Supporting Information

Copper-catalyzed direct decarboxylative fluorosulfonylation of aliphatic carboxylic acids

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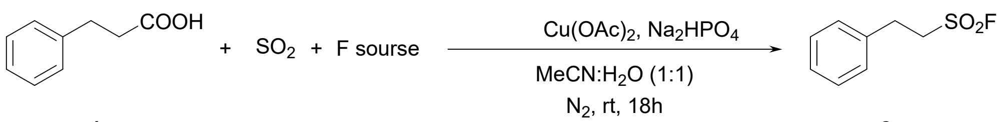
1. General Information

All the commercial reagents were used as such without further purification. All solvents were used as commercial anhydrous grade without further purification. The flash column chromatography was carried out over silica gel (230-400 mesh). ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker Avance-300 MHz spectrometer or Bruker Avance-400 MHz spectrometer, or Bruker Avance-500 MHz spectrometer. Chemical shifts in ^{1}H NMR spectra were reported in parts per million (ppm, δ) downfield from the internal standard Me_4Si (TMS, δ = 0 ppm). Chemical shifts in ^{13}C NMR spectra were reported relative to the central line of the chloroform signal (δ = 77.0 ppm). Peaks were labeled as singlet, doublet (d), triplet (t), quartet (q), and multiplet (m). Low-resolution ions spectrometry (LRMS) was performed on a Fisons Platform spectrometer (ESI). High-resolution mass spectrometry (HRMS) was performed via electron ionization (EI) or electrospray ionization (ESI) sources. The *m/z* ratios are reported in Daltons; high-resolution values are calculated to four decimal places from the molecular formula. Unless otherwise noted, chemical yields refer to pure isolated substances. Acridines were synthesized according to the previous literature.[1]

2. Details for optimization of reaction conditions

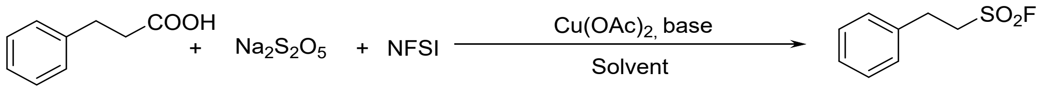
Table S1. Initial evaluation of SO_2 surrogates and fluorine sources



Entry[a]	SO_2 surrogate	F source	ML_n	Yield[b] (%)
1	DABSO	NFSI	$Cu(OAc)_2$	35
2	DABSO	Selectfluor	$Cu(OAc)_2$	N.R
3	$Na_2S_2O_5$	NFSI	$Cu(OAc)_2$	42
4	$Na_2S_2O_5$	Selectfluor	$Cu(OAc)_2$	N.R
5	$Na_2S_2O_4$	NFSI	$Cu(OAc)_2$	24
6	$Na_2S_2O_5$	KHF_2	$Cu(OAc)_2$	N.R
7	H_2SO_3	NFSI	$Cu(OAc)_2$	35

[a]: Reaction conditions: carboxylic acids (0.2 mmol), SO_2 sources (0.3 mmol), F sources (0.4 mmol), Na_2HPO_4 (0.2 mmol), $Cu(OAc)_2$ (10 mol%) in 1.0 mL solvent under N_2 atmosphere;
[b]: Yields calculated with ^{19}F NMR using $PhCF_3$ as the internal standard;

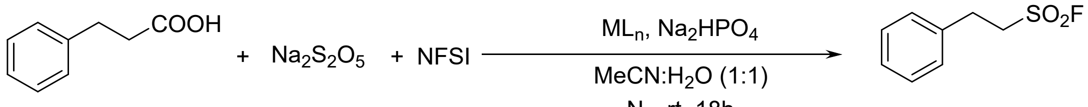
Table S2. Initial evaluation of base and solvent



Entry[a]	base	Solvent (1 mL)	Yield[b] (%)
1	Na_2HPO_4	MeCN	N.R
2	Na_2HPO_4	H_2O	9
3	Na_2HPO_4	DCM	N.R
4	Na_2HPO_4	THF	N.R
5	Na_2HPO_4	ether	N.R
6	Na_2HPO_4	$MeNO_2$	29
7	Na_2HPO_4	DMSO: H_2O (1:1)	6
8	Na_2HPO_4	EtOAc: H_2O (1:1)	2
9	Na_2HPO_4	DCM: H_2O (1:1)	18
10	Na_2HPO_4	MeCN: H_2O (1:1)	42
11	Na_2HPO_4	acetone:H_2O (1:1)	< 1
12	none	MeCN: H_2O (1:1)	39
13	Cs_2CO_3	MeCN: H_2O (1:1)	N.R
14	K_3PO_4	MeCN: H_2O (1:1)	37
15	Et_3N	MeCN: H_2O (1:1)	31
16	DMAP	MeCN: H_2O (1:1)	2

[a]: Reaction conditions: carboxylic acids (0.2 mmol), SO_2 sources (0.3 mmol), F sources (0.4 mmol), base (0.2 mmol), $Cu(OAc)_2$ (10 mol%) in 1.0 mL solvent under N_2 atmosphere;
[b]: Yields calculated with ^{19}F NMR using $PhCF_3$ as the internal standard.

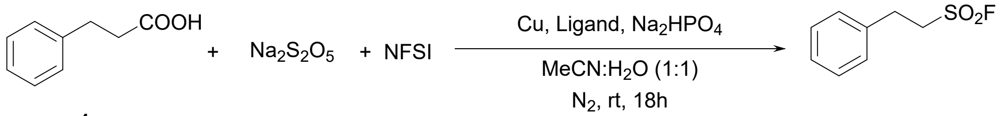
Table S3. Evaluation of metal catalysts



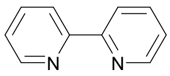
Entry[a]	ML_n	Yield[b] (%)	Entry[a]	ML_n	Yield[b] (%)
1	Cu powder	45	8	$Cu(OTf)_2$	40
2	CuOAc	32	9	$FeCl_3$	26
3	Cu_2O	34	10	$CoBr_2$	7
4	CuCN	32	11	$NiCl_2$	25
5	CuCl	29	12	Zn powder	9
6	$Cu(OAc)_2$	42	13	$Mn_2(CO)_{10}$	41
7	CuF_2	34			

[a]: Reaction conditions: carboxylic acids (0.2 mmol), SO_2 sources (0.3 mmol), F sources (0.4 mmol), Na_2HPO_4 (0.2 mmol), ML_n(10 mol%) in 1.0 mL solvent under N_2 atmosphere;
[b]: Yields calculated with ^{19}F NMR using $PhCF_3$ as the internal standard.

Table S5. Evaluation of ligands [a]



1a **2a**[b]



D1

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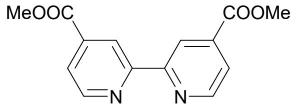

D2

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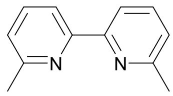

D3

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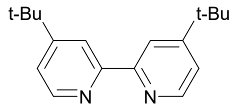

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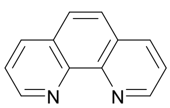

D5

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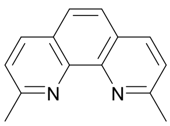

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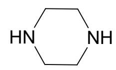

D7

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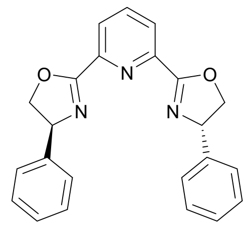
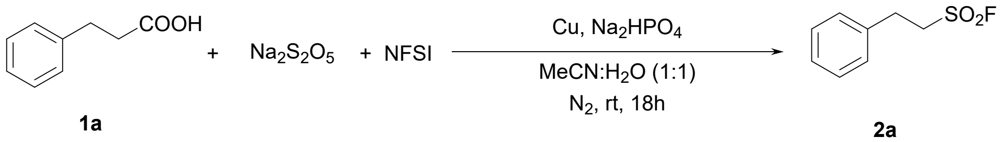


D8

38%

[a]: Reaction conditions: carboxylic acids (0.2 mmol), SO_2 sources (0.3 mmol), F sources (0.4 mmol), Na_2HPO_4 (0.2 mmol), Cu (10 mol%), Ligand (12 mol%) in 1.0 mL solvent under N_2 atmosphere; Yields calculated with ^{19}F NMR using $PhCF_3$ as the internal standard.

Table S5. Evaluation of the reagent loading

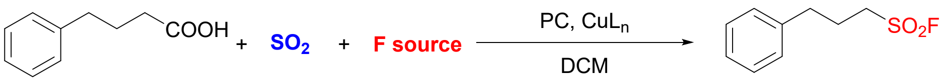


1a **2a**

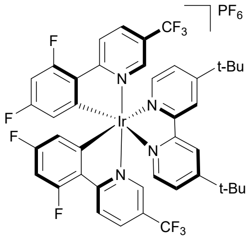
Entry[a]	$Na_2S_2O_5$	NFSI	Cu	Na_2HPO_4	Yield[b] (%)
1	1.5 eq	2.0 eq	10 mol%	1.0 eq	45
2	2.0 eq	3.0 eq	10 mol%	1.0 eq	44
3	2.0 eq	3.0 eq	5 mol%	none	41
4	2.0 eq	3.0 eq	5 mol%	0.8 eq	50
5	2.0 eq	3.0 eq	5 mol%	1.0 eq	45
6	2.0 eq	3.0 eq	5 mol%	1.3 eq	53
7	2.0 eq	3.0 eq	5 mol%	1.5 eq	52
8	2.0 eq	3.0 eq	5 mol%	2.0 eq	49
9	2.0 eq	3.0 eq	10 mol%	1.3 eq	48
10	2.0 eq	3.0 eq	20 mol%	1.3 eq	42

[a]: Reaction conditions: carboxylic acids (0.2 mmol), SO_2 sources, F sources, Na_2HPO_4, Cu in 1.0 mL solvent under N_2 atmosphere;
[b]: Yields calculated with ^{19}F NMR using $PhCF_3$ as the internal standard.

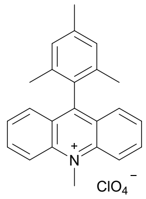
Table S6. Screening of SO_2 surrogates, fluorine sources, copper salts and photocatalysts



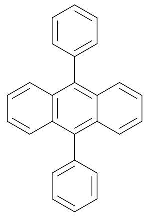
3a **4a**



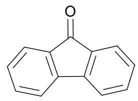
$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$



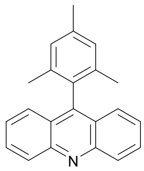
Mes-Acr-Me-ClO_4



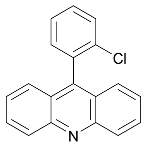
9,10-diphenylanthracene



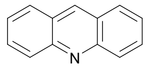
9-fluorenone



A1



A2



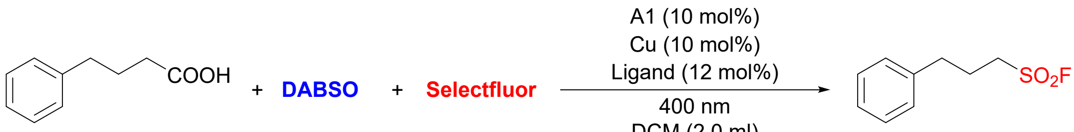
A3

Entry[a]	SO_2 source (2.0 eq)	F source (3.0 eq)	Photocatalyst	CuL_n (10 mol%)	light source	Yield[b] %
1	$Na_2S_2O_5$	NFSI	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (1 mol%)	none	Blue LED	N.R
2	DABSO	Selectfluor	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (1 mol%)	none	Blue LED	<4
3	DABSO	NFSI	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (1 mol%)	none	Blue LED	5
4	DABSO	NFSI	Mes-Acr-Me-ClO_4 (10 mol%)	none	Blue LED	<4
5	DABSO	NFSI	Mes-Acr-Me-ClO4 (10 mol%)	$Cu(OAc)_2$	Blue LED	<5
6	$Na_2S_2O_5$	NFSI	A1 (5 mol%)	Cu (5 mol%)	Blue LED	N.R
7	$Na_2S_2O_5$	NFSI	A1 (10 mol%)	none	Blue LED	N.R

8	DABSO	Selectfluor	A1 (10 mol%)	none	Blue LED	N.R
9	$Na_2S_2O_5$	NFSI	A1 (10 mol%)	none	400 nm	N.R
10	DABSO	NFSI	A1 (10 mol%)	none	400 nm	N.R
11	DABSO	NFSI	A1 (10 mol%)	none	400 nm	16
12	DABSO	NFSI	A1 (10 mol%)	Cu	400 nm	25
13	DABSO	NFSI	A1 (10 mol%)	CuF_2	400 nm	26
14	DABSO	NFSI	A1 (10 mol%)	$Cu(OAc)_2$	400 nm	29
15	DABSO	NFSI	A2 (10 mol%)	$Cu(OAc)_2$	400 nm	22
16	DABSO	NFSI	A3 (10 mol%)	$Cu(OAc)_2$	400 nm	8
17	DABSO	Selectfluor	A1 (10 mol%)	$Cu(OAc)_2$	400 nm	34
18	DABSO	Selectfluor	A1 (10 mol%)	Cu	400 nm	41
19	DABSO	NFSI	9,10-diphenylanthracene (10 mol%)	$Cu(OAc)_2$	400 nm	N.R
20	DABSO	NFSI	9-Fluorenone (10 mol%)	$Cu(OAc)_2$	400 nm	N.R

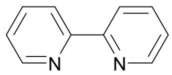
[a]: Reaction conditions: **3a** (0.2 mmol), SO_2 sources (0.3 mmol), F sources (0.4 mmol), CuL_n and PC in 2.0 mL DCM under N_2 atmosphere and light irradiation;
[b]: Yields calculated with ^{19}F NMR using $PhCF_3$ as the internal standard.

Table S7. Effect of ligands [a]

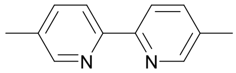


3a + **DABSO** + **Selectfluor** → **4a**[b]

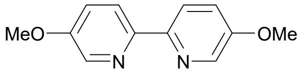
1.0 eq | 2.0 eq | 5.0eq



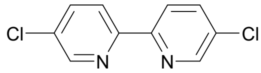
L1 51%



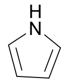
L2 60%



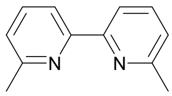
L3 35%



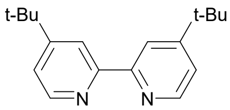
L4 5%



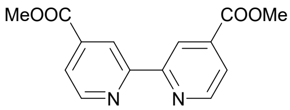
L5 52%



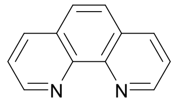
L6 38%



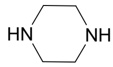
L7 52%



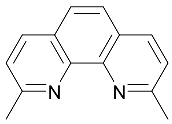
L8 58%



L9 55%



L10 55%



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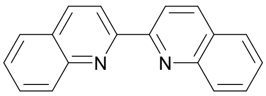

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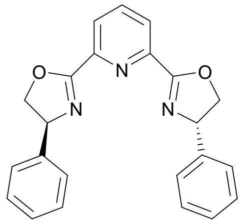
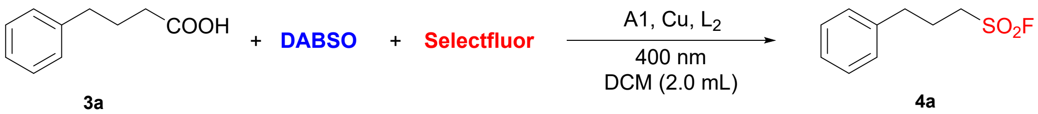


L13 59%

[a]: Reaction conditions: **3a** (0.2 mmol), SO_2 sources(0.4 mmol), F sources (0.5 mmol), Cu (10 mol%), ligand (12 mol%) and A1 (10 mol%) in 2.0 mL DCM under N_2 atmosphere and 400 nm irradiation; Yields calculated with ^{19}F NMR using $PhCF_3$ as the internal standard.

Table S8. Evaluation of the reagent loading



Entry[a]	DABSO	Selectfluor	A1	Cu	L2	Yield[b] %
1	2.0 eq	5.0eq	10 mol%	10 mol%	12 mol%	60
2	2.0 eq	5.0eq	5 mol%	5 mol%	6 mol%	37
3	2.0 eq	5.0eq	5 mol%	10 mol%	12 mol%	50
4	2.0 eq	5.0 eq	10 mol%	5 mol%	6 mol%	51
5	2.0 eq	5.0 eq	10 mol%	15 mol%	18 mol%	46
6	2.0 eq	3.0 eq	10 mol%	10 mol%	12 mol%	57
7	1.5 eq	2.5 eq	10 mol%	10 mol%	12 mol%	58

[a]: Reaction conditions: **3a** (0.2 mmol), SO_2 sources, F sources, Cu, Ligand, A1 in 2.0 mL DCM under N_2 atmosphere and 400 nm irradiation;
[b]: Yields calculated with ^{19}F NMR using $PhCF_3$ as the internal standard.

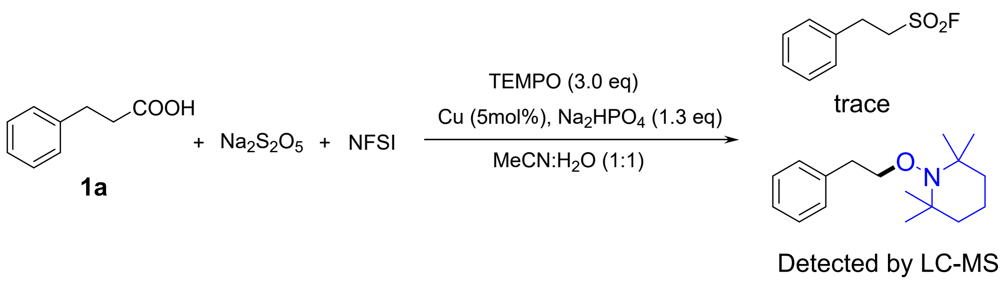
3. General Procedure for the decarboxylative fluorosulfonylation

Method A: Under N_2 atmosphere, a 10 mL reaction tube was charged with carboxylic acids (0.2 mmol, 1.0 eq), $Na_2S_2O_5$ (0.4 mmol, 2.0 eq), NFSI (0.6 mmol, 3.0 eq), Na_2HPO_4 (0.26 mmol, 1.3 eq), electrolytic copper powder (5 mol%), and 1.0 mL solvent ($MeCN:H_2O$=1:1). The reaction mixture was stirred at room temperature for 18 h. Upon completion, dried over Na_2SO_4 was added. The reaction mixture was filtered through a pad of celite, concentrated in vacuo, and purified by flash column chromatography (eluent: petroleum ether/ethyl acetate) on silica gel to give the desired product.

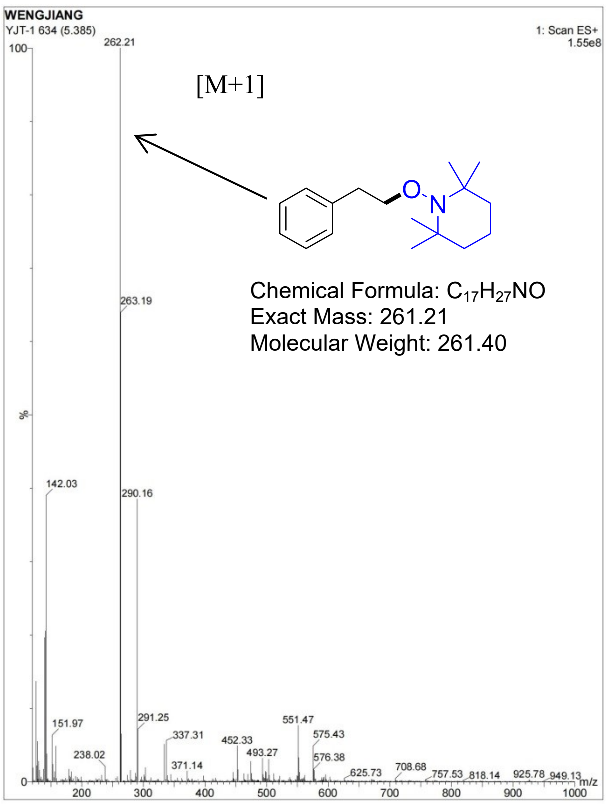
Method B: Under N_2 atmosphere, a 10 mL reaction tube was charged with carboxylic acids (0.2 mmol, 1.0 eq), DABSO (0.3 mmol, 1.5 eq), Selectfluor (0.5 mmol, 2.5 eq), acridine catalyst A1 (10 mol%) , electrolytic copper powder (10 mol%), L_2 (12 mol%) and 2.0 mL dry DCM. The reaction tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at room temperature for 12 h. The reaction mixture was filtered through a pad of celite, concentrated, and purified by flash column chromatography (eluent: petroleum ether/ethyl acetate) on silica gel to give the desired product.

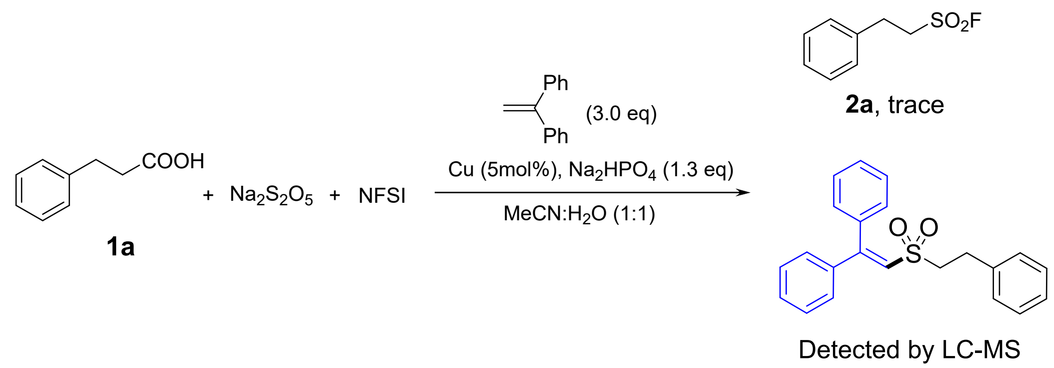
4. Mechanistic Experiments

4.1 Radical trapping experiments

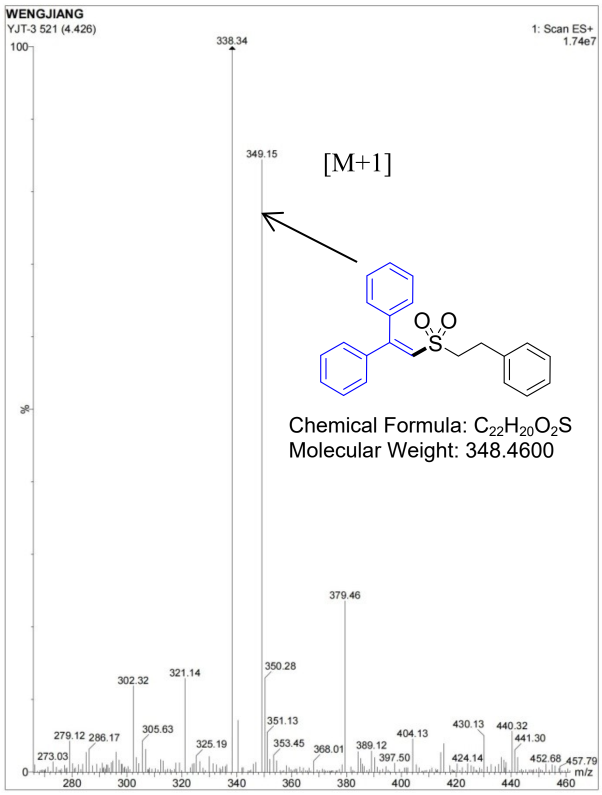


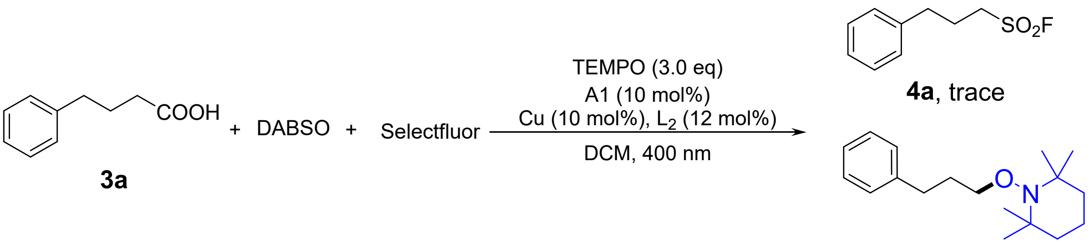
Under N_2 atmosphere, a 10 mL reaction tube was charged with **1a** (0.2 mmol, 1.0 eq), $Na_2S_2O_5$ (0.4 mmol, 2.0 eq), NFSI (0.6 mmol, 3.0 eq), Na_2HPO_4 (0.26 mmol, 1.3 eq), copper powder (5 mol%), TEMPO (0.6 mmol, 3.0 eq) and 1.0 mL solvent ($MeCN:H_2O$=1:1). After stirring for 18 h at room temperature, the yield of **2a** was calculated with ^{19}F NMR using $PhCF_3$ as the internal standard. The LC-MS result of the reaction mixture revealed the combination of an alkyl radical and TEMPO and the formation of the sulfonyl fluoride product was suppressed.





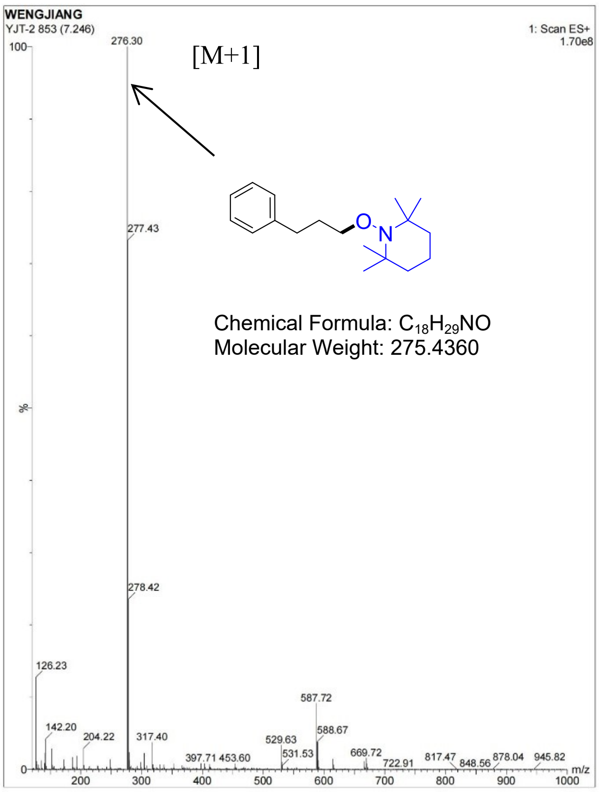
Under N_2 atmosphere, a 10 mL reaction tube was charged with **1a** (0.2 mmol, 1.0 eq), $Na_2S_2O_5$ (0.4 mmol, 2.0 eq), NFSI (0.6 mmol, 3.0 eq), Na_2HPO_4 (0.26 mmol, 1.3 eq), copper powder (5 mol%), 1,1-diphenylethylene (0.6 mmol, 3.0 eq) and 1.0 mL solvent (MeCN:H_2O=1:1). After stirring for 18 h at room temperature, the yield of **2a** was calculated with ^{19}F NMR using $PhCF_3$ as the internal standard. (2-(phenethylsulfonyl)ethene-1,1-diyl)dibenzene was determined by LC-MS and the formation of the sulfonyl fluoride product was suppressed.

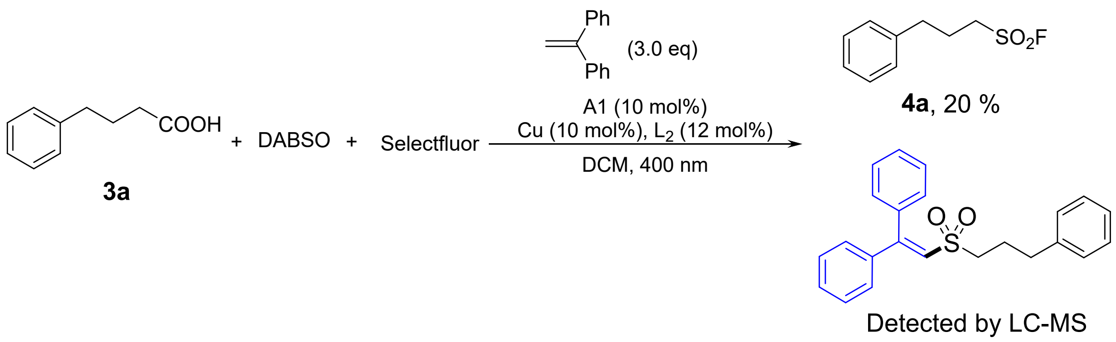




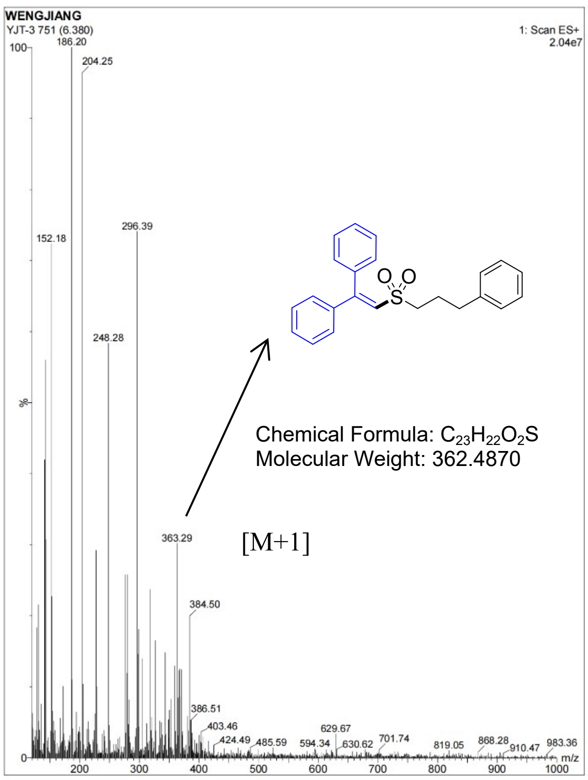
Detected by LC-MS

Under N_2 atmosphere, a 10 mL reaction tube was charged with **3a** (0.2 mmol, 1.0 eq), DABSO (0.3 mmol, 1.5 eq), Selectfluor (0.5 mmol, 2.5 eq), acridine catalyst A1 (10 mol%), copper powder (10 mol%), L_2 (12 mol%), TEMPO (0.6 mmol, 3.0 eq) and 2.0 mL dry DCM. The reaction tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at room temperature for 12 h. the yield of **4a** was calculated with ^{19}F NMR using $PhCF_3$ as the internal standard. The LC-MS result of the reaction mixture revealed the combination of the alkyl radical and TEMPO and the formation of the sulfonyl fluoride product was suppressed.





Under N_2 atmosphere, a 10 mL reaction tube was charged with **3a** (0.2 mmol, 1.0 eq), DABSO (0.3 mmol, 1.5 eq), Selectfluor (0.5 mmol, 2.5 eq), acridine catalyst A1 (10 mol%), copper powder (10 mol%), L_2 (12 mol%), TEMPO (0.6 mmol, 3.0 eq) and 2.0 mL dry DCM. The reaction tube was capped and the reaction mixture was irradiated with LED light (λ = 400 nm) while stirring at room temperature for 12 h. the yield of **4a** was calculated with ^{19}F NMR using $PhCF_3$ as the internal standard. (2-((3-phenylpropyl)sulfonyl)ethene-1,1-diyl)dibenzene was determined by LC-MS and the yield of **4a** was decreased to 20%.

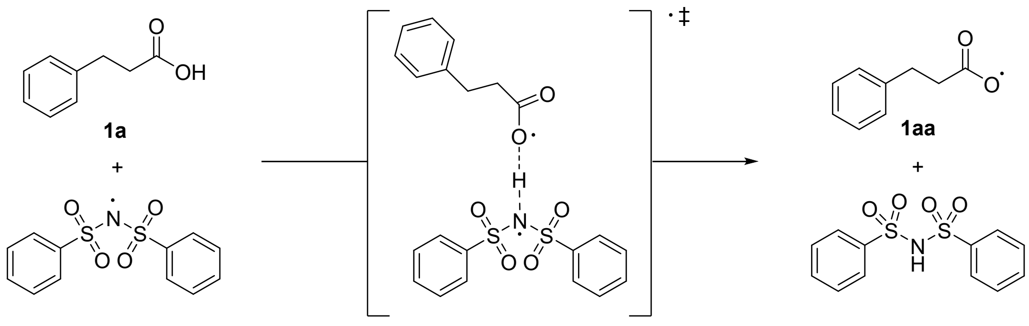


4.2 Computational data

All computations were performed in the Gaussian 16 program[2]. Adapted from an analogous literature procedure[3], we did geometry optimization, vibrational frequencies, transition states (TS) and IRC calculations at B3LYP/6-31G(d) level and single point calculations were performed at the M062X/def2TZVP level. To confirm the nature of stationary points, vibrational frequencies have been calculated for the optimized structures at the same level of theory as geometry optimizations, and it was verified that local minima had only real frequencies, while transition states (TS) were identified by the presence of a single imaginary frequency corresponding to the expected motion along the reaction coordinate. IRC calculations were performed to further corroborate that the located transition states connected reactants to products. The electronic energy was reported in the final calculated thermodynamic values. The simulation has been focused on analyzing the feasibility of Hydrogen Atom Transfer from O-H bond in 3-phenylpropanoic acid (**1a**) promoted by N-(phenylsulfonyl)benzenesulfonamidy radical to give the corresponding carboxyl radical and N-(phenylsulfonyl)benzenesulfonamide. For **1a** and N-(phenylsulfonyl)benzenesulfonamidy radical (**NSI**), only the most stable conformation has been reported and considered for further work. The thermodynamic parameters (energy barrier, $\Delta G^{\ddagger}$) reported in the text have thus been determined according to the following equations in the reference: $\Delta G^{\ddagger}$ = G (TS) - G (reactants), ΔG = G (products) - G (reactants).

G = Electronic Energy at the M062X/def2TZVP level of theory + thermal correction to Gibbs Free Energy at the B3LYP/6-31G(d) level of theory, 1 Hartree = 627.509 kcal·mol^{-1}.

