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Supporting Information

Synthesis and Nitric Oxide Releasing Properties of Novel Fluoro *S*-Nitrosothiols

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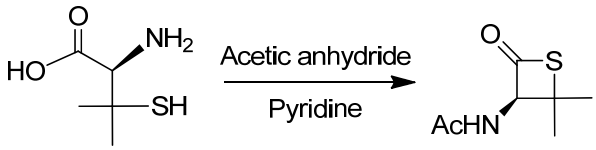
1. General information

All commercial organic solvents and chemicals were directly used in all synthetic reactions. SNAP was purchased from PharmaBlock Sciences Inc (Nanjing, China). Column chromatography was carried out using silica gel (60 Å, 40 - 63 μm) with ACS grade solvents of MeOH and CH_2Cl_2. All novel synthetic compounds were characterized by $^{1}H/^{13}C/^{19}F$ NMR spectroscopy and high-resolution mass spectrometry (HRMS) with an electrospray ionization source. $^{1}H/^{13}C/^{19}F$ NMR spectra were recorded using Varian 400/500 MHz spectrometers. $CFCl_3$ was used in $CDCl_3$ as an internal reference in ^{19}F NMR spectroscopy. The ^{19}F NMR spectra were obtained without proton and carbon decoupled mode. HRMS data was collected using an Agilent 6520 Accurate-Mass Quadrupole Time-of-Flight (Q-TOF) LC/MS in the electrospray positive-ion mode with a ZORBAX RRHD Eclipse Plus C18 reversed-phase column (2.1 x 50 mm, 1.8 Mm). Phosphate-buffered saline (PBS, 10.0 mM, pH 7.40, with 100 MM EDTA) was prepared using Na_2HPO_4, KH_2PO_4, NaCl, KCl and EDTA. The pH of PBS was adjusted by a diluted HCl solution.

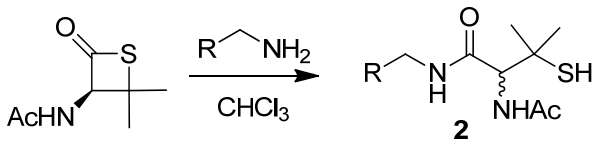
2. Syntheses

2.1 Synthesis of 3(*D*)-acetamido-4,4-dimethylthietan-2-one



To a stirred solution of *D*-penicillamine (2.001 g, 13.41 mmol) in pyridine (25 mL) at room temperature was added acetic anhydride (3.55 mL, 37.52 mmol) in one portion. After stirring for 20 h at room temperature, the reaction solution was washed by HCl solution (1.0 M, 80 mL), and extracted by chloroform (3 x 50 mL). All the organic solution was dried by $NaSO_4$, and taken to dryness to obtain a crude yellow solid. The resulting yellow solid was triturated by petroleum ether to give a pale yellow solid, which was further dried under vacuum overnight to give the desired product (782.8 mg, 34%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.12 (s, 1 H), 5.66 (d, *J* = 7.6 Hz, 1 H), 2.05 (s, 3 H), 1.86 (s, 3 H), 1.62 (s, 3 H).

2.2 Synthesis and characterization of free thiols 2a-2n



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R = 2-FPh (**a**), 3-FPh (**b**), 4-FPh (**c**), 4-FPhCH_2 (**d**), 2,6-diFPh (**e**), 3,5-diFPh (**f**),3-CF_3Ph (**g**), 3-CF_3PhCH_2 (**h**), 3,4,5-triFPh (**i**), 3-F,4-CF_3Ph (**j**), 3-F,5-CF_3Ph (**k**), 3,5-diCF_3Ph (**l**), Ph (**m**), and 3,4,5-triMeOPh (**n**)

All **2a**-**2n** thiol intermediates were prepared using the same procedures as described as follows. To a solution of lactone (600.0 mg, 3.464 mmol) in $CHCl_3$ (25 mL) was added various commercially available amines (4.157 mmol, 1.2 eq. of lactone) in one portion. After stirring at room temperature (**2a**-**2i**, **2m**, **2n** for 24 h; **2j**-**2l** for 48 h), the reaction solution was then taken to dryness. The crude products were purified by column chromatography (silica gel/3:97 MeOH-CH_2Cl_2) to yield the desired products **2a**-**2n** as pale white powers. The corresponding yields for **2a**-**2n** were listed in Table S1. All desired products were characterized by $^1H/^{13}C/^{19}F$ NMR and HRMS.

Table S1. Yields for the synthesis of free thiols **2a**-**2n**.

Compound #	Yields (%)
2a	92
2b	93
2c	71
2d	83
2e	90
2f	92
2g	82
2h	94
2i	91
2j	89
2k	93
2l	85
2m	74
2n	82

Characterization of thiol **2a**: ^1H NMR (500 MHz, $CDCl_3$): δ 7.52 (t, *J* = 5.5 Hz, 1 H), 7.30 (t, *J* = 7.5 Hz, 1 H), 7.25 (q, *J* = 7.5 Hz, 1 H), 7.07 (t, *J* = 7.5 Hz, 1 H), 7.02 (t, *J* = 8.5 Hz, 1 H), 6.72 (d, *J* = 9.5 Hz, 1 H), 4.64 (d, *J* = 9.0 Hz, 1 H), 4.52 (dd, *J* = 14.75, 6.5 Hz, 1 H), 4.35 (dd, *J* = 15.0, 6.5 Hz, 1 H), 2.58 (s, 1 H), 1.94 (s, 3 H), 1.46 (s, 3 H), 1.28 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.31, 169.77, 160.91 (d, *J* = 247.09 Hz), 130.23 (d, *J* = 4.16 Hz), 129.36 (d, *J* = 8.19 Hz), 124.71 (d, *J* = 14.89 Hz), 124.22 (d, *J* = 3.53 Hz), 115.39 (d, *J* = 21.29 Hz), 60.09,

46.20, 37.40 (d, *J* = 4.03 Hz), 30.95, 28.58, 23.10. ^{19}F NMR (377 MHz, $CDCl_3$): -119.01 (m). HRMS m/z (ESI): calculated for MH^+ 299.1224, found 299.1228.

Characterization of thiol **2b**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30-7.28 (m, 1 H), 7.17 (t, *J* = 5.5 Hz, 1 H), 7.03 (d, *J* = 7.5 Hz, 1 H), 6.97-6.94 (m, 2 H), 6.66 (d, *J* = 9.0 Hz 1 H), 4.51 (d, *J* = 9.0 Hz, 1 H), 4.46 (dd, *J* = 15.0, 6.0 Hz, 1 H), 4.35 (dd, *J* = 15.0, 6.0 Hz, 1 H), 2.73 (s, 1 H), 1.99 (s, 3 H), 1.51 (s, 3 H), 1.30 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.42, 169.84, 162.95 (d, *J* = 246.96 Hz), 140.28 (d, *J* = 6.93 Hz), 130.22 (d, *J* = 8.19 Hz), 123.17 (d, *J* = 3.02 Hz) , 114.58 (d, *J* = 21.80 Hz), 114.41 (d, *J* = 21.17 Hz), 60.18, 45.76, 42.96 (d, *J* = 6.5 Hz), 31.13, 28.53, 23.17. ^{19}F NMR (377 MHz, $CDCl_3$): -113.90 (m). HRMS m/z (ESI): calculated for MH^+ 299.1224, found 299.1285.

Characterization of thiol **2c**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 (d, *J* = 5.5 Hz, 1 H), 7.22 (d, *J* = 5.5 Hz, 1 H), 7.02 (d, *J* = 8.5 Hz, 1 H), 7.00 (d, *J* = 8.5 Hz, 1 H), 6.79 (s, 1 H), 6.61 (d, *J* = 9.0 Hz, 1H), 4.44 (dd, *J* = 15.0, 6.0 Hz, 1 H), 4.41 (d, *J* = 8.5 Hz, 1 H), 4.33 (dd, *J* = 15.0, 6.0 Hz, 1 H), 2.73 (s, 1 H), 2.02 (s, 3 H), 1.50 (s, 3 H), 1.28 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): 170.35, 169.67, 162.21 (d, *J* = 246.58 Hz), 133.42 (d, *J* = 3.02 Hz), 129.44 (d, *J* = 8.19 Hz), 115.61 (d, *J* = 21.67 Hz), 60.25, 45.66, 42.86, 31.13, 28.45, 23.22. ^{19}F NMR (377 MHz, $CDCl_3$): -115.28 (m). HRMS m/z (ESI): calculated for MH^+ 299.1224, found 299.1265.

Characterization of thiol **2d**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15 (d, *J* = 5.5 Hz, 1 H), 7.14 (d, *J* = 5.5 Hz, 1 H), 6.99 (t, *J* = 8.5 Hz, 2 H), 6.53 (d, *J* = 7.5 Hz, 1 H), 6.31 (s, 1 H), 4.27 (d, *J* = 9.0 Hz, 1 H), 3.55 (app. sextet, *J* = 6.5 Hz, 1 H), 3.46 (app. sextet, *J* = 7.0 Hz, 1 H), 2.79 (t, *J* = 7.0 Hz, 2 H), 2.68 (s, 1 H), 2.03 (s, 3 H), 1.44 (s, 3 H), 1.25 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.21, 169.70, 161.71 (d, *J* = 245.32 Hz), 134.08 (d, *J* = 3.02 Hz), 130.15 (d, *J* = 7.94 Hz), 115.46 (d, *J* = 21.29 Hz), 60.27, 45.50, 40.57, 34.71, 31.02, 28.40, 23.25. ^{19}F NMR (377 MHz, $CDCl_3$): -116.91 (m). HRMS m/z (ESI): calculated for MH^+ 313.1381, found 313.1476.

Characterization of thiol **2e**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (s, 1 H), 7.24 (app. pentet, *J* = 7.5 Hz, 1 H), 6.87 (t, *J* = 8.0 Hz, 2 H), 6.74 (d, *J* = 9.0 Hz, 1 H), 4.65 (d, *J* = 9.5 Hz, 1 H), 4.59, (dd, *J* = 14.0, 6.0 Hz, 1 H), 4.37 (dd, *J* = 14.5, 5.0 Hz, 1 H), 2.54 (s, 1 H), 1.92 (s, 3 H), 1.44 (s, 3 H), 1.26 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.19, 169.50, 161.54 (dd, *J* = 250.11, 7.94 Hz), 129.60 (t, *J* = 10.21 Hz), 113.43 (t, *J* = 19.40 Hz), 111.42 (d, *J* = 5.80 Hz), 111.26 (d, *J* = 5.54 Hz), 59.94, 46.38, 31.11 (t, *J* = 4.03 Hz), 30.77, 28.52, 23.03. ^{19}F NMR (377 MHz, $CDCl_3$): -115.07 (q, *J* = 5.28 Hz). HRMS m/z (ESI): calculated for MH^+ 317.1130, found 317.1134.

Characterization of thiol **2f**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (s, 1 H), 6.78 (d, *J* = 6.5 Hz, 2 H), 6.73-6.67 (m, 2 H), 4.56 (d, *J* = 9.5 Hz, 1 H), 4.42 (dd, *J* = 15.50, 6.0 Hz, 1 H), 4.33 (dd, *J* = 15.50, 6.0 Hz, 1 H), 2.72 (s, 1 H), 2.01 (s, 3 H), 1.51 (s, 3 H), 1.31 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.55, 170.04, 163.16 (dd, *J* = 249.61, 12.73 Hz), 141.87 (t, *J* = 8.82 Hz), 110.31 (d, *J* = 6.05 Hz), 110.15 (d, *J* = 5.92 Hz), 102.84 (t, *J* = 25.33 Hz), 60.12, 45.71, 42.60, 31.12, 28.56, 23.16. ^{19}F NMR (377 MHz, $CDCl_3$): -109.84 (t, *J* = 7.92 Hz). HRMS m/z (ESI): calculated for MH^+ 317.1130, found 317.1205.

Characterization of thiol **2g**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54-7.50 (m, 3 H), 7.45-7.41 (m, 2 H), 6.70 (d, *J* = 9.0 Hz, 1 H), 4.57 (d, *J* = 9.0 Hz, 1 H), 4.52 (dd, *J* = 15.0, 6.0 Hz, 1 H), 4.38 (dd, *J* = 15.0, 6.0 Hz, 1 H), 2.71 (s, 1 H), 1.96 (s, 3 H), 1.50 (s, 3 H), 1.30 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): 170.47, 169.97, 138.90, 130.97 (q, *J* = 32.26 Hz), 130.93, 129.12, 124.26, 123.97(q, *J* = 272.92 Hz), 60.11, 45.80, 42.87, 31.08, 28.52, 23.08. ^{19}F NMR (377 MHz, $CDCl_3$): -63.22 (s). HRMS m/z (ESI): calculated for MH^+ 349.1192, found 349.1267.

Characterization of thiol **2h**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.38 (m, 4 H), 6.57-6.52 (m, 2 H), 4.31 (d, *J* = 8.8 Hz, 1 H), 3.62 (app. sextet, *J* = 6.8 Hz, 1 H), 3.46 (app. sextet, *J* = 6.8 Hz, 1 H), 2.90 (t, *J* = 6.8 Hz, 2 H), 2.67 (s, 1 H), 2.02 (s, 3 H), 1.43 (s, 3 H), 1.24 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.25, 169.83, 139.49, 132.14, 131.47 (q, *J* = 32.36 Hz), 129.08, 125.48 (q, *J* =3.78 Hz), 123.53 (q, *J* =3.78 Hz), 124.06 (q, *J* = 272.79 Hz), 60.21, 45.52, 40.32, 35.31, 31.00, 28.41, 23.22. ^{19}F NMR (377 MHz, $CDCl_3$): -63.13 (s). HRMS m/z (ESI): calculated for MH^+ 363.1349, found 363.1442.

Characterization of thiol **2i**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (s, 1 H), 6.89 (t, *J* = 7.0 Hz, 2 H), 6.89 (d, *J* = 9.0 Hz, 1 H), 4.52 (d, *J* = 9.0 Hz, 1 H), 4.37 (dd, *J* = 15.5, 6.0 Hz, 1 H), 4.30 (dd, *J* = 15.5, 6.0 Hz, 1 H), 2.72 (s, 1 H), 2.03 (s, 3 H), 1.51 (s, 3 H), 1.31 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.59, 170.08, 151.28 (ddd, *J* = 251.12, 10.08, 3.91 Hz), 139.96 (t, *J* = 15.37 Hz), 137.96 (t, *J* = 15.75 Hz), 134. 34 (m), 111.52 (d, *J* = 5.04 Hz), 111.38 (d, *J* = 5.04 Hz), 60.17, 45.61, 42.27, 31.13, 28.57, 23.20. ^{19}F NMR (377 MHz, $CDCl_3$): -134.07 (m), -162.26 (m). HRMS m/z (ESI): calculated for MH^+ 335.1036, found 335.1081.

Characterization of thiol **2j**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 (s, 1H), 7.53 (t, *J* = 7.5 Hz, 1 H), 7.11 (t, *J* = 7.5 Hz, 2 H), 6.75 (d, *J* = 9.0 Hz, 1 H), 4.60 (d, *J* = 9.5 Hz, 1 H), 4.48 (dd, *J* = 15.5, 6.0 Hz, 1 H), 4.38 (dd, *J* = 15.5, 6.0 Hz, 1 H), 2.68 (s, 1), 1.99 (s, 3 H), 1.51 (s, 3 H), 1.32 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.60, 170.17, 159.86 (dd, *J* = 257.29, 2.27 Hz), 145.13 (d, *J* = 7.43 Hz), 127.40 (qd, *J* = 4.54, 1.64 Hz), 122.85 (d, *J* = 3.40 Hz), 122.48 (q, *J* = 272.54 Hz), 117.29 (qd, *J* = 33.14, 12.47 Hz), 115.67 (d, *J* = 21.29 Hz), 60.22, 45.73, 42.51,

31.13, 28.61, 23.16. ^{19}F NMR (377 MHz, $CDCl_3$): -61.82 (d, *J* = 11.31 Hz), -114.42 (m). HRMS m/z (ESI): calculated for MH^+ 367.1098, found 367.1102.

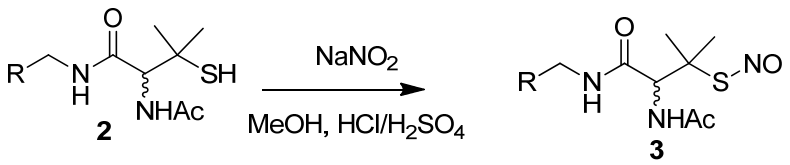
Characterization of thiol **2k**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (s, 1 H), 7.31 (s, 1 H), 7.21 (d, *J* = 8.5 Hz, 1 H), 7.17 (d, *J* = 8.5 Hz, 1 H), 6.68 (d, *J* = 8.0 Hz, 1 H), 4.53 (dd, *J* = 15.5, 6.0 Hz, 1 H), 4.48 (d, *J* = 6.0 Hz, 1 H), 4.42 (dd, *J* = 15.5, 6.0 Hz, 1 H), 2.75 (s, 1 H), 2.01 (s, 3 H), 1.52 (s, 3 H), 1.31 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.61, 170.16, 162.58 (d, *J* = 249.98 Hz), 141.98 (d, *J* = 7.18 Hz), 132.77 (qd, *J* = 33.01, 8.06 Hz), 123.15 (qd, *J* = 273.17, 3.02 Hz), 119.81 (m), 117.85 (d, *J* = 22.05 Hz), 111.83 (dq, *J* = 24.57, 3.78 Hz), 60.13, 45.55, 42.46, 31.10, 28.54, 23.11. ^{19}F NMR (377 MHz, $CDCl_3$): -61.39 (d, *J* = 2.52 Hz), -110.78 (t, *J* = 2.52 Hz). HRMS m/z (ESI): calculated for MH^+ 367.1098, found 367.1101.

Characterization of thiol **2l**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (m, 2 H), 7.72 (s, 1 H), 6.71 (d, *J* = 9.0 Hz, 1 H), 4.58 (d, *J* = 9.5 Hz, 1 H), 4.57 (dd, *J* = 16.0, 6.0 Hz, 1 H), 4.47 (dd, *J* = 16.0, 6.0 Hz, 1 H), 2.73 (s, 1 H), 2.00 (s, 3 H), 1.51 (s, 3 H), 1.31 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.66, 170.28, 140.78, 131.89 (q, *J* = 33.39 Hz), 127.45 (d, *J* = 2.77 Hz), 123.19 (q, *J* = 273.29 Hz), 121.31 (pentet, *J* = 3.78 Hz), 60.12, 45.56, 42.38, 31.05, 28.52, 23.05. ^{19}F NMR (377 MHz, $CDCl_3$): -63.44 (s). HRMS m/z (ESI): calculated for MH^+ 417.1066, found 417.1099.

Characterization of thiol **2m**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34-7.31 (m, 2 H), 7.29-7.25 (m, 3 H), 6.82 (s, 1 H), 6.61 (d, *J* = 9.0 Hz, 1 H), 4.48 (dd, *J* = 15.0, 6.0 Hz, 1 H), 4.44 (d, *J* = 9.5 Hz, 1 H), 4.36 (dd, *J* = 15.0, 6.0 Hz, 1 H), 2.73 (s, 1 H), 2.00 (s, 3 H), 1.51 (s, 3 H), 1.29 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.31, 169.63, 137.54, 128.75, 127.75, 127.62, 60.27, 45.79, 43.61, 31.13, 28.47, 23.20. HRMS m/z (ESI): calculated for MH^+ 281.1318, found 281.1357.

Characterization of thiol **2n**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.93 (s, 1 H), 6.65 (d, *J* = 9.0 Hz, 1 H), 6.49 (s, 2 H), 4.47 (d, *J* = 9.0 Hz, 1 H), 4.46 (dd, *J* = 14.5, 5.0 Hz, 1 H), 4.23 (dd, *J* = 14.5, 5.0 Hz, 1 H), 3.83 (s, 6 H), 3.82 (s, 3 H), 2.72 (s, 1 H), 1.52 (s, 3 H), 1.31 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.30, 169.68, 153.42, 137.30, 133.34, 104.59, 60.85, 60.39, 56.11, 45.81, 43.73, 31.20, 28.46, 23.21. HRMS m/z (ESI): calculated for MH^+ 371.1635, found 371.1664.

2.3 Synthesis and characterization of NO donors 3a-3n



R = 2-FPh (**a**), 3-FPh (**b**), 4-FPh (**c**), 4-FPhCH$_2$ (**d**), 2,6-diFPh (**e**), 3,5-diFPh (**f**),3-CF$_3$Ph (**g**), 3-CF$_3$PhCH$_2$ (**h**), 3,4,5-triFPh (**i**), 3-F,4-CF$_3$Ph (**j**), 3-F,5-CF$_3$Ph (**k**), 3,5-diCF$_3$Ph (**l**), Ph (**m**), and 3,4,5-triMeOPh (**n**)

Due to RSNOs are light sensitive, the synthetic procedure and the workup were performed under dark conditions. To a solution of free thiols **2a**-**2n** (200 mg) in MeOH (10 mL) was added HCl (10 mL, 1.0 M). Then the mixture solution was cooled in ice-water bath. Concentrated H_2SO_4 (2 mL) was added into reaction mixture. When the temperature of reaction solution was below 5 ^oC, $NaNO_2$ (3.0 eq.) dissolved in water (2 mL) was added into the reaction in one portion, and then ice-water bath was removed. After string for 1 h, the reaction mixture was extracted by CH_2Cl_2 (5 mL × 3). All the organic layer was dried by $NaSO_4$, and taken to dryness. The product was dried under vacuum overnight under dark conditions to obtain yields (see Table S2). All desired products were characterized by $^1H/^{13}C/^{19}F$ NMR and HRMS.

Table S2. Yields for the synthesis of NO donors **3a**-**3n**.

Compound #	Yields (%)
3a	90
3b	89
3c	85
3d	93
3e	93
3f	90
3g	91
3h	91
3i	92
3j	90
3k	95
3l	99
3m	92
3n	94

All the donors **3a**-**3n** were re-characterized by ^1H NMR spectroscopy after 7 days stored at -20 ^oC under dark conditions in the refrigerator, and all of them were stable without any decomposition based on ^1H NMR results (data not showed). The stability studies of NO donor **3l** during -20 ^oC storage are summarized in Figure S1. During the storage at -20 ^oC under dark conditions, no disulfide of **3l**

was observed after being stored for 1, 7 and 40 days based on the ^{1}H NMR results. Clean ^{1}H NMR spectra for **3l** in DMSO-d_6 were exactly the same after the storage for 1, 7 and 40 days. Therefore, no decomposition of NO donor **3l** was observed after being stored at -20 ^{o}C under dark conditions for more than one month.

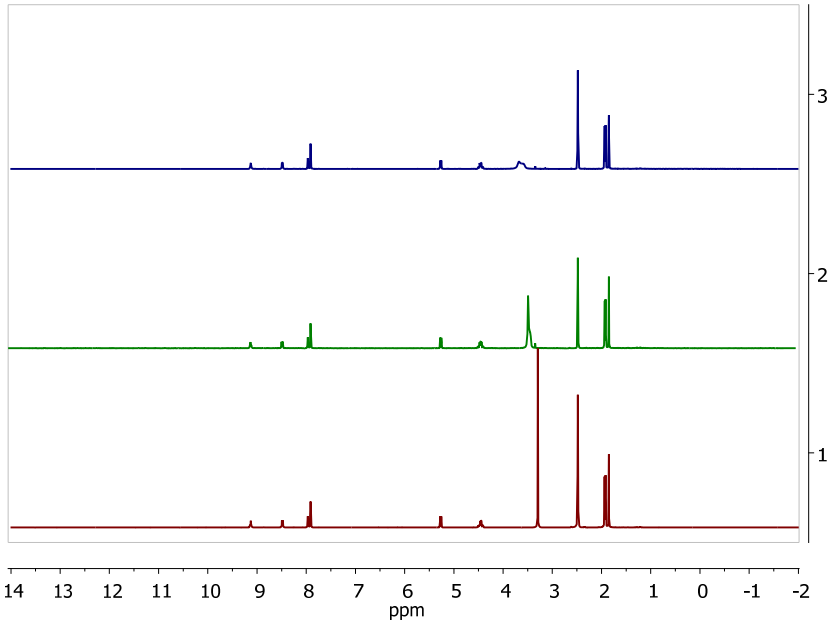


Figure S1. ^{1}H NMR spectra for NO donor **3l** stored at -20 ^{o}C under dark conditions after (1) day 1, (2) day 7, (3) day 40 (spectrum 1: DMSO-d_6 (2.48 ppm) and H_2O (3.30 ppm); spectrum 2: DMSO-d_6 (2.48 ppm) and H_2O (3.49 ppm); spectrum 3: DMSO-d_6 (2.48 ppm) and H_2O (3.65 ppm)).

Characterization of target **3a**: ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.96 (t, J = 5.5 Hz, 1 H), 8.43 (d, J = 10.0 Hz, 1 H), 7.34-7.30 (m, 2 H), 7.19-7.15 (m, 2 H), 5.27 (d, J = 9.5 Hz, 1 H), 4.37 (dd, J = 15.0, 6.0 Hz, 1 H), 4.30 (dd, J = 15.0, 6.0 Hz, 1 H), 1.96 (s, 3 H), 1.92 (s, 3 H), 1.85 (s, 3 H). ^{13}C NMR (126 MHz, DMSO-d_6): δ 169.80, 168.78, 160.53 (d, J = 245.32 Hz), 130.37 (d, J = 4.41 Hz), 129.58 (d, J = 8.06 Hz), 125.80 (d, J = 14.99 Hz), 124.70 (d, J = 3.40 Hz), 115.57 (d, J = 21.80 Hz), 60.06, 59.35, 36.56 (d, J = 4.41 Hz), 27.08, 25.30, 22.75. ^{19}F NMR (377 MHz, DMSO-d_6): -118.66 (m). HRMS m/z (ESI): calculated for MH^+ 328.1126, found 328.1171.

Characterization of target **3b**: ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.00 (t, J = 5.5 Hz, 1 H), 8.45 (d, J = 9.5 Hz, 1 H), 7.36 (q, J = 7.0 Hz, 1 H), 7.10-7.05 (m, 3 H), 5.26 (d, J = 9.5 Hz, 1 H), 4.32 (dd, J = 15.0, 6.0 Hz, 1 H), 4.28 (dd, J = 15.0, 6.0 Hz, 1 H), 1.96 (s, 3 H), 1.94 (s, 3 H), 1.86 (s, 3 H). ^{13}C NMR (126 MHz, DMSO-d_6): δ 169.87, 168.92, 162.59 (d, J = 243.18 Hz), 142.35 (d, J = 6.3 Hz), 130.67 (d, J = 7.56 Hz), 123.79 (d, J = 2.52 Hz), 114.45 (d, J = 21.42 Hz), 114.07 (d, J = 20.16

Hz), 59.92, 59.48, 42.17, 27.00, 25.45, 22.75. ^{19}F NMR (377 MHz, DMSO-d_6): -113.52 (m). HRMS m/z (ESI): calculated for MH^+ 328.1126, found 328.1144.

Characterization of target **3c**: ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.98 (t, J = 5.5 Hz, 1 H), 8.44 (d, J = 10.0 Hz, 1 H), 7.29 (d, J = 8.5 Hz, 1 H), 7.28 (d, J = 8.5 Hz, 1 H), 7.16 (d, J = 8.5 Hz, 1 H), 7.14 (d, J = 8.5 Hz, 1 H), 5.25 (d, J = 9.5 Hz, 1 H), 4.30 (dd, J = 15.0, 6.0 Hz, 1 H), 4.24 (dd, J = 15.0, 6.0 Hz, 1 H), 1.95 (s, 3 H), 1.92 (s, 3 H), 1.85 (s, 3 H). ^{13}C NMR (126 MHz, DMSO-d_6): δ 169.82, 168.71, 162.64 (d, J = 243.05 Hz), 135.55 (d, J = 2.77 Hz), 129.88 (d, J = 8.32 Hz), 115.46 (d, J = 21.29 Hz), 60.04, 59.41, 41.98, 27.09, 25.37, 22.75. ^{19}F NMR (377 MHz, DMSO-d_6): -115.99 (m). HRMS m/z (ESI): calculated for MH^+ 328.1126, found 328.1131.

Characterization of target **3d**: ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.50 (t, J = 5.0 Hz, 1 H), 8.35 (d, J = 9.5 Hz, 1 H), 7.24 (d, J = 8.5 Hz, 1 H), 7.23 (d, J = 8.5 Hz, 1 H), 7.09 (d, J = 8.5 Hz, 1 H), 7.07 (d, J = 8.5 Hz, 1 H), 5.15 (d, J = 10.0 Hz, 1 H), 3.36 (app septet, J = 7.0 Hz, 1 H), 3.28 (app septet, J = 7.0 Hz, 1 H), 2.76-2.66 (m, 2 H), 1.88 (s, 3 H), 1.86 (s, 3 H), 1.83(s, 3 H). ^{13}C NMR (126 MHz, DMSO-d_6): δ 169.67, 168.56, 161.28 (d, J = 241.92 Hz), 135.76 (d, J = 3.15 Hz), 130.89 (d, J = 7.94 Hz), 115.31 (d, J = 2.67 Hz), 60.03, 59.37, 40.47, 34.17, 27.06, 25.23, 22.72. ^{19}F NMR (377 MHz, DMSO-d_6): -117.28 (m). HRMS m/z (ESI): calculated for MH^+ 342.1282, found 342.1323.

Characterization of target **3e**: ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.90 (t, J = 5.0 Hz, 1 H), 8.38 (d, J = 9.5 Hz, 1 H), 7.40 (app pentet, J = 9.5 Hz, 1 H), 7.09 (t, J = 8.0 Hz, 2 H), 5.22 (d, J = 9.5 Hz, 1 H), 4.39 (dd, J = 14.5, 5.5 Hz, 1 H), 4.28 (dd, J = 14.5, 5.5 Hz, 1 H), 1.91 (s, 3 H), 1.88 (s, 3 H), 1.82 (s, 3 H). ^{13}C NMR (126 MHz, DMSO-d_6): δ 169.68, 168.34, 161.50 (dd, J = 248.47, 8.32 Hz), 130.50 (t, J = 10.46 Hz), 113.95 (t, J = 19.40 Hz), 111.88 (dd, J = 19.91, 5.67 Hz), 60.20, 59.06, 30.91 (t, J = 3.65 Hz), 27.07, 25.06, 22.73. ^{19}F NMR (377 MHz, DMSO-d_6): -114.73 (t, J = 5.66 Hz). HRMS m/z (ESI): calculated for MH^+ 346.1031, found 346.1069.

Characterization of target **3f**: ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.03 (t, J = 5.5 Hz, 1 H), 8.47 (d, J = 10.0 Hz, 1 H), 7.11 (t, J = 9.5 Hz, 1 H), 6.95 (d, J = 7.0 Hz, 2 H), 5.26 (d, J = 9.5 Hz, 1 H), 4.30 (app d, J = 6.0 Hz, 2 H), 1.97 (s, 3 H), 1.94 (s, 3 H), 1.87 (s, 3 H). ^{13}C NMR (126 MHz, DMSO-d_6): δ 169.96, 169.14, 162.79 (dd, J = 246.58, 13.36 Hz), 144.18 (t, J = 8.95 Hz), 110.67 (dd, J = 19.78, 5.80 Hz), 102.70 (t, J = 25.70 Hz), 59.72, 59.55, 41.94, 26.88, 25.52, 22.73. ^{19}F NMR (377 MHz, DMSO-d_6): -105.39 (t, J = 6.79 Hz). HRMS m/z (ESI): calculated for MH^+ 346.1031, found 346.1038.

