Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Electrochemical Synthesis of Sulfonyl Fluorides from Sulfonyl Hydrazides

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Contents

1. General information

All the chemicals used were of analytical grade or the highest purity available. Most of the chemicals were purchased from Sigma Aldrich (USA), TCI and Alfa Aesar and used as received without further purification. The solvents for analysis used HPLC-grade, and tertiary distilled water was used. Analytical thin layer chromatography (TLC) was performed on TLC Silica gel 60 F_{254}. The TLC plate were visualized by short-wave (254 nm) or long-wave (360 nm) UV light. Flash chromatography on silica gel (230-400 mesh) was performed. ^{1}H NMR (500 MHz), ^{13}C NMR (126 MHz), and ^{19}F NMR (470 MHz) spectra were recorded in $CDCl_3$. ^{1}H NMR spectra are reported in parts per million (ppm) downfield relative to $CDCl_3$ (7.26 ppm) and all ^{13}C NMR spectra are reported in ppm relative to $CDCl_3$ (77.16 ppm). ^{1}H NMR, ^{13}C NMR and ^{19}F NMR assignment abbreviations are the following; singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), triplet of doublets (td), doublet of a triplets (dt), doublet of doublet of doublet (ddd) and multiplet (m).

2. Electrochemical apparatus and Electrode materials

All reactions for sulfonyl fluoride were performed using an **ElectraSyn 2.0 Pro** from IKA. [Figure S1. (a)] The graphite SK-50 plated electrodes (8 mm × 2mm × 52 mm) and the Nickel plated electrodes (8 mm × 2 mm × 52 mm) were furnished from IKA. [Figure S1. (b)]

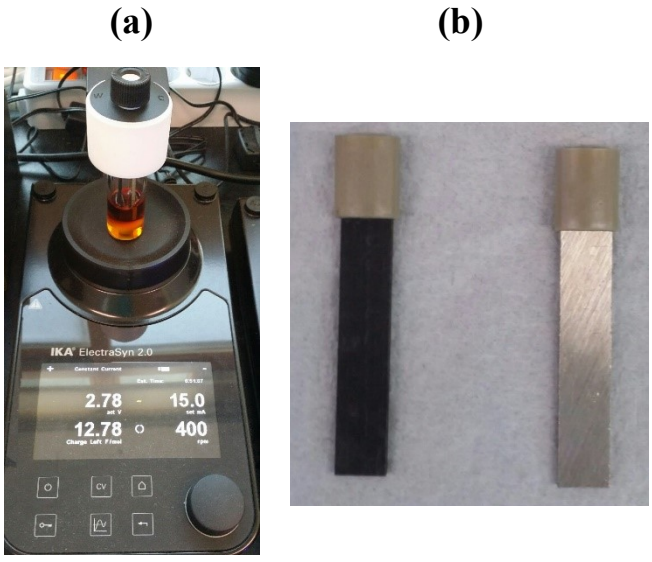
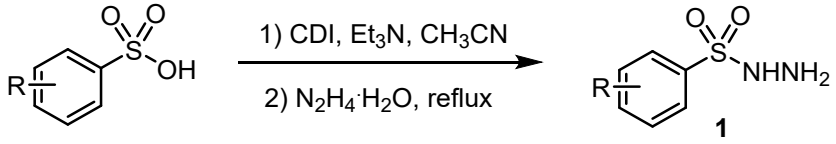


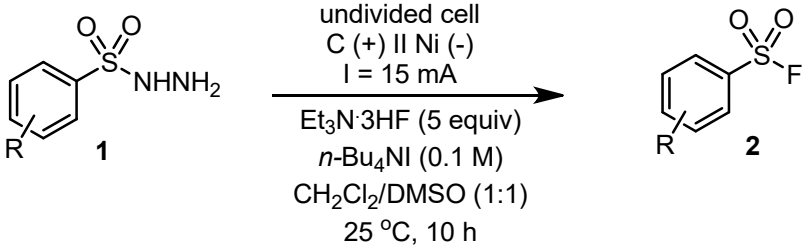
Figure S1. (a) ElectraSyn 2.0 Pro purchased from IKA. (b) Graphite SK-50 plated electrode (left side) (IKA) and nickel plated electrode (right side) (IKA).

3. Experimental Procedures for arylsulfonyl hydrazides.



Arylsulfonic acids (1 mmol), triethylamine (1.2 mmol) and 1,1'-carbonyldiimidazole (1.0 mmol) mixed in acetonitrile (5.0 mL) and reflux for 30 min. Then, eighty percent hydrazine hydrate (2.5 mmol) was added into the reaction mixture and reflux for 6 h. The resulting mixture was diluted with ethyl acetate, and washed with distilled water, and the organic layer was separated and dried over $MgSO_4$. The organic layer was concentrated, and added to petroleum ether and stirred for 30 min. The formed precipitates were filtered and washed with water and then with *n*-hexane. The collected solid was dried in vacuum. The yields for the formation of arylsulfonyl hydrazides range from 51% to 82%.

4. General procedure for the synthesis of sulfonyl fluoride (2)



Graphite (anode) and nickel (cathode) plated electrodes were connected accordingly to an ElectraSyn vial cap. To a clean and dry 10 mL ElectraSyn vial was added sulfonyl hydrazide **1** (0.3 mmol), $Et_3N{\cdot}3HF$ (1.5 mmol), followed by 0.1 M *n*-Bu_4NI in CH_2Cl_2 (2.5 mL)/DMSO (2.5 mL) under air. The electrolyte was allowed to stir and the reaction was carried out at a constant current of 15 mA at 25 °C for 10 h (**2q** was carried out at 1 mA, **2r** and **2s** were carried out at 10 mA). After the reaction, the mixture was extracted with ethyl acetate (1 x 30 mL). The combined organic layers were washed with brine, dried over anhydride $MgSO_4$, filtered and the solvent was removed under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel. The product **2** was eluted with mixture of ethyl acetate and hexane.

5. Cyclic Voltammetry

Cyclic voltammogram of substrate (0.1 M *n*-Bu_4NBF_4 in DMSO was used as an electrolyte) was recorded using Smart Interface Software for WBCS300Le potentiostat at a scan rate of 50 mV/s with a 3.0 mm glassy carbon working electrode, a platinum wire counter electrode, and an Ag/AgCl (3.0 M KClaq) reference electrode. The oxidation peak Ep was determined within -2.0 to 2.0 V potential range (to be + 2.2 V). [**Figure S2**]

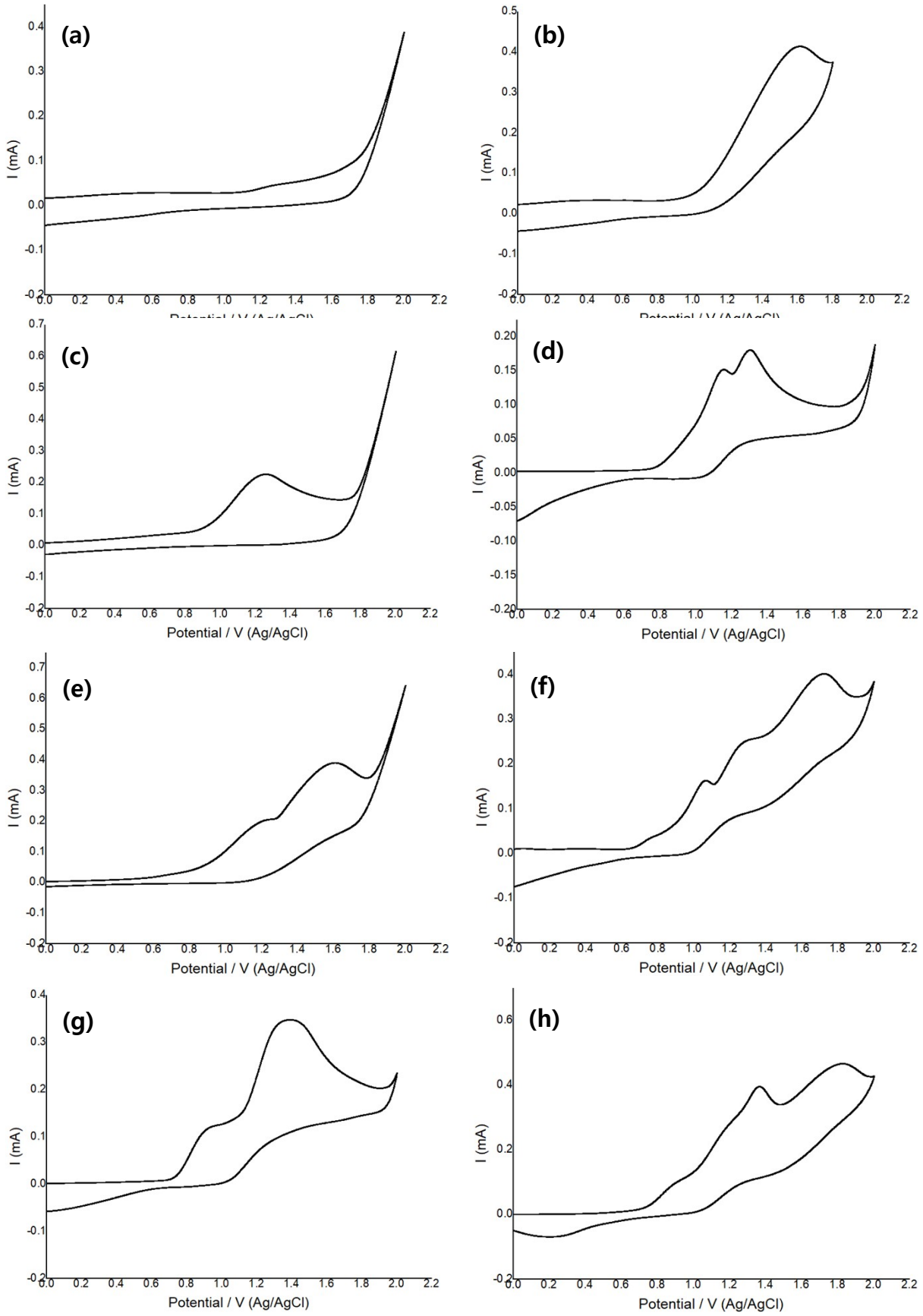
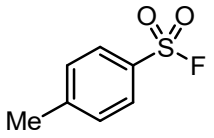

(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
I (mA)
Potential / V (Ag/AgCl)

Figure S2. Cyclic voltammograms of 0.1 M *n*-Bu_4NBF_4 in DMSO, using glassy carbon electrode (d = 3.0 mm) as a working electrode, a platinum wire as a counter electrode and Ag/AgCl as a reference electrode, at a scan rate of 50 mV/s; (a) background; (b) 0.02 M of **1a**; (c) 0.025 M of $Et_3N{\cdot}3HF$; (d) 0.02 M of *n*-Bu_4NI; (e) 0.02 M of **1a** + 0.025 M of $Et_3N{\cdot}3HF$; (f) 0.02 M of **1a** + 0.02 M of *n*-Bu_4NI; (g) 0.025 M of $Et_3N{\cdot}3HF$ + 0.02 M of *n*-Bu_4NI; (h) 0.02 M of **1a** + 0.025 M of $Et_3N{\cdot}3HF$ + 0.02 M of *n*-Bu_4NI.

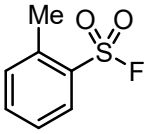
In **Figure S2**. Curve b: the oxidation peak of *p*-tolylsulfonyl hydrazide, **1a** (E_p = 1.61 V *vs.* Ag/AgCl); curve c: the oxidation peak of $Et_3N{\cdot}3HF$ (E_p = 1.26 V *vs.* Ag/AgCl); curve d: the oxidation peak of *n*-Bu_4NI (E_p = 1.16 V, 1.30 V *vs.* Ag/AgCl); curve e: the oxidation peak of **1a** + $Et_3N{\cdot}3HF$ (E_p = 1.25 V, 1.61 V *vs.* Ag/AgCl); curve f: the oxidation peak of **1a** + *n*-Bu_4NI (E_p = 1.07 V, 1.33 V, 1.72 V *vs.* Ag/AgCl); curve g: the oxidation peak of $Et_3N{\cdot}3HF$ + *n*-Bu_4NI (E_p = 0.94 V, 1.39 V *vs.* Ag/AgCl); curve h: the oxidation peak of **1a** + $Et_3N{\cdot}3HF$ + *n*-Bu_4NI (E_p = 1.36 V, 1.82 V *vs.* Ag/AgCl).

6. Analytical data



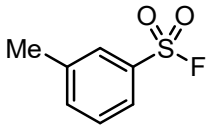
4-Methylbenzenesulfonyl fluoride (**2a**)[1]

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (100:1) and obtained as a white solid (44.9 mg, 0.26 mmol, 86%).
m.p. 39–41 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90–7.89 (m, 2H), 7.43–7.41 (m, 2H), 2.49 (s, 3H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 147.2, 130.4, 130.2 (d, J = 23.9 Hz), 128.6, 22.0;
^{19}F NMR (470 MHz, $CDCl_3$) δ 66.2 (s, 1F);
MS (EI) m/z = 174.0 (M^+)



2-Methylbenzenesulfonyl fluoride (**2b**)[1]

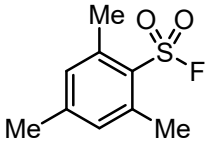
According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (250:1) and obtained as a colorless oil (42.9 mg, 0.25 mmol, 82%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, J = 8.0 Hz, 1H), 7.63 (td, J = 7.6, 1.3 Hz, 1H), 7.44–7.39 (m, 2H), 2.70 (s, 3H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 139.2, 135.4, 133.0, 132.5 (d, J = 22.7 Hz), 130.2 (d, J = 1.7 Hz), 126.8, 20.4 (d, J = 1.2 Hz);
^{19}F NMR (470 MHz, $CDCl_3$) δ 60.3 (s, 1F);
MS (EI) m/z = 174.0 (M^+)



3-Methylbenzenesulfonyl fluoride (**2c**)[1]

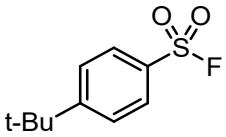
According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (250:1) and obtained as a colorless oil (47.0 mg, 0.27 mmol, 90%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83–7.80 (m, 2H), 7.59–7.56 (m, 1H), 7.53–7.49 (m, 1H), 2.48 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.3, 136.5, 133.1 (d, J = 23.8 Hz), 129.6, 128.8, 125.7, 21.4;
^{19}F NMR (470 MHz, $CDCl_3$) δ 65.8 (s, 1F);
MS (EI) m/z = 174.0 (M^+)



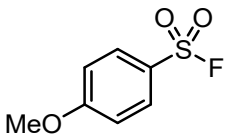
2,4,6-Trimethylbenzenesulfonyl fluoride (**2d**)[2]

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (450:1) and obtained as a white solid (53.4 mg, 0.26 mmol, 88%).
m.p. 70–72 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (s, 2H), 2.64 (d, J = 1.5 Hz, 6H), 2.35 (s, 3H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 145.2, 140.2, 132.0, 129.2 (d, J = 20.4 Hz), 22.5 (d, J = 1.7 Hz), 21.3;
^{19}F NMR (470 MHz, $CDCl_3$) δ 68.2 (s, 1F);
MS (EI) m/z = 202.0 (M^+)



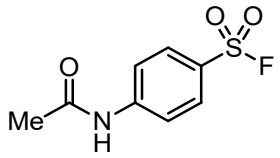
4-*tert*-Butyl-benzenesulfonyl fluoride (**2e**)[1]

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (350:1) and obtained as a white solid (55.8 mg, 0.26 mmol, 86%).
m.p. 61–63 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95–7.92 (m, 2H), 7.64–7.62 (m, 2H), 1.37 (s, 9H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 130.1 (d, J = 24.2 Hz), 128.5, 126.8, 35.7, 31.1;
^{19}F NMR (470 MHz, $CDCl_3$) δ 66.2 (s, 1F);
MS (EI) m/z = 216.1 (M^+)



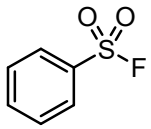
4-Methoxybenzenesulfonyl fluoride (**2f**)[1]

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (100:1) and obtained as a pale yellow oil (49.1 mg, 0.26 mmol, 86%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96–7.93 (m, 2H), 7.08–7.05 (m, 2H), 3.92 (s, 3H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 165.3, 131.0, 124.3 (d, J = 24.8 Hz), 115.0, 56.1;
^{19}F NMR (470 MHz, $CDCl_3$) δ 67.2 (s, 1F);
MS (EI) m/z = 190.0 (M^+)



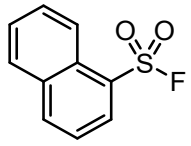
4-(Acetylamino)benzenesulfonyl fluoride (2g)[1]

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (2:1) and obtained as a white solid (58.0 mg, 0.27 mmol, 89%).
m.p. 173–175 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 8.8 Hz, 2H), 7.79 (d, J = 8.7 Hz, 2H), 7.56 (s, 1H), 2.25 (s, 3H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 168.8, 144.6, 130.2, 127.3 (d, J = 24.9 Hz), 119.5, 25.0;
^{19}F NMR (470 MHz, $CDCl_3$) δ 66.7 (s, 1F);
MS (EI) m/z = 217.0 (M^+)



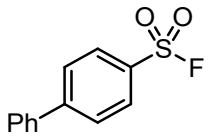
Benzenesulfonyl fluoride (2h)[1]

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (200:1) and obtained as a colorless oil (35.6 mg, 0.22 mmol, 74%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04–8.01 (m, 2H), 7.81–7.77 (m, 1H), 7.66–7.62 (m, 2H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 135.7, 133.3 (d, J = 24.4 Hz), 129.8, 128.6;
^{19}F NMR (470 MHz, $CDCl_3$) δ 65.8 (s, 1F);
MS (EI) m/z = 160.0 (M^+)



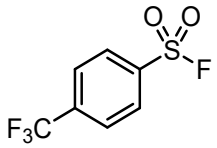
1-Naphthalenesulfonyl fluoride (2i)[2]

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (200:1) and obtained as a white solid (47.3 mg, 0.23 mmol, 75%).
m.p. 51–53 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56–8.54 (m, 1H), 8.38–8.36 (m, 1H), 8.24 (d, *J* = 8.3 Hz, 1H), 8.01–7.99 (m, 1H), 7.78 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.69 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 7.63–7.60 (m, 1H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 137.1, 134.2, 131.2 (d, *J* = 1.9 Hz), 129.7, 129.3, 129.2 (d, *J* = 23.5 Hz), 128.4, 127.9, 124.3, 124.2;
^{19}F NMR (470 MHz, $CDCl_3$) δ 62.6 (s, 1F);
MS (EI) m/z = 210.0 (M^+)



4-Biphenylsulfonyl fluoride (2j)[3]

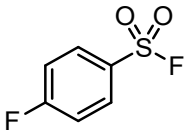
According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (300:1) and obtained as a white solid (62.4 mg, 0.26 mmol, 88%).
m.p. 79–81 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09–8.07 (m, 2H), 7.84–7.81 (m, 2H), 7.64–7.62 (m, 2H), 7.53–7.45 (m, 3H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 148.8, 138.7, 131.5 (d, *J* = 24.6 Hz), 129.4, 129.3, 129.1, 128.3, 127.6;
^{19}F NMR (470 MHz, $CDCl_3$) δ 66.5 (s, 1F);
MS (EI) m/z = 236.0 (M^+)



4-(Trifluoromethyl)benzenesulfonyl fluoride (2k)[3]

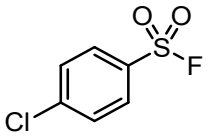
According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (300:1) and obtained as a white solid (42.4 mg, 0.19 mmol, 62%).
m.p. 66–68 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.5 Hz, 2H), 7.92 (d, *J* = 8.7 Hz, 2H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 137.3 (d, *J* = 33.7 Hz), 136.7 (d, *J* = 26.4 Hz), 129.3, 127.0 (q, *J* = 3.7 Hz), 122.9 (q, *J* = 273.4 Hz);
^{19}F NMR (470 MHz, $CDCl_3$) δ 65.9 (s, 1F), -63.5 (s, 3F);

MS (EI) m/z = 228.0 (M^+)



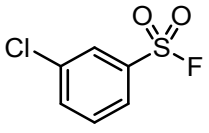
4-Fluorobenzenesulfonyl fluoride (**2l**)[1]

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (250:1) and obtained as a colorless oil (33.7 mg, 0.19 mmol, 63%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08–8.04 (m, 2H), 7.34–7.30 (m, 2H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0 (d, J = 260.5 Hz), 131.7 (d, J = 10.1 Hz), 129.2 (dd, J = 25.7, 3.2 Hz), 137.3 (d, J = 33.7 Hz);
^{19}F NMR (470 MHz, $CDCl_3$) δ 66.7 (s, 1F), -99.3 (s, 1F);
MS (EI) m/z = 178.0 (M^+)



4-Chlorobenzenesulfonyl fluoride (**2m**)[1]

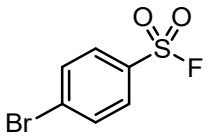
According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (350:1) and obtained as a white solid (47.9 mg, 0.25 mmol, 82%).
m.p. 47–49 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 8.6 Hz, 2H), 7.62 (d, J = 8.2 Hz, 2H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.8, 131.6 (d, J = 25.8 Hz), 130.3, 130.0;
^{19}F NMR (470 MHz, $CDCl_3$) δ 66.5 (s, 1F);
MS (EI) m/z = 194.0 (M^+)



3-Chlorobenzenesulfonyl fluoride (**2n**)[4]

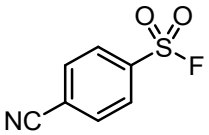
According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (350:1) and obtained as a colorless oil (41.5 mg, 0.21 mmol, 71%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01–8.00 (m, 1H), 7.93–7.90 (m, 1H), 7.77–7.74 (m, 1H), 7.61–7.58 (m, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 136.2, 135.9, 134.7 (d, J = 25.8 Hz), 131.1, 128.6, 126.7;
^{19}F NMR (470 MHz, $CDCl_3$) δ 66.1 (s, 1F);
MS (EI) m/z = 194.0 (M^+)



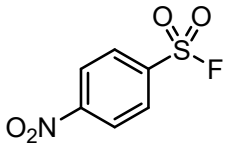
4-Bromobenzenesulfonyl fluoride (2o)[1]

