5051311\PG=C01 [X(C18H29N2O6)]\@\Sum of electronic and thermal Free Energies= -1263.690832

### **TS<sub>HAT\_OH</sub>**

1\1\GINC-SPARTAN-BM121\FTS\UM062X\CC-pVTZ\C18H29N2O6(2)\UWILLE\13-Jun-2022\0\#\#p opt=(ts,noeigentest,calcfc,maxcycle=500) freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,0.2

434817054,-0.3232613977,-0.6263933388\H,-0.7786389715,-0.3521734067,-1.0012047925\C,0.8598540529,-1.702523752,-0.74925178\H,0.9731738286,-0.2415912389,1.344445837\C,-0.8263483351,0.7451045179,1.3000064582\C,-0.6672953443,1.124650977,2.7489171998\H,-0.384815769,2.1771237475,2.7912017854\H,0.0918361677,0.5375721745,3.2594342386\H,-1.6247442349,1.0108576243,3.2502068496\O,1.4794153903,-2.247929981,0.1276378995\O,0.6700166276,-2.2111051967,-1.9592619431\C,1.2732940249,-3.4892213179,-2.2032347491\H,2.3504799833,-3.4229412525,-2.0710001473\H,1.0278464472,-3.7405556537,-3.2283852113\H,0.8656072154,-4.2288862803,-1.5185932008\O,-1.8097878827,1.0664970784,0.649082478\N,0.2052027763,0.0528715455,0.7618172532\C,1.0694390937,0.6682000677,-1.484734762\H,2.1001675621,0.6524602746,-1.1261239332\H,1.059004974,0.3164437328,-2.5156499356\C,0.5119296106,2.0558693818,-1.3962447782\C,-0.4882481809,2.4748158926,-2.2840015431\C,0.9513019321,2.936626966,-0.4037746738\C,-1.0372838024,3.731646754,-2.1892210486\H,-0.8264432657,1.7959677469,-3.0569973706\C,0.3990188157,4.1921971567,-0.279259256\H,1.7356160338,2.6228917513,0.2732967069\C,-0.620552028,4.6123947294,-1.164826952\H,-1.8059068584,4.0677919022,-2.8718541177\H,0.7311515418,4.8812862542,0.4858622442\O,-1.1887383937,5.7856915433,-1.0322003071\H,-0.352456306,6.602441406,-1.0534251837\N,2.7617303187,6.5856117087,-3.9144867389\C,2.9310702824,5.2006758971,-4.3493468789\H,3.9126846008,5.1356419827,-4.8173260857\C,3.9412240427,7.1820598185,-3.288566781\H,4.388885506,6.4946681046,-2.5624433069\H,3.6118002061,8.0533354462,-2.7221411917\C,4.9843595216,7.6104165476,-4.3099629398\H,4.5606226786,8.3400541052,-4.9992906475\H,5.3496731599,6.7641857447,-4.8908343876\H,5.8402464127,8.0617341859,-3.8083336502\C,1.5271737735,6.9731915319,-3.356851521\O,1.4738933387,6.5486821834,-1.9324306637\O,0.5790106561,7.3227689905,-1.2665952392\C,2.8151611669,4.1522994412,-3.2467427336\H,1.8129476897,4.1433146175,-2.8199885769\H,3.518844853,4.3501956807,-2.4373085298\H,3.0270135093,3.1594138812,-3.6457115903\H,2.2079904406,4.9897084506,-5.1375282547\H,1.4839512996,8.0612968406,-3.291896757\C,0.3017120342,6.4392632401,-4.0647541926\H,-0.5897263594,6.7903826461,-3.5487450326\H,0.2856544713,6.8044481679,-5.0904947095\H,0.290554986,5.3513530396,-4.0701855166\\Version=ES64L-G16RevC.01\HF=-1264.0683145\S2=0.767604\S2-1=0.\S2A=0.750239\RMSD=5.345e-09\RMSF=1.148e-06\Dipole=2.2823175,-2.2798455,-1.2005248\Quadrupole=0.7038838,-20.6127968,19.9089131,11.5558969,-3.9385392,1.6029357\PG=C01 [X(C18H29N2O6)]\@\

Frequencies -3462.5369

Sum of electronic and thermal Free Energies= -1263.671712

### O-radical product complex

1\1\GINC-SPARTAN-BM108\FOpt\UM062X\CC-pVTZ\C18H29N2O6(2)\UWILLE\21-Jan-2022\0\#p scf=(qc,direct) opt=(calcfc,maxcycle=500) freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,0.2815464111,-0.5010475372,0.6196502626\H,-0.6106112979,-0.5622354822,1.2418065211\C,0.8614176693,-1.8915109613,0.4447159218\H,0.4465678135,-0.2887118234,-1.4650533696\C,-1.1841813925,0.7989460034,-0.8446102168\C,-1.4178565218,1.2858521965,-2.2500085845\H,-2.485931105,1.2832168883,-2.4498870531\H,-1.0629180379,2.3151555599,-2.3128619186\H,-0.8978703805,0.6901023477,-2.9958570109\O,1.1959011966,-2.3544697269,-0.6151645367\O,0.9882010005,-2.5117842383,1.6085697686\C,1.5805394198,-3.817786

0043,1.5613573297\H,2.5839260651,-3.7552690729,1.1474352602\H,1.609774  
8646,-4.1653803422,2.5872289242\H,0.9719638603,-4.4783939456,0.9488311  
521\O,-1.9104520017,1.1183611786,0.0851582908\N,-0.0940604109,0.014195  
7144,-0.6698085536\C,1.3339893394,0.3887879691,1.3328823531\H,2.235627  
0816,0.4093833363,0.7189964839\H,1.5732331679,-0.0696041081,2.29138115  
35\C,0.8107836764,1.7738034088,1.530622744\C,0.0598351667,2.0888376723  
,2.6850667364\C,1.0178038063,2.7606109779,0.5450063653\C,-0.4780688396  
,3.3279481624,2.8526100228\H,-0.0851096039,1.3244083953,3.4379545706\C  
,0.4905302373,4.0105499343,0.6839504995\H,1.6051040762,2.5104866565,-0  
.3291012962\C,-0.295592437,4.3522213584,1.8489437035\H,-1.0570792229,3  
.5874918465,3.7283977158\H,0.6484109842,4.7818191622,-0.0580654379\O,-  
0.8000336461,5.489165751,1.9900682849\H,0.0117804739,6.7410555224,1.02  
17954567\N,2.5421074166,7.0472309477,3.7719480834\C,2.2385362292,5.665  
2446739,4.14808429\H,2.5199740704,5.5224070813,5.1937845207\C,3.963169  
6901,7.3413790177,3.6101332915\H,4.4013933131,6.7960285773,2.765006811  
\H,4.0641501548,8.4010892065,3.3885723623\C,4.75103952,7.0392220368,4.  
876565987\H,4.3082774817,7.5554286981,5.7287785628\H,4.7758716081,5.97  
31057372,5.0998032105\H,5.7799199222,7.3780559269,4.762367825\C,1.6392  
634892,7.6231515011,2.833714853\H,0.622637839,7.4017178848,3.171506144  
1\C,1.7996746048,9.118895214,2.6363293559\H,0.9584847553,9.4972864376,  
2.0619348155\H,1.8247538619,9.6214810087,3.6020085562\H,2.7117371277,9  
.3478900539,2.0881699711\O,1.7920235163,6.940254449,1.5586074036\O,0.7  
219683558,7.3423532728,0.7095932546\C,2.9017893918,4.5797260867,3.3024  
071407\H,2.6698472904,4.7147586608,2.2476205284\H,3.9860203692,4.58731  
95175,3.4195163106\H,2.5425874545,3.5985021644,3.6156285195\H,1.154054  
1249,5.5525890456,4.0987986595\\Version=ES64L-G16RevC.01\HF=-1264.0919  
58\S2=0.78287\S2-1=0.\S2A=0.750678\RMSE=6.324e-10\RMSF=1.522e-06\Dipol  
e=1.6167203,-3.6788267,0.2525805\Quadrupole=8.1121379,-27.9396158,19.8  
274779,0.9392965,7.5045863,-10.4508809\PG=C01 [X(C18H29N2O6)]\@\@  
Sum of electronic and thermal Free Energies= -1263.692079

#### **Addition complex**

1\1\GINC-SPARTAN-BM006\FOpt\UM062X\CC-pVTZ\C18H29N2O6(2)\UWILLE\21-Jan  
-2022\0\#\#p scf=(qc,direct) opt=(calcfc,maxcycle=500) freq=noraman M06  
2X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,0  
.199922885,-0.3561141962,0.6910014056\H,-0.7516475055,-0.2772435513,1.  
2138089087\C,0.8548959739,-1.6769561309,1.0372459501\H,0.6466476614,-0  
.688560373,-1.3369854112\C,-1.1868535807,0.2215159403,-1.2490499851\C,  
-1.2293718322,0.2855840076,-2.7541311749\H,-2.2422610018,0.0781185765,  
-3.088272207\H,-0.9729407032,1.3023443744,-3.0541763108\H,-0.533414810  
9,-0.4035266774,-3.226177176\O,1.3817783518,-2.4050064391,0.23490878\O  
,0.8232657563,-1.9060739316,2.3444028426\C,1.486670019,-3.0971512806,2  
.7877737879\H,2.5400868212,-3.0576723059,2.521004491\H,1.3652940521,-3  
.11982938,3.8644529167\H,1.0271624517,-3.9707132212,2.331696846\O,-2.0  
997998936,0.6483882167,-0.5569941101\N,-0.0606126663,-0.314564848,-0.7  
241768875\C,1.1272218217,0.7952929029,1.1494561691\H,2.090681874,0.675  
1169903,0.6491565042\H,1.2907284353,0.6946334022,2.2221518767\C,0.5368  
594057,2.1380654338,0.8265058264\C,-0.3253229363,2.770228656,1.7175309  
979\C,0.788568668,2.7558156686,-0.3952257245\C,-0.9180597604,3.9839400  
594,1.4073162958\H,-0.5393311348,2.3056282764,2.6727709413\C,0.2062469  
986,3.9717089164,-0.7204849949\H,1.4595832895,2.2831742736,-1.10248697

57\C,-0.6452017003,4.5940725927,0.1853564944\H,-1.5806255497,4.4693541  
098,2.1123507295\H,0.4167075551,4.4586512715,-1.6629984739\O,-1.185484  
38,5.7937312995,-0.1623524528\H,-1.4046634276,6.2848865106,0.643054948  
1\N,2.7312718132,6.1865450299,2.5294149533\C,2.6400348387,4.7863713993  
,2.1017115533\H,2.5972911345,4.1145625923,2.9708346382\C,4.0014530613,  
6.5602370045,3.1508714516\H,4.7819390503,6.4315541467,2.4018326971\H,3  
.9767966144,7.6235397223,3.3743549319\C,4.3589576186,5.7661019466,4.40  
45633933\H,3.5761408025,5.8444141383,5.1606216708\H,4.5020784518,4.709  
5200704,4.1779429254\H,5.2857433593,6.1435615106,4.8353240111\C,1.5366  
573064,6.6154218796,3.1602591129\H,1.0226623562,5.8246023566,3.7201746  
845\C,1.6038153853,7.8939296768,3.9581008292\H,0.594107541,8.166766380  
3,4.2556392774\H,2.2022668215,7.7562350842,4.8560983724\H,2.0300106015  
,8.697366644,3.359466286\O,0.5931298472,6.8709099431,2.0222877198\O,-0  
.6377550877,6.9008368493,2.4130868665\C,3.7672102248,4.3675879796,1.17  
60876034\H,3.8524157027,5.0633806871,0.340591625\H,4.7287083157,4.3211  
951195,1.6868672687\H,3.5522852855,3.376603682,0.7770396189\H,1.694011  
8181,4.6736180128,1.5736286815\\Version=ES64L-G16RevC.01\HF=-1264.0923  
518\S2=0.755267\S2-1=0.\S2A=0.750016\RMSD=3.927e-09\RMSF=1.760e-06\Dip  
ole=2.9564384,-0.6260786,1.9026429\Quadrupole=-7.131505,-8.3377142,15.  
4692192,18.0990871,10.1276191,14.5051311\PG=C01 [X(C18H29N2O6)]\@\@  
Sum of electronic and thermal Free Energies= -1263.689565

#### TS<sub>addition</sub>

1\1\GINC-SPARTAN-BM007\FTS\UM062X\CC-pVTZ\C18H29N2O6(2)\UWILLE\29-May-  
2022\0\#p opt=(calcf, maxcycle=500, TS, noeigentest) freq=noraman M062X  
/cc-pVTZ scrf=(cpcm, solvent=acetonitrile) nosymm\geom&freq\0,2\C,-2.  
9543614385,2.1331375109,-0.8894007067\H,-3.4312424505,2.8294085613,-1.  
5775473734\C,-3.0007625533,0.7381866695,-1.4781118085\H,-3.5979411429,  
1.3487993586,0.952910658\C,-4.457389635,3.1964306925,0.7280631402\C,-5  
.052994411,3.0948493343,2.1084200221\H,-6.0669474426,3.4851436643,2.08  
51697341\H,-4.4619546003,3.7237979299,2.7751243883\H,-5.0545183734,2.0  
791464819,2.495824009\O,-3.3127912686,-0.2486119314,-0.8619436213\O,-2  
.6048140898,0.7335362364,-2.7447794608\C,-2.5412287389,-0.552334155,-3  
.3759362982\H,-1.843652699,-1.1940722988,-2.8431402015\H,-2.1965560636  
, -0.3687314485,-4.3868278059\H,-3.5267380366,-1.0115361545,-3.38417645  
62\O,-4.6404574612,4.172132852,0.014505084\N,-3.6901876294,2.148851227  
6,0.347183131\C,-1.4749621217,2.5421916435,-0.6921080087\H,-1.00297743  
44,1.8117316692,-0.0325513173\H,-0.9746709983,2.4968223411,-1.65940409  
36\C,-1.3628631778,3.9199510781,-0.103297623\C,-1.4562221506,5.0484370  
538,-0.9462119641\C,-1.2630001737,4.103141846,1.2509575845\C,-1.457845  
5602,6.3329819175,-0.4282974938\H,-1.5488097053,4.9053037193,-2.015342  
1718\C,-1.1456915244,5.404529811,1.822614944\H,-1.2184036387,3.2474906  
646,1.912062912\C,-1.34278522,6.5156592025,0.9402121452\H,-1.556206862  
1,7.1926233881,-1.0793409291\H,-1.4582779939,5.5506127063,2.8483678747  
\O,-1.3637686292,7.7256473141,1.5287872268\H,-1.4616193034,8.419996758  
3,0.8666536023\N,2.7369940401,6.3810094921,0.6837201447\C,4.1352083222  
,6.1054093703,0.9864357786\H,4.6788226286,5.7025617321,0.1201652077\C,  
2.4773071274,7.4711570465,-0.2466951617\H,2.9355590776,8.3771272278,0.  
1500768884\H,1.3994550661,7.6478263545,-0.243963118\C,2.9556163186,7.2  
421414651,-1.6794020291\H,2.4377169655,6.3964484479,-2.1344470588\H,4.  
0276109562,7.0416812974,-1.7104008817\H,2.7618494817,8.1235726986,-2.2

907257798\C,1.9103247843,5.2219741528,0.4950086933\O,1.4393687637,4.71335037,1.7535475551\O,0.6010260948,5.6280532631,2.3507210165\C,4.8744332136,7.3239715698,1.5163967536\H,4.3159455798,7.7834504557,2.3323906518\H,5.0301665432,8.0743696494,0.7418900552\H,5.8541069717,7.0281508692,1.8893943717\H,4.1461865332,5.327384141,1.751283515\C,2.5457440165,4.0109739961,-0.1717099371\H,3.3080714885,3.5656021236,0.4662460063\H,1.7807073141,3.2622257312,-0.3723681997\H,3.00962851,4.3028131263,-1.1127362384\H,1.0340727311,5.533394775,-0.072139356\\Version=ES64L-G16Rev C.01\HF=-1264.0538733\S2=0.786789\S2-1=0.\S2A=0.750808\RMSD=3.317e-09\RMSF=2.597e-06\Dipole=0.3268665,-0.6913669,-2.0795824\Quadrupole=-6.292197,1.9432416,4.3489554,5.9185841,-7.4590066,-18.2309183\PG=C01 [X(C18H29N2O6)]\@  
Frequencies -620.2013  
Sum of electronic and thermal Free Energies= -1263.654012

### Addition product

1\1\GINC-SPARTAN-BM064\FOpt\UM062X\CC-pVTZ\C18H29N2O6(2)\UWILLE\26-May-2022\0\#p opt=(calcf, maxcycle=500) freq=noraman M062X/cc-pVTZ scrf=(cpcm, solvent=acetonitrile) nosymm\geom&freq\0,2\C,-0.8261613983,-0.6341144821,0.4800559267\H,-1.8077659249,-0.327999265,0.1217630063\C,-0.5615178888,-2.0635023986,0.0555507516\H,-0.1220462275,-1.0804677501,2.4105142212\C,-1.6767560474,0.2398268813,2.6056435294\C,-1.4302906945,0.3139902825,4.0905058421\H,-2.3844807516,0.3851169451,4.6051488842\H,-0.8647444049,1.2247302571,4.2918876069\H,-0.8665734303,-0.5360210809,4.4671287584\O,-0.0904921585,-2.9090266029,0.7726621306\O,-0.8652520829,-2.2539230089,-1.2226742112\C,-0.5789005539,-3.5572654998,-1.7466838935\H,0.4845490437,-3.7674400106,-1.6610433276\H,-0.8808884996,-3.53056637,-2.7871497833\H,-1.1445253009,-4.3096561795,-1.202406407\O,-2.5688076573,0.8768567199,2.0642365672\N,-0.8301420126,-0.5600927727,1.9171614861\C,0.2563509149,0.2778553332,-0.1446410074\H,1.2310956026,-0.0532403146,0.2171481128\H,0.2327588392,0.1462714738,-1.2265725136\C,0.0273760423,1.7191481379,0.2155818779\C,-0.9387090875,2.4626818438,-0.5191909703\C,0.6706678877,2.2879540985,1.2619521764\C,-1.2750914704,3.769137762,-0.1409732029\H,-1.4373103362,2.0032734618,-1.3615858082\C,0.4605725591,3.7058972073,1.6696567887\H,1.4049479553,1.7287507117,1.8289900916\C,-0.6548421596,4.3596084679,0.921141938\H,-2.0458054076,4.3095932657,-0.6773206382\H,0.2648899792,3.7850001108,2.7461266192\O,-0.9515510068,5.5918581797,1.388886786\H,-1.6702525798,5.9805493869,0.8758282049\N,2.9122983884,6.6673683138,0.3107644554\C,4.2865755521,6.5977304885,-0.168276991\H,4.395818064,7.0088648791,-1.1816153466\C,2.3837504718,8.0011951344,0.5625008999\H,3.0098143282,8.4788571417,1.3166334914\H,1.3990423998,7.8774058605,1.0168147874\C,2.2747216828,8.9156160641,-0.6568246623\H,1.5744407905,8.5141197042,-1.3900247417\H,3.2425396463,9.0434199023,-1.143738915\H,1.9187648698,9.9014926274,-0.3576613982\C,1.9984218411,5.7608429271,-0.3280966159\O,2.1185747219,4.4450752874,0.2244688218\O,1.6803401575,4.478794662,1.577339806\C,5.2672301763,7.2942696979,0.761786181\H,5.1290643777,6.9509671677,1.7874327527\H,5.1457638177,8.377037249,0.7434104724\H,6.2886605981,7.0722077065,0.4557177447\H,4.5475535928,5.540248404,-0.2294301387\C,2.1818935601,5.5233594164,-1.8219357922\H,3.1130228313,4.9947422666,-2.0211425469\H,1.3550178677,4.9272918681,-2.2040350835\H,2.2060313223,6.4755939184,-2.349043574\H,

0.9889447795,6.1226255619,-0.1306129292\\Version=ES64L-G16RevC.01\HF=-1264.07138\S2=0.78036\S2-1=0.\S2A=0.750547\RMSD=3.364e-09\RMSF=1.267e-06\Dipole=0.0048682,-0.0072731,-1.4277527\Quadrupole=-12.9638962,12.0975689,0.8663273,-4.5787107,1.4152803,-6.5766184\PG=C01 [X(C18H29N2O6)]\@\Sum of electronic and thermal Free Energies= -1263.668754

## b) Entry 2 - Reaction of MeOO<sup>•</sup>

### Reactant complex

1\1\GINC-SPARTAN-BM005\FOpt\UM062X\CC-pVTZ\C13H18N1O6(2)\UWILLE\13-Mar-2022\0\#\#p opt=(calcfc,maxcycle=500) freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,-0.3691323189,5.0326543578,-1.9081424733\H,-0.4343834881,5.4374328915,-2.916634914\C,-0.1353508376,3.5376818013,-1.9808149115\H,-1.8470232955,4.7048881772,-0.4485189878\C,-2.4783678815,6.255848331,-1.6285420243\C,-3.682849097,6.4430328724,-0.7424054464\H,-4.5486692394,6.6560540882,-1.3635751159\H,-3.4993703631,7.3091029817,-0.1054198985\H,-3.881288907,5.5805661054,-0.11102883\O,-0.7095591159,2.7278575534,-1.2974289644\O,0.8191256739,3.2379742416,-2.8512928519\C,1.1768624458,1.8504431248,-2.940309419\H,1.5349147488,1.4935249238,-1.9779828699\H,1.9653546852,1.7921581012,-3.680861424\H,0.3169592152,1.2623033605,-3.2498419555\O,-2.2851509586,6.9547791305,-2.6128540987\N,-1.6207342156,5.2834082407,-1.2421169924\C,0.826570009,5.6867635805,-1.1742299481\H,0.8968635865,5.2422646725,-0.1792846081\H,1.7367770986,5.4377175667,-1.7189220892\C,0.6613572375,7.176013242,-1.071123617\C,1.1271803303,8.0148962694,-2.0779183579\C,-0.0196845233,7.7497494628,-0.0003471128\C,0.9156007062,9.3845165357,-2.0301476805\H,1.6613431167,7.5921561436,-2.9203332083\C,-0.2435787037,9.1158280961,0.0619387115\H,-0.3861991674,7.1164080796,0.7983487998\C,0.2229564049,9.9368571622,-0.9584789631\H,1.286510526,10.0247837591,-2.8209763545\H,-0.7723126355,9.5597226546,0.8943292289\O,-0.0191084224,11.2727722789,-0.8541726128\H,0.3508154307,11.7327387023,-1.6146784442\O,3.4601649891,-0.3452869777,-2.8955458717\O,2.3238922586,-0.8974893006,-3.1841270329\C,4.5286708648,-1.3105908097,-2.8822986694\H,5.4254067357,-0.7542012144,-2.6302214897\H,4.3067686586,-2.0630119167,-2.1305936316\H,4.6054958683,-1.7561621897,-3.8702522208\\Version=ES64L-G16RevC.01\HF=-1012.1978437\S2=0.754965\S2-1=0.\S2A=0.750014\RMSD=2.091e-09\RMSF=1.843e-06\Dipole=2.3663854,-1.4419291,0.3446155\Quadrupole=17.5769596,-15.5988375,-1.9781221,7.1393516,-19.3405654,7.5689647\PG=C01 [X(C13H18N1O6)]\@\Sum of electronic and thermal Free Energies= -1011.953596

### C $\alpha$ \_HAT complex

1\1\GINC-SPARTAN-BM118\FOpt\UM062X\CC-pVTZ\C13H18N1O6(2)\UWILLE\01-Jan-2022\0\#\#p scf=(qc,direct) opt=(calcfc,maxcycle=500) freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,-0.281892829,-0.2936277393,-0.99306465\H,-1.3010845686,-0.1539989462,-1.3501185854\C,0.3349054782,-1.4792349953,-1.7048457281\H,0.4633081373,-1.036215141,0.8293729962\C,-1.3685650406,-0.2010731562,1.2037079709\C,-1.1878727775,-0.461272367,2.6771582788\H,-2.1360629384,-0.7844558767,3.098142737\H,-0.9072244267,0.4796884831,3.1519948445\H,-0.417833302,

-1.200256163,2.8844338109\O,0.9474832331,-2.3607771871,-1.1585510932\O  
,0.155799357,-1.4037645533,-3.0194081425\C,0.7432625128,-2.4563018065,  
-3.7947654068\H,1.8230604351,-2.4568673803,-3.6662829403\H,0.481029371  
7,-2.2459275339,-4.8259274111\H,0.3375094355,-3.4166945446,-3.48655116  
85\O,-2.3774487828,0.3274268048,0.7592159053\N,-0.3291759049,-0.567838  
8788,0.4195010341\C,0.5421718568,0.97535377,-1.3194605055\H,1.57748285  
65,0.7959659802,-1.0214896465\H,0.519254846,1.1224671089,-2.3987224132  
\C,-0.0021594209,2.1838549515,-0.6121752114\C,-0.9873796603,2.96889825  
79,-1.2020974646\C,0.4186008089,2.5122154955,0.6741425768\C,-1.5465800  
549,4.0458499056,-0.530638479\H,-1.3293942221,2.7271741701,-2.20108912  
89\C,-0.1331904631,3.5817685801,1.3613432786\H,1.1894951929,1.91861003  
17,1.1504512282\C,-1.1221640066,4.3502262322,0.7579989254\H,-2.3115068  
473,4.6500118454,-1.002958964\H,0.1945775826,3.8357569115,2.3601576676  
\O,-1.634563876,5.3922067899,1.469909687\H,-2.3062161539,5.8442688072,  
0.9490739102\O,-1.8320009661,0.1489719366,-4.7237293568\O,-2.028855835  
6,0.6805346365,-3.5596642394\C,-0.6755552771,0.7109644188,-5.369799725  
9\H,0.2024487897,0.4499460489,-4.7839773905\H,-0.6394067442,0.25979706  
28,-6.3562869186\H,-0.8005837956,1.78858504,-5.4316102813\\Version=ES6  
4L-G16RevC.01\HF=-1012.2009644\S2=0.754711\S2-1=0.\S2A=0.750013\RMSD=6  
.927e-12\RMSF=4.025e-06\Dipole=1.8149081,-0.0935972,-2.0165672\Quadrup  
ole=-16.7579766,-5.0100437,21.7680202,-4.2361317,-2.298352,-4.3895454\  
PG=C01 [X(C13H18N1O6)]\@\n  
Sum of electronic and thermal Free Energies= -1011.952632

#### TS<sub>HAT\_C $\alpha$</sub>

1\1\GINC-SPARTAN-BM104\FTS\UM062X\CC-pVTZ\C13H18N1O6(2)\UWILLE\21-Dec-  
2021\O\#p scf=(qc,direct) opt=(ts,noeigentest,calcfc,maxcycle=500) fr  
eq=norman M062x/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom  
&freq\0,2\C,-0.8675961667,0.3385897367,-1.7594531158\H,-1.0590476062,  
0.0649278804,-3.0080622502\C,0.2495843309,-0.5954530953,-1.3910908416\  
H,-1.9813448814,-0.9591180134,-0.6173216422\C,-3.2987514897,0.42930159  
18,-1.3573500598\C,-4.4155296628,-0.3358958611,-0.7000382096\H,-4.1768  
121496,-0.5697497657,0.3361461503\H,-4.5631884675,-1.2750910846,-1.234  
8926582\H,-5.3263917898,0.2511176508,-0.7495118397\O,0.086764167,-1.61  
75624058,-0.7667368293\O,1.417784464,-0.1961600308,-1.8705337973\C,2.5  
338472446,-1.0521408022,-1.5897552658\H,2.6787196317,-1.1287350744,-0.  
5147019395\H,3.3898878216,-0.5820954349,-2.0592690988\H,2.3586732431,-  
2.0403783592,-2.0077269522\O,-3.4797947817,1.4163027582,-2.0447857778\  
N,-2.0503851736,-0.0848352872,-1.1224133609\C,-0.5265536823,1.82763311  
69,-1.7263727703\H,0.3742883433,1.9737070795,-2.3179456785\H,-1.339822  
8651,2.3737571654,-2.193931895\C,-0.3140865824,2.303588733,-0.31019736  
83\C,-1.3907613907,2.7368199443,0.4585165525\C,0.9498727558,2.28521736  
53,0.2766106125\C,-1.2179812538,3.1418831651,1.7735017581\H,-2.3796362  
937,2.7673900379,0.0169539918\C,1.1384837217,2.6870314118,1.5893515485  
\H,1.8028570996,1.9587501039,-0.3052386212\C,0.0508067428,3.1143907787  
,2.3421972788\H,-2.0633954399,3.4835227549,2.3580397423\H,2.1207560455  
,2.6791683206,2.0414353259\O,0.2844626961,3.5000841015,3.6262366266\H,  
-0.5405115807,3.7715847015,4.0417148073\O,-2.575627416,-1.0955634757,-  
3.7911715584\O,-1.4969229398,-0.329812649,-4.1205611558\C,-2.153280702  
5,-2.4398129163,-3.5886003148\H,-1.4648288548,-2.4917682558,-2.7438604  
239\H,-3.0584829936,-3.0013112967,-3.3706104516\H,-1.6748621433,-2.818

8145901,-4.489996518\\Version=ES64L-G16RevC.01\HF=-1012.1737663\S2=0.7  
59836\S2-1=0.\S2A=0.750053\RMSD=5.195e-09\RMSF=2.626e-06\Dipole=0.4607  
182,-1.4407516,1.33036\Quadrupole=7.6384413,1.193975,-8.8324163,4.3102  
283,-16.9443422,13.4513571\PG=C01 [X(C13H18N1O6)]\\@  
Frequencies -2030.9705  
Sum of electronic and thermal Free Energies= -1011.926139

### **C $\alpha$ -radical product complex**

1\1\GINC-SPARTAN-BM006\FOpt\UM062X\CC-pVTZ\C13H18N1O6(2)\UWILLE\15-Dec  
-2021\0\#p scf=(qc,direct) opt=(readfc,maxcycle=500) geom=checkpoint  
guess=check freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile  
) nosymm\geom&freq\0,2\C,-0.4090368095,-0.044086917,-1.4709754744\H,  
-4.286280086,0.8838355283,-2.6683670068\C,0.6457740897,-1.0146871944,-  
1.6908334351\H,-1.4892859187,-1.6203734864,-0.8592494024\C,-2.82224339  
7,-0.075123309,-0.9249308297\C,-3.8691720073,-0.9795764957,-0.34347590  
39\H,-4.8207791918,-0.7524756259,-0.8164537762\H,-3.9518788549,-0.7705  
131211,0.723862755\H,-3.6314581381,-2.0316730986,-0.4770927226\O,0.480  
4818858,-2.2185374081,-1.5740069601\O,1.8181528381,-0.4639971312,-2.02  
86888668\C,2.8844226658,-1.3860189859,-2.2657237968\H,3.0838592982,-1.  
9694643641,-1.3695939053\H,3.7458385423,-0.7811099441,-2.5253947089\H,  
2.6279290323,-2.0556761032,-3.0837603845\O,-3.0640641932,1.0775128123,  
-1.2588796172\N,-1.5736460121,-0.6259471476,-1.0359207944\C,-0.2054331  
786,1.4326631954,-1.5429847082\H,0.7232477761,1.6085684553,-2.08087631  
48\H,-1.0161721572,1.9006254758,-2.0956260987\C,-0.1212396873,2.049889  
9122,-0.1579684358\C,-1.063184699,2.9691599608,0.2846568068\C,0.920406  
2424,1.7020637635,0.7011984378\C,-0.9719969509,3.53585315,1.5494994919  
\H,-1.8846494607,3.2417386407,-0.364117365\C,1.0233783903,2.2559846812  
,1.9650127939\H,1.6677242414,0.9896910272,0.3711053949\C,0.0717339615,  
3.1775009524,2.3924868495\H,-1.7116184588,4.2539977157,1.8814403291\H,  
1.8331919466,1.9891255038,2.6300923035\O,0.2147531316,3.6949379273,3.6  
435803819\H,-0.5006054686,4.3130124869,3.8258916795\O,-3.8147631187,-0  
.7604538545,-3.4341869119\O,-4.6443590586,0.3921907701,-3.4332227635\C  
,-2.6575940185,-0.4529979496,-4.1865160185\H,-2.0432411432,-1.35202550  
51,-4.1548518809\H,-2.9193023692,-0.2098491493,-5.2162574\H,-2.1164953  
442,0.3812500217,-3.7327501114\\Version=ES64L-G16RevC.01\HF=-1012.2103  
265\S2=0.756717\S2-1=0.\S2A=0.750036\RMSD=1.136e-09\RMSF=5.543e-06\Dip  
ole=1.0406089,0.1453743,0.5363434\Quadrupole=-4.5462221,3.7513766,0.79  
48454,-4.4372672,-18.6963822,2.9540954\PG=C01 [X(C13H18N1O6)]\\@  
Sum of electronic and thermal Free Energies= -1011.957657

### **C $\beta$ \_HAT complex**

1\1\GINC-SPARTAN-BM125\FOpt\UM062X\CC-pVTZ\C13H18N1O6(2)\UWILLE\15-Dec  
-2021\0\#p scf=(qc,direct) opt=(readfc,maxcycle=500) geom=checkpoint  
guess=check freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile  
) nosymm\geom&freq\0,2\C,1.4514301975,-0.316847496,-0.8789182729\H,1  
.397057271,-0.2811849089,-1.9650210089\C,2.3855357131,-1.428570433,-0.  
4521717186\H,0.057245332,-0.9155832092,0.5779165786\C,-0.9938524021,-0  
.3494519106,-1.0877727788\C,-2.2886613085,-0.5628780144,-0.3468087588\  
H,-3.0073242059,-1.0248596514,-1.0184231764\H,-2.6741889118,0.41525037  
51,-0.0569547948\H,-2.170453103,-1.1712489982,0.546336771\O,2.22272840  
46,-2.1073420588,0.5297104952\O,3.4340485982,-1.5254682941,-1.26147268



