Supporting Information

Aryl sulfonyl fluoride synthesis via organophotocatalytic fluorosulfonylation of diaryliodonium salts

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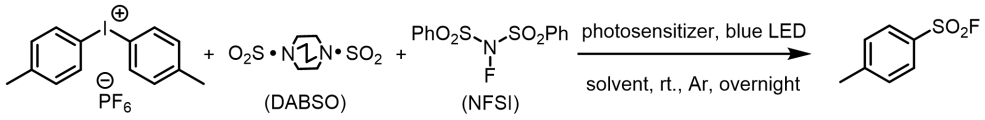
I. General information

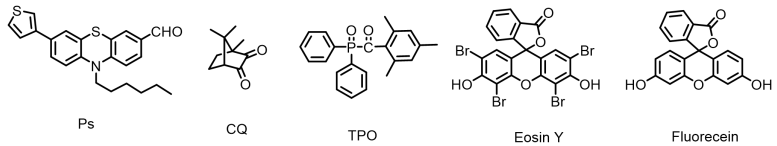
Unless otherwise stated, all reagents were purchased from commercial source and used as received. The solvent MeCN, dichloroethane (DCE), and N, N-dimethylformamide (DMF) and so on were distilled from CaH_2. 1,4-diazabicyclo[2.2.2]octane-1,4-diium-1,4-disulfinate (DABSO) was synthesized with 1,4-diazabicyclo[2.2.2]octane(DABCO) and sulfur dioxide and was purchased from commercial source (TCI). ^{1}H, ^{19}F and ^{13}C NMR spectra were obtained on 400 MHz spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts were determined relative to internal $(CH_3)_4Si$ (TMS) at δ 0.0 ppm and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ at δ 0.0 ppm. Data for ^{1}H, ^{19}F and ^{13}C NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). Coupling constants are reported in hertz (Hz). Flash column chromatograph was carried out using 300-400 mesh silica gel at medium pressure. 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.

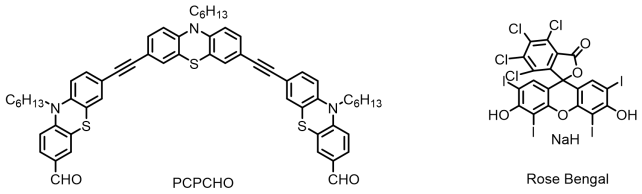
II. Screening reaction conditions for the organophotocatalytic fluorosulfonylation of diaryliodonium salts

Table S1. Initial attempt[a]



1a 2a



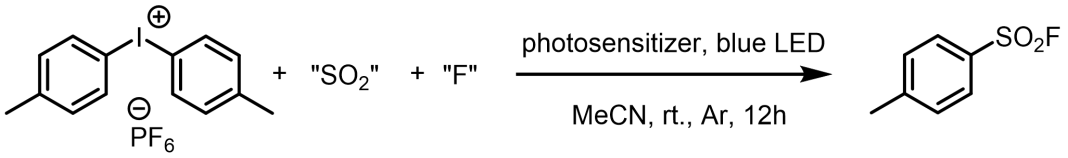


Entry	Photosensitizer	Solvent	Yield[b] (%)
1	Ps	MeCN	5
2	Ps	DCM	9
3	PCPCHO	MeCN	9
4	PCPCHO	DCM	3
5	TPO	MeCN	0
6	TPO	DCM	0
7	CQ	MeCN	14
8	CQ	DCM	10
9	CQ	DCE	13
10	CQ	EtOH	4
11	CQ	DMF	6
12	CQ	DMSO	0
13	CQ	NMP	0
14	CQ	toluene	0

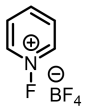
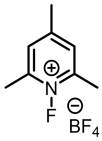
15	CQ	acetone	0

(a) Reaction conditions: 1a (0.2 mmol, 1.0 equiv.), DABSO (0.6 equiv.), KF (1.2 equiv.), photosensitizer (5 mol%), MeCN (2 mL), blue LED, Ar atmosphere, room tempreture, 12 h. (b) Yields were determined by ^{19}F NMR spectroscopy using 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard.

Table S2. Screening on sulfur dioxide source, fluorine source and photosensitizers[a]

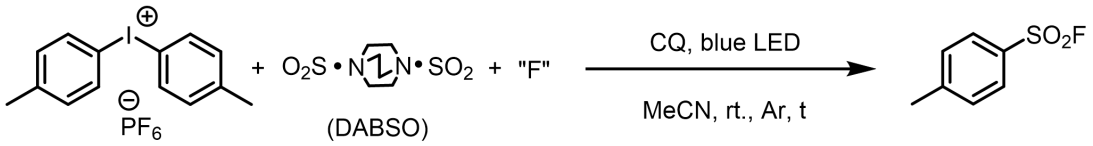


1a **2a**

Entry	"SO_2"	"F"	Photosensitizer	Yield[b] (%)
1	DABSO	Selectfluor	CQ	1
2	DABSO		CQ	7
3	DABSO		CQ	9
4	DABSO	KF	CQ	56
5	DABSO	NaF	CQ	0
6	DABSO	KHF_2	CQ	53
7	DABSO	AgF	CQ	12
8	DABSO	CuF_2	CQ	0
9	$K_2S_2O_5$	KF	CQ	0
10	$Na_2S_2O_4$	KF	CQ	0
11	DABSO	KF	TPO	0
12	DABSO	KF	Ps	4
13	DABSO	KF	PCPCHO	24
14	DABSO	KHF_2	Ps	11
15	DABSO	KHF_2	PCPCHO	27

(a) Reaction conditions: 1a (0.2 mmol, 1.0 equiv.), "SO_2" (0.6 equiv.), "F" (1.2 equiv.), photosensitizer (5 mol%), MeCN (2 mL), blue LED, Ar atmosphere, room tempreture, 12 h. (b) Yields were determined by ^{19}F NMR spectroscopy using 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard.

Table S3. Screening the reaction time[a]

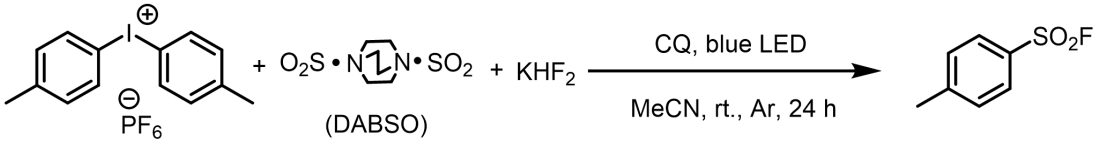


1a **2a**

Entry	DABSO	"F"	t(h)	Yield[b] (%)
1	DABSO	KF	1	9
2	DABSO	KF	4	39
3	DABSO	KF	8	39
4	DABSO	KF	12	56
5	DABSO	KF	24	51
6	DABSO	KF	48	57
7	DABSO	KHF_2	24	67
8[c]	DABSO	KHF_2	12	77
9[c]	DABSO	KHF_2	18	78
10[c]	DABSO	KHF_2	24	83

(a) Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), DABSO (1.2 equiv.), "F" (2.0 equiv.), CQ (5 mol%), MeCN (2 mL), blue LED, Ar atmosphere, room tempreture, t. (b) Yields were determined by ^{19}F NMR spectroscopy using 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard. (c) DABSO was purchased from commercial source.

Table S4. Screening on equivalent of DABSO, KHF_2 and CQ[a]



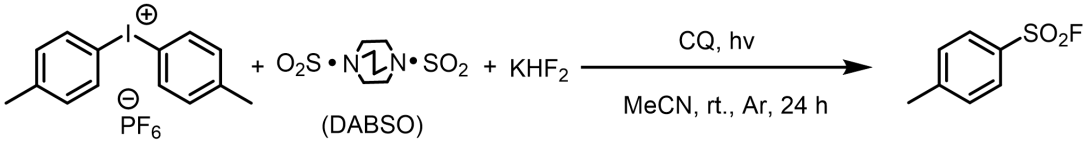
1a **2a**

Entry	DABSO[c] (equiv.)	KHF_2(equiv.)	CQ (equiv.)	Yield[b] (%)
1	1.2	2.0	0.1 mol%	15
2	1.2	2.0	0.5 mol%	35
3	1.2	2.0	1 mol%	80
4	1.2	2.0	2 mol%	75
5	1.2	2.0	10 mol%	82

6	1.2	2.0	5 mol%	83
7	0.6	2.0	5 mol%	80
8	1.5	2.0	5 mol%	84
9	2.0	2.0	5 mol%	81
10	2.0	5.0	5 mol%	71

(a) Reaction conditions: 1a (0.2 mmol, 1.0 equiv.), DABSO, KHF_2, CQ, MeCN (2 mL), blue LED, Ar atmosphere, room tempreture, 24 h. (b) Yields were determined by ^{19}F NMR spectroscopy using 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard. (c) DABSO was purchased from commercial source.

Table S5. Screening on the light sources[a]

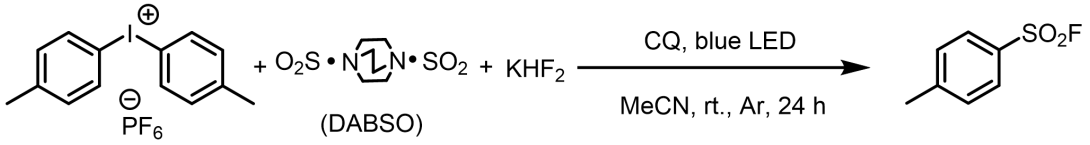


1a **2a**

Entry	DABSO[c]	hv	Yield[b] (%)
1	DABSO	Blue LED	83
2	DABSO	CFL	80
3	DABSO	Green LED	53
4	DABSO	Blue LED (20 W, 440~445 nm)	83

(a) Reaction conditions: 1a (0.2 mmol, 1.0 equiv.), DABSO (1.2 equiv.), KHF_2 (2.0 equiv.), CQ (5 mol%), MeCN (2 mL), hv, Ar atmosphere, room tempreture, 24 h. (b) Yields were determined by ^{19}F NMR spectroscopy using 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard. (c) DABSO was purchased from commercial source.

Table S6. Control experiments[a]



1a **2a**

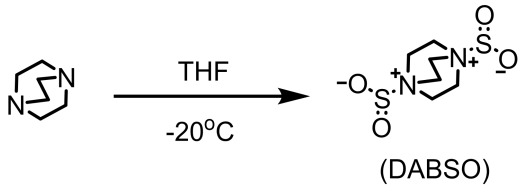
Entry	Variation from standard conditions	Yield[b] (%)
1[c]	**None**	**83**
2[c]	Without KHF_2	0

3[c]	Without CQ	0
4[c]	Without blue LED	0
5[c]	Air instead of Ar	0
6[c]	Eosin Y, Fluorescein and Rose Bengal instead of CQ	<70

(a) Reaction conditions: 1a (0.2 mmol, 1.0 equiv.), DABSO (1.2 equiv.), KHF_2 (2.0 equiv.), CQ (5 mol%), MeCN (2 mL), blue LED (20 W, 440~445 nm), Ar atmosphere, room tempreture, 24 h. (b) Yields were determined by ^{19}F NMR spectroscopy using 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard. (c) DABSO was purchased from commercial source.

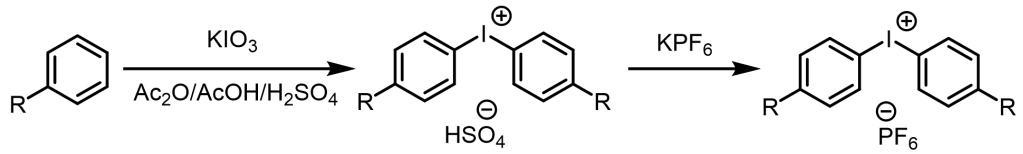
III. Preparation of 1,4-Diazabicyclo[2.2.2]octane bis(sulfur dioxide) adduct (DABSO) and diaryliodonium salts

(1) Preparation of 1,4-Diazabicyclo[2.2.2]octane bis(sulfur dioxide) adduct (DABSO)



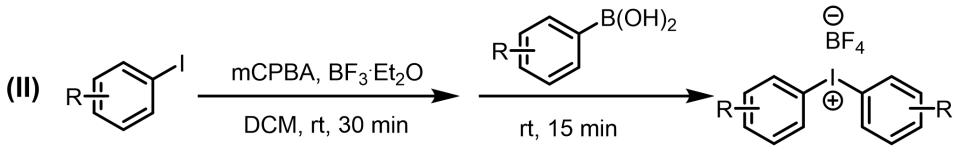
Triethylenediamine (DABCO, 30 mmol, 3.37g) was added into a 250 mL long-neck round-bottomed flask. Then the flask was poured into a slight excess of solvent tetrahydrofuran while stirring, and DABCO was dissolved until the system is clear. The elbow was inserted to about 5 mm above the liquid level of the flask. The elbow was connected to the sulfur dioxide drying tube and the valve of the long-necked round-bottomed bottle was connected to the drying tube to connect to the atmosphere. After that the flask was placed in a low temperature thermostat at minus 20℃, and later SO_2 (air flow rate was about one bubble per second) was accessed 30 minutes. Then the white solid was precipitated. The tempreture was gradually rised up to -10℃ and 0℃ and each continue stirring for 1 hour. Finally after the flask was stirred at room temperature for 1 hour, filter and drain the white solid which weighed about 7 g.

(2) Preparation of diaryliodonium salts

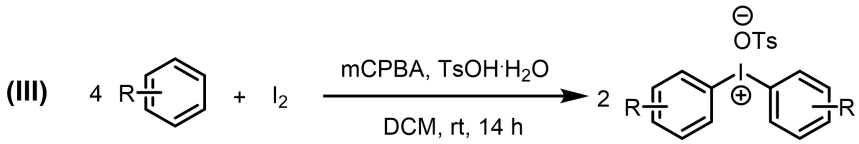


According to related literature[1], weigh potassium iodate (0.023 mol, 5 g) into a 100 mL two-necked flask with a magnet, and then extract aromatic hydrocarbons (0.06 mol) and acetic anhydride (6 mL) by using a syringe and add in the flask. The bottle was placed in an ice-salt bath. After the additional amount of glacial acetic acid (6 mL) and concentrated sulfuric acid (4 mL) was mixed and poured into a constant

pressure dropping funnel, the mixed acid was added slowly by adjusting the flow rate while stirring. The mixture was stirred overnight after the addition is complete. After the reaction, the bottle was added about 10 mL ice water, and filtered. The filtrate was poured into a separatory funnel and extracted with petroleum ether several times. And then add the adjusted saturated potassium hexafluorophosphate solution into the solution while stirring. The precipitate was filtered and recrystallized (EtOH:H_2O=1:1) to obtain diaryliodonium hexafluorophosphate, which is dried under vacuum.



According to related literature[2], m-chloroperoxybenzoic acid (1.1 equiv.) was weighed and added into a 100 mL round-bottomed flask, and add DCM (0.15 M) into the flask to dissolve. Aryl iodide (1.0 equiv.) was added. Boron trifluoride ether (2.5 equiv.) was slowly add dropwise and then stirred at room temperature for 30 min. After that arylboronic acid (1.1 equiv.) was added, and the mixture was stirred at room temperature for 15 min. After the reaction, the system was concentrated and dissolved with a small amount of DCM. Then, ether was added under vigorous stirring. After a period of time, the solid was precipitated (if there is no solid precipitated, you can add a little petroleum ether or try to put it in the refrigerator), and filtered, and dried under vacuum.

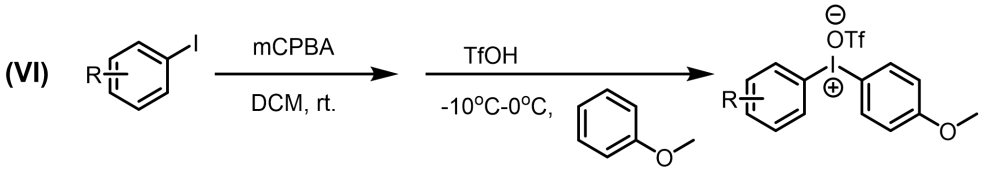


According to related literature[3], m-chloroperoxybenzoic acid (3.0 equiv.) and iodine (1.0 equiv.) was weighed and added into a 100 mL round bottom flask, and add DCM (0.2 M) into the flask to dissolve. Aromatic (4.0 equiv.) was added and then p-toluenesulfonic acid monohydrate (4.0 equiv.) was poured into the bottle. The mixture was stirred at room temperature for 14 h. After the reaction, the system was concentrated and dissolved with a small amount of acetone, and then added diethyl ether under vigorous stirring (you can add a little petroleum ether or try to put it in the

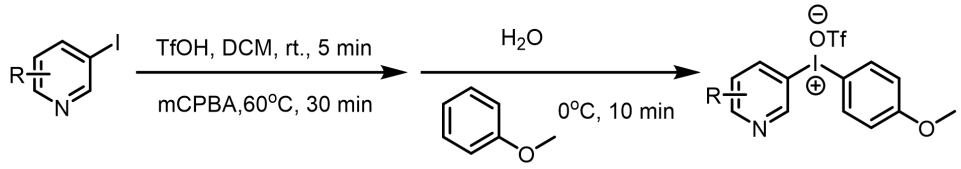
refrigerator if no solids precipitate). After a period of time, the solid was precipitated and filtered, and dried under vacuum.

According to related literature[4-6], m-chloroperoxybenzoic acid (3.0 equiv.) was weighed and added into a 100 mL round-bottomed flask, and add DCM (0.2 M) into the flask to dissolve. Iodine (1.0 equiv.) was added. The system was placed in an ice bath. Aromatic (10.0 equiv.) was added and trifluoromethanesulfonic acid (4.0 equiv.) was slowly added dropwise for about 15 minutes. After the addition, it's returned to room temperature and stirred continuously for 12 hours. After the reaction, the system was concentrated, and ether was added under vigorous stirring. After a period of time, the solid was precipitated (if there is no solid precipitation, add a little petroleum ether or try to put it in the refrigerator) and filtered, and dried under vacuum.

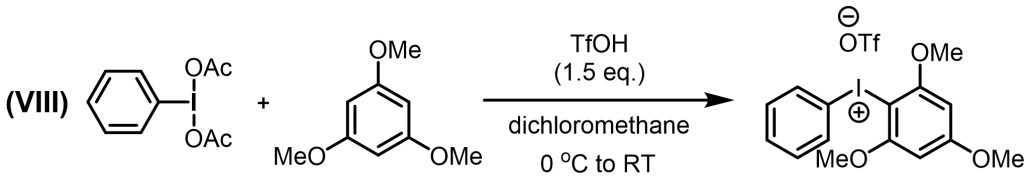
According to related literature [4-6], m-chloroperoxybenzoic acid (1.0 equiv.) was weighed and added into a 100 mL round-bottomed flask, and add DCM (0.1 M) into the flask to dissolve. Then aryl iodide (1.0 equiv.) and aromatic hydrocarbons (1.0 equiv.) were added and trifluoromethanesulfonic acid (2.0 equiv.) was slowly added dropwise at room temperature or in an ice bath (0°C), and stirred for a corresponding time at the corresponding temperature after the addition is complete. After the reaction, the system was concentrated, and ethyl ether was added under vigorous stirring. After a period of time, the solid was precipitated (if there is no solid precipitation, add a little petroleum ether or try to put it in the refrigerator) and filtered, and dried under vacuum.

(VI) 

According to related literature[7], m-chloroperoxybenzoic acid (1.1 equiv.) and aryl iodide (1.0 equiv.) were added into a 100 mL round-bottomed flask, and add DCM (0.2 M) into the flask to dissolve. Trifluoromethanesulfonic acid (2.0 equiv.) was slowly added and then the system was stirred at room temperature for 10 min. Then the system was put in an ice-salt bath. Anisole (1.0 equiv.) dissolved in DCM (0.5 M) was slowly added dropwise, and then the mixture was stirred for 10 min after the addition is complete. After the reaction, the system was concentrated while it was cold, and ether was added under vigorous stirring. After a period of time, the solid was precipitated (if there is no solid precipitation, add a little petroleum ether or try to put it in the refrigerator) and filtered, and dried under vacuum.

(VII) 

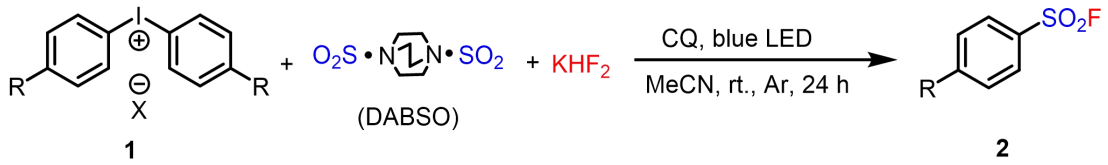
According to related literature[7], iodopyridine compound (1.0 equiv.) was weighed and added into a 100 mL round-bottomed flask, and add DCM (0.15 M) to dissolve. Trifluoromethanesulfonic acid (4.0 equiv.) was added. The mixture was stirred at room temperature for 5 min. Then m-chloroperoxybenzoic acid (1.75 equiv.) was poured. The system was placed under heating at 60℃ and stirred for 30 min. After it's returned to room temperature, put it in an ice bath. Water (2.0 equiv.) and anisole (1.1 equiv.) was added, and stirred continuously for 10 min. After the reaction, the system was concentrated, and ether was added under vigorous stirring. After a period of time, the solid was precipitated (if there is no solid precipitation, add a little petroleum ether or try to put it in the refrigerator) and filtered, and dried under vacuum.

(VIII) 

According to related literature[8], phenyliodine(III) diacetate (1.0 equiv.), 1,3,5-trimethoxybenzene (1.1 equiv.) and DCM (80 mL) was added into a 250 mL round-bottomed flask, triflic acid (TfOH, 1.5 equiv.) in 80 mL of water was slowly added at 0 °C. The solution was warmed up to room temperature and continuously stirred for 3 hours. The resulting mixture was extracted with 100 mL of dichloromethane for three times, and the combined organic layer was dried with anhydrous sodium sulfate. The solvent was evaporated in *vacuo*. To oily residue 100 mL of diethyl ether was added, and the precipitate was filtered and washed with diethyl ether to give the desired iodonium salt as a white powder.

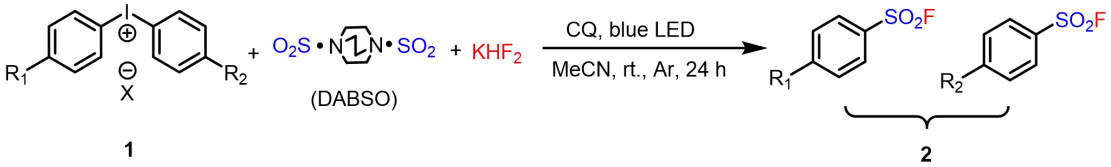
IV. General procedures for the organophotocatalytic fluorosulfonylation of diaryliodonium salts

(1) General procedure A: scope of symmetrical substrates



The above-prepared symmetric diaryliodonium salt substrate (0.4 mmol, 1.0 equiv.), 1,4-diazabicyclo[2.2.2]octane-1,4-dionium-1,4-disulfinate (DABSO, 0.48 mmol, 1.2 equiv.), KHF_2 (0.8 mmol, 2.0 equiv.) and CQ (0.02 mmol, 5 mol %) were added to a 10 mL dried sealed tube which equipped with a magnetic rotor. Then anhydrous MeCN (4.0 mL) was added through a syringe under an argon atmosphere. After the tube is sealed, the mixture is stirred at room temperature under blue light (20 W, 440~445 nm) for 24 hours. The crude yield of the product was measured by ^{19}F NMR spectrum, which 4-(trifluoromethoxy) anisole serves as internal standard. The mixture was filtered through 200-300 mesh silica gel and monitored by thin layer chromatography. After the solvent was removed under reduced pressure with a rotary evaporator, the crude product was purified by silica gel column chromatography to obtain the product.

(2) General procedure B: scope of asymmetric substrates

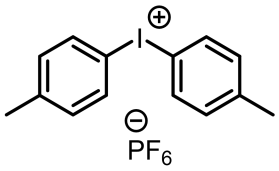


The previously prepared asymmetric diaryliodonium salt substrate (0.4 mmol, 1.0 equiv.), 1,4-diazabicyclo[2.2.2]octane-1,4-dionium-1,4-disulfinate (DABSO, 0.48 mmol), KHF_2 (0.8 mmol) and CQ (0.02 mmol) were added to a 10 mL dried sealed tube which equipped with a magnetic rotor. Then anhydrous MeCN (4.0 mL) was

added through a syringe under an argon atmosphere. After the tube is sealed, the mixture is stirred at room temperature under blue light (20 W, 440~445 nm) for 24 hours. The crude yield of the product was measured by ^{19}F NMR spectrum, which 4-(trifluoromethoxy) anisole serves as internal standard. The mixture was filtered through 200-300 mesh silica gel and monitored by thin layer chromatography. After the solvent was removed under reduced pressure with a rotary evaporator, the crude product was purified by silica gel column chromatography to obtain two mixed or separated fluorosulfonylated products.

V. Characterization data of the substrates and products

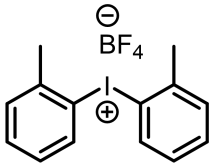
(1) Characterization data of the substrates



1a

di-p-tolyliodonium hexafluorophosphate

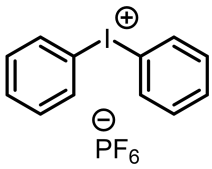
The substrate was prepared according to method **I** from toluene in 48% (white crystal). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.3 Hz, 4H), 7.31 – 7.26 (m, 4H), 2.39 (s, 6H) ppm.



1b

di-o-tolyliodonium tetrafluoroborate

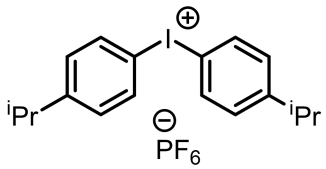
The substrate was prepared according to method **II** from o-iodotoluene and o-iodophenylboronic acid in 54% (white solid). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.1 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 2H), 7.46 (d, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 2H), 2.62 (s, 6H) ppm.



1c

diphenyliodonium hexafluorophosphate

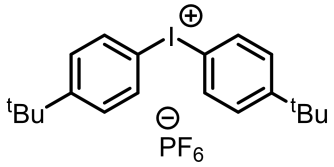
The substrate was prepared according to method **I** from benzene in 31% (white solid). **^{1}H NMR** (400 MHz, Acetone-d_6): δ 8.40 – 8.34 (m, 4H), 7.78 (t, *J* = 7.5 Hz, 2H), 7.67 – 7.60 (m, 4H) ppm.



1d

bis(4-isopropylphenyl)-l2-iodane hexafluorophosphate

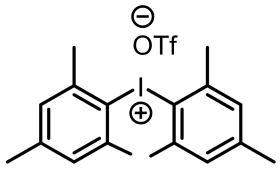
The substrate was prepared according to method **I** from cumene in 56% (white solid). **^{1}H NMR** (400 MHz, Acetone-d_6): δ 8.23 (d, J = 8.0 Hz, 4H), 7.49 (d, J = 8.0 Hz, 4H), 2.99 (p, J = 6.6 Hz, 4H), 1.22 (d, J = 6.8 Hz, 12H) ppm.



1e

bis(4-(tert-butyl)phenyl)iodonium hexafluorophosphate

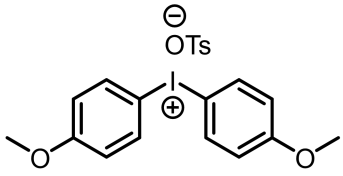
The substrate was prepared according to method **I** from tert-butylbenzene in 16% (white solid). **^{1}H NMR** (400 MHz, Acetone-d_6): δ 8.23 (d, J = 8.5 Hz, 4H), 7.65 (d, J = 8.4 Hz, 4H), 1.32 (s, 18H) ppm.



1f

dimesityliodonium trifluoromethanesulfonate

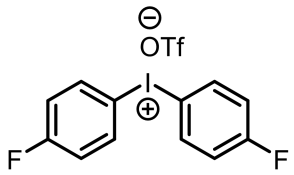
The substrate was prepared according to method **V** from 2,4,6-trimethyliodobenzene and 1,3,5-trimethylbenzene in 41% (white solid). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.04 (s, 4H), 2.50 (s, 12H), 2.32 (s, 6H) ppm.



1g

bis(4-methoxyphenyl)iodonium 4-methylbenzenesulfonate

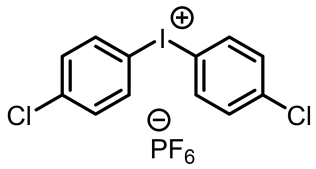
The substrate was prepared according to method **III** from 4-iodoanisole and anisole in 60% (white solid). **^{1}H NMR** (400 MHz, CD_3CN): δ 7.93 (d, *J* = 8.9 Hz, 4H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 7.7 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 4H), 3.79 (s, 6H), 2.34 (s, 3H) ppm.



1h

bis(4-fluorophenyl)-l2-iodane trifluoromethanesulfonate

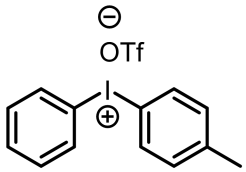
The substrate was prepared according to method **IV** from fluorobenzene in 45% (white solid). **^{1}H NMR** (400 MHz, CD_3CN): δ 8.16 – 8.09 (m, 4H), 7.29 (t, *J* = 8.7 Hz, 4H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -79.3, -106.2 ppm.



1i

bis(4-chlorophenyl)iodonium hexafluorophosphate

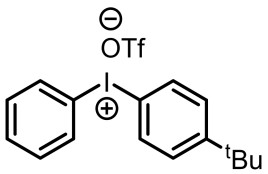
The substrate was prepared according to method **I** from chlorobenzene in 16% (white solid). **^{1}H NMR** (400 MHz, CD_3CN): δ 8.04 (d, *J* = 8.8 Hz, 4H), 7.56 (d, *J* = 8.8 Hz, 4H) ppm.



1j

phenyl(p-tolyl)iodonium trifluoromethanesulfonate

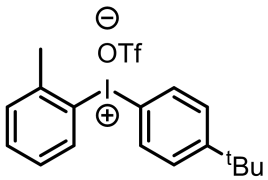
The substrate was prepared according to method **V** from iodobenzene and toluene in 64% (grey solid). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 7.9 Hz, 2H), 7.91 – 7.77 (m, 4H), 7.71 (t, *J* = 7.3 Hz, 1H), 7.54 (t, *J* = 7.9 Hz, 2H) ppm.



1k

(4-(tert-butyl)phenyl)(phenyl)iodonium trifluoromethanesulfonate

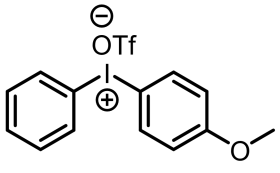
The substrate was prepared according to method **V** from iodobenzene and tert-butylbenzene in 66% (white solid). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95 (dd, *J* = 35.5, 8.2 Hz, 4H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.49 – 7.40 (m, 4H), 1.28 (s, 9H) ppm.



1l

(4-(tert-butyl)phenyl)(o-tolyl)iodonium trifluoromethanesulfonate

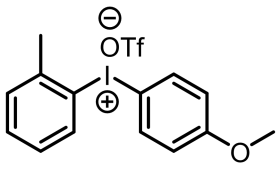
The substrate was prepared according to method **V** from o-iodotoluene and tert-butylbenzene in 68% (white solid). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 9.6 Hz, 3H), 7.24 (d, *J* = 7.4 Hz, 1H), 2.62 (s, 3H), 1.28 (s, 9H) ppm.



1m

(4-methoxyphenyl)(phenyl)iodonium trifluoromethanesulfonate

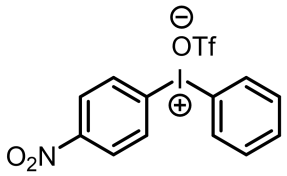
The substrate was prepared according to method **VI** from iodobenzene and anisole in 38% (off white solid). **^{1}H NMR** (400 MHz, CD_3CN): δ 8.03 (t, *J* = 9.2 Hz, 4H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.05 (d, *J* = 9.2 Hz, 2H), 3.83 (s, 3H) ppm.



1n

(4-methoxyphenyl)(o-tolyl)-l2-iodane trifluoromethanesulfonate

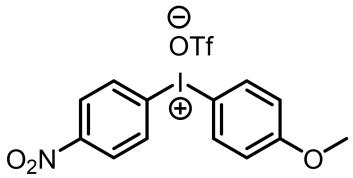
The substrate was prepared according to method **VI** from o-iodotoluene and anisole in 37% (dark gray solid). **^{1}H NMR** (400 MHz, CD_3CN): δ 8.12 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 9.0 Hz, 2H), 7.65 – 7.50 (m, 2H), 7.30 (t, *J* = 7.1 Hz, 1H), 7.04 (d, *J* = 9.0 Hz, 2H), 3.83 (s, 3H), 2.62 (s, 3H) ppm.



1o

(4-nitrophenyl)(phenyl)iodonium trifluoromethanesulfonate

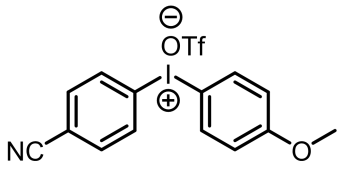
The substrate was prepared according to method **V** from 4-nitroiodobenzene and iodobenzene in 41% (light yellow solid). **^{1}H NMR** (400 MHz, CD_3CN): δ 8.26 (s, 4H), 8.17 – 8.13 (m, 2H), 7.75 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.9 Hz, 2H) ppm.



1p

(4-methoxyphenyl)(4-nitrophenyl)iodonium trifluoromethanesulfonate

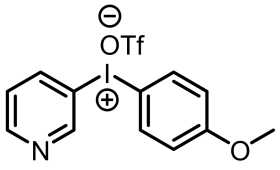
The substrate was prepared according to method **VI** from 4-nitroiodobenzene and anisole in 62% (dark gray solid). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.23 (q, *J* = 9.0 Hz, 4H), 8.07 (d, *J* = 9.1 Hz, 2H), 7.09 (d, *J* = 9.0 Hz, 2H), 3.85 (s, 3H) ppm.



