Electronic Supplementary Material (ESI) for Green Chemistry.
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Supporting information

Important Safety Note:
Safety hazards of all diazoalkanes, described within this manuscript, have not been investigated. However, it should be noted that handling of diazomethane and its derivatives should only be done in a well-ventilated fume cupboard using an additional blast shield. No incidents occurred handling all diazoalkanes during the preparation of this manuscript, yet the reader should be aware of carcinogenicity and potential explosiveness of the herein described diazoalkane derivatives. General safety precautions when working with diazomethane and its derivatives should be followed. Any reactions described in this manuscript should not be performed without strict risk assessment and proper safety precautions.

General: Unless otherwise noted, all commercially available compounds were used as provided without further purification. Chemicals used in this manuscript were purchased from Sigma Aldrich, Fluorochem, Alfa Aesar.

Solvents used in reactions were p.A. grade. Solvents for chromatography were technical grade and distilled prior to use. Analytical thin-layer chromatography (TLC) was performed on Macherey-Nagel silica gel aluminium plates with F-254 indicator, visualised by irradiation with UV light. Column chromatography was performed using silica gel Merck 60 (particle size 0.063 – 0.2 mm). Solvent mixtures are understood as volume/volume.

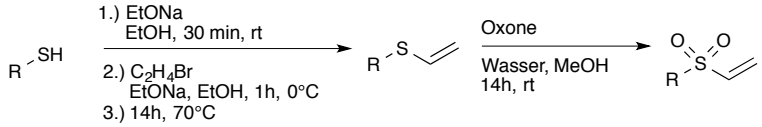
^{1}H-NMR, ^{19}F-NMR and ^{13}C-NMR were recorded on a Varian AV400 or AV600 spectrometer in $CDCl_3$, CD_3OD or DMSO-d_6. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated br (broadened singlet), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants (J) are in Hertz (Hz).

EI MS data were recorded on a Finnigan SSQ 7000 or Finnigan MAT 95 using EI ionization at 70 eV or on a Shimadzu GCMS sytem (QP 2010 SE and GC2010plus, CP-Sil-8-MS column, 30m, 0.25µm ID, method: 60°C 5min, 20K/min to 300°C and keep for 20min).
HRMS data were recorded on a ThermoFisher Scientific LTQ Orbitrap XL using ESI ionization.

IR spectra were recorded on a Perkin Elmer-100 spectrometer and are reported in terms of frequency of absorption (cm^{-1}).

The following equipment was utilized for the continuous-flow generation of substituted diazomethanes:
Syringe pump: Harvard Apparatus 22 syringe pump, Chemyx Inc. Model Fusion 710.
Micromixer: Little Things Factory, MR Lab, Type: MST
PTFE tubing: CS chromatrographie PTFE tubing, Art Nr. 590515, 1/16” AD, 0.8mm ID, max pressure 37 bar. Reactor volume: 0.8 mL / length 1.6 m

General procedure for the preparation of vinyl sulfones



Thiophenol (1 eq, 30 mmol) in ethanol was added to a NaOEt solution (1 eq, 20% w/w), stirred for 30 min at room temperature and cooled down to 0 °C. The solution was added dropwise to 1,2-dibromoethane in ethanol at 0 °C and stirred for 1h at room temperature. NaOEt solution (2.5 eq) was added and the mixture was stirred at 70 °C for 16 h followed by an aqueous workup.
OXONE (3.3 eq) was added to a solution of the crude product in water / methanol and was stirred for 16 h at room temperature. An aqueous workup followed and the product was purified by column chromatography (hexane / ethyl acetate).

General procedure for biphasic batch reactions

A suspension of dipolarophile (0.5 mmol, 1 eq), amine hydrochloride (2 eq) and $NaNO_2$ (3 eq) in DCM (8 mL) / water (2 mL) was vigourosly stirred for 14 h at room temperature. Water (10 mL) and DCM (10 mL) were added. The organic layer was seperated and the aqueous layer was extracted two times with DCM. The combined organic layers were dried over Na_2SO_4, evaporated under vacuum and purified by column chromatography (toluene / ethyl acetate).

Procedure for biphasic batch reaction in gram-scale

A suspension of dipolarophile (5.9 mmol, 1 eq), amine hydrochloride (2 eq) and $NaNO_2$ (3 eq) in DCM (100 mL) / water (20 mL) was vigourosly stirred at 0°C and was allowed to warm up to room temperature over night. Water (50 mL) was added. The organic layer was seperated and the aqueous layer was extracted two times with DCM. The combined organic layers were washed with brine and dried over Na_2SO_4, evaporated under reduced pressure and purified by column chromatography (hexanes / ethyl acetate).

General procedure for the water-free batch reaction

A solution of amine (4 eq), tBuONO (4.8 eq) and acetic acid (1.6 eq) in chloroform (7 mL) was stirred at time and temperature indicated to form the corresponding diazo compound. The dipolarophile (0.5 mmol, 1 eq) dissolved in chloroform (3 mL) was added to the mixture and stirred for either directly at the beginning or after the time indicated at room temperature. The solvent was evaporated under reduced pressure and purified by column chromatography (toluene / ethyl acetate).

General procedure for the continuous-flow reactions

Two stock solutions are prepared:

- 2,2-Difluoroethylamine (c = 0.2 M, 4 eq) is dissolved in $CHCl_3$
- tBuONO (c = 0.24 M, 4.8 eq) and AcOH (c = 0.08 M, 0.2 eq) are dissolved in $CHCl_3$

The stock solutions are transferred into two syringes and placed in a syringe pump and the syringes are connected via PTFE tubing to a micromixer with an internal volume of 0.2 mL that is connected to a self-built microreactor made of PTFE tubing with an internal volume of 0.8 mL. The microreactor is heated up to 55 °C. At a constant flow rate of 50 µL/min per syringe the reactants are transferred into the microreactor. The outlet is added to a solution of dipolarophile (0.5 mmol) dissolved in 5 mL $CHCl_3$.
After complete addition the resulting yellow solution is stirred for 24 h at room temperature. The crude reaction mixture was directly purified by column chromatography (hexanes / ethyl acetate) to yield the desired pyrazolines.

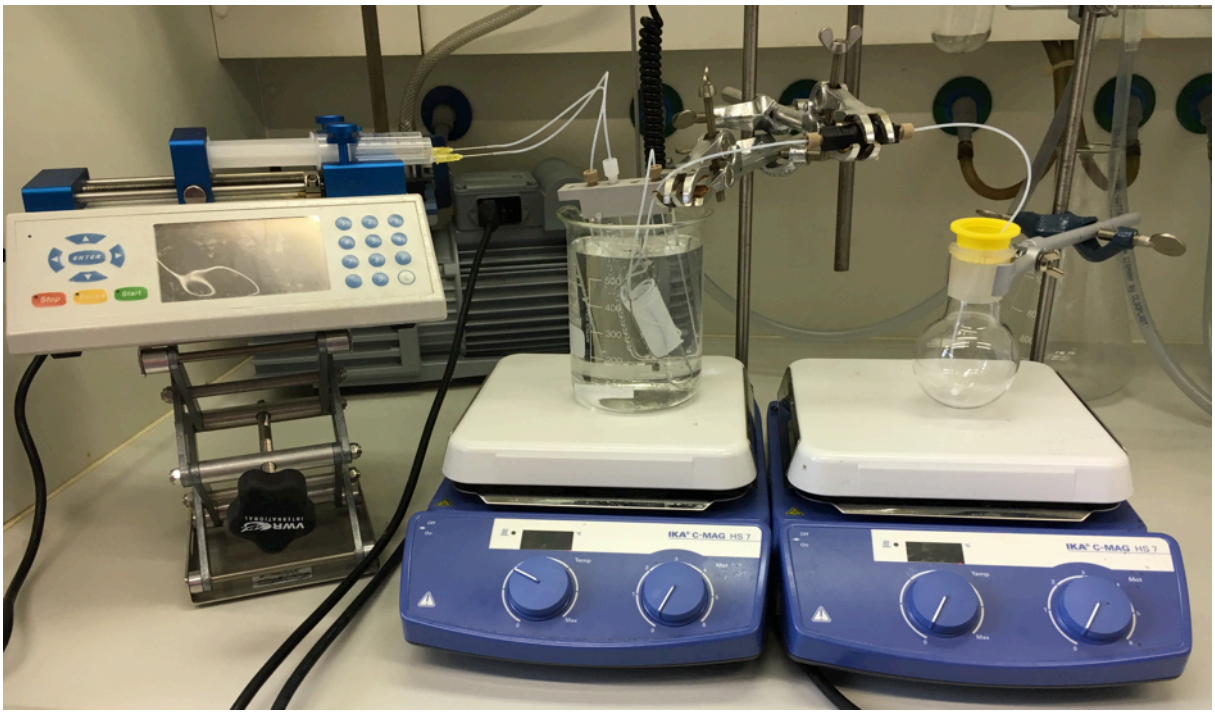


Figure 1: setup of the continuous-flow system (on the left: syringe pump with 2x 10 mL syringes; in the middle: micromixer (Little things factory, MR-Lab type MST) connected to microreactor and back pressure vent (in black); on the right: reaction flask for the cycloadditon reaction

Procedure for the continuous-flow reaction in gram-scale

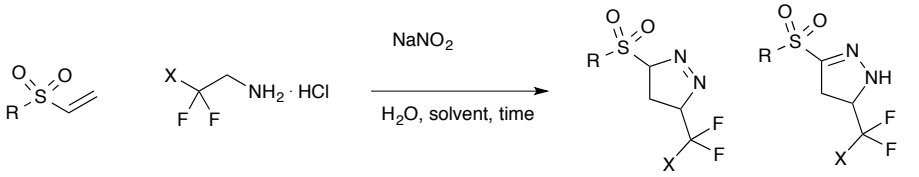
Two stock solutions are prepared:

- 2,2-Difluoroethylamine (c = 0.2 M, 4 eq) is dissolved in $CHCl_3$
- tBuONO (c = 0.24 M, 4.8 eq) and AcOH (c = 0.08 M, 0.2 eq) are dissolved in $CHCl_3$

Because of the high volume the stock solutions are split up and transferred into four syringes and placed in two syringe pumps. The syringes are connected via PTFE tubing to the micromixer with an internal volume of 0.2 mL and a self-built microreactor made of PTFE tubing with an internal volume of 0.8 mL. With an water bath the microreactor is heated up to 55 °C. At a constant flow rate of 50 µL/min per syringe the reactants are transferred into the microreactor. The outlet is added to a solution of dipolarophile (5 mmol) dissolved in 30 mL $CHCl_3$.

After complete addition the resulting yellow solution is stirred for 24 h at room temperature. The solvent was evaporated under reduced pressure and the crude reaction mixture was directly purified by column chromatography (hexanes / ethyl acetate) to yield the desired pyrazolines.

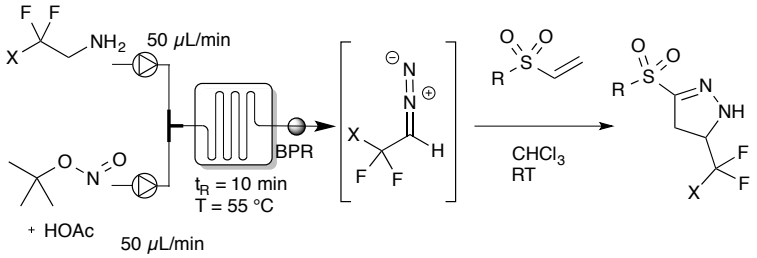
Table 1: Optimization of reaction conditions in Batch



Entry	X	R	solvent	Eq. amine /$NaNO_2$	% yield
1	F	Me	DCM	2/2	>99%
2	F	Me	CHCl3	2/2	87%
3	F	Me	1,2-DCE	2/2	70%
4	F	Me	THF	2/2	79%
5	F	Me	Toluene	2/2	83%
6	F	Me	DMF	2/2	89%
7	F	Ph	DCM	2/2	84%
8	F	Ph	DCM	2/3	87%
9	F	Ph	DCM	3/3	67%
10	H	Me	CHCl3	2/2	no reaction

reaction conditions: vinyl sulfone (0.5 mmol, 1 eq), fluorinated amine hydrochloride (eq. as indicated) and $NaNO_2$ (eq. as indicated) in DCM (8 mL) / water (2 mL) was vigourosly stirred for 14 h at room temperature; isolated yields after column chromatography.

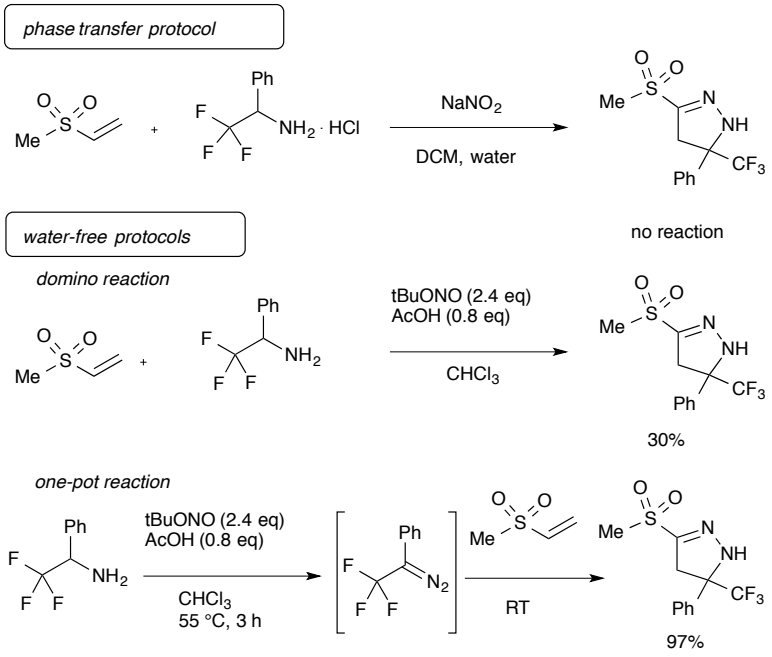
Table 2. Optimization of the continuous-flow protocol



entry[a]	R / X	Solvent	Eq. amine	Yield[b]
1	Me / H	DCM	2	22%
2	Me / H	$CHCl_3$	2	34%
3	Me / H	$CHCl_3$	4	92%
4	Me / F	$CHCl_3$	4	61%
5	Ph / H	$CHCl_3$	4	93%

[a] reaction conditions: a solution of amine (0.2 M in $CHCl_3$, eq. as indicated) and a solution of tBuONO and AcOH (2.4 M / 0.08 M in $CHCl_3$) were placed in two separate syringes and added by syringe pump at a flow rate of 50 µL/min for each syringe into a microreactor (residence time 10 min, temperature 55 °C). The outlet was connected via a back pressure regulator (20 psi) to a reaction flask containing the vinyl sulfone (0.5 mmol) in $CHCl_3$ and stirred for 14 h at room temperature. [b] isolated yields after column chromatography

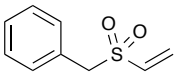
Optimization reactions for Donor-Acceptor fluorinated diazo compounds



Physical data

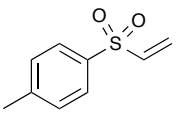
Starting Material

((vinylsulfonyl)methyl)benzene



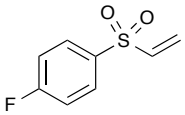
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.42 – 7.31 (m, 5H), 6.50 (dd, *J* = 16.8, 9.8 Hz, 1H), 6.30 (d, *J* = 16.6 Hz, 1H), 6.09 (d, *J* = 9.9 Hz, 1H), 4.24 (s, 2H) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 135.1, 131.2, 131.1, 130.8, 129.0, 128.9, 128.8, 127.6, 61.0 ppm; IR (KBr): υ = 3055, 1492, 1455, 1384, 1305, 1260, 1202, 1156, 1114, 1018, 971, 925, 883, 789, 734, 696 cm^{-1}; MS-EI: m/z = 181.9.

1-(vinylsulfonyl)-4-methyl-benzene



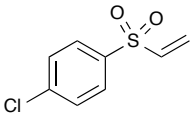
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.80 – 7.74 (m, 2H), 7.37 – 7.32 (m, 2H), 6.63 (dd, *J* = 16.5, 9.9 Hz, 1H), 6.40 (d, *J* = 16.5 Hz, 1H), 5.99 (d, *J* = 9.9 Hz, 1H), 2.42 (d, *J* = 0.9 Hz, 3H) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 144.7, 138.7, 130.0, 127.9, 127.2, 125.2, 21.6 ppm; IR (KBr): υ = 3345, 3015, 2934, 2296, 2085, 1741, 1560, 1428, 1370, 1284, 1107, 956, 865, 758 cm^{-1}; MS-EI: m/z = 182.0.

1-(vinylsulfonyl)-4-fluoro-benzene



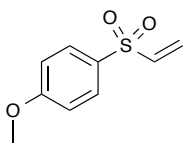
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.96 – 7.81 (m, 2H), 7.30 – 7.10 (m, 2H), 6.62 (dd, *J* = 16.5, 9.8 Hz, 1H), 6.43 (d, *J* = 16.6 Hz, 1H), 6.03 (d, *J* = 9.7 Hz, 1H) ppm; ^{19}F-NMR (564 MHz, $CDCl_3$): δ = –103,46 (m) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 165.8 (d, *J* = 256.6 Hz), 138.3, 130.8, 130.8, 128.0, 117.8, 116.6 ppm; IR (KBr): υ = 3105, 3063, 2106, 1589, 1492, 1383, 1318, 1291, 1234, 1145, 1087, 975, 837, 744, 705, 671 cm^{-1}; MS-EI: m/z = 185.8.

1-(vinylsulfonyl)-4-chloro-benzene



^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.88 – 7.78 (m, 2H), 7.57 – 7.47 (m, 2H), 6.64 (dd, *J* = 16.5, 9.8 Hz, 1H), 6.47 (d, *J* = 16.6, 1H), 6.07 (d, *J* = 9.8, 1H) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 140.4, 138.1, 138.0, 129.7, 129.4, 128.4 ppm; IR (KBr): υ = 3073, 2326, 2095, 1743, 1578, 1474, 1382, 1309, 1141, 977, 830, 760, 659 cm^{-1}; MS-EI: m/z = 201.8.

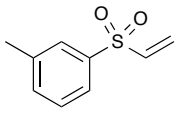
1-(vinylsulfonyl)-4-methoxy-benzene



^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.87 – 7.73 (m, 2H), 7.04 – 6.94 (m, 2H), 6.62 (dd, *J* = 16.5, 9.8 Hz, 1H), 6.37 (d, *J* = 16.5 Hz, 1H), 5.95 (d, *J* = 9.8 Hz, 1H), 3.86 (s, 3H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 163.7, 138.9, 130.9, 130.1, 126.6, 114.5, 55.7 ppm; IR (KBr): υ = 3060,

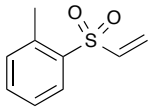
2958, 2851, 1581, 1493, 1466, 1415, 1380, 1292, 1254, 1137 1087, 1015, 966, 832, 803, 740, 672 cm^{-1}; MS-EI: m/z = 198.0.

1-(vinylsulfonyl)-3-methyl-benzene



^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.05 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.57 – 7.27 (m, 3H), 6.65 (dd, *J* = 16.5, 9.9 Hz, 1H), 6.45 (dd, *J* = 16.5, 1.6 Hz, 1H), 6.10 (d, *J* = 9.8 Hz, 1H), 2.59 (s, 3H) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 138.3, 137.9, 137.1, 133.9, 132.6, 129.7, 128.0, 126.7, 20.2 ppm; IR (KBr): υ = 3053, 2334, 2097, 1740, 1603, 1456, 1386, 1302, 1130, 972, 865, 732 cm^{-1}; MS-EI: m/z = 181.9.

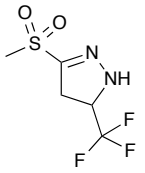
1-(vinylsulfonyl)-2-methyl-benzene



^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.74 – 7.64 (m, 2H), 7.48 – 7.38 (m, 2H), 6.65 (dd, *J* = 16.5, 9.8 Hz, 1H), 6.45 (d, *J* = 16.6 Hz, 1H), 6.03 (d, *J* = 9.9 Hz, 1H), 2.43 (s, 3H) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 139.6, 139.3, 138.5, 134.4, 129.2, 128.2, 127.6, 125.0, 21.3 ppm; IR (KBr): υ = 3057, 2335, 2097, 1740, 1595, 1457, 1383, 1298, 1134, 1055, 972, 737 cm^{-1}; MS-EI: m/z = 181.9.

Trifluoromethyl-substituted pyrazolines

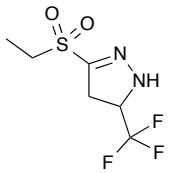
3-(methylsulfonyl)-5-(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole



^{1}H-NMR (600 MHz, $CDCl_3$): δ = 4.57 – 4.44 (m, 1H), 3.40 (dd, *J* = 17.8, 12.3 Hz, 1H), 3.28 (dd, *J* = 17.8, 8.1 Hz, 1 H) , 3.18 (s, 3 H) ppm; ^{19}F-NMR (564 MHz, $CDCl_3$): δ = −77,16 (d, *J* = 6.8 Hz) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 151.1, 124.1 (q, *J* = 279.5 Hz), 61.8 (q, *J* = 31.8 Hz), 41.0,

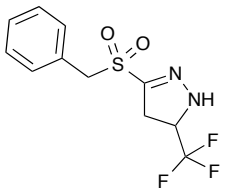
31.0 ppm; IR (KBr): υ = 3345, 3015, 2943, 2296, 2085, 1741, 1560, 1428, 1370, 1284, 1107, 956, 865, 758 cm^{-1}; HRMS (ESI): m/z calcd for $C_5H_7O_2N_2F_3NaS$: 239.00708, found 239.00725.

3-(ethylsulfonyl)-5-(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole



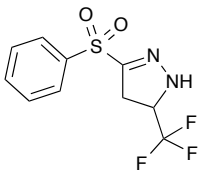
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 4.62 – 4.44 (m, 1H), 3.41 (dd, *J* = 17.8, 12.3 Hz, 1H), 3.34 – 3.23 (m, 3H), 1.41 (t, *J* = 7.5 Hz, 3 H) ppm; ^{19}F-NMR (564 MHz, $CDCl_3$): δ = –77.35 (d, *J* = 6.8 Hz) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 124.0 (q, *J* = 2.79.5), 61.6 (q, *J* = 31.7 Hz), 48.1, 31.6, 29.7, 6.8 ppm; IR (KBr): υ = 3600, 3335, 2937, 2324, 2111, 1924, 1738, 1631, 1569, 1415, 1379, 1280, 1121, 951, 871, 775, 719 cm^{-1}; HRMS (ESI): m/z calcd for $C_6H_9O_2N_2F_3NaS$: 258.0235, found 258.0229.

3-(benzylsulfonyl)-5-(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole



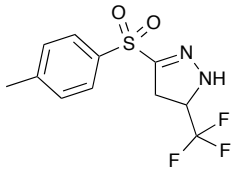
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.42 – 7.35 (m, 5H), 6.52 (b, 1H), 4.50 (d, *J* = 4.5 Hz, 2H), 4.39 – 4.33 (m, 1H), 3.01 (dd, *J* = 17.9, 12.5 Hz, 1H), 2.72 (dd, *J* = 17.9, 8.6 Hz, 1H) ppm; ^{19}F-NMR (564 MHz, $CDCl_3$): δ = −6.82 (d, *J* = 6.5 Hz) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 131.1, 129.3, 129.0, 126.5, 123.9 (q, *J* = 279.4 Hz), 61.8 (q, *J* = 32.0 Hz) 60.9, 33.0 ppm; IR (KBr): υ = 3328, 3079, 2978, 2927, 2853, 2300, 2108, 1988, 1902, 1826, 1738, 1569, 1497, 1425, 1385, 1319, 1286, 1192, 1156, 1128, 1102, 981, 953, 925, 889, 867, 829, 784, 723, 689, 680 cm^{-1}; HRMS (ESI): m/z calcd for $C_{11}H_{11}O_2N_2F_3NaS$: 315.0389, found 315.0386.

3-(phenylsulfonyl)-5-(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole



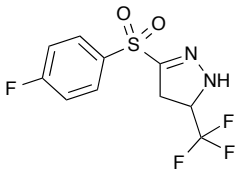
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.00 – 7.92 (m, 2H), 7.74 – 7.54 (m, 3H), 6.57 (b, 1H), 4.54 – 4.40 (m, 1H), 3.32 (dd, *J* = 17.6, 12.4 Hz, 1H), 3.14 (dd, *J* = 17.7, 8.1, 1H) ppm; ^{19}F-NMR (564 MHz, $CDCl_3$): δ = –77.25 (d, *J* = 6.7 Hz) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 150.7, 137.9, 134.4, 129.5, 128.4, 123.9 (q, J = 279.8 Hz), 62.3, 31.8 ppm; IR (KBr): υ = 3322, 3068, 2865, 2322, 2078, 1916, 1702, 1623, 1573, 1443, 1397, 1288, 1127, 1072, 997, 946, 866, 754, 719, 686 cm^{-1}; HRMS (ESI): m/z calcd for $C_{10}H_9O_2N_2F_3NaS$: 301.02191, found 301.02290.

3-tosyl-5-(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole



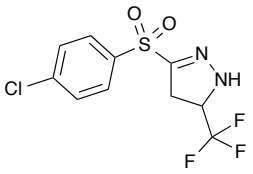
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.87 – 7.77 (m, 2H), 7.36 (d, *J* = 8 Hz, 2H), 4.51 – 4.37 (m, 1H), 3.30 (dd, *J* = 17.6, 12.2 Hz, 1H), 3.12 (dd, *J* = 17.6, 8.2 Hz, 1H) ppm; ^{19}F-NMR (564 MHz, $CDCl_3$): δ = –77.21 (d, J = 6.7 Hz) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 134.8, 130.1, 128.5, 124.0 (d, *J* = 289.4 Hz), 62.1 (q, *J* = 31.8 Hz), 31.8, 21.7 ppm; IR (KBr): υ = 3333, 2961, 2306, 2083, 1926, 1737, 1580, 1400, 1286, 1131, 800, 685 cm^{-1}; HRMS (ESI): m/z calcd for $C_{11}H_{11}O_2N_2F_3NaS$: 315.03857, found 315.03855.

3-((4-fluorophenyl)sulfonyl)-5-(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole



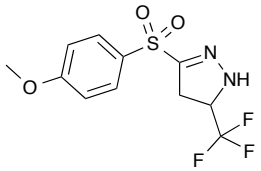
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.03 – 7.95 (m, 2H), 7.32 – 7.25 (m, 2H), 4.47 (m, 1H), 3.35 (dd, *J* = 17.6, 12.3, 1H), 3.17 (dd, *J* = 17.6, 7.9 Hz, 1H) ppm; ^{19}F-NMR (564 MHz, $CDCl_3$): δ = –77.34 (d, *J* = 6.7 Hz, 3F), –101.9 (s, 1F) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 167.1, 165.4, 150.8, 133.9, 131.4, 123.9 (q, *J* = 279.8 Hz), 116.9, 62.2 (q, *J* = 31.9 Hz), 31.7 ppm; IR (KBr): υ = 3349, 2981, 2307, 2092, 1738, 1569, 1383, 1286, 1139, 964, 843, 688 cm^{-1}; HRMS (ESI): m/z calcd for $C_{10}H_8O_2N_2F_4NaS$: 319.01456, found 319.01348.

3-((4-chlorophenyl)sulfonyl)-5-(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole



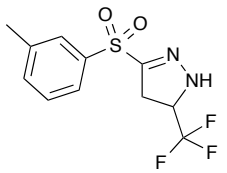
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.96 – 7.86 (m, 2H), 7.58 – 7.52 (m, 2H), 4.47 (m, 1H), 3.34 (dd, *J* = 17.6, 12.3 Hz, 1H), 3.18 (dd, *J* = 17.6, 8.0 Hz, 1H) ppm; ^{19}F-NMR (564 MHz, $CDCl_3$): δ = −77.32 (d, *J* = 6.8 Hz) ppm; ^{13}C-NMR (151MHz, $CDCl_3$): δ = 150.6, 141.4, 136.3, 129.9, 129.8, 124.4 (q, *J* = 279.8), 62.2 (q, *J* = 32.1 Hz), 31.7 ppm; IR (KBr): υ = 3321, 3096, 3011, 2868, 2295, 2111, 1914, 1739, 1646, 1574, 1436, 1396, 1284, 1200, 1130, 1079, 1010, 943, 868, 825, 753, 695 cm^{-1}; HRMS (ESI): m/z calcd for $C_{11}H_{11}O_2N_2F_3NaS$: 315.03857, found 315.03855.

3-((4-methoxyphenyl)sulfonyl)-5-(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole



^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.94 – 7.85 (m, 2H), 7.06 – 6.99 (m, 2H), 4.44 (m, 1H), 3.89 (s, 3H), 3.32 (dd, *J* = 17.6, 12.2 Hz, 1H), 3.16 (dd, *J* = 17.6, 8.1 Hz, 1H) ppm; ^{19}F-NMR (564 MHz, $CDCl_3$): δ = −77.18 (d, *J* = 6.8 Hz) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 164.4, 151.71, 130.8, 129.0, 127.5 (q, *J* = 279.9 Hz), 114.7, 62.1 (q, *J* = 31.8 Hz), 55.8, 31.8 ppm; IR (KBr): υ = 3313, 2969, 2586, 2294, 2070, 1914, 1738, 1588, 1496, 1446, 1264, 1125, 1024, 940, 831, 676 cm^{-1}; HRMS (ESI): m/z calcd for $C_{11}H_{11}O_3N_2F_3NaS$: 331.03360, found 331.03347.

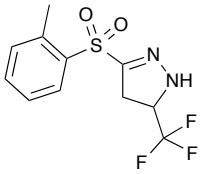
3-(*m*-tolylsulfonyl)-5-(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole



^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.06 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.56 (td, *J* = 7.5, 1.4 Hz, 1H), 7.45 – 7.33 (m, 2H), 4.52 – 4.33 (m, 1H), 3.32 (dd, *J* = 17.7, 12.3 Hz, 1H), 3.13 (dd, *J* = 17.7, 7.7 Hz, 1H), 2.61 (s, 3H) ppm; ^{19}F-NMR (564 MHz, $CDCl_3$): δ = −77.44 (d, *J* = 6.9 Hz) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 150.6, 139.5, 135.7, 134.5, 132.8, 130.2 , 126.6, 124.0 (q, *J* = 279.9

Hz), 61.9 (q, *J* = 31.9 Hz), 31.7, 20.3 ppm; IR (KBr): υ = 3309, 2929, 2087, 1697, 1431, 1286, 1133, 855, 781, 686 cm^{-1}; HRMS (ESI): m/z calcd for $C_{11}H_{11}O_2N_2F_3NaS$: 315.03812, found 315.03855.

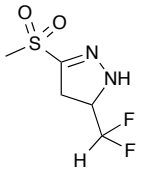
3-(*o*-tolylsulfonyl)-5-(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole



^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.77 – 7.73 (m, 2H), 7.51 – 7.46 (m, 2H), 4.46 (ddq, *J* = 12.2, 8.0, 6.8 Hz, 1H), 3.32 (dd, *J* = 17.6, 12.3 Hz, 1H), 3.15 (dd, *J* = 17.7, 8.1 Hz, 1H), 2.45 (s, 3H) ppm; ^{19}F-NMR (564 MHz, $CDCl_3$): δ = −77.21 (d, *J* = 6.6 Hz) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 150.9, 139.9, 137.7, 135.3, 129.3, 128.7, 125.5, 124.0 (q, *J* = 279.6 Hz), 62.2 (q, *J* = 32.0 Hz), 31.9, 31.3 ppm; IR (KBr): υ = 3350, 2969, 2302, 2089, 1739, 1555, 1282, 1141, 869, 693 cm^{-1}; HRMS (ESI): m/z calcd for $C_{11}H_{11}O_2N_2F_3NaS$: 315.03851, found 315.03855.

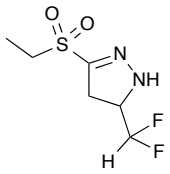
Difluoromethyl-substituted pyrazolines

5-(difluoromethyl)-3-(methylsulfonyl)-4,5-dihydro-1*H*-pyrazole



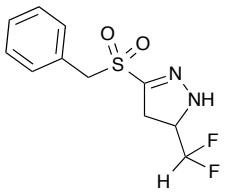
^{1}H-NMR (600 MHz MHz, CD_3OD): δ = 6.00 – 5.75 (td, *J* = 55.7, 4.4 Hz, 1H), 4.40 – 4.23 (m, 1H), 3.25 (dd, *J* = 17.3, 12.4 Hz, 1H), 3.13 (s, 3H) ppm; ^{19}F-NMR (564 MHz, CD_3OD) δ -127.30 (ddd, *J* = 289.4, 55.8, 12.1 Hz), -128.59 (ddd, *J* = 289.5, 55.8, 10.5 Hz).^{13}C-NMR (151 MHz, CD_3OD): δ = 148.8, 115.1, (t, *J* = 242.0 Hz,) 62.7 (t, *J* = 24.1 Hz), 40.0, 30.5 – 28.5 (m) ppm; IR (KBr): υ = 3323, 3022, 2936, 2281, 2085, 1564, 1393, 1298, 1161, 1099, 1059, 1026, 941, 659 cm^{-1}; HRMS (ESI): m/z calcd for $C_5H_8F_2N_2NaO_2S$: 221.01668, found 221.10910.

5-(difluoromethyl)-3-(ethylsulfonyl)-4,5-dihydro-1*H*-pyrazole



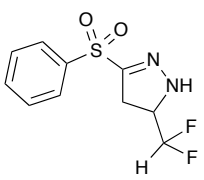
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 6.68 – 6.32 (b, 1H), 5.74 (td, *J* = 55.5, 4.6 Hz, 1H), 4.29 (m, 1H), 3.31 – 3.20 (m, 3H), 3.08 (dd, *J* = 17.5, 8.4 Hz, 1H), 1.38 (t, *J* = 7.5 Hz, 3 H) ppm; ^{19}F-NMR (564 MHz, $CDCl_3$): δ = −125.34 (ddd, *J* = 290.8, 55.6, 12.1 Hz), −126.34 (ddd, *J* = 290.9, 55.4, 9.5 Hz) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 149.5, 114.4 (t, *J* = 243.9 Hz), 62.6 (t, *J* = 24.3 Hz), 48.0, 31.3, 6.7 ppm; IR (KBr): υ = 3600, 3337, 2982, 2323, 2106, 1923, 1739, 1627, 1565, 1412, 1305, 1224, 1055, 871, 775, 719 cm^{-1}; MS (EI): m/z (%): 212.0 ([M], 81%), 161.1 ([M-CF_2H], 100%).

3-(benzylsulfonyl)-5-(difluoromethyl)-4,5-dihydro-1*H*-pyrazole



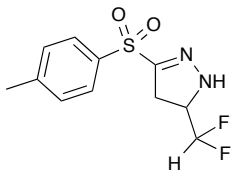
^{1}H-NMR (600 MHz, DMSO-d_6): δ = 8.82 (br, 1H), 7.35 (dtt, *J* = 10.0, 6.6, 3.6 Hz, 5H), 5.98 (dt, *J* = 55.5, 4.0 Hz, 1H), 4.61 (s, 2H), 4.37 – 4.25 (m, 1H), 3.03 (dd, *J* = 17.2, 12.9 Hz, 1H), 2.79 (dd, *J* = 17.2, 9.3 Hz, 1H) ppm; ^{19}F-NMR (564 MHz, DMSO-d_6): δ = −125.89 (ddd, *J* = 284.5, 55.6, 11.7 Hz), –126.17 (ddd, *J* = 284.6, 55.4, 12.5 Hz) ppm; ^{13}C-NMR (151 MHz, DMSO-d_6): δ = 146.4, 131.7, 128.9, 128.4, 115.5 (t, *J* = 241.5 Hz), 78.5, 62.5 (t, *J* = 23.3 Hz), 59.6, 31.8 ppm; IR (KBr): υ = 3336, 2978, 2932, 2658, 2311, 2104, 1904, 1738, 1567, 1496, 1452, 1401, 1307, 1251, 1206, 1157, 1057, 877, 783, 701 cm^{-1}; MS (EI): m/z (%): 273.9 ([M], 5%), 91.0 ([M-$C_4H_5F_2N_2O_2S$], 100%); HRMS (ESI): m/z calcd for $C_{11}H_{12}O_2N_2F_2NaS$: 297.04834, found 297.04798.

5-(difluoromethyl)-3-(phenylsulfonyl)-4,5-dihydro-1*H*-pyrazole



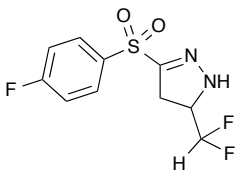
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.09 – 7.82 (m, 2H), 7.74 – 7.62 (m, 1H), 7.61 – 7.51 (m, 2H), 5.64 (td, *J* = 55.6, 5.3 Hz, 1H), 4.30 – 4.15 (m, 1H), 3.21 (dd, *J* = 17.3, 11.8, 1H), 3.00 (dd, *J* = 17.4, 8.6 Hz, 1H) ppm; ^{19}F-NMR (564 MHz, $CDCl_3$): δ = −124.42 (ddd, *J* = 292.6, 55.8 , 11.7 Hz), −125.55 (ddd, *J* = 292.6, 55.3, 8.1 Hz) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 151.1, 137.9, 134.4, 129.5, 128.4, 114.2 (t, *J* = 244.1 Hz), 64.3 – 61.0 (m), 331. – 28.2 (m) ppm; IR (KBr): υ = 3925, 3321, 2857, 1561, 1442, 1319, 1290, 1171, 1134, 1075, 1045, 1006, 945, 861, 791, 718, 691 cm^{-1}; HRMS (ESI): m/z calcd for $C_{10}H_{10}F_2N_2NaO_2S$: 283.03233, found 283.03171.

5-(difluoromethyl)-3-tosyl-4,5-dihydro-1*H*-pyrazole



^{1}H-NMR (600 MHz, CD_3OD): δ = 7.91 – 7.72 (m, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 5.78 (td, *J* = 55.6, 4.1 Hz, 1H), 4.27 (tddd, *J* = 12.6, 10.7, 4.1 Hz, 1H), 3.12 (ddd, *J* = 17.2, 12.5 Hz, 1H), 2.93 (dd, *J* = 17.3 Hz, 9.0 Hz, 1H), 2.44 (s, 3H) ppm; ^{19}F-NMR (376 MHz, CD_3OD): δ = -127.76 (ddd, *J* = 289.0, 55.7, 12.1 Hz), -128.74 (m) ppm; ^{13}C-NMR (151 MHz, CD_3OD): δ = 148.5, 145.4, 1258, 129.8, 127.8, 117.7 – 112.6 (m), 62.8 (t, *J* = 23.9 Hz), 30.3, 20.1 ppm; IR (KBr): υ = 3341, 2974, 2325, 2103, 1920, 1741, 1594, 1381, 1314, 1141, 1064, 957, 868, 810, 666 cm^{-1}; MS (EI): m/z (%): 274.0 ([M], 4%), 223.0 ([M-CF_2H], 7%), 155.0 ([M-$C_4H_5F_2N_2$], 11%), 91.0 ([M-$C_4H_5F_2N_2O_2S$], 100%); HRMS (ESI): m/z calcd for $C_{11}H_{12}O_2N_2F_2NaS$: 297.04868, found 297.04798.

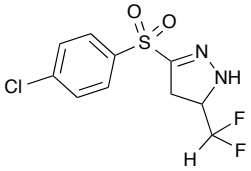
5-(difluoromethyl)-3-((4-fluorophenyl)sulfonyl)-4,5-dihydro-1*H*-pyrazole



^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.01 – 7.92 (m, 2H), 7.30 – 7.21 (m, 2H), 5.68 (td, *J* = 55.5, 5.0 Hz, 1H), 4.27 (ttd, *J* = 11.9, 8.6, 5.0 Hz, 1H), 3.21 (dd, *J* = 17.4, 12.1 Hz, 1H), 3.01 (dd, *J* = 17.4, 8.7 Hz, 1H) ppm^{19}F-NMR (564 MHz, $CDCl_3$): δ = -102.11 (td, *J* = 8.2, 4.1 Hz), -124.81 (ddd, *J* = 291.8, 55.6, 11.8 Hz), -126.00 (ddd, *J* = 292.0, 55.3, 8.6 Hz) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 167.1, 165.3, 150.8, 134.1, 131.3, 116.9, 116.2, 114.3 (t, J = 244.1 Hz), 63.4 – 62.9 (m),

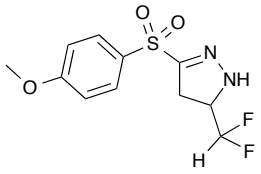
31.3 ppm; IR (KBr): υ = 3346, 3106, 2983, 2327, 2078, 1914, 1743, 1587, 1492, 1406, 1324, 1234, 1146, 1064, 955, 833, 670 cm^{-1}; HRMS (ESI): m/z calcd for $C_{10}H_9O_2N_2F_3NaS$: 301.02229, found 301.02290.

