Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

TBAF-Promoted Carbanion-Mediated Sulfonamide Cyclization of CF_3-substituted *N*-Allenamides: an Access to Fluorinated γ-Sultams

Clément Gommenginger[a], Yongxiang Zheng[a], Daniele Maccarone[b], Ilaria Ciofini[b] and Laurence Miesch[a]*

[a] *Équipe de Synthèse Organique et Phytochimie, Institut de Chimie, Université de Strasbourg, CNRS-UdS UMR 7177, 4, rue Blaise Pascal CS 90032, 67081 Strasbourg, France*

[b] *Chimie ParisTech, PSL University, CNRS, Institute of Chemistry for Life and Health Sciences, Chemical Theory and Modelling Group, F-75005 Paris, France*

Corresponding author**: lmiesch@unistra.fr**

Contents

General remarks

All reactions were carried out under an inert atmosphere of argon in dried glassware, unless otherwise noted. Conventional solvents (THF, Et_2O, CH_2Cl_2) are stored on molecular sieves and sampled under argon. Toluene, CH_3CN, acetic acid, were used as received.

NMR Spectra (^1H, ^{13}C, ^{19}F) were performed at 298 K. ^1H (500 MHz or 300 MHz) and ^{13}C (126 MHz) NMR chemical shifts are reported relative to residual protiated solvent. ^{19}F (281 MHz or 471 MHz) NMR chemical shifts are reported without any calibration. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, m = multiplet, br = broad), coupling constant *J* (Hz) and integration.

HRMS data were recorded on a microTOF spectrometer equipped with an orthogonal electrospray (ESI) interface.

Thin layer chromatography was performed using Merck TLC silica gel 60 F_{254} aluminum sheets using petroleum ether/EtOAc as eluant and visualized using permanganate stain, ninhydrin stain, vanillin stain and/or UV light. Merck Geduran® 40-63 µm silica gel was used for column chromatography.

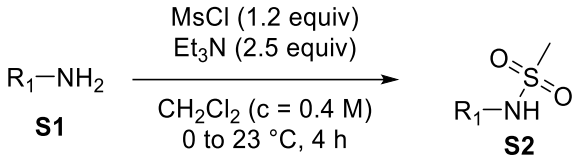
Biotage® Isolera™ One system was used for *flash* chromatography. The wavelength of the UV-detector was calibrated at 254 and 365 nm.

Infrared spectra were reported in frequency of absorption using Alpha Bruker Optics spectrometer.

Melting points were recorded with a SMP3 Stuart Scientific microscope in open capillary tubes and are uncorrected.

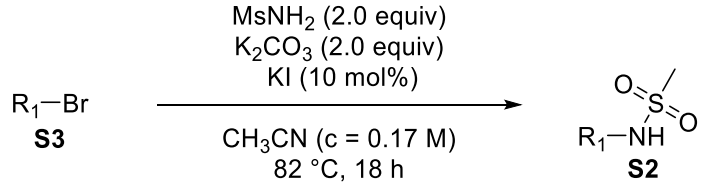
Experimental procedure & characterization data

Synthesis of mesylamides **S2**



General procedure A:

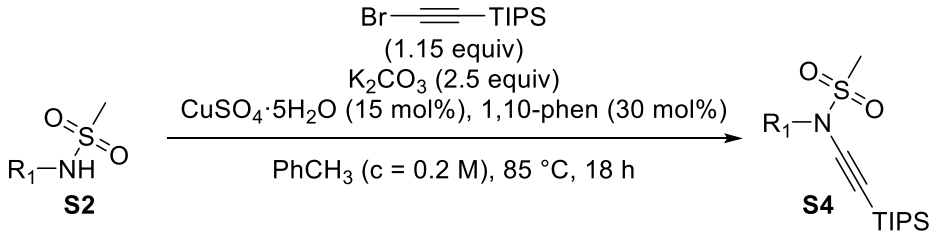
To a solution of amine **S1** (1 equiv) in CH_2Cl_2 (c = 0.4 M) at 0 °C was added dropwise Et_3N (2.5 equiv) and mesityl-chloride (1.2 equiv). The mixture was stirred at 23 °C during 4 h and then hydrolyzed with an aqueous solution of HCl (1 N). The aqueous layer was extracted with CH_2Cl_2 (3x) and Et_2O (1x). The organic layers were washed with a saturated solution of NaCl, dried (Na_2SO_4), filtered and concentrated under vacuum. The crude mesylamide **S2** was used without further purification.



General procedure B:

A solution of mesylamide (2.0 equiv), K_2CO_3 (2.0 equiv) and KI (10 mol%) in CH_3CN (c = 0.17 M) was added bromo-derivative **S3** (1 equiv) and then the mixture was heated at 82 °C for 18 h. The reaction mixture was cooled down to room temperature, filtrated through a pad of Celite® and profusely washed with EtOAc. The filtrate was then concentrated under vacuum. The crude mesylamide **S2** was used without further purification.

Synthesis of mesyl-ynamide **S4**



The (2-bromoethynyl)tris(propan-2-yl)silane was synthesized according to the literature.[1]

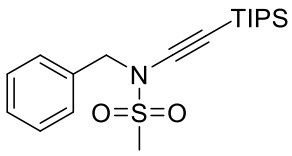
General procedure C:[2]

In a Schlenk tube was introduced $CuSO_4 \cdot 5H_2O$ (15 mol%), 1,10-phenanthroline (30 mol%), K_2CO_3 (2.5 equiv), the mesylamide **S2** (1 equiv), anhydrous toluene (c = 0.2 M) and the

[1] Hofmeister, H.; Annen, K.; Laurent, H.; Wiechert, R. *Angew. Chem. Int. Ed.,* **1984**, *23*, 727.
[2] Zhang, Y. S.; Hsung, R. P.; Tracey, M. R.; Kurtz, K. C. M.; Vera, E. L. *Org. Lett.,* **2004**, *6*, 1151.

bromoacetylenic derivative (1.15 equiv). The reaction mixture was heated to 85 °C for 18 h and then cooled down to room temperature, filtrated through a pad of Celite® and profusely washed with EtOAc. The filtrate was then concentrated under vacuum. The crude material was purified by column chromatography using a step gradient of EtOAc in petroleum ether to afford the title compounds.

_N_-benzyl-N-((triisopropylsilyl)ethynyl)methanesulfonamide (S4a)[3]

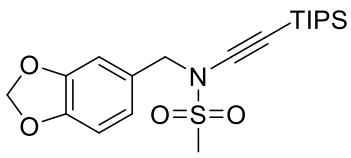


$C_{19}H_{31}NO_2SSi$
MW: 365.18 g.mol^{-1}
Yellow oil
98 % (3.87 g, 10.58 mmol)

The corresponding mesylamide was synthesized following the GP A. The product was obtained by column chromatography on silica gel using a step gradient of ethyl acetate in petroleum ether (0 to 10 %).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.55 – 7.31 (m, 5H), 4.62 (s, 2H), 2.88 (s, 3H), 1.03 (d, J = 0.8 Hz, 21H).

_N_-(benzo[d][1,3]dioxol-5-ylmethyl)-N-((triisopropylsilyl)ethynyl)methanesulfonamide (S4b)



$C_{20}H_{31}NO_4SSi$
MW: 409.17 g.mol^{-1}
Yellow oil
94 % (2.52 g, 6.15 mmol)

The corresponding mesylamide was synthesized following the GP A. The product was obtained by column chromatography on silica gel using a step gradient of ethyl acetate in petroleum ether (0 to 10 %).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.95 (d, *J* = 1.6 Hz, 1H), 6.89 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 5.97 (s, 2H), 4.52 (s, 2H), 2.91 (s, 3H), 1.04 (s, 21H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 148.1, 148.1, 128.2, 123.1, 109.6, 108.4, 101.4, 96.2, 71.1, 55.6, 38.7, 18.7 (x6), 11.4 (x3).

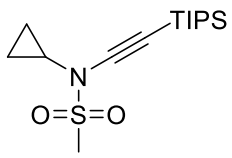
IR (neat): ν = 2941, 2864, 2163, 1491, 1445, 1358, 1245, 1161,1038 cm^{-1}.

ESI-HRMS (ESI-TOF) m/z: $[M+K]^+$ calcd. for $C_{20}H_{31}KNO_4SSi$ 448.1375; found 448.1354.

R_f: 0.58 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain).

_N_-cyclopropyl-N-((triisopropylsilyl)ethynyl)methanesulfonamide (S4c)

[3] Hourtoule, M.; Miesch, L. *Org. Lett*. **2022**, *24*, 3896.



$C_{15}H_{29}NO_2SSi$
MW: 315.55 g.mol^{-1}
Yellow oil
97 % (3.06 g, 9.71 mmol)

The corresponding mesylamide was synthesized following the GP A. The product was obtained by column chromatography on silica gel using a step gradient of ethyl acetate in petroleum ether (0 to 10 %).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.08 (s, 3H), 3.02 (hept, *J* = 7.1, 3.7 Hz, 1H), 1.06 (s, 21H), 1.00 – 0.93 (m, 2H), 0.92 – 0.81 (m, 2H) ppm.

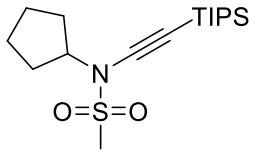
^{13}C NMR ($CDCl_3$, 126 MHz): δ = 94.5, 70.4, 37.2, 32.5, 18.7 (x6), 11.4 (x3), 6.3 (x2) ppm.

IR (neat): ν = 2943, 2865, 2162, 1463, 1367, 1169, 707 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_{15}H_{30}NO_2SSi$ 316.1761; found 316.1784.

R_f: 0.7 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain).

***N*-cyclopentyl-N-((triisopropylsilyl)ethynyl)methanesulfonamide (S4d)**



$C_{17}H_{33}NO_2SSi$
MW: 343.60 g.mol^{-1}
Yellow oil
58 % (1.23 g, 3.58 mmol)

The corresponding mesylamide was synthesized following the GP A. The product was obtained by column chromatography on silica gel using a step gradient of ethyl acetate in petroleum ether (0 to 10 %).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.27 (p, *J* = 7.7 Hz, 1H), 3.06 (s, 3H), 2.05 – 1.92 (m, 2H), 1.92 – 1.69 (m, 4H), 1.63 – 1.55 (m, 2H), 1.08 (s, 21H) ppm.

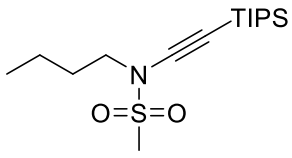
^{13}C NMR ($CDCl_3$, 126 MHz): δ = 93.7, 72.5, 60.6, 38.6, 30.5 (x2), 24.4 (x2), 18.8 (x6), 11.5 (x3) ppm.

IR (neat): ν = 2943, 2865, 2157, 1462, 1360, 1165 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_{17}H_{34}NO_2SSi$ 344.2074; found 344.2058.

R_f: 0.67 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain).

***N*-butyl-*N*-((triisopropylsilyl)ethynyl)methanesulfonamide (S4e)[4]**



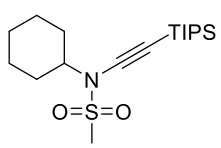
$C_{16}H_{33}NO_2SSi$
MW: 331.59 g.mol^{-1}
Yellow oil
88 % (1.94 g, 5.84 mmol)

[4] Hentz, A.; Retailleau, P.; Gandon, V.; Cariou, K.; Dodd, R. H. *Angew. Chem. Int. Ed*. **2014**, *53*, 8333.

The corresponding mesylamide was synthesized following the GP A. The product was obtained by column chromatography on silica gel using a step gradient of ethyl acetate in petroleum ether (0 to 10 %).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 3.43 (t, *J* = 7.1 Hz, 2H), 3.06 (s, 3H), 1.70 (q, *J* = 7.2 Hz, 2H), 1.40 (hept, *J* = 7.3 Hz, 2H), 1.05 (s, 21H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm.

***N*-cyclohexyl-*N*-((triisopropylsilyl)ethynyl)methanesulfonamide (S4f)**



$C_{18}H_{35}NO_2SSi$
MW: 357.63 g.mol^{-1}
Yellow oil
35 % (710 mg, 2.00 mmol)

The corresponding mesylamide was synthesized following the GP A. The product was obtained by column chromatography on silica gel using a step gradient of ethyl acetate in petroleum ether (0 to 10 %).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.74 (tt, *J* = 11.9, 4.0 Hz, 1H), 3.06 (s, 3H), 1.94 – 1.76 (m, 4H), 1.61 (qd, *J* = 12.1, 3.4 Hz, 3H), 1.33 (qt, *J* = 13.4, 3.4 Hz, 3H), 1.06 (s, 21H) ppm.

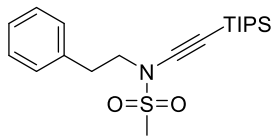
^{13}C NMR ($CDCl_3$, 126 MHz): δ = 93.7, 71.8, 58.8, 39.4, 31.3 (x2), 25.4 (x2), 25.0, 18.7 (x6), 11.44 (x3) ppm.

IR (neat): ν = 2937, 2863, 2157, 1463, 1359, 1162, 732, 660, 632, 521 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_{18}H_{35}NO_2SSi$ 358.2236; found 358.2238.

R_f: 0.67 (Petroleum ether/EtOAc 8:2 *v/v*, UV, ninhydrin stain).

***N*-phenethyl-*N*-((triisopropylsilyl)ethynyl)methanesulfonamide (S4g)**



$C_{20}H_{33}NO_2SSi$
MW: 379.63 g.mol^{-1}
Colorless oil
69 % (1.31 g, 3.46 mmol)

The corresponding mesylamide was synthesized following the GP A. The product was obtained by column chromatography on silica gel using a step gradient of ethyl acetate in petroleum ether (0 to 10 %).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.54 – 7.08 (m, 5H), 3.77 (t, *J* = 7.1 Hz, 2H), 3.07 (d, *J* = 7.0 Hz, 2H), 2.65 (s, 3H), 1.15 (s, 21H) ppm.

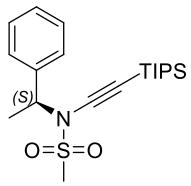
^{13}C NMR ($CDCl_3$, 126 MHz): δ = 137.8, 129.2 (x2), 128.7 (x2), 127.0, 95.4, 70.9, 52.4, 37.9, 34.2, 18.7 (x6), 11.4 (x3) ppm.

IR (neat): ν = 2942, 2864, 2164, 1462, 1365, 1164, 961, 699 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_{20}H_{34}NO_2SSi$ 380.2074; found 380.2078.

R_f: 0.71 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain).

***(S)*-*N*-(1-phenylethyl)-N-((triisopropylsilyl)ethynyl)methanesulfonamide (S4h)**



$C_{20}H_{33}NO_2SSi$
MW: 379.63 g.mol^{-1}
Yellow oil
59 % (1.13 g, 2.97 mmol)

The corresponding mesylamide was synthesized following the GP A. The product was obtained by column chromatography on silica gel using a step gradient of ethyl acetate in petroleum ether (0 to 10 %).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.52 – 7.45 (m, 2H), 7.41 – 7.31 (m, 3H), 5.10 (q, *J* = 7.0 Hz, 1H), 2.68 (s, 3H), 1.72 (d, *J* = 7.1 Hz, 3H), 1.08 (s, 21H).

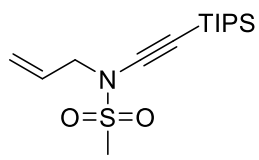
^{13}C NMR ($CDCl_3$, 126 MHz): δ = 139.9, 128.8 (x2), 128.7, 127.1 (x2), 93.8, 73.3, 58.6, 38.5, 20.1, 18.8 (x6), 11.6 (x3).

IR (neat): ν = 2942, 2863, 2157, 1459, 1362, 1164, 959 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{20}H_{33}NNaO_2SSi$ 402.1893; found 402.1893.

R_f: 0.70 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain).

***N*-allyl-*N*-((triisopropylsilyl)ethynyl)methanesulfonamide (S4i)**



$C_{15}H_{29}NO_2SSi$
MW: 315.55 g.mol^{-1}
Colorless oil
77 % (1.80 g, 5.70 mmol)

The corresponding mesylamide was synthesized following the GP A. The product was obtained by column chromatography on silica gel using a step gradient of ethyl acetate in petroleum ether (0 to 20 %).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.90 (ddt, *J* = 16.7, 10.1, 6.4 Hz, 1H), 5.40 – 5.22 (m, 2H), 4.03 (dt, *J* = 6.4, 1.2 Hz, 2H), 3.05 (s, 3H), 1.04 (s, 21H) ppm.

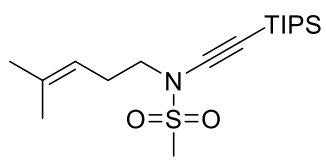
^{13}C NMR ($CDCl_3$, 126 MHz): δ = 130.7, 120.5, 95.9, 70.0, 54.1, 38.5, 18.6 (x6), 11.3 (x3) ppm.

IR (neat): ν = 2942, 2865, 2160, 1361, 1166, 676 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+K]^+$ calcd. for $C_{15}H_{29}KNO_2SSi$ 354.1320; found 354.1341.

R_f: 0.59 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain).

***N*-(4-methylpent-3-en-1-yl)-*N*-((triisopropylsilyl)ethynyl)methanesulfonamide (S4j)**



$C_{18}H_{35}NO_2SSi$
MW: 357.63 g.mol^{-1}
Colorless oil
76 % (1.14 g, 3.19 mmol)

The corresponding mesylamide was synthesized following the GP A. The product was obtained by column chromatography on silica gel using a step gradient of ethyl acetate in petroleum ether (0 to 20 %).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.11 (ddq, *J* = 8.8, 5.9, 1.5 Hz, 1H), 3.44 (d, *J* = 7.6 Hz, 2H), 3.05 (s, 3H), 2.42 (q, *J* = 7.3 Hz, 2H), 1.69 (s, 3H), 1.64 (s, 3H), 1.07 (s, 21H) ppm.

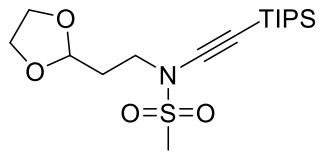
^{13}C NMR ($CDCl_3$, 126 MHz): δ = 135.5, 119.5, 96.0, 70.1, 51.4, 38.1, 27.2, 25.8, 18.7 (x6), 17.9, 11.5 (x3) ppm.

IR (neat): ν = 2941, 2865, 2160, 1463, 1360, 1163, 960, 675, 514 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_{18}H_{36}NO_2SSi$ 358.2231; found 358.2218.

R_f: 0.64 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain).

***N*-(2-(1,3-dioxolan-2-yl)ethyl)-*N*-((triisopropylsilyl)ethynyl)methanesulfonamide (S4k)**



$C_{17}H_{33}NO_4SSi$
MW: 375.60 $g.mol^{-1}$
Colorless oil
8 % (375.6 mg, 0.68 mmol)

The corresponding mesylamide was synthesized following the GP B. The product was obtained by column chromatography on silica gel using a step gradient of ethyl acetate in petroleum ether (0 to 20 %).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.00 (t, *J* = 4.5 Hz, 1H), 4.02 – 3.93 (m, 2H), 3.91 – 3.82 (m, 2H), 3.64 – 3.57 (m, 2H), 3.09 (s, 3H), 2.17 – 2.06 (m, 2H), 1.07 (s, 21H) ppm.

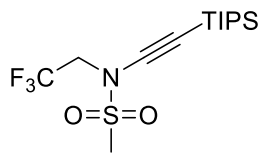
^{13}C NMR ($CDCl_3$, 126 MHz): δ = 101.9, 95.7, 70.6, 65.2 (x2), 46.8, 38.1, 32.6, 18.8 (x6), 11.5 (x3) ppm.

IR (neat): ν = 2942, 2160, 1463, 1361, 1166, 676 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_{17}H_{34}NO_4SSi$ 376.1972; found 376.1961.

R_f: 0.41 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain).

***N*-(2,2,2-trifluoroethyl)-*N*-((triisopropylsilyl)ethynyl)methanesulfonamide (S4l)**



$C_{14}H_{26}F_3NO_2SSi$
MW: 357.51 $g.mol^{-1}$
Yellow oil
18 % (150.0 mg, 0.50 mmol)

The corresponding mesylamide was synthesized following the GP A. The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (2 to 20 %).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 4.09 (q, *J* = 8.3 Hz, 2H), 3.20 (s, 3H), 1.07 (s, 21H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 123.5 (q, *J* = 285.7 Hz), 94.1, 71.3, 51.3 (q, *J* = 35.5 Hz), 39.1 – 38.9 (m), 18.7 (x6), 11.4 (x3) ppm.

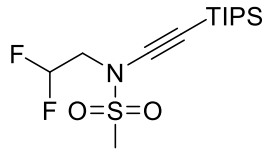
^{19}F NMR (282 MHz, $CDCl_3$): δ = -70.74 ppm.

IR (neat): ν = 2944, 2867, 2163, 1464, 1366, 1328, 1275, 1170, 1044, 966, 785, 650, 531 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{14}H_{26}F_3NNaO_2SSi$ 380.1303; found 380.1305.

R_f: 0.60 (Petroleum ether/EtOAc 9:1 *v/v*, UV, $KMnO_4$ stain).

***N*-(2,2-difluoroethyl)-*N*-((triisopropylsilyl)ethynyl)methanesulfonamide (S4m)**



$C_{14}H_{27}F_2NO_2SSi$
MW: 339.52 g.mol^{-1}
Yellow oil
71 % (772.2 mg, 2.27 mmol)

The corresponding mesylamide was synthesized following the GP A. The product was obtained by *flash* chromatography on 50 g of silica gel using a gradient of ethyl acetate in petroleum ether (5 to 40 %).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.01 (tt, *J* = 55.2, 4.1 Hz, 1H), 3.84 (td, *J* = 13.5, 4.1 Hz, 2H), 3.17 (s, 3H), 1.08 (s, 21H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 113.6 (t, *J* = 244.0 Hz), 94.8, 70.9, 52.4 (t, *J* = 28.3 Hz), 38.7, 18.7 (x6), 11.4 (x3) ppm.

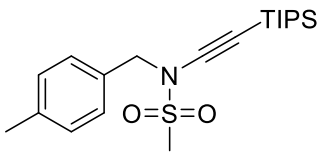
^{19}F NMR (282 MHz, $CDCl_3$): δ = -122.70 ppm.

IR (neat): ν = 2943, 2866, 2165, 1464, 1364, 1169, 1076, 964, 882, 784, 676, 516 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{14}H_{27}F_2NNaO_2SSi$ 362.1392; found 362.1391.

R_f: 0.68 (Petroleum ether/EtOAc 8:2 *v/v*, UV, $KMnO_4$ stain).

***N*-(4-methylbenzyl)-*N*-((triisopropylsilyl)ethynyl)methanesulfonamide (S4n)**



$C_{20}H_{33}NO_2SSi$
MW: 379.63 g.mol^{-1}
Yellow oil
90 % (861.4 mg, 2.27 mmol)

The corresponding mesylamide was synthesized following the GP A. The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (0 to 40 %).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.33 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 7.7 Hz, 2H), 4.57 (s, 2H), 2.85 (s, 3H), 2.35 (s, 3H), 1.03 (s, 21H) ppm.

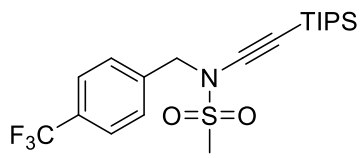
^{13}C NMR ($CDCl_3$, 126 MHz): δ = 138.7, 131.6, 129.5 (x2), 129.2 (x2), 96.4, 70.8, 55.6, 38.7, 21.3, 18.7 (x6), 11.9 (x3) ppm.

IR (neat): ν = 2942, 2865, 2165, 1516, 1463, 1364, 1165, 962, 883, 778, 678 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+K]^+$ calcd. for $C_{20}H_{33}KNO_2SSi$ 418.1633; found 418.1637.

R_f: 0.67 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain).

***N*-(4-(trifluoromethyl)benzyl)-*N*-((triisopropylsilyl)ethynyl)methanesulfonamide (S4o)**



$C_{20}H_{30}F_3NO_2SSi$
MW: 443.61 g.mol^{-1}
Yellow oil
54 % (916.8 mg, 2.11 mmol)

The corresponding mesylamide was synthesized following the GP B. The product was obtained by *flash* chromatography on 50 g of silica gel using a gradient of ethyl acetate in petroleum ether (5 to 40 %).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.64 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 4.66 (s, 2H), 3.01 (s, 3H), 1.00 (s, 21H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 138.6 (q, *J* = 1.3 Hz), 131.0 (q, *J* = 32.6 Hz), 129.3 (x2), 125.9 (q, *J* = 3.7 Hz) (x2), 124.1 (q, *J* = 272.2 Hz), 95.6, 71.7, 54.8, 38.7, 18.7 (x6), 11.4 (x3) ppm.

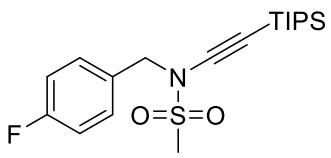
^{19}F NMR (282 MHz, $CDCl_3$): δ = -62.72 ppm.

IR (neat): ν = 2944, 2866, 2167, 1364, 1324, 1165, 1129, 1068 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{20}H_{30}F_3NNaO_2SSi$ 456.1611; found 456.1601.

R_f: 0.58 (Petroleum ether/EtOAc 8:2 *v/v*, UV, ninhydrin stain).

***N*-(4-fluorobenzyl)-*N*-((triisopropylsilyl)ethynyl)methanesulfonamide (S4p)**



$C_{19}H_{30}FNO_2SSi$
MW: 383.60 $g.mol^{-1}$
Yellow oil
86 % (1.22 g, 3.18 mmol)

The corresponding mesylamide was synthesized following the GP A. The product was obtained by *flash* chromatography on 50 g of silica gel using a gradient of ethyl acetate in petroleum ether (0 to 40 %).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.41 – 7.31 (m, 2H), 7.05 – 6.95 (m, 2H), 4.51 (s, 2H), 2.85 (s, 3H), 0.95 (s, 21H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 163.1 (d, *J* = 247.7 Hz), 131.1 (d, *J* = 8.4 Hz) (2), 130.5 (d, *J* = 3.2 Hz), 115.8 (d, *J* = 21.6 Hz) (x2), 95.9, 71.4, 54.9, 38.7, 18.7 (x6), 11.4 (x3) ppm.

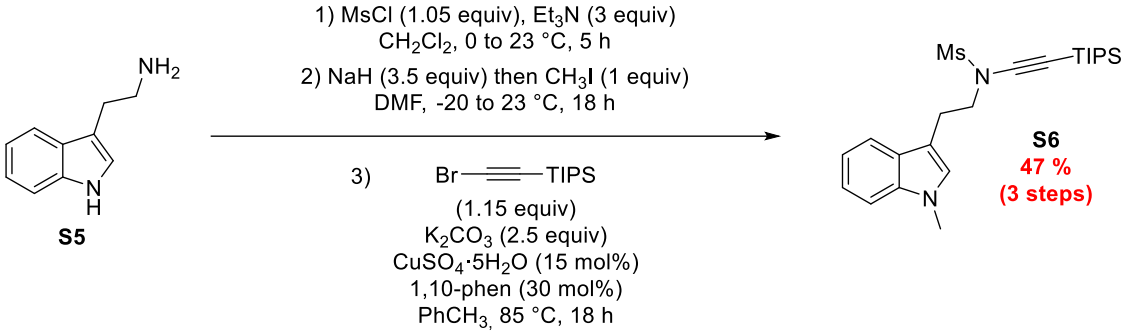
^{19}F NMR (282 MHz, $CDCl_3$): δ = -112.97 ppm.

IR (neat): ν = 2943, 2892, 2865, 2465, 1629, 1511, 1464, 1364, 1323, 1226, 1166, 679 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+K]^+$ calcd. for $C_{19}H_{30}FKNO_2SSi$ 422.1382; found 422.1380.

R_f: 0.50 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain).

Synthesis of tryptamine-derivative mesyl-ynamide **S6**[5]

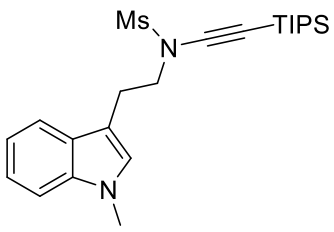


To a solution of tryptamine **S5** (800 mg, 5 mmol, 1 equiv), Et_3N (2.1 mL, 15 mmol, 3 equiv) in CH_2Cl_2 (250 mL) at 0 °C was added in one portion MsCl (0.40 mL, 5.25 mmol, 1.05 equiv). The mixture was stirred at 23 °C during 5 h and hydrolyzed with an aqueous solution of HCl (1 N) (50 mL). The aqueous layer was extracted with CH_2Cl_2 (3x) and Et_2O (1x). The organic layers were washed with a saturated solution of NaCl, dried (Na_2SO_4), filtered and concentrated under vacuum. The crude mesyl-tryptamine was used without further purification.

To a solution of mesyl-tryptamine (1.19 g, 5 mmol, 1 equiv) in DMF (200 mL) at -20 °C was added stepwise NaH (60 % in mineral oil, 700 mg, 17.5 mmol, 3.5 equiv). The solution was stirred at -20 °C for 30 minutes and then a solution of CH_3I (0.31 mL, 5 mmol, 1 equiv) in DMF (8 mL) was added dropwise and **very slowly**. The solution was allowed to warm-up to 23 °C during 18 h and hydrolyzed with an aqueous solution of NH_4Cl (50 mL). The aqueous layer was extracted with EtOAc (3x). The organic layers were washed with a saturated solution of NaCl, dried (Na_2SO_4), filtered and concentrated under vacuum. The crude *N*-methyl-mesyl-tryptamine was used without further purification.

In a Schlenk tube was introduced $CuSO_4·5H_2O$ (187 mg, 0.75 mmol, 15 mol%), 1,10-phenanthroline (270 mg, 1.5 mmol, 30 mol%), K_2CO_3 (1.72 g, 12.5 mmol, 2.5 equiv), the *N*-methyl-mesyl-tryptamine (1.26 g, 5 mmol, 1 equiv), anhydrous toluene (50 mL) and the bromoacetylenic derivative (1.5 g, 5.75 mmol, 1.15 equiv). The reaction mixture was heated to 85 °C for 18 h and then cooled down to room temperature, filtrated through a pad of Celite® and profusely washed with EtOAc. The filtrate was then concentrated under vacuum. The crude material was purified by *flash* chromatography using a gradient of EtOAc in petroleum ether (5 to 40 %) to afford the title compounds.

***N*-(2-(1-methyl-1H-indol-3-yl)ethyl)-*N*-((triisopropylsilyl)ethynyl)methanesulfonamide (S6)**



$C_{23}H_{36}N_2O_2SSi$
MW: 432.23 g.mol^{-1}
Orange oil
47 % (1.0 g, 2.33 mmol)

The product was obtained by *flash* chromatography on 50 g of silica gel using a gradient of ethyl acetate in petroleum ether (5 to 40 %).

[5] N. Zheng, Y.-Y. Chang, L.-J. Zhang, J.-X. Gong and Z. Yang, *Chem. Asian J.*, 2016, **11**, 371–375.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.63 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.33 – 7.20 (m, 2H), 7.13 (ddd, *J* = 8.0, 6.8, 1.3 Hz, 1H), 6.97 (s, 1H), 3.81 – 3.73 (m, 5H), 3.22 (t, *J* = 7.4 Hz, 2H), 2.80 (s, 3H), 1.13 (s, 21H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 137.1, 127.7, 127.5, 122.0, 119.6, 118.8, 110.2, 109.5, 95.9, 70.6, 52.0, 38.1, 32.8, 24.3, 18.8 (x6), 11.5 (x3) ppm.

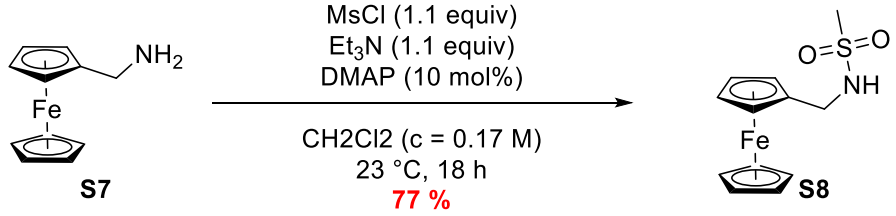
IR (neat): ν = 2941, 2864, 2166, 1464, 1360, 1326, 1164, 961, 883, 740, 677, 563, 515 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M]^+$ calcd. for $C_{23}H_{36}N_2O_2SSi$ 432.2261; found 432.2252.

R_f: 0.53 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain).

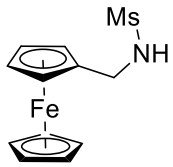
Synthesis of ferrocenyl-derivation mesyl-ynamide **S9**[6]

N-methylaminoferrocene was synthesized in accordance with the literature.[7]



To a degassed solution of **S7** (712.7 mg, 3.31 mmol, 1 equiv) in CH_2Cl_2 (20 mL) were added MsCl (0.28 mL, 3.65 mmol, 1.1 equiv), Et_3N (0.51 mL, 3.65 mmol, 1.1 equiv) and DMAP (40.5 mg, 0.33 mmol, 10 mol%). The solution was stirred at 23 °C for 18 h and hydrolyzed with water. The aqueous layer was extracted with CH_2Cl_2 (3x) and Et_2O (1x). The organic layers were washed with a saturated solution of NaCl, dried (Na_2SO_4), filtered and concentrated under vacuum. The crude material was purified by *flash* chromatography on 50 g of silica gel using a gradient of EtOAc in petroleum ether (0 to 70 %) to afford the title compounds.

***N*-ferrocenyl-methanesulfonamide (S8)**



$C_{12}H_{15}FeNO_2$
MW: 293.16 g.mol^{-1}
Orange solid
77 % (752 mg, 2.57 mmol)

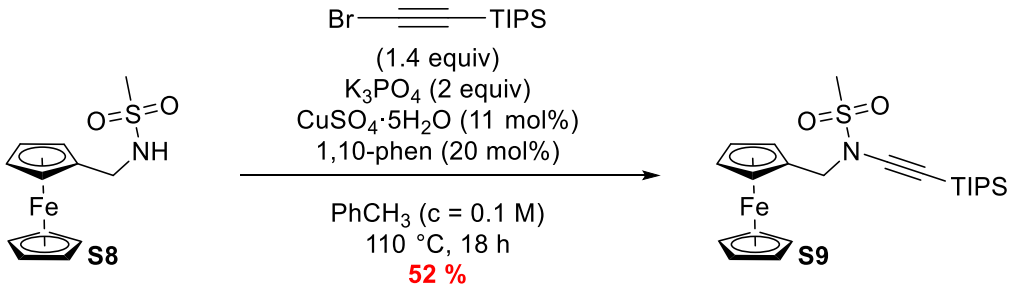
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.40 (s, 1H), 4.23 (t, *J* = 1.8 Hz, 2H), 4.20 – 4.16 (m, 7H), 4.05 (d, J = 5.7 Hz, 2H), 2.90 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 83.8, 68.79 (x5), 68.76 (x2), 68.4 (x2), 43.0, 41.3 ppm.

IR (neat): ν = 3268, 3101, 2935, 1441, 1410, 1307, 1145, 1057, 826, 484 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M]^+$ calcd. for $C_{12}H_{15}FeNO_2$ 293.0167; found 293.0174.

R_f: 0.29 (Petroleum ether/EtOAc 7:3 *v/v*, UV, ninhydrin stain).



In a Schlenk tube was introduced $CuSO_4 \cdot 5H_2O$ (23 mg, 0.09, 11 mol%), 1,10-phenanthroline (30 mg, 0.17 mmol, 20 mol%), K_3PO_4 (362 mg, 1.7 mmol, 2 equiv), the **S8** (250 mg, 0.85 mmol, 1 equiv), anhydrous toluene (10 mL) and the bromoacetylenic derivative (312 mg, 1.19 mmol,

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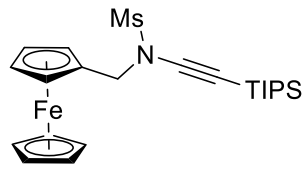
[6] C. Mahe, O. Blacque, G. Gasser, V. Gandon and K. Cariou, *Org. Lett.*, 2023, **25**, 624–629.
[7] Y. Wang, A. Rapakousiou, C. Latouche, J.-C. Daran, A. Singh, I. Ledoux-Rak, J. Ruiz, J.-Y. Saillard and D. Astruc, *Chem. Commun.*, 2013, **49**, 5862.

1.4 equiv). The reaction mixture was heated to 85 °C for 18 h and then cooled down to room temperature, filtrated through a pad of Celite® and profusely washed with EtOAc. The filtrate was then concentrated under vacuum. The crude material was purified by *flash* chromatography on 50 g of silica gel using a gradient of EtOAc in petroleum ether (0 to 20 %) to afford the title compounds.

***N*-ferrocenyl-*N*-((triisopropylsilyl)ethynyl)methanesulfonamide (S9)**



$C_{23}H_{35}FeNO_2SSi$
MW: 473.53 g.mol^{-1}
Orange solid
52 % (212 mg, 0.5 mmol)

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.45 (s, 2H), 4.34 (t, *J* = 1.9 Hz, 2H), 4.19 (d, *J* = 1.8 Hz, 2H), 4.17 (s, 5H), 2.82 (s, 3H), 1.06 (s, 21H) ppm.

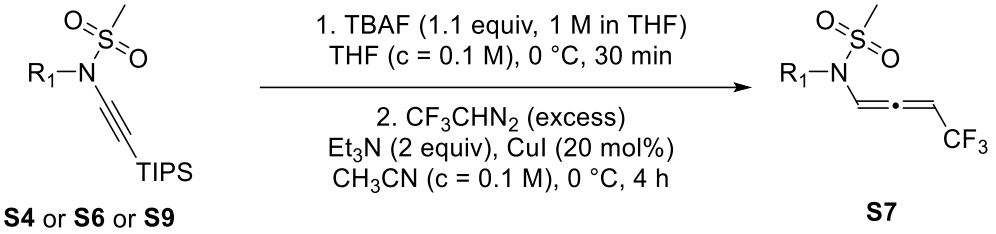
^{13}C NMR ($CDCl_3$, 126 MHz): δ = 96.6, 80.1, 70.5, 69.9 (x2), 69.2 (x2), 68.9 (x5), 52.8, 38.6, 18.8 (x6), 11.5 (x3) ppm.

IR (neat): ν = 2942, 2865, 2165, 1464, 1361, 1164, 1001, 883, 687 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M]^+$ calcd. for $C_{23}H_{35}FeNO_2SSi$ 473.1502; found 473.1507.

R_f: 0.49 (Petroleum ether/EtOAc 8:2 *v/v*, UV, ninhydrin stain).

Synthesis of trifluorinated-mesyl-*N*-allenamide **S7**



S4 or **S6** or **S9** → **S7**

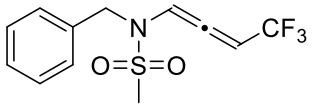
General procedure D:

To a solution of mesyl-ynamide **S4** or **S6** or **S9** (1 equiv) in THF (c = 0.1 M) was added dropwise at 0 °C a solution of TBAF (1.1 equiv, 1 M in THF). The mixture was stirred for 30 minutes at 0 °C and then hydrolyzed with water. The aqueous layer was extracted with Et_2O (3x). The organic layers were washed with a saturated solution of NaCl, dried (Na_2SO_4), filtered and concentrated under vacuum. The crude terminal mesyl-ynamide was used without further purification.[8]

Termial mesyl-ynamide (1 equiv) was dissolved in CH_3CN (c = 0.1 M) in the presence of CuI (20 mol%), and Et_3N (2 equiv). 1,1,1-trifluoro-diazoethane was added dropwise (in excess) and the reaction was stirred for 4 h at 0 °C. The mixture was concentrated under vacuum and the crude material was purified by *flash* chromatography treated with Et_3N using a step gradient of EtOAc in petroleum ether to afford the title compounds.[9]

1,1,1-trifluoro-diazoethane was synthesized according to the previous literature and stored in diethyl ether solution in the presence of Na_2SO_4 at -18 °C for a few weeks.[10]

***N*-benzyl-N-(4,4,4-trifluorobuta-1,2-dien-1-yl)methanesulfonamide (S7a)[11]**



$C_{12}H_{12}F_3NO_2S$
MW: 291.29 g.mol^{-1}
White solid
mp = 75 – 78 °C
91 % (747 mg, 2.23 mmol)

The product was obtained by column chromatography on silica gel using a step gradient of ethyl acetate in petroleum ether (0 to 30 %).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.56 – 7.13 (m, 6H), 5.85 (p, *J* = 5.6 Hz, 1H), 4.66 (d, *J* = 15.3 Hz, 1H), 4.41 (d, *J* = 15.3 Hz, 1H), 2.93 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 198.3 (q, *J* = 5.9 Hz), 134.7, 128.8, 128.2, 127.8, 121.1 (q, *J* = 271.7 Hz), 106.6, 96.8 (q, *J* = 39.4 Hz), 50.9, 39.6 ppm.

^{19}F NMR ($CDCl_3$, 282 MHz): δ = -62.59 ppm.

R_f: 0.46 (Petroleum ether/EtOAc 8:2 *v/v*, UV, ninhydrin stain)

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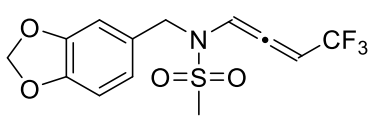
[8] Zhang, X.; Hsung, R. P.; Li, H.; Zhang, Y.; Johnson, W. L.; Figueroa, R. *Org. Lett*. **2008**, *10*, 3477.
[9] Zheng, Y.; Moegle, B.; Ghosh, S.; Perfetto, A.; Luise, D.; Ciofini, I.; Miesch, L. P. *Chem. Eur. J*. **2021**, doi :10.1002/chem.202103598
[10] Gilman, H.; Jones, R. G. *J. Am. Chem. Soc*. **1943**, *65*, 1458.
[11] Hourtoule, M.; Miesch, L. *Org. Lett*. **2022**, *24*, 3896.

<u>*N*-(benzo[*d*][1,3]dioxol-5-ylmethyl)-N-(4,4,4-trifluorobuta-1,2-dien-1-yl)methanesulfonamide (S7b)</u>



$C_{13}H_{12}F_3NO_4S$
MW: 335.30 g.mol^{-1}
White solid
mp = 75 – 78 °C
91 % (747 mg, 2.23 mmol)

The product was obtained by column chromatography on silica gel using a step gradient of ethyl acetate in petroleum ether (10 to 30 %).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.28 – 7.22 (m, 1H), 6.84 (s, 1H), 6.76 (d, *J* = 1.1 Hz, 2H), 5.96 (s, 2H), 5.90 (p, *J* = 5.6 Hz, 1H), 4.55 (d, *J* = 15.1 Hz, 1H), 4.32 (d, *J* = 15.1 Hz, 1H), 2.92 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 198.4 (q, J = 6.0 Hz), 148.2, 147.7, 128.4, 121.8, 121.3 (q, *J* = 271.7 Hz), 108.2 (x2), 106.5, 101.4, 96.9 (q, J = 39.3 Hz), 50.9, 39.8 ppm.

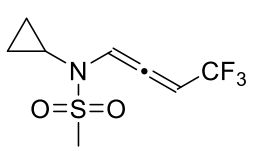
^{19}F NMR ($CDCl_3$, 282 MHz): δ -62.43 ppm.

IR (neat): ν = 3045, 2927, 2359, 2185, 2165, 1491, 1448, 1351, 1244, 1130, 931 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+K]^+$ calcd. for $C_{13}H_{12}KF_3NO_4S$ 374.0071; found 374.0054.

R_f: 0.43 (Petroleum ether/EtOAc 7:3 *v/v*, UV, vanillin stain)

<u>*N*-cyclopropyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)methanesulfonamide (S7c)</u>



$C_8H_{10}F_3NO_2S$
MW: 241.23 g.mol^{-1}
White solid
mp = 80 – 83 °C
46 % (352.9 mg, 1.46 mmol)

The product was obtained by column chromatography on silica gel using a step gradient of ethyl acetate in petroleum ether (0 to 30 %).

^{1}H NMR (C_6D_6, 300 MHz): δ = 6.94 (dq, *J* = 6.1, 3.1 Hz, 1H), 5.58 – 5.31 (m, 1H), 2.06 (s, 3H), 1.53 (tt, *J* = 6.9, 3.5 Hz, 1H), 1.01 – 0.72 (m, 1H), 0.72 – 0.58 (m, 1H), 0.42 – -0.02 (m, 2H).

^{13}C NMR (C_6D_6, 126 MHz): δ = 199.0 (q, *J* = 5.9 Hz), 121.9 (q, *J* = 271.2 Hz), 108.7, 94.6 (q, *J* = 39.0 Hz), 35.9, 28.6, 7.8, 7.4 ppm.

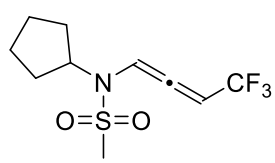
^{19}F NMR (C_6D_6, 282 MHz): δ = -62.06 ppm.

IR (neat): ν = 3052, 3014, 2929, 1431, 1339, 1270, 1160, 1120 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_8H_{11}F_3NO_2S$ 242.0475; found 242.0475.

R_f: 0.60 (Petroleum ether/EtOAc 7:3 *v/v*, UV, vanillin stain)

<u>*N*-cyclopentyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)methanesulfonamide(S7d)</u>



$C_{10}H_{14}F_3NO_2S$
MW: 269.28 g.mol^{-1}
Yellow oil
46 % (360 mg, 1.34 mmol)

The product was obtained by column chromatography on silica gel using a step gradient of ethyl acetate in petroleum ether (0 to 30 %).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.09 (dq, J = 6.1, 3.1 Hz, 1H), 5.92 (p, J = 5.6 Hz, 1H), 4.48 (p, J = 8.9 Hz, 1H), 2.99 (s, 3H), 1.93 – 1.79 (m, 4H), 1.78 – 1.68 (m, 2H), 1.65 – 1.56 (m, 2H) ppm.

^{13}C NMR ($CDCl_3$ 126 MHz): δ = 197.9 (q, *J* = 5.9 Hz), 121.73 (d, *J* = 265.1 Hz), 101.3, 94.7 (q, *J* = 39.1 Hz), 59.1, 40.1, 27.6, 26.6, 24.5 (x2) ppm.

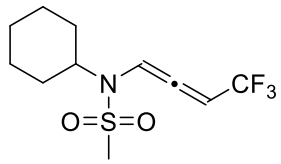
^{19}F NMR ($CDCl_3$, 282 MHz): δ = -62.13 ppm.

IR (neat): ν = 3038, 2959, 2877, 1454, 1350, 1127 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_{10}H_{15}F_3NO_2S$ 270.0770; found 270.0764.

R_f: 0.45 (Petroleum ether/EtOAc 7:3 *v/v*, UV, vanillin stain)

***N*-cyclohexyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)methanesulfonamide (S7e)**



$C_{11}H_{16}F_3NO_2S$
MW: 283.31 g.mol^{-1}
Colorless oil
38 % (135.5 mg, 0.48 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (2 to 40 %).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.05 (dq, *J* = 6.5, 3.3 Hz, 1H), 5.94 (p, *J* = 5.7 Hz, 1H), 3.91 – 3.80 (m, 1H), 3.00 (s, 3H), 1.93 – 1.74 (m, 7H), 1.66 – 1.61 (m, 1H), 1.41 – 1.24 (m, 2H).

^{13}C NMR ($CDCl_3$ 126 MHz): δ = 199.2 (q, *J* = 5.9 Hz), 121.7 (q, *J* = 266.1 Hz), 102.5, 94.7 (q, *J* = 39.2 Hz), 59.3, 41.1, 30.5, 29.8, 26.2, 26.1, 25.1 ppm.

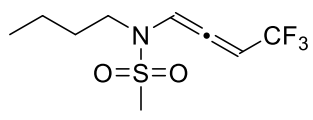
^{19}F NMR ($CDCl_3$, 471 MHz): δ = -61.98 ppm.

IR (neat): ν = 3034, 2937, 2860, 1453, 1355, 1268, 1127, 978, 519 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_{11}H_{17}F_3NO_2S$ 284.0853; found 284.0854.

R_f: 0.48 (Petroleum ether/EtOAc 8:2 *v/v*, UV, ninhydrin stain)

***N*-butyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)methanesulfonamide (S7f)**



$C_9H_{14}F_3NO_2S$
MW: 257.27 g.mol^{-1}
White solid
mp = 41 – 43 °C
55 % (428.3 mg, 1.66 mmol)

The product was obtained by *flash* chromatography on 50 g of silica gel using a gradient of ethyl acetate in petroleum ether (2 to 20 %).

^{1}H NMR (C_6D_6, 300 MHz): δ = 6.97 (dq, *J* = 6.3, 3.2 Hz, 1H), 5.48 (p, *J* = 5.6 Hz, 1H), 3.00 – 2.78 (m, 2H), 2.06 (s, 3H), 1.45 – 1.19 (m, 2H), 1.09 (dt, *J* = 8.2, 7.1 Hz, 2H), 0.76 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (C_6D_6, 126 MHz): δ = 198.1 (q, *J* = 5.9 Hz), 121.7 (q, *J* = 271.5 Hz), 106.7, 95.5 (q, *J* = 38.9 Hz), 46.8, 37.8, 29.3, 19.5, 13.2 ppm.

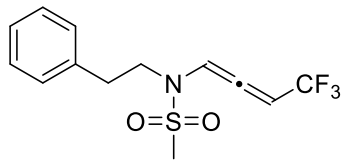
^{19}F NMR (C_6D_6, 282 MHz): δ = -62.19 ppm.

IR (neat): ν = 3045, 2964, 2937, 2876, 1977, 1436, 1350, 1265, 1122, 963, 922, 681, 511 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_9H_{15}F_3NO_2S$ 258.0770; found 258.0760.

R_f: 0.46 (Petroleum ether/EtOAc 8:2 *v/v*, UV, ninhydrin stain)

***N*-phenethyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)methanesulfonamide (S7g)**



$C_{13}H_{14}F_3NO_2S$
MW: 305.32 $g.mol^{-1}$
White solid
mp = 115 - 118 °C
59 % (477 mg, 1.56 mmol)

The product was obtained by column chromatography on silica gel using step a gradient of ethyl acetate in petroleum ether (0 to 20 %).

^{1}H NMR (C_6D_6, 300 MHz): δ = 7.14 – 7.02 (m, 2H), 7.06 – 6.96 (m, 3H), 6.94 (dt, *J* = 6.3, 3.2 Hz, 1H), 5.46 (p, *J* = 5.6 Hz, 1H), 3.26 – 3.03 (m, 2H), 2.64 (dd, *J* = 8.6, 7.1 Hz, 2H), 1.86 (s, 3H).

^{13}C NMR (C_6D_6, 126 MHz): δ = 198.3 (q, *J* = 5.9 Hz), 138.1, 129.2 (x2), 129.0 (x2), 127.1, 122.1 (q, *J* = 271.6 Hz), 106.9, 96.1 (q, *J* = 38.9 Hz), 49.1, 38.4, 34.3 ppm.

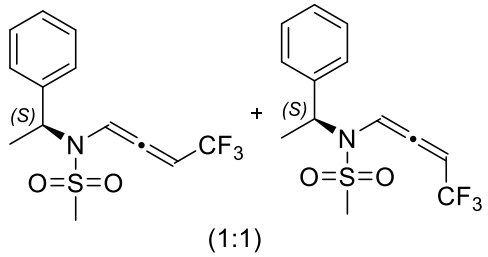
^{19}F NMR (C_6D_6, 282 MHz): δ = -62.02 ppm.

IR (neat): ν = 3049, 2923, 1433, 1336, 1125, 958, 742, 517 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_{13}H_{15}F_3NO_2S$ 306.0770; found 306.0771.

R_f: 0.46 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain)

***N*-((*S*)-1-phenylethyl)-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)methanesulfonamide (S7h)**



(1:1)

$C_{13}H_{14}F_3NO_2S$
MW: 305.32 $g.mol^{-1}$
Yellow oil
68 % (544.5 mg, 1.78 mmol)

The product was obtained by *flash* chromatography on 50 g silica gel using a gradient of ethyl acetate in petroleum ether (0 to 40 %). The mixture of the two diastereosomers cannot be isolated.

^{1}H NMR (C_6D_6, 500 MHz): δ = 7.28 – 7.25 (m, 2H), 7.22 – 7.19 (m, 2H), 7.18 – 7.14 (m, 2H), 7.14 – 7.08 (m, 4H), 6.81 (dqd, *J* = 6.0, 3.5, 0.9 Hz, 1H), 6.65 (dtd, *J* = 6.8, 3.7, 3.0 Hz, 1H),

5.37 (p, *J* = 5.7 Hz, 1H), 5.20 (q, *J* = 7.1 Hz, 2H), 5.15 (q, *J* = 5.9 Hz, 1H), 2.18 (s, 3H), 2.11 (s, 3H), 1.36 (d, *J* = 7.1 Hz, 3H), 1.27 (d, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (C_6D_6, 126 MHz): δ = 199.2 (q, *J* = 6.1 Hz), 198.8 (q, *J* = 6.1 Hz), 138.6, 138.4, 128.8, 128.7, 127.7, 127.5, 122.3 (d, *J* = 271.5 Hz), 122.1 (q, *J* = 271.5 Hz), 102.4, 102.3, 94.3 (q, *J* = 39.0 Hz), 94.3 (q, *J* = 38.7 Hz), 56.6, 56.3, 40.0, 40.0, 17.1, 15.9 ppm.

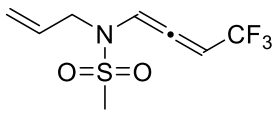
^{19}F NMR (C_6D_6, 471 MHz): δ = -61.97, -62.22 ppm.

IR (neat): ν = 3032, 2955, 2964, 1449, 1349, 1121, 961, 519 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{13}H_{14}F_3NNaO_2S$ 328.0590; found 328.0592.

R_f: 0.55 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain)

***N*-allyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)methanesulfonamide (S7i)**



$C_8H_{10}F_3NO_2S$
MW: 241.23 g.mol^{-1}
Yellow solid
mp = 47 – 49 °C
42 % (481.3 mg, 2.00 mmol)

The product was obtained by column chromatography on silica gel using step a gradient of ethyl acetate in petroleum ether (0 to 20 %).

^{1}H NMR (C_6D_6, 300 MHz): δ = 6.93 (dq, *J* = 6.3, 3.2 Hz, 1H), 5.48 – 5.32 (m, 2H), 4.99 – 4.85 (m, 2H), 3.54 – 3.46 (m, 2H), 2.02 (s, 3H) ppm.

^{13}C NMR (C_6D_6, 126 MHz): δ = 198.6 (q, *J* = 6.0 Hz), 131.1, 122.0 (q, *J* = 271.5 Hz), 119.1, 106.7, 96.1 (q, *J* = 39.0 Hz), 49.4, 39.2 ppm.

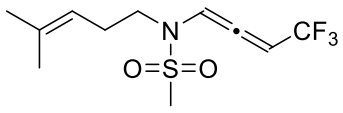
^{19}F NMR (C_6D_6, 282 MHz): δ = -62.16 ppm.

IR (neat): ν = 3047, 2959, 2922, 2875, 2337, 1449, 1351, 1264, 1123, 515 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_8H_{11}F_3NO_2S$ 242.0457; found 242.0458.

R_f: 0.39 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain)

***N*-(4-methylpent-3-en-1-yl)-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)methanesulfonamide (S7j)**



$C_{11}H_{16}F_3NO_2S$
MW: 283.31 g.mol^{-1}
White solid
mp = 89 – 91 °C
29 % (207.4 mg, 0.73 mmol)

The product was obtained by column chromatography on silica gel using step a gradient of ethyl acetate in petroleum ether (0 to 20 %).

^{1}H NMR (C_6D_6, 500 MHz): δ = 6.97 (dq, J = 6.3, 3.2 Hz, 1H), 5.50 (p, *J* = 5.6 Hz, 1H), 5.00 – 4.92 (m, 1H), 2.96 (d, *J* = 8.0 Hz, 2H), 2.19 – 2.11 (m, 2H), 2.03 (s, 3H), 1.56 (s, 3H), 1.48 (s, 3H) ppm.

^{13}C NMR (C_6D_6, 126 MHz): δ = 198.3 (q, *J* = 5.9 Hz), 135.1, 122.1 (q, *J* = 271.5 Hz), 119.8, 107.1, 96.0 (q, J = 38.9 Hz), 47.2, 38.3, 26.9, 25.7, 17.7 ppm.

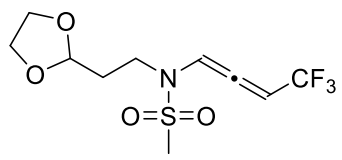
^{19}F NMR (C_6D_6, 282 MHz): δ = -62.10 ppm.

IR (neat): ν = 3050, 2969, 2828, 2869, 1547, 1453, 1433, 1332, 1254, 1123, 953, 515 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{11}H_{16}F_3NNaO_2S$ 306.0746; found 306.0739.

R_f: 0.75 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain)

***N*-(2-(1,3-dioxolan-2-yl)ethyl)-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)methanesulfonamide (S7k)**



$C_{10}H_{14}F_3NO_4S$
MW: 301.28 $g.mol^{-1}$
White solid
mp = 121 – 123 °C
77 % (159.3 mg, 0.53 mmol)

The product was obtained by column chromatography on silica gel using step a gradient of ethyl acetate in petroleum ether (0 to 30 %).

^{1}H NMR (C_6D_6, 500 MHz): δ = 7.25 – 7.22 (m, 1H), 6.06 (p, J = 5.6 Hz, 1H), 4.92 (t, J = 4.4 Hz, 1H), 4.01 – 3.82 (m, 4H), 3.56 – 3.42 (m, 2H), 2.99 (s, 3H), 2.06 – 1.92 (m, 2H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 197.8 (q, *J* = 5.8 Hz), 121.4 (q, *J* = 271.8 Hz), 106.5, 102.0, 96.9 (q, *J* = 39.3 Hz), 65.2, 65.2, 42.6, 39.3, 31.9 ppm.

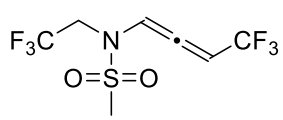
^{19}F NMR ($CDCl_3$, 471 MHz): δ = -62.25 ppm.

IR (neat): ν = 2956, 2915, 1462, 1334, 1125, 965 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_{10}H_{15}F_3NO_4S$ 302.0668; found 302.0652.

R_f: 0.41 (Petroleum ether/EtOAc 7:3 *v/v*, UV, vanillin stain)

***N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)-*N*-(2,2,2-trifluoroethyl)methanesulfonamide (S7l)**



$C_7H_7F_6NO_2S$
MW: 283.19 $g.mol^{-1}$
White solid
mp = 64 – 66 °C
84 % (119.3 mg, 0.42 mmol)

The product was obtained by *flash* chromatography on 10 g of silica gel using a gradient of ethyl acetate in petroleum ether (0 to 40 %).

^{1}H NMR (C_6D_6, 400 MHz): δ = 6.66 (dq, *J* = 6.0, 3.0 Hz, 1H), 5.42 (p, *J* = 5.7 Hz, 1H), 3.48 – 3.33 (m, 1H), 3.30 – 3.13 (m, 1H), 2.02 (s, 3H) ppm.

^{13}C NMR (C_6D_6, 126 MHz): δ = 197.5 (q, *J* = 5.9 Hz), 124.0 (q, *J* = 280.9 Hz), 121.7 (q, *J* = 271.7 Hz), 106.7, 97.4 (q, *J* = 39.3 Hz), 47.5 (q, *J* = 35.6 Hz), 39.5 (d, *J* = 1.5 Hz) ppm.

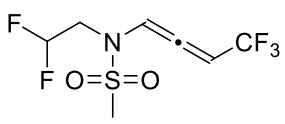
^{19}F NMR (C_6D_6, 282 MHz): δ = -62.37 (q, *J* = 1.6 Hz), -69.45 (q, *J* = 1.7 Hz) ppm.

IR (neat): ν = 2961, 2921, 2852, 1449, 1359, 1272, 1104, 1008, 968, 912, 816, 495 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_7H_7F_6NaNO_2S$ 305.9998; found 306.0000.

R_f: 0.36 (Petroleum ether/EtOAc 8:2 *v/v*, UV, $KMnO_4$ stain).

***N*-(2,2-difluoroethyl)-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)methanesulfonamide (S7m)**



$C_7H_8F_5NO_2S$
MW: 265.20 g.mol^{-1}
White solid
mp = 72 – 74 °C
76 % (455.5 mg, 1.72 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (5 to 40 %).

^{1}H NMR (C_6D_6, 500 MHz): δ = 6.77 (dq, *J* = 6.1, 3.1 Hz, 1H), 5.51 – 5.19 (m, 2H), 3.22 – 2.98 (m, 2H), 2.03 (s, 3H) ppm.

^{13}C NMR (C_6D_6, 126 MHz): δ = 197.7 (q, *J* = 5.9 Hz), 121.8 (q, *J* = 271.7 Hz), 113.5 (t, *J* = 243.9 Hz), 107.2, 97.2 (q, *J* = 39.2 Hz), 48.5 (t, *J* = 28.0 Hz), 38.8 (t, *J* = 1.7 Hz) ppm.

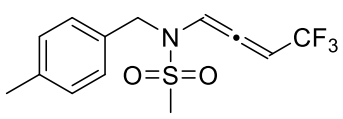
^{19}F NMR (C_6D_6, 282 MHz): δ = -62.17 (d, *J* = 1.9 Hz), -120.66 (d, *J* = 5.6 Hz) ppm.

IR (neat): ν = 3027, 1451, 1344, 1128, 1006, 872, 796, 523 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_7H_8F_5NaNO_2S$ 288.0100; found 288.0096.

R_f: 0.33 (Petroleum ether/EtOAc 8:2 *v/v*, UV, $KMnO_4$ stain).

***N*-(4-methylbenzyl)-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)methanesulfonamide (S7n)**



$C_{13}H_{14}F_3NO_2S$
MW: 305.32 g.mol^{-1}
White solid
mp = 65 – 67 °C
82 % (331.4 mg, 1.09 mmol)

The product was obtained by *flash* chromatography on 10 g of silica gel using a gradient of ethyl acetate in petroleum ether (0 to 40 %).

^{1}H NMR (C_6D_6, 300 MHz): δ = 7.22 – 7.18 (m, 2H), 7.06 – 7.00 (m, 1H), 7.00 – 6.94 (m, 2H), 5.38 (p, *J* = 5.7 Hz, 1H), 4.25 (d, *J* = 15.3 Hz, 1H), 3.99 (d, *J* = 15.3 Hz, 1H), 2.11 (s, 3H), 2.07 (s, 3H) ppm.

^{13}C NMR (C_6D_6, 126 MHz): δ = 198.5 (q, *J* = 6.1 Hz), 137.6 (x2), 132.1 (x2), 129.3, 127.8, 121.7 (q, *J* = 271.5 Hz), 106.7, 95.9 (q, *J* = 38.9 Hz), 50.4, 38.3, 20.7 ppm.

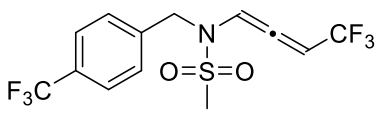
^{19}F NMR (C_6D_6, 282 MHz): δ = -62.36 ppm.

IR (neat): ν = 3029, 2931, 1453, 1266, 1129, 915, 515 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+K]^+$ calcd. for $C_{13}H_{14}F_3KNO_2S$ 344.0329; found 344.0335.

R_f: 0.45 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain).

***N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)-*N*-(4-(trifluoromethyl)benzyl)methanesulfonamide (S7o)**



$C_{13}H_{11}F_6NO_2S$
MW: 359.29 g.mol^{-1}
White solid
mp = 70-72 °C

75 % (156.0 mg, 0.43 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (0 to 40 %).

^{1}H NMR (C_6D_6, 300 MHz): δ = 7.27 (d, *J* = 8.1 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.89 – 6.83 (m, 1H), 5.13 (p, *J* = 5.6 Hz, 1H), 3.98 (d, *J* = 15.8 Hz, 1H), 3.75 (d, *J* = 15.7 Hz, 1H), 1.96 (s, 3H) ppm.

^{13}C NMR (C_6D_6, 126 MHz): δ = 199.1 (q, *J* = 6.0 Hz), 140.2 (d, *J* = 1.5 Hz), 131.1 (q, J = 32.4 Hz), 128.7, 126.6 (q, *J* = 3.8 Hz) (x2), 123.3 (d, *J* = 272.0 Hz), 122.5 (q, *J* = 271.6 Hz), 107.4 (x2), 97.3 (q, *J* = 39.0 Hz), 50.9, 39.1 ppm.

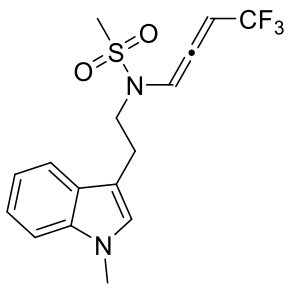
^{19}F NMR (C_6D_6, 282 MHz): δ = -62.35, -62.59 ppm.

IR (neat): ν = 3049, 1451, 1356, 1326, 1268, 1163, 1126, 1067, 924 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{13}H_{11}F_6NaNO_2S$ 382.0307; found 382.0301.

R_f: 0.18 (Petroleum ether/EtOAc 8:2 *v/v*, UV, ninhydrin stain).

***N*-(2-(1-methyl-1H-indol-3-yl)ethyl)-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)methanesulfonamide (S7p)**



$C_{16}H_{17}F_3N_2O_2S$
MW: 358.38 g.mol^{-1}
Orange oil
44 % (69.1 mg, 0.19 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (0 to 40 %).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.59 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.32 – 7.28 (m, 2H), 7.22 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.13 (ddd, *J* = 8.0, 6.8, 1.3 Hz, 1H), 6.89 (s, 1H), 6.02 (p, *J* = 5.6 Hz, 1H), 3.75 (s, 3H), 3.70 – 3.49 (m, 2H), 3.08 (t, *J* = 7.9 Hz, 2H), 2.83 (s, 3H) ppm.

^{13}C NMR (C_6D_6, 126 MHz): δ = 198.1 (q, *J* = 5.9 Hz), 137.1, 127.7, 127.2, 122.7 (q, *J* = 285.8 Hz), 122.0, 119.3, 118.9, 110.4, 109.5, 106.7, 96.7 (q, J = 39.3 Hz), 48.6, 39.4, 32.8, 24.1 ppm.

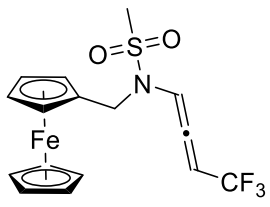
^{19}F NMR ($CDCl_3$, 282 MHz): δ = -61.97 ppm.

IR (neat): ν = 3043, 2927, 2852, 1457, 1352, 1267, 1156, 1130, 956, 743 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+K]^+$ calcd. for $C_{16}H_{17}F_3KN_2O_2S$ 397.0594; found 397.0599.

R_f: 0.38 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain).

***N*-ferrocenyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)methanesulfonamide (S7q)**



$C_{16}H_{16}F_3FeNO_2S$
MW: 399.21 g.mol^{-1}
Yellow solid
73 % (81.9 mg, 0.20 mmol)

The product was obtained by *flash* chromatography on 50 g of silica gel using a gradient of ethyl acetate in petroleum ether (0 to 20 %).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.90 (dq, *J* = 6.5, 3.2 Hz, 1H), 5.54 (p, *J* = 5.7 Hz, 1H), 4.22 (dt, *J* = 2.6, 1.3 Hz, 1H), 4.19 – 4.02 (m, 3H), 3.94 – 3.81 (m, 7H), 1.97 (s, 3H) ppm.

^{13}C NMR (C_6D_6, 126 MHz): δ = 198.4 (q, *J* = 6.0 Hz), 122.2 (q, *J* = 271.5 Hz), 107.3, 96.2 (q, *J* = 38.9 Hz), 80.8, 70.2, 69.9, 69.2, 69.1 (x5), 68.8, 47.3, 39.9 ppm.

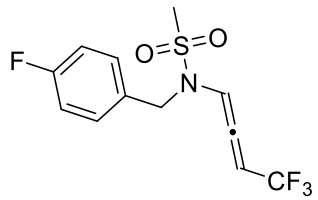
^{19}F NMR (C_6D_6, 282 MHz): δ = -61.89 ppm.

IR (neat): ν = 3100, 3012, 2929, 2358, 2343, 1449, 1354, 1267, 1159, 1129, 1011, 900 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M]^+$ calcd. for $C_{16}H_{16}F_3FeNO_2S$ 399.0498; found 399.0209.

R_f: 0.27 (Petroleum ether/EtOAc 9:1 *v/v*, UV, ninhydrin stain).

***N*-(4-fluorobenzyl)-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)methanesulfonamide (S7r)**



$C_{12}H_{11}F_4NO_2S$
MW: 309.28 $g.mol^{-1}$
Yellow oil
77 % (463.8 mg, 1.50 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (0 to 40 %).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.34 – 7.27 (m, 3H), 7.12 – 6.98 (m, 2H), 5.86 (p, *J* = 5.6 Hz, 1H), 4.60 (d, *J* = 15.2 Hz, 1H), 4.39 (d, *J* = 15.2 Hz, 1H), 2.95 (s, 3H).

^{13}C NMR (C_6D_6, 126 MHz): δ = 198.4 (q, J = 5.9 Hz), 162.7 (d, J = 247.0 Hz), 130.5 (d, J = 3.2 Hz), 129.7 (d, J = 8.3 Hz) (x2), 121.2 (d, J = 271.5 Hz), 115.9 (d, J = 21.7 Hz) (2), 106.5, 97.0 (q, J = 39.4 Hz), 50.4, 39.7 ppm.

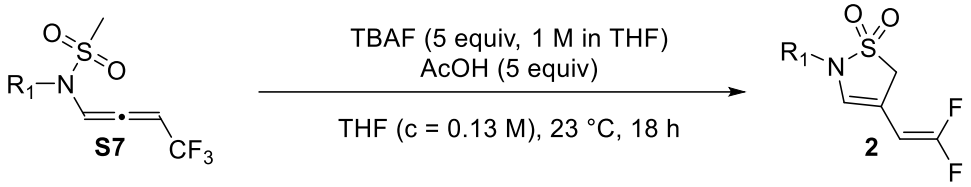
^{19}F NMR ($CDCl_3$, 282 MHz): δ = -62.53, -113.80 ppm.

IR (neat): ν = 2928, 1605, 1510, 1452, 1432, 1350, 1265, 1223, 1158, 1124, 1043, 913, 824, 775, 756, 732, 681, 531, 514 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_{12}H_{12}F_4NO_2S$ 310.0519; found 310.0491.

R_f: 0.52 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain).

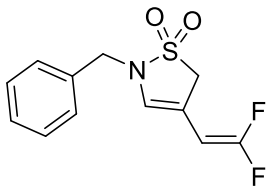
Synthesis of *gem*-difluorinated-sultams **2**



General procedure E:

To a solution of trifluorinated-*N*-allenamide **S7** (1 equiv) in THF (c = 0.13 M) was added dropwise a solution of TBAF (5 equiv, 1 M in THF) and glacial acetic acid (5 equiv). The mixture was stirred at 23 °C during 18 h and then hydrolyzed with a saturated solution of $NaHCO_3$. The aqueous layer was extracted with ethyl acetate (3x). The organic layers were washed with a saturated solution of NaCl, dried (Na_2SO_4), filtered and concentrated under vacuum. The crude material was purified by *flash* chromatography using a gradient of EtOAc in petroleum ether to afford the title compounds.

2-benzyl-4-(2,2-difluorovinyl)-2,5-dihydroisothiazole 1,1-dioxide (2a)



$C_{12}H_{11}F_2NO_2S$
MW: 271.28 g.mol^{-1}
Colorless oil
69 % (47.7 mg, 0.18 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (5 to 40 %).

^{1}H NMR (C_6D_6, 300 MHz): δ = 7.10 – 7.01 (m, 5H), 5.28 (dd, *J* = 1.7, 0.9 Hz, 1H), 4.03 (s, 2H), 3.96 (ddd, *J* = 26.1, 2.7, 0.7 Hz, 1H), 3.31 (dt, *J* = 1.8, 0.9 Hz, 2H) ppm.

^{13}C NMR (C_6D_6, 126 MHz): δ = 155.1 (dd, *J* = 295.5, 286.9 Hz), 135.5, 128.6 (x2), 128.3 (x2), 128.0, 128.0, 100.6 (t, J = 5.6 Hz), 77.1 (dd, J = 32.7, 15.0 Hz), 51.4 (d, J = 5.0 Hz), 46.6 ppm.

^{19}F NMR (C_6D_6, 282 MHz): δ = -86.38 (d, *J* = 39.6 Hz), -88.95 (d, *J* = 39.6 Hz) ppm.

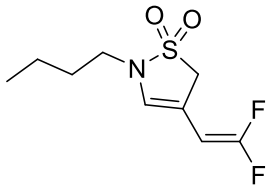
IR (neat): ν = 3033, 2932, 1809, 1732, 1616, 1455, 1324, 1206, 1142, 932, 698, 483 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{12}H_{11}F_2NNaO_2S$ 294.0371; found 294.0371.

R_f: 0.40 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain)

R_f: 0.40 (Petroleum ether/EtOAc 9:1 *v/v*, UV, vanillin stain)

2-butyl-4-(2,2-difluorovinyl)-2,5-dihydroisothiazole 1,1-dioxide (2b)



$C_9H_{13}F_2NO_2S$
MW: 237.29 g.mol^{-1}
Yellow oil
62 % (36.7 mg, 0.15 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (2 to 20 %).

^{1}H NMR (C_6D_6, 500 MHz): δ = 5.30 (dt, *J* = 1.8, 0.9 Hz, 1H), 4.23 (ddd, *J* = 26.0, 2.6, 0.8 Hz, 1H), 3.32 (dq, *J* = 1.8, 0.9 Hz, 2H), 2.90 (t, *J* = 7.3 Hz, 2H), 1.38 – 1.23 (m, 2H), 1.17 – 1.02 (m, 2H), 0.73 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (C_6D_6, 126 MHz): δ = 155.5 (dd, *J* = 295.3, 286.7 Hz), 123.0 (dd, *J* = 9.8, 4.7 Hz), 100.2 (t, *J* = 5.5 Hz), 77.6 (dd, *J* = 32.5, 15.3 Hz), 51.9 (d, *J* = 4.8 Hz), 43.7, 31.2, 19.9, 13.6 ppm.

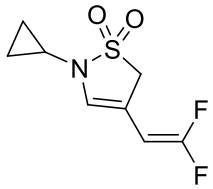
^{19}F NMR (C_6D_6, 282 MHz): δ = -86.64 (d, *J* = 40.3 Hz), -89.21 (d, *J* = 40.3 Hz) ppm.

IR (neat): ν = 3088, 2962, 2936, 2877, 1737, 1620, 1302, 1196, 1133, 694 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+K]^+$ calcd. for $C_9H_{13}F_2NKNO_2S$ 276.0267; found 276.0248.

R_f: 0.68 (Petroleum ether/EtOAc 8:2 *v/v*, UV, ninhydrin stain)

2-cyclopropyl-4-(2,2-difluorovinyl)-2,5-dihydroisothiazole 1,1-dioxide (2c)



$C_8H_9F_2NO_2S$
MW: 221.22 $g.mol^{-1}$
Yellow oil
70 % (39.4 mg, 0.18 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (5 to 40 %).

^{1}H NMR (C_6D_6, 300 MHz): δ = 5.35 (tq, *J* = 1.8, 0.9 Hz, 1H), 4.15 (ddq, *J* = 26.0, 2.7, 0.7 Hz, 1H), 3.30 (tt, *J* = 1.7, 0.8 Hz, 2H), 2.21 (tt, *J* = 6.7, 3.4 Hz, 1H), 0.66 – 0.57 (m, 2H), 0.29 – 0.19 (m, 2H) ppm.

^{13}C NMR (C_6D_6, 126 MHz): δ = 155.7 (dd, *J* = 295.6, 287.1 Hz), 131.4 (dd, *J* = 9.8, 4.7 Hz), 100.9 (t, *J* = 5.6 Hz), 77.4 (dd, *J* = 32.5, 15.1 Hz), 52.4, 52.4, 25.0, 5.4 ppm.

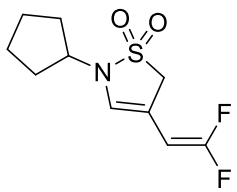
^{19}F NMR (C_6D_6, 282 MHz): δ = -86.23 (d, *J* = 39.0 Hz), -88.50 (d, *J* = 39.0 Hz) ppm.

IR (neat): ν = 3091, 3018, 2937, 1809, 1731, 1618, 1325, 1209, 1142 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_8H_{10}F_2NO_4S$ 222.0400; found 222.0402.

R_f: 0.50 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain)

2-cyclopentyl-4-(2,2-difluorovinyl)-2,5-dihydroisothiazole 1,1-dioxide (2d)



$C_{10}H_{13}F_2NO_2S$
MW: 249.28 $g.mol^{-1}$
Yellow oil
45 % (28.0 mg, 0.11 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (5 to 40 %).

^{1}H NMR (C_6D_6, 300 MHz): δ = 5.51 (tt, *J* = 1.8, 0.9 Hz, 1H), 4.24 – 4.08 (m, 2H), 3.78 – 3.62 (m, 1H), 3.31 (tt, *J* = 1.8, 0.8 Hz, 2H), 1.95 – 1.59 (m, 2H), 1.50 – 1.26 (m, 4H), 1.27 – 1.04 (m, 1H) ppm.

^{13}C NMR (C_6D_6, 126 MHz): δ = 154.3 (dd, *J* = 295.4, 286.6 Hz), 99.5 (t, *J* = 5.7 Hz), 76.5 (dd, J = 32.5, 15.2 Hz), 54.5, 51.1 (d, *J* = 4.8 Hz), 30.3 (x2), 22.5 (x2), 0.2 ppm.

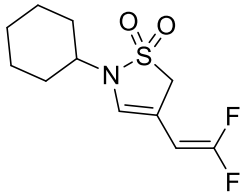
^{19}F NMR (C_6D_6, 282 MHz): δ = -86.60 (d, *J* = 40.2 Hz), -89.26 (d, *J* = 40.2 Hz) ppm.

IR (neat): 2964, 2878, 1732, 1616, 1325, 1210, 1142 cm^{-1}.

ESI-HRMS: calcd. for $C_{10}H_{13}F_2KNO_2S$ $[M+K]^+$: 288.0267, found 288.0282.

R_f: 0.43 (Petroleum ether/EtOAc 8.5:1.5 *v/v*, UV, vanillin stain)

2-cyclohexyl-4-(2,2-difluorovinyl)-2,5-dihydroisothiazole 1,1-dioxide (2e)



$C_{11}H_{15}F_2NO_2S$
MW: 263.30 g.mol^{-1}
Orange oil
30 % (22.4 mg, 0.08 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (2 to 20 %).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 6.34 (s, 1H), 4.95 (dd, *J* = 25.8, 2.0 Hz, 1H), 3.99 (s, 2H), 3.56 (tt, *J* = 11.6, 3.8 Hz, 1H), 2.02 (d, *J* = 12.5 Hz, 2H), 1.83 (d, *J* = 13.4 Hz, 2H), 1.74 – 1.62 (m, 1H), 1.49 – 1.30 (m, 5H) ppm.

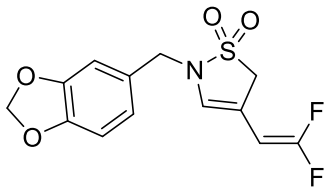
^{13}C NMR ($CDCl_3$, 126 MHz): δ = 155.5 (dd, *J* = 296.5, 292.8 Hz), 126.4 (dd, *J* = 10.0, 4.5 Hz), 100.1 (t, *J* = 5.5 Hz), 77.5 (dd, *J* = 32.6, 15.8 Hz), 53.9, 52.6 (d, *J* = 5.2 Hz), 32.8 (x2), 25.6 (x2), 25.2 ppm.

^{19}F NMR ($CDCl_3$, 471 MHz): δ = -86.16 (d, *J* = 39.6 Hz), -88.00 (d, *J* = 40.2 Hz) ppm.

IR (neat): ν = 2936, 2859, 1732, 1614, 1324, 1200, 1142, 1040, 942 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_{11}H_{16}F_2NO_4S$ 264.0870; found 264.0868.

2-(benzo[*d*][1,3]dioxol-5-ylmethyl)-4-(2,2-difluorovinyl)-2,5-dihydroisothiazole 1,1-dioxide (2f)



$C_{13}H_{11}F_2NO_4S$
MW: 315.29 g.mol^{-1}
Colorless oil
57 % (45.7 mg, 0.14 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (7 to 60 %).

^{1}H NMR (C6D6, 500 MHz): δ = 6.74 (d, *J* = 1.8 Hz, 1H), 6.55 (d, *J* = 7.9 Hz, 1H), 6.49 – 6.43 (m, 1H), 5.37 (dt, *J* = 1.9, 1.0 Hz, 1H), 5.26 (s, 2H), 4.04 (ddd, *J* = 26.1, 2.7, 0.8 Hz, 1H), 3.96 (s, 2H), 3.33 – 3.31 (m, 2H) ppm.

^{13}C NMR (C_6D_6, 126 MHz): δ = 155.2 (dd, *J* = 295.4, 287.0 Hz), 148.3, 147.8, 129.2, 128.6 (dd, *J* = 9.9, 4.6 Hz), 122.0, 108.8, 108.1, 100.9, 100.5 (t, *J* = 5.6 Hz), 77.2 (dd, J = 32.7, 15.1 Hz), 51.6 (d, *J* = 5.0 Hz), 46.5 ppm.

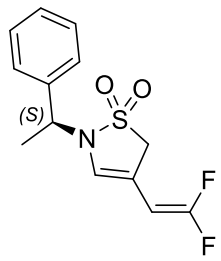
^{19}F NMR (C_6D_6, 282 MHz): δ = -86.40 (d, *J* = 39.8 Hz), -88.96 (d, *J* = 39.7 Hz) ppm.

IR (neat): ν = 3080, 2905, 1732, 1617, 1504, 1491, 1446, 1323, 1244, 1171, 1037, 927 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+K]^+$ calcd. for $C_{13}H_{11}F_2KNO_4S$ 354.0008; found 353.9997.

R_f: 0.47 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain)

(*S*)-4-(2,2-difluorovinyl)-2-(1-phenylethyl)-2,5-dihydroisothiazole 1,1-dioxide (2g)



$C_{13}H_{13}F_2NO_2S$
MW: 285.31 g.mol^{-1}
Yellow oil
34 % (23.6 mg, 0.08 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (2 to 20 %).

^{1}H NMR (C_6D_6, 300 MHz): δ = 6.93 – 6.78 (m, 5H), 5.26 – 5.17 (m, 1H), 4.51 (q, *J* = 6.9 Hz, 1H), 3.69 (dd, *J* = 26.4, 3.0 Hz, 1H), 3.13 (dt, *J* = 1.9, 0.9 Hz, 2H), 1.21 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (C_6D_6, 126 MHz): δ = 155.0 (dd, J = 295.3, 286.6 Hz), 140.5, 128.6 (x2), 127.8, 127.1 (dd, J = 10.0, 4.4 Hz), 127.0 (x2), 100.0 (t, J = 5.6 Hz), 77.2 (dd, J = 32.7, 15.0 Hz), 53.3, 52.2 (d, J = 5.0 Hz), 19.5 ppm.

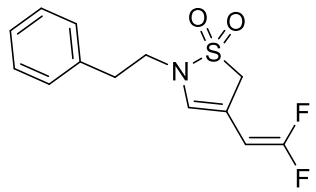
^{19}F NMR (C_6D_6, 282 MHz): δ = -86.88 (d, *J* = 40.4 Hz), -89.47 (d, *J* = 40.4 Hz).

IR (neat): ν = 3091, 2984, 2936, 1810, 1731, 1615, 1322, 1208, 1731, 1615, 1322, 1208, 1180, 1140, 940, 678 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_{13}H_{14}F_2NO_2S$ 286.0708; found 286.0701.

R_f: 0.60 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain)

4-(2,2-difluorovinyl)-2-phenethyl-2,5-dihydroisothiazole 1,1-dioxide (2h)



$C_{13}H_{13}F_2NO_2S$
MW: 285.31 g.mol^{-1}
Colorless oil
41 % (29.0 mg, 0.10 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (2 to 20 %).

^{1}H NMR (C_6D_6, 300 MHz): δ = 7.14 – 6.92 (m, 5H), 5.07 – 5.00 (m, 1H), 4.04 (ddd, *J* = 26.0, 2.7, 0.8 Hz, 1H), 3.27 – 3.23 (m, 2H), 3.17 (t, *J* = 7.2 Hz, 2H), 2.67 (t, *J* = 7.2 Hz, 2H) ppm.

^{13}C NMR (C_6D_6, 126 MHz): δ = 155.4 (dd, *J* = 295.3, 286.8 Hz), 138.5, 130.2 (dd, *J* = 9.8, 4.7 Hz), 129.2 (x2), 128.8 (x2), 127.0, 99.9 (t, J = 5.6 Hz), 77.4 (dd, *J* = 32.6, 15.2 Hz), 51.9 (d, J = 4.9 Hz), 45.7, 36.0 ppm.

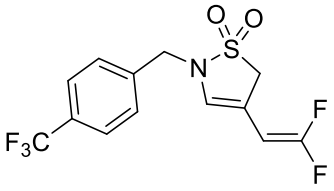
^{19}F NMR (C_6D_6, 282 MHz): δ = -86.59 (d, J = 40.0 Hz), -89.13 (d, J = 40.0 Hz) ppm.

IR (neat): ν = 3080, 2977, 2930, 2360, 1731, 1616, 1298, 1185, 1133, 695, 500 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_{13}H_{14}F_2NO_2S$ 286.0708; found 286.0701.

R_f: 0.73 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain)

4-(2,2-difluorovinyl)-2-(4-(trifluoromethyl)benzyl)-2,5-dihydroisothiazole 1,1-dioxide (2i)



$C_{13}H_{10}F_5NO_2S$
MW: 339.28 g.mol^{-1}
Colorless oil
36 % (30.2 mg, 0.09 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (0 to 40 %).

^{1}H NMR (C_6D_6, 300 MHz): δ = 7.27 (d, *J* = 8.0 Hz, 2H), 6.92 – 6.87 (m, 2H), 5.11 (tq, *J* = 1.8, 1.0 Hz, 1H), 4.03 (ddq, *J* = 25.9, 2.6, 0.7 Hz, 1H), 3.87 (s, 2H), 3.28 (tt, *J* = 1.7, 0.8 Hz, 2H) ppm.

^{13}C NMR (C_6D_6, 126 MHz): δ = 155.2 (dd, *J* = 295.8, 287.7 Hz), 139.5 (q, *J* = 1.4 Hz), 130.1 (q, *J* = 32.4 Hz), 129.1 (d, *J* = 40.6 Hz), 128.3 (dd, *J* = 9.9, 4.7 Hz), 128.3 (x2), 125.4 (q, *J* = 3.8 Hz) (x2), 122.2 (d, *J* = 272.0 Hz), 101.1 (t, *J* = 5.7 Hz), 51.3 (d, *J* = 5.0 Hz), 46.1 ppm.

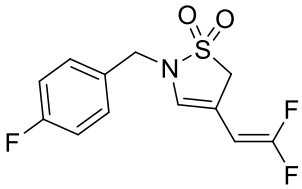
^{19}F NMR (C_6D_6, 282 MHz): δ = -62.33, -85.66 (d, *J* = 37.8 Hz), -88.20 (d, *J* = 37.8 Hz) ppm.

IR (neat): ν = 2961, 1811, 1733, 1620, 1421, 1323, 1208, 1164, 1114, 1067 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{13}H_{10}F_5NNaO_2S$ 362.0245; found 362.0239.

R_f: 0.40 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain).

4-(2,2-difluorovinyl)-2-(4-fluorobenzyl)-2,5-dihydroisothiazole 1,1-dioxide (2j)



$C_{12}H_{10}F_2NO_2S$
MW: 289.27 g.mol^{-1}
Colorless oil
37 % (27 mg, 0.09 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (0 to 40 %).

^{1}H NMR (C_6D_6, 300 MHz): δ = 6.90 – 6.78 (m, 2H), 6.78 – 6.65 (m, 2H), 5.21 (tq, *J* = 1.8, 0.9 Hz, 1H), 4.01 (ddq, *J* = 26.0, 2.6, 0.7 Hz, 1H), 3.89 (s, 2H), 3.29 (tt, *J* = 1.7, 0.8 Hz, 2H) ppm.

^{13}C NMR (C_6D_6, 126 MHz): δ = 163.0 (d, *J* = 246.7 Hz), 155.5 (dd, *J* = 295.6, 287.3 Hz), 131.5 (d, *J* = 3.3 Hz), 130.4 (d, *J* = 8.2 Hz) (x2), 128.8 (dd, *J* = 9.9, 4.7 Hz), 115.8 (d, *J* = 21.6 Hz) (x2), 101.1 (t, *J* = 5.6 Hz), 77.4 (dd, *J* = 32.7, 15.1 Hz), 51.8 (d, *J* = 5.1 Hz), 46.3 ppm.

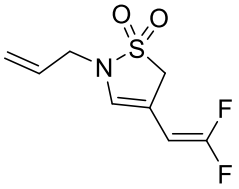
^{19}F NMR (C_6D_6, 282 MHz): δ = -87.34 (dd, *J* = 722.4, 38.8 Hz), -113.76 ppm.

IR (neat): ν = 3094, 2935, 1810, 1732, 1617, 1511, 1325, 1221, 1158, 1142, 866 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{12}H_{10}F_2NNaO_2S$ 312.0280; found 312.0278.

R_f: 0.48 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain).

2-allyl-4-(2,2-difluorovinyl)-2,5-dihydroisothiazole 1,1-dioxide (2k)



$C_8H_9F_2NO_2S$
MW: 221.22 g.mol^{-1}
Yellow oil
51 % (23.8 mg, 0.13 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (5 to 40 %).

^{1}H NMR (C_6D_6, 500 MHz): δ = 5.55 (ddt, *J* = 17.2, 10.2, 6.1 Hz, 1H), 5.37 – 5.34 (m, 1H), 4.97 – 4.85 (m, 2H), 4.11 (ddd, *J* = 26.0, 2.7, 0.7 Hz, 1H), 3.45 (dt, *J* = 6.2, 1.5 Hz, 2H), 3.32 – 3.27 (m, 2H) ppm.

^{13}C NMR (C_6D_6, 126 MHz): δ = 155.5 (dd, *J* = 295.5, 287.1 Hz), 132.8, 129.3 (dd, *J* = 9.9, 4.7 Hz), 119.1, 101.0 (t, *J* = 5.6 Hz), 77.5 (dd, *J* = 32.6, 15.2 Hz), 51.9 (d, *J* = 4.9 Hz), 46.1 ppm.

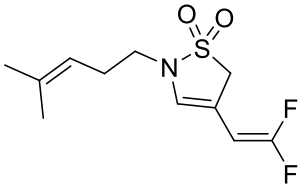
^{19}F NMR (C_6D_6, 282 MHz): δ = -86.18 (d, *J* = 40.1 Hz), -88.76 (d, *J* = 40.3 Hz) ppm.