Characterization of target **3g**: ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.08 (t, J = 5.5 Hz, 1 H), 8.49 (d, J = 9.5 Hz, 1 H), 7.61-7.56 (m, 4 H), 5.28 (d, J = 9.5 Hz, 1 H), 4.41 (dd, J = 15.5, 6.0 Hz, 1 H), 4.35 (dd, J = 15.5, 6.0 Hz, 1 H), 1.96 (s, 3 H), 1.93 (s, 3 H), 1.86 (s, 3 H). ^{13}C NMR (126 MHz, DMSO-d_6): δ 169.87, 169.06, 140.90, 131.91, 129.77, 129.48 (q, J = 31.50 Hz), 124.67 (q, J = 272.54 Hz), 124.19 (q, J = 3.78 Hz), 124.03 (q, J = 3.78 Hz), 59.80, 59.46, 42.16, 26.87, 25.45, 22.70. ^{19}F NMR (377 MHz, DMSO-d_6): -61.19 (s). HRMS m/z (ESI): calculated for MH^+ 378.1094, found 378.1124.

Characterization of target **3h**: ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.54 (t, J = 5.0 Hz, 1 H), 8.37 (d, J = 9.5 Hz, 1 H), 7.58-7.50 (m, 4 H), 5.13 (d, J = 9.5 Hz, 1 H) 3.47 (app septet, J = 7.0 Hz, 1 H), 3.32 (app septet, J = 7.0 Hz, 1 H), 2.85 (t, J = 6.5 Hz, 2 H), 1.82(s, 9 H). ^{13}C NMR (126 MHz, DMSO-d_6): δ 169.65, 168.62, 141.16, 133.40, 129.60, 129.41 (q, J = 31.50 Hz), 125.72 (q, J = 3.78 Hz), 124.75 (q, J = 272.79 Hz), 123.35 (q, J = 3.65 Hz), 59.97, 59.32, 40.06, 34.55, 27.01, 25.09, 22.67. ^{19}F NMR (377 MHz, DMSO-d_6): -61.30 (s). HRMS m/z (ESI): calculated for MH^+ 392.1250, found 392.1341.

Characterization of target **3i**: ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.02 (t, J = 4.0 Hz, 1 H), 8.48 (d, J = 6.5 Hz, 1 H), 7.16 (t, J = 5.0 Hz, 1 H), 5.25 (d, J = 6.5 Hz, 1 H), 4.28 (app d, J = 4.5 Hz, 2 H), 1.97 (s, 3 H), 1.92 (s, 3 H), 1.87 (s, 3 H). ^{13}C NMR (126 MHz, DMSO-d_6): δ 170.01, 169.19, 150.51 (ddd, J = 177.03, 6.93, 2.52 Hz), 138.70 (t, J = 11.09 Hz), 137.29 (t, J = 11.09 Hz), 136.90 (m), 112.10 (dd, J = 12.47, 2.65 Hz), 59.62, 41.58, 26.83, 25.54, 22.71. ^{19}F NMR (377 MHz, DMSO-d_6): -135.50 (dd, J = 21.49, 9.05 Hz), -164.08 (tt, J = 21.87, 6.79 Hz). HRMS m/z (ESI): calculated for MH^+ 364.0937, found 364.0963.

Characterization of target **3j**: ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.09 (t, J = 5.5 Hz, 1 H), 8.48 (d, J = 9.5 Hz, 1 H), 7.74 (t, J = 8.0 Hz, 1 H), 7.33 (d, J = 12.0 Hz, 1 H), 7.28 (d, J = 8.0 Hz, 1 H), 5.28 (d, J = 9.5 Hz, 1 H), 4.39 (app d, J = 5.5 Hz, 2 H), 1.98 (s, 3 H), 1.94 (s, 3 H), 1.88 (s, 3 H). ^{13}C NMR (126 MHz, DMSO-d_6): δ 169.98, 169.22, 159.27 (d, J = 253.76 Hz), 147.96 (d, J = 7.69 Hz), 127.71 (dd, J = 16.13, 4.03 Hz), 124.04 (d, J = 18.77 Hz), 123.12 (q, J = 272.03 Hz), 115.99 (t, J = 20.79 Hz), 115.44 (qd, J = 32.38, 12.22 Hz), 59.69, 59.57 (d, J = 17.51 Hz), 41.99, 26.89 (d, J = 4.16 Hz), 25.49 (d, J = 3.02 Hz), 22.73. ^{19}F NMR (377 MHz, DMSO-d_6): -59.83 (d, J = 12.06 Hz), -116.29 (m). HRMS m/z (ESI): calculated for MH^+ 396.1000, found 396.1009.

Characterization of target **3k**: ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.09 (t, J = 5.5 Hz, 1 H), 8.49 (d, J = 9.5 Hz, 1 H), 7.55 (d, J = 9.0 Hz, 1 H), 7.47 (s, 1 H), 7.41 (d, J = 9.5 Hz, 1 H), 5.28 (d, J = 9.5 Hz, 1 H), 4.41 (dd, J = 15.5, 6.5 Hz, 1 H), 4.37 (dd, J = 15.5, 6.5 Hz, 1 H), 1.96 (s, 3 H), 1.94 (s, 3 H), 1.87 (s, 3 H). ^{13}C NMR (126

MHz, DMSO-d_6): δ 169.96, 169.27, 162.32 (d, J = 246.83 Hz), 144.29 (d, J = 7.56 Hz), 131.28 (qd, J = 32.83, 8.57 Hz) 123.75 (qd, J = 273.17, 3.15 Hz), 120.41 (t, J = 3.28 Hz), 118.75 (d, J = 21.80 Hz), 111.61 (dd, J = 24.95, 3.65 Hz), 59.60, 59.56, 41.84, 26.76, 25.55, 22.69. ^{19}F NMR (377 MHz, DMSO-d_6): -61.36 (s), -111.07 (t, J = 9.05 Hz). HRMS m/z (ESI): calculated for MH^+ 396.1000, found 396.1009.

Characterization of target **3l**: ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.15 (t, J = 7.0 Hz, 1 H), 8.51 (d, J = 12.0 Hz, 1 H), 7.99 (s, 1 H), 7.93 (s, 2 H), 5.28 (d, J = 12.0 Hz, 1 H), 4.51 (dd, J = 20.0, 7.5 Hz, 1 H), 4.44 (dd, J = 20.0, 7.5 Hz, 1 H), 1.96 (s, 3 H), 1.94 (s, 3 H), 1.87 (s, 3 H). ^{13}C NMR (126 MHz, DMSO-d_6): δ 169.97, 169.40, 143.07, 130.57 (q, J = 32.89 Hz), 128.43 (d, J = 2.77 Hz), 123.78 (q, J = 273.29 Hz), 121.00 (septet, J = 3.78 Hz), 59.57, 59.46, 41.80, 26.62, 25.58, 22.64. ^{19}F NMR (377 MHz, DMSO-d_6): -61.48 (s). HRMS m/z (ESI): calculated for MH^+ 446.0968, found 446.0981.

Characterization of target **3m**: ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.96 (t, J = 5.5 Hz, 1 H), 8.43 (d, J = 9.5 Hz, 1 H), 7.34-7.31 (m, 2 H), 7.26-7.23 (m, 3 H), 5.26 (d, J = 9.5 Hz, 1 H), 4.32 (dd, J = 15.0, 6.0 Hz, 1 H), 4.27 (dd, J = 15.0, 6.0 Hz, 1 H), 1.96 (s, 3 H), 1.93 (s, 3 H), 1.85 (s, 3 H). ^{13}C NMR (126 MHz, DMSO-d_6): δ 169.80, 168.70, 139.32, 128.72, 127.87, 127.33, 60.11, 59.44, 42.71, 27.12, 25.40, 22.76. HRMS m/z (ESI): calculated for MH^+ 310.1220, found 310.1243.

Characterization of target **3n**: ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.94 (t, J = 6.0 Hz, 1 H), 8.45 (d, J = 9.5 Hz, 1 H), 6.56 (s, 2 H), 5.27 (d, J = 10.0 Hz, 1 H), 4.28 (dd, J = 15.0, 6.0 Hz, 1 H), 4.21 (dd, J = 15.0, 6.0 Hz, 1 H), 3.74 (s, 6 H), 3.62 (s, 3 H), 1.99 (s, 3 H), 1.97 (s, 3 H), 1.86 (s, 3 H). ^{13}C NMR (126 MHz, DMSO-d_6): δ 169.86, 168.79, 153.19, 136.65, 135.02, 104.73, 60.42, 59.90, 59.61, 56.16, 42.63, 27.06, 25.56, 22.74. HRMS m/z (ESI): calculated for MH^+ 400.1537, found 400.1732.

3. Decompostion kinetic studies of NO donors

All the donors were dissolved in DMSO as the stock solution for kinetic studies. Both aerobic kinetics studies of photolytic and thermal decomposition of NO donors in a mixture of PBS and DMSO (50:50, v/v) were performed using either a PerkinElmer Lambda 35 or Shimadzu UV-1601 UV-Vis spectrophotometer. The photolytic decomposition of fluorinated NO donors in a mixture of PBS and DMSO (50:50, v/v) at room temperature (23 ^{o}C) was irradiated under a Rayonet photochemical reactor (RMR-600), which was equipped with eight 350 nm lamps (4 W). The photolysis was manually scanned by the UV-Vis spectrophotometer at room temperature (23 ◦C) after each irradiation time of 0, 15, 30, 45, 60, 90, 120, 180, 240, 360, 480, 600 and 780 s. The corresponding kinetic data was analyzed

with a first-order rate equation. Kinetics of **3l** were monitored at 282 nm, and the others' kinetics were analyzed at 342 nm. The thermal decomposition kinetic studies in a mixture of PBS and DMSO (50:50, v/v) at 37 ^{o}C were monitored at 342 nm overnight with a time period of 10 min. The kinetic profiles were analyzed using either a zero-order or a first-order rate equation. All UV-Vis data were proceeded using the Origin 8.0 software.

4. Analysis of decomposition products from NO donor 3k

A Sievers 280i chemiluminescence Nitric Oxide Analyzer (NOA) was utilized to determine the NO gas released from NO donor **3k** (1.50×10^{-7} mol). To have a rapid NO release, photolysis of NO donor **3k** in a mixture of PBS and DMSO (3 mL, 50:50, v/v) at room temperature (23 ^{o}C) was performed under a Rayonet photochemical reactor (RMR-600) with 350 nm lamps (4 W, 8 lamps). NO detection signals over time were integrated to calculate the total moles of NO released in each photolysis from the NO donor (1.50×10^{-7} mol). To determine the stoichiometric ratio, the photolysis of NO donor **3k** (1.50×10^{-7} mol) was independently carried out three times.

The disulfide derived from NO donor **3k** during the NO release in pure DMSO-d_6 was characterized by ^{1}H NMR spectroscopy. Before the NO release, NO donor **3k** (2.98 mol) in pure DMSO-d_6 was recorded by ^{1}H NMR spectroscopy. Then two separate sample of NO donor **3k** (2.98 mM) in pure DMSO-d_6 was prepared with trace amount of 3-trimethylsilylpropionic-2,2,3,3-d_4 acid sodium salt (chemical shift: 0 ppm). One sample was photolyzed at room temperature (23 ^{o}C) under a Rayonet photochemical reactor (RMR-600) with 350 nm lamps (4 W, 8 lamps), and the corresponding products was characterized by ^{1}H NMR spectroscopy and HRMS (ESI). The other sample covered by foil paper was kept in the oven set at 37 ^{o}C for 4 day, which was further recorded by ^{1}H NMR spectroscopy.

5. Theoretical calculations

All calculations were performed using Gaussian16.[1] Geometry optimizations were done using UB3LYP[2] with 6-311G(d,p) basis set. NO donors **1**, **3e**, **3l** and **3m** were selected as model compounds in our computational calculations to simulate this system. The trans conformation of RSNO was obtained as the most stable structure. In addition, it is found that the triplet state energy of the reactants is higher than that of the corresponding singlet state by 23-25 kcal/mol. Therefore, singlet state was assigned as the ground state. During the singlet transition state search process, no saddle point was observed, indicating that the S-N bond may not have a transition state in the homolysis process with the formation of NO. The optimized structure for the singlet ground-state of NO donors SNAP (**1**), **3e**, **3l** and **3m** were shown in Figure 1S, and the calculated S-N bond dissociation enthalpies (BDE) were listed in Table S3.

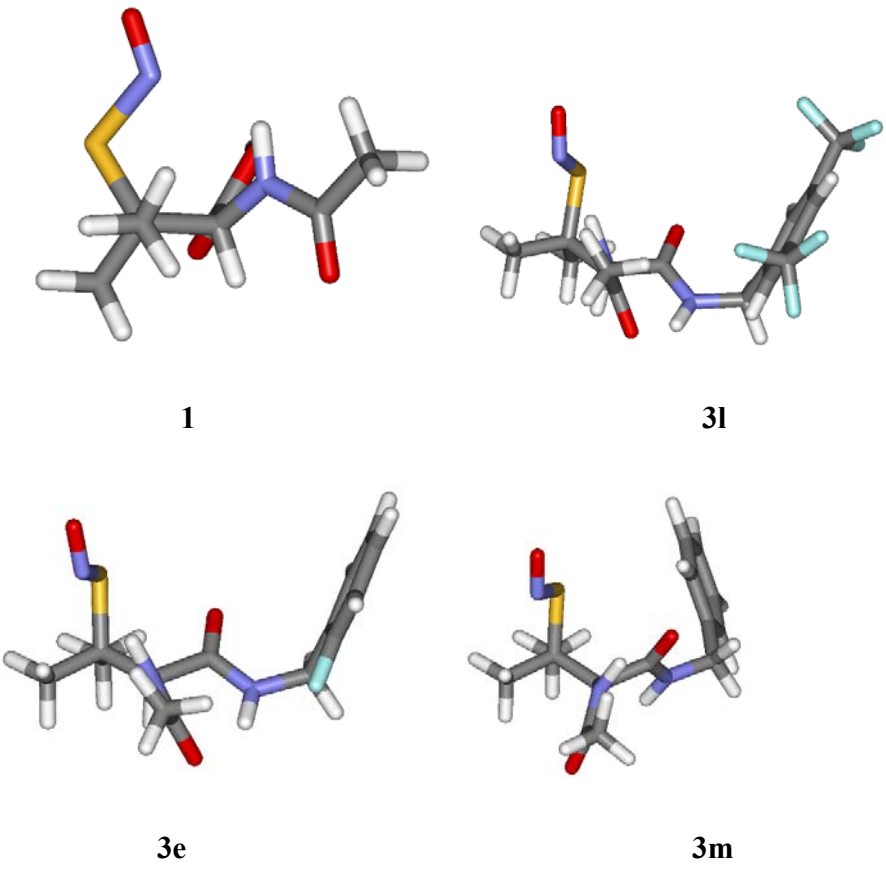


Figure S2. The optimized structures of NO donors (**1**, **3e**, **3l** and **3m**).

Table S3. The calculated S-N bond dissociation enthalpies (BDE) of NO donors (**1**, **3e**, **3l** and **3m**).

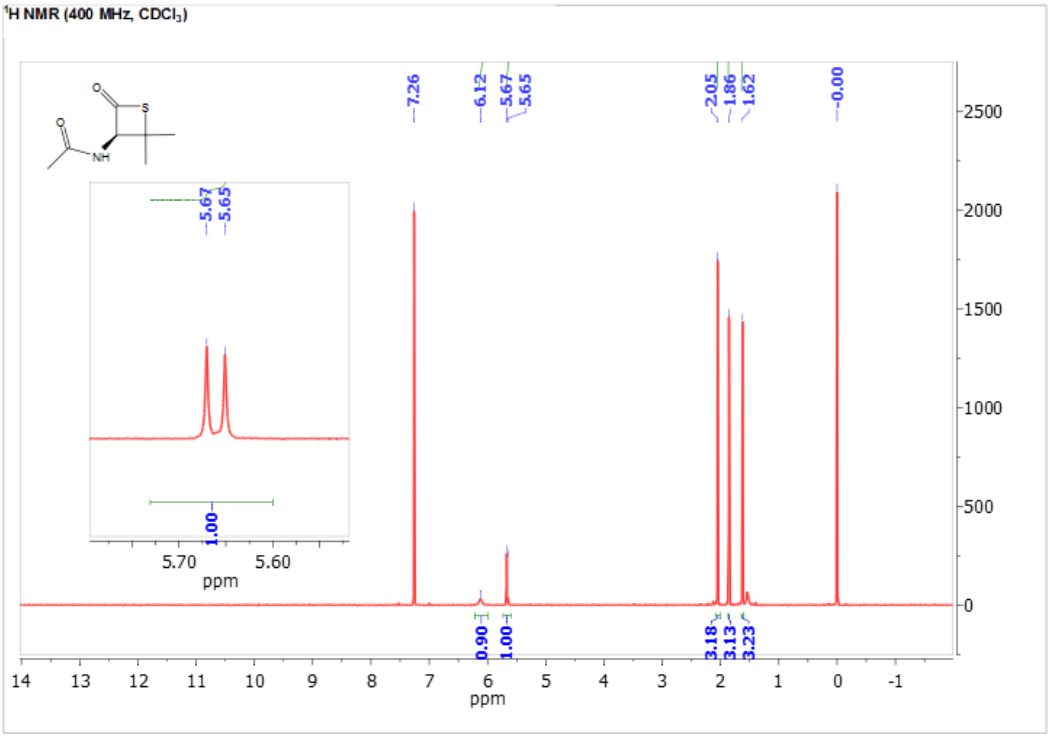
NO donors	BDE (S-N) (kcal/mol)
1	25.11
3e	21.52
3l	21.30
3m	19.01

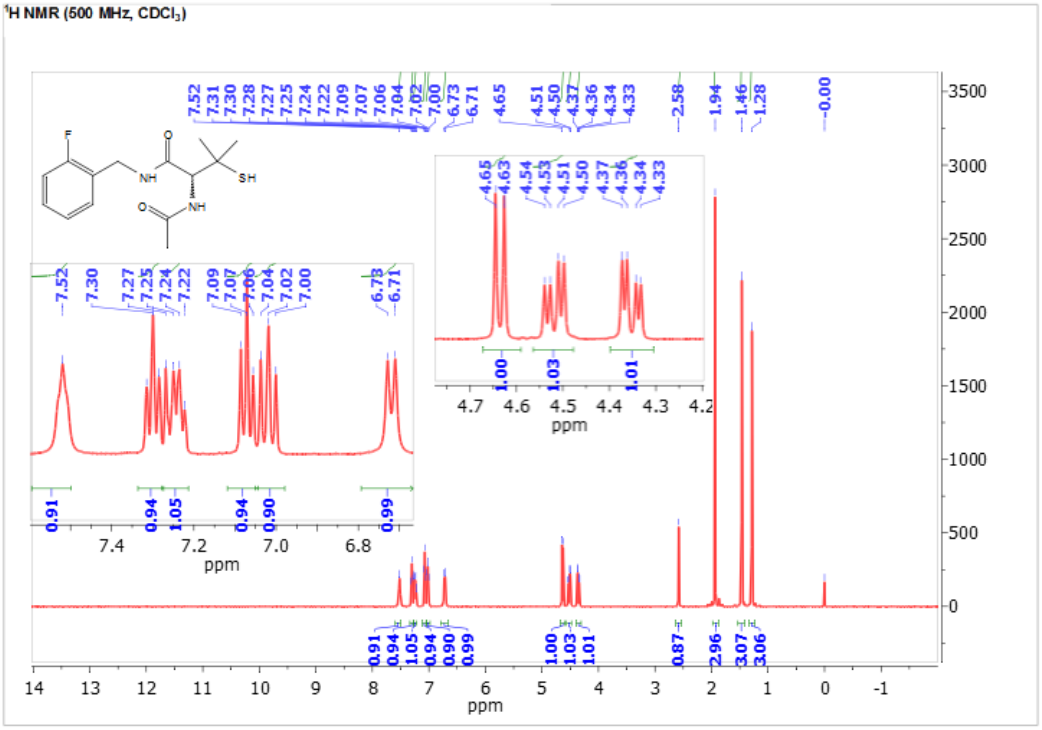
6. References

[1] Gaussian 16, Revision A.03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2016**.

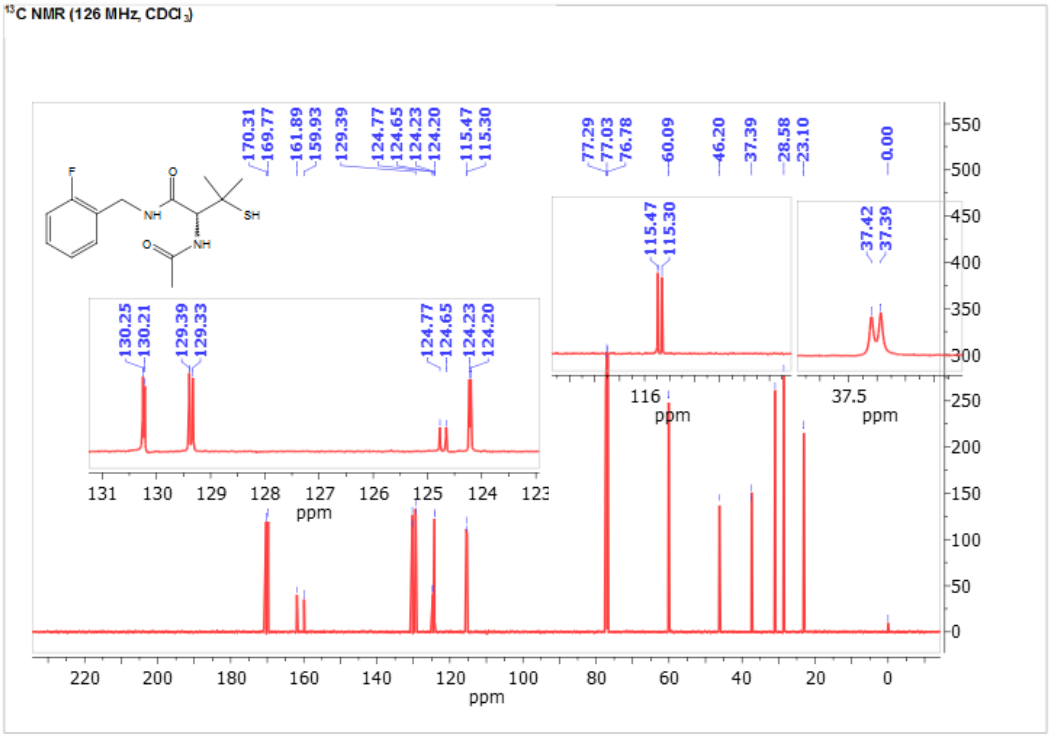
[2] (a) Becke, A. D. *J. Chem. Phys*. **1992**, *96*, 2155. (b) Becke, A. D. *J. Chem. Phys.* **1992**, *97*, 9173. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (d) Lee, C. Yang, W. Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

7. NMR spectra

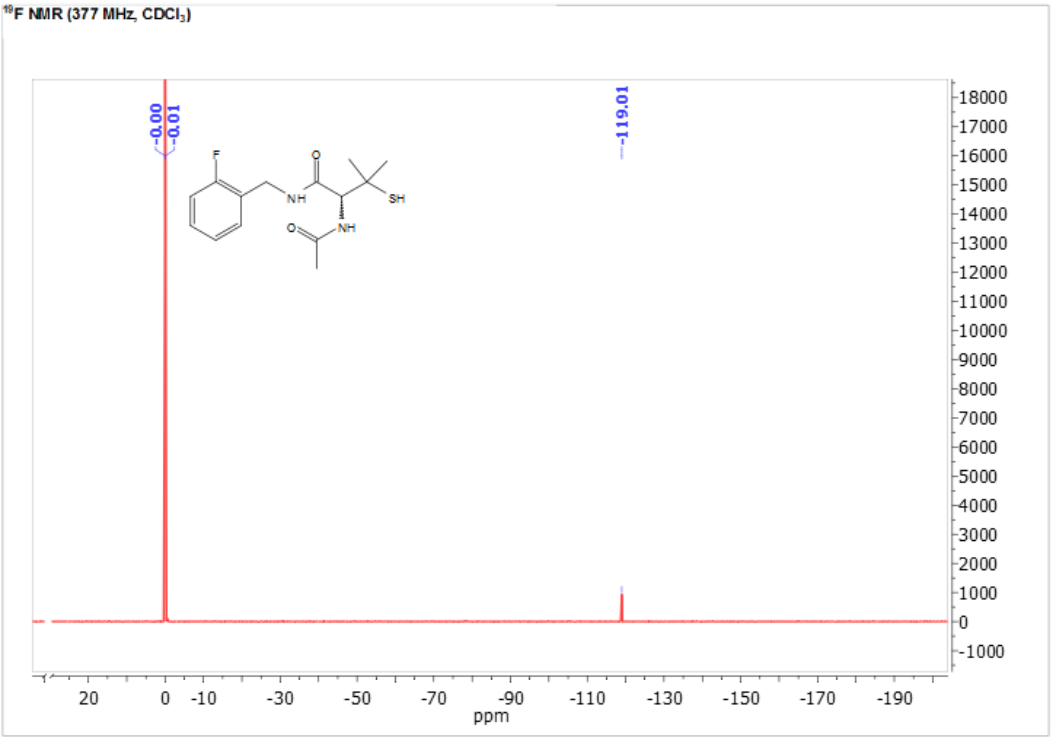


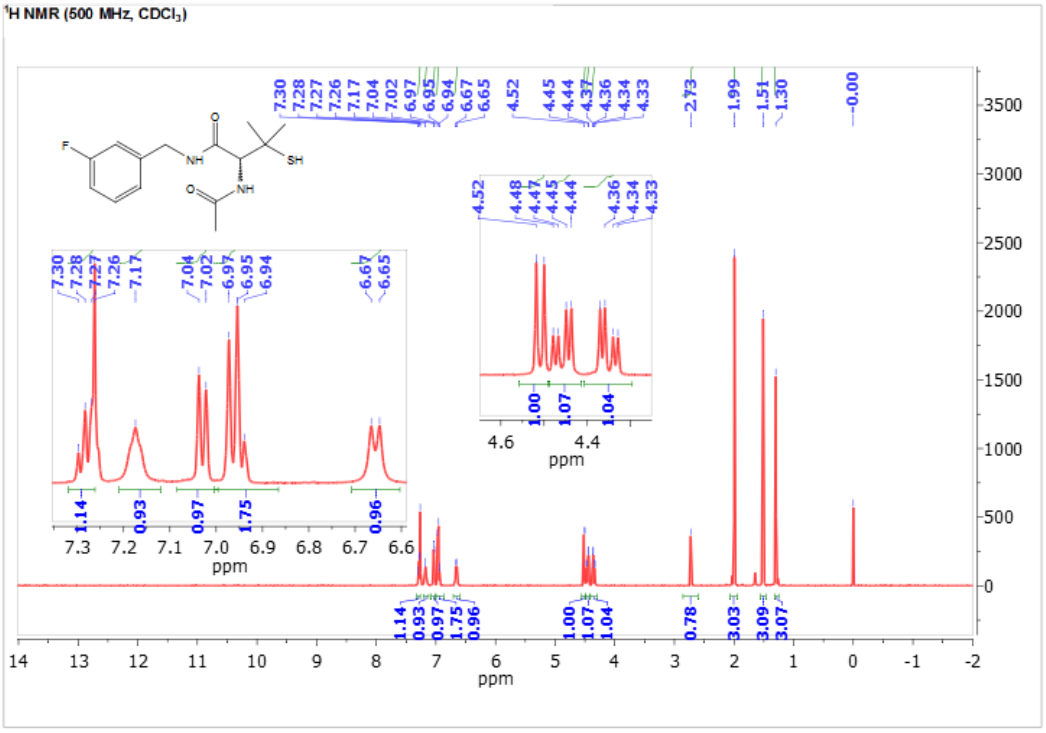


^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (377 MHz, $CDCl_3$)

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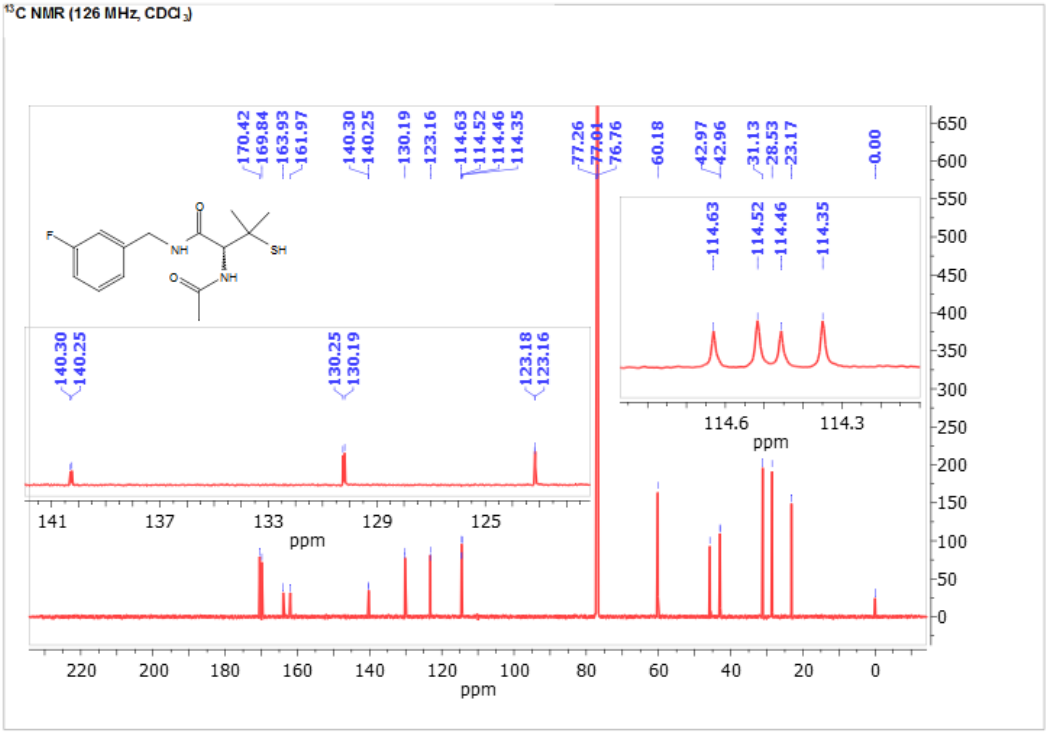
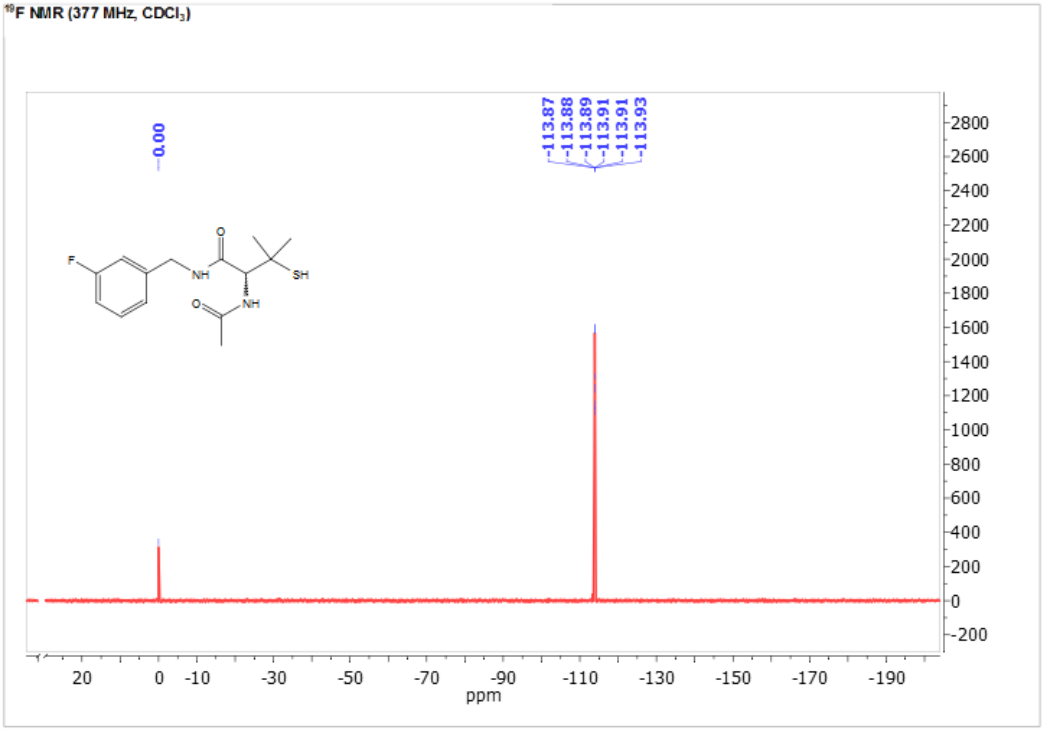
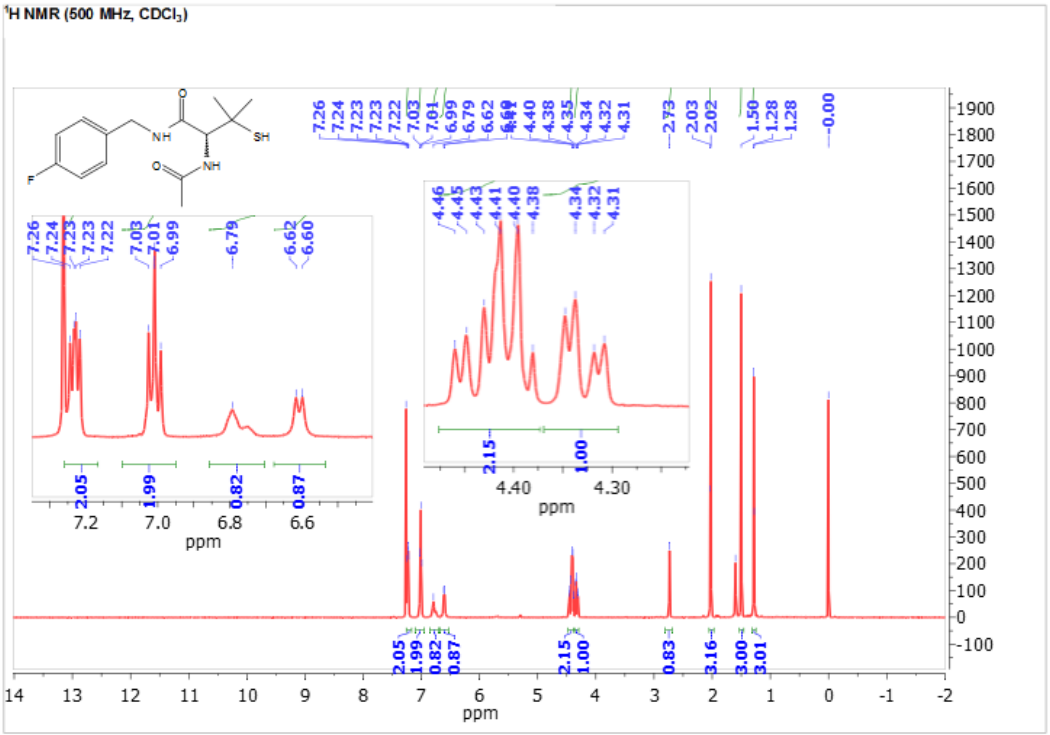
ppm

