Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Tunable Photocatalytic Oxysulfonylation and Chlorosulfonylation of α-CF_3 Alkenes with Sulfonyl Chlorides

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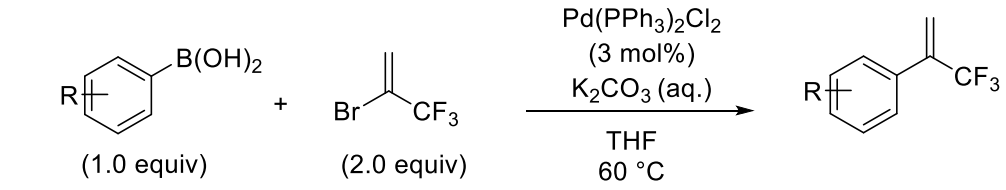
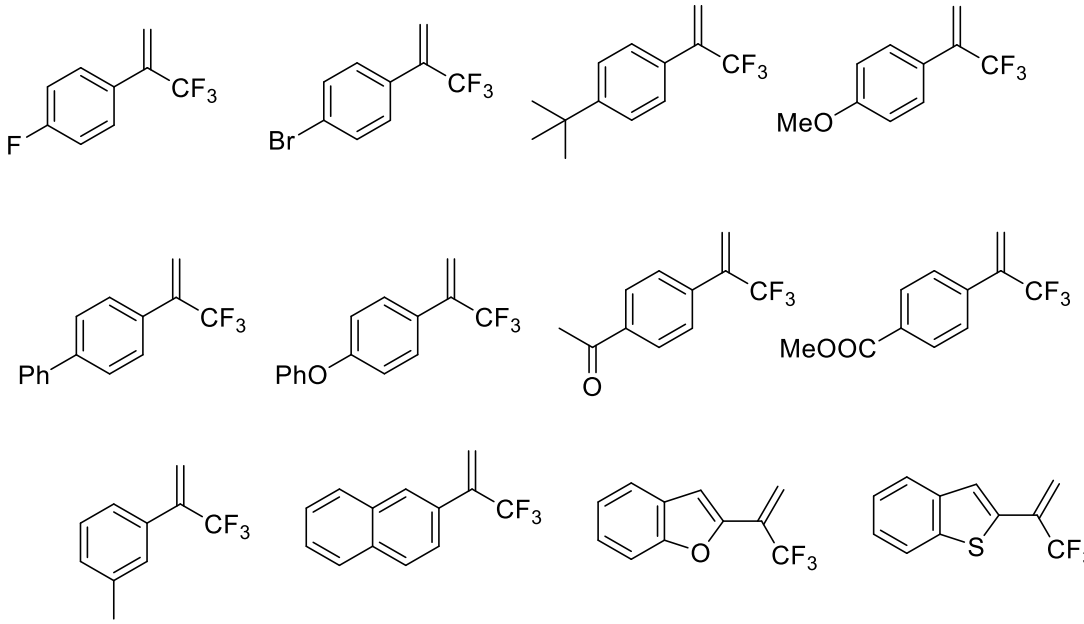
1. General Experimental Informations

Unless otherwise noted, all the reagents were purchased from commercial suppliers and used without further purification. ^{1}H NMR spectra were recorded at 400 or 600 MHz. The chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t =triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. ^{13}C NMR data were collected at 100 or 150 MHz with complete proton decoupling. ^{19}F NMR data were collected at 376 MHz. High resolution mass spectroscopy (HRMS) was recorded on Bruker Compact QTOF-MS with an electrospray ionization (ESI) interface (Bruker co. Bremen, Germany) and Agilent1260HpLC-6545Q-TOFLC-MS. Melting point of all compounds were measured by micro melting point apparatus (SGWX-4). Column chromatography was carried out on silica gel (200-300 mesh).

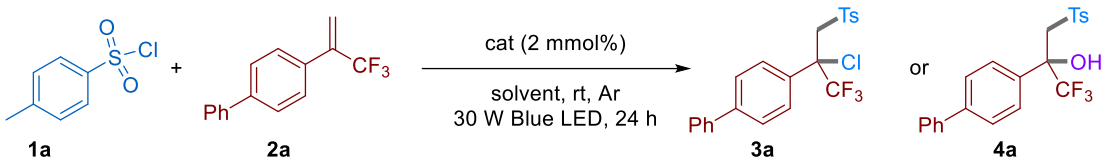
Preparation of Trifluoromethyl Alkenes





Trifluoromethyl alkenes were prepared according to reported synthetic procedures.(*Org. Lett.* **2017**, *19*, 946-949; *Angew. Chem. Int. Ed.*, 2020, **59**, 6706-6710.). To a Schlenk tube equipped with stir bar, arylboronic acid (1.0 equiv., 10 mmol) and $Pd(PPh_3)_2Cl_2$ (3 mol%, 0.3 mmol, 210.6 mg) were added. The vessel was evacuated and filled with argon (three times), and then aqueous K_2CO_3 (2.0 M, 20 mL) and THF (30 mL) were added. After addition of 2-bromo-3,3,3-trifluoropropene (2.0 equiv., 20 mmol, 2.1 mL), the solution was stirred at 60 ℃ for 12 hours (TLC tracking detection). The solvent was removed under reduced pressure and the residue was purified by column chromatography to afford the corresponding trifluoromethyl alkene (PE - PE/EA=100:1).

Optimization of reaction conditions

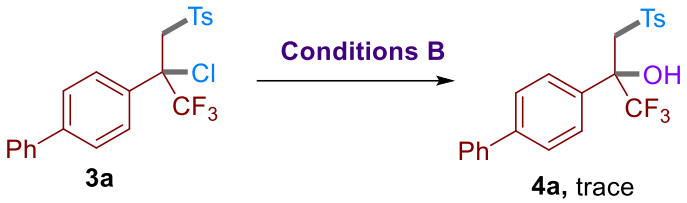


1a 2a 3a 4a

entry	solvent	cat	time	**3a** Yield (%)	**4a** Yield (%)
1	MeCN	$[Ru(bpy)_3][PF_6]$	24	nr	nr
2	MeCN	$[Ir(ppy)_2(dtbbpy)][PF_6]$	24	25	46
3	MeCN	$Ir(ppy)_3$	24	57	trace
4	MeCN	Eosin Y	24	nr	nr
5	DMF	$Ir(ppy)_3$	24	42	trace
6	THF	$Ir(ppy)_3$	24	79	trace
7	THF	$Ir(ppy)_3$	36	**91**	trace
8[b]	THF	$Ir(ppy)_3$	36	nr	nr
9	DMF	$[Ir(ppy)_2(dtbbpy)][PF_6]$	24	trace	31
10	THF	$[Ir(ppy)_2(dtbbpy)][PF_6]$	24	63	trace
11	MeCN/$H_2$0 (3:1)	$[Ir(ppy)_2(dtbbpy)][PF_6]$	24	14	65
12	MeCN/$H_2$0 (1:1)	$[Ir(ppy)_2(dtbbpy)][PF_6]$	24	trace	**86**
13	MeCN/$H_2$0 (1:1)	$Ir(ppy)_3$	24	trace	81
14[b]	MeCN/$H_2$0 (1:1)	$[Ir(ppy)_2(dtbbpy)][PF_6]$	24	nr	nr
15[b]	MeCN/H_2O(1:1)	$[Ir(ppy)_2(dtbbpy)][PF_6]$	24	nr	nr
16[b]	MeCN/H_2O (1:1)	-	24	nr	nr

[a] Reaction conditions: **1a** (0.4 mmol, 2.0 equiv.), **2a** (0.2 mmol, 1.0 equiv.), cat (2 mmol%), solvent (2 mL), 30 W blue LED, argon atmosphere, rt. [b] Without LED.

The control experiment that product **3a** was tested under irradiation of 30 W blue LED for 24 hours in conditions B. which further confirmed that the product **3a** was not an intermediate for producing the final product **4a**.



3a **4a,** trace

Time Profile of the Transformation with the Light ON/OFF over Time

Standard reactions were set up parallel on a 0.40 mmol scale according to the stand condition. After being irradiated for 2 h, an aliquot (200 μL) from the reaction mixture was transferred into a nuclear magnetic tube charged with 0.5 mL of $CDCl_3$-d_1. The yield of product **3a** was determined by ^{19}F NMR. Then the reaction mixture was stirred for 2 h with light-off. All of the following yields were analyzed in the identical way after a 2 hour light on or off.

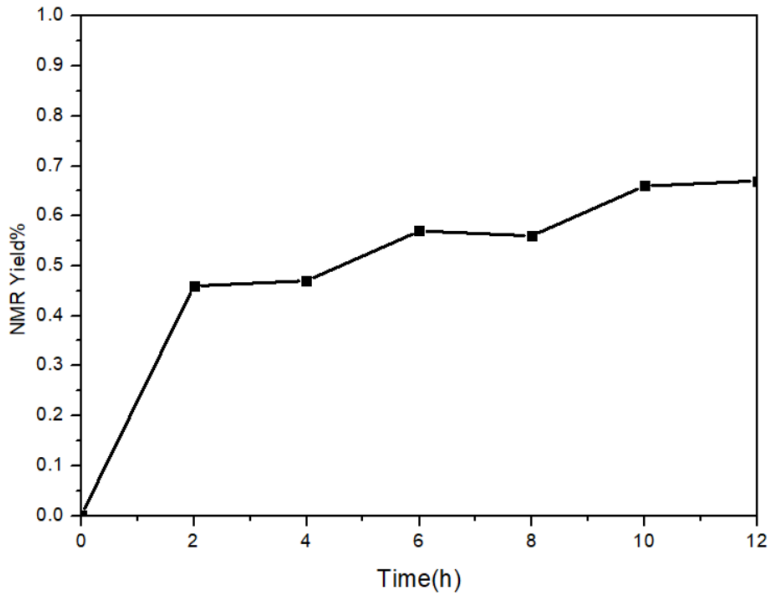
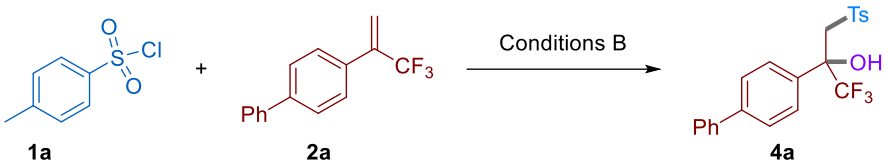
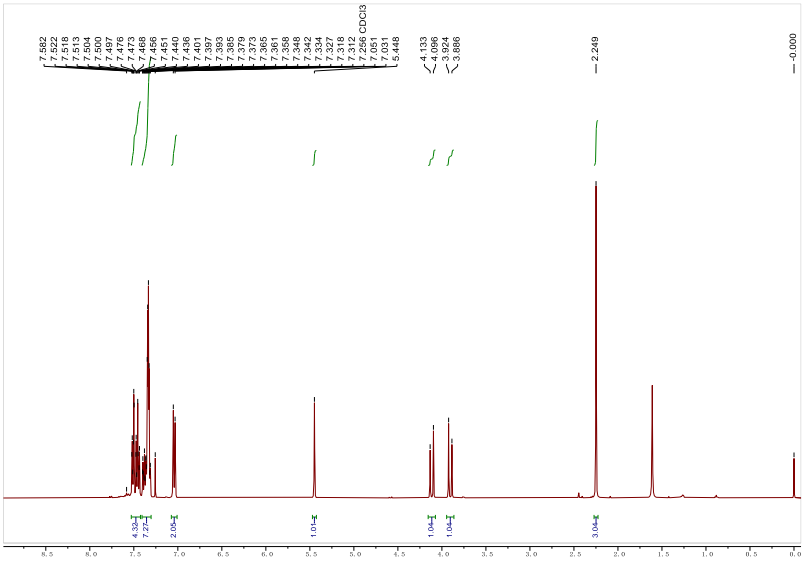


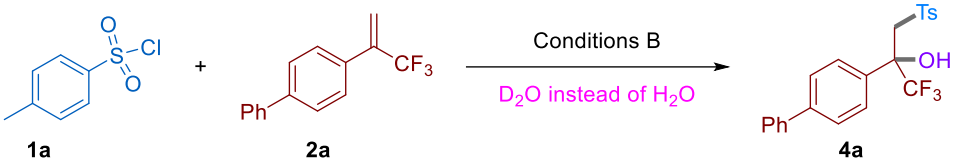
Figure S4. Time profile of the transformation with the light ON/OFF over time.

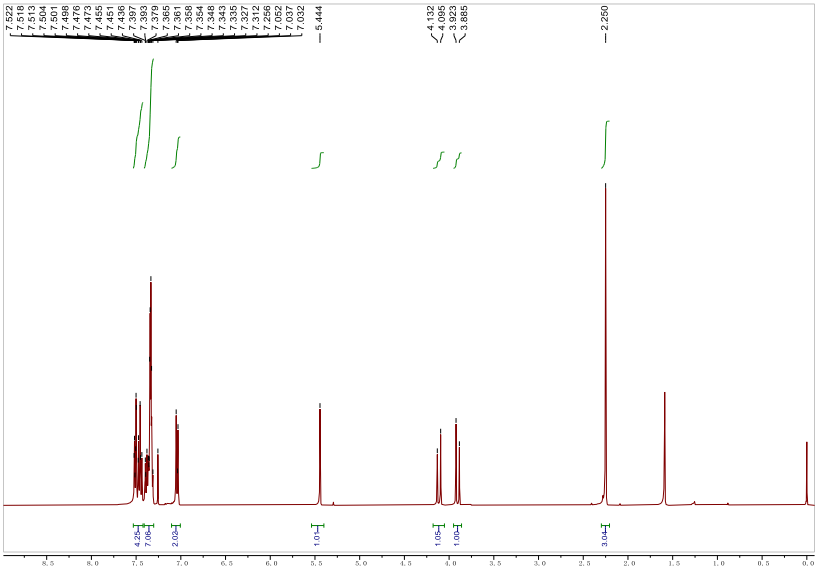
Labelling Experiment by Adding D_2O or $H_2{}^{18}O$

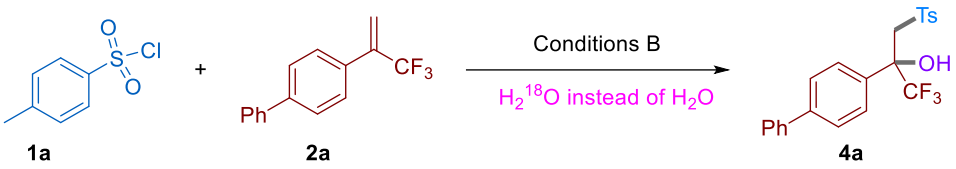
Standard reaction was set up by using deuterated **D_2O** instead of H_2O. As detected by ^1H NMR (Figure S7), deuterated product wasn't observed.



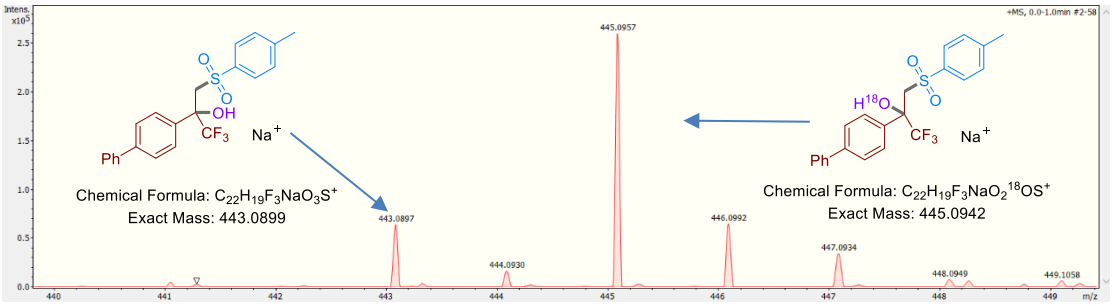




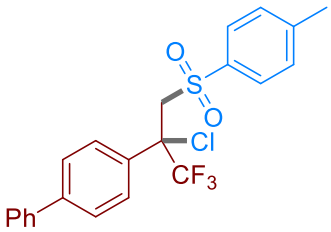




Standard reaction was set up by using deuterated **$H_2{}^{18}O$** instead of H_2O. As detected by ^1H NMR deuterated product wasn't observed. **The resulting mass spectrum clearly shows two peaks corresponding to the product 4a** (HRMS (ESI): $C_{22}H_{19}F_3NaO_3S^+$ $[M+Na]^+$ Calcd 443.0899, Found 443.0897)and ^{18}O-labelled product (HRMS (ESI): $C_{22}H_{19}F_3NaO_2{}^{18}OS^+$ $[M+Na]+$ Calcd 445.0942, Found 445.0957)**.**



Characterization data of compounds 3a-3y, 4a-4y.



3a

3a: 79.7 mg, white solid, yield: 91%;

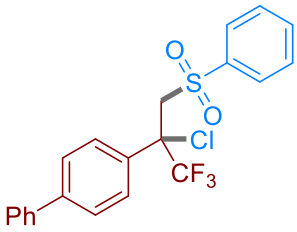
m.p. 112 – 114 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.55 – 7.61 (m, 6H), 7.44 – 7.52 (m, 4H), 7.37 – 7.41 (m, 1H), 7.17 (d, J = 8.0 Hz, 2H), 4.44 (d, J = 15.2 Hz, 1H), 4.12 (d, J = 15.2 Hz, 1H), 2.33 (s, 3H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -76.2 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.2, 142.4, 139.6, 137.3, 129.8, 129.3, 128.9, 128.7, 128.4, 128.0, 127.1, 123.5 (q, $^1J_{C\text{-}F}$ = 282.2 Hz, $\underline{C}F_3$), 68.83 (q, $^2J_{C\text{-}F}$ = 30 Hz, $\underline{C}(Cl)CF_3$), 60.89, 21.60 ppm;

HRMS (ESI): $C_{22}H_{18}ClF_3NaO_2S^+$ $[M+Na]^+$ Calcd 461.0560, Found 461.0564.



3b

3b: 79.8 mg, white solid, yield: 94%;

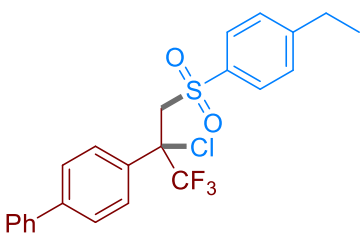
m.p. 100 – 102 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.68 – 7.71 (m, 2H), 7.54 – 7.61 (m, 5H), 7.45 – 7.52 (m, 4H), 7.37 – 7.42 (m, 3H), 4.47 (d, J = 15.6 Hz, 1H), 4.15 (d, J = 15.2 Hz, 1H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -76.2 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.5, 140.3, 139.7, 133.9, 129.3, 129.24, 129.21, 129.0, 128.7, 128.4, 128.0, 127.9, 127.1, 126.9, 123.5 (q, $^1J_{C\text{-}F}$ = 282.1 Hz, $\underline{C}F_3$), 69.8(q, $^2J_{C\text{-}F}$ = 30 Hz, $\underline{C}(Cl)CF_3$), 61.0 ppm;

HRMS (ESI): $C_{21}H_{16}ClF_3NaO_2S^+$ $[M+Na]^+$ Calcd 447.0404, Found 447.0407.



3c

3c: 79.6 mg, white solid, yield: 88%;

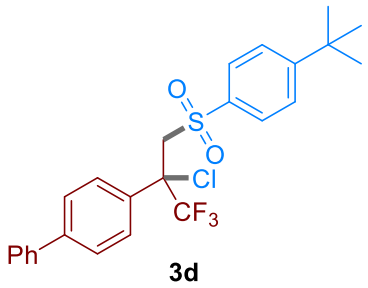
m.p. 85 – 87 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.56 – 7.61 (m, 6H), 7.44 – 7.52 (m, 4H), 7.36 – 7.40 (m, 1H), 7.19 – 7.21 (m, 2H), 4.45 (d, J = 15.2 Hz, 1H), 4.13 (d, J = 15.2 Hz, 1H), 2.62 (q, J = 7.6 Hz, 2H), 1.15 (t, J = 8.0 Hz, 3H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -76.2 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.3, 142.4, 139.7, 137.5, 129.3, 128.9, 128.7, 128.6, 128.4, 128.0, 127.1, 126.8, 123.5 (q, $^{1}J_{C\text{-}F}$ = 282.2 Hz, $\underline{C}F_3$), 69.0 (q, $^{2}J_{C\text{-}F}$ = 30 Hz, $\underline{C}(Cl)CF_3$), 60.9 ppm;

HRMS (ESI): $C_{23}H_{20}ClF_3NaO_2S^+$ $[M+Na]^+$ Calcd 475.0717, Found 475.0730.



3d

3d: 86.4 mg, white solid, yield: 90%;

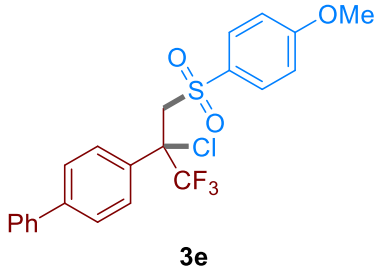
m.p. 99 – 101 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.57 – 7.63 (m, 6H), 7.44 – 7.52 (m, 4H), 7.36 – 7.40 (m, 3H), 4.46 (d, J = 15.2 Hz, 1H), 4.14 (d, J = 15.2 Hz, 1H), 1.22 (s, 9H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -76.2 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.3, 142.4, 139.7, 137.5, 129.3, 128.9, 128.7, 128.6, 128.4, 128.0, 127.1, 126.8, 123.5 (q, $^{2}J_{C\text{-}F}$ = 282.2 Hz, $\underline{C}F_3$), 69.0 (q, $^{2}J_{C\text{-}F}$ = 30 Hz, $\underline{C}(Cl)CF_3$), 60.9; 158.1, 142.4, 139.6, 137.3, 129.3, 128.9, 128.7, 128.1, 128.0, 127.1, 126.8, 126.2, 123.5 (q, $^{1}J_{C\text{-}F}$ = 282.2 Hz, $\underline{C}F_3$), 68.9 (q, $^{2}J_{C\text{-}F}$ = 30 Hz, $\underline{C}(Cl)CF_3$), 60.9, 35.2, 30.9 ppm;

HRMS (ESI): $C_{25}H_{24}ClF_3NaO_2S^+$ $[M+Na]^+$ Calcd 503.1030, Found 503.1022.



3e

3e: 76.3 mg, white solid, yield: 84%;

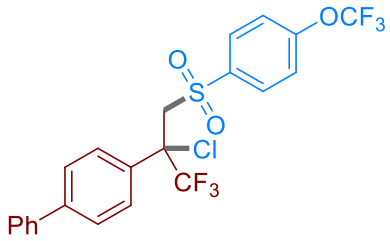
m.p. 114– 116 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.55 – 7.59 (m, 6H), 7.45 – 7.51 (m, 4H), 7.36 – 7.41 (m, 1H), 6.78 – 6.82 (m, 2H), 4.43 (d, J = 15.2 Hz, 1H), 4.11 (d, J = 15.2 Hz, 1H), 3.71 (s, 3H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -76.3 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.0, 142.3, 139.6, 131.5, 130.7, 129.2, 129.0, 128.7, 128.0, 127.1, 126.8, 123.5 (q, $^{1}J_{C\text{-}F}$ = 282.1 Hz, $\underline{C}F_3$), 114.3, 68.9 (q, $^{2}J_{C\text{-}F}$ = 30 Hz, $\underline{C}(Cl)CF_3$), 61.00, 55.6 ppm;

HRMS (ESI): $C_{22}H_{18}ClF_3NaO_3S^+$ $[M+Na]^+$ Calcd 477.0509, Found 477.0531.



3f

3f: 94.5 mg, white solid, yield: 93%;

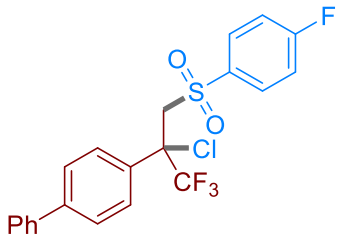
m.p. 118 – 120 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.72 – 7.76 (m, 2H), 7.53 – 7.61 (m, 2H), 7.57 (m, 6H), 7.45 – 7.49 (m, 2H), 7.39 – 7.42 (m, 1H), 7.20 – 7.23 (m, 2H), 4.49 (d, J = 15.6 Hz, 1H), 4.17 (d, J = 15.6 Hz, 1H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -57.7, -76.2 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) 153.2, 142.8, 139.4, 138.2, 130.8, 129.1, 129.0, 129.0 (q, $^1J_{C\text{-}F}$ = 158.8 Hz, O$\underline{C}$F$_3$), 128.7, 128.1, 127.1, 127.0, 123.4 (q, $^1J_{C\text{-}F}$ = 282.2 Hz, $\underline{C}$F$_3$), 118.8, 77.24, 68.90, 68.7 (q, $^2J_{C\text{-}F}$ = 30 Hz, $\underline{C}$(Cl)CF$_3$), 61.3 ppm;

HRMS (ESI): $C_{22}H_{15}ClF_6NaO_3S^+$ $[M+Na]^+$ Calcd 531.0227, Found 531.0224.



3g

3g: 73.4 mg, white solid, yield: 83%;

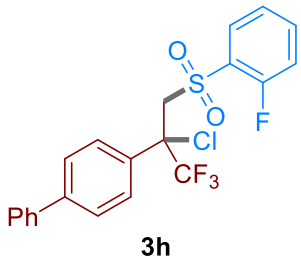
m.p. 113 – 115 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.66 – 7.71 (m, 2H), 7.56 – 7.60 (m, 4H), 7.45 – 7.54 (m, 4H), 7.38 – 7.42 (m, 1H), 7.03 – 7.09 (m, 2H), 4.47 (d, J = 15.2 Hz, 1H), 4.15 (d, J = 15.2 Hz, 1H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -76.2, -102.34 – -102.29(m) ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) 166.0 (d, $^1J_{C\text{-}F}$ = 255.9 Hz), 142.7, 139.5, 136.1 (d, $^4J_{C\text{-}F}$ = 3.5 Hz), 131.5, 131.4, 129.1, 129.0, 128.7, 128.1, 127.2, 127.0, 123.4 (q, $^1J_{C\text{-}F}$ = 282.2 Hz, $\underline{C}$F$_3$), 116.5 (d, $^2J_{C\text{-}F}$ = 22.5 Hz), 68.8 (q, $^2J_{C\text{-}F}$ = 30.1 Hz, $\underline{C}$(Cl)CF$_3$), 61.2 ppm;

HRMS (ESI): $C_{21}H_{15}ClF_4NaO_2S^+$ $[M+Na]^+$ Calcd 465.0310, Found 465.0327.



3h

3h: 70.7 mg, white solid, yield: 80%;

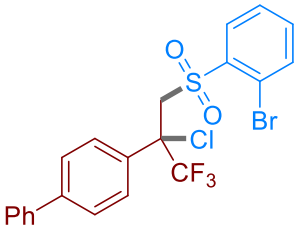
m.p. 85 – 87 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.63 (d, J = 8.4 Hz, 2H), 7.53 – 7.59 (m, 4H), 7.43 – 7.49 (m, 4H), 7.36 – 7.41 (m, 1H), 7.10 – 7.18 (m, 2H), 4.62 (d, J = 15.6 Hz, 1H), 4.32 (d, J = 15.6 Hz, 1H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -75.8, -108.19 – -108.25 (m) ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) 159.3 (d, $^{1}J_{C\text{-}F}$ = 253.9 Hz), 142.6, 139.6, 136.4 (d, $^{3}J_{C\text{-}F}$ = 8.3 Hz), 130.6, 129.2, 129.0, 128.5, 128.3 (d, $^{3}J_{C\text{-}F}$ = 13.9 Hz), 128.0, 127.2, 126.9, 124.8 (d, $^{4}J_{C\text{-}F}$ = 3.8 Hz), 123.5 (q, $^{1}J_{C\text{-}F}$ = 282.0 Hz, $\underline{C}F_3$), 117.0 (d, $^{2}J_{C\text{-}F}$ = 21.1 Hz), 68.7 (q, $^{2}J_{C\text{-}F}$ = 30.2 Hz, $\underline{C}(Cl)CF_3$), 60.2 (d, $J_{C\text{-}F}$ = 2.7 Hz) ppm;

HRMS (ESI): $C_{21}H_{15}ClF_4NaO_2S^+$ $[M+Na]^+$ Calcd 465.0310, Found 465.0312.



3i

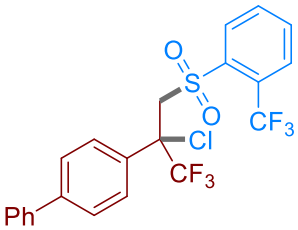
3i: 48.8 mg, colorless oil, yield: 84%;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.67 – 7.72 (m, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.52 – 7.55 (m, 2H), 7.43 – 7.49 (m, 4H), 7.34 – 7.42 (m, 2H), 4.83 (d, *J* = 15.6 Hz, 1H), 4.44 (d, *J* = 15.6 Hz, 1H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -75.8 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.5, 139.6, 139.5, 135.2, 134.7, 132.2, 129.2, 129.0, 128.5, 128.05, 128.03, 127.1, 126.8, 120.6, 69.0 (q, $^{2}J_{C\text{-}F}$ = 29.9 Hz, $\underline{C}(Cl)CF_3$), 58.4 ppm;

HRMS (ESI): $C_{21}H_{15}BrClF_3NaO_2S^+$ $[M+Na]^+$ Calcd 524.9509, Found 524.9531.



3j

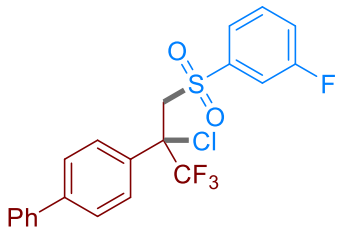
3j: 84.6 mg, colorless oil, yield: 86%;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.85 – 7.88 (m, 2H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.58 (m, 5H), 7.44 – 7.49 (m, 2H), 7.37 – 7.42 (m, 1H), 4.65 (d, *J* = 15.6 Hz, 1H), 4.29 (d, *J* = 15.6 Hz, 1H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -56.3, -75.8 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.6, 139.5, 139.1, 134.1, 133.3, 132.6, 129.4, 129.0, 128.7, 128.4 (q, $^{4}J_{C\text{-}F}$ = 5.9 Hz, $\underline{C}(Cl)CF_3$), 127.1, 126.9, 123.0 (q, $^{1}J_{C\text{-}F}$ = 201.9 Hz), 69.1 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz, $\underline{C}(Cl)CF_3$), 61.3 (q, $^{2}J_{C\text{-}F}$ = 30.5 Hz) ppm;

HRMS (ESI): $C_{22}H_{15}ClF_6NaO_2S^+$ $[M+Na]^+$ Calcd 515.0278, Found 515.0299.



3k

3k: 76.0 mg, white solid, yield: 86%;

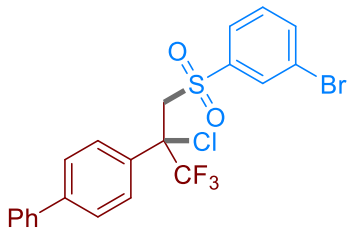
m.p. 97 – 99 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.55 – 7.61 (m, 4H), 7.45 – 7.53 (m, 5H), 7.37 – 7.42 (m, 2H), 7.33 – 7.36 (m, 1H), 7.21 – 7.26 (m, 1H), 4.48 (d, J = 15.2 Hz, 1H), 4.16 (d, J = 15.2 Hz, 1H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -76.2, -108.68 – -108.74 (m) ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.2 (d, $^1J_{C\text{-}F}$ = 251.1 Hz), 142.7, 142.1 (d, $^3J_{C\text{-}F}$ = 6.6 Hz), 139.5, 131.1 (d, $^3J_{C\text{-}F}$ = 7.8 Hz), 129.0, 128.9, 128.6, 128.0, 127.2, 127.0, 124.2 (d, $^4J_{C\text{-}F}$ = 3.5 Hz), 123.4 (q, $^1J_{C\text{-}F}$ = 282.2 Hz, CF_3), 121.3 (d, $^2J_{C\text{-}F}$ = 20.7 Hz), 115.9 (d, $^2J_{C\text{-}F}$ = 24.2 Hz), 68.7 (q, $^2J_{C\text{-}F}$ = 30.0 Hz, C(Cl)CF_3), 61.1;

HRMS (ESI): $C_{21}H_{15}ClF_4NaO_2S^+$ $[M+Na]^+$ Calcd 465.0310, Found 465.0323.



3l

3l: 81.2 mg, white solid, yield: 81%;

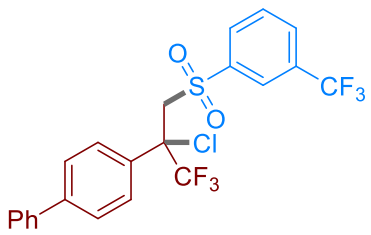
m.p. 114 – 116 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.75 (t, J = 2.0 Hz, 1H), 7.63 – 7.67 (m, 2H), 7.57 – 7.61 (m, 4H), 7.51 – 7.54 (m, 2H), 7.45 – 7.50 (m, 2H), 4.47 (d, J = 15.2 Hz, 1H), 4.16 (d, J = 15.2 Hz, 1H).

^{19}F NMR (375 MHz, Chloroform-*d*) δ -76.2;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.7, 141.7, 139.5, 137.0, 131.6, 130.6, 129.0, 128.8, 128.6, 128.1, 127.2, 127.0, 126.9, 123.2, 69.0 (q, $^2J_{C\text{-}F}$ = 30.0 Hz, C(Cl)CF_3), 61.1.

HRMS (ESI): $C_{21}H_{15}BrClF_3NaO_2S^+$ $[M+Na]^+$ Calcd 524.9509, Found 524.9519.



3m

3m: 70.8 mg, white solid, yield: 72%;

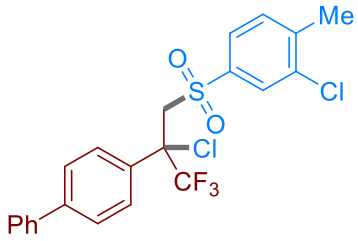
m.p. 1148 – 120 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.98 (s, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.51 – 7.59 (m, 8H), 7.45 – 7.49 (m, 2H), 7.38 – 7.42 (m, 1H), 4.52 (d, J = 15.2 Hz, 1H), 4.19 (d, J = 15.2 Hz, 1H).

^{19}F NMR (375 MHz, Chloroform-*d*) δ -62.8, -76.3;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.8, 141.1, 139.4, 132.1, 131.9, 131.7, 130.7 (q, $^{3}J_{C\text{-}F}$ = 3.6 Hz), 130.0, 129.7, 129.0, 128.8, 128.6, 128.1, 127.1, 127.0, 125.9 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 123.0 (q, $^{1}J_{C\text{-}F}$ = 233.4 Hz, $\underline{C}F_3$), 68.7 (q, $^{2}J_{C\text{-}F}$ = 30.4 Hz, $\underline{C}(Cl)CF_3$), 61.1.

HRMS (ESI): $C_{22}H_{15}ClF_6NaO_2S^+$ $[M+Na]^+$ Calcd 515.0278, Found 515.0288.



3n

3n: 79.3 mg, white solid, yield: 84%;

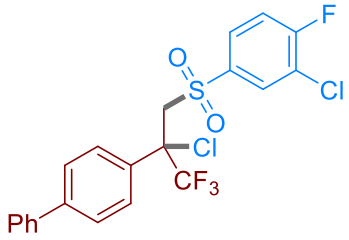
m.p. 136 – 138 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.56 – 7.60 (m, 5H), 7.45 – 7.53 (m, 5H), 7.36 – 7.41 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 4.45 (d, *J* = 15.2 Hz, 1H), 4.13 (d, *J* = 15.2 Hz, 1H), 2.31 (m, 3H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -76.3 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.3, 142.5, 139.4, 138.7, 135.3, 131.5, 129.2, 128.9, 128.6, 128.1, 127.1, 126.8, 126.5, 123.4 (q, $^{1}J_{C\text{-}F}$ = 282.2 Hz, $\underline{C}F_3$), 68.7 (q, $^{2}J_{C\text{-}F}$ = 30.2 Hz, $\underline{C}(Cl)CF_3$), 61.0, 20.4 ppm;

HRMS (ESI): $C_{22}H_{17}Cl_2F_3NaO_2S^+$ $[M+Na]^+$ Calcd 495.0171, Found 495.0188.



3o

3o: 64.7mg, white solid, yield: 68%;

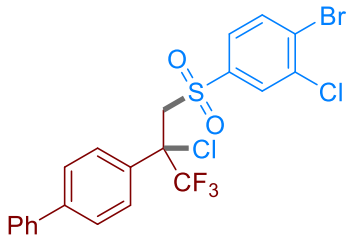
m.p. 127– 129 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.67 (dd, *J* = 6.8, 2.4 Hz, 1H), 7.52 – 7.63 (m, 7H), 7.45 – 7.51 (m, 2H), 7.38 – 7.42 (m, 1H), 7.15 (t, *J* = 8.4 Hz, 1H), 4.73 (d, *J* = 15.2 Hz, 1H), 4.16 (d, *J* = 15.2 Hz, 1H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -76.3, -104.2 – -104.4 (m) ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.5 (d, $^{1}J_{C\text{-}F}$ = 258.7 Hz), 143.0, 139.3, 136.7 (d, $^{4}J_{C\text{-}F}$ = 3.7 Hz), 131.9, 131.8, 129.3, 129.2, 129.0, 128.7, 128.6, 128.2, 127.2, 127.0, 123.6 (q, $^{1}J_{C\text{-}F}$ = 222.5 Hz, $\underline{C}F_3$), 122.5, 117.5 (d, $^{2}J_{C\text{-}F}$ = 22.5 Hz), 68.7 (q, $^{2}J_{C\text{-}F}$ = 30.5 Hz, $\underline{C}(Cl)CF_3$), 61.4 ppm;

HRMS (ESI): $C_{21}H_{14}Cl_2F_4NaO_2S^+$ $[M+Na]^+$ Calcd 498.9920, Found 498.9948.



3p

3p: 82.5 mg, white solid yield: 77%;

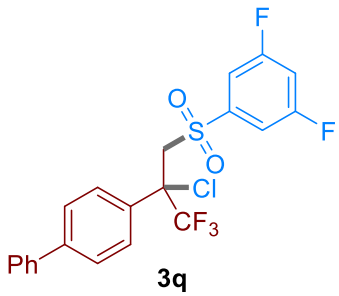
m.p. 113 – 115 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.62 – 7.65 (m, 2H), 7.58–7.61 (m, 2H), 7.52 – 7.57 (m, 4H), 7.45 – 7.50 (m, 2H), 7.34 – 7.43 (m, 2H), 4.47 (d, J = 15.6 Hz, 1H), 4.16 (d, J = 15.6 Hz, 1H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -76.2 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.9, 140.1, 139.2, 135.9, 134.5, 130.3, 129.8, 129.7, 128.9, 128.7, 128.6, 128.2, 127.4, 127.3, 127.0, 123.3 (q, $^{1}J_{C\text{-}F}$ = 284.3 Hz, $\underline{C}F_3$), 77.24, 68.6 (q, $^{2}J_{C\text{-}F}$ = 29.9 Hz, $\underline{C}(Cl)CF_3$), 61.3 ppm;

HRMS (ESI): $C_{21}H_{14}BrCl_2F_3NaO_2S^+$ $[M+Na]^+$ Calcd 558.9119, Found 558.9121.