3-((4-chlorophenyl)sulfonyl)-5-(difluoromethyl)-4,5-dihydro-1*H*-pyrazole



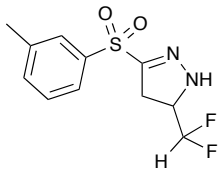
^{1}H-NMR (600 MHz, CD_3OD): δ = 7.91 – 7.84 (m, 2H), 7.68 – 7.60 (m, 2H), 5.78 (td, *J* = 55.6, 4.1 Hz, 1H), 4.29 (tddd, *J* = 12.7, 11.0, 8.9, 4.1 Hz, 1H), 3.14 (dd, *J* = 17.3, 12.6 Hz, 1H), 2.95 (dd, *J* = 17.3, 9.0 Hz, 1H) ppm; ^{19}F-NMR (376 MHz, CD_3OD): δ = -128.00 (ddd, *J* = 289.2, 55.5, 12.0 Hz), -129.13 (ddd, *J* = 289.2, 55.7, 10.9 Hz) ppm; ^{13}C-NMR (151 MHz, CD_3OD): δ = 147.6, 140.3, 137.7, 129.4, 114.9 (t, *J* = 242.2 Hz), 63.0 (q, *J* = 24.1 Hz), 30.2 ppm; IR (KBr): υ = 3333, 2993, 2640, 2323, 2105, 1740, 1566, 1397, 1311, 1057, 826, 753 cm^{-1}; HRMS (ESI): m/z calcd for $C_{10}H_9O_2N_2ClF_2NaS$: 316.99344, found 316.99335.

5-(difluoromethyl)-3-((4-methoxyphenyl)sulfonyl)-4,5-dihydro-1*H*-pyrazole



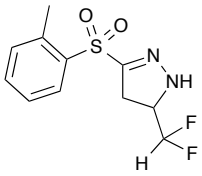
^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.93 – 7.86 (m, 2H), 7.06 – 7.03 (m, 2H), 5.65 (td, *J* = 55.6, 5.3 Hz, 1H), 4.32 – 4.19 (m, 1H), 3.89 (s, 3H), 3.22 (dd, *J* = 17.4, 11.8 Hz, 1H), 3.01 (dd, *J* = 17.4, 8.7 Hz, 1H) ppm; ^{19}F-NMR (564 MHz, $CDCl_3$): δ = –124.15 (ddd, *J* = 292.3, 55.9, 12.0 Hz), –125.31 (ddd, *J* = 292.4, 55.3, 7.7 Hz) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 164.3, 152.1, 130.8, 129.2 114.7, 114.4 (t, *J* = 244.0 Hz), 63.4 – 62.9 (m), 55.8, 31.5 ppm; IR (KBr): υ = 3612, 3339, 2949, 2847, 2578, 2324, 2109, 1999, 1919, 1742, 1587, 1495, 1456, 1309, 1262, 1129, 1066, 956, 833, 729, 670 cm^{-1}; HRMS (ESI): m/z calcd for $C_{11}H_{12}O_3N_2F_2NaS$: 313.04294, found 313.04289.

5-(difluoromethyl)-3-(*m*-tolylsulfonyl)-4,5-dihydro-1*H*-pyrazole



^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.79 – 7.72 (m, 2H), 7.51 – 7.43 (m, 2H), 5.67 (td, *J* = 55.6, 5.1 Hz, 1H), 4.25 (ttd, *J* = 11.9, 8.5, 5.1 Hz, 1H), 3.20 (dd, *J* = 17.4, 12.0 Hz, 1H), 3.00 (ddd, *J* = 17.3, 8.7, 0.7 Hz, 1H), 244 (s, 3H) ppm; ^{19}F-NMR (564 MHz, $CDCl_3$): δ = –124.39 (ddd, *J* = 291.9, 55.7, 11.8 Hz), –125.76 (ddd, *J* = 292.0, 55.4, 8.3 Hz) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 151.1, 139.8, 137.9, 135.2, 129.3, 128.6, 125.5, 114.3 (t, *J* = 243.9 Hz), 63.9 – 62.1 (m), 31.5, 21.3 ppm; IR (KBr): υ = 3343, 2975, 2333, 2096, 2000, 1915, 1819, 1565, 1416, 1307, 1218, 1125, 1064, 956, 865, 787, 691 cm^{-1}; HRMS (ESI): m/z calcd for: $C_{11}H_{12}O_2N_2F_2NaS$: 297.04810, found 297.04798.

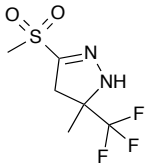
5-(difluoromethyl)-3-(*o*-tolylsulfonyl)-4,5-dihydro-1*H*-pyrazole



^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.04 (dd, J = 7.9, 1.4 Hz, 1H), 7.55 (td, *J* = 7.5, 1.5 Hz, 1H), 7.43 – 7.31 (m, 2H), 5.68 (td, *J* = 55.5, 4.8 Hz, 1H), 4.26 (ttd, *J* = 11.9, 8.7, 4.8 Hz, 1H), 3.17 (dd, *J* = 17.4, 12.0 Hz, 1H), 2.97 (dd, *J* = 17.4, 8.4 Hz, 1H), 2.60 (s, 3H) ppm; ^{19}F-NMR (564 MHz, $CDCl_3$): δ = −125.13 (ddd, *J* = 291.1, 55.7, 12.0 Hz), −126.13 (ddd, *J* = 291.1, 55.3, 8.9 Hz) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 150.6, 139.4, 135.8, 134.4, 132.8, 130.1, 126.6, 114.3 (t, *J* = 244.0 Hz), 64.2 – 61.7 (m), 31.2, 20.3 ppm; IR (KBr): υ = 3343, 3064, 2978, 2331, 2099, 1926, 1739, 1566, 1455, 1308, 1152, 1058, 955, 872, 803, 763, 696 cm^{-1}; HRMS (ESI): m/z calcd for $C_{11}H_{12}O_2N_2F_2NaS$: 297.04813, found 297.04798.

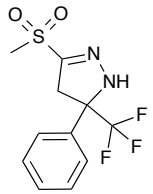
branched pyrazolines

5-methyl-3-(methylsulfonyl)-5-(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole



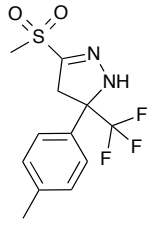
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 3.42 (d, *J* = 17.6 Hz, 1H), 3.17 (s, 3H), 3.04 (dt, *J* = 17.6, 0.9 Hz, 1H), 1.54 – 1.49 (m, 3H) ppm; ^{19}F-NMR (564 MHz, $CDCl_3$): δ = −80.27 (s) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 150.0, 125.3 (q, *J* = 281.8 Hz), 80.2, 69.3 (q, *J* = 29.4 Hz), 40.9, 37.9, 20.4 ppm; IR (KBr): υ = 3254, 2095, 1717, 1149, 778 cm^{-1}; MS (EI): m/z (%): 229.9 (8%), 161.0 (81%).

3-(methylsulfonyl)-5-phenyl-5-(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole



^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.50 – 7.33 (m, 5 H), 3.88 (d, *J* = 17.8 Hz, 1H), 3.54 (dq, *J* = 17.8, 1.0 Hz, 1H), 3.17 (s, 3H) ppm; ^{19}F-NMR (564 MHz, $CDCl_3$): δ = −79.02 (s) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 150.1, 135.5, 129.4, 129.1, 127.9, 125.0 (q, *J* = 285.0 Hz), 74.2 (q, *J* = 28.2 Hz), 41.0, 39.4 ppm; IR (KBr): υ = 3569, 3325, 3020, 2323, 2093, 1709, 1585, 1429, 1298, 1151, 977, 867, 725 cm^{-1}; MS (EI): m/z (%): 291.9 ([M], 10%), 223.0 ([M-CF_3], 100%).

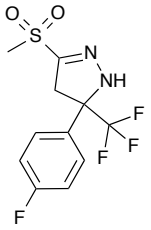
3-(methylsulfonyl)-5-(*p*-tolyl)-5-(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole



^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.29 – 7.22 (m, 4H), 3.85 (d, *J* = 17.7 Hz, 1H), 3.53 (dq, J = 17.8, 1.0 Hz, 1H), 3.17 (s, 3H), 2.37 (s, 3H) ppm; ^{19}F-NMR (564 MHz, $CDCl_3$): δ = −78.94 (s) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 150.1, 139.5, 132.4, 129.7, 127.9, 125.1 (q, *J* = 284.7 Hz), 74.5 – 73.8 (m), 41.1, 39.4, 21.1 ppm; IR (KBr): υ = 3331, 3026, 2930, 2287, 2185, 2077, 1757,

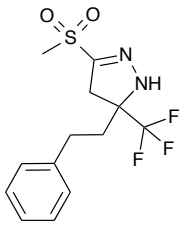
1701, 1619, 1575, 1419, 1306, 1160, 1018, 989, 958, 876, 814, 759, 726, 697 cm^{-1}; HRMS (ESI): m/z calcd for $C_{12}H_{13}O_2N_2F_3NaS$: 329.0548, found 329.0542.

5-(4-fluorophenyl)-3-(methylsulfonyl)-5-(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole



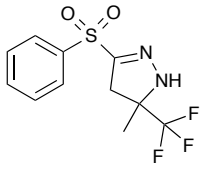
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.36 (hept, *J* = 3.5 Hz, 2H), 7.10 (dt, *J* = 8.6, 4.3 Hz, 1H), 3.86 (ddd, *J* = 17.8, 8.0, 2.9 Hz, 1H), 3.47 (dd, *J* = 18.1, 6.8 Hz, 1H), 3.18 (s, 3H) ppm; ^{19}F-NMR (564 MHz, $CDCl_3$): δ = −111.62 (s, 3F), −79.39 (s, 1F) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 146.5, 140.4, 128.2, 125.9, 72.1 (d, *J* = 27.8 Hz), 40.1, 34.6, 28.3 ppm; IR (KBr): υ = 3328, 2934, 2306, 2089, 1903, 1733, 1594, 1514, 1422, 1299, 1152, 981, 831, 759 cm^{-1}; MS (EI): m/z (%): 310.9 ([M], 6%), 133.0 ([M-$C_8H_4F_4$], 100%); HRMS (ESI): m/z calcd for $C_{11}H_{10}O_2N_2F_4NaS$: 333.0298, found 333.0291.

3-(methylsulfonyl)-5-phenethyl-5-(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole

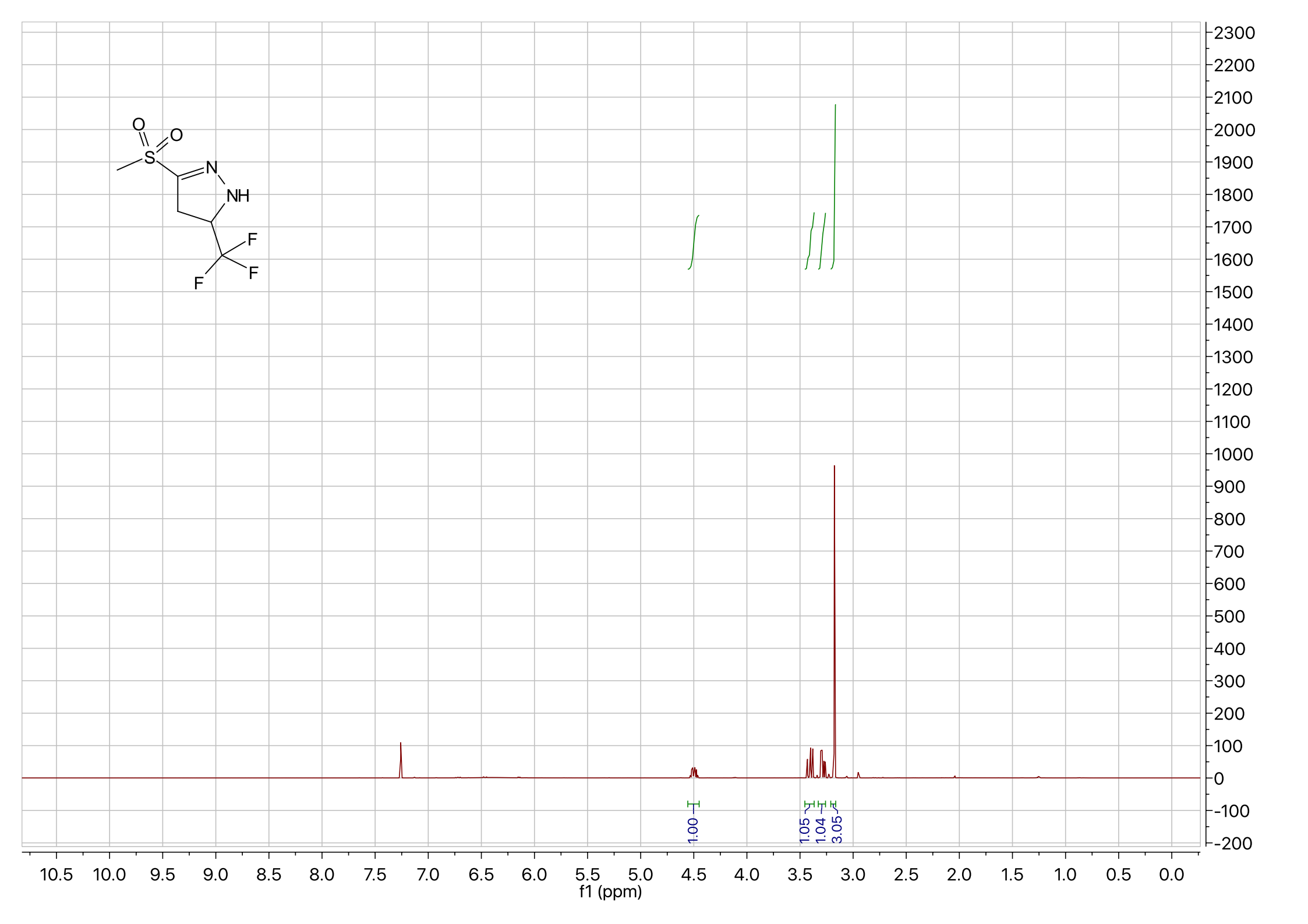


^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.41 – 7.15 (m, 4H), 3.41 (d, *J* = 18.0 Hz, 1H), 3.29 – 3.20 (m, 1H), 3.16 (s, 3H) 2.68 (dddd, *J* = 21.1, 16.7, 13.7, 8.4 Hz, 2H), 2.11 (dd, *J* = 9.4, 7.6 Hz, 1H) ppm; ^{19}F-NMR (564 MHz, $CDCl_3$): δ = −79.17 (s) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 149.4, 139.6, 128.8, 127.9 – 122.2 (m), 126.7, 72.1 (q, *J* = 28.1 Hz), 41.0, 35.5, 34.7, 29.0 ppm; IR (KBr): υ = 3329, 3028, 2932, 2866, 2655, 2327, 2181, 2114, 1994, 1749, 1570, 1497, 1451, 1414, 1305, 1161, 1123, 1049, 989, 957, 866, 817, 758, 700 cm^{-1}; HRMS (ESI): m/z calcd for $C_{13}H_{16}O_2N_2F_3NaS$: 321.08850, found 321.08791.

5-methyl-3-(phenylsulfonyl)-5-(trifluoromethyl)-4,5-dihydro-1*H*-pyrazole



^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.03 – 7.88 (m, 2H), 7.77 – 7.67 (m, 1H), 7.62 – 7.53 (m, 2H), 3.27 (d, *J* = 17.5 Hz, 1H), 2.97 (d, *J* = 17.5, 1.0 Hz, 1H), 1.45 (d, *J* = 1.1 Hz, 3H) ppm; ^{19}F-NMR (564 MHz, $CDCl_3$): δ = −80.33 (s) ppm; ^{13}C-NMR (151 MHz, $CDCl_3$): δ = 149.6, 138.0, 134.4, 129.4, 128.3, 128.2 – 121.5 (m), 69.7 (q, *J* = 29.2 Hz), 38.7, 20.2 ppm; IR (KBr): υ = 3887, 3368, 2340, 2093, 1728, 1377, 1143, 731 cm^{-1}; HRMS (ESI): m/z calcd for $C_{11}H_{12}O_2N_2F_3NaS$: 315.03918, found 315.03855.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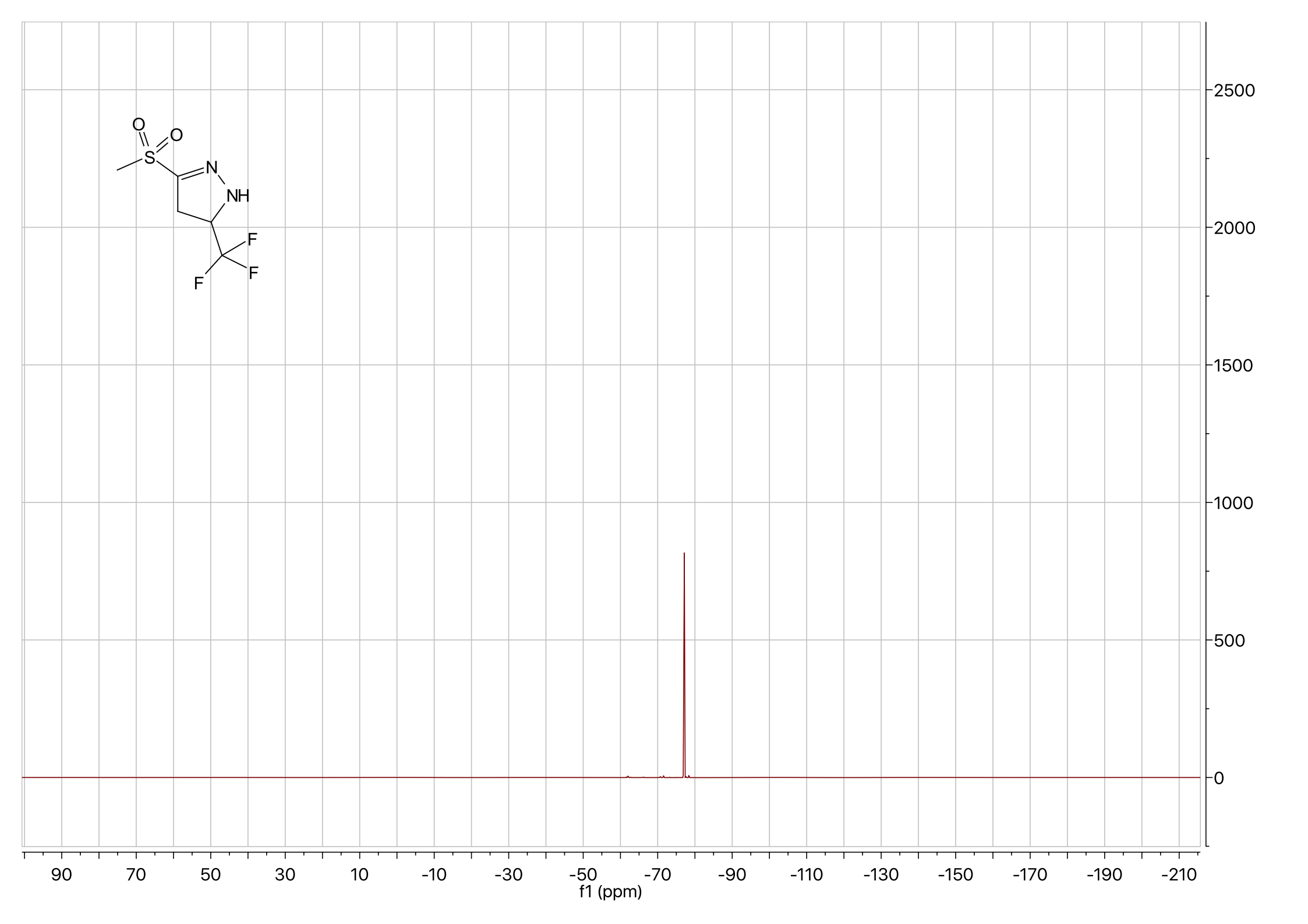
O
S
N
NH
F
F
F
1.00
1.05
1.04
3.05
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200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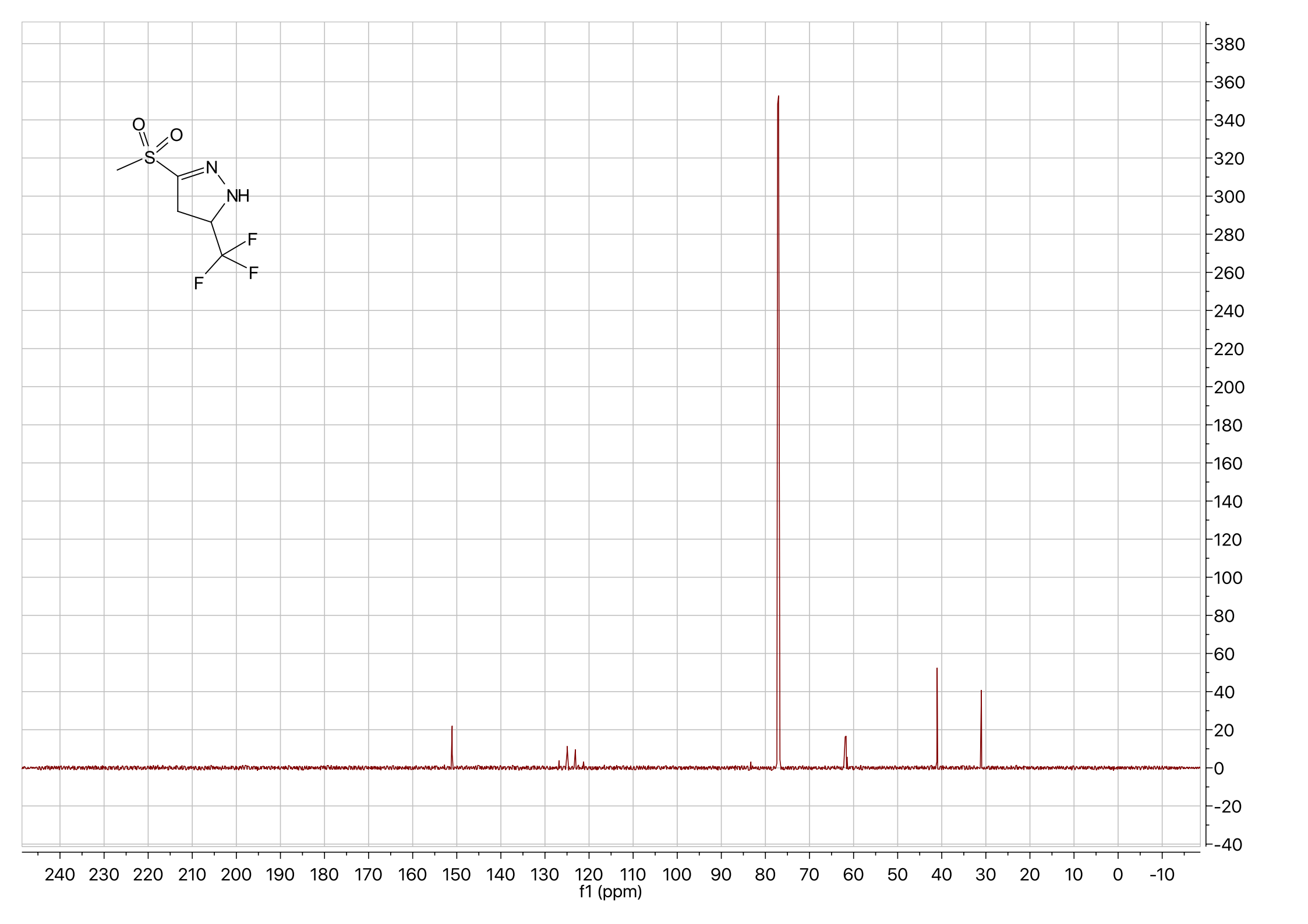
O
S
N
NH
F
F
F
2500
2000
1500
1000
500
0
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)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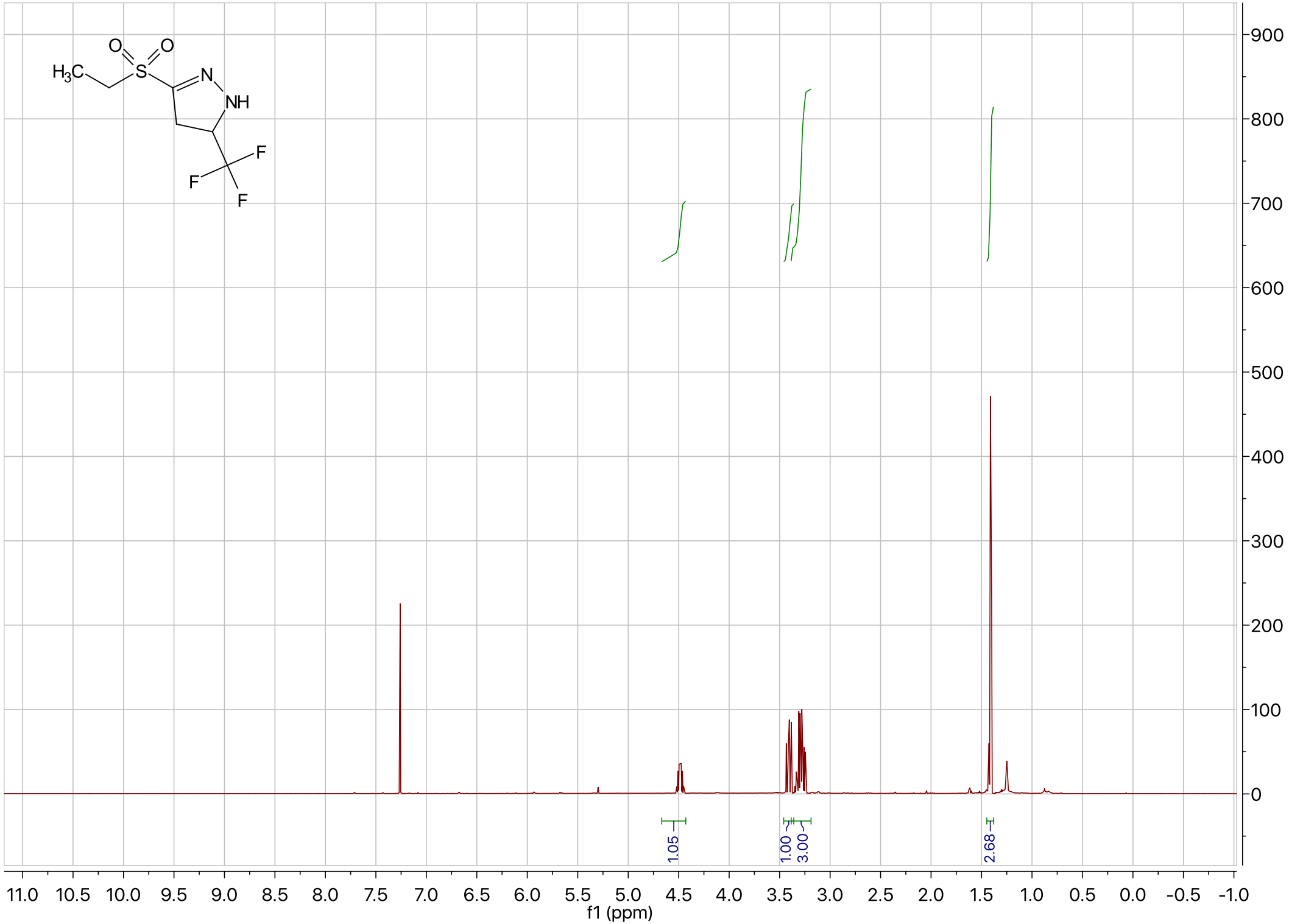
O
S
N
NH
F
F
F
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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O
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H_3C
N
NH
F
F
F
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1.00
3.00
2.68
900
800
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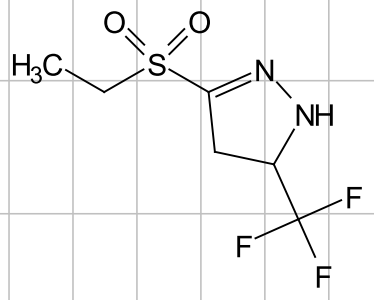
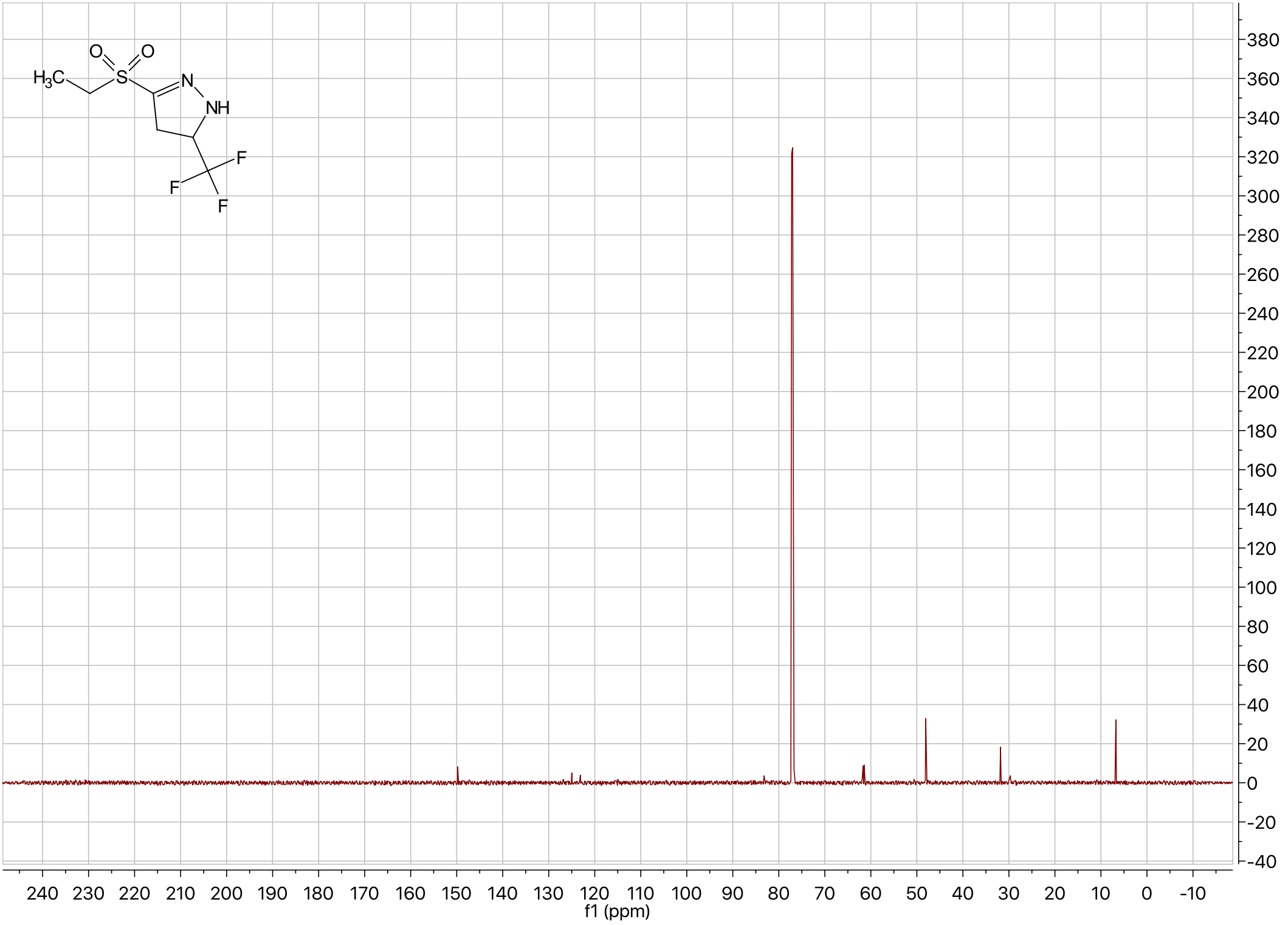
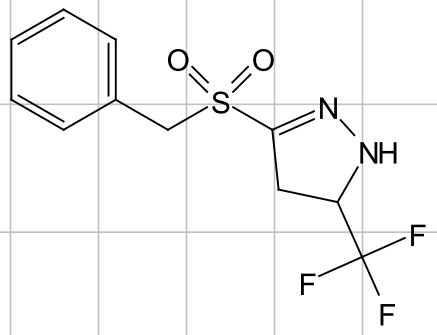
500
400
300
200
100
0
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


O
O
H3C
S
N
NH
F
F
F

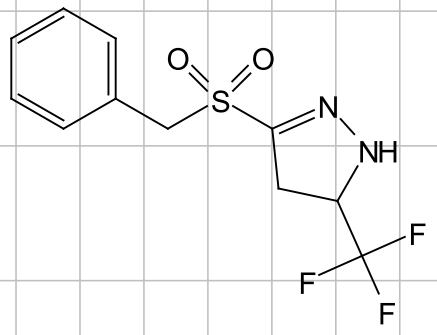
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)


O
O
S
H3C
N
NH
F
F
F
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



4.53
0.84
1.91
1.00
1.06
0.98

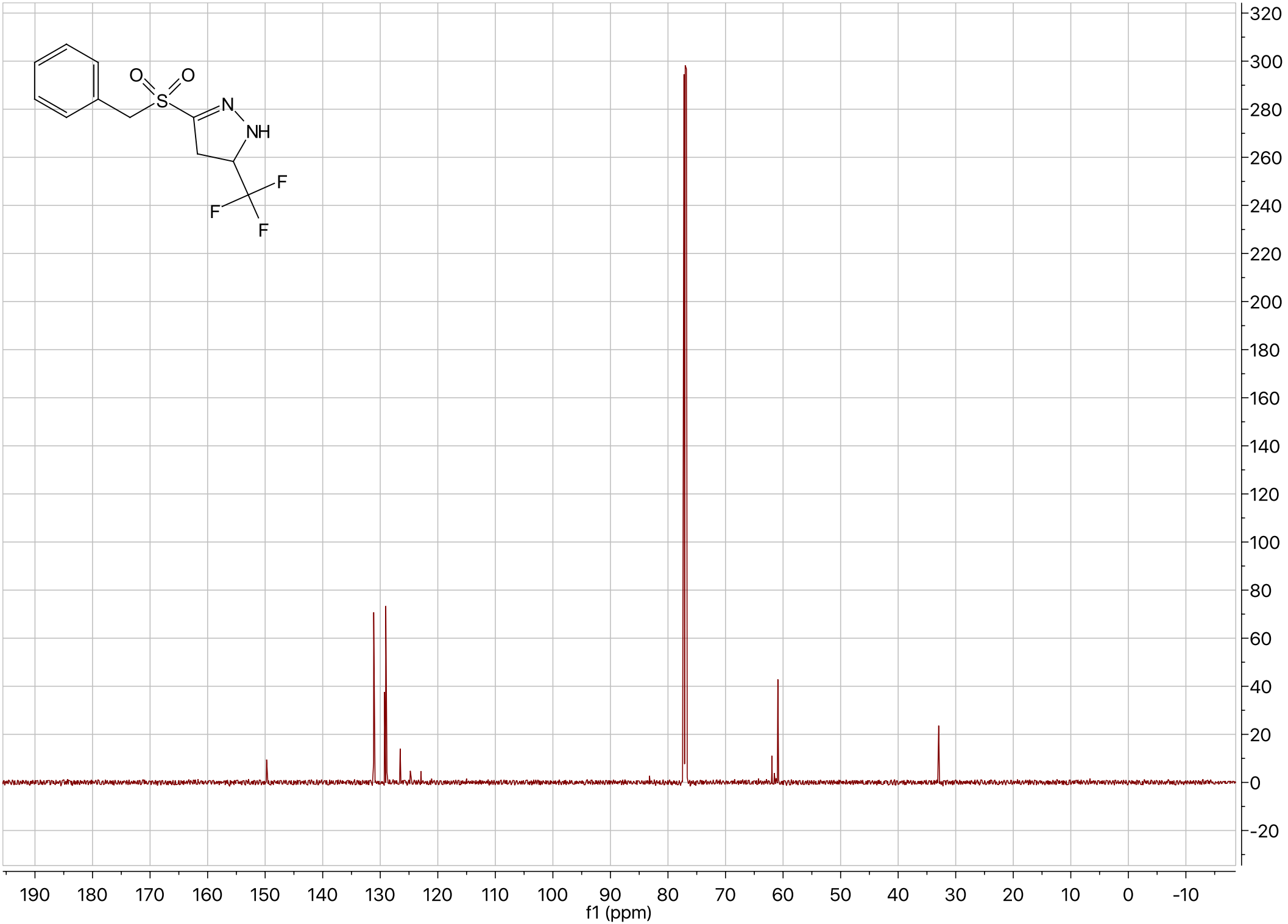
f1 (ppm)

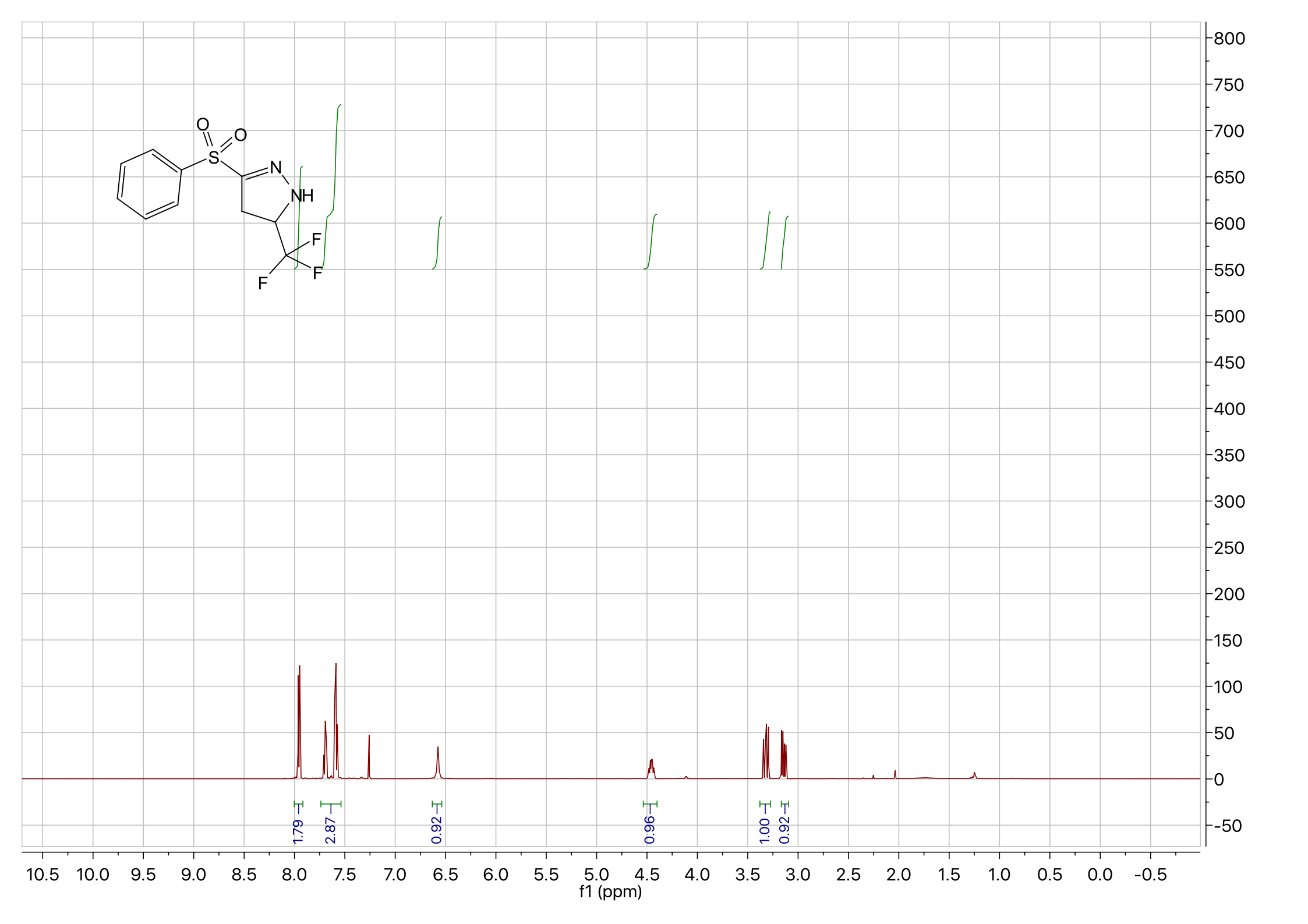


450
400
350
300
250
200
150
100
50
0

90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210

f1 (ppm)