8\C,4.4303264153,-2.4869961951,-0.886808833\H,4.8585543002,-2.21776294  
53,0.0758793672\H,5.1867563443,-2.4450007863,-1.6622335444\H,3.9874970  
266,-3.4783573354,-0.8330405975\O,-0.969151495,0.031609337,-2.24918203  
76\N,0.1298763235,-0.5855597008,-0.3717036972\C,2.013547389,1.02234035  
6,-0.3464477854\H,2.0529643944,0.9592918055,0.7431431924\H,3.036004615  
3,1.1368524984,-0.7073123443\C,1.1593679891,2.1807325195,-0.775580936\  
C,1.3830251032,2.8153705178,-1.9929871093\C,0.0819691108,2.6049884625,  
-0.0017765821\C,0.5571072412,3.8374110563,-2.4354280216\H,2.2152762219  
,2.5037722925,-2.612980672\C,-0.7561544613,3.6222342487,-0.4300362399\  
H,-0.1081516008,2.1289133355,0.9524874406\C,-0.5198818757,4.2393804815  
,-1.6531045849\H,0.7459487362,4.3241002941,-3.3842728905\H,-1.59194991  
03,3.9506856199,0.1724945883\O,-1.3679128598,5.234738748,-2.032819146\  
H,-1.1027433955,5.5800682073,-2.891475162\O,6.0504462402,0.1694234037,  
-1.4809284734\O,5.4830464768,0.4671264752,-0.3544095239\C,5.3814869291  
,0.7916637521,-2.5939160407\H,6.0051137041,0.5960341043,-3.4602570821\  
H,4.4016842286,0.3314811934,-2.7022267551\H,5.2980092238,1.8572058535,  
-2.397620177\Version=ES64L-G16RevC.01\HF=-1012.2006741\S2=0.754795\S2  
-1=0.\S2A=0.750013\RMSD=1.048e-09\RMSF=3.214e-06\Dipole=1.0757672,0.17  
18055,-0.7307134\Quadrupole=1.5657944,-2.6856762,1.1198818,2.9908195,-  
21.1085208,-7.0619498\PG=C01 [X(C13H18N1O6)]\@\@  
Sum of electronic and thermal Free Energies= -1011.952751

#### TS<sub>HAT\_cb</sub>

1\1\GINC-SPARTAN-BM096\FTS\UM062X\CC-pVTZ\C13H18N1O6(2)\UWILLE\18-Jan-  
2022\0\#p opt=(ts,noeigentest,calcf, maxcycle=500) freq=noraman M062X  
/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,1.6  
152587638,-1.0239684128,-0.3399924714\H,1.5119144871,-1.9710441234,-0.  
8715111033\C,2.5808348341,-1.2552158541,0.8139029502\H,0.2233821698,0.  
1233055547,0.7557105296\C,-0.7752074874,-1.4805529567,-0.0180648607\C,  
-2.0593376003,-0.9813727761,0.5901993005\H,-1.9115298007,-0.1546763287  
,1.2799376597\H,-2.5433328913,-1.8081095186,1.1044504552\H,-2.71475258  
2,-0.6584361427,-0.2181454413\O,2.3142021164,-1.0921552819,1.975008999  
9\O,3.7684019342,-1.6455174674,0.3669748993\C,4.7730015501,-1.86910602  
1,1.3643576103\H,4.9529964531,-0.9538506728,1.9231472985\H,5.663452715  
5,-2.1688290301,0.8240488465\H,4.4537703148,-2.6552975086,2.0443489835  
\O,-0.7286906641,-2.5193682952,-0.6627482559\N,0.308496202,-0.69093050  
95,0.1688000446\C,2.178562249,0.0404326404,-1.2793401121\H,2.650865761  
2,0.871340364,-0.7561951454\H,3.1777717591,-0.566930675,-1.8364566257\  
C,1.3613658641,0.4572379878,-2.4161736275\C,0.4362784786,-0.4005250851  
,-3.0271019481\C,1.5393926841,1.7318398284,-2.9737453302\C,-0.27674036  
24,-0.0042685643,-4.1424696972\H,0.2627978805,-1.3893047103,-2.6216820  
766\C,0.8350418662,2.1372365171,-4.0884211637\H,2.2437245699,2.4148481  
143,-2.5149749198\C,-0.0777270429,1.2660177078,-4.6801212231\H,-0.9912  
637197,-0.676005592,-4.6016372447\H,0.9728769294,3.1219672897,-4.51267  
79308\O,-0.7472911735,1.7074206421,-5.7716845007\H,-1.3444207909,1.023  
669575,-6.0938528693\O,3.7133400373,-0.7754716432,-3.8122226945\O,3.98  
49158634,-1.2125401433,-2.5441363652\C,4.5326467571,0.3499910446,-4.09  
44996061\H,5.5840950619,0.0693291753,-4.044487676\H,4.2685090569,0.664  
9224759,-5.1014663781\H,4.3244827557,1.1507783957,-3.3840563104\Versi  
on=ES64L-G16RevC.01\HF=-1012.1685193\S2=0.765778\S2-1=0.\S2A=0.750178\  
RMSD=7.215e-09\RMSF=1.932e-06\Dipole=0.0747688,2.0428661,-0.1103275\Qu

adrupole=10.5986295,-11.9403271,1.3416976,5.3715246,4.9438329,-5.48218  
11\PG=C01 [X(C13H18N1O6)]\ \@  
Frequencies -2029.2327  
Sum of electronic and thermal Free Energies= -1011.923204

### **C $\beta$ -radical product complex**

1\1\GINC-SPARTAN-BM006\FOpt\UM062X\CC-pVTZ\C13H18N1O6(2)\UWILLE\17-Feb  
-2022\0\ \#p opt=(calcfc,maxcycle=500) freq=noraman M062X/cc-pVTZ scrf=  
(cpcm,solvent=acetonitrile) nosymm\ \geom&freq\ \0,2\C,2.6607889274,-1.4  
064281271,2.0358592902\H,2.4837374943,-1.2575544754,0.9684641486\C,3.9  
757907491,-2.162402152,2.1973870892\H,1.9319997393,-2.9942150103,3.205  
7549156\C,0.3196056512,-2.0535466218,2.3756547339\C,-0.6303816852,-2.9  
878843777,3.0712493597\H,-1.2678281918,-3.4515738835,2.3211830891\H,-1  
.2651317653,-2.3992576126,3.7315749545\H,-0.1236412974,-3.7568236549,3  
.6472574931\O,4.1298172977,-3.0897956456,2.9513834603\O,4.9277136639,-  
1.6462134968,1.437616823\C,6.2297262776,-2.2325217802,1.5779828212\H,6  
.5737894389,-2.1294187902,2.6042097519\H,6.8737360875,-1.6839753836,0.  
900778213\H,6.1940435241,-3.2847454266,1.30702907\O,-0.1019860369,-1.1  
568920322,1.6423798211\N,1.6249558826,-2.2494273401,2.5978025246\C,2.7  
618246334,-0.0912679552,2.7546988173\H,2.467436096,-0.1090209928,3.796  
3164698\C,3.2785301459,1.100859264,2.2132564745\C,3.721919835,1.225871  
3378,0.8748057344\C,3.3686463604,2.2558401135,3.0310094936\C,4.2191656  
626,2.4183664528,0.3948213951\H,3.6672167936,0.3756442198,0.2099193083  
\C,3.8626920928,3.4456781277,2.5524710412\H,3.0368865982,2.1917268347,  
4.0595107564\C,4.2943352301,3.5357595334,1.2272186507\H,4.5553885094,2  
.4937297114,-0.632344252\H,3.9264857802,4.3206457028,3.1846042311\O,4.  
7767989817,4.7308078158,0.8044467176\H,5.039421374,4.6733822664,-0.120  
4053661\O,1.6192804169,-0.4838891029,-1.0138639899\C,1.9939324913,0.19  
90780306,-2.185821951\O,0.8553954269,0.4605577557,-0.2573133057\H,0.54  
37701206,-0.1152211758,0.4797392184\H,2.5921198006,-0.5065417384,-2.75  
87135937\H,2.5890280054,1.0820055581,-1.9430436824\H,1.1131836577,0.49  
45799713,-2.7582854667\ \Version=ES64L-G16RevC.01\HF=-1012.2017934\ S2=0  
.777694\ S2-1=0.\ S2A=0.750446\RMSD=9.627e-09\RMSF=1.472e-06\Dipole=1.59  
41453,-0.9610017,-0.058631\Quadrupole=8.1305357,-8.1676617,0.0371259,1  
.0858774,-9.0814244,-8.5510353\PG=C01 [X(C13H18N1O6)]\ \@  
Sum of electronic and thermal Free Energies= -1011.951528

### **OH\_HAT complex**

1\1\GINC-SPARTAN-BM086\FOpt\UM062X\CC-pVTZ\C13H18N1O6(2)\UWILLE\11-Nov  
-2021\0\ \#p scf=(qc,direct) geom=checkpoint guess=check opt=(readfc,ma  
xcycle=500) freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile  
) nosymm\ \geom&freq\ \0,2\C,0.2097370795,-0.566391288,-0.6280090508\H,-  
0.5888534026,-0.2996271672,-1.3180592082\C,0.6548585084,-1.9878708307,  
-0.9015191928\H,0.1873339551,-0.9770004035,1.4351612014\C,-1.401155763  
3,0.2509489209,1.0324508118\C,-1.7203189651,0.3213863496,2.503543201\H  
, -2.7987145641,0.2907988359,2.6335544516\H,-1.3588018349,1.2792653041,  
2.8795476971\H,-1.253761412,-0.4768488677,3.0754316681\O,0.8665051956,  
-2.8104758147,-0.0471659973\O,0.8349947548,-2.1985041438,-2.1999527597  
\C,1.3308564112,-3.4942578573,-2.5608441403\H,2.2975129347,-3.66636640  
18,-2.0935571344\H,1.4240987489,-3.4851680226,-3.6405373278\H,0.630071  
9348,-4.2624920184,-2.2430212903\O,-2.0722389035,0.8379112093,0.195960

2341\N,-0.3107470826,-0.4831036338,0.7116052916\C,1.4114614336,0.38418  
78879,-0.84931522\H,2.2149438854,0.0755513024,-0.177147846\H,1.7621086  
874,0.2554150987,-1.8729457829\C,1.0351604472,1.8155907559,-0.59262755  
97\C,0.5190108612,2.6107593524,-1.6105775067\C,1.1276223807,2.36398596  
37,0.6842619752\C,0.0975001552,3.9095804759,-1.3697105479\H,0.43720831  
62,2.2067597094,-2.6126978842\C,0.7082221641,3.6588499995,0.944070904\  
H,1.5314764378,1.7659531084,1.4923270981\C,0.187681132,4.4387786276,-0  
.0844505705\H,-0.3017983167,4.5145760994,-2.1736530568\H,0.7821977891,  
4.0821714686,1.9366317688\O,-0.2103670709,5.7008014377,0.2137211139\H,  
-0.5221016872,6.1529420702,-0.5883978108\O,0.3862764752,7.3187603823,-  
2.5211258488\O,-0.8407542994,7.1183852523,-2.1599902152\C,0.4603842294  
,8.077879787,-3.744903521\H,-0.0172188124,9.0395390658,-3.580750133\H,  
1.5188002069,8.1894124782,-3.9531069947\H,-0.0426347894,7.5166441563,-  
4.5271543869\Version=ES64L-G16RevC.01\HF=-1012.2037882\S2=0.755206\S2  
-1=0.\S2A=0.750015\RMSD=6.357e-09\RMSF=1.094e-06\Dipole=1.7403833,0.35  
13447,-1.8521043\Quadrupole=-21.9748562,12.7396624,9.2351938,6.6590069  
,-6.3974113,-22.6822765\PG=C01 [X(C13H18N1O6)]\@\  
Sum of electronic and thermal Free Energies= -1011.956407

#### TS<sub>HAT\_OH</sub>

1\1\GINC-SPARTAN-BM007\FTS\UM062X\CC-pVTZ\C13H18N1O6(2)\UWILLE\17-Dec-  
2021\0\#p scf=(qc,direct) opt=(ts,noeigentest,readfc,maxcycle=500) ge  
om=checkpoint guess=check freq=noraman M062X/cc-pVTZ scrf=(cpcm,solven  
t=acetonitrile) nosymm\geom&freq\0,2\C,0.3387081858,-0.1253829106,-0  
.7906969161\H,-0.5665644121,-0.1254021618,-1.3962289599\C,0.9956478374  
,-1.4888350448,-0.8755039924\H,0.5809679316,-0.217825603,1.2959147785\  
C,-1.1731764754,0.7765211843,0.9127910878\C,-1.3681824809,1.0219601107  
,2.3861180367\H,-2.4154964434,0.8696348404,2.6327642293\H,-1.119405447  
,2.064084427,2.5893967936\H,-0.7434921597,0.385082183,3.0072663205\O,1  
.4037171839,-2.1039539055,0.0760184305\O,1.1049587571,-1.8958103954,-2  
.1328214366\C,1.7749303083,-3.1486543057,-2.329754318\H,2.7901145149,-  
3.0914820907,-1.9446190404\H,1.7801353489,-3.3154523733,-3.4004653122\  
H,1.2345999337,-3.9426353726,-1.8200950351\O,-1.9807715729,1.158237862  
6,0.0784794823\N,-0.0302648451,0.1337271283,0.5756332625\C,1.321677069  
,0.9344813259,-1.3496377285\H,2.2391111968,0.8931374851,-0.7601100921\  
H,1.561124636,0.6675399466,-2.3781051216\C,0.7248626441,2.3072158998,-  
1.286807899\C,-0.0654082172,2.7832712926,-2.3426644484\C,0.902104029,3  
.108255014,-0.1560763953\C,-0.6652878529,4.0178081138,-2.2752721942\H,  
-0.1994918273,2.165732153,-3.2220559162\C,0.2930877839,4.3407828695,-0  
.0630187059\H,1.5231176459,2.7507053926,0.6551630838\C,-0.5145962992,4  
.8158650147,-1.120090276\H,-1.2715657512,4.3979680268,-3.0862672792\H,  
0.4245847677,4.9709477059,0.8064942903\O,-1.125176301,5.9781388139,-1.  
035761061\H,-0.3316598213,6.7921297766,-0.947464516\O,1.5849928302,6.5  
58595619,-1.5347350684\O,0.6996135035,7.468155655,-1.0544122163\C,1.62  
3293203,6.647514426,-2.9563413779\H,2.2822945713,5.8491992374,-3.28733  
25764\H,0.6188449765,6.5114970744,-3.3561911877\H,2.0155200482,7.62094  
45849,-3.247557725\Version=ES64L-G16RevC.01\HF=-1012.1774829\S2=0.767  
955\S2-1=0.\S2A=0.750243\RMSD=5.962e-09\RMSF=1.804e-06\Dipole=2.110156  
, -2.3458694,-0.9441949\Quadrupole=0.0424245,-23.5409575,23.4985331,7.5  
232836,-7.9411906,-0.0549343\PG=C01 [X(C13H18N1O6)]\@\  
Frequencies -2807.9687

Sum of electronic and thermal Free Energies= -1011.931950

### O-radical product complex

```
1\1\GINC-SPARTAN-BM121\FOpt\UM062X\CC-pVTZ\C13H18N1O6(2)\UWILLE\15-Dec
-2021\0\#p scf=(qc,direct) opt=(readfc,maxcycle=500) geom=checkpoint
guess=check freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile
) nosymm\geom&freq\0,2\C,0.3015355134,-0.4738469087,-0.6018609185\H,
-0.6603582106,-0.6095108984,-1.095069944\C,0.9007408334,-1.8339718917,
-0.2996574995\H,0.7187575931,0.0294436402,1.3962424146\C,-0.9720609689
,1.050018708,0.8246562595\C,-1.0357165312,1.734251286,2.1641742426\H,-
2.0648371486,1.7270354072,2.5137288424\H,-0.7324676978,2.7725149386,2.
0262809053\H,-0.3882297303,1.2740783999,2.9059782738\O,1.3563278786,-2
.1478866042,0.7696435726\O,0.8933769672,-2.613748539,-1.3707533503\C,1
.4907850849,-3.9080496434,-1.2074578472\H,2.535211474,-3.8013934311,-0
.924844579\H,1.401935611,-4.3972557437,-2.1702144368\H,0.959129364,-4.
4672959726,-0.4415926233\O,-1.8044185117,1.2481353476,-0.0482695847\N,
0.0869137189,0.2270851841,0.6358354052\C,1.2563717188,0.2871201568,-1.
5596362358\H,2.2284033846,0.3755691965,-1.0724546915\H,1.3715939341,-0
.3055854463,-2.4659503812\C,0.7159801233,1.6411832859,-1.8840470375\C,
-0.1717415778,1.8090114868,-2.9701037906\C,1.0475311052,2.7516313843,-
1.0797290305\C,-0.7210711879,3.0239281799,-3.2428564253\H,-0.413350415
2,0.9505249063,-3.5838124027\C,0.5074108345,3.9799819334,-1.3225461594
\H,1.736649922,2.6118794279,-0.2568425557\C,-0.4110361719,4.1729037254
,-2.4220037357\H,-1.4022153587,3.1720128193,-4.0693794978\H,0.74582359
7,4.8440412724,-0.7150701504\O,-0.9194307866,5.2909738851,-2.665221027
6\H,-0.6135520627,6.7471637182,-1.7523435288\O,0.8905143328,7.21047416
75,-0.7129536115\O,-0.3569661959,7.5759852776,-1.287978488\C,1.8802260
548,7.3695471707,-1.7089273766\H,1.9043399648,8.3995426395,-2.06562854
43\H,2.8241780374,7.1182331959,-1.2276559486\H,1.7005105082,6.69077033
84,-2.5462745133\Version=ES64L-G16RevC.01\HF=-1012.2035102\S2=0.78252
8\S2-1=0.\S2A=0.75065\RMSD=3.495e-10\RMSF=3.260e-07\Dipole=2.5303779,-
3.9716256,-0.251254\Quadrupole=11.9827858,-31.2974546,19.3146688,14.25
25664,-7.2100896,12.4574662\PG=C01 [X(C13H18N1O6)]\@\
Sum of electronic and thermal Free Energies= -1011.955005
```

### Addition complex

```
1\1\GINC-SPARTAN-BM095\FOpt\UM062X\CC-pVTZ\C13H18N1O6(2)\UWILLE\14-Nov
-2021\0\#p scf=(qc,direct) geom=checkpoint guess=check opt=(readfc,ma
xcycle=500) freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile
) nosymm\geom&freq\0,2\C,0.5090817426,-0.2562594419,-0.0150611656\H,
0.0274400474,-0.3388842182,-0.9878378175\C,1.4858122603,-1.400564196,0
.1602764282\H,-0.2185590753,-0.6004955726,1.9281253477\C,-1.814072608,
-0.0785844999,0.7530538987\C,-2.7142670063,-0.1044671919,1.9612821544\
H,-3.6849613341,-0.4966824051,1.671186917\H,-2.8484172737,0.9229597275
,2.3023571341\H,-2.3045566941,-0.6920535695,2.7792898624\O,1.592519309
9,-2.0548889887,1.1661115913\O,2.2472494664,-1.5572329548,-0.915767964
3\C,3.2599171613,-2.5679876145,-0.8246573292\H,3.9423485279,-2.3388288
586,-0.009682652\H,3.7801292005,-2.5518493468,-1.7752277138\H,2.801824
3262,-3.5393342443,-0.6548189942\O,-2.2342830181,0.1913513647,-0.36273
56025\N,-0.510067224,-0.3455950534,0.99762501\C,1.2894703657,1.0789464
532,0.0539690006\H,1.798625923,1.1242139254,1.0190395997\H,2.049267060
```

2,1.0697727127,-0.7268639335\C,0.3761824828,2.2600614845,-0.1098782504  
\C,0.1096667693,2.7864154366,-1.3692352091\C,-0.2726522404,2.821487378  
8,0.9881700891\C,-0.7803575355,3.8376898331,-1.5368237418\H,0.60334396  
32,2.3687765879,-2.2383451486\C,-1.1695237177,3.8661526409,0.838159653  
7\H,-0.0714961726,2.4353054926,1.9800716648\C,-1.4252358599,4.37790648  
37,-0.4291534795\H,-0.9733314764,4.2411737937,-2.5232742878\H,-1.66162  
32424,4.3098215426,1.6926836575\O,-2.3058122832,5.4102829506,-0.526949  
7389\H,-2.3889546444,5.683501023,-1.4463444065\O,1.2290605997,5.857064  
1258,1.7876928049\O,0.2757180801,6.6756985164,1.471024885\C,1.97082710  
65,5.4394925273,0.6271234914\H,2.4673039909,6.3087399601,0.2028568971\  
H,2.6917798678,4.7105035148,0.9842727772\H,1.2787339344,4.9931384601,-  
0.0832738896\\Version=ES64L-G16RevC.01\HF=-1012.2006949\S2=0.754699\S2  
-1=0.\S2A=0.750013\RMSD=2.286e-09\RMSF=1.503e-06\Dipole=2.272099,-0.78  
76371,-0.6419968\Quadrupole=6.2905057,-12.2837409,5.9932352,5.3654507,  
-5.9575916,-12.1937108\PG=C01 [X(C13H18N1O6)]\@\@  
Sum of electronic and thermal Free Energies= -1011.952823

#### TS<sub>addition</sub>

1\1\GINC-SPARTAN-BM125\FTS\UM062X\CC-pVTZ\C13H18N1O6(2)\UWILLE\15-Dec-  
2021\0\#p scf=(qc,direct) opt=(ts,noeigentest,readfc,maxcycle=500) ge  
om=checkpoint guess=check freq=noraman M062X/cc-pVTZ scrf=(cpcm,solven  
t=acetonitrile) nosymm\geom&freq\0,2\C,0.4749438898,0.0185026199,-0.  
2470012396\H,-0.0638610099,0.1085990054,-1.1889658855\C,1.4192115137,-  
1.1634910129,-0.3230038866\H,-0.1529595472,-0.6250017173,1.6545141825\  
C,-1.7874352037,0.1461251253,0.6878948958\C,-2.6204717445,-0.052187393  
7,1.9277942714\H,-3.6040867554,-0.412089715,1.6381510246\H,-2.74186424  
71,0.9187196326,2.4094343562\H,-2.1668546694,-0.7401239675,2.636994059  
3\O,1.5515819941,-1.9845196363,0.5483398856\O,2.119944774,-1.151442798  
6,-1.4501634027\C,3.0988844174,-2.1895767098,-1.5902213322\H,3.8243917  
509,-2.1283561764,-0.7826083006\H,3.5765377175,-2.0181395135,-2.547770  
991\H,2.6140102523,-3.1626217691,-1.5725096074\O,-2.2562937184,0.61716  
01197,-0.3382711291\N,-0.4867972688,-0.2101496582,0.7989405601\C,1.302  
4497424,1.3037470935,-0.0062515486\H,1.8571626481,1.1829368004,0.92569  
88526\H,2.022723841,1.4041774319,-0.8178773495\C,0.4172409549,2.515114  
7677,0.0676340626\C,-0.0083774953,3.1421318423,-1.1215666102\C,-0.0595  
083332,2.9756836771,1.2658190202\C,-0.9317982125,4.1758220897,-1.10231  
99302\H,0.3676459384,2.7854673243,-2.0721952063\C,-0.8845130064,4.1362  
836033,1.3356825533\H,0.2392854297,2.5025784607,2.1921892818\C,-1.4186  
795945,4.6326022015,0.1088895132\H,-1.2850048262,4.6158300639,-2.02636  
48996\H,-1.4758113819,4.306605873,2.2264364467\O,-2.346650882,5.606058  
599,0.2196750386\H,-2.6269354197,5.9033249201,-0.653691819\O,1.2952083  
206,5.5959286913,0.9410609946\O,0.2669393742,5.4788846669,1.8551988908  
\C,1.0766129193,6.7576144656,0.1593865465\H,1.0598126834,7.6437901112,  
0.7944571664\H,1.9156075445,6.8111338736,-0.5319004885\H,0.1422236101,  
6.6820730085,-0.3959089761\\Version=ES64L-G16RevC.01\HF=-1012.1693731\  
S2=0.784367\S2-1=0.\S2A=0.750721\RMSD=1.322e-09\RMSF=1.249e-06\Dipole=  
0.6717354,-0.3452273,-1.1187405\Quadrupole=-0.8687313,-1.1192446,1.987  
9759,-7.0813234,-8.1587685,-14.7283717\PG=C01 [X(C13H18N1O6)]\@\@  
Frequencies -601.7533  
Sum of electronic and thermal Free Energies= -1011.916944

### Addition product

```
1\1\GINC-SPARTAN-BM102\FOpt\UM062X\CC-pVTZ\C13H18N1O6(2)\UWILLE\11-Nov
-2021\0\#p scf=(qc,direct) geom=checkpoint guess=check opt=(readfc,ma
xcycle=500) freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile
) nosymm\geom&freq\0,2\C,0.3228489456,-0.5443834192,0.071770039\H,-0
.0593225177,-0.5024382071,-0.9469613988\C,1.0448532128,-1.859329297,0.
2807911863\H,-0.6533561752,-0.7908566777,1.9182551781\C,-1.9810678396,
0.082330578,0.6255387393\C,-2.9821678368,0.2170228976,1.7438209293\H,-
3.9803363698,0.0520473148,1.3479847069\H,-2.9283868552,1.2387136877,2.
1221425375\H,-2.7892492048,-0.4686195905,2.565299308\O,0.9175384729,-2
.5573732125,1.2541876796\O,1.8755423129,-2.1204881479,-0.721230301\C,2
.6658441279,-3.3089824263,-0.5861331017\H,3.2849464156,-3.2449723351,0
.3054989557\H,3.2814882705,-3.3574900469,-1.4766893818\H,2.0188709261,
-4.180301589,-0.5194354903\O,-2.2214698329,0.4665185942,-0.5098825426\
N,-0.7961317868,-0.4703853188,0.9735309041\C,1.3249378214,0.613713211,
0.2916834313\H,1.7105298046,0.543584401,1.3101167299\H,2.1591664475,0.
4798629565,-0.3972308174\C,0.6705442667,1.9492557315,0.073131545\C,0.4
968186722,2.4174246039,-1.2599496142\C,0.1905235919,2.6687480494,1.114
2737019\C,-0.2057509134,3.6016880586,-1.5165232713\H,0.8927959409,1.83
96379703,-2.0837065418\C,-0.4876782341,3.9849781496,0.9470627685\H,0.3
129329604,2.317916503,2.1317426224\C,-0.7109415436,4.340447596,-0.4866
255401\H,-0.3680120737,3.9279548513,-2.5368737421\H,-1.4483965228,4.00
68879307,1.4767784809\O,-1.4384779772,5.4671884391,-0.6403911557\H,-1.
5513960184,5.6671114224,-1.5772902101\O,1.5171362962,5.1530933249,1.09
55746934\O,0.2087188533,5.0403900278,1.6488662273\C,1.6114544073,6.447
3846753,0.5315816821\H,1.441611493,7.2113937325,1.2909352891\H,2.63199
44779,6.520156644,0.1595442564\H,0.9039764441,6.5715799369,-0.28798141
31\Version=ES64L-G16RevC.01\HF=-1012.1853697\S2=0.780127\S2-1=0.\S2A=
0.750537\RMSD=2.269e-09\RMSF=1.883e-06\Dipole=0.8575252,-0.2215704,-0.
6595502\Quadrupole=-2.1034005,2.9747348,-0.8713343,-4.8103367,-7.68344
38,-9.7996103\PG=C01 [X(C13H18N1O6)]\@\
Sum of electronic and thermal Free Energies= -1011.931345
```

### c) Entry 3 - Reaction of MeOO• with Tyr H-bonded with trimethyl amine (TMA) (ArOH•••NMe<sub>3</sub>)

#### Reactant complex

```
1\1\GINC-SPARTAN-BM022\FOpt\UM062X\CC-pVTZ\C16H27N2O6(2)\UWILLE\24-Mar
-2022\0\#p opt=(calcfc,maxcycle=500) freq=noraman M062X/cc-pVTZ scrf=
(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,-1.0086312763,3.0
347428396,-7.2784174427\H,-1.7602372553,2.3276727886,-7.6245156297\C,-
0.4380171448,2.55719148,-5.959210184\H,-1.1783134701,4.9800084303,-6.4
97614762\C,-2.8134097899,4.6469425151,-7.6847712724\C,-3.26147611,6.06
9753281,-7.4693667323\H,-4.3425437235,6.0875725428,-7.361155763\H,-2.9
984276865,6.6422565457,-8.3597048338\H,-2.7935889655,6.5341641308,-6.6
048134248\O,-0.2285796147,3.2727941052,-5.0122157623\O,-0.1463772841,1
.2636484386,-5.9960974162\C,0.4741961958,0.7251183945,-4.8190045411\H,
1.4194036825,1.2278072912,-4.6303407173\H,0.6405842185,-0.325729556,-5
.0231930185\H,-0.1812660764,0.8492141314,-3.9611120872\O,-3.4520945986
,3.8657694749,-8.3753161809\N,-1.6496473749,4.3091481919,-7.0835741791
\C,0.1362391764,3.1101093477,-8.317558295\H,0.8943905466,3.796666429,-
```

7.9343566706\H,0.588263004,2.1216109695,-8.3962013181\C,-0.3620418402,  
3.5737651802,-9.6565819319\C,-0.8271144035,2.6631067553,-10.5998032908  
\C,-0.4333473044,4.9295253231,-9.9682991319\C,-1.3557706507,3.08295683  
42,-11.8107044894\H,-0.7790309589,1.6020636644,-10.3840641323\C,-0.964  
0369605,5.3664614821,-11.1713679594\H,-0.071110148,5.6589352936,-9.253  
4513882\C,-1.4361507548,4.4451168548,-12.1063027219\H,-1.7030829369,2.  
3578384467,-12.5352870134\H,-1.0170702347,6.4210521416,-11.4067010278\  
O,-1.9432851946,4.9054153893,-13.2661469782\O,2.8145207837,-0.96130073  
22,-3.5131835473\O,1.9649981954,-0.6119243669,-2.5991102439\C,3.899459  
7969,-1.7297922876,-2.9600126967\H,4.5484280256,-1.9678533172,-3.79630  
52842\H,4.4143021604,-1.121218423,-2.2217423001\H,3.4915165719,-2.6298  
748083,-2.5083869437\H,-2.3053209676,4.1521901881,-13.830331833\C,-2.2  
716940209,2.0384028129,-15.4501535253\H,-1.3936693099,2.4728686611,-15  
.9254639966\H,-1.9451557549,1.3600944183,-14.6628793766\H,-2.827653532  
1,1.4591575293,-16.1984059192\C,-3.5235235345,4.0305218466,-15.9216513  
302\H,-4.1411696765,3.5306186372,-16.6781151886\H,-4.1028069928,4.8359  
385219,-15.4719401009\H,-2.648512099,4.4578669469,-16.4092654962\C,-4.  
251954454,2.5442476298,-14.1847657606\H,-3.9191159887,1.8666582763,-13  
.3994296479\H,-4.8248033082,3.3517605754,-13.7304721438\H,-4.905342094  
5,1.9902146178,-14.8705041458\N,-3.0957948663,3.0989931366,-14.8812342  
233\\Version=ES64L-G16RevC.01\HF=-1186.6622636\S2=0.754963\S2-1=0.\S2A  
=0.750014\RMSD=2.011e-09\RMSF=3.505e-06\Dipole=1.7314695,-1.801746,-0.  
4899857\Quadrupole=-7.2440325,-16.6766099,23.9206424,-3.4518068,-2.137  
1165,24.6414543\PG=C01 [X(C16H27N2O6)]\@  
Sum of electronic and thermal Free Energies= -1186.306428

#### TS<sub>HAT\_Ca</sub>

1\1\GINC-SPARTAN-BM098\FTS\UM062X\CC-pVTZ\C16H27N2O6(2)\UWILLE\11-Mar-  
2022\O\#p opt=(ts,noeigentest,readfc,maxcycle=500) freq=noraman geom=  
checkpoint guess=check M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile)  
nosymm\geom&freq\0,2\C,-1.1845528957,0.3758112456,-1.6384326342\H,-1  
.3294742543,0.061556214,-2.8830110903\C,-0.0648152097,-0.5247792932,-1  
.2012891317\H,-2.31412022,-0.9033735597,-0.489953385\C,-3.6291264738,0  
.4304501235,-1.3277621882\C,-4.7578819186,-0.3417420145,-0.6999067797\  
H,-4.9327401764,-1.241584578,-1.2916012048\H,-5.6553091195,0.268031882  
8,-0.7102188809\H,-4.520958019,-0.6438991397,0.3182036952\O,-0.2297208  
968,-1.5250548306,-0.542876516\O,1.1110029966,-0.1240749373,-1.6607783  
657\C,2.2318995338,-0.9476437582,-1.3116786973\H,2.3469994087,-0.97515  
87726,-0.2305996359\H,3.0935906785,-0.4835844195,-1.7768491086\H,2.084  
971782,-1.9559486116,-1.6908015234\O,-3.8032871663,1.3921037564,-2.052  
0291551\N,-2.3813656441,-0.0492797156,-1.028537645\C,-0.8685174544,1.8  
710359915,-1.6398260481\H,0.0473486171,2.0133548539,-2.2091330155\H,-1  
.6755622089,2.3885029786,-2.149010495\C,-0.7069358888,2.3924952287,-0.  
2331680053\C,-1.8125165882,2.8308270493,0.490829229\C,0.5372528851,2.4  
137168568,0.3950862682\C,-1.6877079112,3.2789948131,1.796788833\H,-2.7  
8803723,2.8310054527,0.0186012545\C,0.6770923035,2.8590605637,1.699641  
661\H,1.4138784959,2.0838425224,-0.1493229097\C,-0.4366477721,3.295182  
5523,2.417492451\H,-2.5581222413,3.623719992,2.3399998768\H,1.64646323  
,2.8806294903,2.1792655997\O,-0.2606923872,3.7220592272,3.6815427858\O  
, -2.7990976526,-1.1486420765,-3.6829379119\O,-1.7241455851,-0.37151396  
33,-3.9987936278\C,-2.3584357867,-2.4771857062,-3.4250507435\H,-1.6977

419263,-2.489820524,-2.5568679499\H,-3.2595485909,-3.0498867788,-3.219  
4688201\H,-1.8429374546,-2.874034698,-4.2979124953\C,-1.7609815151,4.8  
632648467,6.2719710374\H,-1.0453796599,5.6616150666,6.0802883944\H,-2.  
4730375331,5.2019190733,7.0346635493\H,-1.2242920207,3.9954813157,6.65  
31168721\C,-3.1249491445,5.6691341433,4.4695036855\H,-2.4020915095,6.4  
589439318,4.270722641\H,-3.6121098236,5.3962567361,3.5342649251\H,-3.8  
8703863,6.0535986634,5.1591524078\C,-3.3729097001,3.4087878272,5.24971  
16641\H,-3.8573902962,3.1410716728,4.3115347528\H,-2.8314045912,2.5412  
301255,5.6242310641\H,-4.148029236,3.6820506163,5.9767899548\N,-2.4398  
962876,4.5085208039,5.0282459523\H,-1.1342993112,4.0072447601,4.099653  
4091\Version=ES64L-G16RevC.01\HF=-1186.6383036\S2=0.759839\S2-1=0.\S2  
A=0.750053\RMSD=5.622e-09\RMSF=3.205e-07\Dipole=-0.302548,-0.9269705,2  
.3721371\Quadrupole=4.0811613,0.5524411,-4.6336024,-2.4510315,-26.1437  
703,22.932874\PG=C01 [X(C16H27N2O6)]\@\  
Frequencies -2024.8532  
Sum of electronic and thermal Free Energies= -1186.281514