1q

(4-cyanophenyl)(4-methoxyphenyl)iodonium trifluoromethanesulfonate

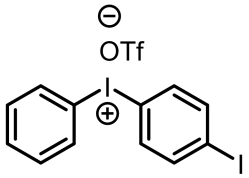
The substrate was prepared according to method **VI** from 4-cyano iodobenzene and anisole in 58% (dark gray solid). **^{1}H NMR** (400 MHz, CD_3CN): δ 8.14 (d, *J* = 8.5 Hz, 2H), 8.04 (d, *J* = 9.0 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 9.0 Hz, 2H), 3.85 (s, 3H) ppm.



1r

(4-methoxyphenyl)(pyridin-3-yl)iodonium trifluoromethanesulfonate

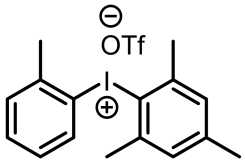
The substrate was prepared according to method **VII** from 3-iodopyridine and anisole in 59% (white solid). **^{1}H NMR** (400 MHz, CD_3CN): δ 9.28 (d, *J* = 1.9 Hz, 1H), 9.02 (dt, *J* = 8.5, 1.6 Hz, 1H), 8.93 (d, *J* = 5.8 Hz, 1H), 8.13 (d, *J* = 2.1 Hz, 1H), 8.13 – 8.08 (m, 2H), 7.14 – 7.09 (m, 2H), 3.87 (s, 3H) ppm.



1s

(4-iodophenyl)(phenyl)iodonium trifluoromethanesulfonate

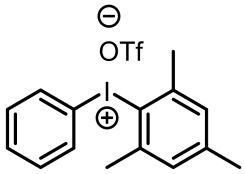
The substrate was prepared according to method **V** from iodobenzene and iodobenzene in 68% (white solid). **^{1}H NMR** (400 MHz, CD_3CN): δ 8.08 (d, *J* = 7.9 Hz, 2H), 7.91 – 7.77 (m, 4H), 7.71 (t, *J* = 7.3 Hz, 1H), 7.54 (t, *J* = 7.9 Hz, 2H) ppm.



1t

mesityl(o-tolyl)iodonium trifluoromethanesulfonate

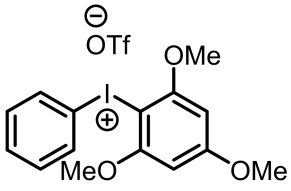
The substrate was prepared according to method **V** from o-iodotoluene and 1,3,5-trimethylbenzene in 35% (silver white solid). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.45 (dt, *J* = 12.0, 7.5 Hz, 3H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.11 (s, 2H), 2.59 (s, 9H), 2.36 (s, 3H) ppm.



1u

mesityl(phenyl)iodonium trifluoromethanesulfonate

The substrate was prepared according to method **V** from iodobenzene and 1,3,5-trimethylbenzene in 15% (grey solid). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 7.9 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.11 (s, 2H), 2.63 (s, 6H), 2.36 (s, 3H) ppm.

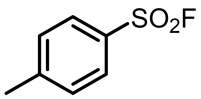


1v

phenyl(2,4,6-trimethoxyphenyl)iodonium trifluoromethanesulfonate

The substrate was prepared according to method **VIII** from phenyliodine(III) diacetate and 1,3,5-trimethoxybenzene in 81% (white solid). **^{1}H NMR** (400 MHz, DMSO): δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 6.48 (s, 2H), 3.96 (s, 6H), 3.88 (s, 3H) ppm.

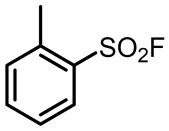
(2) Characterization data of the products



2a

4-methylbenzenesulfonyl fluoride

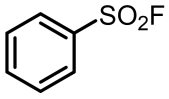
Obtained as a white solid in 75% yield (52.1 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 10:1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 2.49 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$): δ 66.3 ppm. **GC-MS (EI):** m/z = 174.0 (M^+). The analytical data are consistent with literature values[9].



2b

2-methylbenzenesulfonyl fluoride

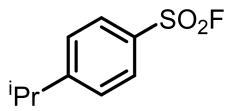
Obtained as a colorless liquid in 58% yield (40.1 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 25:2 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 7.9 Hz, 1H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 8.6 Hz, 2H), 2.69 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$): δ 60.2 ppm. **GC-MS (EI):** m/z = 174.0 (M^+). The analytical data are consistent with literature values[9].



2c

benzenesulfonyl fluoride

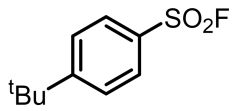
Obtained as a light yellow liquid in 71% yield (45.4 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 10:1 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.64 (t, *J* = 7.8 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$): δ 65.8 ppm. **GC-MS (EI):** m/z = 160.0 (M^+). The analytical data are consistent with literature values[9].



2d

4-isopropylbenzenesulfonyl fluoride

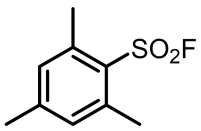
Obtained as a colorless liquid in 70% yield (56.4 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 25:2 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 3.04 (hept, *J* = 6.9 Hz, 1H), 1.29 (d, *J* = 6.9 Hz, 6H); **^{19}F NMR** (376 MHz, $CDCl_3$): δ 66.2; **^{13}C NMR** (101 MHz, $CDCl_3$): δ 157.8, 130.4 (d, *J* = 22 Hz), 128.8, 127.9, 34.6, 23.6 ppm. **HRMS** (FI) m/z: $[M]^+$ Calcd for $C_9H_{11}FO_2S$ 202.0464; Found 202.0459.



2e

4-(*tert*-butyl)benzenesulfonyl fluoride

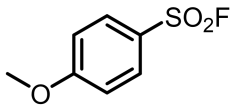
Obtained as a white solid in 48% yield (41.2 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 25:2 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 1.37 (s, 9H); **^{19}F NMR** (376 MHz, $CDCl_3$): δ 66.2 ppm. **GC-MS (EI):** m/z = 216.0 (M^+). The analytical data are consistent with literature values[9].



2f

2,4,6-trimethylbenzenesulfonyl fluoride

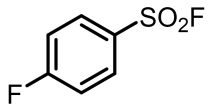
Obtained as a white solid in 69% yield (56.0 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 25:2 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.03 (s, 2H), 2.65 – 2.62 (m, 6H), 2.35 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$): δ 68.2 ppm. **GC-MS (EI):** m/z = 202.0 (M^+). The analytical data are consistent with literature values[10].



2g

4-methoxybenzenesulfonyl fluoride

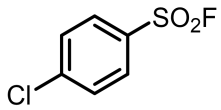
Obtained as a yellow liquid in 16% yield (12.1 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 10:3 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 9.1 Hz, 2H), 7.06 (d, *J* = 9.0 Hz, 2H), 3.92 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$): δ 67.3 ppm. **GC-MS (EI):** m/z = 190.0 (M^+). The analytical data are consistent with literature values[9].



2h

4-fluorobenzenesulfonyl fluoride

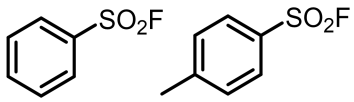
Obtained as a colorless liquid in 74% yield (53.1 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 50:3 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.06 (dd, *J* = 9.0, 4.8 Hz, 2H), 7.32 (t, *J* = 8.5 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$): δ 66.74, -99.34 (tt, *J* = 8.4, 4.9 Hz) ppm. **GC-MS (EI):** m/z = 177.9 (M^+). The analytical data are consistent with literature values[9].



2i

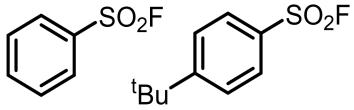
4-chlorobenzenesulfonyl fluoride

Obtained as a white solid in 62% yield (48.2 mg) by silica gel flash column chromatography eluted with petroleum ether: dichloromethane = 25:2 v/v. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.7 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$): δ 66.5 ppm. **GC-MS (EI):** m/z = 193.9 (M^+). The analytical data are consistent with literature values[9].



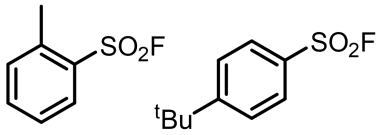
2j

benzenesulfonyl fluoride + 4-methylbenzenesulfonyl fluoride: crude ^{19}F NMR yield: 48% + 27%. After silica gel flash column chromatography purification, the product is obtained as a mixture with the ratio of 4:3 in 66% yield. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 66.2, 65.9 ppm. The analytical data are consistent with literature values[9].



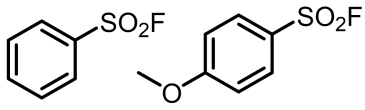
2k

benzenesulfonyl fluoride + 4-(tert-butyl)benzenesulfonyl fluoride: crude ^{19}F NMR yield: 51% + 30%. After silica gel flash column chromatography purification, the product is obtained as a mixture with the ratio of 4:3 in 75% yield. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 66.2, 65.9 ppm. The analytical data are consistent with literature values[9].



2l

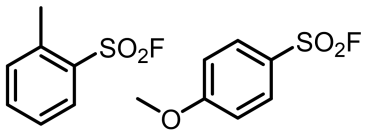
2-methylbenzenesulfonyl fluoride + 4-(tert-butyl)benzenesulfonyl fluoride: crude ^{19}F NMR yield: 40% + 40%. After silica gel flash column chromatography purification, the product is obtained as a mixture with the ratio of 1:0.76 in 42% yield. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 66.2, 60.2 ppm. The analytical data are consistent with literature values[9].



2m

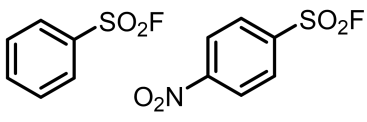
benzenesulfonyl fluoride: crude ^{19}F NMR yield: 43%. After silica gel flash column

chromatography purification, the isolated yield is 37%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$): δ 65.8 ppm. The analytical data are consistent with literature values[9]. **4-methoxybenzenesulfonyl fluoride**: crude ^{19}F NMR yield: 15%. After silica gel flash column chromatography purification, the isolated yield is 13%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.9 Hz, 2H), 3.92 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$): δ 67.2 ppm. The analytical data are consistent with literature values[9].



2n

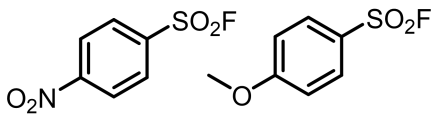
2-methylbenzenesulfonyl fluoride: crude ^{19}F NMR yield: 25%. After silica gel flash column chromatography purification, the isolated yield is 21%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 7.9 Hz, 1H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 8.6 Hz, 2H), 2.69 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$): δ 60.2 ppm. The analytical data are consistent with literature values[9]. **4-methoxybenzenesulfonyl fluoride:** crude ^{19}F NMR yield: 15%. After silica gel flash column chromatography purification, the isolated yield is 20%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 9.1 Hz, 2H), 7.06 (d, *J* = 8.9 Hz, 2H), 3.92 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$): δ 67.2 ppm. The analytical data are consistent with literature values[9].



2o

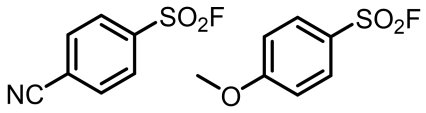
benzenesulfonyl fluoride: crude ^{19}F NMR yield: 17%. After silica gel flash column chromatography purification, benzenesulfonyl fluoride is impure. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 65.9 ppm. The analytical data are consistent with literature values[9]. **p-nitrobenzenesulfonyl fluoride**: crude ^{19}F NMR yield: 27%. After silica gel flash column chromatography purification, the isolated yield is 28%. **^{1}H NMR** (400 MHz,

$CDCl_3$): δ 8.49 (d, *J* = 8.3 Hz, 2H), 8.25 (d, *J* = 8.8 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$): δ 66.2 ppm. The analytical data are consistent with literature values[12].



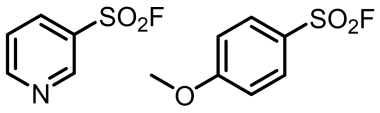
2p

p-nitrobenzenesulfonyl fluoride: crude ^{19}F NMR yield: 12%. **4-methoxybenzenesulfonyl fluoride**: crude ^{19}F NMR yield: 3%.



2q

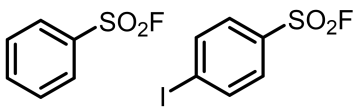
p-cyanobenzenesulfonyl fluoride: crude ^{19}F NMR yield: 63%. After silica gel flash column chromatography purification, the isolated yield is 54%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.5 Hz, 2H), 7.95 (d, *J* = 8.1 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$): δ 66.0 ppm. The analytical data are consistent with literature values[12]. **4-methoxybenzenesulfonyl fluoride**: crude ^{19}F NMR yield: 15%. After silica gel flash column chromatography purification, 4-methoxybenzenesulfonyl fluoride is impure. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 67.2 ppm. The analytical data are consistent with literature values[9].



2r

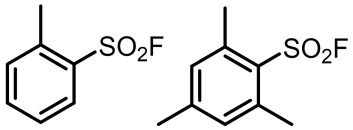
pyridine-3-sulfonyl fluoride: crude ^{19}F NMR yield: 28%. After silica gel flash column chromatography purification, the isolated yield is 23%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.23 (s, 1H), 9.00 (d, *J* = 4.7 Hz, 1H), 8.30 (dt, *J* = 8.1, 1.9 Hz, 1H), 7.61 (dd, *J* = 8.1, 4.9 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$): δ 67.9 ppm. The analytical data are consistent with literature values[13]. **4-methoxybenzenesulfonyl fluoride**: crude ^{19}F NMR yield: 7%. After silica gel flash column chromatography purification, the isolated yield is 5%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 9.1 Hz, 2H), 7.06

(d, J = 9.0 Hz, 2H), 3.92 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$): δ 67.2 ppm. The analytical data are consistent with literature values[9].



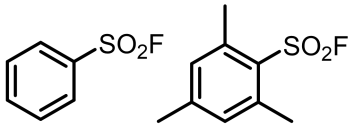
2s

benzenesulfonyl fluoride + 4-iodobenzenesulfonyl fluoride: crude ^{19}F NMR yield: 33% + 44%**.** After silica gel flash column chromatography purification, the product is obtained as a mixture with the ratio of 1.7:4 in 67% yield. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 66.2, 65.9 ppm. The analytical data are consistent with literature values[9,11].



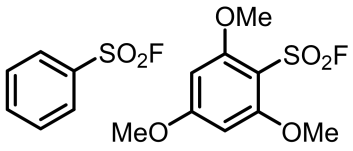
2t

2-methylbenzenesulfonyl fluoride + 2,4,6-trimethylbenzenesulfonyl fluoride: crude ^{19}F NMR yield: 67% + 11%. After silica gel flash column chromatography purification, the product is obtained as a mixture with the ratio of 5:1 in 45% yield. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 68.2, 60.2 ppm. The analytical data are consistent with literature values[9,10].



2u

benzenesulfonyl fluoride + 2,4,6-trimethylbenzenesulfonyl fluoride: crude ^{19}F NMR yield: 62% + 9%. After silica gel flash column chromatography purification, the product is obtained as a mixture with the ratio of 4.4:1 in 58% yield. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 68.2, 65.9 ppm. The analytical data are consistent with literature values[9,10].

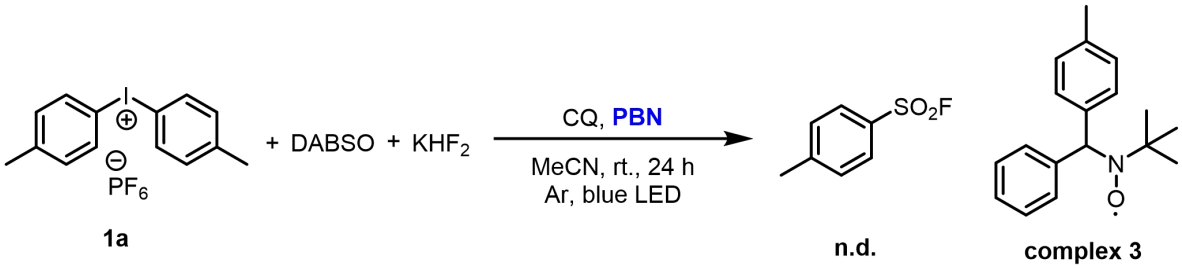


2v

benzenesulfonyl fluoride + 2,4,6-trimethoxybenzenesulfonyl fluoride: crude ^{19}F NMR yield: 11% + 2%. **^{19}F NMR** (376 MHz, $CDCl_3$): δ 69.3, 65.7 ppm. The analytical data are consistent with literature values[8,9].

VI. Preliminary mechanistic studies and gram-scale synthesis

(1) Radical inhibition experiments



Bis(4-methylphenyl)iodonium hexafluorophosphate (0.2 mmol, 1.0 equiv.), 1,4-diazabicyclo[2.2.2]octane-1,4-dionium-1,4-disulfinate (DABSO, 0.24 mmol), KHF_2 (0.4 mmol), CQ (0.01 mmol) and free radical inhibitor N-tert-butyl-#-phenylnitrone (PBN, 0.4 mmol, 2.0 equiv.) were added to a 10 mL dried sealed tube which equipped with a magnetic rotor. The system was evacuated and argon was pumped 2-3 times, and anhydrous MeCN (4.0 mL) was added via a syringe under an argon atmosphere. After the tube is sealed, the mixture is stirred at room temperature under blue light (20 W, 440~445 nm) for 24 hours. The crude yield of the product was measured by ^{19}F NMR spectrum, which 4-(trifluoromethoxy) anisole serves as internal standard, and it can be seen that no product is produced. However, it can be seen from the HRMS analysis and synthesis that there is the formation of complex **3**.

(2) EPR spectroscopy

Spin traps: PBN: TCI chemicals. The irradiation, using a blue led (440~445 nm), was directly done into the EPR cavity while the spectrum is recording.

When diaryliodonium salt **1a** was irradiated in the presence of CQ (Table S7, entry 1), aryl radical was clearly characterised with both spin adducts, which features (a_N=14.8 G, a_H=3.2 G for PBN, Figure S1) are in good agreement with previous works[14].

Finally, when we add simultaneously all the reagents (Table S7, entry 3, Figure S3), the intermediate species in the mechanism proposed are characterised, featuring C-centred phenyl radical S-centred tosyl radicals.

Table S7. EPR simulation with PBN

Irradiation time =3.5mn	PBN				
	%	g	a_N(G)	a_H(G)	Species
1. ION + CQ + MeCN	100	2.005	14.8	3.2	PBN-Ar
2. ION + DABSO + KHF_2 + CQ + MeCN	/	2.006	13.7	1.7	PBN-SO_2Ar

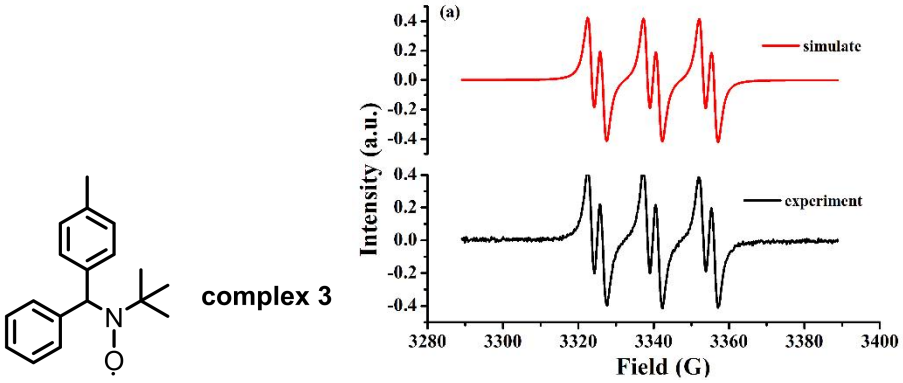


Figure S1. Mixture of ION + CQ, black = experiment, red =simulate

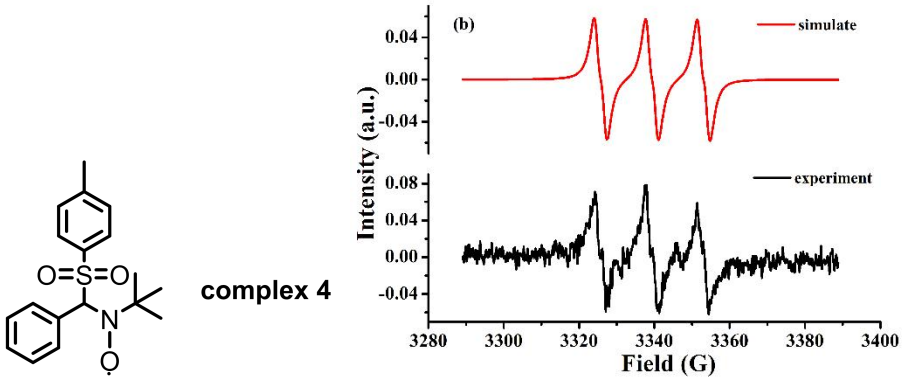
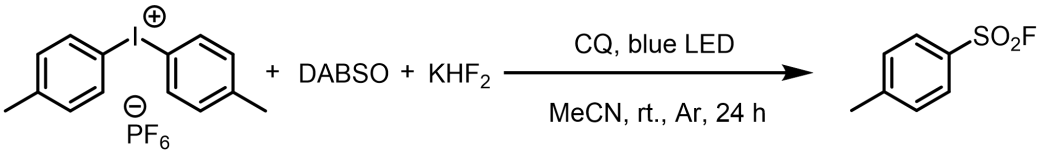


Figure S2. Mixture of ION + DABSO + KHF_2 + CQ, black = experimental, red =simulated

(3) Gram-scale synthesis



3-1a
6 mmol

3-2a
0.85 g, 61%

Bis(4-methylphenyl)iodonium hexafluorophosphate (6.0 mmol, 1.0 equiv.), 1,4-diazabicyclo[2.2.2]octane-1,4-dionium-1,4-disulfinate (DABSO, 7.2 mmol, 1.2 equiv.), KHF_2 (12.0 mmol, 2.0 equiv.) and CQ (0.3 mmol, 5 mol %) were added to a 250 mL dried three-necked bottle which equipped with a magnetic rotor. Then anhydrous MeCN (60 mL) was added through a syringe under an argon atmosphere. After the bottle is sealed, the mixture is stirred at room temperature under blue light (20 W, 440~445 nm) for 24 hours. The mixture was filtered through 200-300 mesh silica gel and monitored by thin layer chromatography. After the solvent was removed under reduced pressure with a rotary evaporator, the crude product was purified by silica gel column chromatography to obtain the product (white solid, 61%).

VII. References

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

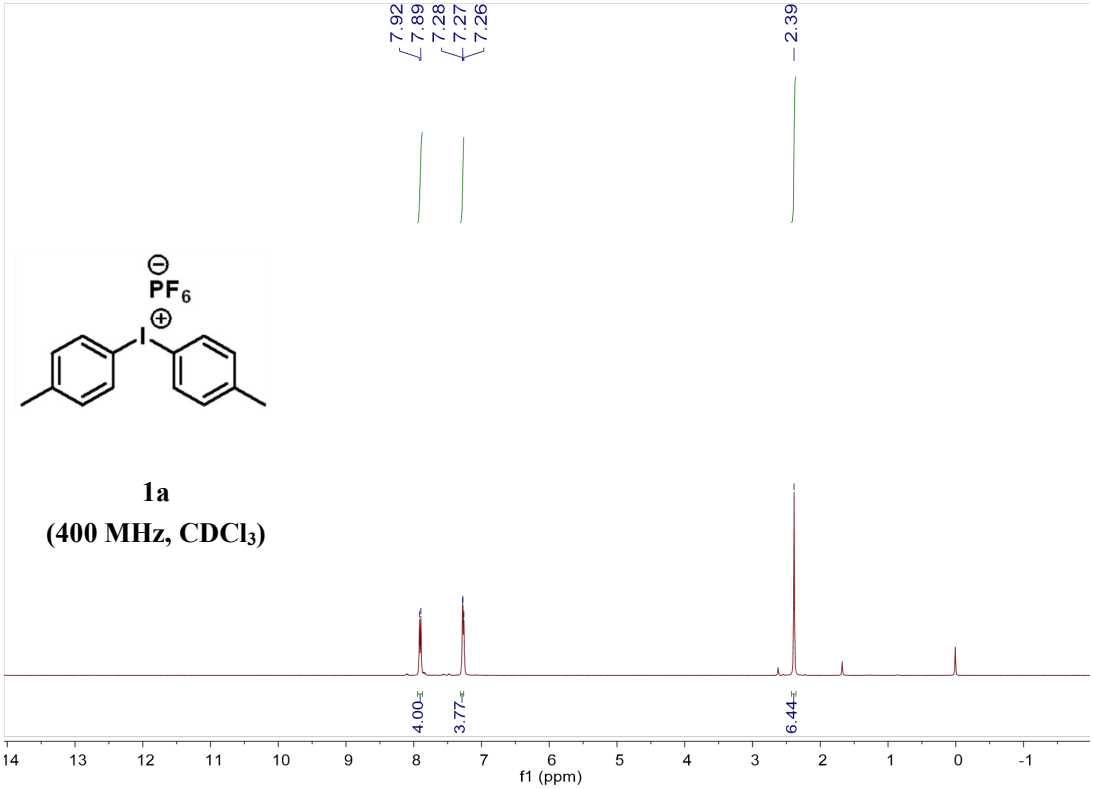


Figure S4. ^{1}H NMR spectrum of di-p-tolyliodonium hexafluorophosphate(V)

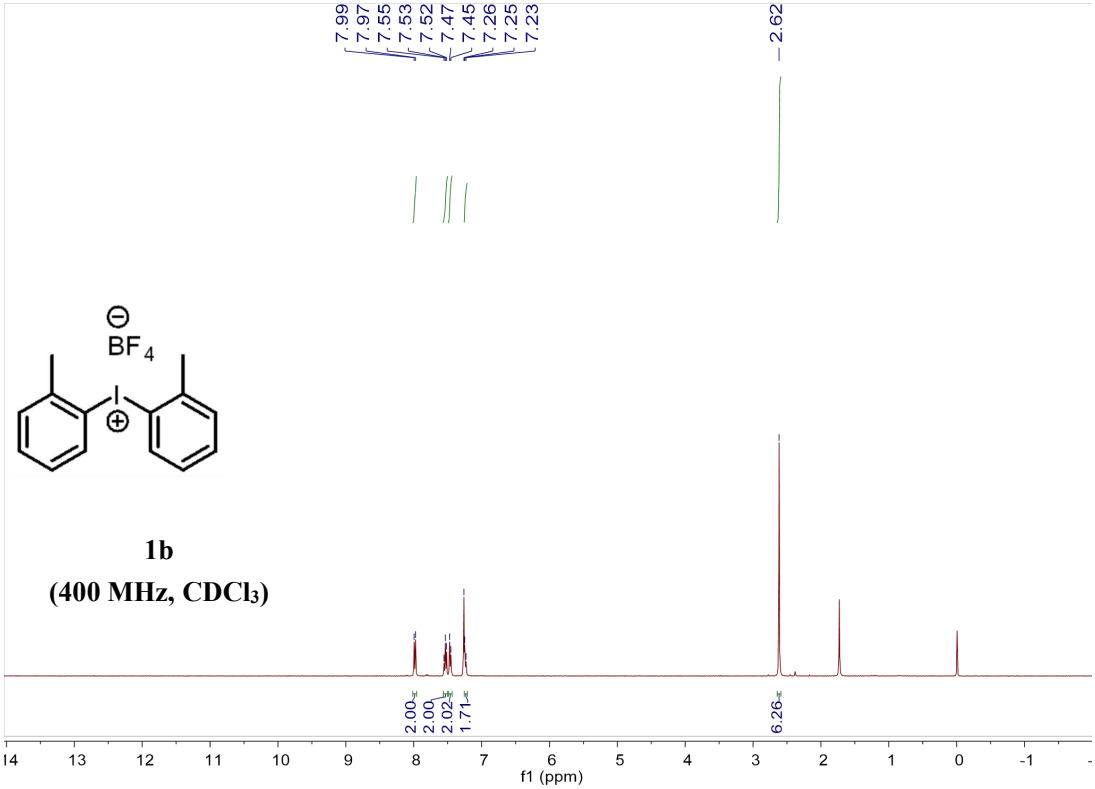


Figure S5. ^{1}H NMR spectrum of di-o-tolyliodonium tetrafluoroborate

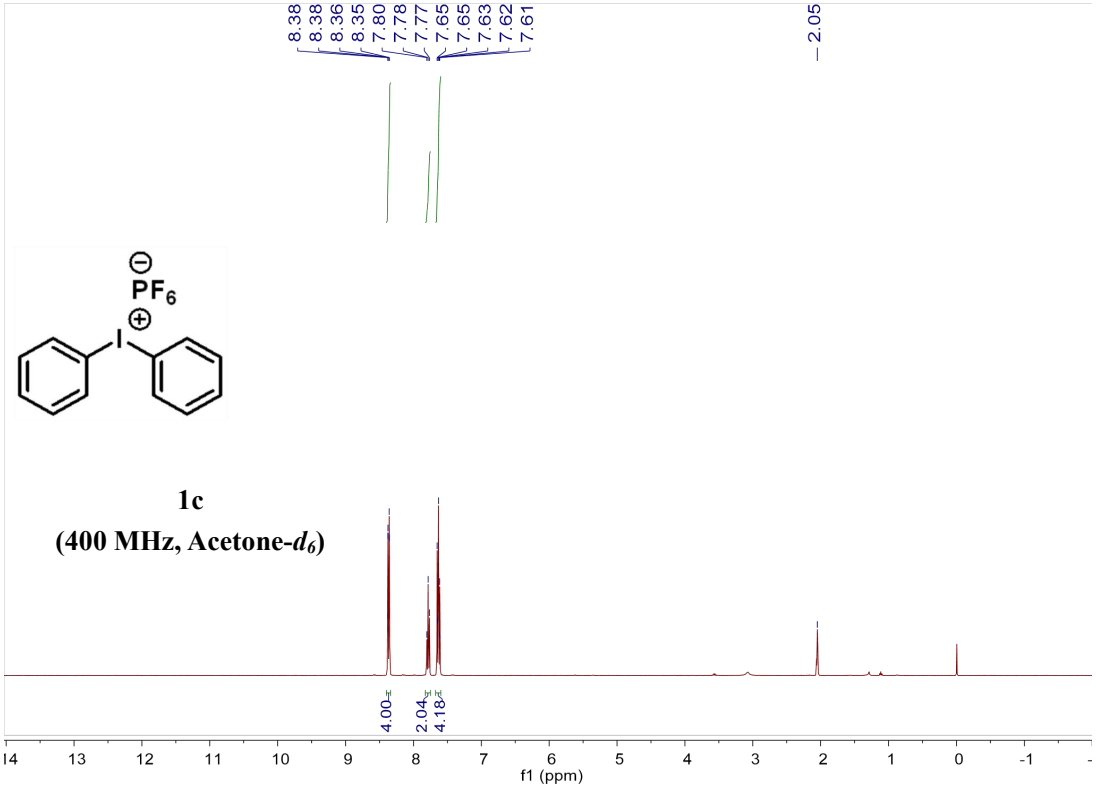


Figure S6. [1]H NMR spectrum of diphenyliodonium hexafluorophosphate(V)

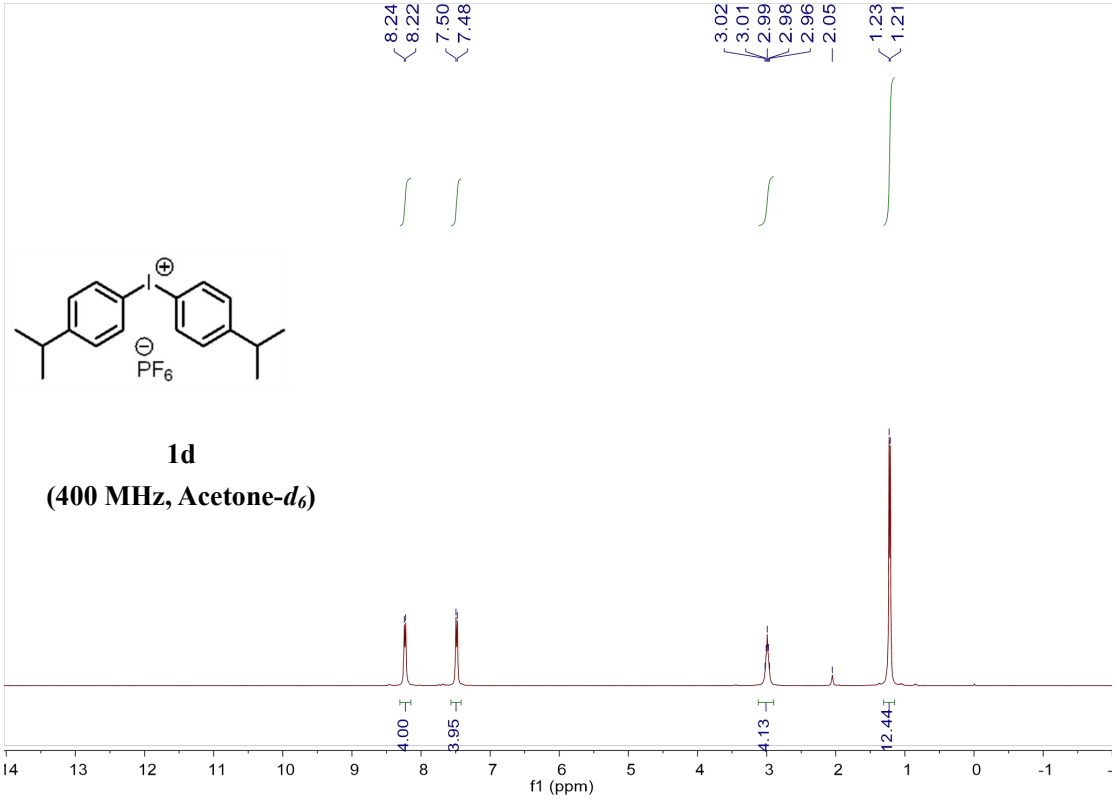


Figure S7. [1]H NMR spectrum of bis(4-isopropylphenyl)-l2-iodane hexafluorophosphate(V)