O
O
S
N
NH
F
F
F
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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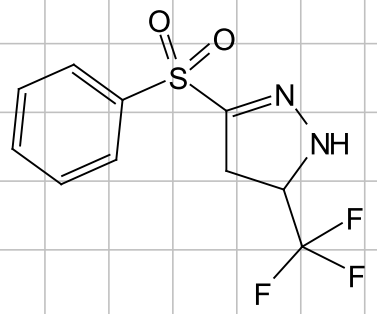
O
S
N
NH
F
F
F
1.79
2.87
0.92
0.96
1.00
0.92
f1 (ppm)



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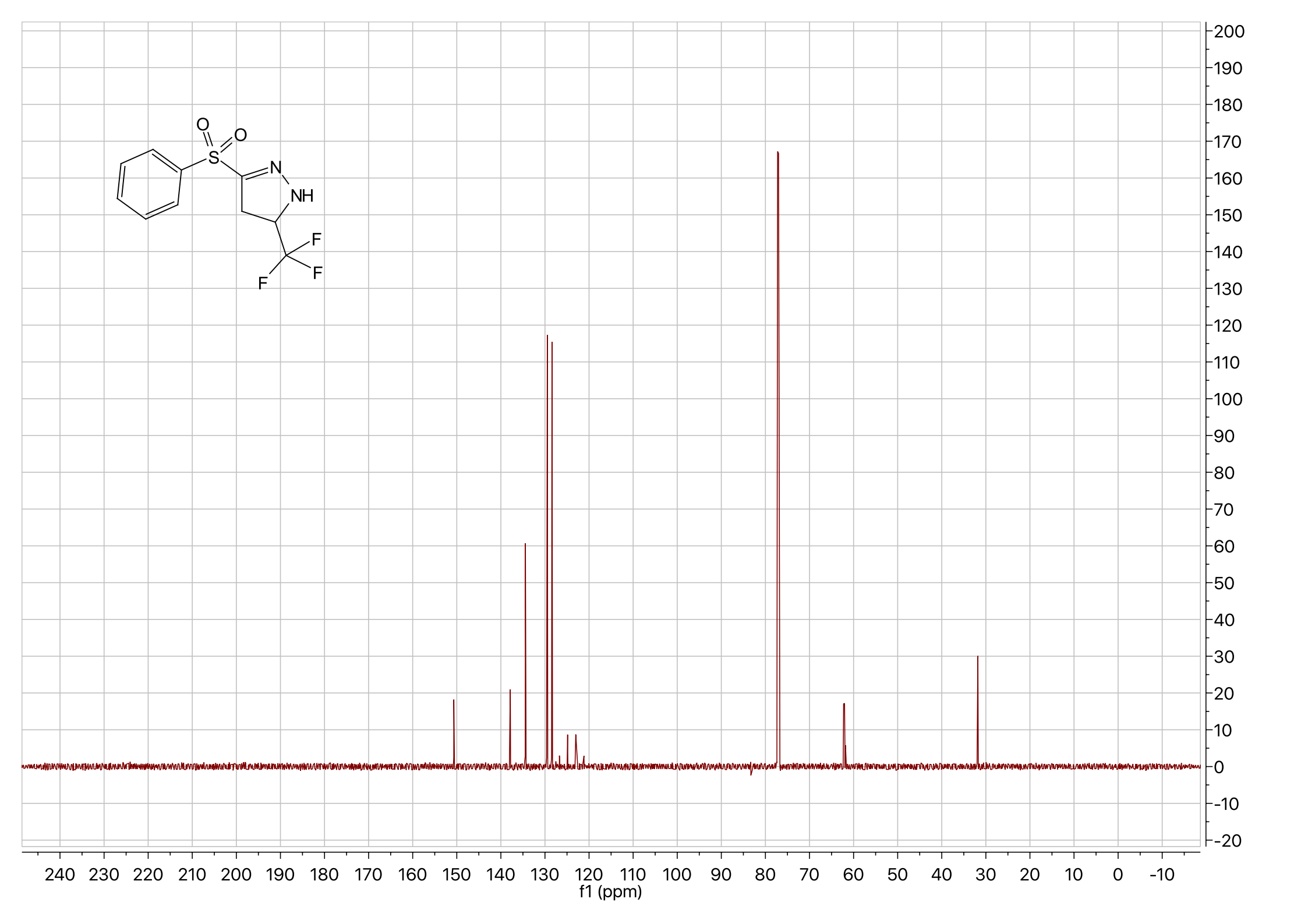
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210

f1 (ppm)


O
O
S
N
NH
F
F
F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
240
230
220
210
200
190
180
170
160
150
140
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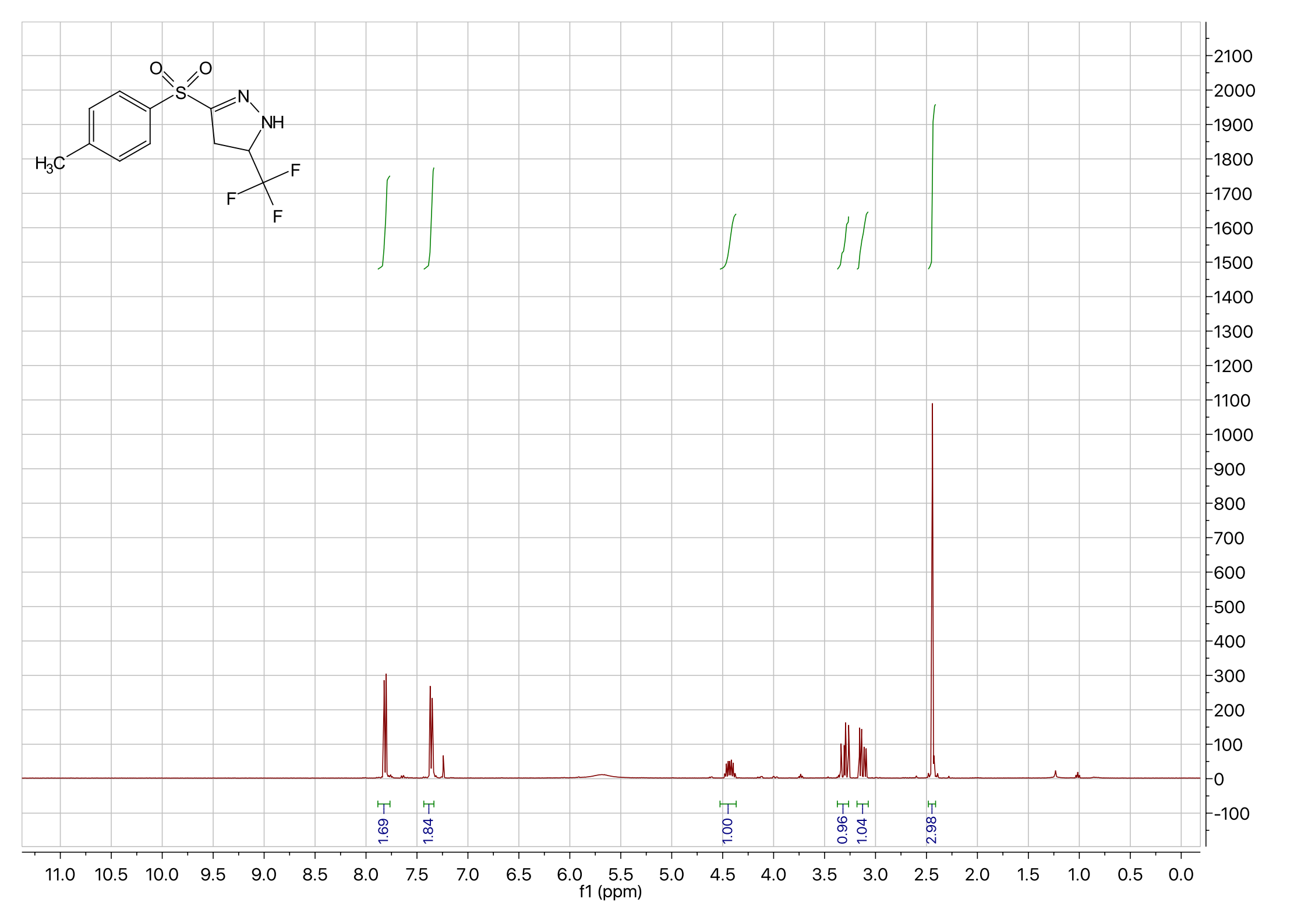
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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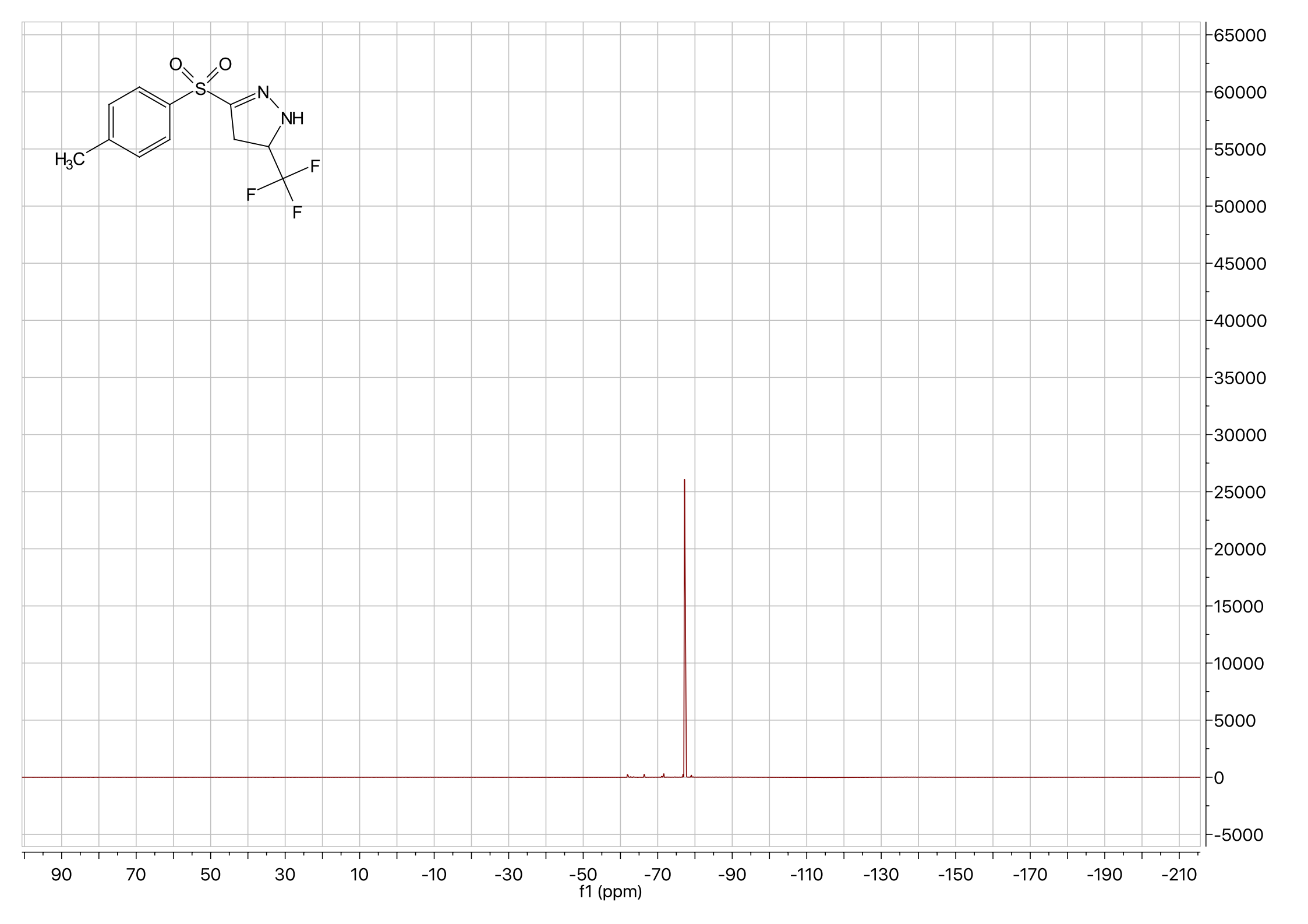
N
NH
H3C
F
F
F
1.69
1.84
1.00
0.96
1.04
2.98
f1 (ppm)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O
S
N
NH
H_3C
F
F
F
65000
60000
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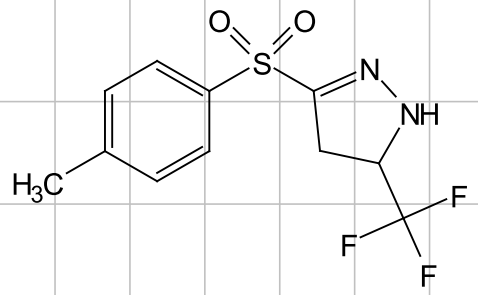
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)



600
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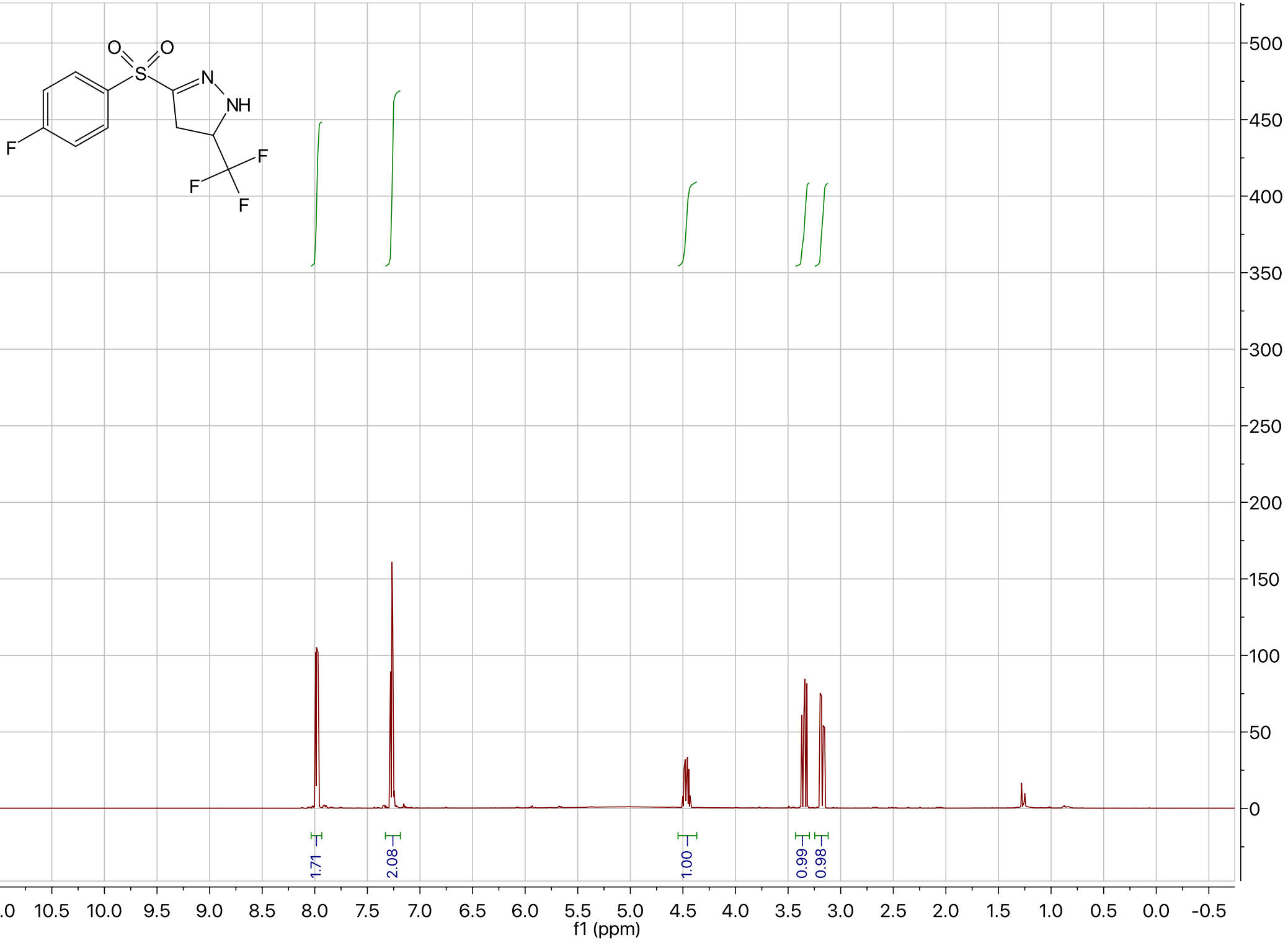
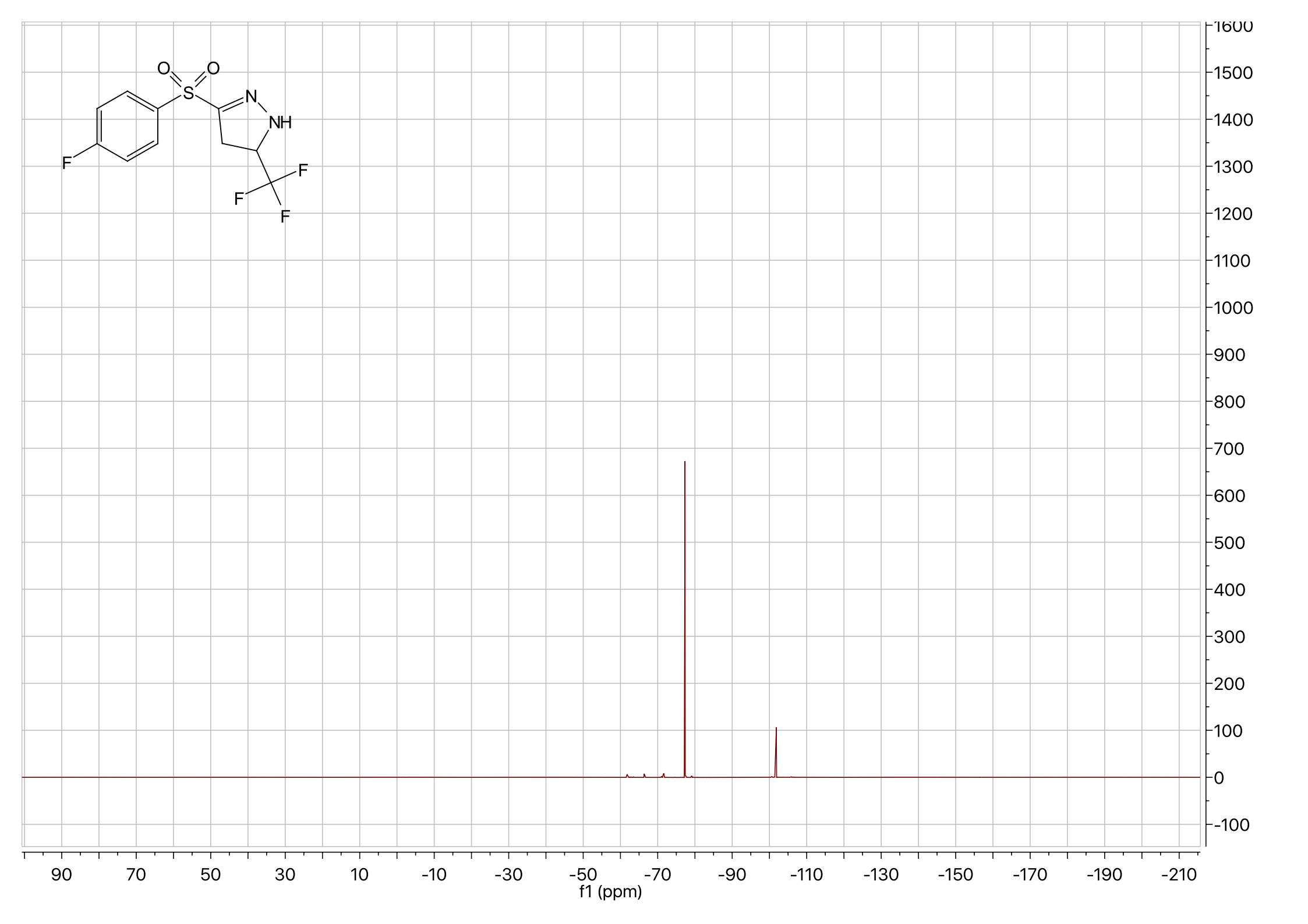
400
350
300
250
200
150
100
50
0
-50

50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20

f1 (ppm)


O
O
S
N
NH
F
F
F
F
1.71
2.08
1.00
0.99
0.98
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
500
450
400
350
300
250
200
150
100
50
0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S
N
NH
F
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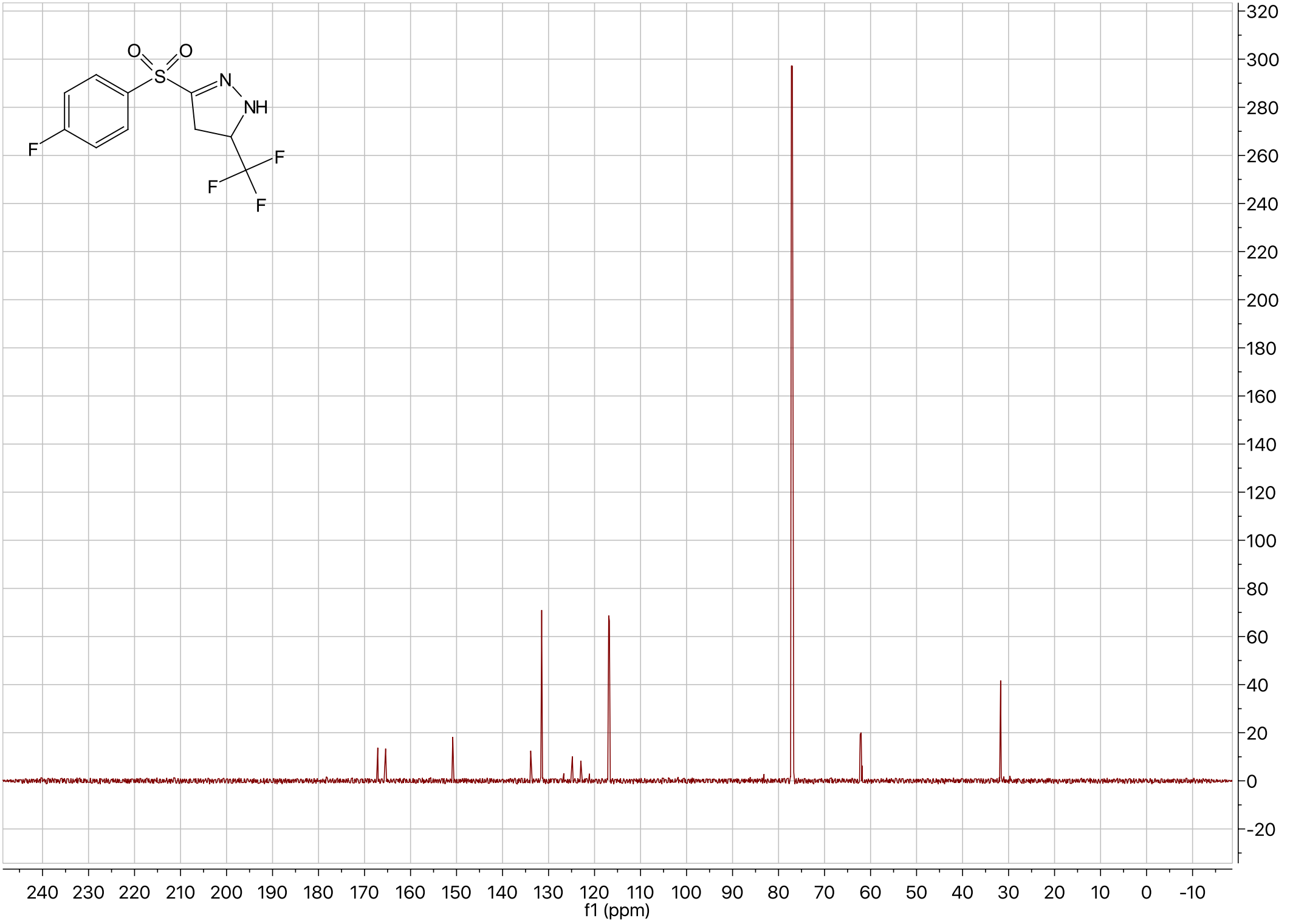
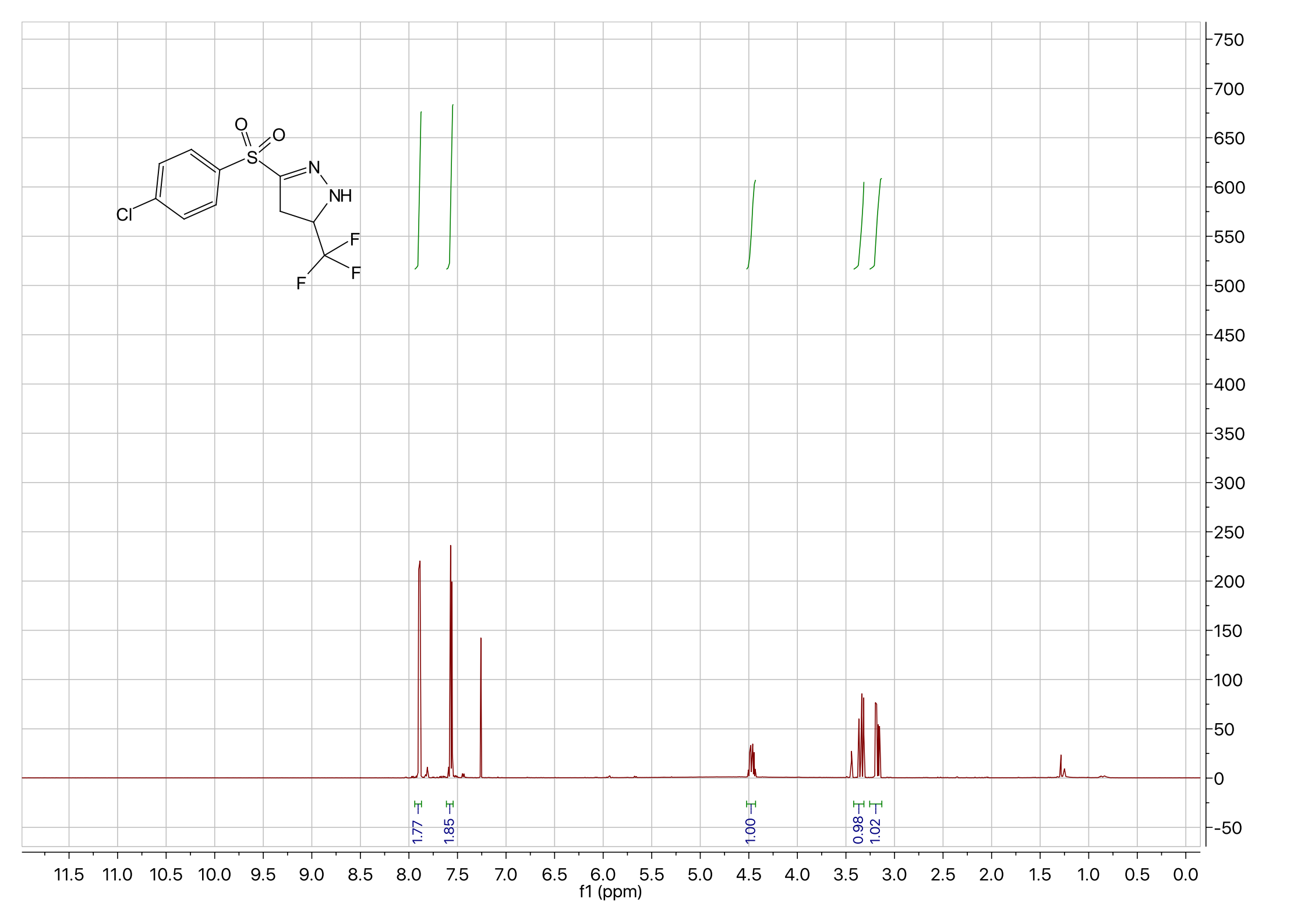
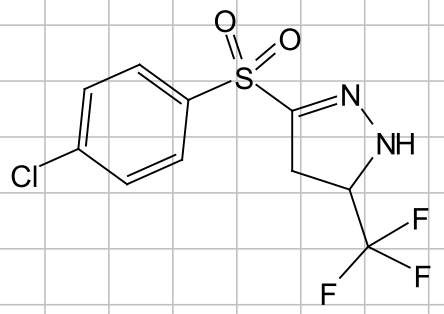
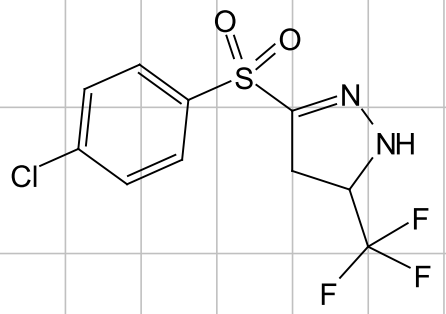
F
F
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)


O
O
S
N
NH
F
F
F
F
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
O
S
N
NH
Cl
F
F
F
1.77
1.85
1.00
0.98
1.02
f1 (ppm)


O
O
S
N
NH
Cl
F
F
F

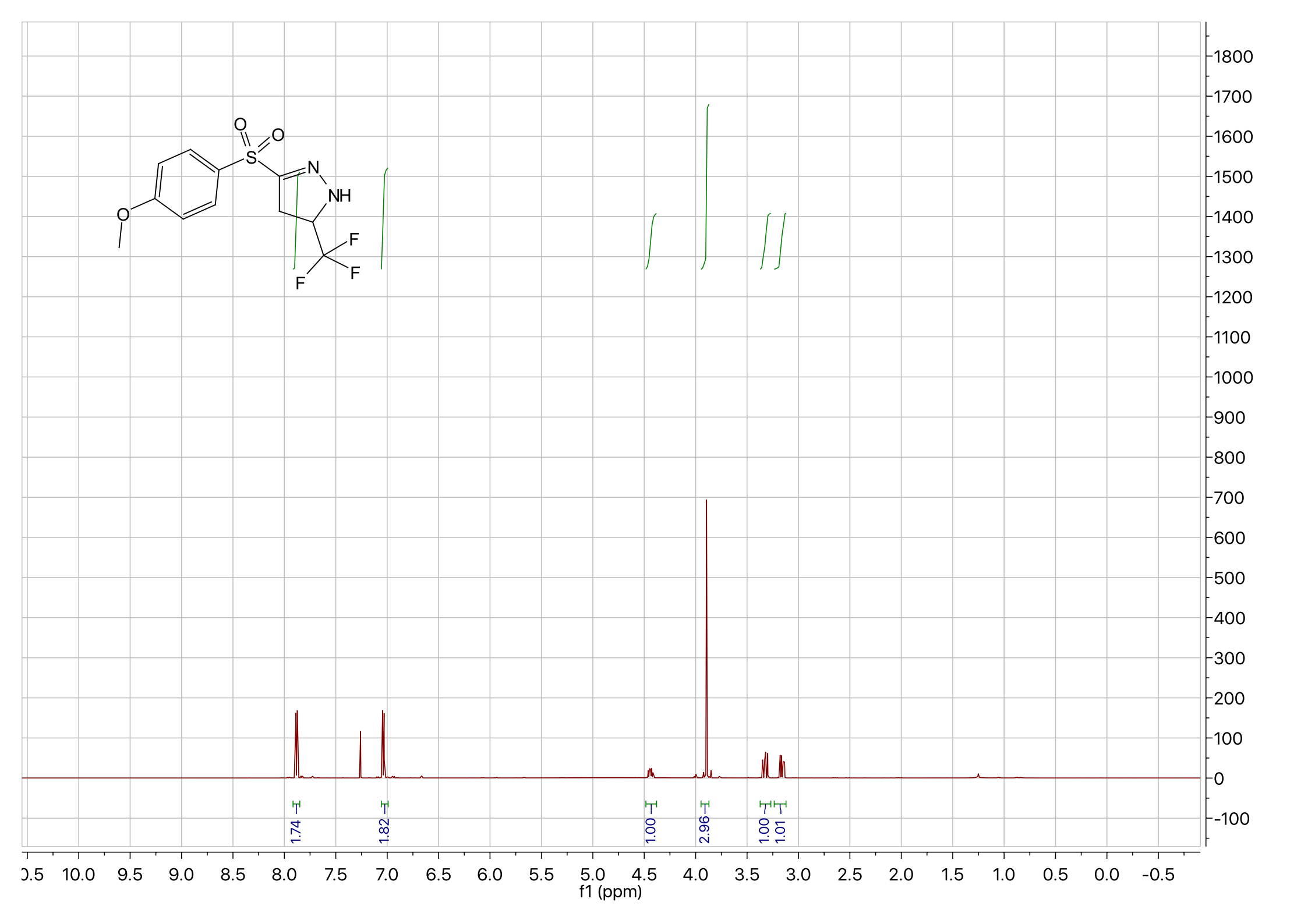
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

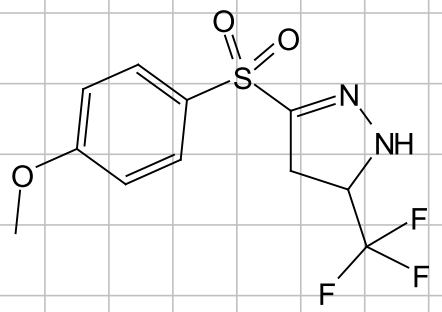


400
350
300
250
200
150
100
50
0

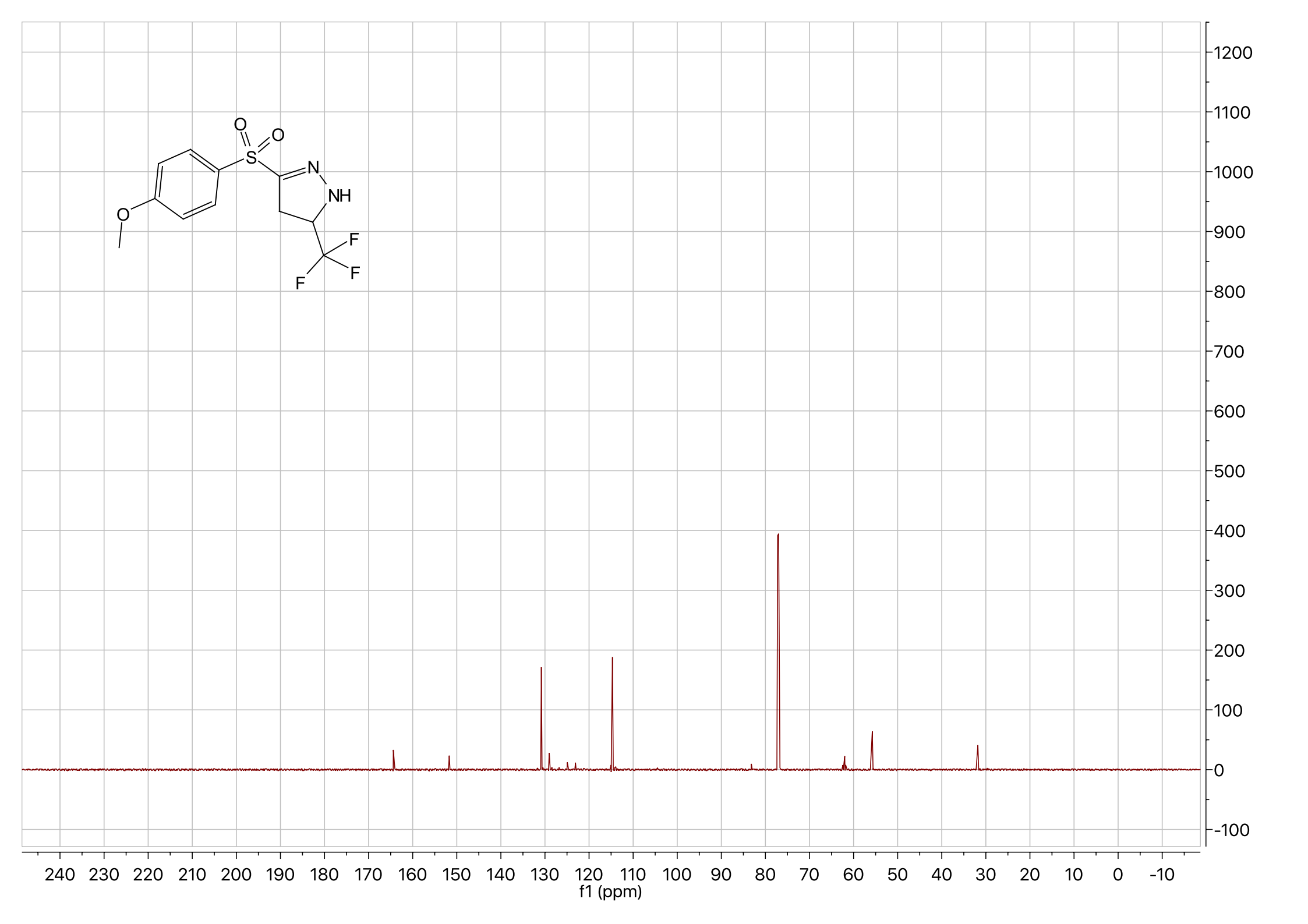
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

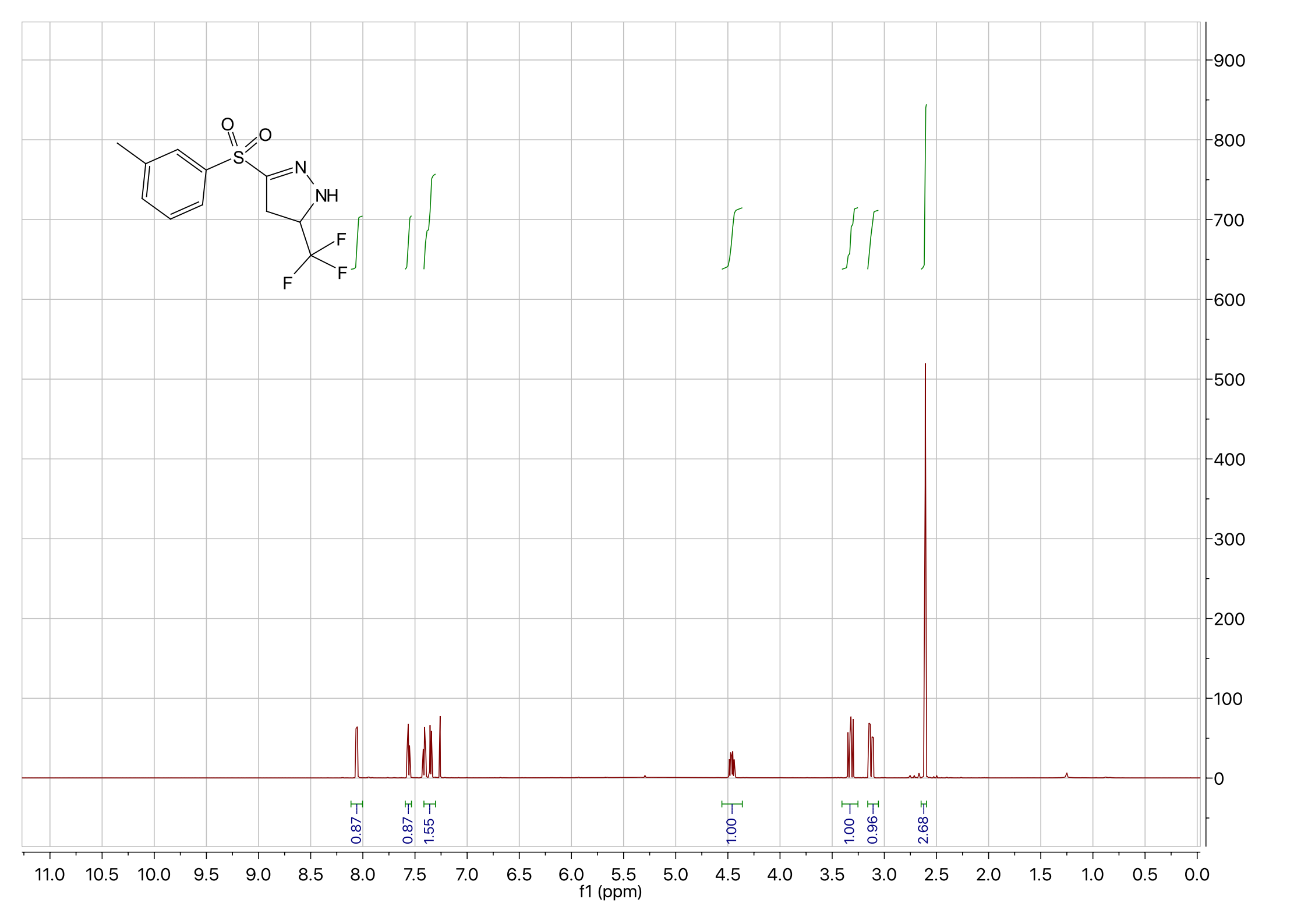
f1 (ppm)