3q

3q: 82.8 mg, white solid, yield: 90%;

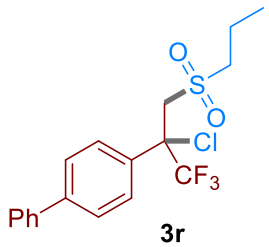
m.p. 115 – 117 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.52 – 7.61 (m, 6H), 7.45–7.50 (m, 2H), 7.38 – 7.43 (m, 1H), 7.18 – 7.24 (m, 2H), 6.94 – 6.99 (m, 1H), 4.48 (d, J = 15.2 Hz, 1H), 4.17 (d, J = 15.2 Hz, 1H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -76.2, -104.52 – -104.57 (m) ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.7 (d, $^{1}J_{C\text{-}F}$ = 254.5 Hz), 162.6 (d, $^{1}J_{C\text{-}F}$ = 254.7 Hz), 143.0, 139.4, 129.0, 128.8, 128.6, 128.5 (d, $^{1}J_{C\text{-}F}$ = 248.6 Hz), 128.2, 127.2, 127.0, 123.4 (q, $^{1}J_{C\text{-}F}$ = 282.2 Hz, $\underline{C}F_3$), 112.4, 112.2 (d, $^{3}J_{C\text{-}F}$ = 11.1 Hz), 109.7 (t, $^{2}J_{C\text{-}F}$ = 24.8 Hz), 68.6 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz, $\underline{C}(Cl)CF_3$), 61.2 ppm;

HRMS (ESI): $C_{21}H_{14}ClF_5NaO_2S^+$ $[M+Na]^+$ Calcd 483.0215, Found 483.0232.



3r

3r: 64.7 mg, white solid, yield: 83%;

m.p. 99– 101 ℃;

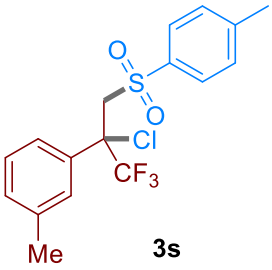
^{1}H NMR (600 MHz, Chloroform-d) δ 7.78 (d, J = 7.8 Hz, 2H), 7.65 – 7.69 (m, 2H), 7.60 – 7.62 (m, 2H), 7.44 – 7.47 (m, 2H), 7.37 – 7.40 (m,

1H), 4.27 (d, *J* = 15.6 Hz, 1H), 4.00 (d, *J* = 15.6 Hz, 1H), 2.99 – 3.10 (m, 2H), 1.84 – 1.92 (m, 2H), 1.04 (t, *J* = 7.2 Hz, 1H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -76.1 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.8, 139.6, 129.8, 129.7, 128.9, 128.6, 128.0, 127.2, 127.1, 123.5 (q, $^{1}J_{C\text{-}F}$ = 282.0 Hz), 68.9 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz, C(Cl)CF_3), 58.7, 57.7, 15.6, 13.0 ppm;

HRMS (ESI): $C_{18}H_{18}ClF_3NaO_2S^+$ $[M+Na]^+$ Calcd 413.0560, Found 413.0563.



3s

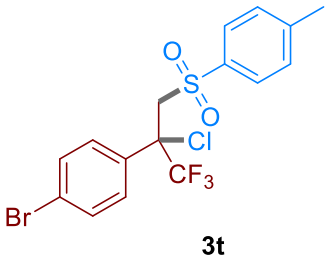
3s: 62.4 mg, colorless oil, yield: 83%;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.52 – 7.55 (m, 2H), 7.34 – 7.39 (m, 2H), 7.15 – 7.24 (m, 4H), 4.40 (d, *J* = 15.2 Hz, 1H), 4.08 (d, *J* = 15.6 Hz, 1H), 2.40 (s, 3H), 2.30 (s, 3H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -76.3 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.0, 138.0, 137.38, 130.4, 130.3, 129.9, 129.7, 128.8, 128.3, 128.2, 127.9, 125.4, 123.5 (q, $^{1}J_{C\text{-}F}$ = 282.1 Hz), 69.0 (q, $^{2}J_{C\text{-}F}$ = 29.9 Hz, C(Cl)CF_3), 61.0, 21.5 ppm;

HRMS (ESI): $C_{17}H_{16}ClF_3NaO_2S^+$ $[M+Na]^+$ Calcd 399.0404, Found 399.0410.



3t

3t: 75.7 mg, white solid, yield: 86%;

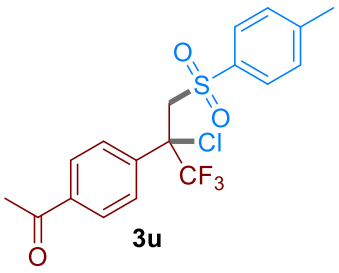
m.p. 95 – 97 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.55 (d, *J* =8.4 Hz, 2H), 7.39 – 7.45 (m, 4H), 7.23 (d, *J* =8.4 Hz, 2H), 4.34 (d, *J* = 15.2 Hz, 1H), 4.06 (d, *J* = 15.2 Hz, 1H), 2.45 (s, 3H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -76.4 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.5, 137.1, 131.5, 129.9, 129.6, 128.3, 124.5, 123.2 (q, $^{1}J_{C\text{-}F}$ = 282.0 Hz), 68.5 (q, $^{2}J_{C\text{-}F}$ = 29.9 Hz, C(Cl)CF_3), 60.6, 21.7 ppm;

HRMS (ESI): $C_{16}H_{13}BrClF_3NaO_2S^+$ $[M+Na]^+$ Calcd 462.9352, Found 462.9382.



3u

3u: 71.1 mg, white solid, yield: 88%;

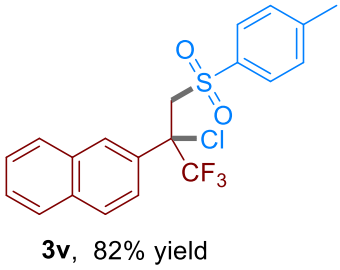
m.p. 106 – 108 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 8.03 (dt, J = 8.0, 1.6 Hz, 1H), 7.66 (t, J = 2.0 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.44 – 7.47 (m, 3H), 7.21 – 7.25 (m, 3H), 2.59 (s, 3H), 2.40 (s, 3H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -67.7 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.8, 145.6, 140.2 (q, $^2J_{C\text{-}F}$ = 31.9 Hz), 137.3 (q, $^3J_{C\text{-}F}$ = 5.0 Hz), 136.8, 136.3, 133.9, 130.0, 129.7, 129.2, 129.0, 128.7, 128.4, 128.2, 128.1, 121.5 (q, $^1J_{C\text{-}F}$ = 274.9 Hz), 70.93, 26.6, 21.6 ppm;

HRMS (ESI): $C_{18}H_{16}ClF_3NaO_3S^+$ $[M+Na]^+$ Calcd 427.0353, Found 427.0364.



3v, 82% yield

3v: 67.6 mg, white solid, yield: 82%;

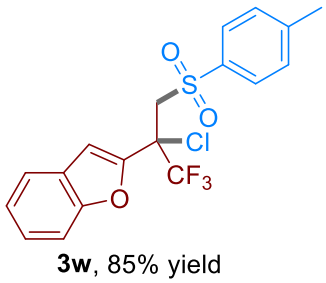
m.p. 109 – 111 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.99 (d, J = 2.4 Hz, 1H), 7.76 – 7.82 (m, 2H), 7.71 (d, J = 8.8 Hz, 1H), 7.49 – 7.56 (m, 3H), 7.43 – 7.46 (m, 2H), 6.94 – 6.96 (m, 2H), 4.52 (d, J = 15.2 Hz, 1H), 4.16 (d, J = 15.2 Hz, 1H), 2.17 (s, 3H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -75.9 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.1, 136.9, 133.3, 132.4, 129.5, 129.0, 128.7, 128.3, 128.1, 127.6, 127.5, 127.4, 126.8, 124.4, 123.6 (q, $^1J_{C\text{-}F}$ = 282.3 Hz), 68.1 (q, $^2J_{C\text{-}F}$ = 29.9 Hz, C(Cl)CF_3), 60.9, 21.4 ppm;

HRMS (ESI): $C_{20}H_{16}ClF_3NaO_2S^+$ $[M+Na]^+$ Calcd 435.0404, Found 435.0423.



3w, 85% yield

3w: 68.3 mg, white solid, yield: 85%;

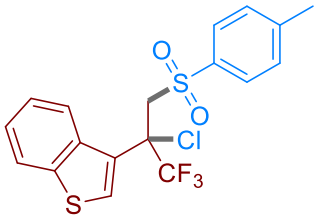
m.p. 113 – 115 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.55 – 7.58 (m, 2H), 7.50 – 7.53 (m, 2H), 7.21 – 7.32 (m, 3H), 6.96 – 6.99 (m, 3H), 4.52 (d, J = 15.2 Hz, 1H), 4.16 (d, J = 15.2 Hz, 1H), 2.16 (s, 3H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -75.8 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.3, 146.0, 145.2, 135.8, 129.3, 128.3, 127.1, 125.7, 123.5, 122.6 (q, $^1J_{C\text{-}F}$ = 283.7 Hz), 111.5, 110.7, 62.6 (q, $^2J_{C\text{-}F}$ = 32.5 Hz, C(Cl)CF_3), 58.4, 21.5 ppm;

HRMS (ESI): $C_{18}H_{14}ClF_3NaO_3S^+$ $[M+Na]^+$ Calcd 425.0196, Found 425.0206.



3x

3u: 69.4 mg, white solid, yield: 83%;

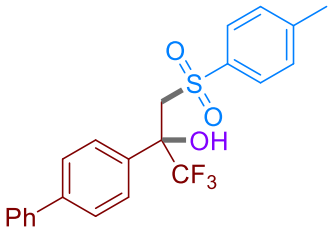
m.p. 117 – 119 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.86 (s, 1H), 7.70 – 7.77 (m, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.24 – 7.30 (m, 2H), 6.92 (d, J = 8.0 Hz, 2H), 4.63 (d, J = 14.4 Hz, 1H), 4.23 (d, J = 15.2 Hz, 1H), 2.25 (s, 3H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -73.8 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.8, 141.1, 135.8, 135.5, 131.3, 129.2, 127.9, 125.4, 124.5, 124.3, 123.7 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 123.5 (q, $^1J_{C\text{-}F}$ = 282.8 Hz), 67.2 (q, $^2J_{C\text{-}F}$ = 32.1 Hz, C(Cl)CF_3), 59.9, 21.5 ppm;

HRMS (ESI): $C_{18}H_{14}ClF_3NaO_2S_2^+$ $[M+Na]^+$ Calcd 440.9968, Found 440.9984.



4a

4a: 69.7 mg, white solid, yield: 83%;

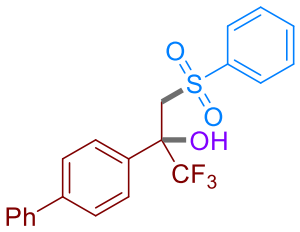
m.p. 155 – 157 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.41 – 7.52 (m, 4H), 7.31 – 7.40 (m, 7H), 7.04 (d, J = 8.0 Hz, 2H), 5.45 (s, 1H), 4.11 (d, J = 14.8 Hz, 1H), 3.90 (d, J = 15.2 Hz, 1H), 2.25 (s, 3H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -80.7 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.1, 141.8, 140.0, 136.1, 132.5, 129.7, 128.9, 127.9, 127.8, 127.3, 127.0, 126.7, 123.8 (q, $^1J_{C\text{-}F}$ = 285.5 Hz), 75.3 (q, $^2J_{C\text{-}F}$ = 29.8 Hz), 58.5, 21.5 ppm;

HRMS (ESI): $C_{22}H_{19}F_3NaO_3S^+$ $[M+Na]^+$ Calcd 443.0899, Found 443.0900.



4b

4b: 74.7 mg, white solid, yield: 92%;

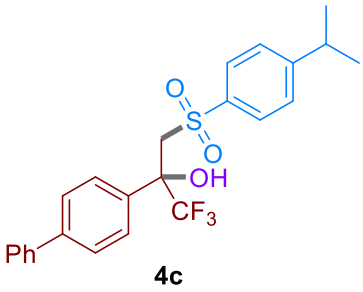
m.p. 137 – 139 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.43 – 7.51 (m, 7H), 7.36 – 7.41 (m, 1H), 7.29 – 7.36 (m, 5H), 7.24 – 7.26 (m, 1H), 5.41 (s, 1H), 4.15 (d, J = 15.2 Hz, 1H), 3.94 (d, J = 14.8 Hz, 1H), 2.25 (s, 3H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -80.6 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 141.9, 140.0, 139.1, 133.7, 132.5, 129.1, 128.9, 128.0, 127.8, 127.7, 127.2, 127.0, 126.9, 123.7 (q, $^{1}J_{C\text{-}F}$ = 283.9 Hz), 75.4 (q, $^{2}J_{C\text{-}F}$ = 29.6 Hz), 58.6 ppm;

HRMS (ESI): $C_{21}H_{17}F_3NaO_3S^+$ $[M+Na]^+$ Calcd 429.0743, Found 429.0743.



4c

4c: 73.5 mg, white solid, yield: 82%;

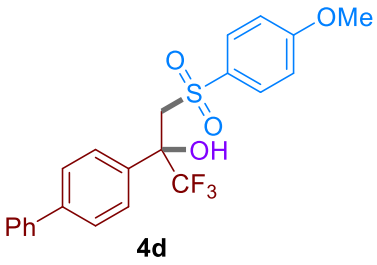
m.p. 139 – 141℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.50 – 7.53 (m, 2H), 7.42 – 7.47 (m, 2H), 7.34 – 7.39 (m, 5H), 7.30 – 7.33 (m, 2H), 7.07 – 7.09 (m, 2H), 5.47 (s, 1H), 4.13 (d, *J* = 14.8 Hz, 1H), 3.92 (d, *J* = 15.2 Hz, 1H), 2.72 – 2.79 (m, 1H), 1.03 (dd, *J* = 16.0, 7.2 Hz, 6H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -80.7 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.9, 141.9, 139.9, 136.4, 132.5, 128.9, 128.0, 127.9, 127.8, 127.3, 127.2, 127.0, 126.7, 123.8 (q, $^{1}J_{C\text{-}F}$ = 283.8 Hz), 75.4 (q, $^{2}J_{C\text{-}F}$ = 29.4 Hz), 58.6, 34.1, 23.4, 23.2 ppm;

HRMS (ESI): $C_{24}H_{23}F_3NaO_3S^+$ $[M+Na]^+$ Calcd 471.1212, Found 471.1222.



4d

4c: 70.6 mg, white solid, yield: 81%;

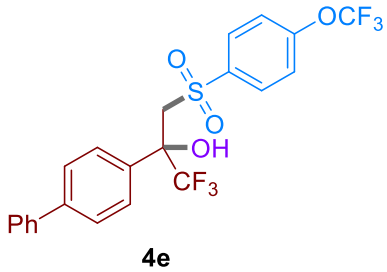
m.p. 146 – 148 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.50 – 7.53 (m, 2H), 7.43 – 7.47 (m, 2H), 7.32 – 7.39 (m, 7H), 6.63 – 6.67 (m, 2H), 5.47 (s, 1H), 4.11 (d, *J* = 15.2 Hz, 1H), 3.90 (d, *J* = 14.8 Hz, 1H), 3.58 (s, 3H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -80.8 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.9, 141.7, 139.9, 132.5, 130.3, 130.0, 129.0, 128.0, 127.9, 127.3, 127.0, 126.7, 123.8 (q, $^{1}J_{C\text{-}F}$ = 283.8 Hz), 114.3, 75.3 (q, $^{2}J_{C\text{-}F}$ = 29.8 Hz), 58.5, 55.5 ppm;

HRMS (ESI): $C_{22}H_{19}F_3NaO_4S^+$ $[M+Na]^+$ Calcd 459.0848, Found 459.0862.



4e

4e: 82.3 mg, white solid, yield: 84%;

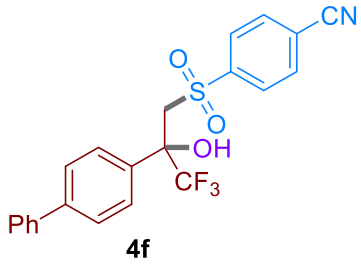
m.p. 117 – 119 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.51 – 7.53 (m, 4H), 7.43 – 7.48 (m, 2H), 7.34 – 7.41 (m, 5H), 7.06 – 7.09 (m, 2H), 5.28 (s, 1H), 4.16 (d, J = 15.2 Hz, 1H), 3.97 (d, J = 15.2 Hz, 1H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -57.8, -80.6 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 153.1 (q, $^4J_{C\text{-}F}$ = 1.1 Hz), 142.4, 139.6, 137.2, 132.3, 130.2, 128.9, 128.0, 127.2, 127.0, 126.9, 123.7 (q, $^1J_{C\text{-}F}$ = 283.7 Hz), 120.6, 120.0 (q, $^1J_{C\text{-}F}$ = 259.0 Hz), 75.3 (q, $^2J_{C\text{-}F}$ = 29.8 Hz), 58.9 ppm;

HRMS (ESI): $C_{22}H_{16}F_6NaO_4S^+$ $[M+Na]^+$ Calcd 513.0566, Found 513.0553.



4f

4f: 68.9 mg, white solid yield: 80%;

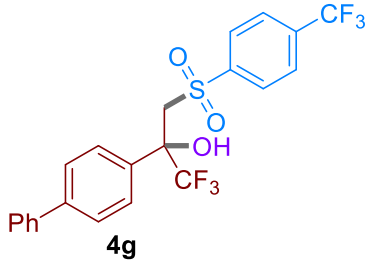
m.p. 184 – 185 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.47 – 7.58 (m, 8H), 7.38 – 7.43 (m, 1H), 7.31 – 7.36 (m, 4H), 7.06 – 7.09 (m, 2H), 5.14 (s, 1H), 4.19 (d, J = 15.2 Hz, 1H), 3.99 (d, J = 15.2 Hz, 1H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -80.5 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.9, 142.4, 139.3, 132.7, 132.1, 129.2, 128.6, 128.3, 127.3, 127.0, 126.9, 123.6 (q, $^1J_{C\text{-}F}$ = 285.9 Hz), 117.4, 116.7, 75.2 (q, $^2J_{C\text{-}F}$ = 30.3 Hz), 59.1 ppm;

HRMS (ESI): $C_{22}H_{16}F_3NNaO_3S^+$ $[M+Na]^+$ Calcd 454.0695, Found 454.0695.



4g

4g: 69.2 mg, white solid, yield:73%;

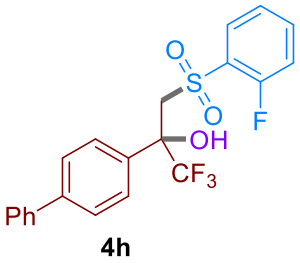
m.p. 132 – 133 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.58 (d, J = 8.4 Hz, 2H), 7.42 – 7.52 (m, 6H), 7.35 – 7.40 (m, 1H), 7.33 (s, 4H), 5.22 (s, 1H), 4.19 (d, J = 15.2 Hz, 1H), 3.99 (d, J = 15.2 Hz, 1H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -63.3, -80.5 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.5, 142.3, 139.4, 135.5 (q, $^{2}J_{C\text{-}F}$ = 33.2 Hz), 132.2, 129.0, 128.5, 128.1, 127.9, 127.2, 126.9, 126.8, 126.2 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 123.7 (q, $^{1}J_{C\text{-}F}$ = 283.8 Hz), 122.8 (q, $^{1}J_{C\text{-}F}$ = 271.6 Hz), 117.4, 116.7, 75.2 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz), 59.0 ppm;

HRMS (ESI): $C_{22}H_{19}F_6NaO_3S^+$ $[M+Na]^+$ Calcd 497.0617, Found 497.0638.



4h

4h: 72.9 mg, white solid, yield: 86%;

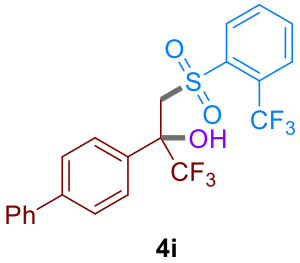
m.p. 141 – 143 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.36 – 7.48 (m, 8H), 7.24 – 7.28 (m, 3H), 7.08 (ddd, *J* = 10.0, 8.4, 1.2 Hz, 1H), 6.90 (td, *J* = 7.6, 1.2 Hz, 1H), 5.23 (s, 1H), 4.41 (d, *J* = 15.2 Hz, 1H), 4.02 (d, *J* = 15.2 Hz, 1H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -80.5, -108.60 – -108.66 (m) ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.11 (d, $^{1}J_{C\text{-}F}$ = 255.4 Hz), 142.0, 140.0, 136.3, 136.2, 132.3, 130.0, 129.0, 128.0, 127.9, 127.0, 126.9, 126.8, 124.71 (d, $^{3}J_{C\text{-}F}$ = 3.6 Hz), 123.7 (q, $^{1}J_{C\text{-}F}$ = 283.7 Hz), 116.8 (q, $^{2}J_{C\text{-}F}$ = 20.7 Hz), 75.2 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz), 58.3 ppm;,

HRMS (ESI): $C_{21}H_{16}F_4NaO_3S^+$ $[M+Na]^+$ Calcd 447.0648, Found 447.0673.



4i

4i: 72.0 mg, white solid, yield: 76%;

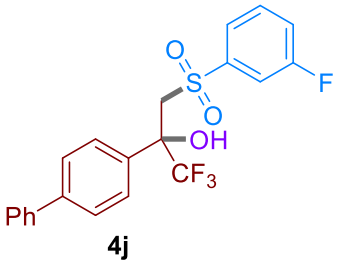
m.p. 151 – 153 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.43 – 7.50 (m, 5H), 7.38 – 7.41 (m, 3H), 7.25 – 7.32 (m, 3H), 5.29 (s, 1H), 4.49 (d, *J* = 15.6 Hz, 1H), 4.00 (d, *J* = 15.2 Hz, 1H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -56.5, -80.6 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.4, 142.1, 139.8, 137.5, 133.7, 132.8, 132.6, 132.4, 129.0, 128.3 (q, $^{3}J_{C\text{-}F}$ = 5.8 Hz), 128.0, 127.3, 126.9, 126.8, 123.6 (d, $^{1}J_{C\text{-}F}$ = 283.5 Hz), 75.4 (q, $^{2}J_{C\text{-}F}$ = 29.4 Hz), 58.3 ppm;,

HRMS (ESI): $C_{22}H_{16}F_6NaO_3S^+$ $[M+Na]^+$ Calcd 497.0617, Found 497.0632.



4j

4j: 78.0 mg, white solid, yield: 92%;

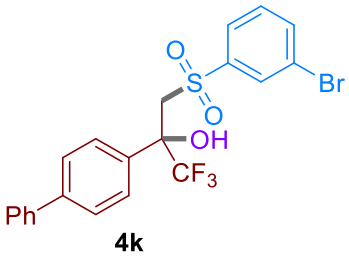
m.p. 159 – 161 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.44 – 7.51 (m, 4H), 7.31 – 7.46 (m, 5H), 7.23 – 7.30 (m, 2H), 7.09 – 7.18 (m, 2H), 5.28 (s, 1H), 4.16 (d, J = 15.2 Hz, 1H), 3.95 (d, J = 15.2 Hz, 1H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ-80.6, -108.43 – -108.48 (m) ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.1 (d, $^1J_{C\text{-}F}$ = 253.2 Hz), 142.3, 140.9 (d, $^3J_{C\text{-}F}$ = 6.6 Hz), 139.9, 132.3, 131.0 (d, $^3J_{C\text{-}F}$ = 7.5 Hz), 128.9, 127.9, 127.2, 127.1, 127.0, 123.7 (d, $^4J_{C\text{-}F}$ = 3.5 Hz) 123.69 (q, $^1J_{C\text{-}F}$ = 283.9 Hz), 121.1 (d, $^2J_{C\text{-}F}$ = 21.0 Hz), 115.4 (q, $^2J_{C\text{-}F}$ = 24.8 Hz), 75.3 (q, $^2J_{C\text{-}F}$ = 29.8 Hz), 58.8 ppm;

HRMS (ESI): $C_{21}H_{16}F_4NaO_3S^+$ $[M+Na]^+$ Calcd 447.0648, Found 447.0653.



4k

4k: 86.2 mg, white solid, yield: 89%;

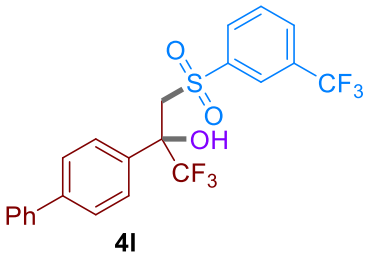
m.p. 136 – 138 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.51 – 7.57 (m, 4H), 7.43 – 7.47 (m, 3H), 7.33 – 7.40 (m, 5H), 7.13 (t, J = 8.0 Hz, 1H), 5.26 (s, 1H), 4.18 (d, J = 14.8 Hz, 1H), 3.95 (d, J = 15.2 Hz, 1H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -80.6 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.1, 140.6, 139.8, 136.8, 132.1, 131.1, 130.6, 128.9, 127.9, 127.2, 127.1, 126.9, 126.4, 123.7 (q, $^1J_{C\text{-}F}$ = 283.7 Hz), 123.2, 75.2 (q, $^2J_{C\text{-}F}$ = 29.8 Hz), 58.6 ppm;

HRMS (ESI): $C_{21}H_{16}BrF_3NaO_3S^+$ $[M+Na]^+$ Calcd 506.9848, Found 506.9871.



4l

4l: 90.0 mg, white solid, yield: 95%;

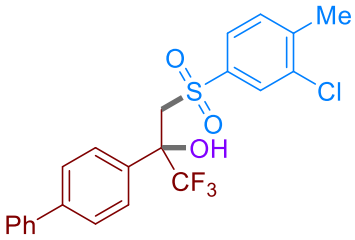
m.p. 105 – 106 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.82 – 7.84 (m, 1H), 7.71 – 7.72 (m, 1H), 7.63 – 7.65 (m, 1H), 7.42 – 7.49 (m, 2H), 7.31 – 7.40 (m, 6H), 5.21 (s, 1H), 4.23 (d, J = 14.8 Hz, 1H), 3.95 (d, J = 15.2 Hz, 1H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -62.9, -80.7 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.1, 140.2, 139.6, 132.1, 132.0, 131.7, 131.3, 130.5 (q, $^{3}J_{C\text{-}F}$ = 3.5 Hz), 130.0, 128.9, 128.0, 127.2, 126.9, 126.89, 125.2 (q, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 122.7 (q, $^{1}J_{C\text{-}F}$ = 271.6 Hz), 120.8 (q, $^{1}J_{C\text{-}F}$ = 289.5 Hz), 75.2 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz), 58.7 ppm;

HRMS (ESI): $C_{22}H_{16}F_6NaO_3S^+$ $[M+Na]^+$ Calcd 497.0617, Found 497.0617.



4m

4m: 74.4mg, white solid, yield: 82%;

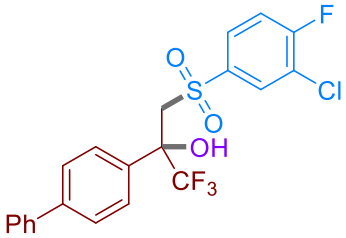
m.p. 164 – 166 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.50 – 7.53 (m, 2H), 7.43 – 7.47 (m, 2H), 7.36 – 7.39 (m, 6H), 7.25 – 7.29 (m, 1H), 7.09 – 7.11 (m, 1H), 5.23 (s, 1H), 4.14 (d, *J* = 14.8 Hz, 1H), 3.92 (d, *J* = 15.2 Hz, 1H), 2.24 (s, 3H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -80.7 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.3, 142.0, 139.7, 137.6, 135.3, 132.2, 131.4, 128.9, 128.7, 127.9, 127.2, 127.0, 126.7, 125.2, 125.4 (q, $^{1}J_{C\text{-}F}$ = 283.7 Hz), 75.2 (q, $^{2}J_{C\text{-}F}$ = 29.9 Hz), 58.5, 20.3 ppm;

HRMS (ESI): $C_{21}H_{18}ClF_3NaO_3S^+$ $[M+Na]^+$ Calcd 447.0509, Found 447.0497.



4n

4n: 71.4 mg, white solid, yield: 78%;

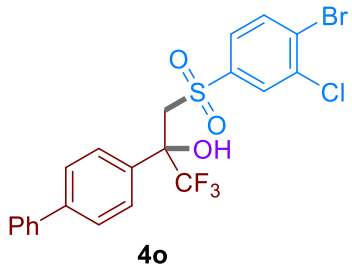
m.p. 152 – 154 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.49 – 7.52 (m, 2H), 7.44 – 7.48 (m, 3H), 7.34 – 7.43 (m, 6H), 7.03 (t, *J* = 8.4 Hz, 1H), 5.18 (s, 1H), 4.16 (d, *J* = 15.2 Hz, 1H), 3.96 (d, *J* = 15.2 Hz, 1H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -80.7, -104.15 – -104.20 (m) ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.4 (d, $^{1}J_{C\text{-}F}$ = 258.2 Hz), 142.5, 139.6, 135.8 (d, $^{3}J_{C\text{-}F}$ = 2.8 Hz), 132.0, 131.4 (d, $^{4}J_{C\text{-}F}$ = 1.4 Hz), 129.0, 128.5 (d,$^{3}J_{C\text{-}F}$ = 8.9 Hz), 128.0, 127.2, 127.1, 126.9, 125.4 (q, $^{1}J_{C\text{-}F}$ = 283.8 Hz), 122.7 (d, $^{2}J_{C\text{-}F}$ = 18.6 Hz), 117.5, 117.3, 75.2 (q, $^{2}J_{C\text{-}F}$ = 29.8 Hz), 58.8 ppm;

HRMS (ESI): $C_{21}H_{15}ClF_4NaO_3S^+$ $[M+Na]^+$ Calcd 481.0259, Found 481.0273.



4o

4o: 86.0 mg, white solid, yield: 83%;

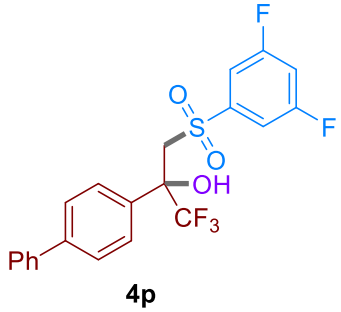
m.p. 149 – 151 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.51 – 7.56 (m, 3H), 7.44 – 7.48 (m, 3H), 7.33 – 7.40 (m, 5H), 7.20 (dd, J = 8.4, 2.2 Hz, 1H), 5.15 (s, 1H), 4.17 (d, J = 15.2 Hz, 1H), 3.95 (d, J = 15.2 Hz, 1H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -80.7 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.5, 139.5, 139.1, 135.9, 134.5, 131.9, 129.7, 128.9, 128.0, 127.9, 127.3, 127.2, 127.0, 126.9, 126.7, 123.6 (q, $^1J_{C\text{-}F}$ = 284.0 Hz), 75.1 (q, $^2J_{C\text{-}F}$ = 30.0 Hz), 58.8 ppm;

HRMS (ESI): $C_{21}H_{15}BrClF_3NaO_3^+$ $[M+Na]^+$ Calcd 540.9458, Found 540.9440.



4p

4p: 82.2 mg, white solid, yield: 93%;

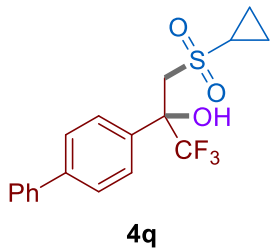
m.p. 171 – 172 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.44 – 7.52 (m, 4H), 7.36 – 7.41 (m, 5H), 6.96 – 7.02 (m, 2H), 6.85 – 6.90 (m, 1H), 5.13 (s, 1H), 4.17 (d, J = 15.2 Hz, 1H), 3.96 (d, J = 15.2 Hz, 1H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -80.6, -104.3 ppm;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.6 (d, $^1J_{C\text{-}F}$ = 255.0 Hz), 162.5 (d, $^1J_{C\text{-}F}$ = 254.9 Hz), 142.6, 142.0 (t, $^3J_{C\text{-}F}$ = 8.3 Hz), 139.7, 132.1, 128.9, 128.0, 127.2, 127.1, 127.0, 123.6 (q, $^1J_{C\text{-}F}$ = 283.9 Hz, $\underline{C}F_3$), 111.72 (d, $^2J_{C\text{-}F}$ = 28.5 Hz), 111.72 (d, $^3J_{C\text{-}F}$ = 11.1 Hz), 109.6 (t, $^2J_{C\text{-}F}$ = 24.8 Hz), 75.2 (q, $^2J_{C\text{-}F}$ = 28.8 Hz, $\underline{C}(OH)CF_3$), 58.9;

HRMS (ESI): $C_{21}H_{15}F_5NaO_3S^+$ $[M+Na]^+$ Calcd 465.0554, Found 465.0555.



4q

4q: 64.4 mg, white solid, yield: 87%;

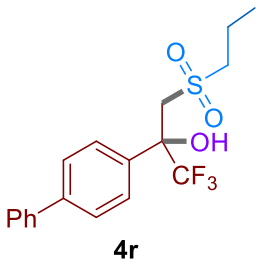
m.p. 111– 113 ℃;

^{1}H NMR (600 MHz, Chloroform-d) δ 7.73 – 7.76 (m, 2H), 7.67 – 7.69 (m, 2H), 7.59 – 7.61 (m, 2H), 7.44 – 7.47 (m, 2H), 7.36 – 7.39 (m, 1H), 5.35 (s, 1H), 4.04 (d, J = 15.0 Hz, 1H), 3.79 (d, J = 15.0 Hz, 1H), 1.78 – 1.82 (m, 1H), 1.17– 1.21 (m, 1H), 1.08 – 1.12 (m, 1H), 0.78 – 0.83 (m, 2H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -80.2 ppm;

^{13}C NMR (150 MHz, Chloroform-*d*) δ 142.4, 139.7, 133.9, 128.9, 128.0, 127.4, 127.2, 127.19, 127.1, 123.9 (q, $^{1}J_{C\text{-}F}$ = 189.2 Hz, $\underline{C}F_3$), 75.1 (q, $^{2}J_{C\text{-}F}$ = 29.6 Hz, $\underline{C}(OH)CF_3$), 56.7, 32.2, 6.4, 5.9 ppm;

HRMS (ESI): $C_{18}H_{17}F_3NaO_3S^+$ $[M+Na]^+$ Calcd 393.0743, Found 393.0726.



4r

4r: 60.3 mg, white solid, yield: 81%;

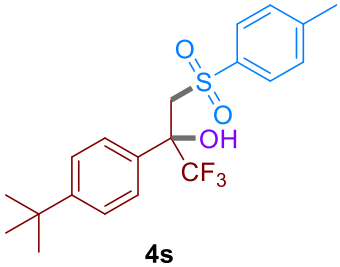
m.p. 117 – 119 ℃;

^{1}H NMR (600 MHz, Chloroform-d) δ 7.68 – 7.72 (m, 4H), 7.59 – 7.61 (m, 2H), 7.45 – 7.48 (m, 2H), 7.37 – 7.40 (m, 1H), 5.40 (s, 1H), 3.93 (d, *J* = 15.6 Hz, 1H), 3.68 (d, *J* = 15.6 Hz, 1H), 2.52 – 2.57 (m, 1H), 2.44– 2.49 (m, 1H), 1.72 – 1.78 (m, 1H), 1.62 – 1.69 (m, 1H), 0.87 (t, *J* = 7.2 Hz, 3H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -80.0 ppm;

^{13}C NMR (150 MHz, Chloroform-*d*) δ 142.6, 139.8, 133.7, 129.0, 128.0, 127.5, 127.1, 127.0, 123.9 (q, $^{1}J_{C\text{-}F}$ = 189.5 Hz, $\underline{C}F_3$), 75.1 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz, $\underline{C}(OH)CF_3$), 57.0, 55.3, 15.7, 12.7 ppm;

HRMS (ESI): $C_{18}H_{19}F_3NaO_3S^+$ $[M+Na]^+$ Calcd 395.0899, Found 395.0897.



4s

4s: 61.6 mg, white solid, yield: 77%;

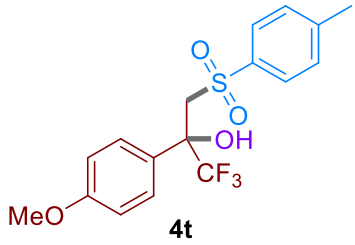
m.p. 161 – 163 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.30 – 7.32 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.09 – 7.12 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 5.38 (s, 1H), 4.10 (d, *J* = 14.8 Hz, 1H), 3.88 (d, *J* = 14.8 Hz, 1H), 2.35 (s, 3H), 1.27 (s, 9H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -80.8 ppm;

^{13}C NMR (150 MHz, Chloroform-*d*) δ 152.0, 144.7, 136.3, 130.5, 129.6, 127.8, 126.4, 125.1, 123.8 (q, $^{1}J_{C\text{-}F}$ = 283.3 Hz, $\underline{C}F_3$), 75.3 (q, $^{2}J_{C\text{-}F}$ = 29.6 Hz, $\underline{C}(OH)CF_3$), 58.4, 34.4, 31.3, 21.6 ppm;

HRMS (ESI): $C_{20}H_{23}F_3NaO_3S^+$ $[M+Na]^+$ Calcd 423.1212, Found 423.1228.



4t

4t: 62.8 mg, white solid,, yield: 84%;

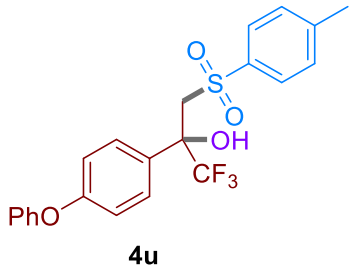
m.p. 66 – 68 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.36 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 6.64 – 6.66 (m, 2H), 5.33 (s, 1H), 4.04 (d, J = 14.8 Hz, 1H), 3.84 (d, J = 14.8 Hz, 1H), 3.77 (s, 3H), 2.34 (s, 3H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -81.1 ppm;

^{13}C NMR (150 MHz, Chloroform-*d*) δ 160.1, 145.0, 136.7, 129.7, 128.1, 127.8, 125.5, 113.5, 123.7 (q, $^{1}J_{C\text{-}F}$ = 291.4 Hz, $\underline{C}F_3$), 75.3 (q, $^{2}J_{C\text{-}F}$ = 29.9 Hz, $\underline{C}(OH)CF_3$), 58.5, 55.2, 21.6 ppm;

HRMS (ESI): $C_{17}H_{17}ClF_3NaO_4S^+$ $[M+Na]^+$ Calcd 397.0692, Found 397.0714.