Table S9. Calculated parameters for describing HAT processes



NSI TS-1 HNSI

Reacting situation	G (reactants) / Hartree	G (TS) / Hartree	G (products) / Hartree	$\Delta G^{\ddagger}$ / kcal·mol^{-1}	ΔG / kcal·mol^{-1}
1a + **NSI**	- 2114.322136	- 2114.298362	-2114.321519	14.92	0.39

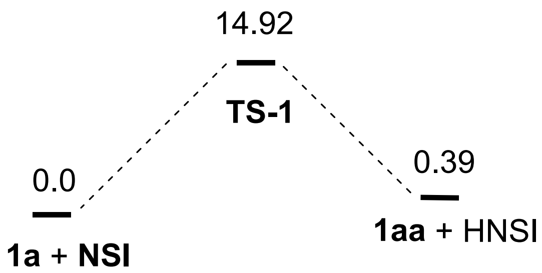
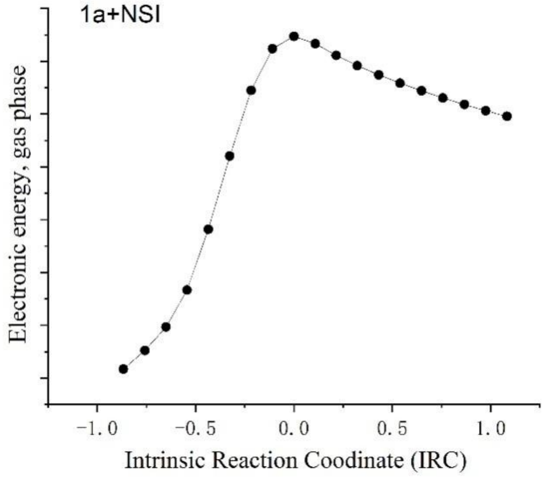


Table S10. Terms adopted to calculate the Gibbs Free Energy (G) values reported in Table S9

	Thermal correction to Gibbs Free Energy (gas phase)	Electronic Energy (gas phase)	G / Hartree
1a	0.134418	- 499.433439	- 499.299021
NSI	0.157340	- 1615.180455	-1615.023115
TS-1	0.30659	- 2114.604952	- 2,114.298362
1aa	0.116976	- 498.742255	- 498.625279
HNSI	0.171363	-1615.867603	-1615.69624



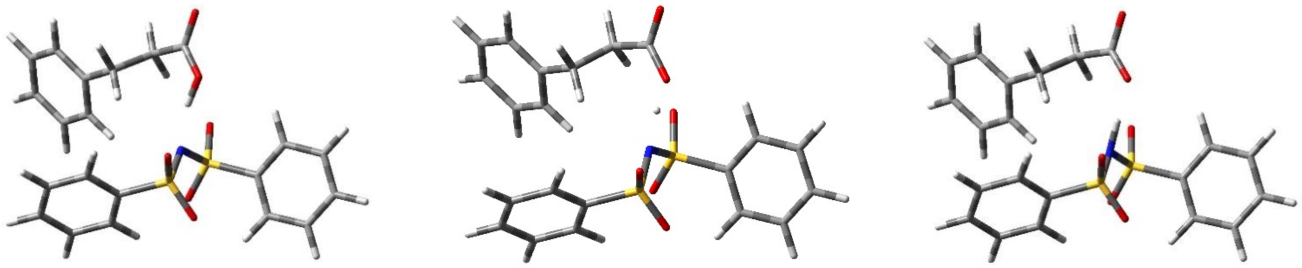
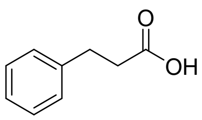


Figure S1. Intrinsic Reaction Coordinate (IRC) plot at the B3LYP/6-31G(d) level of theory (gas phase) obtained for **TS-1**, along with the structures of the starting, TS and end-points.

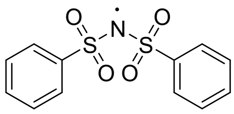
Optimized Structures



1a

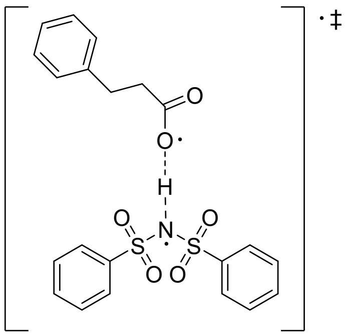
C	2.93100900	1.20640300	-0.19225500
C	1.59534500	1.20261700	0.20839300
C	0.91013300	-0.00088500	0.41273400
C	1.59627600	-1.20340700	0.20594100
C	2.93196100	-1.20532700	-0.19471600
C	3.60363400	0.00100000	-0.39586200
H	3.44762700	2.14993400	-0.34104900
H	1.07670700	2.14421400	0.37067300
H	1.07837100	-2.14573700	0.36627600
H	3.44930500	-2.14815300	-0.34543900
H	4.64447100	0.00172600	-0.70456800
C	-0.54976600	-0.00178300	0.79931300
C	-1.45974800	0.00072800	-0.43515100
H	-0.78384900	0.87248900	1.41417100

H	-0.78369400	-0.87864800	1.41051800
H	-1.26198300	0.87408500	-1.06775800
H	-1.26210700	-0.87011400	-1.07125100
C	-2.92729500	0.00016800	-0.07816300
O	-3.38638700	-0.00138000	1.04279200
O	-3.70946400	0.00162900	-1.18617500
H	-4.62733100	0.00114000	-0.86591500



NSI

C	3.90955000	0.88314200	1.21317900
C	2.66213800	0.27205600	1.14258200
C	2.36393700	-0.49791500	0.01235000
C	3.26877200	-0.66023200	-1.04341900
C	4.51090300	-0.04122300	-0.95350300
C	4.82789300	0.72805500	0.17017100
S	0.77487600	-1.28133100	-0.10802800
O	0.83973200	-2.38763400	-1.05929200
O	0.20802700	-1.47647200	1.22800900
N	0.00013100	0.00014300	-0.98481100
S	-0.77508900	1.28170300	-0.10841300
O	-0.20818600	1.47740100	1.22752400
O	-0.84028200	2.38764800	-1.06005400
C	-2.36393500	0.49793400	0.01228300
C	-3.26862100	0.65930300	-1.04375900
C	-4.51055600	0.03991000	-0.95371300
C	-4.82750000	-0.72878400	0.17036900
C	-3.90932400	-0.88287600	1.21367400
C	-2.66211000	-0.27140900	1.14294700
H	4.16627300	1.48269600	2.07990900
H	1.92291900	0.38733000	1.92465600
H	2.99355900	-1.26838800	-1.89700500
H	5.23146300	-0.15679400	-1.75610100
H	5.79720900	1.21264400	0.23235000
H	-2.99347200	1.26704700	-1.89765900
H	-5.23098300	0.15472700	-1.75653800
H	-5.79665500	-1.21368200	0.23265900
H	-4.16603200	-1.48195000	2.08074000
H	-1.92301500	-0.38590300	1.92525100

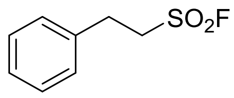


TS-1

C	0.24632500	-2.94867900	1.59725000
O	-0.64317200	-2.05252900	1.83670700
C	-5.37794900	0.61002500	-1.14359400
C	-3.99481800	0.71046300	-1.28384000
C	-3.20207500	-0.37831000	-0.91565400
C	-3.75897400	-1.55658000	-0.40805700
C	-5.14231400	-1.63984300	-0.26826800
C	-5.94974900	-0.55936200	-0.63596400
S	-1.42292900	-0.28028200	-1.10577800
O	-0.94606700	-1.63292900	-1.43807400
O	-1.11085200	0.84128300	-2.00221400
N	-0.75849400	0.00096400	0.41080800
S	-0.95090300	1.47167800	1.22958500
O	-2.09064400	2.22624700	0.70098200
O	-0.87042900	1.11725900	2.64895600
O	0.23755300	-4.03865900	2.19085400
C	1.36197500	-2.72677800	0.57393100
C	2.32922200	-1.59017500	1.01512400
C	2.94963800	-0.51762700	-1.18796200
C	3.84470600	-0.29256900	-2.22921800
C	5.10941800	-0.88862900	-2.20709600
C	5.47693500	-1.71151300	-1.13313300
C	4.58244600	-1.93766700	-0.09259400
C	3.31162800	-1.33544900	-0.09679600
H	-0.63388800	-1.11890500	1.19430800
C	0.55137400	2.37064600	0.81787400
C	1.58101800	2.41904900	1.76168100
C	2.74220400	3.13035300	1.45911600
C	2.86418200	3.77978900	0.22833900
C	1.82247500	3.72719800	-0.70386900
C	0.65575800	3.02211600	-0.41546700
H	-6.00877800	1.44726300	-1.42739000
H	-3.52892600	1.61066000	-1.66542800
H	-3.11931700	-2.38875300	-0.13507100
H	-5.58994000	-2.54789000	0.12487400

H	-7.02834300	-0.62942200	-0.52507000
H	1.91513600	-3.65997200	0.44690700
H	0.86294100	-2.47681100	-0.37134400
H	1.75150600	-0.68783200	1.22846600
H	2.84569200	-1.88763000	1.93379600
H	1.96601300	-0.05695800	-1.20813900
H	3.55611600	0.34484800	-3.05980500
H	5.80701500	-0.71714500	-3.02216700
H	6.46134100	-2.17062600	-1.11252400
H	4.86856100	-2.57378700	0.74170300
H	1.45384800	1.92283500	2.71772600
H	3.54729200	3.18279900	2.18652000
H	3.77077200	4.33163200	-0.00458300
H	1.91814300	4.23970000	-1.65686200
H	-0.15608200	2.96280200	-1.13101900

5. Characterization of products



2-phenylethane-1-sulfonyl fluoride (2a)[4]

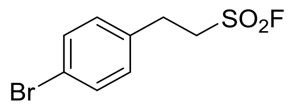
Following the **Method A.** Colorless oil (20 mg, 51% yield).

Following the **Method B**. Colorless oil (23 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (t, J = 7.3 Hz, 2H), 7.30 (t, J = 7.3 Hz, 1H), 7.23 (d, J = 7.3 Hz, 2H), 3.75 – 3.53 (m, 2H), 3.36 – 3.14 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 136.0, 129.2, 128.4, 127.7, 52.3 (d, J = 15.6 Hz), 29.7.

^{19}F NMR (376 MHz, CDCl3): δ 53.22 (t, J = 4.3 Hz)



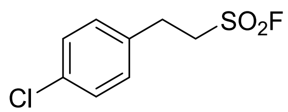
2-(4-bromophenyl)ethane-1-sulfonyl fluoride (2b)[5]

Following the **Method A**. White solid (33 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 – 7.46 (m, 2H), 7.12 (dd, *J* = 8.7, 2.1 Hz, 2H), 3.61 (ddd, *J* = 9.9, 7.0, 4.3 Hz, 2H), 3.29 – 3.12 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 135.0, 132.3, 130.2, 121.7, 51.9 (d, *J* = 15.9 Hz), 29.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ 53.81 (t, *J* = 4.2 Hz).



2-(4-chlorophenyl)ethane-1-sulfonyl fluoride (2c)

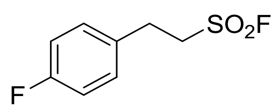
Following the **Method A**. Yellow oil (23 mg, 51% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.28 (m, 2H), 7.22 – 7.12 (m, 2H), 3.65 – 3.54 (m, 2H), 3.27 – 3.16 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 134.5, 133.7, 129.8, 129.4, 52.0 (d, *J* = 15.9 Hz), 29.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ 53.75 (d, *J* = 4.4 Hz).

HRMS (EI): m/z calculated for [$C_8H_8ClFO_2S^+$] [M^+]: 221.9912, found: 221.9910.



2-(4-fluorophenyl)ethanesulfonyl fluoride (2d)

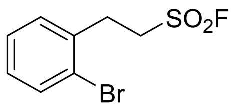
Following the **Method A**. Yellow oil (20 mg, 43% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 – 7.16 (m, 2H), 7.12 – 6.97 (m, 2H), 3.61 (ddd, J = 9.7, 7.0, 4.3 Hz, 2H), 3.23 (dd, J = 9.6, 6.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.3 (d, *J* = 246.6 Hz), 131.8 (d, *J* = 3.2 Hz), 130.1 (d, *J* = 8.1 Hz), 116.1 (d, *J* = 21.7 Hz), 52.3 (d, *J* = 15.7 Hz), 29.0.

^{19}F NMR (376 MHz, $CDCl_3$): δ 53.67 (t, J = 4.3 Hz), -(114.44 – 114.73) (m).

HRMS (EI): m/z calculated for [$C_8H_8O_2F_2S^+$] [M^+]: 206.0208, found: 206.0206.



2-(2-bromophenyl)ethane-1-sulfonyl fluoride (2e)

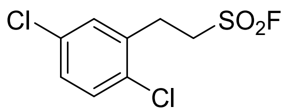
Following the **Method A**. Yellow oil (25 mg, 47% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.59 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.27 (m, 2H), 7.18 (dt, *J* = 8.6, 4.4 Hz, 1H), 3.74 – 3.57 (m, 2H), 3.36 (dd, *J* = 9.4, 6.6 Hz, 2H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 135.5, 133.4, 131.0, 129.6, 128.3, 124.2, 50.3 (d, J = 16.1 Hz), 30.5.

^{19}F NMR (376 MHz, CDCl$_3$): δ 53.52 (t, J = 4.6 Hz).

HRMS (EI): m/z calculated for [$C_8H_8O_2BrFS^+$] [M^+]: 265.9407, found: 202.9407.



2-(2,5-dichlorophenyl)ethane-1-sulfonyl fluoride (2f)

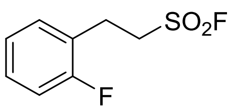
Following the **Method A**. Yellow solid (16 mg, 30% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.43 (d, *J* = 0.9 Hz, 1H), 7.29 – 7.21 (m, 2H), 3.73 – 3.58 (m, 2H), 3.33 (dd, *J* = 9.1, 6.6 Hz, 2H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 134.7, 134.7, 132.3, 131.8, 130.0, 127.9, 50.0 (d, J = 16.4 Hz), 27.7.

^{19}F NMR (376 MHz, CDCl$_3$): δ 53.99 (t, J = 4.5 Hz).

HRMS (EI): m/z calculated for [$C_8H_7Cl_2FO_2S^+$] [M^+]: 255.9522, found: 255.9518.



2-(2-fluorophenyl)ethane-1-sulfonyl fluoride (2g)

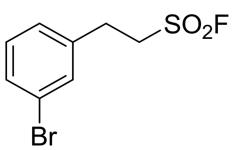
Following the **Method A.** Yellow oil (14 mg, 33% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.35 – 7.21 (m, 2H), 7.18 – 7.04 (m, 2H), 3.78 – 3.54 (m, 2H), 3.44 – 3.17 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 162.4, 130.9 (d, *J* = 4.2 Hz), 129.8 (d, *J* = 8.3 Hz), 124.8 (d, *J* = 3.6 Hz), 123.1, 115.9 (d, *J* = 21.4 Hz), 50.6 (d, *J* = 16.3 Hz), 24.1 (d, *J* = 2.7 Hz).

^{19}F NMR (376 MHz, CDCl$_3$): δ 53.46 (t, J = 4.6 Hz), -(92.37 –138.46) (m).

HRMS (EI): m/z calculated for [$C_8H_7Cl_2FO_2S^+$] [M^+]: 206.0208, found: 206.0204.



2-(3-bromophenyl)ethane-1-sulfonyl fluoride (2h)[5]

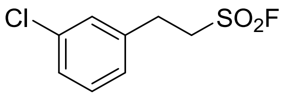
Following the **Method A.** Yellow oil (24 mg, 46% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.43 (t, *J* = 8.5 Hz, 1H), 7.40 (s, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 3.72 – 3.46 (m, 2H), 3.33 – 3.09 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 138.2, 131.6, 130.9, 130.8, 127.1, 123.1, δ 51.9 (d, *J* = 16.3 Hz), 29.3.

^{19}F NMR (376 MHz, CDCl$_3$): δ 53.65 (t, *J* = 4.3 Hz).

HRMS (EI): m/z calculated for [$C_8H_8O_2BrFS^+$] [M^+]: 265.9407, found: 265.9407.



2-(3-chlorophenyl)ethane-1-sulfonyl fluoride (2i)

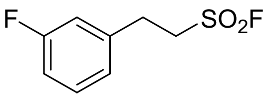
Following the **Method A**. Colorless oil (19 mg, 43% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.21 (m, 3H), 7.13 (d, *J* = 3.0 Hz, 1H), 3.62 (dd, *J* = 7.9, 3.7 Hz, 2H), 3.23 (td, *J* = 8.0, 2.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 137.9, 135.0, 130.5, 128.7, 128.0, 126.7, 51.9 (d, J = 16.3 Hz), 29.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ 53.65 (t, *J* = 4.3 Hz).

HRMS (EI): m/z calculated for [$C_8H_8ClFO_2S^+$] [M^+]: 221.9912, found: 221.9913.



2-(3-fluorophenyl)ethane-1-sulfonyl fluoride (2j)

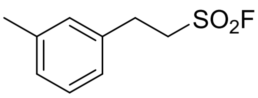
Following the **Method A.** Yellow oil (13 mg, 32% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (td, *J* = 7.9, 6.0 Hz, 1H), 7.10 – 6.85 (m, 3H), 3.63 (ddd, *J* = 9.5, 7.0, 4.4 Hz, 2H), 3.33 – 3.15 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 163.1 (d, *J* = 247.5 Hz), 138.4 (d, *J* = 7.5 Hz), 130.8 (d, *J* = 8.3 Hz), 124.1 (d, *J* = 2.9 Hz), 115.5 (d, *J* = 21.7 Hz), 114.8 (d, *J* = 21.0 Hz), 51.9 (d, *J* = 16.3 Hz), 29.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ 53.63 (t, *J* = 4.3 Hz), -111.94 (td, *J* = 9.0, 6.0 Hz).

HRMS (EI): m/z calculated for [$C_8H_7Cl_2FO_2S^+$] [M^+]: 206.0208 , found: 206.0212.



2-(m-tolyl)ethane-1-sulfonyl fluoride (2k)

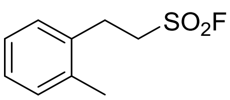
Following the **Method A**. Colorless oil (19 mg, 46% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (t, *J* = 6.4 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.04 (s, 2H), 3.72 – 3.45 (m, 2H), 3.36 – 3.04 (m, 2H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.0, 136.0, 129.2, 129.1, 128.4, 125.4, 52.3 (d, *J* = 15.5 Hz), 29.6, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ 53.06 (t, *J* = 4.3 Hz).

HRMS (EI): m/z calculated for [$C_9H_{11}FO_2S^+$] [M^+]: 202.0458, found: 202.0458.



2-(o-tolyl)ethane-1-sulfonyl fluoride (2l)

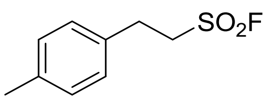
Following the **Method A**. Colorless oil (17 mg, 42% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 – 7.14 (m, 4H), 3.72 – 3.43 (m, 2H), 3.37 – 3.12 (m, 2H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 136.0, 134.3, 131.0, 129.0, 127.9, 126.8, 51.07 (d, *J* = 15.6 Hz), 27.2, 19.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ 52.72 (t, *J* = 4.3 Hz).

HRMS (EI): m/z calculated for [$C_9H_{11}FO_2S^+$] [M^+]: 202.0458, found: 202.0459.



2-(p-tolyl)ethane-1-sulfonyl fluoride (2m)

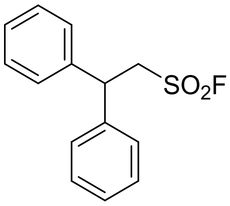
Following the **Method A**. White solid (12 mg, 30% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (dd, *J* = 20.4, 8.0 Hz, 4H), 3.63 – 3.52 (m, 2H), 3.30 – 3.15 (m, 2H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 137.4, 133.0, 129.9, 128.3, 52.4 (d, *J* = 15.3 Hz), 29.3, 21.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ 53.19 (t, *J* = 4.3 Hz).

HRMS (EI): m/z calculated for [$C_9H_{11}FO_2S^+$] [M^+]: 202.0458, found: 202.0457



2,2-diphenylethane-1-sulfonyl fluoride (2n)

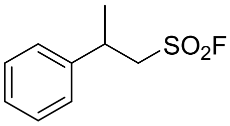
Following the **Method A**. White solid (22 mg, 42% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.32 (m, 4H), 7.32 – 7.26 (m, 6H), 4.70 (t, *J* = 7.3 Hz, 1H), 4.13 (dd, *J* = 7.3, 3.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 140.2, 129.2, 127.8, 127.5, 56.5 (d, *J* = 13.6 Hz), 46.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ 59.20 (t, *J* = 3.5 Hz).

HRMS (EI): m/z calculated for [$C_{14}H_{13}FO_2S^+$] [M^+]: 264.0615, found: 264.0617.



2-phenylpropane-1-sulfonyl fluoride (2o)

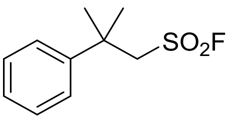
Following the **Method A**. White solid (24 mg, 58% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (t, *J* = 7.3 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.23 (t, *J* = 6.0 Hz, 2H), 3.65 (ddd, *J* = 14.3, 5.7, 3.4 Hz, 1H), 3.60 – 3.42 (m, 2H), 1.51 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 142.4, 129.2, 127.7, 126.7, 58.3 (d, *J* = 13.2 Hz), 35.8, 21.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ 58.57 (s).

HRMS (EI): m/z calculated for [$C_9H_{11}FO_2S^+$] [M^+]: 202.0458, found: 202.0456.



2-methyl-2-phenylpropane-1-sulfonyl fluoride (2p)

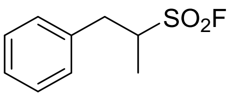
Following the **Method A**. White solid (23 mg, 53% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.34 (m, 4H), 7.33 – 7.25 (m, 1H), 3.69 (d, *J* = 2.3 Hz, 2H), 1.66 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 144.9, 128.8, 127.3, 125.5, 63.6 (d, *J* = 10.6 Hz), 37.5, 27.9.

^{19}F NMR (376 MHz, $CDCl_3$): δ 65.41 (s).

HRMS (EI): m/z calculated for [$C_{10}H_{13}FO_2S^+$] [M^+]: 216.0615, found: 216.0617.



1-phenylpropane-2-sulfonyl fluoride (2q)

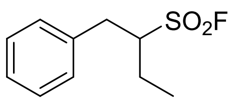
Following the **Method A**. White solid (22 mg, 54% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.40 – 7.28 (m, 3H), 7.21 (d, *J* = 7.0 Hz, 2H), 3.71 – 3.58 (m, 1H), 3.52 (dd, *J* = 13.6, 3.7 Hz, 1H), 2.83 (dd, *J* = 13.5, 10.8 Hz, 1H), 1.44 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 135.4, 129.3, 129.1, 127.7, 59.4 (d, *J* = 12.2 Hz), 36.6, 13.7.

^{19}F NMR (376 MHz, CDCl$_3$): δ 42.20 (s).

HRMS (EI): m/z calculated for [$C_9H_{11}FO_2S^+$] [M$^+$]: 202.0458, found: 202.0457.



1-phenylbutane-2-sulfonyl fluoride (2r)

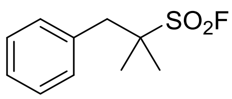
Following the **Method A**. Colorless oil (21 mg, 49% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.33 (t, *J* = 7.2 Hz, 2H), 7.28 (d, *J* = 7.1 Hz, 1H), 7.21 (t, *J* = 8.2 Hz, 2H), 3.53 (qd, *J* = 6.0, 1.4 Hz, 1H), 3.40 (dd, *J* = 14.1, 4.5 Hz, 1H), 2.95 (dd, *J* = 14.1, 9.5 Hz, 1H), 1.96 – 1.84 (m, 2H), 1.06 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 135.7, 129.2, 129.0, 127.6, 65.5 (d, *J* = 9.3 Hz), 34.7, 21.7, 10.8.

^{19}F NMR (376 MHz, CDCl$_3$): δ 49.49 (s).

HRMS (EI): m/z calculated for [$C_{10}H_{13}FO_2S^+$] [M$^+$]: 216.0615, found: 216.0615.



2-methyl-1-phenylpropane-2-sulfonyl fluoride (2s)

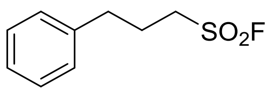
Following the **Method A**. White solid (21 mg, 49% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.39 – 7.30 (m, 3H), 7.23 – 7.15 (m, 2H), 3.20 (s, 2H), 1.48 (s, 6H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 133.6, 131.0, 128.6, 127.8, 65.1 (d, *J* = 9.1 Hz), 41.7, 21.5.

^{19}F NMR (376 MHz, CDCl$_3$): δ 32.16 (s).

HRMS (EI): m/z calculated for [$C_{10}H_{13}FO_2S^+$] [M$^+$]: 216.0615, found: 216.0615.



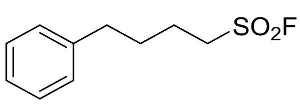
3-phenylpropane-1-sulfonyl fluoride (4a)[5]

Following the **Method B**. Colorless oil (21 mg, 49% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.33 (dd, J = 10.1, 4.5 Hz, 2H), 7.25 (t, J = 7.3 Hz, 1H), 7.18 (d, J = 7.2 Hz, 2H), 3.40 – 3.21 (m, 2H), 2.81 (t, J = 7.3 Hz, 2H), 2.45 – 2.19 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 139.0, 128.9, 128.5, 126.9, 50.0 (d, J = 16.5 Hz), 33.6, 24.9.

^{19}F NMR (376 MHz, CDCl$_3$): δ 53.21 (t, J = 4.1 Hz).



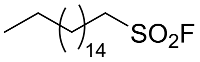
4-phenylbutane-1-sulfonyl fluoride (4b)[6]

Following the **Method B**. Colorless oil (28 mg, 65% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.31 (t, J = 7.4 Hz, 2H), 7.23 (dd, J = 14.6, 7.3 Hz, 1H), 7.18 (d, J = 7.1 Hz, 2H), 3.52 – 3.23 (m, 2H), 2.69 (t, J = 7.5 Hz, 2H), 1.99 (dt, J = 12.1, 7.4 Hz, 2H), 1.91 – 1.74 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$):δ 140.8, 128.7, 128.4, 126.4, 50.8 (d, J = 16.3 Hz), 35.1, 29.6, 23.0.

^{19}F NMR (376 MHz, CDCl$_3$): δ 53.58 (t, J = 4.1 Hz).



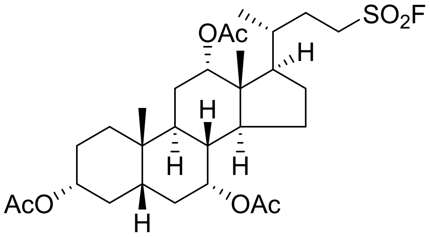
heptadecane-1-sulfonyl fluoride (4c)[6]

Following the **Method B**. White solid (30 mg, 45% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.46 – 3.25 (m, 2H), 1.94 (dt, J = 15.5, 7.7 Hz, 2H), 1.53 – 1.39 (m, 2H), 1.37 – 1.19 (m, 26H), 0.88 (t, J = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 51.0 (d, J = 16.1 Hz), 32.0, 29.8, 29.8, 29.7, 29.6, 29.5, 29.5, 29.3, 28.9, 28.0, 23.5, 22.8, 14.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ 53.24 (t, J = 4.1 Hz).



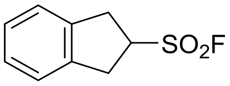
(3R,5S,7R,8R,9S,10S,12S,13R,14S,17R)-17-((R)-4-(fluorosulfonyl)butan-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthrene-3,7,12-triyl triacetate (4d)[5]

Following the **Method B**. White solid (40 mg, 35% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.10 (s, 1H), 4.92 (d, J = 2.5 Hz, 1H), 4.59 (ddd, J = 15.5, 11.2, 4.2 Hz, 1H), 3.41 (ddd, J = 11.3, 9.8, 4.2 Hz, 1H), 3.27 (ddd, J = 14.5, 9.4, 4.7 Hz, 1H), 2.16 (s, 3H), 2.10 (s, 3H), 2.06 (s, 3H), 2.02 – 1.84 (m, 4H), 1.83 – 1.74 (m, 2H), 1.65 (ddd, J = 33.7, 20.4, 15.3 Hz, 8H), 1.55 – 1.42 (m, 3H), 1.30 (dd, J = 29.2, 12.0 Hz, 3H), 1.19 – 1.03 (m, 2H), 0.93 (s, 3H), 0.89 (d, J = 6.3 Hz, 3H), 0.76 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.6, 170.5, 170.4, 75.2, 74.1, 70.6, 48.5 (d, J = 16.2 Hz), 47.1, 45.2, 43.5, 40.9, 37.8, 34.7, 34.7, 34.4, 34.0, 31.3, 29.2, 28.9, 27.2, 26.9, 25.6, 22.8, 22.6, 21.7, 21.6, 21.5, 17.5, 12.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ 52.89 (t, J = 3.8 Hz).



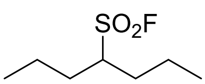
2,3-dihydro-1H-indene-2-sulfonyl fluoride (4e)[7]

Following the **Method B**. White solid (23 mg, 57% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (s, 4H), 4.37 – 4.21 (m, 1H), 3.59 (qd, J = 16.6, 8.2 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 138.3, 127.8, 124.6, 59.6 (d, J = 15.1 Hz), 34.7.

^{19}F NMR (376 MHz, $CDCl_3$): δ 45.49 (d, J = 1.0 Hz).



heptane-4-sulfonyl fluoride (4f)

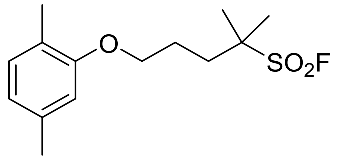
Following the **Method B**. Colorless oil (24 mg, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.54 – 3.23 (m, 1H), 1.98 (ddd, J = 21.5, 14.6, 8.3 Hz, 2H), 1.86 – 1.65 (m, 2H), 1.61 – 1.46 (m, 4H), 0.97 (dd, J = 14.3, 7.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 61.3 (d, J = 10.1 Hz), 29.9, 18.5, 12.7.

^{19}F NMR (376 MHz, $CDCl_3$): δ 47.98 (d, J = 15.2 Hz).

HRMS (EI): m/z calculated for [$C_7H_{15}FO_2S^+$] [M^+]: 182.0771, found: 182.0776 .



5-(2,5-dimethylphenoxy)-2-methylpentane-2-sulfonyl fluoride (4g)

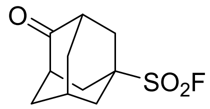
Following the **Method B**. White solid (37 mg, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02 (d, J = 7.5 Hz, 1H), 6.69 (d, J = 7.5 Hz, 1H), 6.62 (s, 1H), 3.99 (t, J = 5.8 Hz, 2H), 2.32 (s, 3H), 2.18 (s, 3H), 2.15 – 2.09 (m, 2H), 2.02 – 1.92 (m, 2H), 1.60 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 156.7, 136.7, 130.5, 123.6, 121.2, 112.0, 67.0, 64.4 (d, J = 10.0 Hz), 33.8, 24.2, 22.3, 21.5, 15.8.

^{19}F NMR (376 MHz, $CDCl_3$): δ 33.65 (s).

HRMS (EI): m/z calculated for [$C_{14}H_{21}FO_3S^+$] [M^+]: 288.1190, found: 288.1193.



(1s,3R,5S,7s)-4-oxoadamantane-1-sulfonyl fluoride (4h)

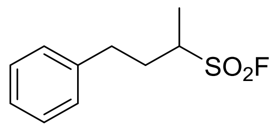
Following the **Method B**. White solid (26 mg, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.76 (s, 2H), 2.60 – 2.44 (m, 5H), 2.41 (s, 2H), 2.08 (q, J = 13.3 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 212.6, 60.8 (d, J = 12.8 Hz), 45.1, 37.5, 37.1, 35.1, 27.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ 29.93 (s).

HRMS (EI): m/z calculated for [$C_{10}H_{13}FO_2S^+$] [M^+]: 232.0564, found: 232.0560.



4-phenylbutane-2-sulfonyl fluoride (4i)[5]

Following the **Method B**. White solid (28 mg, 64% yield).

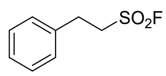
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (t, J = 7.4 Hz, 2H), 7.28 – 7.22 (m, 1H), 7.20 (d, J = 7.2 Hz, 2H), 3.49 – 3.29 (m, 1H), 3.01 – 2.81 (m, 1H), 2.81 – 2.68 (m, 1H), 2.55 – 2.36 (m, 1H), 2.13 – 1.94 (m, 1H), 1.56 (d, J = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.3, 128.9, 128.4, 126.8, 57.2 (d, J = 13.0 Hz), δ 32.1, 32.0, 14.5.

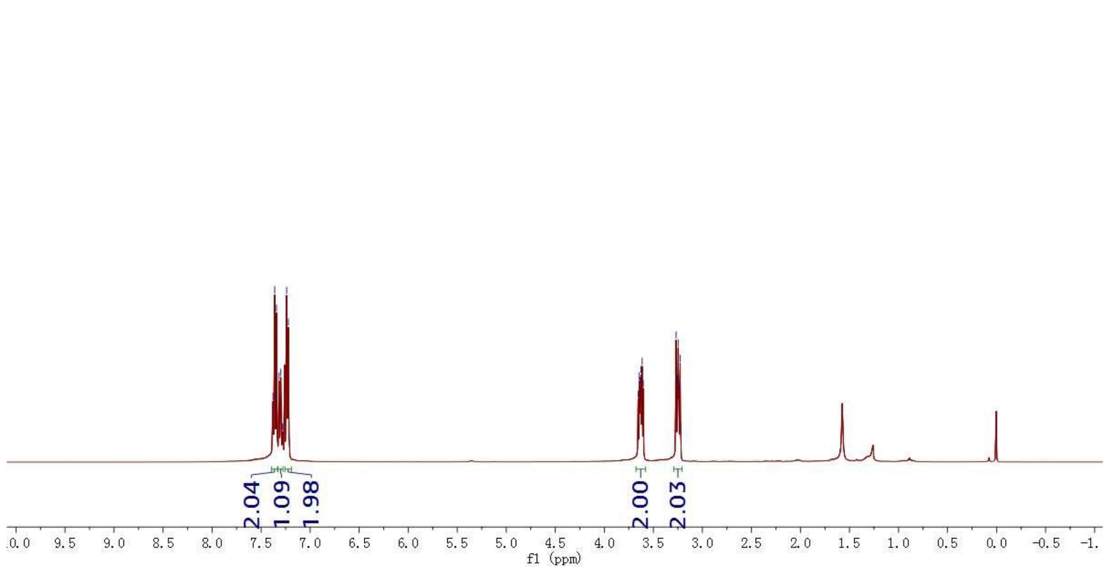
^{19}F NMR (376 MHz, $CDCl_3$): δ 42.76 (d, J = 15.6 Hz).

