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Title:
Oxidative Damage of S-Containing Amino Acids by the Environmental Radical NO3.: A Kinetic, Product and Computational Study

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Table S1. Determination of the second-order rate coefficients from the time-dependent decay at 480 nm and from the 'slower' decay at 630 nm in the reaction of $NO_3^\bullet$ with Ac-Met-OMe in acetonitrile at 298 ± 1K.[a,b]

[Ac-Met-OMe] (mM)	k (10^7 M^{-1} s^{-1}) at 630 nm	k (10^7 M^{-1} s^{-1}) 480 nm
0.66	38.6	30.0
1.3	14.4	11.2
2.0	7.4	6.1
2.6	4.8	3.8
3.3	3.2	2.6

[a] Experimental error ± 10%. [b] Samples were prepared immediately before the laser flash.

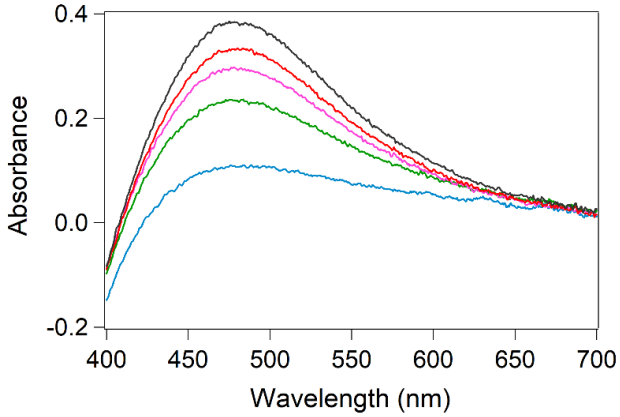


Figure S1. UV/Vis transient absorption spectrum for the reaction of $NO_3^\bullet$ with Tfa-Met-OMe, showing a broad absorption with a maximum at 480 nm. Absorption spectra taken 20 ns after laser flash. [Tfa-Met-OMe] = 1.40 mM (blue), 2.81 mM (green), 4.21 mM (pink), 5.61 mM (red) and 7.01 mM (black). Samples were prepared immediately before the laser flash.

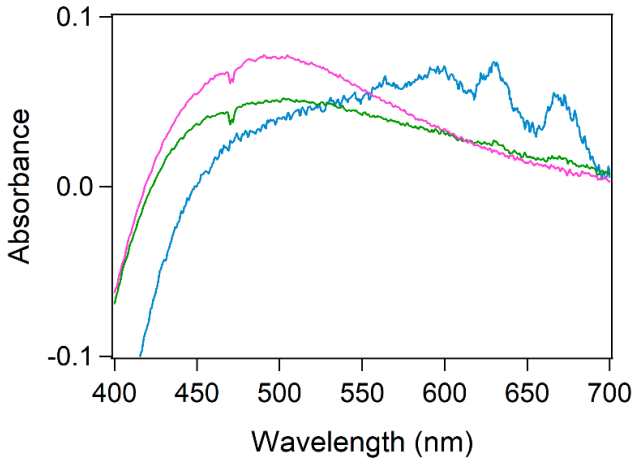


Figure S2. UV/Vis transient absorption spectrum for the reaction of $NO_3^\bullet$ with Phth-Met-OMe, showing a broad absorption with a maximum at 480 nm. Absorption spectra taken 20 ns after laser flash. [Phth-Met-OMe] = 0.33 mM (blue), 1.65 mM (green) and 3.30 mM (pink). Samples were prepared immediately before the laser flash.

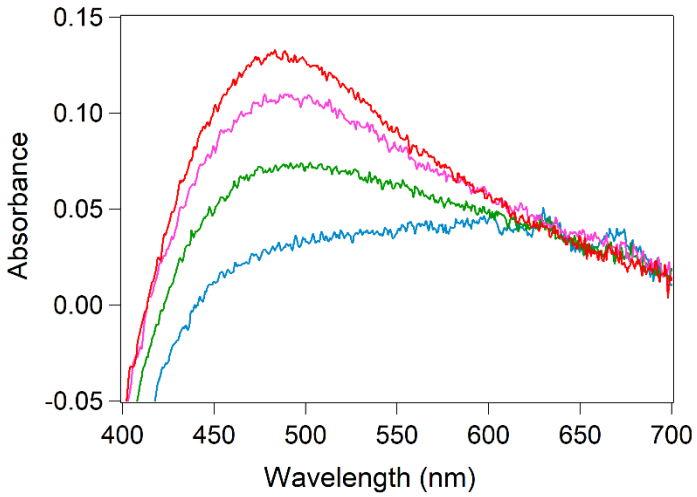


Figure S3. UV/Vis transient absorption spectrum for the reaction of $NO_3^\bullet$ with Ac-(Me)Met-OMe, showing a broad absorption with a maximum at 480 nm. Absorption spectra taken 20 ns after laser flash. [Ac-(Me)Met-OMe] = 0.33 mM (blue), 1.32 mM (green), 2.31 mM (pink) and 3.30 mM (red). Samples were prepared immediately before the laser flash.

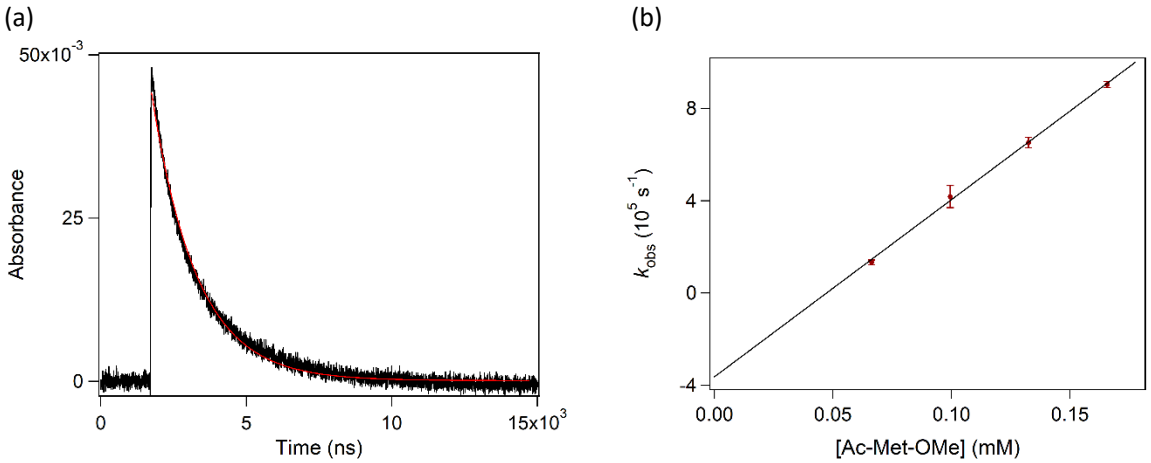


Figure S4. Reaction of $NO_3^\bullet$ with Ac-Met-OMe. (a) Time-dependent decay of the $NO_3^\bullet$ signal (black) at 630 nm in acetonitrile ([CAN] = 0.33 mM) in the presence of Ac-Met-OMe (0.13 mM) and first-order fitting curve (red). (b) Plot of the pseudo-first-order rate coefficient (k_{obs}) vs [Ac-Met-OMe] to confirm that pseudo-first-order conditions were maintained with the lower concentration range. Samples were prepared immediately before the laser flash. Error bars shown are 2σ statistical uncertainties. From the linear regression analysis: Ac-Met-OMe: intercept = -3.6×10^5 s^{-1}, $k = 7.7 \times 10^9$ M^{-1} s^{-1}, $R^2 = 0.9984$. The negative y-intercept is due to experimental errors. However, the value is negligible compared to the actual rate coefficient for the reaction of $NO_3^\bullet$ with Ac-Met-OMe.

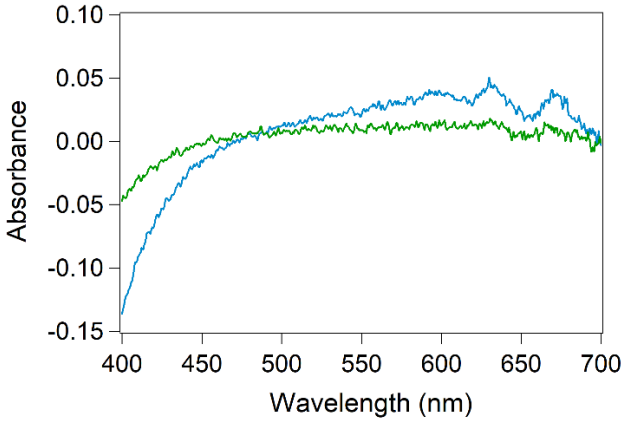


Figure S5. UV/Vis transient absorption spectrum for the reaction of $NO_3^\bullet$ with Ac-MetO_2-OMe, showing no absorption at 480 nm. Absorption spectra taken 20 ns after laser flash. [Ac-MetO_2-OMe] = 1.98 mM (blue) and 9.90 mM (green).

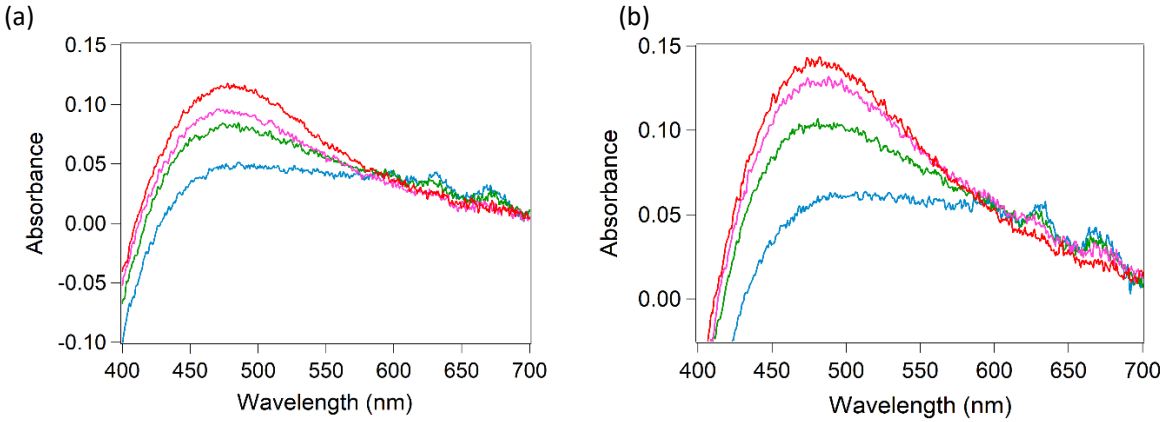
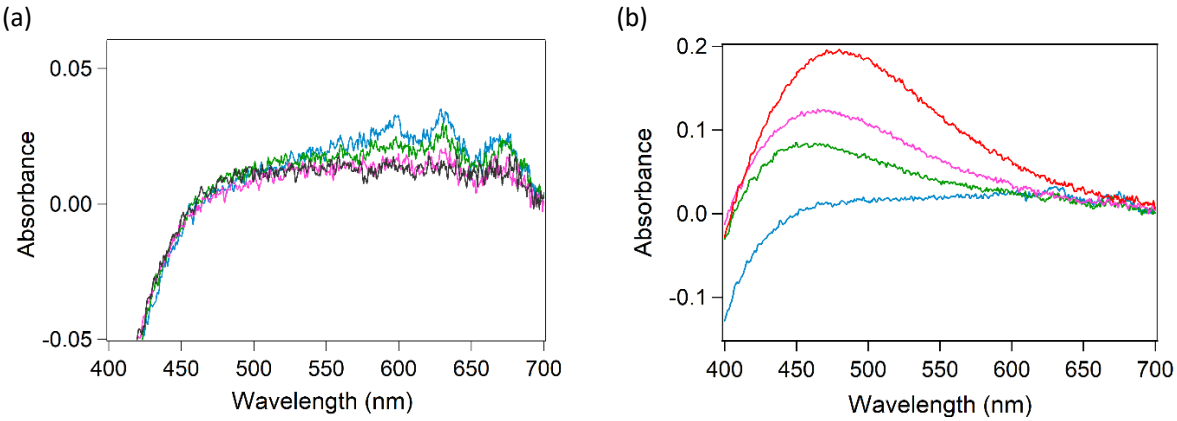


Figure S6. (a) UV/Vis transient absorption spectrum for the reaction of $NO_3^\bullet$ with Ac-Met-Pro-OMe, showing a broad absorption with a maximum at 480 nm. Absorption spectra taken 20 ns after laser flash. [Ac-Met-Pro-OMe] = 0.66 mM (blue), 1.32 mM (green), 1.98 mM (pink) and 3.20 mM (red). (b) UV/Vis transient absorption spectrum for the reaction of $NO_3^\bullet$ with Ac-Pro-Met-OMe, showing a broad absorption with a maximum at 480 nm. Absorption spectra taken 20 ns after laser flash. [Ac-Pro-Met-OMe] = 0.66 mM (blue), 1.32 mM (green), 1.98 mM (pink) and 2.64 mM (red). Samples were prepared immediately before the laser flash.



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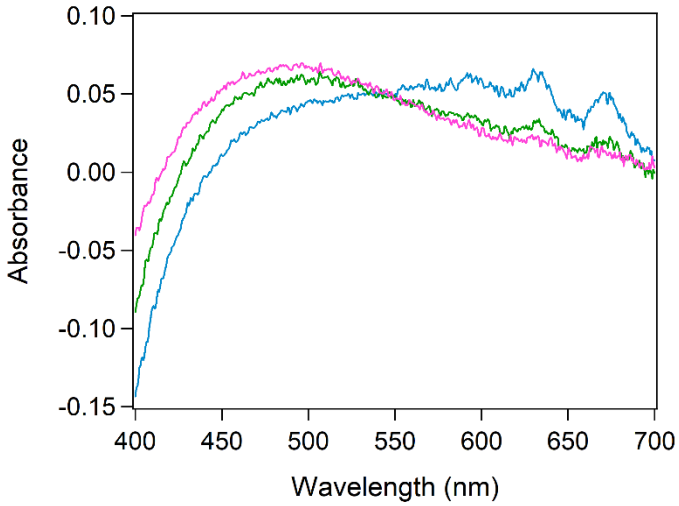


Figure S8. UV/Vis transient absorption spectrum for the reaction of $NO_3^•$ with Ac-Cys(S-S)Cys-OMe, showing a broad absorption with a maximum at 480 nm. Absorption spectra taken 20 ns after laser flash. [Ac-Cys(S-S)Cys-OMe] = 0.33 mM (blue), 0.66 mM (green) and 1.32 mM (pink). Samples were prepared immediately before the laser flash.

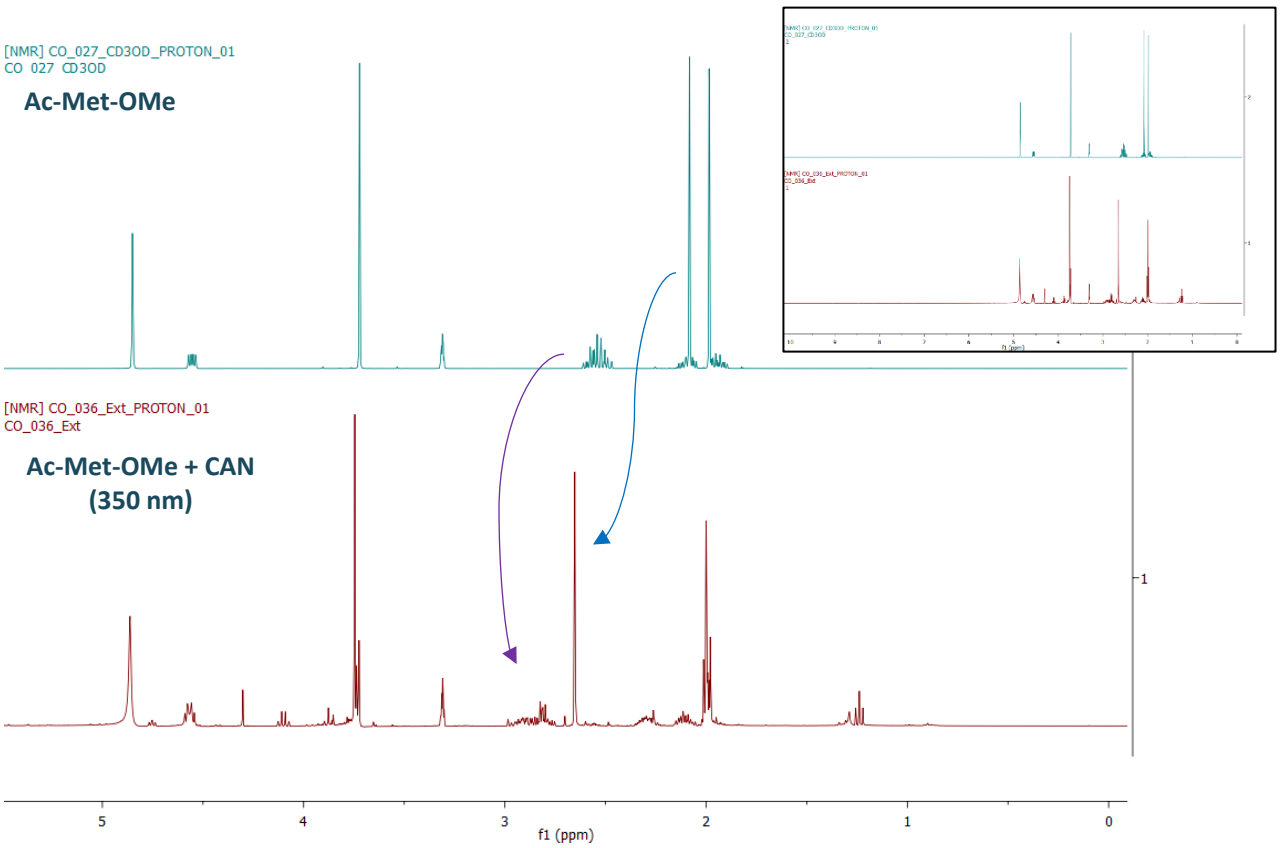
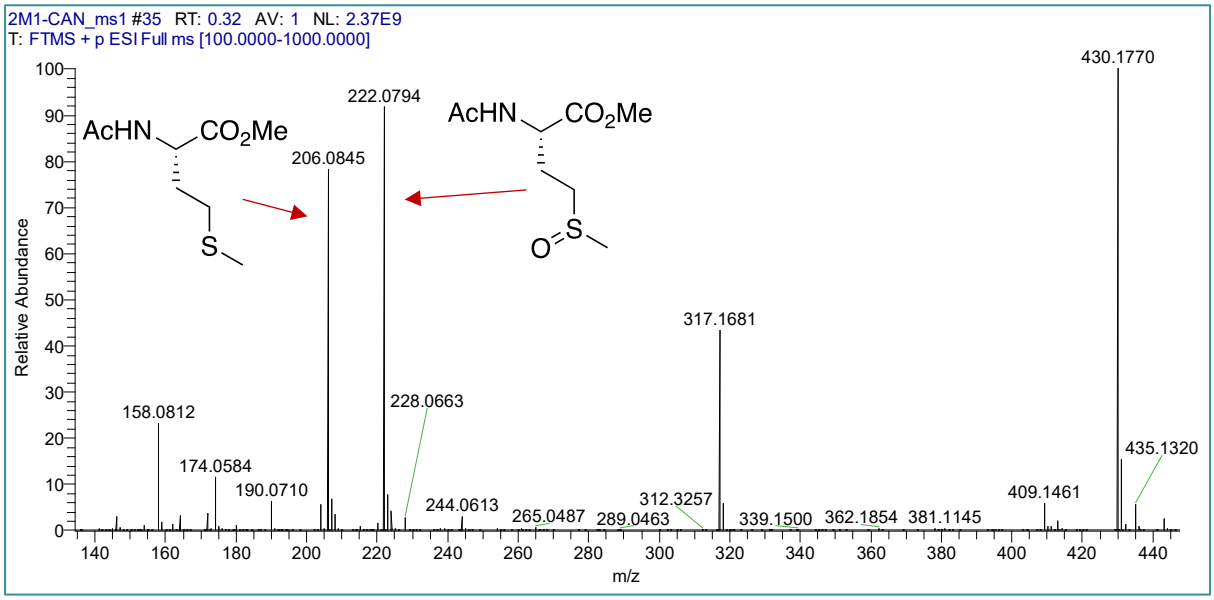


Figure S9. Top image: ^{1}H NMR spectrum of Ac-Met-OMe. Bottom image: ^{1}H NMR spectrum of the reaction mixture of $NO_3^{\bullet}$ with Ac-Met-OMe. The spectra are shown from 0–5 ppm because there is no peak outside this range (see inset). Sulfoxide formation is confirmed by downfield shifts of -SC***H***$_3$ to -SOC***H***$_3$ (2.08 ppm to 2.65 ppm, blue arrow) and -SC***H***$_2$- to -SOC***H***$_2$- (purple arrow).

(a)



(b)

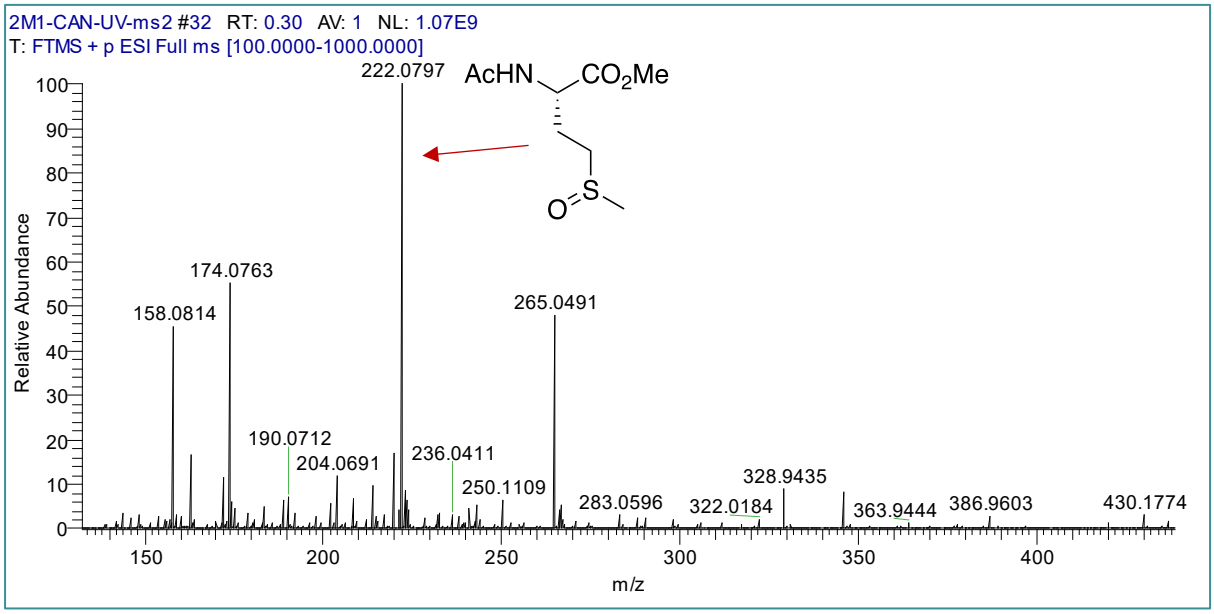
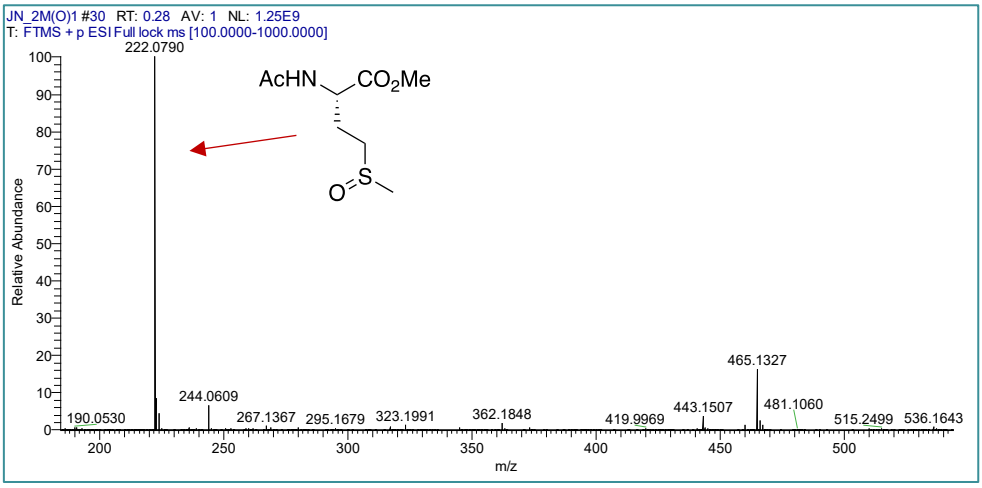
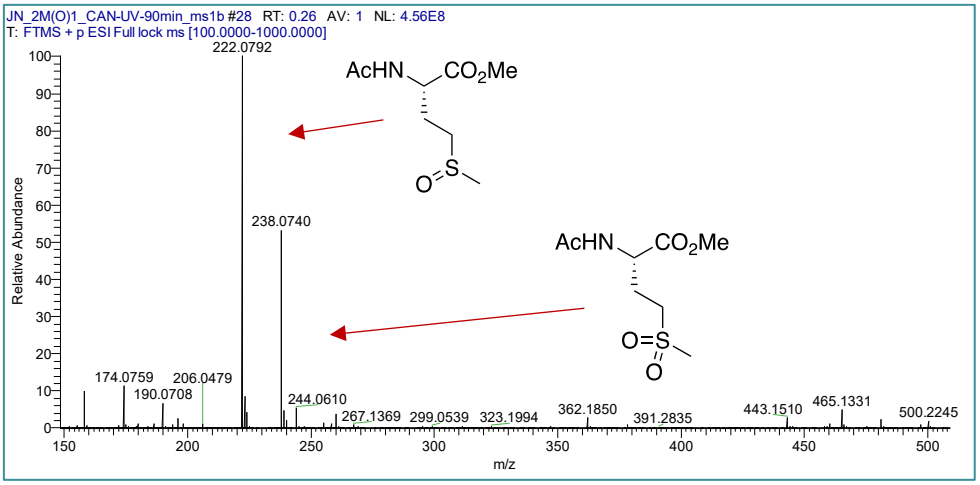


Figure S10. MS spectra of the reaction of CAN with Ac-Met-OMe in (a) the absence of light and (b) the presence of light, where conversion of Ac-Met-OMe to Ac-MetO-OMe was complete under otherwise identical reaction conditions.

(a)



(b)



(c)

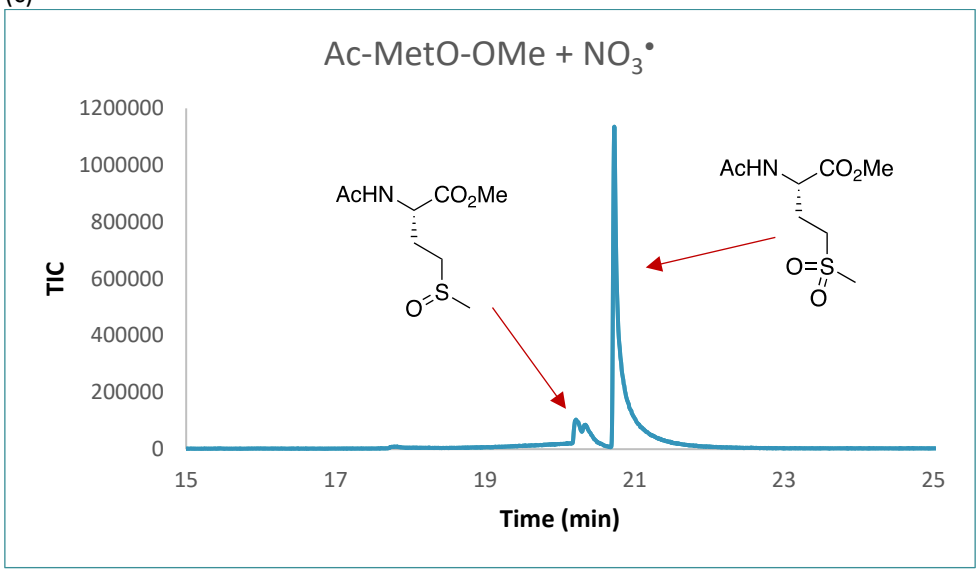
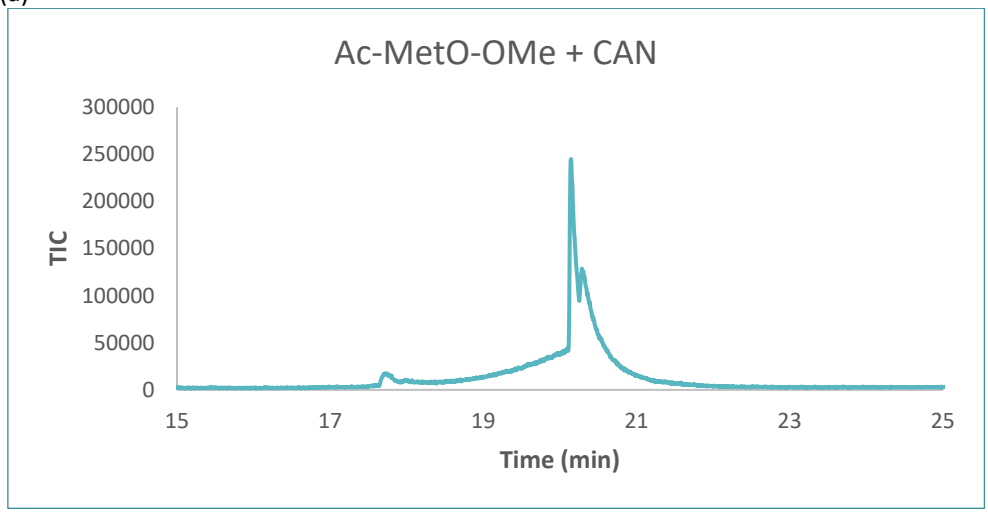


Figure S11. MS spectra of the reaction of CAN with Ac-MetO-OMe in (a) the absence of light and (b) the presence of light. (c) GC chromatogram of the reaction mixture of CAN with Ac-MetO-OMe (dr ~1:1, according to ^{1}H NMR) in the presence of light.

(a)



(b)

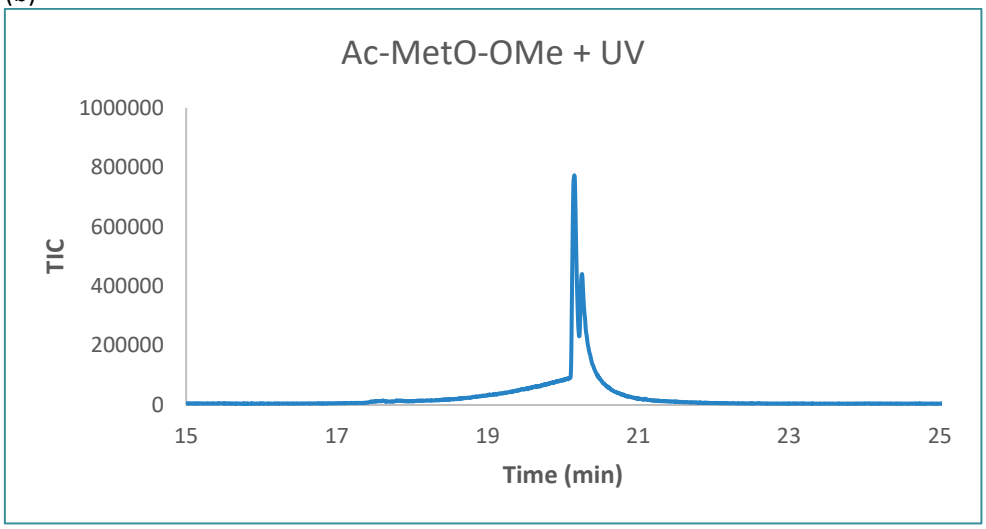


Figure S12. Gas chromatograms of control experiments where Ac-MetO-OMe (dr ~1:1, according to ^{1}H NMR) was (a) treated with CAN in the absence of light or (b) irradiated in the absence of CAN, showing no formation of Ac-MetO_2-OMe in both cases.

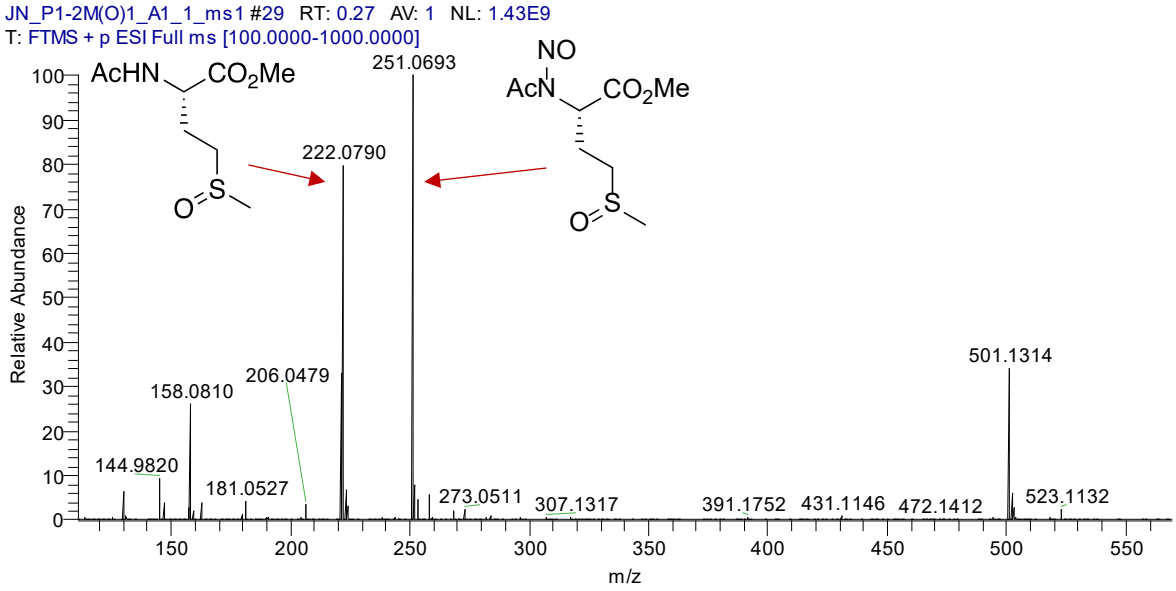


Figure S13. MS spectrum of the reaction of $NO_2^{\bullet}$ with Ac-MetO-OMe, where only *N*-nitrosation occurred but not oxidation to Ac-MetO_2-OMe (which would appear at *m/z* 238; see Figure S11b).

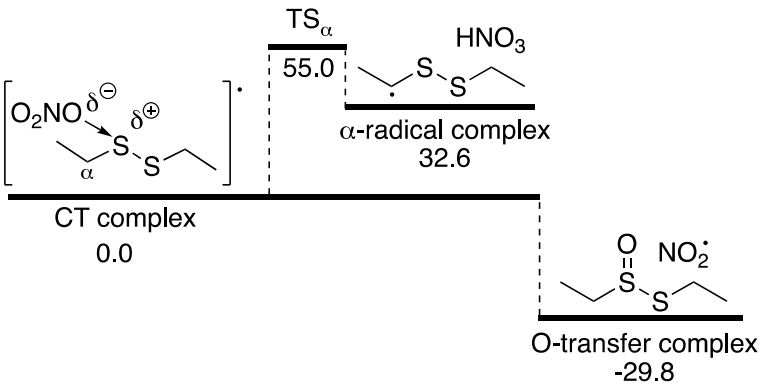


Figure S14. Calculated potential energy surface for the reaction of $NO_3^{\bullet}$ with EtSSEt. M062X/6-31+G* free energies in kJ mol^{-1} (in acetonitrile), relative to the CT complex (a reactant complex without CT interactions could not be located computationally).

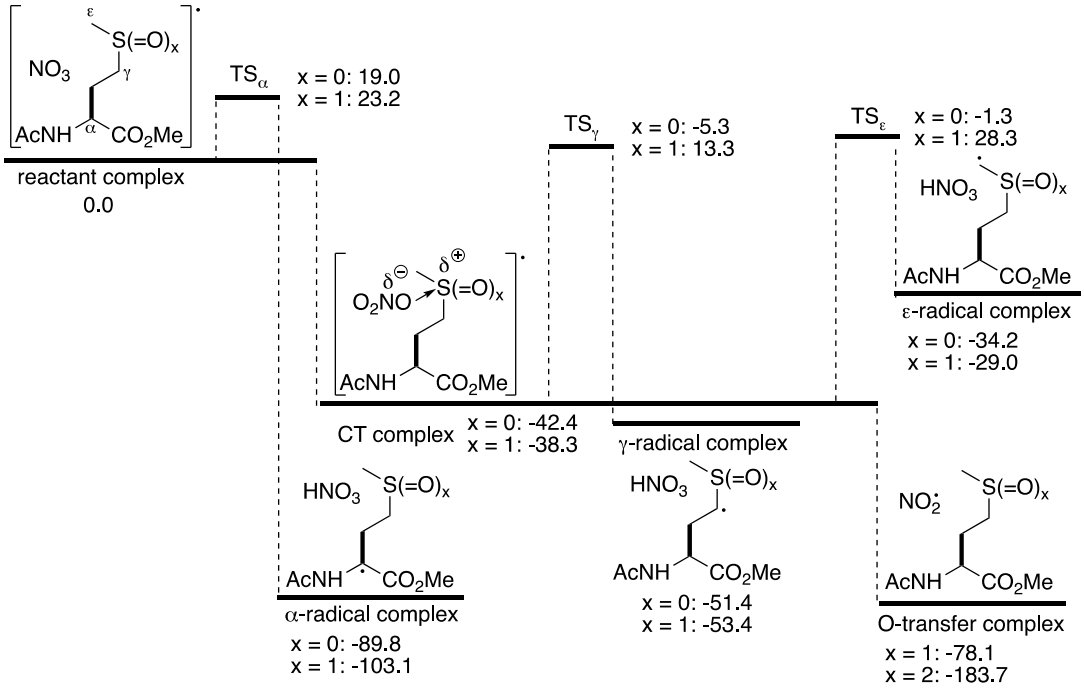


Figure S15. Calculated potential energy surface for the reaction of $NO_3^\bullet$ with Ac-Met-OMe and Ac-MetO-OMe. M062X/6-31+G* free energies in kJ mol^{-1} (in acetonitrile), relative to the reactant complex, which only showed van-der-Waals but no CT interactions. While the reactions occurring at or adjacent to the S-centre should proceed via a CT complex (or pre-reaction complex), this complex is likely not the precursor for HAT from Cα.

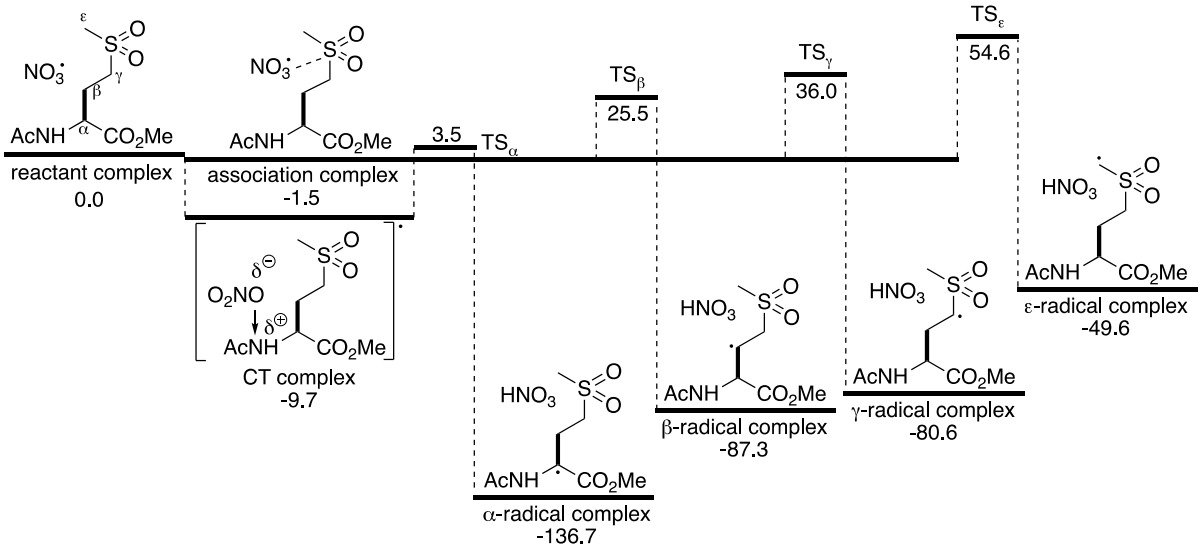


Figure S16. Calculated potential energy surface for the reaction of $NO_3^\bullet$ with Ac-MetO_2-OMe. M062X/6-31+G* free energies in kJ mol^{-1} (in acetonitrile) relative to the reactant (*i.e.*, van-der-Waals) complex. A CT complex between $NO_3^\bullet$ and the amide moiety has been located, which is considered as the precursor to HAT from Cα (and from NH *via* ET; not calculated, see ref. 1). The reactant complex could also transform into a weakly exothermic association complex between $NO_3^\bullet$ and the SO_2 moiety, which could be the precursor for HAT from the side chain.