4u

4u: 54.0 mg, colorless oil, yield: 62%;

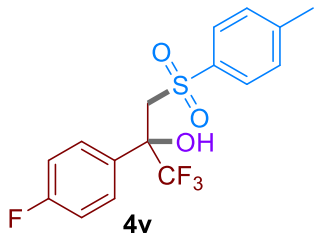
m.p. 134 – 136 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.35 – 7.43 (m, 4H), 7.22 – 7.27 (m, 2H), 7.15 – 7.19 (m, 3H), 7.00 – 7.03 (m, 2H), 6.71 – 6.75 (m, 2H), 5.37 (s, 1H), 4.05 (d, J = 15.2 Hz, 1H), 3.86 (d, J = 15.2Hz, 1H), 2.41 (s, 3H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -90.0 ppm;

^{13}C NMR (150 MHz, Chloroform-*d*) δ 158.4, 156.0, 145.3, 136.4, 130.0, 129.8, 128.4, 127.9, 127.8, 124.2, 123.7 (q, $^{1}J_{C\text{-}F}$ = 283.5 Hz, $\underline{C}F_3$), 119.7, 117.4, 75.3 (q, $^{2}J_{C\text{-}F}$ = 30.2 Hz, $\underline{C}(OH)CF_3$), 58.5, 58.4, 21.7 ppm;

HRMS (ESI): $C_{22}H_{19}F_3NaO_4S^+$ $[M+Na]^+$ Calcd 459.0848, Found 459.0871.



4v

4v: 63.7 mg, white solid, yield: 88%;

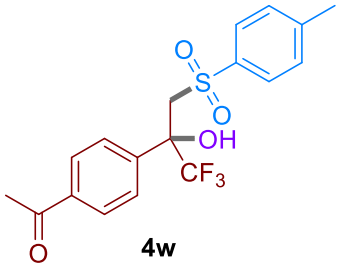
m.p. 130 – 132 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.37 – 7.40 (m, 2H), 7.30 (dd, J = 8.4, 5.2 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 6.81 – 6.85 (m, 2H), 5.41 (s, 1H), 4.03 (d, J = 14.8 Hz, 1H), 3.85 (d, J = 14.8 Hz, 1H), 2.40 (s, 3H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -81.0, -112.7 ppm;

^{13}C NMR (150 MHz, Chloroform-*d*) δ 163.2 (d, $^{1}J_{C\text{-}F}$ = 249.2 Hz), 145.5, 136.1, 129.8, 129.6 (d, $^{3}J_{C\text{-}F}$ = 3.0 Hz), 128.86 (d, $^{3}J_{C\text{-}F}$ = 8.7 Hz), 127.8, 123.6 (q, $^{1}J_{C\text{-}F}$ = 285.3 Hz), 121.1 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 115.2 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz), 75.2 (q, $^{2}J_{C\text{-}F}$ = 29.6 Hz), 58.3, 21.6 ppm

HRMS (ESI): $C_{16}H_{14}F_4NaO_3S^+$ $[M+Na]^+$ Calcd 385.0492, Found 385.0509.



4w

4w: 52.5 mg, white solid, yield: 68%;

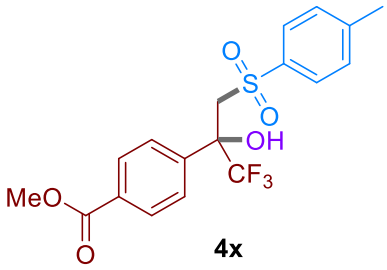
m.p. 163 – 165 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.72 – 7.76 (m, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.40 (m, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 5.46 (s, 1H), 4.07 (d, *J* = 14.8 Hz, 1H), 3.68 (d, *J* = 15.2 Hz, 1H), 2.59 (s, 3H), 2.37 (s, 3H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -80.4 ppm;

^{13}C NMR (150 MHz, Chloroform-*d*) δ 197.3, 145.7, 138.7, 137.4, 136.0, 129.9, 128.0, 127.8, 127.3, 123.9 (q, $^{1}J_{C\text{-}F}$ = 283.1 Hz, $\underline{C}F_3$), 75.4 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz, $\underline{C}(OH)CF_3$), 58.1, 26.6, 21.6 ppm;

HRMS (ESI): $C_{18}H_{17}F_3NaO_4S^+$ $[M+Na]^+$ Calcd 409.0692, Found 409.0717.



4x

4x: 68.2 mg, white solid,, yield: 82%;

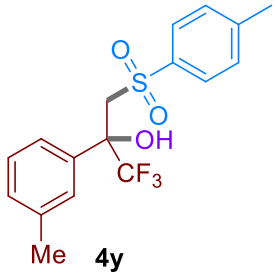
m.p. 152 – 154 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.77 – 7.80 (m, 2H), 7.33 – 7.40 (m, 4H), 7.07 (d, *J* = 8.4 Hz, 2H), 5.46 (s, 1H), 4.07 (d, *J* = 14.8 Hz, 1H), 3.93 (s, 3H), 3.88 (d, *J* = 14.8 Hz, 1H), 2.35 (s, 3H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -80.5 ppm;

^{13}C NMR (150 MHz, Chloroform-*d*) δ 166.3, 145.6, 138.5, 135.8, 130.7, 129.8, 129.3, 129.2, 127.8, 127.0, 123.5 (q, $^{1}J_{C\text{-}F}$ = 283.9 Hz, $\underline{C}F_3$), 75.4 (q, $^{2}J_{C\text{-}F}$ = 29.9 Hz, $\underline{C}(OH)CF_3$), 58.1, 52.3, 21.5 ppm;

HRMS (ESI): $C_{18}H_{17}F_3NaO_5S^+$ $[M+Na]^+$ Calcd 425.0641, Found 425.0659.



4y

4y: 55.8 mg, white solid,, yield: 78%;

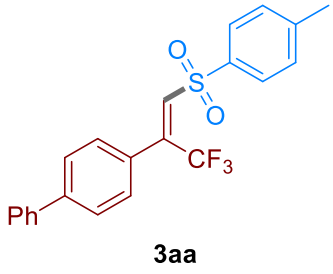
m.p. 89 – 91 ℃;

^{1}H NMR (400 MHz, Chloroform-d) δ 7.31 – 7.33 (m, 2H), 7.21 (d, J = 8.0 Hz, 1H), 7.02 – 7.10 (m, 4H), 6.94 (s, 1H), 5.35 (s, 1H), 4.06 (d, J = 15.2 Hz, 1H), 3.86 (d, J = 14.8 Hz, 1H), 2.37 (s, 3H), 2.13 (s, 3H) ppm;

^{19}F NMR (375 MHz, Chloroform-*d*) δ -80.7 ppm;

^{13}C NMR (150 MHz, Chloroform-*d*) δ 145.0, 137.8, 136.2, 133.5, 129.7, 129.6, 128.3, 127.7, 127.4, 124.0, 123.7 (q, $^{1}J_{C\text{-}F}$ = 284.2 Hz, $\underline{C}F_3$), 75.4 (q, $^{2}J_{C\text{-}F}$ = 29.5 Hz, $\underline{C}(OH)CF_3$), 58.5, 21.6, 21.2 ppm;

HRMS (ESI): $C_{17}H_{17}F_3NaO_3S^+$ $[M+Na]^+$ Calcd 381.0743, Found 381.0763.



3aa

3aa: 68.3 mg, white solid, yield: 85%;

m.p. 102 – 104 ℃;

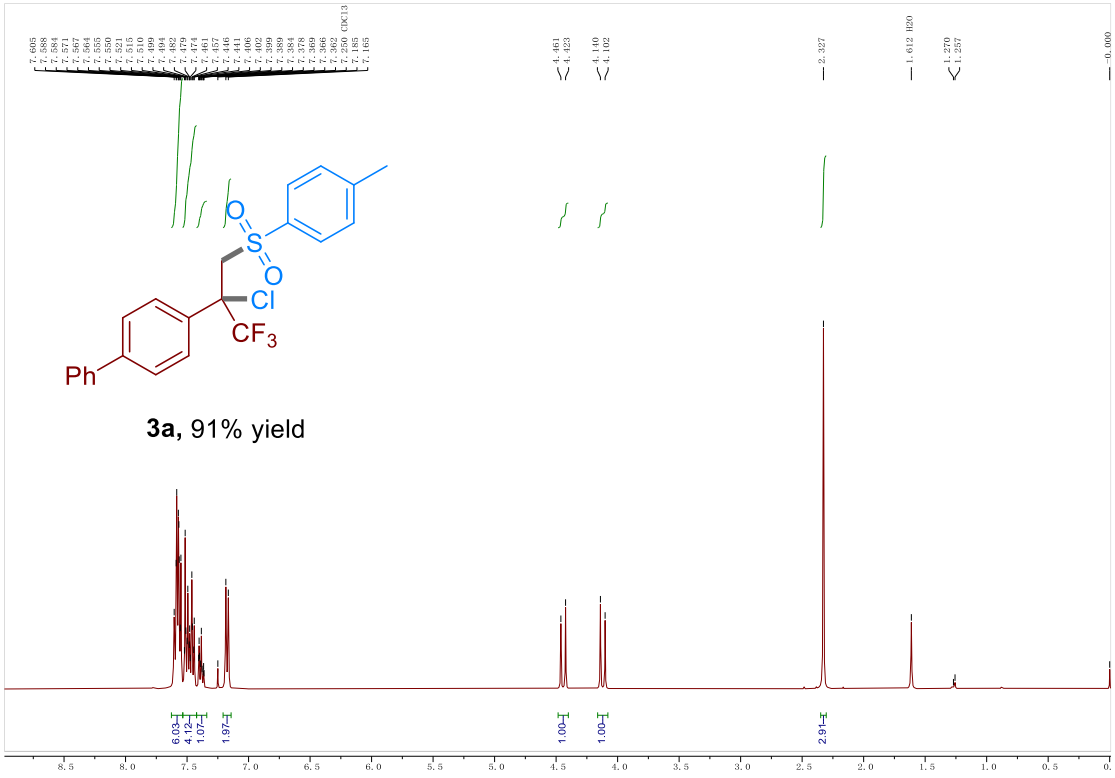
^{1}H NMR (400 MHz, Chloroform-d) δ 7.58 – 7.61 (m, 2H), 7.53 – 7.55 (m, 2H), 7.45 – 7.50 (m, 4H), 7.38– 7.42 (m, 4H), 2.39 (s, 3H) ppm;

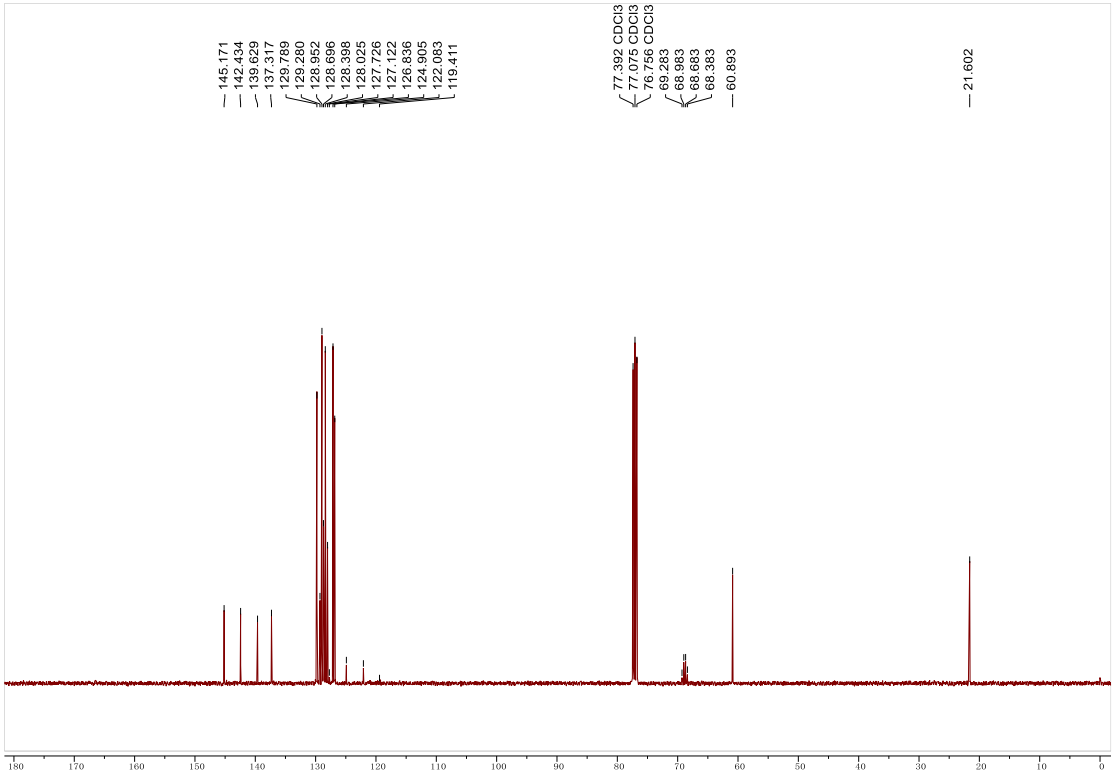
^{19}F NMR (375 MHz, Chloroform-*d*) δ -67.6 ppm;

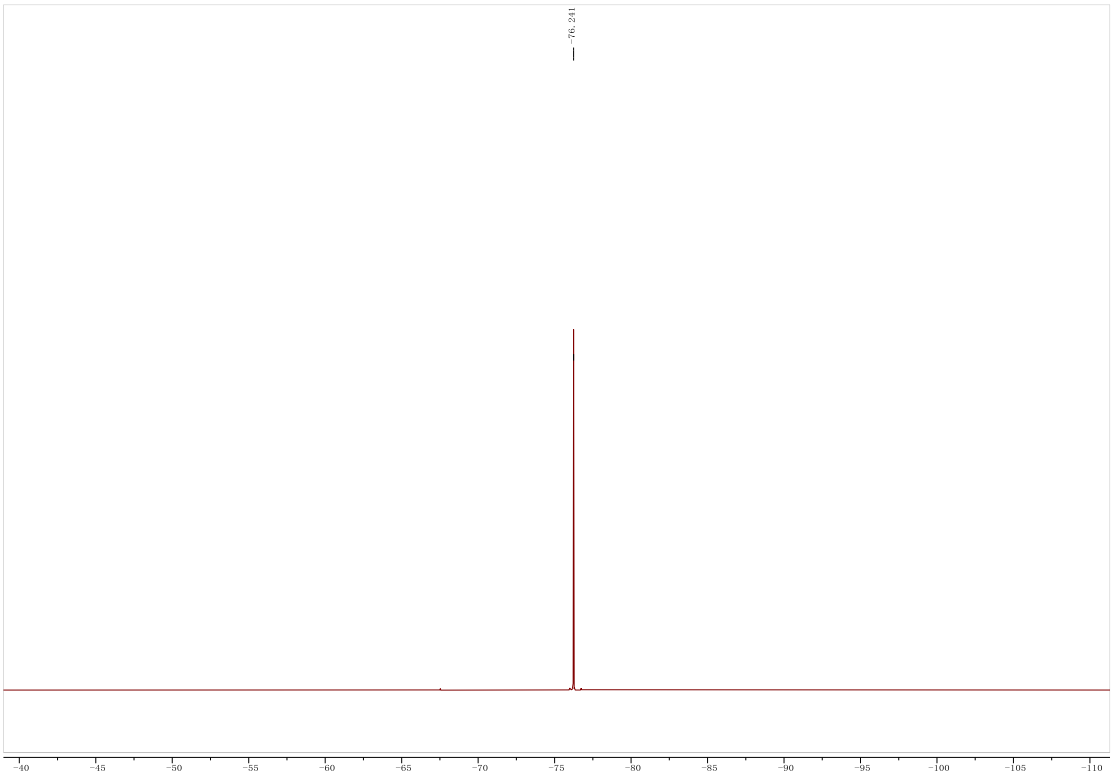
^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.3, 142.9, 141.1, 140.7, 140.0, 136.8 (q, $^{3}J_{C\text{-}F}$ = 5.1 Hz), 129.8, 129.7, 129.0, 128.2, 128.0, 127.2, 126.8, 126.6, 121.7 (q, $^{1}J_{C\text{-}F}$ = 276.1 Hz, $\underline{C}F_3$), 21.7 ppm;

HRMS (ESI): $C_{22}H_{17}F_3NaO_2S^+$ $[M+Na]^+$ Calcd 425.0794, Found 425.0806.

^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3a



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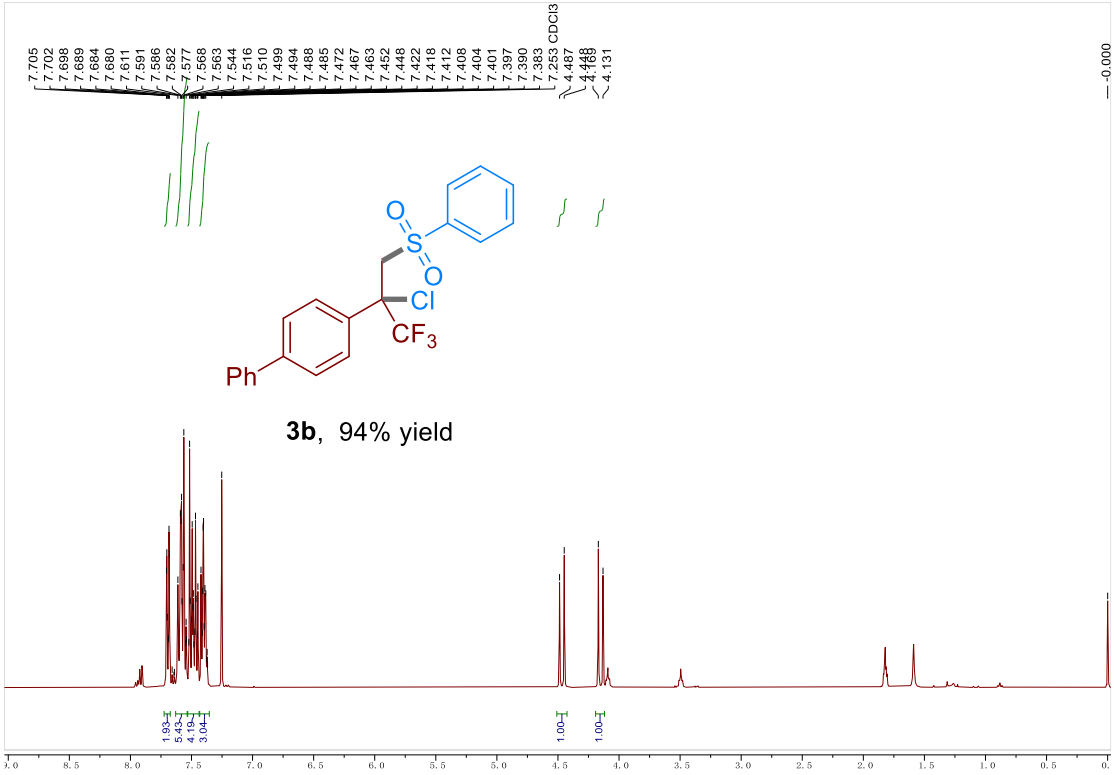
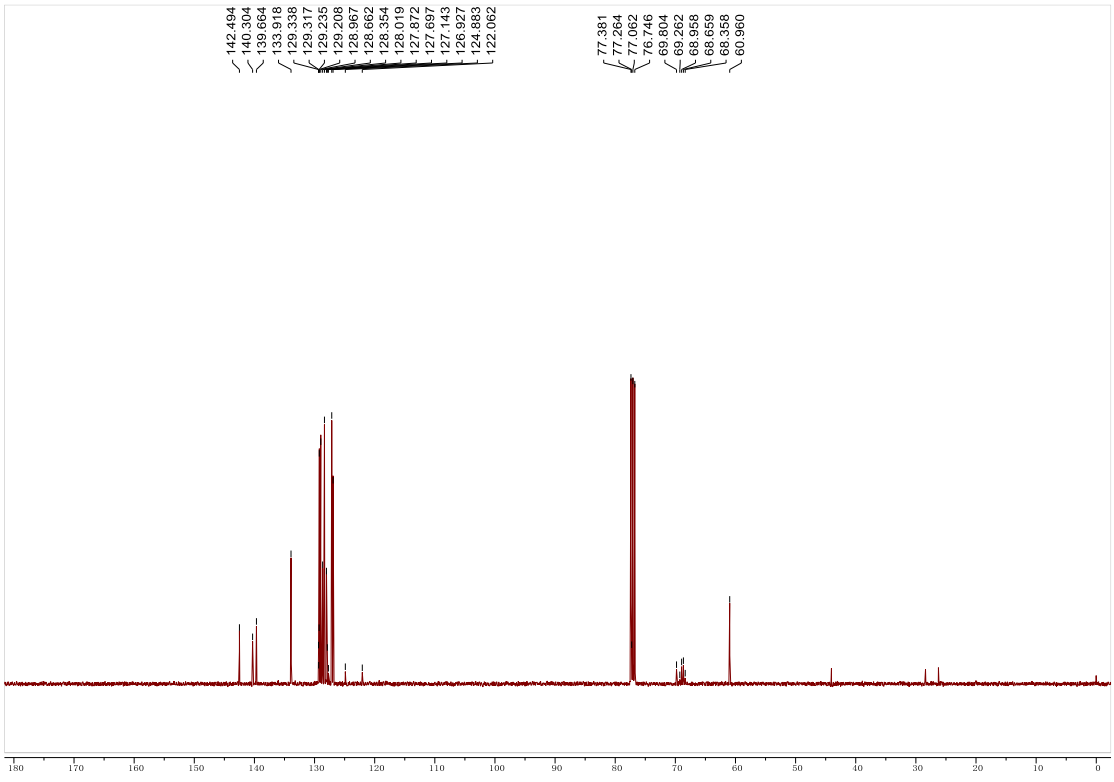
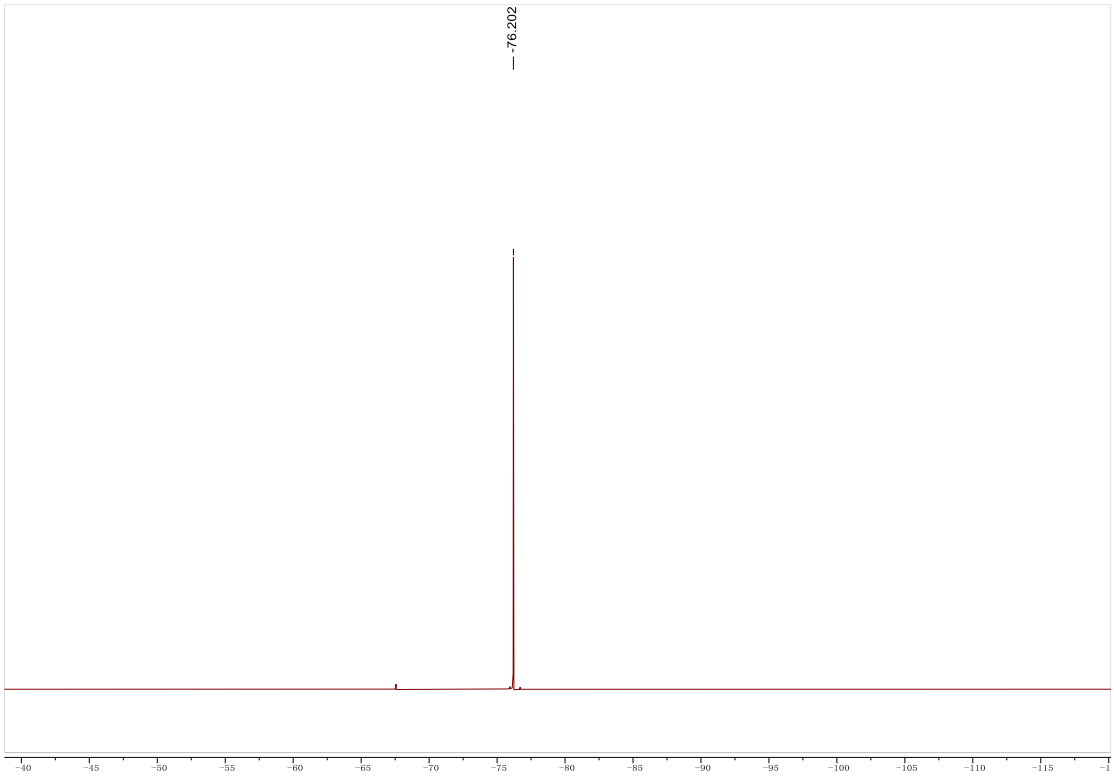
-110

^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3b



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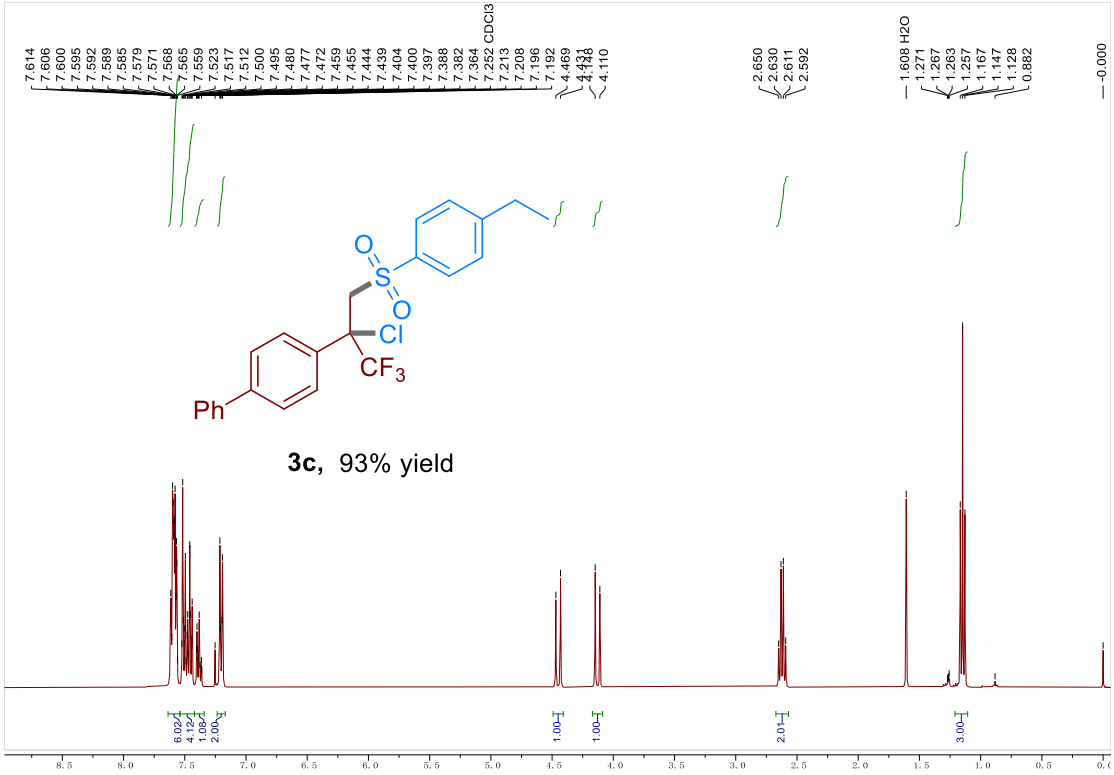
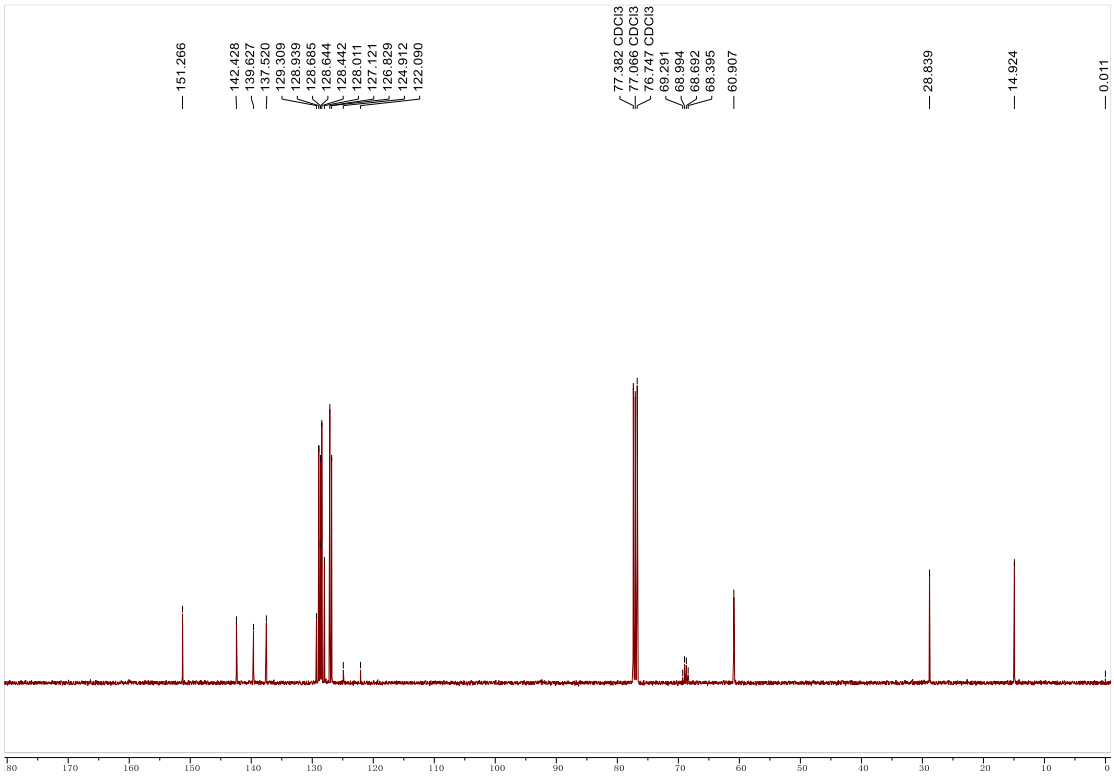
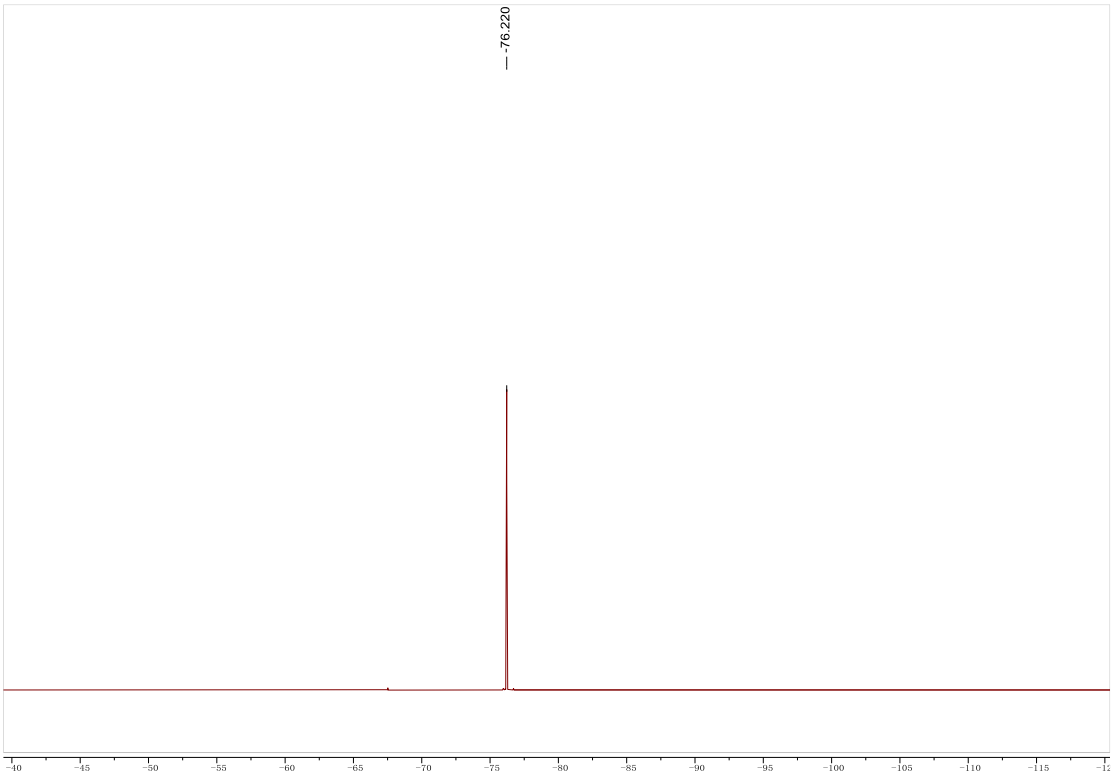
-115

^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3c



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−105
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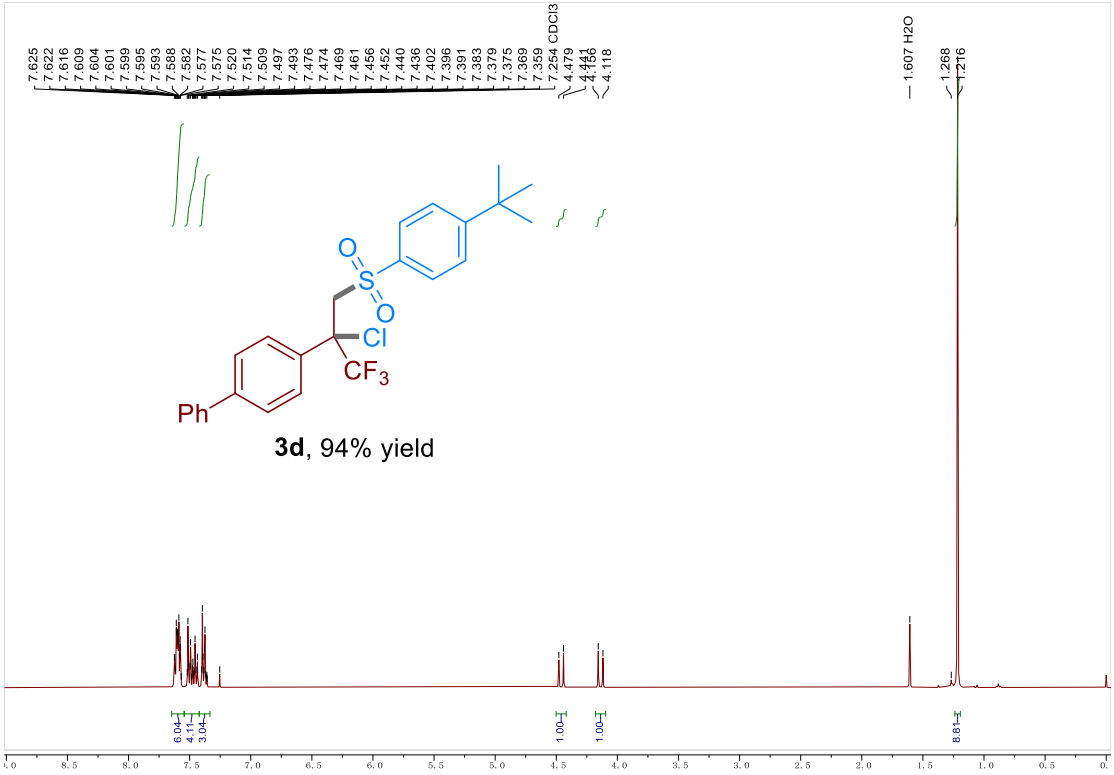
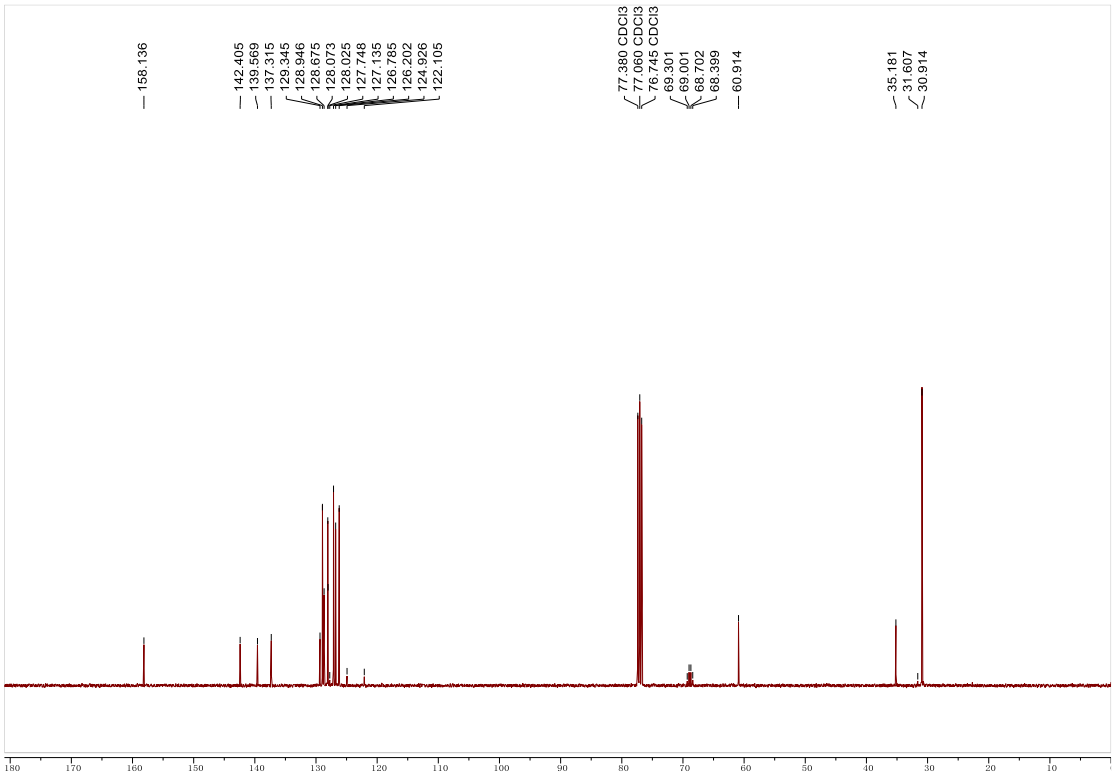
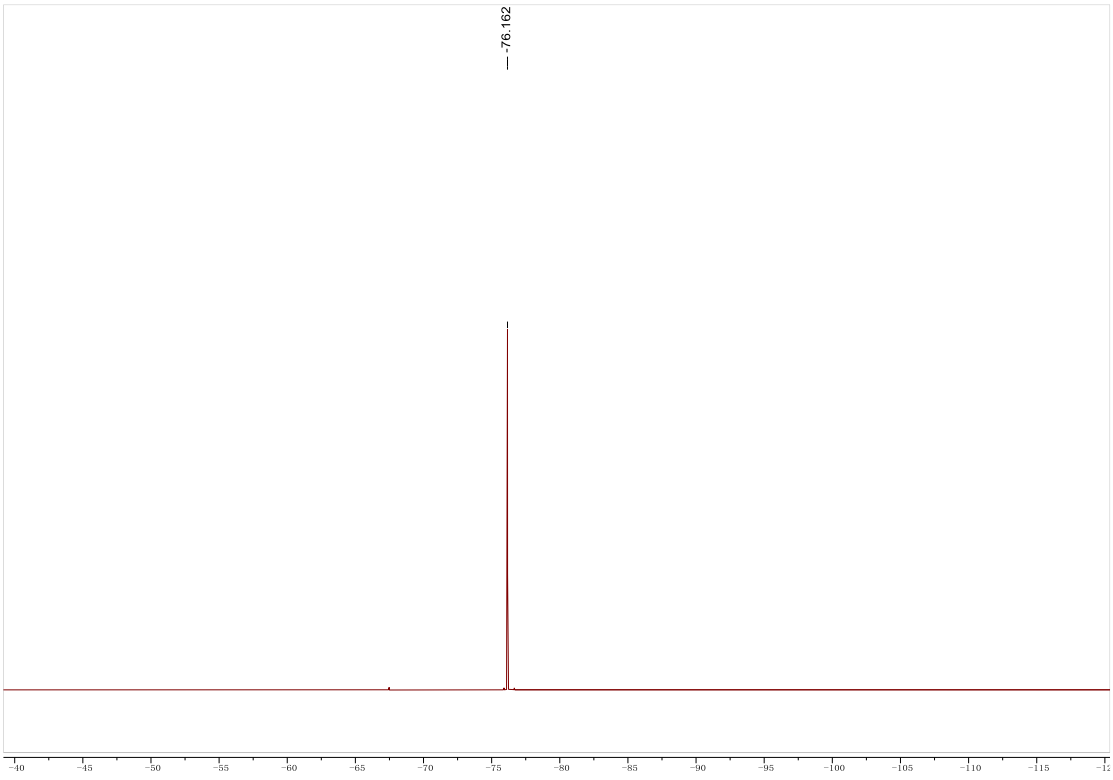
−115