IR (neat): ν = 3087, 2932, 2872, 1731, 1617, 1323, 1185, 1142, 933 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_8H_9F_2NNaO_2S$ 244.0214; found 244.0215.

R_f: 0.53 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain)

4-(2,2-difluorovinyl)-2-(4-methylpent-3-en-1-yl)-2,5-dihydroisothiazole 1,1-dioxide (2l)



$C_{11}H_{15}F_2NO_2S$
MW: 263.30 g.mol^{-1}
Light-yellow oil
57 % (37.2 mg, 0.14 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (5 to 20 %).

^{1}H NMR (C_6D_6, 300 MHz): δ = 5.35 – 5.27 (m, 1H), 5.00 – 4.88 (m, 1H), 4.16 (ddd, *J* = 26.0, 2.7, 0.7 Hz, 1H), 3.28 (dt, *J* = 1.9, 0.9 Hz, 2H), 2.98 (d, *J* = 7.5 Hz, 2H), 2.16 (q, *J* = 7.2 Hz, 2H), 1.58 (d, *J* = 1.4 Hz, 3H), 1.45 (s, 3H) ppm.

^{13}C NMR (C_6D_6, 126 MHz): δ = 154.5 (dd, *J* = 295.3, 286.8 Hz), 133.7, 129.0 (dd, *J* = 9.8, 4.8 Hz), 119.4, 98.9 (t, *J* = 5.6 Hz), 76.5 (dd, *J* = 32.4, 15.4 Hz), 50.9 (d, *J* = 4.8 Hz), 42.9, 27.4, 24.7, 16.7 ppm.

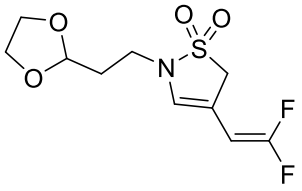
^{19}F NMR (C_6D_6, 282 MHz): δ = -86.59 (d, *J* = 40.2 Hz), -89.22 (d, *J* = 40.2 Hz) ppm.

IR (neat): ν = 2972, 2930, 2876, 1806, 1731, 1617, 1323, 1142 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{11}H_{15}F_2NaNO_2S$ 286.0684; found 286.0697.

R_f: 0.49 (Petroleum ether/EtOAc 9:1 *v/v*, UV, vanillin stain)

2-(2-(1,3-dioxolan-2-yl)ethyl)-4-(2,2-difluorovinyl)-2,5-dihydroisothiazole 1,1-dioxide (2m)



$C_{10}H_{13}F_2NO_4S$
MW: 281.27 g.mol^{-1}
Colorless oil
77 % (54.0 mg, 0.19 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (7 to 60 %).

^{1}H NMR (C_6D_6, 300 MHz): δ = 5.46 – 5.28 (m, 1H), 4.74 (t, *J* = 4.5 Hz, 1H), 4.18 (ddq, *J* = 26.1, 2.7, 0.7 Hz, 1H), 3.46 – 3.36 (m, 2H), 3.35 – 3.25 (m, 6H), 2.12 – 1.88 (m, 2H) ppm.

^{13}C NMR (C_6D_6, 126 MHz): δ = 155.5 (dd, *J* = 295.3, 286.8 Hz), 130.2 (dd, *J* = 9.8, 4.6 Hz), 102.1, 100.5 (t, *J* = 5.6 Hz), 77.6 (dd, *J* = 32.6, 15.2 Hz), 64.9 (x2), 51.9 (d, *J* = 4.9 Hz), 39.6, 33.7 ppm.

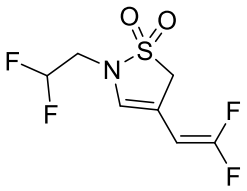
^{19}F NMR (C_6D_6, 282 MHz): δ = -86.65 (d, *J* = 39.8 Hz), -89.17 (d, *J* = 40.1 Hz) ppm.

IR (neat): ν = 2958, 2889, 1731, 1616, 1321, 1212, 1185, 1140, 941 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_{10}H_{14}F_2NO_4S$ 282.0606; found 282.0597.

R_f: 0.38 (Petroleum ether/EtOAc 7:3 *v/v*, UV, vanillin stain)

2-(2,2-difluoroethyl)-4-(2,2-difluorovinyl)-2,5-dihydroisothiazole 1,1-dioxide (2n)



$C_7H_7F_4NO_2S$
MW: 245.19 g.mol^{-1}
Colorless oil
81 % (49.5 mg, 0.20 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (5 to 40 %).

^{1}H NMR (C_6D_6, 500 MHz): δ = 5.56 – 5.30 (m, 1H), 5.31 – 5.29 (m, 1H), 4.03 (dd, *J* = 26.1, 2.6 Hz, 1H), 3.14 (d, *J* = 1.7 Hz, 2H), 2.96 (td, *J* = 14.0, 4.3 Hz, 2H) ppm.

^{13}C NMR (C_6D_6, 126 MHz): δ = 155.61 (dd, *J* = 295.9, 287.7 Hz), 129.41 (dd, *J* = 9.9, 4.7 Hz), 113.81 (t, *J* = 243.4 Hz), 101.59 (t, *J* = 5.8 Hz), 77.18 (dd, *J* = 33.0, 15.0 Hz), 51.04 (d, *J* = 5.2 Hz), 44.97 (t, *J* = 27.8 Hz) ppm ppm.

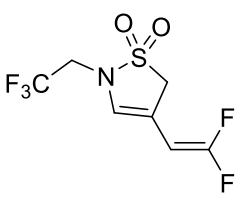
^{19}F NMR (C_6D_6, 282 MHz): δ = -85.56 (d, J = 37.4 Hz), -88.03 (d, J = 36.9 Hz), -120.99 ppm.

IR (neat): ν = 3097, 2995, 2941, 1812, 1734, 1621, 1328, 1202, 1147, 1025, 932 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_7H_7F_4NNaO_2S$ 268.0026; found 268.0030.

R_f: 0.41 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain)

4-(2,2-difluorovinyl)-2-(2,2,2-trifluoroethyl)-2,5-dihydroisothiazole 1,1-dioxide (2o)



$C_7H_6F_5NO_2S$
MW: 263.18 g.mol^{-1}
Colorless oil
32 % (20.9 mg, 0.08 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (0 to 40 %).

^{1}H NMR (C_6D_6, 500 MHz): δ = 5.17 (s, 1H), 3.99 (dd, *J* = 25.8, 2.5 Hz, 1H), 3.07 – 3.00 (m, 4H) ppm.

^{13}C NMR (C_6D_6, 126 MHz): δ = 155.7 (dd, *J* = 298.7, 297.7 Hz), 128.7 (dd, *J* = 9.9, 4.9 Hz), 123.8 (d, *J* = 278.4 Hz), 103.1 (t, *J* = 5.8 Hz), 77.0 (dd, *J* = 33.2, 14.9 Hz), 50.7 (d, *J* = 5.1 Hz), 44.4 (q, *J* = 35.6 Hz) ppm.

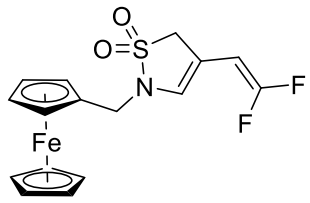
^{19}F NMR (C_6D_6, 282 MHz): δ = -71.61, -84.61 (d, *J* = 35.6 Hz), -87.22 (d, *J* = 36.0 Hz) ppm.

IR (neat): ν = 2955, 1735, 1624, 1328, 1273, 1214, 1158, 1056 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_7H_6F_5NNaO_2S$ 285.9933; found 285.9937.

R_f: 0.54 (Petroleum ether/EtOAc 8:2 *v/v*, UV, $KMnO_4$ stain)

4-(2,2-difluorovinyl)-2-(4-ferrocenyl)-2,5-dihydroisothiazole 1,1-dioxide (2p)



$C_{16}H_{15}F_2FeNO_2S$
MW: 379.20 $g.mol^{-1}$
Yellow solid
56 % (21.4 mg, 0.06 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (0 to 20 %).

^{1}H NMR (C_6D_6, 300 MHz): δ = 5.60 – 5.56 (m, 1H), 4.05 – 4.00 (m, 2H), 3.99 (t, *J* = 1.8 Hz, 2H), 3.94 – 3.88 (m, 3H), 3.87 (s, 5H), 3.30 (tt, *J* = 1.7, 0.8 Hz, 2H) ppm.

^{13}C NMR (C_6D_6, 126 MHz): δ = 155.4 (dd, *J* = 287.8, 278.4 Hz), 129.0 (dd, *J* = 9.9, 4.7 Hz), 100.6 (t, *J* = 5.5 Hz), 81.4, 77.5 (dd, *J* = 32.6, 15.1 Hz), 69.8 (x2), 69.2 (x5), 69.1 (x2), 52.0 (d, *J* = 4.9 Hz), 43.2 ppm.

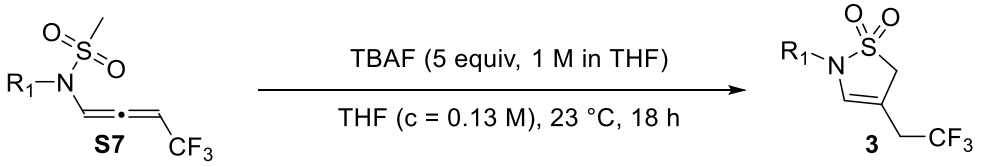
^{19}F NMR (C_6D_6, 282 MHz): δ = -86.51 (d, *J* = 39.8 Hz), -89.14 (d, *J* = 39.8 Hz) ppm.

IR (neat): ν = 3100, 3012, 2929, 2358, 2343, 1449, 1354, 1267, 1159, 1011, 900 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M]^+$ calcd. for $C_{16}H_{15}F_2FeNO_2S$ 379.0135; found 379.0140.

R_f: 0.44 (Petroleum ether/EtOAc 9:1 *v/v*, UV, ninhydrin stain).

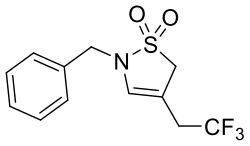
Synthesis of trifluorinated-sultames **3**



General procedure F:

To a solution of trifluorinated-allenamide **S7** (1 equiv) in THF (c = 0.13 M) was added dropwise a solution of TBAF (5 equiv, 1 M in THF). The mixture was stirred at 23 °C during 18 h and then hydrolyzed with a saturated solution of $NaHCO_3$. The aqueous layer was extracted with EtOAc (3x). The organic layers were washed with a saturated solution of NaCl, dried (Na_2SO_4), filtered and concentrated under vacuum. The crude material was purified by column chromatography using a gradient of EtOAc in petroleum ether to afford the title compounds.

2-benzyl-4-(2,2,2-trifluoroethyl)-2,5-dihydroisothiazole 1,1-dioxide (3a)



$C_{12}H_{12}F_3NO_2S$
MW: 291.29 g.mol^{-1}
Colorless oil
57 % (42.2 mg, 0.14 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (0 to 40 %).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.43 – 7.32 (m, 5H), 6.16 – 6.11 (m, 1H), 4.44 (s, 2H), 3.92 (s, 2H), 2.92 – 2.84 (m, 2H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 134.9, 132.5, 129.1 (x2), 128.6 (x2), 128.6, 125.1 (q, *J* = 277.0 Hz), 99.2 (q, *J* = 3.4 Hz), 53.6 (d, *J* = 1.3 Hz), 47.3, 35.0 (q, *J* = 31.3 Hz) ppm.

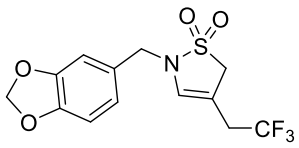
^{19}F NMR ($CDCl_3$, 282 MHz): δ = -65.62 ppm.

IR (neat): ν = 3068, 2928, 2354, 1652, 1368, 1325, 1252, 1137, 1083, 699 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{12}H_{11}F_3NNaO_2S$ 314.0433; found 314.0451.

R_f: 0.33 (Petroleum ether/EtOAc 8:2 *v/v*, UV, ninhydrin stain)

2-(benzo[*d*][1,3]dioxol-5-ylmethyl)-4-(2,2,2-trifluoroethyl)-2,5-dihydroisothiazole 1,1-dioxide (3b)



$C_{13}H_{12}F_3NO_4S$
MW: 335.30 g.mol^{-1}
Colorless oil
31 % (26.0 mg, 0.08 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (5 to 40 %).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.90 – 6.72 (m, 3H), 6.14 (dq, *J* = 1.9, 0.9 Hz, 1H), 5.98 (s, 2H), 4.33 (s, 2H), 3.92 – 3.84 (m, 2H), 2.88 (qd, *J* = 10.3, 1.0 Hz, 2H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 148.4, 148.0, 132.4, 128.5, 125.2 (q, *J* = 277.6 Hz), 122.3, 109.0, 108.6, 101.5, 99.2 (q, *J* = 3.4 Hz), 53.7 (d, J = 1.3 Hz), 47.1, 35.0 (q, *J* = 31.3 Hz) ppm.

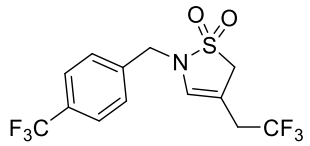
^{19}F NMR ($CDCl_3$, 282 MHz): δ = -65.62 ppm.

IR (neat): ν = 2909, 1652, 1505, 1492, 1447, 1371, 1326, 1248, 1139, 1107, 1038 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+K]^+$ calcd. for $C_{13}H_{12}F_3KNO_4S$ 374.0076; found 374.0071.

R_f: 0.29 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain).

4-(2,2,2-trifluoroethyl)-2-(4-(trifluoromethyl)benzyl)-2,5-dihydroisothiazole 1,1-dioxide (3c)



$C_{13}H_{11}F_6NO_2S$
MW: 359.29 $g.mol^{-1}$
Yellow oil
55 % (49.3 mg, 0.14 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (5 to 40 %).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.65 (d, J = 8.1 Hz, 2H), 7.50 (d, J = 8.6 Hz, 2H), 6.15 (dt, J = 2.0, 0.9 Hz, 1H), 4.50 (s, 2H), 4.01 – 3.89 (m, 2H), 2.91 (qd, J = 10.1, 1.1 Hz, 2H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 139.1 (q, *J* = 1.3 Hz), 132.4, 130.9 (q, *J* = 32.7 Hz), 128.7 (x2), 126.1 (q, *J* = 3.8 Hz) (x2), 124.7 (q, *J* = 279.3 Hz), 124.0 (q, *J* = 272.2 Hz), 100.0 (q, *J* = 3.4 Hz), 53.5 (d, *J* = 1.2 Hz), 47.0, 34.9 (q, *J* = 31.4 Hz) ppm.

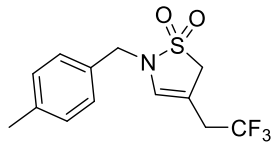
^{19}F NMR ($CDCl_3$, 282 MHz): δ = -62.69, -65.58 ppm.

IR (neat): ν = 2933, 1702, 1656, 1621, 1421, 1371, 1324, 1253, 1137, 1084, 1067, 1019, 824, 680 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{13}H_{11}F_6NNaO_2S$ 382.0307;found 382.0302.

R_f: 0.37 (Petroleum ether/EtOAc 8:2 *v/v*, UV, $KMnO_4$ stain).

2-(4-methylbenzyl)-4-(2,2,2-trifluoroethyl)-2,5-dihydroisothiazole 1,1-dioxide (3d)



$C_{13}H_{14}F_3NO_2S$
MW: 305.32 $g.mol^{-1}$
Yellow oil
59 % (12.8 mg, 0.04 mmol)

The product was obtained by *flash* chromatography on 10 g of silica gel using a gradient of ethyl acetate in petroleum ether (0 to 40 %).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.24 (d, *J* = 7.7 Hz, 2H), 7.19 (d, *J* = 7.7 Hz, 2H), 6.13 (tt, *J* = 1.9, 1.1 Hz, 1H), 4.39 (s, 2H), 3.91 (s, 2H), 2.91 – 2.82 (m, 2H), 2.36 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 138.5, 132.5, 131.8, 129.8 (x2), 128.7 (x2), 125.2 (q, *J* = 277.7 Hz), 99.0 (q, *J* = 3.4 Hz), 53.6 (d, *J* = 1.3 Hz), 47.0, 35.0 (q, *J* = 31.3 Hz), 21.3 ppm.

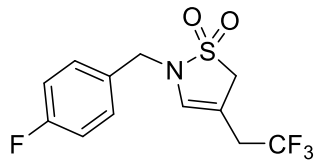
^{19}F NMR ($CDCl_3$, 282 MHz): δ = -65.64 ppm.

IR (neat): ν = 2923, 2358, 1650, 1367, 1326, 1265, 1138, 1084 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{13}H_{14}F_3NNaO_2S$ 328.0590; found 328.0604.

R_f: 0.50 (Petroleum ether/EtOAc 8:2 *v/v*, UV, $KMnO_4$ stain).

2-(4-fluorobenzyl)-4-(2,2,2-trifluoroethyl)-2,5-dihydroisothiazole 1,1-dioxide (3e)



$C_{12}H_{11}F_4NO_2S$
MW: 309.28 g.mol^{-1}
Colorless oil
35 % (27 mg, 0.09 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (0 to 40 %).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.32 – 7.24 (m, 2H), 7.11 – 6.96 (m, 2H), 6.11 – 6.01 (m, 1H), 4.34 (s, 2H), 3.86 – 3.82 (m, 2H), 2.82 (qd, *J* = 10.3, 1.1 Hz, 2H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 162.9 (d, *J* = 247.5 Hz), 132.4, 130.7 (d, *J* = 3.3 Hz), 130.4 (d, *J* = 8.4 Hz) (x2), 125.3 (q, *J* = 278.6 Hz), 116.1 (d, *J* = 21.7 Hz) (x2), 99.5 (d, *J* = 3.3 Hz), 53.6, 46.7, 35.0 (q, *J* = 31.4 Hz) ppm.

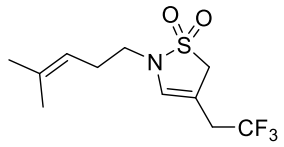
^{19}F NMR ($CDCl_3$, 282 MHz): δ = -65.62, -113.35 ppm.

IR (neat): ν = 2920, 2358, 1645, 1367, 1326, 1265, 1138, 1084 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{12}H_{11}F_4NNaO_2S$ 332.2682; found 332.2680.

R_f: 0.32 (Petroleum ether/EtOAc 8:2 *v/v*, UV, $KMnO_4$ stain).

2-(4-methylpent-3-en-1-yl)-4-(2,2,2-trifluoroethyl)-2,5-dihydroisothiazole 1,1-dioxide (3f)



$C_{11}H_{16}F_3NO_2S$
MW: 283.31 g.mol^{-1}
Colorless oil
56 % (40.0 mg, 0.14 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (0 to 40 %).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.27 (tt, *J* = 2.0, 1.1 Hz, 1H), 5.09 (tdt, *J* = 7.3, 2.9, 1.5 Hz, 1H), 3.87 – 3.81 (m, 2H), 3.30 (d, *J* = 7.4 Hz, 2H), 2.92 (qq, *J* = 10.3, 1.1 Hz, 2H), 2.37 (dddt, J = 8.2, 7.2, 6.3, 1.0 Hz, 2H), 1.71 (d, *J* = 1.3 Hz, 3H), 1.63 (d, *J* = 1.3 Hz, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 135.6, 133.4, 125.5 (q, *J* = 277.6 Hz), 119.6, 98.0 (q, *J* = 3.5 Hz), 53.6 (d, *J* = 1.3 Hz), 43.9, 34.9 (q, *J* = 31.3 Hz), 28.3, 25.8, 18.0 ppm.

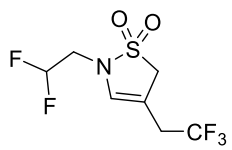
^{19}F NMR ($CDCl_3$, 282 MHz): δ = -65.73 ppm.

IR (neat): ν = 2976, 2930, 1878, 1653, 1550, 1452, 1370, 1324, 1253, 1199, 1139, 1084 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{11}H_{15}F_3NNaO_2S$ 286.0384; found 286.0697.

R_f: 0.48 (Petroleum ether/EtOAc 8:2 *v/v*, UV, $KMnO_4$ stain).

2-(2,2-difluoroethyl)-4-(2,2,2-trifluoroethyl)-2,5-dihydroisothiazole 1,1-dioxide (3g)



$C_7H_8F_5NO_2S$
MW: 265.20 g.mol^{-1}
Colorless oil
39 % (25.9 mg, 0.10 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (5 to 40 %).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.37 (dt, *J* = 2.0, 1.0 Hz, 1H), 5.99 (tt, *J* = 55.4, 4.3 Hz, 1H), 3.90 (s, 2H), 3.65 (td, *J* = 13.7, 4.3 Hz, 2H), 2.96 (dd, *J* = 10.1, 1.1 Hz, 2H) ppm.

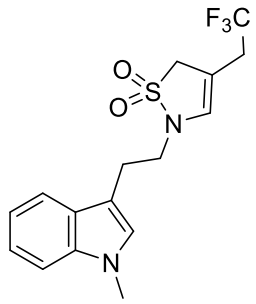
^{13}C NMR ($CDCl_3$, 126 MHz): δ = 133.0, 125.1 (d, *J* = 277.5 Hz), 113.6 (t, *J* = 243.7 Hz), 100.0 (q, *J* = 3.4 Hz), 52.9 (d, *J* = 1.3 Hz), 45.3 (t, *J* = 28.4 Hz), 34.9 (q, *J* = 31.5 Hz) ppm.

^{19}F NMR ($CDCl_3$, 282 MHz): δ = -65.54, -120.86 ppm.

ESI-HRMS (ESI-TOF): $[M]^+$ calcd for $C_7H_8F_5NO_2S$ 265.0190; found 265.0212.

IR (neat): ν = 2490, 2225, 1475, 1250, 1100 cm^{-1}.

2-(2-(1-methyl-1H-indol-3-yl)ethyl)-4-(2,2,2-trifluoroethyl)-2,5-dihydroisothiazole 1,1-dioxide (3h)



$C_{16}H_{17}F_3N_2O_2S$
MW: 358.38 $g.mol^{-1}$
Colorless oil
61 % (20.8 mg, 0.06 mmol)

The product was obtained by *flash* chromatography on 25 g of silica gel using a gradient of ethyl acetate in petroleum ether (0 to 40 %).

^{1}H NMR (C_6D_6, 300 MHz): δ = 7.56 – 7.52 (m, 1H), 7.28 – 7.19 (m, 2H), 7.05 – 6.92 (m, 1H), 6.43 (s, 1H), 5.10 (tt, *J* = 2.0, 1.1 Hz, 1H), 3.38 (t, *J* = 7.0 Hz, 2H), 3.14 (s, 2H), 2.99 (t, *J* = 7.0 Hz, 2H), 2.96 (s, 3H), 1.80 (qd, *J* = 10.5, 1.0 Hz, 2H) ppm.

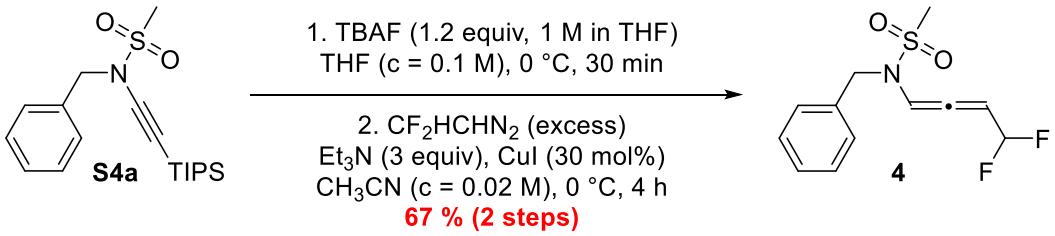
^{13}C NMR (C_6D_6, 126 MHz): δ = 137.6, 133.9, 125.7 (q, *J* = 277.7 Hz), 122.1, 119.5 (x2), 119.0, 110.7, 109.7 (x2), 96.8 (q, *J* = 3.5 Hz), 53.1, 44.8, 33.9 (q, *J* = 30.8 Hz), 31.9, 25.9 ppm.

^{19}F NMR (C_6D_6, 282 MHz): δ = -65.86 ppm.

IR (neat): ν = 3073, 2936, 1654, 1474, 1370, 1325, 1253, 1200, 1139, 1108, 1084, 744, 681 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_{16}H_{18}F_3N_2O_2S$ 359.1036; found 359.1028.

R_f: 0.27 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain).

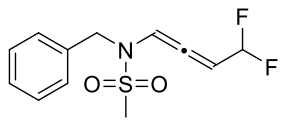


To a solution of **S4a** (300 mg, 0.82 mmol, 1 equiv) in THF (c = 0.1 M) was added dropwise at 0 °C a solution of TBAF (8.0 mL, 0.98 mmol, 1.2 equiv, 1 M in THF). The mixture was stirred for 30 minutes at 0 °C and then hydrolyzed with water. The aqueous layer was extracted with Et_2O (3x). The organic layers were washed with a saturated solution of NaCl, dried (Na_2SO_4), filtered and concentrated under vacuum. The crude terminal mesyl-ynamide was used without further purification.

Terminal mesyl-ynamide (171.7 mg, 0.82 mmol, 1 equiv) was dissolved in CH_3CN (c = 0.1 M) in the presence of CuI (46.9 mg, 0.25 mmol, 30 mol %), and Et_3N (0.34 mL, 2.5 mmol, 3 equiv). 1,1-difluorodiazoethane was added dropwise (in excess) and the reaction was stirred for 4 h at 0 °C. The mixture was concentrated under vacuum and the crude material was purified by *flash* chromatography on 25 g of silica using a gradient of EtOAc in petroleum ether (5 to 40 %).

2,2-difluoro-diazoethane was synthesized according to the previous literature and directly used.[12]

N-benzyl-N-(4,4-difluorobuta-1,2-dien-1-yl)methanesulfonamide (4)



$C_{12}H_{13}F_2NO_2S$
MW: 273.30 g.mol^{-1}
Yellow oil
88 % (196 mg, 0.72 mmol)

^{1}H NMR (C_6D_6, 300 MHz): δ = 7.20 – 7.16 (m, 1H), 7.11 – 6.94 (m, 3H), 6.88 – 6.78 (m, 1H), 5.45 – 5.33 (m, 1H), 5.15 (ddd, *J* = 56.0, 5.8, 0.8 Hz, 1H), 4.16 (d, *J* = 15.3 Hz, 1H), 3.91 (d, J = 15.3 Hz, 1H), 2.05 (s, 3H) ppm.

^{13}C NMR (C_6D_6, 126 MHz): δ = 199.0 (t, *J* = 12.5 Hz), 135.6, 128.8 (x2), 128.4, 128.0 (x2), 113.5 (t, *J* = 239.3 Hz), 104.6 (d, *J* = 1.8 Hz), 99.5 (t, *J* = 28.9 Hz), 50.4, 38.3 ppm.

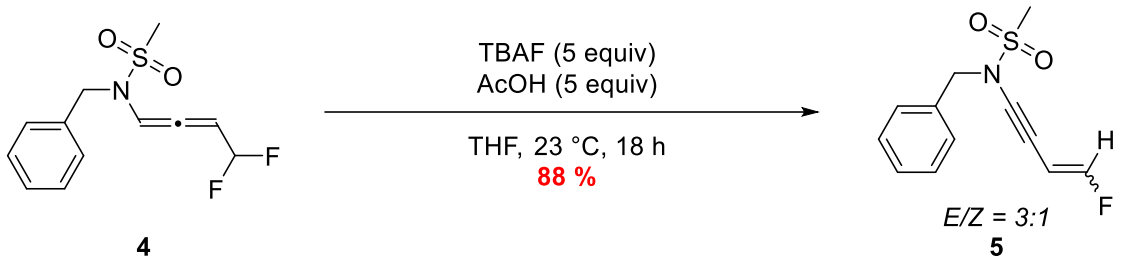
^{19}F NMR (C_6D_6, 282 MHz): δ = -109.05 (d, *J* = 300.4 Hz), -110.40 (d, *J* = 301.0 Hz) ppm.

IR (neat): ν = 3090, 2957, 2928, 1450, 1345, 1185, 1054, 1025, 935, 516 cm^{-1}.

ESI-HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{12}H_{13}F_2NNaO_2S$ 296.0527; found 296.0522.

R_f: 0.29 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain)

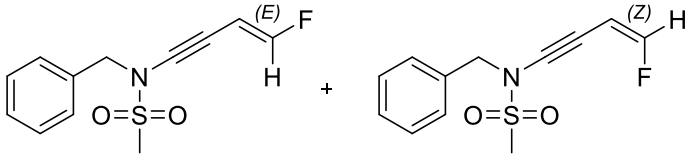
[12] P. K. Mykhailiuk, *Angew. Chem. Int. Ed.*, 2015, **54**, 6558–6561.



4 **5**

To a solution of difluorinated-allenamide **4** (272 mg, 1,0 mmol, 1 equiv) in THF (c = 0.13 M) was added dropwise a solution of TBAF (5.0 mL, 5.0 mmol, 5 equiv, 1 M in THF) and glacial acetic acid (0.29 mL, 5.0 mmol, 5 equiv). The mixture was stirred at 23 °C during 18 h and then hydrolyzed with a saturated solution of $NaHCO_3$. The aqueous layer was extracted with EtOAc (3x). The organic layers were washed with a saturated solution of NaCl, dried (Na_2SO_4), filtered and concentrated under vacuum. The crude material was purified by *flash* chromatography on 25 g of silica using a gradient of EtOAc in petroleum ether (5 to 40 %).

<u>*N*-benzyl-*N*-(4-fluorobut-3-en-1-yn-1-yl)methanesulfonamide (5)</u>



(***E***)-**5** : (***Z***)-**5**

3 : *1*

$C_{12}H_{12}FNO_2S$
MW: 253.29 g.mol^{-1}
Yellow oil
88 % (223 mg, 0.88 mmol)

^{1}H NMR (C_6D_6, 300 MHz): δ = 7.29 – 7.24 (m, 2H), 7.23 – 7.17 (m, 2H), 7.09 – 6.95 (m, 6H), 6.37 (dd, *J* = 81.9, 11.2 Hz, 1H), 5.92 (dd, *J* = 81.2, 4.8 Hz, 1H), 5.29 (dd, *J* = 12.7, 11.2 Hz, 1H), 4.54 (dd, *J* = 37.9, 4.8 Hz, 1H), 4.23 (s, 2H), 4.21 (s, 2H), 2.18 (s, 6H) ppm.

^{13}C NMR (C_6D_6, 126 MHz): δ = 158.8 (d, *J* = 271.3 Hz), 154.9 (d, *J* = 272.7 Hz), 135.2, 135.2, 129.1 (x2), 129.0 (x2), 128.9 (x4), 128.7, 128.7, 95.0 (d, *J* = 26.9 Hz), 92.5 (d, J = 4.4 Hz), 88.3 (d, *J* = 5.8 Hz), 84.8 (d, *J* = 11.9 Hz), 63.2 (d, *J* = 21.6 Hz), 62.9 (d, *J* = 5.1 Hz), 55.6, 55.5, 38.4, 38.4 ppm.

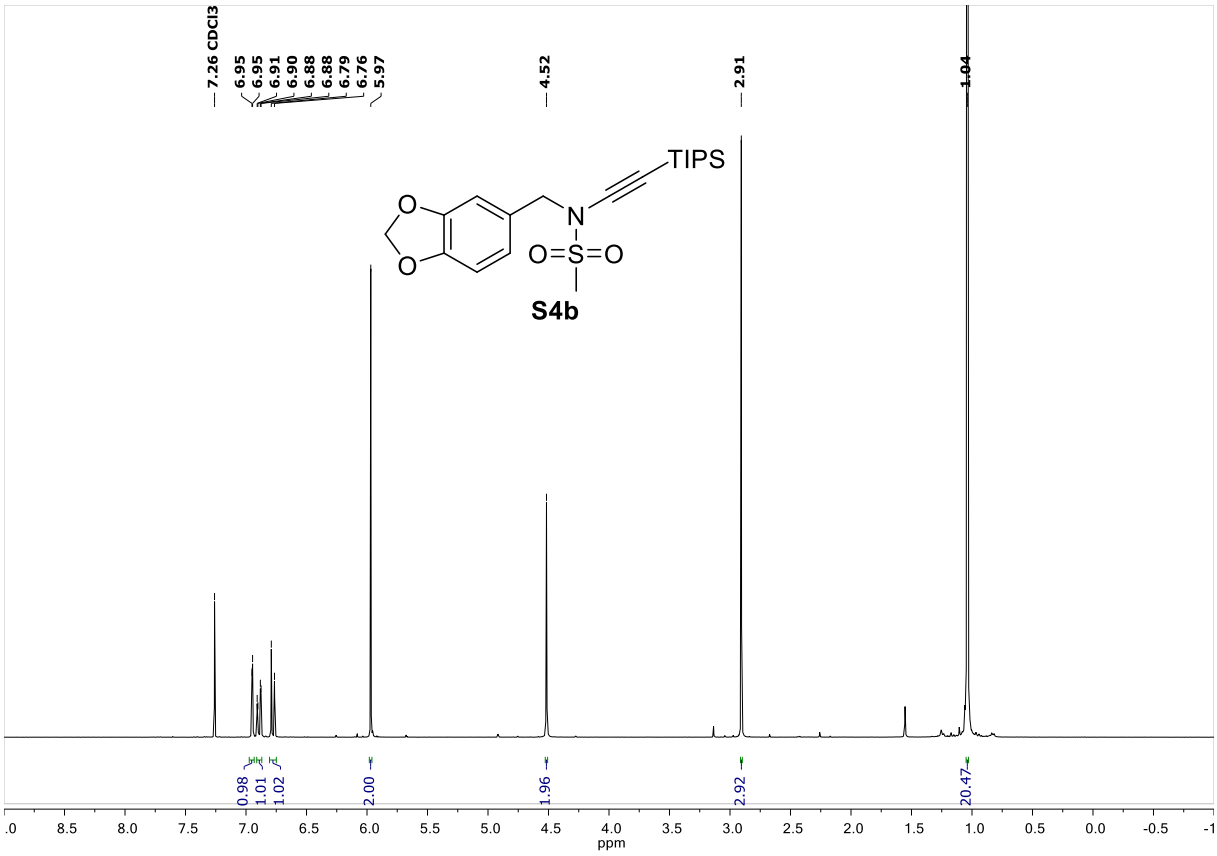
^{19}F NMR (C_6D_6, 282 MHz): δ = -112.74, -113.79 ppm.

IR (neat): ν = 3033, 2932, 2237, 1640, 1354, 1160, 1106, 959, 779, 702, 512 cm^{-1}.

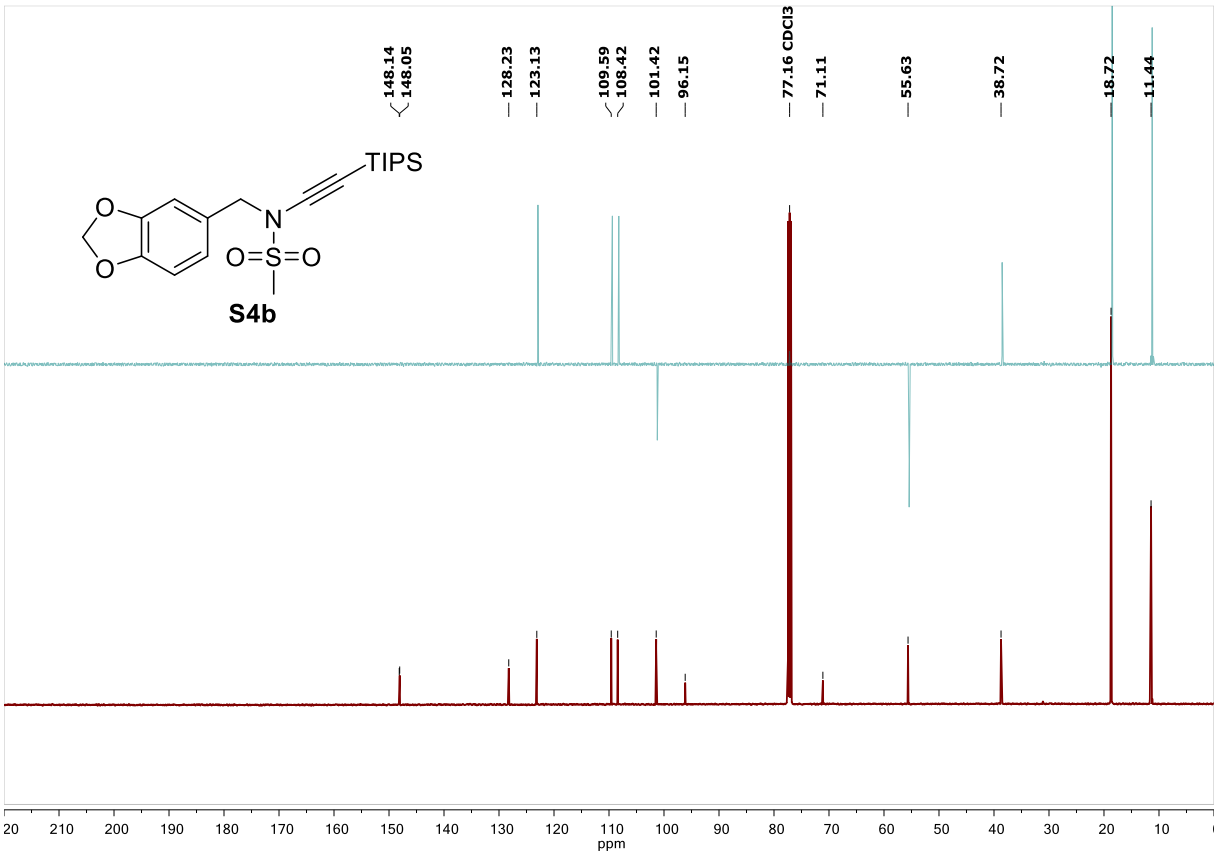
ESI-HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{12}H_{12}FNNaO_2S$ 276.0465, found 276.0467.

R_f: 0.45 (Petroleum ether/EtOAc 8:2 *v/v*, UV, vanillin stain).

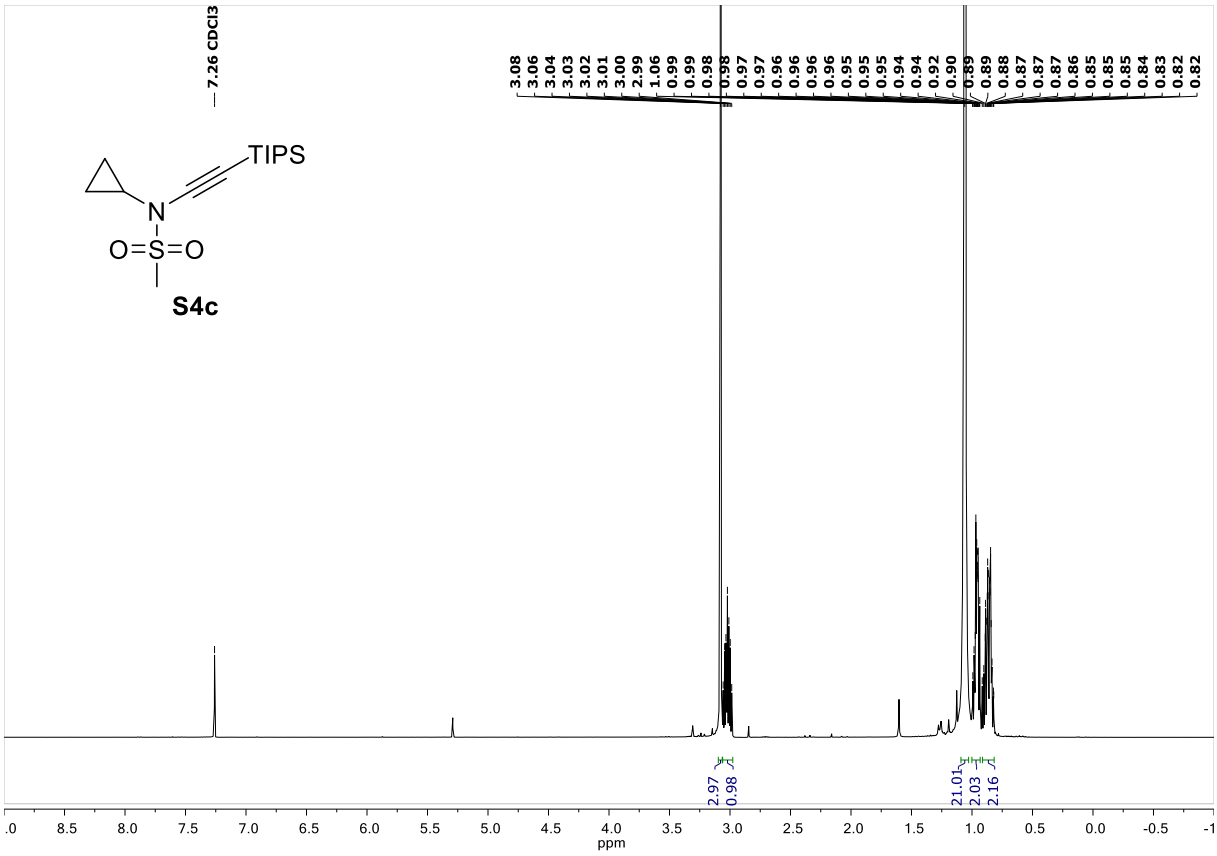
NMR spectrum



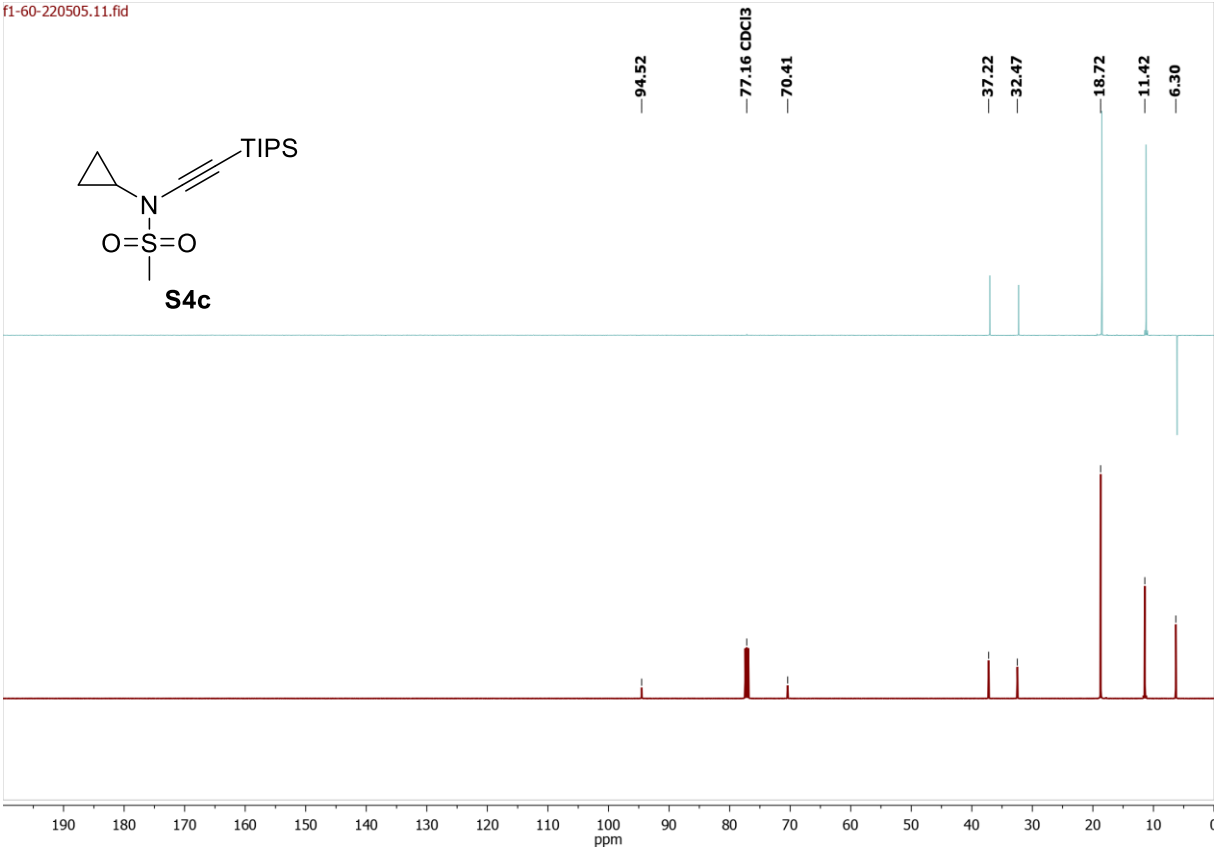
^{1}H NMR ($CDCl_3$, 300 MHz) of **S4b**



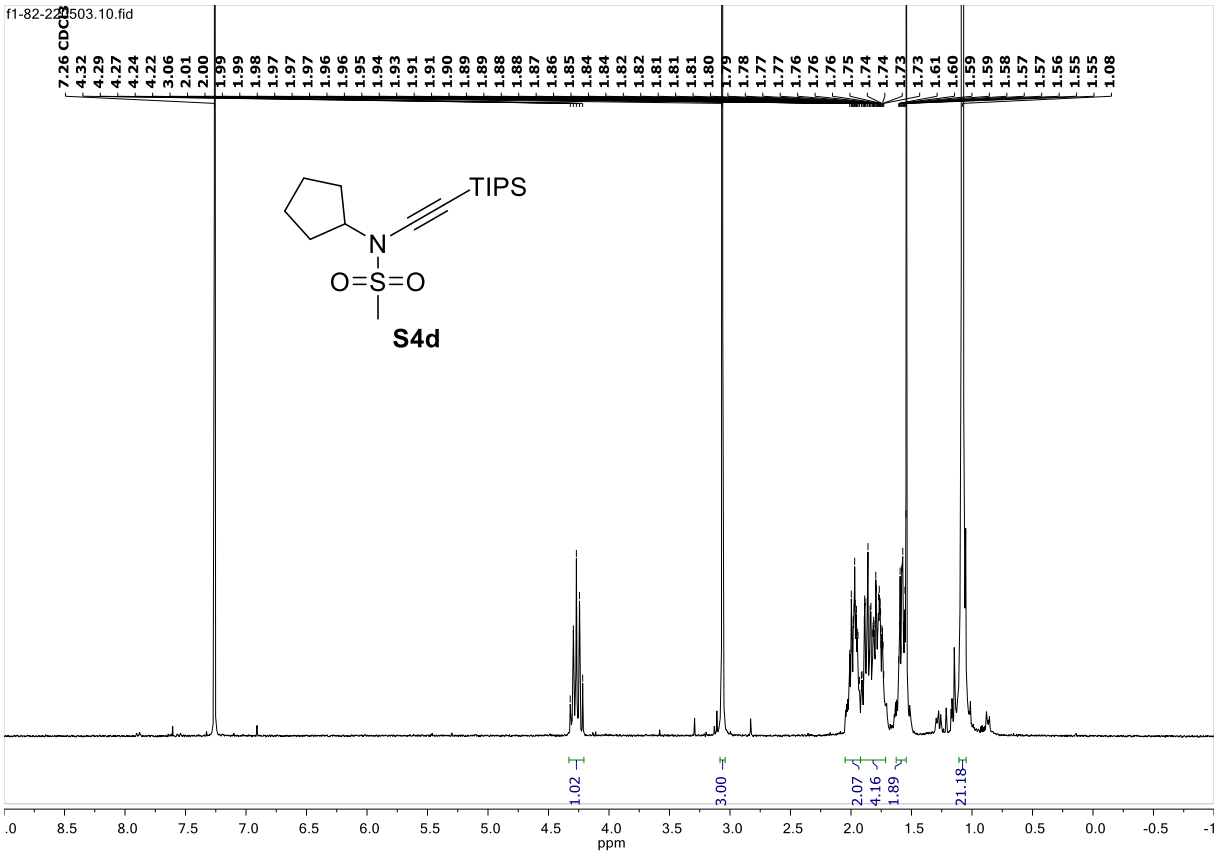
^{13}C NMR ($CDCl_3$, 126 MHz) of **S4b**



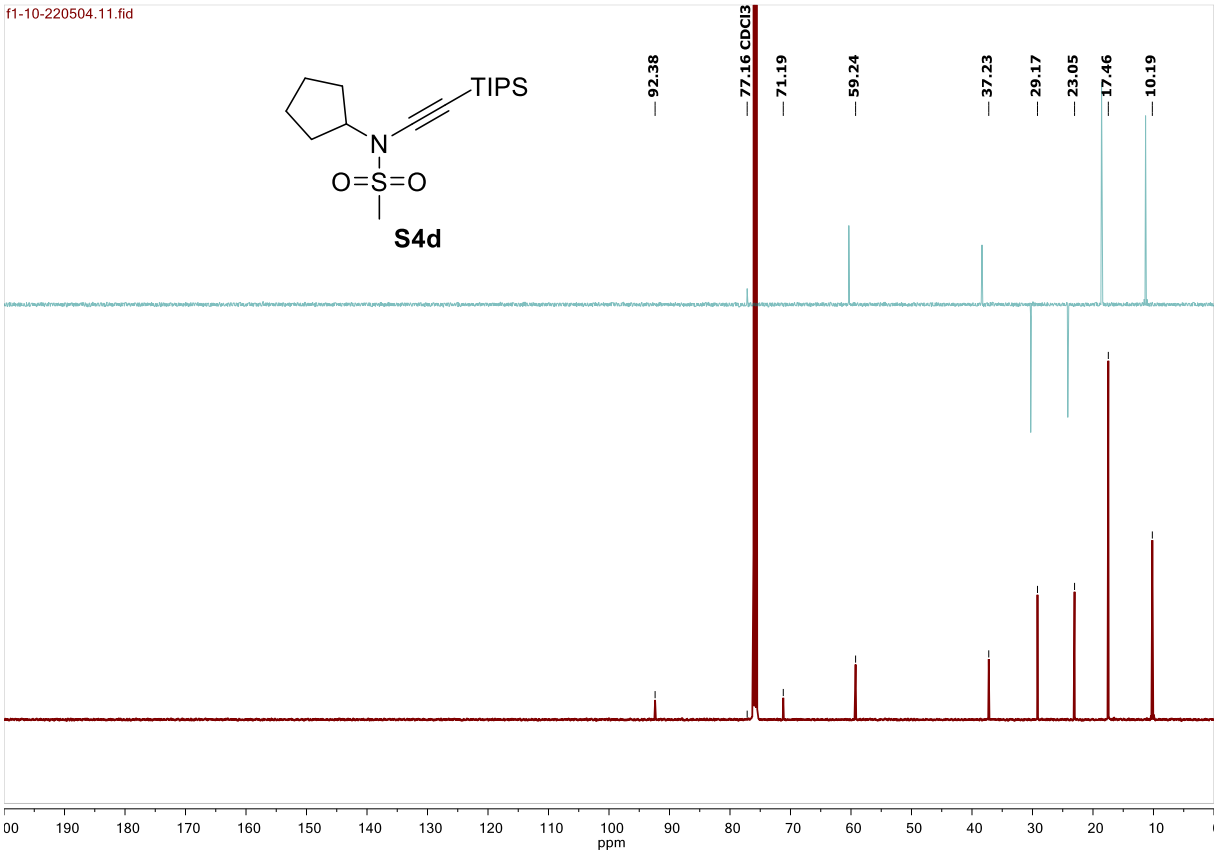
^{1}H NMR ($CDCl_3$, 300 MHz) of **S4c**



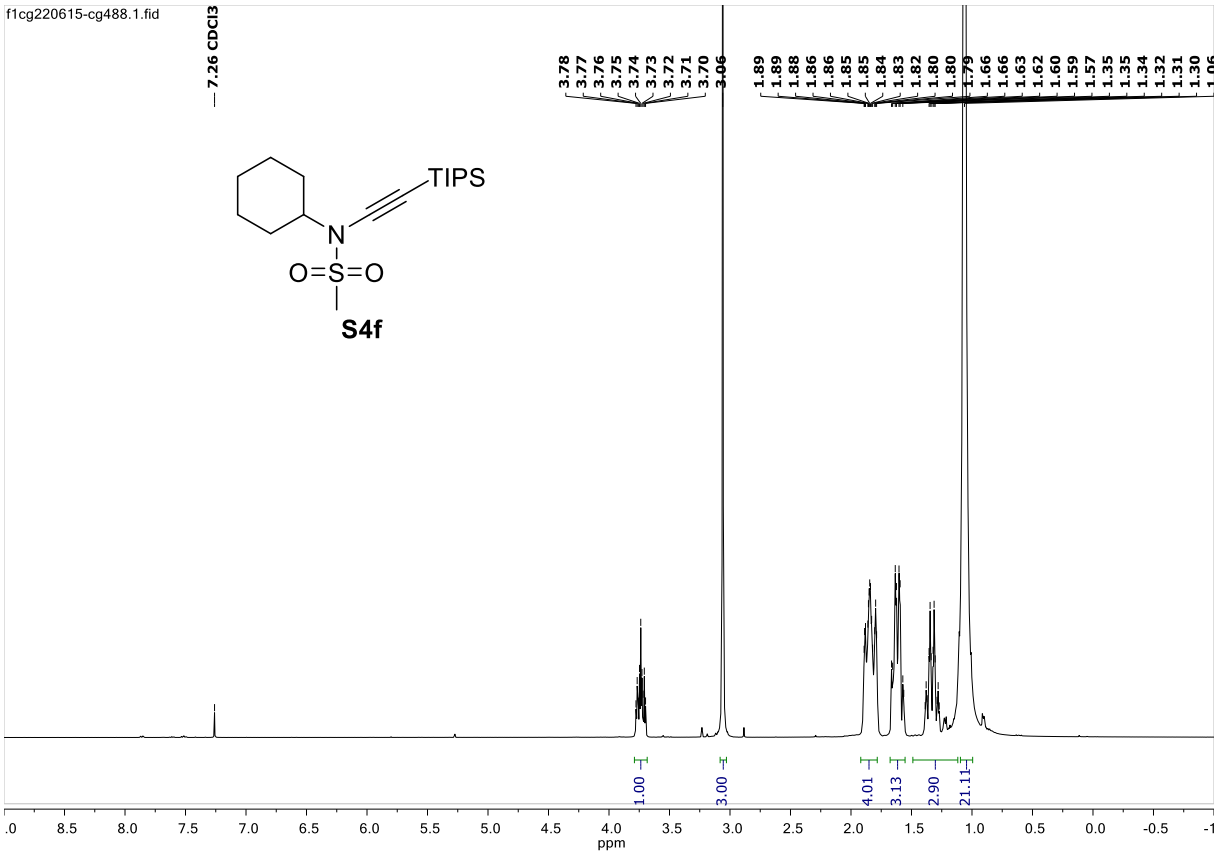
^{13}C NMR ($CDCl_3$, 126 MHz) of **S4c**



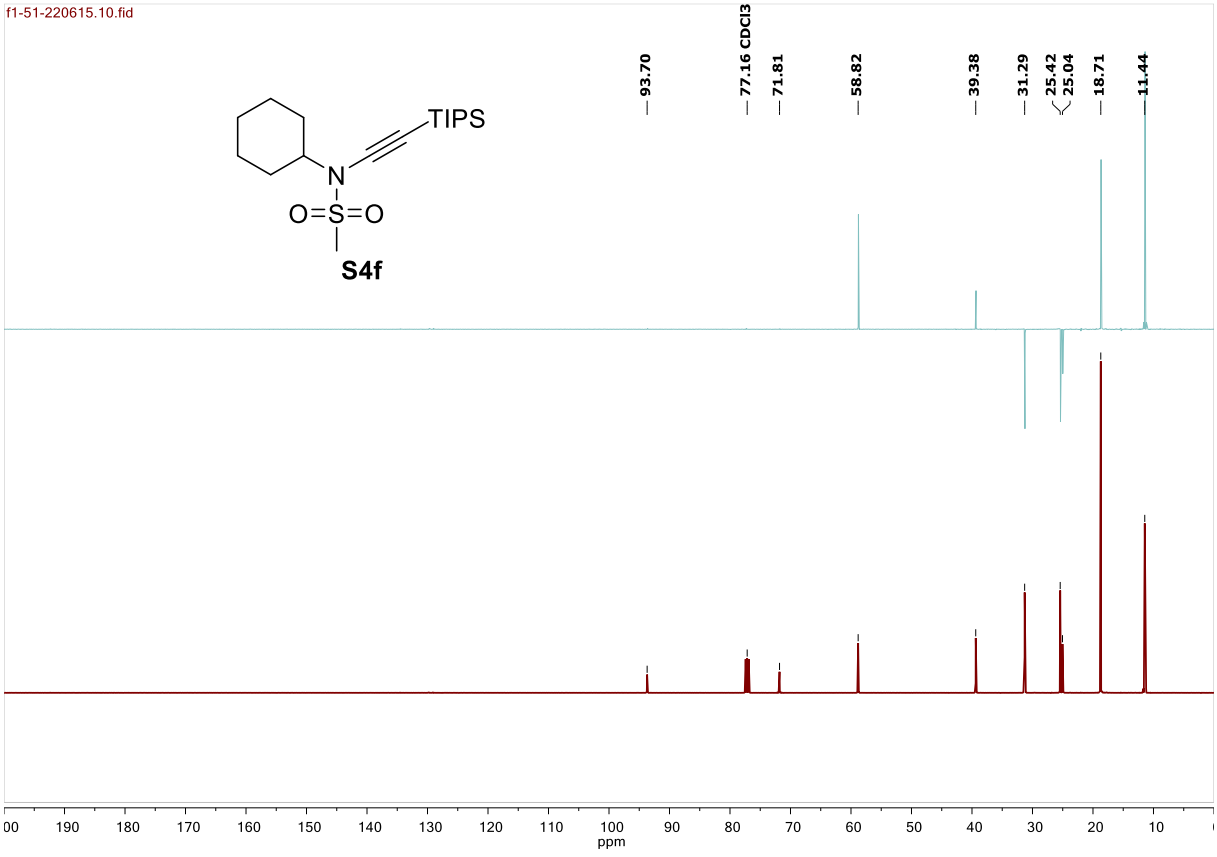
^{1}H NMR ($CDCl_3$, 300 MHz) of **S4d**



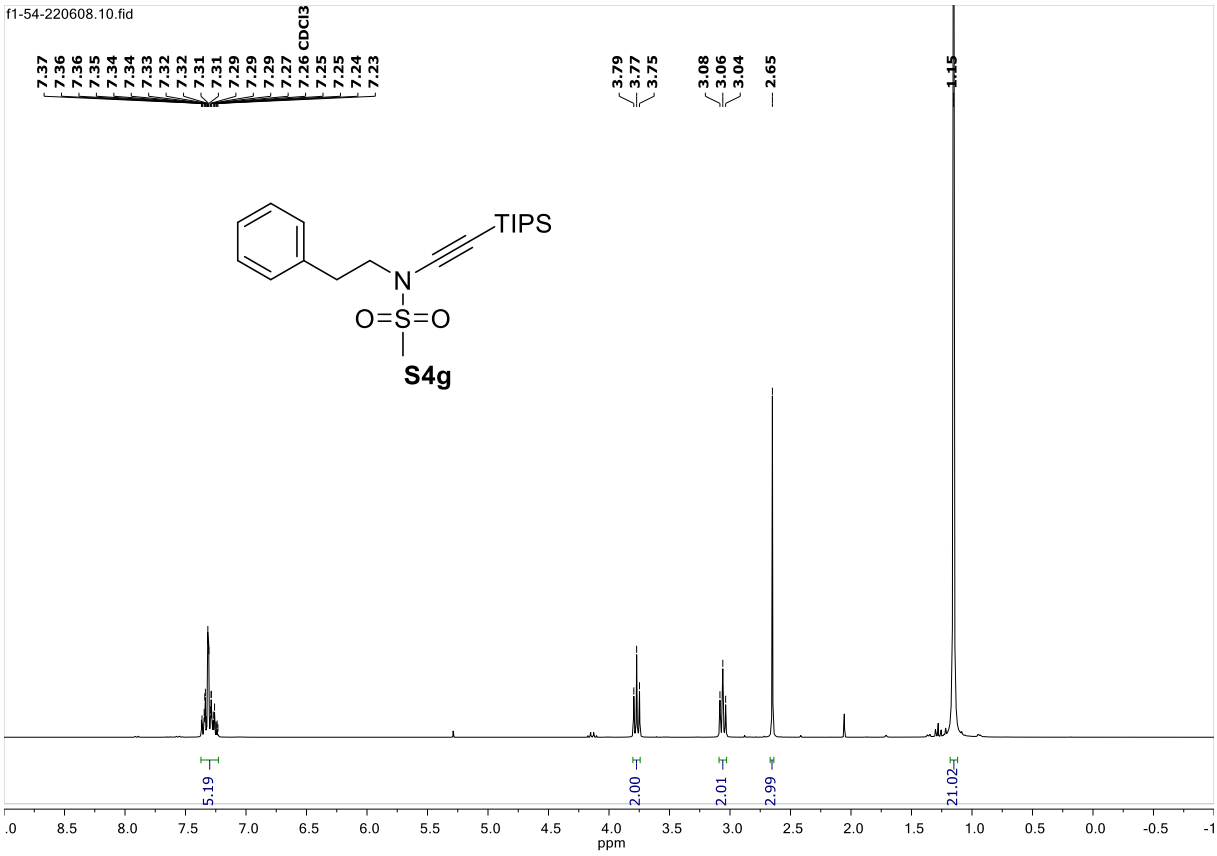
^{13}C NMR ($CDCl_3$, 126 MHz) of **S4d**



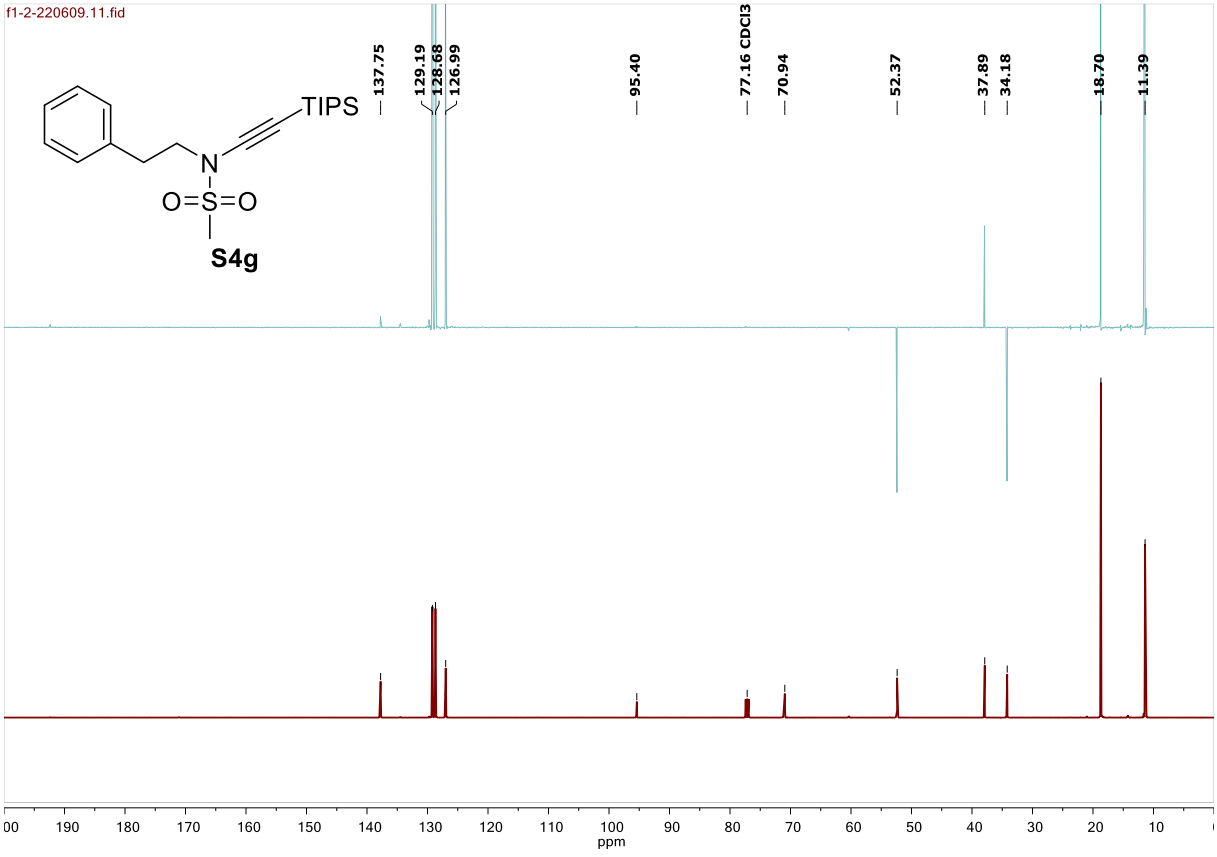
^{1}H NMR ($CDCl_3$, 400 MHz) of **S4f**



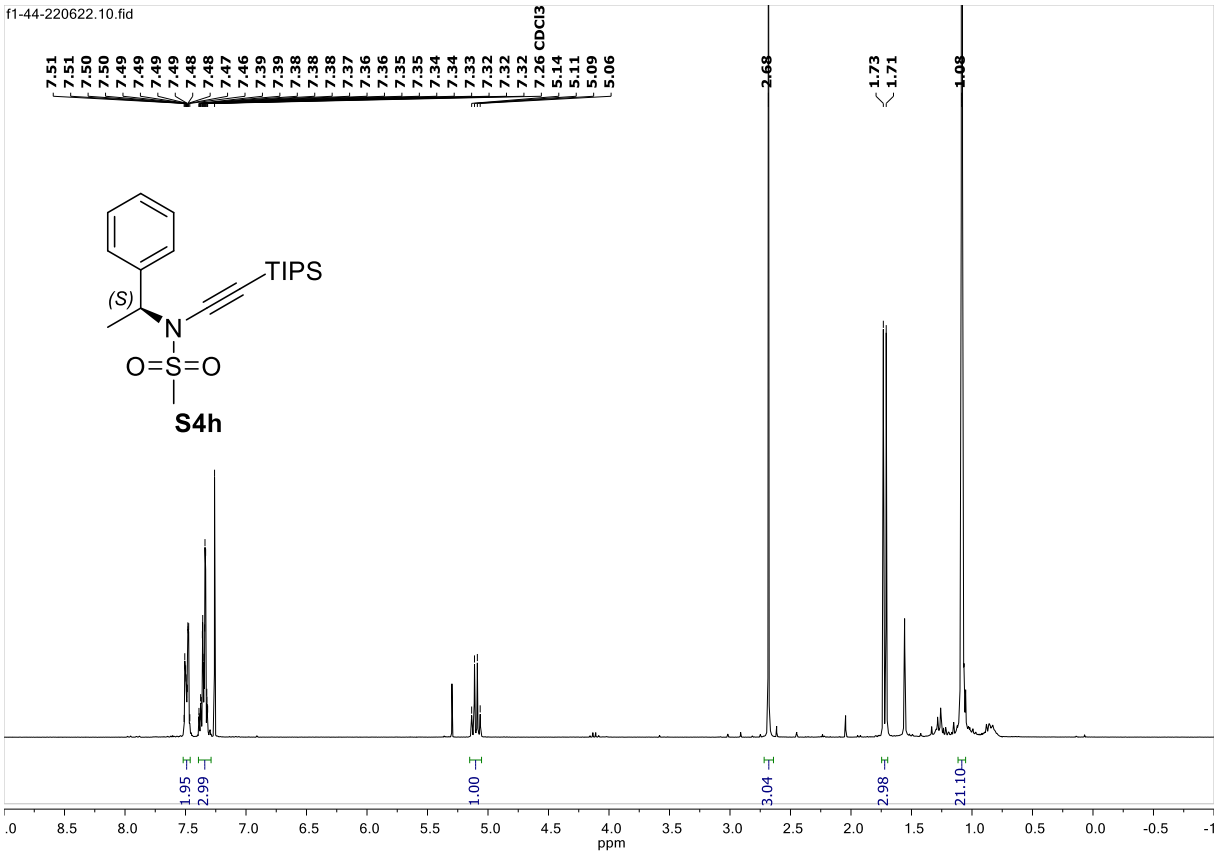
^{13}C NMR ($CDCl_3$, 126 MHz) of **S4f**



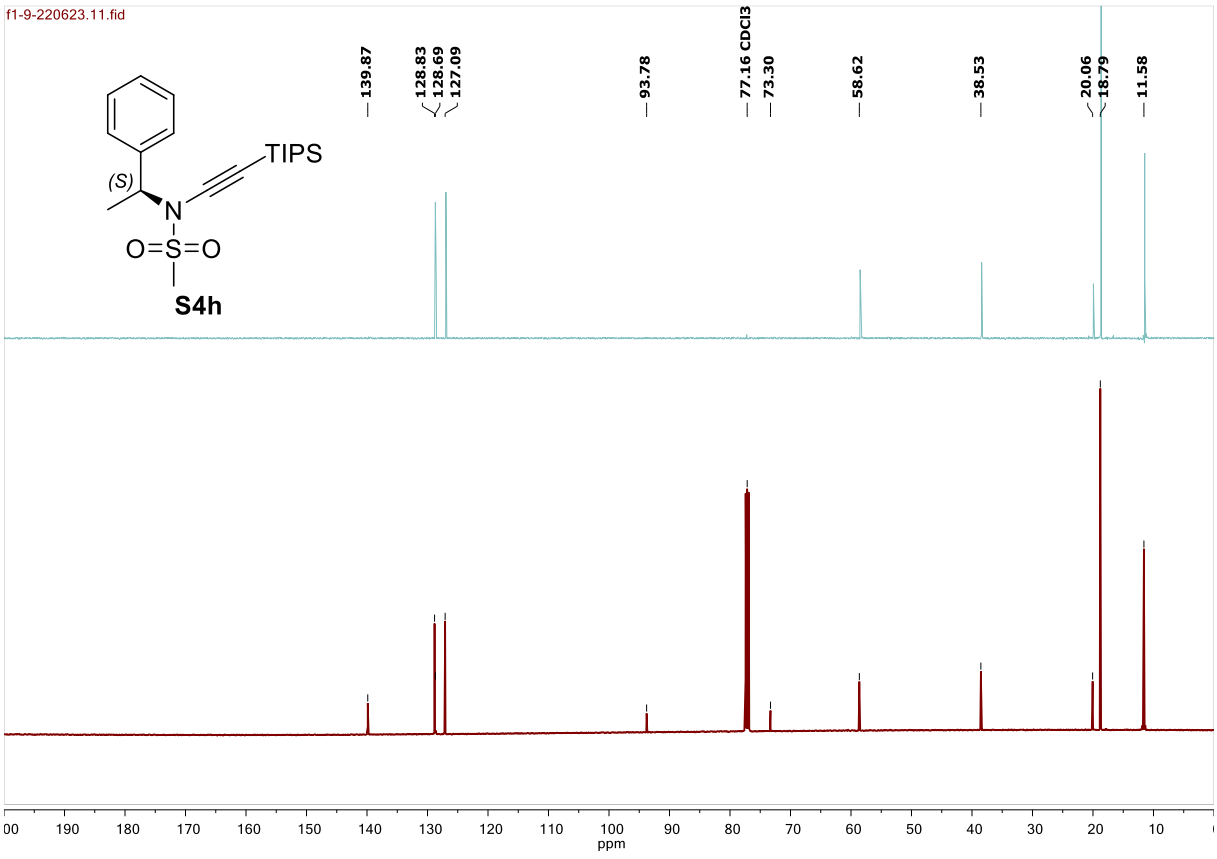
^{1}H NMR ($CDCl_3$, 300 MHz) of **S4g**



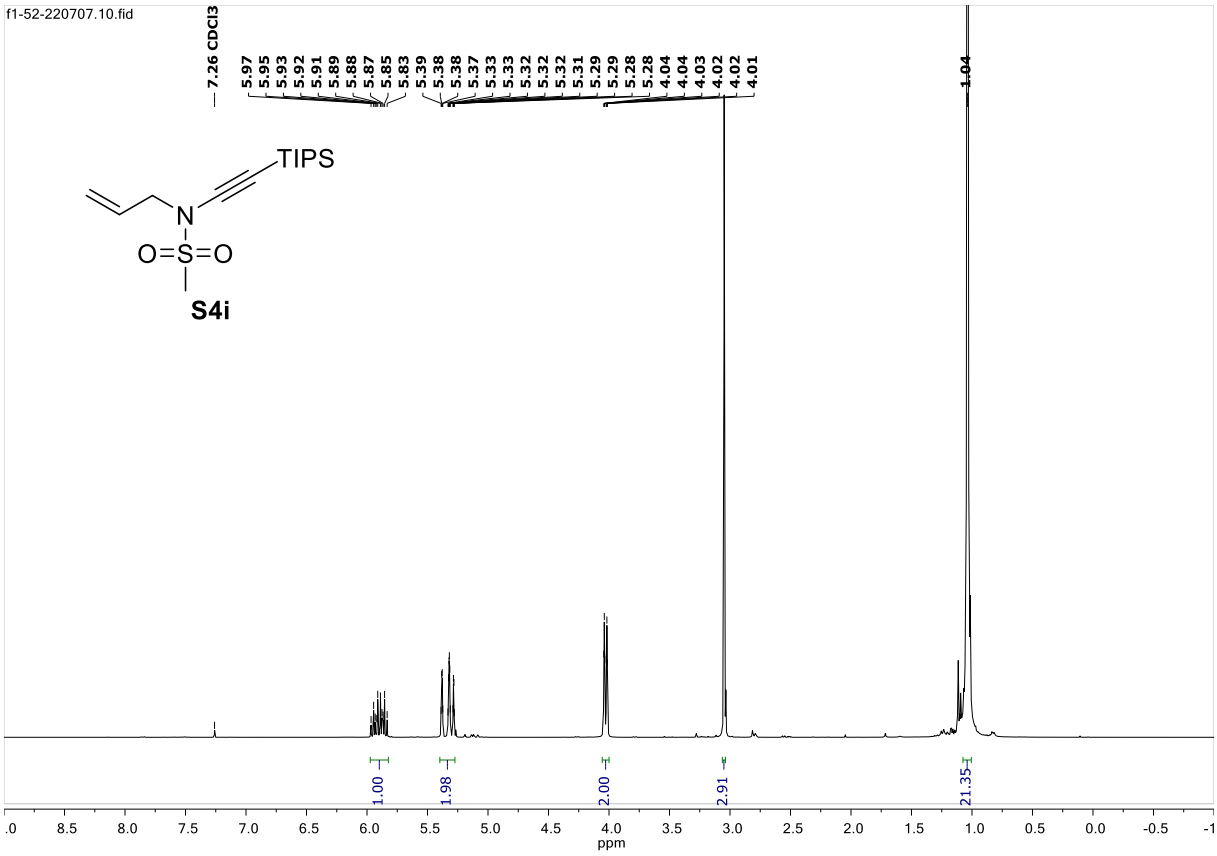
^{13}C NMR ($CDCl_3$, 126 MHz) of **S4g**



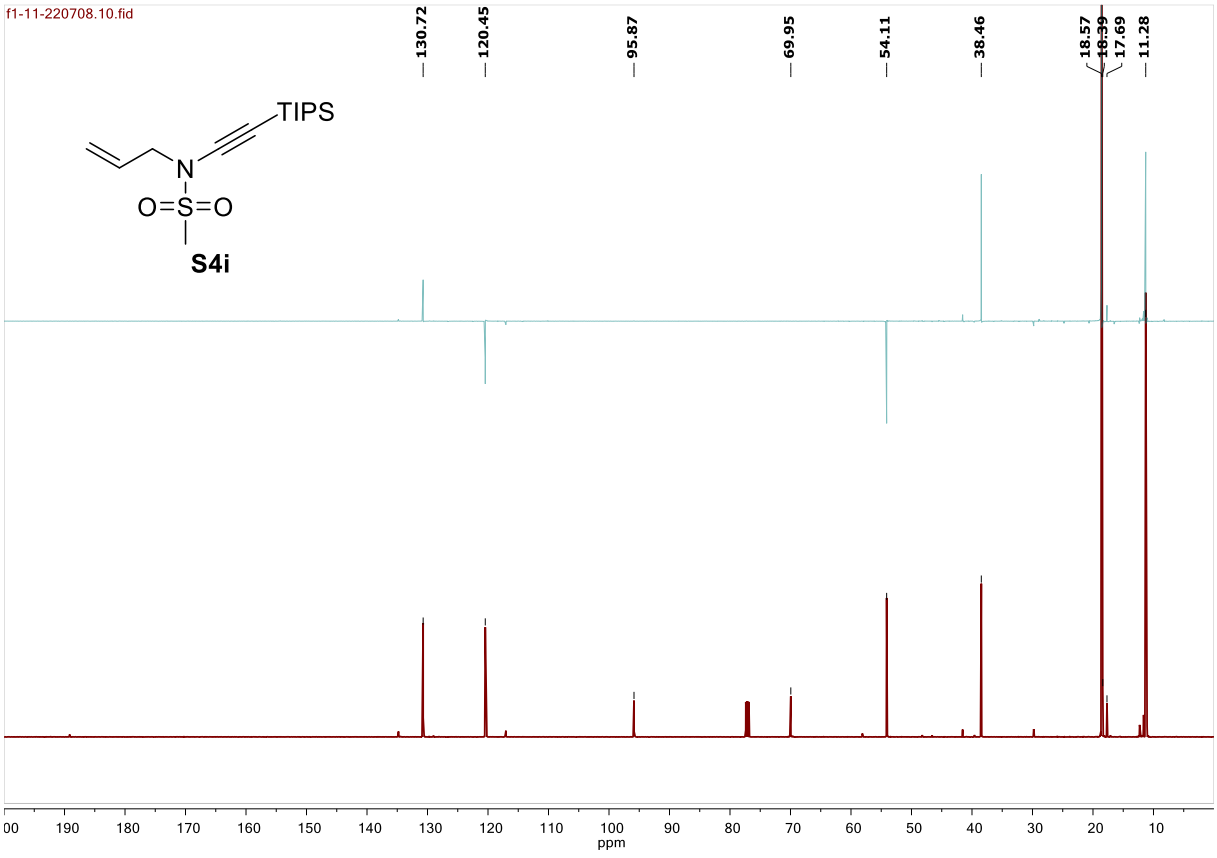
^{1}H NMR ($CDCl_3$, 300 MHz) of **S4h**



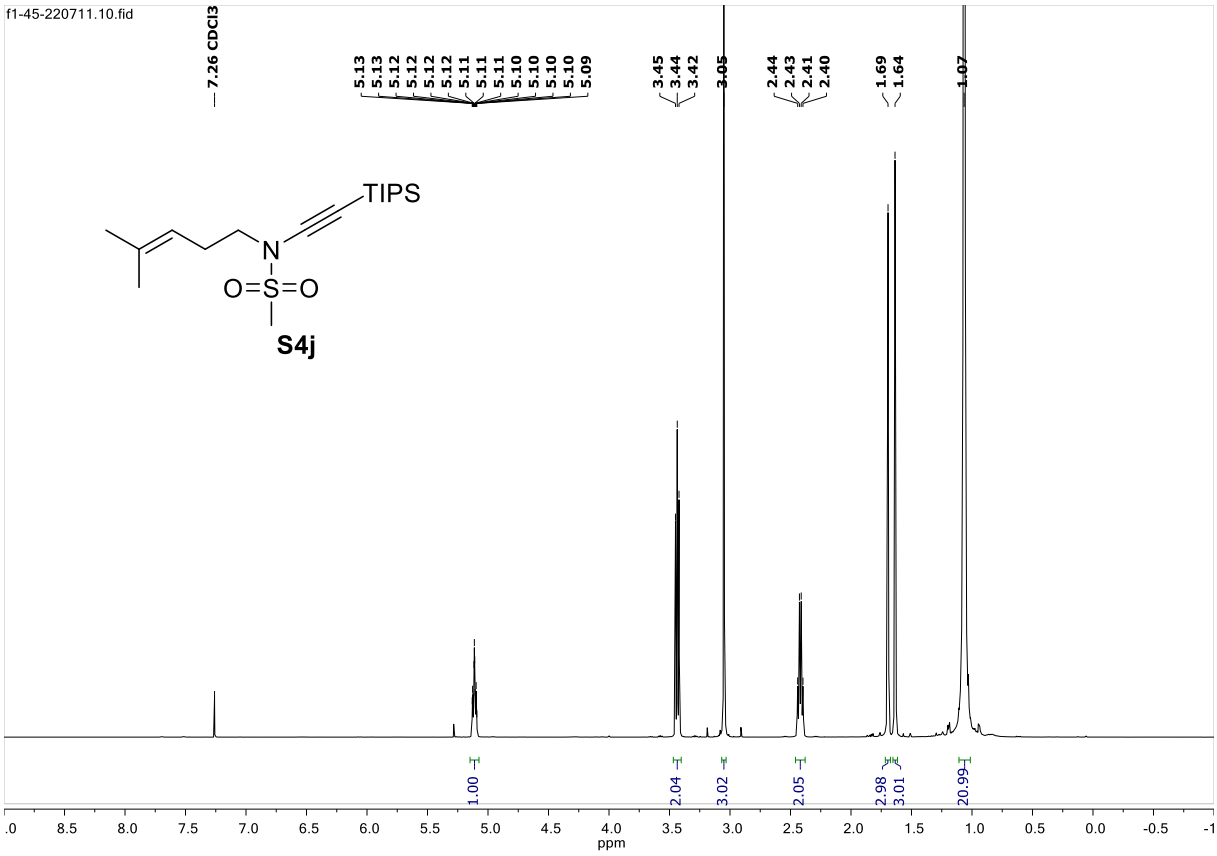
^{13}C NMR ($CDCl_3$, 126 MHz) of **S4h**



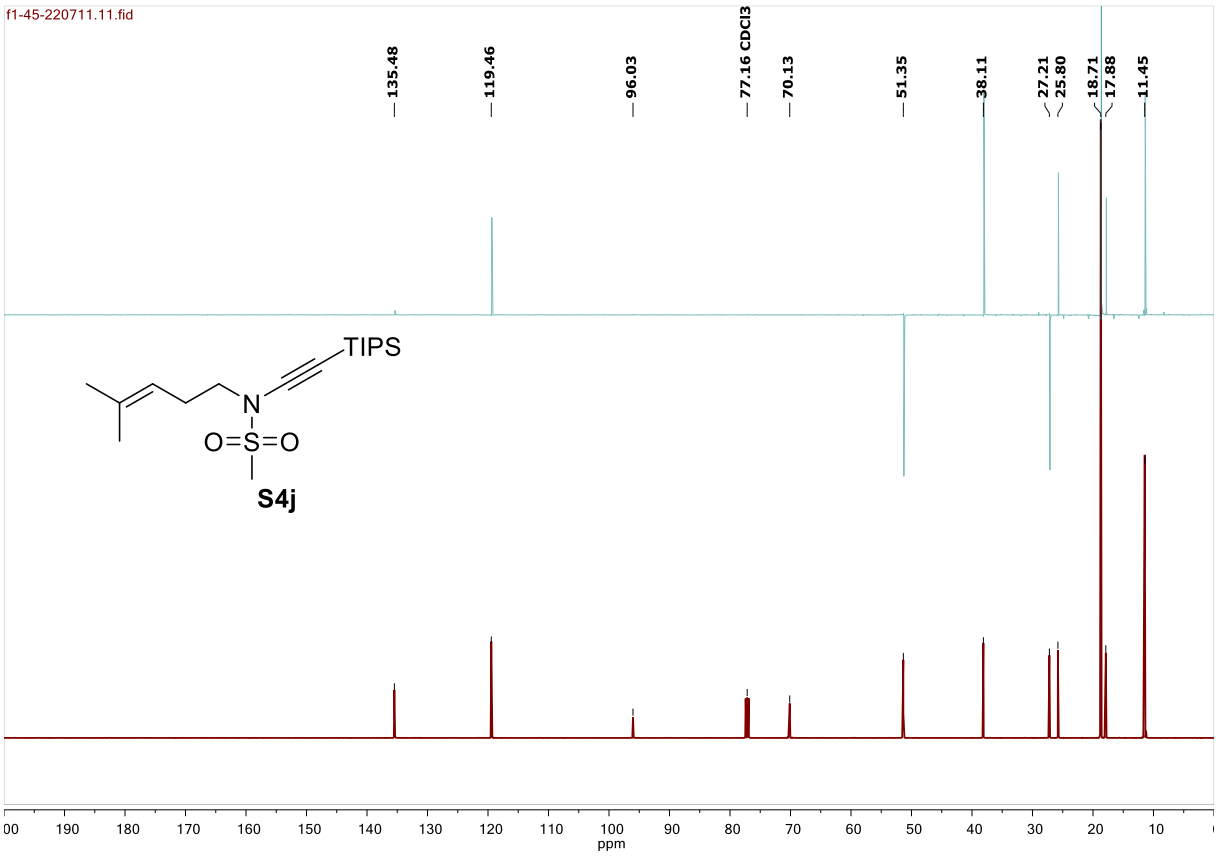
^{1}H NMR ($CDCl_3$, 300 MHz) of **S4i**



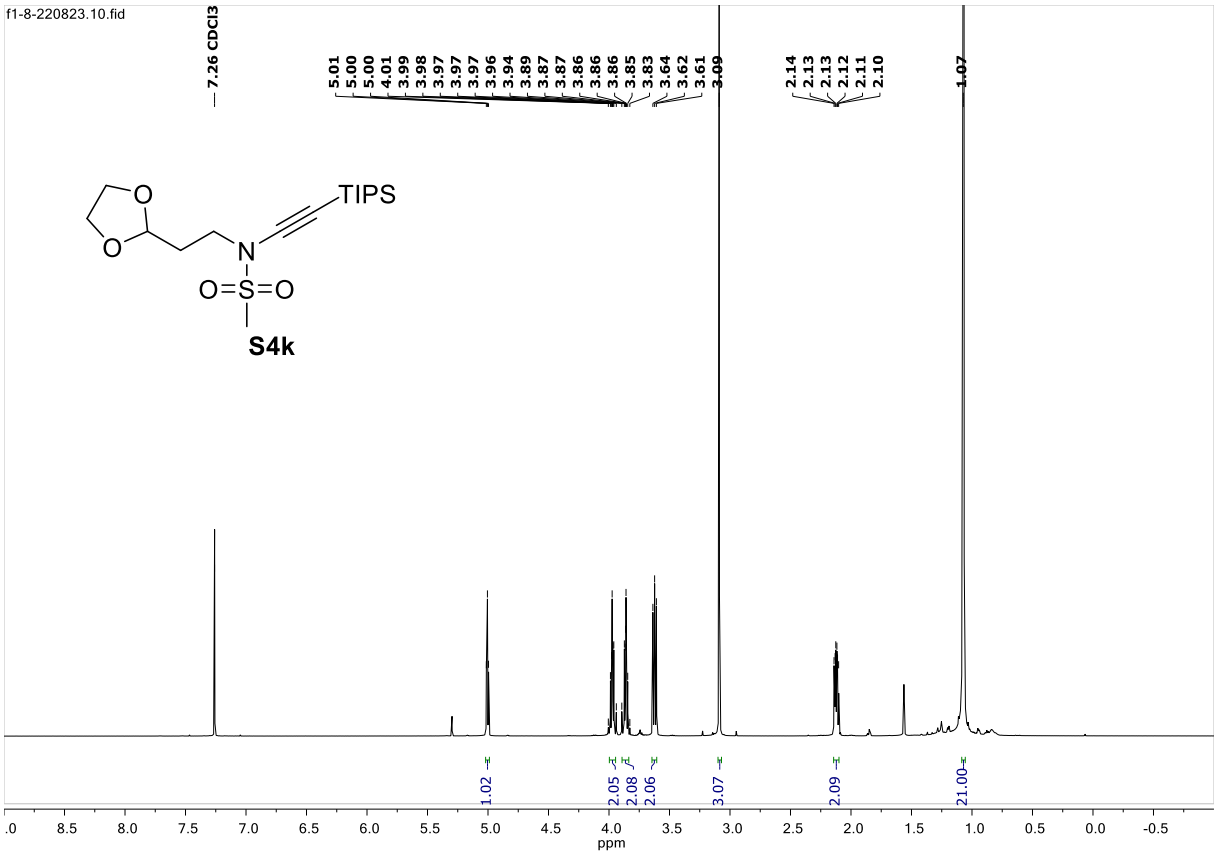
^{13}C NMR ($CDCl_3$, 126 MHz) of **S4i**



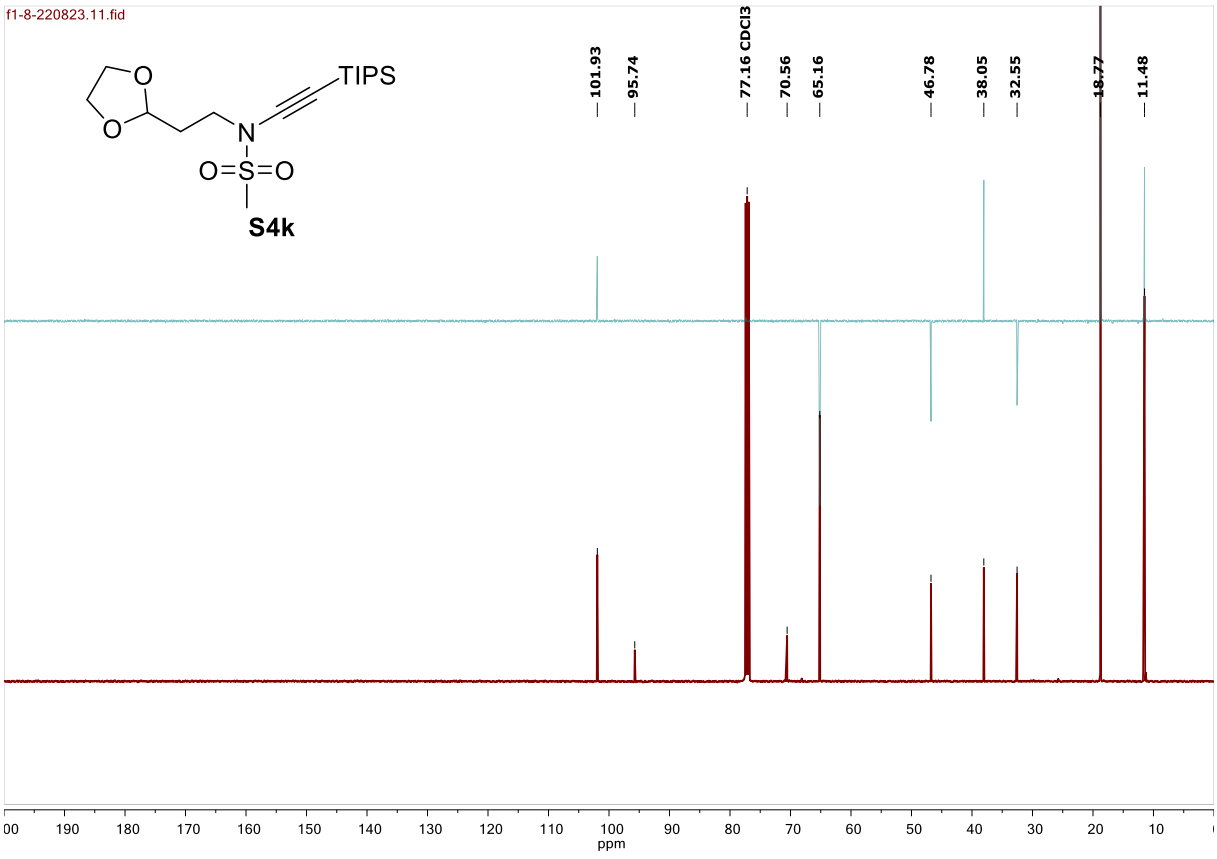
^{1}H NMR ($CDCl_3$, 300 MHz) of **S4j**