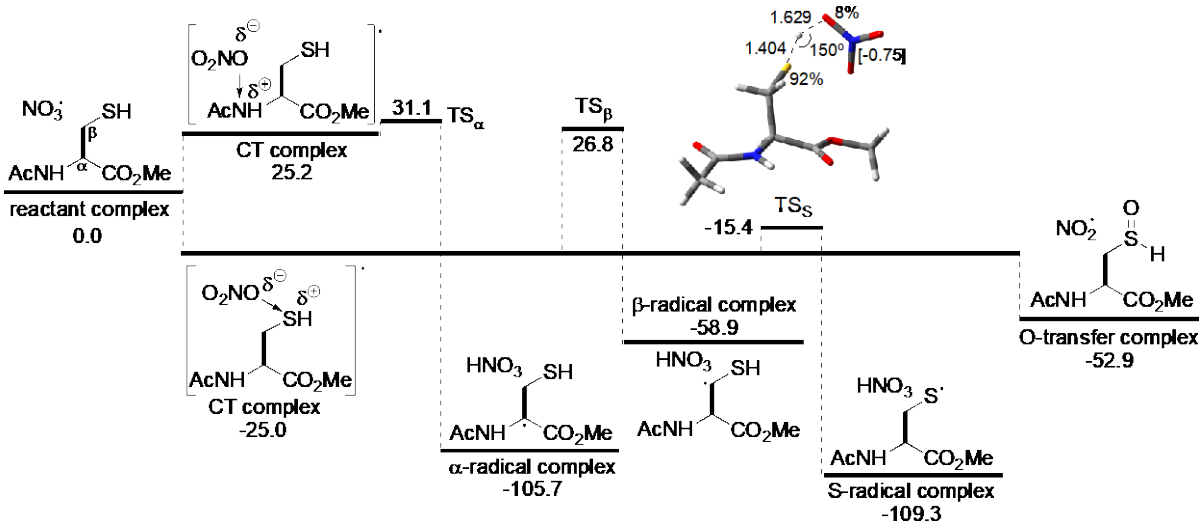


Figure S17. Calculated potential energy surface for the reaction of $NO_3^{\bullet}$ with Ac-Cys-OMe. M062X/6-31+G* free energies in kJ mol^{-1} (in acetonitrile) relative to the reactant (van-der-Waals) complex. The reactant complex has no apparent coordinating interactions but a considerable spin and charge exchange between $NO_3^{\bullet}$ and the S atom of the amino acid. It was not possible to locate a reactant complex as reference point in which the spin remained exclusively on the NO_3 moiety. It was possible to locate a CT complex between $NO_3^{\bullet}$ and the amide moiety without spin density on S, which is considerably higher in energy than the reactant complex and should be the precursor to HAT from Cα (and from NH, which was not calculated; see ref. 1). The reaction pathways through HAT from Cβ and S as well as the O-transfer should proceed via a CT complex between $NO_3^{\bullet}$ and the thiol moiety. Only the shown tautomer of the sulfenic acid in the O-transfer complex was calculated. Optimised geometry of TS_S with distances in Å, spin densities (%) and Mulliken charge on the NO_3 moiety (in square brackets).

2. General Experimental Procedures

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 L-methionine (98%, Acros Organics, Geel, Belgium), *N*-acetyl-L-cysteine (99%, Sigma-Aldrich, Castle Hill, Australia), L-cystine (99%, BDH Chemicals, VWR, Lutterworth, UK), L-proline (99.8%, Chem-Impex, Illinois, USA) and L-proline methyl ester hydrochloride salt (99%, Chem-Impex, Illinois, USA). Thin layer chromatography (TLC) was performed to monitor the reaction progress using aluminium plates coated with silica gel 60 F_{254} (Merck, Hindmarsh, Australia) and visualised with UV light at 254 nm or stained with $KMnO_4$ stain followed by heating. The crude products were purified by recrystallisation from hot solvent or silica column chromatography with approximately 30–60 g of dry silica (Davisil Chromatography Silica Gel LC60A, 40–60 micron, 230–400 mesh) per 1 g of the crude product mixture. The eluting solvent consisted of a mixture of chloroform and methanol. 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^{-1}, flow rate: 1 mL min^{-1}).

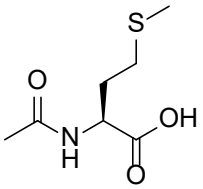
^{1}H and ^{13}C NMR spectra were recorded on an Agilent MR 400 MHz NMR spectrometer or an Agilent DD2 500 MHz NMR spectrometer in deuterated dimethylsulfoxide (DMSO-d_6) at 25.0 °C. Chemical shifts are reported in ppm (δ) using the residual solvent as reference (δ = 2.50 ppm for ^{1}H NMR and 39.5 ppm for ^{13}C NMR). ^{1}H NMR data are reported as follows: chemical shift (δ), multiplicity, coupling constants (in Hz, if any) and relative integral. ^{13}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 $[M - H]^-$, $[M + H]^+$ or $[M + Na]^+$, and in the case of salts, they are $[M – Cl]^+$.

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 and product 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.[2-5] All compounds containing a tertiary amide moiety (i.e., Ac-Pro, Ac-Pro-Met-OMe, Ac-Met-Pro-OMe, and Ac-(Me)Met-OMe) show both isomers in their ^{1}H and ^{13}C NMR spectra. Only chemical shifts for the major isomer (usually *s-trans*) are assigned.

3. Spectroscopic details for the isolated compounds

_N_-Acetyl-L-methionine methyl ester (Ac-Met-OMe)

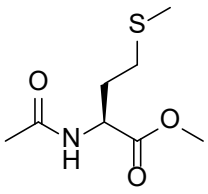
(a) _N_-Acetyl-L-methionine (Ac-Met)[6]



L-Methioine (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%).

^{1}H NMR (400 MHz, DMSO-d_6): 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). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6): δ 173.8, 168.6, 53.0, 32.3, 29.9, 22.8, 14.7 ppm. HRMS (ESI) m/z calcd. for $[C_7H_{14}NO_3S]^+$: 192.0689 $[M + H]^+$, found 192.0689, HRMS (ESI) m/z calcd. for $[C_7H_{13}NO_3SNa]^+$: 214.0509 $[M + Na]^+$, found 214.0508

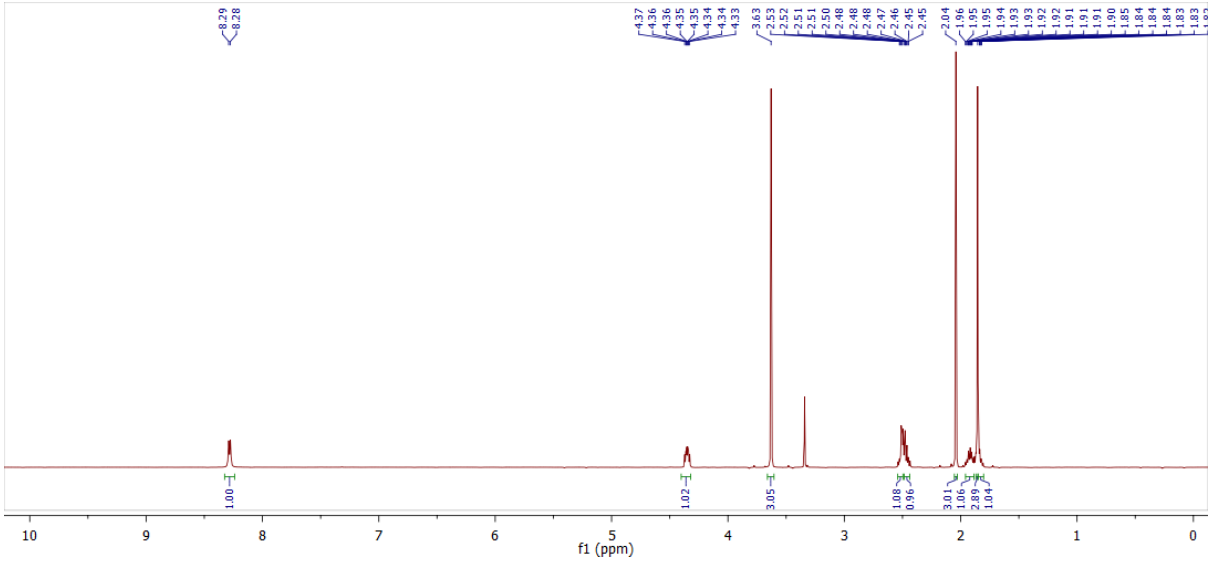
(b) _N_-Acetyl-L-methionine methyl ester (Ac-Met-OMe)[7]



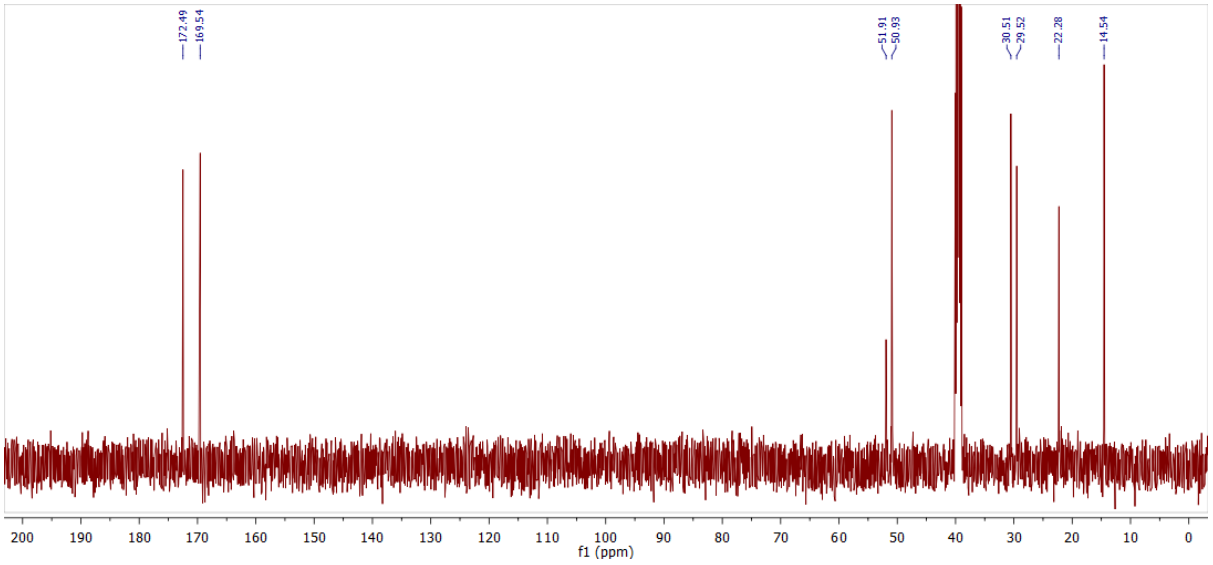
N-Acetyl-L-methionine (10.2 g, 53.5 mmol) was suspended in methanol (50 mL) at 0 °C. Thionyl chloride (4.4 mL, 60.6 mmol) was added dropwise. The resulting mixture was stirred for 4 hours until starting material was fully consumed as monitored using TLC (EtOAc, KMnO4 stain). The solvent was removed under 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%).

^{1}H NMR (500 MHz, DMSO-d_6): 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). ^{13}C {^{1}H} NMR (126 MHz, DMSO-d_6): δ 172.5, 169.5, 51.9, 50.9, 30.5, 29.5, 22.3, 14.5 ppm. HRMS (ESI) m/z calcd. for $[C_8H_{16}NO_3S]^+$: 206.0846 $[M + H]^+$, found 206.0851; HRMS (ESI) m/z calcd. for $[C_8H_{15}NO_3SNa]^+$: 228.0665 $[M + Na]^+$, found 228.0669.

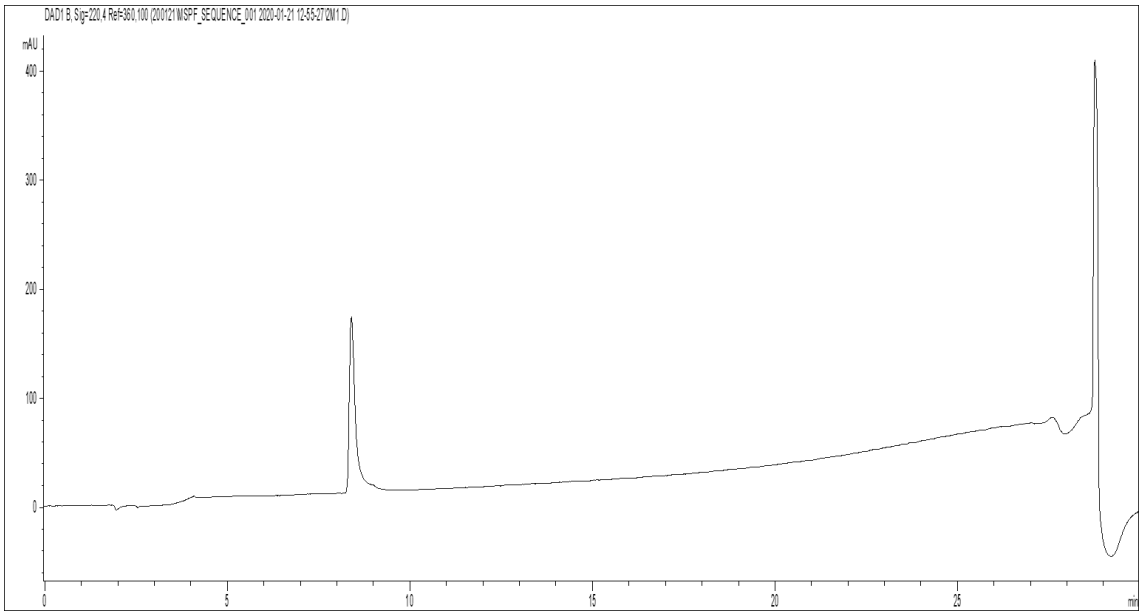
^{1}H NMR spectrum of Ac-Met-OMe



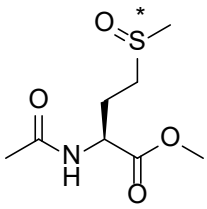
^{13}C NMR spectrum of Ac-Met-OMe



HPLC chromatogram of Ac-Met-OMe



N-Acetyl-L-methionine sulfoxide methyl ester (Ac-MetO-OMe)[8]

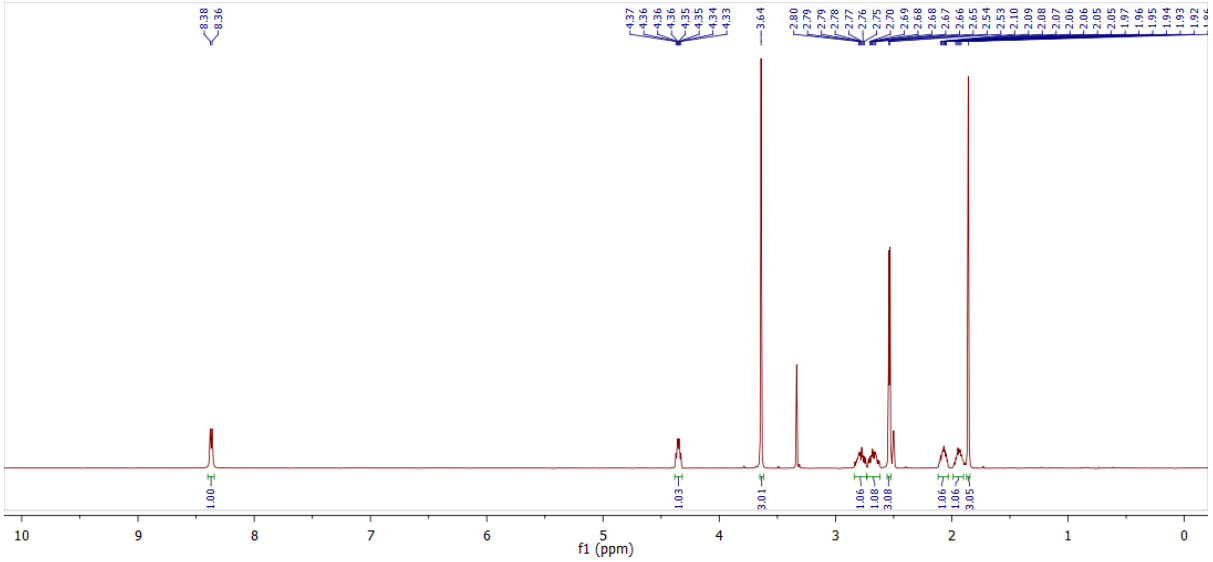


N-Acetyl-L-methionine methyl ester (3.91 g, 19.0 mmol) was added to a solution of sodium periodate (4.28 g, 20.0 mmol) in water (30 mL) at 0 °C. The resulting mixture was stirred at 0 °C for a few hours until starting material was fully consumed as monitored using TLC (EtOAc, $KMnO_4$ stain). Water (50 mL) was added, and the aqueous layer was extracted with chloroform (3 x 50 mL). The combined organic layer was dried over anhydrous magnesium sulfate and filtered. The solvent was removed under reduced pressure to give a yellow oil. The crude product was purified by column chromatography (SiO_2, 24:1 $CHCl_3$/MeOH, $KMnO_4$ stain) to give *N*-acetyl-L-methionine sulfoxide methyl ester as a white solid (0.26 g, 6%).

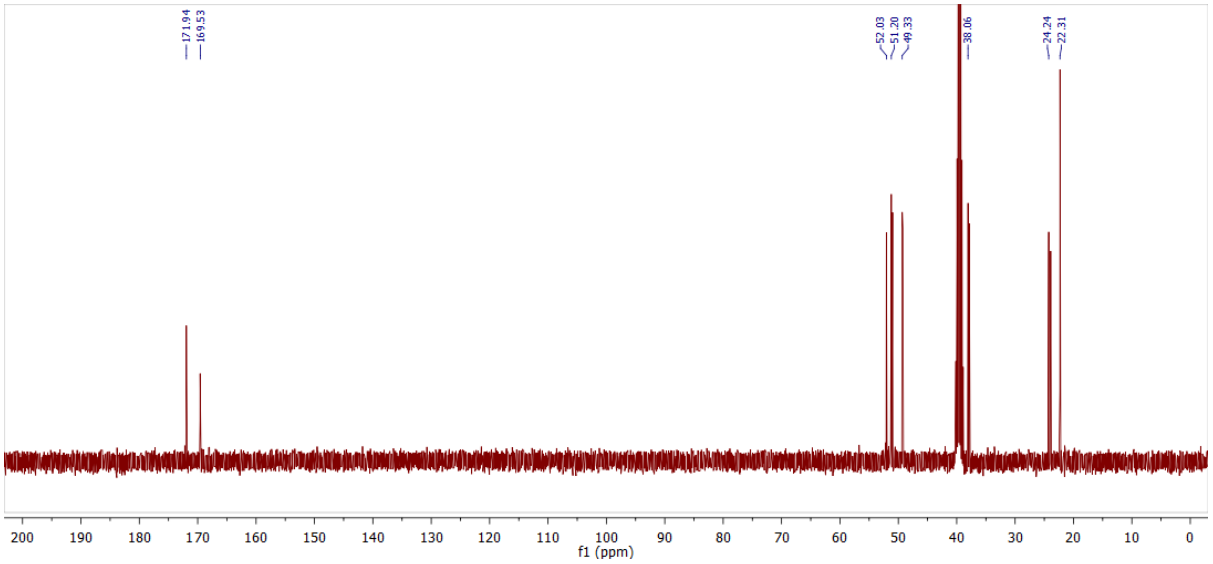
(*) at the sulfur atom denotes chirality. Ac-Met(O)-OMe exists as a mixture of diastereomers. This is reflected in its ^{1}H and ^{13}C NMR spectra. The ^{1}H spectrum shows two distinct peaks at 2.54 ppm that can be assigned to –S(O)C***H***$_3$. However, the other peaks did not show clear chemical shift differences between the two diastereomers. Therefore, chemical shifts reported for ^{1}H NMR are those for the two diastereomers combined. The ^{13}C spectrum shows two distinct peaks for almost each carbon signal. Only chemical shifts for one diastereomer are assigned.

^{1}H NMR (500 MHz, DMSO-d_6): δ 8.37 (d, *J* = 7.6 Hz, 1H), 4.35 (ddd, *J* = 9.6, 7.0, 4.8 Hz, 1H), 3.64 (s, 3H), 2.77 (ddd, *J* = 16.3, 8.4, 4.2 Hz, 1H), 2.66 (ddd, *J* = 22.7, 13.6, 5.2 Hz, 1H), 2.54 (d, *J* = 5.0 Hz, 3H), 2.11–2.03 (m, 1H), 1.98–1.89 (m, 1H), 1.85 ppm (s, 3H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6): δ 171.9, 169.5, 52.0, 51.2, 49.3, 38.1, 24.2, 22.3 ppm. HRMS (ESI) *m*/*z* calcd. for $[C_8H_{16}NO_4S]^+$: 222.0795 $[M + H]^+$, found 222.0795; HRMS (ESI) *m*/*z* calcd. for $[C_8H_{15}NO_4SNa]^+$: 244.0614 $[M + Na]^+$, found 244.0615.

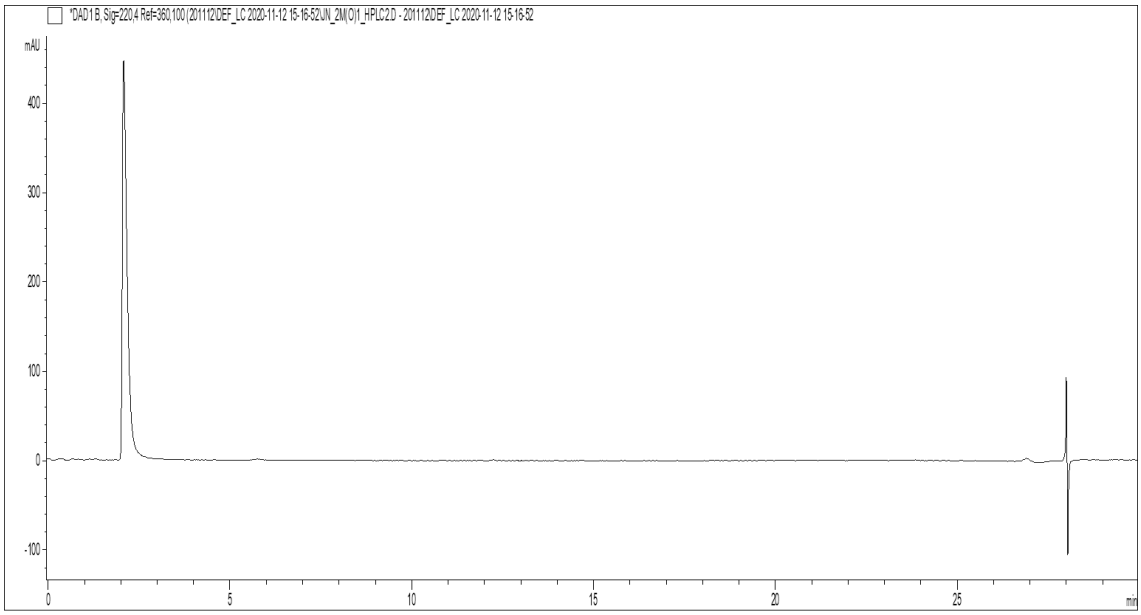
^{1}H NMR spectrum of Ac-MetO-OMe



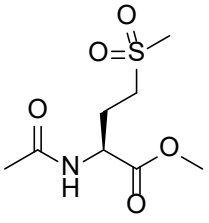
^{13}C NMR spectrum of Ac-MetO-OMe



HPLC chromatogram of Ac-MetO-OMe



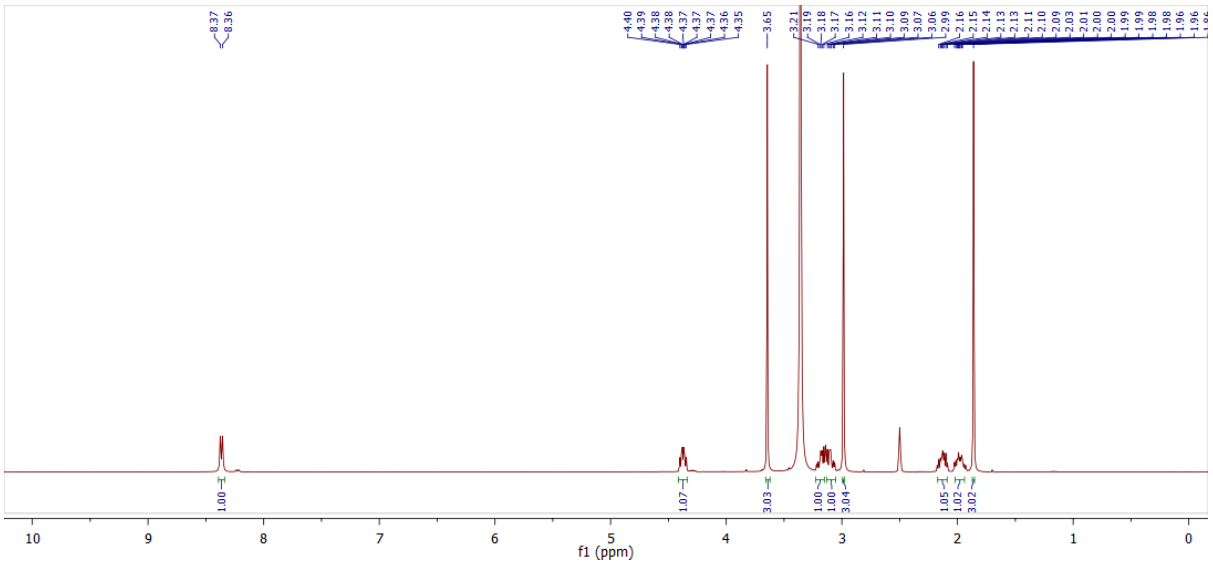
N-Acetyl-L-methionine sulfone methyl ester (Ac-MetO$_2$-OMe)[9]



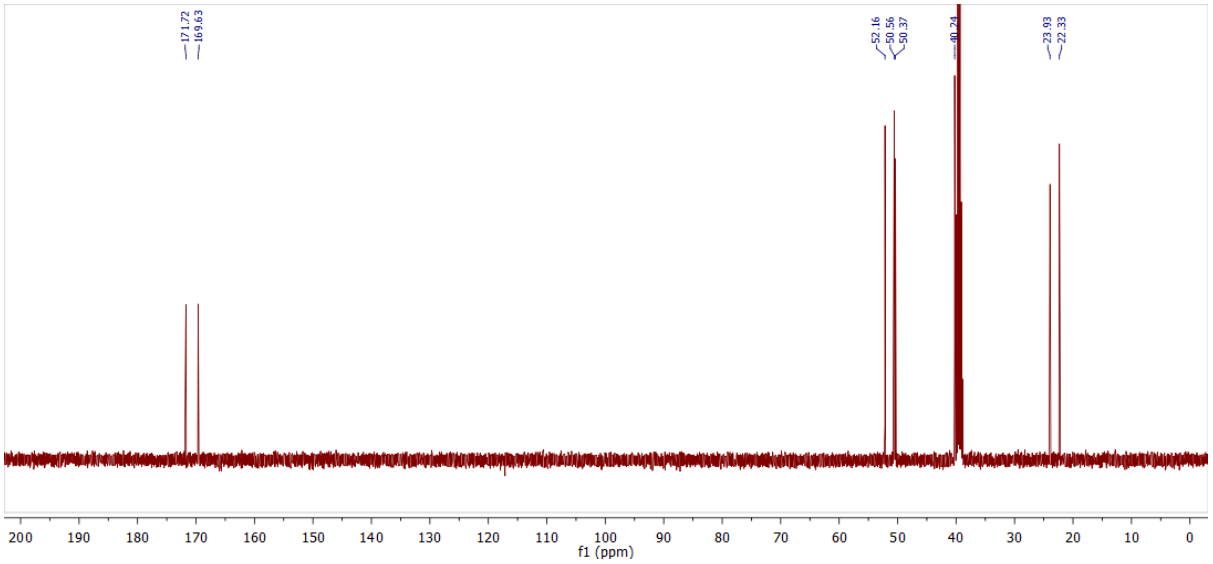
N-Acetyl-L-methionine methyl ester (0.78 g, 3.80 mmol) was dissolved in methanol (20 mL). Hydrogen peroxide 30% (3.50 mL, 34.7 mmol) was added into the solution. The resulting mixture was stirred at room temperature overnight. The solvent was removed under vacuum to give a colourless oil. Upon cooling, the oil crystallised to give *N*-acetyl-L-methionine sulfone methyl ester as white crystals (0.33 g, 36%).

^{1}H NMR (400 MHz, DMSO-d_6): δ 8.37 (d, J = 7.7 Hz, 1H), 4.37 (ddd, J = 9.4, 7.6, 5.0 Hz, 1H), 3.65 (s, 3H), 3.22–3.15 (m, 1H), 3.13–3.06 (m, 1H), 2.99 (s, 3H), 2.18–2.08 (m, 1H), 2.03–1.93 (m, 1H), 1.86 ppm (s, 3H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6): δ 171.7, 169.6, 52.2, 50.6, 50.4, 40.2, 23.9, 22.3 ppm. HRMS (ESI) m/z calcd. for $[C_8H_{16}NO_5S]^+$: 238.0744 $[M + H]^+$, found 238.0745; HRMS (ESI) m/z calcd. for $[C_8H_{15}NO_5SNa]^+$: 260.0564 $[M + Na]^+$, found 260.0564.

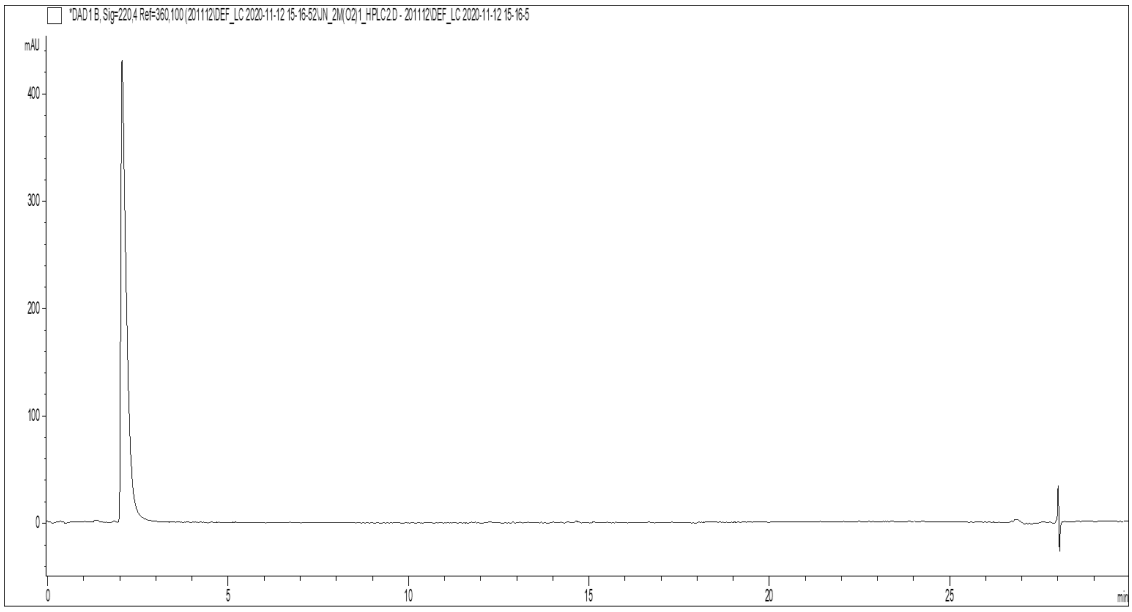
^{1}H NMR spectrum of Ac-MetO_2-OMe



^{13}C NMR spectrum of Ac-MetO_2-OMe

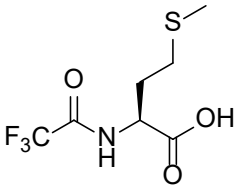


HPLC chromatogram of Ac-MetO_2-OMe



N-Trifluoroacetyl-L-methionine methyl ester (Tfa-Met-OMe)

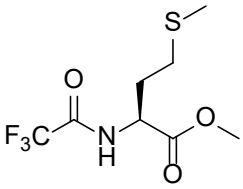
(a) *N*-Trifluoroacetyl-L-methionine (Tfa-Met)[10]



L-Methionine (1.52 g, 10.2 mmol) was suspended in methanol (5 mL). Triethylamine (2.0 mL, 14.3 mmol) was added at room temperature and the resulting mixture was stirred for 15 minutes. Ethyl trifluoroacetate (1.55 mL, 13.0 mmol) was added and the resulting mixture was stirred overnight. Ethyl acetate (200 mL) and 0.5M hydrochloric acid solution (200 mL) was added. The organic layer was separated and washed with brine (100 mL), dried over anhydrous magnesium sulfate and filtered. The solvent was removed under reduced pressure to give a colourless oil. Petroleum ether (5 mL) was added to induce crystallisation. The solid was filtered and washed with cold petroleum ether (2 x 5 mL) to give *N*-trifluoroacetyl-L-methionine as a white solid (2.31 g, 92%).

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.73 (d, J = 7.9 Hz, 1H), 4.41 (ddd, J = 9.7, 7.8, 4.6 Hz, 1H), 2.58–2.51 (m, 1H), 2.48–2.41 (m, 1H), 2.12–2.06 (m, 1H), 2.04 (s, 3H), 2.03 – 1.98 ppm (m, 1H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6): δ 171.8, 156.7 (q, J = 36.5 Hz), 115.9 (q, J = 288.0 Hz), 51.5, 29.8, 29.4, 14.5 ppm. HRMS (ESI) m/z calcd. for $[C_7H_9NO_3SF_3]^-$: 244.0260 [M – H]$^-$, found 244.0233; HRMS (ESI) m/z calcd. for $[C_7H_{11}NO_3SF_3]^+$: 246.0407 [M + H]$^+$, found 246.0403.

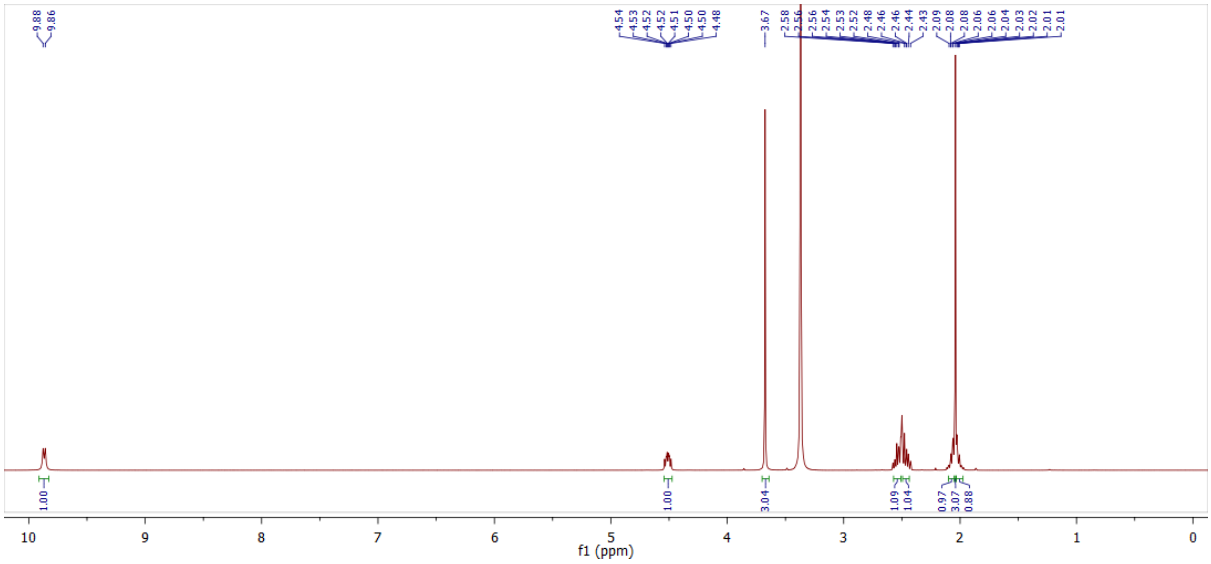
(b) *N*-Trifluoroacetyl-L-methionine methyl ester (Tfa-Met-OMe)[7]



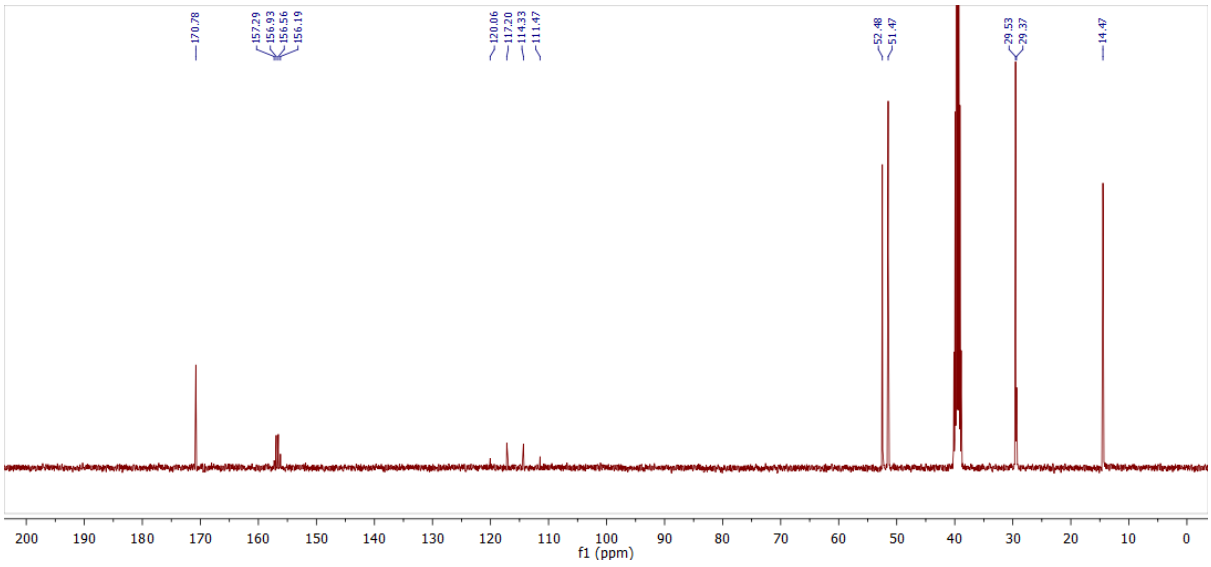
N-Trifluoroacetyl-L-methionine (1.13 g, 4.61 mmol) was suspended in methanol (8 mL) at 0 °C. Thionyl chloride (0.4 mL, 5.51 mmol) was added dropwise. The resulting mixture was stirred for 4 hours until starting material was fully consumed as monitored using TLC (EtOAc, $KMnO_4$ stain). The solvent was removed under reduced pressure and the residue was suspended in water (8 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 a yellow oil. The crude product was purified by column chromatography (SiO_2, 99:1 $CHCl_3$/MeOH, $KMnO_4$ stain) to give *N*-trifluoroacetyl-L-methionine methyl ester as a colourless oil (0.18 g, 15%).

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.87 (d, J = 7.6 Hz, 1H), 4.51 (ddd, J = 9.4, 7.4, 5.2 Hz, 1H), 3.67 (s, 3H), 2.58–2.52 (m, 1H), 2.48–2.42 (m, 1H), 2.10–2.06 (m, 1H), 2.04 (s, 3H), 2.03–2.00 ppm (m, 1H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6): 170.8, 156.7 (q, J = 36.5 Hz), 115.8 (q, J = 287.9 Hz), 52.5, 51.5, 29.5, 29.4, 14.5 ppm. HRMS (ESI) m/z calcd. for $[C_8H_{11}NO_3SF_3]^-$: 258.0417 $[M - H]^-$, found 258.0415; HRMS (ESI) m/z calcd. for $[C_8H_{13}NO_3SF_3]^+$: 260.0563 $[M + H]^+$, found 260.0562.