### **C $\alpha$ -radical product complex**

1\1\GINC-SPARTAN-BM019\FOpt\UM062X\CC-pVTZ\C16H27N2O6(2)\UWILLE\09-Mar  
-2022\0\#p opt=(calcf, maxcycle=500) freq=noraman M062X/cc-pVTZ scrf=  
(cp, solvent=acetonitrile) nosymm\geom&freq\0,2\C,-0.6902552268,0.1  
527767062,-1.4450094573\H,-4.5895268673,0.9290756755,-2.6771654854\C,0  
.4061618037,-0.7761912812,-1.6381032395\H,-1.7118908768,-1.4604073791,  
-0.8290592214\C,-3.1065005652,0.0273251175,-0.9251810887\C,-4.12205176  
83,-0.9165115636,-0.3501702197\H,-5.0817370716,-0.7166613707,-0.818855  
2508\H,-4.2086829439,-0.7219720089,0.7196315713\H,-3.8496541392,-1.958  
7243987,-0.4954635801\O,0.2900790654,-1.98423917,-1.5041411009\O,1.558  
8719968,-0.1828997592,-1.9724391212\C,2.6648523463,-1.0637832072,-2.18  
12792016\H,2.8776548542,-1.623038992,-1.2728588491\H,3.5036902807,-0.4  
283103719,-2.4419507088\H,2.4460667278,-1.7577154624,-2.9900266181\O,-  
3.3915433968,1.1673145956,-1.2687399457\N,-1.8355964135,-0.4724236176,  
-1.0180983891\C,-0.546902953,1.6355842849,-1.5340317132\H,0.3774603979  
,1.8422698668,-2.0686208494\H,-1.371904005,2.0621559549,-2.0990693658\  
C,-0.5004294561,2.2746196345,-0.1569916137\C,-1.475256544,3.1710515684  
,0.2617058425\C,0.5396045791,1.97494996,0.7223551391\C,-1.4177097508,3  
.7609530572,1.5174724094\H,-2.2974802552,3.4067533128,-0.4010566682\C,  
0.6089328282,2.5535534651,1.9772341025\H,1.3134003242,1.2807668912,0.4  
140085931\C,-0.37306396,3.4567974234,2.3898634913\H,-2.1864195768,4.45  
75701625,1.8264340212\H,1.4202546991,2.3217202466,2.6541547627\O,-0.27  
11282571,3.9990403988,3.61808678\O,-4.0692632152,-0.7006071096,-3.4426  
055504\O,-4.9281776762,0.4304712457,-3.4468684766\C,-2.9144088238,-0.3  
624739932,-4.1852598357\H,-2.2766216071,-1.2448378235,-4.1484017939\H,  
-3.1737978257,-0.1261571648,-5.2172303294\H,-2.3992343818,0.4856785157  
,-3.7271831753\C,-2.0136887156,7.0039157423,3.4536328383\H,-2.38247738  
71,6.7731719897,2.454956597\H,-2.5995935474,7.8393547766,3.8572639325\  
H,-0.9711762731,7.3105190116,3.3795905804\C,-1.6002184801,6.1064384614  
,5.6403034751\H,-2.176954449,6.8994601974,6.1322217462\H,-1.6524380153  
,5.20494237,6.2491663454\H,-0.5599695082,6.4214374452,5.5689553945\C,-  
3.493714996,5.349076353,4.3754001378\H,-3.8600172283,5.1232352081,3.37  
47381763\H,-3.5378260355,4.442903494,4.9776018078\H,-4.1522225247,6.10  
35025261,4.8243666713\N,-2.115658864,5.8222874428,4.3035357031\H,-1.02



04563217,4.6512595722,3.7941737302\\Version=ES64L-G16RevC.01\HF=-1186.674749\S2=0.756745\S2-1=0.\S2A=0.750037\RMSD=7.223e-09\RMSF=1.295e-06\  
Dipole=0.4231403,1.1068699,1.2334144\Quadrupole=-11.0033517,11.4630878  
,-0.4597361,-12.244197,-25.1171842,14.1104667\PG=C01 [X(C16H27N2O6)]\ \@  
Sum of electronic and thermal Free Energies= -1186.312084

#### TS<sub>HAT\_cβ</sub>

1\1\GINC-SPARTAN-BM125\FTS\UM062X\CC-pVTZ\C16H27N2O6(2)\UWILLE\10-Mar-2022\0\#p opt=(ts,noeigentest,calcfc,maxcycle=500) freq=noraman M062X  
/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,1.4  
50473773,-1.2593714201,-0.3788698114\H,1.3625471171,-2.228058747,-0.87  
17791837\C,2.4340077985,-1.4175605906,0.7711515837\H,0.0465670008,-0.0  
94360195,0.6815115686\C,-0.9283623233,-1.7472601014,-0.0155465898\C,-2  
.2179122821,-1.2425753084,0.5770028974\H,-2.07856032,-0.3922077959,1.2  
392232562\H,-2.6934583455,-2.0569957138,1.1179642199\H,-2.8765165812,-  
0.9523559753,-0.2412078051\O,2.1924259129,-1.1611756813,1.9211314109\O  
,3.6092481828,-1.8539860989,0.3340255747\C,4.6328766942,-2.0031977345,  
1.3256531819\H,4.8277085799,-1.0476413546,1.8066408536\H,5.5111787282,  
-2.3493887357,0.7932516796\H,4.3249329563,-2.7314918367,2.0721467927\O  
,-0.8685377644,-2.8121941672,-0.6152895574\N,0.1426265657,-0.933245541  
6,0.1322116981\C,1.9823116937,-0.2189054383,-1.364025843\H,2.427522748  
2,0.6461230499,-0.8724611479\H,2.993175987,-0.8145543155,-1.8948918915  
\C,1.1483519942,0.1315460648,-2.509110741\C,0.2435641534,-0.7731645817  
,-3.084417082\C,1.2853583122,1.3888712013,-3.1179043512\C,-0.485336638  
5,-0.4401313107,-4.2083737542\H,0.1000855282,-1.7505187722,-2.64067389  
06\C,0.5644737413,1.7309095759,-4.2417175109\H,1.9722314979,2.10874162  
34,-2.6889357146\C,-0.3332499972,0.8174494948,-4.8067150667\H,-1.18098  
18275,-1.1507640453,-4.6349529265\H,0.673665383,2.7035900017,-4.701548  
0261\O,-1.0158911662,1.183215173,-5.8959264243\O,3.5534538927,-1.04868  
82125,-3.8656954222\O,3.8328364232,-1.4577869664,-2.5891262722\C,4.337  
8933544,0.0973191488,-4.1607674871\H,5.3976578742,-0.1489788193,-4.102  
2388172\H,4.0692715616,0.3902432365,-5.1732926181\H,4.1015968301,0.901  
3485179,-3.4627826208\C,-2.1762426796,-1.8095865367,-7.3731052855\H,-1  
.8431957484,-2.4010318956,-6.5213453682\H,-2.9090018378,-2.3973698289,  
-7.9395298108\H,-1.3201041985,-1.6042375737,-8.0138250942\C,-3.1853497  
915,0.2634352648,-8.0423212264\H,-3.9669446674,-0.2425893649,-8.621514  
173\H,-3.57568436,1.2129425037,-7.6786413117\H,-2.3353475965,0.4597457  
081,-8.6941755471\C,-3.866290415,-0.7916637297,-5.996298273\H,-3.52697  
05765,-1.3832635813,-5.1470276276\H,-4.2488460472,0.1600480521,-5.6303  
165628\H,-4.6804081269,-1.3317448927,-6.4949468138\N,-2.7520892671,-0.  
5510776091,-6.908614837\H,-1.6442127263,0.4492008555,-6.2159312307\\Ve  
rsion=ES64L-G16RevC.01\HF=-1186.6341228\S2=0.766116\S2-1=0.\S2A=0.7501  
8\RMSD=6.102e-09\RMSF=9.963e-07\Dipole=-1.093531,1.5331117,-1.0936152\  
Quadrupole=8.1149032,-21.3316589,13.2167557,7.1029241,18.7900849,0.879  
2149\PG=C01 [X(C16H27N2O6)]\ \@  
Frequencies -2005.9419  
Sum of electronic and thermal Free Energies= -1186.277456

#### Cβ-radical product complex

1\1\GINC-SPARTAN-BM116\FOpt\UM062X\CC-pVTZ\C16H27N2O6(2)\UWILLE\07-Mar-2022\0\#p opt=(calcfc,maxcycle=500) freq=noraman M062X/cc-pVTZ scrf=

(cpcm,solvent=acetonitrile) nosymm\\geom&freq\\0,2\C,2.7231275189,-1.4  
795968763,1.7589546716\H,2.5854089727,-1.3712239234,0.6810632627\C,4.0  
03900096,-2.2708885402,1.9989988214\H,1.9009255428,-2.9821738398,2.978  
5977157\C,0.3514321956,-2.043181034,2.0357861271\C,-0.6525773947,-2.91  
32082996,2.7391260472\H,-1.2696764261,-3.4023799714,1.9881633945\H,-1.  
2988770338,-2.2729711579,3.337261968\H,-0.1924084346,-3.6611356054,3.3  
783806794\O,4.1059283926,-3.1551625993,2.8119878697\O,4.9938041244,-1.  
8360696223,1.2360754935\C,6.2700570994,-2.4544735796,1.4519083577\H,6.  
5908642368,-2.293996067,2.478364658\H,6.9506297609,-1.9745573025,0.758  
4644761\H,6.2050282897,-3.520898492,1.250782802\O,-0.0154181822,-1.175  
8289865,1.2402493097\N,1.640390206,-2.2627351675,2.3204634611\C,2.8488  
745599,-0.1390642537,2.4258638773\H,2.5266347334,-0.1045039186,3.45896  
09802\C,3.4187718544,1.0096725823,1.850648573\C,3.9071213609,1.0641660  
689,0.5216433084\C,3.5234926928,2.1993700688,2.617849497\C,4.451933525  
1,2.2186062598,0.0050588643\H,3.8509328832,0.1852101058,-0.1051672696\  
C,4.0639774536,3.3511947745,2.1011681598\H,3.1615174887,2.1907623081,3  
.6385131249\C,4.5378401624,3.3826390154,0.781623541\H,4.8275807009,2.2  
332052869,-1.0103696325\H,4.1338478225,4.2508170148,2.6977300879\O,5.0  
594792881,4.5247188398,0.3149395003\O,1.8156850793,-0.6472573882,-1.38  
08832159\C,2.2752035089,-0.0038922261,-2.5447091765\O,1.0461372119,0.3  
397236201,-0.6870454931\H,0.7021573431,-0.1997728326,0.0629727394\H,2.  
8780469409,-0.7415766601,-3.0704562762\H,2.8865847495,0.8639773638,-2.  
2880972318\H,1.4367831416,0.308406616,-3.1696398434\C,4.3530021738,4.5  
250477223,-3.001411035\H,4.4626547626,4.8109537787,-4.0547848447\H,3.9  
903426958,3.498808605,-2.9558895928\H,3.6159250299,5.1776977825,-2.535  
3340189\C,6.1088517184,6.0097613578,-2.3135847135\H,7.038643927,6.0773  
303735,-1.7507883878\H,6.2910190947,6.3482568554,-3.3407448362\H,5.371  
1989423,6.6655905286,-1.8529352871\C,6.6156242026,3.7246636629,-2.8465  
451327\H,7.535484272,3.7872165508,-2.2674987075\H,6.2457221152,2.70082  
30547,-2.8094862682\H,6.8380228492,3.9749346047,-3.8913449271\N,5.6206  
939467,4.6326913733,-2.2852679839\H,5.2982984139,4.4523988788,-0.66849  
95745\\Version=ES64L-G16RevC.01\HF=-1186.6672738\S2=0.777828\S2-1=0.\S  
2A=0.750435\RMSD=3.385e-09\RMSF=1.501e-06\Dipole=1.9389308,-0.3666379,  
-1.1877225\Quadrupole=10.1150854,-7.472866,-2.6422194,7.6953084,-22.73  
53658,-16.9621833\PG=C01 [X(C16H27N2O6)]\\@  
Sum of electronic and thermal Free Energies= -1186.305126

#### TS<sub>HAT\_OH</sub>

1\1\GINC-SPARTAN-BM090\FTS\UM062X\CC-pVTZ\C16H27N2O6(2)\UWILLE\22-Mar-  
2022\0\#p opt=(ts,noeigentest,calcf, maxcycle=500) freq=noraman M062X  
/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\\geom&freq\\0,2\C,0.6  
974139335,-0.5080443855,-0.9837389943\H,-0.1080846426,-0.5125025693,-1  
.716607838\C,1.3799870415,-1.8612755896,-0.9830693462\H,0.6348037354,-  
0.6090364243,1.1158965474\C,-1.0634679902,0.3554262258,0.4836221675\C,  
-1.473012052,0.5942616656,1.9133106884\H,-2.5443759497,0.4370848118,2.  
004131792\H,-1.2605549683,1.636554511,2.153930979\H,-0.9425210104,-0.0  
423471665,2.6168667286\O,1.6602301125,-2.477619134,0.0128982143\O,1.67  
07023422,-2.2572180411,-2.2149010822\C,2.3808183483,-3.4986900303,-2.3  
226841586\H,3.3325583645,-3.4286200982,-1.8016277374\H,2.5356466573,-3  
.659049762,-3.3831547827\H,1.78822322,-4.3037773459,-1.895185329\O,-1.  
7475961144,0.7272807445,-0.4585808611\N,0.1258431831,-0.2693298711,0.3

149196562\C,1.7367636806,0.5713121323,-1.379906819\H,2.5588080684,0.53  
16315877,-0.66330042\H,2.127576345,0.3218056561,-2.3655560376\C,1.1180  
929673,1.9359357064,-1.3867043858\C,0.4882500678,2.4213294994,-2.54038  
97006\C,1.1122793795,2.7192880849,-0.2290518248\C,-0.1338760548,3.6473  
313742,-2.5431031043\H,0.4959692352,1.8185637781,-3.4399904177\C,0.476  
8493379,3.9411179051,-0.2074979821\H,1.6106363335,2.3547343535,0.66005  
9616\C,-0.1718743877,4.4264117538,-1.3654184352\H,-0.6177063656,4.0338  
693407,-3.4300121217\H,0.467090769,4.556484658,0.6823120486\O,-0.81067  
08564,5.5742645439,-1.351442798\O,1.9162810315,6.169116262,-1.54584733  
45\O,0.9956692775,7.0622438064,-1.0974629251\C,2.0642773797,6.32574727  
85,-2.9533824202\H,2.7502170354,5.5454510525,-3.2728781689\H,1.0936334  
316,6.2094144956,-3.4359177367\H,2.4726597636,7.3128461423,-3.16702313  
71\H,-0.0608585282,6.4201762218,-1.1334433537\N,-1.6104294729,8.486209  
1477,-0.7837155981\C,-1.472073969,8.639820632,-2.2197073067\H,-0.47198  
9672,9.0019937838,-2.4559386007\H,-1.61126626,7.6740237599,-2.70505075  
32\H,-2.2093261027,9.3498776614,-2.6297815736\C,-1.3710042307,9.747775  
9993,-0.1097049455\H,-1.4556491209,9.6150914961,0.9687545428\H,-0.3658  
308364,10.1028195474,-0.3375450022\H,-2.0894563144,10.5255555251,-0.41  
7648553\C,-2.9220121904,7.9630722415,-0.4522643569\H,-3.0590995396,6.9  
95362942,-0.9334348789\H,-3.0067273449,7.8300587966,0.6263560168\H,-3.  
7309700678,8.6368792929,-0.7802201761\\Version=ES64L-G16RevC.01\HF=-11  
86.6288769\S2=0.768807\S2-1=0.\S2A=0.750266\RMSD=3.501e-09\RMSF=7.922e  
-07\Dipole=1.95043,-1.9895462,-0.7475214\Quadrupole=-0.2940113,-17.036  
6584,17.3306697,1.4483894,-11.8161112,0.3045537\PG=C01 [X(C16H27N2O6)]\@\@  
Frequencies -2801.5254

Sum of electronic and thermal Free Energies= -1186.272900

### O-radical product complex

1\1\GINC-SPARTAN-BM012\FOpt\UM062X\CC-pVTZ\C16H27N2O6(2)\UWILLE\13-Mar  
-2022\0\#p opt=(calcf, maxcycle=500) freq=noraman M062X/cc-pVTZ scrf=  
(cpcm, solvent=acetonitrile) nosymm\geom&freq\0,2\C,0.1208277463,-0.1  
540791296,-0.9649882026\H,-0.5396405137,-0.3164714891,-1.8158559388\C,  
0.5432747032,-1.4973680468,-0.4025461999\H,-0.340016819,0.4265239408,1  
.004282269\C,-1.6699753471,1.3533126986,-0.2585049606\C,-2.2844290378,  
2.0785443701,0.9095337571\H,-3.3003188893,2.3664129929,0.656876454\H,-  
1.7019553325,2.9813194625,1.0997445868\H,-2.2775982542,1.473829311,1.8  
140841345\O,0.511113026,-1.7804680696,0.7672769228\O,0.989769345,-2.30  
13705134,-1.3569455385\C,1.47200117,-3.5811484624,-0.9236793059\H,2.30  
47687085,-3.4506638439,-0.2369536274\H,1.7929433657,-4.0949282451,-1.8  
221176206\H,0.6737455969,-4.1307150757,-0.4310242218\O,-2.0749855067,1  
.4859711825,-1.404268389\N,-0.6072886201,0.5691414825,0.0425676164\C,1  
.3862367424,0.6029735525,-1.444539527\H,2.0654514342,0.7064379685,-0.5  
970927188\H,1.8734042838,-0.0030199569,-2.2076093709\C,1.0367761741,1.  
949589798,-1.9924391022\C,0.6266034697,2.0830602996,-3.3373585614\C,1.  
0800444693,3.0897066194,-1.1654461754\C,0.2674609467,3.2955708927,-3.8  
428710441\H,0.5989448266,1.2007407294,-3.964719155\C,0.7313585635,4.32  
0343276,-1.6444868342\H,1.4020650025,2.9766535365,-0.1378780912\C,0.29  
7847055,4.4838494194,-3.0164705468\H,-0.0506712613,3.413990877,-4.8697  
406707\H,0.7713385721,5.2051457454,-1.0233457931\O,-0.0406410976,5.596  
1109118,-3.4685269384\H,-0.1889773742,6.9665796445,-1.8426915109\O,1.6  
278080047,7.5381011286,-1.9646368465\O,0.3128037918,7.7197272933,-1.46

366632\C,1.7194633991,8.2444371209,-3.1839247568\H,1.5103786826,9.3042  
287672,-3.0307744142\H,2.7483693791,8.1160505774,-3.517703052\H,1.0345  
610941,7.8261747575,-3.9220087339\C,-1.8551789678,6.0958903428,0.30675  
76769\H,-1.392720724,7.0180342097,0.657081234\H,-2.8063552572,5.952249  
0392,0.8432582899\H,-1.1931135609,5.2647319627,0.5531385281\C,-2.64808  
39297,4.9339736653,-1.6245112502\H,-3.6522927647,4.7739159025,-1.20013  
54434\H,-2.7319015789,4.9760757843,-2.7105568787\H,-2.0289518294,4.075  
3780005,-1.3623776796\C,-2.8484591339,7.3123136734,-1.4971087101\H,-2.  
3627486668,8.2242014937,-1.1500906837\H,-2.9451747002,7.3616735117,-2.  
5818159049\H,-3.8580388524,7.2660225648,-1.0602185381\N,-2.0440805338,  
6.1583463253,-1.1313842122\\Version=ES64L-G16RevC.01\HF=-1186.6599838\  
S2=0.785213\S2-1=0.\S2A=0.750783\RMSD=4.928e-09\RMSF=1.237e-06\Dipole=  
0.8837035,-3.2911423,0.7784184\Quadrupole=11.8909208,-22.4936305,10.60  
27096,-7.4053045,-8.382688,16.398107\PG=C01 [X(C16H27N2O6)]\@\@  
Sum of electronic and thermal Free Energies= -1186.298541

#### TS<sub>addition</sub>

1\1\GINC-SPARTAN-BM010\FTS\UM062X\CC-pVTZ\C16H27N2O6(2)\UWILLE\23-Mar-  
2022\0\#p opt=(ts,noeigentest,calcf, maxcycle=500) freq=noraman M062X  
/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,0.3  
65451032,0.0190038687,-0.528132064\H,-0.1830168757,0.0687185571,-1.467  
3099242\C,1.3045789564,-1.1686294542,-0.5581233036\H,-0.2402842583,-0.  
5057320547,1.4161717116\C,-1.8854662613,0.2063255302,0.4243619345\C,-2  
.6969283194,0.0987975315,1.6896274252\H,-2.2520296155,-0.5719316449,2.  
4206386118\H,-3.7000332315,-0.2357010015,1.4397857168\H,-2.7682359799,  
1.0953853417,2.1272575568\O,1.4529828914,-1.9409669428,0.3543169268\O,  
1.9840491261,-1.2205453287,-1.6975061031\C,2.9587644124,-2.2670007801,  
-1.7979980859\H,3.7023715055,-2.1599272973,-1.0118592145\H,3.415197860  
4,-2.1532444172,-2.774319234\H,2.4738642738,-3.2363961803,-1.712008737  
2\O,-2.3687134309,0.6130772672,-0.6224010248\N,-0.5864080456,-0.155434  
2417,0.5369589722\C,1.2011624665,1.3103938156,-0.3542611521\H,1.765959  
7993,1.2270354075,0.5759455855\H,1.9131102432,1.369626146,-1.177408477  
2\C,0.3227345164,2.5283308009,-0.3242940089\C,-0.1114552168,3.10704887  
9,-1.5361642694\C,-0.1458612417,3.0406460412,0.8559718219\C,-1.0285208  
542,4.141957284,-1.5546921958\H,0.2561096695,2.7069511104,-2.473186940  
6\C,-0.9676491612,4.203400696,0.880939124\H,0.1576660467,2.6047731527,  
1.7993448614\C,-1.5169327967,4.6625309267,-0.3590692658\H,-1.386554397  
,4.5388195812,-2.4956253206\H,-1.5458033673,4.4177143617,1.7708921676\  
O,-2.4299963598,5.6272555647,-0.296588943\O,1.2208488076,5.6578881046,  
0.4115199083\O,0.1960801419,5.577770745,1.337110259\C,0.9776227988,6.7  
643782221,-0.4374817059\H,0.9338030389,7.6867288367,0.1431079089\H,1.8  
180898282,6.8001079703,-1.1286001489\H,0.04823467,6.6321742895,-0.9914  
603696\C,-4.2244376983,7.619631659,-2.0176542224\H,-3.7542934266,8.257  
9014541,-1.2709473218\H,-4.6600496073,8.2509942009,-2.8007944326\H,-5.  
020092228,7.0485799976,-1.5417323723\C,-2.1300808732,7.4442098032,-3.1  
806354171\H,-1.6733317287,8.0956987841,-2.4367536212\H,-1.3763227442,6  
.7500692307,-3.5513507221\H,-2.4821272285,8.0585608572,-4.0179435156\C  
, -3.847151699,5.7963267466,-3.5342645421\H,-3.0982261373,5.1155383702,  
-3.9361709332\H,-4.6244490204,5.2138844377,-3.0424045431\H,-4.29401071  
45,6.3518947075,-4.3674233656\N,-3.2288262056,6.7011751358,-2.56891652  
32\H,-2.702623361,5.9626259263,-1.2258964711\\Version=ES64L-G16RevC.01

\HF=-1186.6361828\S2=0.781637\S2-1=0.\S2A=0.750599\RMSD=4.226e-09\RMSF=1.541e-06\Dipole=-0.1078656,0.4934094,-2.08929\Quadrupole=-5.5332553,5.623823,-0.0905677,-19.5836272,-1.3801165,-27.8268103\PG=C01 [X(C16H27N2O6)]\@\nFrequencies -566.5653  
Sum of electronic and thermal Free Energies= -1186.272812

#### Addition product

1\1\GINC-SPARTAN-BM121\FOpt\UM062X\CC-pVTZ\C16H27N2O6(2)\UWILLE\07-Mar-2022\0\#p opt=(calcfc,maxcycle=500) freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,0.290068904,-0.5470198936,-0.181438747\H,-0.0978437661,-0.5474843978,-1.198704942\C,1.0169103408,-1.8498948882,0.0781227366\H,-0.6670154478,-0.6851961345,1.6859226635\C,-2.0142809975,0.093770069,0.3560957698\C,-2.9987052245,0.3000910726,1.4784519783\H,-4.0041667863,0.1266131294,1.1055788978\H,-2.9268490158,1.3396931788,1.8011191008\H,-2.801829006,-0.3430128921,2.3328211832\O,0.9067414177,-2.5013480764,1.0853748536\O,1.832894287,-2.1577285203,-0.9233152013\C,2.628400036,-3.3365277899,-0.7431813535\H,3.2630963324,-3.2271007188,0.1329692283\H,3.228398143,-3.4285139778,-1.6409946889\H,1.98521406,-4.2047066496,-0.6213853438\O,-2.2723004422,0.4038687543,-0.7978873418\N,-0.8247162861,-0.4371343244,0.7220101486\C,1.289441535,0.6222770158,-0.0135933711\H,1.6736478373,0.5981721563,1.0076858657\H,2.1252212812,0.4578441123,-0.6941988251\C,0.6331278025,1.9453152924,-0.2944805595\C,0.4652579868,2.3533231951,-1.6482302041\C,0.1410691862,2.7070563566,0.7108599294\C,-0.2473980574,3.5137909596,-1.9621689434\H,0.8703765829,1.7399914907,-2.4418983896\C,-0.5346248154,4.0135538029,0.4775388324\H,0.256052979,2.3992867146,1.7433387923\C,-0.773205661,4.3072048358,-0.9723181609\H,-0.4090807656,3.7854292506,-2.9976807742\H,-1.4892282104,4.0722990581,1.0151951836\O,-1.5015909366,5.4002174363,-1.1865267762\O,1.471370859,5.194970326,0.5363322871\O,0.174174837,5.1036380761,1.1191435612\C,1.5429591418,6.4526476476,-0.107211671\H,1.3839517487,7.2609162849,0.6077229424\H,2.5543318788,6.5102198637,-0.5064150789\H,0.8152477389,6.5222897112,-0.9156898993\C,-0.4955854288,6.5304348238,-4.2766463176\H,0.0819805935,5.6221429831,-4.4426793871\H,-0.6199761246,7.046044445,-5.2364490744\H,0.0575528333,7.1794613293,-3.5990883542\C,-2.5655352412,7.4050299159,-3.4284787528\H,-2.7777853709,7.9461216585,-4.3580180678\H,-3.5081629242,7.1369642985,-2.953729646\H,-2.0082007479,8.0590268031,-2.7592713763\C,-2.5326062205,5.2769859498,-4.542573722\H,-1.9490744597,4.3730997188,-4.7113457432\H,-3.4694622373,5.0053145482,-4.0588291898\H,-2.7551955201,5.7349468858,-5.5138012103\N,-1.7875016945,6.193884943,-3.6843643732\H,-1.5848971547,5.61856872,-2.1853509581\\Version=ES64L-G16RevC.01\HF=-1186.6518435\S2=0.778135\S2-1=0.\S2A=0.750459\RMSD=6.167e-09\RMSF=7.177e-07\Dipole=0.4490647,0.6627925,-1.816933\Quadrupole=-10.4187252,8.511951,1.9067742,-11.0200225,-3.2482121,-25.4716164\PG=C01 [X(C16H27N2O6)]\@\nSum of electronic and thermal Free Energies= -1186.286688

#### d) Entry 4 - Reaction of CCl<sub>3</sub>OO\*

##### Reactant complex

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1\1\GINC-SPARTAN-BM015\FOpt\UM062X\CC-pVTZ\C13H15Cl3N1O6(2)\UWILLE\10-
Apr-2022\0\#p freq=norman opt=(calcf, maxcycle=500) M062X/cc-pVTZ sc
rf=(cpcm, solvent=acetonitrile) nosymm\geom&freq\0,2\C,-1.26751916,3.
7274514403,-0.9218207509\H,-0.7809138981,4.6724395515,-1.157398556\C,-
0.6044382628,2.6136065253,-1.7047872698\H,-3.1496191377,2.9635863738,-
1.4683663231\C,-3.2885651365,5.0079180975,-1.4622652554\C,-4.762497143
5,4.9101219006,-1.7603958051\H,-5.0405656566,5.712845278,-2.4376107659
\H,-5.3045730121,5.0492836665,-0.8241195859\H,-5.043400848,3.949813327
8,-2.1859700284\O,-1.2003786382,1.748216755,-2.2938032075\O,0.71913503
59,2.6795627467,-1.6173236356\C,1.4398516169,1.6262018662,-2.267769496
8\H,1.1572617101,0.6638281215,-1.8450548051\H,2.4902267089,1.828435671
8,-2.0877762137\H,1.2269368198,1.6298414233,-3.3344508544\O,-2.7226559
576,6.0841133147,-1.3363432407\N,-2.6482343332,3.8246028465,-1.3172309
746\C,-1.1093962664,3.4390649069,0.5908192251\H,-1.5631017364,2.468195
0871,0.8002416685\H,-0.04530127,3.3682242707,0.8141131423\C,-1.7569546
231,4.5087693796,1.4231426198\C,-1.0509095815,5.6485347357,1.792909905
2\C,-3.0982088219,4.4197801405,1.7871810597\C,-1.6593983997,6.67654408
25,2.4968723603\H,-0.0059460709,5.7405014057,1.5219181731\C,-3.7235654
331,5.4389727342,2.4875240597\H,-3.6666577355,3.5388770491,1.514692880
9\C,-3.0025891915,6.5736335903,2.8416977859\H,-1.0951120597,7.55658506
52,2.77966635\H,-4.7650295461,5.3678332588,2.770004554\O,-3.6581585085
,7.547960202,3.531017526\H,-3.0582695497,8.2772011539,3.718571615\O,3.
0619258614,-0.4679672939,-3.7788321155\O,1.9404059716,-1.1136616295,-3
.8372247062\C,4.0770040245,-1.1978333314,-3.0552169573\Cl,4.3929325159
,-2.7191207169,-3.8720699513\Cl,5.4660836675,-0.134680063,-3.103618084
\Cl,3.5293380458,-1.4702279343,-1.4073643423\Version=ES64L-G16RevC.01
\HF=-2390.9982538\S2=0.754324\S2-1=0.\S2A=0.750012\RMSD=1.677e-09\RMSF
=1.132e-06\Dipole=1.428501,-1.1740788,0.4828656\Quadrupole=14.903273,-
12.8381539,-2.0651191,10.0384537,-2.9152611,9.6608529\PG=C01 [X(C13H15
Cl3N1O6)]\@
Sum of electronic and thermal Free Energies= -2390.789059

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### **C $\alpha$ \_HAT complex**

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1\1\GINC-SPARTAN-BM098\FOpt\UM062X\CC-pVTZ\C13H15Cl3N1O6(2)\UWILLE\20-
Nov-2021\0\#p scf=(qc,direct) geom=checkpoint guess=check freq=norma
n M062X/cc-pVTZ scrf=(cpcm, solvent=acetonitrile) nosymm opt=(readfc,ma
xcycle=500)\geom&freq\0,2\C,-0.0326937138,-0.2310357792,-1.032549678
2\H,-0.9960123348,-0.0468395294,-1.5051897315\C,0.6535169316,-1.385532
1004,-1.7336033623\H,0.4522138201,-1.0835528709,0.8285853391\C,-1.4209
469796,-0.2725390473,0.9901412486\C,-1.4509790447,-0.6264082779,2.4547
226227\H,-2.4450947514,-0.9822380391,2.7114186825\H,-1.2581668962,0.28
39729973,3.0235955751\H,-0.707735951,-1.3719023492,2.7261964081\O,1.13
61161723,-2.3359173626,-1.1731944919\O,0.7055878841,-1.189224767,-3.04
6798771\C,1.4320227029,-2.167903208,-3.8008510312\H,2.4352052957,-2.27
93583533,-3.3970351487\H,1.4671012749,-1.7906085835,-4.8166741308\H,0.
9139436445,-3.1237630764,-3.7664360226\O,-2.3613030819,0.2825154105,0.
440484297\N,-0.2753538305,-0.585050936,0.3411930329\C,0.8467509488,1.0
351041957,-1.1696149429\H,1.8137404887,0.8280894584,-0.7059453521\H,1.
0149285817,1.2159657657,-2.2310085859\C,0.2003950418,2.2303054668,-0.5
300221931\C,-0.6147493758,3.0771847046,-1.2733391043\C,0.3507568342,2.
4897841839,0.8304549592\C,-1.2777630654,4.1423835038,-0.6817907806\H,-

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0.738746206,2.9016249458,-2.3355447595\C,-0.3062912027,3.5471377983,1.4383057538\H,0.9904825953,1.8511924983,1.4273315902\C,-1.1281584817,4.3743857506,0.680644647\H,-1.9079431222,4.7939348737,-1.2745073014\H,-0.1889179396,3.7469896509,2.4946147898\O,-1.7534289135,5.4005285827,1.3210548737\H,-2.2886112712,5.8988233759,0.6948657742\O,-2.1188643127,0.064137515,-3.8208816408\O,-2.4215822211,1.1695440866,-3.2179264369\C,-1.668550029,0.285037484,-5.174048666\Cl,-1.3673399926,-1.3281187348,-5.7815191101\Cl,-2.9379091827,1.0889290118,-6.0853952023\Cl,-0.2056475163,1.2586219546,-5.1508279298\\Version=ES64L-G16RevC.01\HF=-2391.0020705\S2=0.75445\S2-1=0.\S2A=0.750013\RMSD=3.796e-10\RMSF=1.552e-06\Dipole=1.4160105,-0.3064414,-1.4136015\Quadrupole=-11.750135,-3.6450916,15.3952266,-3.1172215,0.5891128,-2.3722536\PG=C01 [X(C13H15Cl3N1O6)]\@\@  
Sum of electronic and thermal Free Energies= -2390.781588

