Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Aliphatic sulfonyl fluoride synthesis via reductive decarboxylative fluorosulfonylation of aliphatic carboxylic acids NHPI esters

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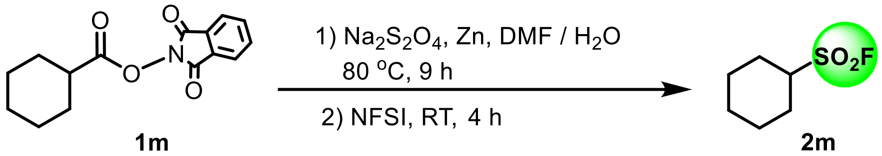
I. General information

The solvents were dried and distilled by the standard methods, other commercially available reagents were purchased and used without further purification. ^{1}H NMR ($(CH_3)_4Si$ (TMS) as the internal standard) and ^{19}F NMR spectra ($CFCl_3$ as the outside standard and low field is positive) were recorded on a 400MHz spectrometer. ^{13}C NMR also was recorded on 400MHz spectrometer. Data for ^{1}H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, number of hydrogens). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). The NMR yield was determined by ^{19}F NMR using 1-methoxy-4-(trifluoromethoxy) benzene (^{19}F NMR: δ -58.4 ppm) as an internal standard before working up the reaction. GC-MS (EI) data were determined on an Agilent 5975C. LRMS (EI) and HRMS (EI) data were tested on a Waters Micromass GCT Premier.

II. Screening reaction conditions for Fluorosulfonylation of alkyl carboxylic acids

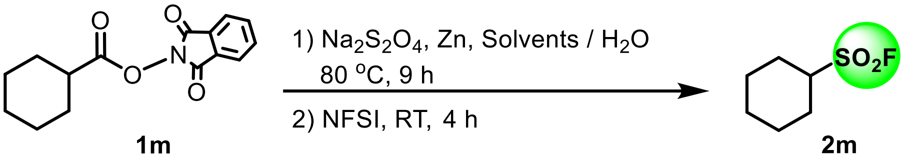
Table S1. Initial attemp[a]



Entry	"SO_2"	"F"	Zinc (mol%)	Solvent	Yield (%)[b]
1	$Na_2S_2O_4$	NFSI	0	DMF/H_2O	30
2	$Na_2S_2O_4$	NFSI	10	DMF/H_2O	40

[a] Reaction conditions: **1m** (0.1 mmol, 1.0 equiv.), $Na_2S_2O_4$ (0.15 mmol, 1.5 equiv.), Zinc (0.01 mmol, 10 mol%), DMF : H_2O (1.0 : 0.3 mL), Ar atmosphere, 80 °C, 9 h, and then NFSI (0.3 mmol, 3.0 equiv.), RT, 4 h. [b]Yields were determined by ^{19}F NMR spectroscopy using 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard.

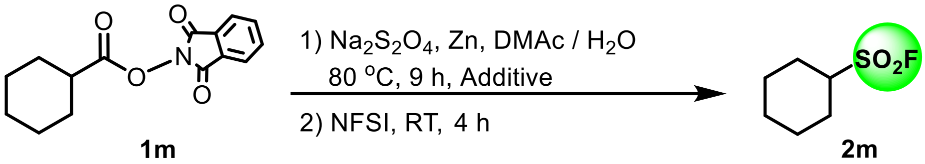
Table S2. Screening the solvents[a]



Entry	Solvents	Yield (%)[b]
1	DMF	40
2	DMSO	7
3	DMAc	59
4	NMP	45
5	DCM	0
6	THF	17
7	Toluene	0

[a] Reaction conditions: **1m** (0.1 mmol, 1.0 equiv.), $Na_2S_2O_4$ (0.15 mmol, 1.5 equiv.), Zinc (0.01 mmol, 10 mol%), Solvent : H_2O (1.0 : 0.3 mL), Ar atmosphere, 80 °C, 9 h, and then NFSI (0.3 mmol, 3.0 equiv.), RT, 4 h. [b]Yields were determined by ^{19}F NMR spectroscopy using 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard.

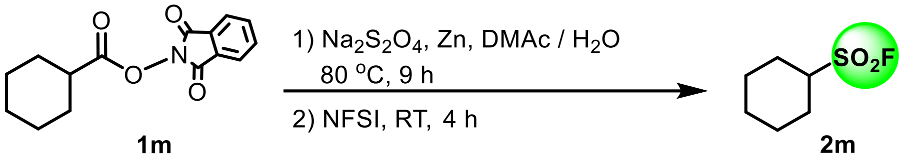
Table S3. Screening the additives[a]



Entry	Additive	Yield (%)[b]
1	Na_2CO_3	61
2	NaOH	0
3	$BF_3 \cdot OEt_2$	6
4	CH_3COOH	0

[a] Reaction conditions: **1m** (0.1 mmol, 1.0 equiv.), $Na_2S_2O_4$ (0.15 mmol, 1.5 equiv.), Zinc (0.01 mmol, 10 mol%), DMF : H_2O (1.0 : 0.3 mL), additives (0.1 mmol, 1.0 equiv.), Ar atmosphere, 80 °C, 9 h, and then NFSI (0.3 mmol, 3.0 equiv.), RT, 4 h. [b]Yields were determined by ^{19}F NMR spectroscopy using 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard.

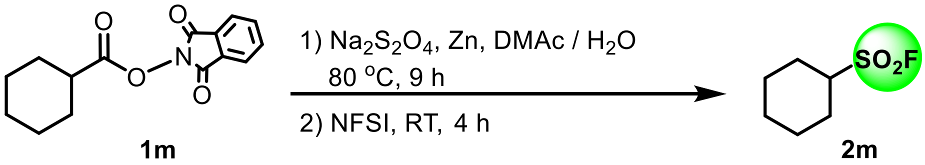
Table S4. Survey on the amount of Zinc[a]



Entry	Zinc (mol%)	Yield (%)[b]
1	10	59
2	100	52
3	200	63

[a] Reaction conditions: **1m** (0.1 mmol, 1.0 equiv.), $Na_2S_2O_4$ (0.15 mmol, 1.5 equiv.), Zinc, DMAc : H_2O (1.0 : 0.3 mL), Ar atmosphere, 80 °C, 9 h, and then NFSI (0.3 mmol, 3.0 equiv.), RT, 4 h. [b]Yields were determined by ^{19}F NMR spectroscopy using 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard.

Table S5. Survey on the amount of water[a]

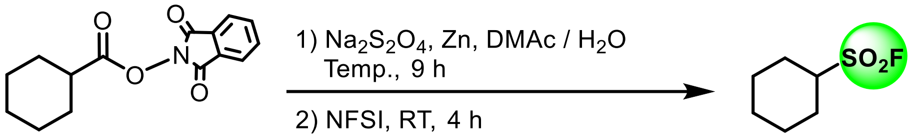


Entry	H_2O	Yield (%)[b]

1	0.1	25
2	0.2	46
3	0.3	56
4	0.4	64
5	0.5	54
6	0.6	52
7	0.7	49
8	0.8	48

[a] Reaction conditions: **1m** (0.2 mmol, 1.0 equiv.), $Na_2S_2O_4$ (0.3 mmol, 1.5 equiv.), Zinc (0.4 mmol, 2.0 equiv.), DMAc (2.0 mL): H_2O, Ar atmosphere, 80 °C, 9 h, and then NFSI (0.6 mmol, 3.0 equiv.), RT, 4 h. [b] Yields were determined by ^{19}F NMR spectroscopy using 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard.

Table S6. Survey on the reaction temperatures[a]

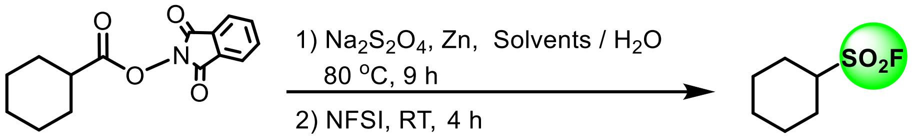


1m **2m**

Entry	Temp.	Yield (%)[b]
1	RT	7
2	60	50
3	80	63
4	100	58

[a] Reaction conditions: **1m** (0.2 mmol, 1.0 equiv.), $Na_2S_2O_4$ (0.3 mmol, 1.5 equiv.), Zinc (0.4 mmol, 2.0 equiv.), DMAc : H_2O (2.0 : 0.4 mL), Ar atmosphere, Temp., 9 h, and then NFSI (0.6 mmol, 3.0 equiv.), RT, 4 h. [b] Yields were determined by ^{19}F NMR spectroscopy using 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard.

Table S7. Survey on the effect of solvent[a]

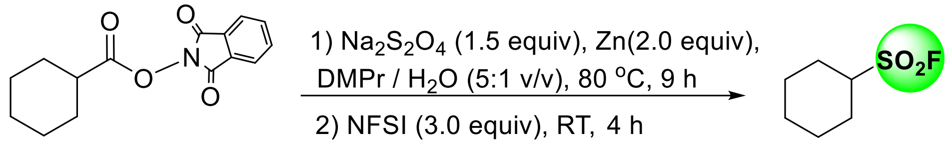


1m **2m**

Entry	Solvent	Yield (%)[b]
1	DMAc	64
2	DMPr	78

[a] Reaction conditions: **1m** (0.2 mmol, 1.0 equiv.), $Na_2S_2O_4$ (0.3 mmol, 1.5 equiv.), Zinc (0.4 mmol, 2.0 equiv.), Solvent : H_2O (2.0 : 0.4 mL), Ar atmosphere, 80 °C, 9 h, and then NFSI (0.6 mmol, 3.0 equiv.), RT, 4 h. [b] Yields were determined by ^{19}F NMR spectroscopy using 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard.

Table S8. Optimization of the reaction conditions[a]

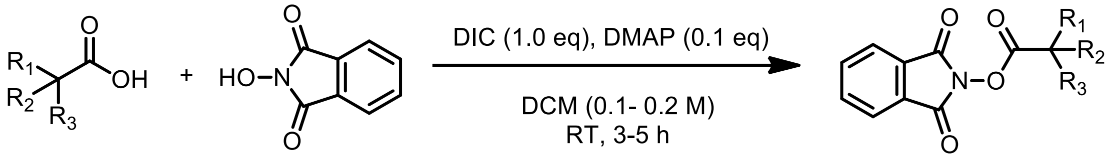


1m **2m**

entry	variations from the standard conditions	yield (%)[b]
1	none	76
2	DABSO instead of $Na_2S_2O_4$	20
3	$K_2S_2O_5$ instead of $Na_2S_2O_4$	21
4	10 eq. SO_2 gas instead of $Na_2S_2O_4$	0
5	without Zn	47
6	Cu instead of Zn	18
7	Mn instead of Zn	40
8	CH_3CN instead of DMPr	55
9	DMF instead of DMPr	50
10	without H_2O	0
11	20 °C	6
12	60 °C	45
13	100 °C	61

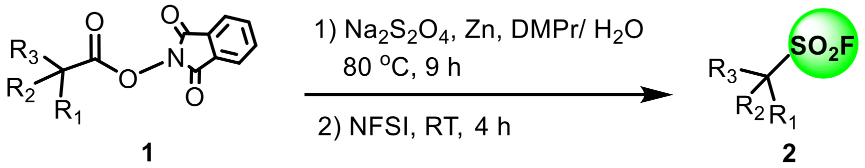
[a] Reaction conditions: **1m** (0.2 mmol), $Na_2S_2O_4$ (0.3 mmol), Zinc (0.4 mmol), DMPr/H_2O (2.0 mL, 5/1 v/v), Ar atmosphere, 80 °C, 9 h, then NFSI (0.6 mmol), room temperature, 4 h. [b] Yields were determined by ^{19}F NMR spectroscopy using 1-methoxy-4-(trifleoromethoxy)benzene as an internal standard.

III. General procedures for synthesis of aliphatic carboxylic acid NHPI redox-active esters



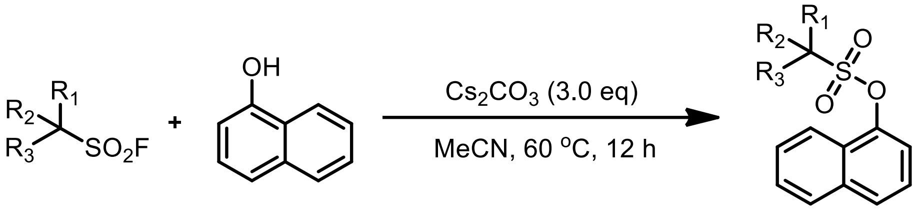
Various aliphatic carboxylic acid NHPI esters were prepared according to the known procedures.[1] Aliphatic carboxylic acid (5 mmol, 1.0 equiv.), N-hydroxyphthalimide (5 - 5.5 mmol, 1.0 - 1.1 equiv.), DMAP (0.5 mmol, 0.1 equiv.) and dichloromethane (50 mL) was added to an round-bottomed flask, and the mixture was stirred vigorously. DIC (5.5 mmol, 1.1 equiv.) was then added and the mixture was stirred for 3-5 h. The mixture was filtered through a pad of Celite or silica gel, and rinsed with DCM. The filtrate was collected and dried under reduced pressure. Purification of the resulting residue by column chromatography afforded the desired aliphatic carboxylic acid NHPI ester products.

IV. General procedures for the reductive decarboxylative fluorosulfonylation of various aliphatic carboxylic acids



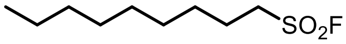
R-COO-NHPI **1** (0.4 mmol, 1.0 equiv.), $Na_2S_2O_4$ (0.6 mmol, 1.5 equiv.), zinc (0.8 mmol, 2 equiv.) were added to an oven-dried sealed tube (10 mL) equipped with a magnetic stirring bar. The tube was evacuated and backfilled with Ar (3 times) and DMPr (N,N'-Dimethylpropionamide) : H_2O (4 : 0.8 mL) was added via syringe under Ar atmosphere. The mixture was sealed and stirred smoothly at 80 °C for 9 h. After cooled to room temperature, NFSI (1.2 mmol, 1.5 equiv.) was added and the reaction mixture was stirred at room temperature for 4 h. Yields of the desired product were measured by ^{19}F NMR spectroscopy before working-up. Then the reaction mixture was filtered through a pad of celite, diluted with DCM (20 mL) and H_2O (50 mL). The resulting mixture was extracted with DCM (2 × 20 mL). The organic layers were combined, washed with brine (50 mL), dried over Na_2SO_4, filtered and concentrated. The crude product was purified by silica gel column chromatography to give the desired product.

V. General procedures for derivatization of sulfonyl fluorides 2c, 2n, 2w, 2x, and 2y with 1-naphthol

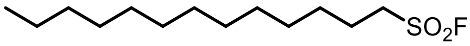


For aliphatic sulfonyl fluorides **2c**, **2n**, **2w**, **2x**, and **2y**, their derivatization with 1-naphthol was performed to unambiguously characterize them due to their high volatility or unstability. After the reductive decarboxylative fluorosulfonylation reaction was complete (see general procedure IV), the crude product was filtered, washed with water, extracted with DCM, and concentrated under reduced pressure. The resulting crude product was dissolved in CH_3CN (4 mL). 1-Naphthol (3 equiv.) and cesium carbonate (3 equiv.) were added subsequently. The reaction mixutre was stirred and heated to 60 °C for 12 h. After cooled to room temperature, the reaction mixture was filtered through a pad of celite, diluted with DCM (20 mL) and H_2O (50 mL). The resulting mixture was extracted with DCM (2 × 20 mL). The organic layers were combined, washed with brine (50 mL), dried over Na_2SO_4, filtered and concentrated. The crude product was purified by silica gel chromatography to give the desired product.

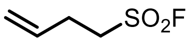
VI. Analytical data for compounds 2a–x, 2aa–gg



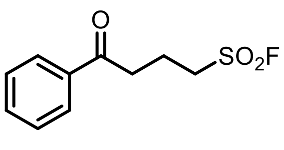
nonane-1-sulfonyl fluoride (2a): Obtained as a colorless oil in 58% yield (97.1 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethan = 25:4 v/v. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.41 – 3.29 (m, 2H), 2.01 – 1.86 (m, 2H), 1.53 – 1.41 (m, 2H), 1.40 – 1.17 (m, 10H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ 53.15 (t, *J* = 3.8 Hz, 0.94F), 53.11 (t, *J* = 3.8 Hz, 0.06F). ^{13}C NMR (101 MHz, $CDCl_3$): δ 51.0 (d, *J* = 16.2 Hz), 31.9, 29.2, 29.2, 28.9, 28.0, 23.5, 22.8, 14.2 ppm. HRMS (FI) m/z: $[M]^+$ Calcd for $C_9H_{19}O_2FS$ 210.1084; Found 210.1083. The analytical data are consistent with literature values.[3]



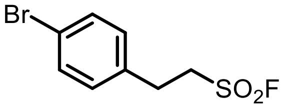
tridecane-1-sulfonyl fluoride (2b): Obtained as a white soild (m.p. 31-32 °C) in 60% yield (63.8 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 50:3 v/v. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.39 – 3.32 (m, 2H), 1.99 – 1.89 (m, 2H), 1.52 – 1.42 (m, 2H), 1.39 – 1.17 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ 53.13 (t, *J* = 3.8 Hz, 0.94F), 53.08 (t, *J* = 3.8 Hz, 0.06F). ^{13}C NMR (101 MHz, $CDCl_3$): δ 51.1 (d, *J* = 16.2 Hz), 32.0, 29.8, 29.8, 29.7, 29.6, 29.5, 29.3, 29.0, 28.0, 23.5, 22.8, 14.2 ppm. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{13}H_{27}O_2FS$ 266.1710; Found 266.1717.



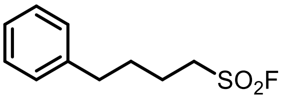
but-3-ene-1-sulfonyl fluoride (2c): Obtained in 50% ^{19}F NMR yield. Crude ^{19}F NMR (376 MHz) δ 53.9 ppm. HRMS (EI) m/z: $[M]^+$ Calcd for $C_8H_8O_2BrFS$ 138.0145; Found 138.0147. Due to its high volatility, its derivatization with 1-naphthol was performed to unambiguously characterize it (See characterization data of **2cc**).



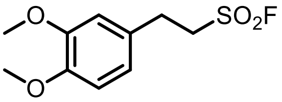
4-oxo-4-phenylbutane-1-sulfonyl fluoride (2d): Obtained as a white solid (m.p. 97 - 98 °C) in 50% yield (46.0 mg) by silica gel flash column chromatography eluted with petroleum ether: ethyl acetate = 5:1 v/v. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 3.63 – 3.52 (m, 2H), 3.26 (t, *J* = 6.5 Hz, 2H), 2.46 – 2.33 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ 58.63 (t, *J* = 3.8 Hz, 0.94F), 58.58 (t, *J* = 3.8 Hz, 0.06F). ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.9, 136.3, 133.8, 128.9, 128.1, 50.2 (d, *J* = 17.2 Hz), 35.5, 18.0 ppm. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{10}H_{11}O_3FS$ 230.0407; Found 230.0409.



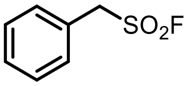
2-(4-bromophenyl)ethanesulfonyl fluoride (2e): Obtained as a white solid (m.p. 63-64 °C) in 49% yield (52.1 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane= 5:1 v/v. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 3.62 – 3.55 (m, 2H), 3.22 – 3.15 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ 53.72 (t, *J* = 3.8 Hz, 0.94F), 53.68 (t, *J* = 3.8 Hz, 0.06F). ^{13}C NMR (101 MHz, $CDCl_3$): δ 135.0, 132.4, 130.2, 121.8, 51.9 (d, *J* = 16.2 Hz), 29.2 ppm. HRMS (FI) m/z: $[M]^+$ Calcd for $C_8H_8O_2BrFS$ 265.9407; Found 265.9402. The analytical data are consistent with literature values.[4]



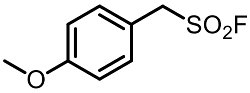
4-phenylbutane-1-sulfonyl fluoride (2f): Obtained as a white soild (m.p. 30-31 °C) in 63% yield (54.5 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane= 25:4 v/v. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (t, *J* = 7.3 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 6.9 Hz, 2H), 3.41 – 3.32 (m, 2H), 2.69 (t, *J* = 7.5 Hz, 2H), 2.04 – 1.93 (m, 2H), 1.88 – 1.78 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ 53.54 (t, *J* = 3.8 Hz, 0.94F), 53.49 (t, *J* = 3.8 Hz, 0.06F). ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.8, 128.7, 128.5, 126.4, 50.8 (d, *J* = 16.2 Hz), 35.2, 29.6, 23.1 ppm. HRMS (FI) m/z: $[M]^+$ Calcd for $C_{10}H_{13}O_2FS$ 216.0615; Found 216.0612. The analytical data are consistent with literature values.[5]



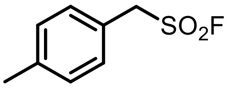
2-(3,4-dimethoxyphenyl)ethanesulfonyl fluoride (2g): Obtained as a white soild (m.p. 100-101 °C) in 50% yield (46.0 mg) by silica gel flash column chromatography eluted with petroleum ether: ethyl acetate= 10:1 v/v. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.83 (d, *J* = 8.2 Hz, 1H), 6.80 – 6.74 (m, 1H), 6.72 (d, *J* = 1.9 Hz, 1H), 3.88 (d, *J* = 5.5 Hz, 6H), 3.65 – 3.55 (m, 2H), 3.23 – 3.14 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ 53.31 (t, *J* = 3.8 Hz, 0.94F), 53.27 (t, *J* = 3.8 Hz, 0.06F). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.5, 148.6, 128.5, 120.6, 111.7, 111.6, 56.1, 52.5 (d, *J* = 15.2 Hz), 29.4 ppm. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{10}H_{13}O_4FS$ 248.0513; Found 248.0520.



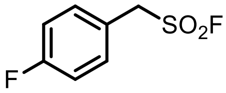
phenylmethanesulfonyl fluoride (2h): Obtained as a white soild (m.p. 86-87 ℃) in 68% yield (43.8 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane= 25:4 v/v. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 – 7.40 (m, 5H), 4.60 (d, *J* = 3.2 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ 51.31 (t, *J* = 3.8 Hz, 0.94F), 51.26 (t, *J* = 3.8 Hz, 0.06F). ^{13}C NMR (101 MHz, $CDCl_3$): δ 130.8, 130.0, 129.4, 125.6, 56.9 (d, *J* = 16.2 Hz) ppm. HRMS (EI) m/z: $[M]^+$ Calcd for $C_7H_7O_2FS$ 174.0145; Found 174.0150. The analytical data are consistent with literature values.[6]



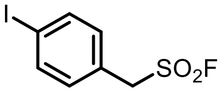
(4-methoxyphenyl)methanesulfonyl fluoride (2i)： Obtained as a white soild (m.p. 87-88 ℃) in 71% yield (58.0 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane= 25:4 v/v. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 4.54 (d, *J* = 2.9 Hz, 2H), 3.83 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ 50.25 (t, *J* = 3.8 Hz, 0.94F), 50.21 (t, *J* = 3.8 Hz, 0.06F). ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.9, 132.1, 117.3, 114.9, 56.6 (d, *J* = 17.2 Hz), 55.5 ppm. HRMS (EI) m/z: $[M]^+$ Calcd for $C_8H_9O_3N_2FS$ 204.0251; Found 204.0252.



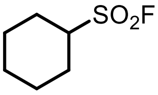
p-tolylmethanesulfonyl fluoride (2j): Obtained as a white soild (m.p. 135-136 ℃) in 70% yield (52.6 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane= 5:1 v/v. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 4.54 (d, *J* = 3.2 Hz, 2H), 2.37 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ 55.64 (t, *J* = 3.8 Hz, 0.94F), 55.60 (t, *J* = 3.8 Hz, 0.06F). ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.2, 130.6, 130.1, 122.5, 56.7 (d, *J* = 17.2 Hz), 21.4 ppm. HRMS (EI) m/z: $[M]^+$ Calcd for $C_8H_9FO_2S$ 188.0302; Found 188.0301.



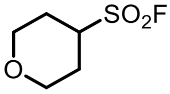
(4-fluorophenyl)methanesulfonyl fluoride (2k)： Obtained as a white solid (m.p. 94-95 °C) in 66% yield (49.9 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane= 5:1 v/v. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.42 (dd, *J* = 8.5, 5.2 Hz, 2H), 7.13 (t, *J* = 8.6 Hz, 2H), 4.58 (d, *J* = 3.1 Hz, 2H). ^{19}F NMR (376 MHz, CDCl$_3$): δ 50.96 (t, *J* = 3.8 Hz, 0.94F), 50.92 (t, *J* = 3.8 Hz, 0.06F), -110.7 – -110.5 (m, 1F). ^{13}C NMR (101 MHz, CDCl$_3$): δ 163.8 (d, *J* = 251.5 Hz), 132.7 (d, *J* = 9.1 Hz), 121.5 (d, *J* = 3.0 Hz), 116.6 (d, *J* = 22.2 Hz), 56.2 (d, *J* = 16.2 Hz) ppm. HRMS (EI) m/z: [M]$^+$ Calcd for $C_7H_6O_2F_2S$ 192.0051; Found 192.0047.



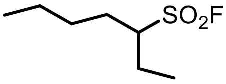
(4-iodophenyl)methanesulfonyl fluoride (2l): Obtained as a white soild (m.p. 179-180 °C) in 20% yield (24.0 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane= 10:3 v/v. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 4.53 (s, 2H). ^{19}F NMR (376 MHz, CDCl$_3$): δ 51.68 (s, 0.94F), 50.92 (s, 0.06F). ^{13}C NMR (101 MHz, CDCl$_3$): δ 138.7, 132.4, 125.2, 96.5, 56.4 (d, *J* = 18.3 Hz) ppm. HRMS (EI) m/z: [M]$^+$ Calcd for $C_7H_6O_2FIS$ 299.9112; Found 299.9116.



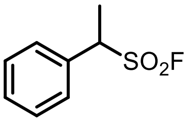
cyclohexanesulfonyl fluoride (2m)： Obtained as a colorless oil in 66% yield (43.8 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane= 5:1 v/v. ^{1}H NMR (400 MHz, CDCl$_3$): δ 3.30 (t, *J* = 12.6 Hz, 1H), 2.29 (d, *J* = 12.7 Hz, 2H), 1.95 (d, *J* = 13.0 Hz, 2H), 1.80 – 1.61 (m, 3H), 1.43 – 1.17 (m, 3H). ^{19}F NMR (376 MHz, CDCl$_3$): δ 40.77 (s, 0.94F), 40.73 (s, 0.06F). ^{13}C NMR (101 MHz, CDCl$_3$): δ 61.1(d, *J* = 12.1 Hz), 26.6, 24.9, 24.8 ppm. HRMS (FI) m/z: [M+H]$^+$ Calcd for $C_6H_{12}O_2FS$ 167.0537; Found 167.0535. The analytical data are consistent with literature values.[10]



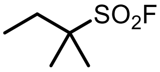
tetrahydro-2H-pyran-4-sulfonyl fluoride (2n): Obtained in 56% ^{19}F NMR yield. Crude ^{19}F NMR (376 MHz, CDCl$_3$): δ 40.3 ppm. Due to its unstability, it can not be purified by silica gel flash column chromatography from impurities, and its derivatization with 1-naphthol was then performed to unambiguously characterize it (See characterization data of **2dd**).



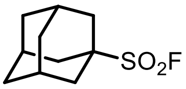
heptane-3-sulfonyl fluoride (2o): Obtained as a colorless oil in 85% yield (61.9 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 10:1 v/v. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.32 – 3.22 (m, 1H), 2.10 – 1.96 (m, 2H), 1.95 – 1.86 (m, 1H), 1.86 – 1.75 (m, 1H), 1.51 – 1.42 (m, 2H), 1.41 – 1.31 (m, 2H), 1.15 – 1.06 (m, 3H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ 48.74 (s, 0.94F), 48.70 (s, 0.06F). ^{13}C NMR (101 MHz, $CDCl_3$): δ 64.2 (d, *J* = 10.1 Hz), 28.4, 22.5, 22.2, 13.8, 10.8 ppm. HRMS (FI) m/z: $[M+H]^+$ Calcd for $C_7H_{16}O_2FS$ 183.0850; Found 183.0853.



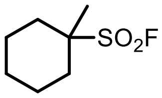
phenylethanesulfonyl fluoride (2p): Obtained as a colorless oil in 88% yield (66.2 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane= 5:1 v/v. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (dq, *J* = 7.1, 3.9 Hz, 5H), 4.71 – 4.61 (m, 1H), 1.94 (d, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ 42.56 (s, 0.94F), 42.52 (s, 0.06F). ^{13}C NMR (101 MHz, $CDCl_3$): δ 131.5, 130.0, 129.3, 129.1, 63.2 (d, *J* = 12.2 Hz), 16.1 ppm. HRMS (EI) m/z: $[M]^+$ Calcd for $C_8H_9O_2FS$ 188.0302; Found 188.0229.



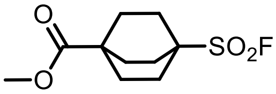
2-methylbutane-2-sulfonyl fluoride (2q): Obtained as a colorless oil in 60% yield (36.8 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane= 10:1 v/v. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.95 (qd, *J* = 7.5, 1.1 Hz, 2H), 1.52 (s, 6H), 1.06 (td, *J* = 7.6, 0.9 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ 33.48 (s, 0.95F), 33.44 (s, 0.05F). ^{13}C NMR (101 MHz, $CDCl_3$): δ 65.0 (d, *J* = 9.0 Hz), 29.9, 21.7, 8.3 ppm. HRMS (FI) m/z: $[M+H]^+$ Calcd for $C_5H_{11}O_2FS$ 155.0536; Found 155.0531.



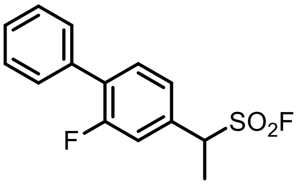
(3s,5s,7s)-adamantane-1-sulfonyl fluoride (2r)： Obtained as a colorless oil in 48% yield (34.8 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 5:1 v/v. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.22 (s, 3H), 2.18 (s, 6H), 1.83 – 1.69 (m, 6H). ^{19}F NMR (376 MHz, CDCl$_3$): δ 26.44 (s, 0.94F), 26.40 (s, 0.06F). ^{13}C NMR (101 MHz, CDCl$_3$): δ 62.6 (d, *J* = 11.1 Hz), 36.1, 35.5, 28.0 ppm. HRMS (FI) m/z: [M-H]$^+$ Calcd for $C_{10}H_{14}O_2FS$ 217.0693; Found 217.0690. The analytical data are consistent with literature values.[4]



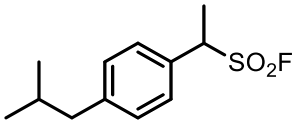
1-methylcyclohexane-1-sulfonyl fluoride (2s)： Obtained as a colorless oil in 55% yield (39.6 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 10:1 v/v. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.02 (td, *J* = 12.8, 4.1 Hz, 2H), 1.89 (d, *J* = 13.0 Hz, 2H), 1.79 (dt, *J* = 13.1, 3.7 Hz, 2H), 1.70 (dt, *J* = 13.1, 3.7 Hz, 1H), 1.58 (s, 3H), 1.54 – 1.40 (m, 2H), 1.35 – 1.22 (m, 1H). ^{19}F NMR (376 MHz, CDCl$_3$): δ 29.0 (s, 1F). ^{13}C NMR (101 MHz, CDCl$_3$): δ 65.1 (d, *J* = 9.1 Hz), 31.3, 24.8, 21.2, 18.6 ppm. HRMS (FI) m/z: [M+H]$^+$ Calcd for $C_7H_{14}O_2FS$ 181.0693; Found 181.0697.



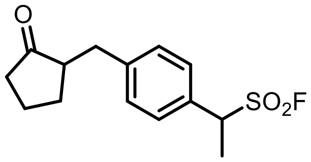
Methyl-4-(fluorosulfonyl)bicyclo[2.2.2]octane-1-carboxylate (2t): Obtained as a white solid (m.p. 90-91 °C) in 20% yield (20 mg) by silica gel flash column chromatography eluted with petroleum ether: ethyl acetate = 10:1 v/v. ^{1}H NMR (400 MHz, CDCl$_3$): δ 3.67 (s, 3H), 2.11 (dd, *J* = 9.9, 5.9 Hz, 6H), 1.95 (dd, *J* = 10.1, 5.7 Hz, 6H). ^{19}F NMR (376 MHz, CDCl$_3$): δ 33.58 (s, 0.95F), 33.54 (s, 0.05F). ^{13}C NMR (101 MHz, CDCl$_3$): δ 176.2, 60.4 (d, *J* = 13.1 Hz), 52.2, 38.1, 27.4, 25.5 ppm. HRMS (ESI) m/z: [M]$^+$ Calcd for $C_{10}H_{15}O_4FS$ 250.0670; Found 250.0672.



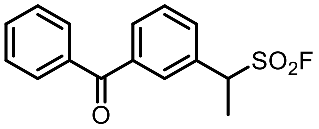
1-(2-fluoro-[1,1'-biphenyl]-4-yl)ethanesulfonyl fluoride (2u)： Obtained as a white solid (m.p. 100-101 °C) in 84% yield (94.7 mg) by silica gel flash column chromatography eluted with petroleum ether: ethyl acetate= 10:1 v/v. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.61 – 7.55 (m, 2H), 7.55 – 7.45 (m, 3H), 7.45 – 7.39 (m, 1H), 7.36 – 7.27 (m, 2H), 4.69 (q, J = 7.2 Hz, 1H), 1.97 (d, J = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, CDCl$_3$): δ 43.10 (s, 0.94F), 43.06 (s, 0.06F), -115.9 (t, J = 11.3 Hz, 1F). ^{13}C NMR (101 MHz, CDCl$_3$): δ 161.0, 159.8 (d, J = 250.5 Hz), 134.8 (d, J = 2.0 Hz), 132.4 (d, J = 8.1 Hz), 131.5 (d, J = 4.0 Hz), 129.1 (d, J = 2.0 Hz), 128.7, 128.4, 125.2 (d, J = 3.0 Hz), 116.9 (d, J = 25.3 Hz), 62.5 (d, J = 16.2 Hz), 16.0 ppm. HRMS (EI) m/z: [M]$^+$ Calcd for $C_{14}H_{12}O_2F_2S$ 282.0521; Found 282.0519.



1-(4-isobutylphenyl)ethanesulfonyl fluoride (2v): Obtained as a colorless oil in 82% yield (80.1 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane= 5:1 v/v. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.36 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 4.63 (q, J = 7.2 Hz, 1H), 2.50 (d, J = 7.2 Hz, 2H), 1.93 (d, J = 7.2 Hz, 3H), 1.91 – 1.80 (m, 1H), 0.92 (d, J = 6.6 Hz, 6H). ^{19}F NMR (376 MHz, CDCl$_3$): δ 42.21 (s, 0.94F), 42.17 (s, 0.06F). ^{13}C NMR (101 MHz, CDCl$_3$): δ 143.9, 129.9, 128.8, 128.7, 63.0 (d, J = 14.1 Hz), 45.2, 30.2, 22.4, 16.1 ppm. HRMS (EI) m/z: [M]$^+$ Calcd for $C_{12}H_{17}O_2FS$ 244.0928; Found 244.0926.

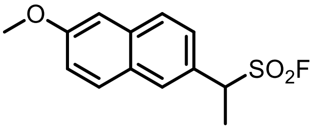


1-(4-((2-oxocyclopentyl)methyl)phenyl)ethanesulfonyl fluoride (2w): Obtained in 91% ^{19}F NMR yield. Crude ^{19}F NMR (376 MHz): δ 41.1 ppm. Due to its unstability, it can not be purified by silica gel flash column chromatography from impurities, and its derivatization with 1-naphthol was then performed to unambiguously characterize it (See characterization data of **2ee**).

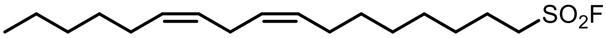


1-(3-benzoylphenyl)ethanesulfonyl fluoride (2x): Obtained in 82% ^{19}F NMR yield. Crude ^{19}F NMR (376 MHz): δ 42.3 ppm. Due to its unstability, it can not be purified by silica gel flash column chromatography from impurities, and its derivatization with

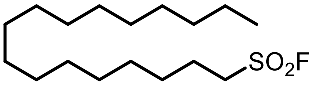
1-naphthol was then performed to unambiguously characterize it (See characterization data of **2ff**).



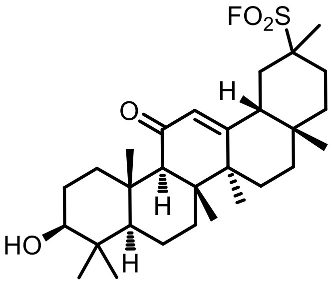
1-(6-methoxynaphthalen-2-yl)ethanesulfonyl fluoride (2y): Obtained in 83% ^{19}F NMR yield. Crude ^{19}F NMR (376 MHz): δ 42.0 ppm. Due to its unstability, it can not be purified by silica gel flash column chromatography from impurities, and its derivatization with 1-naphthol was then performed to unambiguously characterize it (See characterization data of **2gg**).



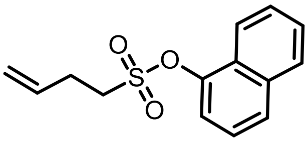
(8Z,11Z)-heptadeca-8,11-diene-1-sulfonyl fluoride (2z): Obtained as a colorless oil in 52% yield (65.0 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 100:13 v/v. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.47 – 5.27 (m, 4H), 3.41 – 3.28 (m, 2H), 2.77 (t, *J* = 5.8 Hz, 2H), 2.14 – 2.00 (m, 4H), 1.99 – 1.87 (m, 2H), 1.53 – 1.42 (m, 2H), 1.32 (d, *J* = 15.9 Hz, 12H), 0.89 (t, *J* = 6.5 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ 53.20 (t, *J* = 3.8 Hz, 0.94F), 53.16 (t, *J* = 3.8 Hz, 0.06F). ^{13}C NMR (101 MHz, $CDCl_3$): δ 130.4, 129.9, 128.4, 127.9, 51.0 (d, *J* = 16.2 Hz), 31.7, 29.6, 29.5, 28.9, 27.9, 28.0, 27.4, 27.2, 25.8, 23.5, 22.7, 14.2 ppm. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{31}O_2FS$ 318.2023; Found 318.2025.



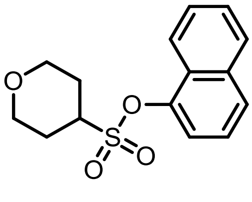
heptadecane-1-sulfonyl fluoride (2aa): Obtained as a white solid (m.p. 46-47 °C) in 51% yield (65.7 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 10:1 v/v. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.40 – 3.31 (m, 2H), 2.00 – 1.89 (m, 2H), 1.47 (p, *J* = 7.0 Hz, 2H), 1.25 (s, 26H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ 53.15 (t, *J* = 3.8 Hz, 0.94F), 53.11 (t, *J* = 3.8 Hz, 0.06F). ^{13}C NMR (101 MHz, $CDCl_3$): δ 51.0 (d, *J* = 16.2 Hz), 32.1, 29.9, 29.8, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 29.3, 29.0, 28.0, 28.0, 23.5, 22.8, 14.3 ppm. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{35}O_2FS$ 322.2336; Found 322.2342. The analytical data are consistent with literature values.[4]



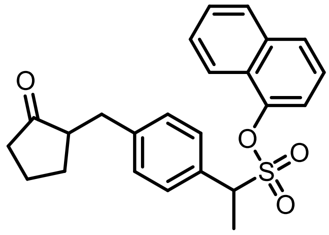
(4aS,6aS,6bR,8aR,10S,12aS,12bR,14bR)-10-hydroxy-2,4a,6a,6b,9,9,12a-heptamethyl-13-oxo-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-icosahydropicene-2-sulfonyl fluoride (2bb): Obtained as a white solid (m.p. 247-248 °C) in 32% yield (65.0 mg) by silica gel flash column chromatography eluted with petroleum ether: ethyl acetate = 5: 2 v/v. ^{1}HNMR (400 MHz, CDCl$_3$): δ 5.61 (s, 1H), 3.22 (dd, J = 10.3, 5.6 Hz, 1H), 2.73 (d, J = 13.5 Hz, 1H), 2.50 (t, J = 13.4 Hz, 1H), 2.32 (s, 1H), 2.26 – 1.99 (m, 3H), 1.86 – 1.73 (m, 2H), 1.60 (q, J = 15.5, 14.2 Hz, 10H), 1.39 (d, J = 14.2 Hz, 5H), 1.22 (d, J = 12.7 Hz, 2H), 1.11 (s, 8H), 0.99 (s, 3H), 0.91 (s, 3H), 0.79 (s, 3H), 0.69 (d, J = 11.4 Hz, 1H). ^{19}F NMR (376 MHz, CDCl$_3$): δ 29.1 (s, 1F). ^{13}C NMR (101 MHz, CDCl$_3$): δ 199.8, 166.2, 129.4, 78.7, 65.1 (d, J = 10.1 Hz), 62.0, 54.9, 46.0, 45.6, 43.3, 39.2, 39.2, 37.2, 35.4, 34.8, 32.8, 32.2, 28.2, 28.1, 27.3, 26.3, 26.2 (2C), 23.6, 18.8, 17.6, 17.4, 16.4, 15.7 ppm. HRMS (ESI) m/z: [M+H]$^+$ Calcd for $C_{29}H_{46}O_4FS$ 509.3095; Found 509.3089.



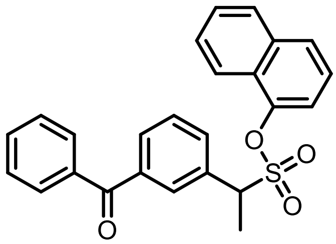
naphthalen-1-yl but-3-ene-1-sulfonate (2cc): Obtained as a colorless oil in 47% yield (49.2 mg) by silica gel flash column chromatography eluted with petroleum ether: ethyl acetate = 20:1 v/v. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.15 (d, J = 8.1 Hz, 1H), 7.89 (d, J = 7.7 Hz, 1H), 7.81 (d, J = 7.7 Hz, 1H), 7.64 – 7.54 (m, 2H), 7.54 – 7.44 (m, 2H), 5.94 – 5.77 (m, 1H), 5.24 – 5.09 (m, 2H), 3.51 – 3.39 (m, 2H), 2.80 (q, J = 6.7 Hz, 2H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 145.2, 135.0, 133.4, 128.1, 127.4, 127.3, 127.3, 127.1, 125.5, 121.7, 118.4, 118.0, 50.6, 27.9 ppm. HRMS (EI) m/z: [M]$^+$ Calcd for $C_{14}H_{14}O_3S$ 262.0658; Found 262.0662.



naphthalen-1-yl tetrahydro-2H-pyran-4-sulfonate (2dd): Obtained as a colorless oil in 50% yield (58.6 mg) by silica gel flash column chromatography eluted with petroleum ether: ethyl acetate = 4:1 v/v. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.13 (d, *J* = 7.7 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 6.7 Hz, 1H), 7.64 – 7.51 (m, 2H), 7.51 – 7.40 (m, 2H), 4.25 – 4.09 (m, 2H), 3.69 – 3.58 (m, 1H), 3.54 – 3.40 (m, 2H), 2.37 – 2.15 (m, 4H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 144.9, 135.0, 128.1, 127.5, 127.3, 127.2, 127.1, 125.4, 121.7, 118.4, 66.5 (2C), 58.2, 26.9 (2C) ppm. HRMS (EI) m/z: [M]$^+$ Calcd for $C_{15}H_{16}O_4S$ 292.0764; Found 292.0768.

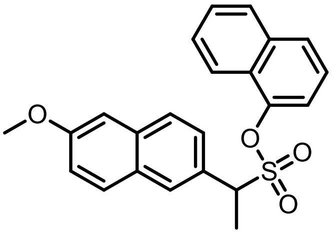


naphthalen-1-yl-1-(4-((2-oxocyclopentyl)methyl)phenyl)ethanesulfonate (2ee): Obtained as a yellow oil in 34% yield (56.0 mg) by silica gel flash column chromatography eluted with petroleum ether: ethyl acetate = 20:7 v/v. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.54 – 7.41 (m, 4H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 7.6 Hz, 1H), 4.74 (q, *J* = 7.1 Hz, 1H), 3.20 (dd, *J* = 13.8, 3.7 Hz, 1H), 2.63 – 2.51 (m, 1H), 2.43 – 2.30 (m, 2H), 2.17 – 2.07 (m, 2H), 2.03 (d, *J* = 7.2 Hz, 3H), 2.01 – 1.93 (m, 1H), 1.83 – 1.70 (m, 1H), 1.62 – 1.49 (m, 1H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 219.9, 145.2, 141.6, 134.9, 131.4, 129.6, 129.5, 127.8, 127.5, 127.0, 126.9, 126.8, 125.3, 121.9, 118.0, 62.8, 51.0, 38.2, 35.4, 29.3, 20.6, 16.3 ppm. HRMS (ESI) m/z: [M+Na]$^+$ Calcd for $C_{24}H_{24}O_4NaS$ 431.1288; Found 431.1289.



naphthalen-1-yl 1-(3-benzoylphenyl)ethanesulfonate (2ff): Obtained as a yellow oil in 40% yield (66.0 mg) by silica gel flash column chromatography eluted with petroleum ether: ethyl acetate = 5:1 v/v. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.98 (s, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.86 – 7.72 (m, 6H), 7.61 – 7.53 (m, 2H), 7.52 – 7.45 (m, 2H), 7.44 – 7.36 (m, 3H), 7.25 (dd, *J* = 8.1, 2.2 Hz, 1H), 4.83 (q, *J* = 7.2 Hz, 1H), 2.07 (d, *J*

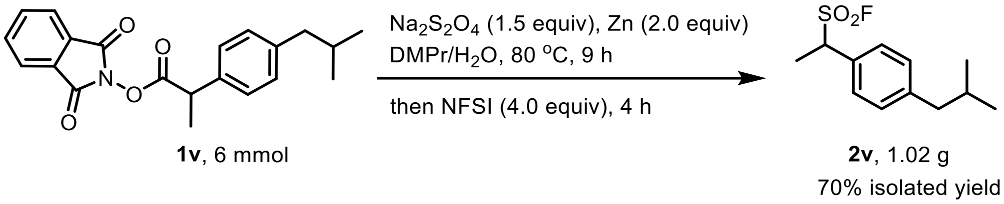
= 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 195.9, 145.1, 138.3, 137.1, 134.9, 134.0, 133.2, 132.8, 131.1, 130.9, 130.2, 129.1, 128.5, 127.9, 127.4, 127.2, 127.1, 127.0, 125.3, 121.7, 118.0, 62.8, 16.3 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{21}O_4S$ 417.1155; Found 417.1154.



naphthalen-1-yl-1-(6-methoxynaphthalen-2-yl)ethanesulfonate (2gg): Obtained as a yellow oil in 43% yield (72.0 mg) by silica gel flash column chromatography eluted with petroleum ether: ethyl acetate = 5:1 v/v. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.80 (dd, *J* = 8.4, 3.2 Hz, 2H), 7.72 (dd, *J* = 11.9, 8.6 Hz, 3H), 7.64 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.36 – 7.28 (m, 2H), 7.24 – 7.15 (m, 3H), 4.90 (q, *J* = 7.2 Hz, 1H), 3.95 (s, 3H), 2.14 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.6, 145.3, 135.0, 134.9, 129.8, 129.1, 128.8, 128.6, 127.8, 127.6, 127.5, 127.0, 127.0, 126.9, 126.8, 125.3, 121.9, 119.6, 118.0, 105.8, 63.3, 55.5, 16.5 ppm. HRMS (ESI) m/z: $[M+Na^+]$ Calcd for $C_{23}H_{20}O_4NaS$ 415.0975; Found 415.0976.