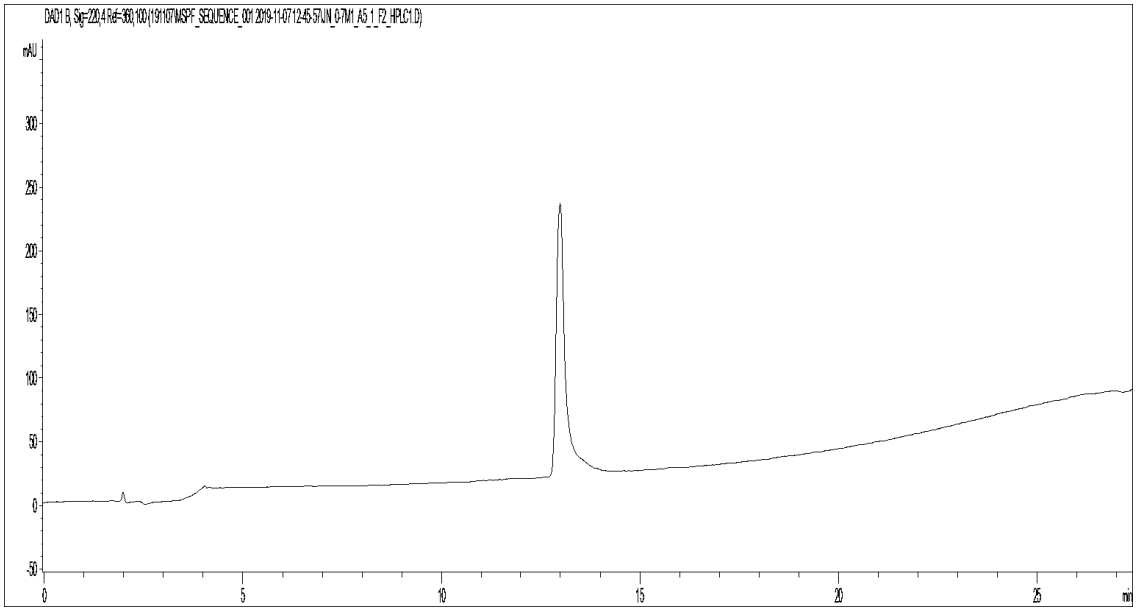
^{1}H NMR spectrum of Tfa-Met-OMe



^{13}C NMR spectrum of Tfa-Met-OMe

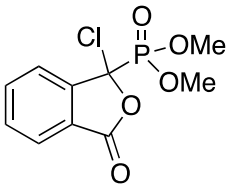


HPLC chromatogram of Tfa-Met-OMe



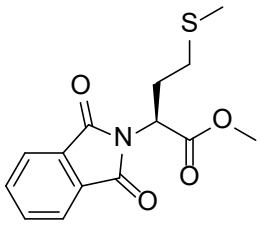
_N_-Phthaloyl-L-methionine methyl ester (Phth-Met-OMe)

(a) Synthesis of the phthaloylating agent Phth-P(O)(OMe)$_2$-Cl[11]



Trimethyl phosphite (8.0 mL, 67.7 mmol) was added dropwise to 90% phthaloyl chloride (10.0 mL, 62.5 mmol) over 30 minutes, keeping the temperature below 50 °C. The mixture was stirred for 3 hours at room temperature and excess trimethyl phosphite was removed under reduced pressure to give a sticky oil. Petroleum ether (10 mL) was repeatedly added and removed under reduced pressure to induce precipitation. The resulting solid was washed with cold petroleum ether (2 x 10 mL) to give the precursor as a white solid (16.1 g, 86%). This acylphosphonate derivative was used without further purification to introduce the phthaloyl group in the amino acid.

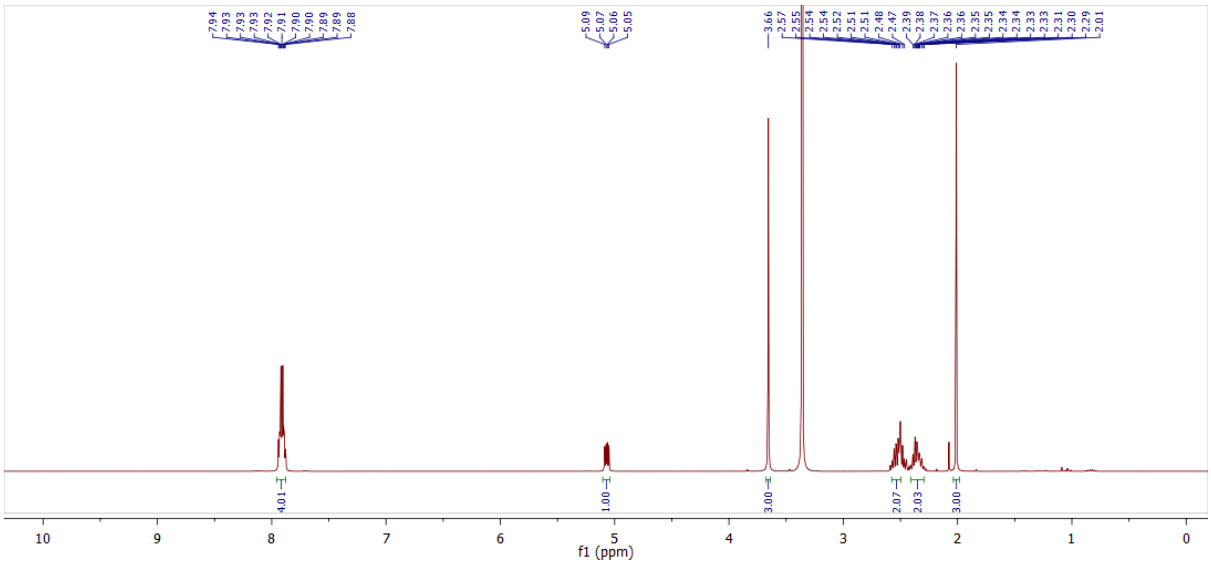
(b) _N_-Phthaloyl-L-methionine methyl ester (Phth-Met-OMe)[7,12]



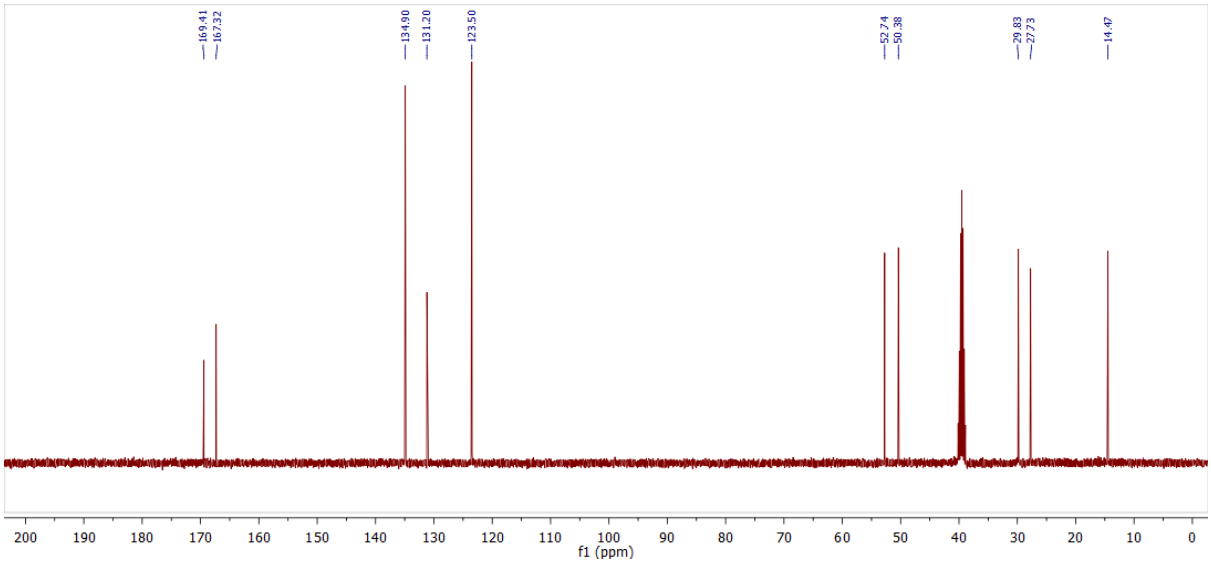
The acylphosphonate derivative (1.38 g, 4.97 mmol) and L-methionine (0.79 g, 5.29 mmol) were dissolved in a 1:1 acetonitrile/water mixture (25 mL). Diisopropylethylamine (3.5 mL, 20.1 mmol) was added dropwise and the mixture was stirred for 30 minutes at room temperature. Acetonitrile was removed under reduced pressure. The remaining solution was acidified with 1M hydrochloric acid solution dropwise. The resulting precipitate was collected by filtration and washed with 1M cold hydrochloric acid solution (2 x 2 mL) to give _N_-phthaloyl-L-methionine as a white solid. The white solid was suspended in methanol (15 mL) at 0 °C. Thionyl chloride (0.4 mL, 5.51 mmol) was added dropwise. The resulting mixture was stirred for 5 hours until starting material was fully consumed as monitored using TLC (EtOAc, UV light). The solvent was removed under reduced pressure and the residue was suspended in water (8 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 a yellow oil. The crude product was purified by column chromatography (SiO_2, 4:1 Pet. Ether/EtOAc, UV light) to give _N_-phthaloyl-L-methionine methyl ester as white crystals (0.77 g, 50%).

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.94–7.88 (m, 4H), 5.07 (dd, J = 9.5, 5.1 Hz, 1H), 3.66 (s, 3H), 2.58–2.46 (m, 2H), 2.40–2.29 (m, 2H), 2.01 ppm (s, 3H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6): 169.4, 167.3, 134.9, 131.2, 123.5, 52.7, 50.4, 29.8, 27.7, 14.5 ppm. HRMS (ESI) m/z calcd. for $[C_{14}H_{16}NO_4S]^+$: 294.0795 $[M + H]^+$, found 294.0794; HRMS (ESI) m/z calcd. for $[C_{14}H_{15}NO_4SNa]^+$: 316.0614 $[M + Na]^+$, found 316.0610.

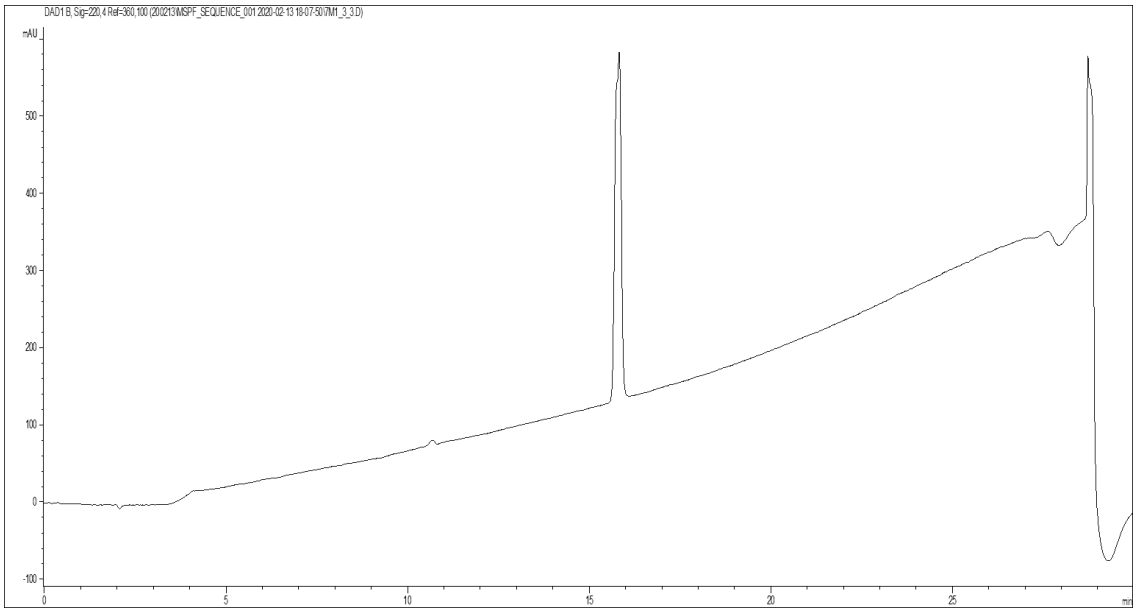
^{1}H NMR spectrum of Phth-Met-OMe



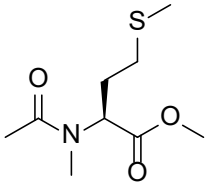
^{13}C NMR spectrum of Phth-Met-OMe



HPLC chromatogram of Phth-Met-OMe



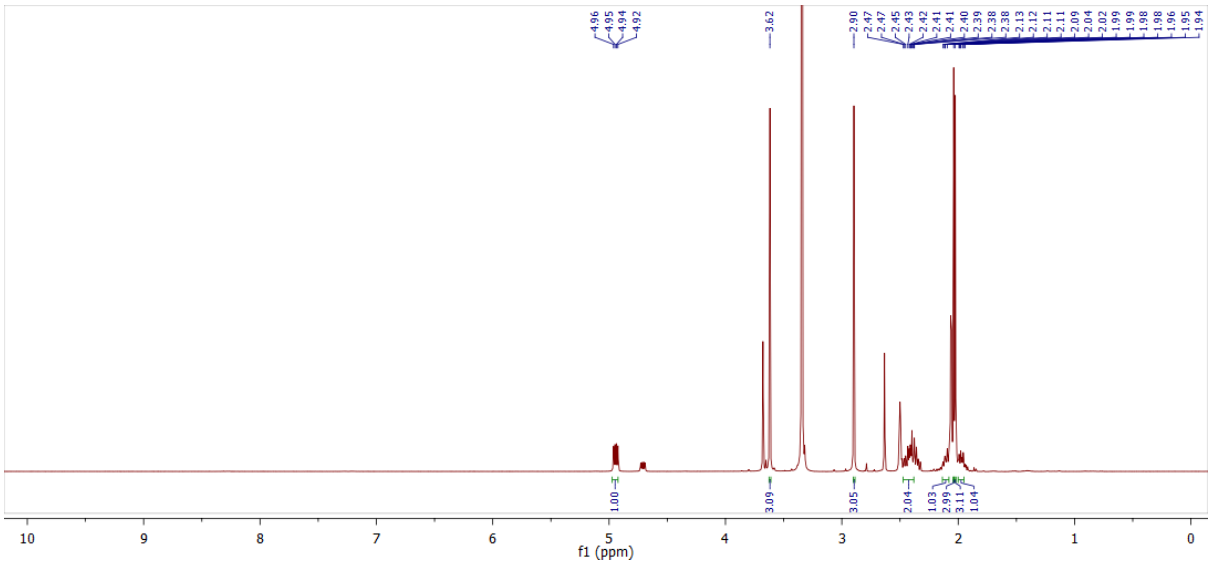
N-Acetyl-*N*-methyl-L-methionine methyl ester (Ac-(Me)Met-OMe)[13]



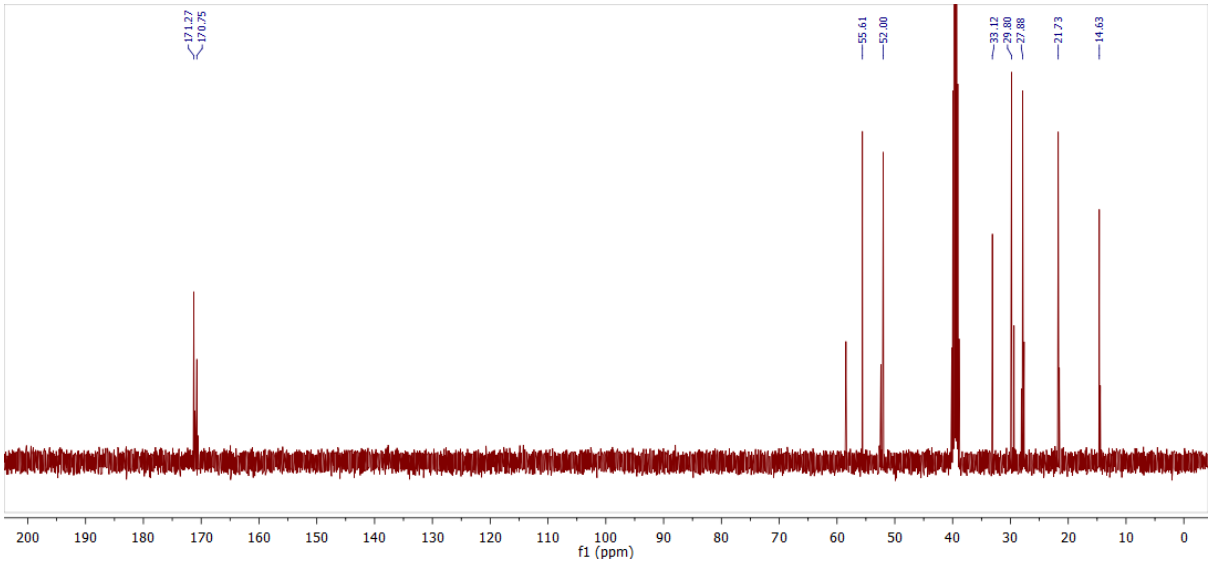
N-Acetyl-L-methionine (3.81 g, 19.9 mmol) was added to a suspension of sodium hydride (60% dispersion in mineral oil, 2.13 g, 53.3 mmol) in dry dimethylformamide (70 mL) under inert atmosphere at 0 °C. The resulting mixture was stirred for 1 hour at room temperature and cooled again to 0 °C. Methyl iodide (3.5 mL, 56.2 mmol) was then added dropwise. The resulting mixture was stirred overnight at room temperature. Nitrogen was blown over the mixture for 3 days to remove the solvent and water (60 mL) was added. The aqueous layer was extracted with dichloromethane (3 x 80 mL). The combined organic layers were washed with water (100 mL) and 5% aqueous lithium chloride solution (100 mL). The organic layer was dried over anhydrous magnesium sulfate and filtered. The solvent was removed under reduced pressure to give a dark orange oil. The crude product was purified by column chromatography (SiO_2, 497:3 $CHCl_3$/MeOH) to yield *N*-acetyl-*N*-methyl-L-methionine methyl ester as a colourless oil (0.11 g, 3%).

^{1}H NMR (400 MHz, DMSO-d_6) major isomer: δ 4.94 (dd, J = 10.1, 5.1 Hz, 1H), 3.62 (s, 3H), 2.90 (s, 3H), 2.47–2.38 (m, 2H), 2.13–2.09 (m, 1H), 2.04 (s, 3H), 2.02 (s, 3H), 1.99–1.95 ppm (m, 1H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) major isomer: δ 171.3, 170.8, 55.6, 52.0, 33.1, 29.8, 27.9, 21.7, 14.6 ppm. HRMS (ESI) m/z calcd. for $[C_9H_{18}NO_3S]^+$: 220.1002 $[M + H]^+$, found 220.1001, HRMS (ESI) m/z calcd. for $[C_9H_{17}NO_3SNa]^+$: 242.0822 $[M + Na]^+$, found 242.0819.

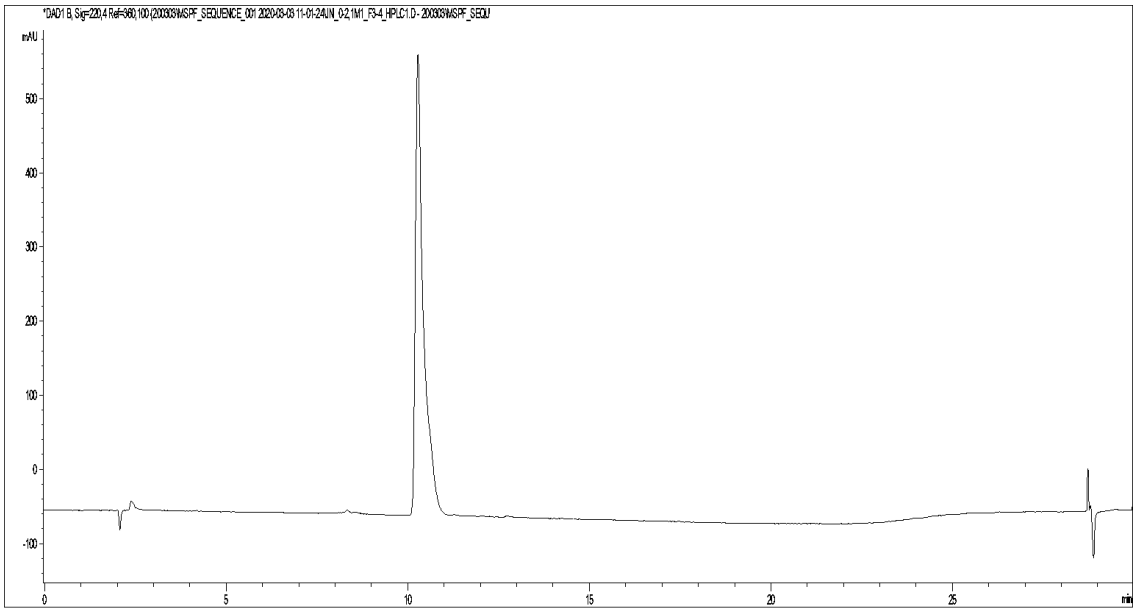
^{1}H NMR spectrum of Ac-(Me)Met-OMe



^{13}C NMR spectrum of Ac-(Me)Met-OMe

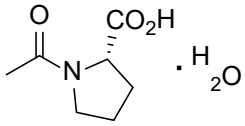


HPLC chromatogram of Ac-(Me)Met-OMe



N-Acetyl-L-prolyl-L-methionine methyl ester (Ac-Pro-Met-OMe)

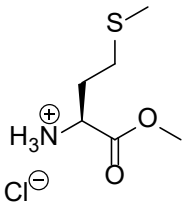
(a) *N*-Acetyl-L-proline monohydrate (Ac-Pro)[14]



L-Proline (8.07 g, 70.1 mmol) was dissolved in water (8 mL). The solution was 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%).

^{1}H NMR (400 MHz, DMSO-d_6) 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). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) major isomer: δ 173.5, 168.2, 58.1, 47.2, 29.1, 24.4, 22.1 ppm. HRMS (ESI) m/z calcd. for $[C_7H_{12}NO_3]^+$: 158.0812 $[M + H]^+$, found 158.0813, HRMS (ESI) m/z calcd. for $[C_{14}H_{23}N_2O_6]^+$: 315.1551 $[2M + H]^+$, found 315.1550.

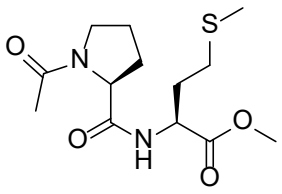
(b) L-Methionine methyl ester hydrochloride salt (Met-OMe·HCl)[6]



L-Methionine (4.48 g, 30.0 mmol) was suspended in methanol (50 mL) at 0 °C. Thionyl chloride (2.4 mL, 33.0 mmol) was added dropwise. The resulting mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure. Acetone (10 mL) was added and the solid was collected by filtration to give L-methionine methyl ester hydrochloride salt as an amorphous white solid (4.67 g, 78%).

^{1}H NMR (500 MHz, DMSO-d_6): δ 8.83 (s, 3H), 4.07 (t, J = 6.2 Hz, 1H), 3.73 (s, 3H), 2.65 (ddd, J = 13.6, 8.3, 6.6 Hz, 1H), 2.55 (ddd, J = 13.6, 8.5, 6.6 Hz, 1H), 2.12–2.07 (m, 2H), 2.04 ppm (s, 3H). ^{13}C {^{1}H} NMR (126 MHz, DMSO-d_6): δ 169.6, 52.9, 50.8, 29.3, 28.4, 14.3 ppm. HRMS (ESI) m/z calcd. for $[C_6H_{14}NO_2S]^+$: 164.0740 $[M - Cl]^+$, found 164.0740.

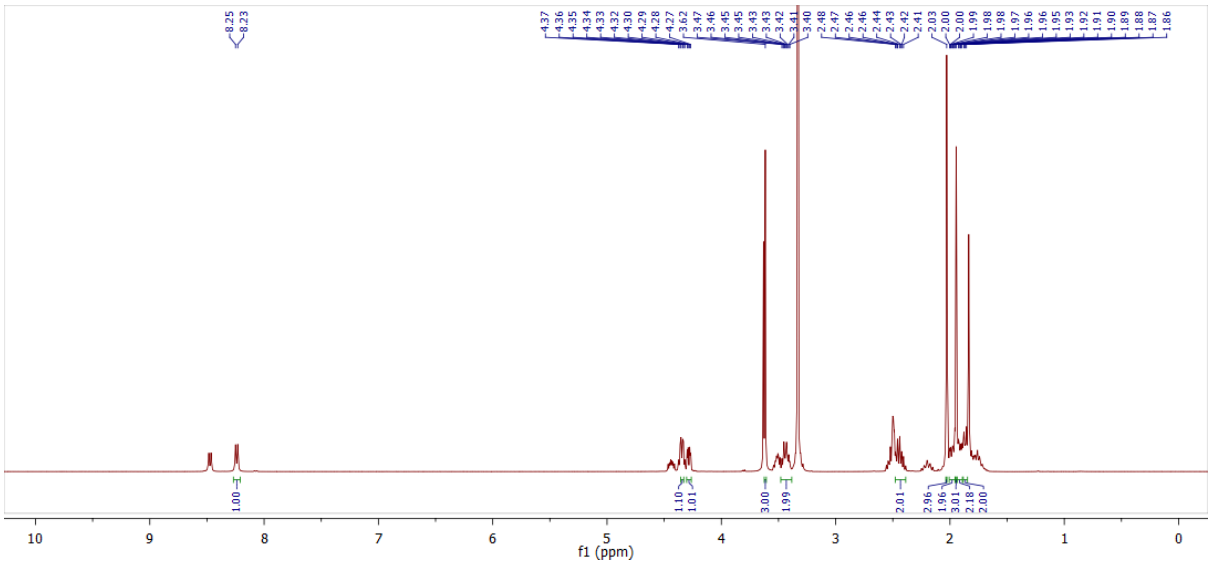
(c) *N*-Acetyl-L-prolyl-L-methionine methyl ester (Ac-Pro-Met-OMe)[15]



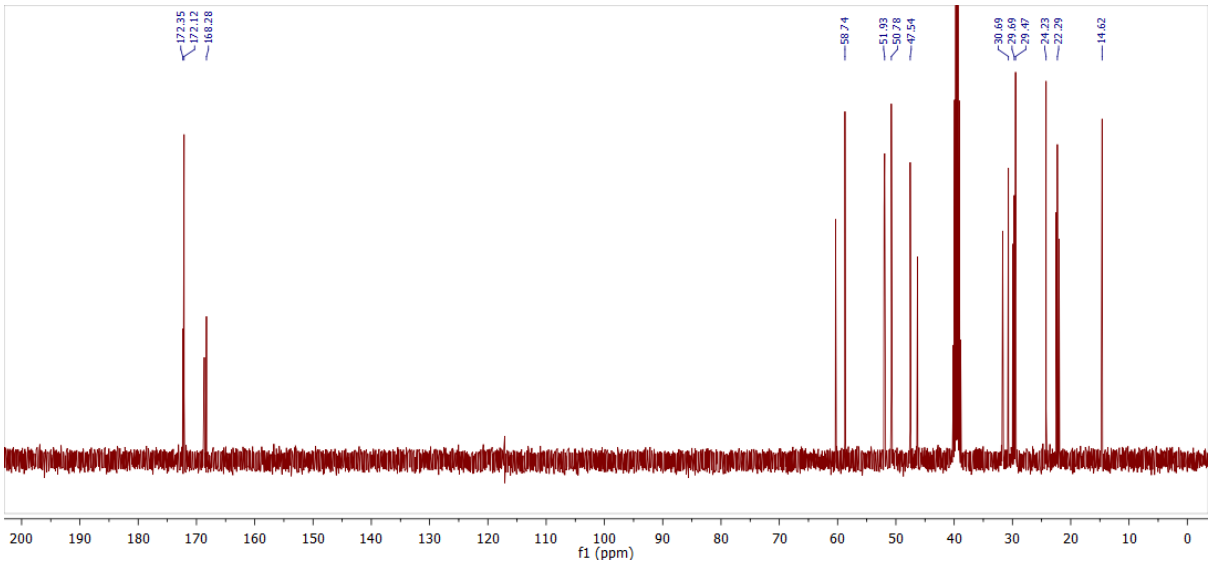
N-Acetyl-L-proline monohydrate (1.01 g, 5.78 mmol) was suspended in dichloromethane (15 mL) at 0 °C, followed by addition of HOBt·H_2O (1.35 g, 8.82 mmol) and EDC·HCl (1.65 g, 8.60 mmol). After 10 minutes, L-methionine methyl ester hydrochloride salt (1.25 g, 6.28 mmol) was added, followed by dropwise addition of diisopropylethylamine (3.0 mL, 17.2 mmol). After the resulting mixture was stirred overnight at room temperature, saturated aqueous sodium bicarbonate solution (50 mL) was added. The aqueous layer was then extracted with dichloromethane (3 x 50 mL). The combined organic layers were dried over anhydrous sodium sulfate and filtered. The solvent was removed under reduced pressure to give a yellow oil. The crude product was purified by column chromatography (SiO_2, 97:3 $CHCl_3$/MeOH, $KMnO_4$ stain) to give *N*-acetyl-L-prolyl-L-methionine methyl ester as a white solid (1.16 g, 67%).

^{1}H NMR (400 MHz, DMSO-d_6) major isomer: δ 8.24 (d, J = 7.7 Hz, 1H), 4.35 (td, J = 8.0, 4.9 Hz, 1H), 4.28 (dd, J = 8.5, 3.1 Hz, 1H), 3.62 (s, 3H), 3.47–3.39 (m, 2H), 2.48–2.39 (m, 2H), 2.03 (s, 3H), 2.01–1.96 (m, 2H), 1.95 (s, 3H), 1.93–1.89 (m, 2H), 1.88–1.85 ppm (m, 2H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) major isomer: δ 172.4, 172.1, 168.3, 58.7, 51.9, 50.8, 47.5, 30.7, 29.7, 29.5, 24.2, 22.3, 14.6 ppm. HRMS (ESI) m/z calcd. for $[C_{13}H_{23}N_2O_4S]^+$: 303.1374 $[M + H]^+$, found 303.1372, HRMS (ESI) m/z calcd. for $[C_{13}H_{22}N_2O_4SNa]^+$: 325.1193, found 325.1190.

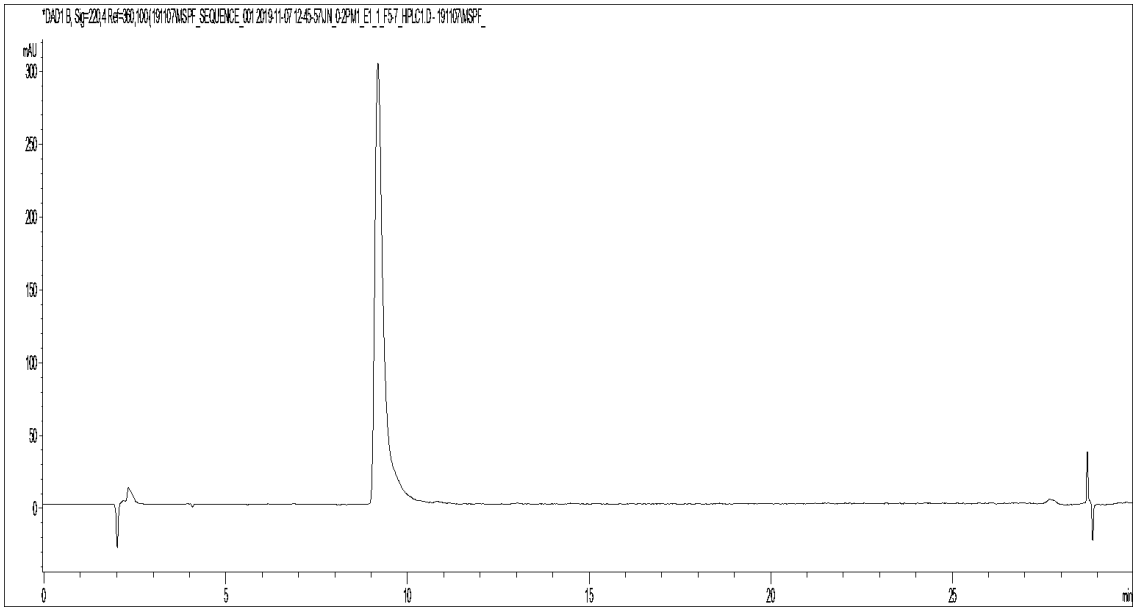
^{1}H NMR spectrum of Ac-Pro-Met-OMe



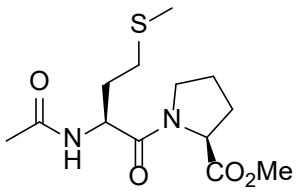
^{13}C NMR spectrum of Ac-Pro-Met-OMe



HPLC chromatogram of Ac-Pro-Met-OMe



_N_-Acetyl-L-methionyl-L-proline methyl ester (Ac-Met-Pro-OMe)[15]

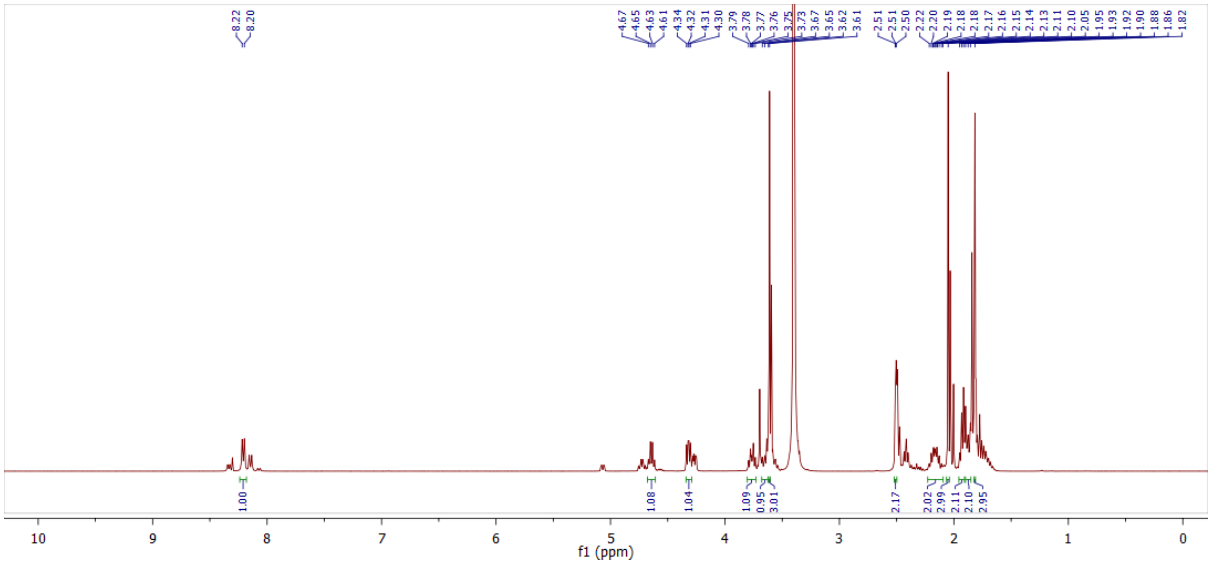


*A small amount of *N*-acetyl-D-methionyl-L-proline methyl ester was observed from ^{1}H and ^{13}C NMR, which was not expected to affect the kinetics with $NO_3^{\bullet}$.

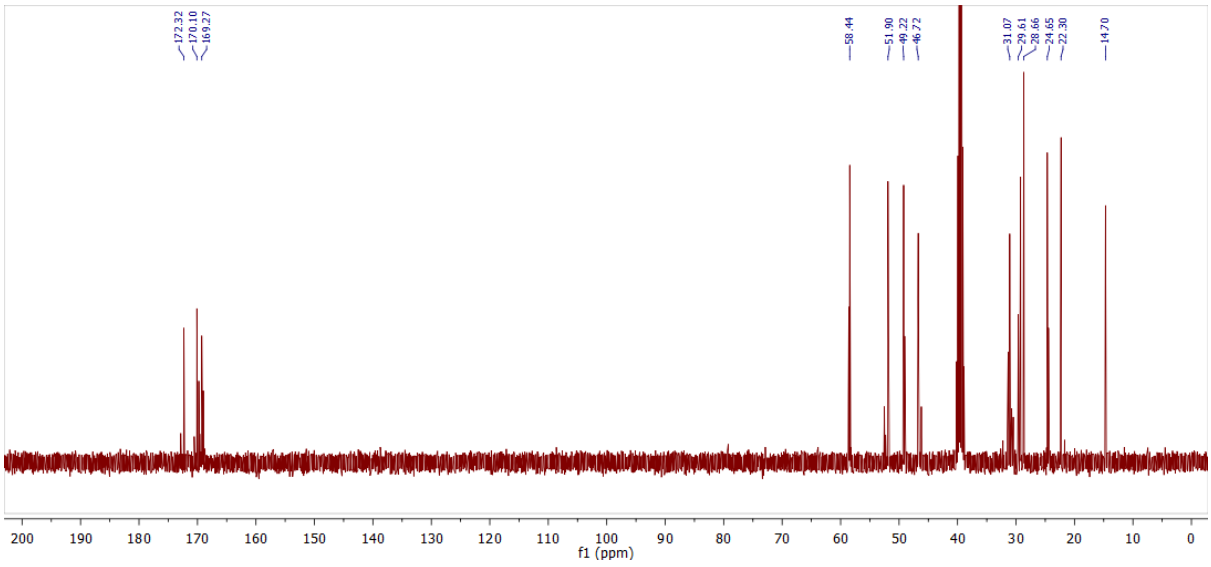
N-Acetyl-L-methionine (1.10 g, 5.75 mmol) was suspended in dichloromethane (15 mL) at 0 °C, followed by addition of HOBt·H_2O (1.32 g, 8.62 mmol) and EDC·HCl (1.66 g, 8.65 mmol). After 10 minutes, L-proline methyl ester hydrochloride salt (1.11 g, 6.71 mmol) was added, followed by dropwise addition of diisopropylethylamine (3.0 mL, 17.2 mmol). After the resulting mixture was stirred overnight at room temperature, saturated aqueous sodium bicarbonate solution (50 mL) was added. The aqueous layer was then extracted with dichloromethane (3 x 50 mL). The combined organic layers were dried over anhydrous sodium sulfate and filtered. The solvent was removed under reduced pressure to give a yellow oil. The crude product was purified by column chromatography (SiO_2, 49:1 $CHCl_3$/MeOH, $KMnO_4$ stain) to give *N*-acetyl-L-methionyl-L-proline methyl ester as a colourless oil (0.53 g, 30%).

^{1}H NMR (400 MHz, DMSO-d_6) major isomer: δ 8.21 (d, *J* = 7.8 Hz, 1H), 4.64 (q, *J* = 7.2 Hz, 1H), 4.32 (dd, *J* = 8.6, 5.0 Hz, 1H), 3.76 (dt, *J* = 9.9, 6.8 Hz, 1H), 3.68–3.62 (m, 1H), 3.61 (s, 3H), 2.52–2.50 (m, 2H), 2.22–2.09 (m, 2H), 2.05 (s, 3H), 1.95–1.91 (m, 2H), 1.90–1.85 (m, 2H), 1.82 ppm (s, 3H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6) major isomer: δ 172.3, 170.1, 169.3, 58.4, 51.9, 49.2, 46.7, 31.1, 29.6, 28.7, 24.7, 22.3, 14.7 ppm. HRMS (ESI) *m/z* calcd. for $[C_{13}H_{23}N_2O_4S]^+$: 303.1374 $[M + H]^+$, found 303.1374, HRMS (ESI) *m/z* calcd. for $[C_{13}H_{22}N_2O_4SNa]^+$: 325.1193 $[M + Na]^+$, found 325.1191.