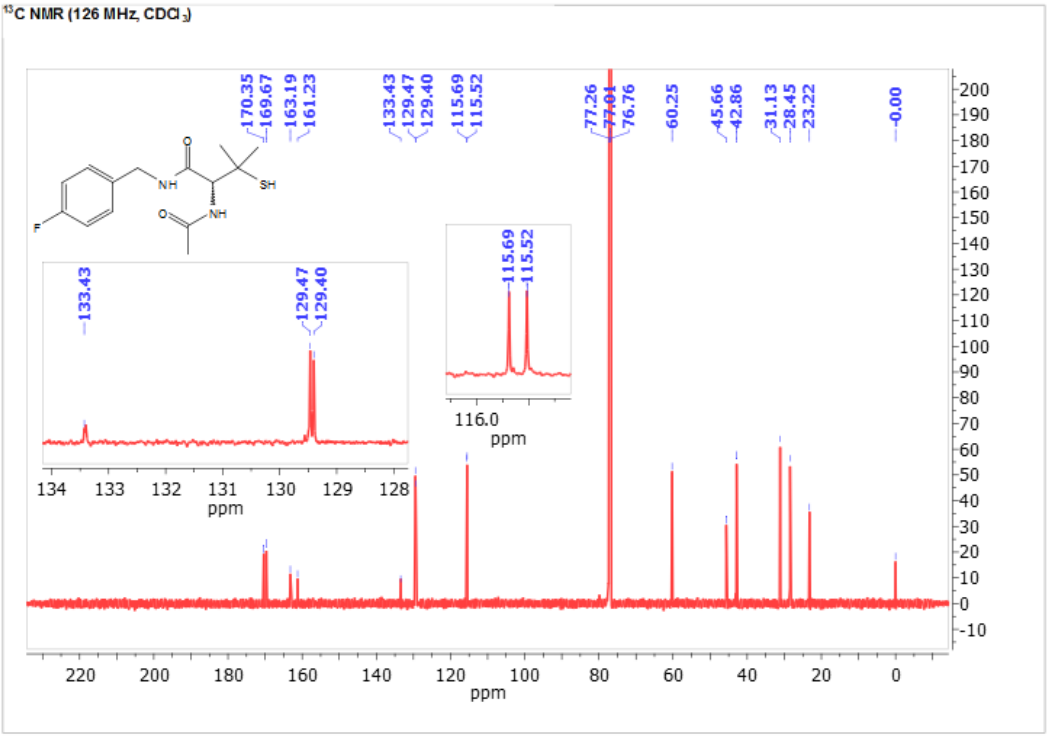

^{13}C NMR (126 MHz, CDCl$_3$)
ppm

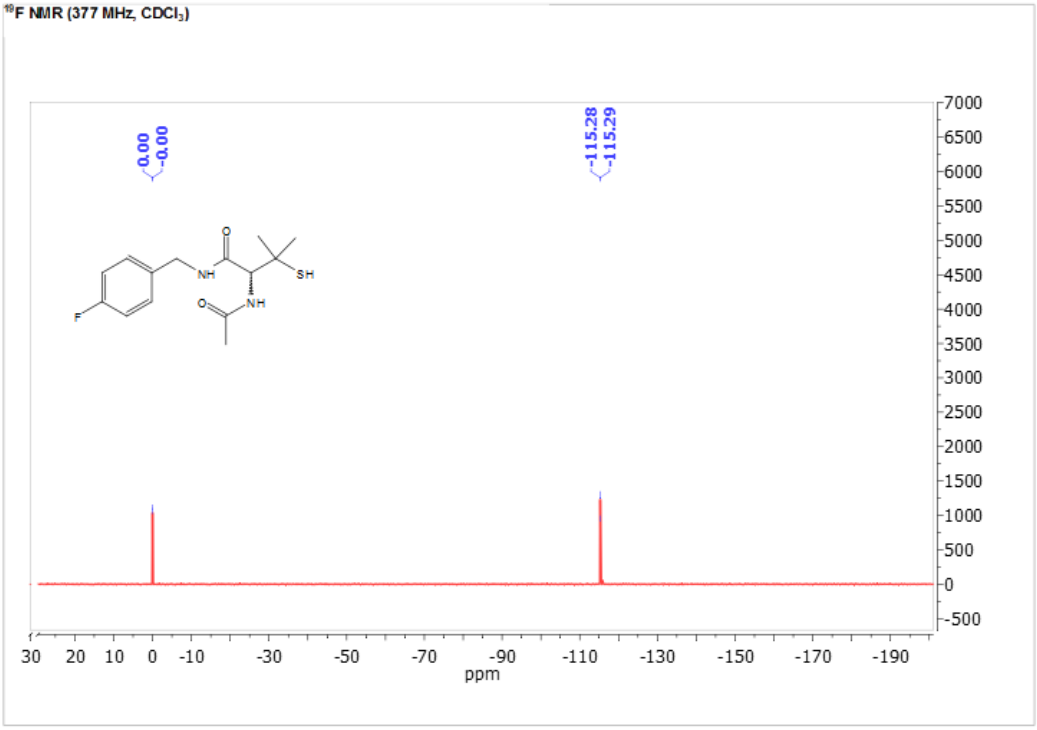
^{19}F NMR (377 MHz, $CDCl_3$)

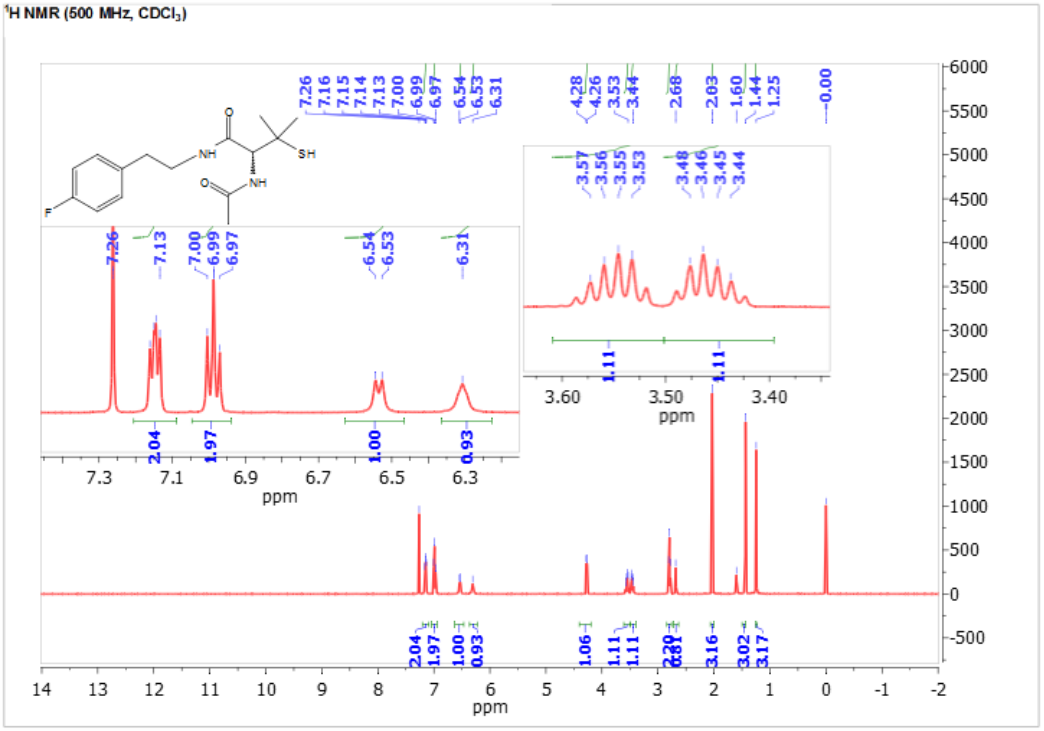


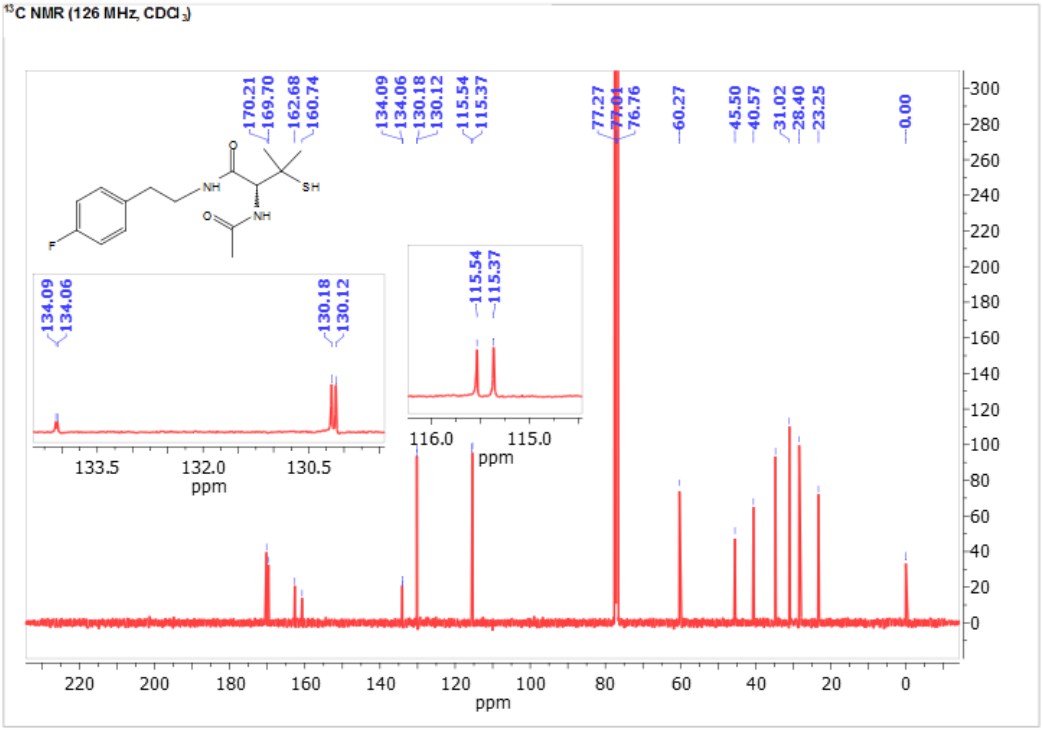
^{1}H NMR (500 MHz, $CDCl_3$)



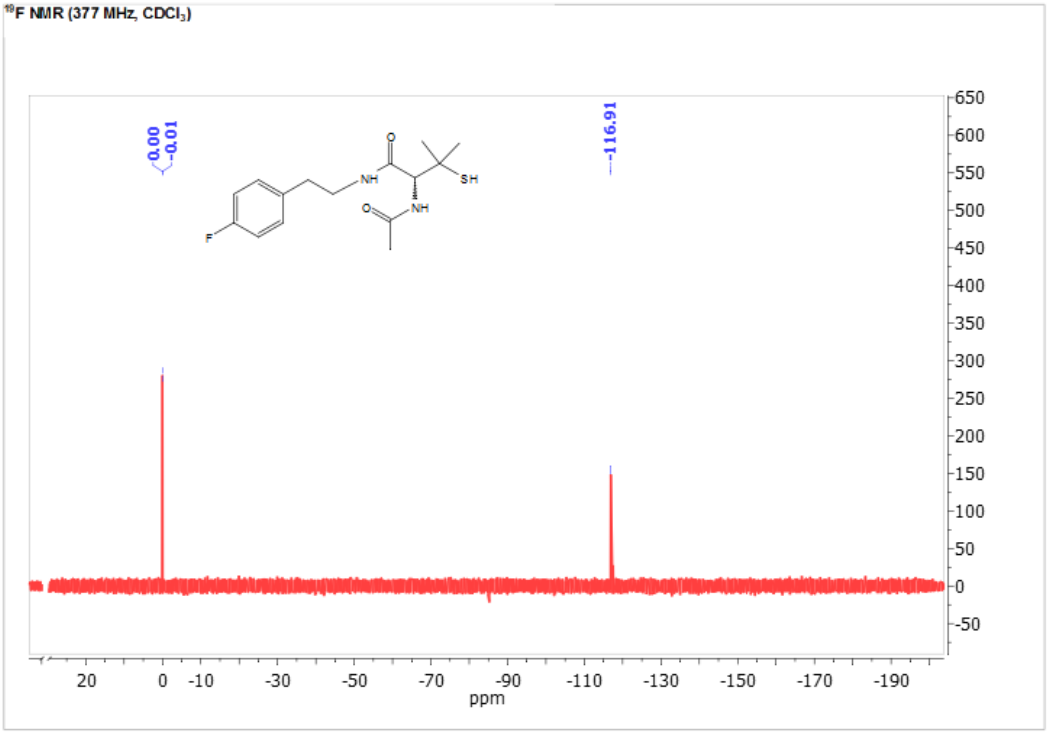

13C NMR (126 MHz, CDCl3)
170.35
169.67
163.19
161.23
133.43
129.47
129.40
115.69
115.52
77.26
77.01
76.76
60.25
45.66
42.86
31.13
28.45
23.22
0.00
ppm


19F NMR (377 MHz, CDCl3)
0.00
-0.00
-115.28
-115.29
ppm

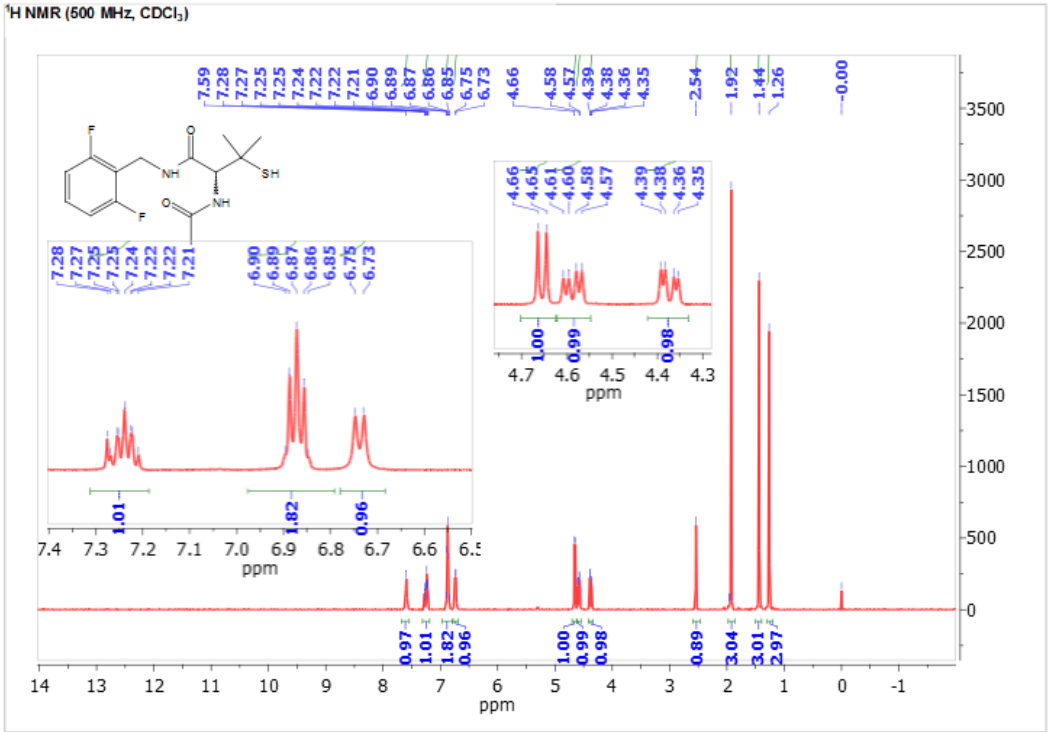

^{1}H NMR (500 MHz, CDCl$_3$)
ppm

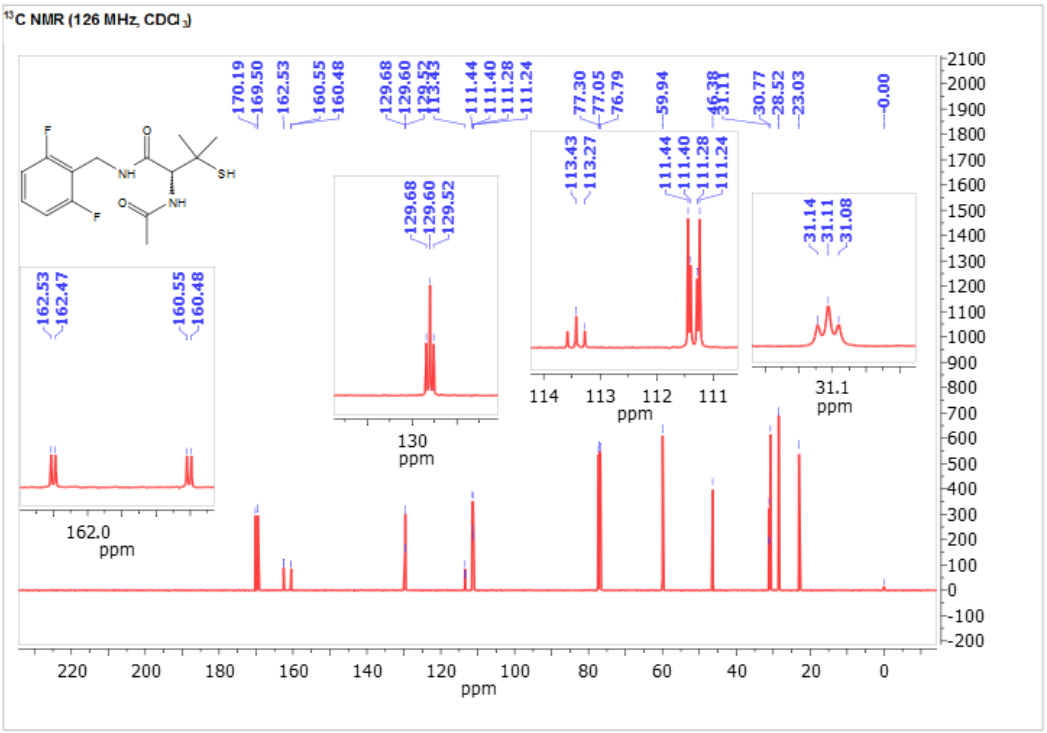

^{13}C NMR (126 MHz, CDCl$_3$)
ppm

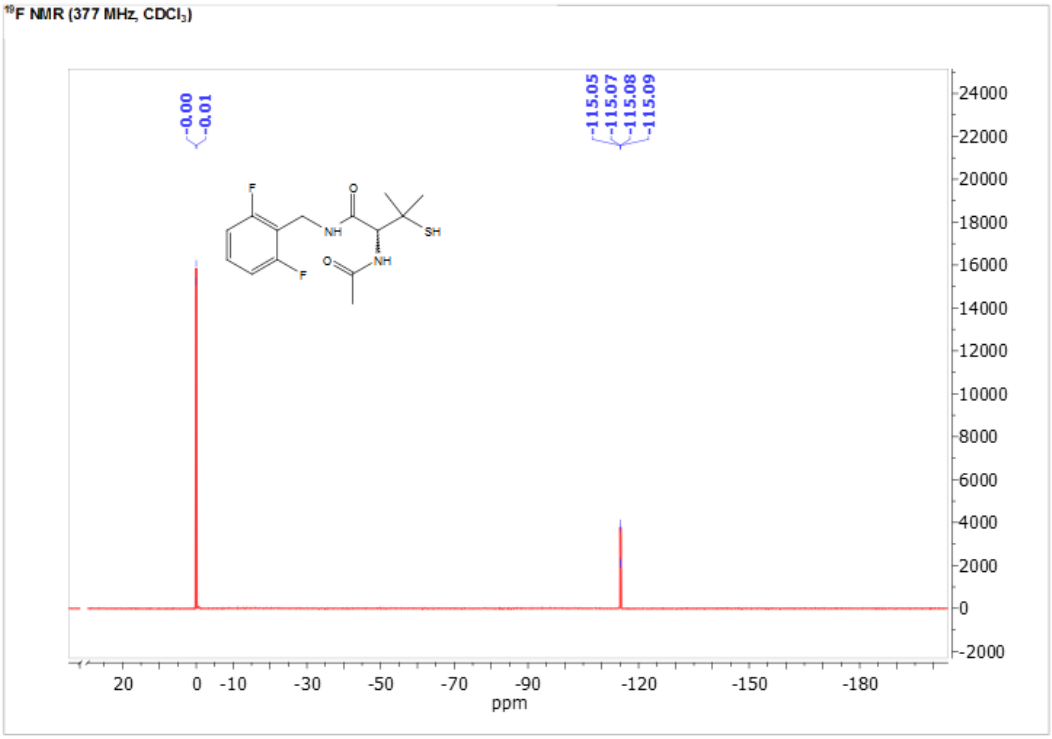
^{19}F NMR (377 MHz, $CDCl_3$)

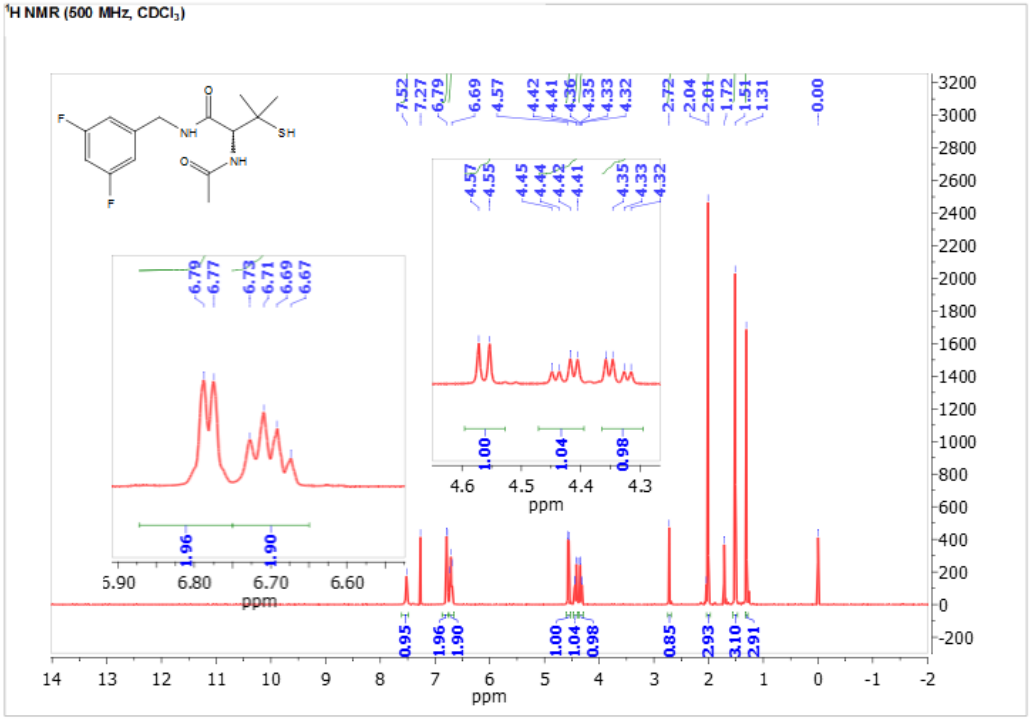


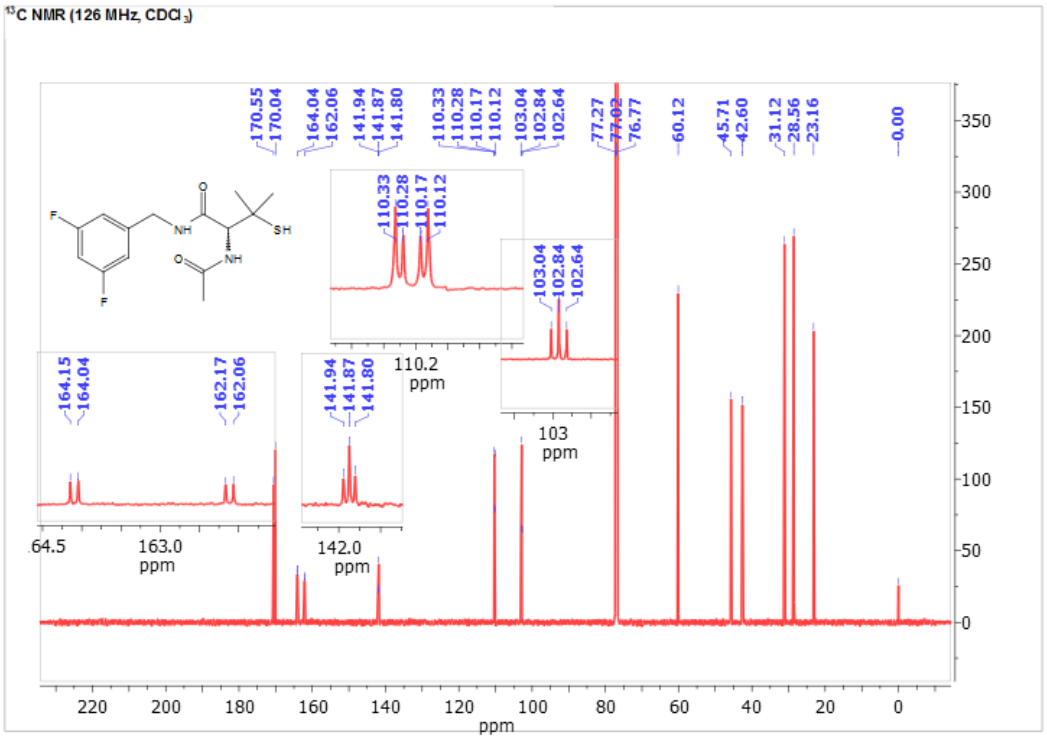
^{1}H NMR (500 MHz, $CDCl_3$)

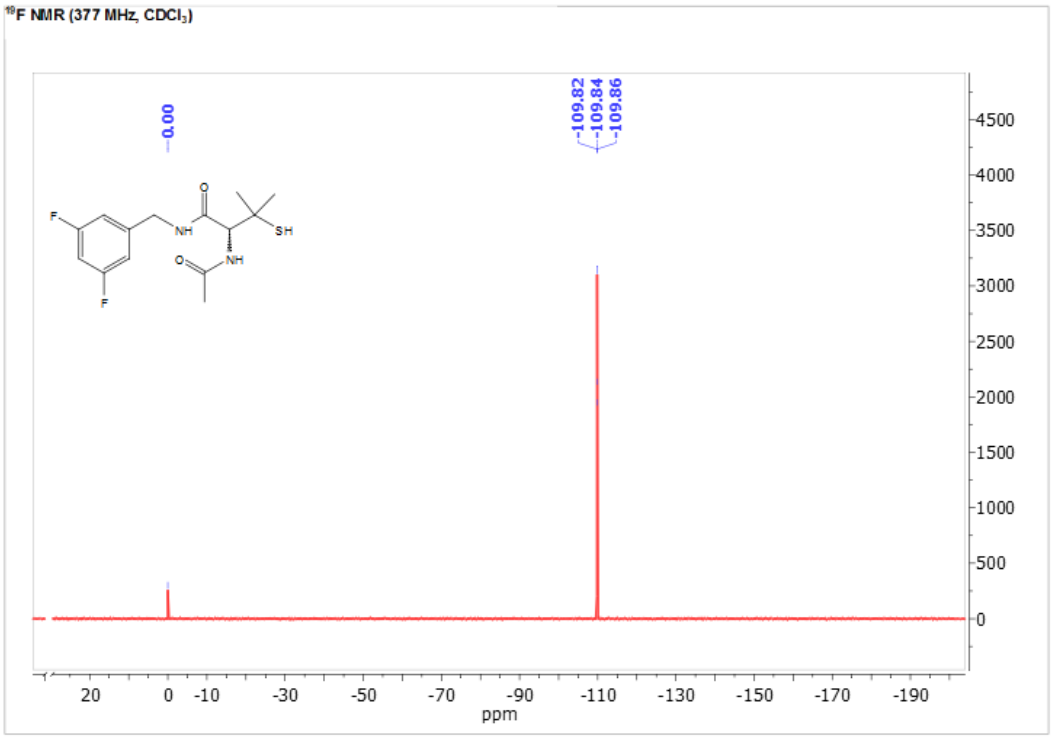


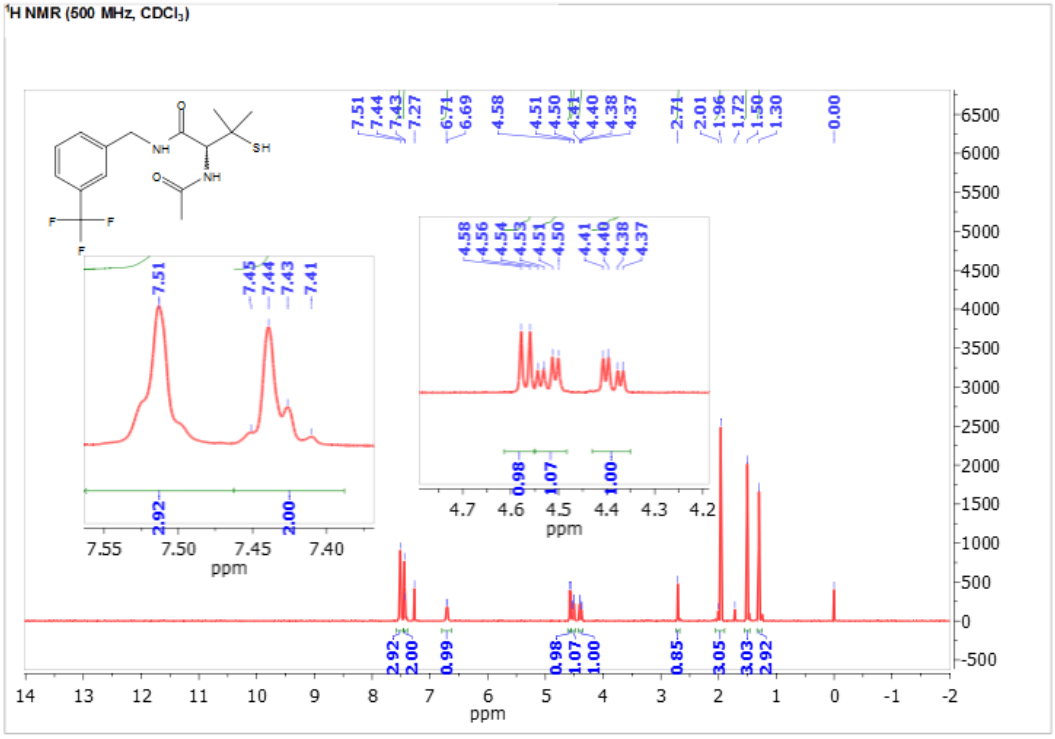

13C NMR (126 MHz, CDCl3)
170.19
169.50
162.53
160.55
160.48
129.68
129.60
129.52
113.43
111.44
111.40
111.28
111.24
77.30
77.05
76.79
59.94
46.38
31.11
30.77
28.52
23.03
0.00
ppm