#### TS<sub>HAT\_cα</sub>

1\1\GINC-SPARTAN-BM094\FTS\UM062X\CC-pVTZ\C13H15Cl3N1O6(2)\UWILLE\09-Dec-2021\0\#p scf=(qc,direct) geom=checkpoint guess=check freq=noraman opt=(ts,noeigentest,readfc,maxcycle=500) M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,-0.8022842644,0.277799301,-1.6080776174\H,-0.8962314959,-0.0298391303,-2.7900061719\C,0.3438093751,-0.5525992281,-1.0749783364\H,-1.9135524709,-0.9436735764,-0.3798516265\C,-3.2446401889,0.3600539792,-1.2549523618\C,-4.3509144153,-0.3183775251,-0.4953079054\H,-4.3370730712,-1.390688446,-0.689064657\H,-5.3028836821,0.1001098292,-0.8029425735\H,-4.2102809952,-0.1675266932,0.5750199386\O,0.2329926503,-1.3543019932,-0.1821482751\O,1.4692467466,-0.2968660828,-1.7209675204\C,2.6181806873,-1.0432991286,-1.2925394867\H,2.8306193665,-0.8259529191,-0.2483575092\H,3.4336134538,-0.7172035216,-1.9269230961\H,2.4330338641,-2.1075625402,-1.4167342802\O,-3.4245140779,1.2722437487,-2.0373586396\N,-1.9929272164,-0.1342405473,-0.9827368859\C,-0.4968495623,1.7827493048,-1.647434908\H,0.4096117209,1.9140784202,-2.2345638846\H,-1.3152923586,2.2825931224,-2.1550521525\C,-0.3130496992,2.3231370247,-0.2528352499\C,-1.4060560571,2.773382807,0.4820426644\C,0.9426341345,2.3417052267,0.3517490724\C,-1.2563154487,3.2338477766,1.7810360866\H,-2.3891267546,2.775649998,0.0265817703\C,1.1081964281,2.7987067967,1.6490428397\H,1.808632054,2.0037184,-0.2049072762\C,0.004853676,3.2450000568,2.3678625876\H,-2.113824146,3.5884382372,2.3392719848\H,2.0837911802,2.8204828014,2.1146809144\O,0.2160131753,3.6867793292,3.6365560141\H,-0.6157672613,3.9740419349,4.0274525589\O,-2.4473281192,-1.0636786426,-3.8152256127\O,-1.2993850533,-0.359243292,-4.0445518653\C,-2.2238217792,-2.4321989581,-3.918502023\Cl,-1.6589152532,-2.860213264,-5.5437192531\Cl,-3.7975673085,-3.1506003378,-3.597877935\Cl,-1.0360858332,-2.9853352684,-2.7194733281\\Version=ES64L-G16RevC.01\HF=-2390.9853149\S2=0.759345\S2-1=0.\S2A=0.750047\RMSD=1.806e-10\RMSF=5.995e-07\Dipole=0.4022441,-0.4552144,1.6508017\Quadrupole=11.0077741,-0.6338326,-10.3739415,0.1871665,-17.1951906,7.8953487\PG=C01 [X(C13H15Cl3N1O6)]\@\@  
Frequencies -1398.2397  
Sum of electronic and thermal Free Energies= -2390.772054

#### Cα-radical product complex

1\1\GINC-SPARTAN-BM094\FOpt\UM062X\CC-pVTZ\C13H15Cl3N1O6(2)\UWILLE\23-

Nov-2021\0\#p scf=(qc,direct) geom=checkpoint guess=check freq=norama  
n opt=(readfc,maxcycle=500) M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitr  
ile) nosymm\geom&freq\0,2\C,-0.2969785488,0.0046107922,-1.4212869982  
\H,-4.0660141664,1.1300504026,-2.688317459\C,0.7589897295,-0.971297441  
4,-1.6129676731\H,-1.4092771324,-1.5725992708,-0.8712960405\C,-2.73101  
36574,-0.0259566514,-0.9811478876\C,-3.7965702696,-0.9456890742,-0.458  
878327\H,-4.7678677417,-0.5675049678,-0.7625108306\H,-3.7460842474,-0.  
9619948479,0.6306043764\H,-3.6624763226,-1.9614910904,-0.8259288416\O,  
0.5811450484,-2.1747838686,-1.5149802788\O,1.9453814507,-0.4245894841,  
-1.9024091026\C,3.0143013061,-1.3508400657,-2.1106275093\H,3.179946398  
2,-1.9420837169,-1.2127365642\H,3.8871285278,-0.7487079144,-2.33627245  
04\H,2.7816456783,-2.0126563981,-2.942035115\O,-2.959706663,1.13260516  
77,-1.3141000017\N,-1.4835028281,-0.5766585797,-1.0478263273\C,-0.0846  
6341,1.4803066405,-1.4626151328\H,0.8624699114,1.660990703,-1.96605074  
48\H,-0.8758282708,1.9569752987,-2.0354113466\C,-0.0465263358,2.073946  
6712,-0.0653649922\C,-1.0017599394,2.9879410441,0.3595357519\C,0.96324  
64471,1.7084348677,0.8240974134\C,-0.9542301652,3.5326409098,1.6364461  
485\H,-1.7986700535,3.2749129654,-0.3133489709\C,1.0226330476,2.240405  
0368,2.1000014278\H,1.7201332178,0.9996107533,0.5085305431\C,0.0584100  
369,3.1571205019,2.5093768098\H,-1.7036706243,4.2469325578,1.954394246  
\H,1.8077253832,1.9599363023,2.7887037165\O,0.1584381473,3.6526225673,  
3.7733287595\H,-0.5609203469,4.2702739699,3.9406918937\O,-4.0326810473  
, -0.552353364,-3.4758273705\O,-4.5553595854,0.7631711993,-3.4625862112  
\C,-3.1607214994,-0.6991413743,-4.5253082148\Cl,-1.8048587525,0.452358  
3312,-4.4404189064\Cl,-3.9847525498,-0.5026373383,-6.0890971757\Cl,-2.  
5608951724,-2.3487392343,-4.345894614\\Version=ES64L-G16RevC.01\HF=-23  
91.0271379\S2=0.757126\S2-1=0.\S2A=0.750041\RMSD=2.918e-09\RMSF=8.537e  
-06\Dipole=0.5497173,0.03533,1.124252\Quadrupole=2.7174527,4.9472732,-  
7.6647259,-2.8851638,-17.4462424,3.4938257\PG=C01 [X(C13H15Cl3N1O6)]\@\@  
Sum of electronic and thermal Free Energies= -2390.809193

### C $\beta$ \_HAT complex\_

1\1\GINC-SPARTAN-BM106\FOpt\UM062X\CC-pVTZ\C13H15Cl3N1O6(2)\UWILLE\25-  
Nov-2021\0\#p scf=(qc,direct) geom=checkpoint guess=check opt=(calcfc  
,maxcycle=500) freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitr  
ile) nosymm\geom&freq\0,2\C,1.2973423406,-0.4510730082,-0.8579515289  
\H,1.1763239983,-0.487749916,-1.9392157216\C,2.1873590973,-1.591463125  
6,-0.4112292776\H,-0.0343412395,-0.8823025732,0.711588137\C,-1.1533912  
4,-0.3293337673,-0.9130916981\C,-2.4075564535,-0.4197985947,-0.0823924  
265\H,-3.2047369634,-0.8381521825,-0.690734505\H,-2.6938338888,0.59250  
76542,0.2054408794\H,-2.2756187698,-1.0145330424,0.8180273356\O,1.9990  
379624,-2.2544573563,0.5772232933\O,3.2344190473,-1.7260057238,-1.2142  
202042\C,4.2125341757,-2.6975952857,-0.8255763265\H,4.5928968262,-2.46  
69968853,0.1667335093\H,5.0049723155,-2.6275178098,-1.562931665\H,3.77  
24649098,-3.6920993814,-0.8286064202\O,-1.1810001466,-0.0135088232,-2.  
0938541688\N,-0.002007496,-0.5953328828,-0.2540729791\C,1.9801572971,0.  
.8808844345,-0.4663258524\H,2.102876705,0.8911620104,0.6190533297\H,2.  
9734782163,0.8974624883,-0.9146991538\C,1.1737030453,2.0654158544,-0.9  
148083678\C,1.3533668905,2.6071074906,-2.1835461821\C,0.1818703178,2.6  
092417699,-0.1023765264\C,0.5660249539,3.6541918686,-2.6381691994\H,2.  
1197667549,2.2006785751,-2.8331012497\C,-0.6166156014,3.6532405595,-0.



5416311265\H,0.0279245268,2.2068221023,0.8914833234\C,-0.4256743659,4.1766382141,-1.8153168319\H,0.7184504985,4.0669740031,-3.6278216241\H,-1.3860742607,4.074760912,0.0906064134\O,-1.2314767147,5.2032945233,-2.2037281763\H,-1.001917602,5.4778890816,-3.0974045856\O,6.3581463557,0.5163060567,-1.4612462238\O,5.4657612792,0.2011970619,-0.577533836\C,5.8156641255,1.3418527174,-2.5140970586\Cl,5.1336261638,2.805528658,-1.8205429385\Cl,7.1988691813,1.6899883485,-3.5270247493\Cl,4.5888368774,0.432565214,-3.3843447974\\Version=ES64L-G16RevC.01\HF=-2391.001763\S2=0.754272\S2-1=0.\S2A=0.750012\RMSD=3.246e-09\RMSF=1.904e-06\Dipole=1.4547952,0.146902,-0.0534684\Quadrupole=6.1118373,-4.2938224,-1.8180149,2.1075523,-15.5050735,-5.308495\PG=C01 [X(C13H15Cl3N1O6)]\\@\nSum of electronic and thermal Free Energies= -2390.788136

#### TS<sub>HAT\_Cβ</sub>

1\1\GINC-SPARTAN-BM056\FTS\UM062X\CC-pVTZ\C13H15Cl3N1O6(2)\UWILLE\21-Jan-2022\0\#p freq=noraman opt=(ts,noeigentest,readfc,maxcycle=500) geom=checkpoint guess=check M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\\geom&freq\\0,2\C,1.3271379655,-1.2287289491,-0.8986637077\H,1.806007203,-1.4629864214,0.0524858069\C,1.8767608986,0.1091755812,-1.3711999566\H,-0.6738405967,-0.7773222113,-1.3844243984\C,-0.6269679606,-1.340635978,0.5792008276\C,-2.1197696787,-1.1660049333,0.6715493193\H,-2.342877667,-0.5526788371,1.5413906387\H,-2.5671148532,-2.1468251756,0.8289562426\H,-2.5530274663,-0.7151675302,-0.2171813263\O,1.2079298491,1.0804014828,-1.6050447187\O,3.1952605356,0.0541040092,-1.5140057637\C,3.826750532,1.2498428401,-1.9904503438\H,3.4333123485,1.5130968455,-2.9692946214\H,4.8841539052,1.0204250685,-2.051761309\H,3.6503490101,2.0657942538,-1.293775455\O,0.0431132103,-1.6818405379,1.5435673401\N,-0.0848547232,-1.1211776396,-0.6430218523\C,1.6649051013,-2.3100249303,-1.9311028888\H,1.5124698448,-1.9759289174,-2.9578896026\H,2.8809210928,-2.4119651499,-1.8310291309\C,1.1587679049,-3.6609452808,-1.6915657965\C,1.0252723521,-4.1851987229,-0.3967206833\C,0.8598101905,-4.5007150786,-2.7761976784\C,0.6138203297,-5.4859601482,-0.1941254513\H,1.2374178579,-3.5635362039,0.4634228167\C,0.4457731531,-5.800964716,-2.5860990202\H,0.950546631,-4.113765536,-3.7824565407\C,0.325784993,-6.3018036222,-1.2896893936\H,0.5130355471,-5.8795561248,0.809366309\H,0.210558593,-6.4448766088,-3.4217692707\O,-0.0775533306,-7.5826449118,-1.1516557413\H,-0.1245134407,-7.8206852543,-0.2190060422\O,4.0949663978,-4.1116037351,-1.492508342\O,4.1537768583,-2.7431503024,-1.4420715038\C,4.6975356864,-4.5934754209,-2.6408304431\Cl,3.9915907503,-3.8922509542,-4.1124153518\Cl,4.412159347,-6.3309926498,-2.5889920763\Cl,6.4444443883,-4.2517318893,-2.6243803904\\Version=ES64L-G16RevC.01\HF=-2390.9821149\S2=0.764855\S2-1=0.\S2A=0.750146\RMSD=8.288e-09\RMSF=1.480e-06\Dipole=-1.4595134,-0.3235682,-0.9775732\Quadrupole=-7.8901109,7.9278187,-0.0377079,14.6663052,-0.4550402,-3.6887853\PG=C01 [X(C13H15Cl3N1O6)]\\@\nFrequencies -1367.8482\nSum of electronic and thermal Free Energies= -2390.771486

#### Cβ-radical product complex

1\1\GINC-SPARTAN-BM022\FOpt\UM062X\CC-pVTZ\C13H15Cl3N1O6(2)\UWILLE\23-Feb-2022\0\#p opt=(calcfc,maxcycle=500) freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\\geom&freq\\0,2\C,2.1218793955,0

.1931623928,3.0421706711\H,2.548614899,0.1609691026,2.0372258022\C,3.2  
804786505,0.295958914,4.0293142923\H,1.6550802408,-1.4943343809,4.2080  
80489\C,0.4867561779,-1.5553726501,2.5331575743\C,-0.2060536129,-2.800  
8151569,3.0041483431\H,-0.0810234882,-3.5714636409,2.2460461121\H,-1.2  
699000372,-2.5863659806,3.0902959961\H,0.1704889583,-3.1595413362,3.95  
76064129\O,3.3732041829,-0.3721963217,5.0271466826\O,4.1394403194,1.23  
20607173,3.664307598\C,5.2345391255,1.4643003409,4.5626774082\H,4.8567  
881778,1.7746887269,5.5337557867\H,5.8232215912,2.2534271941,4.1101735  
65\H,5.8242011799,0.557381668,4.6700867159\O,0.1815010674,-1.034629585  
8,1.4545469123\N,1.432500618,-1.0487003885,3.3298438002\C,1.2147399129  
,1.3772994581,3.2058899635\H,0.4404203221,1.2647948023,3.9538226895\C,  
1.3114322311,2.5885821169,2.4991186427\C,2.3089769072,2.8570871046,1.5  
325325741\C,0.3504803137,3.6059500665,2.7323980379\C,2.3291564072,4.04  
64709486,0.8375535891\H,3.0758127757,2.1241738197,1.3271932868\C,0.368  
6366911,4.7907454115,2.0379293396\H,-0.4214095882,3.4321736691,3.47129  
25631\C,1.3572035222,5.0170206315,1.0765421779\H,3.0968234255,4.230074  
6923,0.0960586648\H,-0.3735582435,5.5566561697,2.2164081922\O,1.325019  
8861,6.1974291324,0.4098048152\H,2.0448394436,6.2353215207,-0.22904822  
62\O,0.6082748962,0.1707168388,-1.3898682892\C,0.1381759473,1.41576376  
,-1.7000298327\Cl,-0.6879173916,2.1828997522,-0.3231545489\Cl,1.445946  
5308,2.4929427742,-2.2594325462\Cl,-1.0049512093,1.1324248762,-3.01805  
00593\O,1.5397791255,0.2750854512,-0.3271844101\H,1.0232346886,-0.1528  
753315,0.4170375444\Version=ES64L-G16RevC.01\HF=-2391.0210486\S2=0.77  
7794\S2-1=0.\S2A=0.750451\RMSD=5.580e-09\RMSF=3.204e-06\Dipole=1.32918  
61,-0.2639945,2.068658\Quadrupole=5.562556,-3.5265573,-2.0359986,10.71  
86341,4.535179,-4.8921491\PG=C01 [X(C13H15Cl3N1O6)]\@\@  
Sum of electronic and thermal Free Energies= -2390.804385

### **OH\_HAT complex**

1\1\GINC-SPARTAN-BM006\FOpt\UM062X\CC-pVTZ\C13H15Cl3N1O6(2)\UWILLE\19-  
Nov-2021\0\#p scf=(qc,direct) geom=checkpoint guess=check opt=(readfc  
,maxcycle=500) freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitr  
ile) nosymm\geom&freq\0,2\C,0.1915052261,-0.3333183402,-0.715584449\  
H,-0.8288988744,-0.355614413,-1.0942397296\C,0.8830608101,-1.637041382  
8,-1.0555669026\H,0.9481616571,-0.4665707775,1.2424776335\C,-0.9377773  
016,0.3249349207,1.3604582328\C,-0.7675686915,0.5149567457,2.845633219  
3\H,-1.6977717239,0.2558780224,3.3440963147\H,-0.5667086467,1.57140004  
2,3.0275617211\H,0.0501895663,-0.0721393322,3.2560192926\O,1.574775846  
4,-2.2586176332,-0.2896705768\O,0.6753925755,-1.981272938,-2.320638053  
8\C,1.3501955063,-3.1651582589,-2.7662765123\H,2.4256879728,-3.0410275  
644,-2.6649984587\H,1.075511399,-3.2878770672,-3.8074106991\H,1.024966  
4221,-4.021395152,-2.1803320202\O,-1.9685286233,0.6373011143,0.7821161  
648\N,0.1354851553,-0.1881459553,0.7155628726\C,0.9597122796,0.8277420  
416,-1.392970158\H,1.9909210769,0.8057962951,-1.0342998034\H,0.9733396  
145,0.6454817685,-2.4671717551\C,0.3287468652,2.1563190337,-1.08790621  
4\C,-0.6791821184,2.6688232254,-1.8977251892\C,0.6885844822,2.87563231  
43,0.0493771563\C,-1.3178320722,3.8593268777,-1.5862368534\H,-0.975710  
9909,2.1272852701,-2.7880361786\C,0.0611719769,4.0668084262,0.37641317  
13\H,1.4763137493,2.4987252463,0.6903806227\C,-0.9487141394,4.55928199  
85,-0.4423380969\H,-2.1004441366,4.2477123326,-2.2262313305\H,0.346409  
5749,4.6283032568,1.2556355342\O,-1.5396066849,5.7312259905,-0.0824526

427\H,-2.1051050512,6.0416082137,-0.7980614098\O,0.4354681488,6.914883  
1545,-1.9926433482\O,-0.4807378006,6.4962956158,-2.807709038\C,1.76462  
42574,6.6075342458,-2.4596273675\Cl,1.9370737367,4.87014398,-2.6291644  
442\Cl,2.7986691652,7.2371169619,-1.1930278108\Cl,2.0462366311,7.42429  
14107,-3.9914364638\\Version=ES64L-G16RevC.01\HF=-2391.0026597\S2=0.75  
4448\S2-1=0.\S2A=0.750014\RMSD=4.607e-09\RMSF=1.620e-06\Dipole=1.64895  
42,-0.4529824,-0.8719649\Quadrupole=-6.9015783,-1.4073357,8.308914,4.3  
318617,1.1619566,1.3245661\PG=C01 [X(C13H15Cl3N1O6)]\@\n  
Sum of electronic and thermal Free Energies= -2390.788088

#### TS<sub>HAT\_OH</sub>

Could not be located.

#### O-radical product complex

1\1\GINC-SPARTAN-BM061\FOpt\UM062X\CC-pVTZ\C13H15Cl3N1O6(2)\UWILLE\25-  
Nov-2021\0\#p scf=(qc,direct) geom=checkpoint guess=check opt=(calcfc  
,maxcycle=500) freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitr  
ile) nosymm\geom&freq\0,2\C,0.2873998967,-0.5063981487,-0.597133727\  
H,-0.6951676828,-0.6379572353,-1.0491495987\C,0.8876117611,-1.86994435  
4,-0.3114897194\H,0.7852654347,-0.0044209702,1.382030936\C,-0.91229444  
14,1.0376486678,0.8708222508\C,-0.9200447283,1.7243727278,2.2104641723  
\H,-1.937371885,1.7361265315,2.5927997763\H,-0.6027307022,2.7568486326  
,2.0611156053\H,-0.2572381791,1.2538300522,2.9319525418\O,1.3774766206  
, -2.183692928,0.7425180291\O,0.8364906258,-2.6530099201,-1.3787466533\  
C,1.427534268,-3.9522575872,-1.2315337149\H,2.4815485484,-3.8541665569  
, -0.9836657117\H,1.3026686263,-4.4429570614,-2.1895004758\H,0.91629316  
67,-4.5046892092,-0.4470558406\O,-1.7731115068,1.2441075897,0.02796603  
82\N,0.1302911007,0.203230963,0.6441503803\C,1.2069835626,0.2409686197  
, -1.5994225677\H,2.1980644999,0.3296107005,-1.1523712167\H,1.282734188  
2,-0.3603799458,-2.5041319139\C,0.6597762507,1.5937754725,-1.915351992  
6\C,-0.2699775196,1.7551293712,-2.9670715893\C,1.0278190838,2.71098511  
16,-1.1356736965\C,-0.8219765068,2.9702137721,-3.2309936501\H,-0.54134  
59673,0.8917367918,-3.5609537052\C,0.4873318187,3.9395043831,-1.372441  
095\H,1.7452895684,2.5762902898,-0.3366914725\C,-0.4686403281,4.126302  
1725,-2.4395815032\H,-1.5340834545,3.1148597007,-4.0314562239\H,0.7533  
016727,4.8017086705,-0.7757873997\O,-0.9773880722,5.2446660599,-2.6876  
886634\H,-0.5641990479,6.6630627516,-2.0371441897\O,0.7924336498,7.269  
0448858,-0.8724698808\O,-0.3290196608,7.5703987295,-1.6818511455\C,1.9  
422901707,7.6031738566,-1.5346499593\Cl,2.1300202231,6.6777463842,-3.0  
48968964\Cl,2.007144977,9.3415847578,-1.9140271216\Cl,3.2315290683,7.1  
782423307,-0.406330928\\Version=ES64L-G16RevC.01\HF=-2391.0215874\S2=0  
.781336\S2-1=0.\S2A=0.750598\RMSD=2.444e-09\RMSF=9.659e-07\Dipole=1.74  
49931,-4.4233503,0.2444271\Quadrupole=12.9313808,-34.9486928,22.017312  
,3.3720633,-2.9505105,21.7606\PG=C01 [X(C13H15Cl3N1O6)]\@\n  
Sum of electronic and thermal Free Energies= -2390.807521

#### Addition complex

1\1\GINC-SPARTAN-BM114\FOpt\UM062X\CC-pVTZ\C13H15Cl3N1O6(2)\UWILLE\03-  
Dec-2021\0\#p scf=(qc,direct) opt=(calcfc,maxcycle=500) freq=noraman  
M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\  
C,-2.3147630815,0.427824698,3.5406510409\H,-1.5774438634,-0.2261417603

,3.0781345884\C,-2.721739547,-0.144692683,4.8823640244\H,-4.3413609189  
,0.7701984178,3.0924483848\C,-3.4112519934,0.1972989528,1.3588085445\C  
,-4.6880959378,0.4304952912,0.5931553492\H,-4.8000100678,-0.3504423723  
, -0.1540233744\H,-4.5992309685,1.3867358818,0.0760643326\H,-5.56567139  
81,0.4606306079,1.2341147088\O,-3.858561487,-0.2148630961,5.2749471682  
\O,-1.6630086872,-0.5112866157,5.5943901455\C,-1.9348729167,-0.9984885  
905,6.9149991628\H,-2.4329064463,-0.229250703,7.5003695856\H,-0.970271  
4938,-1.2417659785,7.344906492\H,-2.5654175173,-1.8827479485,6.8627843  
412\O,-2.3920304889,-0.1986207941,0.8121009677\N,-3.4679904029,0.48153  
40151,2.6805845006\C,-1.684931109,1.8242691172,3.7637676119\H,-2.42240  
34293,2.4524006823,4.267934953\H,-0.8298527072,1.70918453,4.4292059501  
\C,-1.2671142,2.4507557854,2.4641304186\C,-0.0037965472,2.2127975205,1  
.9322373558\C,-2.1563616443,3.2263743012,1.7251048819\C,0.3663967345,2  
.7266222091,0.6992807834\H,0.7051467754,1.6118521311,2.489014133\C,-1.  
8050097821,3.7437801878,0.4879558249\H,-3.1442693125,3.4271255349,2.12  
15168702\C,-0.5391767019,3.4913436891,-0.0271292447\H,1.3562569197,2.5  
405231939,0.3009809549\H,-2.4959796089,4.3471242763,-0.0843623427\O,-0  
.2297680218,4.034166506,-1.2373214589\H,0.6842314084,3.8308265221,-1.4  
632773644\O,1.0098501269,6.0258603145,0.6038366128\O,0.3837278956,5.98  
62149694,1.73762916\C,0.6413755414,7.1748092108,-0.1819201925\Cl,-1.09  
34686589,7.1965393147,-0.4453888599\Cl,1.5224704776,6.9600388224,-1.68  
04558342\Cl,1.1578440602,8.6325728586,0.6611498241\\Version=ES64L-G16R  
evC.01\HF=-2391.0016467\S2=0.754286\S2-1=0.\S2A=0.750013\RMSD=5.702e-1  
2\RMSF=2.436e-06\Dipole=0.2293522,0.5966682,0.9028301\Quadrupole=-0.52  
13196,-6.7389771,7.2602967,-1.1909937,-2.663241,-5.7117277\PG=C01 [X(C  
13H15Cl3N1O6)]\@

Sum of electronic and thermal Free Energies= - 2390.788620

#### TS<sub>addition</sub>

1\1\GINC-SPARTAN-BM095\FTS\UM062X\CC-pVTZ\C13H15Cl3N1O6(2)\UWILLE\04-J  
an-2022\0\#p geom=checkpoint guess=check opt=(ts,noeigentest,readfc,m  
axcycle=500) freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitril  
e) nosymm\geom&freq\0,2\C,0.1701923464,-0.0360870356,0.0921737193\H,  
0.0047279726,-1.0377060863,-0.3023582484\C,1.4462034922,-0.0277775204,  
0.9090570019\H,-0.7799147254,0.9909368122,1.6626317356\C,-2.1555107622  
, -0.278136513,0.8221350564\C,-3.2243139129,0.2609342905,1.7370285619\H  
, -3.8376974663,0.9577707827,1.164651263\H,-2.817343046,0.7815184037,2.  
6003575471\H,-3.857174242,-0.5602478378,2.0622942035\O,1.5503132681,0.  
4724971629,1.9996866256\O,2.4458724946,-0.5988559914,0.2499609319\C,3.  
7201003081,-0.5824265915,0.9076991001\H,4.0317852675,0.4434168837,1.08  
86979107\H,4.4075612905,-1.0778483605,0.2321885816\H,3.6575244011,-1.1  
174731193,1.8521102996\O,-2.383072747,-1.1605764196,0.0072032463\N,-0.  
9381836132,0.300365023,0.9459021745\C,0.3240524622,0.9568017525,-1.084  
8354423\H,0.5361970516,1.9462886088,-0.6757903487\H,1.1792393703,0.648  
2480384,-1.686009393\C,-0.9192460919,1.0049686736,-1.9236847527\C,-1.1  
345655024,0.0241834456,-2.9178596139\C,-1.8914286591,1.9423446648,-1.6  
987429265\C,-2.3078558507,-0.0316309725,-3.645729241\H,-0.3678711909,-  
0.7195512082,-3.0954165053\C,-3.0434306523,2.0044853026,-2.5212122952\  
H,-1.7628269395,2.6931513493,-0.9314785922\C,-3.2867550614,0.923995756  
2,-3.4220222273\H,-2.4712324539,-0.8132478189,-4.3761202619\H,-3.89499  
15868,2.5961294114,-2.2146644162\O,-4.4651652086,0.9452361236,-4.05654

31042\H,-4.525453339,0.2176121359,-4.6872344555\O,-1.4425234161,2.9262  
384044,-4.4598391161\O,-2.6302296094,3.3468463962,-3.8510957952\C,-0.5  
109063945,3.9155539883,-4.4310285405\Cl,-0.1095048763,4.473967137,-2.7  
849428306\Cl,0.9235859818,3.2036810212,-5.1831777777\Cl,-1.0461733593,  
5.3390879064,-5.3805850745\\Version=ES64L-G16RevC.01\HF=-2390.986126\S  
2=0.776765\S2-1=0.\S2A=0.750434\RMSD=7.043e-09\RMSF=1.398e-06\Dipole=0  
.839722,-1.2896375,0.9578551\Quadrupole=14.4146132,-12.2146509,-2.1999  
623,0.1233192,-2.4236334,21.7015873\PG=C01 [X(C13H15Cl3N1O6)]\@  
Frequencies -323.8464  
Sum of electronic and thermal Free Energies= -2390.768858

#### Addition product

1\1\GINC-SPARTAN-BM116\FTS\UM062X\CC-pVTZ\C13H15Cl3N1O6(2)\UWILLE\28-N  
ov-2021\0\#p scf=(qc,direct) opt=(ts,noeigentest,calcfc,maxcycle=500)  
freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\g  
eom&freq\0,2\C,0.3277829664,-0.5065316614,0.0920583102\H,-0.047631653  
8,-0.4985046727,-0.9301353601\C,1.0919344482,-1.7922695349,0.333584279  
9\H,-0.6599168249,-0.774982252,1.9291635965\C,-2.0027192808,0.04103677  
4,0.613727876\C,-3.0420814702,0.1140442454,1.7024713971\H,-3.944380961  
7,-0.3864752082,1.3575910979\H,-3.2836868671,1.1635183757,1.8676556422  
\H,-2.7132048736,-0.3283628071,2.6390522681\O,0.9735846467,-2.47805196  
21,1.3166699416\O,1.9449865779,-2.0407195418,-0.6521813033\C,2.7735332  
882,-3.1991701479,-0.4865917504\H,3.3778803238,-3.0988349362,0.4117725  
306\H,3.4024017916,-3.2411665941,-1.3681667168\H,2.1556160534,-4.09078  
31692,-0.413280028\O,-2.2395885809,0.4113825735,-0.5273258643\N,-0.799  
3471344,-0.4519847479,0.9849905397\C,1.2890021602,0.6884256241,0.29595  
34152\H,1.6659570333,0.6535272749,1.3192142225\H,2.1341271918,0.568202  
0083,-0.3819235088\C,0.5951812664,1.9967600627,0.0407016557\C,0.424391  
347,2.4313066058,-1.3054703685\C,0.0767367941,2.7206561773,1.060105947  
\C,-0.3430965345,3.5604463946,-1.6029268255\H,0.8606445312,1.853728007  
6,-2.1087595563\C,-0.6094620948,4.0193149289,0.8393946312\H,0.19155273  
43,2.3976892233,2.0869088334\C,-0.9021945076,4.2947362232,-0.593986105  
7\H,-0.5273651178,3.8401359817,-2.6329211847\H,-1.5248557732,4.1124619  
645,1.4329941414\O,-1.7346107286,5.3367778577,-0.7692763617\H,-1.85809  
2003,5.5165501805,-1.7091556382\O,1.4637494399,5.0728153273,0.88171928  
76\O,0.1462421427,5.1297545656,1.4350919887\C,1.9035090661,6.343394722  
7,0.656515067\Cl,1.9431147813,7.3065215597,2.1582898012\Cl,3.545775436  
2,6.1207765591,0.04158829\Cl,0.9174003862,7.2056040175,-0.5491431884\\  
Version=ES64L-G16RevC.01\HF=-2390.9990297\S2=0.77925\S2-1=0.\S2A=0.750  
499\RMSD=4.095e-10\RMSF=1.788e-05\Dipole=0.425299,-1.2826113,-0.381820  
7\Quadrupole=4.7359667,-12.3614047,7.6254379,-11.8748547,-6.9399109,-7  
.9750534\PG=C01 [X(C13H15Cl3N1O6)]\@  
Sum of electronic and thermal Free Energies= -2390.780505

#### d) Entry 4 - Reaction of 4-hydroxytoluene (as model of Ac-Tyr-Me) with CCl<sub>3</sub>OO\*

##### Reactant complex

1\1\GINC-SPARTAN-BM107\FOpt\UM062X\CC-pVTZ\C8H8Cl3O3(2)\UWILLE\05-Mar-  
2022\0\#p scf=(qc,direct) opt=(calcfc,maxcycle=500) freq=noraman M062  
X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,0.

5810976367,1.604066343,-1.7987022552\H,1.1299999446,1.6385532631,-2.74  
14899157\H,-0.0372669938,0.7059889727,-1.8147082861\C,-0.257713834,2.8  
399673657,-1.6225606589\C,-1.2989265535,3.1267928487,-2.5062227819\C,-  
0.0156193527,3.7435379179,-0.5954692452\C,-2.063647954,4.2727167332,-2  
.3773446752\H,-1.5105211058,2.439918617,-3.3170495723\C,-0.7753049904,  
4.8984388387,-0.4476706294\H,0.7888411589,3.5516078096,0.1041500102\C,  
-1.7992389812,5.1666951265,-1.3434446613\H,-2.8666362211,4.4912436931,  
-3.0683033497\H,-0.5625847747,5.5941764102,0.3552088726\O,-2.574405048  
8,6.2855121542,-1.2629122336\H,-2.2929629285,6.8224326341,-0.515195907  
\O,2.2003061377,6.0760356513,-1.0853471433\O,1.587077516,7.2155051986,  
-1.0862371541\C,2.539126712,5.6340394947,-2.4161887922\H,1.3062107934,  
1.5050605701,-0.9925623375\Cl,3.7133594931,6.750771647,-3.1051289919\C  
l,1.0963043852,5.5523117481,-3.4073768623\Cl,3.238363081,4.0478336625,  
-2.15883568\\Version=ES64L-G16RevC.01\HF=-1915.7876708\S2=0.754313\S2-  
1=0.\S2A=0.750012\RMSD=4.145e-09\RMSF=9.658e-06\Dipole=0.6199623,-0.39  
63203,0.1184531\Quadrupole=0.4983256,-3.6762658,3.1779402,3.5031116,-2  
.5162384,5.5389896\PG=C01 [X(C8H8Cl3O3)]\@\  
Sum of electronic and thermal Free Energies= -1915.685496

#### TS<sub>HAT\_OH</sub>

1\1\GINC-SPARTAN-BM087\FTS\UM062X\CC-pVTZ\C8H8Cl3O3(2)\UWILLE\18-Feb-2  
022\O\#p freq=noraman opt=(calcf, maxcycle=500, ts, noeigentest) M062X/  
cc-pVTZ scrf=(cpcm, solvent=acetonitrile) nosymm\geom&freq\0,2\C,1.32  
1127964,0.897592471,-1.3223814966\H,1.8987626611,0.8113036283,-2.24411  
14784\H,0.5982637837,0.0805848813,-1.3212523024\C,0.6205928204,2.21999  
24554,-1.2643963131\C,-0.3118288417,2.5660730884,-2.256949198\C,0.8747  
602131,3.1325646397,-0.2390253289\C,-0.9574399697,3.7786772692,-2.2362  
987601\H,-0.5146219503,1.8634378358,-3.0551310391\C,0.226101018,4.3495  
563719,-0.1923673477\H,1.5917495449,2.8795445537,0.530724965\C,-0.7032  
498402,4.6871140313,-1.1926368279\H,-1.6684926374,4.0576479784,-3.0013  
017752\H,0.4199800154,5.0587398036,0.6012595828\O,-1.3704974534,5.8373  
276627,-1.1628488573\H,-0.7301998175,6.6149048555,-0.9677117287\O,1.37  
36147281,6.5882009816,-1.513123545\O,0.4302195999,7.4947073402,-1.1850  
080595\C,1.7561346545,6.6974346755,-2.8544583339\H,1.9945758686,0.7667  
151525,-0.4788812839\Cl,2.6180884348,8.2268364856,-3.1112354212\Cl,0.3  
653863962,6.6146286379,-3.9432138979\Cl,2.8283818075,5.3256342008,-3.1  
093155528\\Version=ES64L-G16RevC.01\HF=-1915.7738504\S2=0.763875\S2-1=  
0.\S2A=0.750141\RMSD=7.676e-09\RMSF=5.786e-06\Dipole=0.4644571,-2.1232  
337,-0.0212841\Quadrupole=10.5599582,-24.357109,13.7971507,1.2443571,1  
.4237441,6.9394394\PG=C01 [X(C8H8Cl3O3)]\@\  
Frequencies -2403.8591  
Sum of electronic and thermal Free Energies= -1915.675246

#### O-radical product complex

1\1\GINC-SPARTAN-BM022\FOpt\UM062X\CC-pVTZ\C8H8Cl3O3(2)\UWILLE\08-Mar-  
2022\O\#p scf=(qc, direct) opt=(calcf, maxcycle=500) freq=noraman M062  
X/cc-pVTZ scrf=(cpcm, solvent=acetonitrile) nosymm\geom&freq\0,2\C,0.  
7412916438,0.3089274122,-1.027106951\H,0.7815093816,-0.2085847264,-1.9  
87692491\H,0.0570947032,-0.2588080563,-0.3937331344\C,0.2363050456,1.6  
988693762,-1.2142345525\C,-1.0493511657,1.9102956801,-1.769398142\C,1.  
0155583757,2.8159394988,-0.8477489037\C,-1.5374856603,3.1659801114,-1.

