Supporting Information

Photocatalytic Fluorosulfonylation of Aliphatic Carboxylic Acid NHPI Esters

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Electronic Supplementary Information (ESI) available: Experimental procedures, data for all the products. See DOI: 10.1039/x0xx00000x.

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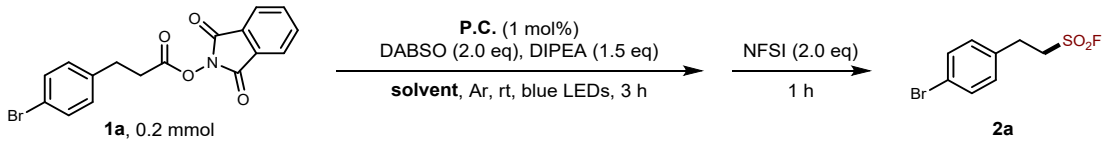
1. General Information

Solvents and reagents were bought from Sigma-Aldrich, J&K, Alfa-Aesar and TCI chemicals, and used directly without further purification. Column chromatography was performed with silica gel (300-400 mesh) or analytical thin layer chromatography was performed on 0.25 mm silica gel 60-F254. Visualization was carried out with UV light and Vogel's permanganate. ^{1}H NMR spectra were recorded on Bruker AMX-400 instrument (400 MHz) or JEOL ECX-500 (500 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to 0.00 ppm for TMS, 7.26 ppm for chloroform-*d*. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants, *J*, were reported in Hertz unit (Hz). ^{13}C NMR spectra were recorded on Bruker DRX-400 instrument (101 MHz) or JEOL ECX-500 (126 MHz). Chemical shifts were reported in ppm referenced to 77.16 ppm for chloroform-*d*. ^{19}F NMR spectra were recorded on Bruker DRX-400 instrument (376 MHz) or JEOL ECX-500 (471 MHz). High-resolution mass spectra (HRMS) were recorded on Thermo Fisher Scientific using ESI mode. NHPI esters were prepared according to the literature.[1]

2. Optimization of Reaction Conditions

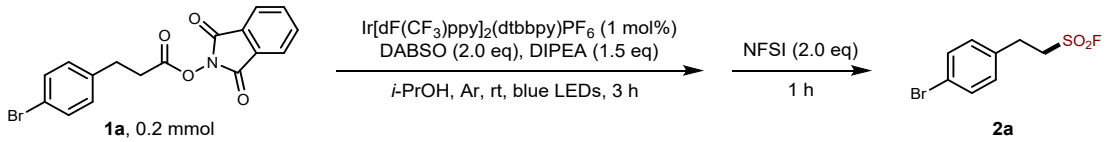
Table S1. Screening of photocatalysts (P.C.) and solvents[a]



Entry	P.C.	Solvent	Yield (^{19}F)[b]
1	Eosin Y-Na_2	*i*-PrOH	6%
2	$Ru(bpy)_3Cl_2$	*i*-PrOH	5%
3	*fac*-$Ir(ppy)_3$	*i*-PrOH	17%
4	Rodamine 6G	*i*-PrOH	N.P.
5	**$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$**	***i*-PrOH**	**63%**
6	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	MeCN	13%
7	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	THF	N.P.
8	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DCM	N.P.
9	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DMF	17%
10	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	EA	N.P.
11	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	NMP	5%
12	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	EtOH	trace
13	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	*t*-BuOH	26%

[a] Reaction conditions: NHPI esters (**1a**, 0.2 mmol), DABSO (0.4 mmol), DIPEA (0.3 mmol), P.C. (1 mol%), argon, blue LEDs (λ_{max} = 460 nm), room temperature; N.P. = no product was detected. [b] Yields were determined by ^{19}F NMR analysis with 4-iodofluorobenzene as an internal standard.

Table S2. Further screening of reaction conditions[a]

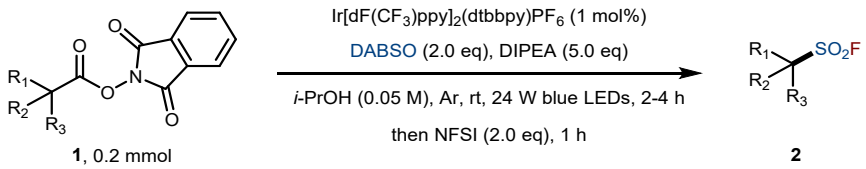


1a, 0.2 mmol **2a**

Entry	Variation from entry 13 (Table S1)	Yield (^{19}F)[b]
1	DIPEA (3.0 eq)	61%
2	**DIPEA (5.0 eq)**	**91% (85%)**[c]
3	Addition of Hantzsch Esters (2.0 eq)	85%
4	DABSO (1.5 eq)	84%
5	Selectfluor^{TM} instead of NFSI	18%
6	KF instead of NFSI	N.P.
7	KHF_2 instead of NFSI	N.P.
8	NFSI (3.0 eq)	90%
9	Without DIPEA	N.P.
10	Addition of Hantzsch Esters (2.0 eq), without DIPEA	trace
11	Without P.C.	N.P.
12	No light	trace
13	In air	trace

[a] Reaction conditions: NHPI esters (**1a**, 0.2 mmol), DABSO (0.4 mmol), DIPEA (0.3 mmol), P.C. (1 mol%), argon, blue LEDs (λ_{max} = 460 nm), room temperature; N.P. = no product was detected. [b] Yields were determined by ^{19}F NMR analysis with 4-iodofluorobenzene as an internal standard. [c] In parenthesis is isolated yield.

3. General Procedure and Characterizations for the Syntheses of 2



1, 0.2 mmol **2**

General Procedure for 2: The $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2.3 mg, 0.002 mmol, 1 mol%) was weighed into an oven-dried Schlenk tube, followed by the NHPI ester (0.2 mmol), DABSO (0.4 mmol, 96.1 mg). The flask was evacuated and backfilled with argon for three times, then DIPEA (1.0 mmol, 129.1 mg) and anhydrous isopropyl alcohol (4 ml, 0.05 M) was added under argon. The reaction mixture was allowed to stir at room temperature under irradiation with blue LEDs for 2-4 h. NFSI was added to the reaction under argon flow, and stirred for additional 1 h without light before extracted with ethyl acetate. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated. Further purification by column chromatography or preparative thin layer chromatography on silica gel gave the desired pure product **2**.

Photo-induced reactions were conducted in photo-reactors, which comprise a fan for cooling (approximately room temperature) and six 1W blue LED beads for each place (6 W). The average power output of the photo-reactor was ca. 30 mW/cm^2. The emission spectra of the blue LEDs were recorded on an Ocean Optics HR4000CG-UVNIR spectrometer. The spectra was normalized to 1.0 at the maximum (460 nm).

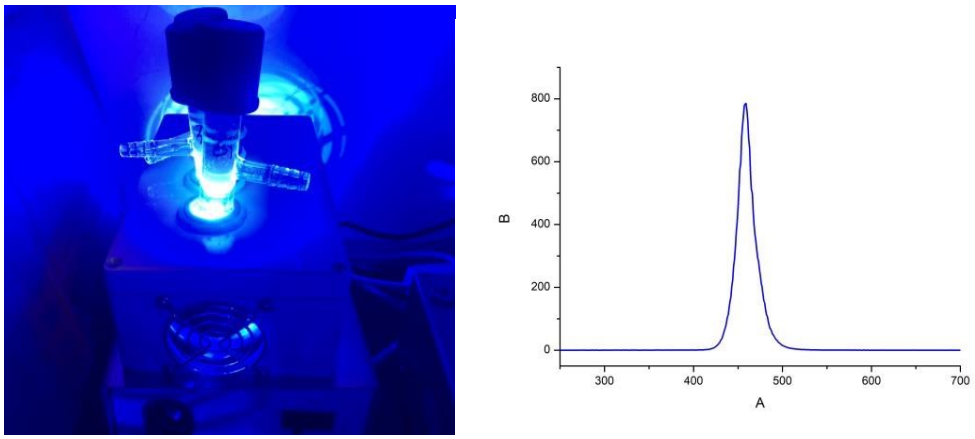
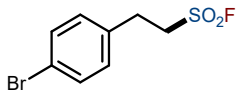


Figure S1. Photo-reactor and reaction setup.



2a, 85%

2-(4-bromophenyl)ethane-1-sulfonyl fluoride (2a):

45 mg, 85%, colorless oil.

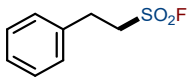
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 6.7 Hz, 2H), 7.12 (d, J = 7.6 Hz, 2H), 3.65 – 3.57 (m, 2H), 3.25 – 3.17 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.0, 132.4, 130.2, 121.8, 51.2 (d, J = 16.0 Hz), 29.2;

^{19}F NMR (376 MHz, $CDCl_3$) δ 53.7;

HRMS (ESI): *m/z* calculated for $C_8H_9BrFO_2S$ $[M+H]^+$ 266.9485, found 266.9481.

The analytical data are consistent with literature values.[2]



2b, 86%

2-phenylethane-1-sulfonyl fluoride (2b):

32 mg, 86%, colorless oil.

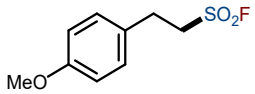
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.30 – 7.25 (m, 1H), 7.20 (d, J = 7.2 Hz, 1H), 3.62 – 3.54 (m, 2H), 3.23 – 3.17 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 136.1, 129.2, 128.4, 127.6, 52.1 (d, J = 15.5 Hz), 29.6;

^{19}F NMR (471 MHz, $CDCl_3$) δ 53.4;

HRMS (ESI): *m/z* calculated for $C_8H_{10}FO_2S$ $[M+H]^+$ 189.0380, found 189.0385.

The analytical data are consistent with literature values.[3]



2c, 79%

2-(4-methoxyphenyl)ethane-1-sulfonyl fluoride (2c):

34 mg, 79%, colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 – 7.12 (m, 2H), 6.90 – 6.86 (m, 2H), 3.80 (s, 3H),

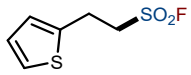
3.62 – 3.55 (m, 2H), 3.22 – 3.16 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 129.6, 128.0, 114.8, 55.5, 52.5 (d, J = 15.0 Hz), 28.9;

^{19}F NMR (471 MHz, $CDCl_3$) δ 53.4;

HRMS (ESI): *m/z* calculated for $C_9H_{12}FO_3S$ $[M+H]^+$ 219.0486, found 219.0490.

The analytical data are consistent with literature values.[4]



2d, 78%

2-(thiophen-2-yl)ethane-1-sulfonyl fluoride (2d):

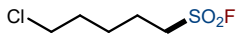
30 mg, 78%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 5.1 Hz, 1H).7.00 – 6.90 (m, 2H), 3.72 – 3.64 (m, 2H), 3.51 – 3.44 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.9, 127.5, 126.4, 125.3, 52.4 (d, J = 16.0 Hz), 24.2;

^{19}F NMR (376 MHz, $CDCl_3$) δ 53.7;

HRMS (ESI): *m/z* calculated for $C_6H_8FO_2S_2$ $[M+H]^+$ 194.9944, found 194.9946.



2e, 73%

5-chloropentane-1-sulfonyl fluoride (2e):

27 mg, 73%, colorless oil.

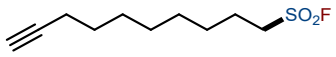
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.57 (t, J = 6.3 Hz, 2H), 3.44 – 3.34 (m, 2H), 1.99 (p, J = 7.8 Hz, 2H), 1.85 (p, J = 6.6 Hz, 2H), 1.72-1.62 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 50.8 (d, J = 16.5 Hz), 44.3, 31.8, 25.3, 23.0;

^{19}F NMR (376 MHz, $CDCl_3$) δ 53.6;

HRMS (ESI): *m/z* $C_5H_{10}ClFNaO_2S$ $[M+Na]^+$ 210.9966, found 210.9966.

The analytical data are consistent with literature values.[2]



2f, 70%

Dec-9-yne-1-sulfonyl fluoride (2f):

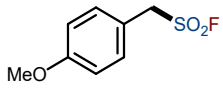
31 mg, 70%, colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.40 – 3.33 (m, 2H), 2.19 (td, J = 7.0, 2.7 Hz, 2H), 1.99 – 1.91 (m, 3H), 1.55 – 1.29 (m, 10H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 84.7, 68.4, 51.0 (d, J = 16.1 Hz), 28.8, 28.7, 28.6, 28.4, 27.9, 23.5, 18.5;

^{19}F NMR (471 MHz, $CDCl_3$) δ 53.4;

HRMS (ESI): *m/z* calculated for $C_{10}H_{18}FO_2S$ $[M+H]^+$ 221.1006, found 221.1001.



2g, 71%

(4-methoxyphenyl)methanesulfonyl fluoride (2g):

29 mg, 71% colorless oil.

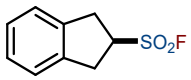
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.6 Hz, 2H). 6.95 (d, J = 8.7 Hz, 2H), 4.55 (d, J = 3.1 Hz, 2H), 3.83 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 132.1, 117.3, 114.9, 56.5(d, J = 17.5 Hz), 55.5;

^{19}F NMR (376 MHz, $CDCl_3$) δ 50.3;

HRMS (ESI): *m/z* calculated for $C_8H_{10}FO_3S$ $[M+H]^+$ 205.0329, found 205.0327.

The analytical data are consistent with literature values.[5]



2h, 85%

2,3-dihydro-1H-indene-2-sulfonyl fluoride (2h):

34 mg, 85%, colorless oil.

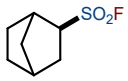
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (s, 4H), 4.34 – 4.22 (m, 1H), 3.65 – 3.47 (m, 4H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 127.9, 124.9, 59.7 (d, J = 15.1 Hz), 34.7;

^{19}F NMR (376 MHz, $CDCl_3$) δ 45.5;

HRMS (ESI): *m/z* calculated for $C_9H_{10}FO_2S$ $[M+H]^+$ 201.0380, found 201.0382.

The analytical data are consistent with literature values.[2]



2i, 90%

Bicyclo[2.2.1]heptane-2-sulfonyl fluoride (2i):

32 mg, 90%, colorless oil.

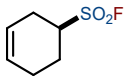
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.33 (t, J = 7.5 Hz, 1H), 2.87 (s, J = 4.2 Hz, 1H), 2.49 (s, 1H), 2.12 – 2.02 (m, 1H), 1.84 (dd, J = 22.8, 10.1 Hz, 2H), 1.76 – 1.59 (m, 2H), 1.33 (t, J = 9.2 Hz, 2H), 1.29-1.22 (m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 63.6 (d, J = 12.0 Hz), 39.9, 36.4, 36.1, 33.7, 29.5, 27.9;

^{19}F NMR (376 MHz, $CDCl_3$) δ 47.4;

HRMS (ESI): *m/z* calculated for $C_7H_{12}FO_2S$ $[M+H]^+$ 179.0537, found 179.0537.

The analytical data are consistent with literature values.[2]



2j, 92%

Cyclohex-3-ene-1-sulfonyl fluoride (2j)：

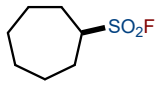
30 mg, 92%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 – 5.76 (m, 1H), 5.74 – 5.66 (m, 1H), 3.62 – 3.50 (m, 1H), 2.67 – 2.50 (m, 2H), 2.44 – 2.27 (m, 2H), 2.27 – 2.14 (m, 1H), 2.00 – 1.85 (m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 127.0, 122.7, 57.8 (d, J = 13.8 Hz), 25.3, 24.0, 22.8;

^{19}F NMR (376 MHz, $CDCl_3$) δ 42.0;

HRMS (ESI): *m/z* calculated for $C_6H_9FNaO_2S$ $[M+Na]^+$ 187.0199, found 187.0204.



2k, 88%

Cycloheptanesulfonyl fluoride (2k):

32 mg, 88%, colorless oil.

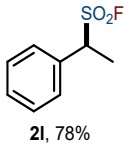
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.50 – 3.40 (m, 1H), 2.40 – 2.30 (m, 2H), 2.06 – 1.82 (m, 4H), 1.64 – 1.53 (m, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 63.0 (d, J = 10.3 Hz), 28.3, 28.2, 25.5;

^{19}F NMR (376 MHz, $CDCl_3$) δ 41.5;

HRMS (ESI): *m/z* calculated for $C_7H_{14}FO_2S$ $[M+H]^+$ 181.0693, found 181.0686.

The analytical data are consistent with literature values.[2]



2l, 78%

1-phenylethane-1-sulfonyl fluoride (2l):

29 mg, 78%, colorless oil.

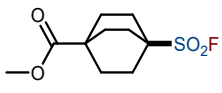
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 5H), 4.64 (q, J = 7.2 Hz, 1H), 1.94 (d, J = 8.0 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 131.5, 130.1, 129.3, 129.1, 63.2 (d, J = 14.0 Hz), 16.2;

^{19}F NMR (376 MHz, $CDCl_3$) δ 42.7;

HRMS (ESI): *m/z* calculated for $C_8H_{10}FO_2S$ $[M+H]^+$ 189.0380, found 189.0382.

The analytical data are consistent with literature values.[5]



2m, 81%

Methyl 4-(fluorosulfonyl)bicyclo[2.2.2]octane-1-carboxylate (2m):

41 mg, 81%, white solid.

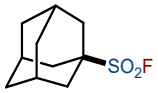
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.67 (s, 3H), 2.16 – 2.10 (m, 6H), 1.99 – 1.93 (m, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.3, 60.3 (d, J = 12.7 Hz), 52.3, 38.1, 27.4, 25.5;

^{19}F NMR (471 MHz, $CDCl_3$) δ 33.7;

HRMS (ESI): *m/z* calculated for $C_{10}H_{16}FO_4S$ $[M+H]^+$ 251.0748, found 251.0745.

The analytical data are consistent with literature values.[5]



2n, 93%

Adamantane-1-sulfonyl fluoride (2n):

41 mg, 93%, colorless oil.

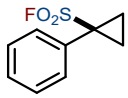
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22 (s, 3H), 2.18 (d, J = 3.0 Hz, 6H), 1.83 – 1.71 (m, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 62.6 (d, J = 10.7 Hz), 36.1, 35.5, 28.0;

^{19}F NMR (376 MHz, $CDCl_3$) δ 26.5;

HRMS (ESI): *m/z* calculated for $C_{10}H_{15}FNaO_2S$ $[M+Na]^+$ 241.0669, found 241.0676.

The analytical data are consistent with literature values.[2]



2o, 67%

1-phenylcyclopropane-1-sulfonyl fluoride (2o):

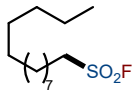
27 mg, 67%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 7.44 – 7.38 (m, 3H), 2.01 – 1.96 (m, 2H), 1.54 – 1.49 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 131.9, 130.0, 129.1, 43.4 (d, J = 24.2 Hz), 14.2;

^{19}F NMR (376 MHz, $CDCl_3$) δ 47.4;

HRMS (ESI): *m/z* calculated for $C_9H_9FKO_2S$ $[M+K]^+$ 238.9939, found 238.9935.



2p,77%
from Myristic acid

Tridecane-1-sulfonyl fluoride (2p):

41 mg, 77%, white solid.

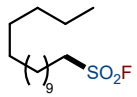
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.39 – 3.32 (m, 2H), 1.99 – 1.89 (m, 2H), 1.52 – 1.43 (m, 2H), 1.36 – 1.21 (m, 18H), 0.88 (t, J = 6.8 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 51.0 (d, J = 16.1 Hz) 32.0, 29.8, 29.7, 29.6, 29.5, 29.3, 28.9, 28.0, 23.5, 22.8, 14.3;

^{19}F NMR (471 MHz, $CDCl_3$) δ 53.2;

HRMS (ESI): *m/z* calculated for $C_{13}H_{27}FNaO_2S$ $[M+Na]^+$ 289.1608, found 289.1611.

The analytical data are consistent with literature values.[4]



2q, 83%
from Palmitic acid

Pentadecane-1-sulfonyl fluoride (2q):

49 mg, 83%, white solid.

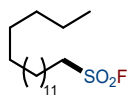
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.39 – 3.32 (m, 2H), 2.00 – 1.89 (m, 2H), 1.52 – 1.43 (m, 2H), 1.32 – 1.25(m, 22H), 0.88 (t, J = 6.7 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 50.9 (d, J = 16.0 Hz) 31.9, 29.68, 29.67, 29.64, 29.60, 29.5, 29.42, 29.35, 29.1, 28.8, 27.8, 23.4, 22.7, 14.1;

^{19}F NMR (471 MHz, $CDCl_3$) δ 53.2;

HRMS (ESI): *m/z* calculated for $C_{15}H_{31}FKO_2S$ $[M+K]^+$ 333.1660, found 333.1666.

The analytical data are consistent with literature values.[5]



2r, 80%
from stearic acid

Heptadecane-1-sulfonyl fluoride (2r):

52 mg, 80%, white solid.

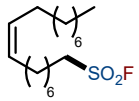
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.37 – 3.31 (m, 2H), 1.97 – 1.89 (m, 2H), 1.50 – 1.43 (m, 2H), 1.32 – 1.23 (m, 26H), 0.87 (t, J = 6.9 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 50.9 (d, J = 16.0 Hz), 31.9, 29.67, 29.65, 29.61, 29.5, 29.4, 29.35, 29.1, 28.8, 27.9, 23.4, 22.7, 14.1;

^{19}F NMR (471 MHz, $CDCl_3$) δ 53.3;

HRMS (ESI): *m/z* calculated for $C_{17}H_{35}FNaO_2S$ $[M+Na]^+$ 345.2234, found 345.2228.

The analytical data are consistent with literature values.[2]



2s, 81%
from Oleic acid

Heptadic-8-ene-1-sulfonyl fluoride (2s):

52 mg, 81%, colorless oil.

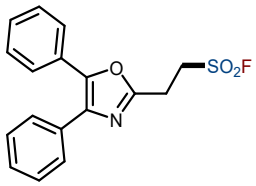
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.40 – 5.29 (m, 2H), 3.39 – 3.32 (m, 2H), 2.06 – 1.98 (m, 4H), 1.97 – 1.91 (m, 2H), 1.52 – 1.43 (m, 2H), 1.39 – 1.25 (m, 18H), 0.88 (t, J = 6.9 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 130.4, 129.6, 51.0 (d, J = 16.0 Hz), 32.0, 29.9, 29.66, 29.64, 29.5, 28.9, 28.8, 28.0, 27.4, 27.2, 23.5, 22.8, 14.2;

^{19}F NMR (471 MHz, $CDCl_3$) δ 53.3;

HRMS (ESI): *m/z* calculated for $C_{17}H_{34}FO_2S$ $[M+H]^+$ 321.2258, found 321.2256.

The analytical data are consistent with literature values.[4]



2t, 79%
from Oxaprozin

2-(4,5-diphenyloxazol-2-yl)ethane-1-sulfonyl fluoride (2t):

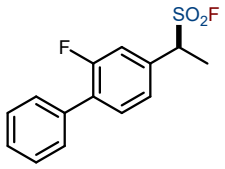
52 mg, 79%, colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 2H), 7.59 – 7.55 (m, 2H), 7.41 – 7.33 (m, 6H), 4.03 – 3.96 (m, 2H), 3.53 – 3.47 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.7, 146.6, 135.5, 131.9, 129.1, 128.9, 128.8, 128.6, 128.5, 127.9, 126.7, 47.9 (d, J = 18.9 Hz), 22.9;

^{19}F NMR (471 MHz, $CDCl_3$) δ 53.6;

HRMS (ESI): *m/z* calculated for $C_{17}H_{15}FNO_3S$ $[M+H]^+$ 332.0751, found 332.0751.



2u, 86%
from Flubiprofen

(2-fluoro-[1,1'-biphenyl]-4-yl)ethane-1-sulfonyl fluoride (2u):

49 mg, 86%, white solid.

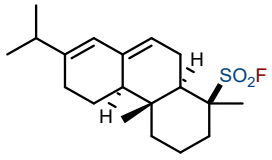
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.37 (m, 6H), 7.34 – 7.26 (m, 2H), 4.67 (q, J = 7.2 Hz, 1H), 1.97 (d, J = 7.1 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.58 (d, J = 250.2 Hz), 134.79 (d, J = 1.4 Hz), 132.42 (d, J = 7.9 Hz), 131.61 (d, J = 4.0 Hz), 131.00 (d, J = 13.5 Hz), 129.10 (d, J = 3.0 Hz), 128.74, 128.40, 125.21 (d, J = 3.6 Hz), 116.94 (d, J = 24.9 Hz), 62.51 (dd, J = 14.8, 1.7 Hz), 16.11;

^{19}F NMR (376 MHz, $CDCl_3$) δ 43.2, -115.8 (t, J = 9.4 Hz);

HRMS (ESI): *m/z* calculated for $C_{14}H_{13}F_2O_2S_2$ $[M+H]^+$ 283.0599, found 283.0603.

The analytical data are consistent with literature values.[5]



2v, 84%
from Abietic acid

(1R,4a*R*,4b*R*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,4b,5,6,10,10a-

decahydrophenanthrene-1-sulfonyl fluoride (2v):

57 mg, 84%, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 (s, 1H), 5.41 – 5.35 (m, 1H),2.48 – 2.38 (m, 1H), 2.32 – 2.19 (m, 3H), 2.15 – 1.89 (m, 7H), 1.85 – 1.75 (m, 2H), 1.65-1.63 (s, 2H), 1.27 – 1.16 (m, 3H), 1.01 (dd, J = 6.8, 3.6 Hz, 6H), 0.86 (s, 3H);

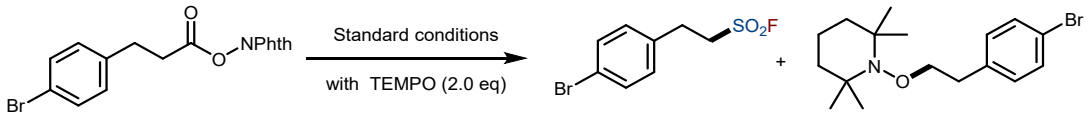
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 135.1, 122.1, 119.4, 71.1 (d, J = 5.7 Hz), 50.5, 43.3, 37.6, 36.1, 35.0, 34.6, 27.4, 25.30 (d, J = 1.8Hz), 22.7, 21.5, 21.0, 18.0, 16.6, 14.2;

^{19}F NMR (471 MHz, $CDCl_3$) δ 36.9;

HRMS (ESI): *m*/*z* calculated for $C_{19}H_{30}FO_2S$ $[M+H]^+$ 341.1945, found 341.1942.

4. Mechanism Studies

4.1 TEMPO trapping experiment



1a, 0.2 mmol

2a, 18%

3, detected by HRMS: 340.1271

HRMS (ESI): *m/z* calculated for $C_{17}H_{27}BrNO$ $[M+H]^+$ 340.1271, found 340.1271.