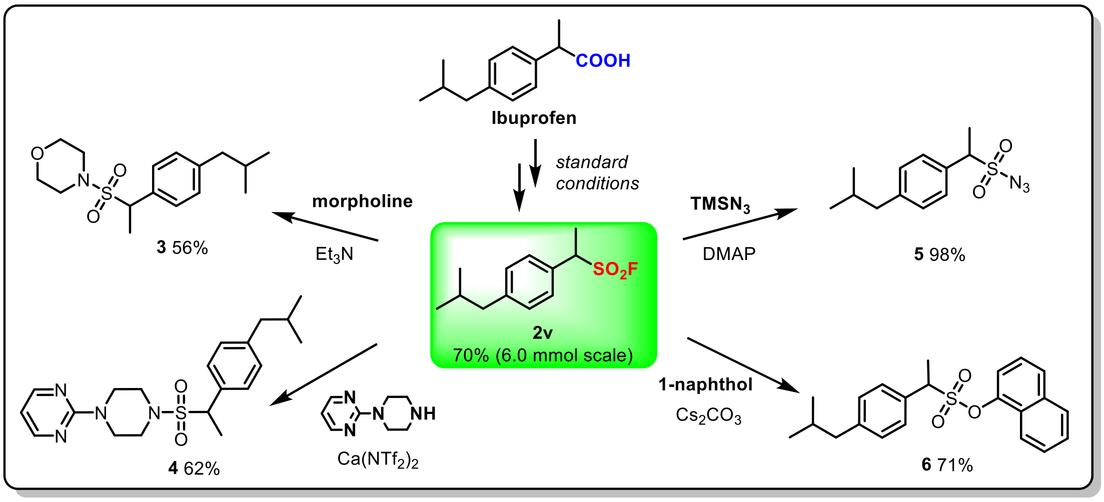
VII. Scale-up and derivatization reactions of the aliphatic sulfonyl fluoride 2v

1. Gram-scale synthesis of 1-(4-isobutylphenyl)ethanesulfonyl fluoride (2v)



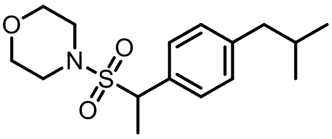
To a 100 mL round-bottomed flask equipped with a magnetic stirring bar were added 1,3-dioxoisoindolin-2-yl 2-(4-isobutylphenyl)propanoate **1v** (6.0 mmol, 1.0 equiv.), $Na_2S_2O_4$ (9 mmol, 1.0 equiv.), zinc (12 mmol, 2.0 equiv.). The tube was then evacuated and backfilled with Ar (3 times) and DMPr (N,N-Dimethylpropionamide) : H_2O (60 : 12 mL) was added via syringe under Ar atmosphere. The mixture was sealed and stirred smoothly at 80 °C for 9 h. Then NFSI (18 mmol, 3 equiv.) was added and the reaction mixture was stirred smoothly at room temperature for 4 h. The reaction mixture was filtered through a pad of celite, diluted with DCM (20 mL) and H_2O (50 mL). The resulting mixture was extracted with DCM (2 × 20 mL). The organic layers were combined, washed with brine (50 mL), dried over Na_2SO_4. filtered and concentrated. The crude product was purified by silica gel chromatography to give the desired product (1.02 g, 70%).

2. Derivatization of 1-(4-isobutylphenyl)ethanesulfonyl fluoride 2v with various O- or N-nucleophiles



(a) The procedure for the preparation of sulfonamides 3[7]

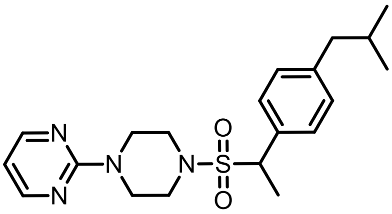
A 10 mL sealed tube equipped with a magnetic stirring bar was charged with **2v** (0.4 mmol, 1.0 equiv.), morpholine (0.8 mmol, 2.0 equiv.), Et_3N (0.8 mmol, 2.0 equiv.) and anhydrous MeCN (4 mL). The reaction mixture was stirred vigorously at 80 °C under Ar atmosphere for 24 h. The resulting mixture was filtered through a pad of silica gel and concentrated under reduced pressure. The residue was subjected to flash column chromatography to afford the desired product.



((1-(4-isobutylphenyl)ethyl)sulfonyl)morpholine (3): Obtained as a colorless oil in 56% yield (69.3 mg) by silica gel flash column chromatography eluted with petroleum ether : ethyl acetate = 5:1 v/v. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.7 Hz, 2H), 4.19 (q, *J* = 7.0 Hz, 1H), 3.58 – 3.39 (m, 4H), 3.10 – 2.95 (m, 2H), 2.80 (s, 2H), 2.46 (d, *J* = 7.1 Hz, 2H), 1.84 (dd, *J* = 13.3, 6.5 Hz, 1H), 1.74 (d, *J* = 7.1 Hz, 3H), 0.86 (d, *J* = 6.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.8, 132.1, 129.5, 128.9, 66.8, 62.9, 46.3, 45.0, 30.2, 22.3, 22.3, 16.2 ppm. HRMS (FI) m/z: $[M]^+$ Calcd for $C_{16}H_{25}O_3NS$ 311.1550; Found 311.1546.

(b) The procedure for the preparation of sulfonamides 4[8]

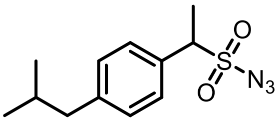
A 10 mL sealed tube equipped with a magnetic stirring bar was charged with **2v** (0.2 mmol, 1.0 equiv.), 2-(piperazin-1-yl)pyrimidine (0.22 mmol, 1.1 equiv.), $Ca(NTf_2)_2$ (0.2 mmol, 1.0 equiv.), DABCO (0.3 mmol, 1.5 equiv.) and anhydrous THF (2 mL). The reaction mixture was stirred vigorously at 25 °C under Ar atmosphere for 24 h. The mixture was filtered through a pad of silica gel and concentrated under reduced pressure. The residue was subjected to flash column chromatography to afford the desired product.



(4-((1-(4-isobutylphenyl)ethyl)sulfonyl)piperazin-1-yl)pyrimidine (4): Obtained as a white solid (m.p. 126-127 °C) in 62% yield (48.2 mg) by silica gel flash column chromatography eluted with petroleum ether : ethyl acetate = 5:1 v/v. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, *J* = 4.6 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 6.50 (t, *J* = 4.6 Hz, 1H), 4.21 (q, *J* = 7.0 Hz, 1H), 3.69 (q, *J* = 15.5, 14.6 Hz, 4H), 3.11 (dd, *J* = 11.9, 4.1 Hz, 2H), 2.92 (s, 2H), 2.45 (d, *J* = 7.1 Hz, 2H), 1.83 (dd, *J* = 13.4, 6.8 Hz, 1H), 1.77 (d, *J* = 7.1 Hz, 3H), 0.86 (d, *J* = 6.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.5, 157.8, 142.8, 132.2, 129.6, 128.9, 110.5, 63.2, 46.1, 45.2, 44.1, 30.3, 22.4, 16.3 ppm. HRMS (FI) m/z: $[M]^+$ Calcd for $C_{20}H_{28}O_2N_4S$ 388.1927; Found 388.1925.

(c) The procedure for the preparation of 4-methoxybenzenesulfonyl azide 5[7]

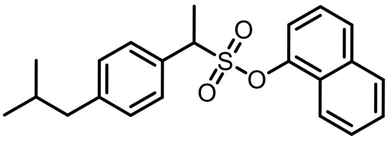
To a stirred solution of **2v** (0.4 mmol, 1.0 equiv.) in MeCN (4 mL) was added DMAP (0.6 mmol, 1.5 equiv.) followed by $TMSN_3$ (0.3 mmol, 0.75 equiv.). The resulting solution was stirred at room temperature for 70 min, then a further portion of $TMSN_3$ (0.3 mmol, 0.75 equiv.) was added. The reaction mixture was stirred at 50 °C for 8 h. After cooled to room temperature, the reaction mixture was filtered through a pad of celite, eluted with DCM, and concentrated under reduced pressure. The residue was subjected to flash column chromatography to afford the desired product.



(isobutylphenyl)ethanesulfonyl azide (5): Obtained as a colorless oil in 98% yield (104.7 mg) by silica gel flash column chromatography eluted with petroleum ether : ethyl acetate = 4:1 v/v. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.9 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 4.54 (q, *J* = 7.2 Hz, 1H), 2.51 (d, *J* = 7.2 Hz, 2H), 1.89 (d, *J* = 7.2 Hz, 3H), 1.85 (d, *J* = 6.7 Hz, 1H), 0.90 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.0, 129.9, 129.6, 129.3, 67.5, 45.5, 30.2, 22.3, 22.3, 15.0 ppm. HRMS (FI) m/z: $[M]^+$ Calcd for $C_{12}H_{17}O_2N_3S$ 267.1036; Found 267.1038.

(d) The procedure for the preparation of sulfonic ester 6[9]

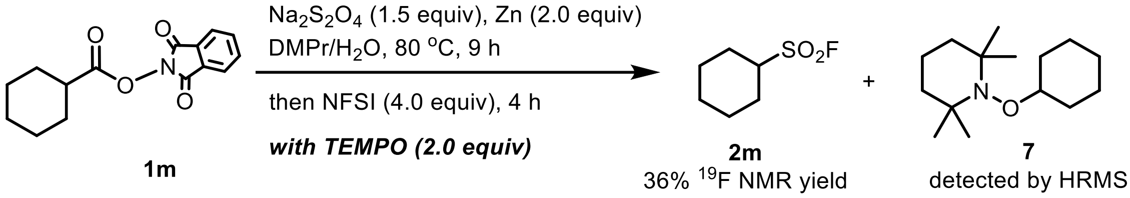
A 10 mL sealed tube equipped with a magnetic stirring bar was charged with **2v** (0.4 mmol, 1.0 equiv.), 1-naphthol (0.8 mmol, 2.0 equiv.), Cs_2CO_3 (0.8 mmol, 2.0 equiv.) and anhydrous MeCN (3 mL). The reaction mixture was stirred vigorously at 60 °C under argon atmosphere for 12 h. The mixture was filtered through a short plug of silica gel and concentrated under reduced pressure. The residue was subjected to flash column chromatography to afford the desired product.



naphthalen-1-yl 1-(4-isobutylphenyl)ethanesulfonate (6): Obtained as a white solid (m.p. 71-73 °C) in 71% yield (105.0 mg) by silica gel flash column chromatography eluted with petroleum ether : ethyl acetate = 5:1 v/v. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (dd, *J* = 7.9, 3.4 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.53 – 7.41 (m, 4H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 7.6 Hz, 1H), 4.75 (q, *J* = 7.2 Hz, 1H), 2.54 (d, *J* = 7.2 Hz, 2H), 2.05 (d, *J* = 7.2 Hz, 3H), 2.01 – 1.84 (m, 1H), 0.96 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.3, 143.2, 134.9, 130.8, 129.7, 129.3, 127.8, 127.6, 127.0, 126.9, 126.8, 125.3, 122.0, 118.1, 63.0, 45.2, 30.3, 22.5, 16.2 ppm. HRMS (FI) m/z: $[M]^+$ Calcd for $C_{22}H_{24}O_3S$ 368.1441; Found 368.1445.

VIII. Preliminary mechanistic studies

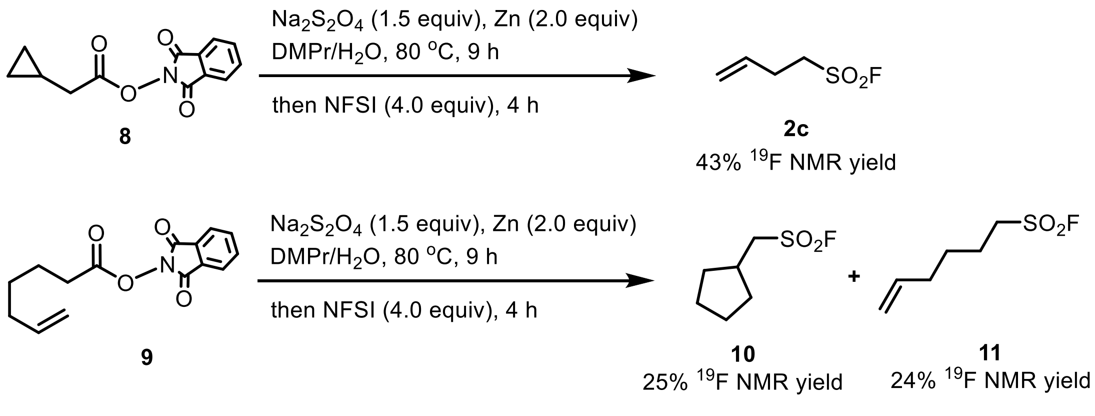
1. Radical inhibition experiments



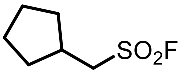
To an oven-dried sealed tube (10 mL) equipped with a magnetic stirring bar were added 1,3-dioxoisoindolin-2-yl-cyclohexanecarboxylate **1m** (0.4 mmol, 1.0 equiv.), $Na_2S_2O_4$ (0.6 mmol, 1.5 equiv.), Zinc (0.8 mmol, 2 equiv.), TEMPO (125 mg, 0.8 mmol). The tube was then evacuated and backfilled with Ar (3 times) and DMPr (N, N-Dimethylpropionamide) : H_2O (4 : 0.8 mL) was added via syringe under Ar atmosphere. The mixture was sealed and stirred smoothly at 80 °C for 9 h. Then NFSI (1.2 mmol, 3.0 equiv.) was added and the reaction mixutre was stirred smoothly at room temperature for 4 h. The crude reaction mixture was then analyzed by ^{19}F NMR spectroscopy and HRMS.

Compound 7: HRMS (FI) m/z: $[M]^+$ Calcd for $C_{15}H_{29}ON$ 239.2244; Found 239.2238.

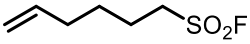
2. Radical clock experiments



Following the general procedure for reductive decarboxylative fluorosulfonylation of aliphatic carboxylic acids, substrate **8** (0.4 mmol) afforded 43% ^{19}F NMR yield of **2c**, and substrate **9** gave 25% ^{19}F NMR yield of **10** and 24% ^{19}F NMR yield of **11**.



cyclopentylmethanesulfonyl fluoride (10): Obtained as a colorless oil in 25% yield (16.6 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 100:14 v/v. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.48 – 3.30 (m, 2H), 2.52 – 2.35 (m, 1H), 2.11 – 1.93 (m, 2H), 1.80 – 1.59 (m, 4H), 1.41 – 1.27 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ 56.04 (s, 0.96F), 56.00 (s, 0.06F). ^{13}C NMR (101 MHz, $CDCl_3$): δ 56.4 (d, *J* = 13.1 Hz), 35.1, 32.4, 24.9 ppm. HRMS (EI) m/z: $[M]^+$ Calcd for $C_6H_{11}O_2FS$ 166.0458; Found 166.0462.



hex-5-ene-1-sulfonyl fluoride (11): Obtained as a colorless oil in 23% yield (15.8 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 100:16 v/v. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.83 – 5.69 (m, 1H), 5.09 – 5.00 (m, 2H), 3.41 – 3.33 (m, 2H), 2.13 (q, *J* = 7.0 Hz, 2H), 2.01 – 1.92 (m, 2H), 1.64 – 1.57 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ 53.30 (t, *J* = 3.8 Hz, 0.94F), 53.26 (t, *J* = 3.8 Hz, 0.06F). ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.2, 116.0, 50.9 (d, *J* = 16.2 Hz), 32.9, 27.1, 22.9 ppm. HRMS (FI) m/z: $[M]^+$ Calcd for $C_6H_{11}O_2FS$ 166.0458; Found 166.0459.

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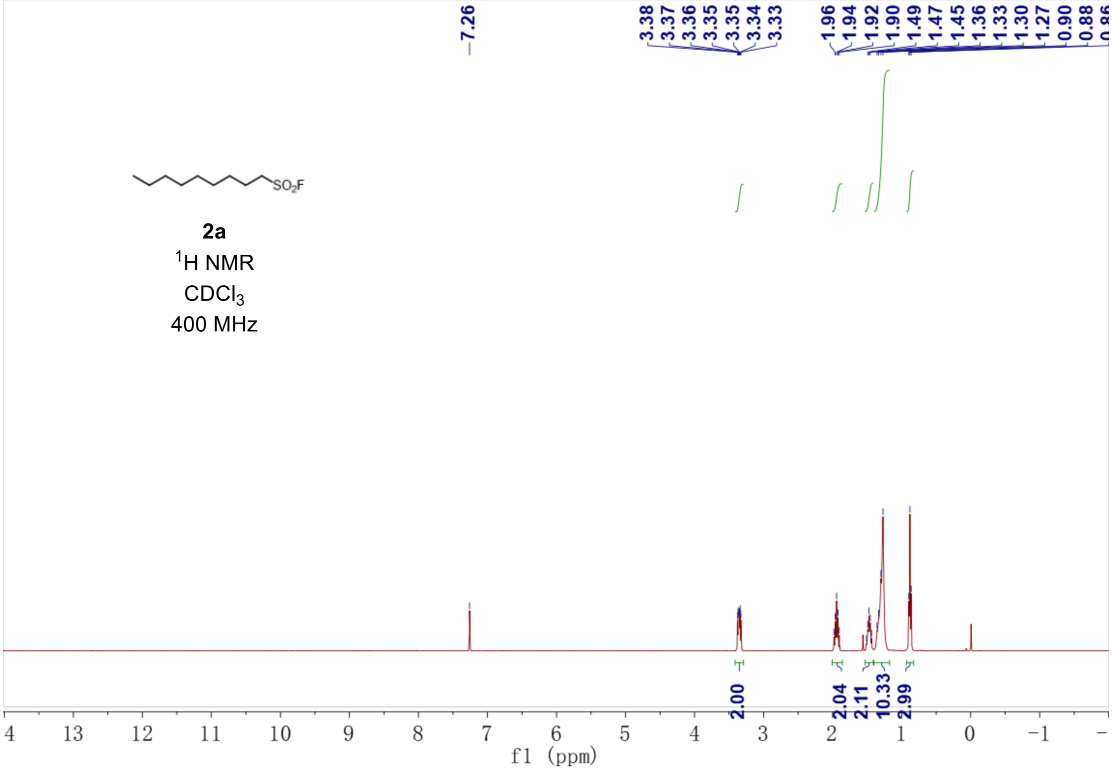
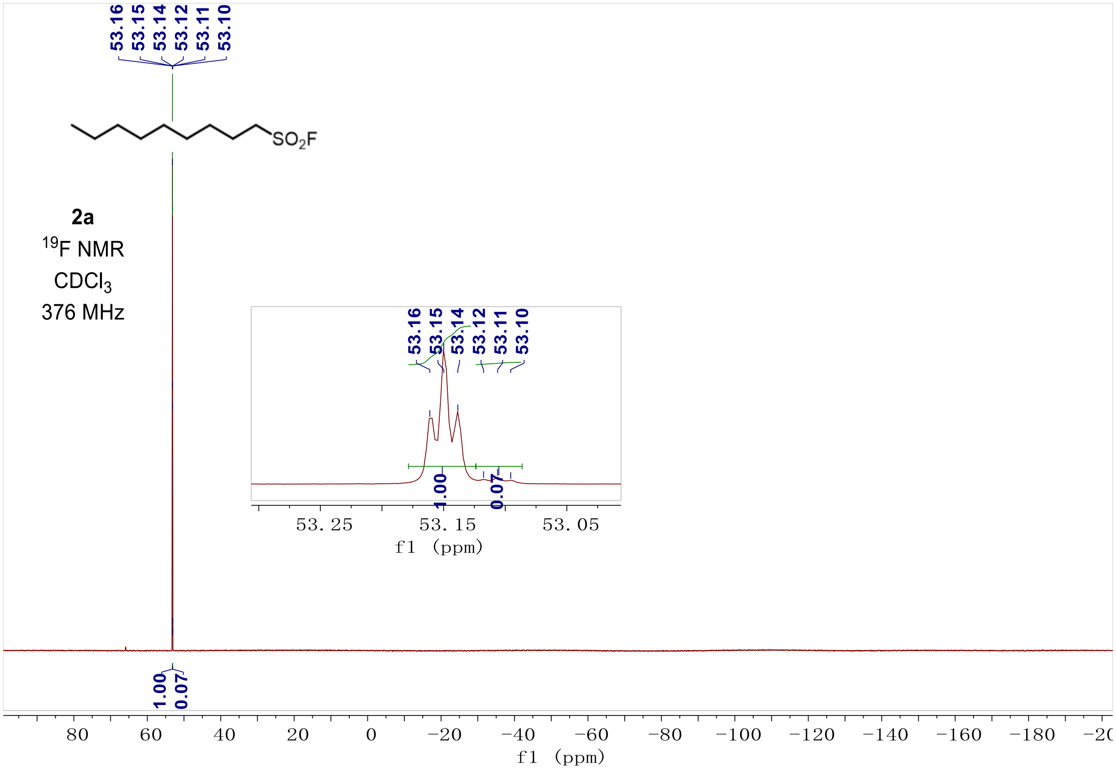
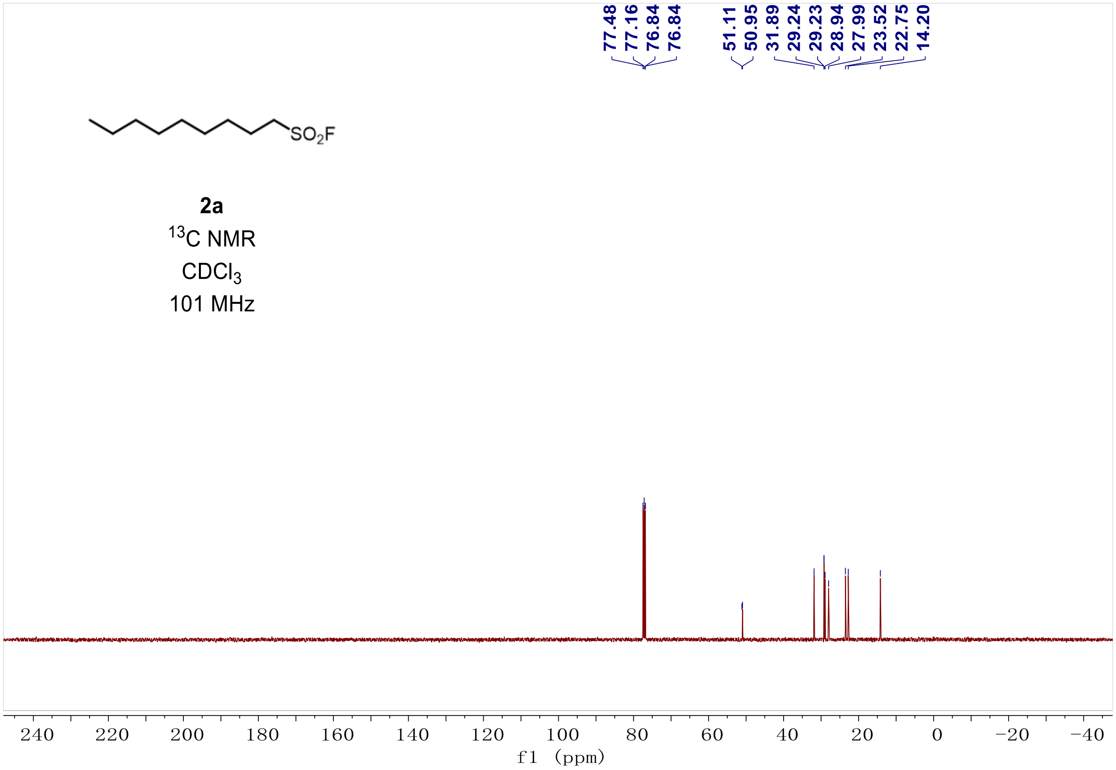
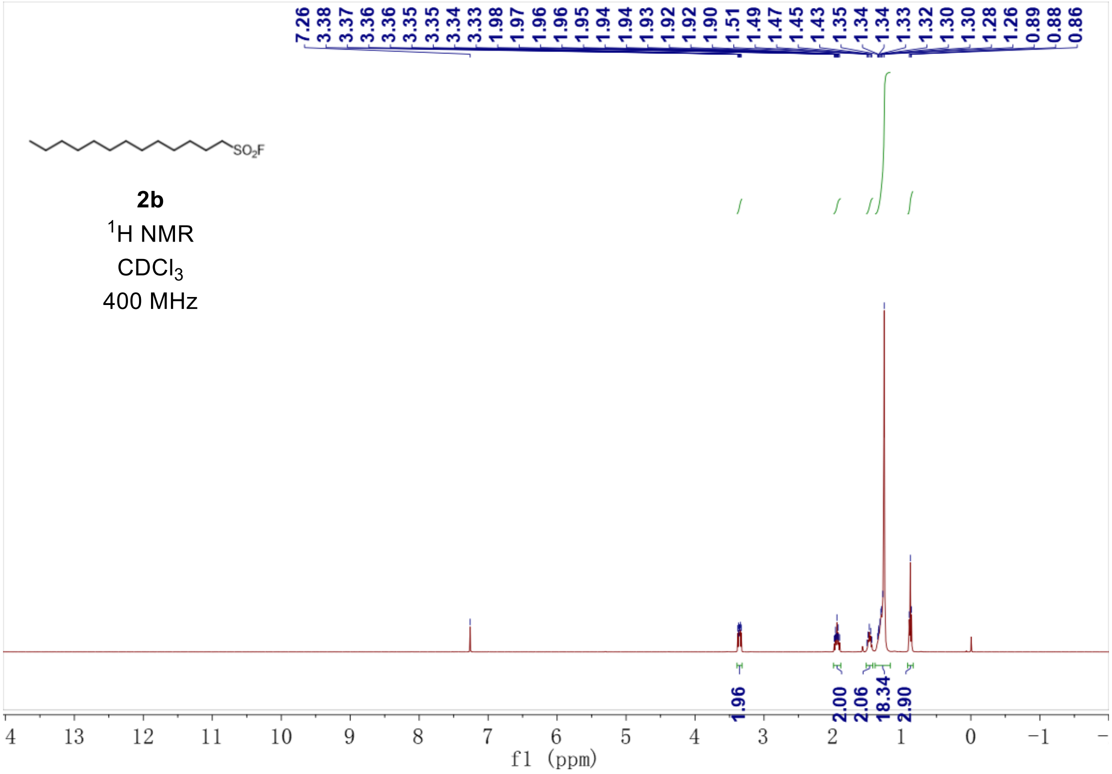
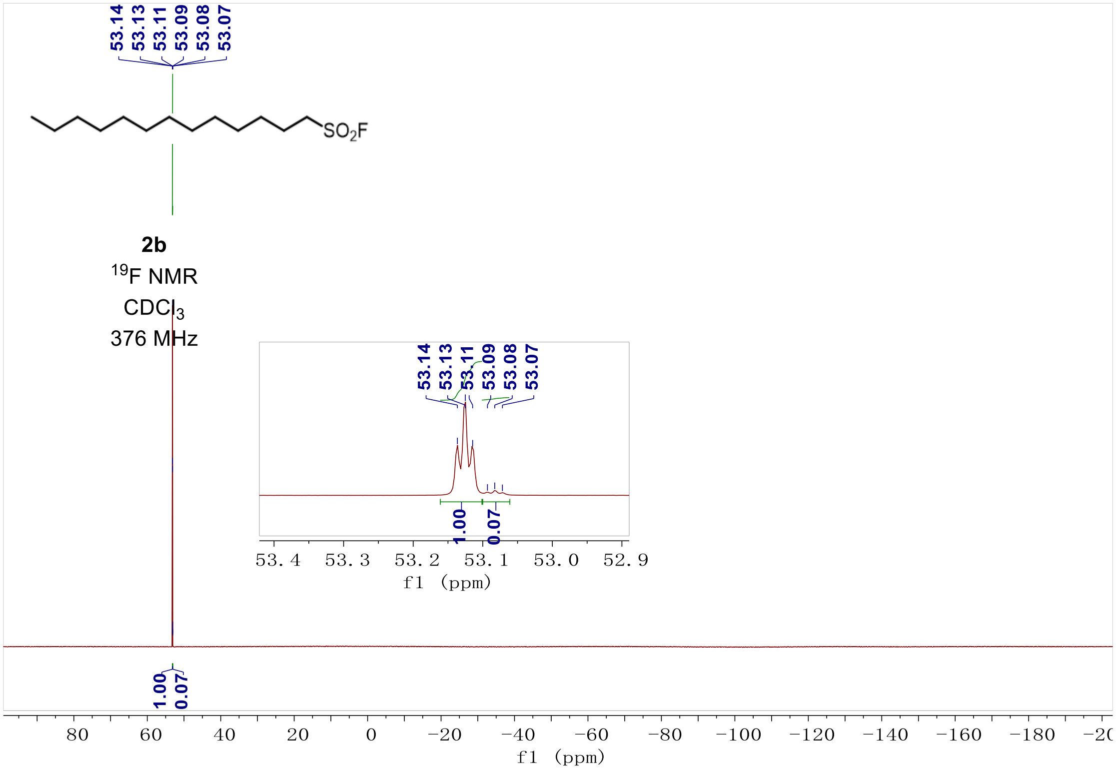
X. Copies of ^{1}H, ^{19}F, and ^{13}C NMR spectra

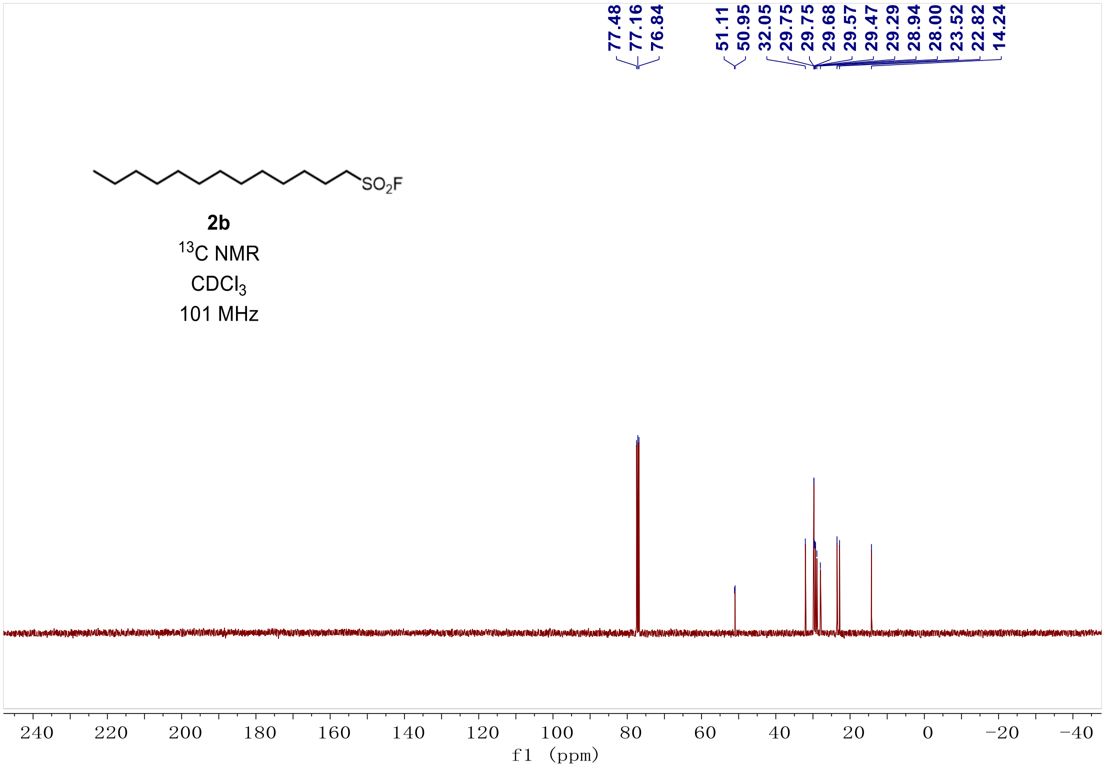


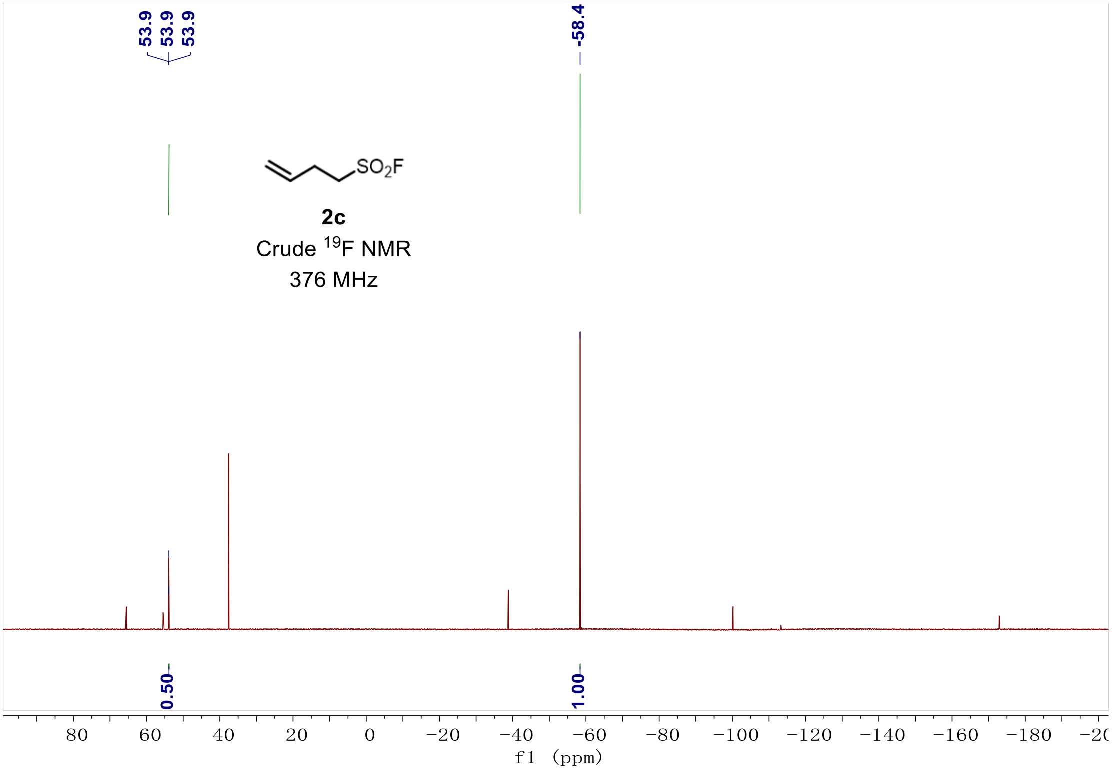



77.48
77.16
76.84
76.84
51.11
50.95
31.89
29.24
29.23
28.94
27.99
23.52
22.75
14.20
SO2F
2a
13C NMR
CDCl3
101 MHz
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
−40
f1 (ppm)


7.26
3.38
3.37
3.36
3.36
3.35
3.35
3.34
3.33
1.98
1.97
1.96
1.96
1.95
1.94
1.94
1.93
1.92
1.92
1.90
1.51
1.49
1.47
1.45
1.43
1.35
1.34
1.34
1.33
1.32
1.30
1.30
1.28
1.26
0.89
0.88
0.86
SO2F
2b
1H NMR
CDCl3
400 MHz
1.96
2.00
2.06
18.34
2.90
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)


53.14
53.13
53.11
53.09
53.08
53.07
SO2F
2b
19F NMR
CDCl3
376 MHz
53.14
53.13
53.11
53.09
53.08
53.07
1.00
0.07
53.4 53.3 53.2 53.1 53.0 52.9
f1 (ppm)
1.00
0.07
80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −20
f1 (ppm)

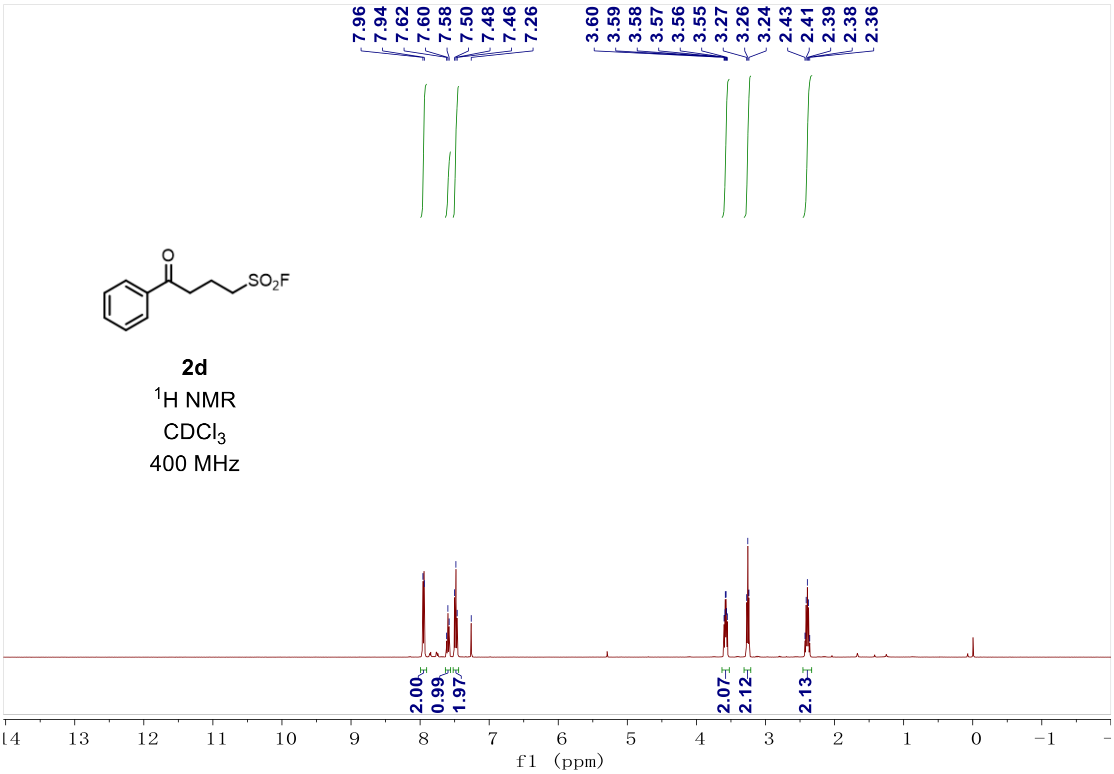

77.48
77.16
76.84
51.11
50.95
32.05
29.75
29.75
29.68
29.57
29.47
29.29
28.94
28.00
23.52
22.82
14.24
SO2F
2b
13C NMR
CDCl3
101 MHz
240 220 200 180 160 140 120 100 80 60 40 20 0 −20 −40
f1 (ppm)