6. ^{1}H, ^{13}C and ^{19}F NMR Spectra

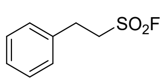
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$):



2a



^{13}C-NMR Spectrum (101 MHz, $CDCl_3$):



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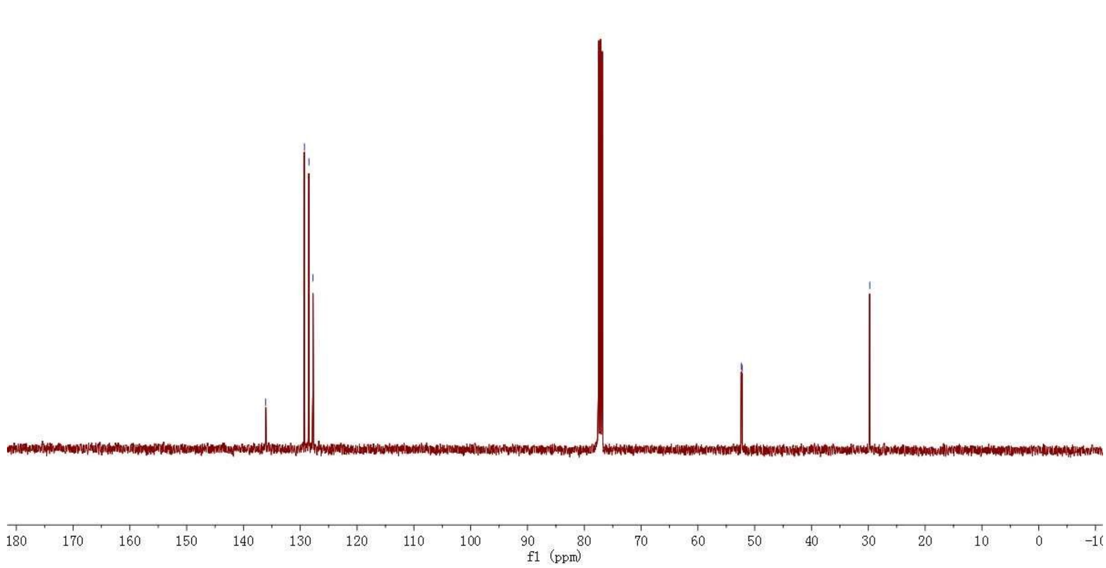
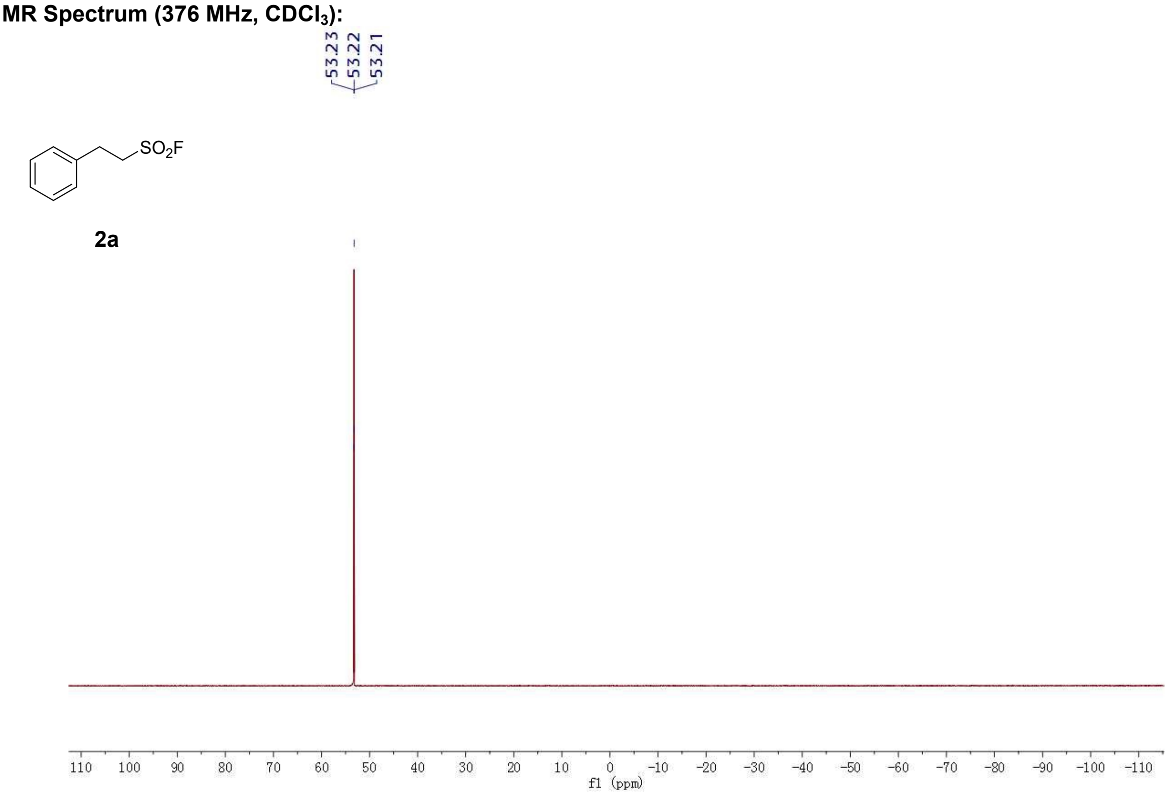
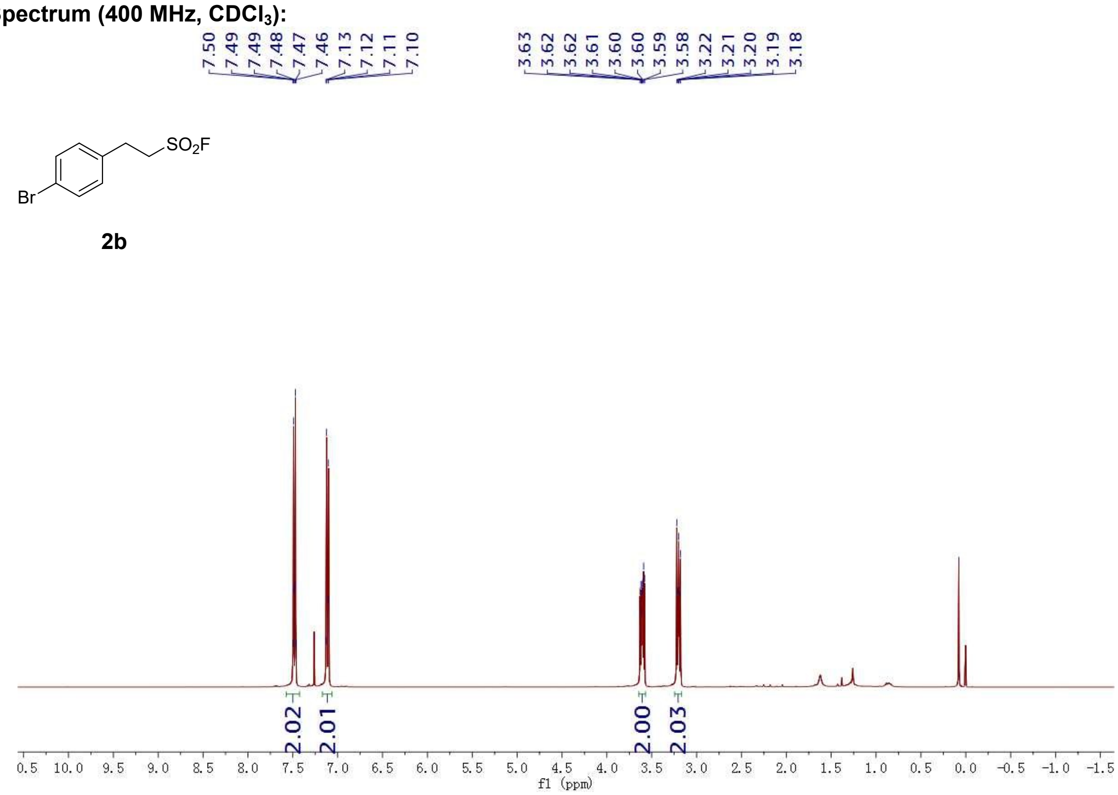


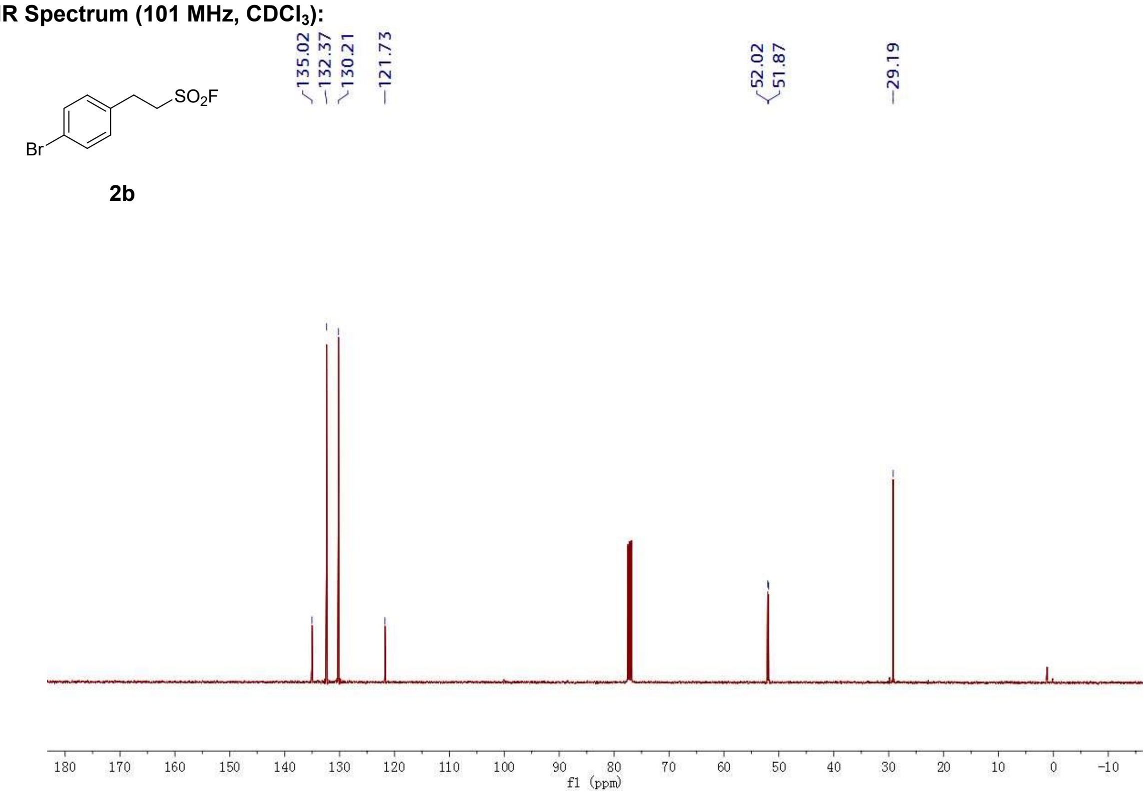
^{19}F-NMR Spectrum (376 MHz, $CDCl_3$):



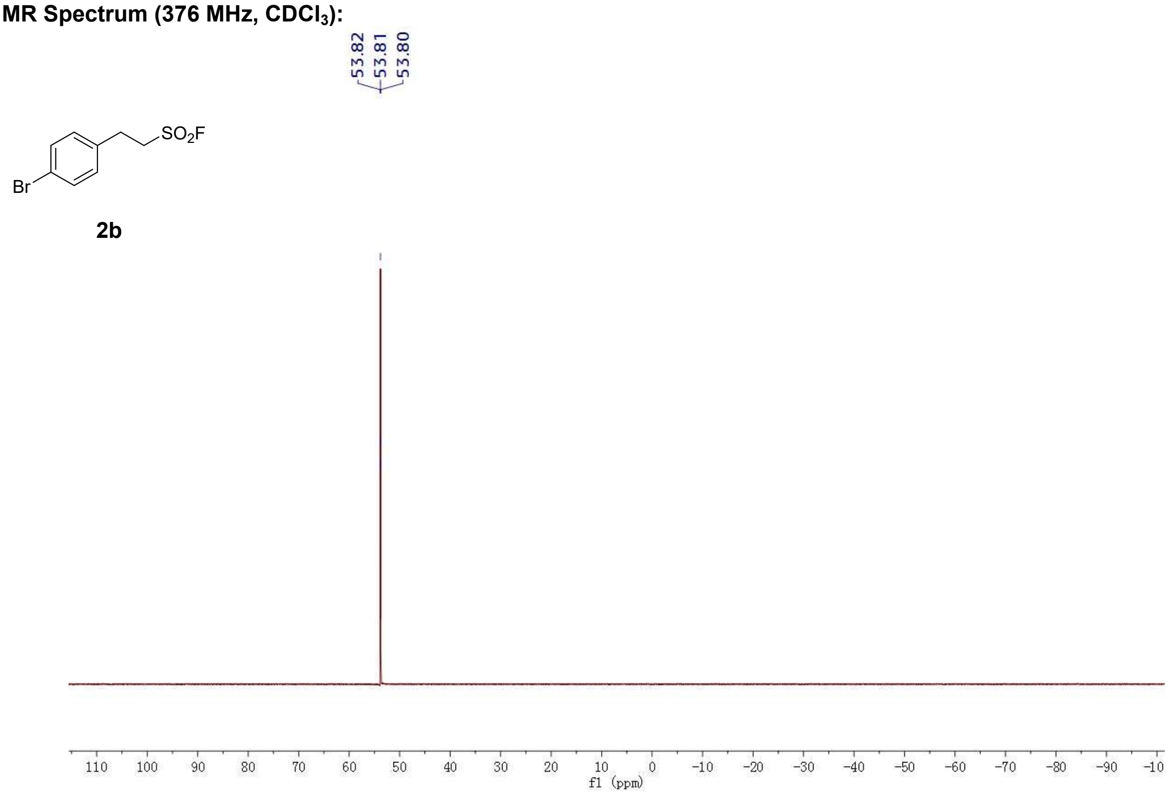
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$):



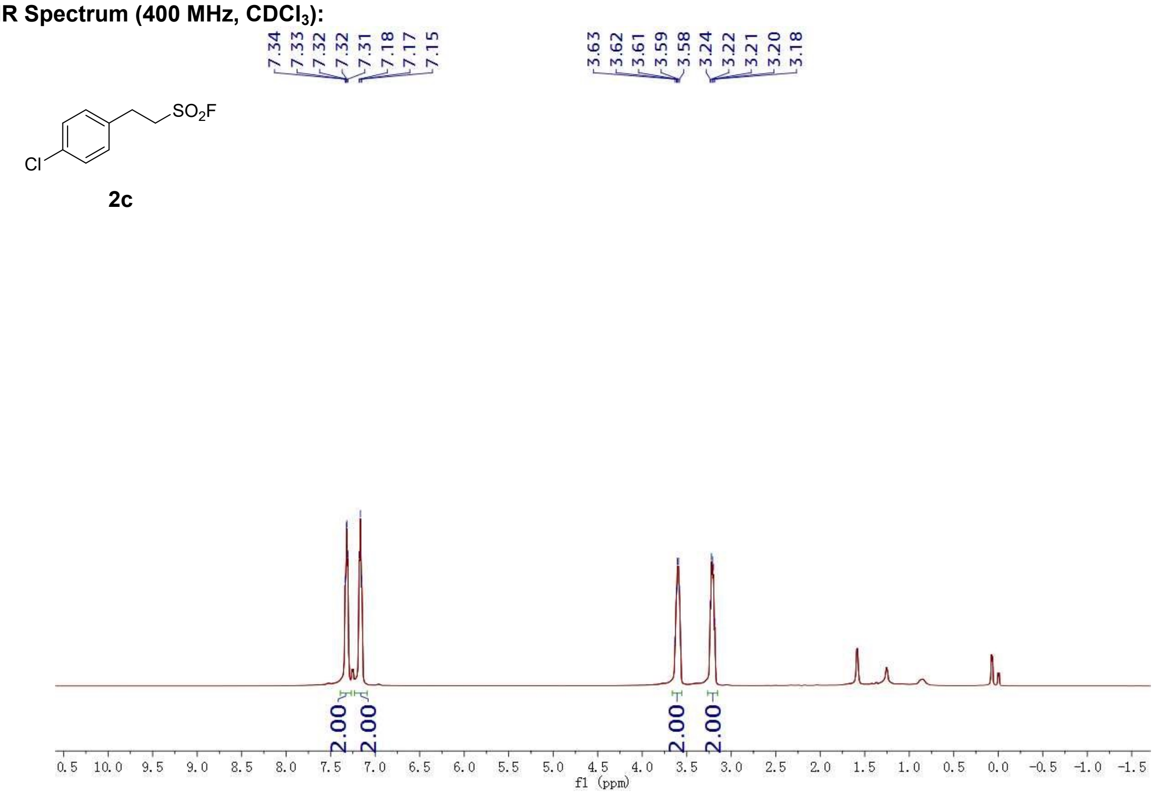
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$):



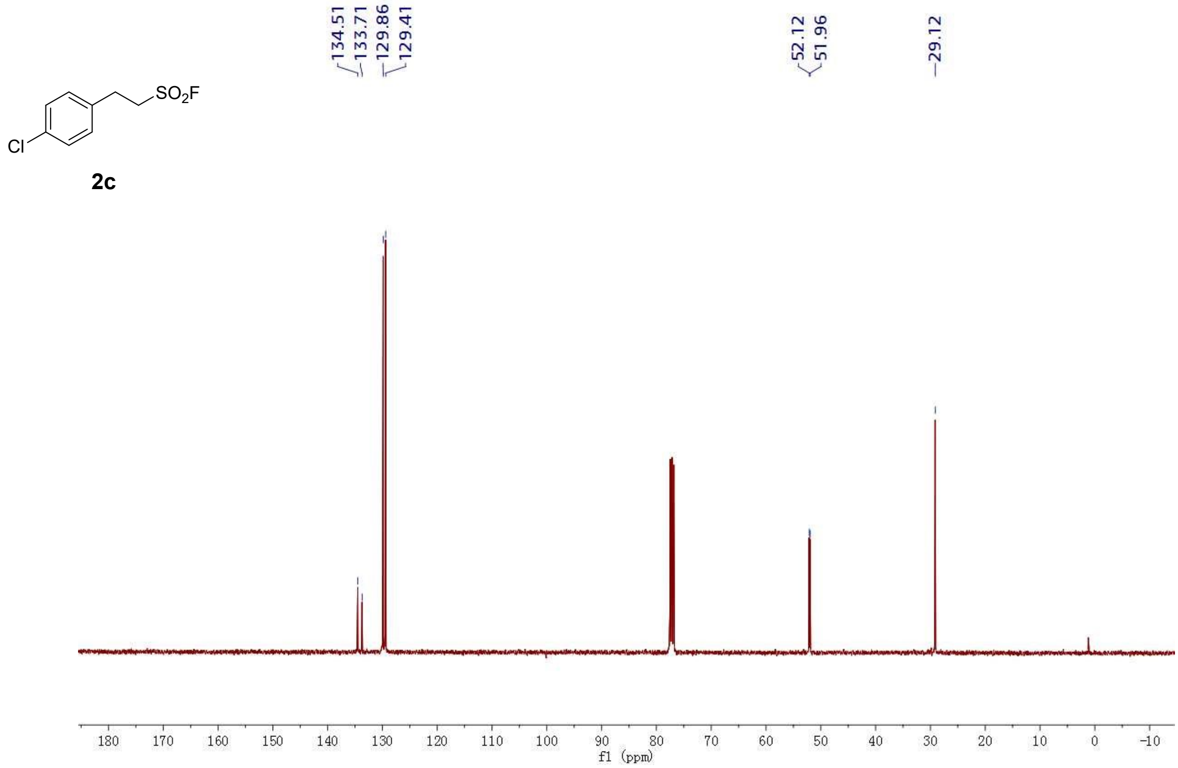
^{19}F-NMR Spectrum (376 MHz, $CDCl_3$):



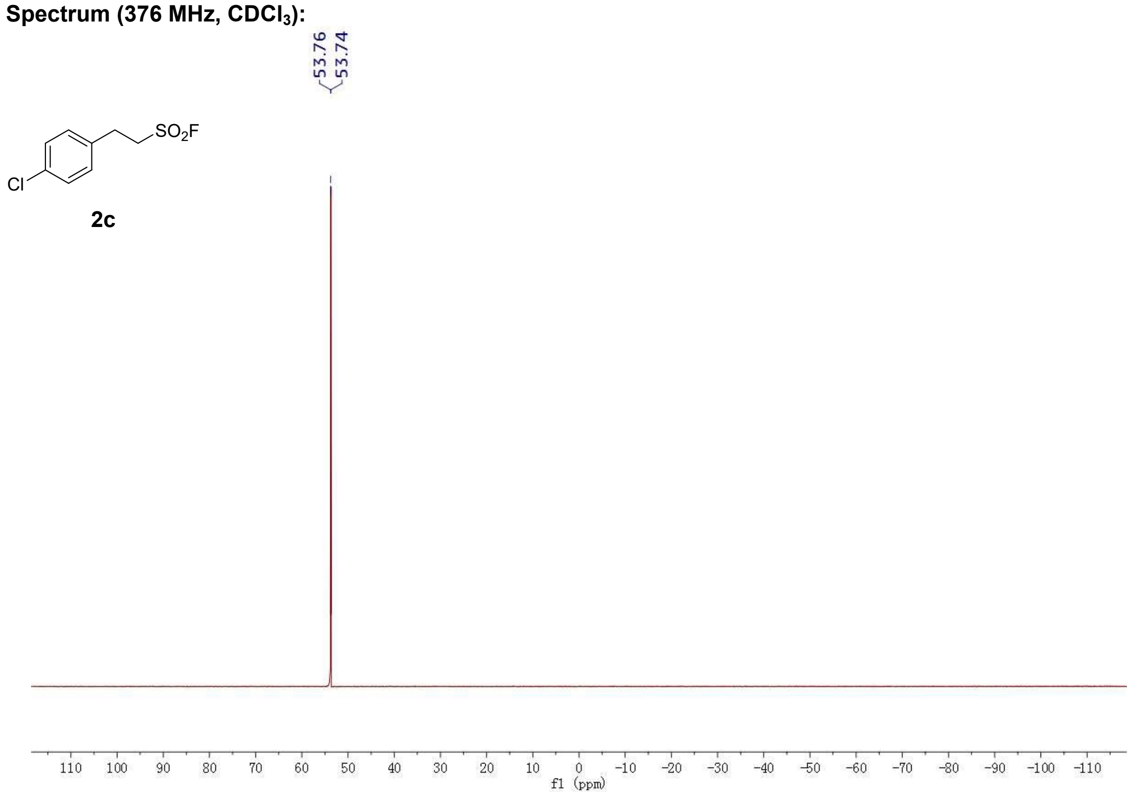
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$):



^{13}C-NMR Spectrum (101 MHz, $CDCl_3$):



^{19}F-NMR Spectrum (376 MHz, $CDCl_3$):



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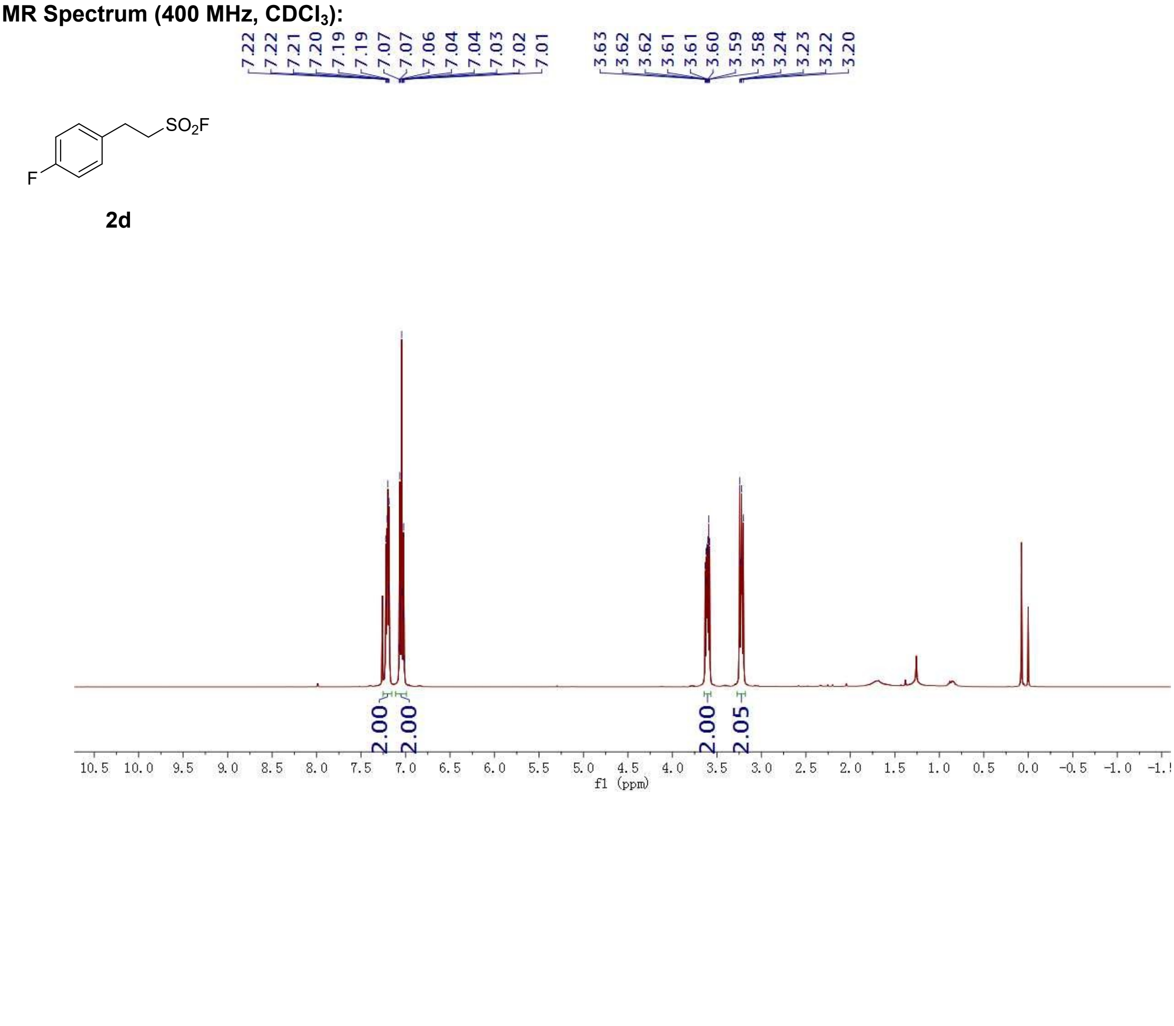
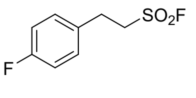


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$):



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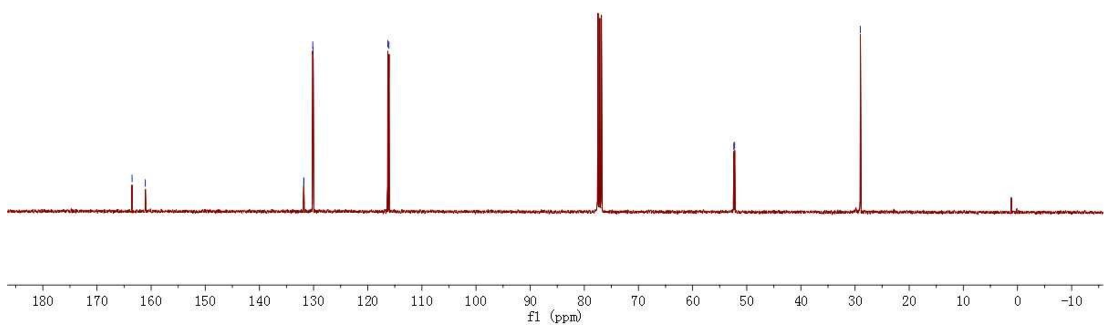

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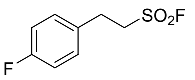

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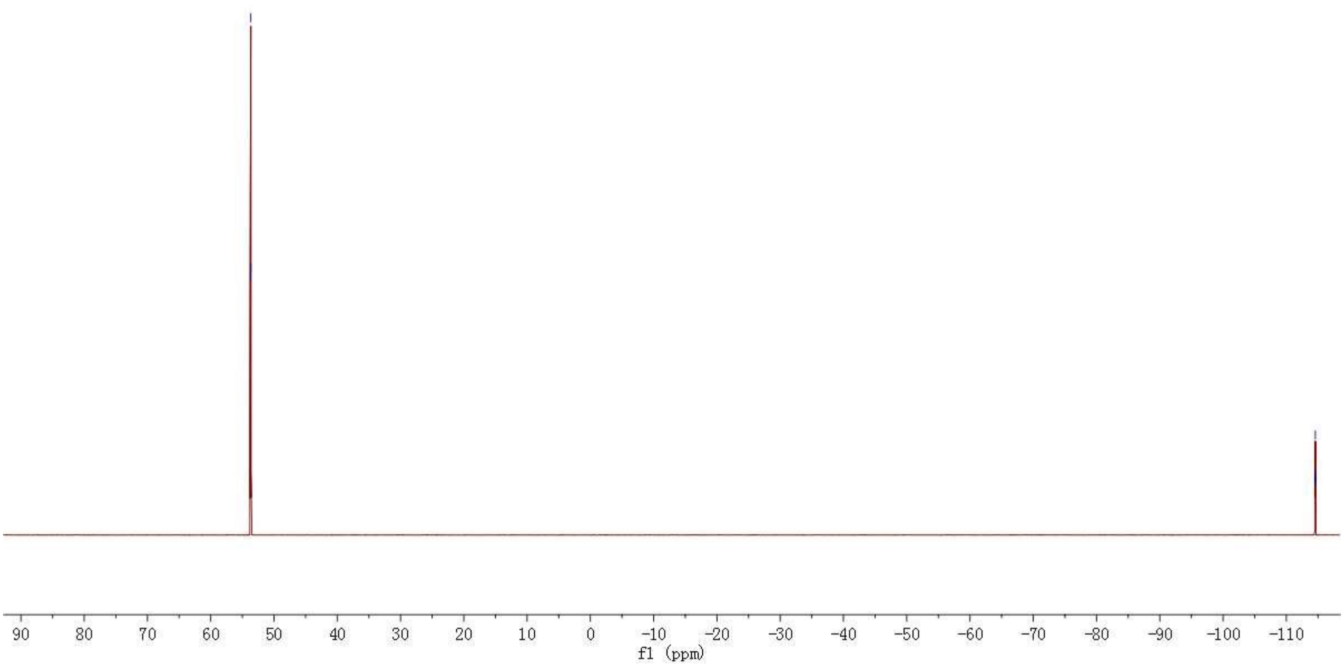
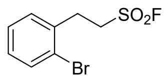


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$):



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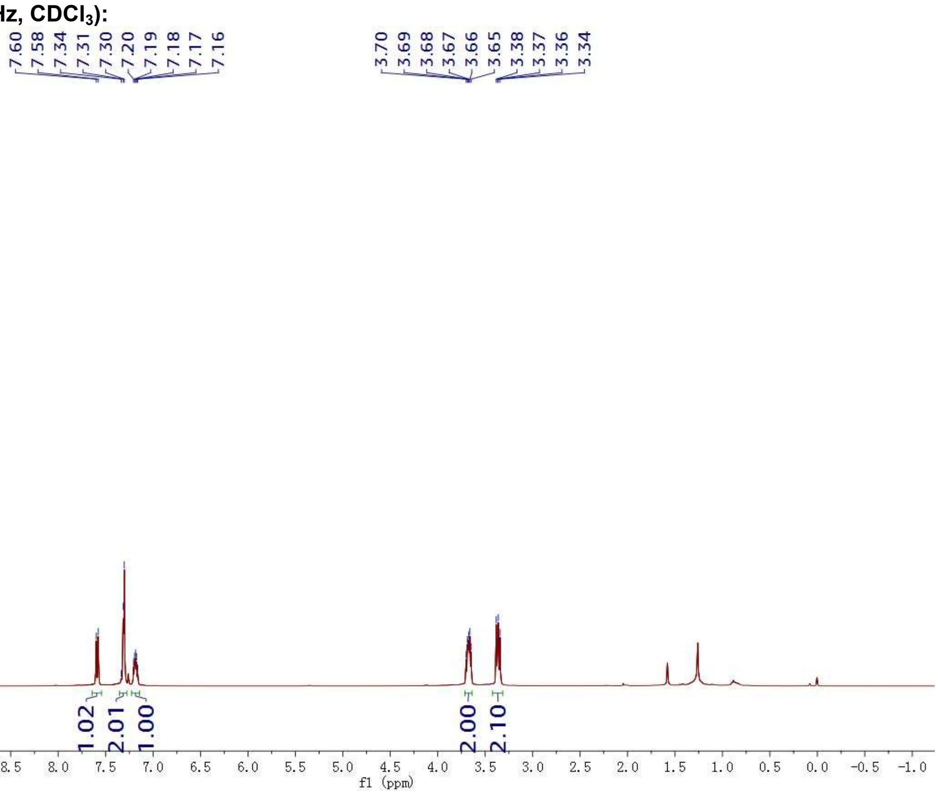
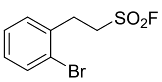


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$):