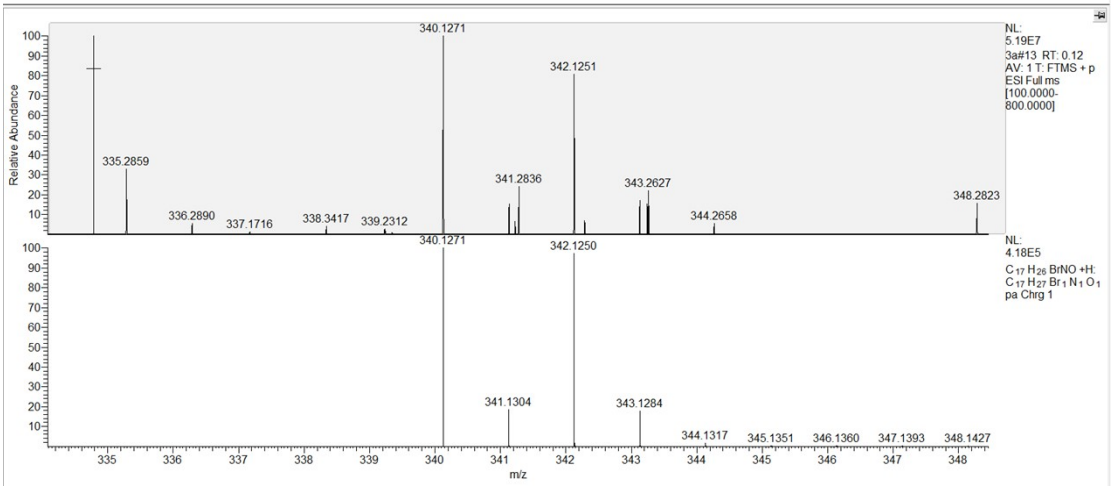
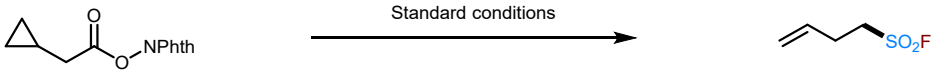


Figure S2. HRMS spectra for the TEMPO trapping reaction

4.2 Radical clock experiment



4, 0.2 mmol

5, 66% detected by ^{19}F

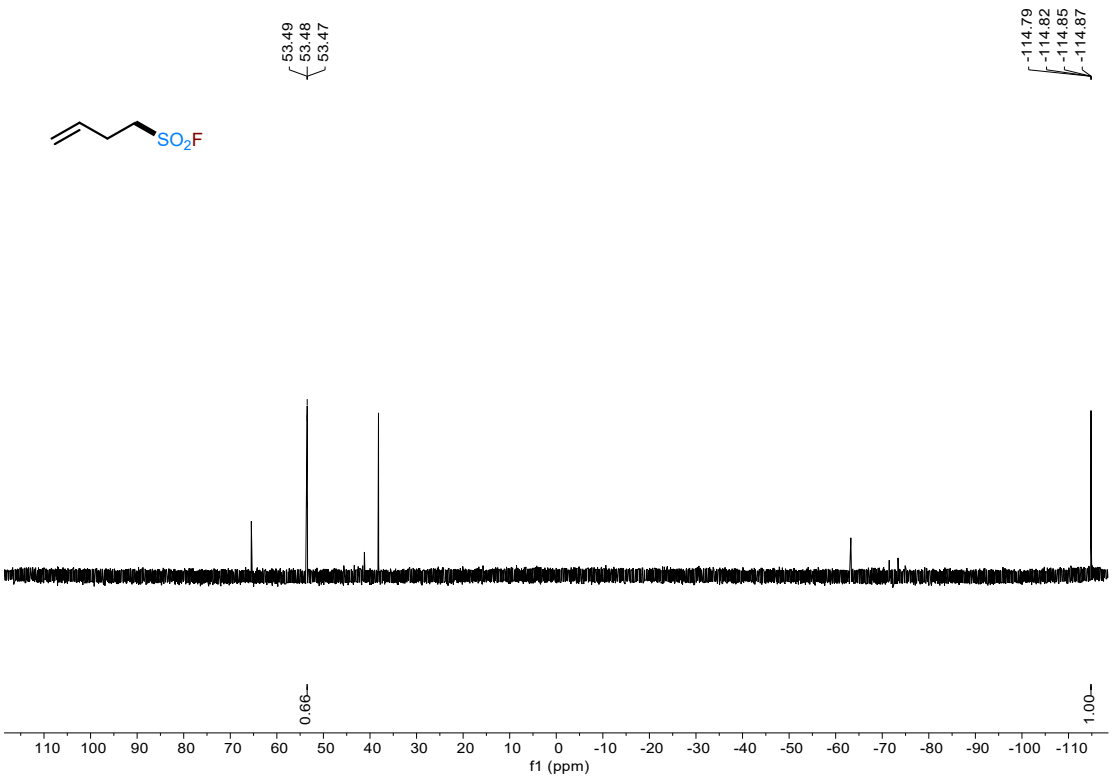
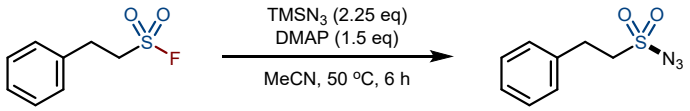


Figure S3. ^{19}F NMR spectra for radical clock experiment[5]

5. General Procedure and Characterizations for the Syntheses of 6-8



2b, 0.2 mmol **6**, 62%

2-phenylethane-1-sulfonyl azide (6):

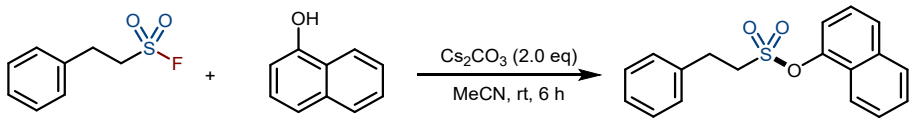
26 mg, 62%, colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.31 – 7.26 (m, 1H), 7.24 – 7.20 (m, 2H), 3.61 – 3.55 (m, 2H), 3.24 – 3.18 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 136.4, 129.2, 128.5, 127.6, 57.1, 29.7;

HRMS (ESI): *m/z* calculated for $C_8H_9N_3NaO_2S$ $[M+Na]^+$ 234.0308, found 234.0312.

The analytical data are consistent with literature values.[6]



2b, 0.2 mmol (2.0 eq) **7**, 92%

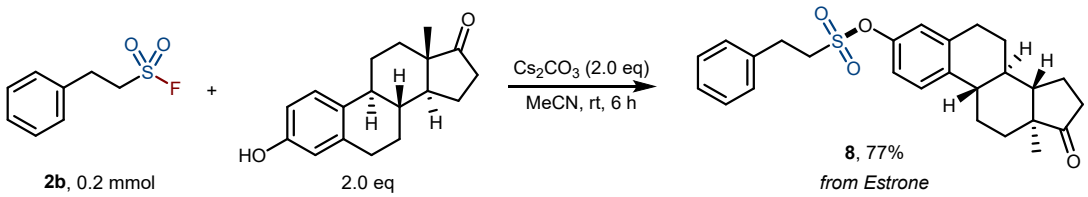
Naphthalen-1-yl 2-phenylethane-1-sulfonate (7):

57 mg, 92%, colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 8.4 Hz, 1H), 7.90 – 7.85 (m, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.61 – 7.52 (m, 2H), 7.51 – 7.43 (m, 2H), 7.34 – 7.29 (m, 2H), 7.28 – 7.23 (m, 1H), 7.22 – 7.17 (m, 2H), 3.66 – 3.58 (m, 2H), 3.36 – 3.29 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.2, 137.1, 135.0, 129.1, 128.5, 128.1, 127.41, 120.40, 127.31, 127.26, 127.1, 125.5, 121.6, 118.3, 52.6, 30.0;

HRMS (ESI): *m/z* calculated for $C_{18}H_{17}O_3S$ $[M+H]^+$ 313.0893, found 313.0888.



2b, 0.2 mmol 2.0 eq **8**, 77% *from Estrone*

(9*R*,14*R*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl 2-phenylethane-1-sulfonate (8):

67 mg, 77%, colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.21 (m, 6H), 7.03 – 6.93 (m, 2H), 3.52 – 3.45 (m, 2H), 3.30 – 3.24 (m, 2H), 2.92 (dd, J = 9.0, 4.3 Hz, 2H), 2.51 (dd, J = 19.5, 8.3 Hz, 1H), 2.43 – 2.36 (m, 1H), 2.28 (td, J = 10.9, 4.2 Hz, 1H), 2.20 – 2.10 (m, 1H), 2.10 – 2.00 (m, 2H), 1.99 – 1.92 (m, 1H), 1.69 – 1.40 (m, 6H), 0.91 (s, 3H);

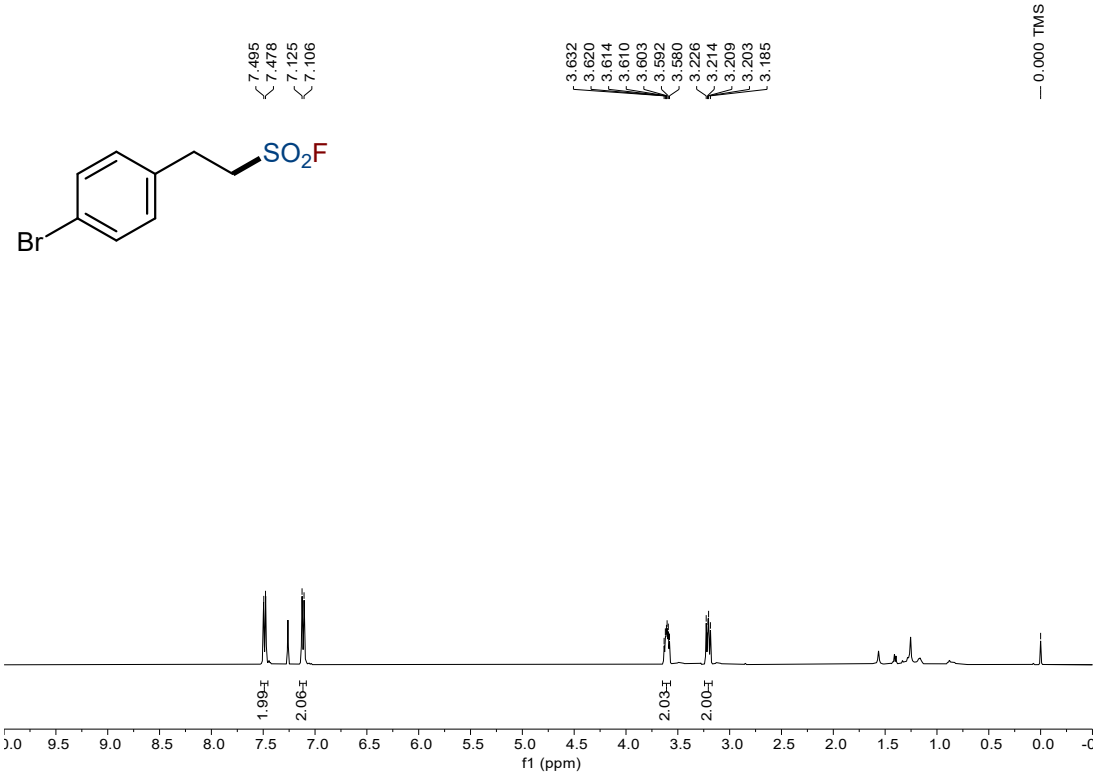
^{13}C NMR (126 MHz, $CDCl_3$) δ 220.8, 147.1, 139.2, 138.9, 137.3, 129.1, 128.6, 127.4, 127.0, 122.1, 119.1, 51.7, 50.5, 48.0, 44.2, 37.4, 35.9, 31.6, 29.9, 29.5, 26.3, 25.8, 21.7, 13.9;

HRMS (ESI): *m*/*z* calculated for $C_{26}H_{31}O_2S$ $[M+H]^+$ 439.1938, found 439.1950.

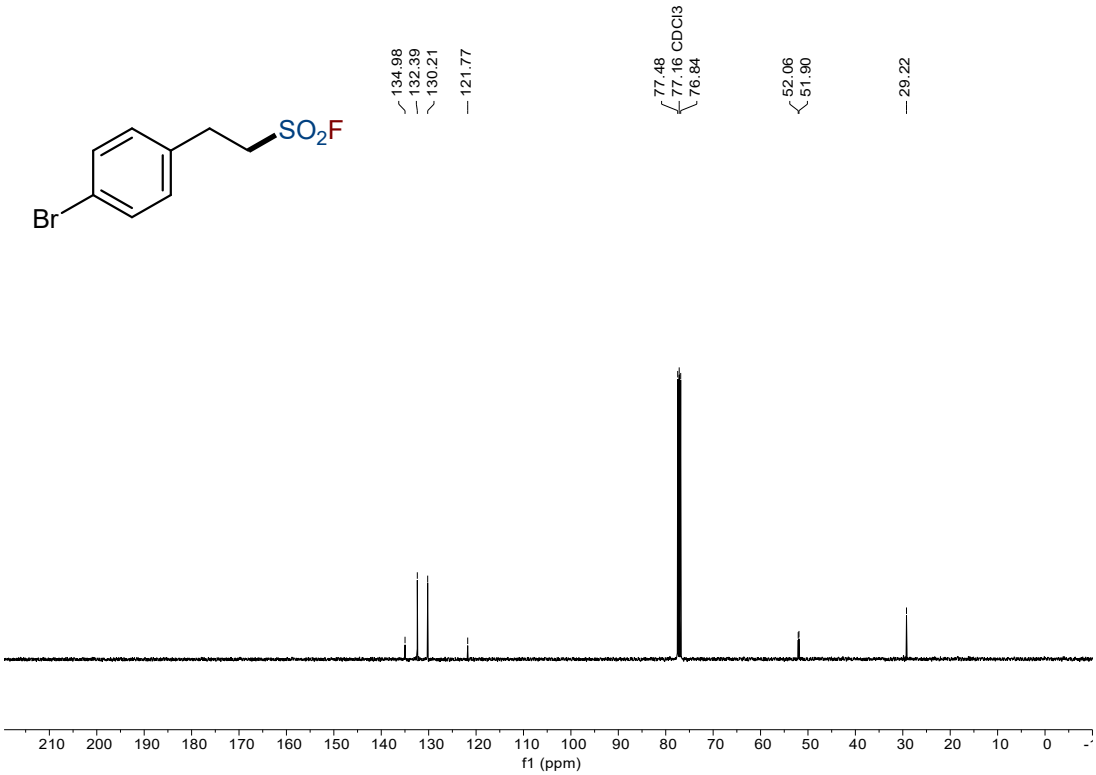
6. References

1. J. Cornella, J. T. Edwards, T. Qin, S. Kawamura, J. Wang, C. M. Pan, R. Gianatassio, M. Schmidt, M. D. Eastgate and P. S. Baran, Practical Ni-Catalyzed Aryl-Alkyl Cross-Coupling of Secondary Redox-Active Esters, *J. Am. Chem. Soc.,* 2016, **138**, 2174-2177.
2. T. Xu, T. Cao, M. Yang, R. Xu, X. Nie and S. Liao, Decarboxylative Thiolation of Redox-Active Esters to Thioesters by Merging Photoredox and Copper Catalysis, *Org. Lett.,* 2020, **22**, 3692-3696.
3. G. Laudadio, A. Bartolomeu, L. M. H. M. Verwijlen, Y. Cao K. T. Oliveira and T. Noel, Sulfonyl Fluoride Synthesis through Electrochemical Oxidative Coupling of Thiols and Potassium Fluoride, *J. Am. Chem. Soc.,* 2019, **141**, 11832-11836.
4. Z. Chen, X. Zhou, J. Yi, H. Diao, Q. Chen, G. Lu and J. Weng, Catalytic Decarboxylative Fluorosulfonylation Enabled by Energy-Transfer-Mediated Photocatalysis, *Org. Lett.*, 2022, **24**, 2474-2478.
5. Z. Ma, Y. Liu, X. Ma, X. Hu, Y. Guo, Q. Chen and C. Liu, Aliphatic Sulfonyl Fluoride Synthesis via Reductive Decarboxylative Fluorosulfonylation of Aliphatic Carboxylic Acid NHPI Esters, *Org. Chem. Front.,* 2022, **9**, 1115-1120.
6. S. P. McManus, M. R. Smith, R. A. Abramovitch and M. N. Offor, Thermolysis of Sulfonyl Azides Bearing Nucleophilic Neighboring Groups. A search for Anchimeric Assistance, *J. Org. Chem.* 1984*,* **49***,* 683-687.

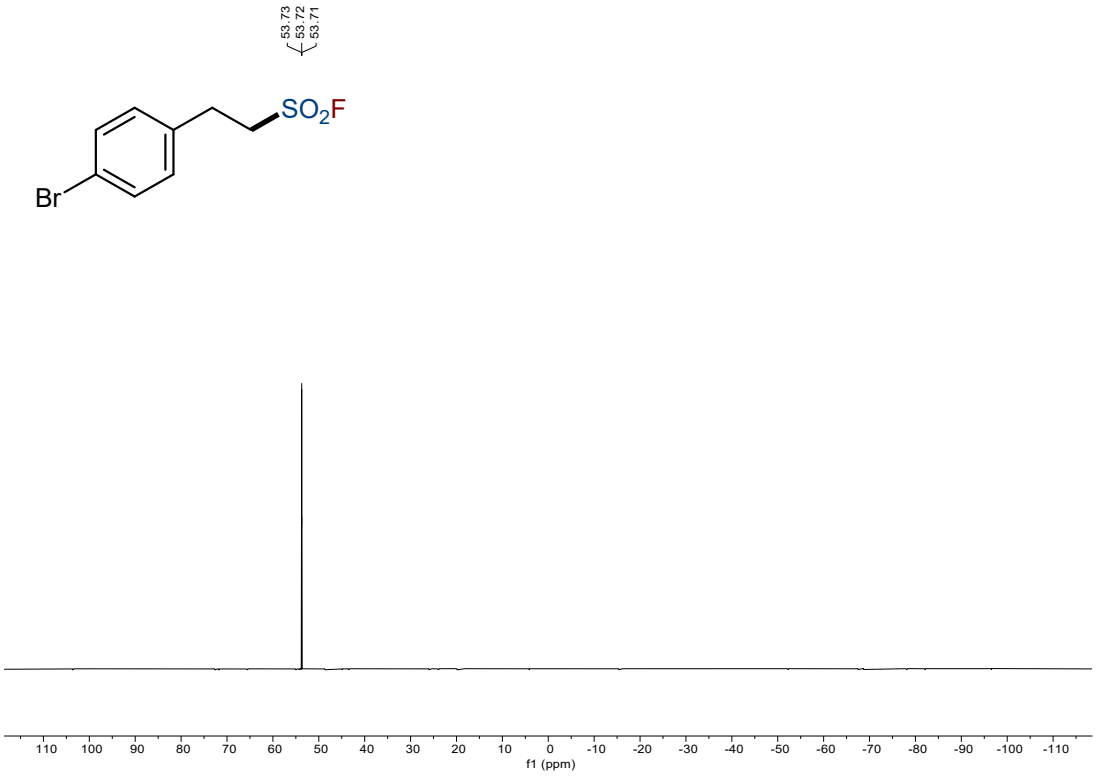
7. NMR Spectra



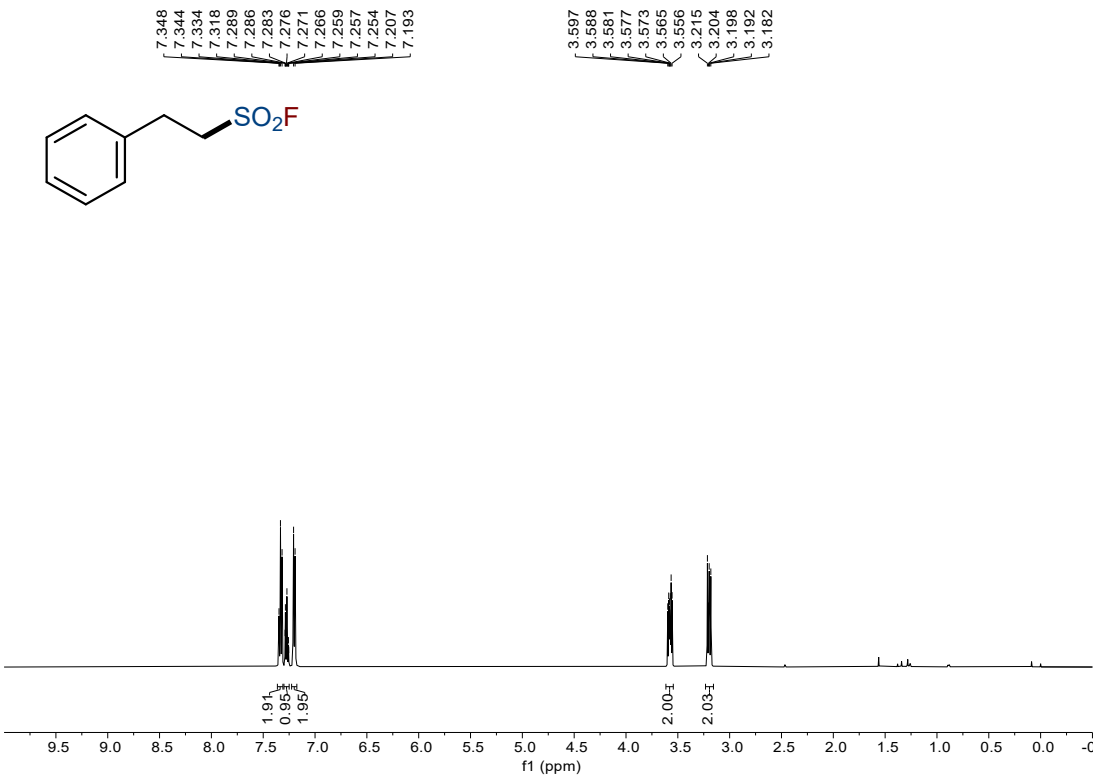
^{1}H NMR (400 MHz, $CDCl_3$) – (**2a**)



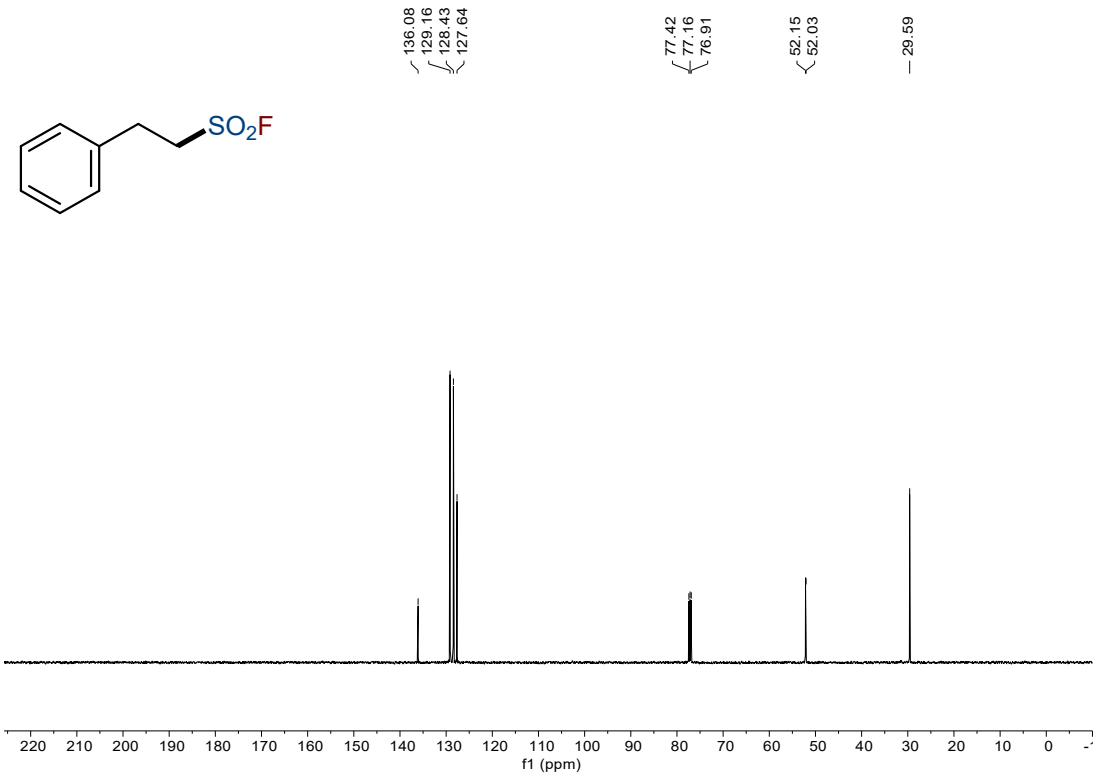
^{13}C NMR (101 MHz, $CDCl_3$) – **(2a)**



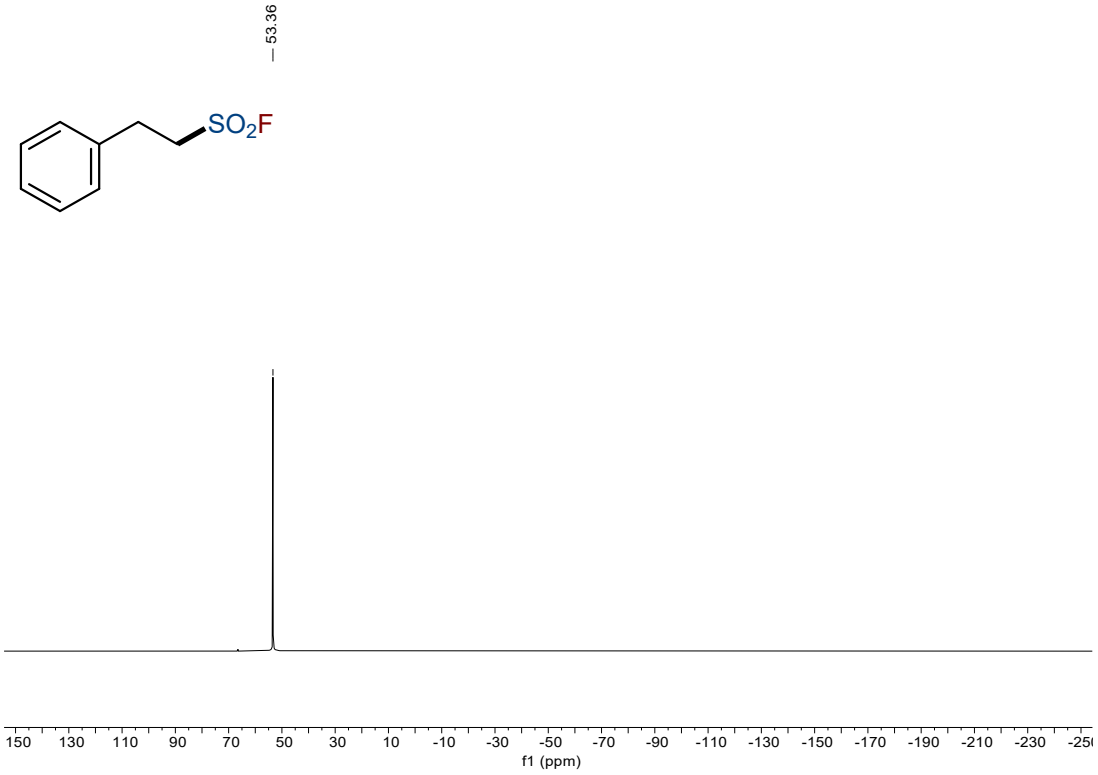
^{19}F NMR (376 MHz, $CDCl_3$) – **(2a)**



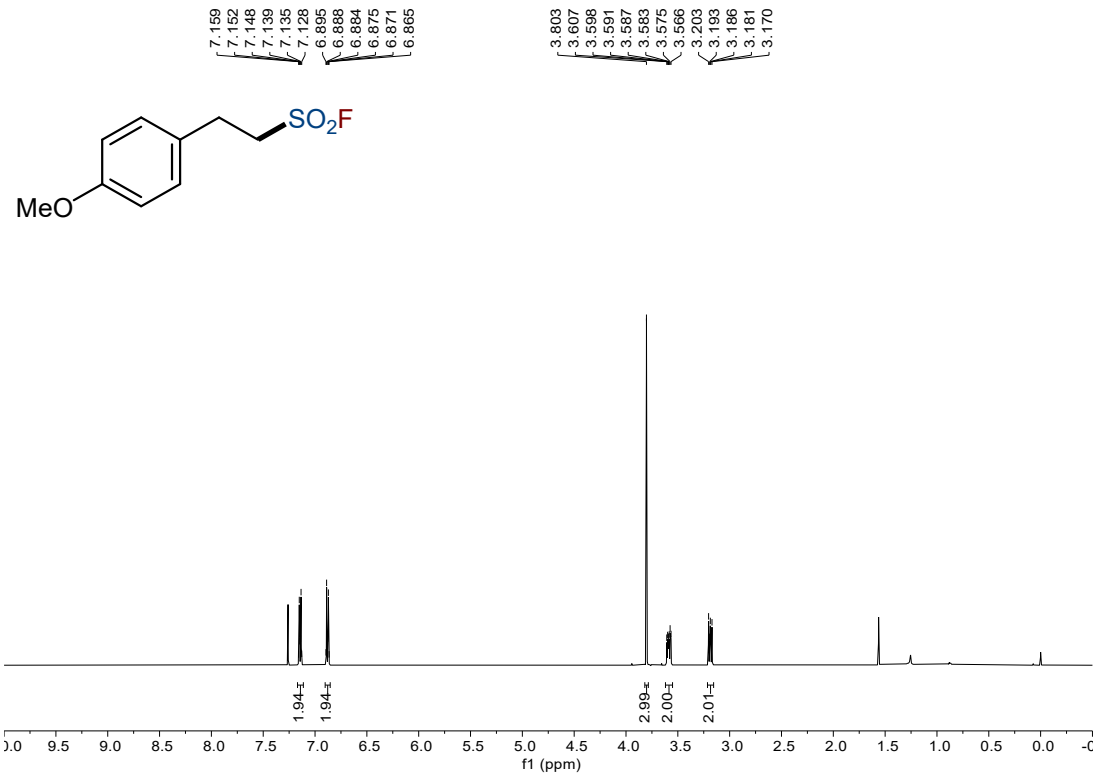
^{1}H NMR (500 MHz, $CDCl_3$) – **(2b)**