2c

Crude ^{19}F NMR

376 MHz

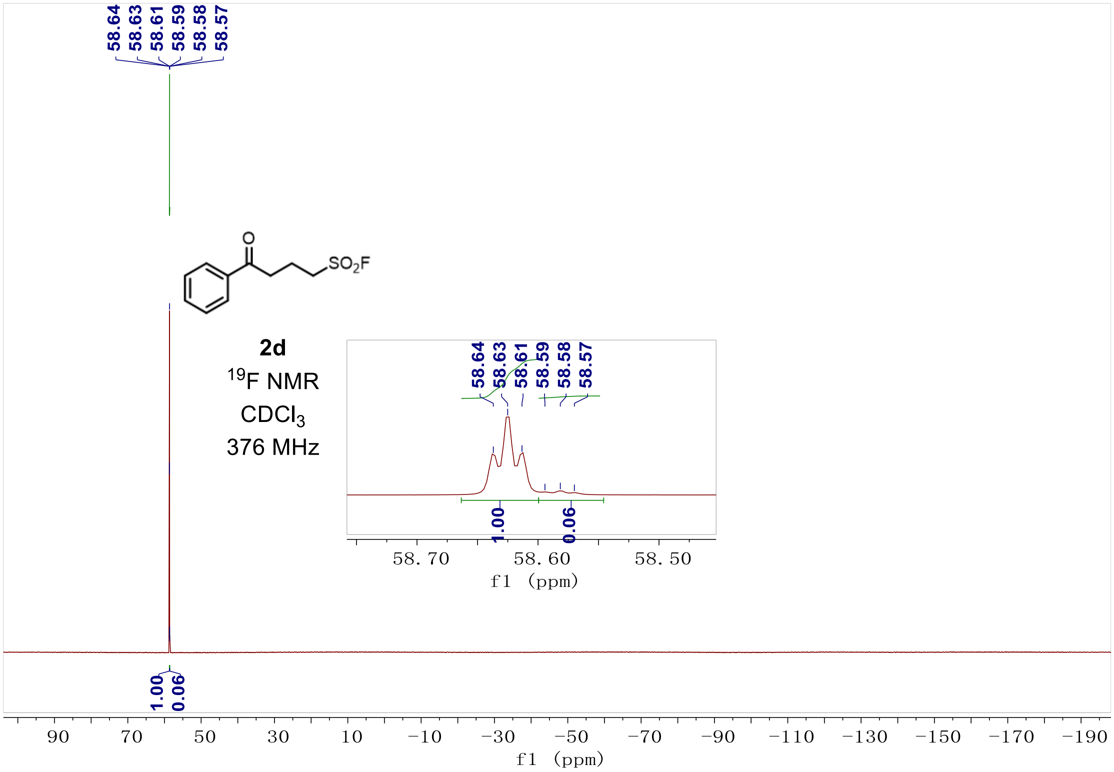


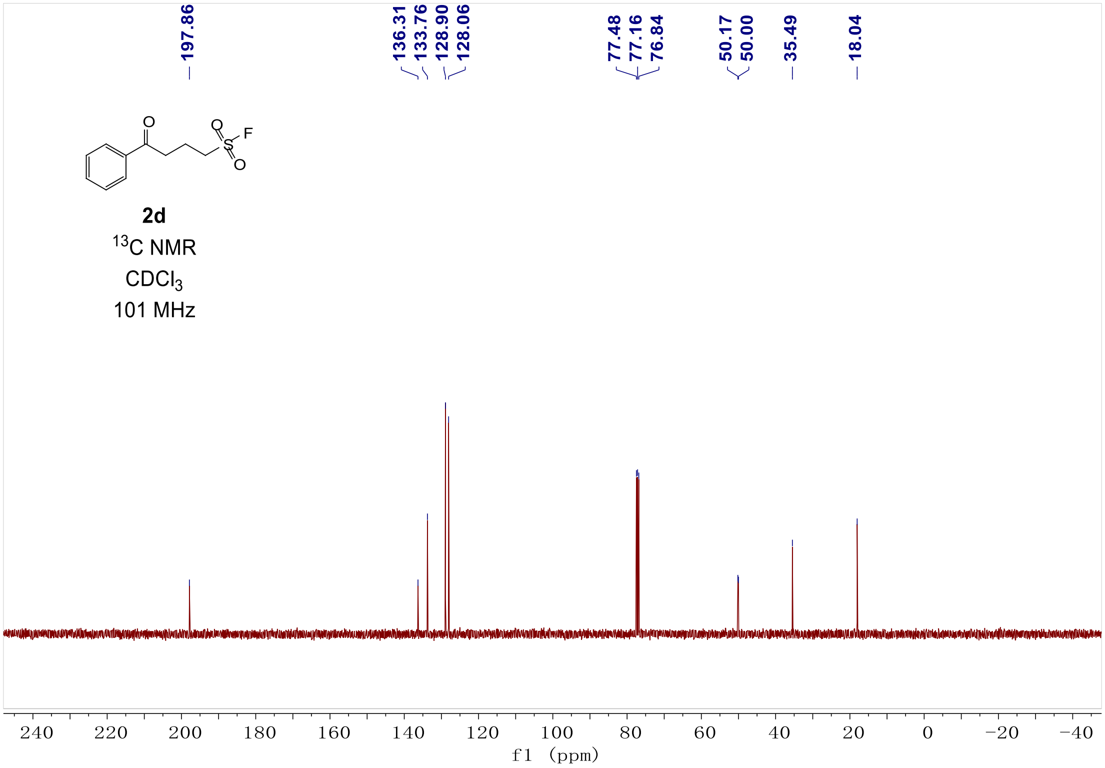
2d

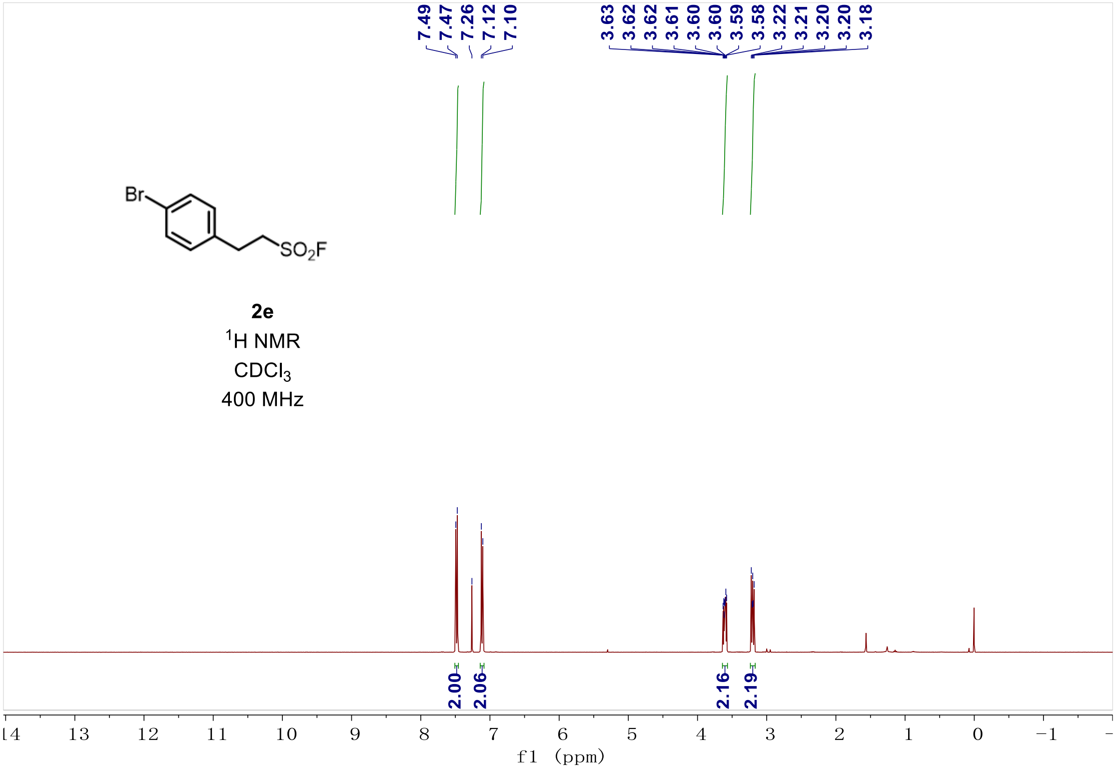
^1H NMR

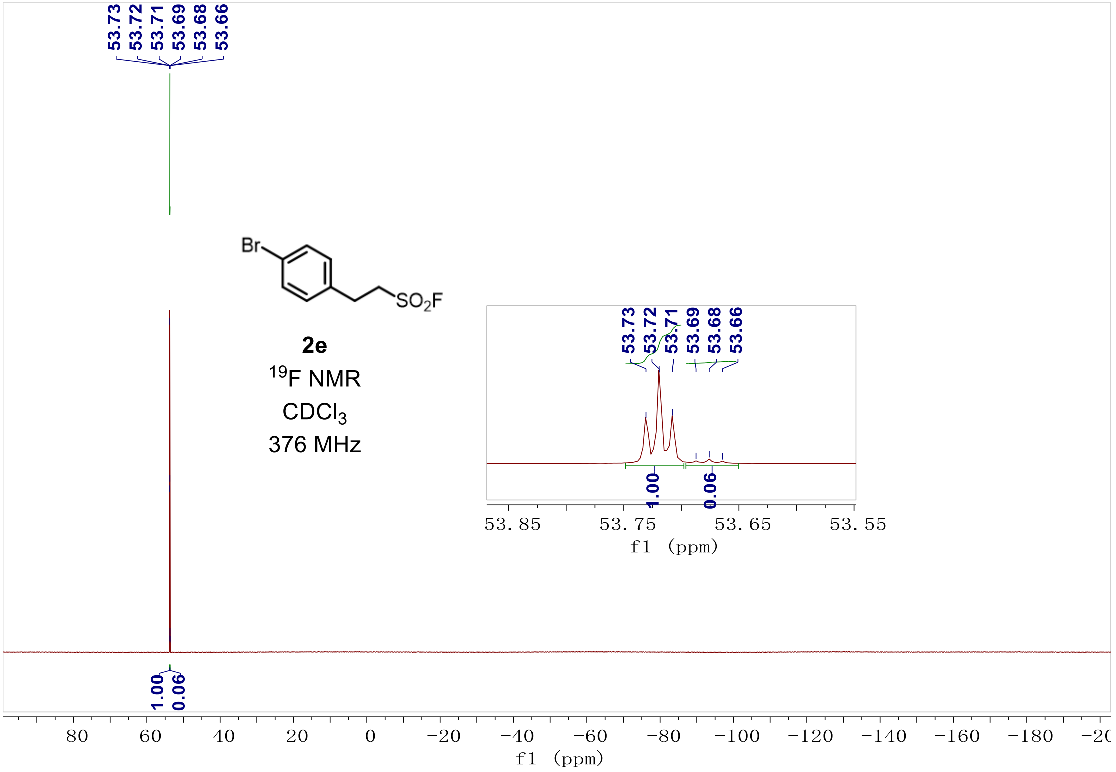
$CDCl_3$

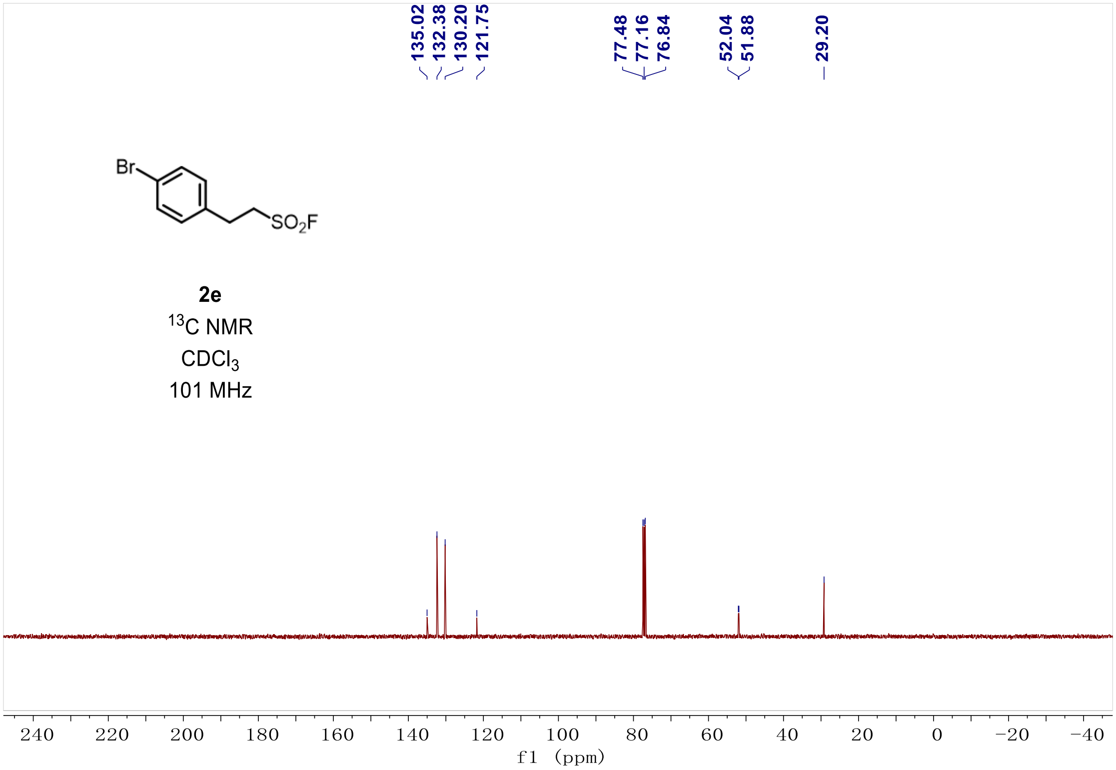
400 MHz

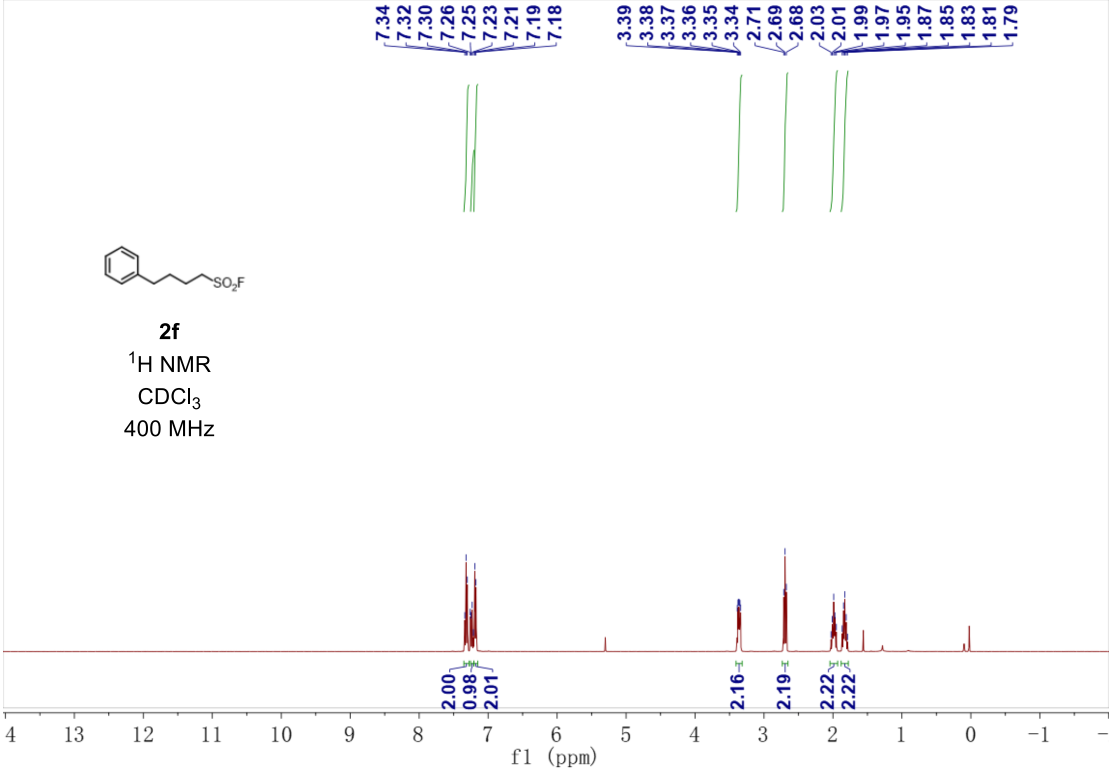

58.64
58.63
58.61
58.59
58.58
58.57
O
SO$_2$F
2d
^{19}F NMR
CDCl$_3$
376 MHz
58.64
58.63
58.61
58.59
58.58
58.57
1.00
0.06
58.70
58.60
58.50
f1 (ppm)
1.00
0.06
90
70
50
30
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
−190
f1 (ppm)

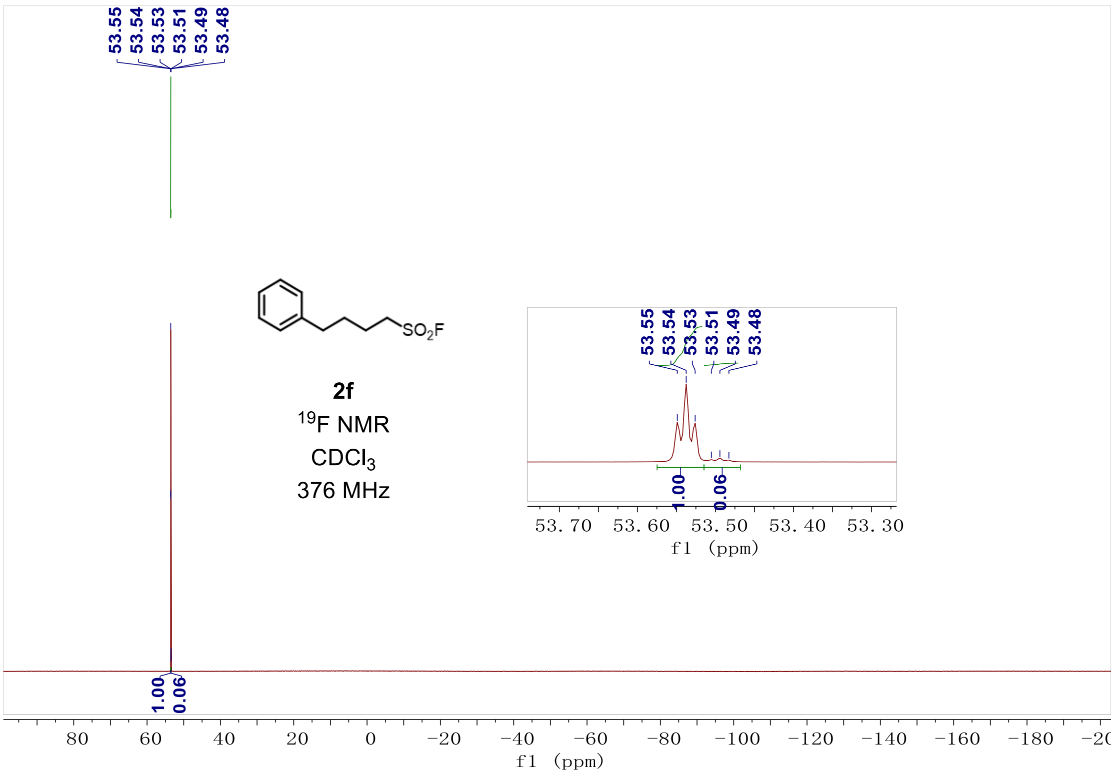

197.86
136.31
133.76
128.90
128.06
77.48
77.16
76.84
50.17
50.00
35.49
18.04
O
O
S
F
O
2d
^{13}C NMR
CDCl$_3$
101 MHz
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
−40
f1 (ppm)

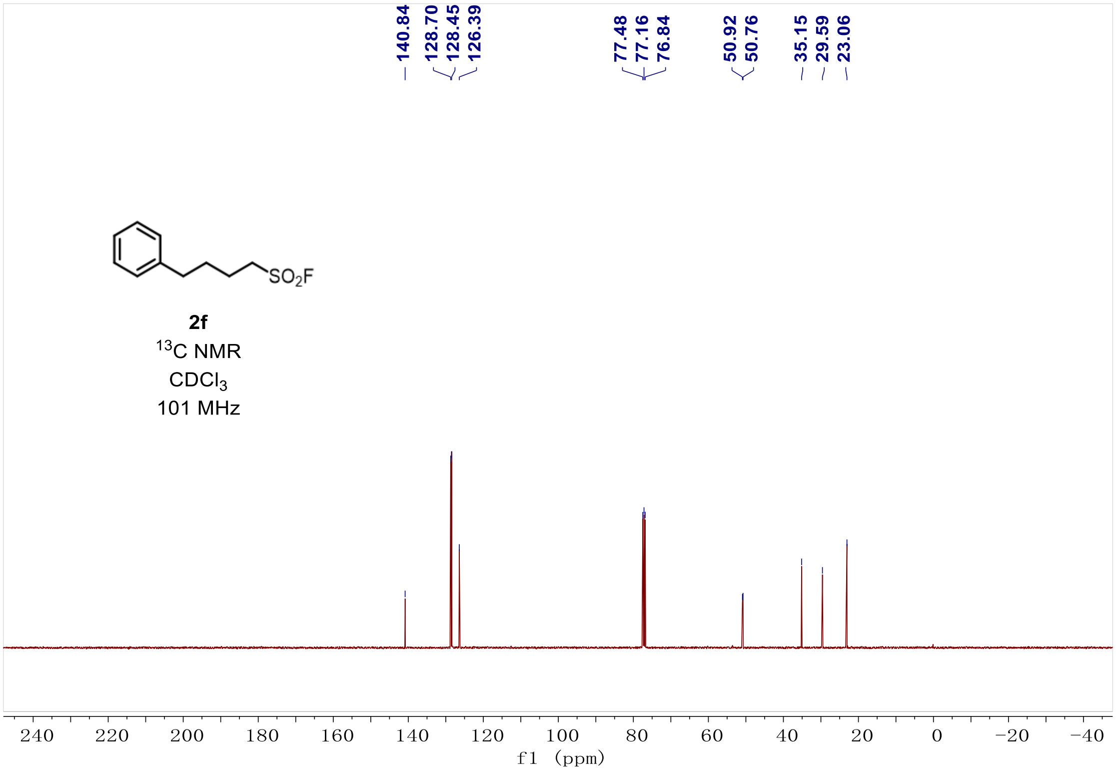

7.49
7.47
7.26
7.12
7.10
3.63
3.62
3.62
3.61
3.60
3.60
3.59
3.58
3.22
3.21
3.20
3.20
3.18
Br
SO$_2$F
2e
^{1}H NMR
CDCl$_3$
400 MHz
2.00
2.06
2.16
2.19
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)

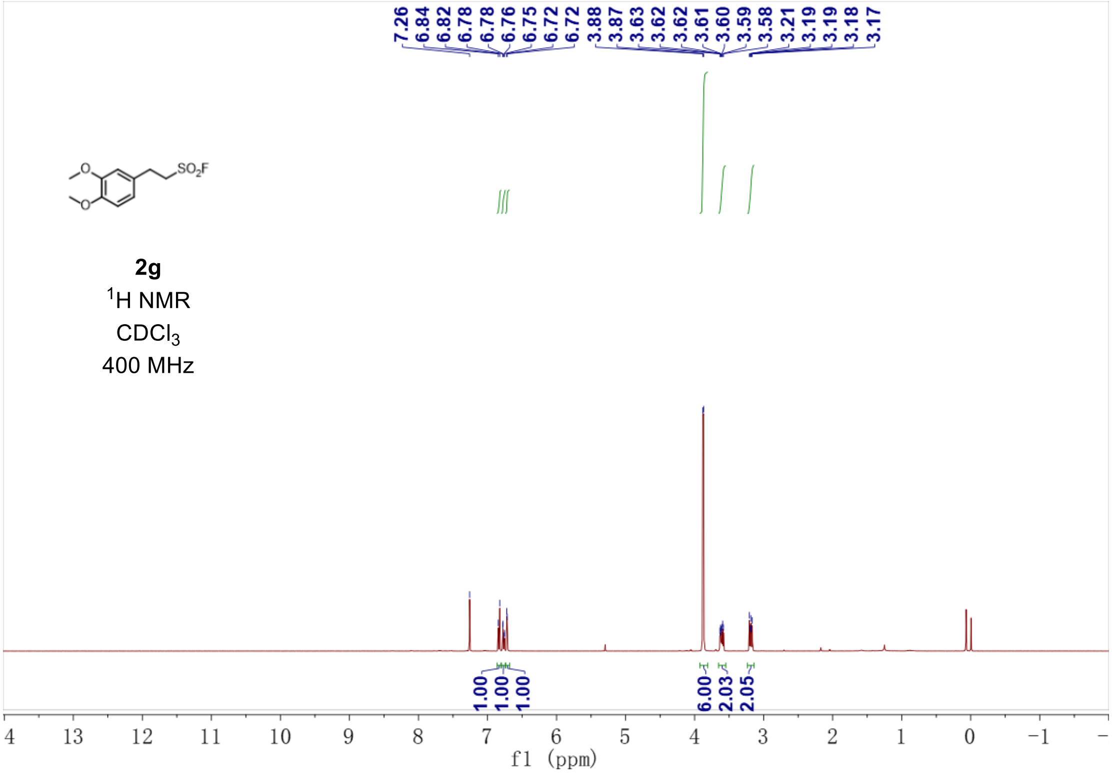

53.73
53.72
53.71
53.69
53.68
53.66
Br
SO$_2$F
2e
^{19}F NMR
CDCl$_3$
376 MHz
1.00
0.06
53.85
53.75
53.65
53.55
f1 (ppm)
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
f1 (ppm)

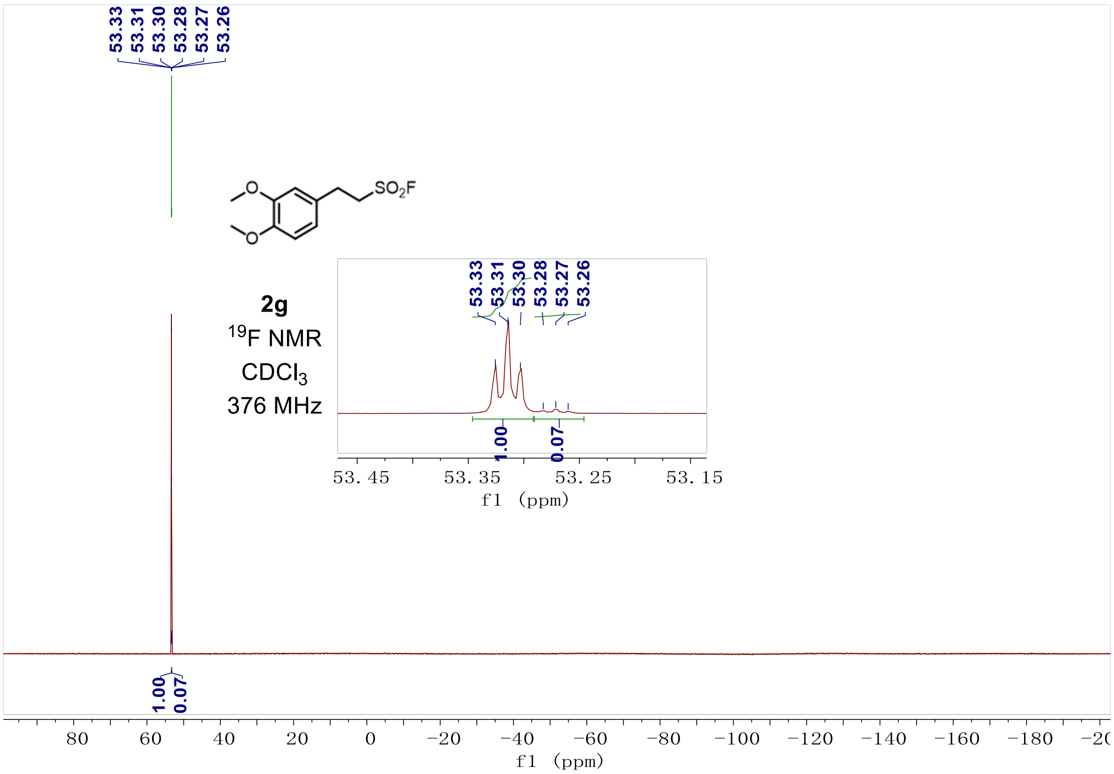

135.02
132.38
130.20
121.75
77.48
77.16
76.84
52.04
51.88
29.20
Br
SO2F
2e
13C NMR
CDCl3
101 MHz
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
−40
f1 (ppm)

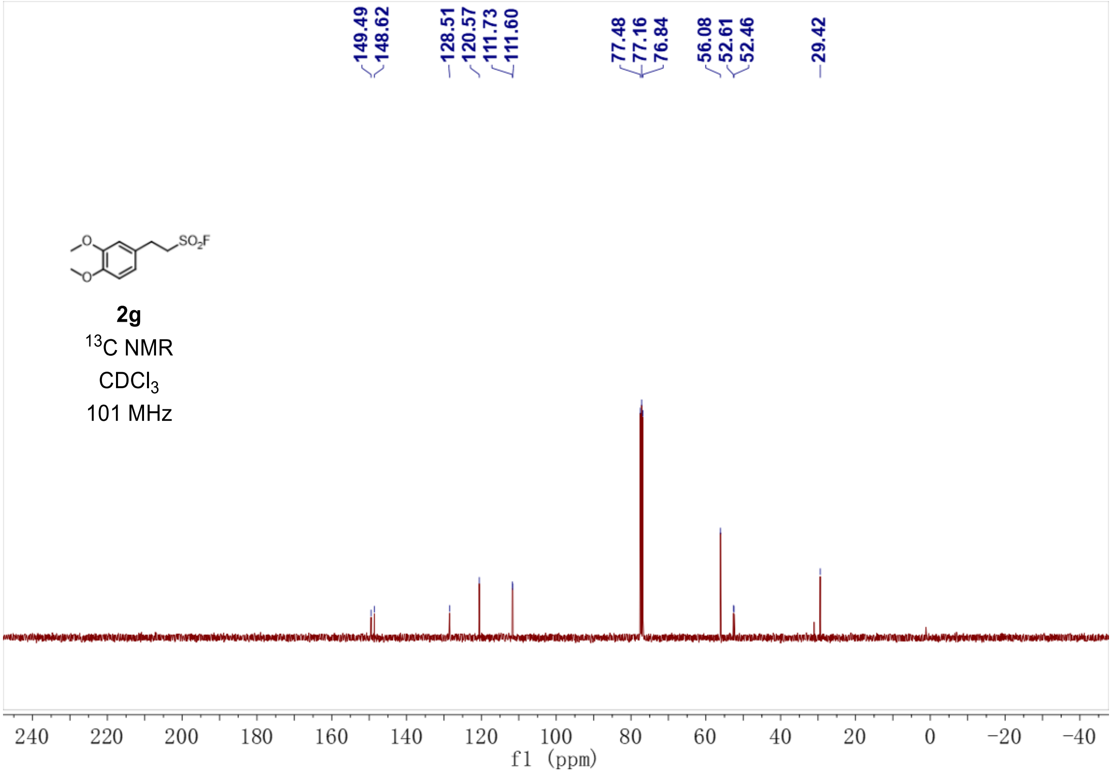

7.34
7.32
7.30
7.26
7.25
7.23
7.21
7.19
7.18
3.39
3.38
3.37
3.36
3.35
3.34
2.71
2.69
2.68
2.03
2.01
1.99
1.97
1.95
1.87
1.85
1.83
1.81
1.79
SO2F
2f
1H NMR
CDCl3
400 MHz
2.00
0.98
2.01
2.16
2.19
2.22
2.22
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)

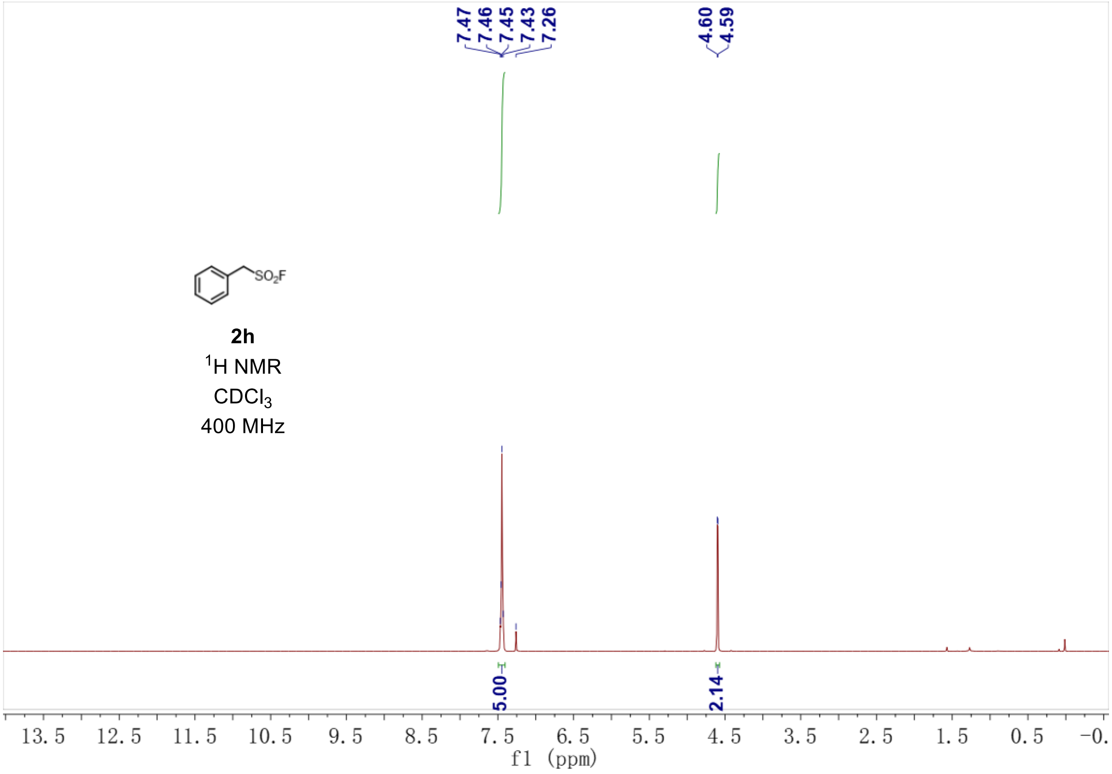

53.55
53.54
53.53
53.51
53.49
53.48
SO$_2$F
2f
^{19}F NMR
CDCl$_3$
376 MHz
1.00
0.06
53.70
53.60
53.50
53.40
53.30
f1 (ppm)
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−20

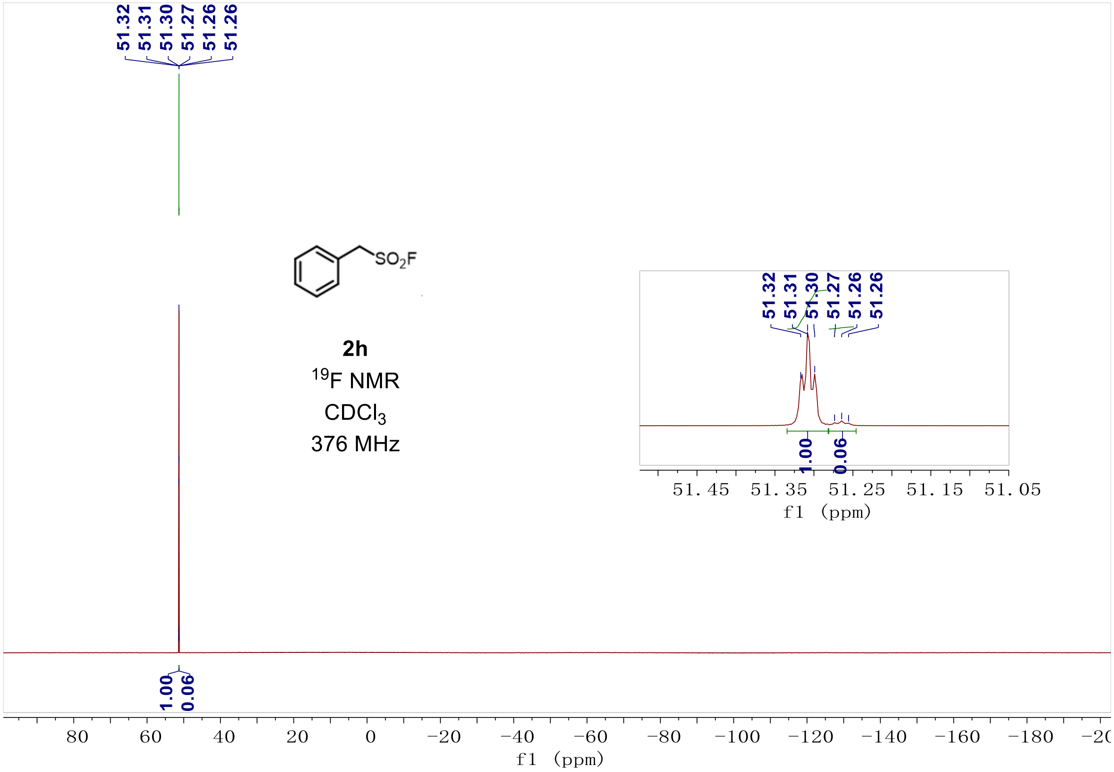

140.84
128.70
128.45
126.39
77.48
77.16
76.84
50.92
50.76
35.15
29.59
23.06
SO$_2$F
2f
^{13}C NMR
CDCl$_3$
101 MHz
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
−40
f1 (ppm)

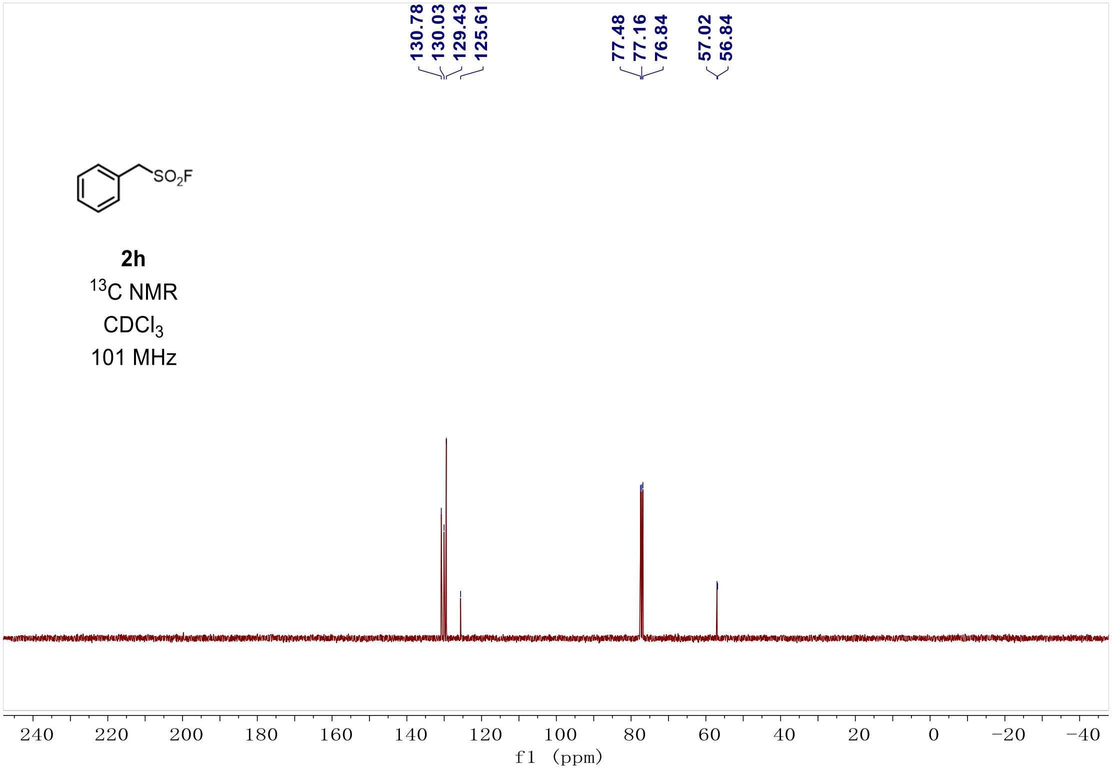

7.26
6.84
6.82
6.78
6.78
6.76
6.75
6.72
6.72
3.88
3.87
3.63
3.62
3.61
3.60
3.59
3.58
3.21
3.19
3.19
3.18
3.17
SO2F
2g
1H NMR
CDCl3
400 MHz
1.00
1.00
1.00
6.00
2.03
2.05
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)

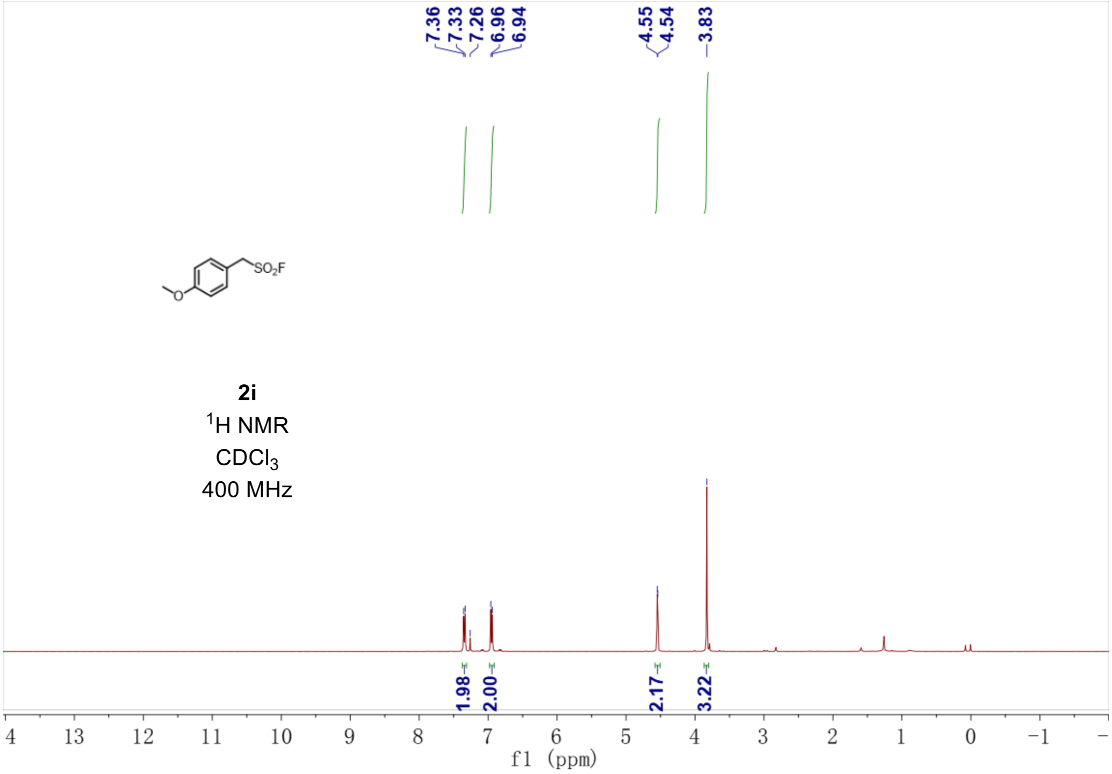

53.33
53.31
53.30
53.28
53.27
53.26
SO2F
2g
19F NMR
CDCl3
376 MHz
53.33
53.31
53.30
53.28
53.27
53.26
1.00
0.07
53.45
53.35
53.25
53.15
f1 (ppm)
1.00
0.07
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
f1 (ppm)


149.49
148.62
128.51
120.57
111.73
111.60
77.48
77.16
76.84
56.08
52.61
52.46
29.42
SO2F
O
O
2g
13C NMR
CDCl3
101 MHz
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
−40
f1 (ppm)

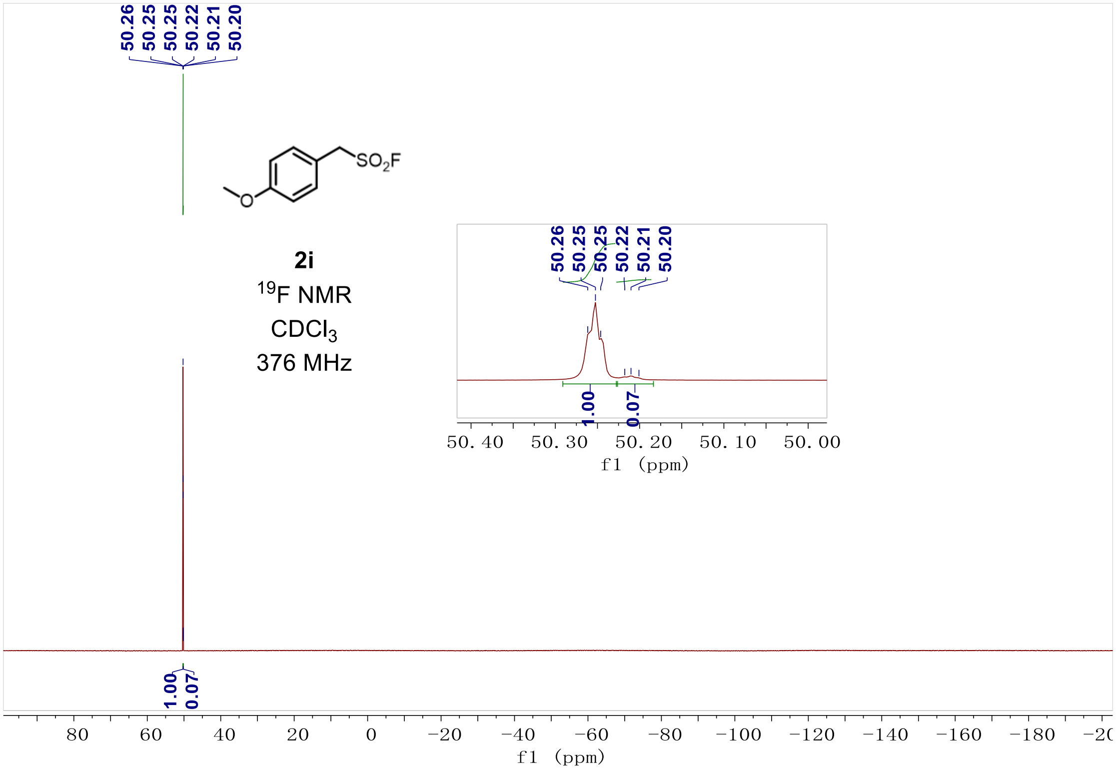

7.47
7.46
7.45
7.43
7.26
4.60
4.59
SO2F
2h
1H NMR
CDCl3
400 MHz
5.00
2.14
13.5
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.
f1 (ppm)


51.32
51.31
51.30
51.27
51.26
51.26
SO2F
2h
19F NMR
CDCl3
376 MHz
51.32
51.31
51.30
51.27
51.26
51.26
1.00
0.06
51.45
51.35
51.25
51.15
51.05
f1 (ppm)
1.00
0.06
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−2(
f1 (ppm)

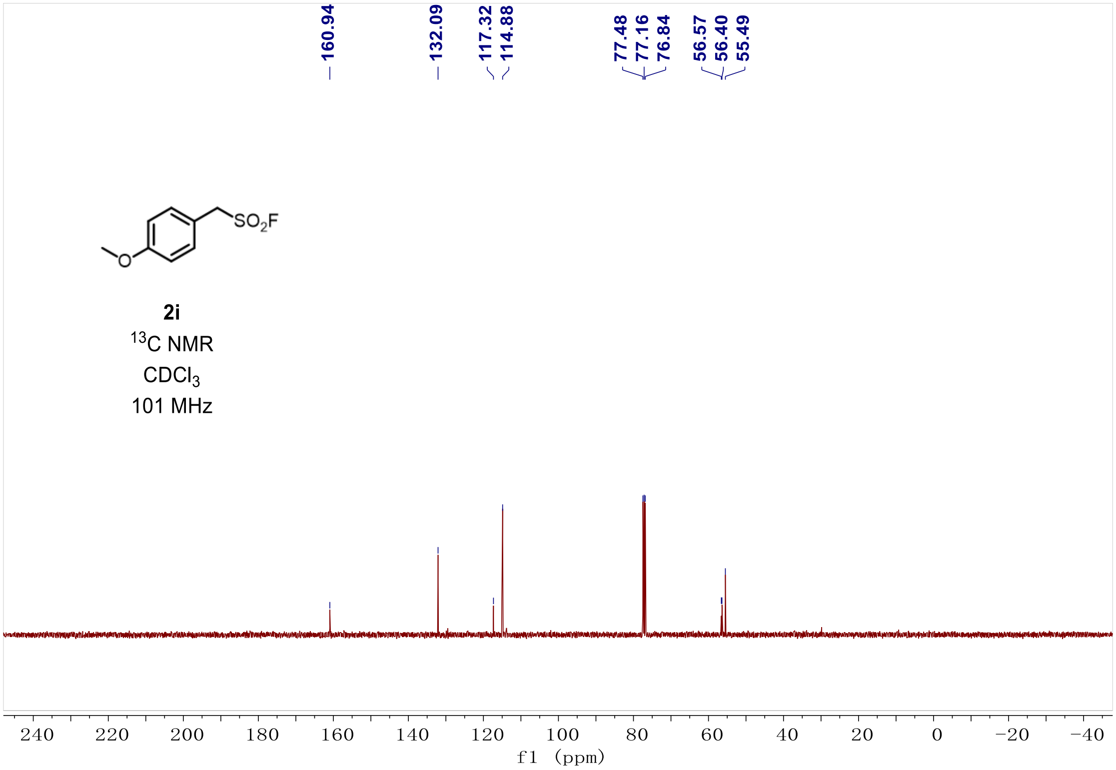

130.78
130.03
129.43
125.61
77.48
77.16
76.84
57.02
56.84
SO2F
2h
13C NMR
CDCl3
101 MHz
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
−40
f1 (ppm)