^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3d



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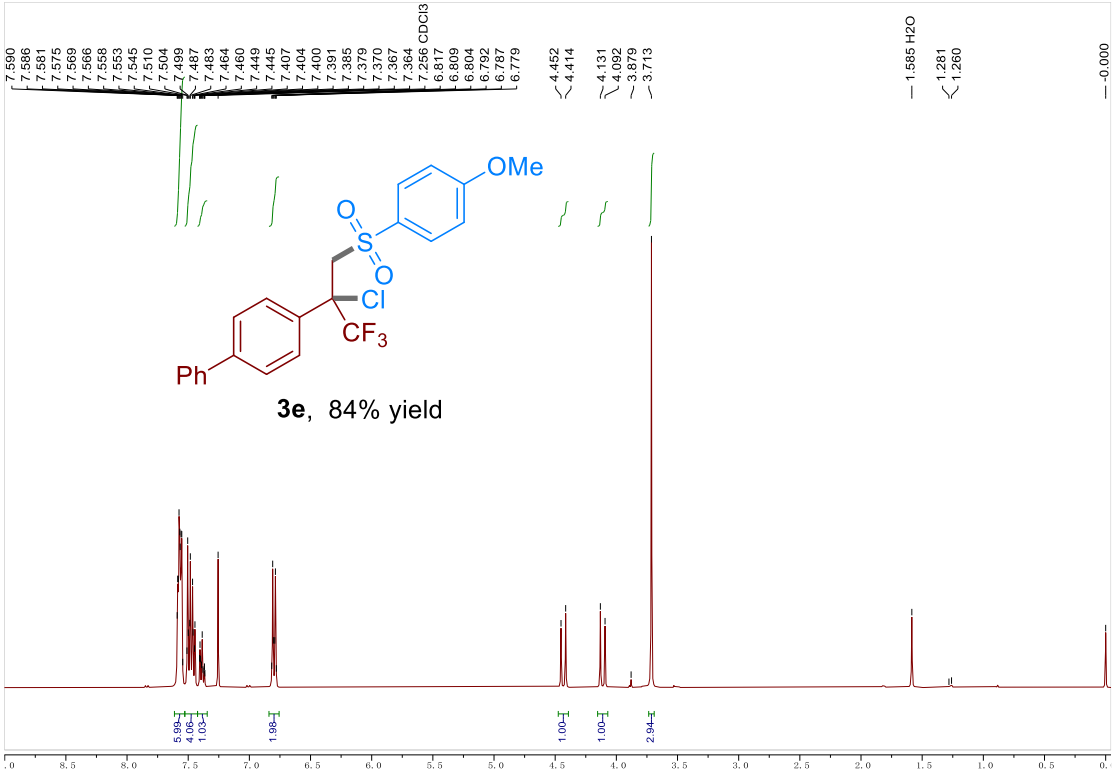
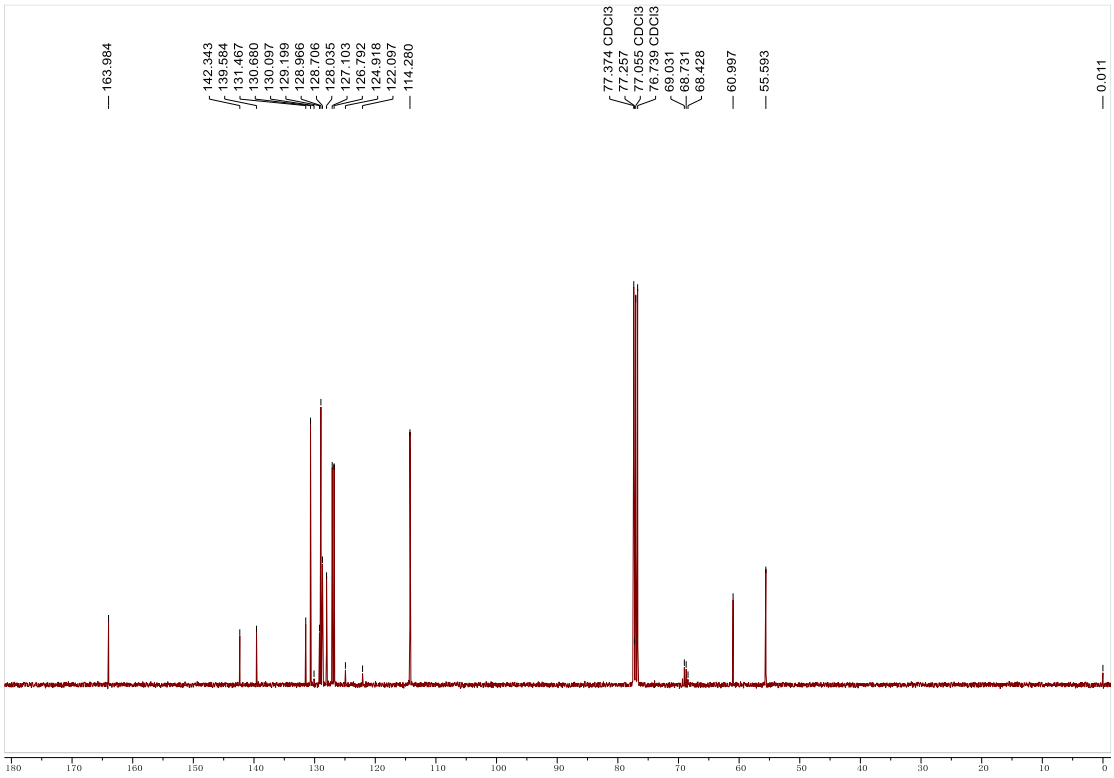
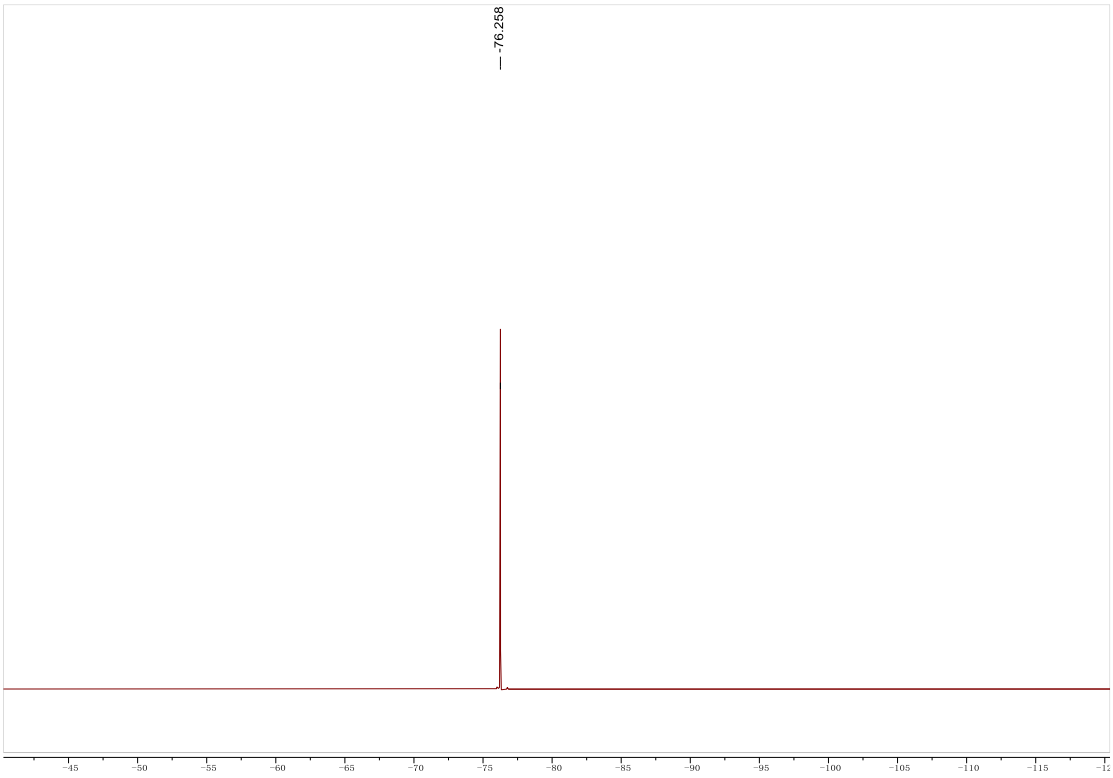
−95
−100
−105
−110
−115

^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3e



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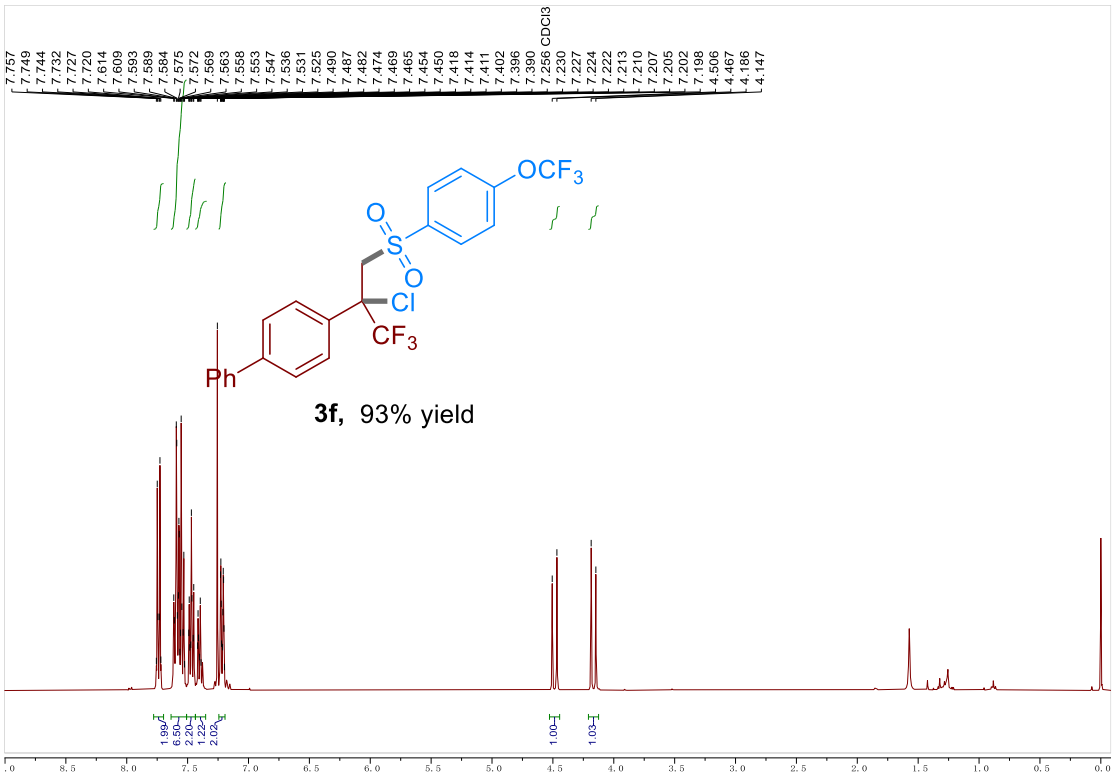
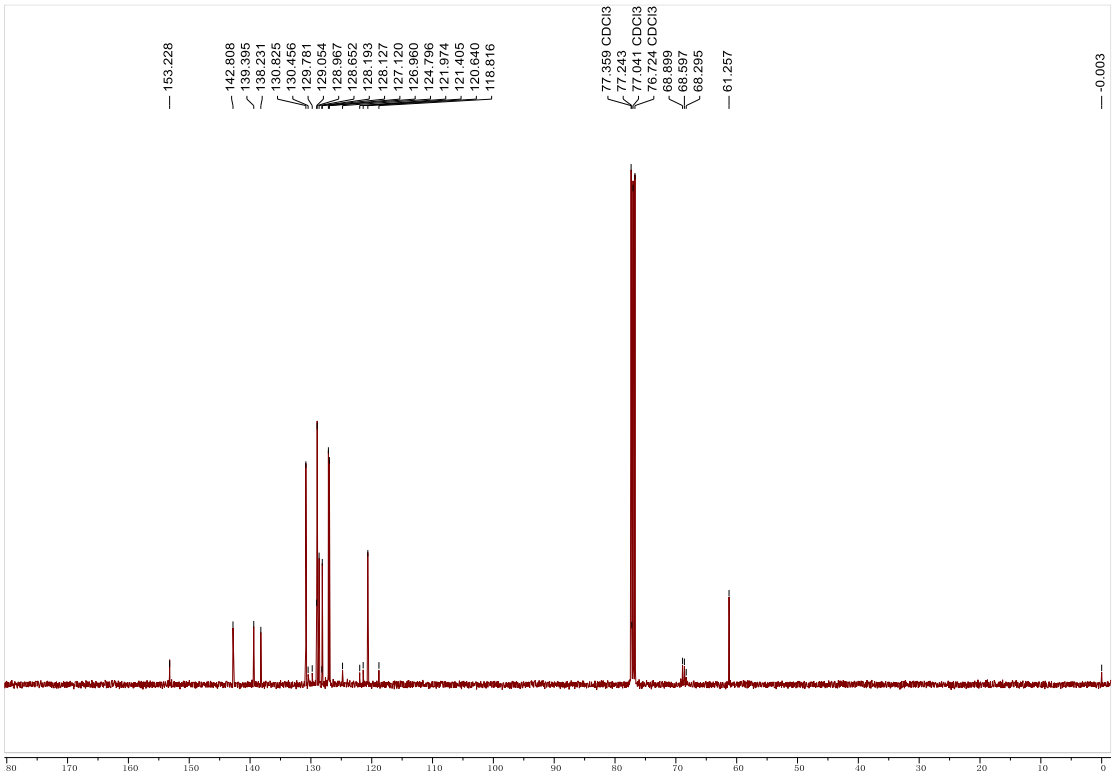
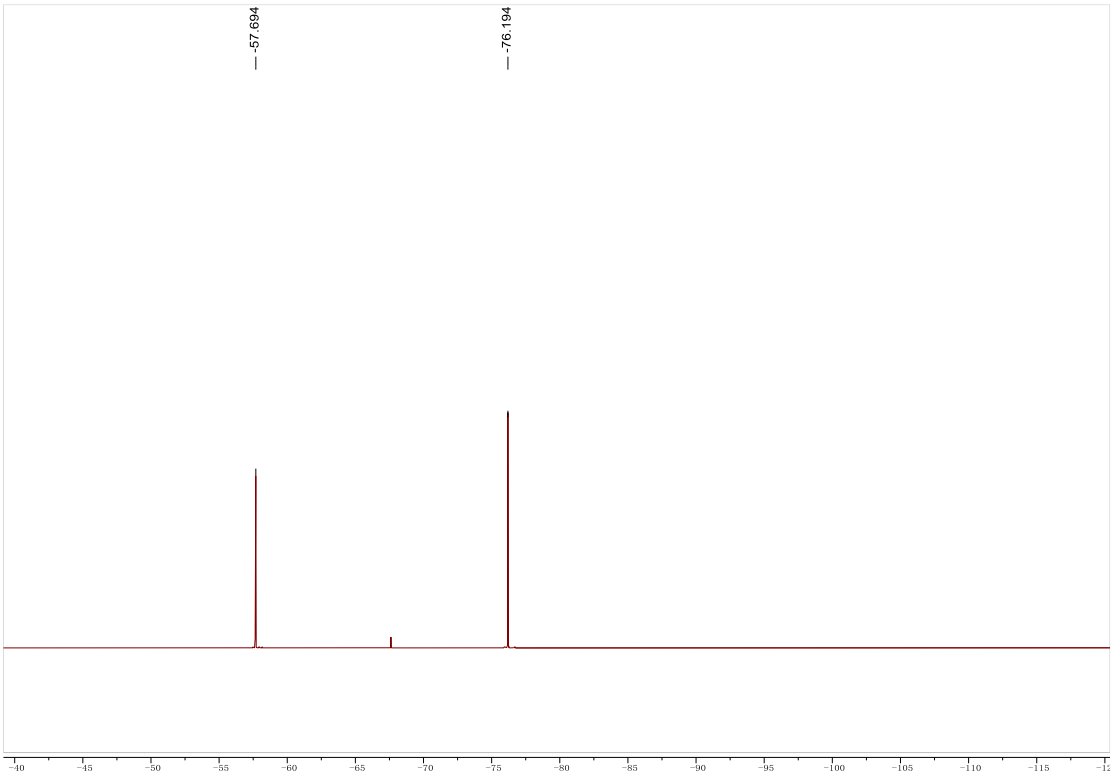
-85
-90
-95
-100
-105
-110
-115

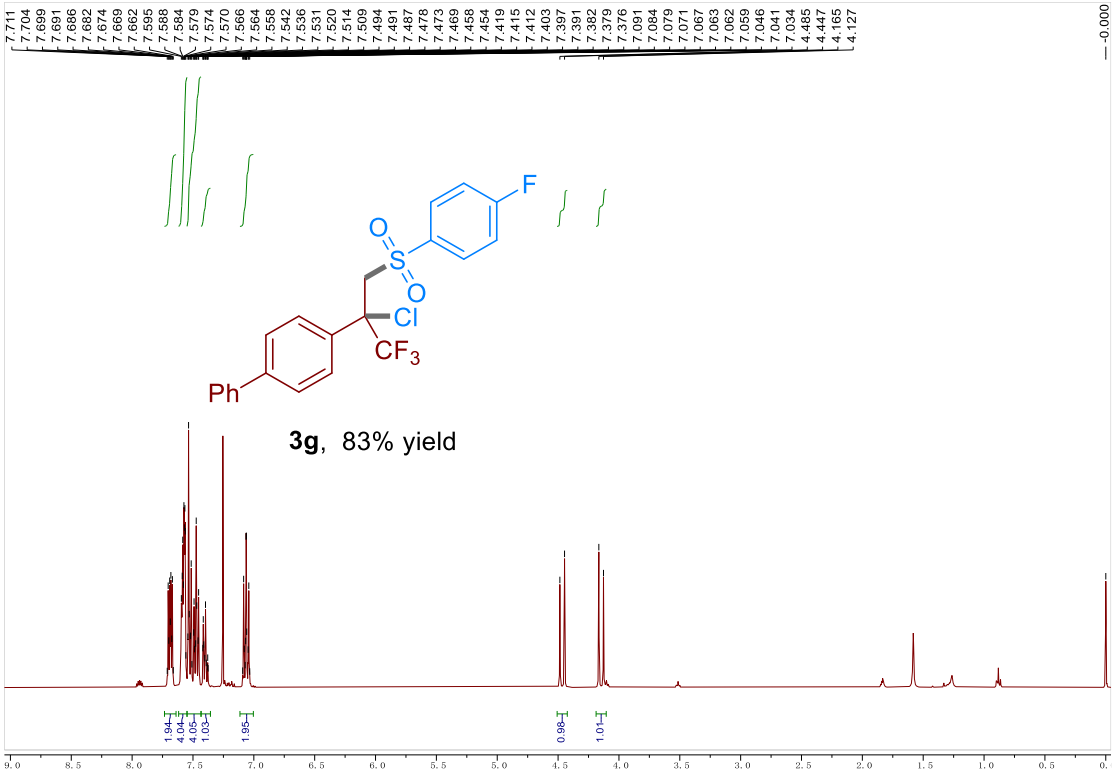
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3f

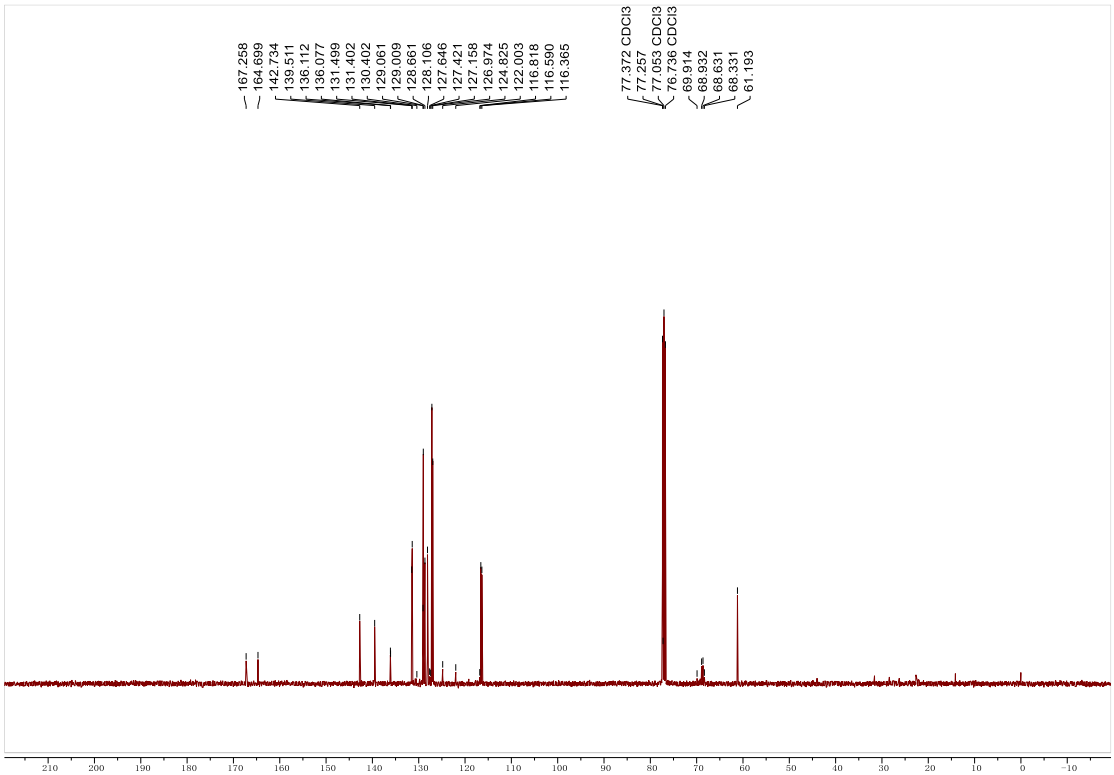


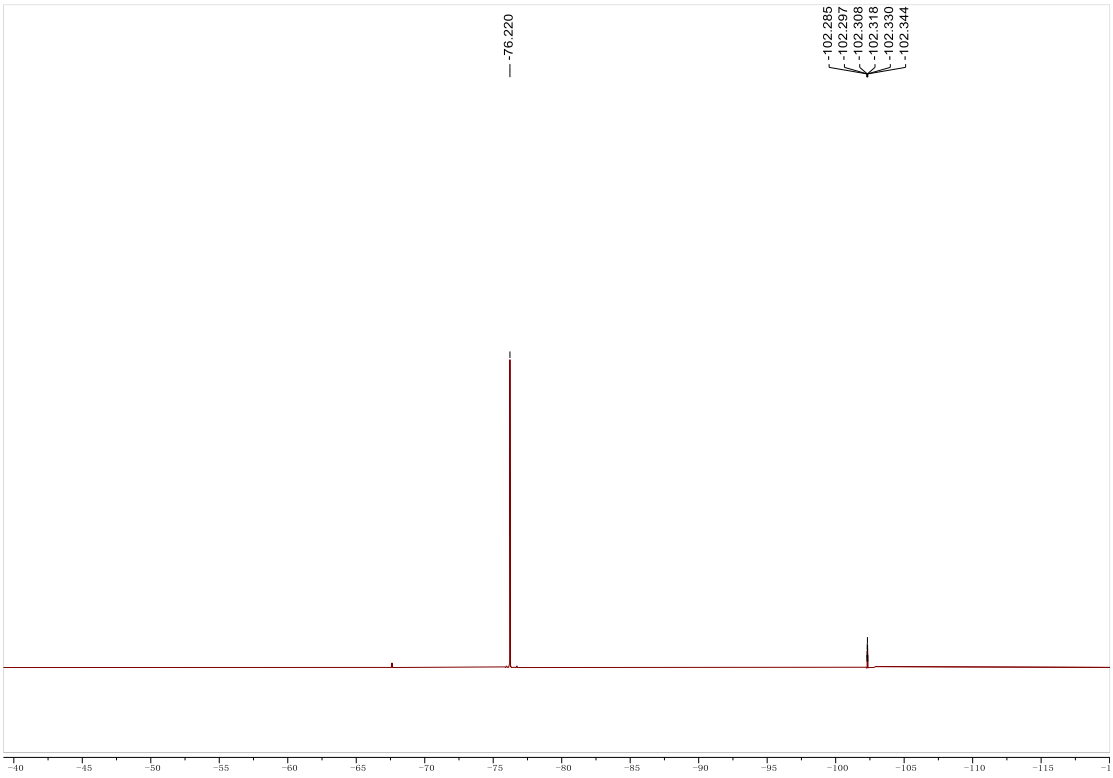



-57.694
-76.194
−40
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115

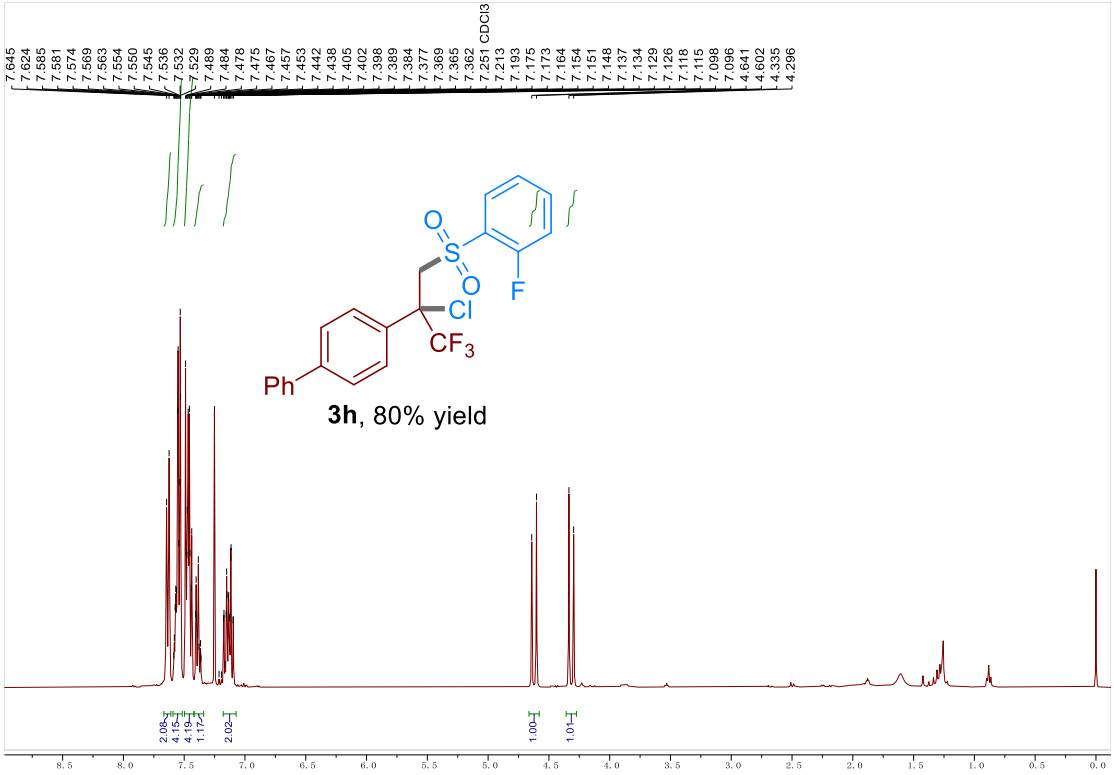
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3g

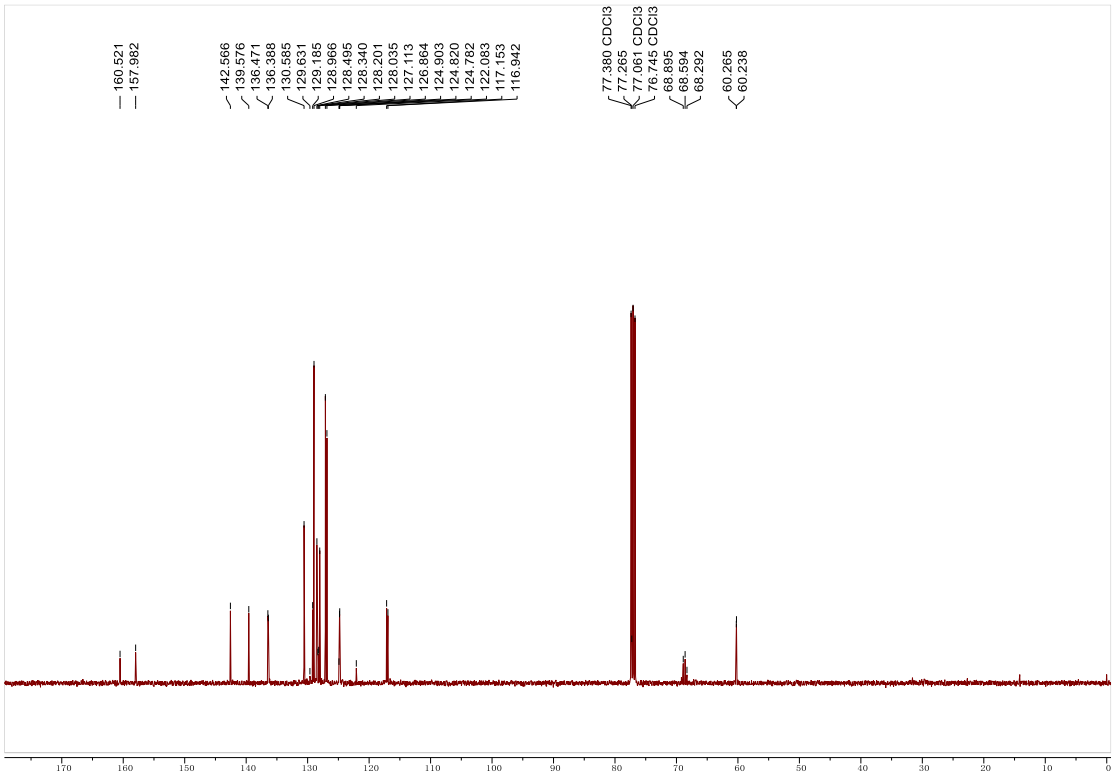


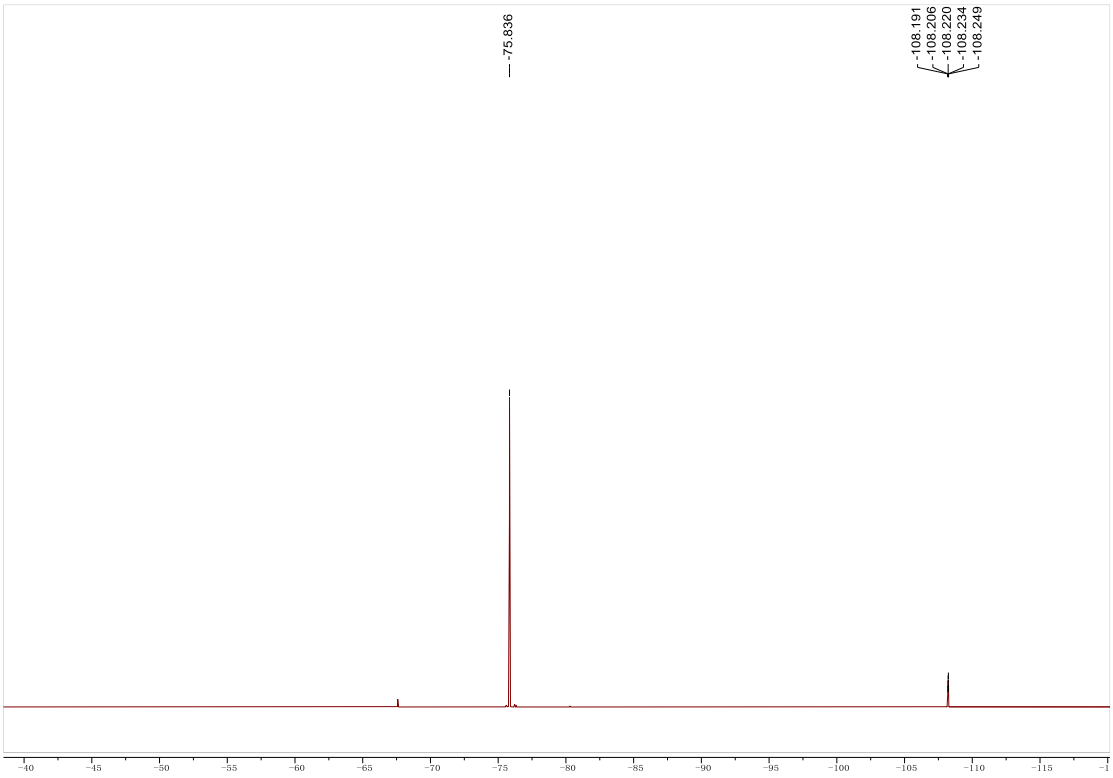



-76.220
-102.285
-102.297
-102.308
-102.318
-102.330
-102.344
−40
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115

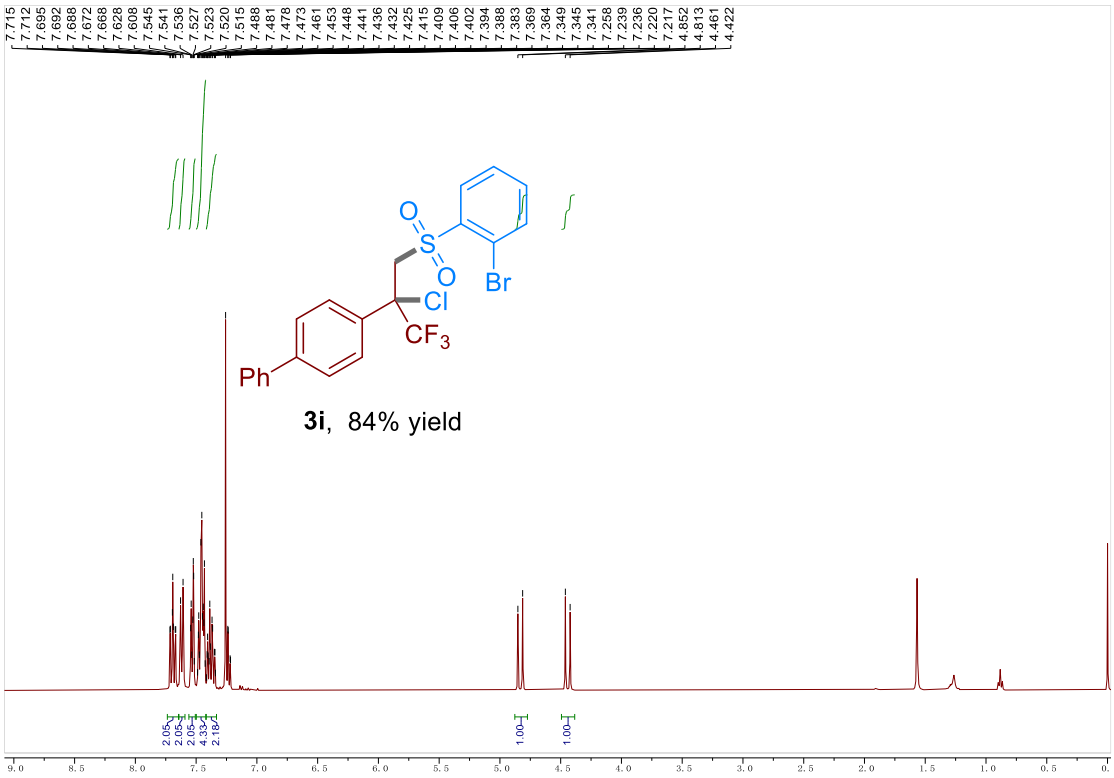
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3h