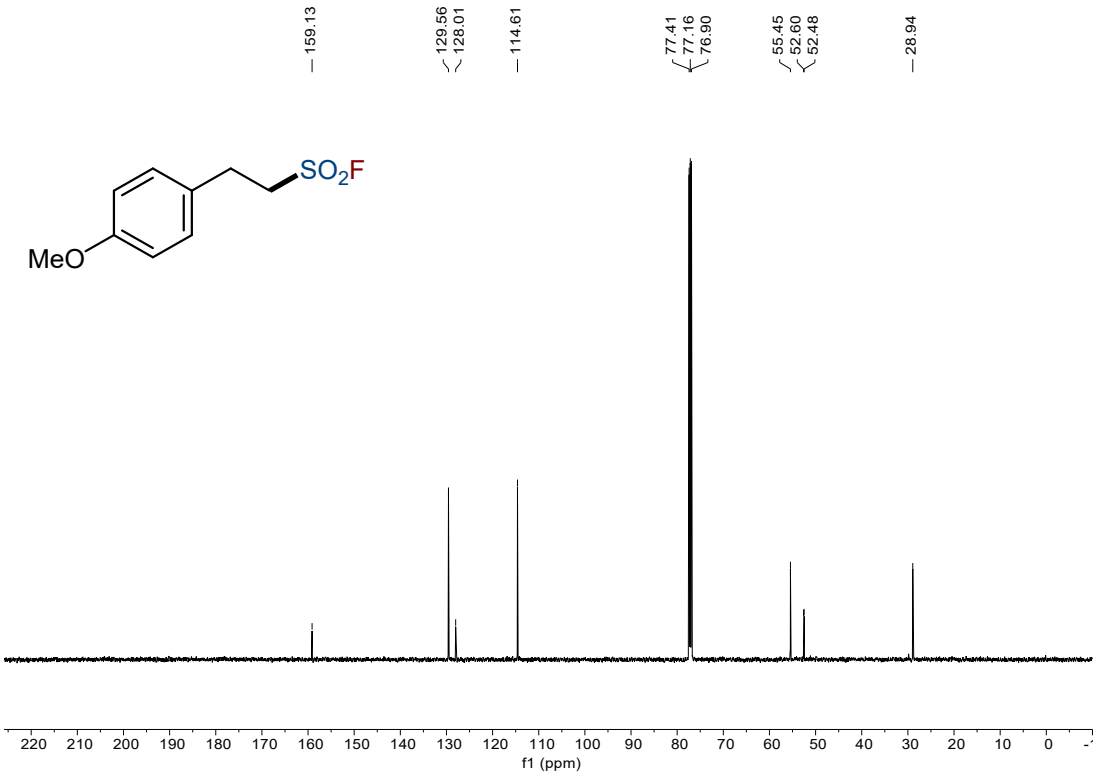
^{13}C NMR (126 MHz, $CDCl_3$) – **(2b)**



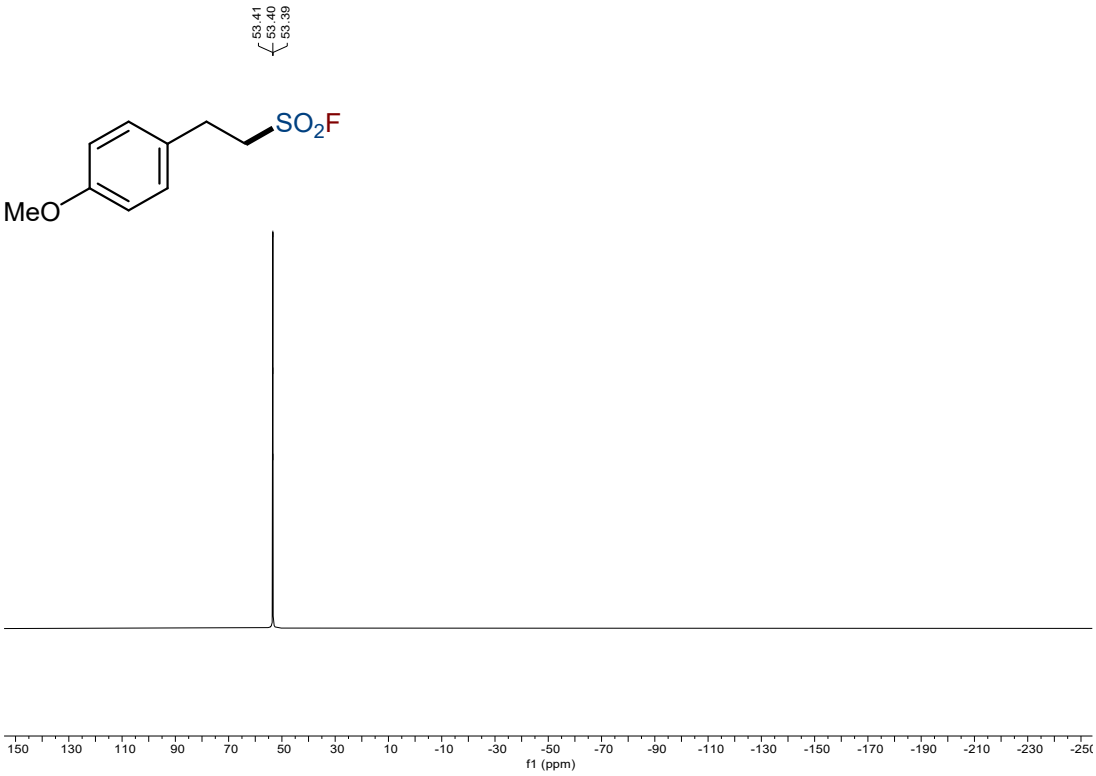
^{19}F NMR (471 MHz, $CDCl_3$) – **(2b)**



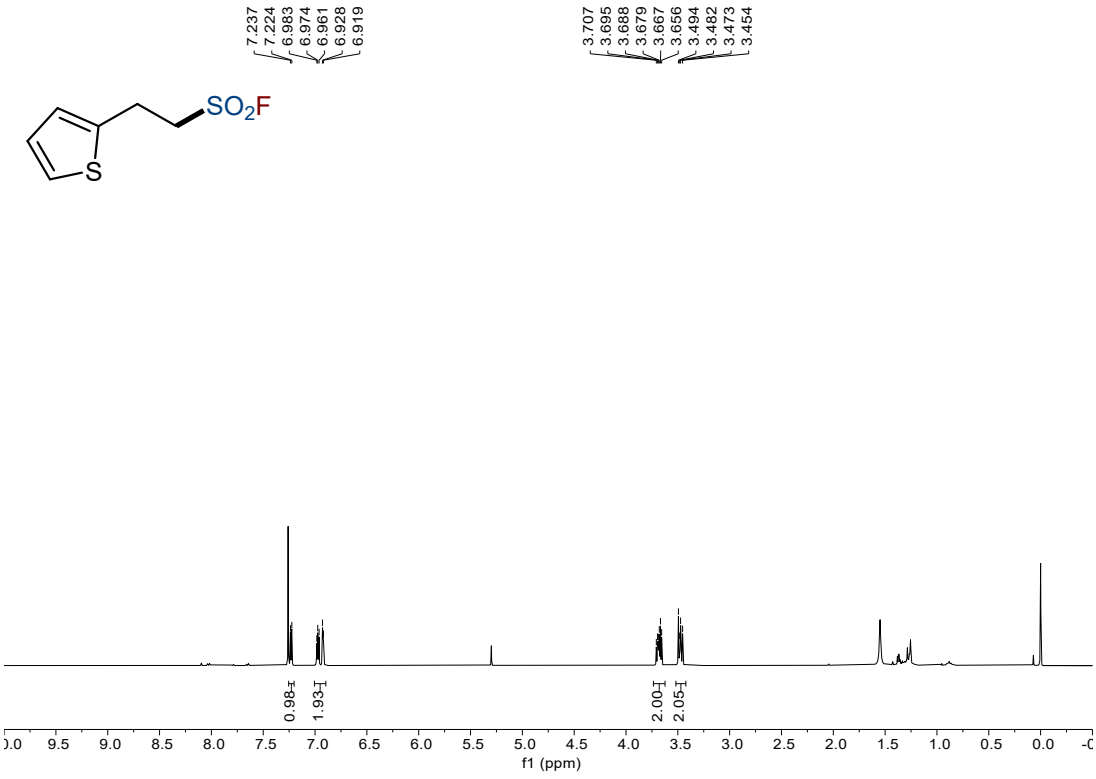
^{1}H NMR (500 MHz, $CDCl_3$) – **(2c)**



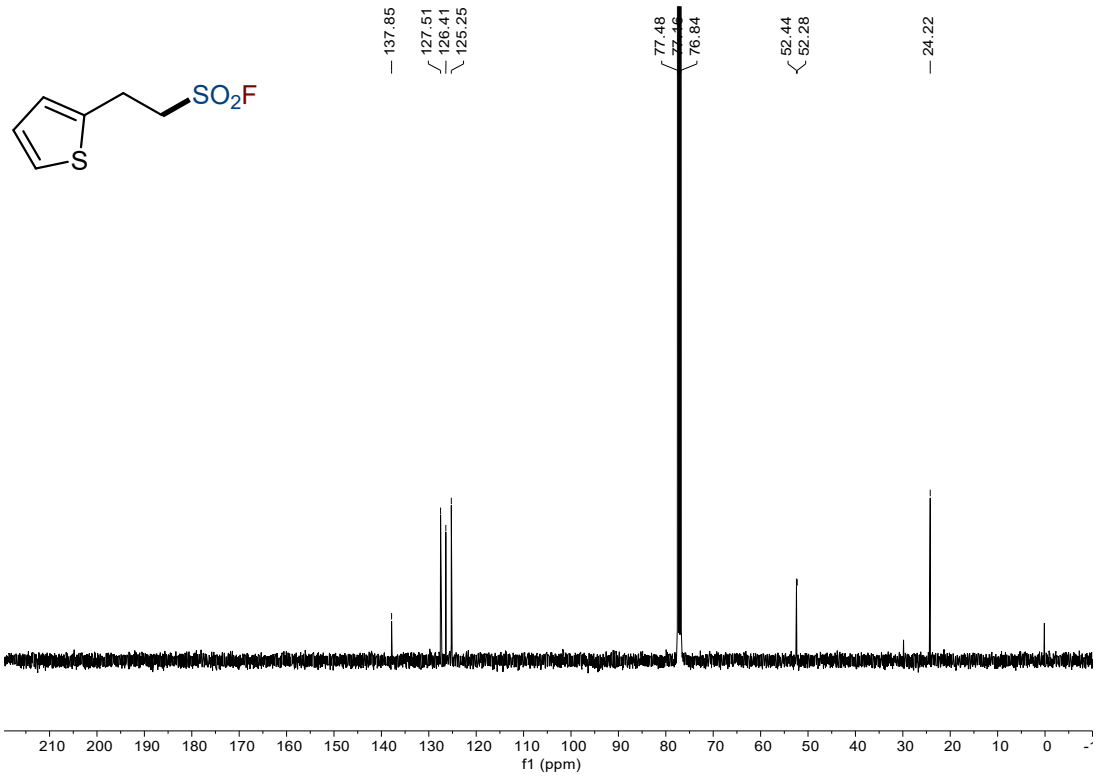
^{13}C NMR (126 MHz, $CDCl_3$) – **(2c)**



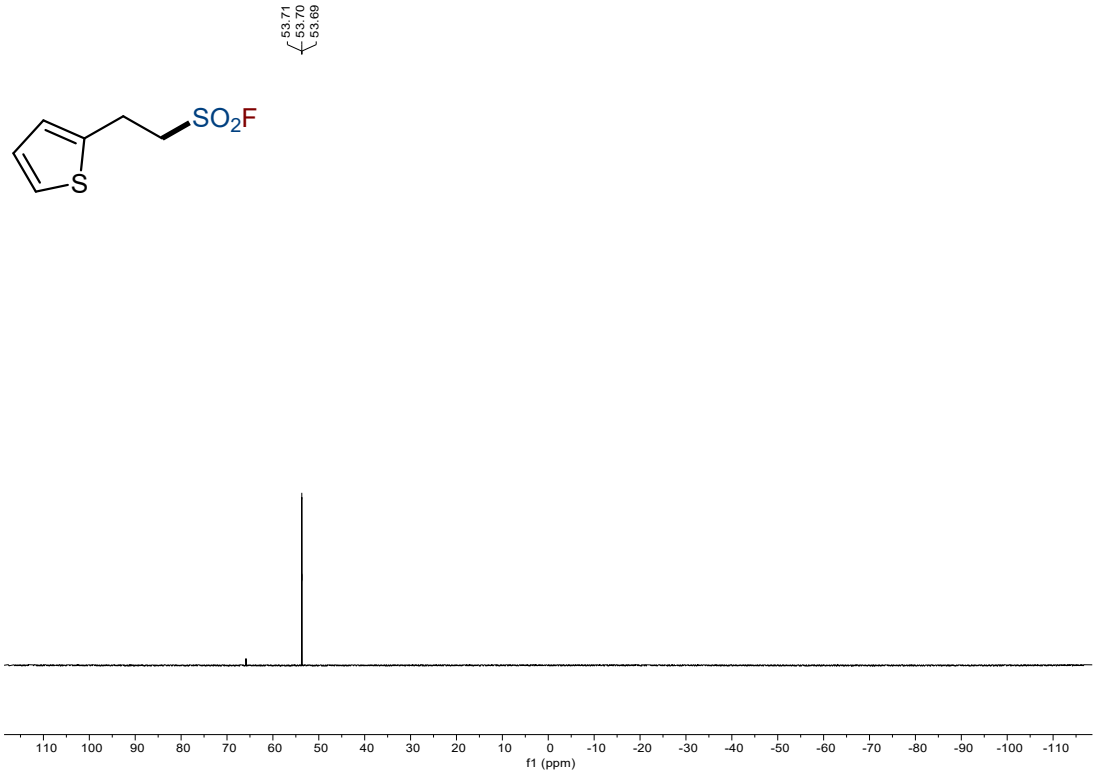
^{19}F NMR (471 MHz, $CDCl_3$) – **(2c)**



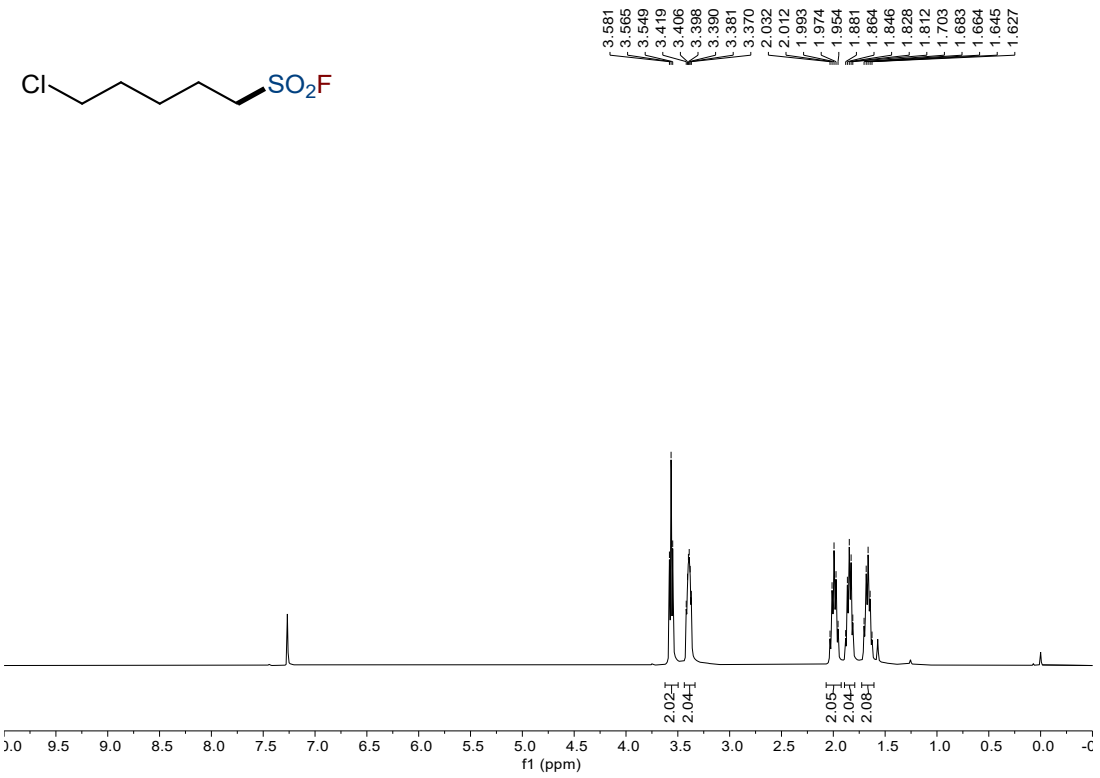
^{1}H NMR (400 MHz, $CDCl_3$) – **(2d)**



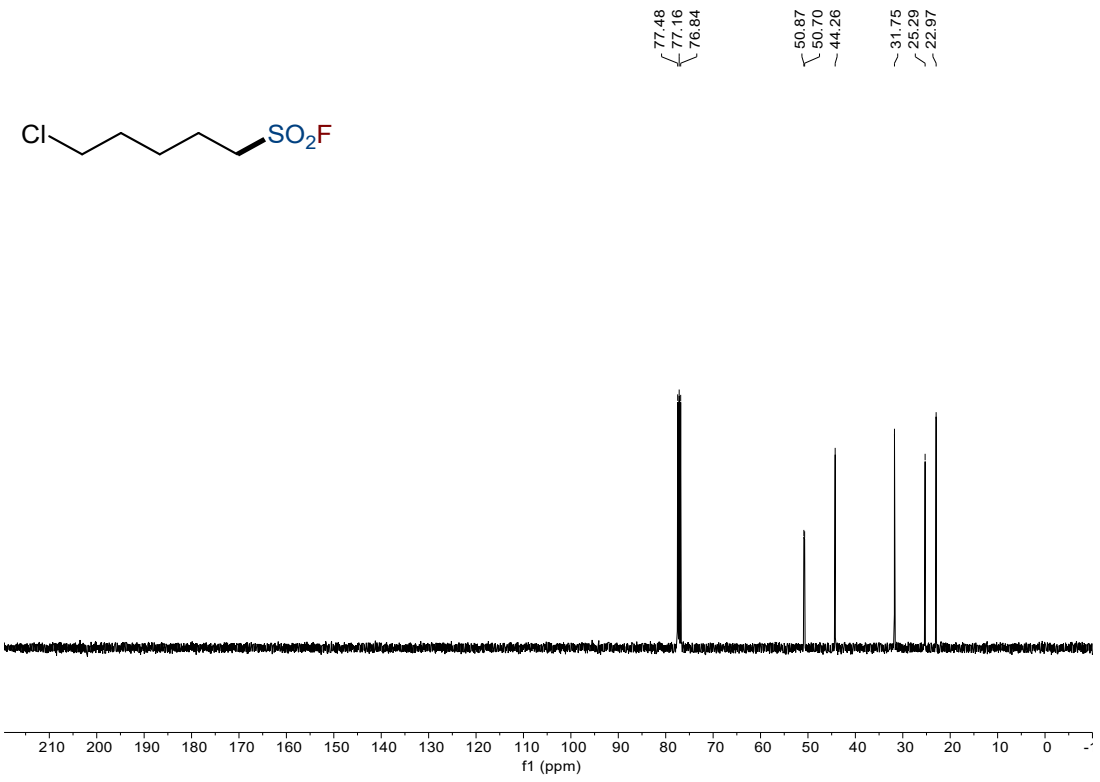
^{13}C NMR (101 MHz, $CDCl_3$) – **(2d)**



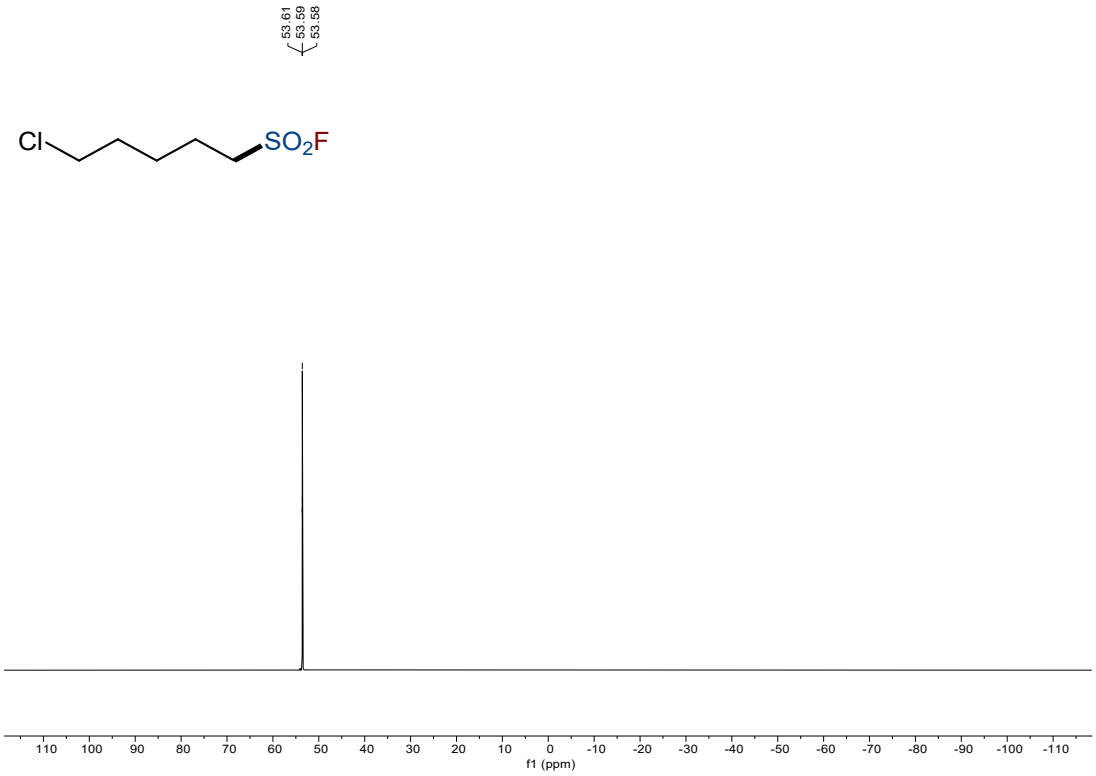
^{19}F NMR (376 MHz, $CDCl_3$) – **(2d)**



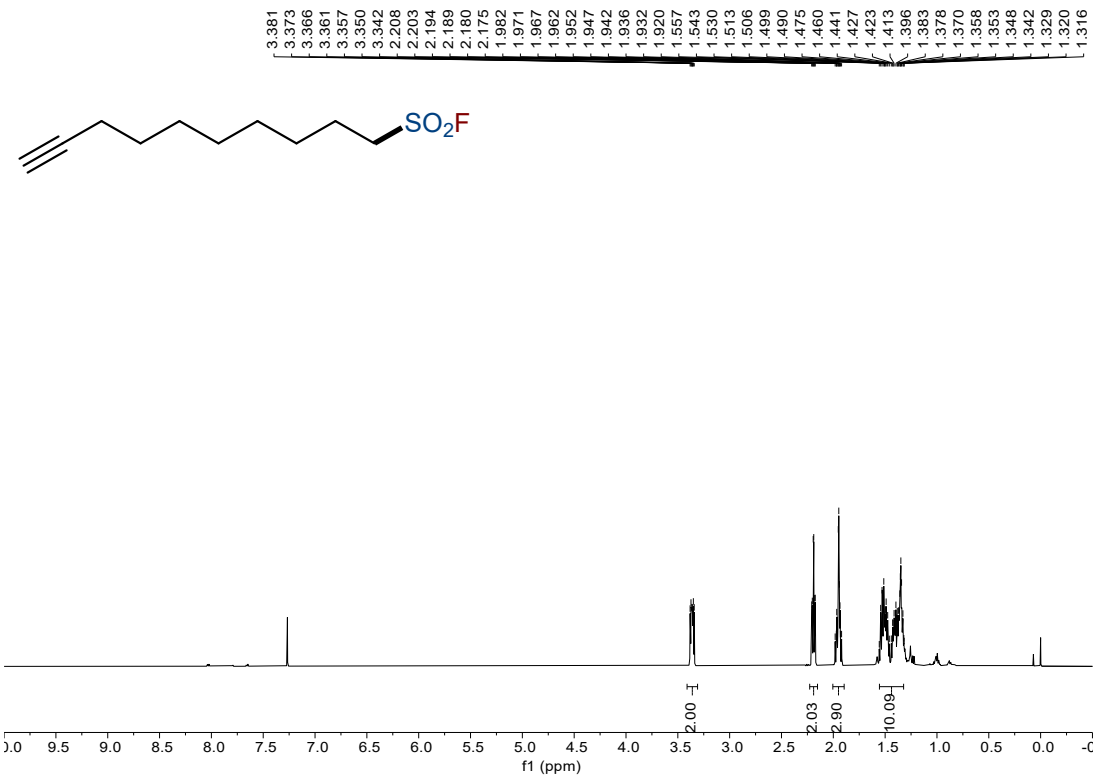
^{1}H NMR (400 MHz, $CDCl_3$) – **(2e)**



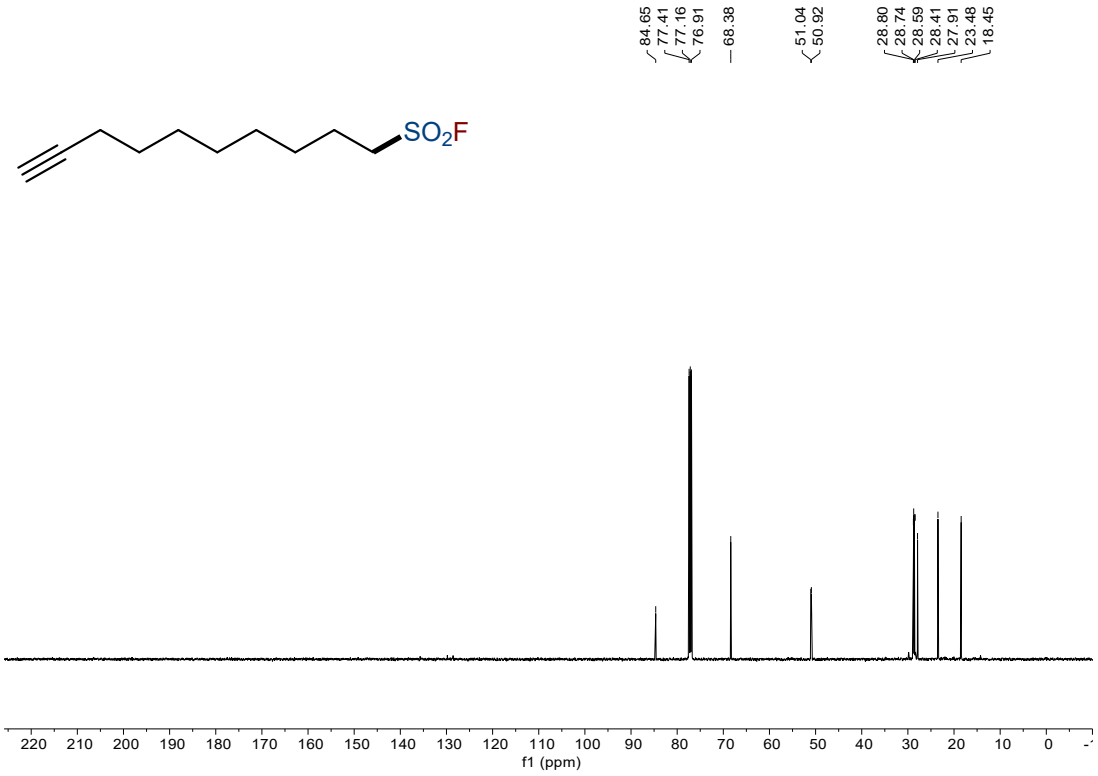
^{13}C NMR (101 MHz, $CDCl_3$) – **(2e)**



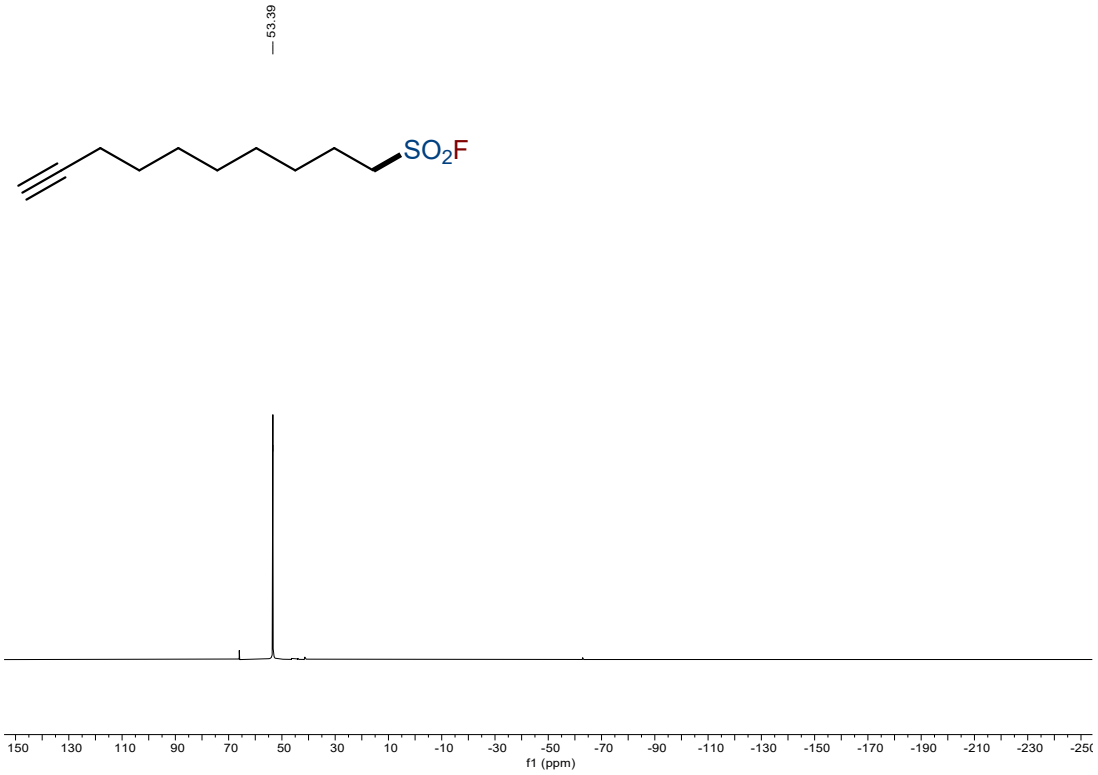
^{19}F NMR (376 MHz, $CDCl_3$) – **(2e)**