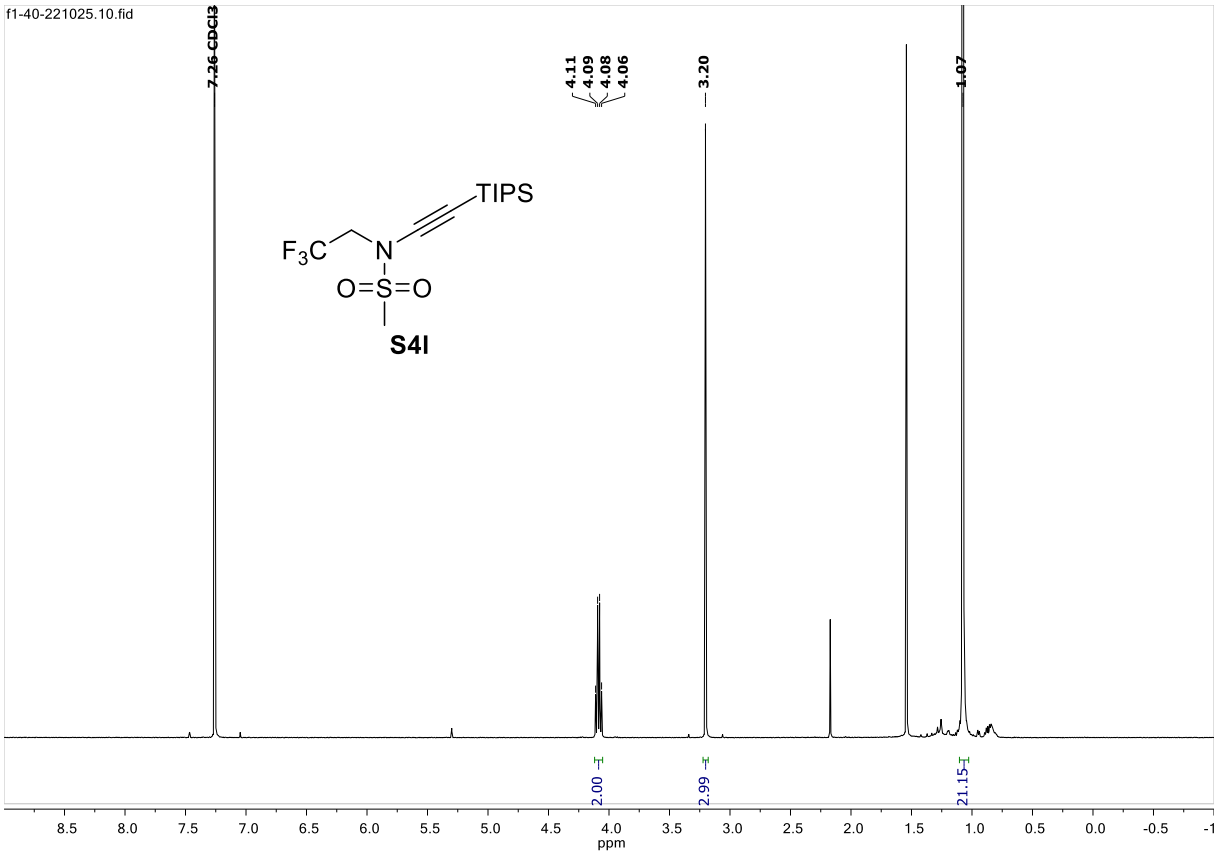
^{13}C NMR ($CDCl_3$, 126 MHz) of **S4j**



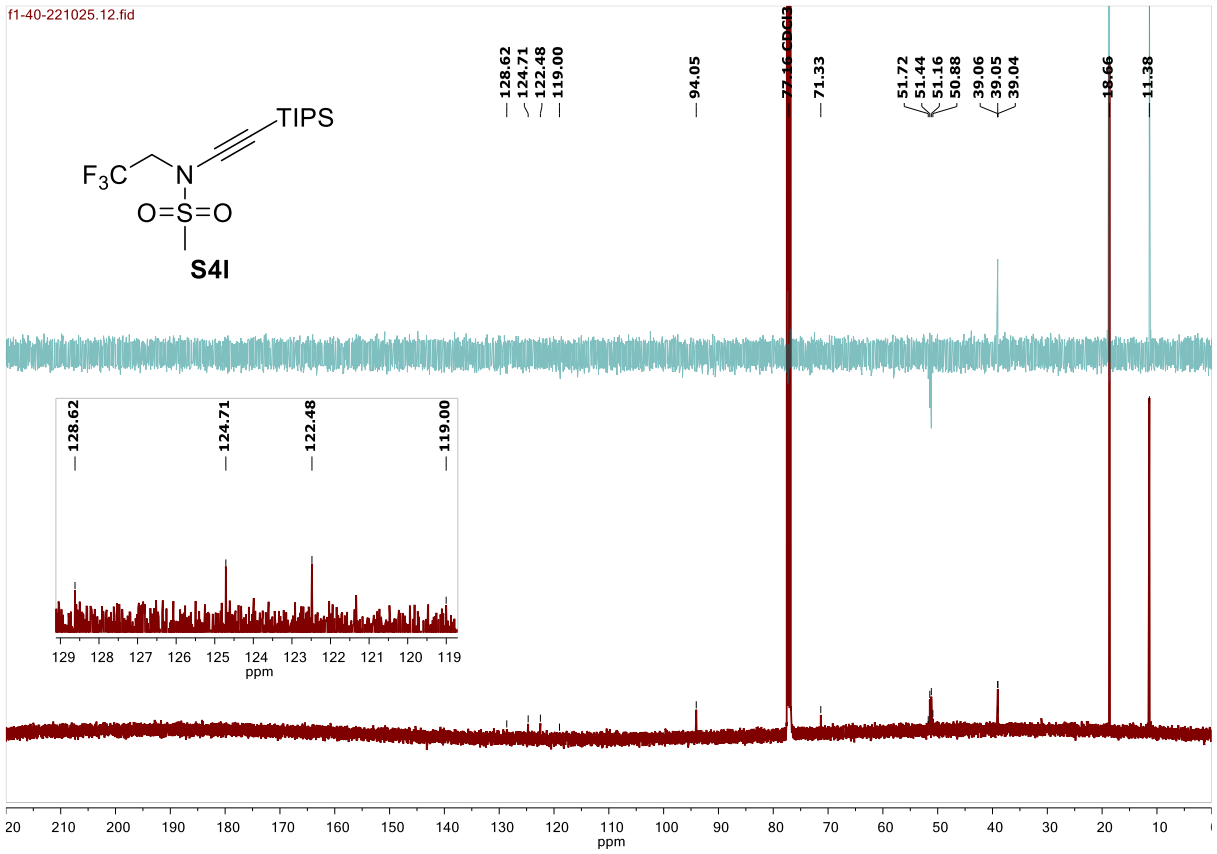
^{1}H NMR ($CDCl_3$, 500 MHz) of **S4k**



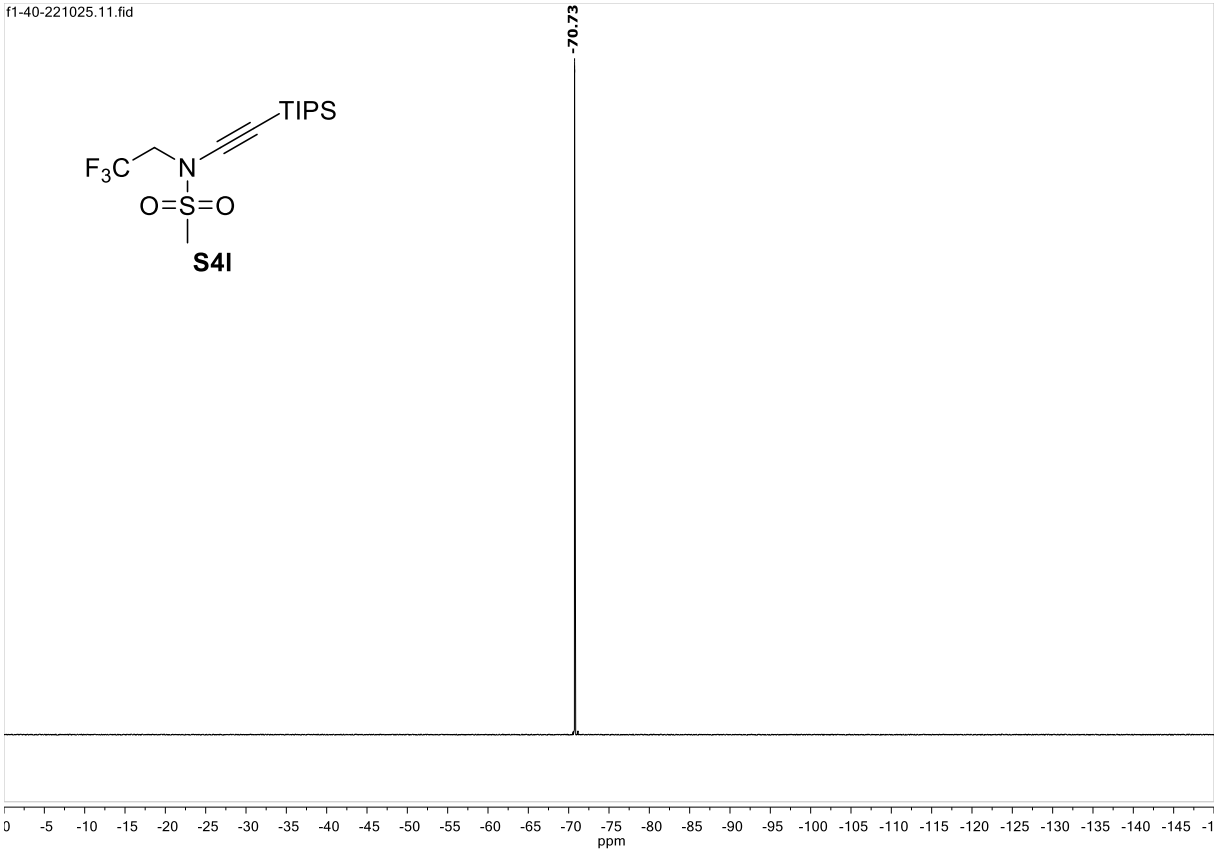
^{13}C NMR ($CDCl_3$, 126 MHz) of **S4k**



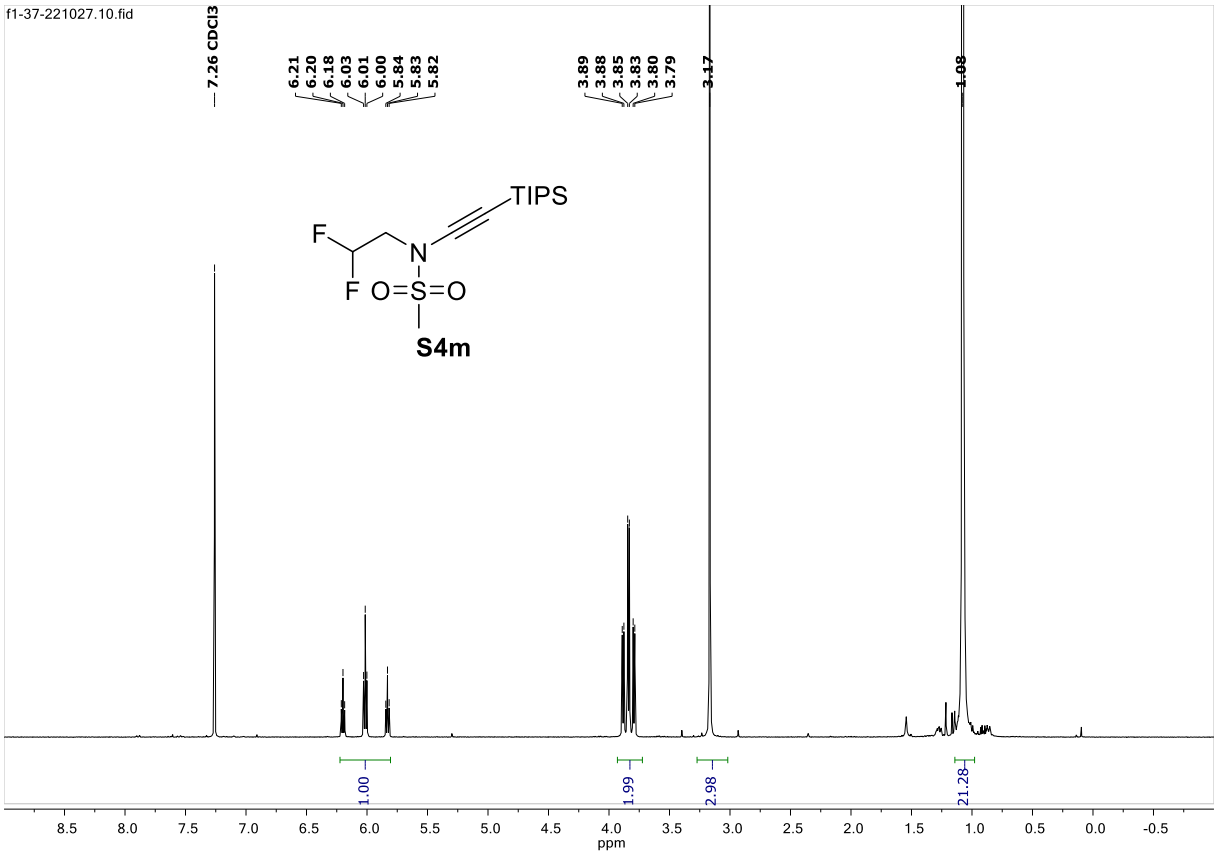
^{1}H NMR ($CDCl_3$, 500 MHz) of **S4l**



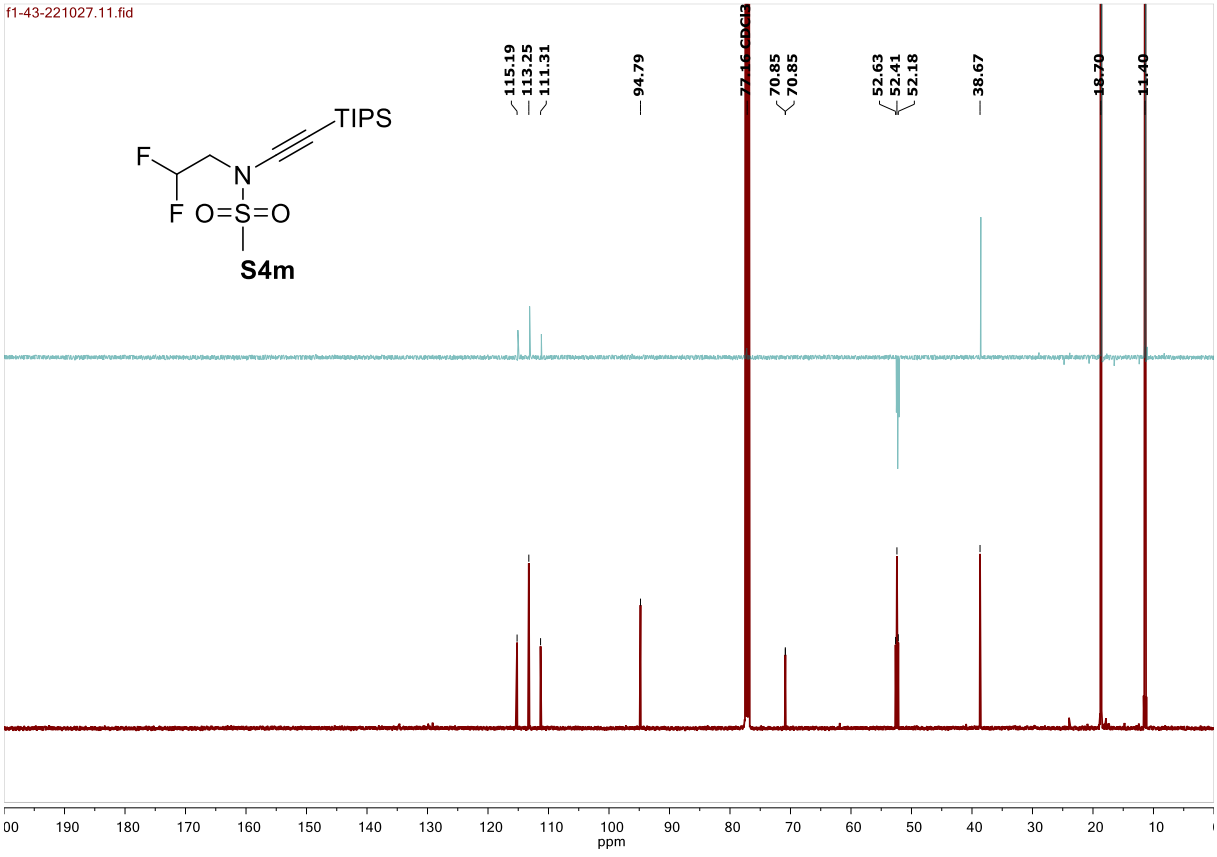
^{13}C NMR ($CDCl_3$, 126 MHz) of **S4l**



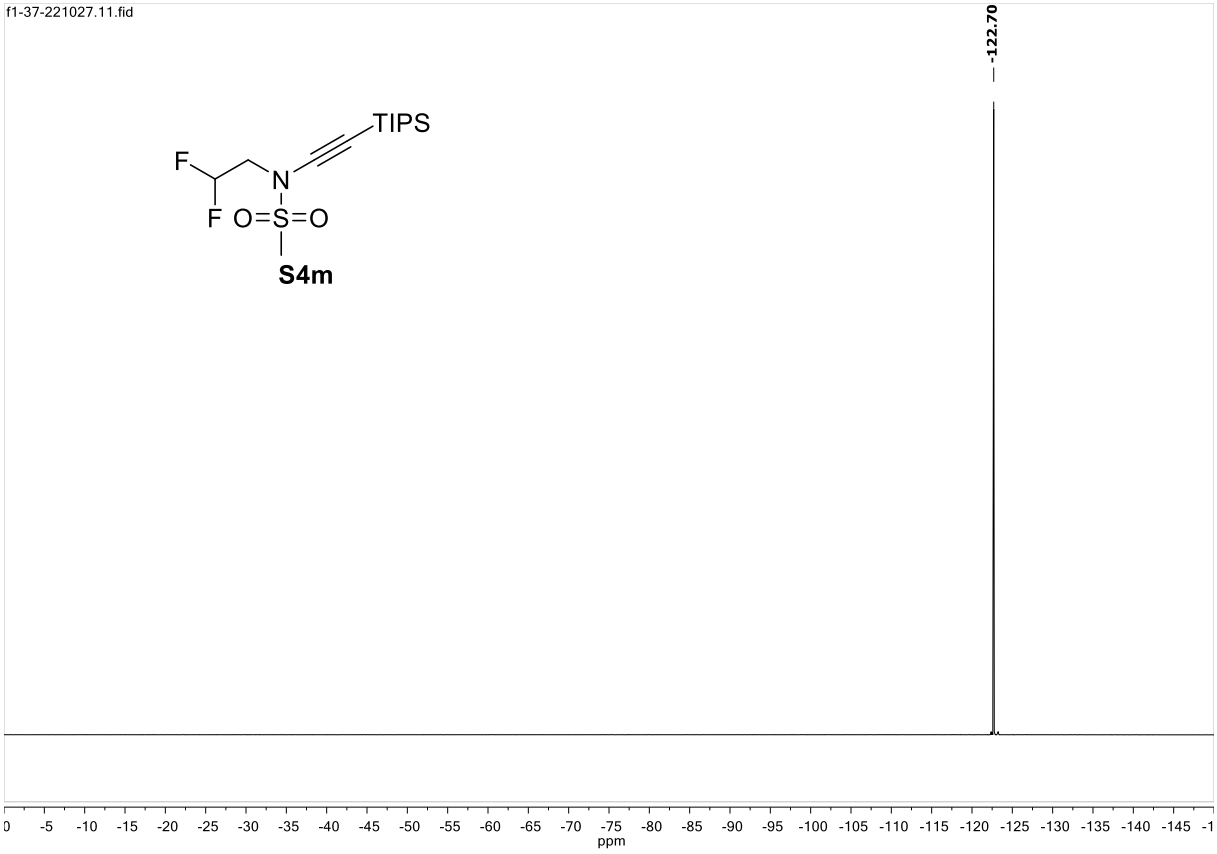
^{19}F NMR ($CDCl_3$, 282 MHz) of **S4l**



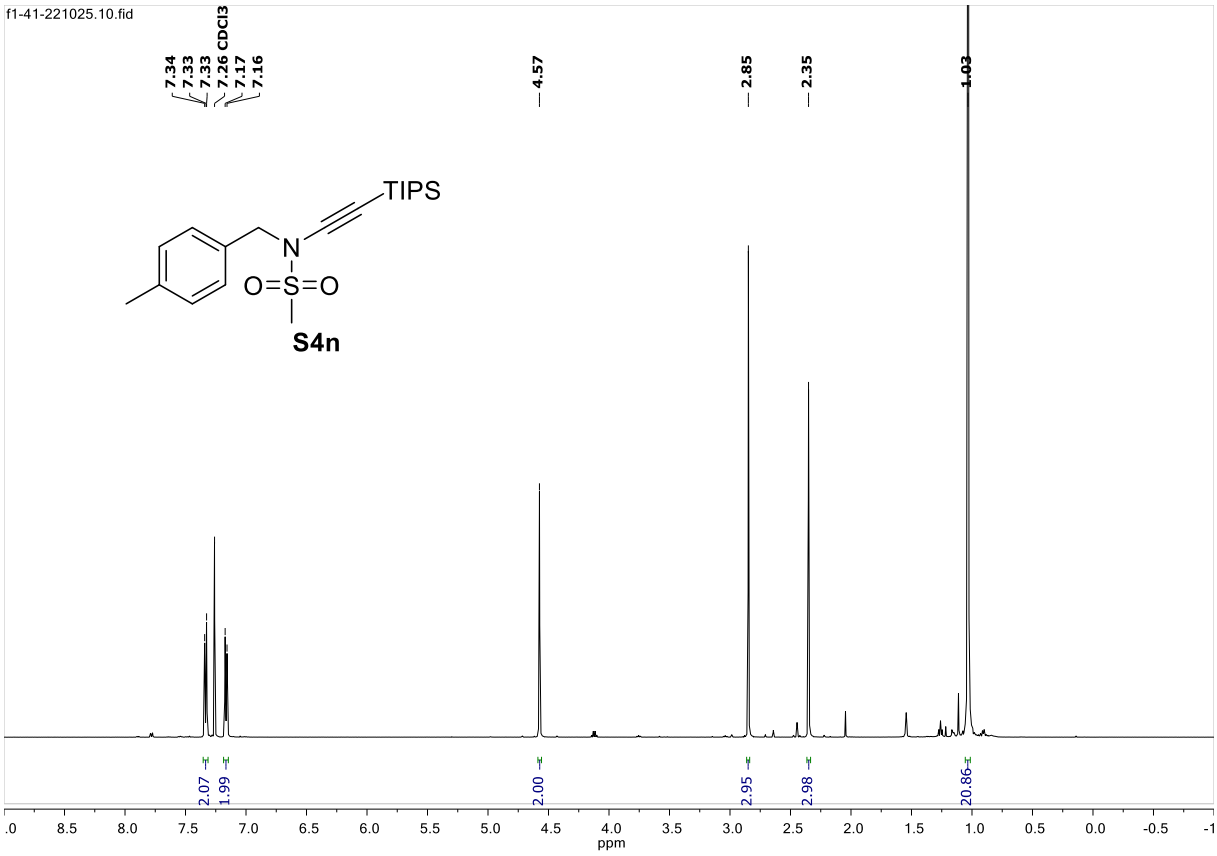
^{1}H NMR ($CDCl_3$, 300 MHz) of **S4m**



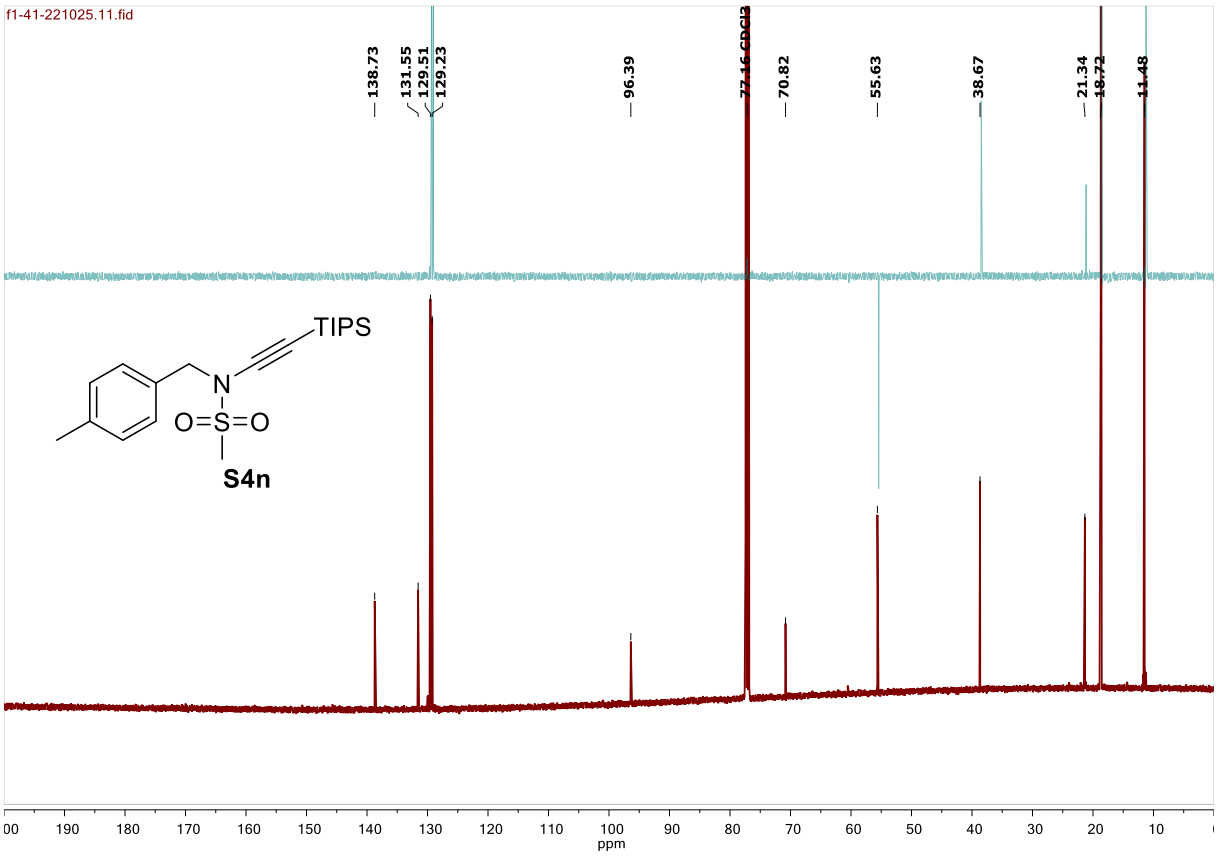
^{13}C NMR ($CDCl_3$, 126 MHz) of **S4m**



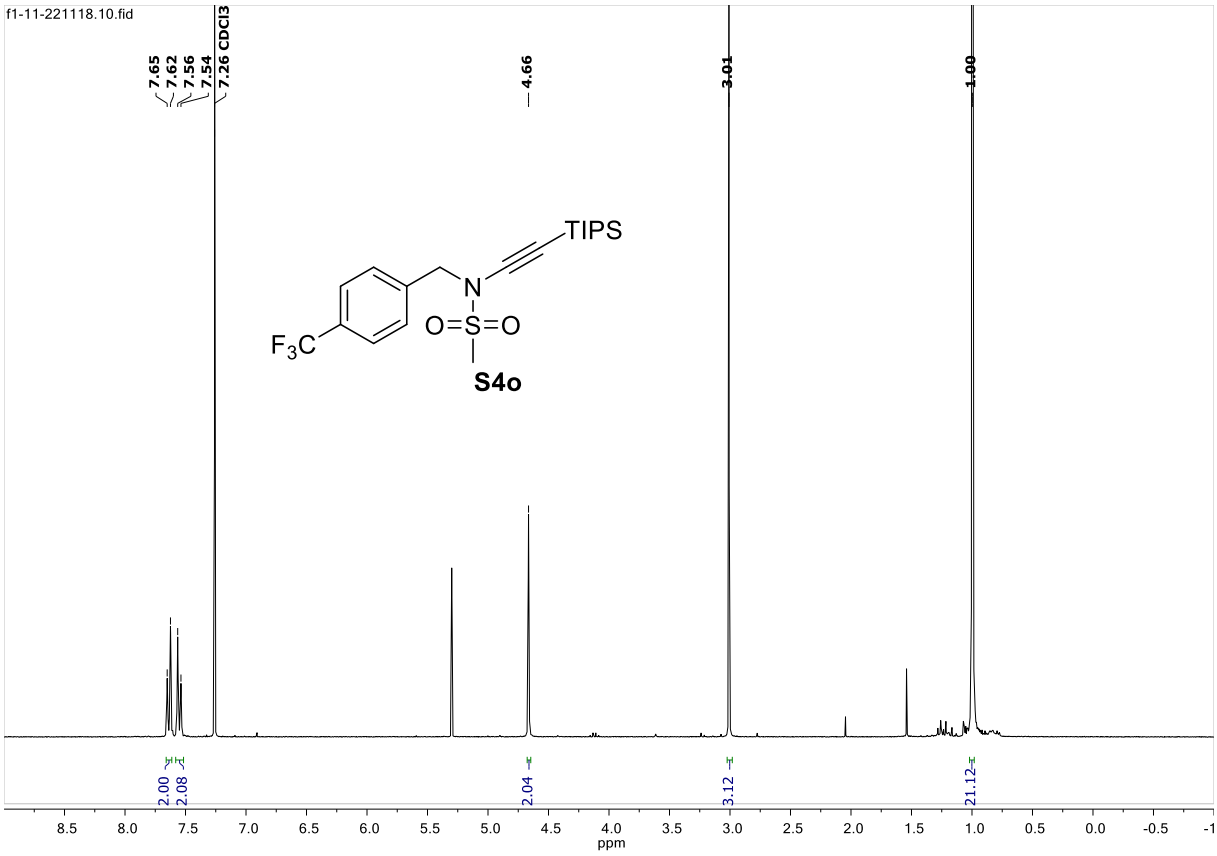
^{19}F NMR ($CDCl_3$, 282 MHz) of **S4m**



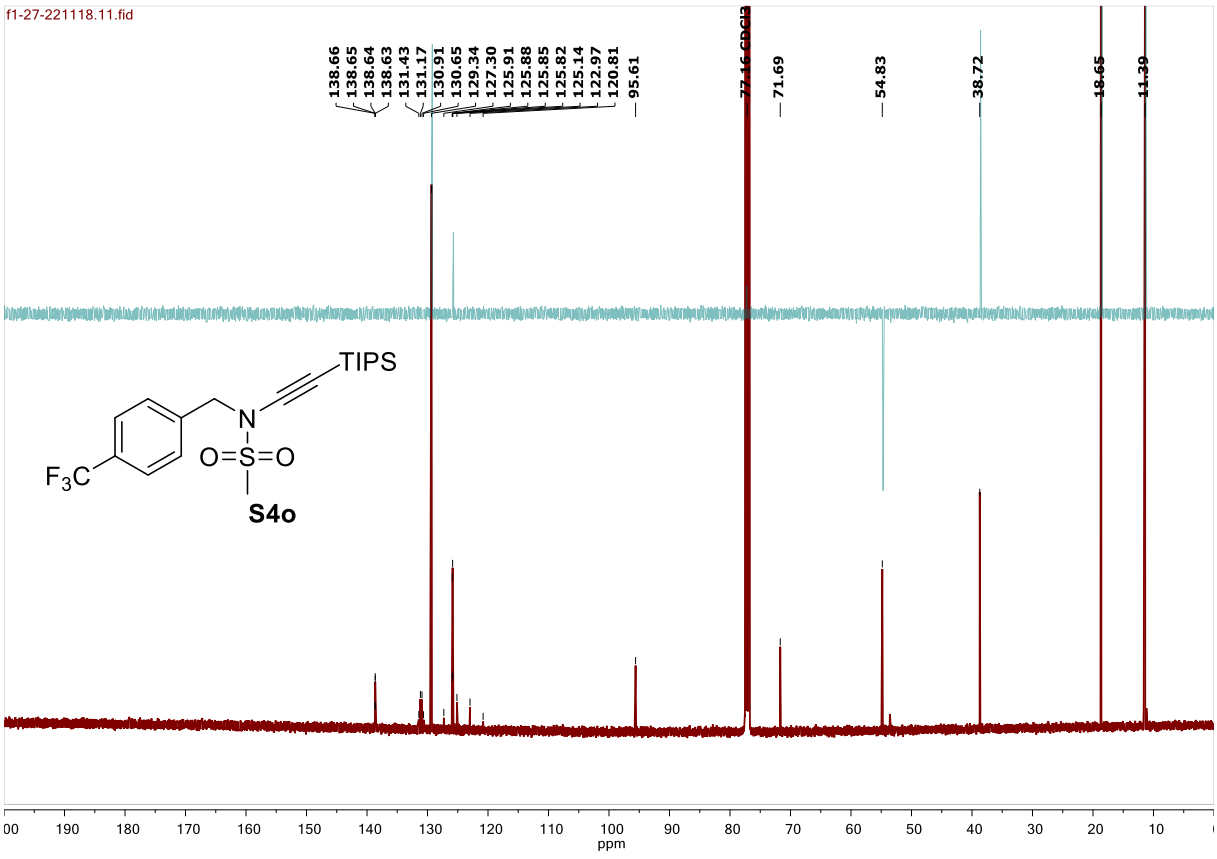
^{1}H NMR ($CDCl_3$, 500 MHz) of **S4n**



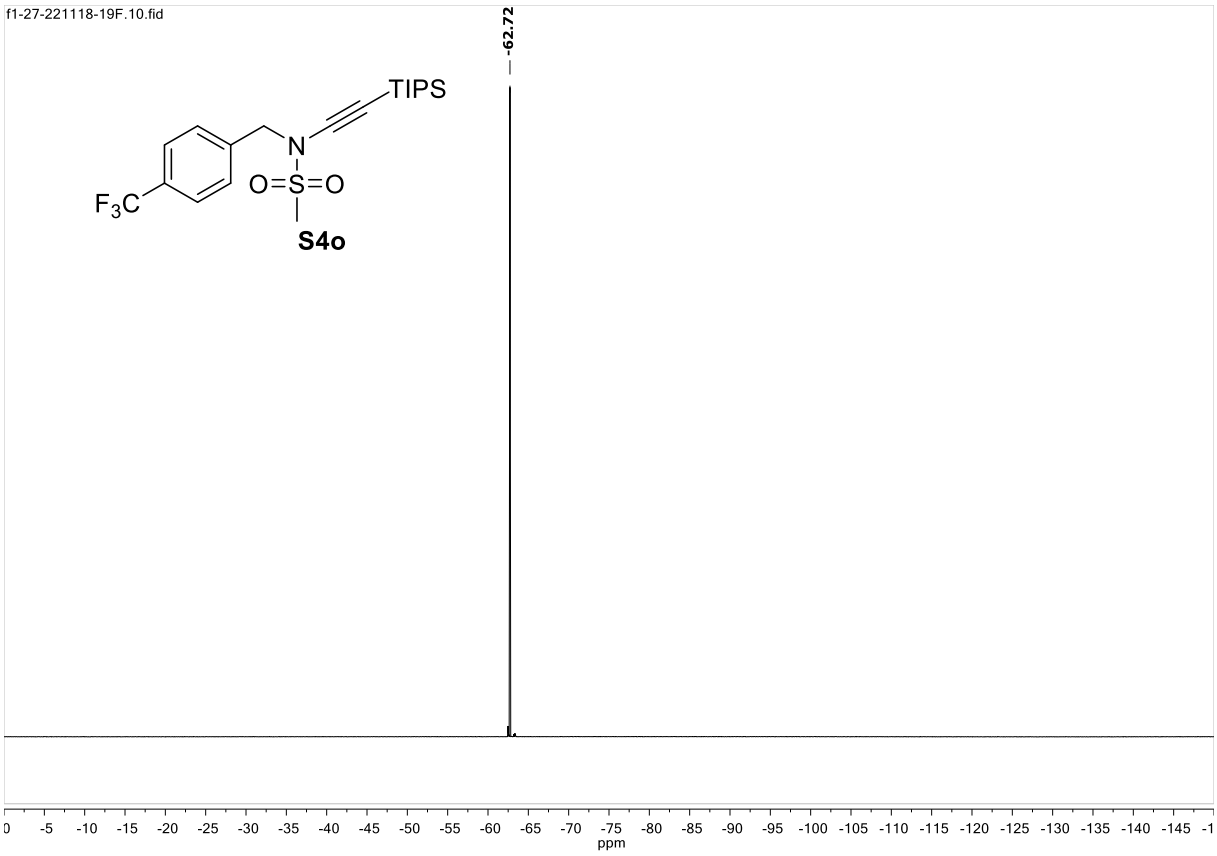
^{13}C NMR ($CDCl_3$, 126 MHz) of **S4n**



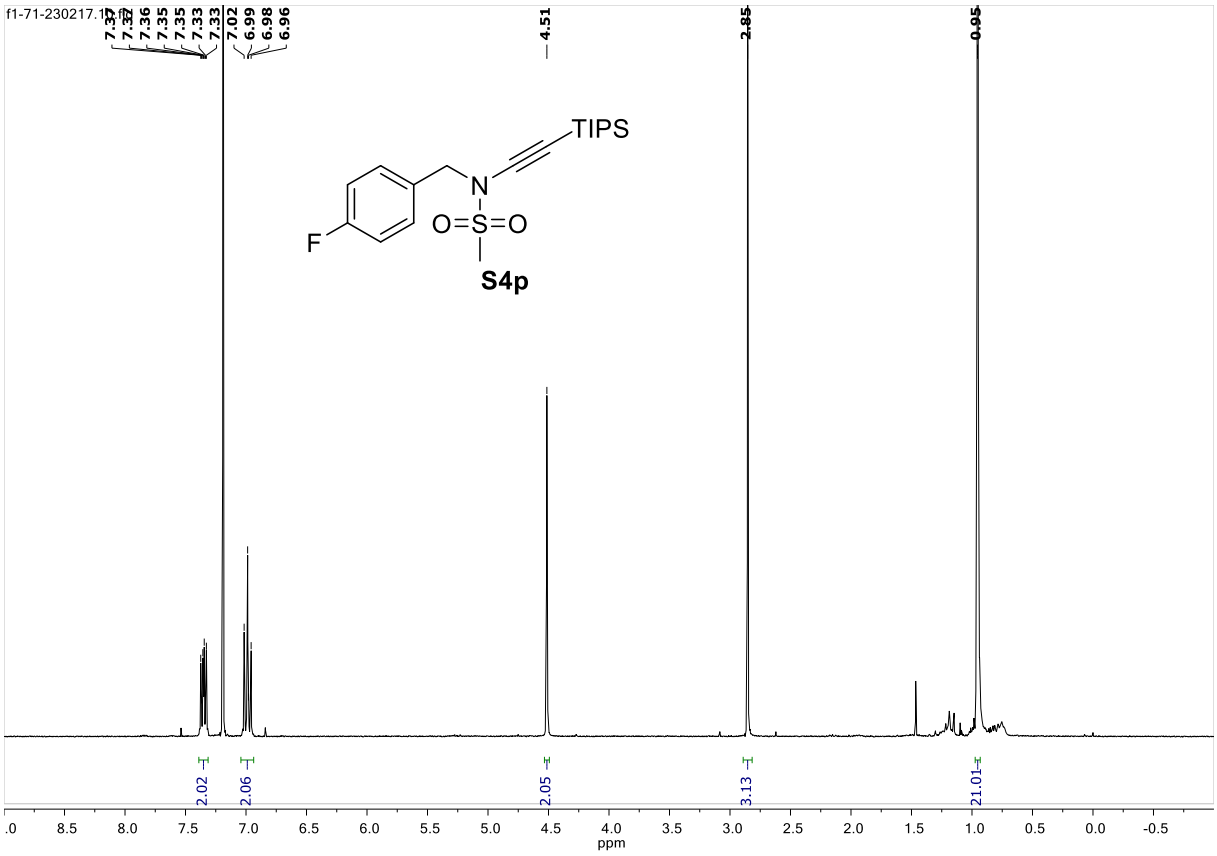
^{1}H NMR ($CDCl_3$, 500 MHz) of **S4o**



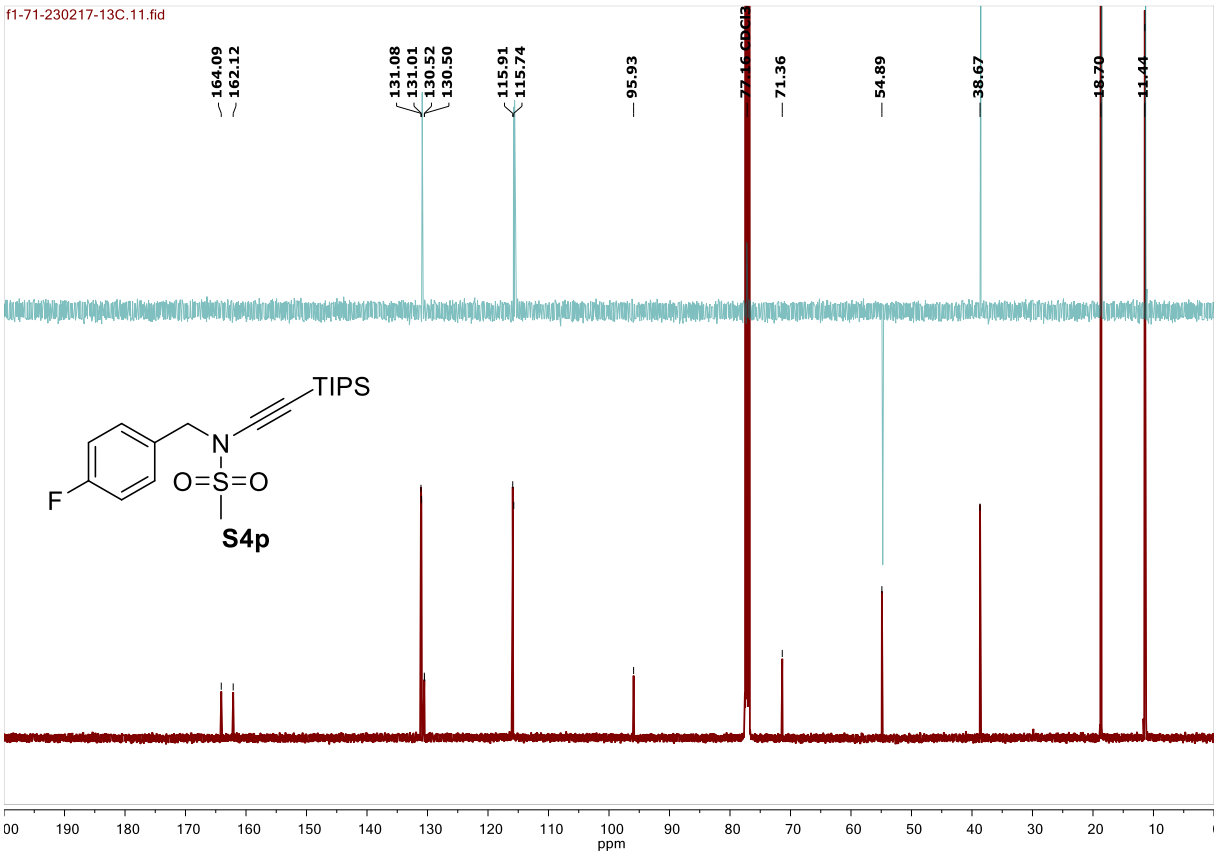
^{13}C NMR ($CDCl_3$, 126 MHz) of **S4o**



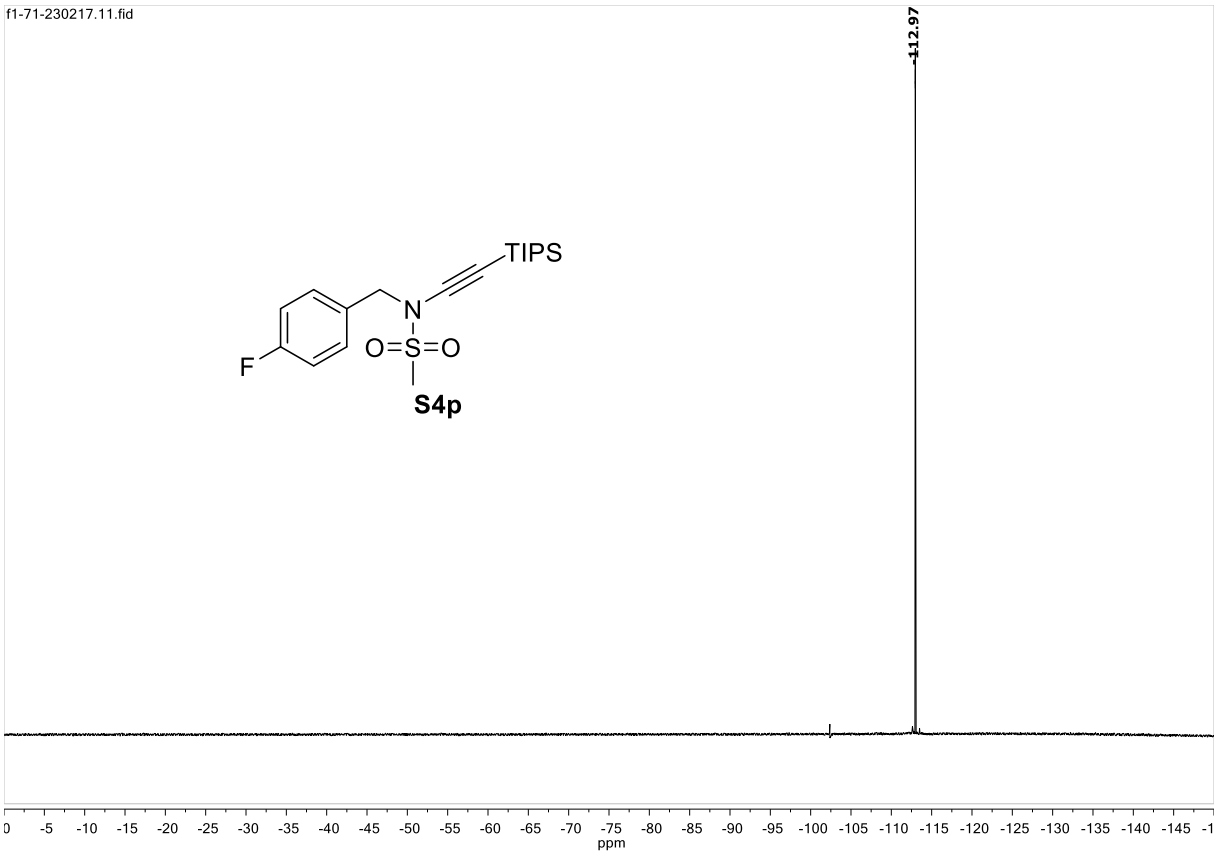
^{19}F NMR ($CDCl_3$, 282 MHz) of **S4o**



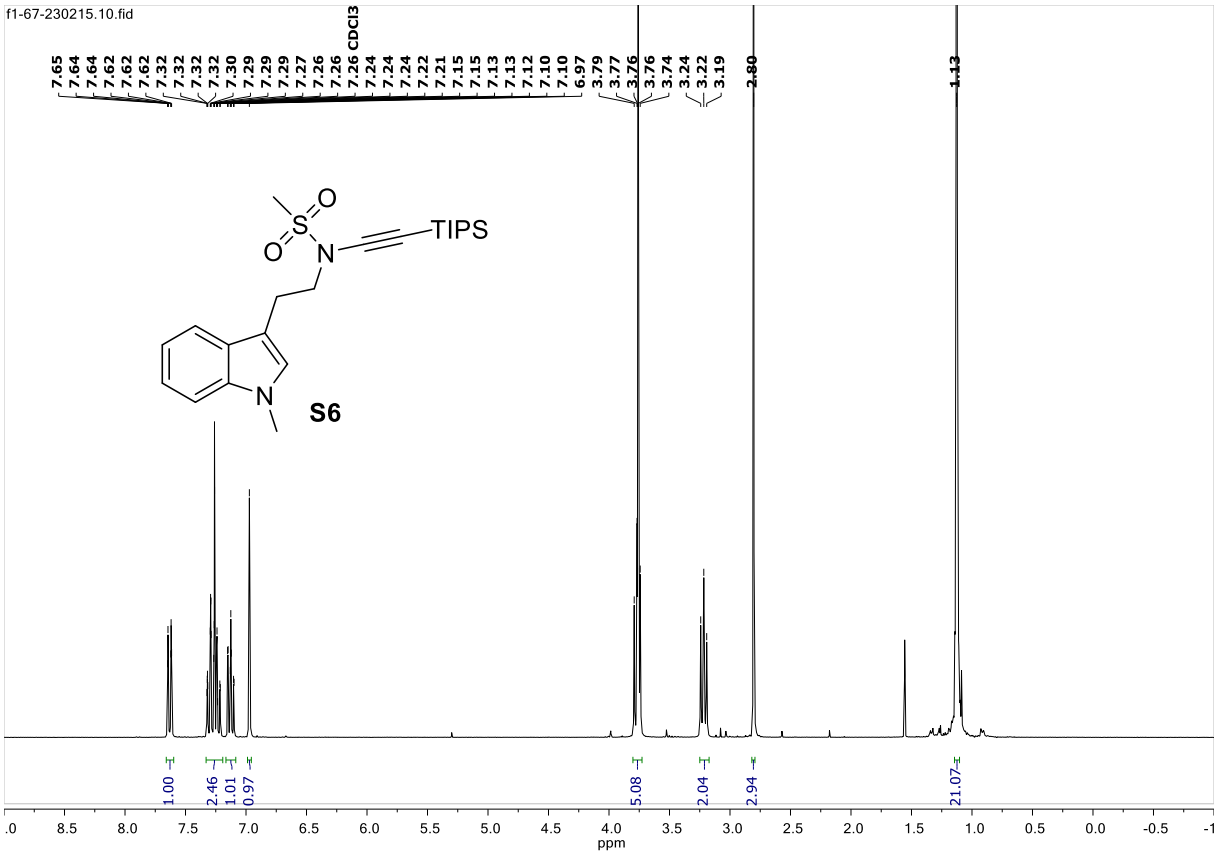
^{1}H NMR ($CDCl_3$, 300 MHz) of **S4p**



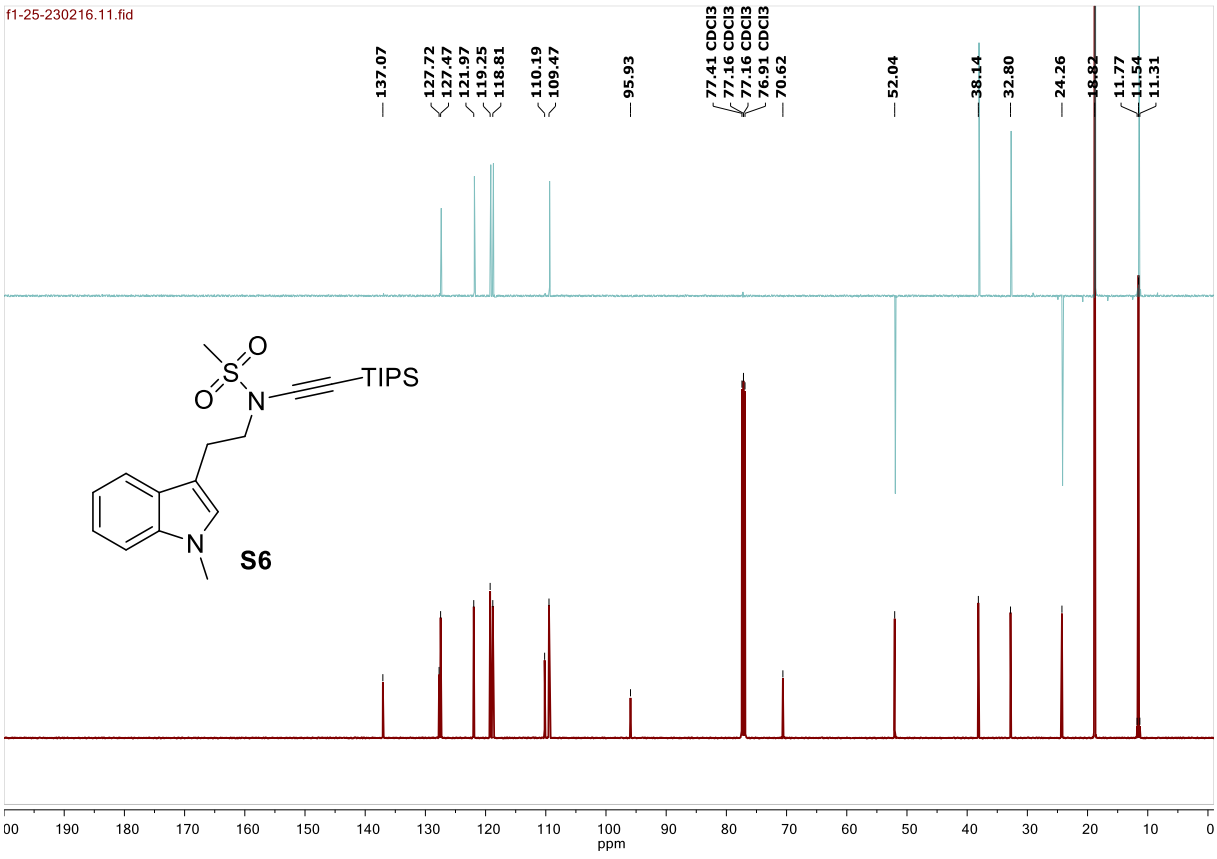
^{13}C NMR ($CDCl_3$, 126 MHz) of **S4p**



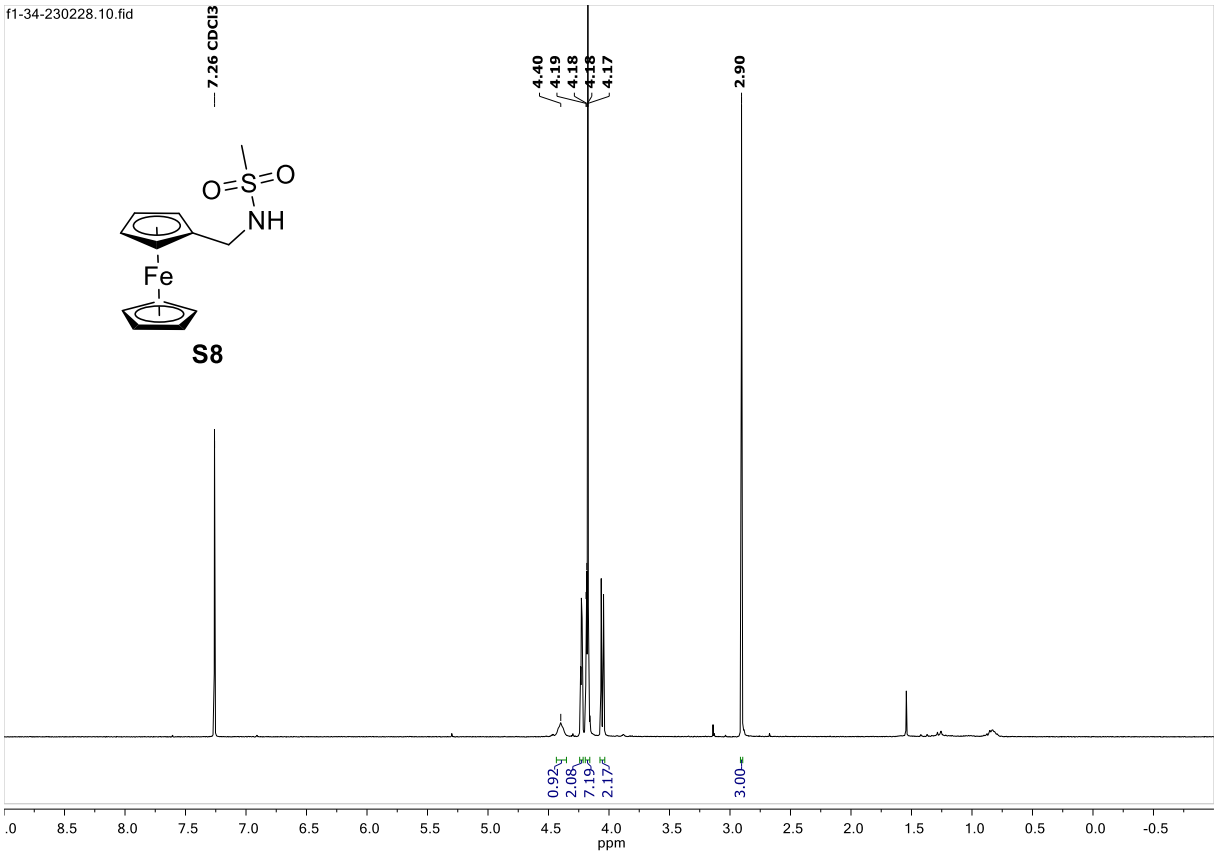
^{19}F NMR ($CDCl_3$, 282 MHz) of **S4p**



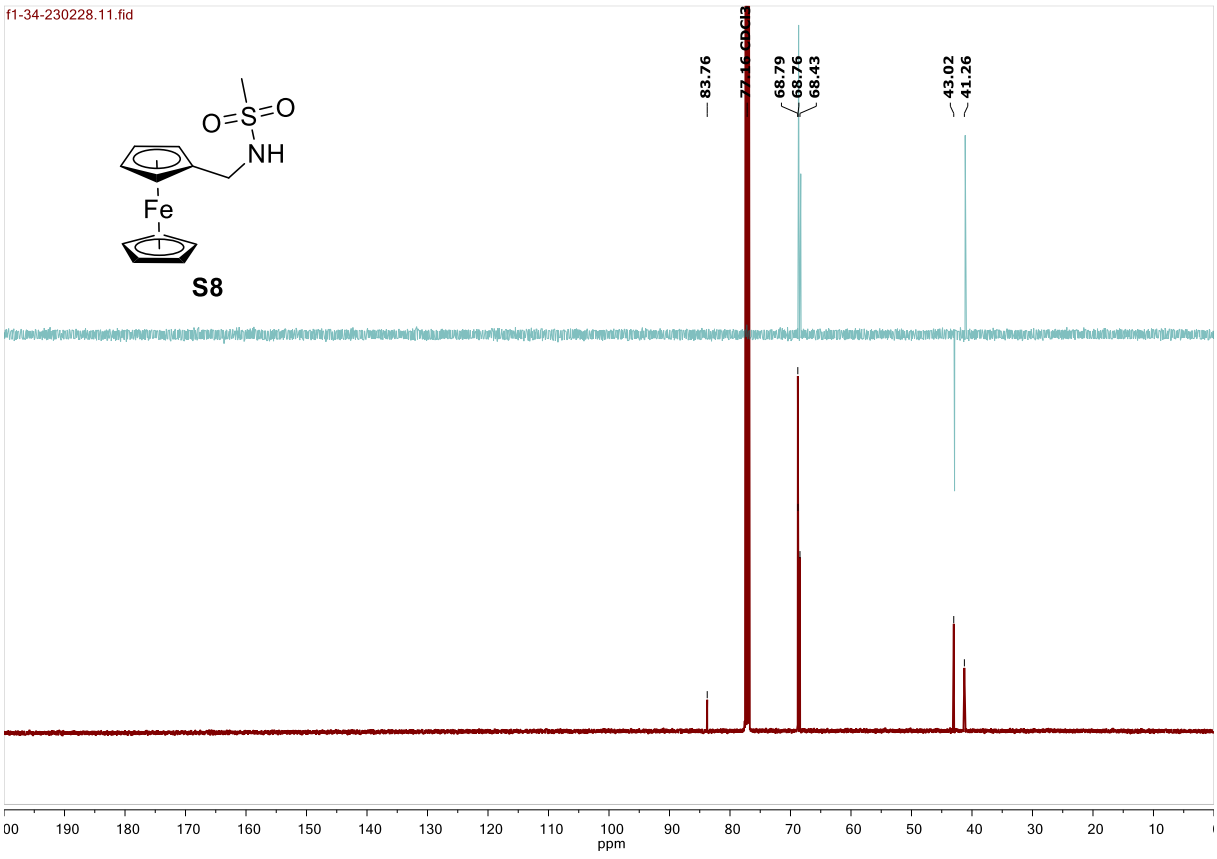
^{1}H NMR ($CDCl_3$, 300 MHz) of **S6**



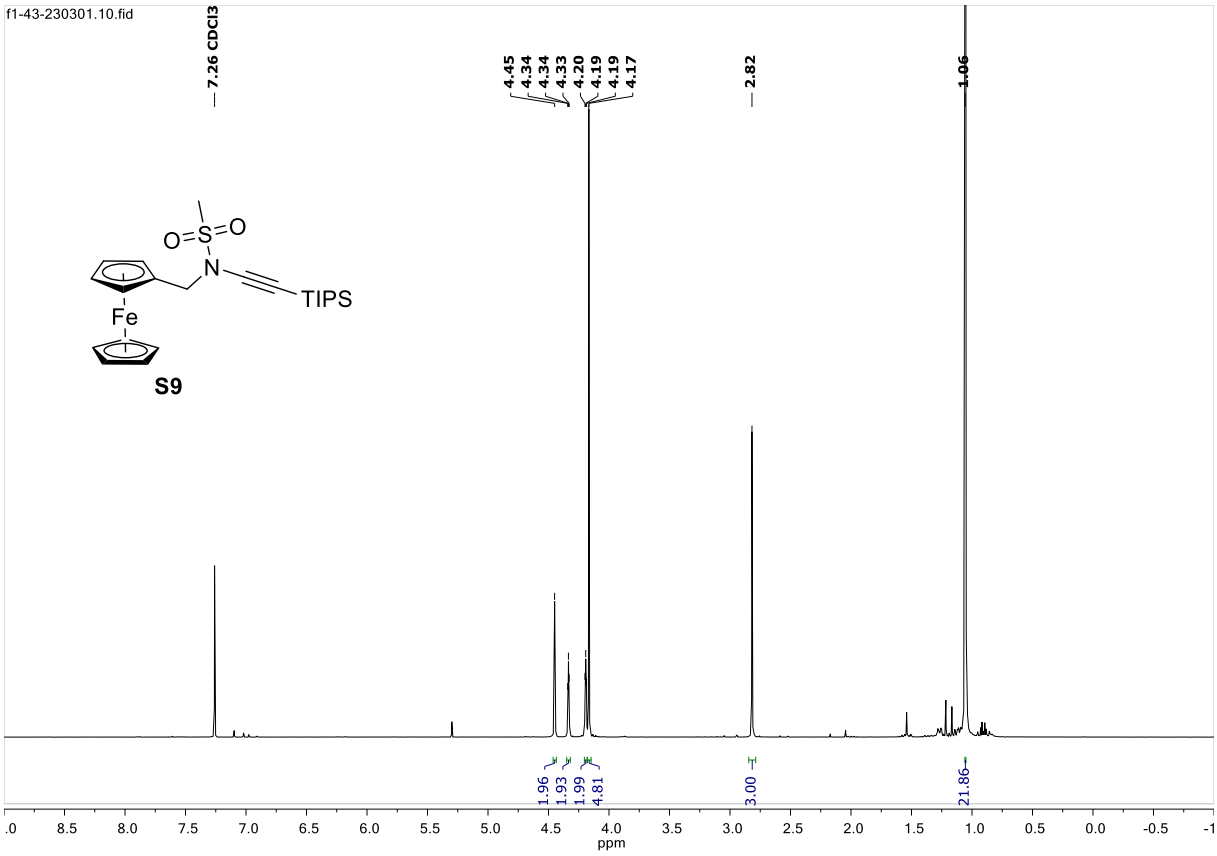
^{13}C NMR ($CDCl_3$, 126 MHz) of **S6**



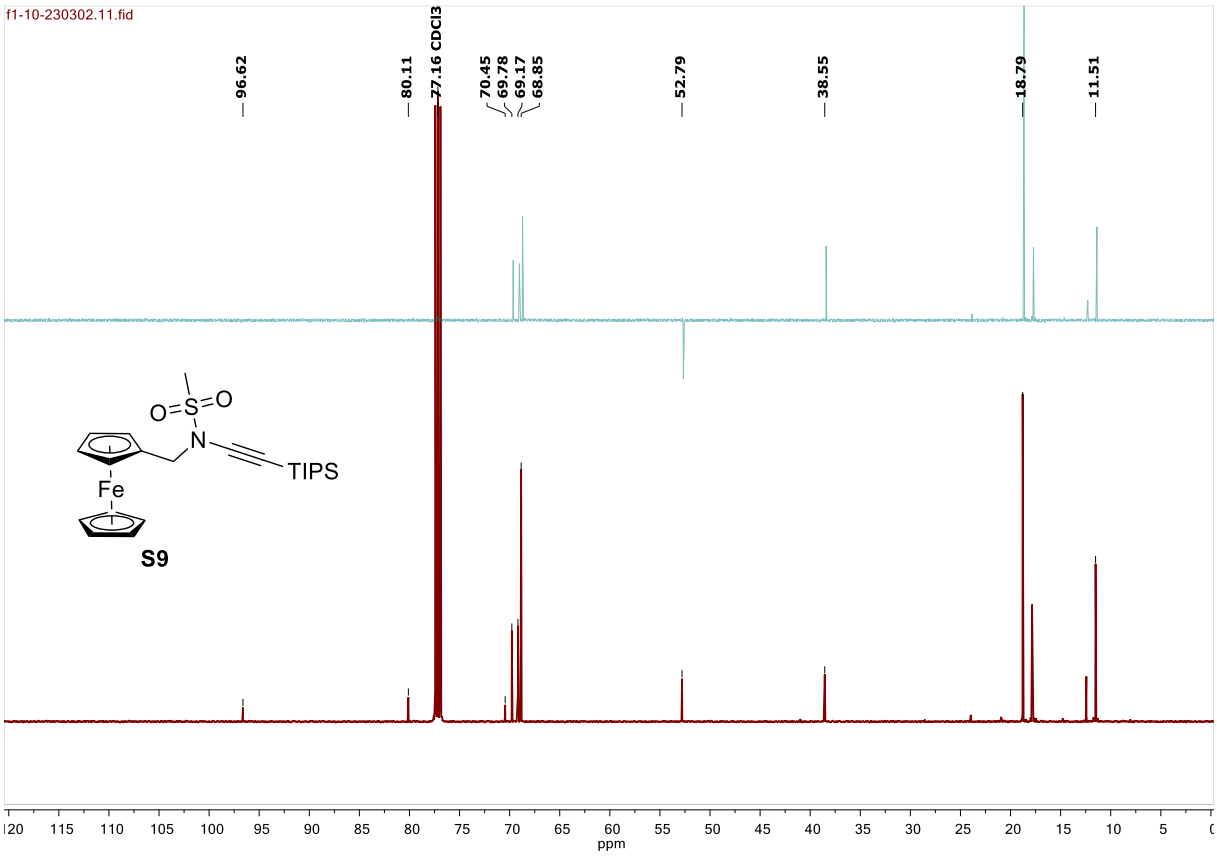
^{1}H NMR ($CDCl_3$, 300 MHz) of **S8**



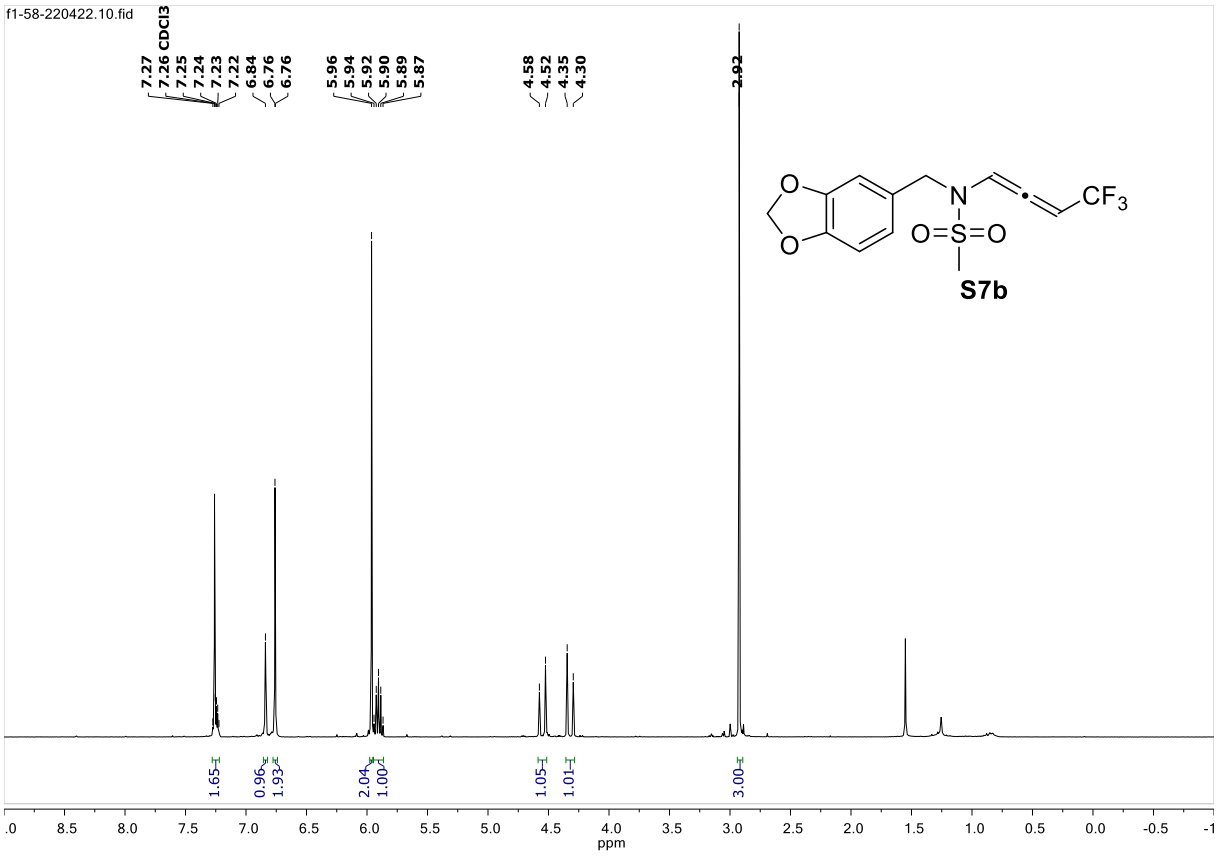
^{13}C NMR ($CDCl_3$, 126 MHz) of **S8**



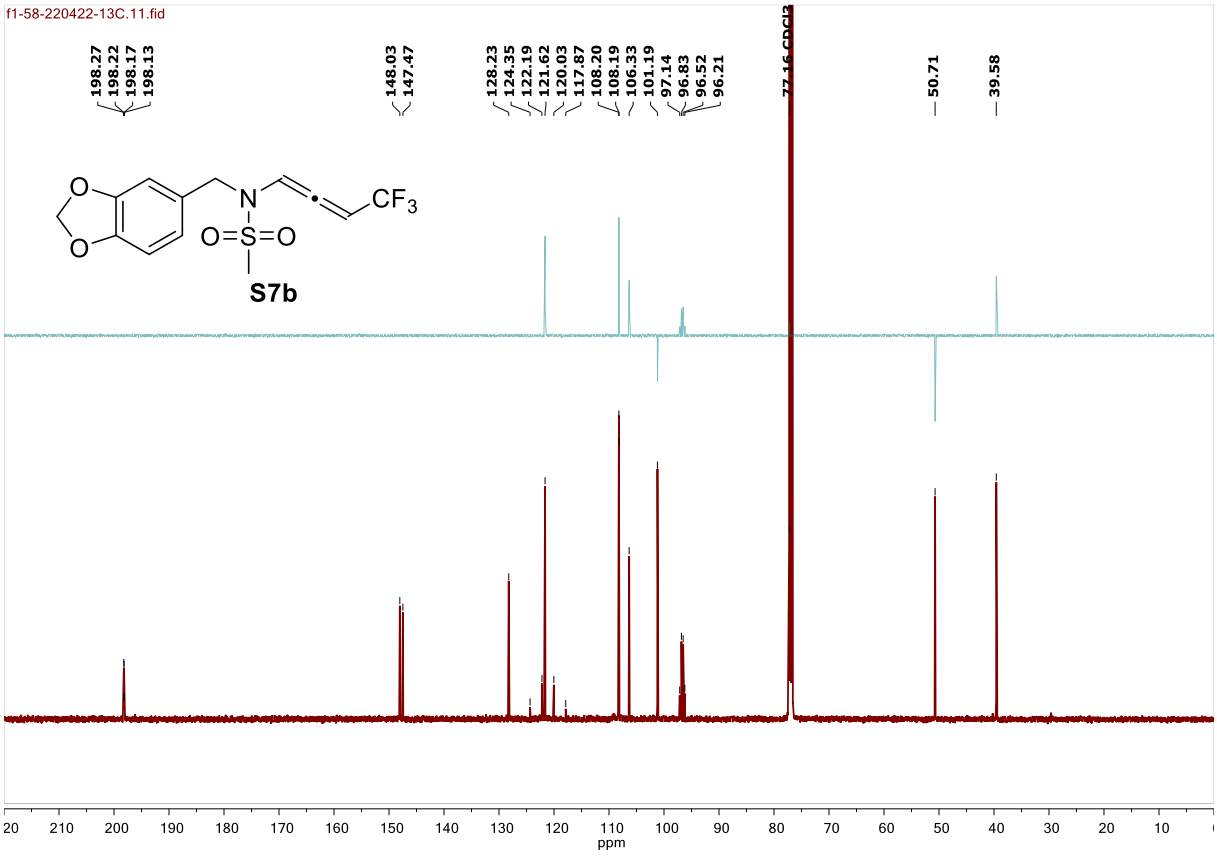
^{1}H NMR ($CDCl_3$, 300 MHz) of **S9**



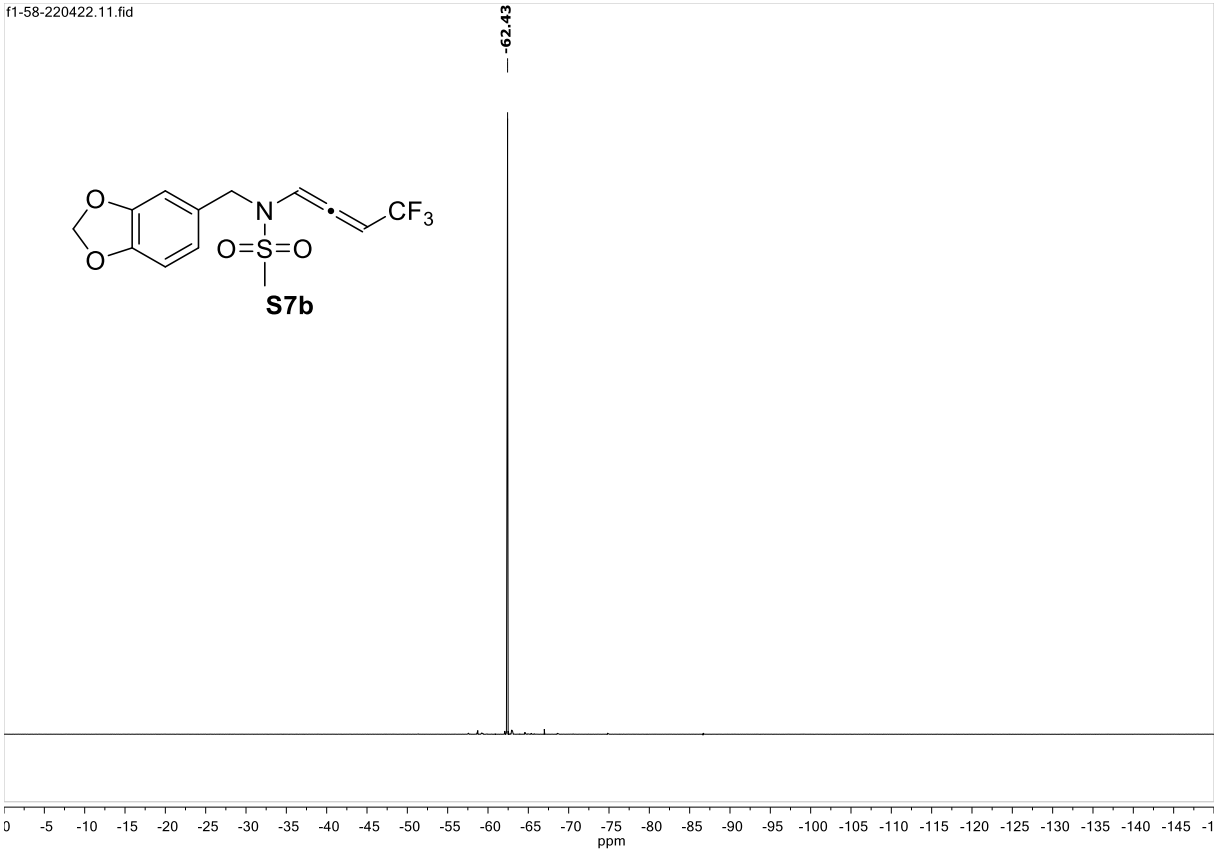
^{13}C NMR ($CDCl_3$, 126 MHz) of **S9**