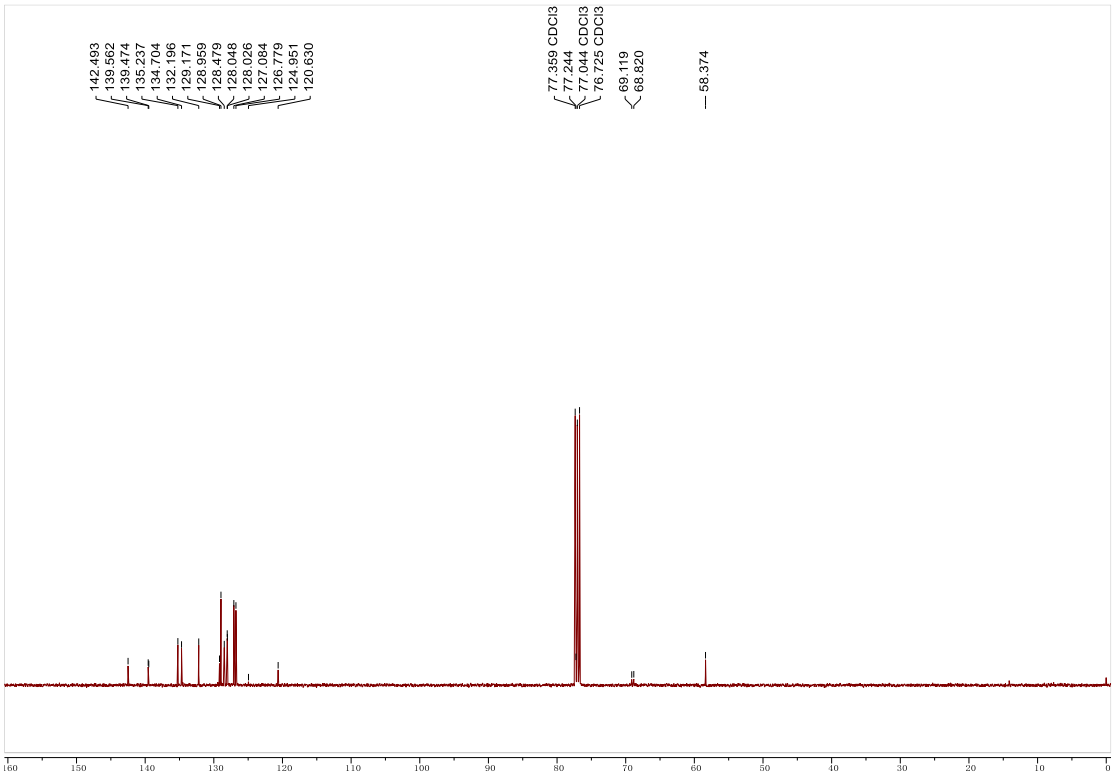


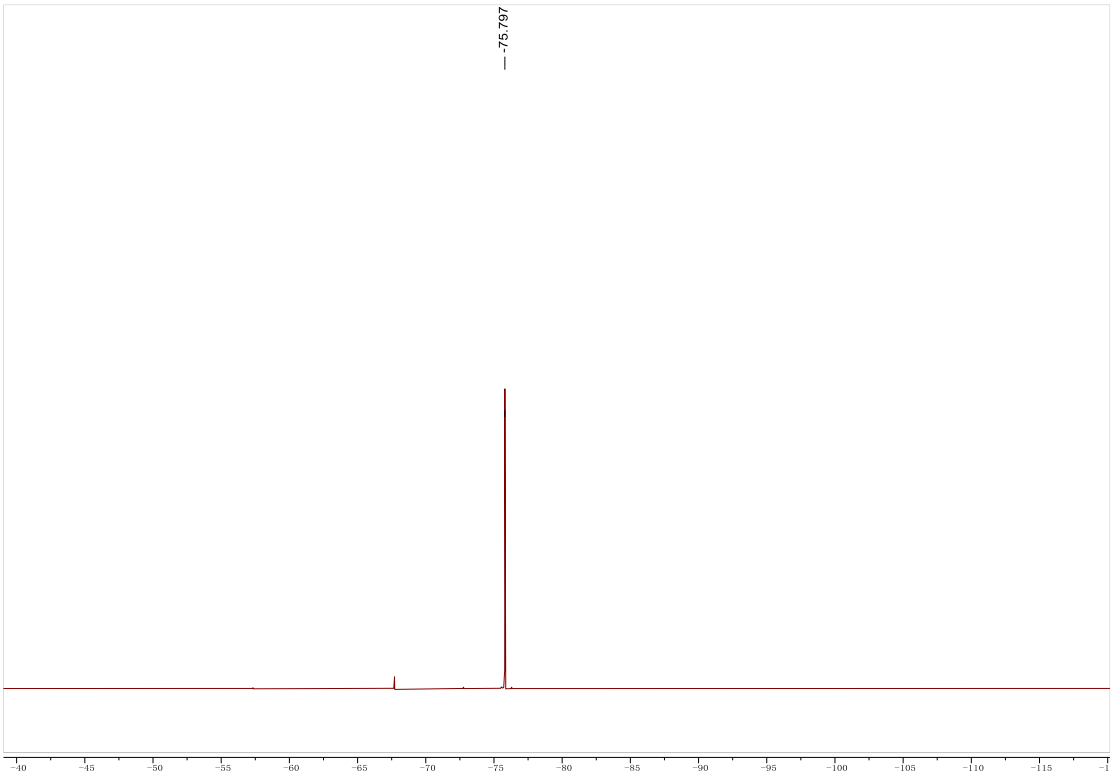



-75.836
-108.191
-108.206
-108.220
-108.234
-108.249
−40
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115

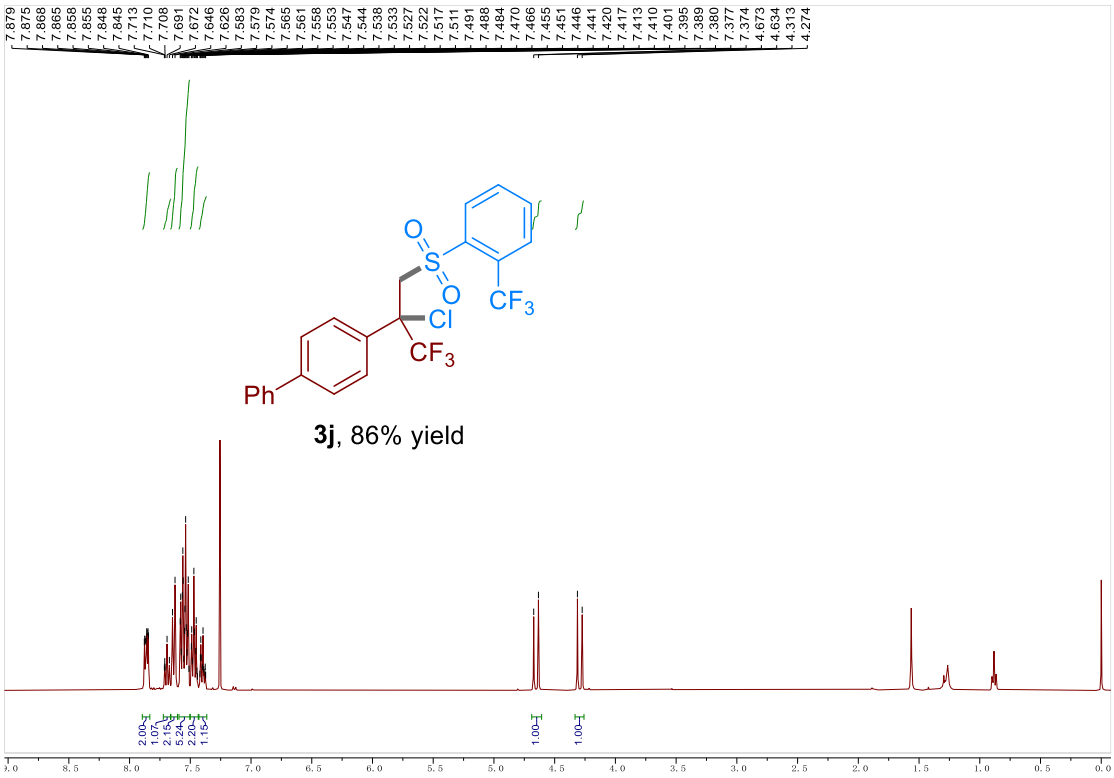
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3i

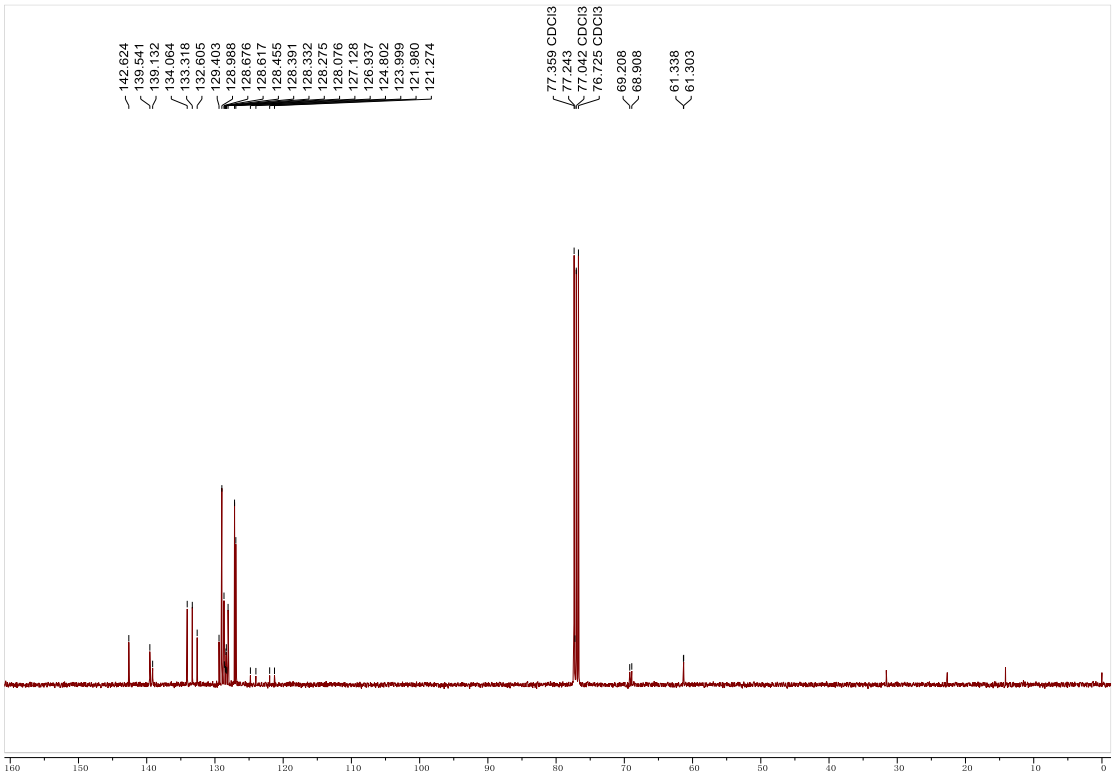


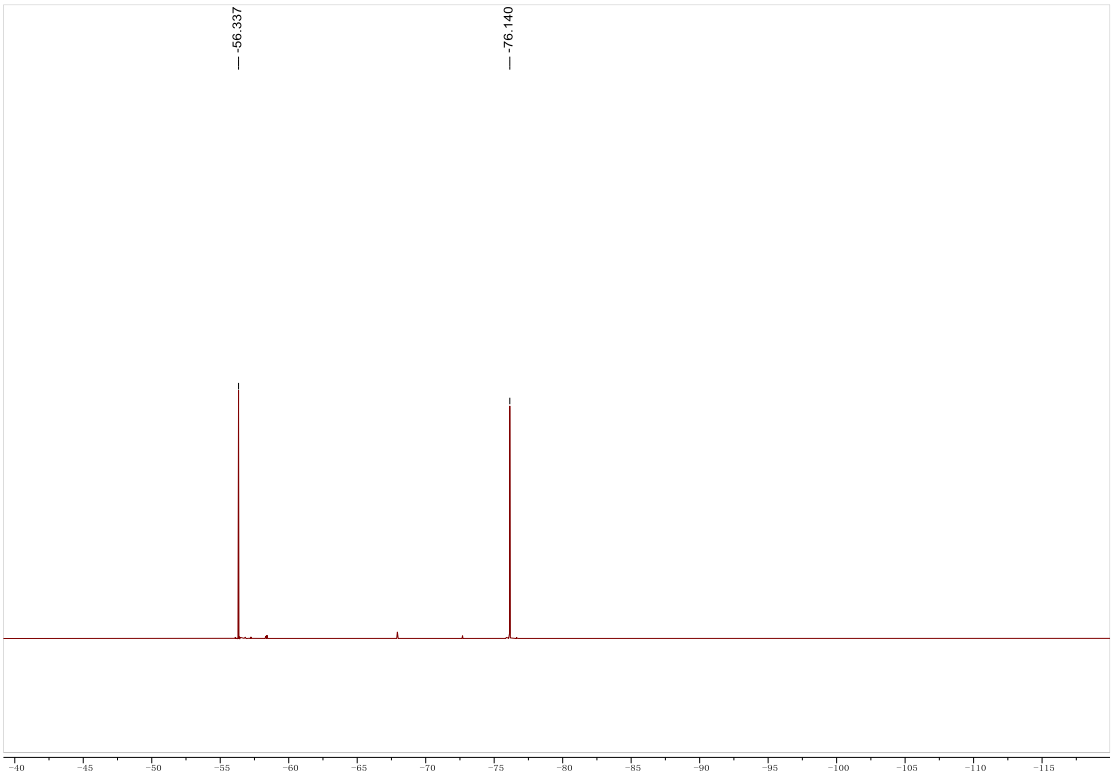



-75.797
−40
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115

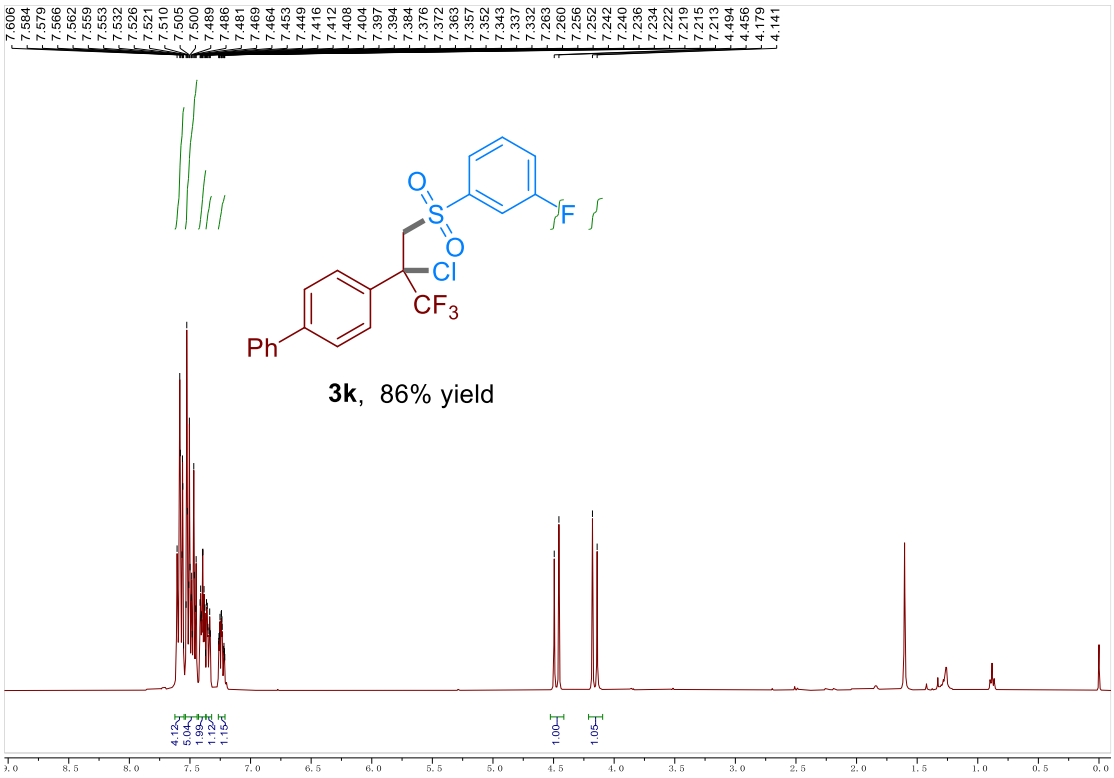
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3j

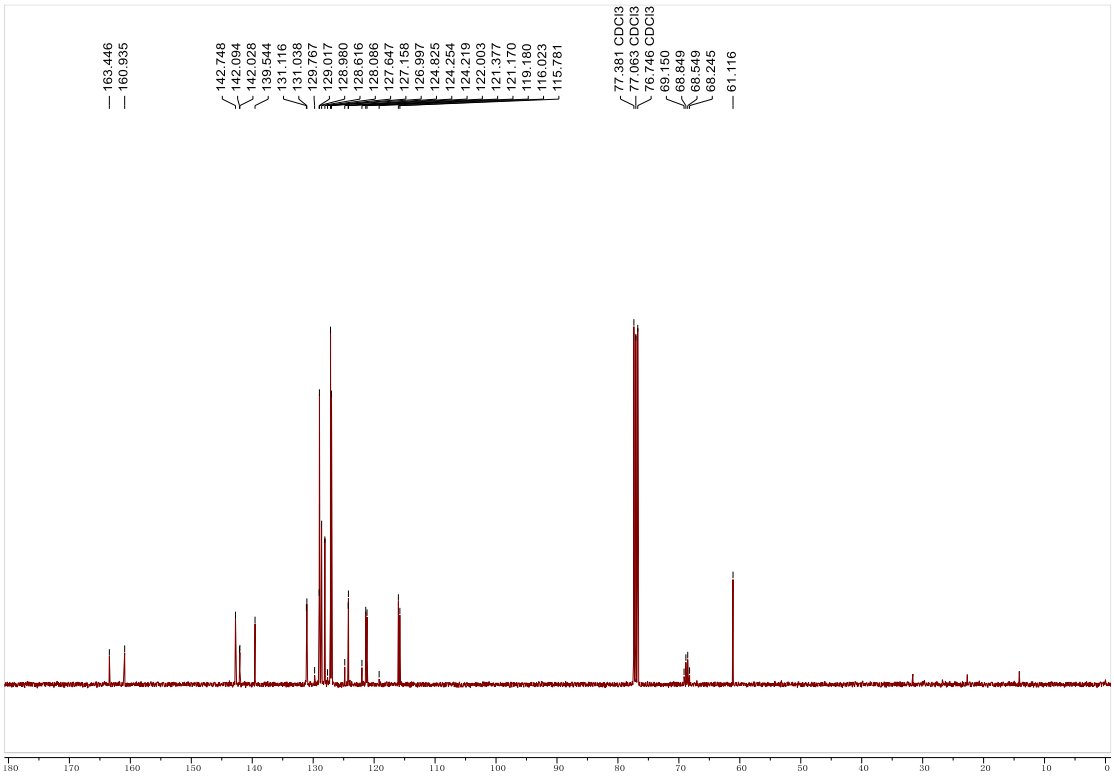


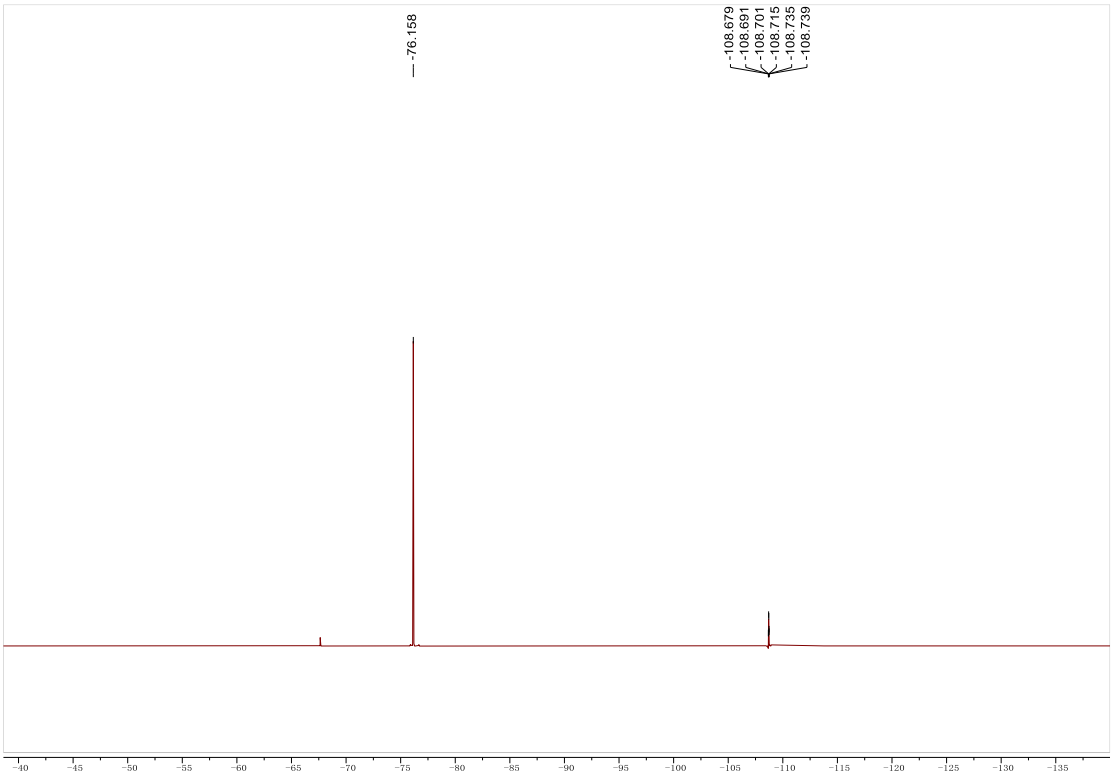



-56.337
-76.140
−40
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115

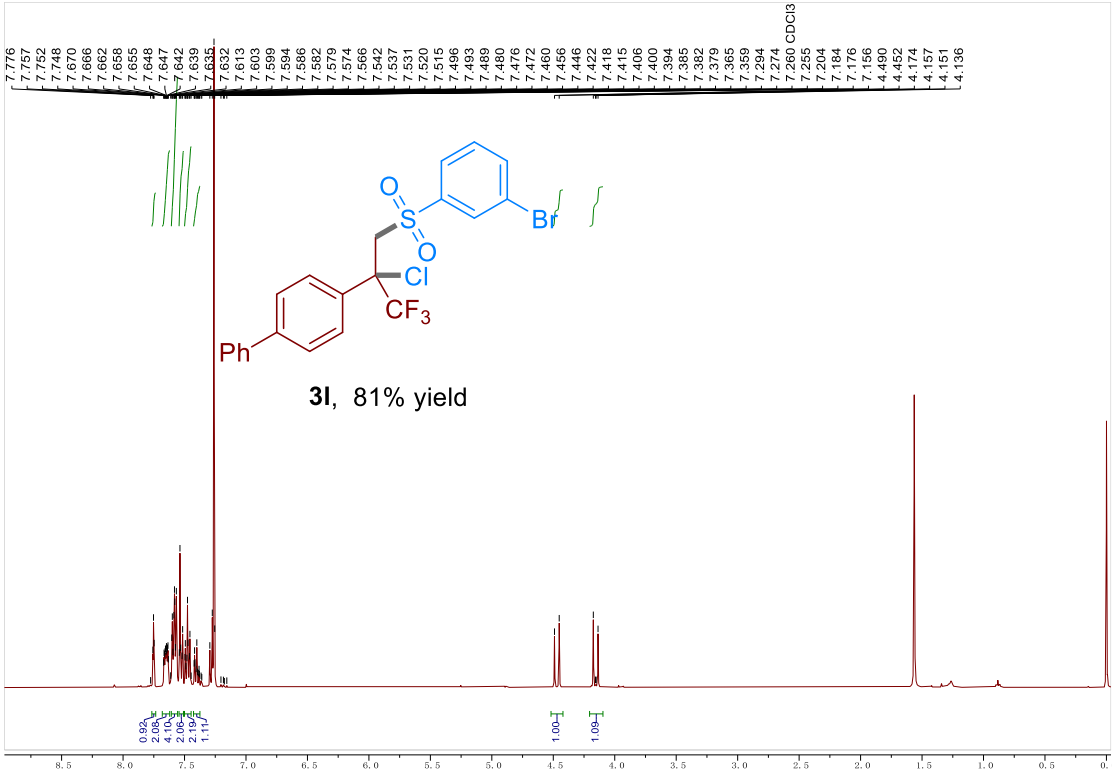
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3k

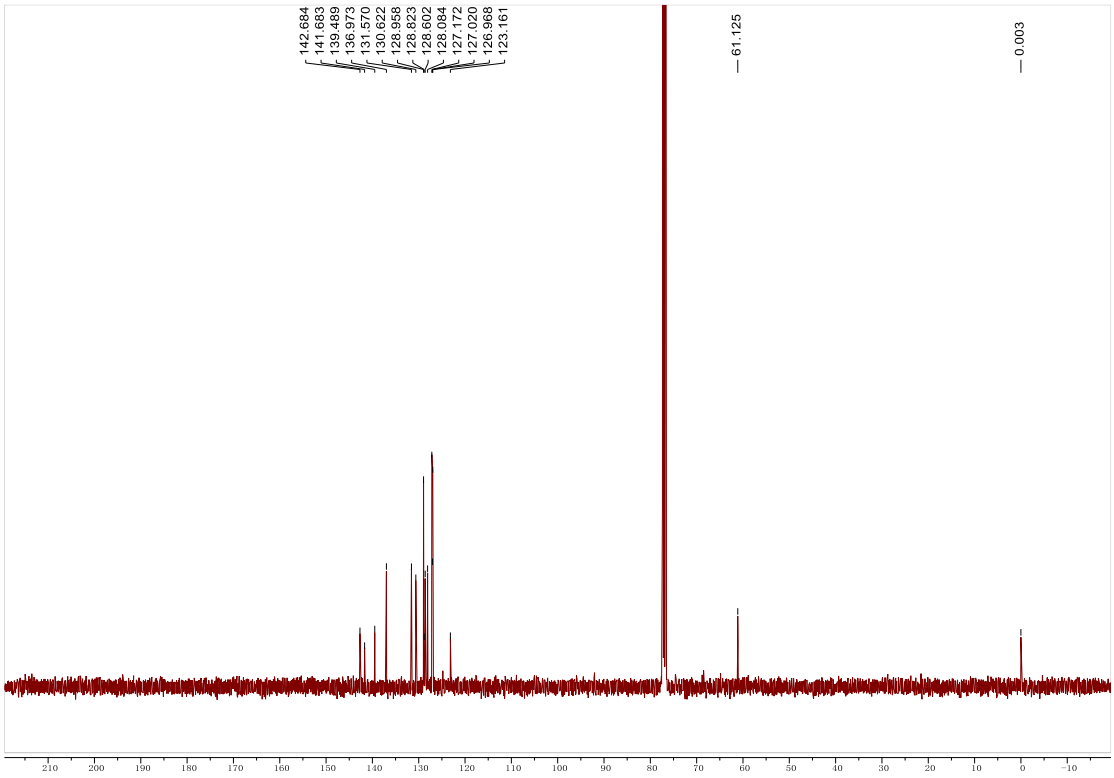


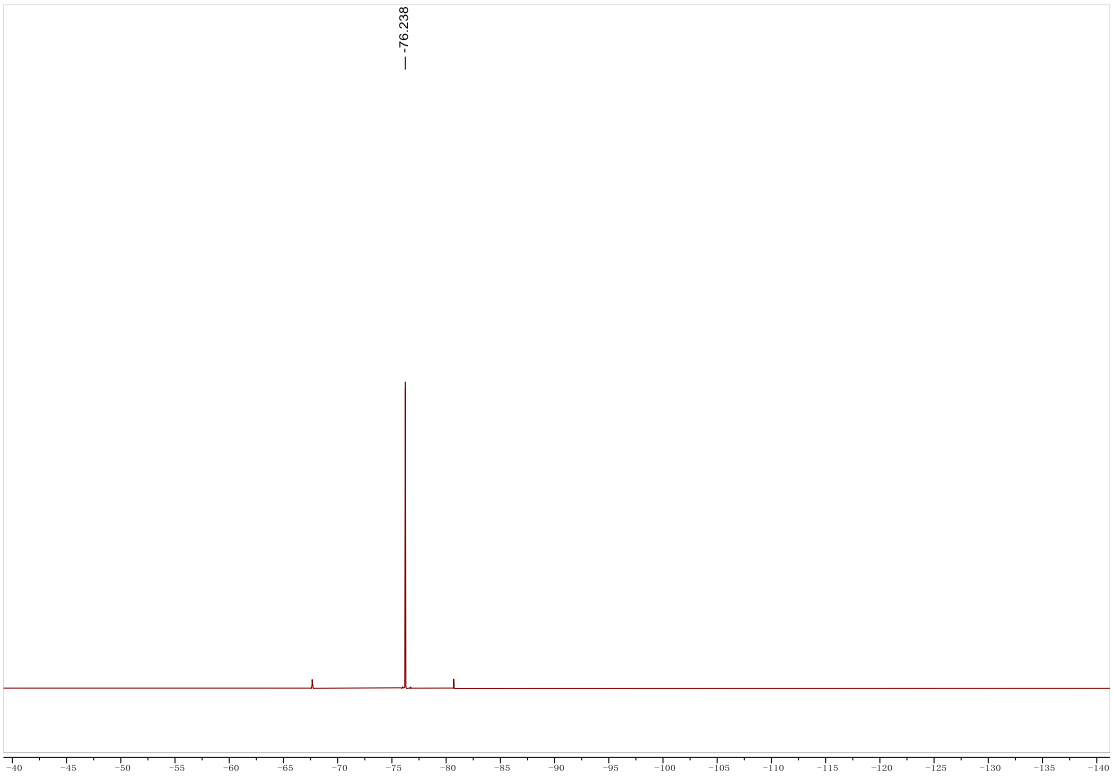



-76.158
-108.679
-108.691
-108.701
-108.715
-108.735
-108.739
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135

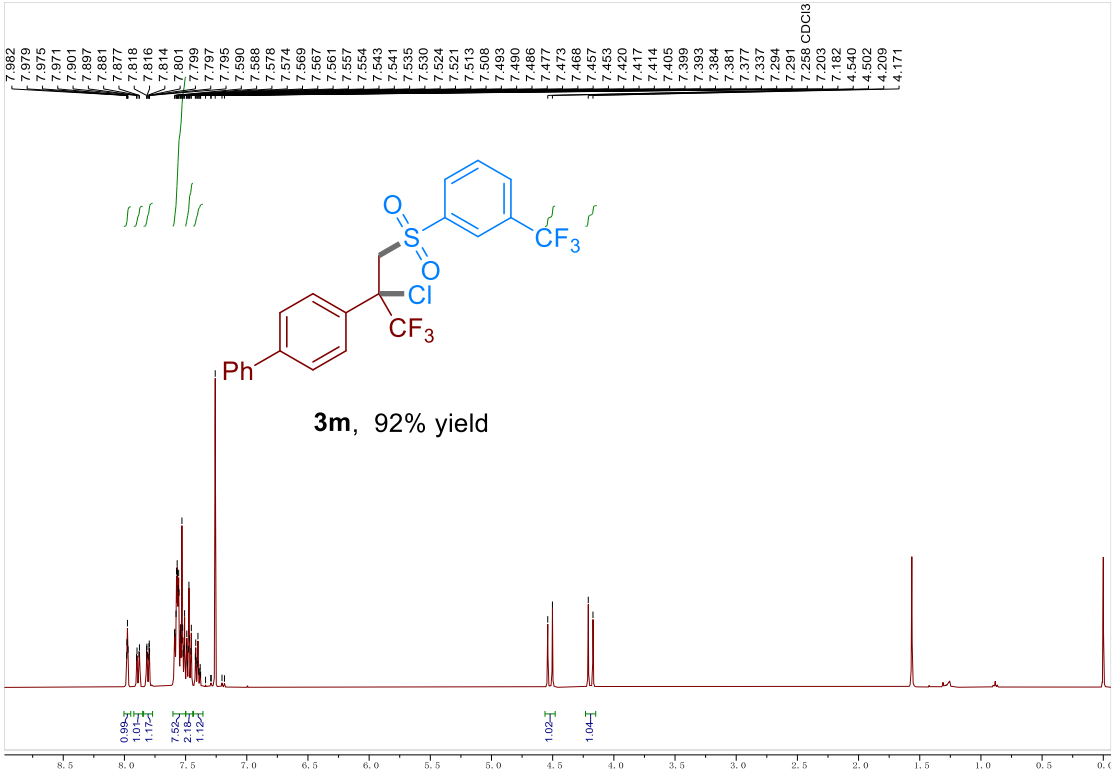
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3l

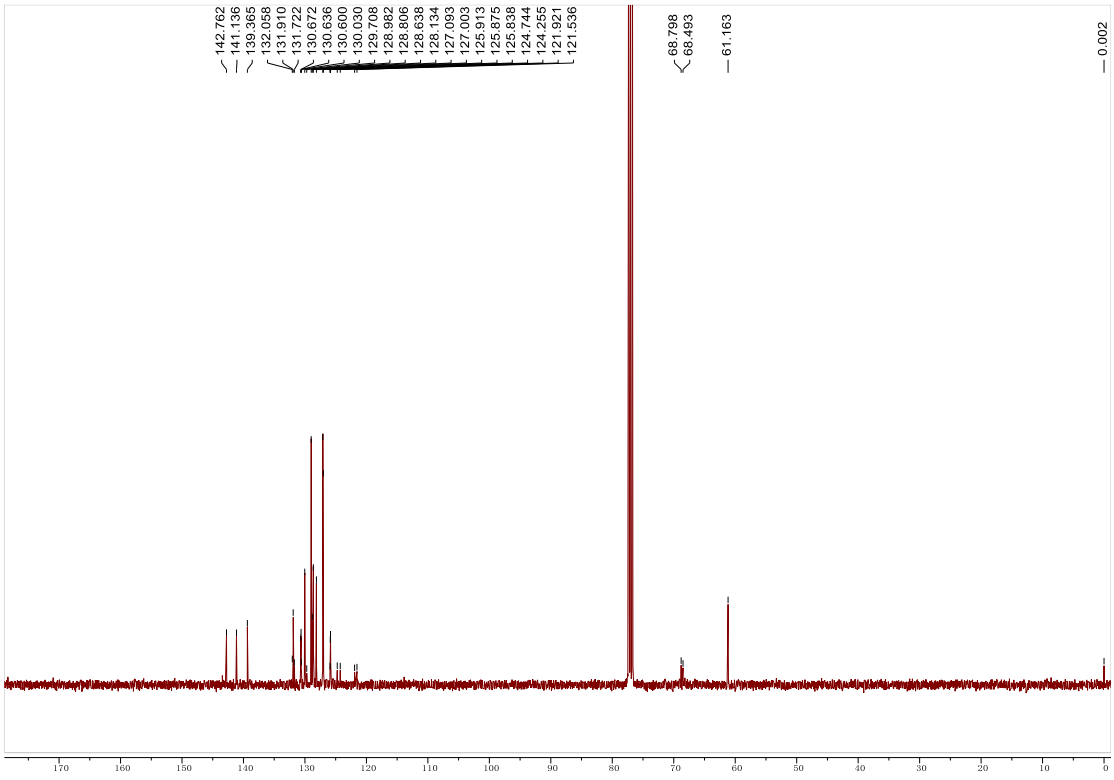


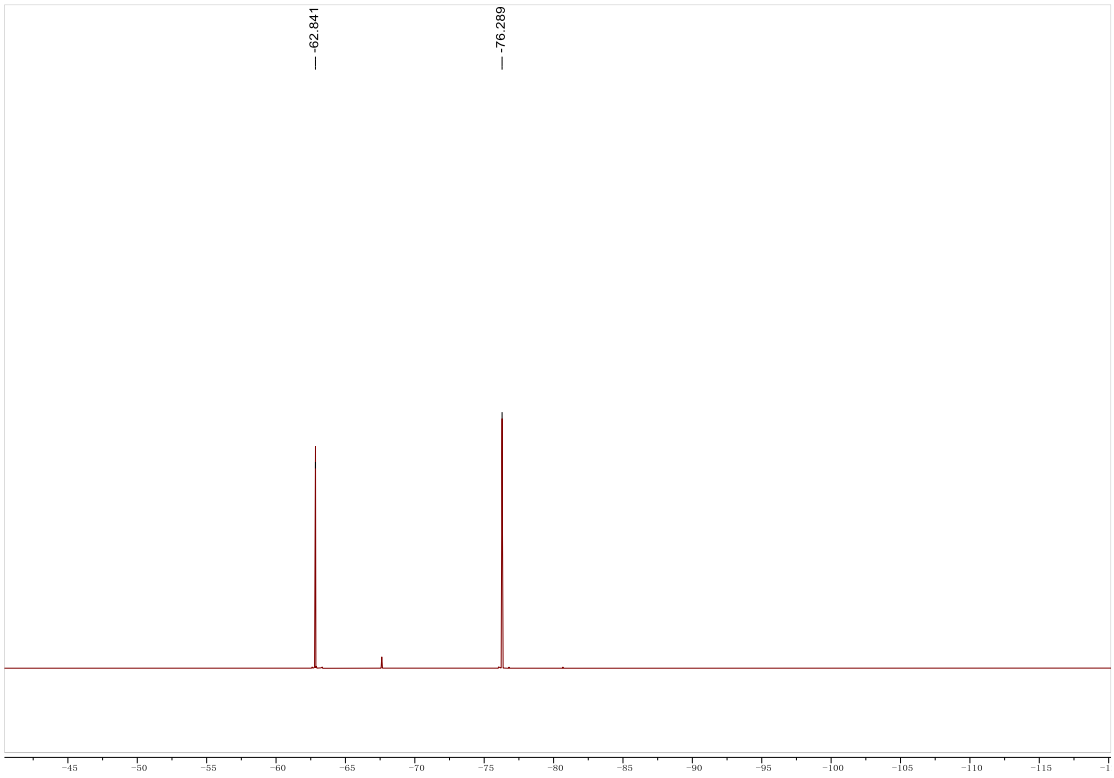



-76.238
−40
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115
−120
−125
−130
−135
−140