9550693904\H,-1.6423817094,1.0481754488,-2.0463398029\C,0.5533158017,4  
.0875848028,-1.022426582\H,1.9955805504,2.6496176845,-0.4206729074\C,-  
0.7521374212,4.3228581439,-1.5914065935\H,-2.5163534535,3.3432771646,-  
2.3787014364\H,1.1432065644,4.9486817499,-0.7384092957\O,-1.2026090207  
,5.479593971,-1.7717511621\H,-0.40769881,6.8648944813,-1.5795728802\O,  
1.3776041937,7.3591072876,-1.2130586206\O,0.0484175737,7.7548041888,-1  
.4963689327\C,2.1386680419,7.4532452341,-2.3459794121\H,1.7309686408,0  
.2953407888,-0.5788006985\Cl,2.2018267091,9.1217243812,-2.9648804316\C  
l,1.5377497856,6.3830536599,-3.641592931\Cl,3.7457412295,6.9332457168,  
-1.8331707484\\Version=ES64L-G16RevC.01\HF=-1915.8089667\S2=0.779962\S  
2-1=0.\S2A=0.750541\RMSD=5.403e-10\RMSF=2.336e-06\Dipole=0.1711895,-3.  
8057359,0.3395214\Quadrupole=23.3407637,-41.2669072,17.9261435,0.25241  
13,2.2927587,13.7434877\PG=C01 [X(C8H8Cl3O3)]\\@  
Sum of electronic and thermal Free Energies= -1915.708541

### e) Entry 5- Reaction of MeOO<sup>•</sup> with deprotonated Tyr

#### Reactant complex

1\1\GINC-SPARTAN-BM005\FOpt\UM062X\CC-pVTZ\C13H17N1O6(1-,2)\UWILLE\10-  
Mar-2022\0\#p opt=(calcf, maxcycle=500) freq=noraman M062X/cc-pVTZ sc  
rf=(cp, solvent=acetonitrile) nosymm\geom&freq\1,2\C,0.0944053096,  
5.067138951,-1.7487153314\H,-0.2912451475,5.2602923839,-2.7472419057\C  
,0.3839671085,3.5912800659,-1.5928702608\H,-0.7647195161,5.2067010205,  
0.1638083651\C,-1.9122570122,6.3235244518,-1.1008633601\C,-2.71507021,  
6.8116945402,0.0780245175\H,-3.7531418627,6.9281546565,-0.2206028305\H  
,-2.3262096641,7.7912176908,0.3603579244\H,-2.6467477347,6.1491354511,  
0.9377295188\O,0.1516436414,2.9503314771,-0.5986673596\O,0.992321596,3  
.0983737002,-2.6677964242\C,1.3984160326,1.7272039195,-2.5842157209\H,  
2.0899680509,1.5914111949,-1.755220876\H,1.8836082079,1.5012377923,-3.  
5271727778\H,0.5328492593,1.0850572943,-2.4398027954\O,-2.1474158298,6  
.6976947787,-2.2411919455\N,-0.913437298,5.4627324767,-0.7993229946\C,  
1.4152248785,5.8559506579,-1.547565388\H,1.7926012671,5.6125094424,-0.  
5502973183\H,2.1387978445,5.4817351575,-2.2732471185\C,1.2246653269,7.  
3367071536,-1.6965548976\C,1.3519643548,7.9638271655,-2.9380033549\C,0  
.8373130399,8.1390405085,-0.6213272852\C,1.1049079041,9.3130809211,-3.  
1076730838\H,1.652146986,7.3692871526,-3.7965135741\C,0.5818239305,9.4  
908881309,-0.7681821535\H,0.7334800476,7.6857121767,0.3605188711\C,0.6  
975611418,10.1612868923,-2.0278077229\H,1.2204734588,9.768154464,-4.08  
51705375\H,0.288683501,10.0841458529,0.0911819804\O,0.4654468407,11.40  
54518825,-2.1753078335\O,3.2001119938,-0.981081601,-1.8788936872\O,2.2  
9945538,-1.0941111446,-2.8042521636\C,4.4889006112,-0.6571202517,-2.43  
35542388\H,5.1694968853,-0.6085401929,-1.5899924457\H,4.7749671164,-1.  
4416947603,-3.1284459648\H,4.41823156,0.3033965469,-2.9378728269\\Vers  
ion=ES64L-G16RevC.01\HF=-1011.7104446\S2=0.754779\S2-1=0.\S2A=0.750013  
\RMSD=2.312e-09\RMSF=2.345e-06\Dipole=2.602988,-9.9785018,1.3152121\Qu  
adrupole=148.1764324,-265.3063197,117.1298873,-12.3643045,-12.1370661,  
93.6387766\PG=C01 [X(C13H17N1O6)]\\@  
Sum of electronic and thermal Free Energies= -1011.479242

TS<sub>HAT\_Ca</sub>

1\1\GINC-SPARTAN-BM021\FTS\UM062X\CC-pVTZ\C13H17N1O6(1-,2)\UWILLE\05-M  
ar-2022\0\#p opt=(ts,noeigentest,calcf, maxcycle=500) freq=noraman M0  
62X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\|-1,2\C  
,-0.9245246458,0.3951760216,-1.7838673143\H,-1.0958215393,0.1154258033  
,-3.0234535495\C,0.1907947855,-0.5271379495,-1.3829385528\H,-2.0438036  
122,-0.8668050277,-0.5964656116\C,-3.3591000765,0.4662421945,-1.431871  
5852\C,-4.4873690728,-0.2849906654,-0.7759439322\H,-5.365740157,0.3513  
220496,-0.7402017135\H,-4.2243218593,-0.617465563,0.2260600906\H,-4.71  
23873299,-1.1647547619,-1.3808787319\O,0.0429451214,-1.5008467538,-0.6  
812694074\O,1.3469443518,-0.1777389158,-1.9288648891\C,2.4700822376,-1  
.0004128463,-1.5911759402\H,2.6366400461,-0.9743243054,-0.5164489403\H  
,3.3159631045,-0.5759859454,-2.1193185512\H,2.2925071148,-2.0249401972  
,-1.9091659096\O,-3.5385561986,1.4225654462,-2.1637101077\N,-2.1156477  
066,-0.027256541,-1.1558533913\C,-0.5711096983,1.8865654578,-1.7224213  
145\H,0.299927672,2.0432550814,-2.3560466517\H,-1.4040249515,2.4453616  
962,-2.1388098428\C,-0.2878886577,2.2935225765,-0.3016613236\C,-1.3260  
989324,2.6540351706,0.5642384487\C,1.0042935249,2.265266511,0.23399748  
91\C,-1.0965952864,2.9785831491,1.886018635\H,-2.3400042317,2.68927383  
07,0.1755188056\C,1.2557100894,2.5862671819,1.5543037329\H,1.833451545  
5,1.993757348,-0.4122030989\C,0.21505832,2.9590948911,2.4652633455\H,-  
1.9218571696,3.2670762899,2.5274066473\H,2.2711031254,2.5681738302,1.9  
341349082\O,0.4340388282,3.2529203471,3.6829410318\O,-2.558657085,-1.1  
122177992,-3.8467609543\O,-1.4764113283,-0.3344536117,-4.1545976897\C,  
-2.118558922,-2.4350088094,-3.5710650453\H,-1.4722737493,-2.4405932858  
,-2.691683953\H,-3.0202767702,-3.0107085419,-3.3752104726\H,-1.5867268  
866,-2.839356356,-4.4311346606\Version=ES64L-G16RevC.01\HF=-1011.6880  
737\S2=0.760334\S2-1=0.\S2A=0.750064\RMSD=9.608e-09\RMSF=2.812e-06\Dip  
ole=-0.8369953,-5.5816658,-4.9937821\Quadrupole=28.9253928,-5.9425135,  
-22.9828793,6.1112102,-17.5627166,-19.715064\PG=C01 [X(C13H17N1O6)]\@  
Frequencies -1984.8606  
Sum of electronic and thermal Free Energies= -1011.454294

### **α-radical product complex**

1\1\GINC-SPARTAN-BM060\FOpt\UM062X\CC-pVTZ\C13H17N1O6(1-,2)\UWILLE\04-  
Mar-2022\0\#p opt=(calcf, maxcycle=500) freq=noraman M062X/cc-pVTZ sc  
rf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\|-1,2\C,-0.5562454868  
,0.0639281476,-1.456408216\H,-4.3331450553,0.7425327137,-3.0376584022\  
C,0.4992251262,-0.9232824719,-1.5495687691\H,-1.6644009763,-1.45376520  
61,-0.7470592311\C,-3.0050669471,0.0404667685,-1.07963334\C,-4.0779770  
534,-0.8160937782,-0.4710405635\H,-4.9817941109,-0.7075499677,-1.06512  
83098\H,-4.2800030518,-0.4502103108,0.536492201\H,-3.7968404647,-1.864  
4201202,-0.4139924009\O,0.3264870499,-2.1153357357,-1.3394939359\O,1.6  
86936889,-0.4079042821,-1.8939222335\C,2.757208384,-1.3474177514,-1.99  
6853236\H,2.9161022836,-1.8453313694,-1.0426114266\H,3.6325056741,-0.7  
702400119,-2.27368163\H,2.5359479737,-2.0917497725,-2.7589698514\O,-3.  
2510734419,1.139217541,-1.5655001955\N,-1.7454951555,-0.4853838738,-1.  
0337858565\C,-0.3148129615,1.5350493945,-1.5587441867\H,0.5553991366,1  
.6888543604,-2.1925709011\H,-1.170374365,2.0232975222,-2.0158177807\C,  
-0.0583636322,2.0983090029,-0.1724957042\C,-1.1013849983,2.5644036534,  
0.6320832445\C,1.2273241816,2.113896485,0.3752110353\C,-0.8775091461,3  
.034052578,1.9130460086\H,-2.1102359249,2.5640484922,0.2317868064\C,1.



4704117126,2.5825345125,1.6523707046\H,2.0554144734,1.7512932669,-0.22  
58778944\C,0.4266703406,3.0693750381,2.5039643271\H,-1.7057675633,3.40  
1258302,2.5090500439\H,2.4819888592,2.5941776768,2.0429391824\O,0.6401  
079655,3.501437437,3.6824600899\O,-3.7404463976,-0.9479452585,-3.58313  
81142\O,-4.6084068657,0.1599941635,-3.7727881211\C,-2.5285248693,-0.65  
90712885,-4.2523791253\H,-1.8837831343,-1.5179656317,-4.0687875793\H,-  
2.6981221158,-0.5349481292,-5.3220467662\H,-2.0689543326,0.2424939034,  
-3.8392208723\\Version=ES64L-G16RevC.01\HF=-1011.7235913\S2=0.756897\S  
2-1=0.\S2A=0.750039\RMSD=3.793e-09\RMSF=3.030e-06\Dipole=-0.8880591,-4  
.6727441,-5.7623756\Quadrupole=20.9802597,-12.0838364,-8.8964233,-4.43  
18499,-23.2771395,-32.7976482\PG=C01 [X(C13H17N1O6)]\@\@  
Sum of electronic and thermal Free Energies= -1011.483624

#### TS<sub>HAT\_Cβ</sub>

1\1\GINC-SPARTAN-BM060\FTS\UM062X\CC-pVTZ\C13H17N1O6(1-,2)\UWILLE\06-M  
ar-2022\0\#p opt=(ts,noeigentest,calcfc,maxcycle=500) freq=noraman M0  
62X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\1,2\C  
,1.6690163548,-1.0071610247,-0.3393321338\H,1.5613089654,-1.9669093053  
, -0.840386531\C,2.6414995705,-1.1781554719,0.8136200775\H,0.2717343487  
,0.2559011122,0.612143298\C,-0.7209066282,-1.4341952594,0.0486563216\C  
, -2.0112457019,-0.8523318089,0.566780916\H,-2.5334601732,-1.6157028857  
,1.1382281424\H,-2.6322739782,-0.5889359629,-0.2892280483\H,-1.8633162  
333,0.0315095235,1.1818891433\O,2.509602658,-0.6706275128,1.8982736084  
\O,3.6871003764,-1.9191115597,0.4639267478\C,4.7092870177,-2.067741145  
9,1.4554541078\H,5.1071661731,-1.0938644358,1.7313165522\H,5.479152191  
5,-2.6785370464,0.997996427\H,4.3058317104,-2.5584701725,2.3382027444\  
O,-0.6797095705,-2.544070596,-0.4677797352\N,0.3664297931,-0.641931536  
,0.1657955992\C,2.2522385834,0.0334211047,-1.3043246618\H,2.6186779059  
,0.9070092657,-0.7602110462\H,3.2162759438,-0.498630675,-1.7727742409\  
C,1.4082697297,0.4163117589,-2.4295264674\C,0.4768308405,-0.4699210333  
, -3.0246003246\C,1.5238414737,1.7066036294,-3.0003573064\C,-0.27108451  
54,-0.1059359645,-4.1077344856\H,0.3475340407,-1.4610430145,-2.6049205  
971\C,0.7879473012,2.0912294537,-4.0840722902\H,2.2209092315,2.4056357  
225,-2.550766753\C,-0.1583632092,1.200616745,-4.7125430415\H,-0.981418  
1636,-0.7952008468,-4.5475066016\H,0.8890360557,3.0853024198,-4.501737  
7042\O,-0.8396189469,1.5393285638,-5.7107569646\O,3.7083230862,-0.7510  
538383,-3.8362888013\O,4.1999552376,-1.2142701096,-2.6190510748\C,4.40  
69122083,0.4217300385,-4.179977656\H,5.4678825468,0.206323402,-4.32901  
61458\H,3.9666681688,0.7907608822,-5.1061273746\H,4.298471607,1.175306  
584,-3.3963876995\\Version=ES64L-G16RevC.01\HF=-1011.695467\S2=0.77226  
1\S2-1=0.\S2A=0.750203\RMSD=1.718e-09\RMSF=6.587e-06\Dipole=1.2800132,  
0.6201085,4.6808274\Quadrupole=19.866543,20.603777,-40.47032,9.6688771  
,5.296424,3.0717759\PG=C01 [X(C13H17N1O6)]\@\@  
Frequencies -749.2687  
Sum of electronic and thermal Free Energies= -1011.462113

#### Cβ-radical product complex

1\1\GINC-SPARTAN-BM060\FOpt\UM062X\CC-pVTZ\C13H17N1O6(1-,2)\UWILLE\04-  
Mar-2022\0\#p opt=(calcfc,maxcycle=500) freq=noraman M062X/cc-pVTZ sc  
rf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\1,2\C,2.6498884499,  
-1.3680399972,2.0696946825\H,2.4454480255,-1.1934337076,1.0124758267\C

,3.9501897261,-2.1436041782,2.1910038866\H,1.9131870276,-2.908784703,3.2994789937\C,0.3101247582,-2.0584891574,2.3736412165\C,-0.6370472176,-2.9686726629,3.1067940543\H,-1.2654003284,-3.4743546561,2.3765843371\H,-1.2816685206,-2.3553054426,3.7345969708\H,-0.1275396741,-3.7037220967,3.7234995076\O,4.1480255977,-3.0133236497,3.006207882\O,4.8643917108,-1.7086834141,1.3329943756\C,6.1665791922,-2.2923523331,1.4571506196\H,6.5710606521,-2.0946209043,2.4472576301\H,6.7761494907,-1.8203858109,0.6951579492\H,6.1128098842,-3.3660590716,1.2936916655\O,-0.1188796855,-1.2195887887,1.5769035371\N,1.6110723676,-2.2122391043,2.6349147882\C,2.8039720553,-0.0756872694,2.82189801\H,2.6027792594,-0.1360235797,3.8850568678\C,3.2824710757,1.1178072183,2.2809967908\C,3.6443002657,1.28934805,0.9102432506\C,3.4359976588,2.2745565386,3.1074190454\C,4.1010964174,2.484875744,0.4230887713\H,3.5553103105,0.4460332329,0.2368595829\C,3.8906606775,3.46855017,2.6242587005\H,3.1747114191,2.1860740455,4.1569494907\C,4.256667567,3.6549693656,1.2440410751\H,4.3684170466,2.5788300063,-0.6241049294\H,3.9914976732,4.3228439243,3.2841272772\O,4.6829940268,4.7588921697,0.7925855069\O,1.6393434299,-0.588789372,-1.1232995161\C,2.1566734014,0.1609926043,-2.1958362095\O,0.7238947718,0.2894058793,-0.4615144456\H,0.4890658999,-0.2542535239,0.3264818482\H,2.8661110467,-0.494624044,-2.6971394968\H,2.6656720062,1.0551268636,-1.8303666788\H,1.3607455347,0.445266655,-2.8867948644\\Version=ES64L-G16RevC.01\HF=-1011.7236836\S2=0.775775\S2-1=0.\S2A=0.750224\RMSD=3.239e-09\RMSF=3.353e-06\Dipole=-0.8767841,-6.9324147,1.0108265\Quadrupole=-15.505254,-17.4041544,32.9094085,-51.6883892,-20.3034271,-12.7792414\PG=C01 [X(C13H17N1O6)]\@\

Sum of electronic and thermal Free Energies= -1011.485742

#### TS<sub>addition</sub>

1\1\GINC-SPARTAN-BM066\FTS\UM062X\CC-pVTZ\C13H17N1O6(1-,2)\UWILLE\05-M ar-2022\0\#p opt=(ts,noeigentest,calcf, maxcycle=500) freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\|-1,2\C,0.4985258778,0.0012341939,-0.236558486\H,-0.0498489722,0.0620066119,-1.1744333181\C,1.4768812913,-1.151297142,-0.2965822353\H,-0.0828010681,-0.4856422516,1.7232141412\C,-1.7618093528,0.0862430913,0.7099315779\C,-2.5518842708,0.0074439874,1.9910446198\H,-2.6300522236,1.0177600028,2.3951909241\H,-2.082847532,-0.6303624385,2.7365416512\H,-3.5533869213,-0.3515816275,1.7708869396\O,1.6822530116,-1.92019769,0.6082075633\O,2.1302756635,-1.1742857431,-1.4539019242\C,3.1464428797,-2.1766760107,-1.5787840753\H,3.9033242441,-2.0385422613,-0.8102073671\H,3.5749961345,-2.0427790205,-2.5652635484\H,2.7073898297,-3.1669076384,-1.4833677969\O,-2.2754897089,0.4253468635,-0.3463704742\N,-0.4506546105,-0.2296917139,0.8206628119\C,1.2925284805,1.3148065217,-0.0205914568\H,1.8517609215,1.2166644197,0.9126349172\H,2.0129248066,1.4094857867,-0.8340348265\C,0.3860050996,2.5101086314,0.0327243731\C,-0.0329920845,3.1307542065,-1.1720503552\C,-0.1299759845,2.9640661097,1.2215698188\C,-0.9544013128,4.1433433573,-1.1720165252\H,0.3719093941,2.7695491734,-2.1117325203\C,-0.9830683436,4.0911971624,1.2774219302\H,0.1634393505,2.4865520041,2.1501137398\C,-1.5401966463,4.6350182423,0.0443268174\H,-1.2957292641,4.584434445,-2.1010819218\H,-1.5683627033,4.2635349485,2.1722115781\O,-2.4517450234,5.502376234,0.0586523455\O,1.2824672063,5.6832160875,1.096013259\O,0.1482827231,5.5544454313,1.9028267287\C,1.059382106

5,6.7323585019,0.1823727935\H,0.8675357114,7.6692424896,0.7114010836\H  
,1.9719232936,6.8268613758,-0.4069435681\H,0.2184509968,6.5057836579,-  
0.4747372145\\Version=ES64L-G16RevC.01\HF=-1011.6984883\S2=0.772942\S2  
-1=0.\S2A=0.750248\RMSD=4.475e-09\RMSF=3.801e-06\Dipole=3.4980148,-5.8  
440387,-0.6439301\Quadrupole=23.1355562,-59.7496548,36.6140986,21.9467  
443,-11.7134654,-13.5189221\PG=C01 [X(C13H17N1O6)]\ \@  
Frequencies -324.5092  
Sum of electronic and thermal Free Energies= -1011.459481

#### Addition product

1\1\GINC-SPARTAN-BM009\FOpt\UM062X\CC-pVTZ\C13H17N1O6(1-,2)\UWILLE\04-  
Mar-2022\0\#p opt=(calcfc,maxcycle=500) freq=noraman M062X/cc-pVTZ sc  
rf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\ -1,2\C,0.3265266712,  
-0.5574523412,0.0813705078\H,-0.0492433818,-0.4917361665,-0.9375513696  
\C,1.0469306405,-1.8750861712,0.2681288225\H,-0.6195023184,-0.64108855  
41,1.9541108419\C,-1.9945309657,0.0317314173,0.6084750157\C,-2.9544477  
055,0.2874026749,1.7422077821\H,-3.971712899,0.1465683558,1.3885628763  
\H,-2.8355099309,1.3271483805,2.0509407943\H,-2.7659209273,-0.35252050  
41,2.6011697493\O,0.9570855216,-2.5720548254,1.2469305426\O,1.84339361  
17,-2.1432404682,-0.7628066602\C,2.6385940669,-3.3290312566,-0.6470683  
01\H,3.2858121101,-3.2613223827,0.2242788418\H,3.2264832511,-3.3818909  
652,-1.5561497887\H,1.9963500353,-4.2018131413,-0.5558059919\O,-2.2798  
426198,0.2905785189,-0.5516112784\N,-0.8011231643,-0.4922131416,0.9740  
428419\C,1.3273396466,0.5963279324,0.3352186471\H,1.6870363331,0.50745  
79725,1.3630799876\H,2.1789229584,0.4553448731,-0.3318812886\C,0.69414  
10729,1.9424928948,0.1100819889\C,0.5947187721,2.4390795623,-1.2180522  
545\C,0.146307088,2.6337996916,1.147303973\C,-0.1148877215,3.602627421  
3,-1.487528509\H,1.0458936625,1.874092124,-2.0254270774\C,-0.493777902  
9,3.9626762112,0.9713788726\H,0.2022213113,2.2382162652,2.156194427\C,  
-0.7294357285,4.3720090018,-0.4776153992\H,-0.2329866271,3.94870541,-2  
.5085032837\H,-1.4481402784,4.033792244,1.5087216511\O,-1.4330074411,5  
.3998284643,-0.6879463014\O,1.5173382743,5.1737510246,1.0971140443\O,0  
.2311940582,5.0146764399,1.690847084\C,1.5331506053,6.4541993145,0.498  
6359598\H,1.3805928654,7.2322754554,1.249508499\H,2.5277191579,6.55831  
21089,0.0659929837\H,0.7706418978,6.5306591587,-0.2758502309\\Version=  
ES64L-G16RevC.01\HF=-1011.7124794\S2=0.768449\S2-1=0.\S2A=0.750168\RMS  
D=8.552e-09\RMSF=3.856e-06\Dipole=2.4643679,-5.2719006,1.4148313\Quadr  
upole=22.3404728,-44.9120439,22.5715711,9.7589248,-12.4409898,5.870482  
9\PG=C01 [X(C13H17N1O6)]\ \@  
Sum of electronic and thermal Free Energies= -1011.471051

## Scheme 4 - Reaction of MeOO<sup>•</sup> with Ac-Trp-OMe

### Reactant complex

```
1\1\GINC-SPARTAN-BM097\FOpt\UM062X\CC-pVTZ\C15H19N2O5(2)\UWILLE\11-Dec
-2021\0\#p scf=(qc,direct) freq=noraman opt=(calcf, maxcycle=500) M06
2X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,-
0.5286192899,3.1661237569,4.8353840979\H,-0.4622551795,3.7443453329,3.
915334736\C,-0.2340613406,1.7117570945,4.5373745771\H,-2.1793579061,2.
589487208,6.0026866942\C,-2.7034100468,4.2898738216,4.9896075681\O,-0.
8615613498,0.785082993,4.9840918626\O,0.8378791389,1.5824211435,3.7645
10705\C,1.2485310209,0.2376416115,3.4838669931\H,0.4522525954,-0.29704
09233,2.970932562\H,2.1232171036,0.3201646982,2.8486155506\H,1.4957990
54,-0.2809341214,4.4069290534\O,-2.4046370196,5.1365157427,4.159452734
9\N,-1.8700997015,3.2850119154,5.3425035735\O,1.9146097451,-2.58153718
99,2.8568801409\C,0.5194658855,3.6927197998,5.8468417695\H,1.513495501
,3.5117795287,5.4352151102\H,0.4289537393,3.1064752707,6.7633731754\C,
-4.0297485379,4.3124538453,5.7058524563\H,-3.9930271689,5.0995417471,6
.4593219103\H,-4.8099400349,4.5642899052,4.992300837\H,-4.2642908735,3
.3698042437,6.1939530255\O,2.7364965419,-2.2812424278,1.9006329935\C,2
.1104006225,-2.4003903302,0.609360521\H,2.8793503355,-2.1536314874,-0.
1152217143\H,1.7627381623,-3.4221550247,0.4850653651\H,1.2824013309,-1
.6978324437,0.5593335178\C,0.3231010327,5.1410160104,6.1341806936\C,0.
7416555867,6.2370052996,5.3067884102\C,-0.3647207753,5.6887055272,7.17
757769\C,0.2737219159,7.4219281671,5.9172927371\C,1.4604040069,6.32494
67111,4.1082998235\H,-0.8428242901,5.2016252375,8.0117340532\C,0.51568
69314,8.6825014049,5.3713850487\C,1.6982809625,7.5706153605,3.56260862
72\H,1.8248097134,5.4303439499,3.6182095096\H,-0.8243210377,7.68711029
17,7.7114803713\C,1.2303002205,8.7382621697,4.190983487\H,0.1549028443
,9.58057463,5.8542506249\H,2.2525882187,7.6552856675,2.637863497\H,1.4
342936416,9.6998680909,3.7399452334\N,-0.4001532991,7.0562027715,7.053
8123769\Version=ES64L-G16RevC.01\HF=-1068.5395007\S2=0.754807\S2-1=0.
\S2A=0.750013\RMSD=9.192e-09\RMSF=2.199e-06\Dipole=-0.0045296,-0.76813
33,0.4297813\Quadrupole=-8.2303228,-15.3610173,23.59134,-5.2389433,-17
.2239585,23.8536932\PG=C01 [X(C15H19N2O5)]\@\@
Sum of electronic and thermal Free Energies= -1068.271984
```

### C $\alpha$ \_HAT complex

```
1\1\GINC-SPARTAN-BM010\FOpt\UM062X\CC-pVTZ\C15H19N2O5(2)\UWILLE\29-Jan
-2022\0\#p scf=(qc,direct) opt=(readfc, maxcycle=500) geom=checkpoint
guess=check freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile
) nosymm\geom&freq\0,2\C,-1.3367893098,1.1645694712,-1.8960475015\H,
-1.5433898887,1.0681570135,-2.9619674263\C,0.0840401708,0.7112217,-1.6
455713079\H,-1.8477887844,-0.1949853275,-0.3702913006\C,-3.5075563406,
0.1136750585,-1.5444082676\C,-4.3216809726,-0.8281507644,-0.6954183543
\H,-4.7997201365,-1.5559077537,-1.3481463518\H,-5.1064282766,-0.255831
3627,-0.2025499795\H,-3.729594425,-1.3443735115,0.0560078978\O,0.40191
86062,-0.1035724749,-0.8141987237\O,0.9409373538,1.3420374509,-2.43537
49411\C,2.3191687982,0.9873834644,-2.2669416746\H,2.6376424468,1.21060
36289,-1.250549803\H,2.8690254424,1.5903324649,-2.9806119673\H,2.45297
26276,-0.0721818282,-2.473362518\O,-3.9862765052,0.6920450341,-2.51146
45279\N,-2.221331014,0.2854727619,-1.1738142935\C,-1.5175936117,2.6444
```

906717,-1.4862093477\H,-0.9105710446,3.2612421047,-2.1493833127\H,-2.5  
628561697,2.8888916496,-1.6724745292\O,-1.3101850966,-1.6190734691,-3.  
3853600915\O,-0.1601017333,-1.1632732826,-3.773340197\C,-1.1641612893,  
-2.6598348579,-2.3997172208\H,-0.5996077494,-2.2601788572,-1.561161994  
3\H,-2.1742912686,-2.9304865942,-2.1079125505\H,-0.6496431401,-3.49977  
88705,-2.8591995773\C,-1.1537184192,2.8938576996,-0.0592710929\C,0.135  
9208589,3.2817936229,0.4450043738\C,0.0361914179,3.3242945503,1.854418  
8376\C,1.3569561005,3.6123671592,-0.1589049427\C,1.115439496,3.6743783  
074,2.6662835189\C,2.4273111812,3.9570722111,0.6414376643\H,1.45647387  
48,3.6011369425,-1.2369232935\H,-1.6218919222,2.9347620581,3.115051408  
9\C,2.307050415,3.9846943771,2.0424826535\H,1.0194185723,3.7011931181,  
3.7432620719\H,3.3749718546,4.2136155786,0.1876857429\H,3.1643295865,4  
.2586285137,2.6421797757\C,-1.954639751,2.7239200708,1.034397697\H,-2.  
9925418478,2.437412831,1.082561744\N,-1.2484411067,2.9800384396,2.1827  
387024\\Version=ES64L-G16RevC.01\HF=-1068.548129\S2=0.754916\S2-1=0.\S  
2A=0.750014\RMSD=2.523e-09\RMSF=1.096e-06\Dipole=0.0531619,-1.093876,2.  
.3605182\Quadrupole=1.587712,2.7766964,-4.3644084,7.3015647,-18.271552  
1,8.6119393\PG=C01 [X(C15H19N2O5)]\@\  
Sum of electronic and thermal Free Energies= -1068.273537

#### TS<sub>HAT\_Cα</sub>

1\1\GINC-SPARTAN-BM116\FTS\UM062X\CC-pVTZ\C15H19N2O5(2)\UWILLE\10-Dec-  
2021\0\#p scf=(qc,direct) geom=checkpoint guess=check opt=(ts,noeigen  
test,readfc,maxcycle=500) freq=norman M062X/cc-pVTZ scrf=(cpcm,solven  
t=acetonitrile) nosymm\geom&freq\0,2\C,-1.1392575913,0.6499567598,-1  
.835703282\H,-1.4329004171,0.2817150605,-3.0380816562\C,0.2902950332,0  
.2123541491,-1.6993508898\H,-1.4709017453,-0.922950027,-0.5525581859\C  
, -3.3129414312,-0.1127495264,-0.9567230225\C,-3.9336466179,-1.20145065  
98,-0.1231586121\H,-3.8736102125,-2.1429000997,-0.6709606988\H,-4.9754  
793021,-0.960041624,0.0588166057\H,-3.4078123981,-1.3247030448,0.82190  
84605\O,0.6397187378,-0.7401761251,-1.0422898374\O,1.1134174424,0.9559  
872722,-2.4238285172\C,2.5006007653,0.5986224309,-2.3570499141\H,2.856  
7808953,0.6965069683,-1.3336579225\H,3.014957235,1.295069856,-3.009134  
7702\H,2.6386857825,-0.4241661323,-2.6986176309\O,-3.9651117283,0.7307  
363636,-1.5433293825\N,-1.9461459545,-0.1568851885,-1.0121262624\C,-1.  
3848776807,2.1618935193,-1.8222249692\H,-0.670428392,2.616463932,-2.50  
60973083\H,-2.3843974729,2.3468336908,-2.2020049881\O,-2.5618952797,-1  
.3607773892,-3.5713493366\O,-1.9020712894,-0.2751940641,-4.0665027297\  
C,-1.6607855749,-2.4590402241,-3.4882588465\H,-0.8561131098,-2.2303685  
368,-2.7875689136\H,-2.2509105608,-3.2954838736,-3.1217828852\H,-1.251  
6735959,-2.6798747474,-4.4726398917\C,-1.2347939898,2.7301978656,-0.44  
54699673\C,-0.0312775349,3.2179956519,0.1715242048\C,-0.3661016673,3.5  
877427103,1.4946416566\C,1.286660854,3.4023846237,-0.2701294299\C,0.57  
31627956,4.1176018242,2.3797943923\C,2.2182967811,3.9249777363,0.60365  
0994\H,1.564828164,3.1460735804,-1.2838855447\H,-2.2285940609,3.508955  
5595,2.5029689449\C,1.8643480475,4.2761000863,1.9187777494\H,0.2968964  
018,4.394951549,3.3880585037\H,3.2378909682,4.0723088517,0.274320805\H  
,2.6176020296,4.6832389691,2.5794102399\C,-2.2157563562,2.8207949615,0  
.5012975375\H,-3.2575084061,2.5537961994,0.4281741687\N,-1.7016604438,  
3.3332499414,1.664782302\\Version=ES64L-G16RevC.01\HF=-1068.5155042\S2  
=0.759899\S2-1=0.\S2A=0.750054\RMSD=2.649e-12\RMSF=2.249e-06\Dipole=0.