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (400:1) and obtained as a white solid (52.4 mg, 0.22 mmol, 73%).
m.p. 63–65 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89–7.86 (m, 2H), 7.80–7.77 (m, 2H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 133.3, 132.1 (d, J = 25.8 Hz), 131.5, 130.0;
^{19}F NMR (470 MHz, $CDCl_3$) δ 66.4 (s, 1F);
MS (EI) m/z = 237.9 (M^+)



4-Cyanobenzenesulfonyl fluoride (2p)[5]

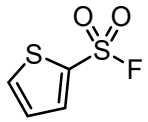
According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (12:1) and obtained as a white solid (33.3 mg, 0.18 mmol, 60%).
m.p. 88–90 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, J = 8.6 Hz, 2H), 7.95 (d, J = 8.1 Hz, 2H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 137.1 (d, J = 26.8 Hz), 133.5, 129.3, 119.6, 116.6;
^{19}F NMR (470 MHz, $CDCl_3$) δ 66.0 (s, 1F);
MS (EI) m/z = 185.0 (M^+)



4-Nitrobenzenesulfonyl fluoride (2q)[5]

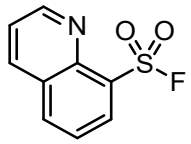
According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (100:1) and obtained as a white solid (22.8 mg, 0.11 mmol, 37%).
m.p. 74–76 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50–8.48 (m, 2H), 8.26–8.23 (m, 2H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 151.9, 138.5 (d, *J* = 27.1 Hz), 130.1, 125.0;
^{19}F NMR (470 MHz, $CDCl_3$) δ 66.2 (s, 1F);
MS (EI) m/z = 205.0 (M^+)



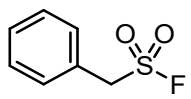
2-Thiophenesulfonyl fluoride (**2r**)[2]

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (100:1) and obtained as a yellow oil (34.4 mg, 0.21 mmol, 69%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dt, *J* = 3.9, 1.3 Hz, 1H), 7.88 (ddd, *J* = 5.0, 1.3, 0.3 Hz, 1H), 7.24 (ddd, *J* = 4.9, 3.9, 0.9 Hz, 1H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 137.0, 136.6 (d, *J* = 2.0 Hz), 131.7 (d, *J* = 30.9 Hz), 128.3;
^{19}F NMR (470 MHz, $CDCl_3$) δ 71.7 (s, 1F);
MS (EI) m/z = 166.0 (M^+)



8-Quinolinesulfonyl fluoride (**2s**)[6]

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (4:1) and obtained as a white solid (48.8 mg, 0.23 mmol, 77%).
m.p. 119–121 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.19 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.52 (dd, *J* = 7.4, 1.3 Hz, 1H), 8.32 (dd, *J* = 8.3, 1.6 Hz, 1H), 8.23 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.73–7.70 (m, 1H), 7.63 (dd, *J* = 8.3, 4.2 Hz, 1H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 152.8, 143.9, 136.8, 136.3, 133.3 (d, *J* = 1.9 Hz), 131.5 (d, *J* = 21.3 Hz), 129.2, 125.4, 123.2;
^{19}F NMR (470 MHz, $CDCl_3$) δ 60.3 (s, 1F);
MS (EI) m/z = 211.0 (M^+)



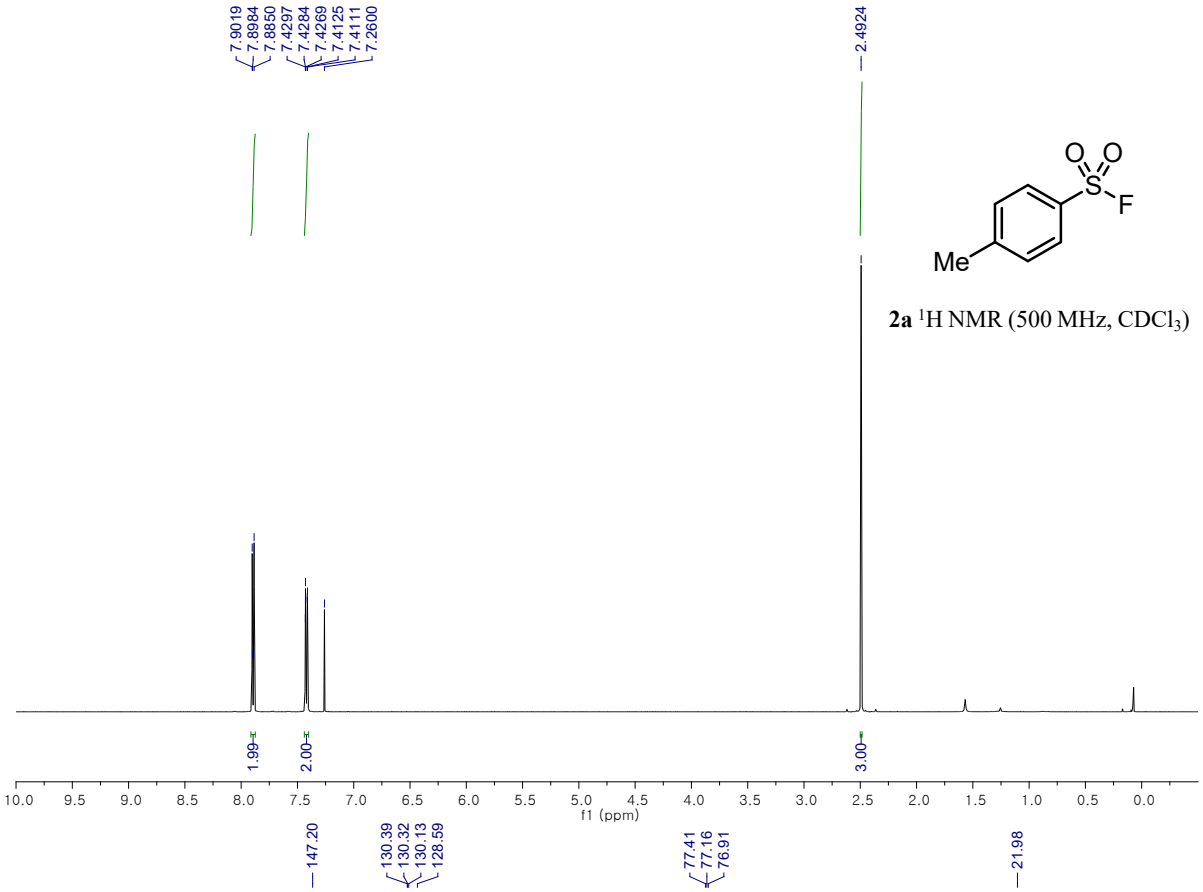
Phenylmethanesulfonyl fluoride (**2t**)[1]

According to the general procedure, the product was purified by chromatography on silica gel eluting with *n*-hexane/EtOAc (250:1) and obtained as a white solid (36.6 mg, 0.21 mmol, 70%).
m.p. 91–93 ^{o}C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.42 (m, 5H), 4.60 (d, J = 3.2 Hz, 2H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 130.8, 130.1, 129.5, 125.6, 57.0 (d, J = 17.7 Hz);
^{19}F NMR (470 MHz, $CDCl_3$) δ 51.4 (t, J = 3.1 Hz, 1F);
MS (EI) m/z = 174.0 (M^+)

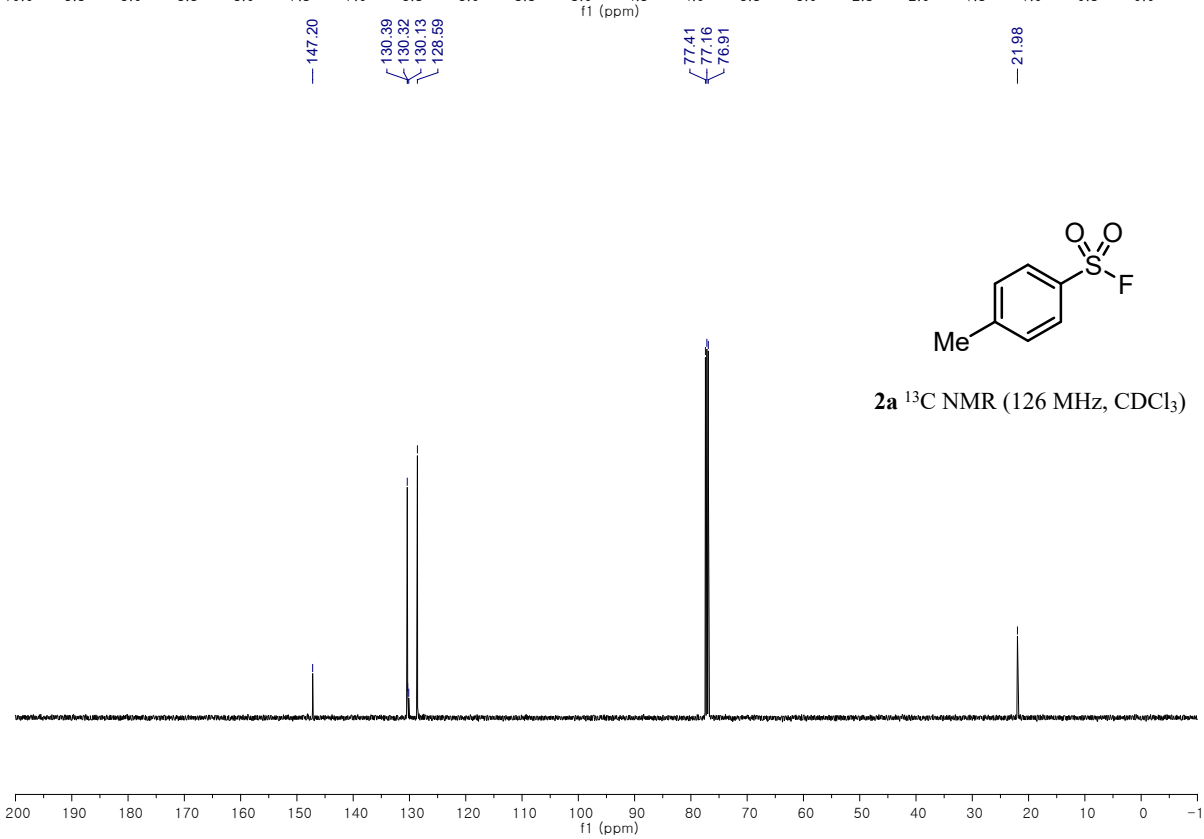
7. References

(1) G. Laudadio, A. de A. Bartolomeu, L. M. H. M. Verwijlen, Y. Cao, K. T. de Oliveira and T. Noël, Sulfonyl Fluoride Synthesis through Electrochemical Oxidative Coupling of Thiols and Potassium Fluoride, *J. Am. Chem. Soc.,* 2019, **141**, 11832-11836.
(2) C. Lee, N. D. Ball and G. M. Sammis, One-pot fluorosulfurylation of Grignard reagents using sulfuryl fluoride, *Chem. Commun.,* 2019, **55**, 14753-14756.
(3) L. Wang and J. Cornella, A Unified Strategy for Arylsulfur(VI) Fluorides from Aryl Halides: Access to Ar-SOF_3 Compounds, *Angew. Chem. Int. Ed.,* 2020, **59**, 23510-23515.
(4) M. Pérez-Palau and J. Cornella, Synthesis of Sulfonyl Fluorides from Sulfonamides, *Eur. J. Org. Chem.,* 2020, **2020**, 2497-2500.
(5) T. Zhong, M.-K. Pang, Z.-D. Chen, B. Zhang, J. Weng and G. Lu, Copper-free Sandmeyer-type Reaction for the Synthesis of Sulfonyl Fluorides, *Org. Lett.,* 2020, **22**, 3072-3078.
(6) P. Chatelain, C. Muller, A. Sau, D. Brykczyńska, M. Bahadori, C. N. Rowley and J. Moran, Desulfonative Suzuki–Miyaura Coupling of Sulfonyl Fluorides, *Angew. Chem. Int. Ed.,* 2021, **60**, 25307-25312.

8. ^{1}H, ^{13}C and ^{19}F NMR spectra of products

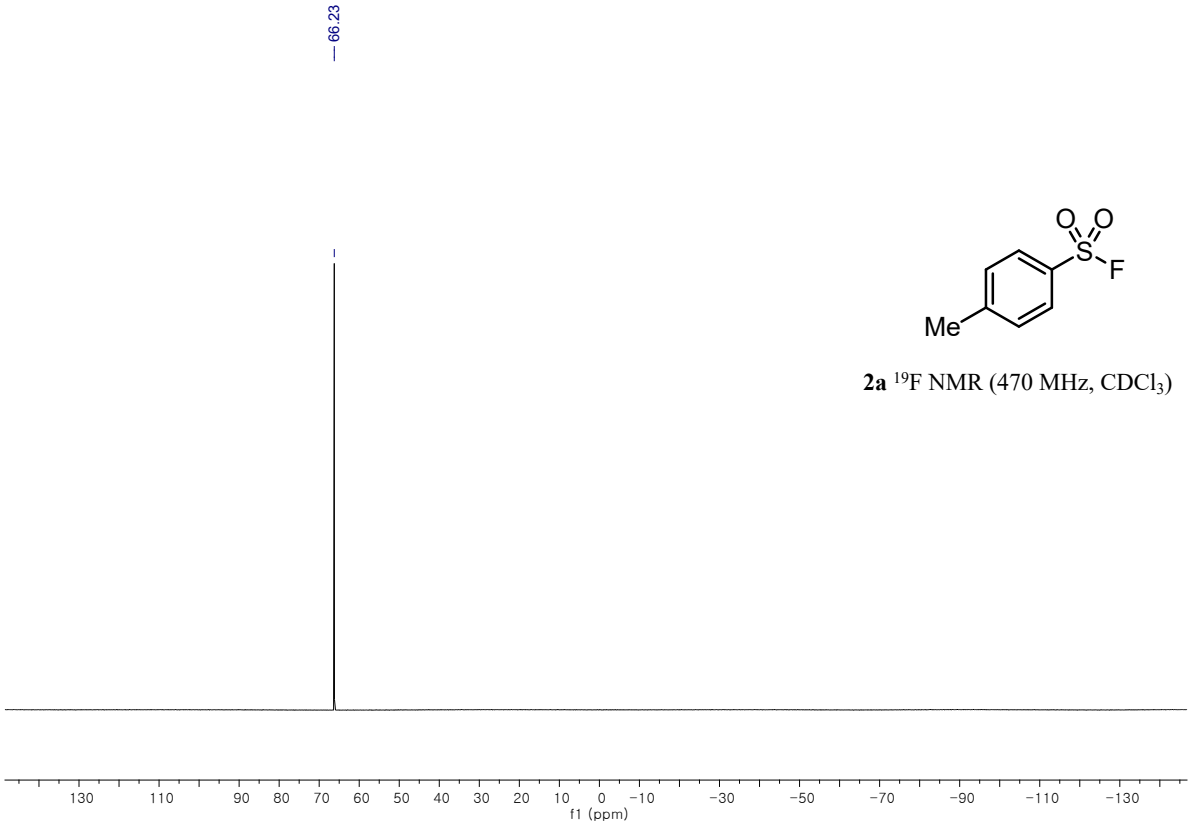


2a ^{1}H NMR (500 MHz, $CDCl_3$)



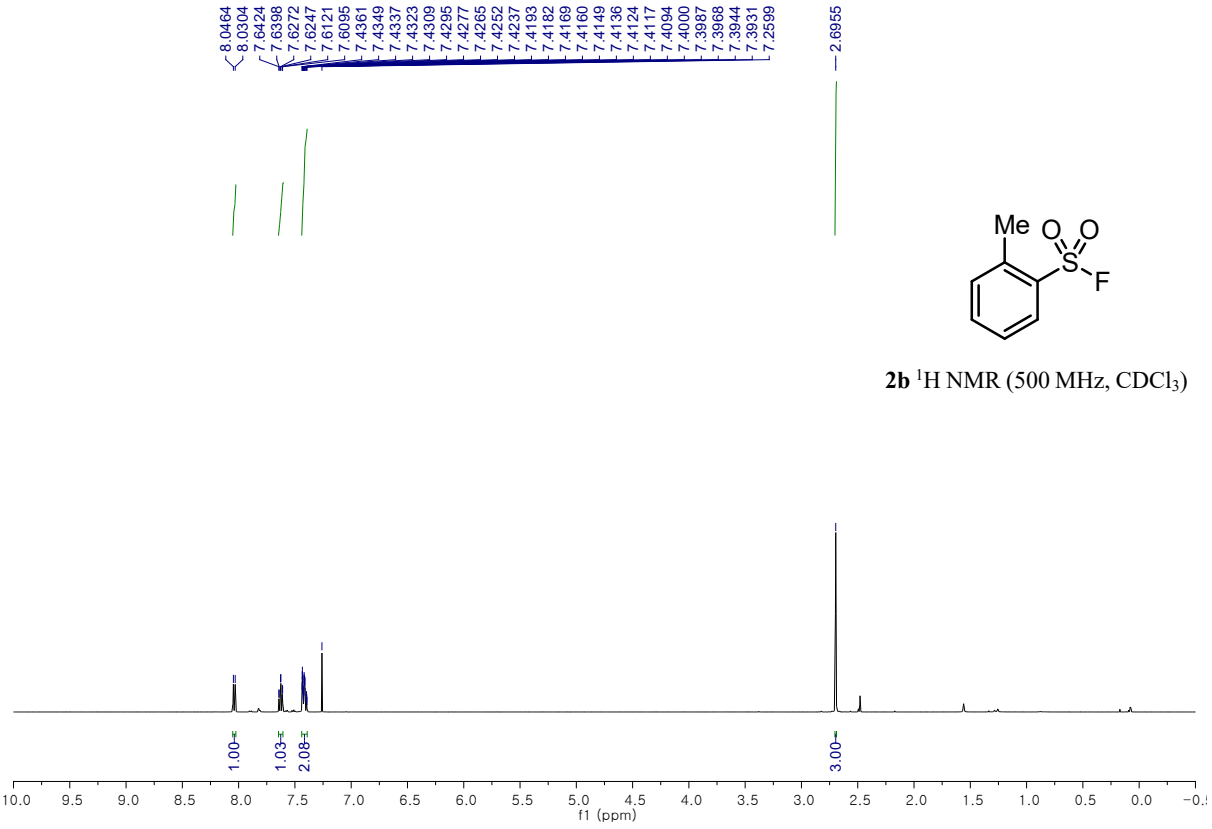
2a ^{13}C NMR (126 MHz, $CDCl_3$)

4-Methylbenzenesulfonyl fluoride (2a)

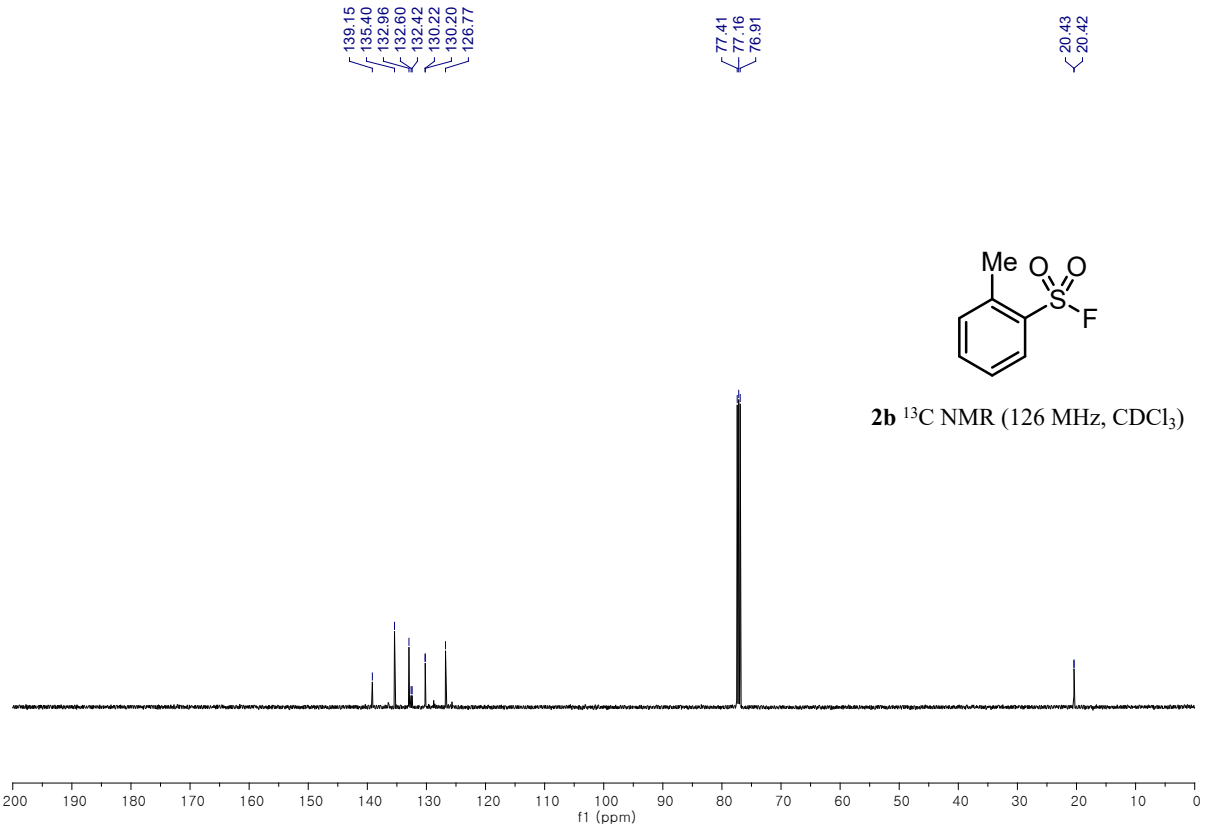


2a ^{19}F NMR (470 MHz, $CDCl_3$)