19F NMR (377 MHz, CDCl3)
-0.00
-0.01
-115.05
-115.07
-115.08
-115.09
ppm

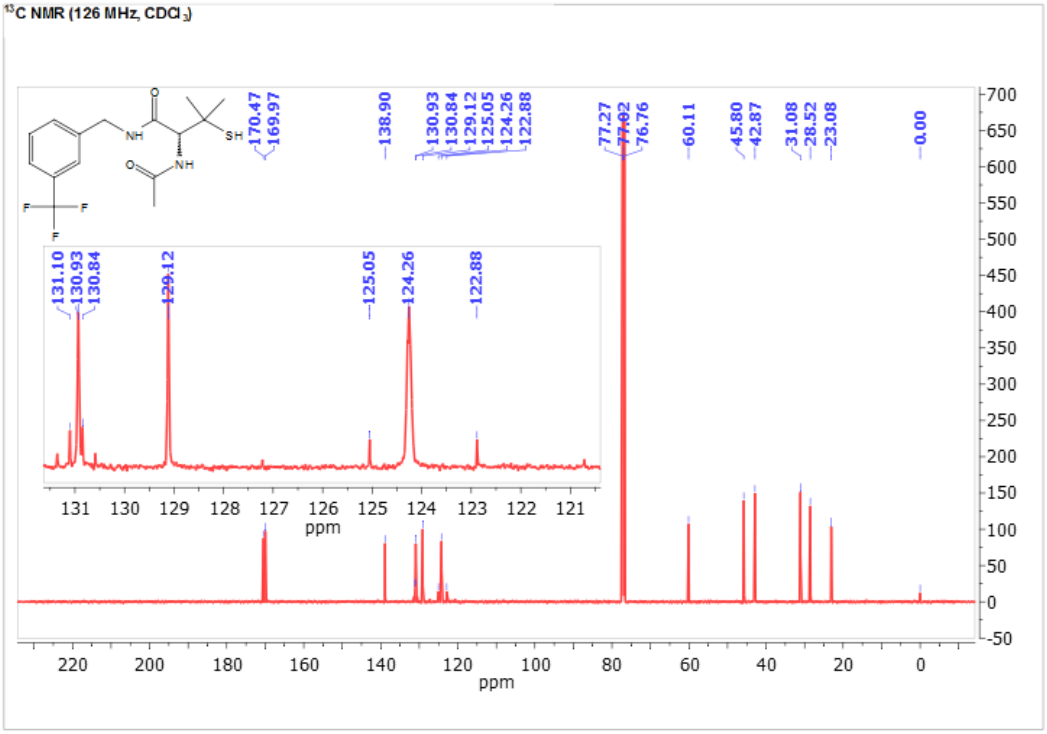

^{1}H NMR (500 MHz, CDCl$_3$)
7.52
7.27
6.79
6.69
4.57
4.42
4.41
4.36
4.35
4.33
4.32
2.72
2.04
2.01
1.72
1.51
1.31
0.00
ppm


^{13}C NMR (126 MHz, CDCl$_3$)
170.55
170.04
164.04
162.06
141.94
141.87
141.80
110.33
110.28
110.17
110.12
103.04
102.84
102.64
77.27
77.02
76.77
60.12
45.71
42.60
31.12
28.56
23.16
0.00
ppm

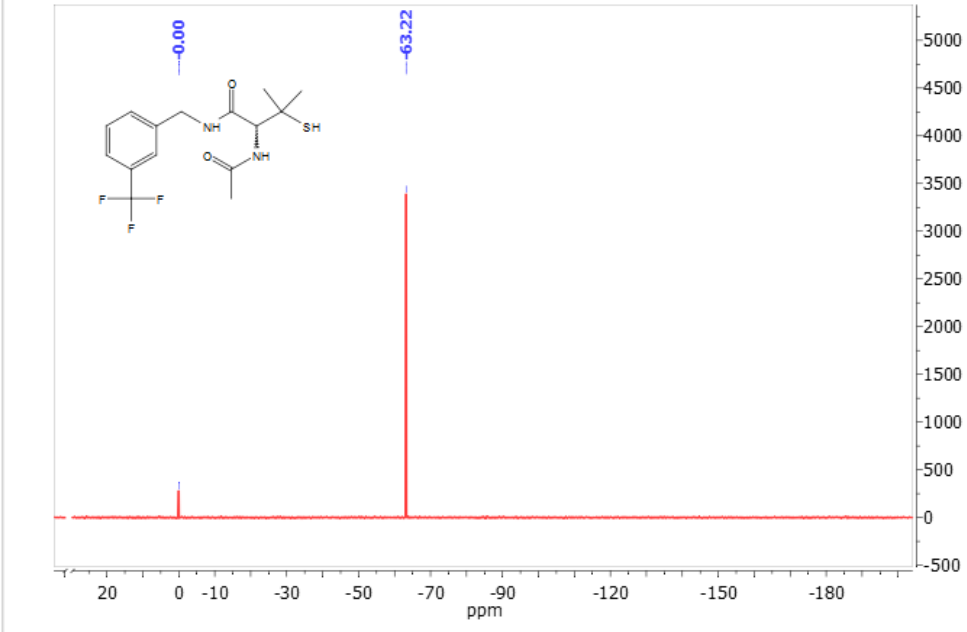

19F NMR (377 MHz, CDCl3)
0.00
-109.82
-109.84
-109.86
ppm

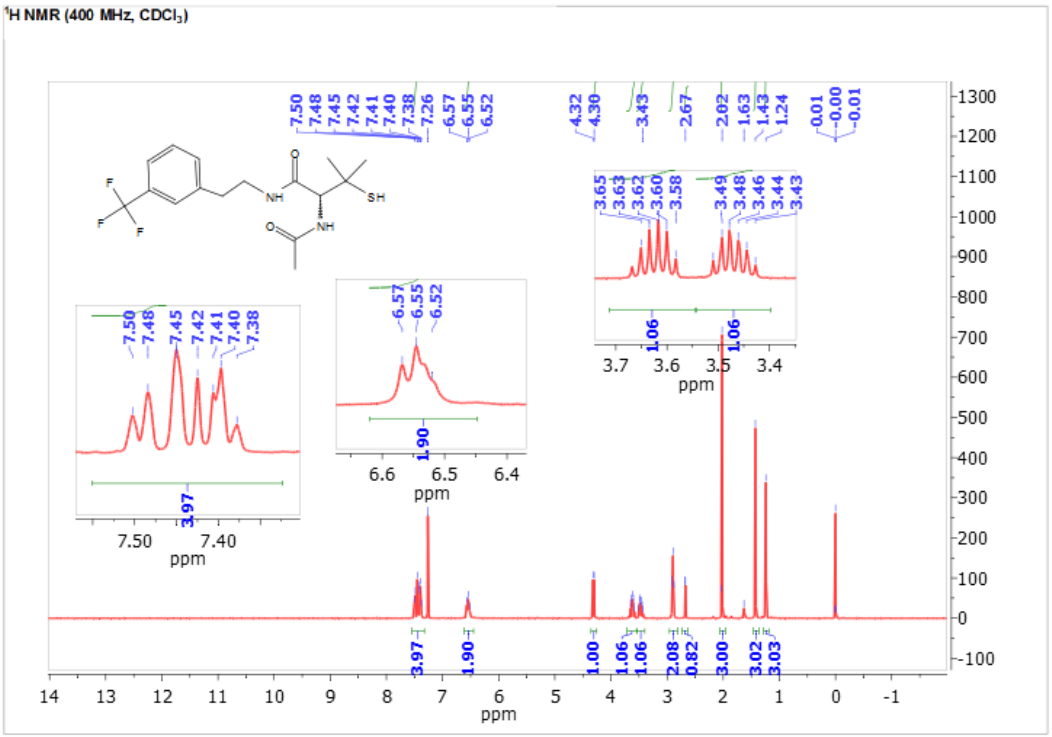

1H NMR (500 MHz, CDCl3)
7.51
7.44
7.43
7.27
6.71
6.69
4.58
4.51
4.50
4.41
4.40
4.38
4.37
2.71
2.01
1.96
1.72
1.50
1.30
0.00
2.92
2.00
0.99
0.98
1.07
1.00
0.85
3.05
3.03
2.92
ppm

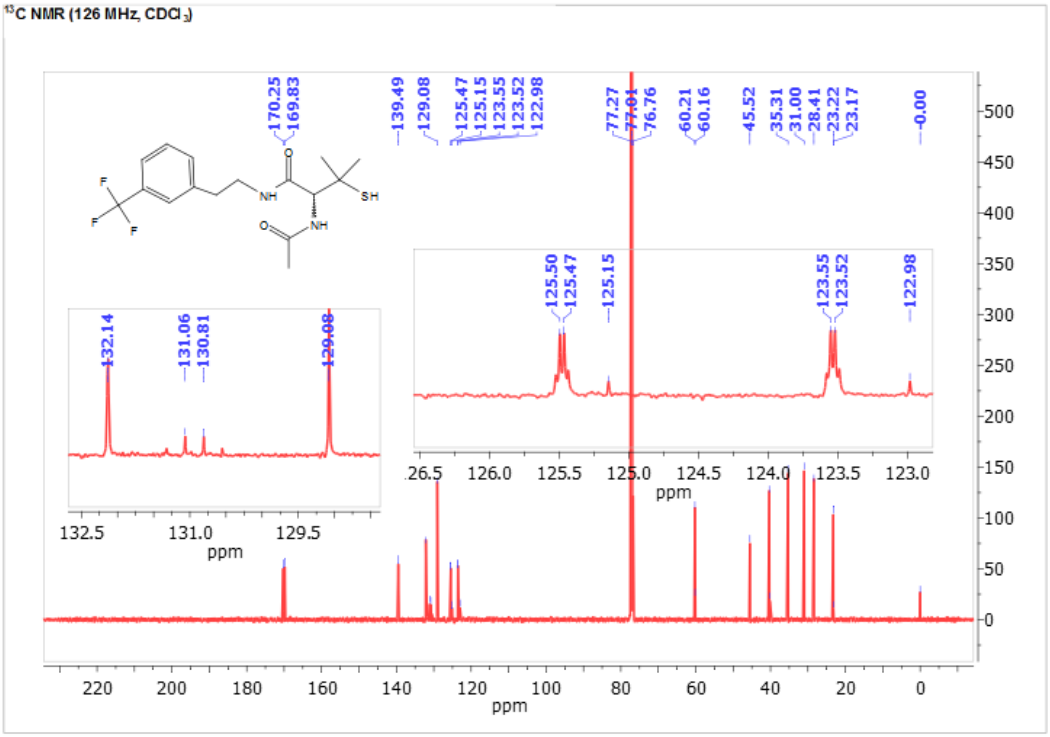
^{13}C NMR (126 MHz, $CDCl_3$)

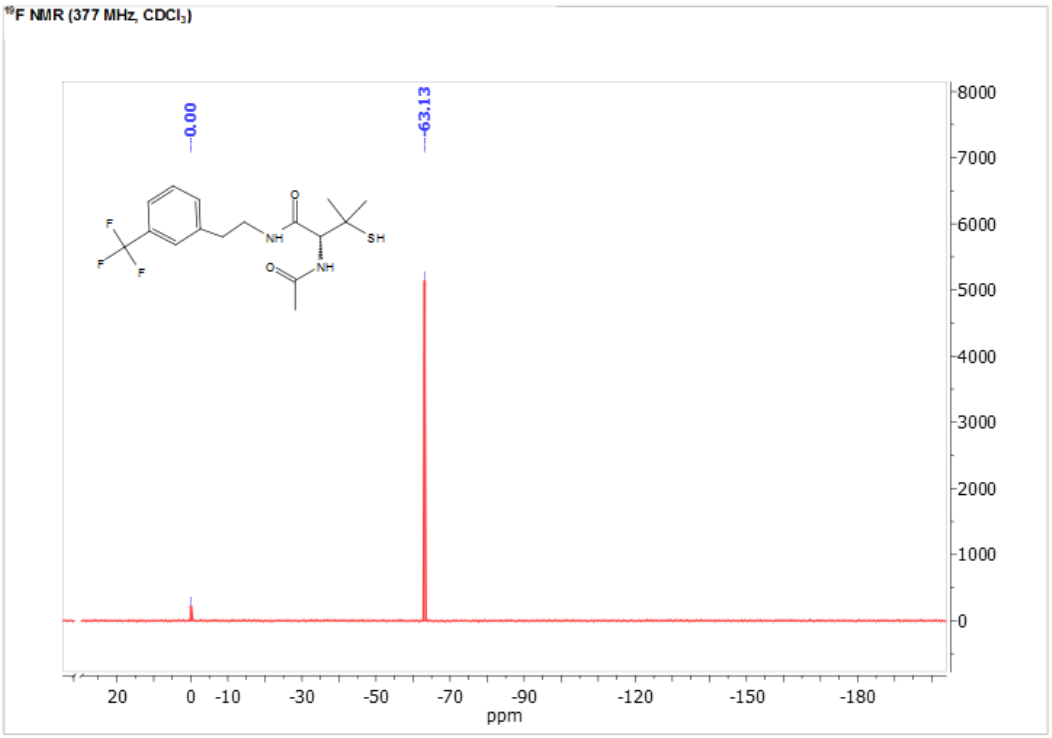


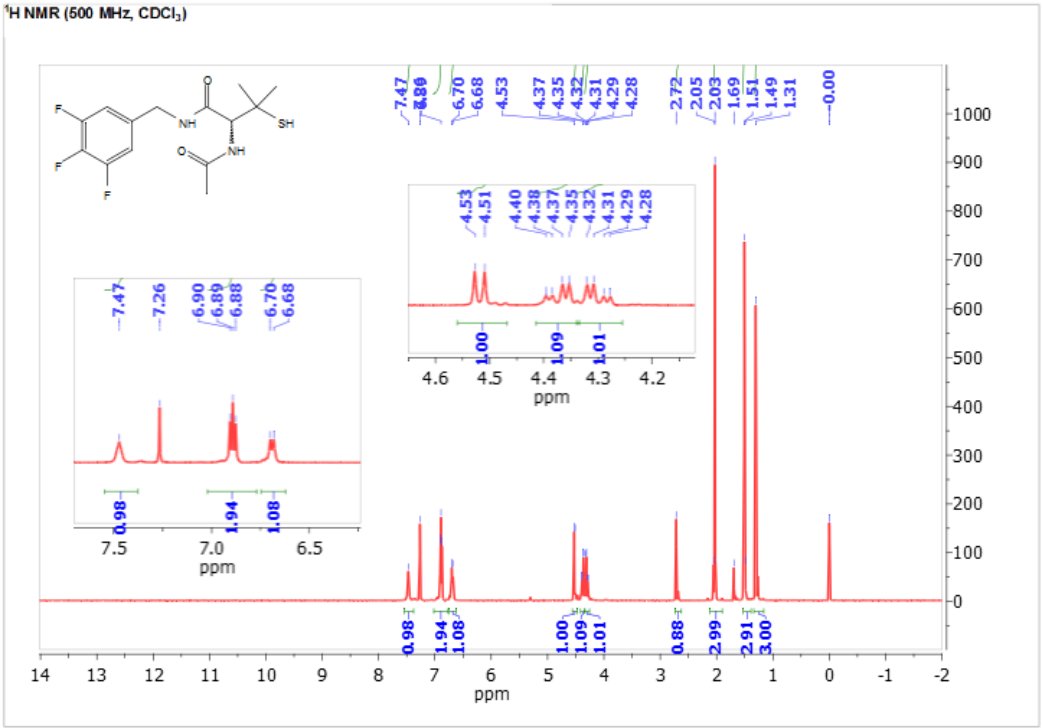
^{19}F NMR (377 MHz, $CDCl_3$)

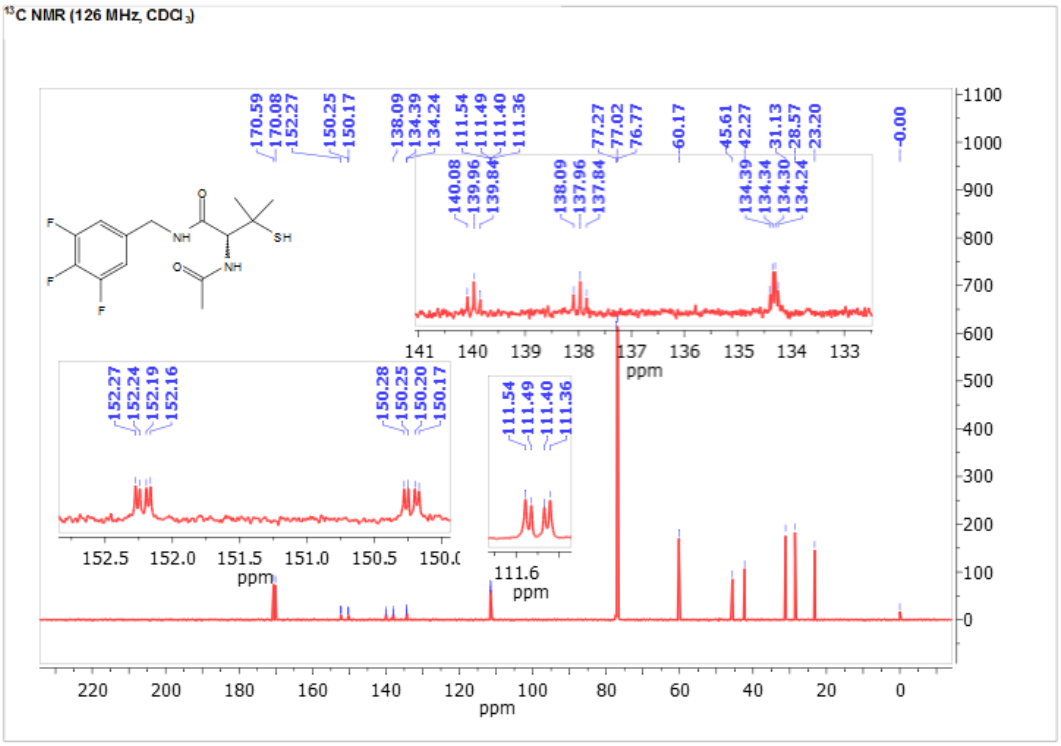


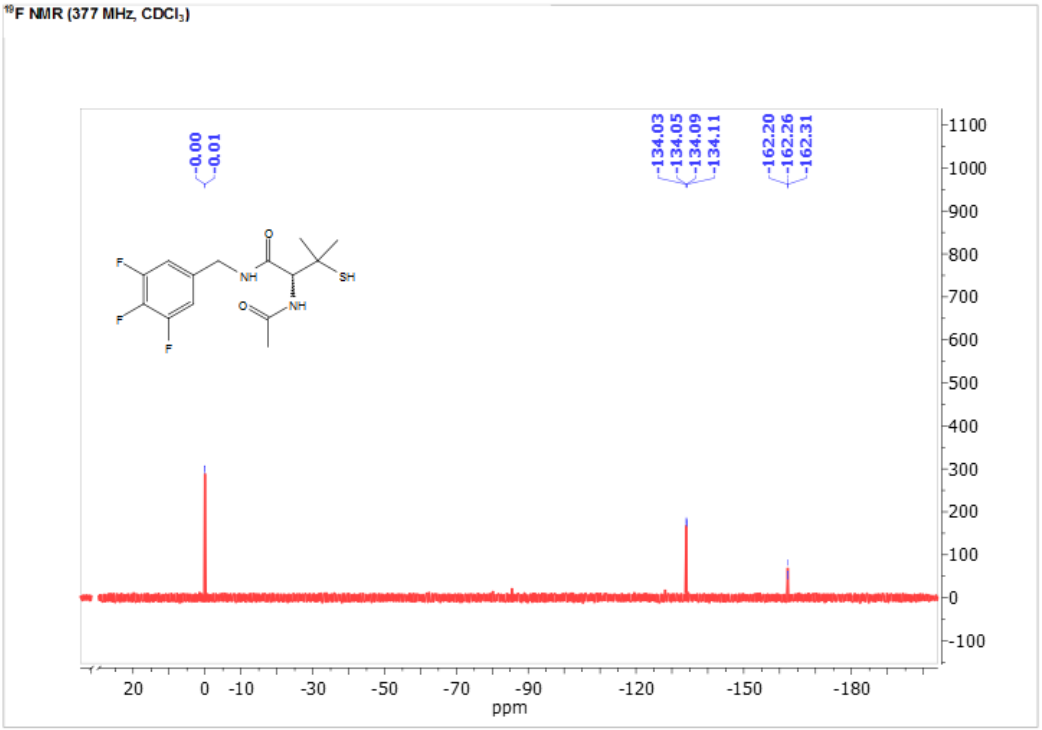

1H NMR (400 MHz, CDCl3)
ppm

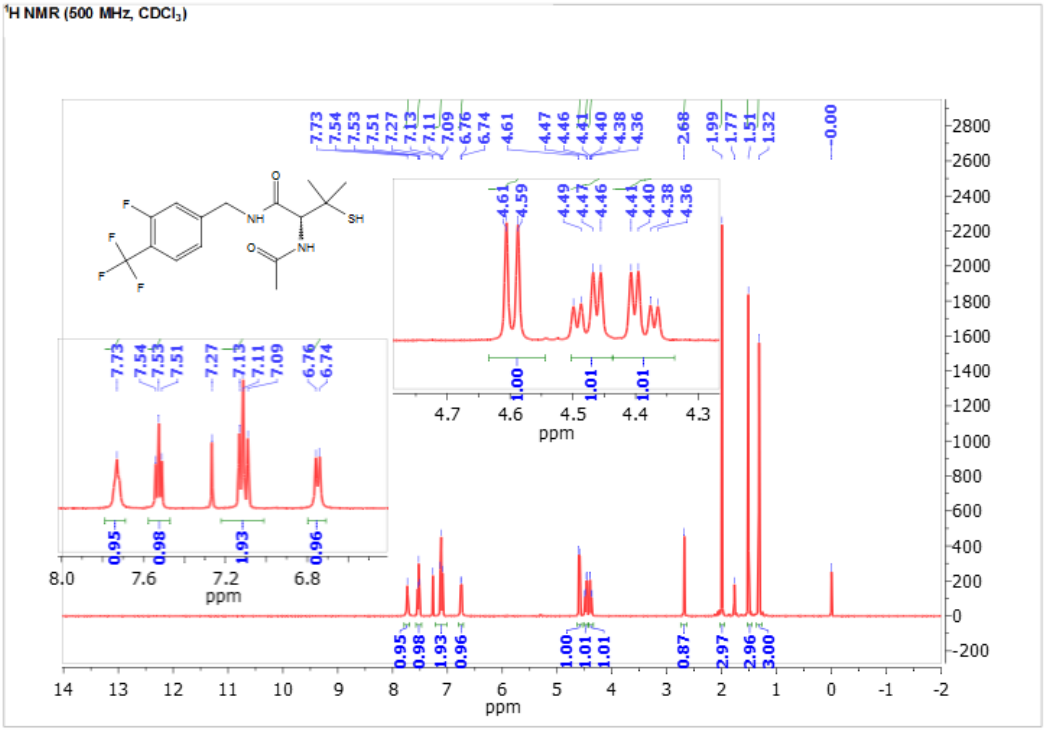

13C NMR (126 MHz, CDCl3)
ppm

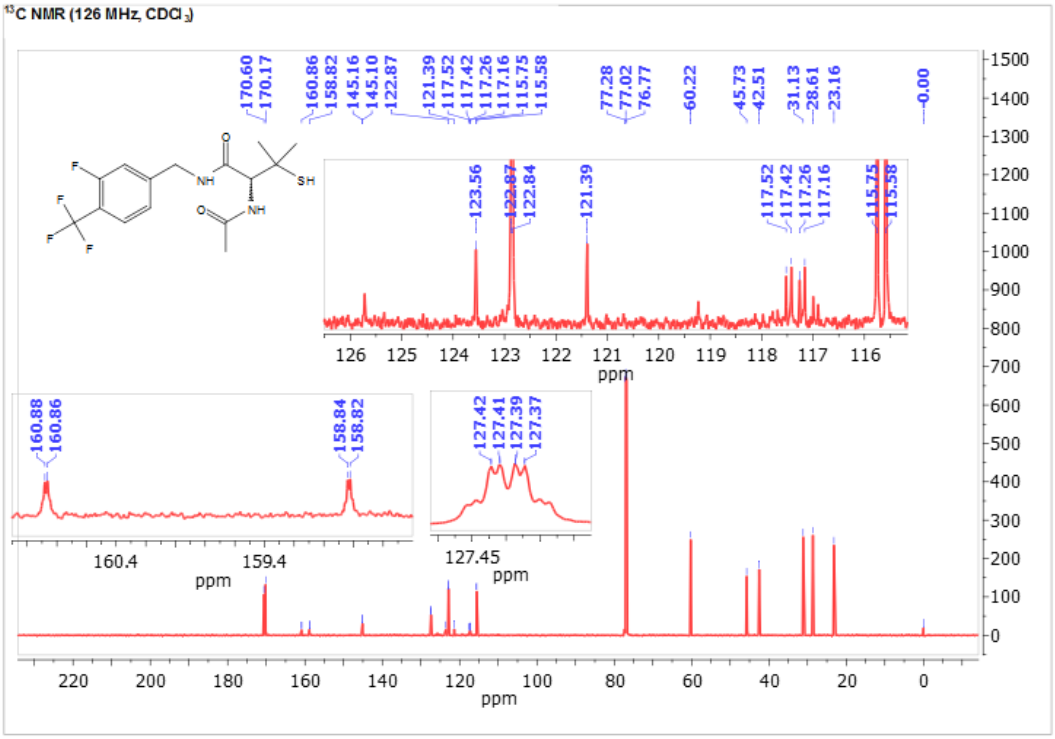

^{19}F NMR (377 MHz, $CDCl_3$)
-0.00
-63.13
ppm

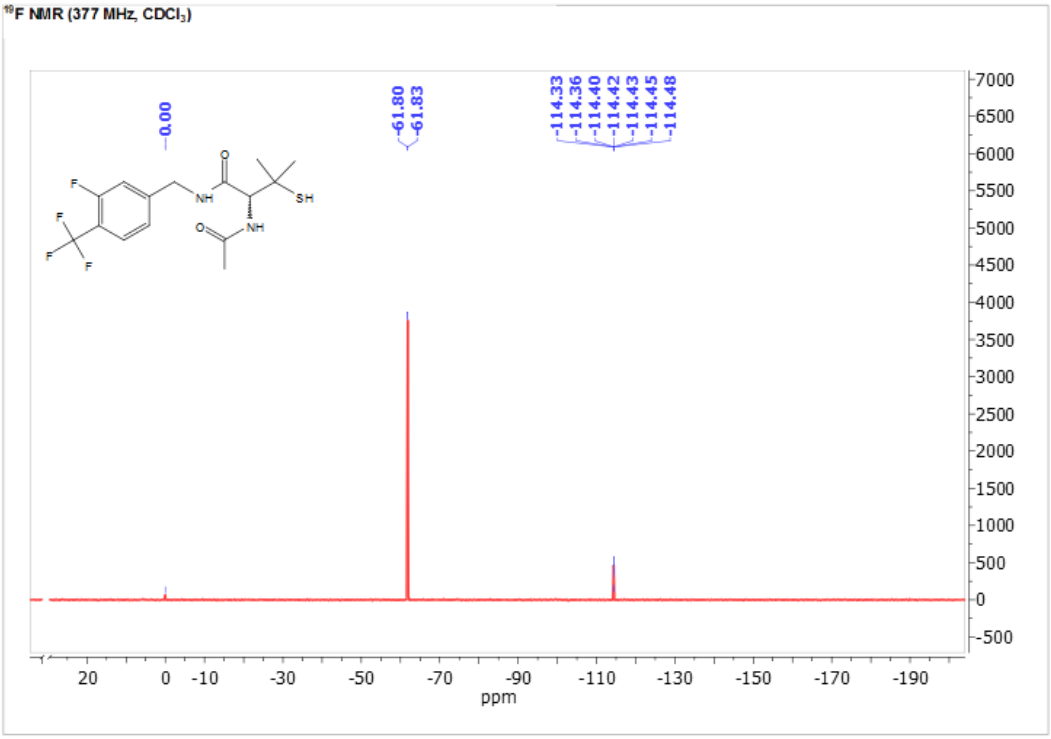

^{1}H NMR (500 MHz, $CDCl_3$)
ppm

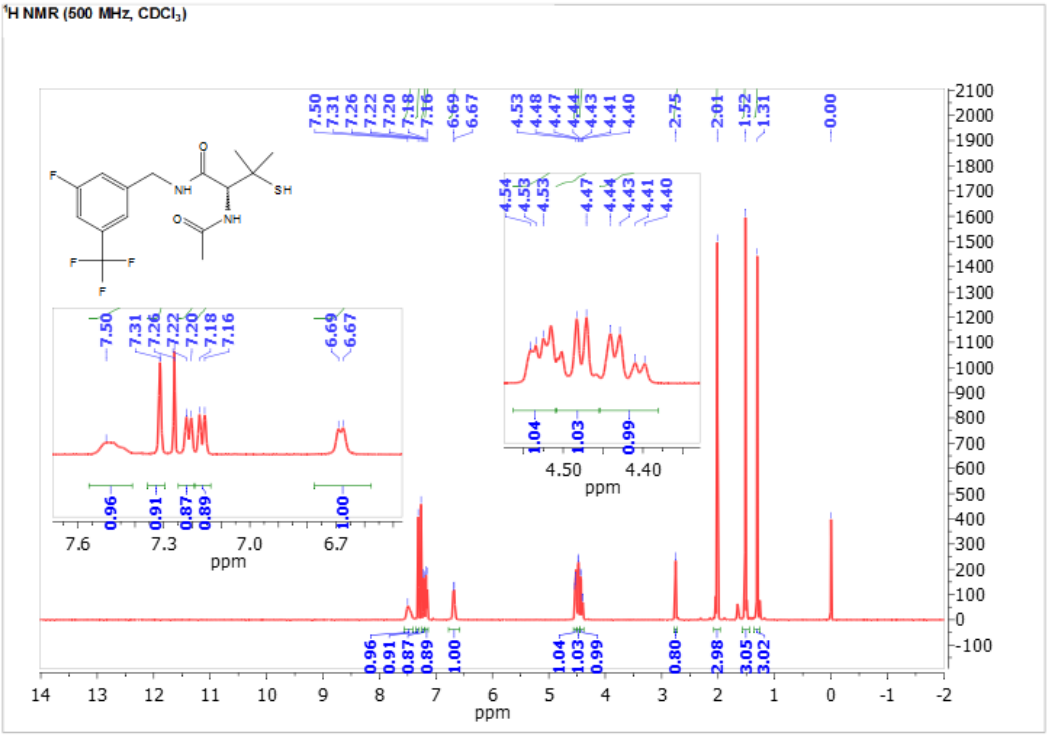

13C NMR (126 MHz, CDCl3)
170.59
170.08
152.27
150.25
150.17
138.09
134.39
134.24
111.54
111.49
111.40
111.36
77.27
77.02
76.77
60.17
45.61
42.27
31.13
28.57
23.20
-0.00
140.08
139.96
139.84
138.09
137.96
137.84
134.39
134.34
134.30
134.24
152.27
152.24
152.19
152.16
150.28
150.25
150.20
150.17
111.54
111.49
111.40
111.36
ppm
111.6
ppm
220 200 180 160 140 120 100 80 60 40 20 0
ppm