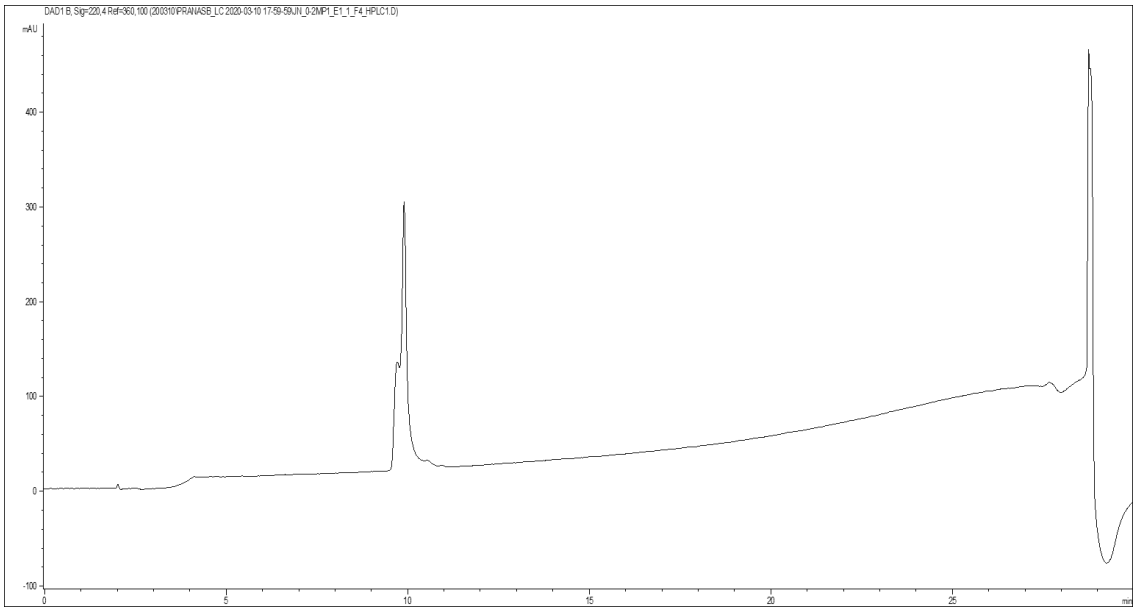
^{1}H NMR spectrum of Ac-Met-Pro-OMe



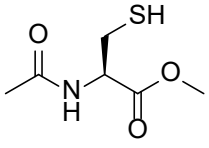
^{13}C NMR spectrum of Ac-Met-Pro-OMe



HPLC chromatogram of Ac-Met-Pro-OMe



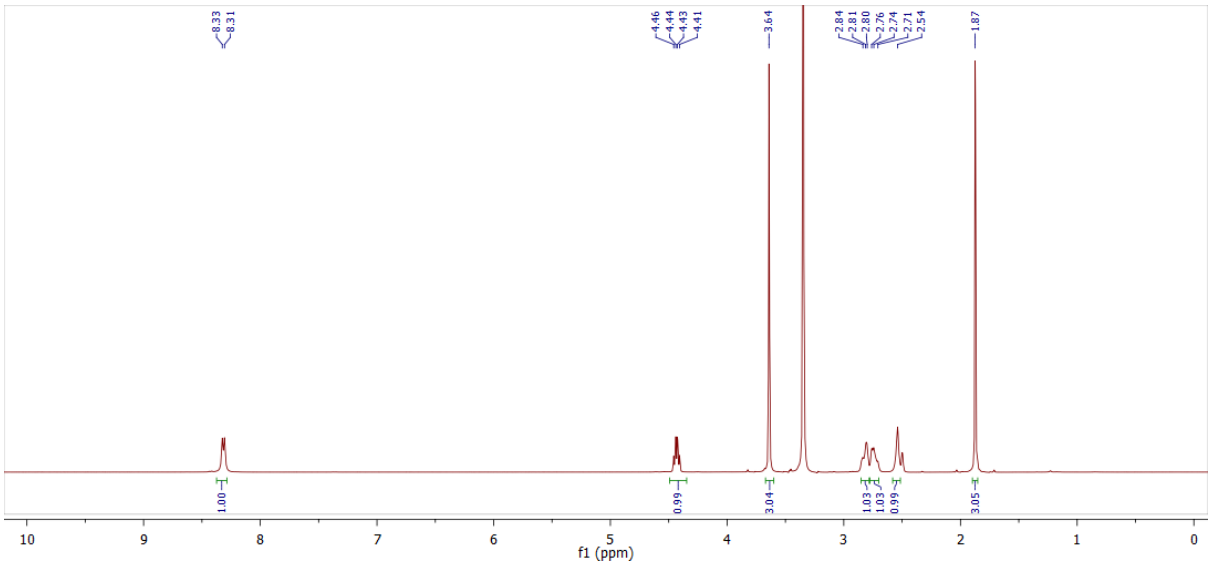
N-Acetyl-L-cysteine methyl ester (Ac-Cys-OMe)[16]



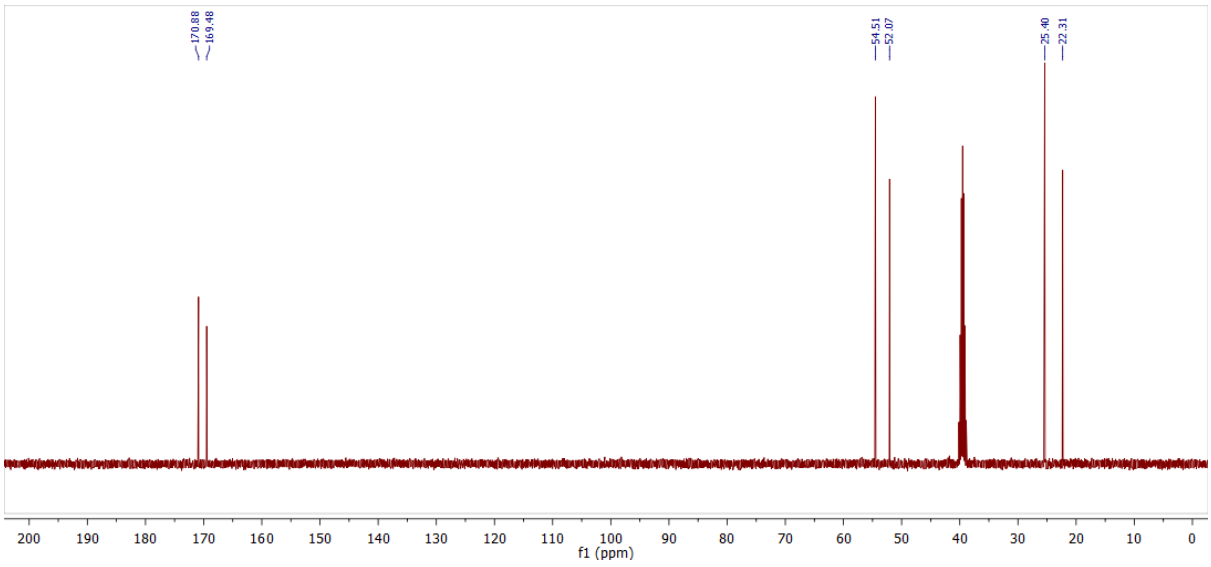
N-Acetyl-L-cysteine (1.04 g, 6.37 mmol) was suspended in methanol (13 mL) at 0 °C. Acetyl chloride (6.6 mL, 92.8 mmol) was added dropwise under inert atmosphere. The resulting mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure to give a yellow oil. The crude product was purified by column chromatography (SiO_2, 19:1 EtOAc/MeOH, $KMnO_4$ stain) to give *N*-acetyl-L-cysteine methyl ester as a white solid (0.46 g, 41%).

^{1}H NMR (400 MHz, DMSO-d_6): δ 8.32 (d, J = 7.9 Hz, 1H), 4.43 (q, J = 7.2 Hz, 1H), 3.64 (s, 3H), 2.84–2.79 (m, 1H), 2.74 (t, J = 10.8 Hz, 1H), 2.54 (s, 1H), 1.87 ppm (s, 3H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6): δ 170.9, 169.5, 54.5, 52.1, 25.4, 22.3 ppm. HRMS (ESI) m/z calcd. for $[C_6H_{12}NO_3S]^+$: 178.0533 $[M + H]^+$, found 178.0533, HRMS (ESI) m/z calcd. for $[C_6H_{11}NO_3SNa]^+$: 200.0352 $[M + Na]^+$, found 200.0351.

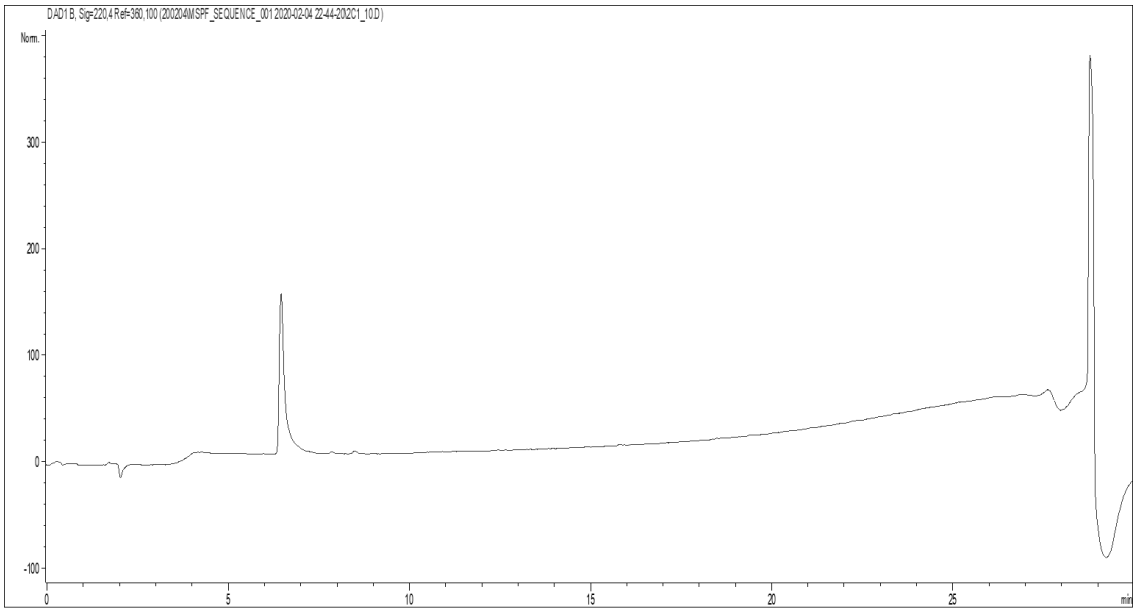
^{1}H NMR spectrum of Ac-Cys-OMe



^{13}C NMR spectrum of Ac-Cys-OMe

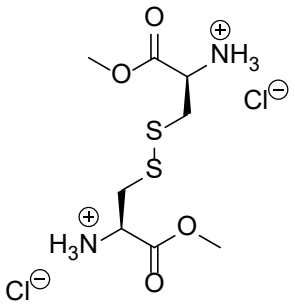


HPLC chromatogram of Ac-Cys-OMe



_N_-Acetyl-L-cystine methyl ester (Ac-Cys(S-S)Cys-OMe)

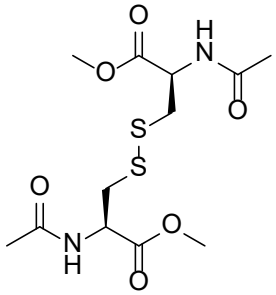
(a) L-Cystine methyl ester hydrochloride salt (Cys(S-S)Cys-OMe·2HCl)[7]



L-Cystine (2.54g, 10.6 mmol) was suspended in methanol (30 mL) and cooled at 0 °C. Thionyl chloride (2.4 mL, 33.0 mmol) was added dropwise. The resulting mixture was heated at 40 °C for a few hours until starting material was fully consumed as monitored using TLC (9:1 EtOH/AcOH, ninhydrin stain). The solvent was removed under reduced pressure. Diethyl ether (30 mL) was added. The solid was collected by filtration to give L-cystine methyl ester hydrochloride salt as a white solid (3.50 g, 97%).

^{1}H NMR (500 MHz, DMSO-d_6): δ 8.99 (s, 6H), 4.34 (t, J = 5.8 Hz, 2H), 3.75 (s, 6H), 3.38 (dd, J = 14.6, 5.4 Hz, 2H), 3.31 ppm (dd, J = 14.6, 6.3 Hz, 2H). ^{13}C {^{1}H} NMR (126 MHz, DMSO-d_6): δ 168.4, 53.0, 51.0, 36.7 ppm. HRMS (ESI) m/z calcd. for $[C_8H_{18}N_2O_4S_2]^{2+}$: 135.0349 [M − 2Cl]$^{2+}$, found 135.0349; HRMS (ESI) m/z calcd. for $[C_8H_{17}N_2O_4S_2]^+$: 269.0625 [M – H − 2Cl]$^+$, found 269.0623.

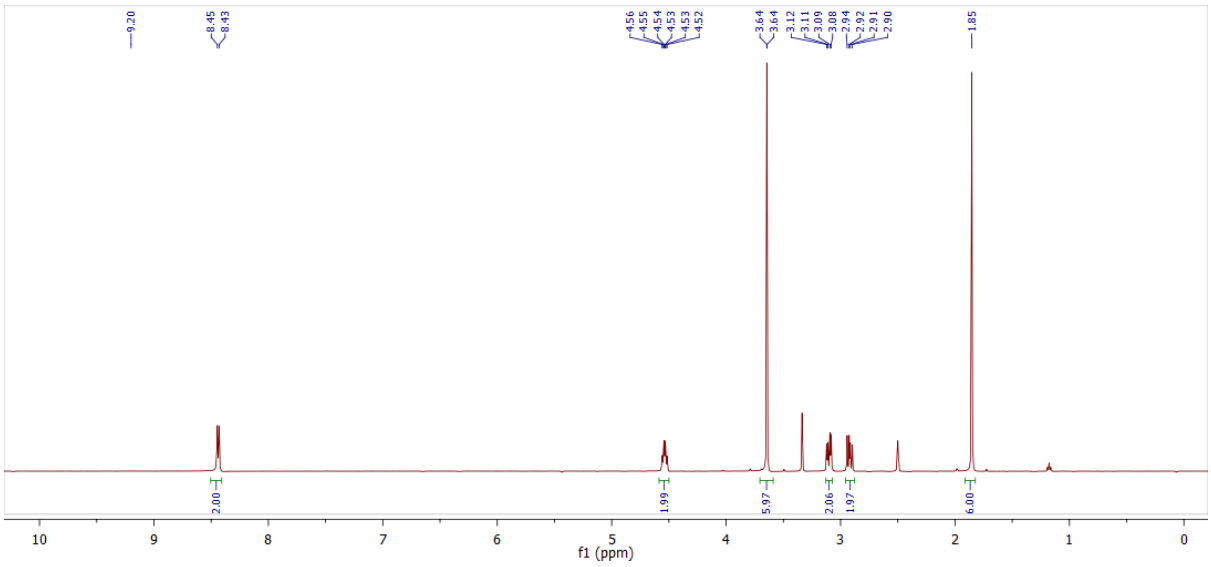
(b) _N_-Acetyl-L-cystine methyl ester (Ac-Cys(S-S)Cys-OMe)[17]



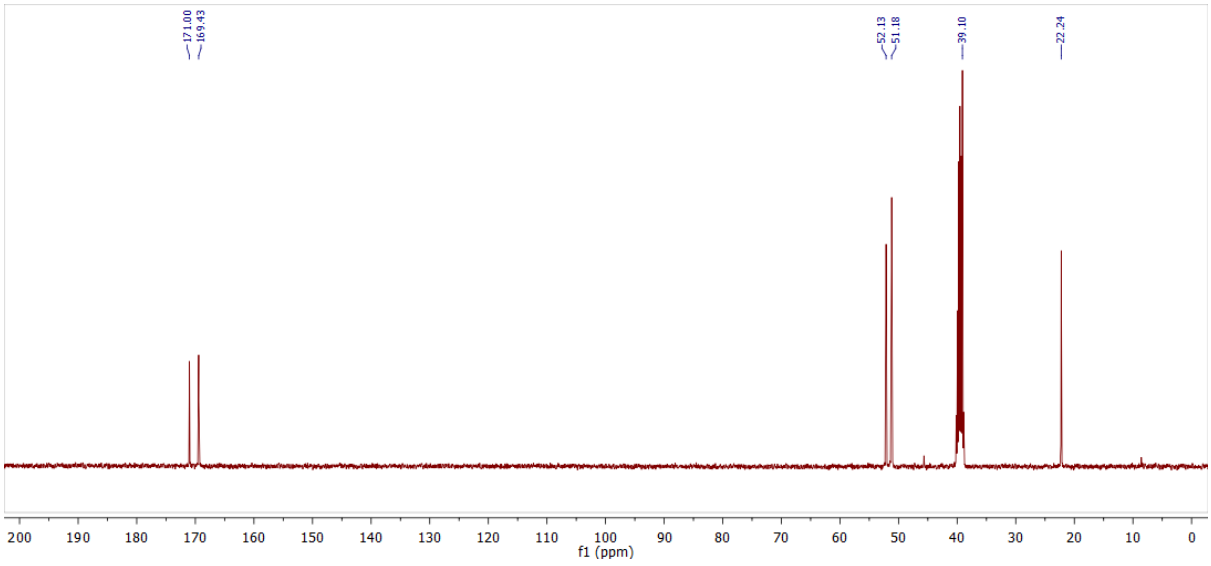
L-Cystine methyl ester hydrochloride salt (1.70 g, 4.99 mmol) and triethylamine (2.8 mL, 20.1 mmol) were dissolved in dichloromethane (35 mL) at 0 °C. Acetyl chloride (0.75 mL, 10.5 mmol) was then added dropwise. The mixture was stirred for 1 hour and the solvent was removed under reduced pressure. Ethyl acetate (30 mL) was added. The mixture was filtered cooled down. The solid was collected and washed with cold ethyl acetate (2 x 2 mL) to give _N_-acetyl-L-cystine methyl ester as white crystals (0.90 g, 51%).

^{1}H NMR (500 MHz, DMSO-d_6): δ 8.44 (d, J = 7.9 Hz, 2H), 4.54 (td, J = 8.3, 5.2 Hz, 2H), 3.64 (s, 6H), 3.10 (dd, J = 13.8, 5.1 Hz, 2H), 2.92 (dd, J = 13.8, 8.8 Hz, 2H), 1.85 ppm (s, 6H). ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6): δ 171.0, 169.4, 52.1, 51.2, 39.1, 22.2 ppm. HRMS (ESI) m/z calcd. for $[C_{12}H_{21}N_2O_6S_2]^+$: 353.0836 $[M + H]^+$, found 353.0834; HRMS (ESI) m/z calcd. for $[C_{12}H_{20}N_2O_6S_2Na]^+$: 375.0655 $[M + Na]^+$, found 375.0652.

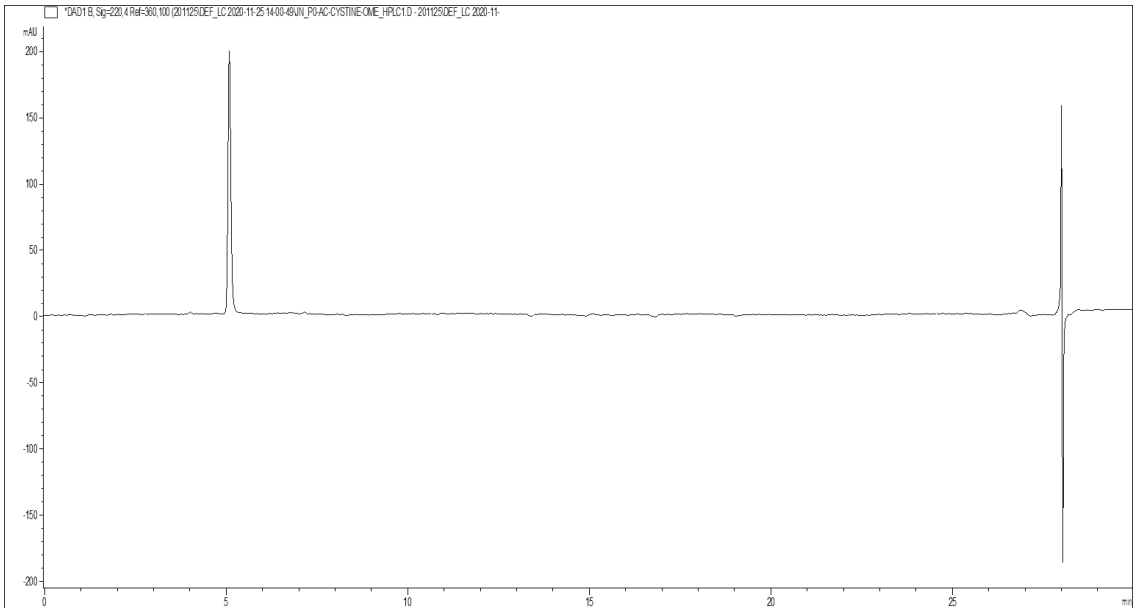
^{1}H NMR spectrum of Ac-Cys(S-S)Cys-OMe



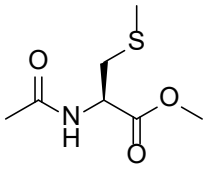
^{13}C NMR spectrum of Ac-Cys(S-S)Cys-OMe



HPLC chromatogram of Ac-Cys(S-S)Cys-OMe



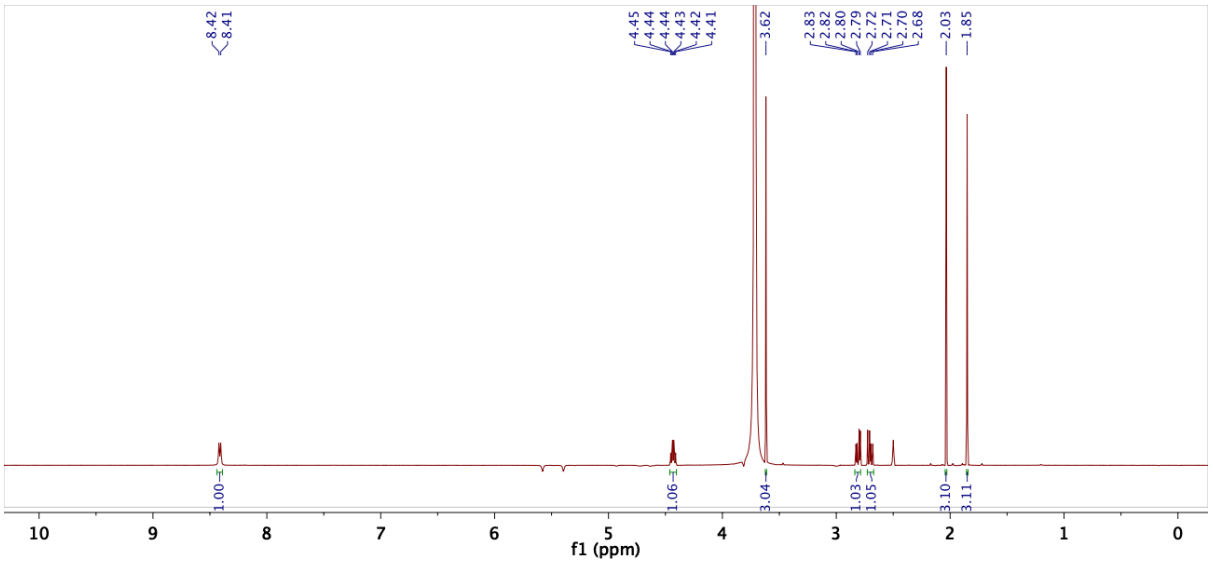
N-Acetyl-*S*-methyl-L-cysteine methyl ester (Ac-Cys(SMe)-OMe)[17]



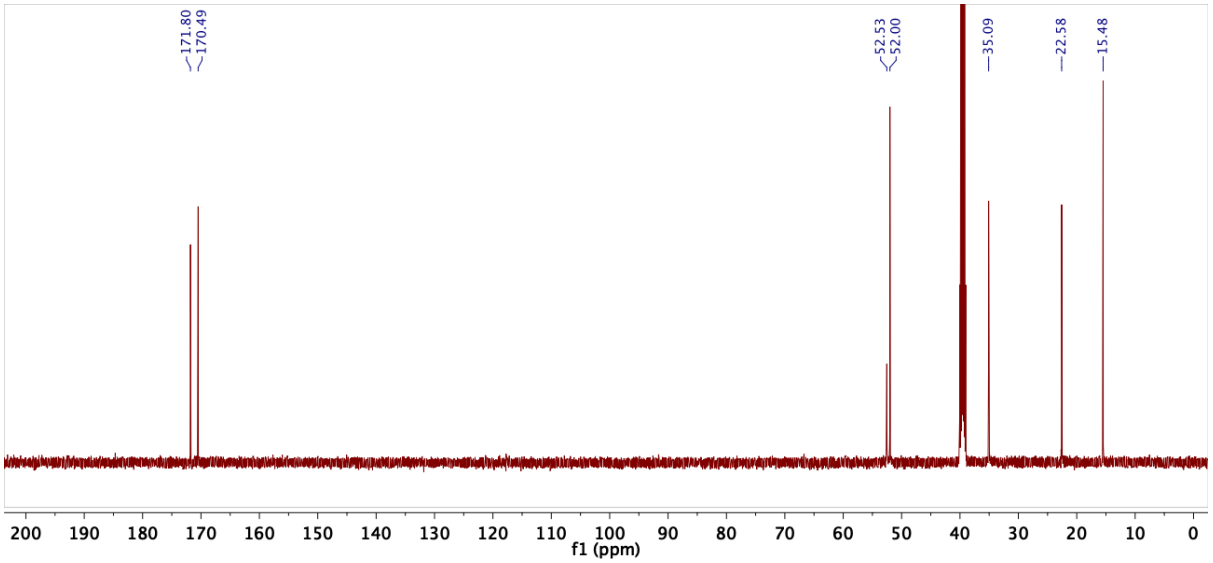
N-Acetyl-L-cysteine methyl ester (0.71 g, 4.03 mmol) was dissolved in acetonitrile (40 mL) at room temperature under inert atmosphere. Methyl iodide (1.76 mL, 28.3 mmol) and silver(I) oxide (3.53 g, 15.2 mmol) were added. The reaction mixture was stirred for 5 days under the exclusion of light at room temperature and filtered through a pad of celite. The filtrate was concentrated under reduced pressure and the crude product was purified by column chromatography (SiO_2, 3:7 Pet. ether/EtOAc, $KMnO_4$ stain) to give *N*-acetyl-*S*-methyl-L-cysteine methyl as a white solid (0.14 g, 18%).

^{1}H NMR (500 MHz, DMSO-d_6): δ 8.41 (d, *J* = 7.8 Hz, 1H), 4.43 (td, *J* = 8.1 5.5 Hz, 1H), 3.62 (s, 3H), 2.81 (dd, *J* = 13.8, 5.5 Hz, 1H), 2.70 (dd, *J* = 13.8, 8.4 Hz, 1H), 2.03 (s, 3H), 1.85 ppm (s, 3H). ^{13}C {^{1}H} NMR (126 MHz, DMSO-d_6): δ 171.8, 170.5, 52.5, 52.0, 35.1, 22.6, 15.5 ppm. HRMS (ESI) *m/z* calcd. for $[C_7H_{14}NO_3S]^+$: 192.0689 $[M + H]^+$, found 192.0691; HRMS (ESI) *m/z* calcd. for $[C_7H_{13}NO_3SNa]^+$: 214.0509 $[M + Na]^+$, found 214.0509.

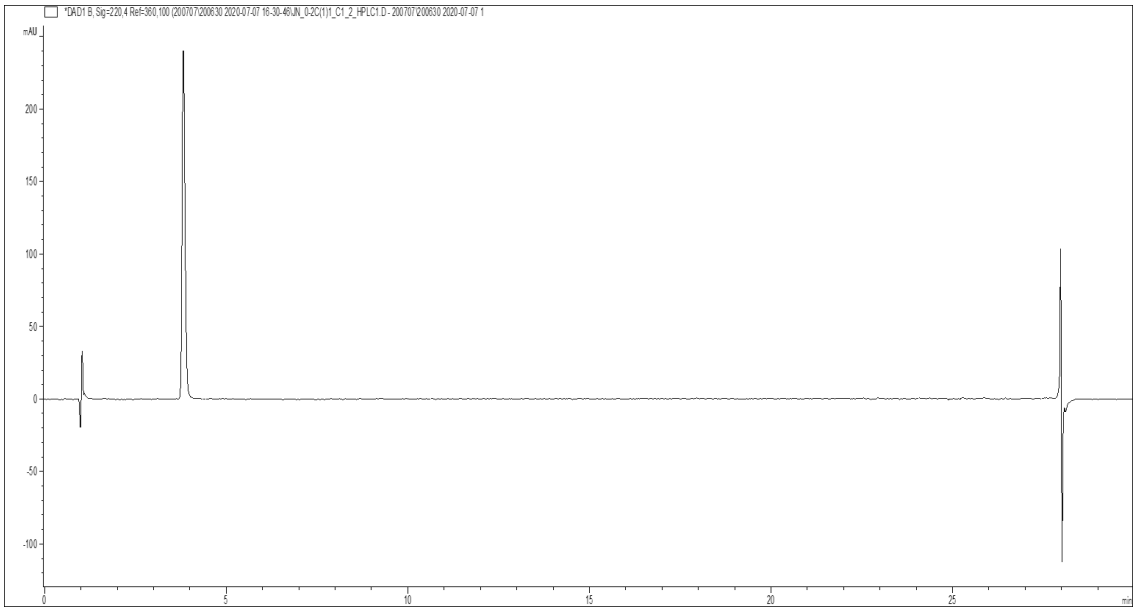
^{1}H NMR spectrum of Ac-Cys(SMe)-OMe



^{13}C NMR spectrum of Ac-Cys(SMe)-OMe



HPLC chromatogram of Ac-Cys(SMe)-OMe



4. Laser Flash Photolysis Studies

The kinetic experiments were performed at 298 ± 1 K on an Edinburgh Instrument LP920 spectrometer using the third harmonic of a Quantel Brilliant B Nd:YAG laser (6 ns pulse, 10–20 mJ, λ = 355 nm) to generate the reaction transient, as described previously.[1,18-20] The detection system employed a Hamamatsu R2856 photomultiplier tube (PMT) interfaced with a Tektronix TDS 3012C Digital Phosphor oscilloscope for transient absorption spectra. Kinetic measurements were carried out under pseudo-first order conditions in triplicate for each substrate, and the results are reported as the average of these three runs. To avoid a potential dark reaction between CAN and the amino acid, the samples were prepared by mixing the CAN and substrate solutions in the cuvette immediately before exposing to the laser flash.

Time-dependent decay plots of $NO_3^\bullet$ signals at 630 nm for its reaction with each compound are fitted according to the exponential decay fitting available on Igor Pro 6.03 (WaveMetrics, Inc.; Lake Oswego, OR, USA). The fitting used for the calculations follows the equation: $y = y_o + Ae^{-invTau*x}$; where y is the optical density, OD (proportional to [$NO_3^\bullet$]) and x is the time (unit in ns). The value of k_{obs} corresponds to the value of $invTau$.

Second-order rate coefficients, k, for the reactions of $NO_3^\bullet$ with various substrates were obtained from the slopes of k_{obs} vs [substrate] plots. These plots are shown in Figure S18–21 below. Negative y-intercepts for these very fast reactions are due to experimental errors in the gradient. However, the value is usually in the 10^5 s^{-1} range and thus insignificant compared with the determined rate coefficients (usually in the 10^9 M^{-1} s^{-1} range). The positive y-intercept, specifically in the reaction of $NO_3^\bullet$ with Ac-MetO_2-OMe is due to the reaction of $NO_3^\bullet$ with the solvent.[19]

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 σ is the overall standard deviation obtained following the statistical equation below:

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

where x_1, x_2, x_3 are the results from each respective run and $\sigma_1, \sigma_2, \sigma_3$ is the standard deviation of each result. Overall errors are given as 2σ statistical uncertainties. Typical errors measured in these experiments are around 5–15%.

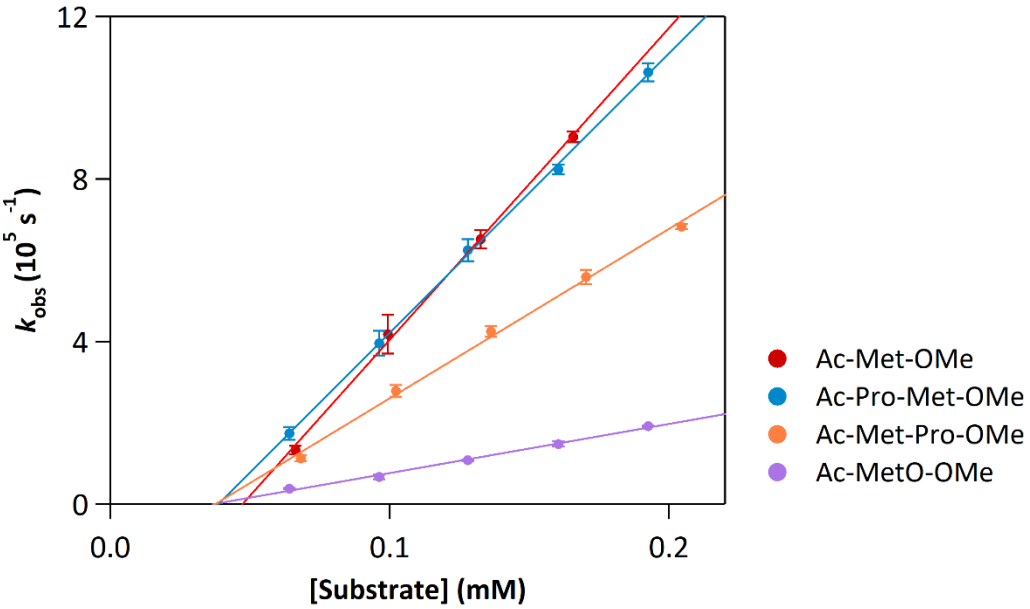


Figure S18. Plot of pseudo-first-order rate coefficient (k_{obs}) versus [substrate] containing methionine or methionine sulfoxide residue (see Table 1). To reduce interference of the transient signal with the $NO_3^{\bullet}$ signal at 630 nm only a narrow excess concentration range could be explored. Error bars shown are 2σ statistical uncertainties. From the linear regression analysis: Ac-Met-OMe: intercept = -3.6×10^5 s^{-1}, $k = 7.7 \times 10^9$ M^{-1} s^{-1}, $R^2 = 0.9984$; Ac-Pro-Met-OMe: intercept = -2.7×10^5 s^{-1}, $k = 6.9 \times 10^9$ M^{-1} s^{-1}, $R^2 = 0.9993$; Ac-Met-Pro-OMe: intercept = -1.6×10^5 s^{-1}, $k = 4.2 \times 10^9$ M^{-1} s^{-1}, $R^2 = 0.9967$; Ac-MetO-OMe: intercept = -4.4×10^4 s^{-1}, $k = 1.2 \times 10^9$ M^{-1} s^{-1}, $R^2 = 0.9953$.

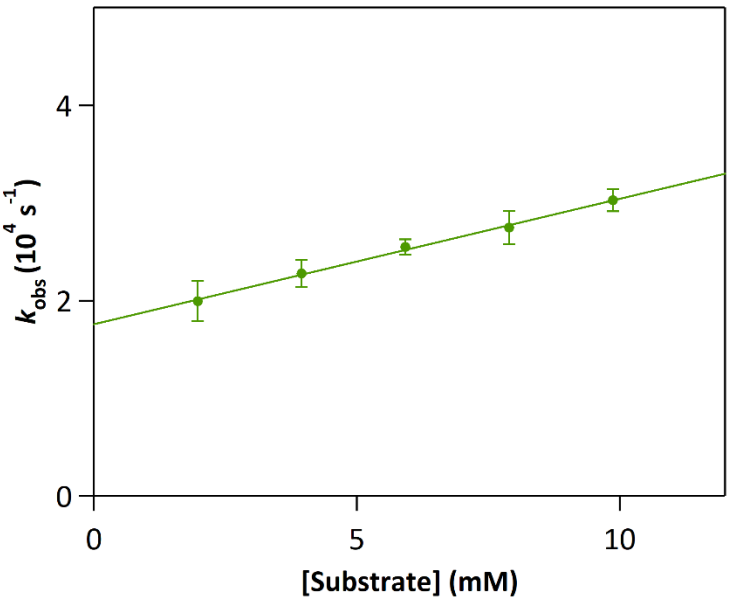


Figure S19. Plot of pseudo-first-order rate coefficient (k_{obs}) versus [Ac-MetO_2-OMe] (see Table 1). Error bars shown are 2σ statistical uncertainties. From the linear regression analysis: intercept = 1.8×10^4 s^{-1}, $k = 1.3 \times 10^6$ M^{-1} s^{-1}, $R^2 = 0.9966$.

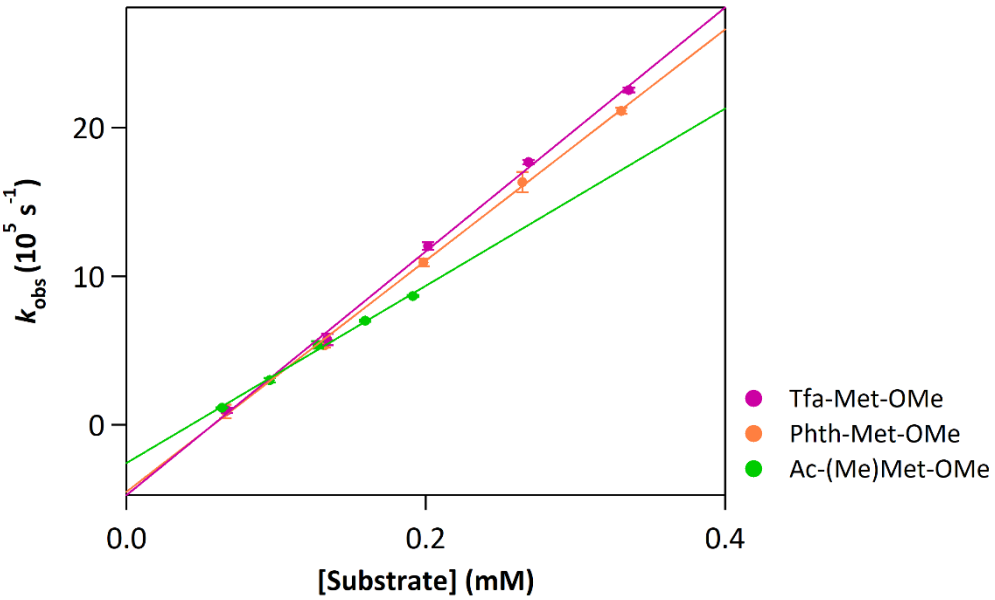


Figure S20. Plot of pseudo-first-order rate coefficient (k_{obs}) versus [substrate] containing methionine with different N-terminal protecting groups (see Table 1). To reduce interference of the transient signal with the $NO_3^{\bullet}$ signal at 630 nm only a narrow excess concentration range could be explored. Error bars shown are 2σ statistical uncertainties. From the linear regression analysis: Tfa-Met-OMe: intercept = −4.7 x 10^5 s^{-1}, k = 8.2 x 10^9 M^{-1} s^{-1}, R^2 = 0.9980; Phth-Met-OMe: intercept = −4.5 x 10^5 s^{-1}, k = 7.8 x 10^9 M^{-1} s^{-1}, R^2 = 0.9987; Ac-(Me)Met-OMe: intercept = −2.6 x 10^5 s^{-1}, k = 6.0 x 10^9 M^{-1} s^{-1}, R^2 = 0.9954.

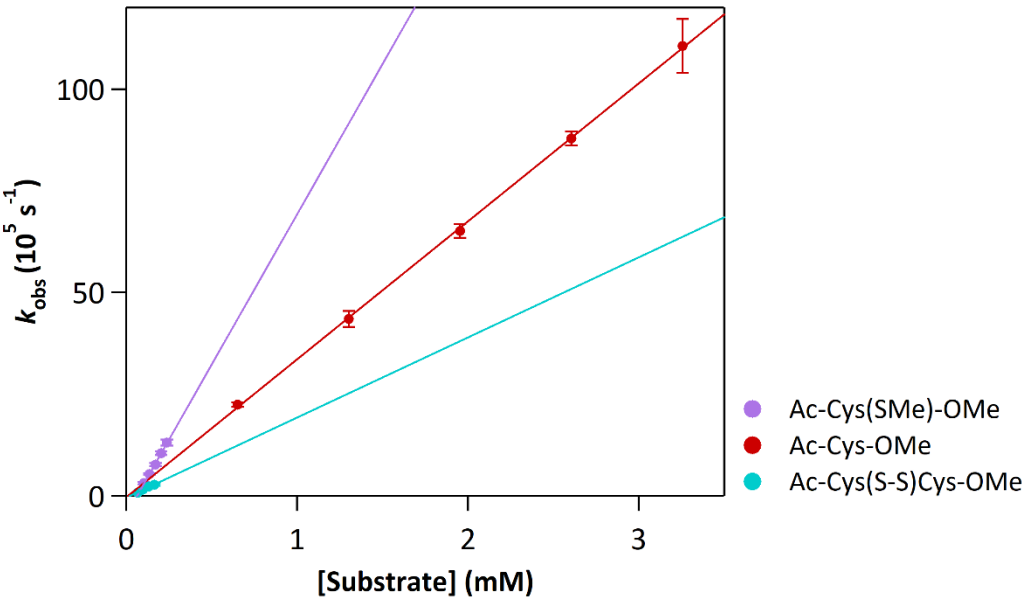


Figure S21. Plot of pseudo-first-order rate coefficient (k_{obs}) versus [substrate] containing cysteine or cystine derivatives (see Table 1). Error bars shown are 2σ statistical uncertainties. From the linear regression analysis: Ac-Cys(SMe)-OMe: intercept = −4.5 x 10^5 s^{-1}, k = 7.4 x 10^9 M^{-1} s^{-1}, R^2 = 0.9980; Ac-Cys-OMe: intercept = −2.9 x 10^4 s^{-1}, k = 3.4 x 10^9 M^{-1} s^{-1}, R^2 = 0.9997; Ac-Cys(S-S)Cys-OMe: intercept = −3.7 x 10^4 s^{-1}, k = 2.0 x 10^9 M^{-1} s^{-1}, R^2 = 0.9940. To reduce interference of the transient signal in the reactions involving Ac-Cys(SMe)-OMe and Ac-Cys(S-S)Cys-OMe with the $NO_3^{\bullet}$ signal at 630 nm only a narrow excess concentration range could be explored.

5. Product Studies

Product studies were carried out using the method that was previously developed in our group.[6] Nitrate radicals ($NO_3^\bullet$) can be generated from irradiation of CAN in acetonitrile or from $NO_2^\bullet/O_3$ mixtures.

Reactions of substrates with $NO_3^\bullet$ from CAN irradiation

The substrate (0.25 mmol) was dissolved in acetonitrile (5 mL). CAN (0.14 g, 0.26 mmol) in acetonitrile (20 mL) was added and the reaction mixture was irradiated at 350 nm in a Rayonet photoreactor under inert atmosphere for 90 minutes. The reaction mixture was concentrated under reduced pressure, resuspended in water (25 mL) and extracted with ethyl acetate (3 x 25 mL). The combined organic layers were dried over anhydrous magnesium sulfate and filtered. The solvent was removed under reduced pressure. The crude product was analysed by ^{1}H NMR, ^{13}C NMR, HPLC and HRMS, when possible, or purified by column chromatography, followed by spectroscopic characterisation.