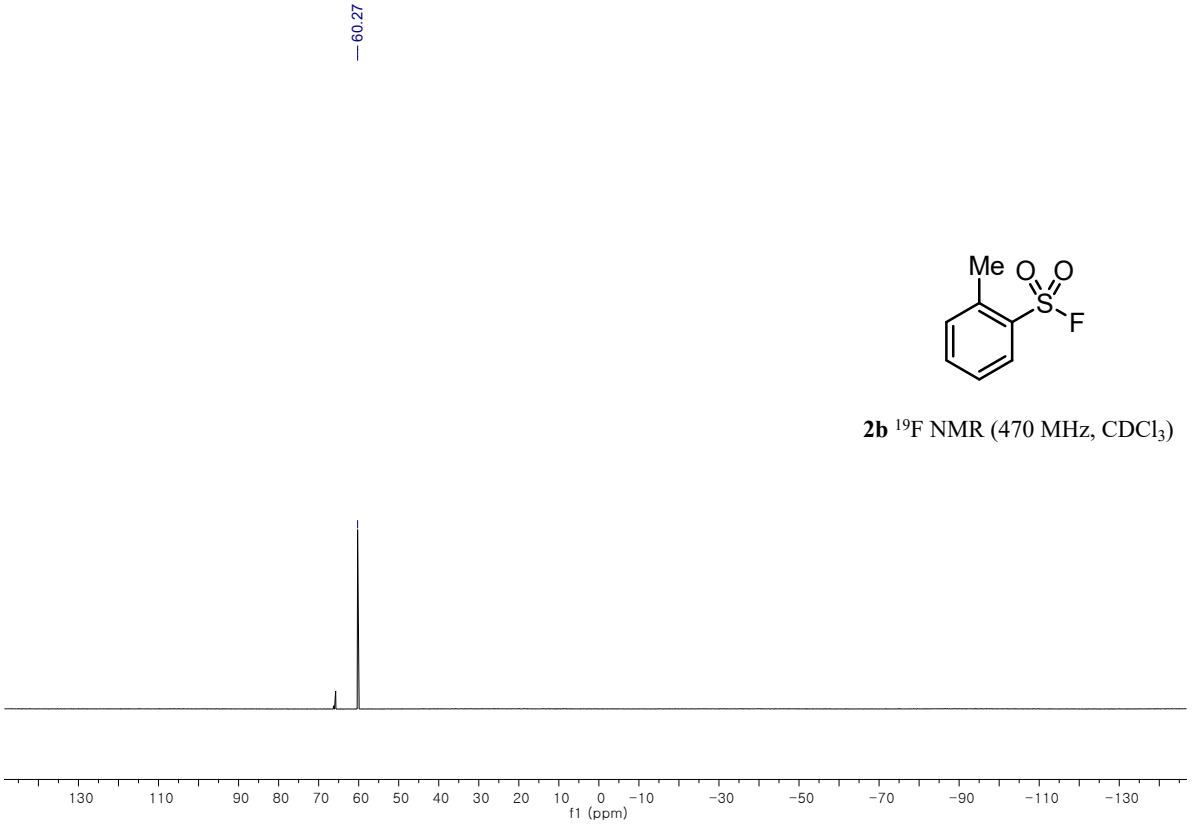
2-Methylbenzenesulfonyl fluoride (2b)



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

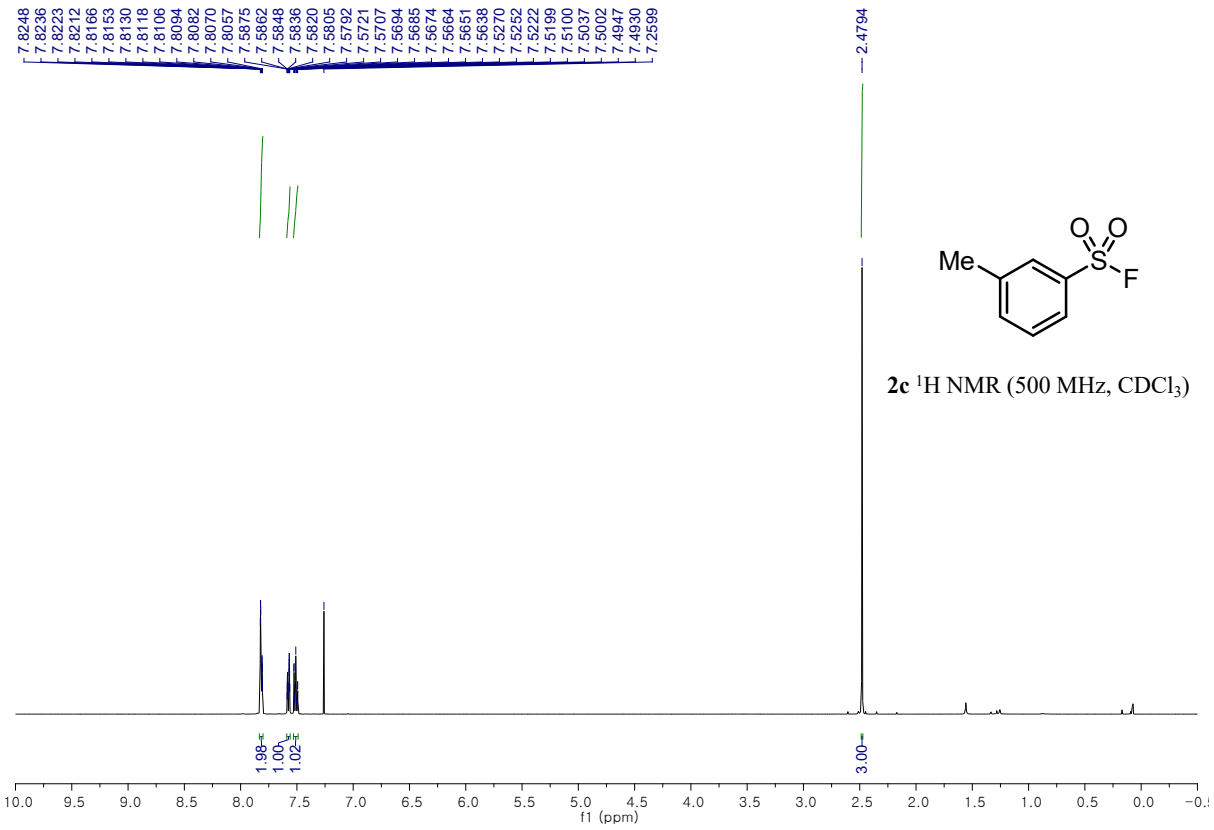


2b ^{13}C NMR (126 MHz, $CDCl_3$)

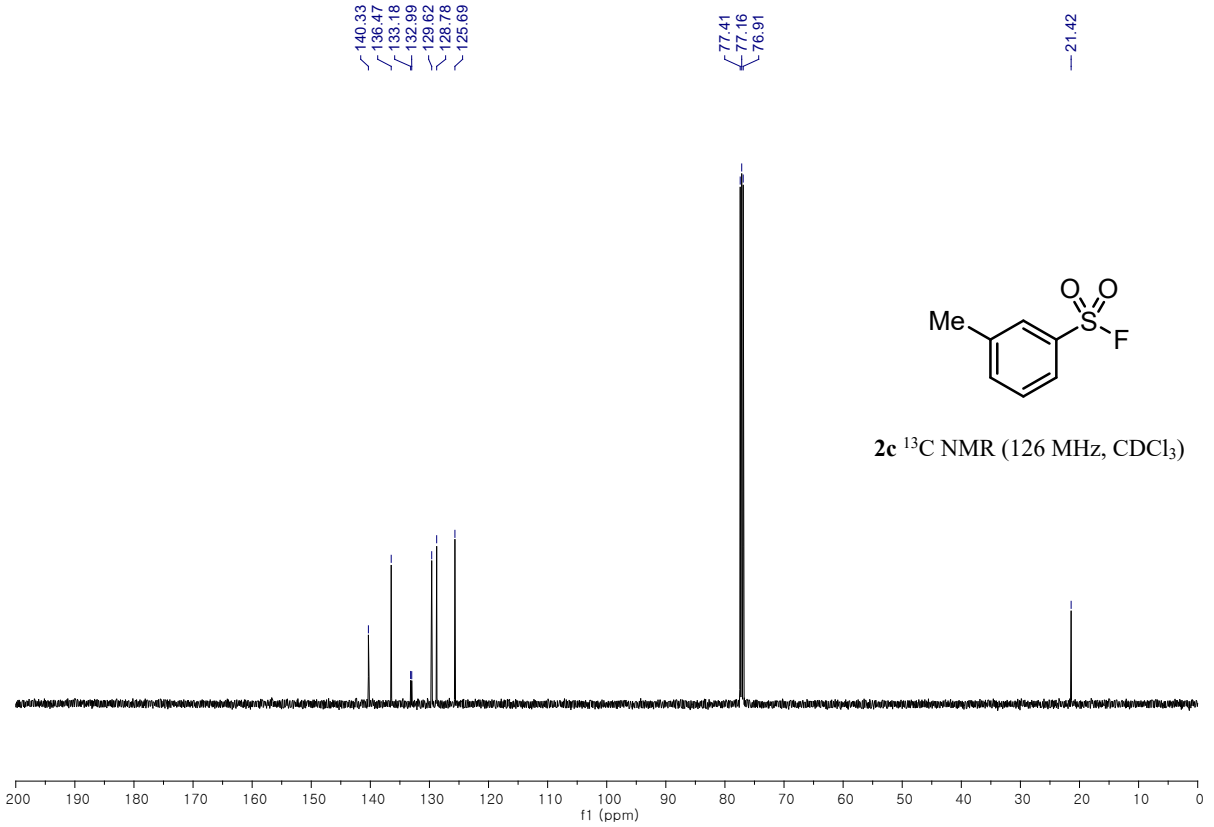


2b ^{19}F NMR (470 MHz, $CDCl_3$)

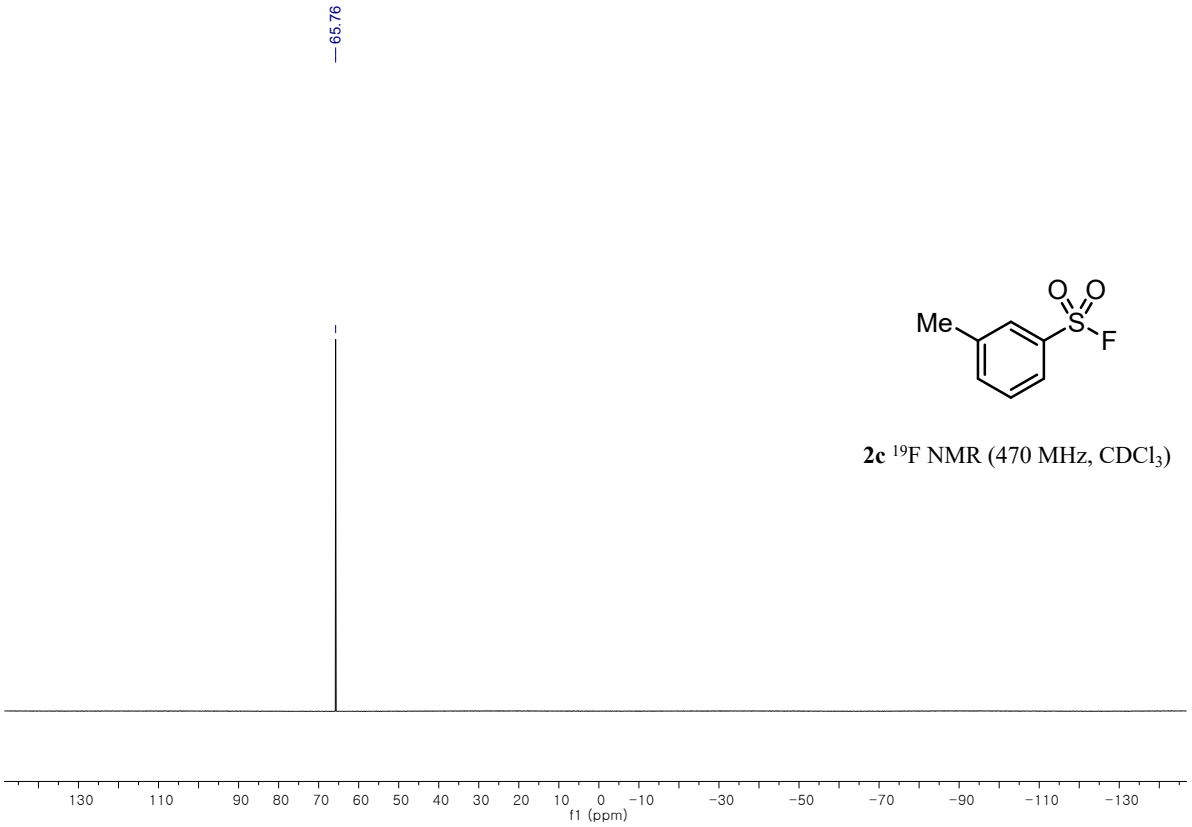
3-Methylbenzenesulfonyl fluoride (2c)



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

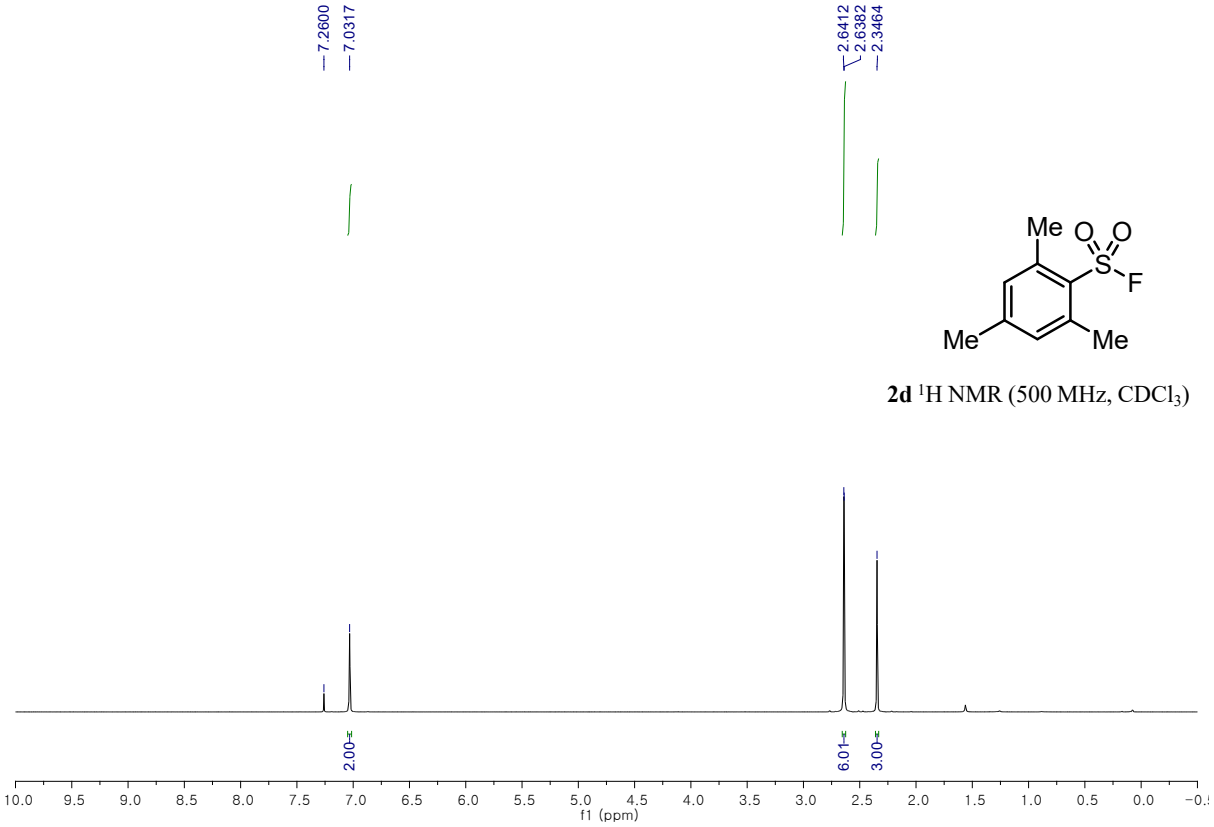


2c ^{13}C NMR (126 MHz, $CDCl_3$)

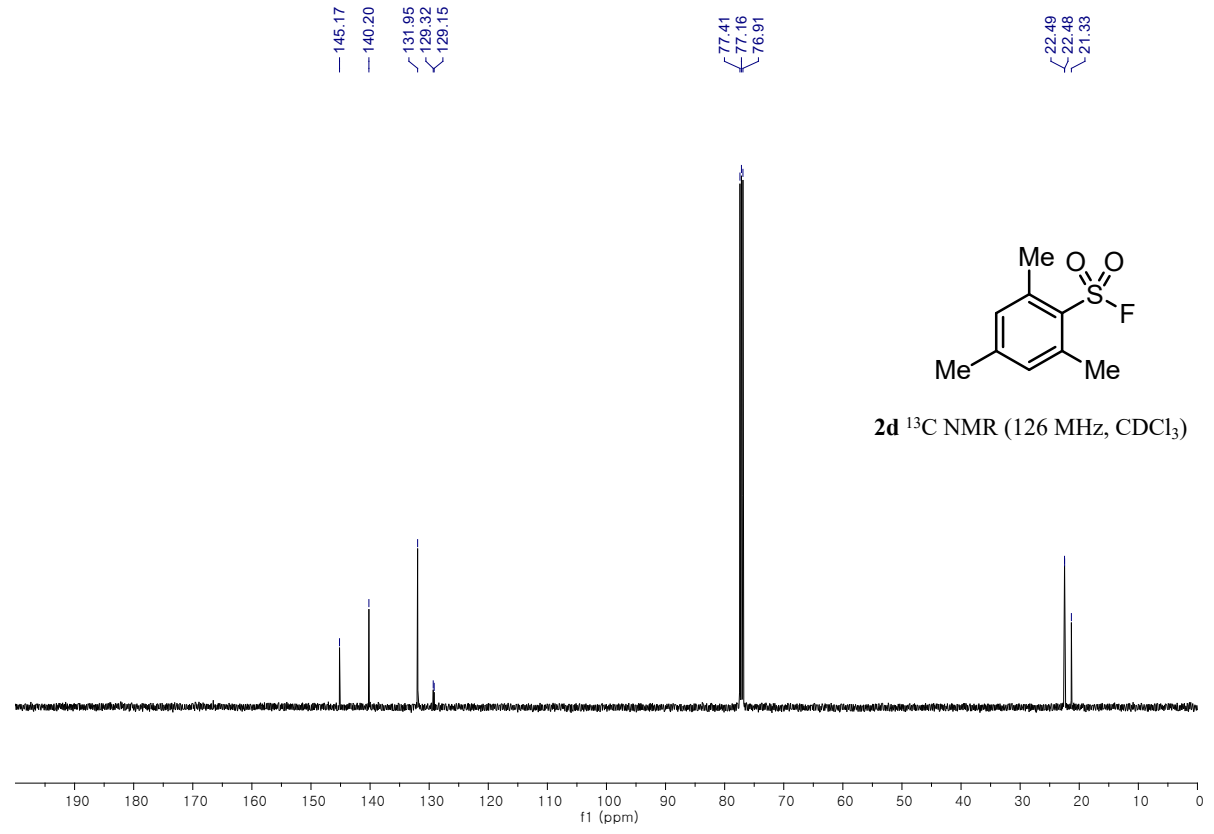


2c ^{19}F NMR (470 MHz, $CDCl_3$)

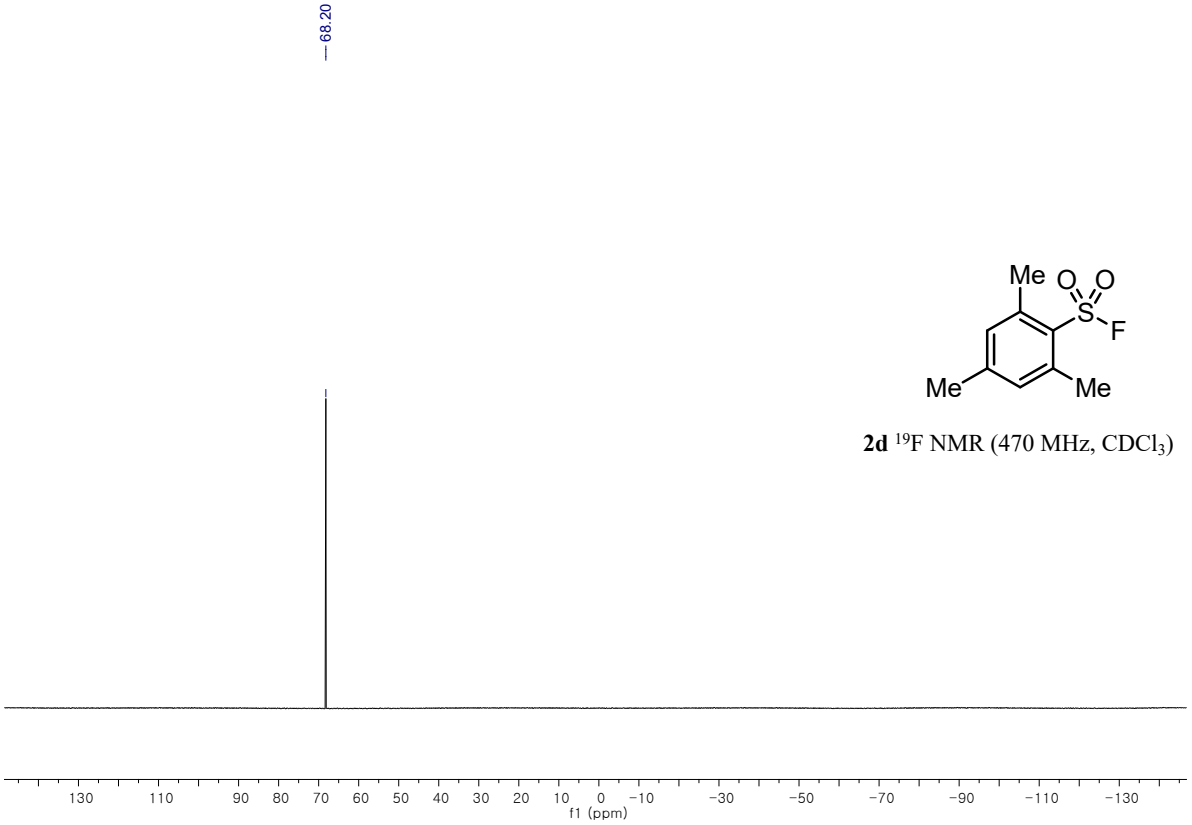
2,4,6-Trimethylbenzenesulfonyl fluoride (2d)



2d ^{1}H NMR (500 MHz, $CDCl_3$)