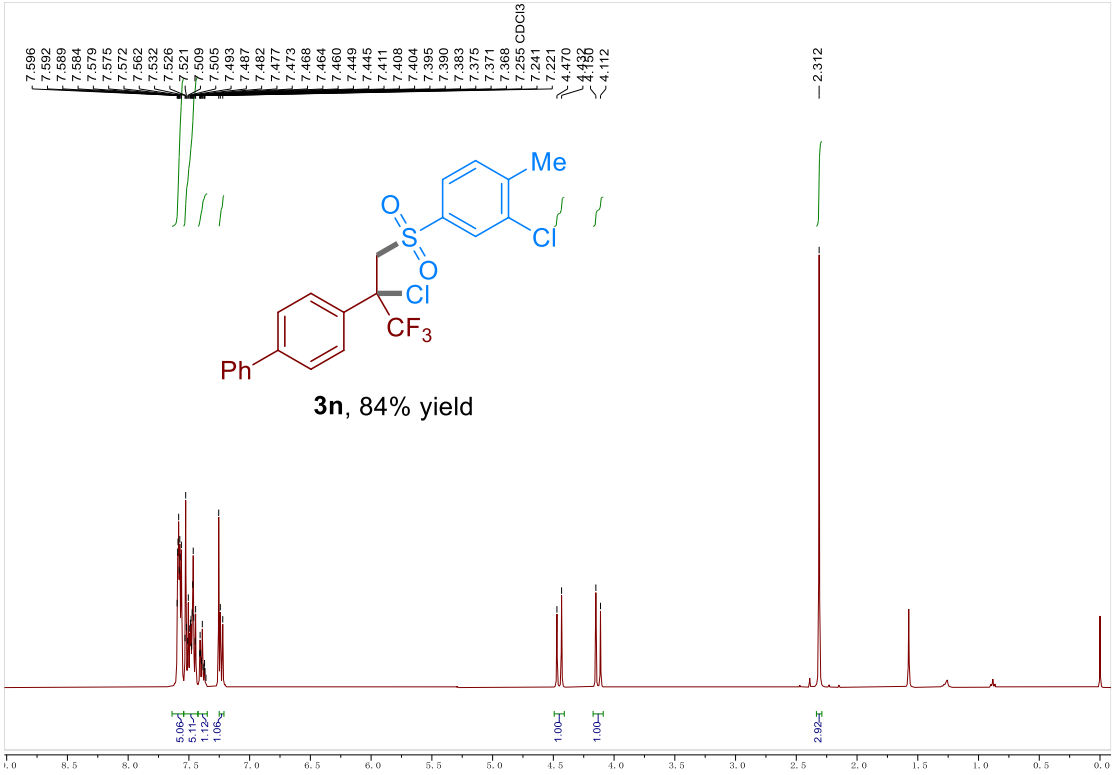
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3m

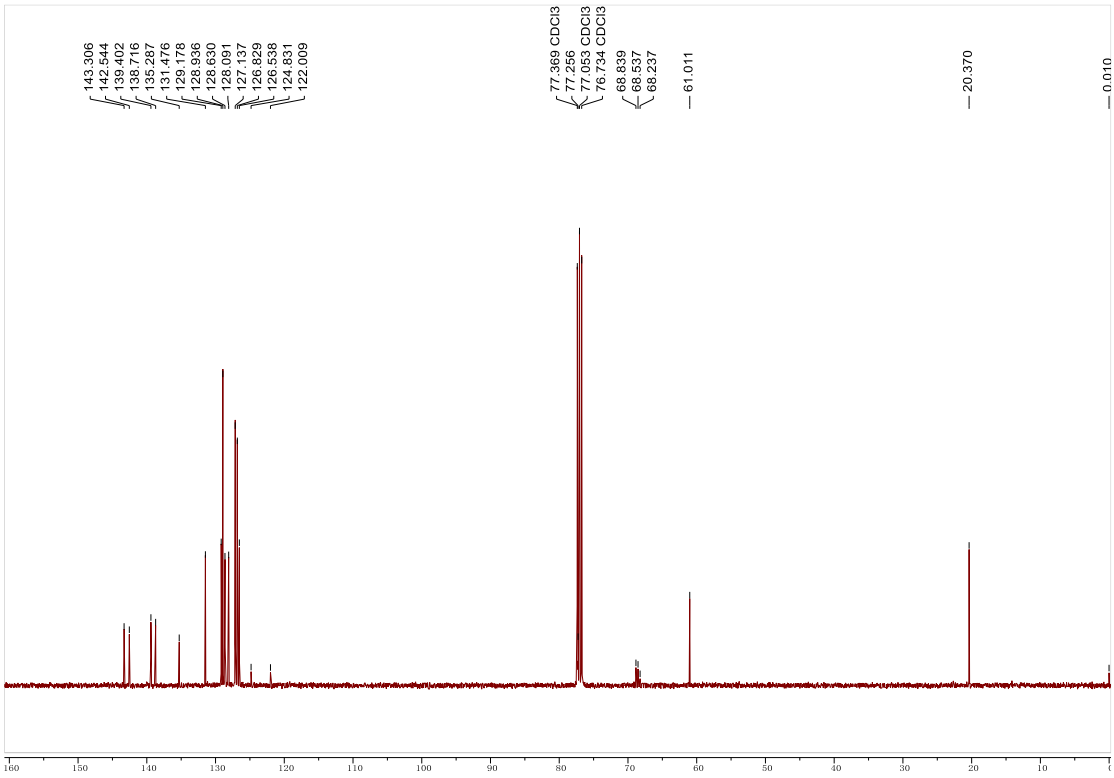


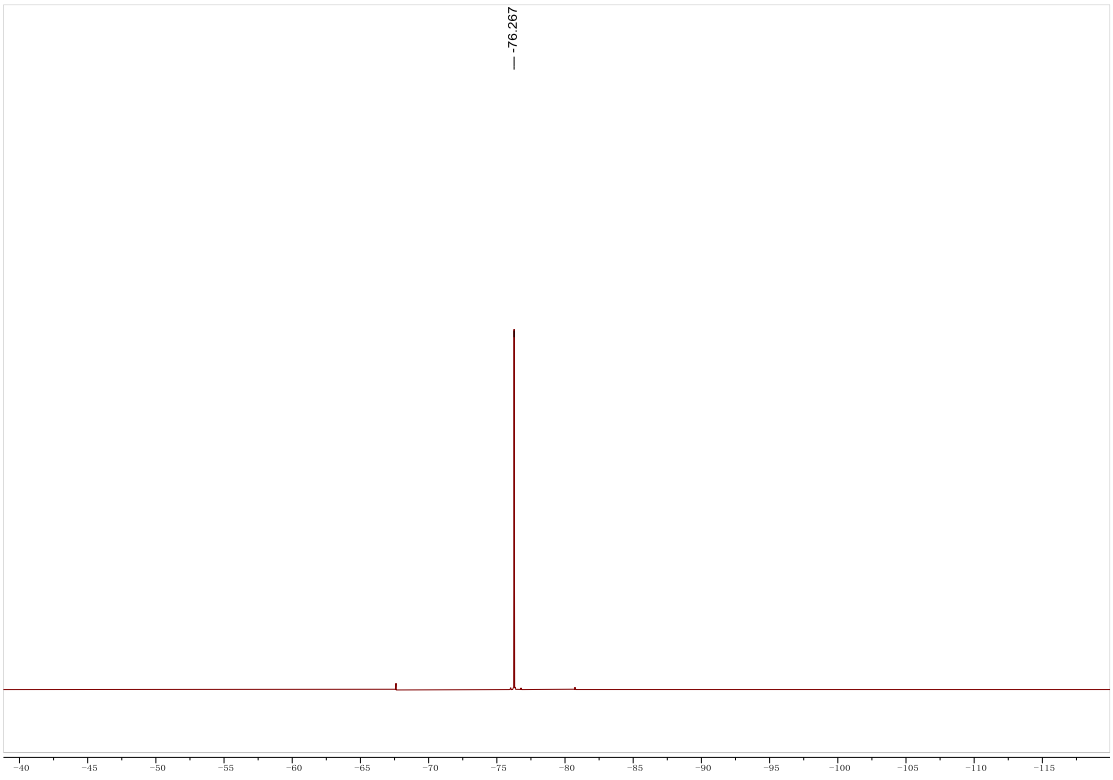



-62.841
-76.289
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115

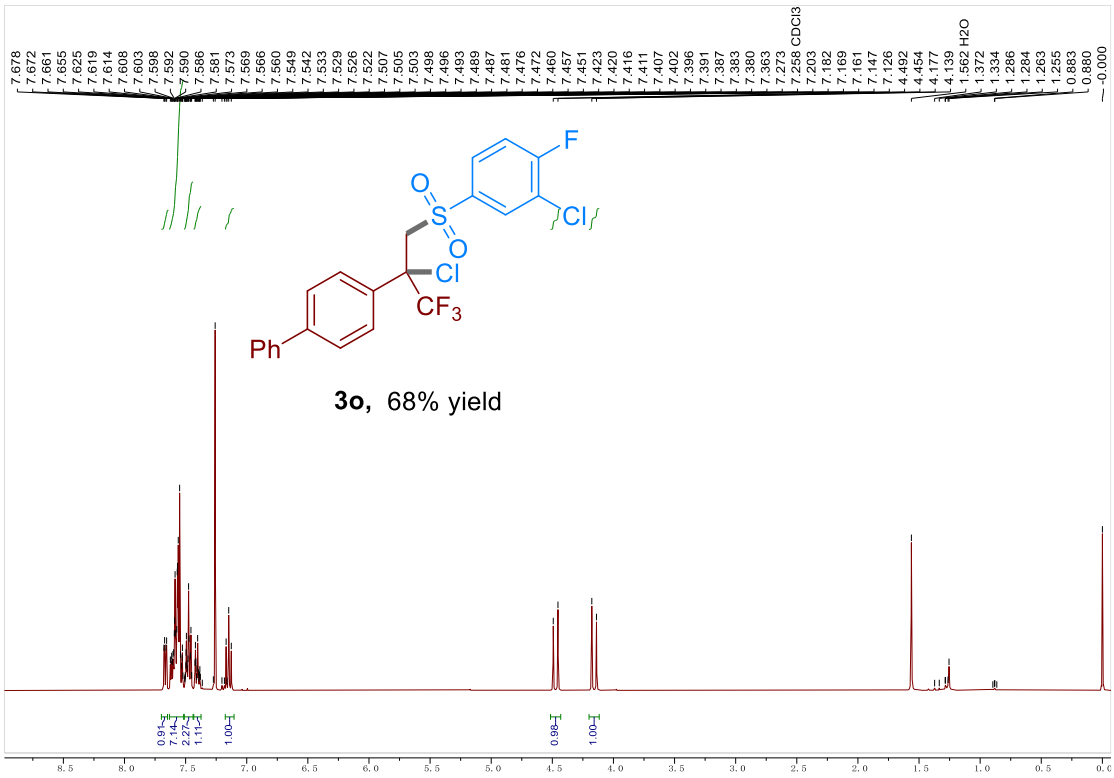
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3n

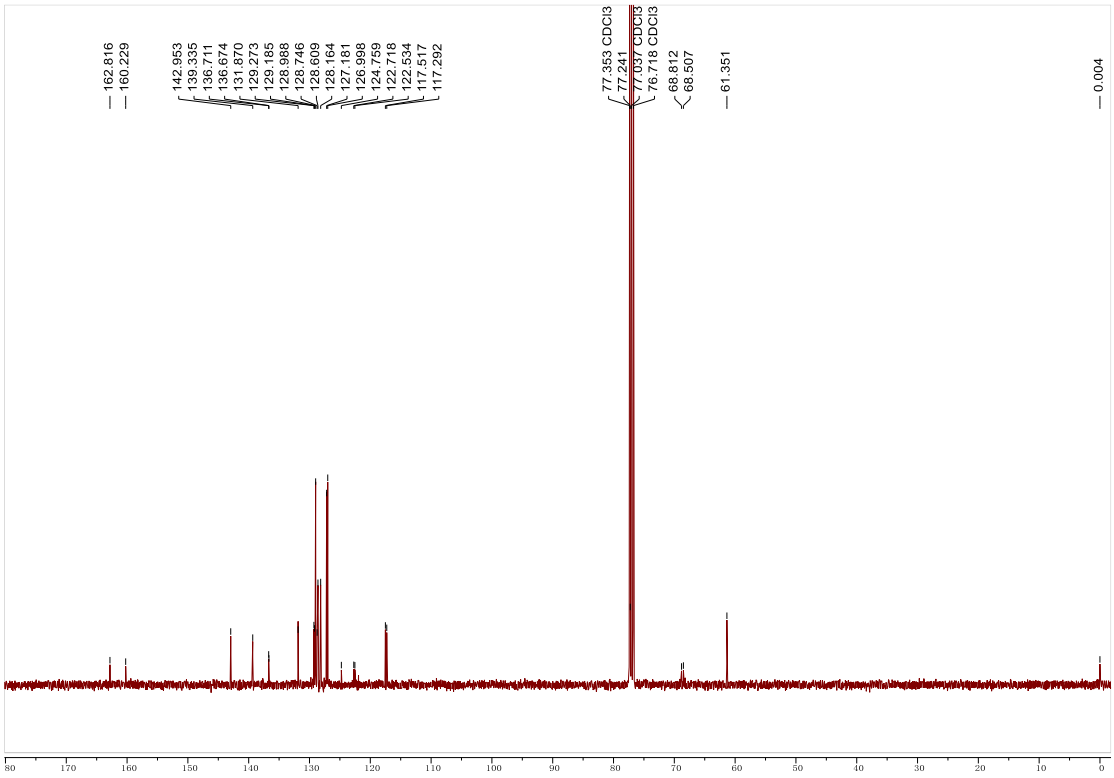


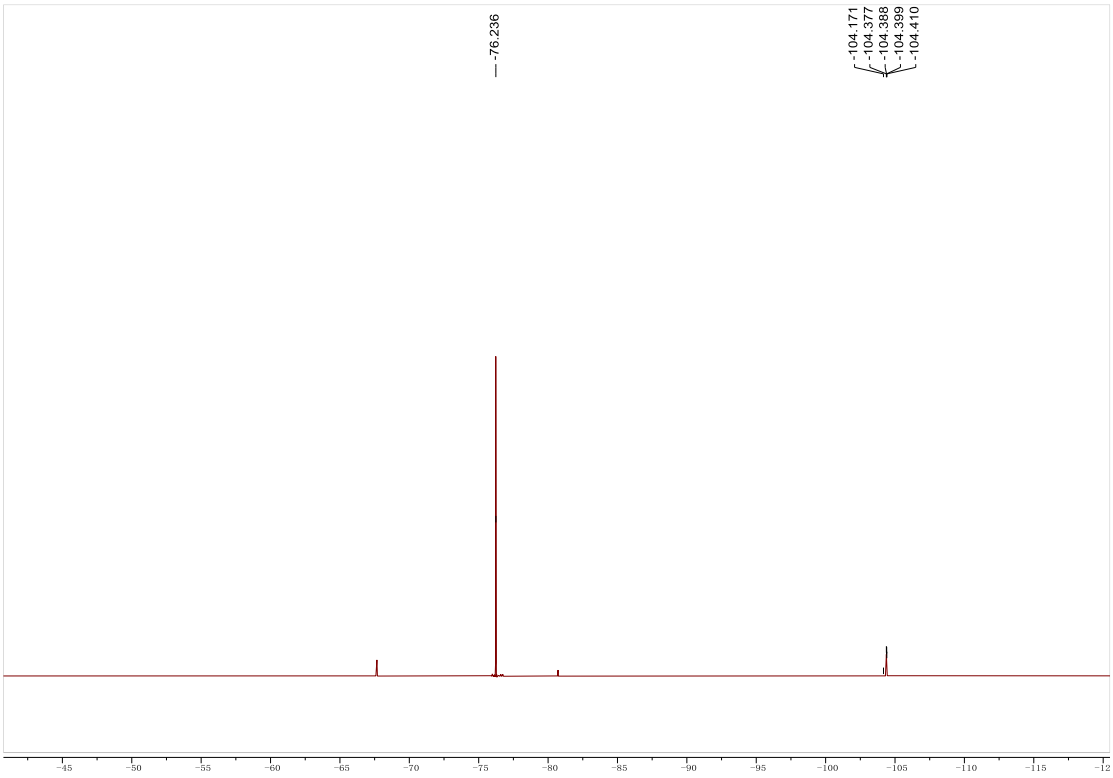



-76.267
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115

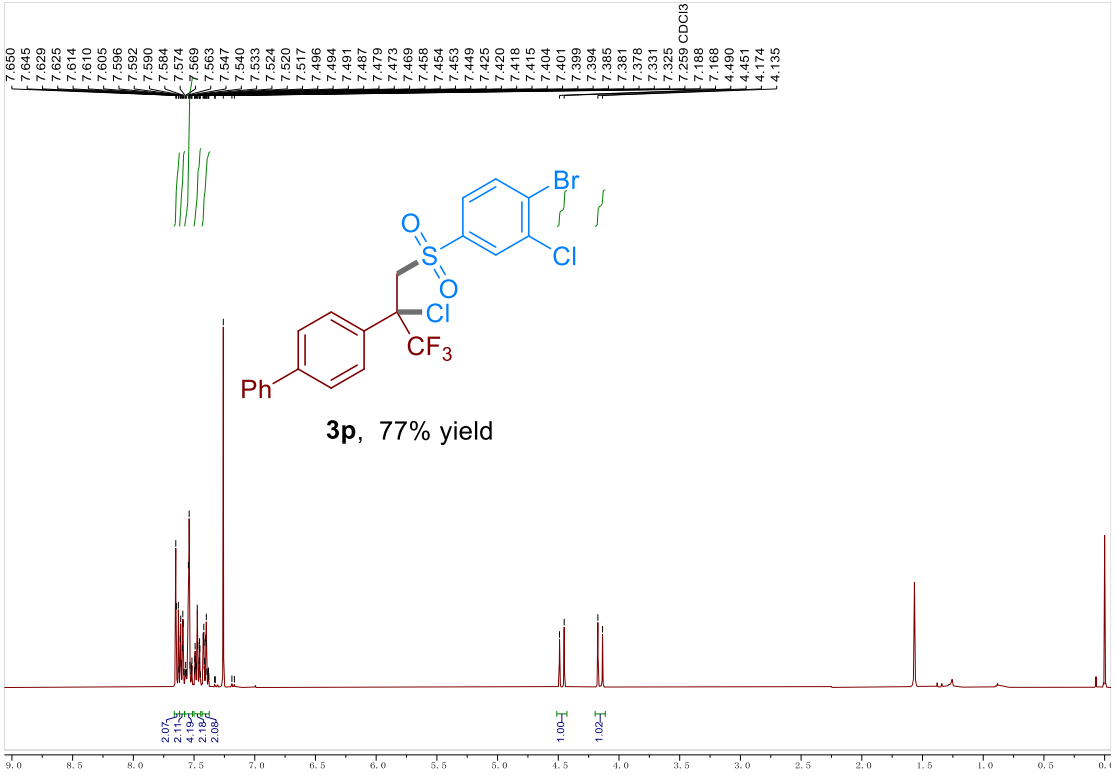
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3o

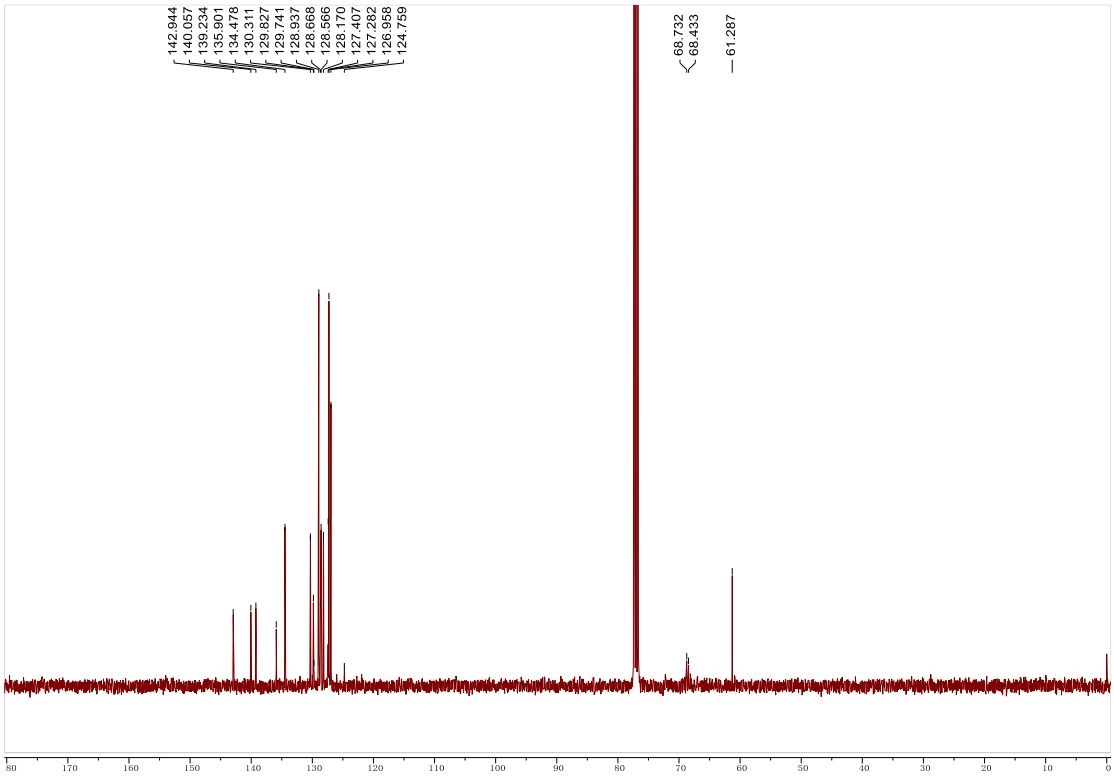


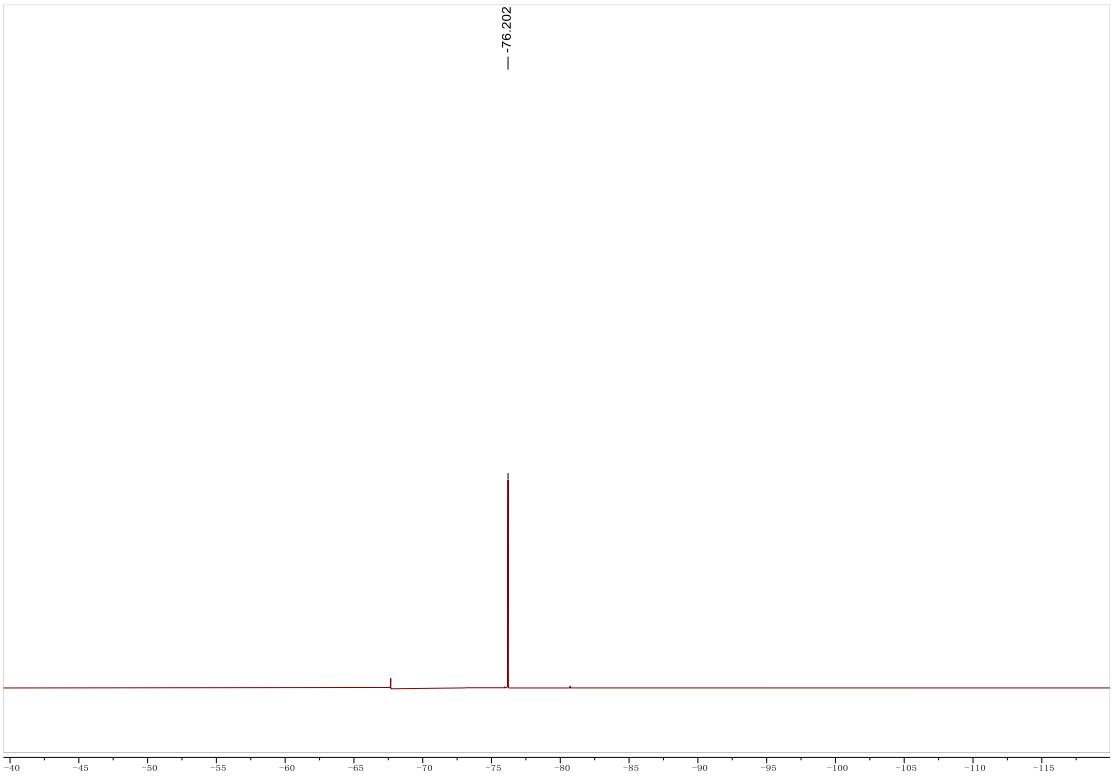



-76.236
-104.171
-104.377
-104.388
-104.399
-104.410
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-12

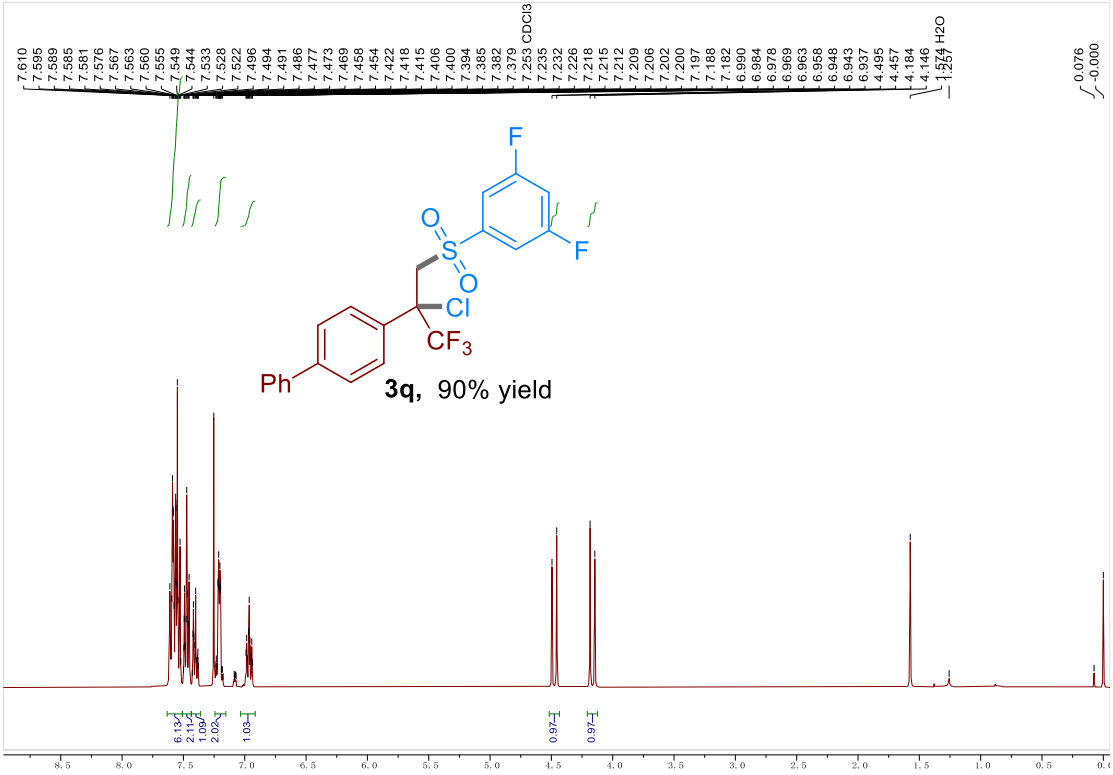
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3p

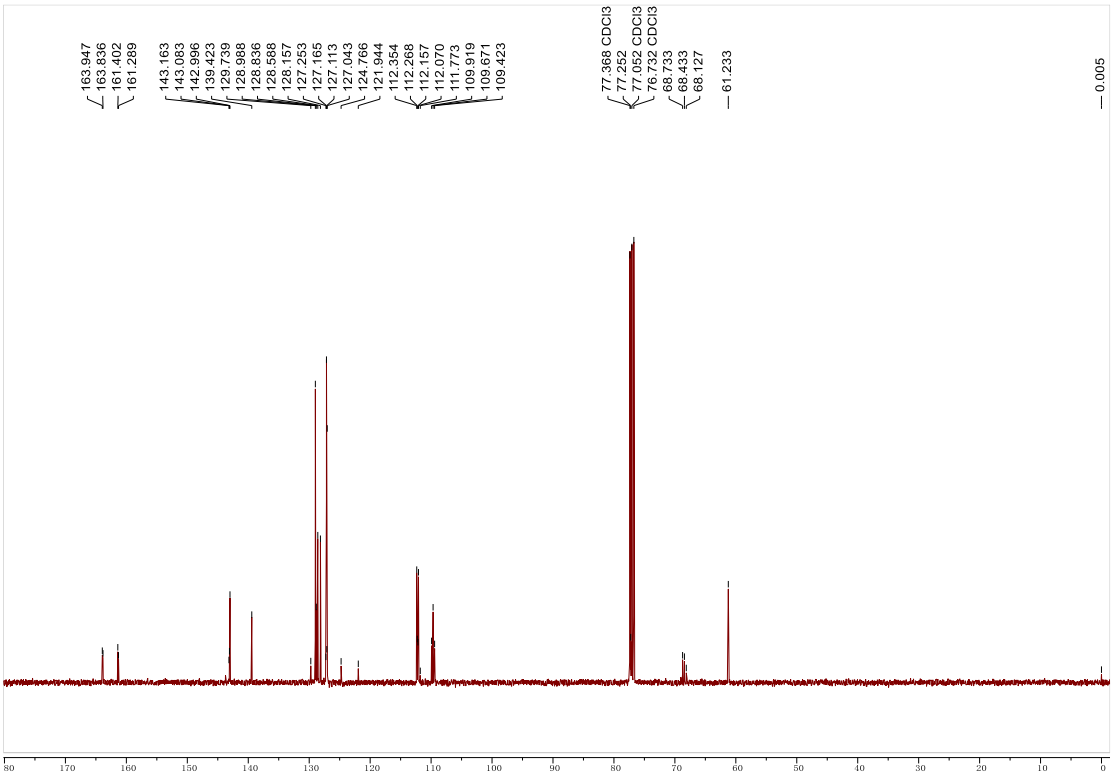


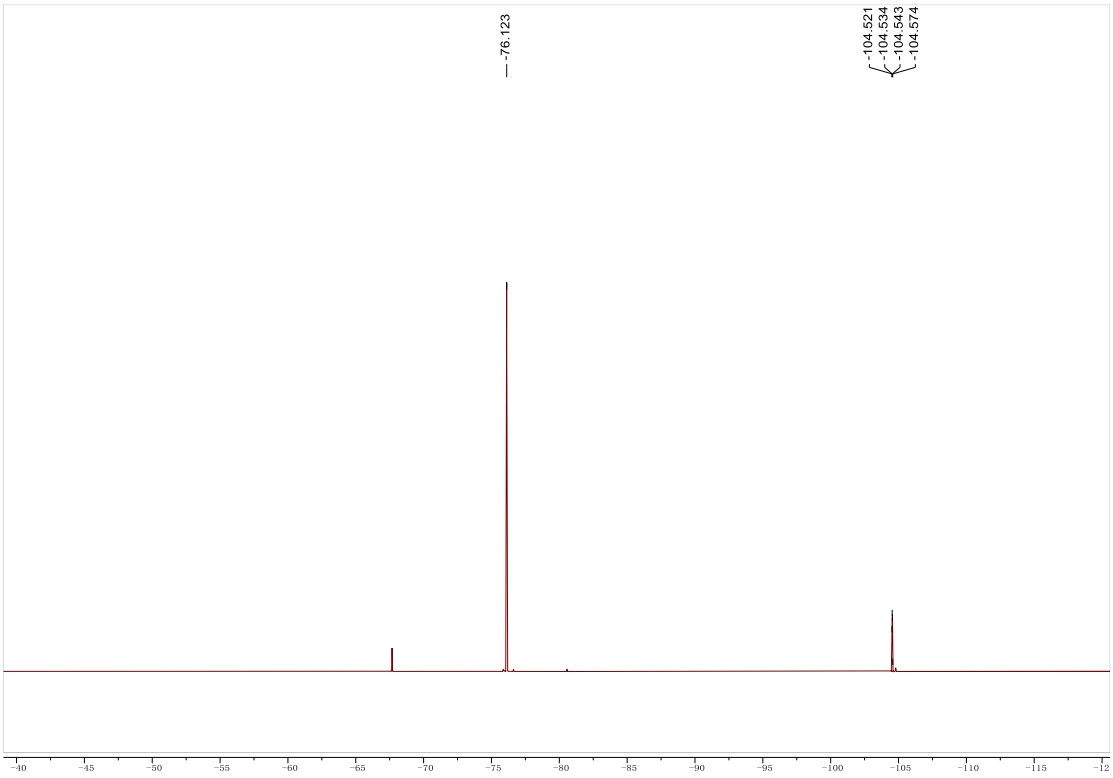



-76.202
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115

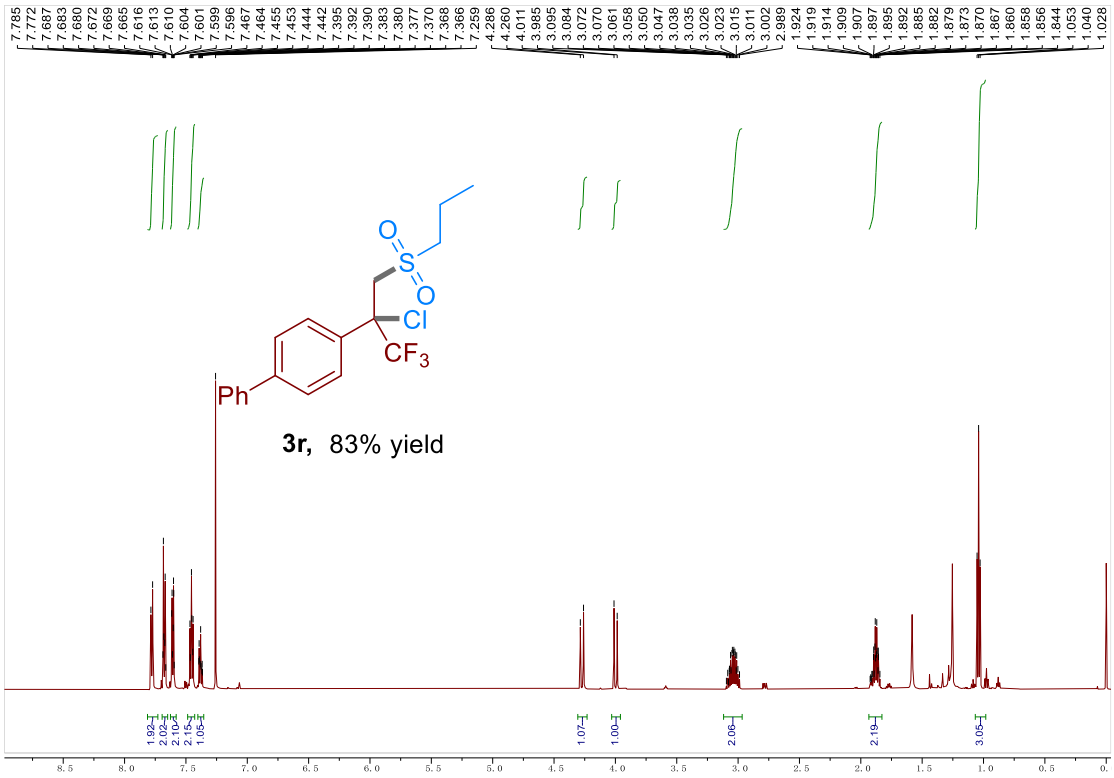
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3q

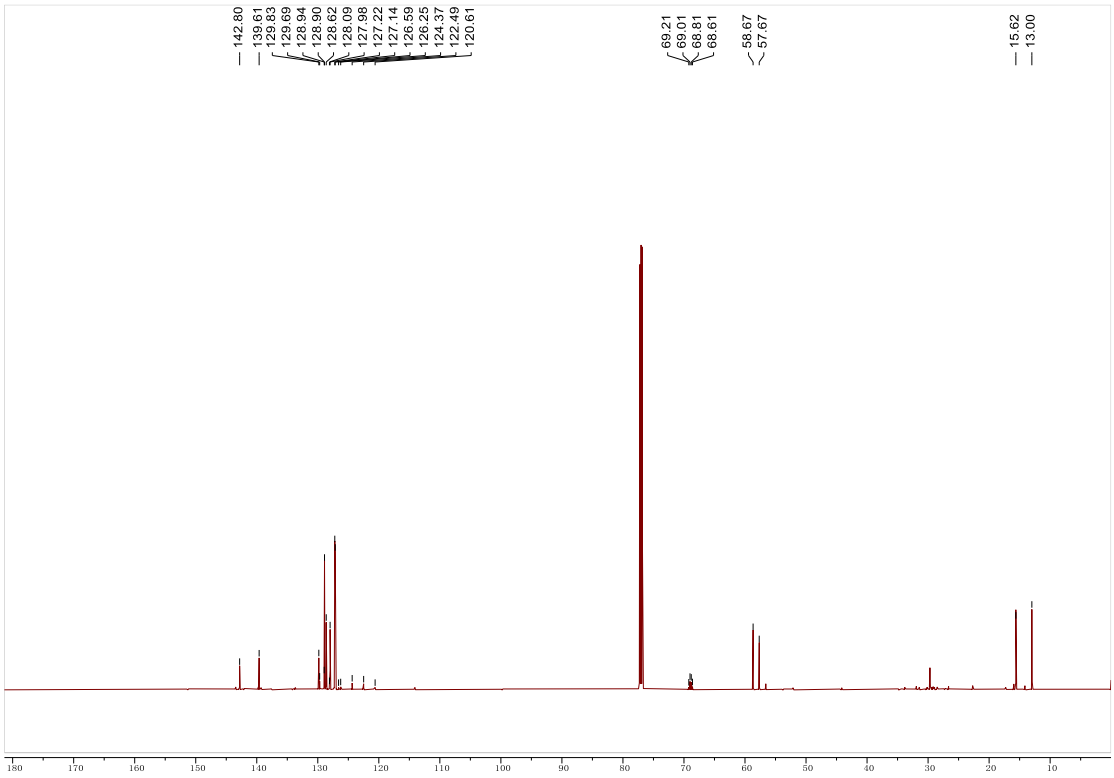


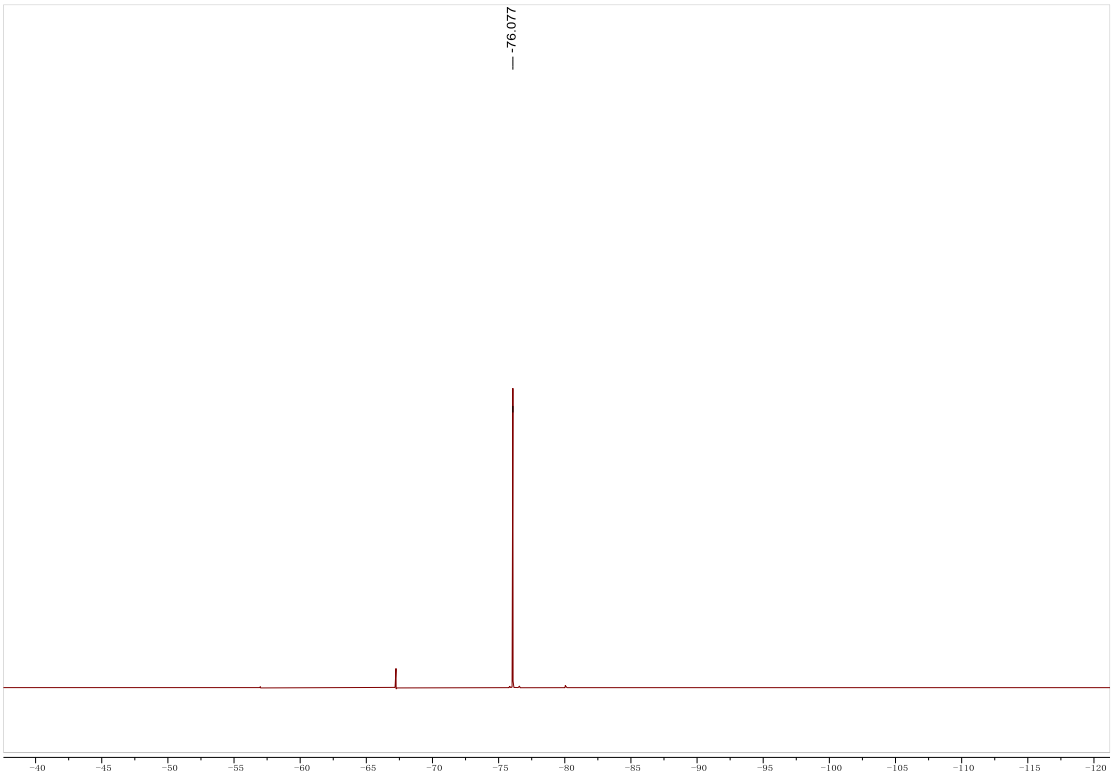



-76.123
-104.521
-104.534
-104.543
-104.574
−40
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115
−12