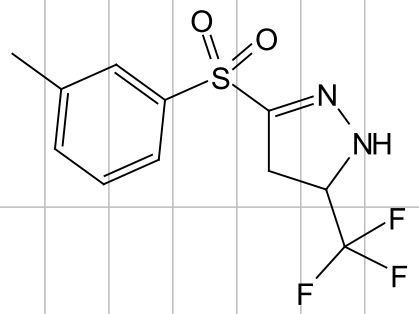

O
O
S
N
NH
O
F
F
F
1.74
1.82
1.00
2.96
1.00
1.01
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


O
O
S
N
NH
O
F
F
F

18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)


O
O
S
N
NH
O
F
F
F
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

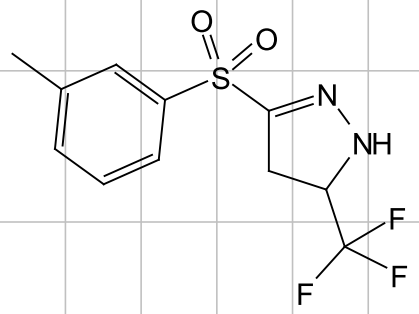

O
O
S
N
NH
F
F
F
0.87
0.87
1.55
1.00
1.00
0.96
2.68
900
800
700
600
500
400
300
200
100
0
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



25000
20000
15000
10000
5000
0

90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210

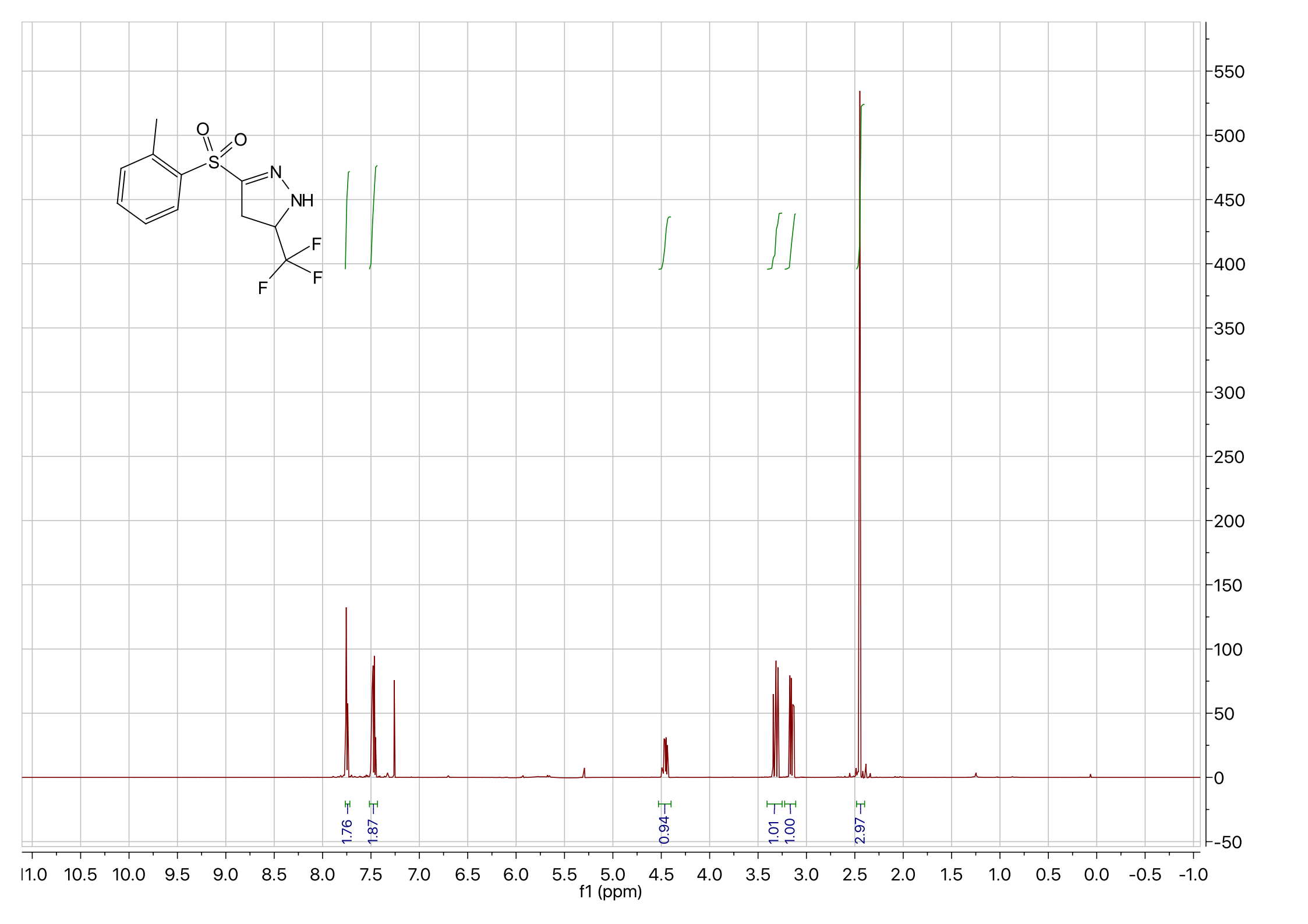
f1 (ppm)

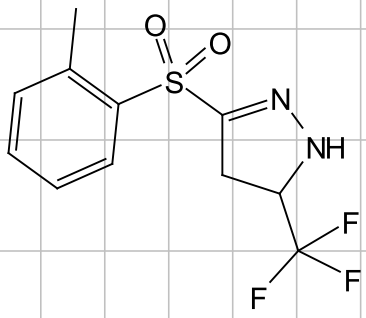


400
350
300
250
200
150
100
50
0

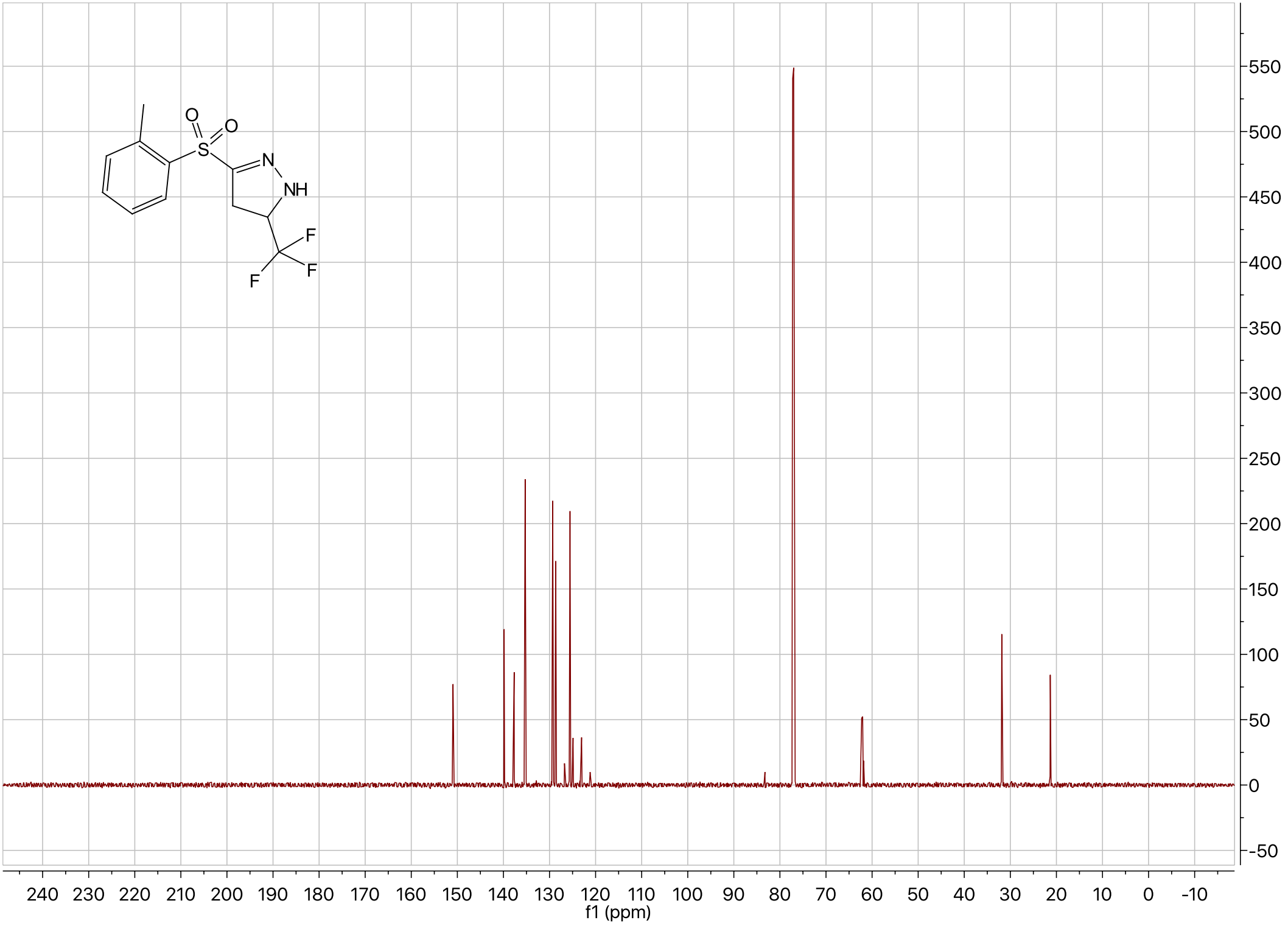
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

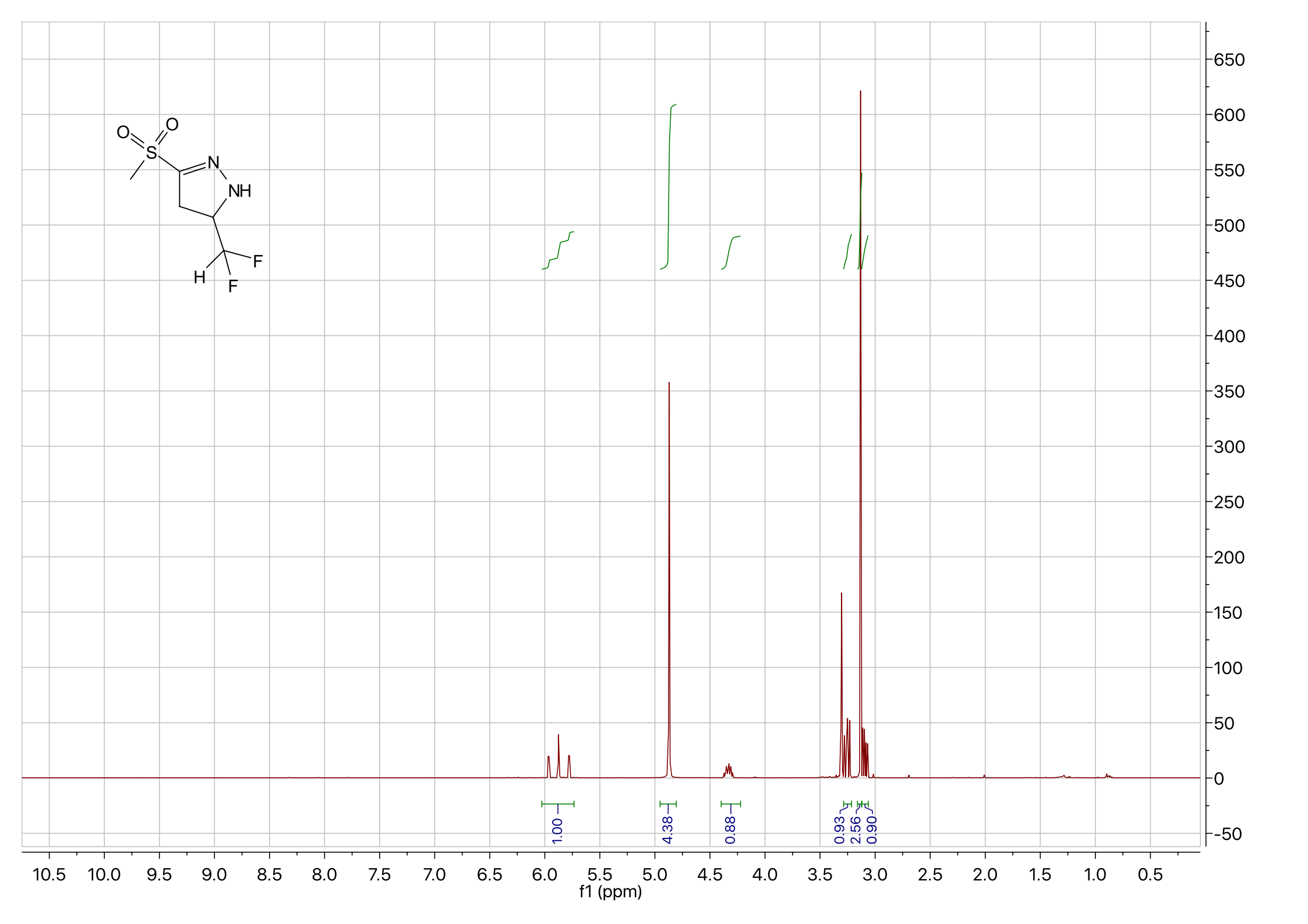
f1 (ppm)

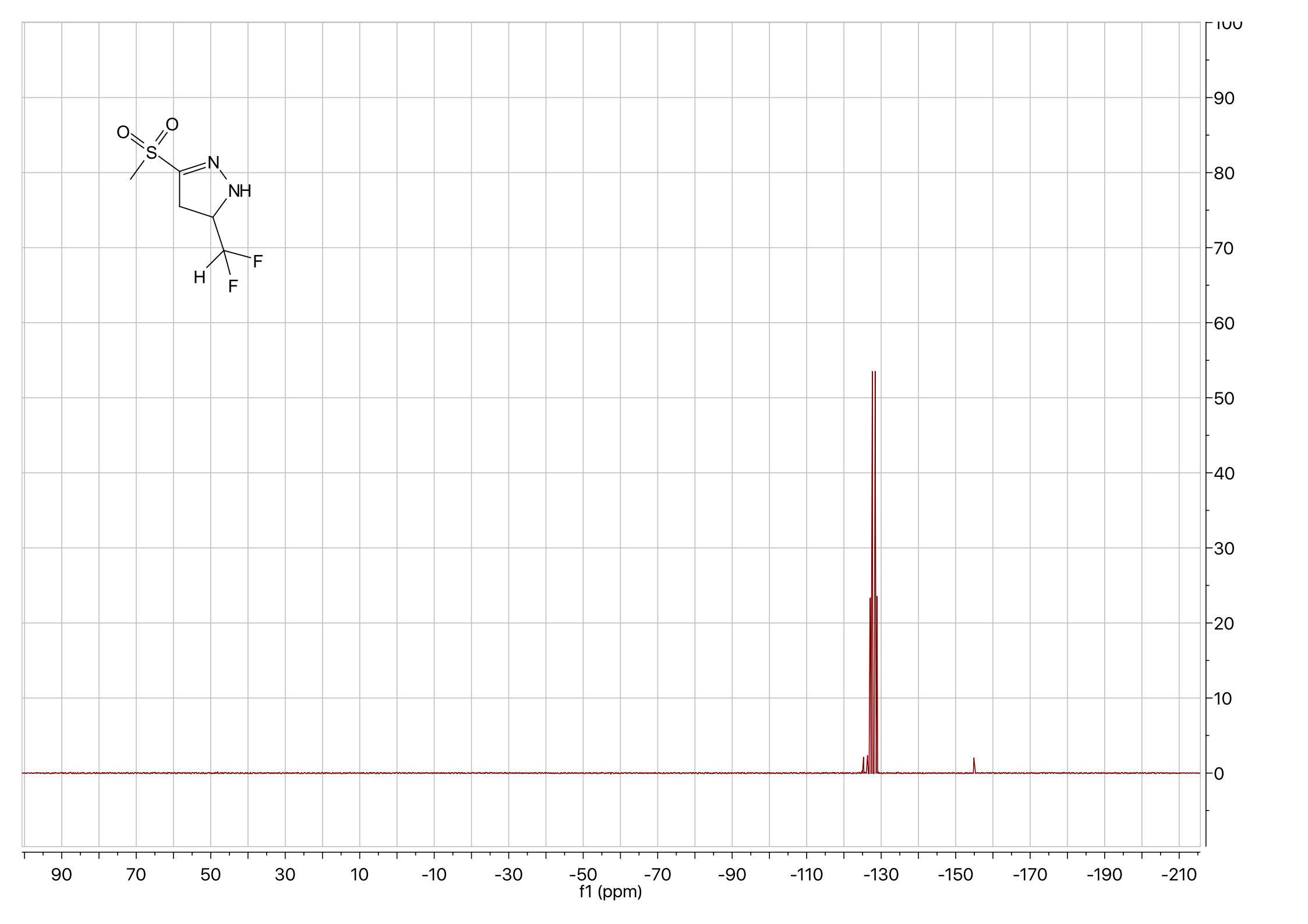

O
O
S
N
NH
F
F
F
1.76
1.87
0.94
1.01
1.00
2.97
f1 (ppm)

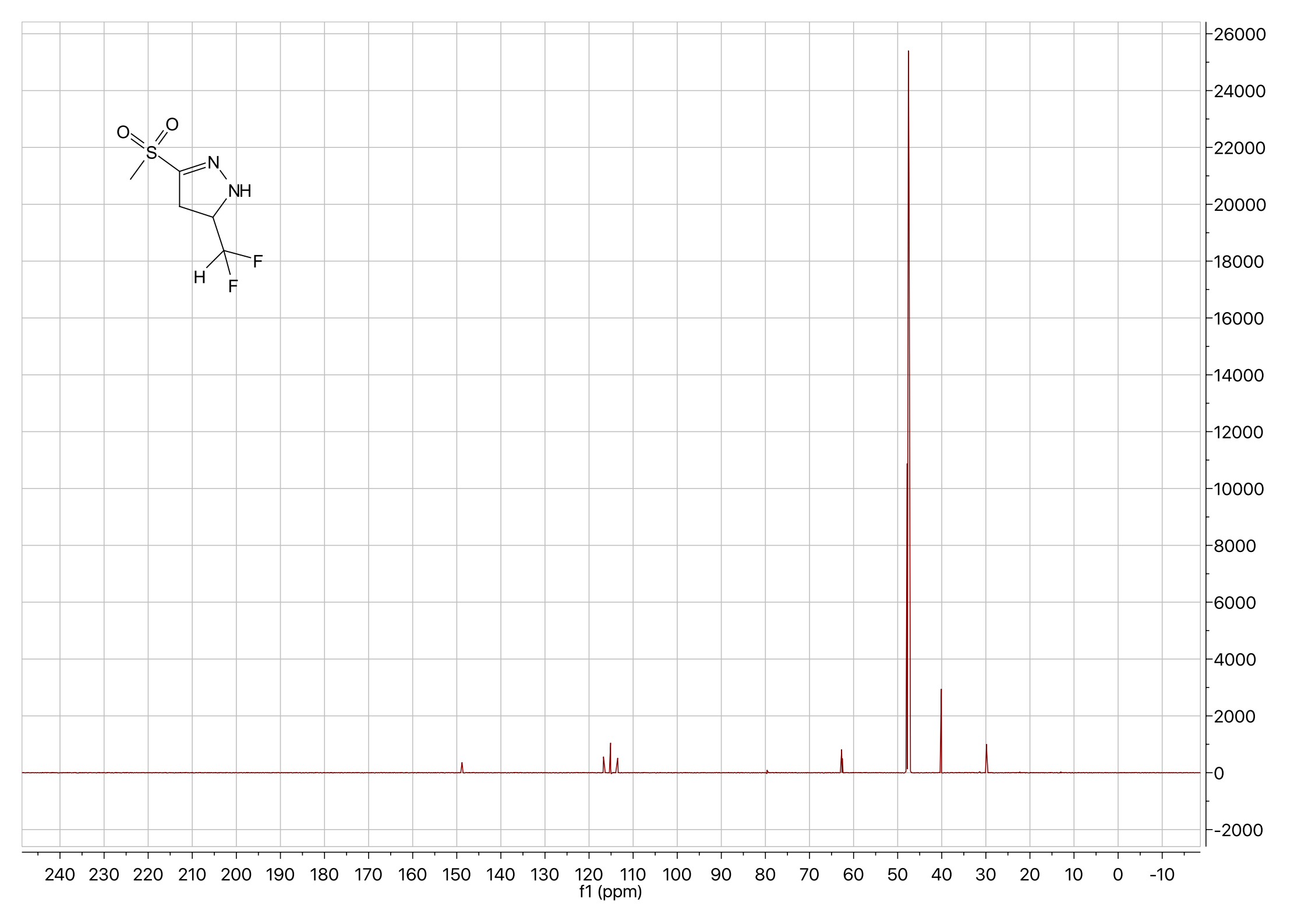

O
O
S
N
NH
F
F
F

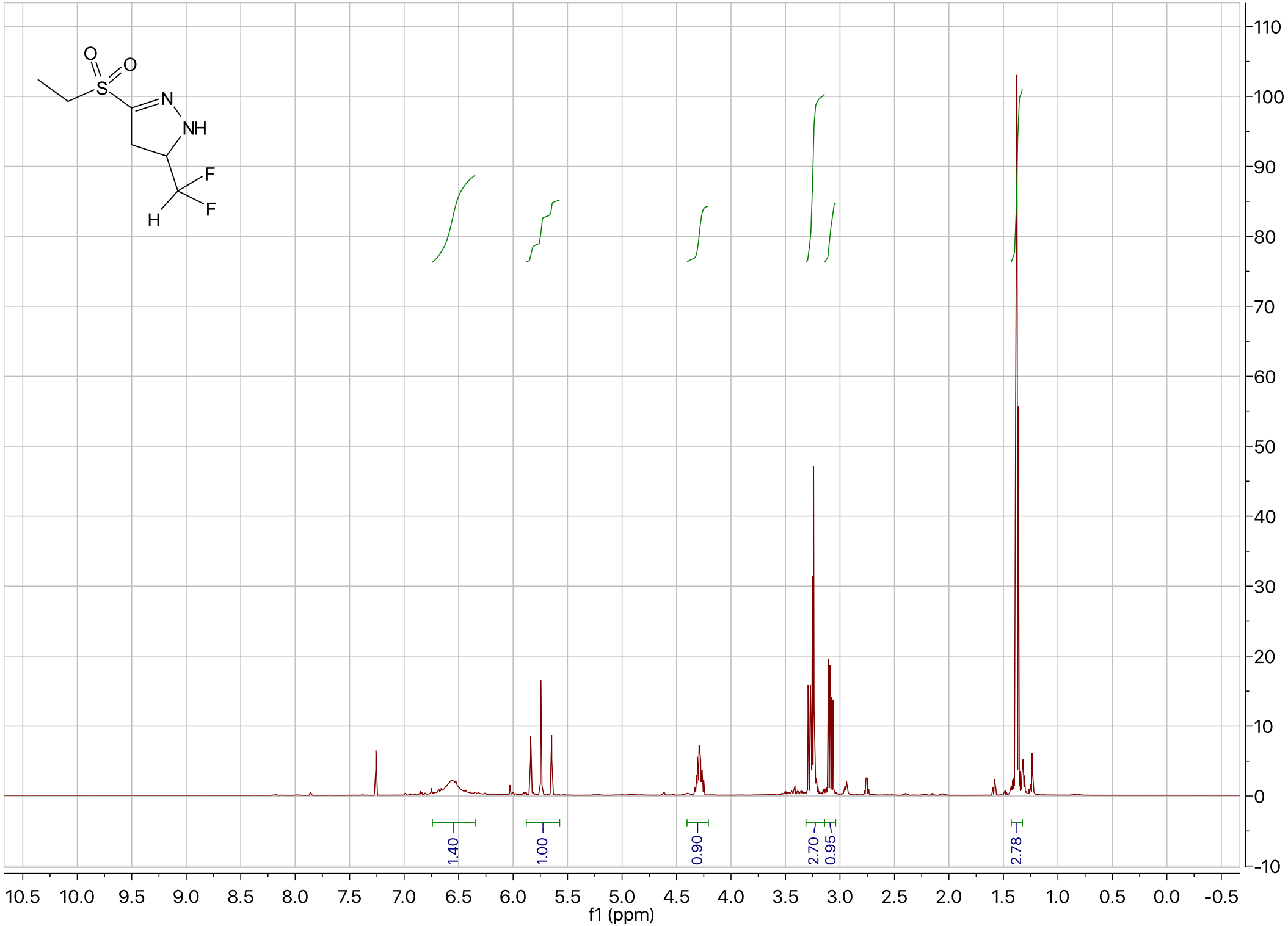
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

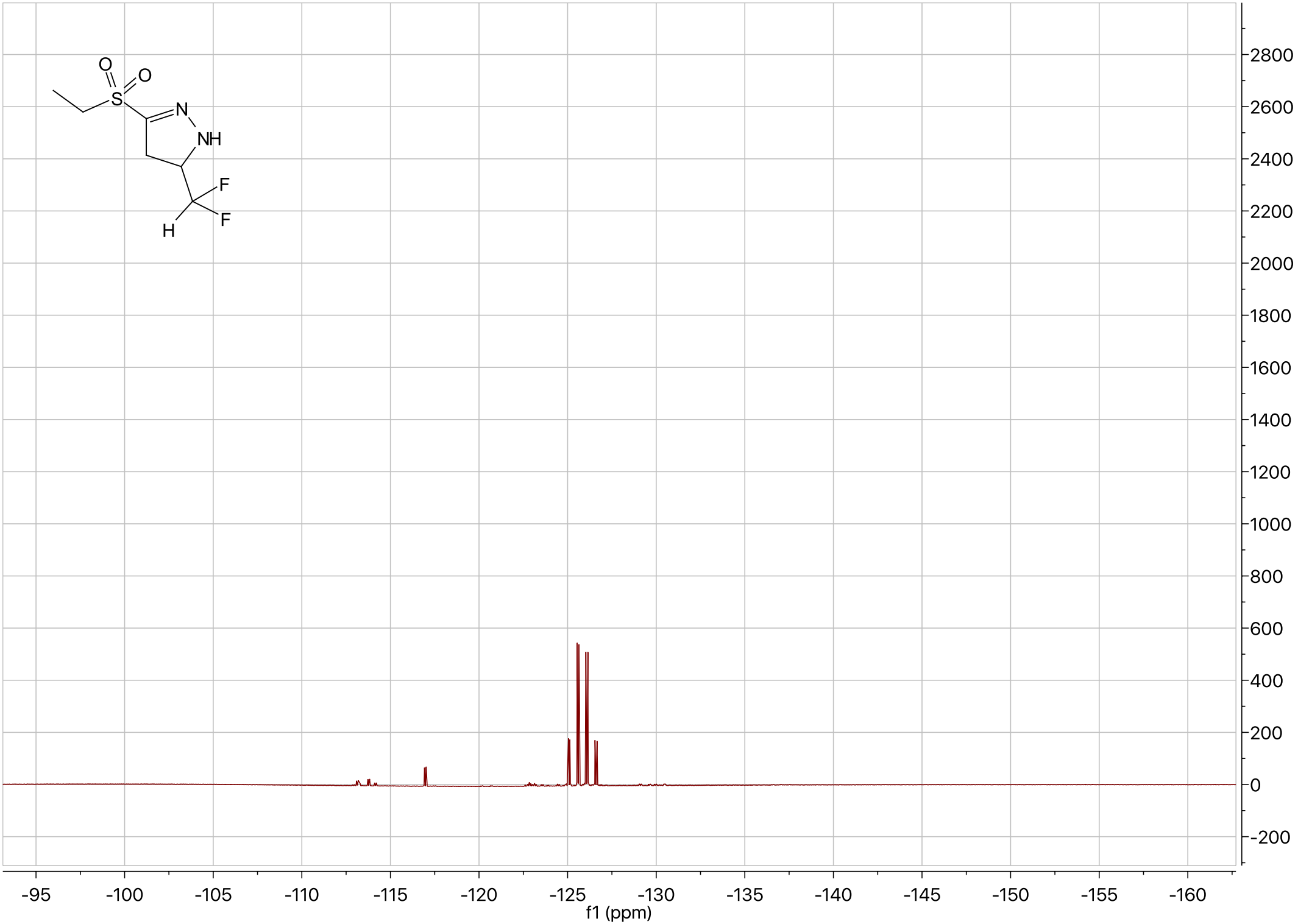

O
O
S
N
NH
F
F
F
550
500
450
400
350
300
250
200
150
100
50
0
-50
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

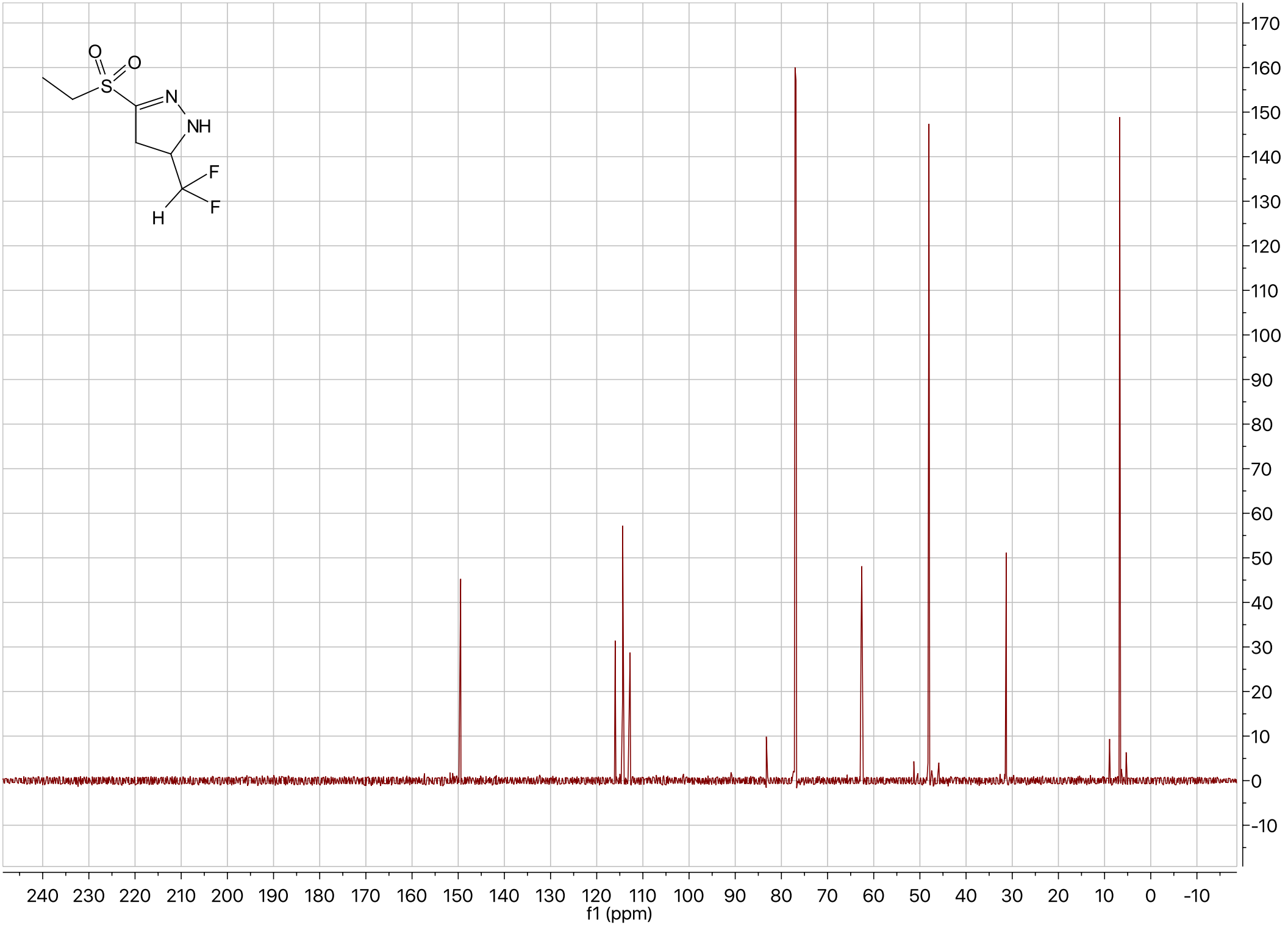

O
O
S
N
NH
F
H
F
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
1.00
4.38
0.88
0.93
2.56
0.90
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

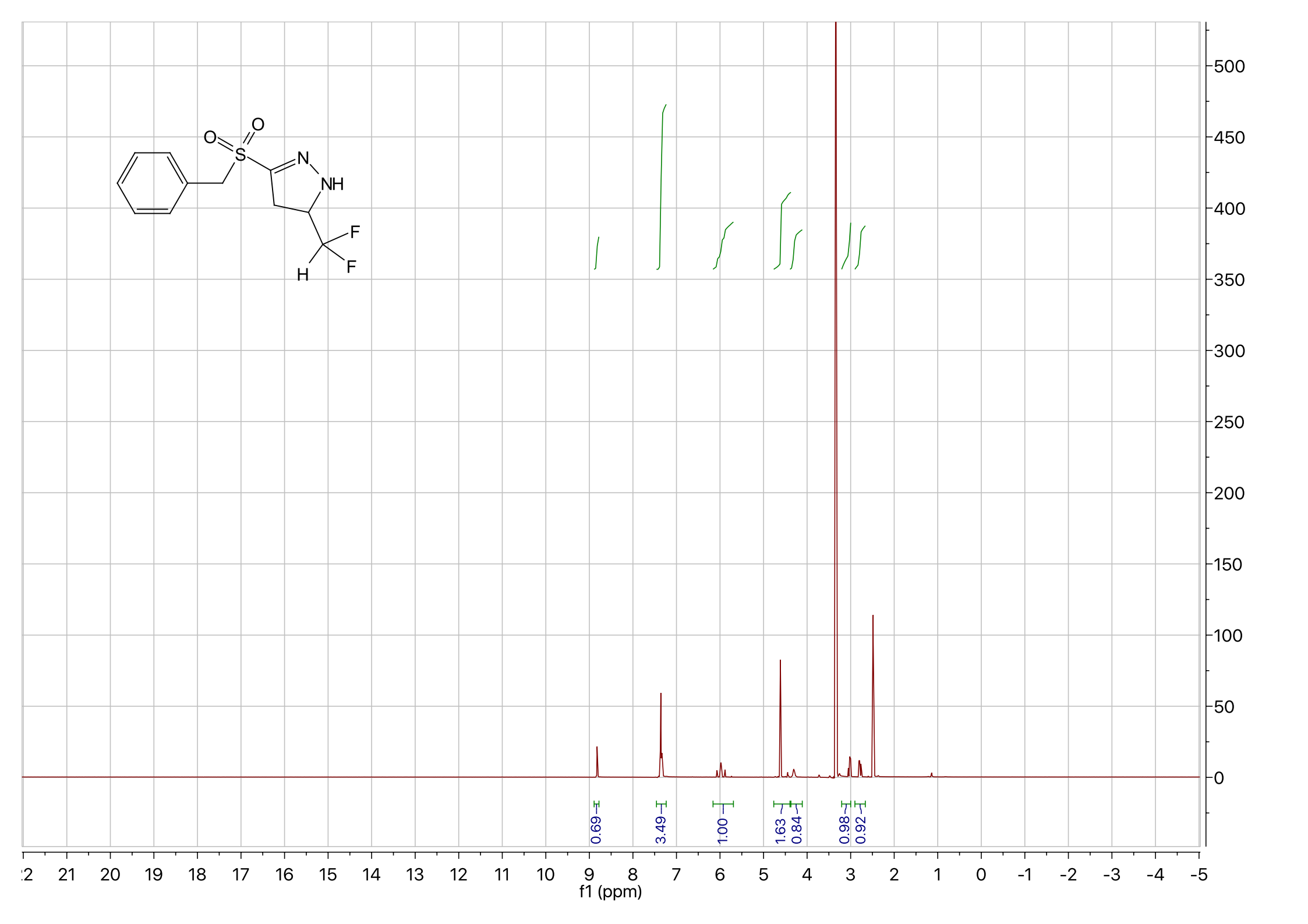

O
O
S
N
NH
F
H
F
100
90
80
70
60
50
40
30
20
10
0
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