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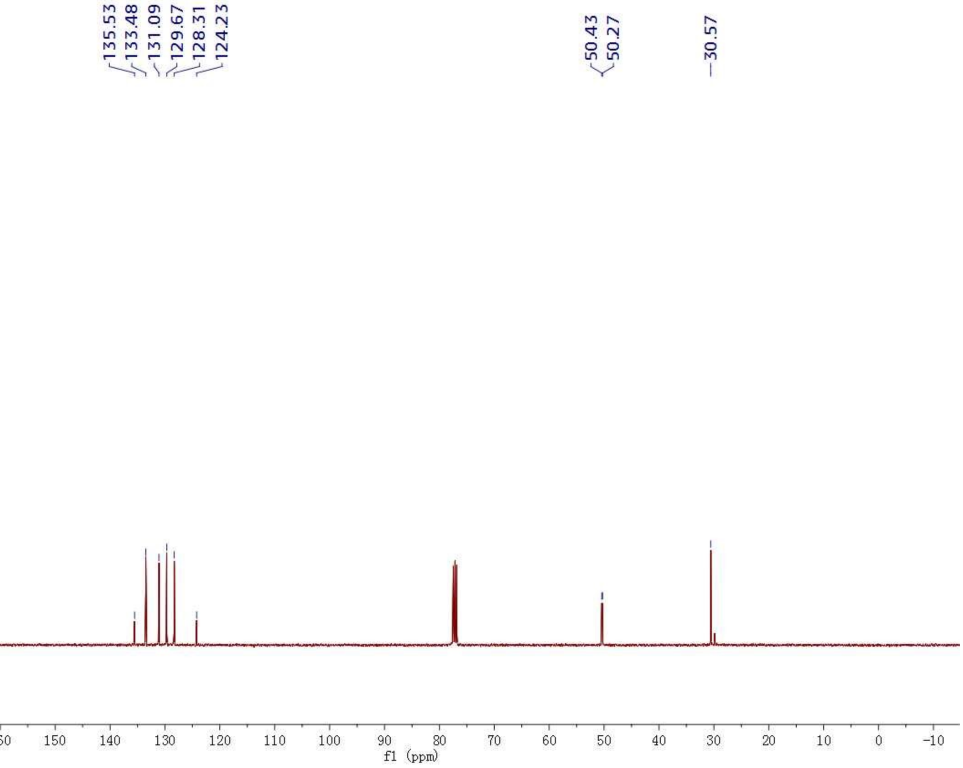
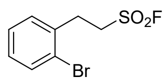


^{19}F-NMR Spectrum (376 MHz, $CDCl_3$):



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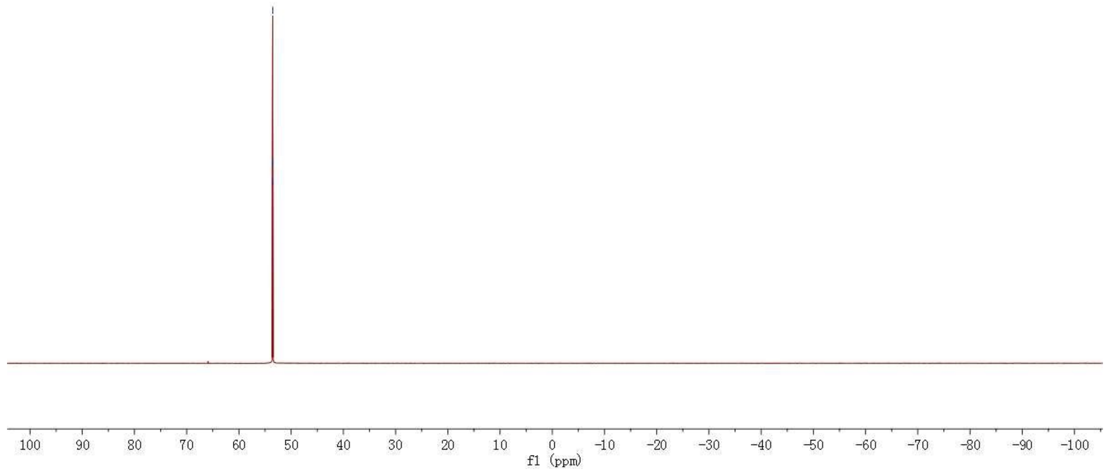
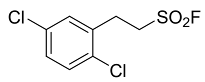


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$):



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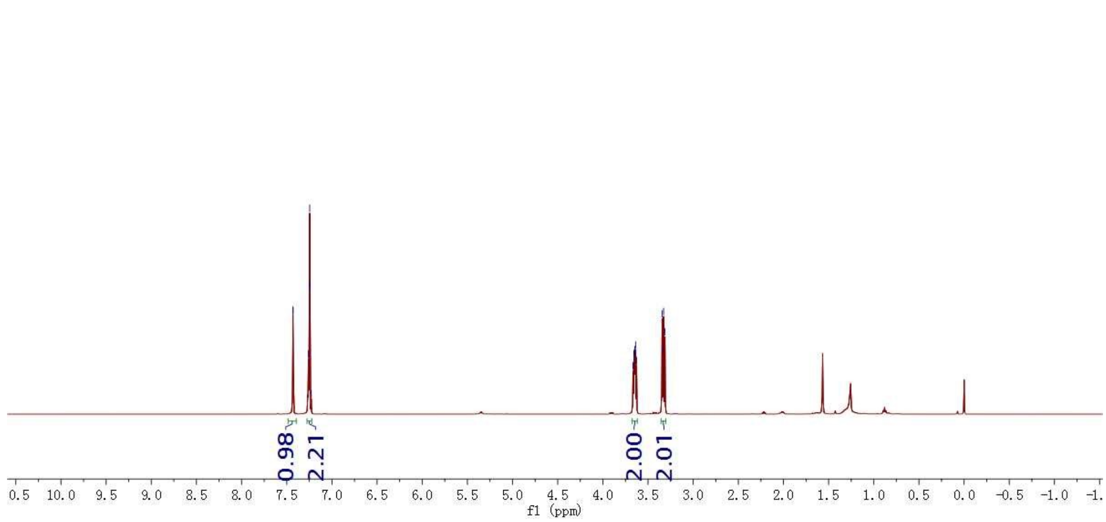
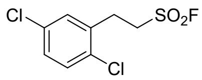


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$):



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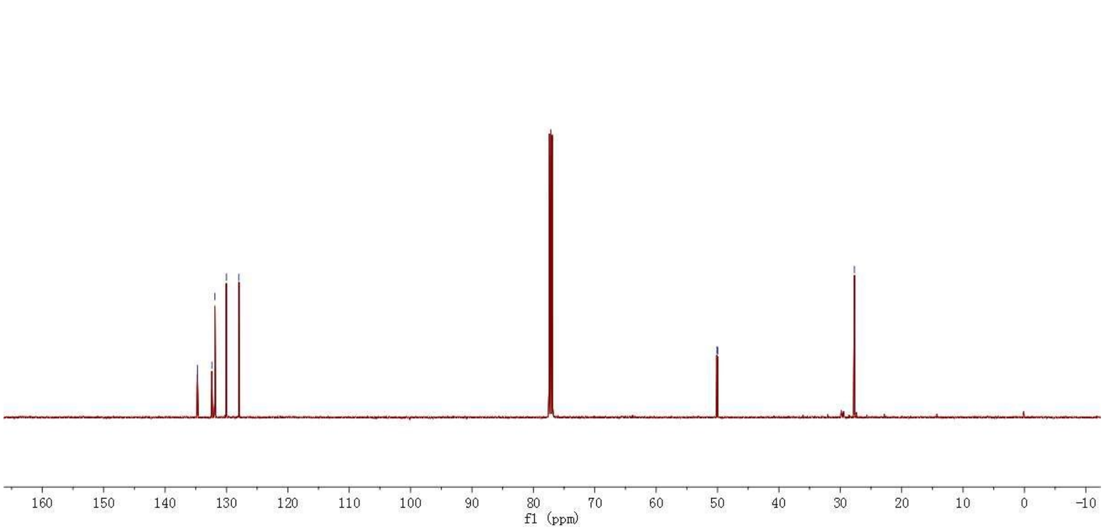
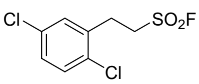


^{19}F-NMR Spectrum (376 MHz, $CDCl_3$):



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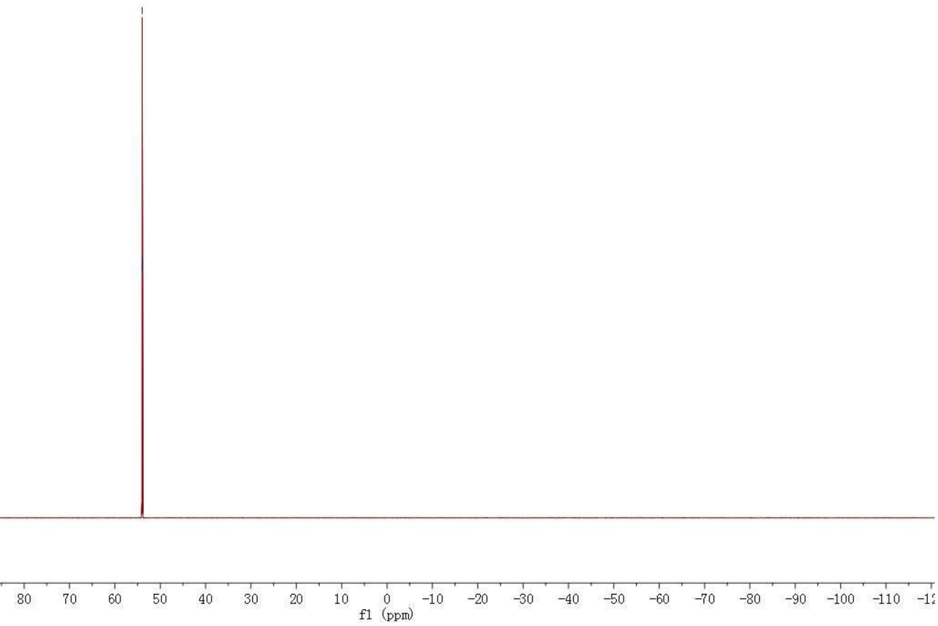
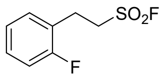


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$):



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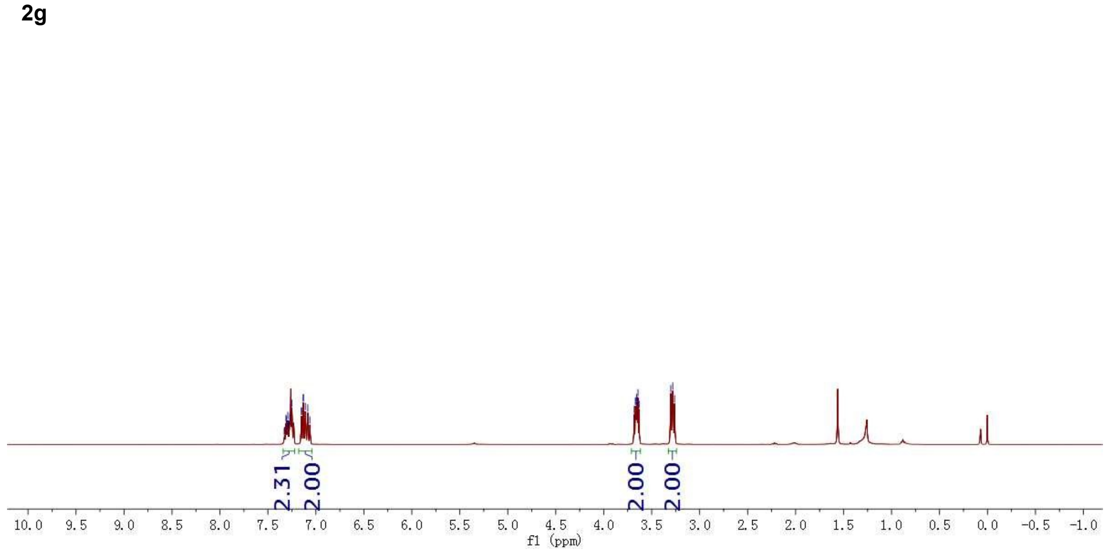
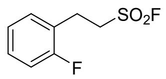


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$):



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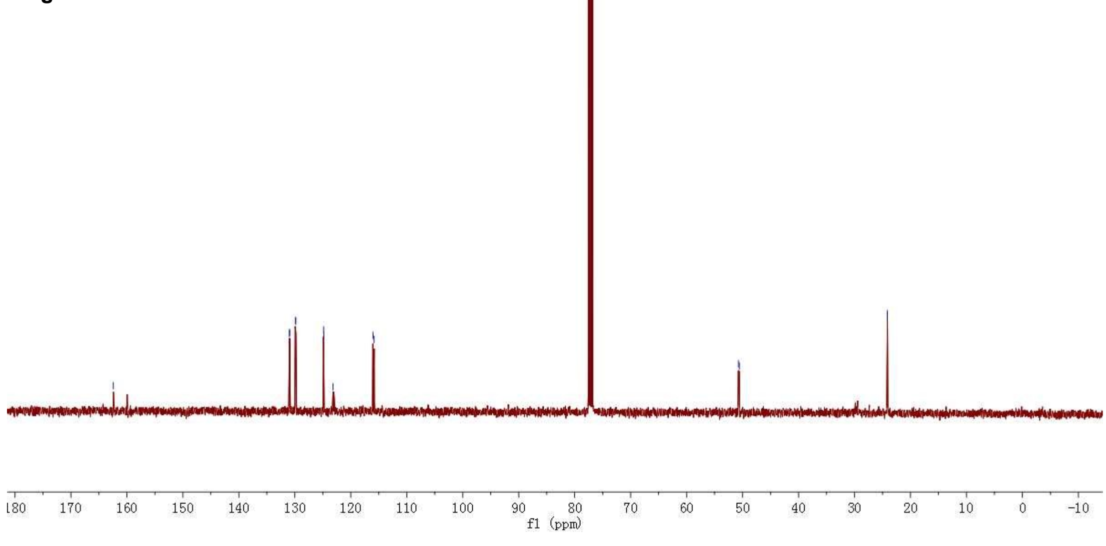
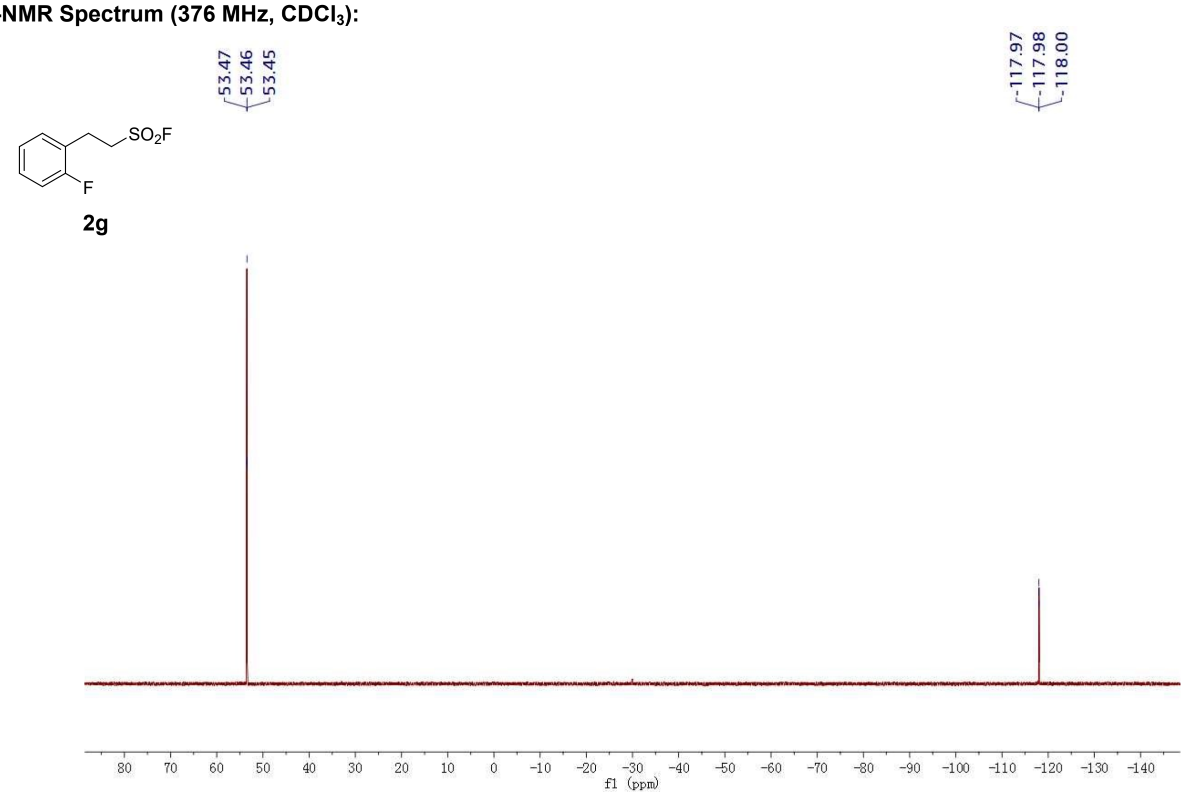
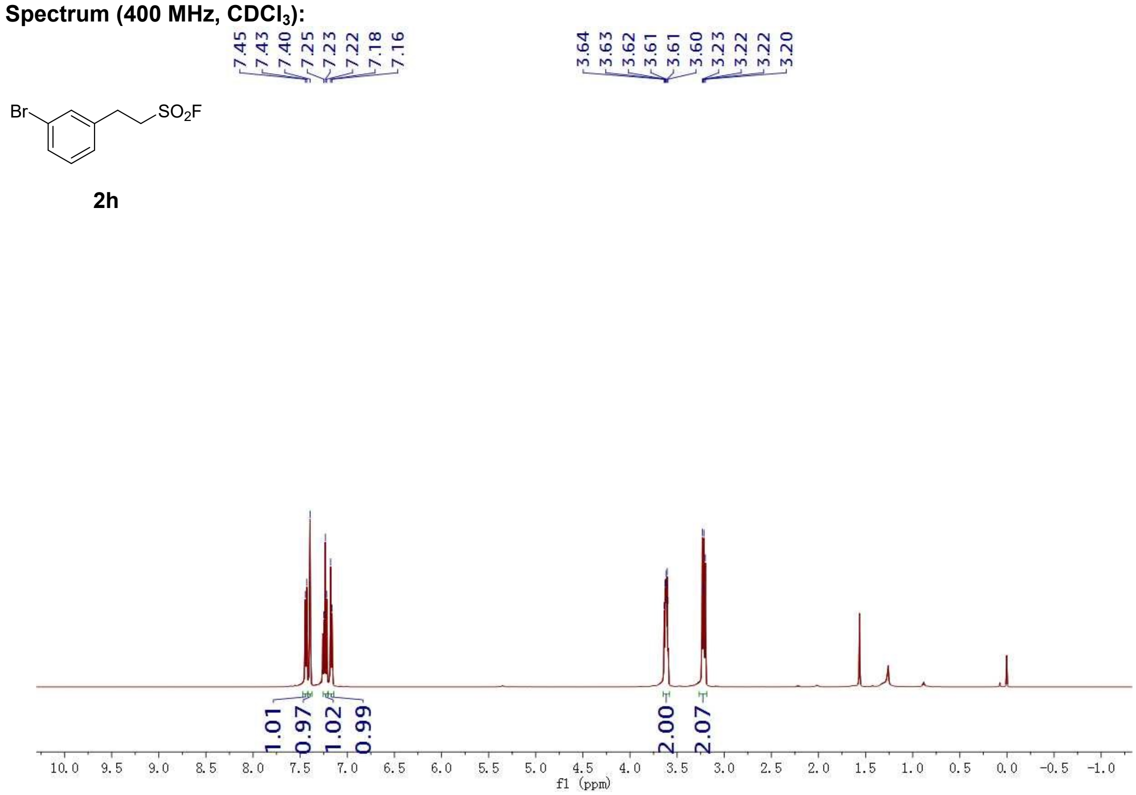


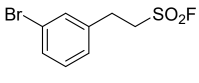
[19]F-NMR Spectrum (376 MHz, $CDCl_3$):



[1]H-NMR Spectrum (400 MHz, $CDCl_3$):



^{13}C-NMR Spectrum (101 MHz, $CDCl_3$):



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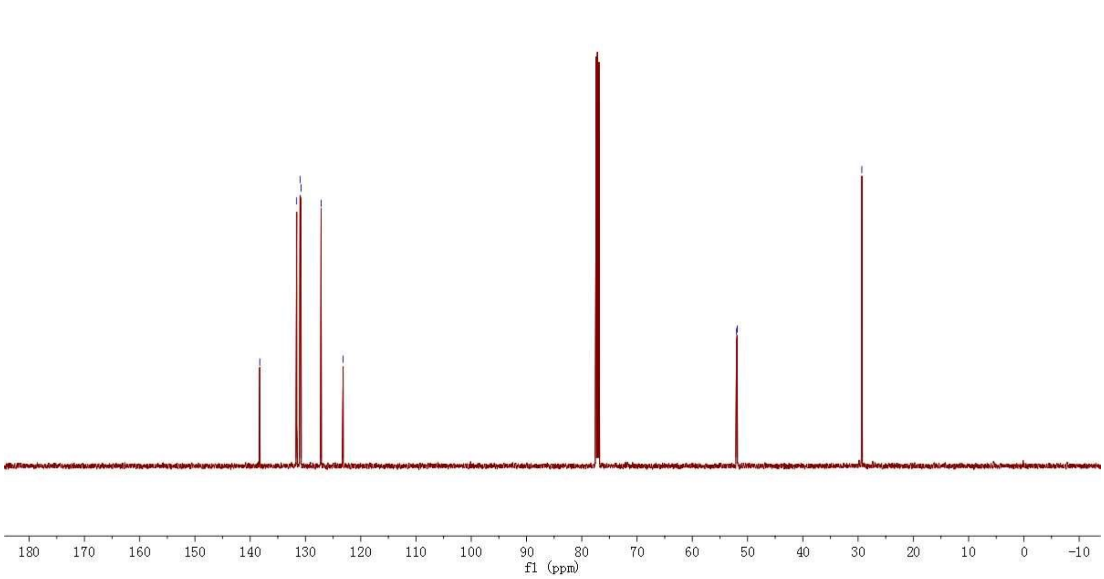
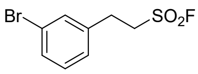


^{19}F-NMR Spectrum (376 MHz, $CDCl_3$):



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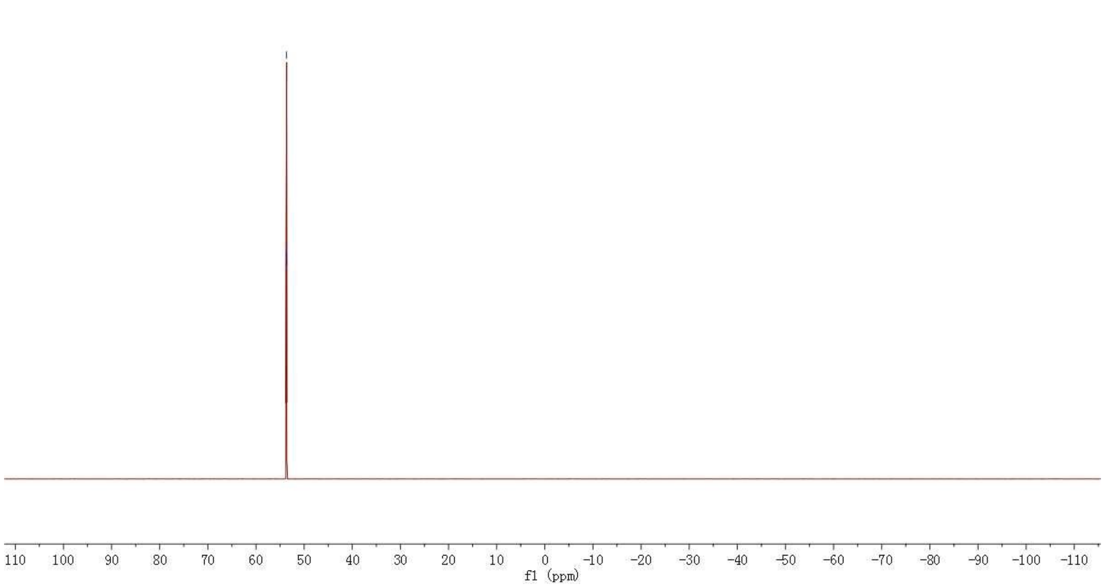

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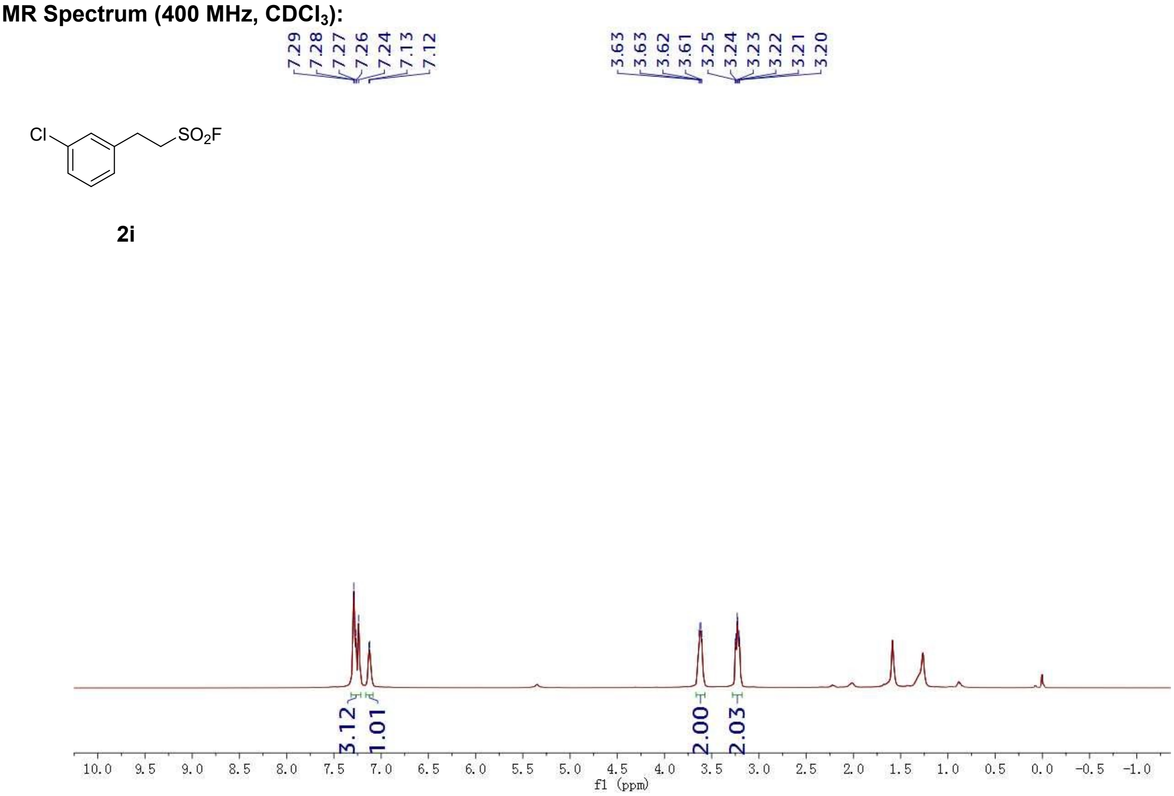

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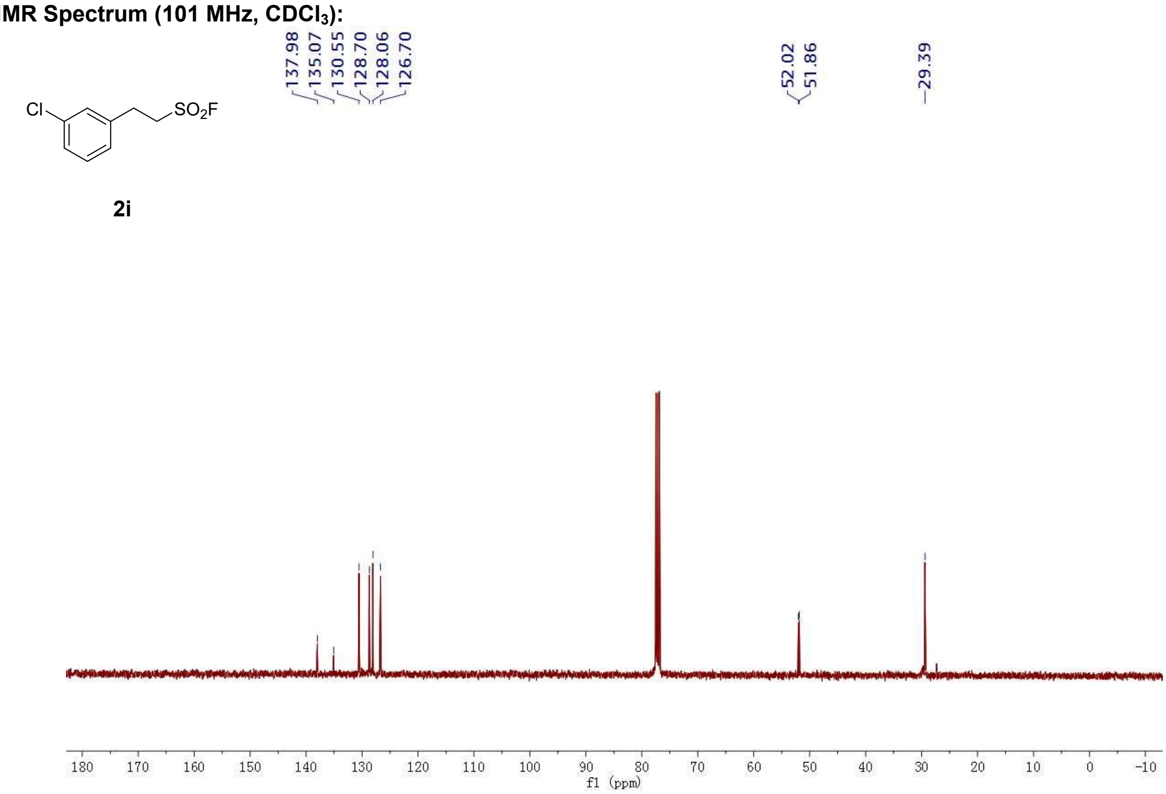

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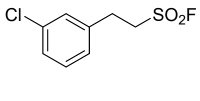

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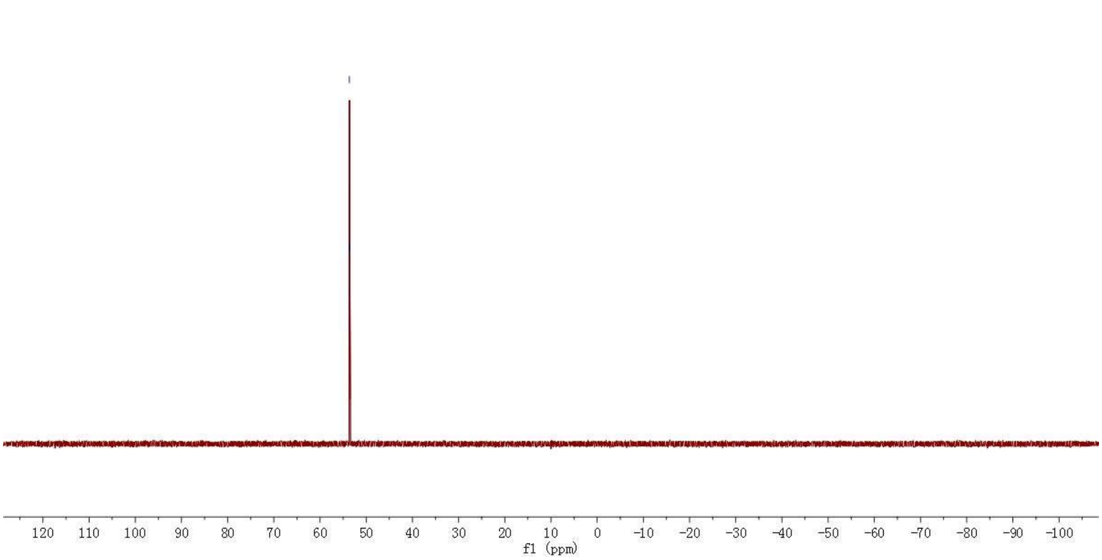

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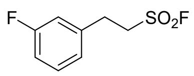

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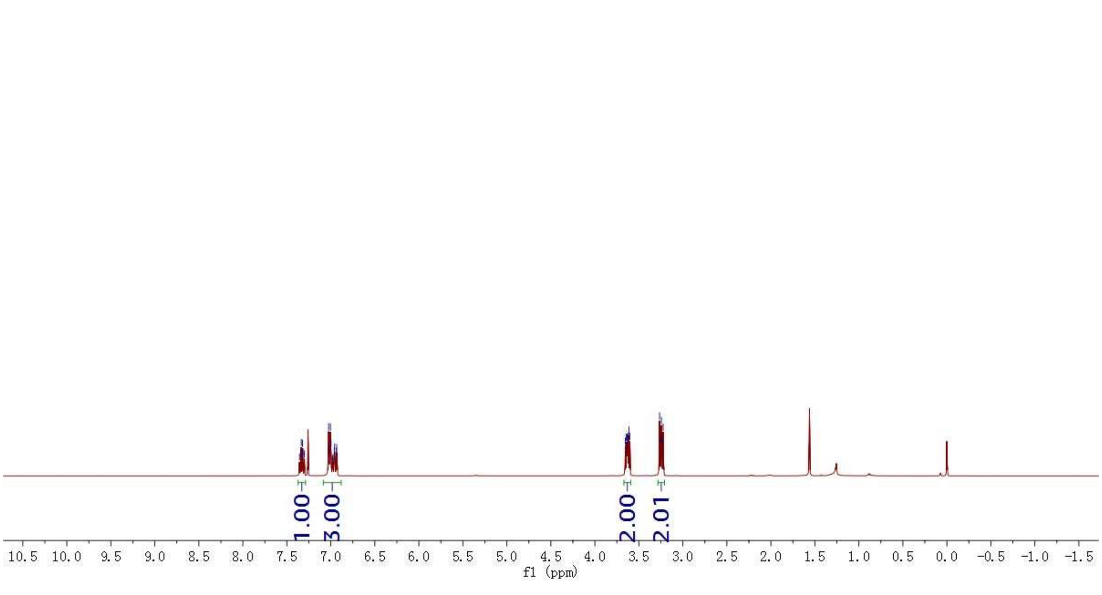
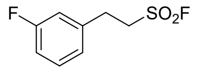


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$):