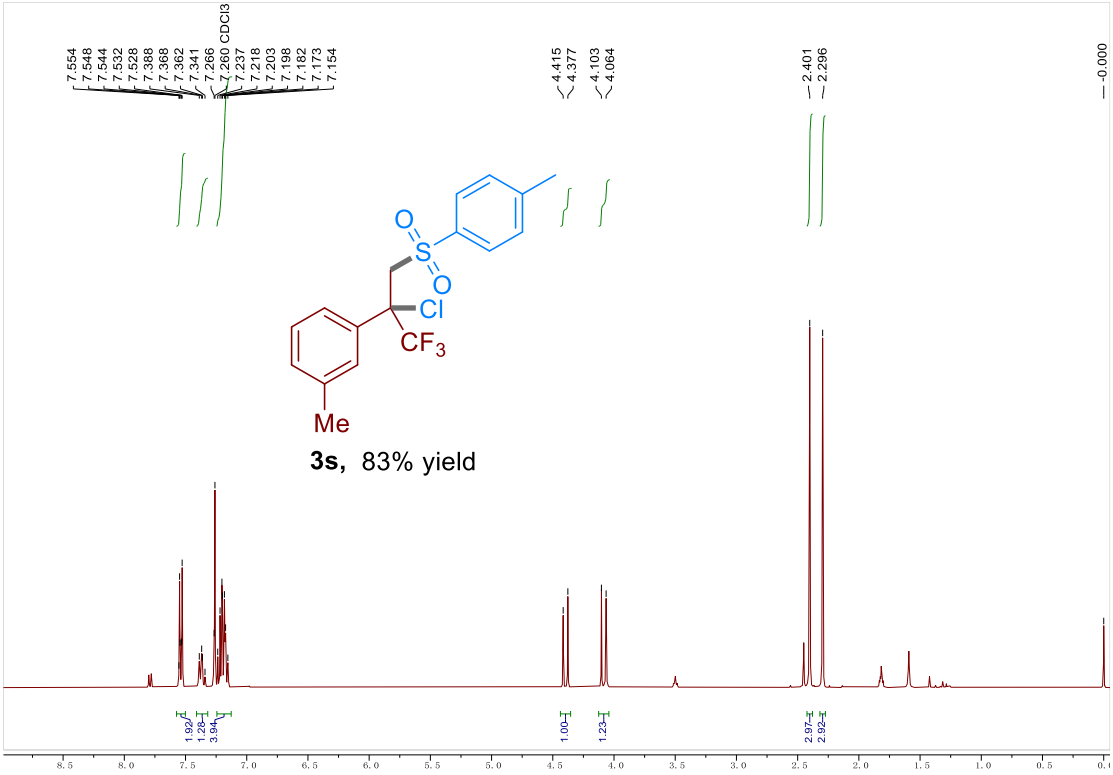
^{1}H NMR (600 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of product 3r

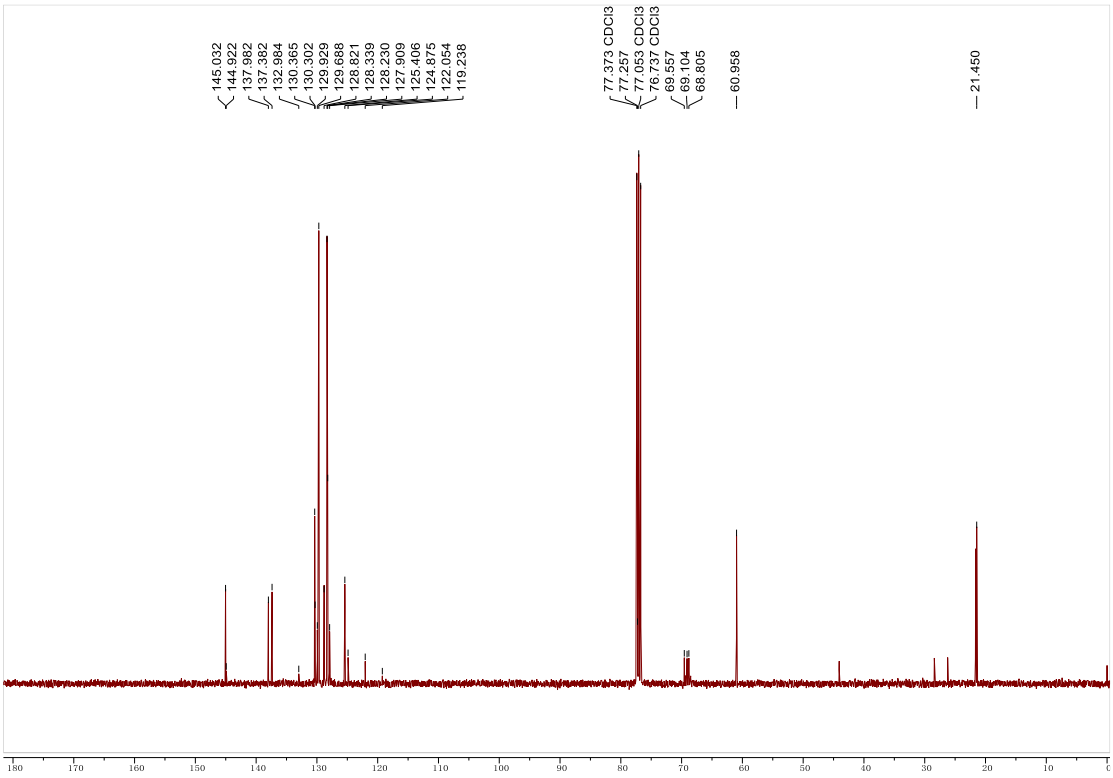


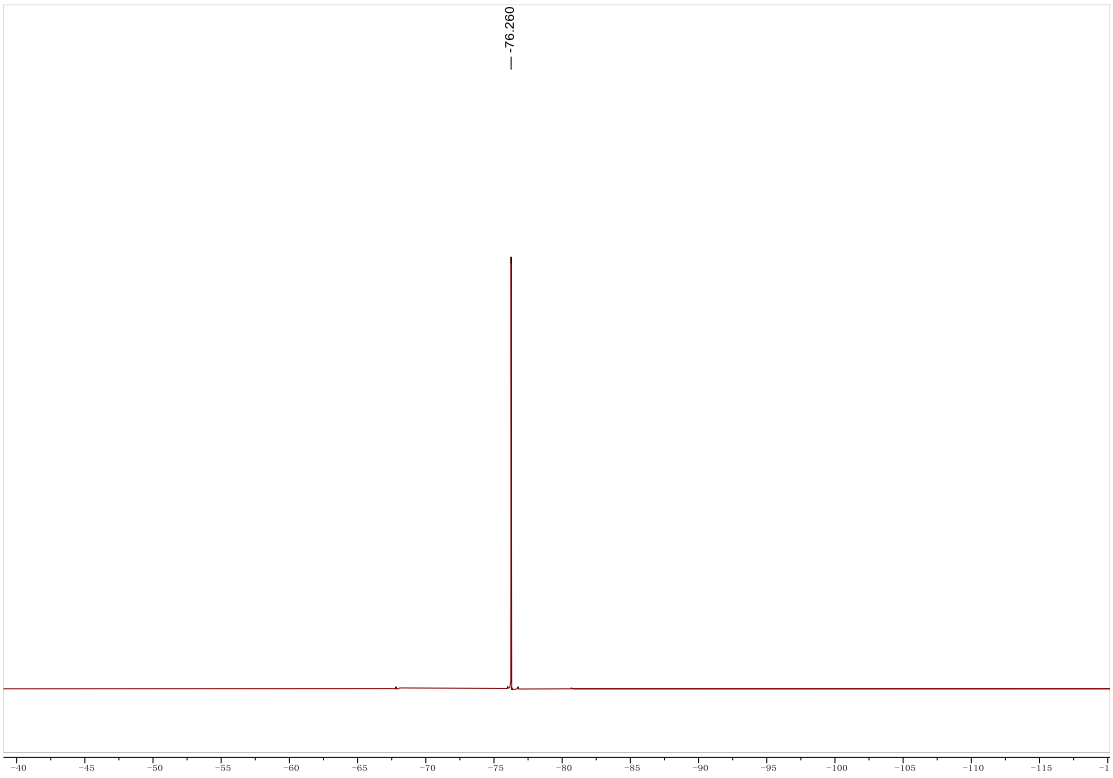



-76.077
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120

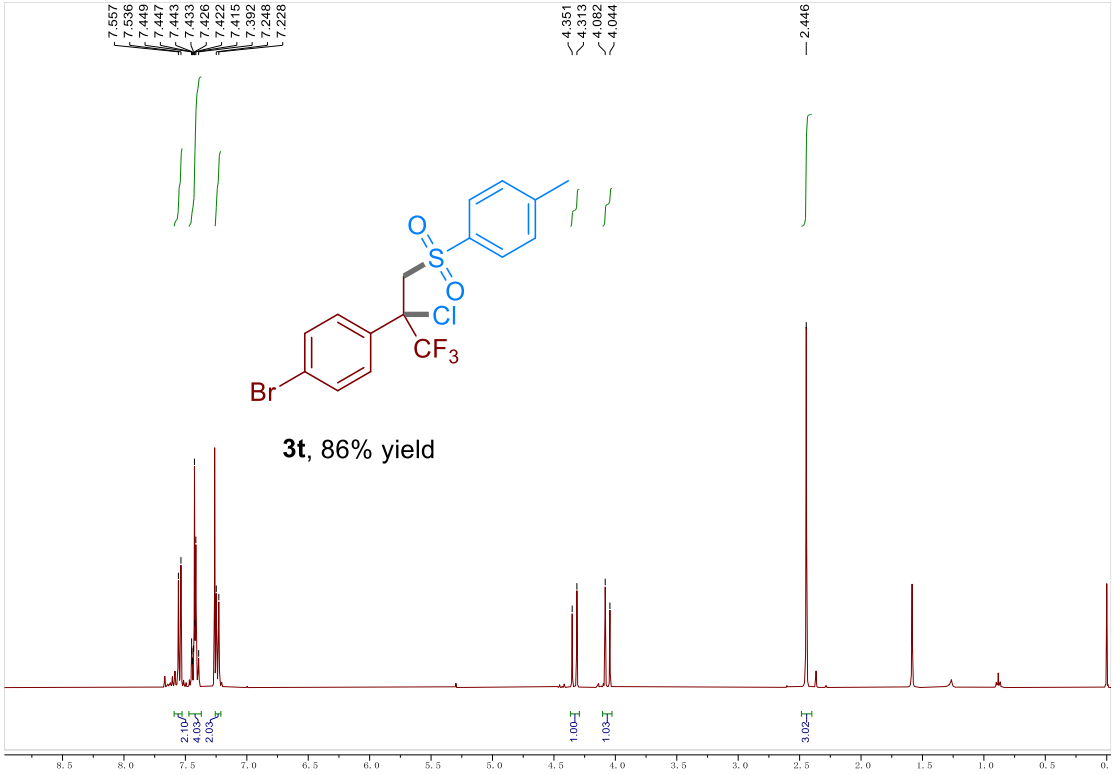
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3s

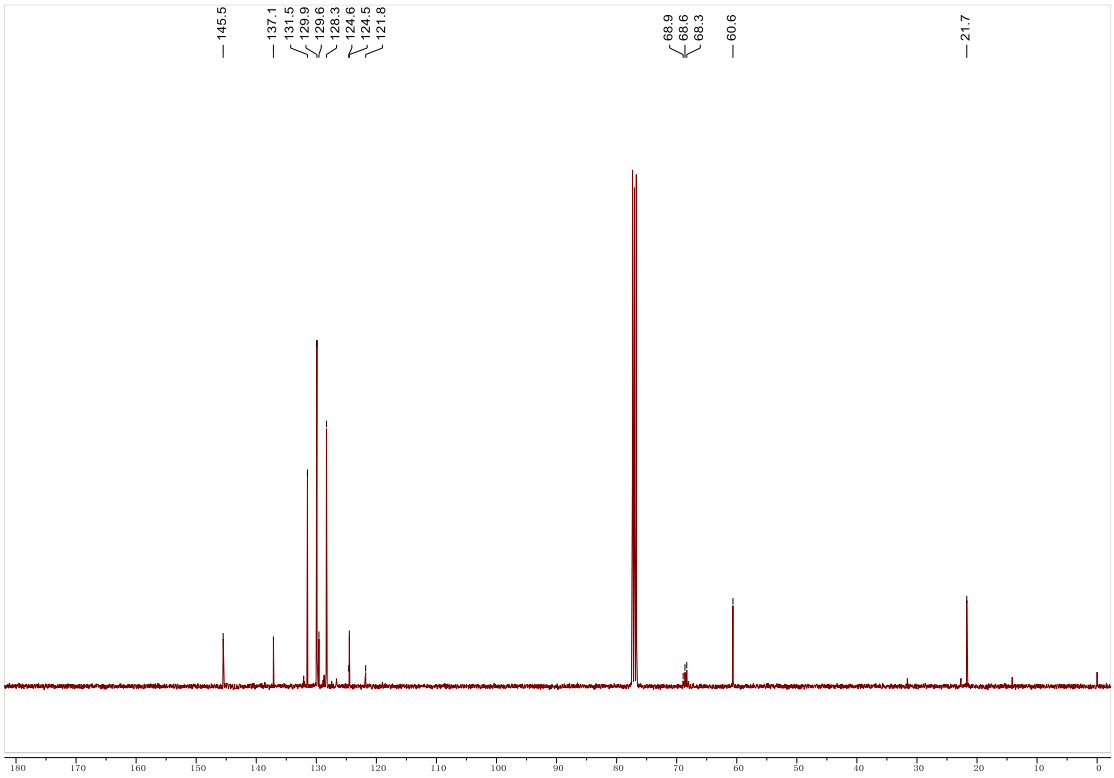


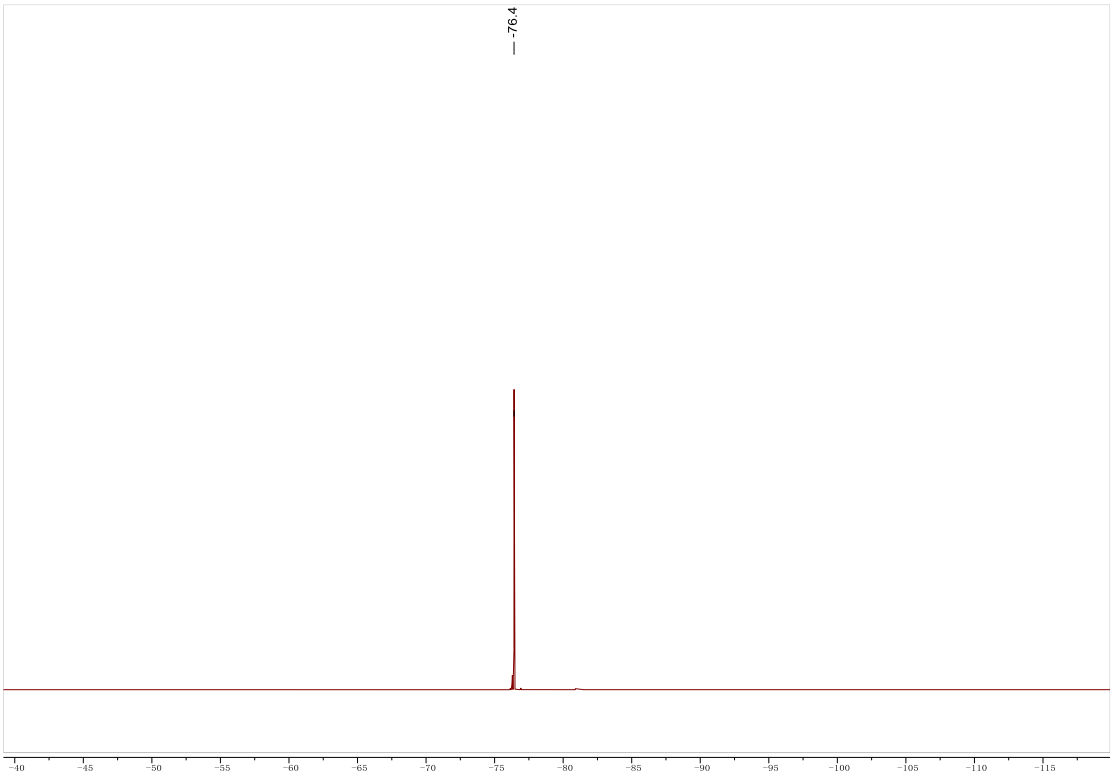



-76.260
−40
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115

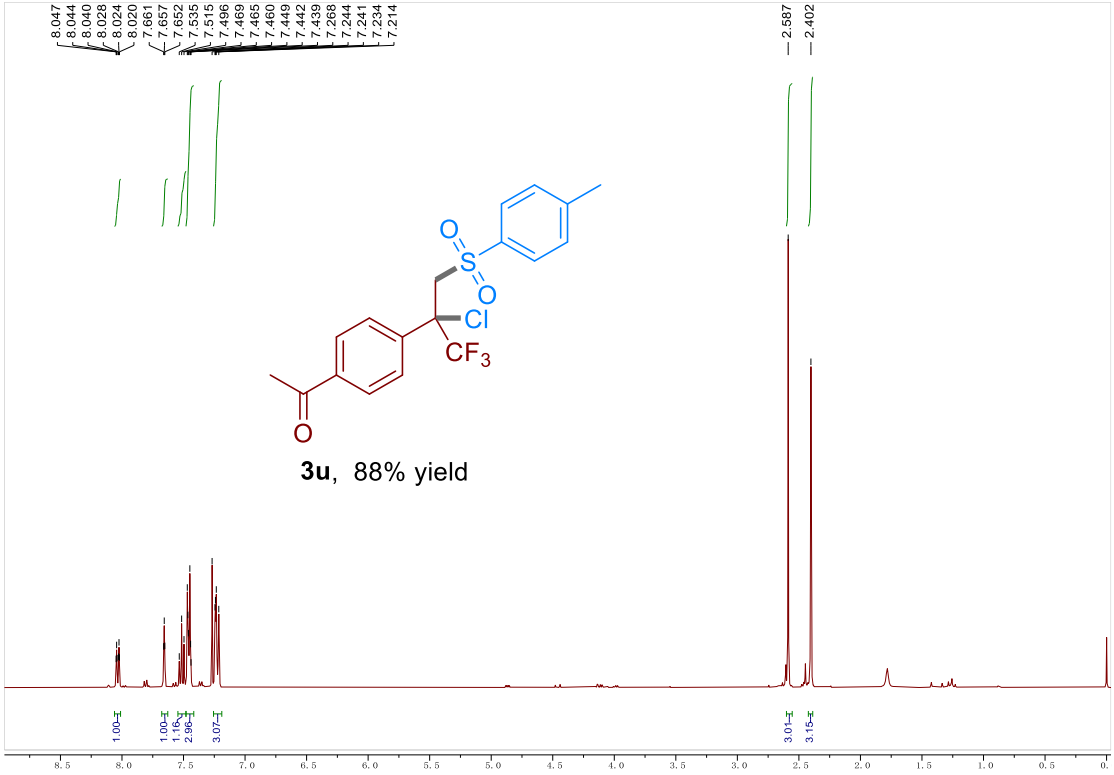
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3t

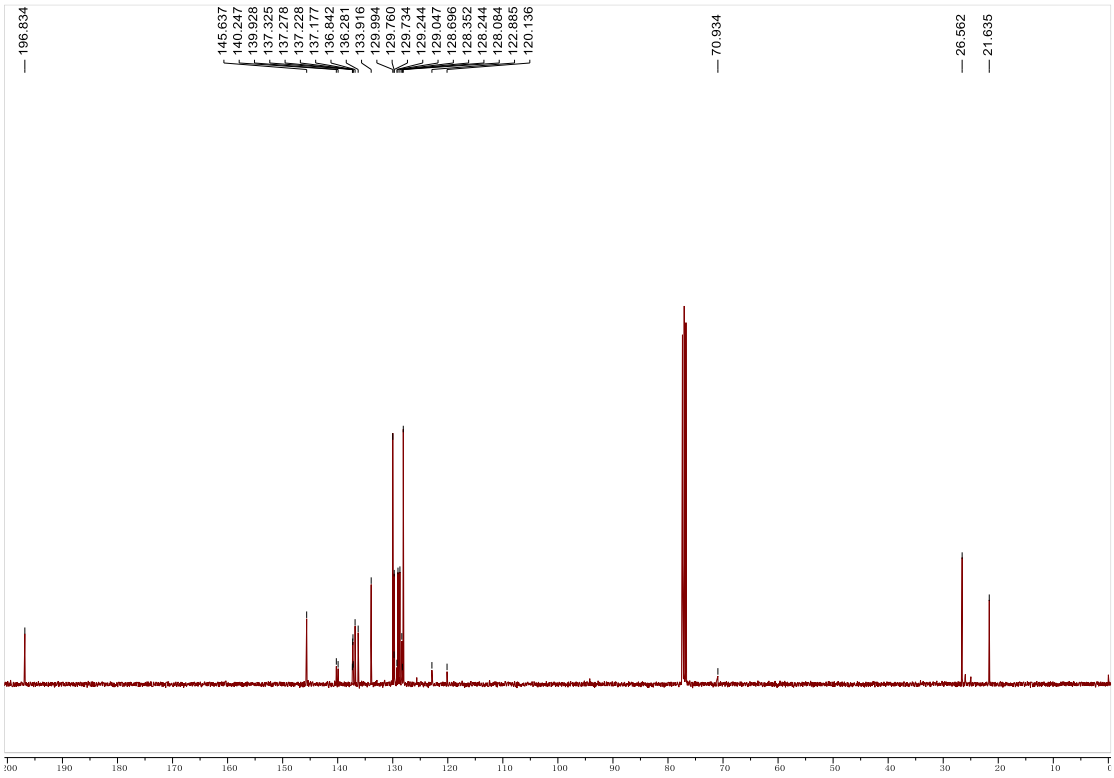


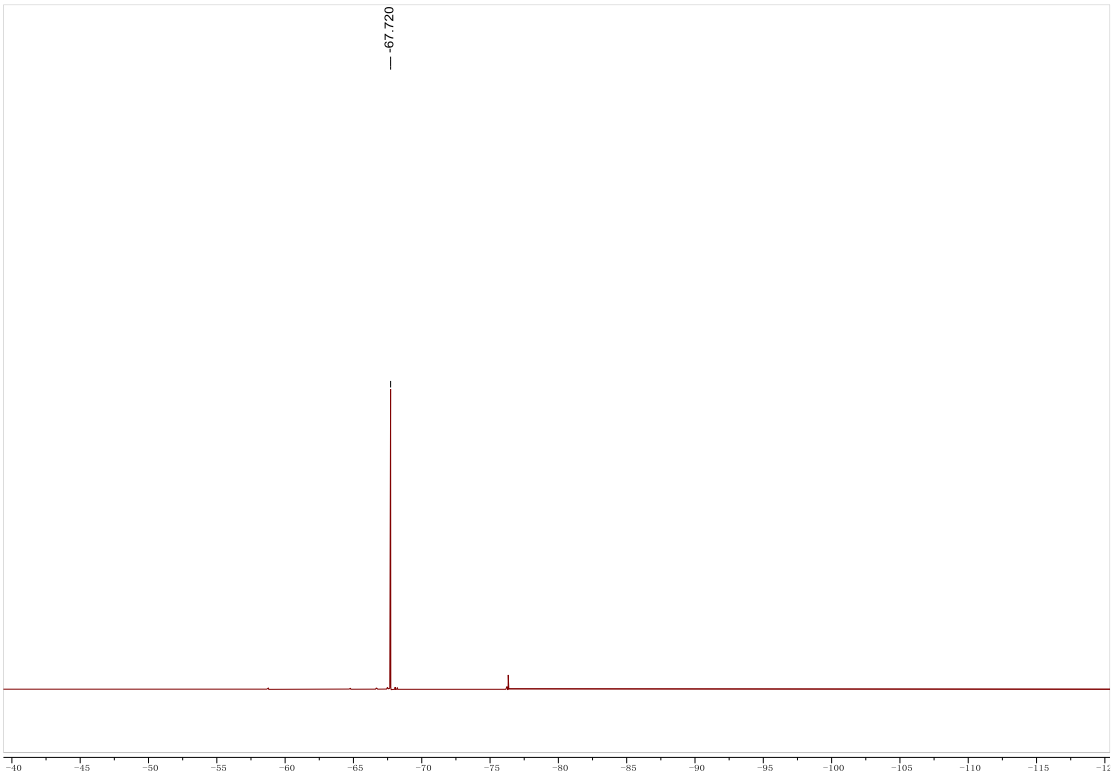



-76.4
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115

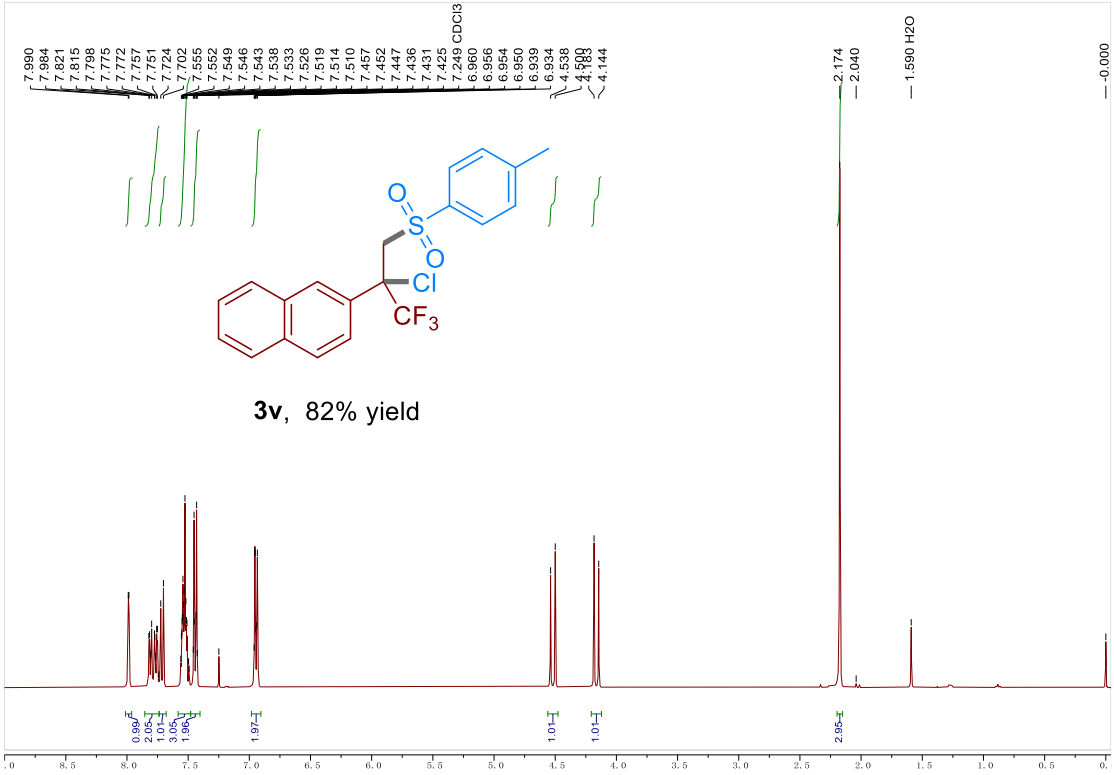
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3u

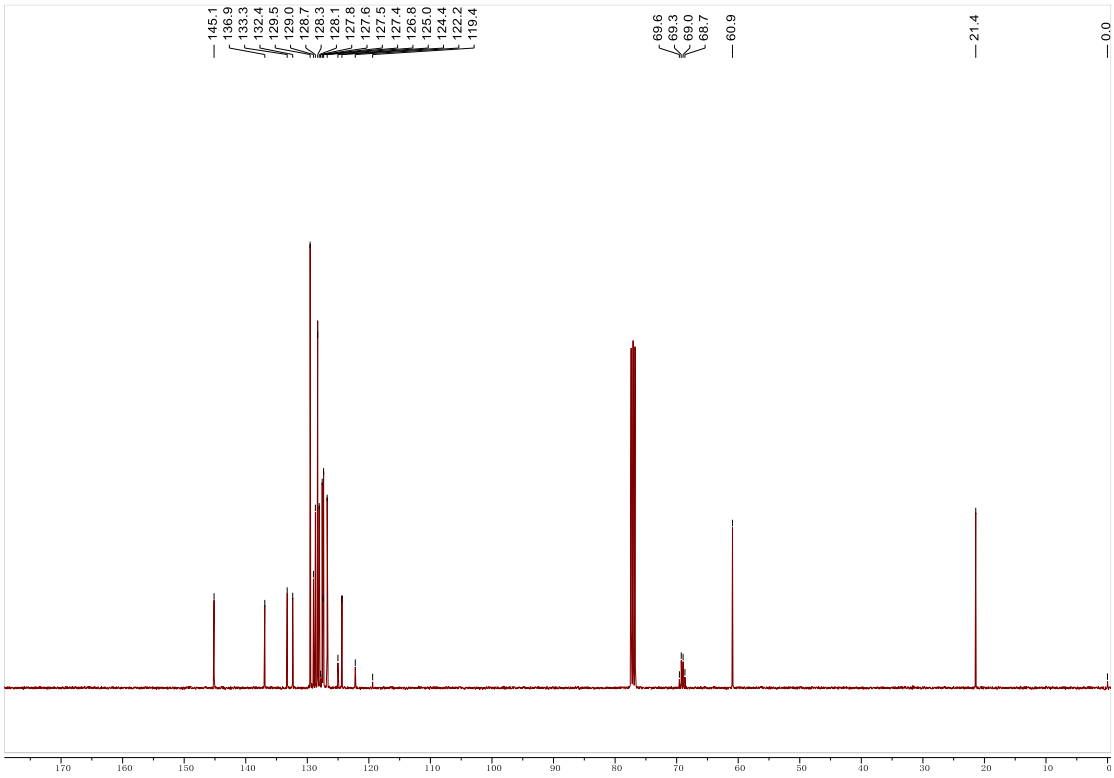


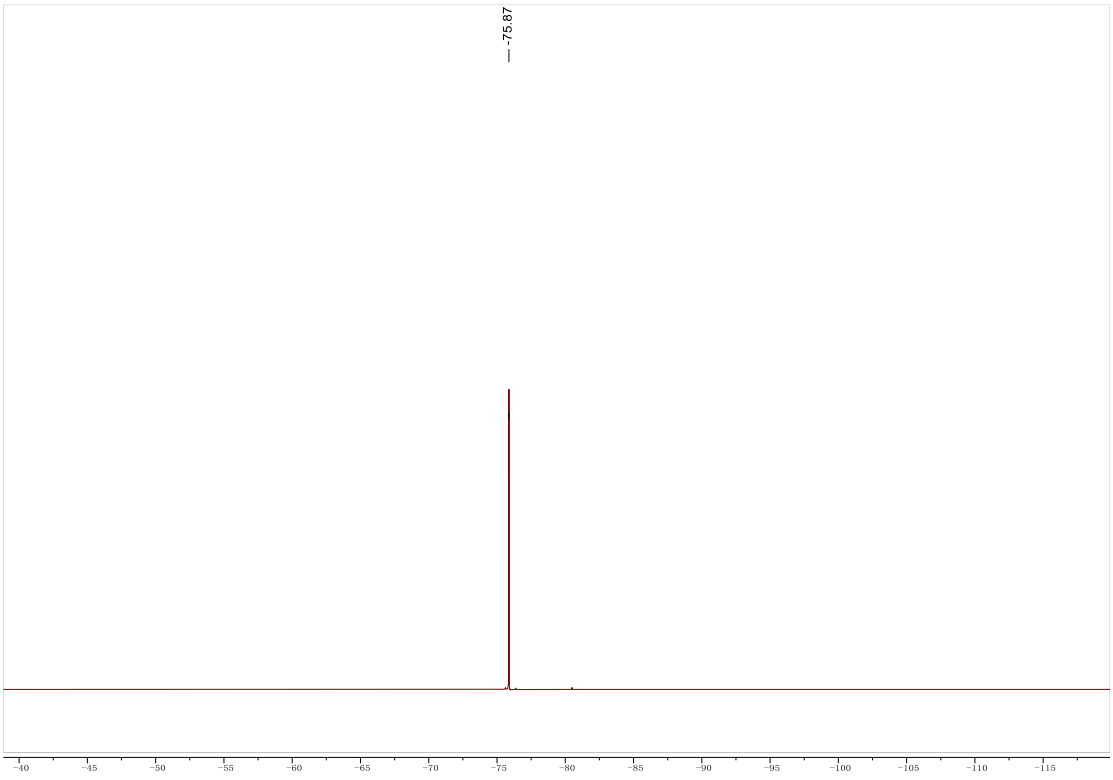



-67.720
−40
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115

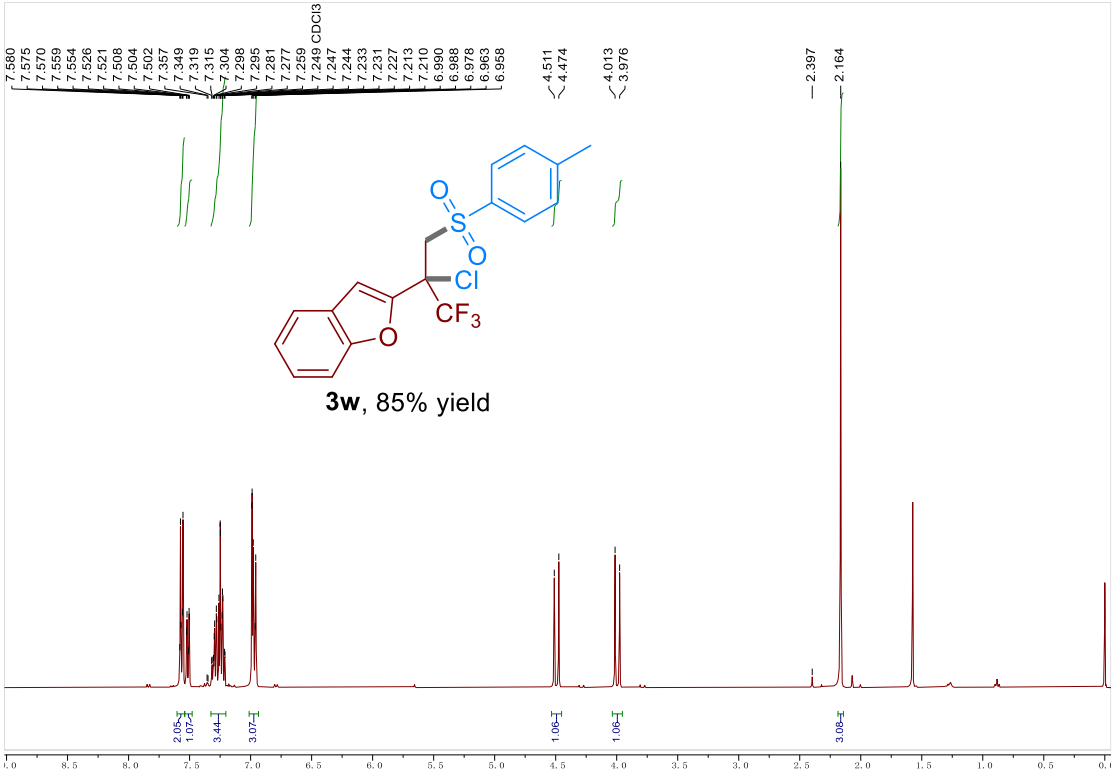
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3v