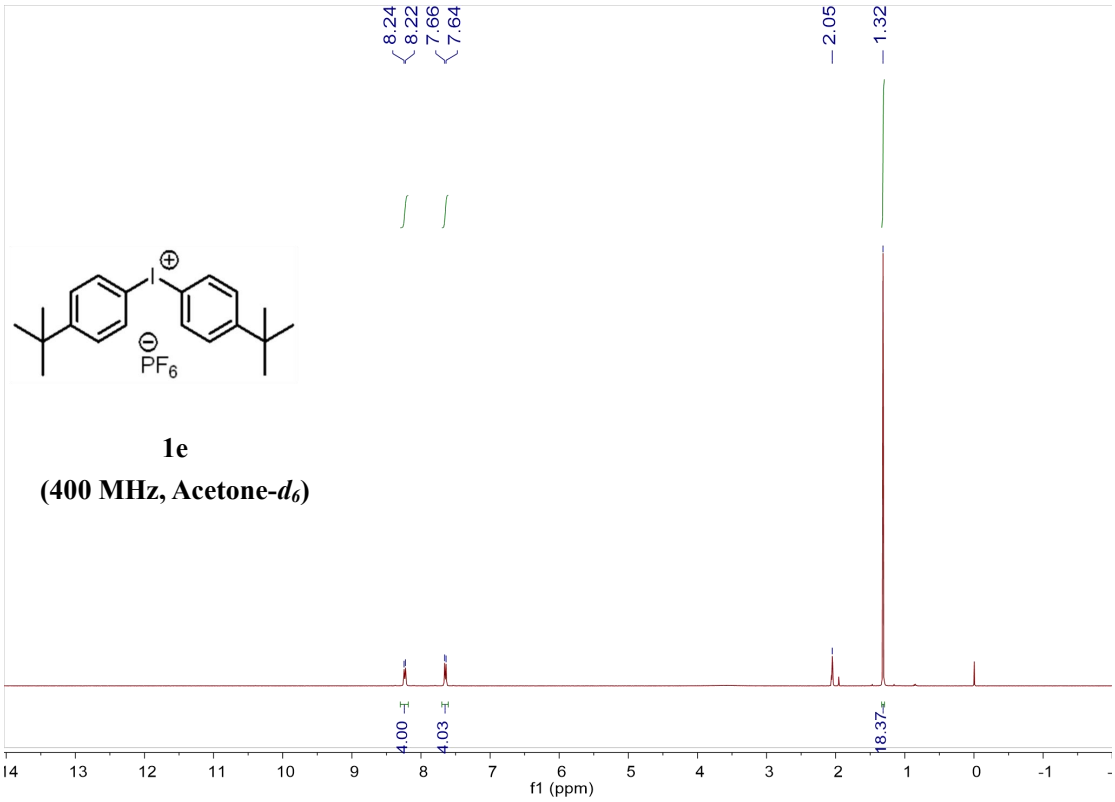


Figure S8. [1]H NMR spectrum of bis(4-(tert-butyl)phenyl)iodonium hexafluorophosphate(V)

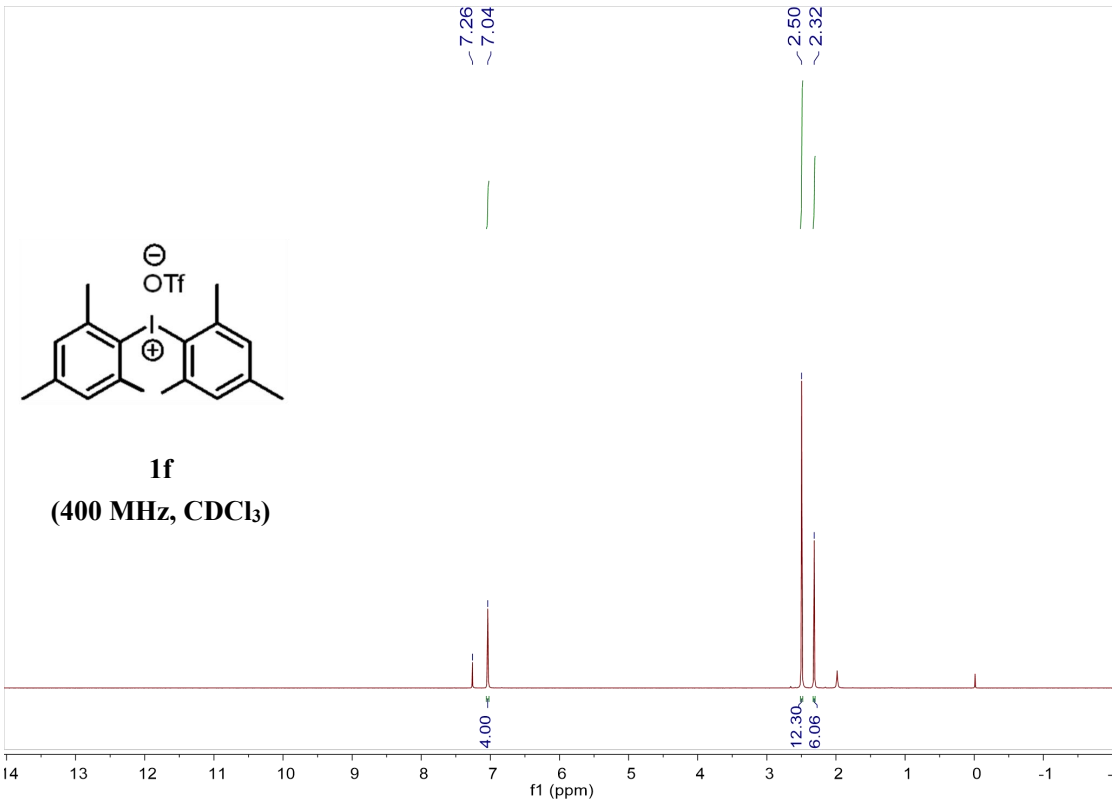


Figure S9. [1]H NMR spectrum of dimesityliodonium trifluoromethanesulfonate

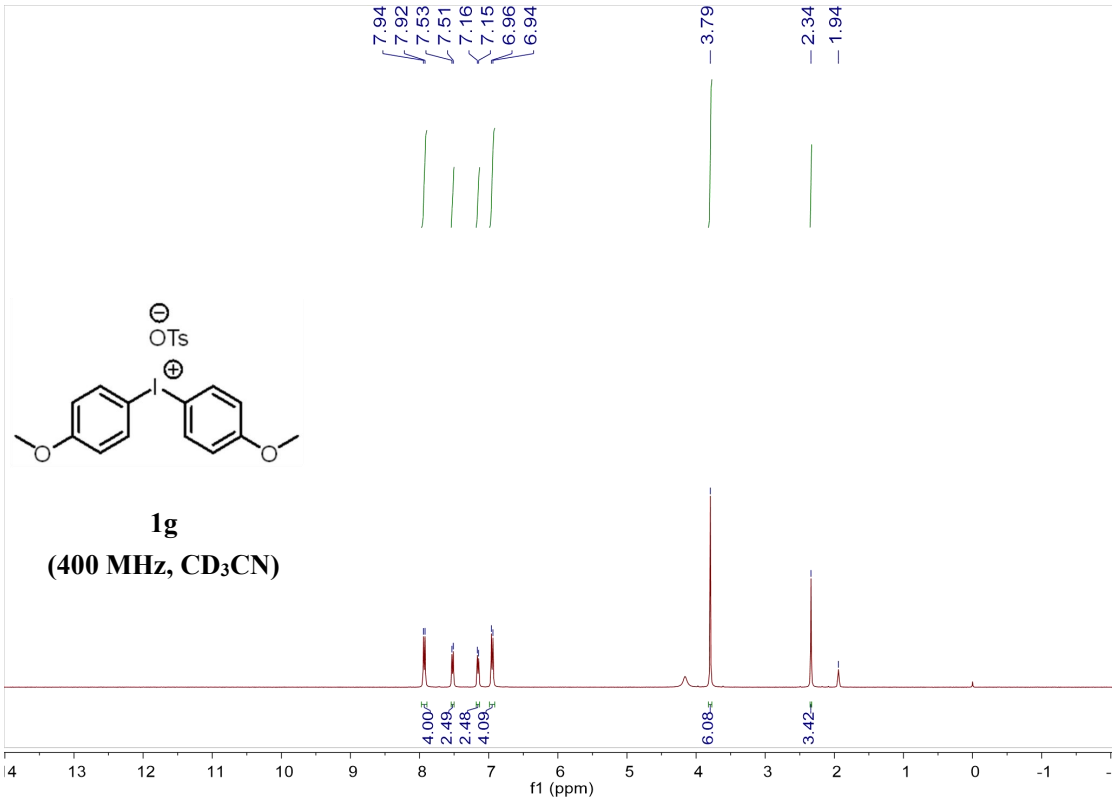


Figure S10. [1]H NMR spectrum of bis(4-methoxyphenyl)iodonium 4-methylbenzenesulfonate

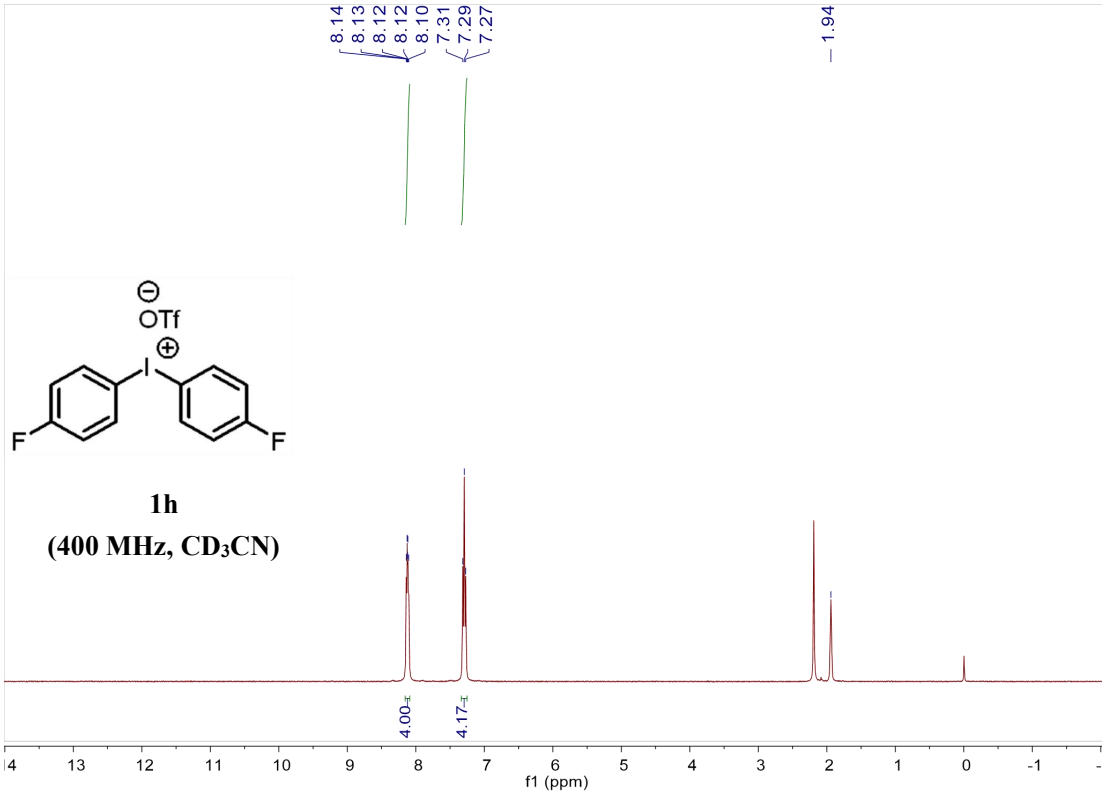


Figure S11. [1]H NMR spectrum of bis(4-fluorophenyl)-l2-iodane trifluoromethanesulfonate

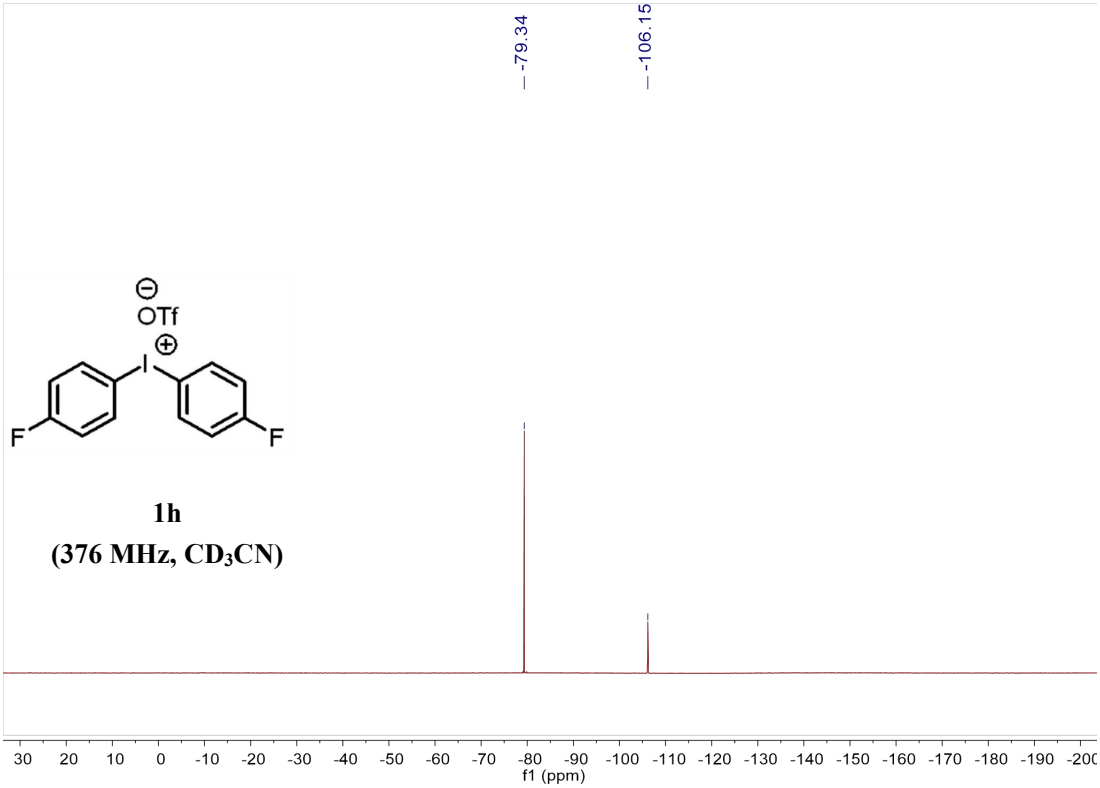


Figure S12. ^{19}F NMR spectrum of bis(4-fluorophenyl)-l2-iodane trifluoromethanesulfonate

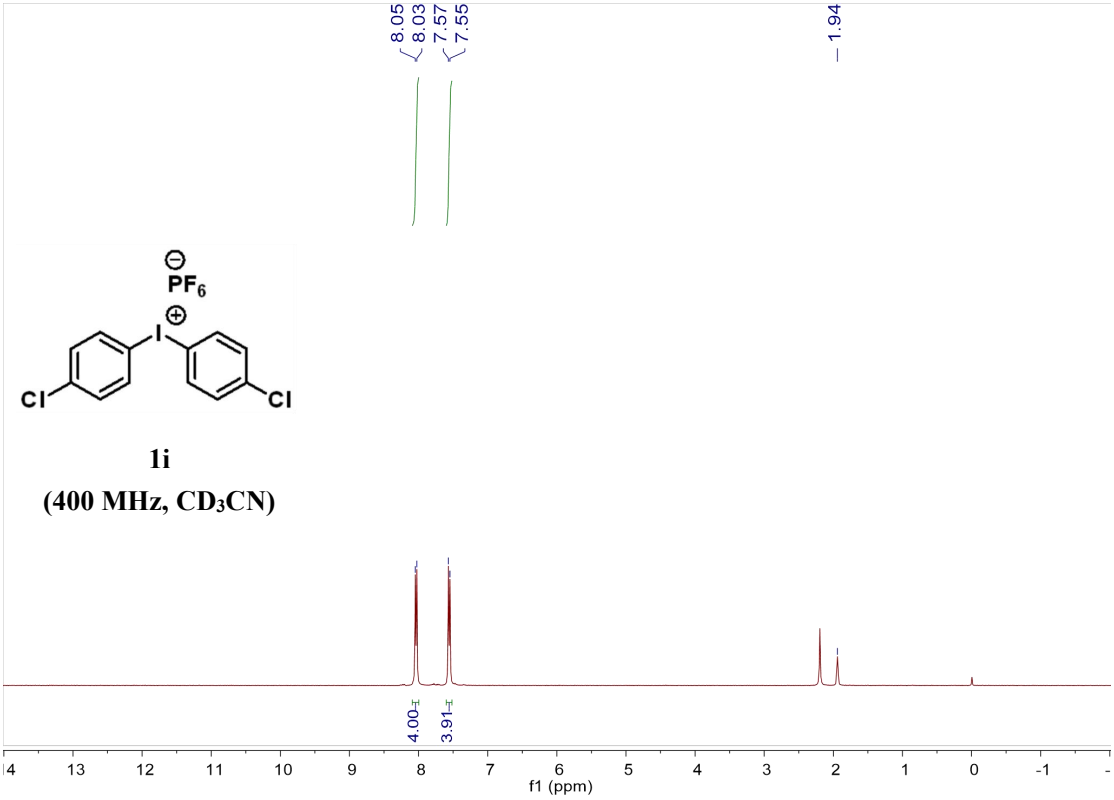


Figure S13. ^{1}H NMR spectrum of bis(4-chlorophenyl)iodonium hexafluorophosphate(V)

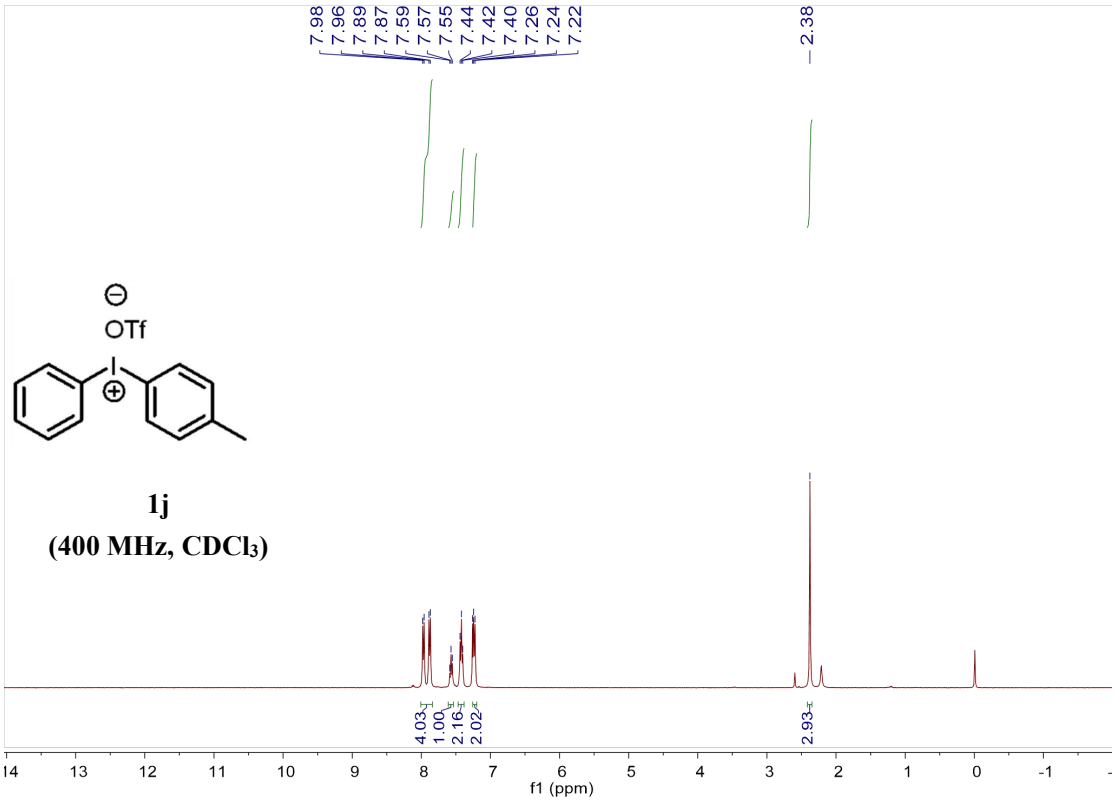


Figure S14. ^{1}H NMR spectrum of phenyl(p-tolyl)iodonium trifluoromethanesulfonate

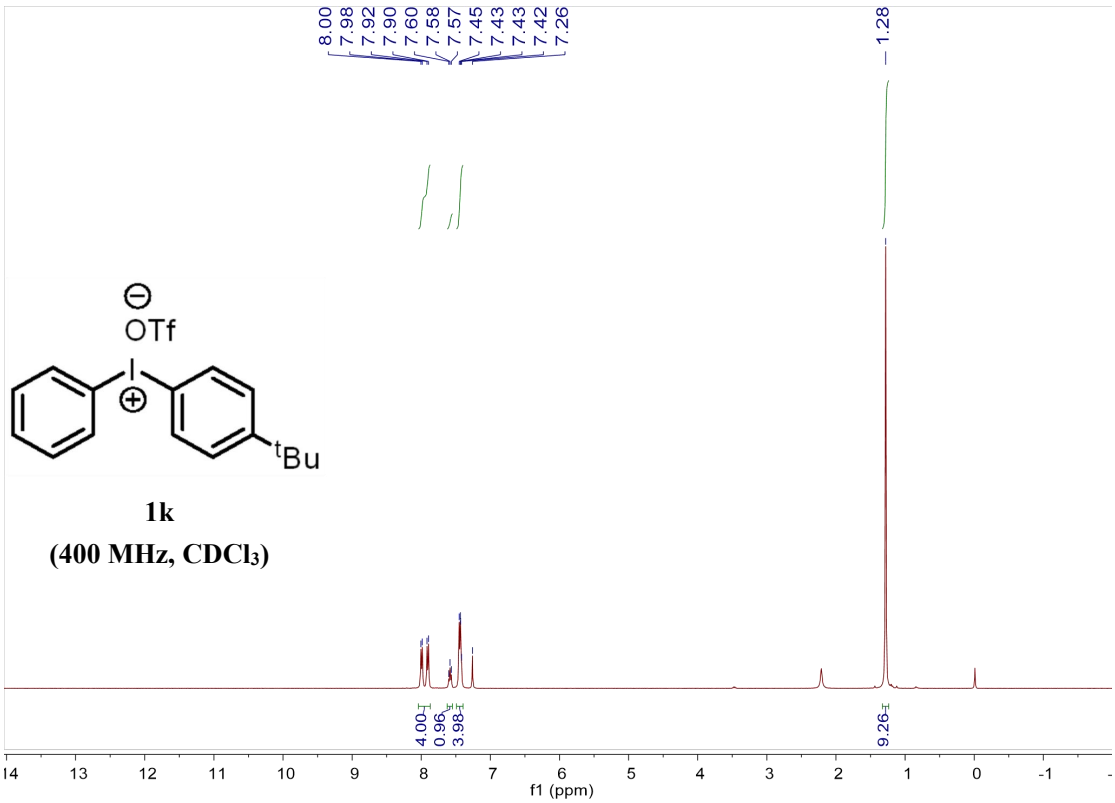


Figure S15. ^{1}H NMR spectrum of (4-(tert-butyl)phenyl)(phenyl)iodonium trifluoromethanesulfonate

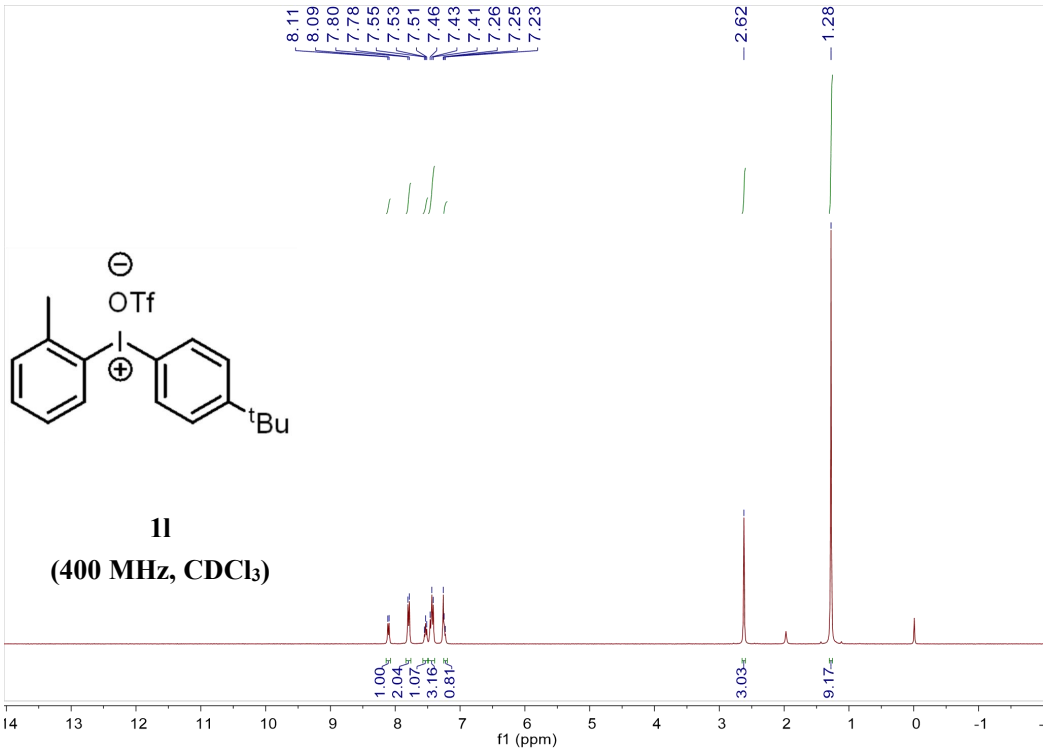


Figure S16. ^{1}H NMR spectrum of (4-(tert-butyl)phenyl)(o-tolyl)iodonium trifluoromethanesulfonate

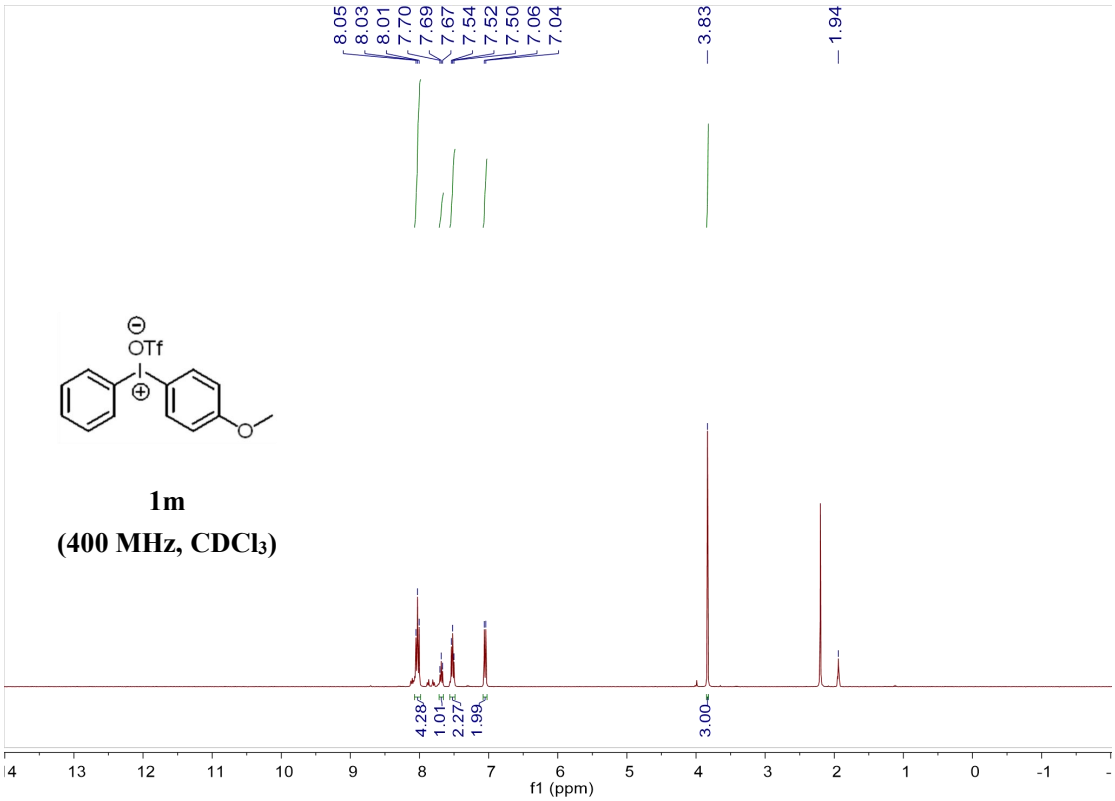


Figure S17. ^{1}H NMR spectrum of (4-methoxyphenyl)(phenyl)iodonium trifluoromethanesulfonate

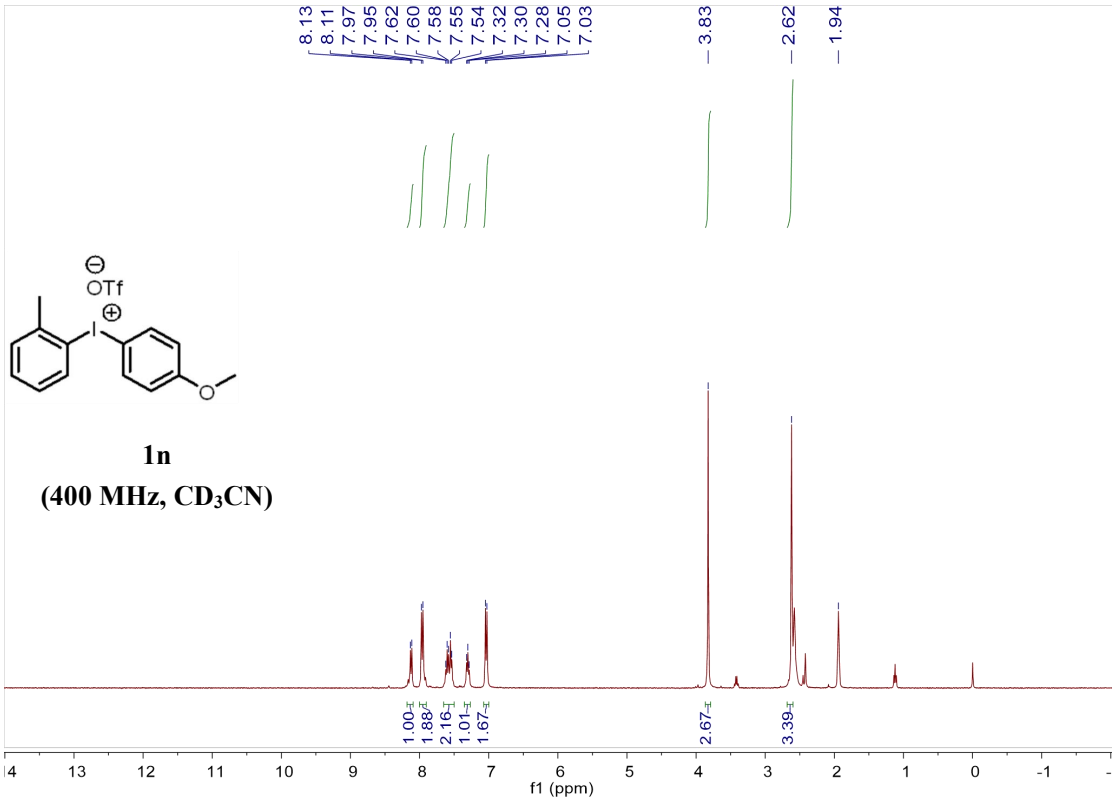


Figure S18. ^{1}H NMR spectrum of (4-methoxyphenyl)(o-tolyl)-l2-iodane trifluoromethanesulfonate

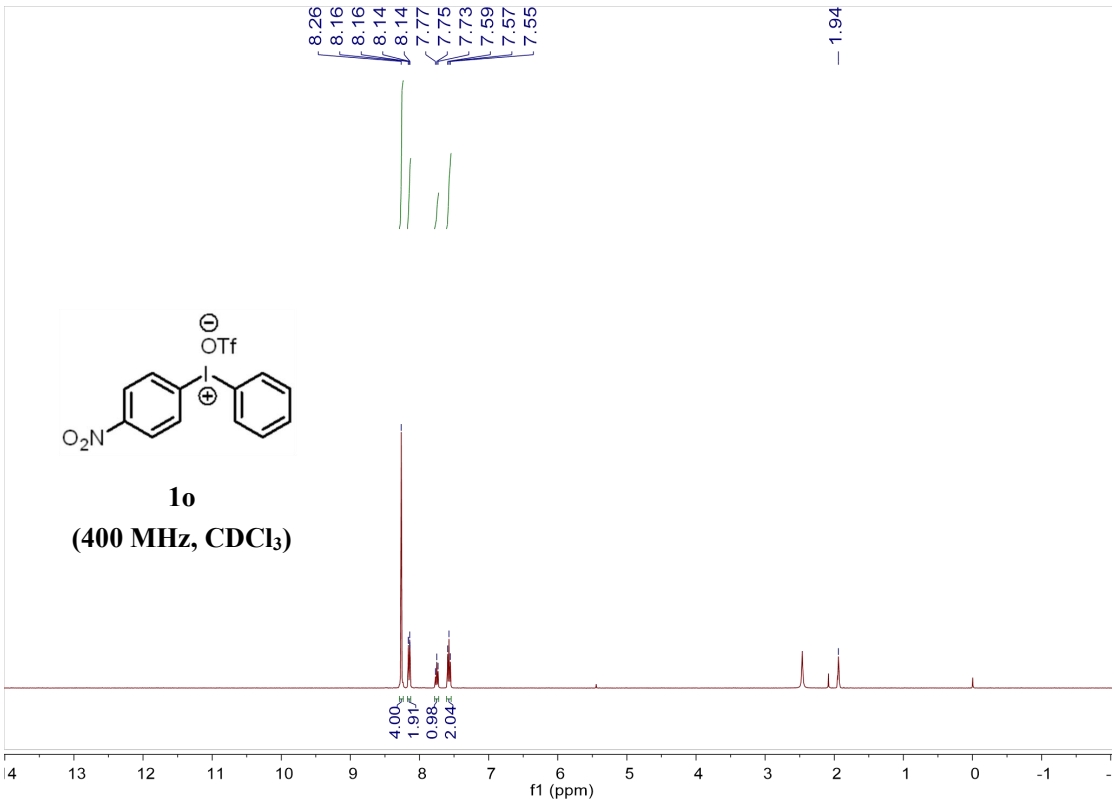


Figure S19. ^{1}H NMR spectrum of (4-nitrophenyl)(phenyl)iodonium trifluoromethanesulfonate