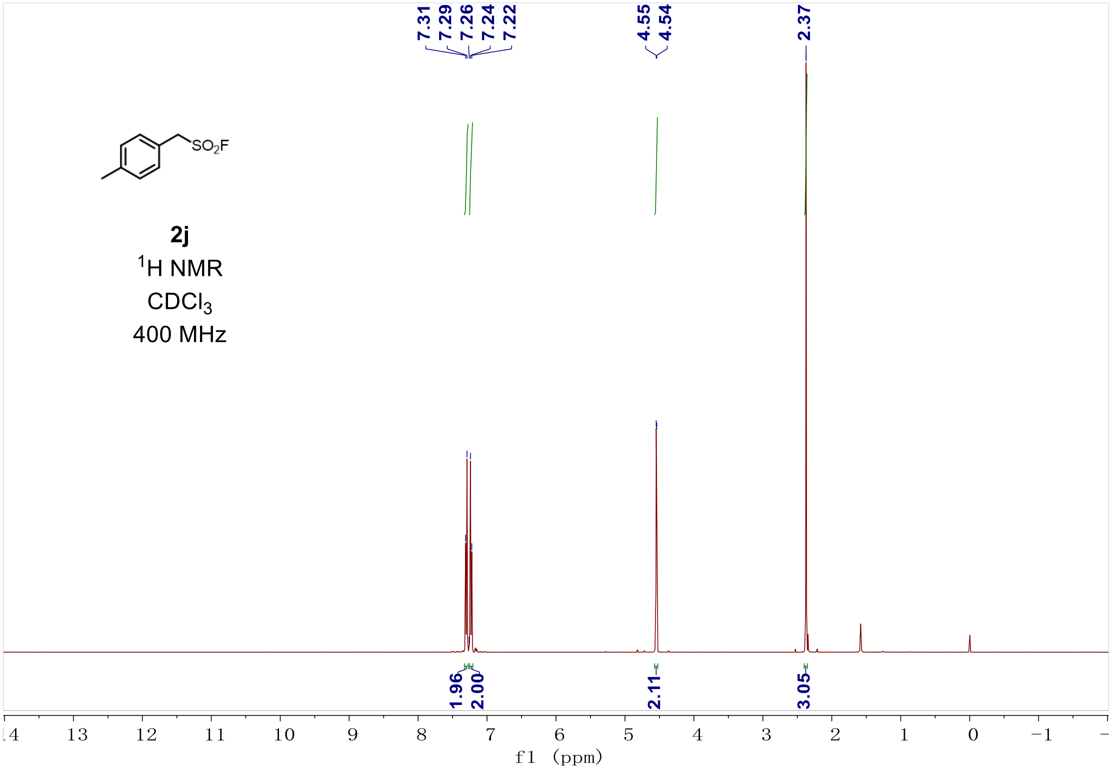


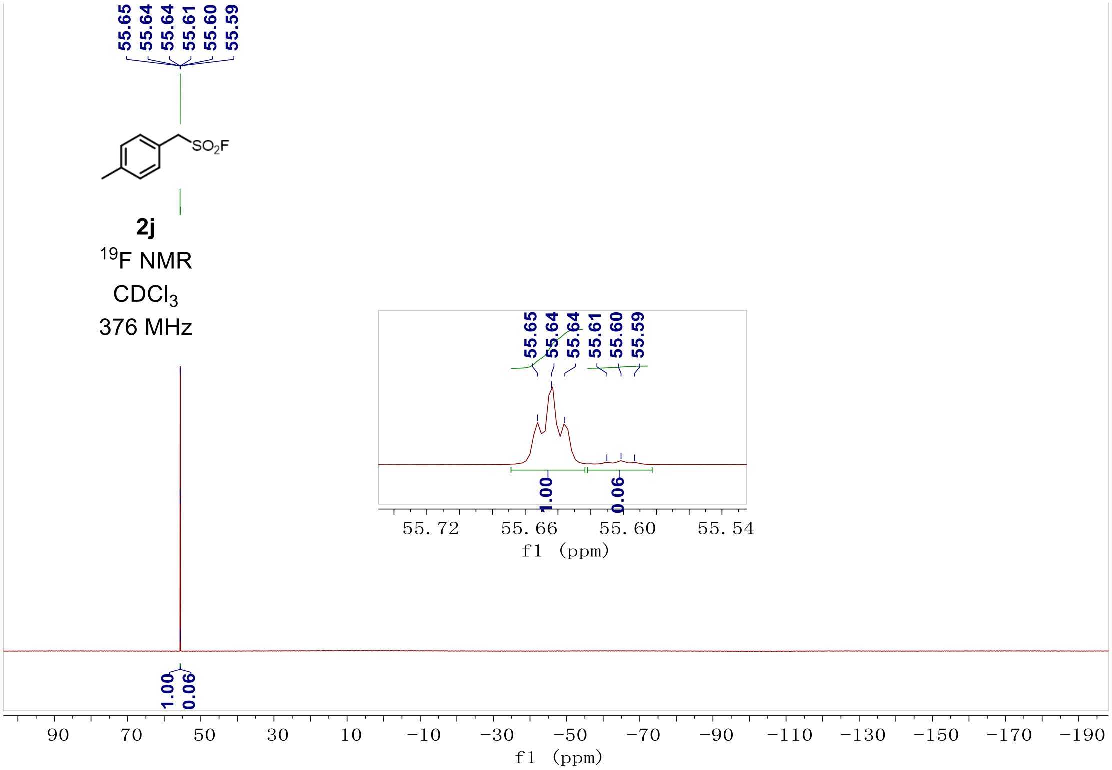
7.36
7.33
7.26
6.96
6.94
4.55
4.54
3.83
SO$_2$F
O
2i
^{1}H NMR
CDCl$_3$
400 MHz
1.98
2.00
2.17
3.22
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)

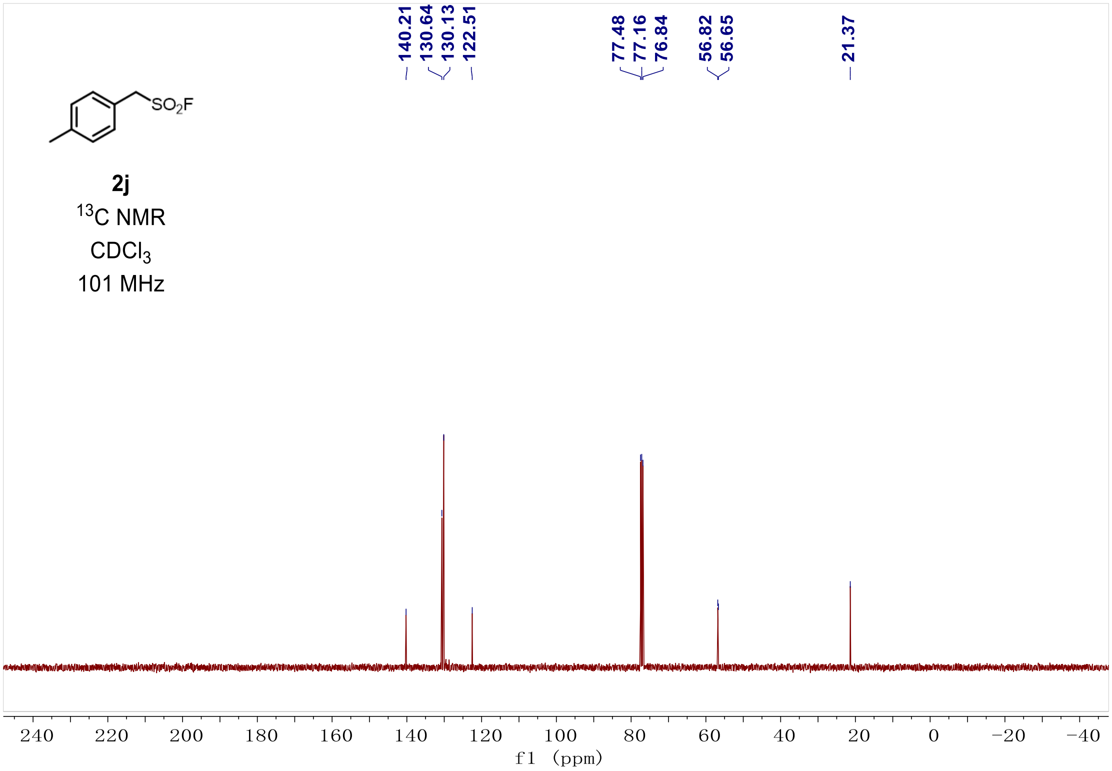


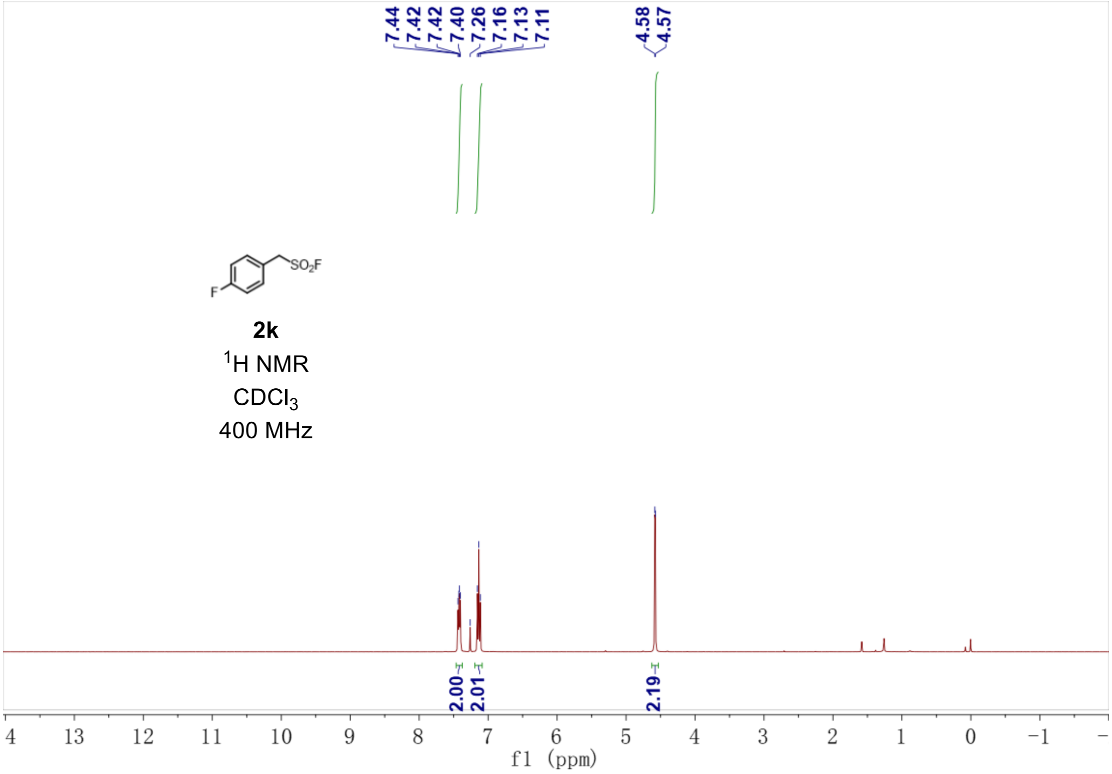
50.26
50.25
50.25
50.22
50.21
50.20
SO$_2$F
O
2i
^{19}F NMR
CDCl$_3$
376 MHz
50.26
50.25
50.25
50.22
50.21
50.20
1.00
0.07
50.40
50.30
50.20
50.10
50.00
f1 (ppm)
1.00
0.07
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
f1 (ppm)

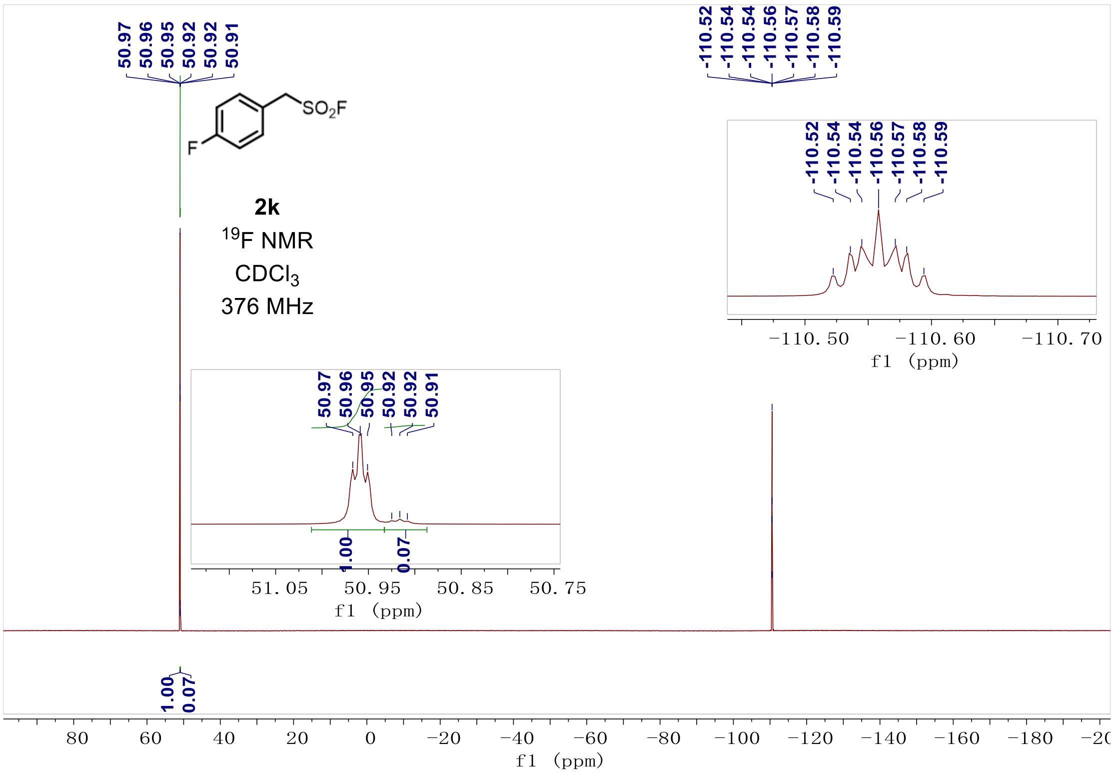

160.94
132.09
117.32
114.88
77.48
77.16
76.84
56.57
56.40
55.49
SO2F
O
2i
13C NMR
CDCl3
101 MHz
240 220 200 180 160 140 120 100 80 60 40 20 0 −20 −40
f1 (ppm)

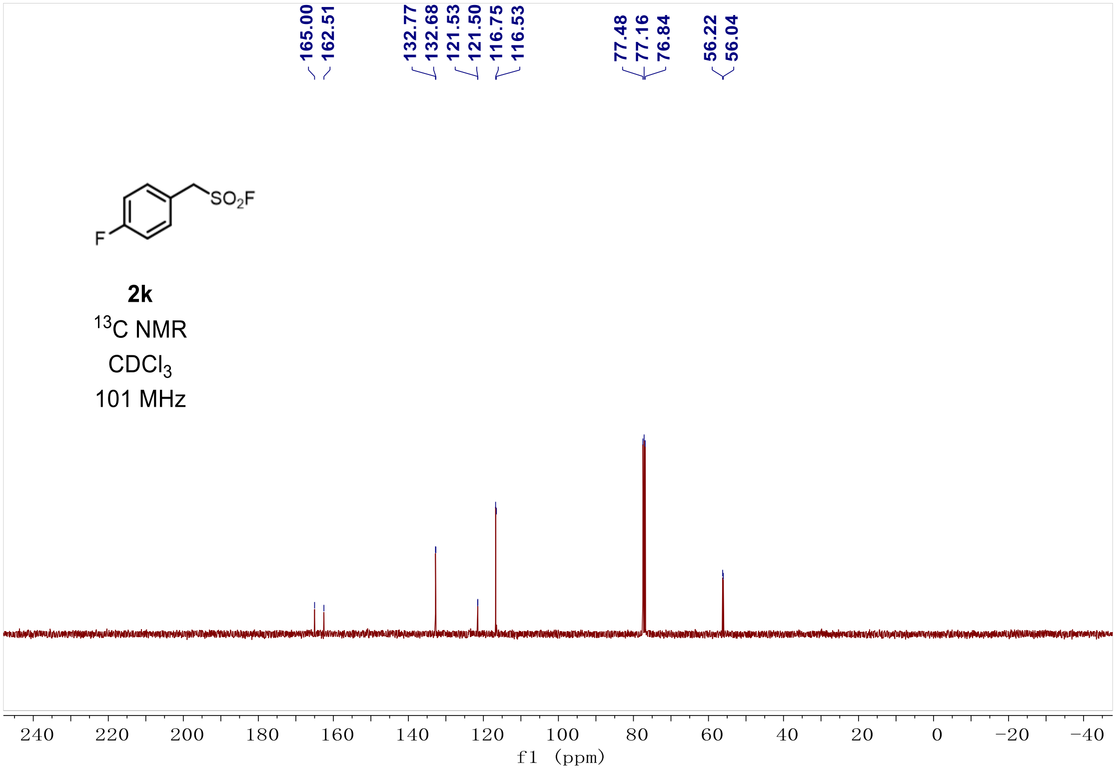

7.31
7.29
7.26
7.24
7.22
4.55
4.54
2.37
SO2F
2j
1H NMR
CDCl3
400 MHz
1.96
2.00
2.11
3.05
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)

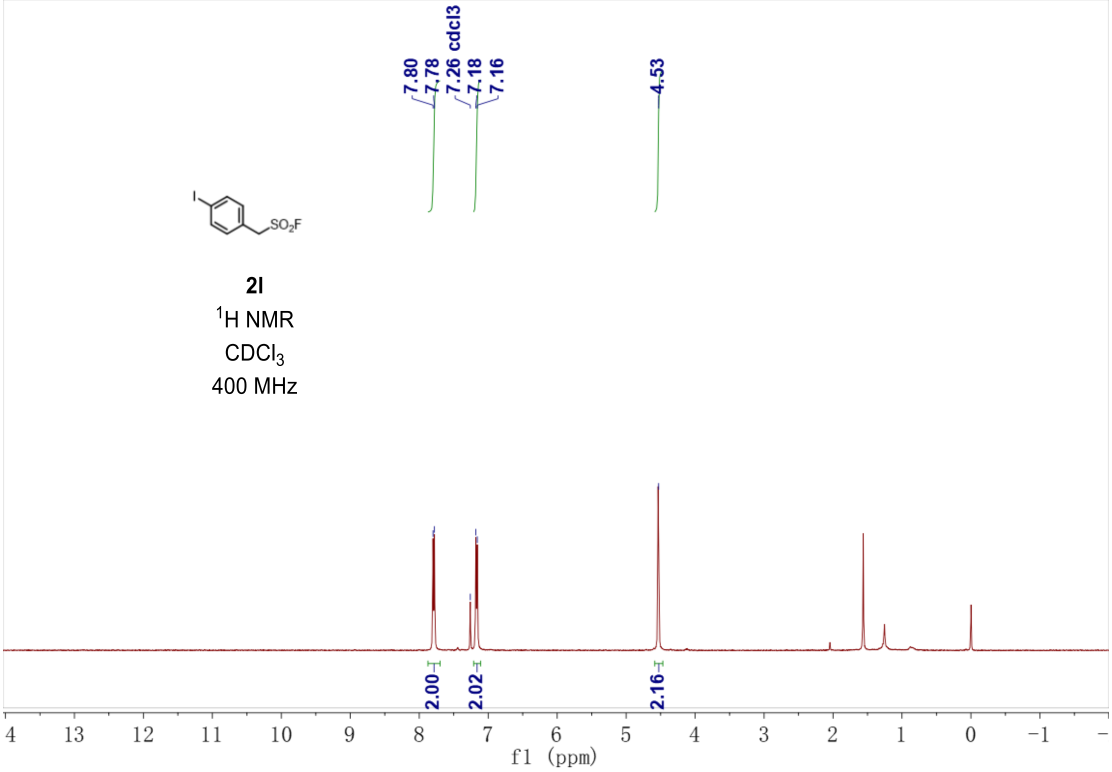

55.65
55.64
55.64
55.61
55.60
55.59
SO2F
2j
19F NMR
CDCl3
376 MHz
1.00
0.06
55.72
55.66
55.60
55.54
f1 (ppm)
90
70
50
30
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
−190
f1 (ppm)

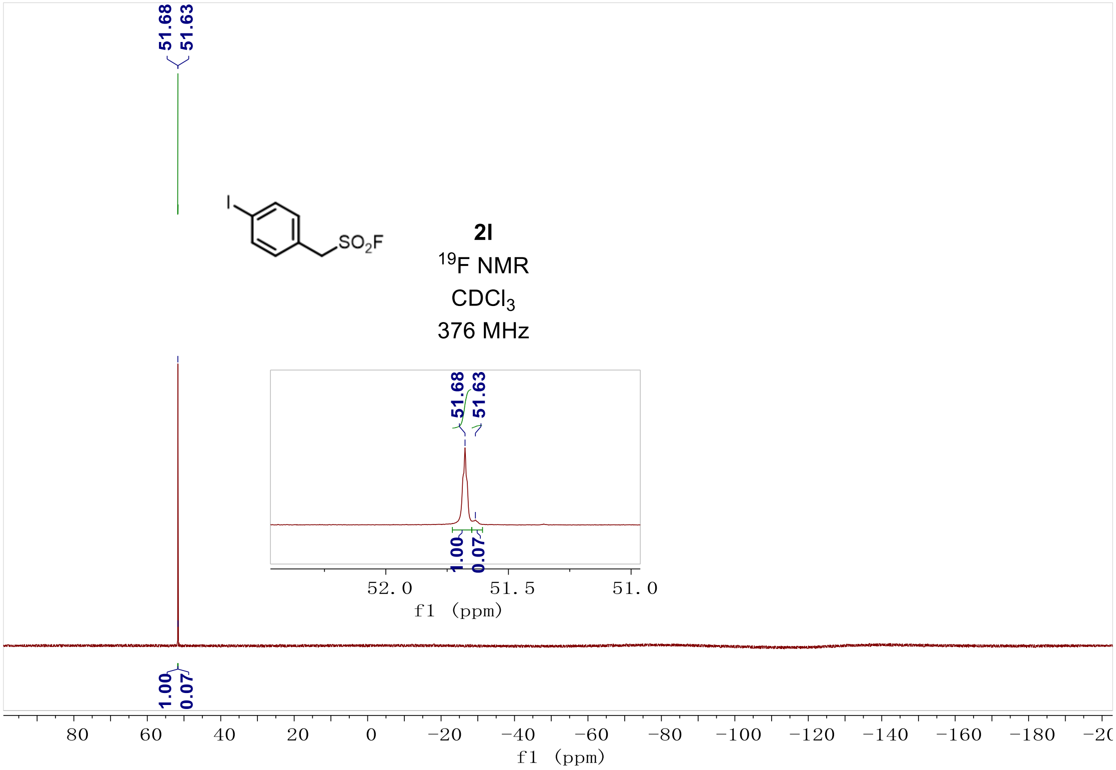

140.21
130.64
130.13
122.51
77.48
77.16
76.84
56.82
56.65
21.37
SO2F
2j
13C NMR
CDCl3
101 MHz
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
−40
f1 (ppm)

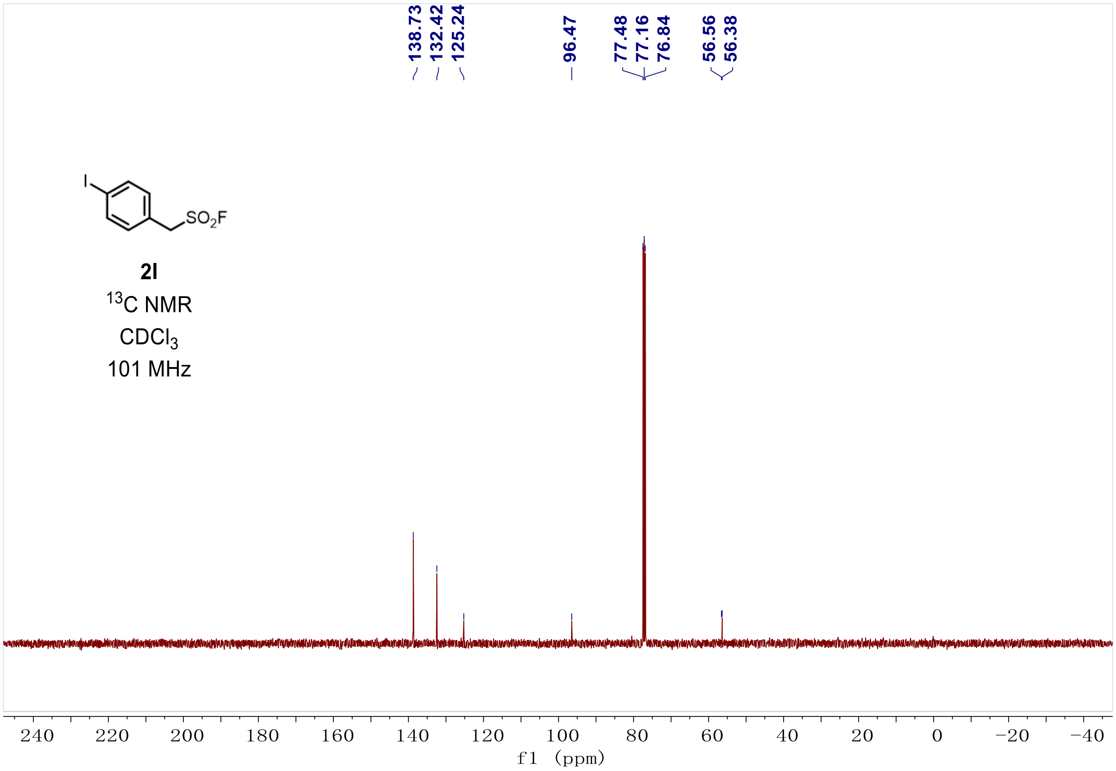

7.44
7.42
7.42
7.40
7.26
7.16
7.13
7.11
4.58
4.57
SO2F
F
2k
1H NMR
CDCl3
400 MHz
2.00
2.01
2.19
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)

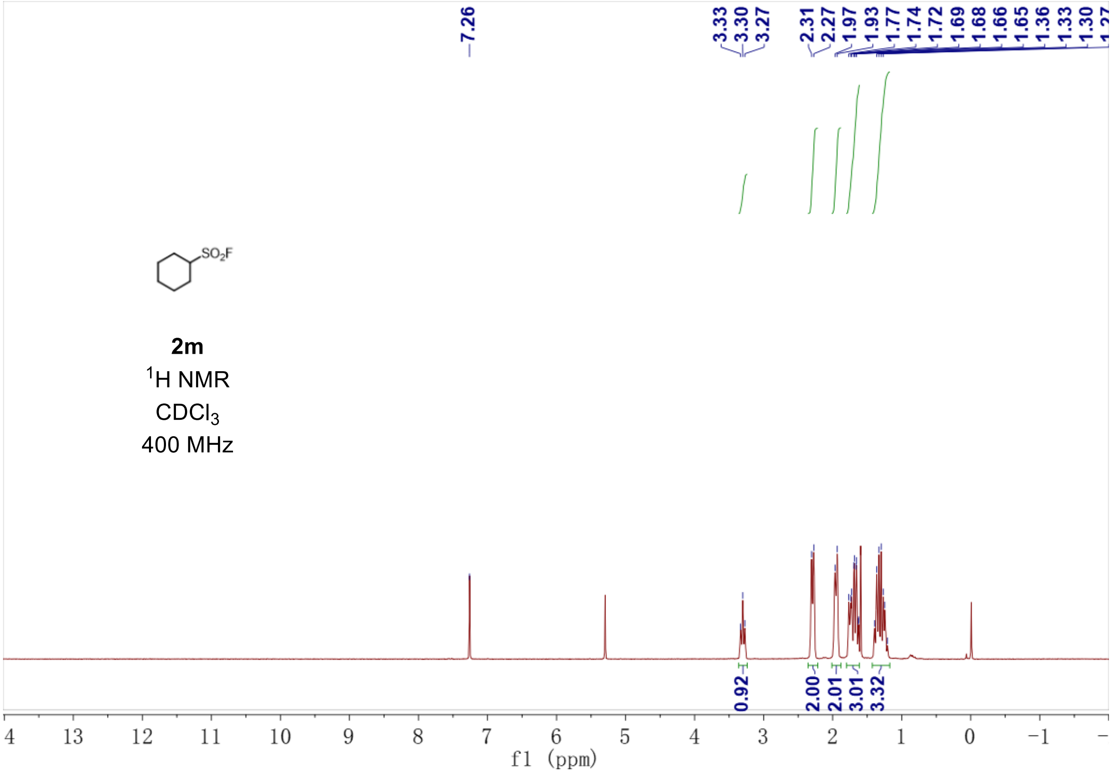

50.97
50.96
50.95
50.92
50.92
50.91
-110.52
-110.54
-110.54
-110.56
-110.57
-110.58
-110.59
SO2F
F
2k
19F NMR
CDCl3
376 MHz
−110.50
−110.60
−110.70
f1 (ppm)
1.00
0.07
51.05
50.95
50.85
50.75
f1 (ppm)
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
f1 (ppm)


165.00
162.51
132.77
132.68
121.53
121.50
116.75
116.53
77.48
77.16
76.84
56.22
56.04
F
SO2F
2k
13C NMR
CDCl3
101 MHz
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
−40
f1 (ppm)

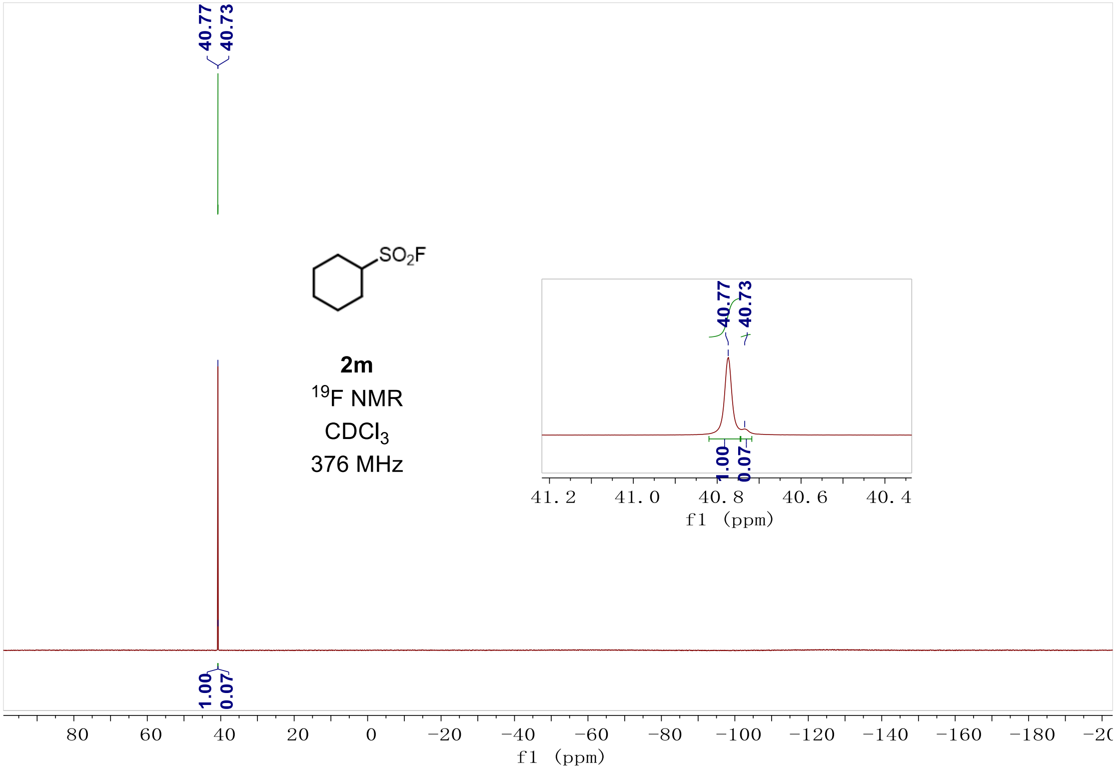

7.80
7.78
7.26 cdcl3
7.18
7.16
4.53
I
SO2F
2l
1H NMR
CDCl3
400 MHz
2.00
2.02
2.16
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)


51.68
51.63
I
SO2F
2l
19F NMR
CDCl3
376 MHz
51.68
51.63
1.00
0.07
52.0
51.5
51.0
f1 (ppm)
1.00
0.07
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
f1 (ppm)

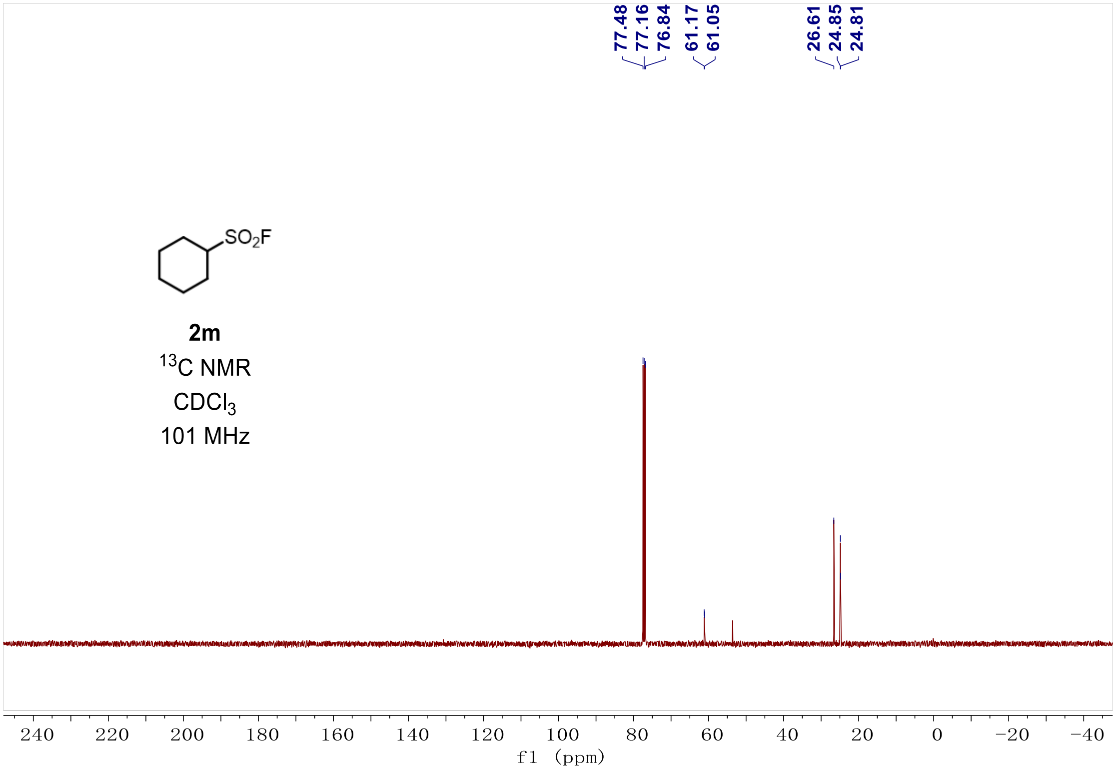

138.73
132.42
125.24
96.47
77.48
77.16
76.84
56.56
56.38
I
SO2F
2l
13C NMR
CDCl3
101 MHz
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
−40
f1 (ppm)

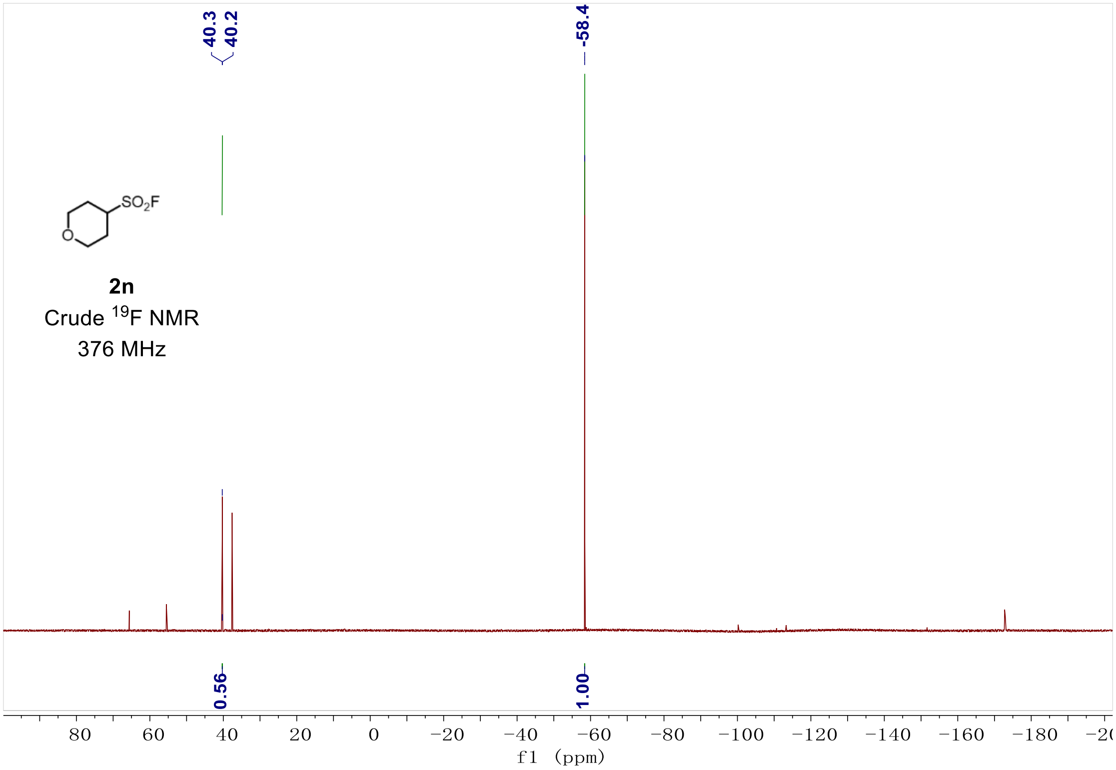


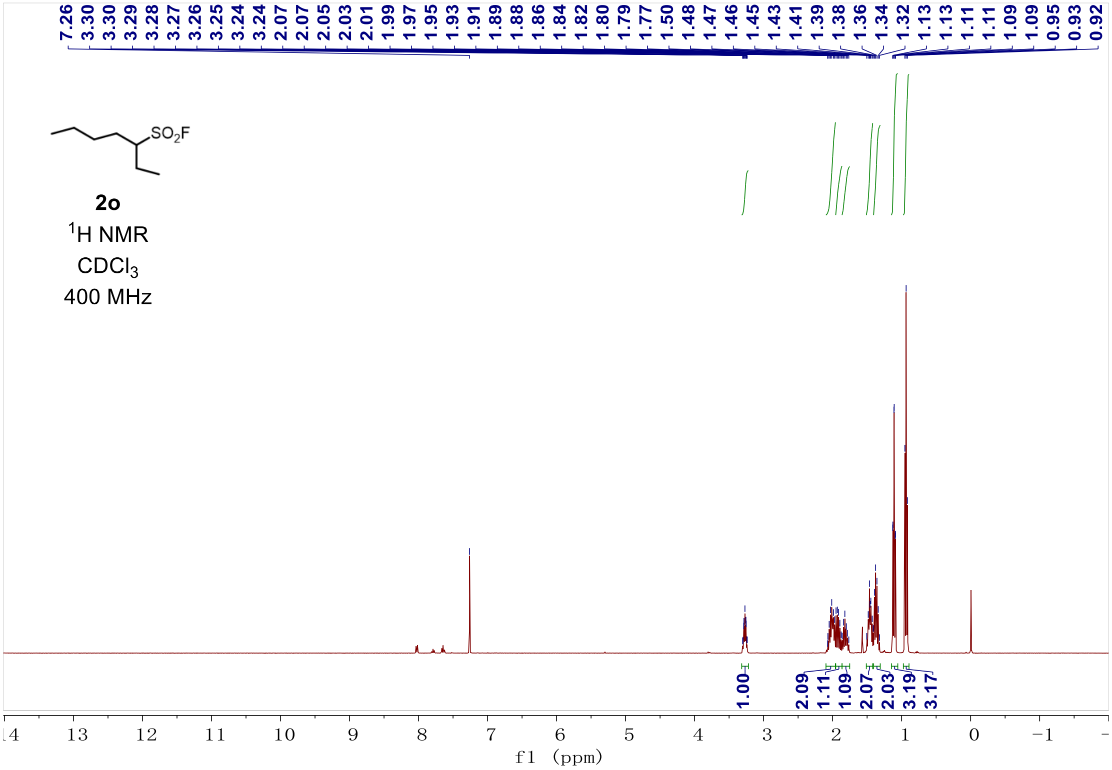
7.26
3.33
3.30
3.27
2.31
2.27
1.97
1.93
1.77
1.74
1.72
1.69
1.68
1.66
1.65
1.36
1.33
1.30
1.27
SO2F
2m
1H NMR
CDCl3
400 MHz
0.92
2.00
2.01
3.01
3.32
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)

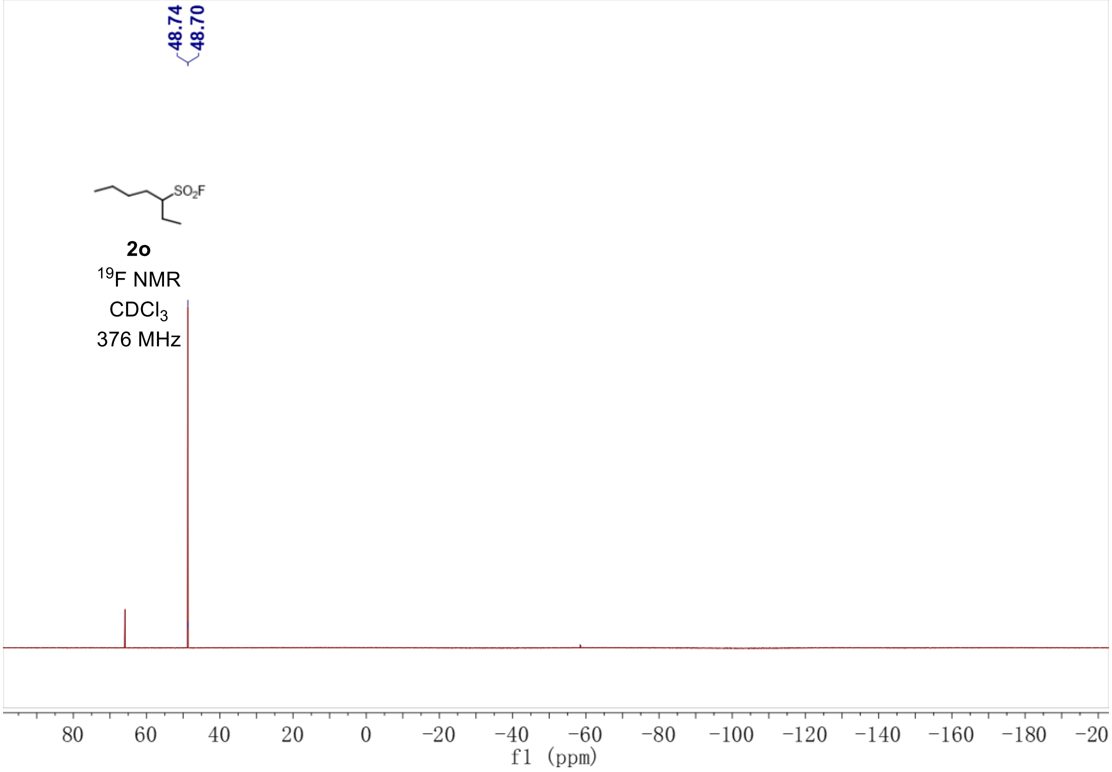


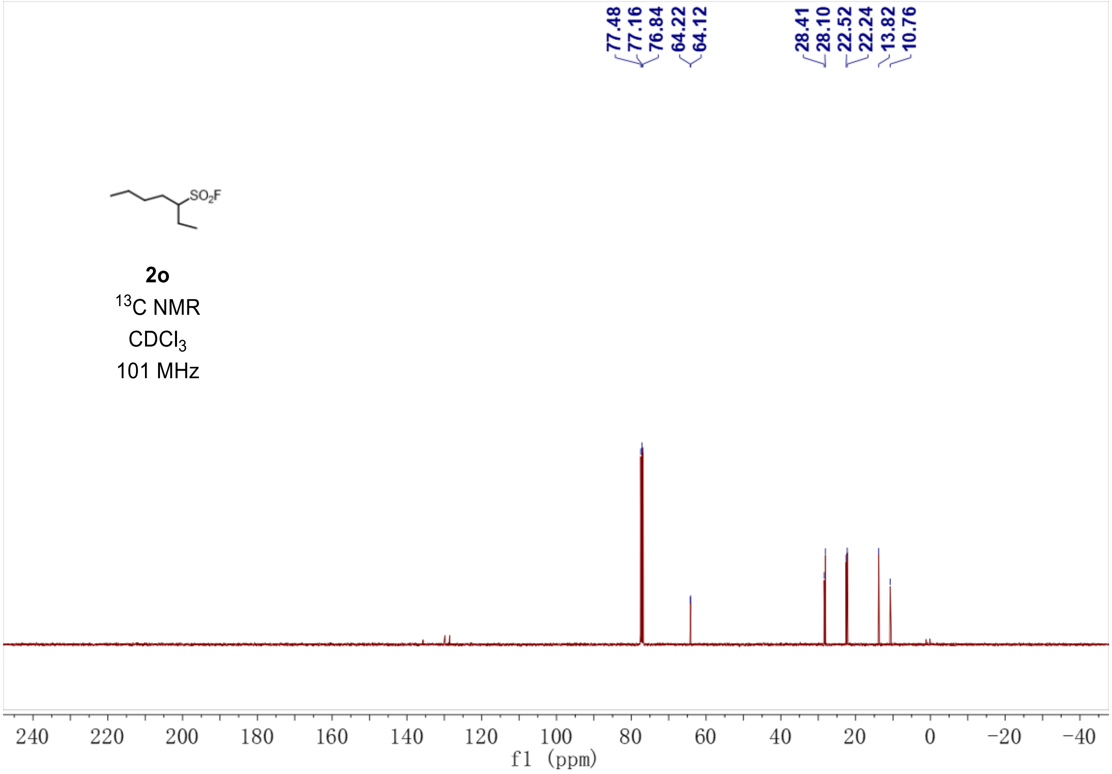
40.77
40.73
SO2F
2m
19F NMR
CDCl3
376 MHz
40.77
40.73
1.00
0.07
41.2
41.0
40.8
40.6
40.4
f1 (ppm)
1.00
0.07
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
f1 (ppm)


77.48
77.16
76.84
61.17
61.05
26.61
24.85
24.81
SO2F
2m
13C NMR
CDCl3
101 MHz
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
−40
f1 (ppm)