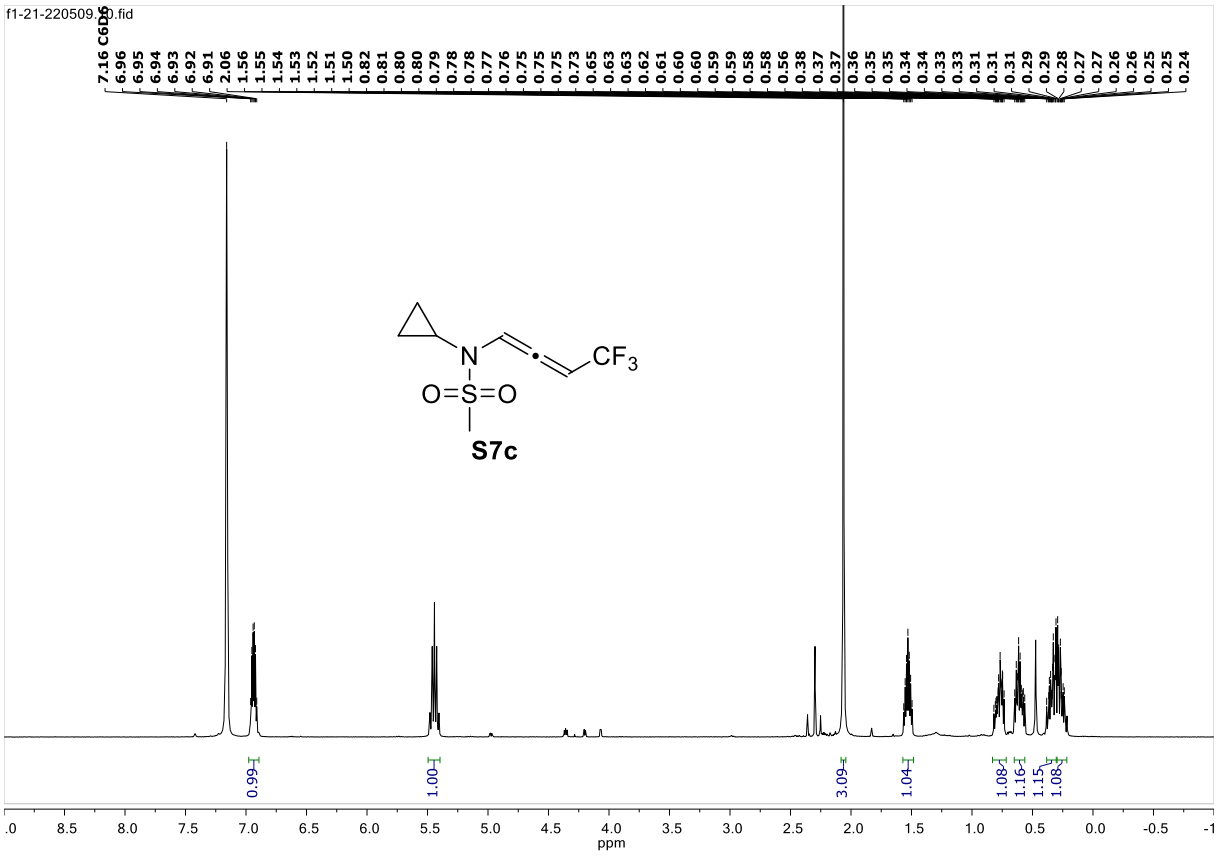
^{1}H NMR (C_6D_6, 300 MHz) of **S7b**



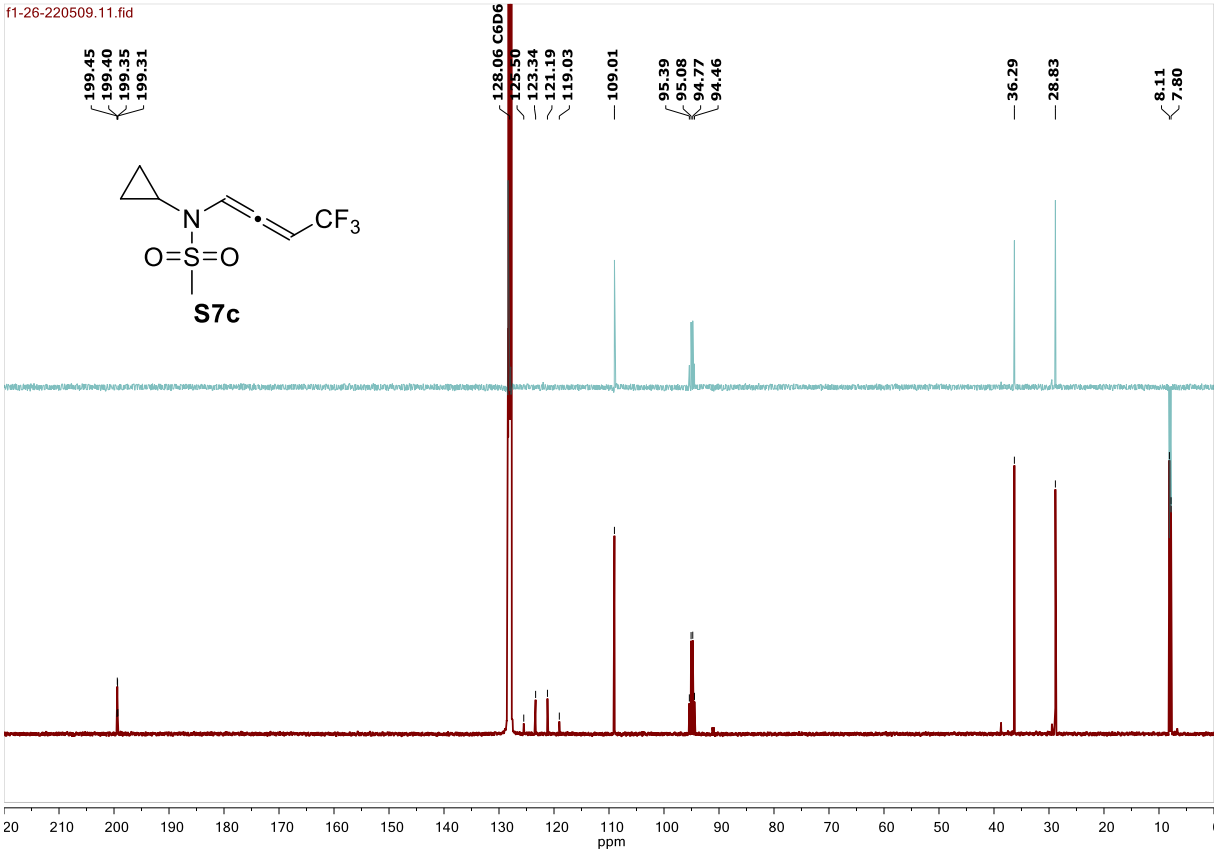
^{13}C NMR (C_6D_6, 126 MHz) of **S7b**



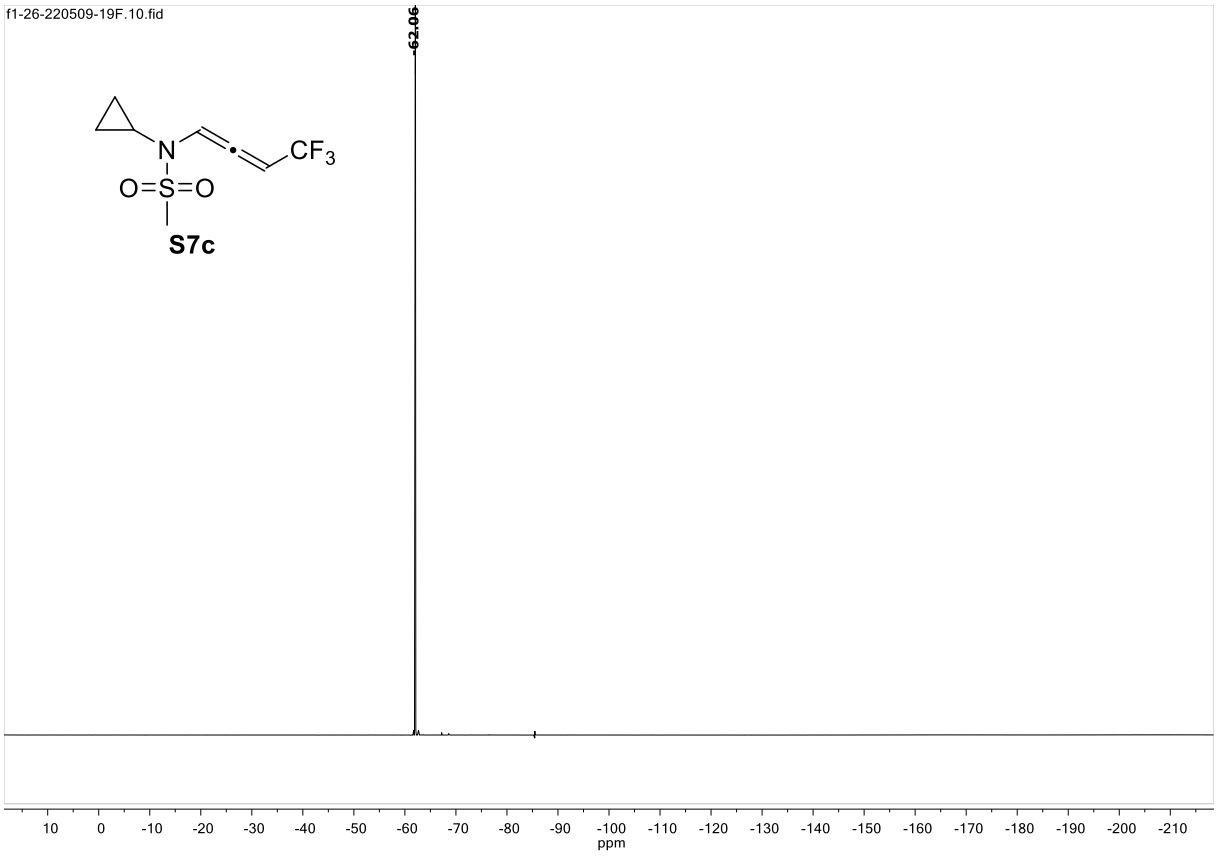
^{19}F NMR (C_6D_6, 282 MHz) of **S7b**



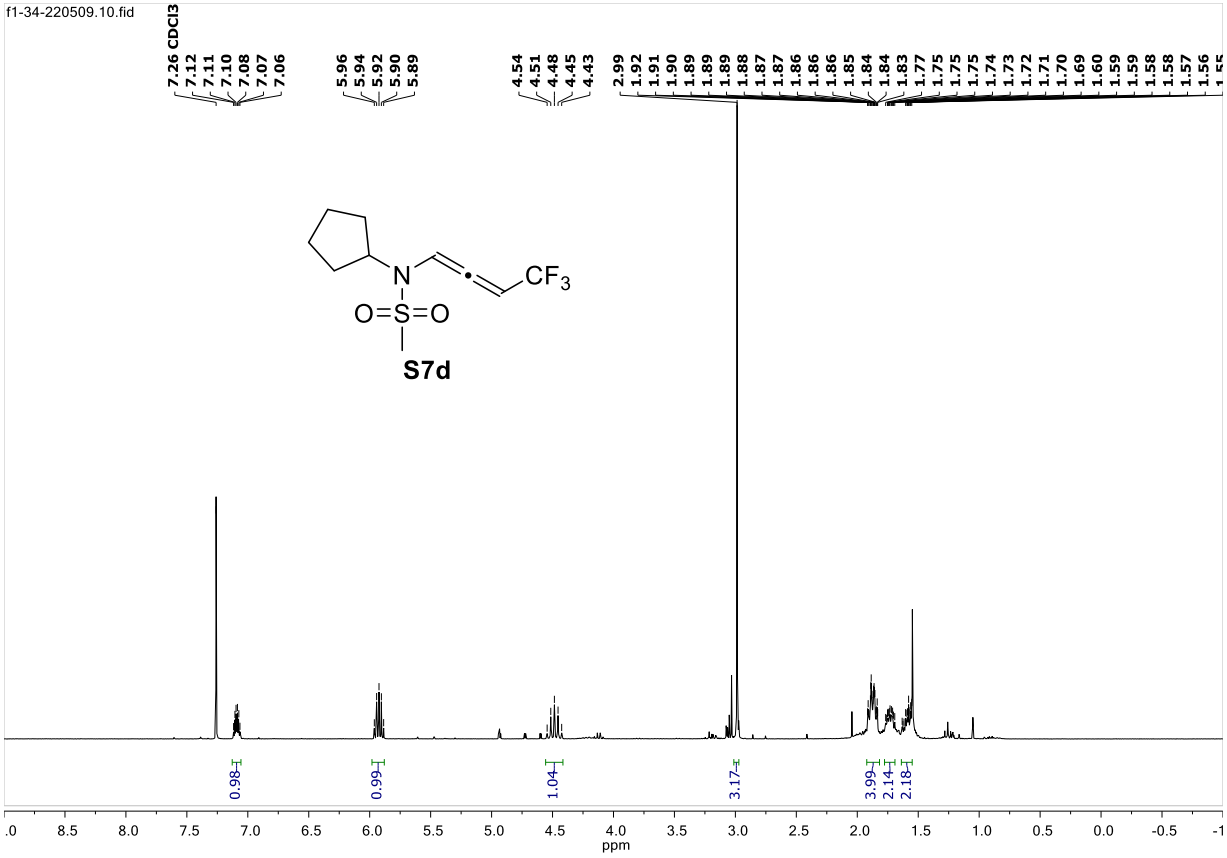
^{1}H NMR (C_6D_6, 300 MHz) of **S7c**



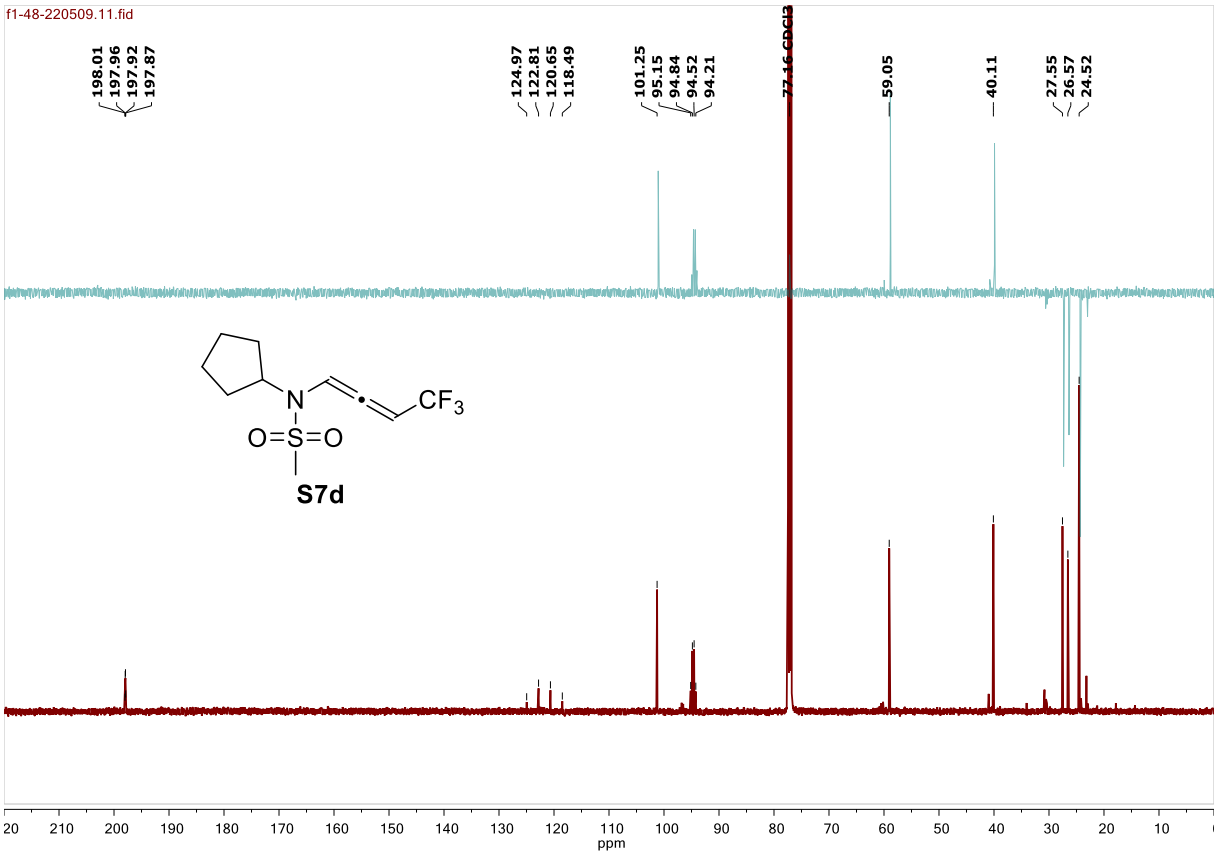
^{13}C NMR (C_6D_6, 126 MHz) of **S7c**



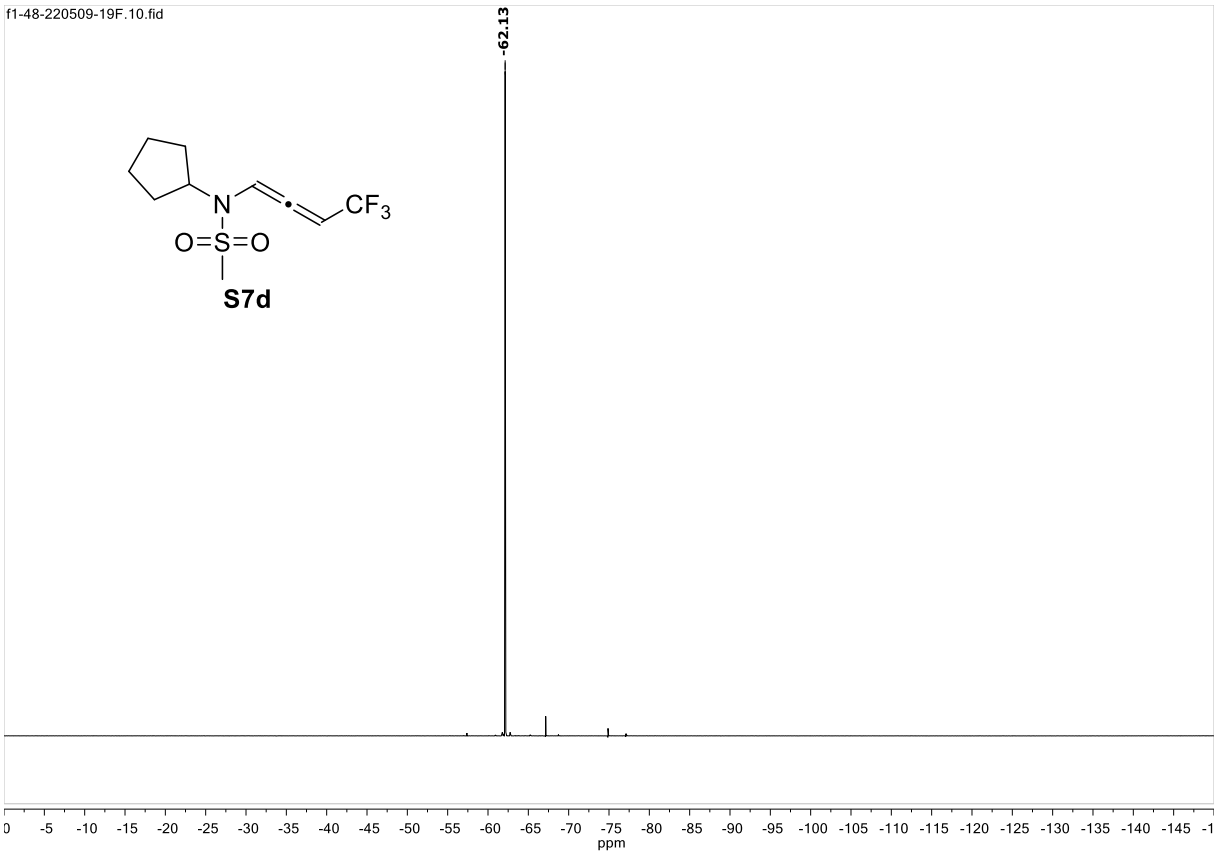
^{19}F NMR (C_6D_6, 282 MHz) of **S7c**



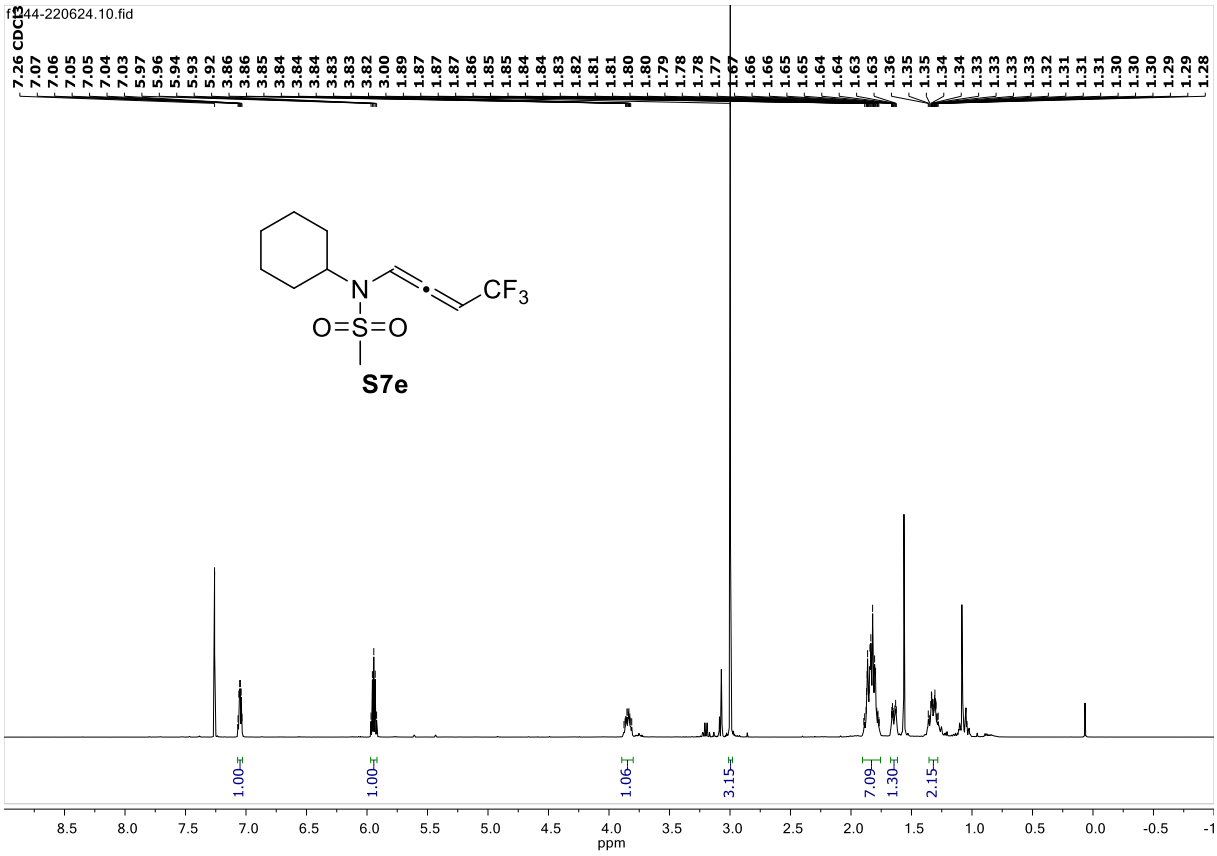
^{1}H NMR (C_6D_6, 300 MHz) of **S7d**



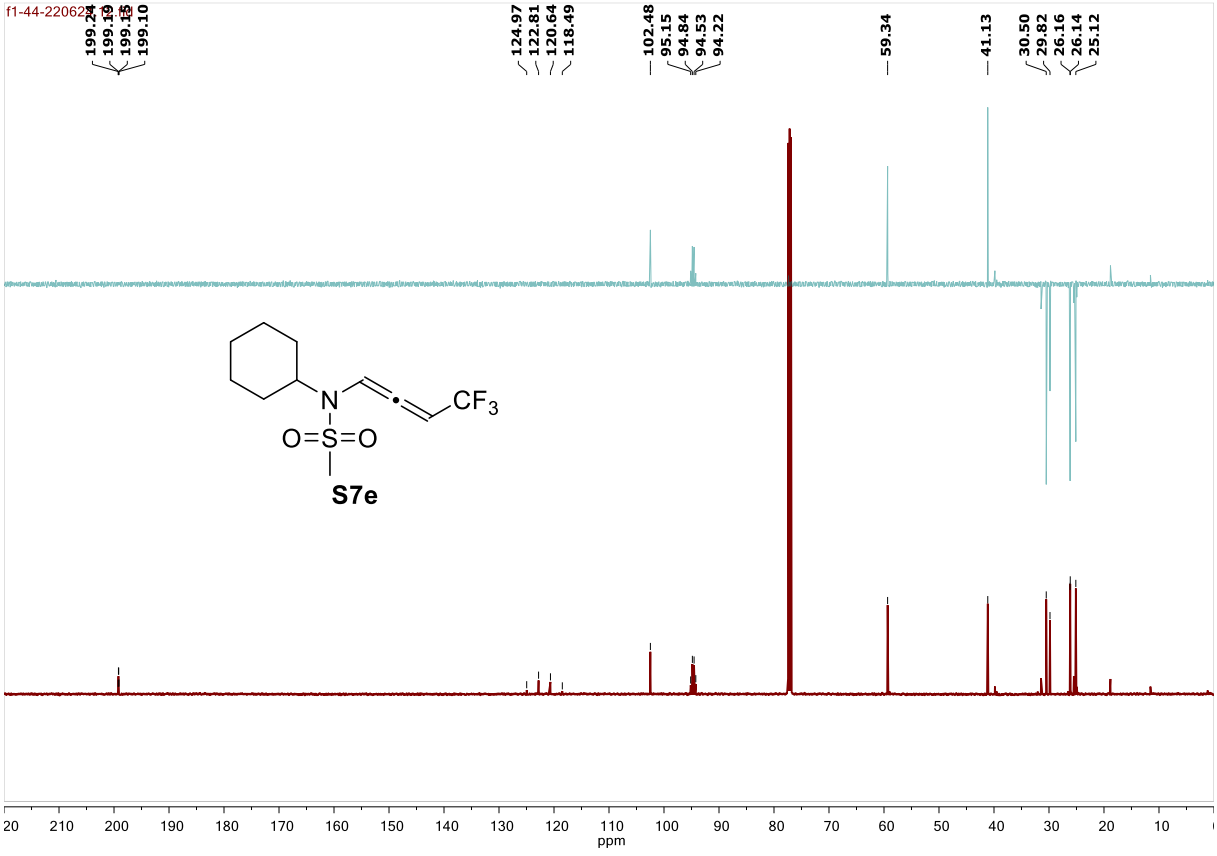
^{13}C NMR (C_6D_6, 126 MHz) of **S7d**



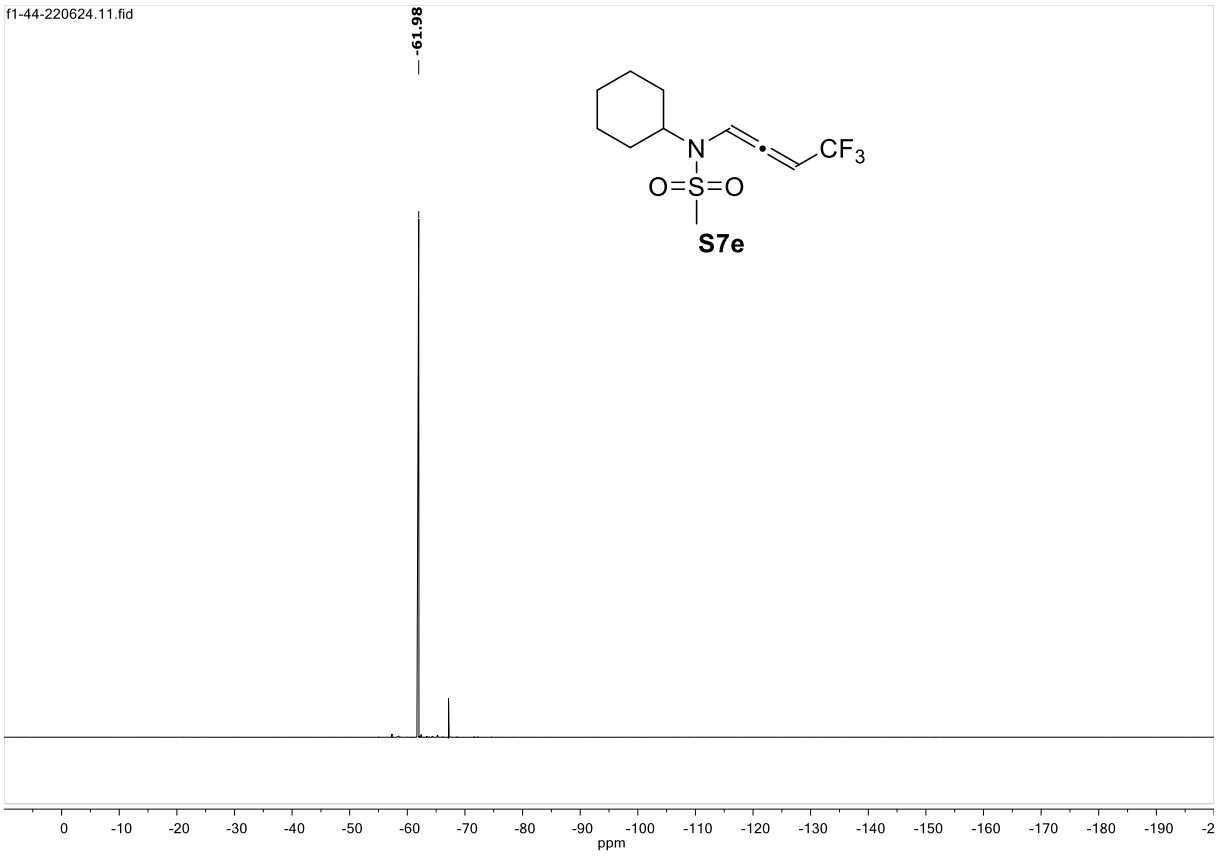
^{19}F NMR (C_6D_6, 282 MHz) of **S7d**



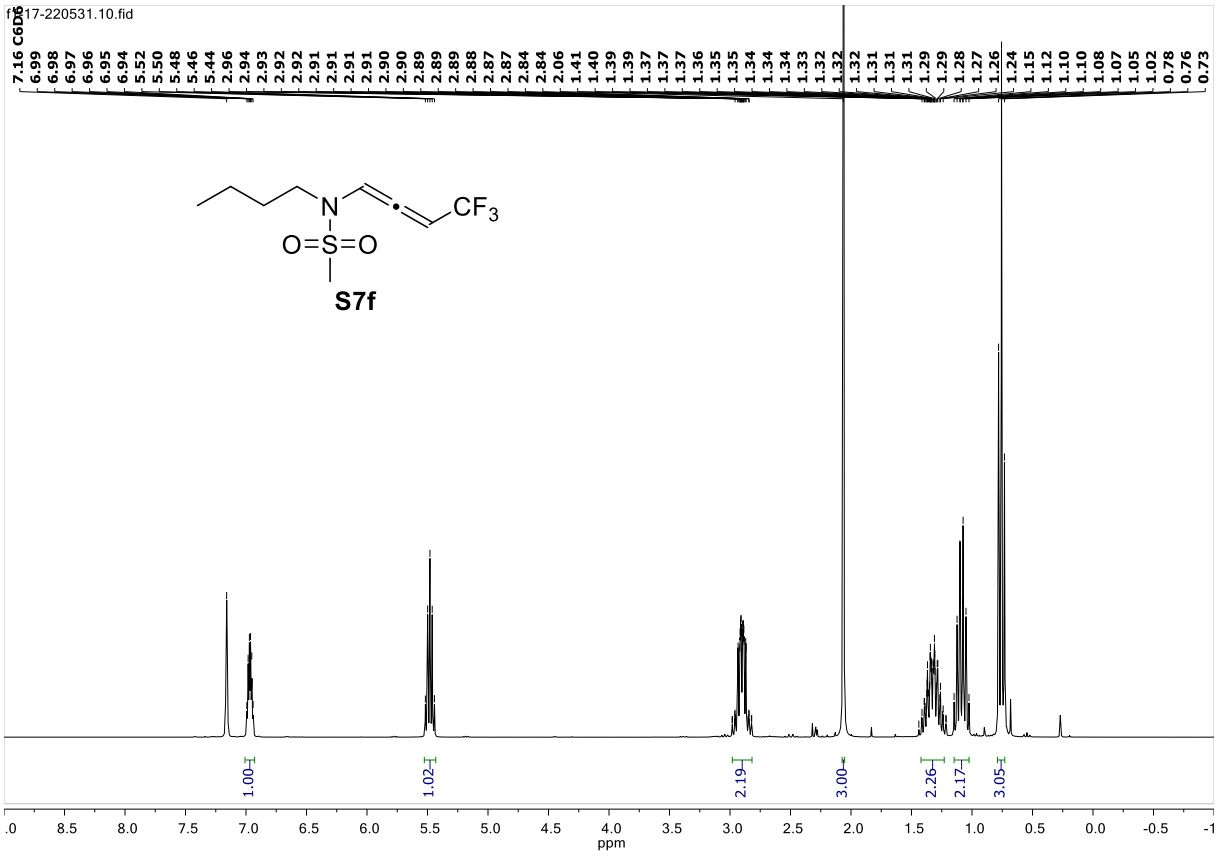
^{1}H NMR ($CDCl_3$, 500 MHz) of **S7e**



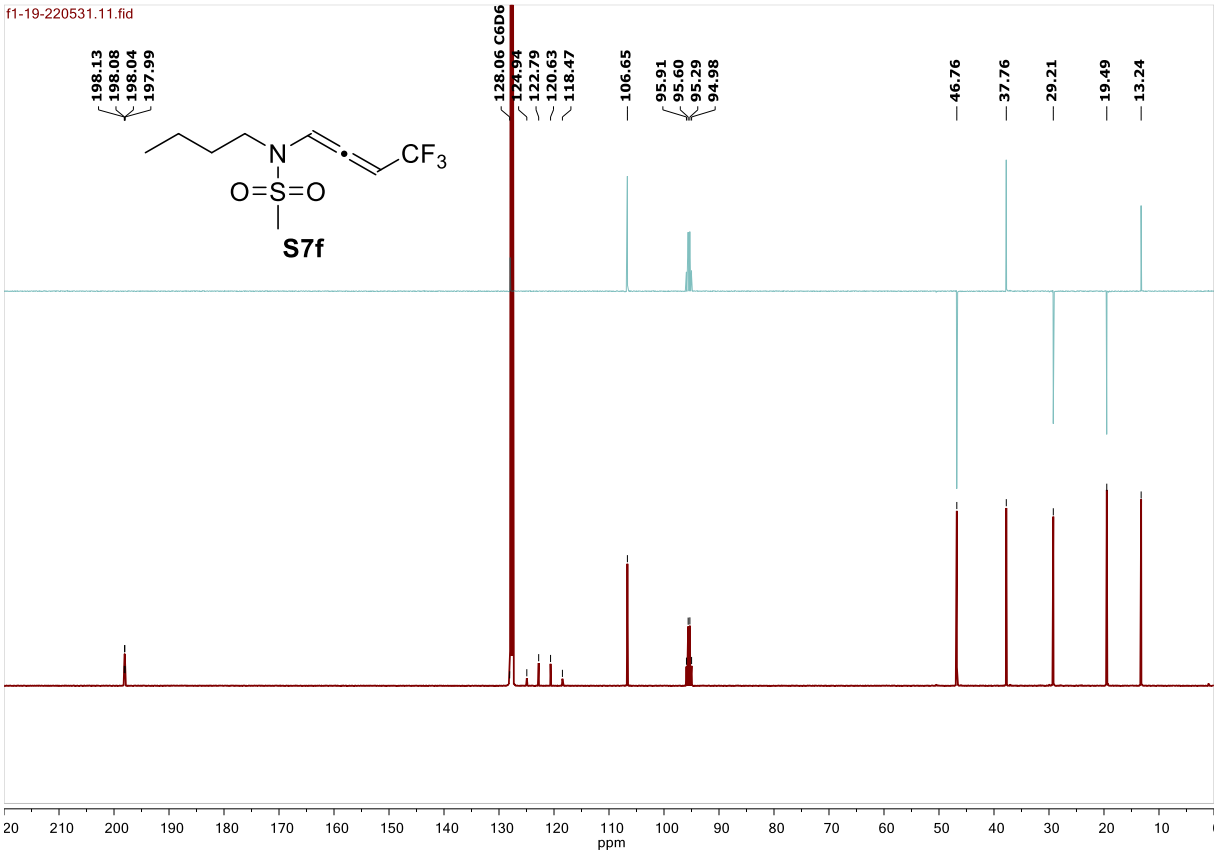
^{13}C NMR ($CDCl_3$, 126 MHz) of **S7e**



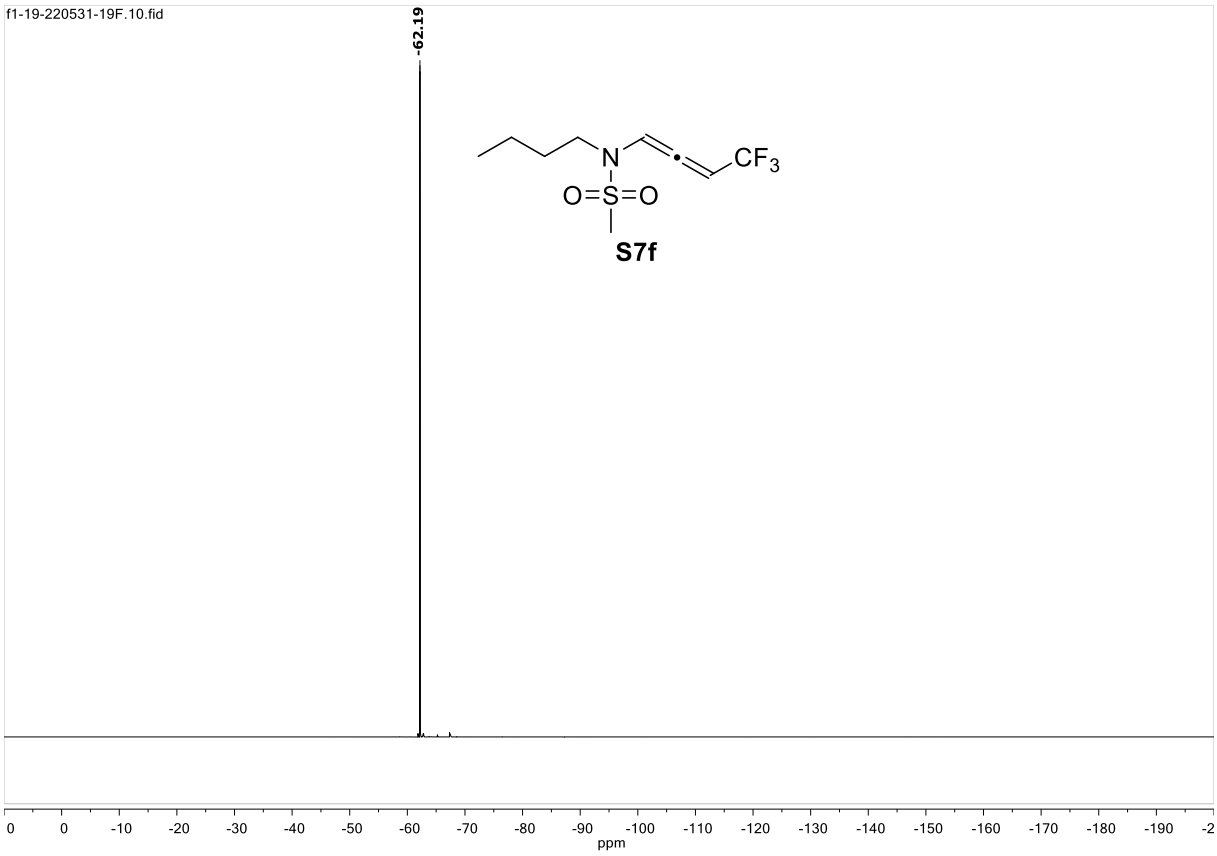
^{19}F NMR ($CDCl_3$, 282 MHz) of **S7e**



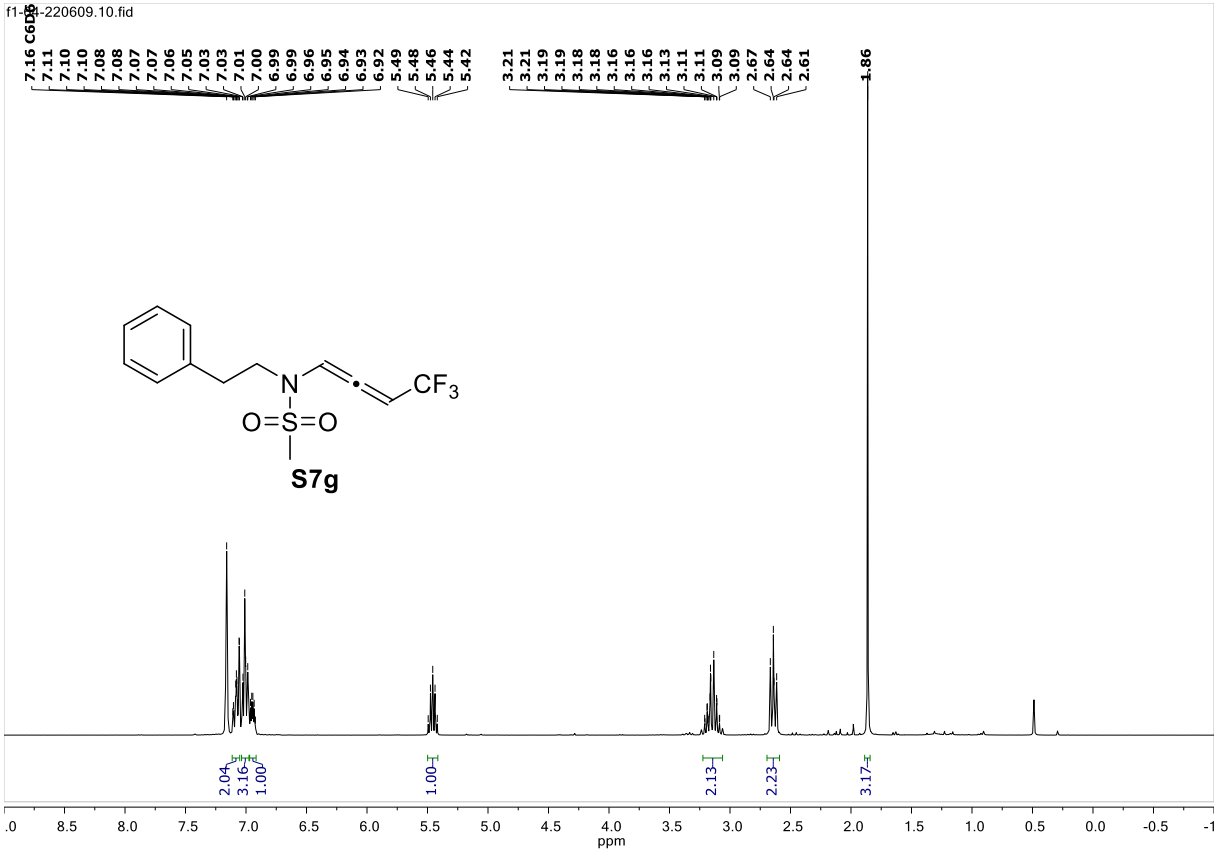
^{1}H NMR (C_6D_6, 300 MHz) of **S7f**



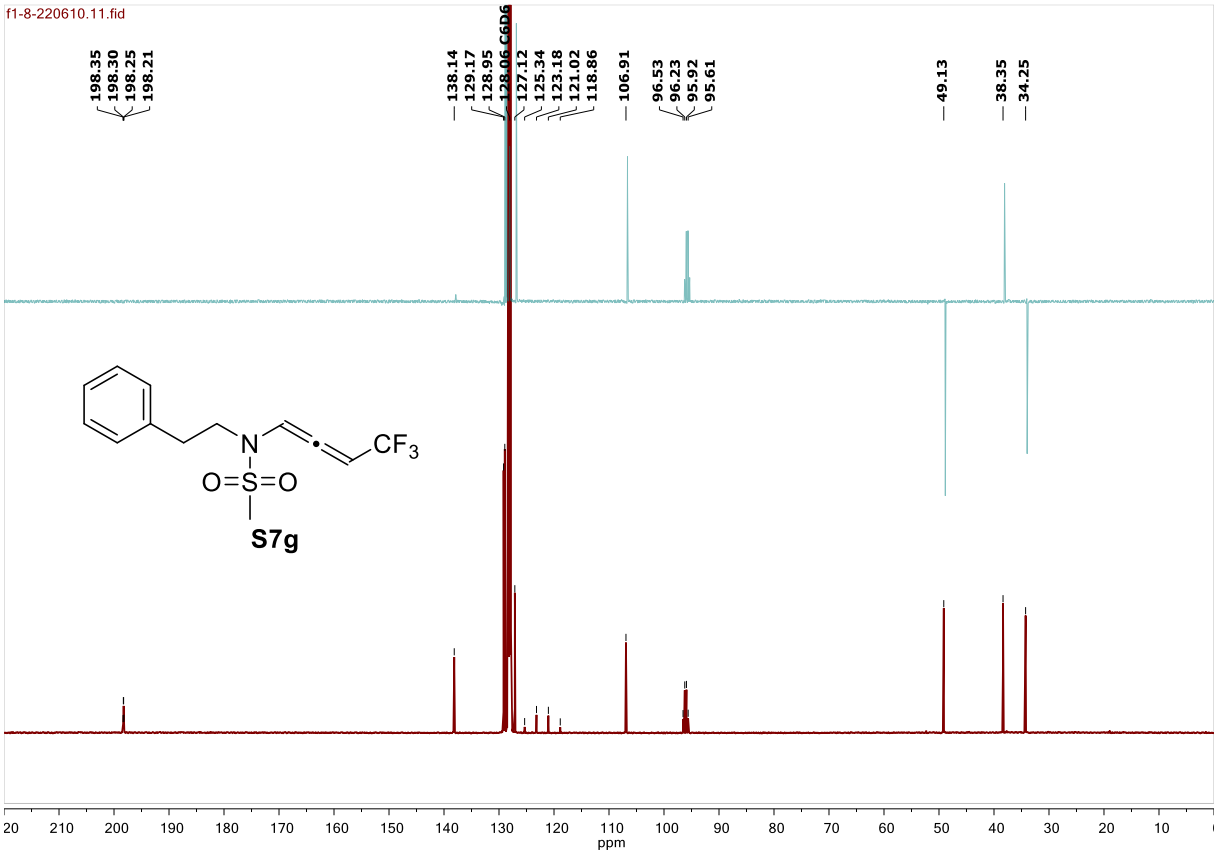
^{13}C NMR (C_6D_6, 126 MHz) of **S7f**



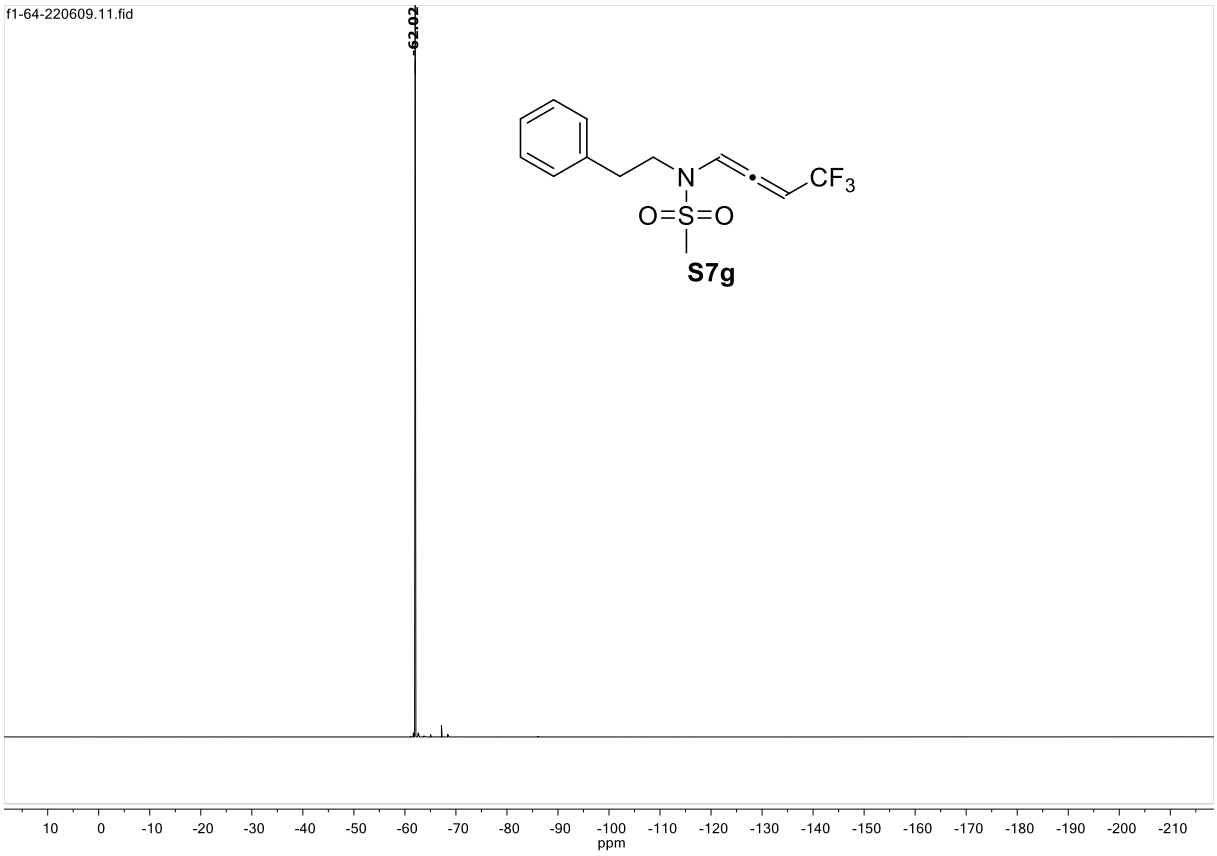
^{19}F NMR (C_6D_6, 471 MHz) of **S7f**



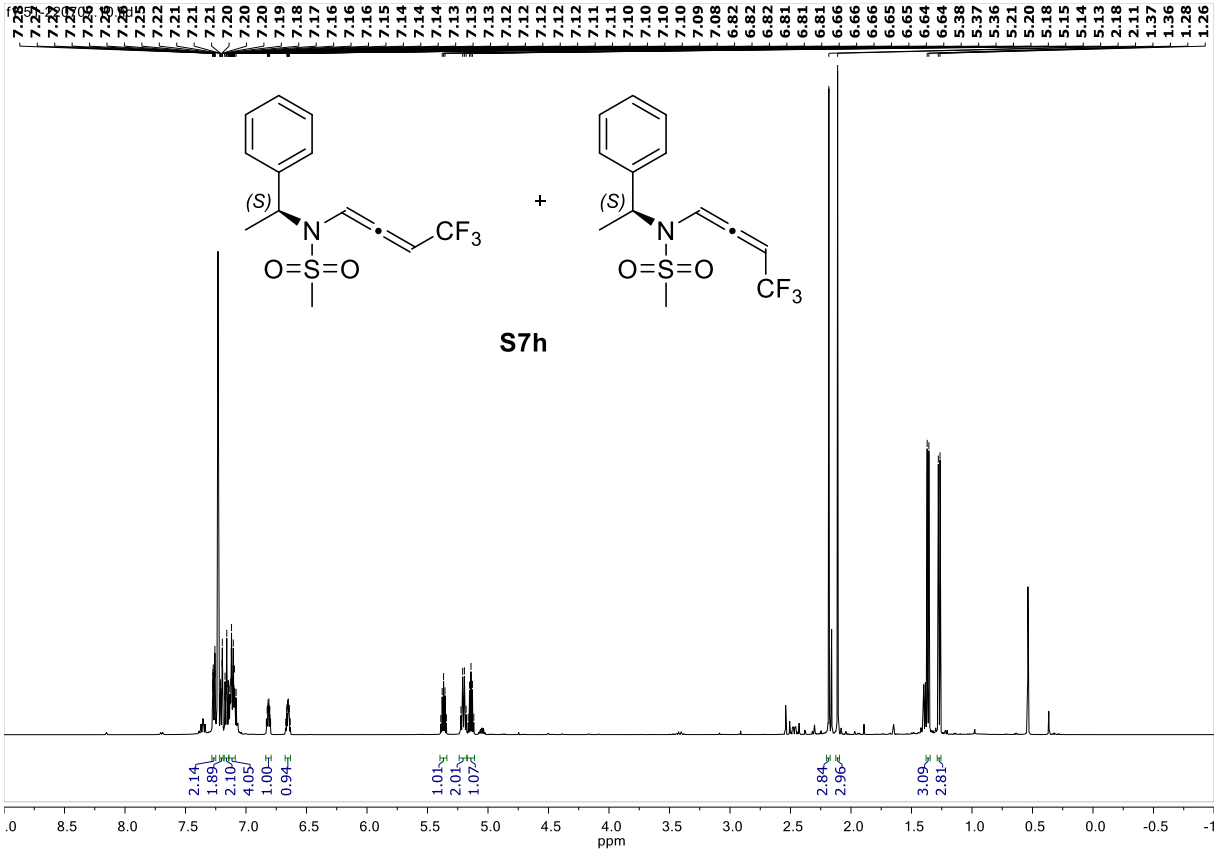
^{1}H NMR (C_6D_6, 300 MHz) of **S7g**



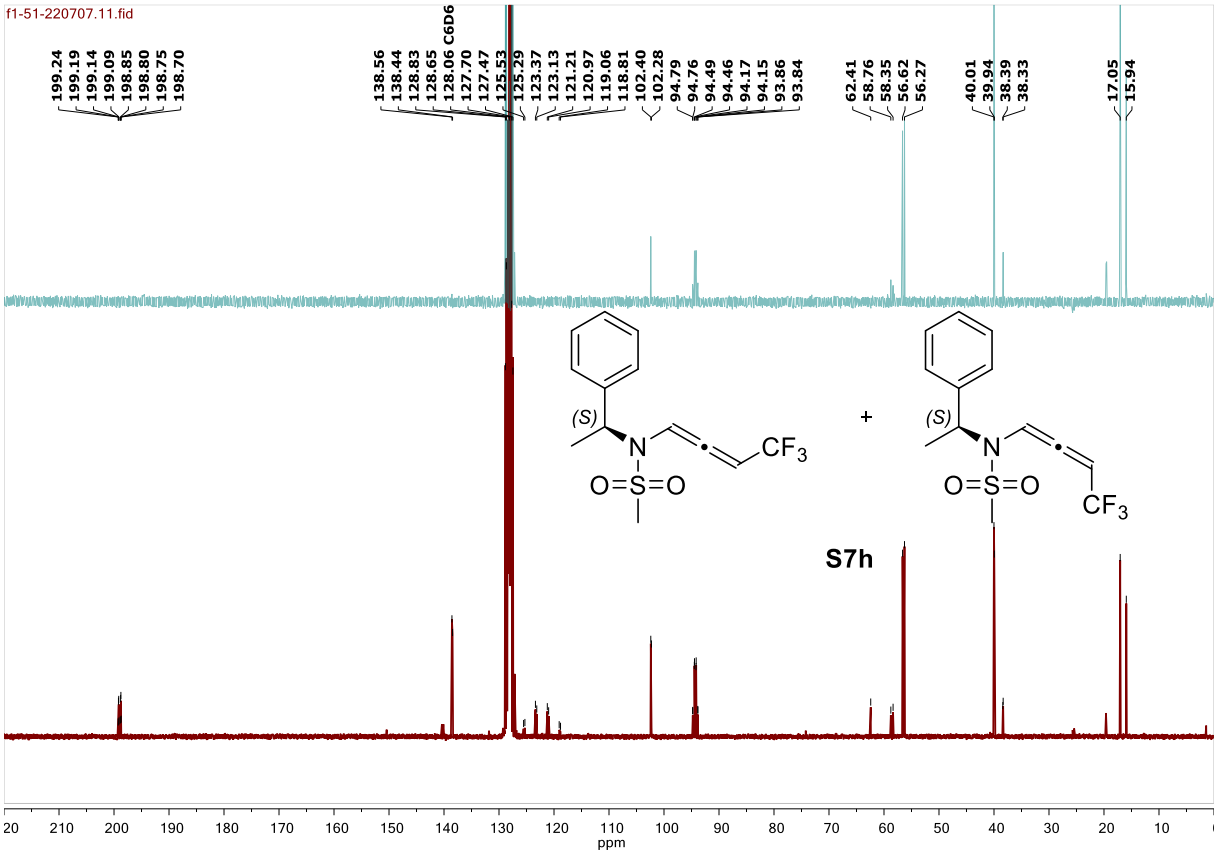
^{13}C NMR (C_6D_6, 126 MHz) of **S7g**



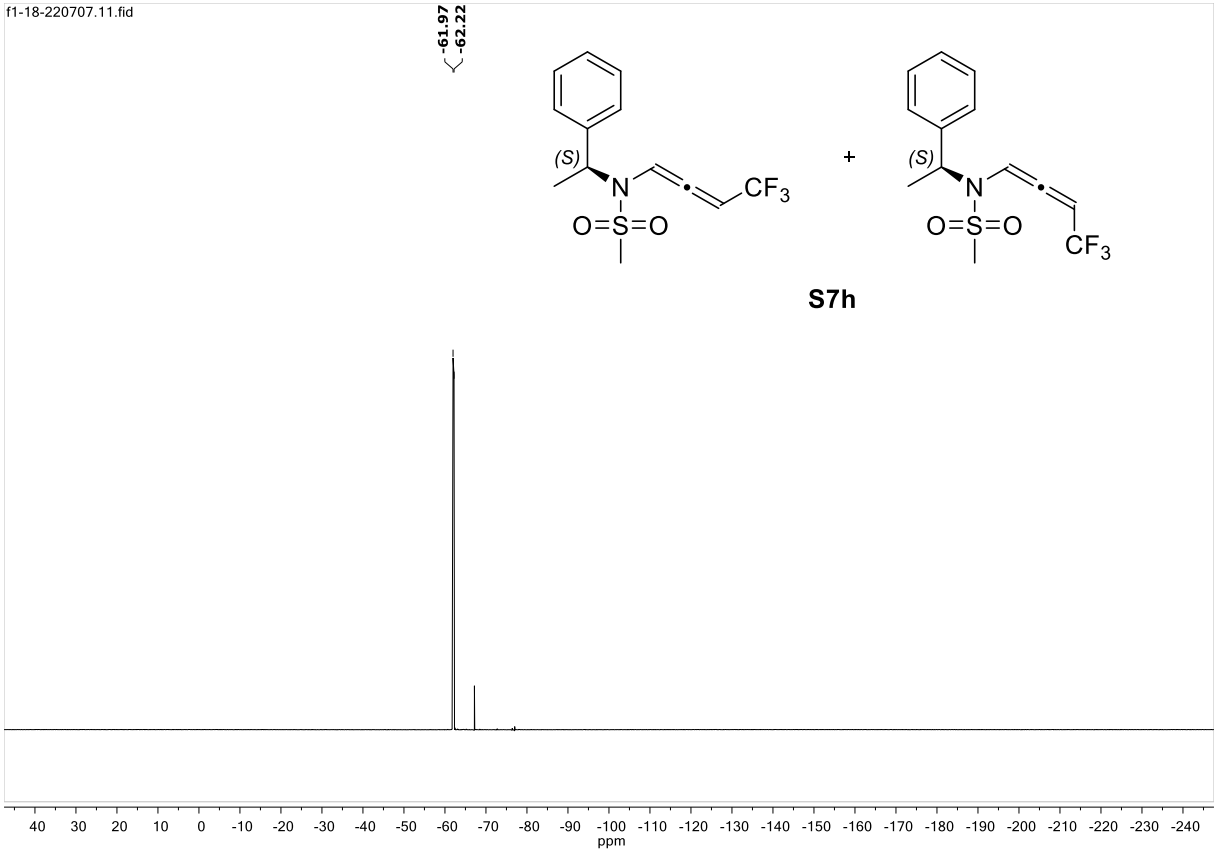
^{19}F NMR (C_6D_6, 282 MHz) of **S7g**



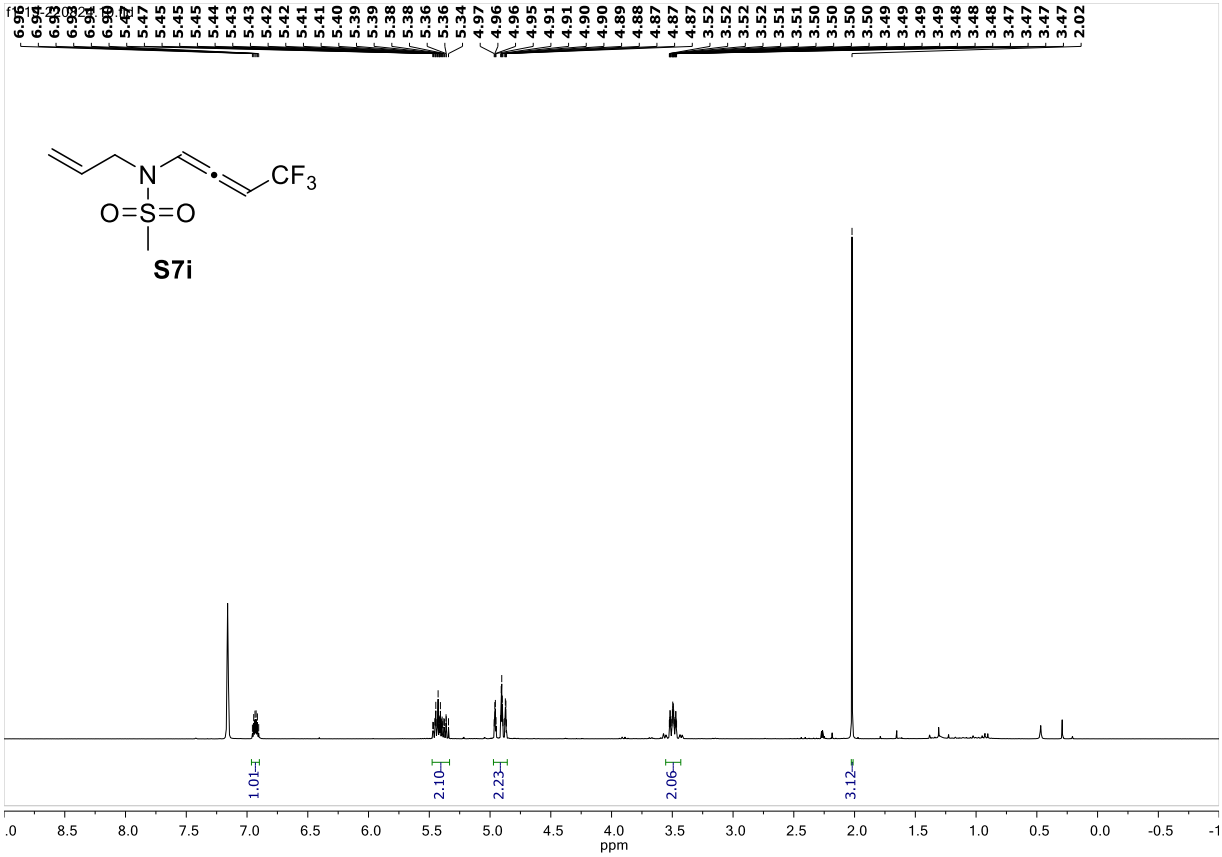
^{1}H NMR (C_6D_6, 500 MHz) of **S7h**



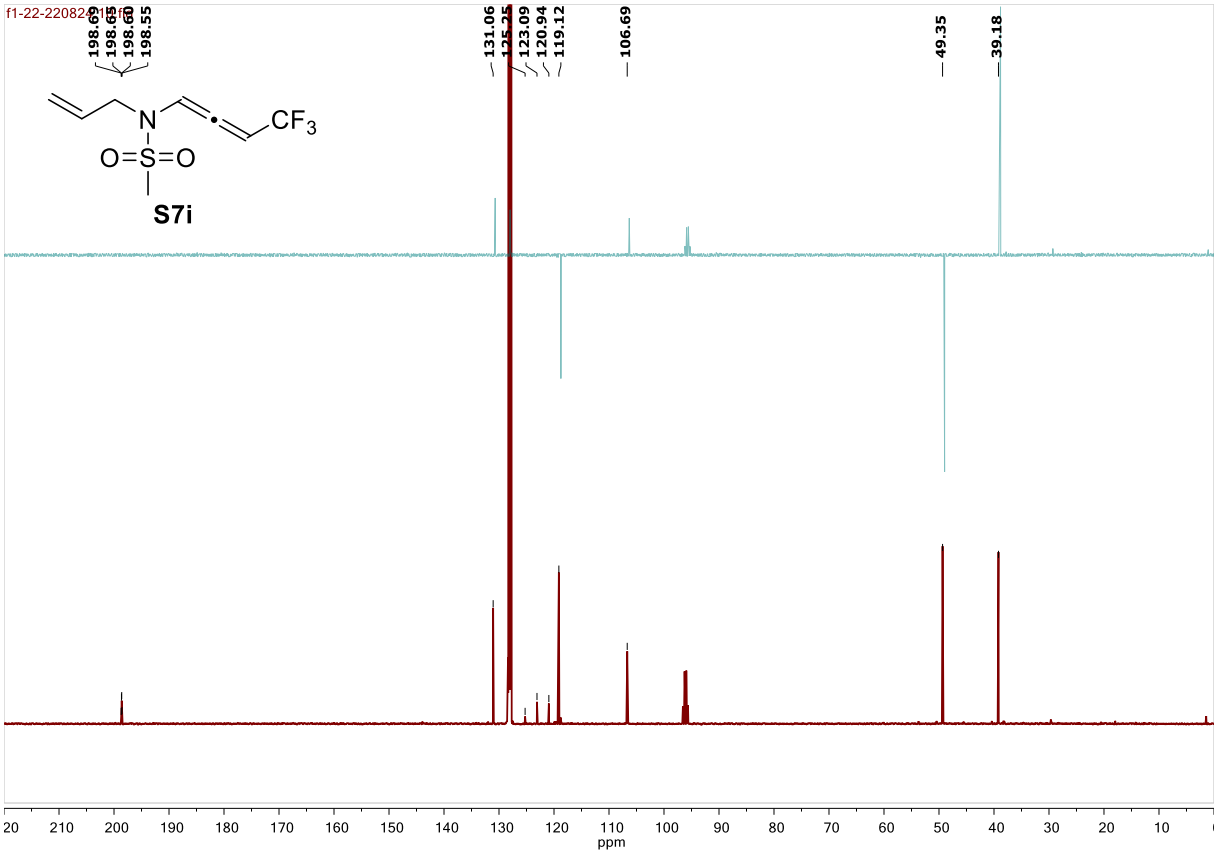
^{13}C NMR (C_6D_6, 126 MHz) of **S7h**



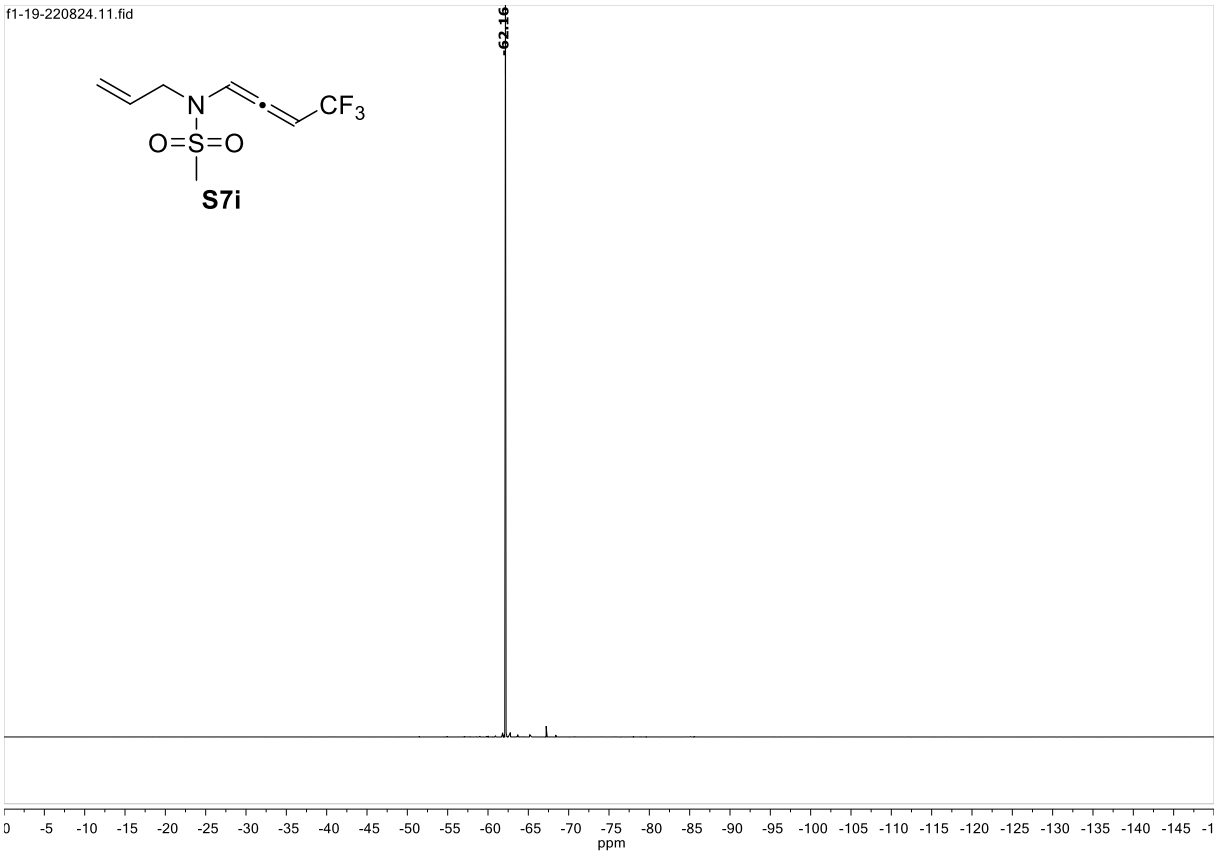
^{19}F NMR (C_6D_6, 471 MHz) of **S7h**



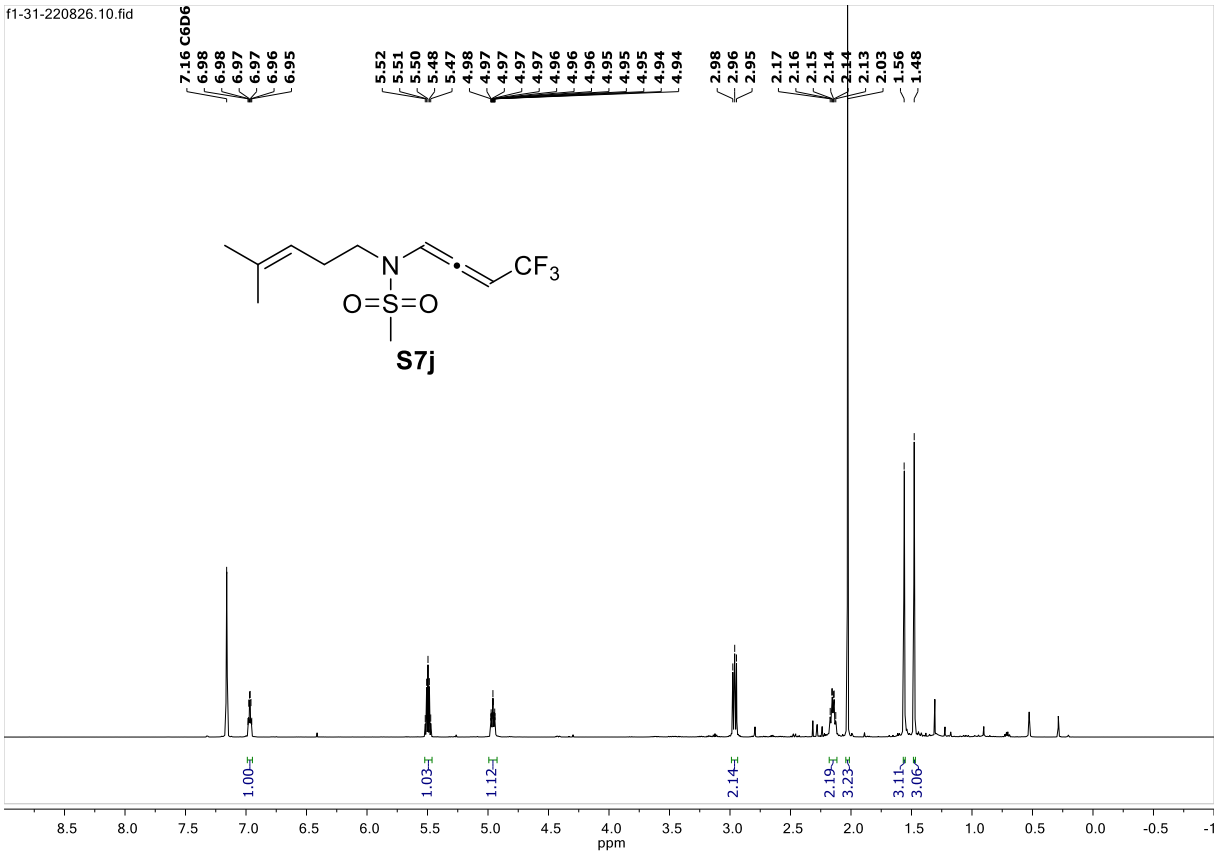
^{1}H NMR (C_6D_6, 300 MHz) of **S7i**



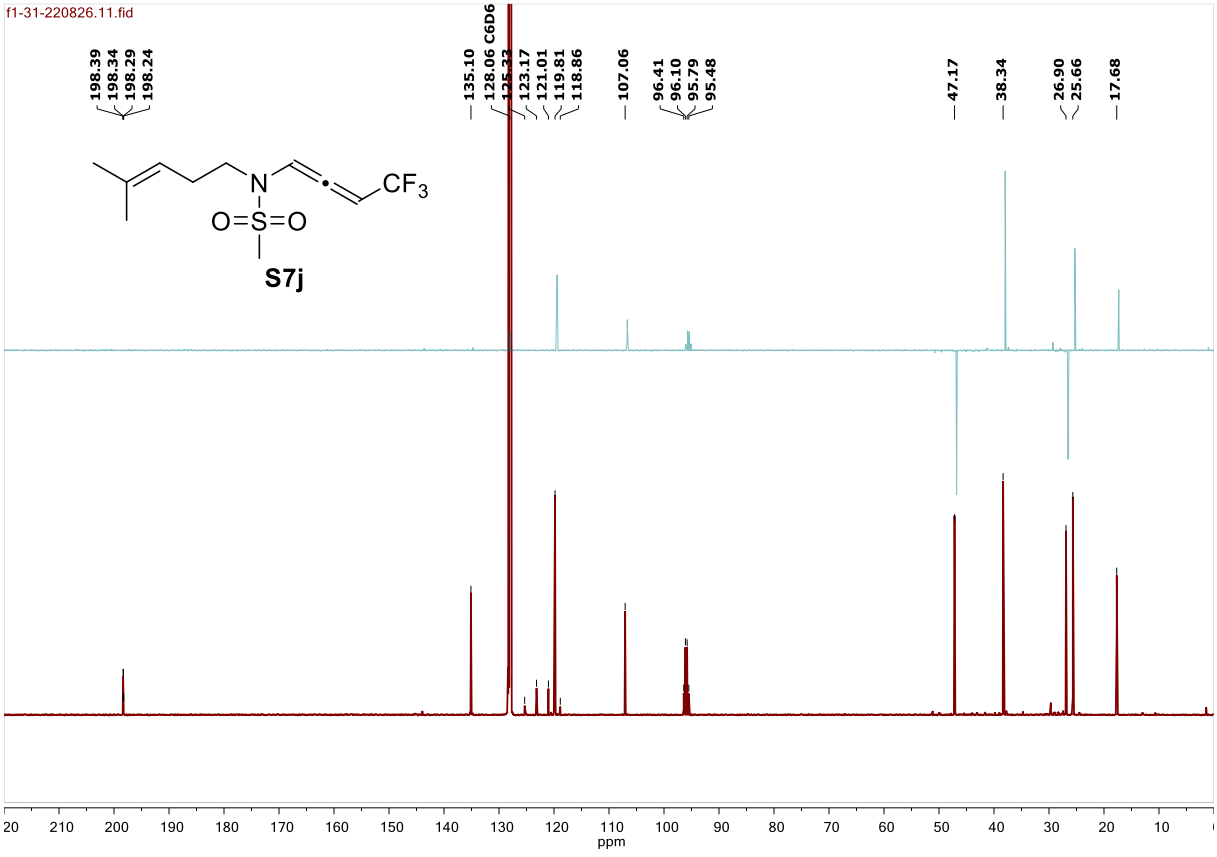
^{13}C NMR (C_6D_6, 126 MHz) of **S7i**



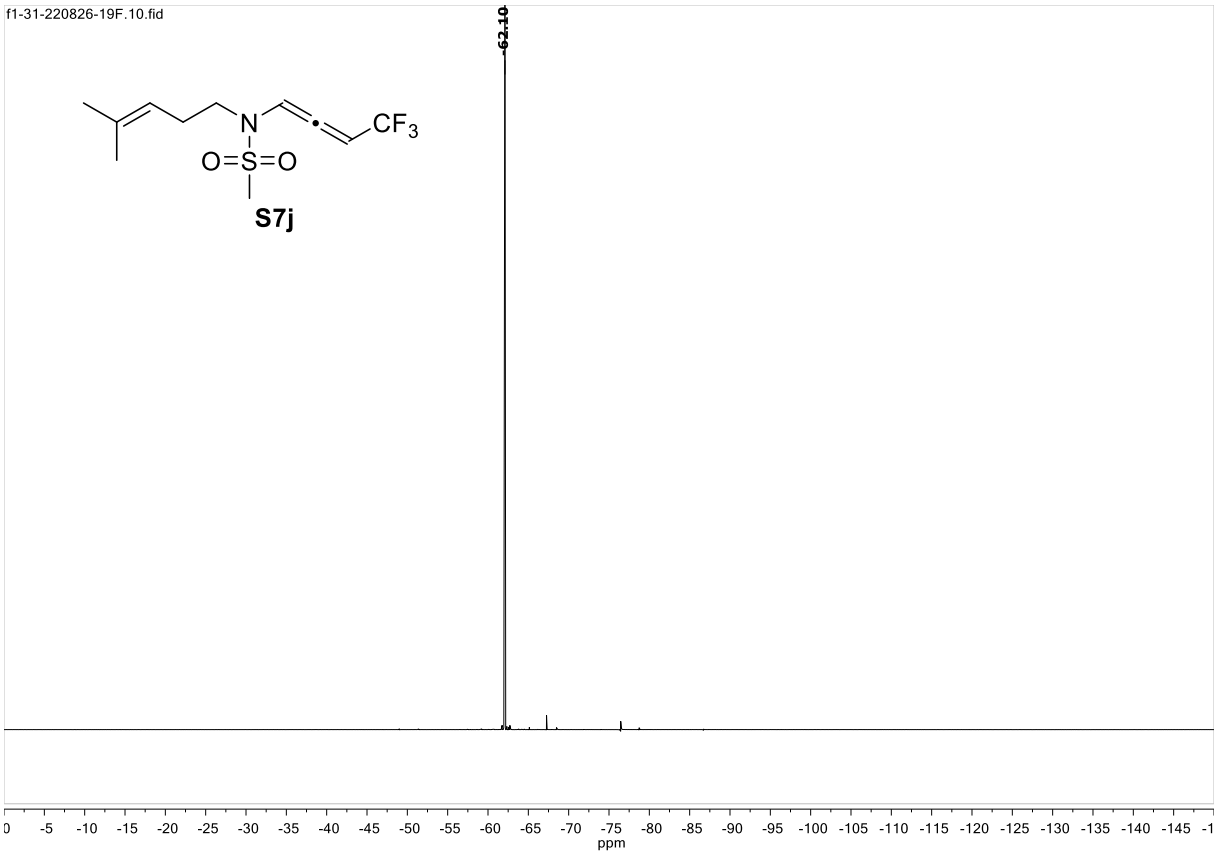
^{19}F NMR (C_6D_6, 282 MHz) of **S7i**



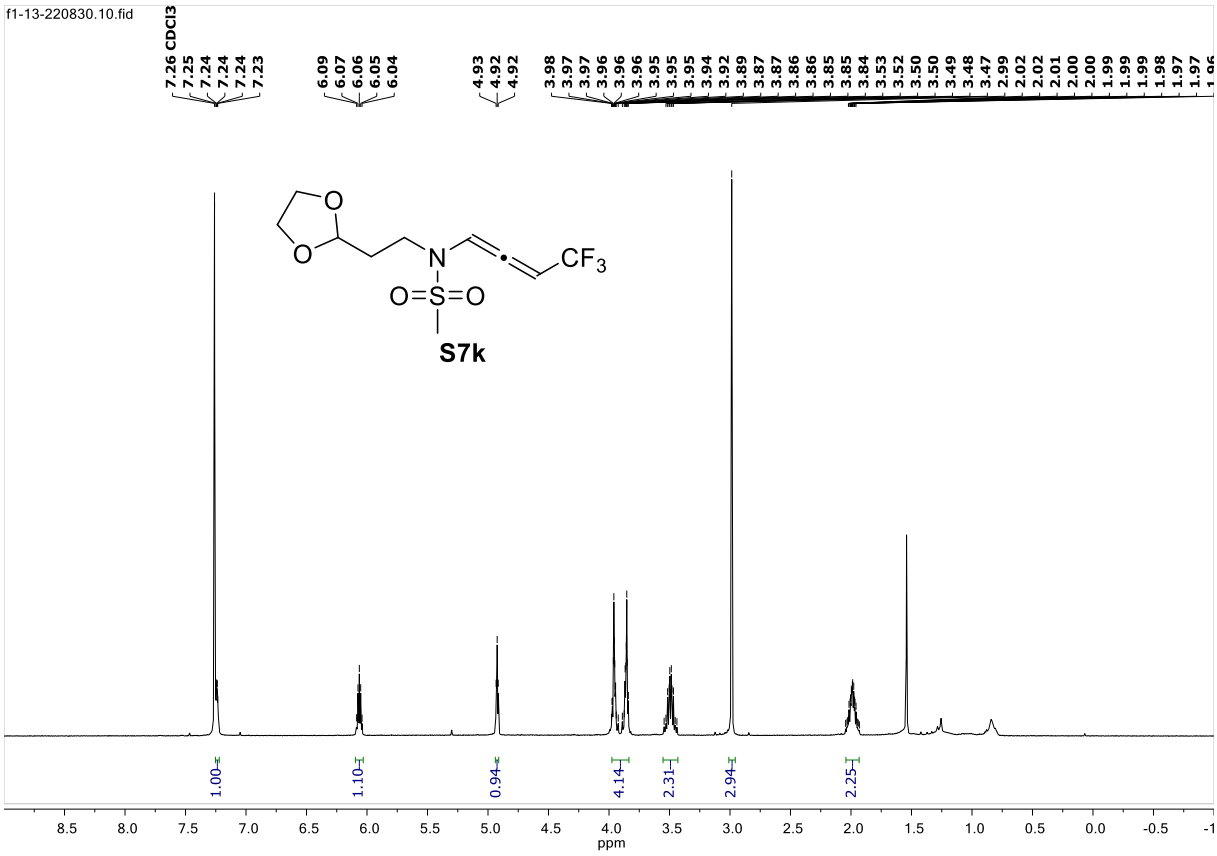
^{1}H NMR (C_6D_6, 500 MHz) of **S7j**



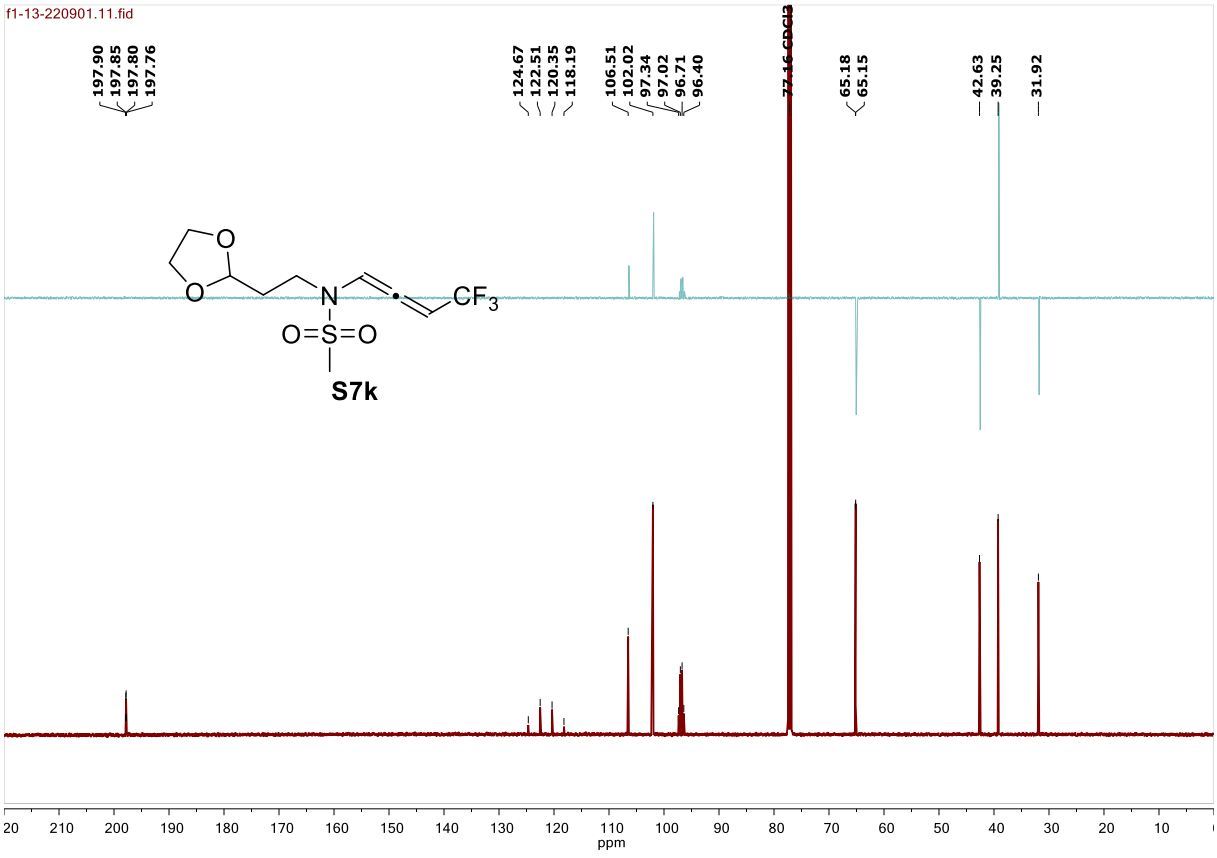
^{13}C NMR (C_6D_6, 126 MHz) of **S7j**



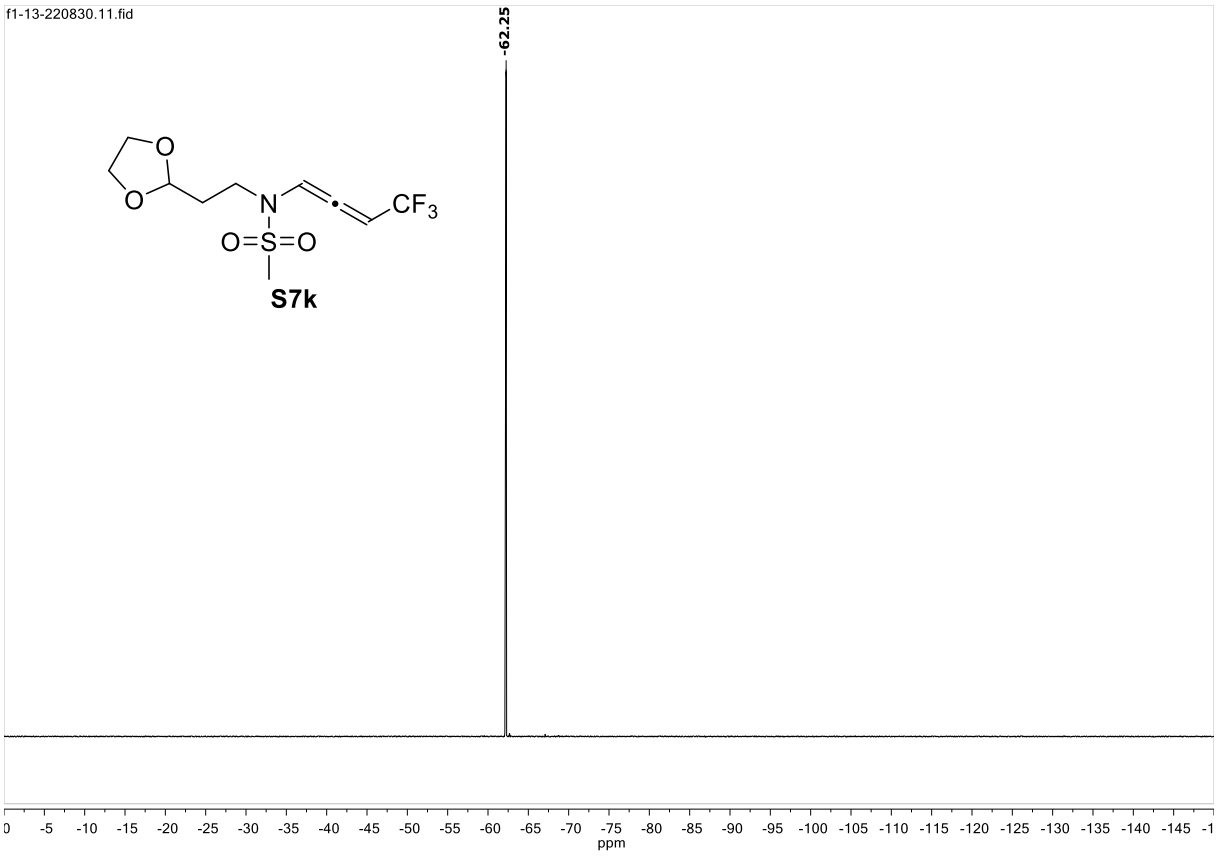
^{19}F NMR (C_6D_6, 282 MHz) of **S7j**



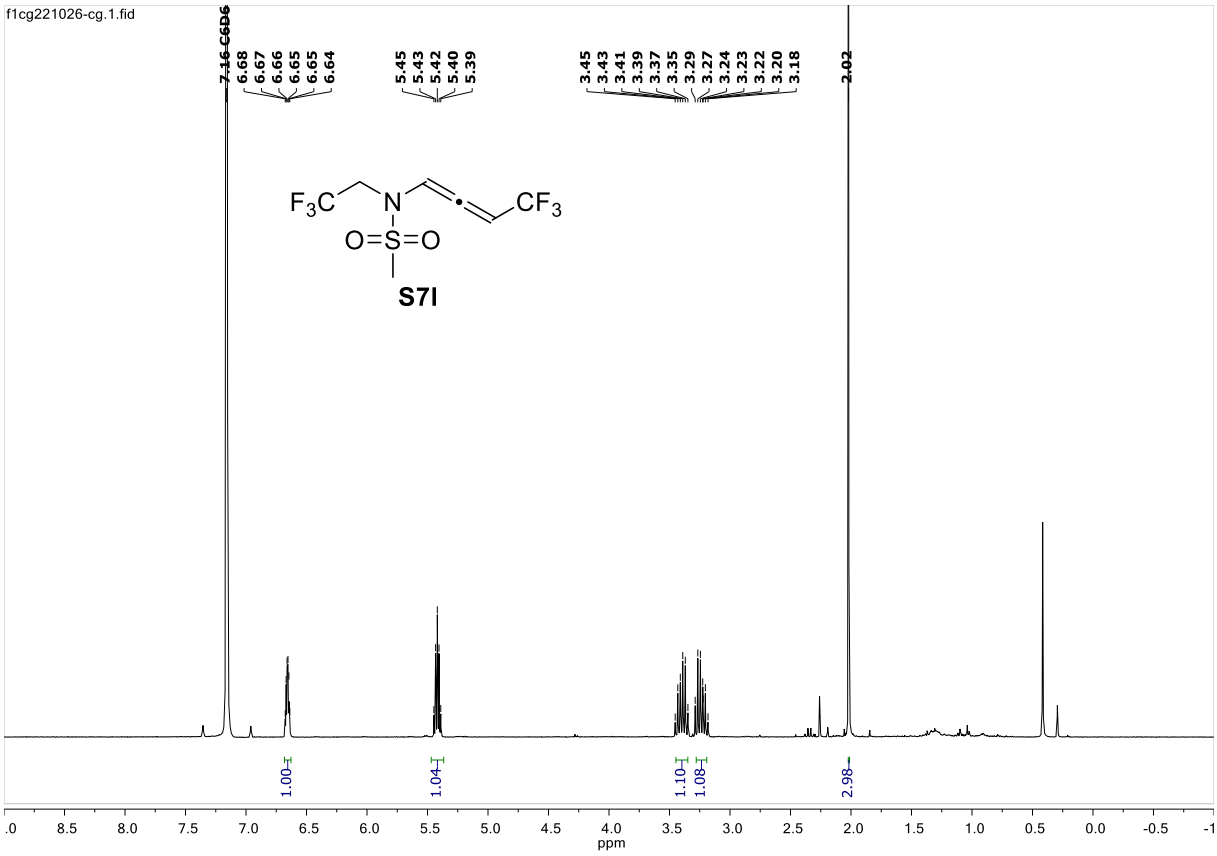
^{1}H NMR ($CDCl_3$, 500 MHz) of **S7k**



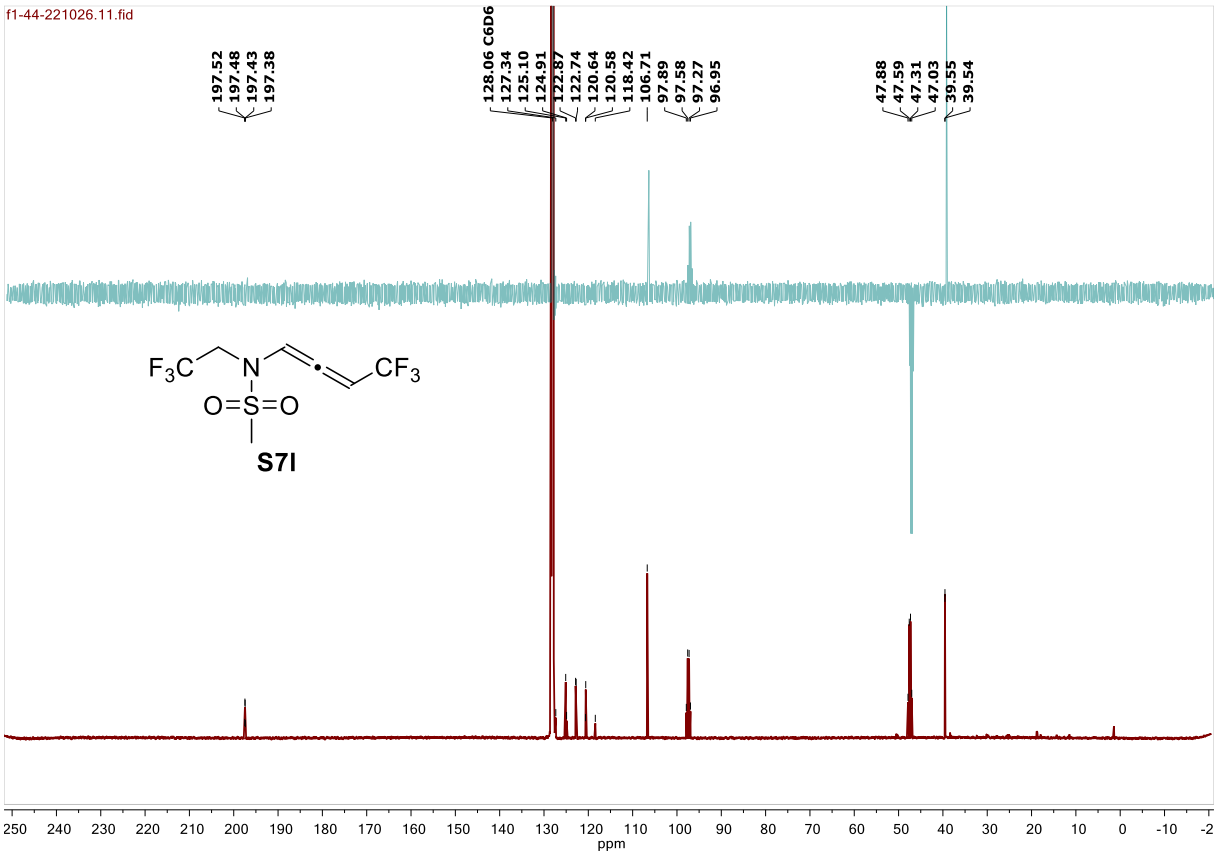
^{13}C NMR ($CDCl_3$, 126 MHz) of **S7k**



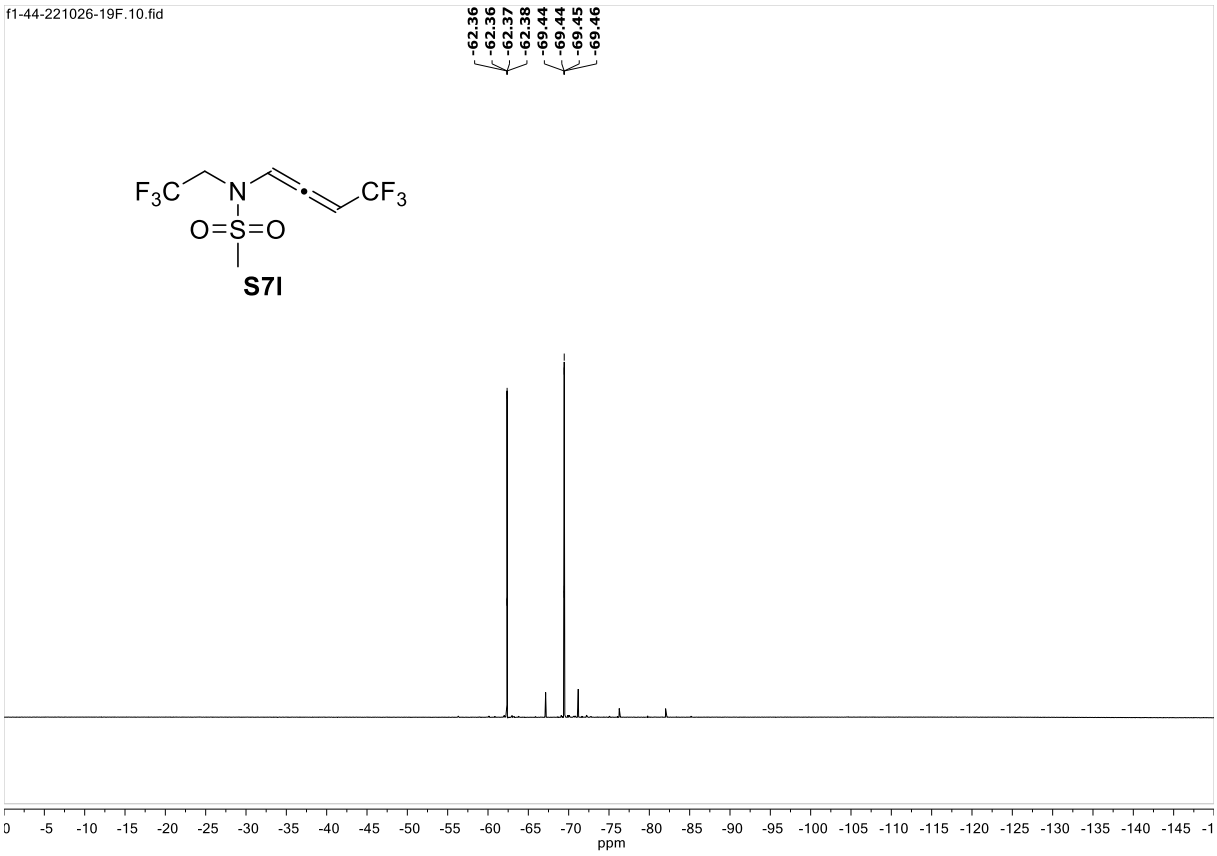
^{19}F NMR ($CDCl_3$, 471 MHz) of **S7k**