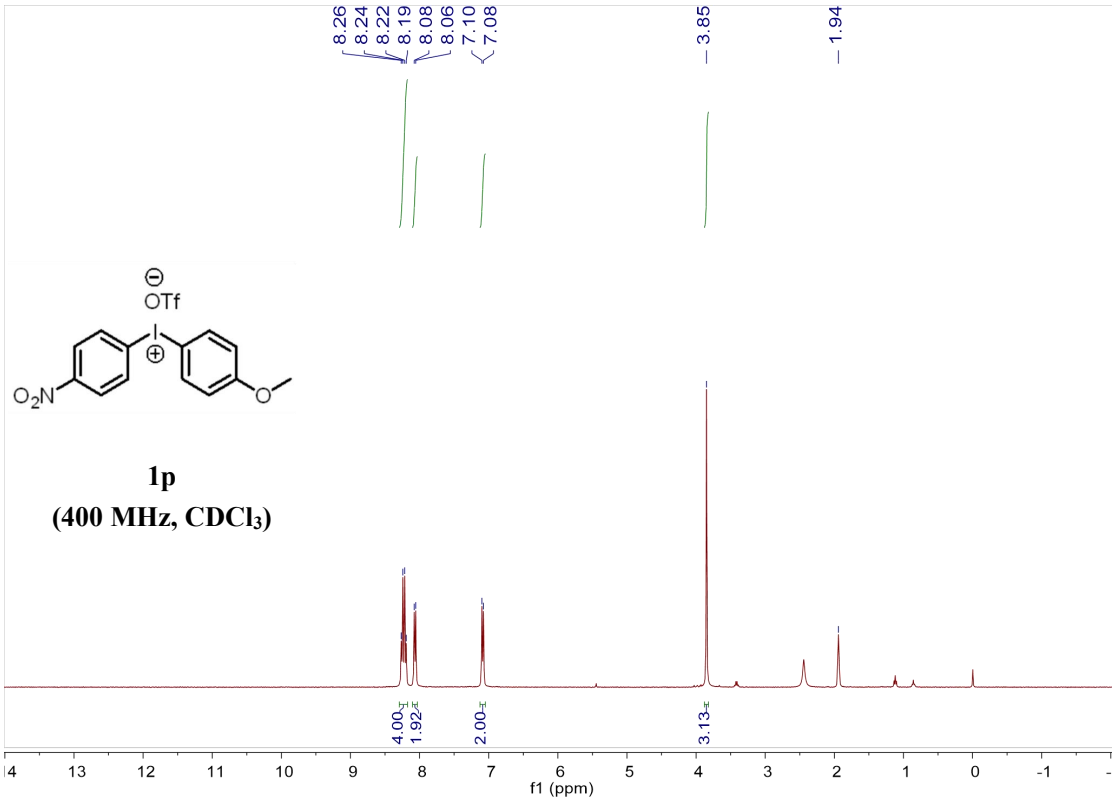


Figure S20. ^{1}H NMR spectrum of (4-methoxyphenyl)(4-nitrophenyl)iodonium trifluoromethanesulfonate

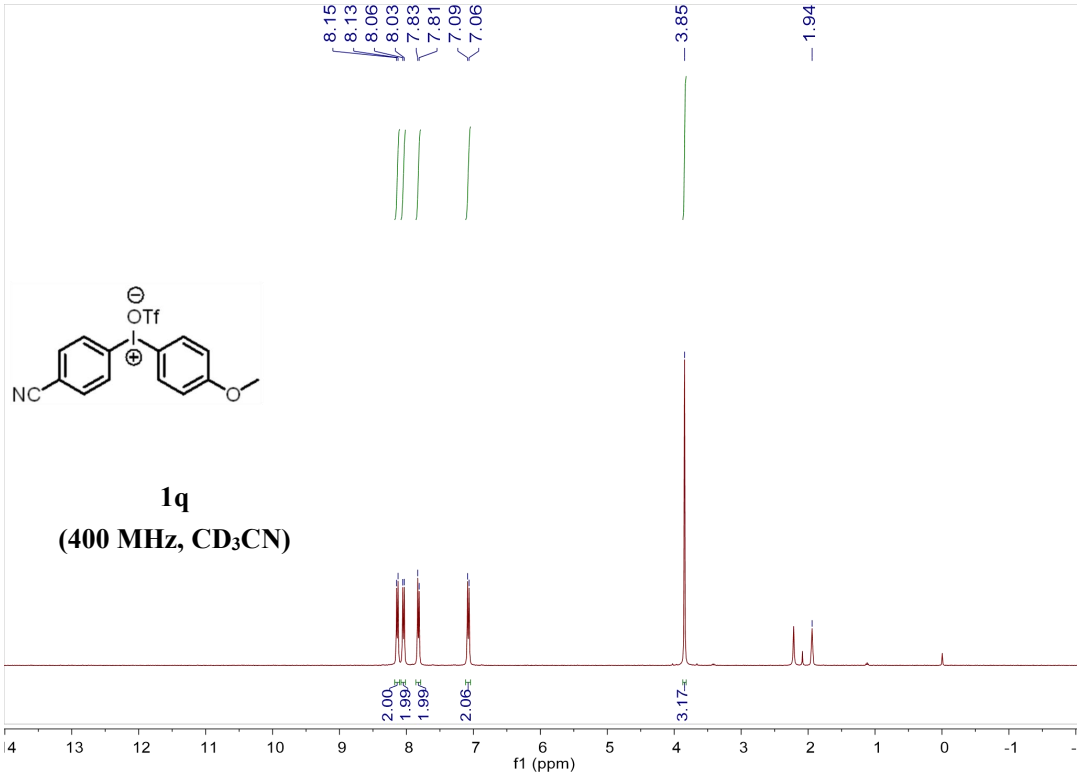


Figure S21. ^{1}H NMR spectrum of (4-cyanophenyl)(4-methoxyphenyl)iodonium trifluoromethanesulfonate

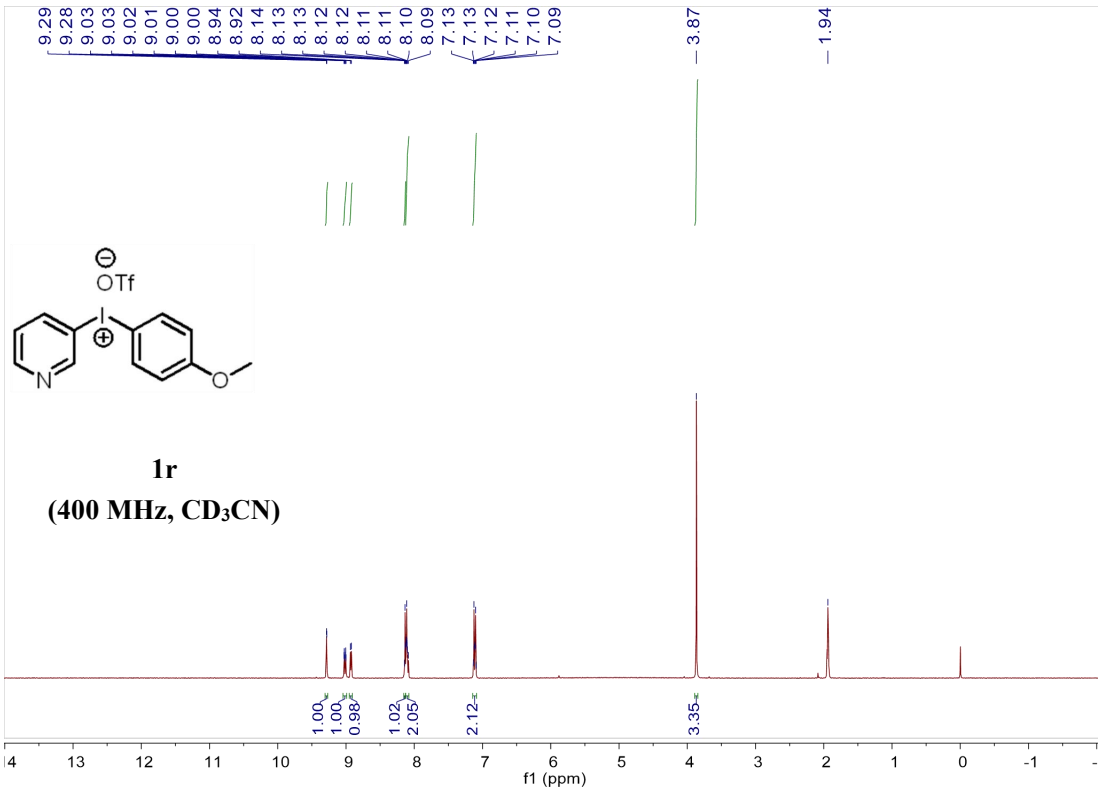


Figure S22. ^{1}H NMR spectrum of (4-methoxyphenyl)(pyridin-3-yl)iodonium trifluoromethanesulfonate

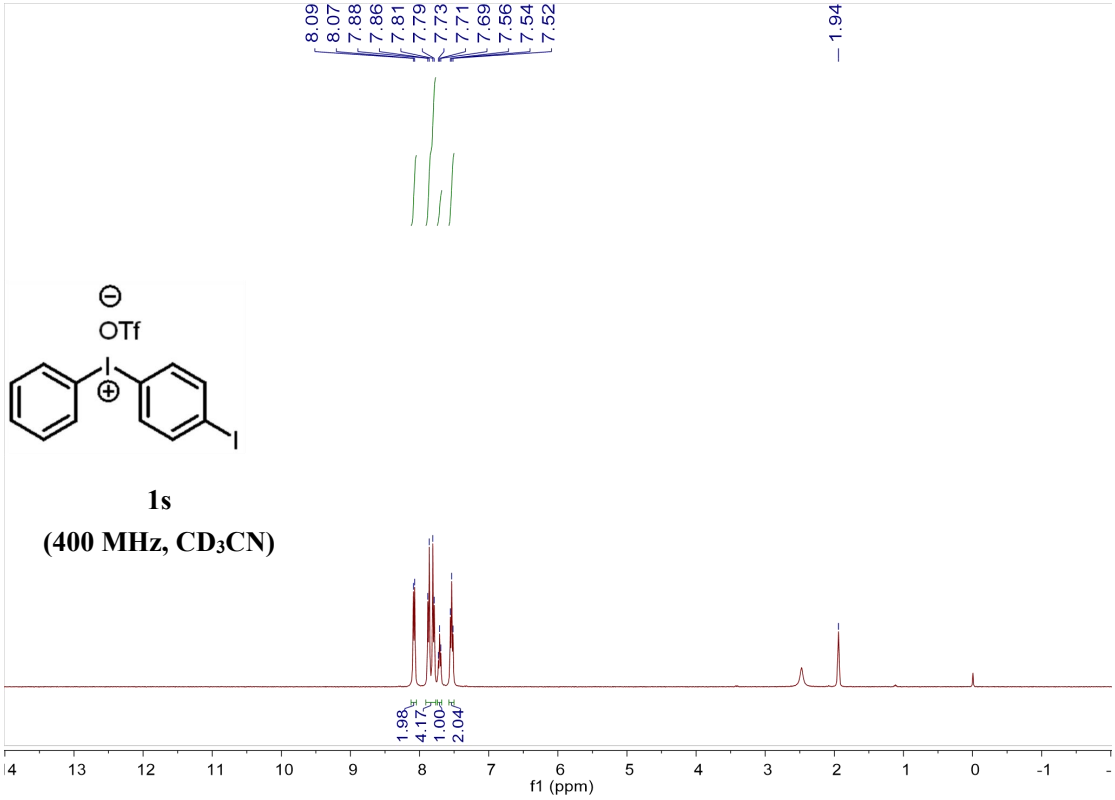


Figure S123. ^{1}H NMR spectrum of (4-iodophenyl)(phenyl)iodonium trifluoromethanesulfonate

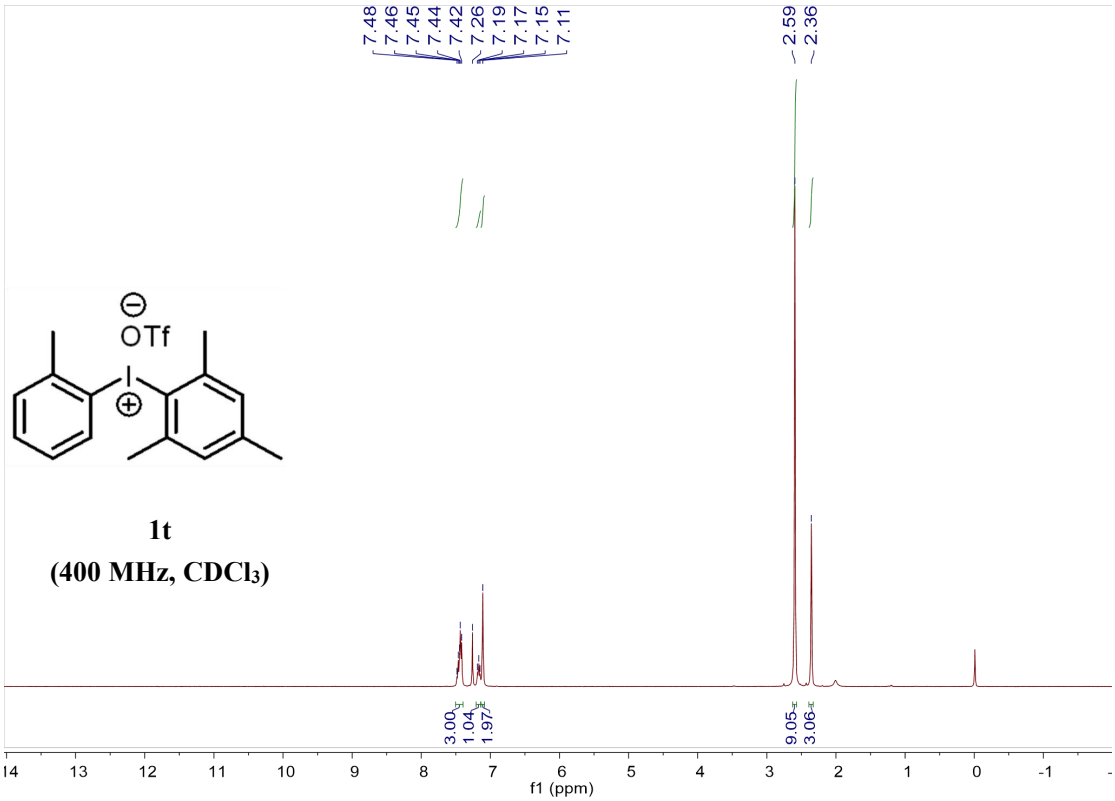


Figure S24. ^{1}H NMR spectrum of mesityl(o-tolyl)iodonium trifluoromethanesulfonate

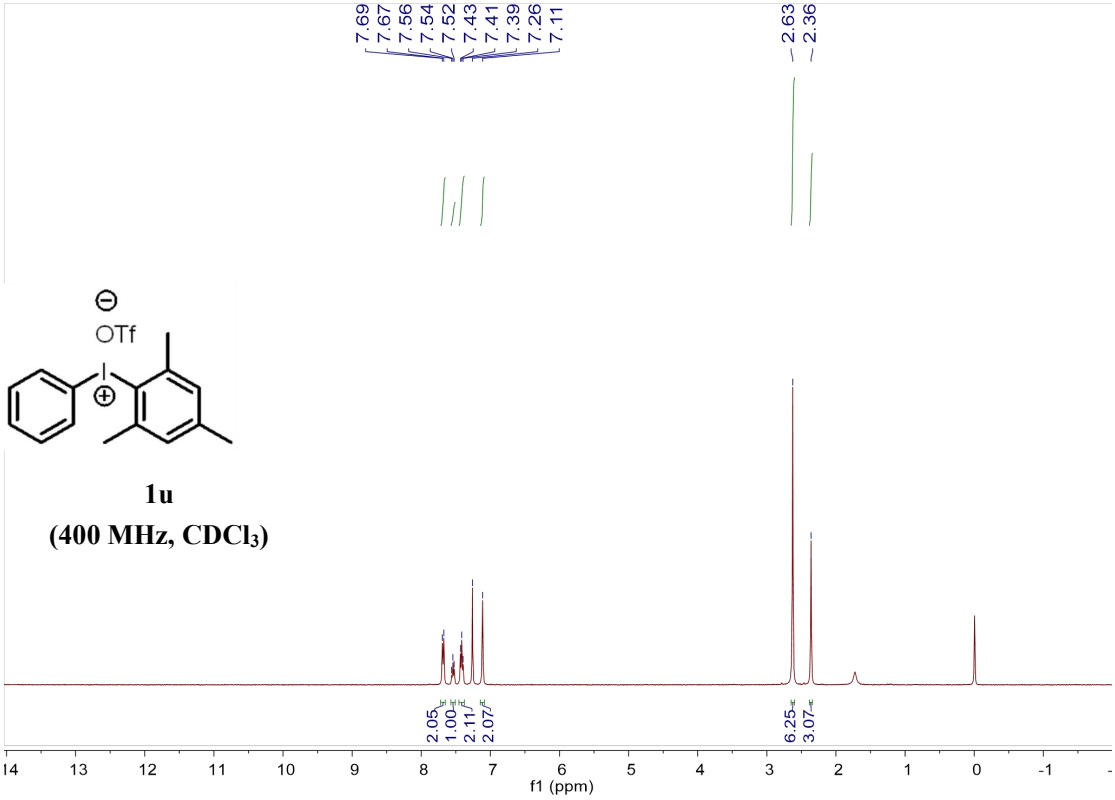


Figure S25. ^{1}H NMR spectrum of mesityl(phenyl)iodonium trifluoromethanesulfonate

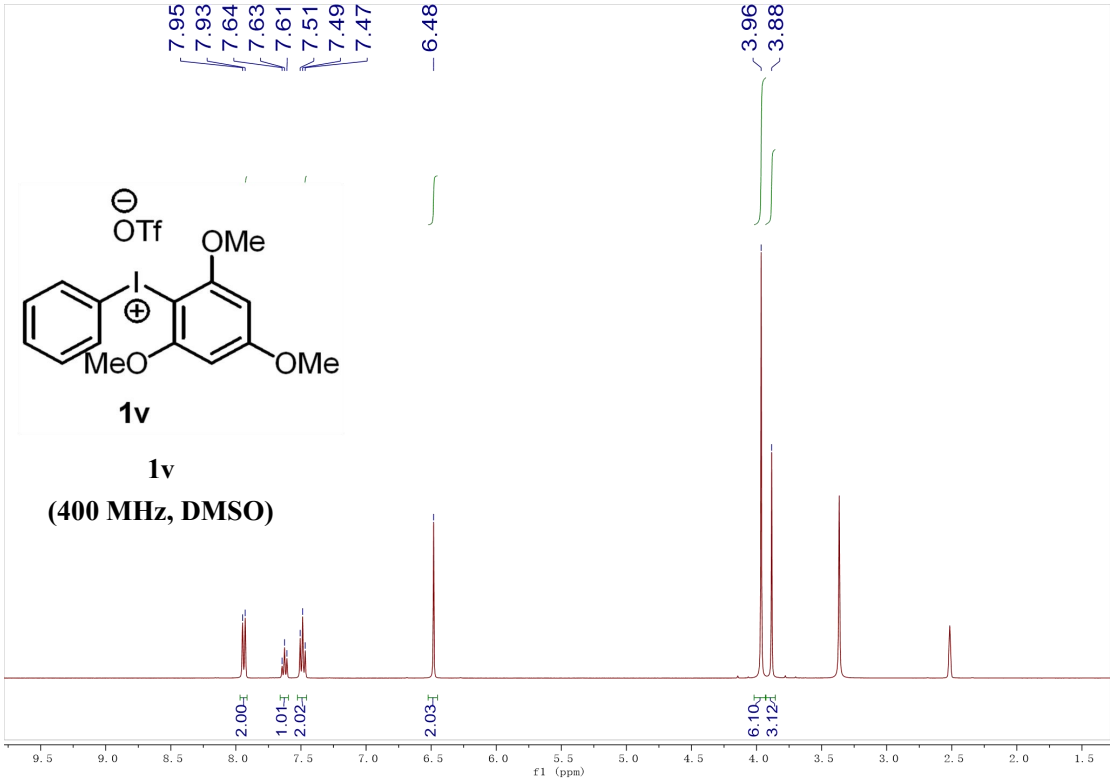


Figure S26. ^{1}H NMR spectrum of phenyl(2,4,6-trimethoxyphenyl)iodonium trifluoromethanesulfonate