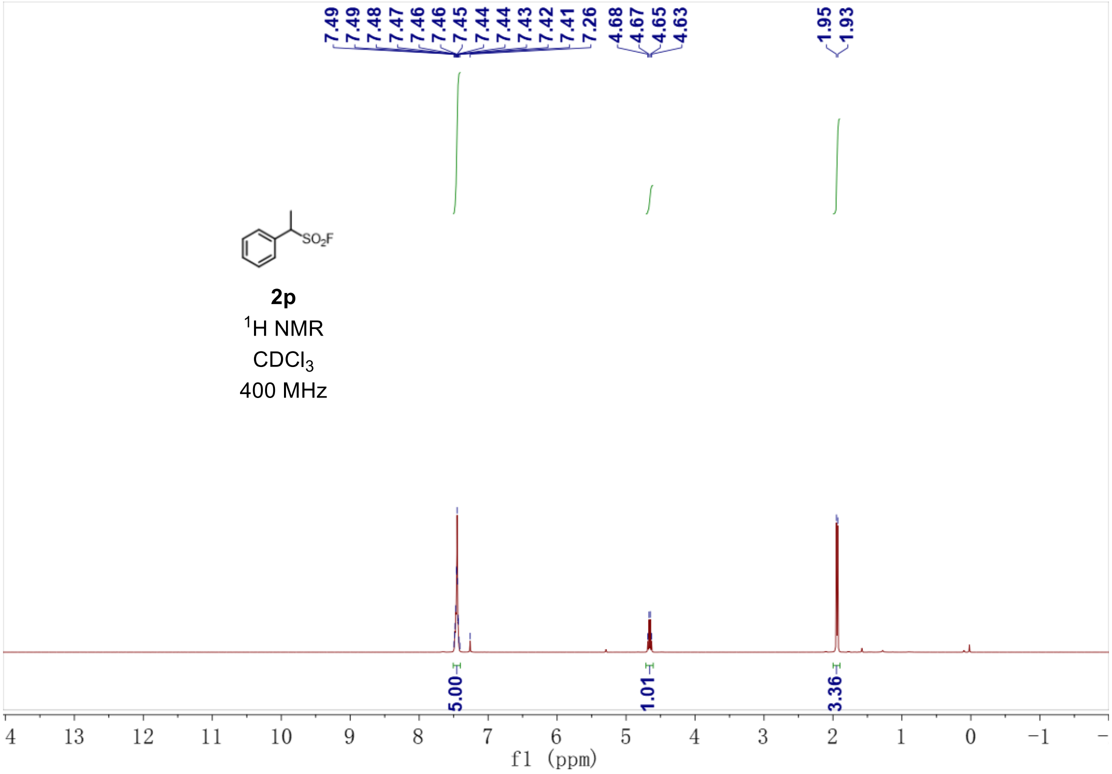

40.3
40.2
-58.4
SO2F
O
2n
Crude 19F NMR
376 MHz
0.56
1.00
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−20
f1 (ppm)


7.26
3.30
3.30
3.29
3.28
3.27
3.26
3.25
3.24
3.24
2.07
2.07
2.05
2.03
2.01
1.99
1.97
1.95
1.93
1.91
1.89
1.88
1.86
1.84
1.82
1.80
1.79
1.77
1.50
1.48
1.47
1.46
1.45
1.43
1.41
1.39
1.38
1.36
1.34
1.32
1.13
1.13
1.11
1.11
1.09
1.09
0.95
0.93
0.92
SO2F
2o
1H NMR
CDCl3
400 MHz
1.00
2.09
1.11
1.09
2.07
2.03
3.19
3.17
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)

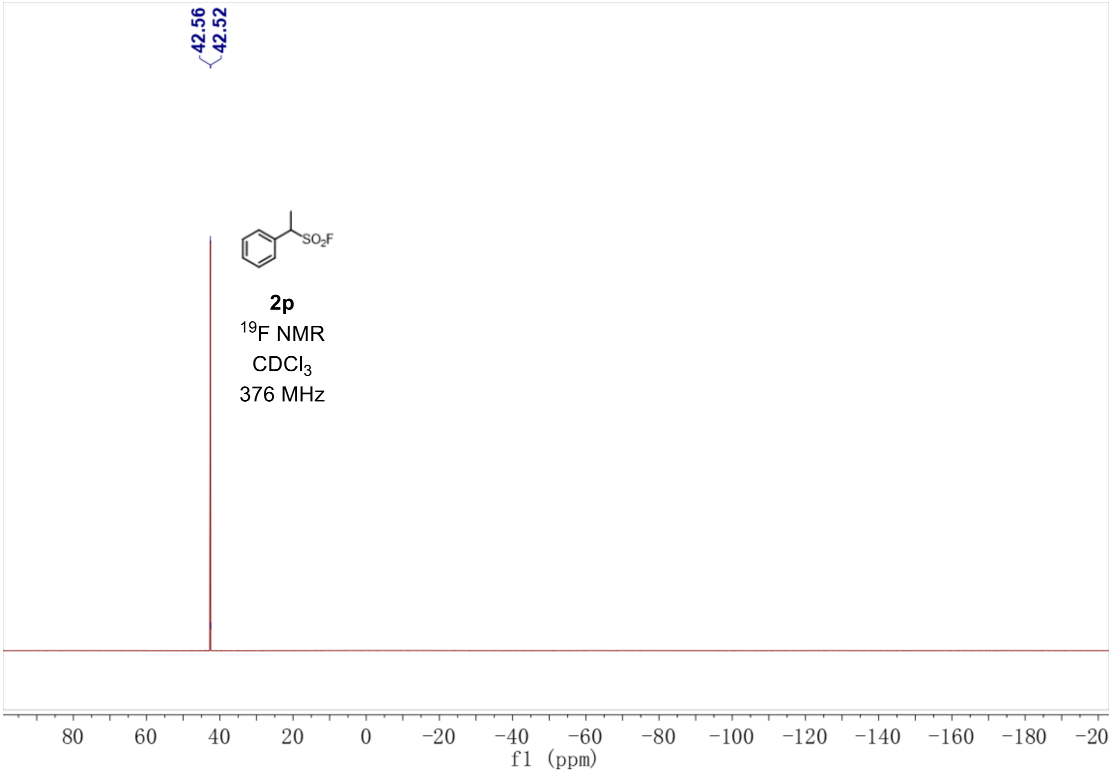

48.74
48.70
SO2F
2o
19F NMR
CDCl3
376 MHz
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−20
f1 (ppm)



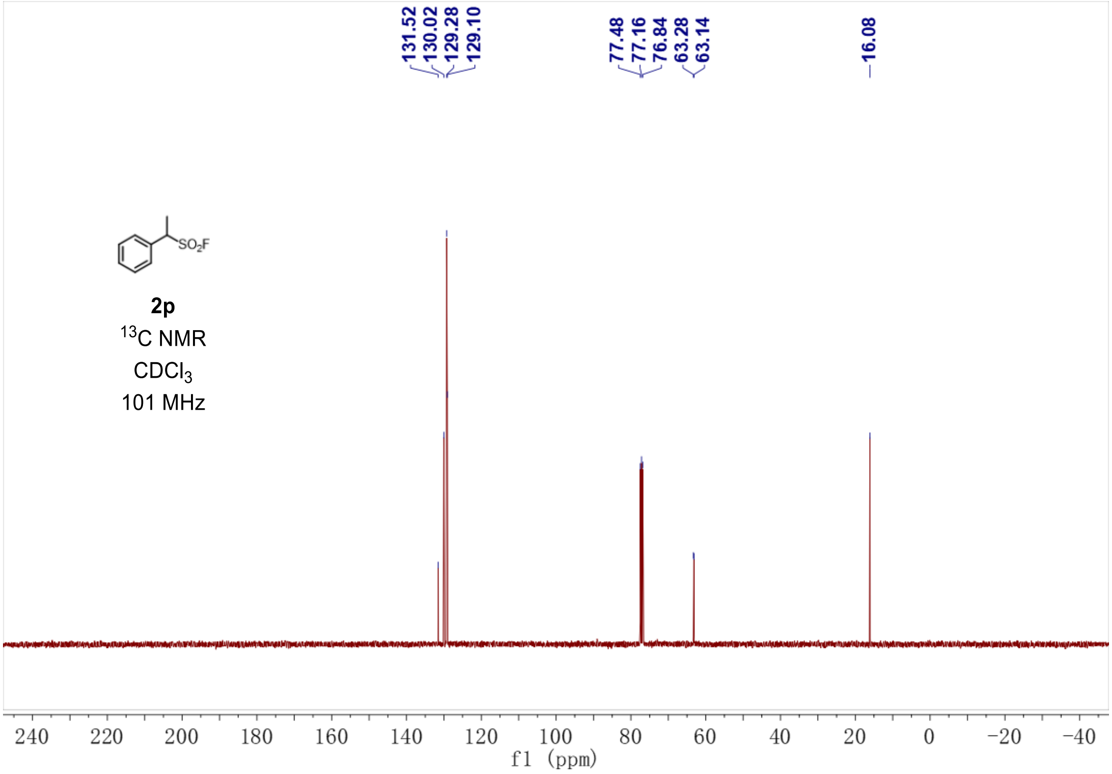
2o
^{13}C NMR
CDCl$_3$
101 MHz

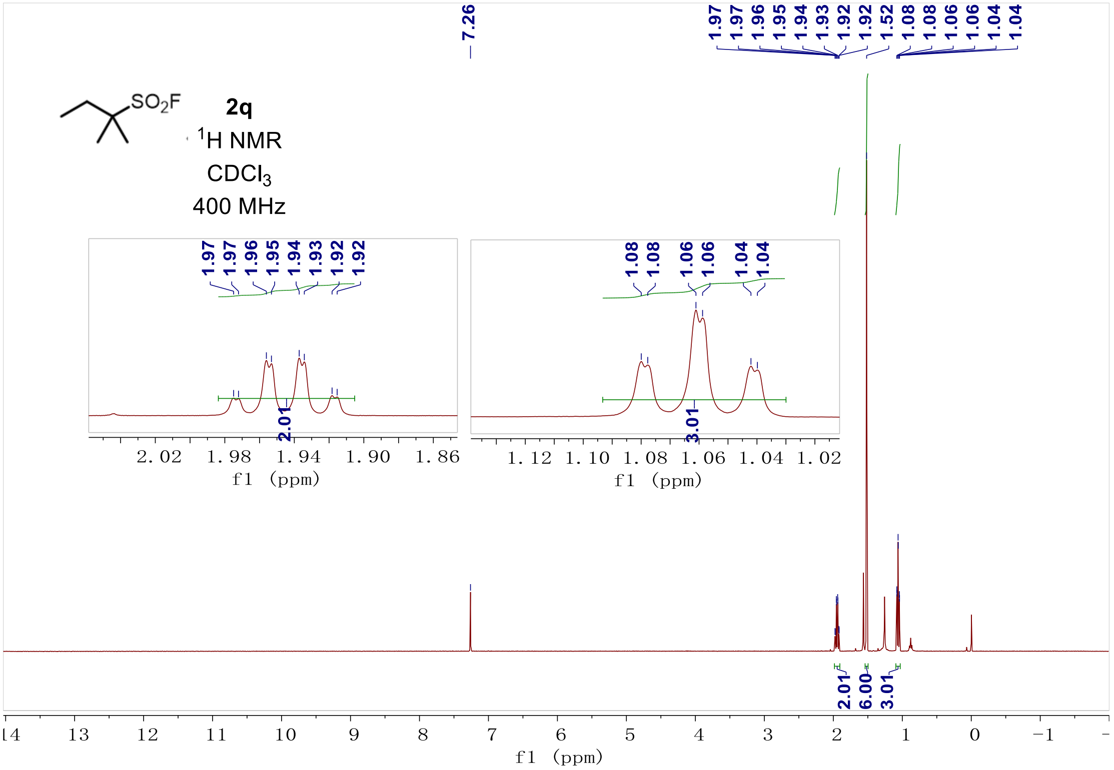


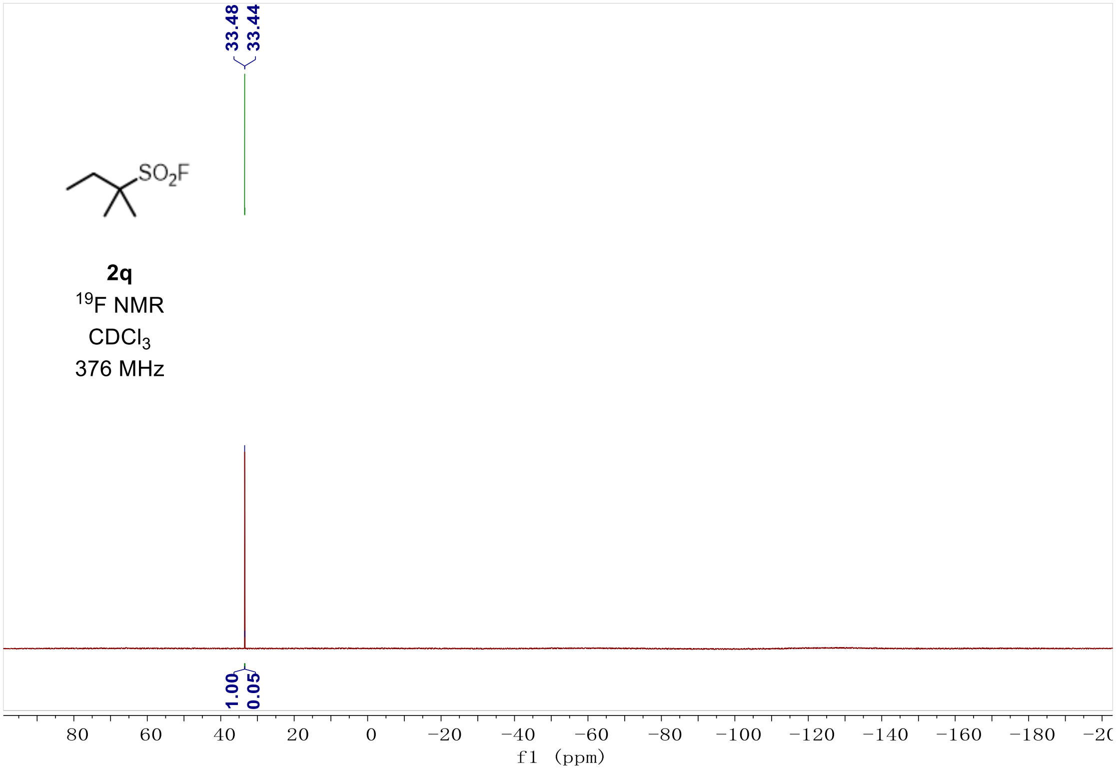
2p
^{1}H NMR
CDCl$_3$
400 MHz

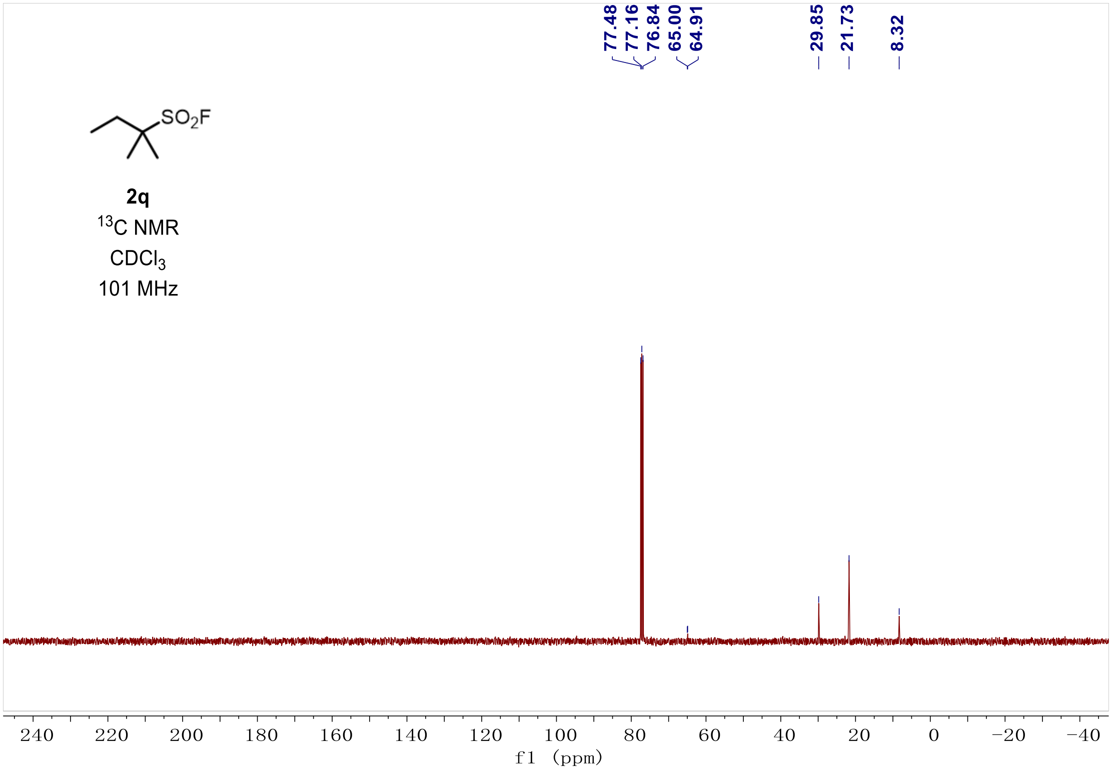


^{13}C NMR spectrum of phenylethanesulfonyl fluoride (101 MHz, CDCl3):




7.26
1.97
1.97
1.96
1.95
1.94
1.93
1.92
1.92
1.52
1.08
1.08
1.06
1.06
1.04
1.04
SO2F
2q
1H NMR
CDCl3
400 MHz
2.01
3.01
2.02 1.98 1.94 1.90 1.86
1.12 1.10 1.08 1.06 1.04 1.02
f1 (ppm)
2.01
6.00
3.01
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)

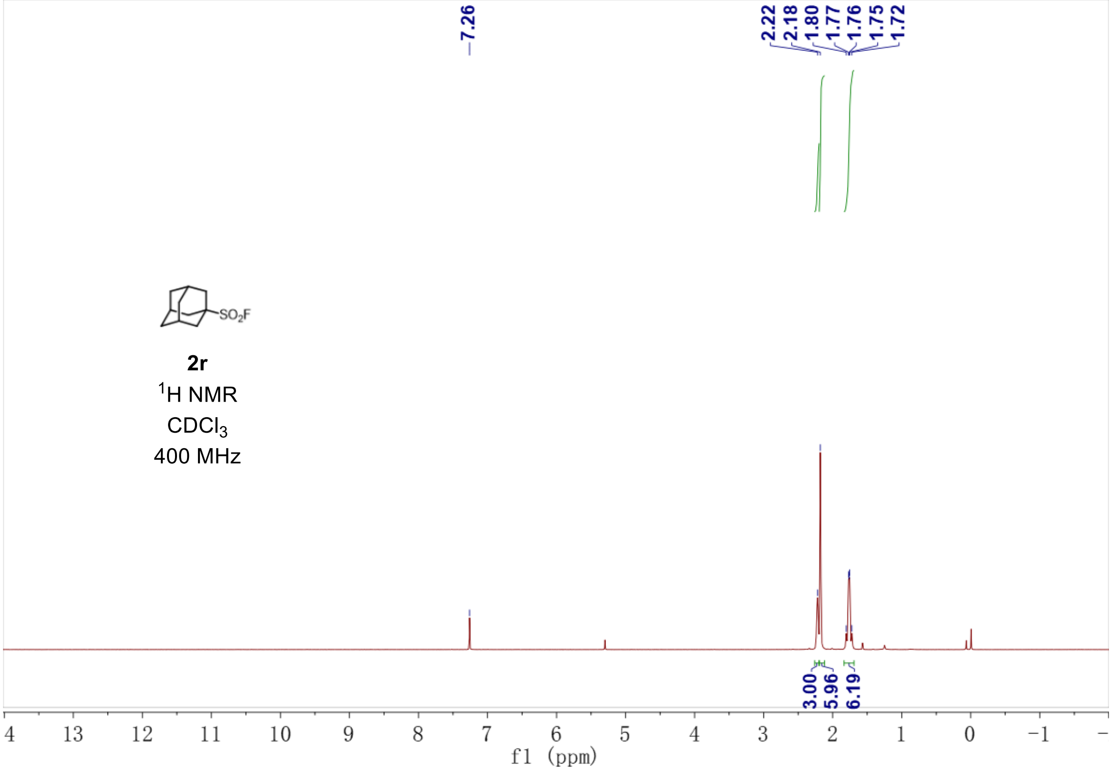

33.48
33.44
SO2F
2q
19F NMR
CDCl3
376 MHz
1.00
0.05
80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −20
f1 (ppm)


2q

^{13}C NMR

$CDCl_3$

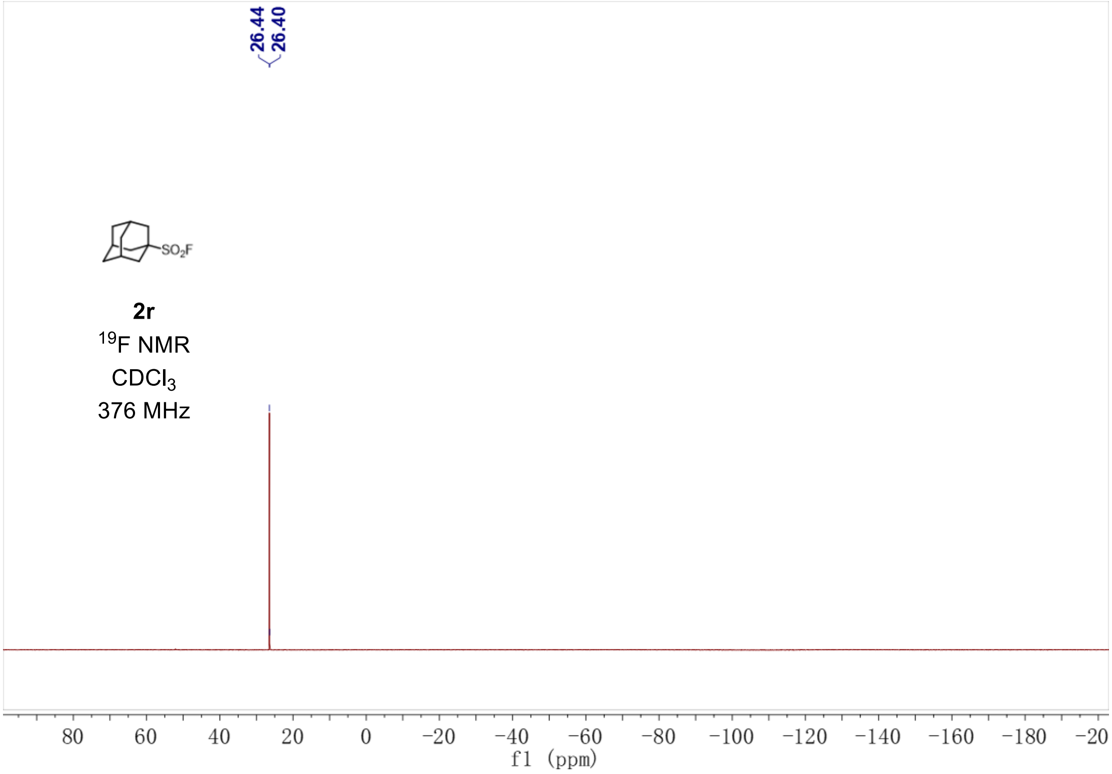
101 MHz

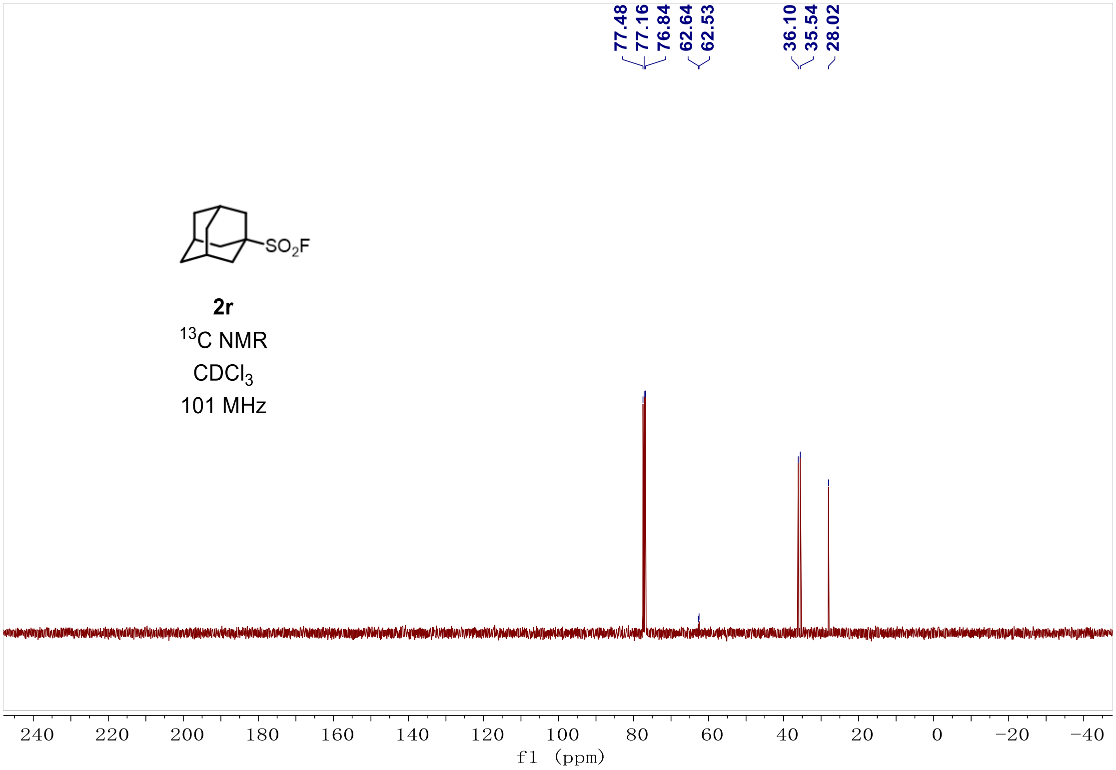

2r

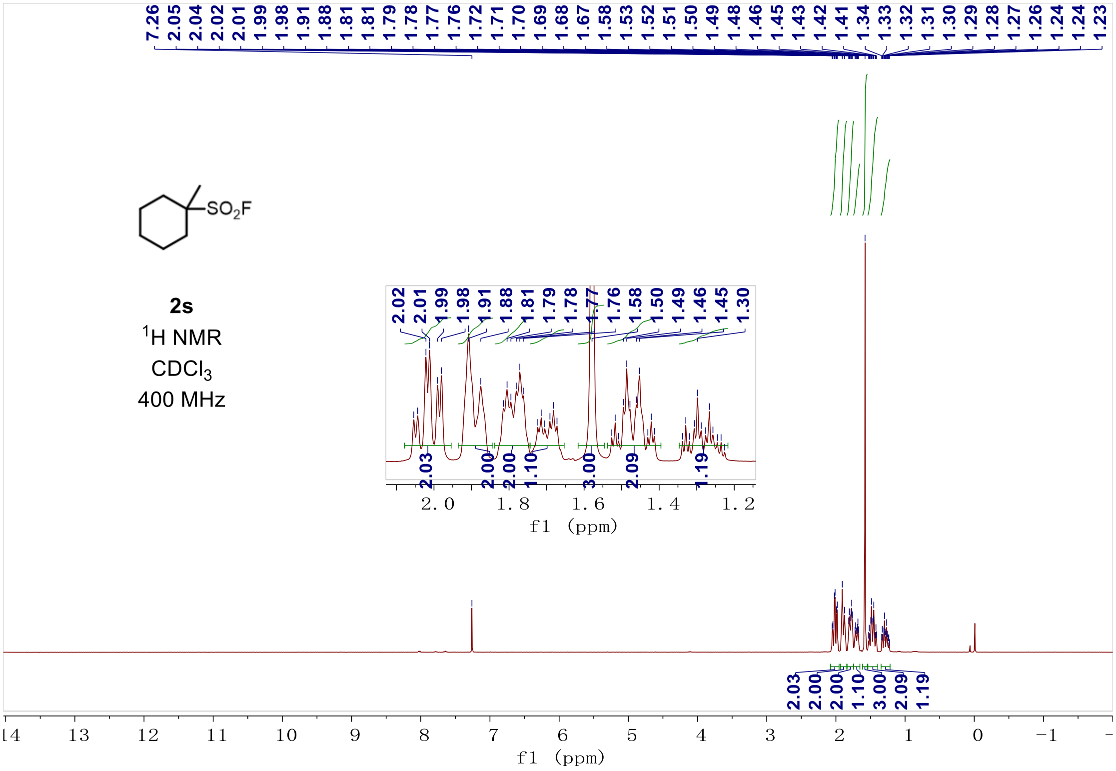
^{1}H NMR

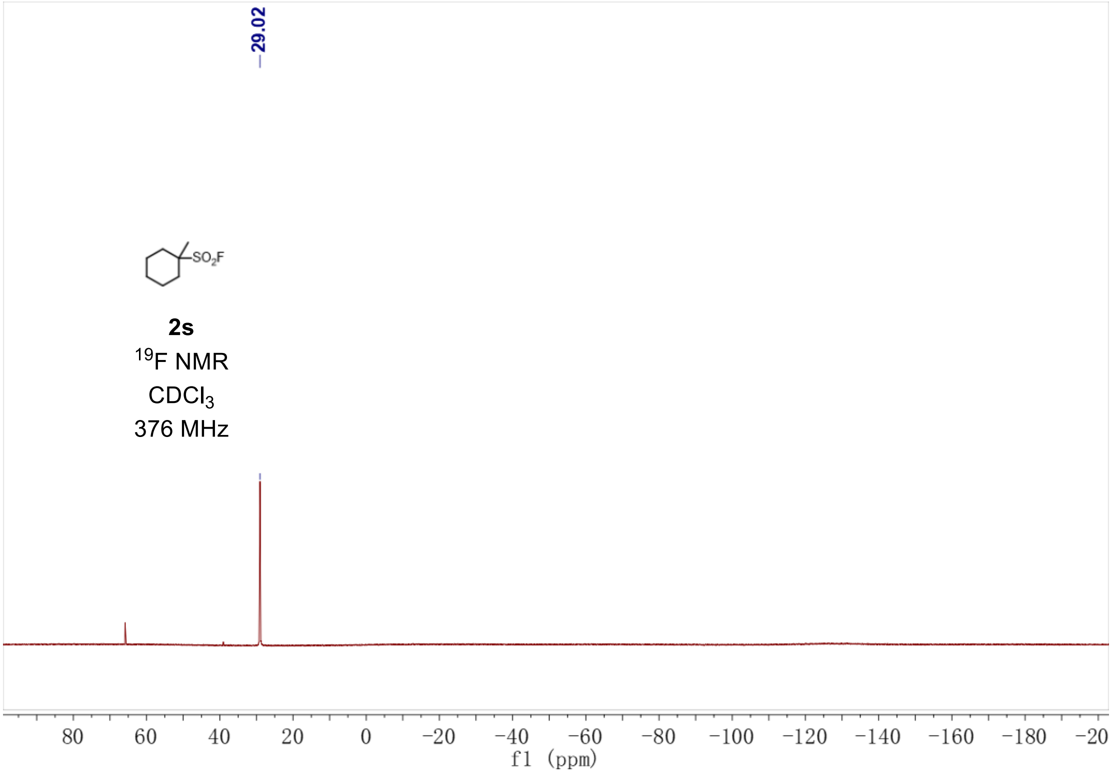
$CDCl_3$

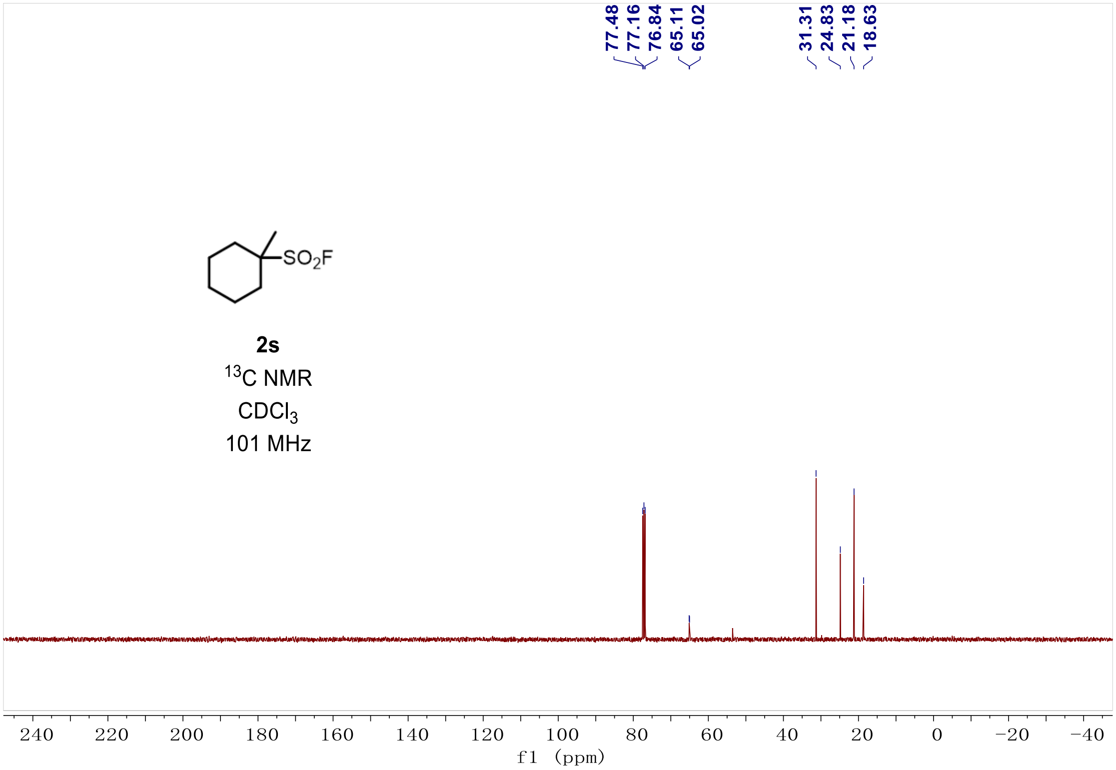
400 MHz

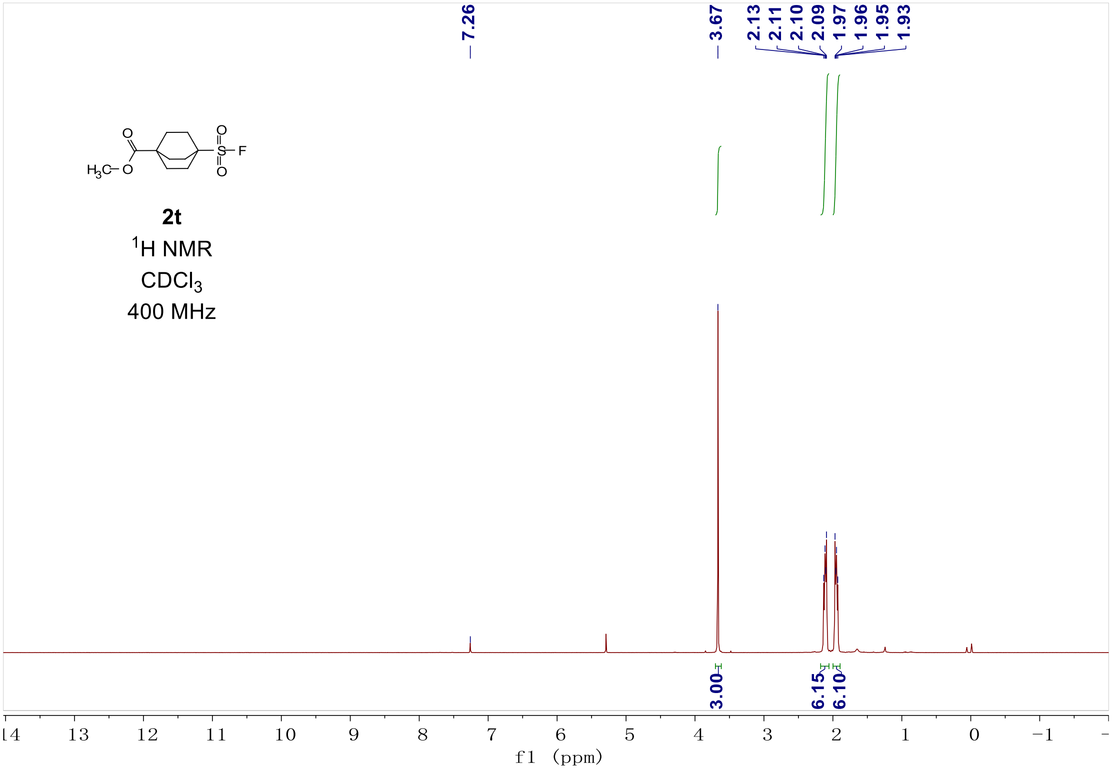

26.44
26.40
SO2F
2r
19F NMR
CDCl3
376 MHz
80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −20
f1 (ppm)

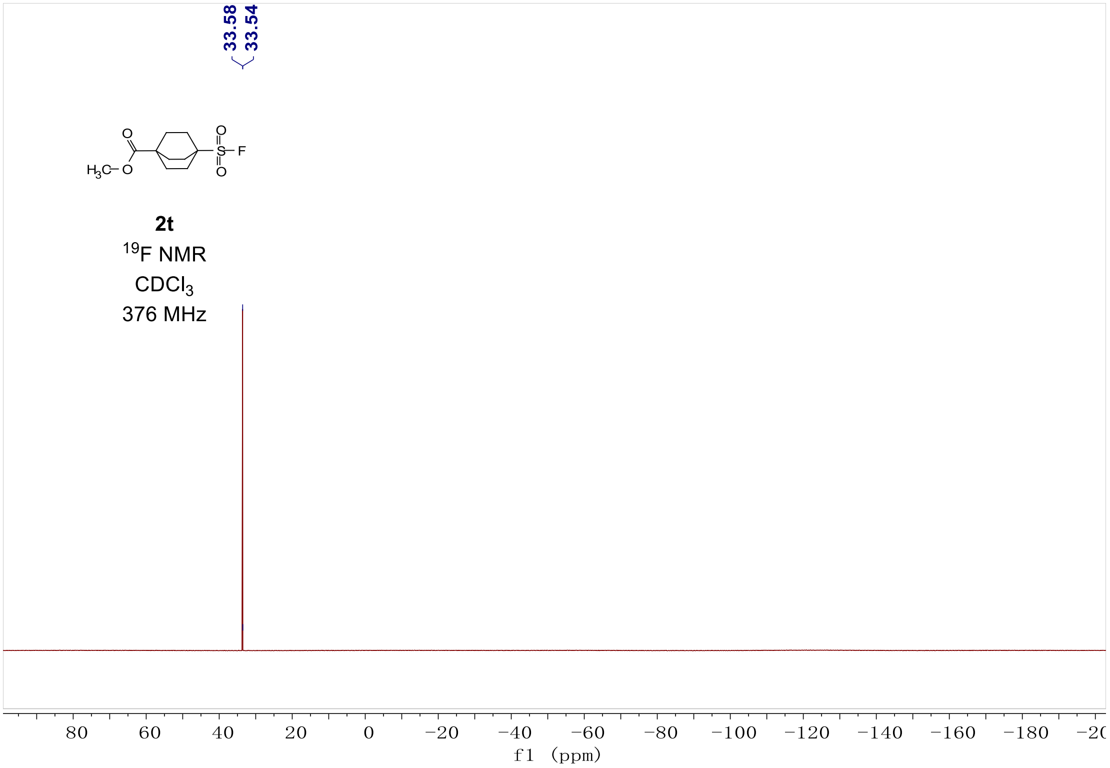

77.48
77.16
76.84
62.64
62.53
36.10
35.54
28.02
SO2F
2r
13C NMR
CDCl3
101 MHz
240 220 200 180 160 140 120 100 80 60 40 20 0 −20 −40
f1 (ppm)

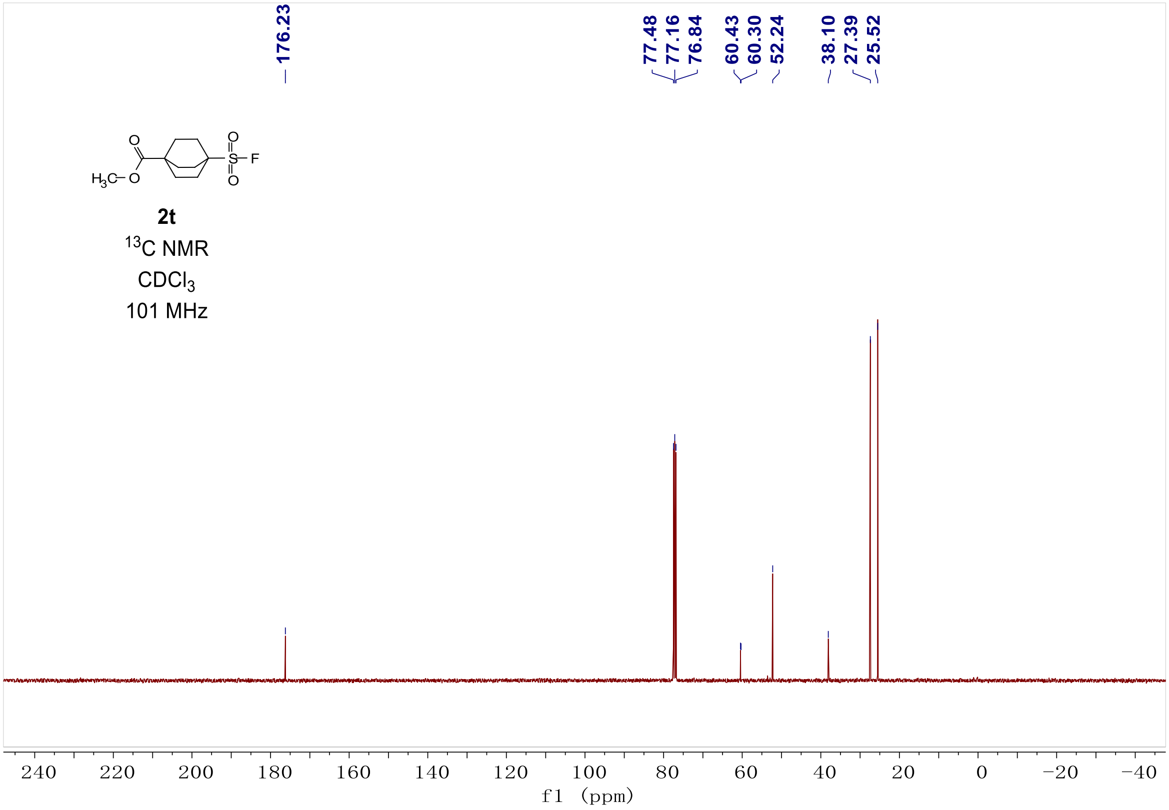

7.26 2.05 2.04 2.02 2.01 1.99 1.98 1.91 1.88 1.81 1.81 1.79 1.78 1.77 1.76 1.72 1.71 1.70 1.69 1.68 1.67 1.58 1.53 1.52 1.51 1.50 1.49 1.48 1.46 1.45 1.43 1.42 1.41 1.34 1.33 1.32 1.31 1.30 1.29 1.28 1.27 1.26 1.24 1.24 1.23
SO2F
2s
1H NMR
CDCl3
400 MHz
2.02 2.01 1.99 1.98 1.91 1.88 1.81 1.79 1.78 1.77 1.76 1.58 1.50 1.49 1.46 1.45 1.30
2.03 2.00 2.00 1.10 3.00 2.09 1.19
2.0 1.8 1.6 1.4 1.2
f1 (ppm)
2.03 2.00 2.00 1.10 3.00 2.09 1.19
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

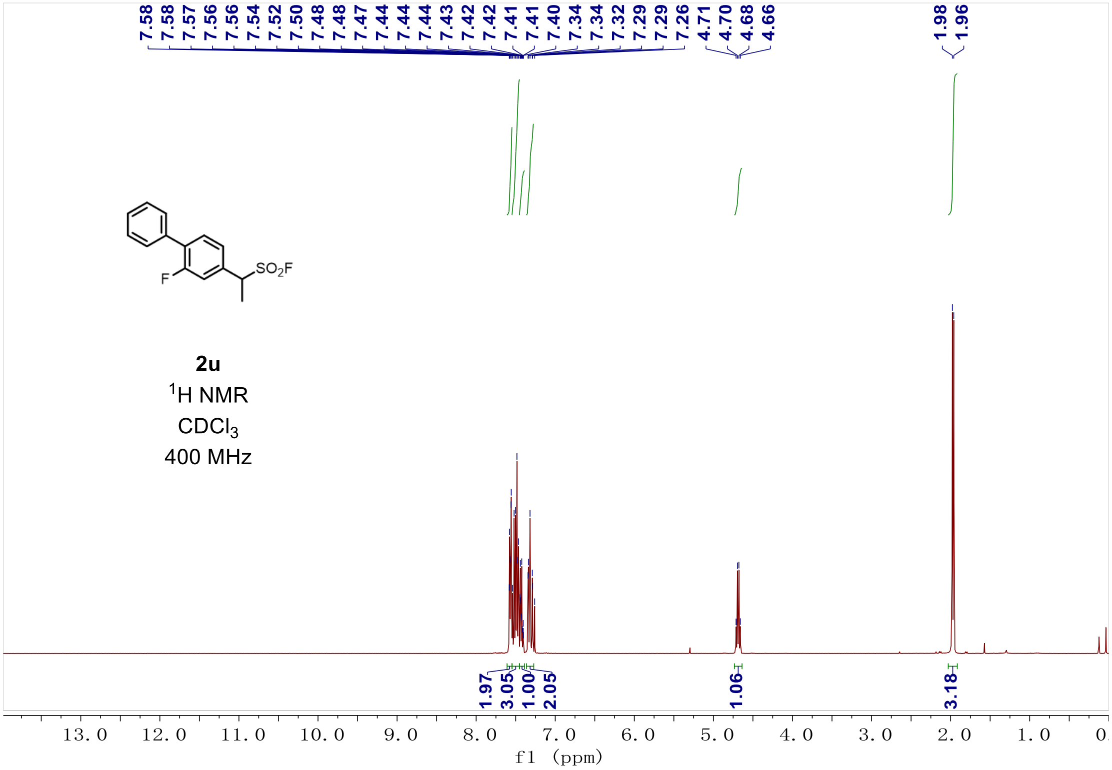

29.02
SO2F
2s
19F NMR
CDCl3
376 MHz
80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -20
f1 (ppm)

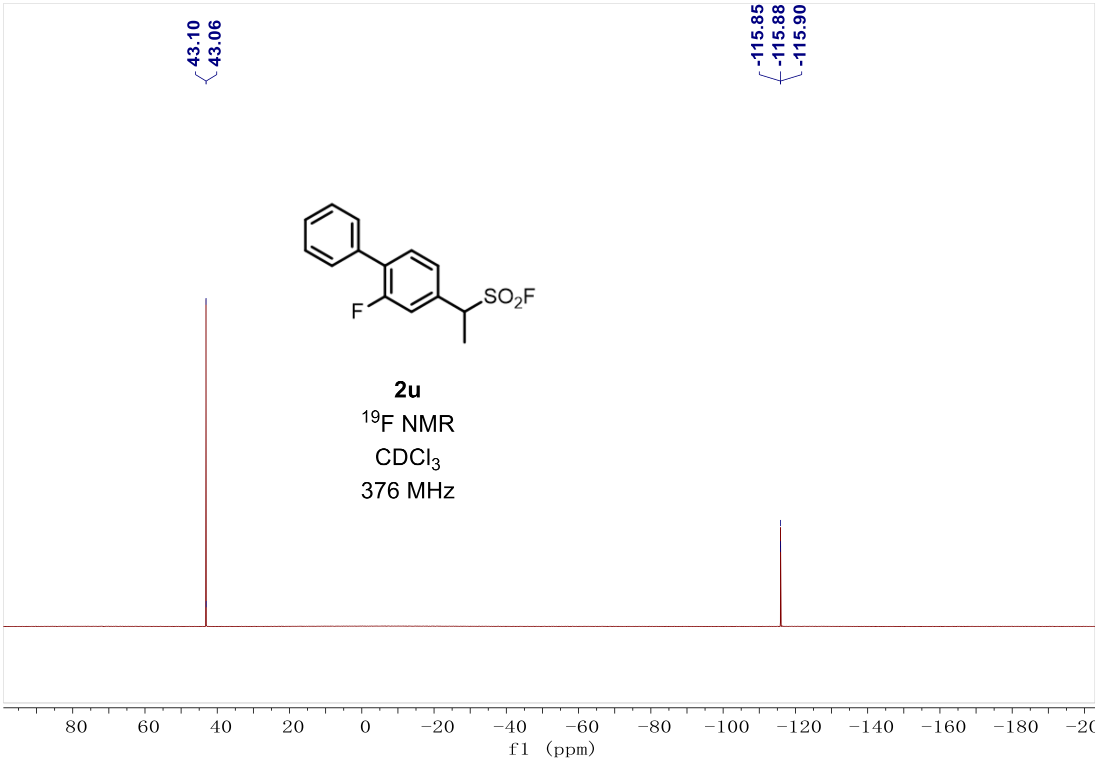

77.48
77.16
76.84
65.11
65.02
31.31
24.83
21.18
18.63
SO2F
2s
13C NMR
CDCl3
101 MHz
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
−40
f1 (ppm)