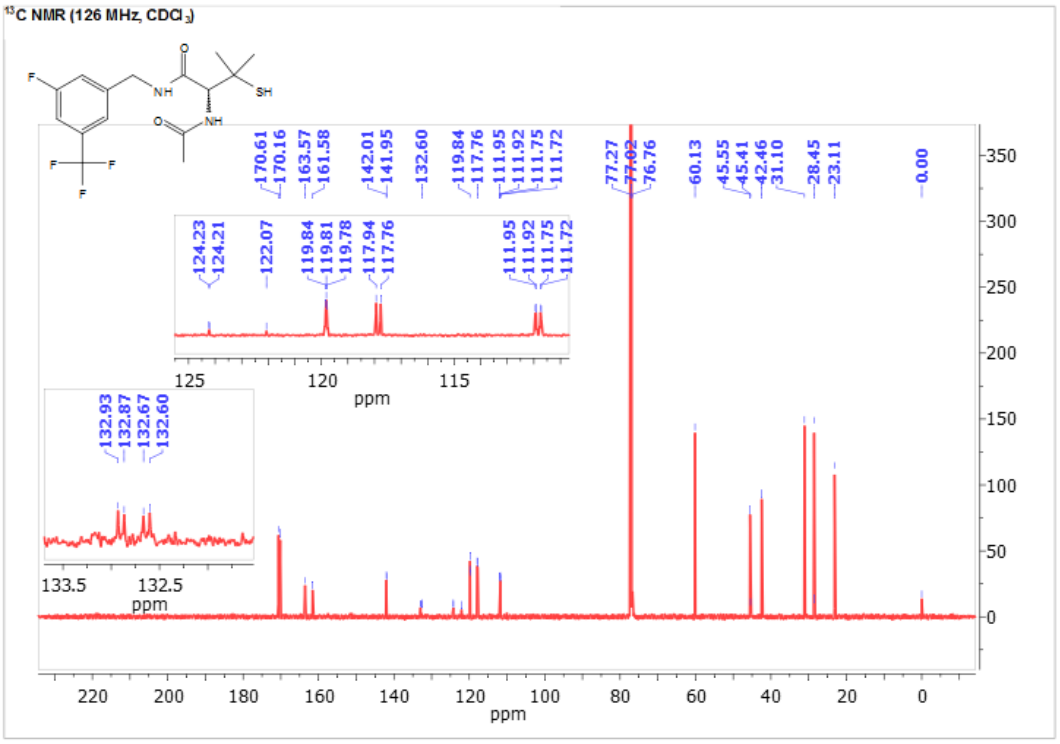

19F NMR (377 MHz, CDCl3)
-0.00
-0.01
-134.03
-134.05
-134.09
-134.11
-162.20
-162.26
-162.31
20 0 -10 -30 -50 -70 -90 -120 -150 -180
ppm

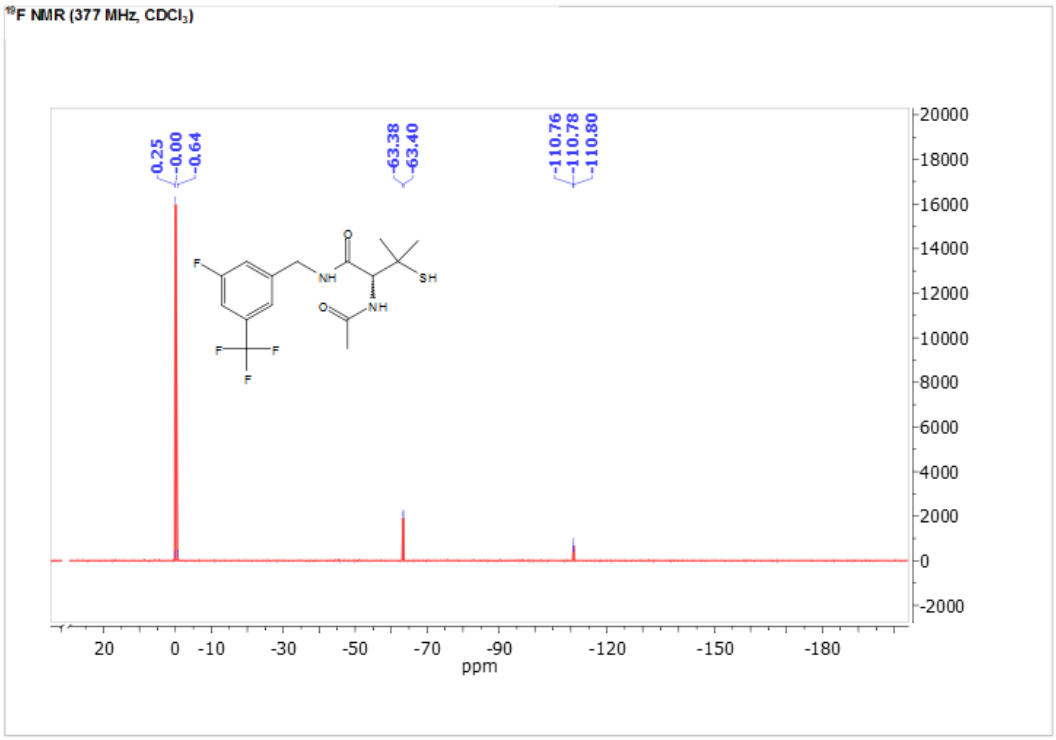

^{1}H NMR (500 MHz, CDCl$_3$)
ppm

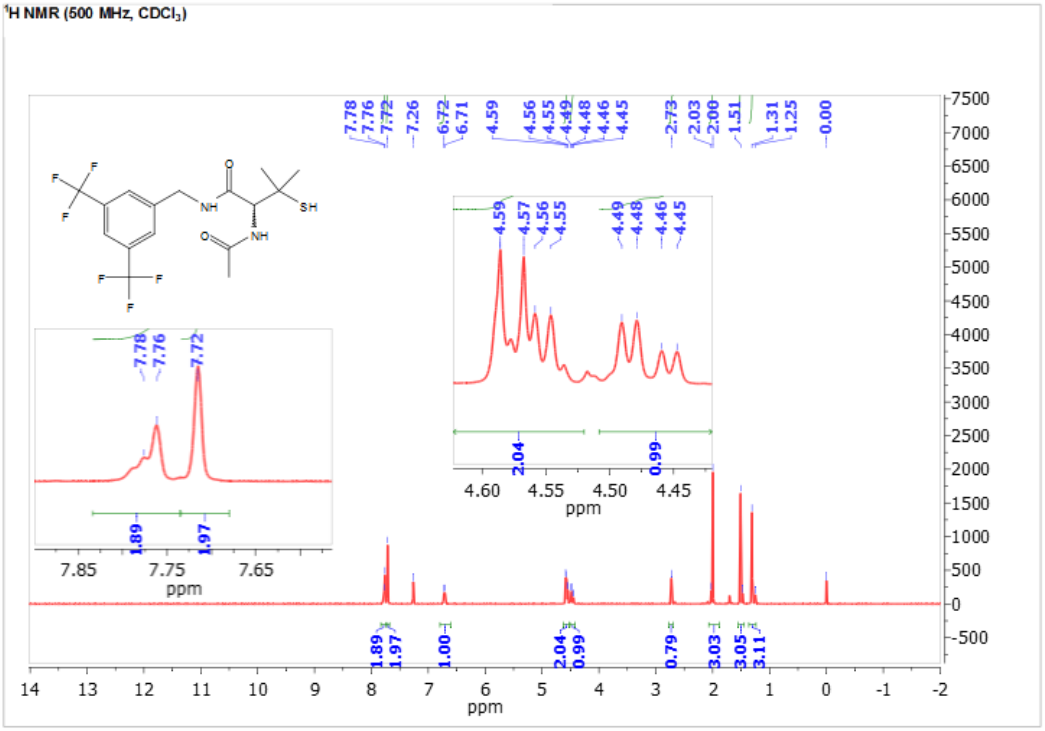

^{13}C NMR (126 MHz, CDCl$_3$)
ppm

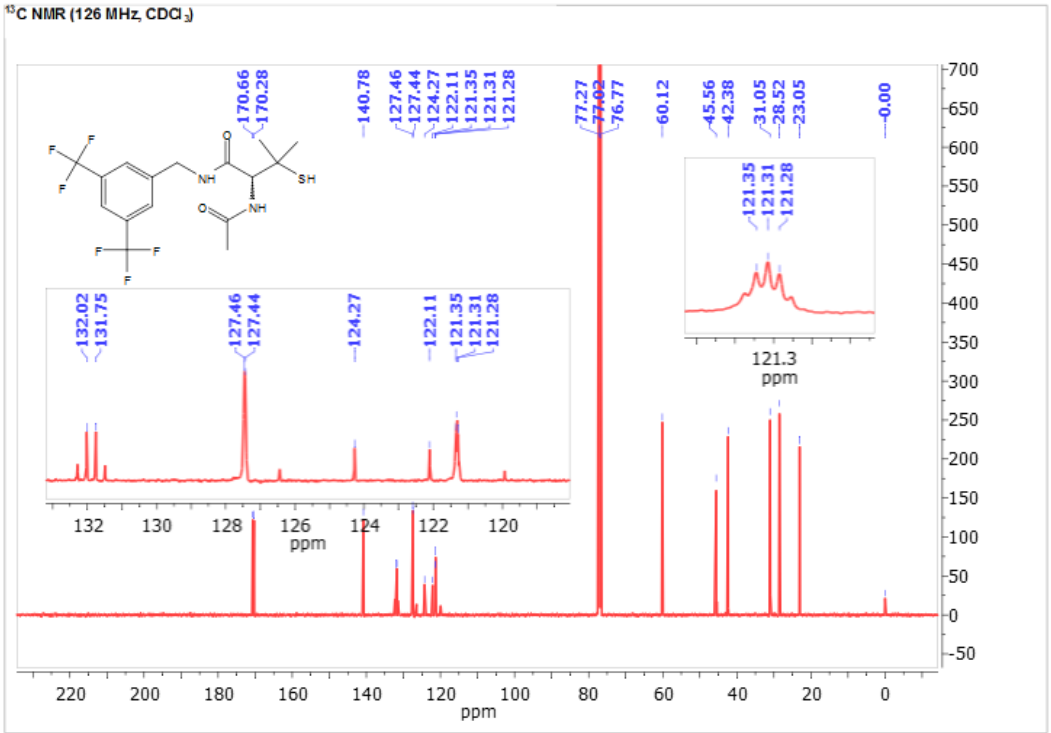

^{19}F NMR (377 MHz, CDCl$_3$)
-0.00
-61.80
-61.83
-114.33
-114.36
-114.40
-114.42
-114.43
-114.45
-114.48
ppm


^{1}H NMR (500 MHz, CDCl$_3$)
7.50
7.31
7.26
7.22
7.20
7.18
7.16
6.69
6.67
4.53
4.48
4.47
4.44
4.43
4.41
4.40
2.75
2.01
1.52
1.31
0.00
0.96
0.91
0.87
0.89
1.00
1.04
1.03
0.99
0.80
2.98
3.05
3.02
ppm

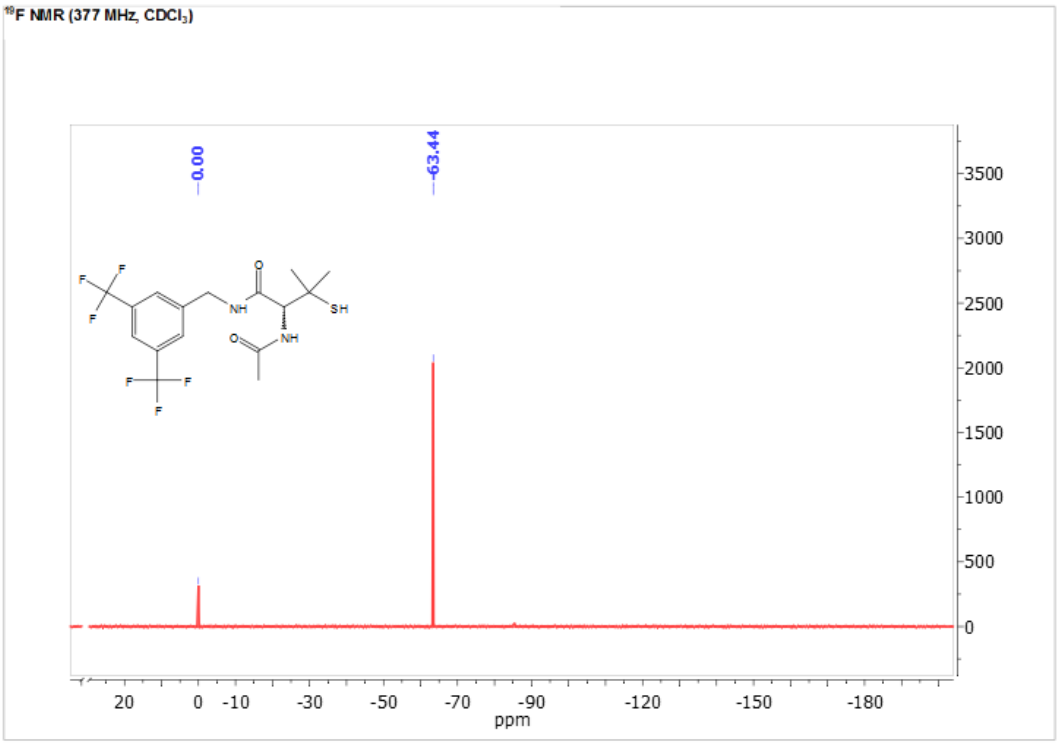

13C NMR (126 MHz, CDCl3)
170.61
170.16
163.57
161.58
142.01
141.95
132.60
119.84
117.76
111.95
111.92
111.75
111.72
77.27
77.02
76.76
60.13
45.55
45.41
42.46
31.10
28.45
23.11
0.00
124.23
124.21
122.07
119.84
119.81
119.78
117.94
117.76
111.95
111.92
111.75
111.72
132.93
132.87
132.67
132.60
ppm


19F NMR (377 MHz, CDCl3)
0.25
0.00
-0.64
-63.38
-63.40
-110.76
-110.78
-110.80
ppm

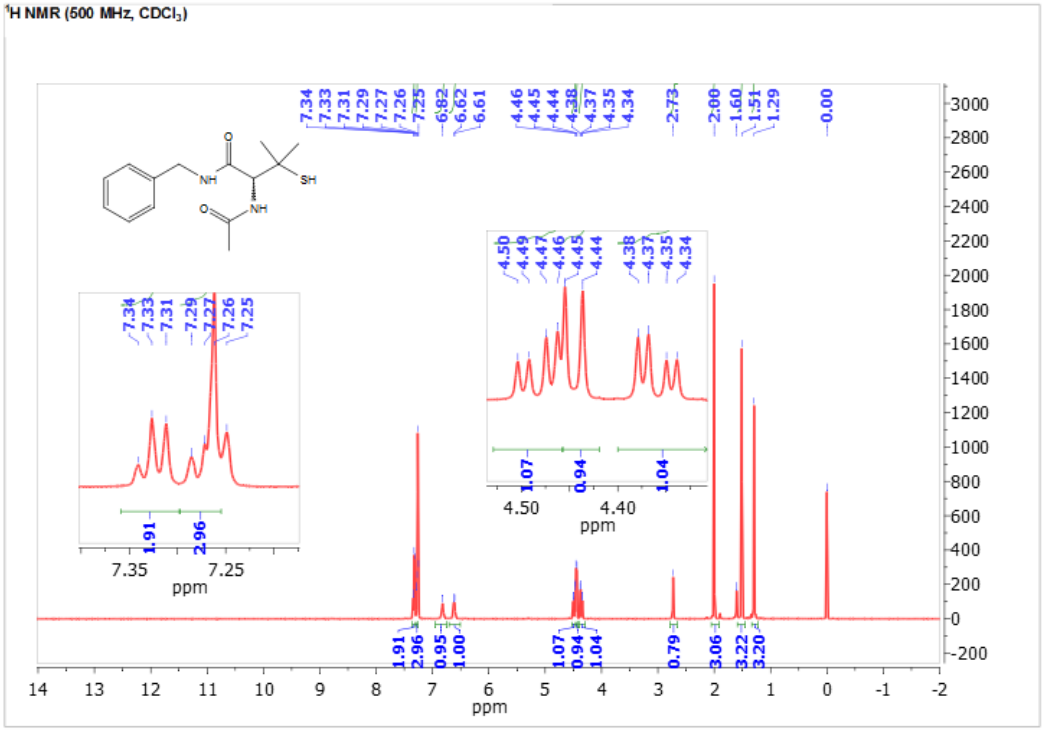

^{1}H NMR (500 MHz, CDCl$_3$)
ppm


^{13}C NMR (126 MHz, CDCl$_3$)
ppm

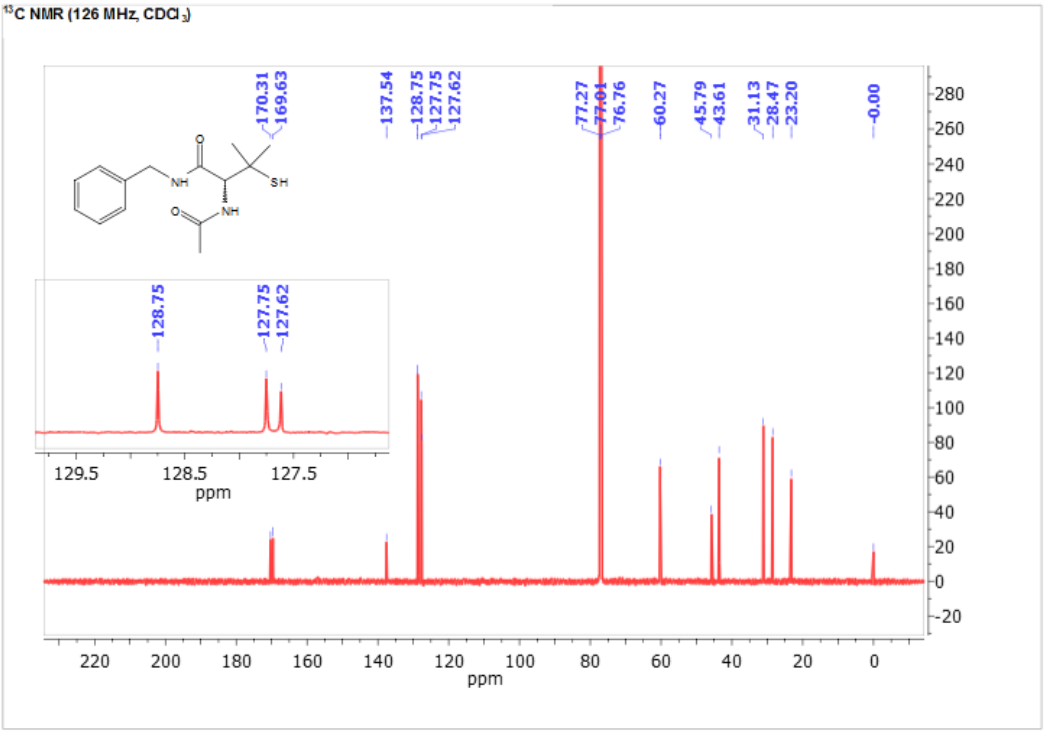
^{19}F NMR (377 MHz, $CDCl_3$)



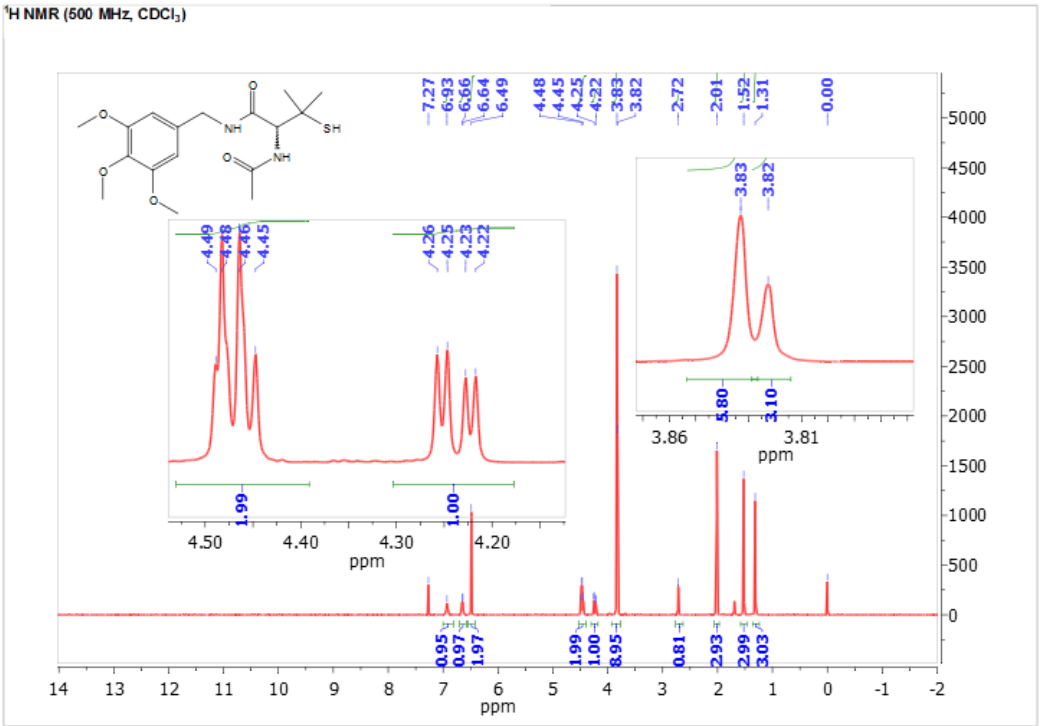
^{1}H NMR (500 MHz, $CDCl_3$)



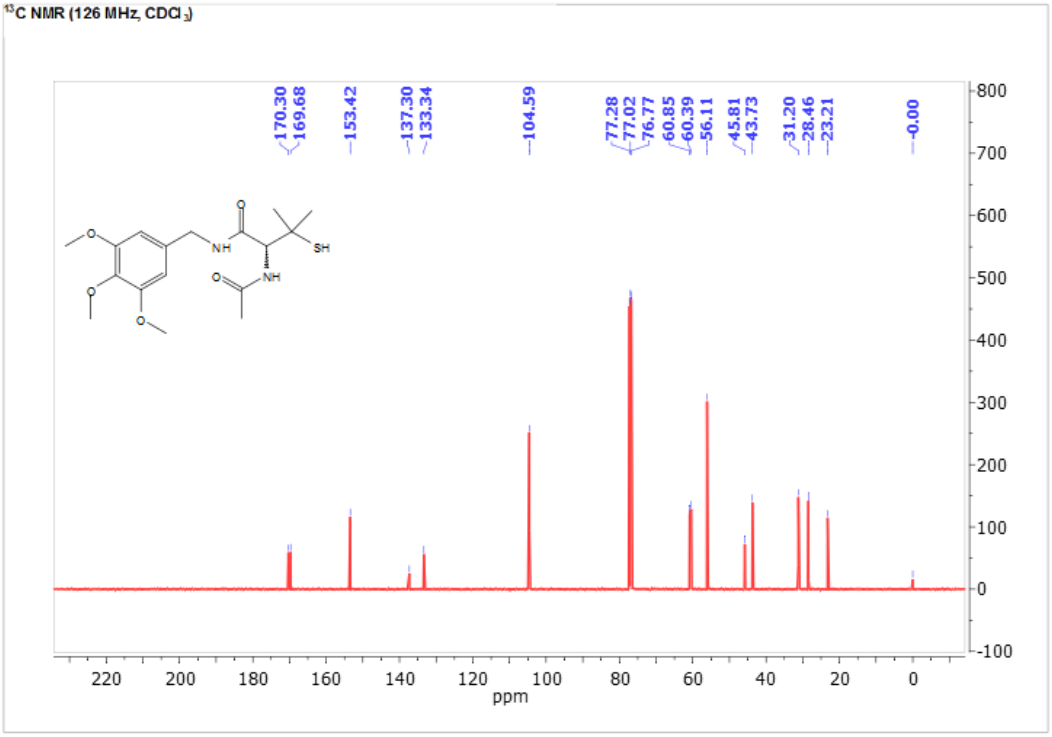
^{13}C NMR (126 MHz, $CDCl_3$)



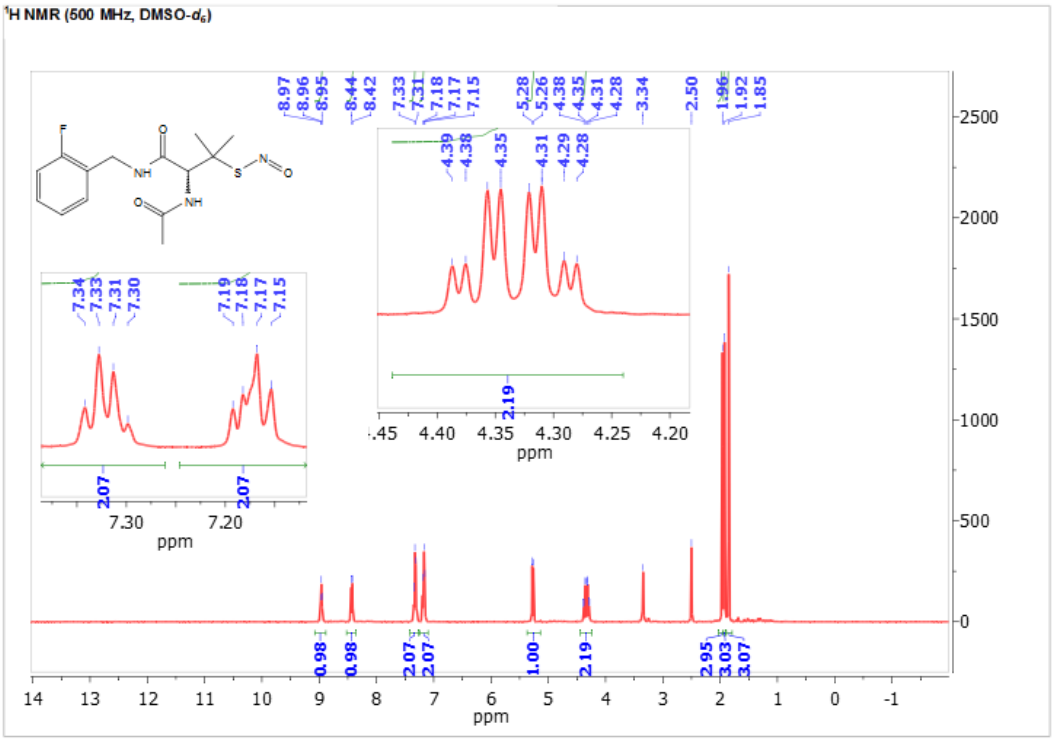
^{1}H NMR (500 MHz, $CDCl_3$)



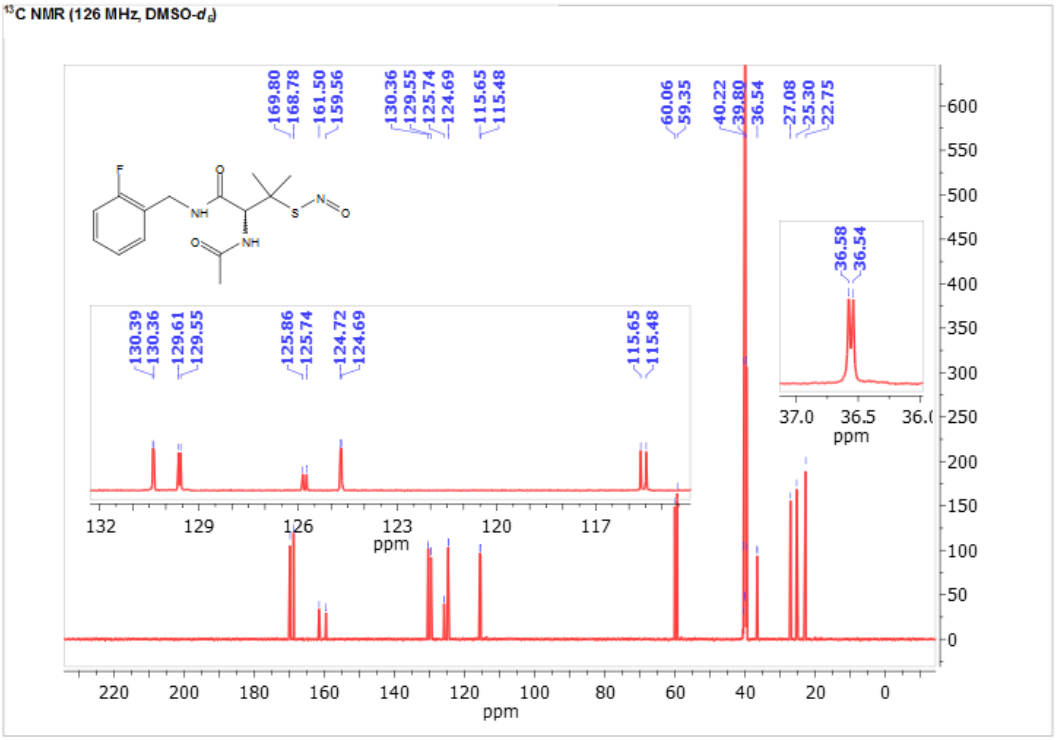
^{13}C NMR (126 MHz, $CDCl_3$)



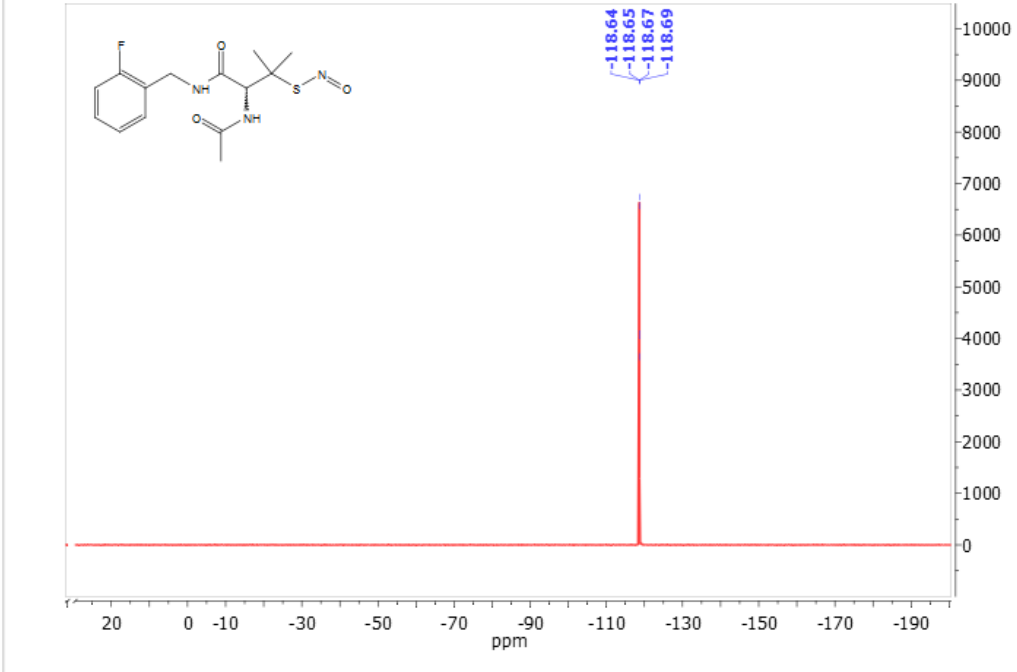
^{1}H NMR (500 MHz, DMSO-d_6)