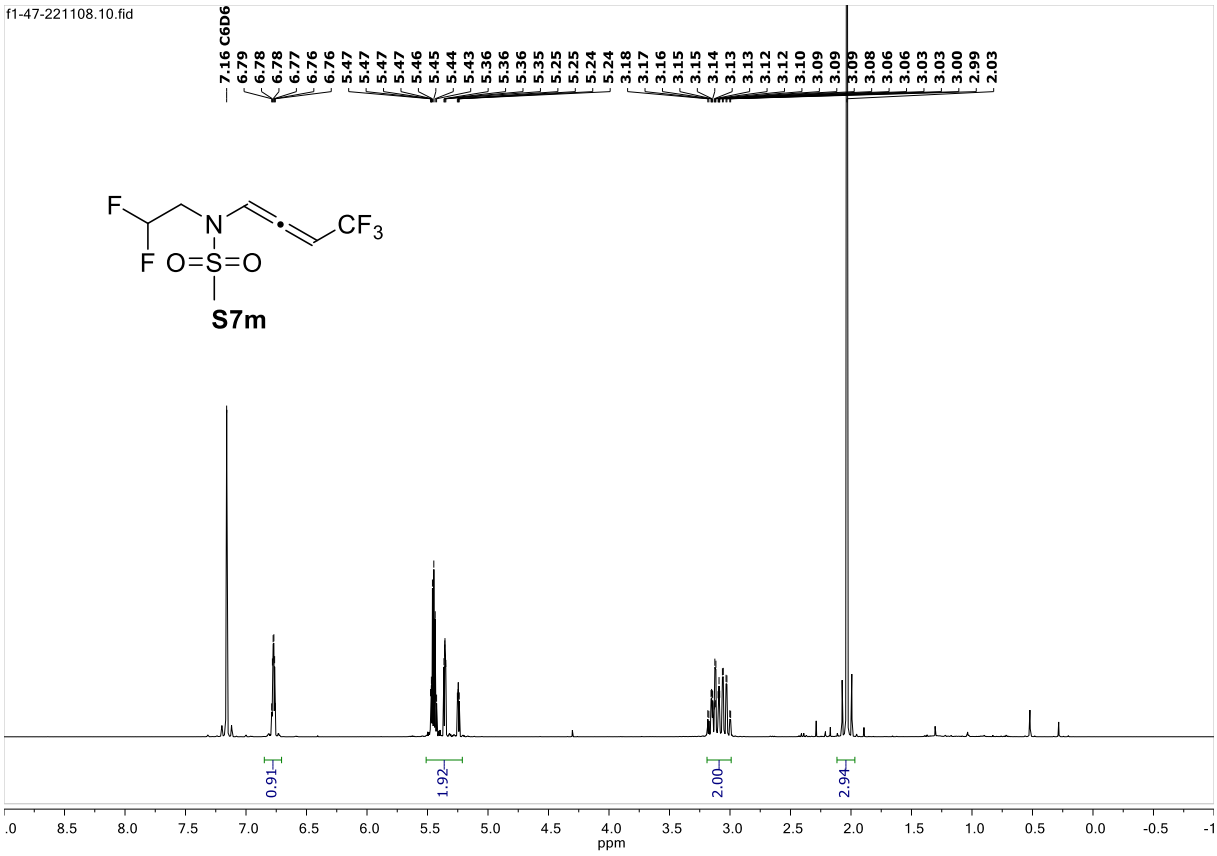
^{1}H NMR (C_6D_6, 400 MHz) of **S7l**



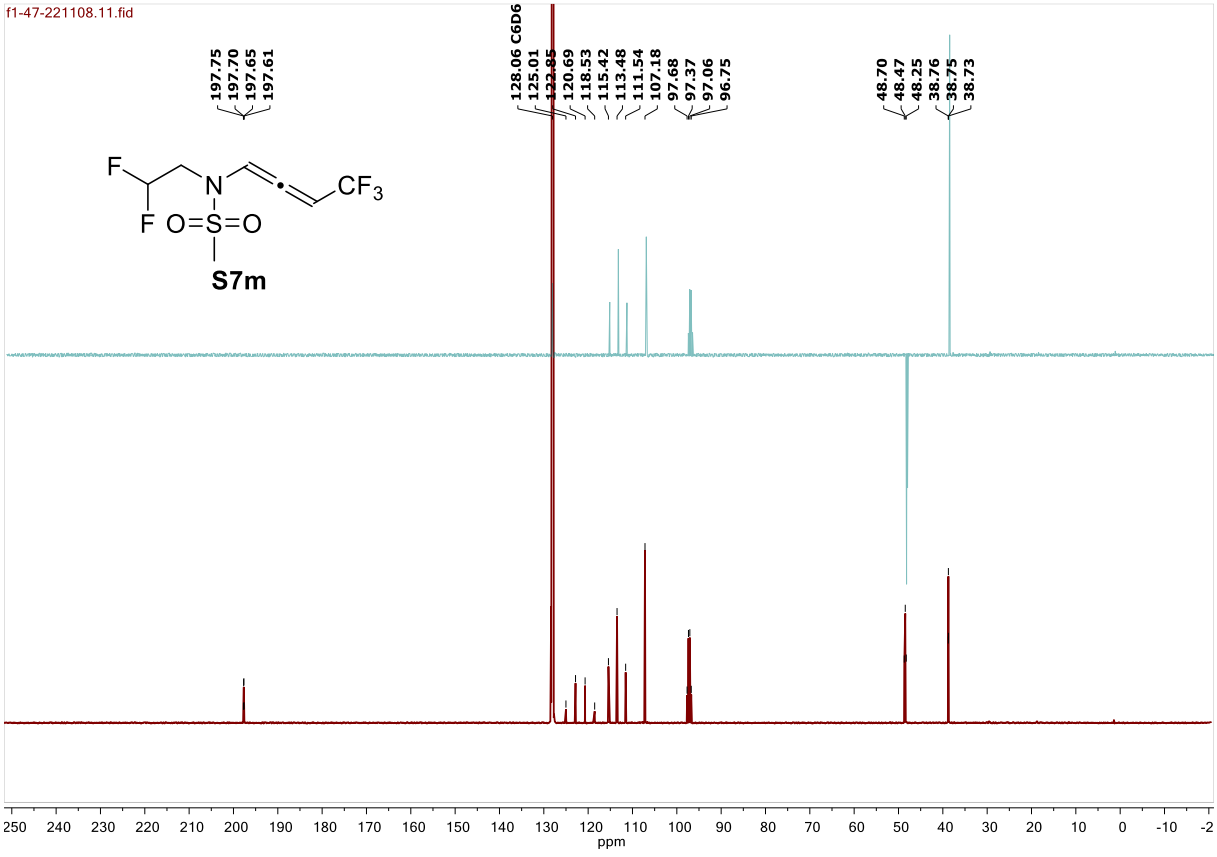
^{13}C NMR (C_6D_6, 126 MHz) of **S7l**



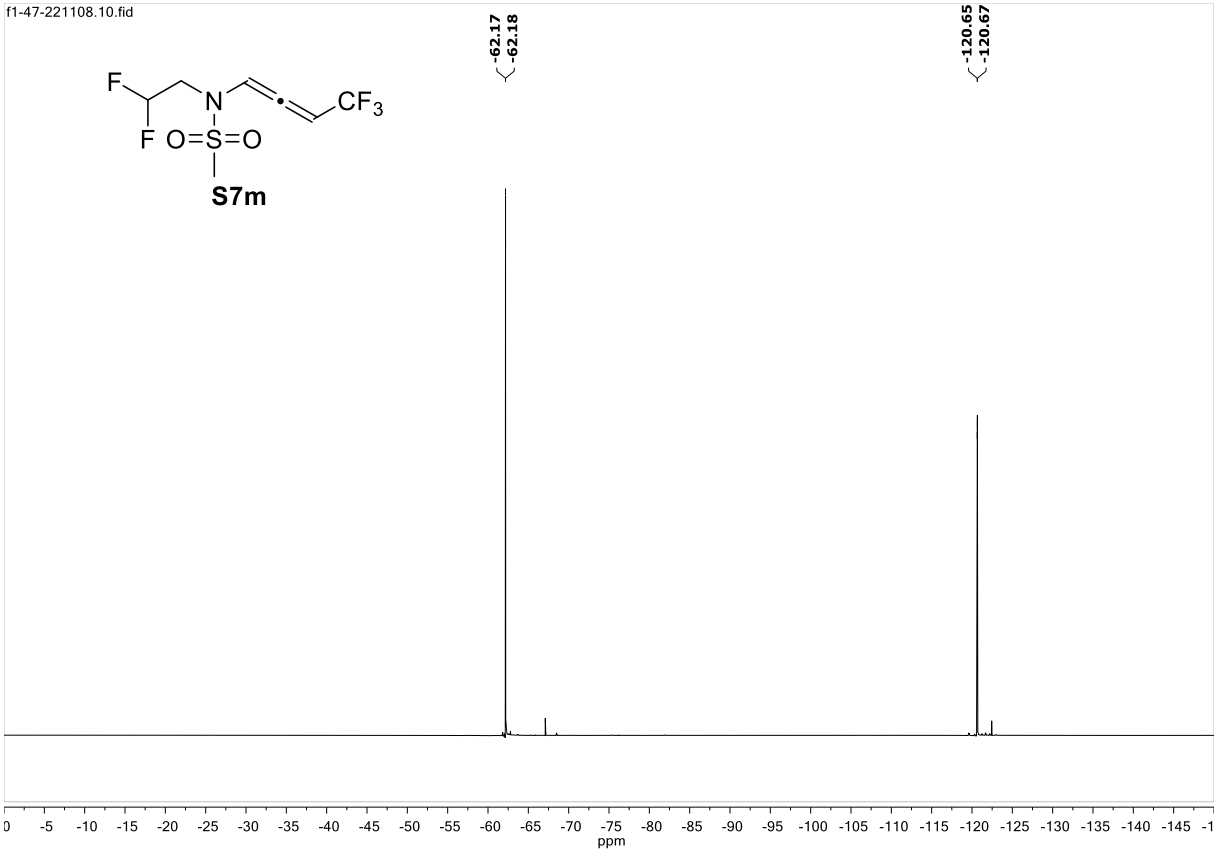
^{19}F NMR (C_6D_6, 282 MHz) of **S7l**



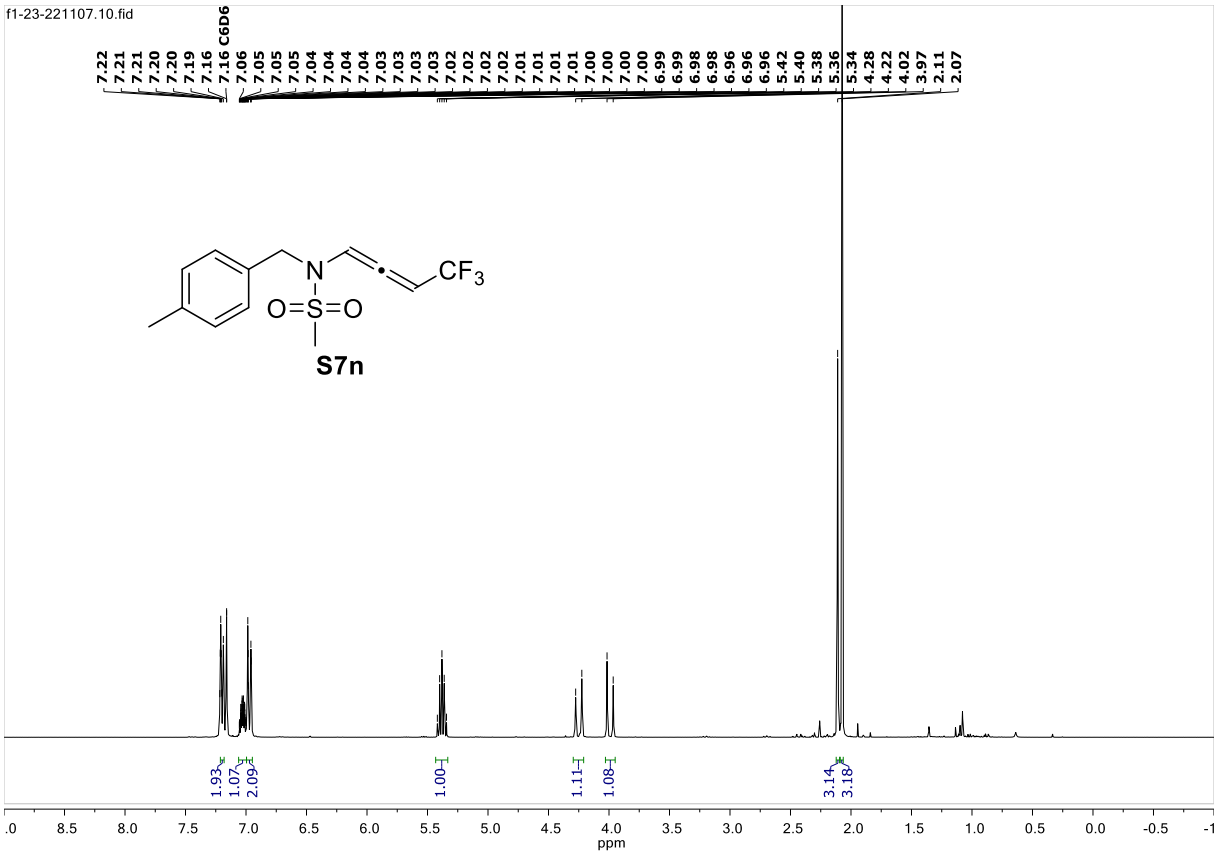
^{1}H NMR (C_6D_6, 500 MHz) of **S7m**



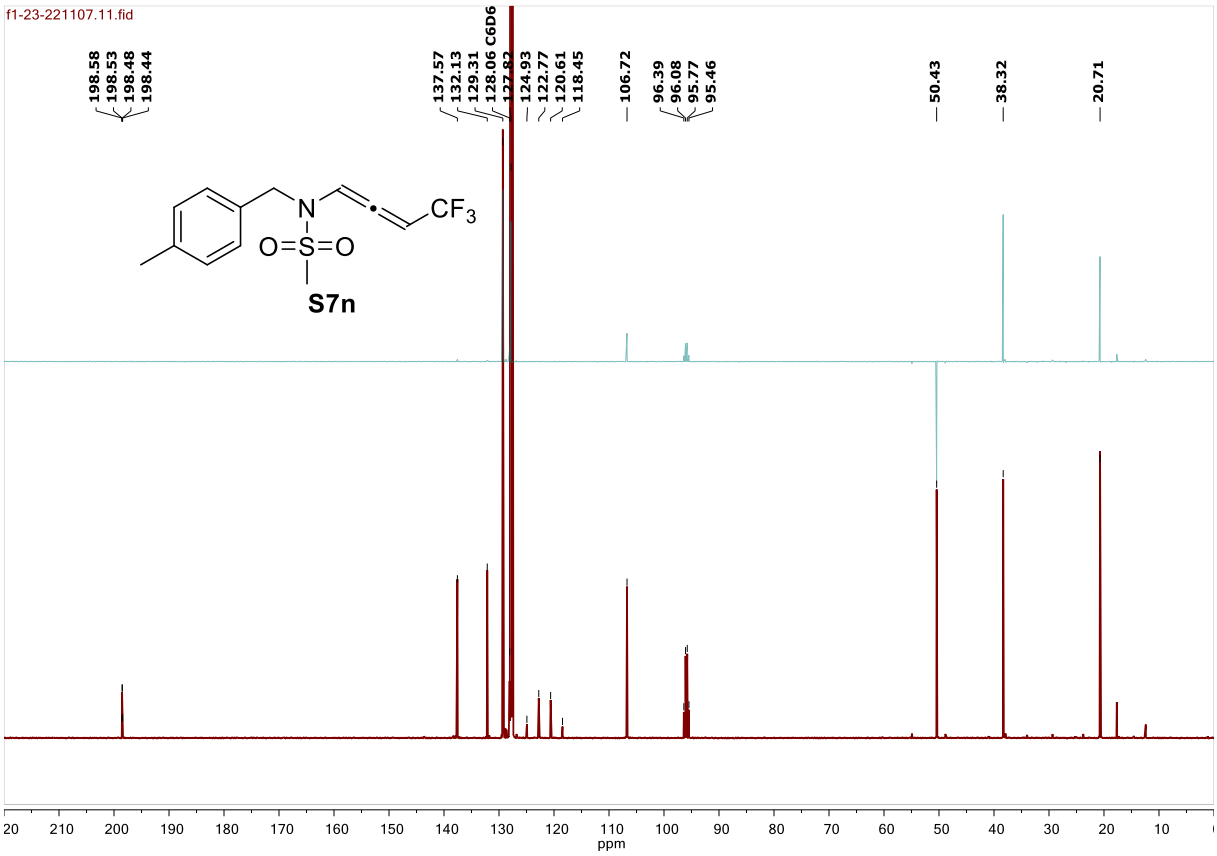
^{13}C NMR (C_6D_6, 126 MHz) of **S7m**



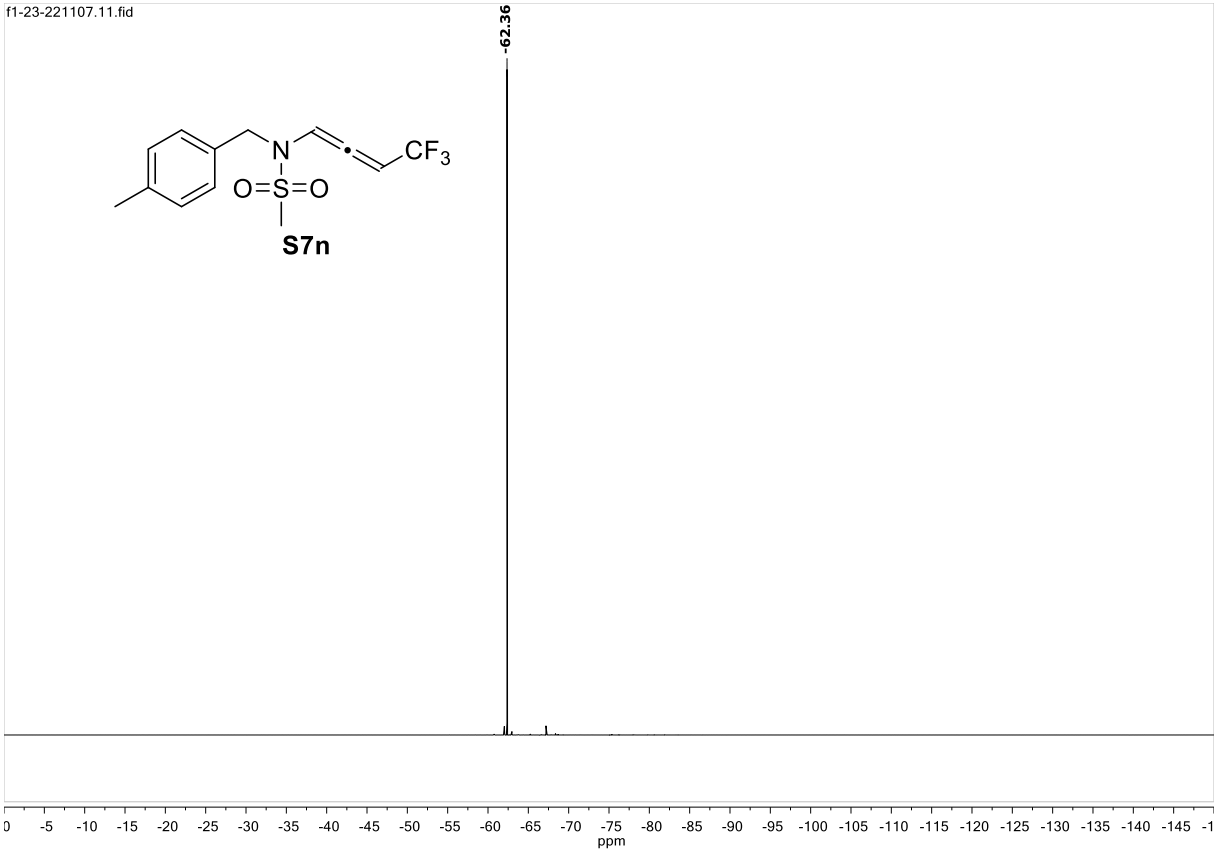
^{19}F NMR (C_6D_6, 282 MHz) of **S7m**



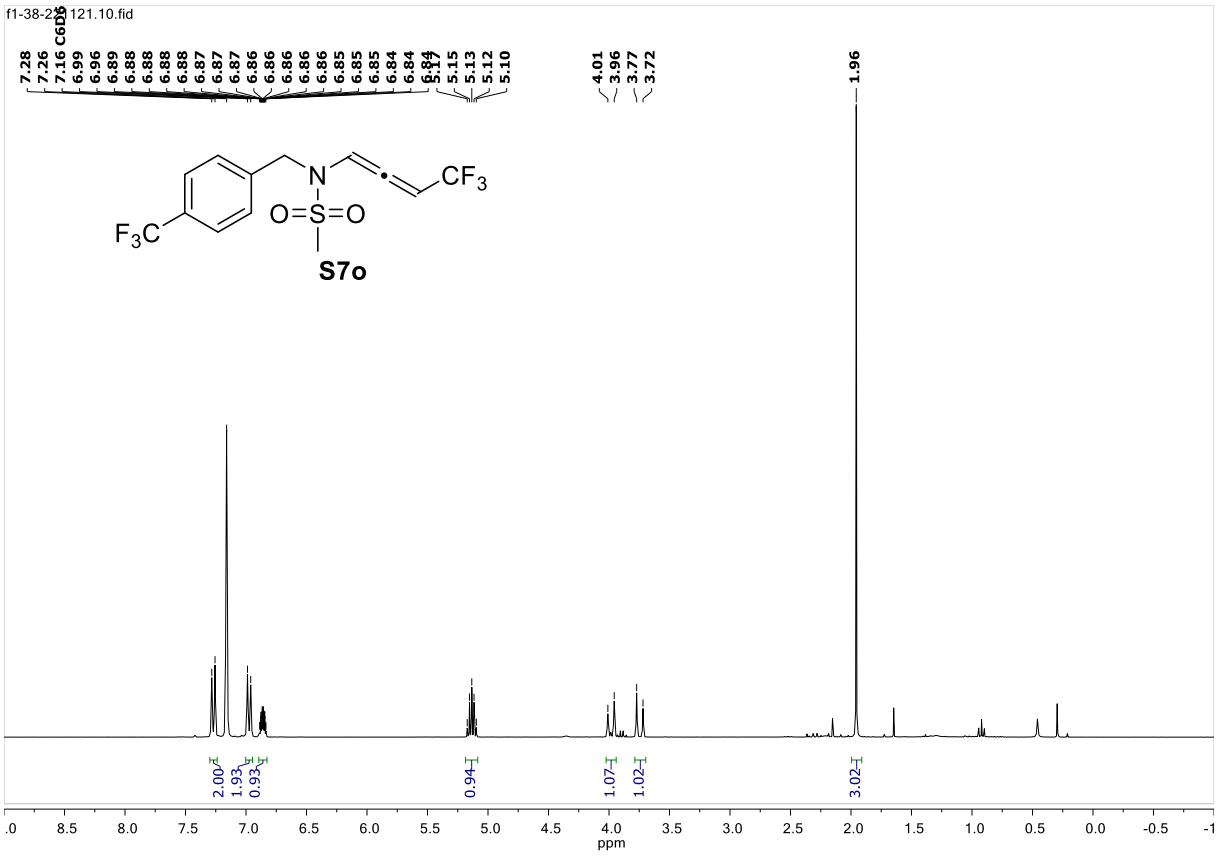
^{1}H NMR (C_6D_6, 500 MHz) of **S7n**



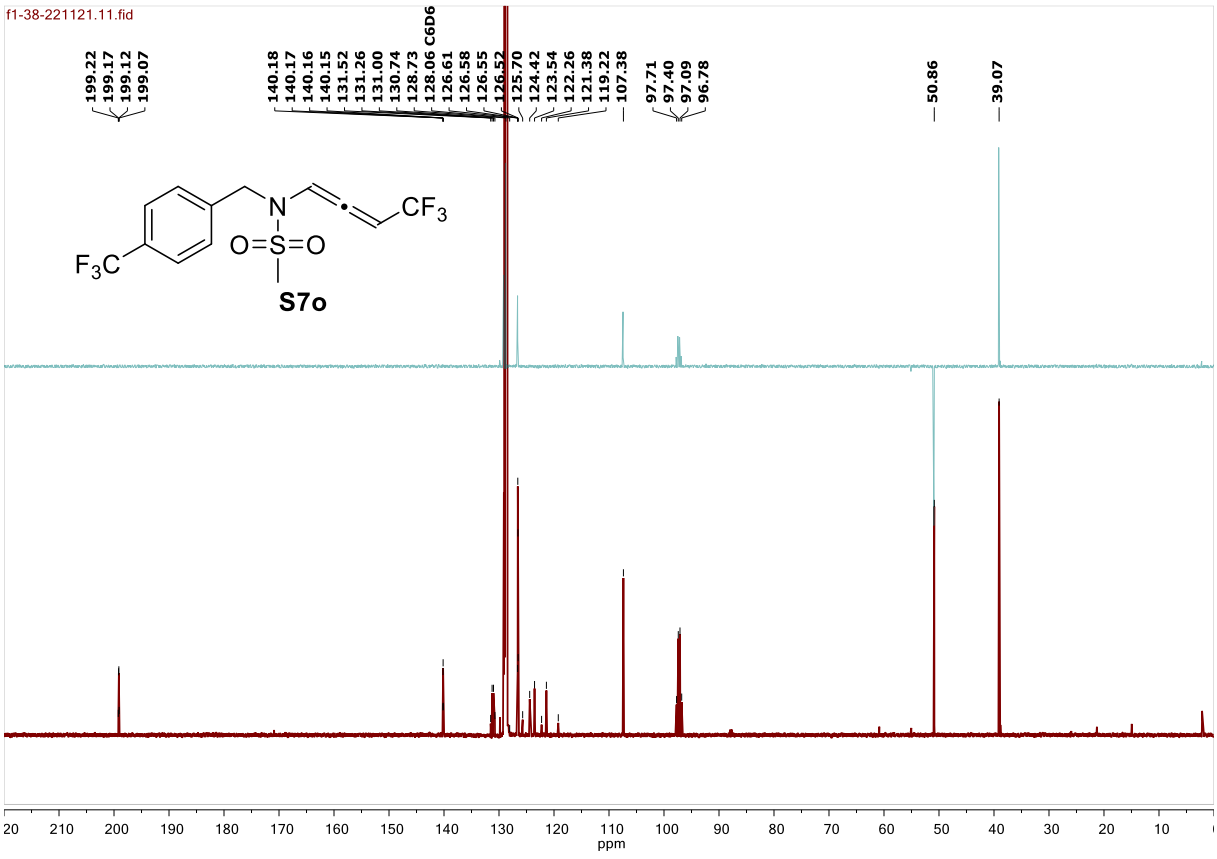
^{13}C NMR (C_6D_6, 126 MHz) of **S7n**



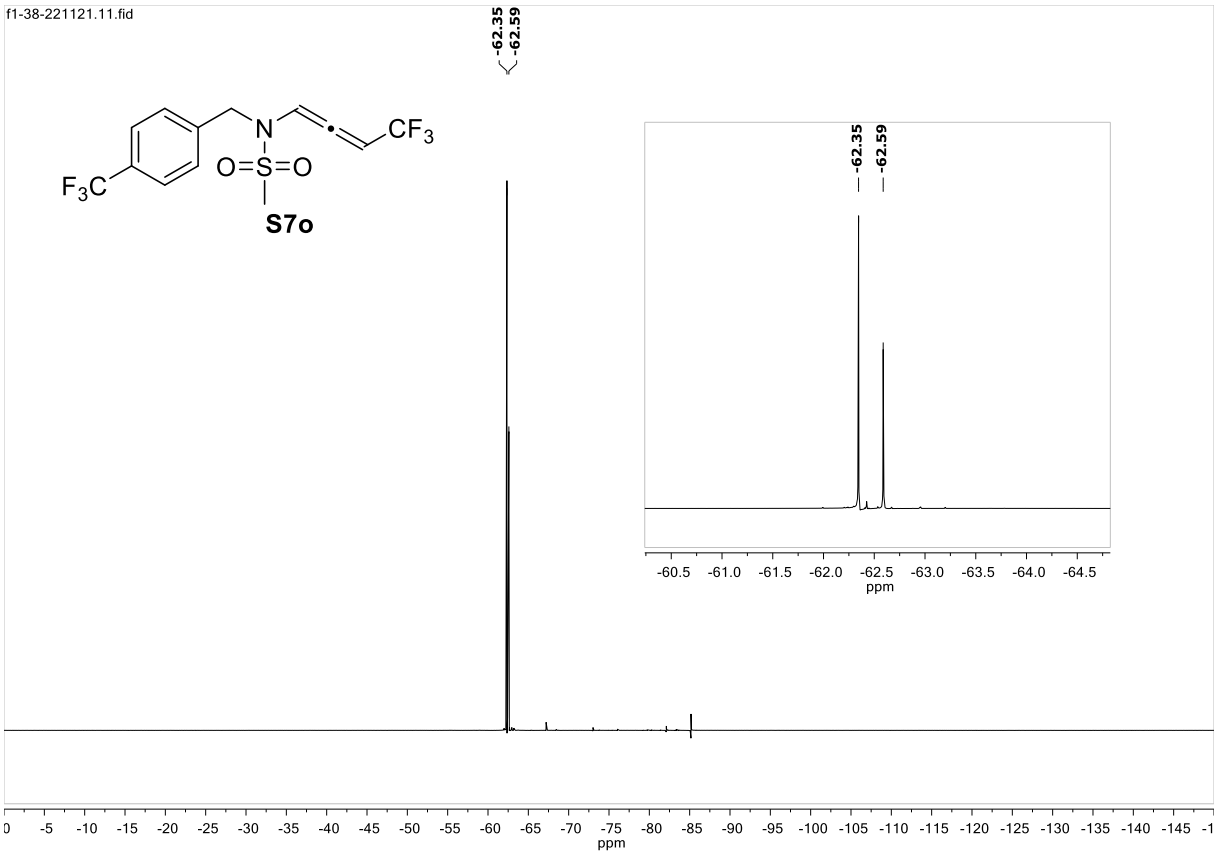
^{19}F NMR (C_6D_6, 282 MHz) of **S7n**



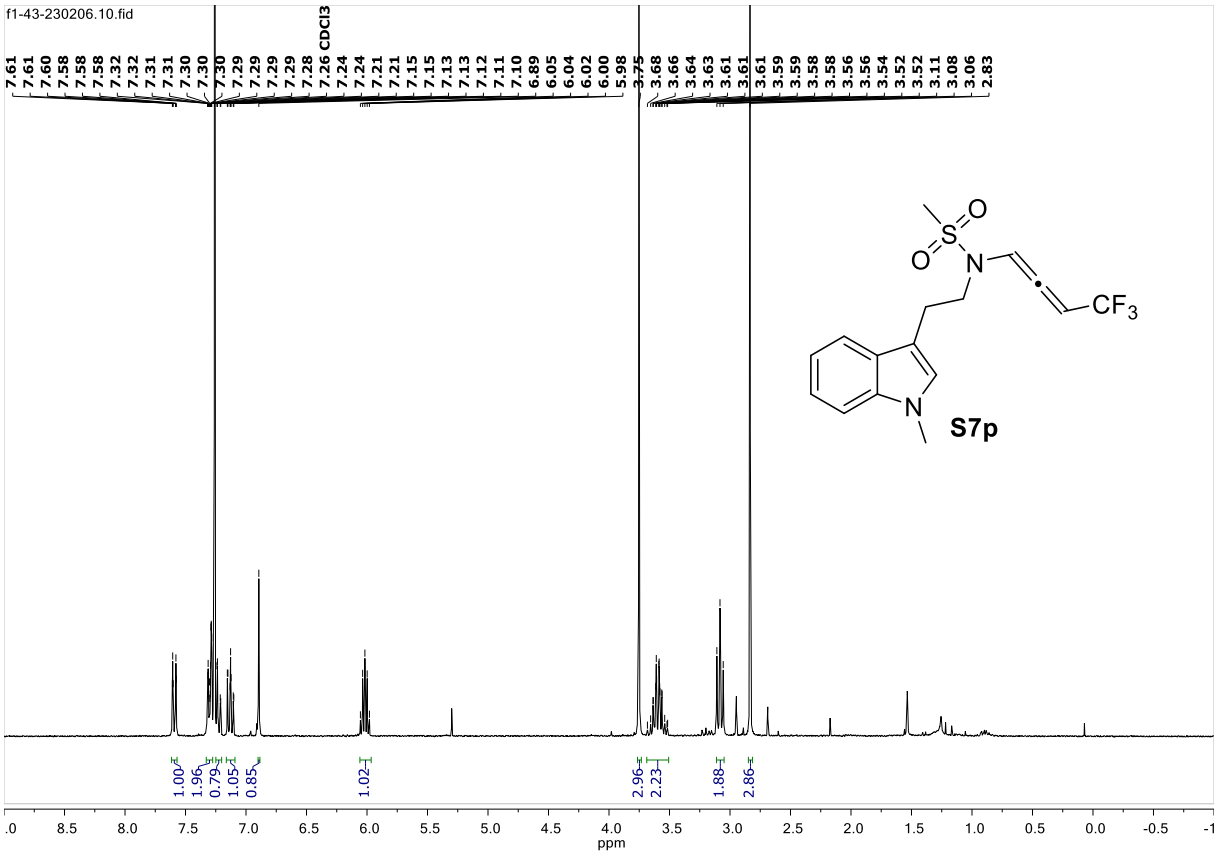
^{1}H NMR (C_6D_6, 300 MHz) of **S7o**



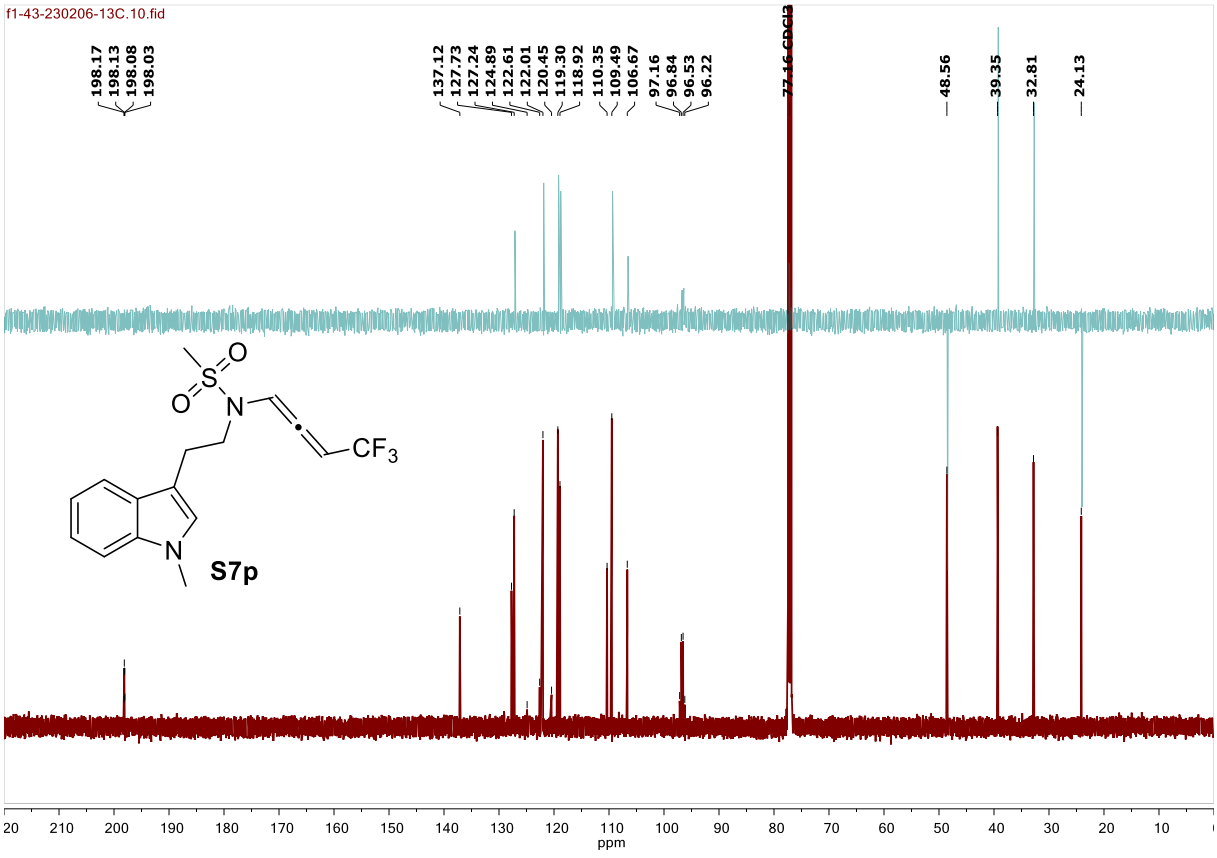
^{13}C NMR (C_6D_6, 126 MHz) of **S7o**



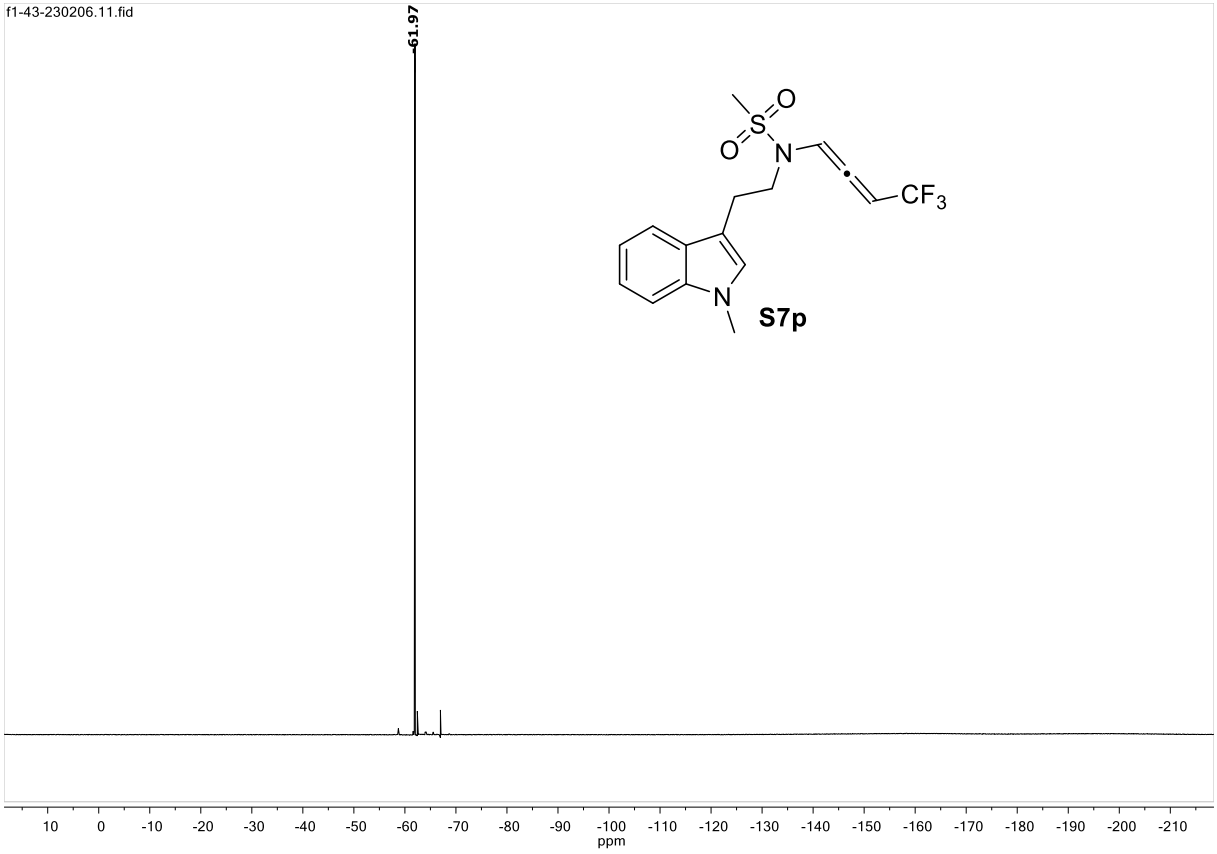
^{19}F NMR (C_6D_6, 282 MHz) of **S7o**



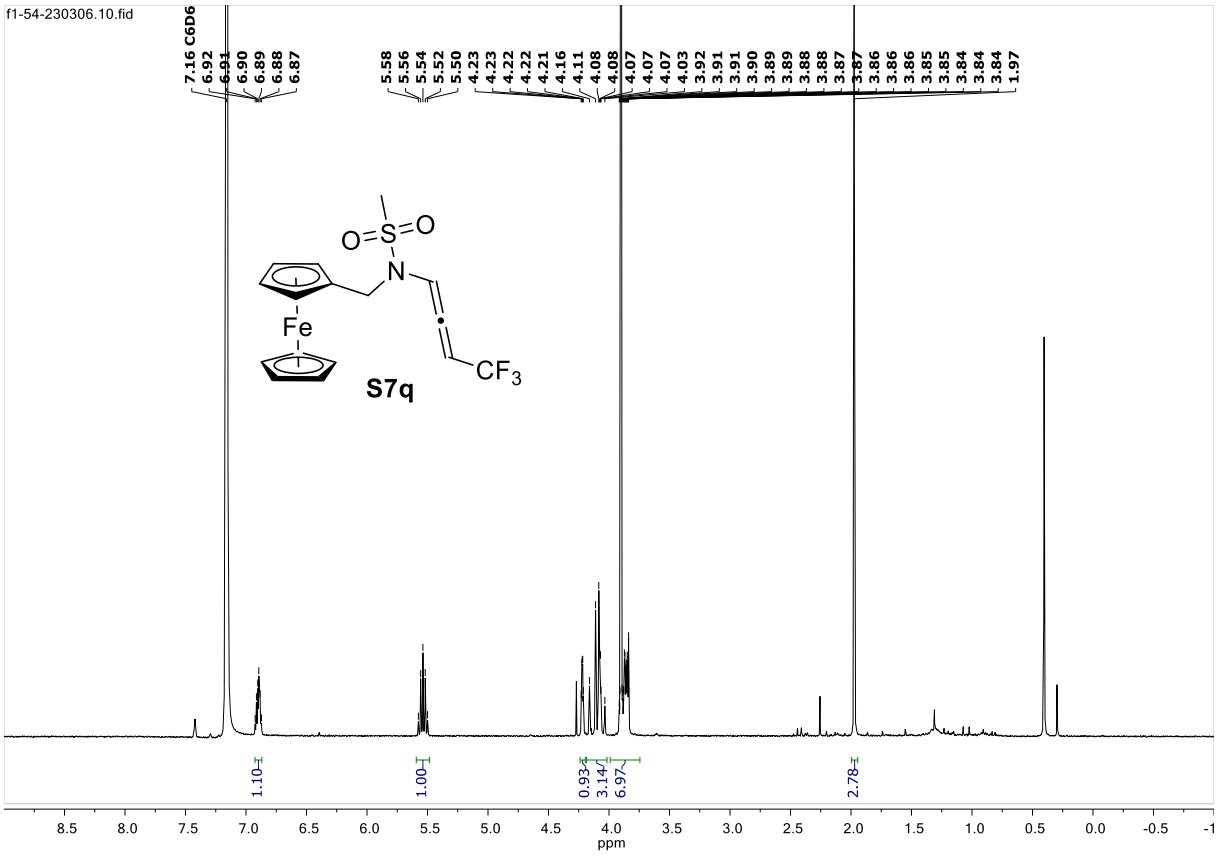
^{1}H NMR ($CDCl_3$, 300 MHz) of **S7p**



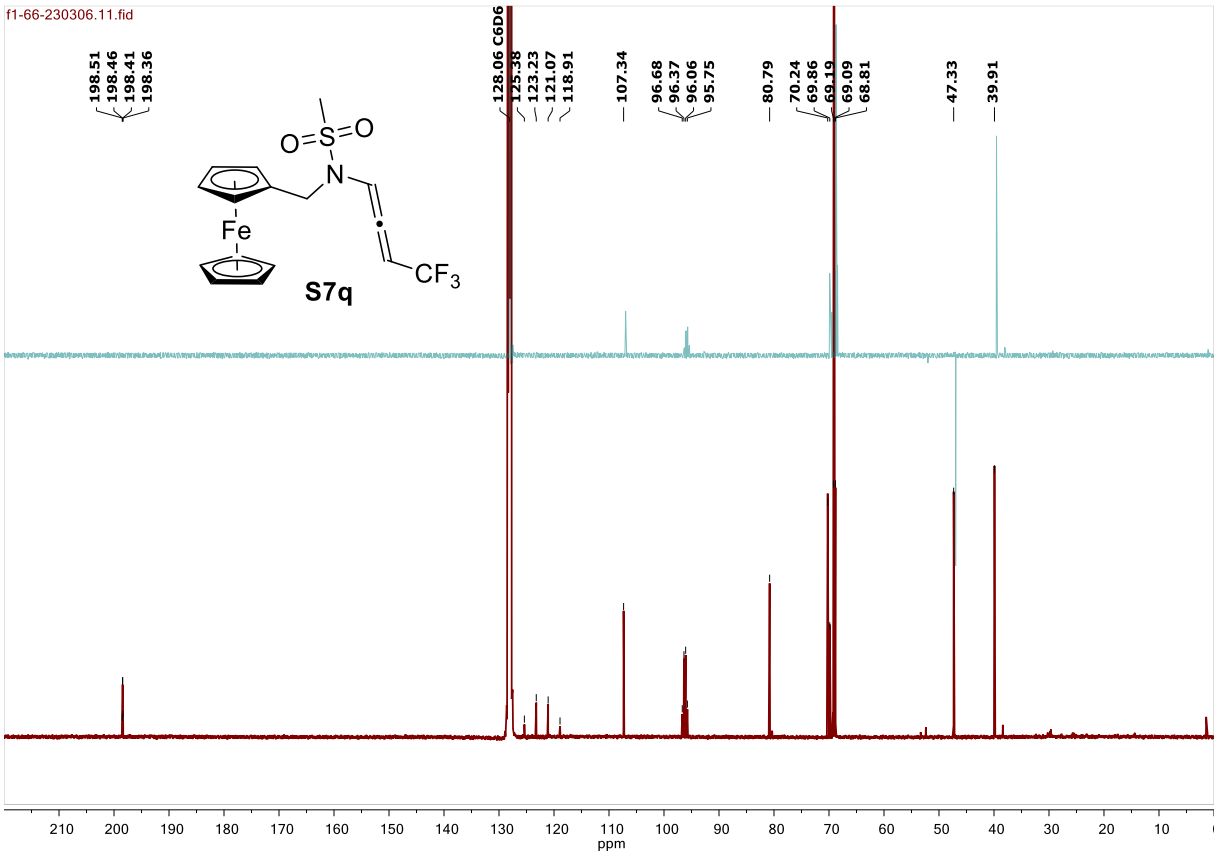
^{13}C NMR ($CDCl_3$, 126 MHz) of **S7p**



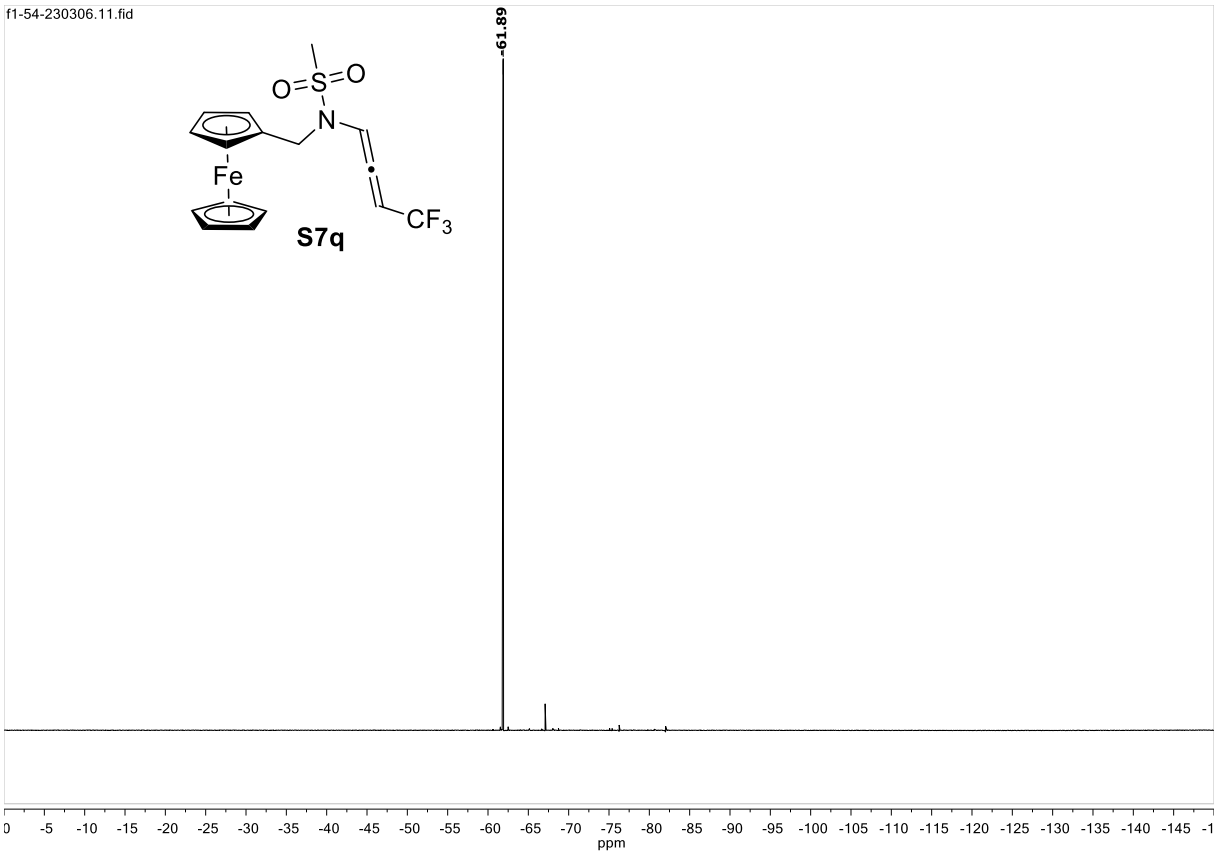
^{19}F NMR ($CDCl_3$, 282 MHz) of **S7p**



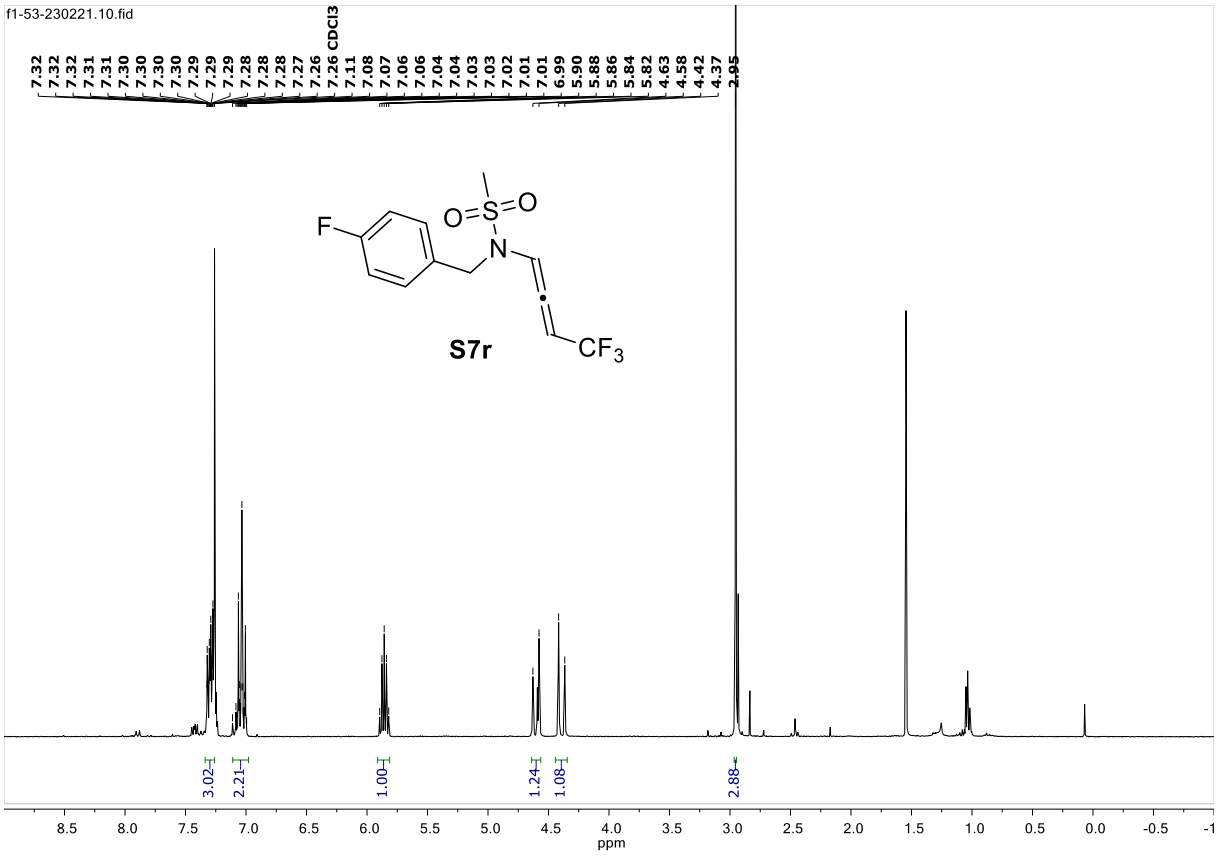
^{1}H NMR (C_6D_6, 300 MHz) of **S7q**



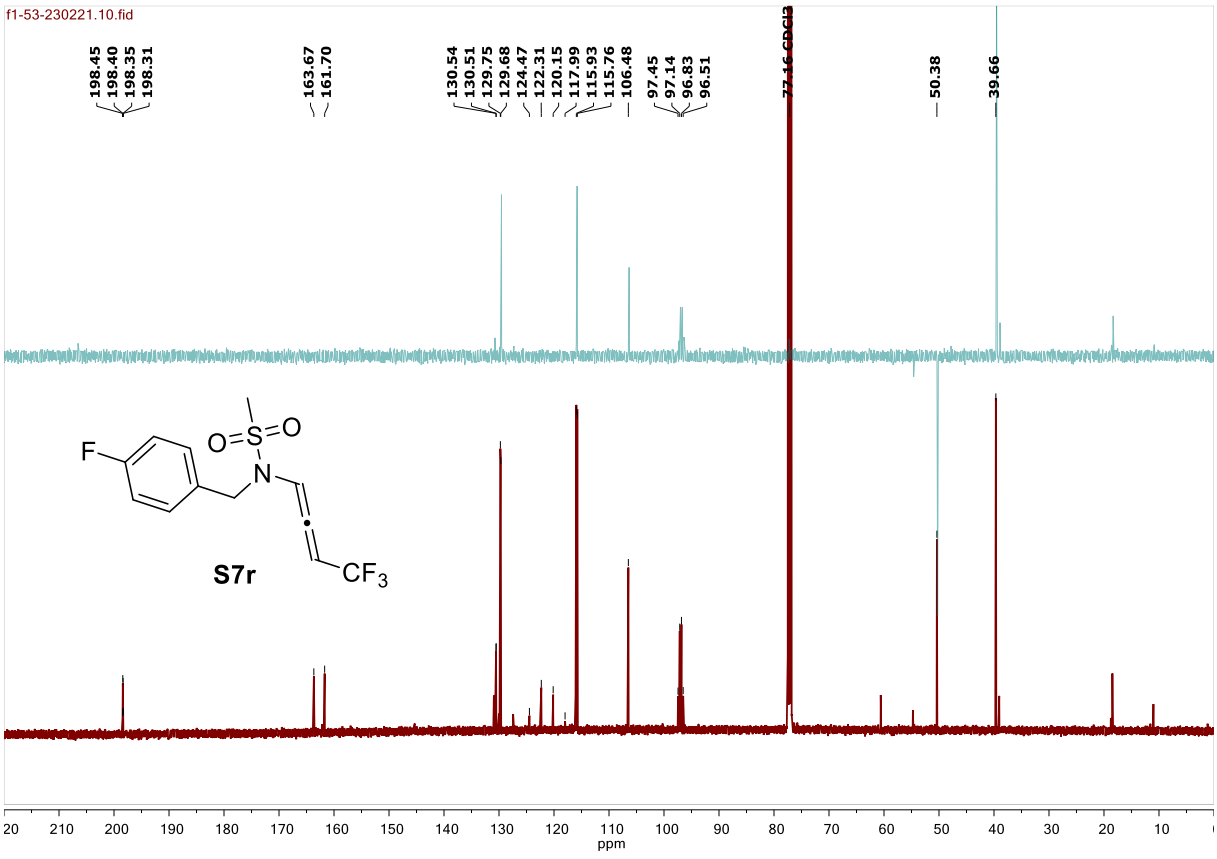
^{13}C NMR (C_6D_6, 126 MHz) of **S7q**



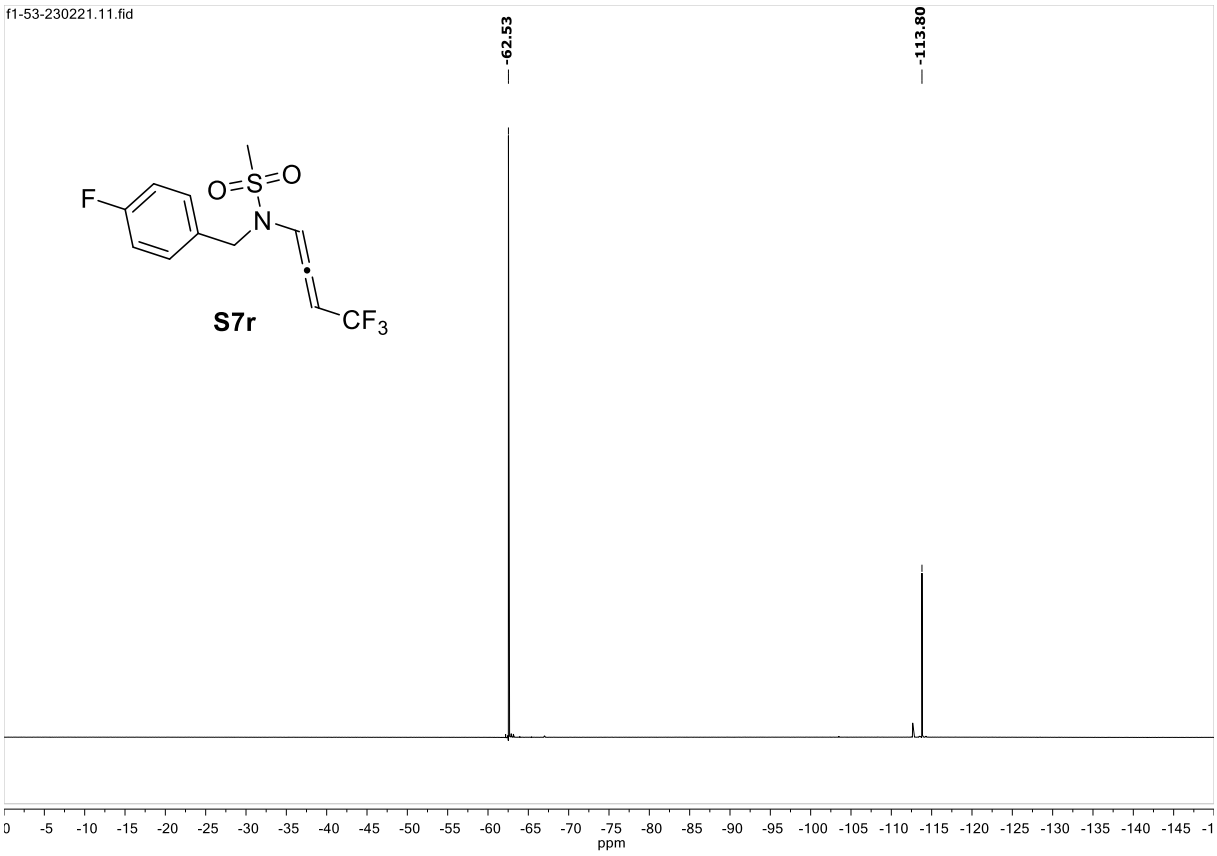
^{19}F NMR (C_6D_6, 282 MHz) of **S7q**



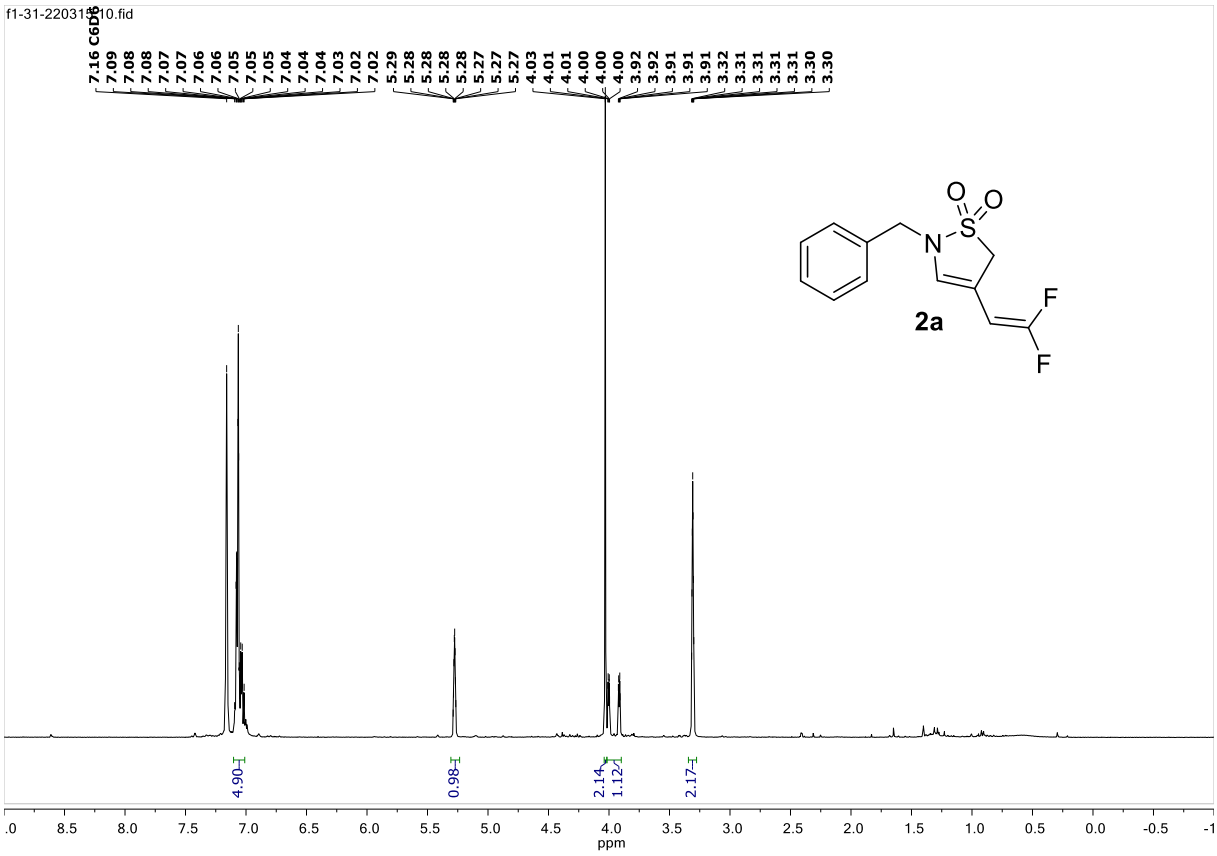
^{1}H NMR ($CDCl_3$, 300 MHz) of **S7r**