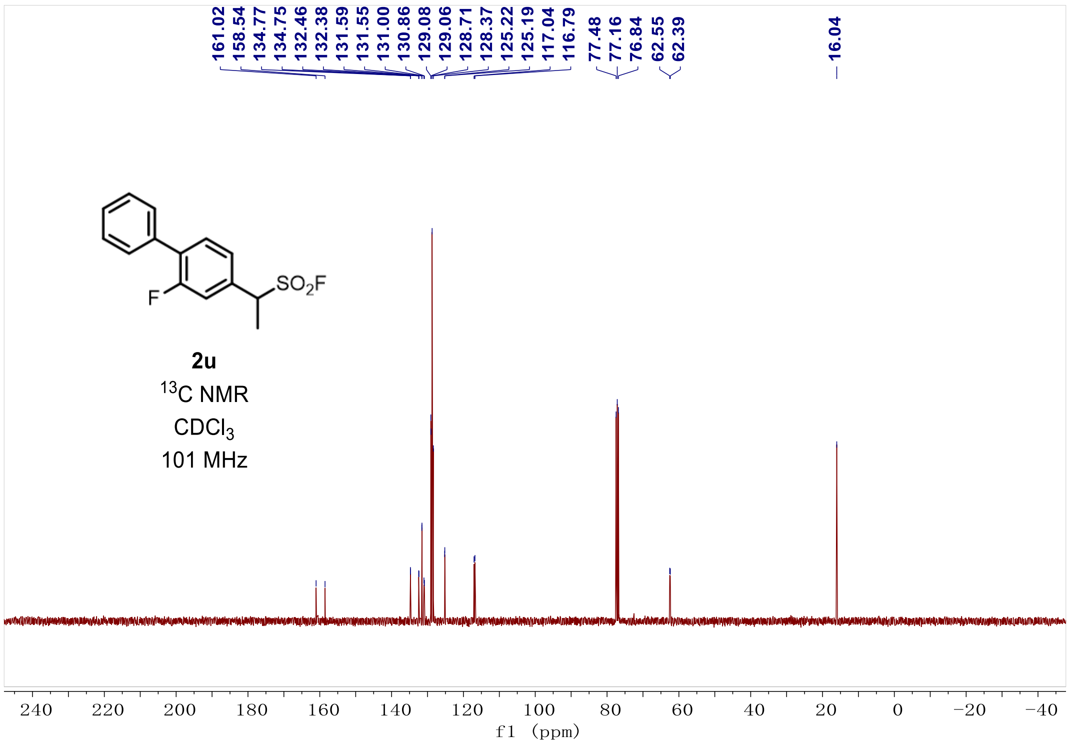

7.26
3.67
2.13
2.11
2.10
2.09
1.97
1.96
1.95
1.93
O
H3C–O
O
S–F
O
2t
1H NMR
CDCl3
400 MHz
3.00
6.15
6.10
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)

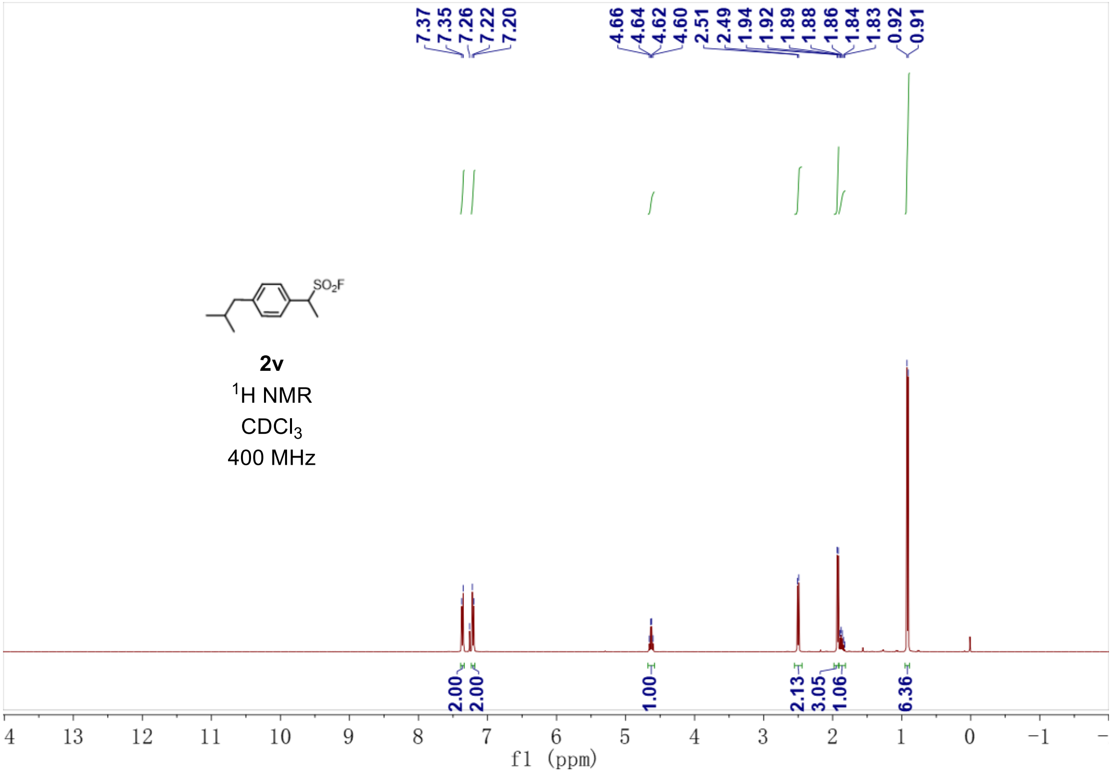

33.58
33.54
O
O
S
F
O
H3C
O
2t
19F NMR
CDCl3
376 MHz
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−2(
f1 (ppm)

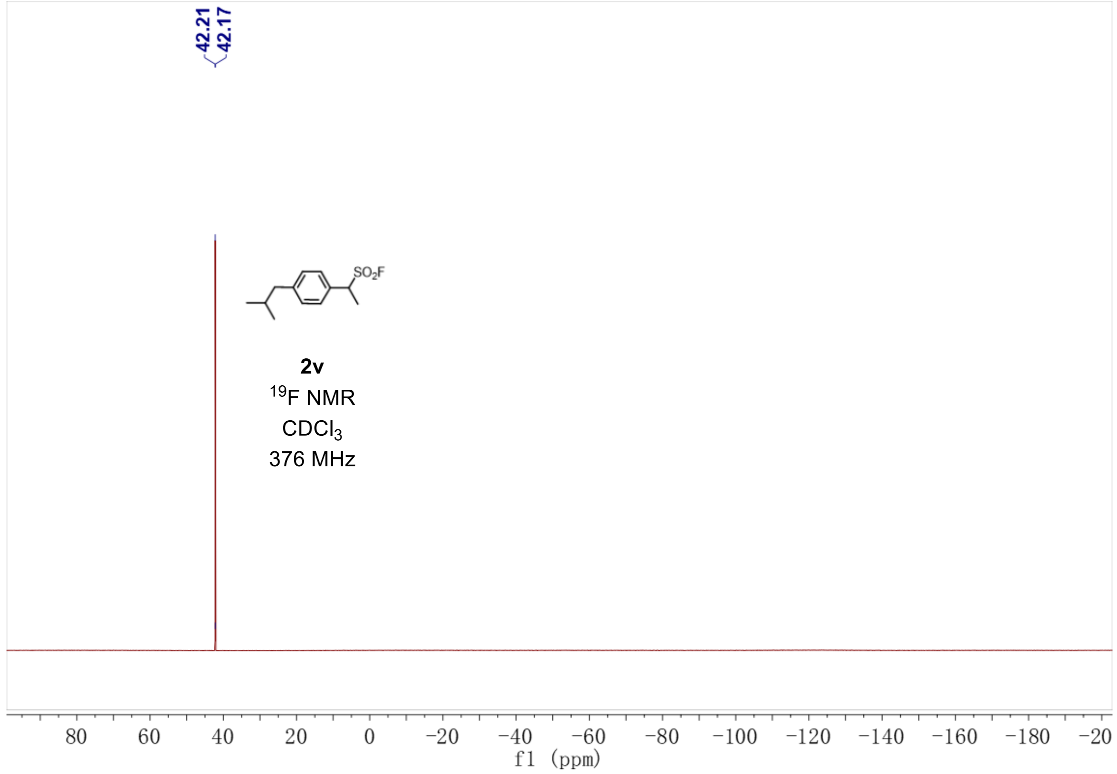

176.23
77.48
77.16
76.84
60.43
60.30
52.24
38.10
27.39
25.52
O
O
S
F
O
H3C
O
2t
13C NMR
CDCl3
101 MHz
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
−40
f1 (ppm)

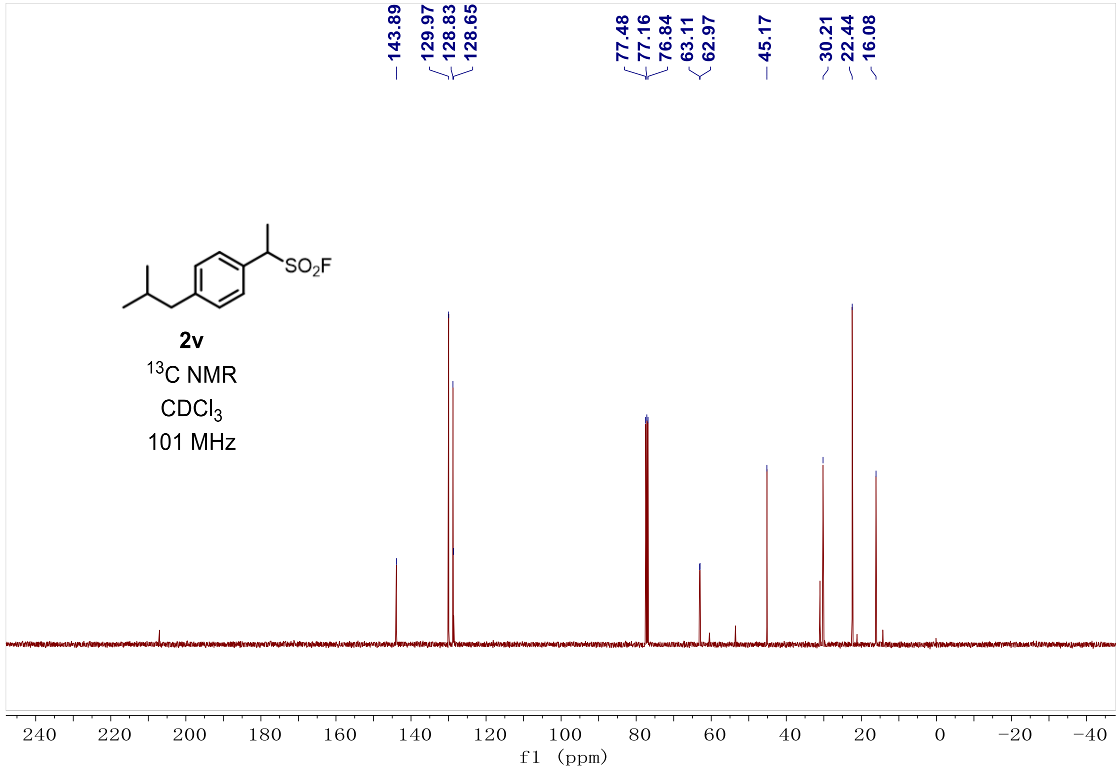

7.58
7.58
7.57
7.56
7.56
7.54
7.52
7.50
7.48
7.48
7.47
7.44
7.44
7.44
7.43
7.42
7.42
7.41
7.41
7.40
7.34
7.34
7.32
7.29
7.29
7.26
4.71
4.70
4.68
4.66
1.98
1.96
F
SO_2F
2u
^1H NMR
$CDCl_3$
400 MHz
1.97
3.05
1.00
2.05
1.06
3.18
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
f1 (ppm)

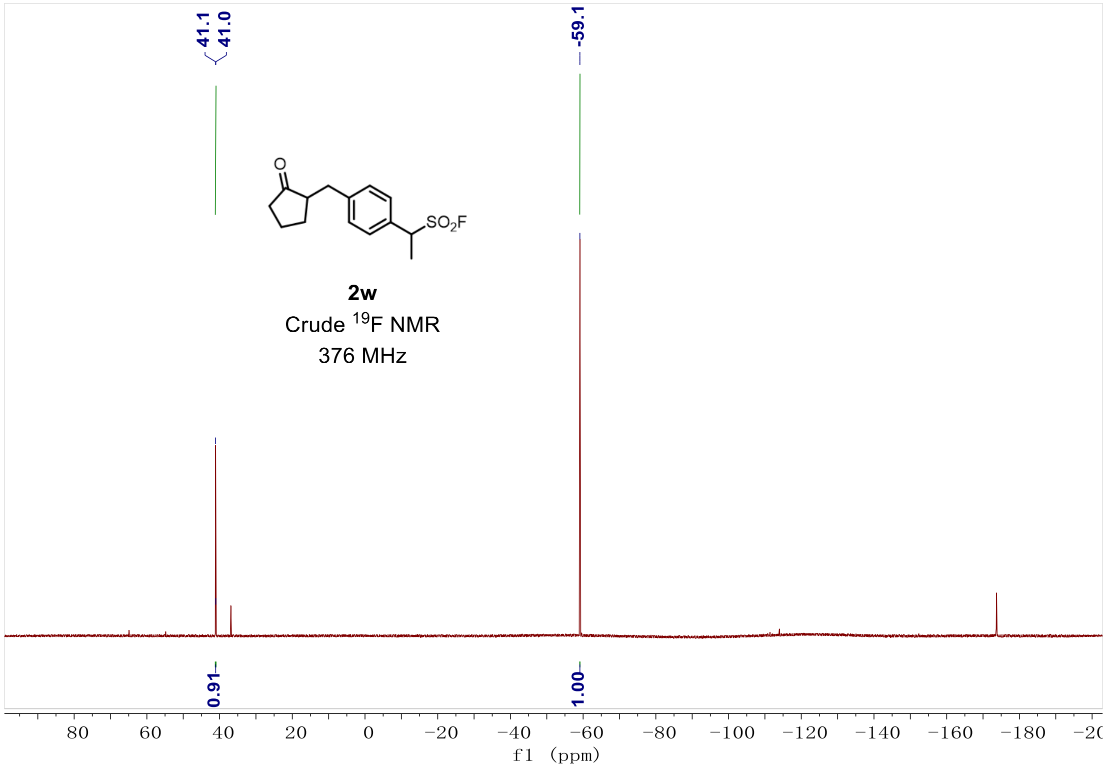

43.10
43.06
-115.85
-115.88
-115.90
F
SO_2F
2u
^{19}F NMR
$CDCl_3$
376 MHz
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−20
f1 (ppm)

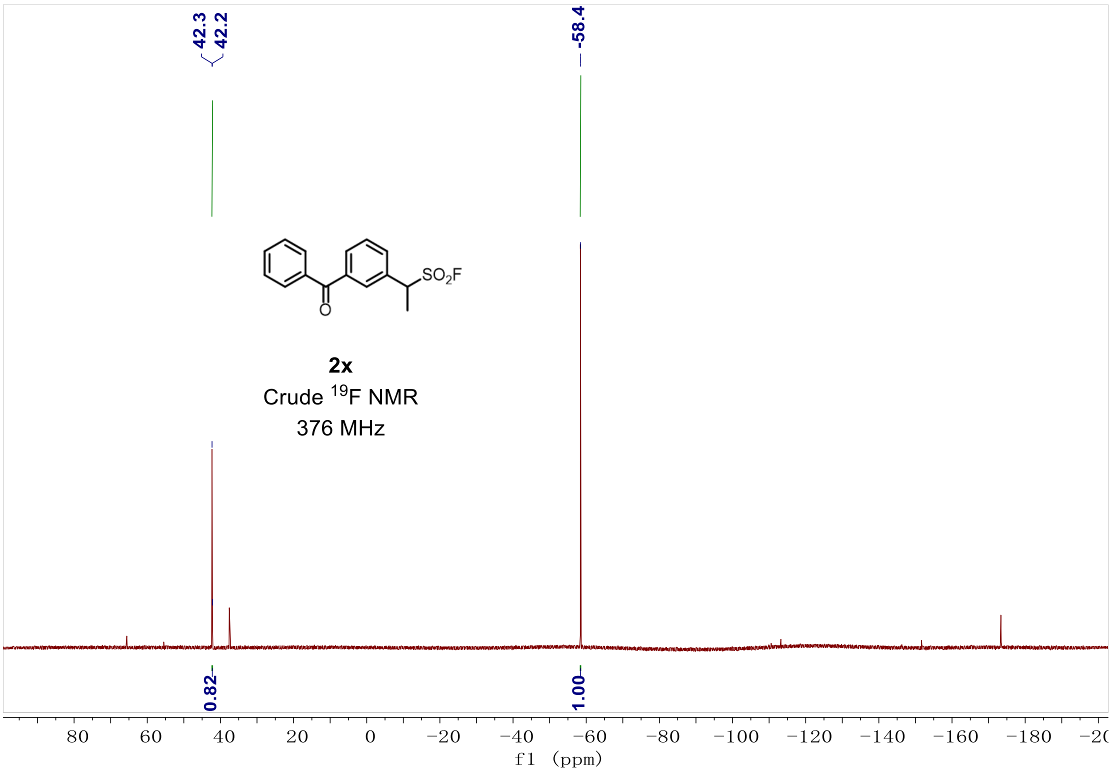

161.02
158.54
134.77
134.75
132.46
132.38
131.59
131.55
131.00
130.86
129.08
129.06
128.71
128.37
125.22
125.19
117.04
116.79
77.48
77.16
76.84
62.55
62.39
16.04
F
SO2F
2u
13C NMR
CDCl3
101 MHz
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
−40
f1 (ppm)

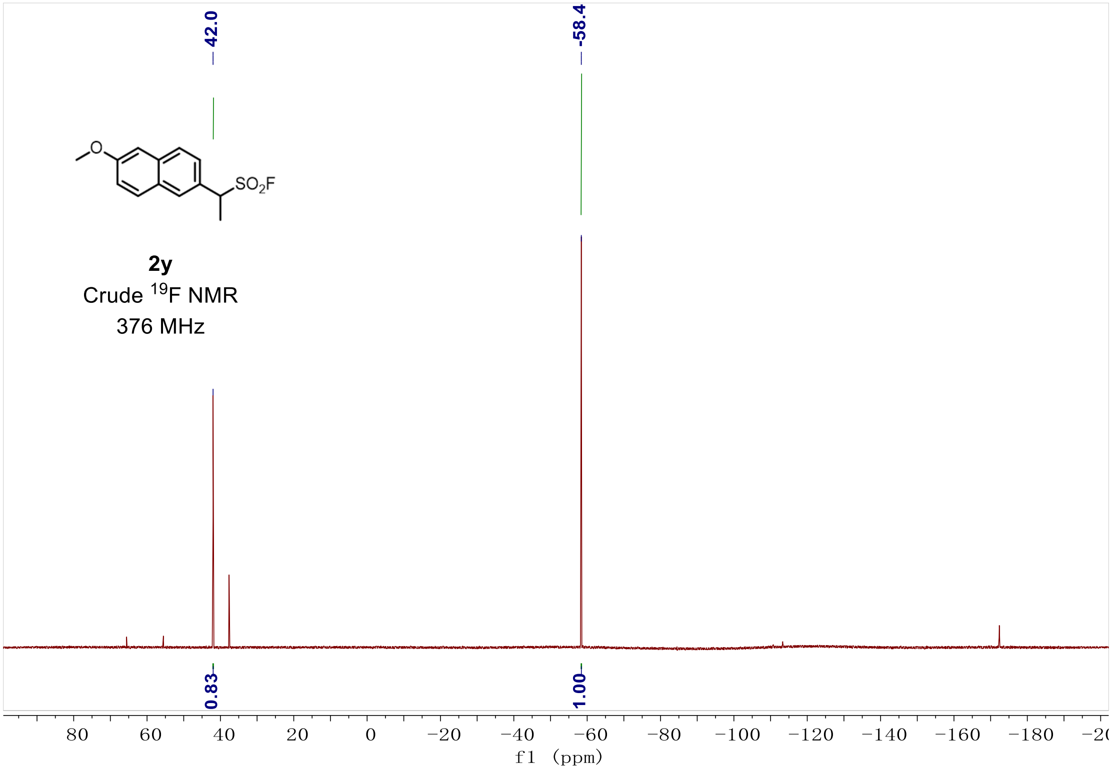

7.37
7.35
7.26
7.22
7.20
4.66
4.64
4.62
4.60
2.51
2.49
1.94
1.92
1.89
1.88
1.86
1.84
1.83
0.92
0.91
SO2F
2v
1H NMR
CDCl3
400 MHz
2.00
2.00
1.00
2.13
3.05
1.06
6.36
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)

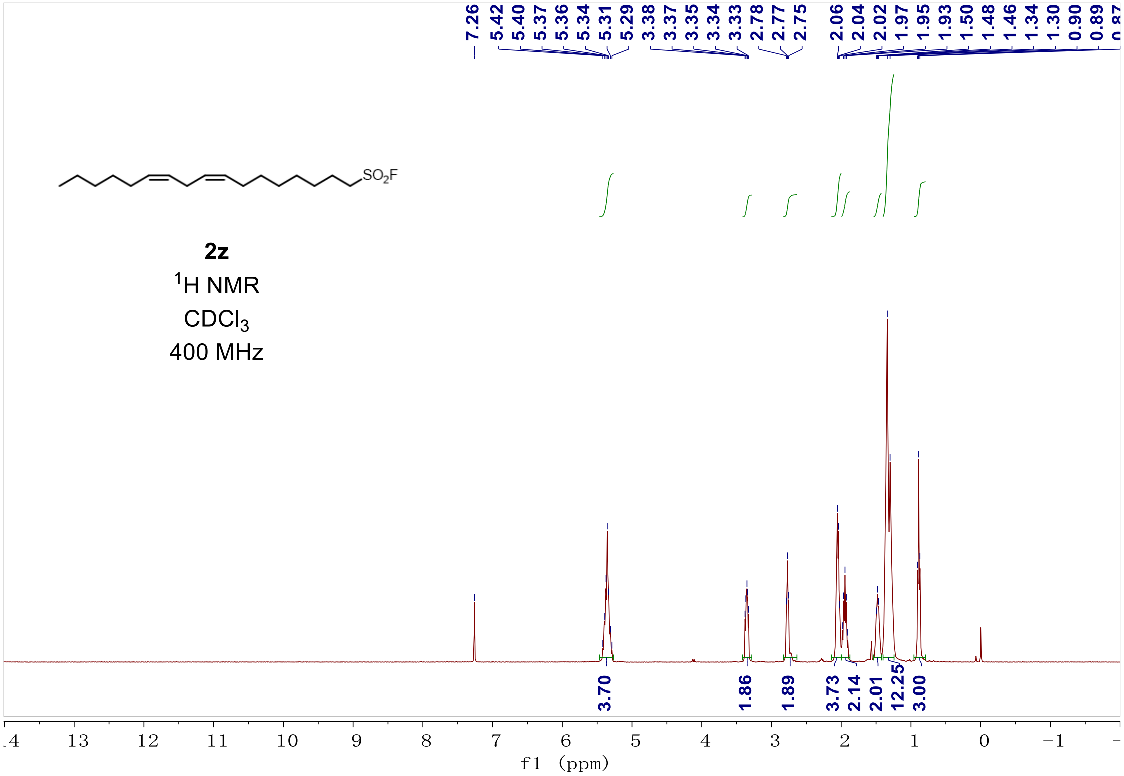

42.21
42.17
SO$_2$F
2v
^{19}F NMR
CDCl$_3$
376 MHz
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−20
f1 (ppm)

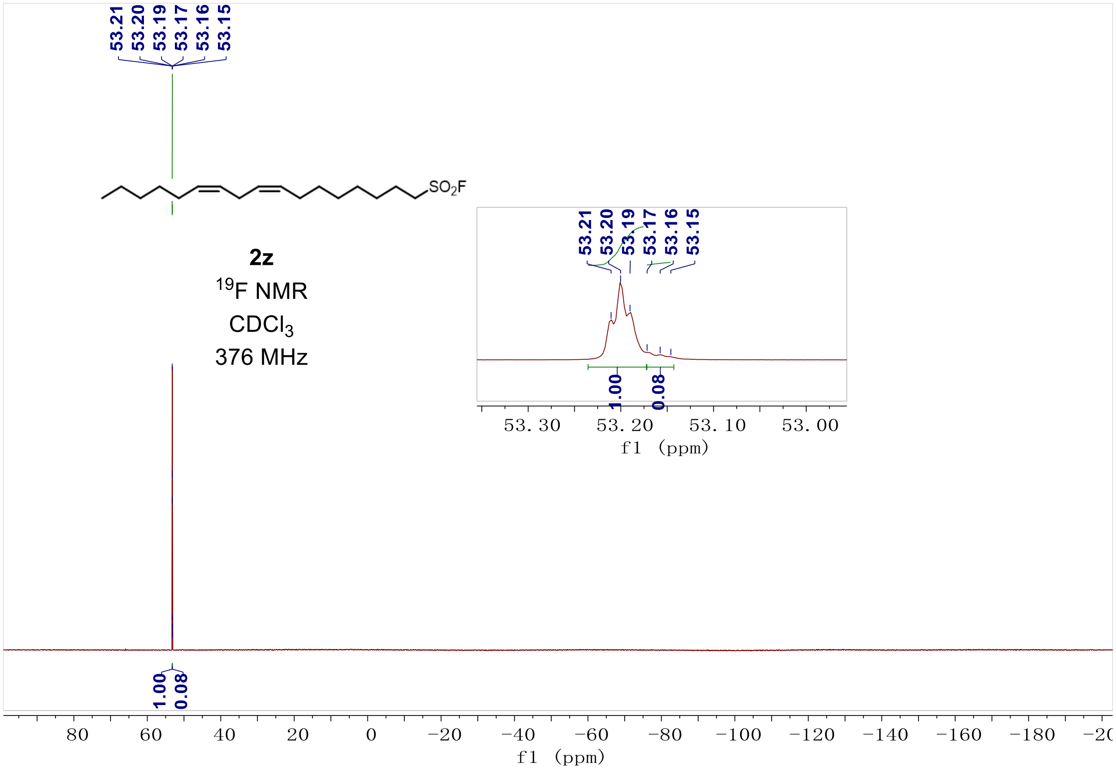

143.89
129.97
128.83
128.65
77.48
77.16
76.84
63.11
62.97
45.17
30.21
22.44
16.08
SO$_2$F
2v
^{13}C NMR
CDCl$_3$
101 MHz
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
−40
f1 (ppm)

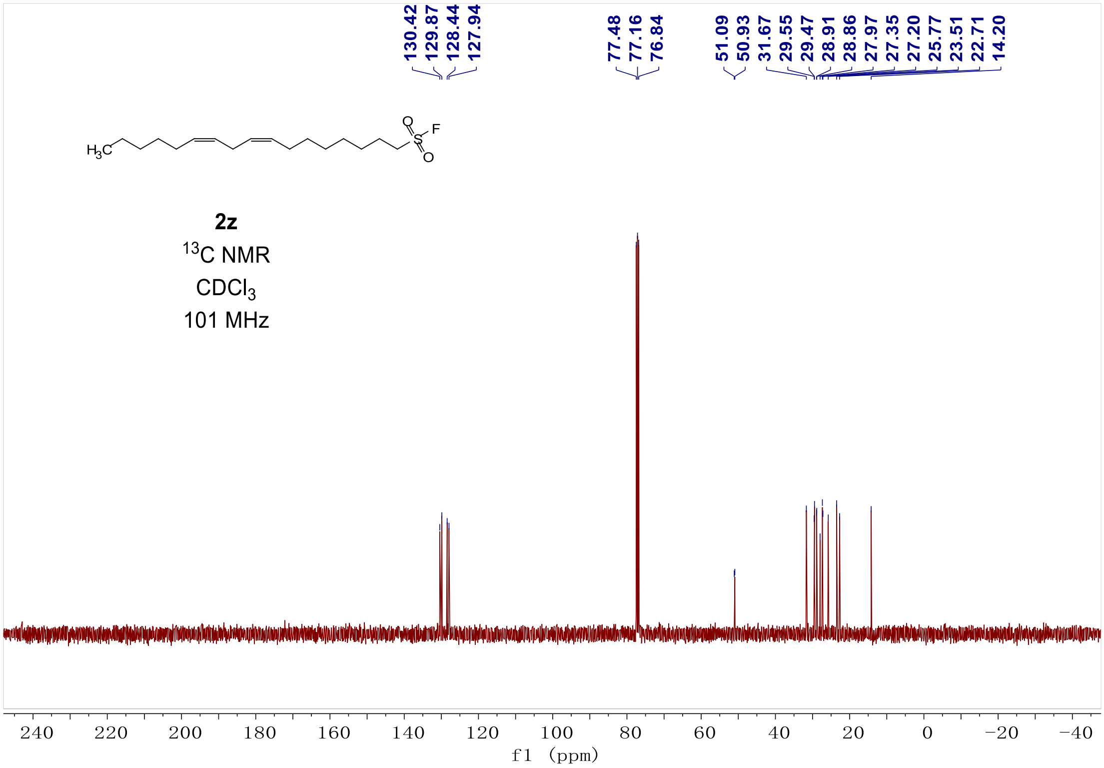

41.1
41.0
-59.1
SO$_2$F
O
2w
Crude ^{19}F NMR
376 MHz
0.91
1.00
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−20
f1 (ppm)

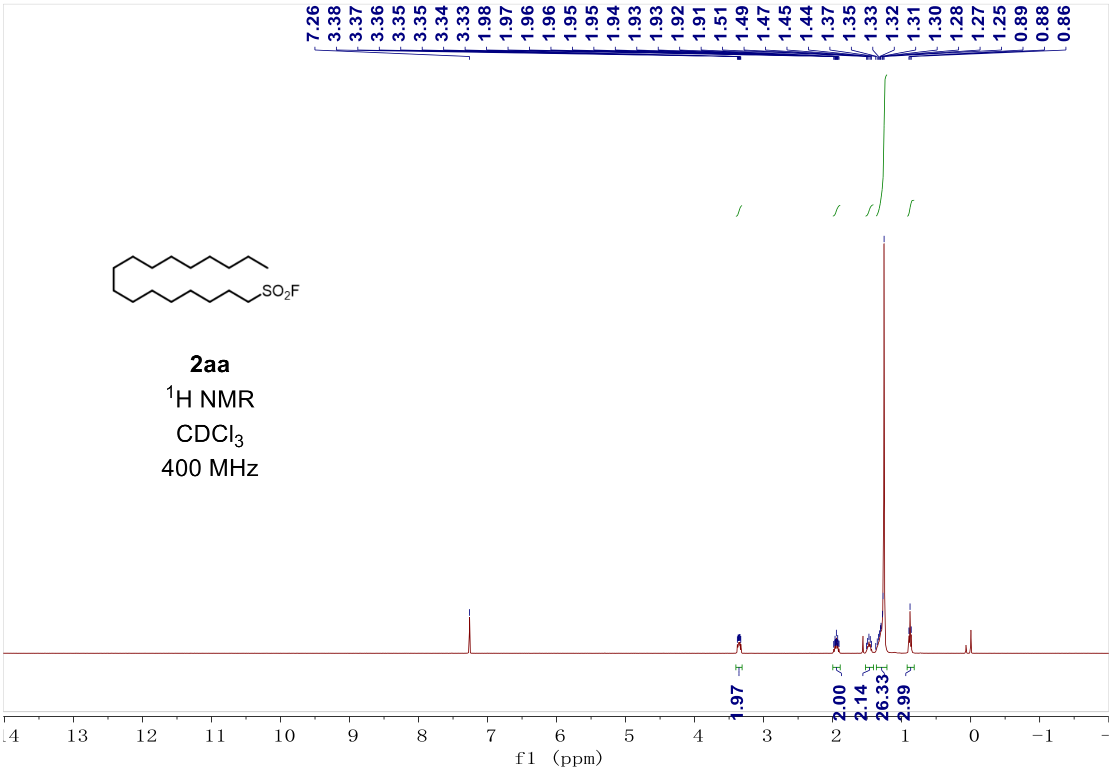

42.3
42.2
-58.4
SO$_2$F
O
2x
Crude ^{19}F NMR
376 MHz
0.82
1.00
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−20
f1 (ppm)

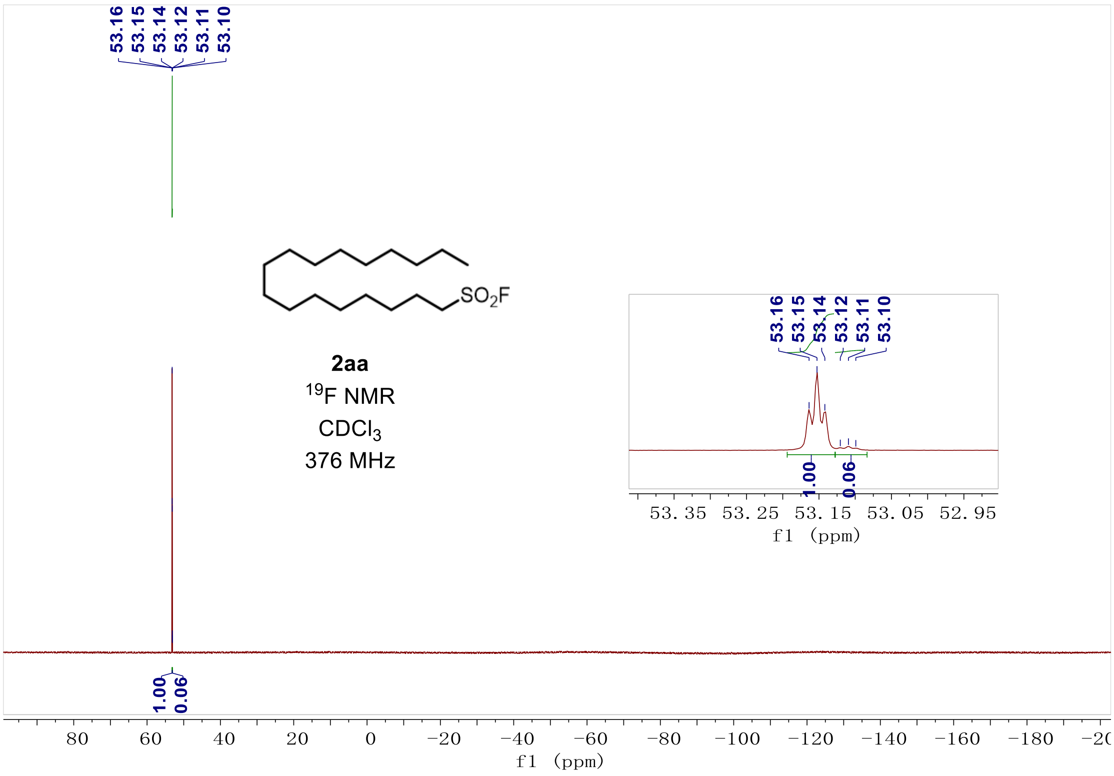

42.0
-58.4
O
SO2F
2y
Crude 19F NMR
376 MHz
0.83
1.00
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
f1 (ppm)

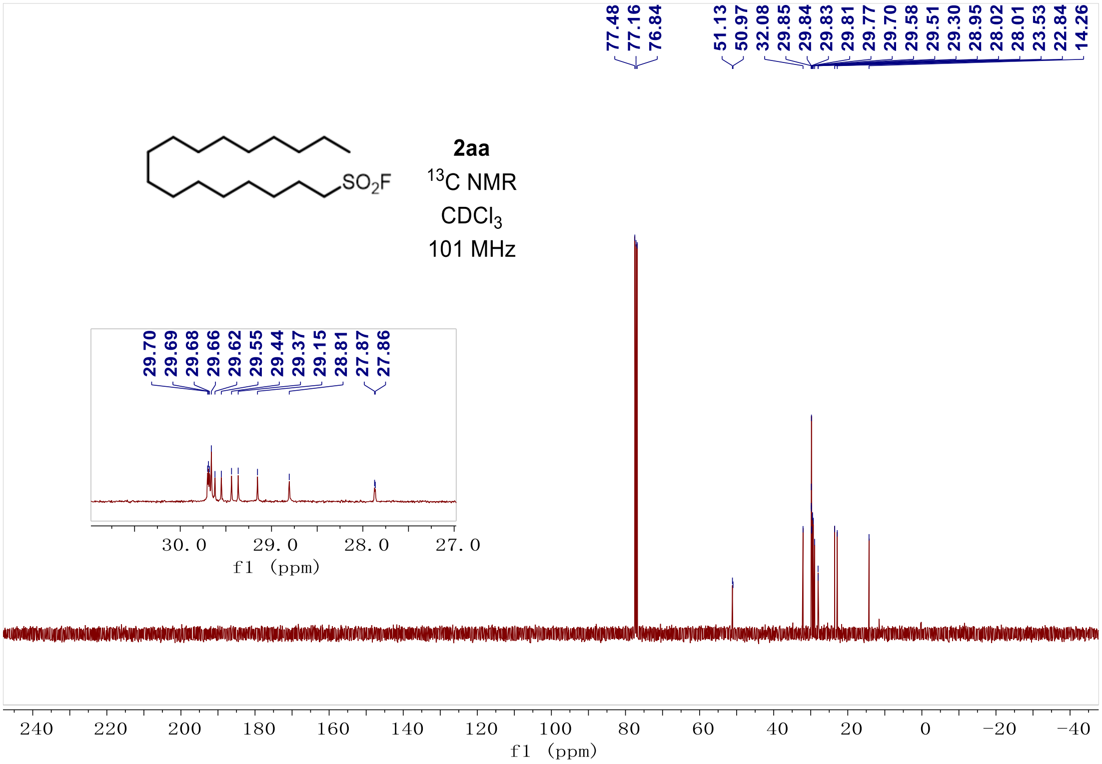

7.26
5.42
5.40
5.37
5.36
5.34
5.31
5.29
3.38
3.37
3.35
3.34
3.33
2.78
2.77
2.75
2.06
2.04
2.02
1.97
1.95
1.93
1.50
1.48
1.46
1.34
1.30
0.90
0.89
SO2F
2z
1H NMR
CDCl3
400 MHz
3.70
1.86
1.89
3.73
2.14
2.01
12.25
3.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)


53.21
53.20
53.19
53.17
53.16
53.15
SO2F
2z
19F NMR
CDCl3
376 MHz
1.00
0.08
53.30
53.20
53.10
53.00
f1 (ppm)
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
f1 (ppm)


130.42
129.87
128.44
127.94
77.48
77.16
76.84
51.09
50.93
31.67
29.55
29.47
28.91
28.86
27.97
27.35
27.20
25.77
23.51
22.71
14.20
H3C
O
S
F
O
2z
13C NMR
CDCl3
101 MHz
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
−40
f1 (ppm)


7.26 3.38 3.37 3.36 3.35 3.35 3.34 3.33 1.98 1.97 1.96 1.96 1.95 1.95 1.94 1.93 1.93 1.92 1.91 1.51 1.49 1.47 1.45 1.44 1.37 1.35 1.33 1.32 1.31 1.30 1.28 1.27 1.25 0.89 0.88 0.86
SO2F
2aa
1H NMR
CDCl3
400 MHz
1.97 2.00 2.14 26.33 2.99
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)


53.16 53.15 53.14 53.12 53.11 53.10
SO2F
2aa
19F NMR
CDCl3
376 MHz
53.16 53.15 53.14 53.12 53.11 53.10
1.00 0.06
53.35 53.25 53.15 53.05 52.95
f1 (ppm)
1.00 0.06
80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200
f1 (ppm)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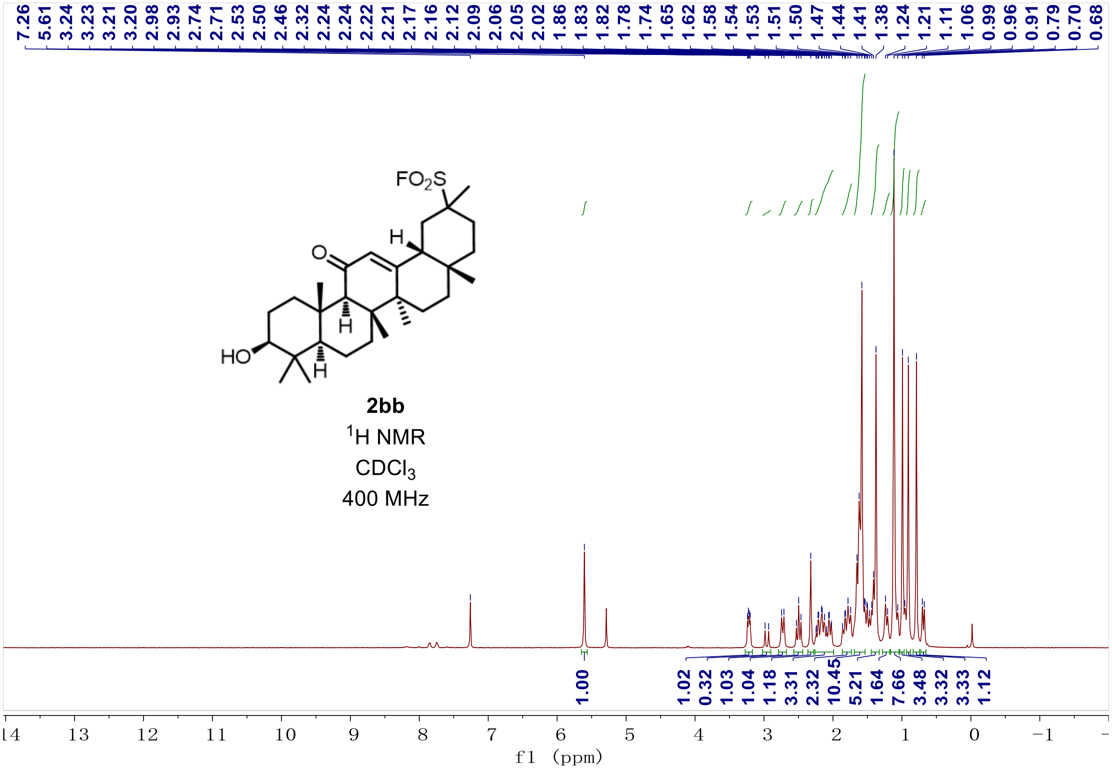
77.16
76.84
51.13
50.97
32.08
29.85
29.84
29.83
29.81
29.77
29.70
29.58
29.51
29.30
28.95
28.02
28.01
23.53
22.84
14.26
SO$_2$F
2aa
^{13}C NMR
CDCl$_3$
101 MHz
29.70
29.69
29.68
29.66
29.62
29.55
29.44
29.37
29.15
28.81
27.87
27.86
30.0
29.0
28.0
27.0
f1 (ppm)
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
f1 (ppm)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3.24
3.23
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3.20
2.98
2.93
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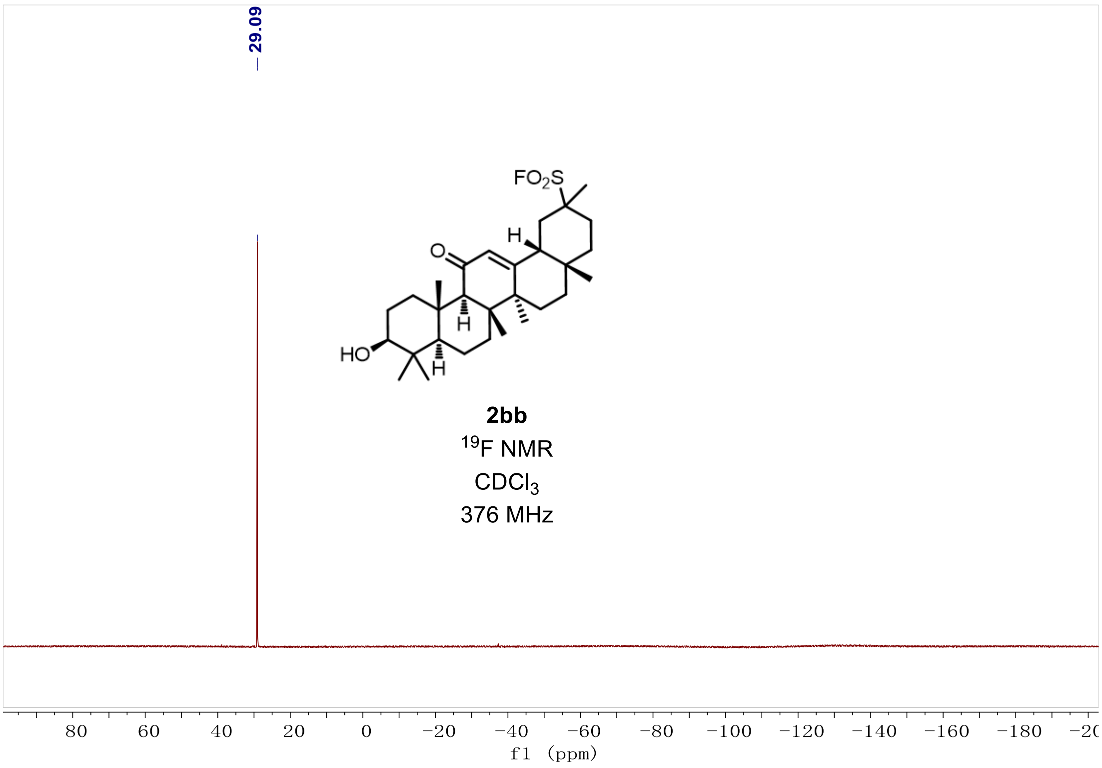
2.71
2.53
2.50
2.46
2.32
2.24
2.24
2.22
2.21
2.17
2.16
2.12
2.09
2.06
2.05
2.02
1.86
1.83
1.82
1.78
1.74
1.65
1.62
1.58
1.54
1.53
1.51
1.50
1.47
1.44
1.41
1.38
1.24
1.21
1.11
1.06
0.99
0.96
0.91
0.79
0.70
0.68
FO$_2$S
H
O
H
HO
H
2bb
^{1}H NMR
CDCl$_3$
400 MHz
1.00
1.02
0.32
1.03
1.04
1.18
3.31
2.32
10.45
5.21
1.64
7.66
3.48
3.32
3.33
1.12
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