Reactions of substrates with $NO_2^\bullet$

Liquid $NO_2^\bullet$ (0.25 mL, condensed at –20 °C, taken at –10 °C) was injected into a solution of the substrate (0.5 mmol) in acetonitrile (50 mL) at 10 °C. The reaction mixture was stirred for 20 minutes and saturated aqueous sodium bicarbonate solution (25 mL) was added. Acetonitrile was removed under reduced pressure. The aqueous layer was extracted with ethyl acetate (3 x 50 mL) and the combined organic layers were dried over magnesium sulfate and filtered. The solvent was removed under reduced pressure. The crude product was analysed by ^{1}H NMR, ^{13}C NMR, HPLC and HRMS, when possible, or purified by column chromatography, followed by spectroscopic characterisation.

Reactions of substrates with $NO_2^\bullet/O_3$ mixtures

Liquid $NO_2^\bullet$ (0.25 mL, condensed at –20 °C, taken at –10 °C) was injected into a solution of the substrate (0.5 mmol) in acetonitrile (50 mL) at 10 °C, with a stream of ozonized oxygen passing through the solution. The reaction mixture was stirred for 20 minutes and saturated aqueous sodium bicarbonate solution (25 mL) was added. Acetonitrile was removed under reduced pressure. The aqueous layer was extracted with ethyl acetate (3 x 50 mL) and the combined organic layers were dried over magnesium sulfate and filtered. The solvent was removed under reduced pressure. The crude product was analysed by ^{1}H NMR, ^{13}C NMR, HPLC and HRMS, when possible, or purified by column chromatography, followed by spectroscopic characterisation.

6. DFT Calculations

The DFT computations were carried out with the Gaussian 09 program[21] using the M062X method[22-24] in combination with the 6-31+G* basis set, which has been employed previously to investigate radical induced damage in amino acids.[1,20] Calculations in acetonitrile were performed using the Conductor-like Polarizable Continuum Model (CPCM) for acetonitrile.[25] The ground and transition structures were verified by vibrational frequency analysis at the same level of theory, and all identified transition structures showed only one imaginary frequency.

Gaussian Archive Entries

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

Reaction of $NO_3^•$ with EtSMe (Table 2)

Reactant complex

1\1\GINC-SPARTAN-BM095\FOpt\UM062X\6-31+G(d)\C3H8N1O3S1(2)\UWILLE\07-D
ec-2020\0\\#p M062X/6-31+G* nosymm opt=(calcfc,maxcycle=500) freq=nora
man scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\N,6.7647053536,-4
.7233388897,-0.3493461359\O,6.6237400495,-5.9408519107,-0.1048204011\O
,5.967215029,-3.8906405013,0.1238819701\O,7.723489615,-4.3420023304,-1
.0595956683\C,11.5116650743,-7.4396585085,-0.5349814226\H,10.906252811
4,-7.1962402411,-1.4124429729\H,12.5680552003,-7.5015621978,-0.7923242
691\H,11.1671860015,-8.3856328061,-0.1041535615\C,9.526564944,-6.03876
63643,0.8278929457\H,9.1543584225,-5.7539377423,-0.1688627141\H,9.1603
148436,-7.0505708292,1.0411853683\S,11.3121124925,-6.1539788836,0.6872
53837\C,9.1169630151,-5.0223831622,1.8829536465\H,9.4527074955,-4.0170
995403,1.6173934581\H,8.02491141,-5.0181169186,1.9360509712\H,9.504414
242,-5.2838921739,2.8705579485\\Version=AM64L-G09RevB.01\HF=-797.35717
94\S2=0.753825\S2-1=0.\S2A=0.750012\RMSD=5.179e-09\RMSF=3.702e-05\Dipo
le=7.0261722,-3.3446851,1.2044826\Quadrupole=131.2652931,-31.7057421,-
99.559551,-131.7807696,20.0981497,-10.8863151\PG=C01 [X(C3H8N1O3S1)]\\@

Sum of electronic and thermal Free Energies= -797.276273

CT complex (pre-reaction complex)

1\1\GINC-SPARTAN-BM057\FOpt\UM062X\6-31+G(d)\C3H8N1O3S1(2)\UWILLE\07-D
ec-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcycl
e=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\N
,7.7980807403,0.0091911304,2.1199100437\O,8.2455909417,1.1532487952,2.
1679279512\O,6.5904038788,-0.2398187088,2.099149996\O,8.6376166038,-0.
9641825909,2.0803051217\C,5.2530703276,-3.0423137239,1.1319408601\H,4.
8605867156,-3.8608516427,1.7410403462\H,4.96496797,-2.0892980765,1.580
7955026\C,6.7642325039,-3.1407804192,0.9837801989\H,7.1748167087,-2.33
47177786,0.3679514193\H,7.0722572161,-4.1009103522,0.5587792004\H,4.79
91910715,-3.1079364145,0.1392654921\S,7.5795862328,-3.0082950227,2.598
3875206\C,9.195699054,-3.7043181073,2.2351892549\H,9.5876371183,-3.248
6632606,1.3240787957\H,9.8488118434,-3.4870748104,3.0805422454\H,9.091
5250734,-4.7849140175,2.1097140512\\Version=AM64L-G09RevB.01\HF=-797.3
740548\S2=0.755691\S2-1=0.\S2A=0.750025\RMSD=0.000e+00\RMSF=5.858e-06\
Dipole=0.0036244,-4.3911349,-0.5269579\Quadrupole=-7.1818466,16.577795
7,-9.3959491,-65.9228463,-5.626457,-14.6794222\PG=C01 [X(C3H8N1O3S1)]\\@

Sum of electronic and thermal Free Energies= -797.289638

$TS_{C\text{-}1}$

1\1\GINC-SPARTAN-BM113\FTS\UM062X\6-31+G(d)\C3H8N1O3S1(2)\UWILLE\26-Oc
t-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(ts,noeigentest,
calcfc,maxcycle=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\ge
om&freq\\0,2\N,2.9238997334,3.025809198,2.5906414841\O,2.2052389929,2.
5554187359,1.7141613193\O,3.9591200779,2.3412950735,2.9853910149\O,2.7
331998783,4.1074110826,3.1258687891\S,4.30767998,0.6797375964,-0.11789
89996\C,6.0786233893,1.060680645,-0.2947244932\H,6.620574746,0.1139193
068,-0.2152264254\H,6.3543750809,1.6937996541,0.5536654323\C,4.2056997
197,0.1763174803,1.5169299877\H,5.1101032834,-0.2843347126,1.920313425
8\H,4.0659103061,1.2588486882,2.2179114431\C,6.3381373456,1.7532255877
,-1.6251149903\H,7.4084180546,1.9559187641,-1.7164197536\H,6.038905729
8,1.1241463954,-2.4677867051\H,5.8029569176,2.7042210266,-1.6879829714
\H,3.2836492346,-0.3684737321,1.7217482123\\Version=AM64L-G09RevB.01\H
F=-797.350202\S2=0.753964\S2-1=0.\S2A=0.750011\RMSD=0.000e+00\RMSF=6.1
06e-06\Dipole=2.5728082,-2.7188853,-2.2231889\Quadrupole=37.8835932,-2
3.4070586,-14.4765346,-9.5060413,-13.593508,-19.0989385\PG=C01 [X(C3H8
N1O3S1)]\\@

Frequencies -- -954.1402

Sum of electronic and thermal Free Energies= -797.272599

Product association complex (C-1 radical)

1\1\GINC-SPARTAN-BM087\FOpt\UM062X\6-31+G(d)\C3H8N1O3S1(2)\UWILLE\27-O
ct-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcycl
e=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\N
,2.8829087013,3.0283141419,2.6236035839\O,2.0744653991,2.4079524048,1.
9685596067\O,4.0942068716,2.46597267,2.8184244173\O,2.7395800582,4.109
6461428,3.1356503236\S,4.3040693561,0.5874510305,-0.2443998459\C,6.098
1277557,0.8840929856,-0.4049207557\H,6.6060784413,-0.0794676725,-0.312
0303371\H,6.4052904173,1.5249014782,0.4259803914\C,4.1996158082,-0.028
7417011,1.3482309672\H,5.0872531965,-0.4631792443,1.8024964\H,4.082102
2153,1.5813807104,2.3260142957\C,6.3938742705,1.5404777591,-1.74666549
44\H,7.4708558981,1.7044088735,-1.8416412469\H,6.0723318642,0.90676296
05,-2.5783675977\H,5.8923911718,2.5087013757,-1.8326225299\H,3.2279917
649,-0.4158692153,1.6410648618\\Version=AM64L-G09RevB.01\HF=-797.35766
75\S2=0.754108\S2-1=0.\S2A=0.750012\RMSD=0.000e+00\RMSF=4.608e-06\Dipo
le=1.7989085,-1.5288519,-0.8801915\Quadrupole=25.0232731,-16.7214819,-
8.3017912,-4.7015895,-5.0318828,-11.3165494\PG=C01 [X(C3H8N1O3S1)]\\@

Sum of electronic and thermal Free Energies= -797.277044

$TS_{C\text{-}3}$

1\1\GINC-SPARTAN-BM086\FTS\UM062X\6-31+G(d)\C3H8N1O3S1(2)\UWILLE\26-Oc
t-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(ts,noeigentest,
calcfc,maxcycle=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\ge
om&freq\\0,2\N,2.9906423806,3.022308732,2.581778382\O,2.2705541143,2.6
082643448,1.6767080901\O,3.9622249155,2.2684107958,3.0002515799\O,2.85
00415886,4.1107025286,3.1216631883\C,2.8482659241,-0.612605494,1.75279
77571\H,1.9842126391,-0.0622427445,1.370959565\H,2.8604517,-1.61189405
37,1.3053781656\S,4.3089805182,0.7069366157,-0.1565142205\C,6.06749763
33,1.1116521836,-0.22575362\H,6.6602931925,0.2025147196,-0.1087489212\
H,6.2587828674,1.5629543078,-1.1992284472\H,6.3054639602,1.8254789516,
0.5662319641\C,4.1373251984,0.1289176169,1.4591879316\H,5.0522152298,-

0.3285804874,1.8497675618\H,4.0649664714,1.1955046201,2.1510599818\H,2
.7335358267,-0.7228032968,2.8344996618\\Version=AM64L-G09RevB.01\HF=-7
97.352657\S2=0.754072\S2-1=0.\S2A=0.750012\RMSD=0.000e+00\RMSF=1.217e-
05\Dipole=2.2550356,-2.9673157,-2.0395768\Quadrupole=34.8798158,-22.08
60064,-12.7938094,-11.9701101,-12.3874335,-19.3618235\PG=C01 [X(C3H8N1O3S1)]\\@
Frequencies -- -719.2694
Sum of electronic and thermal Free Energies= - -797.275345

Product association complex (C-3 radical)
1\1\GINC-SPARTAN-BM114\FOpt\UM062X\6-31+G(d)\C3H8N1O3S1(2)\UWILLE\26-O
ct-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm freq=noraman opt=(c
alcfc,z-matrix,maxcycle=500) scrf=(cpcm,solvent=acetonitrile)\\geom&fr
eq\\0,2\N,2.9733414087,2.974338639,2.5827421283\O,2.1477479292,2.43700
46016,1.8776599425\O,4.1405200242,2.3257879023,2.7822193205\O,2.883006
0518,4.03756005,3.1423665118\C,2.8308849998,-0.7678253058,1.6117943246
\H,1.9904866718,-0.1860087759,1.220591464\H,2.7554734378,-1.7864920635
,1.2047322887\S,4.3275712282,0.510483733,-0.3313668248\C,6.1033902696,
0.8789356191,-0.3629290751\H,6.6810336039,-0.037654364,-0.2308470127\H
,6.3239155617,1.3116888448,-1.3396327938\H,6.3544613706,1.6008851774,0
.4167400886\C,4.144931073,-0.1373044363,1.2595686409\H,5.0527511718,-0
.5173537249,1.7290933332\H,4.0876849026,1.4689585367,2.2445735701\H,2.
7207533162,-0.8391890322,2.698481849\\Version=AM64L-G09RevB.01\HF=-797
.3614059\S2=0.754081\S2-1=0.\S2A=0.750013\RMSD=0.000e+00\RMSF=2.749e-0
5\Dipole=1.4823602,-1.6928898,-0.6069867\Quadrupole=21.3773627,-14.652
9539,-6.7244088,-6.5540264,-3.2958026,-11.2442732\PG=C01 [X(C3H8N1O3S1)]\\@
Sum of electronic and thermal Free Energies= -797.282303

TS_{C-4}
1\1\GINC-SPARTAN-BM102\FTS\UM062X\6-31+G(d)\C3H8N1O3S1(2)\UWILLE\20-No
v-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(ts,noeigentest,
calcfc,maxcycle=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\ge
om&freq\\0,2\N,3.4850783832,3.1571351782,2.1248563526\O,3.0030598382,2
.9248700937,1.0393673368\O,3.8850271914,2.1460800239,2.8870331326\O,3.
6513034801,4.2471824807,2.6319638584\C,3.9229767358,-0.0729018047,1.49
58106247\H,4.6275338902,-0.6426578326,2.1072797748\H,3.7380534944,0.91
1967692,2.1499109111\C,6.0941492216,2.0144346513,-1.3417129981\H,6.206
3341473,1.1951420125,-2.0549744111\H,5.2144682784,2.61209516,-1.591755
0804\H,2.9441689364,-0.5533064034,1.4334207893\C,4.456724337,0.3911292
003,0.1741910873\H,3.7083386823,0.9694413185,-0.3752016285\H,4.6962662
985,-0.5045487398,-0.4219135892\S,5.9649034688,1.3817241624,0.35232586
92\H,6.9826326166,2.6469388068,-1.3821910295\\Version=AM64L-G09RevB.01
\HF=-797.3222526\S2=0.758612\S2-1=0.\S2A=0.750046\RMSD=0.000e+00\RMSF=
7.522e-06\Dipole=0.1078211,-2.0568323,-1.4375038\Quadrupole=6.8676617,
-8.8745834,2.0069217,-12.4918208,-14.2692403,-11.9296669\PG=C01 [X(C3H
8N1O3S1)]\\@
Frequencies -- -847.5196
Sum of electronic and thermal Free Energies= -797.245529

Product association complex (C-4 radical)
1\1\GINC-SPARTAN-BM112\FOpt\UM062X\6-31+G(d)\C3H8N1O3S1(2)\UWILLE\18-N
ov-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcycl
e=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\N
,4.0264784719,2.8907284559,2.6052754255\O,4.3447438205,1.9128789342,3.
2405582122\O,3.0019802757,2.7504952151,1.7239079506\O,4.4970731937,3.9

955589158,2.6498662649\C,3.3172618372,-0.2054242422,0.8240694958\H,3.7
822900312,-0.7460018933,1.6415582058\H,2.8112879847,1.7814154253,1.701
9208965\C,6.462321309,1.4381872686,-1.2853851077\H,5.8309704078,2.0862
688517,-1.8976296036\H,7.4052343488,1.9485705473,-1.0807115205\H,6.668
4149803,0.5079290361,-1.8202440411\H,2.2478813903,-0.3235778648,0.6807
937459\S,5.6715563066,1.0961641295,0.3111843387\C,4.1516190439,0.28560
76533,-0.3060650118\H,4.4622575736,-0.5536627112,-0.9470866974\H,3.593
5160248,0.9894922788,-0.9322385538\\Version=AM64L-G09RevB.01\HF=-797.3
453598\S2=0.754799\S2-1=0.\S2A=0.750019\RMSD=0.000e+00\RMSF=1.100e-05\
Dipole=-0.922397,-1.3525477,-1.6693485\Quadrupole=-2.1956667,-2.131482
7,4.3271494,-11.7246129,-19.5929277,-8.4184303\PG=C01 [X(C3H8N1O3S1)]\\@
Sum of electronic and thermal Free Energies= -797.265419

Reaction of $NO_3^\bullet$ with EtSOMe (Table 2)

Reactant complex

1\1\GINC-SPARTAN-BM116\FOpt\UM062X\6-31+G(d)\C3H8N1O4S1(2)\UWILLE\24-N
ov-2020\0\\#p M062X/6-31+G* nosymm opt=(calcfc,maxcycle=500) freq=nora
man scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\N,0.5597453509,2.
3252112738,1.6306869744\O,-0.0903305818,1.4039423607,2.1695120588\O,1.
631375836,2.7156213431,2.1418705236\O,0.1389784283,2.8558161205,0.5806
420792\C,5.4823108783,-2.0892355426,1.0849902004\H,5.54514135,-1.22169
71029,1.743662488\H,5.1355611527,-1.7776770376,0.0976371439\C,9.703765
0279,-2.483972998,0.5514981329\H,9.6954689005,-3.4394136394,0.02341737
91\H,10.434943825,-1.8008159516,0.1178432399\H,9.8537094263,-2.6126714
231,1.6256119142\C,6.8063062993,-2.8279747361,1.0087623142\H,6.7879379
163,-3.6878426152,0.3344076626\H,7.1986090886,-3.1258445662,1.98654821
26\H,4.7512741168,-2.7867395247,1.5014487032\S,8.0910074224,-1.7356469
93,0.3107464159\O,8.0314125625,-0.3778079677,0.9311435571\\Version=AM6
4L-G09RevB.01\HF=-872.5039849\S2=0.756414\S2-1=0.\S2A=0.750014\RMSD=7.
314e-09\RMSF=1.981e-05\Dipole=14.2050933,-9.7211161,-2.0388084\Quadrup
ole=160.4361199,-73.1387493,-87.2973706,-87.3328208,9.7915977,-18.2216
153\PG=C01 [X(C3H8N1O4S1)]\\@
Sum of electronic and thermal Free Energies= -872.424985

CT complex (pre-reaction complex)

1\1\GINC-SPARTAN-BM090\FOpt\UM062X\6-31+G(d)\C3H8N1O4S1(2)\UWILLE\23-N
ov-2020\0\\#p M062X/6-31+G* nosymm opt=(calcfc,maxcycle=500) freq=nora
man scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\N,3.4269628835,1.
3843321971,-0.1549352752\O,2.8815293334,2.1764246422,-0.9229597377\O,2
.8765763338,0.9757702329,0.8788685247\O,4.6002351603,0.9634281077,-0.4
320267912\C,3.6829309307,-1.6262103875,2.6105601362\H,4.2228210656,-1.
6842669638,3.5575132319\H,2.9680562877,-0.8019662608,2.6430070633\C,7.
0232840351,-0.0982356558,0.5255161293\H,6.6651199093,-0.4194880687,-0.
4530771055\H,7.4940464988,0.8834653027,0.4625297178\H,7.6890970771,-0.
8328786081,0.9818969064\C,4.6358886393,-1.476835695,1.438385319\H,4.13
00159556,-1.3874982502,0.4753695166\H,5.3898706037,-2.2698257825,1.400
7827271\H,3.1326185839,-2.5603133357,2.4698671498\S,5.5862586191,0.067
8704558,1.5861972031\O,6.0407540433,0.2376969397,3.0026846646\\Version
=AM64L-G09RevB.01\HF=-872.5275227\S2=0.757381\S2-1=0.\S2A=0.750026\RMS
D=4.247e-09\RMSF=1.501e-05\Dipole=2.9449596,-3.2233052,0.9711407\Quadr
upole=37.0772683,-16.6756362,-20.4016321,-22.4403534,6.8854589,-1.8020
035\PG=C01 [X(C3H8N1O4S1)]\\@
Sum of electronic and thermal Free Energies= -872.441035

TS_{C-1}

1\1\GINC-SPARTAN-BM114\FTS\UM062X\6-31+G(d)\C3H8N1O4S1(2)\UWILLE\19-Fe
b-2021\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(ts,noeigentest,
calcfc,maxcycle=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\ge
om&freq\\0,2\N,1.5482388086,-0.8536795012,2.7645010134\O,2.0040350441,
-0.0527823395,3.5685283232\O,2.1388619558,-0.972644598,1.5964096244\O,
0.576649932,-1.5610708294,2.9587273138\C,5.1825622931,-1.5312114313,-0
.0789247113\H,4.1723214569,-1.9421495245,0.0135365261\H,5.7706637969,-
1.797977823,0.8030572067\C,4.2289250284,0.571742338,1.5427624129\H,3.8
97931754,1.6089861644,1.6198537108\H,3.1136821928,-0.2368066777,1.5822
403924\H,4.9023707198,0.2741858607,2.3499821521\C,5.8577916368,-1.9142
679594,-1.3851203618\H,6.860230239,-1.4858418686,-1.4597469189\H,5.945
1448753,-3.0030405895,-1.4186380735\H,5.2638138336,-1.592566543,-2.243
4848383\S,4.977248073,0.2761865674,0.0145749317\O,4.18242512,0.7537120
947,-1.1555935337\\Version=AM64L-G09RevB.01\HF=-872.4940333\S2=0.75694
4\S2-1=0.\S2A=0.750029\RMSD=0.000e+00\RMSF=1.395e-05\Dipole=3.9367766,
-0.286265,-1.1764237\Quadrupole=37.9699211,-10.5281004,-27.4418207,-11
.0730646,5.0839448,6.7167337\PG=C01 [X(C3H8N1O4S1)]\\@
Frequencies -- -1370.2302
Sum of electronic and thermal Free Energies= - 872.415157

Product association complex (C-1 radical)

1\1\GINC-SPARTAN-BM088\FOpt\UM062X\6-31+G(d)\C3H8N1O4S1(2)\UWILLE\27-O
ct-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcycl
e=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\N
,3.343971219,3.1029471626,2.4966670727\O,3.5475232236,2.8540337372,1.3
294267071\O,3.7017129832,2.1542996694,3.4043497987\O,2.8614501967,4.09
04932532,2.9759001041\C,5.7796501953,1.0761005481,-0.396666403\H,6.454
7232256,0.31595396,0.0100793263\H,5.6920925109,1.9050925983,0.31141615
62\C,4.0406363093,-0.3013903984,1.1433629656\H,4.914858254,-0.79013688
21,1.5654771512\H,4.0578054805,1.4070800649,2.8742535926\C,6.223447679
1,1.5464049026,-1.7748422966\H,7.2149576526,2.0007326342,-1.7007821858
\H,6.2824994022,0.7066683034,-2.4720549407\H,5.5346275418,2.2935481747
,-2.1804545307\H,3.0521695555,-0.5165680814,1.533900016\S,4.1335995331
,0.3107035009,-0.5124568858\O,4.3279760376,-0.9329151476,-1.3889226478
\\Version=AM64L-G09RevB.01\HF=-872.5006499\S2=0.756533\S2-1=0.\S2A=0.7
50033\RMSD=0.000e+00\RMSF=1.673e-05\Dipole=1.0562286,0.2157944,1.58284
56\Quadrupole=18.4921558,-13.1329644,-5.3591914,8.1329037,14.1947286,-
10.2171315\PG=C01 [X(C3H8N1O4S1)]\\@
Sum of electronic and thermal Free Energies= -872.417896

TS_{C-3}

1\1\GINC-SPARTAN-BM104\FTS\UM062X\6-31+G(d)\C3H8N1O4S1(2)\UWILLE\28-Oc
t-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(ts,noeigentest,
calcfc,maxcycle=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\ge
om&freq\\0,2\N,3.1945623868,3.0861602384,2.7092364748\O,3.0017890546,2
.1783945619,3.5075712611\O,3.6070847823,2.7814497442,1.5022220113\O,3.
0293286457,4.2692783179,2.9491123297\C,2.5486796283,-0.4122535807,1.43
52263891\H,2.0547210875,-0.091024163,2.3564841157\H,1.953422006,-0.080
6923252,0.5806295428\C,6.1083141618,1.2162851662,-0.0292191014\H,6.648
2894283,1.1046350025,0.9128306017\H,6.767186285,1.0300649409,-0.877455
2422\H,5.6327719581,2.1965735136,-0.1030062905\C,3.9264392008,0.200988
7449,1.4128076848\H,4.5785127607,-0.0744049619,2.2475961143\H,3.794068

0007,1.5248878331,1.4561510752\H,2.5871893026,-1.5074837043,1.43769101
49\S,4.8142604881,-0.036649109,-0.0831393905\O,3.9604568226,0.17565778
05,-1.2914965908\\Version=AM64L-G09RevB.01\HF=-872.4968767\S2=0.757302
\S2-1=0.\S2A=0.750034\RMSD=0.000e+00\RMSF=4.100e-06\Dipole=2.3832915,-
2.641285,-0.7828814\Quadrupole=40.8174589,-22.5777372,-18.2397217,-11.
6430339,-1.7538708,-15.9735881\PG=C01 [X(C3H8N1O4S1)]\\@
Frequencies -- -1454.1364
Sum of electronic and thermal Free Energies= -872.417461

Product association complex (C-3 radical)
1\1\GINC-SPARTAN-BM087\FOpt\UM062X\6-31+G(d)\C3H8N1O4S1(2)\UWILLE\28-O
ct-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcycl
e=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\N
,3.9368666734,3.1983845963,1.582019455\O,4.5197205856,3.4304557953,0.5
493716137\O,4.5852967498,2.4150437586,2.4932376198\O,2.8429077119,3.54
99423101,1.9244717517\C,4.9909727348,0.2257505241,0.1558312316\H,5.619
5586574,-0.3825279237,0.7998786933\H,5.4683642551,2.2413913903,2.10269
81327\C,5.4966736868,0.8086099136,-1.1145676605\H,6.4872832675,1.24956
48796,-0.9662173275\H,5.5946777333,0.0327038307,-1.8867664064\H,4.8232
351587,1.5800922459,-1.500504371\S,3.2530209089,0.236272855,0.44638018
79\O,2.5739691298,-0.5530302888,-0.676653534\C,3.2335869153,-0.8283313
672,1.9041152978\H,3.7896953361,-0.341096495,2.7086265229\H,2.18919671
52,-0.9503041393,2.1947301465\H,3.6731390604,-1.7943629055,1.645304446
7\\Version=AM64L-G09RevB.01\HF=-872.5080502\S2=0.756251\S2-1=0.\S2A=0.
750032\RMSD=0.000e+00\RMSF=1.915e-05\Dipole=2.6806564,-0.2798199,1.750
1431\Quadrupole=28.7177891,-18.7223117,-9.9954774,2.4802673,13.7158861
,-2.9742539\PG=C01 [X(C3H8N1O4S1)]\\@
Sum of electronic and thermal Free Energies= -872.425933

$TS_{C\text{-}4}$
1\1\GINC-SPARTAN-BM117\FTS\UM062X\6-31+G(d)\C3H8N1O4S1(2)\UWILLE\18-No
v-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(ts,noeigentest,
calcfc,maxcycle=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\ge
om&freq\\0,2\N,3.6077469675,3.0867858352,2.4048958354\O,2.9719190362,2
.9113487974,1.3902990319\O,4.3001472017,2.0709855427,2.9156369884\O,3.
7088471043,4.1123680847,3.042044071\C,3.9919203451,-0.0519097677,1.381
3879827\H,4.7655651116,-0.7146005308,1.7748297844\H,4.0069396184,0.862
2604845,2.1413898914\C,6.0614223359,1.6832326639,-1.6961100953\H,5.186
7791454,2.0803407094,-2.2169221318\H,6.9125759732,2.3516316213,-1.8350
691666\H,6.305733178,0.6771902112,-2.0444341653\H,2.983357518,-0.45410
88627,1.4967738944\S,5.7158632197,1.6219276531,0.0739177386\O,6.845072
0266,0.8255411315,0.7088430622\C,4.2800677333,0.4799362639,0.012359318
9\H,4.5798501873,-0.3374441151,-0.6564172932\H,3.4396682979,1.03031727
74,-0.4163757473\\Version=AM64L-G09RevB.01\HF=-872.4830483\S2=0.759154
\S2-1=0.\S2A=0.750055\RMSD=0.000e+00\RMSF=9.862e-06\Dipole=-1.1019717,
-1.3231636,-2.340863\Quadrupole=-13.0856321,3.1883082,9.8973239,-7.191
421,-25.4885517,-13.389641\PG=C01 [X(C3H8N1O4S1)]\\@
Frequencies -- -582.8082
Sum of electronic and thermal Free Energies= -872.401848

Product association complex (C-4 radical)
1\1\GINC-SPARTAN-BM095\FOpt\UM062X\6-31+G(d)\C3H8N1O4S1(2)\UWILLE\18-N
ov-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcycl
e=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\N

,4.1974183433,2.7930364614,2.5989278621\O,4.4198504676,1.7515956868,3.
1710156683\O,3.1068125859,2.8289570104,1.7849478911\O,4.8194242652,3.8
187431666,2.6401383879\C,3.2800024393,-0.189344558,0.6845038625\H,3.70
42534427,-0.7893643979,1.4811010036\H,2.7319814382,1.9203863189,1.8209
457485\C,6.4567885093,1.3759577995,-1.3691593284\H,5.8488719551,2.0251
467299,-2.0034726796\H,7.416321467,1.8520184227,-1.1606844566\H,6.6110
485623,0.4005106561,-1.83672835\H,2.2017801106,-0.1469456804,0.5834125
341\S,5.6230282604,1.1344563415,0.2139358589\O,6.4243873392,0.06696836
05,0.9536858942\C,4.1435849265,0.2609064889,-0.433857843\H,4.549843960
3,-0.5851523609,-1.0087691596\H,3.625068297,0.9423223139,-1.1146375639
\\Version=AM64L-G09RevB.01\HF=-872.5068708\S2=0.755167\S2-1=0.\S2A=0.7
50022\RMSD=0.000e+00\RMSF=2.528e-05\Dipole=-2.0549081,0.0023978,-2.416
3783\Quadrupole=-19.3088086,8.4748173,10.8339913,0.3976836,-30.699942,
-6.7411542\PG=C01 [X(C3H8N1O4S1)]\\@
Sum of electronic and thermal Free Energies= -872.422959

Reaction of $NO_3^\bullet$ with $EtSO_2Me$ (Table 2)

Reactant complex

1\1\GINC-SPARTAN-BM089\FOpt\UM062X\6-31+G(d)\C3H8N1O5S1(2)\UWILLE\23-N
ov-2020\0\\#p M062X/6-31+G* nosymm opt=(calcfc,maxcycle=500) freq=nora
man scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\N,1.0007226624,1.
0232186272,1.3830375378\O,0.5695049629,-0.0003923388,1.8423616084\O,1.
7339392341,1.844967228,1.8635867362\O,0.6104767672,1.2825898429,0.1475
315356\C,4.115728327,-0.2158490024,1.4651924122\H,4.3502819509,0.64132
89004,2.1012334111\H,3.8020995035,0.1449504601,0.4815464707\C,8.016028
1956,-1.4714344883,0.5499697731\H,7.6955948647,-2.2916655812,-0.093850
3655\H,8.8765125061,-0.9576031633,0.1161073674\H,8.2460242925,-1.82131
65873,1.5572566968\C,5.3116686208,-1.1521237592,1.3418043803\H,5.11198
23882,-1.9936716506,0.6730119206\H,5.6437918986,-1.5292640321,2.312714
8239\H,3.2867642896,-0.7653113928,1.9193525554\S,6.7075053036,-0.26661
31494,0.642188693\O,6.3583608793,0.1470071223,-0.7274490353\O,7.110437
4729,0.7867100046,1.5891738885\\Version=AM64L-G09RevB.01\HF=-947.68221
81\S2=0.756156\S2-1=0.\S2A=0.750029\RMSD=8.269e-09\RMSF=8.270e-06\Dipo
le=-0.317476,-2.3934715,0.4163632\Quadrupole=0.4034046,3.0372699,-3.44
06745,-33.323074,4.8736855,-4.8925412\PG=C01 [X(C3H8N1O5S1)]\\@
Sum of electronic and thermal Free Energies= -947.597692

CT complex (pre-reaction complex)

1\1\GINC-SPARTAN-BM106\FOpt\UM062X\6-31+G(d)\C3H8N1O5S1(2)\UWILLE\27-O
ct-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm freq=noraman opt=(c
alcfc,maxcycle=500) scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\N
,2.9967353522,3.4055592357,2.3121313053\O,2.5291628237,2.4560468862,2.
8854763174\O,4.3056067074,3.5135633281,2.433332145\O,2.4651275382,4.26
35875494,1.6658449765\C,2.6733264087,-0.6839126943,1.6514428392\H,1.95
59377032,0.1401039893,1.6744432699\H,2.4284899624,-1.3508348033,0.8211
316242\C,5.9639296297,1.3541481528,0.0189777754\H,6.6275023944,0.48848
48223,0.0305438671\H,6.0953697429,1.9266336352,-0.9018689627\H,6.12118
44606,1.9903224949,0.8913716635\C,4.0994705646,-0.1607899925,1.5299189
807\H,4.8367196405,-0.9664949142,1.4756154525\H,4.3607362055,0.5157317
867,2.3489417522\H,2.5834819235,-1.2456338674,2.5841780758\S,4.2764417
896,0.7869182869,0.0172208832\O,3.3947192779,1.9658367575,0.1077976865
\O,4.0857718749,-0.1138156533,-1.1305116515\\Version=AM64L-G09RevB.01\
HF=-947.6880737\S2=0.756421\S2-1=0.\S2A=0.750031\RMSD=0.000e+00\RMSF=1

.444e-05\Dipole=2.0603859,-0.5501657,1.822905\Quadrupole=23.4292817,-1
4.153287,-9.2759947,3.5076956,14.9032458,-0.2748092\PG=C01 [X(C3H8N1O5
S1)]\\@
Sum of electronic and thermal Free Energies= -947.600035

TS_{C-1}
1\1\GINC-SPARTAN-BM110\FTS\UM062X\6-31+G(d)\C3H8N1O5S1(2)\UWILLE\29-Oc
t-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(ts,noeigentest,
calcfc,maxcycle=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\ge
om&freq\\0,2\N,2.9329033092,2.9624957382,2.4720619736\O,2.0075660541,2
.2141015382,2.2974292389\O,4.1817895116,2.4497815719,2.563462303\O,2.9
183355019,4.1625892905,2.603612378\C,5.9883424349,1.1815222546,-0.3261
839675\H,6.6035108496,0.3150276089,-0.0705680708\H,6.1267197217,1.9654
238309,0.424381945\C,4.1070944252,0.1380013108,1.5169458984\H,4.933103
6847,-0.4719534983,1.8861377462\H,4.1363585484,1.2061228934,2.14436287
49\S,4.284479959,0.6486598645,-0.1808699274\O,4.0794261984,-0.55477605
91,-0.9983156344\O,3.4040349559,1.8031531685,-0.3925769655\C,6.2515366
802,1.682993982,-1.7417761619\H,5.6136420321,2.5366684457,-1.981882181
5\H,7.2941786871,2.0015749098,-1.807320037\H,6.0861260351,0.8917607478
,-2.4767997857\H,3.1103964108,-0.2711545982,1.6920333737\\Version=AM64
L-G09RevB.01\HF=-947.6615745\S2=0.760674\S2-1=0.\S2A=0.75007\RMSD=0.00
0e+00\RMSF=3.521e-06\Dipole=2.6013279,-1.1867889,0.8537041\Quadrupole=
32.836661,-22.8826978,-9.9539632,-0.4639908,6.9446879,-8.1415797\PG=C0
1 [X(C3H8N1O5S1)]\\@
Frequencies -- -1560.7052
Sum of electronic and thermal Free Energies= -947.576658

Product association complex (C-1 radical)
1\1\GINC-SPARTAN-BM089\FOpt\UM062X\6-31+G(d)\C3H8N1O5S1(2)\UWILLE\10-N
ov-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm freq=noraman opt=(c
alcfc,z-matrix,maxcycle=500) scrf=(cpcm,solvent=acetonitrile)\\geom&fr
eq\\0,2\N,3.6379226538,3.3723199084,1.7292851716\O,2.4835876506,3.7088
083585,1.8242763133\O,4.0687244403,2.3876342629,2.5690491559\O,4.48590
10365,3.7960810568,0.9926184513\C,2.7878252513,-1.5002333035,1.5352397
886\H,1.9994124981,-0.7827414645,1.7754938581\H,2.4728173127,-2.105625
7984,0.6817052414\C,5.4481181134,1.110064331,-0.2930526409\H,6.3420480
458,0.6197882404,0.0718191542\H,5.4783971528,1.9841549871,-0.93063894\
H,3.2755959933,2.1262620602,3.0813615995\H,2.9270266601,-2.161315382,2
.3936790046\S,3.9170948251,0.2910896988,-0.170482769\O,3.7101063963,-0
.5409630058,-1.3687308236\O,2.8824023992,1.2972987128,0.1262233786\C,4
.1044558861,-0.7888026062,1.2477533174\H,4.4241941954,-0.1519961799,2.
0767128813\H,4.9071344892,-1.4867598767,0.9940878575\\Version=AM64L-G0
9RevB.01\HF=-947.6932846\S2=0.755835\S2-1=0.\S2A=0.750027\RMSD=0.000e+
00\RMSF=9.610e-06\Dipole=1.5217893,-1.3203476,2.4581301\Quadrupole=15.
949054,-16.2081917,0.2591377,-6.2255901,14.8090206,-2.4915205\PG=C01 [
X(C3H8N1O5S1)]\\@
Sum of electronic and thermal Free Energies= -947.604903

TS_{C-3}
1\1\GINC-SPARTAN-BM113\FTS\UM062X\6-31+G(d)\C3H8N1O5S1(2)\UWILLE\28-Oc
t-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(ts,noeigentest,
calcfc,maxcycle=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\ge
om&freq\\0,2\N,3.0538599548,3.0564063421,2.5971709873\O,2.0543471643,2
.4378592056,2.3352578242\O,4.243094656,2.4375073566,2.5049081351\O,3.1

545674632,4.2058794147,2.9552648167\C,2.6422740145,-0.53524236,1.64195
91501\H,1.8524744726,0.0517987373,1.1696335929\H,2.6449540156,-1.54632
13042,1.2160887781\C,5.9397152513,1.2591468024,-0.2629003184\H,6.65692
39956,0.5096291002,0.0738525697\H,6.1463369684,1.5537083811,-1.2943221
395\H,5.9308386138,2.1330848835,0.3906377647\C,3.9950373939,0.08824606
77,1.4378485088\H,4.8412430358,-0.4658393463,1.8550152202\H,4.03934952
13,1.1623982482,1.9891729346\H,2.438936846,-0.6214843036,2.7122613958\
S,4.3127137621,0.5408046281,-0.2726244359\O,4.33991501,-0.7106739299,-
1.0410506595\O,3.3398538606,1.5739890763,-0.6448671249\\Version=AM64L-
G09RevB.01\HF=-947.66863\S2=0.759705\S2-1=0.\S2A=0.750057\RMSD=0.000e+
00\RMSF=1.425e-05\Dipole=1.9340987,-1.2259954,1.1887038\Quadrupole=26.
2283201,-18.4404995,-7.7878206,-0.7446591,9.2439246,-9.2720483\PG=C01
[X(C3H8N1O5S1)]\\@
Frequencies -- -1080.1518
Sum of electronic and thermal Free Energies= -947.584882

Product association complex (C-3 radical)
1\1\GINC-SPARTAN-BM089\FOpt\UM062X\6-31+G(d)\C3H8N1O5S1(2)\UWILLE\29-O
ct-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm freq=noraman opt=(c
alcfc,z-matrix,maxcycle=500) scrf=(cpcm,solvent=acetonitrile)\\geom&fr
eq\\0,2\N,3.1478337485,2.9018850404,2.0766543117\O,2.2346611168,2.2013
381014,2.4414042662\O,4.4100722891,2.4804369401,2.3907761244\O,3.11078
35337,3.9343591384,1.470090134\C,2.5931751673,-0.9244137928,1.53023264
04\H,1.8417185643,-0.2270910044,1.1503322959\H,2.393062103,-1.91801220
01,1.1051394414\C,5.8930554738,0.9367542907,-0.2725807713\H,6.55644520
22,0.0752111703,-0.1836559708\H,6.0650174026,1.4541596127,-1.219041071
\H,6.0056478104,1.6235927273,0.5672640062\C,3.968754024,-0.4777184778,
1.1871165485\H,4.8570401364,-0.9169562266,1.6313879553\H,4.2837191853,
1.66174704,2.9158372751\H,2.4864891698,-1.0026140174,2.6158981042\S,4.
2088169874,0.3693556492,-0.3273306068\O,4.0718943701,-0.5803841711,-1.
4453884022\O,3.3145637155,1.5399721775,-0.33486228\\Version=AM64L-G09R
evB.01\HF=-947.700333\S2=0.755396\S2-1=0.\S2A=0.750024\RMSD=0.000e+00\
RMSF=1.890e-05\Dipole=2.1540114,-1.5015373,2.4170883\Quadrupole=25.360
8795,-20.7833412,-4.5775383,-4.126889,19.2411013,-3.8772738\PG=C01 [X(
C3H8N1O5S1)]\\@
Sum of electronic and thermal Free Energies= -947.611598