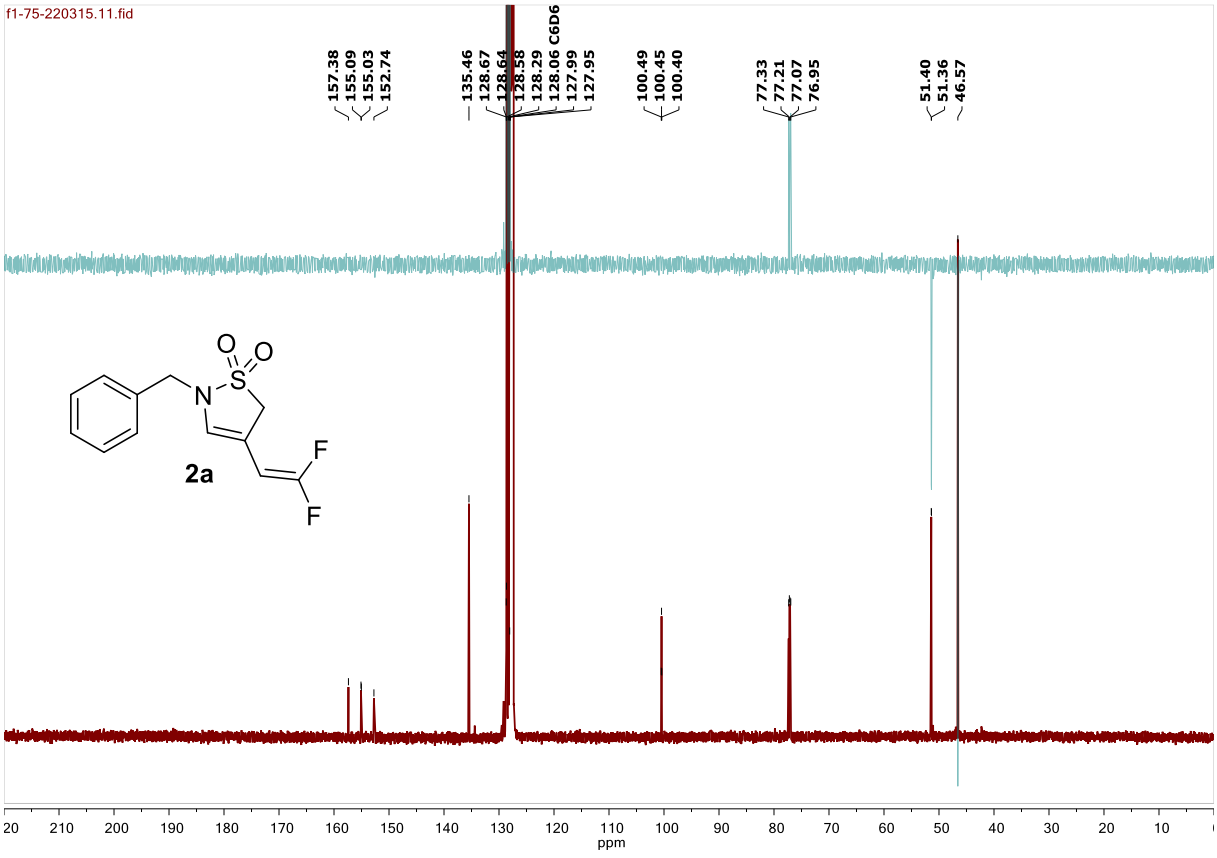
^{13}C NMR (C_6D_6, 126 MHz) of **S7r**



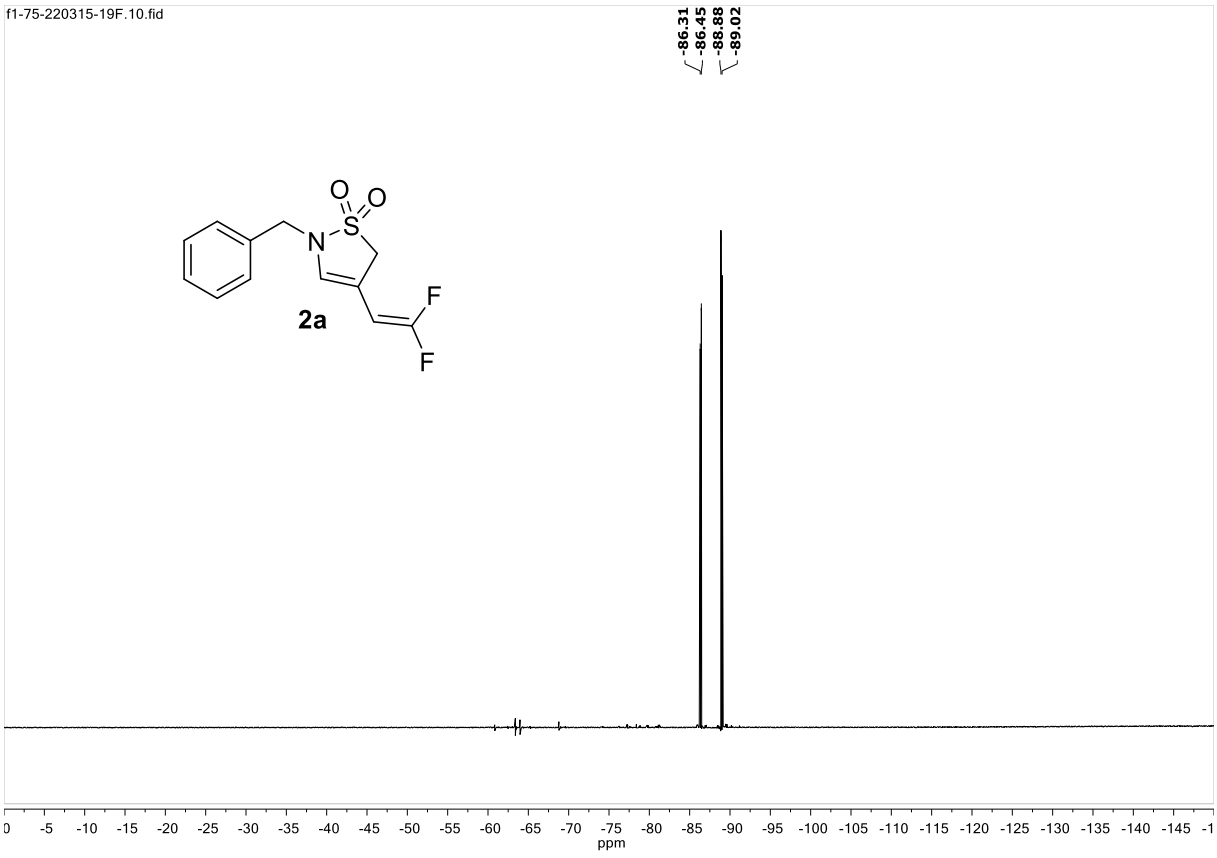
^{19}F NMR (C_6D_6, 282 MHz) of **S7r**



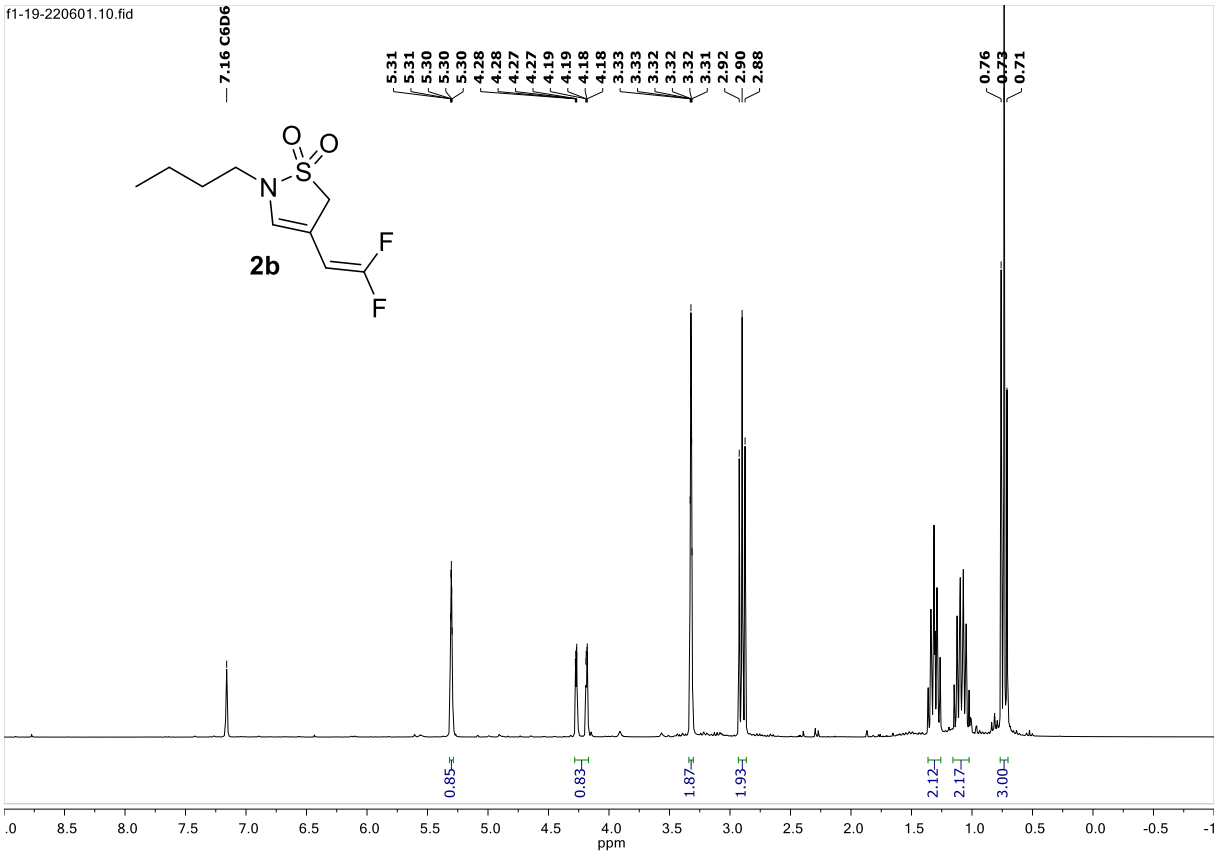
^{1}H NMR (C_6D_6, 300 MHz) of **2a**



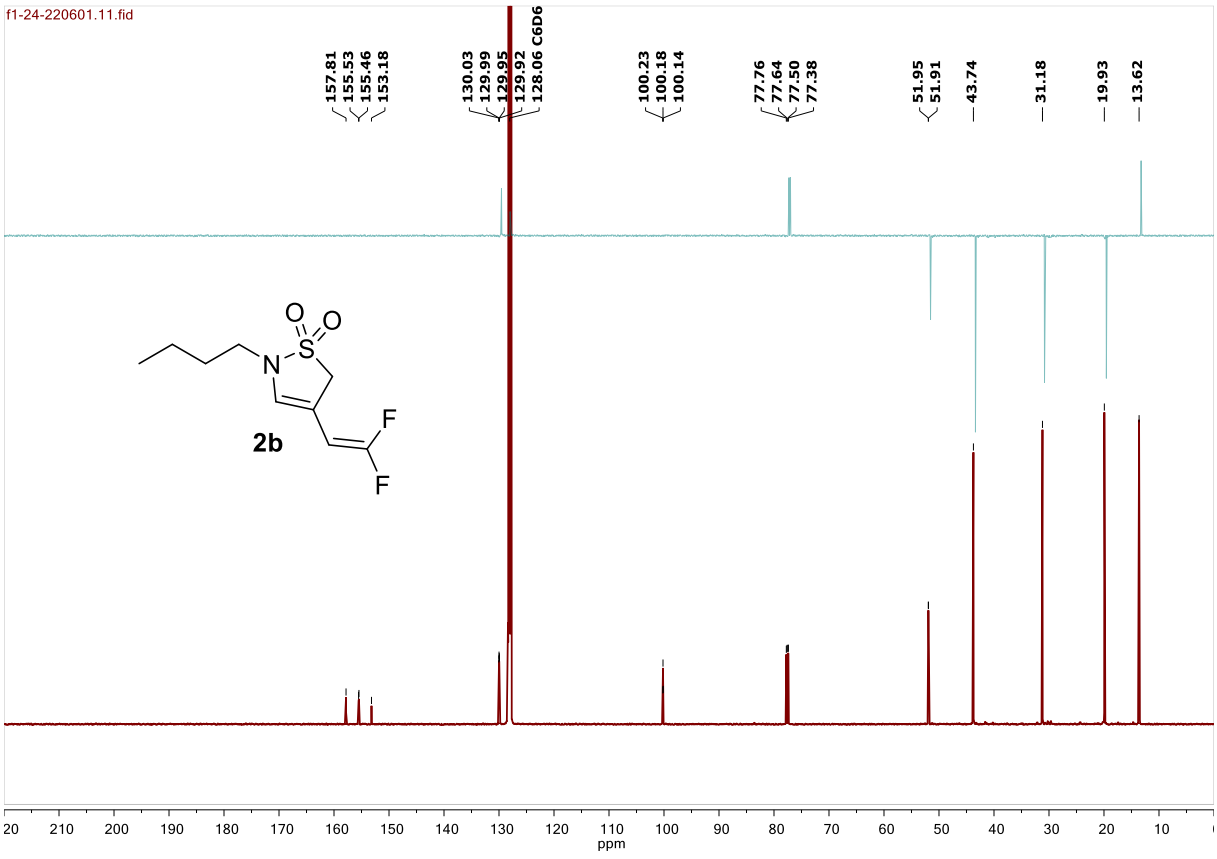
^{13}C NMR (C_6D_6, 126 MHz) of **2a**



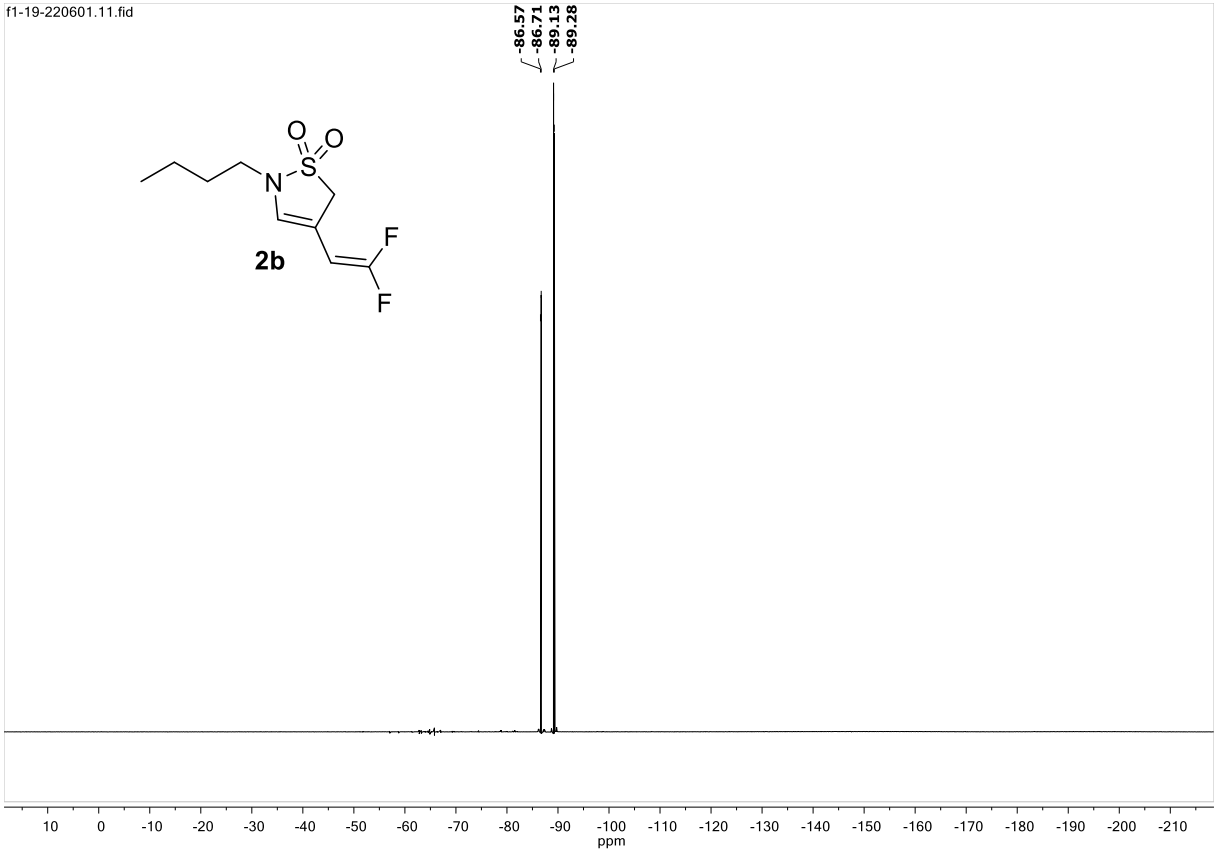
^{19}F NMR (C_6D_6, 282 MHz) of **2a**



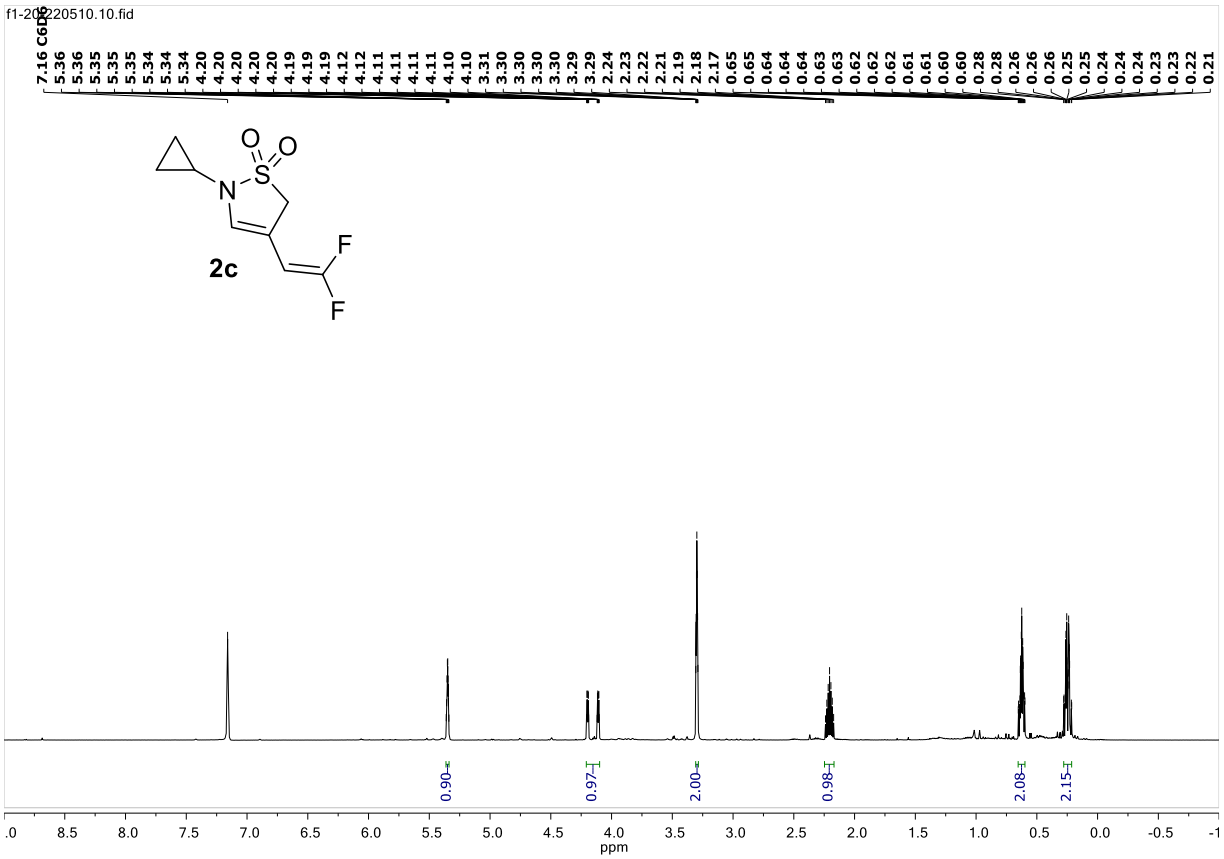
^{1}H NMR (C_6D_6, 500 MHz) of **2b**



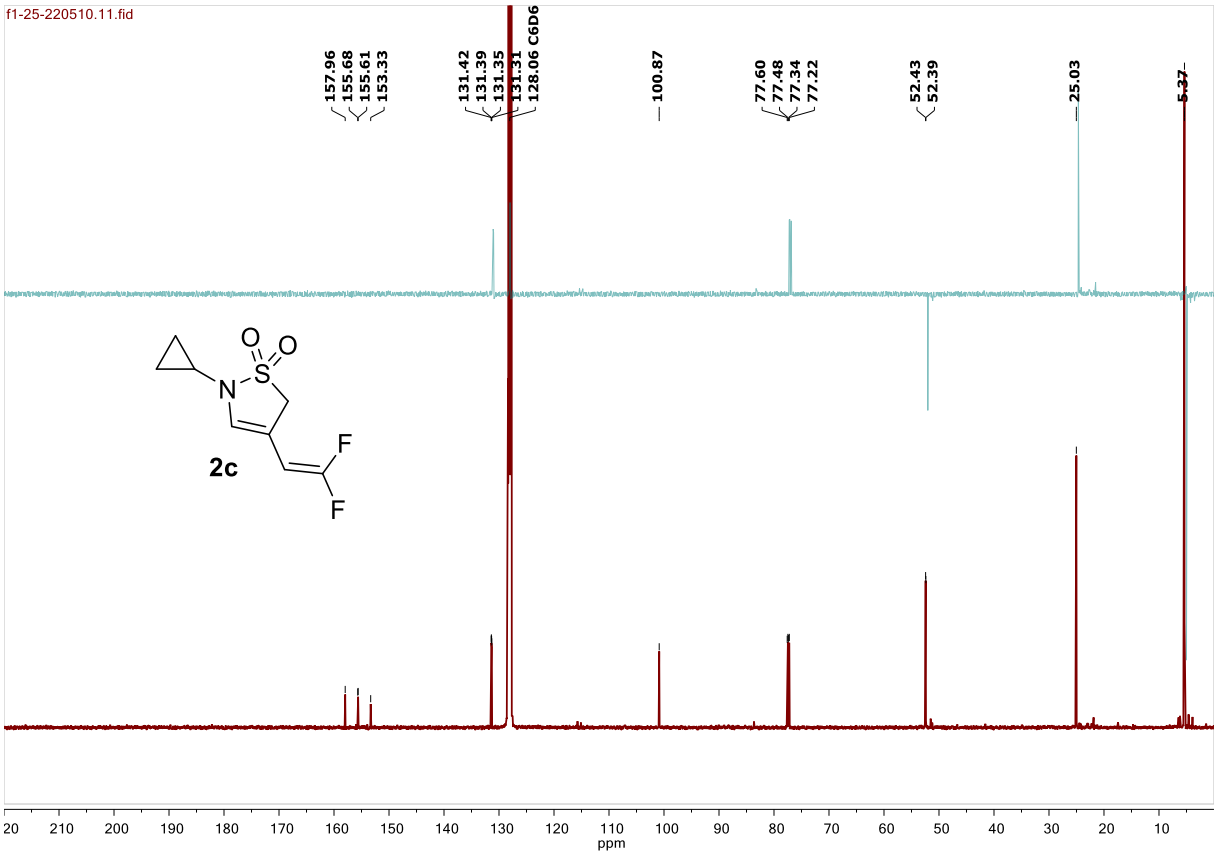
^{13}C NMR (C_6D_6, 126 MHz) of **2b**



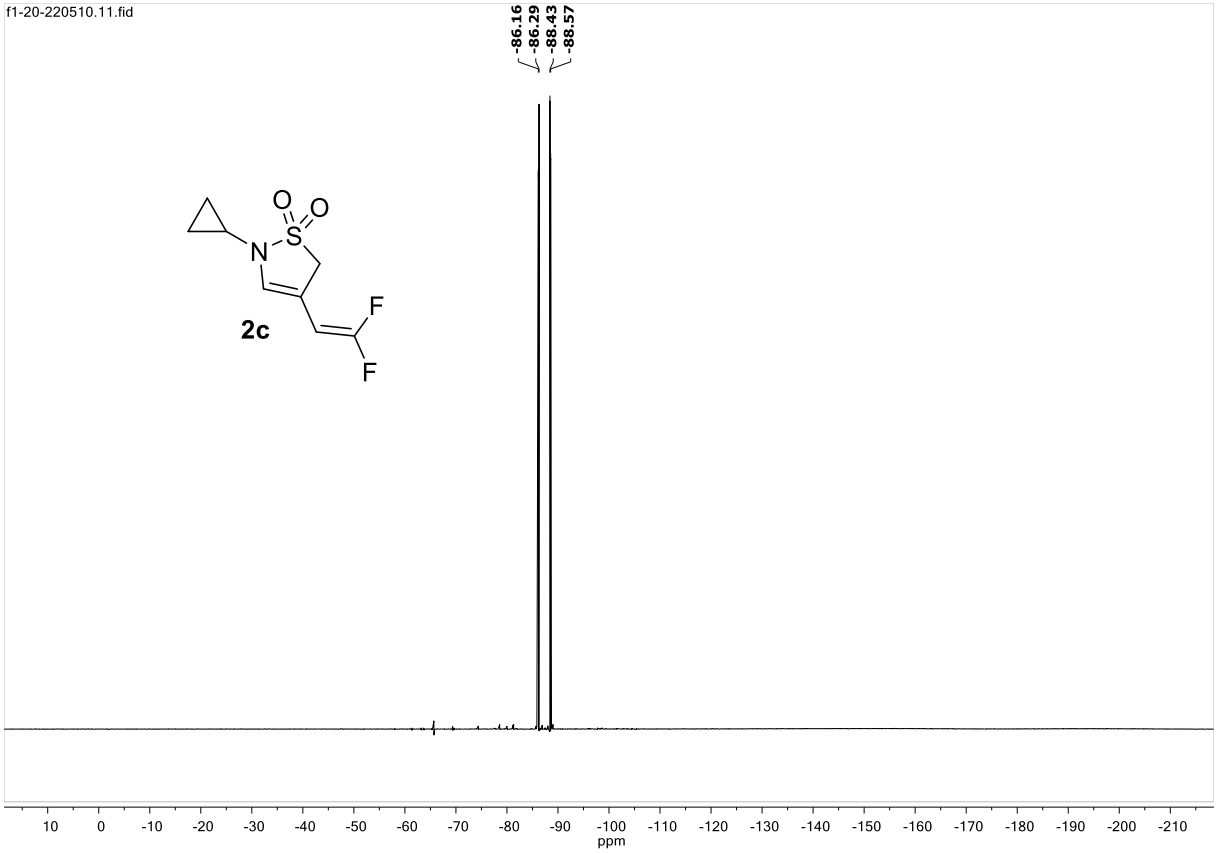
^{19}F NMR (C_6D_6, 282 MHz) of **2b**



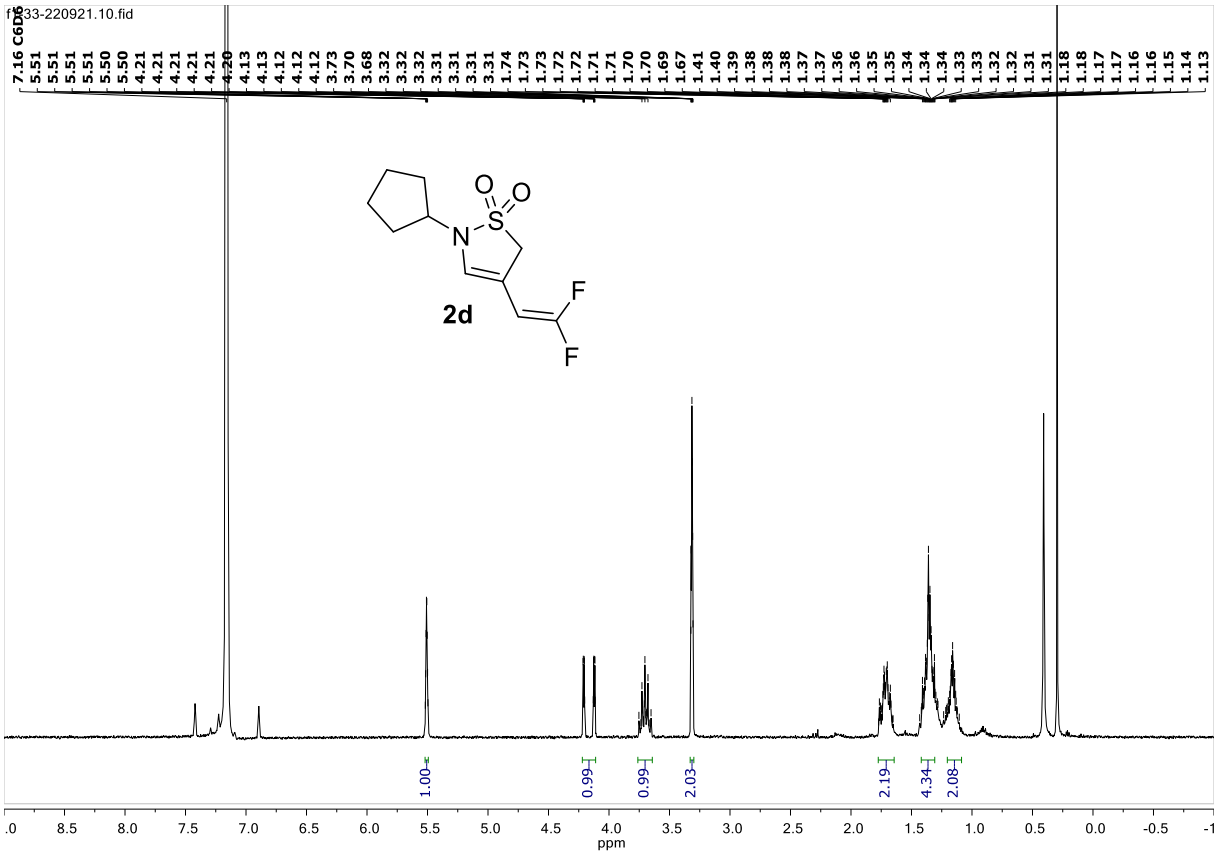
^{1}H NMR (C_6D_6, 300 MHz) of **2c**



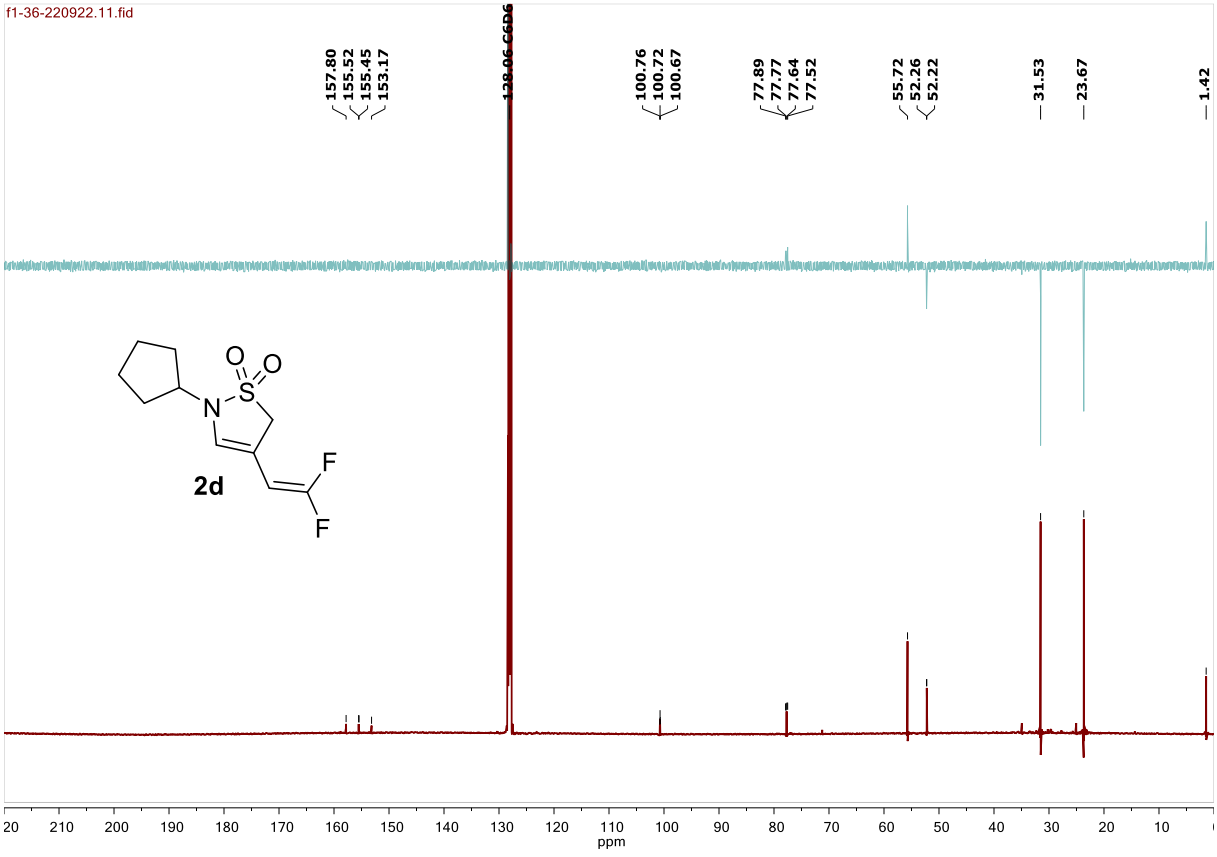
^{13}C NMR (C_6D_6, 126 MHz) of **2c**



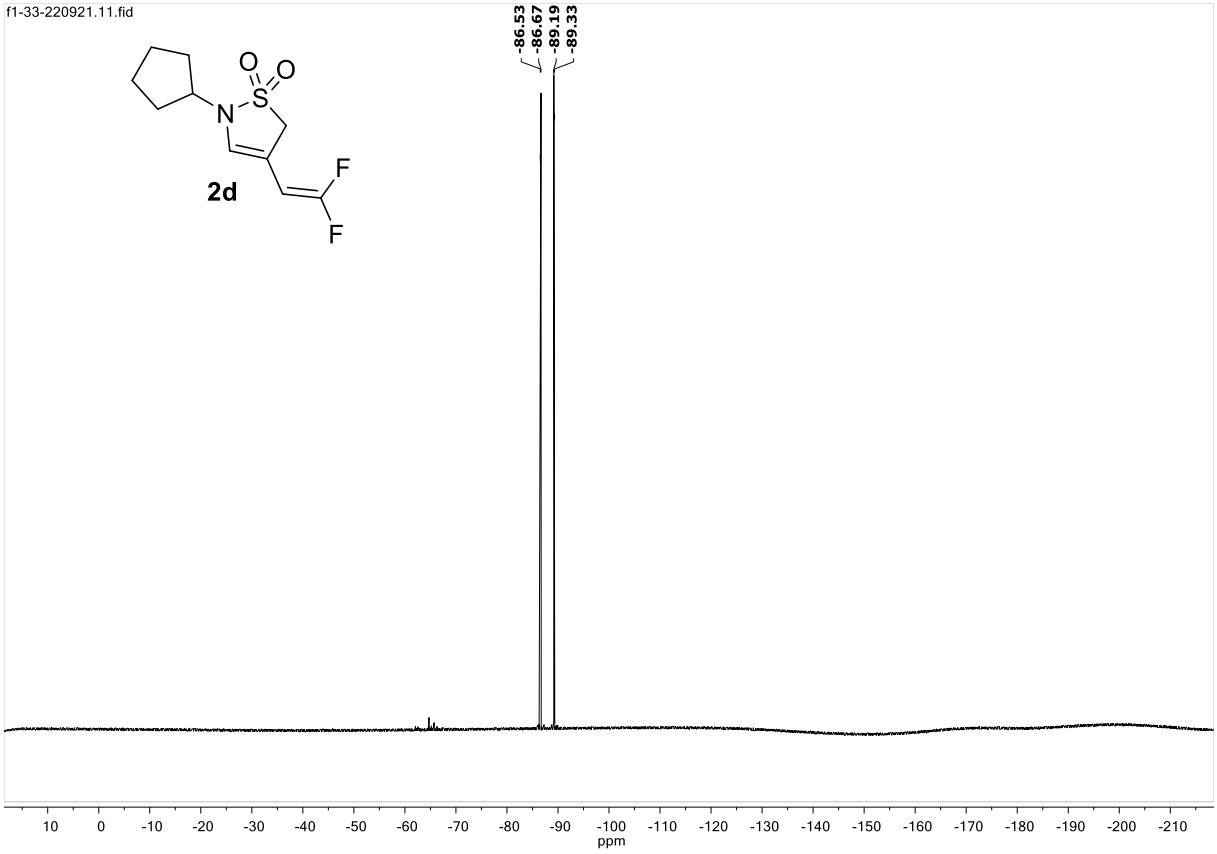
^{19}F NMR (C_6D_6, 282 MHz) of **2c**



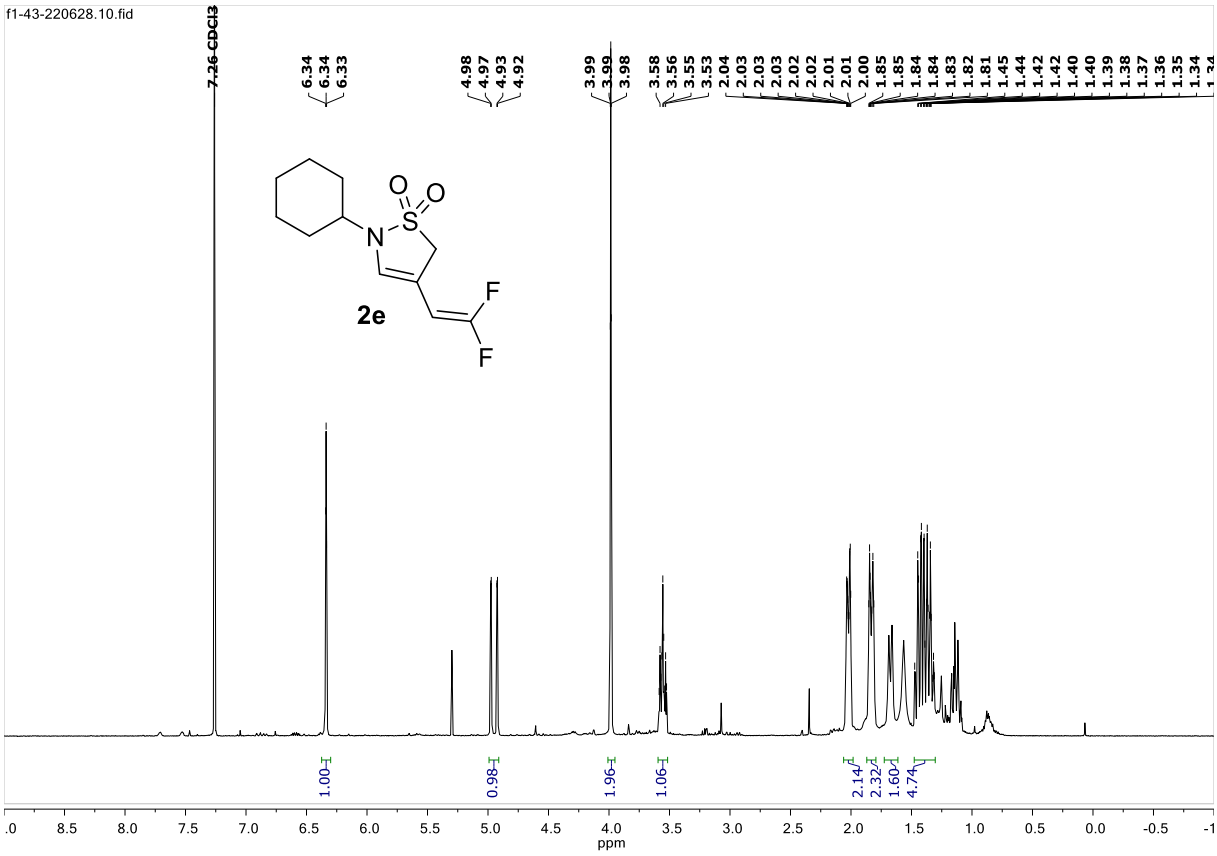
^{1}H NMR (C_6D_6, 300 MHz) of **2d**



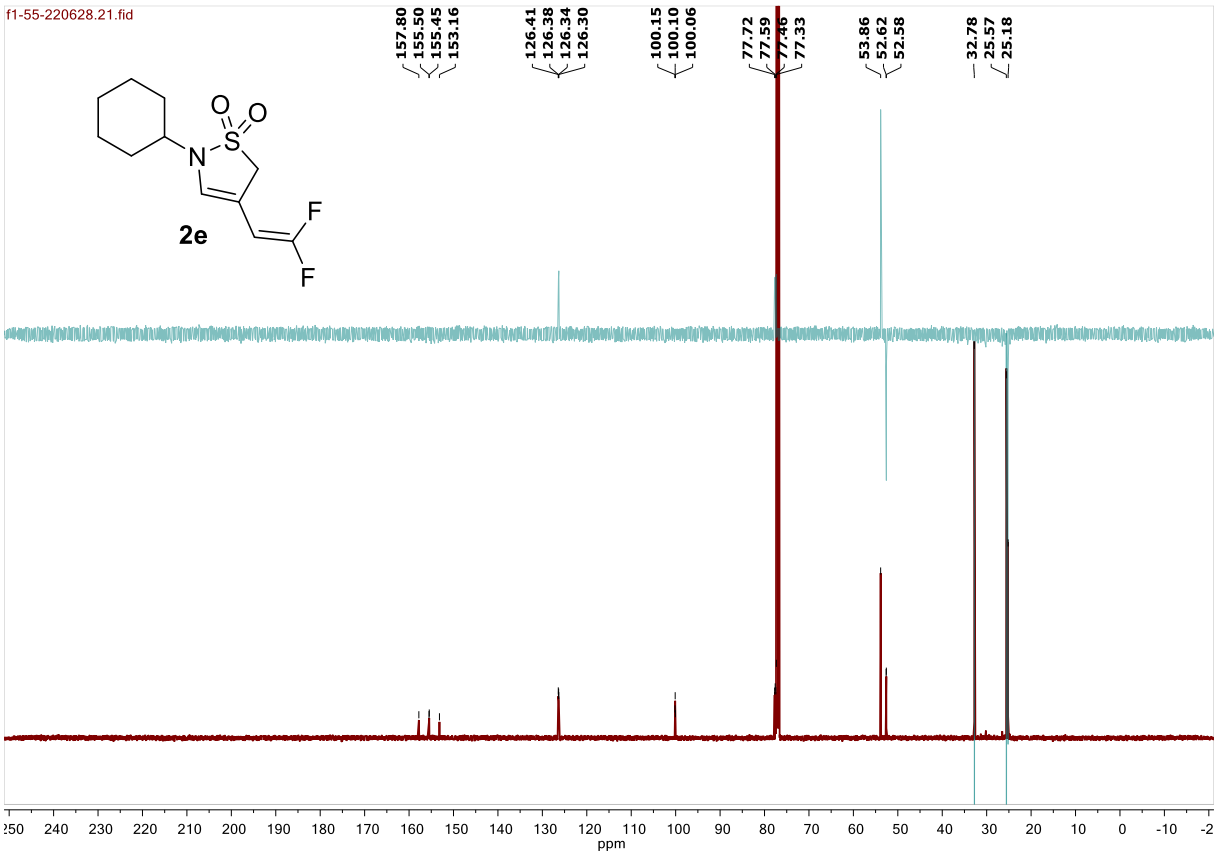
^{13}C NMR (C_6D_6, 126 MHz) of **2d**



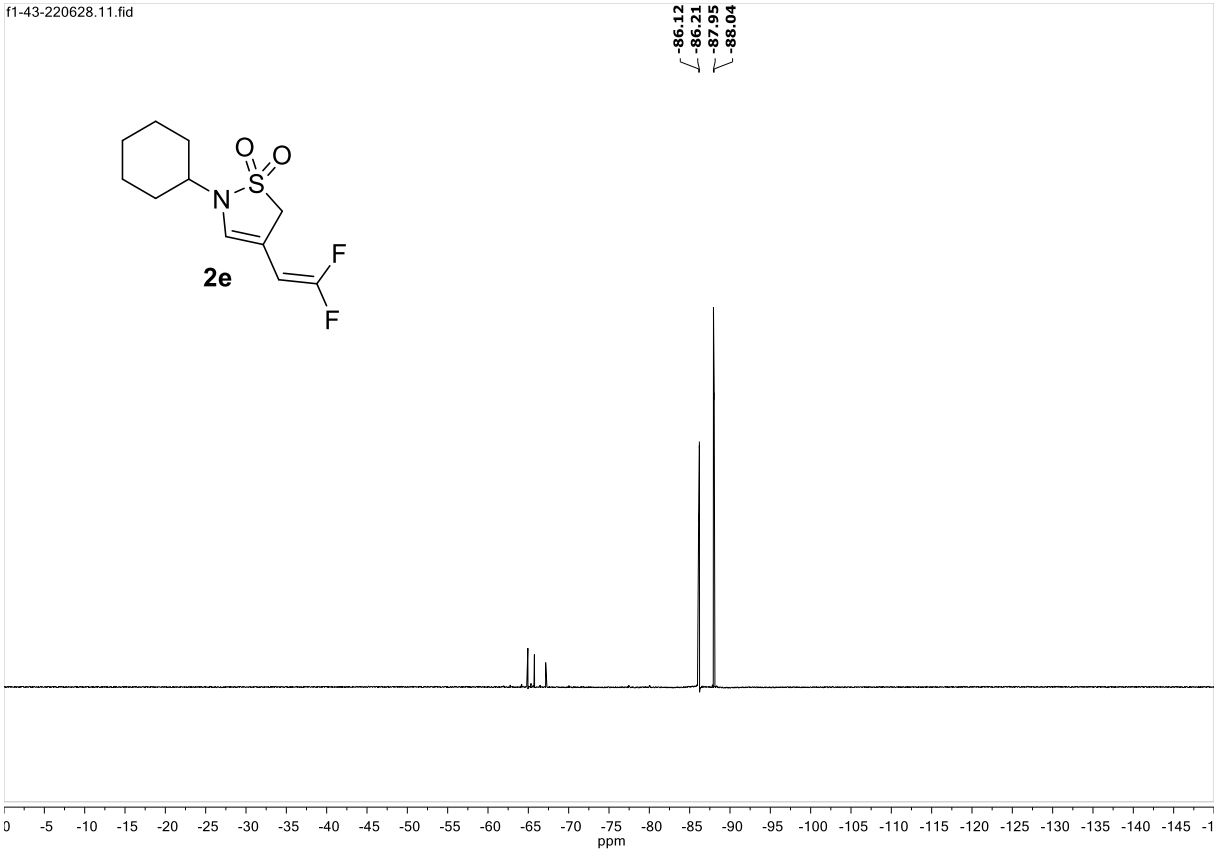
^{19}F NMR (C_6D_6, 282 MHz) of **2d**



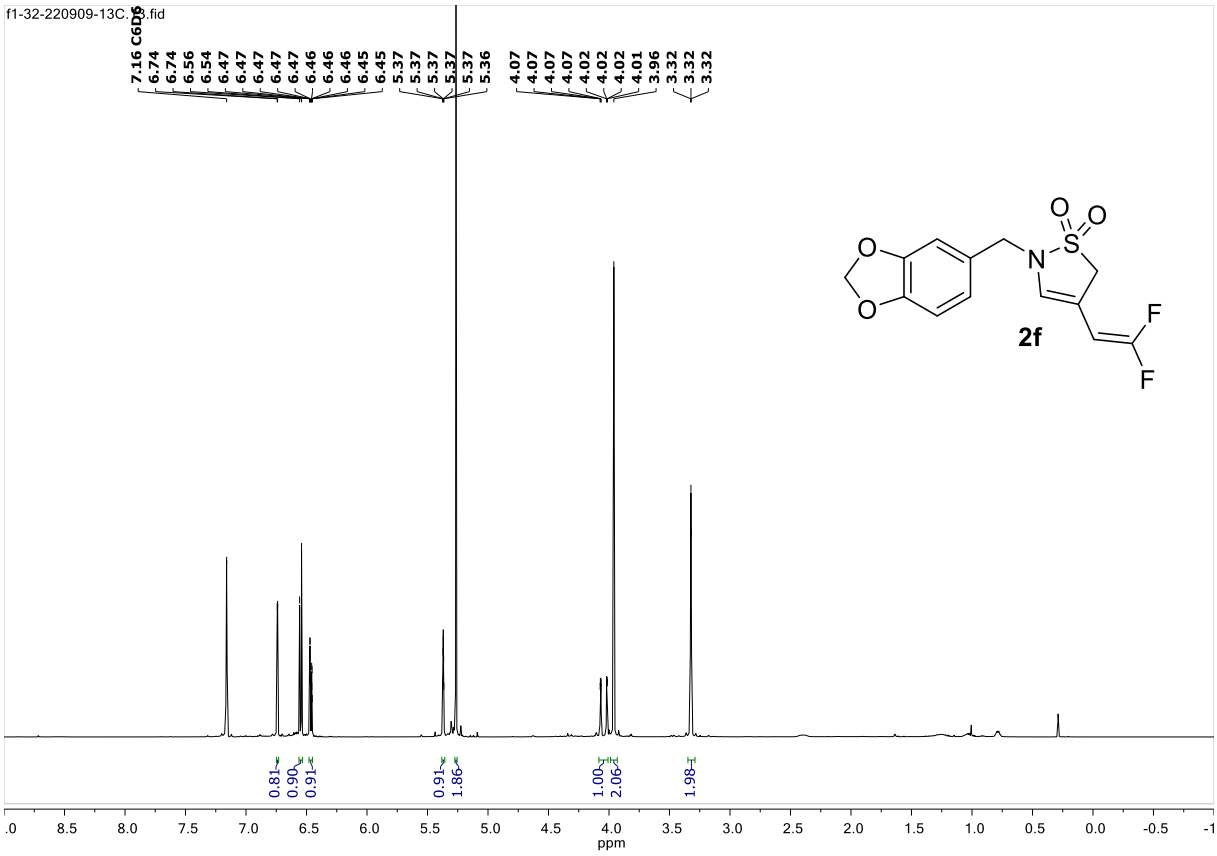
^{1}H NMR ($CDCl_3$, 500 MHz) of **2e**



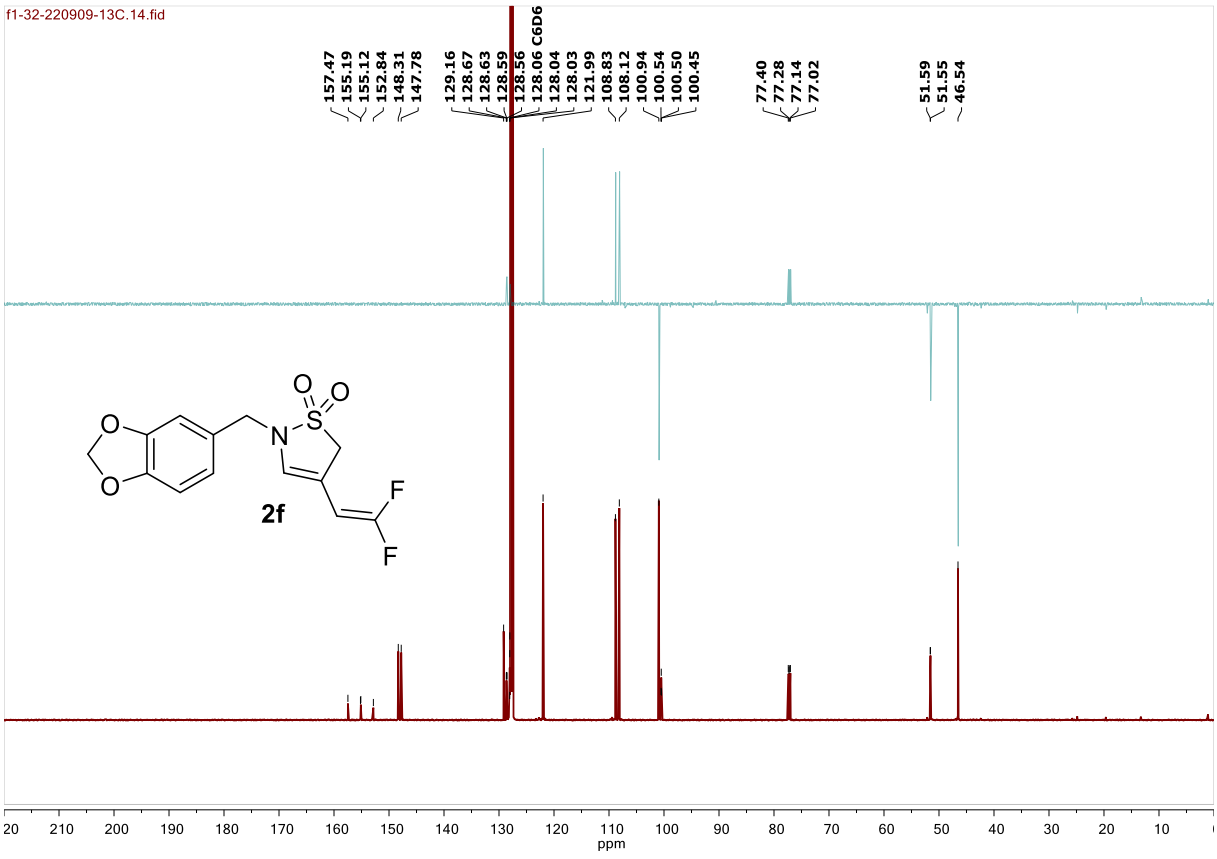
^{13}C NMR ($CDCl_3$, 126 MHz) of **2e**