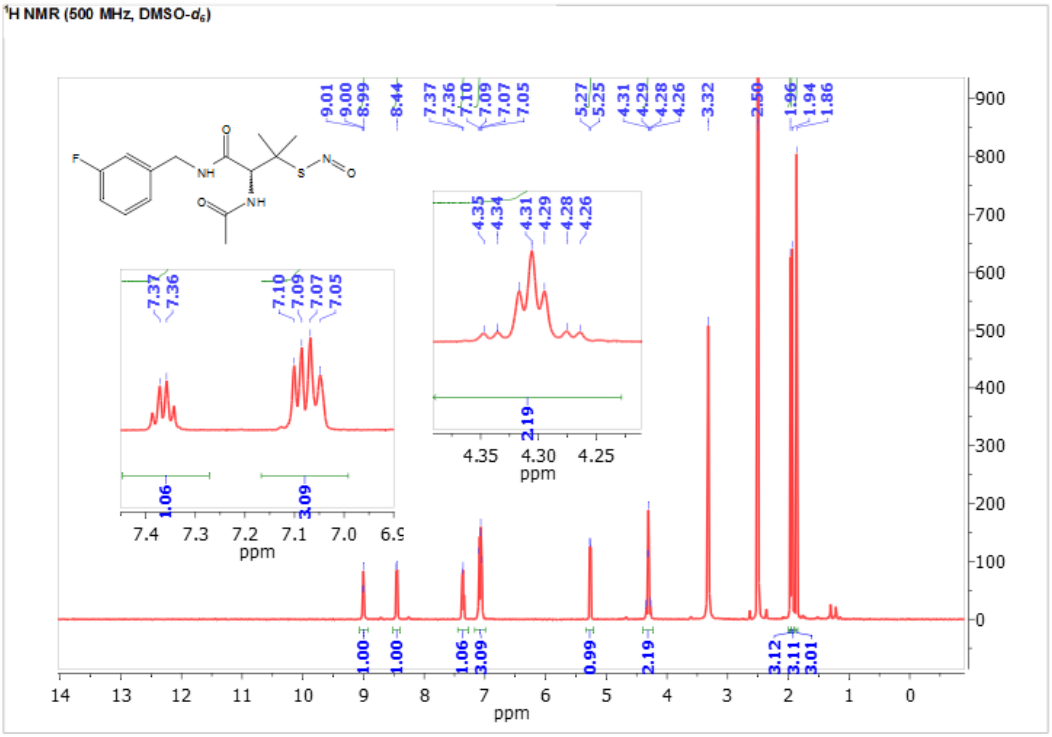
^{13}C NMR (126 MHz, DMSO-d_6)



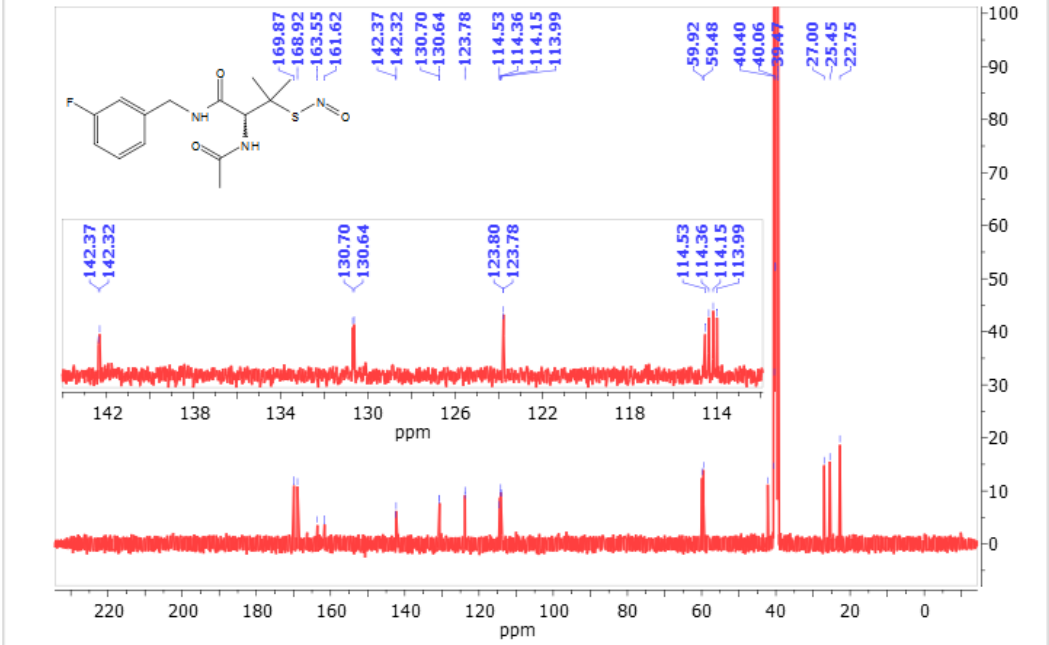
^{19}F NMR (377 MHz, DMSO-d_6)



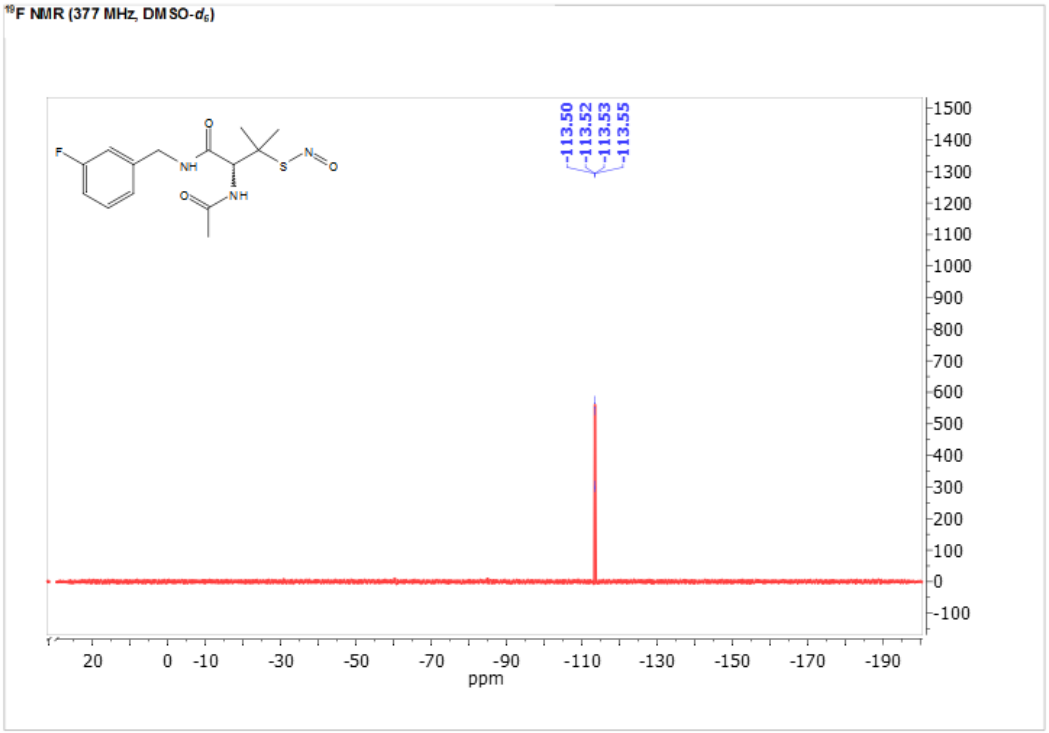
^{1}H NMR (500 MHz, DMSO-d_6)



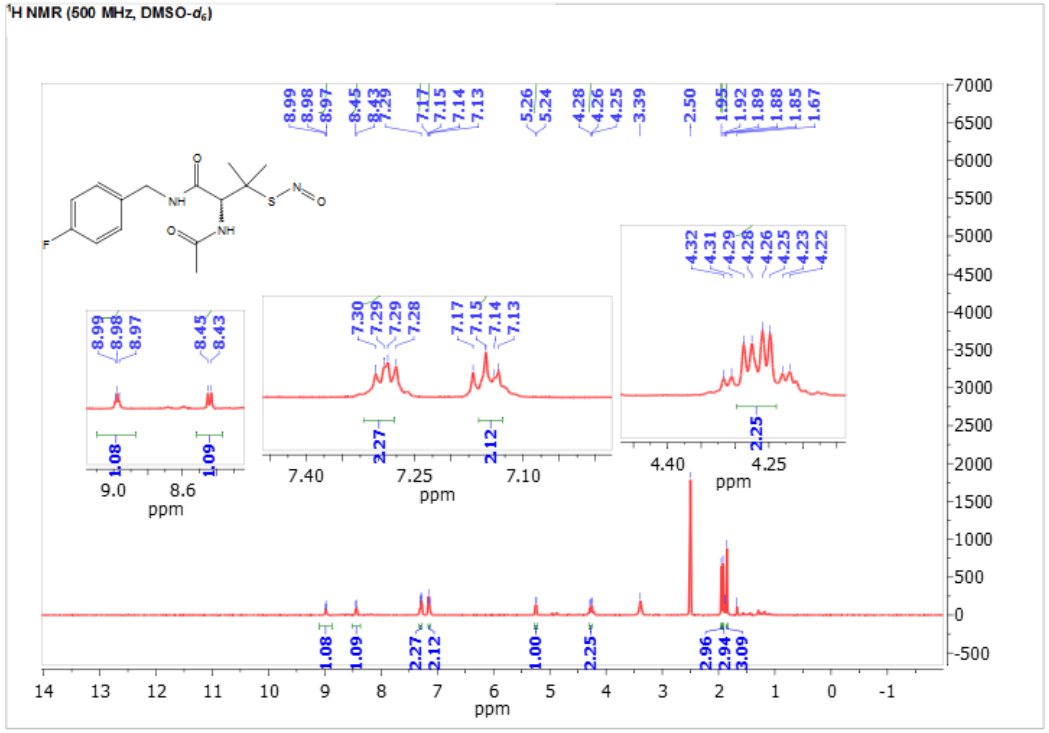
^{13}C NMR (126 MHz, DMSO-d_6)



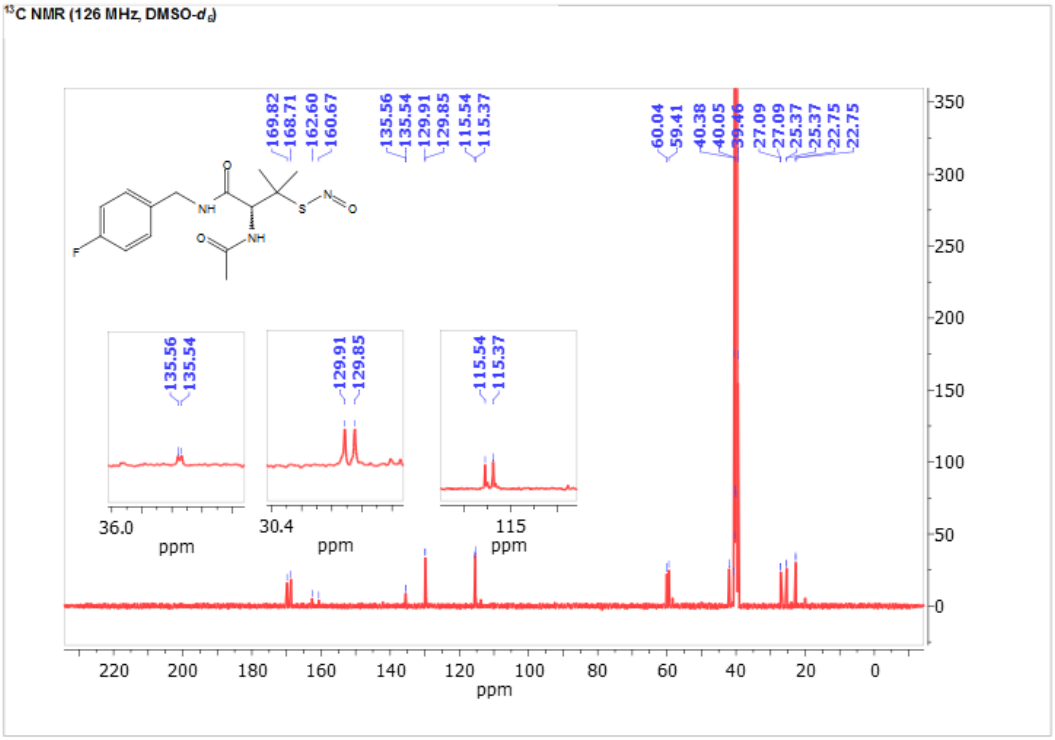
^{19}F NMR (377 MHz, DMSO-d_6)



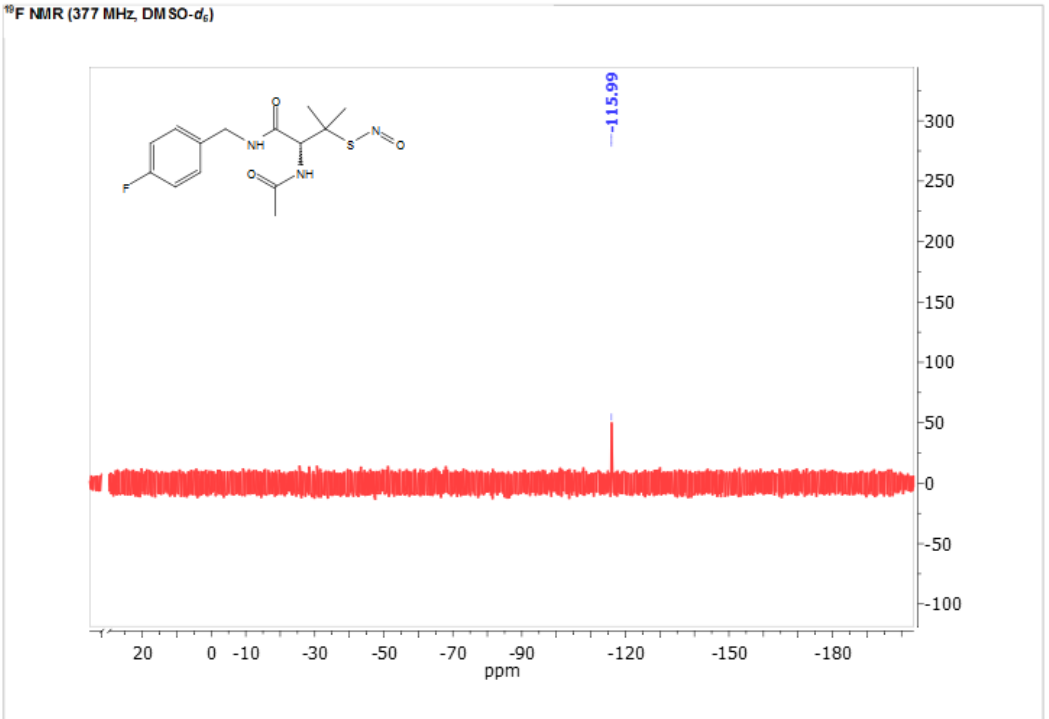
^{1}H NMR (500 MHz, DMSO-d_6)

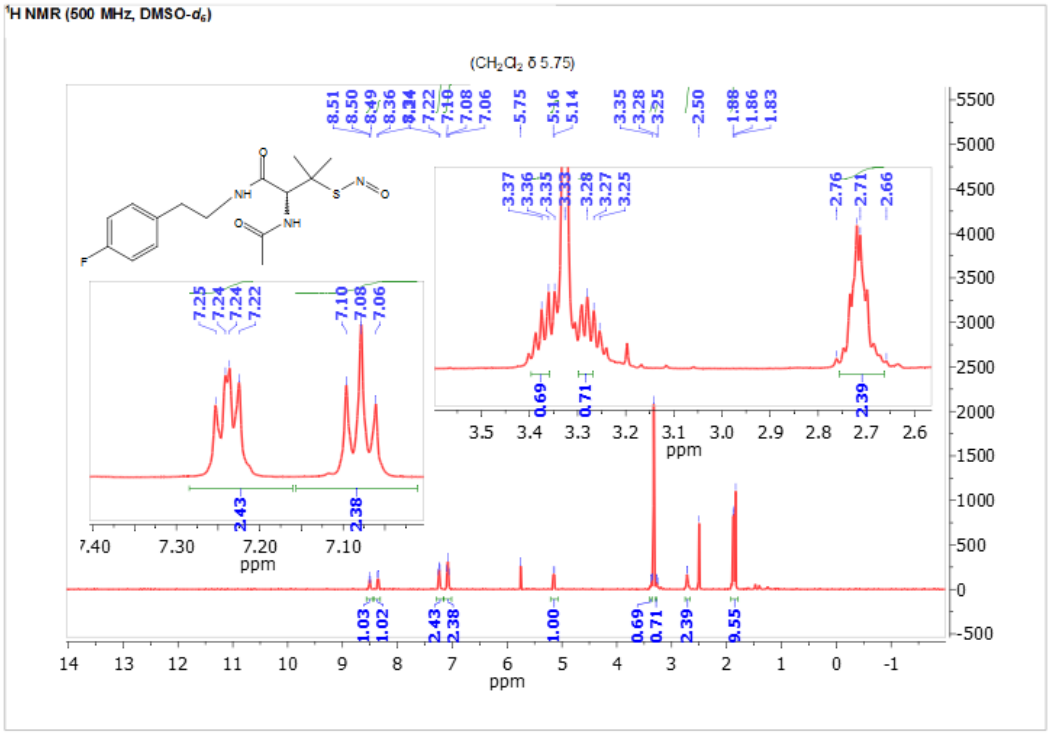


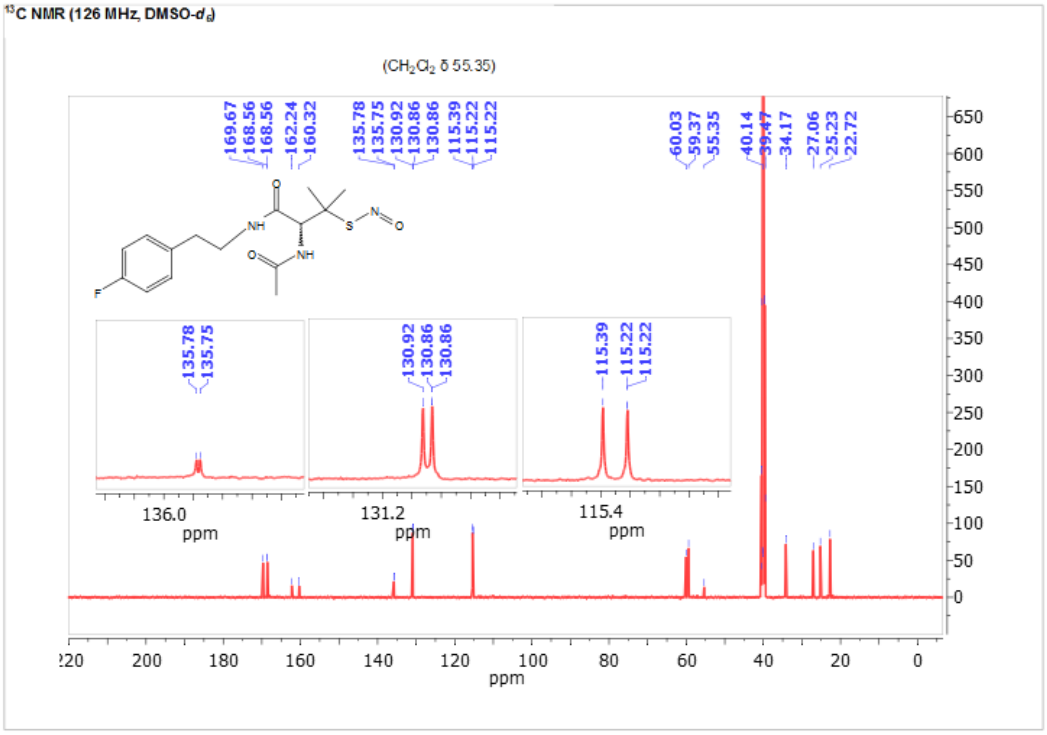
^{13}C NMR (126 MHz, DMSO-d_6)



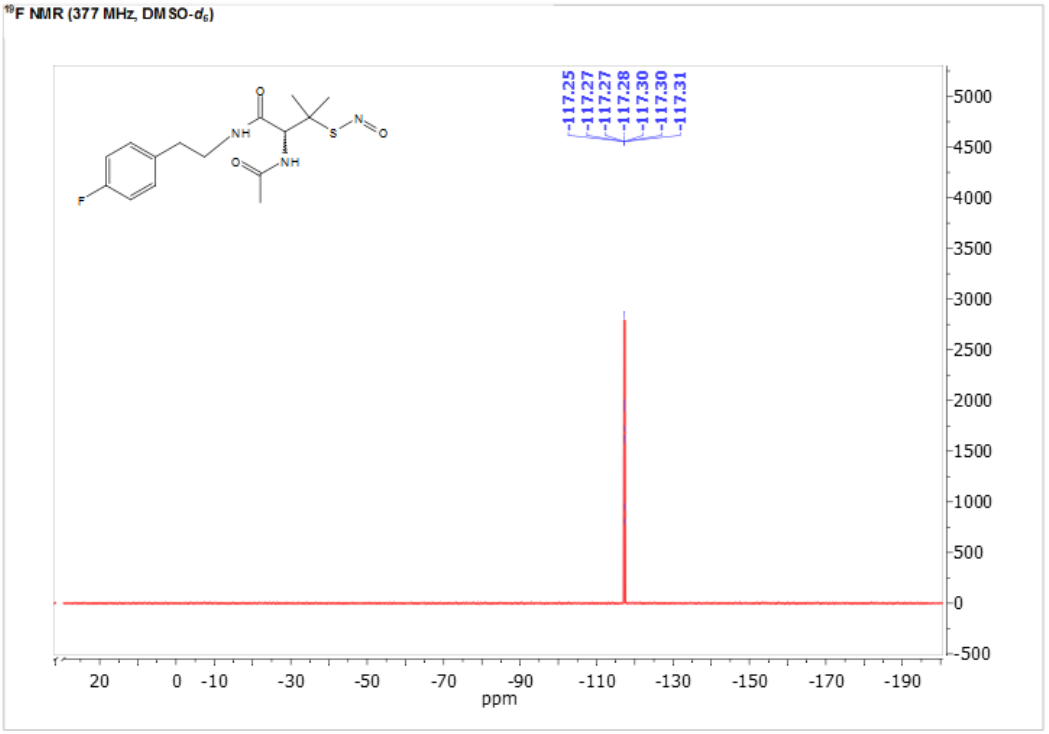
^{19}F NMR (377 MHz, DMSO-d_6)



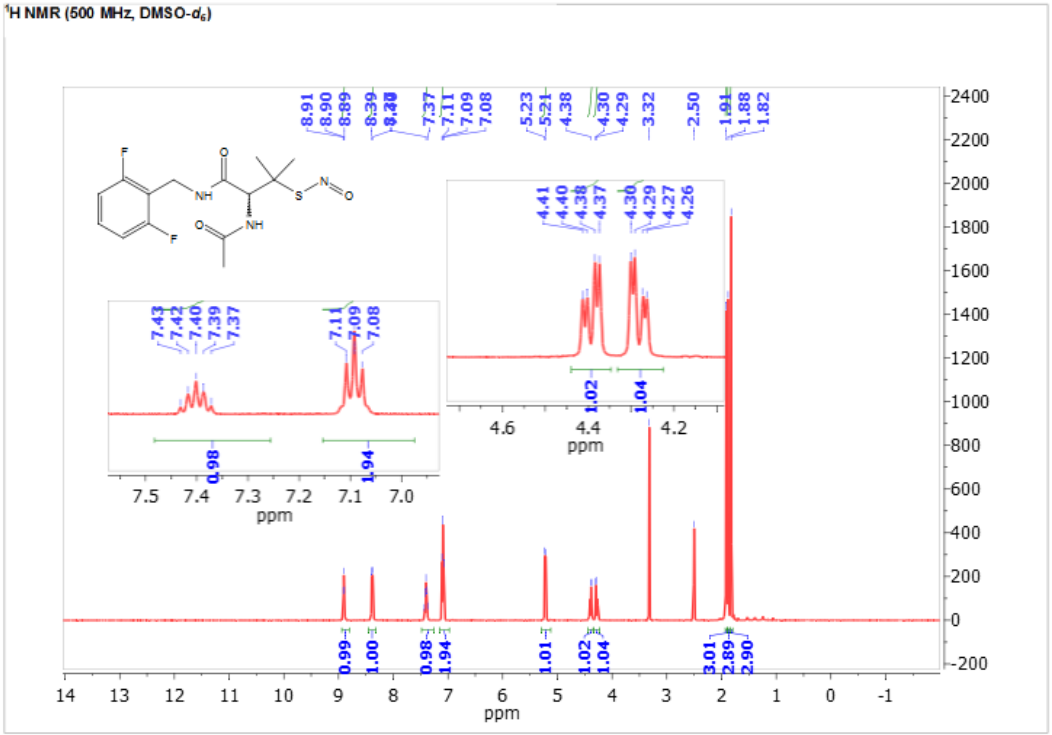

^{1}H NMR (500 MHz, DMSO-d_6)
(CH_2Cl_2 δ 5.75)
ppm


^{13}C NMR (126 MHz, DMSO-d_6)
(CH_2Cl_2 δ 55.35)
ppm

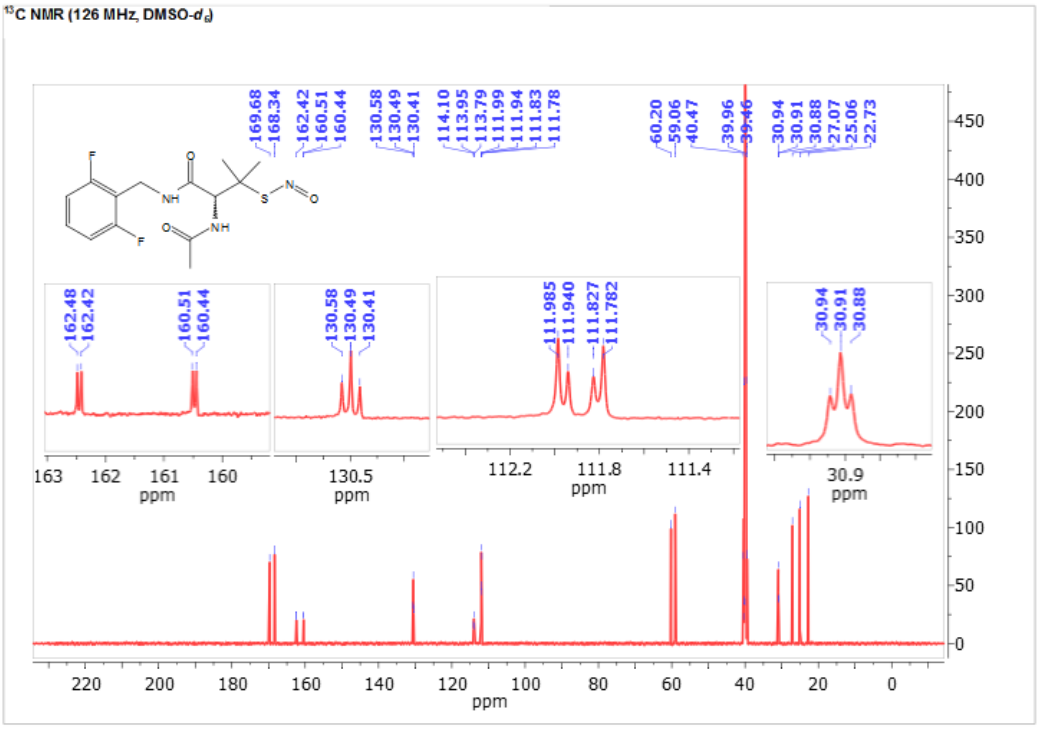
^{19}F NMR (377 MHz, DMSO-d_6)



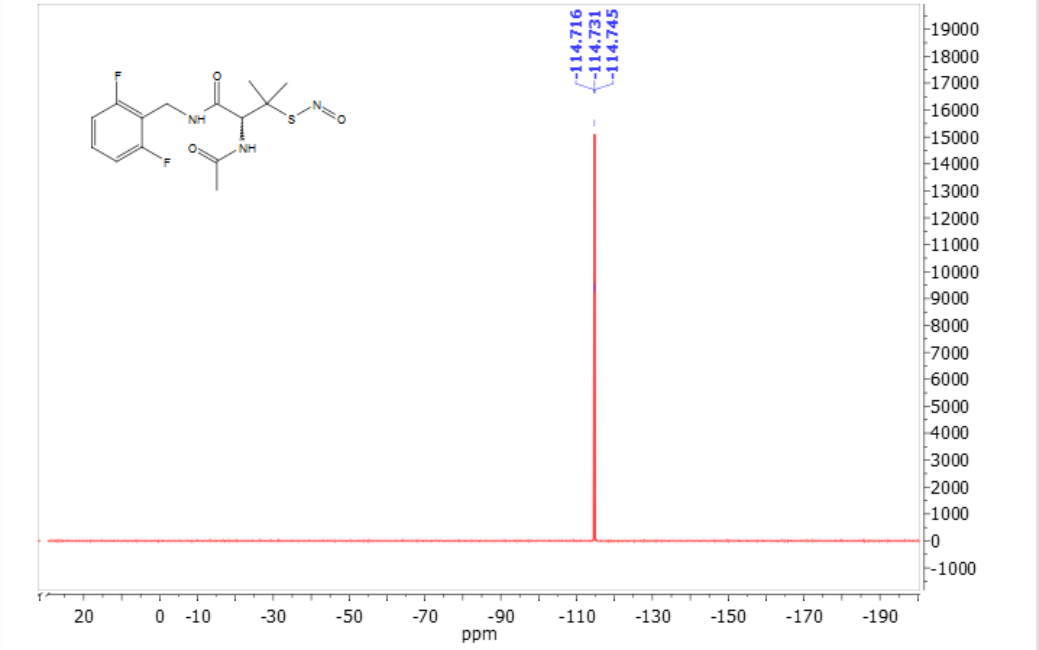
^{1}H NMR (500 MHz, DMSO-d_6)