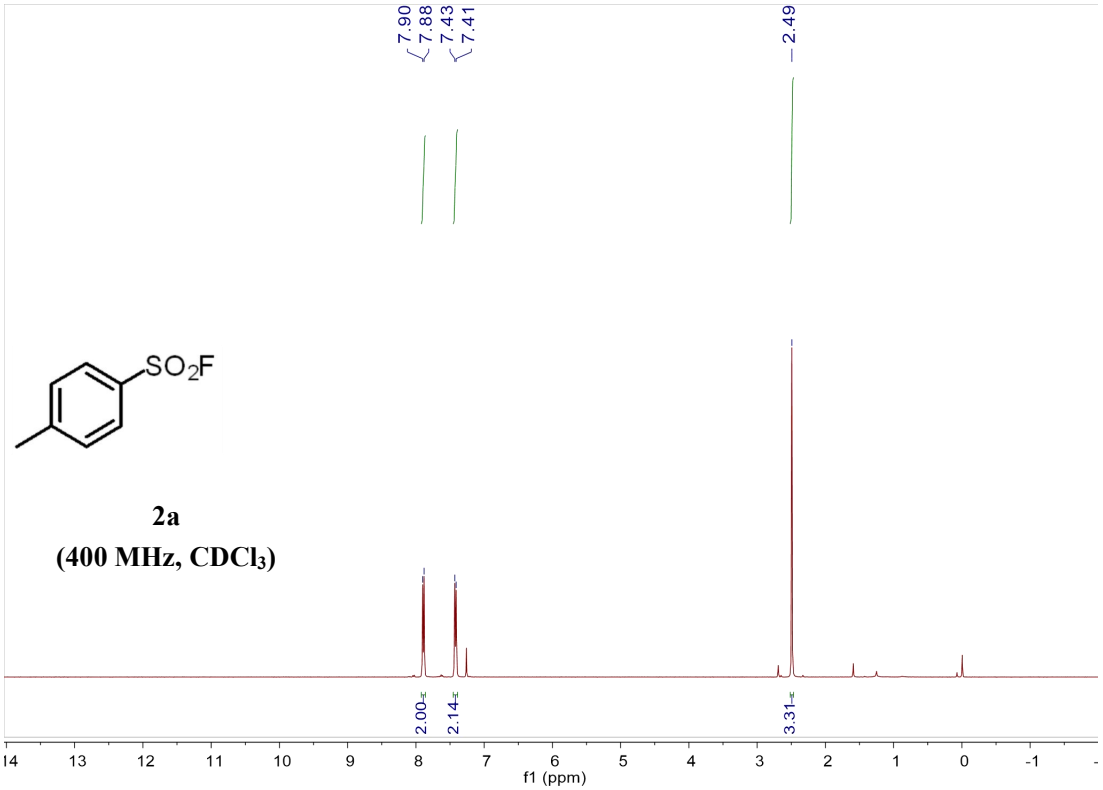


Figure S27. ^{1}H NMR spectrum of 4-methylbenzenesulfonyl fluoride

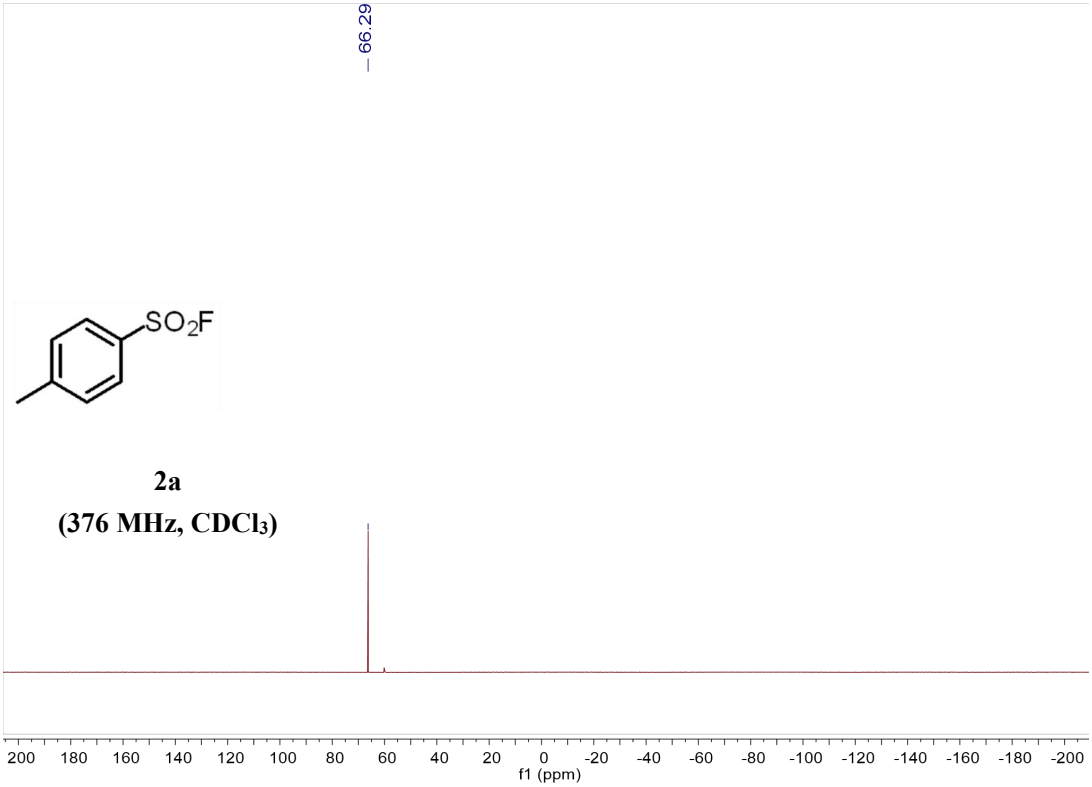


Figure S28. ^{19}F NMR spectrum of 4-methylbenzenesulfonyl fluoride

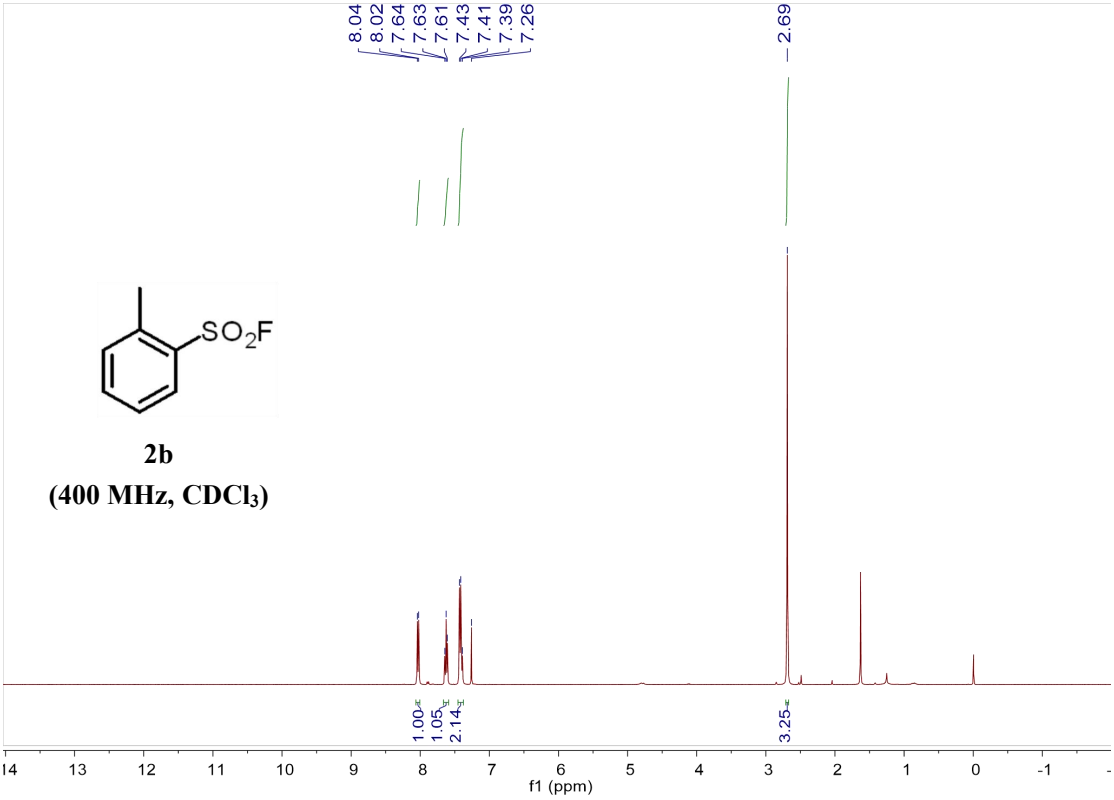


Figure S29. ^{1}H NMR spectrum of 2-methylbenzenesulfonyl fluoride

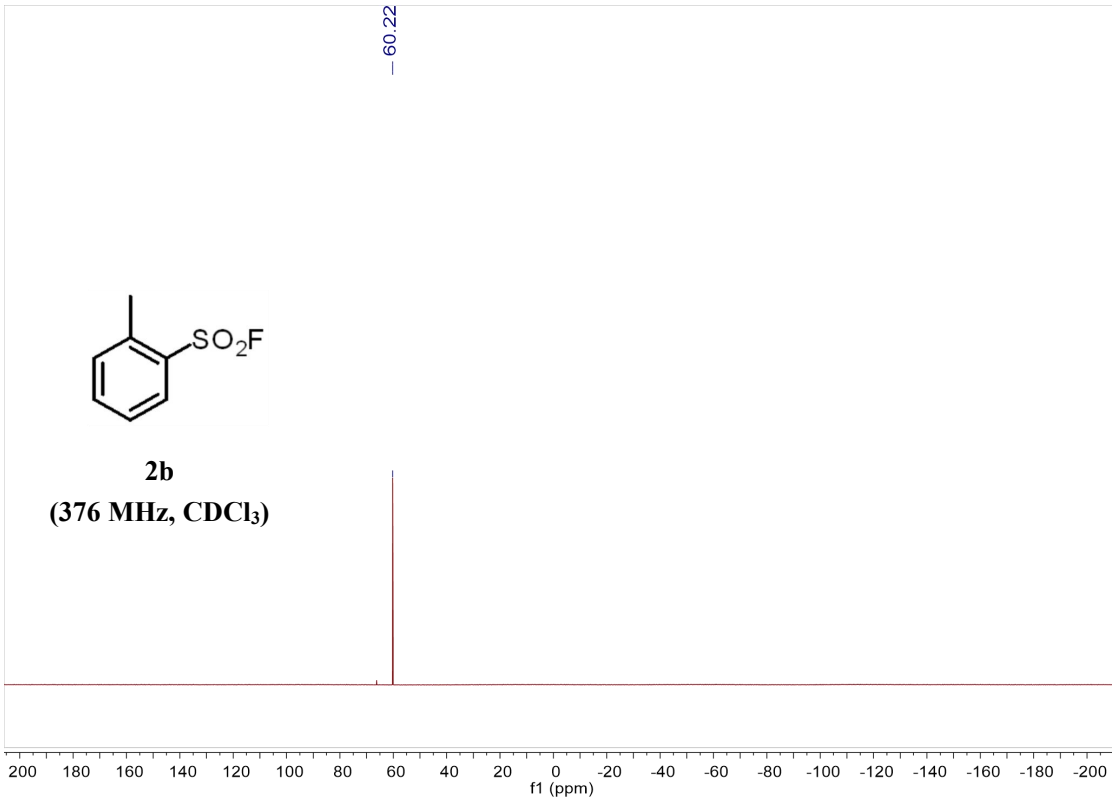


Figure S30. ^{19}F NMR spectrum of 2-methylbenzenesulfonyl fluoride

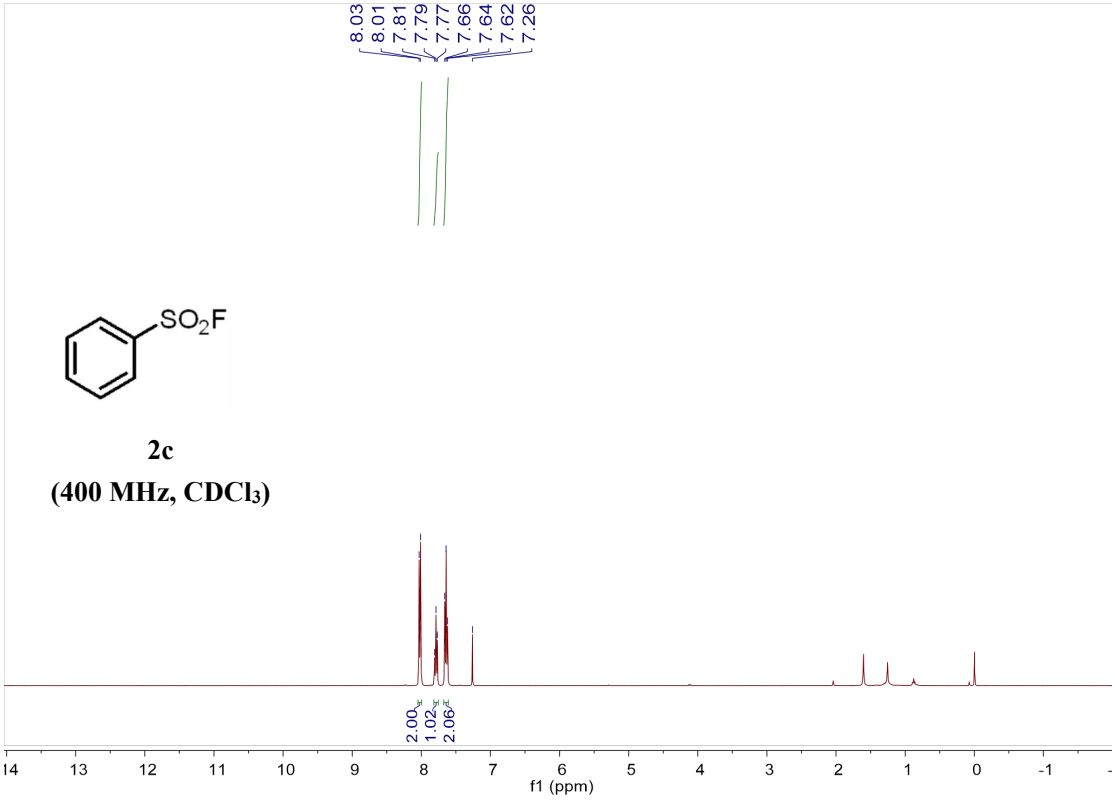


Figure S31. ^{1}H NMR spectrum of benzenesulfonyl fluoride

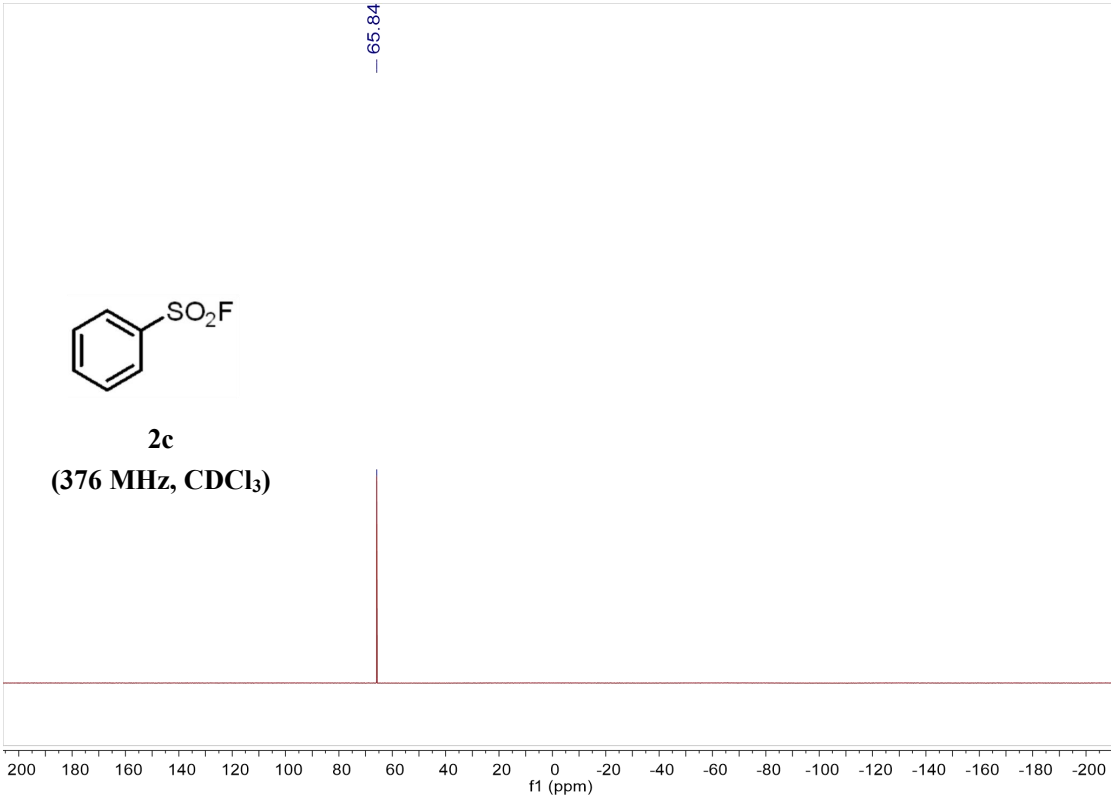


Figure S32. ^{19}F NMR spectrum of benzenesulfonyl fluoride

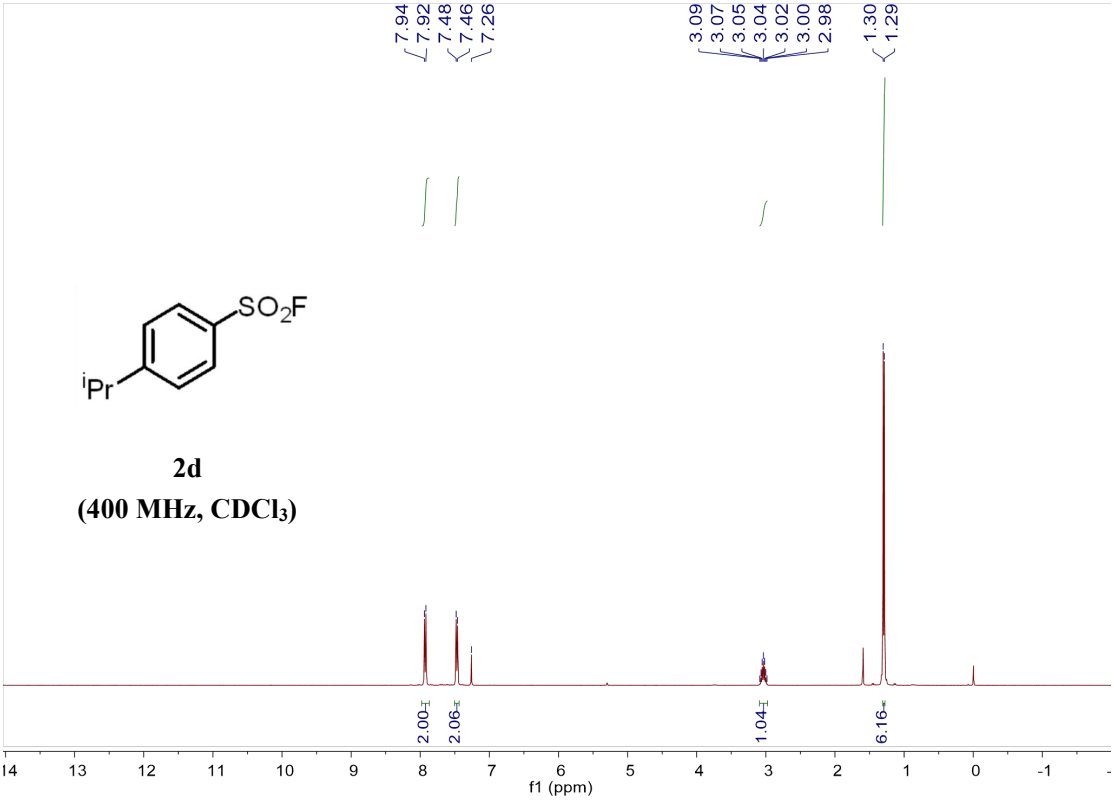


Figure S33. ^{1}H NMR spectrum of 4-isopropylbenzenesulfonyl fluoride

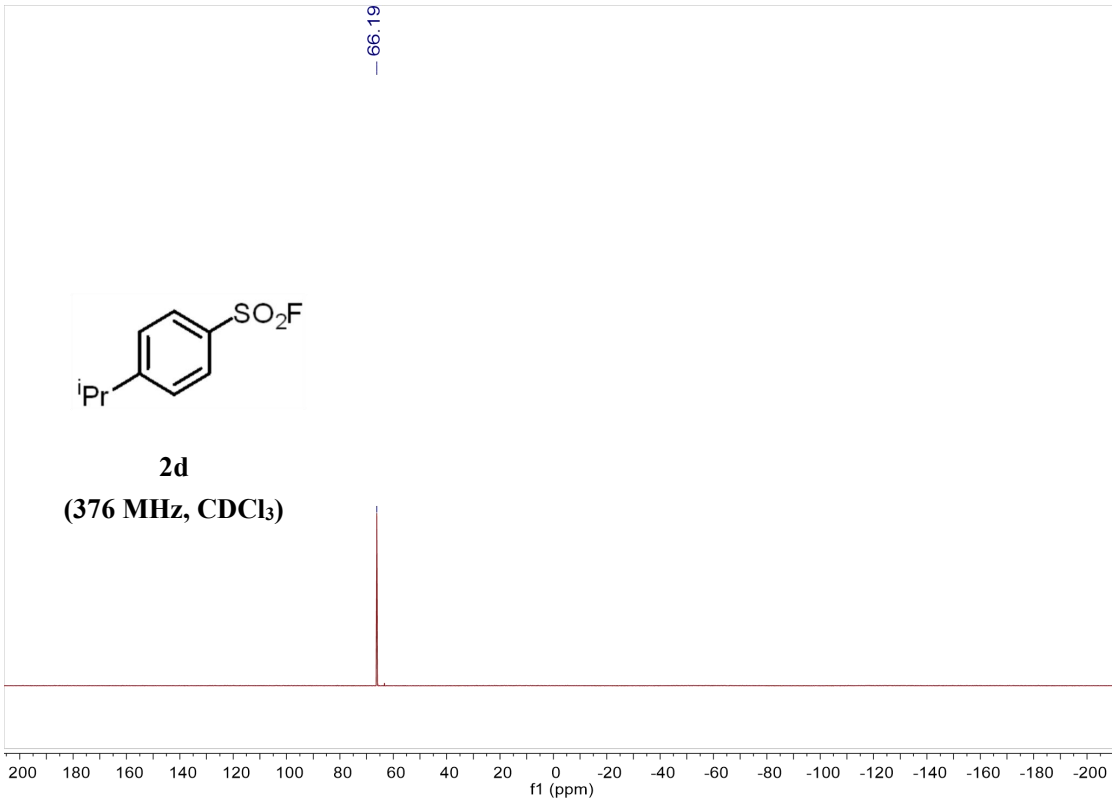


Figure S34. ^{19}F NMR spectrum of 4-isopropylbenzenesulfonyl fluoride

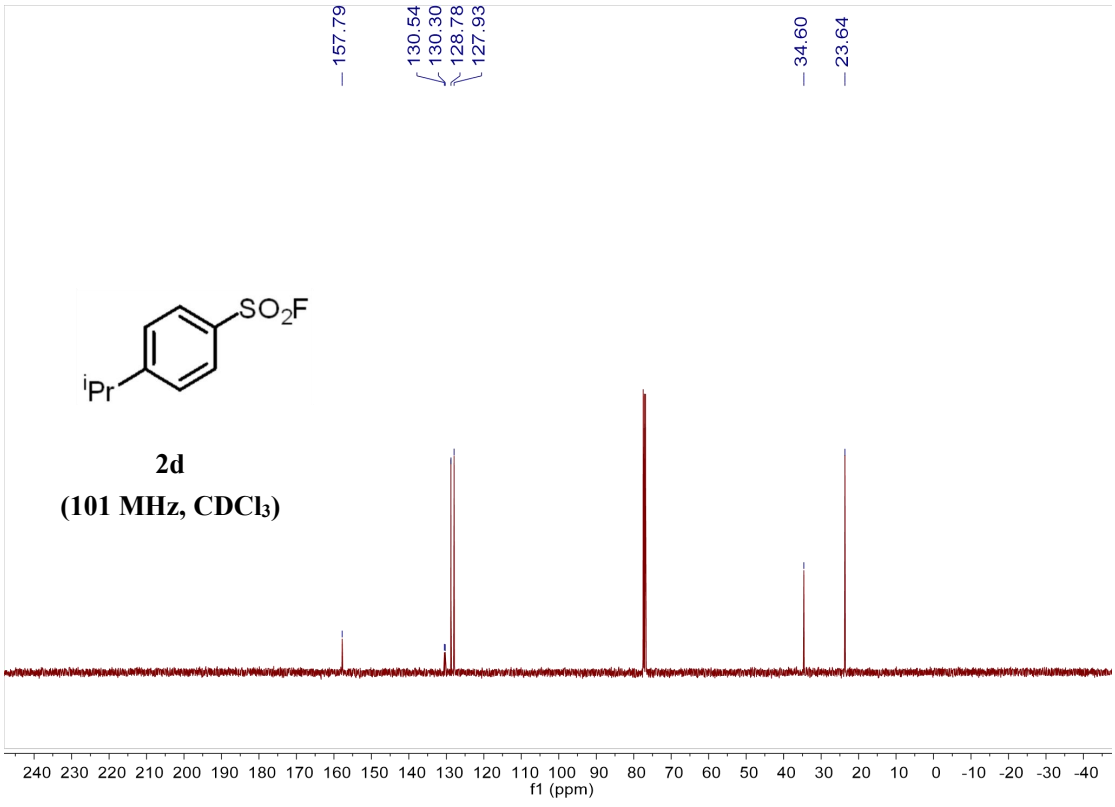


Figure S35. ^{13}C NMR spectrum of 4-isopropylbenzenesulfonyl fluoride

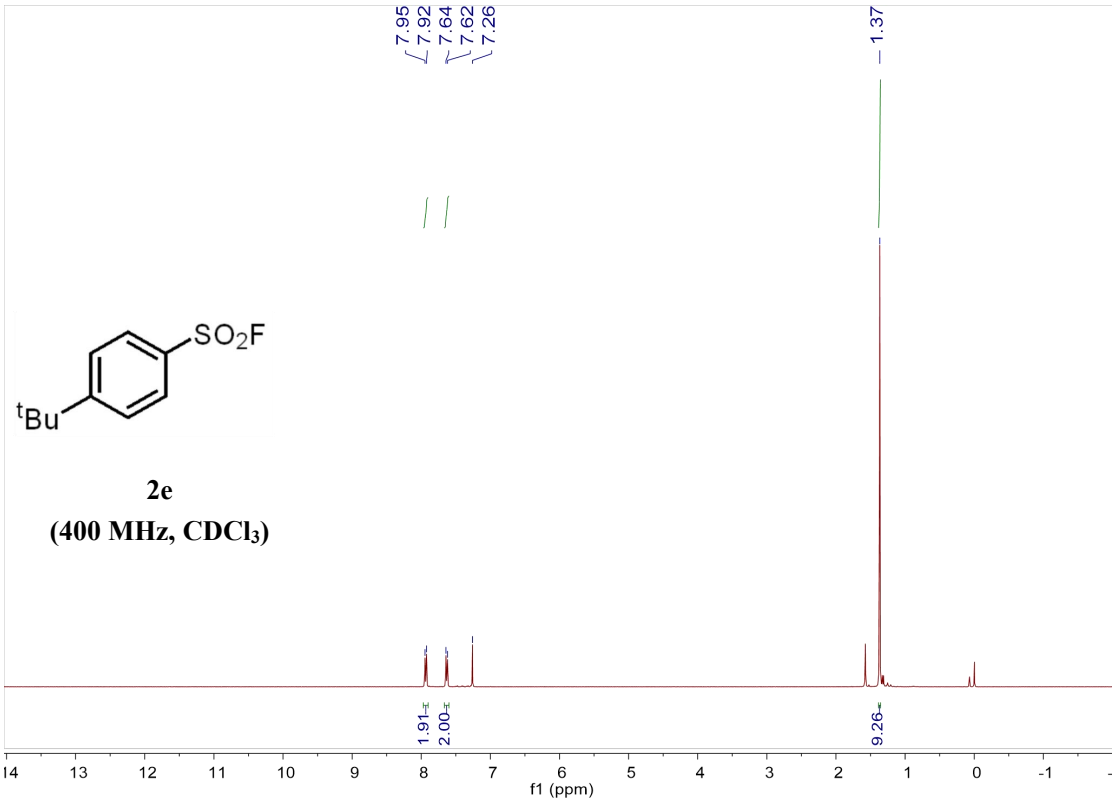


Figure S36. [1]H NMR spectrum of 4-(*tert*-butyl)benzenesulfonyl fluoride

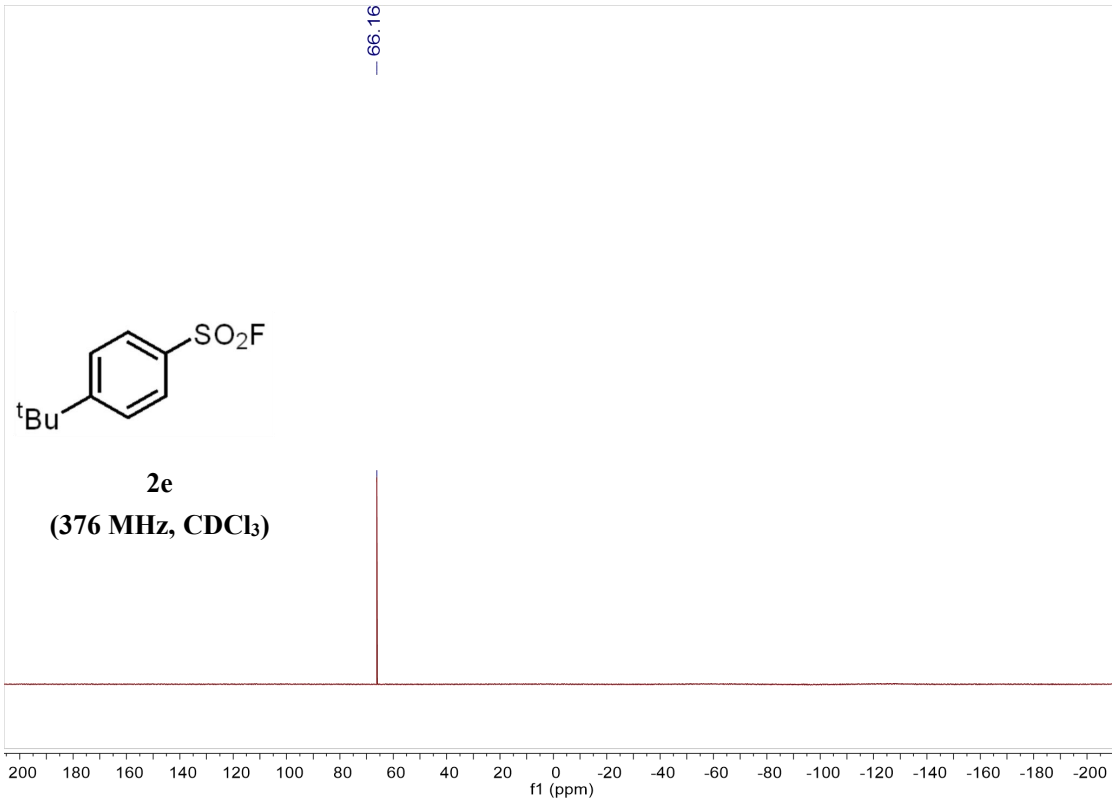


Figure S37. [19]F NMR spectrum of 4-(*tert*-butyl)benzenesulfonyl fluoride

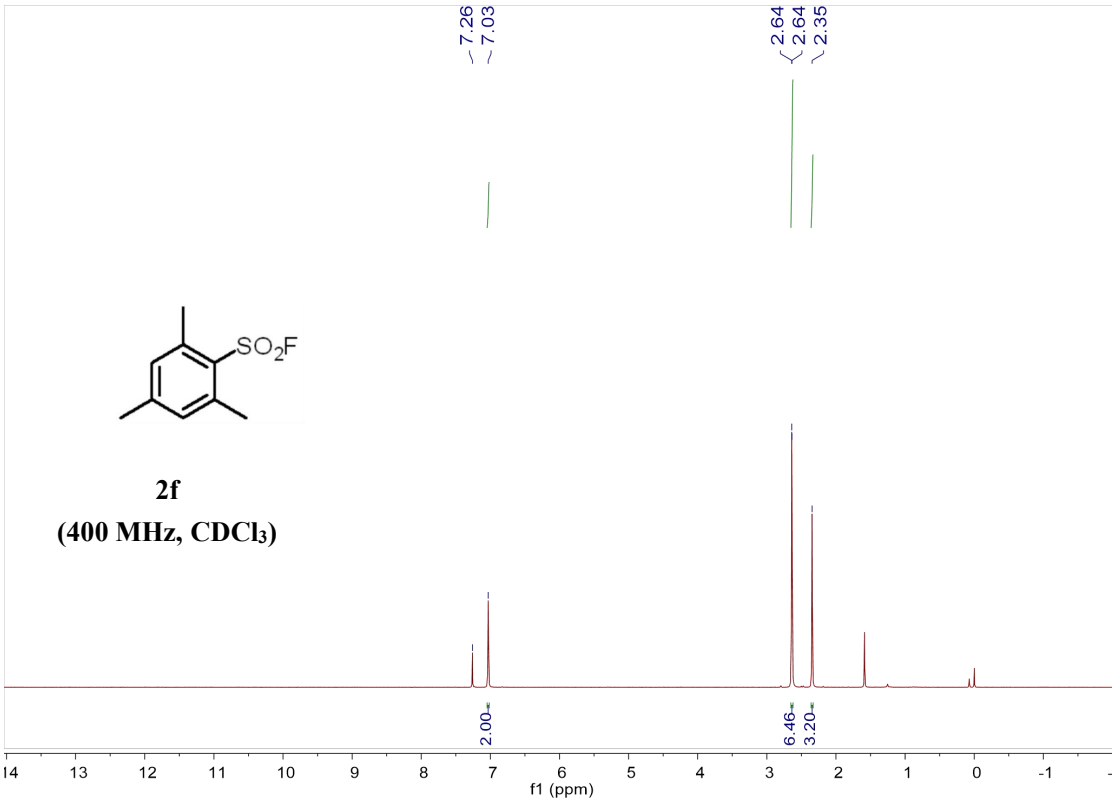