8521881,-1.0076833,1.6397598\Quadrupole=-1.828644,3.0411018,-1.2124578  
,6.1435468,-21.0589567,11.8562907\PG=C01 [X(C15H19N2O5)]\ \@  
Frequencies -2023.1658  
Sum of electronic and thermal Free Energies= -1068.243883

### **C $\alpha$ -radical product complex**

1\1\GINC-SPARTAN-BM004\FOpt\UM062X\CC-pVTZ\C15H19N2O5(2)\UWILLE\08-Dec  
-2021\0\ \#p scf=(qc,direct) geom=checkpoint guess=check freq=noraman o  
pt=(readfc,maxcycle=500) M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile  
) nosymm\ \geom&freq\ \0,2\C,0.0894338008,0.5135560251,-0.6098244711\H,3  
.5251294954,0.2321451469,2.4261757814\C,-1.2129042052,0.4711689057,-1.  
2465881771\H,-0.9114203329,0.0693023824,1.072647743\C,1.061511284,0.05  
23536902,1.6109201743\O,-2.2324713849,0.1490981749,-0.6578965127\O,-1.  
1885831315,0.826360587,-2.5352601277\C,-2.4522449603,0.8015448959,-3.2  
028660761\H,-3.1451120718,1.4889257255,-2.7224811709\H,-2.2540158419,1  
.112069452,-4.2224667032\H,-2.8683646032,-0.2033618852,-3.1841559224\O  
,2.2327041297,0.0707216466,1.256562796\N,0.0308204241,0.2140878393,0.7  
279558677\O,4.3003562448,0.5411292243,2.9422700464\C,1.3278726598,0.99  
80360809,-1.2803329412\H,1.1501631255,0.9918821853,-2.3544524667\H,2.1  
517144115,0.3154956653,-1.0767092938\C,0.6690310674,-0.1295306161,3.04  
84138884\H,1.2329544365,-0.9631211011,3.4612335421\H,0.9571924339,0.77  
21936983,3.5902284288\H,-0.3948358763,-0.2992350358,3.1846640945\C,4.3  
041819243,2.666463744,2.0985114399\H,3.2425994774,2.6015633174,1.84307  
3151\H,4.4267976506,3.0725539079,3.1040301552\H,4.8117881454,3.2982692  
041,1.3693764268\O,4.9216451732,1.4002081481,1.9939211827\C,1.71297972  
7,2.3808468804,-0.8274139386\C,2.9895086631,3.005807303,-1.0247324651\  
C,0.9290076177,3.2992865143,-0.1915457205\C,2.8989994931,4.3123249656,  
-0.4937584142\C,4.2048168314,2.5735187582,-1.5688080028\H,-0.093305121  
5,3.2197347219,0.1411852801\C,3.977922537,5.1961724402,-0.5097747636\C  
,5.2785536114,3.4414401767,-1.5758443701\H,4.3020232204,1.5735926707,-  
1.9722874656\H,1.2773369434,5.2839190516,0.464381073\C,5.1626435356,4.  
7430562856,-1.0555431477\H,3.8906949431,6.1935340015,-0.1007230665\H,6  
.2251673647,3.1211047657,-1.9890133176\H,6.0208685523,5.400699943,-1.0  
800016576\N,1.6347026049,4.4615145129,0.0100181215\ \Version=ES64L-G16R  
evC.01\HF=-1068.553192\ S2=0.757241\ S2-1=0.\ S2A=0.750042\ RMSD=7.376e-09  
\ RMSF=2.440e-06\ Dipole=-2.9760067,1.3063052,-0.1858493\ Quadrupole=-27.  
2035318,21.4576186,5.7459132,-1.5099689,-8.3882833,5.2747321\ PG=C01 [X  
(C15H19N2O5)]\ \@  
Sum of electronic and thermal Free Energies= -1068.276837

### **C $\beta$ \_HAT complex**

1\1\GINC-SPARTAN-BM004\FOpt\UM062X\CC-pVTZ\C15H19N2O5(2)\UWILLE\21-Jan  
-2022\0\ \#p scf=(qc,direct) opt=(readfc,maxcycle=500) freq=noraman geo  
m=checkpoint guess=check M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile  
) nosymm\ \geom&freq\ \0,2\C,-1.2435582085,2.8894653083,5.1134031083\H,-  
1.9860891606,2.1927742637,4.7278593474\C,-0.5559708635,2.274031851,6.3  
129866058\H,-1.4447145312,4.7010945691,6.1608956824\C,-3.1524639146,4.  
4297874081,5.0641001229\O,-0.3212221362,2.860311148,7.3390984304\O,-0.  
1947887526,1.0186427686,6.072999753\C,0.5345143834,0.3660598959,7.1204  
076309\H,-0.070781111,0.3203832313,8.0225454871\H,0.7500378582,-0.6308  
836957,6.7540751357\H,1.4552684218,0.9068076663,7.3260055873\O,-3.8065

371361,3.709014151,4.3236244325\N,-1.9256024597,4.0901763947,5.5199485  
64\O,1.4275949167,1.023906073,1.4601512086\C,-0.1883692562,3.168832838  
3,4.0165698212\H,0.3415579948,2.2394952768,3.7983942127\H,0.5378841401  
,3.8799455921,4.4153266711\C,-3.663171088,5.7744733119,5.5156087141\H,  
-4.7065110174,5.6741202037,5.8040402443\H,-3.0907329654,6.1930887982,6  
.3393446751\H,-3.6120667877,6.4569983253,4.6672816391\O,1.5209079748,2  
.3079600621,1.3136848577\C,1.1050439594,2.7320855999,0.0018298968\H,0.  
1971072394,2.1971083175,-0.2656870737\H,0.9237233913,3.8008028323,0.08  
29975785\H,1.911360854,2.5219844927,-0.6975419368\C,-0.814166583,3.704  
9231503,2.7769597207\C,-1.5156240479,2.9360224559,1.7910742047\C,-0.87  
32096265,5.0041530715,2.365085927\C,-1.9654000856,3.8364041833,0.80103  
95047\C,-1.7615240928,1.5673060637,1.6358356692\H,-0.467747779,5.88844  
86466,2.8288850089\C,-2.6421444989,3.4046215876,-0.3394510027\C,-2.429  
8568197,1.1350307312,0.5075015804\H,-1.4168531365,0.8587774973,2.37920  
92241\H,-1.7273172266,5.9393310049,0.6645357328\C,-2.8647315195,2.0476  
70146,-0.4707269217\H,-2.9718982789,4.1048167606,-1.0949203293\H,-2.62  
24507529,0.0801880817,0.3670999585\H,-3.3835129006,1.6781860895,-1.344  
7917876\N,-1.5660851968,5.0919092958,1.1807235137\Version=ES64L-G16Re  
vC.01\HF=-1068.5447612\S2=0.755083\S2-1=0.\S2A=0.750015\RMSD=7.383e-10  
\RMSF=1.521e-06\Dipole=1.1780011,2.0749582,-0.674232\Quadrupole=-24.58  
26504,30.3974175,-5.814767,0.9586867,9.8822525,-0.8658834\PG=C01 [X(C1  
5H19N2O5)]\@  
Sum of electronic and thermal Free Energies= -1068.272300

#### TS<sub>HAT\_CB</sub>

1\GINC-SPARTAN-BM094\FTS\UM062X\CC-pVTZ\C15H19N2O5(2)\UWILLE\08-Dec-  
2021\O\#p scf=(qc,direct) opt=(ts,noeigentest,readfc,maxcycle=500) fr  
eq=norman geom=checkpoint guess=check M062X/cc-pVTZ scrf=(cpcm,solven  
t=acetonitrile) nosymm\geom\0,2\C,-1.1400206151,2.9354135797,4.82549  
53865\H,-1.8554575172,2.2564389708,4.3704042542\C,-0.2834663496,2.1797  
993593,5.8212239079\H,-1.4071666758,4.4385212707,6.2735249936\C,-3.167  
4030292,4.2582991789,5.2324261191\O,0.0866370662,2.6327076142,6.874231  
0759\O,0.0554754472,0.9861633488,5.3553456543\C,0.9950760021,0.2461063  
3,6.1456321752\H,0.5834654068,0.0548155453,7.133555381\H,1.1614694725,  
-0.6830495163,5.6132774831\H,1.9222281644,0.8076516674,6.2355294674\O,  
-3.7960854856,3.6746983303,4.3613912021\N,-1.8809303703,3.958523516,5.  
5242736433\O,1.7147413463,2.0118022892,3.1445209451\C,-0.2215865952,3.  
5430732186,3.7598828089\H,0.6870009693,2.6751932814,3.4938021723\H,0.3  
745098047,4.3497828199,4.187783754\C,-3.7817368353,5.3665755907,6.048  
4323881\H,-4.7143141434,5.0039228568,6.4754739529\H,-3.131334262,5.725  
0947092,6.8417174263\H,-4.0195073975,6.1918307593,5.378847907\O,2.1704  
022865,2.7230350406,2.0597651365\C,1.744738061,2.0747560463,0.86962710  
7\H,0.6568815051,2.0164958581,0.835427927\H,2.113919753,2.6904576688,0  
.0519179411\H,2.1771707089,1.0758647119,0.813100336\C,-0.7956091812,3.  
8926464354,2.4773326368\C,-1.6198669178,3.0839120296,1.6105046559\C,-0  
.5601571589,5.0670043547,1.7894377318\C,-1.8531587281,3.8397051783,0.4  
436137422\C,-2.1200219793,1.7789805076,1.6792396733\H,0.0173559461,5.9  
23812589,2.0947504131\C,-2.6002537844,3.3566436468,-0.6262787755\C,-2.  
8581979497,1.2894434569,0.6184696521\H,-1.9206583568,1.1486703048,2.53  
56328889\H,-1.1905159064,5.790225914,-0.0835434411\C,-3.103677665,2.07  
41785227,-0.5187974395\H,-2.7696206401,3.9584759206,-1.5085533669\H,-3

.2505508313,0.2828094877,0.6602465771\H,-3.6875980125,1.663396818,-1.3  
308394965\N,-1.1953025525,5.0426067879,0.5900943812\\Version=ES64L-G16  
RevC.01\HF=-1068.5110354\S2=0.763205\S2-1=0.\S2A=0.75011\RMSD=5.043e-1  
0\RMSF=1.647e-06\Dipole=0.2265542,1.4998379,-1.1291624\Quadrupole=-22.  
9192709,28.3071056,-5.3878346,-3.409705,1.5272754,-3.4304052\PG=C01 [X  
(C15H19N2O5)]\@\@  
Frequencies -1972.8804  
Sum of electronic and thermal Free Energies= -1068.242122

### **C $\beta$ -radical product complex**

1\1\GINC-SPARTAN-BM121\FOpt\UM062X\CC-pVTZ\C15H19N2O5(2)\UWILLE\08-Dec  
-2021\0\#p scf=(qc,direct) geom=checkpoint guess=check freq=noraman o  
pt=(readfc,maxcycle=500) M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile  
) nosymm\geom&freq\0,2\C,0.6566929734,-0.5137754679,-1.915718305\H,0  
.6883338815,0.4752709592,-1.4557236038\C,0.706544708,-0.3208657376,-3.  
4265207431\H,-1.1684501899,-1.4580257874,-2.401655535\C,-1.0570759132,  
-1.3335475718,-0.3655058098\C,-2.37571905,-2.0384802701,-0.2115431934\  
H,-2.2106147445,-2.9460932663,0.3667591965\H,-3.0456571513,-1.39699964  
55,0.3575124876\H,-2.8338547159,-2.2938742099,-1.1628203588\O,-0.03278  
28089,-0.8734660179,-4.2026161779\O,1.6826576961,0.4998974601,-3.77600  
58761\C,1.8578322842,0.7001248958,-5.185804846\H,0.9532525698,1.122505  
0848,-5.6162755391\H,2.6873458366,1.3902994362,-5.2840804113\H,2.08634  
16417,-0.2468618117,-5.6688211035\O,-0.4278120793,-0.9476991402,0.6220  
541441\N,-0.612444609,-1.1553476987,-1.6158218558\O,1.7857469985,0.527  
790066,1.0152105206\C,1.8628147469,-1.2887985856,-1.4634524031\H,2.617  
2394656,-0.743607306,-0.9165871308\H,1.0433958866,-0.0922053276,0.8234  
397332\O,1.1649765292,1.4520470157,1.8997577056\C,0.5195778771,2.42550  
44722,1.106787602\H,1.2331410647,2.9213741137,0.4472379063\H,-0.283125  
4978,1.9769326971,0.5169869084\H,0.0999861132,3.1453423876,1.807962690  
3\C,2.0764777621,-2.6333615013,-1.7775451375\C,3.2230598546,-3.4313206  
674,-1.3659937979\C,1.2792577341,-3.4997786969,-2.5319859957\C,3.05009  
88335,-4.7223319543,-1.8955727772\C,4.3555831078,-3.152693786,-0.60153  
72079\H,0.345763353,-3.3137739664,-3.0337379315\C,3.9740888471,-5.7421  
588448,-1.6866472782\C,5.2804362495,-4.1590910797,-0.3887123629\H,4.50  
83792418,-2.1679779648,-0.1788759979\H,1.4819690228,-5.5215161087,-3.0  
853003685\C,5.0895153825,-5.4401916385,-0.9273287348\H,3.8237339752,-6  
.7291874229,-2.101675826\H,6.1637944552,-3.9596189623,0.2019306268\H,5  
.8290330257,-6.2077095243,-0.7443985268\N,1.8642856415,-4.7291436259,-  
2.5973486858\\Version=ES64L-G16RevC.01\HF=-1068.5459938\S2=0.76995\S2-  
1=0.\S2A=0.750141\RMSD=3.022e-10\RMSF=1.185e-06\Dipole=-1.5354978,-1.1  
702885,-3.0840467\Quadrupole=-10.5179859,15.0651064,-4.5471205,0.22915  
51,-6.4079638,8.5844905\PG=C01 [X(C15H19N2O5)]\@\@  
Sum of electronic and thermal Free Energies= -1068.273336

### **NH\_HAT complex**

1\1\GINC-SPARTAN-BM001\FOpt\UM062X\CC-pVTZ\C15H19N2O5(2)\UWILLE\17-Feb  
-2022\0\#p opt=(calcf, maxcycle=500) freq=noraman M062X/cc-pVTZ scrf=  
(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,-0.7392580173,0.3  
191331167,-6.0598324409\H,-0.9750453083,0.6650840977,-7.0665318096\C,0  
.7568526375,0.1252279501,-5.9514724843\H,-0.8309448684,-1.6665255445,-  
5.3682440401\C,-2.6455663188,-1.1938468156,-6.2113356676\C,-3.19389112



54,-2.5555221602,-5.8719113386\H,-3.6535328136,-2.9773322138,-6.762943  
9671\H,-3.9725102109,-2.4323071499,-5.1199588782\H,-2.43664871,-3.2365  
158554,-5.4925141918\O,1.2861832687,-0.8730847098,-5.5320271271\O,1.41  
54308198,1.2064925172,-6.3485780905\C,2.8426252483,1.1488773761,-6.222  
5878418\H,3.1144853916,0.9929674016,-5.1805756642\H,3.2086082026,2.107  
2868625,-6.5730366756\H,3.2373948051,0.3400056387,-6.8325856989\O,-3.3  
212806829,-0.3475920096,-6.7839910978\N,-1.371789166,-0.9571553113,-5.  
8373073961\C,-1.213507957,1.3912364813,-5.0494874437\H,-0.7998719745,2  
.3532189665,-5.3528290934\H,-2.2962482784,1.4500898256,-5.1516715704\O  
,-1.2495885786,0.4698306684,1.5553832229\O,-1.0706578265,-0.7708351525  
,1.2282038299\C,-1.2881704769,0.6399132283,2.9860830913\H,-0.340306448  
9,0.3053988373,3.3981287781\H,-1.4389414181,1.7015140842,3.1496382084\  
H,-2.1153944247,0.055897384,3.3795101036\C,-0.8190400071,1.0718145109,  
-3.6451469057\C,0.3699942882,1.5097226287,-2.9665903415\C,0.3651031312  
,0.9024712614,-1.6897696022\C,1.4265115057,2.3660294467,-3.3068152971\  
C,1.3827026044,1.1188856073,-0.7592244497\C,2.4350889564,2.5809099566,  
-2.3892448685\H,1.4491234881,2.8526622163,-4.2739774243\H,-1.040293747  
8,-0.3906517486,-0.7844507522\C,2.4136290504,1.9597956694,-1.127119933  
1\H,1.3604938792,0.6437057934,0.212376647\H,3.2563467597,3.2387419157,  
-2.6396513272\H,3.2195677519,2.1482300608,-0.4309068443\C,-1.470524106  
5,0.2438860144,-2.7733417285\H,-2.4015316995,-0.2841104974,-2.90220000  
03\N,-0.7665136228,0.1370886506,-1.6019178892\\Version=ES64L-G16RevC.0  
1\HF=-1068.5461617\S2=0.755199\S2-1=0.\S2A=0.750015\RMSD=1.862e-09\RMS  
F=1.032e-06\Dipole=0.4589072,-0.1751492,2.663853\Quadrupole=0.5100135,  
4.1197575,-4.629771,9.2912524,-21.355173,4.9333464\PG=C01 [X(C15H19N2O  
5)]\@  
Sum of electronic and thermal Free Energies= -1068.274430

**TS<sub>HAT\_N</sub>**

Could not be located.

### **N-radical product complex**

1\1\GINC-SPARTAN-BM006\FOpt\UM062X\CC-pVTZ\C15H19N2O5(2)\UWILLE\09-Dec  
-2021\0\#p scf=(qc,direct) geom=checkpoint guess=check freq=norman o  
pt=(readfc,maxcycle=500) M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile  
) nosymm\geom&freq\0,2\C,-2.9439337908,-2.2524484463,1.8812296993\H,  
-3.8287843054,-1.8384923644,2.3674312559\C,-3.2026198581,-2.3206519132  
,0.3881980956\H,-2.5691530892,-4.3073917712,1.6543511114\C,-2.72707725  
13,-3.9019312067,3.6658809088\C,-2.4696722923,-5.3450762668,4.00968709  
24\H,-1.5066242045,-5.411884965,4.5156870102\H,-3.2362370167,-5.677198  
4853,4.7062116136\H,-2.4590119459,-5.9936195951,3.137942631\O,-3.11852  
11001,-3.3279197162,-0.2666838459\O,-3.501549939,-1.128849864,-0.10553  
94408\C,-3.7491849547,-1.0793667849,-1.5190173163\H,-4.5967741385,-1.7  
129739967,-1.7676564405\H,-3.96591108,-0.0417269227,-1.7430497516\H,-2  
.8689621012,-1.4153888912,-2.0619928028\O,-2.9191761832,-3.0512021173,  
4.5253483713\N,-2.7101798544,-3.5924012761,2.3517032748\O,2.9035188895  
,-1.7943479042,-2.158577955\C,-1.7642131606,-1.2878483404,2.1816334316  
\H,-1.6392295452,-1.2763975515,3.2632745766\H,-2.0521754912,-0.2917995  
587,1.8490733215\O,3.3566003333,-0.4834353774,-1.8429919229\C,4.324303  
086,-0.6054971549,-0.8228591242\H,3.8816570597,-1.0134317195,0.0888980  
582\H,5.1505964896,-1.2394653629,-1.1477516861\H,4.6842615166,0.405207

0574,-0.6353900469\C,-0.5168710894,-1.7246768419,1.515958875\C,0.45851  
32641,-2.6369816133,2.0033056774\C,-0.0638979366,-1.3767588733,0.18891  
62568\C,1.4033663906,-2.7809719739,0.9624547986\C,0.6144405626,-3.3283  
564618,3.2025000458\H,-0.5608378759,-0.6854666578,-0.4789147673\C,2.49  
31457898,-3.6084420168,1.091448218\C,1.7165703858,-4.1672199,3.3361720  
461\H,-0.0944951357,-3.2072473244,4.0127615237\H,2.1610600207,-1.89883  
28332,-1.5093921326\C,2.6362209499,-4.3053982563,2.2993364446\H,3.2118  
791775,-3.7179650382,0.2902081254\H,1.8638410899,-4.7169524703,4.25490  
35605\H,3.4837860144,-4.9640021955,2.429438076\N,1.04356987,-1.9808465  
783,-0.1448584873\\Version=ES64L-G16RevC.01\HF=-1068.5393756\S2=0.7662  
86\S2-1=0.\S2A=0.750192\RMSD=4.765e-09\RMSF=3.334e-06\Dipole=-1.214136  
7,-0.4507835,1.1734807\Quadrupole=4.4304942,11.1547944,-15.5852887,-2.  
0209891,19.2094462,-12.3943217\PG=C01 [X(C15H19N2O5)]\@\  
Sum of electronic and thermal Free Energies= -1068.267696

### Cy-addition complex

1\1\GINC-SPARTAN-BM125\FOpt\UM062X\CC-pVTZ\C15H19N2O5(2)\UWILLE\21-Jan  
-2022\0\#\#p scf=(qc,direct) opt=(readfc,maxcycle=500) freq=noraman M06  
2X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm geom=checkpoint gue  
ss=check\geom&freq\0,2\C,-2.6394972675,-2.8673858994,2.0510838934\H,  
-3.3970593758,-2.2970089753,2.5931880905\C,-2.7799798419,-2.5074574744  
,0.5837953728\H,-3.0182054132,-4.8197371037,1.3541978667\C,-3.27755251  
44,-4.8063269679,3.3890827387\C,-3.6268433985,-6.2721150288,3.38542417  
86\H,-3.5223615356,-6.7331759671,2.4069787325\H,-2.9796660181,-6.78170  
83792,4.0967356286\H,-4.6535069826,-6.3819268418,3.7305019592\O,-2.985  
002432,-3.3071452423,-0.2962219897\O,-2.6715770349,-1.2025690204,0.395  
1450398\C,-2.8091520923,-0.7502525345,-0.9590005317\H,-3.8014014635,-0  
.9957951214,-1.330498061\H,-2.6683707512,0.3239747327,-0.9252604751\H,  
-2.0507437349,-1.2167368638,-1.5812647797\O,-3.3083686995,-4.136898296  
5,4.4138889414\N,-2.926203316,-4.2764409489,2.1984427495\O,0.202407953  
3,-1.2957403405,-0.5327665688\C,-1.2739541362,-2.4557925596,2.61323958  
69\H,-1.2861950988,-2.692982051,3.6784481446\H,-1.2002992384,-1.368885  
3626,2.5369162727\O,1.4017354381,-1.5773870207,-0.9418125347\C,2.37445  
79116,-0.6710622225,-0.3893667705\H,3.3368864013,-1.015582825,-0.75482  
448\H,2.1534260159,0.3315046245,-0.7475221493\H,2.3275452134,-0.725363  
422,0.6957884342\C,-0.0837436658,-3.079077621,1.9550642131\C,1.2743239  
374,-2.71962324,2.2525281864\C,-0.0159596676,-4.0329415042,0.979124931  
8\C,2.1090707163,-3.4904723147,1.413440194\C,1.8550555906,-1.805272547  
8,3.1403237852\H,-0.8028773758,-4.5561446239,0.4636580957\C,3.49815611  
1,-3.3681792785,1.4357486727\C,3.2303096035,-1.6794903102,3.1636666729  
\H,1.2352223095,-1.2034954852,3.7930275914\H,1.5990226954,-4.928659964  
3,-0.0556708112\C,4.0428570918,-2.454452237,2.3169053421\H,4.123386517  
6,-3.9624381572,0.783068093\H,3.6943091652,-0.97546077,3.8408139806\H,  
5.1166738865,-2.3317579944,2.356709729\N,1.2944074065,-4.2860715394,0.  
6545631738\\Version=ES64L-G16RevC.01\HF=-1068.5451137\S2=0.755136\S2-1  
=0.\S2A=0.750016\RMSD=7.912e-10\RMSF=9.248e-07\Dipole=1.2505098,-0.027  
0487,-1.9720484\Quadrupole=7.0521848,14.7293217,-21.7815065,-4.2887742  
,5.6469861,11.600363\PG=C01 [X(C15H19N2O5)]\@\  
Sum of electronic and thermal Free Energies= -1068.269636

TS<sub>addition\_Cy</sub>

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1\1\GINC-SPARTAN-BM105\FTS\UM062X\CC-pVTZ\C15H19N2O5(2)\UWILLE\11-Dec-
2021\0\#p scf=(qc,direct) opt=(ts,noeigentest,calcf, maxcycle=500) fr
eq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom
&freq\0,2\C,-2.5941055142,-2.4693891226,1.6722406177\H,-3.3318598207,
-1.9313104507,2.2688078767\C,-2.7579905001,-2.042769707,0.2281452454\H
,-2.9509109227,-4.3966442446,0.8949985192\C,-3.1732784548,-4.476122786
,2.9354039728\C,-3.5002720564,-5.9454028726,2.8757351083\H,-3.43819462
48,-6.3553771996,1.8712792348\H,-2.8099338084,-6.4777847519,3.52742507
92\H,-4.5061969372,-6.090360688,3.2656689487\O,-2.7569799724,-2.809187
5622,-0.7037081301\O,-2.9112971341,-0.7334841919,0.1270795273\C,-2.850
1170864,-0.2059042429,-1.2027071043\H,-3.6495809521,-0.622268827,-1.81
07253938\H,-2.9670252711,0.8671035045,-1.1021892458\H,-1.8824625234,-0
.450658506,-1.6364615295\O,-3.1807857629,-3.8529205339,3.989350404\N,-
2.8669518206,-3.8864276299,1.7603679862\O,-0.1001393644,-1.2529933402,
0.1663272838\C,-1.2103914532,-2.0815466212,2.2180570503\H,-1.161303579
1,-2.455228529,3.2409932727\H,-1.1543317209,-0.9930309689,2.2650468103
\O,0.7942462406,-1.5344107498,-0.867472665\C,1.9004339041,-0.657785728
5,-0.7594561495\H,2.5342069115,-0.876415237,-1.6179517672\H,1.56867471
43,0.3809699049,-0.8031702236\H,2.4552512693,-0.8313701228,0.163423538
3\C,-0.0174049859,-2.5826540787,1.4497701341\C,1.3415410061,-2.4243105
005,1.9783336095\C,0.0468108174,-3.7859068658,0.6970517936\C,2.1514175
893,-3.3957797342,1.3753910973\C,1.9037115026,-1.4924556258,2.84054297
69\H,-0.7326088581,-4.2778228666,0.1441283725\C,3.5223391245,-3.448858
7121,1.5842711045\C,3.2710396068,-1.5398093637,3.0677619045\H,1.290576
676,-0.7351834795,3.3119851828\H,1.64312948,-4.9838423513,0.0489292152
\C,4.0684105077,-2.5020252,2.4379591906\H,4.1383773182,-4.1962407872,1
.1039676756\H,3.73089883,-0.8233170394,3.7339177844\H,5.1334148576,-2.
5127921093,2.6250035999\N,1.331883768,-4.2039410812,0.6037570919\Vers
ion=ES64L-G16RevC.01\HF=-1068.5185955\S2=0.769032\S2-1=0.\S2A=0.750125
\RMSD=3.030e-10\RMSF=2.176e-06\Dipole=1.2320955,-1.0681188,-1.1042649\
Quadrupole=2.4317963,20.0484174,-22.4802137,-7.1554932,8.3757225,6.085
0013\PG=C01 [X(C15H19N2O5)]\@
Frequencies -421.4743
Sum of electronic and thermal Free Energies= -1068.239589

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#### **γ-Addition product**

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1\1\GINC-SPARTAN-BM100\FOpt\UM062X\CC-pVTZ\C15H19N2O5(2)\UWILLE\08-Dec
-2021\0\#p scf=(qc,direct) opt=(readfc, maxcycle=500) geom=checkpoint
guess=check freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile
) nosymm\geom&freq\0,2\C,-2.5239208351,-2.3807085442,1.7633458499\H,
-3.1790680168,-2.0073852443,2.5559474115\C,-2.8604599213,-1.5780702061
,0.5199717973\H,-3.0657624632,-4.0021929894,0.5393785184\C,-2.95335201
31,-4.6752340491,2.4803586894\C,-3.2460654795,-6.0856781975,2.04029430
56\H,-2.3173830021,-6.6549845474,2.0949141443\H,-3.9557605844,-6.53135
59001,2.7324038982\H,-3.6321874426,-6.1407455719,1.0255991684\O,-3.346
8472987,-2.0451321023,-0.4786144696\O,-2.5908698403,-0.2911037258,0.68
62180562\C,-2.8248492945,0.5439071924,-0.4532547888\H,-3.8741537896,0.
5082908196,-0.7359782513\H,-2.5441863425,1.5457687387,-0.1495244248\H,
-2.2097797962,0.2086142975,-1.2858302148\O,-2.7843063918,-4.3824690789
,3.6572874682\N,-2.8539699776,-3.7596838882,1.495045051\O,-0.252411080
4,-2.0722076042,0.0825542879\C,-1.0851868578,-2.1651833791,2.256991984

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8\H,-0.9917769246,-2.6463002266,3.2277674212\H,-0.9360318898,-1.094408  
3954,2.3944211855\O,0.7057912295,-2.5149438981,-0.8700792891\C,1.37130  
11245,-1.3595578279,-1.343575989\H,2.0623587684,-1.7226996689,-2.10237  
99444\H,0.6623862108,-0.6640865437,-1.7944131369\H,1.9208980915,-0.869  
3324086,-0.5397710266\C,0.0318003885,-2.7068979054,1.3592128102\C,1.41  
20350035,-2.3435435184,1.8682244386\C,0.1533794066,-4.2009063584,1.254  
1095124\C,2.2163314438,-3.4866379089,1.8798438015\C,1.9313742061,-1.12  
1636249,2.2454742743\H,-0.5239934527,-4.8626441717,0.7450645337\C,3.54  
90733389,-3.4319242181,2.266816645\C,3.2666795399,-1.0473018715,2.6360  
299988\H,1.3153045537,-0.2307536334,2.2266111812\H,1.80284688,-5.51241  
60255,1.4220231243\C,4.057994836,-2.1947518561,2.6423754662\H,4.167728  
3172,-4.3185472278,2.2749607093\H,3.6914387511,-0.099189869,2.93361969  
94\H,5.0933661138,-2.1239999879,2.9477779855\N,1.4624720408,-4.5676257  
896,1.4680564873\\Version=ES64L-G16RevC.01\HF=-1068.5303565\S2=0.75647  
3\S2-1=0.\S2A=0.750033\RMSD=4.667e-10\RMSF=1.987e-05\Dipole=1.0748036,  
0.1988593,-1.1533449\Quadrupole=2.7800224,16.2407975,-19.02082,-9.8999  
593,7.0917765,6.9440819\PG=C01 [X(C15H19N2O5)]\@\  
Sum of electronic and thermal Free Energies= -1068.251206

### Cδ-addition complex

1\1\GINC-SPARTAN-BM011\FOpt\UM062X\CC-pVTZ\C15H19N2O5(2)\UWILLE\21-Jan  
-2022\0\#p scf=(qc,direct) opt=(calcf, maxcycle=500) freq=noraman M06  
2X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,2  
.8695692512,4.4929795232,4.6709060638\H,2.0192606422,5.1407691405,4.46  
40443894\C,4.0783130884,5.3408012977,5.003143605\H,4.0583158726,3.3086  
71193,3.403982725\C,2.219809494,3.504495152,2.5229274368\O,5.188000104  
4,5.1405739473,4.5787066524\O,3.7728394403,6.3024831441,5.8665678786\C  
,4.8661491211,7.1175820725,6.3085801603\H,5.3174117978,7.6264991123,5.  
4602649879\H,4.4399561559,7.8337993065,7.0013296652\H,5.6130633118,6.5  
020383838,6.8042270194\O,1.1080278332,4.0130222513,2.5456049566\N,3.14  
21136632,3.7195170051,3.4884305329\O,-0.6430768017,-1.0113269693,7.212  
5583106\C,2.5410796964,3.5910544805,5.8866408915\H,2.4079200732,4.2293  
193347,6.761303402\H,3.4031243951,2.947775953,6.0734407534\C,2.6452883  
06,2.5743606932,1.4156613374\H,3.7185310565,2.403303825,1.3930902919\H  
,2.1391756724,1.6203143173,1.5642997734\H,2.3158444717,2.9859567371,0.  
4650771028\O,-1.4198895771,-0.0277274573,7.5416296111\C,-0.7094470156,  
0.9870600601,8.276907921\H,-1.3735703972,1.8464999938,8.3110776642\H,-  
0.5019634727,0.6054456533,9.2739154851\H,0.2097344787,1.2210272182,7.7  
443004277\C,1.3225669644,2.7699599801,5.6431641581\C,-0.0379900384,3.2  
115875252,5.7590532356\C,1.2714568927,1.4851584701,5.1839904169\C,-0.8  
602505146,2.138477105,5.3510082993\C,-0.6349322442,4.3995552323,6.1983  
785851\H,2.0779889878,0.8041666397,4.9662972676\C,-2.2523725411,2.2147  
699364,5.3846291145\C,-2.0126735819,4.4800924529,6.2322747424\H,-0.025  
9170563,5.2377289298,6.5141441814\H,-0.3364314526,0.1782611286,4.74182  
31762\C,-2.8129987176,3.3953206894,5.8300271145\H,-2.865881687,1.37700  
5971,5.0824769778\H,-2.489543726,5.388733574,6.5735576686\H,-3.8896490  
044,3.4887418945,5.8716282585\N,-0.0349319429,1.1033131021,4.997174758  
3\\Version=ES64L-G16RevC.01\HF=-1068.5440884\S2=0.754796\S2-1=0.\S2A=0  
.750013\RMSD=6.606e-12\RMSF=1.875e-06\Dipole=1.428483,-0.1234639,1.171  
5949\Quadrupole=-4.5329068,-10.4836154,15.0165223,9.2879571,14.9782885  
,19.5008224\PG=C01 [X(C15H19N2O5)]\@\