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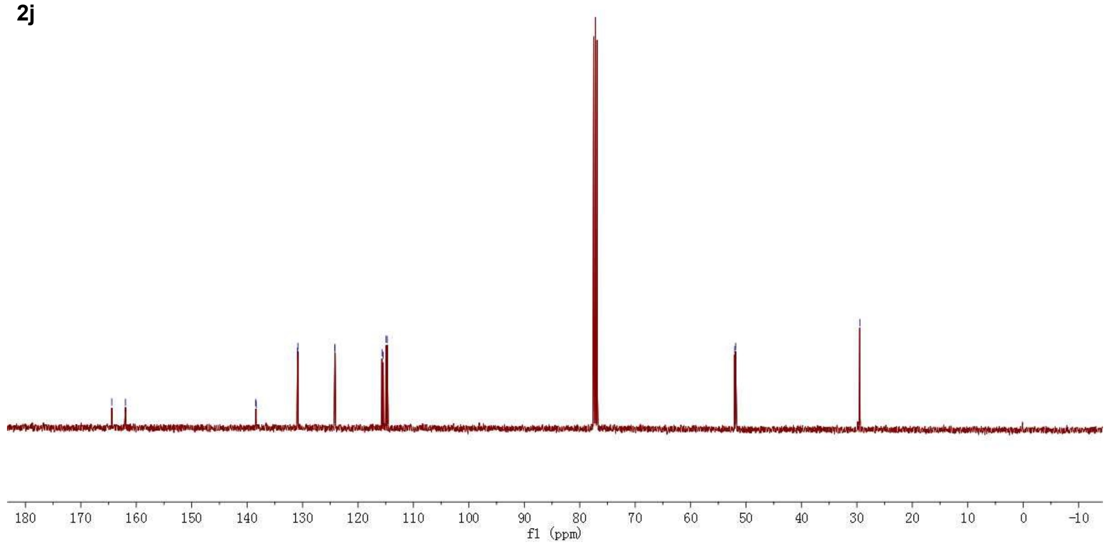
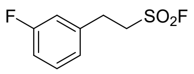


^{19}F-NMR Spectrum (376 MHz, $CDCl_3$):



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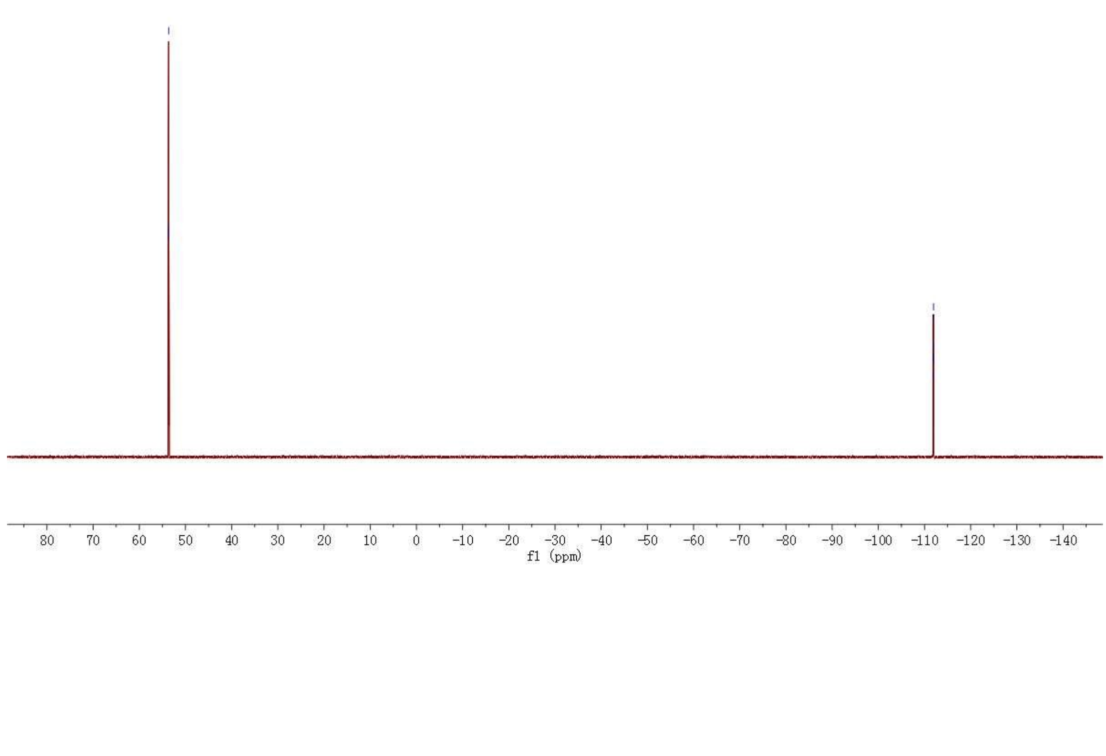
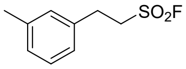


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$):



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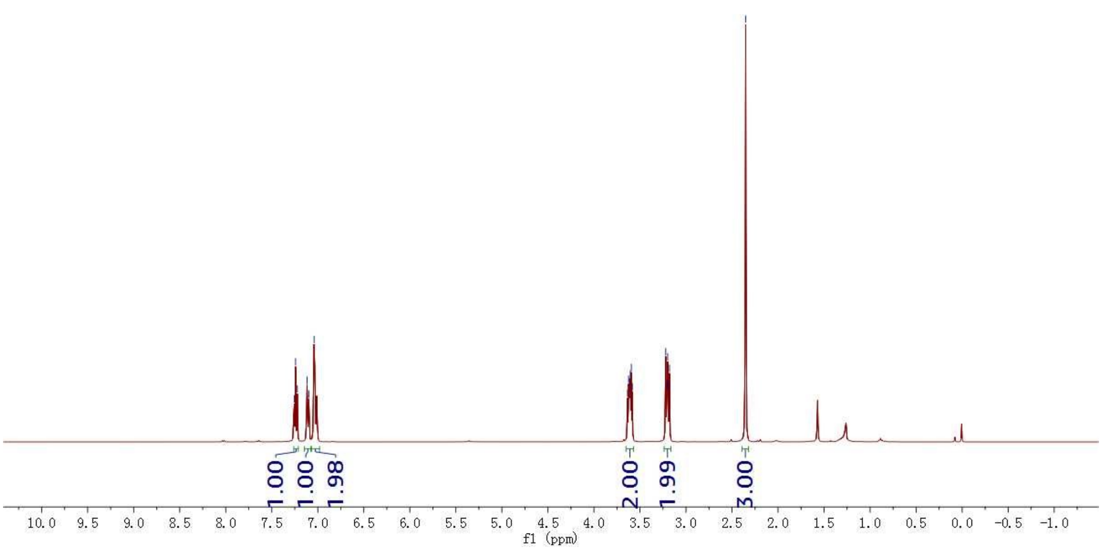
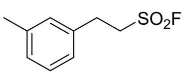


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$):



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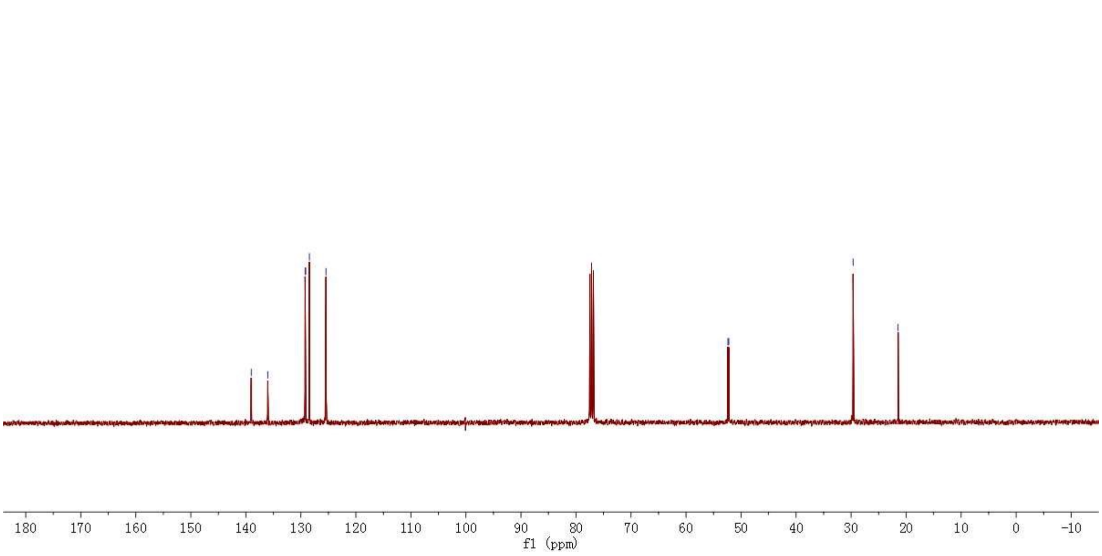
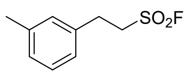


^{19}F-NMR Spectrum (376 MHz, $CDCl_3$):



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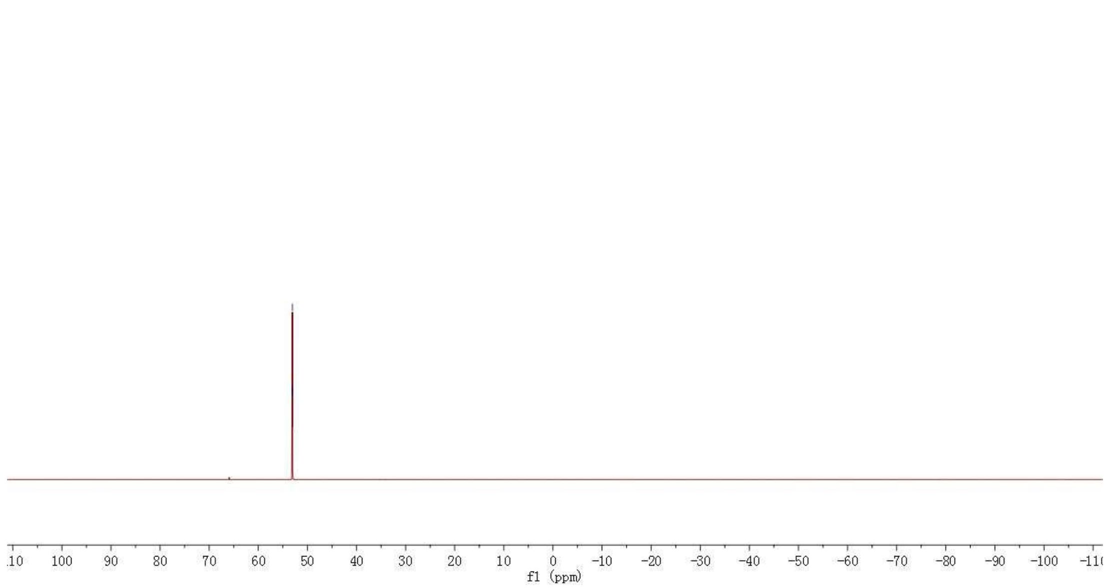
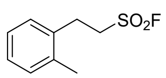


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$):



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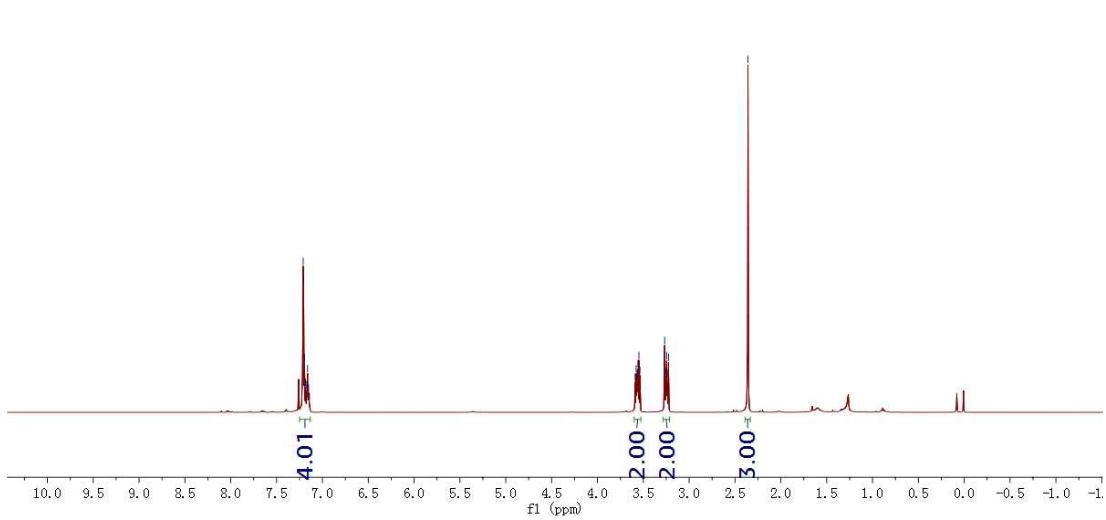
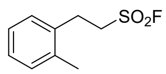


[13]C-NMR Spectrum (101 MHz, $CDCl_3$):



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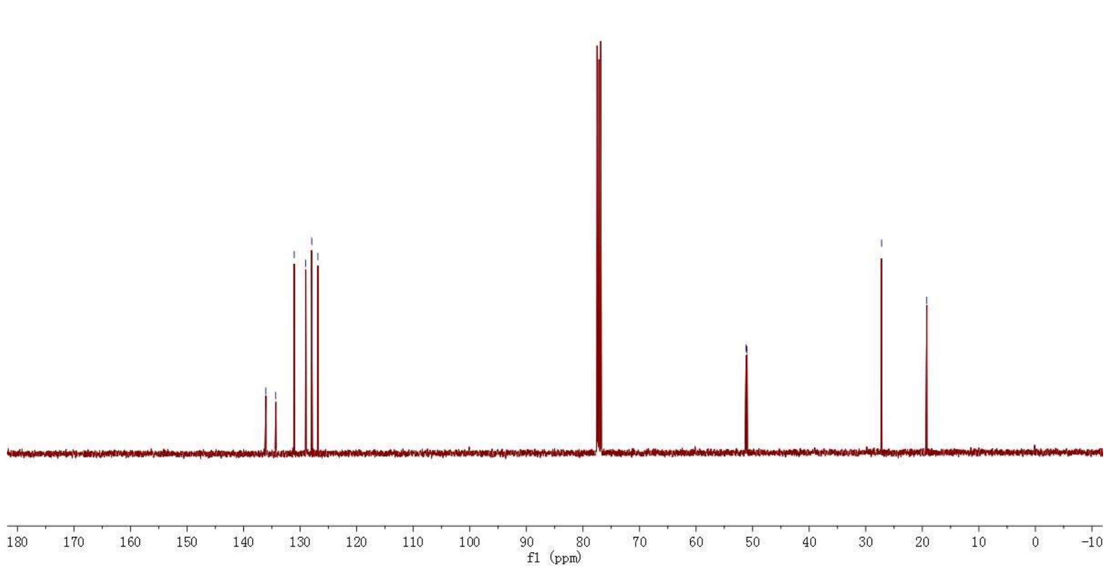

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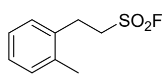

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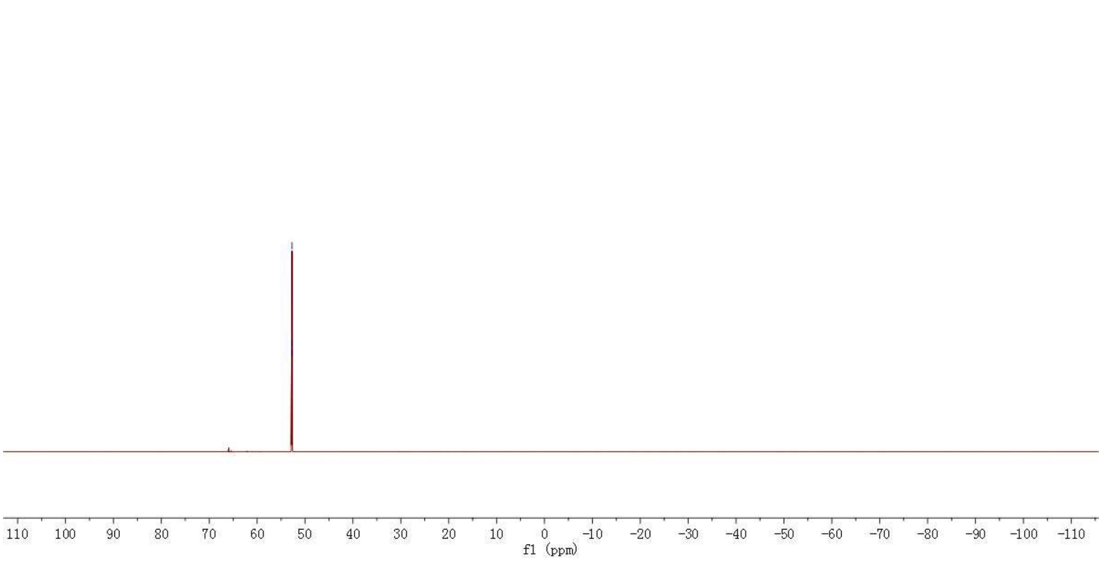

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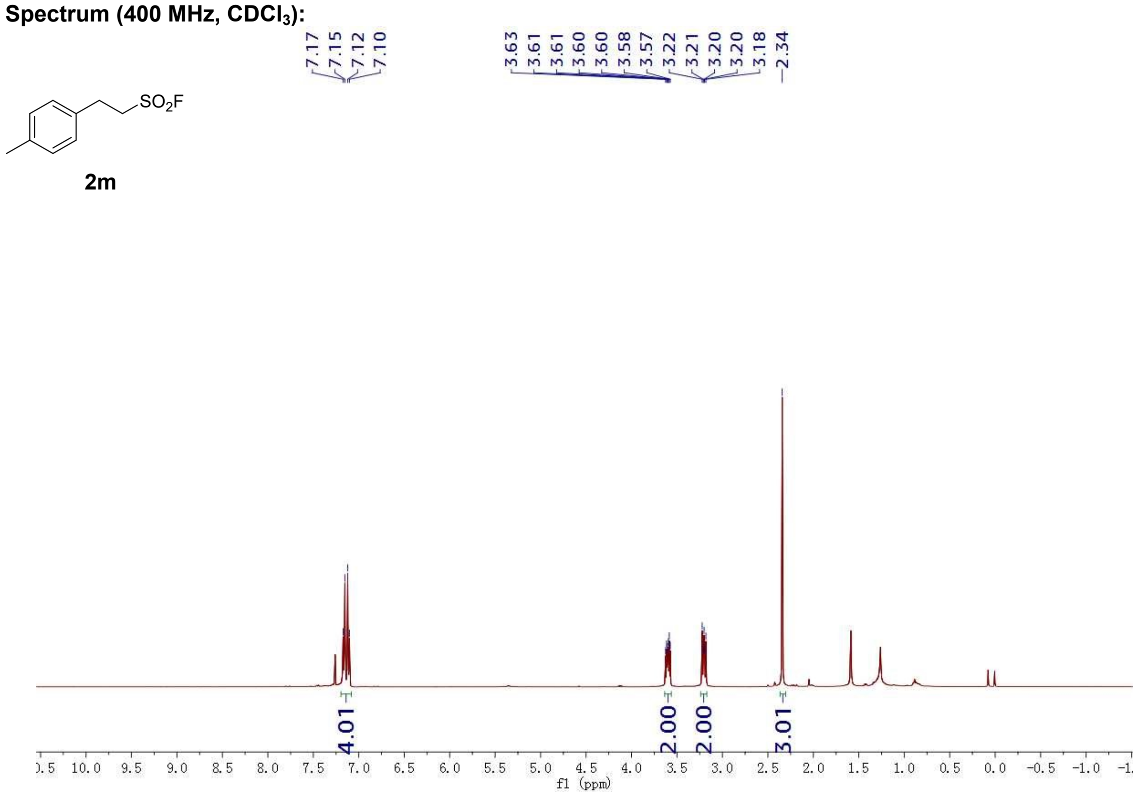
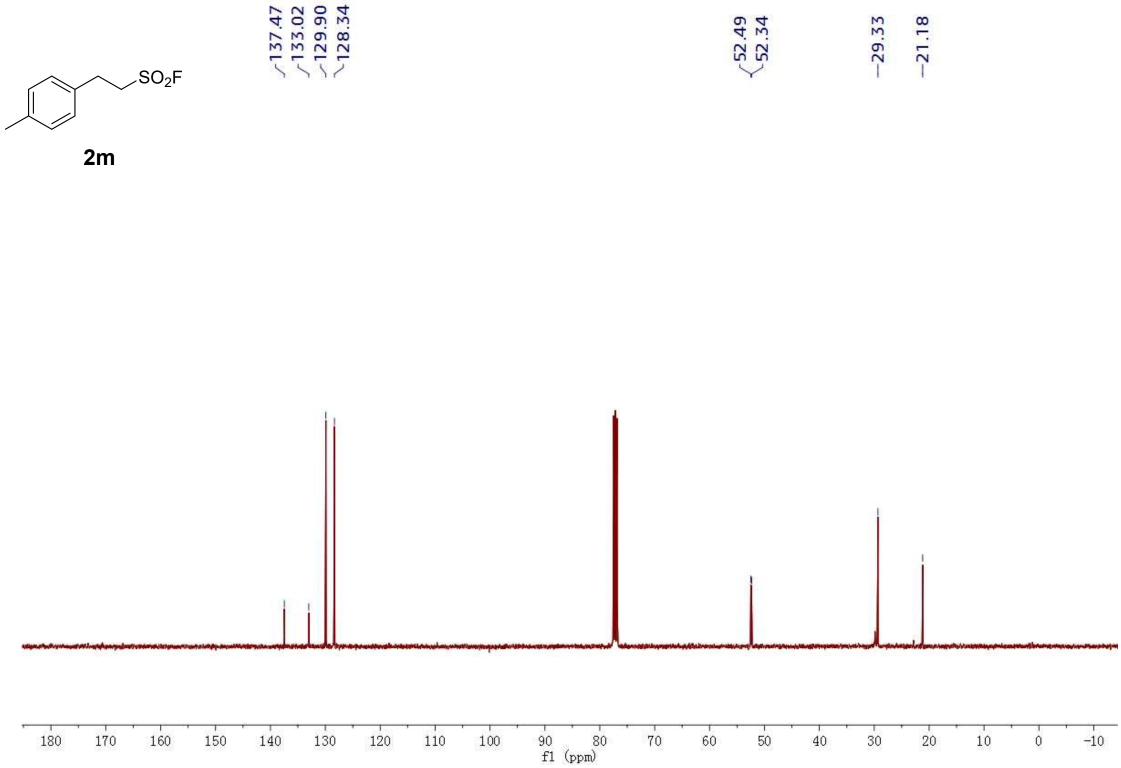


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$):



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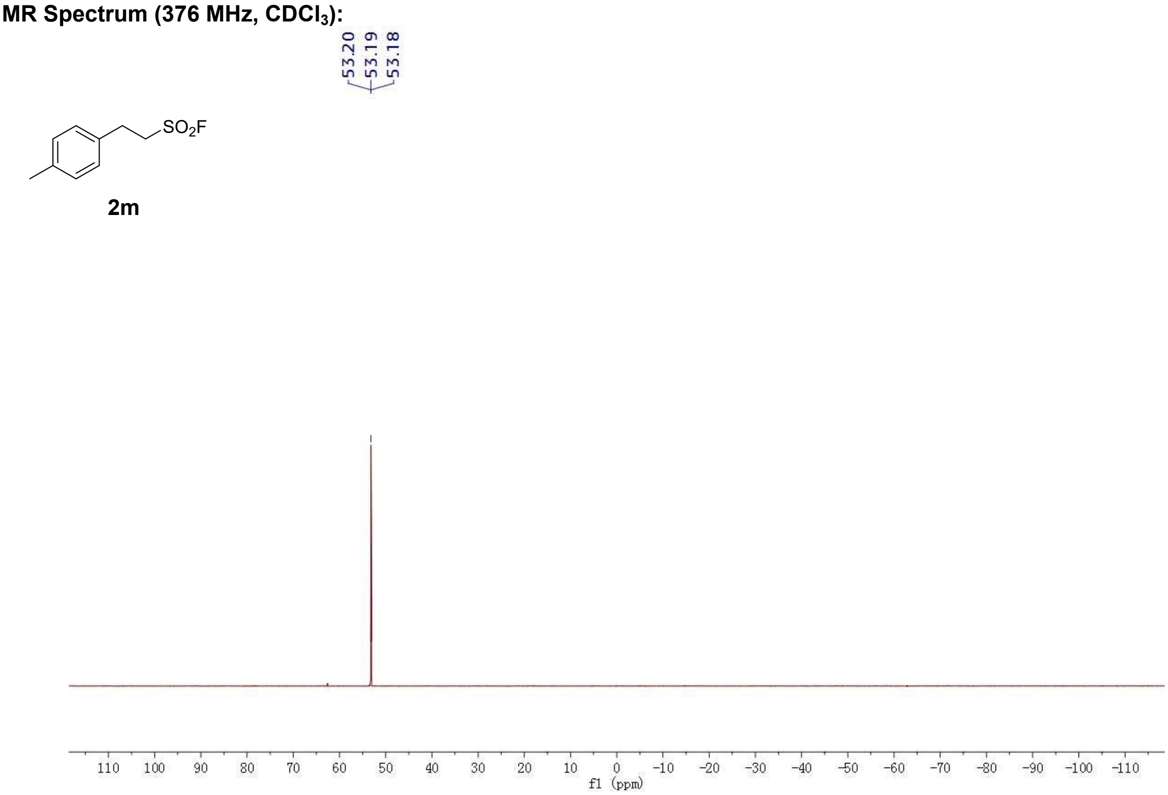
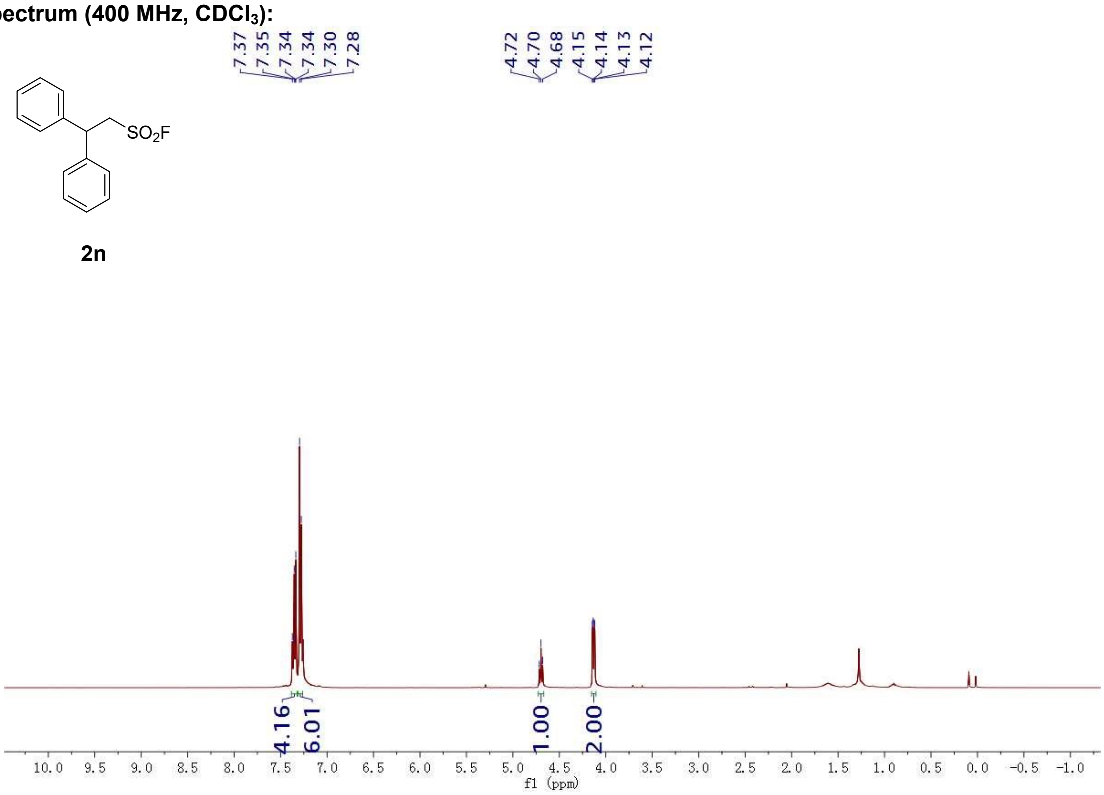
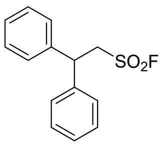


[1]H-NMR Spectrum (400 MHz, $CDCl_3$):



^{13}C-NMR Spectrum (101 MHz, $CDCl_3$):



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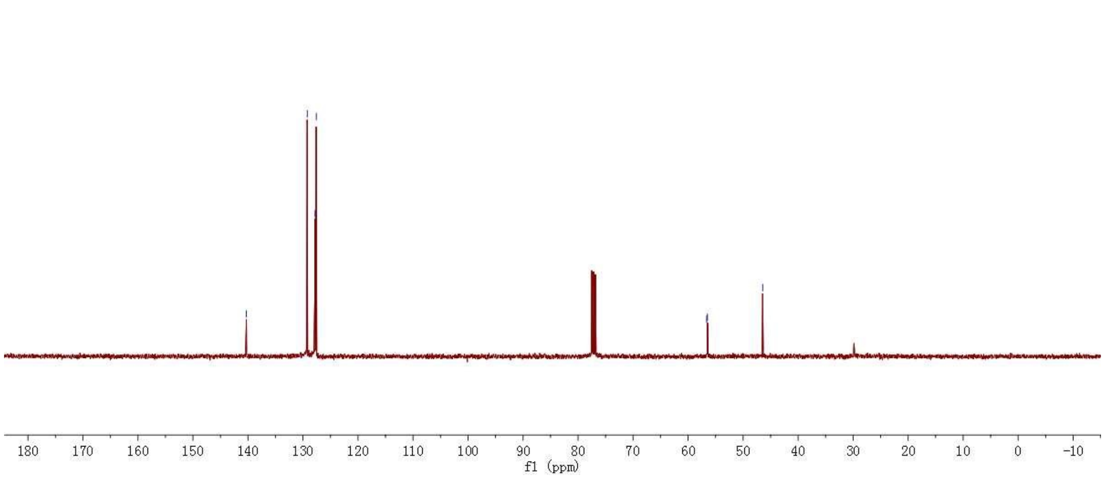
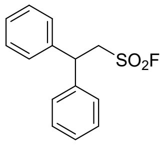


^{19}F-NMR Spectrum (376 MHz, $CDCl_3$):



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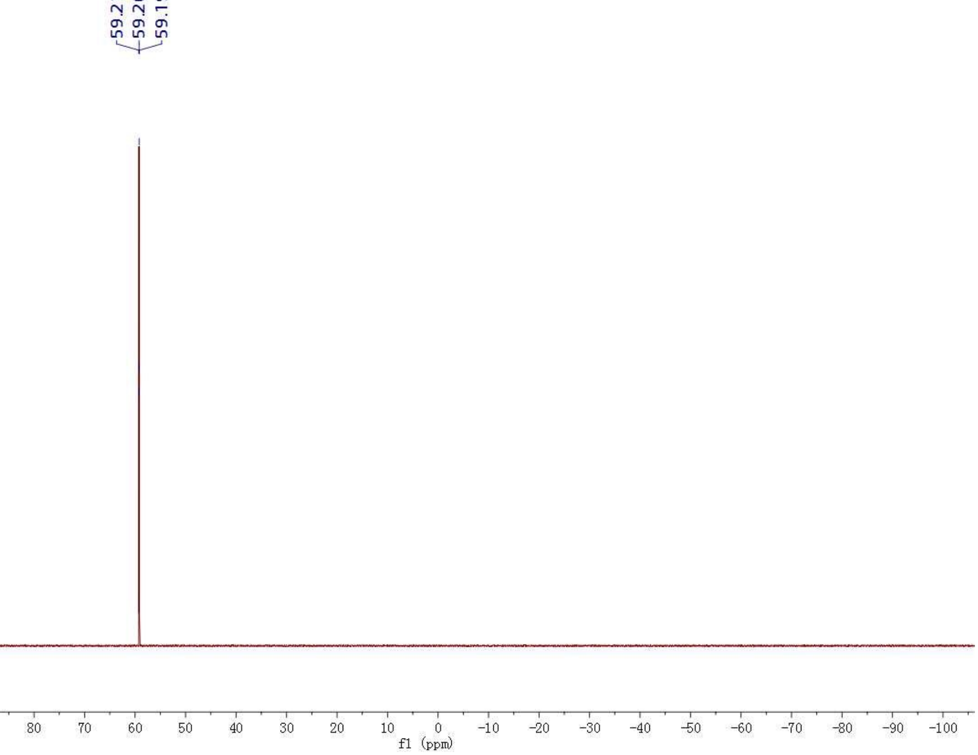

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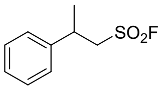

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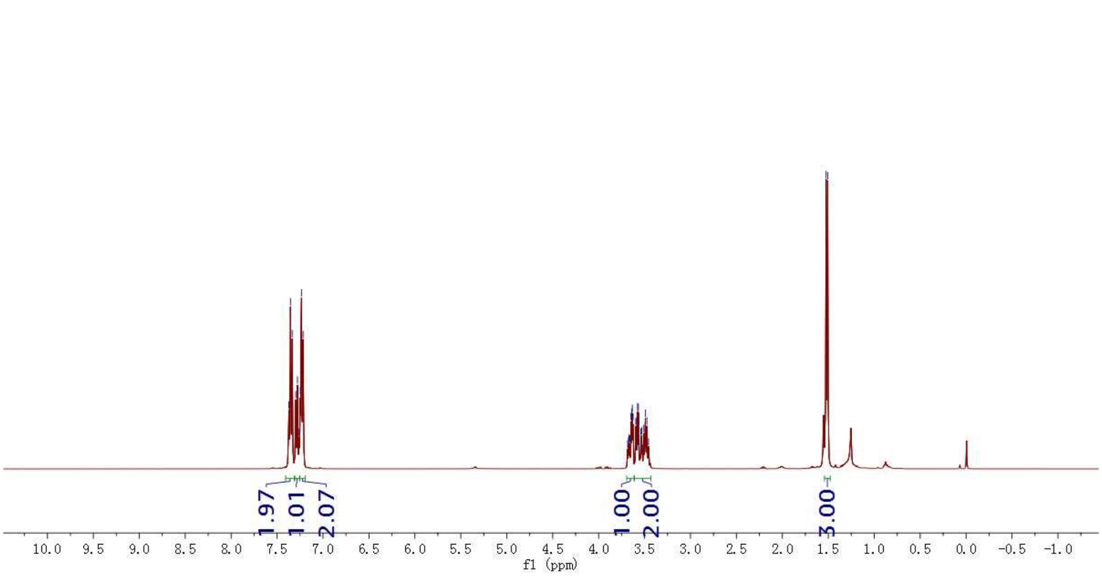
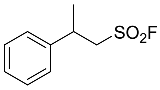


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$):