Figure S38. [1]H NMR spectrum of 2,4,6-trimethylbenzenesulfonyl fluoride

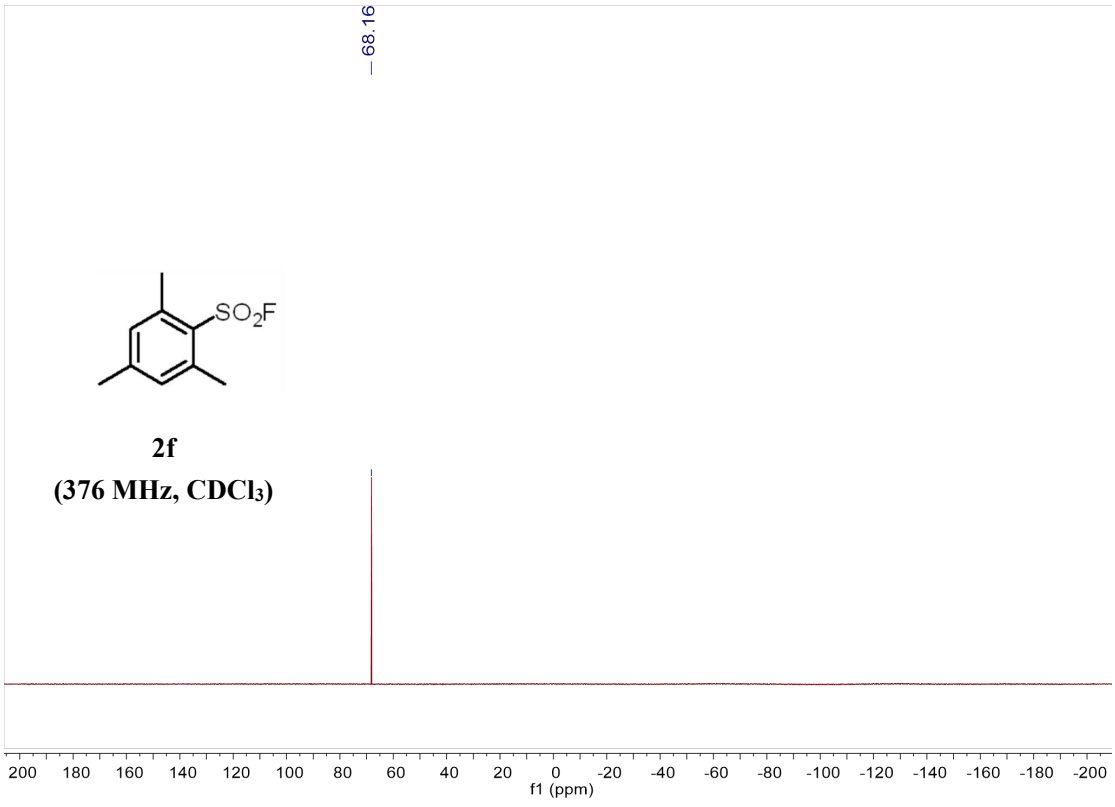


Figure S39. [19]F NMR spectrum of 2,4,6-trimethylbenzenesulfonyl fluoride

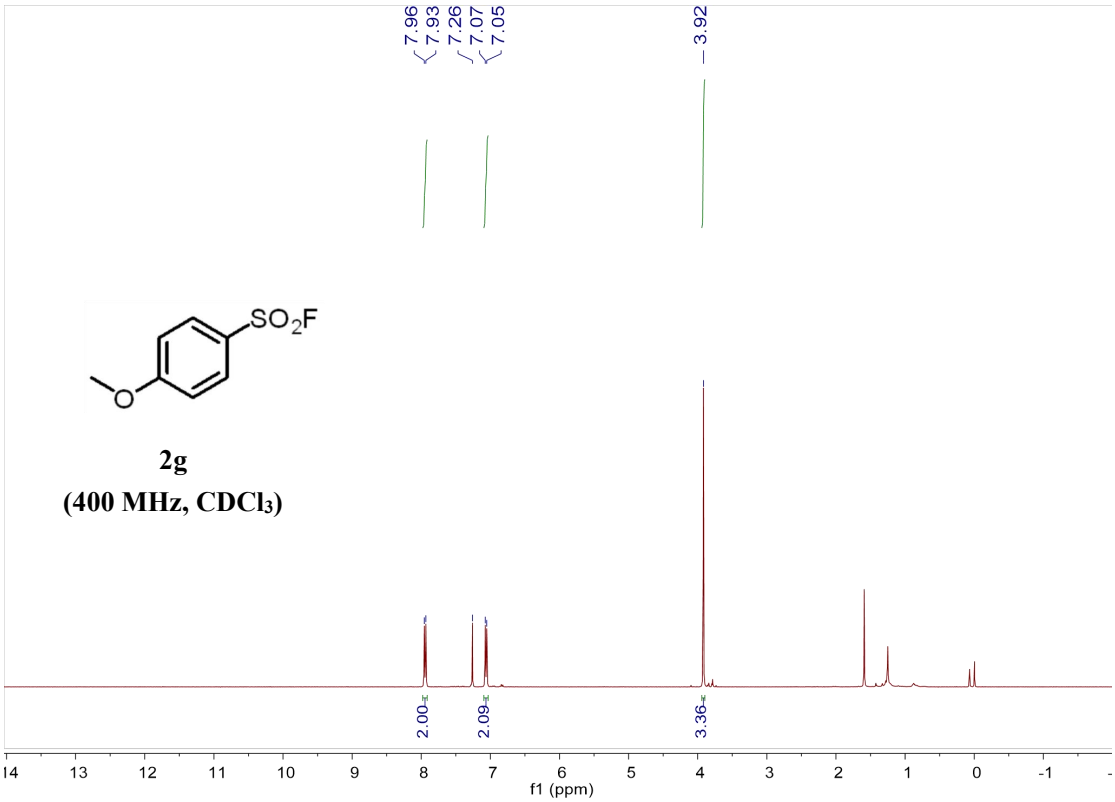


Figure S40. ^{1}H NMR spectrum of 4-methoxybenzenesulfonyl fluoride

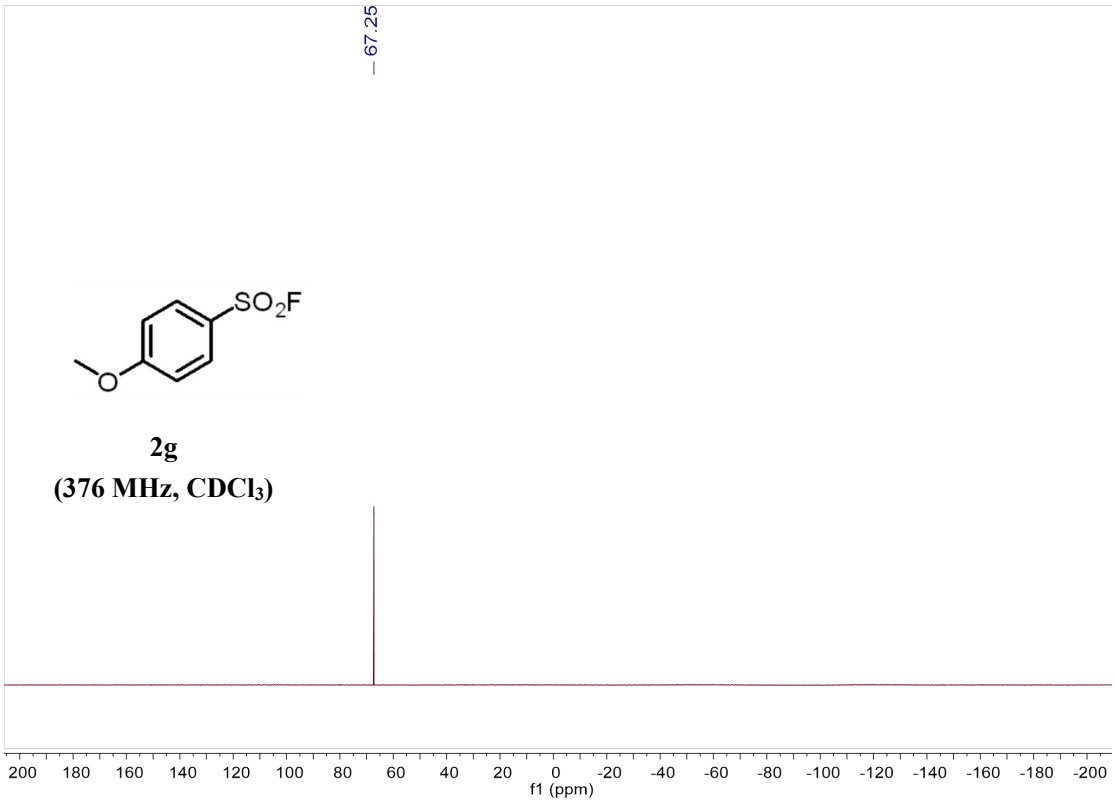


Figure S41. ^{19}F NMR spectrum of 4-methoxybenzenesulfonyl fluoride

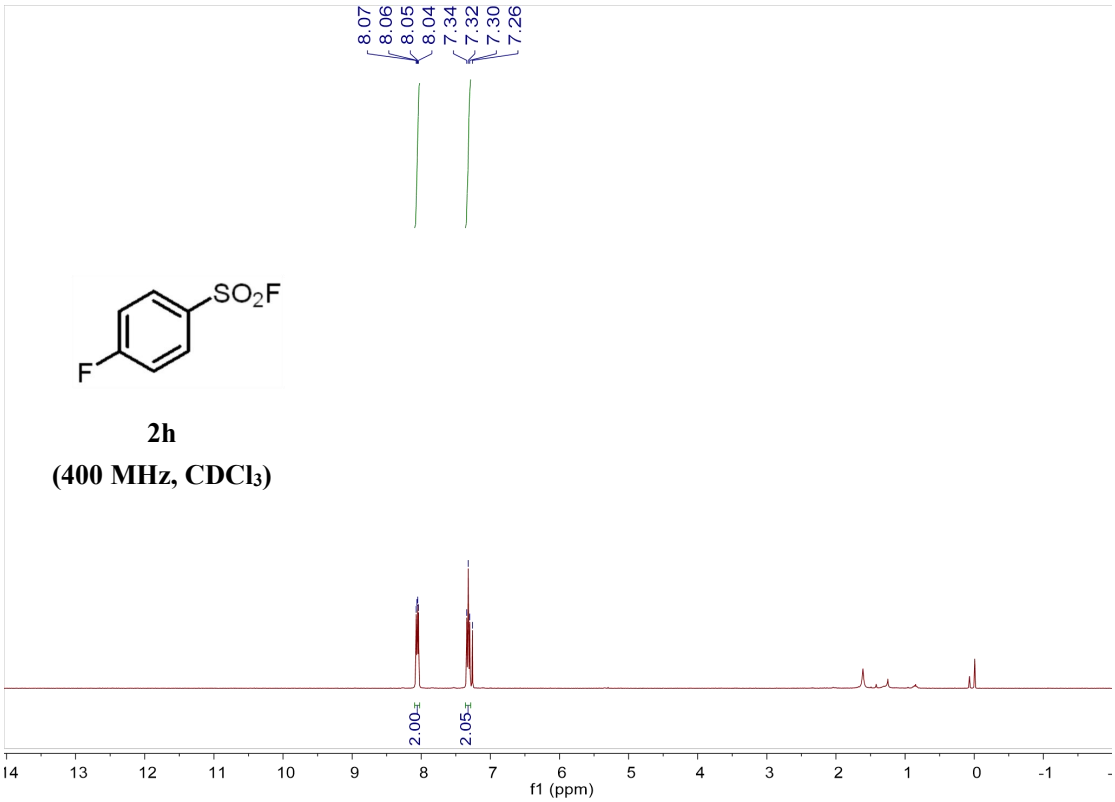


Figure S42. ^{1}H NMR spectrum of 4-fluorobenzenesulfonyl fluoride

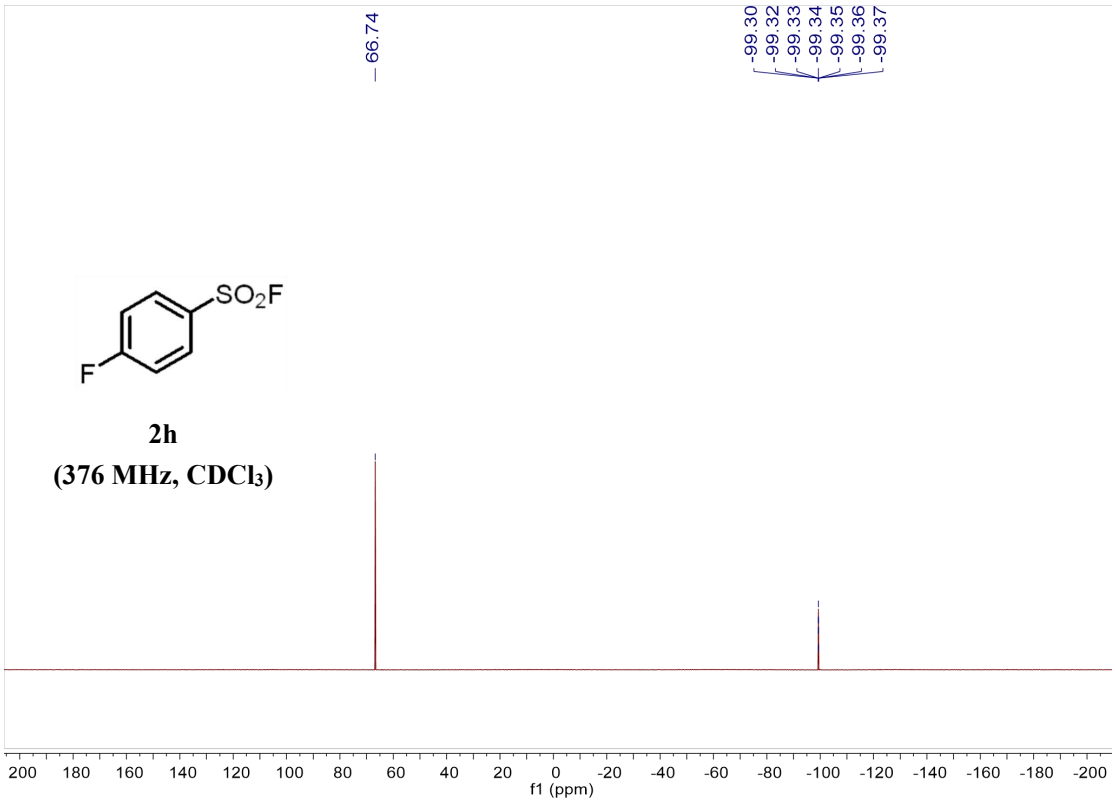


Figure S43. ^{19}F NMR spectrum of 4-fluorobenzenesulfonyl fluoride

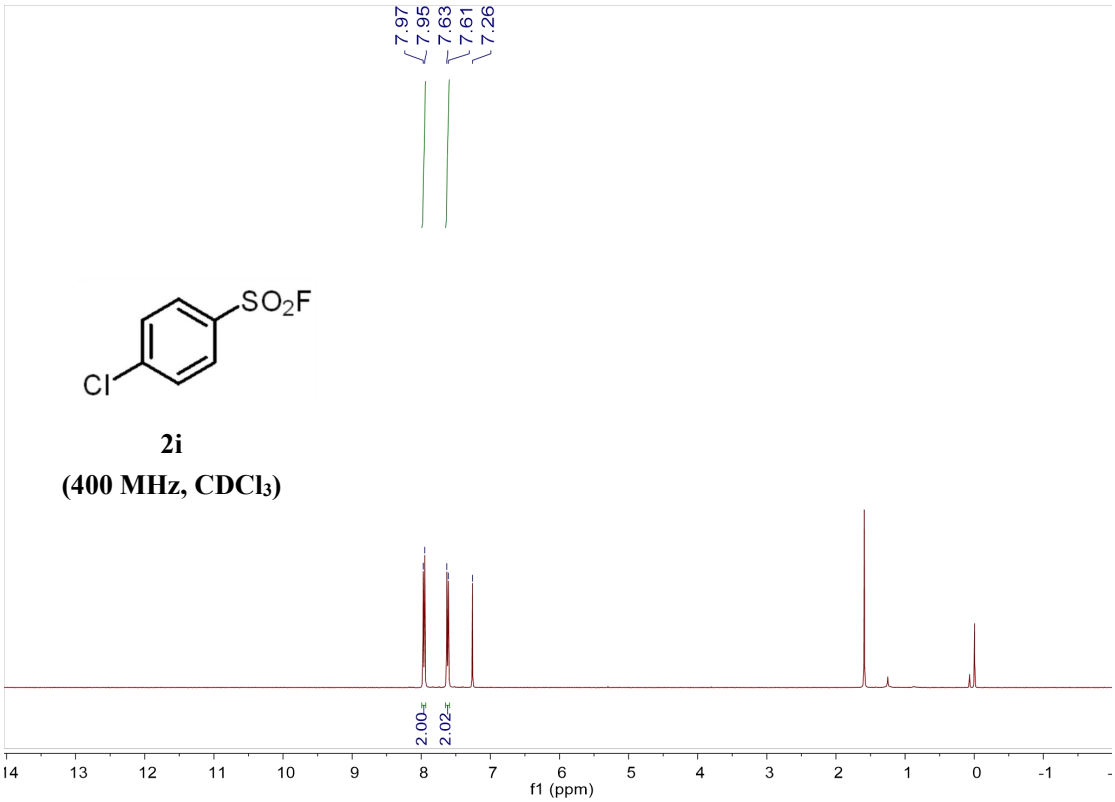


Figure S44. ^{1}H NMR spectrum of 4-chlorobenzenesulfonyl fluoride

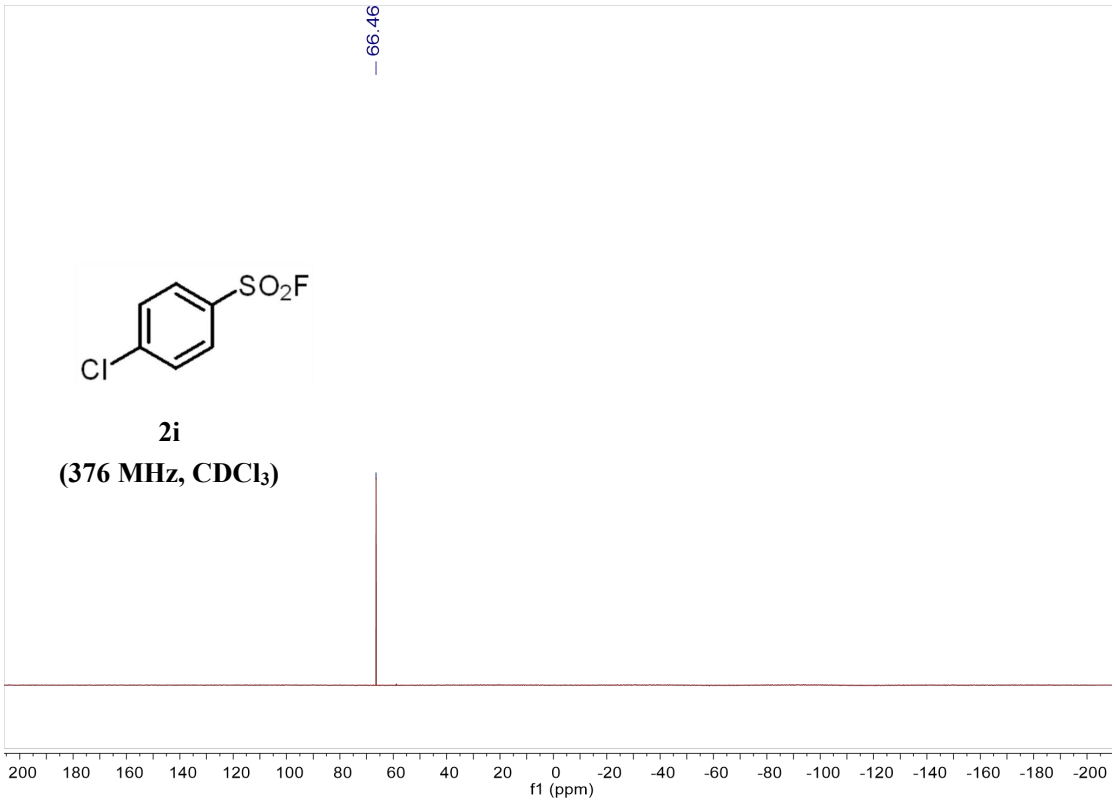


Figure S45. ^{19}F NMR spectrum of 4-chlorobenzenesulfonyl fluoride

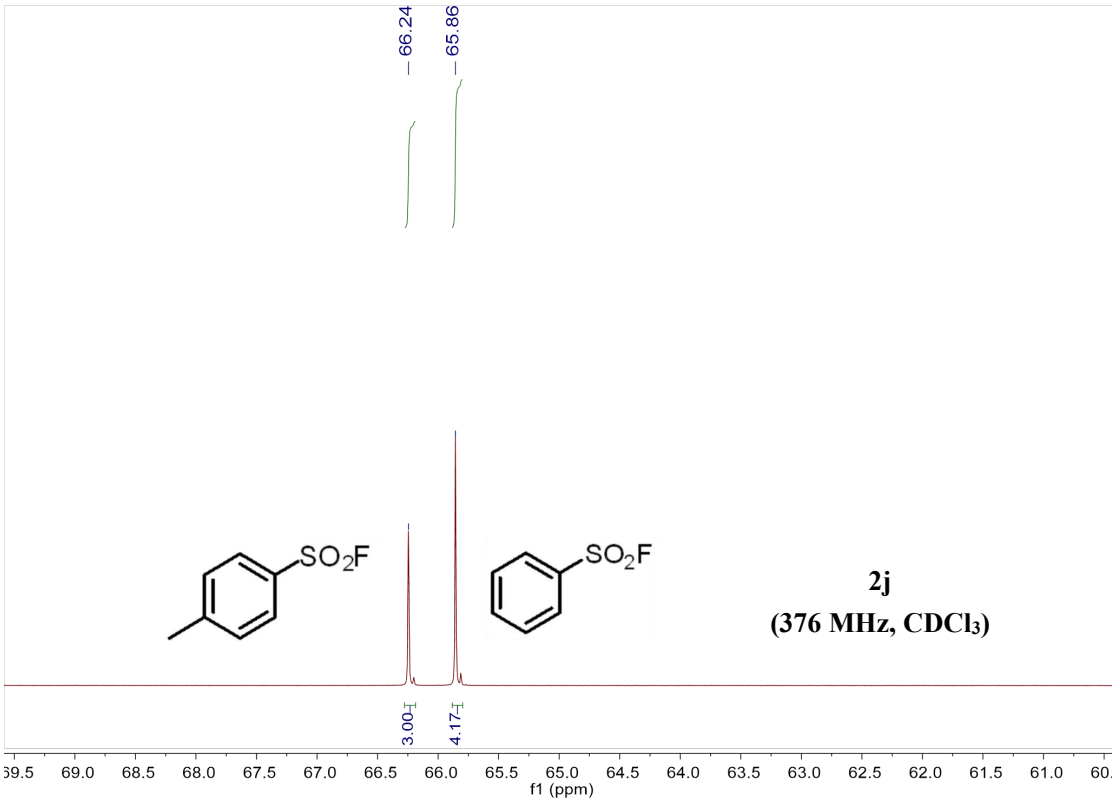


Figure S46. Crude ^{19}F NMR spectrum of benzenesulfonyl fluoride and 4-methylbenzenesulfonyl fluoride

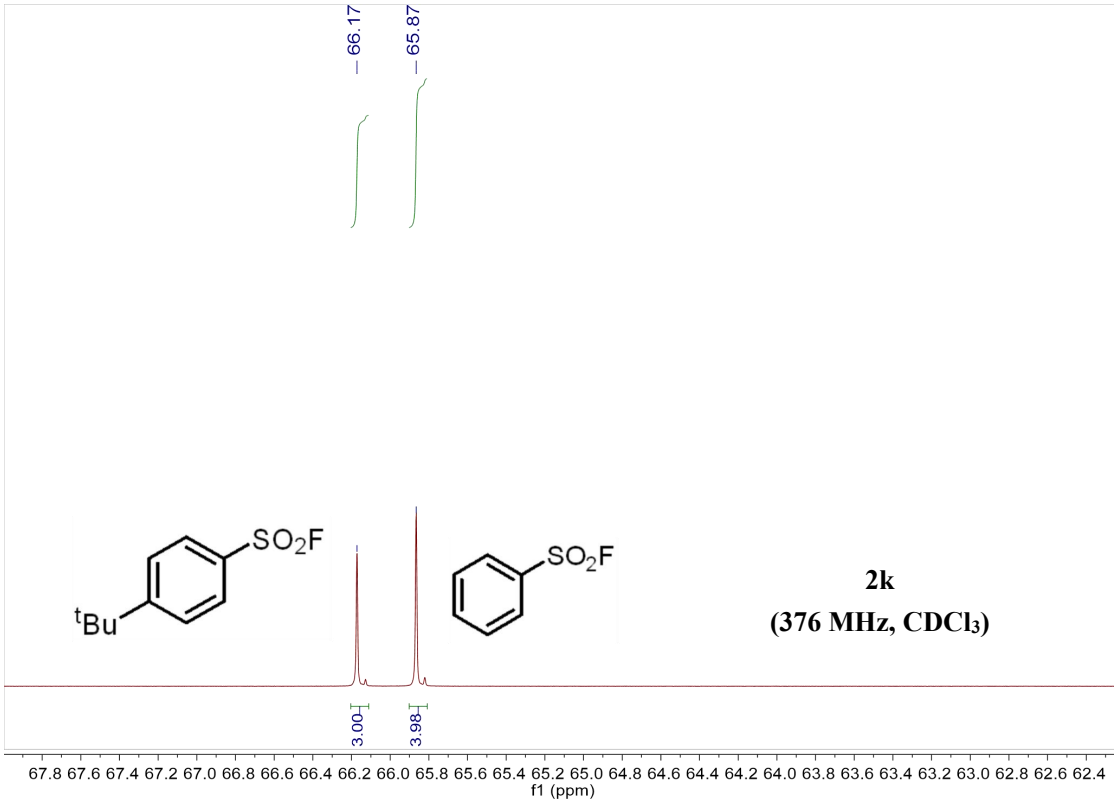


Figure S47. Crude ^{19}F NMR spectrum of benzenesulfonyl fluoride and 4-(*tert*-butyl)benzenesulfonyl fluoride

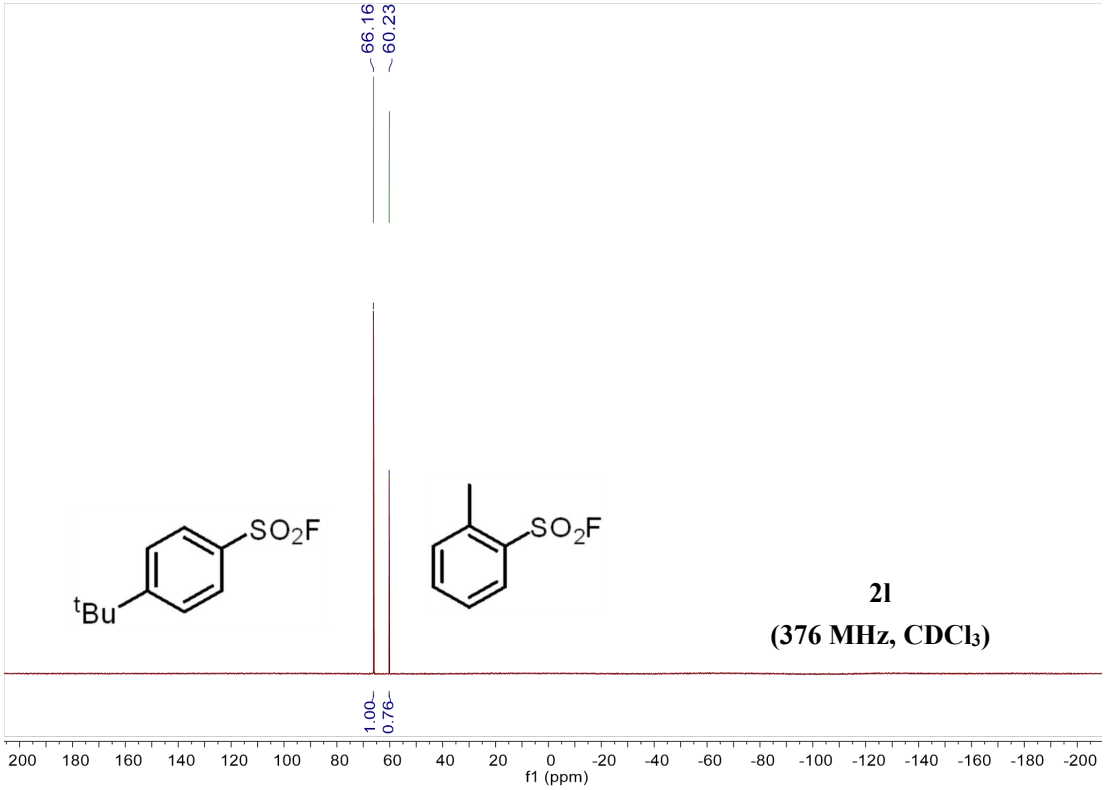


Figure S48. Crude ^{19}F NMR spectrum of 2-methylbenzenesulfonyl fluoride and 4-(*tert*-butyl)benzenesulfonyl fluoride