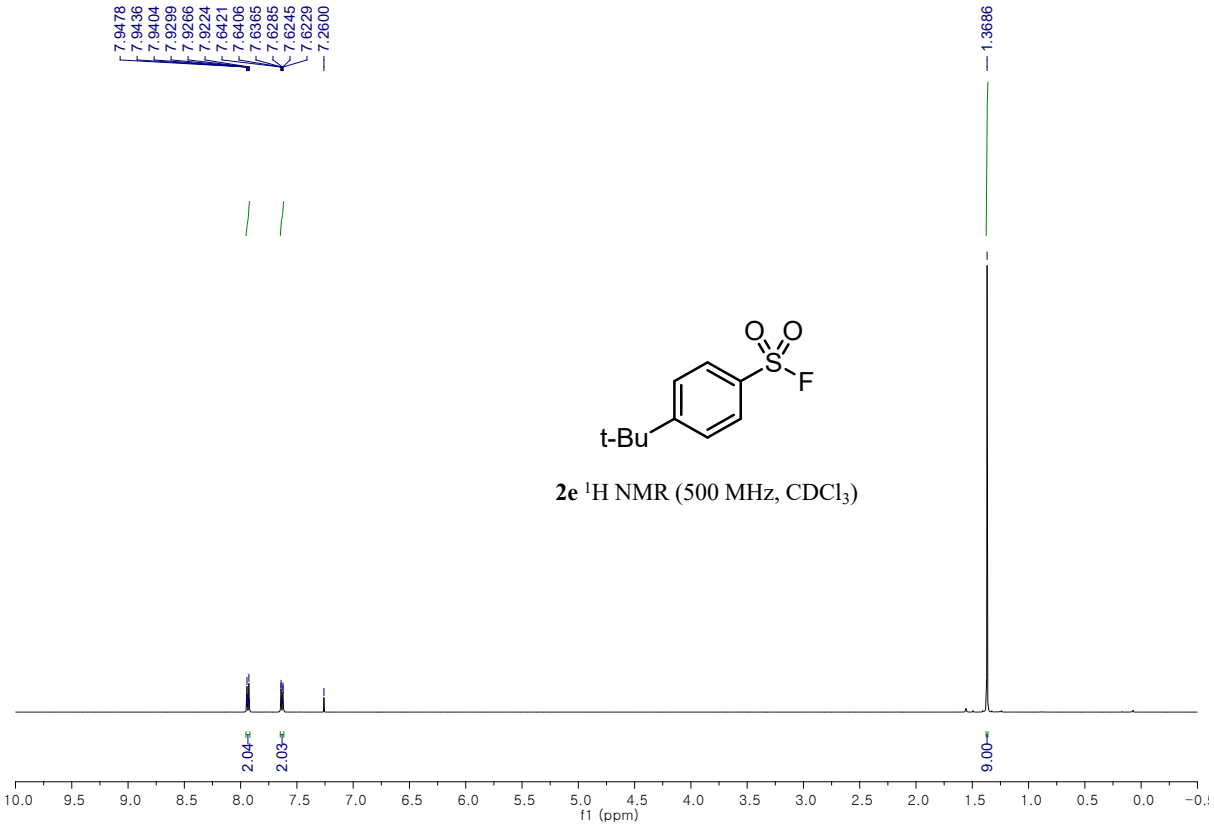


2d ^{13}C NMR (126 MHz, $CDCl_3$)

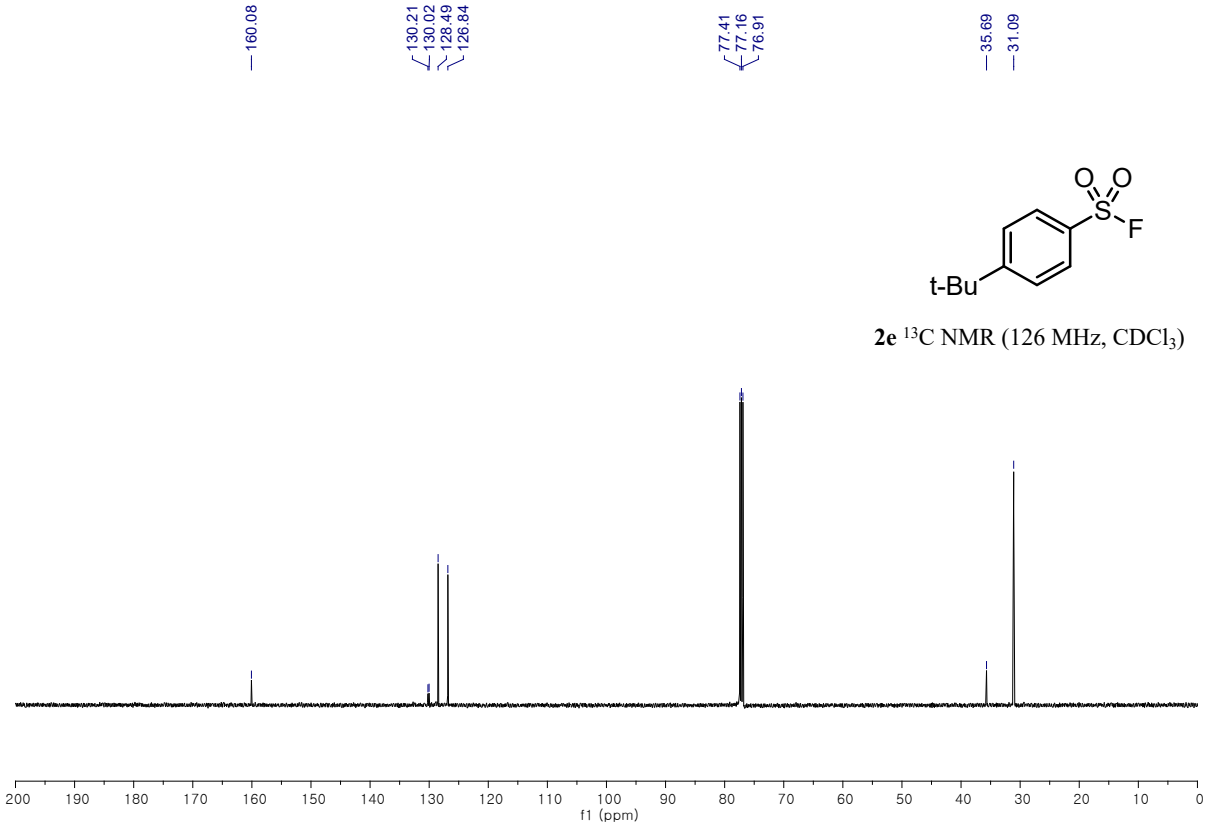


2d ^{19}F NMR (470 MHz, $CDCl_3$)

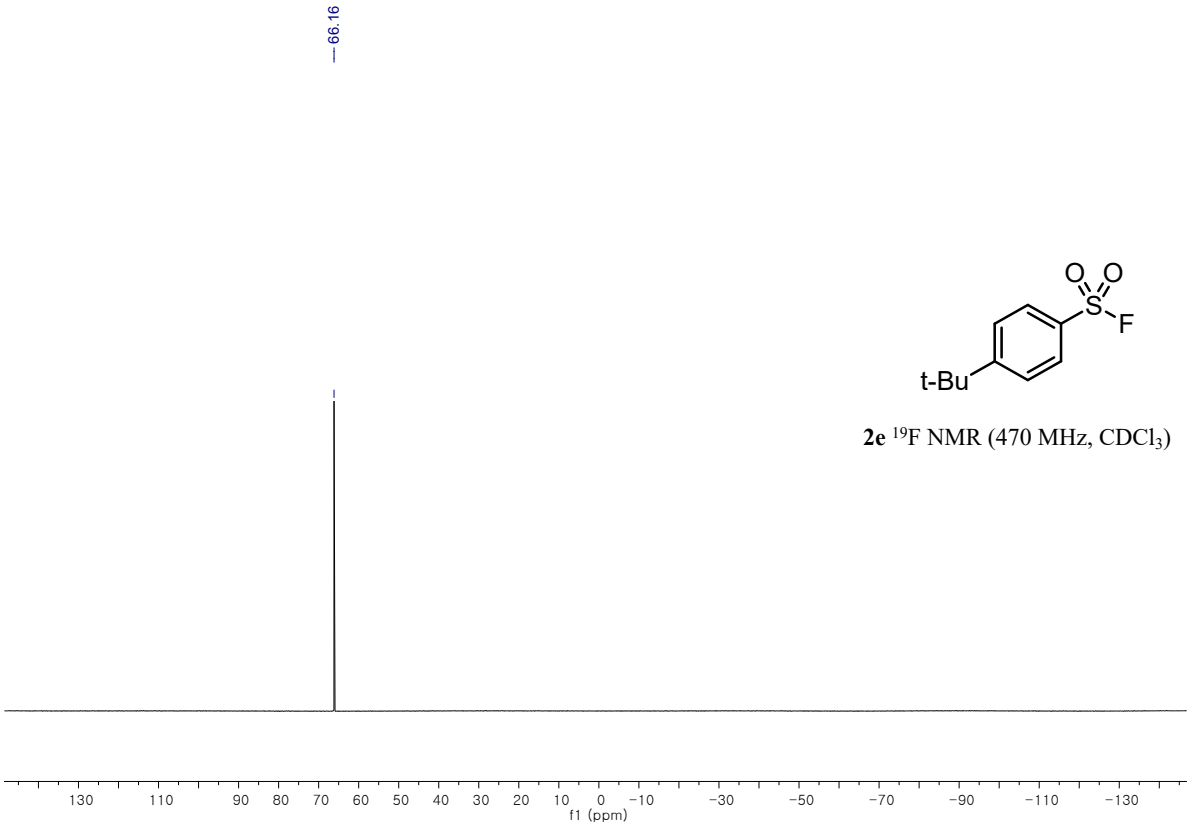
4-*tert*-Butyl-benzenesulfonyl fluoride (2e)



2e ^{1}H NMR (500 MHz, $CDCl_3$)

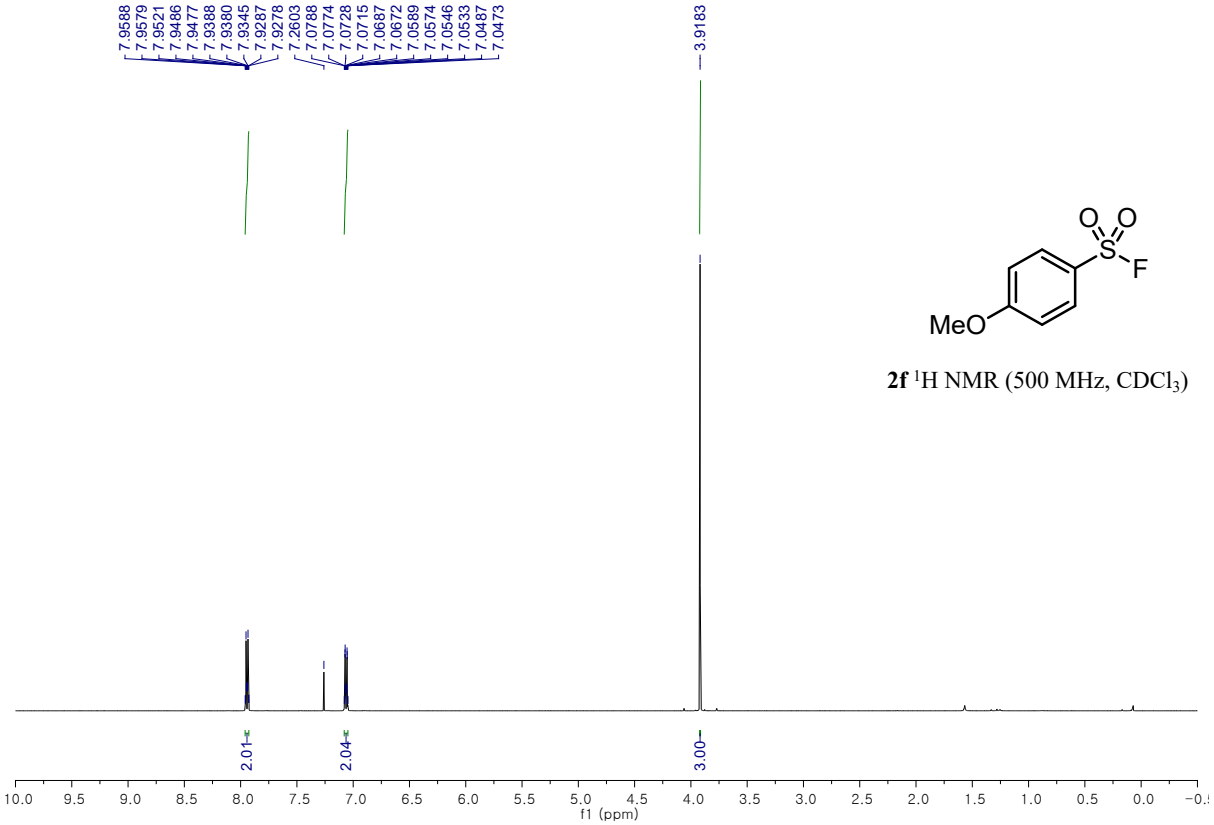


2e ^{13}C NMR (126 MHz, $CDCl_3$)

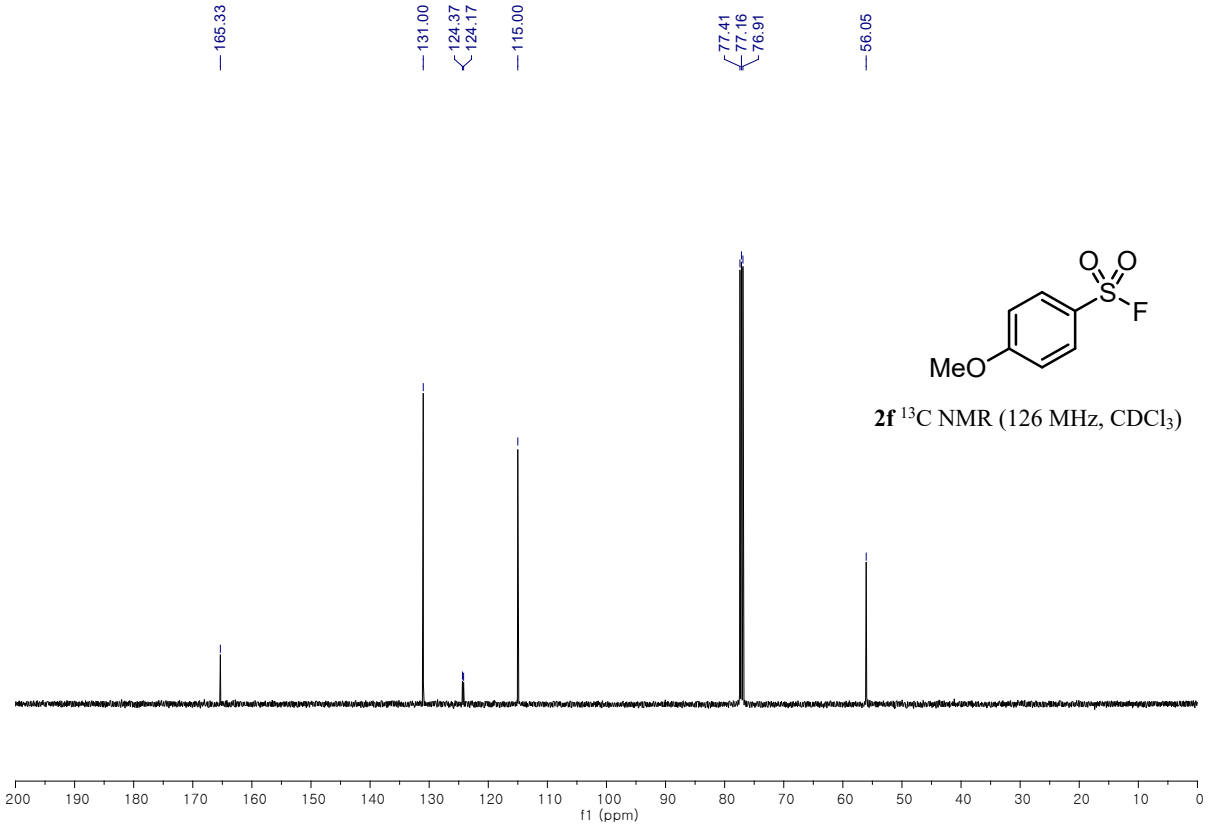


2e ^{19}F NMR (470 MHz, $CDCl_3$)

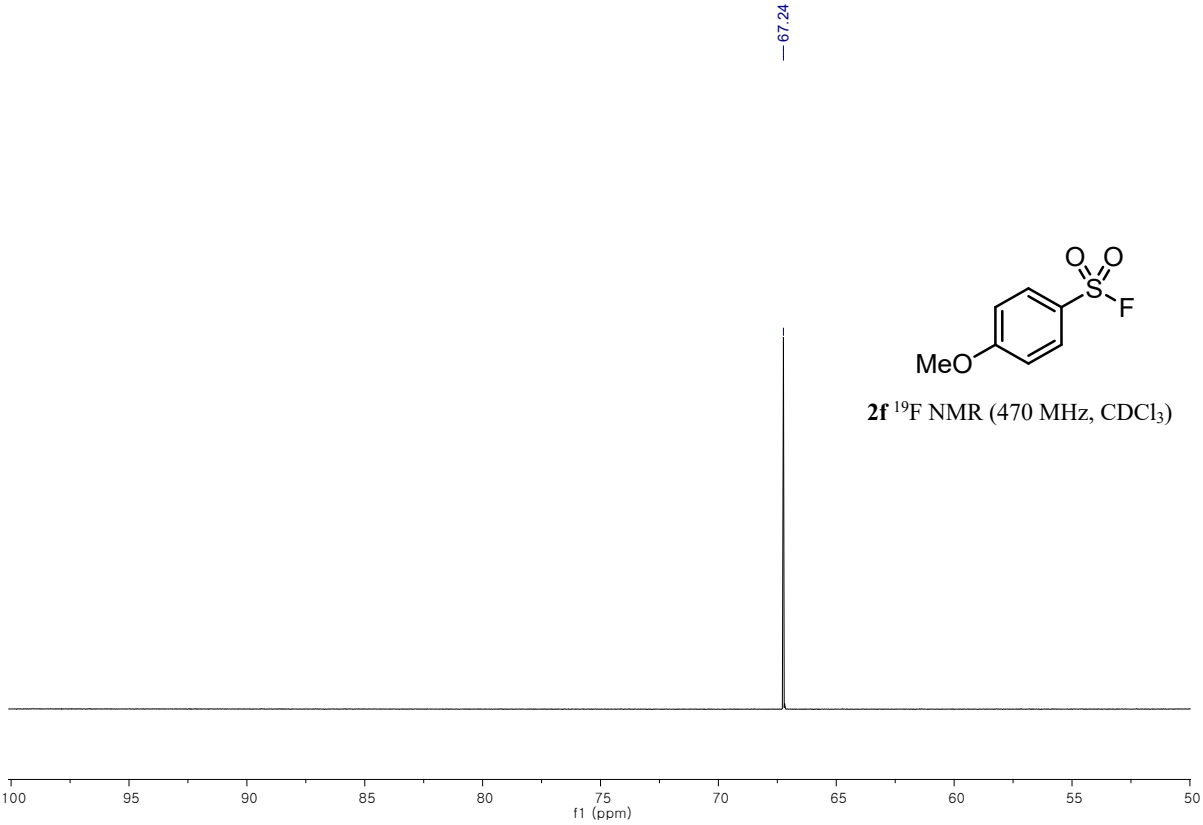
4-Methoxybenzenesulfonyl fluoride (2f)



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

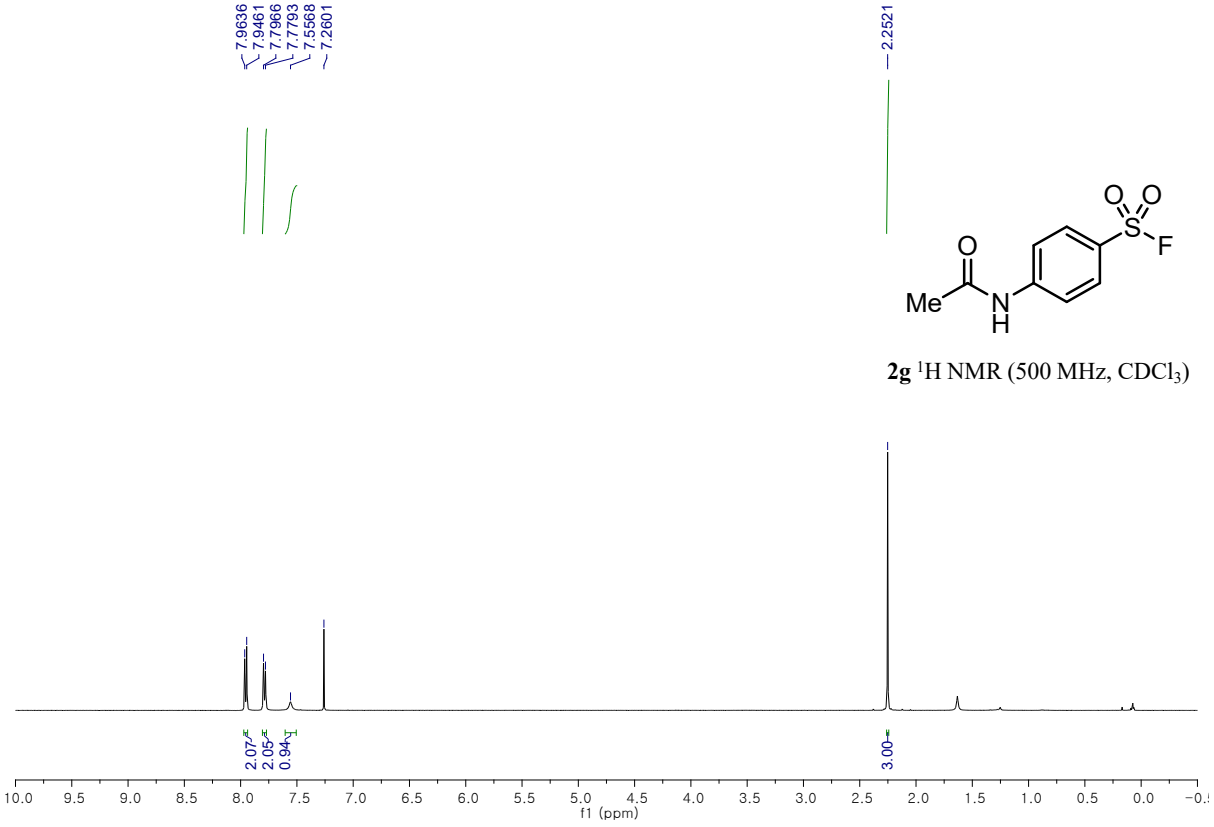


2f ^{13}C NMR (126 MHz, $CDCl_3$)