TS_{C-4}
1\1\GINC-SPARTAN-BM117\FTS\UM062X\6-31+G(d)\C3H8N1O5S1(2)\UWILLE\18-No
v-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(ts,noeigentest,
calcfc,maxcycle=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\ge
om&freq\\0,2\N,3.4486545992,3.0785664892,2.3385386872\O,2.8398208731,2
.8515209329,1.3227079555\O,3.9406253129,2.0518000693,3.0455663583\O,3.
6703011754,4.1514302454,2.8505523565\C,4.0573127291,-0.0234438177,1.47
49423875\H,4.853208034,-0.6103732324,1.938959089\H,3.9665256377,0.9344
724582,2.1918199267\C,6.1126540369,1.7761546399,-1.6976531266\H,5.2839
726678,2.420967606,-1.9936587634\H,7.0610373381,2.313759701,-1.7630382
856\H,6.1452803438,0.8649612445,-2.296062936\H,3.0762605157,-0.4920870
419,1.5684579163\S,5.9095928939,1.3356866848,0.0140962326\O,5.75083963
67,2.5680322227,0.8016621356\O,6.9794371232,0.4051899423,0.4017318687\
C,4.3492529493,0.4384454893,0.0718844411\H,4.4652702692,-0.4273880546,
-0.5921172054\H,3.5721078639,1.0980234211,-0.3210970381\\Version=AM64L
-G09RevB.01\HF=-947.6733514\S2=0.759659\S2-1=0.\S2A=0.750057\RMSD=0.00
0e+00\RMSF=1.269e-05\Dipole=-1.121792,-2.1089758,-2.4261139\Quadrupole

=-11.5855158,-2.0951692,13.680685,-15.3821608,-26.9171062,-14.7582034\
PG=C01 [X(C3H8N1O5S1)]\\@
Frequencies -- -875.8145
Sum of electronic and thermal Free Energies= -947.586842

Product association complex (C-4 radical)
1\1\GINC-SPARTAN-BM062\FOpt\UM062X\6-31+G(d)\C3H8N1O5S1(2)\UWILLE\19-N
ov-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcycl
e=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\N
,2.015326854,2.0712101127,3.4822305824\O,0.8879273712,2.1194801962,3.0
506644223\O,2.9425924449,1.4204180143,2.7238861046\O,2.4465769092,2.52
41622225,4.5064929132\C,6.4948947065,0.8810929545,1.2086705158\H,6.751
0318934,0.2989943219,2.0837178456\H,2.4560984819,1.1066247941,1.933556
316\C,9.4796067964,3.302596199,-0.4290000147\H,8.9705416345,3.42144054
15,-1.3863518079\H,9.9348046617,4.2448601926,-0.1161410848\H,10.228272
9199,2.510302788,-0.4708068551\H,5.488814835,1.2638646745,1.1043070543
\S,8.2743137283,2.8889061351,0.8178686082\O,7.2155336161,3.9106151222,
0.8027836376\O,8.978872665,2.6516449001,2.0882656716\C,7.5485459157,1.
3075111761,0.2646521684\H,8.3891644082,0.6094044013,0.216153592\H,7.16
49947782,1.5063564334,-0.7405537993\\Version=AM64L-G09RevB.01\HF=-947.
693372\S2=0.755634\S2-1=0.\S2A=0.750025\RMSD=0.000e+00\RMSF=1.214e-05\
Dipole=0.7019155,-1.9882605,-3.2041198\Quadrupole=23.2070543,-10.54786
31,-12.6591912,-15.3855988,-39.3172414,-21.0270632\PG=C01 [X(C3H8N1O5S1)]\\@
Sum of electronic and thermal Free Energies= -947.610860

O-Transfer (Scheme 2)

Product complex 3 (x = 0)
1\1\GINC-SPARTAN-BM109\FOpt\UM062X\6-31+G(d)\C3H8N1O3S1(2)\UWILLE\04-N
ov-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcycl
e=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\N
,0.8817867321,0.0886065577,-0.0504181239\O,2.5253348425,2.105808812,-0
.9723241042\O,0.9519981869,-0.5317570455,-1.0617260649\O,1.4523906679,
0.0374382812,0.9918443501\S,3.8152987932,1.2888424058,-0.8569329905\C,
4.8195870332,1.7450474068,-2.284872243\H,5.8079618627,1.2891785077,-2.
190836072\H,4.3160935169,1.3602211357,-3.1732474828\H,4.8928050947,2.8
344721454,-2.3317119896\C,4.8078249266,2.117494755,0.4206792214\H,5.79
55959956,1.6457234484,0.413056313\H,4.9030508301,3.1641716409,0.112027
4647\C,4.1230910794,1.9847854199,1.773573761\H,4.6933230094,2.53323110
43,2.5281211401\H,3.1119837896,2.4000511641,1.7380253976\H,4.059631299
1,0.9378400508,2.0847305332\\Version=AM64L-G09RevB.01\HF=-797.3843566\
S2=0.754943\S2-1=0.\S2A=0.750015\RMSD=0.000e+00\RMSF=1.609e-05\Dipole=
2.2593452,-0.1214814,0.1326718\Quadrupole=21.417825,-12.9903534,-8.427
4717,7.4653124,-3.6393463,1.2644766\PG=C01 [X(C3H8N1O3S1)]\\@
Sum of electronic and thermal Free Energies= -797.304053

Product complex 3 (x = 1)
1\1\GINC-SPARTAN-BM116\FOpt\UM062X\6-31+G(d)\C3H8N1O4S1(2)\UWILLE\04-N
ov-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcycl
e=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\N
,4.8834407279,0.2224690582,-0.9162599889\O,0.6255187018,0.266359988,1.
9679631456\O,4.2083109683,1.0716530008,-1.404186494\O,5.3373993169,0.0
489434152,0.1670946409\C,1.0126209548,1.6778871511,-0.2370179607\H,1.8
133219212,1.9838914913,-0.912221269\H,0.2636697191,1.0890577225,-0.771

0094588\H,0.5495284258,2.5380424591,0.2486175066\C,2.9200043802,1.6046
812665,1.8601394309\H,3.6294369492,1.9331982352,1.0940643926\H,2.39001
07863,2.4749617325,2.2572537854\C,3.5892895232,0.7844163103,2.95602990
83\H,4.3433924335,1.4025779945,3.4488160789\H,2.8604736315,0.464629771
4,3.7049350146\H,4.0837018436,-0.096224262,2.5387769486\S,1.6928140991
,0.6075108949,1.0131285595\O,2.3870726678,-0.5063191996,0.3431393996\\
Version=AM64L-G09RevB.01\HF=-872.576311\S2=0.754838\S2-1=0.\S2A=0.7500
14\RMSD=0.000e+00\RMSF=2.339e-05\Dipole=0.7745231,2.2707899,-0.4721051
\Quadrupole=2.3894711,1.7520248,-4.1414959,9.0440795,3.8494384,3.86237
37\PG=C01 [X(C3H8N1O4S1)]\\@
Sum of electronic and thermal Free Energies= -872.490032

Intermediate 5 (x = 0)
1\1\GINC-SPARTAN-BM121\FOpt\RM062X\6-31+G(d)\C3H8N1O3S1(1+)\UWILLE\04-
Nov-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcyc
le=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\1,1\
N,1.5159006647,0.4418817172,-0.5832754158\O,2.5497950585,1.4889115173,
-0.6071847737\O,0.4427629629,0.9348945316,-0.5410733766\O,1.8995948374
,-0.6820559105,-0.6192263177\S,4.1096088288,0.923753418,-0.5443753562\
C,4.665229438,1.3828671254,-2.1848713781\H,5.7450189704,1.2138318706,-
2.203652106\H,4.171095004,0.7145823321,-2.8915609281\H,4.4208024875,2.
4287021528,-2.3718037547\C,4.7729076661,2.2439124946,0.5105258309\H,5.
8495405077,2.0433753903,0.5153445261\H,4.5796470869,3.19072144,0.00070
84647\C,4.1625418749,2.1682418601,1.9016151544\H,4.6343988757,2.944787
3175,2.5084101868\H,3.0882784928,2.3614807428,1.876982197\H,4.35063490
39,1.20126779,2.3734261571\\Version=AM64L-G09RevB.01\HF=-797.1791131\R
MSD=0.000e+00\RMSF=2.030e-05\Dipole=2.9326837,0.8393038,-0.4936571\Qua
drupole=46.5112546,-23.8641663,-22.6470883,27.2804575,-10.4759671,-1.3
341007\PG=C01 [X(C3H8N1O3S1)]\\@
Sum of electronic and thermal Free Energies= -797.091900

Product complex 6 (x = 0)
1\1\GINC-SPARTAN-BM115\FOpt\RM062X\6-31+G(d)\C3H8N1O3S1(1+)\UWILLE\05-
Nov-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcyc
le=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\1,1\
N,4.8569121599,0.2111911255,-1.6911632886\O,0.5980793949,0.1765151775,
1.9128207263\O,4.177209017,0.2156422776,-2.5753772068\O,5.5315253314,0
.2076401799,-0.8029906307\S,1.8036566276,0.598571092,1.071954763\C,1.1
927377635,1.8362426973,-0.0920300514\H,2.0376576093,2.2715608049,-0.63
15802894\H,0.5288367239,1.3267515072,-0.7923958124\H,0.6445631139,2.60
40205669,0.4601468667\C,2.7758375018,1.7196041863,2.121981688\H,3.5575
418653,2.1482487193,1.4863585449\H,2.0976059449,2.5157836883,2.4475185
116\C,3.3587844613,0.95491532,3.3015844103\H,3.9202796706,1.6402247937
,3.9420571389\H,2.5642017354,0.5015828932,3.9005739258\H,4.0390486493,
0.1661146703,2.9659165335\\Version=AM64L-G09RevB.01\HF=-797.1276019\RM
SD=0.000e+00\RMSF=1.711e-05\Dipole=5.3398952,0.4611859,-5.1045115\Quad
rupole=57.658036,-30.4917314,-27.1663046,9.9613777,-24.3136068,1.49928
06\PG=C01 [X(C3H8N1O3S1)]\\@
Sum of electronic and thermal Free Energies= -797.045423

Intermediate 5 (x = 1)
1\1\GINC-SPARTAN-BM121\FOpt\RM062X\6-31+G(d)\C3H8N1O4S1(1+)\UWILLE\04-
Nov-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcyc
le=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\1,1\

N,3.9661741941,2.4630918248,-0.5193009851\O,2.7423448092,-1.103810774,
0.3062033424\O,4.9056392111,2.7124816687,-1.1776334984\O,3.1460739859,
3.1188732836,0.0403560072\C,1.0824343627,0.9247315948,-0.3116282299\H,
0.9992793126,2.0002556844,-0.1525593009\H,1.157945551,0.665063956,-1.3
705075873\H,0.2630250132,0.3844272881,0.1707135898\C,2.7372804265,0.89
068041,2.1372864089\H,2.6850815197,1.9818333008,2.1051012471\H,1.84062
14837,0.4998601635,2.6306991366\S,2.5609533673,0.321609066,0.451138006
4\O,3.8167981836,0.9905044713,-0.3832144196\C,4.0283461723,0.341835435
4,2.7340984692\H,4.0697070529,0.6897710419,3.7683326844\H,4.0325065589
,-0.749169079,2.7336778\H,4.9109026452,0.7149780437,2.2107081494\\Vers
ion=AM64L-G09RevB.01\HF=-872.3250261\RMSD=0.000e+00\RMSF=2.235e-05\Dip
ole=-2.1369419,0.4368684,1.1900024\Quadrupole=7.7872183,-8.870229,1.08
30107,11.2985031,13.006909,2.559577\PG=C01 [X(C3H8N1O4S1)]\\@
Sum of electronic and thermal Free Energies= -872.233224

TS 5 → 6 (x = 1)
1\1\GINC-SPARTAN-BM059\FTS\RM062X\6-31+G(d)\C3H8N1O4S1(1+)\UWILLE\05-N
ov-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(ts,noeigentest
,calcfc,maxcycle=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\g
eom&freq\\1,1\N,4.1173343491,-0.7850917772,-0.3213300225\O,4.624168344
5,3.4472160675,0.2969688044\O,3.5851071193,-0.7473605504,-1.3333676179
\O,4.5551741977,-1.36087315,0.5549237383\C,6.488365301,2.1724982109,-1
.8843460068\H,6.8538994667,3.0502792871,-1.3476031341\H,6.7880328339,1
.2686149228,-1.3493475098\C,2.4210844257,2.3455521327,-0.7422709663\H,
2.1263672554,1.491561493,-1.3549273729\H,1.9594492647,2.2990295534,0.2
466508732\H,2.1851415138,3.2863742015,-1.2430260609\C,4.9762188197,2.2
359432597,-2.0703471362\H,4.57332523,1.3625323451,-2.5920780947\H,4.65
2907794,3.1421200573,-2.5917664979\S,4.1719202983,2.298152358,-0.47606
45334\O,4.4855192707,0.9734254074,0.2394383479\H,6.9471016155,2.155133
2311,-2.8751301804\\Version=AM64L-G09RevB.01\HF=-872.3212388\RMSD=0.00
0e+00\RMSF=2.221e-05\Dipole=-1.412316,-1.7253778,-1.9085359\Quadrupole
=30.2652448,-15.7898162,-14.4754286,1.4426422,-27.0831562,-11.9104531\
PG=C01 [X(C3H8N1O4S1)]\\@
Frequencies -- -214.6960
Sum of electronic and thermal Free Energies= -872.229814

Product complex 6 (x = 1)
1\1\GINC-SPARTAN-BM111\FOpt\RM062X\6-31+G(d)\C3H8N1O4S1(1+)\UWILLE\04-
Nov-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcyc
le=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\1,1\
N,4.7120732061,0.0032965816,-1.242260128\O,0.8035889956,-0.0094108364,
1.7273387227\O,4.0542900953,-0.0068685411,-2.1429782482\O,5.4166049603
,0.0133808103,-0.3775233338\C,1.1058060043,1.8256283783,-0.1657379915\
H,1.8953766299,2.3737693731,-0.6820547167\H,0.5309354602,1.2196543936,
-0.8692077837\H,0.4501583876,2.4993816587,0.388054906\C,2.7978777933,1
.7127343989,2.1134770731\H,3.4943407786,2.289670809,1.498413465\H,2.07
79172091,2.3919723928,2.5782036547\C,3.5101116706,0.8349831706,3.13575
756\H,4.0792371741,1.4773936921,3.8112908063\H,2.792678544,0.260788103
7,3.7267700305\H,4.2051017514,0.1456062319,2.6496703112\S,1.8550188547
,0.6923561865,0.9815492045\O,2.8088895349,-0.1565997736,0.2285001077\\
Version=AM64L-G09RevB.01\HF=-872.3305054\RMSD=0.000e+00\RMSF=1.048e-05
\Dipole=3.4797611,1.6049614,-3.0454456\Quadrupole=45.8840503,-23.72178
29,-22.1622674,10.2707832,-12.6193487,4.9823268\PG=C01 [X(C3H8N1O4S1)]\\@
Sum of electronic and thermal Free Energies= -872.240481

Reaction of $NO_3^\bullet$ with EtSSEt (Figure S14)

CT complex

1\1\GINC-SPARTAN-BM121\FOpt\UM062X\6-31+G(d)\C4H10N1O3S2(2)\UWILLE\01-Feb-2021\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcycle=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\N,9.4491369978,-7.6688242339,2.4662651826\O,8.8653879995,-6.8621507787,3.2205230467\O,8.9731463573,-8.8022089662,2.2649986514\O,10.5115381262,-7.3230728301,1.8965017313\C,9.1995591034,-4.897165061,0.6886075767\H,9.3913638398,-5.1159692107,1.7418086517\H,8.94820568,-3.8424282999,0.5521546529\S,10.7631913007,-5.1787125485,-0.2207983636\C,13.6644053206,-4.8113609809,0.2171094127\H,13.5895503075,-4.2781383653,-0.732726636\H,13.7630312774,-5.8832916347,0.032296852\C,14.7957814183,-4.2757806463,1.0857403497\H,14.8504776202,-4.8006803683,2.0426982934\H,15.7370872203,-4.4377197048,0.5543433568\H,14.6865305828,-3.2042322259,1.2695548686\S,12.0920924228,-4.5609918476,1.1238245827\C,8.1363569984,-5.825539122,0.1169957279\H,7.2079188881,-5.6519946058,0.6679443183\H,7.9465261727,-5.626325954,-0.941086191\H,8.4194391364,-6.8746834453,0.2381134955\\Version=AM64L-G09RevB.01\HF=-1234.8271478\S2=0.75353\S2-1=0.\S2A=0.750009\RMSD=0.000e+00\RMSF=8.247e-06\Dipole=3.5593766,4.9697688,-3.5735018\Quadrupole=150.5171645,-125.8905018,-24.6266627,56.2806261,-58.4283023,54.9196477\PG=C01 [X(C4H10N1O3S2)]\\@

Sum of electronic and thermal Free Energies= -1234.719579

α-radical complex

1\1\GINC-SPARTAN-BM087\FOpt\UM062X\6-31+G(d)\C4H10N1O3S2(2)\UWILLE\28-Jan-2021\0\\#p M062X/6-31+G* nosymm opt=(calcfc,maxcycle=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\N,2.0480929071,4.1956083025,-0.1707672132\O,1.4457469707,3.1638399672,-0.3666063822\O,3.1695979673,4.1267630147,0.5842672788\O,1.7749114765,5.2991422518,-0.5657795473\C,2.4447738766,0.9813682833,2.0135824078\H,1.5613329998,0.9807227484,1.3673952503\H,2.5202153116,-0.0095311168,2.4840430565\S,3.8777970579,0.5534573969,-0.3092234036\C,3.6897366298,1.311618647,1.2479227914\H,4.6109639279,1.5442370648,1.7804853117\H,3.2949918147,3.1545509423,0.8075987026\H,2.2876812154,1.7136377051,2.811374711\C,5.5685082698,2.6602054091,-1.6955888099\H,4.7993153507,2.5394423015,-2.4620618758\H,5.2265291746,3.3892685027,-0.9571508514\C,6.8989720287,3.0842585468,-2.3062564237\H,7.2420091799,2.3610082381,-3.0517800492\H,6.7765969744,4.0526208885,-2.7998536747\H,7.6731349091,3.1902839507,-1.540433745\S,5.8072715375,1.0439489356,-0.862822044\\Version=AM64L-G09RevB.01\HF=-1234.8123994\S2=0.754438\S2-1=0.\S2A=0.750016\RMSD=9.490e-09\RMSF=4.879e-06\Dipole=0.9501024,-0.4541104,0.6961967\Quadrupole=9.2895459,-13.6466106,4.3570647,8.1985894,-0.3394421,0.7256295\PG=C01 [X(C4H10N1O3S2)]\\@

Sum of electronic and thermal Free Energies= -1234.706282

O-transfer complex

1\1\GINC-SPARTAN-BM089\FOpt\UM062X\6-31+G(d)\C4H10N1O3S2(2)\UWILLE\27-Jan-2021\0\\#p M062X/6-31+G* nosymm opt=(calcfc,maxcycle=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\N,1.1724272009,-0.4276027606,-1.390703577\O,2.5206582988,1.6662640844,-0.3219598449\O,0.6429781652,0.2616658686,-2.2001686199\O,2.1616500057,-1.0887677318,-1.387680478\S,3.9970546169,1.3361383024,-0.3553436492\C,4.8066426818,2.5597046055,0.7308404405\H,5.8809337708,2.362084486,0.6744115872\H,4.5

928401817,3.5517130372,0.321603647\C,4.2638684491,2.401775254,2.144373
4218\H,4.7461871981,3.1358496788,2.7952421935\H,3.1855809638,2.5776284
188,2.1687708418\H,4.4691872934,1.4040111218,2.5433265724\C,4.17098041
36,0.8009749063,-3.2621453968\H,3.0786674174,0.8407999582,-3.223590875
1\H,4.5072598262,-0.1753308817,-2.9040026156\C,4.6701863241,1.06902831
59,-4.6772905206\H,5.7620349381,1.0290903564,-4.7259768911\H,4.2690057
704,0.3066995758,-5.3511516079\H,4.3394698879,2.0482355617,-5.03521143
79\S,4.8330423463,2.0930532524,-2.1450446001\\Version=AM64L-G09RevB.01
\HF=-1234.8356877\S2=0.754905\S2-1=0.\S2A=0.750014\RMSD=4.503e-09\RMSF
=3.973e-06\Dipole=1.5641119,-0.2386234,0.1300767\Quadrupole=10.1649765
,-9.8503555,-0.314621,4.9914175,0.2138512,4.8747234\PG=C01 [X(C4H10N1O3S2)]\\@

Sum of electronic and thermal Free Energies= -1234.730064

TS_{α}

1\1\GINC-SPARTAN-BM103\FTS\UM062X\6-31+G(d)\C4H10N1O3S2(2)\UWILLE\27-J
an-2021\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(ts,noeigentest
,calcfc,maxcycle=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\g
eom&freq\\0,2\N,3.2789727775,3.0874396868,1.9158707539\O,2.456988466,2
.5263124849,1.1985801446\O,4.2110967925,2.3681664269,2.4776075816\O,3.
2871586488,4.2865665368,2.1449061239\C,2.8354916246,-0.6833552257,1.97
68442288\H,1.9775224639,-0.1946340119,1.5068491792\H,2.8004435528,-1.7
546733882,1.7526401286\S,4.2550303548,0.1718179335,-0.2016280992\C,4.1
380001393,-0.0663718075,1.5163234078\H,5.0504463047,-0.4760642451,1.96
07716046\H,4.1577006049,1.1578854175,1.9603575141\H,2.7492909165,-0.55
82132294,3.0599377217\S,6.2688858985,0.4392217162,-0.4988241632\C,6.24
48169511,2.0131238593,-1.4425720562\H,5.6243962796,1.8779118096,-2.331
0722242\H,5.8060558548,2.7828570539,-0.8038964189\C,7.6825158688,2.349
9278131,-1.8194463479\H,8.1216201422,1.5718864111,-2.4500785824\H,7.68
95263506,3.2884757106,-2.3804403492\H,8.307687458,2.4791471176,-0.9314
574575\\Version=AM64L-G09RevB.01\HF=-1234.8006293\S2=0.753898\S2-1=0.\
S2A=0.750012\RMSD=0.000e+00\RMSF=9.226e-06\Dipole=1.5784757,-2.4633492
,-1.6446742\Quadrupole=24.4710158,-20.8918943,-3.5791215,-8.1025121,-1
5.7329014,-17.3894515\PG=C01 [X(C4H10N1O3S2)]\\@
Frequencies -- -1199.0372
Sum of electronic and thermal Free Energies= -1234.698618

Reaction of $NO_3^{\bullet}$ with Ac-Met-OMe (Figure S15)

Reactant complex

1\1\GINC-SPARTAN-BM103\FOpt\UM062X\6-31+G(d)\C8H15N2O6S1(2)\UWILLE\14-
Oct-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcyc
le=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\
C,-0.9362443289,2.9068702392,5.7567215324\H,-0.9606219488,3.93834393,5
.388186753\C,-1.8301385371,2.0474890485,4.8705382258\H,-2.0719439012,2
.1021749998,7.3358809313\C,-1.4322227285,3.9773872254,7.9036420192\O,-
2.7049410804,1.3253942226,5.2954203214\O,-1.5013747125,2.1669557769,3.
5931575805\C,-2.2404284824,1.3472626488,2.6665820016\H,-3.3077087002,1
.5621327455,2.748816102\H,-1.8676470437,1.6138311691,1.6798698537\H,-2
.054092247,0.2936011655,2.879415471\O,-0.8023381243,4.9866686129,7.586
6321654\N,-1.4692481135,2.8832453752,7.0997446167\N,-4.2163117116,1.15
91755944,0.3091308733\O,-3.6157857544,1.9347491549,-0.4645527966\O,-3.
7815498614,0.0022589215,0.4948442607\O,-5.2423057782,1.5440306542,0.90
96121972\C,0.5070044882,2.3719327413,5.6706020663\H,0.8336207403,2.419

5015882,4.6282907827\H,0.5194187193,1.3239963107,5.9901058842\S,3.1113
953034,2.5518694796,6.4854363748\C,4.0364498349,3.8353381405,7.3100586
771\H,3.5570922612,4.0660934386,8.265352117\H,5.0544060249,3.475847951
1,7.454337333\H,4.030999701,4.7251093891,6.6714274886\C,1.4338060678,3
.1984666253,6.5549991008\H,1.1425489653,3.1551863716,7.6134322043\H,1.
4735072913,4.2553307814,6.265327209\C,-2.187094685,3.8783298476,9.2058
677576\H,-1.5056424295,4.1166788578,10.0258511421\H,-2.9829800144,4.62
83161231,9.201067954\H,-2.6248734645,2.8927959399,9.3728303697\\Versio
n=AM64L-G09RevB.01\HF=-1272.3915241\S2=0.753877\S2-1=0.\S2A=0.750012\R
MSD=0.000e+00\RMSF=6.530e-06\Dipole=12.5079899,2.567835,11.4450639\Qua
drupole=-76.1100506,-37.6489346,113.7589851,47.7521012,68.8471042,59.8
146082\PG=C01 [X(C8H15N2O6S1)]\\@
Sum of electronic and thermal Free Energies= -1272.199954

CT complex (pre-reaction complex)
1\1\GINC-SPARTAN-BM116\FOpt\UM062X\6-31+G(d)\C8H15N2O6S1(2)\UWILLE\03-
Oct-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcyc
le=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\
C,-2.2786164187,1.3835767151,2.8062671316\H,-2.1199877903,2.4672112254
,2.7700133474\C,-3.5697419034,1.0593049825,2.0681651191\H,-3.085278316
4,0.2445334947,4.386129559\C,-1.9334330166,1.7381353113,5.2088745814\O
,-4.4750145472,0.4054864717,2.5375303528\O,-3.5627797929,1.5597170627,
0.8387557388\C,-4.7254395942,1.2882624965,0.0389912338\H,-5.6105478704
,1.7113279667,0.5171254699\H,-4.5380592696,1.7684697158,-0.9186377014\
H,-4.847190122,0.210919395,-0.0855420028\O,-1.2247045652,2.7241460725,
5.0053851098\N,-2.4313879336,0.9937536725,4.1895731859\N,1.0052930807,
2.2666521718,-0.3938484627\O,1.2535747738,1.0201106492,-0.2126613615\O
,0.8769292753,3.0054120949,0.5874968873\O,0.9020207679,2.6705784215,-1
.5495212766\C,-1.0974302072,0.6810252681,2.1099842156\H,-1.060860814,1
.0027636016,1.0651362043\H,-1.2617339541,-0.4032036231,2.1297380714\S,
1.5909691979,0.1668116634,2.0099469623\C,2.9532090576,1.2841355586,2.3
569752161\H,3.0796216359,1.3531529533,3.4407977639\H,3.8497990673,0.86
62936383,1.8994542823\H,2.7167254901,2.2642515461,1.9368441472\C,0.213
5611068,1.0354209935,2.8013745091\H,0.2215250419,0.7128058857,3.848903
0432\H,0.4177147794,2.1065646525,2.7516395336\C,-2.279579712,1.2764722
929,6.6037518271\H,-1.3510753203,1.0818054497,7.1464873235\H,-2.805093
9102,2.0859082794,7.1169728913\H,-2.8994030864,0.3782867301,6.61750764
75\\Version=AM64L-G09RevB.01\HF=-1272.4131457\S2=0.755942\S2-1=0.\S2A=
0.750026\RMSD=0.000e+00\RMSF=4.770e-06\Dipole=-0.2110144,-2.6605728,2.
9681324\Quadrupole=13.4838126,-24.0728411,10.5890285,-3.3014292,9.1212
91,-4.2716142\PG=C01 [X(C8H15N2O6S1)]\\@
Sum of electronic and thermal Free Energies= -1272.216103

TS_{α}
1\1\GINC-SPARTAN-BM114\FTS\UM062X\6-31+G(d)\C8H15N2O6S1(2)\UWILLE\09-O
ct-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(ts,noeigentest
,calcfc,maxcycle=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\g
eom&freq\\0,2\C,-0.5556005409,-0.5852832255,0.3591947562\H,-0.30049432
86,0.2423937857,-0.6099618351\C,-1.5555784209,-1.5535824044,-0.2066503
169\H,-2.1745603742,0.0395813674,1.462265442\C,-0.6279183131,1.3628621
026,1.8798721555\C,-1.5309136225,2.0813787547,2.840037068\H,-0.9704995
005,2.8735076868,3.3351400575\H,-2.3661133288,2.5226832013,2.284825565
1\H,-1.9395003583,1.3896596599,3.5822177027\O,-2.7445358283,-1.5086361
962,0.0447586135\O,-0.9939786095,-2.4288144475,-1.029424286\C,-1.88481

31728,-3.369355173,-1.6529957371\H,-2.6147191543,-2.8364898917,-2.2646
604713\H,-1.2515782278,-4.0022941693,-2.269969902\H,-2.3955322058,-3.9
572603292,-0.8886549753\O,0.4697755926,1.7453665321,1.5325141336\N,-1.
1651229146,0.1705282014,1.3660072939\N,-0.6580034512,2.1747024941,-1.4
681457981\O,-1.646893763,2.1531564364,-0.73758228\O,0.0730868987,1.105
1184169,-1.5617408295\O,-0.3177771922,3.1486186031,-2.1228418961\C,0.8
134660473,-1.1419033557,0.7025653179\H,1.4851530303,-0.3260938781,0.97
13652267\H,1.2276172432,-1.6558769827,-0.1684556467\C,0.7241251049,-2.
1576371485,1.8694411042\H,1.7411686185,-2.492670808,2.093116673\H,0.13
16225051,-3.0325299608,1.58616471\S,0.0406997987,-1.4617852815,3.39039
36012\C,-1.5362169593,-2.3499335307,3.5132296629\H,-1.3521308297,-3.40
5962518,3.7197674882\H,-2.0915728975,-1.9067347614,4.341568546\H,-2.11
42608454,-2.2460901801,2.592025856\\Version=AM64L-G09RevB.01\HF=-1272.
3869407\S2=0.755871\S2-1=0.\S2A=0.750028\RMSD=0.000e+00\RMSF=2.400e-06
\Dipole=-0.8525199,-4.7625479,3.2508321\Quadrupole=-3.3607524,-1.87301
75,5.2337699,1.6989351,-7.6700812,7.6834619\PG=C01 [X(C8H15N2O6S1)]\\@
Frequencies -- -1546.2564
Sum of electronic and thermal Free Energies= -1272.192709

α-radical complex
1\1\GINC-SPARTAN-BM096\FOpt\UM062X\6-31+G(d)\C8H15N2O6S1(2)\UWILLE\05-
Oct-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcyc
le=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\
C,-0.0465453564,-0.3349204012,-0.2703802912\H,2.600775919,0.8489207673
,3.0096496823\C,-1.2323704594,-0.5812210095,-1.0786993685\H,-1.3673748
658,0.1577167374,1.1651314124\C,0.4606074399,0.4255109215,2.0298250578
\O,-2.3729827712,-0.448615741,-0.6468018953\O,-0.9513270668,-0.9618311
804,-2.3295053757\C,-2.0834161826,-1.2185006711,-3.1694740178\H,-2.687
3076345,-0.314652586,-3.2710256418\H,-1.6698561863,-1.514635935,-4.131
2976889\H,-2.6891778972,-2.0224748354,-2.7467496598\O,1.6948363659,0.3
66979378,1.9102474917\N,-0.3634183797,0.0947672551,0.9997870518\N,3.19
41625469,2.4324841163,3.9186815847\O,3.9617676977,2.9042333325,4.72342
40204\O,3.2878400554,1.1119814069,3.7394307279\O,2.3580283014,3.034665
3346,3.2725788208\C,1.3473911261,-0.4646461536,-0.7845492771\H,1.32076
57998,-1.0949268351,-1.6761660184\H,1.9792946767,-0.9495771928,-0.0365
694644\C,-0.1960584298,0.8839427844,3.2998890958\H,0.2609200921,0.3591
707698,4.142752542\H,-0.00055267,1.9542640021,3.4205863042\H,-1.272972
6634,0.7130721576,3.3092476711\S,3.665821367,0.6894467342,-1.682602934
7\C,4.0759868471,2.4291210709,-1.9933808056\H,3.9831142905,3.015791247
4,-1.0762103722\H,5.1114417488,2.4659866217,-2.3372871483\H,3.42750930
84,2.8461881658,-2.7674588087\C,1.9394530995,0.9065279029,-1.145152352
2\H,1.922034932,1.5702046113,-0.2759531729\H,1.363224579,1.365189473,-
1.9556937092\\Version=AM64L-G09RevB.01\HF=-1272.428127\S2=0.757629\S2-
1=0.\S2A=0.750045\RMSD=0.000e+00\RMSF=6.172e-06\Dipole=-2.5818242,-0.7
787294,-1.6004559\Quadrupole=-10.7636165,5.2402581,5.5233583,-4.683522
,-16.3340216,-11.5912325\PG=C01 [X(C8H15N2O6S1)]\\@
Sum of electronic and thermal Free Energies= -1272.234166

TS_{γ}
1\1\GINC-SPARTAN-BM093\FTS\UM062X\6-31+G(d)\C8H15N2O6S1(2)\UWILLE\15-O
ct-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(ts,noeigentest
,calcfc,maxcycle=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\g
eom&freq\\0,2\C,2.349414153,-0.6922821451,3.3253139591\H,1.6690627934,
-0.0619383655,3.9097021328\C,1.5706083004,-1.8898203849,2.8011714537\H

,3.7397090009,-2.1109320218,4.0279872869\C,3.7444395189,-0.5288440129,
5.3428246707\O,1.9267316927,-3.040858035,2.9264746766\O,0.4689823052,-
1.5084752667,2.165546415\C,-0.3244209148,-2.5581878168,1.5882799481\H,
-0.6691709341,-3.2357244388,2.3712045336\H,-1.1651963083,-2.0584565717
,1.1126514557\H,0.2656580983,-3.1073201681,0.8525366391\O,3.2729725296
,0.5689849956,5.6386764836\N,3.3937014286,-1.1739387513,4.2023090523\N
,0.582342067,2.8477124941,3.0733424222\O,0.6619446075,2.3811075792,1.9
382034374\O,1.5208301397,2.5728071328,3.9271882634\O,-0.337620962,3.55
7996837,3.4540055611\C,2.9028362235,0.1177204356,2.1377197962\H,2.0892
304066,0.3304282145,1.437798546\H,3.6564114649,-0.4894357388,1.6201499
236\C,4.7501250543,-1.2320991569,6.2225763308\H,4.2625344167,-1.489503
6805,7.1670799373\H,5.1551917472,-2.1397142922,5.7714036583\H,5.566832
1584,-0.5409790603,6.4432008524\C,4.9818347902,3.705061557,2.222281367
4\H,5.8993287327,3.2069919968,2.5408573872\H,5.2119399701,4.5110170148
,1.5254643053\H,4.4440897202,4.1018778589,3.0863271294\C,3.5171921596,
1.4230422987,2.61317784\H,4.2939886731,1.3377405149,3.3798461031\H,2.5
789824877,2.0117745887,3.2436410247\S,3.9223494788,2.5283513889,1.3531
974074\\Version=AM64L-G09RevB.01\HF=-1272.3931583\S2=0.754155\S2-1=0.\
S2A=0.750012\RMSD=0.000e+00\RMSF=5.106e-06\Dipole=3.9400594,-1.6963008
,-1.7444574\Quadrupole=37.850159,-9.6698146,-28.1803444,17.9529257,16.
8239745,-18.7246022\PG=C01 [X(C8H15N2O6S1)]\\@
Frequencies -- -767.9404
Sum of electronic and thermal Free Energies= - -1272.201980

γ-radical complex
1\1\GINC-SPARTAN-BM095\FOpt\UM062X\6-31+G(d)\C8H15N2O6S1(2)\UWILLE\05-
Oct-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcyc
le=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\
C,-0.0996118812,0.8942963903,0.4571609803\H,-0.0310637867,1.8892805515
,0.9035203122\C,-1.536677409,0.6321104727,0.0371884147\H,-0.1678057171
,-0.9981660829,1.3872593089\C,0.9706751292,0.2122212038,2.5624768758\O
,-2.1610617356,-0.3656261959,0.3261348931\O,-2.0031339112,1.6161917027
,-0.722419855\C,-3.3387170925,1.4467971468,-1.2254290345\H,-4.04082153
76,1.3662404338,-0.3939158696\H,-3.5420710971,2.336807176,-1.816493244
9\H,-3.3898856841,0.5501527715,-1.8452717534\O,1.4570479812,1.33875344
06,2.7698197775\N,0.2608475138,-0.0816592857,1.4640524533\N,2.28469580
6,4.0674264437,0.9065178952\O,2.9900083997,4.9576777544,0.4979380857\O
,2.8721325515,3.2220680003,1.7598103722\O,1.1191888172,3.871852916,0.6
247962599\C,0.820981815,0.8373184559,-0.7851699377\H,0.5131183066,1.64
0416335,-1.4637331484\H,0.6395504412,-0.1169019159,-1.3056476587\C,1.1
588151063,-0.8874200749,3.5727939038\H,2.2301963937,-1.0488556032,3.71
56818975\H,0.7396662002,-0.5538337871,4.5256395163\H,0.6863213992,-1.8
250638347,3.2770394281\S,3.275499596,1.9770927716,-1.4058447076\C,4.86
68896829,1.7916696253,-0.5562702522\H,5.1687965389,0.7423863288,-0.543
4133226\H,5.6005500749,2.3720270557,-1.1180985004\H,4.7925388499,2.179
8689252,0.4613802309\C,2.2625745638,0.9791715462,-0.4192238638\H,2.745
9535962,0.2215702608,0.192857137\H,2.1971070886,2.4994900716,2.0032264
063\\Version=AM64L-G09RevB.01\HF=-1272.4161483\S2=0.755123\S2-1=0.\S2A
=0.750022\RMSD=0.000e+00\RMSF=6.581e-06\Dipole=-0.8506878,-2.9043478,0
.0764358\Quadrupole=11.0278753,-18.392482,7.3646067,-17.6430823,3.1698
965,-7.2072782\PG=C01 [X(C8H15N2O6S1)]\\@
Sum of electronic and thermal Free Energies= -1272.219528

TS_{ϵ}

1\1\GINC-SPARTAN-BM117\FTS\UM062X\6-31+G(d)\C8H15N2O6S1(2)\UWILLE\08-O
ct-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(ts,noeigentest
,calcfc,maxcycle=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\g
eom&freq\\0,2\C,1.7430286139,3.4742692128,4.514725752\H,2.3159486161,4
.2248355762,5.0709379532\C,0.4814171156,3.146737796,5.3005417702\H,2.0
51089992,1.3890750392,4.4659399362\C,3.8964996152,2.2980899871,4.50743
03886\O,0.137956155,2.0237410979,5.5983961853\O,-0.2080726838,4.243978
9267,5.5894405191\C,-1.4441613426,4.0470107039,6.2953532379\H,-1.25008
95746,3.5708206381,7.2578693373\H,-1.8610398668,5.0418093806,6.4343533
796\H,-2.1157653859,3.4260191746,5.700277407\O,4.5252531471,3.35500850
32,4.5638219616\N,2.5431225996,2.2741666387,4.4153867328\N,2.097744183
6,8.4053347052,2.7605555628\O,1.8279464202,7.2626508431,3.1236843312\O
,2.7726909214,8.5669558942,1.6586816223\O,1.7724892449,9.410974094,3.3
690467297\C,1.354720734,4.0575419247,3.1430214205\H,0.7418142864,4.949
1301355,3.304805817\H,0.7548352105,3.320185259,2.5958681802\C,4.586116
4726,0.9554091782,4.5278220412\H,5.0539252001,0.8205416144,5.507100679
5\H,3.9061274671,0.122813171,4.3392617192\H,5.3769240452,0.9559920181,
3.7741887488\S,2.1126371735,5.1646207249,0.7538569073\C,3.3630930767,6
.3017121367,0.4769920812\H,4.3315460663,6.0473900061,0.9123808456\H,3.
4011095463,6.6230228292,-0.5644062487\H,3.0217229259,7.3984837987,1.12
03448756\C,2.5988660001,4.4280782528,2.3444472522\H,3.2158305731,3.552
8259848,2.1188856807\H,3.2048404512,5.1669907543,2.873182193\\Version=
AM64L-G09RevB.01\HF=-1272.3923914\S2=0.753979\S2-1=0.\S2A=0.750011\RMS
D=0.000e+00\RMSF=1.618e-06\Dipole=-0.5131357,-3.7118608,-1.4178357\Qua
drupole=31.7160308,-56.1707636,24.4547329,-21.9133675,-17.5874298,-36.
2993262\PG=C01 [X(C8H15N2O6S1)]\\@
Frequencies -- -1107.1734
Sum of electronic and thermal Free Energies= -1272.200445