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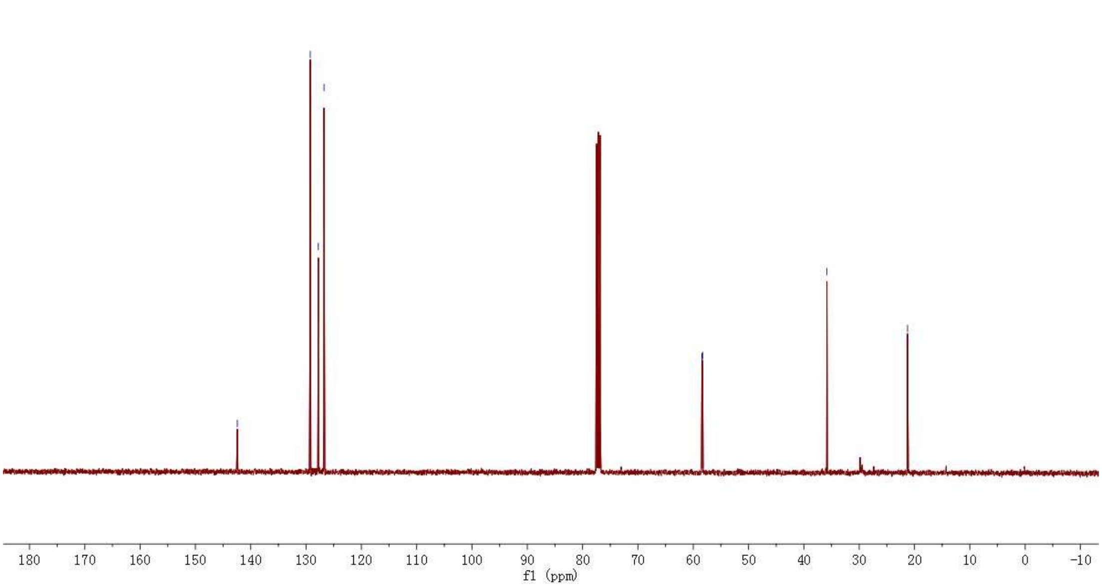
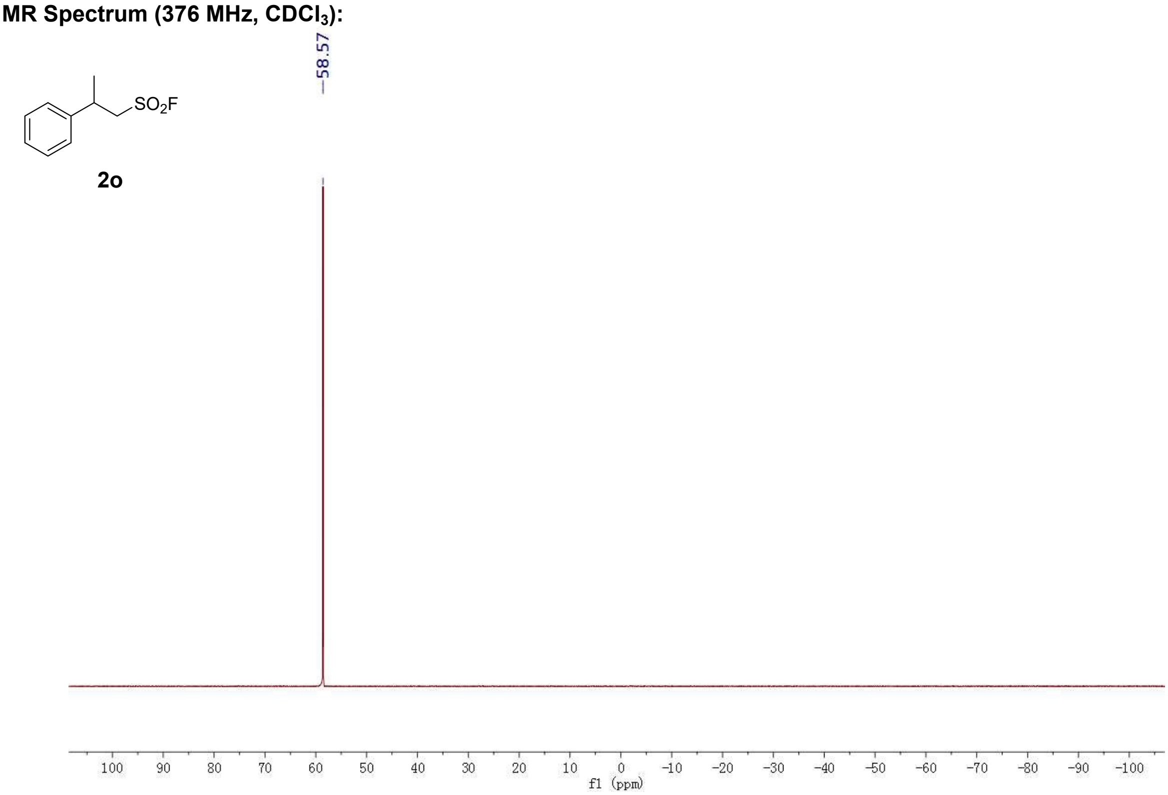
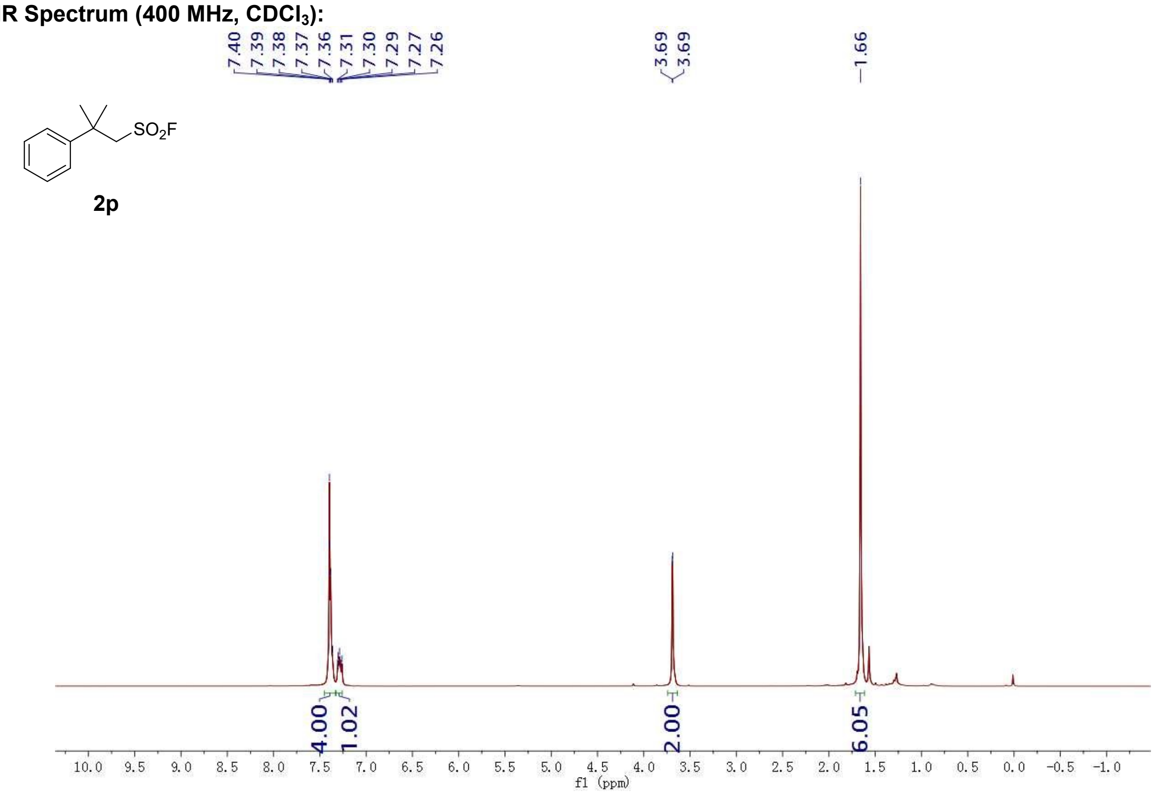


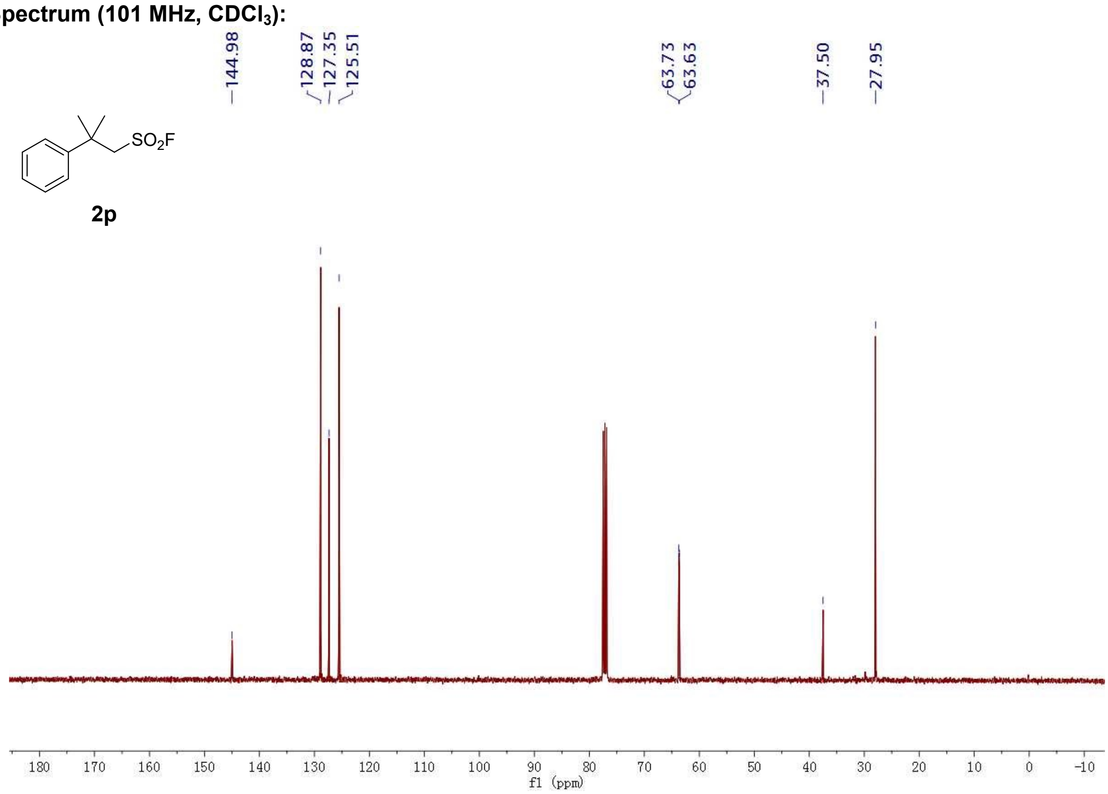
^{19}F-NMR Spectrum (376 MHz, CDCl$_3$):



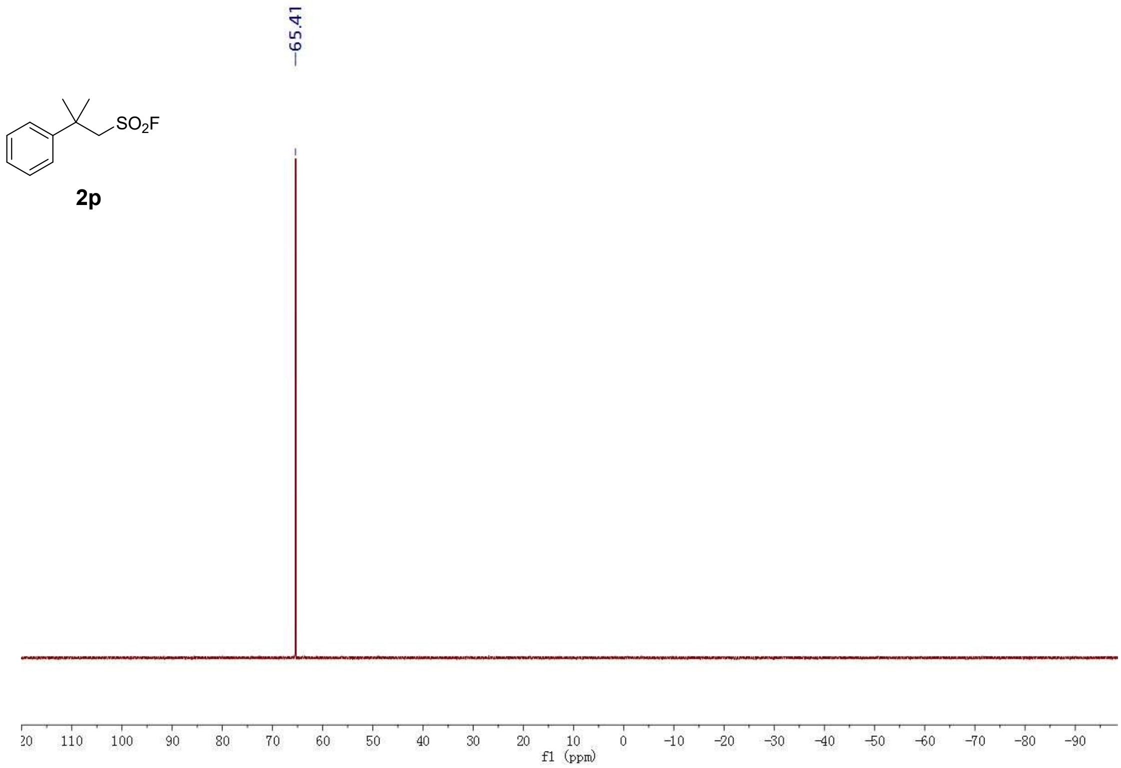
^{1}H-NMR Spectrum (400 MHz, CDCl$_3$):



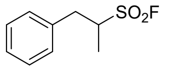
^{13}C-NMR Spectrum (101 MHz, CDCl$_3$):



^{19}F-NMR Spectrum (376 MHz, CDCl$_3$):



^{1}H-NMR Spectrum (400 MHz, $CDCl_3$):



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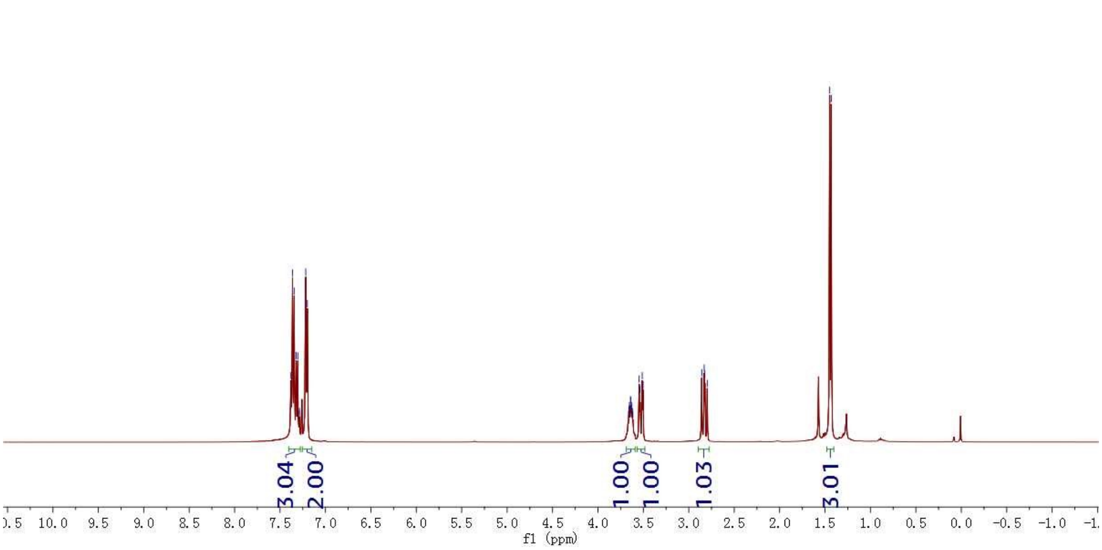
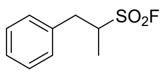


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$):



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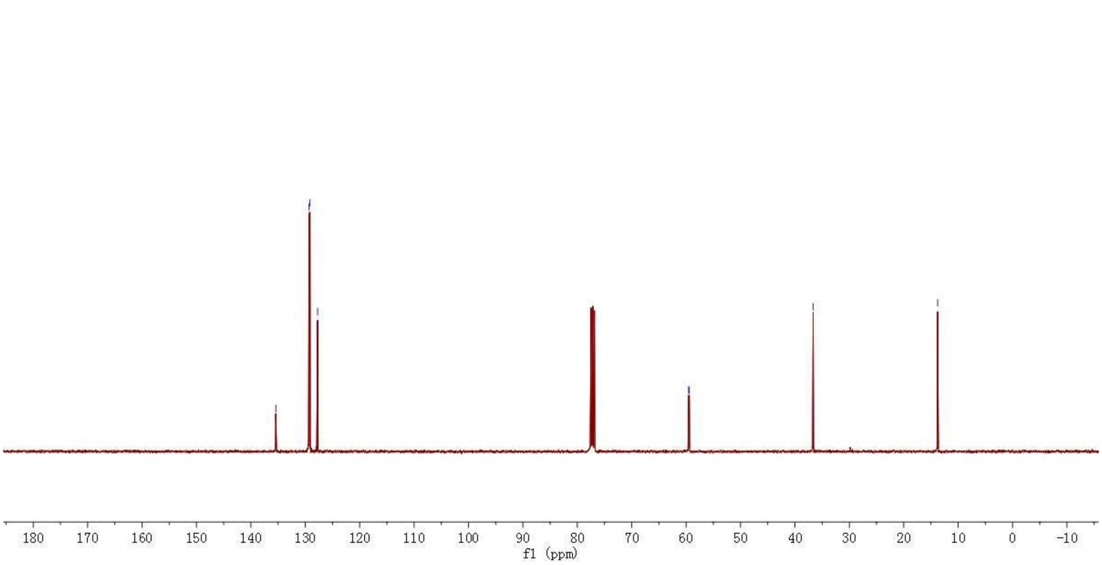
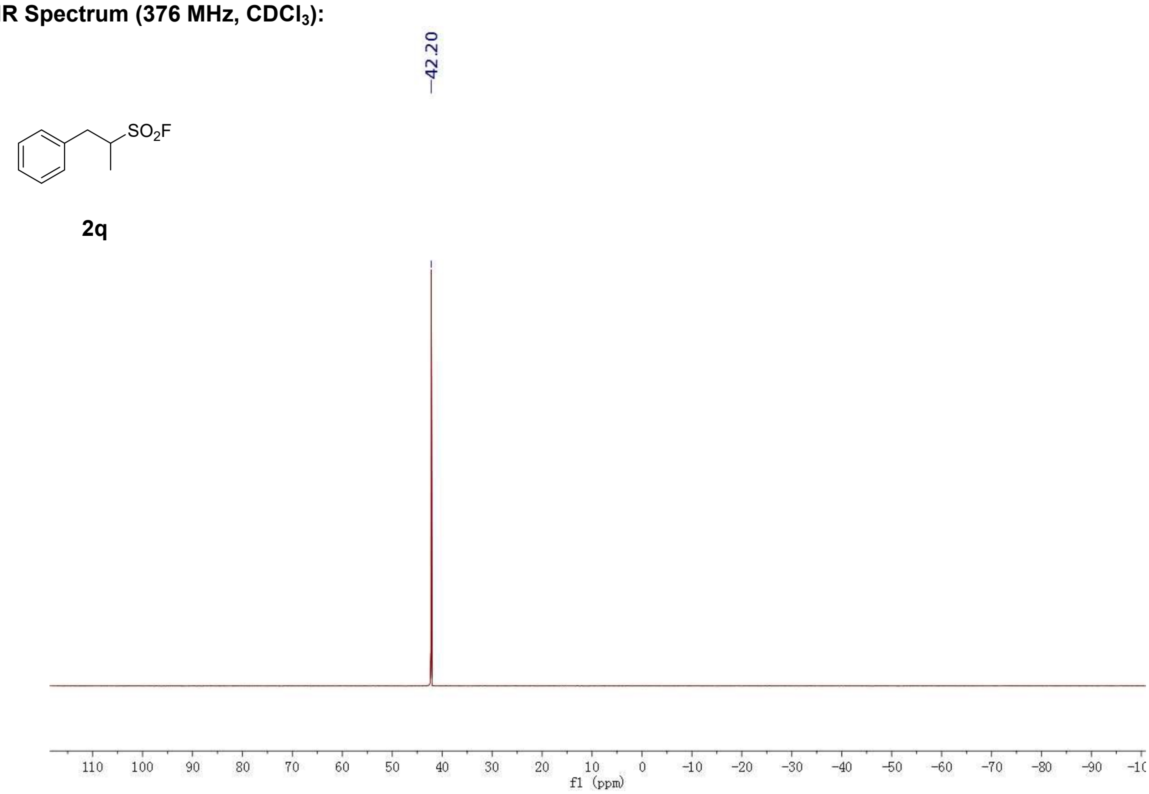


^{19}F-NMR Spectrum (376 MHz, $CDCl_3$):



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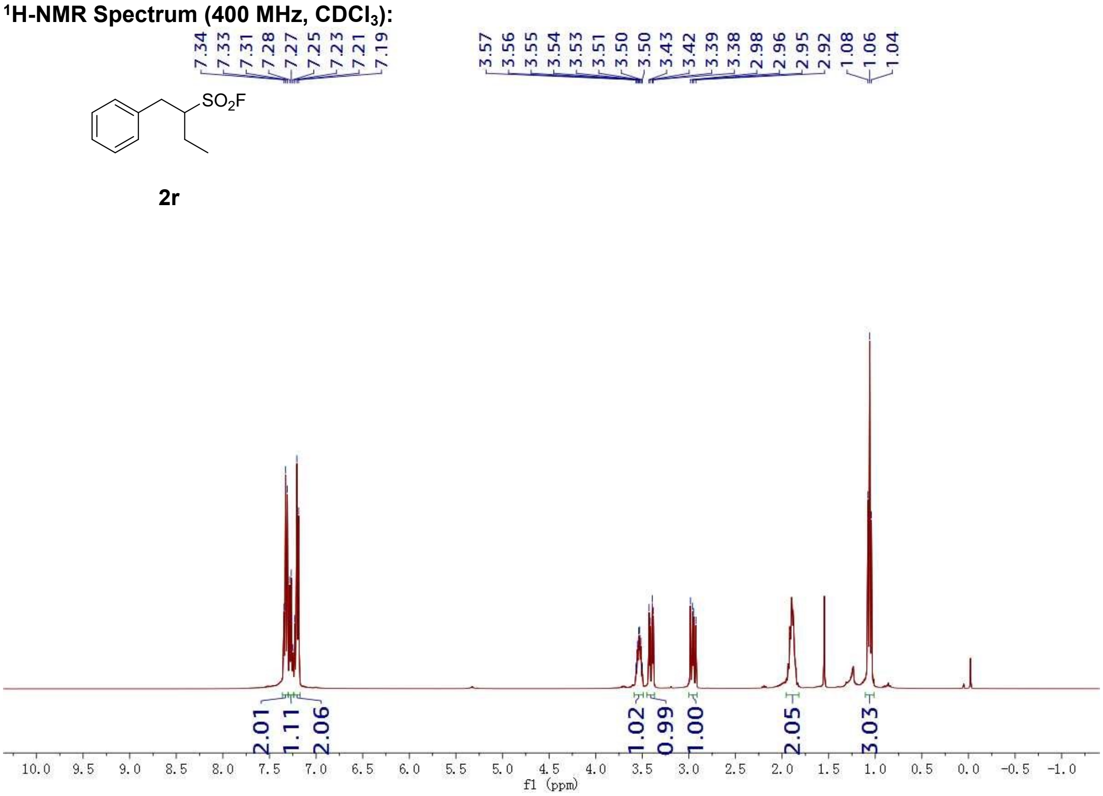
^{1}H-NMR Spectrum (400 MHz, $CDCl_3$):



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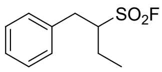
^{13}C-NMR Spectrum (101 MHz, $CDCl_3$):



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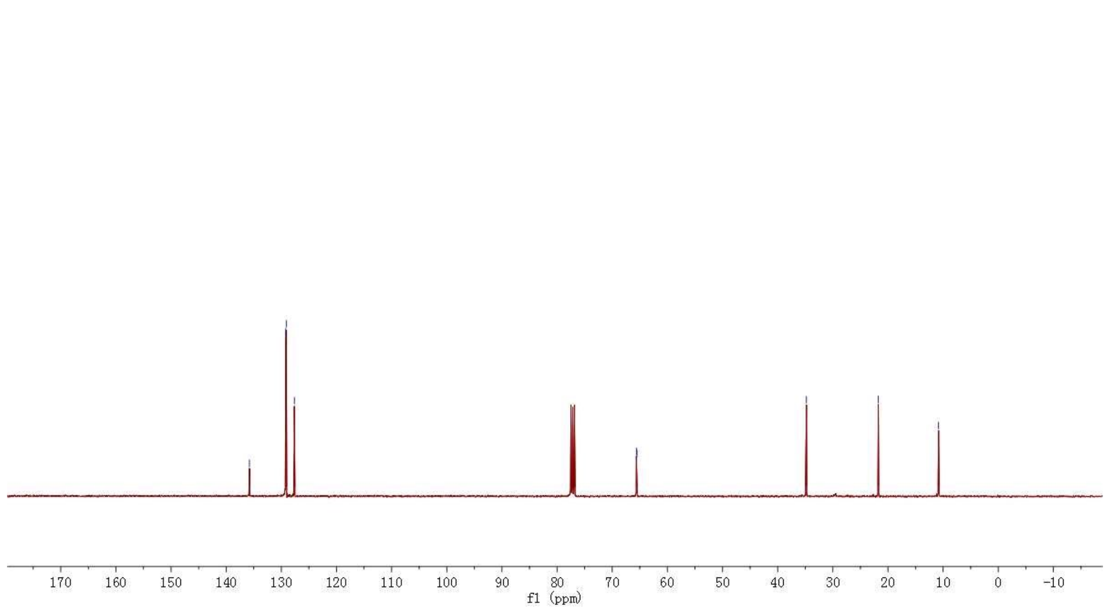
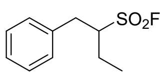


^{19}F-NMR Spectrum (376 MHz, $CDCl_3$):



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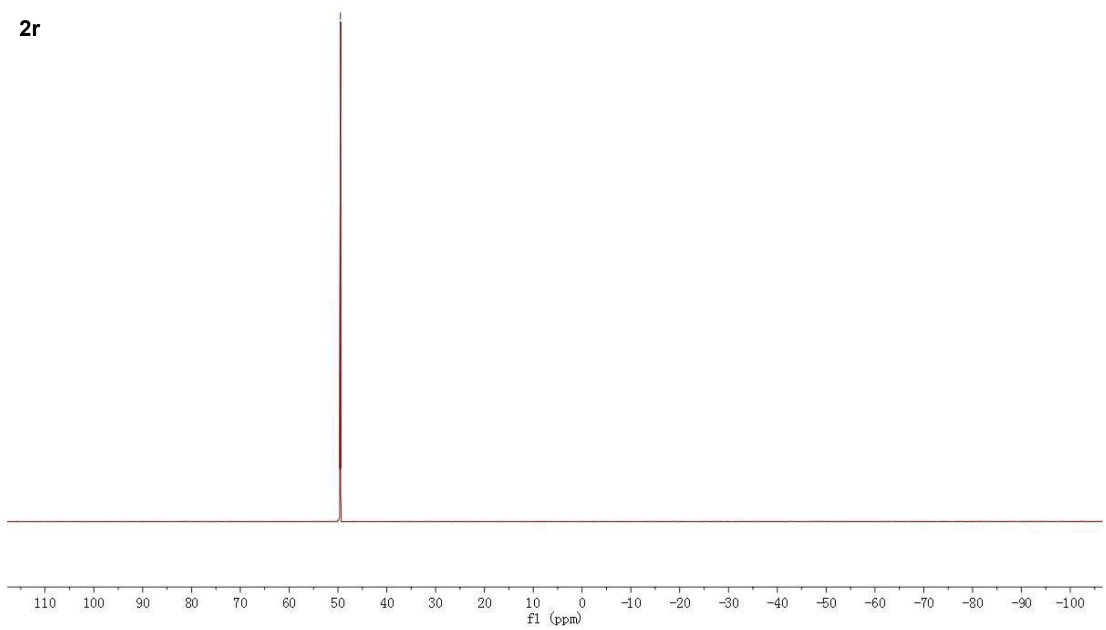

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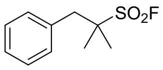

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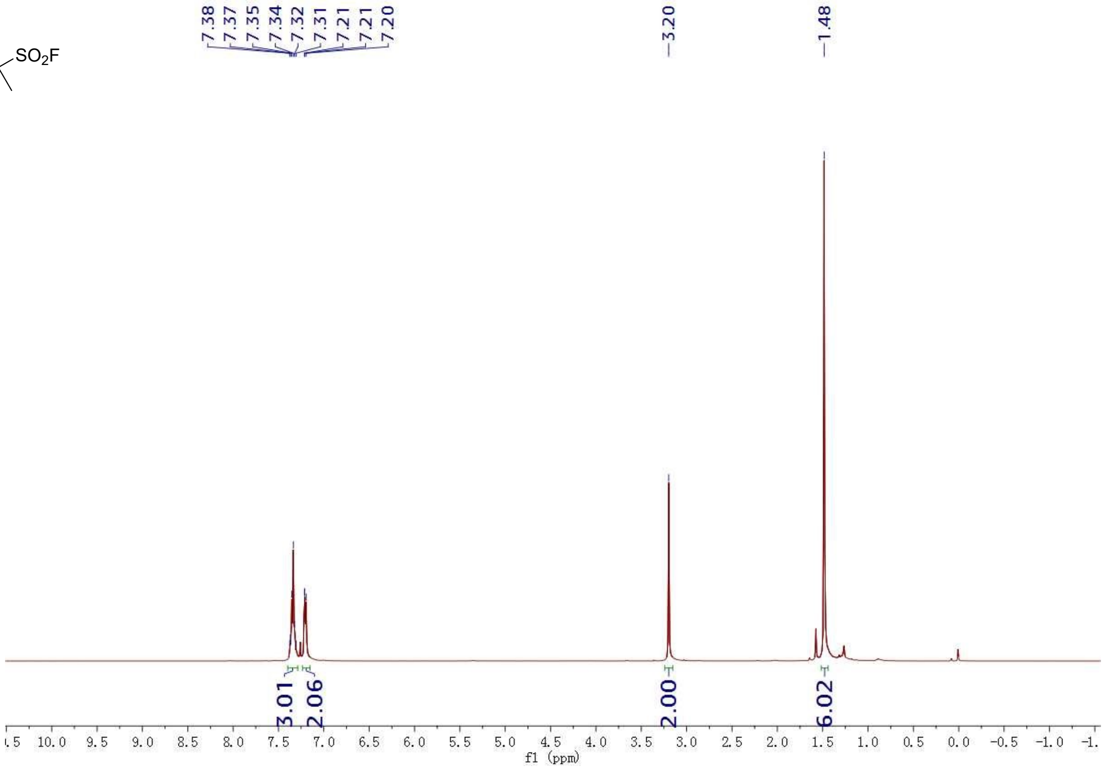
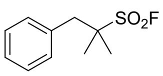


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$):



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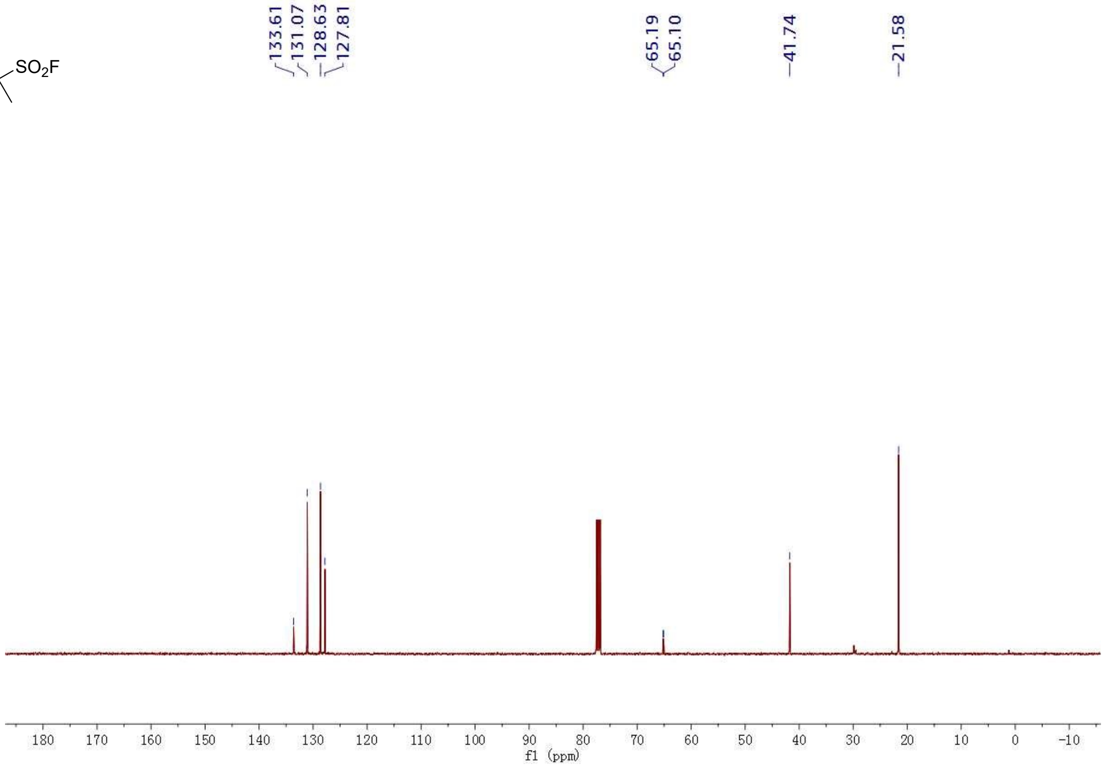

^{19}F-NMR Spectrum (376 MHz, $CDCl_3$):