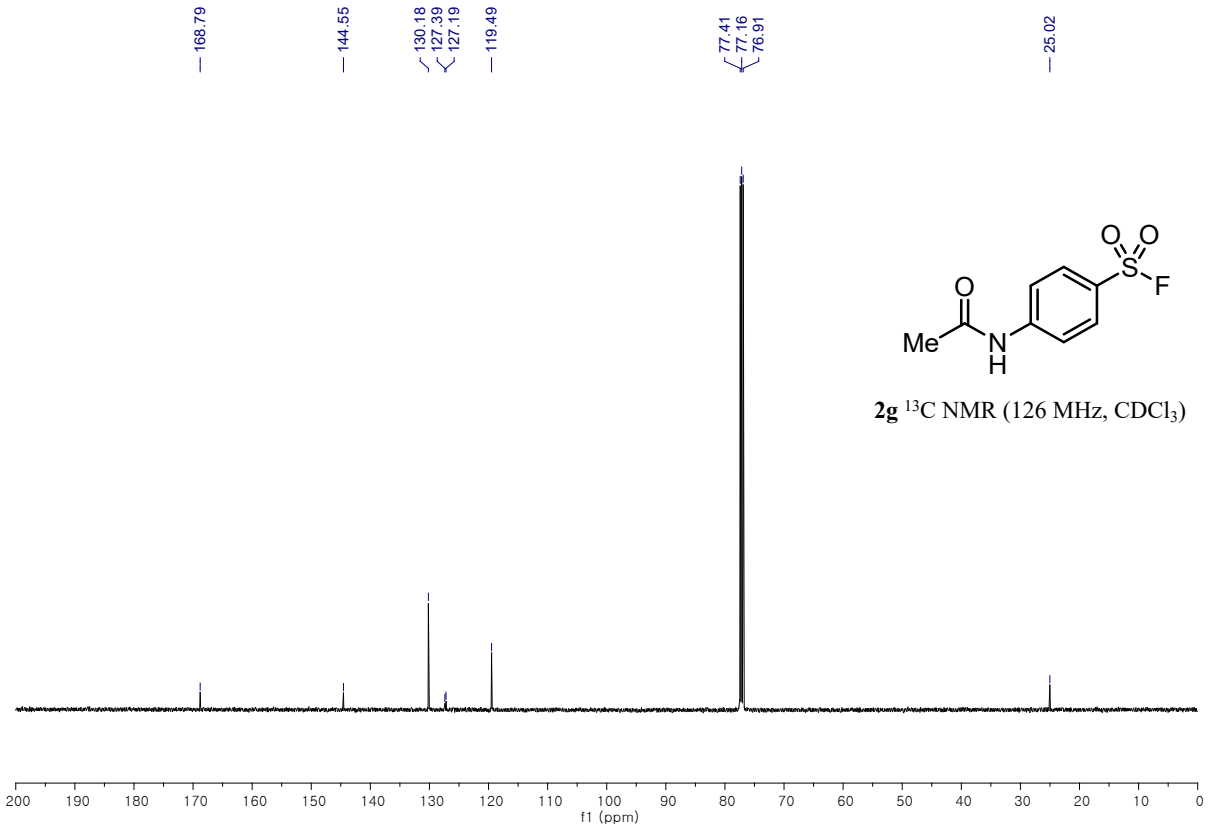


2f ^{19}F NMR (470 MHz, $CDCl_3$)

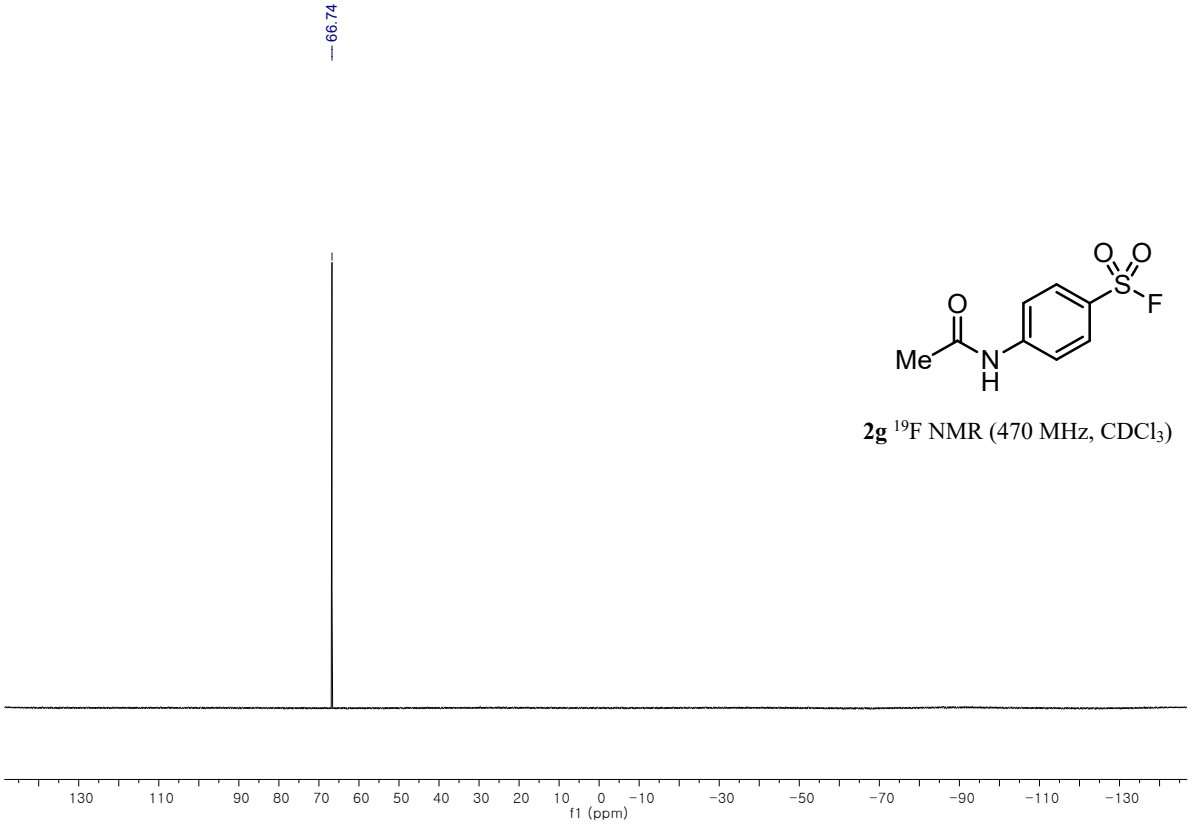
4-(Acetylamino)benzenesulfonyl fluoride (2g)



2g ^{1}H NMR (500 MHz, $CDCl_3$)

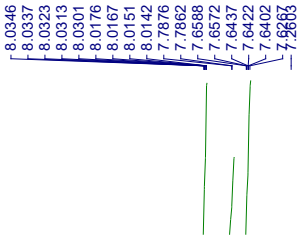


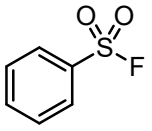
2g ^{13}C NMR (126 MHz, $CDCl_3$)



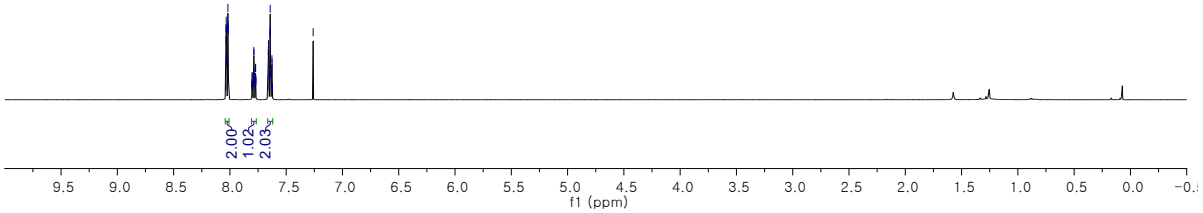
2g ^{19}F NMR (470 MHz, $CDCl_3$)

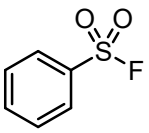
Benzenesulfonyl fluoride (2h)



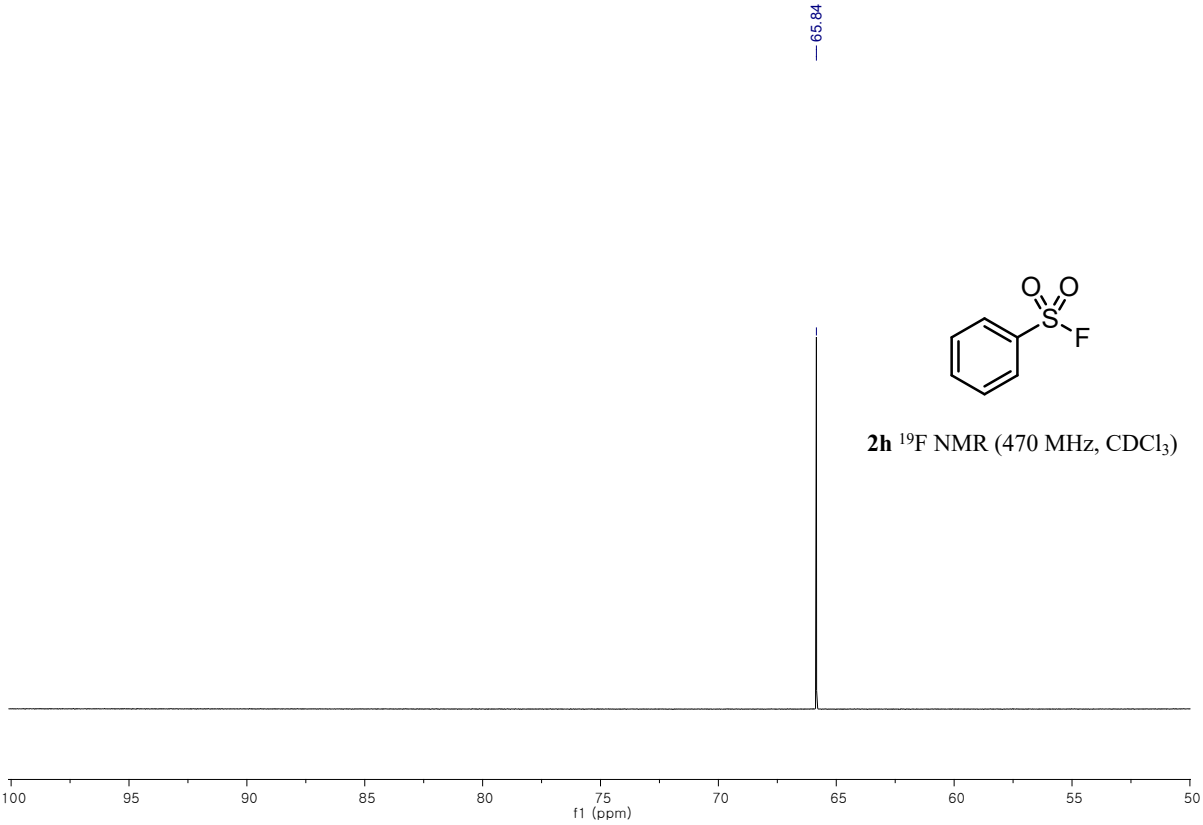


2h ^{1}H NMR (500 MHz, $CDCl_3$)



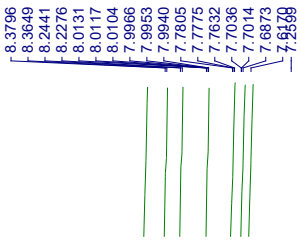


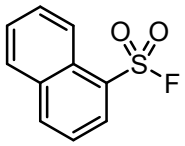
2h ^{13}C NMR (126 MHz, $CDCl_3$)



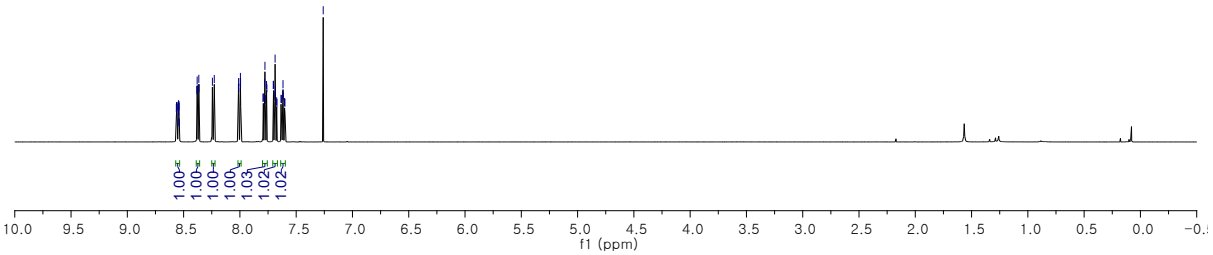
2h ^{19}F NMR (470 MHz, $CDCl_3$)

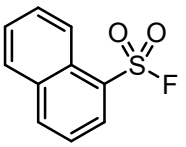
1-Naphthalenesulfonyl fluoride (2i)



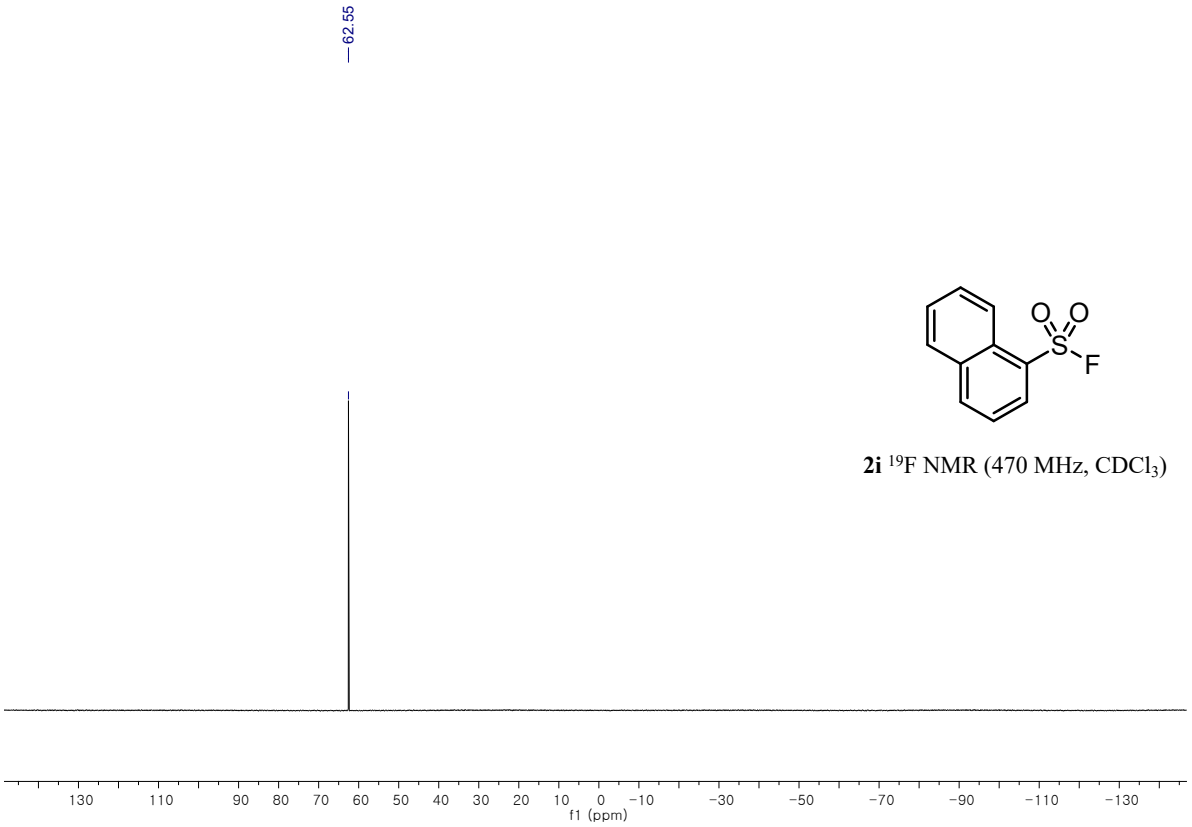


2i ^{1}H NMR (500 MHz, $CDCl_3$)



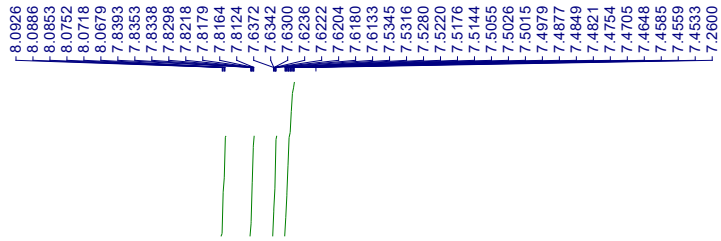


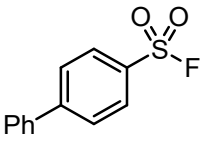
2i ^{13}C NMR (126 MHz, $CDCl_3$)



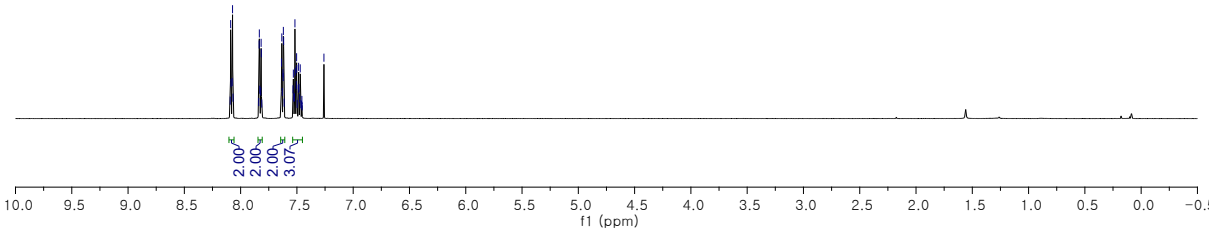
2i ^{19}F NMR (470 MHz, $CDCl_3$)

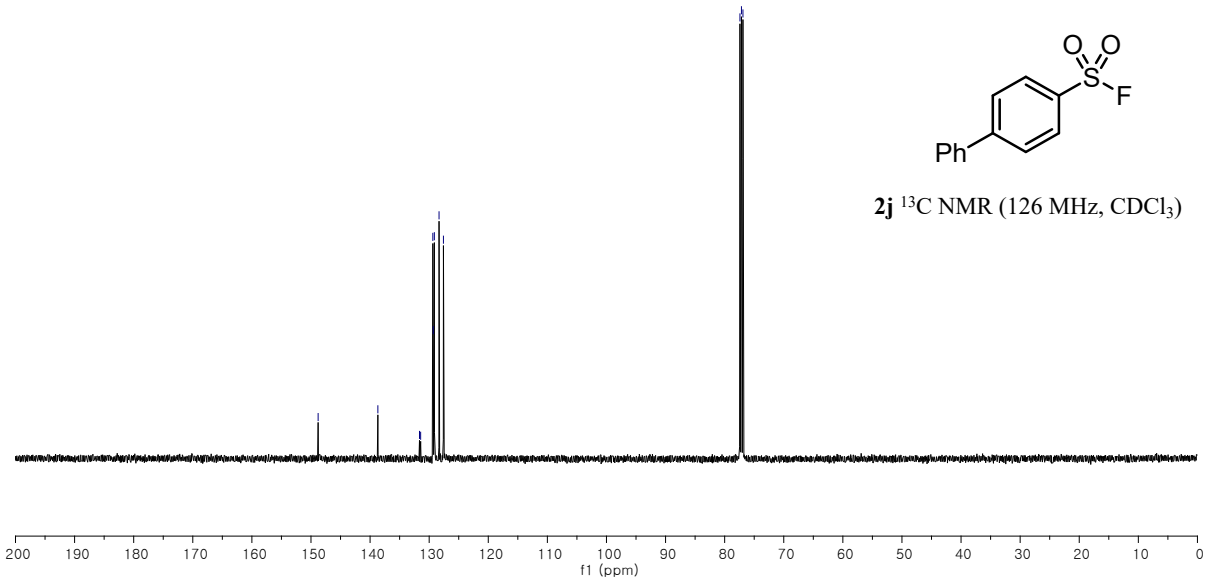
4-Biphenylsulfonyl fluoride (2j)