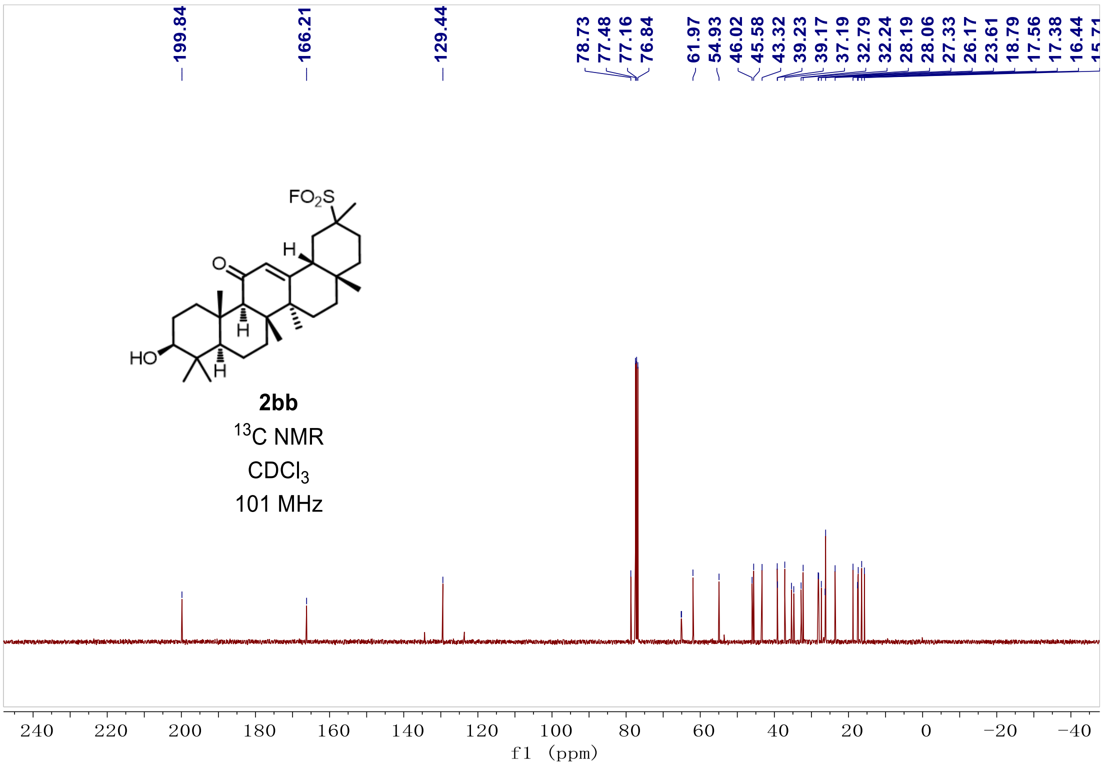


2bb

^{19}F NMR

$CDCl_3$

376 MHz

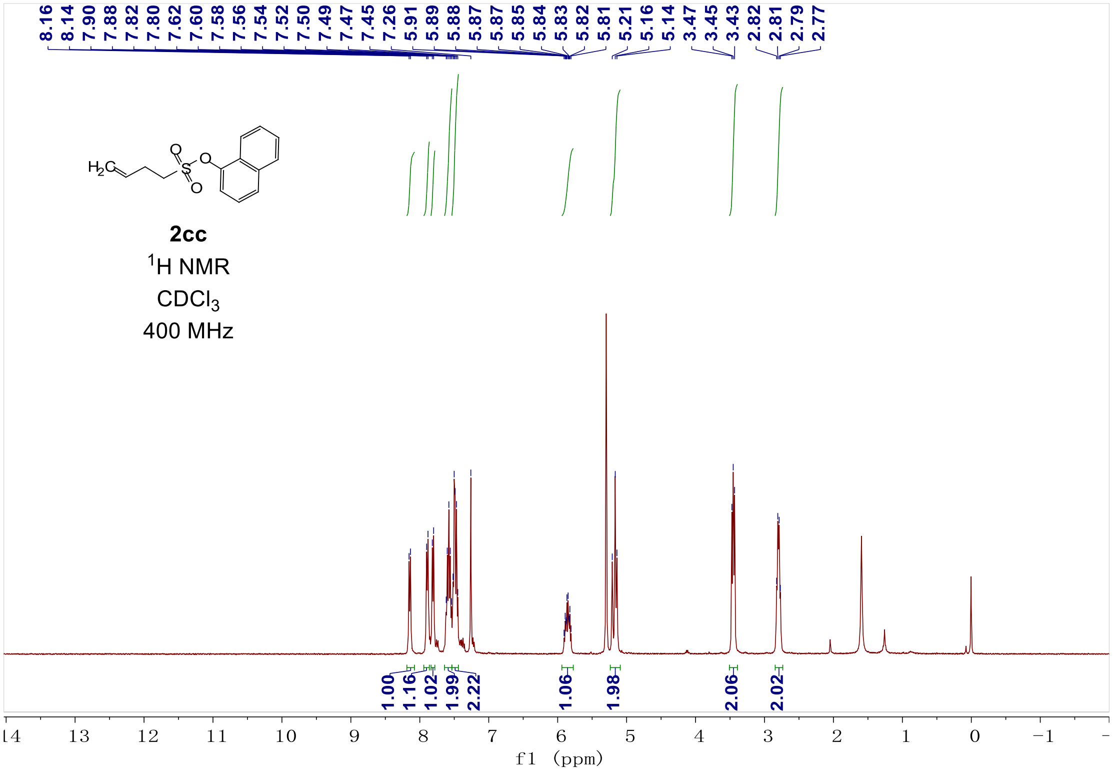


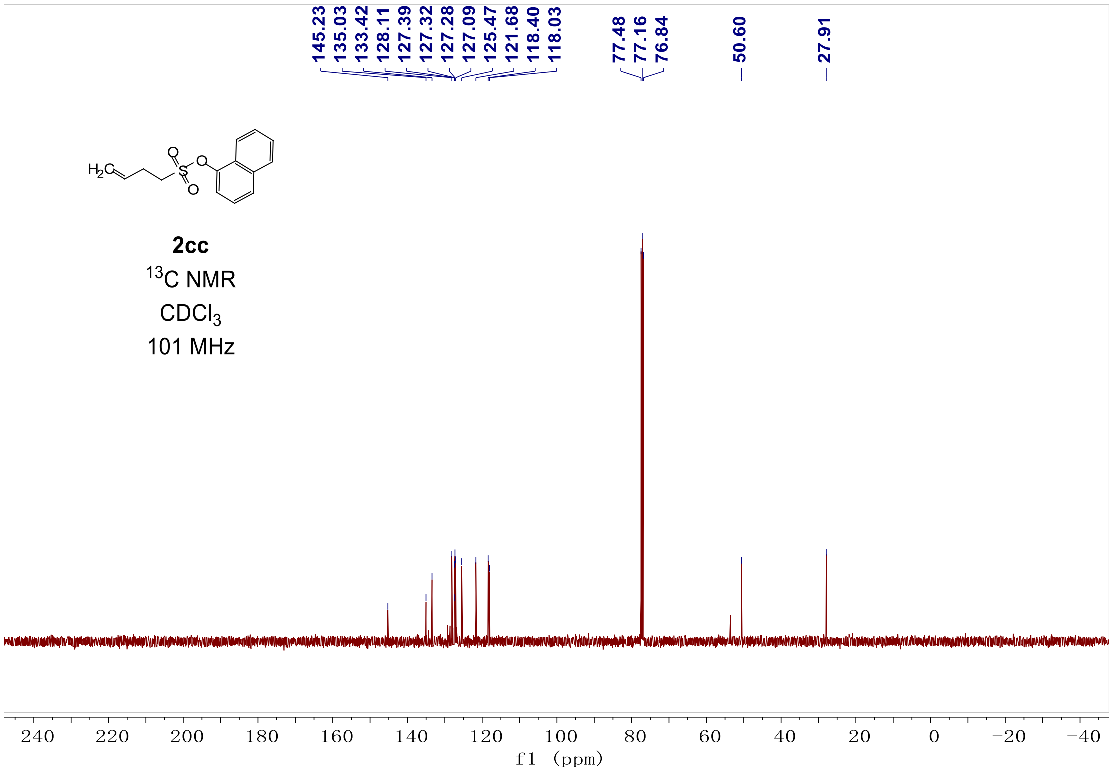
2bb

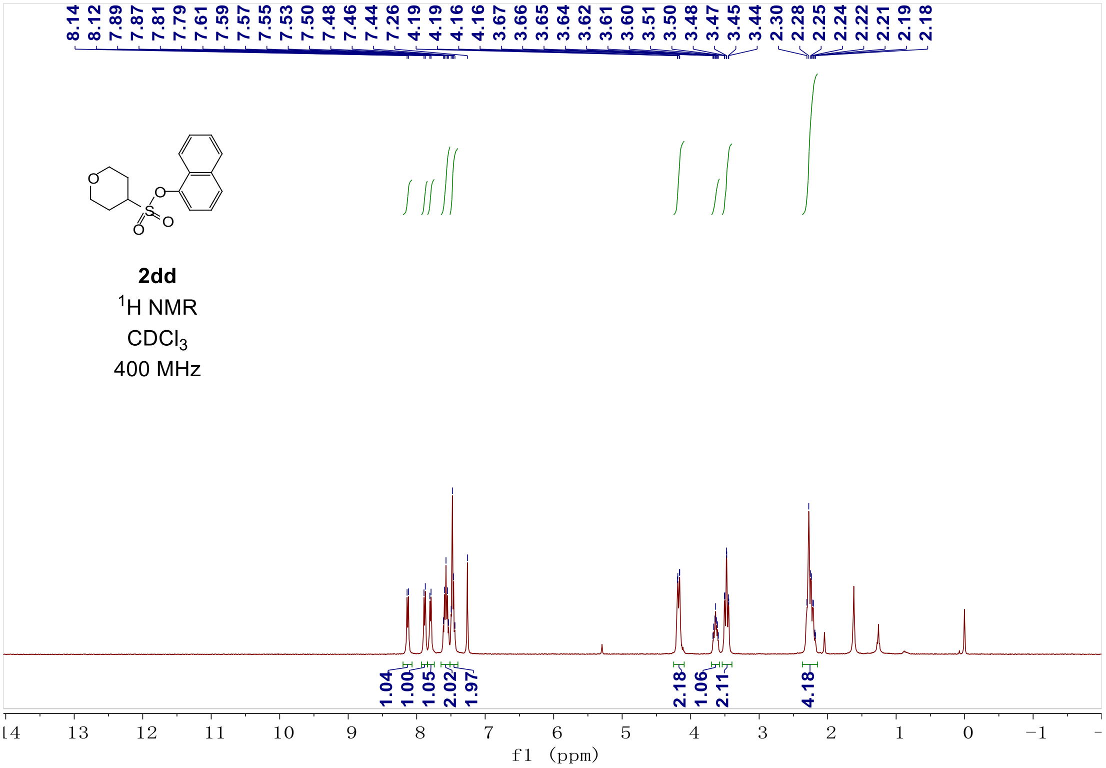
^{13}C NMR

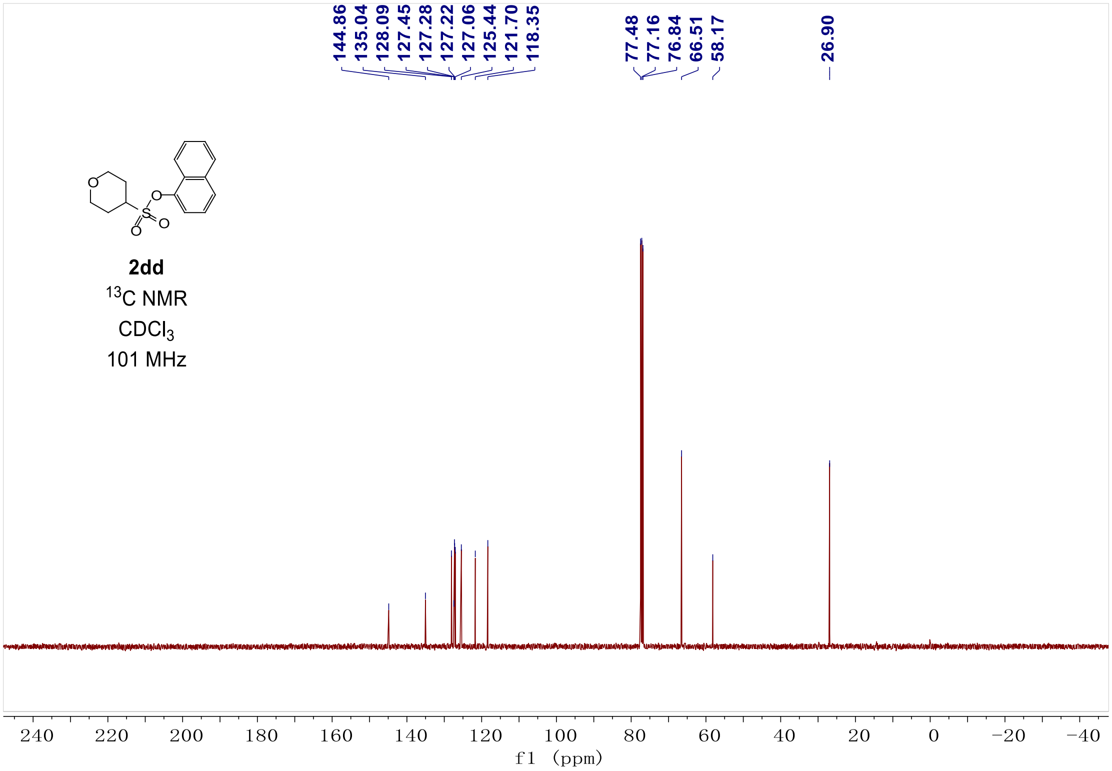
$CDCl_3$

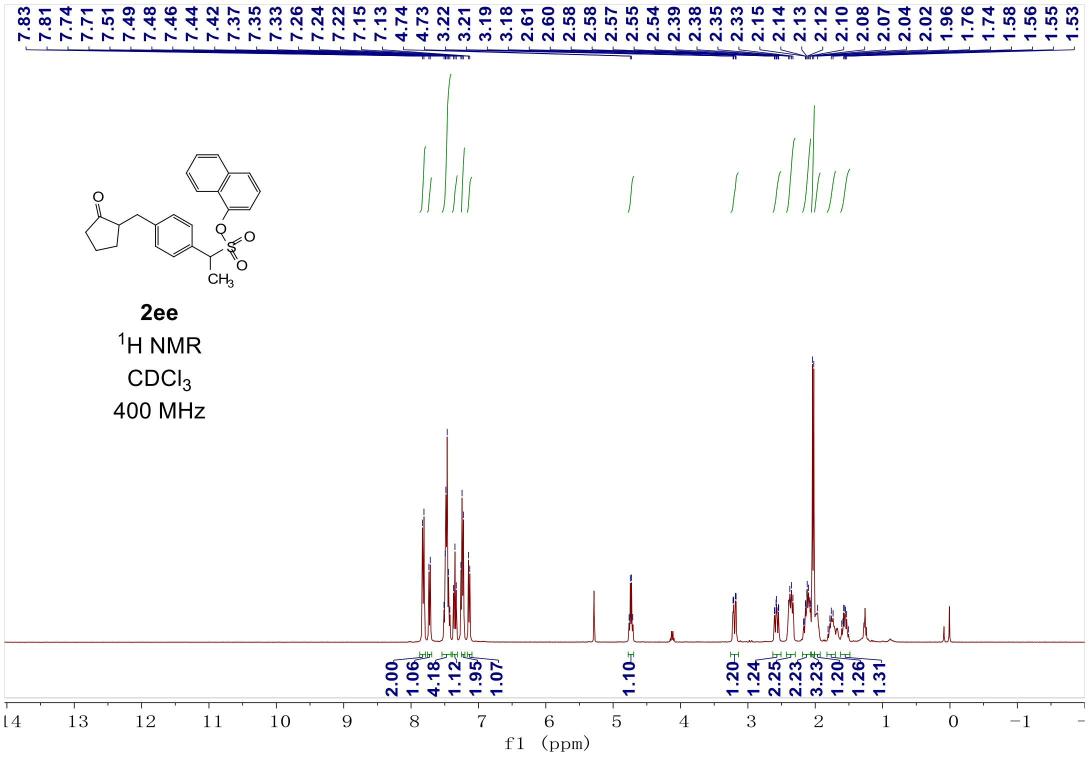
101 MHz


8.16
8.14
7.90
7.88
7.82
7.80
7.62
7.60
7.58
7.56
7.54
7.52
7.50
7.49
7.47
7.45
7.26
5.91
5.89
5.88
5.87
5.87
5.85
5.84
5.83
5.82
5.81
5.21
5.16
5.14
3.47
3.45
3.43
2.82
2.81
2.79
2.77
H2C
O
S
O
O
2cc
1H NMR
CDCl3
400 MHz
1.00
1.16
1.02
1.99
2.22
1.06
1.98
2.06
2.02
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)


145.23
135.03
133.42
128.11
127.39
127.32
127.28
127.09
125.47
121.68
118.40
118.03
77.48
77.16
76.84
50.60
27.91
H2C
O
S
O
O
2cc
13C NMR
CDCl3
101 MHz
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
−40
f1 (ppm)


8.14 8.12 7.89 7.87 7.81 7.79 7.61 7.59 7.57 7.55 7.53 7.50 7.48 7.46 7.44 7.26 4.19 4.19 4.16 4.16 3.67 3.66 3.65 3.64 3.62 3.61 3.60 3.51 3.50 3.48 3.47 3.45 3.44 2.30 2.28 2.25 2.24 2.22 2.21 2.19 2.18
O
S
O
O
O
2dd
^{1}H NMR
$CDCl_3$
400 MHz
1.04 1.00 1.05 2.02 1.97 2.18 1.06 2.11 4.18
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)


144.86 135.04 128.09 127.45 127.28 127.22 127.06 125.44 121.70 118.35
77.48 77.16 76.84 66.51 58.17
26.90
O
S
O
O
O
2dd
^{13}C NMR
$CDCl_3$
101 MHz
240 220 200 180 160 140 120 100 80 60 40 20 0 −20 −40
f1 (ppm)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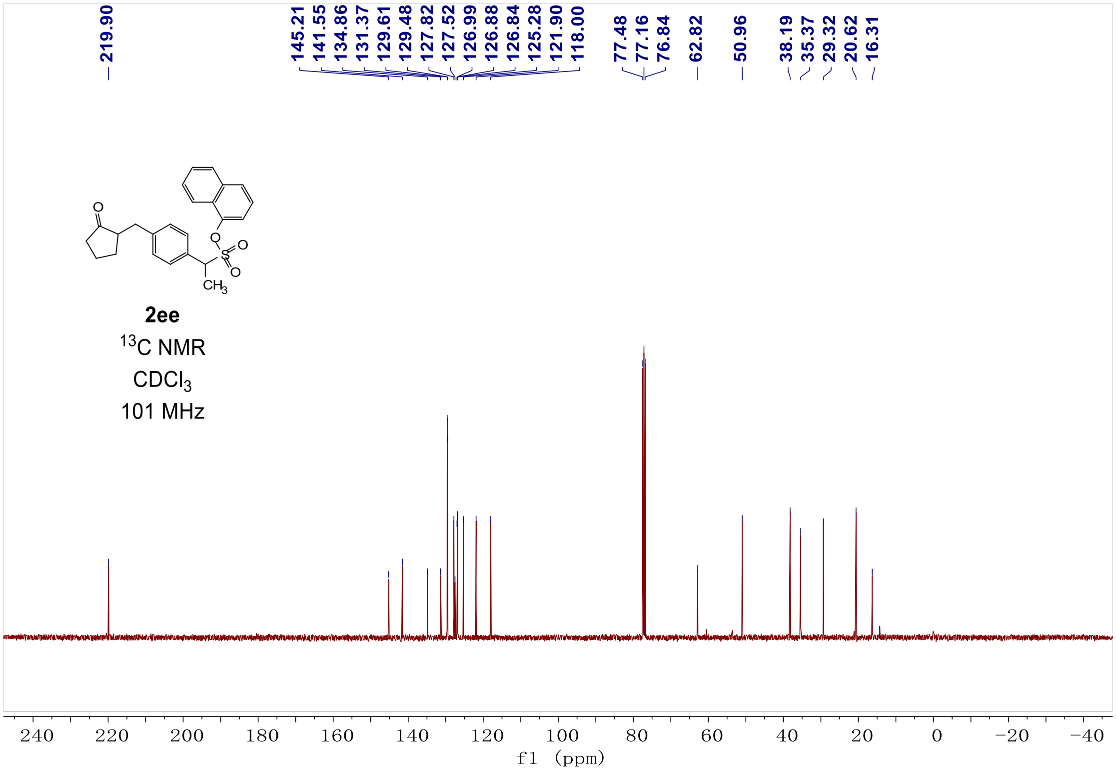
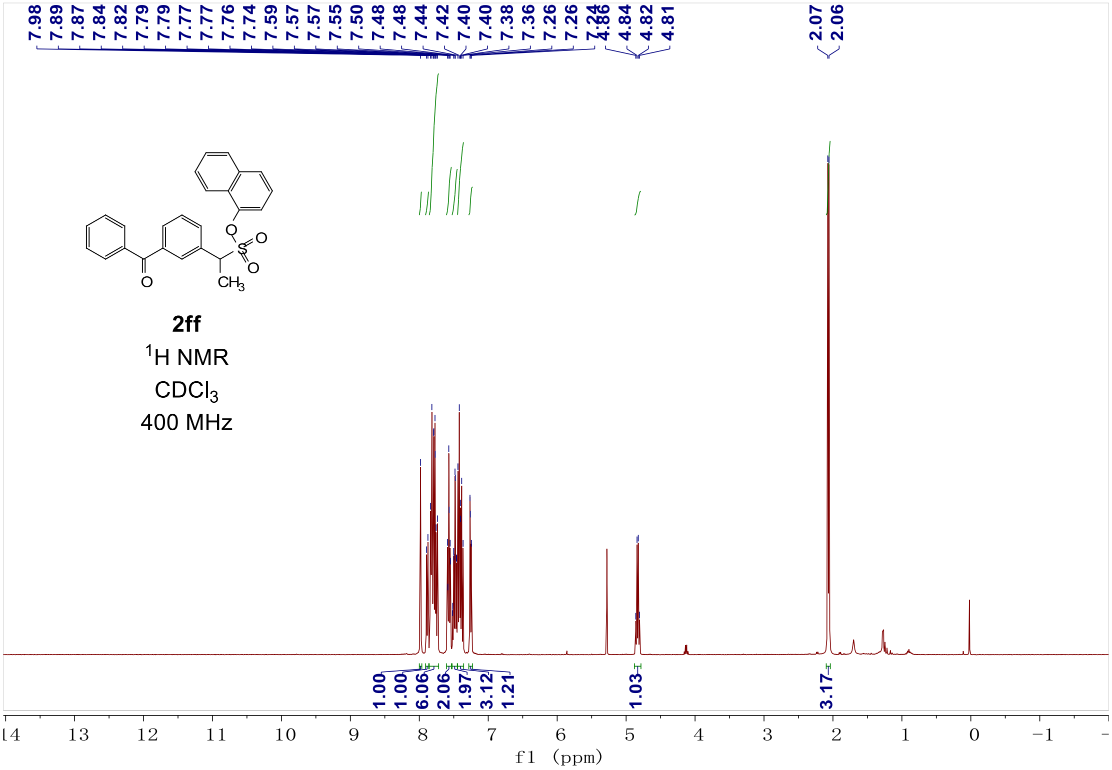
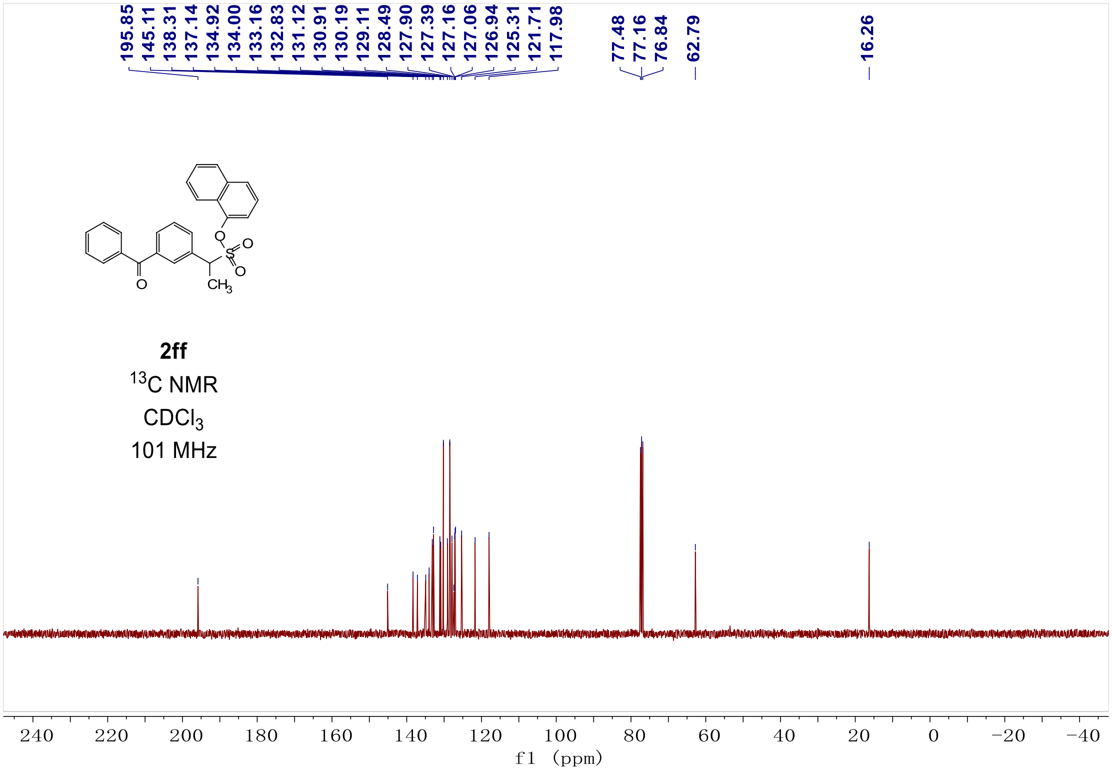
7.81
7.74
7.71
7.51
7.49
7.48
7.46
7.44
7.42
7.37
7.35
7.33
7.26
7.24
7.22
7.15
7.13
4.74
4.73
3.22
3.21
3.19
3.18
2.61
2.60
2.58
2.58
2.57
2.55
2.54
2.39
2.38
2.35
2.33
2.15
2.14
2.13
2.12
2.10
2.08
2.07
2.04
2.02
1.96
1.76
1.74
1.58
1.56
1.55
1.53
2ee
^{1}H NMR
CDCl$_3$
400 MHz
2.00
1.06
4.18
1.12
1.95
1.07
1.10
1.20
1.24
2.25
2.23
3.23
1.20
1.26
1.31
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)


219.90
145.21
141.55
134.86
131.37
129.61
129.48
127.82
127.52
126.99
126.88
126.84
125.28
121.90
118.00
77.48
77.16
76.84
62.82
50.96
38.19
35.37
29.32
20.62
16.31
2ee
^{13}C NMR
CDCl$_3$
101 MHz
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
−40
f1 (ppm)


7.98
7.89
7.87
7.84
7.82
7.79
7.79
7.77
7.77
7.76
7.74
7.59
7.57
7.57
7.55
7.50
7.48
7.48
7.44
7.42
7.40
7.40
7.38
7.36
7.26
7.26
7.24
4.86
4.84
4.82
4.81
2.07
2.06
O
S
O
O
O
CH3
2ff
1H NMR
CDCl3
400 MHz
1.00
1.00
6.06
2.06
1.97
3.12
1.21
1.03
3.17
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
f1 (ppm)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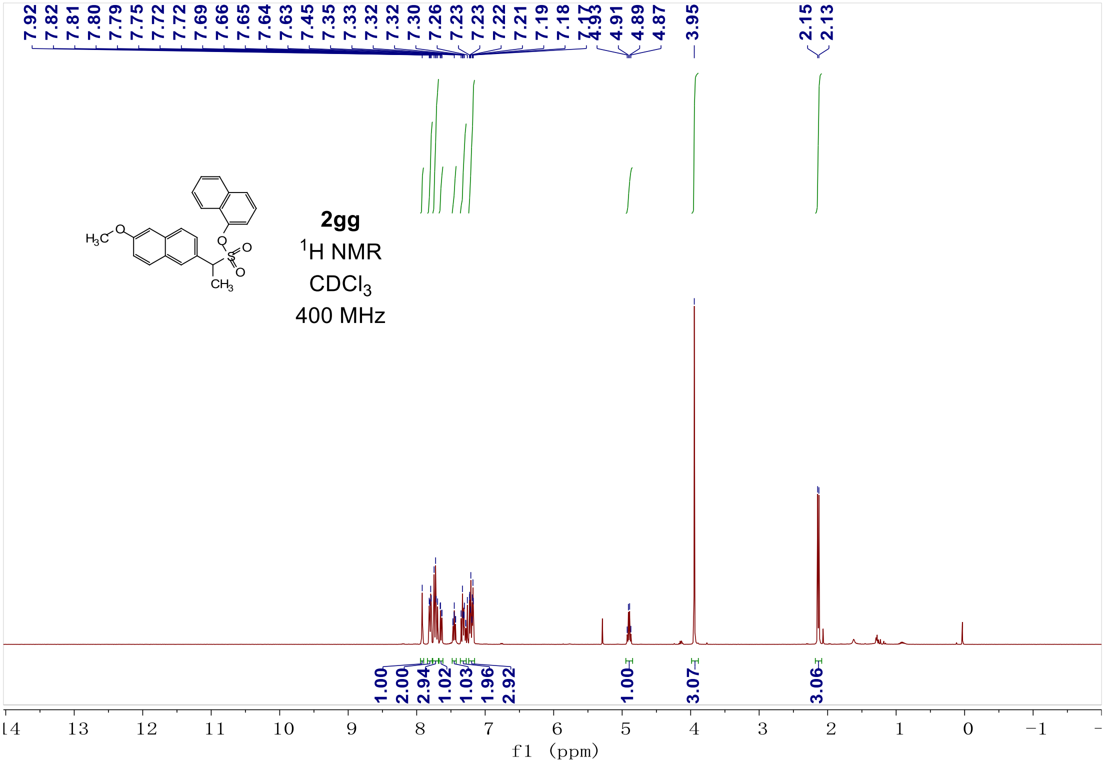
145.11
138.31
137.14
134.92
134.00
133.16
132.83
131.12
130.91
130.19
129.11
128.49
127.90
127.39
127.16
127.06
126.94
125.31
121.71
117.98
77.48
77.16
76.84
62.79
16.26
O
S
O
O
O
CH3
2ff
13C NMR
CDCl3
101 MHz
240 220 200 180 160 140 120 100 80 60 40 20 0 −20 −40
f1 (ppm)


7.92
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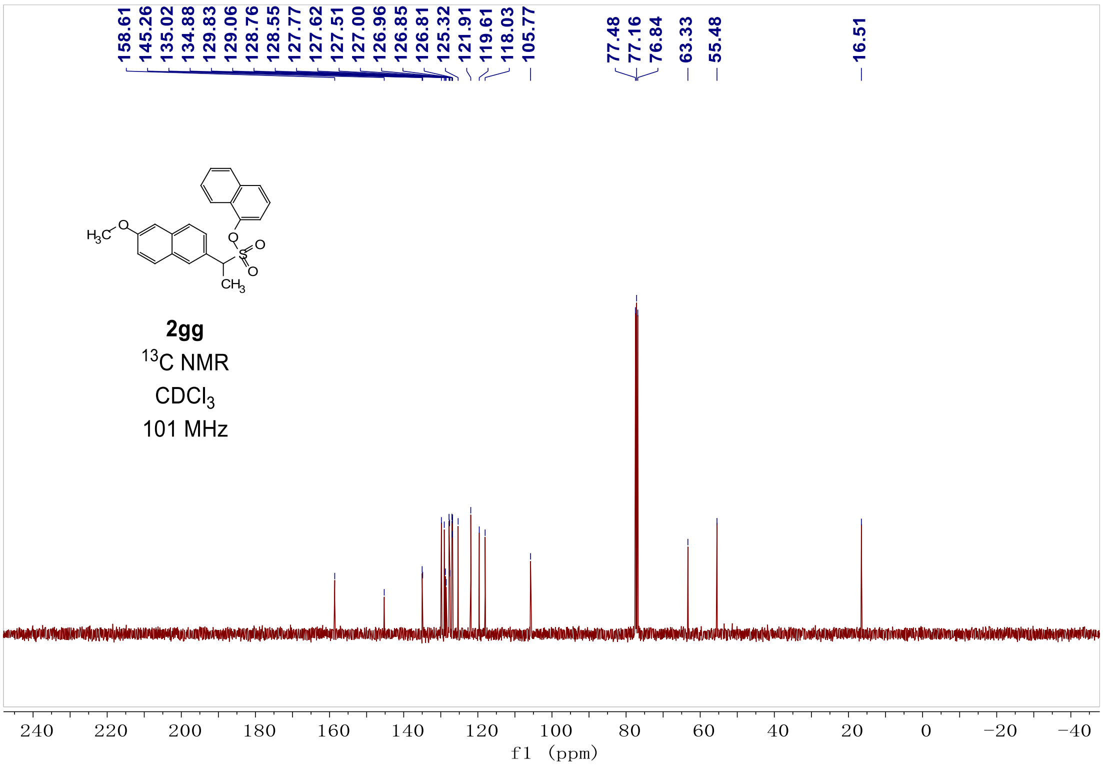
7.81
7.80
7.79
7.75
7.72
7.72
7.69
7.66
7.65
7.64
7.63
7.45
7.35
7.33
7.32
7.32
7.30
7.26
7.23
7.23
7.22
7.21
7.19
7.18
7.17
4.93
4.91
4.89
4.87
3.95
2.15
2.13
H_3C
O
S
O
O
CH_3
2gg
^{1}H NMR
$CDCl_3$
400 MHz
1.00
2.00
2.94
1.02
1.03
1.96
2.92
1.00
3.07
3.06
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)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134.88
129.83
129.06
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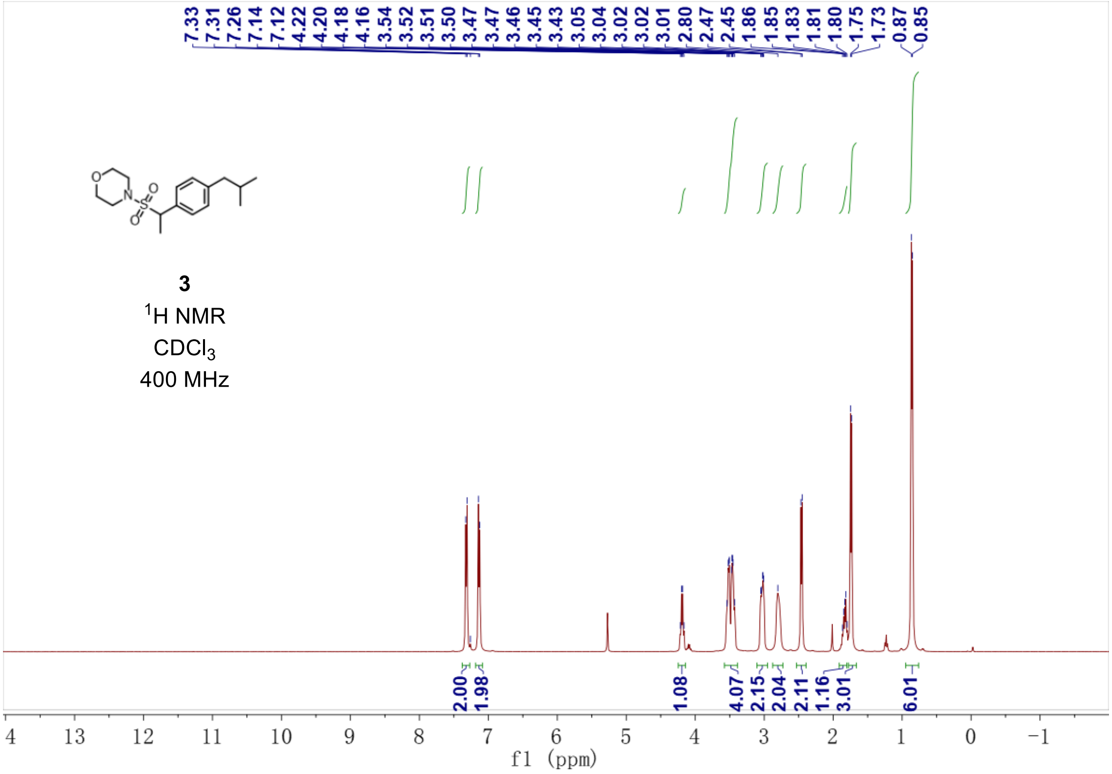
128.55
127.77
127.62
127.51
127.00
126.96
126.85
126.81
125.32
121.91
119.61
118.03
105.77
77.48
77.16
76.84
63.33
55.48
16.51
H_3C
O
O
S
O
O
CH_3
2gg
^{13}C NMR
$CDCl_3$
101 MHz
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
−40
f1 (ppm)