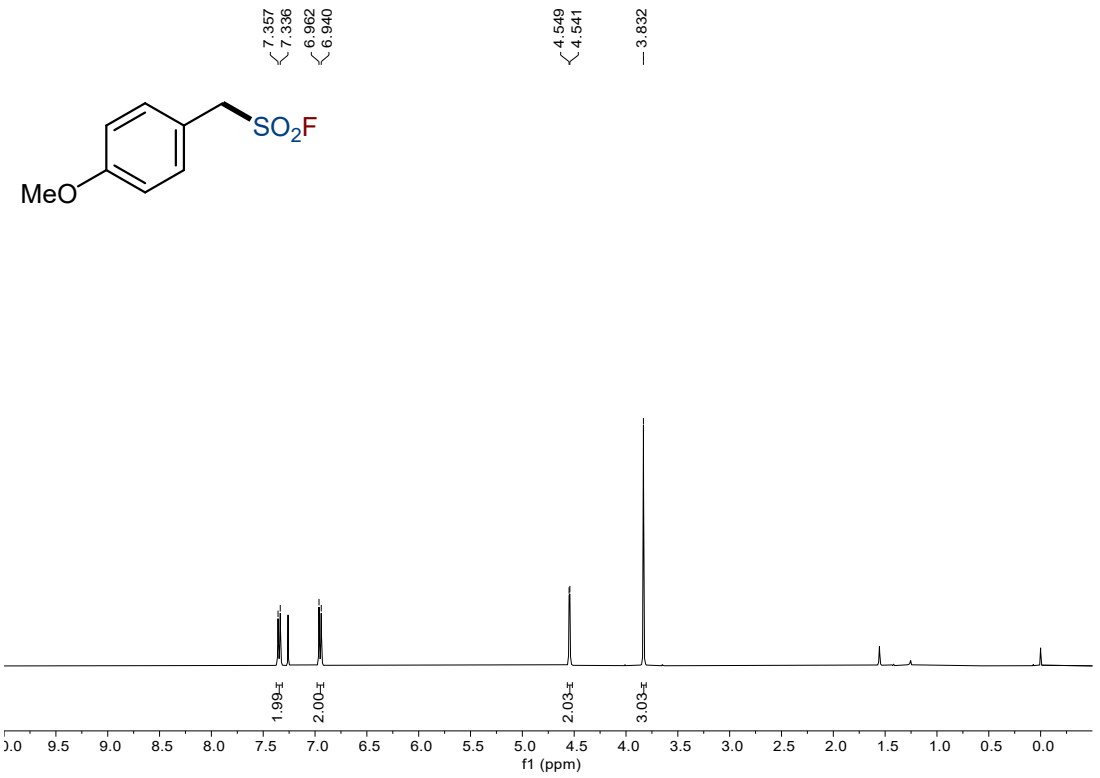
^{1}H NMR (500 MHz, $CDCl_3$) – **(2f)**



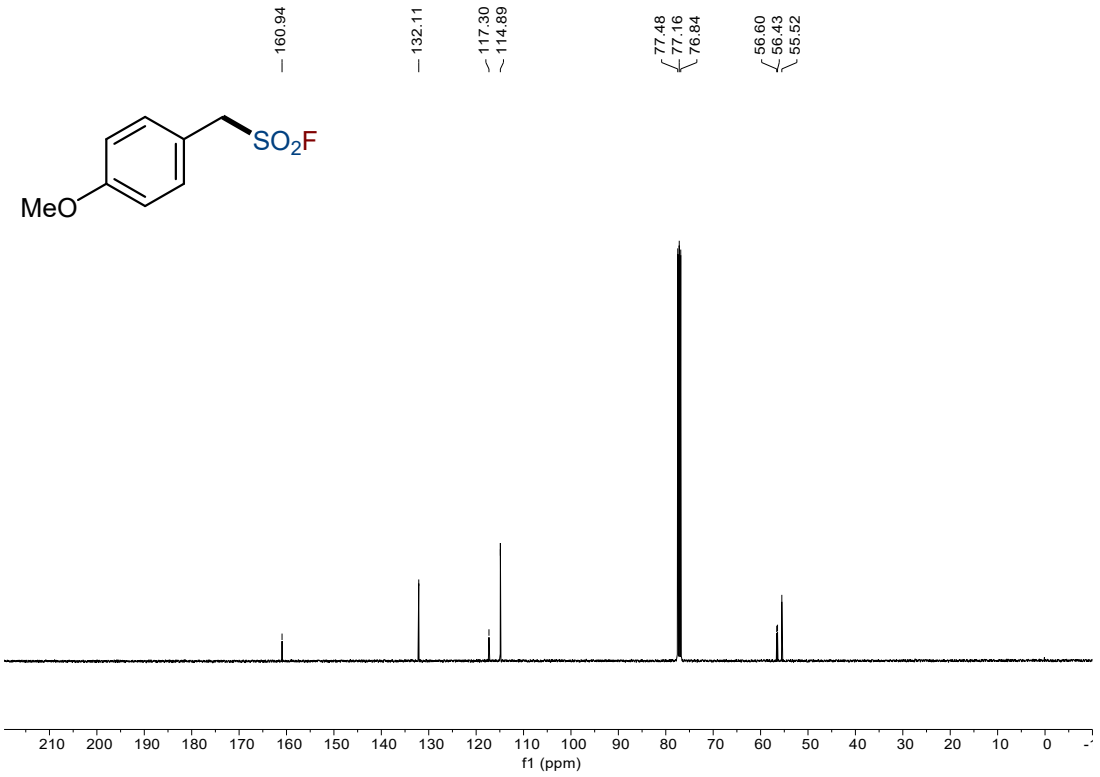
^{13}C NMR (126 MHz, $CDCl_3$) – **(2f)**



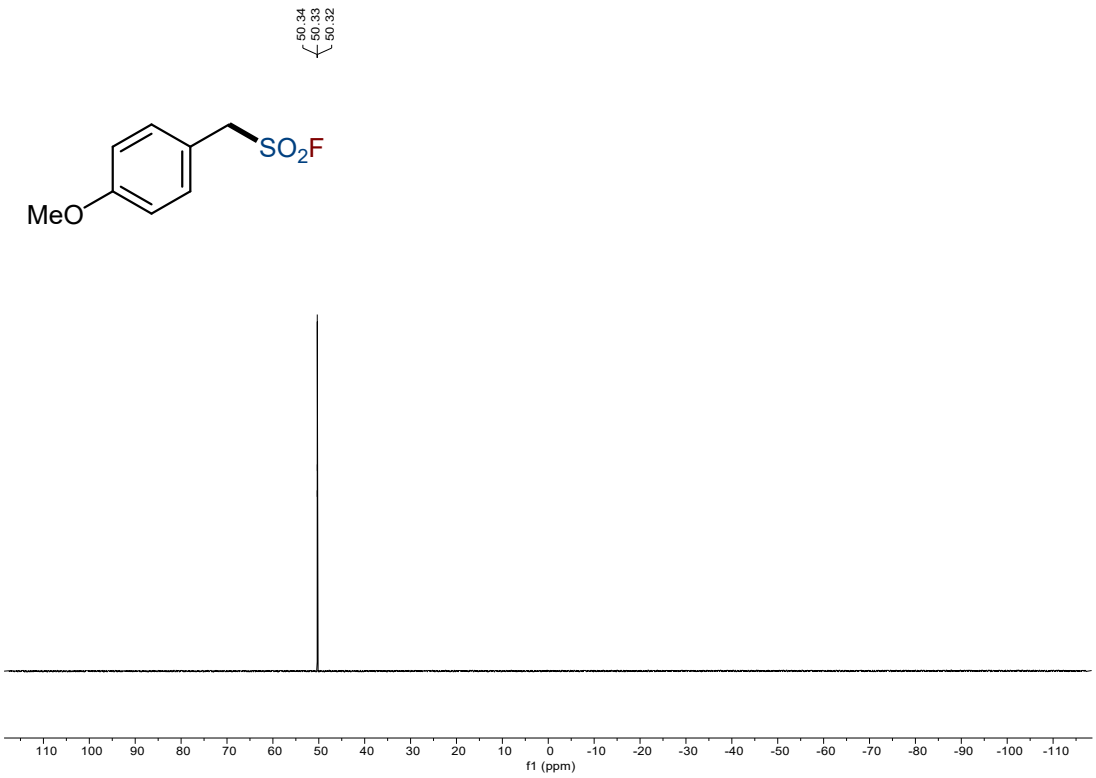
^{19}F NMR (471 MHz, $CDCl_3$) – **(2f)**



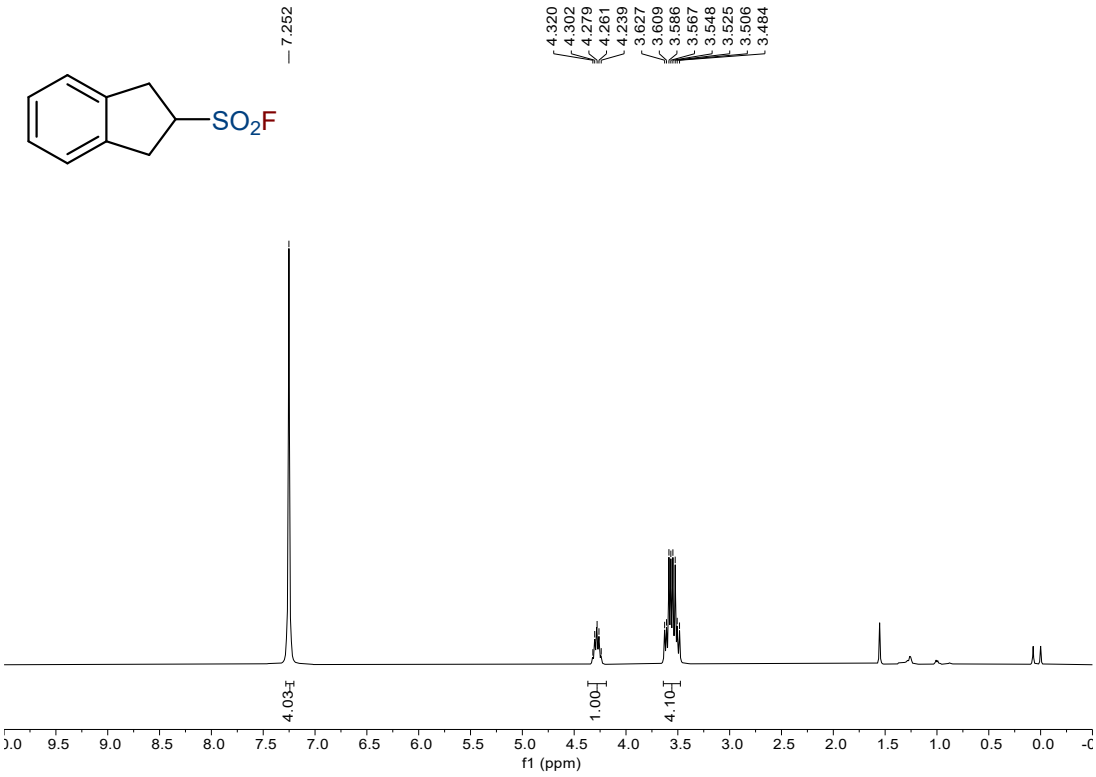
^{1}H NMR (400 MHz, $CDCl_3$) – **(2g)**



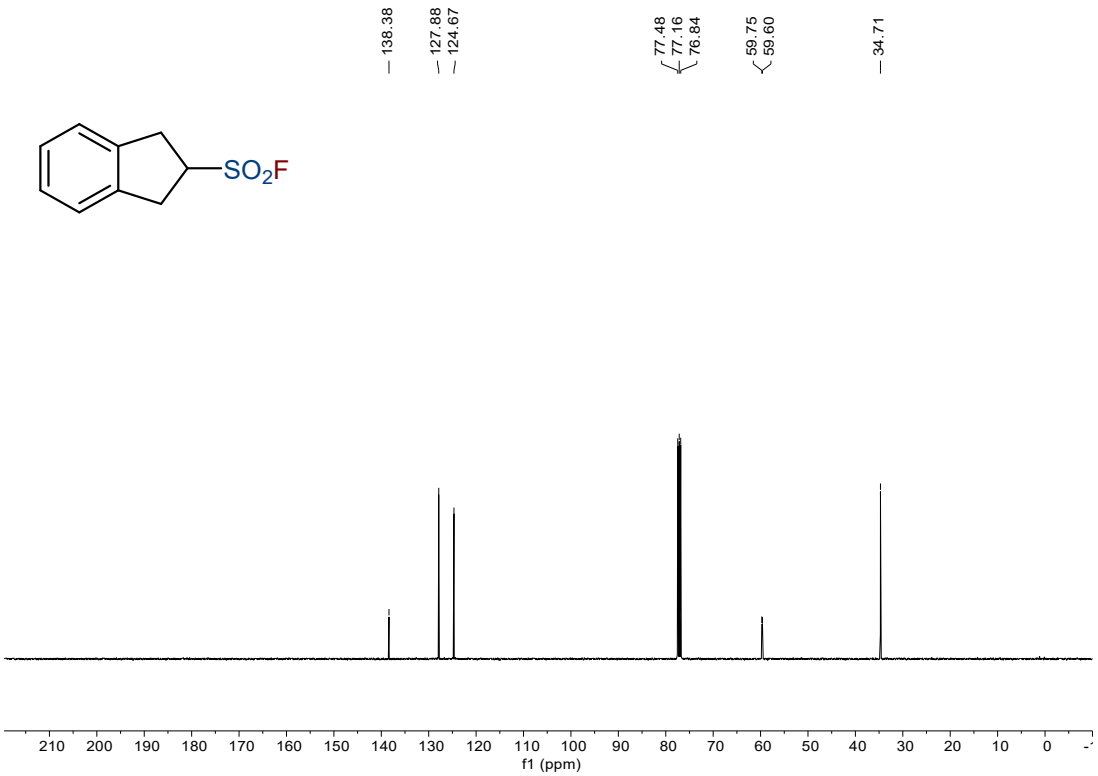
^{13}C NMR (101 MHz, $CDCl_3$) – **(2g)**



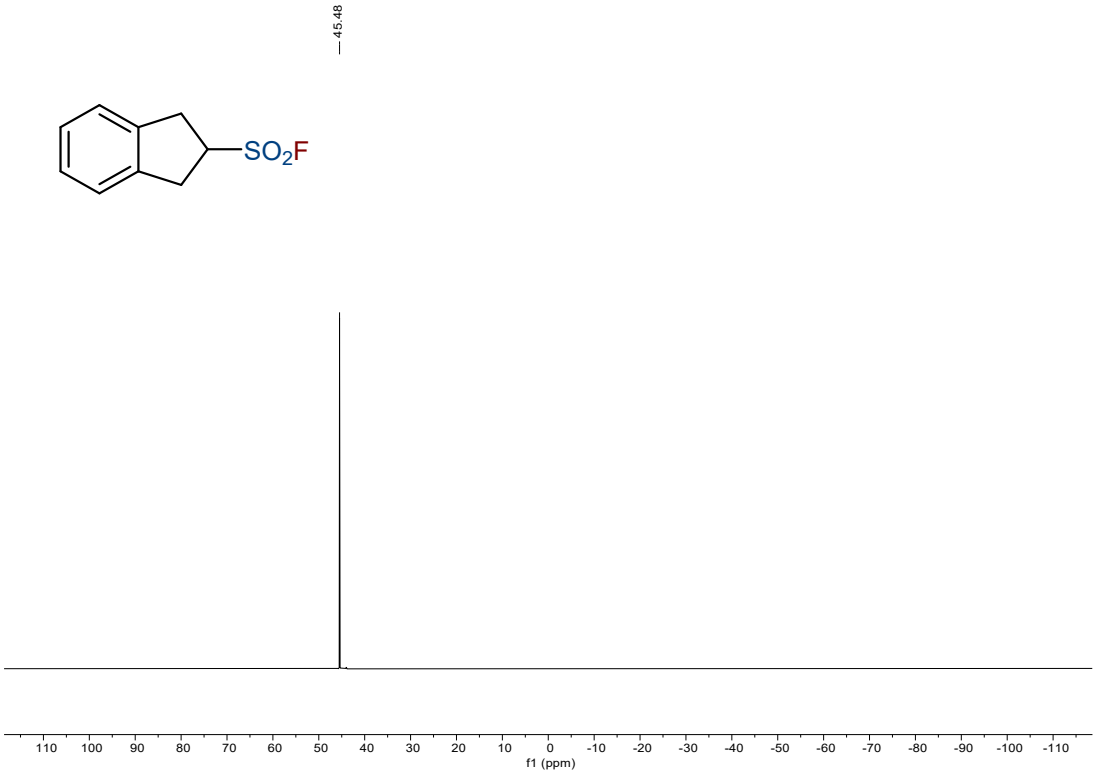
^{19}F NMR (376 MHz, $CDCl_3$) – **(2g)**



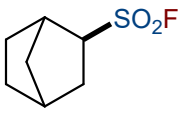
^{1}H NMR (400 MHz, $CDCl_3$) – **(2h)**



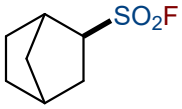
^{13}C NMR (101 MHz, $CDCl_3$) – **(2h)**



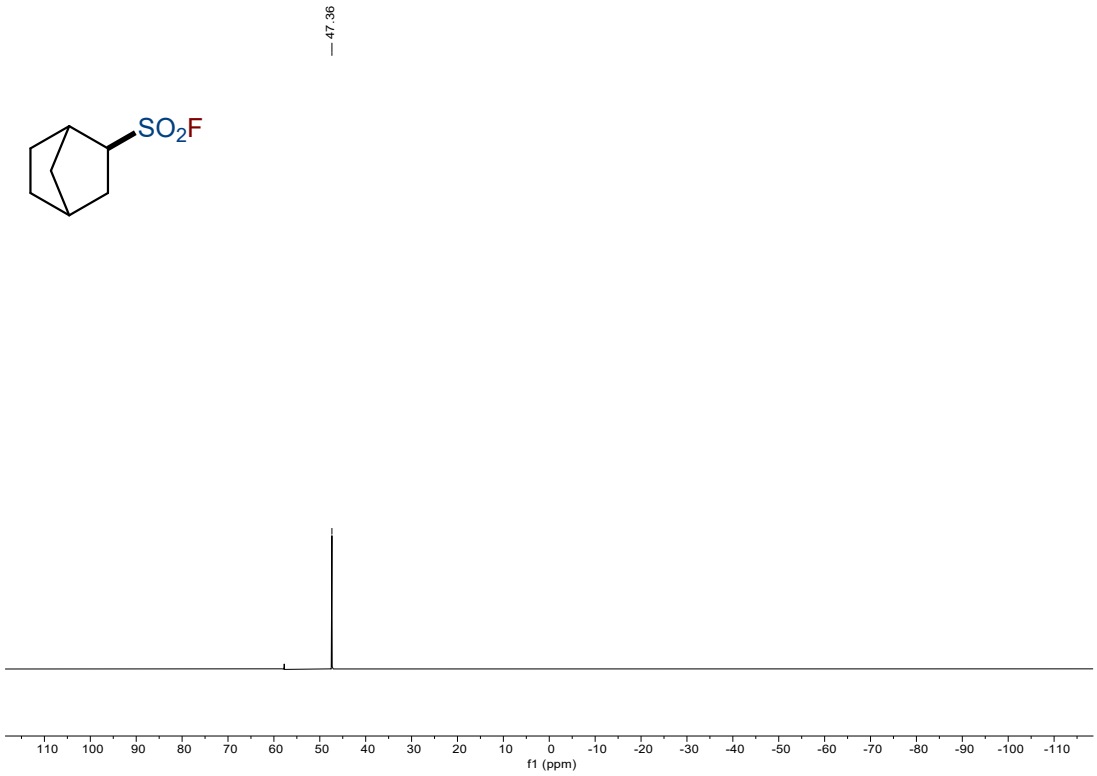
^{19}F NMR (376 MHz, $CDCl_3$) – **(2h)**



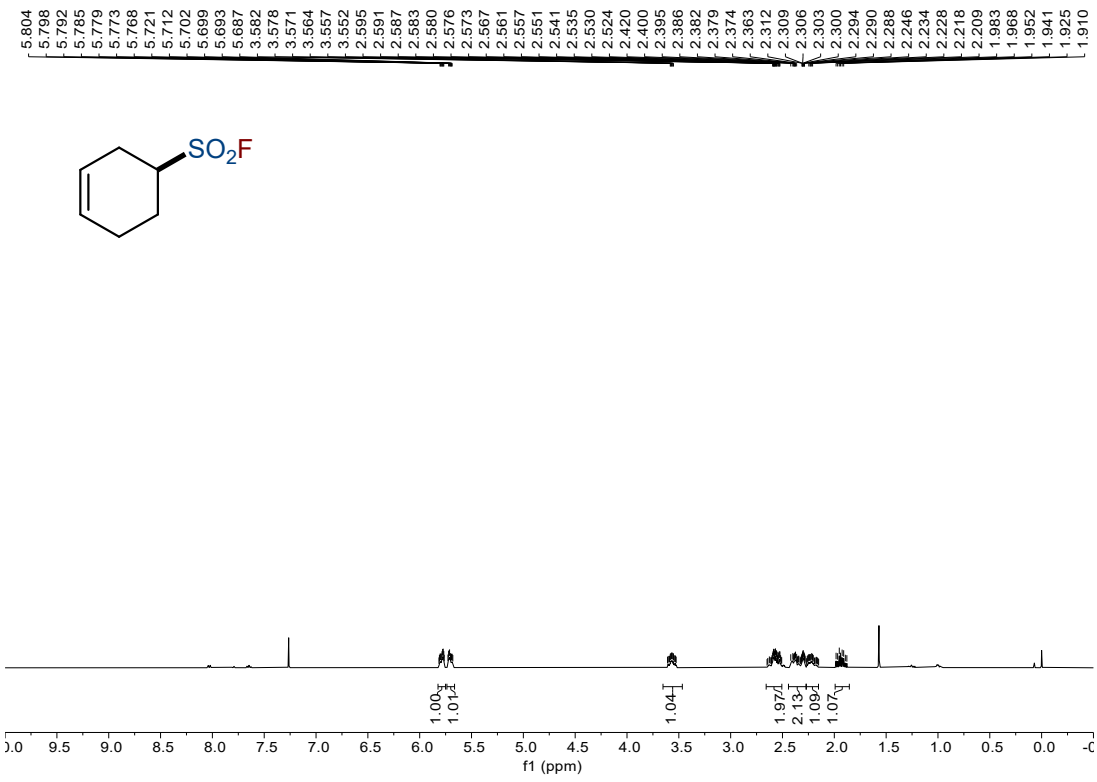
^{1}H NMR (400 MHz, $CDCl_3$) – **(2i)**



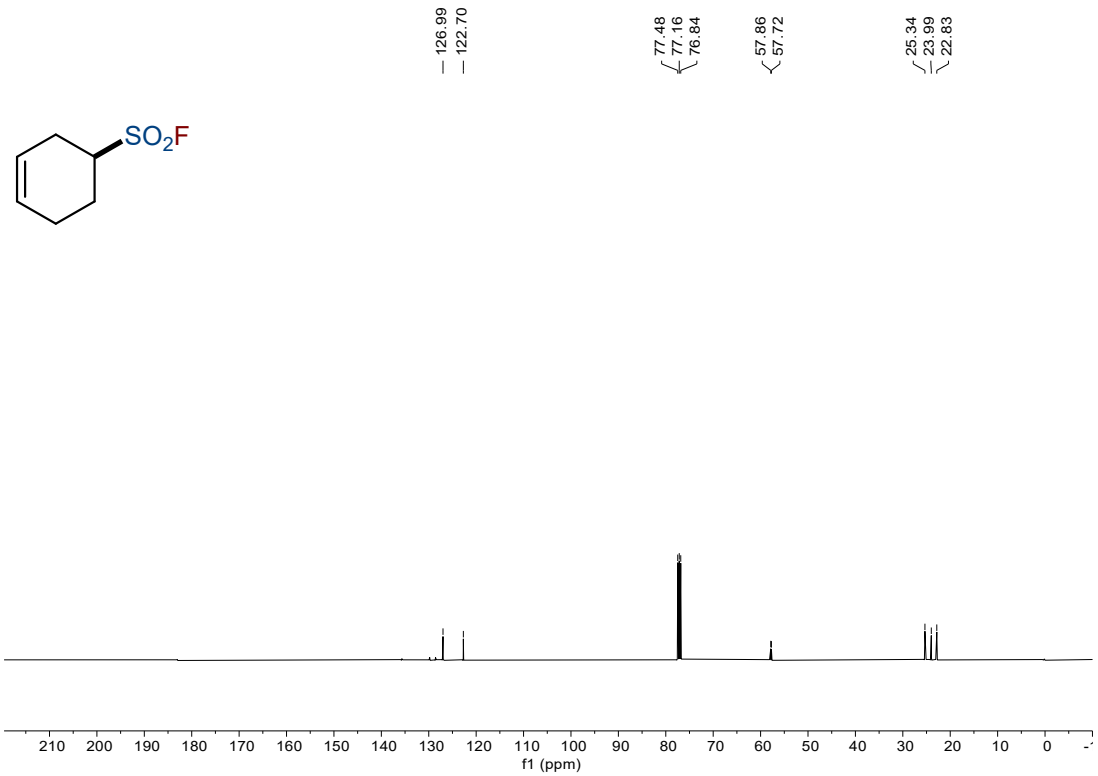
^{13}C NMR (101 MHz, $CDCl_3$) – **(2i)**



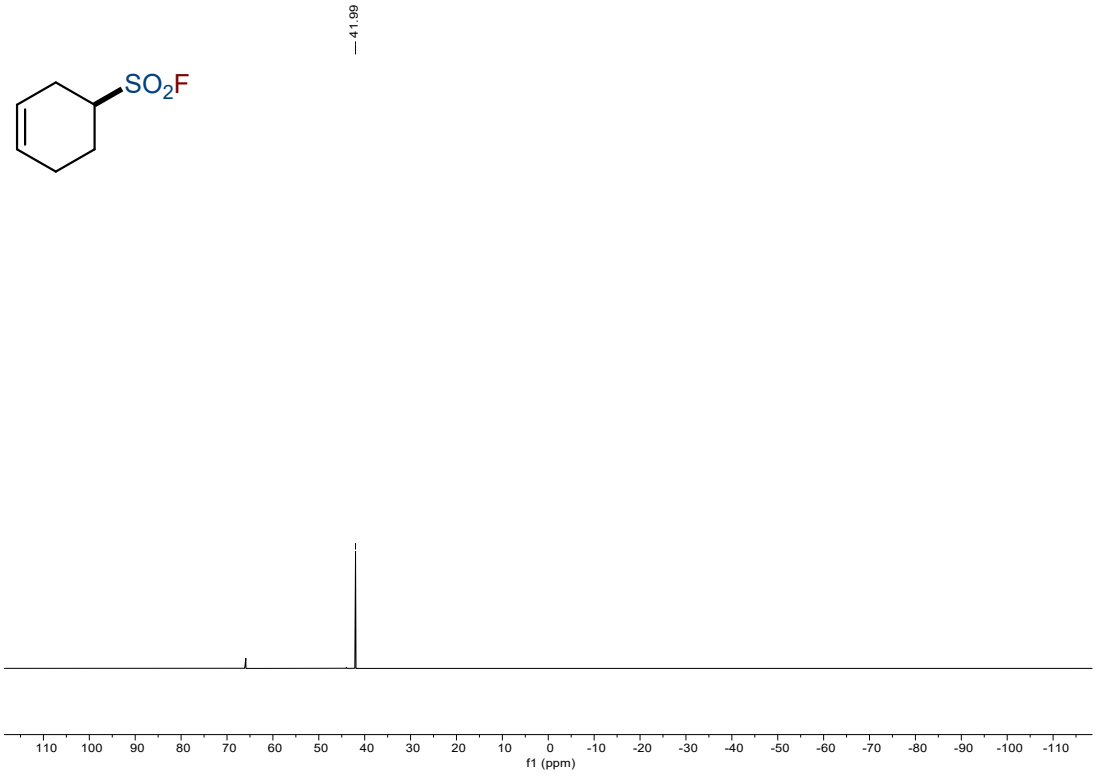
^{19}F NMR (376 MHz, $CDCl_3$) – **(2i)**