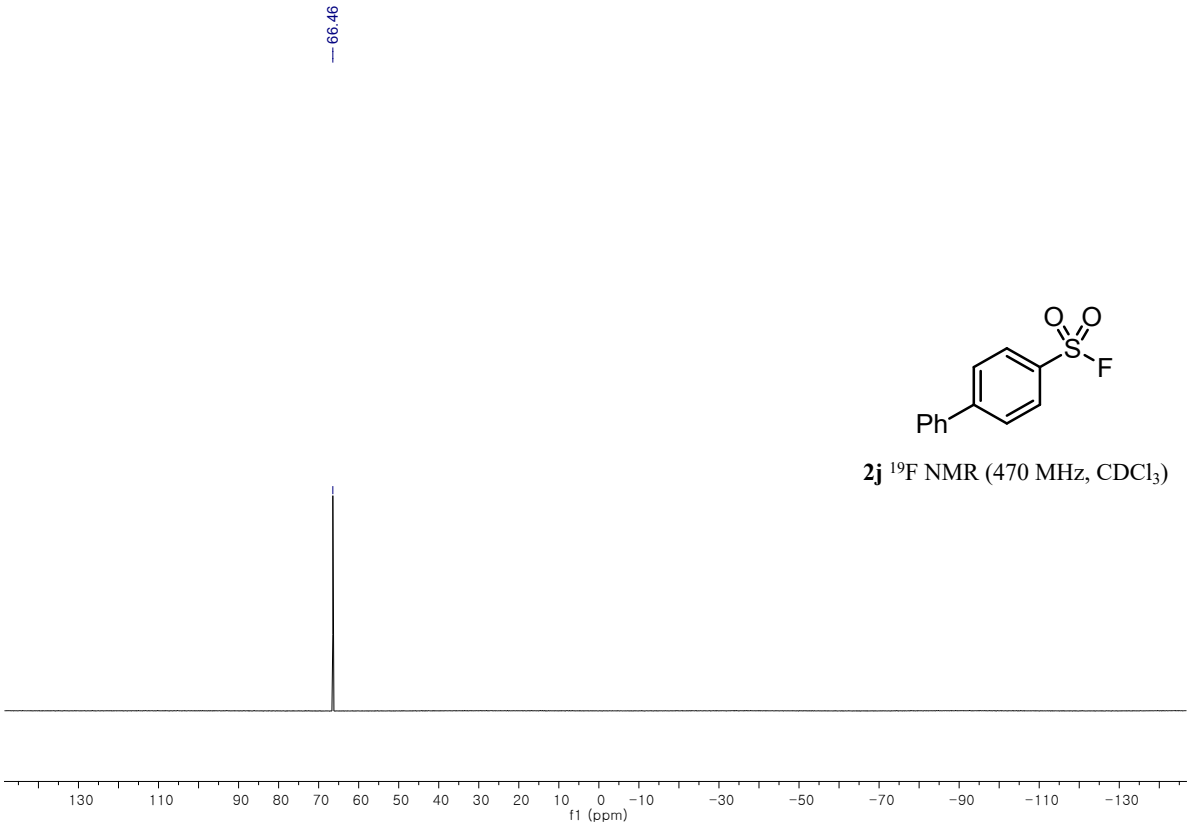


2j ^{1}H NMR (500 MHz, $CDCl_3$)



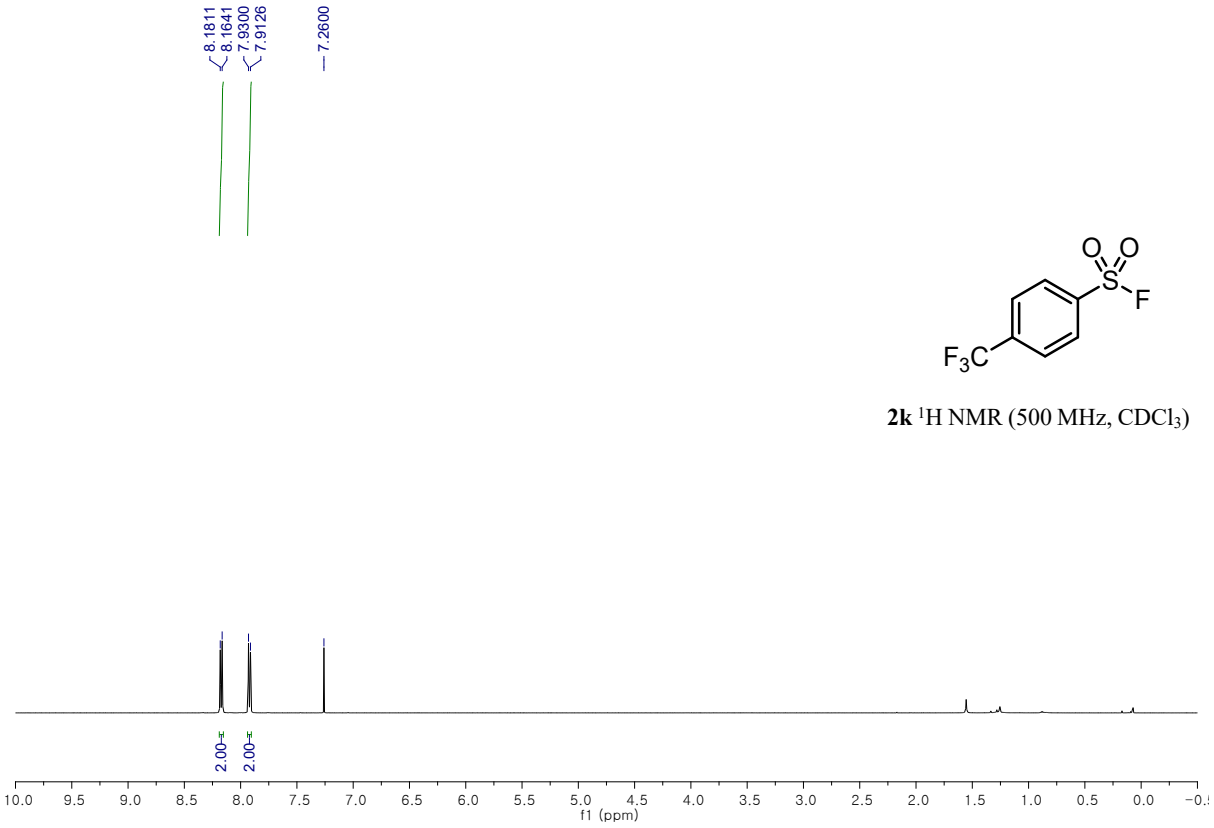


2j ^{13}C NMR (126 MHz, $CDCl_3$)

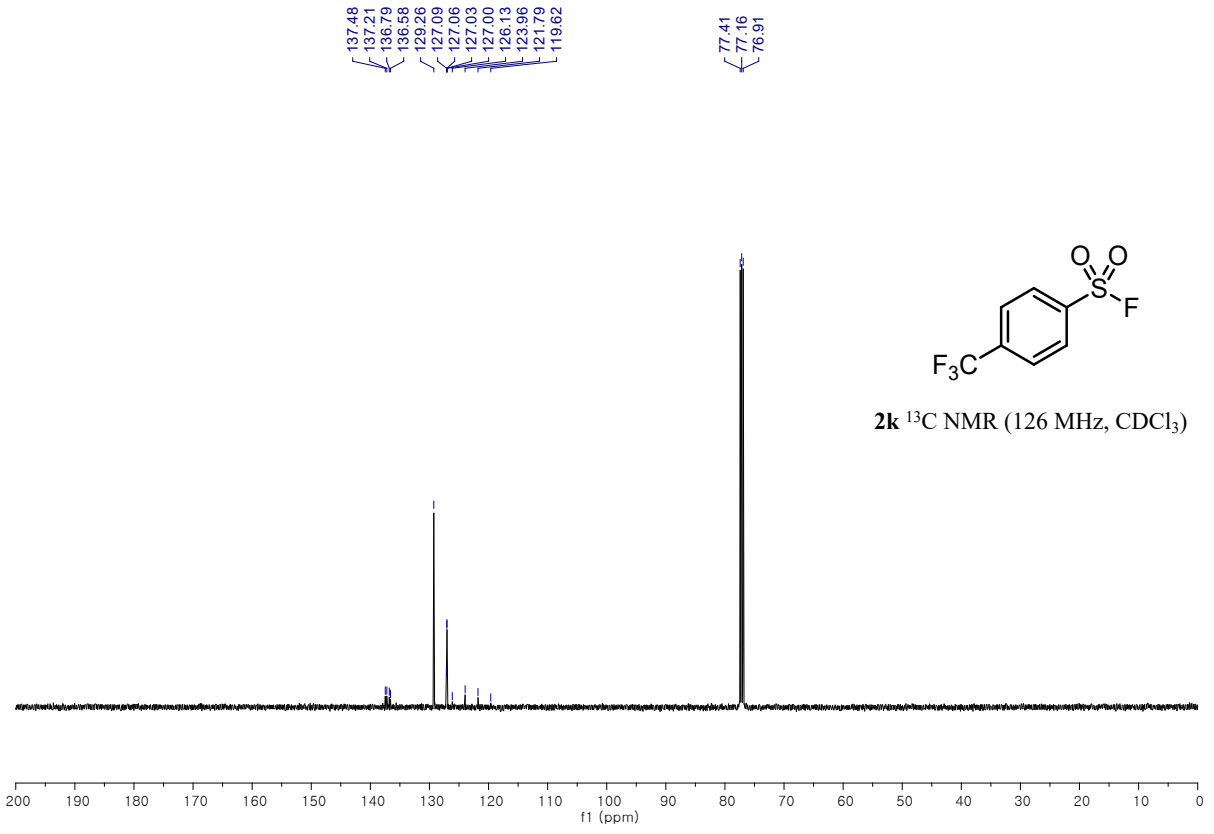


2j ^{19}F NMR (470 MHz, $CDCl_3$)

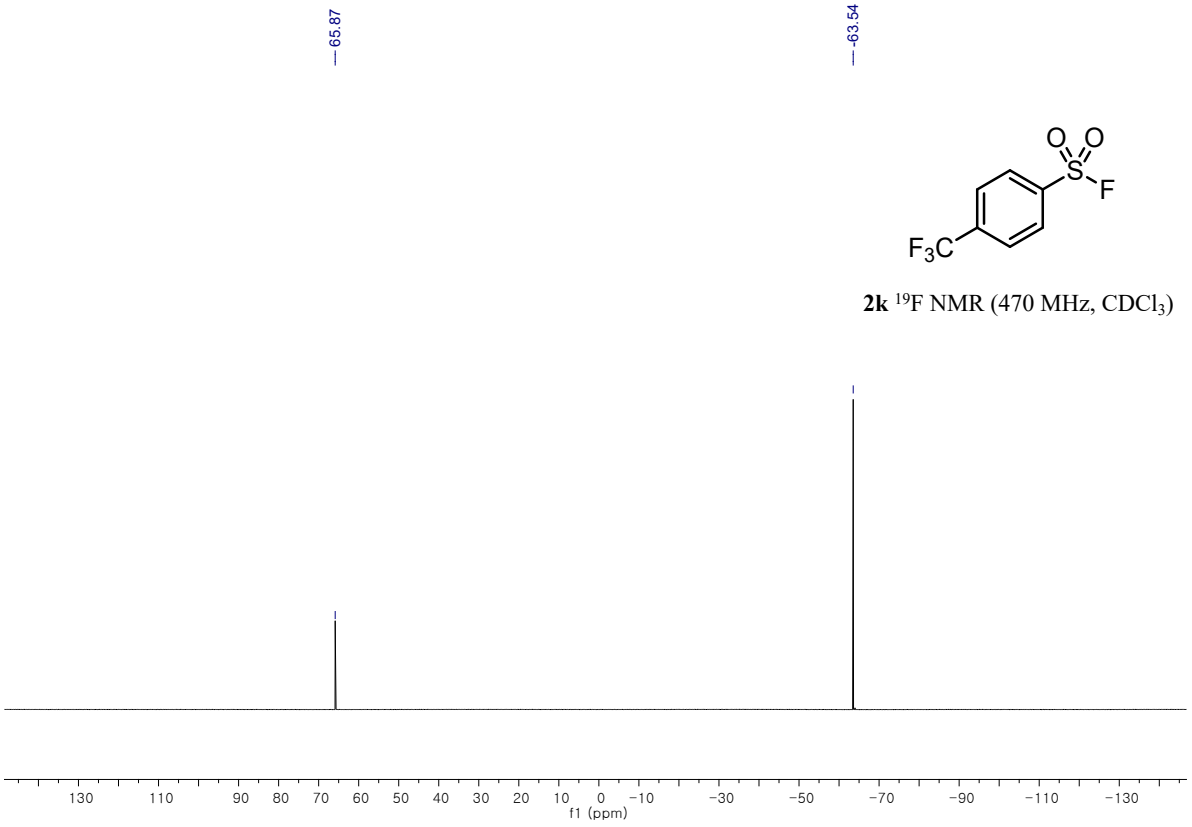
4-(Trifluoromethyl)benzenesulfonyl fluoride (2k)



2k ^{1}H NMR (500 MHz, $CDCl_3$)

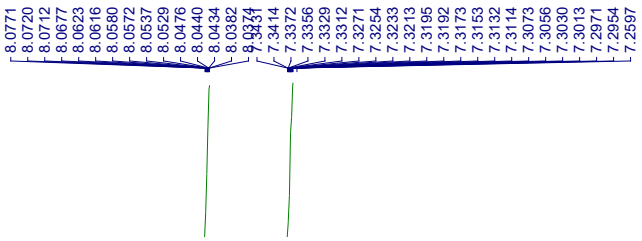


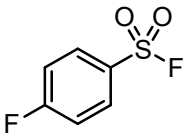
2k ^{13}C NMR (126 MHz, $CDCl_3$)



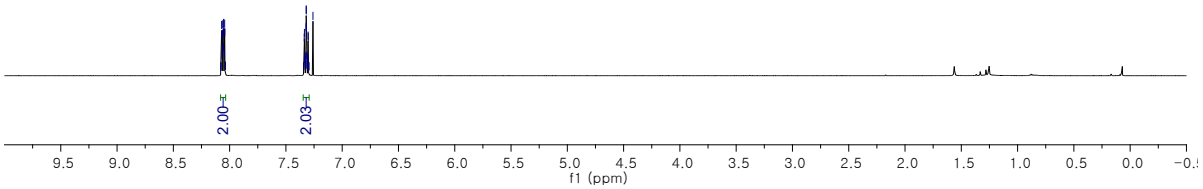
2k ^{19}F NMR (470 MHz, $CDCl_3$)

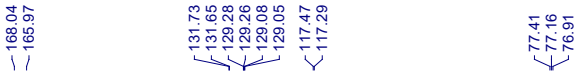
4-Fluorobenzenesulfonyl fluoride (2l)

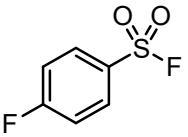




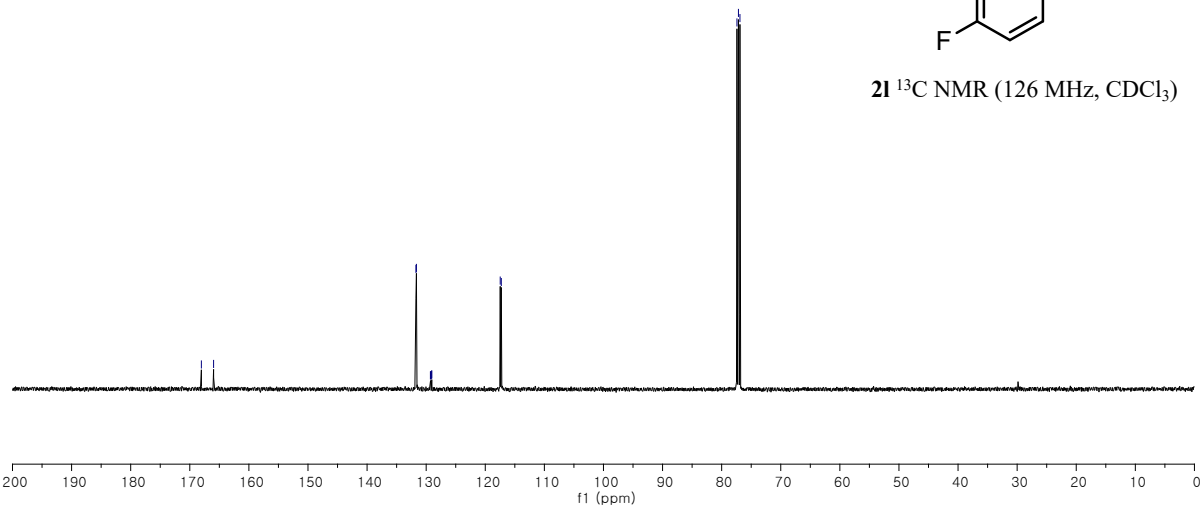
2l ^{1}H NMR (500 MHz, $CDCl_3$)

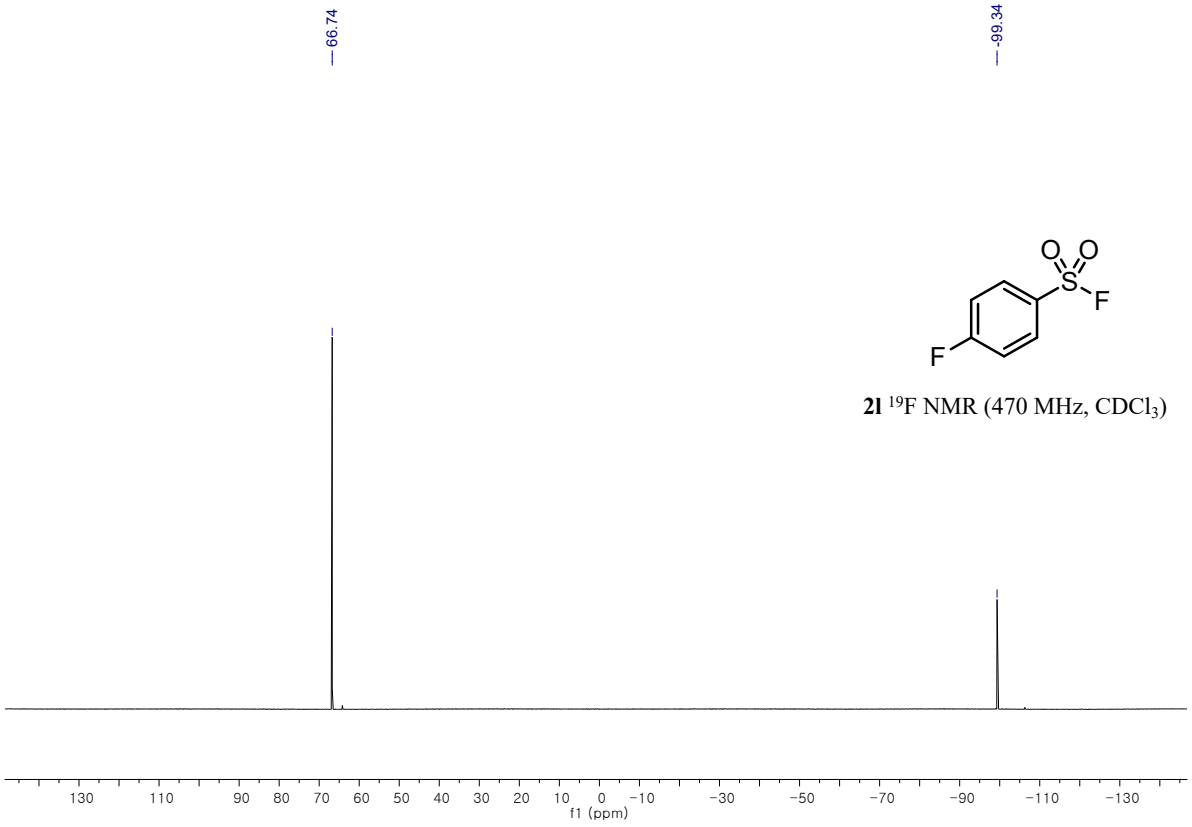






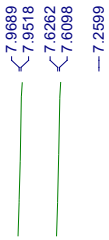
2l ^{13}C NMR (126 MHz, $CDCl_3$)

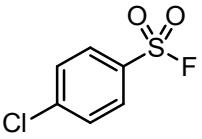




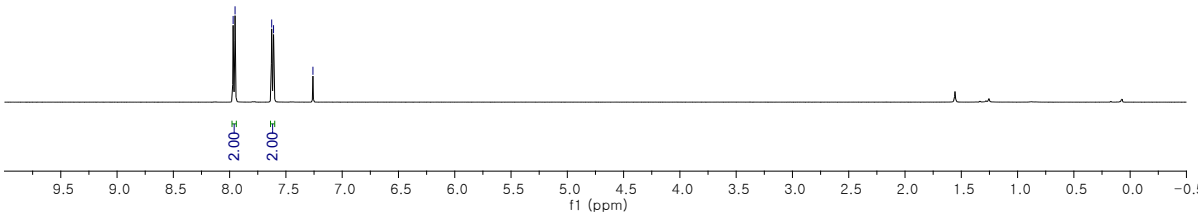
2l ^{19}F NMR (470 MHz, $CDCl_3$)

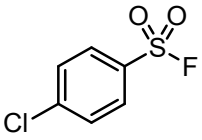
4-Chlorobenzenesulfonyl fluoride (2m)



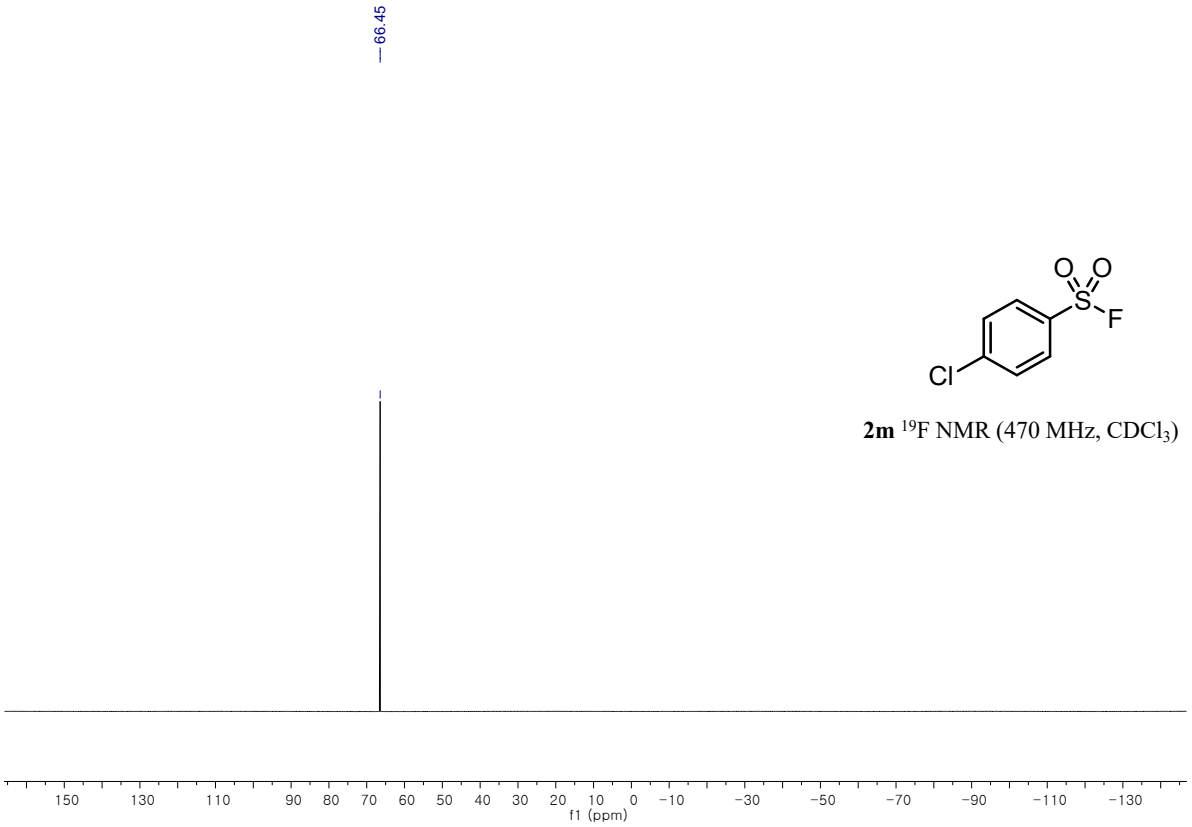


2m ^{1}H NMR (500 MHz, $CDCl_3$)