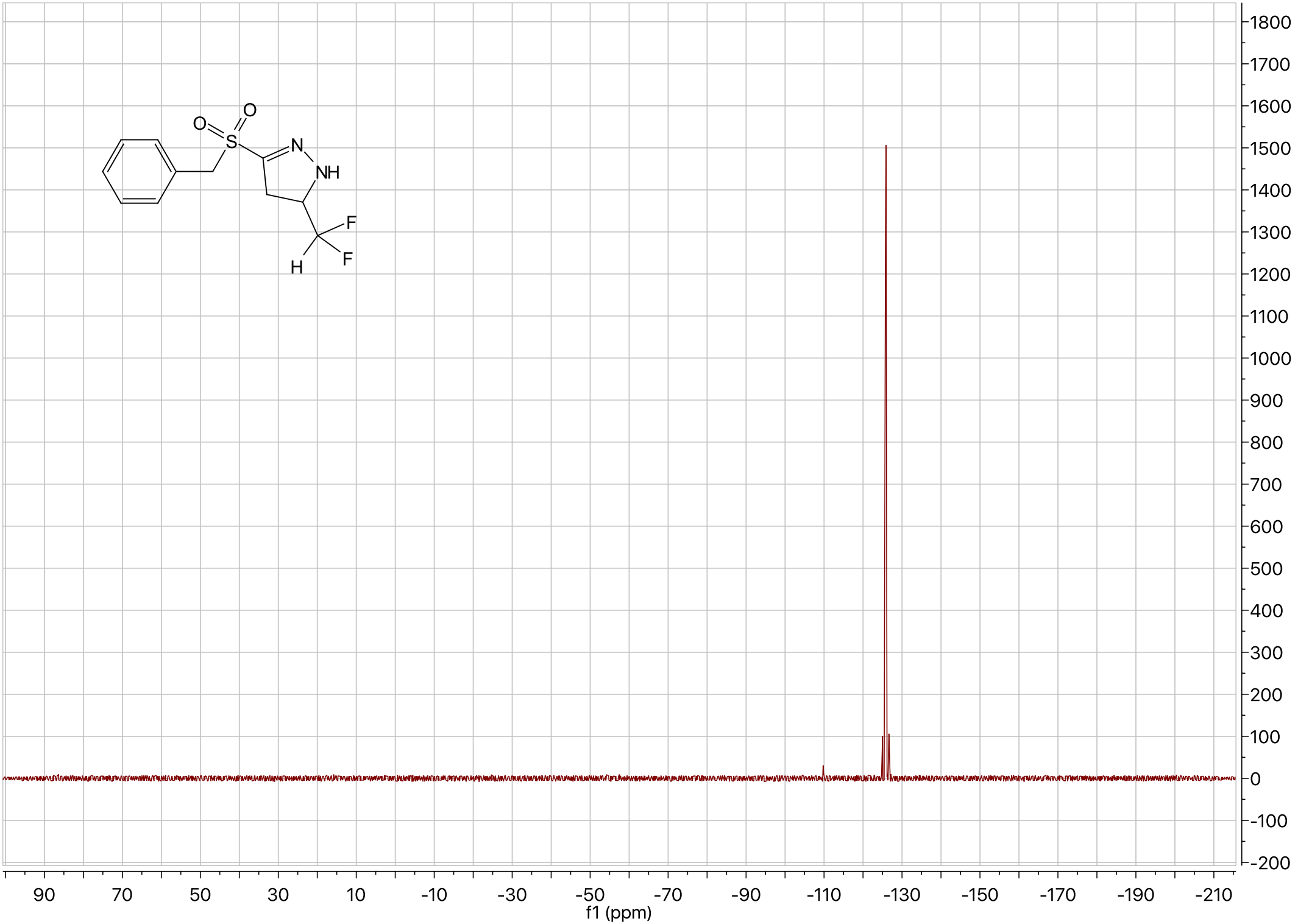

O
O
S
N
NH
F
H
F
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

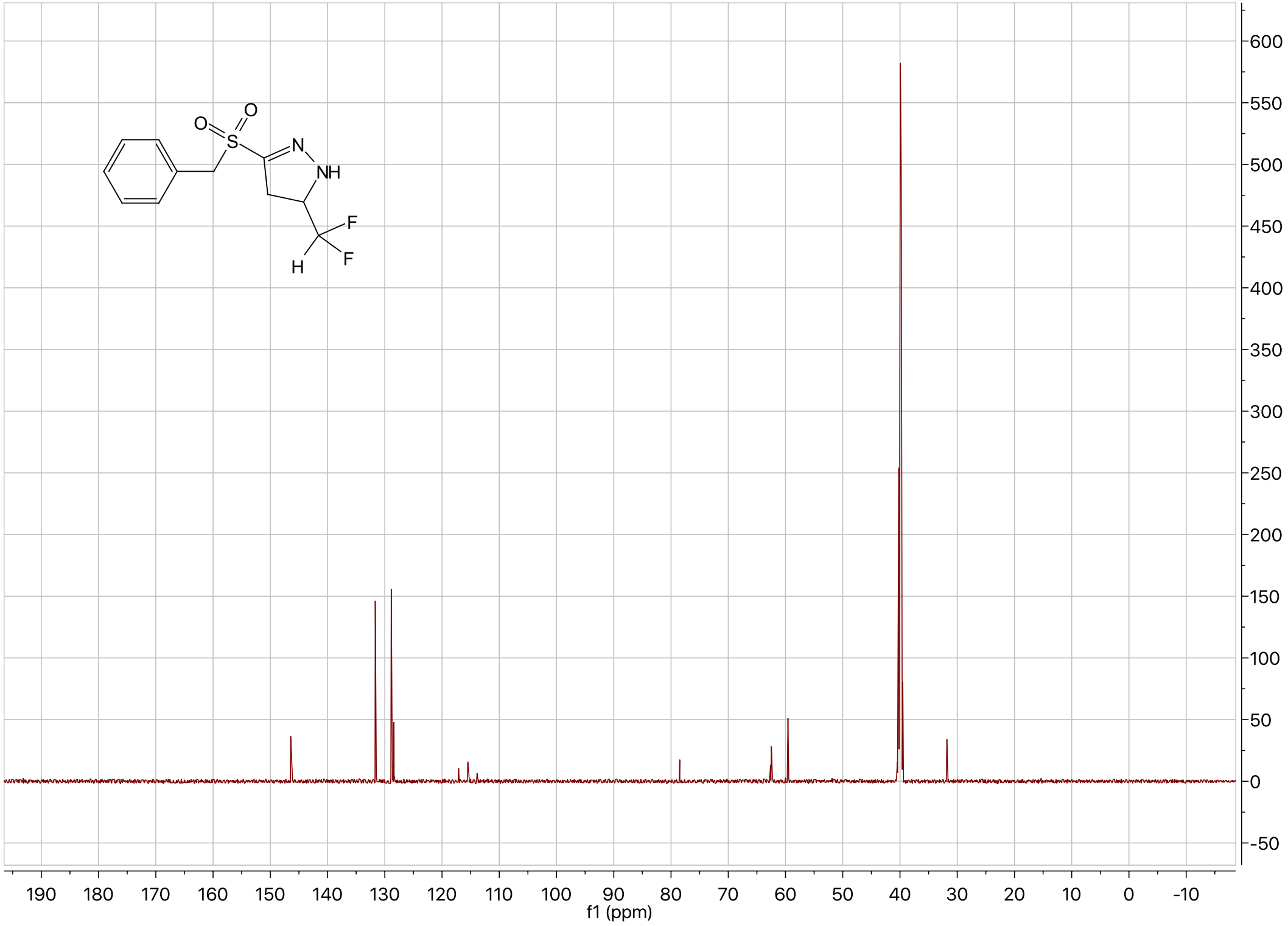

O
O
S
N
NH
F
F
H
1.40
1.00
0.90
2.70
0.95
2.78
f1 (ppm)

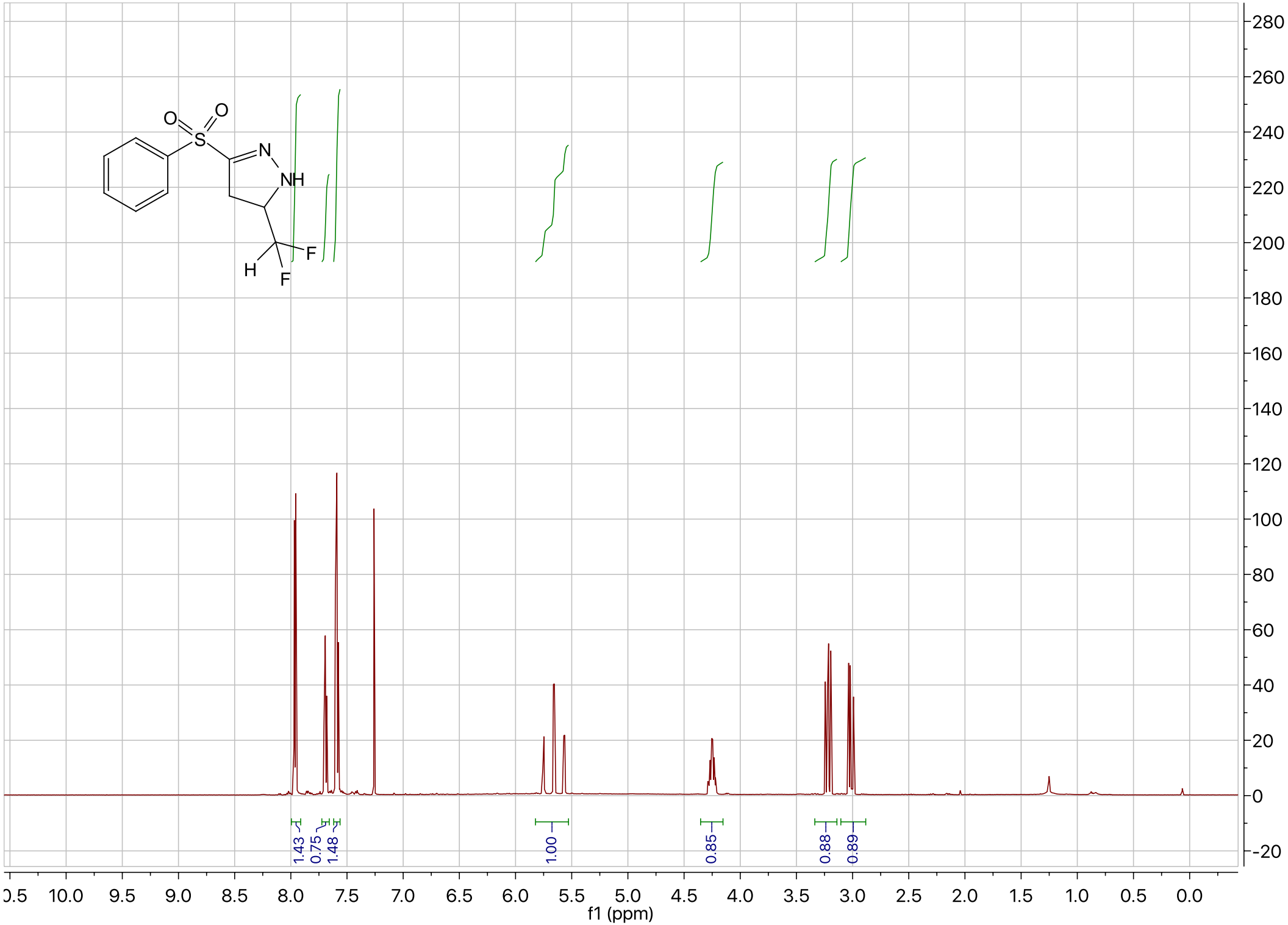

O
O
S
N
NH
F
F
H
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
f1 (ppm)

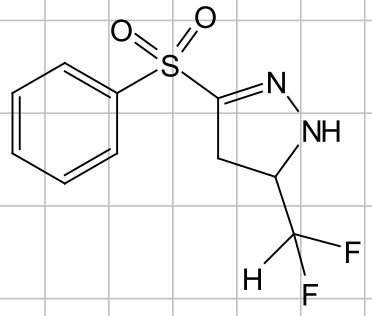

O
O
S
N
NH
F
F
H
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
O
S
N
NH
F
F
H
0.69
3.49
1.00
1.63
0.84
0.98
0.92
f1 (ppm)


O
O
S
N
NH
F
F
H
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)


O
O
S
N
NH
F
F
H
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

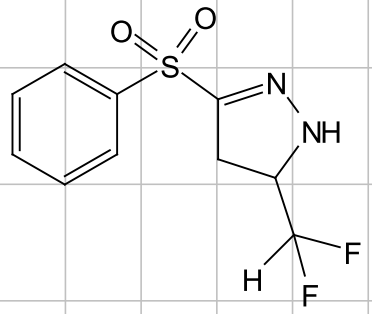

O
O
S
N
NH
F
H
F
1.43
0.75
1.48
1.00
0.85
0.88
0.89
f1 (ppm)



65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5

90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210

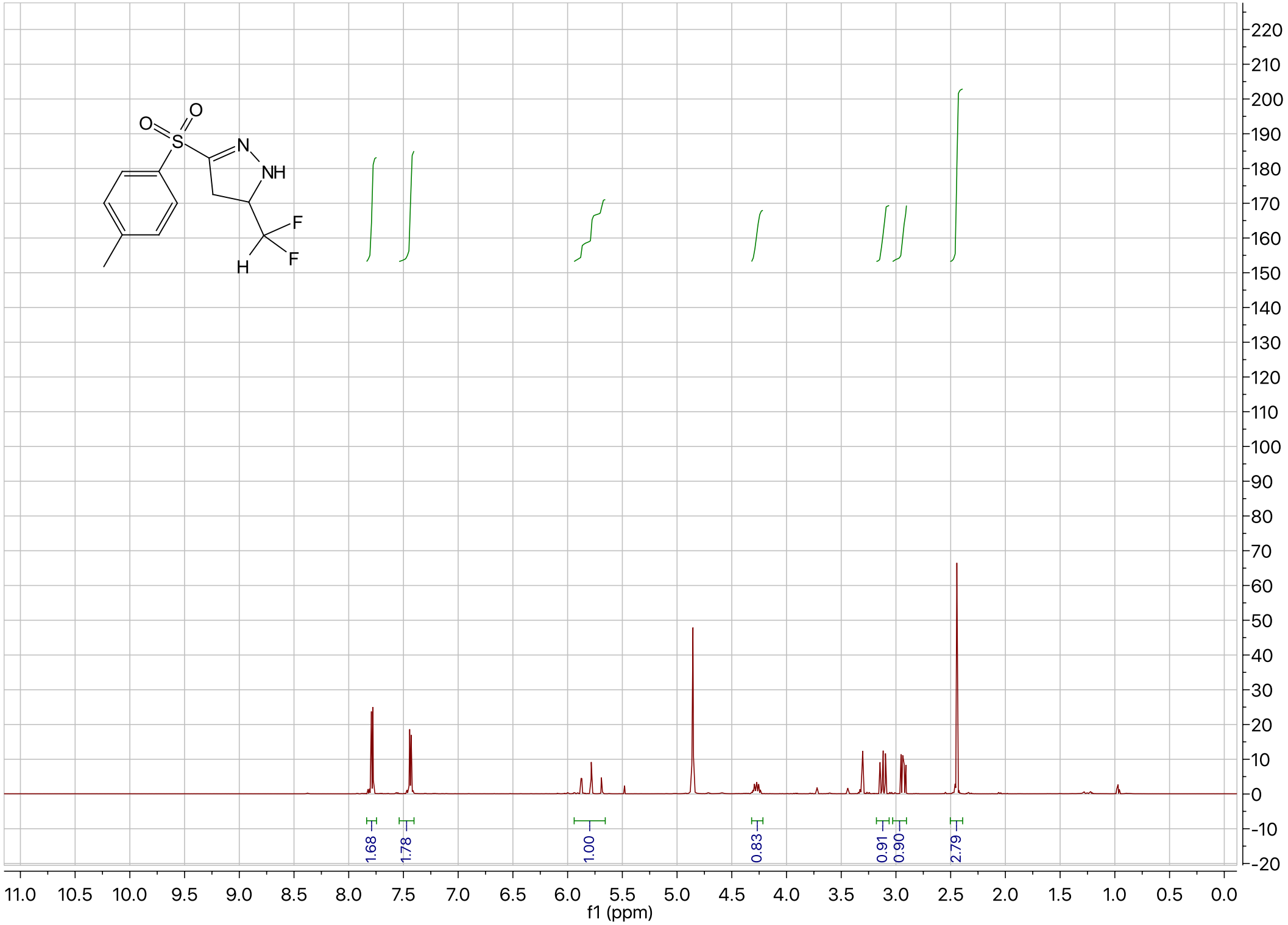
f1 (ppm)

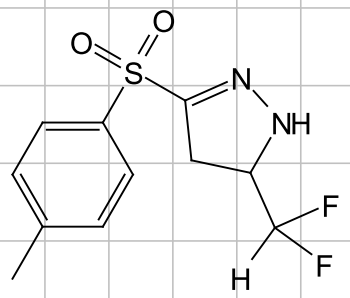


500
450
400
350
300
250
200
150
100
50
0
-50

240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

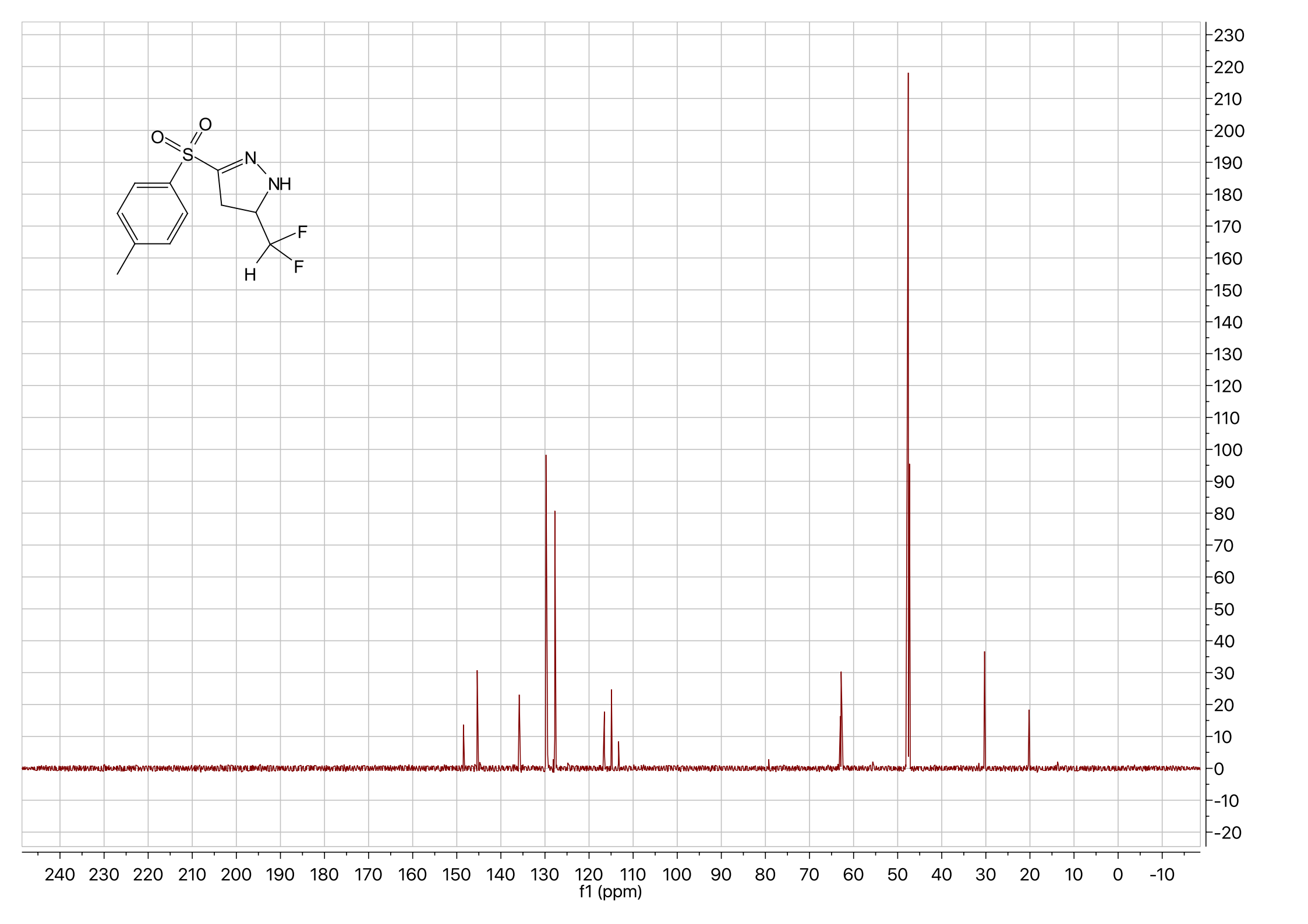

O
O
S
N
NH
F
F
H
1.68
1.78
1.00
0.83
0.91
0.90
2.79
f1 (ppm)

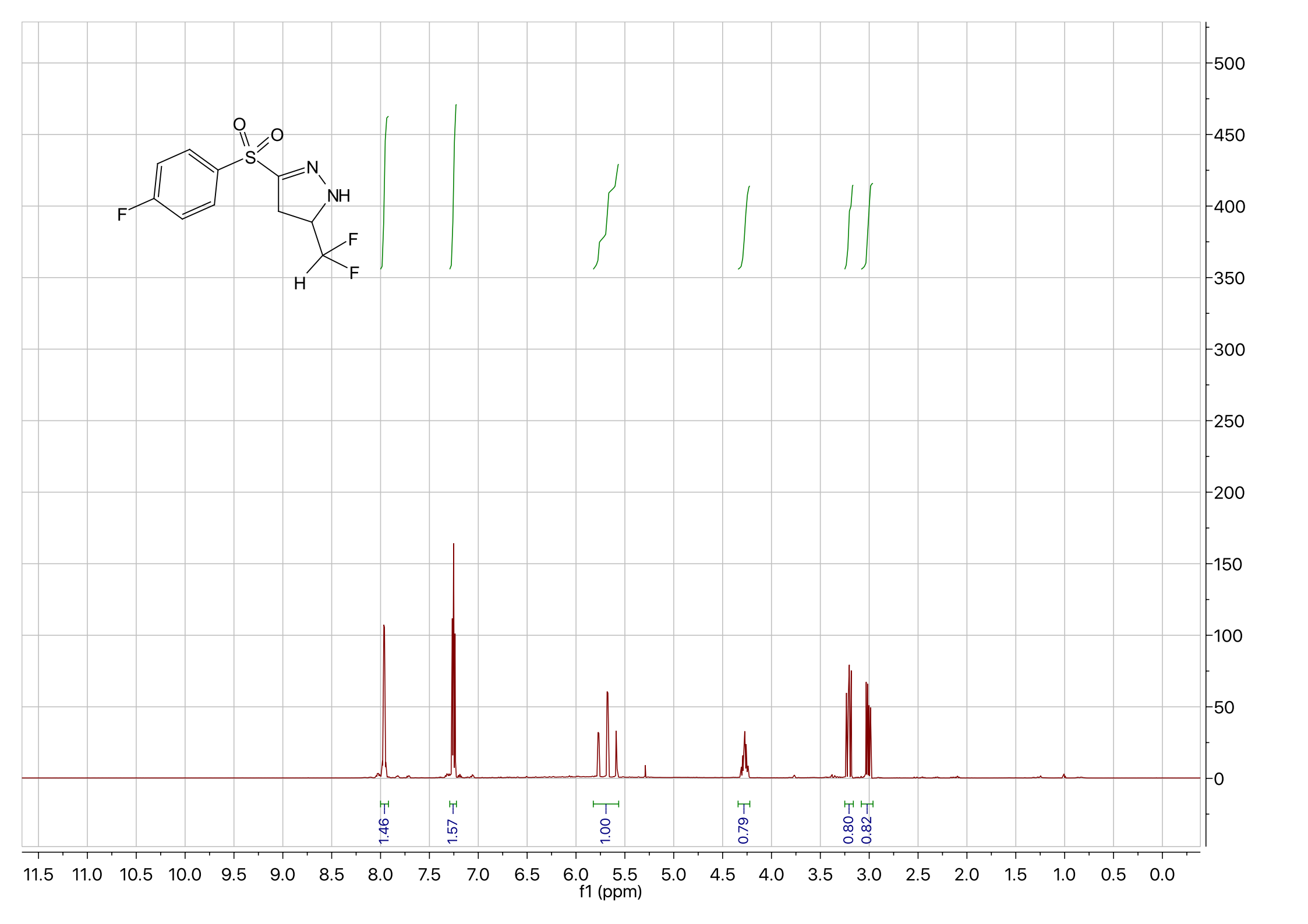


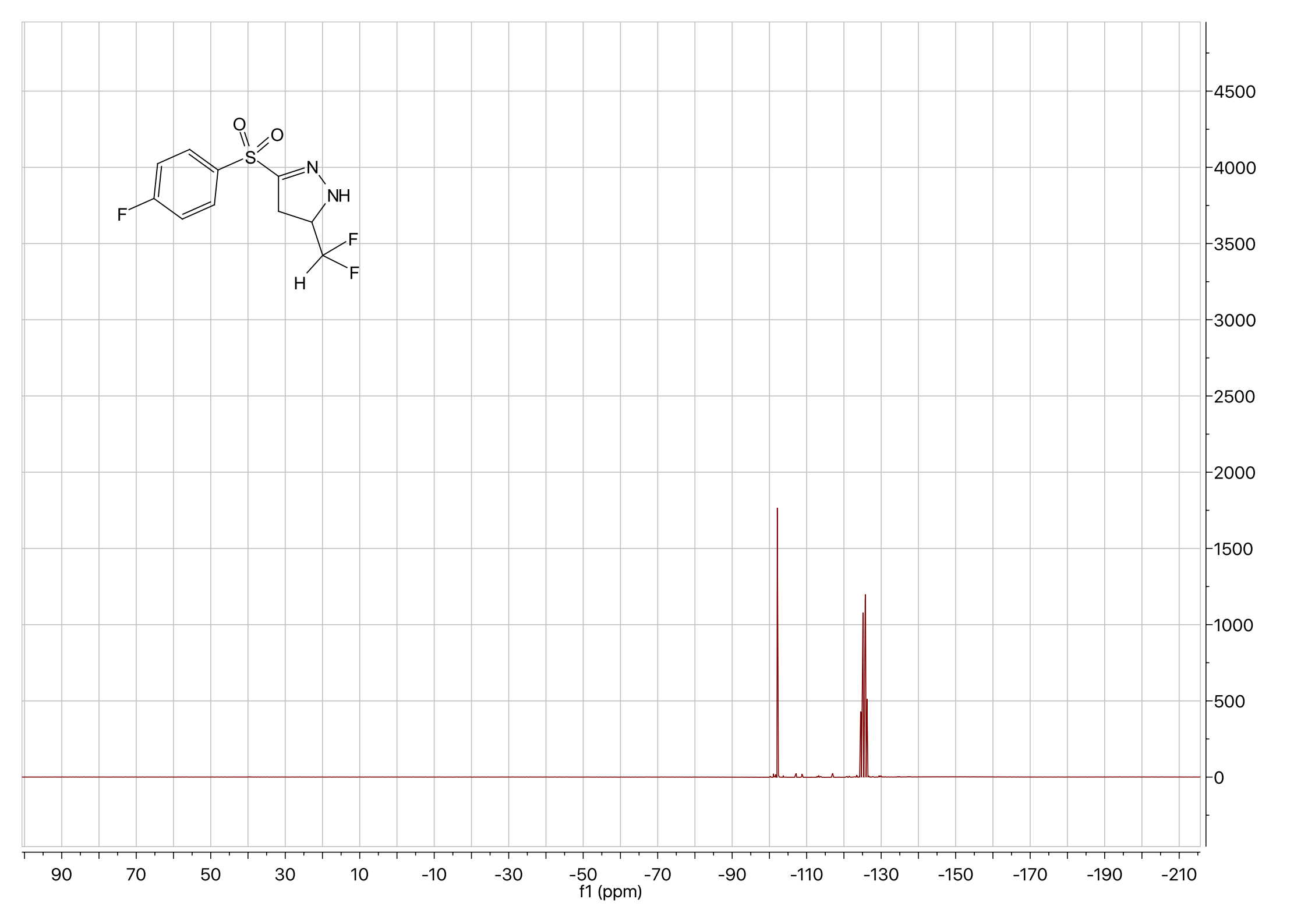
85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5

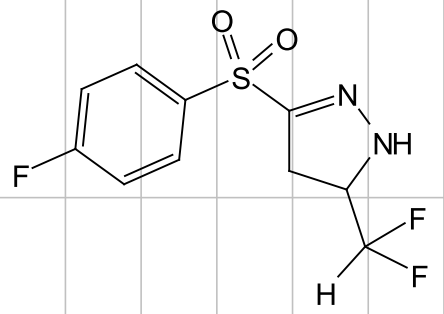
90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210

f1 (ppm)


O
O
S
N
NH
F
F
H
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
O
S
N
NH
F
F
F
H
1.46
1.57
1.00
0.79
0.80
0.82
500
450
400
350
300
250
200
150
100
50
0
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

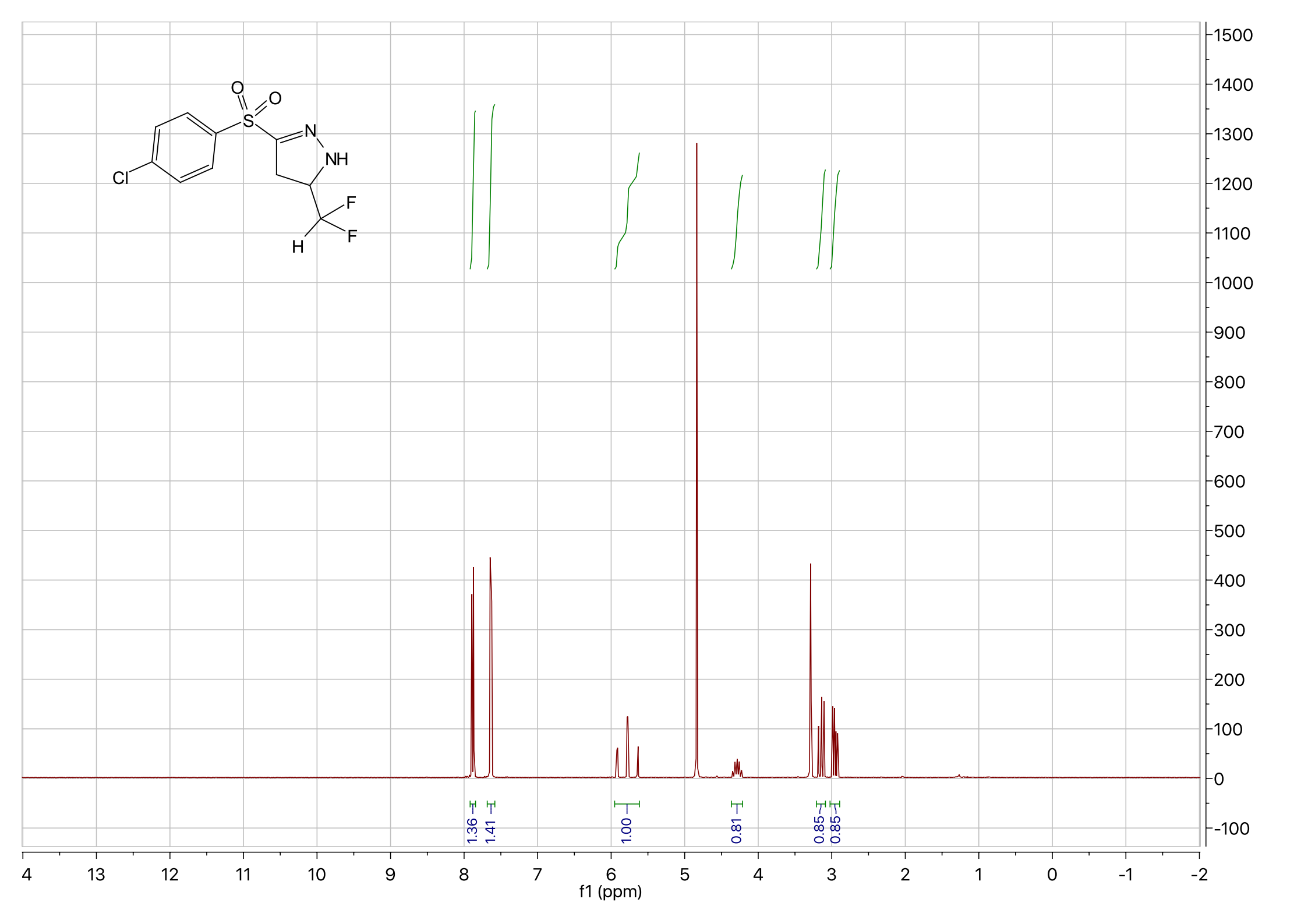

O
O
S
N
NH
F
F
F
H
4500
4000
3500
3000
2500
2000
1500
1000
500
0
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

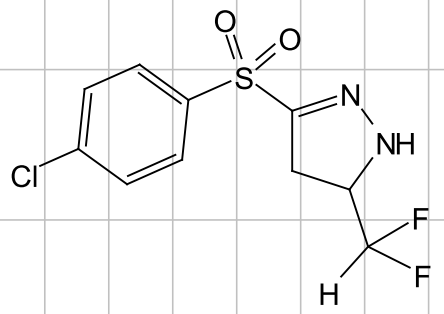


250
200
150
100
50
0

240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

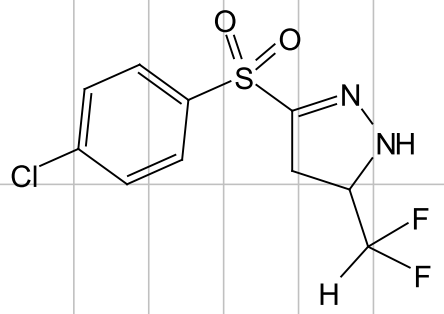

O
O
S
N
NH
Cl
F
F
H
1.36
1.41
1.00
0.81
0.85
0.85
f1 (ppm)



4000
3500
3000
2500
2000
1500
1000
500
0

90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210

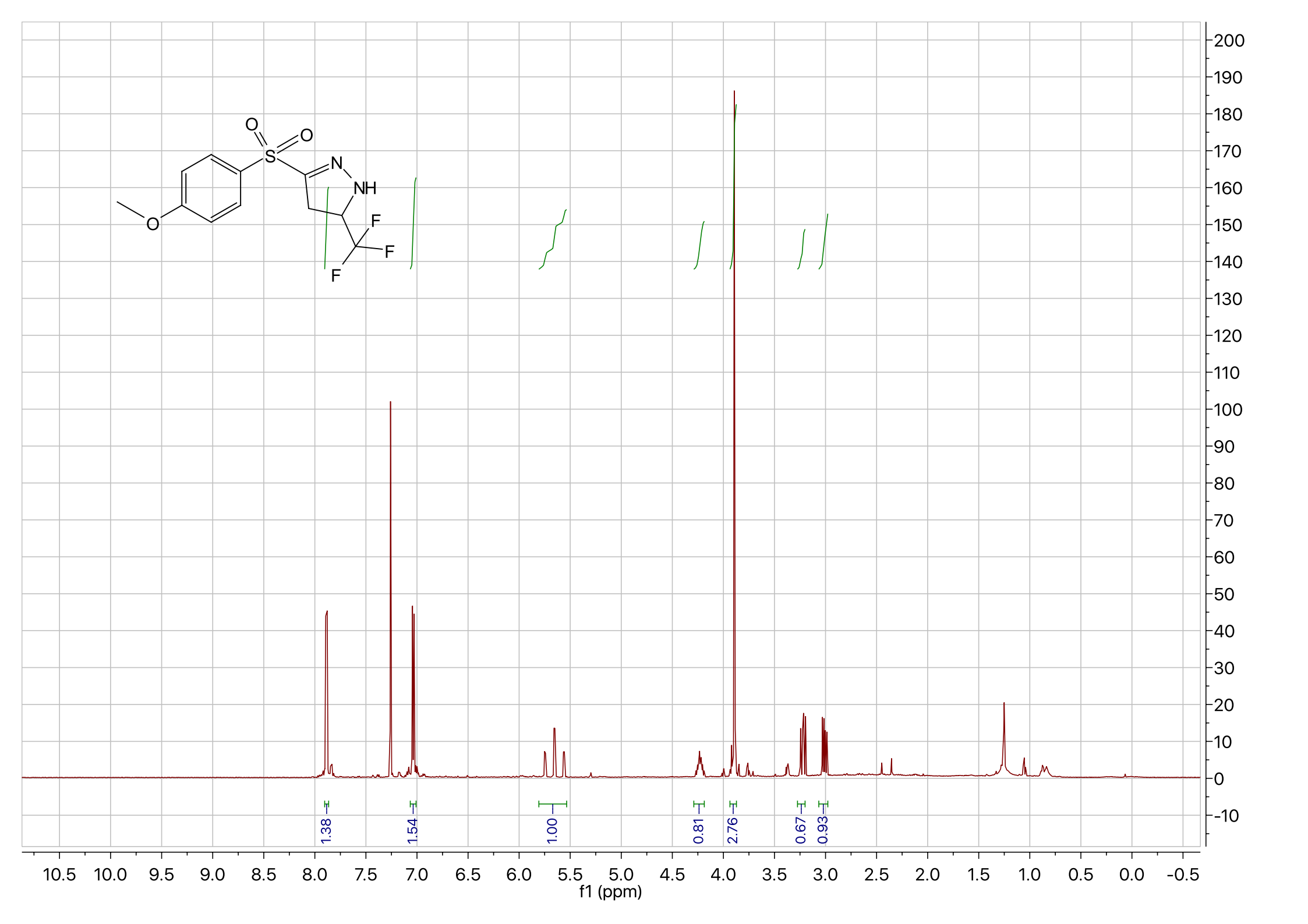
f1 (ppm)