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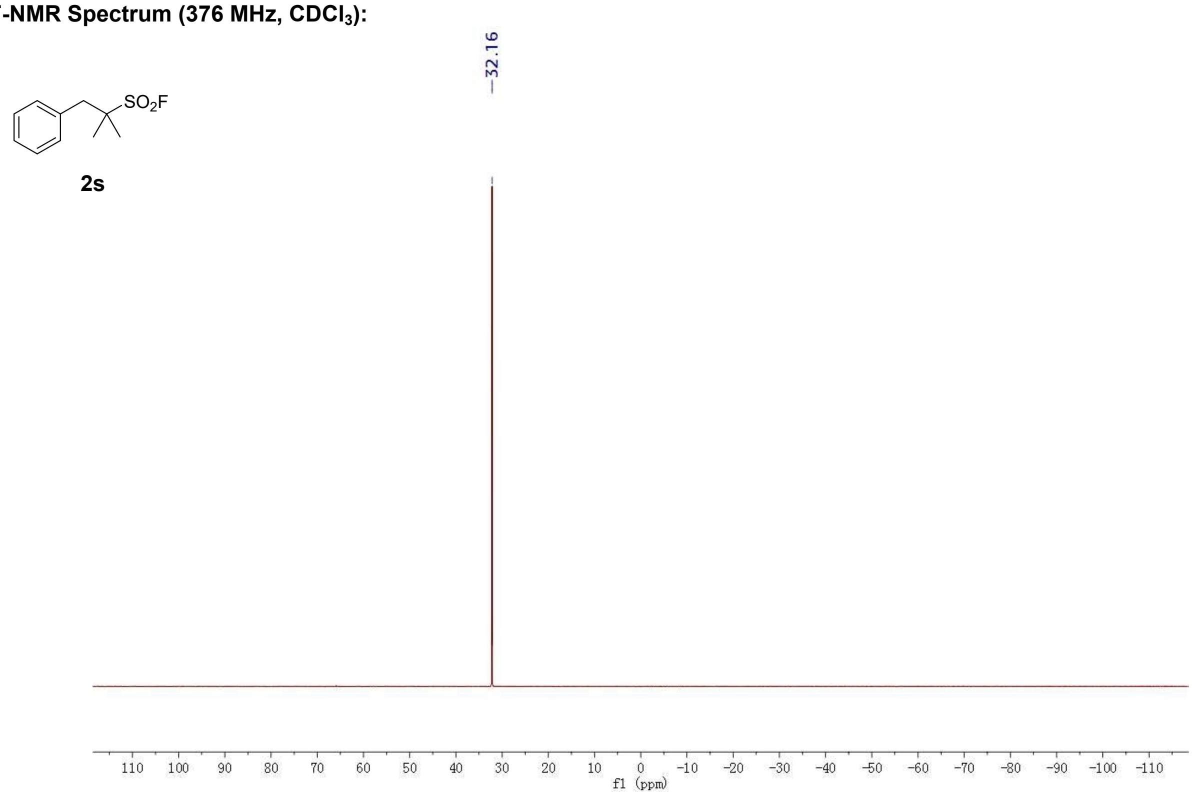

^{1}H-NMR Spectrum (400 MHz, $CDCl_3$):

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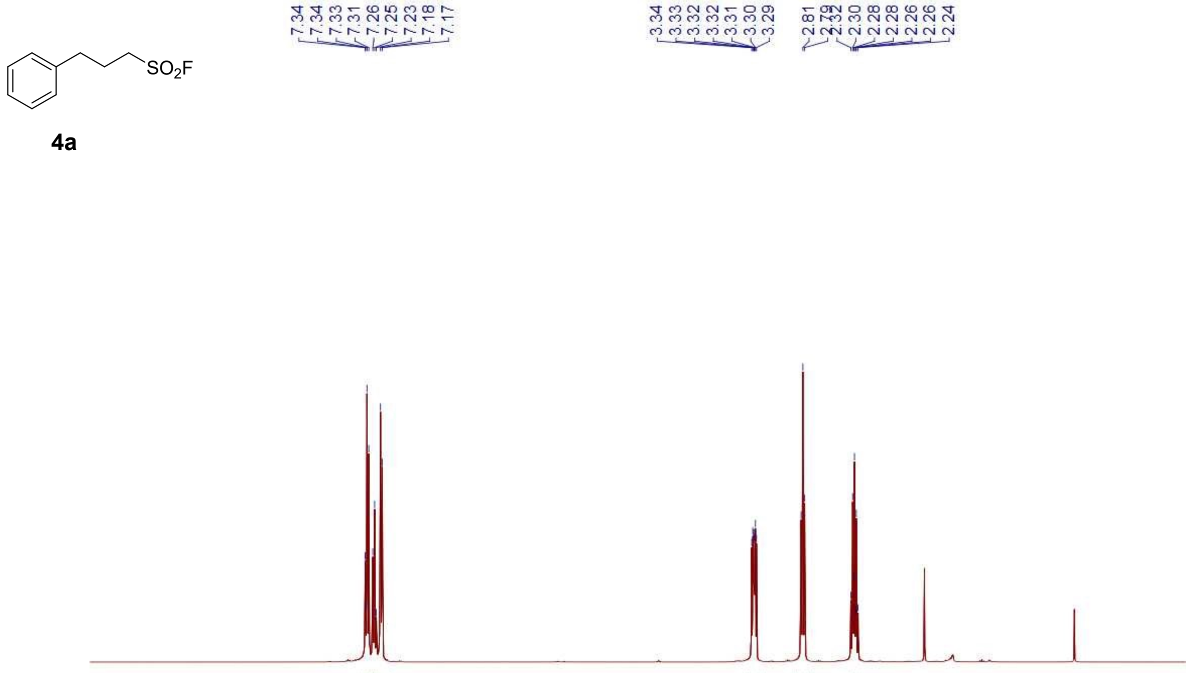
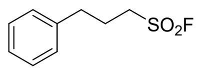


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$):



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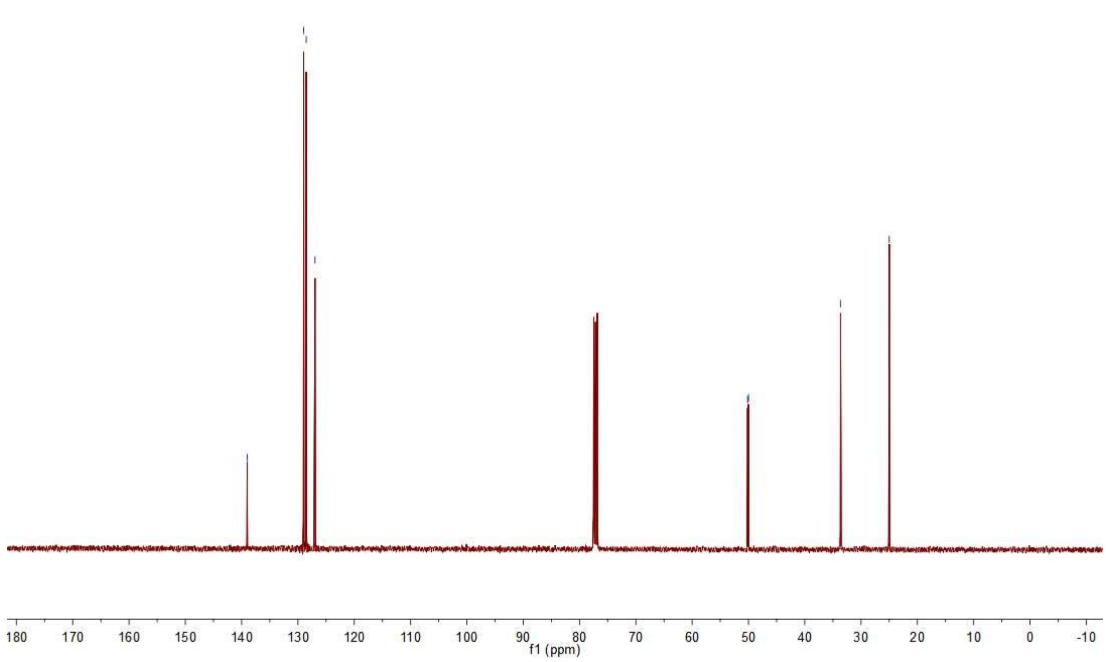
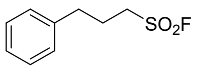


^{19}F-NMR Spectrum (376 MHz, $CDCl_3$):



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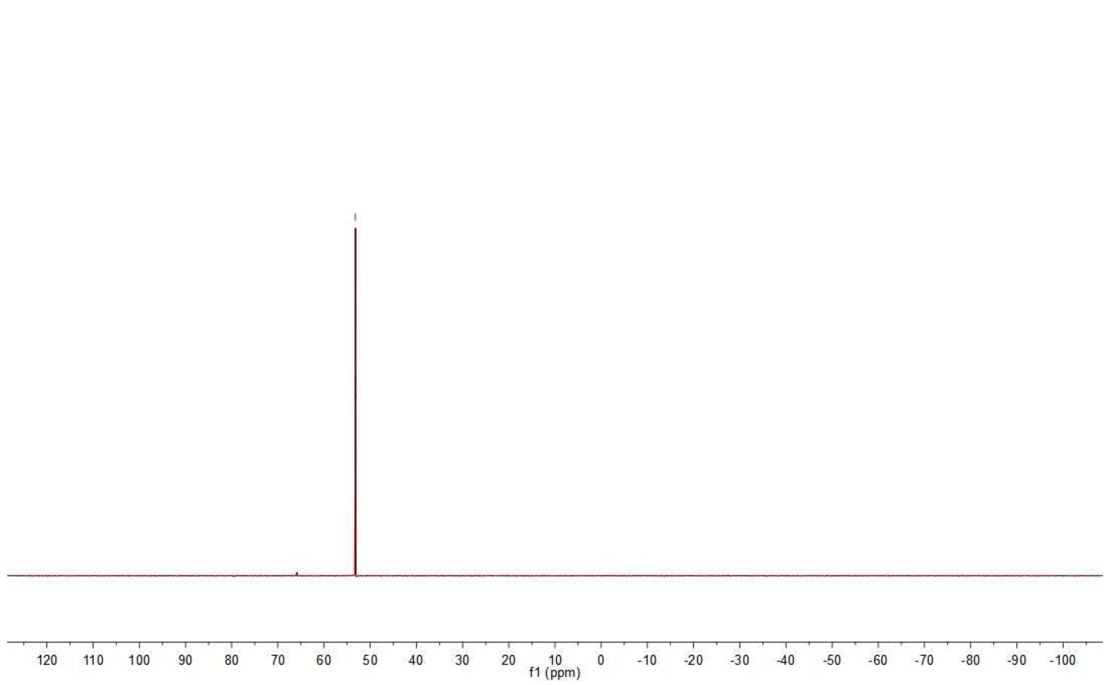
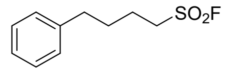


[1]H-NMR Spectrum (400 MHz, $CDCl_3$):



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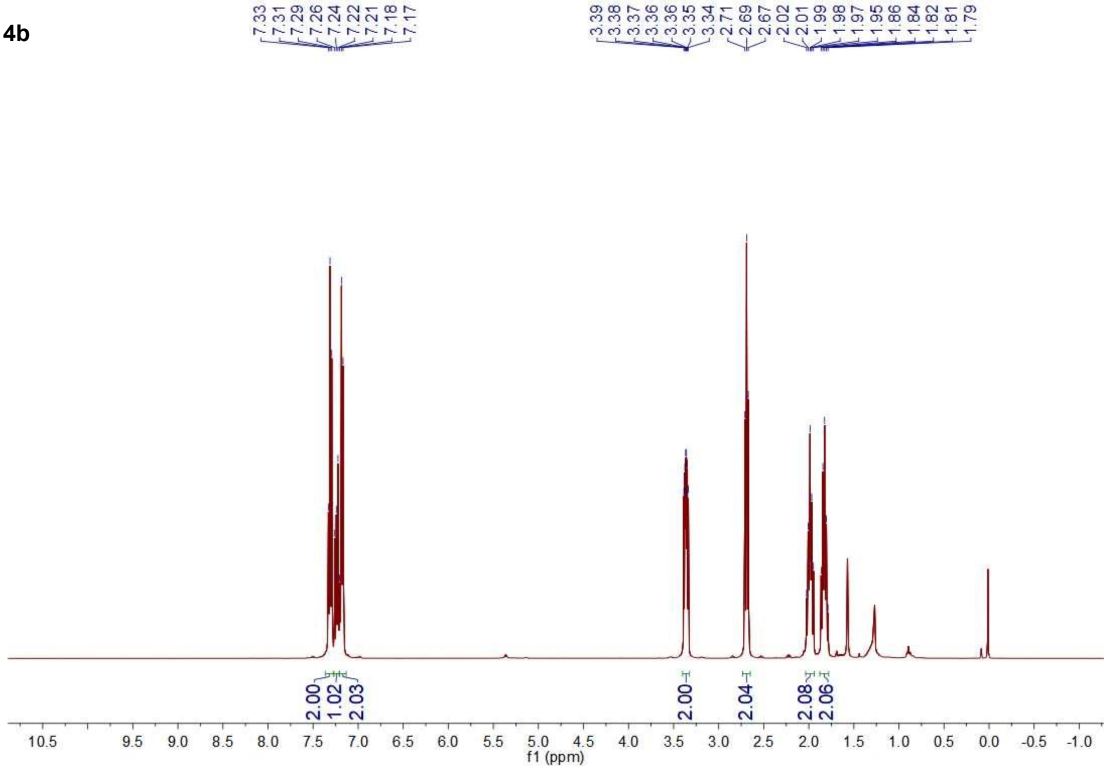
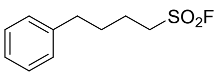


[13]C-NMR Spectrum (101 MHz, $CDCl_3$):



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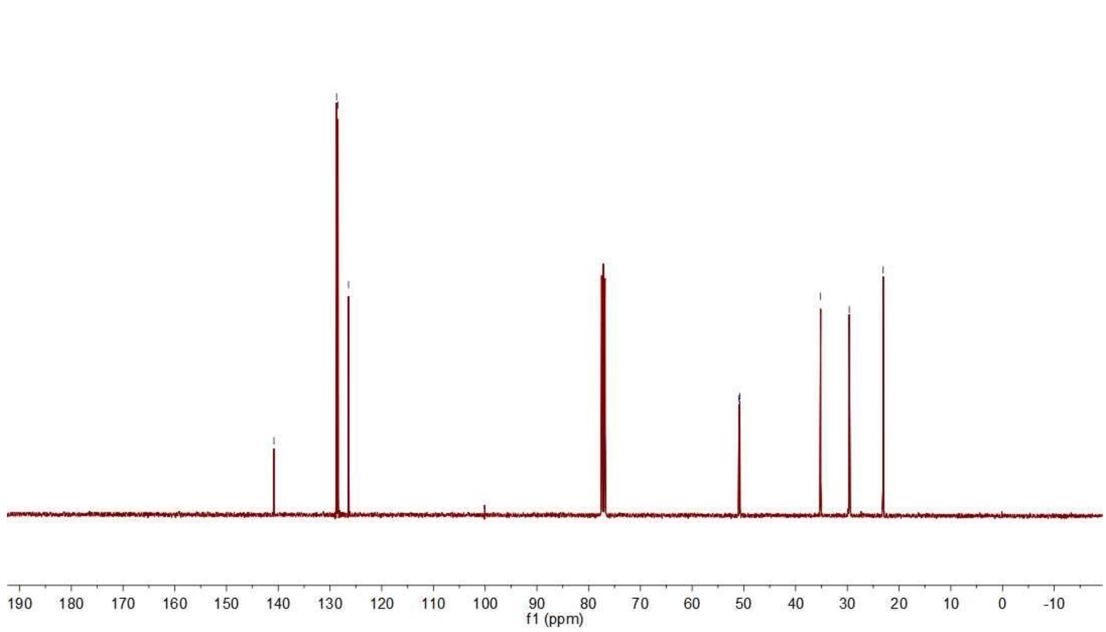
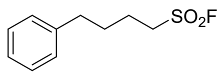


^{19}F-NMR Spectrum (376 MHz, $CDCl_3$):



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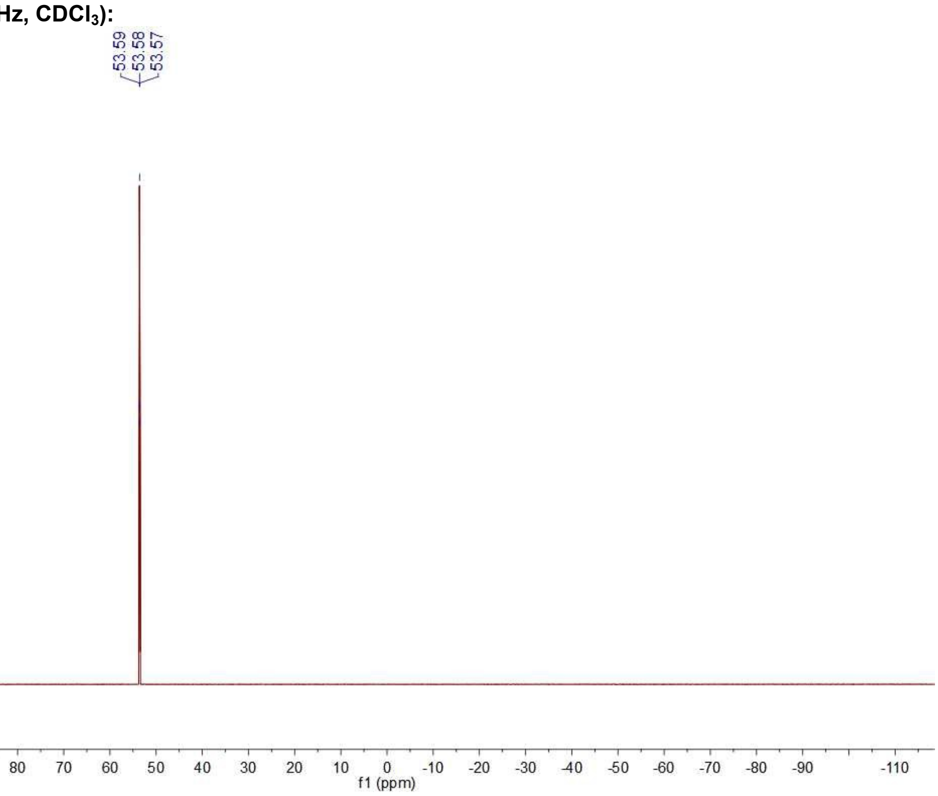
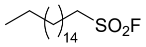


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$):



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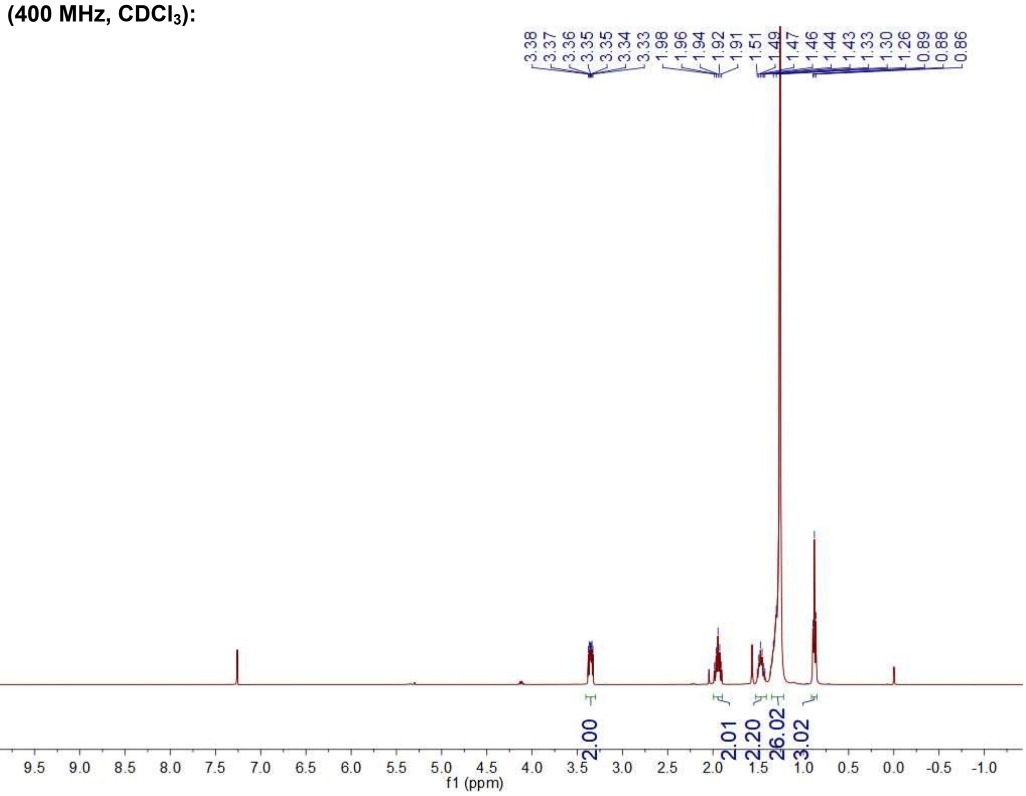
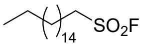


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$):



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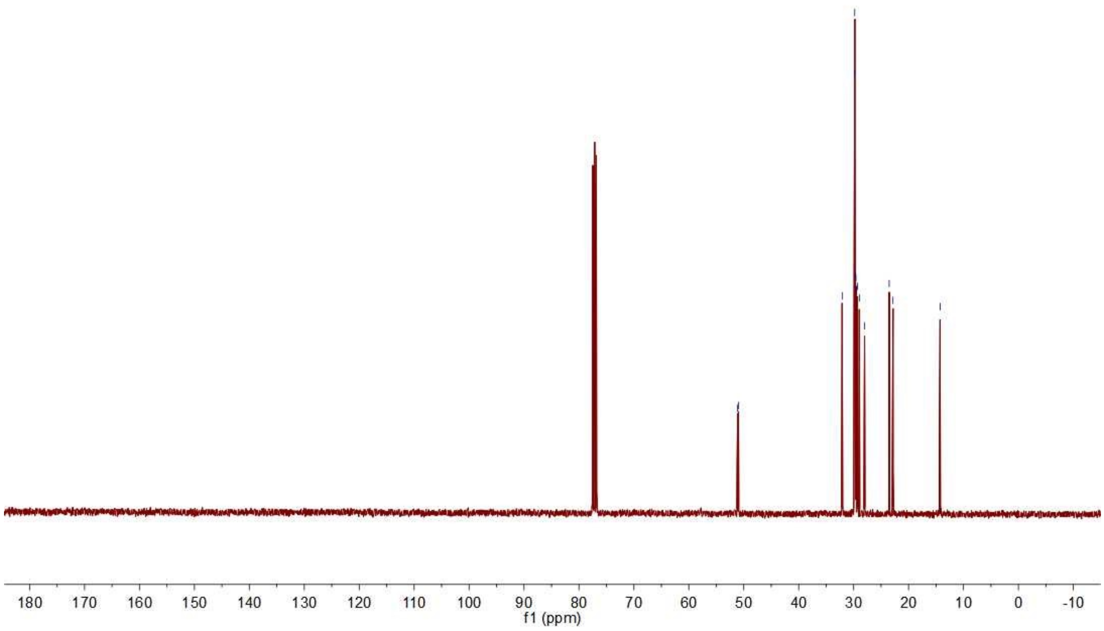
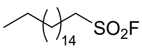


^{19}F-NMR Spectrum (376 MHz, $CDCl_3$):



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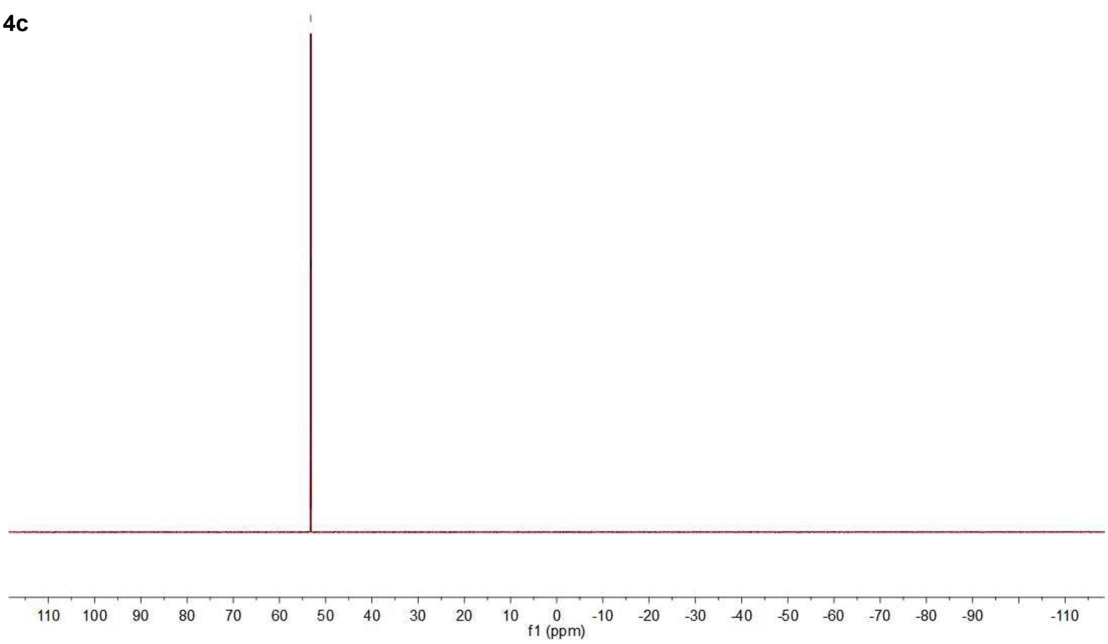

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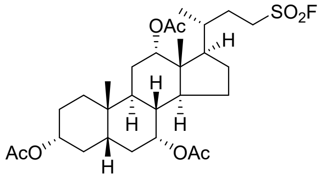

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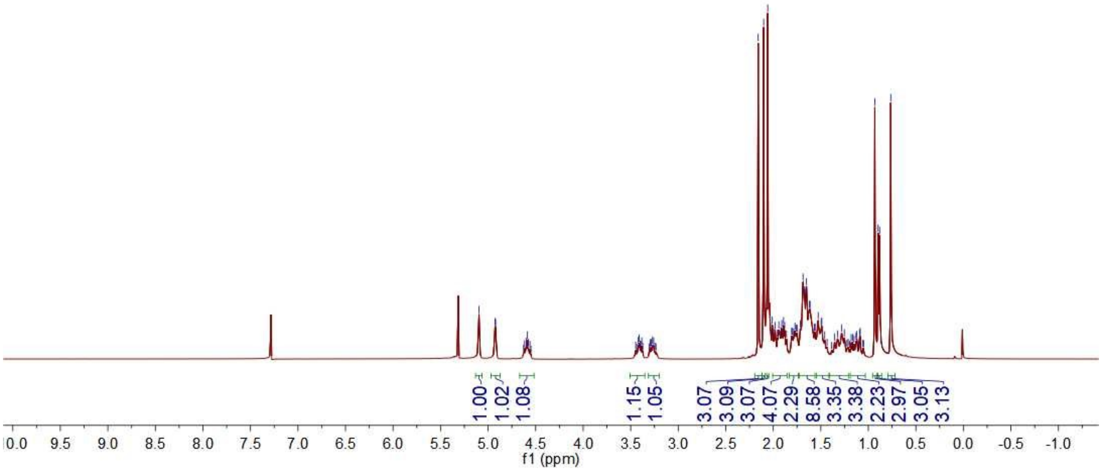
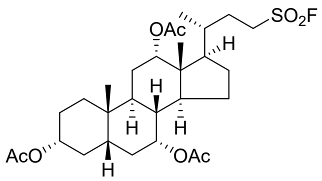


[13]C-NMR Spectrum (101 MHz, $CDCl_3$):



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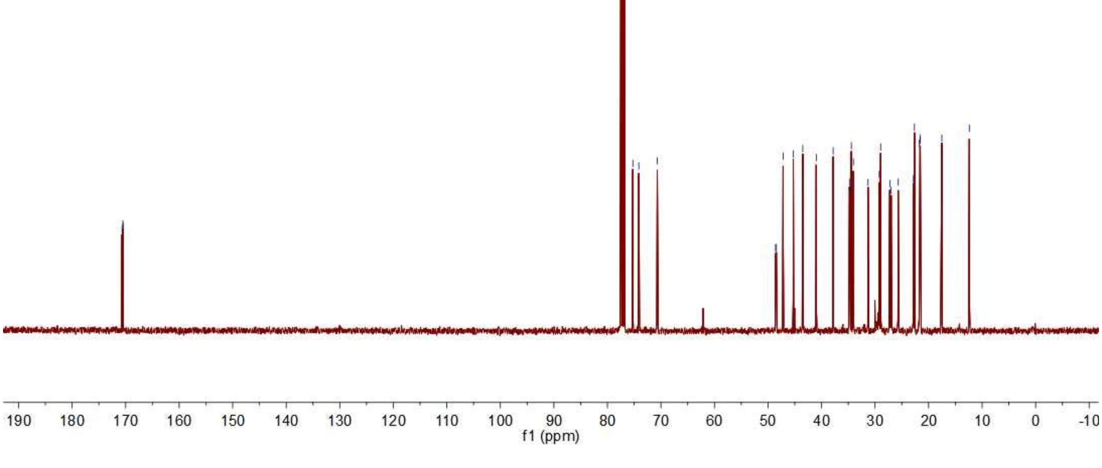
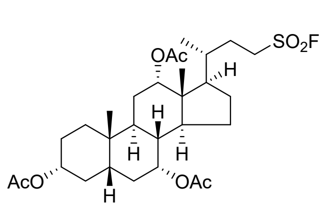


^{19}F-NMR Spectrum (376 MHz, $CDCl_3$):



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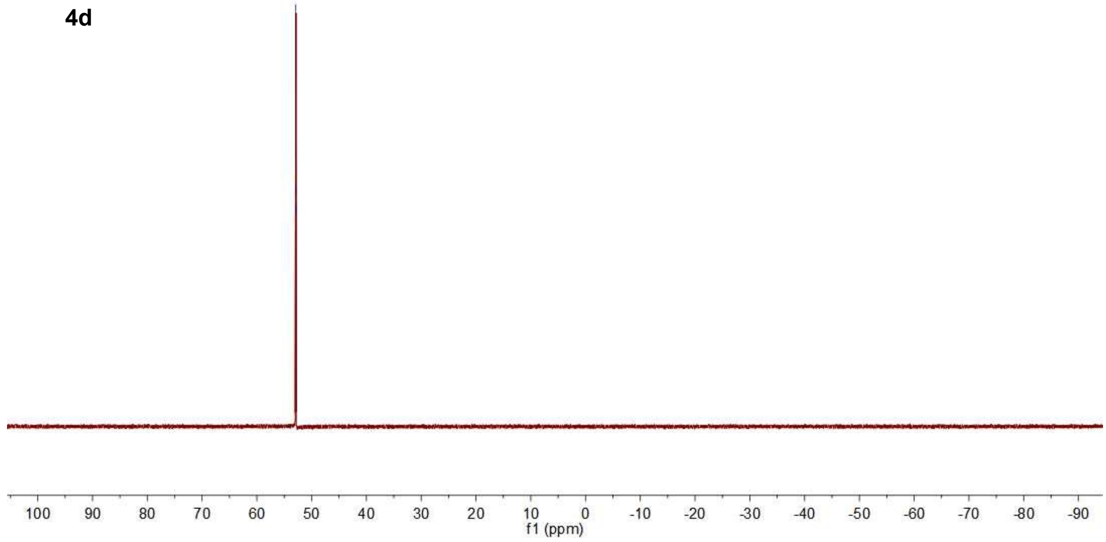
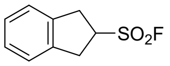


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$):



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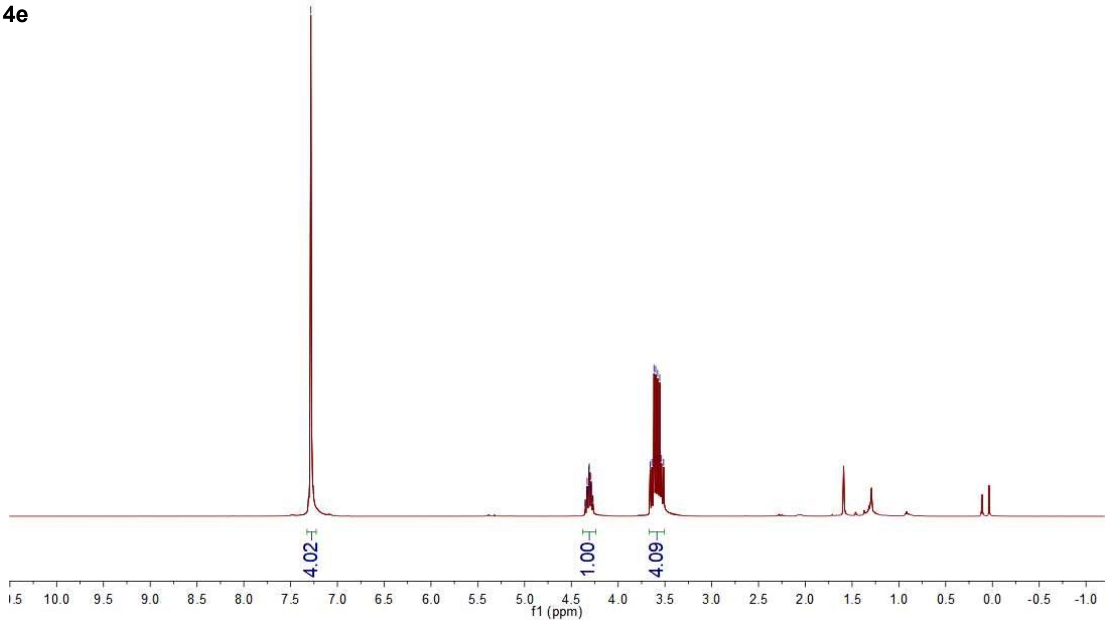
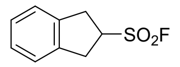


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$):