ε-radical complex
1\1\GINC-SPARTAN-BM097\FOpt\UM062X\6-31+G(d)\C8H15N2O6S1(2)\UWILLE\06-
Oct-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcyc
le=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\
C,1.5914657795,0.8363145366,-0.3633989038\H,1.3633951686,1.7448109303,
0.2010125561\C,0.3388733439,0.3973836252,-1.1066776424\H,1.7473550554,
-1.1628553794,0.2922577649\C,2.3765008695,0.0231686584,1.8229354663\O,
-0.0932310985,-0.7342712515,-1.10026696\O,-0.1934198453,1.4036088194,-
1.788795142\C,-1.357881094,1.0921530357,-2.571873095\H,-2.1531727241,0
.7234363699,-1.9219883615\H,-1.6483288812,2.0275152254,-3.0447396107\H
,-1.1095648282,0.3395138625,-3.3221910109\O,2.5764035141,1.1684438242,
2.2636786318\N,1.9463561014,-0.2088608549,0.5752414731\N,2.5240957506,
4.4640522418,1.405506222\O,2.8023510131,5.633218475,1.4926633453\O,3.2
110631866,3.6491593246,2.217123535\O,1.7041404082,3.9605032449,0.66154
24472\C,2.7131325054,1.125056735,-1.3788970042\H,2.3496269607,1.878201
6618,-2.0858376539\H,2.925961395,0.2080717591,-1.9424416578\C,2.624570
7829,-1.1753255956,2.6983184377\H,3.6779520694,-1.1785719313,2.9901981
81\H,2.0250180365,-1.0703744627,3.6059035469\H,2.3820032873,-2.1190927
901,2.2083071284\S,5.2791046034,1.9023656652,-1.9364576295\C,6.5836354
493,2.3911184803,-0.9281388854\H,6.5842038675,2.132625708,0.1245523643
\H,7.5021188377,2.6834064311,-1.4204326511\H,2.8642556254,2.7049052602
,2.0820175146\C,3.9783054632,1.6219201993,-0.6912384555\H,4.3506666141
,0.8899069438,0.0320227988\H,3.7921843426,2.5674181677,-0.1746041496\\
Version=AM64L-G09RevB.01\HF=-1272.4061304\S2=0.755732\S2-1=0.\S2A=0.75
0024\RMSD=0.000e+00\RMSF=6.953e-06\Dipole=-0.8097304,-2.9266244,-0.473

4824\Quadrupole=7.1254411,-18.3199777,11.1945366,-20.5779583,3.7991207
,-11.3475413\PG=C01 [X(C8H15N2O6S1)]\\@
Sum of electronic and thermal Free Energies= -1272.212971

O-transfer complex
1\1\GINC-SPARTAN-BM104\FOpt\UM062X\6-31+G(d)\C8H15N2O6S1(2)\UWILLE\29-
Oct-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm geom=checkpoint gu
ess=check opt=(readfc,maxcycle=500) freq=noraman scrf=(cpcm,solvent=ac
etonitrile)\\geom&freq\\0,2\C,-0.9280018223,2.9947890923,6.2087005889\
H,-1.3899129464,3.9850296171,6.2777093121\C,-1.1975151105,2.4129695656
,4.8321506275\H,-1.7191981084,1.1624210013,6.9095976769\C,-1.860072549
7,2.5597916465,8.4256544518\O,-1.4456187191,1.2436746136,4.6307576073\
O,-1.0928734613,3.3320985913,3.8791461217\C,-1.2503999215,2.8652216292
,2.528465871\H,-2.2399305347,2.4233019585,2.4006760209\H,-1.137722546,
3.748971101,1.9030682553\H,-0.480066734,2.1264514123,2.2986648479\O,-1
.6419132979,3.721044852,8.775932705\N,-1.5448762924,2.1224709094,7.184
3085378\N,-1.2625616902,3.0141739268,-1.0423382391\O,-0.9844306855,4.1
42105674,-0.7920401967\O,-1.5569600724,2.0683106939,-0.3850975813\C,0.
5890792213,3.1184312786,6.4694381435\H,1.0533522615,2.1343168229,6.341
3938516\H,0.6932172991,3.4043831891,7.5221357331\C,3.5536897555,5.4106
322869,4.7795394107\H,3.018122713,6.3588868638,4.8674575622\H,4.624441
1996,5.5764375492,4.9099003749\H,3.3586748823,4.9367963192,3.814244254
1\C,1.2826452665,4.1466132466,5.5841569217\H,0.8306028348,5.1394462814
,5.6876553125\H,1.2857271293,3.8573410238,4.5287839795\C,-2.4954563397
,1.5518854659,9.3529368543\H,-1.8823395276,1.4730108701,10.254257041\H
,-3.480196729,1.9233779141,9.6485025925\H,-2.604730462,0.5633815426,8.
9034939335\S,3.0225597773,4.2955300512,6.0973989665\O,3.6594958207,2.9
419075199,5.7845272115\\Version=AM64L-G09RevB.01\HF=-1272.4196577\S2=0
.754858\S2-1=0.\S2A=0.750014\RMSD=0.000e+00\RMSF=1.594e-06\Dipole=-1.1
764395,1.0229235,-1.9018147\Quadrupole=0.2594795,23.2895947,-23.549074
2,7.3919558,-13.4670985,-11.1820671\PG=C01 [X(C8H15N2O6S1)]\\@
Sum of electronic and thermal Free Energies= -1272.229711

Reaction of $NO_3^\bullet$ with Ac-MetO-OMe (Figure S15)

Reactant complex
1\1\GINC-SPARTAN-BM113\FOpt\UM062X\6-31+G(d)\C8H15N2O7S1(2)\UWILLE\22-
Oct-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcyc
le=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\
C,-1.0291360329,2.8653277877,5.8180407141\H,-0.9625527985,3.9117272238
,5.4989305871\C,-1.9616940918,2.1325450334,4.8592822599\H,-2.295061207
8,2.0953751714,7.3130811129\C,-1.494973687,3.8654139586,8.0016795268\O
,-2.9408776483,1.5143621638,5.2134957044\O,-1.5518518035,2.2499940176,
3.6059199246\C,-2.3627455365,1.5983107939,2.6086053574\H,-3.3756054299
,2.0050378433,2.6355924766\H,-1.8852203663,1.816677722,1.6558231121\H,
-2.3854109571,0.5236804593,2.7957270543\O,-0.7563491883,4.8197402966,7
.7562068227\N,-1.6078484379,2.8213241231,7.1404185691\N,-4.0384270289,
2.1694258568,0.098021587\O,-3.1217396259,2.76056299,-0.5109707063\O,-4
.0259721898,0.9229746896,0.1871498305\O,-4.9581054532,2.823819456,0.63
39178942\C,0.3750866018,2.2291549259,5.7481635528\H,0.7335493595,2.280
0507181,4.7169878129\H,0.3093113486,1.1777592821,6.0473757609\C,4.1441
767973,3.3843959008,7.3664070965\H,3.7963428964,3.5555491154,8.3868912
21\H,5.1171814377,2.8915565212,7.358804893\H,4.1470503061,4.3022512828
,6.774842118\C,1.316959046,2.9859772869,6.673208799\H,1.0370661225,2.9

185345465,7.7277922871\H,1.4533549395,4.0361311231,6.3922750093\S,2.98
29480978,2.247498567,6.6030850501\O,3.3807449067,1.9373487625,5.196711
4966\C,-2.3129317838,3.7841714348,9.2659610099\H,-1.6729847291,4.02653
20777,10.1168061355\H,-3.1041205688,4.537801179,9.2124571417\H,-2.7665
996646,2.8031932896,9.4173135182\\Version=AM64L-G09RevB.01\HF=-1347.54
55696\S2=0.756501\S2-1=0.\S2A=0.750014\RMSD=0.000e+00\RMSF=9.453e-06\D
ipole=11.6413795,0.4158849,12.6134302\Quadrupole=-75.4053682,-54.98125
2,130.3866202,55.2438961,64.6827967,57.4836547\PG=C01 [X(C8H15N2O7S1)]\\@
Sum of electronic and thermal Free Energies= -1347.348408

CT complex (pre-reaction complex)
1\1\GINC-SPARTAN-BM113\FOpt\UM062X\6-31+G(d)\C8H15N2O7S1(2)\UWILLE\23-
Oct-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcyc
le=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\
C,-1.7097671197,-0.3481624384,1.0047306322\O,-1.4115290294,0.778591862
6,1.3321076197\O,-5.6338410485,-4.4214776426,1.4250719017\O,-5.0647399
562,-5.8630282409,2.9274329149\O,-3.8070021225,-5.566380295,1.19262621
71\N,-4.8235682366,-5.2992065775,1.8598651022\C,-2.6100986999,-1.26355
46396,1.8184668665\H,-2.0754654166,-2.20370931,2.0046745197\H,-2.64061
99529,0.3635122898,3.1668551026\C,-3.3123445611,-1.3319040266,4.148491
629\C,-3.5299951809,-0.564816409,5.4293540622\H,-4.5960258609,-0.58839
34479,5.6717951317\H,-2.9909650163,-1.0692097727,6.2346517325\H,-3.201
3581855,0.4740578269,5.3672576041\N,-2.8764076266,-0.6187329044,3.0819
227706\O,-3.532143531,-2.5407974252,4.0623939719\C,-0.4777184387,-0.14
64656162,-0.985733636\H,0.4373781223,0.1326527374,-0.4614158344\H,-0.2
563257961,-0.7869845815,-1.8361802663\H,-1.0162658475,0.7480516218,-1.
3023031798\O,-1.3118243889,-0.9349992988,-0.1183401689\C,-3.9278936776
,-1.5793629453,1.0737371071\H,-4.6148037895,-1.9835596785,1.8230157668
\H,-4.3558670658,-0.6571091689,0.6674088971\C,-3.7261493594,-2.6224403
038,-0.0196627329\H,-3.1523029406,-2.2658081224,-0.8787506596\H,-3.305
3355189,-3.5563616877,0.3685548144\C,-5.0728741948,-4.6326361588,-1.62
46735193\H,-6.0536324675,-4.9640658682,-1.9678994308\H,-4.4132768735,-
4.3939522547,-2.4616885126\H,-4.6238272721,-5.3458709412,-0.9301276301
\S,-5.329563153,-3.1241324516,-0.6897701796\O,-5.8704722337,-2.0477821
612,-1.5788781638\\Version=AM64L-G09RevB.01\HF=-1347.5632259\S2=0.7570
96\S2-1=0.\S2A=0.750022\RMSD=0.000e+00\RMSF=4.149e-06\Dipole=1.4194552
,3.2477215,-4.2308243\Quadrupole=4.9462885,-22.3787863,17.4324978,-29.
3331769,34.5759118,50.1509455\PG=C01 [X(C8H15N2O7S1)]\\@
Sum of electronic and thermal Free Energies= -1347.362992

TS_{α}
1\1\GINC-SPARTAN-BM107\FTS\UM062X\6-31+G(d)\C8H15N2O7S1(2)\UWILLE\18-N
ov-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(ts,noeigentest
,calcfc,maxcycle=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\g
eom&freq\\0,2\C,-1.313635036,0.0899213589,0.9789179134\H,-1.2877005452
,1.0069488673,0.2211645403\C,-2.3879636125,-0.8322583872,0.4411166815\
H,-2.7353010185,0.4643734964,2.4324244218\C,-1.1113807091,1.7631000725
,2.8081649453\C,-1.7790290759,2.2192737847,4.0652264978\H,-1.981224388
4,1.3660926671,4.716859807\H,-1.1340403612,2.937991891,4.5694030536\H,
-2.7283766402,2.7021316648,3.8077345711\O,-3.4891597408,-0.9288964173,
0.9410614715\O,-1.9782457336,-1.4791765091,-0.6344463374\C,-2.94136819
29,-2.3547279854,-1.2522234905\H,-3.8205650532,-1.7813901541,-1.548555
4016\H,-2.4365219452,-2.7709176769,-2.1204211889\H,-3.2230132066,-3.14
17525579,-0.5508348679\O,-0.1500037852,2.2613695741,2.2772131171\N,-1.

7627763745,0.6611014467,2.1713762403\N,-2.1017506128,3.121295835,-0.17
40195857\O,-2.8324959001,2.7635449103,0.7615182558\O,-1.2886811425,2.2
753995537,-0.6837977621\O,-2.1296791759,4.2583287618,-0.6320840412\C,0
.1222485418,-0.4695177204,0.9743091032\H,0.7794083088,0.2597831843,1.4
483353847\H,0.4307604864,-0.5656838331,-0.0699262278\C,0.2809831965,-1
.8425328093,1.6224944653\H,1.3099739312,-2.180387877,1.4788109732\H,-0
.3850295248,-2.593001373,1.1862158571\C,-1.6503227059,-2.5182275298,3.
5218826005\H,-1.6281705419,-3.5517757389,3.1674534195\H,-1.9537730783,
-2.4913550822,4.5699653696\H,-2.33439917,-1.9172865641,2.9179064801\S,
0.0253483548,-1.8466536424,3.453138065\O,-0.0983055484,-0.3780612104,3
.8794206684\\Version=AM64L-G09RevB.01\HF=-1347.5382716\S2=0.75848\S2-1
=0.\S2A=0.750056\RMSD=0.000e+00\RMSF=1.024e-05\Dipole=-0.0506868,-6.32
36663,1.6237125\Quadrupole=-1.2563616,-10.439852,11.6962136,16.7282393
,-9.7633817,-0.3577462\PG=C01 [X(C8H15N2O7S1)]\\@
Frequencies -- -354.4002
Sum of electronic and thermal Free Energies= -1347.339589

α-radical complex
1\1\GINC-SPARTAN-BM090\FOpt\UM062X\6-31+G(d)\C8H15N2O7S1(2)\UWILLE\23-
Oct-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm freq=noraman opt=(
calcfc,z-matrix,maxcycle=500) scrf=(cpcm,solvent=acetonitrile)\\geom&f
req\\0,2\C,-1.1315758954,-0.4428633408,0.6337106571\H,0.583849127,1.67
79064944,-0.0238494338\C,-2.0301947313,-1.2480762631,-0.1839110723\H,-
2.7764750655,0.5178811398,1.3498950305\C,-1.2012779688,1.7863192827,1.
6560652553\C,-2.0417214214,2.6825126962,2.5168666118\H,-1.7742499898,2
.5009125191,3.5634534249\H,-1.8142988206,3.7219937606,2.2778535929\H,-
3.1100510095,2.4943202232,2.3973276144\O,-3.2043150144,-0.9660463028,-
0.3721865012\O,-1.4245743479,-2.3220550903,-0.7038456978\C,-2.24978491
08,-3.1696097305,-1.5128402216\H,-2.6004450615,-2.6223863424,-2.390222
6058\H,-1.6134065517,-4.0009764089,-1.808482466\H,-3.1037719282,-3.524
4334855,-0.9326716793\O,-0.0391254642,2.0909450323,1.3463881838\N,-1.7
655207415,0.6117041952,1.26736644\N,0.1045814551,1.4878022724,-1.86369
78527\O,-1.0263412773,1.7797591292,-1.5297404911\O,1.0441135739,1.4402
757789,-0.9072111657\O,0.4892877085,1.225416155,-2.977044502\C,0.23648
95769,-0.905652933,1.0377035878\H,0.7565984559,-0.1074967761,1.5702721
688\H,0.8248786794,-1.1469602587,0.1462661954\C,0.1998969571,-2.166225
3705,1.9201562999\H,1.1995121766,-2.3722771556,2.3146972549\H,-0.16893
19865,-3.0363362655,1.3682154015\C,-0.5845572845,-3.5276827473,4.13429
7954\H,0.4468055213,-3.5358421865,4.4940268882\H,-1.2731750495,-3.6150
134758,4.9763732798\H,-0.7580291782,-4.3330996228,3.4161733217\S,-0.92
75495113,-1.9463381367,3.3321156301\O,-2.3330072388,-2.0747170214,2.73
82585659\\Version=AM64L-G09RevB.01\HF=-1347.5877411\S2=0.756778\S2-1=0
.\S2A=0.750037\RMSD=0.000e+00\RMSF=2.167e-05\Dipole=1.2239801,-1.67930
87,2.9588393\Quadrupole=-15.7859216,11.2136704,4.5722511,-10.5310478,3
.8744099,1.8053833\PG=C01 [X(C8H15N2O7S1)]\\@
Sum of electronic and thermal Free Energies= -1347.387671

TS_{γ}
1\1\GINC-SPARTAN-BM105\FTS\UM062X\6-31+G(d)\C8H15N2O7S1(2)\UWILLE\03-N
ov-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm freq=noraman opt=(t
s,noeigentest,calcfc,maxcycle=500) scrf=(cpcm,solvent=acetonitrile)\\g
eom&freq\\0,2\C,0.7412893904,0.6910697549,7.6173479308\H,1.7533173392,
0.2714126087,7.6509997784\C,0.272712691,0.9720976406,9.0343843566\H,-1
.0685920392,-0.381219994,7.4472447608\C,0.226247984,-1.0381593059,5.97

23030987\O,-0.8399518161,0.7196461671,9.4402700194\O,1.2233978208,1.55
61024631,9.7551487685\C,0.8606144241,1.9349435002,11.0948262531\H,0.56
95726754,1.0501884358,11.6628076528\H,1.7529665128,2.3898106826,11.518
4899977\H,0.036363299,2.6496312139,11.0660330635\O,1.3409846274,-0.922
3435917,5.4628603789\N,-0.1473708498,-0.2836247151,7.0351462949\C,0.75
45334405,1.9904353725,6.7634417693\H,-0.2590027107,2.4058043592,6.7402
839091\H,1.0182263315,1.6882540336,5.7442403922\C,4.2183329664,4.27101
07713,7.3340553245\H,3.8564505756,4.7711001733,8.2342508881\H,5.285403
9133,4.061056398,7.4097029818\H,3.986373692,4.8450826772,6.4344247498\
H,1.4434048821,3.5388765074,8.19860503\S,3.381095793,2.6812820317,7.21
08257624\O,3.7848951582,1.9856364483,5.9519091084\C,-0.7965024547,-2.0
187191849,5.4528898206\H,-1.0438447231,-1.7508427271,4.4222461127\H,-0
.349040349,-3.0156968921,5.4427916581\H,-1.7113570611,-2.0387771821,6.
0475349837\N,0.3796627055,5.4246033708,5.3367554065\O,0.1793351834,6.3
045549957,4.5186915286\O,-0.4670008389,4.9706116768,6.0962015879\O,1.5
955741075,4.9380314864,5.3945930261\C,1.6768568077,3.0917822202,7.2279
972848\H,1.6272296419,4.0611413037,6.3095401414\\Version=AM64L-G09RevB
.01\HF=-1347.5361215\S2=0.757139\S2-1=0.\S2A=0.750032\RMSD=0.000e+00\R
MSF=4.394e-06\Dipole=1.2555929,-0.7088936,4.2651751\Quadrupole=-23.955
5359,-53.2678097,77.2233456,26.6284191,36.9397709,21.1915434\PG=C01 [X
(C8H15N2O7S1)]\\@
Frequencies -- -1429.8220
Sum of electronic and thermal Free Energies= -1347.343330

γ-radical complex
1\1\GINC-SPARTAN-BM110\FOpt\UM062X\6-31+G(d)\C8H15N2O7S1(2)\UWILLE\21-
Nov-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcyc
le=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\
C,5.7465809323,3.4190189328,6.2214247444\H,6.3973663409,3.2090712584,5
.3668834156\C,6.6026917996,3.8019515054,7.4170413572\H,4.8737407806,2.
0216273718,7.5454840823\C,4.6137068081,1.3396145419,5.6354577215\O,6.4
988078746,3.2948589575,8.5124741977\O,7.4405972127,4.7832959455,7.1139
133104\C,8.2665030461,5.265762675,8.1878683653\H,8.9037058443,4.459415
9556,8.5544676694\H,8.8647685888,6.0647144309,7.7560215593\H,7.6386195
919,5.6444836848,8.9959277579\O,4.8600746316,1.5423038373,4.4263730339
\N,5.0183175162,2.2153349527,6.559597549\N,2.1730067205,1.1763856845,2
.7821780598\O,1.4471270208,1.1539402515,1.8151381981\O,3.3663990984,0.
605145143,2.6218658789\O,1.9027041431,1.6368040504,3.8745998123\C,4.80
14744571,4.6034921151,5.8634899572\H,5.4375800603,5.4647305258,5.62567
86519\H,4.2099092168,4.8595185799,6.7493453915\C,3.8540766555,0.128469
0459,6.0942736433\H,4.312911959,-0.7609944074,5.6557297732\H,3.8314339
509,0.0319196693,7.1805098349\H,2.8297235573,0.205912316,5.7174669126\
C,4.0802712155,6.08072572,2.7322688162\H,4.6468724985,6.7198798308,3.4
137450286\H,4.3744586149,6.2804220092,1.6997417236\H,3.005212551,6.221
3439067,2.8642591388\C,3.8817063866,4.28763458,4.7362691787\H,2.924307
0734,3.7910566542,4.8649036948\H,3.9674298287,0.9414531646,3.402055639
9\S,4.4753974617,4.3408565206,3.0755566702\O,3.5019362122,3.53109905,2
.2269744616\\Version=AM64L-G09RevB.01\HF=-1347.5695053\S2=0.756336\S2-
1=0.\S2A=0.750034\RMSD=0.000e+00\RMSF=1.178e-05\Dipole=2.8661135,2.386
9525,4.2796666\Quadrupole=-5.7206852,-7.3403434,13.0610286,39.2016269,
53.8630031,38.0583062\PG=C01 [X(C8H15N2O7S1)]\\@
Sum of electronic and thermal Free Energies= -1347.368748

TS_{ϵ}

1\1\GINC-SPARTAN-BM122\FTS\UM062X\6-31+G(d)\C8H15N2O7S1(2)\UWILLE\24-N
ov-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm freq=noraman opt=(t
s,noeigentest,calcfc,z-matrix,maxcycle=500) scrf=(cpcm,solvent=acetoni
trile)\\geom&freq\\0,2\C,5.7501566848,6.655892849,2.3085676088\H,5.166
4110635,7.4433017993,1.8199627022\C,5.4933411495,6.6903154758,3.807341
1732\H,7.7778968507,6.7746265553,2.8904447569\C,7.6304910065,7.3220384
956,0.9005487092\O,6.3652547346,6.5696478096,4.6400698685\O,4.20385197
87,6.8346188666,4.0862637837\C,3.8509435079,6.7657150022,5.478380912\H
,4.3016805389,7.6030113605,6.0140453553\H,2.765235152,6.8295343095,5.5
061895802\H,4.1984335613,5.8204418834,5.8995786258\O,6.8808840711,7.49
12533165,-0.0625848744\N,7.1570477661,6.9139356484,2.1011732902\N,3.54
5431326,3.2787094614,5.024210524\O,2.4526715408,2.6959202528,4.5868613
065\O,3.7455362637,3.240908159,6.2212712136\O,4.2825338556,3.819741377
4,4.2079220207\C,5.3625253596,5.2758878191,1.7270296604\H,5.8009536925
,4.4916790957,2.3509705351\H,5.8137447513,5.2116275826,0.7328417114\C,
9.1199944393,7.5477782909,0.8071657145\H,9.5364015467,6.83090437,0.094
3016743\H,9.2971458639,8.5523757741,0.4158399509\H,9.6305530252,7.4365
32268,1.7653774563\C,2.0323423279,2.9647257542,2.0261833001\H,1.691310
2455,1.9636112442,1.7532354106\H,2.3528000224,2.8765860791,3.424299894
4\H,1.2763519771,3.7352356517,1.8572445919\C,3.8535892102,5.1013721553
,1.6243725476\H,3.4150518265,5.7197000192,0.8365118276\H,3.338609255,5
.2785827554,2.5695764399\S,3.4638530931,3.3714078091,1.1664797305\O,4.
6164663675,2.4563341965,1.4161254635\\Version=AM64L-G09RevB.01\HF=-134
7.5359143\S2=0.757025\S2-1=0.\S2A=0.750029\RMSD=0.000e+00\RMSF=5.944e-
06\Dipole=-1.4997371,1.2212251,-1.5020314\Quadrupole=-1.025848,24.8416
133,-23.8157653,-0.3484765,-14.7870983,6.7133673\PG=C01 [X(C8H15N2O7S1)]\\@
Frequencies -- -1285.9692
Sum of electronic and thermal Free Energies= -1347.337611

ε-radical complex
1\1\GINC-SPARTAN-BM108\FOpt\UM062X\6-31+G(d)\C8H15N2O7S1(2)\UWILLE\28-
Oct-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm freq=noraman opt=(
calcfc,z-matrix,maxcycle=500) scrf=(cpcm,solvent=acetonitrile)\\geom&f
req\\0,2\C,1.6162615474,0.9442585394,-0.4279045932\H,1.4341068345,1.86
70893535,0.1284177809\C,0.3333142252,0.5474036807,-1.1419684126\H,1.67
98603124,-1.0512001381,0.2611348518\C,2.5220598375,0.1214698334,1.7027
329811\O,-0.1547303559,-0.560158469,-1.0941598607\O,-0.1544124146,1.55
79575418,-1.8493544147\C,-1.3431270783,1.2838606355,-2.6097504809\H,-2
.1482499551,0.9768938569,-1.9401674531\H,-1.5901907968,2.2183748028,-3
.1081659354\H,-1.1433915065,0.49714012,-3.3391996465\O,2.8318852353,1.
2627277507,2.0885342394\N,1.9530998216,-0.1062111203,0.510606358\N,2.1
342346437,4.5319434188,1.4097019555\O,1.8932106187,5.6875363952,1.6514
312158\O,2.2048809649,3.7262752731,2.4775207693\O,2.3150473104,4.03598
28156,0.3138365051\C,2.7230028552,1.1916205827,-1.4719510447\H,2.41493
19398,2.0356115579,-2.0975534554\H,2.8151269698,0.3070871544,-2.114980
4913\C,2.8126306592,-1.0753764502,2.566668659\H,3.8935579329,-1.134286
6002,2.7196721206\H,2.3432730208,-0.9228141987,3.5413798567\H,2.458793
0938,-2.0111130897,2.1321600448\C,6.6328457157,2.2664175738,-1.0814501
431\H,7.0063386839,1.486076297,-0.4282092395\H,7.2501402269,3.10899187
95,-1.3694665011\H,2.4207754587,2.7905345426,2.1517614341\C,4.06127622
63,1.4998377674,-0.815204279\H,4.4625253229,0.641684672,-0.2662129544\
H,4.0052448627,2.3701049164,-0.1562284983\S,5.2792116496,1.9013551575,
-2.1201589868\O,4.8136421368,3.2054159481,-2.7557253835\\Version=AM64L
-G09RevB.01\HF=-1347.5569163\S2=0.756967\S2-1=0.\S2A=0.750038\RMSD=0.0

00e+00\RMSF=1.070e-05\Dipole=0.0300786,-4.2167555,0.5642785\Quadrupole
=26.4778103,-28.6804957,2.2026854,-26.9821377,13.3351463,-0.9123819\PG
=C01 [X(C8H15N2O7S1)]\\@
Sum of electronic and thermal Free Energies= -1347.359470

O-transfer complex
1\1\GINC-SPARTAN-BM124\FOpt\UM062X\6-31+G(d)\C8H15N2O7S1(2)\UWILLE\16-
Oct-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm freq=noraman opt=(
calcfc,maxcycle=500) scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\
C,6.824440398,5.0223402362,1.2362696516\H,6.3573158934,5.7568978202,0.
570966443\C,6.919172143,5.6221732313,2.6321790133\H,8.8820431775,4.618
4421698,1.4590008647\C,8.5193483515,4.9776758195,-0.5350396376\O,7.944
0972145,5.6900958921,3.2743035256\O,5.7331818544,6.0322681545,3.065311
5906\C,5.7028056878,6.5901417848,4.3895084858\H,6.3291124154,7.4828896
248,4.4288136794\H,4.6610467151,6.8414875022,4.5748892861\H,6.05774258
53,5.8528924811,5.1114185392\O,7.6902388724,5.2777211943,-1.3943287571
\N,8.1648696753,4.7682439293,0.7580727825\N,1.8729260383,-0.1060813948
,0.9603274641\O,3.4267076985,2.1030140351,0.3421887757\O,0.8892675254,
0.5563636509,1.0001152669\O,2.4159650036,-0.7371170917,0.1100713355\C,
5.9497372822,3.7550308306,1.2824085438\H,4.9570952455,4.0271868673,1.6
53487861\H,6.3932455088,3.0351209989,1.9796124524\C,9.9823057717,4.803
5146084,-0.862927124\H,10.0778019393,4.0457334399,-1.6445226488\H,10.3
63141317,5.7473733136,-1.2617760264\H,10.5829237081,4.509078244,-0.000
7732268\C,4.7561725788,1.0493360993,-1.6893493652\H,5.7717076457,0.782
1159254,-1.9849805098\H,4.1158128128,0.1647048588,-1.6692149332\H,4.33
61842512,1.8131290486,-2.3453079999\C,5.83569576,3.1290185898,-0.10317
89244\H,6.8045454076,2.7909190591,-0.482009027\H,5.3807349859,3.810579
5268,-0.8275290369\S,4.7890148057,1.6749315458,-0.0225104884\O,5.44208
87299,0.6776280043,0.840677144\\Version=AM64L-G09RevB.01\HF=-1347.6149
241\S2=0.754953\S2-1=0.\S2A=0.750015\RMSD=0.000e+00\RMSF=3.393e-06\Dip
ole=1.4152458,0.8784657,-0.2368966\Quadrupole=14.9611427,-6.7813118,-8
.1798309,14.2283331,-2.8491421,14.3865771\PG=C01 [X(C8H15N2O7S1)]\\@
Sum of electronic and thermal Free Energies= -1347.418380

Reaction of $NO_3^\bullet$ with Ac-MetO_2-OMe (Figure S16)

Reactant complex
1\1\GINC-SPARTAN-BM125\FOpt\UM062X\6-31+G(d)\C8H15N2O8S1(2)\UWILLE\18-
Nov-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcyc
le=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\
C,-0.8691647865,2.9402764381,5.7842570076\H,-0.8787925241,3.983107399,
5.4497564826\C,-1.7768585418,2.1249104001,4.874267661\H,-1.9645285441,
2.0767253359,7.3643963144\C,-1.3751014949,3.9592894606,7.9570477085\O,
-2.6384348576,1.3724634373,5.2731341496\O,-1.4795973728,2.3164671766,3
.5948574932\C,-2.2408601259,1.5490417399,2.6474302074\H,-3.3031187119,
1.7777864616,2.7532849637\H,-1.8747120985,1.8515710498,1.6687051359\H,
-2.0715550492,0.4834065795,2.8119623596\O,-0.790705726,4.9994996123,7.
6531102376\N,-1.403534849,2.8869873194,7.1262027967\N,-4.5371044232,0.
6344365754,-0.1105113243\O,-4.2626729341,0.9474055755,-1.363896036\O,-
3.6806781794,0.0022317893,0.4489850898\O,-5.5996118674,1.0287612754,0.
2873674063\C,0.565924942,2.3875924591,5.6866052106\H,0.8906413142,2.43
46290808,4.6428116529\H,0.5676292505,1.3379232013,6.002286906\C,4.1665
392216,3.5612597866,7.4796437127\H,3.7918567571,3.4884524219,8.5014603
76\H,5.1869893103,3.1773377957,7.4159147344\H,4.1176141792,4.585877705

9,7.1088043147\C,1.5170389219,3.1928673784,6.5644038386\H,1.2469706936
,3.1389293601,7.6228087287\H,1.5730495909,4.2411007121,6.2566785879\C,
-2.0804151563,3.7975781236,9.281773172\H,-1.3558987842,3.9607318125,10
.0836649759\H,-2.849954574,4.5697037918,9.3624992427\H,-2.5404012992,2
.8159398376,9.407265858\S,3.1755051658,2.5199822021,6.4298613415\O,3.6
310967361,2.6850861634,5.0399480051\O,3.171970717,1.1591787014,6.99135
24188\\Version=AM64L-G09RevB.01\HF=-1422.7218222\S2=0.756148\S2-1=0.\S
2A=0.750029\RMSD=0.000e+00\RMSF=6.915e-06\Dipole=-1.1940337,0.7129396,
0.3256359\Quadrupole=-11.1630062,-10.36771,21.5307162,5.2259225,-0.845
1829,13.5286562\PG=C01 [X(C8H15N2O8S1)]\\@
Sum of electronic and thermal Free Energies= -1422.523996

CT complex (pre-reaction complex between $NO_3^•$ and amide moiety)
1\1\GINC-SPARTAN-BM116\FOpt\UM062X\6-31+G(d)\C8H15N2O8S1(2)\UWILLE\23-
Nov-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcyc
le=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\
C,-0.7141129206,-1.644585817,1.1164044957\H,-2.5679668617,-2.555870025
2,1.5892357241\C,-2.6498259489,-0.5497601357,2.2281359226\O,-2.0663918
975,0.5091866246,2.1414239738\N,-2.0015852622,-1.7227037829,1.78070585
28\O,-3.2631098495,-3.8745905501,3.0502592354\O,-2.1083815363,-4.40457
34843,4.8056383869\O,-1.5506985662,-2.6732033194,3.6790302565\N,-2.348
7642116,-3.6985599991,3.8437444246\C,-4.0164792933,-0.7508300134,2.809
5360304\H,-3.9205820971,-1.2241154721,3.7919751749\H,-4.4955049138,0.2
210879773,2.9227776065\H,-4.625181422,-1.4026769744,2.1783830742\H,-0.
776114548,-0.8475290111,0.36235764\C,-0.5087190956,-2.9755942443,0.404
5442717\O,0.6442696784,-3.0043203882,-0.2415717226\O,-1.3101884503,-3.
8818848676,0.4423951014\C,0.9459594839,-4.2231550813,-0.9480589674\H,1
.9199951281,-4.0589223543,-1.4022260642\H,0.979186556,-5.0564301073,-0
.2449339673\H,0.1861311896,-4.4017019131,-1.709974491\C,0.4281513354,-
1.3186342741,2.1063984332\H,0.0295165391,-0.63087716,2.8570058631\H,0.
7433445454,-2.2324041365,2.6173009925\C,1.6110650305,-0.6609005909,1.4
021415021\H,2.1079378822,-1.3334936795,0.6990334851\H,1.3199599517,0.2
619174818,0.8903864519\C,4.1685319341,0.5135000242,1.6918349348\H,4.92
85470562,0.812028044,2.4173733066\H,4.5618559173,-0.2436397176,1.01246
62272\H,3.7944228294,1.3828150796,1.1493336538\S,2.8342424064,-0.19529
80329,2.6336215328\O,3.3171858376,-1.4215453266,3.2871116942\O,2.25232
83533,0.8528438275,3.4864492936\\Version=AM64L-G09RevB.01\HF=-1422.733
3979\S2=0.759998\S2-1=0.\S2A=0.750081\RMSD=0.000e+00\RMSF=1.039e-05\Di
pole=0.8069382,1.175552,-4.8432184\Quadrupole=28.4678008,-4.052334,-24
.4154669,-8.9805592,-8.1633912,23.9487097\PG=C01 [X(C8H15N2O8S1)]\\@
Sum of electronic and thermal Free Energies= -1422.527708

Association complex
1\1\GINC-SPARTAN-BM102\FOpt\UM062X\6-31+G(d)\C8H15N2O8S1(2)\UWILLE\06-
Oct-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcyc
le=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\
C,-2.8123017351,1.9617121934,2.4254293385\H,-2.1359227182,2.7455334737
,2.0702331412\C,-4.2399176558,2.3869381711,2.1213020247\H,-3.466730474
9,1.638914982,4.4102052201\C,-1.5245491227,2.3096428383,4.4749518669\O
,-5.1184157633,2.4769441947,2.950039736\O,-4.4034388754,2.6153321529,0
.8232248641\C,-5.7282439927,2.9849204393,0.40616636\H,-6.0302286506,3.
9073214714,0.9050350344\H,-5.6632437913,3.1314117161,-0.6695870558\H,-
6.4293781724,2.1837679093,0.6461477\O,-0.5417729395,2.695510734,3.8357
91302\N,-2.6463646508,1.8635162385,3.858382055\N,1.0309903315,2.838753

1655,1.6066511026\O,0.001236591,2.6241753875,0.7956989703\O,1.64182944
05,1.8735303966,1.9734364141\O,1.1992257389,4.0054714754,1.8477097934\
C,-2.4886265394,0.6557553495,1.67034838\H,-2.3918196578,0.9046073589,0
.6081640665\H,-3.3113738878,-0.0588627627,1.7701741865\C,-1.5332804358
,2.2923690523,5.9827700752\H,-0.6895140569,1.6906060194,6.3294659306\H
,-1.3868686723,3.3145040431,6.341818665\H,-2.4585017578,1.8926585472,6
.4008776742\C,1.0829883712,-1.5490794319,1.6533219062\H,0.7857520283,-
2.2225744475,2.4582064232\H,1.6136655283,-2.0949136243,0.8702595328\H,
1.689789549,-0.7218055065,2.0244980144\C,-1.1985674239,0.024352103,2.2
026154269\H,-1.3869747902,-0.6832582649,3.0141588763\H,-0.478492383,0.
7729112478,2.5452153866\S,-0.3788308077,-0.8781792874,0.8922010925\O,0
.0370558072,0.0978156394,-0.1320750118\O,-1.2468181906,-1.9855689153,0
.4608816072\\Version=AM64L-G09RevB.01\HF=-1422.7287674\S2=0.756284\S2-
1=0.\S2A=0.750031\RMSD=0.000e+00\RMSF=7.360e-06\Dipole=-1.1682898,-0.3
6338,2.0007972\Quadrupole=4.0891607,-14.2060862,10.1169255,-14.5423011
,-4.5712067,-9.0530825\PG=C01 [X(C8H15N2O8S1)]\\@
Sum of electronic and thermal Free Energies= -1422.524575

TS_{α}
1\1\GINC-SPARTAN-BM125\FTS\UM062X\6-31+G(d)\C8H15N2O8S1(2)\UWILLE\17-O
ct-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm freq=noraman opt=(t
s,noeigentest,calcfc,z-matrix,maxcycle=500) scrf=(cpcm,solvent=acetoni
trile)\\geom&freq\\0,2\C,-0.6949798809,-0.4137213003,0.2294607356\H,-0
.2315352616,0.2595775653,-0.5926844596\C,-1.7067950548,-1.3154157882,-
0.4656283567\H,-2.4355008768,0.4621037531,0.9279539022\C,-0.8286872785
,1.6050809328,1.7158971038\C,-1.8185518955,2.4633142286,2.4320210578\H
,-2.3825391811,1.8528957381,3.1433604761\H,-1.2876048703,3.2573002286,
2.9552404369\H,-2.5163790095,2.8973642042,1.7088388837\O,-2.8987742552
,-1.1031639395,-0.4416987404\O,-1.1168016844,-2.3117854724,-1.09726585
89\C,-1.9846132257,-3.2090890958,-1.8176722432\H,-2.5070677456,-2.6606
180824,-2.6025609908\H,-1.3270804386,-3.9636156266,-2.2416827452\H,-2.
7011183347,-3.6571045652,-1.1281165696\O,0.3664534647,1.7540372628,1.6
582510507\N,-1.4132299894,0.500508774,1.016595952\N,-0.4814430598,2.48
36301027,-1.5149912968\O,-1.4975172743,2.4018943725,-0.7956252343\O,0.
2973066404,1.4860552496,-1.5950394314\O,-0.2204126398,3.5035863438,-2.
1432592717\C,0.4926150955,-1.1506649282,0.8827094407\H,1.2041316411,-0
.4278103084,1.2851580103\H,0.9950195988,-1.6868092808,0.0754470558\C,0
.096422089,-2.1775695235,1.9460954465\H,0.9248504301,-2.8721514493,2.1
125010506\H,-0.7969579518,-2.7526941243,1.6836152064\C,-0.573840473,-2
.7617426922,4.6387239523\H,0.2942423233,-3.4209893071,4.6835461469\H,-
0.7671898715,-2.3152104908,5.6165914731\H,-1.4583398268,-3.2849352272,
4.2731592207\S,-0.2092104741,-1.408291939,3.5440896411\O,1.034454817,-
0.7588250206,3.9784200346\O,-1.4131525436,-0.5602575926,3.4327789238\\
Version=AM64L-G09RevB.01\HF=-1422.7276742\S2=0.759427\S2-1=0.\S2A=0.75
0065\RMSD=0.000e+00\RMSF=1.046e-05\Dipole=-1.5533976,-6.1833311,2.5226
213\Quadrupole=-6.4483707,6.2710568,0.1773139,1.5027184,-8.0923556,1.0
98128\PG=C01 [X(C8H15N2O8S1)]\\@
Frequencies -- -118.6615
Sum of electronic and thermal Free Energies= - 1422.522661