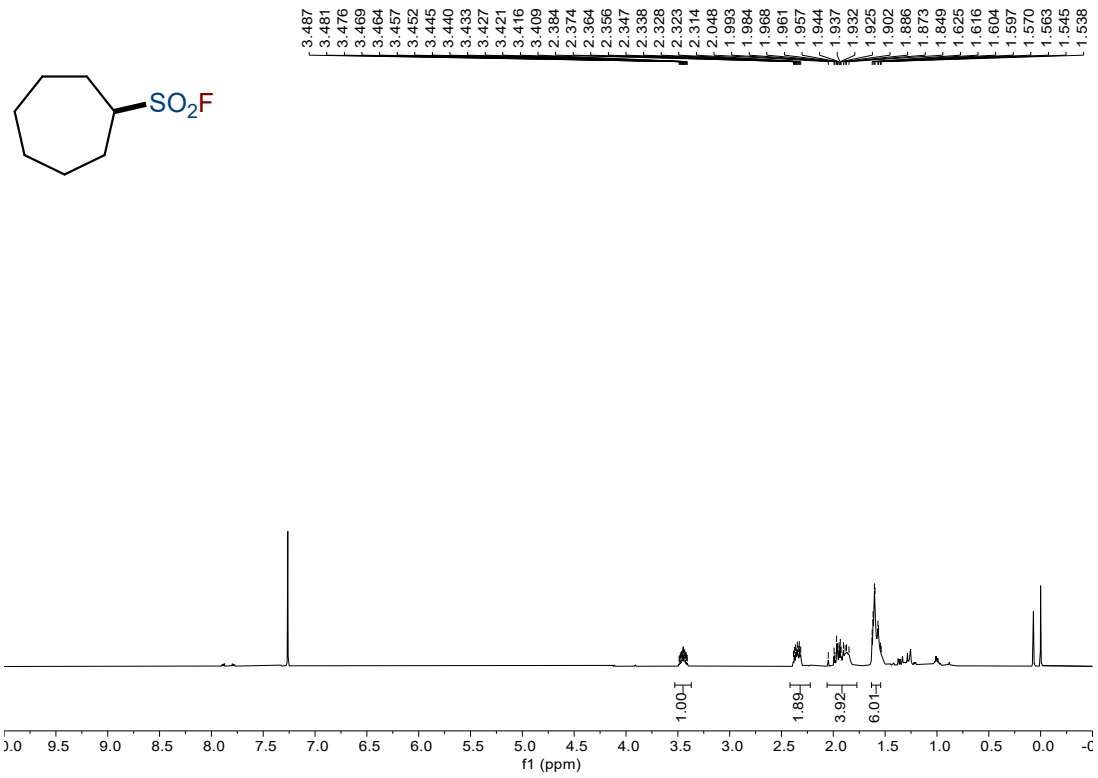
^{1}H NMR (400 MHz, $CDCl_3$) – **(2j)**



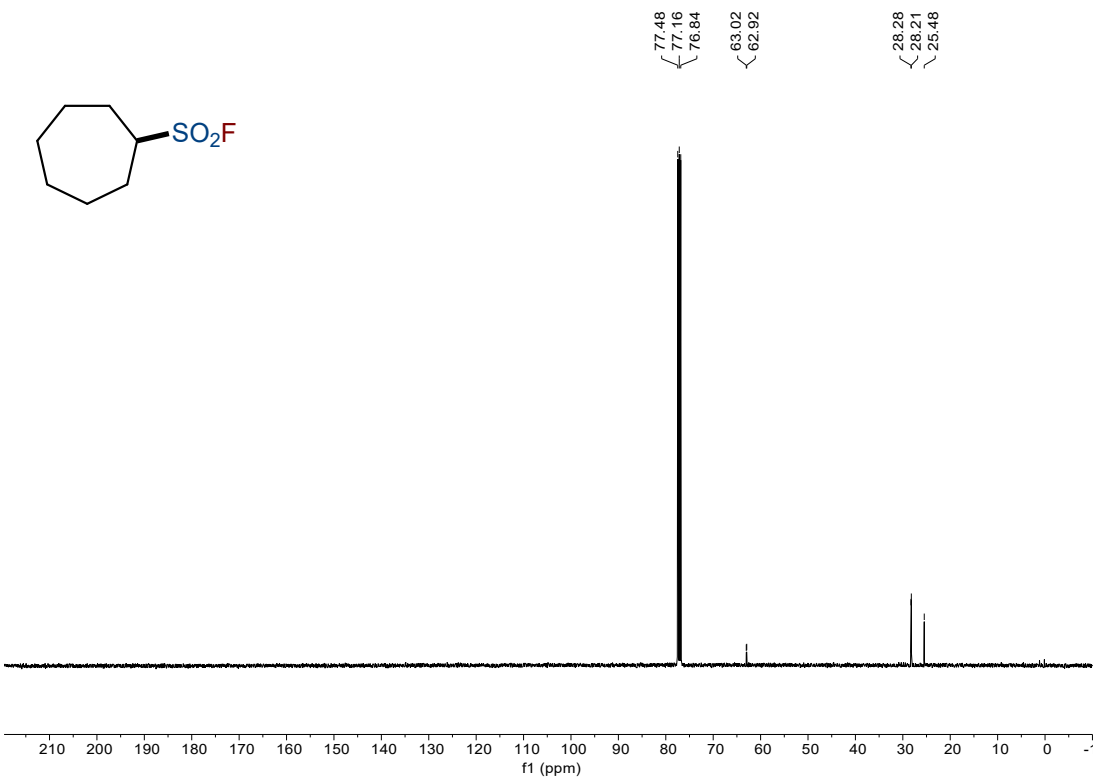
^{13}C NMR (101 MHz, $CDCl_3$) – **(2j)**



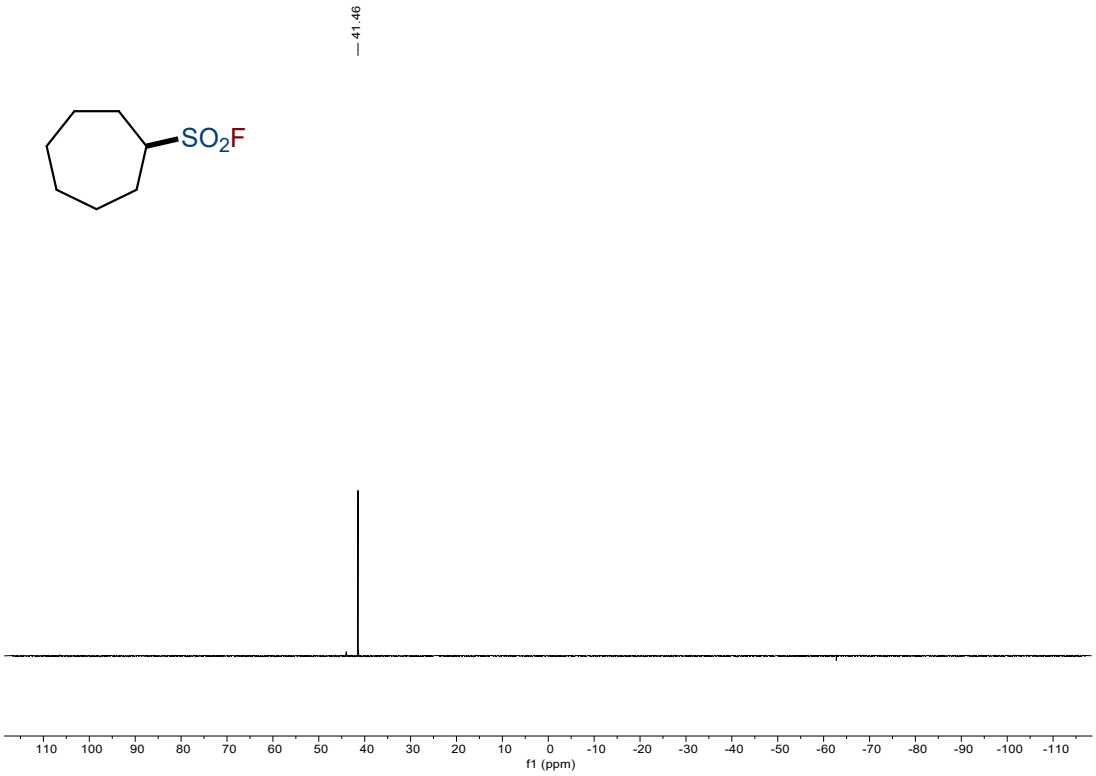
^{19}F NMR (376 MHz, $CDCl_3$) – **(2j)**



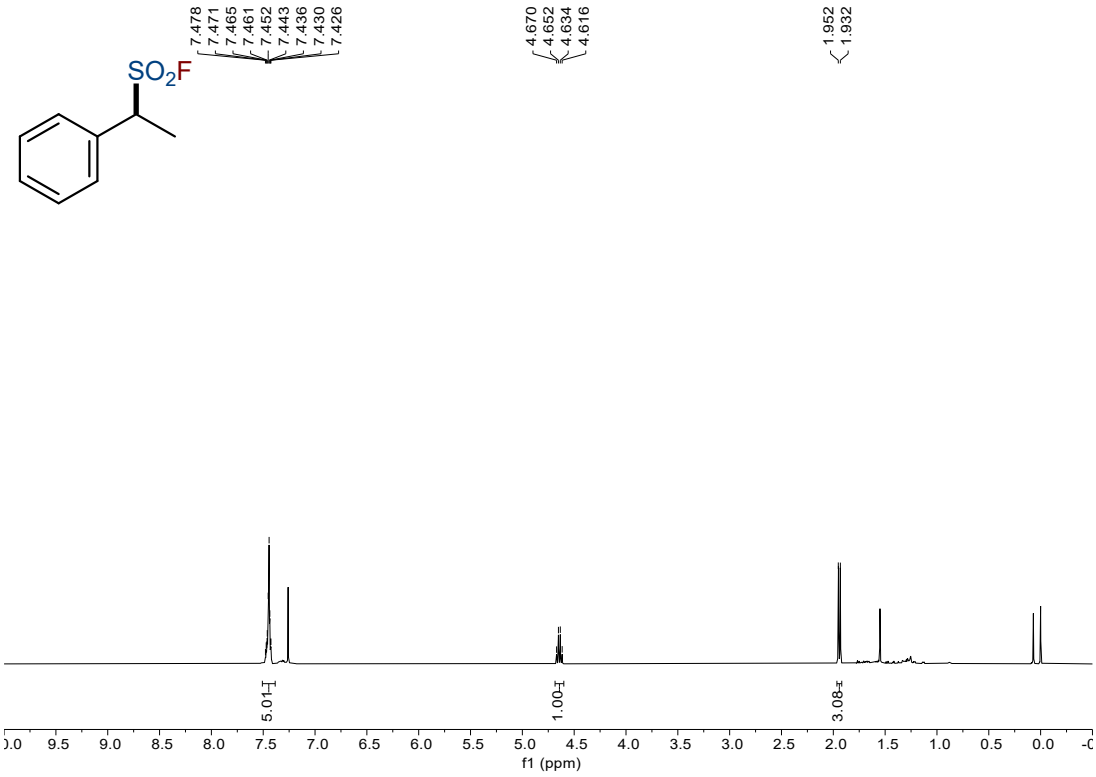
^{1}H NMR (400 MHz, $CDCl_3$) – **(2k)**



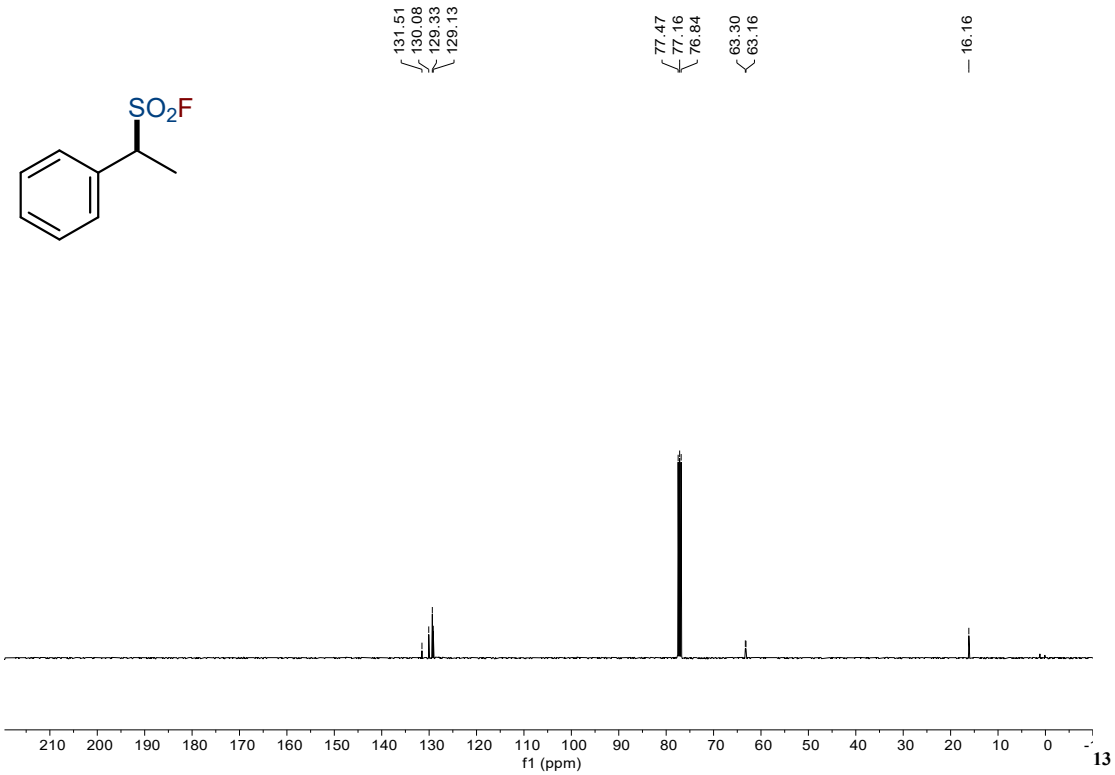
^{13}C NMR (101 MHz, $CDCl_3$) – **(2k)**



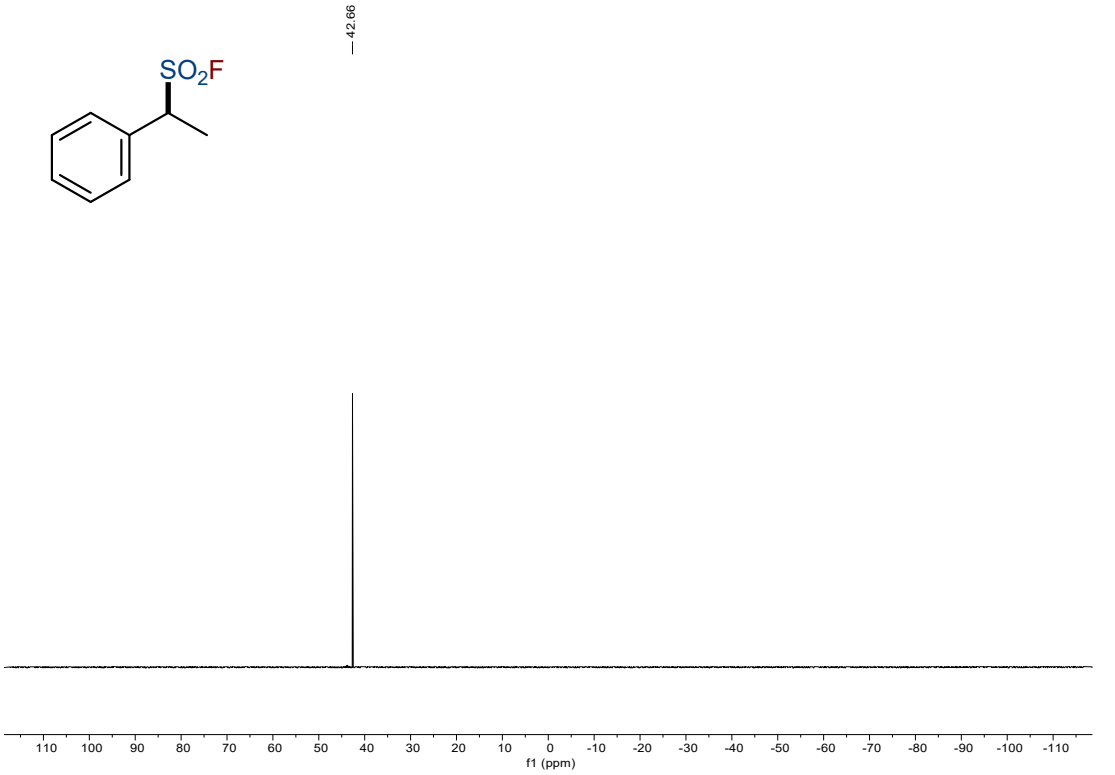
^{19}F NMR (376 MHz, $CDCl_3$) – **(2k)**



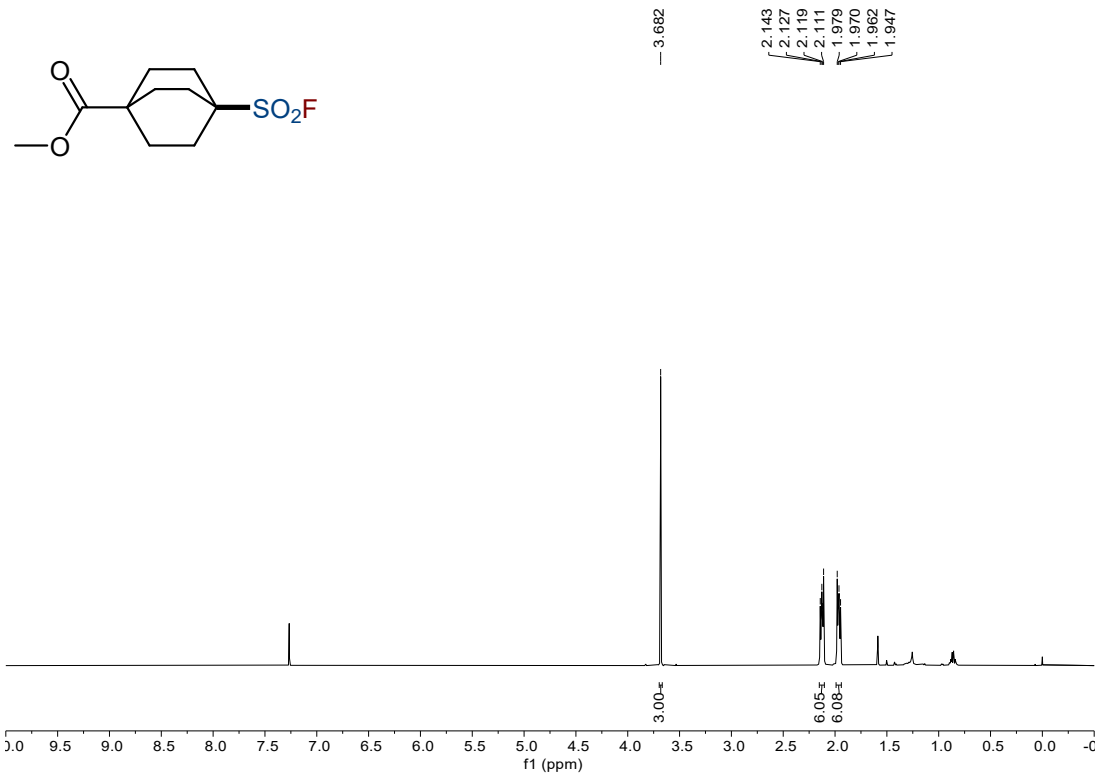
^{1}H NMR (400 MHz, $CDCl_3$) – **(2l)**



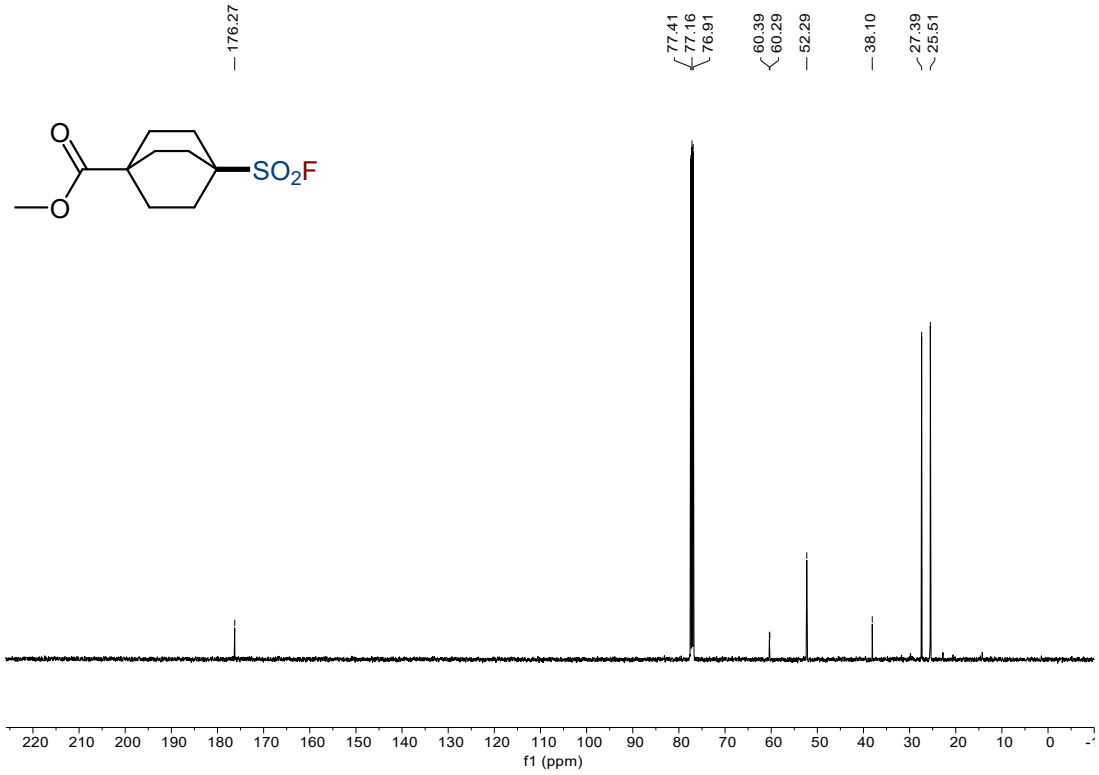
C NMR (101 MHz, $CDCl_3$) – **(2l)**



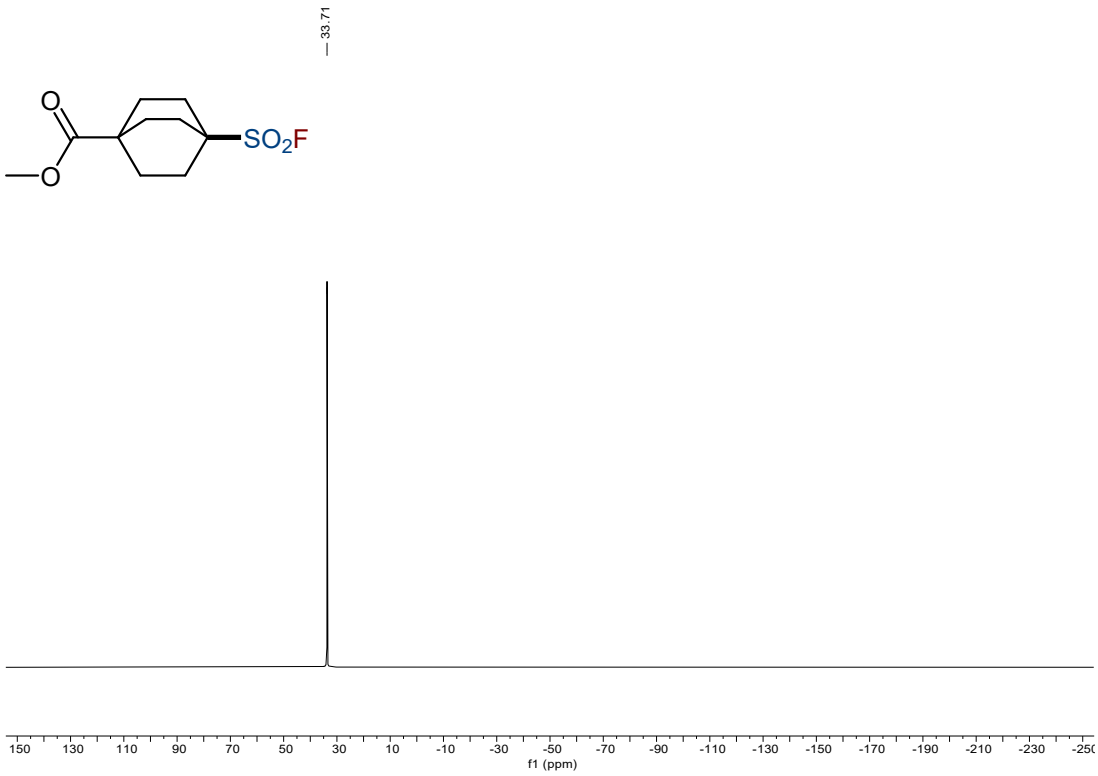
^{19}F NMR (376 MHz, $CDCl_3$) – **(2l)**



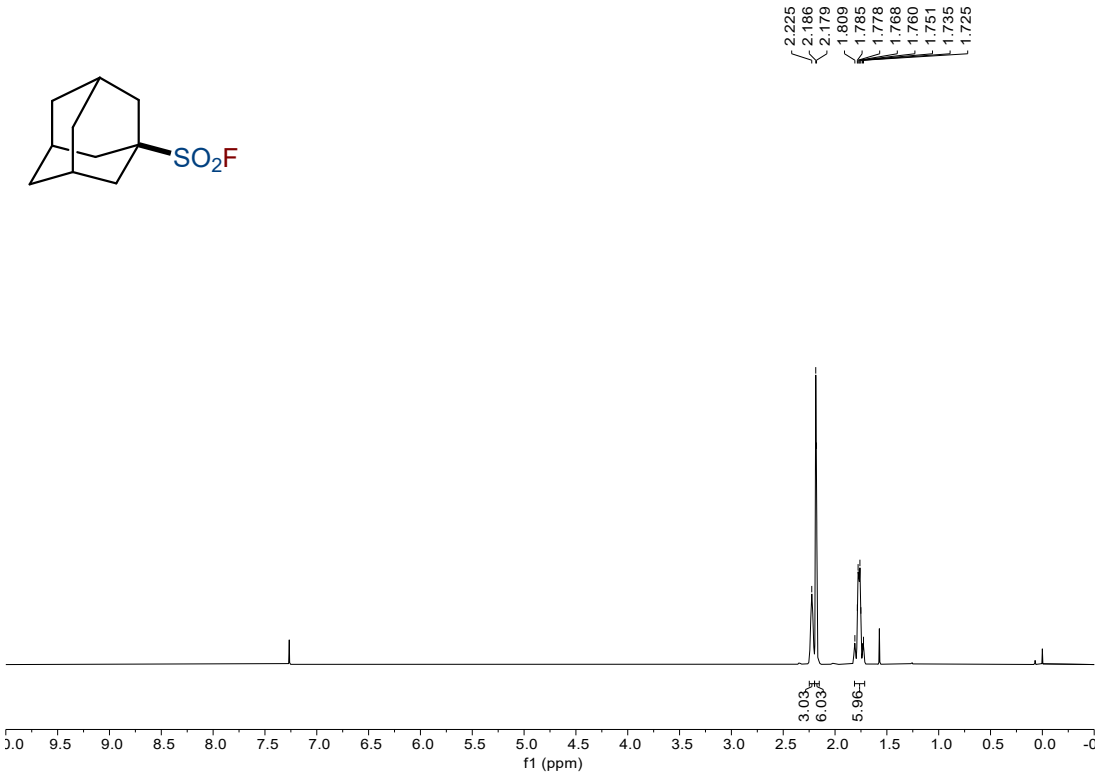
^{1}H NMR (500 MHz, $CDCl_3$) – **(2m)**



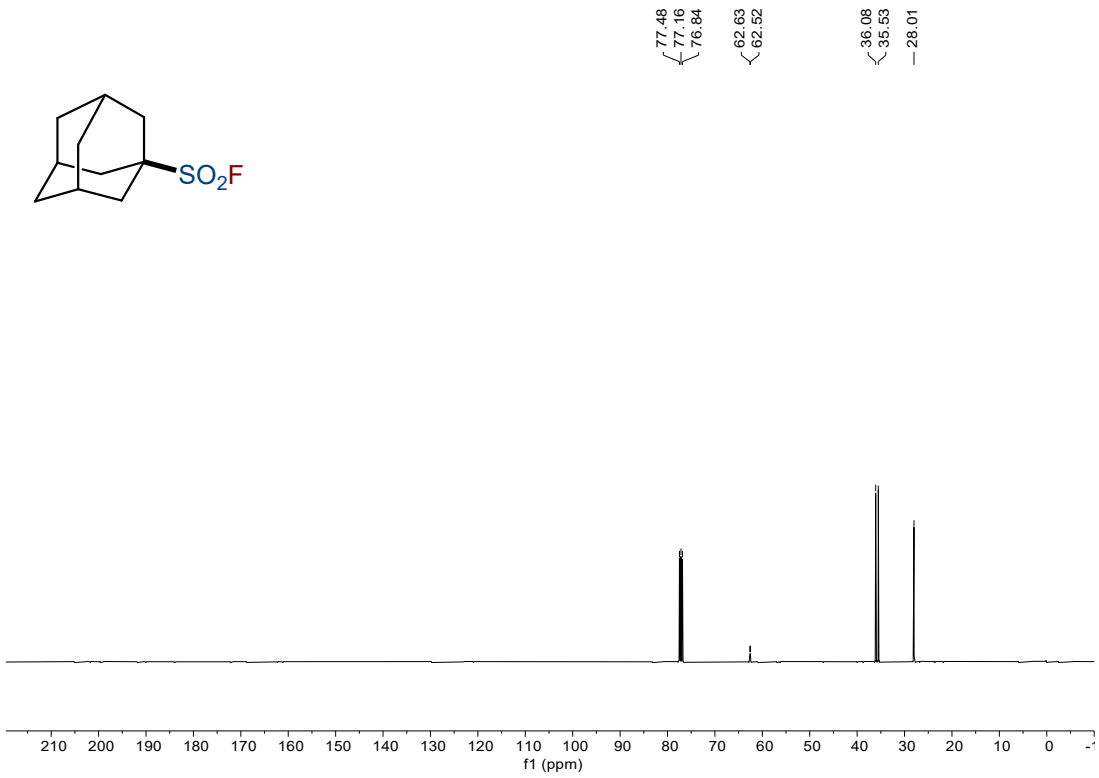
^{13}C NMR (126 MHz, $CDCl_3$) – **(2m)**