Sum of electronic and thermal Free Energies= -1068.270616

#### TS<sub>addition\_c8</sub>

```
1\1\GINC-SPARTAN-BM100\FTS\UM062X\CC-pVTZ\C15H19N2O5(2)\UWILLE\07-Dec-2021\0\#p geom=checkpoint guess=check freq=noraman opt=(ts, noeigenes t, readfc, maxcycle=500) M062X/cc-pVTZ scrf=(cpcm, solvent=acetonitrile) nosymm\geom&freq\0,2\C,2.7827266041,4.2057329474,4.994476607\H,2.0409507914,4.9411065782,4.6861340483\C,4.0249131613,4.9219026032,5.4820637679\H,4.0448835993,2.9868824931,3.8364417811\C,2.2968884899,3.24551849,2.7932872164\O,5.1483541099,4.624571135,5.1647204146\O,3.721174411,5.8865870019,6.3404336\C,4.8330077615,6.5860879409,6.9159550128\H,5.4114701734,7.0714175557,6.1336551378\H,4.4041276818,7.3213149061,7.5866361319\H,5.466921633,5.8915646698,7.4618332776\O,1.2045104629,3.7910495017,2.7297084684\N,3.1247152826,3.3980367588,3.8528662583\O,1.1466908494,0.2740284151,6.8315801271\C,2.2016430603,3.3610713168,6.1573174529\H,1.9913596815,4.029975482,6.9928421407\H,2.963571282,2.6486424017,6.4809954345\C,2.7954135264,2.3348608048,1.7011448394\H,3.8464651829,2.078884676,1.805365786\H,2.2030479527,1.4202809717,1.7278244114\H,2.6256317211,2.8160313895,0.7410027296\O,-0.0200807683,0.3965858718,7.547659781\C,0.2061215185,1.2479935023,8.6564051132\H,-0.7394869934,1.3006263225,9.1931940364\H,0.9806661361,0.8316364767,9.3011164538\H,0.4988527963,2.2429459912,8.3186739519\C,0.974387566,2.6344317633,5.7451083877\C,-0.3643348082,3.0888439898,5.7983088771\C,0.9356190421,1.3184040833,5.2290661019\C,-1.175552773,2.0737095241,5.2309000224\C,-0.9653242736,4.2628360077,6.2790061457\H,1.7657300778,0.7863189539,4.7923155409\C,-2.5566192473,2.1994620354,5.146340233\C,-2.3357550711,4.3895233968,6.1931061181\H,-0.3613768357,5.0508593138,6.710688675\H,-0.6632640346,0.1545549716,4.5069723444\C,-3.1213142302,3.3659568487,5.6342784786\H,-3.1658685246,1.4167122637,4.7164076854\H,-2.8184971394,5.2847414481,6.5594870708\H,-4.194023047,3.4935839148,5.5835124391\N,-0.347248809,1.060626281,4.8084669\Version=ES64L-G16RevC.01\HF=-1068.5229327\S2=0.781495\S2-1=0.\S2A=0.750554\RMSD=6.464e-09\RMSF=1.862e-06\Dipole=0.8662937,0.3238891,0.5079695\Quadrupole=-1.0613873,-2.1019321,3.1633195,11.1943429,9.3222365,22.9974512\PG=C01 [X(C15H19N2O5)]\@\nFrequencies -541.1062
```

Sum of electronic and thermal Free Energies= -1068.247721

#### δ-Addition product

```
1\1\GINC-SPARTAN-BM002\FOpt\UM062X\CC-pVTZ\C15H19N2O5(2)\UWILLE\08-Dec-2021\0\#p scf=(qc,direct) opt=(readfc, maxcycle=500) geom=checkpoint guess=check freq=noraman M062X/cc-pVTZ scrf=(cpcm, solvent=acetonitrile) nosymm\geom&freq\0,2\C,2.7553361976,4.2930475438,5.0215058826\H,2.0181269072,4.93520179,4.5400363835\C,4.0039515024,5.1004370304,5.3118566827\H,4.0536705615,2.8976183827,4.1442795692\C,2.2729645082,2.8026762285,3.1333253214\O,5.1235485096,4.7295931043,5.0652641645\O,3.710799694,6.2462191659,5.9112106947\C,4.8296379277,7.0604280345,6.2889250102\H,5.4018163218,7.3371380435,5.4068074576\H,4.4083069991,7.9391077743,6.7629230609\H,5.4667064054,6.5174960755,6.9828325371\O,1.1392734087,3.2411492071,2.9980495729\N,3.1002720705,3.2251229504,4.116371458\O,1.2451893924,0.950504039,7.0774829211\C,2.166438244,3.7749209595,6.3605654108\H,2.0399856306,4.6308345505,7.0250496624\H,2.8943050235,3.09912181
```

57,6.8135704406\C,2.8251745981,1.7338795114,2.2257862172\H,2.210321837  
4,0.8412486077,2.3333029199\H,2.7361008253,2.0768479486,1.196924818\H,  
3.861012612,1.4843632608,2.4391814245\O,1.2238839693,-0.4470951631,6.7  
867126187\C,0.376017356,-1.0495411659,7.7469451226\H,0.402291489,-2.11  
37840375,7.5193154633\H,0.7550667488,-0.8791972763,8.7548644492\H,-0.6  
413742204,-0.6700456845,7.6580948429\C,0.8681934756,3.0874282423,6.162  
9579333\C,-0.3989520543,3.674660481,6.0759485386\C,0.7186294946,1.6124  
957127,5.9314989346\C,-1.3465699139,2.649764211,5.7929553412\C,-0.8302  
638178,5.008159556,6.1740799889\H,1.2655572864,1.2302121315,5.06381427  
84\C,-2.6809215901,2.942487759,5.586833043\C,-2.1693536356,5.294929132  
9,5.9751945176\H,-0.1208340842,5.7969404352,6.389662392\H,-1.052707180  
7,0.6757437837,5.2067581841\C,-3.0809069185,4.2762875411,5.6795871138\  
H,-3.3939985662,2.1612866376,5.3619547413\H,-2.5170824106,6.316420924,  
6.0415615821\H,-4.1212347176,4.5254911578,5.5212053678\N,-0.7072858369  
,1.4263011178,5.7821041067\\Version=ES64L-G16RevC.01\HF=-1068.5435748\  
S2=0.774064\S2-1=0.\S2A=0.750344\RMSD=2.762e-10\RMSF=2.201e-06\Dipole=  
0.6688734,-0.166266,0.3018268\Quadrupole=-1.706945,7.2815757,-5.574630  
7,13.958257,6.2133734,6.2834869\PG=C01 [X(C15H19N2O5)]\ \@  
Sum of electronic and thermal Free Energies= -1068.266195

## Scheme 5 - Reaction of MeOO• with Ac-Met-OMe

### Reactant complex

```
1\1\GINC-SPARTAN-BM001\FOpt\UM062X\CC-pVTZ\C9H18N1O5S1(2)\UWILLE\22-De
c-2021\0\#p scf=(qc,direct) geom=checkpoint guess=check opt=(readfc,m
axcycle=500) freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitril
e) nosymm\geom&freq\0,2\C,-1.0468612325,2.7913941752,6.0122880655\H,
-1.3046540837,3.8123298106,5.7296831333\C,-1.9102596126,1.8316138947,5
.2165933648\H,-1.6646369298,1.7073146906,7.7028404785\C,-1.4245253796,
3.6618412731,8.2718865734\O,-2.5179041025,0.9088950998,5.697595784\O,-
1.8814203805,2.1117634955,3.9211722756\C,-2.6194792342,1.2230126329,3.
0708545915\H,-3.6719209601,1.2315078557,3.3449856983\H,-2.4845318891,1
.5974090726,2.0624578693\H,-2.2305285274,0.2114930145,3.1571402444\O,-
1.1568547102,4.8073002026,7.935174425\N,-1.3474800147,2.6198333434,7.4
137473591\O,-4.2836296984,-0.5604934178,1.3947672317\C,0.4315527641,2.
533251778,5.679100872\H,0.5643627654,2.6270341192,4.6010832384\H,0.679
8486286,1.5063482313,5.958327946\S,3.0751861106,3.1478146397,5.9678312
507\C,3.8807606666,4.4134025966,6.9764471154\H,3.6583979901,4.25711887
18,8.0297174737\H,4.9521574021,4.3227097458,6.8178932634\H,3.554804681
8,5.4053465958,6.6714408747\C,1.3490270349,3.5043598189,6.4027831227\H
,1.2365090177,3.4103969754,7.4824626189\H,1.1165003974,4.5316994683,6.
1227656364\C,-1.8510424205,3.3272377299,9.6777636106\H,-1.0756349958,3
.6659871136,10.3622324771\H,-2.7595146804,3.8836920239,9.901703257\H,-
2.029514672,2.2662706233,9.8298025695\O,-4.220273785,0.1850002827,0.33
6336576\C,-5.3951032229,1.0060861996,0.1977092801\H,-5.2576047918,1.56
50778007,-0.7219780135\H,-6.2659447988,0.359028649,0.1412309971\H,-5.4
57466917,1.6700415928,1.0562280293\Version=ES64L-G16RevC.01\HF=-1182.
7330796\S2=0.754797\S2-1=0.\S2A=0.750013\RMSD=1.518e-09\RMSF=2.025e-06
\Dipole=-1.2587294,0.0941038,-0.6964827\Quadrupole=12.5453166,-16.3313
043,3.7859877,-5.3476075,5.0853447,-8.9475542\PG=C01 [X(C9H18N1O5S1)]\@\@
Sum of electronic and thermal Free Energies= -1182.515986
```

### C $\alpha$ \_HAT complex

```
1\1\GINC-SPARTAN-BM117\FOpt\UM062X\CC-pVTZ\C9H18N1O5S1(2)\UWILLE\29-Ja
n-2022\0\#p scf=(qc,direct) opt=(calcfc,maxcycle=500) freq=noraman M0
62X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,
0.1619049002,-0.6197554365,0.7318328301\H,0.8715807479,-0.0984728865,0
.0867209474\C,-0.8558066718,-1.2908134669,-0.164300267\H,-1.5306487133
,0.3037399435,1.5913604292\C,0.1285993641,1.4014438612,2.0925324166\C,
-0.7311509851,2.411287829,2.8068811824\H,-0.8251678901,3.2897318372,2.
167852754\H,-1.7251603246,2.0321204836,3.0323695461\H,-0.2334483477,2.
7115581453,3.7253151655\O,-2.0505685449,-1.1452364844,-0.0686671721\O,
-0.2739613711,-2.0824365959,-1.0519982721\C,-1.1561981363,-2.776707721
2,-1.9446838479\H,-1.7300682699,-2.0598188982,-2.5275993178\H,-0.51771
65252,-3.3703339889,-2.5882047781\H,-1.8317318788,-3.413874098,-1.3790
468482\O,1.3440735389,1.5213249535,2.0102307525\N,-0.5274549387,0.3678
762393,1.5265887228\O,0.0206391745,2.1092872934,-0.9598657188\C,0.9546
789376,-1.6570966752,1.542123558\H,1.6066315833,-1.1077227609,2.220158
844\H,1.595423498,-2.1904731355,0.8381154443\C,0.1450365864,-2.6936478
82,2.3138967096\H,0.8236767209,-3.473390296,2.653302215\H,-0.601447873
6,-3.1790195152,1.6821990493\S,-0.7116865731,-2.0884466713,3.808474137
```

4\C,-2.4345734952,-2.0811455699,3.2550547251\H,-2.760332949,-3.0915871  
91,3.0190810237\H,-3.0277973894,-1.6982831409,4.081993943\H,-2.5726120  
153,-1.4427037331,2.3862266117\C,-2.1714804481,1.7192342727,-1.3764136  
503\H,-2.3990717866,1.8402561507,-0.3203294527\H,-2.2763441913,2.65915  
50354,-1.9115638214\H,-2.7788618688,0.9365016682,-1.8186051755\O,-0.80  
85608639,1.2717874343,-1.500785686\\Version=ES64L-G16RevC.01\HF=-1182.  
7362622\S2=0.754642\S2-1=0.\S2A=0.750013\RMSD=1.021e-09\RMSF=2.269e-06  
\Dipole=-2.5654151,-1.1554248,-1.4975608\Quadrupole=1.1402897,4.583269  
6,-5.7235593,-7.8985746,-2.7453115,4.2087785\PG=C01 [X(C9H18N1O5S1)]\@  
Sum of electronic and thermal Free Energies= -1182.512729

#### TS<sub>HAT\_Cα</sub>

1\1\GINC-SPARTAN-BM109\FTS\UM062X\CC-pVTZ\C9H18N1O5S1(2)\UWILLE\10-Feb  
-2022\0\#p opt=(ts,noeigentest,calcfc,maxcycle=500) freq=noraman M062  
X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,-1  
.4485151824,0.2837119155,-1.2614123707\H,-1.4966845228,-0.4074533241,-  
2.3486344326\C,-1.171654927,-0.7713242434,-0.2278940892\H,-3.330149514  
6,0.2271648195,-0.4354771977\C,-3.4040376568,1.6380683988,-1.923979077  
3\C,-4.8759137535,1.7956391596,-1.6534923892\H,-5.0993272696,1.7553201  
084,-0.589573578\H,-5.404761822,0.9786581635,-2.1466391214\H,-5.215651  
5904,2.7374966557,-2.0718500949\O,-2.0375887434,-1.28850884,0.43905668  
94\O,0.1085154584,-1.1016380502,-0.1674769284\C,0.4386220339,-2.155010  
8551,0.7487475936\H,0.1679384428,-1.8640800611,1.7605969458\H,1.509759  
0122,-2.2937754263,0.662806143\H,-0.0913882018,-3.0638492599,0.4743444  
747\O,-2.8245168238,2.2301376692,-2.813471389\N,-2.767208136,0.7540061  
01,-1.0909568782\C,-0.3491757327,1.3018826073,-1.508601329\H,0.5935969  
203,0.763671111,-1.5832019105\H,-0.5340334634,1.8044237161,-2.45334613  
46\O,-3.2110391187,-0.9160183965,-3.3853316513\O,-1.8515511001,-0.9738  
826399,-3.4239099035\C,-3.7125163415,-2.0699059516,-2.7178482559\H,-3.  
3598157322,-2.0852332964,-1.6857373085\H,-4.7954045897,-1.9768965541,-  
2.7455683261\H,-3.3914937917,-2.9690446576,-3.2407801578\C,-0.28258204  
68,2.3277697166,-0.3819492233\H,-1.2110021162,2.8968654912,-0.33296709  
07\H,-0.121711631,1.8387448123,0.5805357379\S,1.089168473,3.4729577813  
,-0.6924454126\C,0.8774326124,4.5584811698,0.7375324655\H,1.6550127004  
,5.3161620029,0.6858936114\H,-0.0972215722,5.0403658335,0.7073271267\H  
,0.9856702069,3.994870963,1.6615162523\\Version=ES64L-G16RevC.01\HF=-1  
182.708269\S2=0.759968\S2-1=0.\S2A=0.750054\RMSD=6.966e-09\RMSF=1.404e  
-06\Dipole=-0.8470316,-1.199184,2.546828\Quadrupole=13.8809167,3.64579  
68,-17.5267134,0.4339734,-0.873192,12.3791106\PG=C01 [X(C9H18N1O5S1)]\@  
Frequencies -2043.3651  
Sum of electronic and thermal Free Energies= -1182.489092

#### Cα-radical product complex

1\1\GINC-SPARTAN-BM013\FOpt\UM062X\CC-pVTZ\C9H18N1O5S1(2)\UWILLE\17-Fe  
b-2022\0\#p opt=(calcfc,maxcycle=500) freq=noraman M062X/cc-pVTZ scrf  
=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,1.7383658485,-0.  
3703635526,0.7273626723\H,2.9274434455,3.0982823354,2.5973710082\C,1.2  
482717203,-1.2873554751,-0.2820098427\H,-0.0902410052,0.4453027371,0.6  
25627234\C,0.8657013124,1.5115962151,2.0837155825\O,0.0974879596,-1.28  
10338172,-0.6895101181\O,2.1816284106,-2.1364252149,-0.7268256098\C,1.  
7449968045,-3.0602155503,-1.7260468511\H,1.3932029056,-2.5252646198,-2



.6054909748\H,2.6120338873,-3.6636871291,-1.9699416866\H,0.9430345485,  
-3.6844035577,-1.3378860603\O,1.8451125798,1.6527456355,2.8022948152\N  
,0.7889154779,0.5379970314,1.1226560019\O,3.3383611626,3.86417099,2.15  
17447121\C,3.1520229588,-0.3131695623,1.1844156254\H,3.6431410855,-1.2  
426259414,0.9087685126\H,3.1890756188,-0.2053738416,2.2663955743\C,-0.  
345790956,2.3953419647,2.1662666668\H,-0.3448667633,3.0756598399,1.313  
5582143\H,-1.2651866475,1.8131071489,2.1342581668\H,-0.302513206,2.970  
4119715,3.0853223625\S,5.504691691,1.0936043978,1.2973846024\C,6.00864  
44417,2.5785885855,0.3979550215\H,5.2875457593,3.372329195,0.581656938  
6\H,6.983975581,2.8747707266,0.7757220284\H,6.0838113881,2.3706389014,  
-0.6671541102\C,3.8759391851,0.870824227,0.5326005844\H,3.3110464841,1  
.7919874784,0.6697146543\H,4.0015115028,0.6908611504,-0.5354234247\C,1  
.6684871985,5.2262081841,1.4071084541\H,1.0992657332,5.0764476236,2.32  
60362035\H,2.3227218781,6.091853187,1.5121349628\H,0.9896867805,5.3737  
618218,0.5685201534\O,2.4185902482,4.071460424,1.0863948061\\Version=E  
S64L-G16RevC.01\HF=-1182.7472924\S2=0.756923\S2-1=0.\S2A=0.750038\RMSD  
=5.100e-09\RMSF=4.834e-06\Dipole=-1.77083,0.1912892,-0.8889086\Quadrup  
ole=-13.195692,14.0307621,-0.8350701,-9.6146225,-15.4181542,0.9994816\  
PG=C01 [X(C9H18N1O5S1)]\\@  
Sum of electronic and thermal Free Energies= -1182.522823

### Cβ\_HAT complex

1\1\GINC-SPARTAN-BM012\FOpt\UM062X\CC-pVTZ\C9H18N1O5S1(2)\UWILLE\21-Ja  
n-2022\0\#p scf=(qc,direct) opt=(calcf, maxcycle=500) freq=noraman M0  
62X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,  
-0.540444377,-0.1604512277,-0.2422048443\H,-0.4922108986,0.913786165,-  
0.4303551037\C,-0.5913553218,-0.8665632124,-1.5803733223\H,-2.28054785  
14,-1.2716487085,0.1748261277\C,-2.1641878315,0.2646378381,1.530939115  
4\C,-3.4073595589,-0.2201770603,2.2287286294\H,-4.0644858693,0.6282182  
098,2.4045599771\H,-3.9360693155,-0.9869882907,1.6686508567\H,-3.11499  
11982,-0.6258957226,3.1970389284\O,-1.4318479507,-1.6704498437,-1.8962  
10239\O,0.4312697227,-0.5154359757,-2.3476183201\C,0.5123256122,-1.169  
3976629,-3.6212788855\H,-0.3763215163,-0.9516465237,-4.2085919953\H,1.  
3969653317,-0.7691576555,-4.1023937696\H,0.6041101618,-2.2440559036,-3  
.4813483715\O,-1.5467519272,1.2513692035,1.9177633654\N,-1.7597442573,  
-0.4606215783,0.4708506611\O,1.4982660909,2.3592658895,-0.8598081854\C  
,0.7310725489,-0.5620336918,0.5243072487\H,0.662730858,-0.1269353189,1  
.5220235533\H,1.5809577777,-0.1018941517,0.0207878764\C,0.9938123132,-  
2.0590908369,0.6130410724\H,1.9415442936,-2.2202882725,1.1253234243\H,  
1.0764201863,-2.5012044984,-0.3824347352\S,-0.2803173442,-2.9688338468  
,1.5459417576\C,0.5825479835,-4.5535185656,1.6593399364\H,1.5172890611  
, -4.4395206028,2.2042360782\H,-0.0669888632,-5.2395788951,2.1966581168  
\H,0.7784598241,-4.9499267926,0.6653341002\O,2.0868818835,2.5513125548  
,0.2787921246\C,1.1829094745,3.1031759817,1.2568743961\H,0.8370624246,  
4.068939053,0.8968359002\H,0.3510871642,2.4142080958,1.3966689647\H,1.  
7676919386,3.2116896873,2.1649271908\\Version=ES64L-G16RevC.01\HF=-118  
2.7374505\S2=0.754853\S2-1=0.\S2A=0.750013\RMSD=7.689e-09\RMSF=1.095e-  
05\Dipole=0.577387,-0.9217161,-0.1308918\Quadrupole=-1.6974551,2.27265  
05,-0.5751955,-3.7777247,-0.6274831,0.7879975\PG=C01 [X(C9H18N1O5S1)]\\@  
Sum of electronic and thermal Free Energies= -1182.515355

### TS<sub>HAT\_cβ</sub>

```
1\1\GINC-SPARTAN-BM010\FTS\UM062X\CC-pVTZ\C9H18N1O5S1(2)\UWILLE\19-Jan-2022\0\#p scf=(qc,direct) opt=(ts,noeigentest,calcfc,maxcycle=500) f req=noraman M062x/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,-0.5904322753,-0.0030086899,-0.234690155\H,-0.6397029905,1.0742877607,-0.4088652518\C,-0.5143321558,-0.6890918274,-1.583898803\H,-2.2514452095,-1.2621115806,0.1097736969\C,-2.316322217,0.3095908774,1.447896275\C,-3.5769473489,-0.2200912992,2.0766534108\H,-4.3384245756,0.5560094759,2.0305416041\H,-3.9452306837,-1.1215339249,1.5947004037\H,-3.3743418432,-0.428154962,3.1259851289\O,-1.2921189414,-1.5217969247,-1.9707161144\O,0.5371944962,-0.264480707,-2.2697367536\C,0.7360781588,-0.8737628517,-3.5538240649\H,-0.123453444,-0.6829514045,-4.1914338145\H,1.6276073671,-0.4136469821,-3.9629809036\H,0.8753654815,-1.9460137695,-3.4367995578\O,-1.7755304721,1.3379433983,1.835885614\N,-1.8052589186,-0.4161288581,0.4300876237\O,2.3249210927,1.3888468579,-0.1862565228\C,0.6428263577,-0.296664894,0.6084472324\H,0.5401754981,0.1236829514,1.6077056826\H,1.5810695737,0.529385326,0.1240075299\C,1.236455288,-1.6701784056,0.5736672117\H,2.1550870989,-1.6933897978,1.1581228989\H,1.4652671171,-1.9870447977,-0.444860185\S,0.0877694783,-2.8979122956,1.3102007274\C,1.1868275358,-4.332690339,1.2509998497\H,2.0746597311,-4.1559877057,1.8538655216\H,0.6346910643,-5.1749732027,1.6600530997\H,1.4691277928,-4.552055862,0.2238195715\O,2.4978054755,2.1219433184,0.9685704264\C,1.4374173295,3.0618587753,1.0741615005\H,1.3958577039,3.6824141924,0.1800337009\H,0.4855802184,2.5460871886,1.2247163356\H,1.6718752162,3.6687789595,1.9458290806\Version=ES64L-G16RevC.01\HF=-1182.6974838\S2=0.75995\S2-1=0.\S2A=0.750053\RMSD=8.349e-09\RMSF=1.466e-06\Dipole=-0.1494908,-1.2575526,-0.7856843\Quadrupole=-3.3339609,2.9159008,0.41806,-5.3870273,-3.3311539,-3.3174479\PG=C01 [X(C9H18N1O5S1)]\@\@Frequencies -1993.2795Sum of electronic and thermal Free Energies= -1182.479168
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### Cβ-radical product complex

```
1\1\GINC-SPARTAN-BM020\FOpt\UM062X\CC-pVTZ\C9H18N1O5S1(2)\UWILLE\23-Dec-2021\0\#p scf=(qc,direct) geom=checkpoint opt=(readfc,maxcycle=500) guess=check freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,1.0910243136,-0.3778788177,-1.5768711054\H,1.0147527753,0.664100175,-1.2618976054\C,1.3634439363,-0.4001507954,-3.0767642318\H,-0.5410229895,-1.5949590491,-2.1291430689\C,-0.7928845235,-1.0391178492,-0.1722619205\C,-2.0426093526,-1.8622750013,-0.0535151045\H,-1.8053627448,-2.7349407924,0.5553434115\H,-2.7988463815,-1.2801925612,0.4669418161\H,-2.4232345912,-2.1923017993,-1.0161095969\O,0.796981231,-1.1293752993,-3.8504876715\O,2.326831435,0.4449857383,-3.4020020264\C,2.7161766802,0.4492914819,-4.7835732674\H,1.8677403941,0.719997697,-5.4069953742\H,3.5033796351,1.1893375346,-4.8647705809\H,3.0817603747,-0.534410347,-5.067796347\O,-0.3623348804,-0.3907377571,0.7830312336\N,-0.1660464499,-1.0626893728,-1.3580363786\O,1.8395824338,1.0751195759,1.3065062435\C,2.242617632,-1.0305138977,-0.8694722105\H,3.011521129,-0.402070123,-0.4484070559\H,1.1010943206,0.4588649575,1.0946036977\C,2.3550943975,-2.5004638327,-0.8063249614\H,3.3962530656,-2.8164046501,-0.8600317761\H,1.7919171458,-2.9831647647,-1.6065709887\S,1.6966989178,-3.1321401747,0.7956928357\C,2.2099126562,-4.8586525608,0.62
```

67886405\H,3.2929003628,-4.9284256949,0.5517048448\H,1.8767685028,-5.3  
818375074,1.5195216566\H,1.746070903,-5.3095792053,-0.2476970546\O,1.1  
49458414,2.1284561559,1.9676102953\C,0.6793409817,3.0126359033,0.97236  
39017\H,1.5070295816,3.3967291324,0.3745801477\H,-0.0487771112,2.51775  
50416,0.3257123491\H,0.197899005,3.8294246597,1.5079746528\\Version=ES  
64L-G16RevC.01\HF=-1182.7248535\S2=0.756066\S2-1=0.\S2A=0.750031\RMSD=  
3.389e-09\RMSF=3.133e-06\Dipole=-0.2464616,-1.0227058,-3.030747\Quadru  
pole=-0.1184108,7.3215953,-7.2031845,-3.9309868,-12.4935812,-4.4007694  
\PG=C01 [X(C9H18N1O5S1)]\@\n  
Sum of electronic and thermal Free Energies= -1182.504219

### C<sub>γ</sub>,δ\_HAT complex

1\1\GINC-SPARTAN-BM009\FOpt\UM062X\CC-pVTZ\C9H18N1O5S1(2)\UWILLE\21-Jan-2022\0\#p scf=(qc,direct) opt=(calcf, maxcycle=500) freq=noraman M0  
62X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,  
2.8329003045,-0.701701218,3.4063955954\H,2.2311814,-0.3802414876,4.256  
4256802\C,1.9786049957,-1.5652530892,2.4998471702\H,4.2503765793,-2.25  
12612868,3.3036551245\C,4.3847285177,-1.4096082714,5.1665873377\O,2.31  
97478111,-2.6352723383,2.0626515878\O,0.8228854964,-0.9796917104,2.216  
0971512\C,-0.03575368,-1.6928760583,1.3161659393\H,-0.3022159233,-2.65  
71149345,1.74219933\H,-0.9158762622,-1.0724854408,1.1939536536\H,0.465  
1784429,-1.8409855009,0.3625010645\O,3.9519018463,-0.5841396745,5.9596  
346237\N,3.9297086273,-1.502169595,3.8973273795\O,1.1091327526,1.90919  
27549,4.5077717196\C,3.293813712,0.5425755388,2.631381601\H,2.40875586  
68,1.0749340362,2.2833467277\H,3.8648101857,0.2265256638,1.7550666469\  
C,5.4687341973,-2.3838405583,5.5497227154\H,5.1000888875,-3.0026948428  
,6.3661514881\H,5.7820607081,-3.0205860124,4.7268571857\H,6.3233873303  
, -1.8201956537,5.9186199764\S,4.5488212166,2.9626582442,2.5707117957\C  
,5.6431690798,3.7497036136,3.7745814961\H,6.5070880613,3.1186096967,3.  
9709665834\H,5.9748718993,4.6917499616,3.345858375\H,5.1125449687,3.94  
68896083,4.7042833522\C,4.143131958,1.4573559889,3.4984530212\H,5.0727  
599686,0.9658513804,3.7847911054\H,3.6070679017,1.724937029,4.41002173  
18\C,1.7107362351,4.0882888698,4.4235656851\H,0.9369860469,4.368464828  
2,5.1335617272\H,2.6424413306,3.8546404938,4.9331808737\H,1.8594223808  
,4.8553052214,3.6710526416\O,1.2733123564,2.9174857331,3.7094933233\\V  
ersion=ES64L-G16RevC.01\HF=-1182.7376674\S2=0.754815\S2-1=0.\S2A=0.750  
013\RMSD=2.056e-09\RMSF=1.932e-06\Dipole=0.3266539,0.6026349,-0.499750  
8\Quadrupole=8.7559399,9.659037,-18.4149768,2.070567,5.2979282,8.25816  
63\PG=C01 [X(C9H18N1O5S1)]\@\n  
Sum of electronic and thermal Free Energies= -1182.514796

### TS<sub>HAT\_C<sub>γ</sub></sub>

1\1\GINC-SPARTAN-BM008\FTS\UM062X\CC-pVTZ\C9H18N1O5S1(2)\UWILLE\19-Jan-2022\0\#p scf=(qc,direct) opt=(ts,noeigentest,calcf, maxcycle=500) f  
req=noraman M062x/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geo  
m&freq\0,2\C,2.5625182898,-0.6803490345,3.4531662519\H,1.9367026617,-  
0.2881463112,4.2550913408\C,1.7241928645,-1.5856014386,2.5718092694\H,  
3.9392568041,-2.266091507,3.5139987725\C,4.0215046059,-1.3049013402,5.  
3215593011\O,2.0480449006,-2.6964293245,2.2363078617\O,0.6045680316,-0  
.987229465,2.1890122852\C,-0.238530739,-1.7405925326,1.3067888029\H,-0  
.5560891752,-2.6603296845,1.7919515365\H,-1.0904007498,-1.1041989142,1

.0978331603\H,0.2984159638,-1.9766866886,0.3912705205\O,3.584169739,-0.4120432559,6.0343625155\N,3.6226012015,-1.4655534359,4.0390695904\O,1.9122709073,2.2099617793,4.927199958\C,3.0853666928,0.4983143852,2.616188644\H,2.2364822597,0.9998916446,2.1485747226\H,3.7256392592,0.1083962348,1.8194449005\C,5.0476018142,-2.2889481365,5.8205080502\H,4.610345921,-2.848643446,6.6458455297\H,5.3846042192,-2.981415382,5.0539940203\H,5.8985596159,-1.7330853979,6.2088371233\S,4.336772285,2.924201357,2.5973696788\C,5.4670510739,3.6534459438,3.8023185792\H,6.3312909373,3.0093744205,3.9419840008\H,5.7834453579,4.6149647063,3.4082431692\H,4.953348344,3.7988821655,4.7505264608\C,3.8462030879,1.485554506,3.4701110868\H,4.6515427169,1.057813222,4.0646580222\H,2.972893782,1.8663113062,4.3346692427\C,1.7109518014,4.4453204633,4.5632441042\H,1.2832032629,4.5908252157,5.5549213245\H,2.7919149764,4.5772700463,4.5982572066\H,1.2742395993,5.1484452989,3.8571478051\O,1.3826656875,3.1540826552,4.0747521618\Version=ES64L-G16RevC.01\HF=-1182.707769\S2=0.75918\S2-1=0.\S2A=0.750049\RMSD=5.411e-09\RMSF=2.164e-06\Dipole=1.1493871,0.0569445,-1.2324772\Quadrupole=19.6704617,7.4149799,-27.0854415,4.9441154,8.3543539,-0.021217\PG=C01 [X(C9H18N1O5S1)]\@\@  
Frequencies -1891.0318  
Sum of electronic and thermal Free Energies= -1182.488734

#### Cy-radical product complex

1\1\GINC-SPARTAN-BM125\FOpt\UM062X\CC-pVTZ\C9H18N1O5S1(2)\UWILLE\22-Dec-2021\0\#p scf=(qc,direct) geom=checkpoint guess=check freq=norman M062X/cc-pVTZ opt=(readfc,maxcycle=500) scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,2.8494801299,-0.6711387827,2.8203738068\H,2.5177589699,0.2206156675,3.3521291805\C,1.6319270224,-1.4338508304,2.3377714316\H,3.5517379188,-2.5070387758,3.5552935016\C,4.1658723323,-1.072893429,4.862437404\O,1.4939758192,-2.6263080724,2.4371628738\O,0.7600252679,-0.6240301366,1.7531296613\C,-0.4051001742,-1.2510687451,1.1989233704\H,-0.9620866603,-1.7577051053,1.9832265485\H,-0.9938790506,-0.4502511378,0.7673388\H,-0.1130886761,-1.9680205435,0.4354510872\O,4.1835453132,0.1143245856,5.1863887117\N,3.5828188467,-1.5147334824,3.7360151631\O,3.5180560511,2.6319104223,4.4263221512\C,3.7032223102,-0.2619739392,1.5996390124\H,3.0684704286,0.2782328774,0.8952939235\H,4.0243305792,-1.1850713016,1.1008305306\C,4.8159500854,-2.1151643586,5.7297543883\H,5.8636875193,-1.8499231021,5.857490356\H,4.3427774384,-2.0864466995,6.7096766969\H,4.7417176771,-3.1180802449,5.3192456722\S,5.3491925204,1.9055205192,1.0313799858\C,6.4724477305,2.7440693999,2.173102039\H,7.2819594542,2.0752869774,2.454804417\H,6.8776906755,3.6077267984,1.6534051858\H,5.9163340042,3.0608458813,3.0519732393\C,4.8605813594,0.5788040191,2.0081968749\H,5.5412555083,0.2395100764,2.7769008085\H,3.8073132686,1.70837852,4.5931804985\C,1.944383441,2.8612649149,2.7945109284\H,2.1974861431,3.9173356309,2.6887510447\H,2.5480739314,2.2713414372,2.102620923\H,0.8847129393,2.7113686726,2.5929708346\O,2.1390075657,2.4328905669,4.1256274039\Version=ES64L-G16RevC.01\HF=-1182.7330204\S2=0.755735\S2-1=0.\S2A=0.750026\RMSD=3.703e-10\RMSF=1.760e-06\Dipole=0.014133,-1.6577631,-1.1689136\Quadrupole=15.0077015,-0.4517199,-14.5559816,-11.6638753,0.7715125,-18.4391562\PG=C01 [X(C9H18N1O5S1)]\@\@  
Sum of electronic and thermal Free Energies= -1182.510960

**TS<sub>HAT\_C8</sub>**