^{19}F NMR ($CDCl_3$, 282 MHz) of **2e**

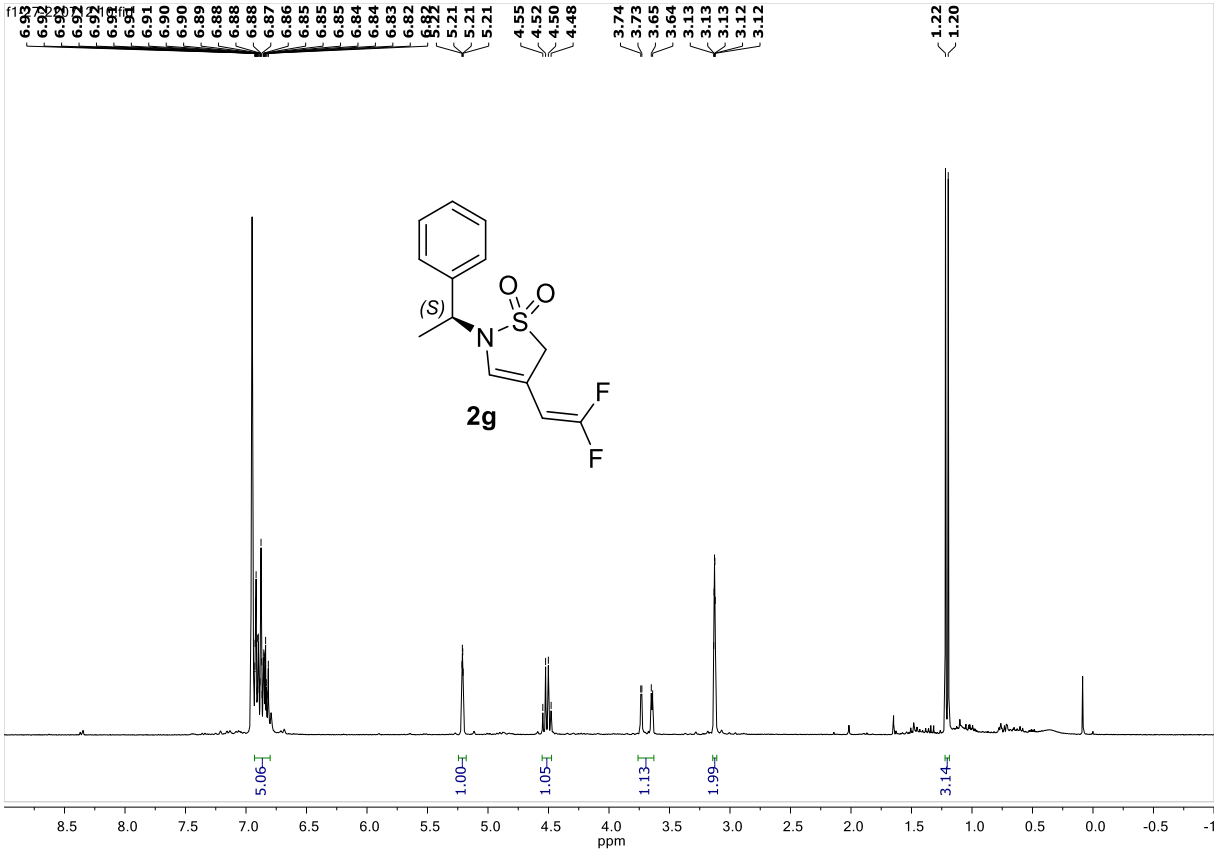


^{1}H NMR (C_6D_6, 500 MHz) of **2f**

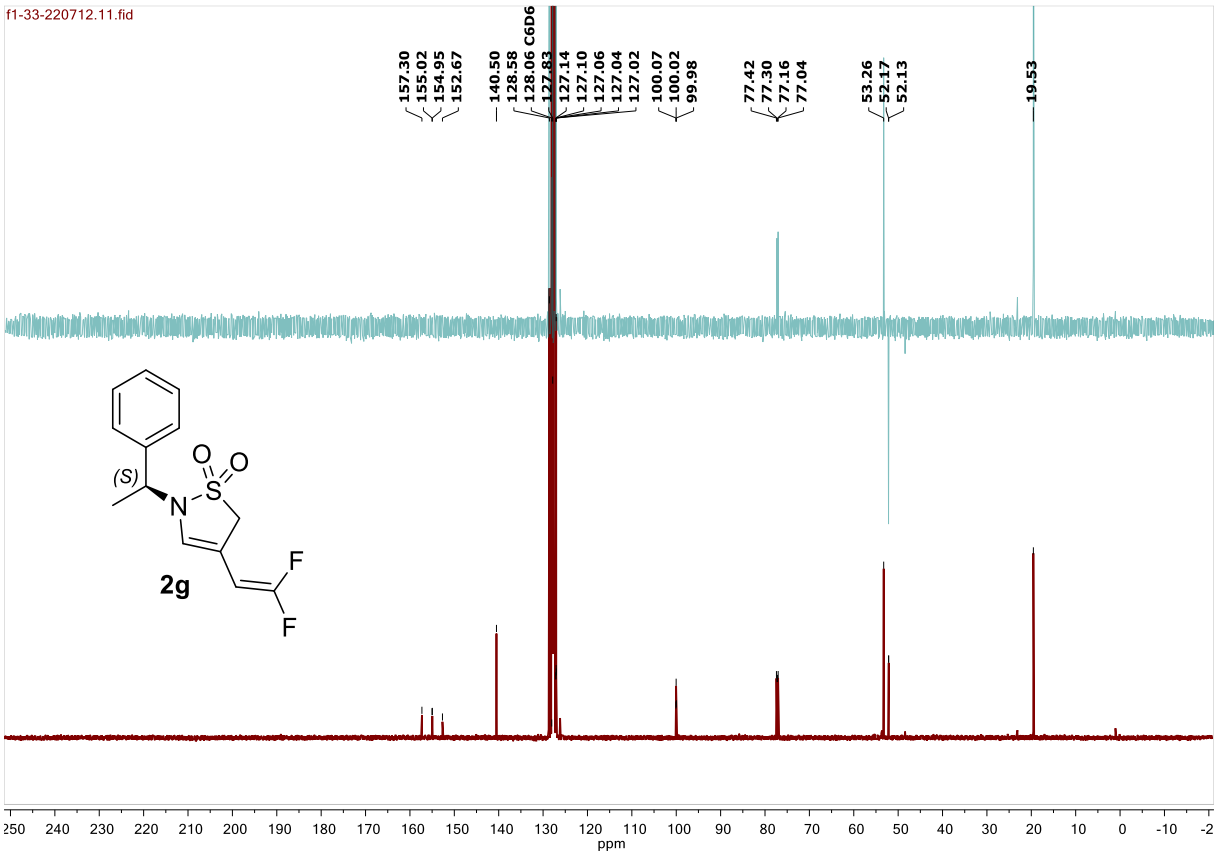


^{13}C NMR (C_6D_6, 126 MHz) of **2f**

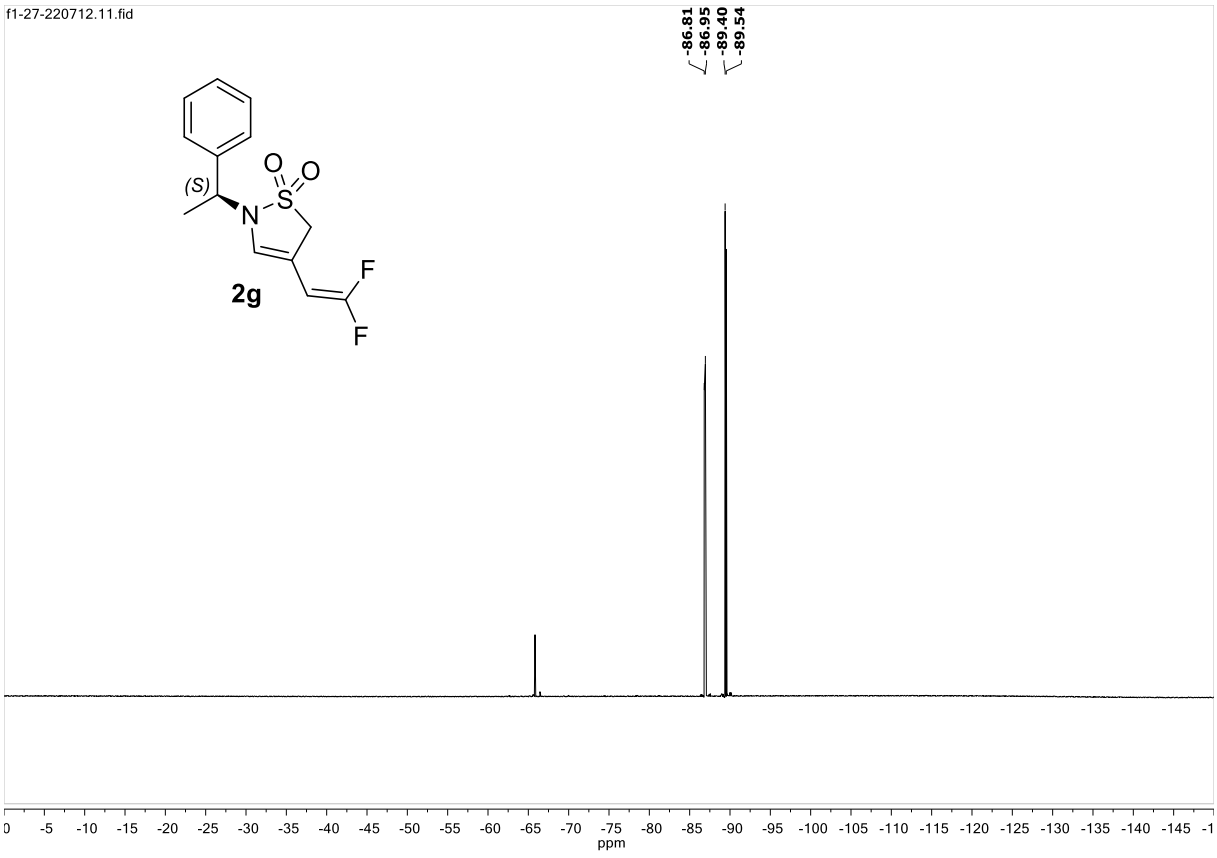
^{19}F NMR (C_6D_6, 282 MHz) of **2f**



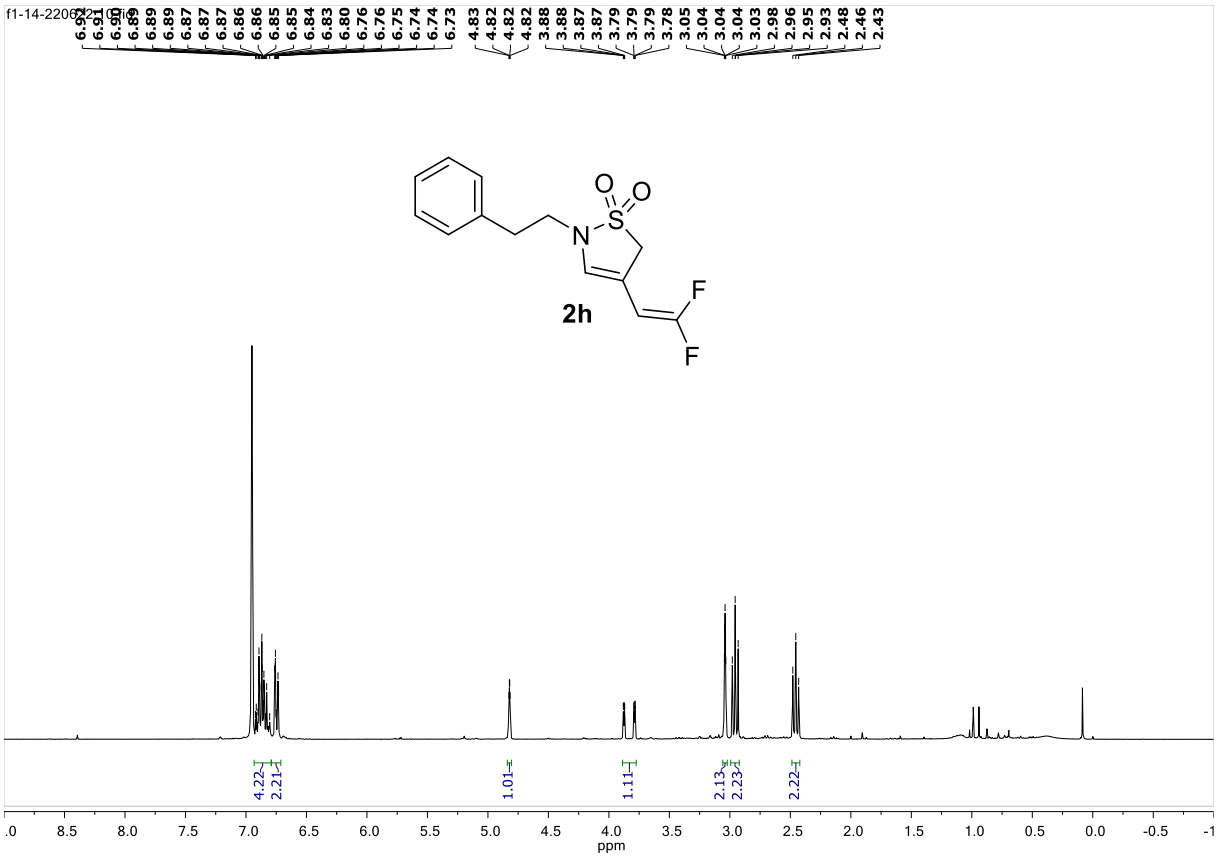
^{1}H NMR (C_6D_6, 300 MHz) of **2g**



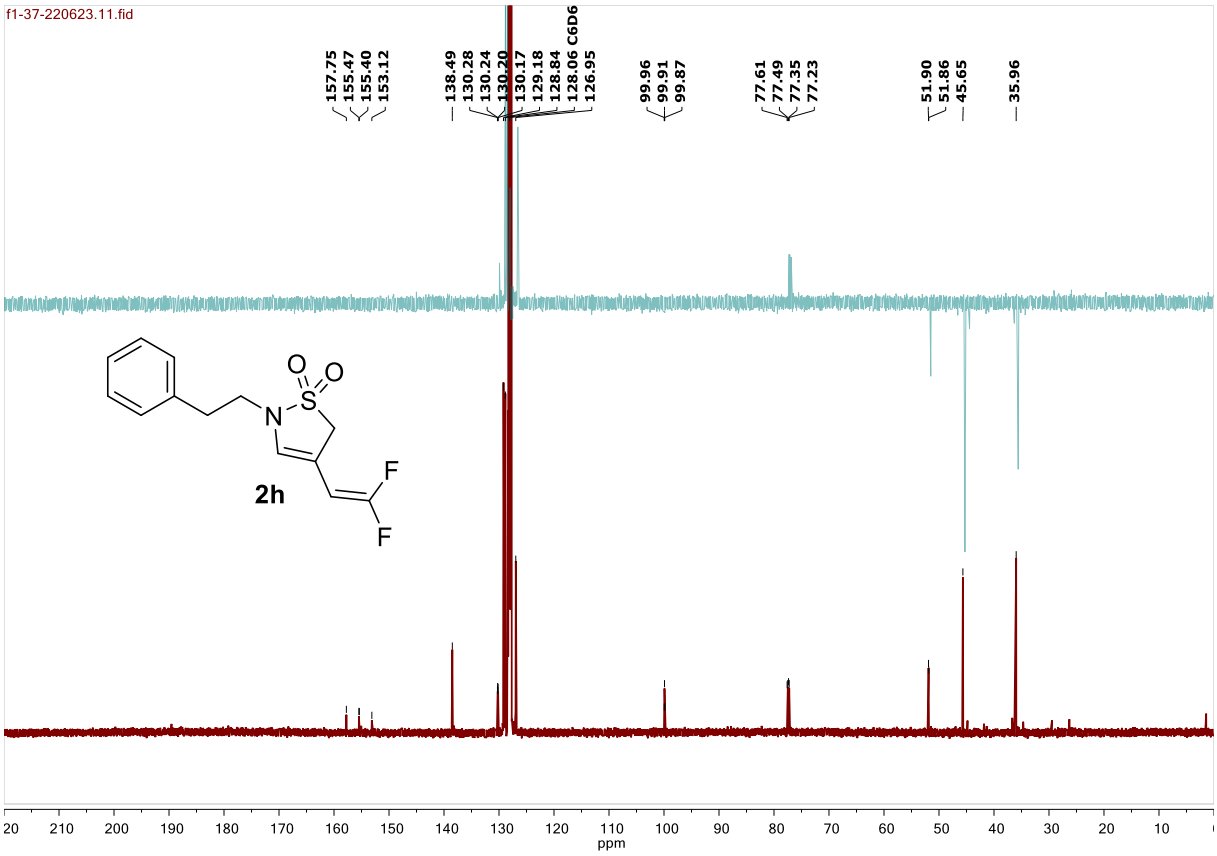
^{13}C NMR (C_6D_6, 126 MHz) of **2g**



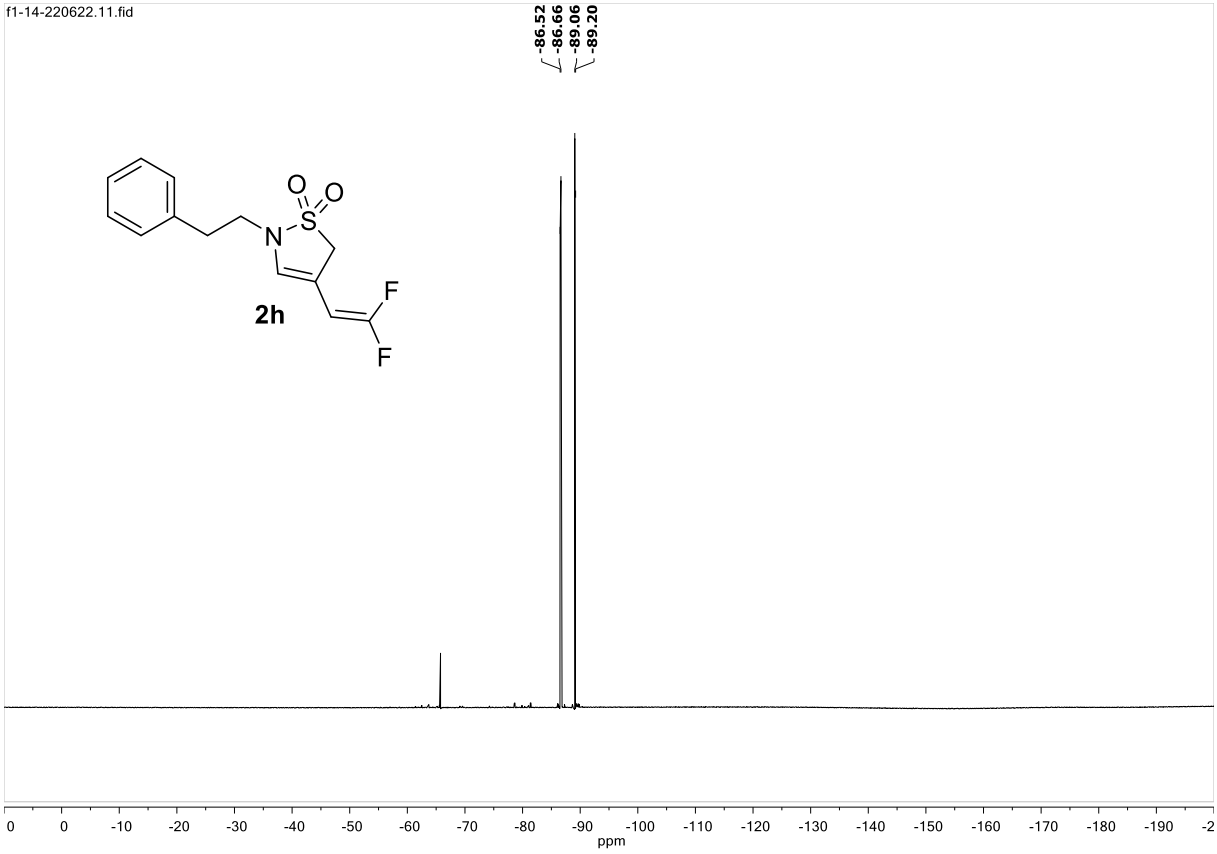
^{19}F NMR (C_6D_6, 282 MHz) of **2g**



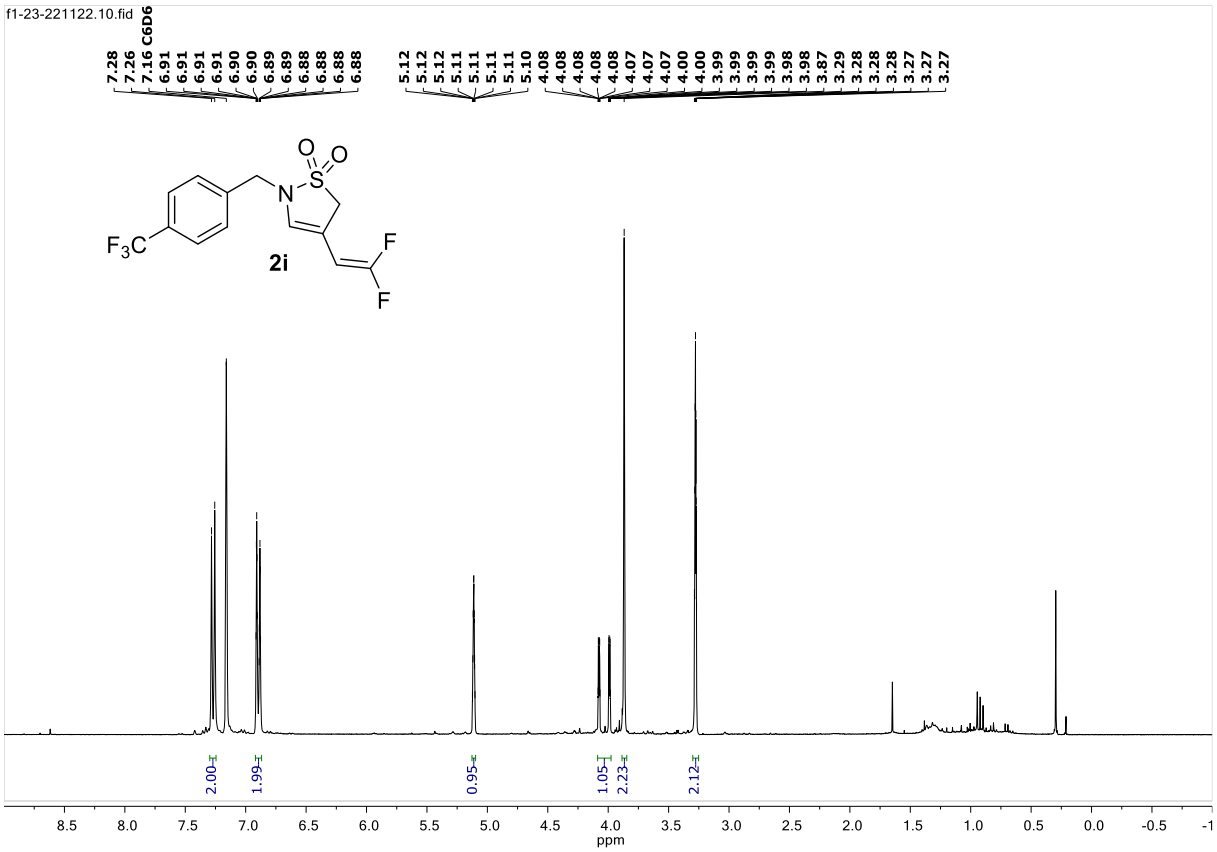
^{1}H NMR (C_6D_6, 300 MHz) of **2h**



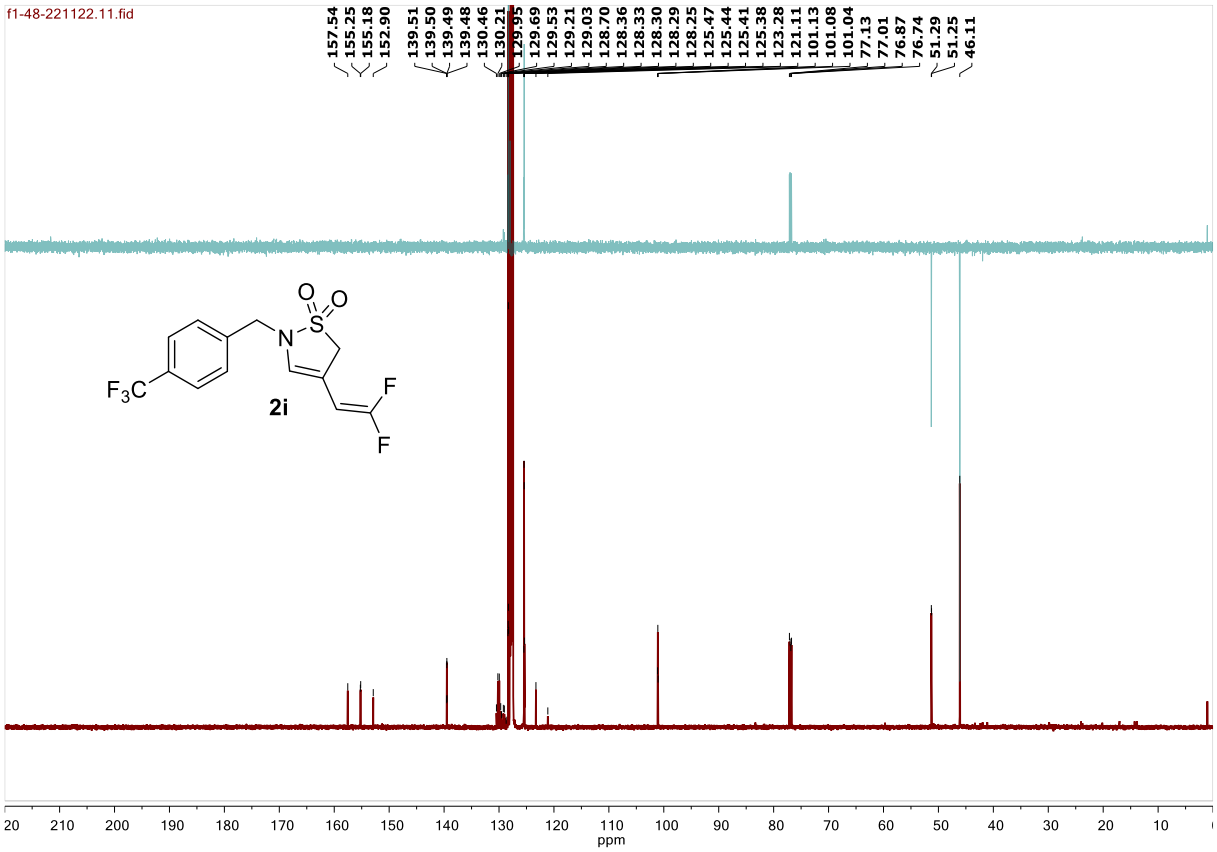
^{13}C NMR (C_6D_6, 126 MHz) of **2h**



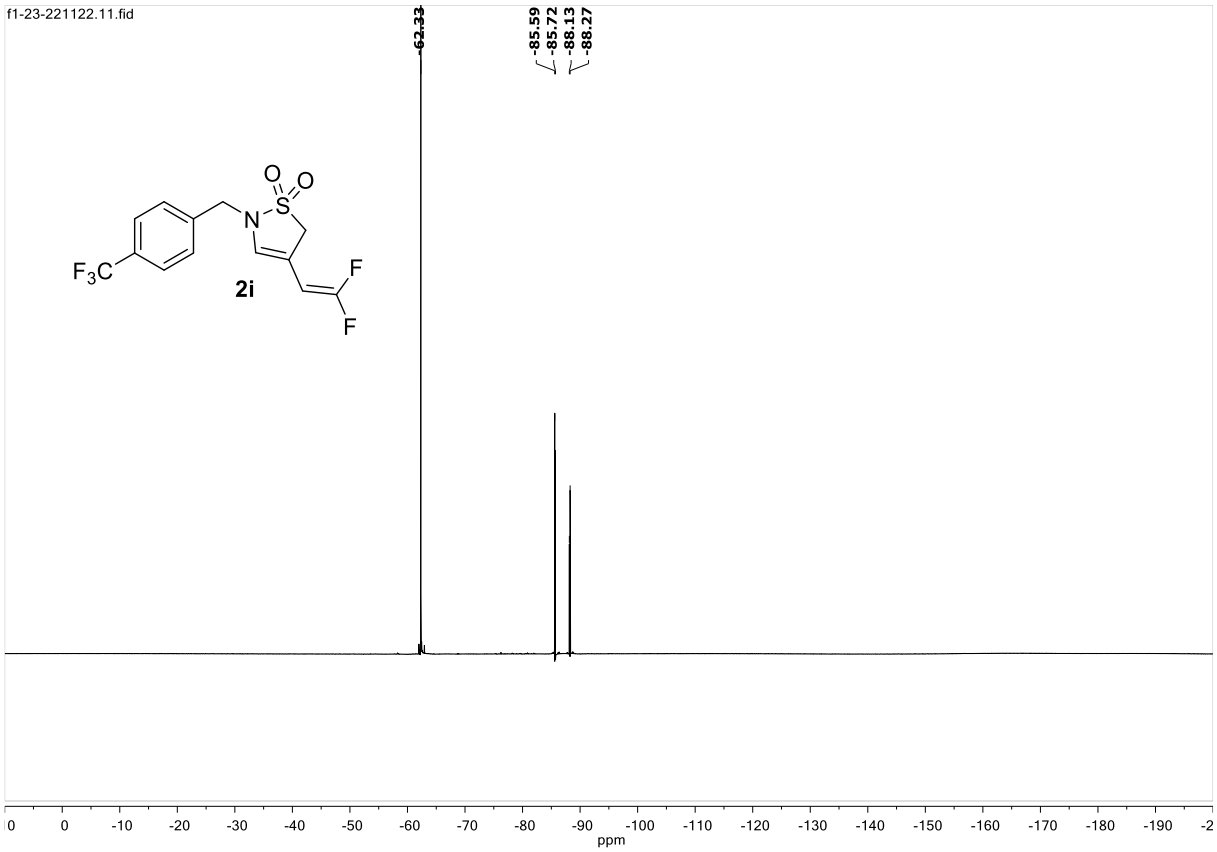
^{19}F NMR (C_6D_6, 282 MHz) of **2h**



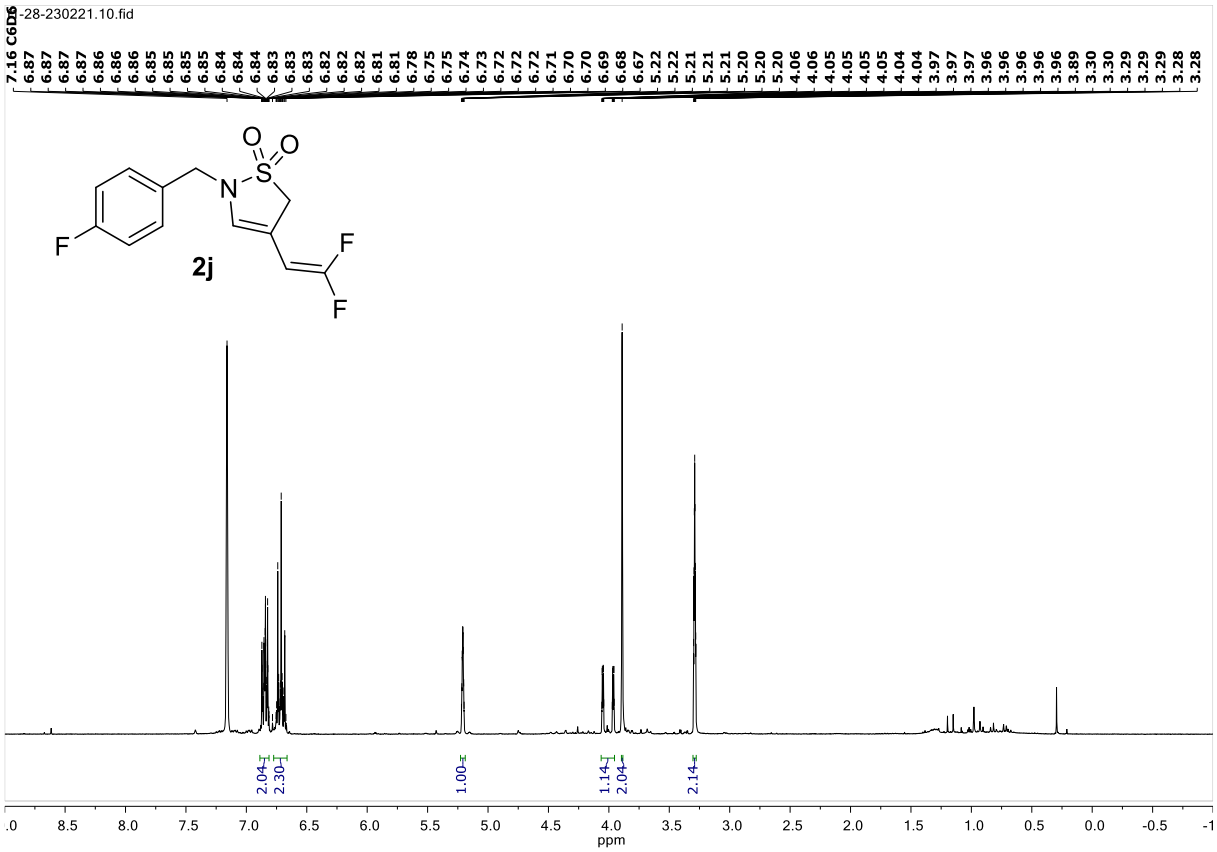
^{1}H NMR (C_6D_6, 300 MHz) of **2i**



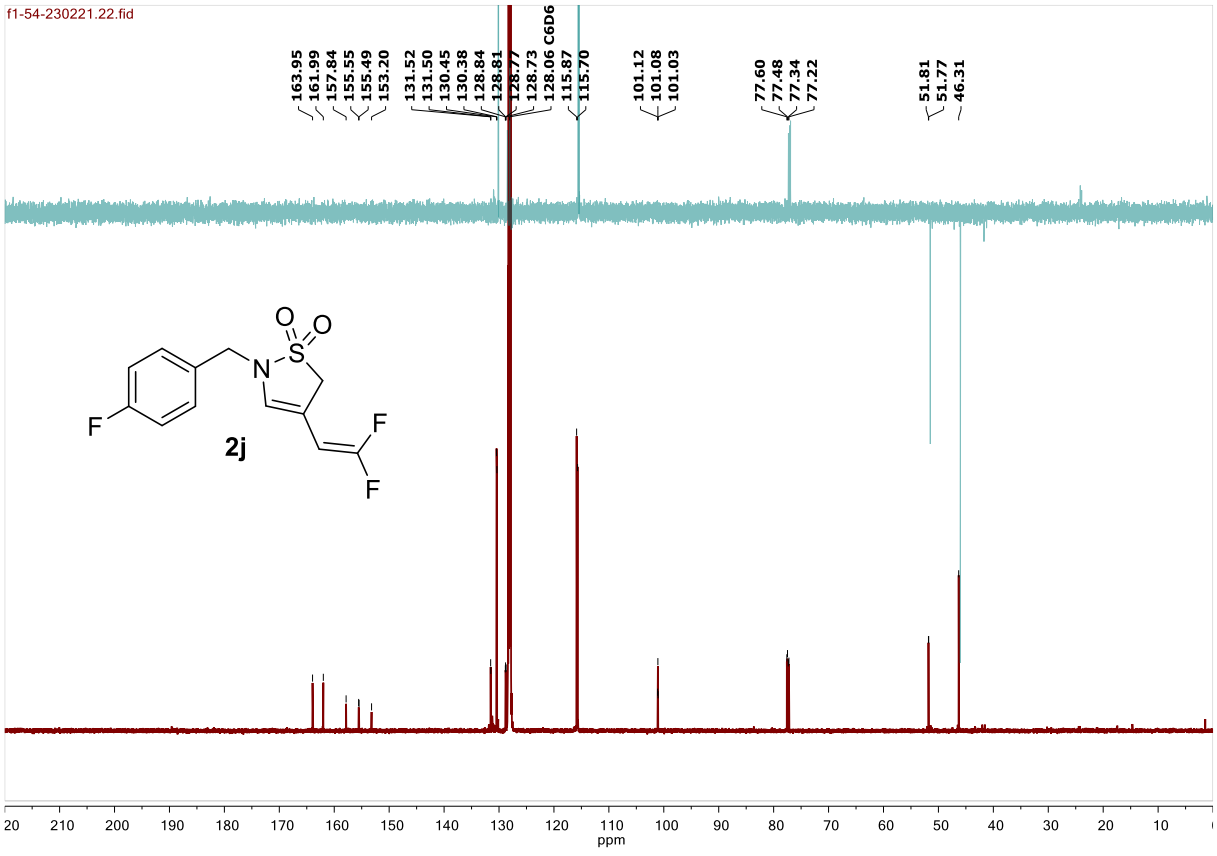
^{13}C NMR (C_6D_6, 126 MHz) of **2i**



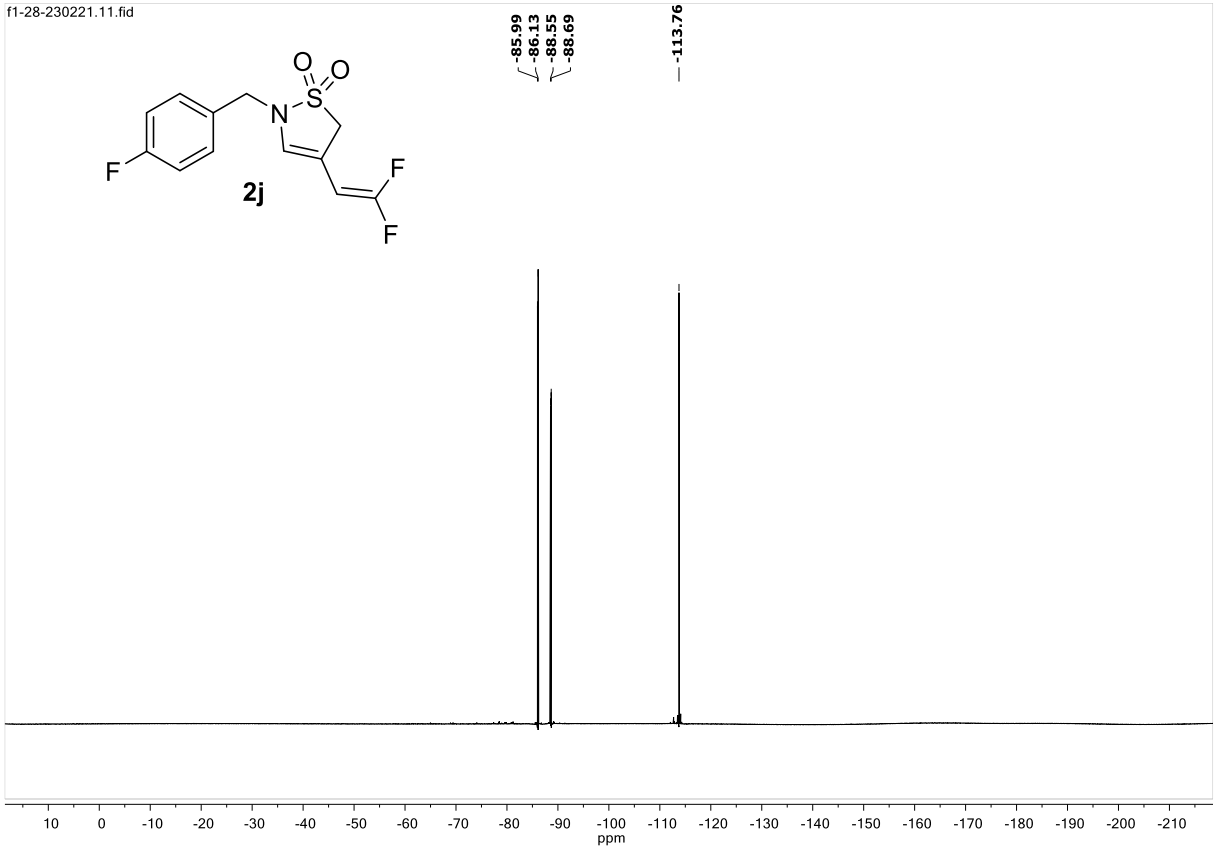
^{19}F NMR (C_6D_6, 282 MHz) of **2i**



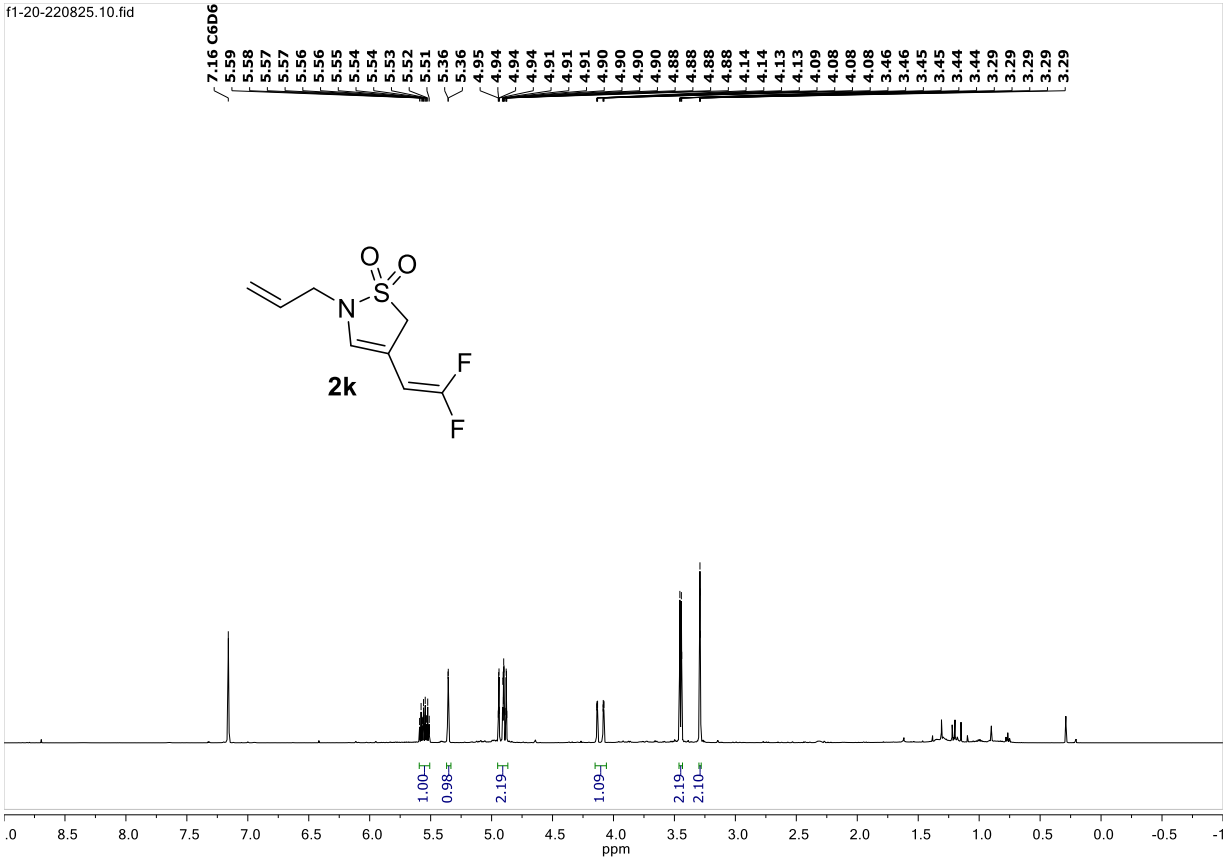
^{1}H NMR (C_6D_6, 300 MHz) of **2j**



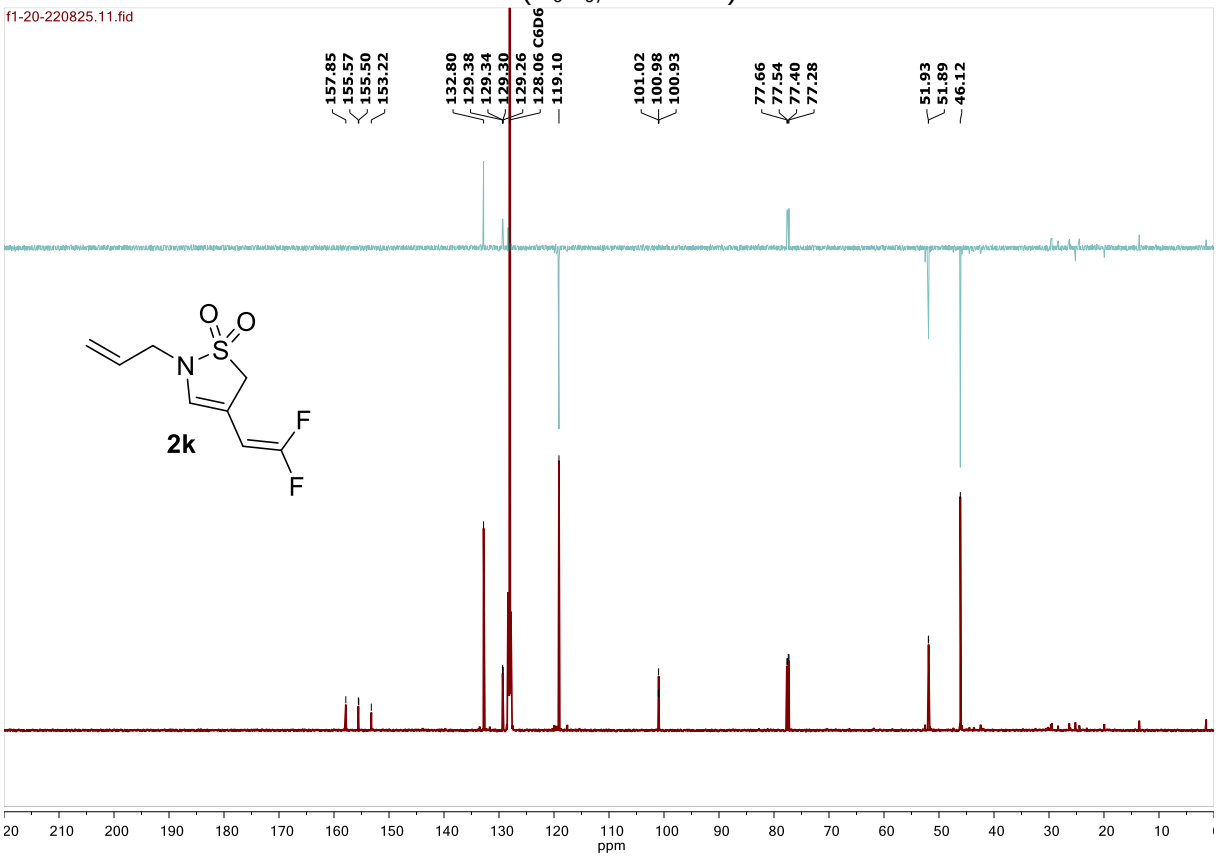
^{13}C NMR (C_6D_6, 126 MHz) of **2j**



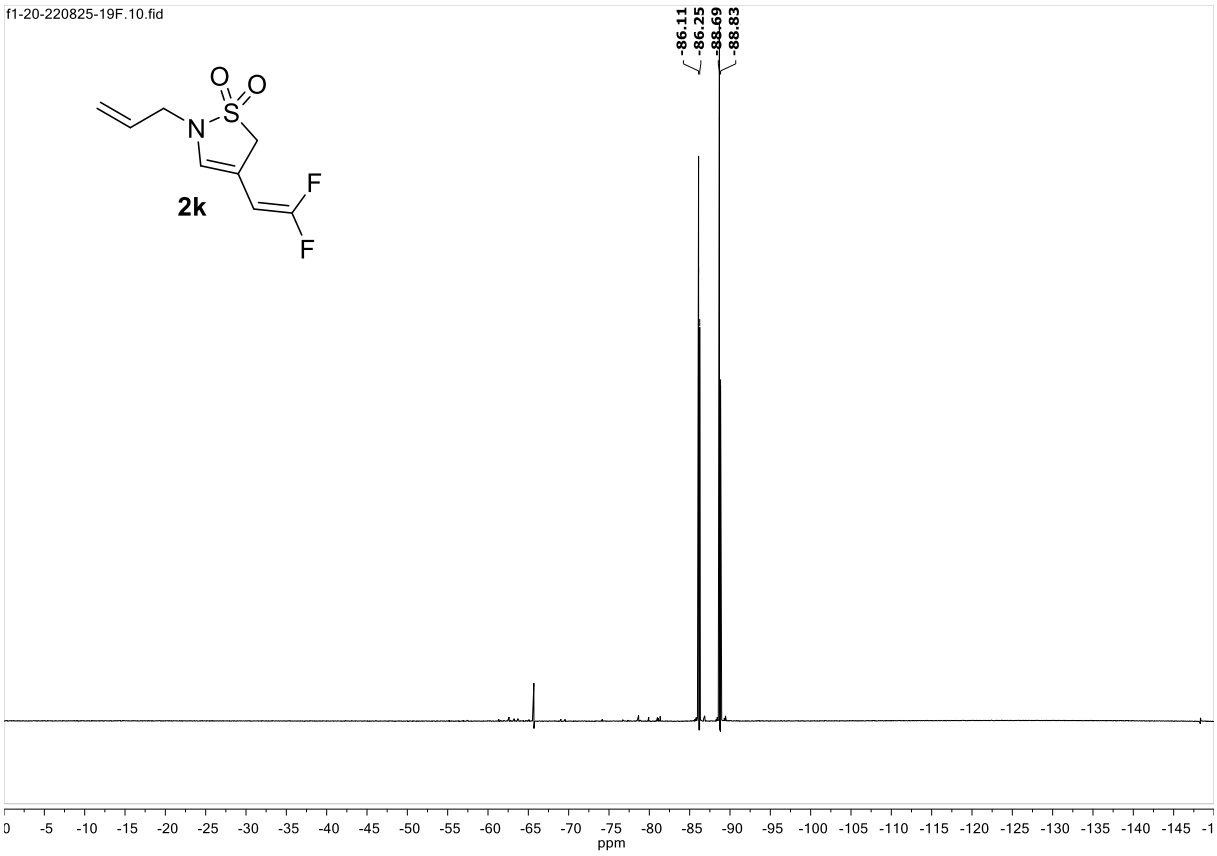
^{19}F NMR (C_6D_6, 282 MHz) of **2j**



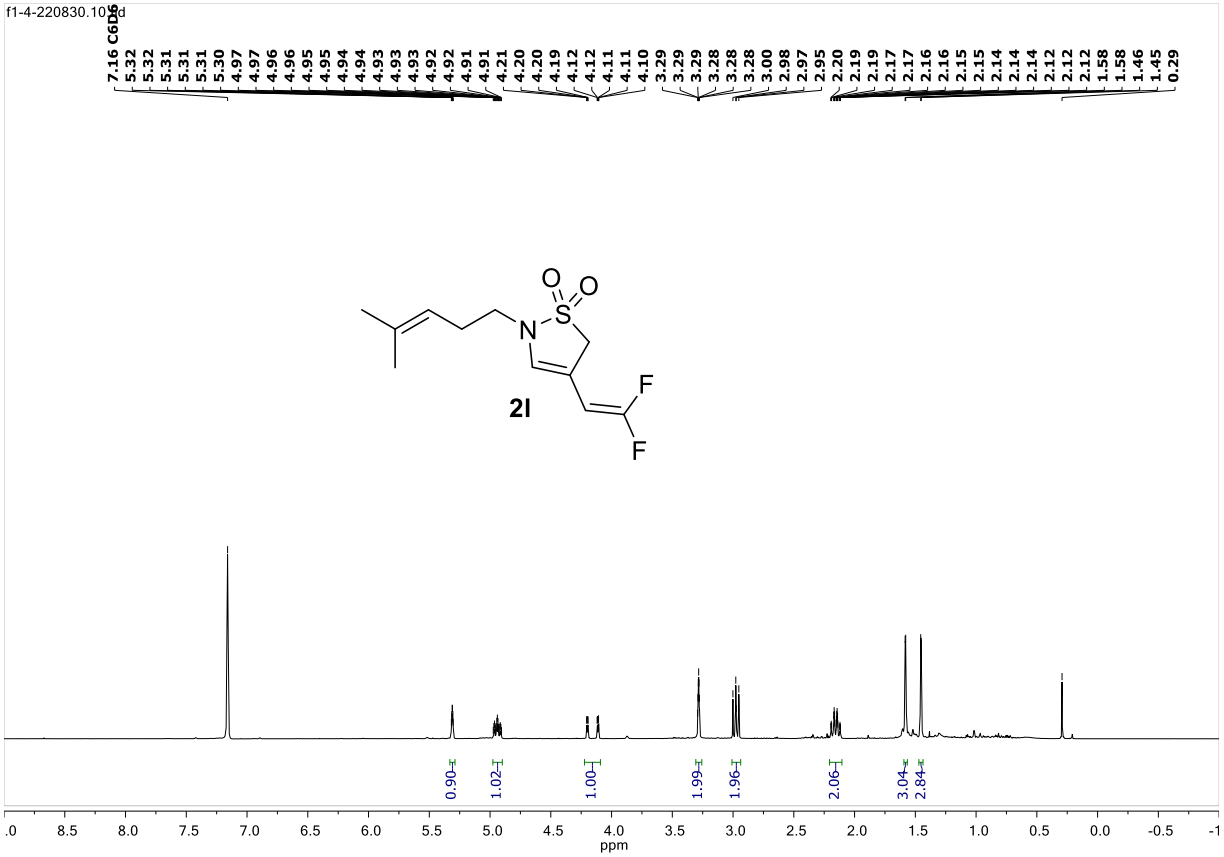
^{1}H NMR (C_6D_6, 500 MHz) of **2k**



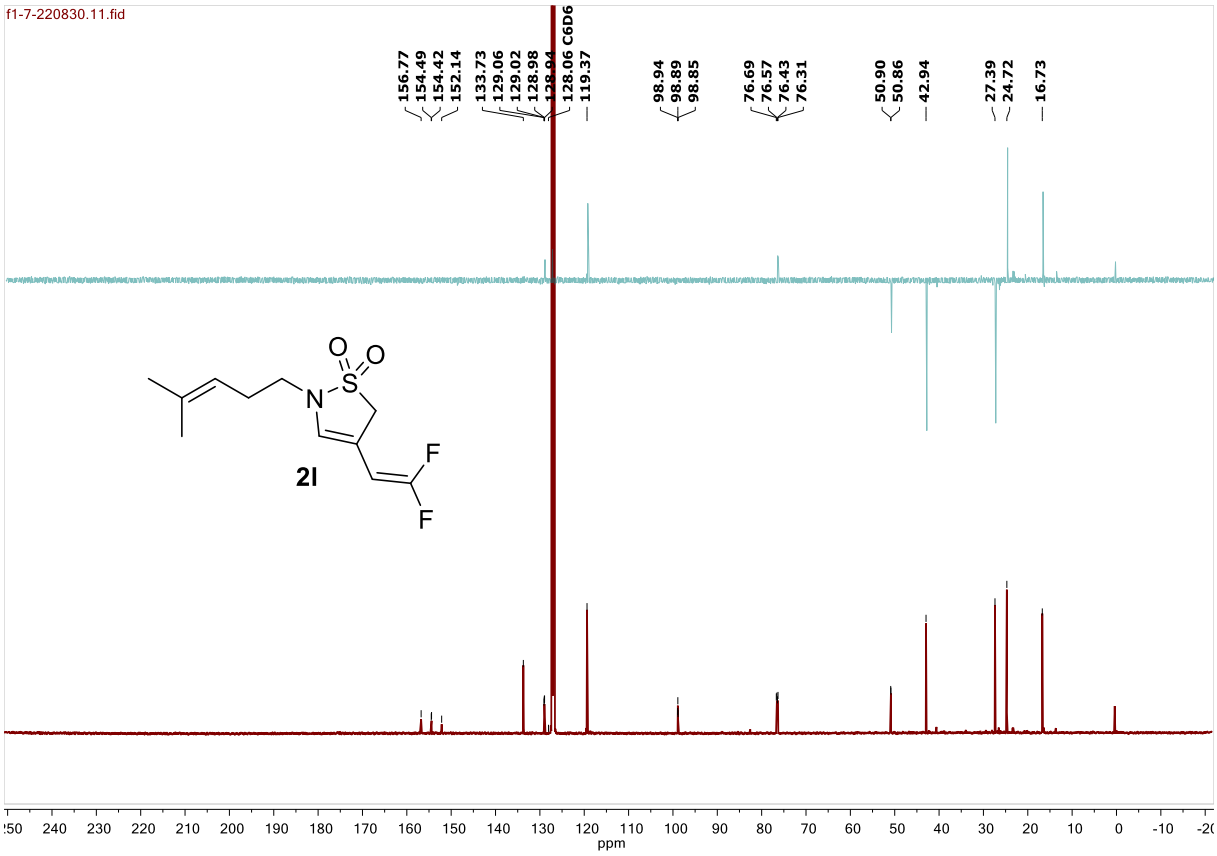
^{13}C NMR (C_6D_6, 126 MHz) of **2k**



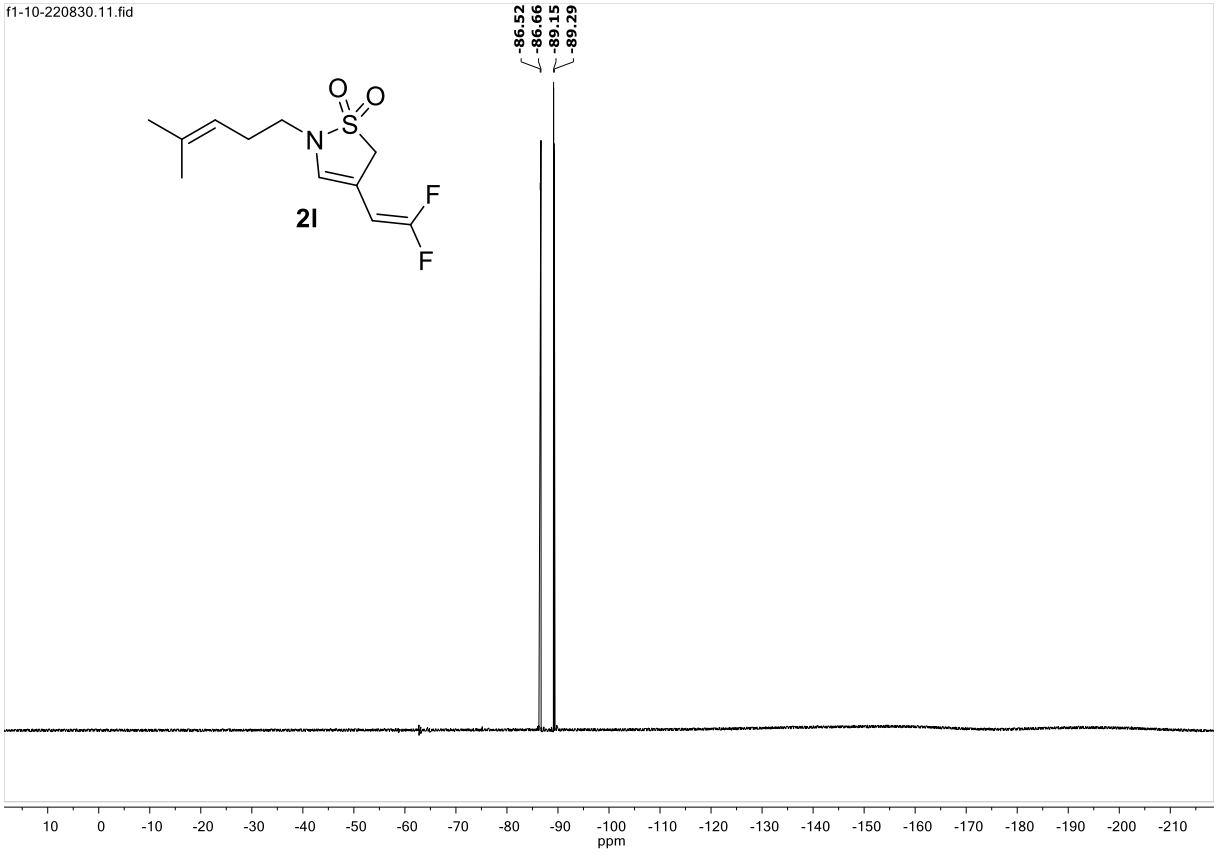
^{19}F NMR (C_6D_6, 282 MHz) of **2k**



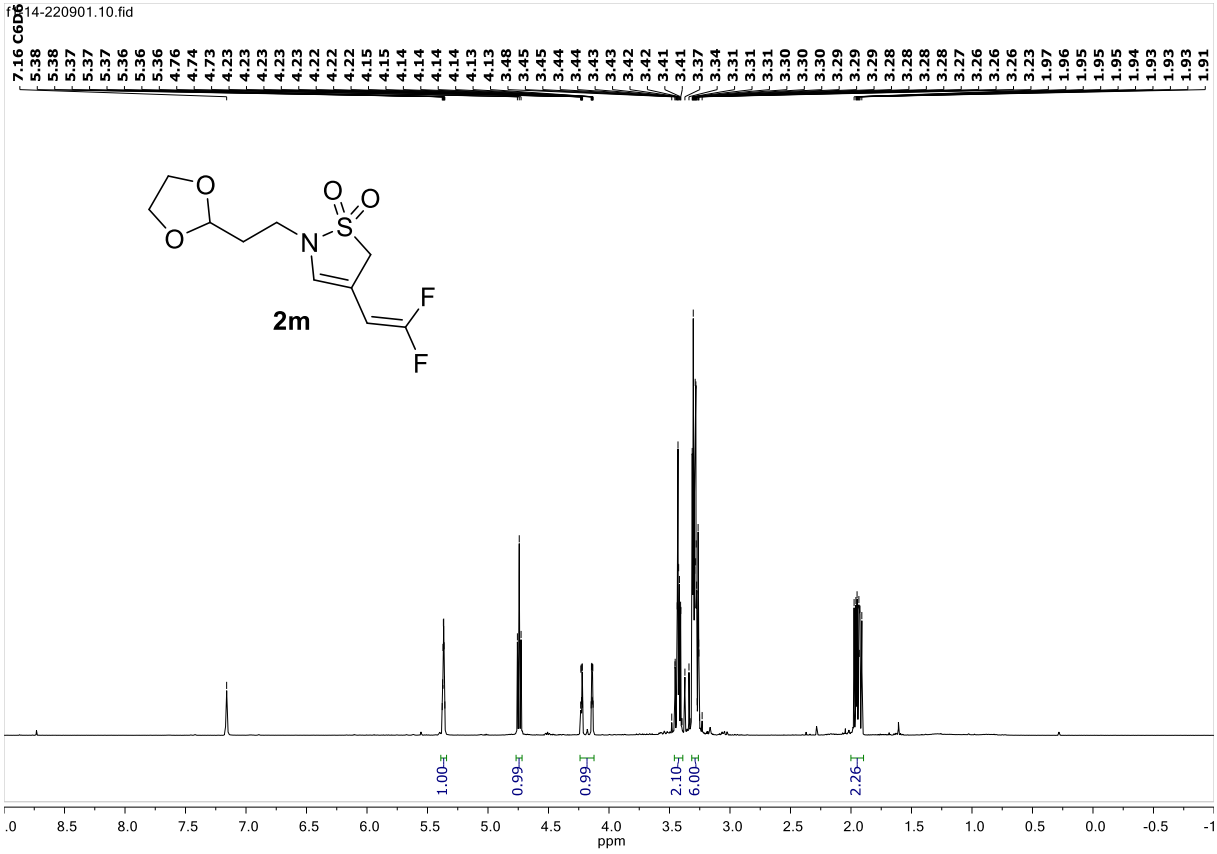
^{1}H NMR (C_6D_6, 300 MHz) of **2l**



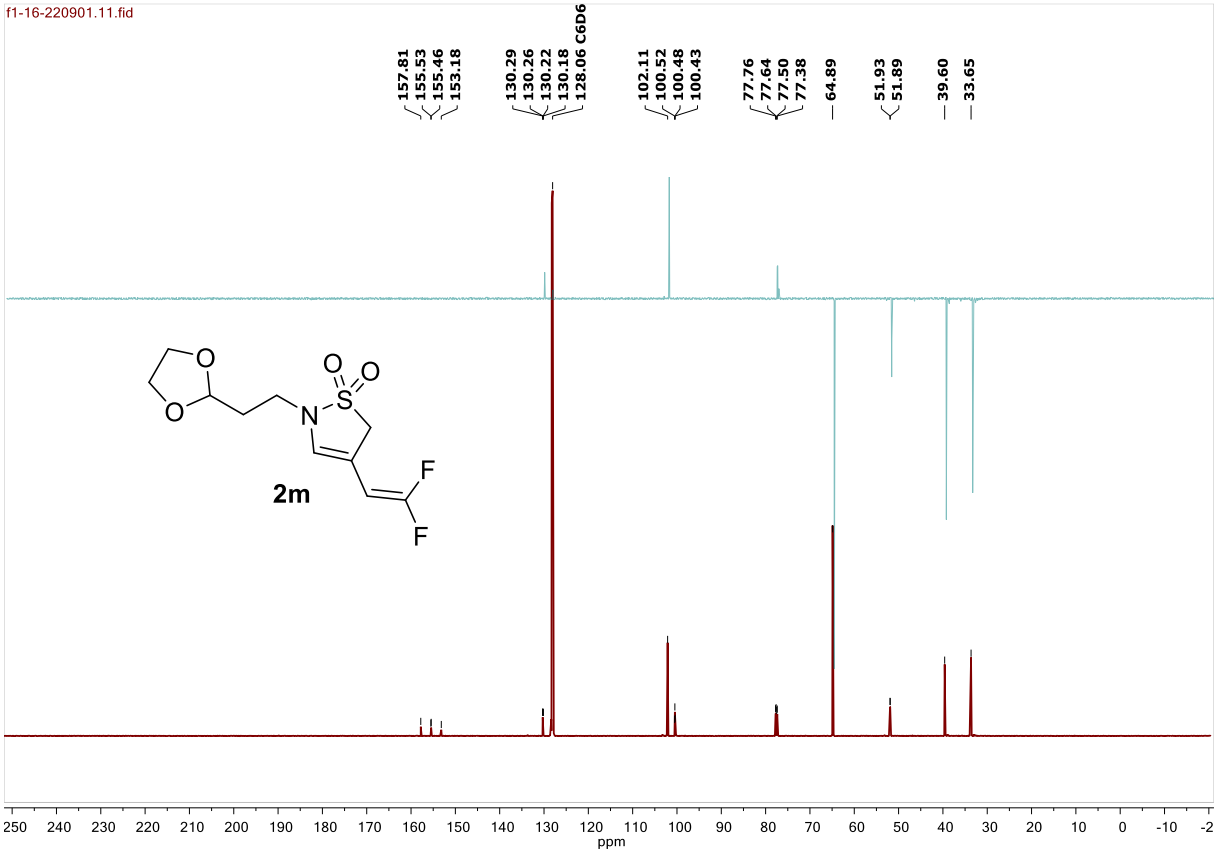
^{13}C NMR (C_6D_6, 126 MHz) of **2l**



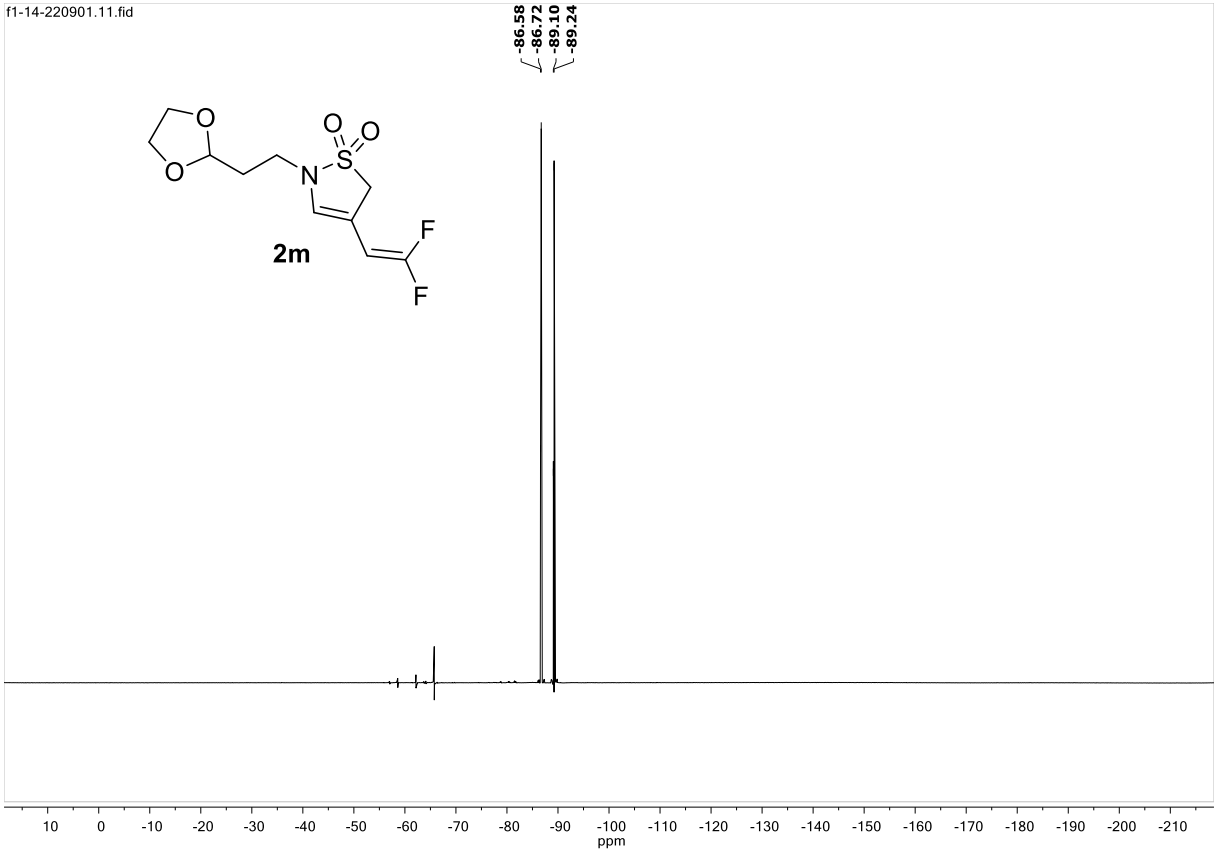
^{19}F NMR (C_6D_6, 282 MHz) of **2l**



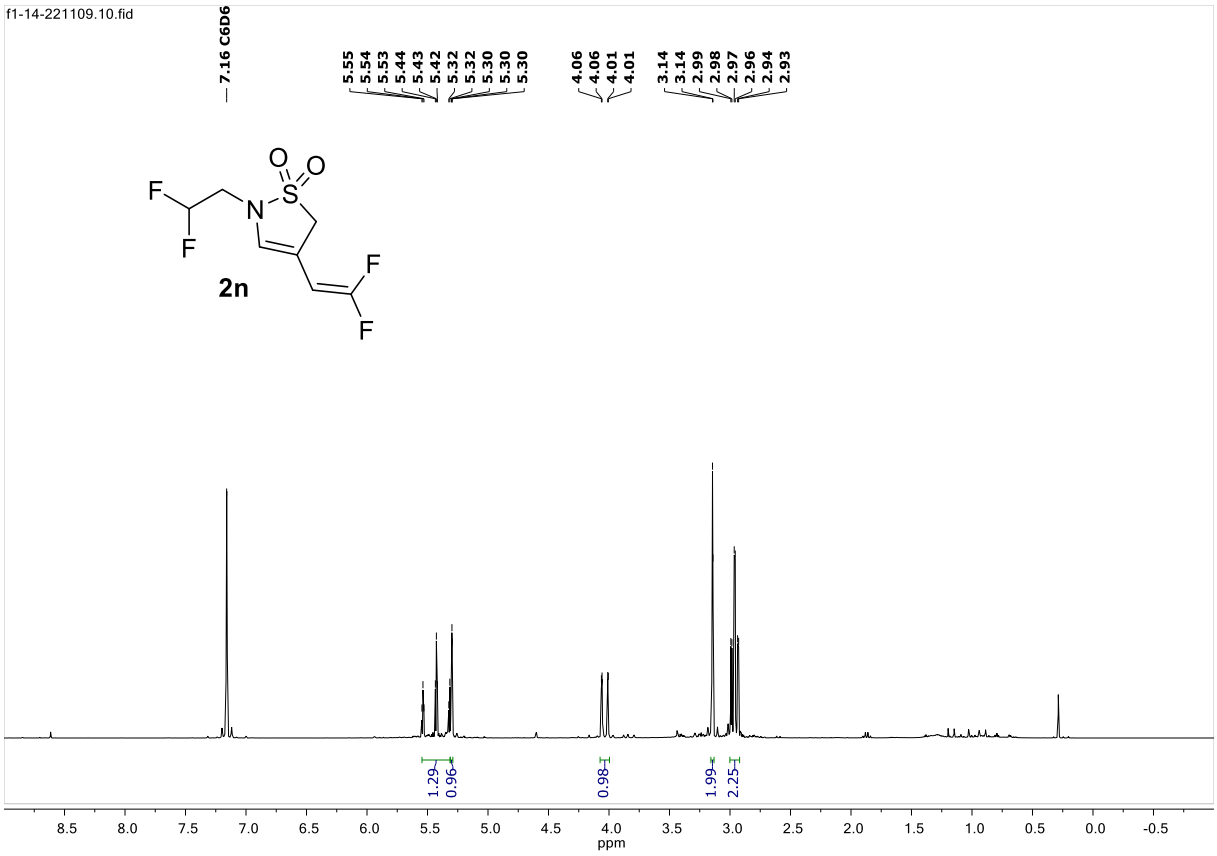
^{1}H NMR (C_6D_6, 300 MHz) of **2m**



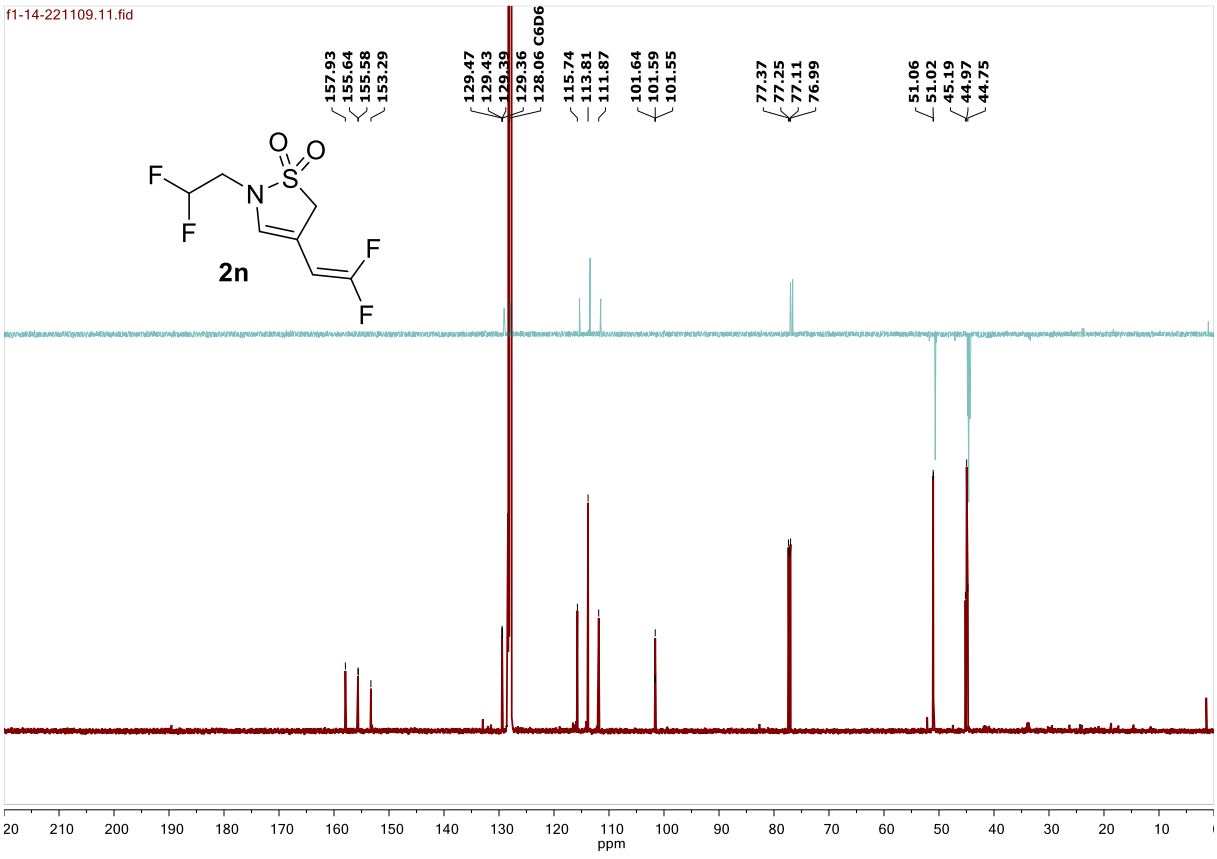
^{13}C NMR (C_6D_6, 126 MHz) of **2m**



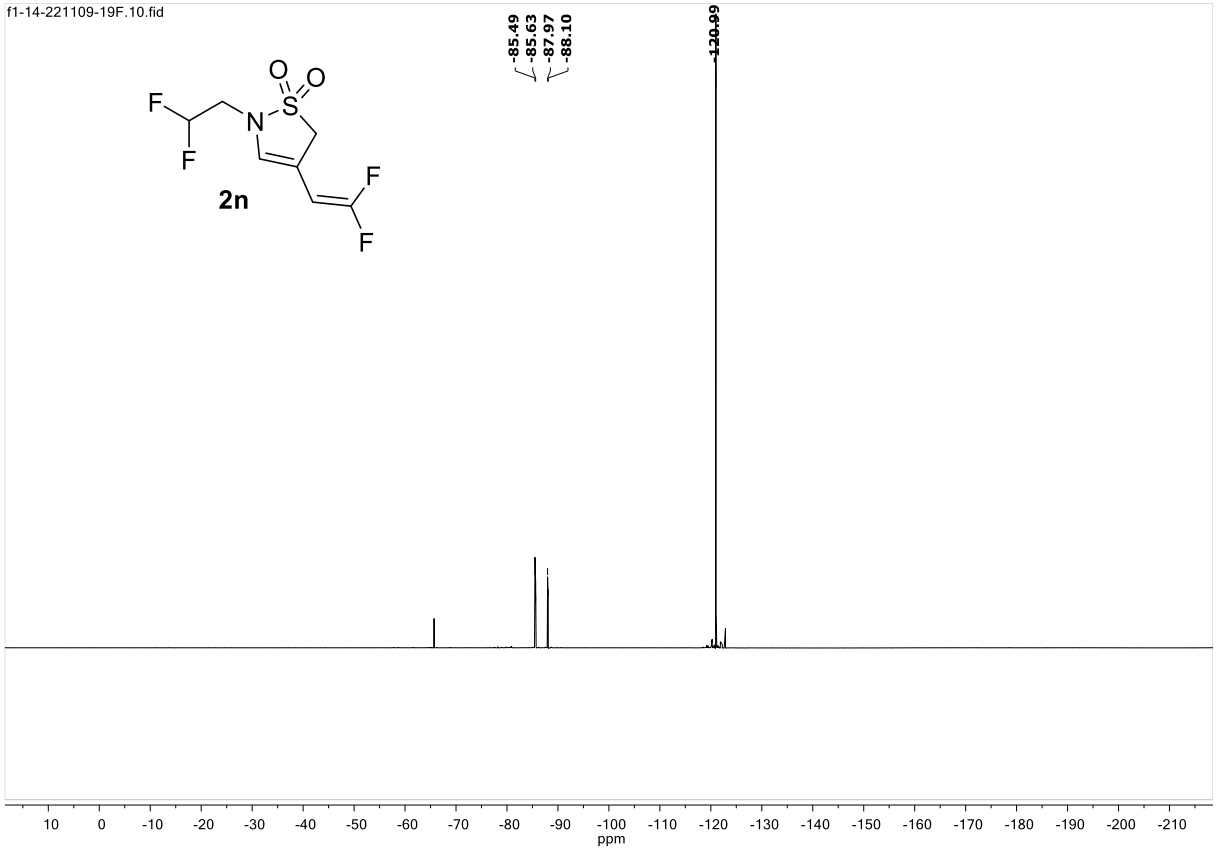
^{19}F NMR (C_6D_6, 282 MHz) of **2m**



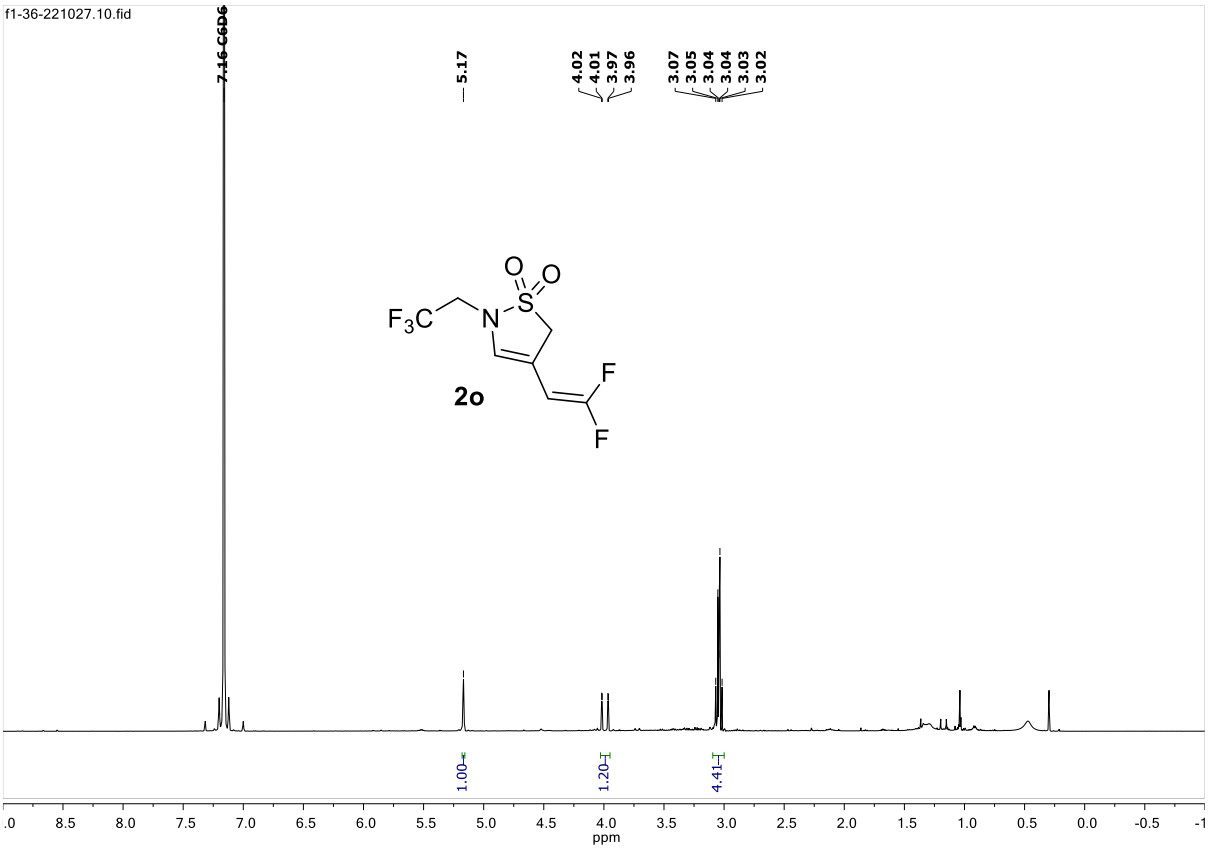
^{1}H NMR (C_6D_6, 500 MHz) of **2n**



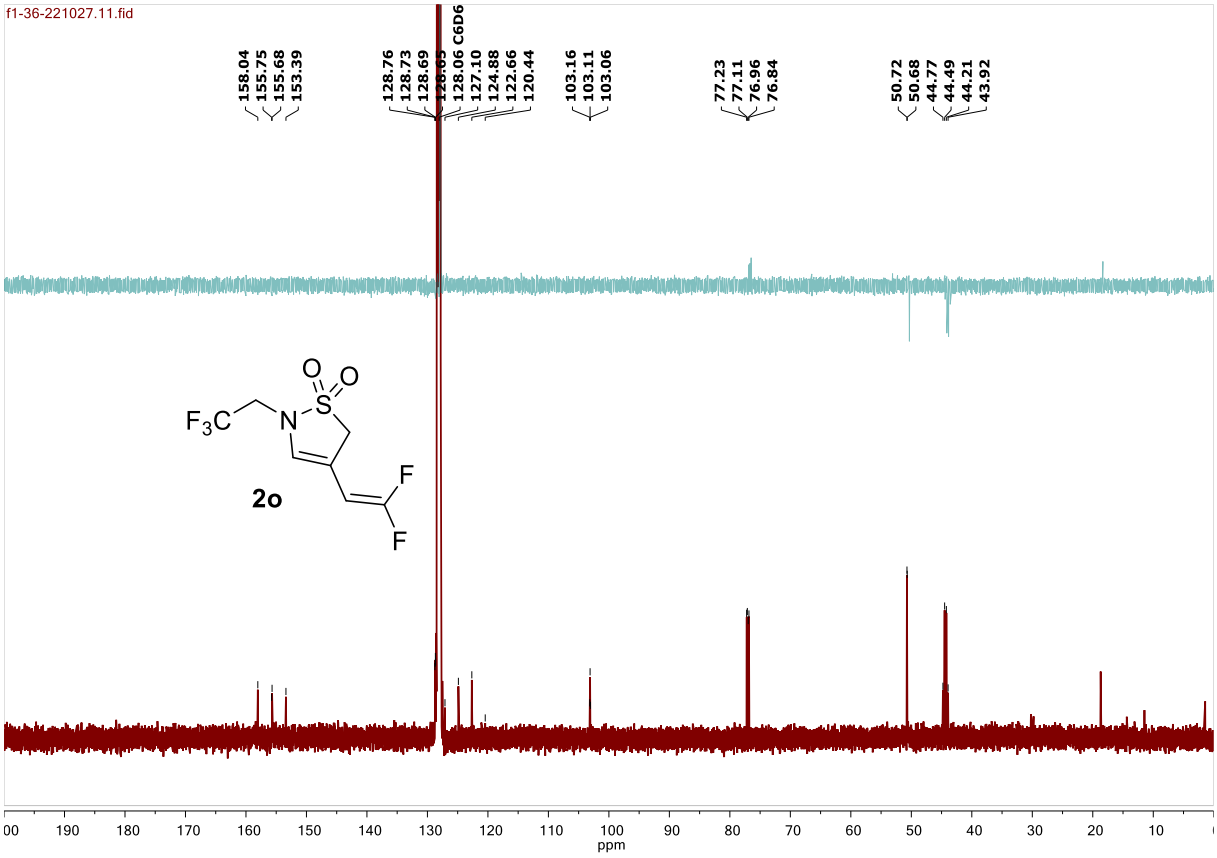
^{13}C NMR (C_6D_6, 126 MHz) of **2n**



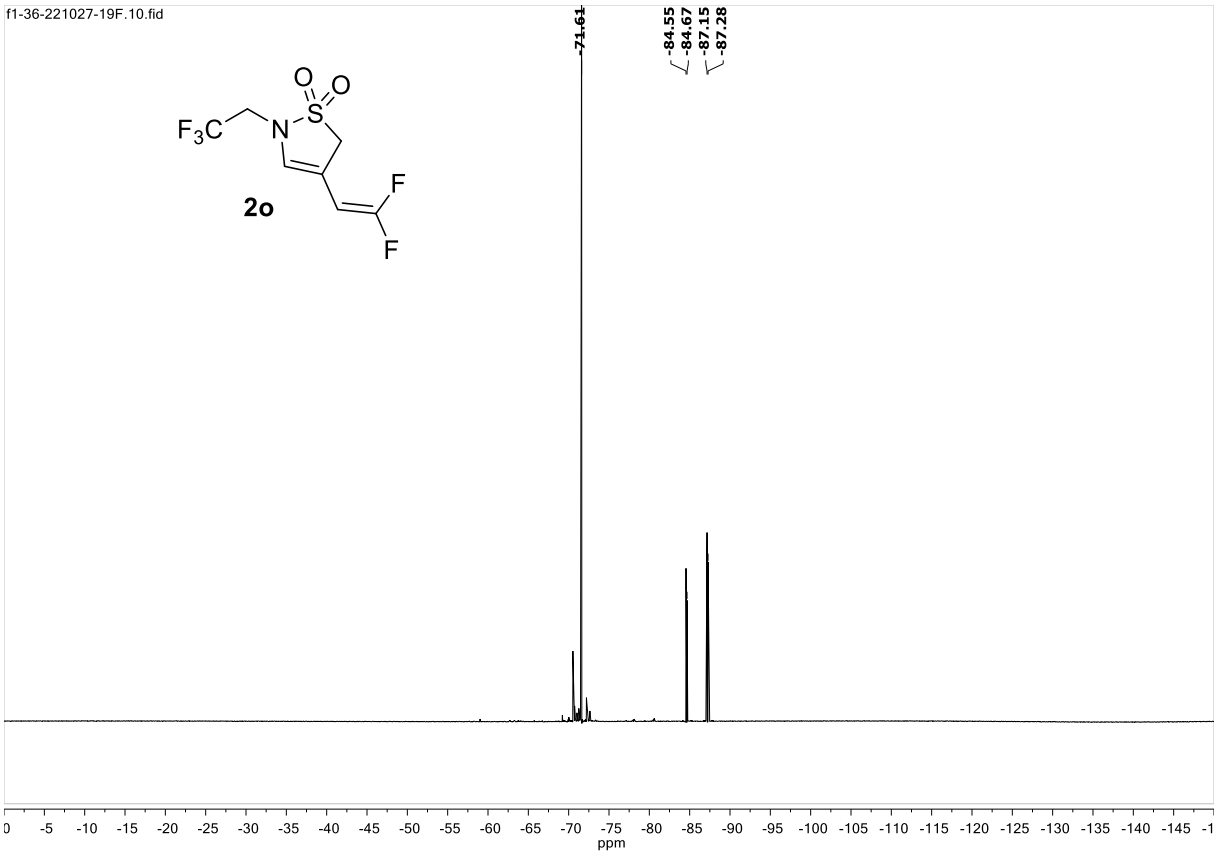
^{19}F NMR (C_6D_6, 282 MHz) of **2n**



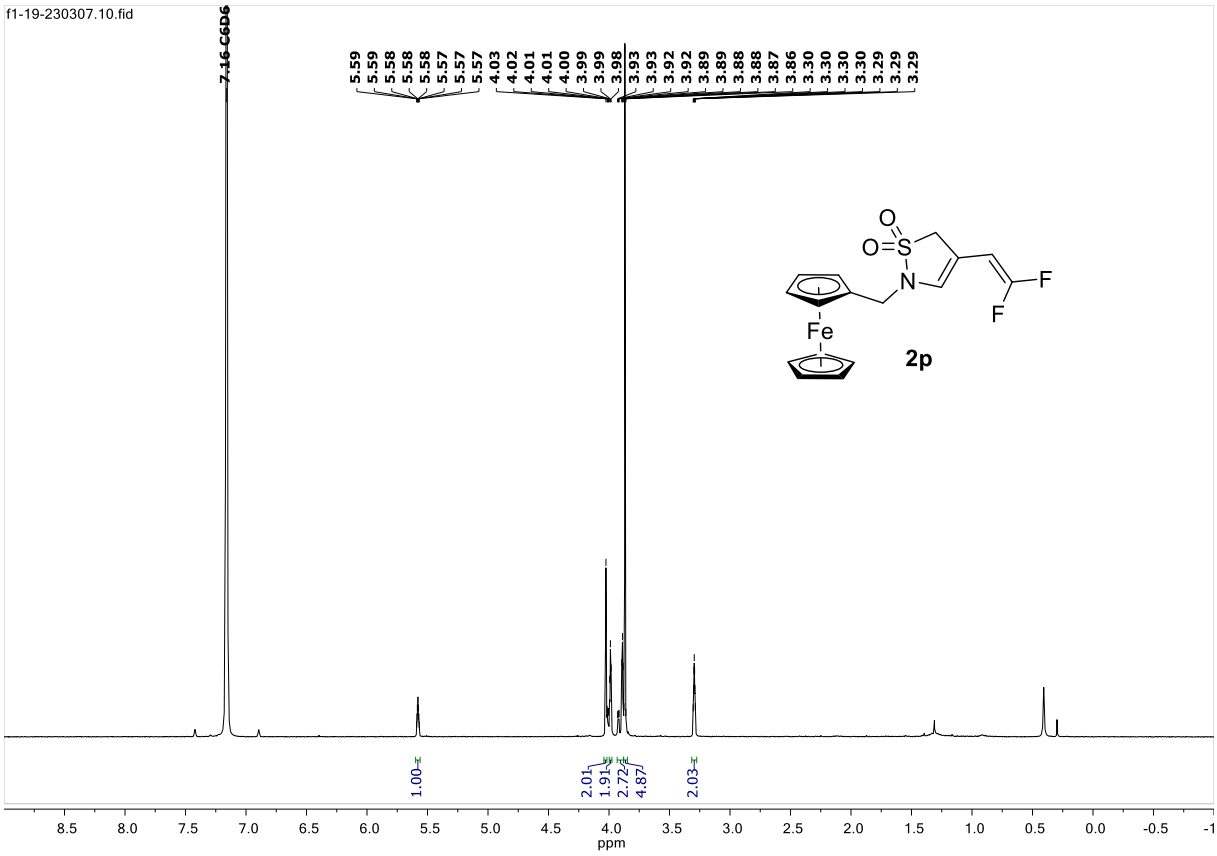
^{1}H NMR (C_6D_6, 500 MHz) of **2o**



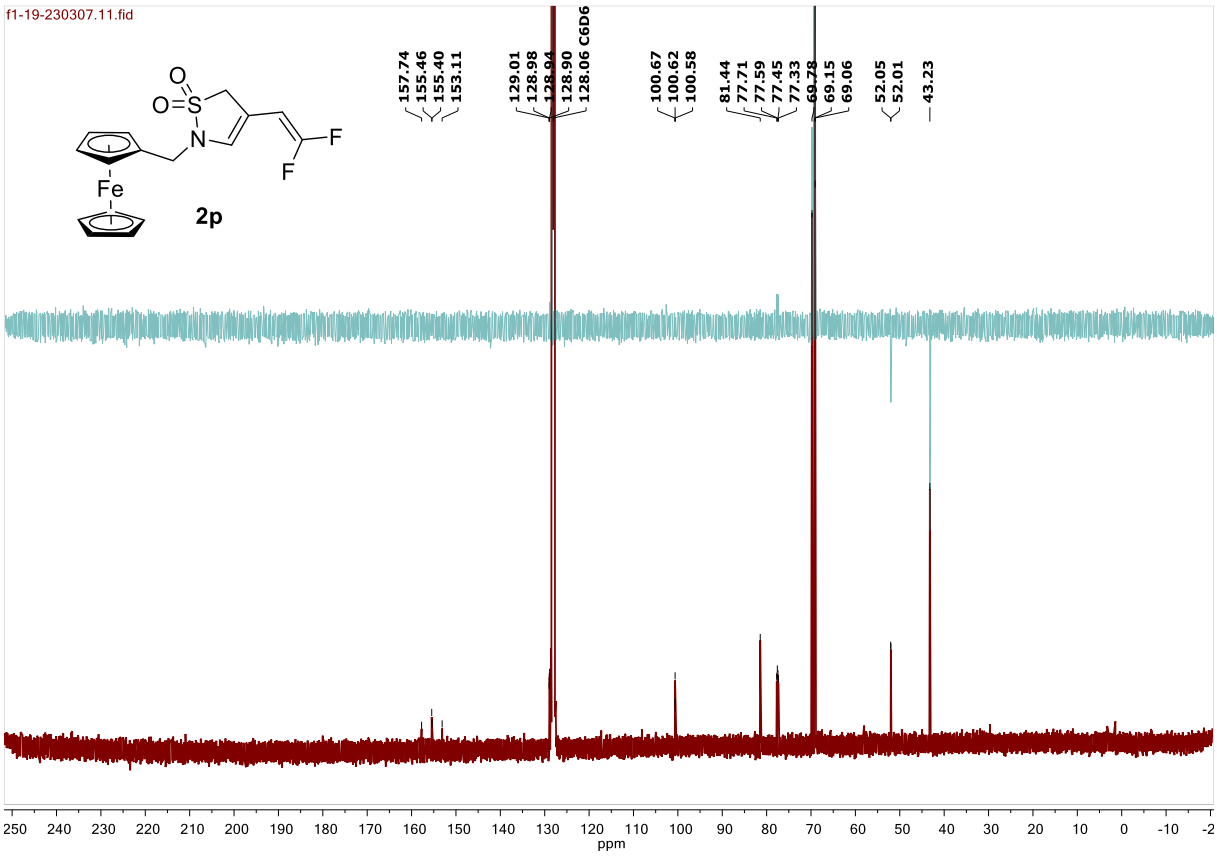
^{13}C NMR (C_6D_6, 126 MHz) of **2o**



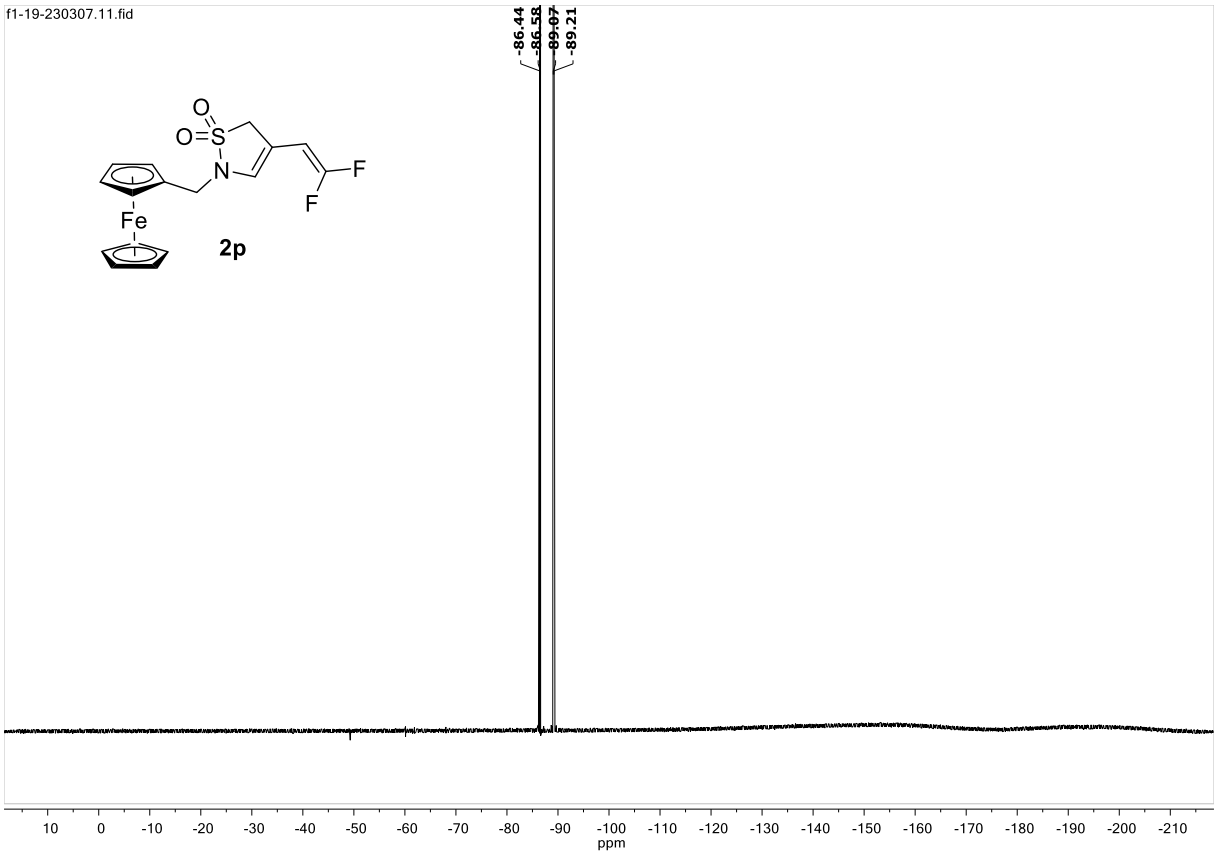
^{19}F NMR (C_6D_6, 282 MHz) of **2o**



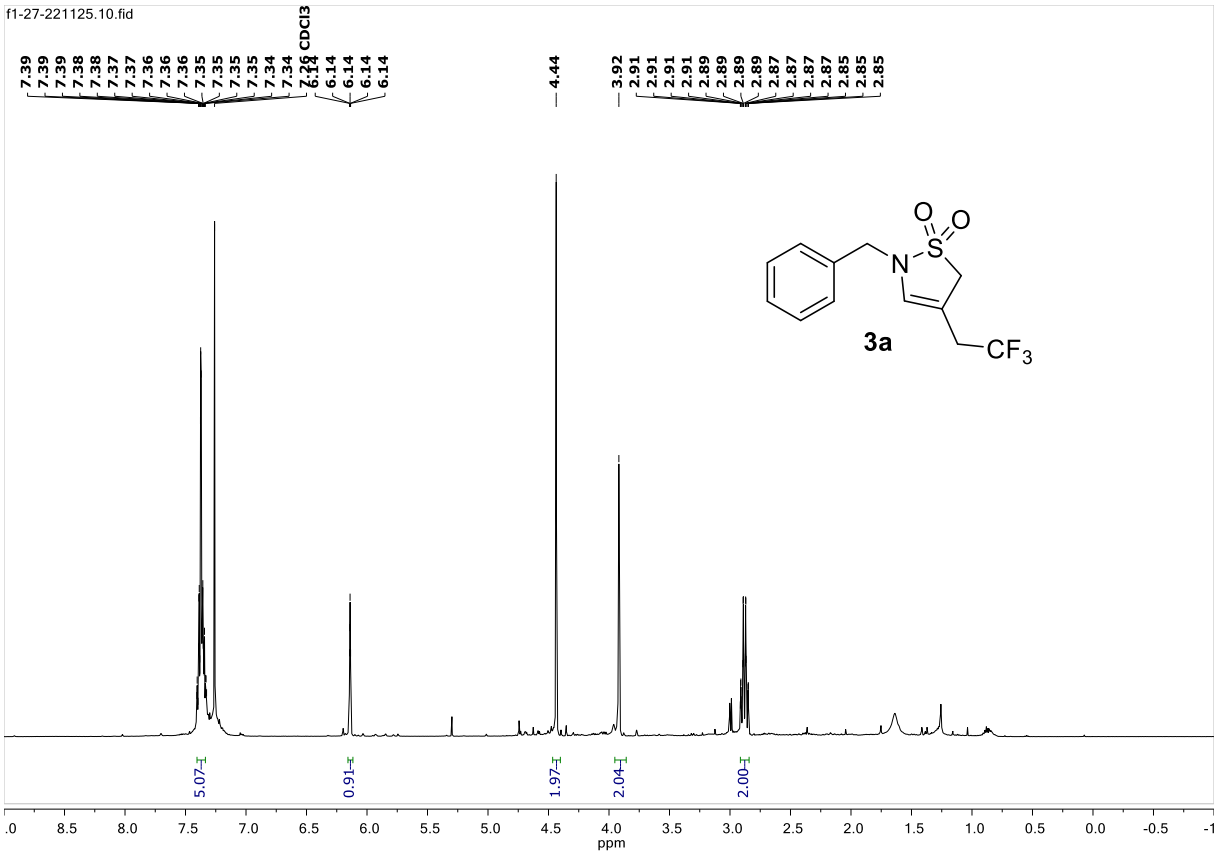
^{1}H NMR (C_6D_6, 300 MHz) of **2p**



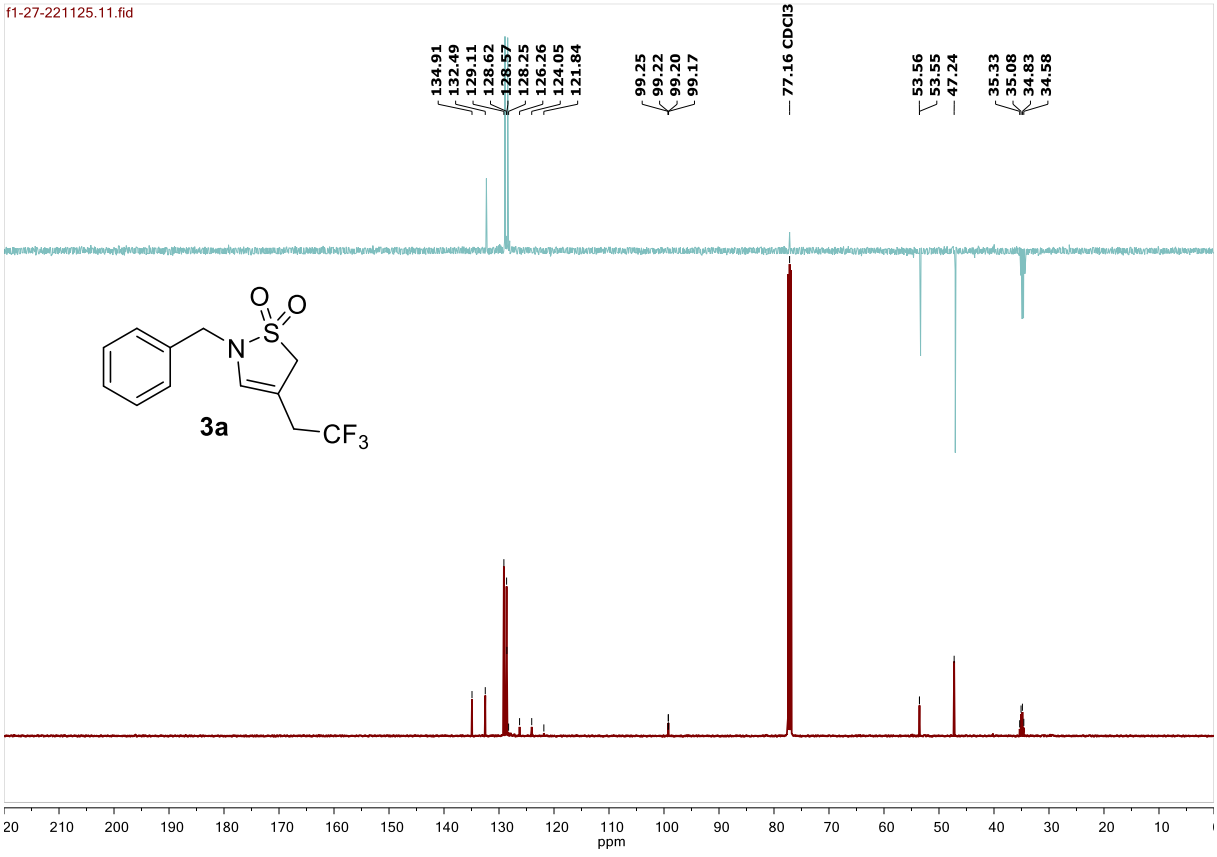
^{13}C NMR (C_6D_6, 126 MHz) of **2p**



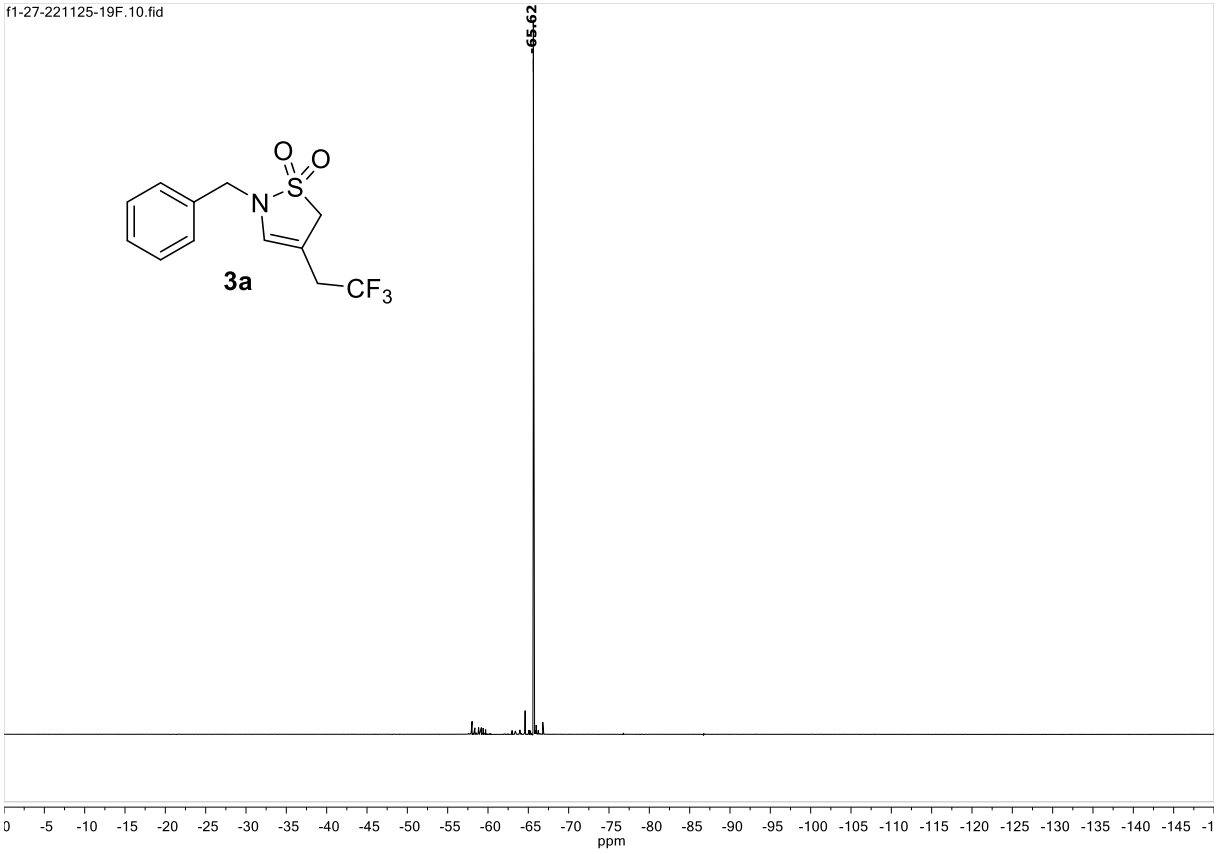
^{19}F NMR (C_6D_6, 282 MHz) of **2p**



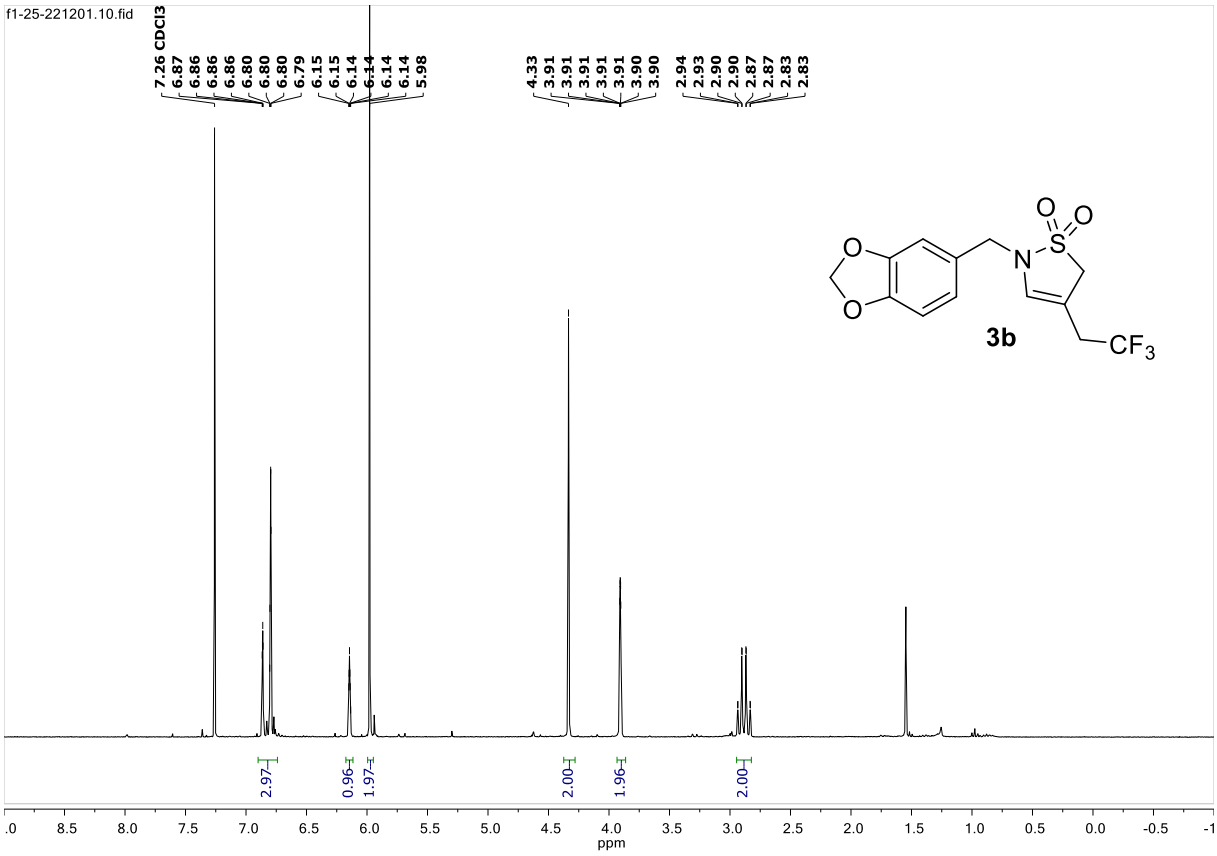
^{1}H NMR ($CDCl_3$, 500 MHz) of **3a**



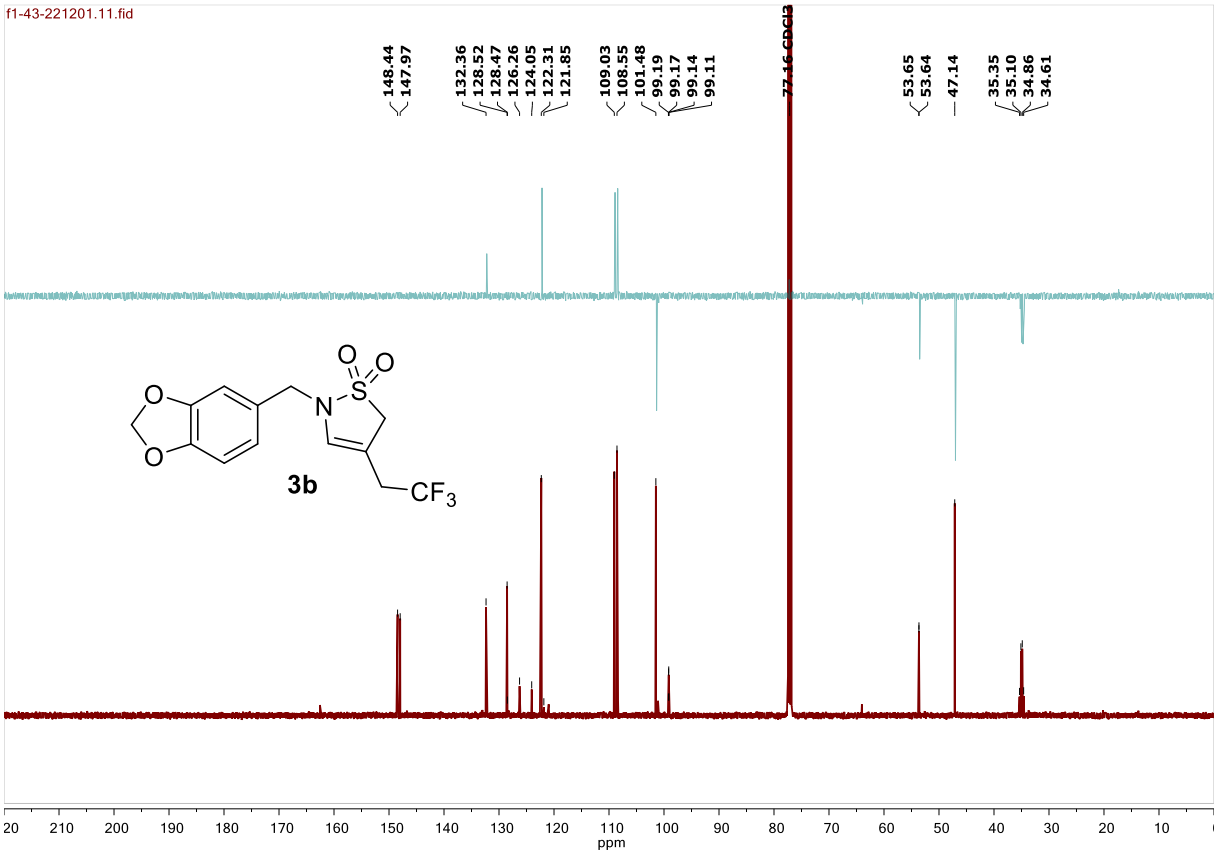
^{13}C NMR ($CDCl_3$, 126 MHz) of **3a**



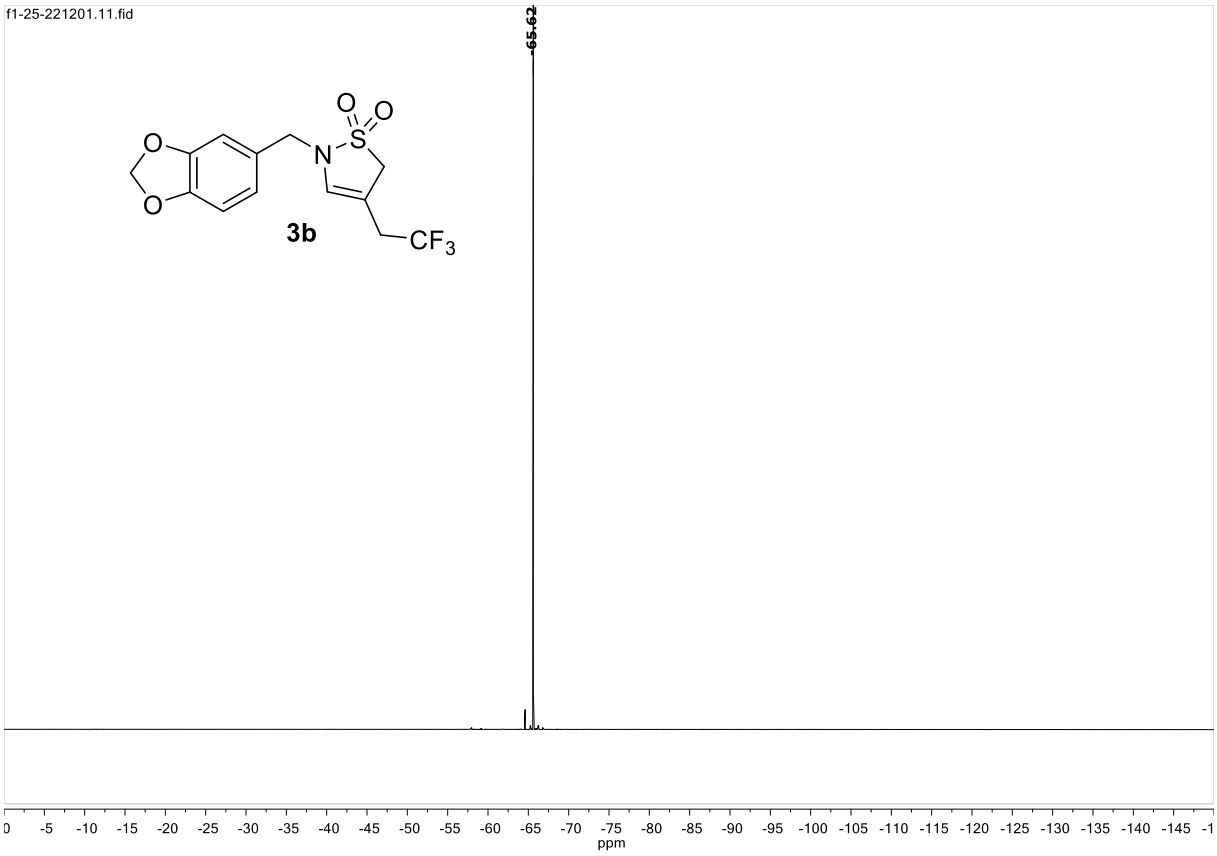
^{19}F NMR ($CDCl_3$, 282 MHz) of **3a**



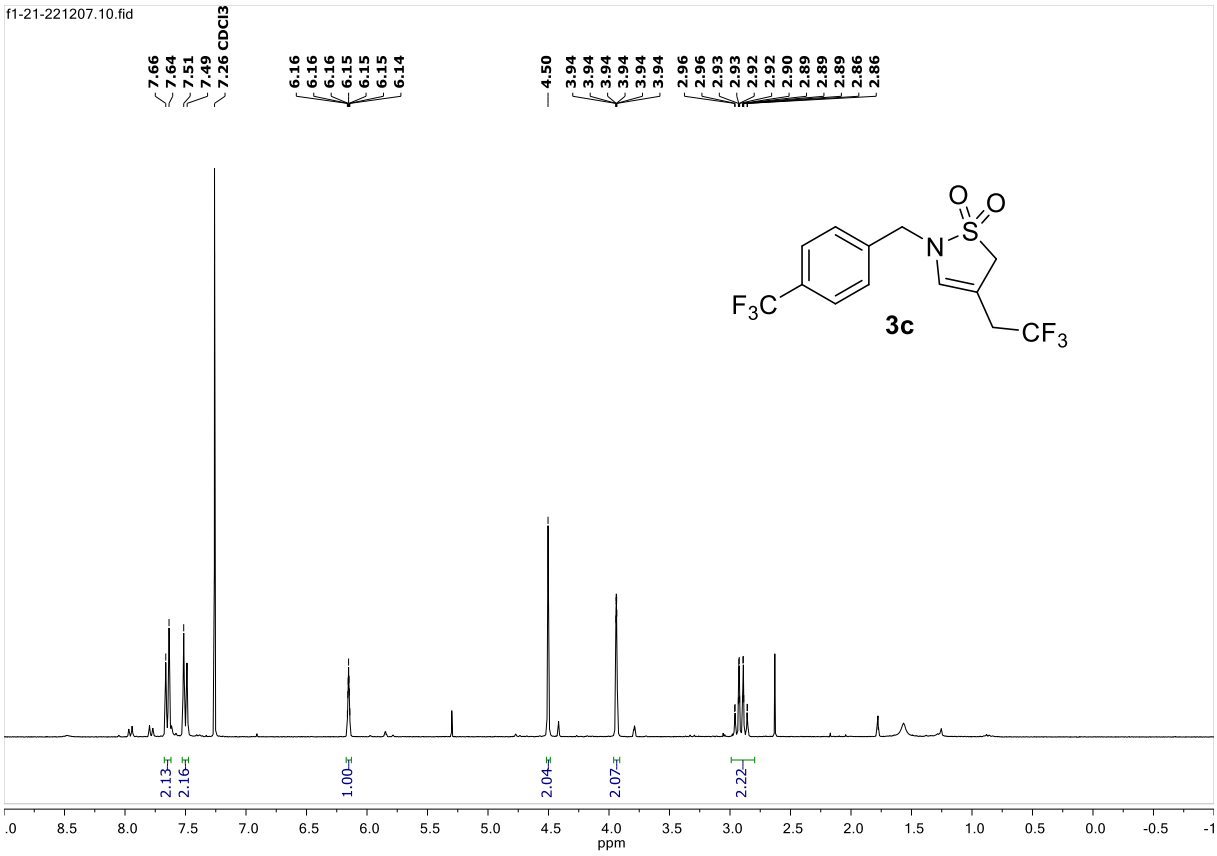
^{1}H NMR ($CDCl_3$, 500 MHz) of **3b**



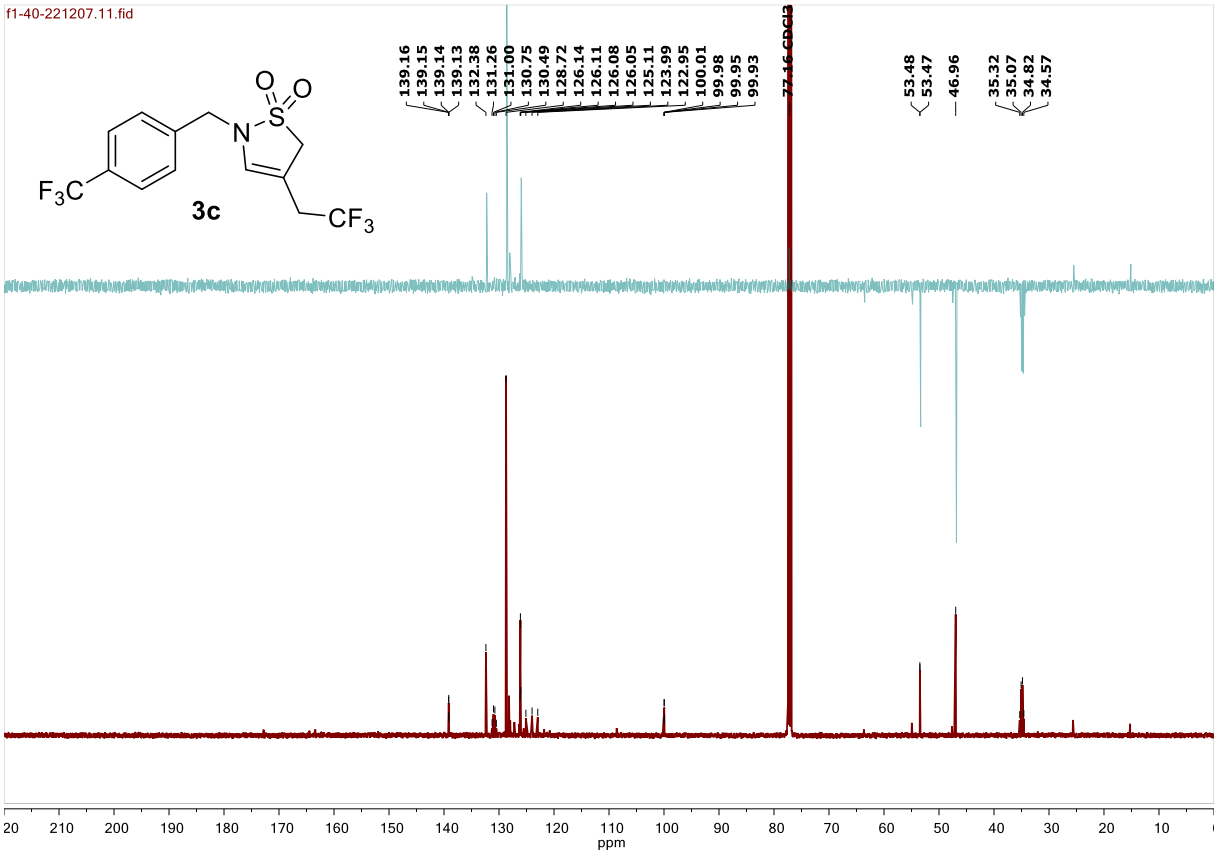
^{13}C NMR ($CDCl_3$, 126 MHz) of **3b**



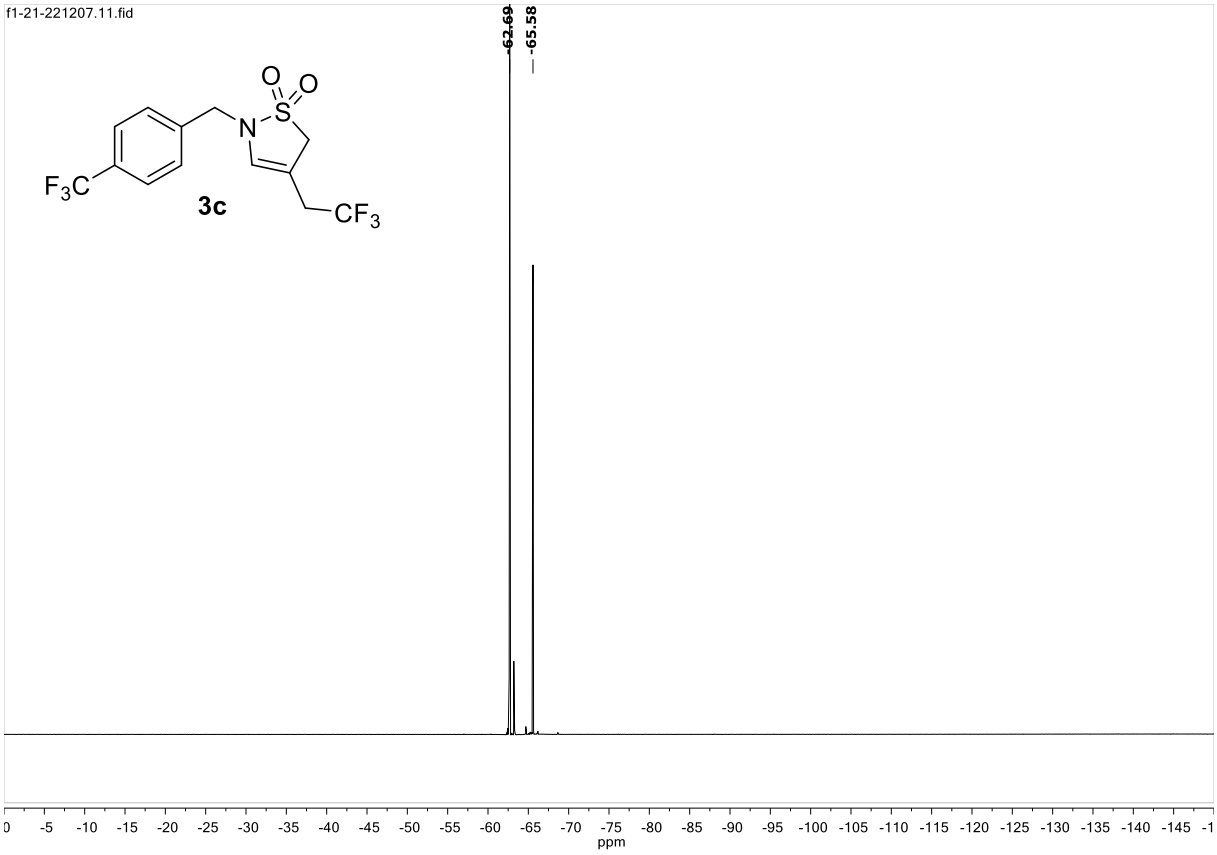
^{19}F NMR ($CDCl_3$, 282 MHz) of **3b**



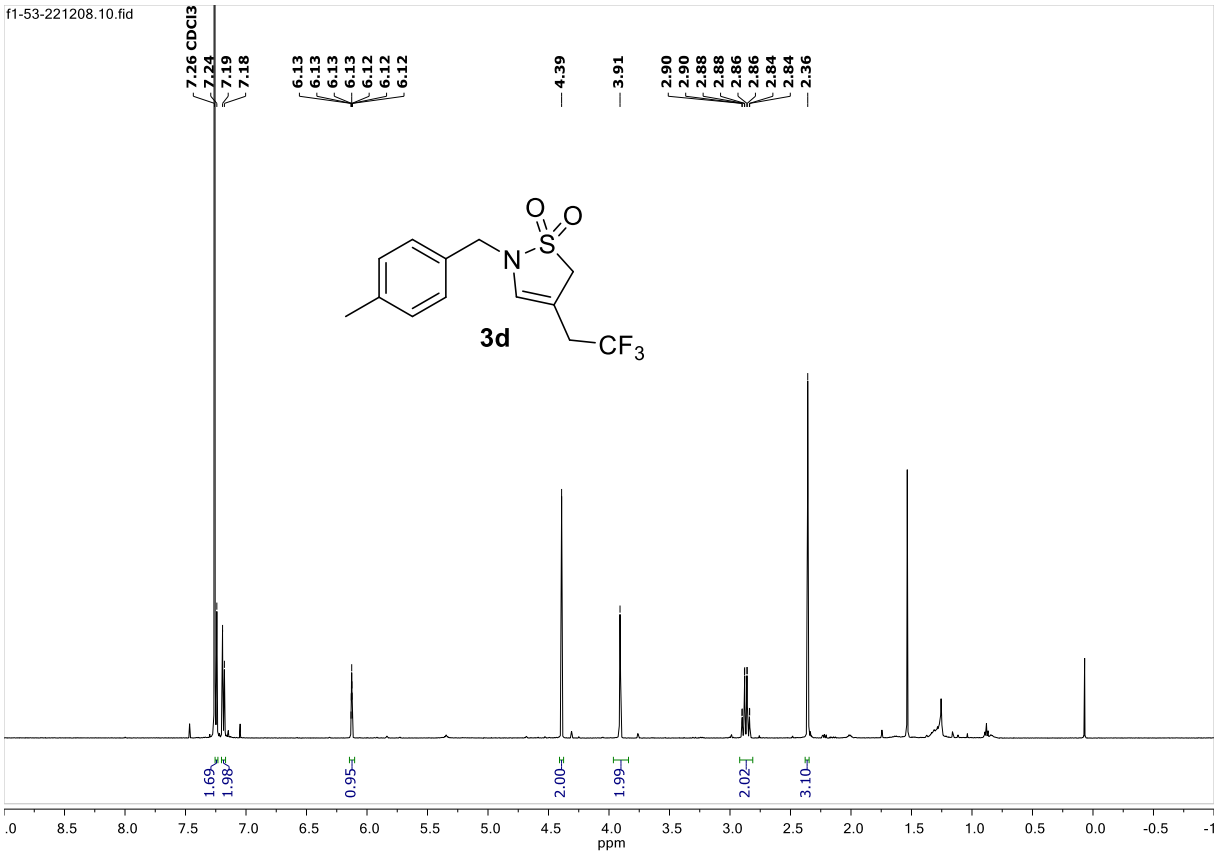
^{1}H NMR ($CDCl_3$, 300 MHz) of **3c**



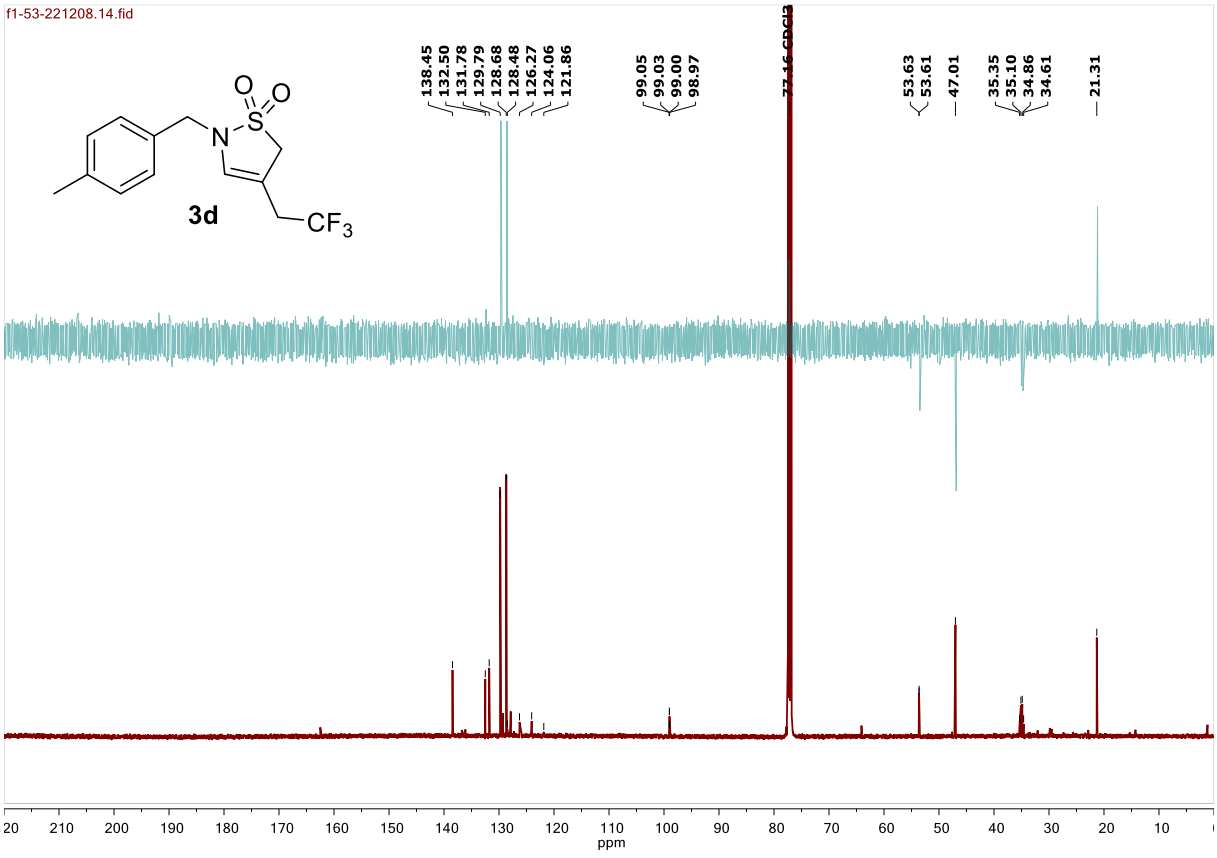
^{13}C NMR ($CDCl_3$, 126 MHz) of **3c**



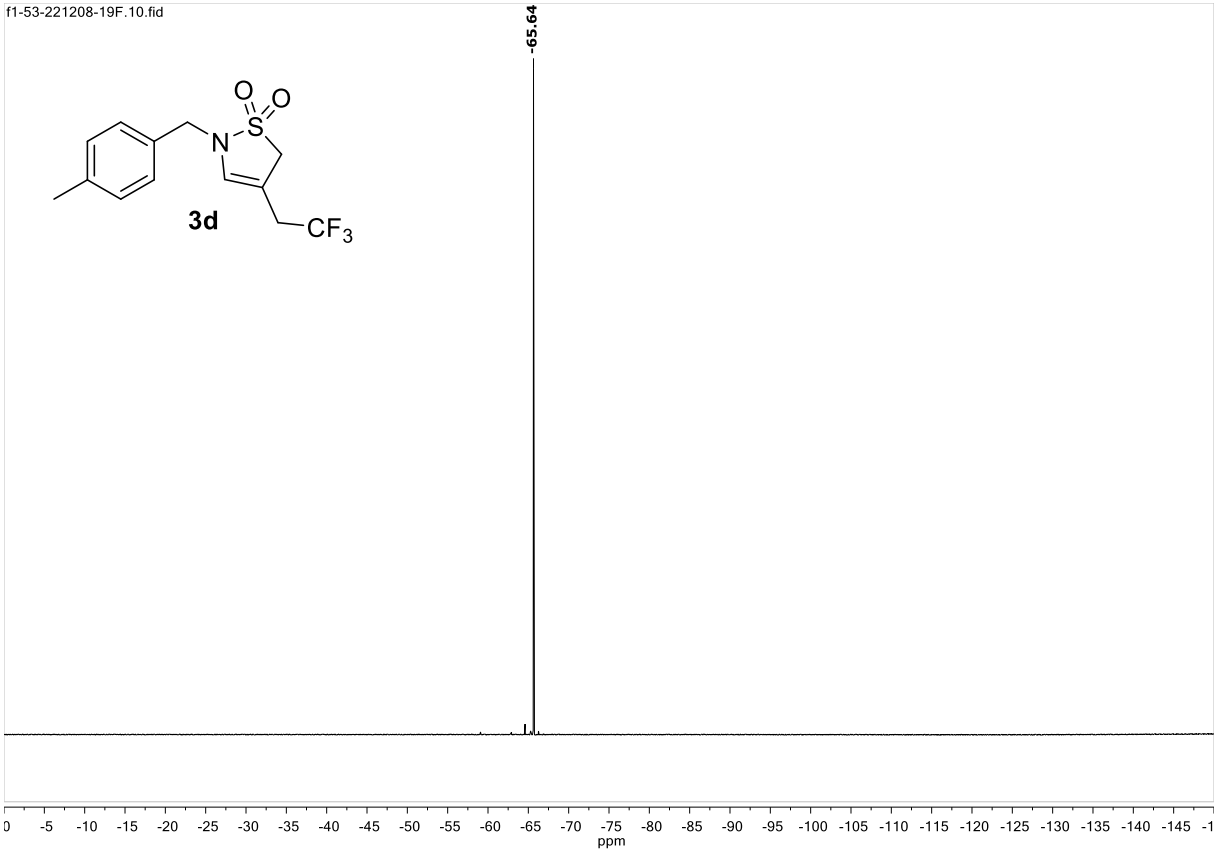
^{19}F NMR ($CDCl_3$, 282 MHz) of **3c**



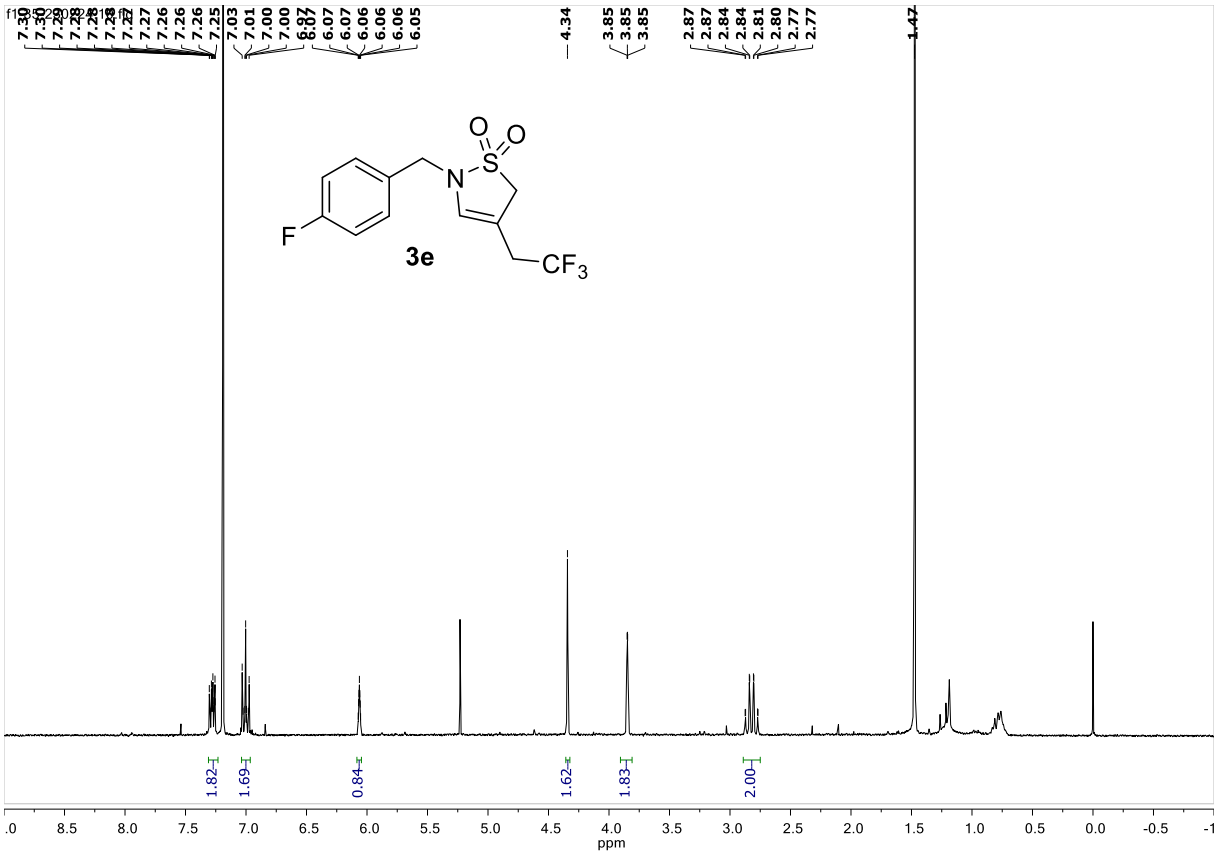
^{1}H NMR ($CDCl_3$, 500 MHz) of **3d**



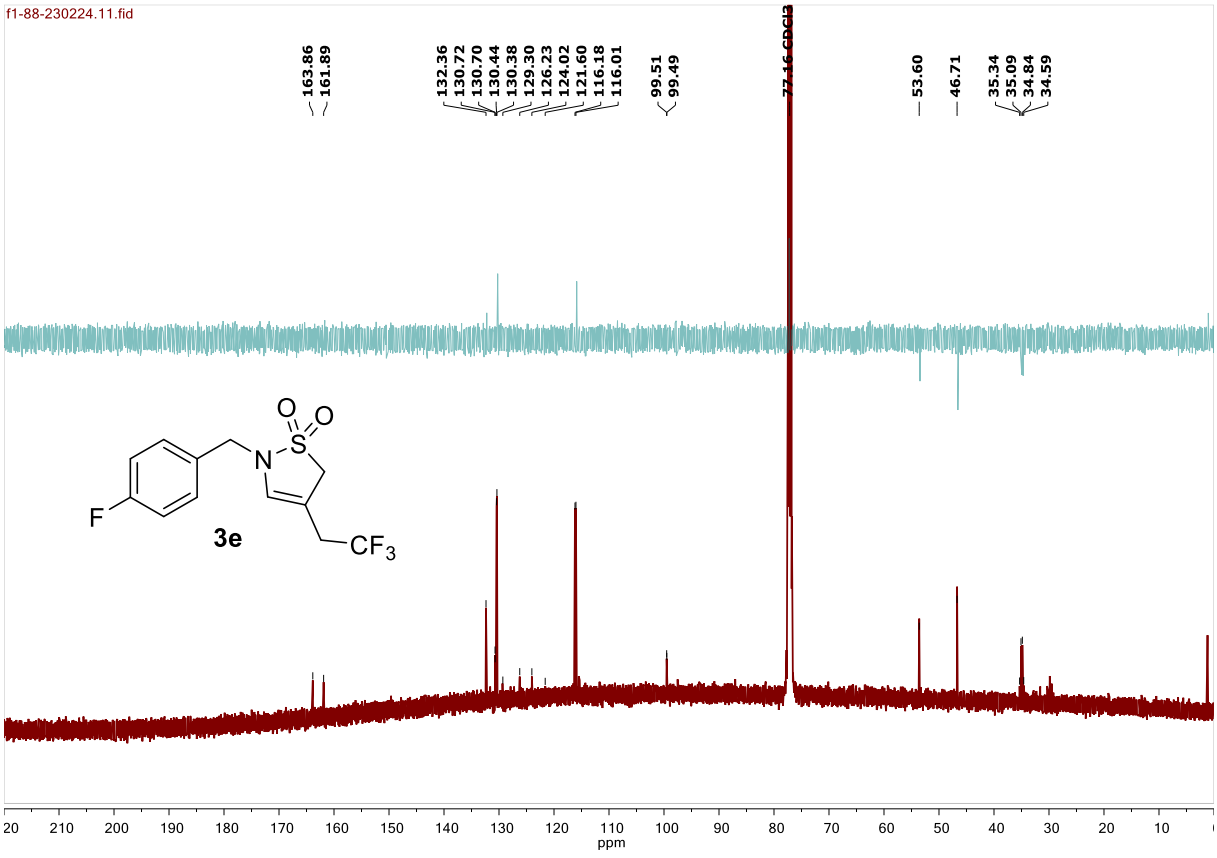
^{13}C NMR ($CDCl_3$, 126 MHz) of **3d**



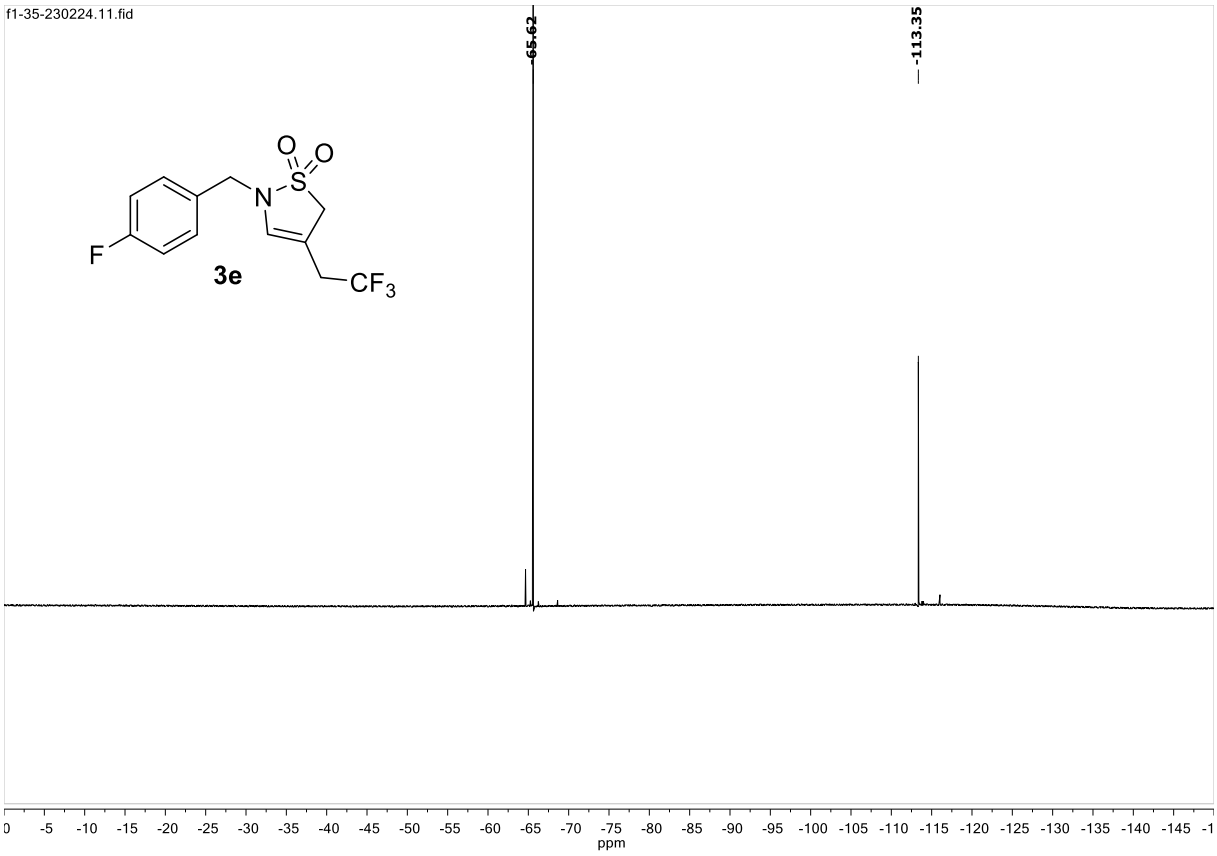
^{19}F NMR ($CDCl_3$, 282 MHz) of **3d**



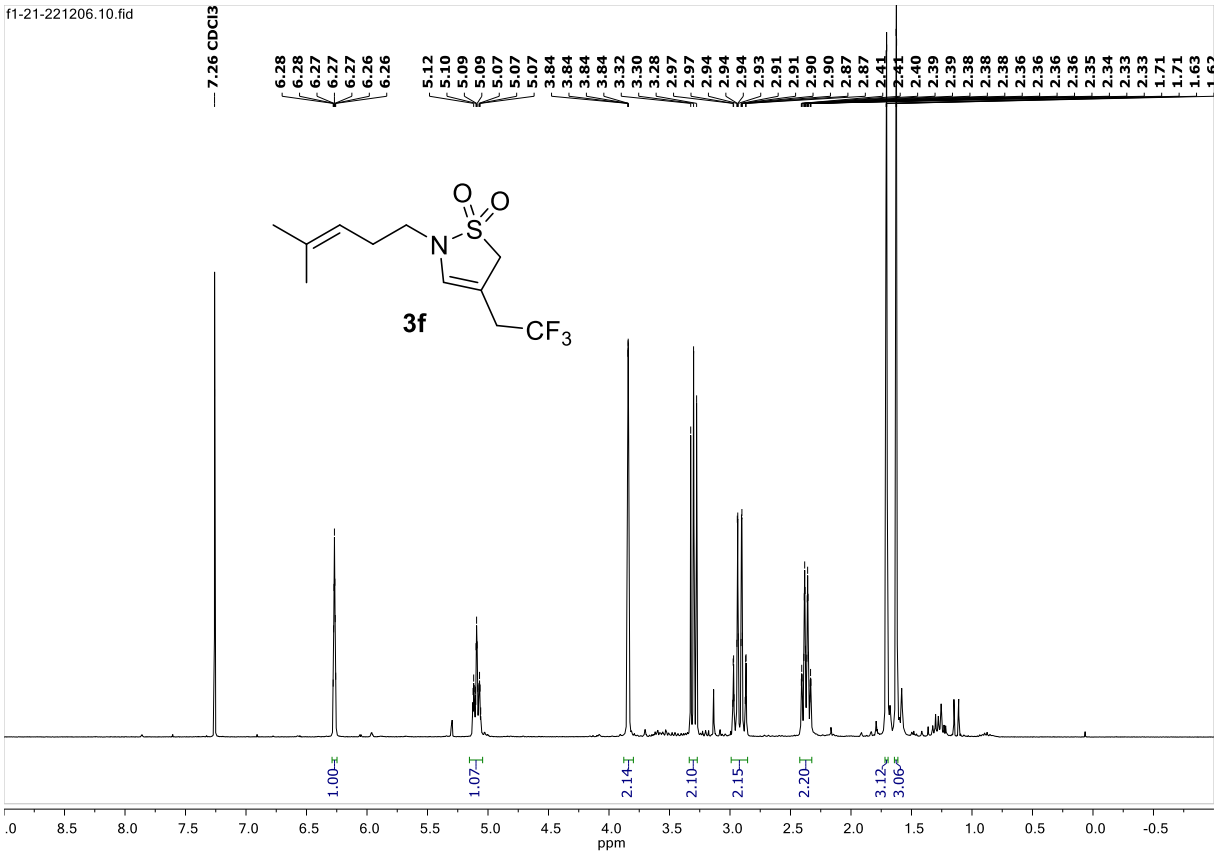
^{1}H NMR ($CDCl_3$, 300 MHz) of **3e**



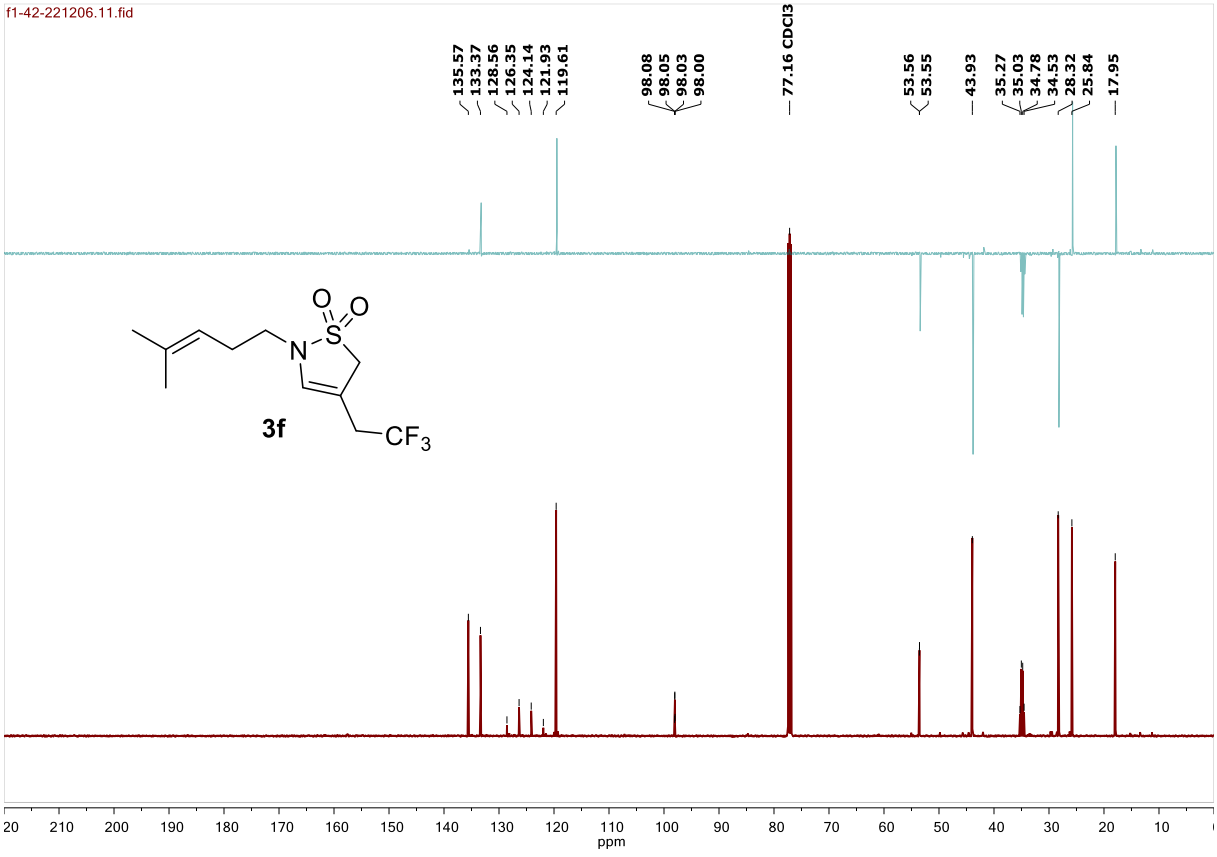
^{13}C NMR ($CDCl_3$, 126 MHz) of **3e**



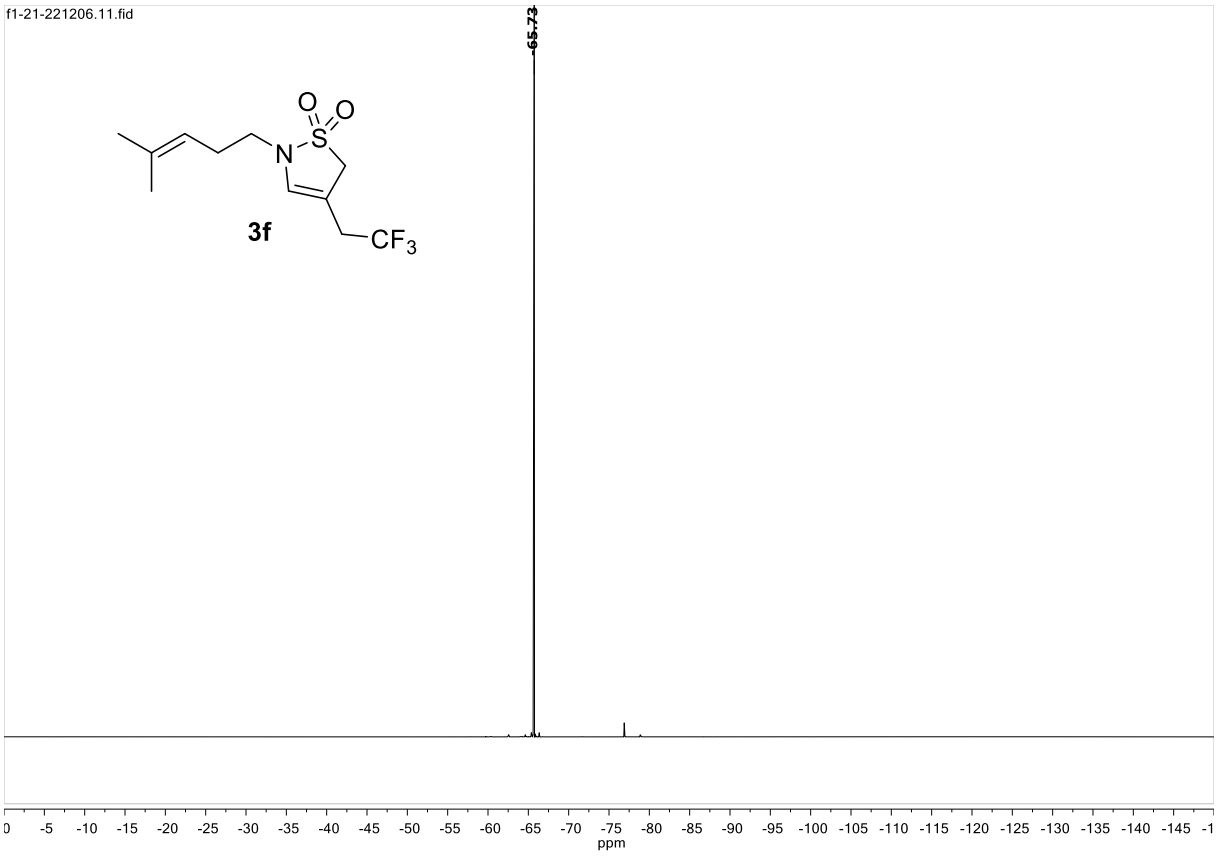
^{19}F NMR ($CDCl_3$, 282 MHz) of **3e**