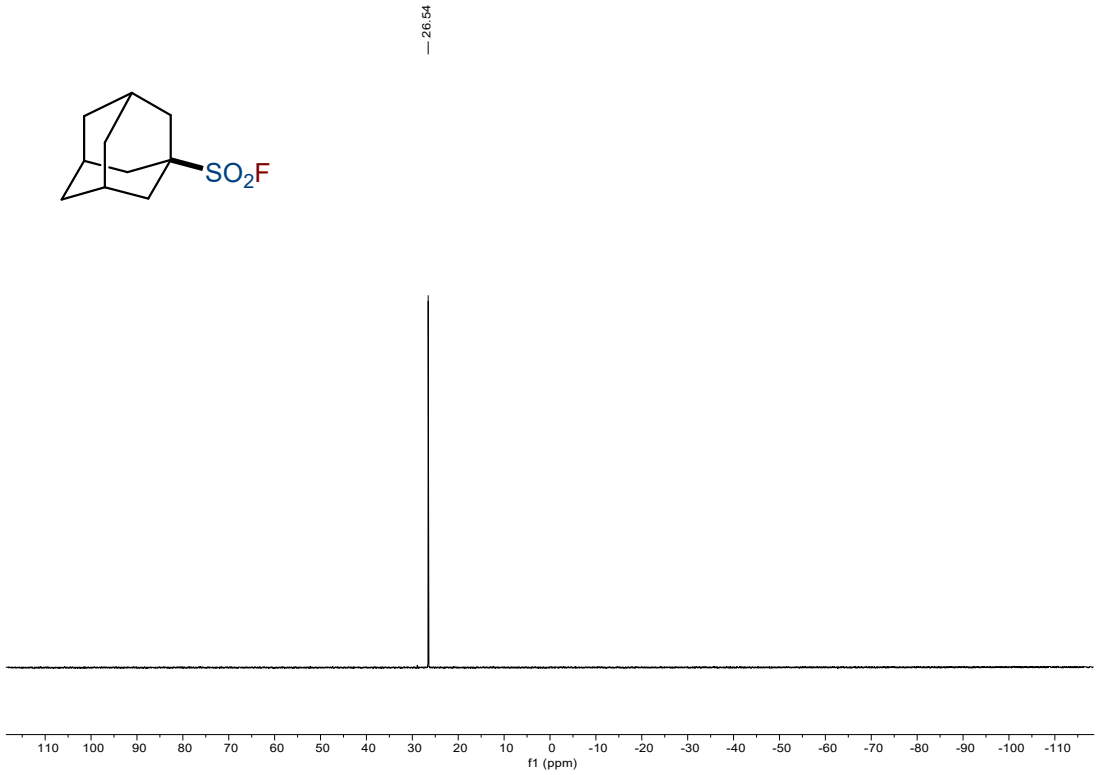
^{19}F NMR (471 MHz, $CDCl_3$) – **(2m)**



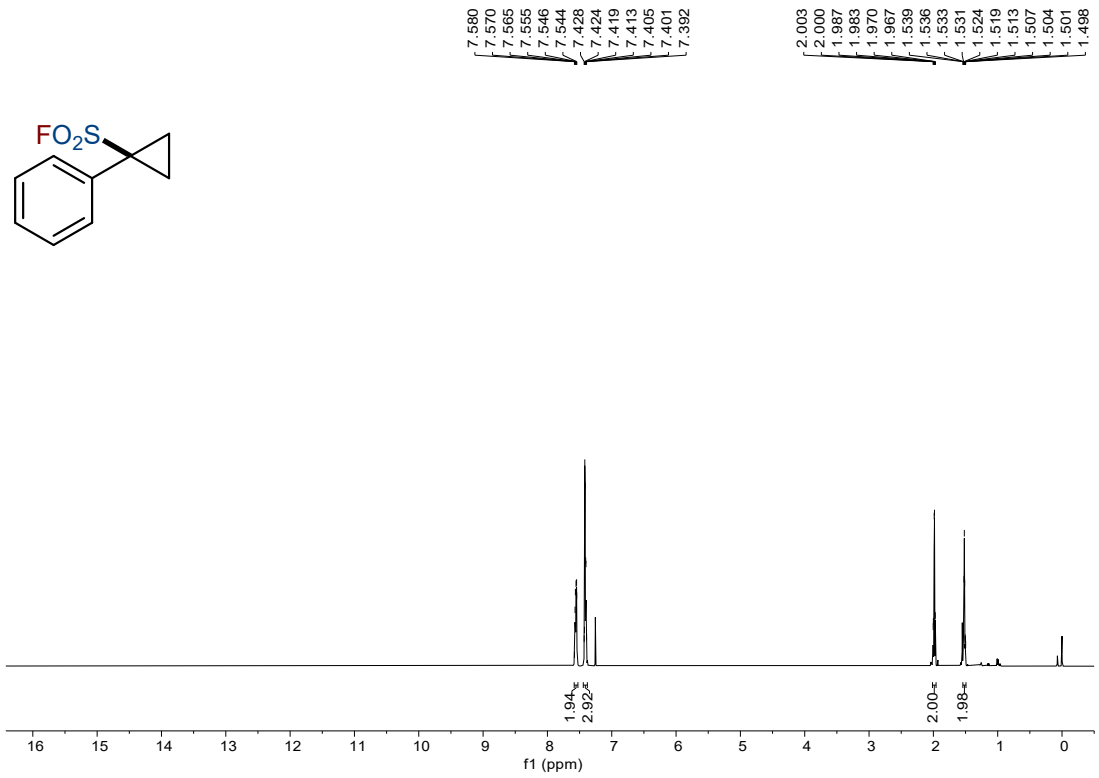
^{1}H NMR (400 MHz, $CDCl_3$) – **(2n)**



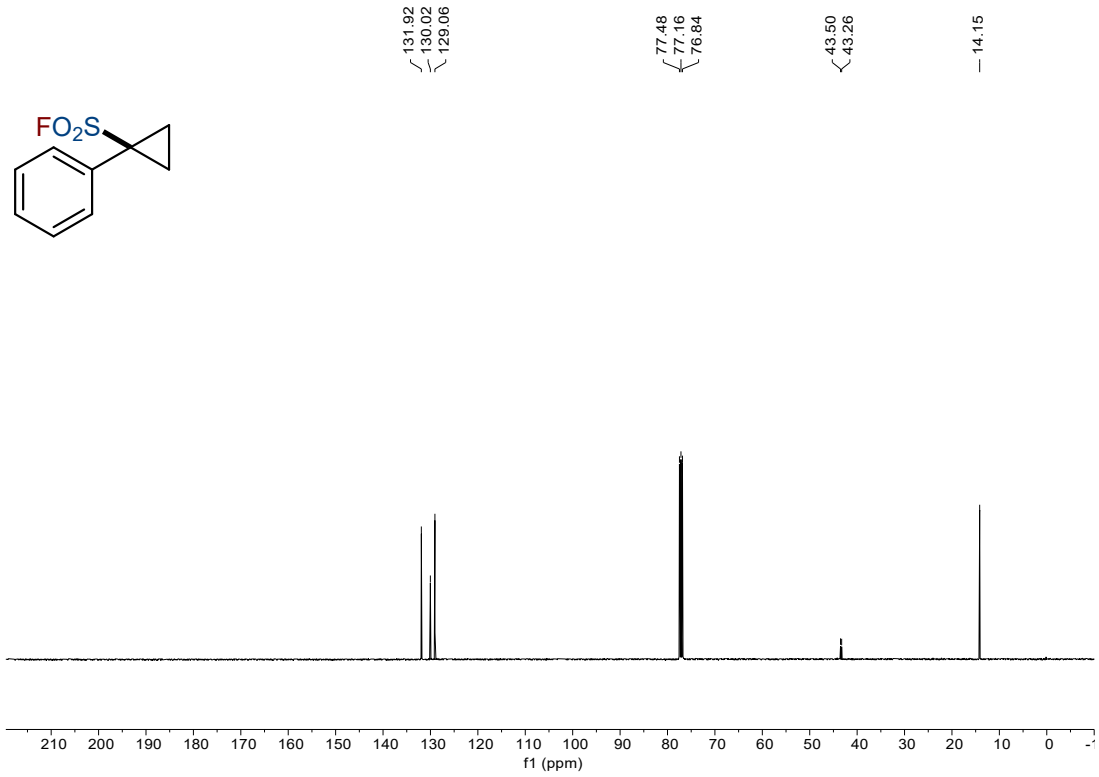
^{13}C NMR (101 MHz, $CDCl_3$) – **(2n)**



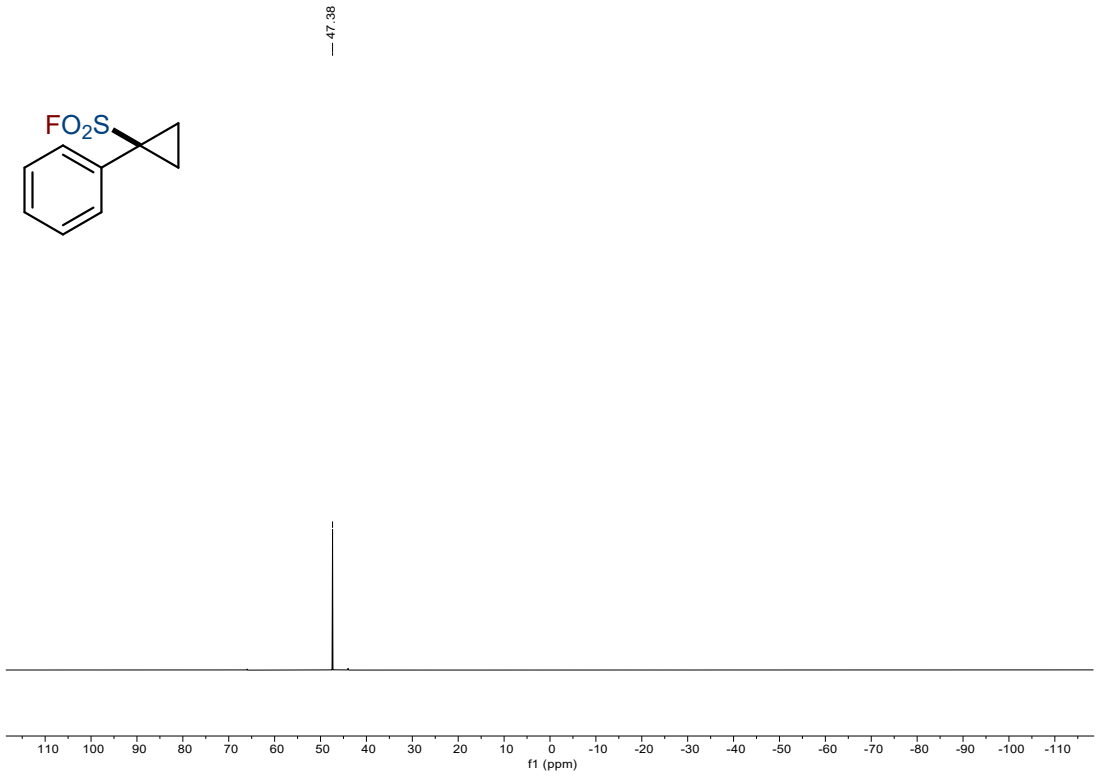
^{19}F NMR (376 MHz, $CDCl_3$) – **(2n)**



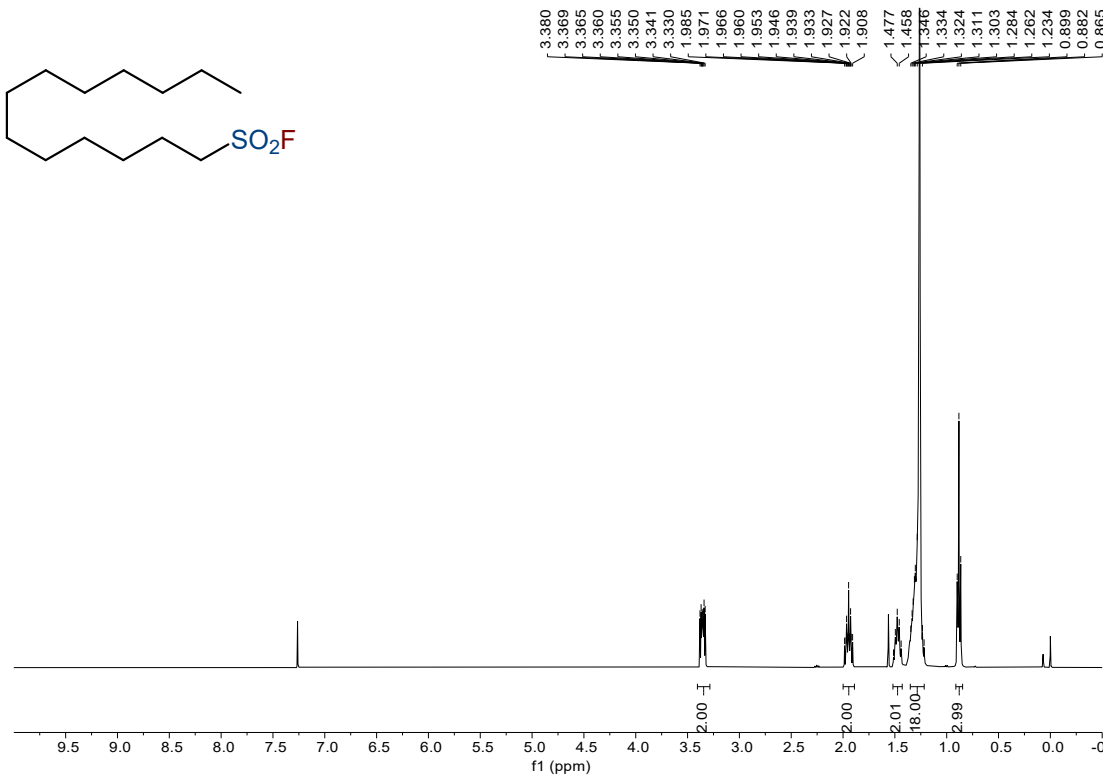
^{1}H NMR (400 MHz, $CDCl_3$) – **(2o)**



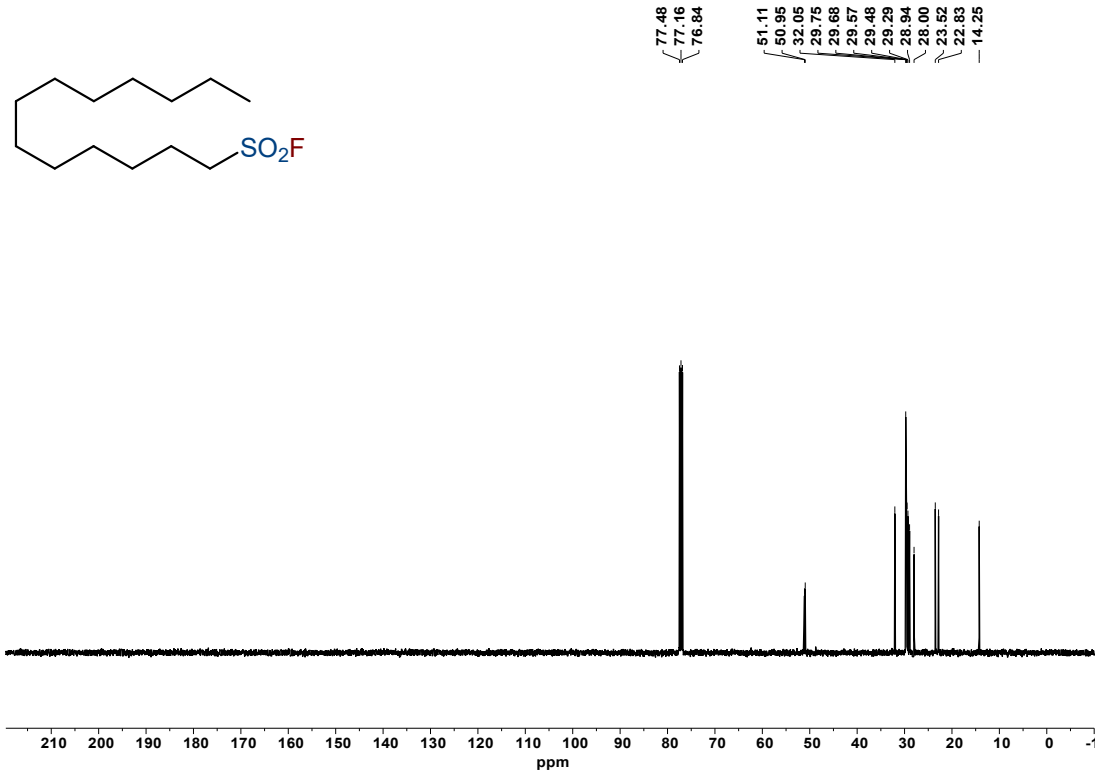
^{13}C NMR (101 MHz, $CDCl_3$) – **(2o)**



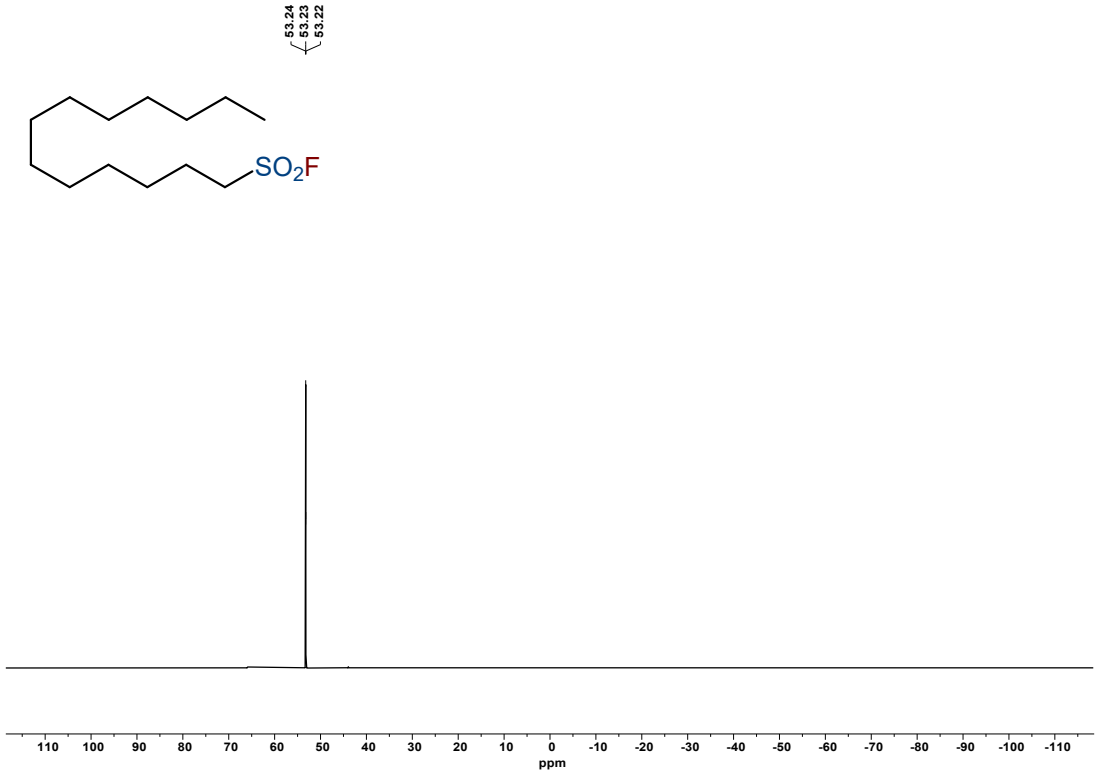
^{19}F NMR (376 MHz, $CDCl_3$) – **(2o)**



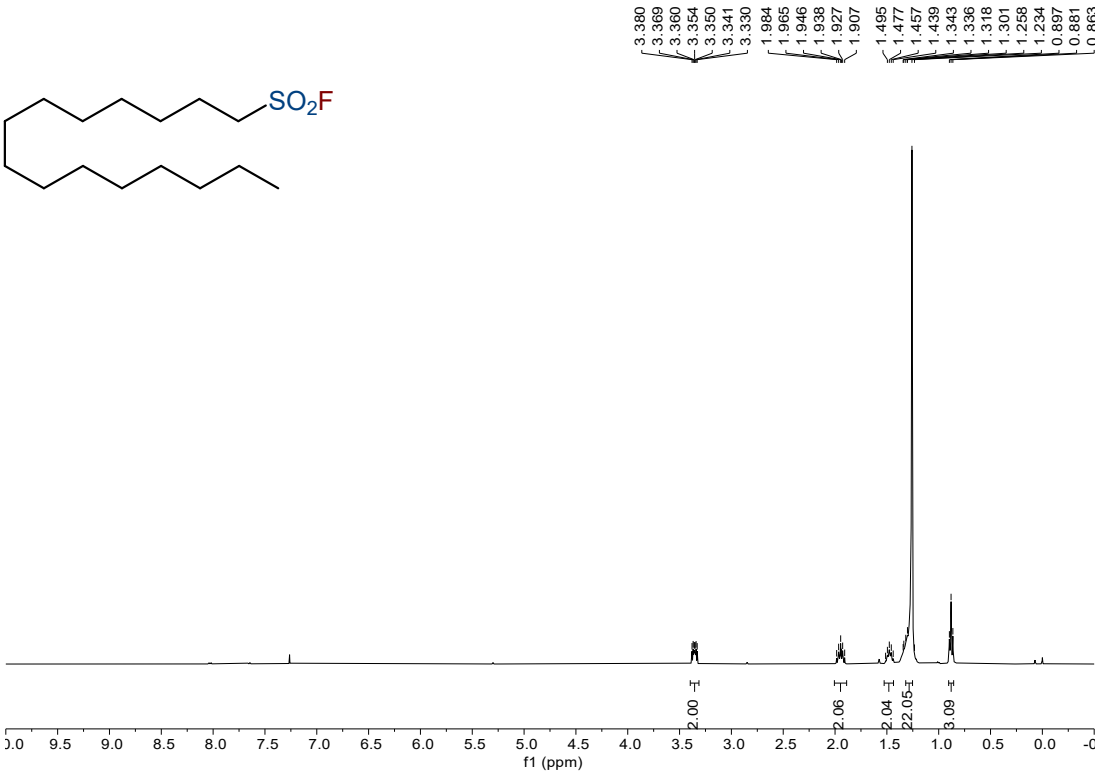
^{1}H NMR (400 MHz, $CDCl_3$) – **(2p)**



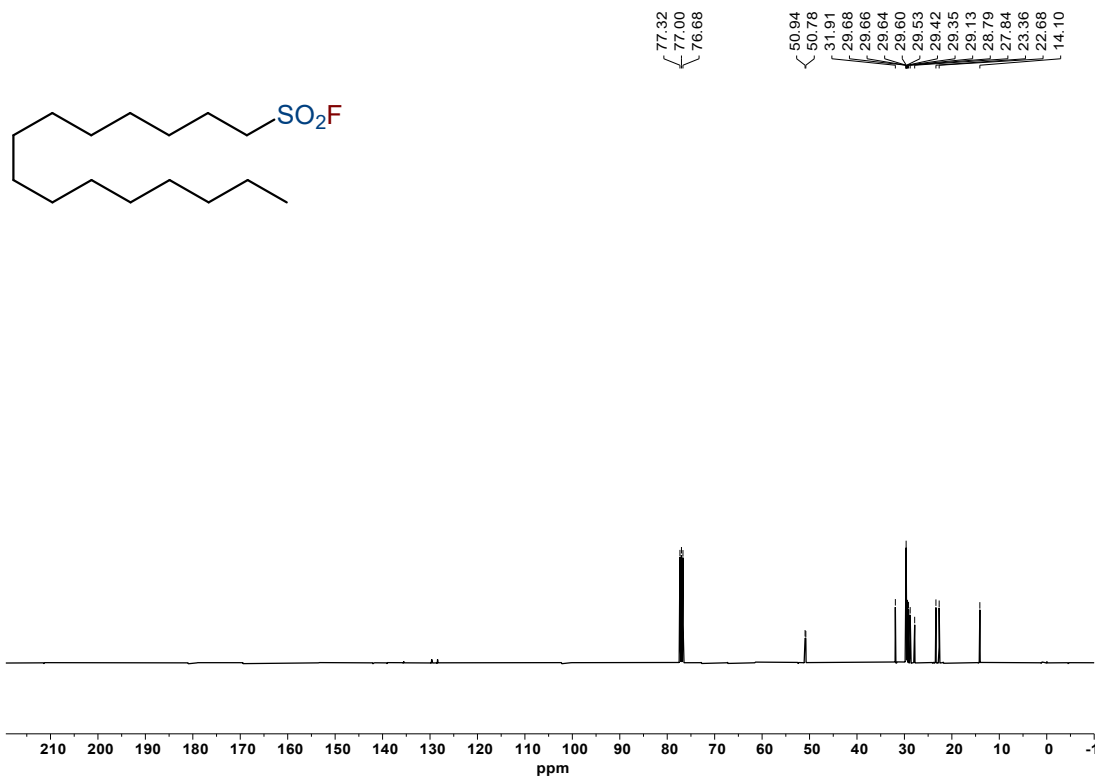
^{13}C NMR (101 MHz, $CDCl_3$) – **(2p)**



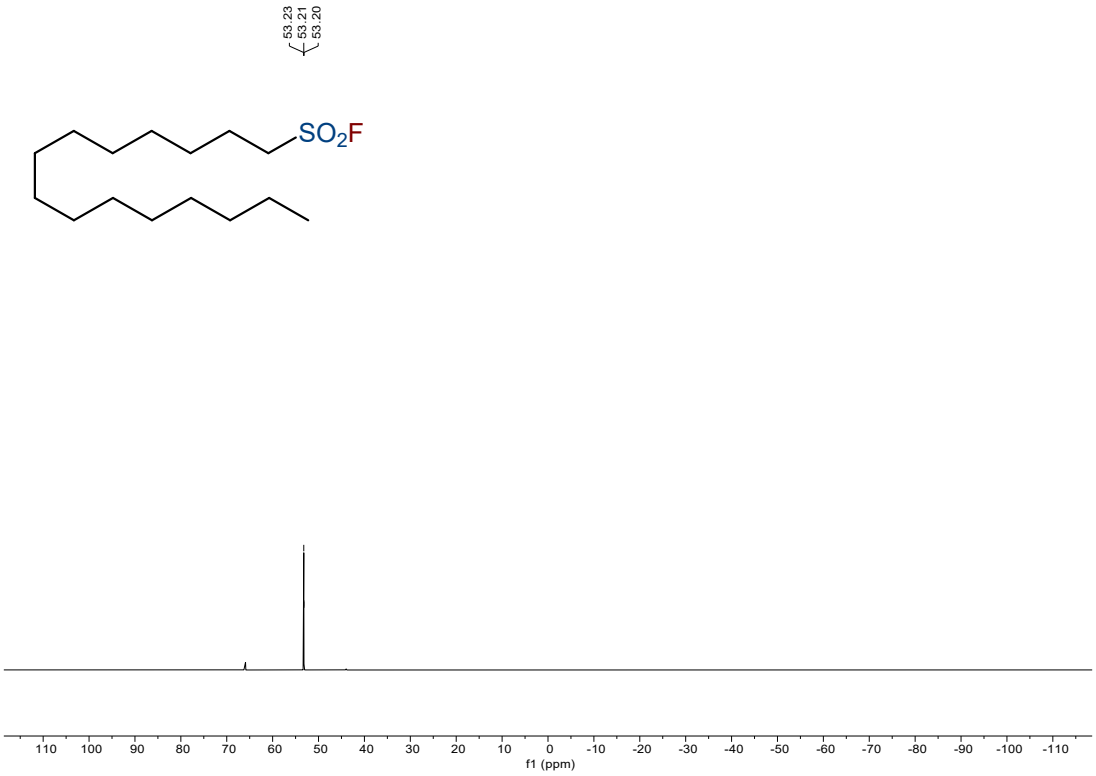
^{19}F NMR (376 MHz, $CDCl_3$) – **(2p)**