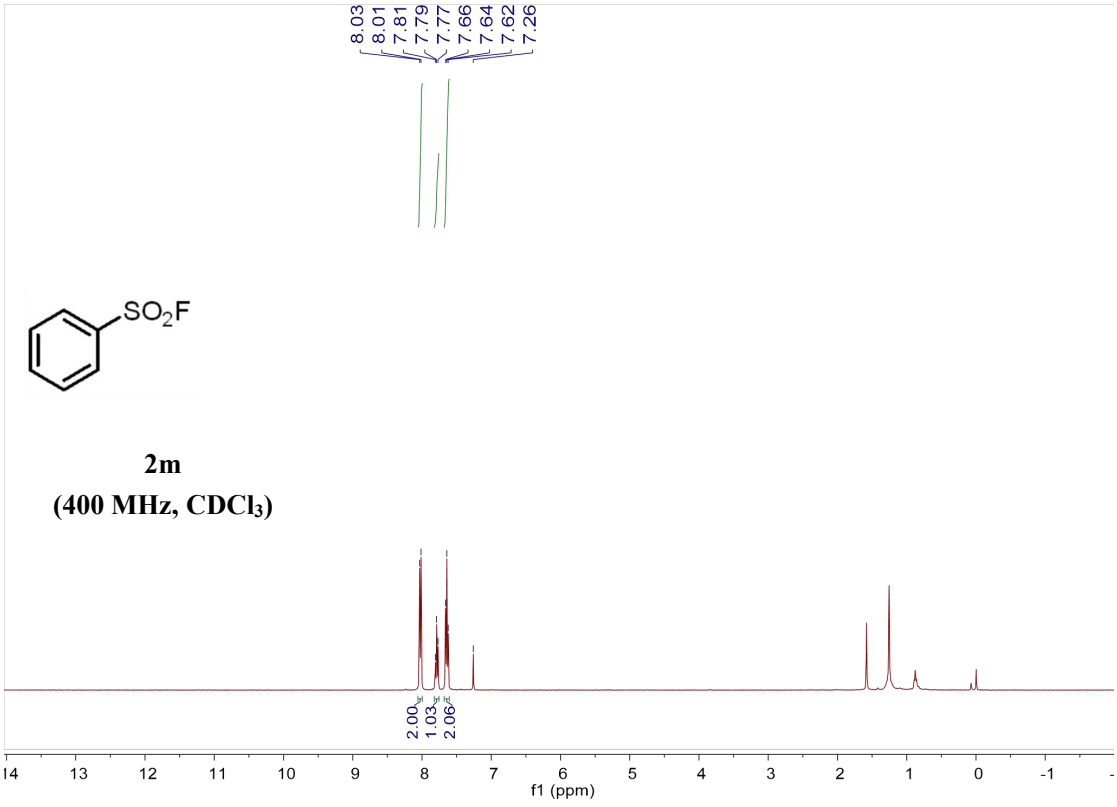


Figure S49. [1]H NMR spectrum of benzenesulfonyl fluoride

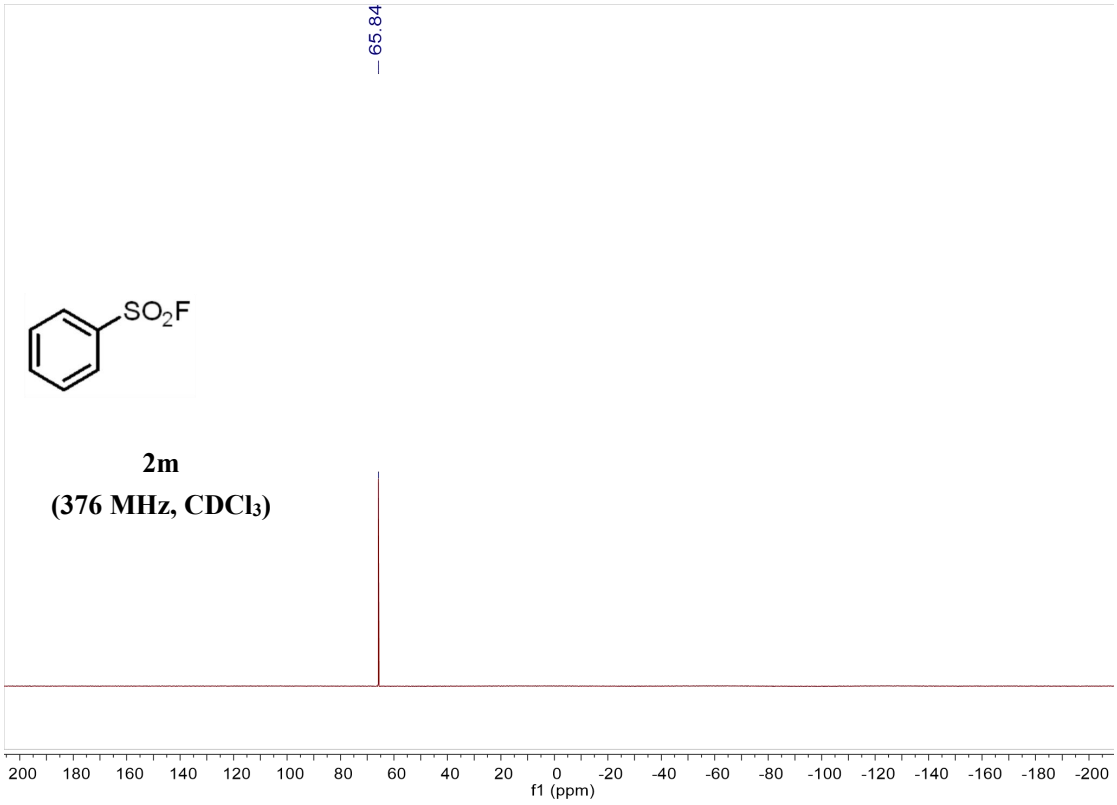


Figure S50. [19]F NMR spectrum of benzenesulfonyl fluoride

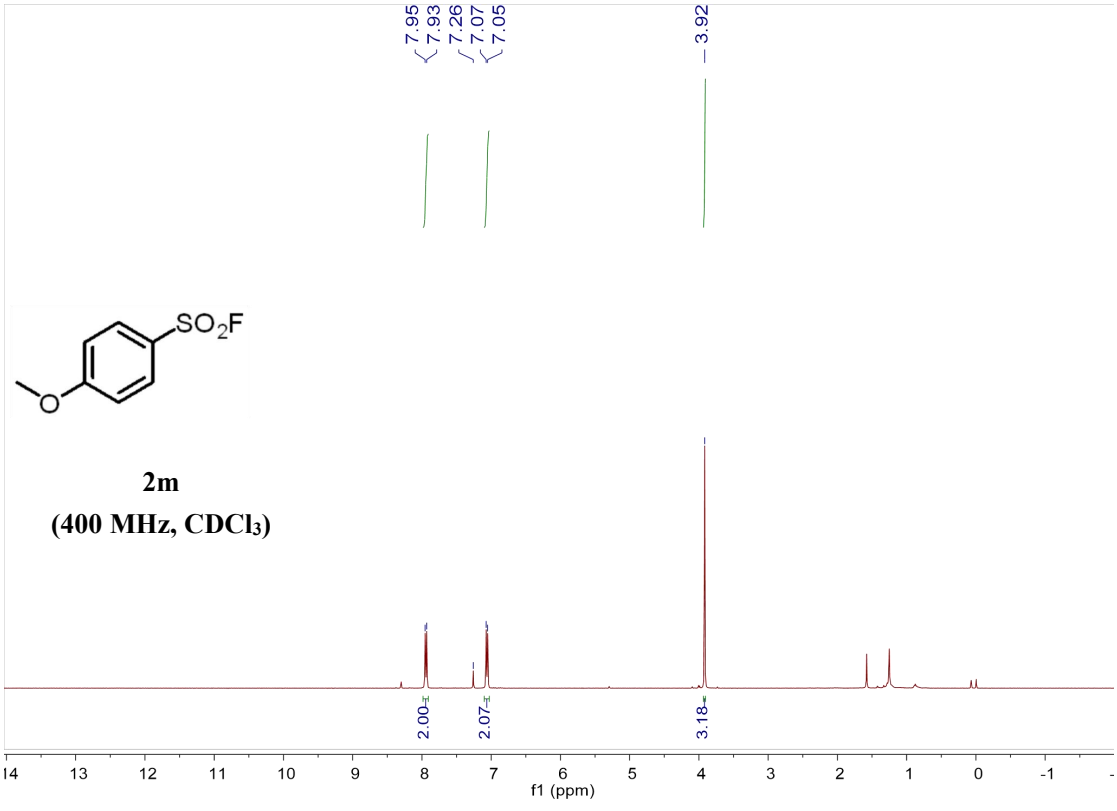


Figure S51. ^{1}H NMR spectrum of 4-methoxybenzenesulfonyl fluoride

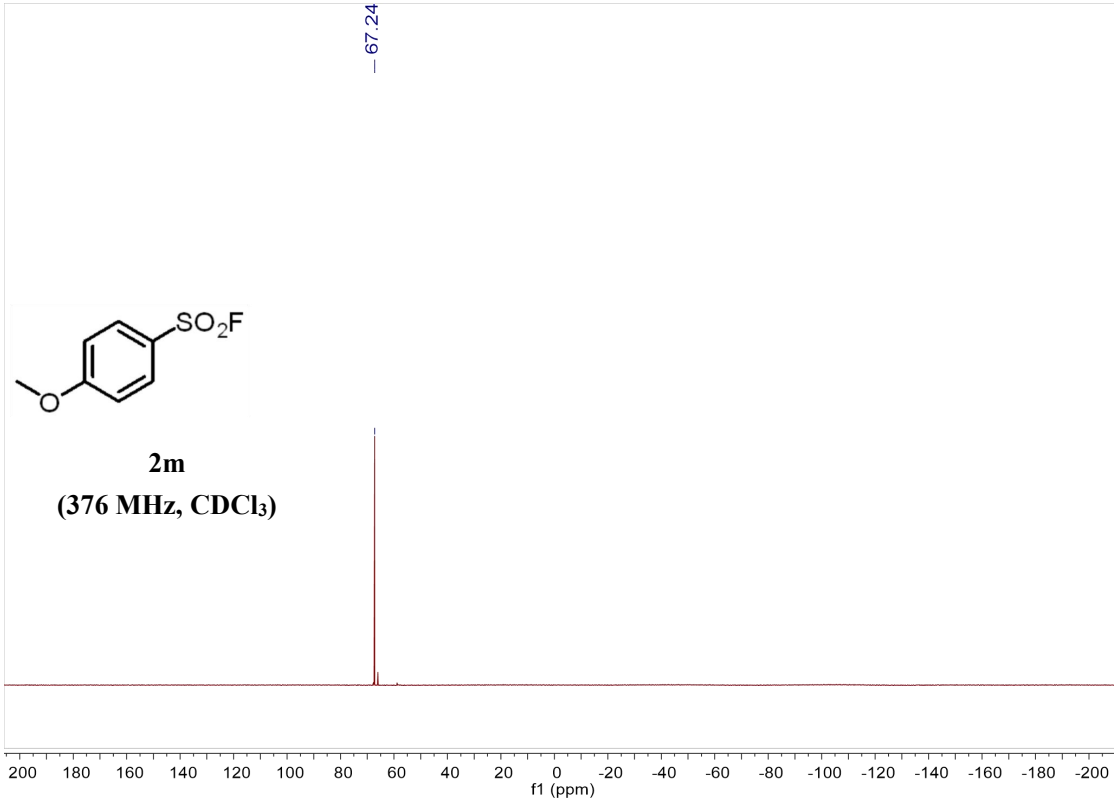


Figure S52. ^{19}F NMR spectrum of 4-methoxybenzenesulfonyl fluoride

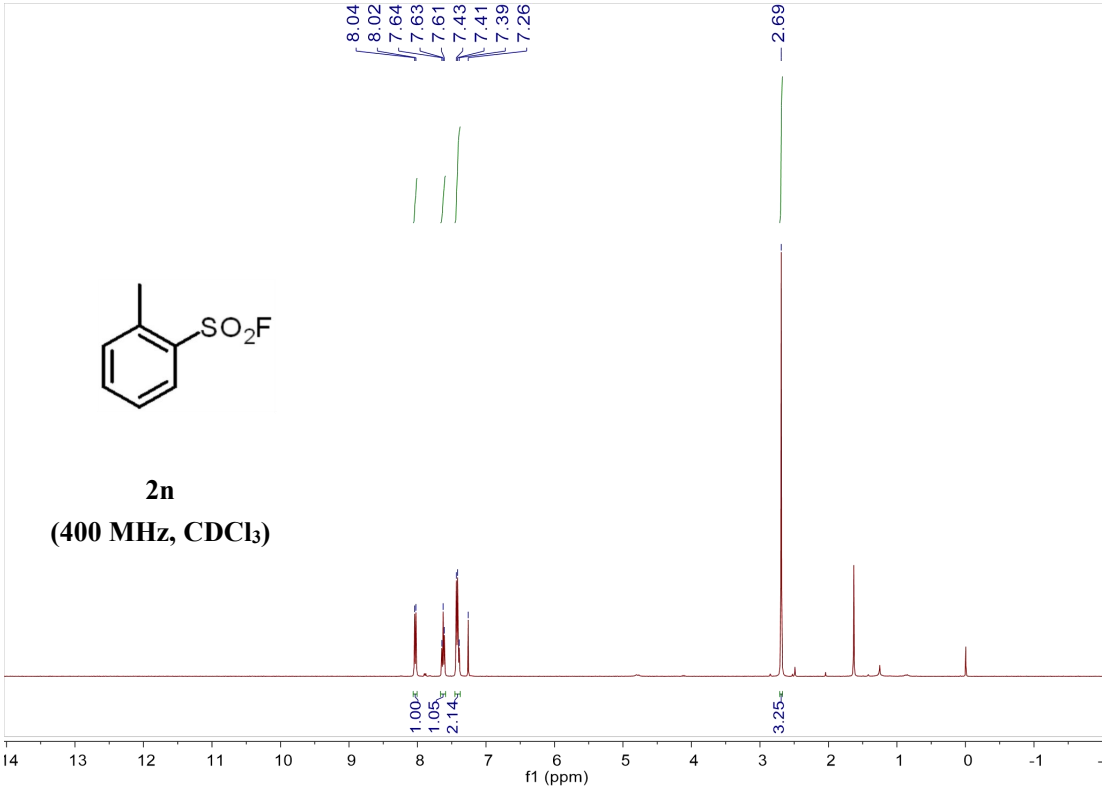


Figure S53. [1]H NMR spectrum of 2-methylbenzenesulfonyl fluoride

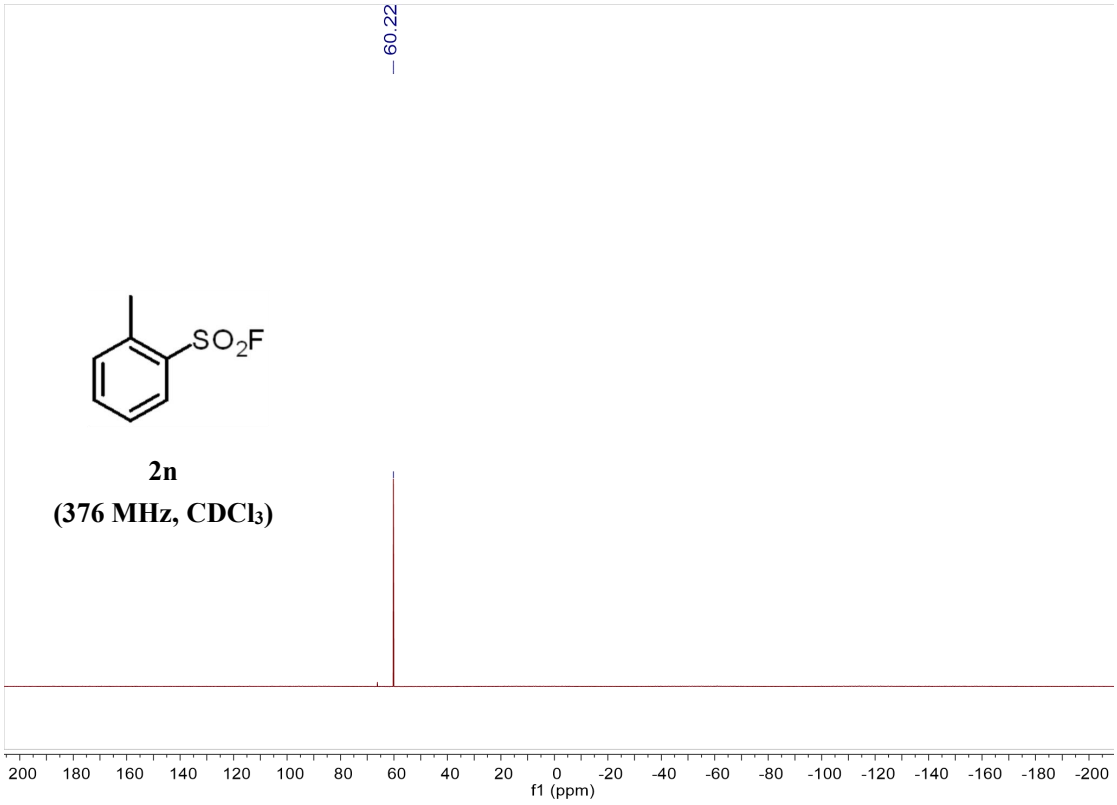


Figure S54. [19]F NMR spectrum of 2-methylbenzenesulfonyl fluoride

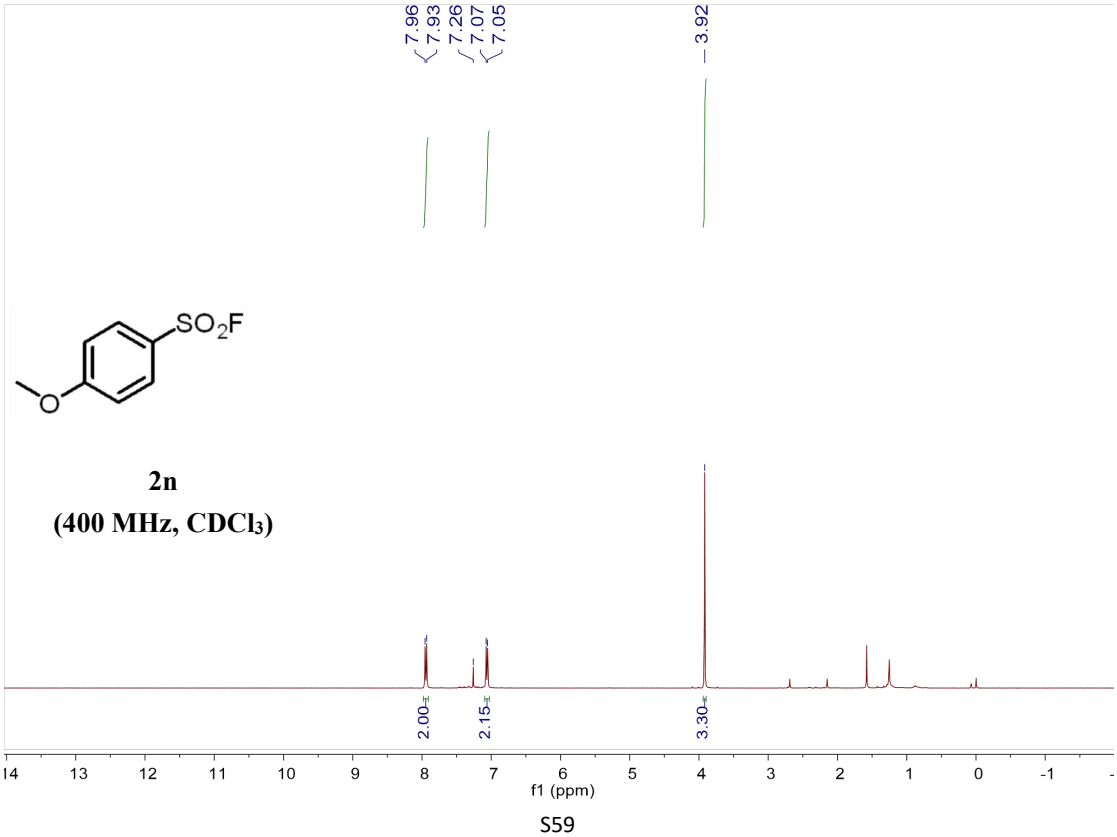


Figure S55. ^{1}H NMR spectrum of 4-methoxybenzenesulfonyl fluoride

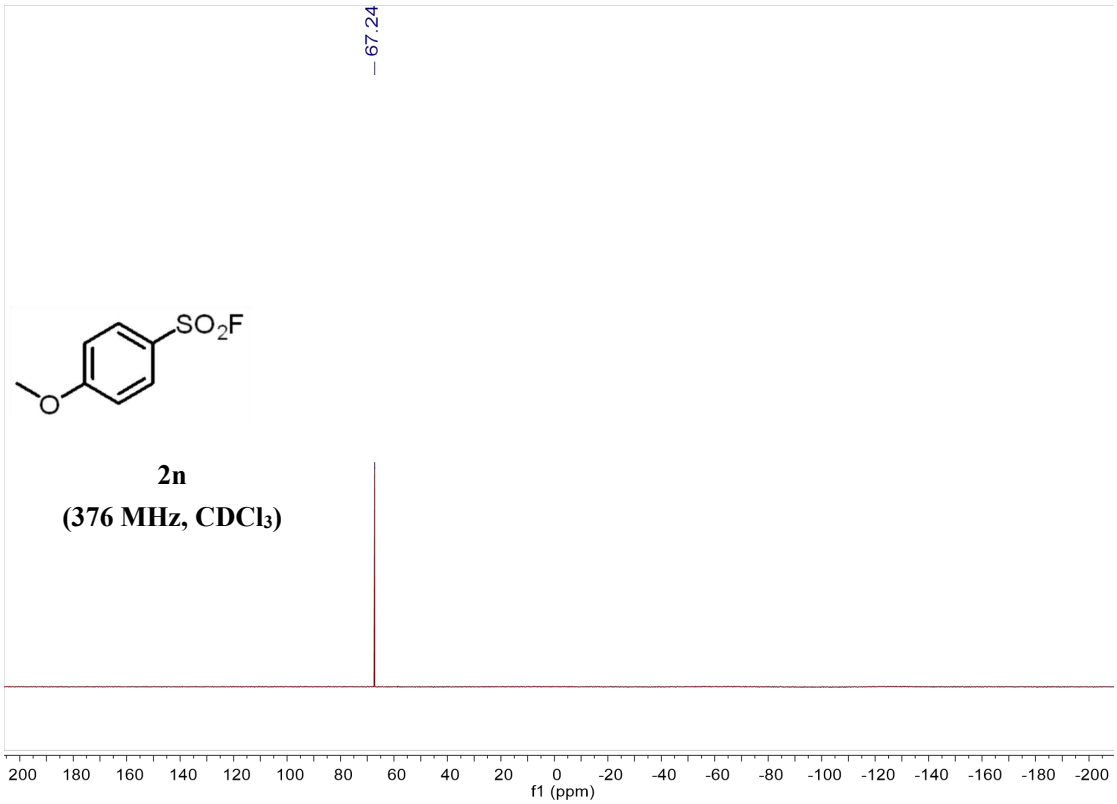


Figure S56. ^{19}F NMR spectrum of 4-methoxybenzenesulfonyl fluoride

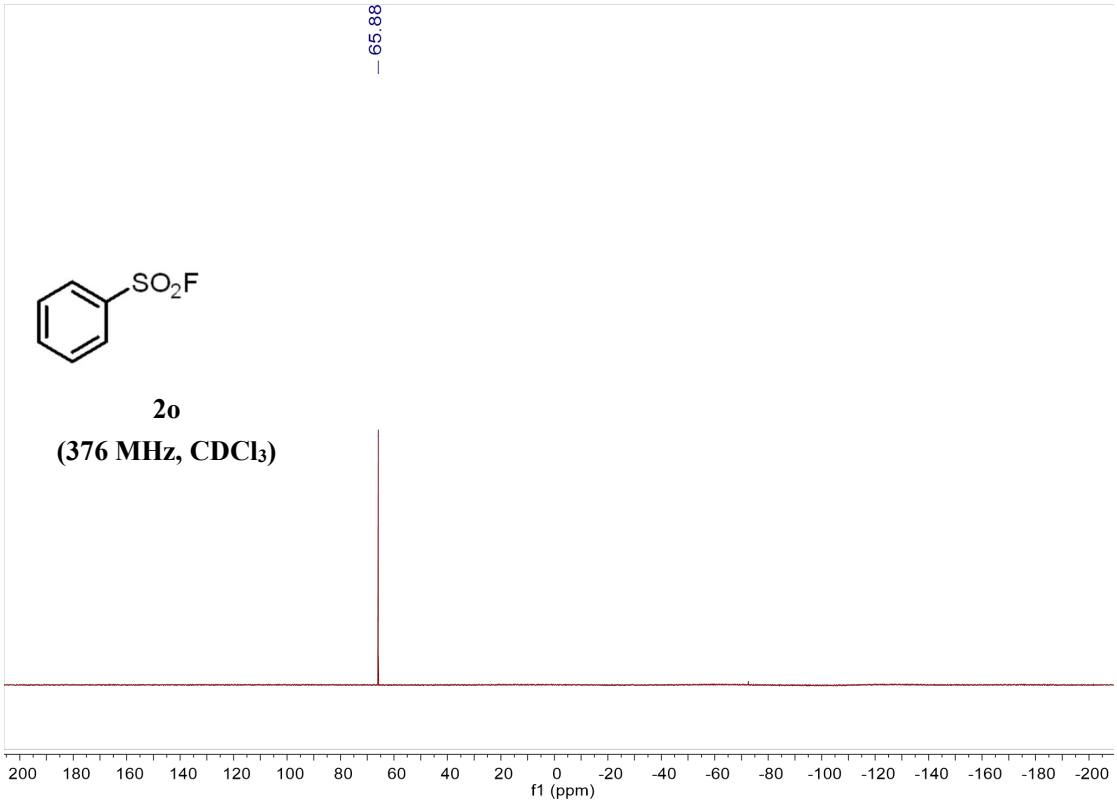


Figure S57. ^{19}F NMR spectrum of benzenesulfonyl fluoride

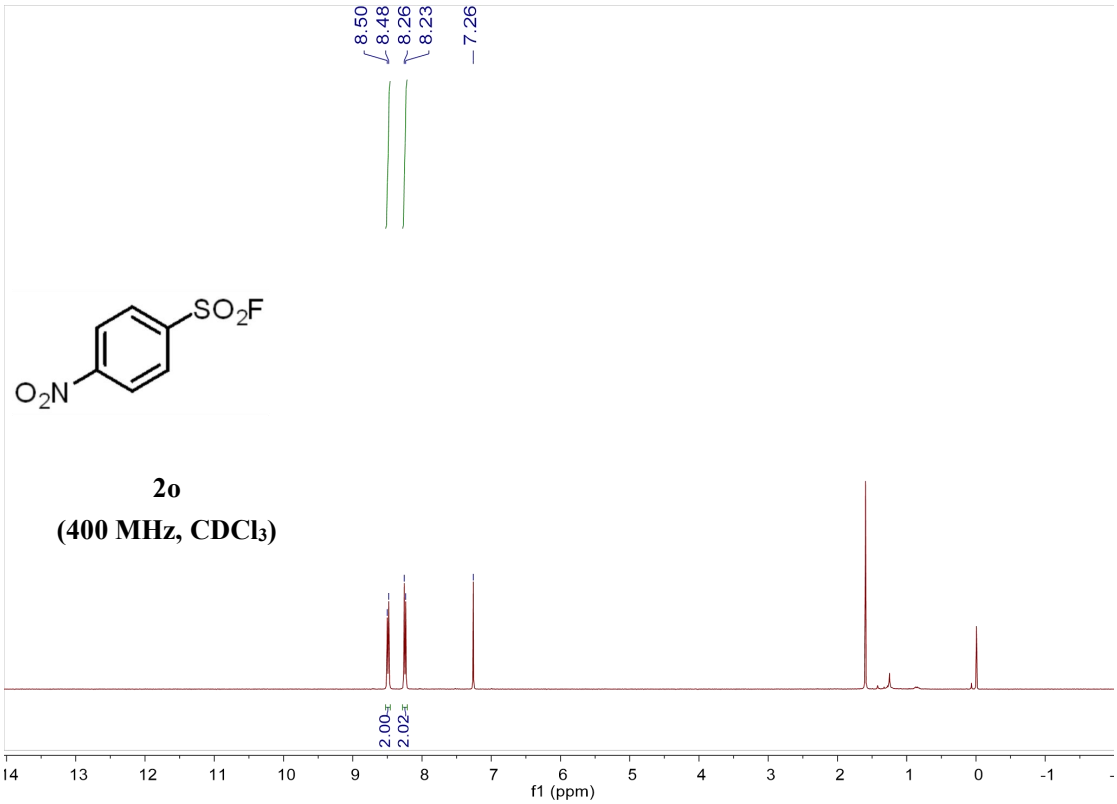


Figure S58. ^{1}H NMR spectrum of p-nitrobenzenesulfonyl fluoride

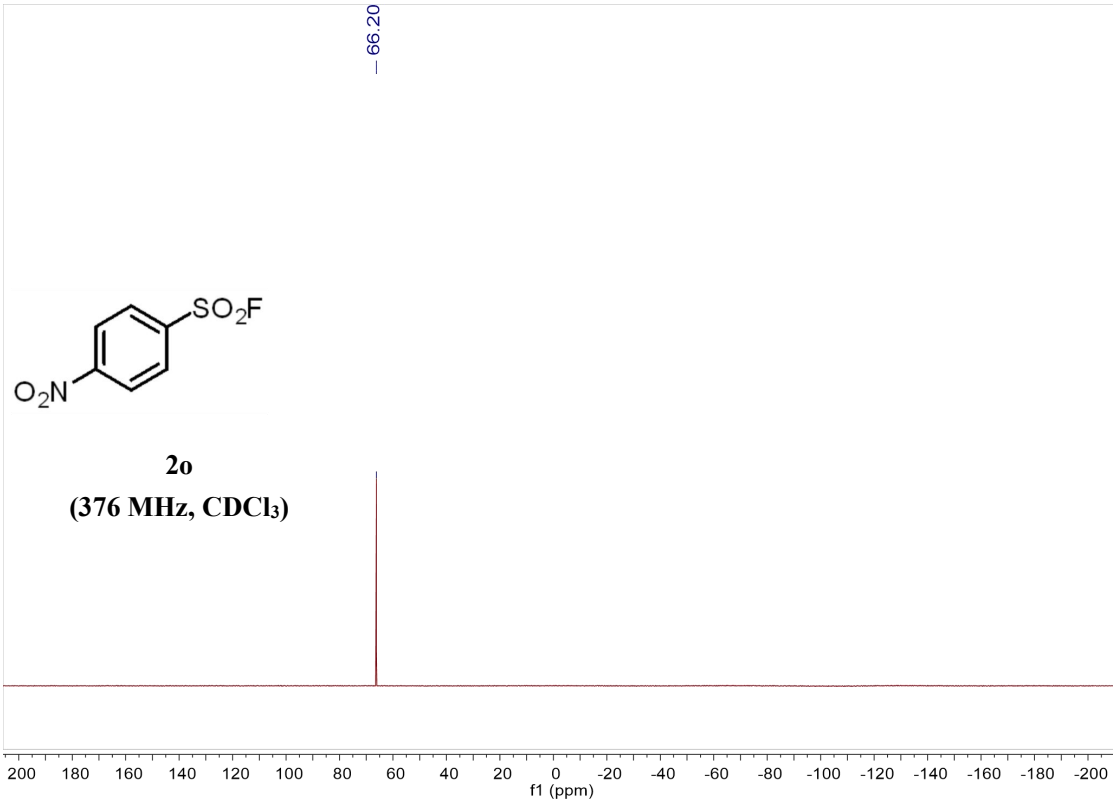


Figure S59. ^{19}F NMR spectrum of p-nitrobenzenesulfonyl fluoride

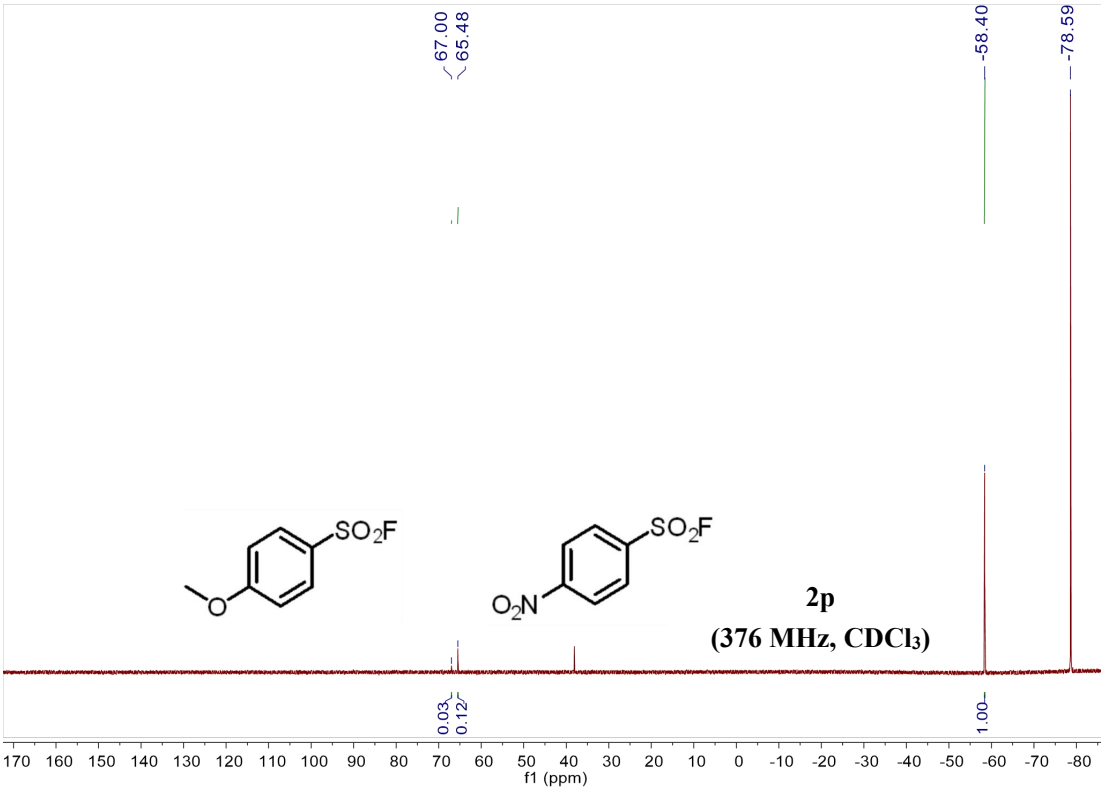


Figure S60. Crude ^{19}F NMR spectrum of p-nitrobenzenesulfonyl fluoride and 4-methoxybenzenesulfonyl fluoride