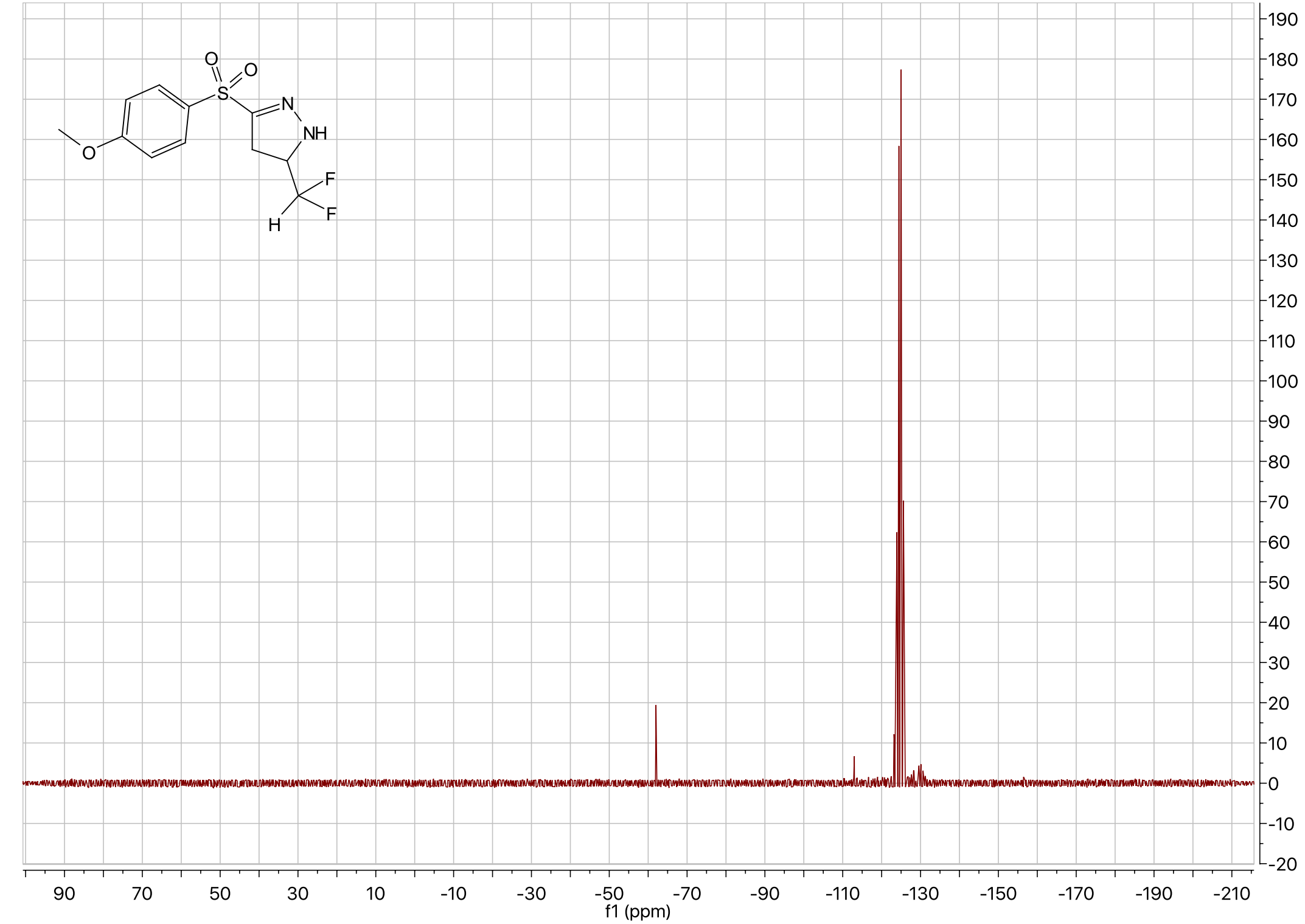


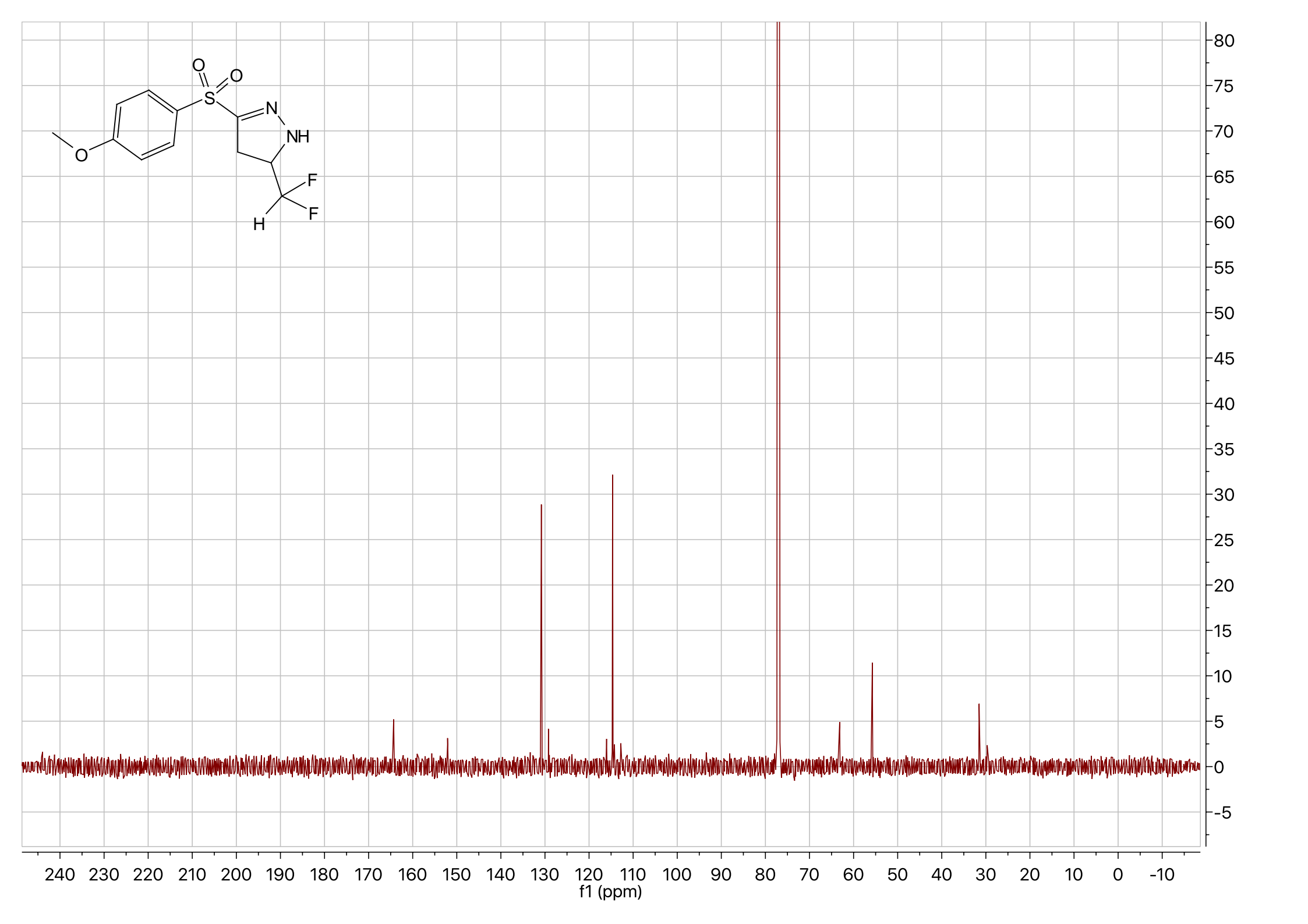
250
200
150
100
50
0

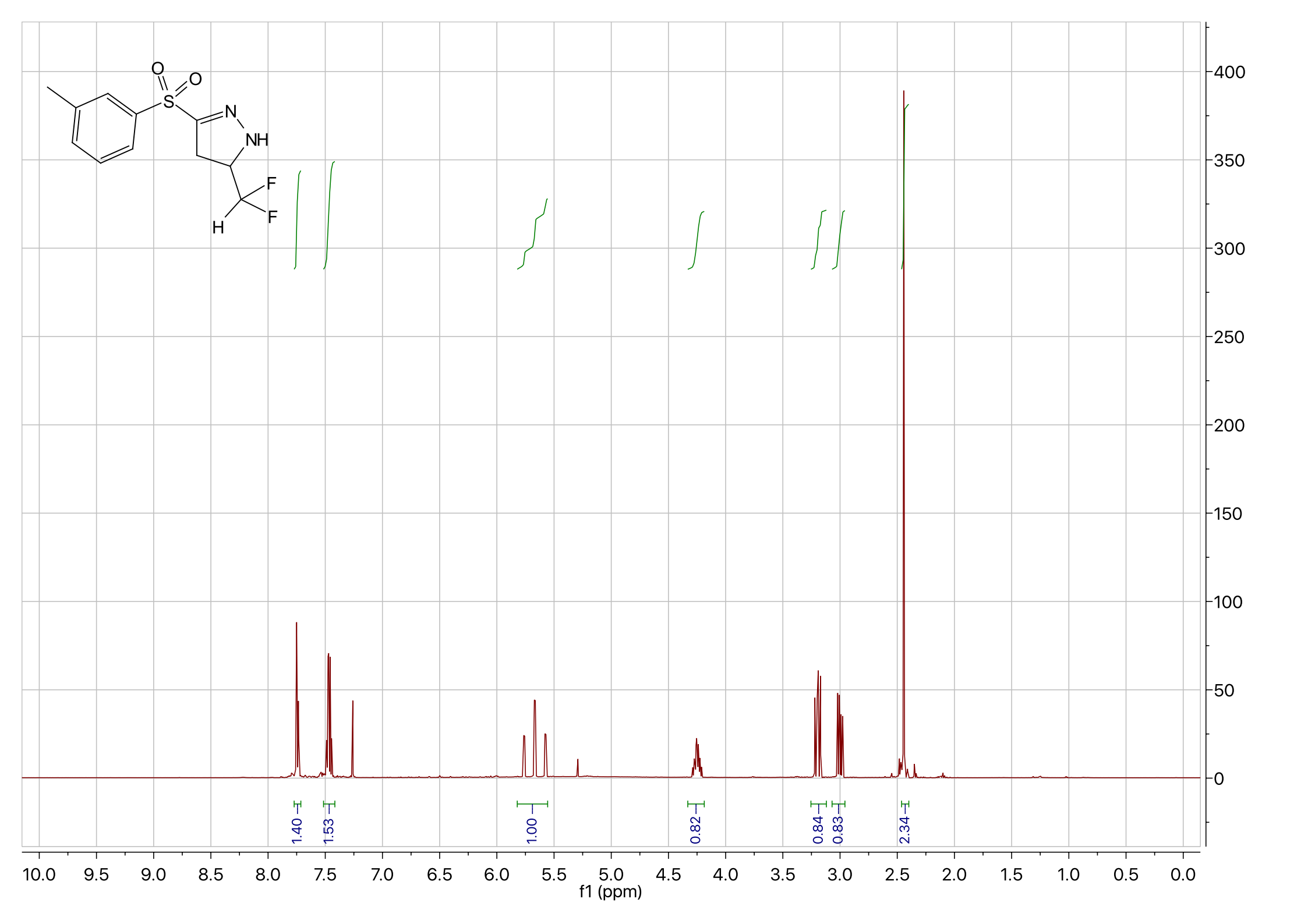
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20

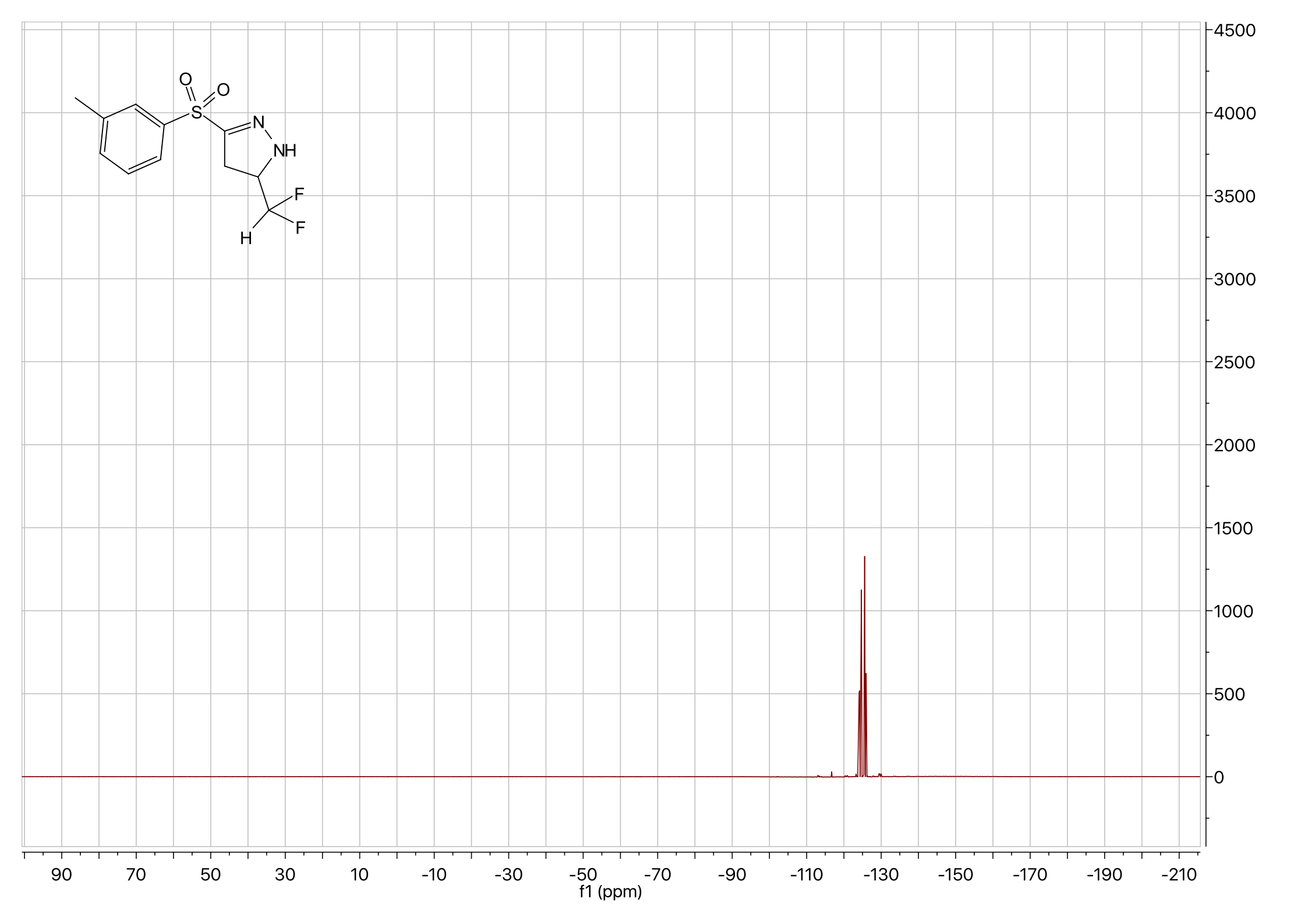
f1 (ppm)

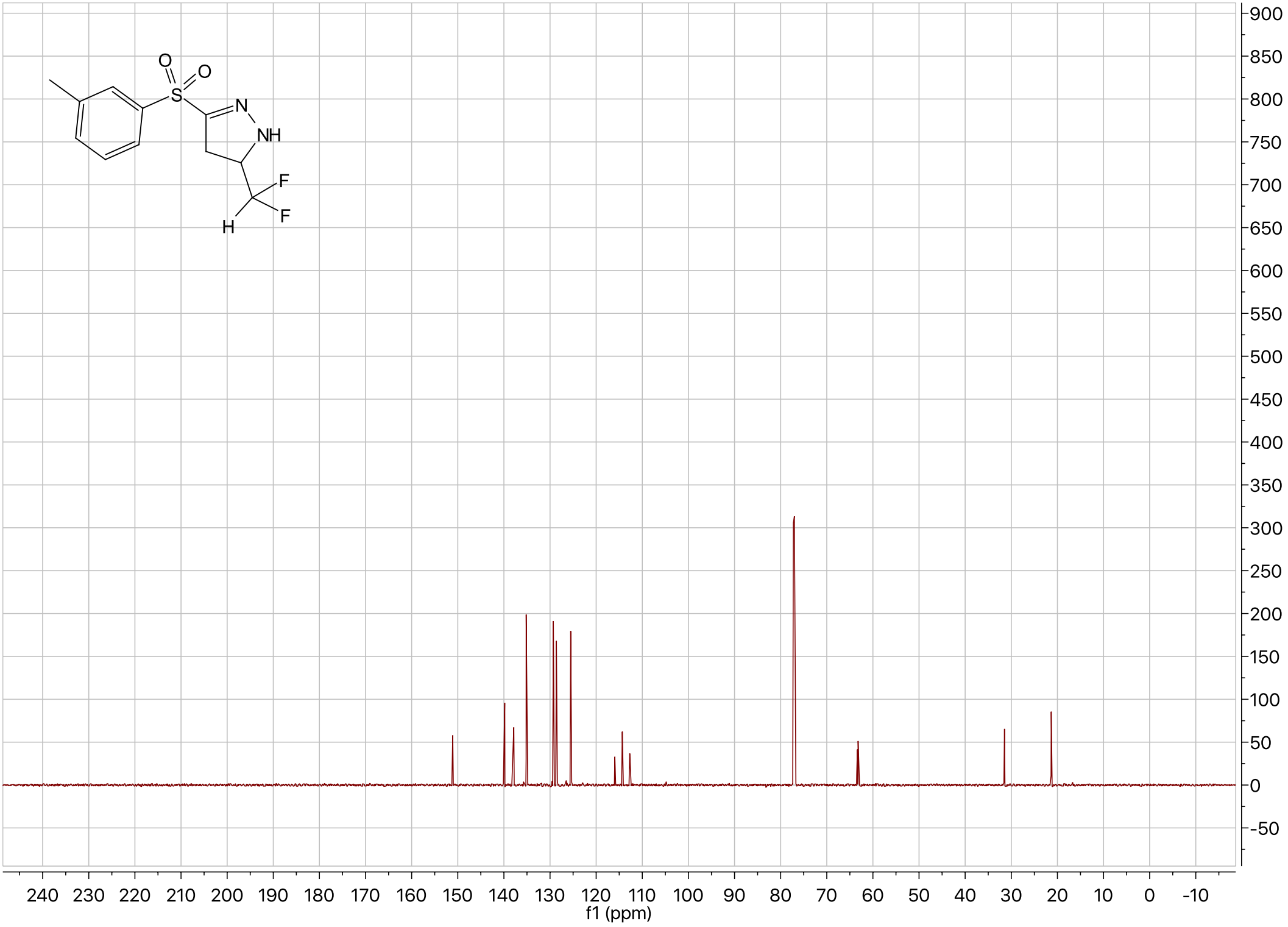

O
O
S
N
NH
O
F
F
F
1.38
1.54
1.00
0.81
2.76
0.67
0.93
f1 (ppm)

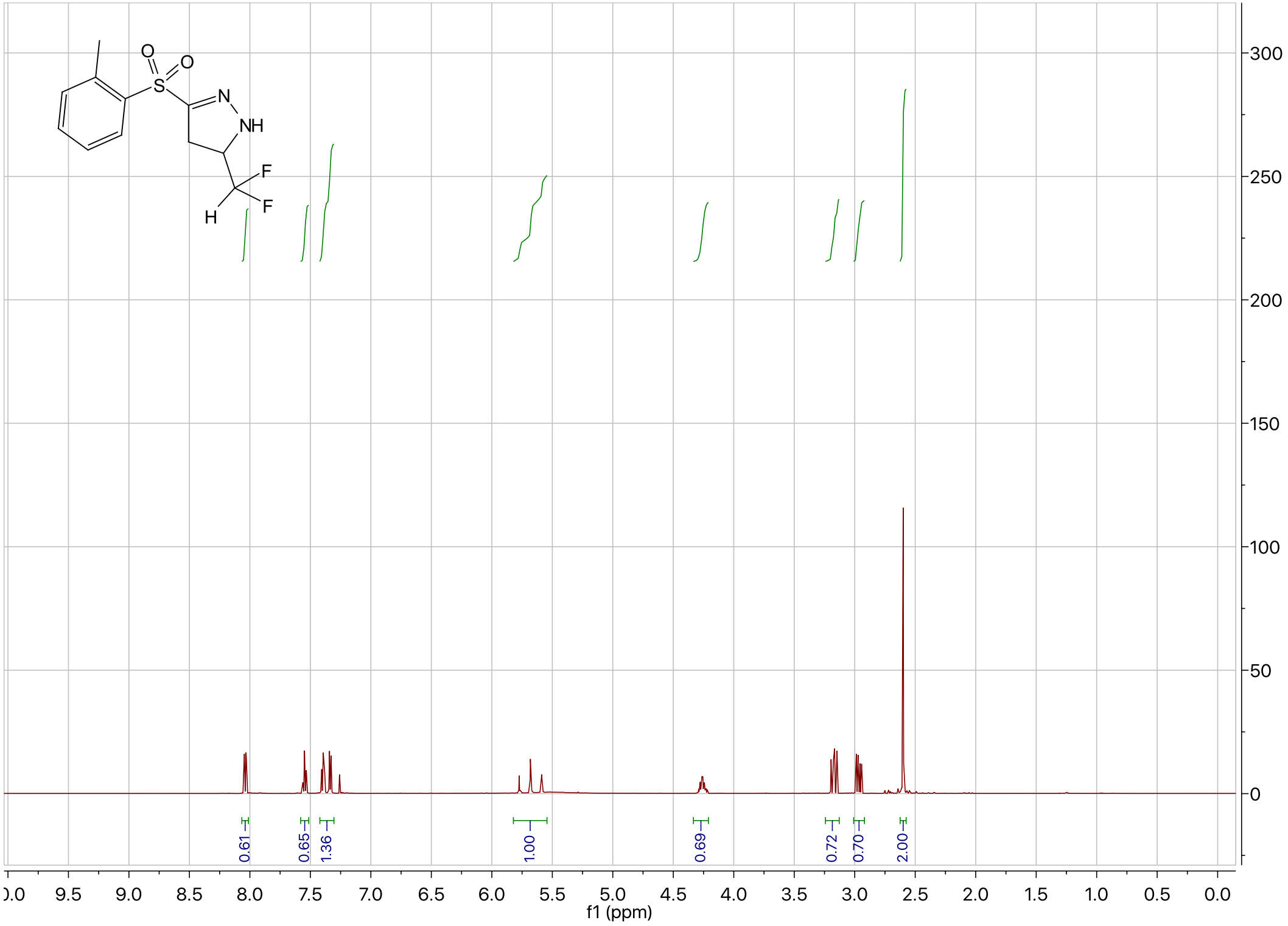

O
O
S
N
NH
O
F
F
H
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

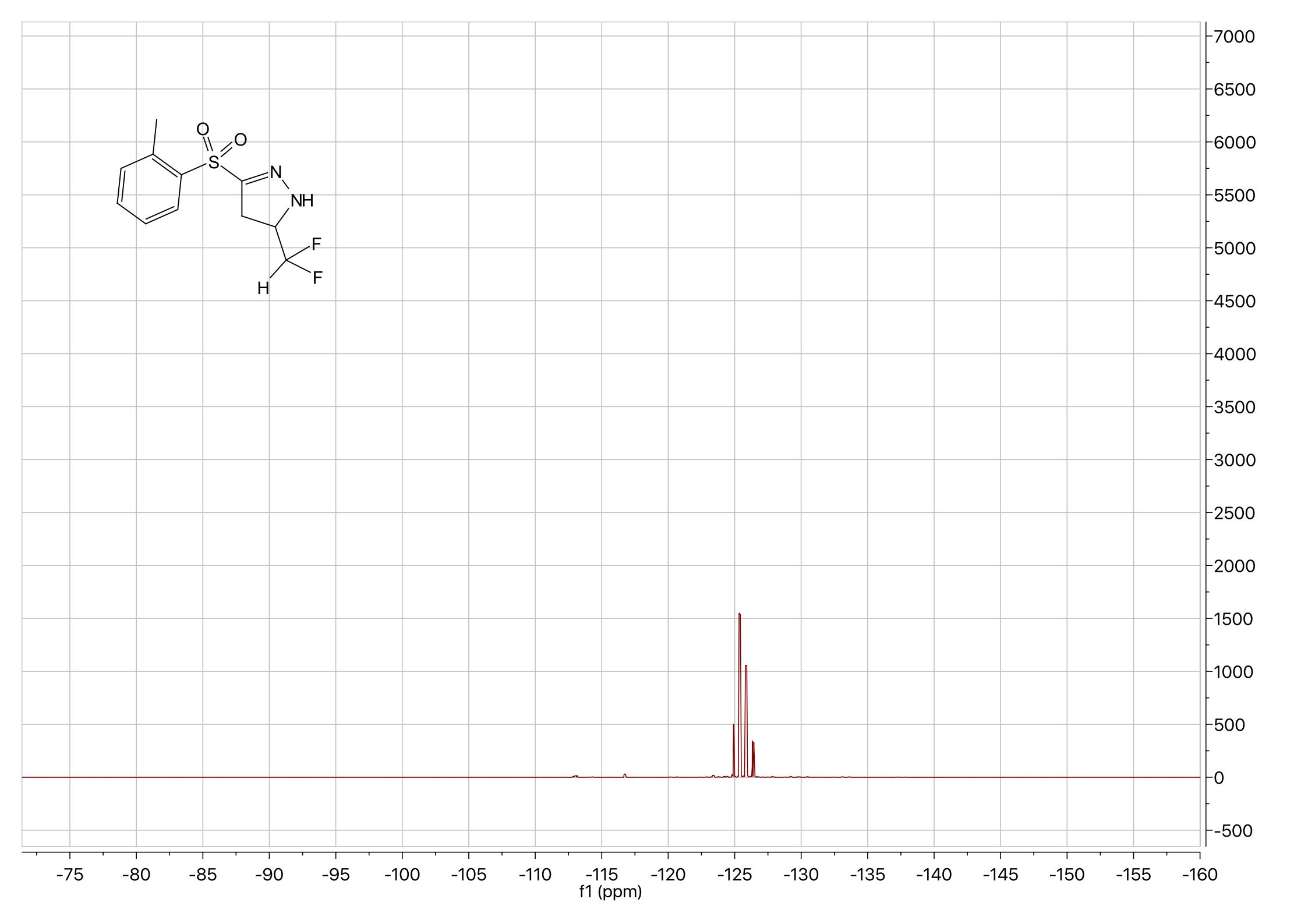

O
O
S
N
NH
O
F
F
H
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

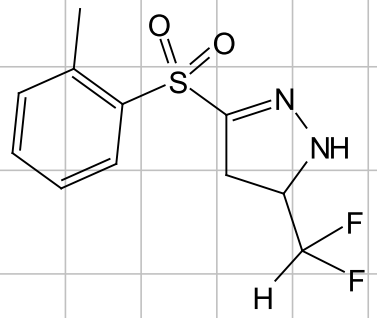

O
O
S
N
NH
F
F
H
1.40
1.53
1.00
0.82
0.84
0.83
2.34
400
350
300
250
200
150
100
50
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


O
O
S
N
NH
F
F
H
4500
4000
3500
3000
2500
2000
1500
1000
500
0
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)


O
O
S
N
NH
F
F
H
900
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
O
S
N
NH
F
F
H
0.61
0.65
1.36
1.00
0.69
0.72
0.70
2.00
300
250
200
150
100
50
0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

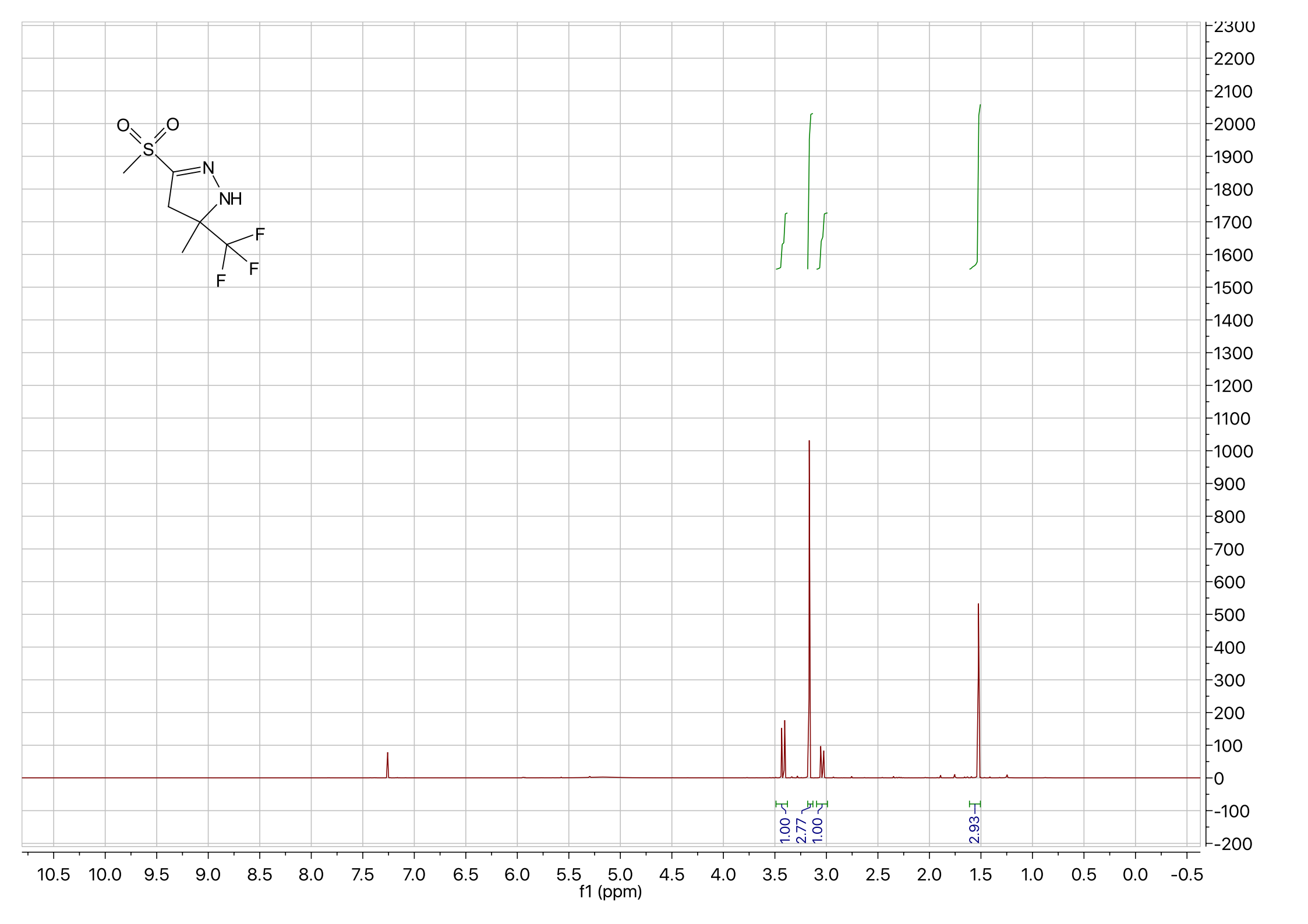

O
O
S
N
NH
F
F
H
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
f1 (ppm)

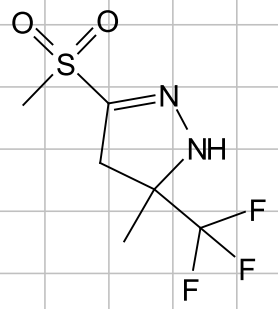


600
550
500
450
400
350
300
250
200
150
100
50
0
-50

240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

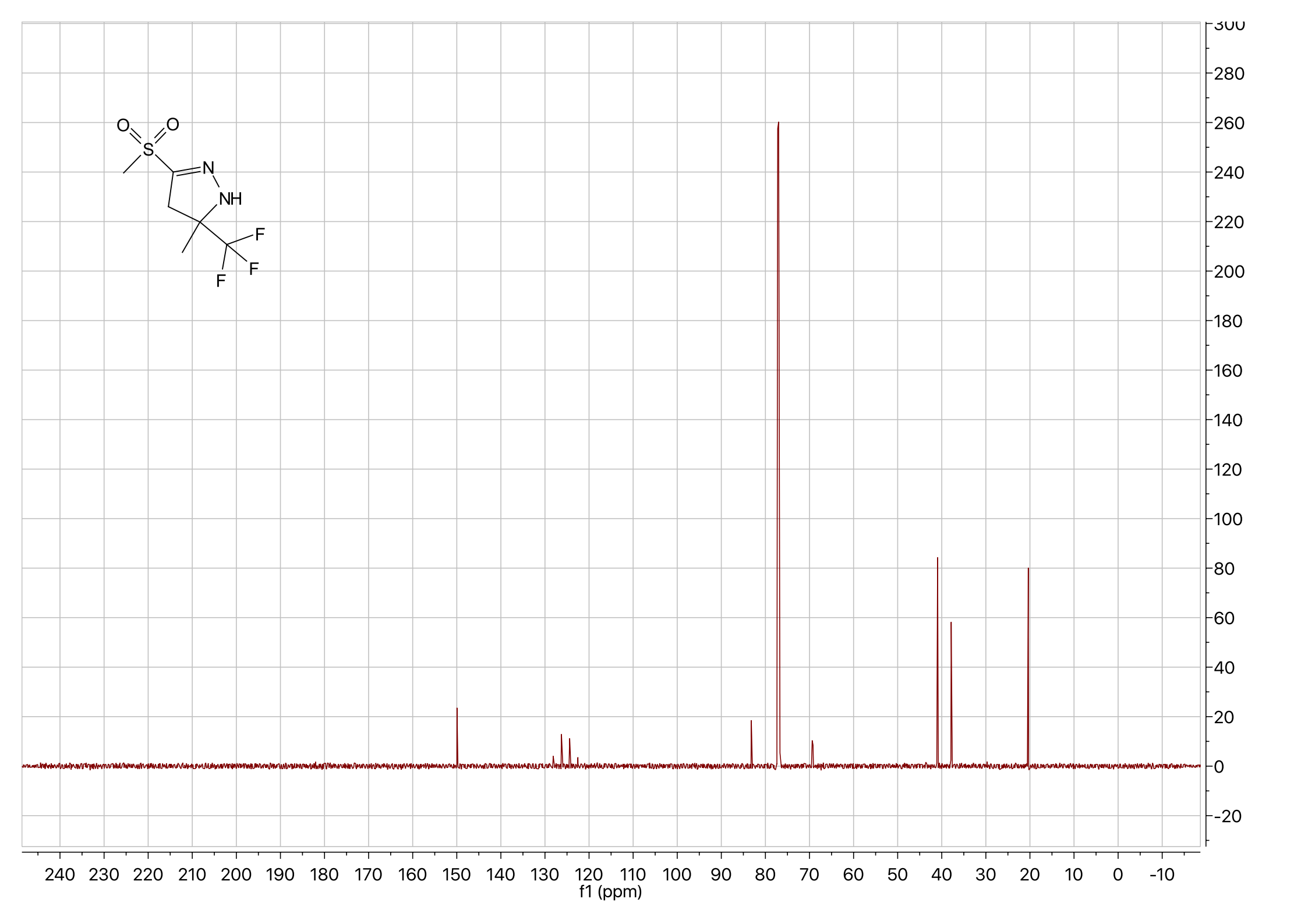

O
O
S
N
NH
F
F
F
1.00
2.77
1.00
2.93
f1 (ppm)

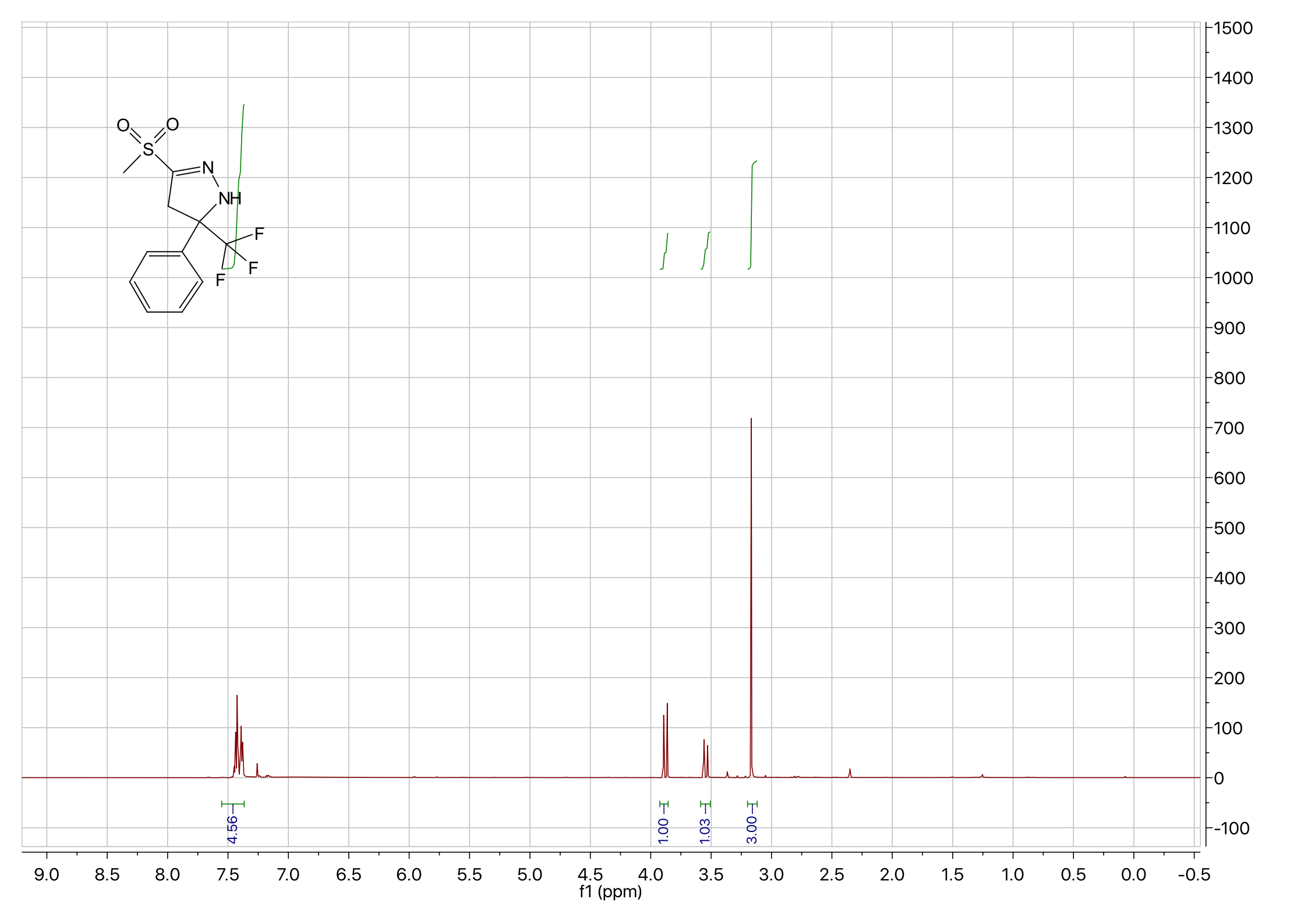


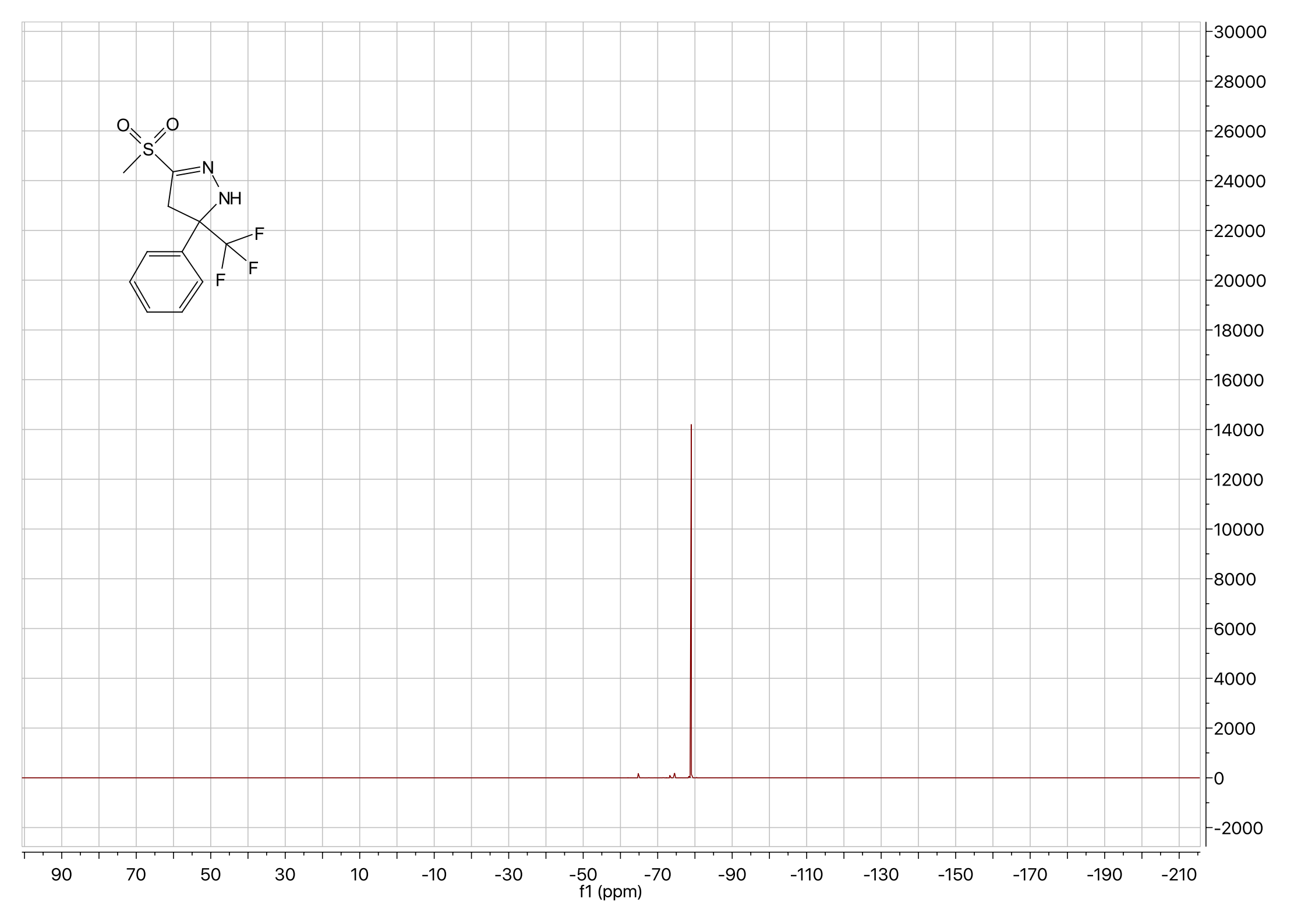
40000
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000

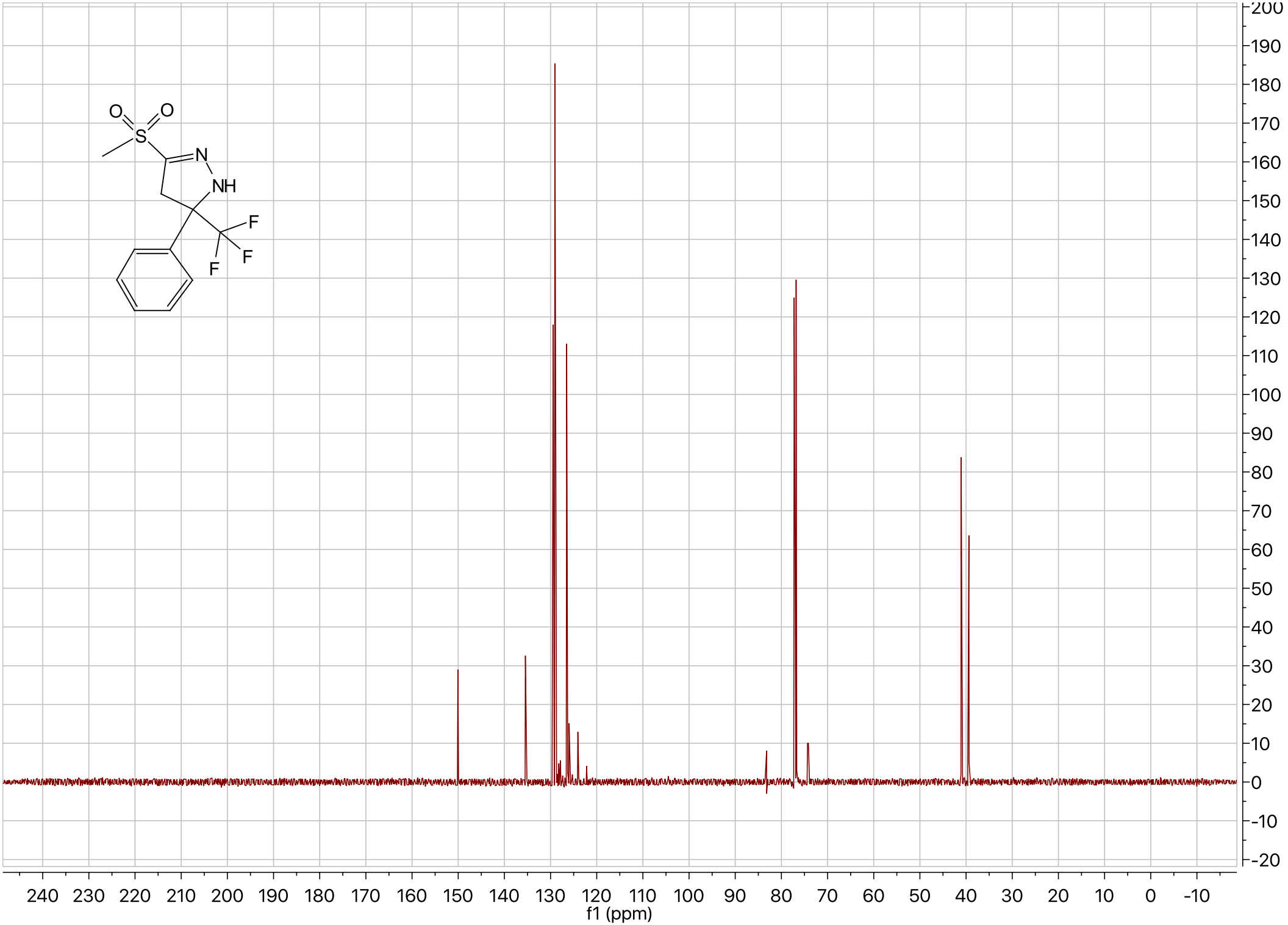
90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210