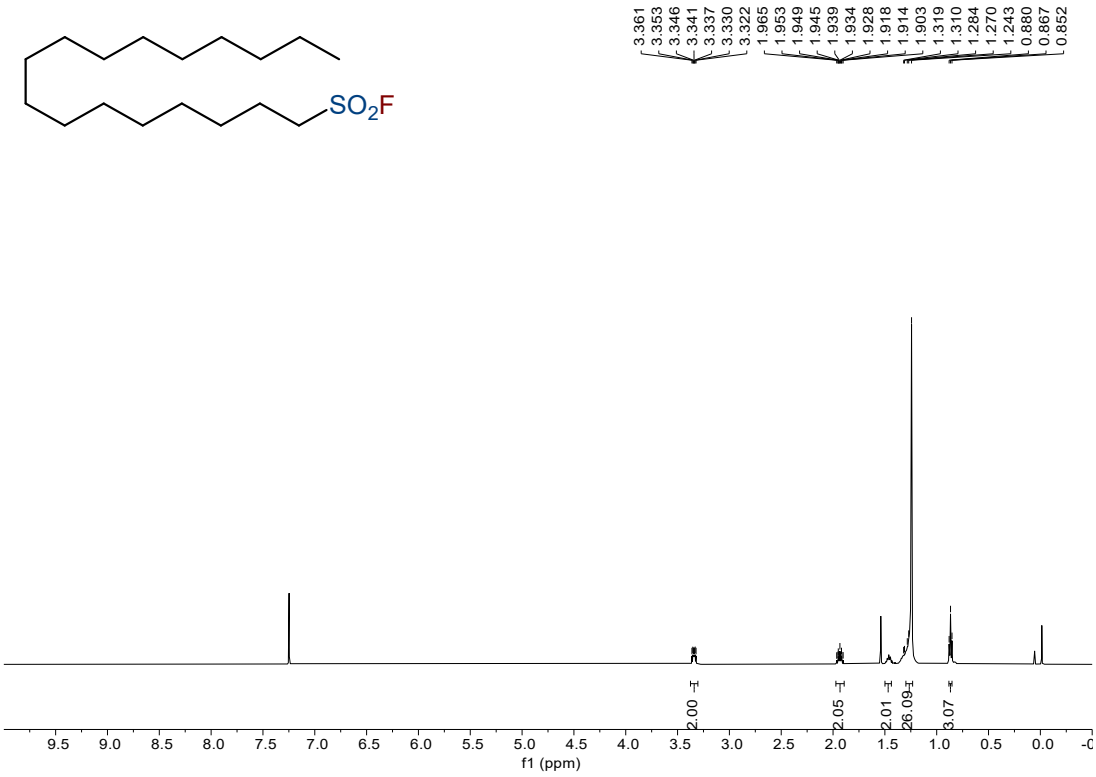
^{1}H NMR (400 MHz, $CDCl_3$) – **(2q)**



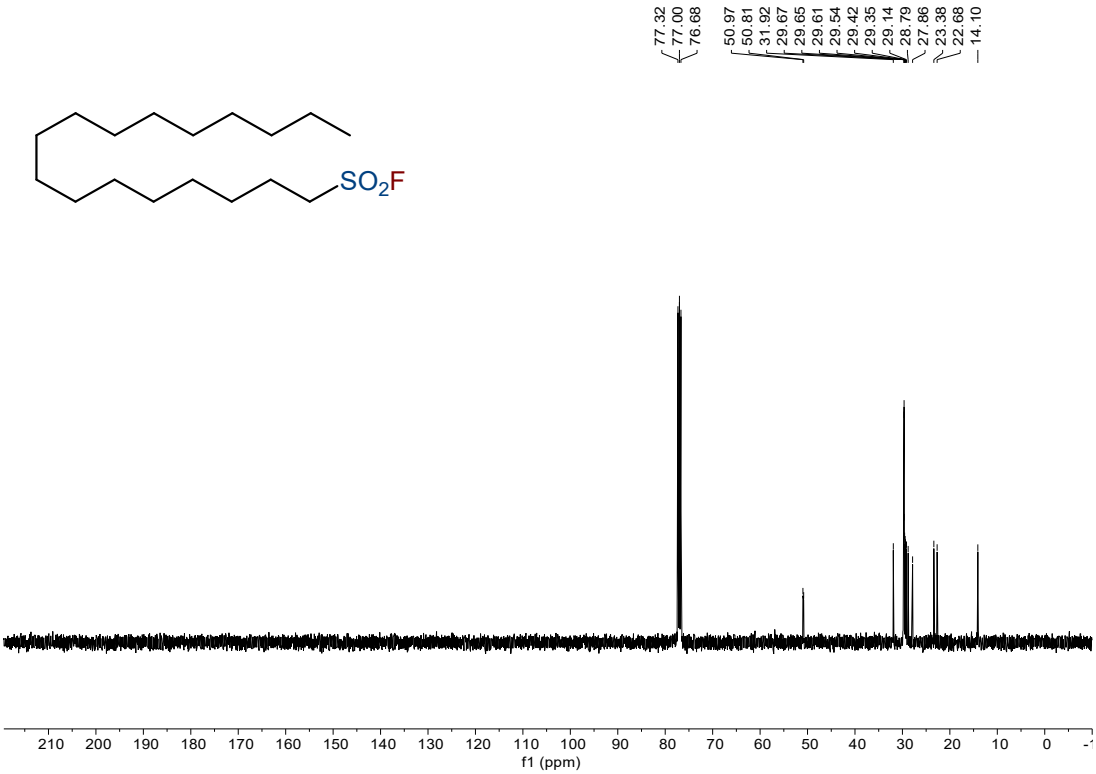
^{13}C NMR (101 MHz, $CDCl_3$) – **(2q)**



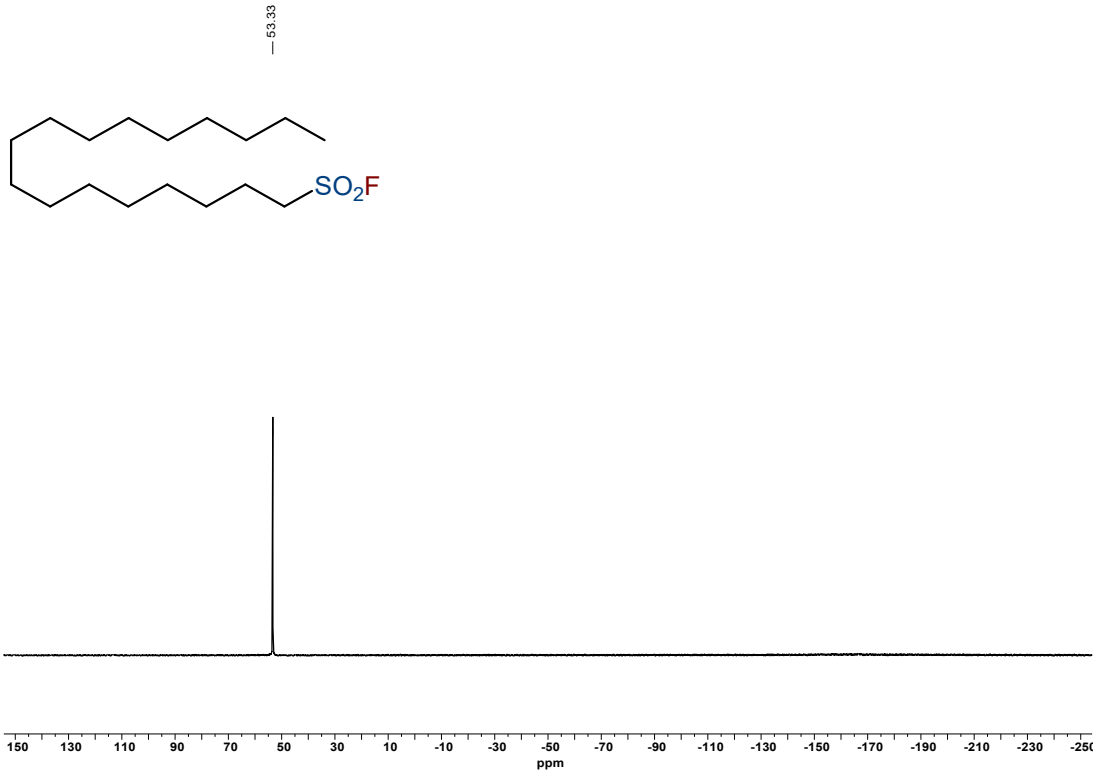
^{19}F NMR (376 MHz, $CDCl_3$) – **(2q)**



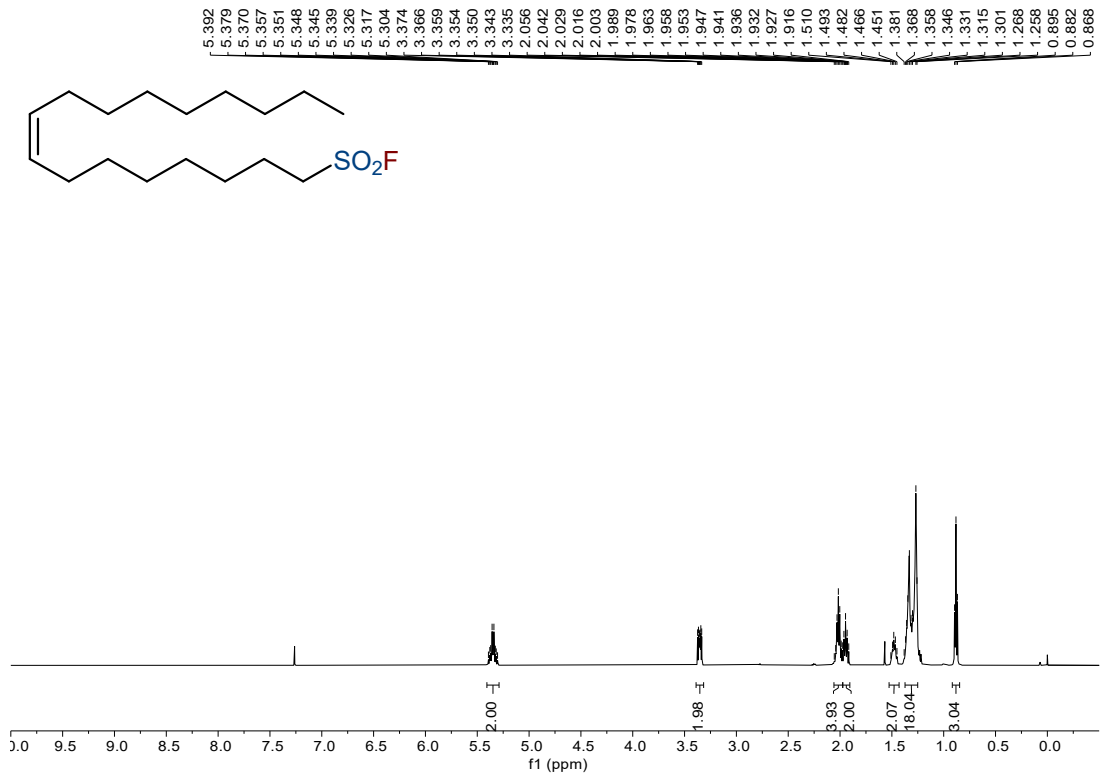
^{1}H NMR (500 MHz, $CDCl_3$) – **(2r)**



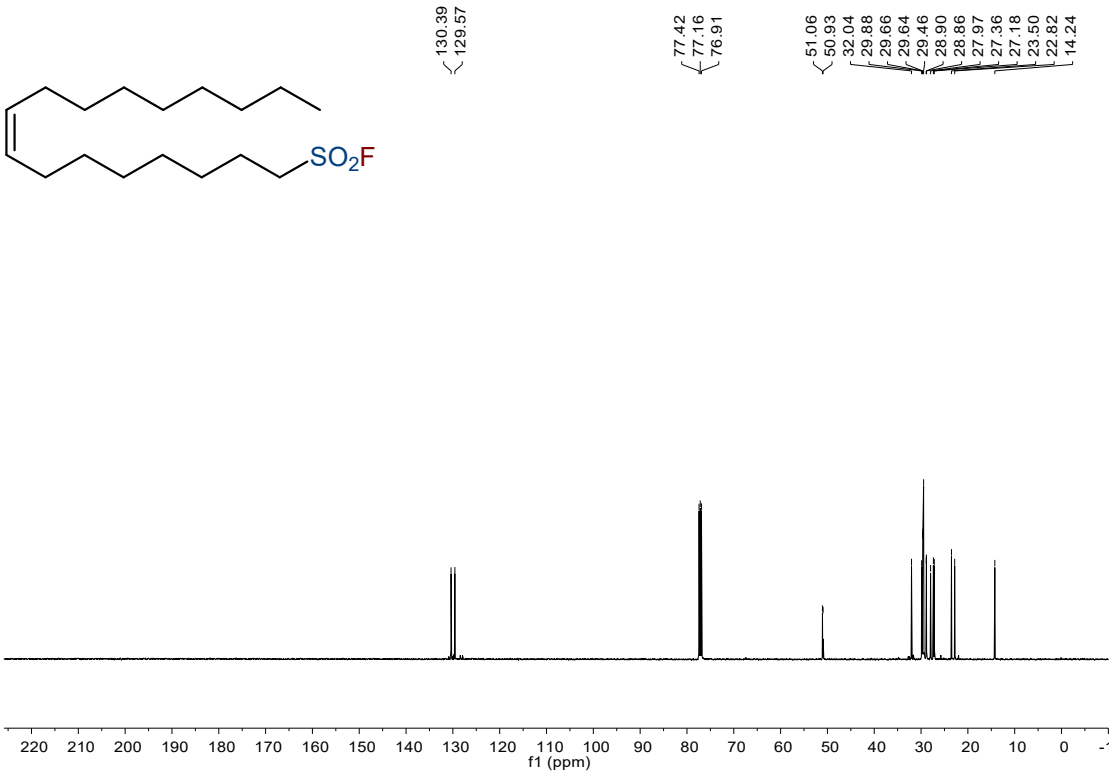
^{13}C NMR (126 MHz, $CDCl_3$) – **(2r)**



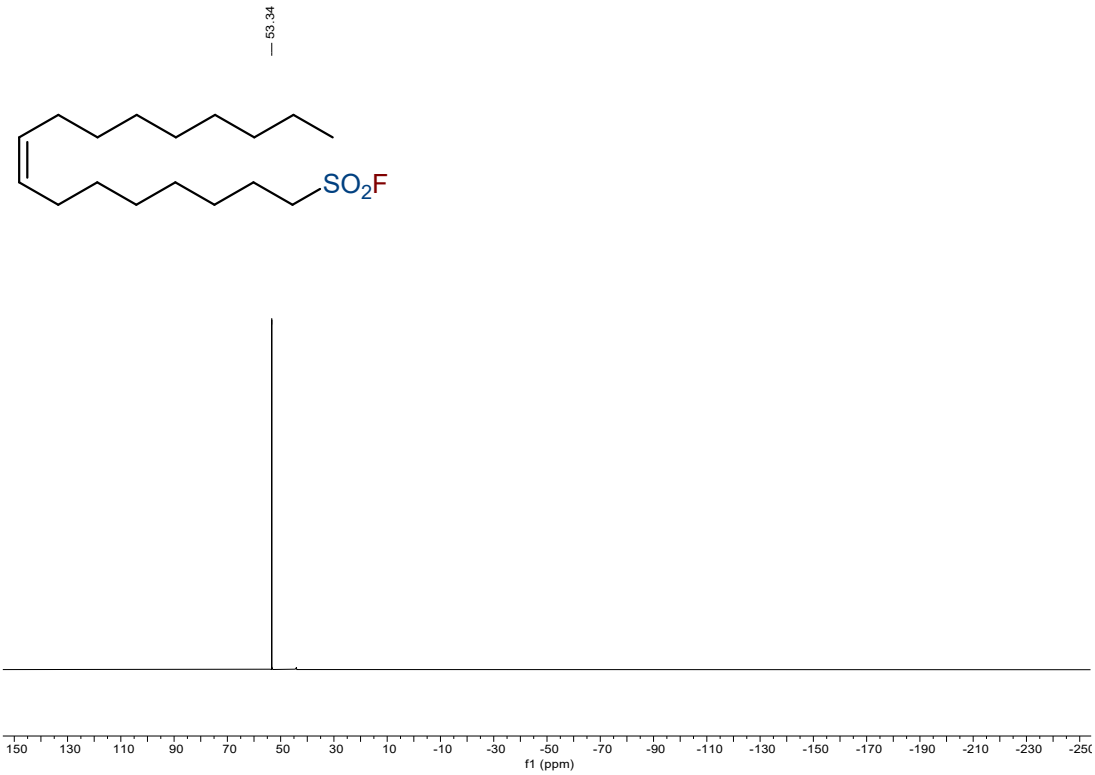
^{19}F NMR (471 MHz, $CDCl_3$) – **(2r)**



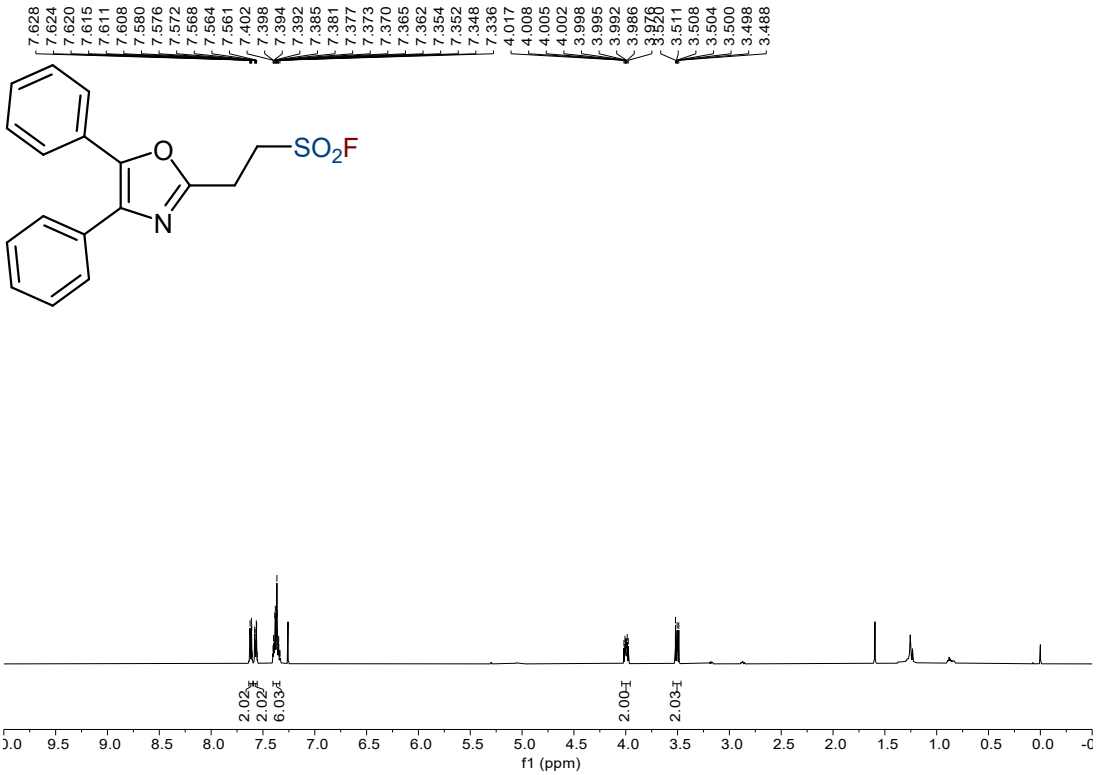
^{1}H NMR (500 MHz, $CDCl_3$) – **(2s)**



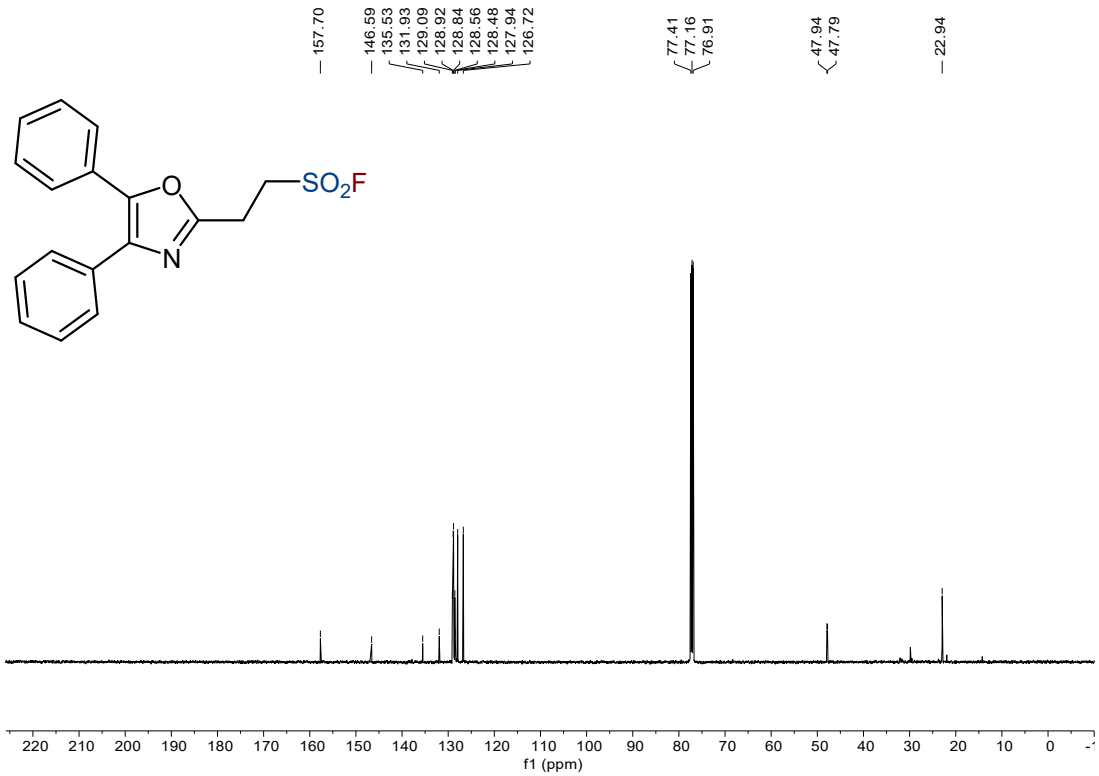
^{13}C NMR (126 MHz, $CDCl_3$) – **(2s)**



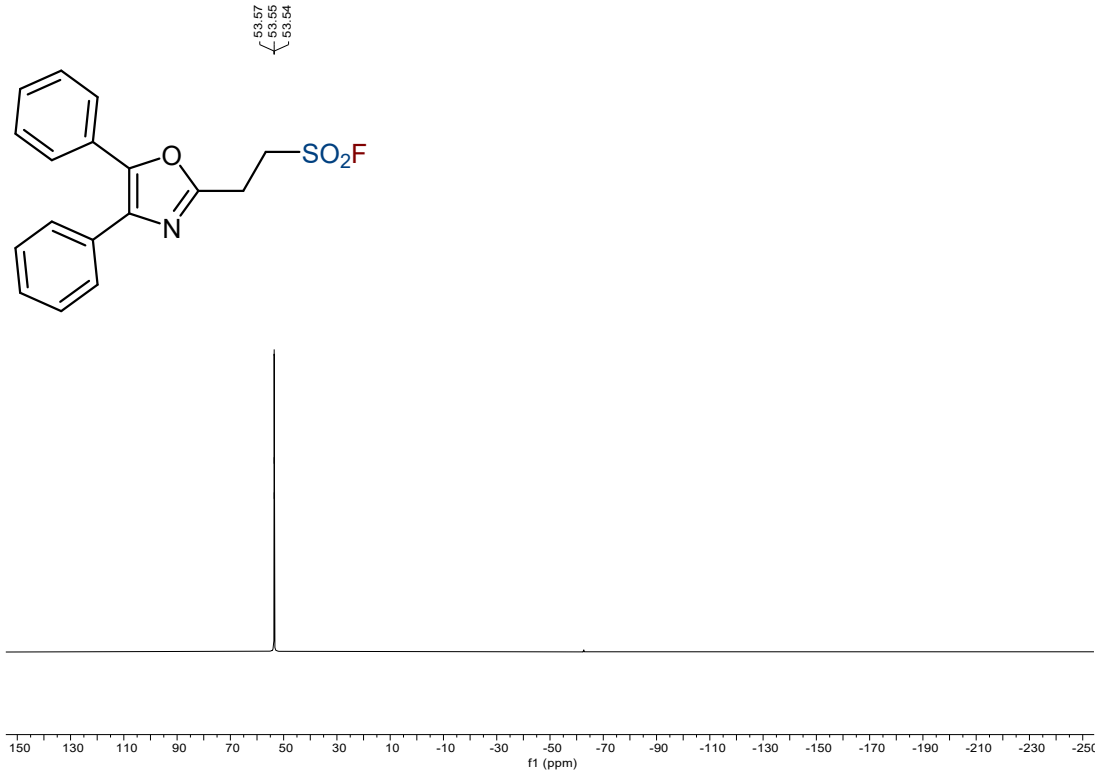
^{19}F NMR (471 MHz, $CDCl_3$) – **(2s)**



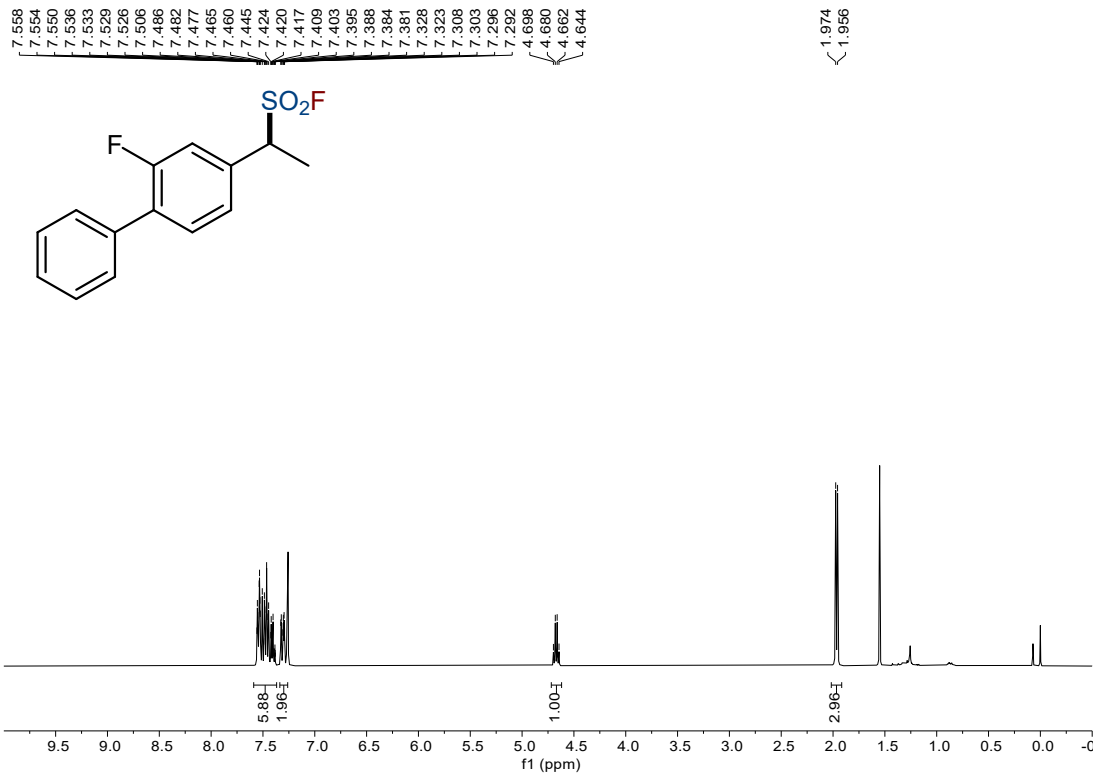
^{1}H NMR (500 MHz, $CDCl_3$) – **(2t)**



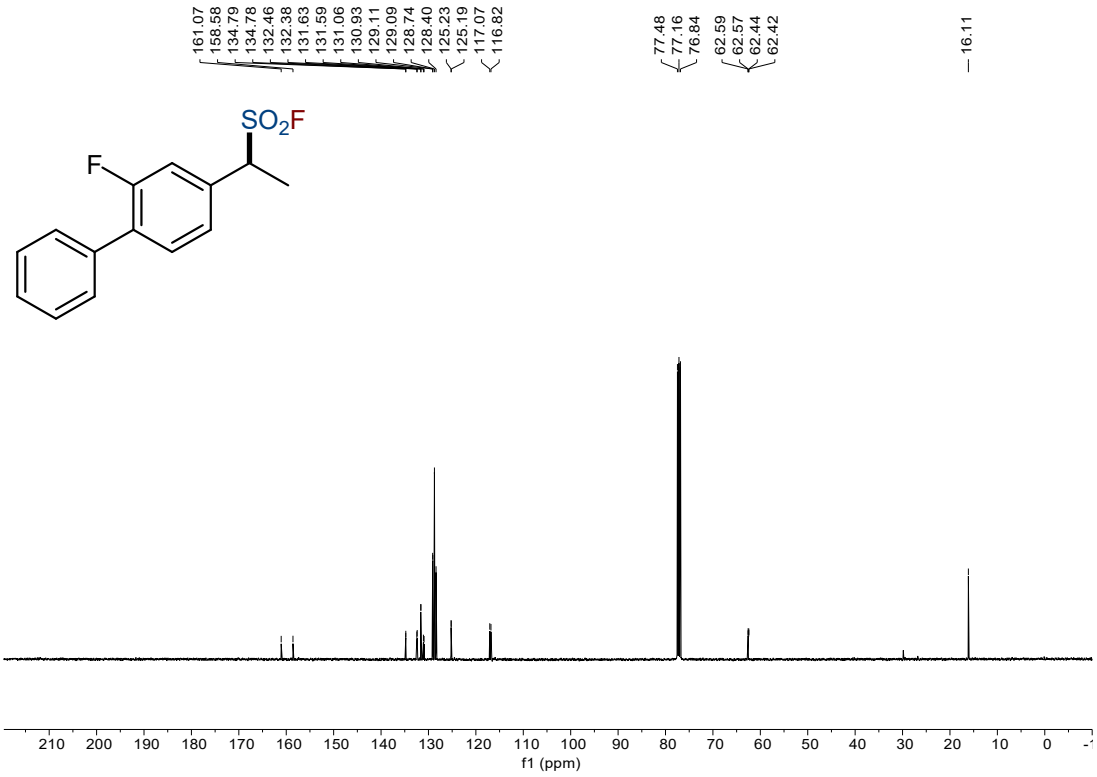
^{13}C NMR (126 MHz, $CDCl_3$) – **(2t)**