```
1\1\GINC-SPARTAN-BM110\FTS\UM062X\CC-pVTZ\C9H18N1O5S1(2)\UWILLE\23-Dec
-2021\0\#p freq=noraman scf=(qc,direct) geom=checkpoint guess=check M
062X/cc-pVTZ opt=(ts,noeigentest,readfc,maxcycle=500) scrf=(cpcm,solve
nt=acetonitrile) nosymm\geom&freq\0,2\C,1.9695918484,3.6483293196,4.
4772156926\H,2.1251499419,3.8773756204,5.5318539985\C,0.5098452902,3.2
934367811,4.2671274254\H,2.3907303389,1.8595162555,3.4589756291\C,3.86
26490584,2.1411948067,4.8573003613\O,0.1283977393,2.3175587393,3.67259
07851\O,-0.2921566112,4.2108794467,4.7890795729\C,-1.6974424204,3.9971
986224,4.5979497152\H,-1.9969329012,3.0606239623,5.061907013\H,-2.1908
173654,4.835604139,5.0753925573\H,-1.9280938612,3.9696532324,3.5357897
901\O,4.2956421862,2.8299364201,5.771066995\N,2.7721839012,2.497018261
5,4.1406779995\O,4.4341035288,8.1104306317,5.8374314533\C,2.3139917131
,4.8888717474,3.6378006259\H,1.6355012349,5.6963564705,3.9127472754\H,
2.1510592223,4.6544368933,2.5829733172\C,4.5216115329,0.8475884932,4.4
552253897\H,5.5643187029,1.0508459483,4.2191009064\H,4.4987681875,0.17
24646211,5.3090382107\H,4.0431769684,0.3705545819,3.6041103315\S,4.108
2168516,6.7785241976,2.8273014412\C,5.5123687042,7.3894392642,3.650985
5295\H,6.2300106017,6.6269418224,3.9440947532\H,5.9557675143,8.2245972
034,3.1189262257\H,5.0578685566,7.8282142861,4.7948495764\C,3.74887274
8,5.3317122395,3.8640776152\H,4.4559300201,4.5423153757,3.6158280247\H
,3.9023042649,5.6342420061,4.8990775755\C,2.7386435059,9.300646741,4.9
068217364\H,2.8166391626,10.0577023199,5.686778419\H,3.3676162946,9.57
14328505,4.0575710625\H,1.7051652165,9.1909700686,4.584630074\O,3.1240
120729,8.0342301706,5.4160692914\HF=-1182.70
69495\S2=0.759027\S2-1=0.\S2A=0.750049\RMSD=3.147e-09\RMSF=3.230e-06\D
ipole=-1.1703245,-0.2320247,-1.7076242\Quadrupole=9.3259153,15.3133508
,-24.6392661,-16.6391031,-27.2283696,-19.8749799\PG=C01 [X(C9H18N1O5S1)]\@
Frequencies -1851.1281
Sum of electronic and thermal Free Energies= -1182.487481
```

**Cδ-radical product complex**

```
1\1\GINC-SPARTAN-BM125\FOpt\UM062X\CC-pVTZ\C9H18N1O5S1(2)\UWILLE\26-De
c-2021\0\#p freq=noraman scf=(qc,direct) opt=(readfc,maxcycle=500) ge
om=checkpoint guess=check M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitril
e) nosymm\geom&freq\0,2\C,1.8317557881,1.1010539714,-0.2528326137\H,
1.8036839966,2.0432335364,0.2915596991\C,0.4989824037,0.8986375618,-0.
9456912541\H,1.620600554,-0.868513062,0.4533546784\C,2.544974888,0.208
0496321,1.9157275655\O,-0.1229001754,-0.1327093075,-0.929847225\O,0.12
58384622,1.9889965183,-1.6005376335\C,-1.0967124744,1.8857516023,-2.34
41679492\H,-1.9206624901,1.656200943,-1.6730627212\H,-1.2406746359,2.8
531246073,-2.8106864622\H,-1.0085445553,1.1054143258,-3.0961560444\O,2
.9746850363,1.2971712871,2.2987112176\N,2.0210353187,0.0259829614,0.69
33244634\O,3.5836200278,3.8793342801,1.7091257066\C,2.944758707,1.1770
675455,-1.3097978095\H,2.7055090197,1.9882284842,-1.9977137307\H,2.957
2262223,0.2450394546,-1.8797058678\C,2.5978789549,-0.9978971978,2.8107
776785\H,3.6401120515,-1.1988091705,3.0527010467\H,2.0803830635,-0.758
403229,3.7376714281\H,2.1531642846,-1.8809151431,2.3608728182\S,5.5745
975381,1.4860794543,-1.9671882766\C,6.9680543057,1.8056831133,-1.03234
63181\H,6.8735541716,2.1031439284,0.0000142479\H,7.9077265496,1.887417
1279,-1.552854215\H,3.3733534953,2.9412866903,1.9106204996\C,4.3023192
```

354,1.4199041211,-0.6723318193\H,4.5653533864,0.6166485427,0.014006794  
1\H,4.3147498419,2.3666565448,-0.1351222195\O,2.6959949929,4.153061416  
5,0.6321199051\C,1.4812757989,4.6145841138,1.1901992779\H,1.0234113902  
,3.8421197376,1.8127436204\H,1.6472264705,5.5159272317,1.780123937\H,0  
.8361533657,4.8350640263,0.3409857657\\Version=ES64L-G16RevC.01\HF=-11  
82.7286291\S2=0.7559\S2-1=0.\S2A=0.750025\RMSD=3.294e-10\RMSF=2.896e-0  
6\Dipole=-2.069513,-1.2828516,-0.1823912\Quadrupole=-10.2267903,1.3314  
996,8.8952907,-21.5095115,2.8645898,-8.1382136\PG=C01 [X(C9H18N1O5S1)]\@  
Sum of electronic and thermal Free Energies= -1182.507870

### S\_addition complex

Not calculated.

### TS<sub>addition\_s</sub>

Could not be located.

### S-addition product

1\1\GINC-SPARTAN-BM005\FOpt\UM062X\CC-pVTZ\C9H18N1O5S1(2)\UWILLE\23-De  
c-2021\0\#p scf=(qc,direct) M062X/cc-pVTZ geom=checkpoint guess=check  
opt=(readfc,maxcycle=500) freq=norman scrf=(cpcm,solvent=acetonitril  
e) nosymm\geom&freq\0,2\C,-1.9188002977,2.034371184,5.9836062941\H,-  
2.1448974513,2.8134873441,5.2601653634\C,-3.1034255153,1.0854246263,6.  
1682630354\H,-2.0701100721,2.1122108037,8.0520414439\C,-1.222210227,3.  
8863388121,7.4680121638\O,-3.07052492,0.300805595,7.1827773927\O,-3.37  
03841412,0.5253986413,4.8811197454\C,-4.4556661035,-0.3669718347,4.885  
5592485\H,-5.3662029333,0.1292441328,5.2425569145\H,-4.6113845535,-0.7  
042337353,3.8620641963\H,-4.26560335,-1.2296447702,5.5258626344\O,-0.7  
973089511,4.5819563945,6.5411092242\N,-1.6981235483,2.6503910669,7.280  
901261\O,-0.5389032226,3.5727175406,3.6507673245\C,-0.6826874006,1.230  
2776391,5.5390788472\H,-0.8766701505,0.7932237604,4.5593307432\H,-0.57  
04049855,0.4037034257,6.2427629898\S,0.9157610444,2.9106922004,4.01705  
45345\C,1.7045951074,4.4012396312,4.5928167609\H,2.6428073144,4.085232  
357,5.045280443\H,1.8876280274,5.0259534602,3.724235628\H,1.0383697064  
,4.8579329756,5.3224321869\C,0.6366239455,1.9965121277,5.5498835114\H,  
1.4952783927,1.323382412,5.5625030867\H,0.7102170189,2.7019110884,6.37  
21688103\C,-1.2189468029,4.3971201056,8.8862983516\H,-0.2126358262,4.7  
280386112,9.1354271238\H,-1.8764181037,5.2638007114,8.9396388435\H,-1.  
5472552497,3.6522805087,9.6061281993\O,-1.1643145115,2.7341223179,2.68  
04055513\C,-0.9322099691,3.3222425598,1.4038292679\H,-1.4671975811,2.6  
731428862,0.7146310657\H,-1.33896275,4.3303392749,1.3744334395\H,0.132  
2900904,3.3204751255,1.1689243734\\Version=ES64L-G16RevC.01\HF=-1182.6  
212691\S2=0.75391\S2-1=0.\S2A=0.750009\RMSD=8.451e-10\RMSF=2.639e-05\D  
ipole=6.2011802,2.8713144,-3.1346392\Quadrupole=-3.0235003,33.6727571,  
-30.6492569,18.3074273,70.8769022,17.9727578\PG=C01 [X(C9H18N1O5S1)]\@  
Sum of electronic and thermal Free Energies= -1182.393103

## Scheme 6 - Reaction of MeOO• with Ac-Pro-OMe

### Reactant complex

```
1\1\GINC-SPARTAN-BM016\FOpt\UM062X\CC-pVTZ\C9H16N1O5(2)\UWILLE\19-Feb-2022\0\#p opt=(calcfc,maxcycle=500) freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,-3.8948333634,-2.1837268293,3.1928488621\H,-3.7149529279,-2.08480704,4.2610007488\C,-2.9671885912,-1.2247799796,2.467112674\C,-5.8422270731,-0.7487807583,3.2591803893\O,-3.2101285016,-0.6916738795,1.4151004754\O,-1.8144055624,-1.0931994193,3.1182987497\C,-0.8296203576,-0.2699576147,2.4831972565\H,0.0271114308,-0.2590388801,3.147858489\H,-0.5546268564,-0.6863000454,1.5168924233\H,-1.2181727168,0.736674705,2.3440707268\O,-5.2039365769,0.0726264303,3.9113910319\N,-5.2791220357,-1.9085713955,2.8643249607\C,-3.6920580902,-3.6217834187,2.6880813693\H,-3.9840327734,-4.3128817644,3.4777621047\H,-2.6578269366,-3.8251847761,2.4200730783\C,-5.8773741621,-2.9275558469,1.9970401511\H,-6.4321049854,-2.4681010254,1.1820044935\H,-6.55866152,-3.5619449897,2.5683654358\C,-4.6626088661,-3.714229123,1.5096787146\H,-4.9122308457,-4.7385178992,1.2463591348\H,-4.2353940906,-3.2236119942,0.6357172042\O,1.5670739299,1.1621032338,1.4060127282\C,-7.2745442362,-0.5229152672,2.8523754091\H,-7.3244797053,-0.3222806673,1.7813866043\H,-7.8877701056,-1.3996726926,3.055146492\H,-7.6608219526,0.3346277348,3.3932036199\O,0.8794479649,2.2520795663,1.2668857976\C,1.1179271525,3.1689407091,2.3514951882\H,0.8115544271,2.6949471194,3.280566009\H,2.1756945302,3.416209833,2.3705260778\H,0.5117123972,4.0429729746,2.1374326001\Version=ES64L-G16RevC.01\HF=-783.334654\S2=0.754814\S2-1=0.\S2A=0.750013\RMSD=2.519e-09\RMSF=9.403e-07\Dipole=-0.1967425,-0.9094004,0.138974\Quadrupole=3.9367755,11.4900768,-15.4268523,22.7564281,6.4831153,-3.3747652\PG=C01 [X(C9H16N1O5)]\@\Sum of electronic and thermal Free Energies= -783.131423
```

### α<sub>1</sub> HAT complex

```
1\1\GINC-SPARTAN-BM004\FOpt\UM062X\CC-pVTZ\C9H16N1O5(2)\UWILLE\18-Jan-2022\0\#p geom=checkpoint guess=check opt=(readfc,maxcycle=500) freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,-1.6928616751,-1.7927367749,-0.4414884446\C,-1.9861468695,0.6014354932,1.3287219266\C,-2.4504346586,1.1905043202,2.6344787468\H,-1.6106372835,1.4631288912,3.272378603\H,-3.0594477661,2.0640788283,2.4267270916\H,-3.0506958123,0.4562509097,3.1735058443\O,-2.6042550242,-2.2921323532,0.1663917939\O,-1.5076556029,-1.9324931794,-1.7516189121\C,-2.4681393764,-2.7466530206,-2.4337188884\H,-3.4616381699,-2.3168591153,-2.3293712204\H,-2.1644357793,-2.7568127675,-3.4742198611\H,-2.4632568785,-3.7539288611,-2.023550949\O,-2.455877142,0.9455493761,0.2466846053\N,-1.0148995289,-0.3313078752,1.3947780844\O,2.0117780098,0.94271671,-0.3111170501\C,0.5529810021,-1.9226055915,0.676207204\H,1.4936134312,-1.3749392431,0.657654506\H,0.6567712204,-2.8065118458,0.0507577516\C,-0.4282730141,-0.9075025889,2.6091374552\H,-1.1824429198,-1.0346114403,3.3820207888\H,0.3619660103,-0.25681757,2.9910123691\C,0.1375243018,-2.2358795628,2.1143286547\H,0.9646742441,-2.5857942009,2.726110096\H,-0.6466390745,-2.9922246858,2.1215596373\C,0.6714044168,2.409867912,0.7709301304\H,1.2428620829,3.2532205095,0.3928822657\H,-0.1594856141,2.1685689197,0.1110304042\H,0.3291416296,2.5919703037,1.7855433181\O,1
```

.5423067612,1.265871513,0.8531157562\C,-0.565807433,-0.9894910923,0.18  
27926413\H,-0.2116254877,-0.2708488778,-0.555042669\\Version=ES64L-G16  
RevC.01\HF=-783.3396904\S2=0.754869\S2-1=0.\S2A=0.750014\RMSD=6.150e-0  
9\RMSF=4.454e-06\Dipole=0.8608143,0.0208035,1.3710685\Quadrupole=-14.4  
864525,5.1710252,9.3154273,0.3190901,1.5291434,6.9415712\PG=C01 [X(C9H  
16N1O5)]\@\@  
Sum of electronic and thermal Free Energies= -783.130558

#### TS<sub>HAT\_C $\alpha$</sub>

1\1\GINC-SPARTAN-BM123\FTS\UM062X\CC-pVTZ\C9H16N1O5(2)\UWILLE\22-Dec-2  
021\0\#p scf=(qc,direct) opt=(ts,noeigentest,readfc,maxcycle=500) geo  
m=checkpoint guess=check freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent  
=acetonitrile) nosymm\geom&freq\0,2\C,-1.5273194801,-1.5711769451,-0  
.5746160162\C,-1.8938002377,0.6495178952,1.4320221381\C,-2.3265218137,  
1.2410980241,2.7436240219\H,-1.4631994823,1.5944398469,3.3079847062\H,  
-3.000693185,2.0674084343,2.5460061311\H,-2.8354454222,0.4913004999,3.  
3492834152\O,-2.6201368644,-1.9281962403,-0.2210880831\O,-1.0571190457  
, -1.7078337244,-1.8117664803\C,-1.9364289435,-2.3482486675,-2.74399210  
11\H,-2.8525391152,-1.7715953551,-2.8474362253\H,-1.3982011207,-2.3822  
773955,-3.6841132169\H,-2.1751441949,-3.3527855379,-2.4023479279\O,-2.  
3159961883,1.0385025161,0.354128292\N,-0.9684109326,-0.3542556799,1.49  
43860729\O,0.9447402972,0.7580133926,-0.7979424828\C,0.6294939348,-1.9  
150352893,0.7821780758\H,1.5851072348,-1.3930792996,0.7055400332\H,0.6  
82661656,-2.8163053444,0.1770874365\C,-0.2906210974,-0.8345820314,2.70  
83667216\H,-0.9978936322,-0.9296825799,3.5277329362\H,0.4969885673,-0.  
1356624861,2.9967327772\C,0.2810423959,-2.1721702341,2.2519980342\H,1.  
1395829835,-2.4793132036,2.8425553372\H,-0.4883239168,-2.9405673585,2.  
3238672884\C,0.7901350851,2.5805358029,0.5579677802\H,1.1249886077,3.2  
72981011,-0.2137431737\H,-0.2941444204,2.483314688,0.5247317525\H,1.11  
58341982,2.9226518113,1.5378952692\O,1.4046585022,1.3113011476,0.37235  
88425\C,-0.4796025109,-0.9723235936,0.3245379556\H,0.1211261411,-0.073  
4671037,-0.3905003104\\Version=ES64L-G16RevC.01\HF=-783.3058904\S2=0.7  
60005\S2-1=0.\S2A=0.750059\RMSD=1.469e-09\RMSF=1.714e-06\Dipole=0.7922  
304,-0.6146544,1.9170312\Quadrupole=-14.720306,3.3517857,11.3685203,-0  
.6510131,0.5996877,5.3832576\PG=C01 [X(C9H16N1O5)]\@\@  
Frequencies -2060.3531  
Sum of electronic and thermal Free Energies= -783.101892

#### C $\alpha$ -radical product complex

1\1\GINC-SPARTAN-BM012\FOpt\UM062X\CC-pVTZ\C9H16N1O5(2)\UWILLE\19-Feb-  
2022\0\#p opt=(calcfc,maxcycle=500) freq=noraman M062X/cc-pVTZ scrf=(  
cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,-5.1771399635,-0.4  
584964157,1.673040917\C,-4.5380735512,0.0505258739,0.477579297\C,-4.39  
21619305,1.1399494597,3.3506063835\O,-4.2440069032,1.2093302209,0.2655  
589062\O,-4.3380224035,-0.937496264,-0.4130435964\C,-3.703696098,-0.53  
98745195,-1.6274124266\H,-3.6059986476,-1.4417487549,-2.2219582462\H,-  
4.3098411794,0.1963719302,-2.1515693483\H,-2.7247647367,-0.1166446716,  
-1.4110844746\O,-3.2562203732,1.2013948345,2.9068417145\N,-5.343768363  
3,0.302580381,2.8105718693\C,-6.0682535577,-1.6534536064,1.7425819614\  
H,-5.5427451162,-2.4860550199,2.2207978306\H,-6.400861127,-1.982726816  
4,0.7631000801\H,-2.3484839099,0.0987415184,1.8639190684\C,-7.20344804



03,-1.1422629009,2.6420942937\H,-7.7165360121,-1.9369219555,3.17540207  
25\H,-7.930309521,-0.6020561402,2.0377625889\O,-1.6917842008,-0.414335  
2214,1.3458904212\C,-4.8312014698,1.9516305282,4.5345635751\H,-5.72767  
55489,2.5241025841,4.300652876\H,-5.064067123,1.2977252715,5.375632150  
4\H,-4.0240739429,2.6201501131,4.8129447059\O,-0.567438423,0.455328766  
2,1.3993717348\C,-0.6495160941,1.3149867472,0.2815153411\H,-0.56750640  
45,0.7491821431,-0.6482349912\H,-1.5867872651,1.8736743868,0.293785375  
4\H,0.1961978539,1.9950337427,0.3734044642\C,-6.5058931088,-0.17704058  
69,3.5974188792\H,-7.1337260447,0.6591547601,3.8929221777\H,-6.1468027  
941,-0.6842683881,4.4932003989\\Version=ES64L-G16RevC.01\HF=-783.33906  
62\S2=0.756624\S2-1=0.\S2A=0.750035\RMSD=5.591e-09\RMSF=1.146e-06\Dipole  
le=-3.2115689,-0.4341857,1.0142138\Quadrupole=27.0258524,-23.4606486,-  
3.5652038,7.4126006,-28.5809295,1.08735\PG=C01 [X(C9H16N1O5)]\ \@  
Sum of electronic and thermal Free Energies= -783.130093

### Cδ\_HAT complex

1\1\GINC-SPARTAN-BM087\FOpt\UM062X\CC-pVTZ\C9H16N1O5(2)\UWILLE\19-Jan-  
2022\0\#p geom=checkpoint guess=check freq=norman M062X/cc-pVTZ opt=  
(readfc,maxcycle=500) scrf=(cpcm,solvent=acetonitrile) nosymm\geom&fr  
eq\0,2\C,0.1440775911,-1.2920895197,0.0547323566\H,0.9056529182,-0.71  
02344191,-0.4602270821\C,-0.0015053099,-2.616368582,-0.6758210823\C,-1  
.684426805,-0.1381718331,-1.0389388628\C,-3.0513044522,0.4806905886,-0  
.9195577517\H,-3.1074320417,1.1608085641,-0.0715020019\H,-3.2734926428  
,1.013469601,-1.838540103\H,-3.7928097969,-0.306540057,-0.774131935\O,  
-1.0233791892,-3.2456822288,-0.7689791989\O,1.1703853755,-3.0238944158  
,-1.1559420891\C,1.1699821588,-4.3022563641,-1.8018473395\H,0.49711028  
58,-4.2874706055,-2.6560455196\H,2.1908792496,-4.4734027153,-2.1234409  
462\H,0.8538888319,-5.0739142302,-1.1036788653\O,-1.0976233337,-0.2457  
998938,-2.1125296911\N,-1.1227899,-0.589770277,0.102635477\O,-1.186827  
4505,2.7330076441,0.9705009745\C,0.4745689809,-1.5214272035,1.53805933  
16\H,0.9972430189,-0.644950436,1.9209112084\H,1.1098799874,-2.39056855  
42,1.6914627609\C,-1.7355072022,-0.6027411859,1.435108355\H,-2.7879781  
708,-0.8709598415,1.3773658868\H,-1.6507116882,0.384933553,1.895883304  
\C,-0.9062177043,-1.6439166566,2.1837802856\H,-0.8890217012,-1.4655511  
916,3.2554620589\H,-1.3153593196,-2.6373365697,2.0027597629\C,0.580028  
8508,2.1933361781,-0.3510477243\H,1.1464807765,3.1210835334,-0.3236648  
169\H,0.8474232274,1.5504692034,0.4832814157\H,0.6975930313,1.68565146  
58,-1.3043588422\O,-0.8210624658,2.5089761889,-0.252347796\\Version=ES  
64L-G16RevC.01\HF=-783.3392726\S2=0.754995\S2-1=0.\S2A=0.750014\RMSD=4  
.005e-09\RMSF=3.094e-06\Dipole=1.3905252,-0.3187434,1.5026362\Quadrupo  
le=2.3917782,1.401052,-3.7928301,-2.301299,-4.4927337,-2.9358354\PG=CO  
1 [X(C9H16N1O5)]\ \@  
Sum of electronic and thermal Free Energies= -783.130780

### TS<sub>HAT\_cδ</sub>

1\1\GINC-SPARTAN-BM092\FTS\UM062X\CC-pVTZ\C9H16N1O5(2)\UWILLE\22-Dec-2  
021\0\#p geom=checkpoint guess=check opt=(ts,noigentest,readfc,maxcy  
cle=500) freq=norman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) n  
osymm\geom&freq\0,2\C,0.1588905532,-1.2455835314,-0.1603971142\H,0.8  
729322211,-0.7117802998,-0.7837859322\C,-0.0210551987,-2.6430746512,-0  
.7297142905\C,-1.7364348717,-0.1800034158,-1.280757688\C,-3.0850498543

,0.4668336228,-1.1465636113\H,-3.0667129208,1.2580914886,-0.3997314341  
\H,-3.3751694353,0.8686370733,-2.1116198283\H,-3.815379218,-0.28165046  
32,-0.835147018\O,-1.0531720615,-3.261220342,-0.7178200072\O,1.1310590  
808,-3.1148572402,-1.1915526323\C,1.1023845636,-4.4615317268,-1.681992  
5489\H,0.4047900656,-4.5392500349,-2.5124334363\H,2.1123160833,-4.6793  
800097,-2.0093453636\H,0.8013362163,-5.1407521774,-0.887904723\O,-1.19  
45186097,-0.3967124222,-2.3521172811\N,-1.122114163,-0.5595393473,-0.1  
173328435\O,-1.2252534481,2.0861520122,1.5190063696\C,0.5775803507,-1.  
3088034299,1.3197150925\H,1.163048167,-0.4240374304,1.5645754395\H,1.1  
836126254,-2.1846656261,1.5363884257\C,-1.6185045929,-0.4004988741,1.1  
975161947\H,-2.6977577019,-0.4900699047,1.2880271626\H,-1.4152776011,0  
.8386145574,1.4966315807\C,-0.7566690195,-1.2868628435,2.0698341587\H,  
-0.6658617068,-0.9158464075,3.0872737841\H,-1.1933423256,-2.287250142,  
2.1075480252\C,0.5101906148,2.3949324575,0.0758411523\H,0.9447681195,3  
.1484029984,0.7315416825\H,0.9265004116,1.4149449062,0.3116714105\H,0.  
7035908632,2.6402271514,-0.9662436834\O,-0.9007921572,2.3784472824,0.2  
119070871\\Version=ES64L-G16RevC.01\HF=-783.3102887\S2=0.759214\S2-1=0  
\S2A=0.750049\RMSD=7.896e-09\RMSF=7.744e-06\Dipole=1.1952029,-0.88349  
88,1.2657667\Quadrupole=3.458937,1.7154234,-5.1743604,-2.7668029,-2.90  
95595,-3.8016559\PG=C01 [X(C9H16N1O5)]\@\@  
Frequencies -1851.2177  
Sum of electronic and thermal Free Energies= -783.105113

### Cδ-radical product complex

1\1\GINC-SPARTAN-BM002\FOpt\UM062X\CC-pVTZ\C9H16N1O5(2)\UWILLE\19-Feb-  
2022\O\#p opt=(calcfc,maxcycle=500) freq=noraman M062X/cc-pVTZ scrf=(  
cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,-1.0923950799,-1.2  
504217462,0.983270325\H,-1.4115770197,-0.9681338609,1.9856403622\C,-0.  
1987064637,-0.1373586526,0.4507644666\C,-3.2938758887,-0.5685694847,0.  
1157514804\O,-0.4631451393,0.5706730806,-0.4840006481\O,0.9266663181,-  
0.0631586325,1.1525421509\C,1.7961766805,1.022342353,0.8126261616\H,2.  
6477899318,0.9414609661,1.4789533623\H,2.1122894871,0.9407416259,-0.22  
44420333\H,1.2765577319,1.9669816629,0.9643127213\O,-3.3511916363,0.36  
48322258,0.9217811691\N,-2.2412201904,-1.4213240658,0.0963829964\C,-0.  
4132956471,-2.6258696623,0.9342003444\H,-0.8952396618,-3.2787483126,1.  
6589937953\H,0.6449960536,-2.5642682538,1.1654080715\C,-2.0373419086,-  
2.4906208422,-0.7646853749\H,-2.6552704304,-2.6172514122,-1.6348280895  
\H,-2.6032462394,0.9026736198,2.3371616468\C,-0.7115899212,-3.11027215  
8,-0.4916985944\H,-0.7276734477,-4.1956815992,-0.5722587317\H,0.050465  
3585,-2.7454506144,-1.1913160493\O,-2.2294114829,1.2561831164,3.176008  
1739\C,-4.3803821154,-0.8229864356,-0.8851891373\H,-3.9976620863,-0.68  
88393544,-1.8978467755\H,-4.7477189499,-1.8460102394,-0.8014986545\H,-  
5.1895396364,-0.1233275346,-0.7074218015\O,-0.8997196914,1.5787759654,  
2.7685429216\C,-0.0529183036,1.0812550799,3.7802482677\H,-0.3198650494  
,1.5118787094,4.7462615804\H,-0.0999296783,-0.0084062869,3.8314432396\  
H,0.9523671065,1.3932837432,3.503050653\\Version=ES64L-G16RevC.01\HF=-  
783.3342365\S2=0.759638\S2-1=0.\S2A=0.750051\RMSD=3.534e-09\RMSF=2.607  
e-06\Dipole=1.3417182,-2.5880264,-0.7821173\Quadrupole=1.363041,2.1266  
948,-3.4897358,12.275188,12.631288,-2.1265624\PG=C01 [X(C9H16N1O5)]\@\@  
Sum of electronic and thermal Free Energies= -783.124960

### Cε\_HAT complex

```
1\1\GINC-SPARTAN-BM087\FOpt\UM062X\CC-pVTZ\C9H16N1O5(2)\UWILLE\18-Jan-2022\O\#p opt=(readfc,maxcycle=500) geom=checkpoint guess=check freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,-0.1274361575,-0.9594288114,0.3680429817\C,0.0131923627,-0.6864792623,3.3751105991\C,-0.6719907017,-0.3545007845,4.6744510589\H,-0.8546051369,-1.2501585372,5.2664209884\H,-0.0505030518,0.3392673153,5.2308117504\H,-1.6366765137,0.1125012553,4.4718361152\O,-1.0291610706,-0.162045263,0.3843448418\O,0.7926800263,-1.0218271389,-0.5919102037\C,0.6502627544,-0.0733013649,-1.6543399989\H,-0.3111140384,-0.2055726463,-2.1473709298\H,0.7168423754,0.9398715133,-1.2626553453\H,1.4636474793,-0.2725703651,-2.3429480269\O,0.9919861193,-0.0673514049,2.9677933825\N,-0.5072137516,-1.7066547254,2.6632572645\O,-0.8137744215,3.0371914564,-1.6113242378\C,-0.7015306688,-3.3278744226,0.9844617695\H,-0.2090245002,-4.1962332599,1.4201386407\H,-0.7428249587,-3.4626204318,-0.0938956231\C,-1.7240712636,-2.4639255542,2.9703820748\H,-2.5106826709,-1.8061306732,3.3332541438\H,-1.5207605084,-3.2183004676,3.7336518749\C,-2.0705504335,-3.1085774584,1.6299915886\H,-2.6349891262,-4.0295699486,1.7482870551\H,-2.6585751871,-2.4141484274,1.0307513524\C,-1.0327280009,2.4845720011,-3.7942784651\H,-1.0560437731,3.5283426039,-4.0954476651\H,-0.0158633039,2.10006682,-3.8081925726\H,-1.690556686,1.8815233717,-4.4115598885\O,-1.5476976334,2.3803666588,-2.4540131349\C,0.0785776702,-2.0659166625,1.3877861207\H,1.147419581,-2.2453878558,1.4799338984\\Version=ES64L-G16RevC.01\HF=-783.3342322\S2=0.754818\S2-1=0.\S2A=0.750013\RMSD=3.369e-09\RMSF=3.338e-06\Dipole=-1.0298912,-2.0129202,-1.4243905\Quadrupole=-11.1855162,-1.8504771,13.0359934,4.3539268,-7.2978838,-13.8549518\PG=C01 [X(C9H16N1O5)]\@\nSum of electronic and thermal Free Energies= -783.129171
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### TS<sub>HAT\_Cε</sub>

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1\1\GINC-SPARTAN-BM123\FTS\UM062X\CC-pVTZ\C9H16N1O5(2)\UWILLE\23-Dec-2021\O\#p scf=(qc,direct) opt=(ts,noeigentest,readfc,maxcycle=500) geom=checkpoint guess=check freq=noraman M062X/cc-pVTZ scrf=(cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,-0.3772840883,-1.0093176546,0.1904569356\C,-0.3098117323,0.0280190399,2.9895790642\C,-1.0379167531,0.5057308152,4.2174869812\H,-0.9587208281,-0.2145901564,5.0303382271\H,-0.6207854355,1.4595900613,4.5227021403\H,-2.0965858682,0.6350953392,3.9888000878\O,-1.4574397303,-0.5099631323,0.0501106812\O,0.5668074061,-1.0201655588,-0.7757949063\C,0.2435320834,-0.4114928936,-1.9793984992\H,-0.790430928,-0.5470028104,-2.2839640811\H,0.304687996,0.9064191943,-1.7717020555\H,1.0058651736,-0.6332565531,-2.7150808437\O,0.4533035425,0.7465839226,2.3505615234\N,-0.5407892141,-1.2451399728,2.6066196526\O,0.2844818845,2.0635948159,-1.5034313327\C,-0.3412928801,-3.229573559,1.3735067054\H,0.3662738531,-3.8220920432,1.951605695\H,-0.3723442972,-3.6257019572,0.3610958699\C,-1.5036669152,-2.1849088942,3.1879952656\H,-2.4244883023,-1.6764056706,3.4637680473\H,-1.0846864246,-2.6569604356,4.0792814641\C,-1.7055864482,-3.1984912553,2.0640678193\H,-2.0125147759,-4.1725034946,2.435244408\H,-2.4654260402,-2.8330670403,1.3740280377\C,-0.9062604305,2.8503652492,-3.2716801162\H,-0.1542701183,3.62295175,-3.4252505718\H,-0.6773204364,1.9766947083,-3.8845351892\H,-1.895607949,3.2289167464,-3.5179410963\O,-0.9660068181,2.4855821691,-1.90
```

1696026\C,0.1053759175,-1.7581399447,1.4159529617\H,1.1862460873,-1.64  
94031149,1.4716325706\\Version=ES64L-G16RevC.01\HF=-783.2948277\S2=0.7  
5957\S2-1=0.\S2A=0.750043\RMSD=9.810e-10\RMSF=1.094e-05\Dipole=-0.7051  
907,-2.626185,-0.2066491\Quadrupole=-10.5932233,-2.3383781,12.9316014,  
-0.0537341,-5.4559708,-11.5398569\PG=C01 [X(C9H16N1O5)]\@\  
Frequencies -2079.8127  
Sum of electronic and thermal Free Energies= -783.092442

### C $\alpha$ -radical product complex

1\1\GINC-SPARTAN-BM018\FOpt\UM062X\CC-pVTZ\C9H16N1O5(2)\UWILLE\18-Feb-  
2022\0\#p opt=(calcfc,maxcycle=500) freq=norman M062X/cc-pVTZ scrf=(  
cpcm,solvent=acetonitrile) nosymm\geom&freq\0,2\C,-0.876028479,-2.75  
12024723,-1.875220639\C,-0.6391769068,-0.2056615045,-0.2537913941\C,-1  
.2221931738,0.7364206132,0.7612417236\H,-0.6733723803,0.6870000228,1.7  
004993818\H,-1.197727633,1.7486137025,0.3693998243\H,-2.2566045695,0.4  
56750129,0.9644373507\O,-2.0656007514,-2.632217272,-1.783328077\O,-0.2  
553297843,-3.2532888736,-2.962839401\C,-1.0204155845,-3.6675836664,-4.  
0155384155\H,-2.0804602393,-3.7672167704,-3.8642248744\H,-0.5709093248  
,1.7572580808,-1.8505922487\H,-0.4554448828,-4.1459068282,-4.793957074  
2\O,-0.3819513044,0.1413559509,-1.414842131\N,-0.4073526403,-1.4629900  
276,0.1394857642\O,-0.5563215179,2.7252865964,-2.0527292856\C,0.402276  
4088,-3.6614754429,0.090437961\H,1.395128614,-3.5661402344,0.527518516  
4\H,0.3620360341,-4.5915848112,-0.4711019349\C,-0.7323792043,-2.046835  
2169,1.4467156622\H,-1.712698239,-1.7182336863,1.7830412252\H,0.012267  
7069,-1.7476477931,2.1866206124\C,-0.6739997511,-3.5468719113,1.170461  
0707\H,-0.4396707136,-4.1204757753,2.0627759687\H,-1.6333620126,-3.885  
8906741,0.7807197288\C,1.3844747713,3.2034832412,-0.9477998328\H,0.895  
2907788,4.0578692173,-0.4779316707\H,1.2941244705,2.3248998794,-0.3047  
134212\H,2.4371664564,3.4254419885,-1.11683285\O,0.8369416533,2.952901  
6064,-2.2239811603\C,0.136970899,-2.431666665,-0.7942783252\H,1.038125  
6996,-2.0552055629,-1.2728334644\\Version=ES64L-G16RevC.01\HF=-783.320  
5958\S2=0.754858\S2-1=0.\S2A=0.750018\RMSD=2.484e-09\RMSF=1.667e-06\Di  
pole=0.8063033,-2.6062302,2.9590747\Quadrupole=-1.4833139,5.8014652,-4  
.3181513,0.1517124,-3.2667638,10.3329783\PG=C01 [X(C9H16N1O5)]\@\  
Sum of electronic and thermal Free Energies= -783.115403

## 6. References

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