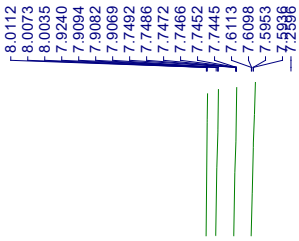


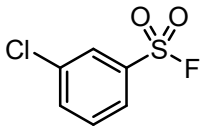
2m ^{13}C NMR (126 MHz, $CDCl_3$)



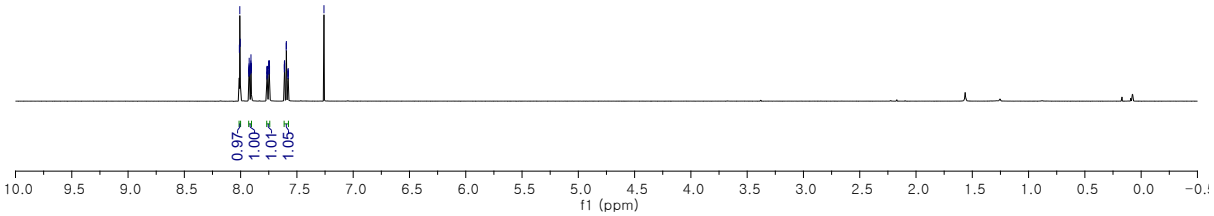
2m ^{19}F NMR (470 MHz, $CDCl_3$)

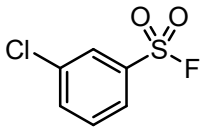
3-Chlorobenzenesulfonyl fluoride (2n)



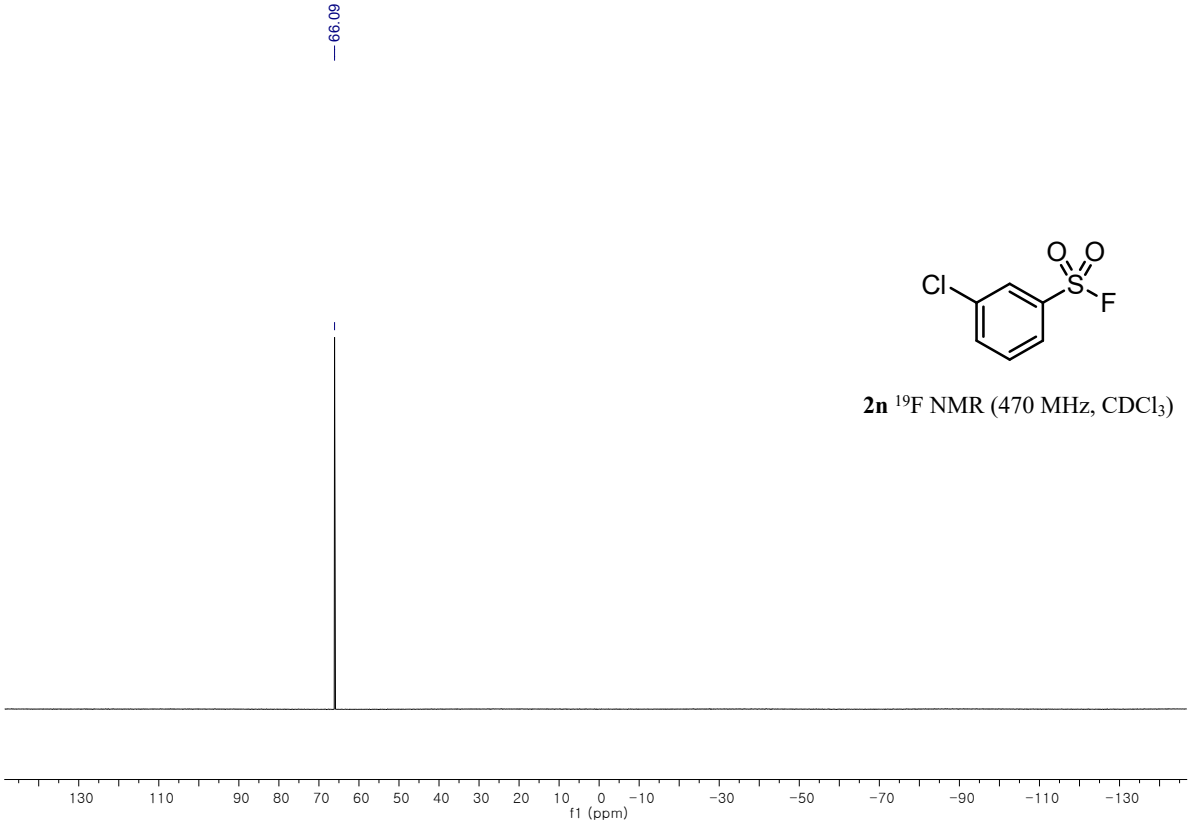


2n ^{1}H NMR (500 MHz, $CDCl_3$)



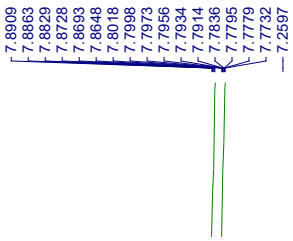


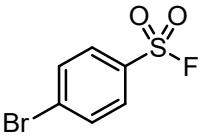
2n ^{13}C NMR (126 MHz, $CDCl_3$)



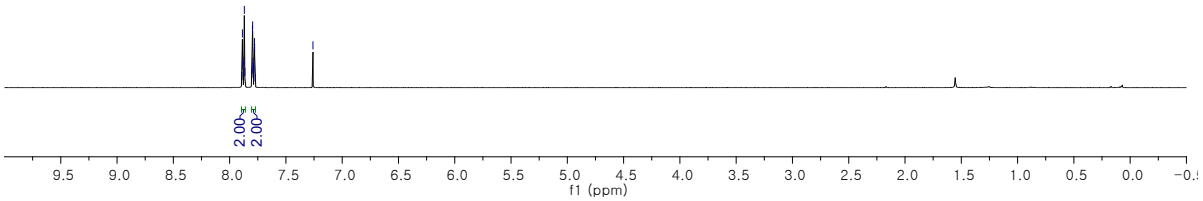
2n ^{19}F NMR (470 MHz, $CDCl_3$)

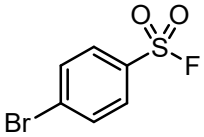
4-Bromobenzenesulfonyl fluoride (2o)



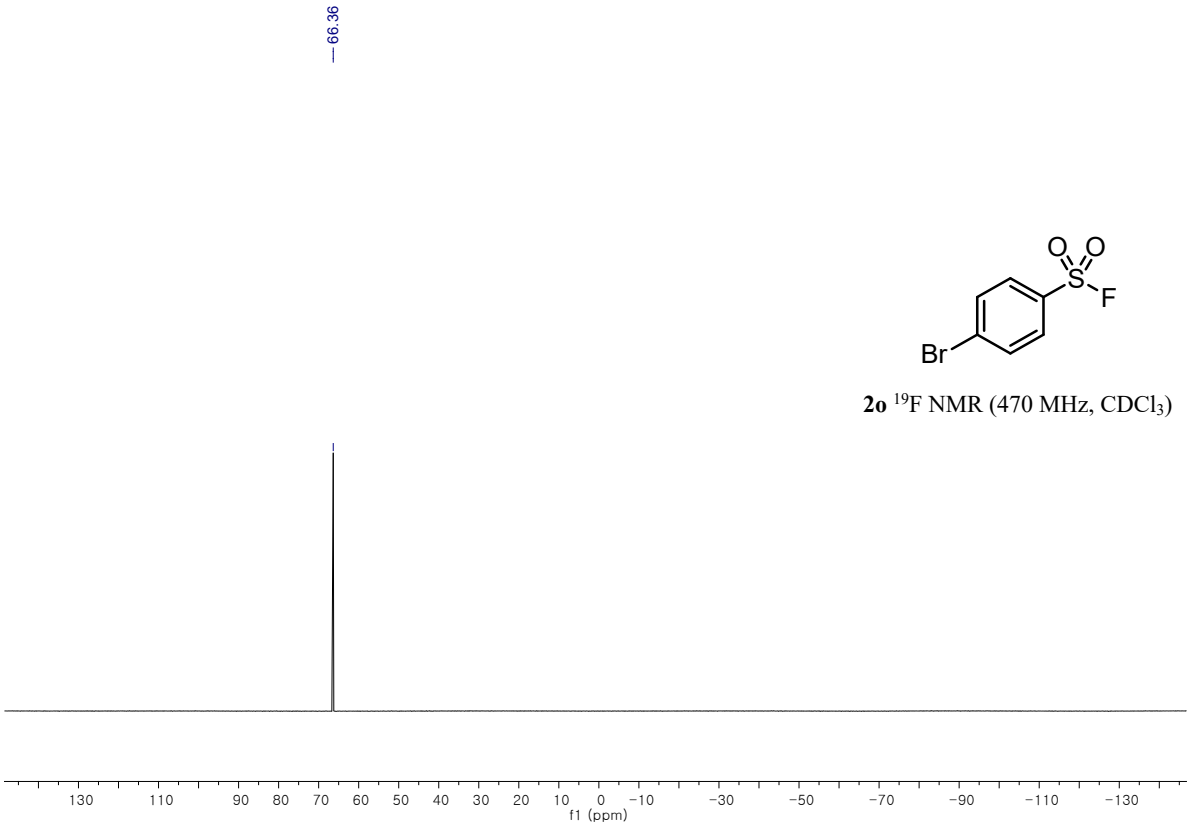


2o ^{1}H NMR (500 MHz, $CDCl_3$)



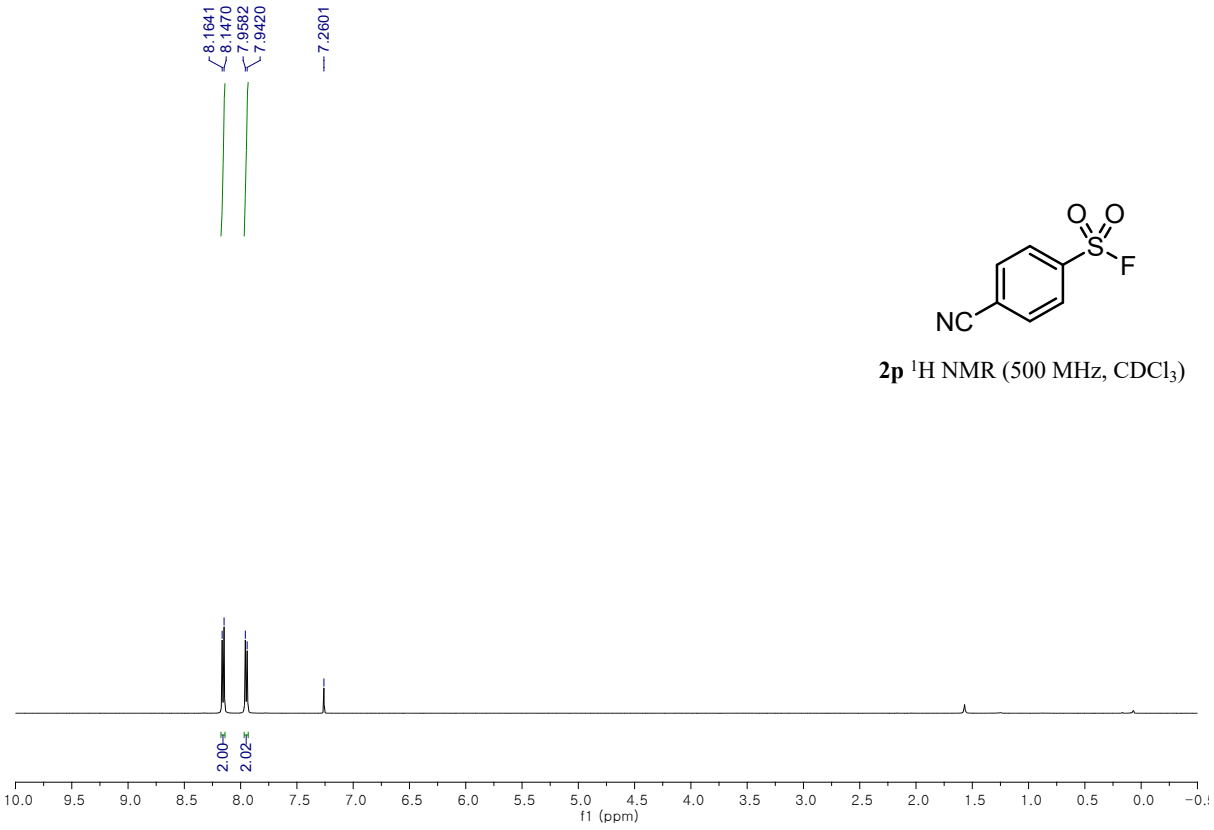


2o ^{13}C NMR (126 MHz, $CDCl_3$)

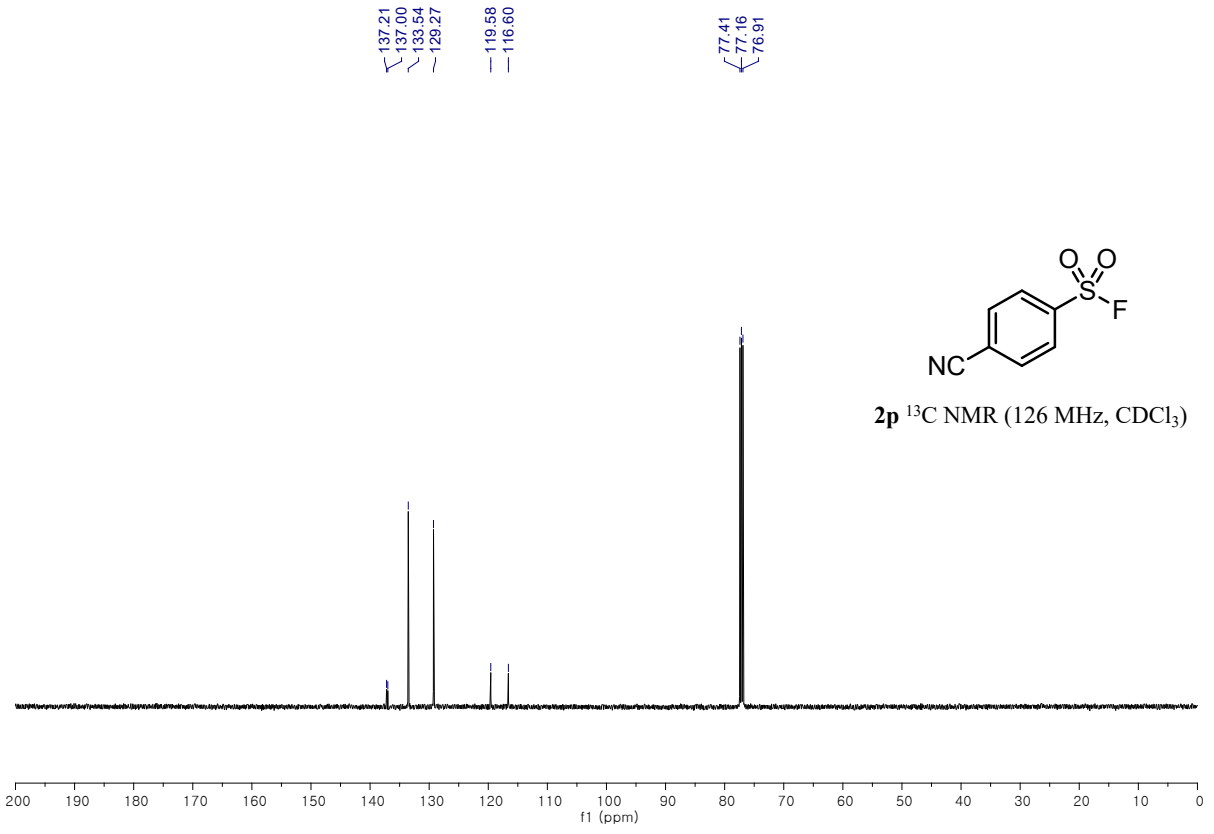


2o ^{19}F NMR (470 MHz, $CDCl_3$)

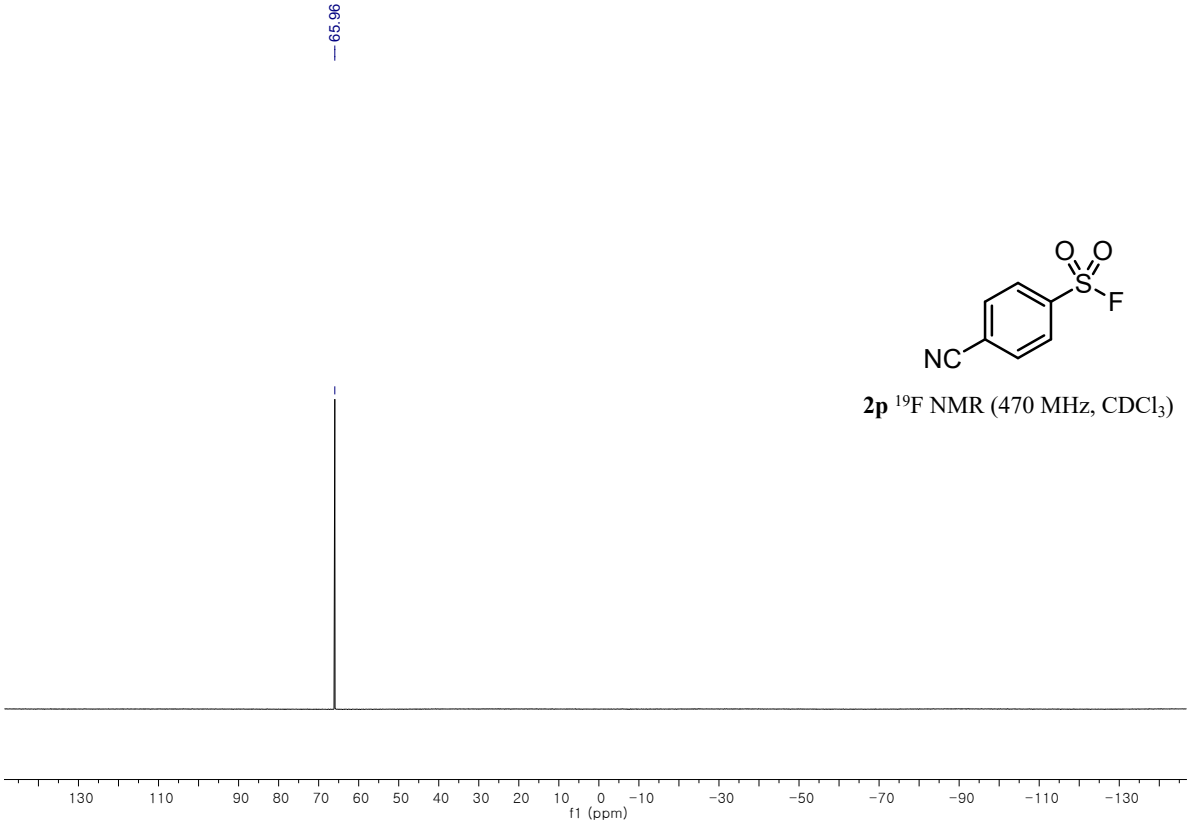
4-Cyanobenzenesulfonyl fluoride (2p)



2p ^{1}H NMR (500 MHz, $CDCl_3$)

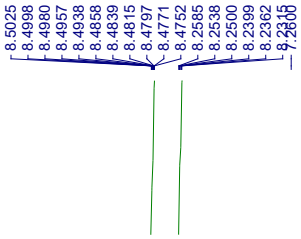


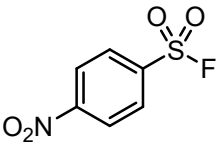
2p ^{13}C NMR (126 MHz, $CDCl_3$)



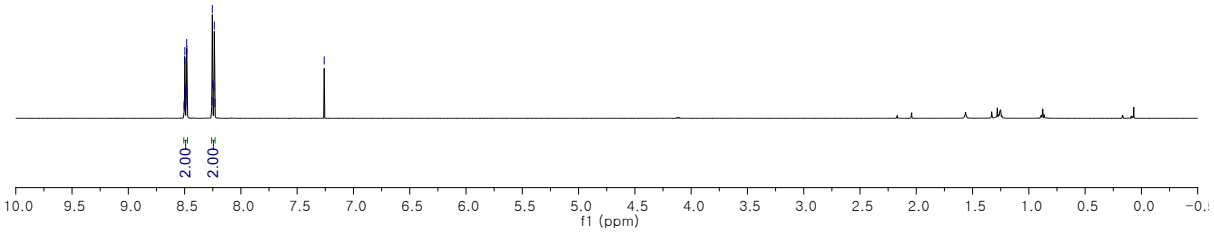
2p ^{19}F NMR (470 MHz, $CDCl_3$)

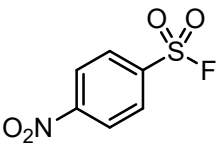
4-Nitrobenzenesulfonyl fluoride (2q)