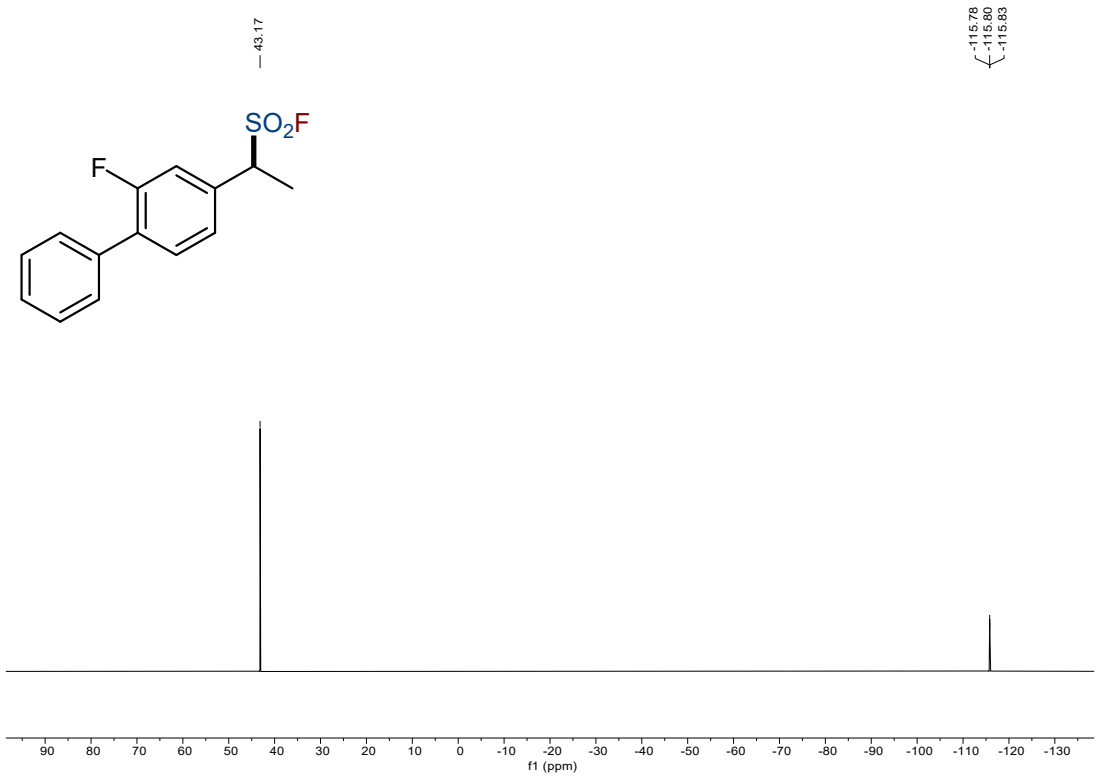
^{19}F NMR (471 MHz, $CDCl_3$) – **(2t)**



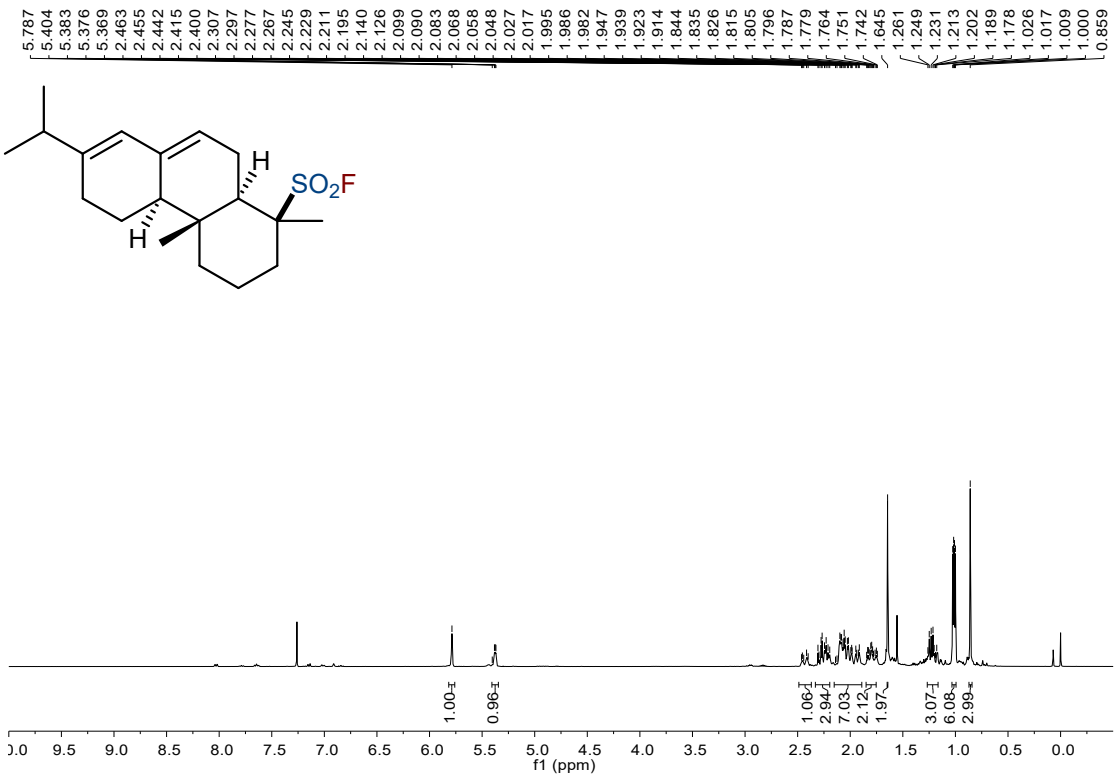
^{1}H NMR (400 MHz, $CDCl_3$) – **(2u)**



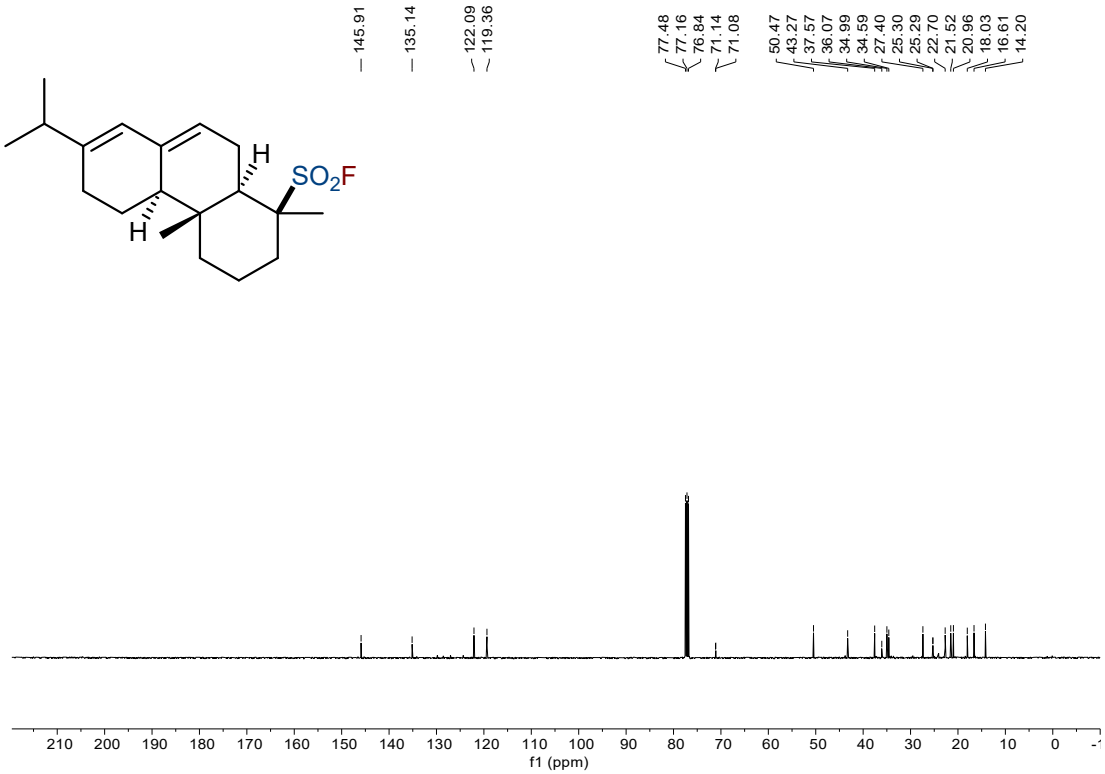
^{13}C NMR (126 MHz, $CDCl_3$) – **(2u)**



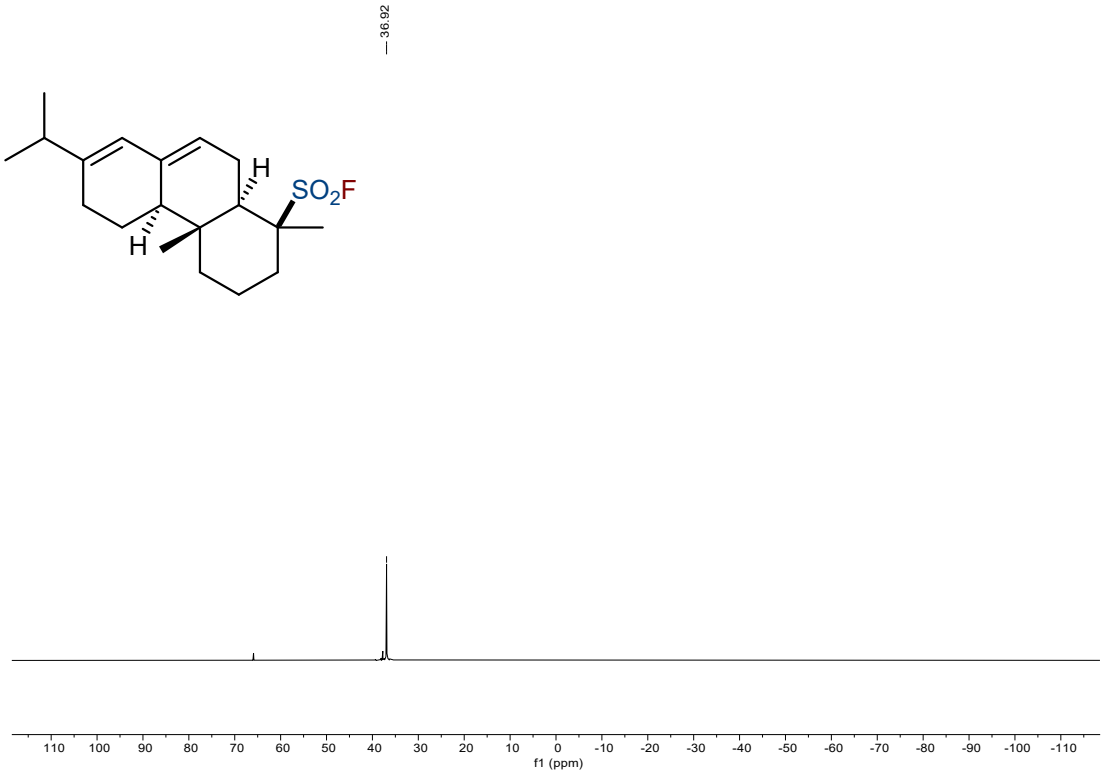
^{19}F NMR (376 MHz, $CDCl_3$) – **(2u)**



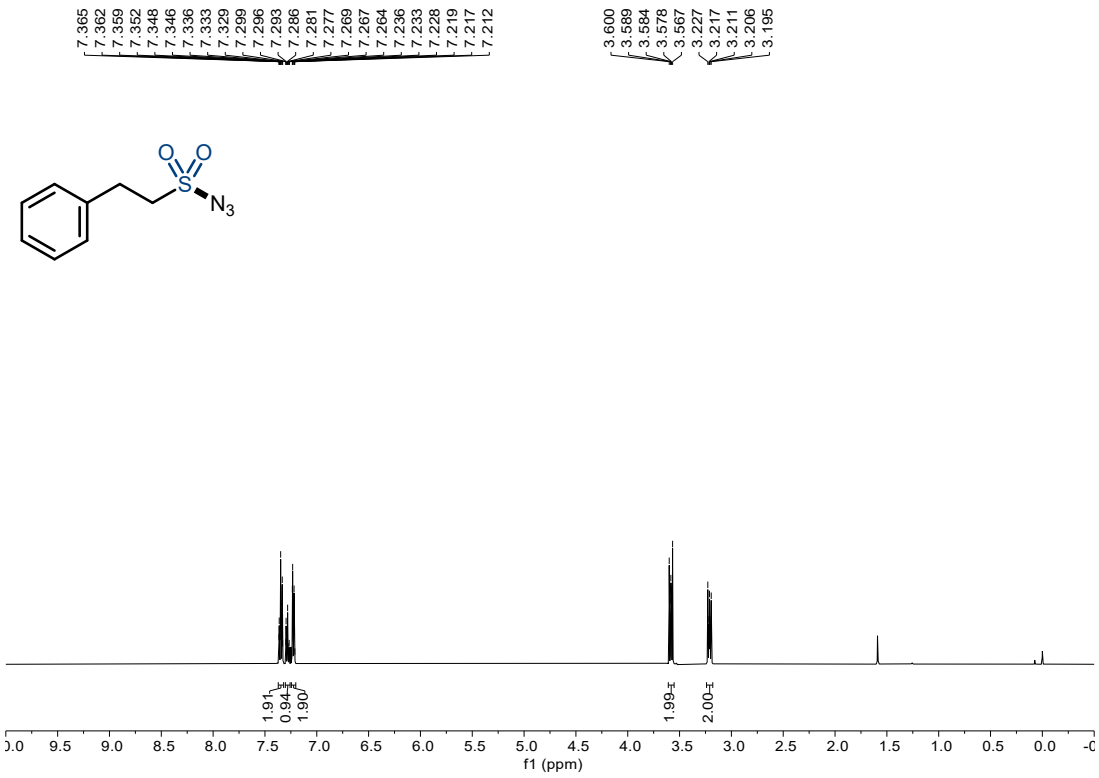
^{1}H NMR (400 MHz, $CDCl_3$) – **(2v)**



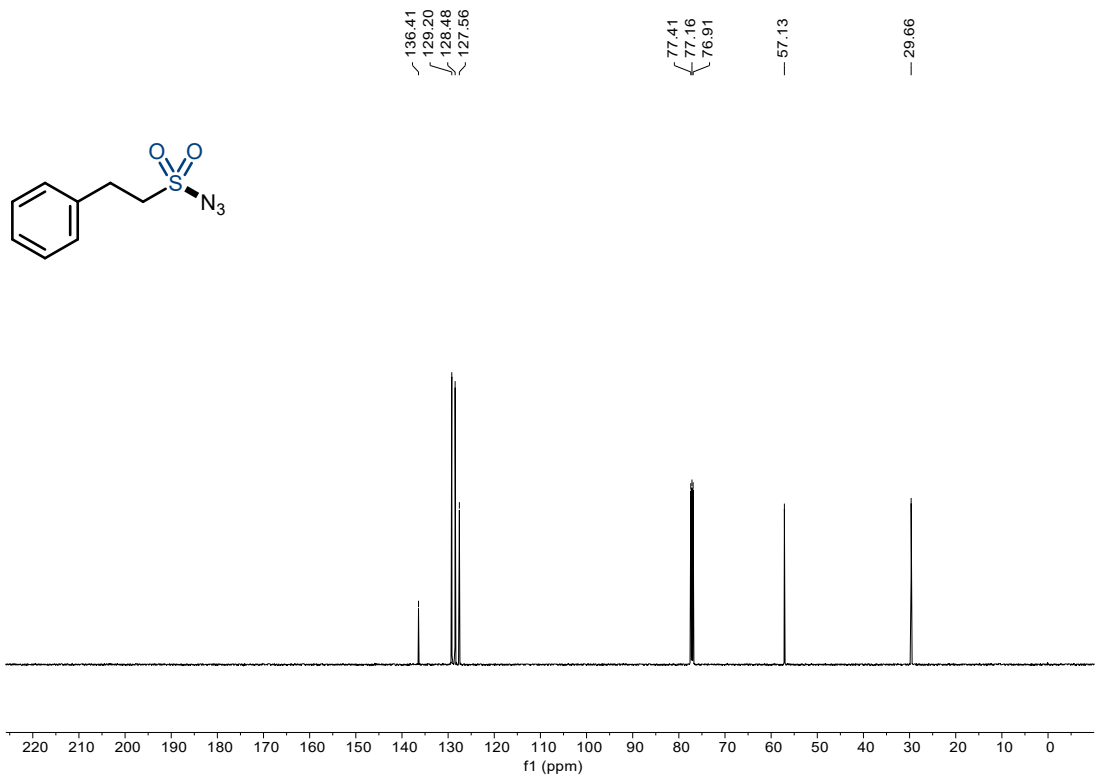
^{13}C NMR (101 MHz, $CDCl_3$) – **(2v)**



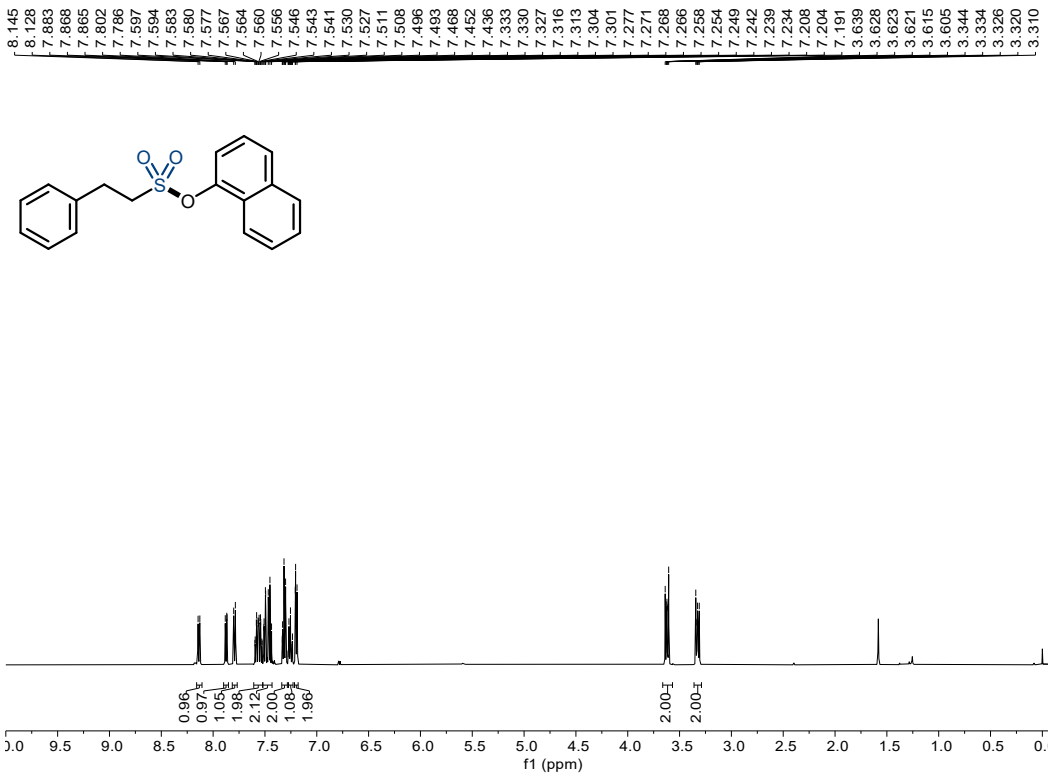
^{19}F NMR (376 MHz, $CDCl_3$) – **(2v)**



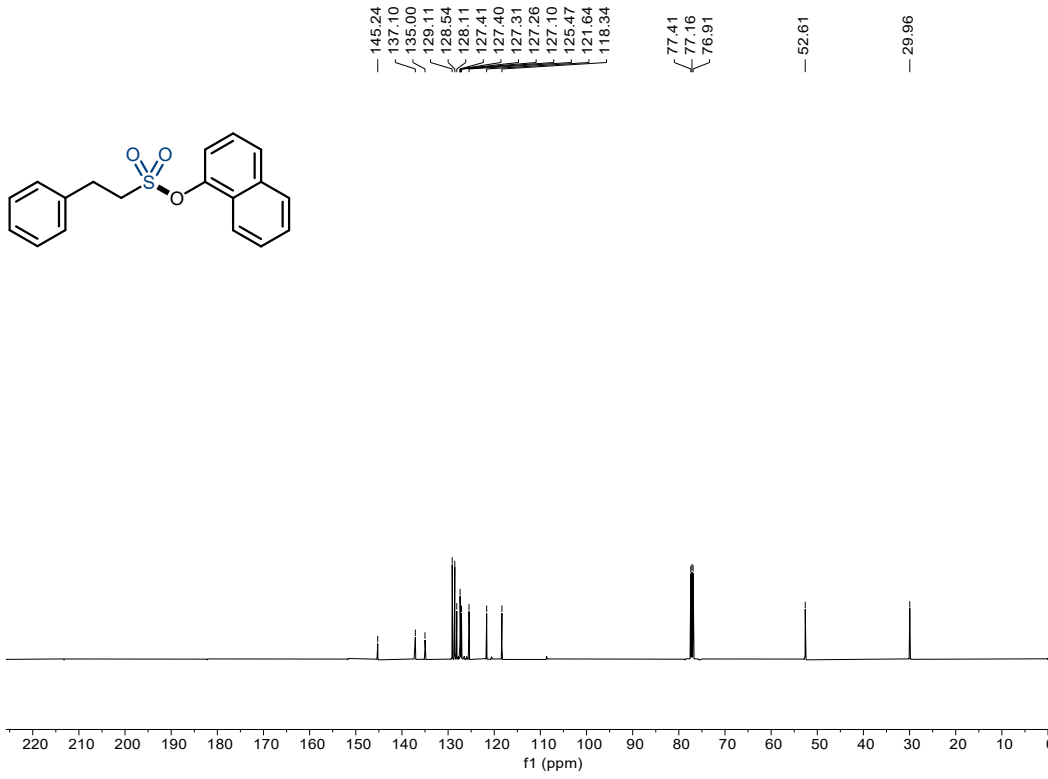
^{1}H NMR (500 MHz, $CDCl_3$) – **(6)**



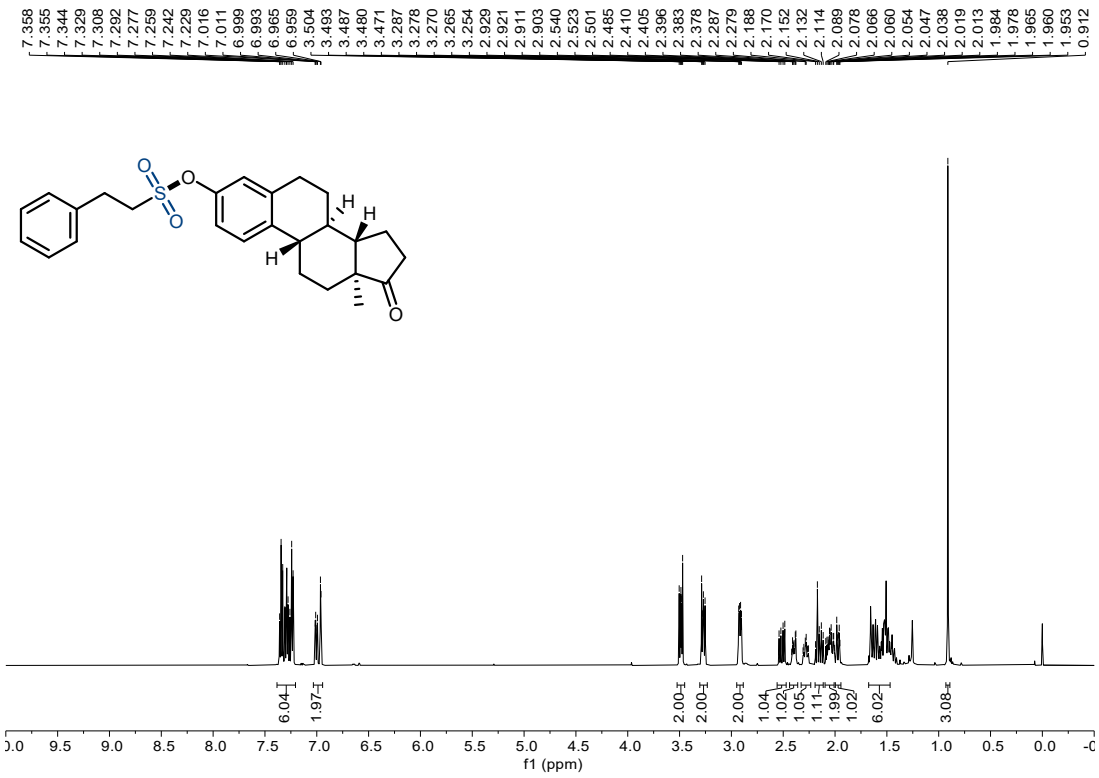
^{13}C NMR (126 MHz, $CDCl_3$) – **(6)**



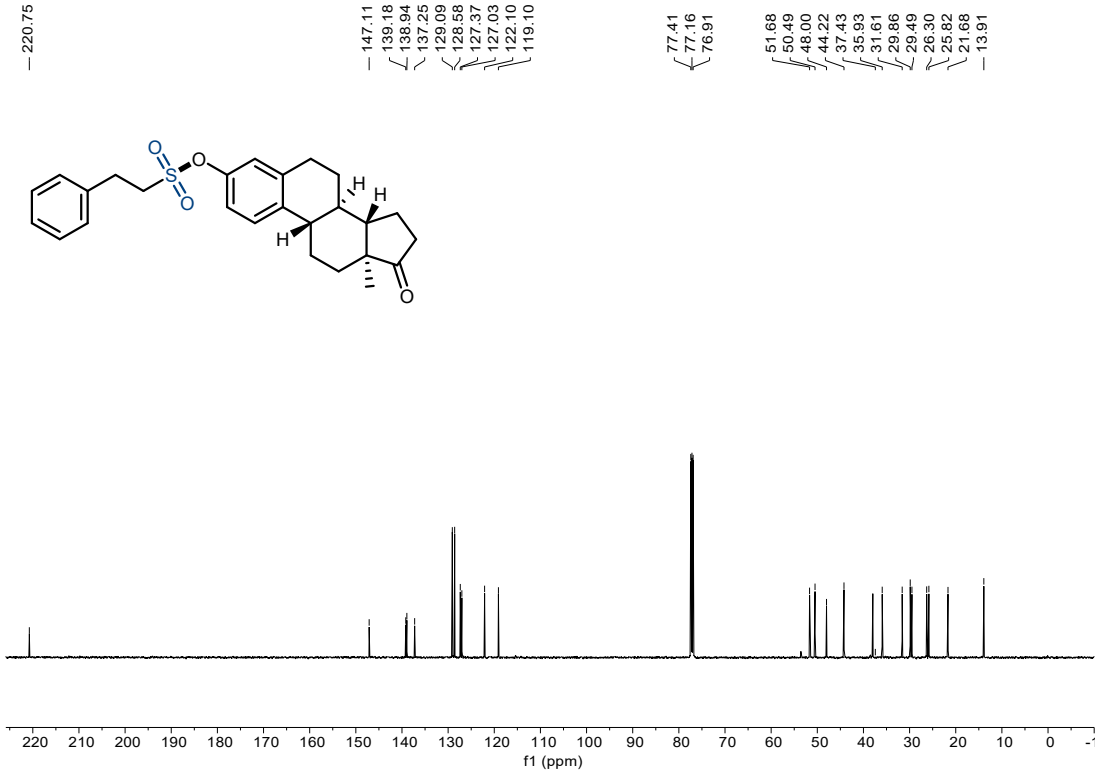
^{1}H NMR (500 MHz, $CDCl_3$) – **(7)**



^{13}C NMR (126 MHz, $CDCl_3$) – **(7)**



^{1}H NMR (500 MHz, $CDCl_3$) – **(8)**



^{13}C NMR (126 MHz, $CDCl_3$) – **(8)**