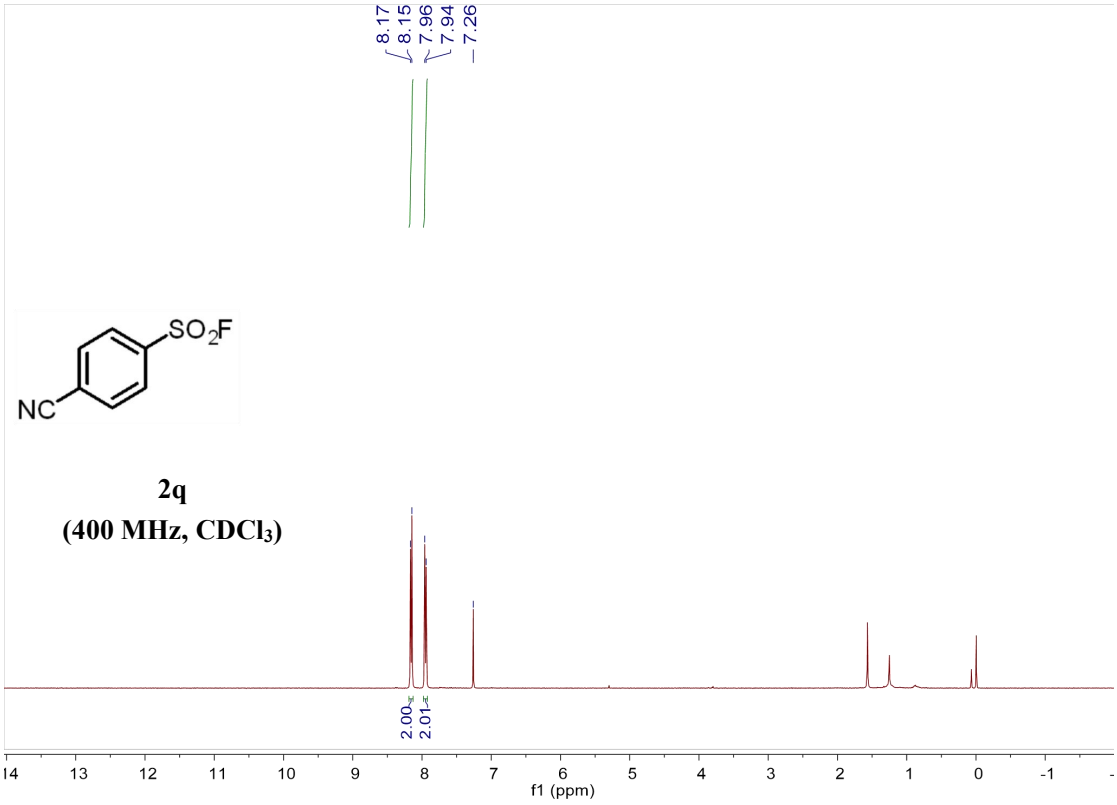


Figure S61. ^{1}H NMR spectrum of p-cyanobenzenesulfonyl fluoride

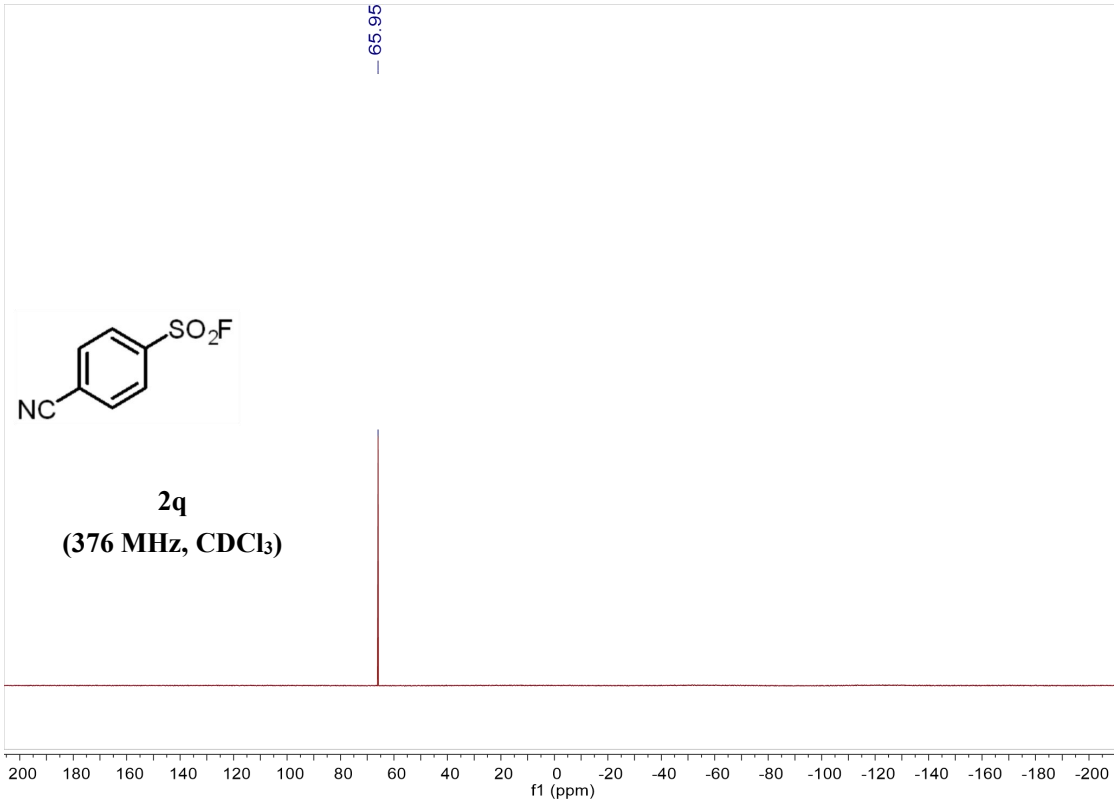


Figure S62. ^{19}F NMR spectrum of p-cyanobenzenesulfonyl fluoride

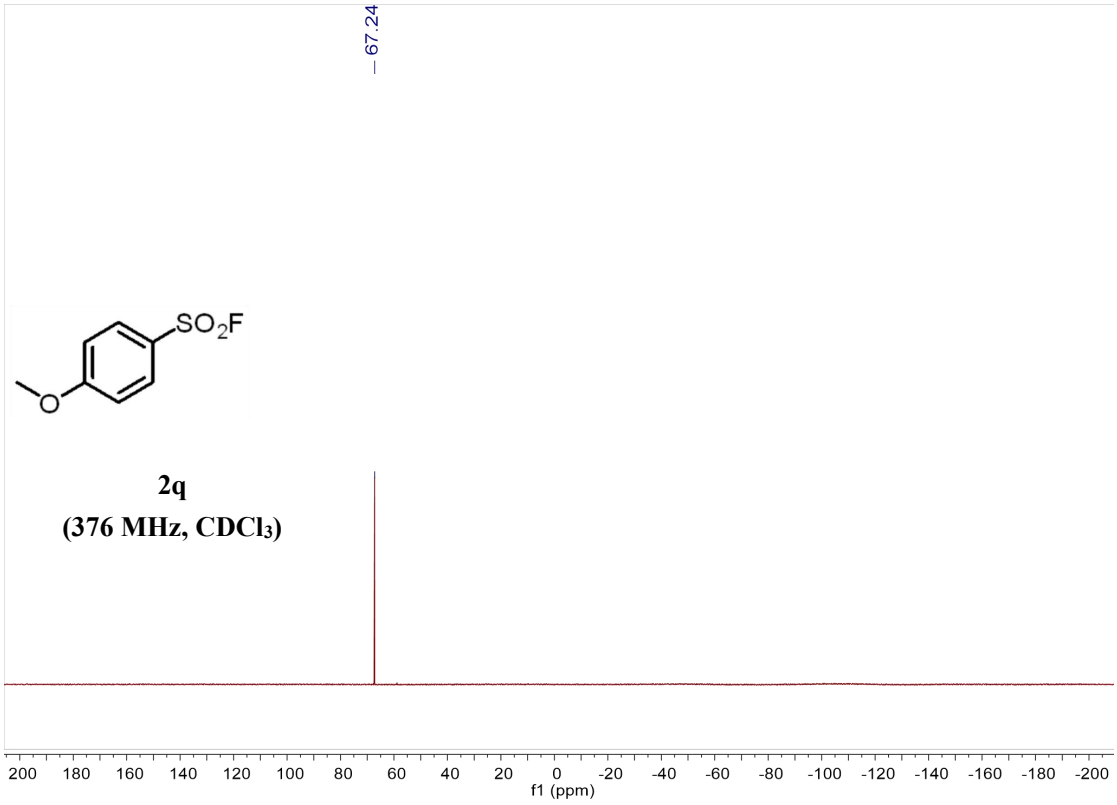


Figure S63. ^{19}F NMR spectrum of 4-methoxybenzenesulfonyl fluoride

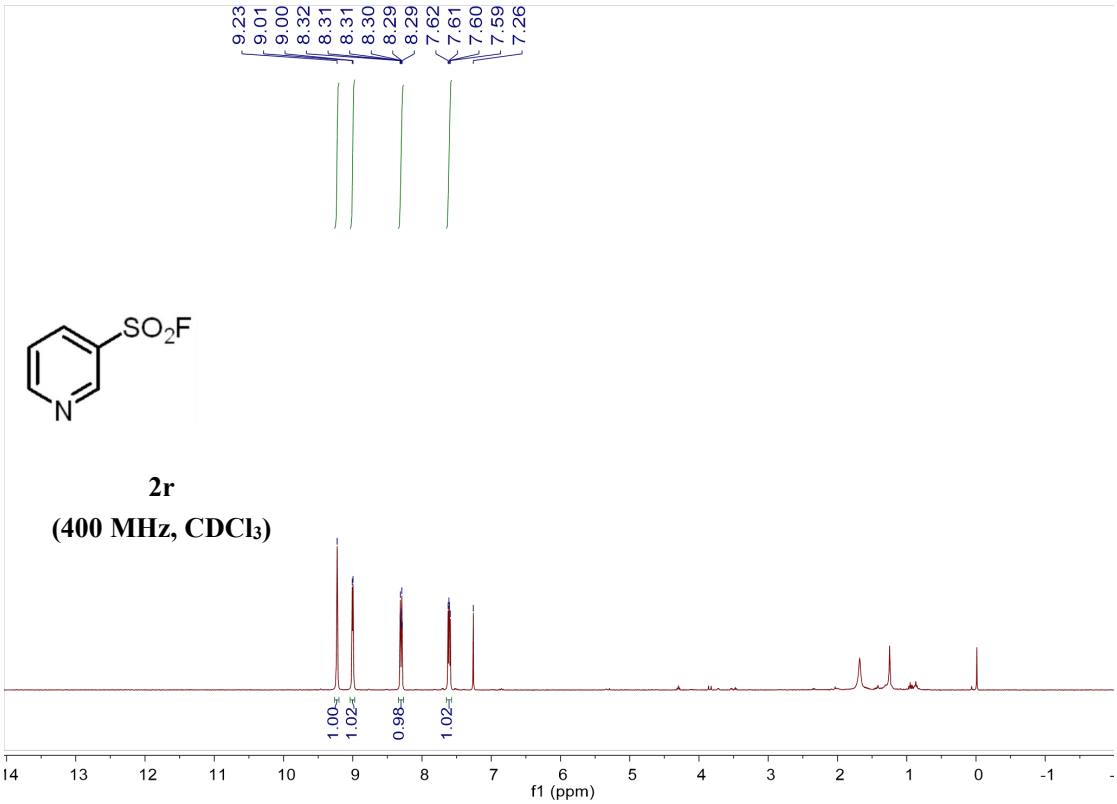


Figure S64. ^{1}H NMR spectrum of pyridine-3-sulfonyl fluoride

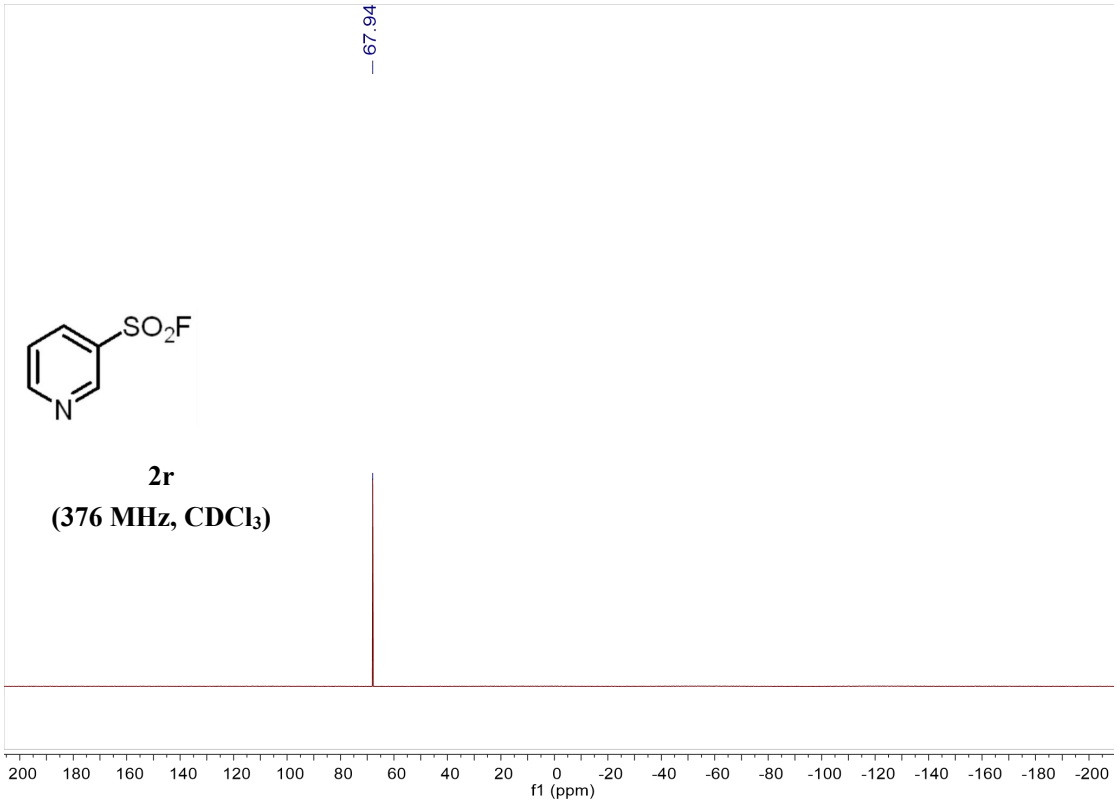


Figure S65. ^{19}F NMR spectrum of pyridine-3-sulfonyl fluoride

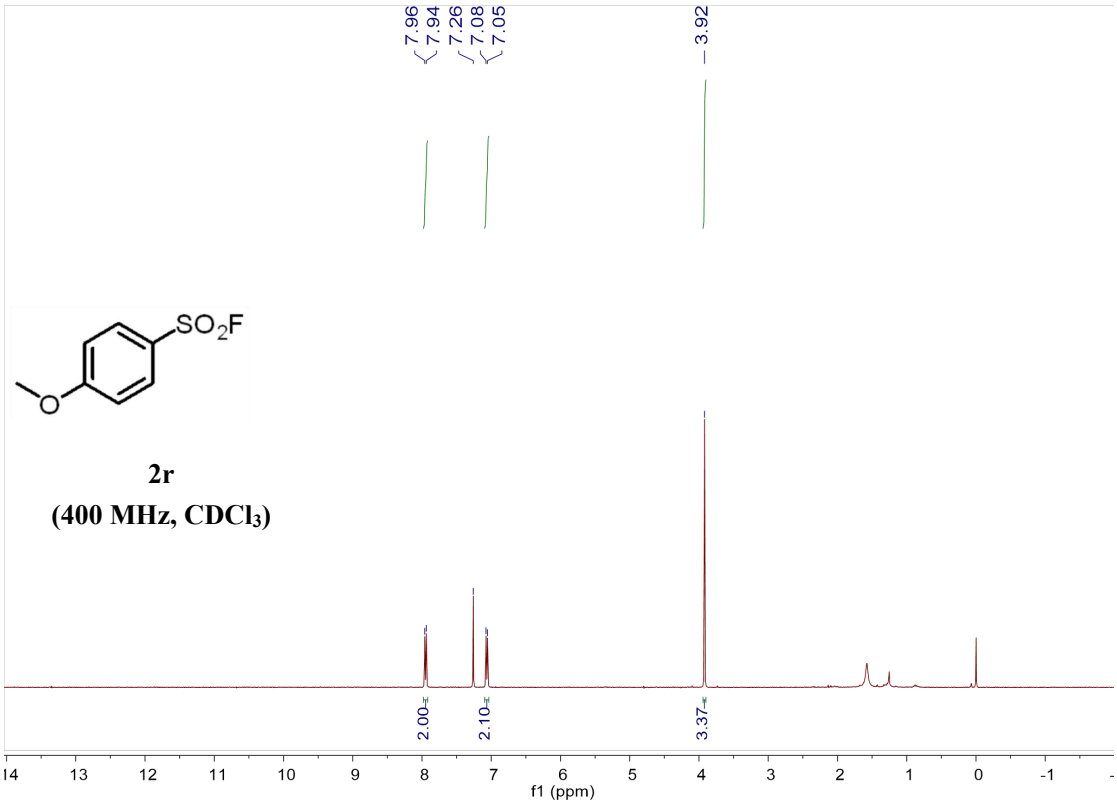


Figure S66. ^{1}H NMR spectrum of 4-methoxybenzenesulfonyl fluoride

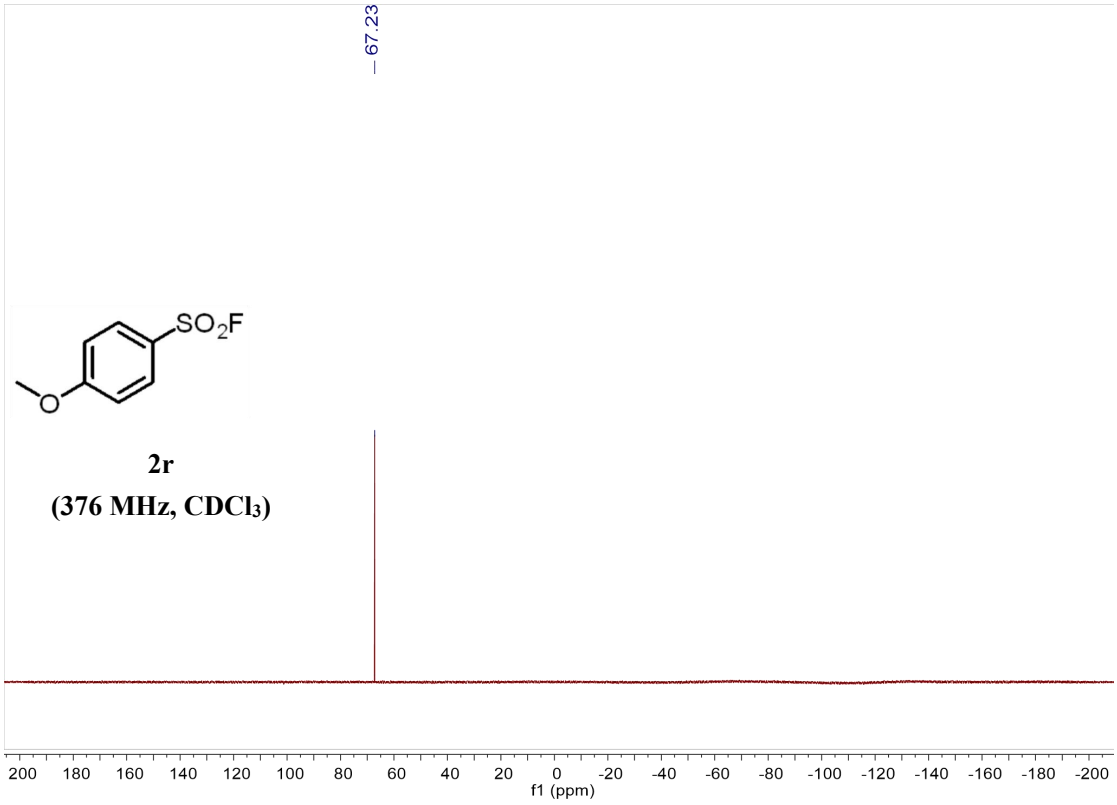


Figure S67. ^{19}F NMR spectrum of 4-methoxybenzenesulfonyl fluoride

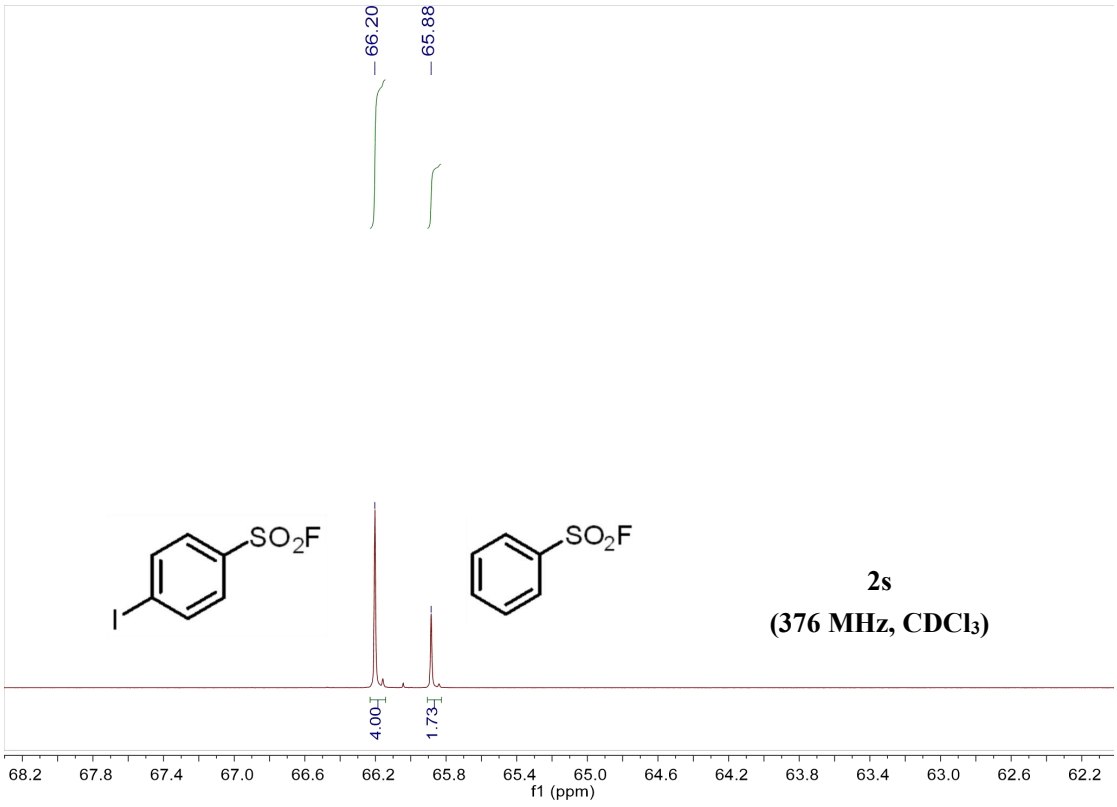


Figure S68. Crude ^{19}F NMR spectrum of benzenesulfonyl fluoride and 4-iodobenzenesulfonyl fluoride

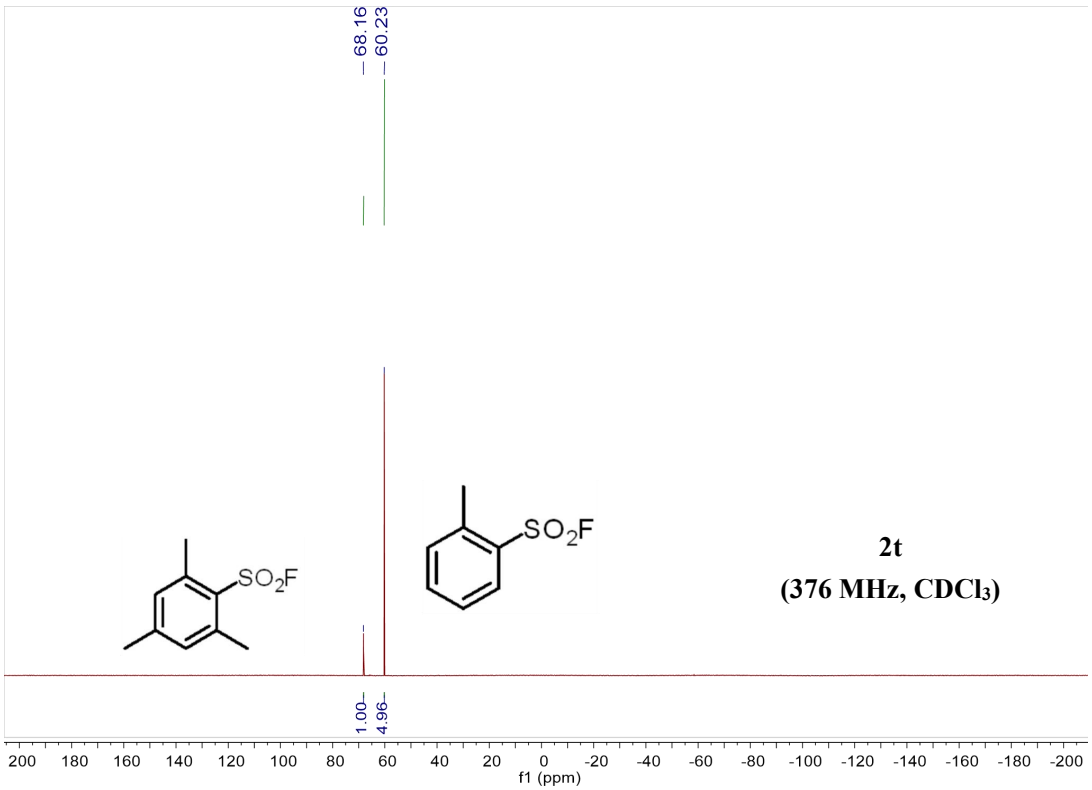


Figure S69. Crude ^{19}F NMR spectrum of 2-methylbenzenesulfonyl fluoride and 2,4,6-trimethylbenzenesulfonyl fluoride

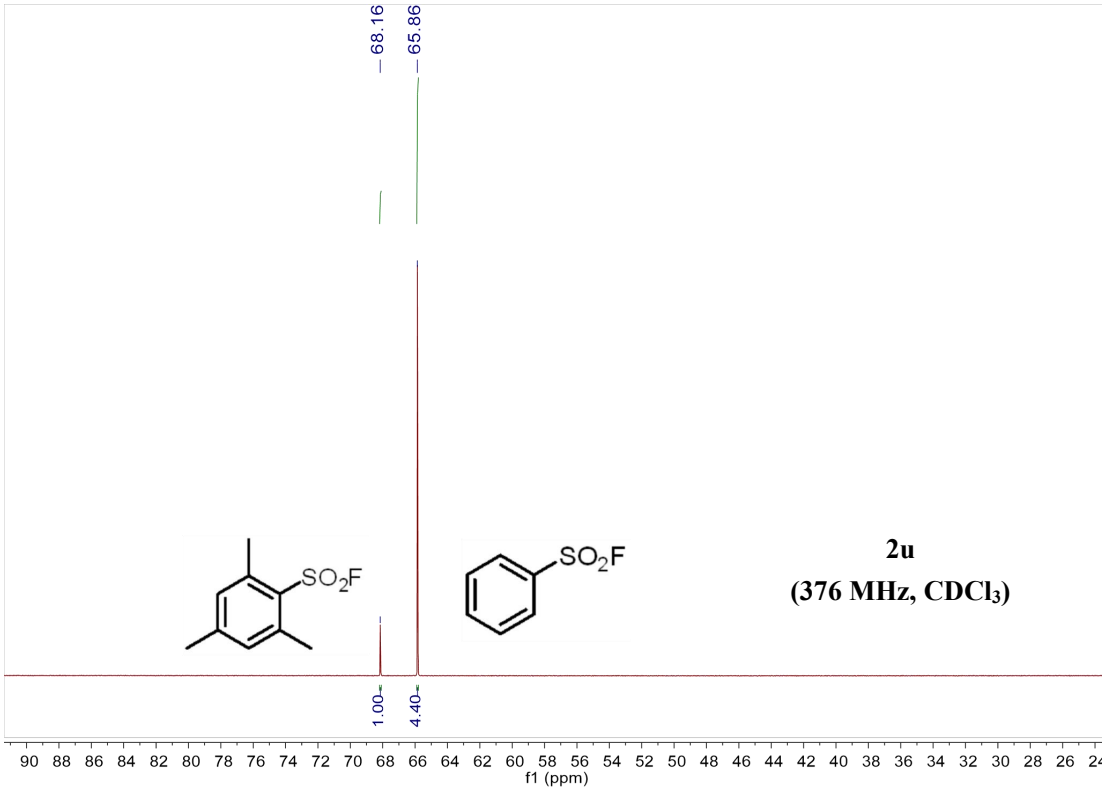


Figure S70. Crude ^{19}F NMR spectrum of benzenesulfonyl fluoride and 2,4,6-trimethylbenzenesulfonyl fluoride

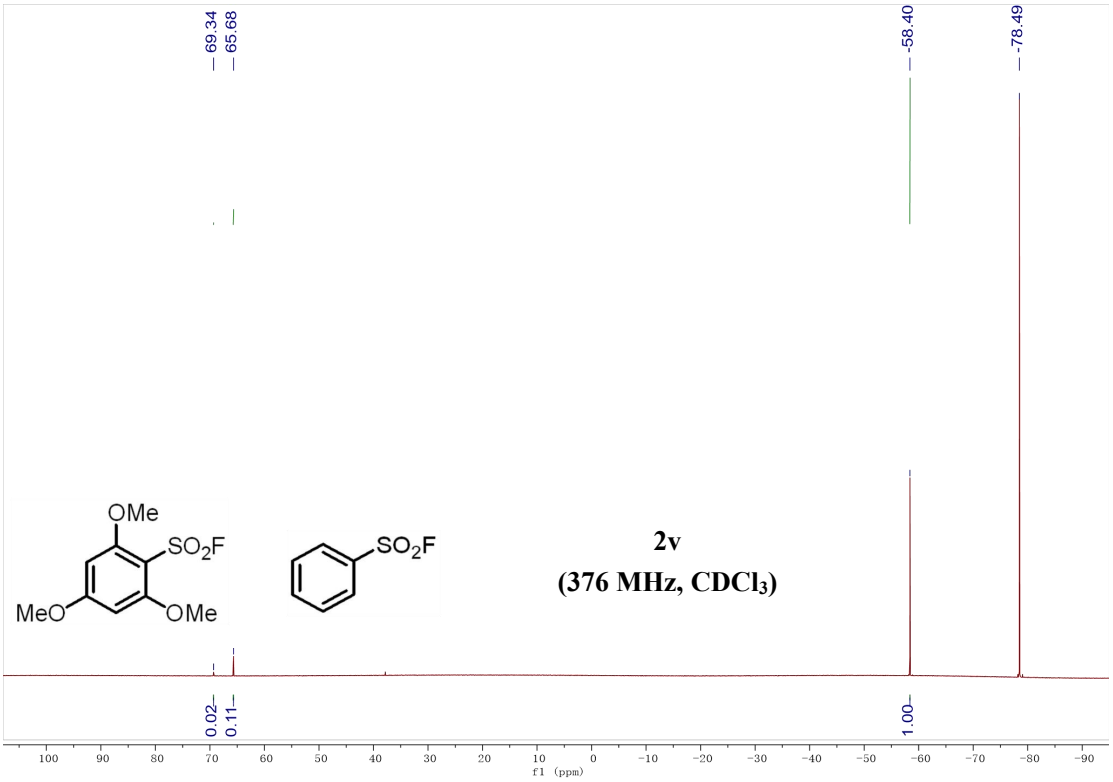


Figure S71. crude ^{19}F NMR spectrum of benzenesulfonyl fluoride and 2,4,6-trimethoxybenzenesulfonyl fluoride

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS DATA REPORT

Instrument: Thermo Fisher Scientific LTQ FTICR-MS

Card Serial Number : D20214535

Sample Serial Number: 2019558-5-13-4

Operator : DONG Date: 2021/09/06

Operation Mode: DART POSITIVE

Elemental composition search on mass 248.2007

m/z= 243.2007-253.2007

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
248.2007	248.2009	-0.77	4.5	$C_{16}H_{26}ON$

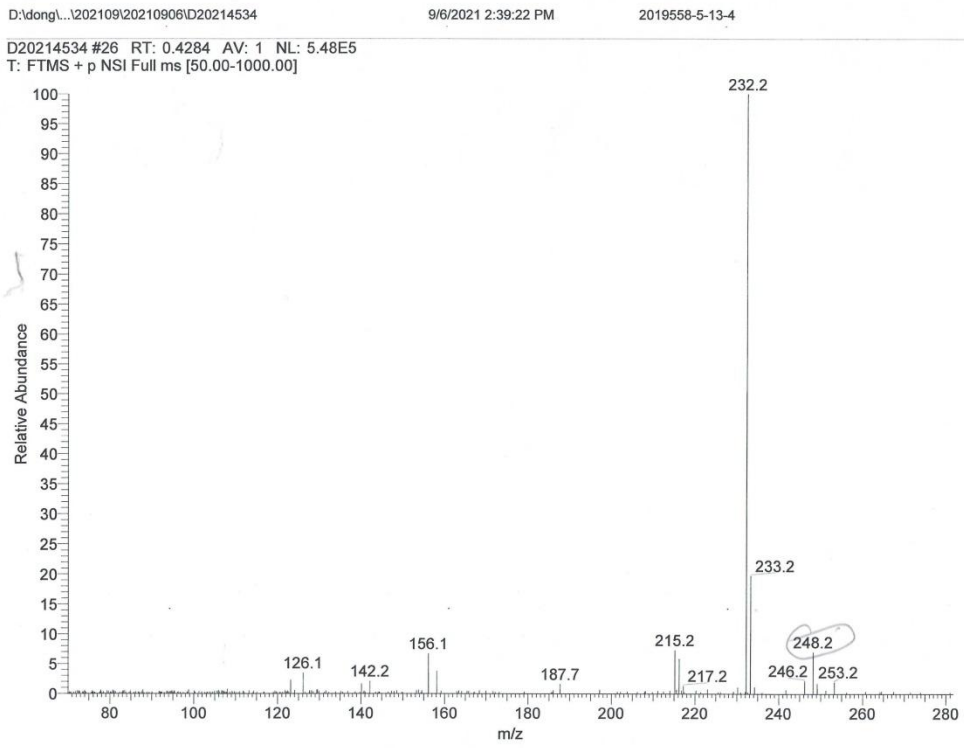


Figure S72. HRMS data of complex **3**

National Center for Organic Mass Spectrometry in Shanghai
Shanghai Institute of Organic Chemistry
Chinese Academic of Sciences
High Resolution MS DATA REPORT

Instrument: Thermo Fisher Scientific LTQ FTICR-MS

Card Serial Number : D20214533

Sample Serial Number: 2019558-5-13-5

Operator : DONG Date: 2021/09/06

Operation Mode: DART POSITIVE

Elemental composition search on mass 268.1694

m/z= 263.1694-273.1694

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
268.1694	268.1696	-0.75	8.5	$C_{18}H_{22}ON$

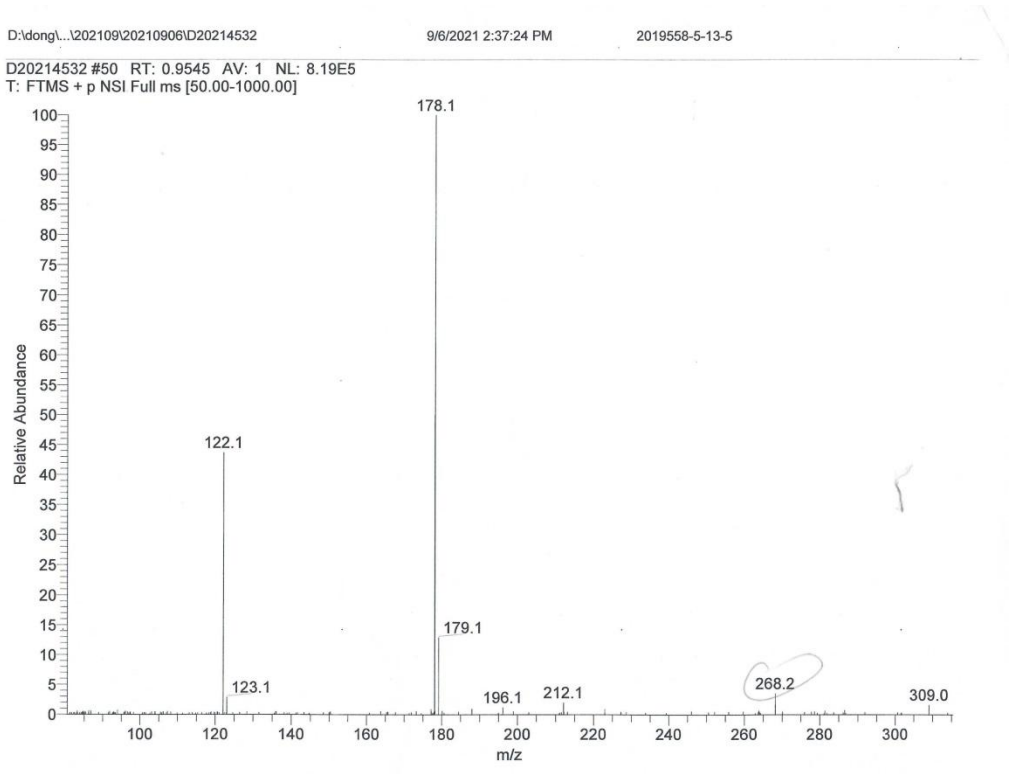
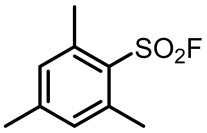


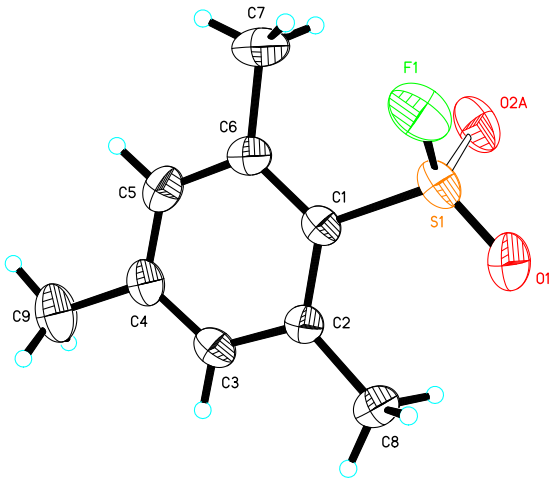
Figure S73. HRMS data of complex **4**

IX. Single crystal structure data of 2,4,6-trimethylbenzenesulfonyl fluoride (2f)



2f

CCDC：2122882



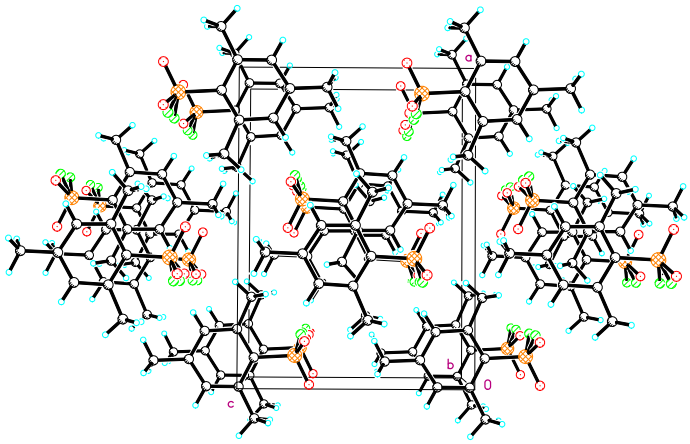


Figure S74. Single crystal structure of 2,4,6-trimethylbenzenesulfonyl fluoride (**2f**)

Table S7. Crystal data and structure refinement for **2f**

Compound	**2f**
Solvent system for crystal growth	petroleum ether / CH_2Cl_2
Identification code	d8v21630
Empirical formula	$C_9H_{11}FO_2S$
Formula weight	202.24
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P n m a
Unit cell dimensions	a = 13.407(2) Å α= 90°
	b = 7.2877(13) Å β= 90°
	c = 9.8840(17) Å γ= 90°
Volume	965.7(3) $Å^3$
Z	4
Density (calculated)	1.391 Mg/m^3
Absorption coefficient	0.314 mm^{-1}
F(000)	424
Crystal size	0.200 x 0.140 x 0.120 mm^3
Theta range for data collection	4.395 to 25.994°.
Index ranges	-16<=h<=15, -8<=k<=8, -10<=l<=12
Reflections collected	4423
Independent reflections	1006 [R(int) = 0.0207]
Completeness to theta = 25.242°	97.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6345
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1006 / 10 / 107
Goodness-of-fit on F^2	1.114
Final R indices [I>2sigma(I)]	R1 = 0.0402, wR2 = 0.1178
R indices (all data)	R1 = 0.0471, wR2 = 0.1253
Extinction coefficient	0.16(4)
Largest diff. peak and hole	0.184 and -0.226 $e.Å^{-3}$

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2f**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
S(1)	5965(1)	2500	7356(1)	72(1)
O(1)	5038(2)	2500	7980(2)	114(1)
F(1)	6669(11)	3990(20)	7641(15)	92(3)
O(2)	6455(15)	4240(20)	7810(17)	86(3)
C(1)	5896(2)	2500	5585(2)	49(1)
C(2)	4965(2)	2500	4938(2)	48(1)
C(3)	4972(2)	2500	3537(2)	57(1)
C(4)	5832(2)	2500	2781(2)	61(1)
C(5)	6732(2)	2500	3453(3)	65(1)
C(6)	6797(2)	2500	4855(3)	58(1)
C(7)	7827(2)	2500	5463(5)	93(1)
C(8)	3959(2)	2500	5624(3)	68(1)
C(9)	5786(4)	2500	1253(3)	96(1)

Table S9. Bond lengths [Å] and angles [°] for **2f**

S(1)-O(1)	1.387(2)
S(1)-F(1)	1.466(16)
S(1)-F(1)#1	1.466(16)
S(1)-O(2)#1	1.495(19)
S(1)-O(2)	1.495(19)
S(1)-C(1)	1.753(2)
C(1)-C(2)	1.402(3)
C(1)-C(6)	1.408(3)
C(2)-C(3)	1.385(3)
C(2)-C(8)	1.510(3)
C(3)-C(4)	1.374(3)
C(3)-H(3)	0.9300
C(4)-C(5)	1.377(4)
C(4)-C(9)	1.512(4)
C(5)-C(6)	1.389(4)
C(5)-H(5)	0.9300
C(6)-C(7)	1.506(4)
C(7)-H(7A)	0.943(19)
C(7)-H(7B)	0.939(17)
C(8)-H(8A)	0.99(2)
C(8)-H(8B)	0.99(4)
C(9)-H(9A)	0.946(17)
C(9)-H(9B)	0.98(2)
O(1)-S(1)-F(1)	119.4(5)
O(1)-S(1)-F(1)#1	119.4(5)
F(1)-S(1)-F(1)#1	95.6(11)
O(1)-S(1)-O(2)#1	105.1(7)
O(1)-S(1)-O(2)	105.1(7)
O(2)#1-S(1)-O(2)	115.6(14)
O(1)-S(1)-C(1)	113.39(12)
F(1)-S(1)-C(1)	103.1(6)
F(1)#1-S(1)-C(1)	103.1(6)
O(2)#1-S(1)-C(1)	108.9(7)
O(2)-S(1)-C(1)	108.9(7)
C(2)-C(1)-C(6)	122.0(2)

C(2)-C(1)-S(1)	120.14(16)
C(6)-C(1)-S(1)	117.82(16)
C(3)-C(2)-C(1)	116.7(2)
C(3)-C(2)-C(8)	117.1(2)
C(1)-C(2)-C(8)	126.2(2)
C(4)-C(3)-C(2)	123.3(2)
C(4)-C(3)-H(3)	118.3
C(2)-C(3)-H(3)	118.3
C(3)-C(4)-C(5)	118.2(2)
C(3)-C(4)-C(9)	120.6(3)
C(5)-C(4)-C(9)	121.2(3)
C(4)-C(5)-C(6)	122.4(2)
C(4)-C(5)-H(5)	118.8
C(6)-C(5)-H(5)	118.8
C(5)-C(6)-C(1)	117.2(2)
C(5)-C(6)-C(7)	117.2(3)
C(1)-C(6)-C(7)	125.6(2)
C(6)-C(7)-H(7A)	109(2)
C(6)-C(7)-H(7B)	113.3(17)
H(7A)-C(7)-H(7B)	115(2)
C(2)-C(8)-H(8A)	113.5(11)
C(2)-C(8)-H(8B)	112.3(19)
H(8A)-C(8)-H(8B)	108.6(17)
C(4)-C(9)-H(9A)	111(2)
C(4)-C(9)-H(9B)	115(3)
H(9A)-C(9)-H(9B)	108(3)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1/2,z

Table S10. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2f**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	82(1)	85(1)	48(1)	0	-13(1)	0
O(1)	101(2)	190(3)	53(1)	0	10(1)	0
F(1)	115(6)	78(4)	83(4)	-31(2)	-30(4)	-5(4)
O(2)	122(7)	67(4)	68(3)	-19(3)	-19(4)	4(3)
C(1)	56(1)	43(1)	48(1)	0	-6(1)	0
C(2)	50(1)	42(1)	53(1)	0	-2(1)	0
C(3)	62(1)	54(1)	55(1)	0	-13(1)	0
C(4)	78(2)	56(1)	49(1)	0	2(1)	0
C(5)	66(1)	61(1)	68(2)	0	17(1)	0
C(6)	51(1)	55(1)	67(1)	0	-4(1)	0
C(7)	53(2)	121(3)	107(3)	0	-15(2)	0
C(8)	54(1)	75(2)	75(2)	0	6(1)	0
C(9)	131(3)	106(3)	51(2)	0	5(2)	0

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **2f**

	x	y	z	U(eq)
H(3)	4364	2500	3085	68
H(5)	7318	2500	2948	78
H(7A)	8300(20)	2500	4760(30)	126(14)
H(8A)	3864(14)	1460(30)	6260(20)	90(7)
H(9A)	5419(19)	1480(30)	930(30)	147(11)
H(7B)	7920(19)	1580(30)	6120(20)	134(11)
H(8B)	3400(30)	2500	4970(40)	96(10)
H(9B)	6440(20)	2500	800(50)	190(20)

Table S12. Torsion angles [°] for **2f**

O(1)-S(1)-C(1)-C(2)	0.000(1)
F(1)-S(1)-C(1)-C(2)	-130.5(5)
F(1)#1-S(1)-C(1)-C(2)	130.5(5)
O(2)#1-S(1)-C(1)-C(2)	116.6(7)
O(2)-S(1)-C(1)-C(2)	-116.6(7)
O(1)-S(1)-C(1)-C(6)	180.000(1)
F(1)-S(1)-C(1)-C(6)	49.5(5)
F(1)#1-S(1)-C(1)-C(6)	-49.5(5)
O(2)#1-S(1)-C(1)-C(6)	-63.4(7)
O(2)-S(1)-C(1)-C(6)	63.4(7)
C(6)-C(1)-C(2)-C(3)	0.000(1)
S(1)-C(1)-C(2)-C(3)	180.000(1)
C(6)-C(1)-C(2)-C(8)	180.000(1)
S(1)-C(1)-C(2)-C(8)	0.000(1)
C(1)-C(2)-C(3)-C(4)	0.000(1)
C(8)-C(2)-C(3)-C(4)	180.000(1)
C(2)-C(3)-C(4)-C(5)	0.000(1)
C(2)-C(3)-C(4)-C(9)	180.000(1)
C(3)-C(4)-C(5)-C(6)	0.000(1)
C(9)-C(4)-C(5)-C(6)	180.000(1)
C(4)-C(5)-C(6)-C(1)	0.000(1)
C(4)-C(5)-C(6)-C(7)	180.000(1)
C(2)-C(1)-C(6)-C(5)	0.000(1)
S(1)-C(1)-C(6)-C(5)	180.000(1)
C(2)-C(1)-C(6)-C(7)	180.000(1)
S(1)-C(1)-C(6)-C(7)	0.000(1)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1/2,z

Table S13. Hydrogen bonds for **2f** [Å and °]

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