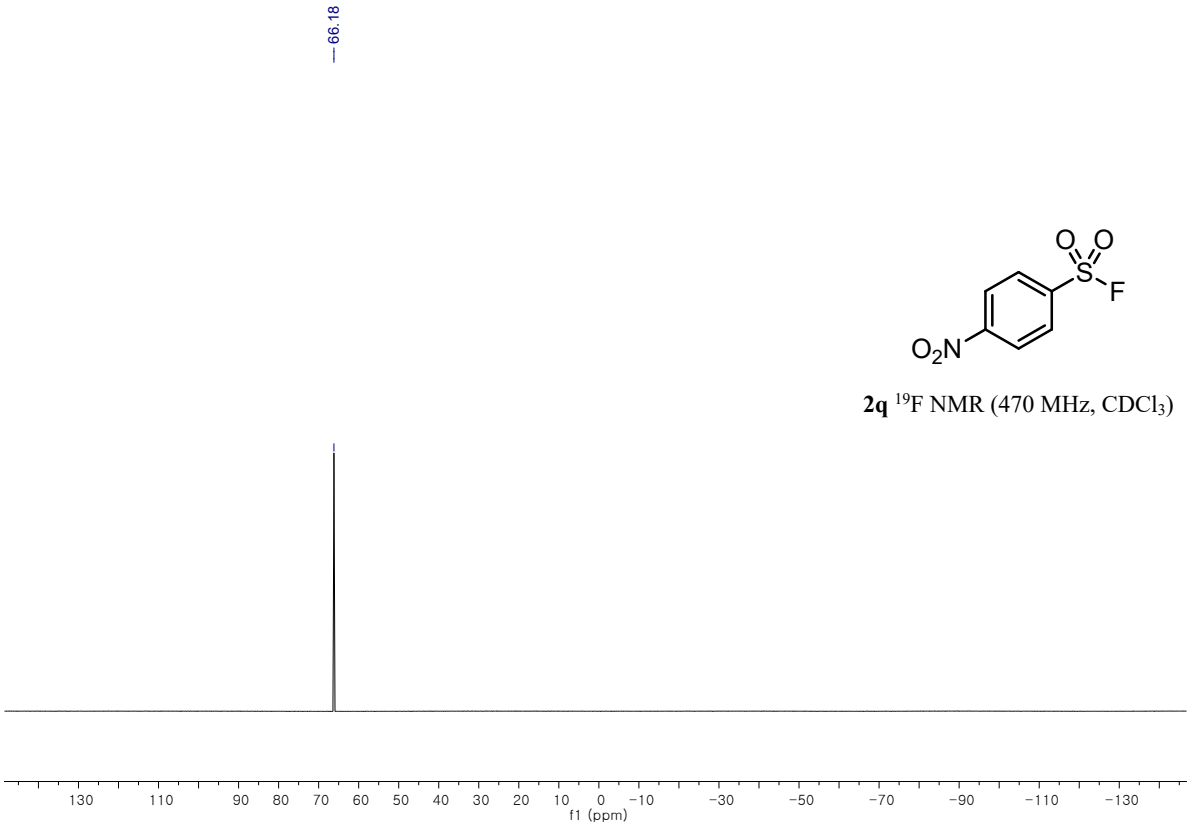


2q ^{1}H NMR (500 MHz, $CDCl_3$)



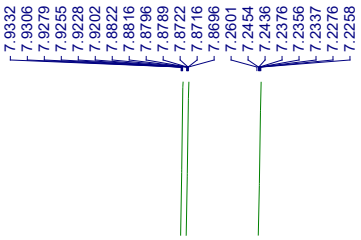


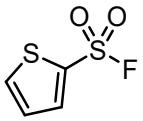
2q ^{13}C NMR (126 MHz, $CDCl_3$)



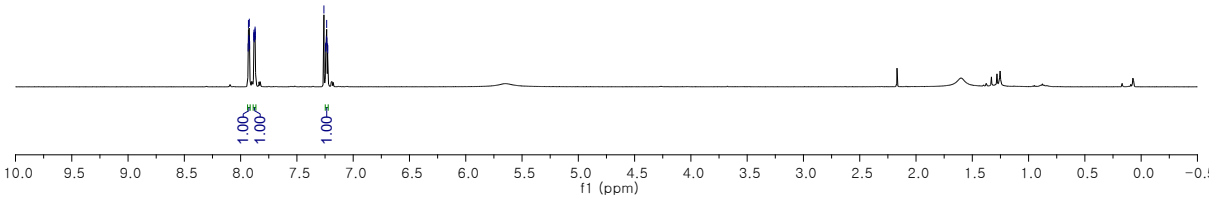
2q ^{19}F NMR (470 MHz, $CDCl_3$)

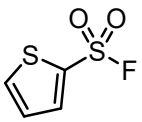
2-Thiophenesulfonyl fluoride (2r)



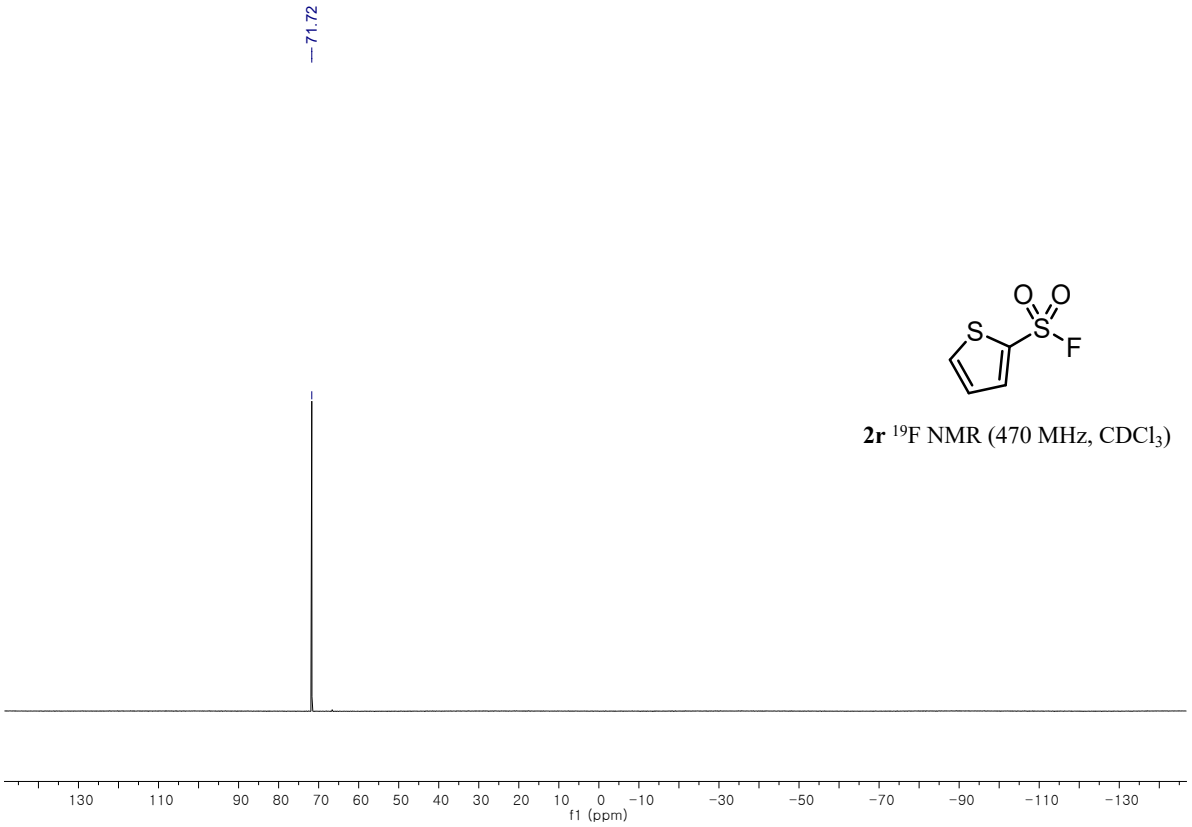


2r ^{1}H NMR (500 MHz, $CDCl_3$)



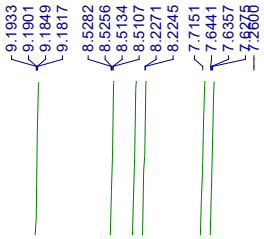


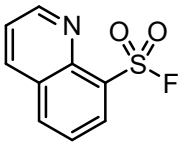
2r ^{13}C NMR (126 MHz, $CDCl_3$)



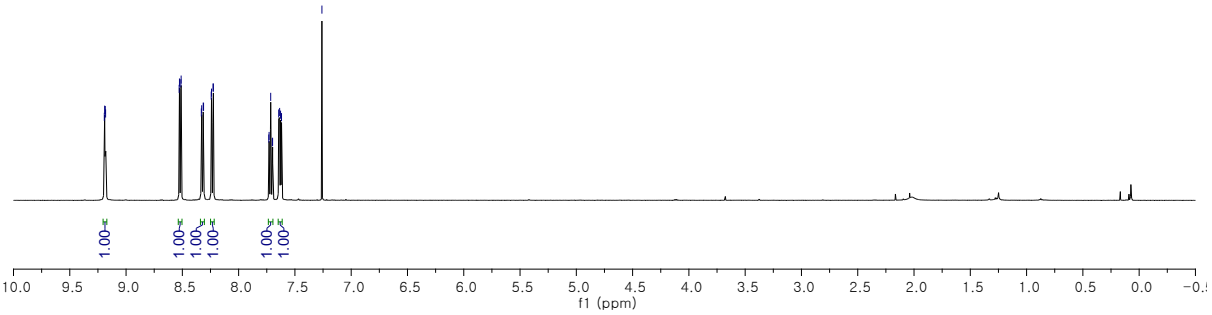
2r ^{19}F NMR (470 MHz, $CDCl_3$)

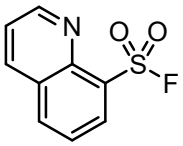
8-Quinolinesulfonyl fluoride (2s)



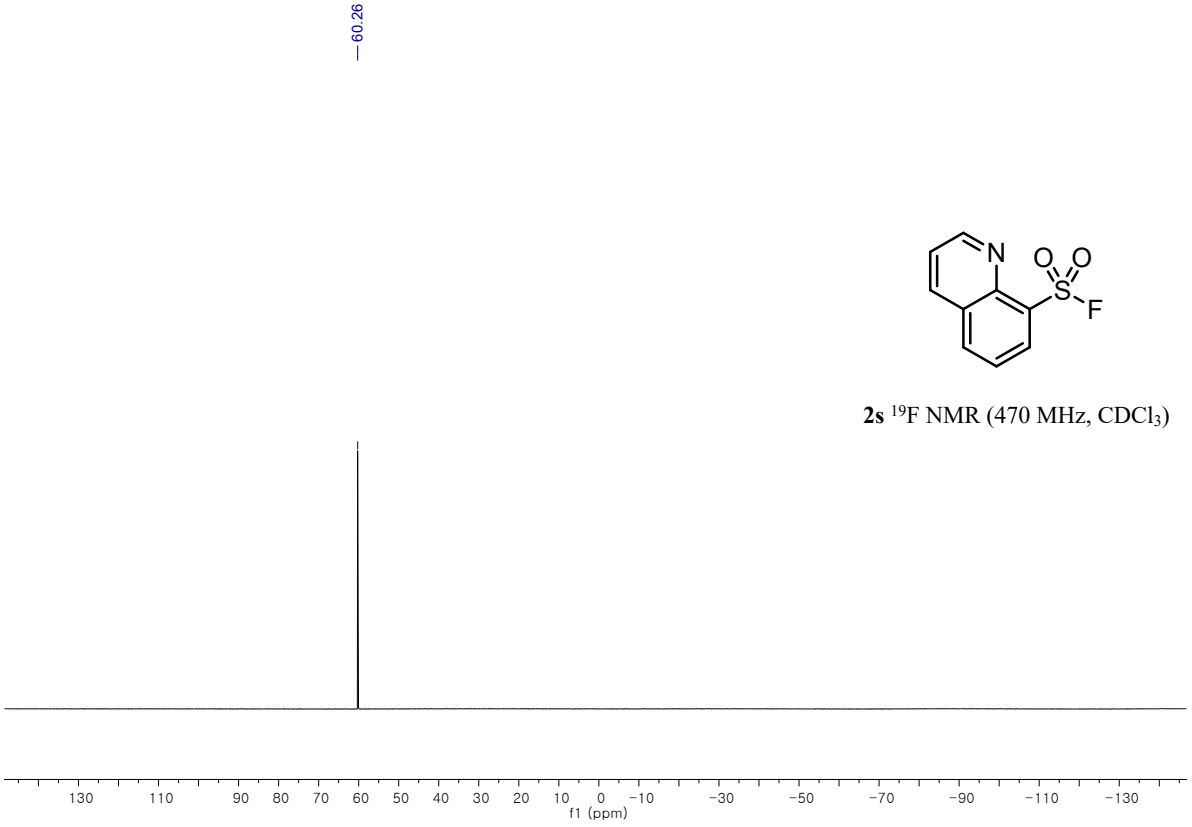


2s ^{1}H NMR (500 MHz, $CDCl_3$)



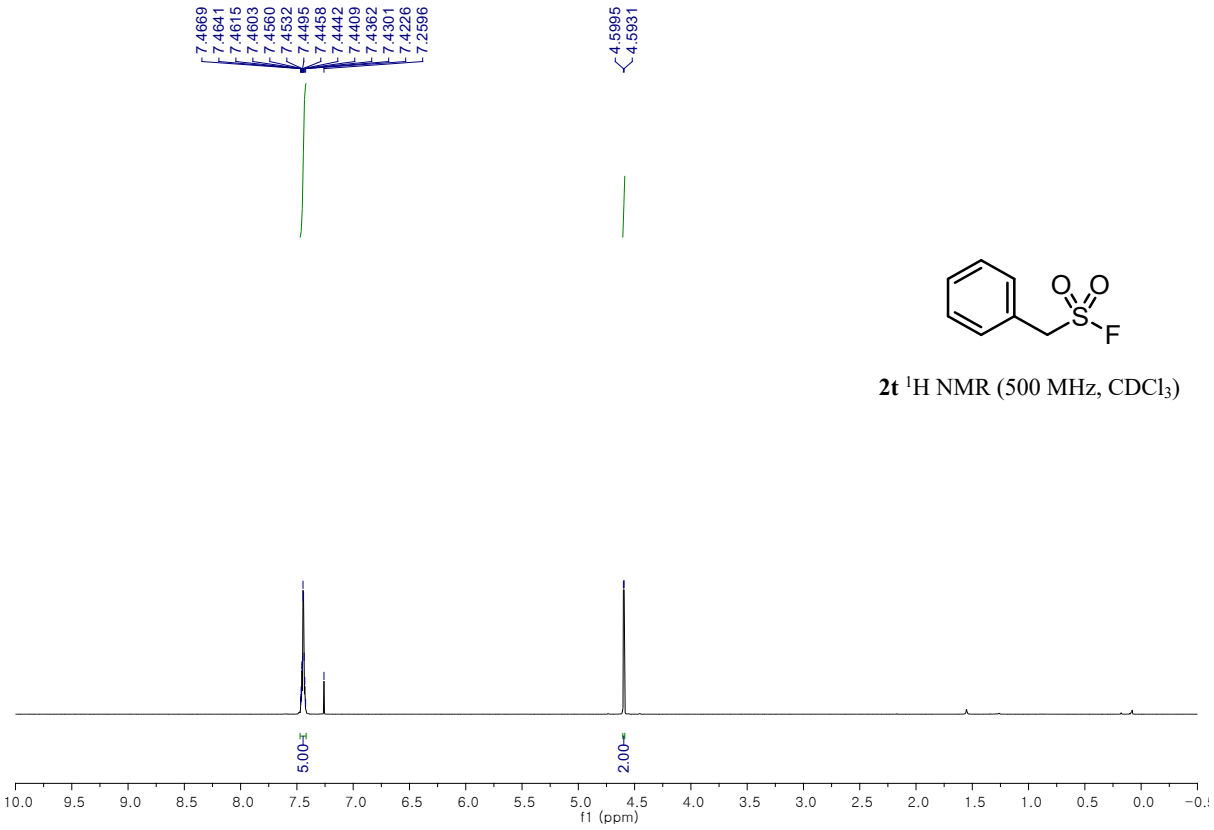


2s ^{13}C NMR (126 MHz, $CDCl_3$)

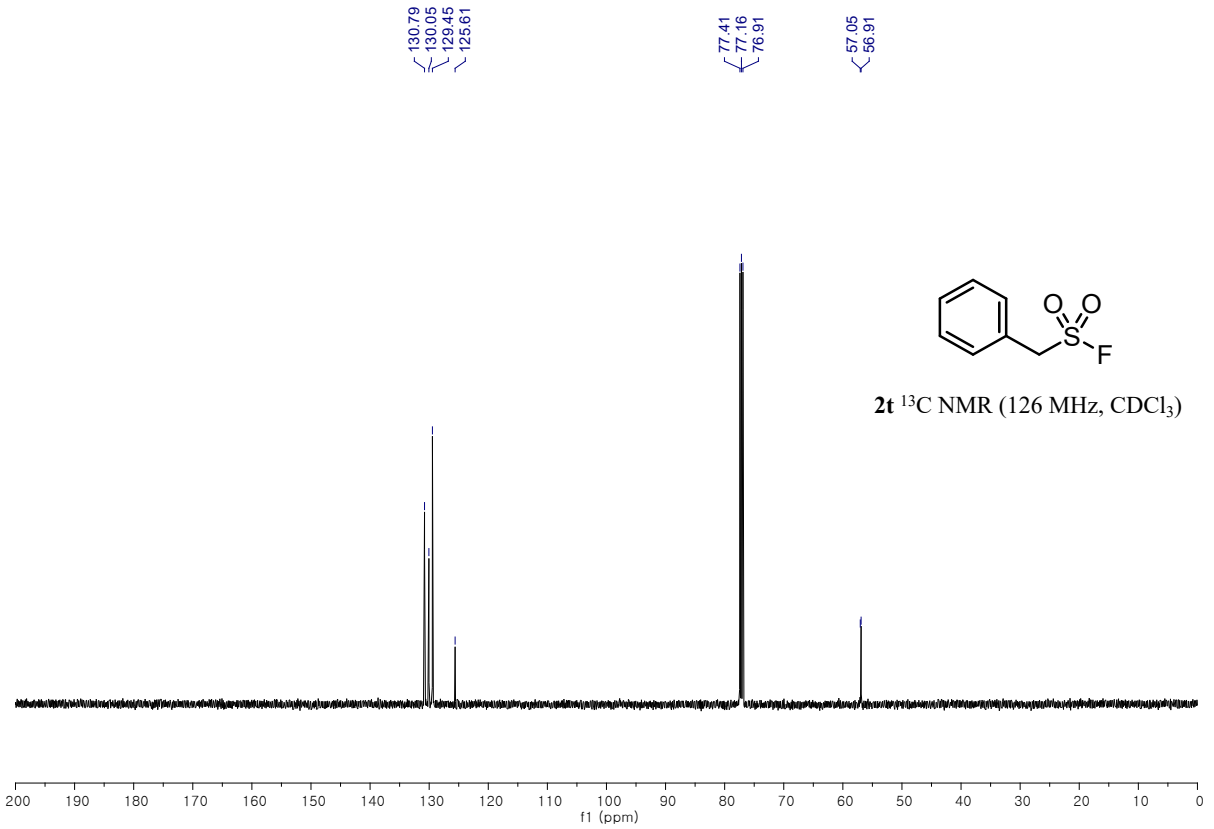


2s ^{19}F NMR (470 MHz, $CDCl_3$)

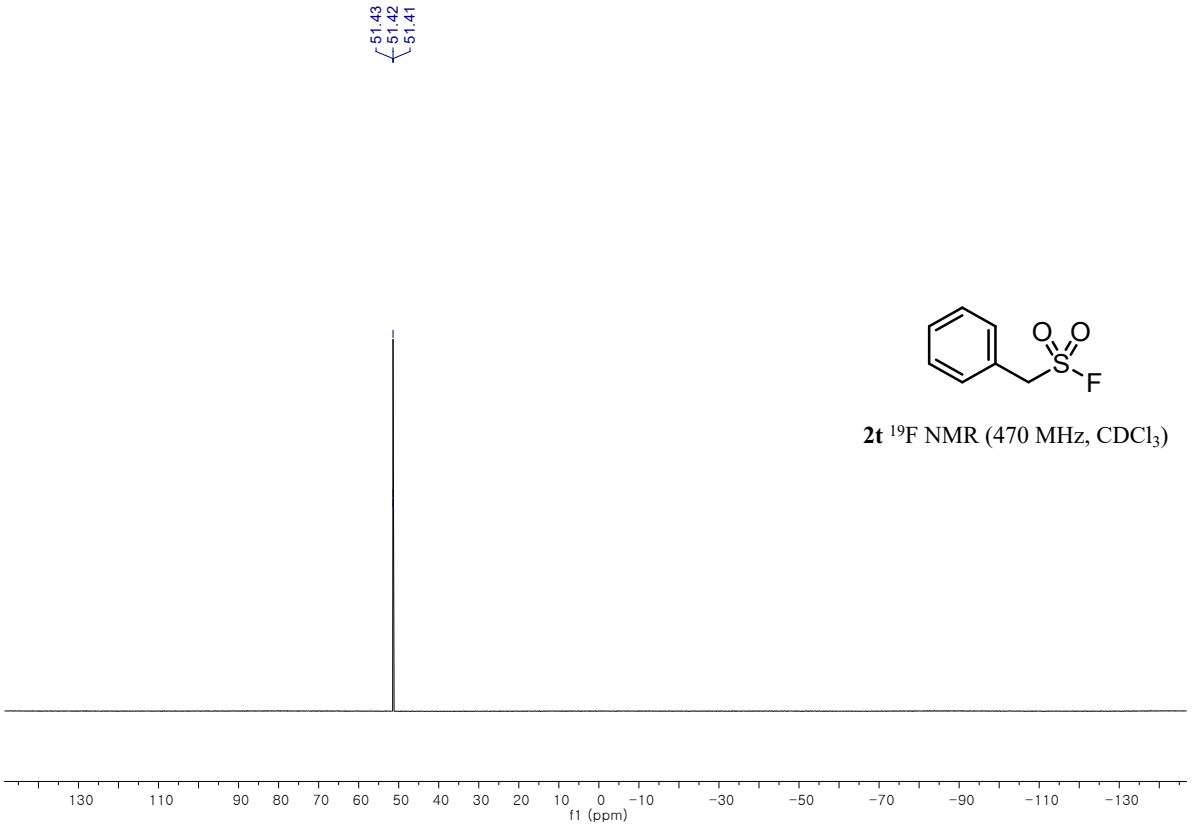
Phenylmethanesulfonyl fluoride (2t)



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



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



2t ^{19}F NMR (470 MHz, $CDCl_3$)