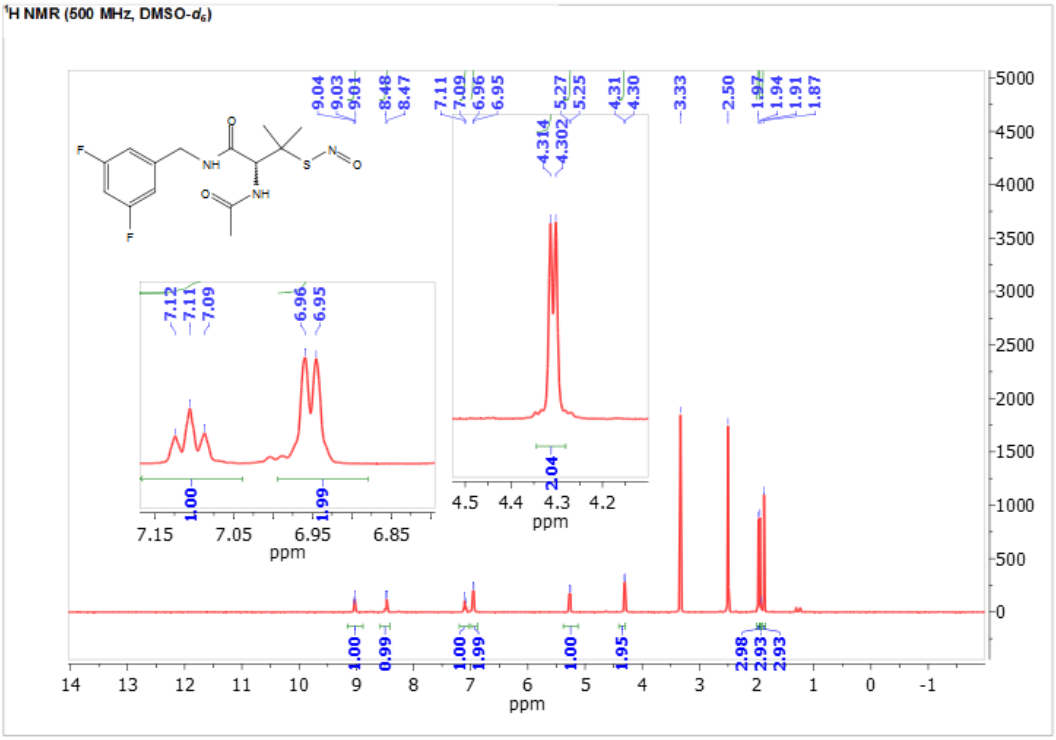
^{13}C NMR (126 MHz, DMSO-d_6)



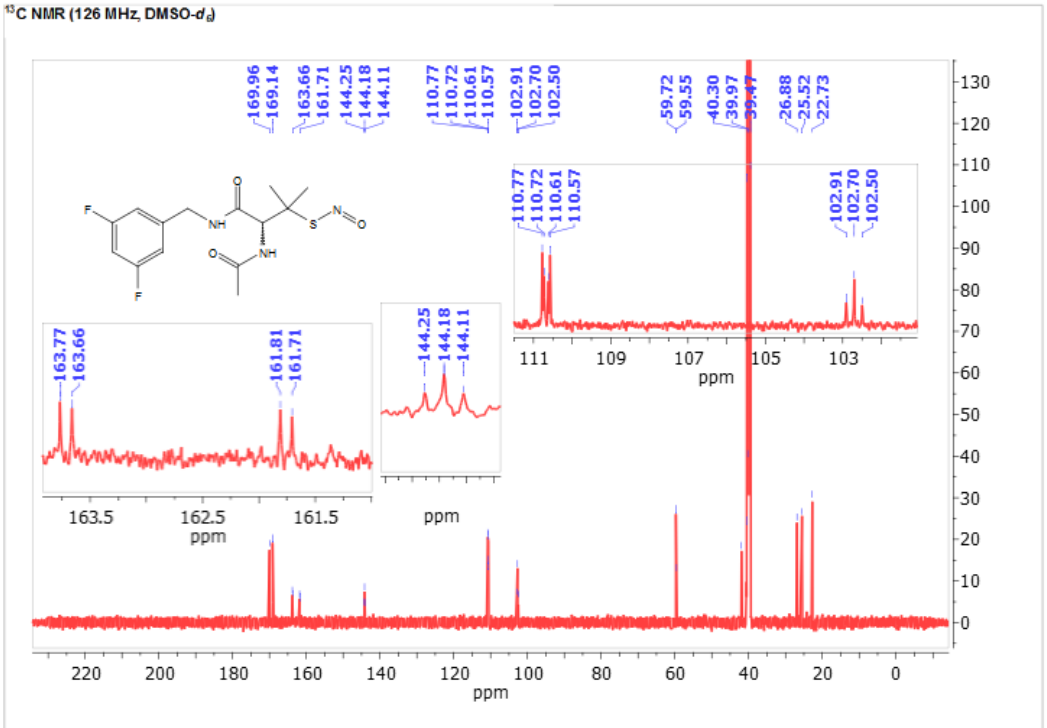
^{19}F NMR (377 MHz, DMSO-d_6)



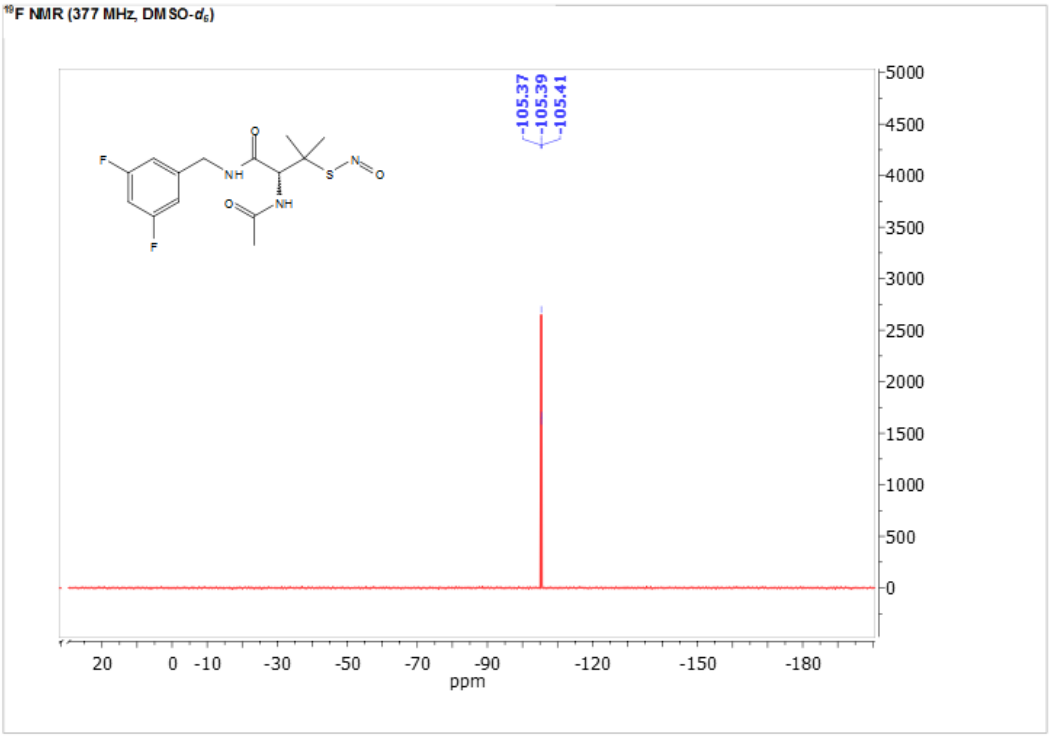
^{1}H NMR (500 MHz, DMSO-d_6)



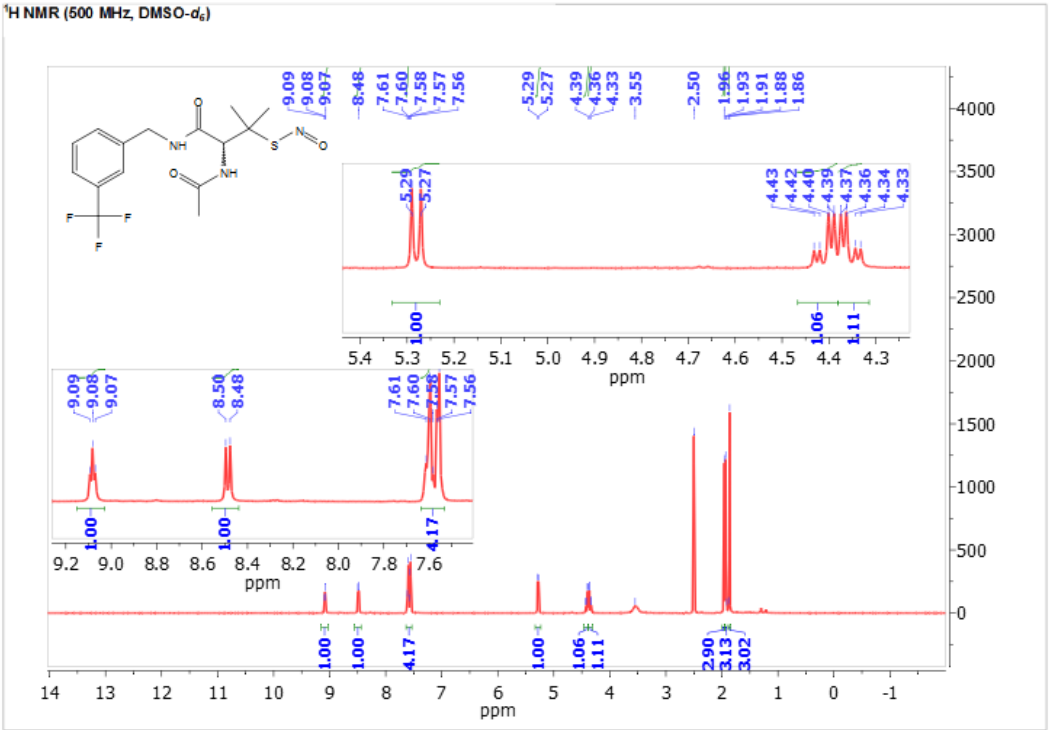
^{13}C NMR (126 MHz, DMSO-d_6)



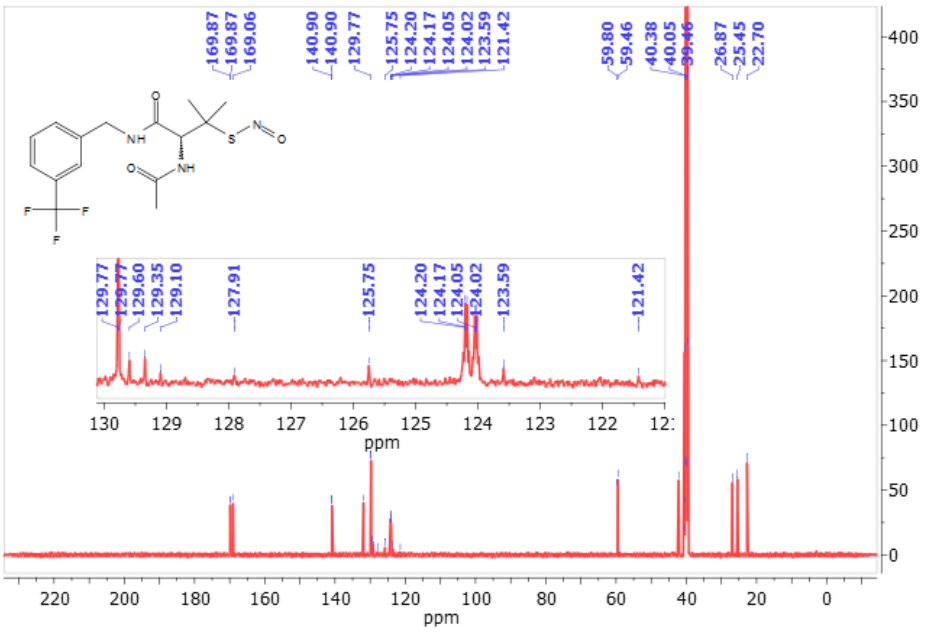
^{19}F NMR (377 MHz, DMSO-d_6)



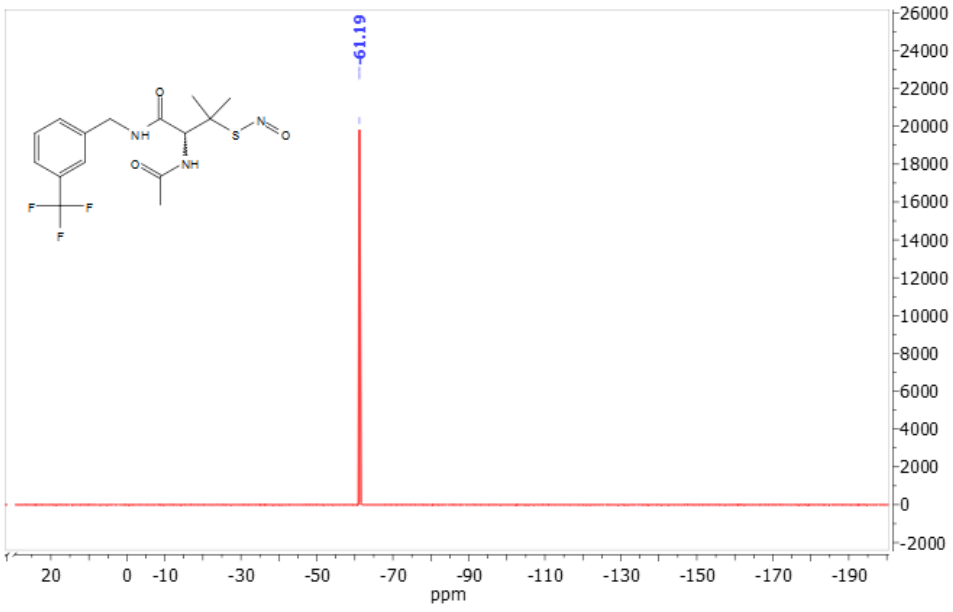
^{1}H NMR (500 MHz, DMSO-d_6)

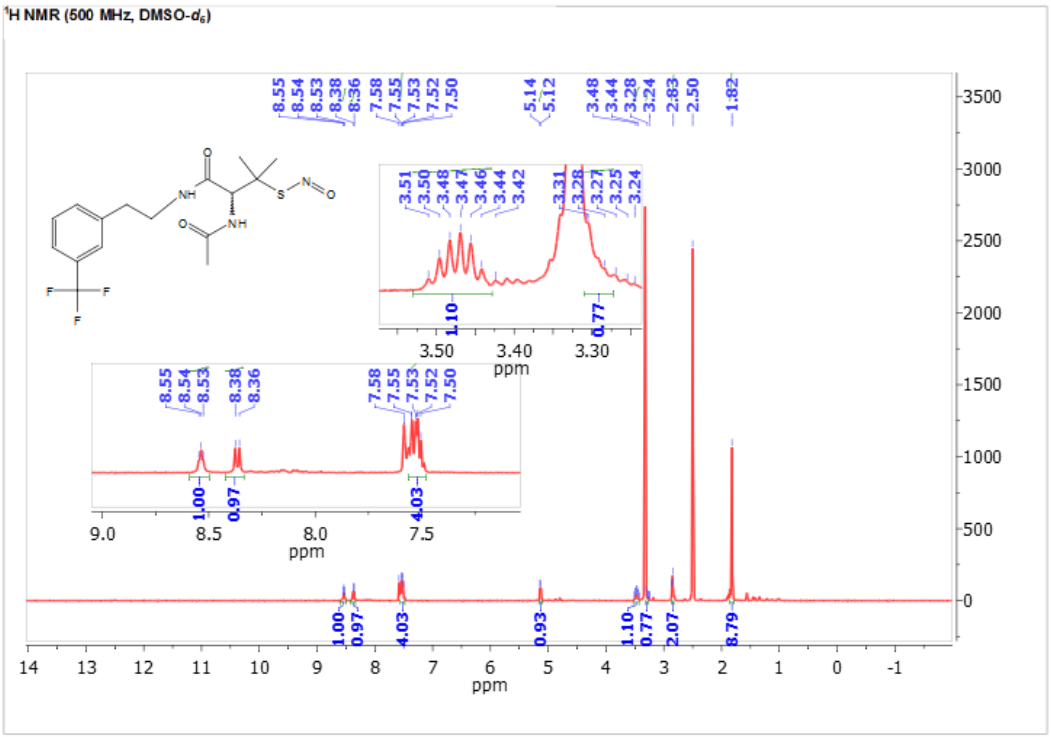


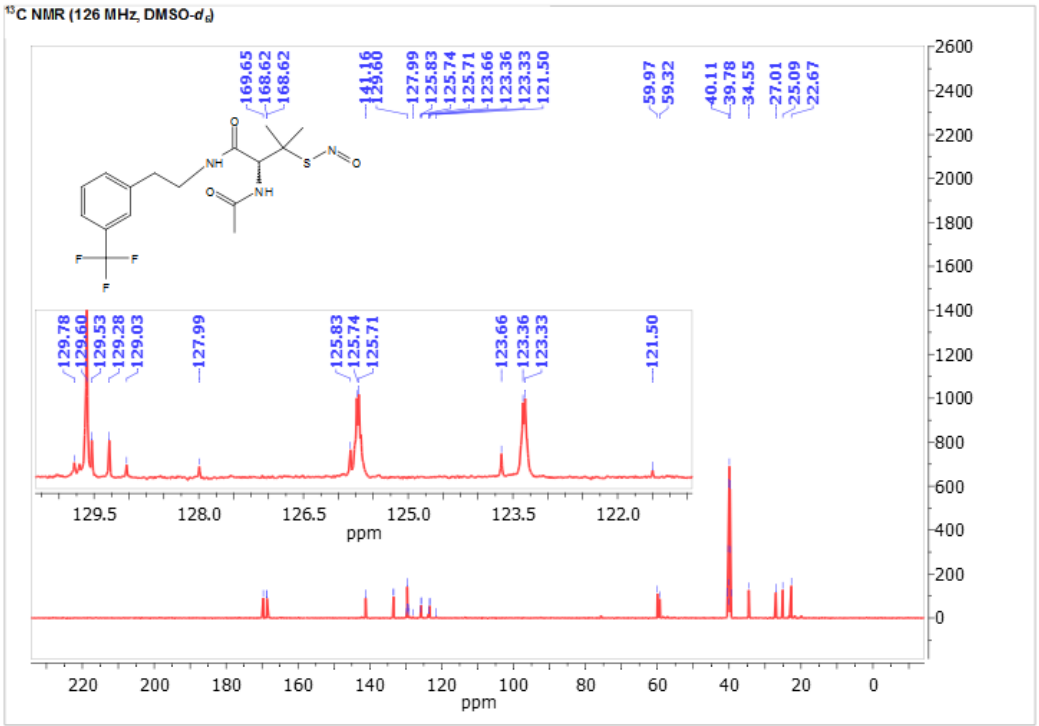
^{13}C NMR (126 MHz, DMSO-d_6)



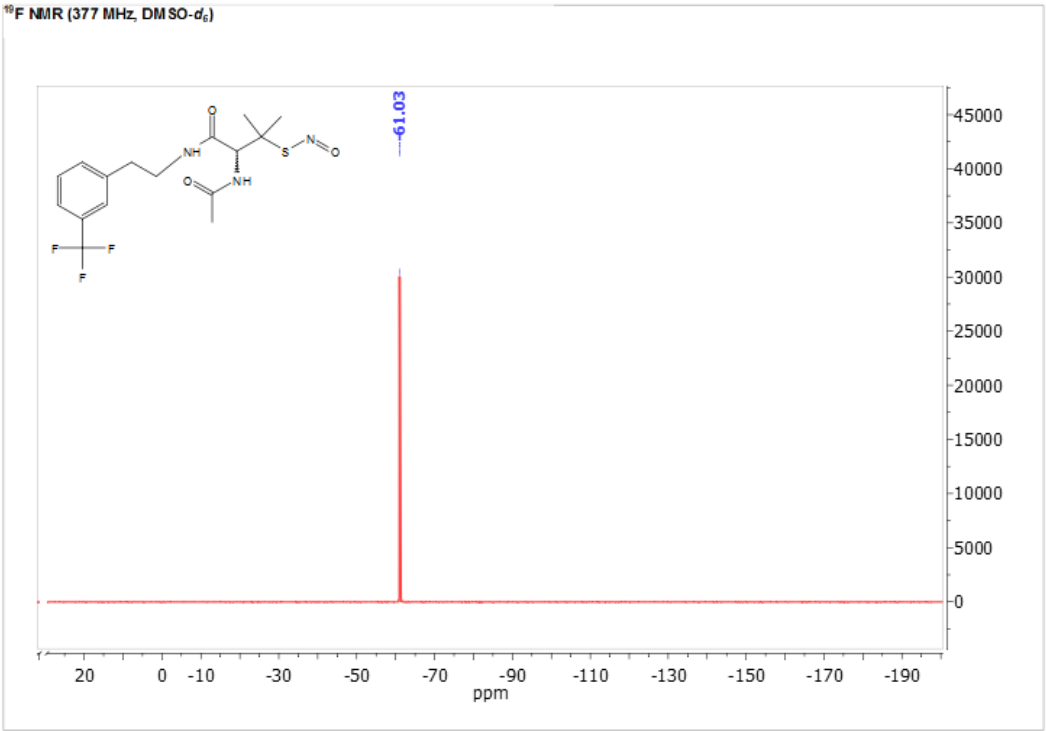
^{19}F NMR (377 MHz, DMSO-d_6)



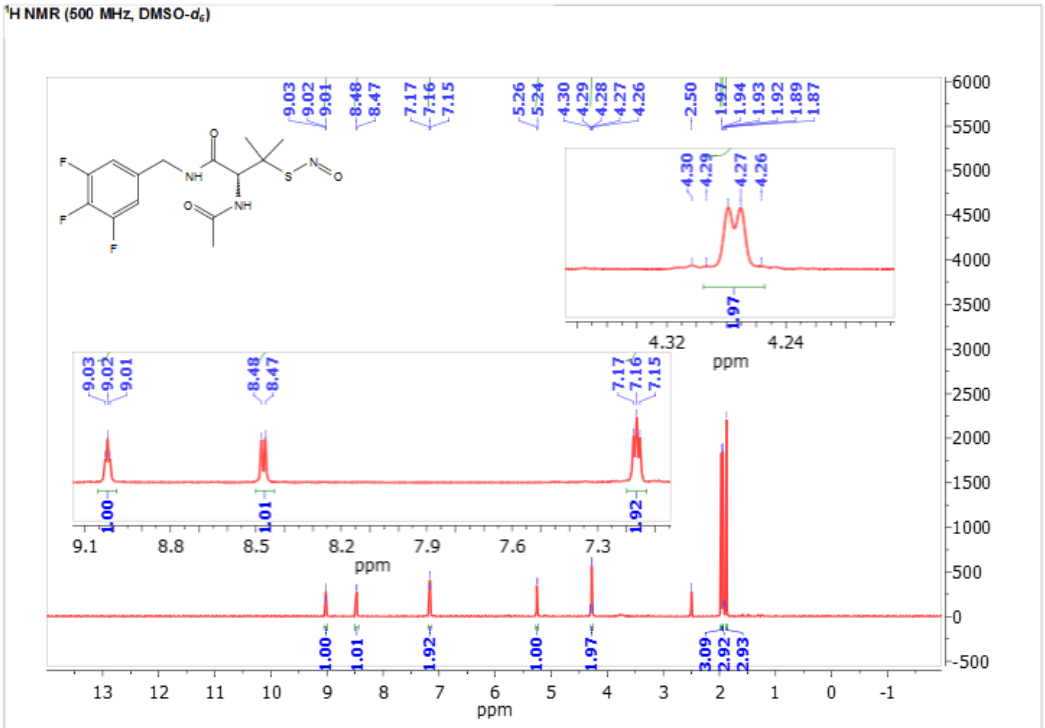

^{1}H NMR (500 MHz, DMSO-d_6)
8.55 8.54 8.53 8.38 8.36 7.58 7.55 7.53 7.52 7.50 5.14 5.12 3.48 3.44 3.28 3.24 2.83 2.50 1.82
3.51 3.50 3.48 3.47 3.46 3.44 3.42 3.31 3.28 3.27 3.25 3.24
1.10 0.77
3.50 3.40 3.30
ppm
8.55 8.54 8.53 8.38 8.36 7.58 7.55 7.53 7.52 7.50
1.00 0.97 4.03
9.0 8.5 8.0 7.5
ppm
1.00 0.97 4.03 0.93 1.10 0.77 2.07 8.79
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
ppm
3500 3000 2500 2000 1500 1000 500 0


^{13}C NMR (126 MHz, DMSO-d_6)
169.65 168.62 168.62 141.16 129.60 127.99 125.83 125.74 125.71 123.66 123.36 123.33 121.50 59.97 59.32 40.11 39.78 34.55 27.01 25.09 22.67
129.78 129.60 129.53 129.28 129.03 127.99 125.83 125.74 125.71 123.66 123.36 123.33 121.50
129.5 128.0 126.5 125.0 123.5 122.0
ppm
220 200 180 160 140 120 100 80 60 40 20 0
ppm
2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0

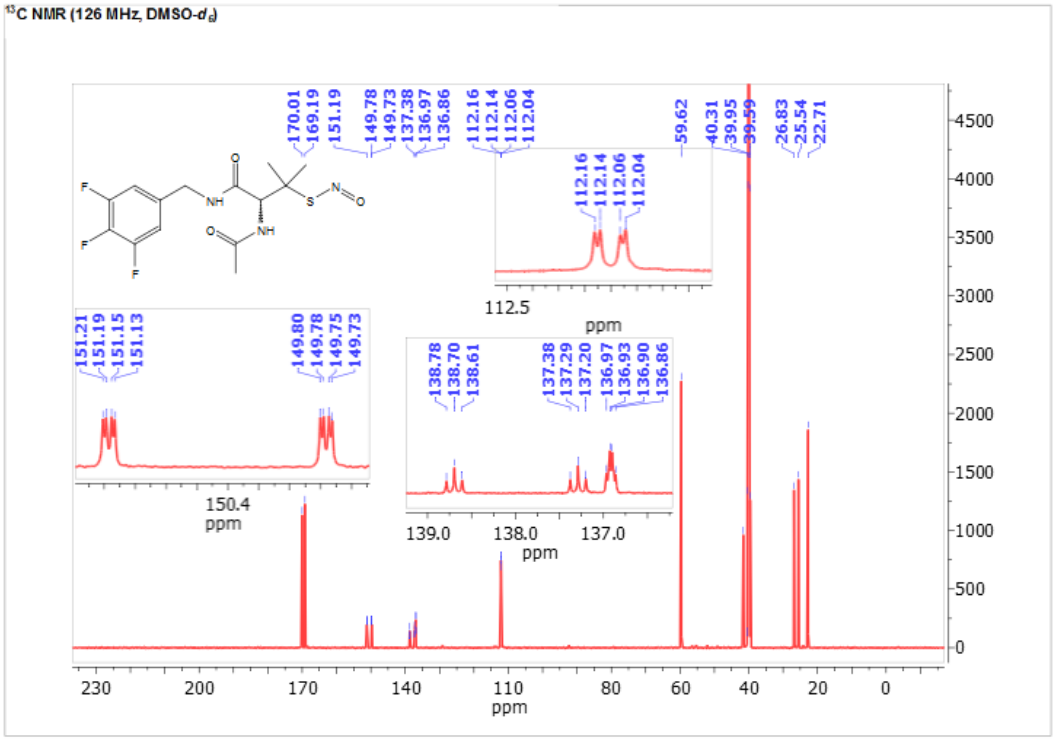
^{19}F NMR (377 MHz, DMSO-d_6)



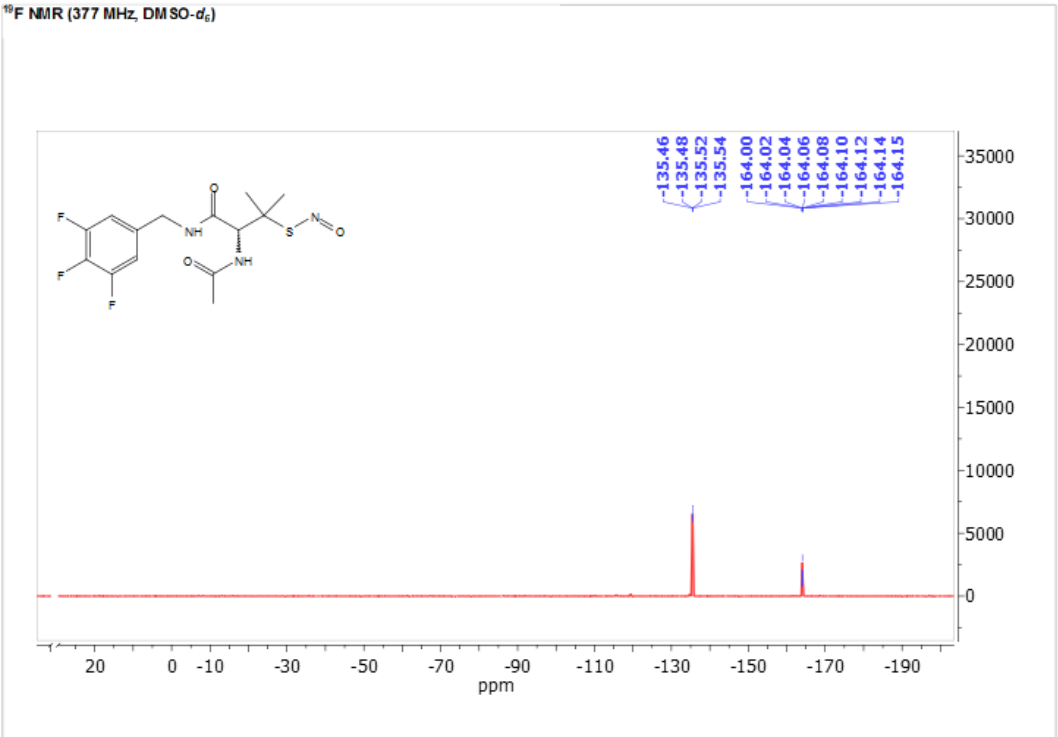
^{1}H NMR (500 MHz, DMSO-d_6)