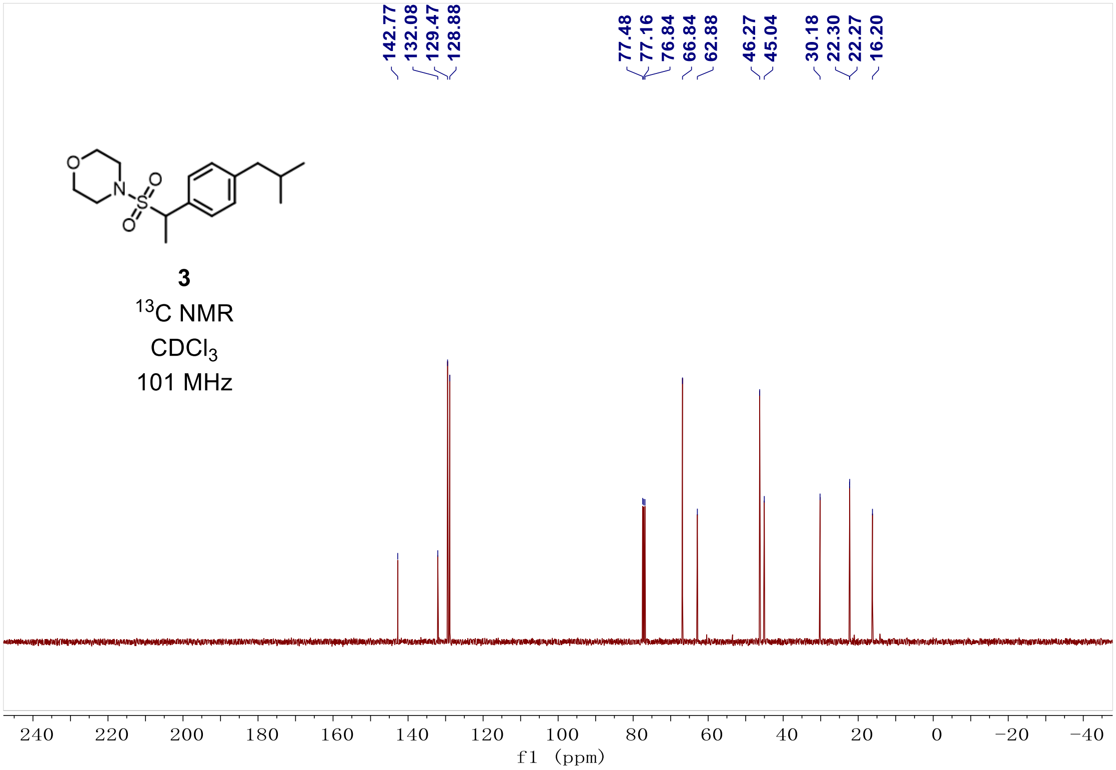


3

^{1}H NMR

$CDCl_3$

400 MHz

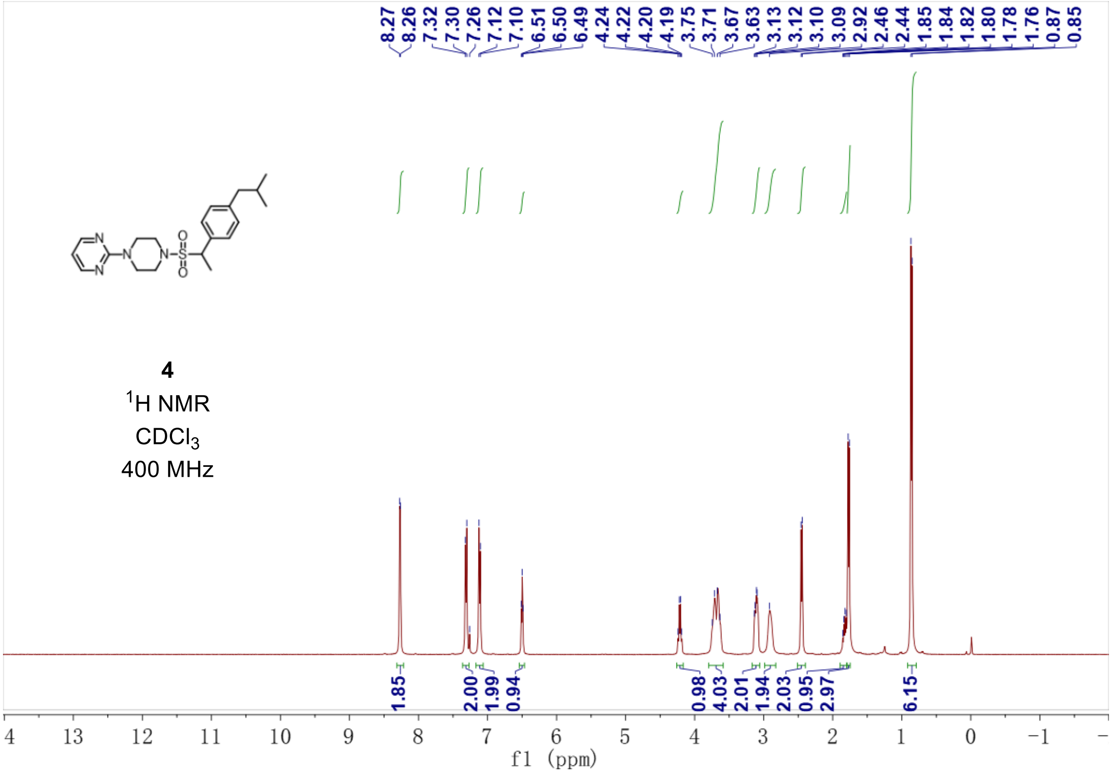


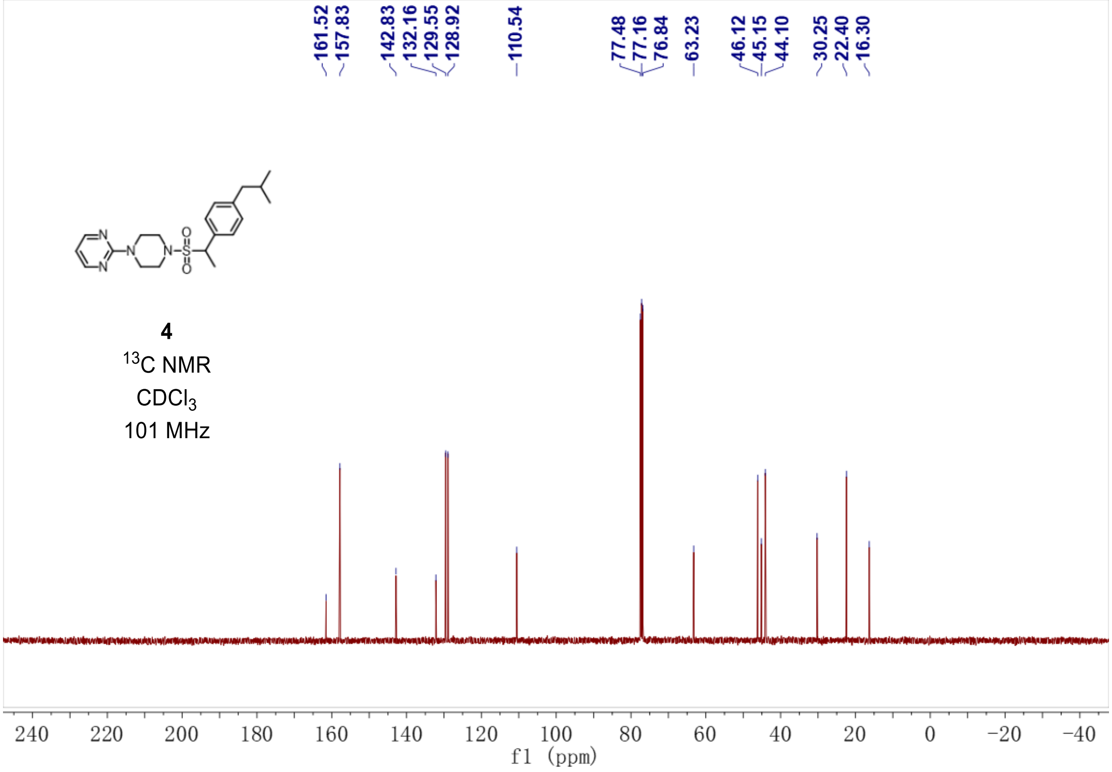
3

^{13}C NMR

$CDCl_3$

101 MHz


8.27
8.26
7.32
7.30
7.26
7.12
7.10
6.51
6.50
6.49
4.24
4.22
4.20
4.19
3.75
3.71
3.67
3.63
3.13
3.12
3.10
3.09
2.92
2.46
2.44
1.85
1.84
1.82
1.80
1.78
1.76
0.87
0.85
4
^{1}H NMR
CDCl$_3$
400 MHz
1.85
2.00
1.99
0.94
0.98
4.03
2.01
1.94
2.03
0.95
2.97
6.15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)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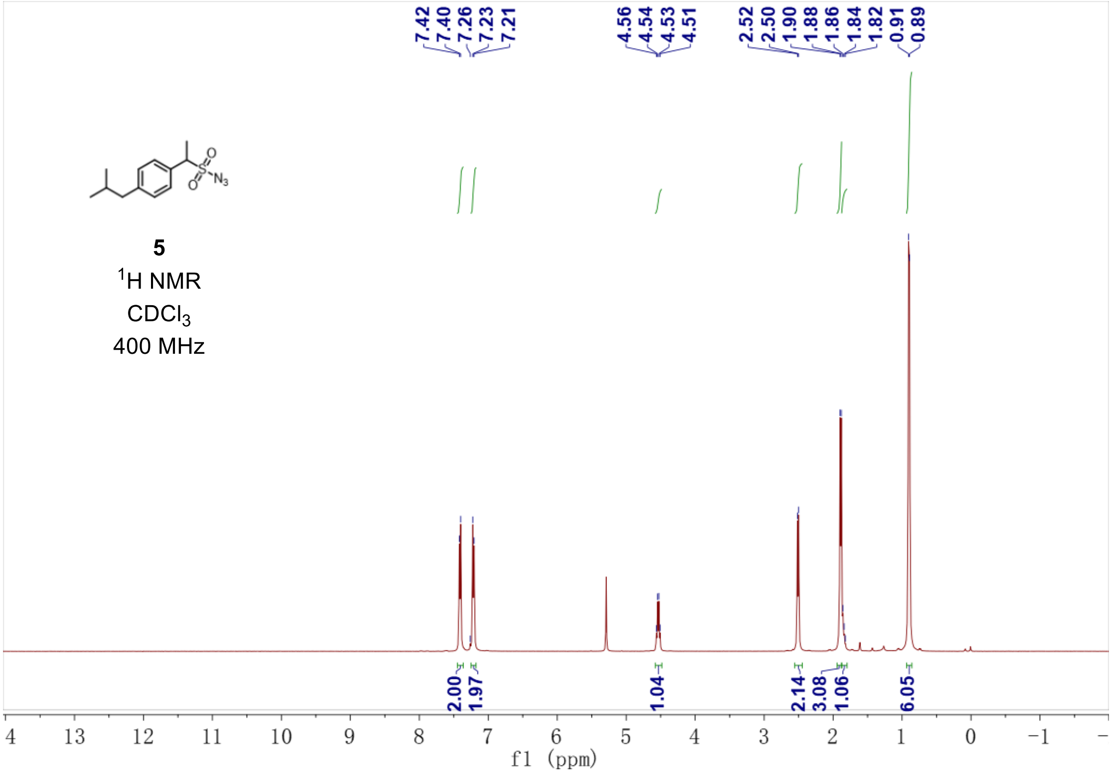
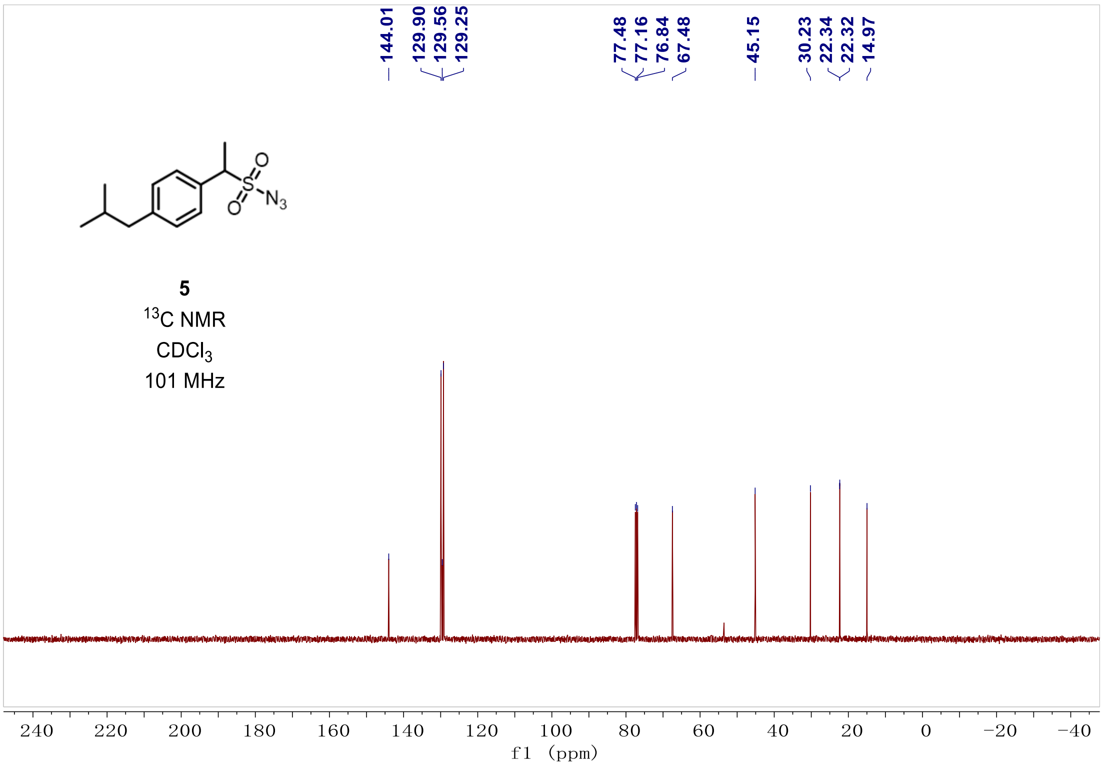
157.83
142.83
132.16
129.55
128.92
110.54
77.48
77.16
76.84
63.23
46.12
45.15
44.10
30.25
22.40
16.30
4
^{13}C NMR
CDCl$_3$
101 MHz
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
−40
f1 (ppm)


7.42
7.40
7.26
7.23
7.21
4.56
4.54
4.53
4.51
2.52
2.50
1.90
1.88
1.86
1.84
1.82
0.91
0.89
O
S
N3
O
5
^{1}H NMR
CDCl$_3$
400 MHz
2.00
1.97
1.04
2.14
3.08
1.06
6.05
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−
f1 (ppm)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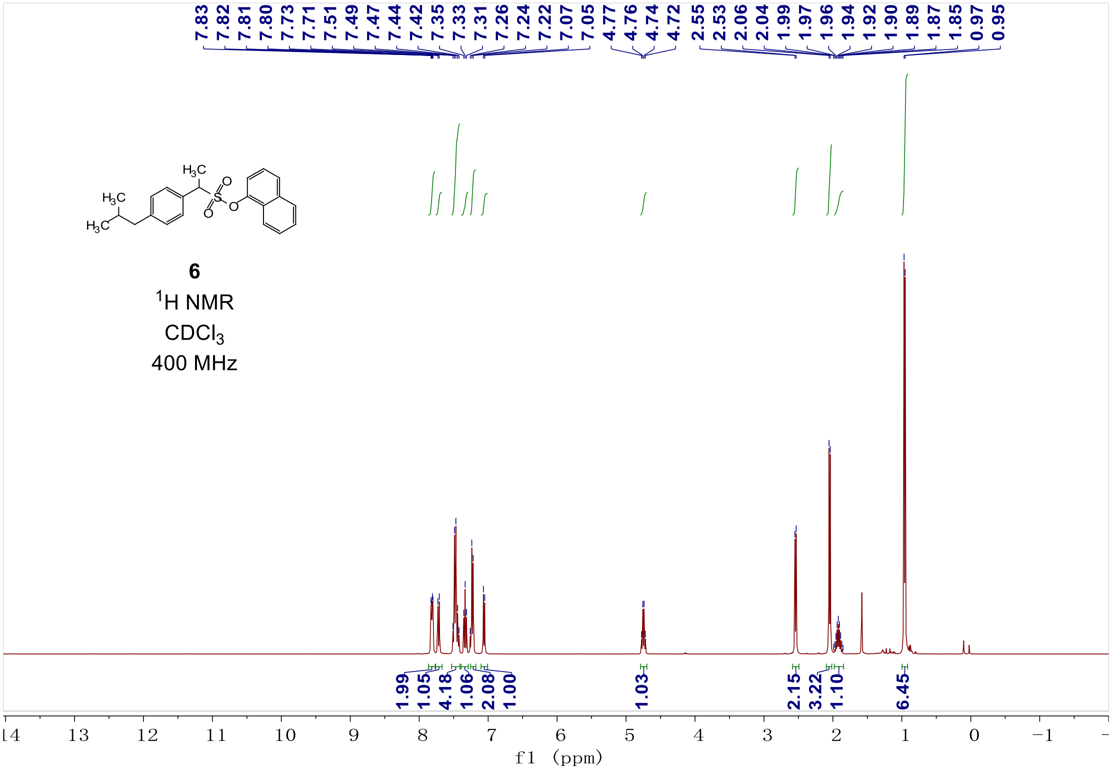
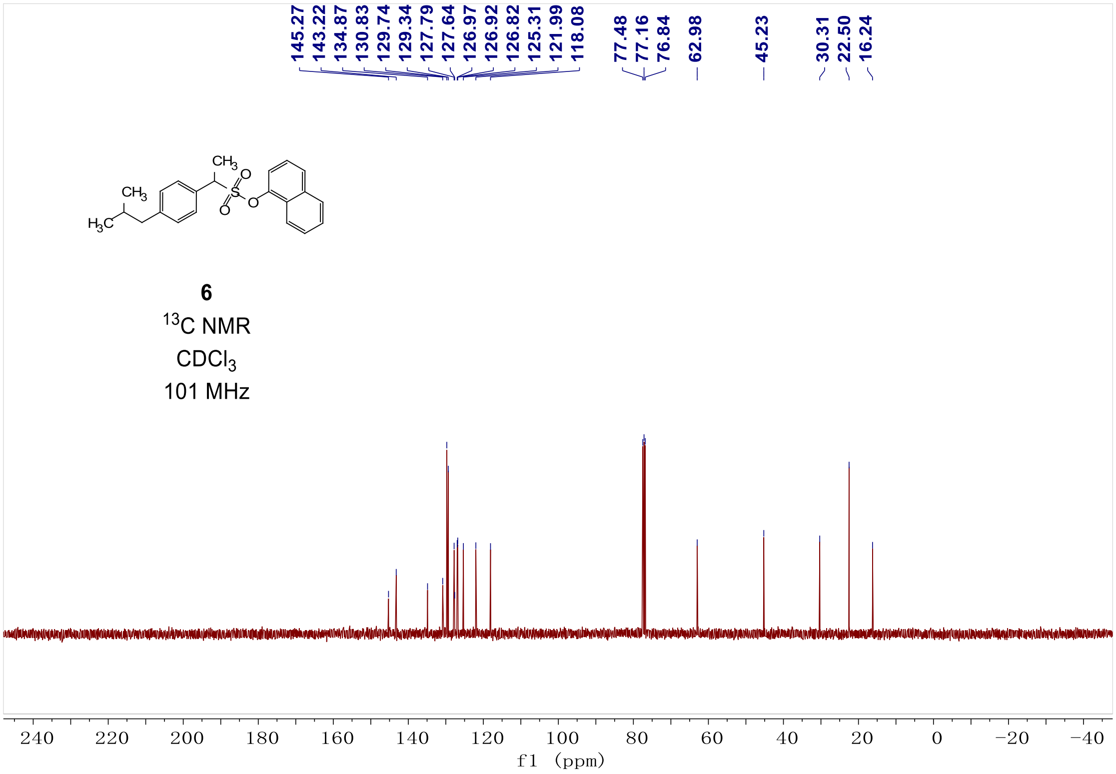
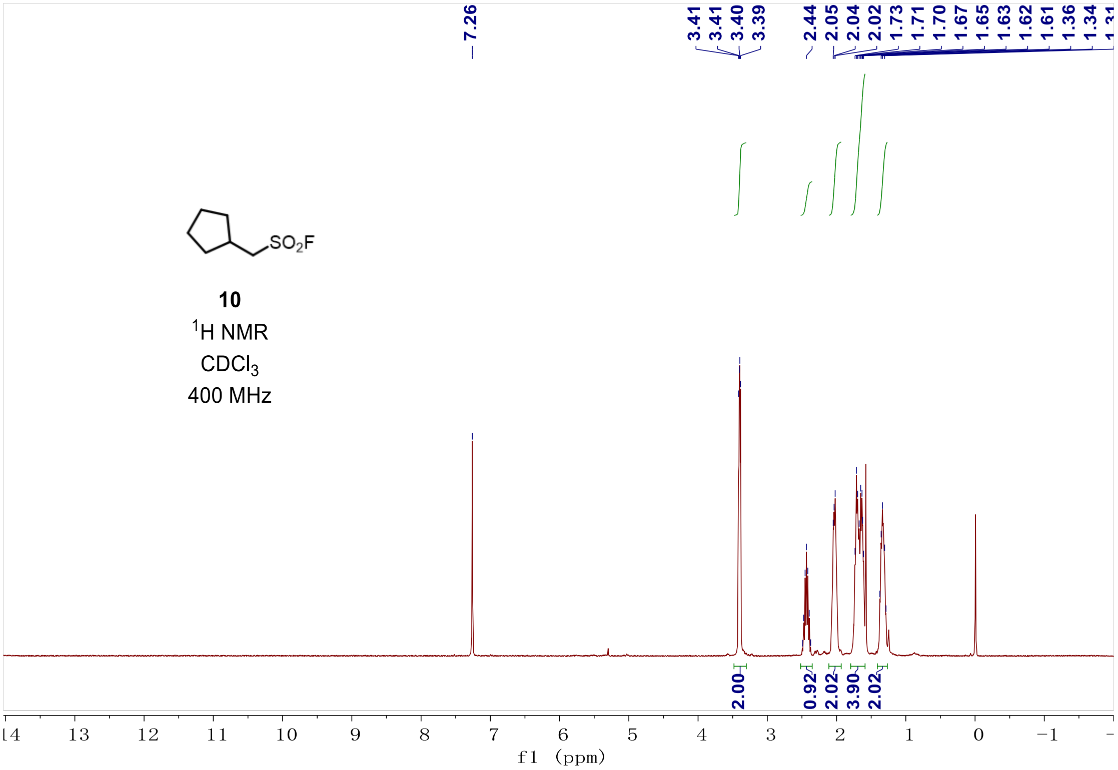
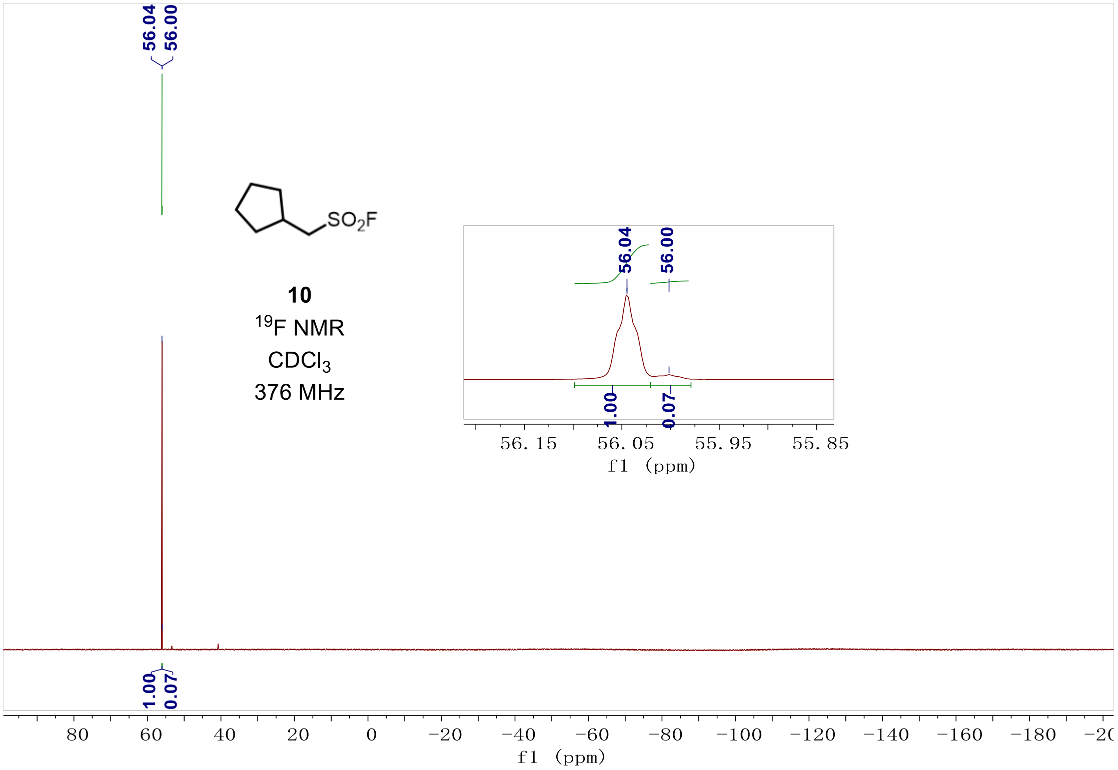
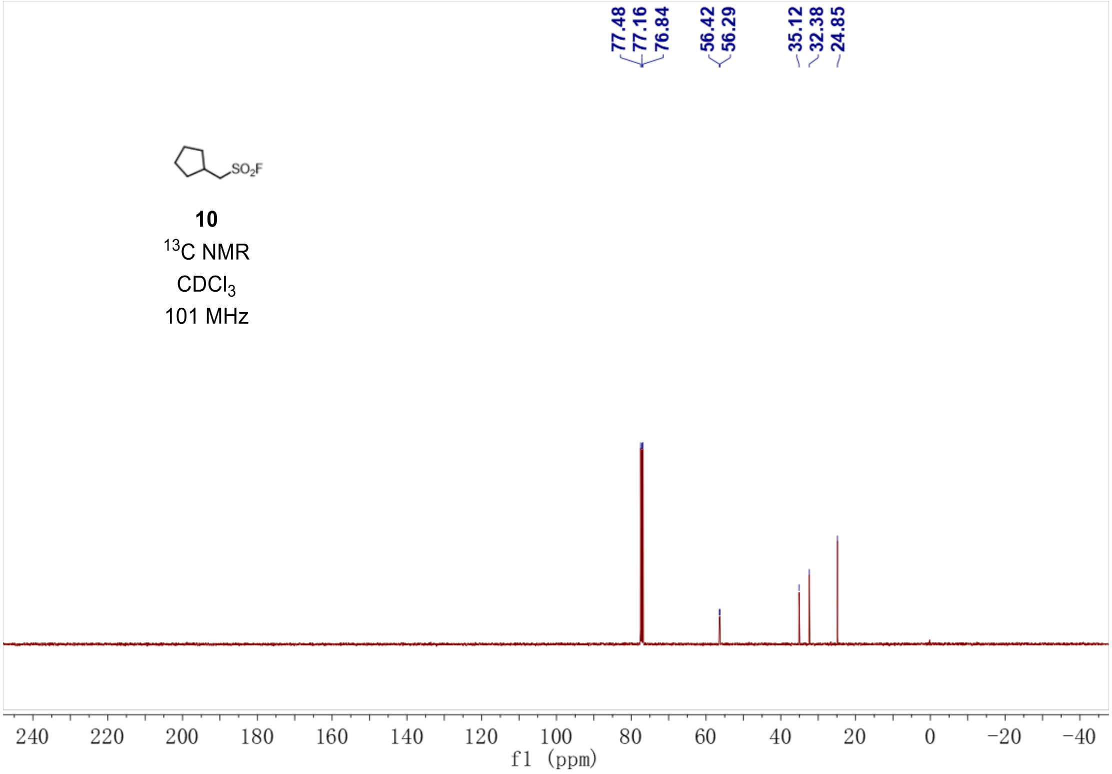
129.90
129.56
129.25
77.48
77.16
76.84
67.48
45.15
30.23
22.34
22.32
14.97
O
S
N3
O
5
^{13}C NMR
CDCl$_3$
101 MHz
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
−40
f1 (ppm)

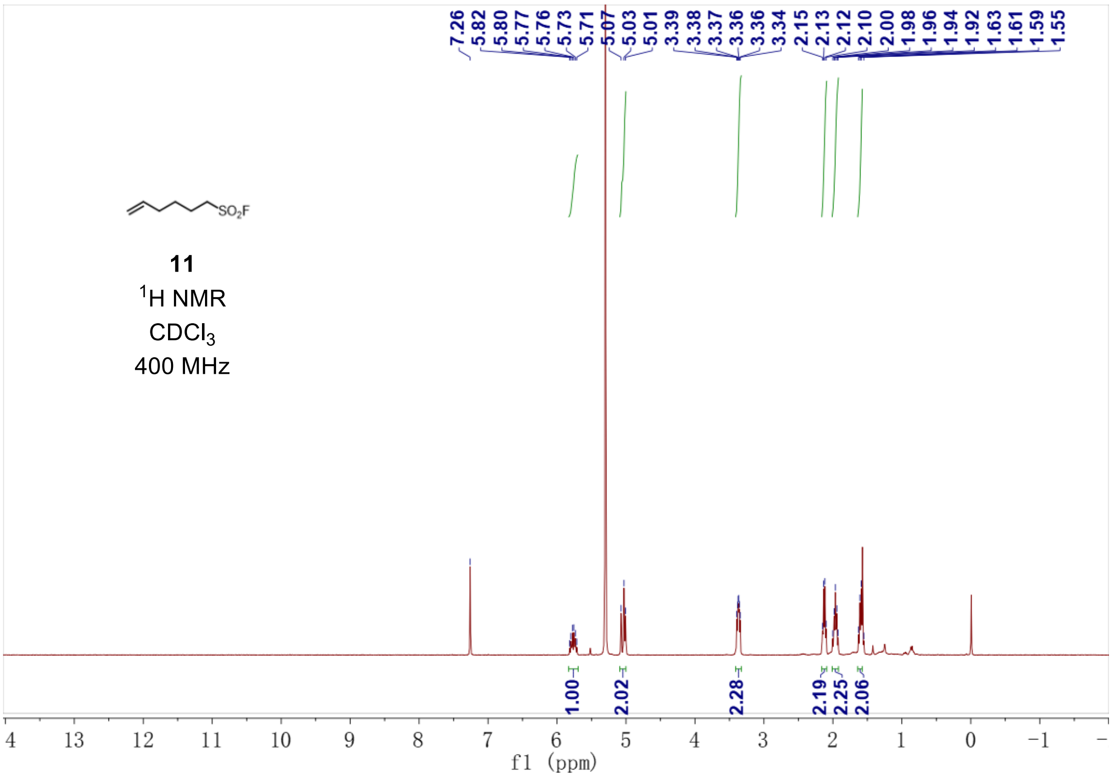

7.83
7.82
7.81
7.80
7.73
7.71
7.51
7.49
7.47
7.44
7.42
7.35
7.33
7.31
7.26
7.24
7.22
7.07
7.05
4.77
4.76
4.74
4.72
2.55
2.53
2.06
2.04
1.99
1.97
1.96
1.94
1.92
1.90
1.89
1.87
1.85
0.97
0.95
H3C
H3C
H3C
O
S
O
O
6
1H NMR
CDCl3
400 MHz
1.99
1.05
4.18
1.06
2.08
1.00
1.03
2.15
3.22
1.10
6.45
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


145.27
143.22
134.87
130.83
129.74
129.34
127.79
127.64
126.97
126.92
126.82
125.31
121.99
118.08
77.48
77.16
76.84
62.98
45.23
30.31
22.50
16.24
CH3
CH3
H3C
O
S
O
O
6
13C NMR
CDCl3
101 MHz
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
f1 (ppm)


SO2F
10
1H NMR
CDCl3
400 MHz
7.26
3.41
3.41
3.40
3.39
2.44
2.05
2.04
2.02
1.73
1.71
1.70
1.67
1.65
1.63
1.62
1.61
1.36
1.34
2.00
0.92
2.02
3.90
2.02
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)


56.04
56.00
SO2F
10
19F NMR
CDCl3
376 MHz
56.04
56.00
1.00
0.07
56.15
56.05
55.95
55.85
f1 (ppm)
1.00
0.07
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
f1 (ppm)


77.48
77.16
76.84
56.42
56.29
35.12
32.38
24.85
SO2F
10
13C NMR
CDCl3
101 MHz
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
−40
f1 (ppm)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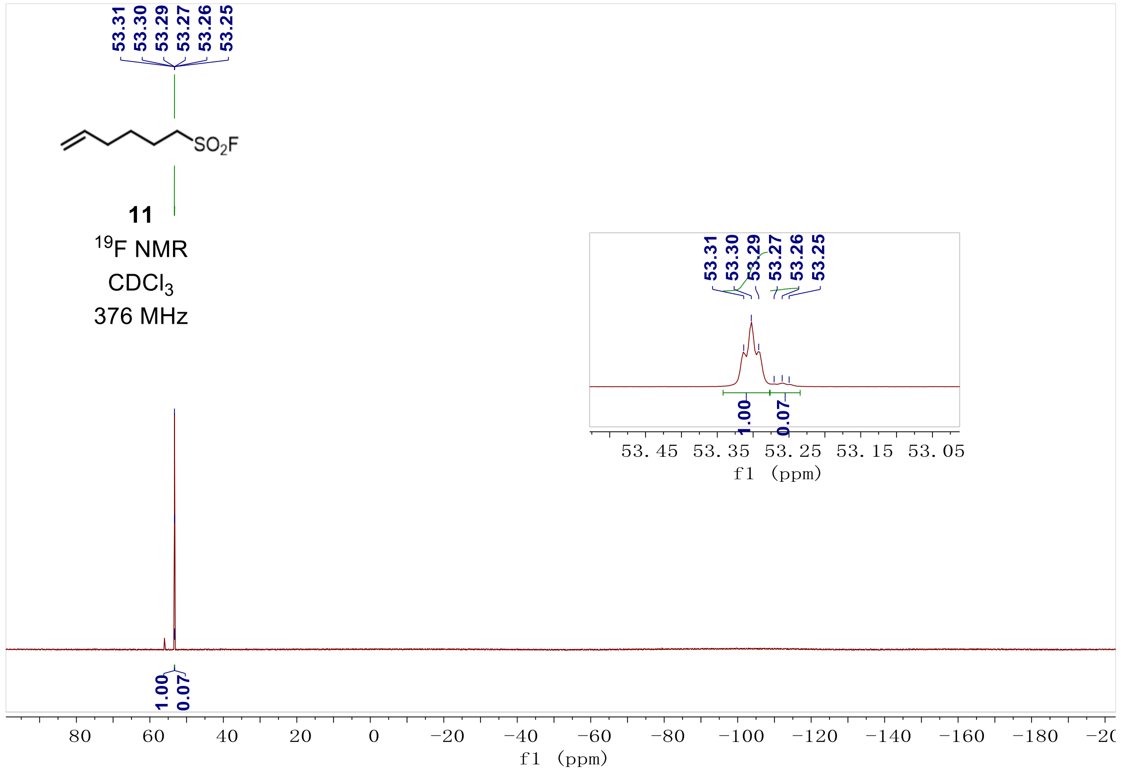
5.82
5.80
5.77
5.76
5.73
5.71
5.07
5.03
5.01
3.39
3.38
3.37
3.36
3.36
3.34
2.15
2.13
2.12
2.10
2.00
1.98
1.96
1.94
1.92
1.63
1.61
1.59
1.55
SO2F
11
1H NMR
CDCl3
400 MHz
1.00
2.02
2.28
2.19
2.25
2.06
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)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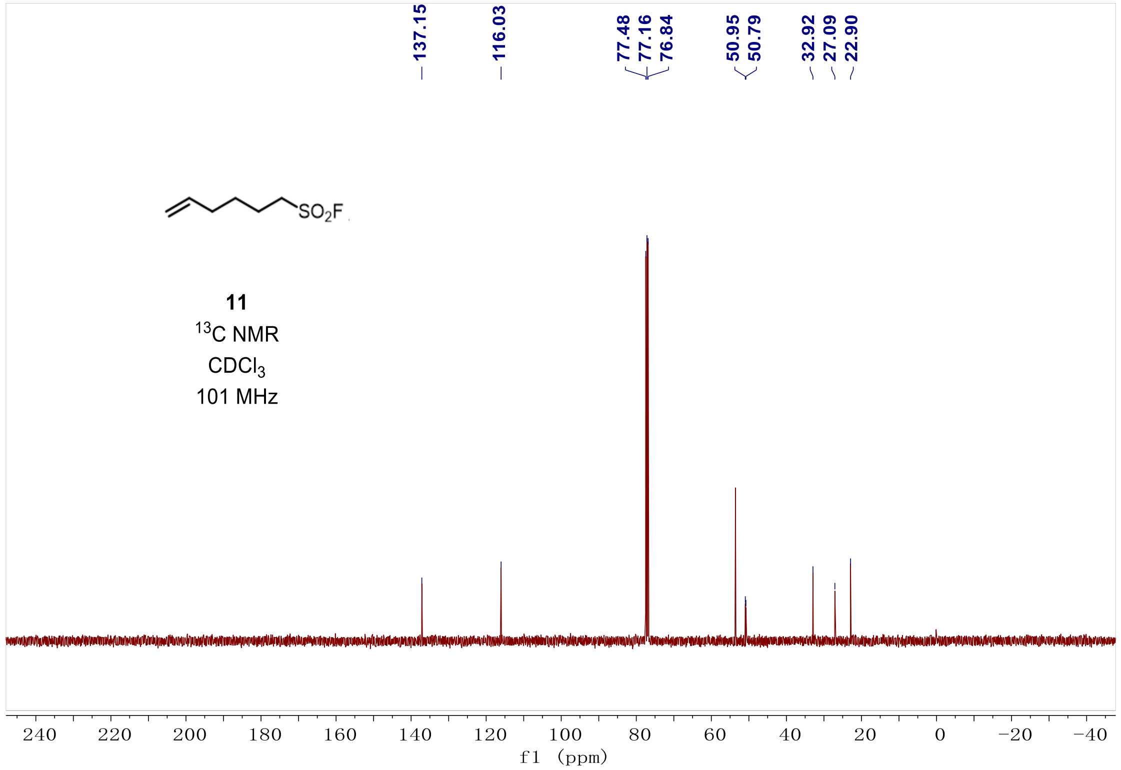
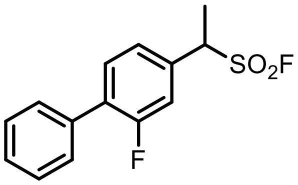
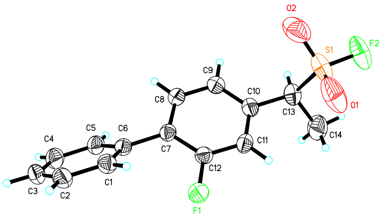
53.30
53.29
53.27
53.26
53.25
SO2F
11
19F NMR
CDCl3
376 MHz
1.00
0.07
53.45
53.35
53.25
53.15
53.05
f1 (ppm)
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−20
f1 (ppm)


137.15
116.03
77.48
77.16
76.84
50.95
50.79
32.92
27.09
22.90
SO2F
11
13C NMR
CDCl3
101 MHz
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
−40
f1 (ppm)

XI. Single crystal structure data of 2u





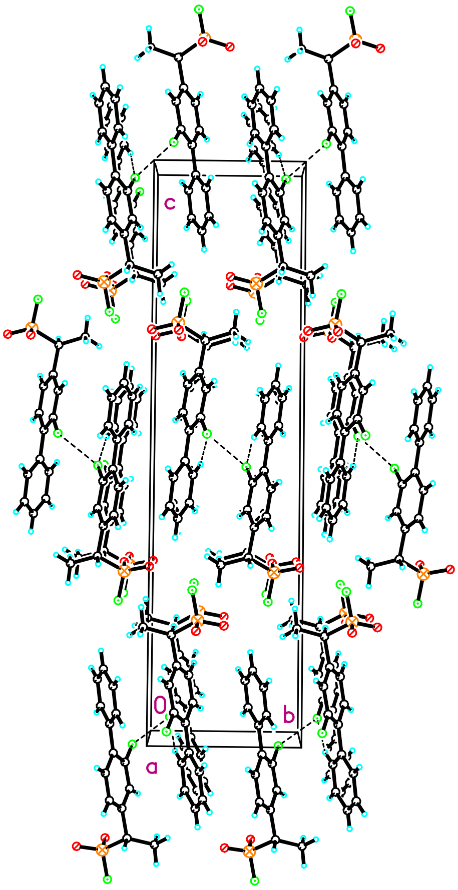


Table S9. Crystal data and structure refinement for mo_d8v21634_0m.

Identification code	mo_d8v21634_0m	
Empirical formula	$C_{14}H_{12}F_2O_2S$	
Formula weight	282.30	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 6.1569(6) Å	a= 90°.
	b = 7.4390(7) Å	b= 94.592(3)°.
	c = 28.410(2) Å	g = 90°.
Volume	1297.1(2) Å^3	
Z	4	
Density (calculated)	1.446 Mg/m^3	
Absorption coefficient	0.268 mm^{-1}	
F(000)	584	
Crystal size	0.200 x 0.150 x 0.110 mm^3	
Theta range for data collection	2.831 to 25.997°.	
Index ranges	-6<=h<=7, -9<=k<=9, -34<=l<=34	
Reflections collected	20165	
Independent reflections	2539 [R(int) = 0.0451]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5985	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2539 / 2 / 174	
Goodness-of-fit on F^2	1.067	
Final R indices [I>2sigma(I)]	R1 = 0.0579, wR2 = 0.1645	
R indices (all data)	R1 = 0.0764, wR2 = 0.1815	
Extinction coefficient	0.016(5)	
Largest diff. peak and hole	0.422 and -0.215 e.Å^{-3}	

Table S10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for mo_d8v21634_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	5321(2)	1797(2)	7118(1)	97(1)
F(1)	6247(2)	3709(3)	5279(1)	74(1)
F(2)	5295(5)	2172(4)	7632(1)	136(1)
O(1)	7434(5)	1885(6)	6981(1)	140(1)
O(2)	4248(7)	103(4)	7021(1)	134(1)
C(1)	3925(5)	1591(4)	4549(1)	60(1)
C(2)	3512(6)	1372(4)	4068(1)	71(1)
C(3)	1522(6)	1853(4)	3849(1)	78(1)
C(4)	-44(6)	2576(5)	4110(1)	76(1)
C(5)	338(5)	2790(4)	4590(1)	61(1)
C(6)	2340(4)	2295(3)	4819(1)	51(1)
C(7)	2718(4)	2550(3)	5338(1)	50(1)
C(8)	1147(4)	2103(4)	5643(1)	57(1)
C(9)	1452(5)	2390(4)	6123(1)	61(1)
C(10)	3355(4)	3158(4)	6320(1)	57(1)
C(11)	4961(4)	3608(4)	6027(1)	58(1)
C(12)	4634(4)	3279(3)	5551(1)	52(1)
C(13)	3634(5)	3520(4)	6848(1)	71(1)
C(14)	4494(8)	5350(6)	6988(1)	106(1)

Table S11. Bond lengths [Å] and angles [°] for mo_d8v21634_0m.

S(1)-O(1)	1.390(3)
S(1)-O(2)	1.439(4)
S(1)-F(2)	1.486(2)
S(1)-C(13)	1.784(3)
F(1)-C(12)	1.346(3)
C(1)-C(2)	1.379(4)
C(1)-C(6)	1.391(4)
C(1)-H(1)	0.9300
C(2)-C(3)	1.377(5)
C(2)-H(2)	0.9300
C(3)-C(4)	1.372(5)
C(3)-H(3)	0.9300
C(4)-C(5)	1.376(4)
C(4)-H(4)	0.9300
C(5)-C(6)	1.396(4)
C(5)-H(5)	0.9300
C(6)-C(7)	1.486(3)
C(7)-C(8)	1.390(4)
C(7)-C(12)	1.393(3)
C(8)-C(9)	1.380(4)
C(8)-H(8)	0.9300
C(9)-C(10)	1.380(4)
C(9)-H(9)	0.9300
C(10)-C(11)	1.384(4)
C(10)-C(13)	1.522(4)
C(11)-C(12)	1.372(3)
C(11)-H(11)	0.9300
C(13)-C(14)	1.502(5)
C(13)-H(13)	0.9800
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
O(1)-S(1)-O(2)	114.4(2)
O(1)-S(1)-F(2)	110.52(19)
O(2)-S(1)-F(2)	108.1(2)

O(1)-S(1)-C(13)	111.81(19)
O(2)-S(1)-C(13)	107.74(19)
F(2)-S(1)-C(13)	103.60(15)
C(2)-C(1)-C(6)	120.6(3)
C(2)-C(1)-H(1)	119.7
C(6)-C(1)-H(1)	119.7
C(3)-C(2)-C(1)	120.3(3)
C(3)-C(2)-H(2)	119.9
C(1)-C(2)-H(2)	119.9
C(4)-C(3)-C(2)	119.8(3)
C(4)-C(3)-H(3)	120.1
C(2)-C(3)-H(3)	120.1
C(3)-C(4)-C(5)	120.6(3)
C(3)-C(4)-H(4)	119.7
C(5)-C(4)-H(4)	119.7
C(4)-C(5)-C(6)	120.4(3)
C(4)-C(5)-H(5)	119.8
C(6)-C(5)-H(5)	119.8
C(1)-C(6)-C(5)	118.3(2)
C(1)-C(6)-C(7)	122.3(2)
C(5)-C(6)-C(7)	119.4(2)
C(8)-C(7)-C(12)	115.4(2)
C(8)-C(7)-C(6)	121.8(2)
C(12)-C(7)-C(6)	122.8(2)
C(9)-C(8)-C(7)	122.2(2)
C(9)-C(8)-H(8)	118.9
C(7)-C(8)-H(8)	118.9
C(10)-C(9)-C(8)	120.6(3)
C(10)-C(9)-H(9)	119.7
C(8)-C(9)-H(9)	119.7
C(9)-C(10)-C(11)	118.8(2)
C(9)-C(10)-C(13)	119.8(2)
C(11)-C(10)-C(13)	121.4(2)
C(12)-C(11)-C(10)	119.6(2)
C(12)-C(11)-H(11)	120.2
C(10)-C(11)-H(11)	120.2
F(1)-C(12)-C(11)	117.9(2)
F(1)-C(12)-C(7)	118.7(2)

C(11)-C(12)-C(7)	123.4(2)
C(14)-C(13)-C(10)	115.5(3)
C(14)-C(13)-S(1)	110.9(2)
C(10)-C(13)-S(1)	108.2(2)
C(14)-C(13)-H(13)	107.3
C(10)-C(13)-H(13)	107.3
S(1)-C(13)-H(13)	107.3
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S12. Anisotropic displacement parameters ($Å^2 \times 10^3$) for mo_d8v21634_0m. The anisotropic displacement factor exponent takes the form: $-2p^2$ [$h^2 a^{2*}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	120(1)	115(1)	54(1)	5(1)	-2(1)	37(1)
F(1)	60(1)	92(1)	68(1)	4(1)	4(1)	-12(1)
F(2)	158(2)	195(3)	53(1)	1(1)	-4(1)	43(2)
O(1)	112(2)	230(4)	77(2)	25(2)	5(1)	72(2)
O(2)	227(4)	85(2)	90(2)	15(2)	10(2)	23(2)
C(1)	68(2)	55(2)	56(2)	1(1)	3(1)	1(1)
C(2)	95(2)	63(2)	56(2)	-2(1)	13(2)	-4(2)
C(3)	112(3)	73(2)	46(2)	5(1)	-7(2)	-18(2)
C(4)	81(2)	77(2)	65(2)	9(2)	-20(2)	-7(2)
C(5)	59(2)	64(2)	59(2)	1(1)	-6(1)	-2(1)
C(6)	58(1)	43(1)	51(1)	3(1)	-3(1)	-2(1)
C(7)	54(1)	43(1)	51(1)	0(1)	-3(1)	0(1)
C(8)	56(1)	58(2)	56(2)	0(1)	0(1)	-5(1)
C(9)	62(2)	65(2)	56(2)	1(1)	6(1)	-5(1)
C(10)	64(2)	57(2)	50(1)	0(1)	-1(1)	5(1)
C(11)	56(2)	56(2)	60(2)	-4(1)	-11(1)	-2(1)
C(12)	49(1)	54(1)	54(1)	5(1)	3(1)	0(1)
C(13)	77(2)	79(2)	57(2)	-8(1)	-2(1)	6(2)
C(14)	139(3)	101(3)	76(2)	-29(2)	-4(2)	-11(3)

Table 13. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for mo_d8v21634_0m.

	x	y	z	U(eq)
H(1)	5276	1265	4694	72
H(2)	4583	897	3891	85
H(3)	1240	1688	3526	93
H(4)	-1376	2926	3960	91
H(5)	-744	3266	4764	74
H(8)	-155	1592	5519	69
H(9)	367	2065	6316	73
H(11)	6254	4130	6152	70
H(13)	2195	3403	6970	86
H(14A)	4502	5489	7324	159
H(14B)	3579	6254	6834	159
H(14C)	5951	5477	6894	159

Table S14. Torsion angles [°] for mo_d8v21634_0m.

C(6)-C(1)-C(2)-C(3)	0.2(4)
C(1)-C(2)-C(3)-C(4)	0.9(5)
C(2)-C(3)-C(4)-C(5)	-1.4(5)
C(3)-C(4)-C(5)-C(6)	0.9(5)
C(2)-C(1)-C(6)-C(5)	-0.7(4)
C(2)-C(1)-C(6)-C(7)	179.9(2)
C(4)-C(5)-C(6)-C(1)	0.2(4)
C(4)-C(5)-C(6)-C(7)	179.6(3)
C(1)-C(6)-C(7)-C(8)	-137.1(3)
C(5)-C(6)-C(7)-C(8)	43.5(3)
C(1)-C(6)-C(7)-C(12)	44.1(4)
C(5)-C(6)-C(7)-C(12)	-135.3(3)
C(12)-C(7)-C(8)-C(9)	1.1(4)
C(6)-C(7)-C(8)-C(9)	-177.8(2)
C(7)-C(8)-C(9)-C(10)	0.5(4)
C(8)-C(9)-C(10)-C(11)	-1.0(4)
C(8)-C(9)-C(10)-C(13)	178.1(3)
C(9)-C(10)-C(11)-C(12)	-0.2(4)
C(13)-C(10)-C(11)-C(12)	-179.2(2)
C(10)-C(11)-C(12)-F(1)	-179.0(2)
C(10)-C(11)-C(12)-C(7)	1.9(4)
C(8)-C(7)-C(12)-F(1)	178.6(2)
C(6)-C(7)-C(12)-F(1)	-2.5(4)
C(8)-C(7)-C(12)-C(11)	-2.3(4)
C(6)-C(7)-C(12)-C(11)	176.5(2)
C(9)-C(10)-C(13)-C(14)	-133.3(3)
C(11)-C(10)-C(13)-C(14)	45.7(4)
C(9)-C(10)-C(13)-S(1)	101.7(3)
C(11)-C(10)-C(13)-S(1)	-79.3(3)
O(1)-S(1)-C(13)-C(14)	-61.1(3)
O(2)-S(1)-C(13)-C(14)	172.4(3)
F(2)-S(1)-C(13)-C(14)	58.0(3)
O(1)-S(1)-C(13)-C(10)	66.6(3)
O(2)-S(1)-C(13)-C(10)	-60.0(3)
F(2)-S(1)-C(13)-C(10)	-174.4(2)

Symmetry transformations used to generate equivalent atoms:

Table S15. Hydrogen bonds for mo_d8v21634_0m [Å and °].

D-H…A	d(D-H)	d(H...A)	d(D...A)	<(DHA)