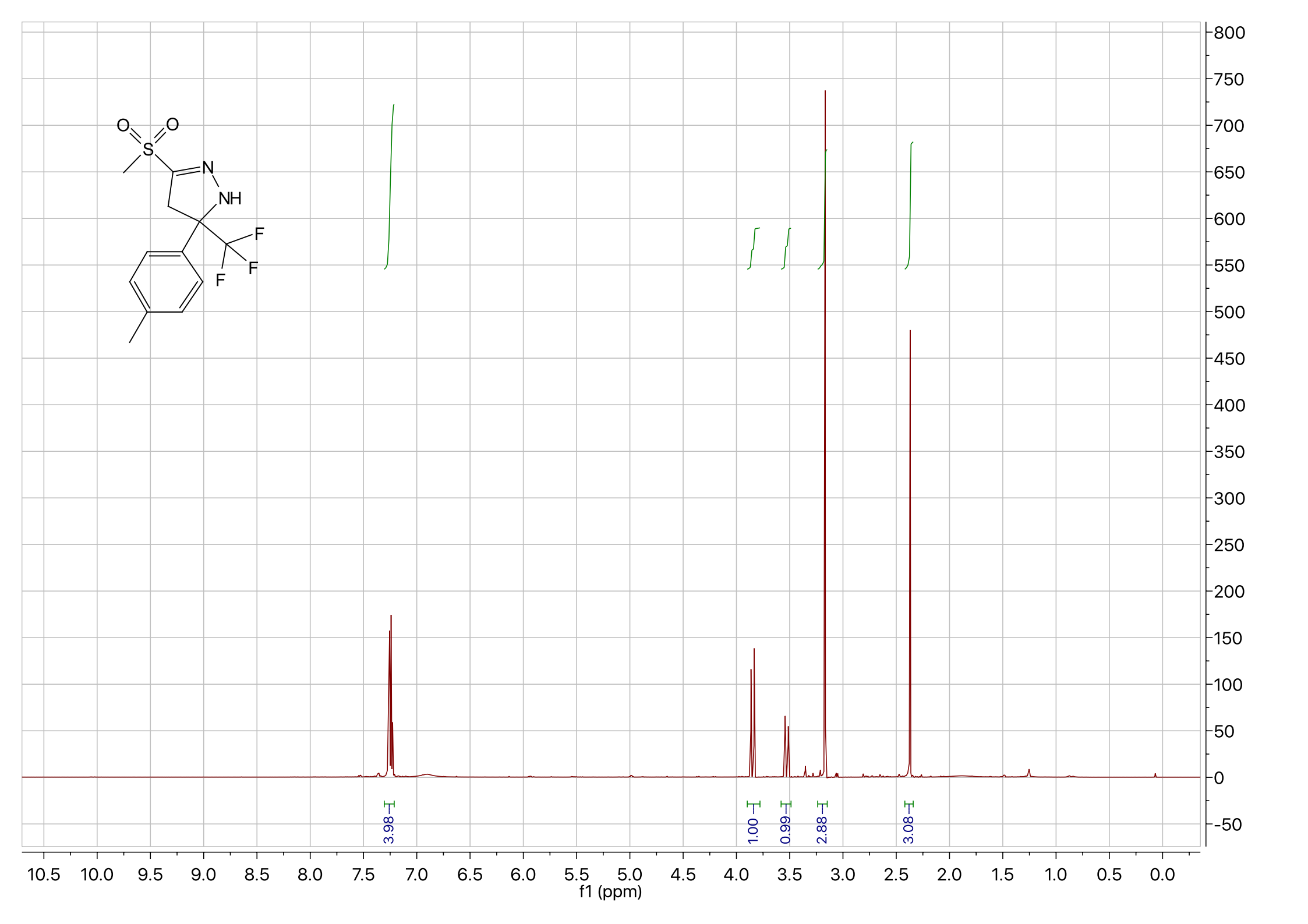
f1 (ppm)

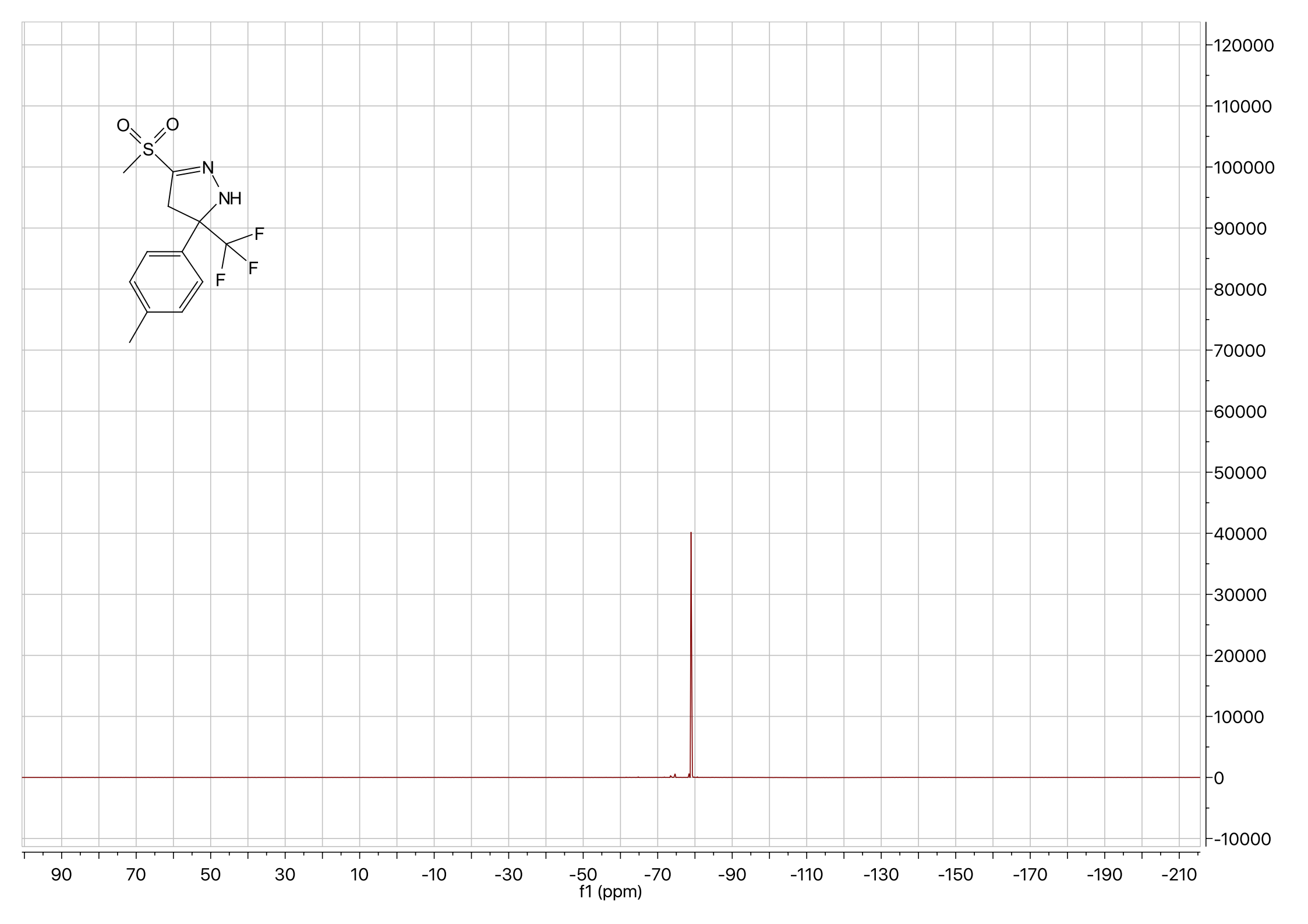

O
O
S
N
NH
F
F
F
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

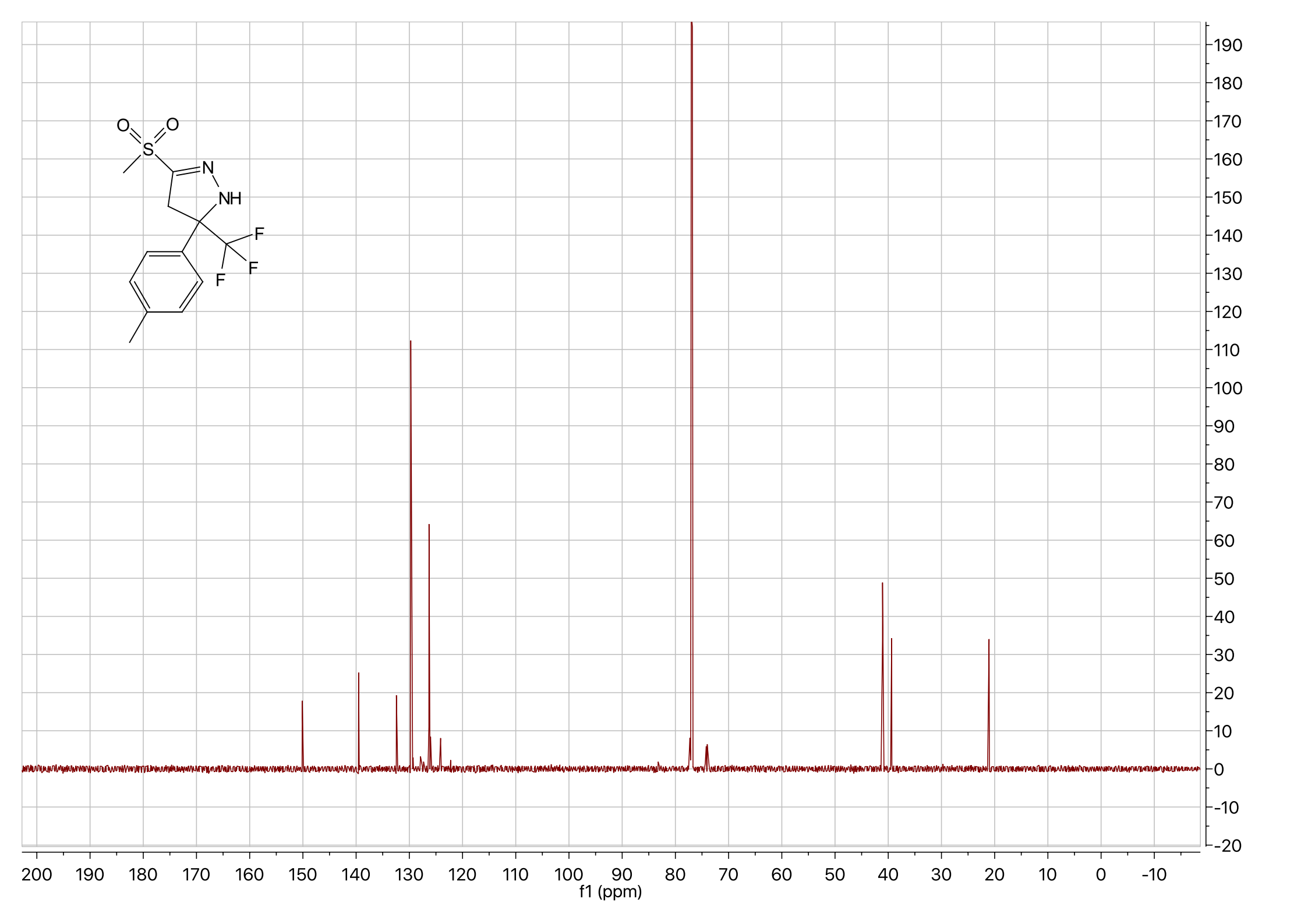

O
O
S
N
NH
F
F
F
4.56
1.00
1.03
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

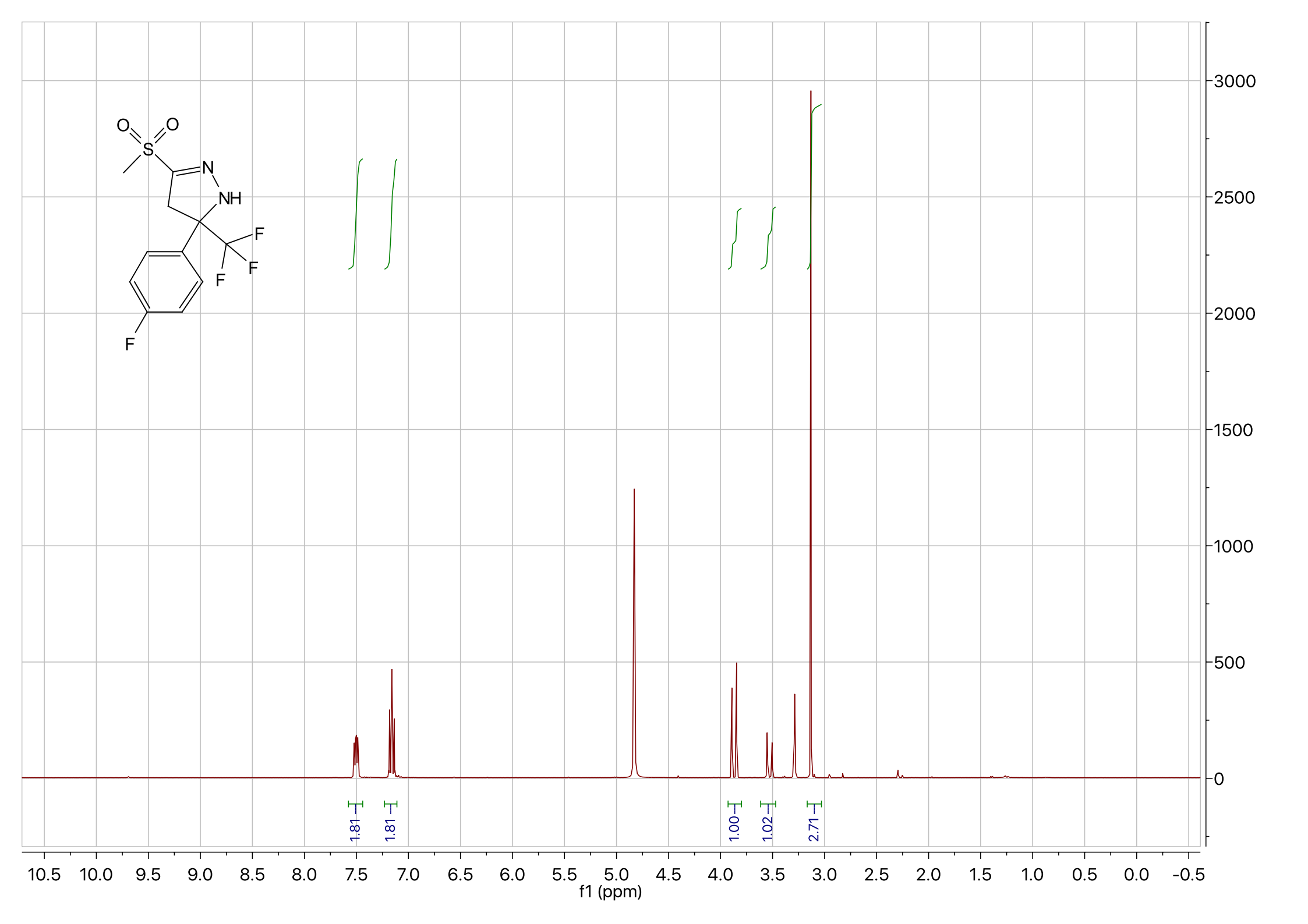

O
O
S
N
NH
F
F
F
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

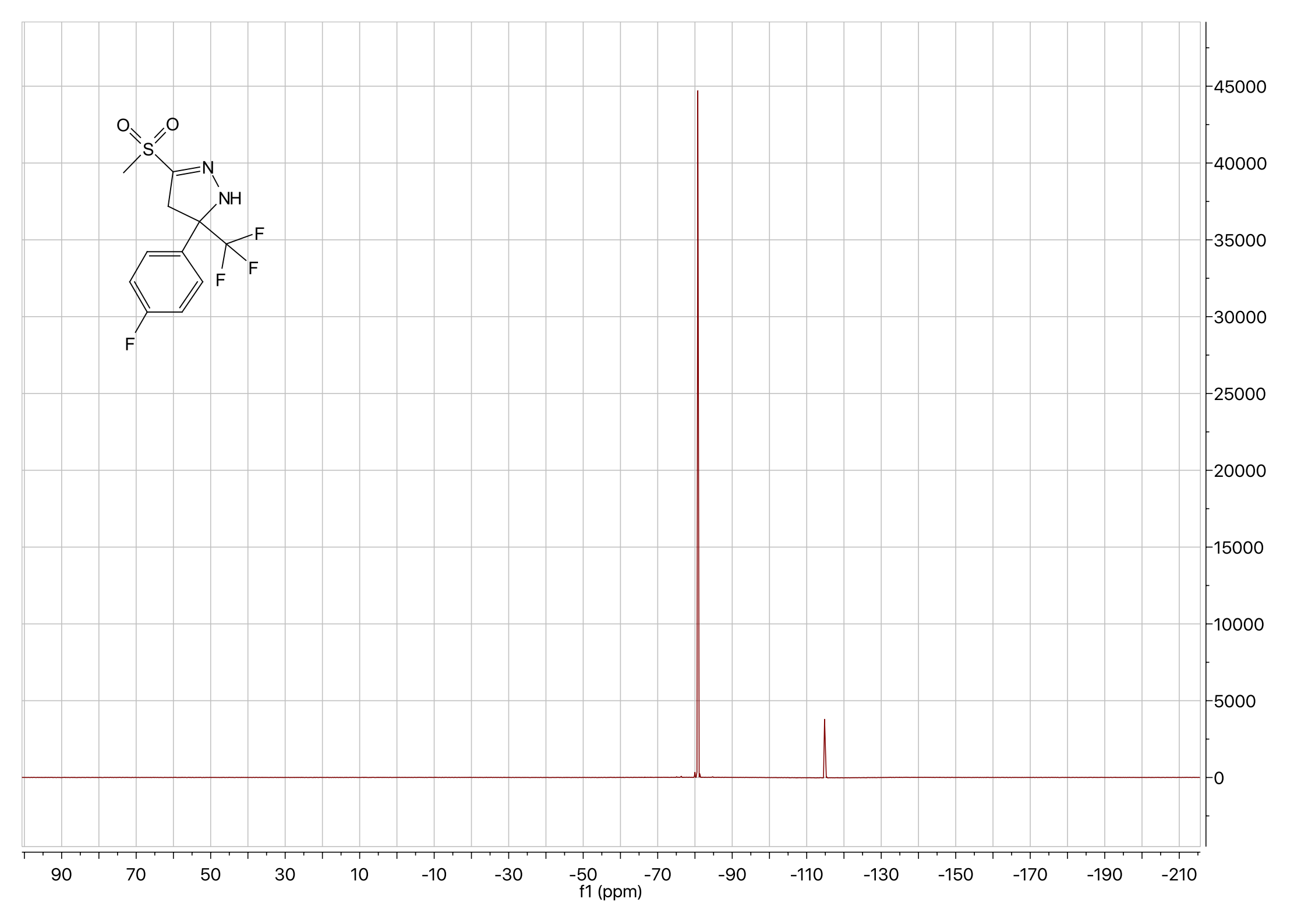

O
O
S
N
NH
F
F
F
f1 (ppm)

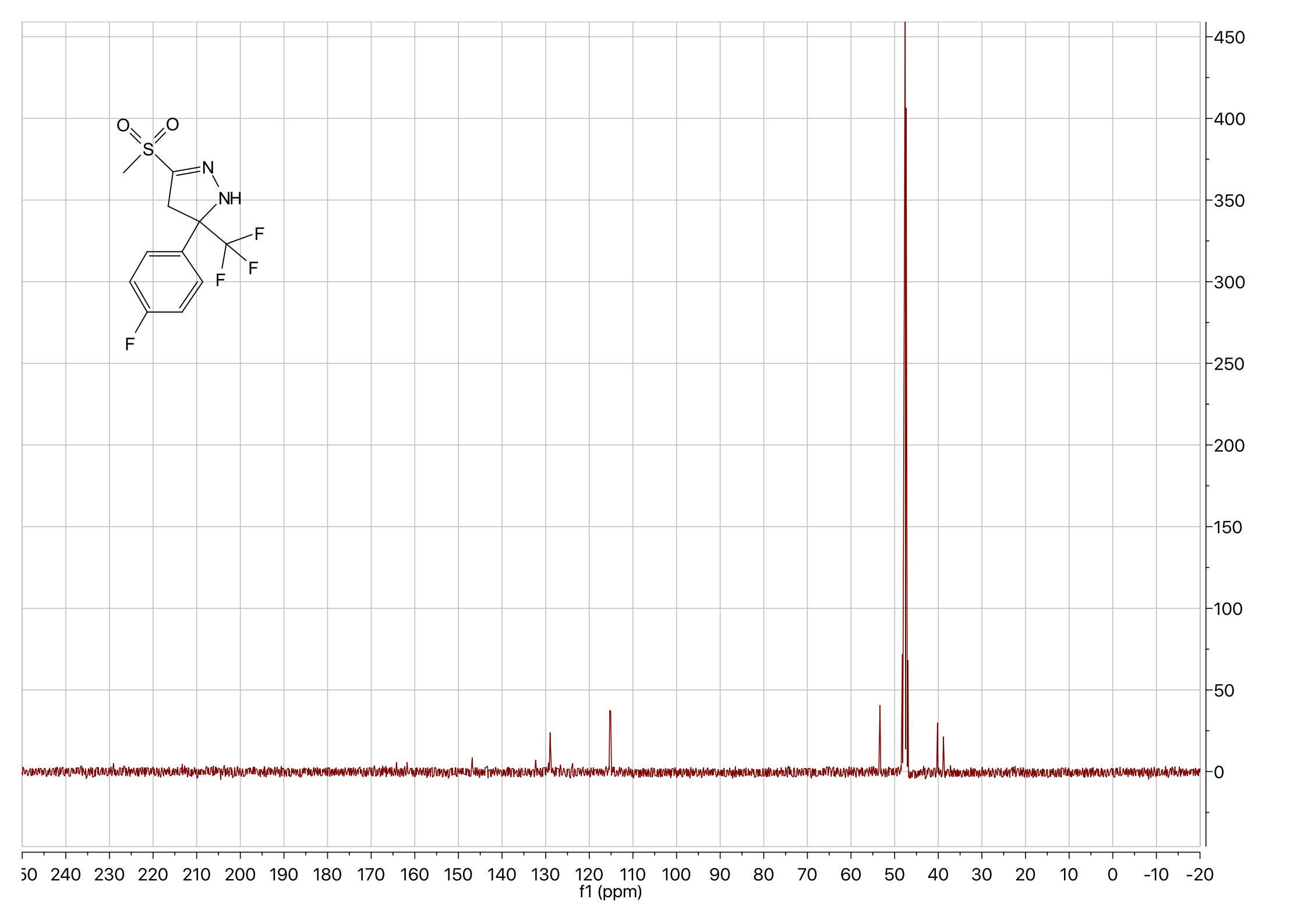

O
O
S
N
NH
F
F
F
3.98
1.00
0.99
2.88
3.08
f1 (ppm)

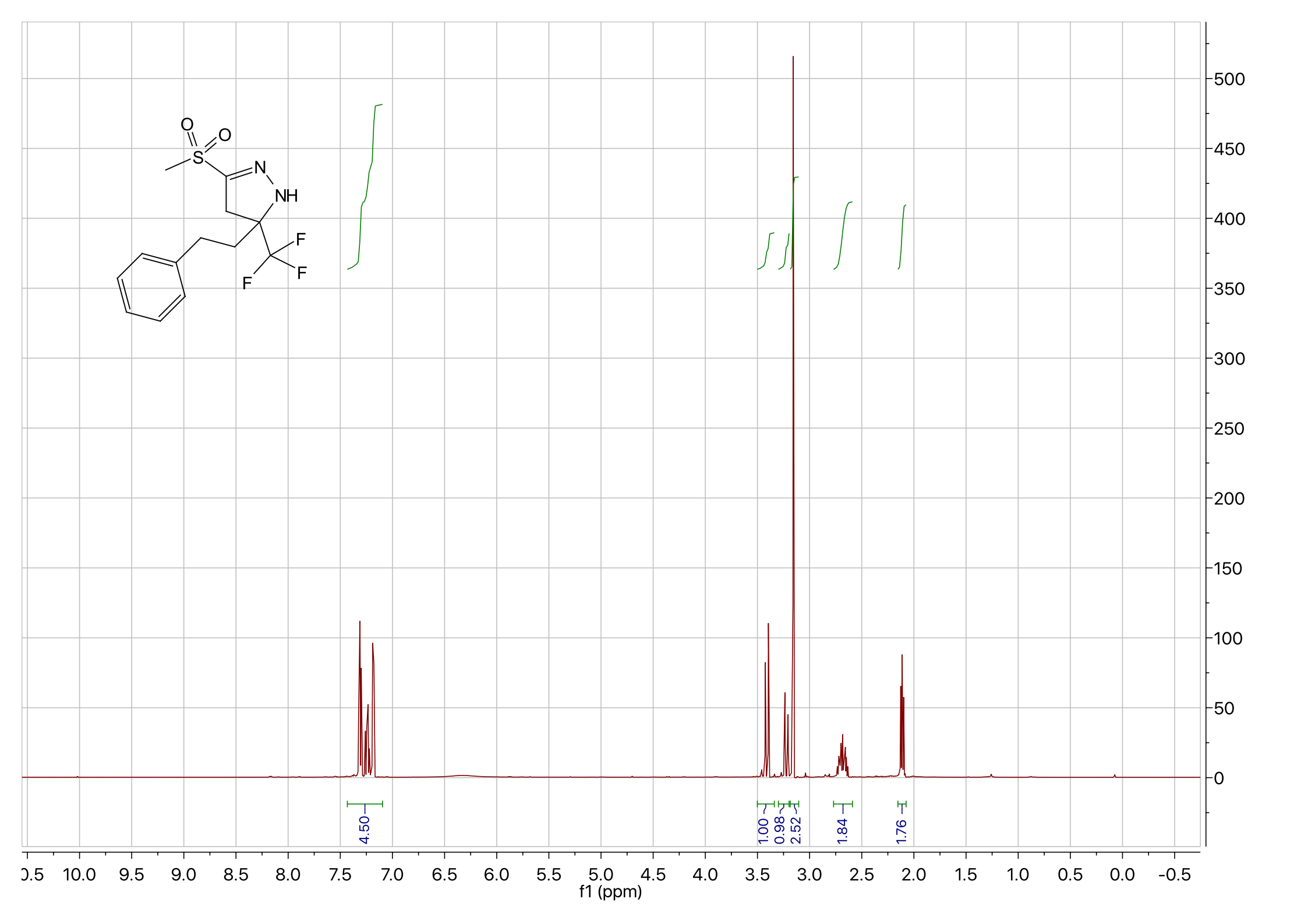

O
O
S
N
NH
F
F
F
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

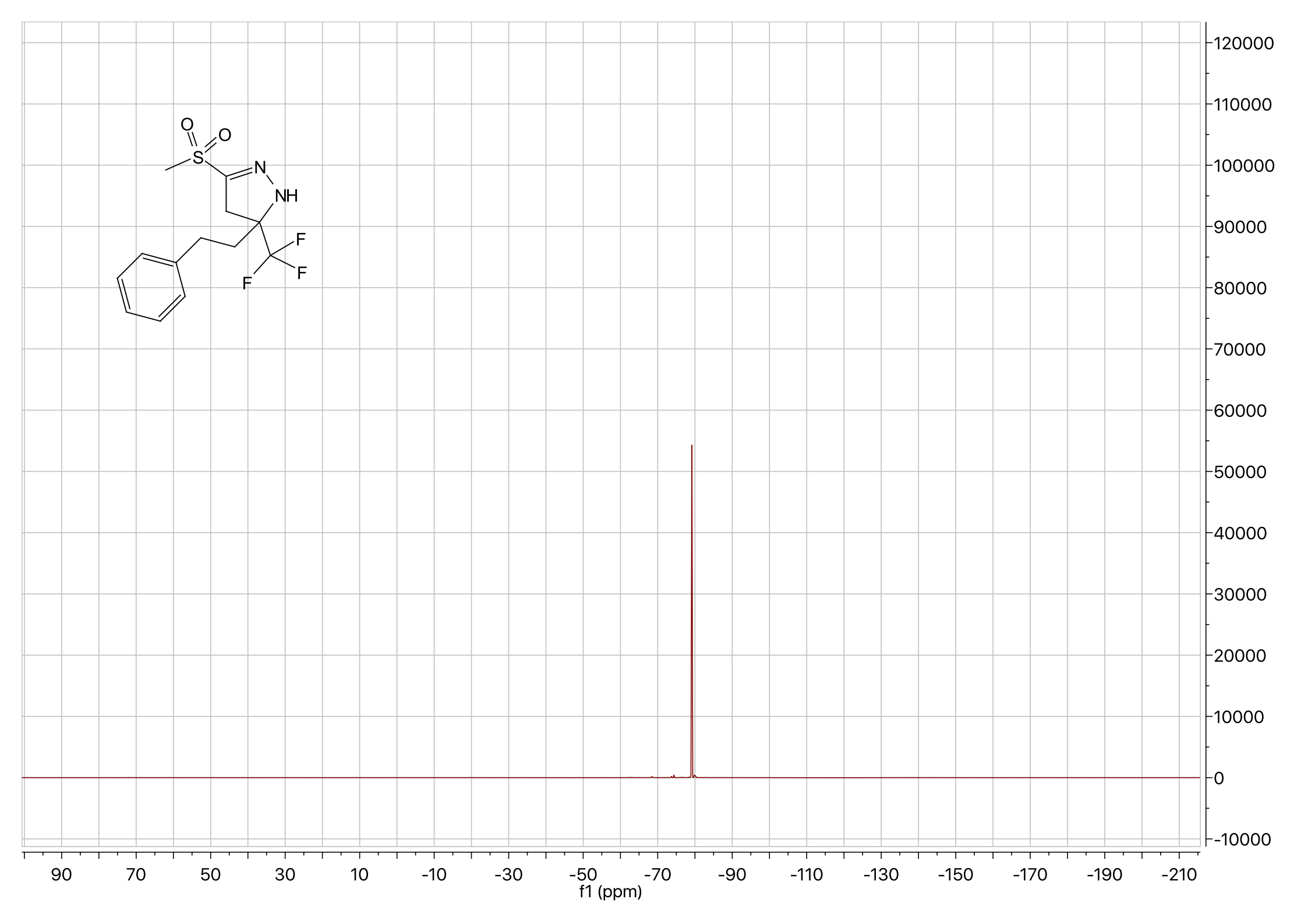

O
O
S
N
NH
F
F
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

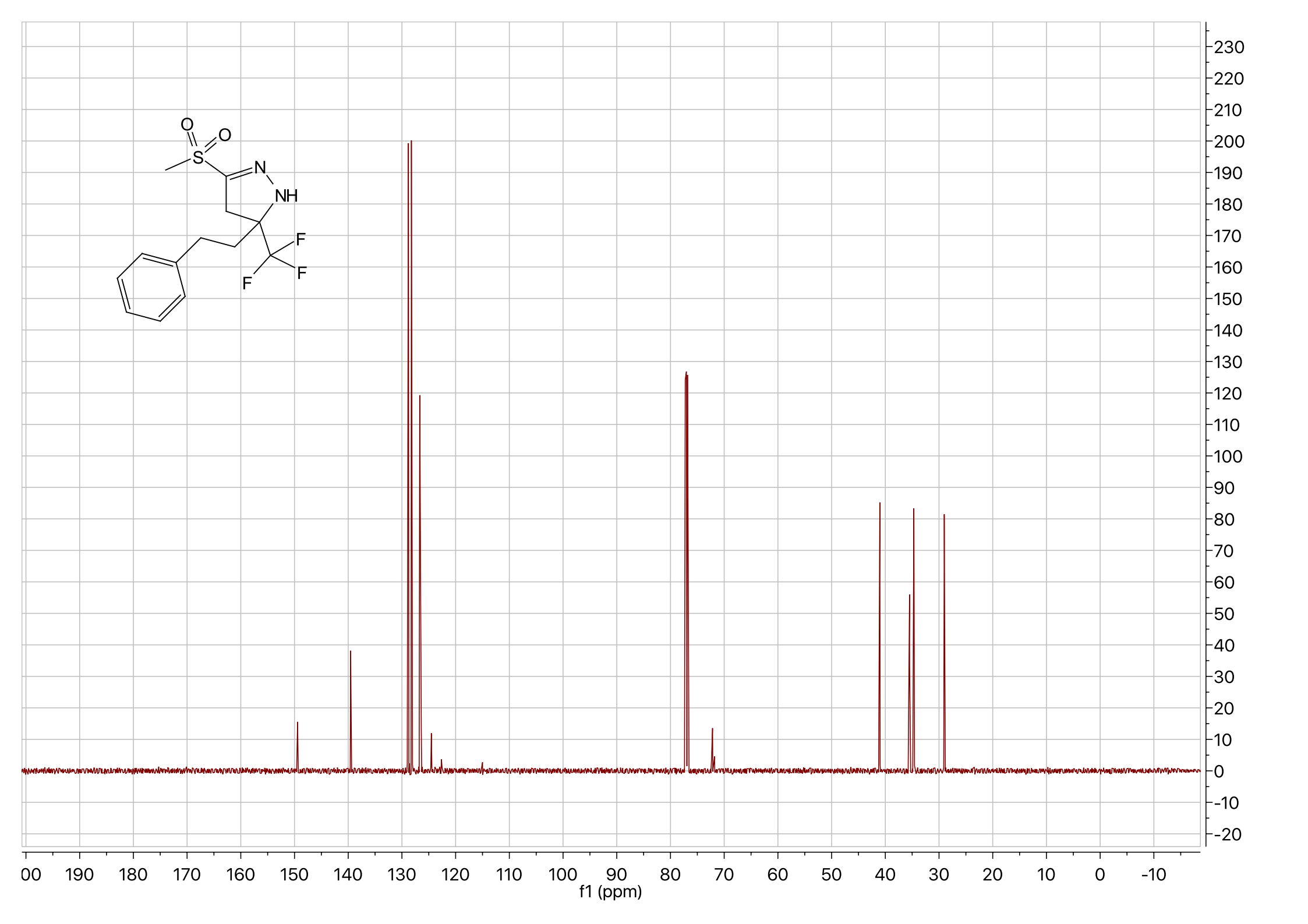

O
O
S
N
NH
F
F
F
F
1.81
1.81
1.00
1.02
2.71
3000
2500
2000
1500
1000
500
0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

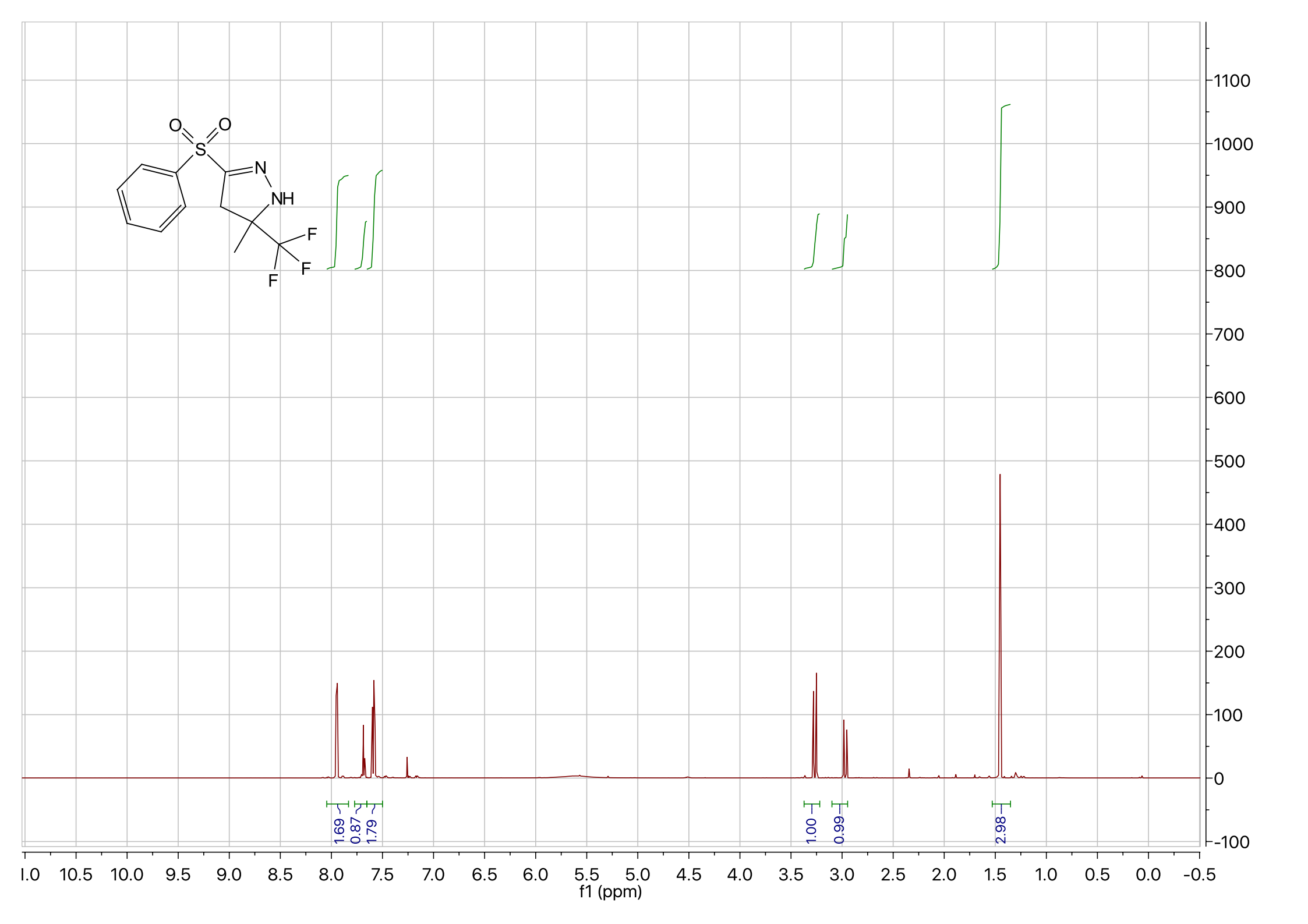

O
O
S
N
NH
F
F
F
F
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

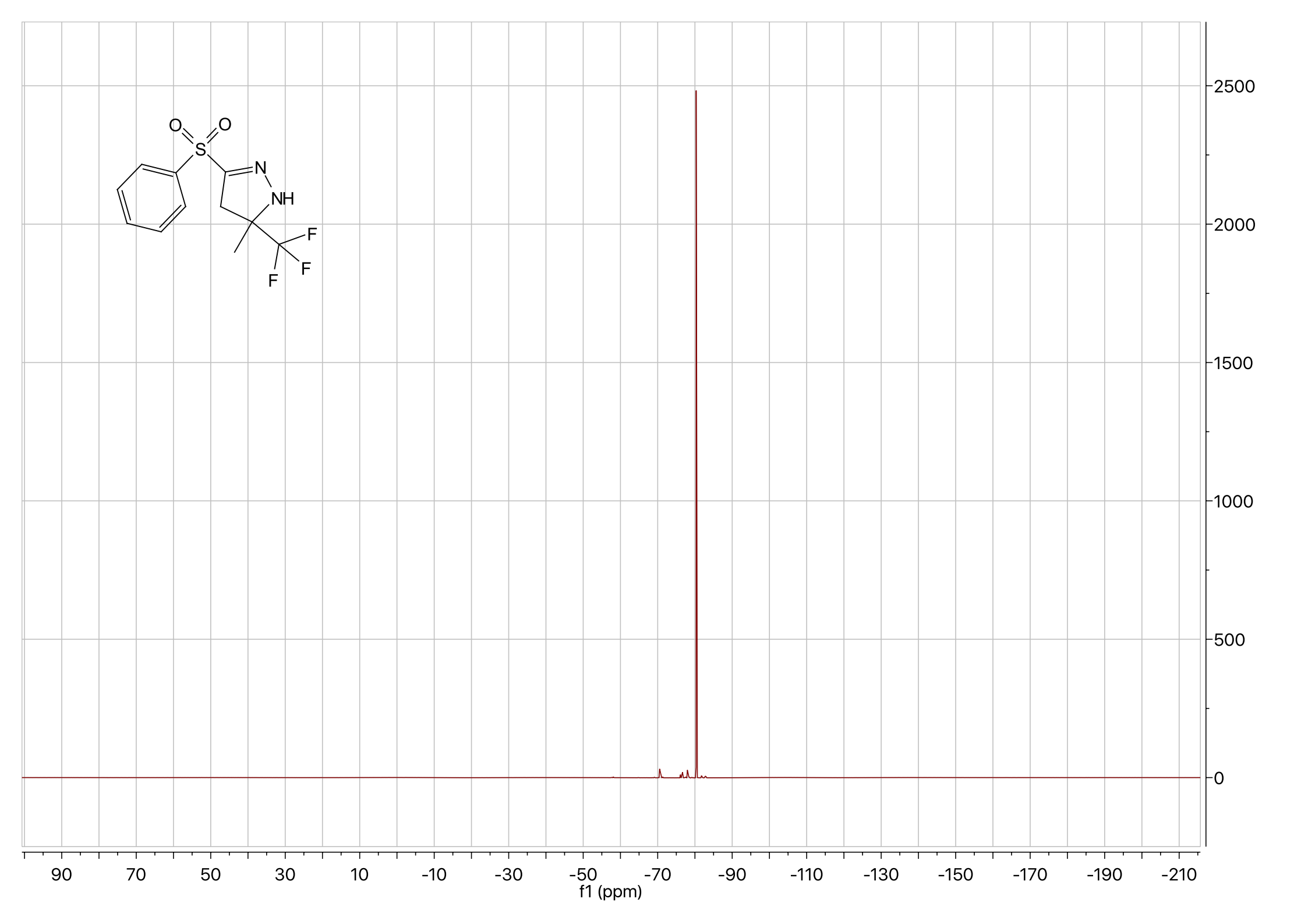

O
O
S
N
NH
F
F
F
F
450
400
350
300
250
200
150
100
50
0
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