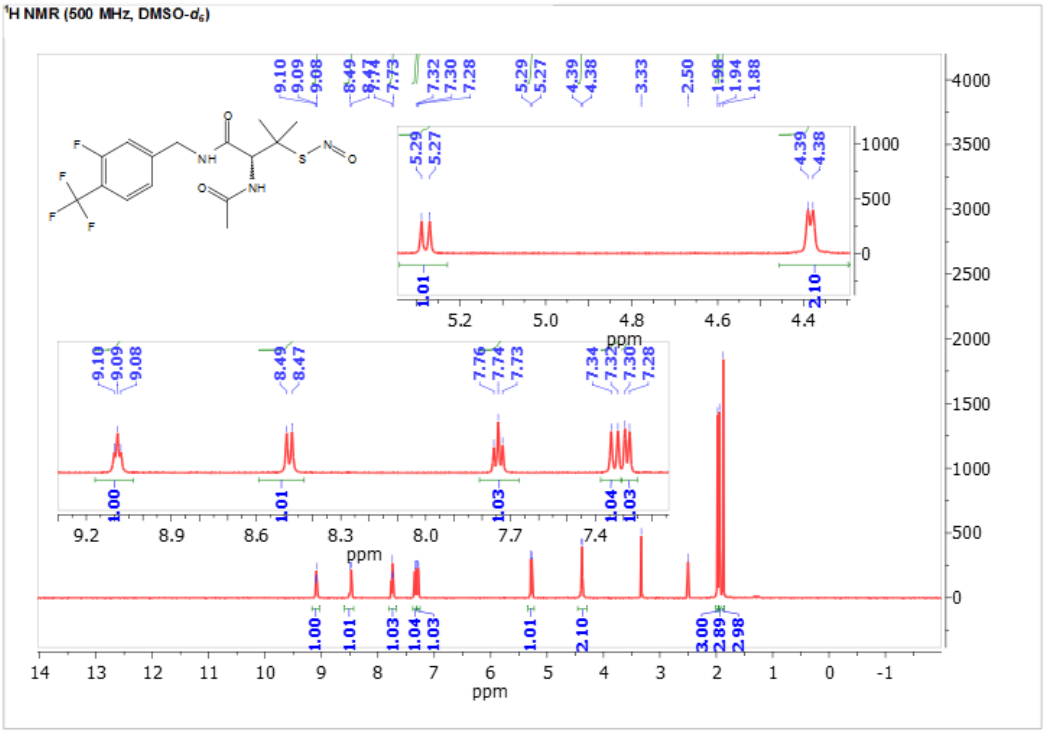


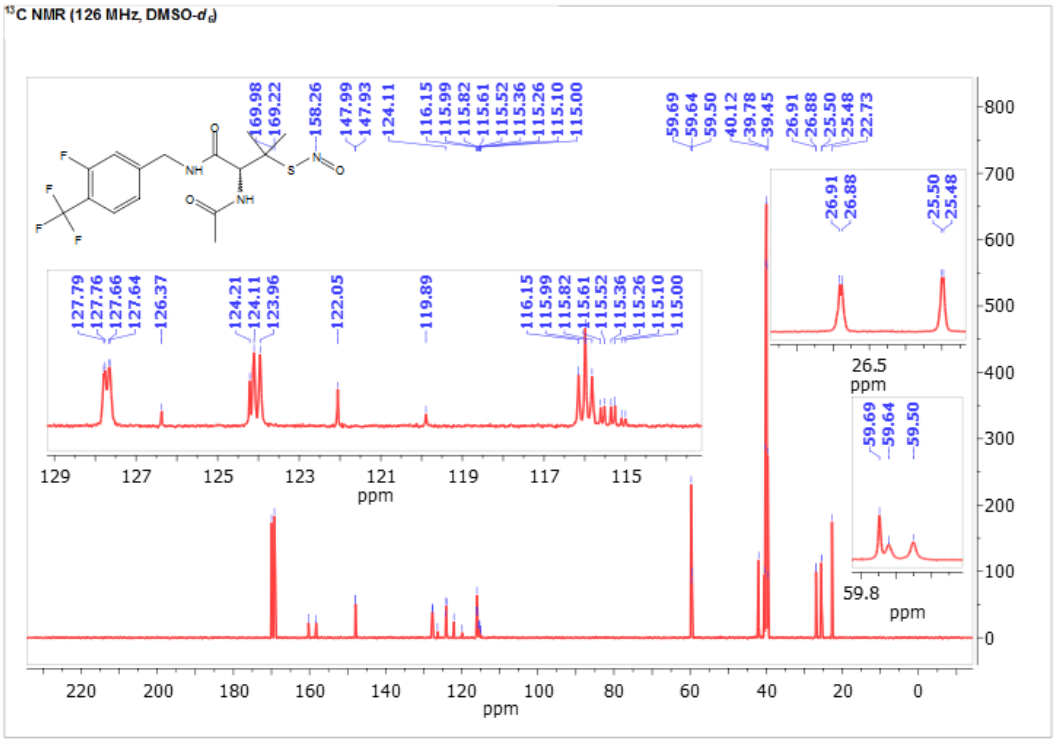
^{13}C NMR (126 MHz, DMSO-d_6)



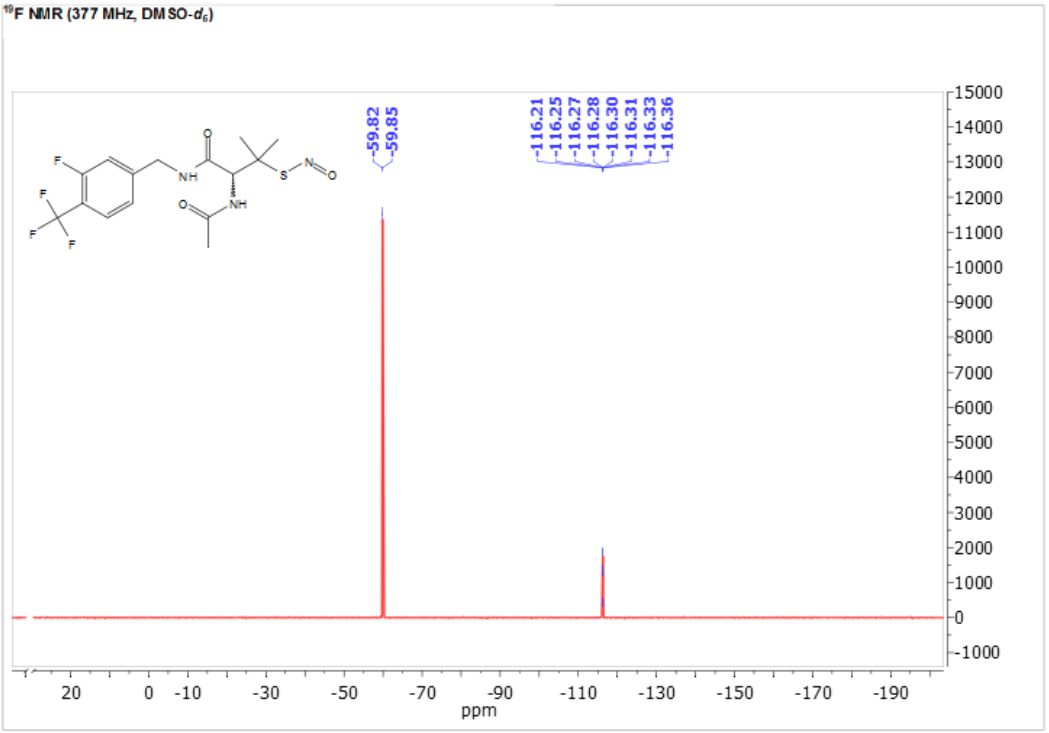
^{19}F NMR (377 MHz, DMSO-d_6)



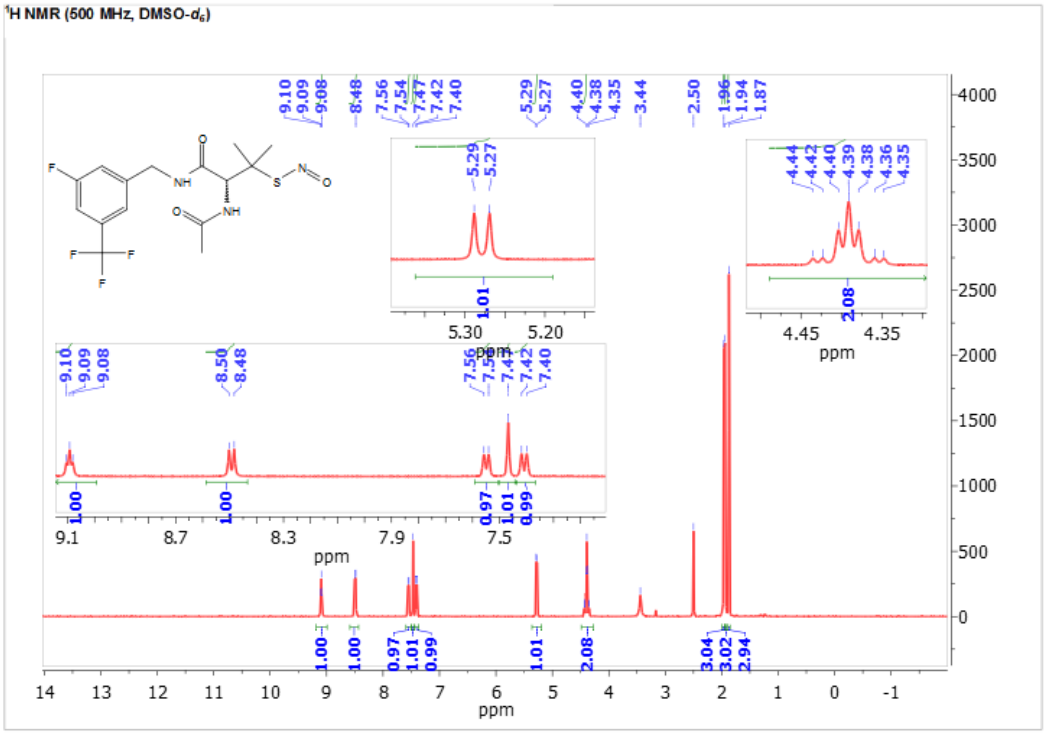

^{1}H NMR (500 MHz, DMSO-d_6)
ppm


^{13}C NMR (126 MHz, DMSO-d_6)
ppm

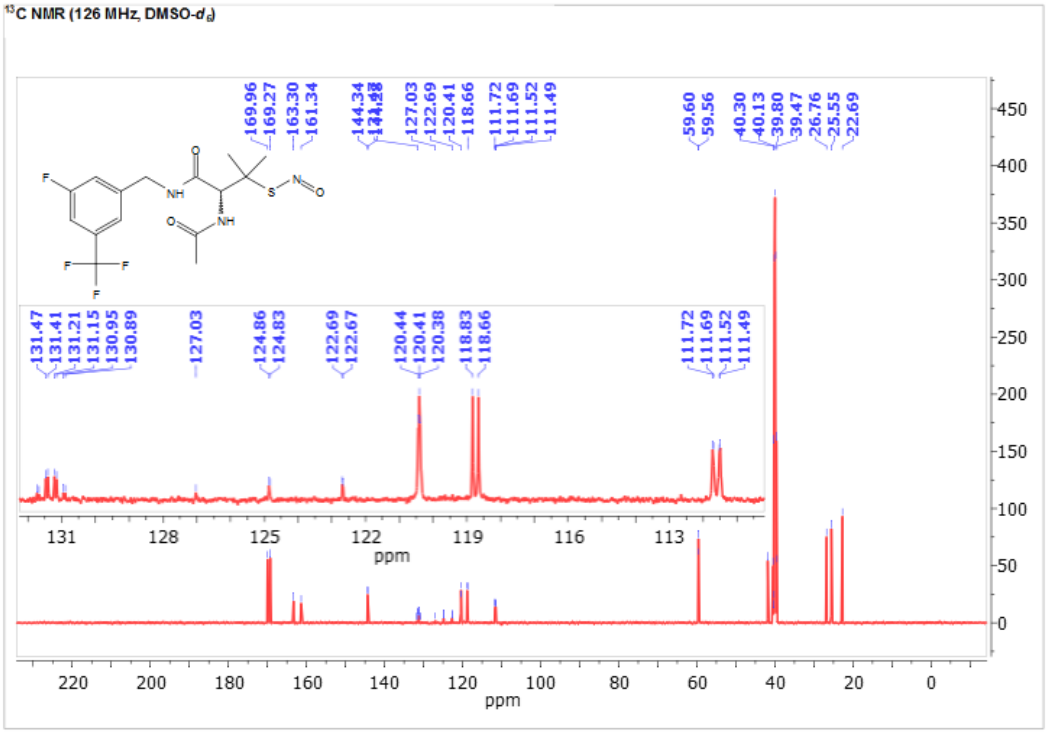
^{19}F NMR (377 MHz, DMSO-d_6)



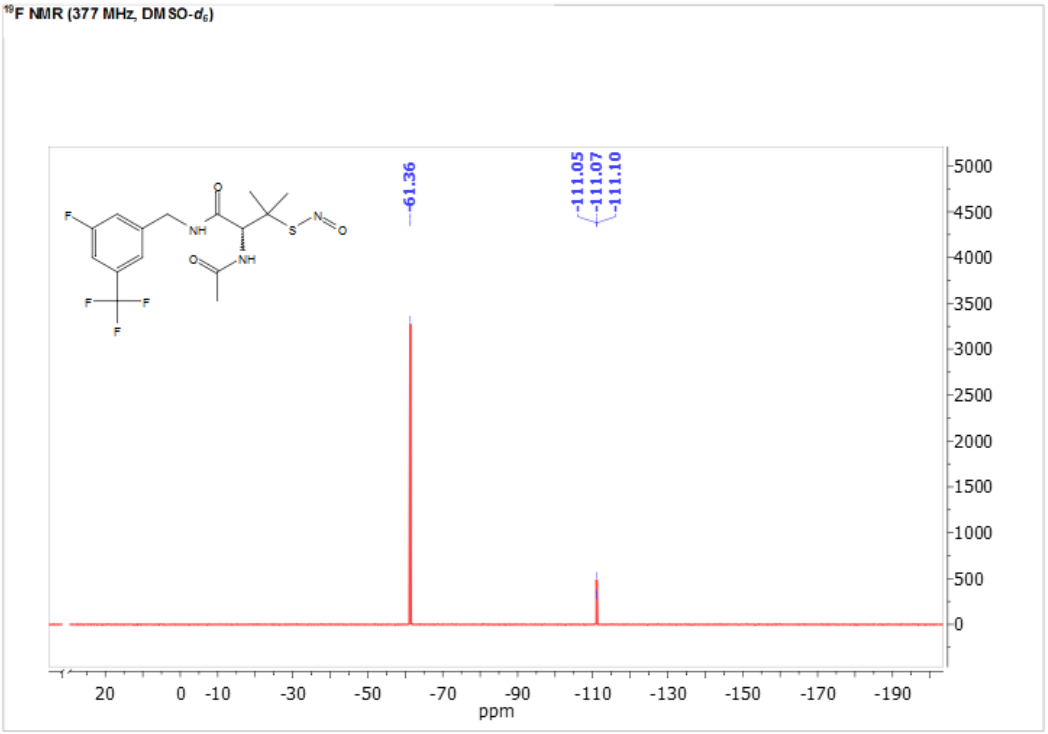
^{1}H NMR (500 MHz, DMSO-d_6)



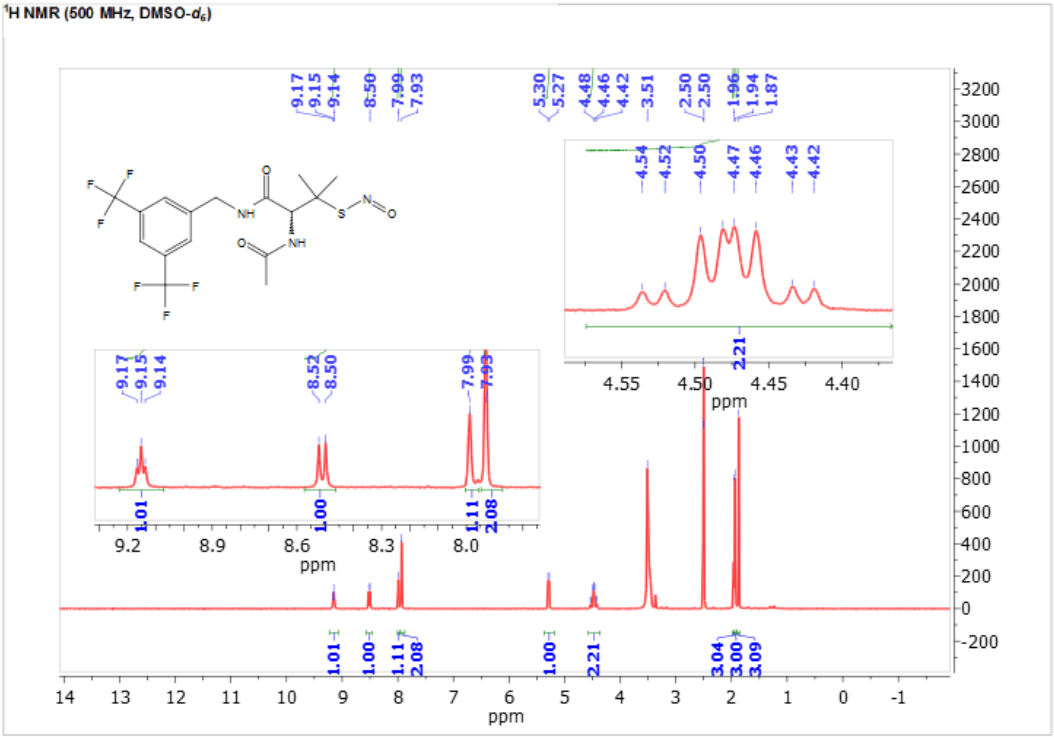
^{13}C NMR (126 MHz, DMSO-d_6)



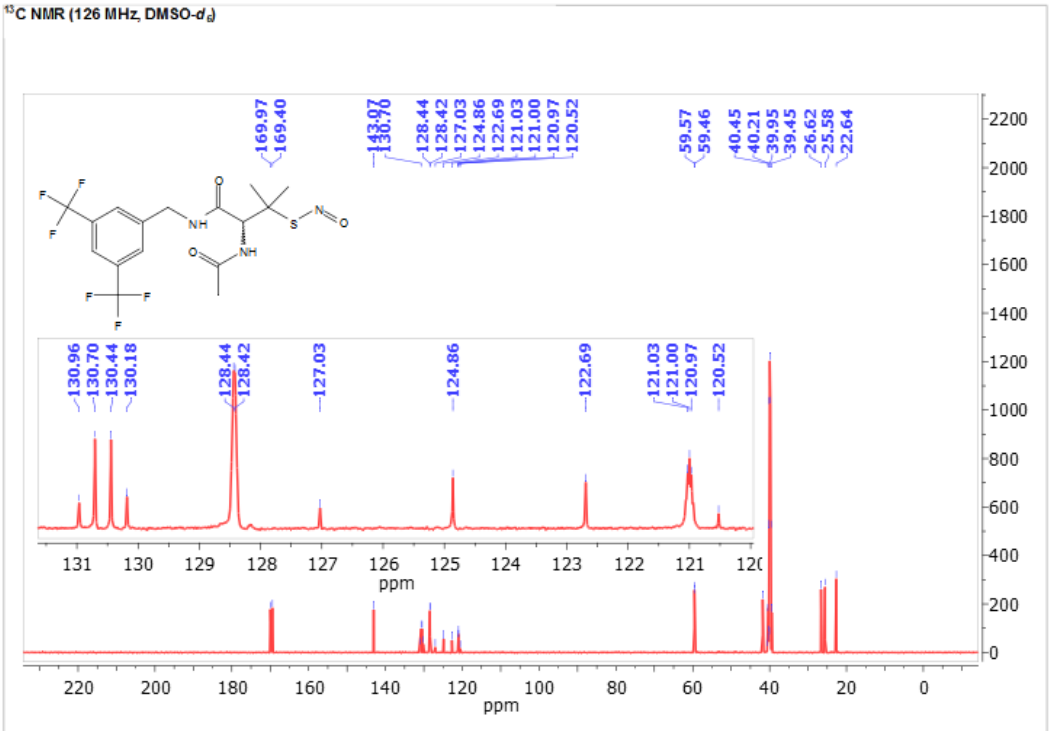
^{19}F NMR (377 MHz, DMSO-d_6)

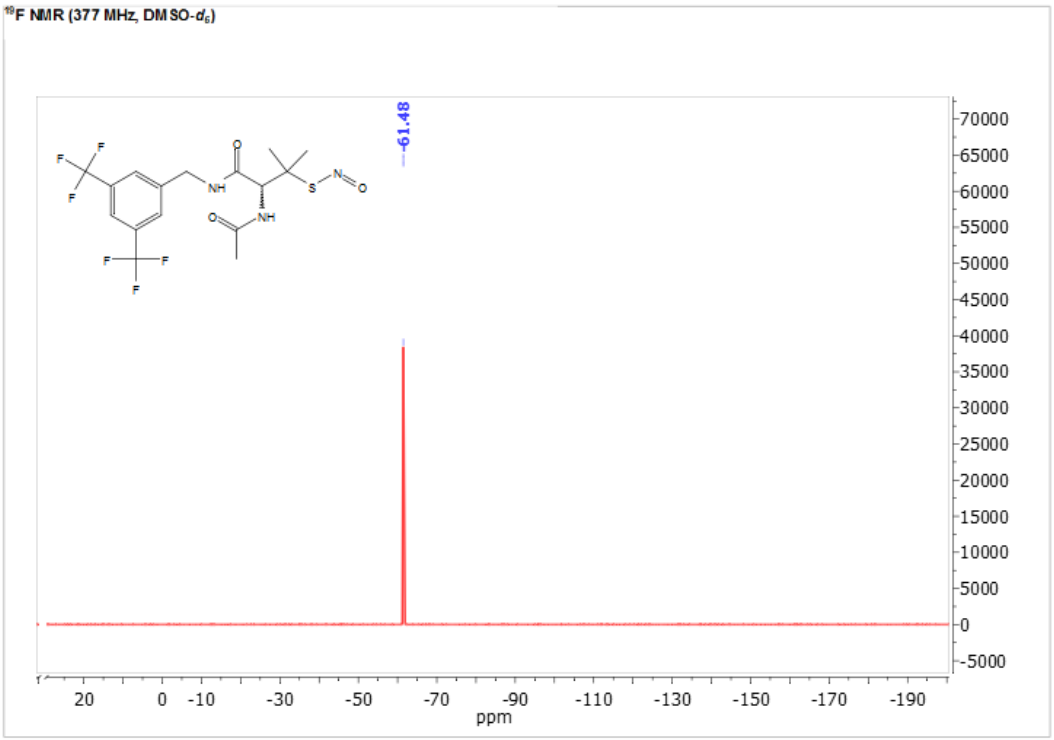


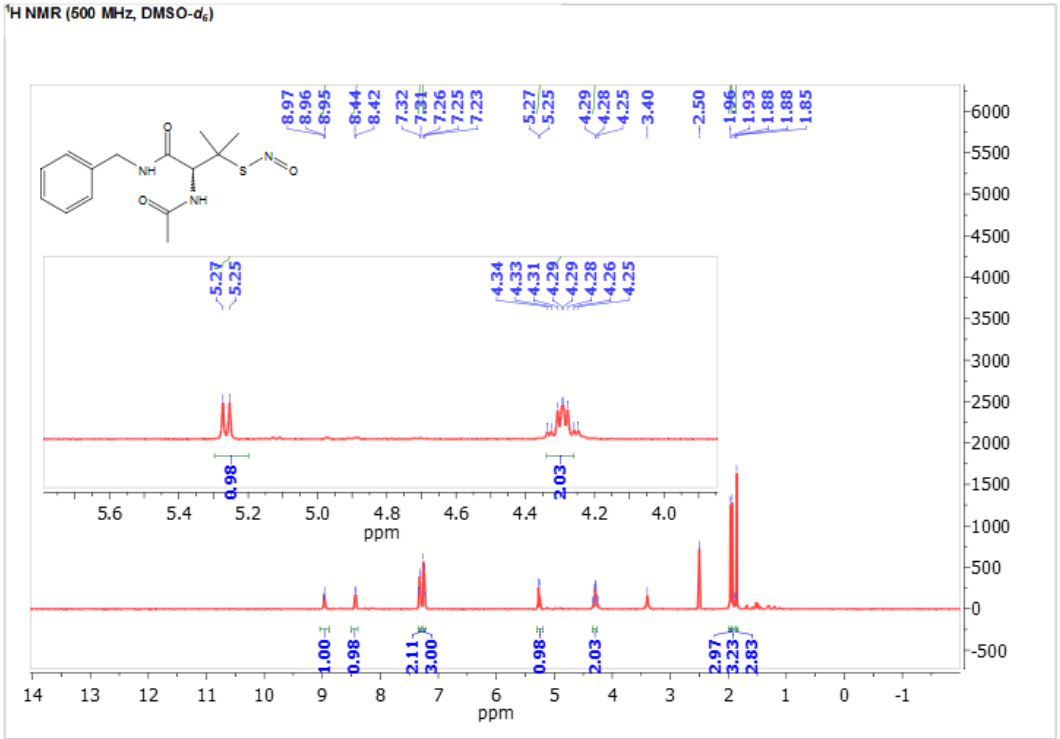
^{1}H NMR (500 MHz, DMSO-d_6)

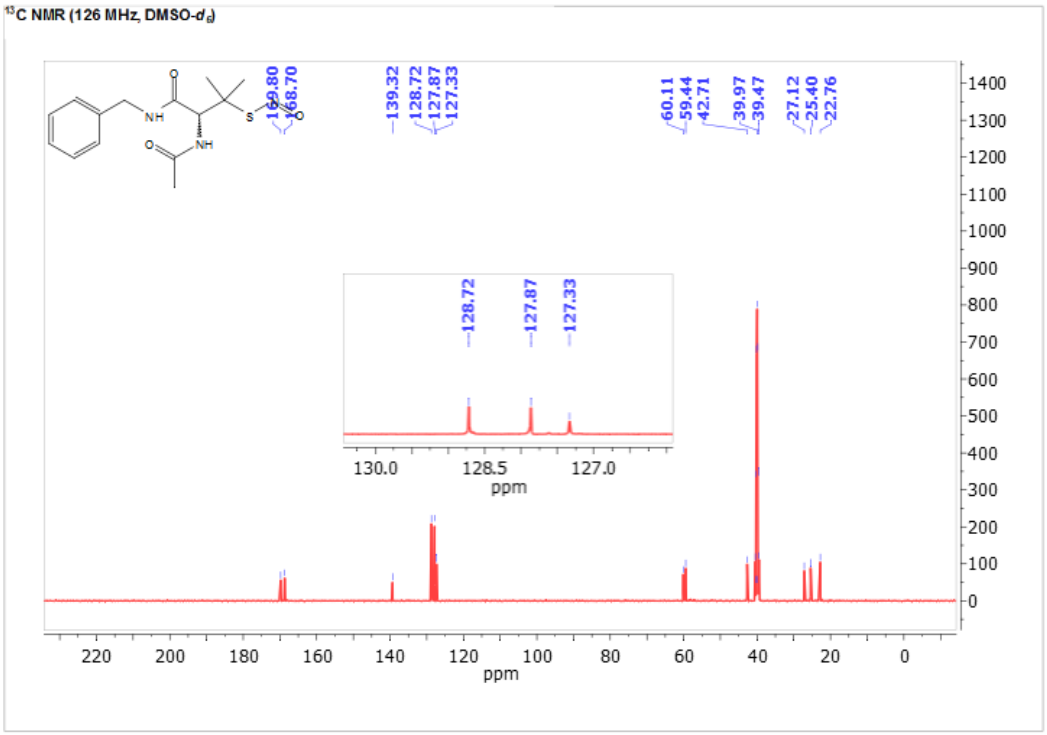


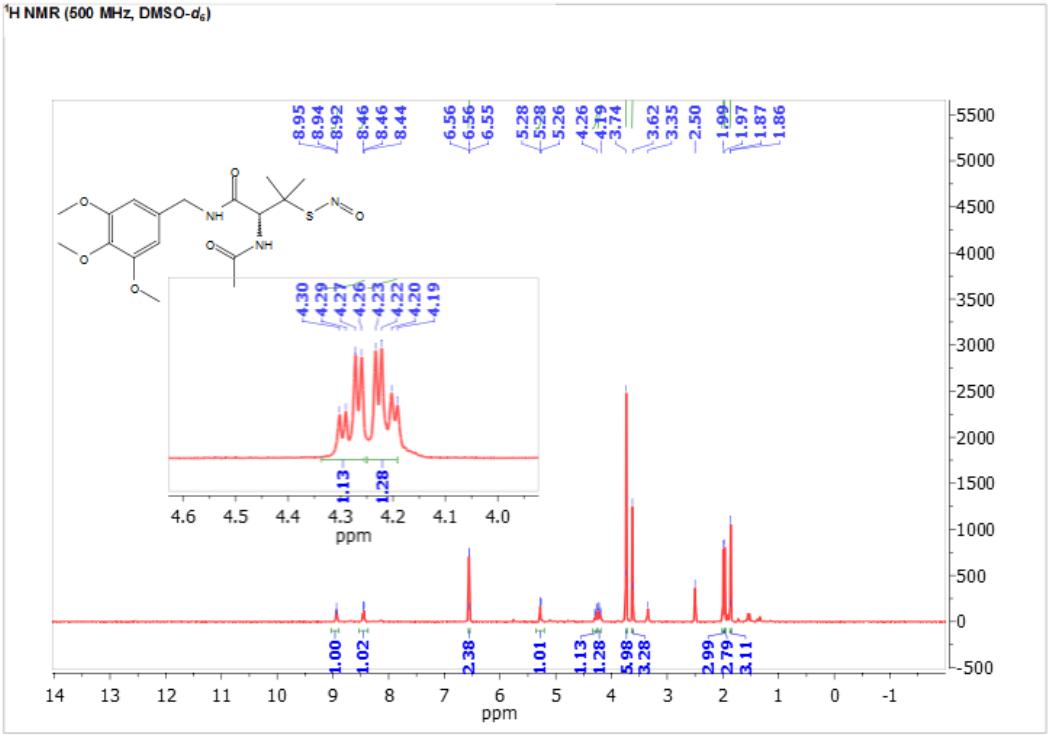
^{13}C NMR (126 MHz, DMSO-d_6)

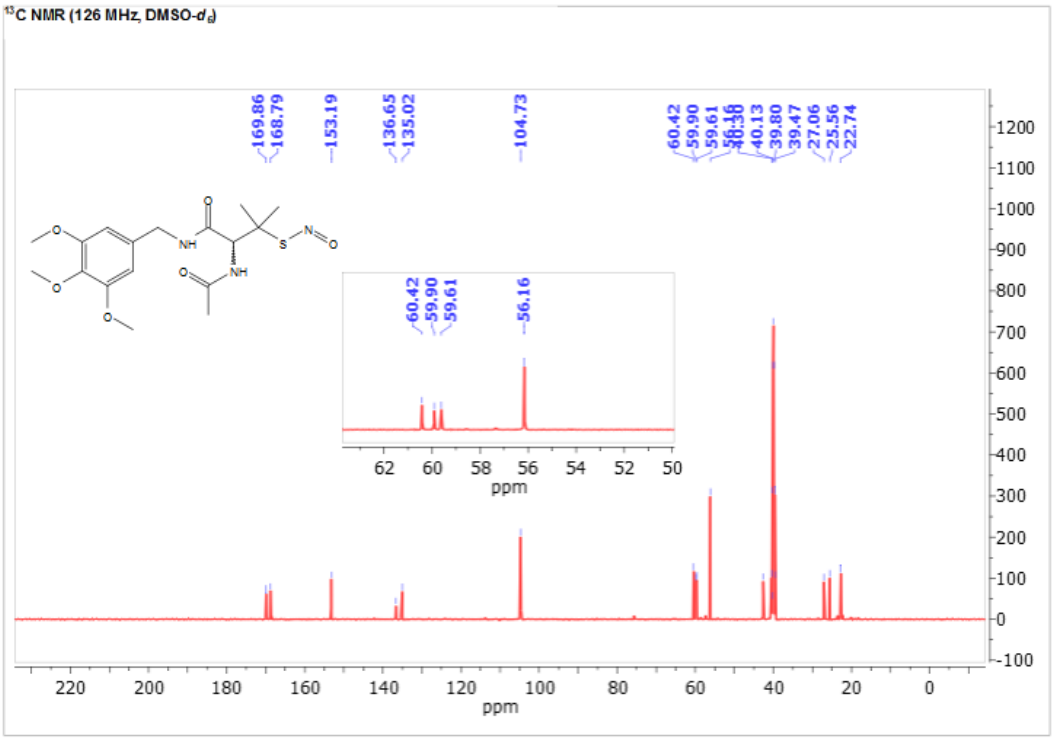



19F NMR (377 MHz, DMSO-d6)
-61.48
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
20 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190
ppm


1H NMR (500 MHz, DMSO-d6)
8.97
8.96
8.95
8.44
8.42
7.32
7.31
7.26
7.25
7.23
5.27
5.25
4.29
4.28
4.25
3.40
2.50
1.96
1.93
1.88
1.88
1.85
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0
ppm
0.98
2.03
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
ppm
1.00
0.98
2.11
3.00
0.98
2.03
2.97
3.23
2.83


13C NMR (126 MHz, DMSO-d6)
170.80
168.70
139.32
128.72
127.87
127.33
60.11
59.44
42.71
39.97
39.47
27.12
25.40
22.76
ppm


1H NMR (500 MHz, DMSO-d6)
8.95
8.94
8.92
8.46
8.46
8.44
6.56
6.56
6.55
5.28
5.28
5.26
4.26
4.19
3.74
3.62
3.35
2.50
1.99
1.97
1.87
1.86
4.30
4.29
4.27
4.26
4.23
4.22
4.20
4.19
1.13
1.28
1.00
1.02
2.38
1.01
1.13
1.28
5.98
3.28
2.99
2.79
3.11
ppm


13C NMR (126 MHz, DMSO-d6)
169.86
168.79
153.19
136.65
135.02
104.73
60.42
59.90
59.61
56.16
40.13
39.80
39.47
27.06
25.56
22.74
ppm