α-radical complex
1\1\GINC-SPARTAN-BM090\FOpt\UM062X\6-31+G(d)\C8H15N2O8S1(2)\UWILLE\10-
Oct-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm freq=noraman opt=(
calcfc,z-matrix,maxcycle=500) scrf=(cpcm,solvent=acetonitrile)\\geom&f

req\\0,2\C,-0.0391098778,-0.3208888088,-0.2381461097\H,2.5972137134,0.
9903574448,3.0075041465\C,-1.2135391542,-0.5634260815,-1.0650810914\H,
-1.3697542367,0.0409548743,1.2266090182\C,0.4530709486,0.4262172705,2.
0648876272\O,-2.3584858448,-0.476410918,-0.6364422213\O,-0.9104299849,
-0.8820382715,-2.3270548694\C,-2.0266301335,-1.1306697279,-3.191416166
6\H,-2.6666467184,-0.2478035272,-3.2389635088\H,-1.5952396775,-1.34612
73145,-4.1666450392\H,-2.5997708896,-1.9849530831,-2.8257895426\O,1.68
03356517,0.5039592816,1.8994575414\N,-0.3663095734,0.0467921904,1.0468
65839\N,3.0910952539,2.5360889741,4.0284940187\O,3.8473245249,3.001342
3234,4.8470182685\O,3.2879544608,1.2478468133,3.7301922564\O,2.1838469
151,3.115679285,3.463352668\C,1.3585469551,-0.4587855256,-0.7423574506
\H,1.3351328236,-1.1060756128,-1.6216898318\H,1.9922209265,-0.91846344
14,0.0189324672\C,-0.2009001251,0.7599687599,3.3737745455\H,0.30927667
52,0.2125239932,4.1708362423\H,-0.0694372913,1.8302361857,3.5607254095
\H,-1.2638394229,0.517903991,3.3937466861\C,4.1780494821,2.30239161,-2
.178461329\H,4.1920251756,2.9093150756,-1.2725001555\H,5.187898469,2.1
807830766,-2.5763261392\H,3.5168433124,2.7271089059,-2.9350361589\C,1.
9427720252,0.9063242537,-1.1363071691\H,2.0227846523,1.5752143298,-0.2
757529897\H,1.3654936186,1.3808922863,-1.9350911317\S,3.6066683866,0.6
663792826,-1.768304184\O,3.5160631268,-0.1229417089,-3.0069683515\O,4.
440066332,0.1366444146,-0.6774965652\\Version=AM64L-G09RevB.01\HF=-142
2.7803862\S2=0.757534\S2-1=0.\S2A=0.750044\RMSD=0.000e+00\RMSF=7.327e-
06\Dipole=-3.3441365,0.4842499,-1.3465491\Quadrupole=-16.4185193,11.75
37899,4.6647293,5.1417735,-14.0181602,-18.8109841\PG=C01 [X(C8H15N2O8S1)]\\@
Sum of electronic and thermal Free Energies= -1422.576077

TS_{β}

1\1\GINC-SPARTAN-BM087\FTS\UM062X\6-31+G(d)\C8H15N2O8S1(2)\UWILLE\10-M
ar-2021\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(ts,noeigentest
,calcfc,maxcycle=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\g
eom&freq\\0,2\C,2.2103170197,3.8617856112,4.2624312365\H,1.6539978937,
4.6781725635,3.7872140348\C,1.3066114441,3.1731075267,5.2808314849\H,3
.601505018,3.9987056872,5.8399611357\C,3.9083214767,5.5980545563,4.568
0953682\O,1.5290509889,3.1403253111,6.4691059352\O,0.2702137372,2.6029
978179,4.6848603914\C,-0.6452700276,1.8938296107,5.537529207\H,-1.0825
020033,2.5821100517,6.26241584\H,-1.4078520698,1.4950979067,4.87251439
73\H,-0.1202745406,1.0882975861,6.053137824\O,3.5484458393,6.170918390
9,3.5420508184\N,3.3451381944,4.4202100635,4.9538815545\N,0.6177690271
,0.8904510316,1.5603402993\O,-0.0708684544,0.5387715917,0.6286677724\O
,0.5932506239,2.2138638386,1.7512890055\O,1.2703379438,0.2011142158,2.
3034728303\C,2.6546974727,2.8547983626,3.1907365951\H,1.6435701646,2.5
155269549,2.6425832245\H,3.0405128888,1.9228192857,3.6209301486\C,5.00
83950614,6.1322899674,5.4504276486\H,5.1366129568,5.5596505274,6.37042
99267\H,5.9443673909,6.1171421512,4.8852520157\H,4.7805952095,7.171856
3385,5.6968814536\C,5.250490767,2.9262163878,-0.0849432742\H,6.0805244
302,3.3412423882,0.4881454755\H,5.6047244651,2.1569188122,-0.774640523
6\H,4.7060802151,3.703626307,-0.6229713263\C,3.5578977043,3.4275284045
,2.1228262638\H,4.4590068522,3.862889326,2.5702499476\H,3.0596392965,4
.1866834579,1.5132118963\S,4.1305309372,2.1112605186,1.031195974\O,4.8
809666468,1.1499238278,1.8517376303\O,2.9820884298,1.608368621,0.26374
07885\\Version=AM64L-G09RevB.01\HF=-1422.7133112\S2=0.759804\S2-1=0.\S
2A=0.75006\RMSD=0.000e+00\RMSF=2.141e-06\Dipole=1.4648715,2.4071588,1.
6940301\Quadrupole=7.088349,-9.6137686,2.5254196,26.3512631,5.0749996,
15.559385\PG=C01 [X(C8H15N2O8S1)]\\@

Frequencies -- -928.0061
Sum of electronic and thermal Free Energies= - 1422.514285

β-radical complex

1\1\GINC-SPARTAN-BM099\FOpt\UM062X\6-31+G(d)\C8H15N2O8S1(2)\UWILLE\05-Mar-2021\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcycle=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\C,1.5666802301,-0.6728860555,6.271608094\H,0.8058263498,-0.4730122221,5.5071448331\C,1.1822959511,-1.9604355525,6.9930068873\H,1.4941290089,0.1361866537,8.2414682644\C,1.4970463537,1.6795592384,6.8874247614\O,0.964803097,-2.0291479004,8.1824242496\O,1.1310283489,-2.9824470161,6.1532080879\C,0.7829666947,-4.2546705673,6.7258014286\H,-0.2087141174,-4.1977061188,7.1775465664\H,0.7894366009,-4.9565316321,5.8952109268\H,1.5217379454,-4.5364003743,7.4779254159\O,1.5082021074,1.9579829801,5.6675556102\N,1.5303895502,0.4011695209,7.2616586509\N,2.0733097041,3.9987117544,3.3362280615\O,2.1747324227,4.9884617619,2.6486308932\O,1.6421572009,4.2006889188,4.5788382328\O,2.3274462428,2.8568232112,2.994995387\C,2.9132579012,-0.8060521787,5.6148848314\H,3.7026724916,-1.3232584066,6.1482219933\C,1.451440339,2.7425704696,7.9453916859\H,0.5849721307,3.3827972623,7.7608125067\H,1.3910151924,2.3293303113,8.952645585\H,2.3519459112,3.3576215367,7.8608039767\C,2.8477058613,-0.3367327074,1.4731223988\H,3.9323204121,-0.3410621457,1.3546913299\H,2.3678959726,-0.8709530994,0.6501810044\H,2.4593715062,0.6803701508,1.5527236705\H,1.5906814223,3.2664963278,5.0599200416\O,0.9700718199,-1.1670985222,3.148329854\S,2.4303072516,-1.2202790838,2.9627693349\O,3.0666751122,-2.5457582724,2.9270297923\C,3.1936513922,-0.2269832133,4.2814350339\H,4.2631730484,-0.2081216212,4.0582253724\H,2.7579189742,0.7719793919,4.1606970575\\Version=AM64L-G09RevB.01\HF=-1422.7586098\S2=0.755919\S2-1=0.\S2A=0.750029\RMSD=0.000e+00\RMSF=5.692e-06\Dipole=0.9086637,-0.5014908,2.8280342\Quadrupole=-7.8971843,-35.5311499,43.4283342,-0.0535312,15.4661124,4.4000611\PG=C01 [X(C8H15N2O8S1)]\\@
Sum of electronic and thermal Free Energies= - 1422.557240

TS_{γ}

1\1\GINC-SPARTAN-BM088\FTS\UM062X\6-31+G(d)\C8H15N2O8S1(2)\UWILLE\10-Oct-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(ts,noeigentest,calcfc,maxcycle=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\C,2.2735508353,-0.7547034131,3.3007550803\H,1.5479077632,-0.1678101482,3.8758323577\C,1.5612466702,-1.9713429412,2.7261459405\H,3.6420834253,-2.1620359131,4.068997226\C,3.6507285144,-0.5104528932,5.3047579834\O,1.9316152141,-3.1123625788,2.8891642997\O,0.5021157382,-1.6146686296,2.0122987003\C,-0.23688229,-2.6845377952,1.3983495302\H,-0.6128464267,-3.3624647503,2.1662417677\H,-1.0576335182,-2.2038486771,0.87142854\H,0.4062486838,-3.22668169,0.7031262055\O,3.180628776,0.6072215018,5.5213852404\N,3.3137728908,-1.2102374357,4.1916106787\N,0.8526392544,2.9707849001,3.4151279247\O,0.5009569682,1.9746297811,2.8324601218\O,2.093351497,3.0187032406,3.9237678583\O,0.2133657205,3.9722965762,3.635357187\C,2.8031217677,0.1175160138,2.144087148\H,1.9684427551,0.421834778,1.5070825747\H,3.5043983755,-0.4757618927,1.5393900977\C,4.6313680734,-1.1675152034,6.2429533266\H,4.1192218851,-1.3777050338,7.1861622004\H,5.0449338928,-2.0962388783,5.8462049165\H,5.4427500996,-0.4659997937,6.4492926384\C,4.8475346756,3.7869016759,2.1519008882\H,5.7724107774,3.3599171051,2.5412799402\H,5.0601037442,4.5322328895,1.381993285\H,4.2347319665,4.2194413896,2.9445982028\C,3.5447089647,1.3244

950147,2.6543555397\H,4.4343553355,1.1190519744,3.2567844473\H,2.82180
42155,1.9758487728,3.3899385053\S,3.9101182235,2.5075973681,1.34930880
49\O,4.7613100831,1.8146736755,0.3746324504\O,2.6316436181,3.06815576,
0.8967990317\\Version=AM64L-G09RevB.01\HF=-1422.7101617\S2=0.759909\S2
-1=0.\S2A=0.75006\RMSD=0.000e+00\RMSF=2.451e-06\Dipole=1.8716403,-1.95
62472,0.9404795\Quadrupole=18.1139292,-11.0653759,-7.0485534,7.5847462
,24.9396931,-8.9416518\PG=C01 [X(C8H15N2O8S1)]\\@
Frequencies -- -1253.7622
Sum of electronic and thermal Free Energies= -1422.510271

γ-radical complex
1\1\GINC-SPARTAN-BM113\FOpt\UM062X\6-31+G(d)\C8H15N2O8S1(2)\UWILLE\22-
Nov-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcyc
le=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\
C,5.8135990177,3.375687651,6.225079532\H,6.4481756836,3.1684436966,5.3
585416969\C,6.6848228104,3.7479941188,7.4132115214\H,4.9334886512,1.98
18929297,7.551626356\C,4.6418473241,1.3247838752,5.6357375559\O,6.5993
352642,3.2262784216,8.5030917962\O,7.516949192,4.733203922,7.107993976
9\C,8.3632914663,5.2013058774,8.1725106372\H,9.0062020012,4.3896747431
,8.5167081105\H,8.9541619709,6.0051229693,7.7395797102\H,7.7510373786,
5.5701467209,8.9969384851\O,4.8807894911,1.5450035479,4.4277774148\N,5
.0750473391,2.1791890639,6.5660140774\N,2.2129749666,1.2552011894,2.76
28033469\O,1.4867917198,1.2218748712,1.795846408\O,3.3804960493,0.6301
099929,2.6313813914\O,1.9625134239,1.7809972343,3.8316102925\C,4.87466
17789,4.5678189233,5.8804289311\H,5.5116880514,5.427566537,5.645972391
8\H,4.2744915966,4.8115206909,6.7632400561\C,3.858603358,0.1242185146,
6.0810522279\H,4.2990360835,-0.7696648825,5.6327879071\H,3.8338958902,
0.016328838,7.1661348627\H,2.835561693,0.2258657596,5.7058255898\C,4.0
245858518,6.0783359461,2.6187179521\H,4.4859342245,6.8000803464,3.2948
252384\H,4.3764126558,6.2295858805,1.595299128\H,2.9359713524,6.130901
0515,2.6655180636\C,3.9652031993,4.2579749693,4.745833196\H,2.96864504
08,3.8454211936,4.8545576192\H,3.9926943838,0.9649314573,3.4099144402\
O,3.8169182255,3.4817689892,2.2379287982\S,4.5328785896,4.4364192993,3
.0953369483\O,6.004821855,4.4111580706,3.1161813604\\Version=AM64L-G09
RevB.01\HF=-1422.7604071\S2=0.755874\S2-1=0.\S2A=0.750028\RMSD=0.000e+
00\RMSF=1.298e-05\Dipole=1.0315034,2.3614556,4.2851517\Quadrupole=-28.
5768798,3.7718967,24.8049831,24.410303,44.2572189,37.3953815\PG=C01 [X
(C8H15N2O8S1)]\\@
Sum of electronic and thermal Free Energies= -1422.554704

TS_{ε}
1\1\GINC-SPARTAN-BM064\FTS\UM062X\6-31+G(d)\C8H15N2O8S1(2)\UWILLE\20-N
ov-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm freq=noraman opt=(t
s,noeigentest,calcfc,z-matrix,maxcycle=500) scrf=(cpcm,solvent=acetoni
trile)\\geom&freq\\0,2\C,2.1767005401,3.9077170587,4.5506385529\H,2.59
94555549,3.107501483,5.1686166707\C,0.6685294104,3.7241029664,4.467252
525\H,2.063531379,3.9226490734,2.4400945205\C,4.012847289,3.5073120748
,2.9931880376\O,0.035853548,3.7889629182,3.4364936716\O,0.1327036834,3
.5178367924,5.6654354942\C,-1.3009914846,3.4099202639,5.7128788171\H,-
1.6284399146,2.5683442286,5.1005191257\H,-1.5428243698,3.2458808251,6.
7606564704\H,-1.7518434334,4.3358176332,5.3509958963\O,4.7988781483,3.
3346548048,3.9258020698\N,2.7086739553,3.7984343516,3.212047775\N,-1.0
79509624,5.8144431811,8.7298055088\O,-0.3311264662,4.8716192916,8.6345
748152\O,-0.5550955109,7.0534242946,8.8254618202\O,-2.2847041345,5.815

2859836,8.743833111\C,2.5406478683,5.276538619,5.1708958274\H,2.007944
0662,6.0690862321,4.6350735078\H,3.6140574255,5.4162108886,5.010753992
8\C,4.4474945235,3.4118379901,1.5509650637\H,4.8974409128,2.4295374644
,1.3870310852\H,3.6276651267,3.5559818833,0.8451176355\H,5.2154506931,
4.1680795469,1.3685047774\C,1.992686078,6.9465605312,8.9681304757\H,2.
2403460501,6.0468738559,9.5339480782\H,2.2381372593,7.8854806013,9.469
608101\H,0.7601344539,6.9562945441,8.8493725558\C,2.2290999615,5.33821
31466,6.6628426619\H,2.8092768781,4.6111829354,7.2397177819\H,1.167418
5502,5.1972806255,6.8740823659\S,2.645989161,6.9540236089,7.3105925319
\O,1.9298025527,7.9732493555,6.5389814549\O,4.1027598683,7.0733379567,
7.453847212\\Version=AM64L-G09RevB.01\HF=-1422.7000169\S2=0.76056\S2-1
=0.\S2A=0.750067\RMSD=0.000e+00\RMSF=4.963e-06\Dipole=-1.1752867,-1.05
79287,0.5604822\Quadrupole=-19.3589451,-20.7561328,40.1150779,-11.6264
302,-11.9826713,-2.0060421\PG=C01 [X(C8H15N2O8S1)]\\@
Frequencies -- -1518.5734
Sum of electronic and thermal Free Energies= -1422.503205

ε-radical complex
1\1\GINC-SPARTAN-BM103\FOpt\UM062X\6-31+G(d)\C8H15N2O8S1(2)\UWILLE\15-
Oct-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm freq=noraman opt=(
calcfc,z-matrix,maxcycle=500) scrf=(cpcm,solvent=acetonitrile)\\geom&f
req\\0,2\C,1.6200603033,0.8846867279,-0.3455072238\H,1.429501228,1.813
091267,0.1989698956\C,0.3412694598,0.4743268479,-1.061269894\H,1.66505
91047,-1.0980853788,0.3797969886\C,2.5221983582,0.0954205519,1.7971295
669\O,-0.1585120278,-0.6255138079,-0.9777079702\O,-0.127357829,1.46403
9055,-1.80862094\C,-1.3127233401,1.1765089757,-2.5701054676\H,-2.12724
61152,0.9035373629,-1.8972667367\H,-1.5439333647,2.0951195499,-3.10416
20315\H,-1.1149662903,0.3615051556,-3.2683146614\O,2.845754285,1.24231
68687,2.1538243055\N,1.95616943,-0.1526470818,0.6069903772\N,2.1579938
271,4.4900447838,1.4199422942\O,1.898844024,5.6482261196,1.6250460057\
O,2.1795073373,3.7064763107,2.506292207\O,2.3959444469,3.972512285,0.3
445736685\C,2.7284681189,1.1282973881,-1.3889114604\H,2.4264432861,1.9
767453453,-2.0106561337\H,2.823271637,0.2466082454,-2.0329876261\C,2.7
923379357,-1.0831210654,2.6914520367\H,3.8700391745,-1.1438644512,2.86
43426607\H,2.3072214166,-0.9060861511,3.6543589646\H,2.4402269419,-2.0
262727607,2.2720231069\C,6.7468908976,2.0998013564,-1.063941275\H,6.99
66192033,1.4330532439,-0.248313738\H,7.4461850151,2.8162021876,-1.4757
430028\H,2.4156533999,2.7668978171,2.2084309545\C,4.0669642573,1.42109
95931,-0.7182439508\H,4.4522258815,0.55546524,-0.1708532468\H,4.014668
2863,2.2869360999,-0.0536901611\S,5.2875547011,1.8153399606,-1.9711564
698\O,4.9038239991,3.0753547407,-2.6245494375\O,5.468011011,0.63214461
74,-2.8289476072\\Version=AM64L-G09RevB.01\HF=-1422.7442508\S2=0.75583
2\S2-1=0.\S2A=0.750027\RMSD=0.000e+00\RMSF=7.602e-06\Dipole=-0.2958326
,-2.9132125,1.539413\Quadrupole=22.8505094,-19.9978107,-2.8526987,-14.
7194583,24.2830304,-5.2499416\PG=C01 [X(C8H15N2O8S1)]\\@
Sum of electronic and thermal Free Energies= -1422.542888

Reaction of $NO_3^\bullet$ with Ac-Cys-OMe (Figure S17)

Reactant complex
1\1\GINC-SPARTAN-BM109\FOpt\UM062X\6-31+G(d)\C6H11N2O6S1(2)\UWILLE\23-
Nov-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcyc
le=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\
C,-1.0769037118,2.9006998216,5.7482296179\H,-1.0980299267,3.9119778624

,5.3228591568\C,-1.9831923049,2.0113919276,4.8940322375\H,-2.4350868606,2.3274215679,7.2527816314\C,-1.1744221989,3.734412719,8.0351088581\O,-2.9606516343,1.4520612582,5.3339846958\O,-1.5497588881,1.9522332154,3.6516255894\C,-2.3227696963,1.14062108,2.7403686053\H,-3.343483869,1.5235493878,2.6859510243\H,-1.8237786347,1.2311387238,1.7785016381\H,-2.3243943258,0.1059324078,3.0851557262\O,-0.1620097241,4.458545046,7.8437466726\N,-1.6300124038,2.9264335005,7.082279721\N,-3.8956357403,1.2292945441,0.1285723368\O,-2.9757914259,1.7708435981,-0.5205598818\O,-3.8220459812,0.0167069518,0.422211926\O,-4.879875188,1.9026613544,0.5012425935\C,0.3638511939,2.3595945824,5.7041693027\H,0.6989755903,2.2766851559,4.6668086385\H,0.4320110116,1.384407472,6.1909891596\C,-1.8834973116,3.780652439,9.35441546\H,-1.199740867,3.4181435104,10.1261996876\H,-2.1301853813,4.8206905376,9.5795129133\H,-2.7931471645,3.1793875034,9.353409829\S,1.5279798708,3.4373585774,6.5680562452\H,1.3890275724,4.5177156654,5.7795128053\\Version=AM64L-G09RevB.01\HF=-1193.7996343\S2=0.756139\S2-1=0.\S2A=0.750025\RMSD=0.000e+00\RMSF=8.641e-06\Dipole=6.7532143,3.0150572,10.9307857\Quadrupole=-88.243286,-17.0668757,105.3101617,14.6537761,-4.124661,64.1076243\PG=C01 [X(C6H11N2O6S1)]\\@
Sum of electronic and thermal Free Energies= -1193.657757

CT complex (pre-reaction complex between $NO_3^\bullet$ and amide moiety)
1\1\GINC-SPARTAN-BM057\FOpt\UM062X\6-31+G(d)\C6H11N2O6S1(2)\UWILLE\21-Nov-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcycle=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\C,-0.6048771745,-1.766422277,1.0104113429\H,-2.5115695336,-2.5275530771,1.5440523687\C,-2.3417276301,-0.581518186,2.3364323851\O,-1.6546525063,0.416308116,2.294930601\N,-1.8515580111,-1.770548396,1.752213687\O,-3.224475826,-3.8879473864,2.9572138234\O,-2.0784339038,-4.5780450531,4.6616264066\O,-1.3823306422,-2.8814184561,3.5599174752\N,-2.2740133772,-3.8246705942,3.7254920538\C,-3.6797252174,-0.6935602506,3.0024491718\H,-3.5480741463,-1.1743388349,3.9776584014\H,-4.0838339417,0.3075691117,3.1498865874\H,-4.3718852455,-1.300792854,2.4154706984\H,-0.6167357684,-0.9022576945,0.3330623684\C,-0.5865987556,-3.0446274661,0.1813250107\O,0.5583023673,-3.188103302,-0.4643745419\O,-1.5132242513,-3.8221562551,0.1367226186\C,0.6839833808,-4.3686162716,-1.2801153263\H,1.6723614269,-4.3035551837,-1.7284848109\H,0.5972652014,-5.2580653464,-0.654559721\H,-0.0923430555,-4.3689085731,-2.0465473131\C,0.6259960761,-1.6457137254,1.9397797498\H,0.3552692934,-1.017369425,2.7895109607\H,0.9141583883,-2.6254842185,2.3239397779\S,2.0515877215,-0.817351533,1.1773713557\H,2.3892041308,-1.8061248179,0.3354785388\\Version=AM64L-G09RevB.01\HF=-1193.792209\S2=0.760022\S2-1=0.\S2A=0.750081\RMSD=0.000e+00\RMSF=1.300e-05\Dipole=0.2946577,0.3255442,-2.2940638\Quadrupole=10.6862594,-5.3150051,-5.3712542,-17.2618591,0.2789311,21.6486575\PG=C01 [X(C6H11N2O6S1)]\\@
Sum of electronic and thermal Free Energies= -1193.648150

TS_α
1\1\GINC-SPARTAN-BM057\FTS\UM062X\6-31+G(d)\C6H11N2O6S1(2)\UWILLE\03-Nov-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(ts,noeigentest,calcfc,maxcycle=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\C,-0.5266375872,-0.0760054207,0.5899658311\H,-1.1648180176,-0.0955227649,1.5418533645\C,0.906347789,-0.45372356,0.921387209\H,0.3264963748,1.6343604972,-0.209518602\C,-1.7490435586,1.9162529818,-0

.1188021608\C,-1.5932935553,3.2909061987,-0.7037570885\H,-0.962387606,
3.9068105797,-0.0556754512\H,-1.1160607002,3.23317373,-1.6866588148\H,
-2.5770056718,3.7484677671,-0.7987808916\O,1.8415530064,0.299350823,0.
7798738794\O,0.9752661155,-1.6910551506,1.385173536\C,2.2909424031,-2.
1666853439,1.7281629887\H,2.7264766899,-1.522422409,2.4929050626\H,2.1
430050275,-3.1748202016,2.1070016152\H,2.9200992166,-2.1734556589,0.83
65234269\O,-2.8044076833,1.4098013754,0.2148498443\N,-0.5636469902,1.1
99517821,0.033248048\N,-3.1701994326,-0.174809685,2.7352291347\O,-3.29
34688369,-1.1270831043,1.9517967193\O,-2.0099426605,0.2945245476,2.957
9012006\O,-4.1415636841,0.3310055452,3.3075832067\C,-1.3060523613,-1.2
169060628,-0.2452880267\H,-2.2534236721,-0.7701255759,-0.5453440336\H,
-1.4722350717,-2.0562372488,0.4259230906\S,-0.3505796363,-1.6699751055
,-1.6649531921\H,0.3237961029,-2.6900755749,-1.1055478962\\Version=AM6
4L-G09RevB.01\HF=-1193.7839343\S2=0.756615\S2-1=0.\S2A=0.750035\RMSD=0
.000e+00\RMSF=5.783e-06\Dipole=4.9524231,-0.9872275,-4.5108401\Quadrup
ole=-24.0113008,30.127025,-6.1157242,-6.6024845,29.0037441,-4.3364683\
PG=C01 [X(C6H11N2O6S1)]\\@
Frequencies -- -285.2414
Sum of electronic and thermal Free Energies= - -1193.645900

α-radical complex
1\1\GINC-SPARTAN-BM085\FOpt\UM062X\6-31+G(d)\C6H11N2O6S1(2)\UWILLE\01-
Mar-2021\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcyc
le=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\
C,0.8657769334,-5.6356351702,3.2570001951\H,-0.5682411853,-8.260518560
3,0.0958043876\C,1.0156284687,-4.5192250773,4.1839156048\H,-1.05027777
29,-5.0313741893,3.1322299644\C,-0.9090634795,-6.6150644608,1.84898378
41\O,0.0787034199,-3.8021954883,4.5146384257\O,2.2655281681,-4.3668401
232,4.6285399047\C,2.4727912179,-3.2831989694,5.5440918354\H,1.8654305
581,-3.4287855205,6.4395509476\H,3.5321571658,-3.3097553308,5.78990011
48\H,2.210807527,-2.3365058901,5.0677344663\O,-0.1923475033,-7.5090868
673,1.3713704152\N,-0.4142821057,-5.7351132405,2.7593751058\N,-0.25468
03064,-8.0793507997,-1.7814095664\O,0.353464356,-7.0608970743,-1.51372
85092\O,-0.7867778105,-8.7742354162,-0.7688655937\O,-0.435417951,-8.54
47515791,-2.8803558242\C,2.0020352802,-6.4699545143,2.7997448526\H,1.7
343029702,-7.521514903,2.7179541242\H,2.8276189393,-6.3588730528,3.501
9997237\C,-2.3414279348,-6.4352547515,1.437429884\H,-2.873935901,-5.70
92063105,2.0523041707\H,-2.363243702,-6.0992990416,0.3953865473\H,-2.8
475367604,-7.4019288812,1.4933196704\S,2.6684187276,-5.9084836789,1.17
14298511\H,1.6655586805,-6.4049231087,0.4243915182\\Version=AM64L-G09R
evB.01\HF=-1193.8407124\S2=0.757744\S2-1=0.\S2A=0.750048\RMSD=0.000e+0
0\RMSF=5.192e-06\Dipole=-0.9766406,0.9178109,3.0002613\Quadrupole=10.4
462241,-21.9536906,11.5074666,13.569783,5.1678233,-38.7643439\PG=C01 [
X(C6H11N2O6S1)]\\@
Sum of electronic and thermal Free Energies= -1193.698032

CT complex (pre-reaction complex between $NO_3^\bullet$ and SH moiety)
1\1\GINC-SPARTAN-BM056\FOpt\UM062X\6-31+G(d)\C6H11N2O6S1(2)\UWILLE\03-
Oct-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcyc
le=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\
C,-2.6846163019,1.6300127794,2.3804972769\H,-2.1257975185,2.5312292824
,2.1050156385\C,-4.1658784123,1.8702543534,2.108531983\H,-3.2897826476
,1.0291489455,4.3089219968\C,-1.433869899,1.916344752,4.4600816411\O,-
5.0287583651,1.7986654618,2.953045623\O,-4.3774507329,2.1462104652,0.8

288404389\C,-5.7458174692,2.3723722361,0.4474625601\H,-6.137117657,3.2
417774655,0.9783343891\H,-5.7213248236,2.5529775,-0.6245553893\H,-6.34
43588805,1.4903884358,0.6799092796\O,-0.5138574977,2.4702485155,3.8619
941614\N,-2.4946811926,1.3853737604,3.789203748\N,0.9344397925,2.71732
23167,1.3367565448\O,-0.065389035,2.0956314613,0.7850254963\O,1.845120
5907,2.0653911011,1.8308016218\O,0.906746509,3.9424214899,1.3038356831
\C,-2.1991906325,0.470476925,1.4964789958\H,-2.2758931548,0.7313902758
,0.4400705527\H,-2.7663440893,-0.4441948455,1.6967930021\C,-1.46961801
46,1.7862562794,5.9618304782\H,-0.4536606349,1.6400706669,6.3310260663
\H,-1.8570158405,2.7205360481,6.3806179886\H,-2.1062109742,0.964327518
9,6.2956463559\S,-0.4582587165,0.1163645075,1.8794564231\H,-0.16873400
21,-0.518853598,0.7302436742\\Version=AM64L-G09RevB.01\HF=-1193.811373
3\S2=0.756404\S2-1=0.\S2A=0.750029\RMSD=0.000e+00\RMSF=1.035e-05\Dipol
e=-3.936236,-3.5312151,-0.1678499\Quadrupole=12.2352326,-21.5656018,9.
3303692,-13.2826416,-9.8935273,-11.9245805\PG=C01 [X(C6H11N2O6S1)]\\@

Sum of electronic and thermal Free Energies= -1193.667272

TS_{β}

1\1\GINC-SPARTAN-BM099\FTS\UM062X\6-31+G(d)\C6H11N2O6S1(2)\UWILLE\22-O
ct-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(ts,noeigentest
,calcfc,maxcycle=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\g
eom&freq\\0,2\C,-0.5299873282,-0.9964411262,-0.0022372172\H,-0.6465314
915,0.0112975942,-0.4252337912\C,0.3720322381,-1.7710646944,-0.9608070
861\H,-1.9180698144,-2.4998488336,-0.5210220026\C,-2.8896746296,-1.059
4285392,0.6006795785\C,-4.2015725579,-1.7957156366,0.4970745519\H,-4.0
985512398,-2.7879110929,0.0548255138\H,-4.6322265114,-1.8873593058,1.4
967811752\H,-4.8856769029,-1.1991184974,-0.1124807506\O,-0.0440892617,
-2.579506906,-1.7586900292\O,1.6424529009,-1.4358067923,-0.8070535643\
C,2.587233909,-2.0605038512,-1.6946285791\H,2.3474176692,-1.7989949497
,-2.7263681629\H,3.555415389,-1.656788787,-1.4074499237\H,2.5560203224
,-3.1429905037,-1.5618301948\O,-2.7870249501,0.0336811577,1.1562623212
\N,-1.8072592798,-1.6709911631,0.0537218844\N,2.3662019606,1.135143729
8,-0.1268962165\O,1.2639849576,1.5112192676,-0.5478696696\O,2.45156005
67,0.6838040676,1.0620020649\O,3.3839463875,1.1767604184,-0.8222590049
\C,0.0844144841,-0.7803243071,1.3830041847\H,-0.5772372678,-0.18443668
43,2.0217586801\H,1.0578665289,-0.1482644526,1.3013801518\S,0.56810993
47,-2.2670195648,2.1694466491\H,0.7262354964,-1.7734085474,3.412818437
1\\Version=AM64L-G09RevB.01\HF=-1193.7883523\S2=0.754493\S2-1=0.\S2A=0
.750015\RMSD=0.000e+00\RMSF=7.678e-06\Dipole=-2.0371102,-4.7702479,2.4
937258\Quadrupole=-11.4519298,2.9037609,8.5481689,-4.7670512,4.1464503
,-10.131176\PG=C01 [X(C6H11N2O6S1)]\\@
Frequencies -- -225.4396
Sum of electronic and thermal Free Energies= - -1193.647537

β-radical complex

1\1\GINC-SPARTAN-BM057\FOpt\UM062X\6-31+G(d)\C6H11N2O6S1(2)\UWILLE\13-
Nov-2020\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcyc
le=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\
C,0.6529230149,-2.399779128,-0.0988082755\H,0.7691102846,-1.6760633507
,-0.9153004389\C,1.3331289563,-3.7024696008,-0.5287791572\H,-1.0028404
076,-3.6866377479,0.1410482565\C,-1.6966197431,-1.76326558,0.237604883
3\C,-3.1054492229,-2.228479435,0.4764963183\H,-3.4160202599,-1.8847983
06,1.4670735051\H,-3.7584840925,-1.7599090853,-0.2631048075\H,-3.20983

56694,-3.3126874209,0.4228460105\O,0.8275713594,-4.7963617474,-0.40669
26539\O,2.5478470438,-3.4725058276,-1.0011240792\C,3.3109289242,-4.632
7732907,-1.376567384\H,2.7910865153,-5.1766212748,-2.1667060781\H,4.26
31099911,-4.2488592387,-1.7347417558\H,3.4537678243,-5.2777843606,-0.5
080163476\O,-1.444092035,-0.5459484501,0.1748434174\N,-0.7503734411,-2
.7032750207,0.1087910418\N,1.0722730617,1.3814226119,0.9952191509\O,0.
4117266534,1.1751611404,1.9921241703\O,0.6466088612,0.857306583,-0.158
6940535\O,2.0957624544,2.0227295827,0.9256546414\C,1.3200699065,-1.858
91315,1.1358664327\H,2.3039958257,-1.4142350565,1.0426937033\H,-0.1732
923946,0.2637935758,0.0501954043\S,0.8051492464,-2.4816069705,2.673451
2964\H,1.8171823429,-1.9691674515,3.387715799\\Version=AM64L-G09RevB.0
1\HF=-1193.8215745\S2=0.755239\S2-1=0.\S2A=0.750022\RMSD=0.000e+00\RMS
F=8.993e-06\Dipole=-0.1067203,-2.9858134,-0.8079007\Quadrupole=7.28672
12,-2.9326859,-4.3540353,-7.7621205,-1.3916687,0.3237841\PG=C01 [X(C6H
11N2O6S1)]\\@
Sum of electronic and thermal Free Energies= -1193.680181

TS_S
1\1\GINC-SPARTAN-BM122\FTS\UM062X\6-31+G(d)\C6H11N2O6S1(2)\UWILLE\03-D
ec-2020\0\\#p M062X/6-31+G* freq=noraman scf=verytight opt=(ts,noeigen
test,calcfc,maxcycle=500) nosymm scrf=(cpcm,solvent=acetonitrile)\\geo
m&freq\\0,2\C,3.6856996252,-1.0248062204,0.1849971978\H,4.7299144,-0.7
523526622,0.3711449465\C,3.0686279823,-1.5621128032,1.4701844623\H,2.9
950415375,-2.8376731893,-0.6401835686\C,4.3844972002,-2.0017458073,-1.
9362972543\O,2.3599231882,-2.5417133329,1.5144729769\O,3.4027681468,-0
.8108844232,2.5074893308\C,2.8123416439,-1.1706077817,3.7699165429\H,3
.1282861283,-2.1777885151,4.0464550308\H,3.1869397668,-0.4388508678,4.
481884902\H,1.7260991919,-1.1170664304,3.6904470581\O,5.1372742538,-1.
0505553289,-2.1437462177\N,3.623723473,-2.0609221138,-0.8137381089\N,-
0.0740503713,1.0702531629,1.4132415087\O,0.9377762414,0.506505369,1.91
3239166\O,0.1032195688,1.931889435,0.5042811112\O,-1.2008641962,0.7884
643084,1.7947055623\C,2.9168482942,0.2110032341,-0.3247561865\H,1.8639
033049,-0.0229780826,-0.4994709062\H,3.3802414133,0.5319542572,-1.2661
044955\C,4.2495605368,-3.1516704355,-2.9021513836\H,3.8955285375,-2.76
18738559,-3.8599647323\H,5.2378488252,-3.5900614825,-3.0610598545\H,3.
5632343772,-3.924680097,-2.5526321142\H,1.723119877,2.1036639706,0.471
0631224\S,3.0070334133,1.6306032125,0.7858696338\\Version=AM64L-G09Rev
B.01\HF=-1193.8066272\S2=0.754806\S2-1=0.\S2A=0.750019\RMSD=7.984e-09\
RMSF=4.380e-06\Dipole=2.6565868,-0.5655891,-0.4652445\Quadrupole=-4.38
67415,3.742514,0.6442275,0.5122388,11.9378496,4.6049448\PG=C01 [X(C6H1
1N2O6S1)]\\@
Frequencies -- -340.0868
Sum of electronic and thermal Free Energies= -1193.663624

S-radical complex
1\1\GINC-SPARTAN-BM099\FOpt\UM062X\6-31+G(d)\C6H11N2O6S1(2)\UWILLE\25-
Feb-2021\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcyc
le=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\
C,1.1588079547,-2.8505263755,5.823284942\H,1.7865603188,-2.4891173815,
5.0005210252\C,0.8312767749,-4.3186495571,5.5860143097\H,-0.9511019368
,-2.6707561052,5.8715744035\C,-0.1468067381,-0.8016160856,5.6691283672
\O,-0.2934012366,-4.7444133766,5.4439607494\O,1.9263667242,-5.06436657
45,5.5840470918\C,1.7335989401,-6.4783993507,5.4003219981\H,1.28041822

83,-6.6632896088,4.425253192\H,2.7283221239,-6.9143148857,5.4542520913
\H,1.0940929175,-6.8696866202,6.1928706715\O,0.9164344622,-0.147762877
6,5.5645792759\N,-0.0961426701,-2.1253741514,5.8216507325\N,0.41516879
9,2.6458617284,4.0483628143\O,0.0448376199,1.7463229101,3.3152221746\O
,0.4054656594,3.8282658666,3.7898876631\C,1.9163832764,-2.6610536147,7
.1519699666\H,1.3984644243,-3.1731282695,7.968019252\H,1.9249972069,-1
.5879029054,7.3820337551\C,-1.4935492315,-0.1407505729,5.6264204799\H,
-1.5250706603,0.6499931187,6.3809097794\H,-1.6211029654,0.3202430857,4
.6426924065\H,-2.3080497507,-0.843495765,5.8048364472\S,3.6506715894,-
3.1369256104,7.0853524959\O,0.8737945022,2.3195140463,5.2527292242\H,0
.8482416674,1.2619929326,5.340904691\\Version=AM64L-G09RevB.01\HF=-119
3.8432821\S2=0.753264\S2-1=0.\S2A=0.750008\RMSD=0.000e+00\RMSF=7.256e-
06\Dipole=-1.0754238,-3.6140276,1.4974843\Quadrupole=-12.7458496,-4.30
09589,17.0468084,-6.6346353,-13.9324867,-31.4489486\PG=C01 [X(C6H11N2O
6S1)]\\@
Sum of electronic and thermal Free Energies= -1193.699379

O-transfer complex
1\1\GINC-SPARTAN-BM099\FOpt\UM062X\6-31+G(d)\C6H11N2O6S1(2)\UWILLE\25-
Feb-2021\0\\#p M062X/6-31+G* scf=(qc,direct) nosymm opt=(calcfc,maxcyc
le=500) freq=noraman scrf=(cpcm,solvent=acetonitrile)\\geom&freq\\0,2\
C,-1.332688334,-2.8267298946,1.5188797018\H,-0.5316543386,-3.510192496
,1.2026088866\C,-2.4488523327,-3.6572901077,2.1311476007\H,-2.85221594
91,-2.1272978298,0.2247117302\C,-1.0100934886,-1.6842230004,-0.6058265
028\O,-3.5485575075,-3.7971674259,1.6507585626\O,-2.045578184,-4.19489
85324,3.278244152\C,-3.0026068432,-5.0083388291,3.9806234346\H,-3.2883
333827,-5.8571306872,3.3579646466\H,-2.4922089739,-5.3423125517,4.8808
613965\H,-3.8798259211,-4.4100265621,4.2301620937\O,0.2123578558,-1.77
74194001,-0.4856248491\N,-1.8469989277,-2.1501267138,0.3539401136\N,2.
2143914446,-2.2506083074,1.3319716572\O,2.0955676826,-3.4351834551,1.3
86698315\O,1.5371407361,-1.7943737423,3.9126335225\O,3.0908962793,-1.5
264157205,0.9914955148\C,-0.7587165149,-1.823976433,2.5306900459\H,-1.
5496020488,-1.2095637167,2.9691911774\H,-0.0384722072,-1.1772562181,2.
0213625855\C,-1.6534189939,-1.052940312,-1.8147435109\H,-1.3807131261,
-1.6378603197,-2.6971771582\H,-2.7408177175,-0.9990522261,-1.741259516
4\H,-1.2479964845,-0.0460859302,-1.9400348941\S,0.2139592469,-2.556282
9667,3.9105231177\H,0.4581092307,-3.7198242211,3.2396297765\\Version=A
M64L-G09RevB.01\HF=-1193.8212152\S2=0.754814\S2-1=0.\S2A=0.750015\RMSD
=0.000e+00\RMSF=2.323e-05\Dipole=-3.5592302,-1.0743871,0.0581865\Quadr
upole=-9.6320375,10.5228943,-0.8908568,12.2526162,-15.8489431,-13.2355
748\PG=C01 [X(C6H11N2O6S1)]\\@
Sum of electronic and thermal Free Energies= -1193.677910

7. References

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Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2010**.

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