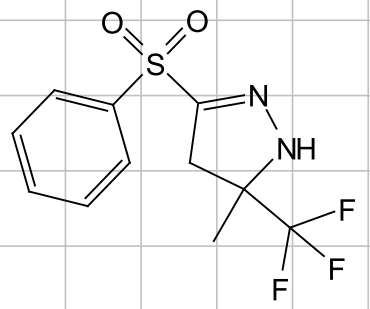

O
O
S
N
NH
F
F
F
4.50
1.00
0.98
2.52
1.84
1.76
500
450
400
350
300
250
200
150
100
50
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


O
O
S
N
NH
F
F
F
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)


O
O
S
N
NH
F
F
F
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
O
S
N
NH
F
F
F
1.69
0.87
1.79
1.00
0.99
2.98
f1 (ppm)


O
O
S
N
NH
F
F
F
2500
2000
1500
1000
500
0
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

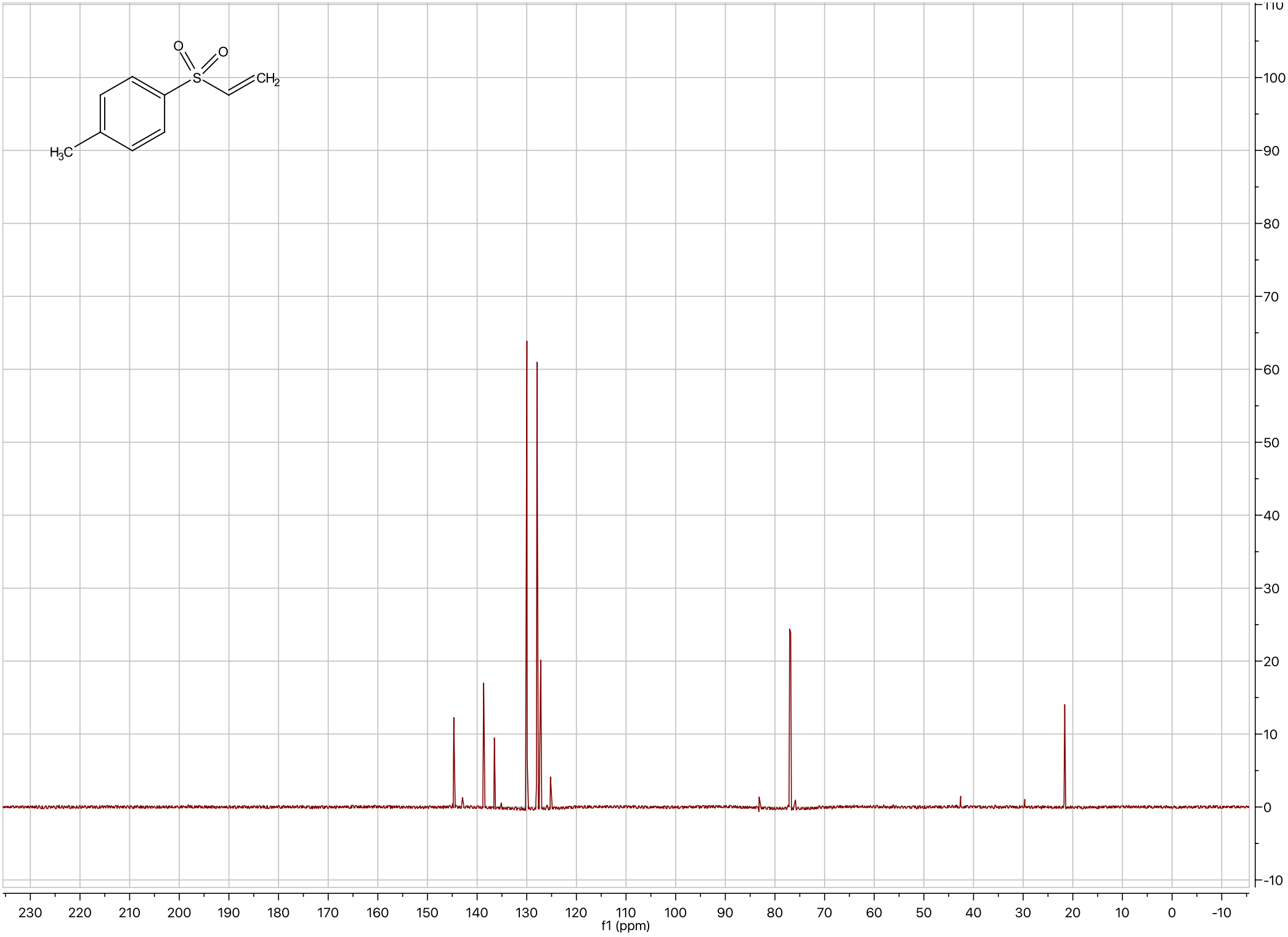


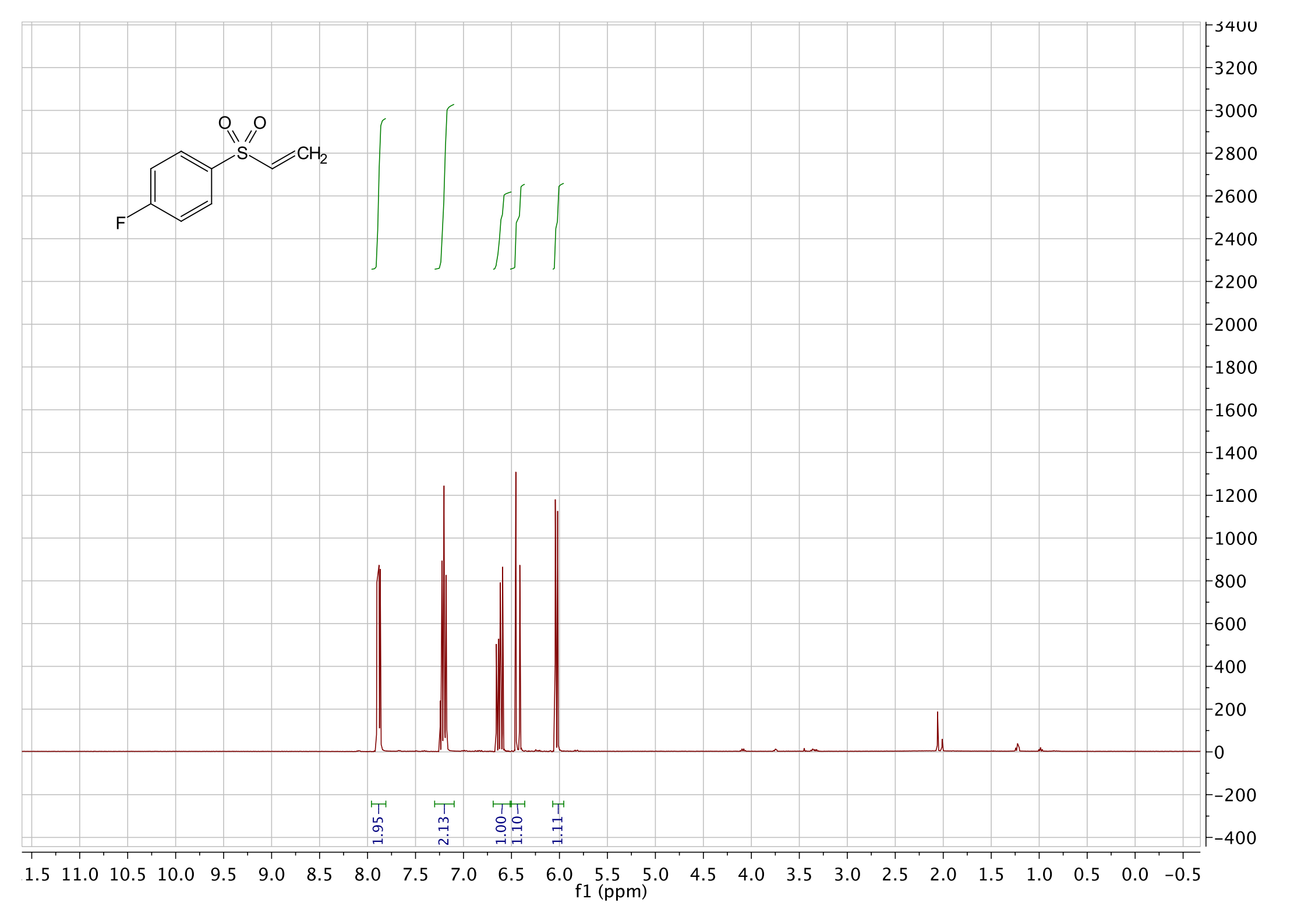
320 300 280 260 240 220 200 180 160 140 120 100 80 60 40 20 0 -20 -40

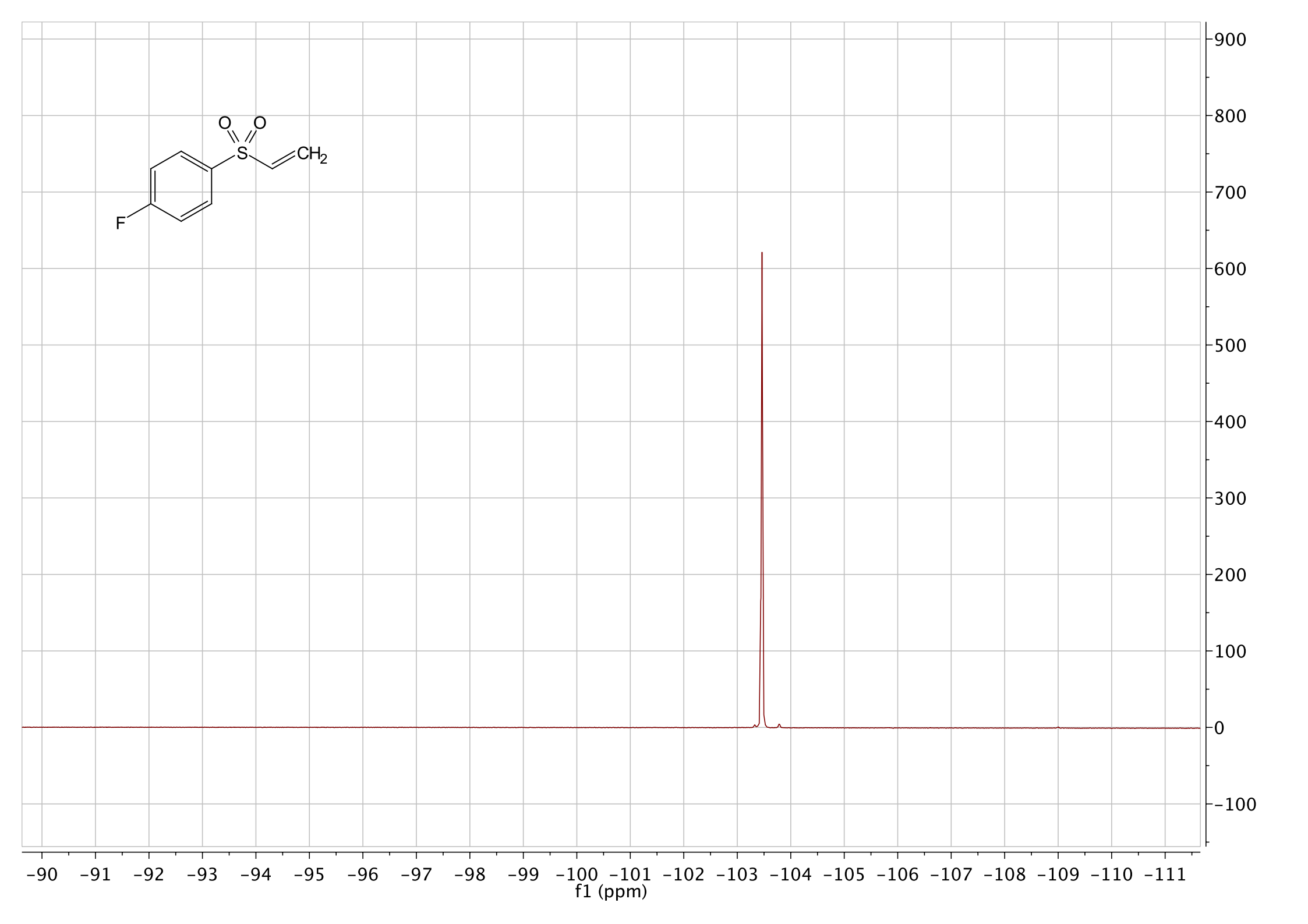
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

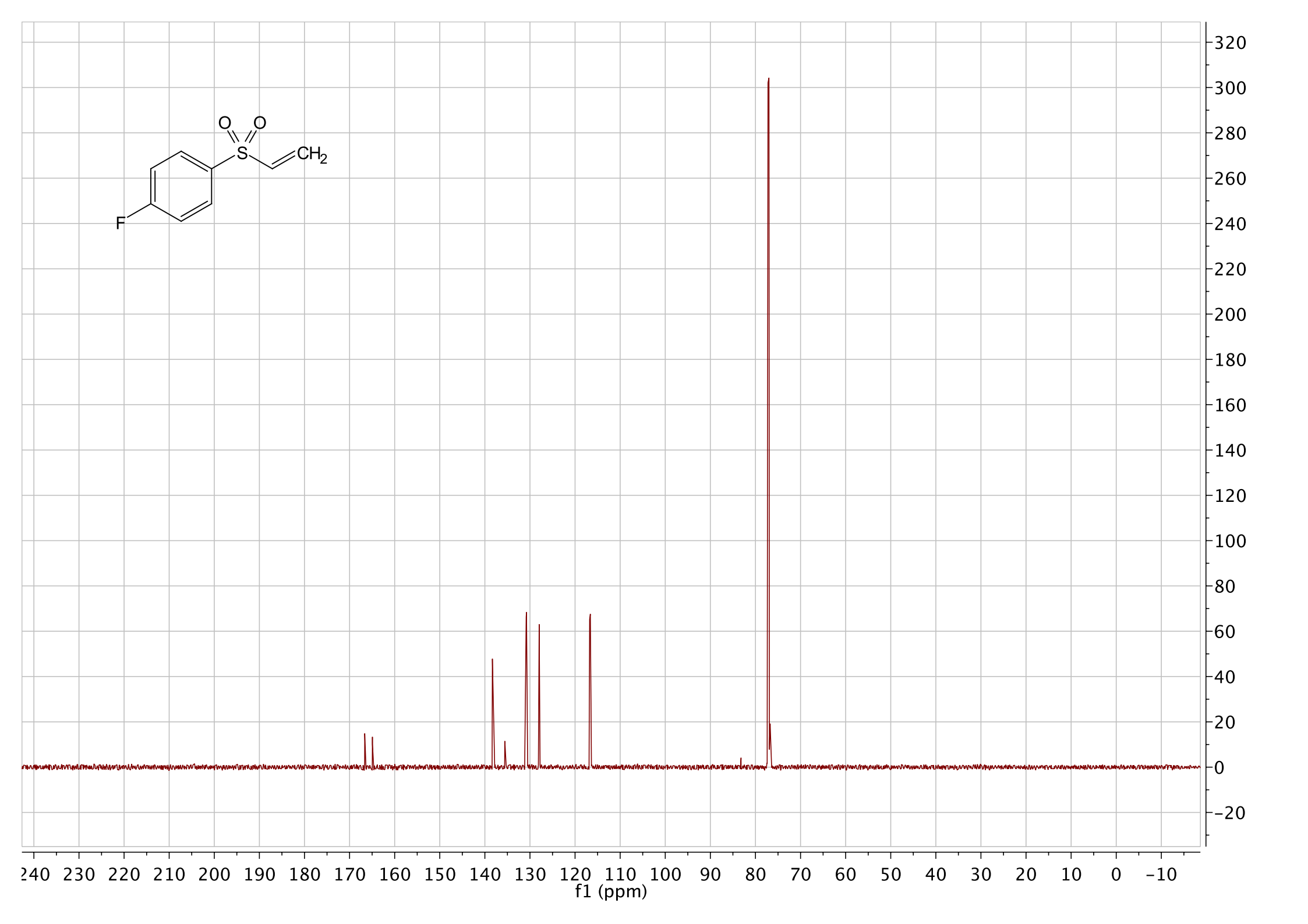
f1 (ppm)

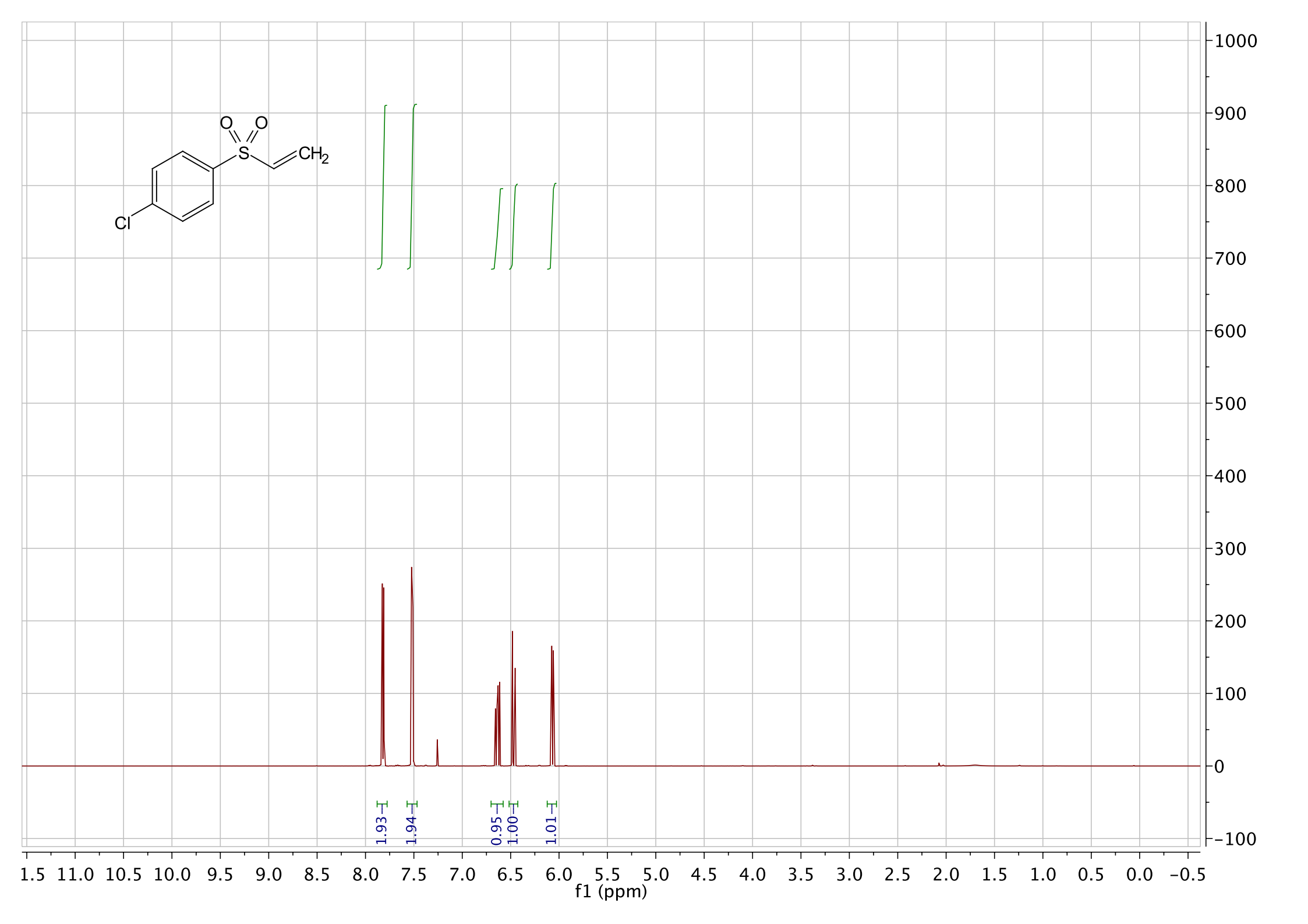

O
O
S
CH2
H3C
1.96
2.03
0.92
1.00
1.00
3.57
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50

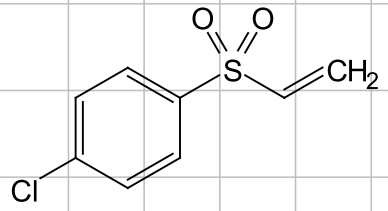

O
O
S
CH2
H3C
110
100
90
80
70
60
50
40
30
20
10
0
-10
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
O
S
CH2
F
1.95
2.13
1.00
1.10
1.11
f1 (ppm)


O
O
S
CH2
F
900
800
700
600
500
400
300
200
100
0
−100
−90 −91 −92 −93 −94 −95 −96 −97 −98 −99 −100 −101 −102 −103 −104 −105 −106 −107 −108 −109 −110 −111
f1 (ppm)


O
O
S
CH2
F
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

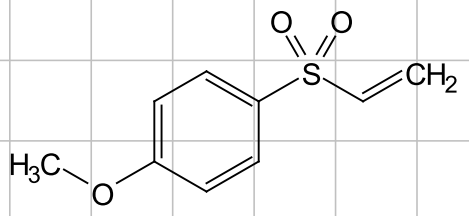

O
O
S
CH2
Cl
1.93
1.94
0.95
1.00
1.01
1000
900
800
700
600
500
400
300
200
100
0
−100
1.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)



280 260 240 220 200 180 160 140 120 100 80 60 40 20 0 −20

240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

f1 (ppm)

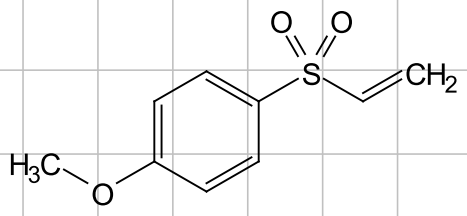


1.91 2.05 0.88 1.00 1.02 3.35

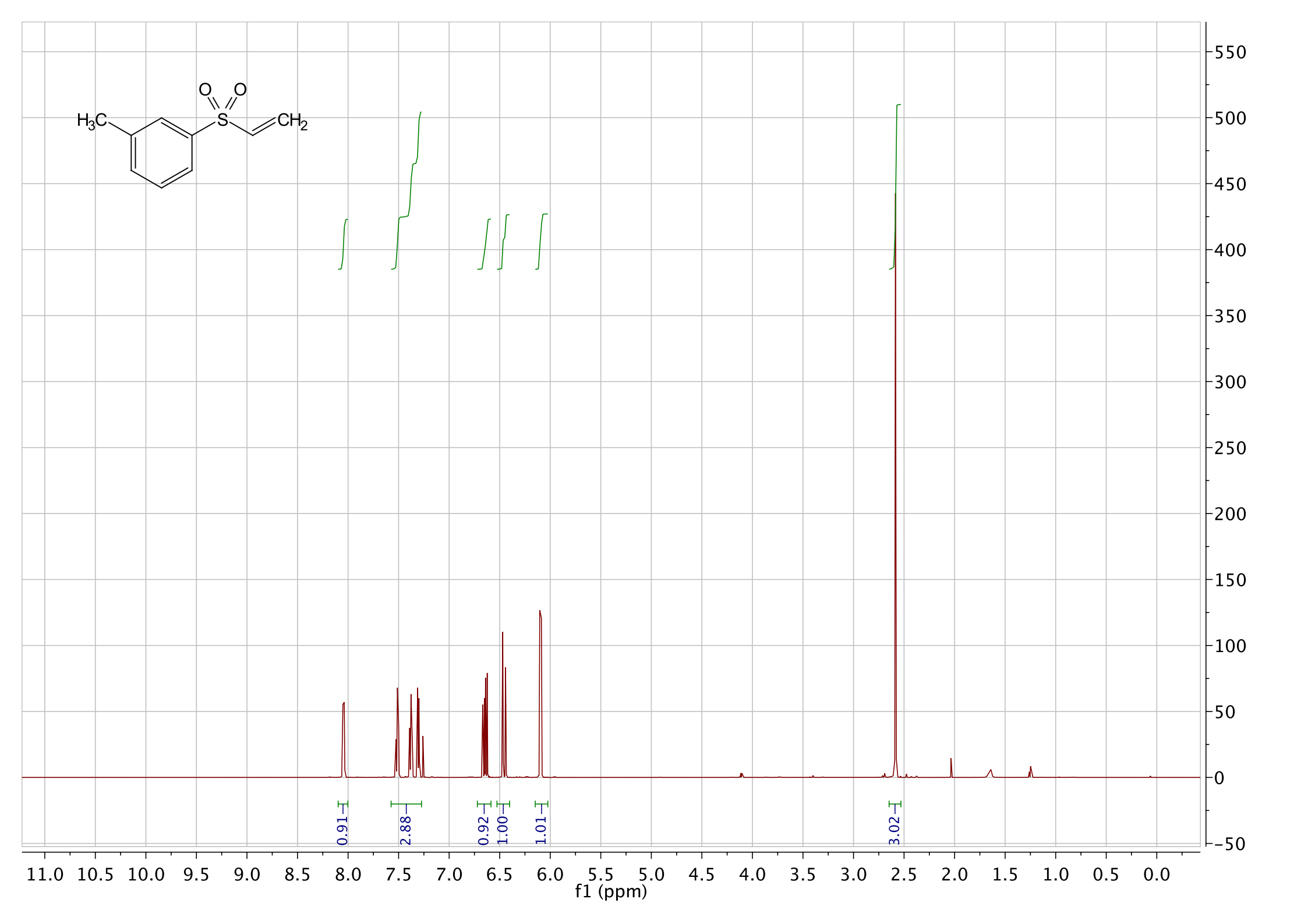
8000 7500 7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 −500

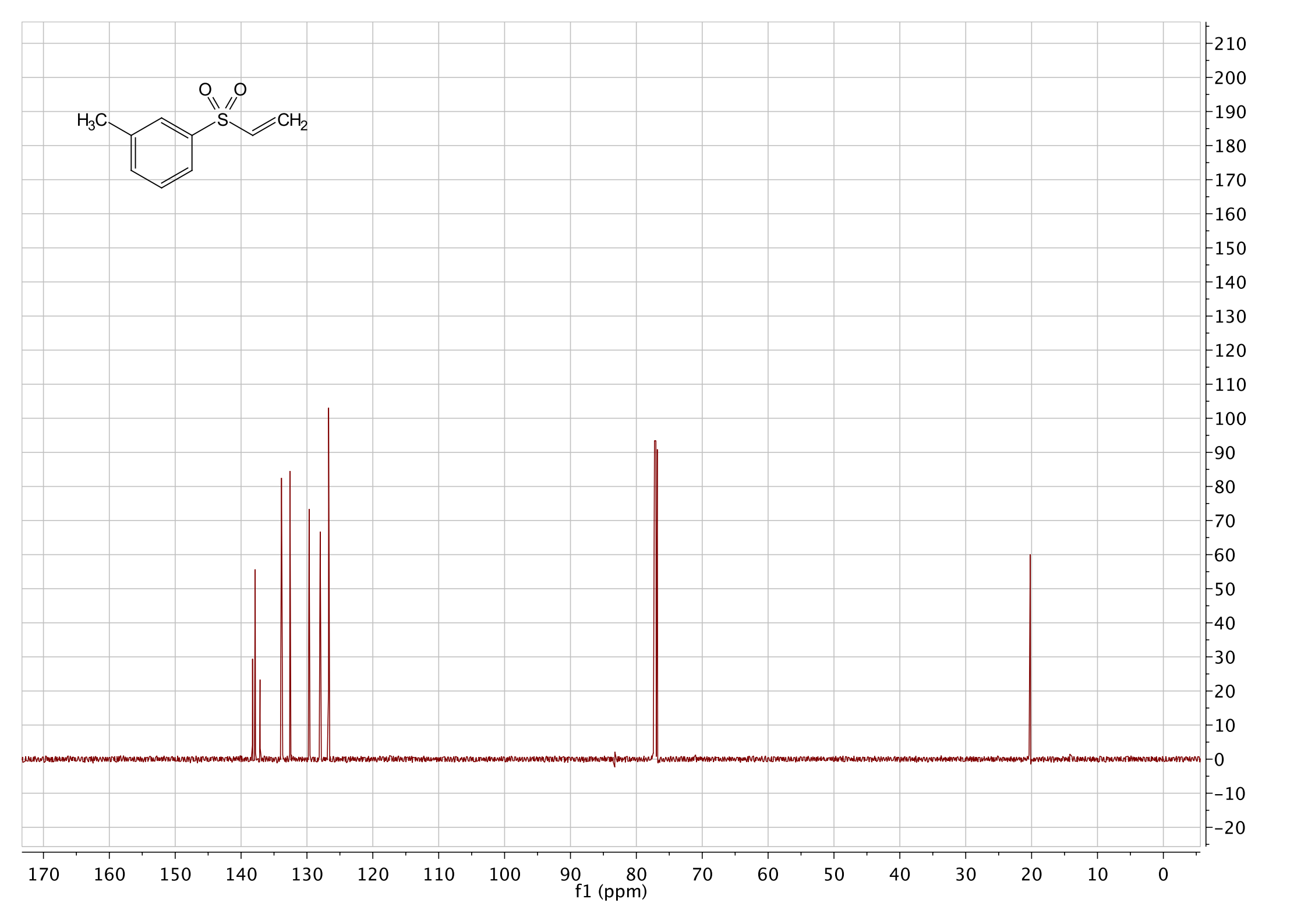
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0

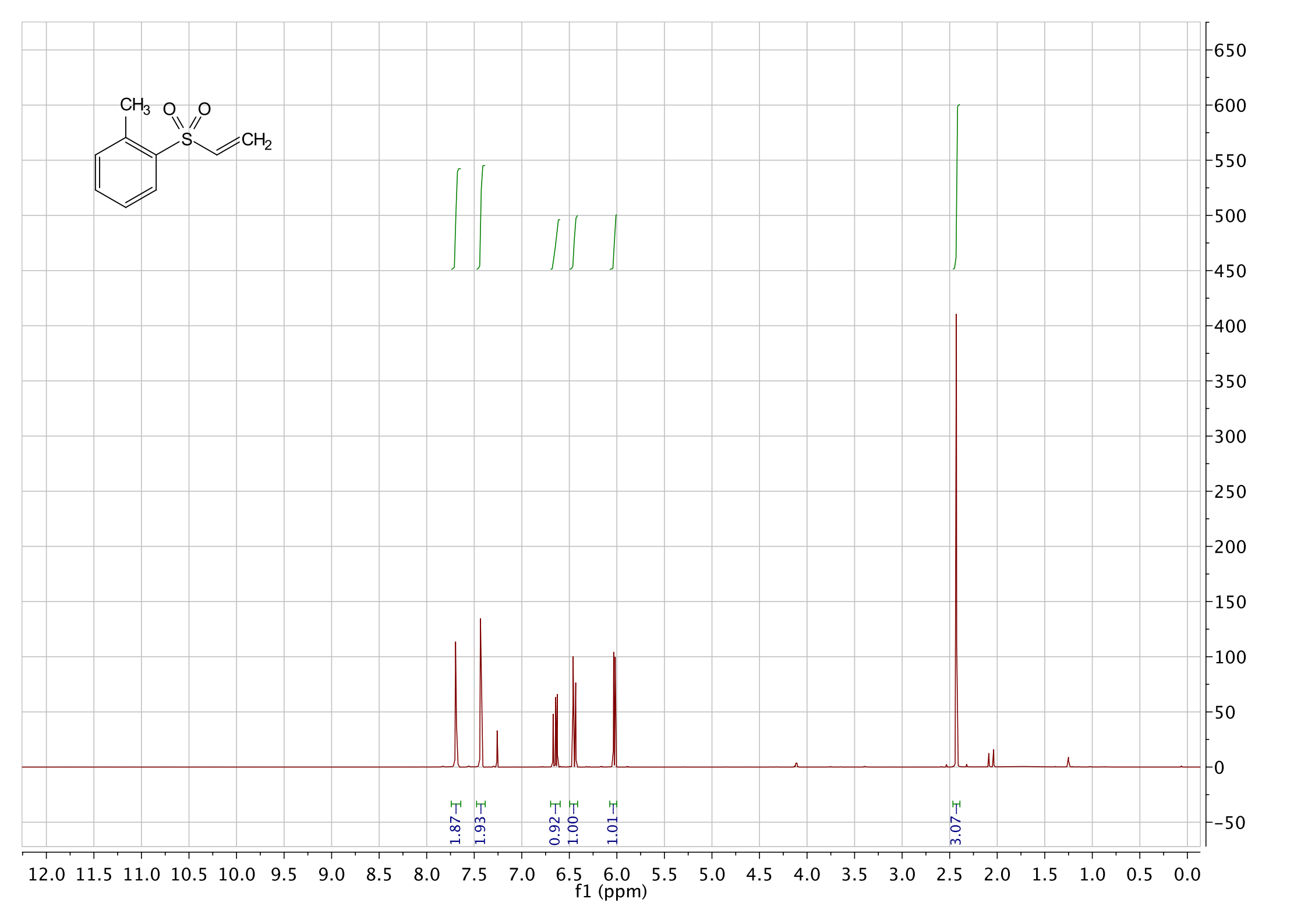
f1 (ppm)

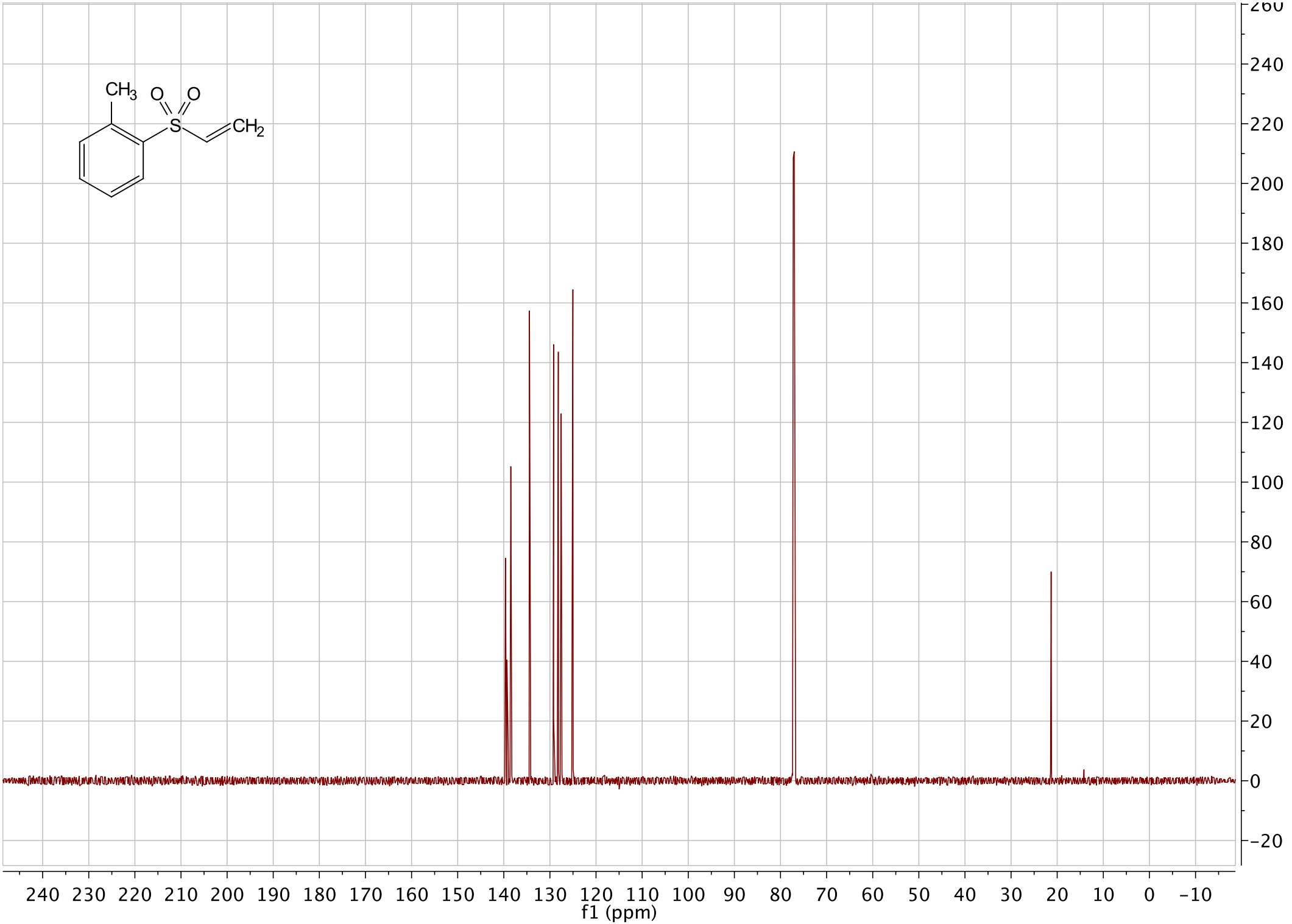


f1 (ppm)


O
O
S
H3C
CH2
0.91
2.88
0.92
1.00
1.01
3.02
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
550 500 450 400 350 300 250 200 150 100 50 0 -50


O
O
H3C
S
CH2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


CH3
O
O
S
CH2
1.87
1.93
0.92
1.00
1.01
3.07
650
600
550
500
450
400
350
300
250
200
150
100
50
0
−50
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


CH3
O
O
S
CH2
260
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)