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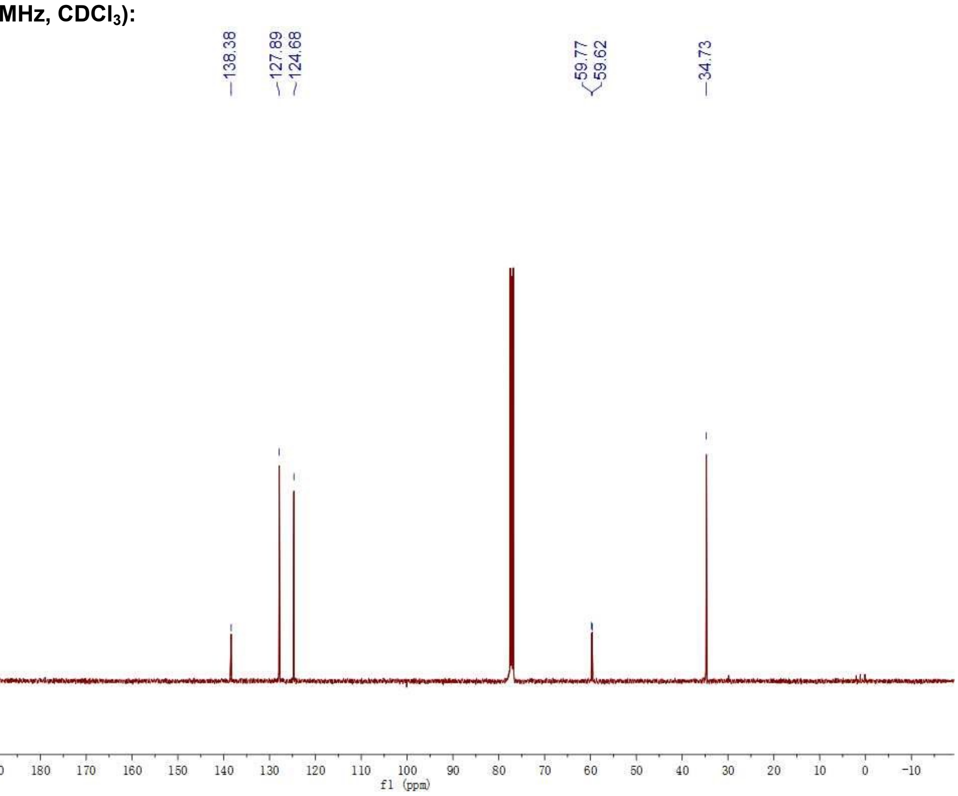
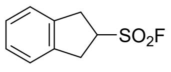


^{19}F-NMR Spectrum (376 MHz, $CDCl_3$):



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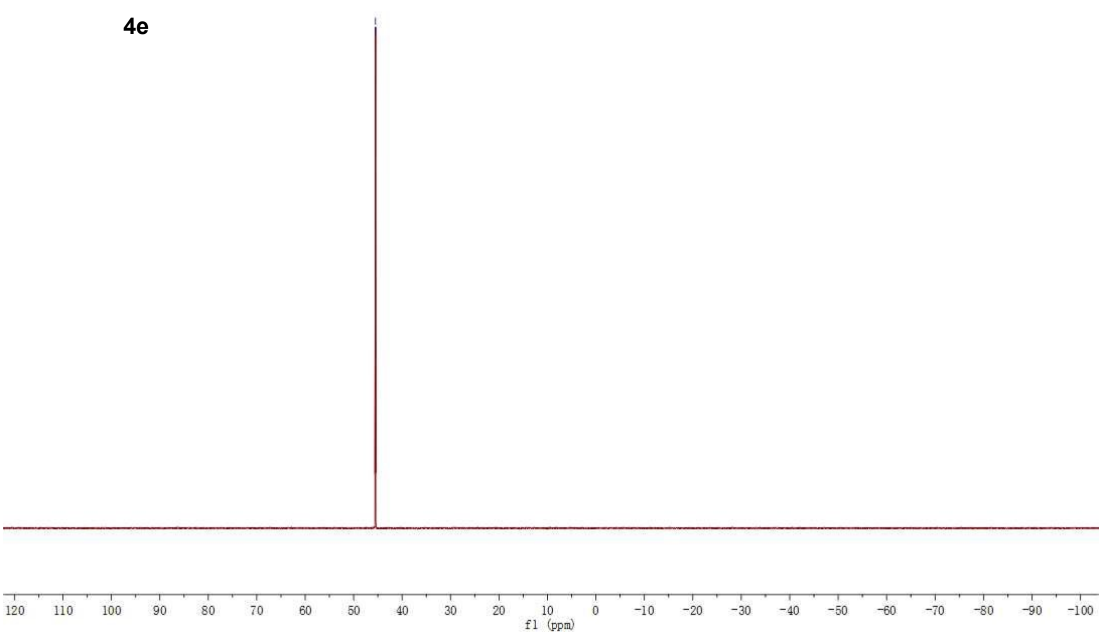

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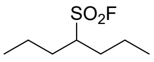

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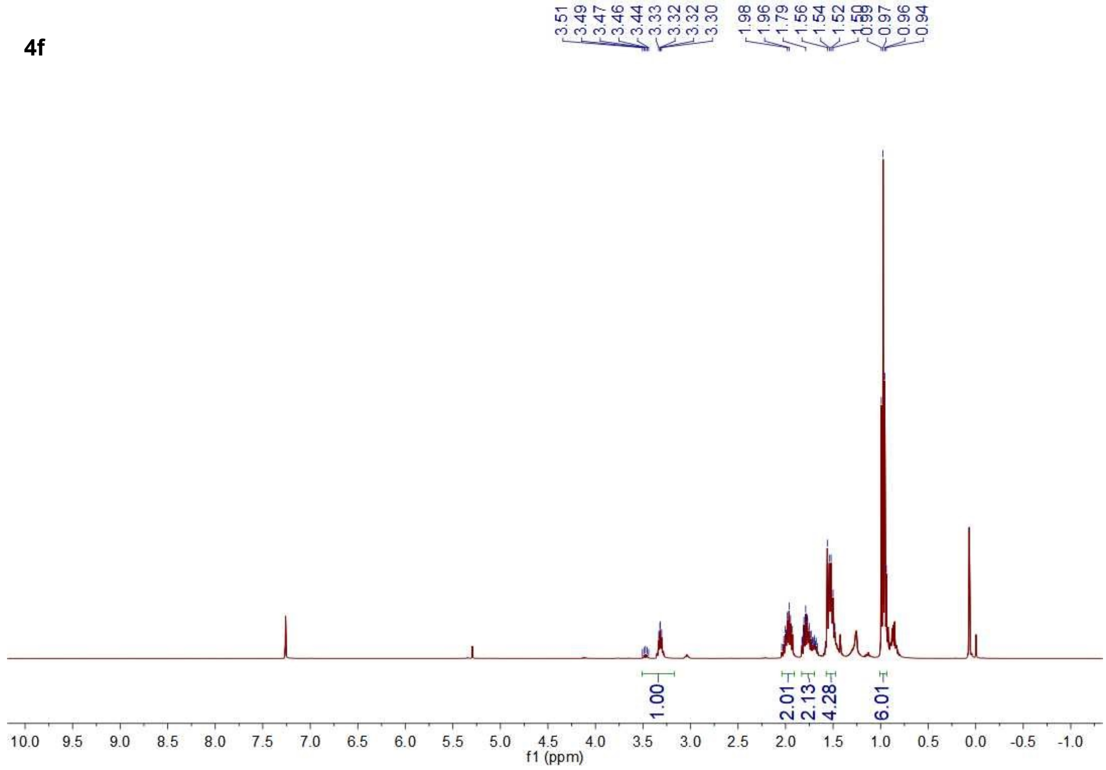
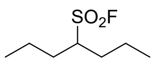


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$):



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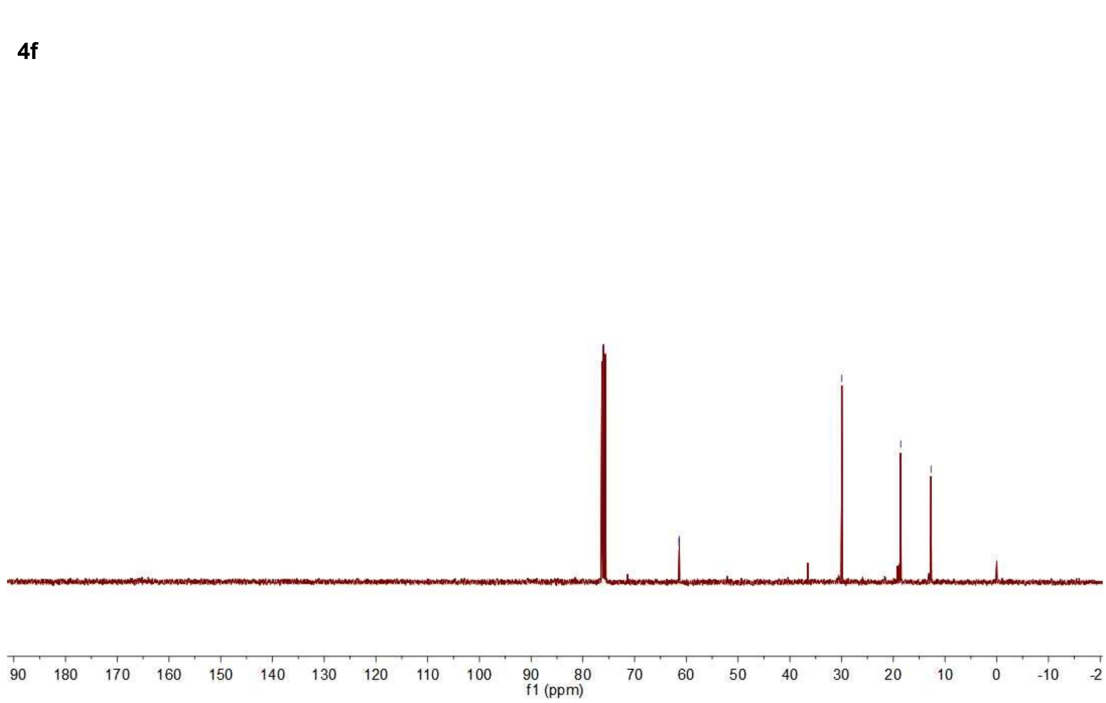
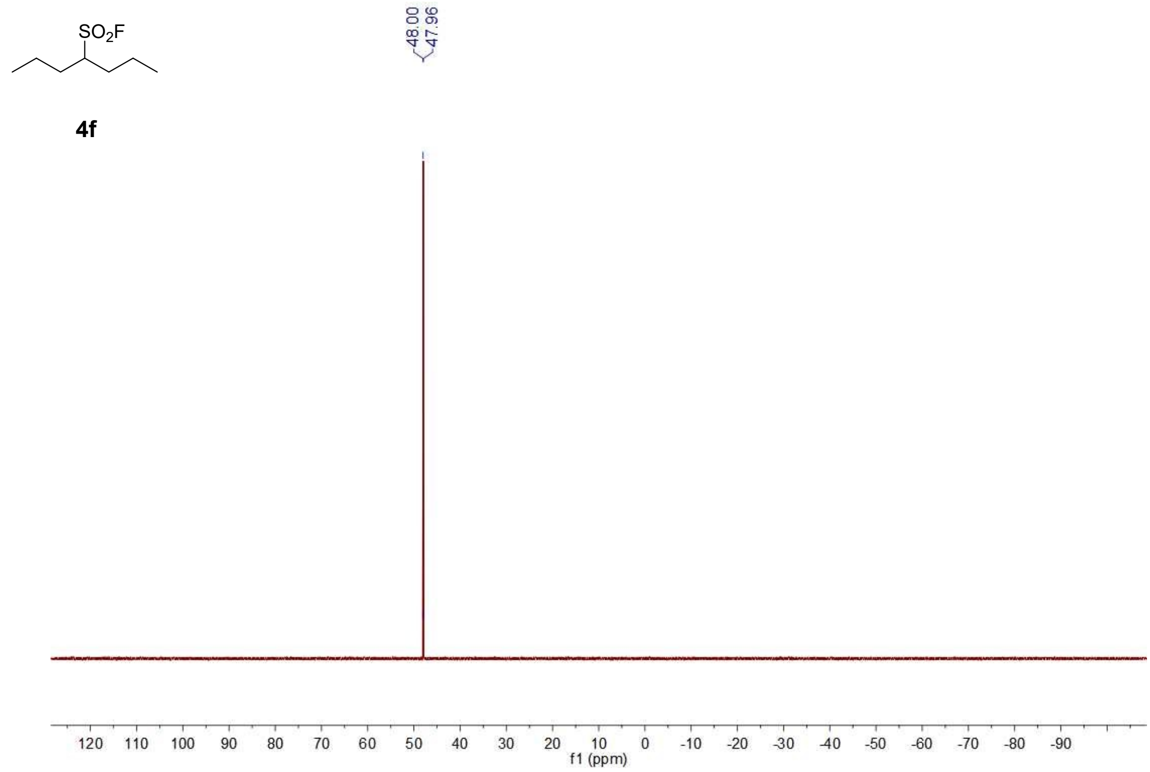
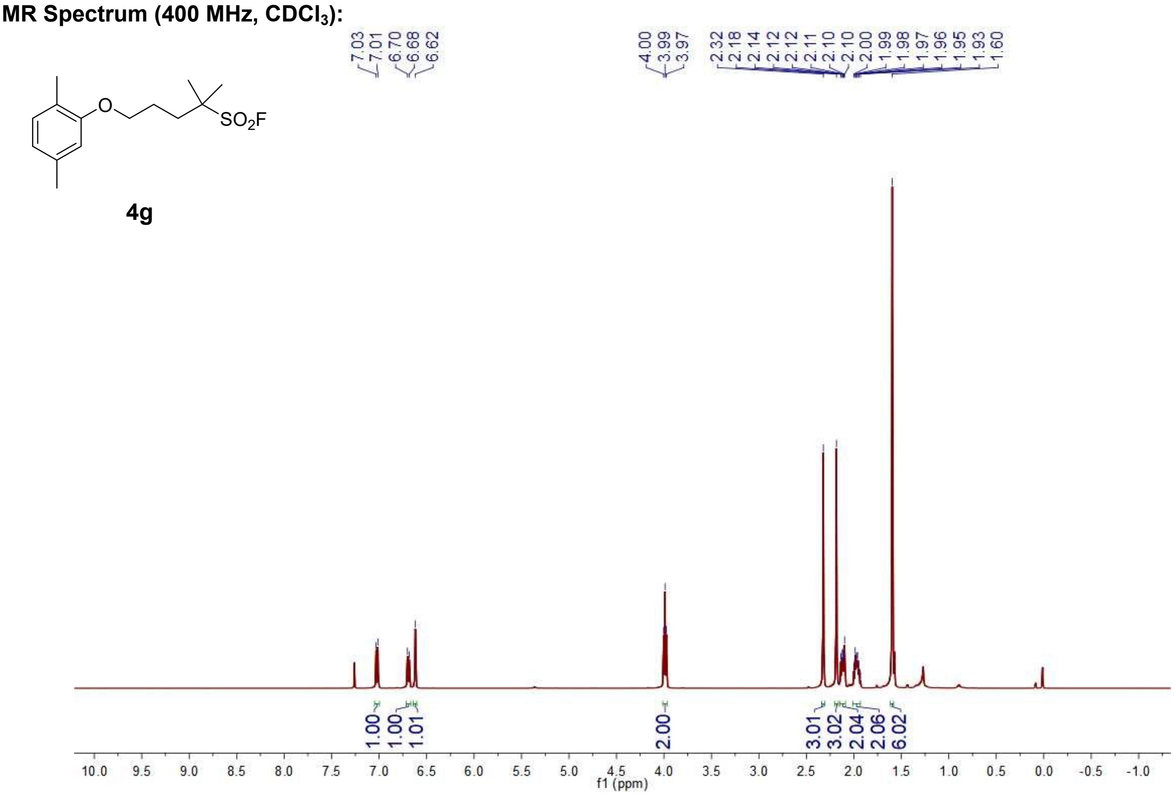


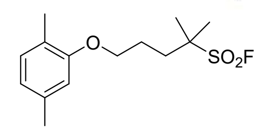
^{19}F-NMR Spectrum (376 MHz, $CDCl_3$):



^{1}H-NMR Spectrum (400 MHz, $CDCl_3$):



^{13}C-NMR Spectrum (101 MHz, $CDCl_3$):



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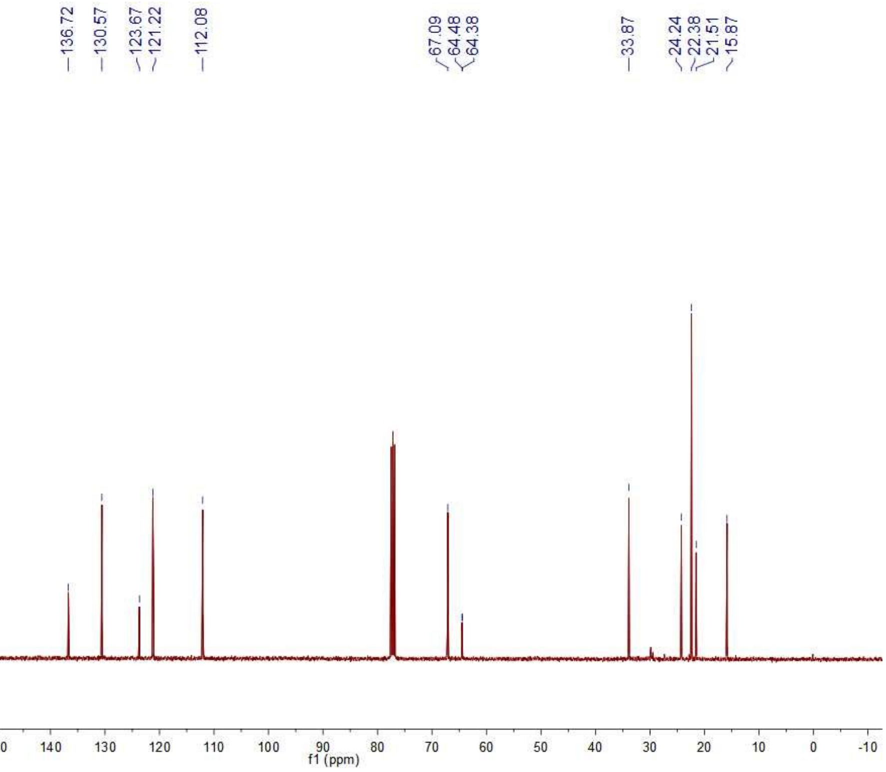
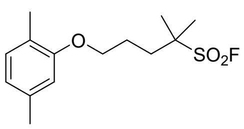


^{19}F-NMR Spectrum (376 MHz, $CDCl_3$):



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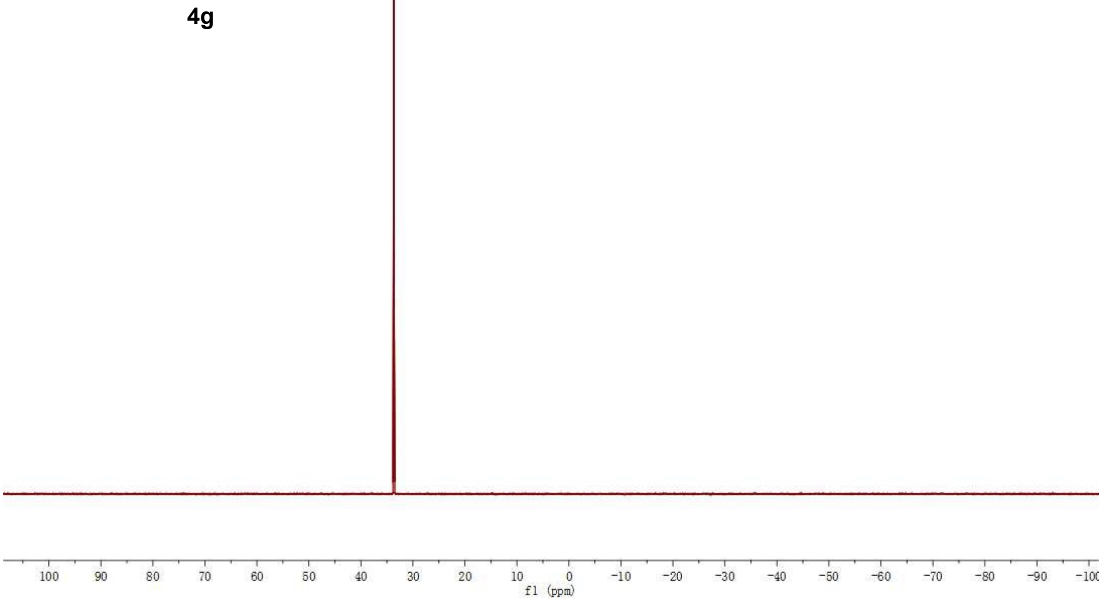
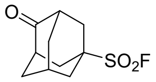


^{1}H-NMR Spectrum (400 MHz, $CDCl_3$):



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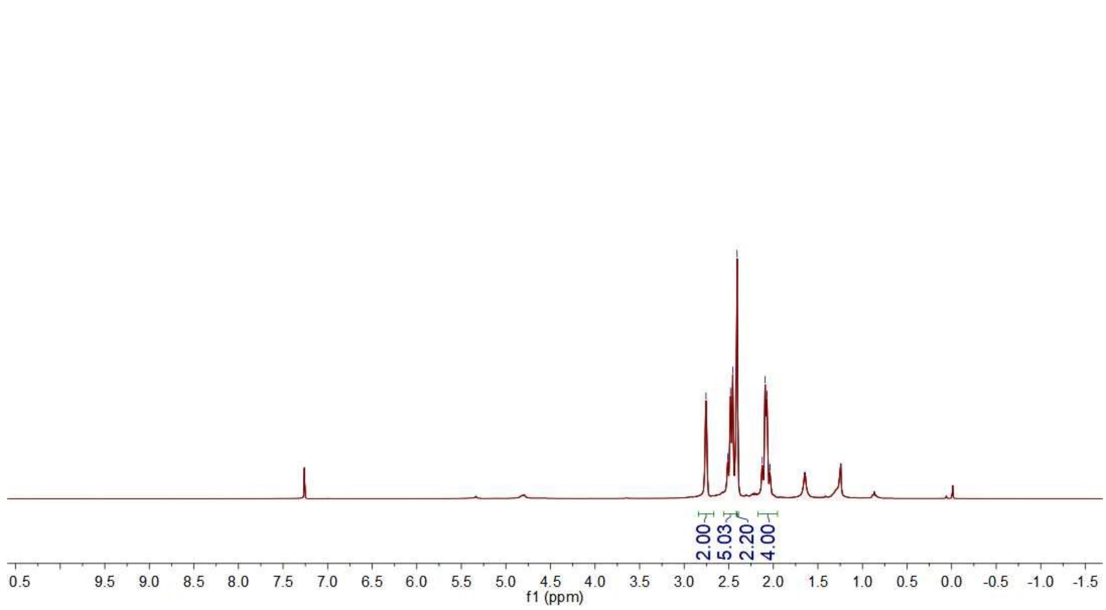
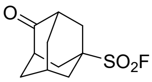


^{13}C-NMR Spectrum (101 MHz, $CDCl_3$):



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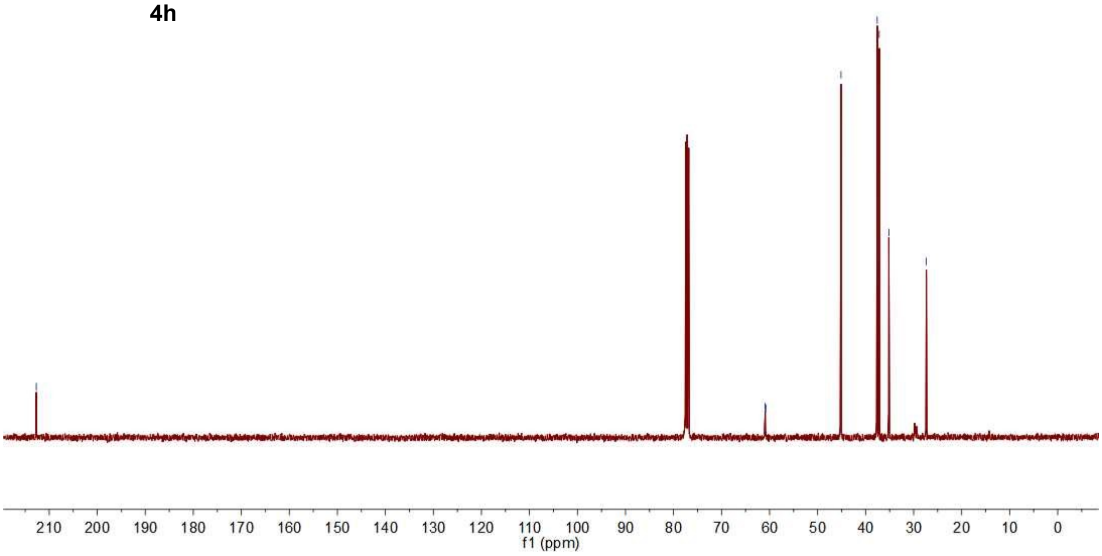
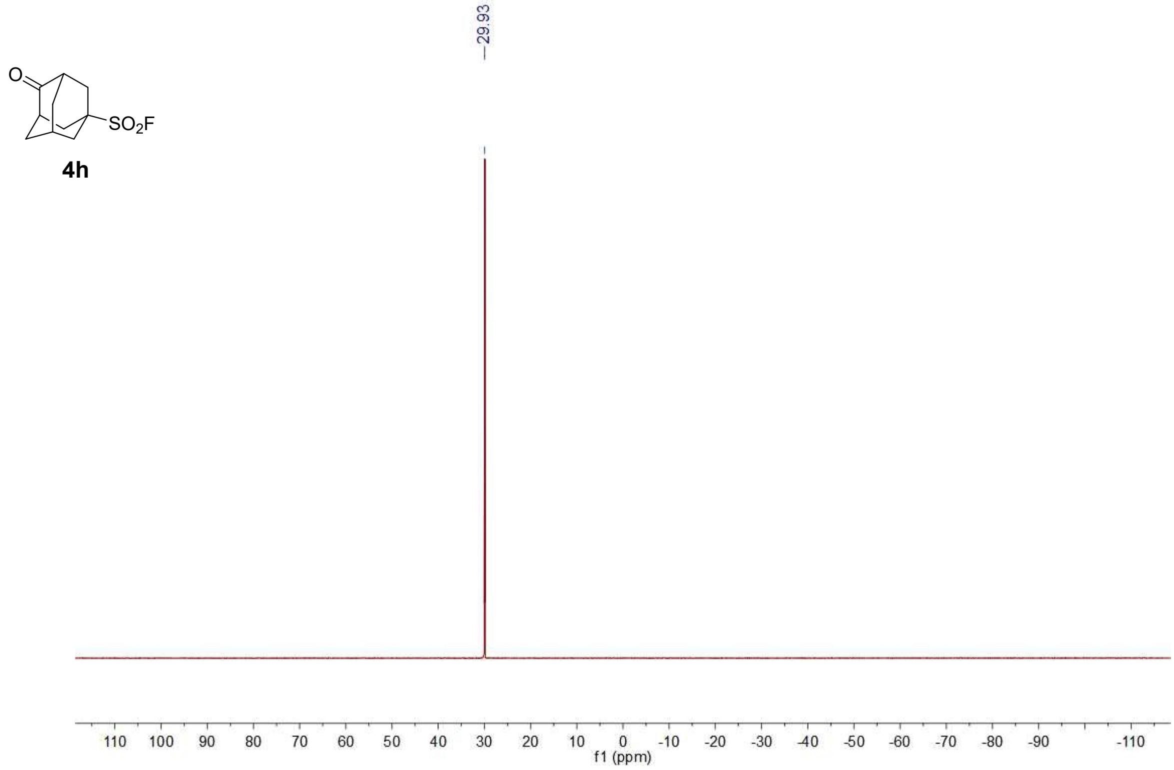
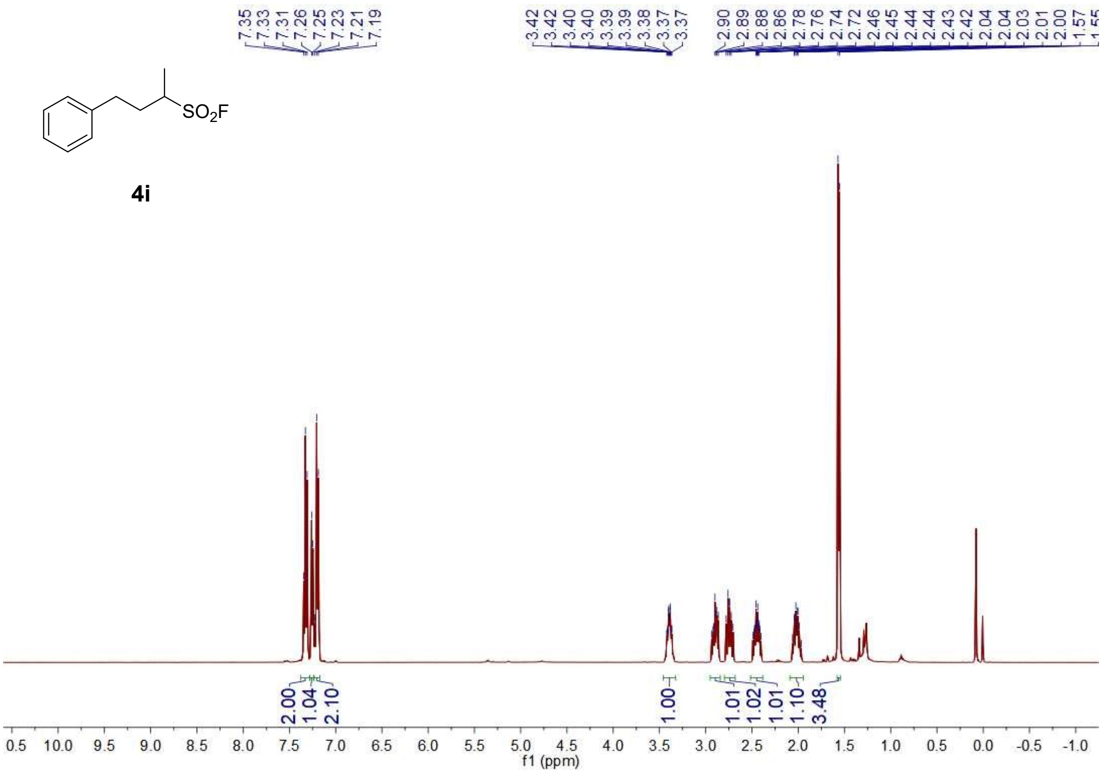


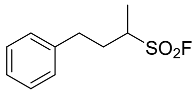
^{19}F-NMR Spectrum (376 MHz, $CDCl_3$):



^{1}H-NMR Spectrum (400 MHz, $CDCl_3$):



^{13}C-NMR Spectrum (101 MHz, $CDCl_3$):



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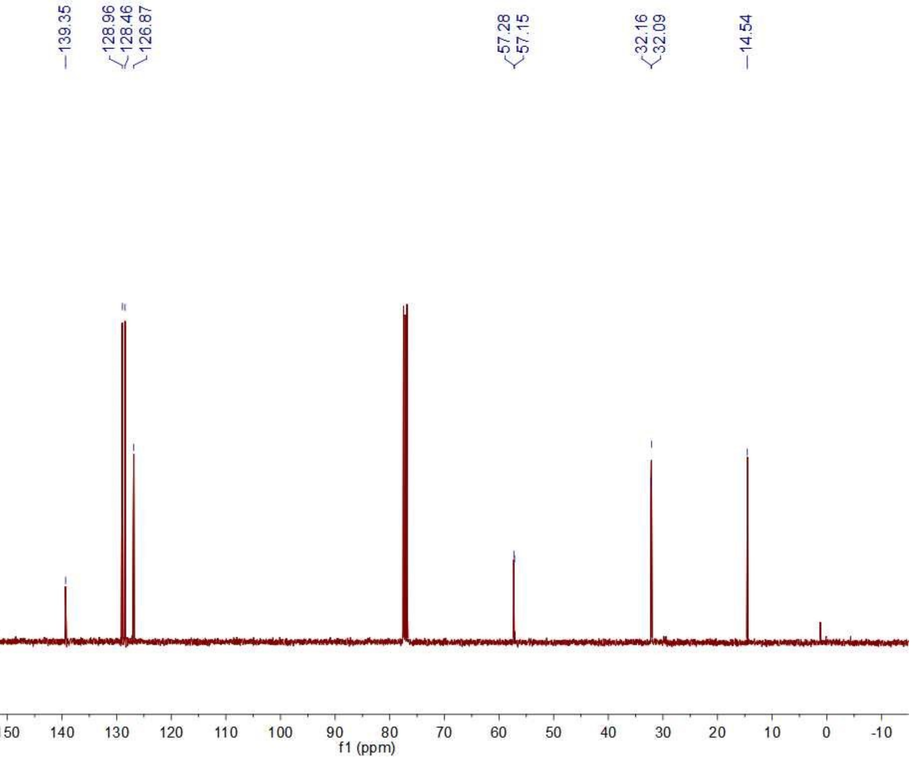
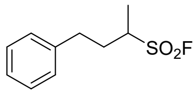
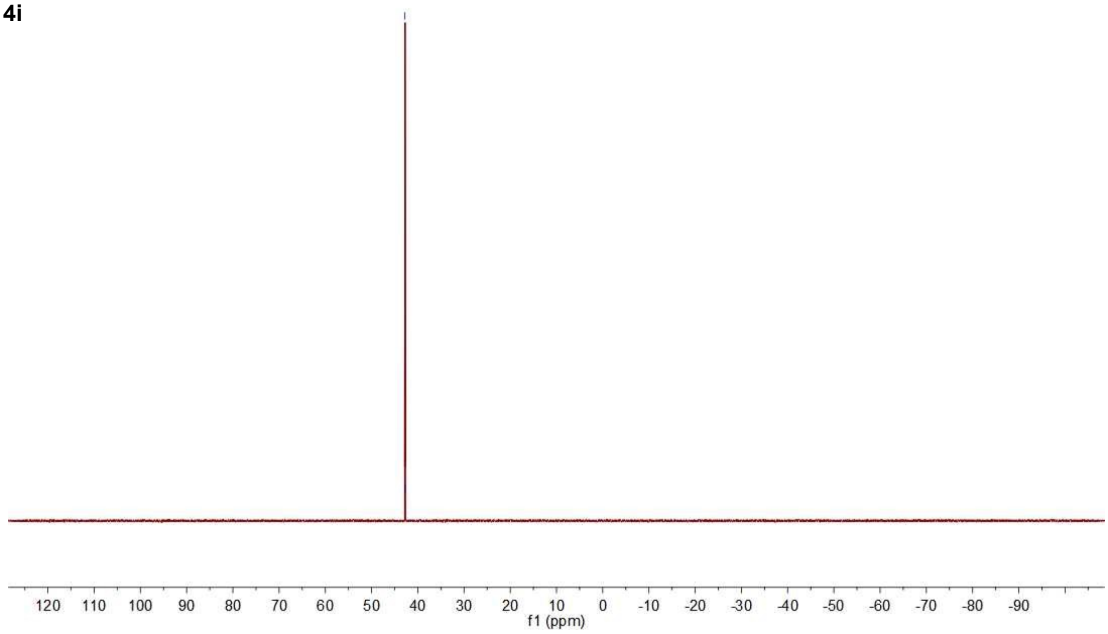


^{19}F-NMR Spectrum (376 MHz, $CDCl_3$):



4i



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