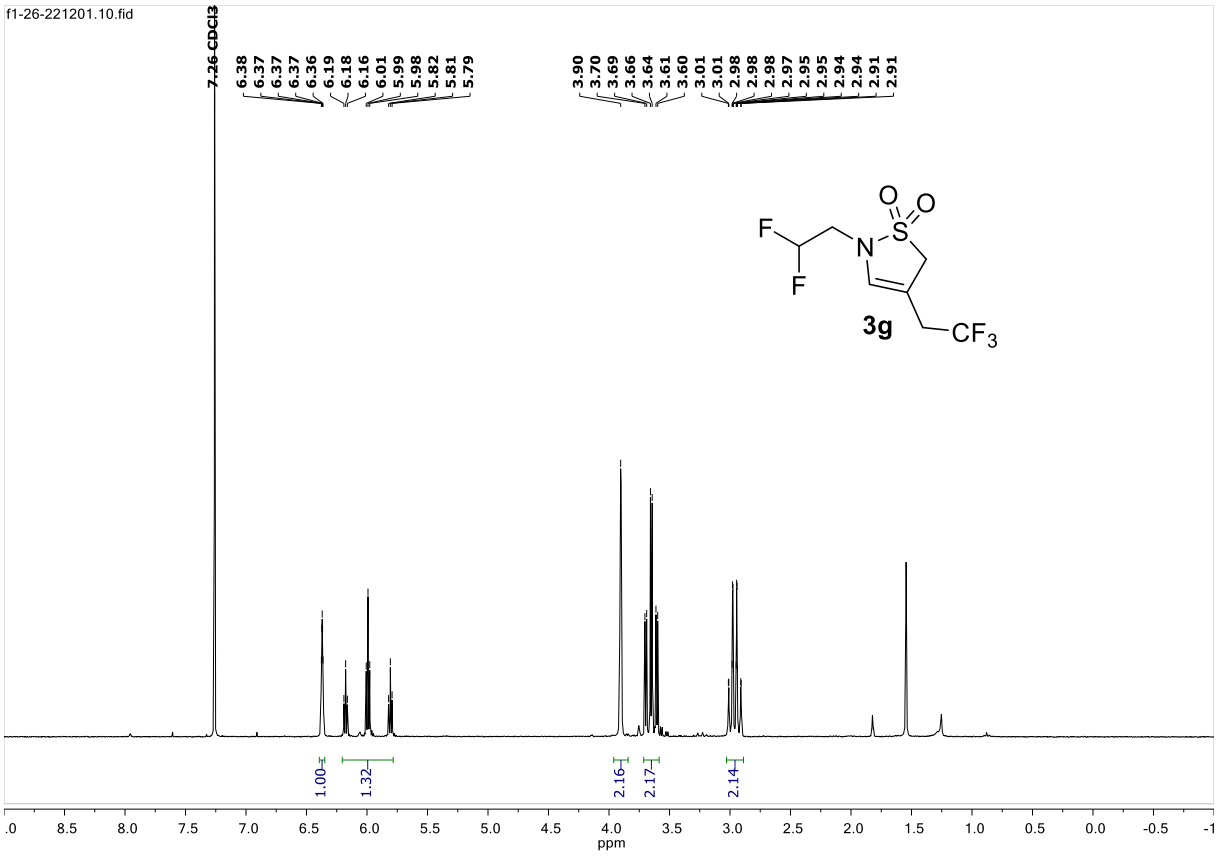
^{1}H NMR ($CDCl_3$, 500 MHz) of **3f**



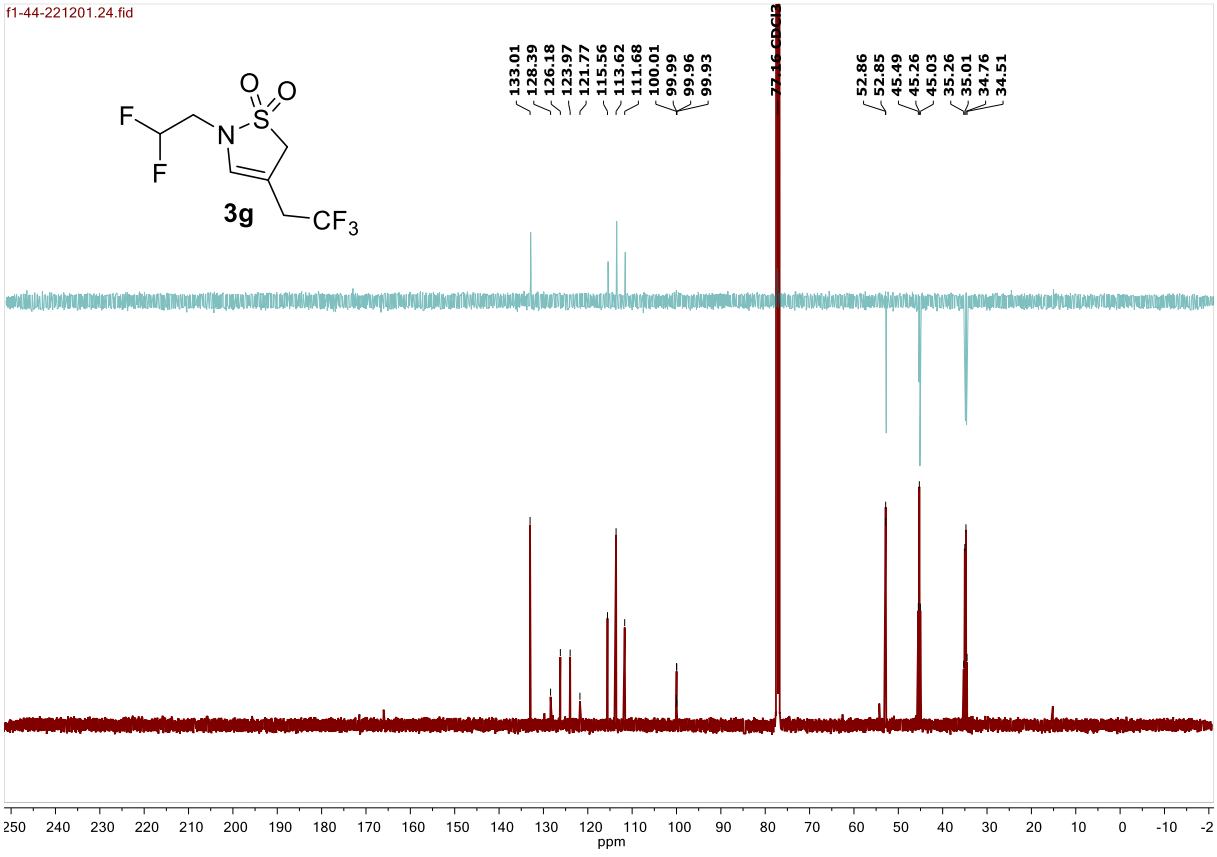
^{13}C NMR ($CDCl_3$, 126 MHz) of **3f**



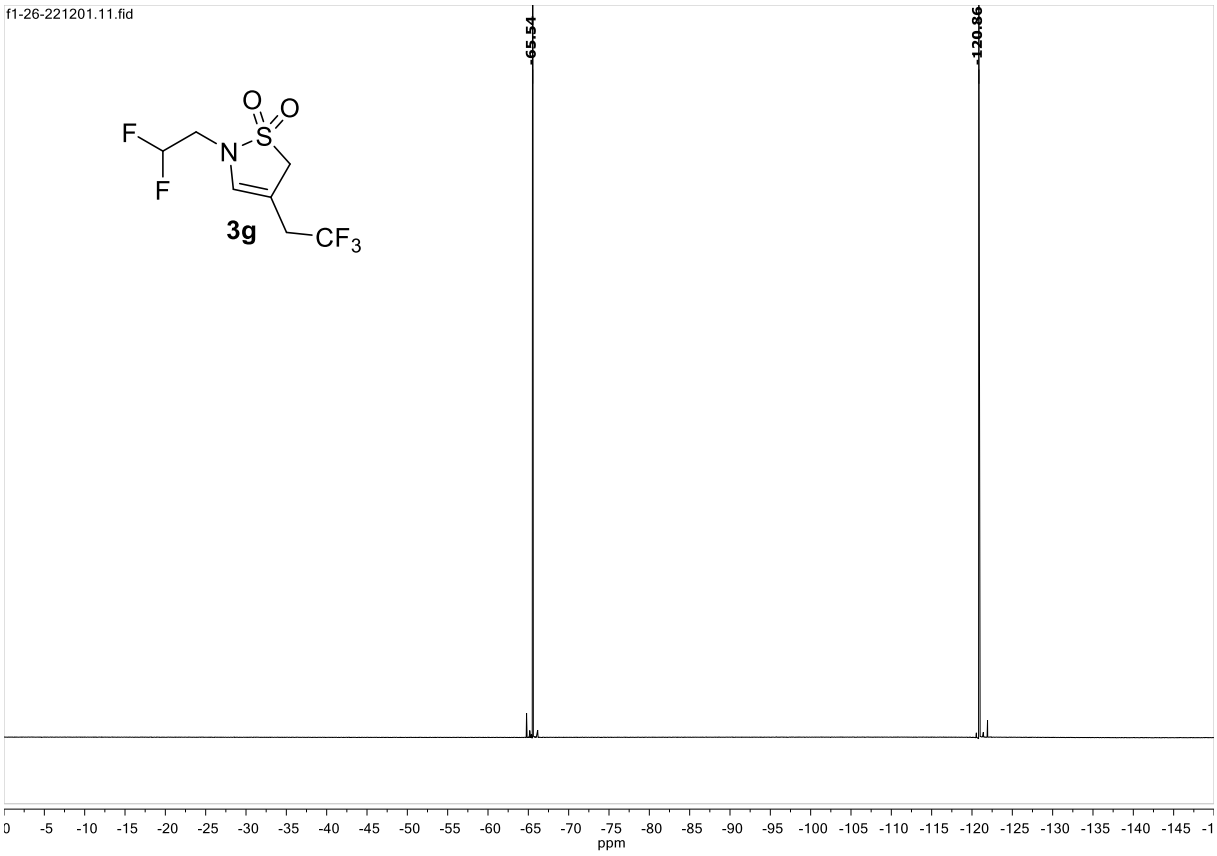
^{19}F NMR ($CDCl_3$, 282 MHz) of **3f**



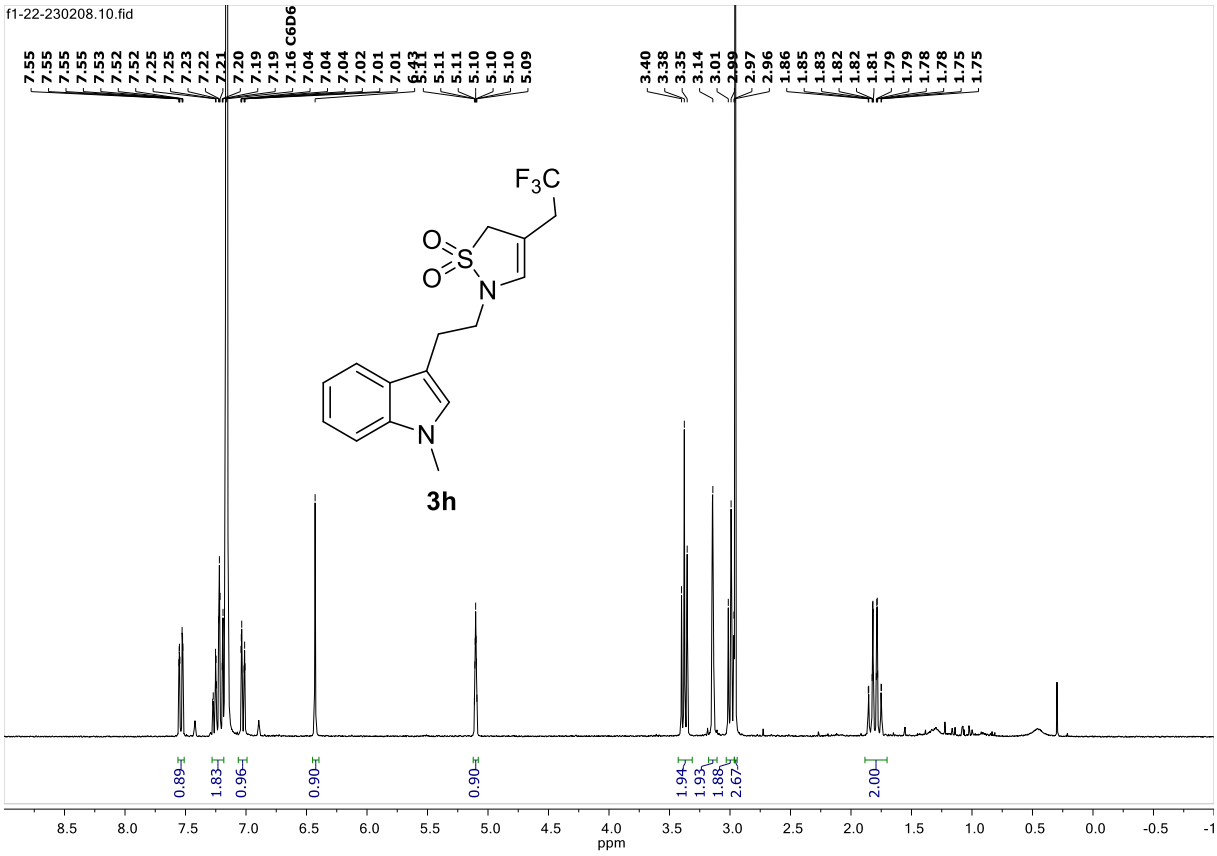
^{1}H NMR ($CDCl_3$, 300 MHz) of **3g**



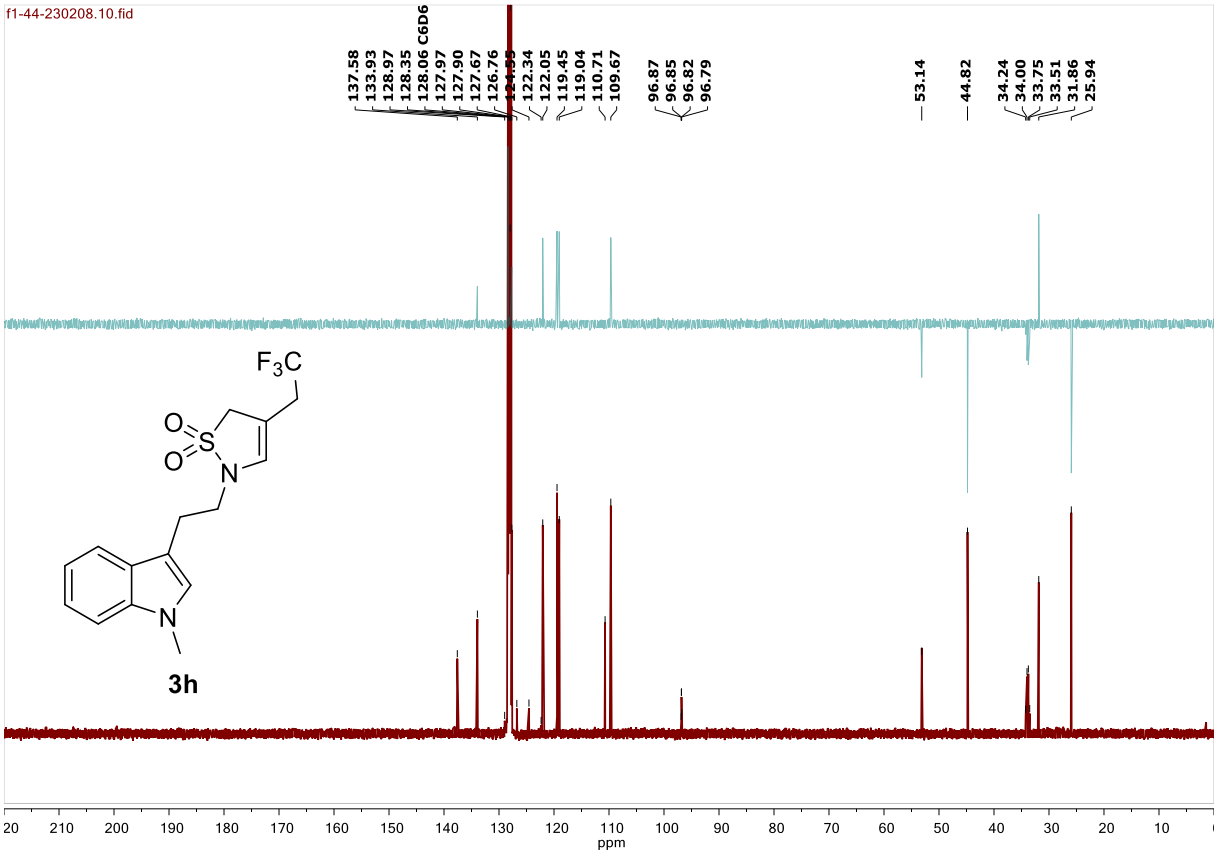
^{13}C NMR ($CDCl_3$, 126 MHz) of **3g**



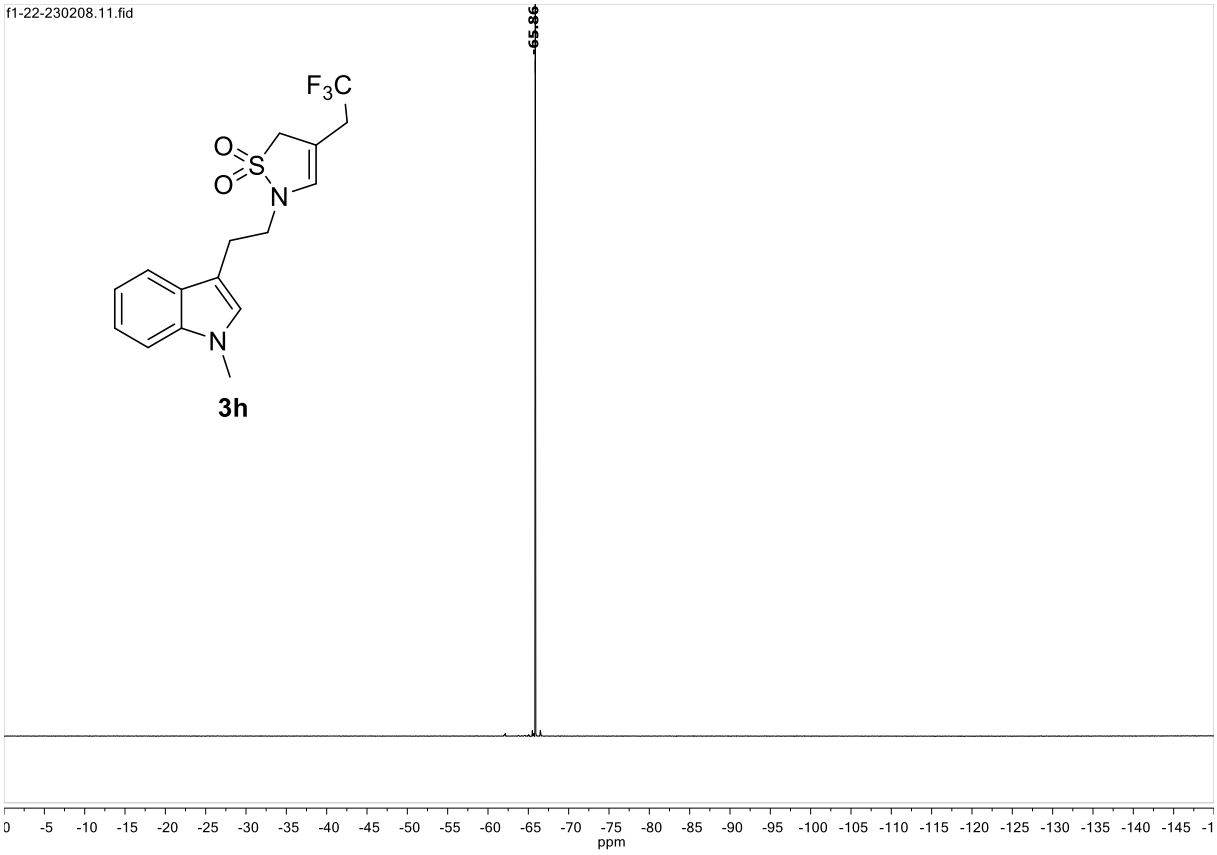
^{19}F NMR ($CDCl_3$, 282 MHz) of **3g**



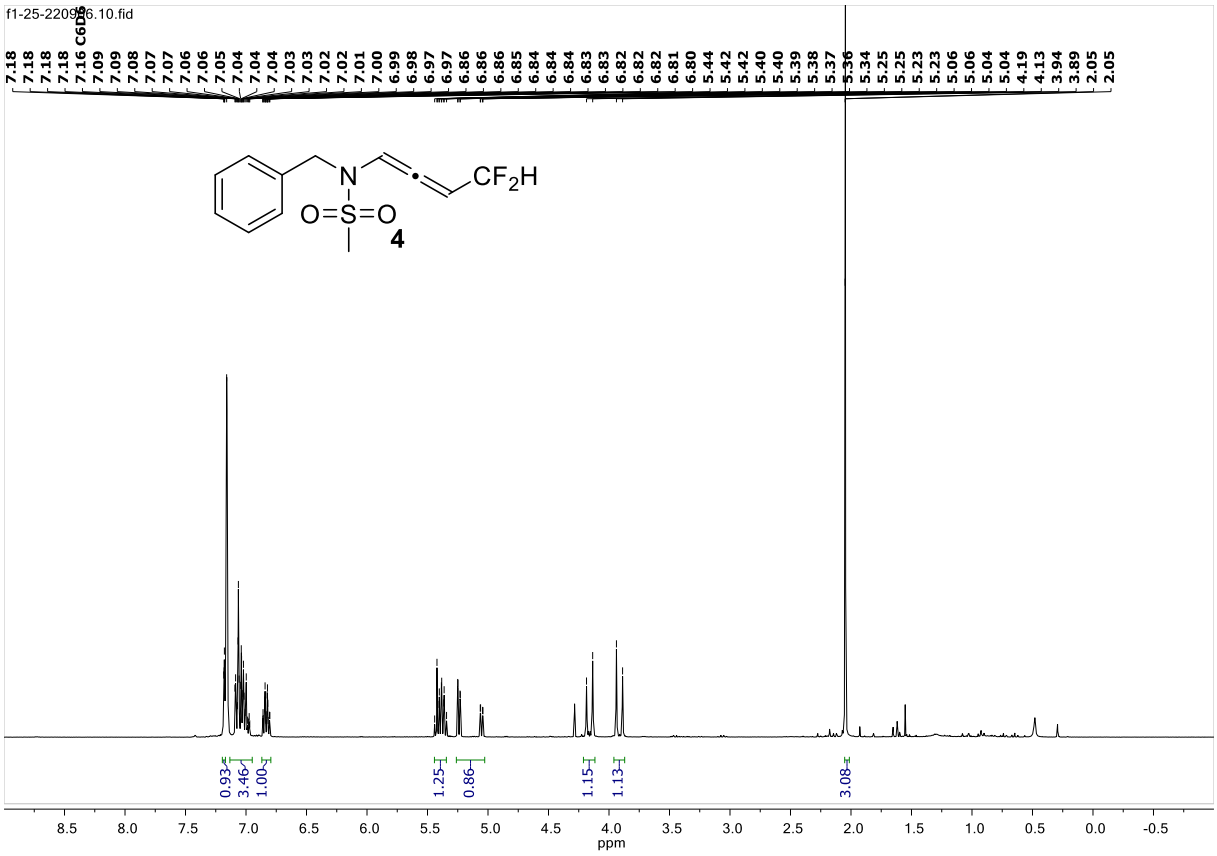
^{1}H NMR ($CDCl_3$, 300 MHz) of **3h**



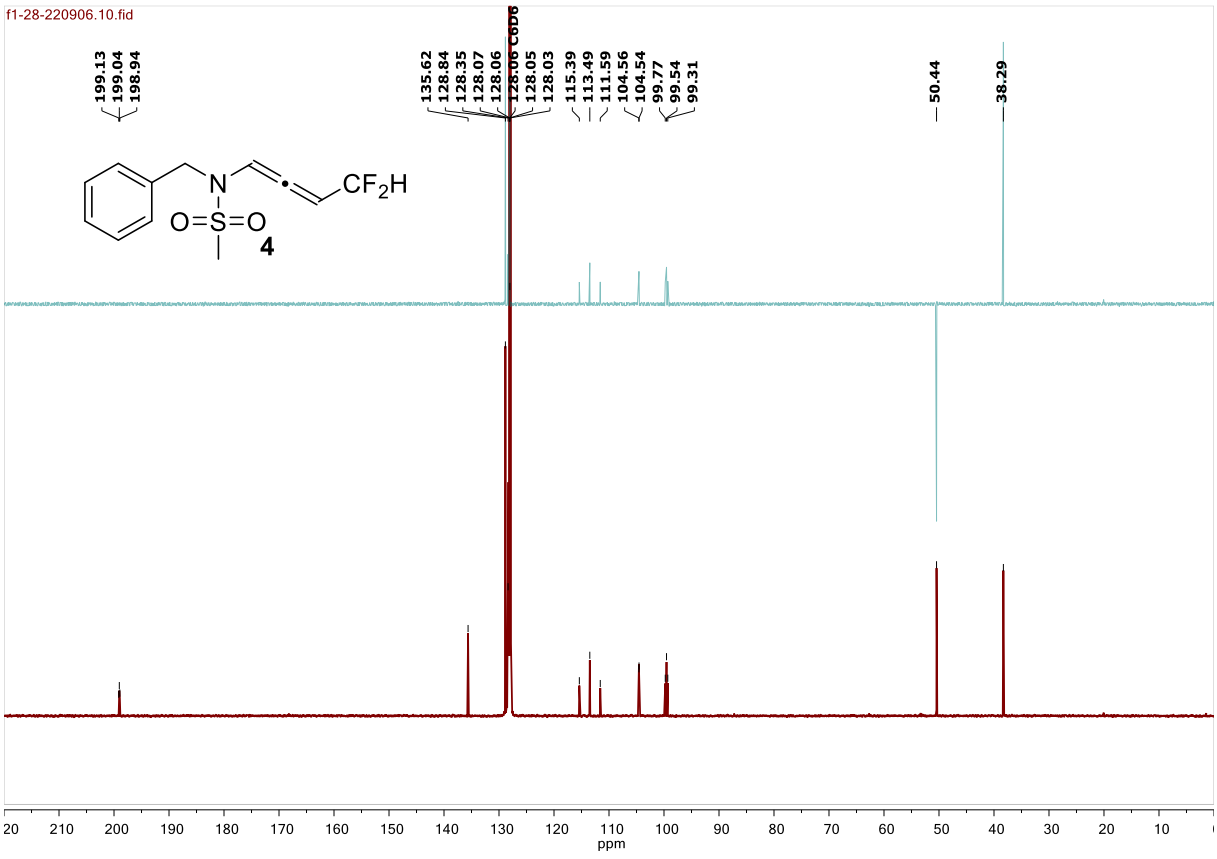
^{13}C NMR ($CDCl_3$, 126 MHz) of **3h**



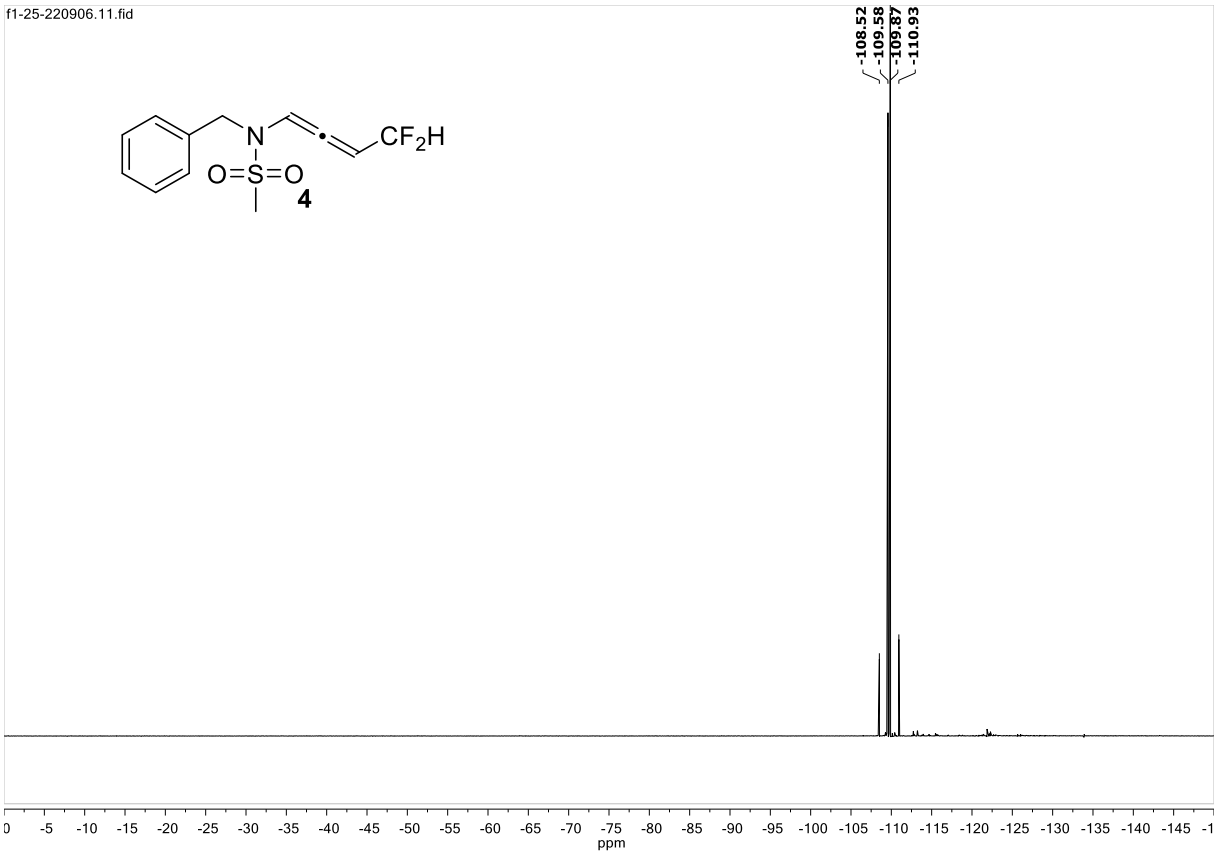
^{19}F NMR ($CDCl_3$, 282 MHz) of **3h**



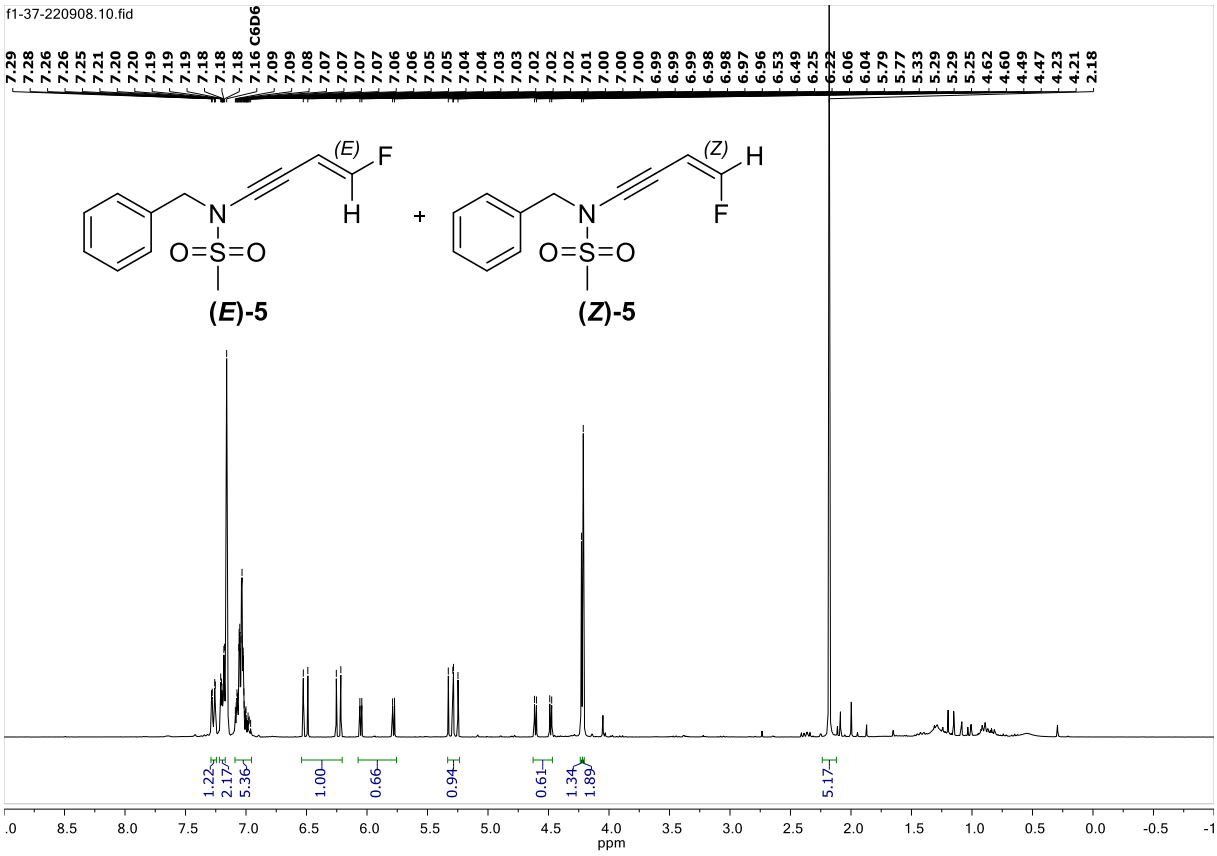
^{1}H NMR (C_6D_6, 300 MHz) of **4**



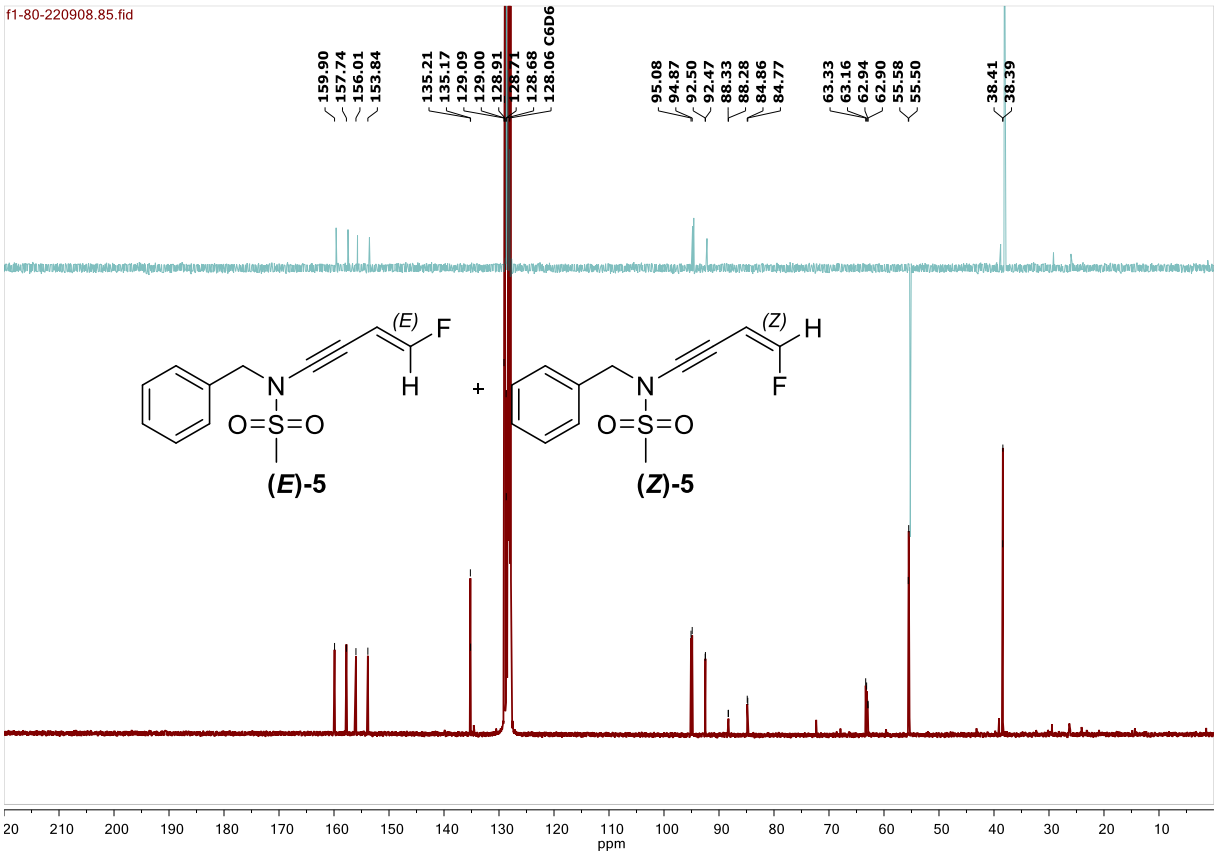
^{13}C NMR (C_6D_6, 126 MHz) of **4**



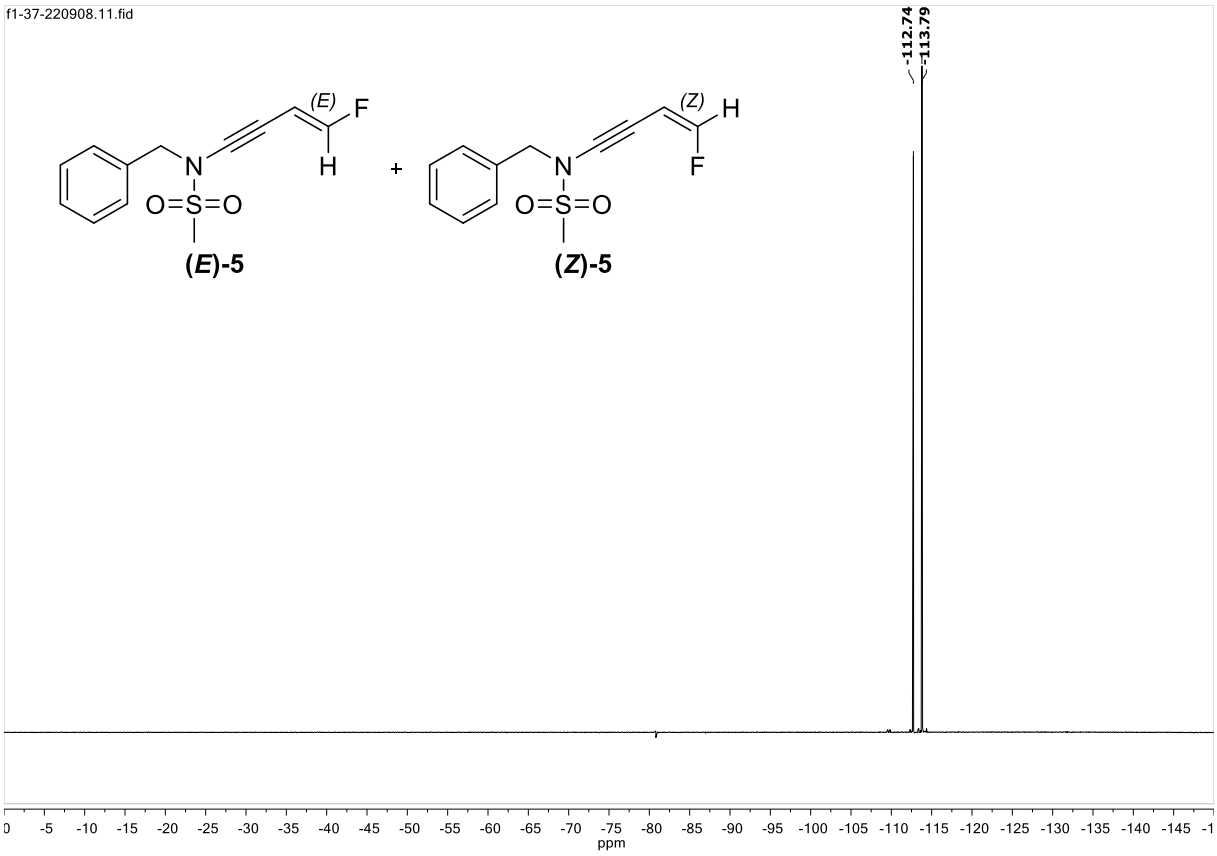
^{19}F NMR (C_6D_6, 282 MHz) of **4**



^{1}H NMR (C_6D_6, 300 MHz) of **5**



^{13}C NMR (C_6D_6, 126 MHz) of **5**



^{19}F NMR (C_6D_6, 282 MHz) of **5**

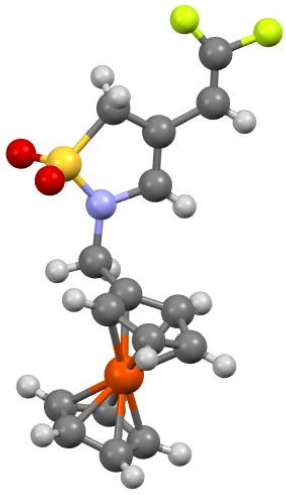
X-Ray Crystallography data

CCDC 2259326 (**2p**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge crystallographic Data Centre.

Compound 4a was dissolved in a 0.5 mL dichloromethane, and *n*-hexane 2 mL were added. The sample was maintained at 4 °C for several days. Crystals were obtained through diffusion.

The X-ray diffraction data were collected at and 173 K on a Bruker SMART CCD diffractometer with MoKα radiation (λ = 0.71073 Å). The diffraction data were corrected for absorption using the SADABS program.[13] The structures were solved using SHELXS977[14] and refined by full matrix leastsquares on F2 using SHELXL-2014 in the anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms were introduced at calculated positions and not refined (riding model).[15]

Crystallography date of 2p:



Structure of **2p** (CCDC 2259326): ellipsoid contour probability 50 %

[13] Bruker. SADABS. Bruker AXS Inc.: Madison, Wisconsin, USA 2001
[14] M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr*. 2008, **64**, 112–122
[15] G. M. Sheldrick, Acta Crystallogr. Sect. C Struct. Chem. 2015, **71**, 3-8

Crystal Structure Report for **2p** (CCDC 2259326)

Table 1. Crystal data and structure refinement for **2p** (CCDC 2259326)

Identification code	**2p** (CCDC 2259326)
Empirical formula	C16 H15 F2 Fe N O2 S
Formula weight	379.20
Temperature	173(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P 21/n
Unit cell dimensions	a = 6.0568(9) A alpha = 90 deg. b = 11.538(3) A beta = 92.696(14) deg. c = 22.723(4) A gamma = 90 deg.
Volume	1586.2(5) A^3
Z, Calculated density	4, 1.588 Mg/m^3
Absorption coefficient	9.128 mm^-1
F(000)	776
Crystal size	0.200 x 0.100 x 0.050 mm
Theta range for data collection	3.895 to 67.738 deg.

Limiting indices	-5<=h<=7, -11<=k<=13, -26<=l<=26
Reflections collected / unique	4914 / 2701 [R(int) = 0.0733]
Completeness to theta = 67.679	94.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6542
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2701 / 0 / 209
Goodness-of-fit on F^2	1.311
Final R indices [I>2sigma(I)]	R1 = 0.1850, wR2 = 0.3970
R indices (all data)	R1 = 0.3103, wR2 = 0.4758
Extinction coefficient	0.00123(11)
Largest diff. peak and hole	1.323 and -1.218 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for elmcg_a.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Fe(1)	5086(4)	4960(4)	1819(1)	85(1)
C(1)	3930(40)	6050(30)	1194(12)	133(10)
C(2)	5530(50)	5420(30)	968(9)	139(11)
C(3)	7500(40)	5470(30)	1280(11)	146(11)
C(4)	7210(40)	6280(30)	1727(9)	140(10)
C(5)	5090(40)	6733(15)	1659(9)	93(7)
C(6)	4350(30)	4560(20)	2654(7)	85(8)
C(7)	6160(50)	3870(30)	2518(11)	124(10)
C(8)	5460(70)	3270(20)	1980(14)	148(11)
C(9)	3290(70)	3520(30)	1919(15)	166(13)
C(10)	2500(40)	4290(30)	2303(13)	132(10)
C(11)	4500(50)	5430(30)	3151(8)	152(12)
N(1)	3770(60)	4930(30)	3701(12)	205(15)
S(1)	1691(8)	5075(8)	4030(2)	110(3)
O(1)	0(40)	4780(30)	3672(10)	260(17)
O(2)	1500(50)	6170(20)	4263(9)	211(13)
C(12)	2260(40)	3900(20)	4591(8)	117(8)
C(13)	4300(30)	3497(19)	4428(7)	78(6)
C(14)	5140(40)	3980(30)	3924(9)	119(9)
C(15)	5470(40)	2460(30)	4737(9)	113(10)
C(16)	4730(50)	2050(40)	5206(15)	167(16)
F(1)	5960(30)	1090(20)	5438(8)	221(10)

F(2)	3070(30)	2200(20)	5493(7)	218(9)

Table 3. Selected bond lengths [A] and angles [deg] for elmcg_a.

Symmetry transformations used to generate equivalent atoms:

Table 4. Bond lengths [A] and angles [deg] for elmcg_a.

Fe(1)-C(9)	2.00(3)
Fe(1)-C(8)	2.00(2)
Fe(1)-C(1)	2.00(2)
Fe(1)-C(4)	2.01(3)
Fe(1)-C(6)	2.025(17)
Fe(1)-C(3)	2.04(2)
Fe(1)-C(2)	2.03(2)
Fe(1)-C(10)	2.103(19)
Fe(1)-C(7)	2.10(2)
Fe(1)-C(5)	2.077(16)
C(1)-C(2)	1.34(4)
C(1)-C(5)	1.47(3)
C(1)-H(1)	1.0000
C(2)-C(3)	1.36(3)
C(2)-H(2)	1.0000
C(3)-C(4)	1.40(4)
C(3)-H(3)	1.0000
C(4)-C(5)	1.39(3)

C(4)-H(4)	1.0000
C(5)-H(5)	1.0000
C(6)-C(10)	1.38(3)
C(6)-C(7)	1.40(3)
C(6)-C(11)	1.51(3)
C(7)-C(8)	1.45(3)
C(7)-H(7)	1.0000
C(8)-C(9)	1.35(4)
C(8)-H(8)	1.0000
C(9)-C(10)	1.35(4)
C(9)-H(9)	1.0000
C(10)-H(10)	1.0000
C(11)-N(1)	1.47(3)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
N(1)-C(14)	1.45(3)
N(1)-S(1)	1.50(2)
S(1)-O(1)	1.32(2)
S(1)-O(2)	1.38(3)
S(1)-C(12)	1.88(2)
C(12)-C(13)	1.39(3)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(14)	1.39(3)
C(13)-C(15)	1.54(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.27(4)
C(15)-H(15)	0.9500
C(16)-F(2)	1.23(3)
C(16)-F(1)	1.42(4)

C(9)-Fe(1)-C(8)	39.4(12)

C(9)-Fe(1)-C(1)	115.4(13)
C(8)-Fe(1)-C(1)	141.2(14)
C(9)-Fe(1)-C(4)	173.2(16)
C(8)-Fe(1)-C(4)	133.8(14)
C(1)-Fe(1)-C(4)	69.7(10)
C(9)-Fe(1)-C(6)	63.8(12)
C(8)-Fe(1)-C(6)	68.4(11)
C(1)-Fe(1)-C(6)	136.4(11)
C(4)-Fe(1)-C(6)	116.2(8)
C(9)-Fe(1)-C(3)	135.9(16)
C(8)-Fe(1)-C(3)	108.4(14)
C(1)-Fe(1)-C(3)	68.2(10)
C(4)-Fe(1)-C(3)	40.4(10)
C(6)-Fe(1)-C(3)	145.7(8)
C(9)-Fe(1)-C(2)	114.7(12)
C(8)-Fe(1)-C(2)	114.0(13)
C(1)-Fe(1)-C(2)	38.8(11)
C(4)-Fe(1)-C(2)	66.0(9)
C(6)-Fe(1)-C(2)	174.6(10)
C(3)-Fe(1)-C(2)	39.1(8)
C(9)-Fe(1)-C(10)	38.3(12)
C(8)-Fe(1)-C(10)	68.1(13)
C(1)-Fe(1)-C(10)	110.9(11)
C(4)-Fe(1)-C(10)	145.8(12)
C(6)-Fe(1)-C(10)	38.9(8)
C(3)-Fe(1)-C(10)	173.7(13)
C(2)-Fe(1)-C(10)	136.6(11)
C(9)-Fe(1)-C(7)	64.6(12)
C(8)-Fe(1)-C(7)	41.5(10)
C(1)-Fe(1)-C(7)	175.9(13)
C(4)-Fe(1)-C(7)	110.7(10)
C(6)-Fe(1)-C(7)	39.6(9)

C(3)-Fe(1)-C(7)	114.9(11)
C(2)-Fe(1)-C(7)	145.3(13)
C(10)-Fe(1)-C(7)	66.3(10)
C(9)-Fe(1)-C(5)	147.2(15)
C(8)-Fe(1)-C(5)	173.4(14)
C(1)-Fe(1)-C(5)	42.1(9)
C(4)-Fe(1)-C(5)	39.6(8)
C(6)-Fe(1)-C(5)	113.1(10)
C(3)-Fe(1)-C(5)	66.6(11)
C(2)-Fe(1)-C(5)	65.0(11)
C(10)-Fe(1)-C(5)	117.3(11)
C(7)-Fe(1)-C(5)	135.8(12)
C(2)-C(1)-C(5)	104(2)
C(2)-C(1)-Fe(1)	71.9(15)
C(5)-C(1)-Fe(1)	71.7(10)
C(2)-C(1)-H(1)	126.9
C(5)-C(1)-H(1)	128.6
Fe(1)-C(1)-H(1)	127.0
C(1)-C(2)-C(3)	114(3)
C(1)-C(2)-Fe(1)	69.3(13)
C(3)-C(2)-Fe(1)	70.8(13)
C(1)-C(2)-H(2)	122.8
C(3)-C(2)-H(2)	122.9
Fe(1)-C(2)-H(2)	122.8
C(2)-C(3)-C(4)	106(3)
C(2)-C(3)-Fe(1)	70.2(13)
C(4)-C(3)-Fe(1)	68.7(15)
C(2)-C(3)-H(3)	126.9
C(4)-C(3)-H(3)	127.3
Fe(1)-C(3)-H(3)	126.9
C(5)-C(4)-C(3)	108(2)
C(5)-C(4)-Fe(1)	72.7(13)

C(3)-C(4)-Fe(1)	70.9(16)
C(5)-C(4)-H(4)	126.6
C(3)-C(4)-H(4)	124.8
Fe(1)-C(4)-H(4)	125.1
C(4)-C(5)-C(1)	107(2)
C(4)-C(5)-Fe(1)	67.7(14)
C(1)-C(5)-Fe(1)	66.2(12)
C(4)-C(5)-H(5)	126.6
C(1)-C(5)-H(5)	126.2
Fe(1)-C(5)-H(5)	127.0
C(10)-C(6)-C(7)	112(2)
C(10)-C(6)-C(11)	127(3)
C(7)-C(6)-C(11)	121(2)
C(10)-C(6)-Fe(1)	73.6(11)
C(7)-C(6)-Fe(1)	73.2(11)
C(11)-C(6)-Fe(1)	122.5(16)
C(6)-C(7)-C(8)	105(2)
C(6)-C(7)-Fe(1)	67.3(12)
C(8)-C(7)-Fe(1)	65.5(12)
C(6)-C(7)-H(7)	127.0
C(8)-C(7)-H(7)	127.8
Fe(1)-C(7)-H(7)	127.2
C(9)-C(8)-C(7)	103(3)
C(9)-C(8)-Fe(1)	70.5(19)
C(7)-C(8)-Fe(1)	73.0(15)
C(9)-C(8)-H(8)	128.2
C(7)-C(8)-H(8)	127.9
Fe(1)-C(8)-H(8)	128.4
C(8)-C(9)-C(10)	117(3)
C(8)-C(9)-Fe(1)	70.1(19)
C(10)-C(9)-Fe(1)	74.8(18)
C(8)-C(9)-H(9)	121.3

C(10)-C(9)-H(9)	121.7
Fe(1)-C(9)-H(9)	120.9
C(9)-C(10)-C(6)	103(2)
C(9)-C(10)-Fe(1)	66.9(17)
C(6)-C(10)-Fe(1)	67.5(10)
C(9)-C(10)-H(10)	128.1
C(6)-C(10)-H(10)	129.4
Fe(1)-C(10)-H(10)	128.9
N(1)-C(11)-C(6)	111(3)
N(1)-C(11)-H(11A)	109.0
C(6)-C(11)-H(11A)	109.0
N(1)-C(11)-H(11B)	109.8
C(6)-C(11)-H(11B)	109.8
H(11A)-C(11)-H(11B)	108.0
C(14)-N(1)-C(11)	114(2)
C(14)-N(1)-S(1)	113.1(19)
C(11)-N(1)-S(1)	132(3)
O(1)-S(1)-O(2)	113(2)
O(1)-S(1)-N(1)	108(2)
O(2)-S(1)-N(1)	112(2)
O(1)-S(1)-C(12)	110.0(14)
O(2)-S(1)-C(12)	114.8(11)
N(1)-S(1)-C(12)	97.0(14)
C(13)-C(12)-S(1)	101.4(15)
C(13)-C(12)-H(12A)	111.5
S(1)-C(12)-H(12A)	111.6
C(13)-C(12)-H(12B)	111.4
S(1)-C(12)-H(12B)	111.4
H(12A)-C(12)-H(12B)	109.3
C(12)-C(13)-C(14)	117(2)
C(12)-C(13)-C(15)	122.2(19)
C(14)-C(13)-C(15)	121(2)

C(13)-C(14)-N(1)	111.4(19)
C(13)-C(14)-H(14)	124.3
N(1)-C(14)-H(14)	124.3
C(16)-C(15)-C(13)	120(3)
C(16)-C(15)-H(15)	119.7
C(13)-C(15)-H(15)	120.2
C(15)-C(16)-F(2)	136(4)
C(15)-C(16)-F(1)	114(3)
F(2)-C(16)-F(1)	110(3)

Symmetry transformations used to generate equivalent atoms:

Table 5. Anisotropic displacement parameters (A^2 x 10^3) for elmcg_a.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Fe(1)	61(2)	133(3)	61(2)	2(2)	0(1)	-7(2)
C(1)	76(13)	190(30)	131(19)	96(19)	-18(15)	-24(19)
C(2)	123(18)	230(30)	60(13)	28(16)	3(13)	-100(20)
C(3)	68(13)	260(40)	113(18)	-10(20)	8(13)	-36(18)
C(4)	95(16)	270(30)	60(13)	-16(16)	3(12)	45(19)
C(5)	99(15)	53(11)	130(17)	66(11)	29(14)	-9(12)
C(6)	46(8)	150(20)	61(10)	18(12)	-3(8)	-48(13)
C(7)	109(19)	170(30)	90(16)	68(18)	10(15)	-10(20)
C(8)	250(40)	53(14)	140(20)	32(14)	20(30)	0(20)
C(9)	190(30)	200(40)	110(30)	-10(20)	-20(30)	-70(30)

C(10)	68(12)	160(30)	170(30)	30(20)	53(16)	-51(15)
C(11)	210(30)	190(30)	60(13)	-22(14)	49(16)	-60(20)
N(1)	250(30)	220(30)	160(20)	30(20)	160(20)	110(30)
S(1)	75(3)	191(8)	65(3)	1(4)	19(2)	-34(5)
O(1)	200(20)	400(40)	171(19)	110(20)	-74(19)	-180(30)
O(2)	320(30)	210(30)	115(14)	54(15)	97(17)	80(20)
C(12)	100(15)	180(30)	77(13)	22(14)	34(12)	-14(17)
C(13)	85(12)	90(15)	60(10)	-33(10)	11(10)	-20(12)
C(14)	104(17)	160(30)	100(16)	-37(16)	48(14)	14(18)
C(15)	98(16)	160(30)	78(13)	18(16)	4(13)	-35(18)
C(16)	100(20)	280(60)	120(20)	-20(30)	10(20)	-40(30)
F(1)	135(14)	360(30)	166(16)	107(17)	13(12)	47(17)
F(2)	159(13)	340(30)	162(13)	120(15)	84(12)	28(16)

Table 6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for elmcg_a.

	x	y	z	U(eq)
H(1)	2369	6147	1039	159
H(2)	5251	4870	630	167
H(3)	8893	5046	1197	175
H(4)	8368	6537	2028	168
H(5)	4430	7346	1907	112
H(7)	7651	3858	2725	149
H(8)	6310	2687	1754	178
H(9)	2331	3197	1588	200
H(10)	955	4593	2329	158

H(11A)	6051	5697	3210	183
H(11B)	3575	6113	3045	183
H(12A)	2339	4208	4997	141
H(12B)	1128	3278	4559	141
H(14)	6451	3727	3750	143
H(15)	6747	2131	4576	136

Table 7. Selected torsion angles [deg] for elmcg_a.

Symmetry transformations used to generate equivalent atoms:

Table 8. Torsion angles [deg] for elmcg_a.

C(5)-C(1)-C(2)-C(3)	9(3)
Fe(1)-C(1)-C(2)-C(3)	-56(2)
C(5)-C(1)-C(2)-Fe(1)	65.2(13)
C(1)-C(2)-C(3)-C(4)	-4(3)
Fe(1)-C(2)-C(3)-C(4)	-59.8(19)
C(1)-C(2)-C(3)-Fe(1)	56(2)
C(2)-C(3)-C(4)-C(5)	-3(3)
Fe(1)-C(3)-C(4)-C(5)	-63.4(17)
C(2)-C(3)-C(4)-Fe(1)	60.8(17)
C(3)-C(4)-C(5)-C(1)	8(3)
Fe(1)-C(4)-C(5)-C(1)	-54.5(13)
C(3)-C(4)-C(5)-Fe(1)	62(2)
C(2)-C(1)-C(5)-C(4)	-10(3)

Fe(1)-C(1)-C(5)-C(4)	55.4(15)
C(2)-C(1)-C(5)-Fe(1)	-65.3(17)
C(10)-C(6)-C(7)-C(8)	9(3)
C(11)-C(6)-C(7)-C(8)	-173(2)
Fe(1)-C(6)-C(7)-C(8)	-54.8(16)
C(10)-C(6)-C(7)-Fe(1)	63.9(16)
C(11)-C(6)-C(7)-Fe(1)	-118.3(19)
C(6)-C(7)-C(8)-C(9)	-9(3)
Fe(1)-C(7)-C(8)-C(9)	-65(2)
C(6)-C(7)-C(8)-Fe(1)	55.9(16)
C(7)-C(8)-C(9)-C(10)	6(4)
Fe(1)-C(8)-C(9)-C(10)	-60(3)
C(7)-C(8)-C(9)-Fe(1)	66.5(17)
C(8)-C(9)-C(10)-C(6)	-1(4)
Fe(1)-C(9)-C(10)-C(6)	-58.6(16)
C(8)-C(9)-C(10)-Fe(1)	58(3)
C(7)-C(6)-C(10)-C(9)	-5(3)
C(11)-C(6)-C(10)-C(9)	177(3)
Fe(1)-C(6)-C(10)-C(9)	58(2)
C(7)-C(6)-C(10)-Fe(1)	-63.7(16)
C(11)-C(6)-C(10)-Fe(1)	119(2)
C(10)-C(6)-C(11)-N(1)	84(3)
C(7)-C(6)-C(11)-N(1)	-94(3)
Fe(1)-C(6)-C(11)-N(1)	177(2)
C(6)-C(11)-N(1)-C(14)	64(4)
C(6)-C(11)-N(1)-S(1)	-105(4)
C(14)-N(1)-S(1)-O(1)	-111(3)
C(11)-N(1)-S(1)-O(1)	58(4)
C(14)-N(1)-S(1)-O(2)	123(3)
C(11)-N(1)-S(1)-O(2)	-67(4)
C(14)-N(1)-S(1)-C(12)	2(3)
C(11)-N(1)-S(1)-C(12)	172(4)

O(1)-S(1)-C(12)-C(13)	113(2)
O(2)-S(1)-C(12)-C(13)	-118(2)
N(1)-S(1)-C(12)-C(13)	1(2)
S(1)-C(12)-C(13)-C(14)	-4(2)
S(1)-C(12)-C(13)-C(15)	-176.6(15)
C(12)-C(13)-C(14)-N(1)	6(3)
C(15)-C(13)-C(14)-N(1)	179(2)
C(11)-N(1)-C(14)-C(13)	-177(3)
S(1)-N(1)-C(14)-C(13)	-5(4)
C(12)-C(13)-C(15)-C(16)	-10(4)
C(14)-C(13)-C(15)-C(16)	178(3)
C(13)-C(15)-C(16)-F(2)	7(6)
C(13)-C(15)-C(16)-F(1)	180(2)

Symmetry transformations used to generate equivalent atoms:

Table 9. Hydrogen bonds for elmcg_a [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

Computational details

All calculations have been performed at Density Functional Theory (DFT)[16] level using the Gaussian 16 software.[17] All structural optimizations and subsequent harmonic frequency calculations confirming the nature of the stationary points as minima or first order transition states have been performed using the PBE0[18] global hybrid exchange and correlation functional and the 6-311++G(d,p) Pople basis set. Bulk solvent effects (THF) were included using the conductor-like polarizable continuum model (CPCM)[19]. The above described level of theory applies to all data reported.

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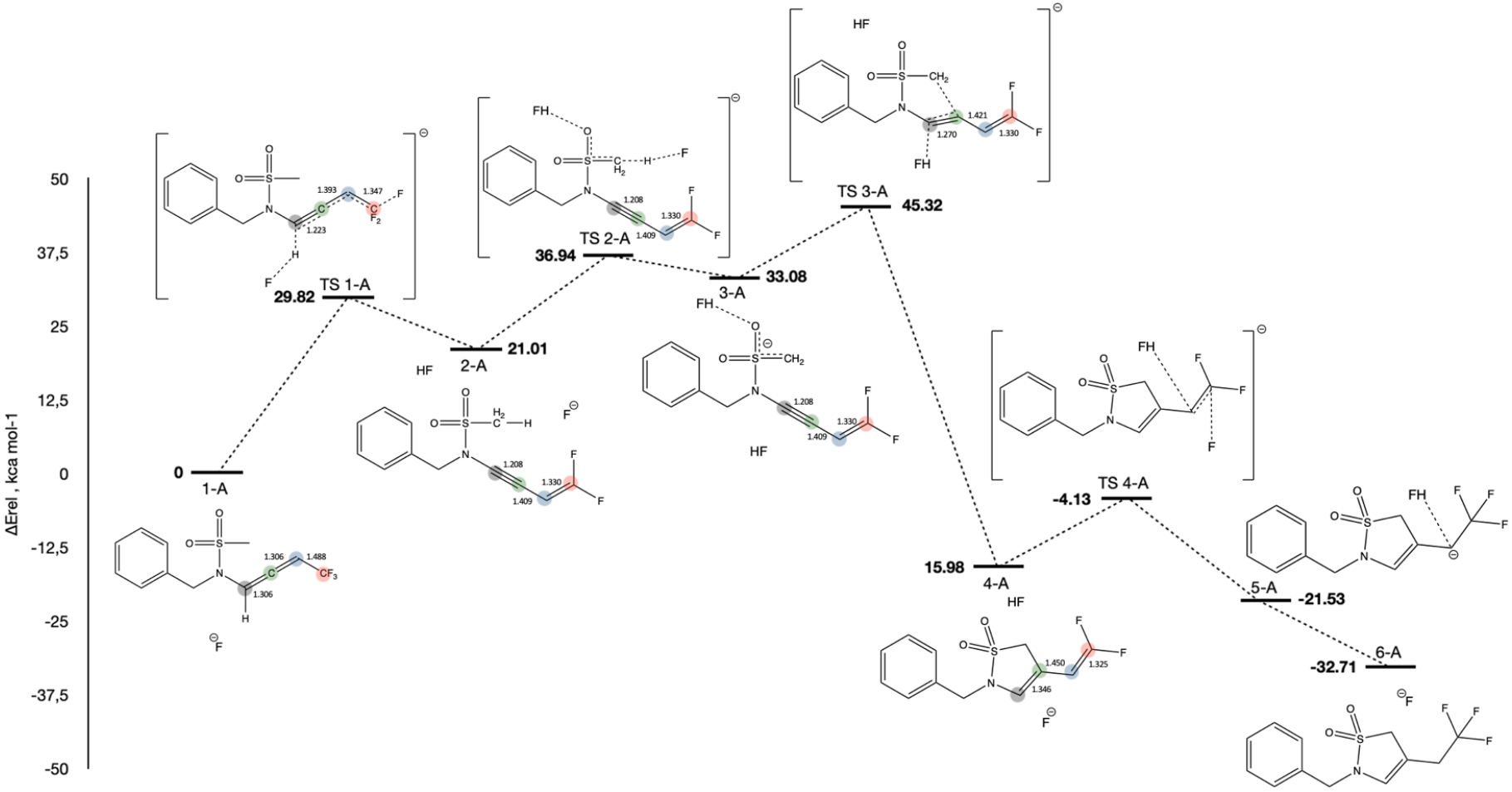
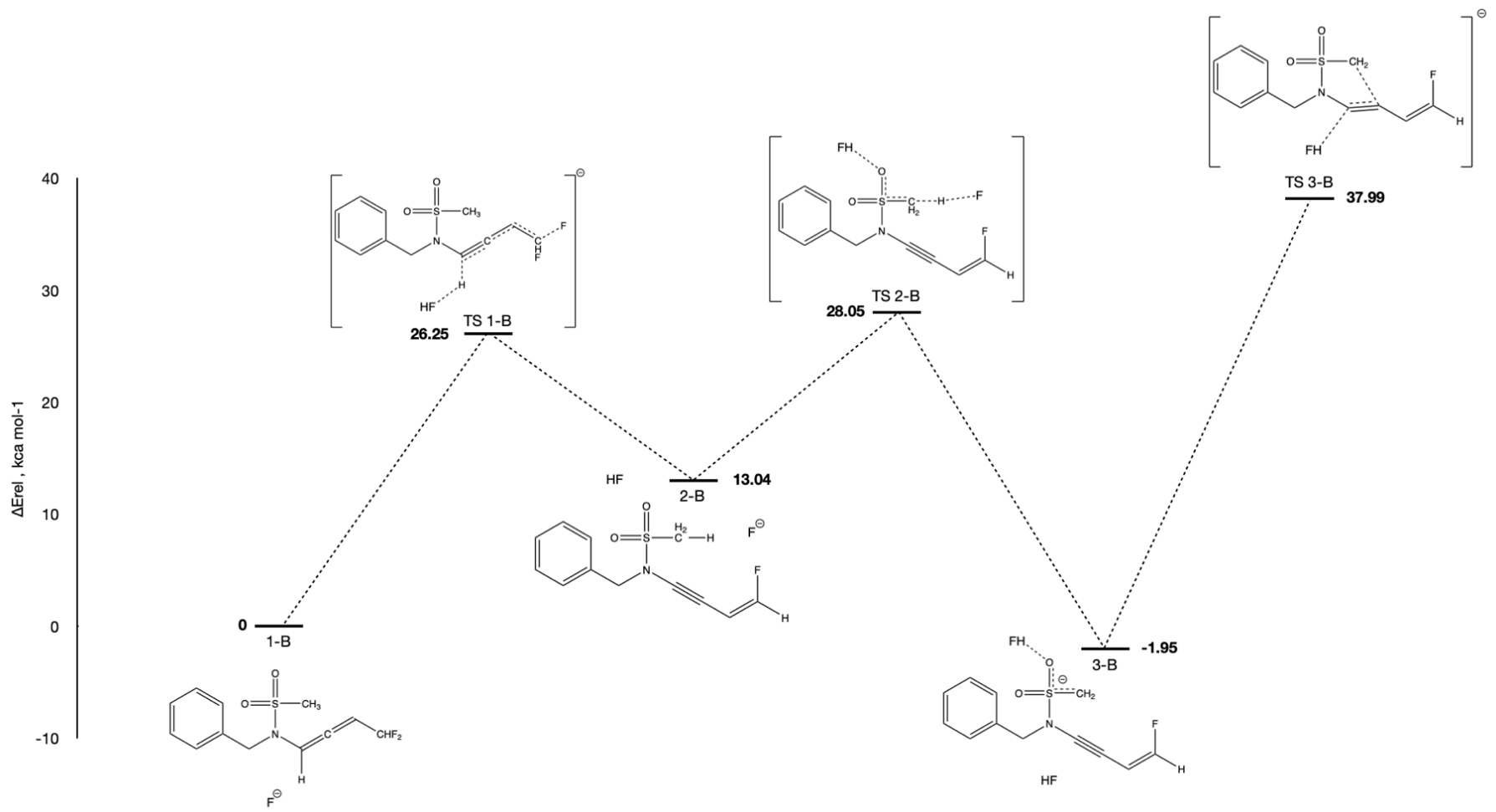
Computed reaction profiles

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-10
0
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2-B
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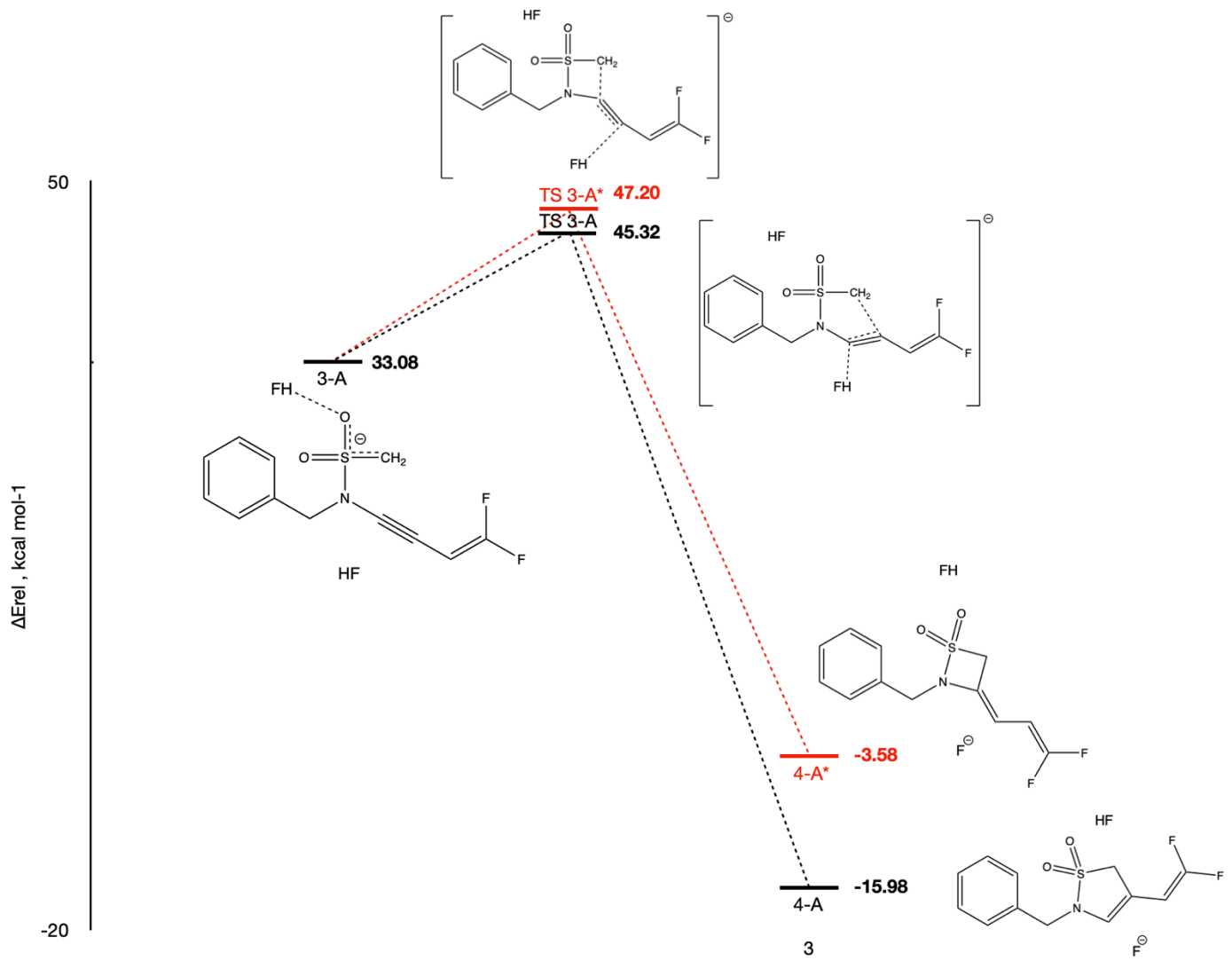
TS 2-B
-1.95
3-B
TS 3-B
37.99
HF
HF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-20
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TS 3-A 45.32
33.08
3-A
-3.58
4-A*
-15.98
4-A
3

Table 1. Optimized geometry and related energy for **1 A** compound.

C	-5.27222200	-0.36496600	-0.10591100
C	-4.12082100	-0.21391200	-0.87011800
C	-2.85755100	-0.33151600	-0.28876800
C	-2.76931900	-0.60057800	1.07567300
C	-3.92054100	-0.74982600	1.84336200
C	-5.17616500	-0.63374100	1.25651300
H	-6.24661800	-0.26624900	-0.57422000
H	-4.20348900	0.00223800	-1.93206700
H	-1.79393100	-0.68903900	1.54320500
H	-3.83412200	-0.95716600	2.90548000
H	-6.07345400	-0.74791100	1.85624200
C	-1.63412000	-0.22500500	-1.16509700
H	-1.80970600	0.50085100	-1.96271000
H	-1.42575200	-1.20090000	-1.62855900
N	-0.40532600	0.11673100	-0.44283000
C	0.55231700	-0.88444800	-0.24471000
H	0.26698500	-1.84300400	-0.77103900
C	1.68170200	-0.81490400	0.40840200
C	2.82991400	-0.88316200	1.02852100
H	2.92411100	-1.17757000	2.07241800
C	4.12283900	-0.53967200	0.37651600
F	3.99155900	-0.13376400	-0.89505900
F	4.97749700	-1.58753500	0.36482300
F	4.76977500	0.44905500	1.03594300
S	-0.06121100	1.71564700	-0.10594100
O	-1.27303900	2.46901500	-0.39616700
O	0.52909500	1.79418800	1.22257000
C	1.18714800	2.16143400	-1.29184900
H	0.74751000	2.10265600	-2.28689900
H	2.02883900	1.47712200	-1.18737100
H	1.49068500	3.18266300	-1.05948100
F	-0.41015700	-2.98053600	-1.71977000

Energy = -1466.32607096 Hartree

Table 2. Optimized geometry and related energy for **TS 1 A** compound.

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.39053800
C	1.20039400	0.00000000	2.10105400
C	2.40361200	0.01342600	1.39707100
C	2.40435900	0.01898900	0.00578500
C	1.20409000	0.00967500	-0.69731000
H	-0.94213900	0.00222400	-0.53892000
H	-0.94332500	0.00466900	1.92994800
H	3.34683800	0.02588200	1.93529700
H	3.34825800	0.03263500	-0.52993100
H	1.20672500	0.01672100	-1.78250600
C	1.16235700	-0.05375500	3.60940200
H	1.16558500	-1.09116900	3.95367100

H	0.24341700	0.40689000	3.98249500
N	2.29100300	0.60820100	4.26208800
C	2.49321700	1.93229000	4.17385200
H	0.92295200	3.05705700	3.85295900
C	3.05120100	3.01210000	4.31026900
C	3.65929600	4.22990300	4.60675800
H	4.34893600	4.71237000	3.92479600
C	3.63959500	4.66054100	5.88329000
F	2.75695400	4.30448300	6.77282800
F	4.30264100	5.71323500	6.28129000
F	5.03035700	3.17372300	6.88269700
S	3.59134200	-0.30370800	4.90200600
O	3.07659600	-1.66345600	5.02399500
O	4.78358700	-0.08916400	4.09174200
C	3.84326400	0.41609300	6.49950600
H	2.89875400	0.35579400	7.04008700
H	4.22594800	1.45197300	6.43536300
H	4.59021800	-0.22612200	6.97124900
F	0.06419000	3.42038100	3.70067000

Energy = -1466.27855186 Hartree
Frequency = 129.9694i cm^{-1}

Table 3. Optimized geometry and related energy for **2 A** compound.

C	-0.35161400	4.27256200	-0.96556800
C	-0.13553700	2.94546600	-1.32839900
C	0.73942700	2.14733200	-0.59650000
C	1.39437800	2.68971600	0.51056000
C	1.17680900	4.01139900	0.87646100
C	0.30347900	4.80699600	0.13734400
H	-1.03623900	4.88519800	-1.54320800
H	-0.65246900	2.52671200	-2.18704600
H	2.07331000	2.06841200	1.08753300
H	1.69112600	4.42457100	1.73821900
H	0.13469800	5.84013300	0.42355100
C	0.99006500	0.72081700	-1.00559400
H	2.05621700	0.56423000	-1.18264300
H	0.44602000	0.47990200	-1.92328000
N	0.59498800	-0.22391600	0.05974800
C	-0.69281300	-0.30432600	0.41664500
C	-1.86371300	-0.31550300	0.71577100
C	-3.21301500	-0.32729200	1.12142400
H	-3.49646700	-0.01004200	2.11965800
C	-4.20207100	-0.71263400	0.31978700
F	-4.07201700	-1.12118100	-0.91523700
F	-5.46727500	-0.71957500	0.67106000
F	-0.96232000	-3.61583600	-1.50926200
S	1.62203000	-1.51474400	0.45476400
O	2.95342900	-0.88361400	0.51460500
O	1.08895800	-2.11151200	1.66310700
C	1.56141000	-2.65226500	-0.88393900

H	1.97397900	-2.14725100	-1.75939100
H	0.49912100	-3.00097700	-1.05918600
H	2.21043000	-3.48172700	-0.59165400
F	5.27993500	-1.72489700	-0.05787800
H	4.39805900	-1.44503400	0.15520100

Energy = -1466.29258566 Hartree

Table 4. Optimized geometry and related energy for **TS 2 A** compound.

C	-0.38152700	3.95506600	-1.75779700
C	0.08241000	2.64215700	-1.72292200
C	0.92318000	2.21308300	-0.69841200
C	1.29000100	3.11944400	0.29910700
C	0.82667400	4.42832500	0.26909600
C	-0.01084000	4.85051200	-0.76165400
H	-1.03519400	4.27526300	-2.56300100
H	-0.21181800	1.94297000	-2.50052800
H	1.94081400	2.79074300	1.10415100
H	1.12117500	5.12342100	1.04908800
H	-0.37162700	5.87386200	-0.78581100
C	1.43853200	0.79930600	-0.66577000
H	2.52541200	0.79222500	-0.57607300
H	1.16587600	0.27984600	-1.59414300
N	0.92794700	0.07082100	0.51178100
C	-0.39471500	-0.06141900	0.57520700
C	-1.59221100	-0.25879700	0.63126700
C	-2.99346800	-0.32925900	0.78625700
H	-3.57590200	0.58551400	0.82833500
C	-3.67269800	-1.46419500	0.90059400
F	-3.15466100	-2.67235500	0.88243900
F	-4.97842100	-1.53211500	1.06700700
S	1.75882300	-1.52394500	0.88291300
O	3.15518700	-1.04507600	0.65435300
O	1.31750500	-1.71226000	2.26798700
C	1.35131000	-2.75059400	-0.09792800
H	0.48689800	-3.33410000	0.18448600
H	1.76366800	-2.75000600	-1.09715900
H	4.33681600	-1.94566900	0.38041100
F	5.13656700	-2.45429900	0.19308800
F	-1.26175000	-2.04334500	-1.98983600
H	-0.87164200	-1.79400400	-1.17987600

Energy = -1466.26719702 Hartree
Frequency = 313.0870i cm^{-1}

Table 5. Optimized geometry and related energy for **3 A** compound.

C	0.20901200	-0.17809600	-0.00222300
C	-0.13196200	-0.04150900	1.34155800
C	0.85773300	0.05650500	2.31677800
C	2.19963700	0.02172800	1.93084000
C	2.54064600	-0.11046300	0.59090800
C	1.54596700	-0.21217500	-0.38012200
H	-0.57203300	-0.25164400	-0.75237900
H	-1.17795800	-0.00839900	1.63356800
H	2.96726700	0.10259700	2.69490100
H	3.58648000	-0.13706800	0.30108000
H	1.81446300	-0.31547400	-1.42668100
C	0.48375600	0.18359300	3.77107900
H	0.83264300	-0.69088200	4.32966400
H	-0.60379900	0.22579100	3.88135600
N	1.08199200	1.35545100	4.41742000
C	0.69696600	2.54812700	4.13147700
C	0.19640200	3.67654000	3.95556400
C	0.35686900	4.88101000	3.20773800
H	1.19754900	5.01453000	2.53299700
C	-0.48664000	5.90548400	3.27970800
F	-1.56676700	5.97092100	4.02232200
F	-0.34851400	7.02108800	2.59211500
S	2.20450700	1.02788800	5.87812200
O	3.20351100	0.19752600	5.14144700
O	2.55860200	2.41088700	6.19502200
C	1.51296200	0.19479700	7.08115900
H	0.81257300	0.74804000	7.69340000
H	1.39809200	-0.86869600	6.91964100
H	4.16555000	-0.78108800	5.78980800
F	4.79666700	-1.42785900	6.12705100
F	-1.82224700	3.32296700	5.74299700
H	-1.09621900	3.45376800	5.10834500

Energy = -1466.27334739 Hartree

Table 6. Optimized geometry and related energy for **TS 3 A** compound.

C	0.42125300	-0.27787300	-0.27299200
C	0.02902500	-0.23131400	1.06277000
C	0.96506700	-0.00328500	2.06878500
C	2.30431800	0.18381200	1.72113700
C	2.69621700	0.14113000	0.38885800
C	1.75596200	-0.09120400	-0.61305200
H	-0.31947000	-0.45351500	-1.04682600
H	-1.01651600	-0.36983100	1.32401800
H	3.03328000	0.36669600	2.50613700
H	3.74019200	0.28779400	0.12952600
H	2.06373800	-0.12299900	-1.65341100

C	0.53717800	0.01473000	3.51529500
H	0.92621300	-0.86625100	4.03377800
H	-0.55272700	-0.02723700	3.58990600
N	1.02893000	1.18157500	4.23750000
C	0.60174500	2.39184400	4.16124500
C	0.76101700	3.40659300	4.97900000
C	1.25167600	4.74007400	4.75315700
H	1.76918900	5.01476900	3.83835000
C	1.14772900	5.70946700	5.65702100
F	0.59019700	5.61087700	6.84008700
F	1.63358200	6.92423800	5.49474400
S	2.25608600	0.90548500	5.65280900
O	1.58763700	-0.22937500	6.36466100
O	3.50540000	0.59576300	4.93802600
C	2.22084000	2.33853900	6.44892900
H	3.07230700	2.98561700	6.29899200
H	1.61781700	2.38089200	7.34373000
H	2.08484400	-0.89124500	7.64072400
F	2.36069200	-1.33642800	8.44960800
F	-1.20849000	3.00591400	6.69053200
H	-0.46245700	3.15768800	6.04221800

Energy = -1466.25385251 Hartree
Frequency = 366.0099i cm^{-1}

Table 7. Optimized geometry and related energy for **4 A** compound.

C	4.91670700	-0.24813800	0.45473500
C	3.64609400	0.04536700	0.94350300
C	2.52103000	-0.60080100	0.43536500
C	2.68797900	-1.54768700	-0.57757000
C	3.95289200	-1.83824800	-1.07162100
C	5.07310900	-1.18946000	-0.55573200
H	5.78264900	0.26539400	0.86054300
H	3.52698400	0.78744000	1.72814400
H	1.81657700	-2.05441600	-0.98129500
H	4.06771400	-2.57621300	-1.85941300
H	6.06147900	-1.41725600	-0.94201800
C	1.15910600	-0.32100100	1.00903400
H	1.21030200	0.49889000	1.73467400
H	0.74812700	-1.20817200	1.52472300
N	0.15405000	-0.02286800	-0.02103000
C	-1.17214500	-0.44113600	0.16880300
C	-2.12062400	0.26146200	-0.47815500
C	-3.55139800	0.02338700	-0.51381400
H	-4.20413400	0.84708500	-0.78155600
C	-4.16894900	-1.12196600	-0.26404200
F	-3.59056500	-2.26139100	0.05178200

F	-5.48195800	-1.28010800	-0.29579200
S	0.16081100	1.49339200	-0.75153800
O	0.33919200	2.54169400	0.27274500
O	1.09861100	1.55327000	-1.85931700
C	-1.55774700	1.39803700	-1.28413400
H	-2.01887800	2.37136200	-1.09876200
H	-1.52809900	1.20419000	-2.36022600
F	-1.15337700	3.46425600	2.12787800
H	-0.61622900	3.08674000	1.44447500
F	-0.55779900	-2.53498100	2.02247100
H	-1.26327800	-1.30784100	0.83982600

Energy = -1466.35154696 Hartree

Table 8. Optimized geometry and related energy for **TS 4 A** compound.

C	-5.19894300	-0.09901100	-0.19859000
C	-3.95906800	-0.11767500	-0.83261200
C	-2.84464200	-0.65481500	-0.19328700
C	-2.98523000	-1.17107500	1.09619600
C	-4.21928700	-1.15043300	1.73220500
C	-5.33105200	-0.61448000	1.08511300
H	-6.05893300	0.32406600	-0.70778900
H	-3.85606500	0.29235400	-1.83322400
H	-2.11817200	-1.58394600	1.60309100
H	-4.31665200	-1.55476100	2.73473300
H	-6.29533400	-0.59829500	1.58287600
C	-1.51558100	-0.71055600	-0.89985500
H	-1.59348800	-0.25691100	-1.89458300
H	-1.20933700	-1.75117100	-1.03811000
N	-0.43437000	-0.08715100	-0.12804700
C	0.88941000	-0.47609600	-0.39411900
C	1.85064900	0.44497300	-0.24296900
C	3.27420000	0.17101500	-0.41527600
H	3.84848100	0.74578100	-1.13677200
C	3.80146000	-1.01574000	-0.05954700
F	3.34237500	-1.77472900	0.90416900
F	5.03248600	-1.35476400	-0.35947500
S	-0.46620700	1.62201400	-0.03422800
O	-0.93427300	2.16967900	-1.30549900
O	-1.16485900	2.04149400	1.17240500
C	1.32516900	1.79726800	0.13298800
H	1.64017600	2.61103600	-0.52548600
H	1.51180300	2.07243500	1.17465700
F	4.41535800	1.54389400	1.76570400
H	4.08006000	1.00496400	1.05326600
F	2.91448100	-2.49425700	-1.47048800
H	1.09446900	-1.49820200	-0.70420700

Energy = -1466.33265417 Hartree
Frequency = 125.2252i cm^{-1}

Table 9. Optimized geometry and related energy for **5 A** compound.

C	-5.22652800	-0.49214000	-0.59602200
C	-3.90442700	-0.68507300	-0.98922100
C	-2.90727700	-0.90334400	-0.04171200
C	-3.25169500	-0.92283900	1.31136600
C	-4.56823300	-0.72704500	1.70701900
C	-5.56071600	-0.51159000	0.75275200
H	-5.99291500	-0.32143100	-1.34535600
H	-3.64346800	-0.66076200	-2.04326200
H	-2.47794600	-1.08585300	2.05565900
H	-4.82334900	-0.74415700	2.76190600
H	-6.58966500	-0.35838200	1.06222400
C	-1.48434600	-1.14501600	-0.47154900
H	-1.41168200	-1.15232800	-1.56636800
H	-1.15385500	-2.12454400	-0.11418400
N	-0.54019300	-0.18273400	0.11312200
C	0.84753000	-0.54521300	0.03376300
C	1.74815600	0.43995200	-0.13633300
C	3.20340100	0.43065900	-0.08739800
H	3.65670600	1.15383100	-0.76838600
C	3.87505000	-0.85440100	-0.22339800
F	3.55074800	-1.75497800	0.74829200
F	5.22692000	-0.73250600	-0.18860300
S	-0.65957900	1.39487800	-0.51876500
O	-0.97546500	1.34847300	-1.94820500
O	-1.53156500	2.20751500	0.32191900
C	1.07954600	1.77990500	-0.27119900
H	1.41218300	2.36716200	-1.13042600
H	1.14714300	2.38350200	0.63783000
F	3.85804500	1.42835400	2.32851300
H	3.62596000	1.03612700	1.41472900
F	3.63940300	-1.55974800	-1.39540200
H	1.06293700	-1.59320600	0.19070800

Energy = -1466.36037509 Hartree

Table 10. Optimized geometry and related energy for **6 A** compound.

C	-4.27109100	-0.91195000	1.68689700
C	-3.01978300	-0.91214900	1.08168800
C	-2.90387100	-0.78404400	-0.30234300
C	-4.06058700	-0.65113600	-1.06845500

C	-5.31454900	-0.65575900	-0.46530900
C	-5.42299800	-0.78631600	0.91508400
H	-4.34731700	-1.00830000	2.76536300
H	-2.12130800	-0.99903100	1.68415000
H	-3.97956100	-0.53703400	-2.14591700
H	-6.20640300	-0.54797300	-1.07441900
H	-6.39949900	-0.78334900	1.38866700
C	-1.55830100	-0.84397400	-0.98065300
H	-1.63308700	-0.44432700	-1.99898600
H	-1.23708500	-1.88704800	-1.06732100
N	-0.50186700	-0.16774300	-0.23206400
C	0.82534300	-0.63040800	-0.32667100
C	1.78939100	0.28576900	-0.44906900
C	3.27310900	0.12692500	-0.38263200
H	3.73119200	0.35023400	-1.35365200
C	3.77341900	-1.21952800	0.03638300
F	3.37068300	-1.57307200	1.27083900
F	5.12031800	-1.25102500	0.04710500
S	-0.48010500	1.54254100	-0.26693000
O	-1.25438600	1.99933200	-1.42079200
O	-0.87188700	2.04570600	1.04289200
C	1.28746200	1.69540300	-0.52268200
H	1.44286900	2.16850800	-1.49695400
H	1.75774800	2.29984800	0.28183200
F	3.26409700	2.60204800	1.30422000
H	3.64159000	0.88358500	0.33383800
F	3.37900400	-2.21567300	-0.78980400
H	0.96362600	-1.69937400	-0.22275300

Energy = -1466.37819862 Hartree