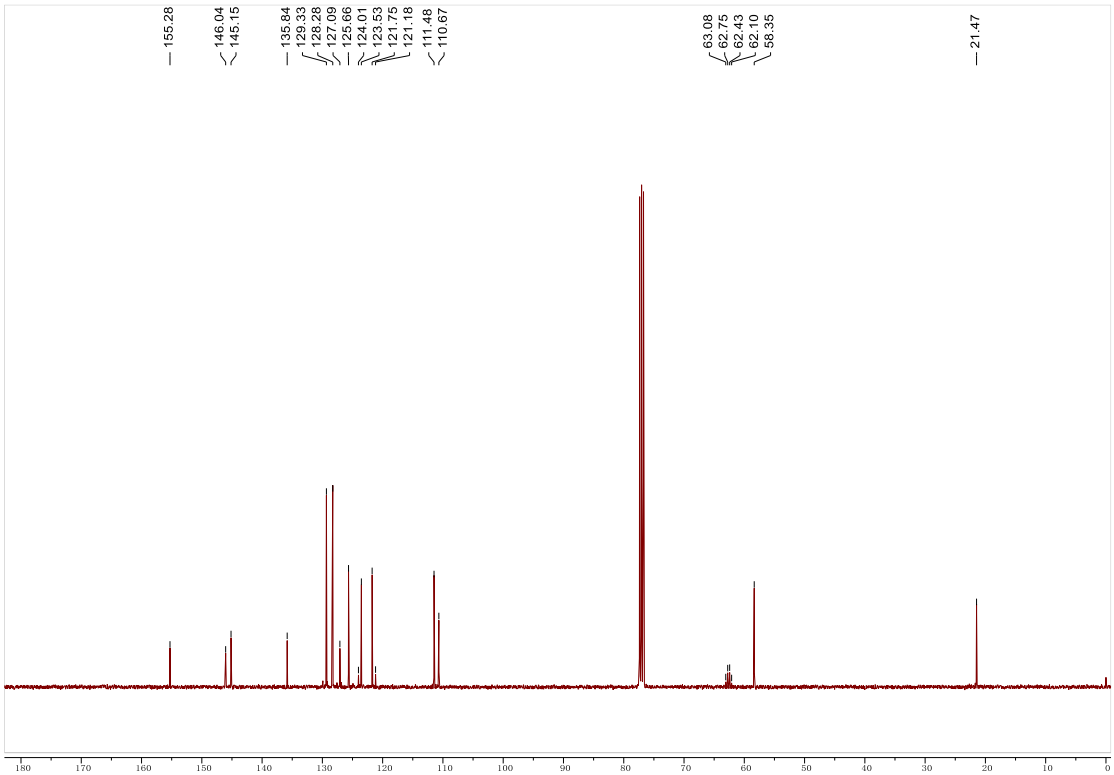


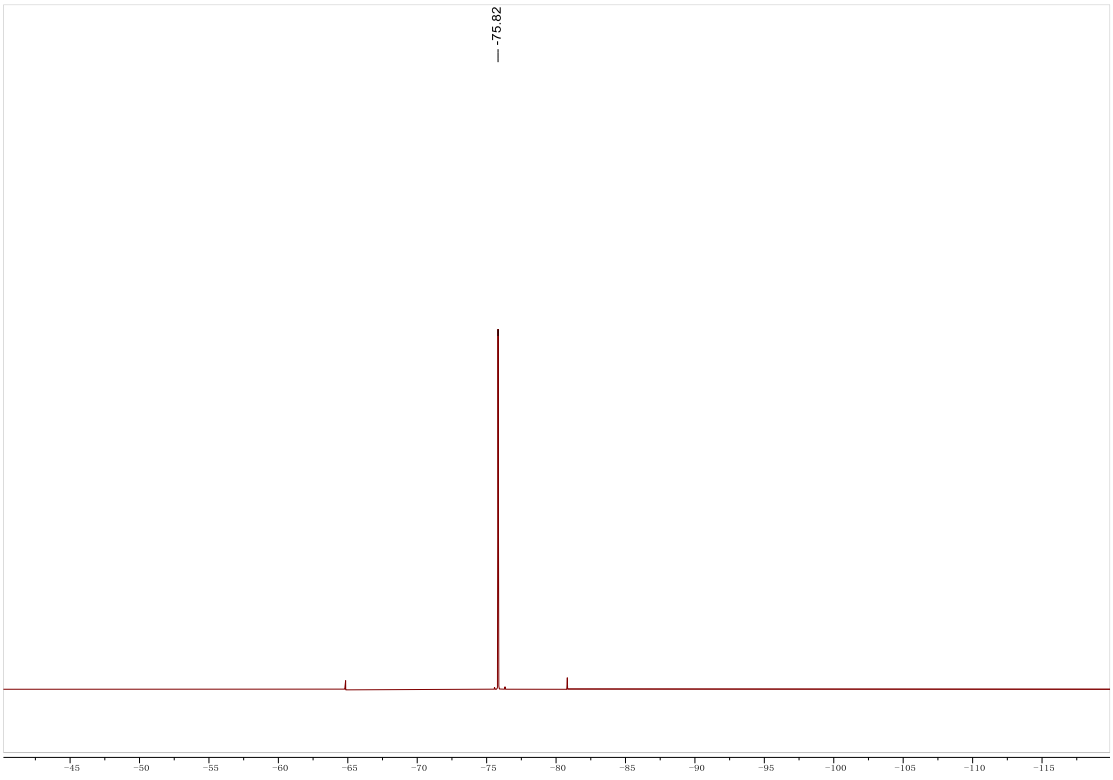



-75.87
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115

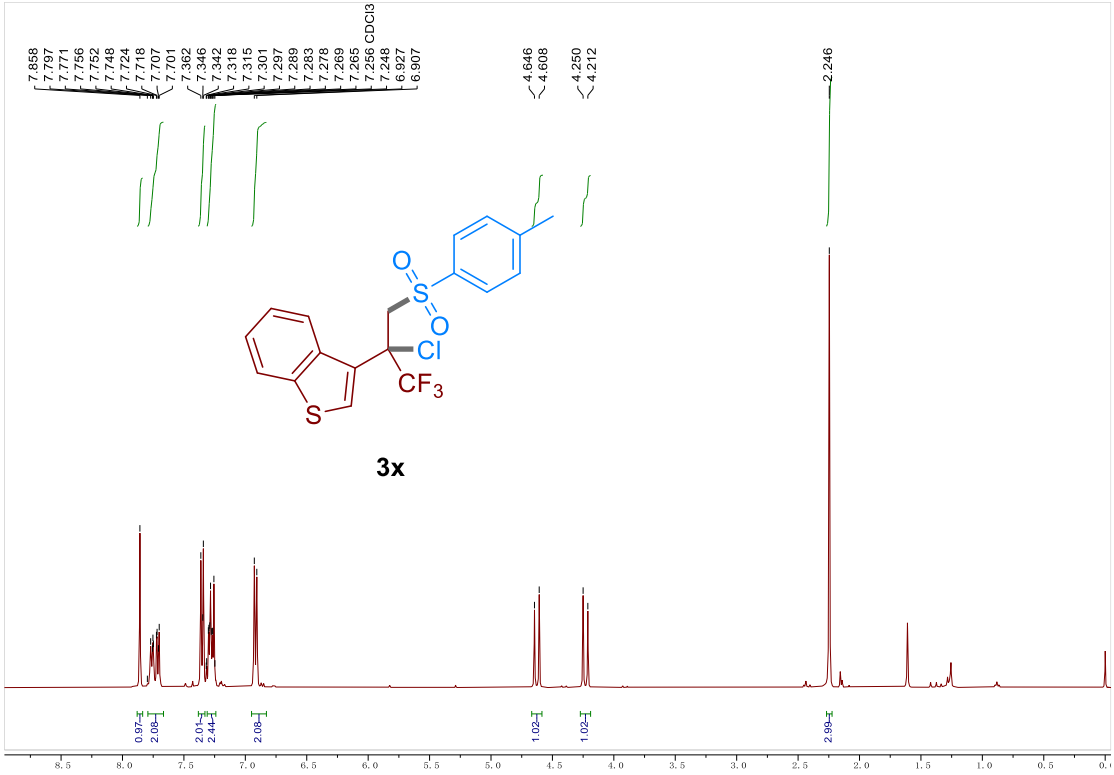
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3w

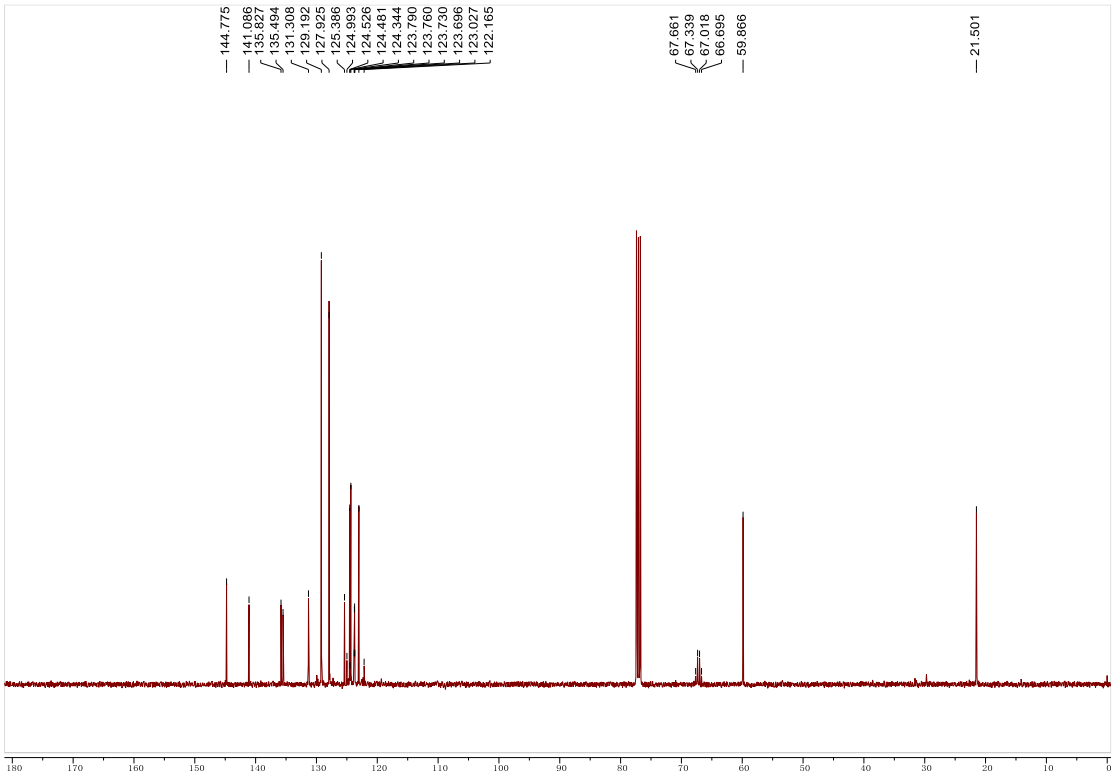


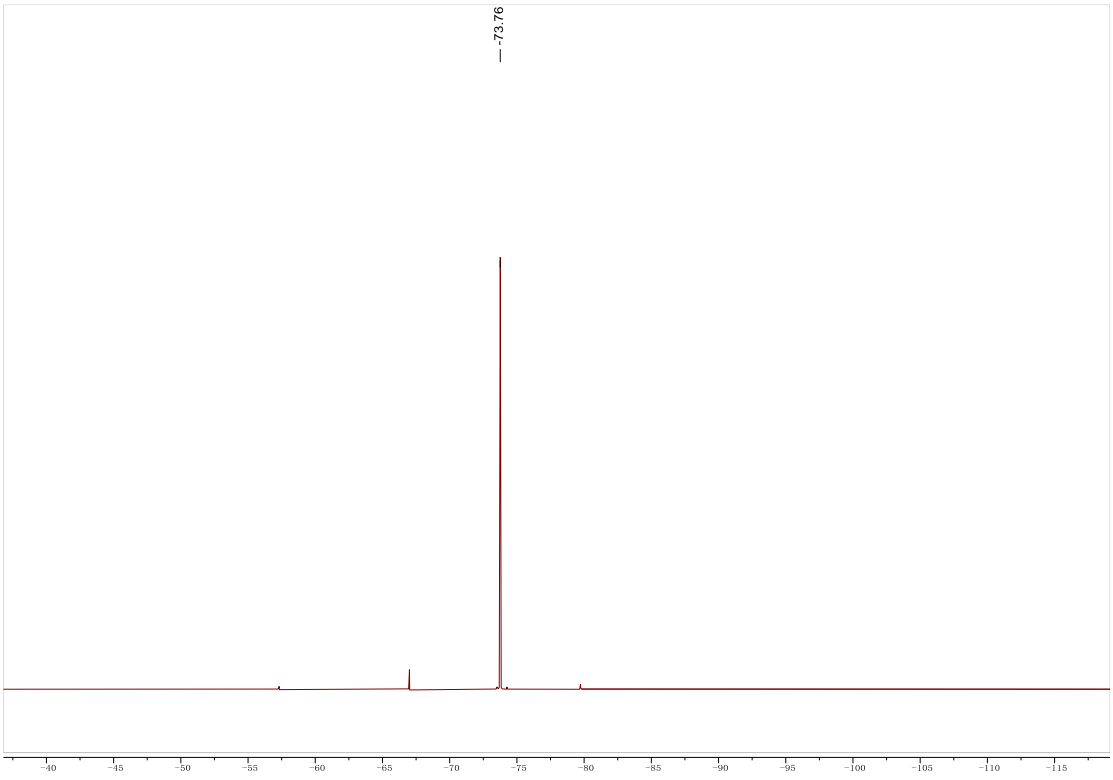



-75.82
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115

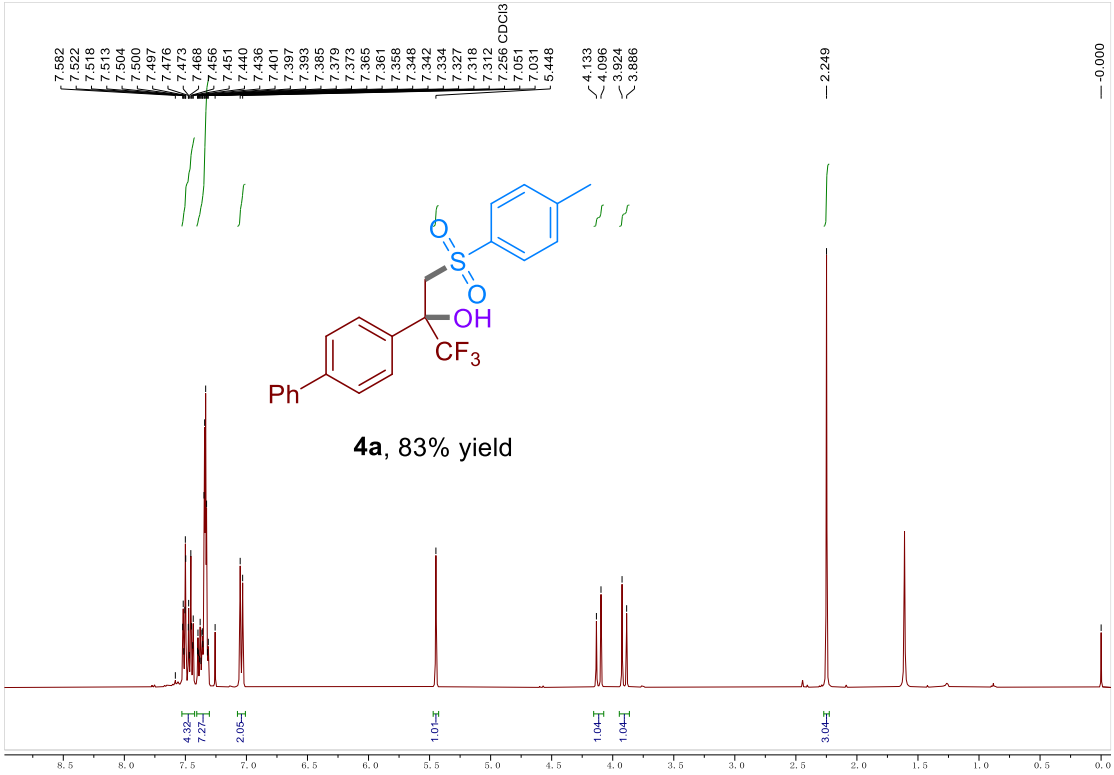
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3x

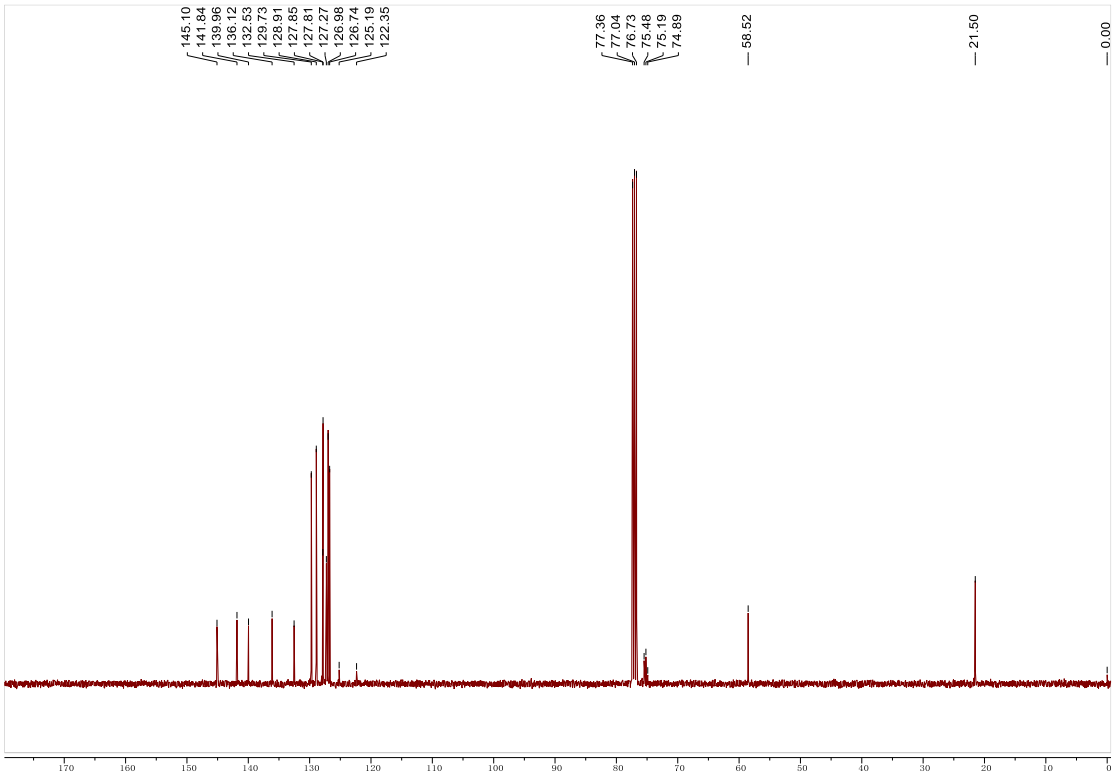


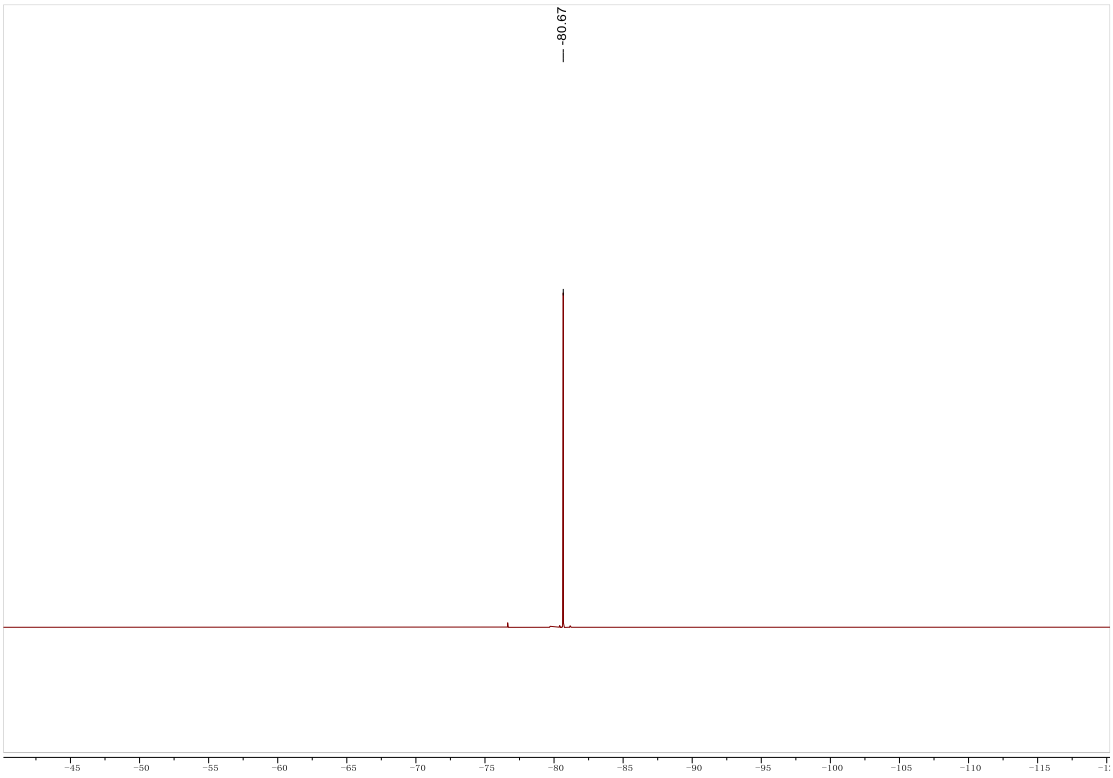



-73.76
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115

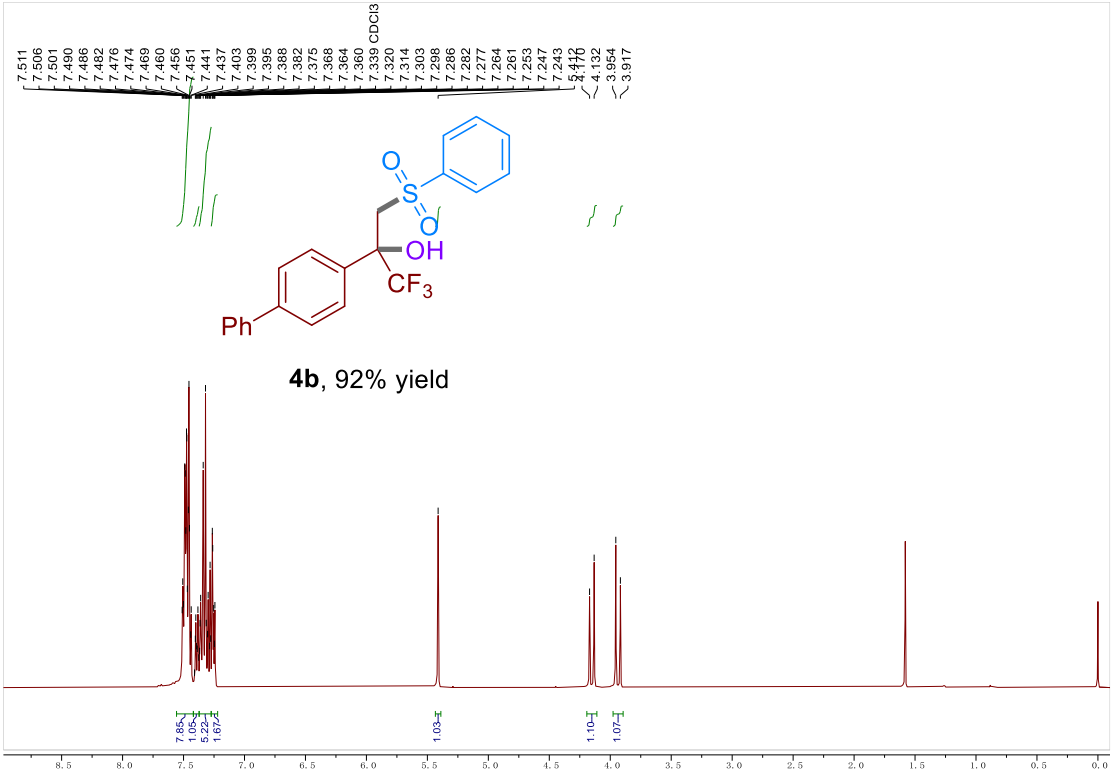
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4a

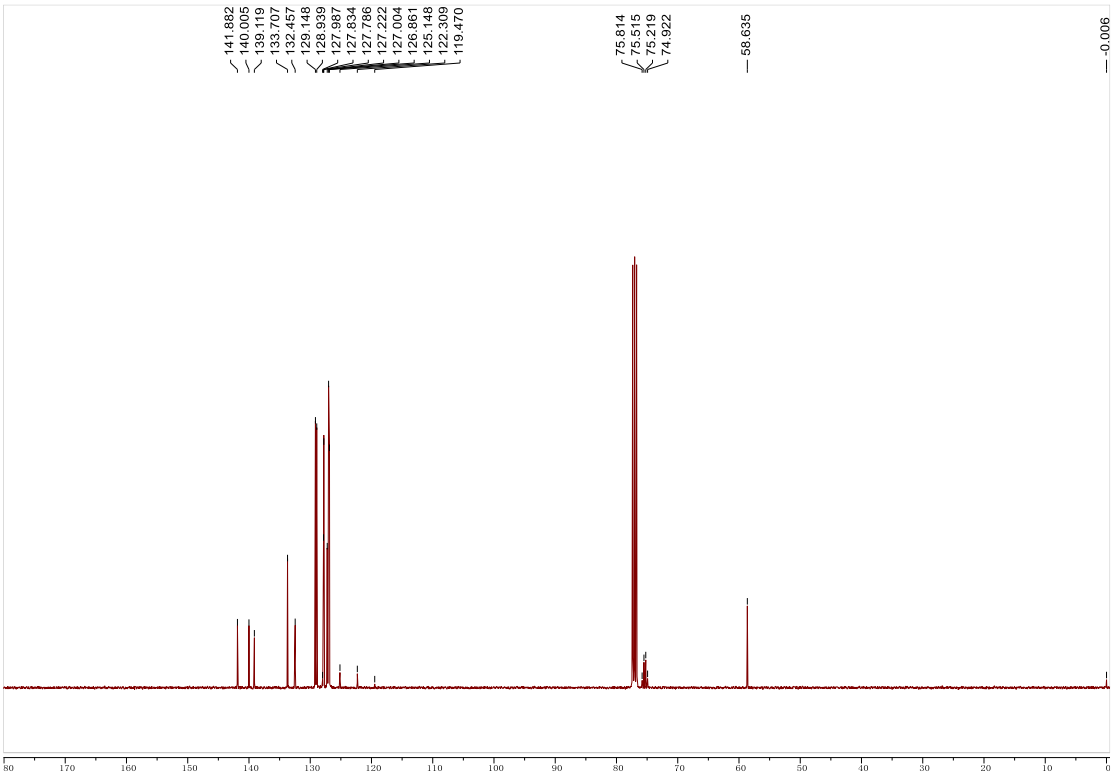


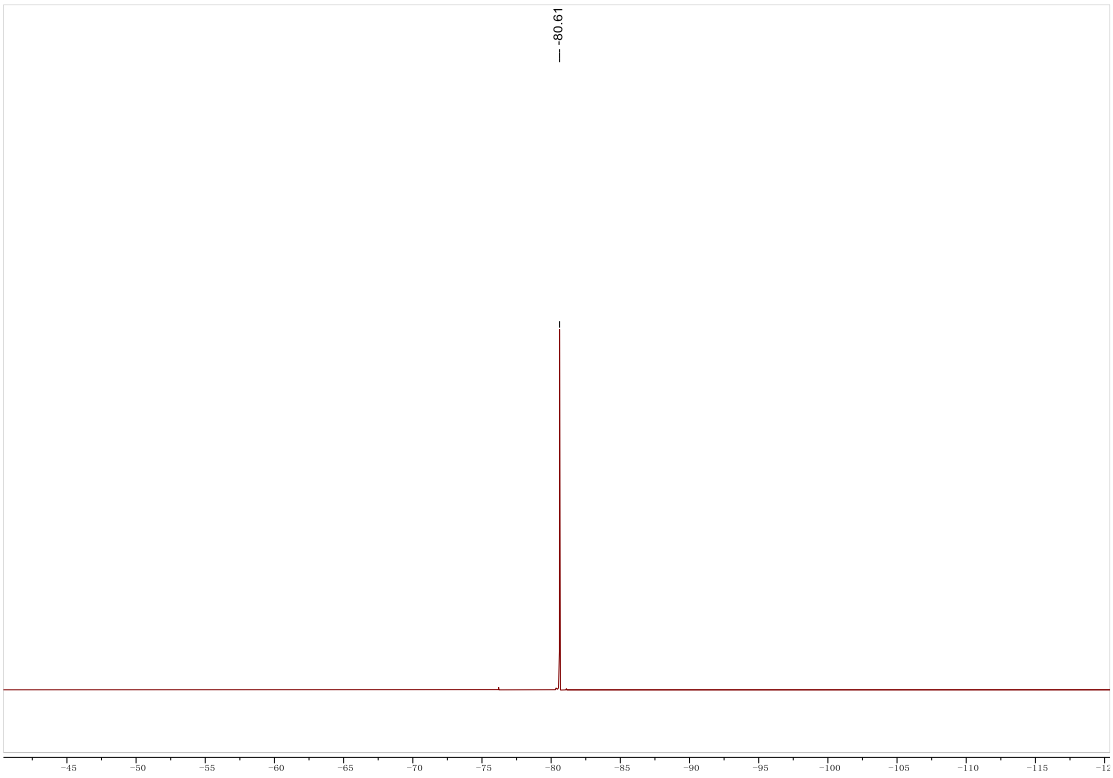



-80.67
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115

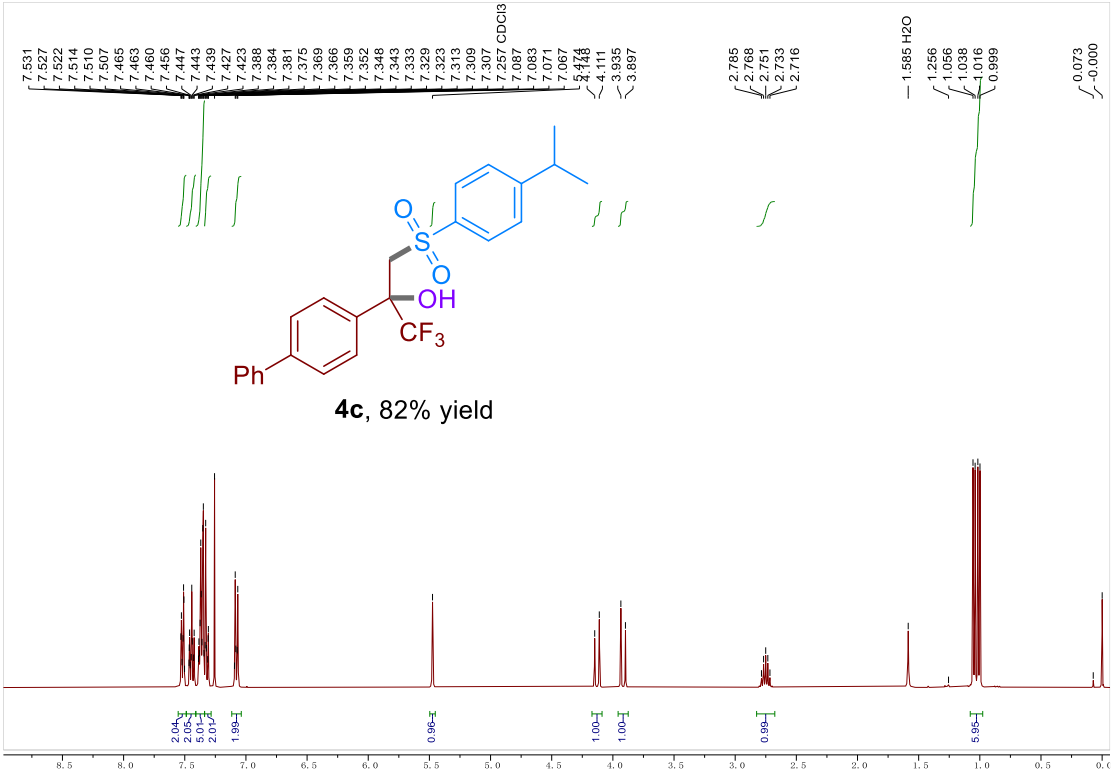
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4b

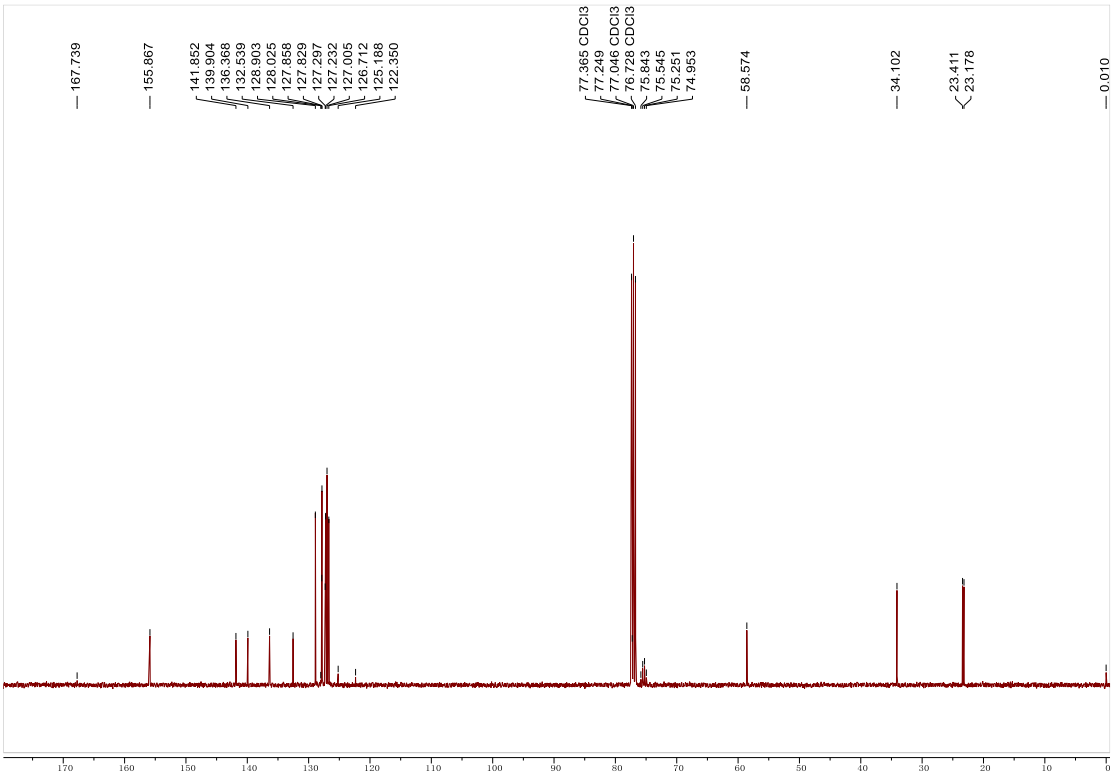


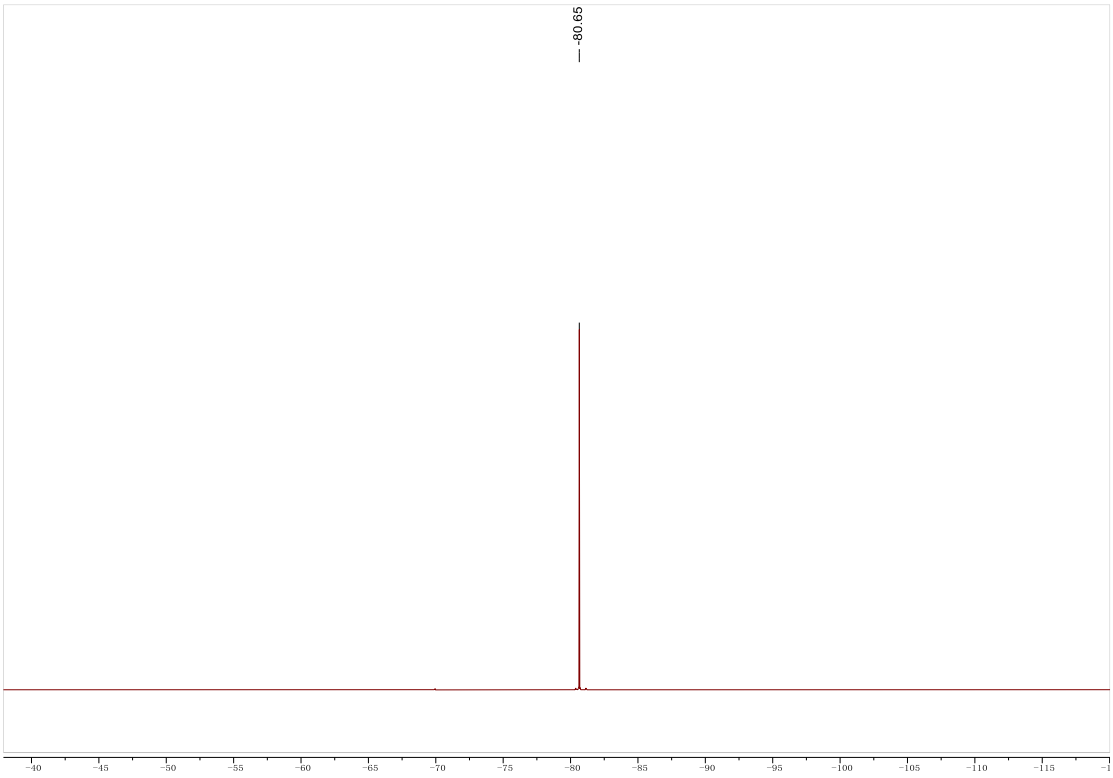



-80.61
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115

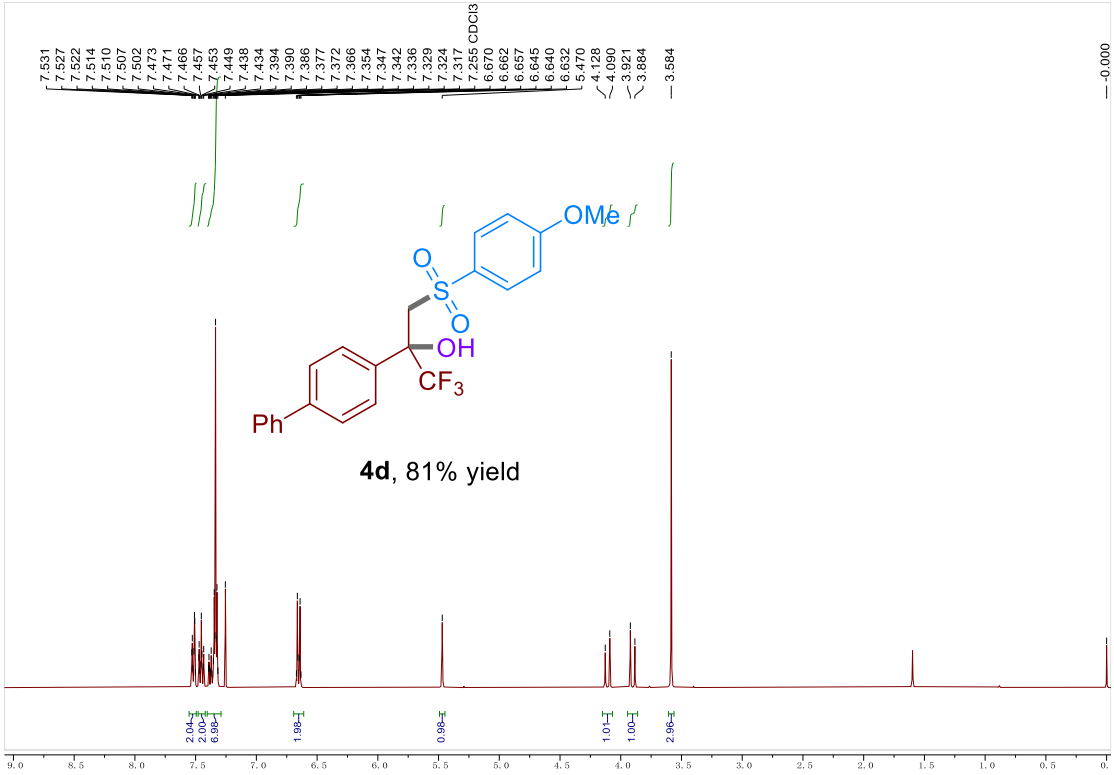
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4c

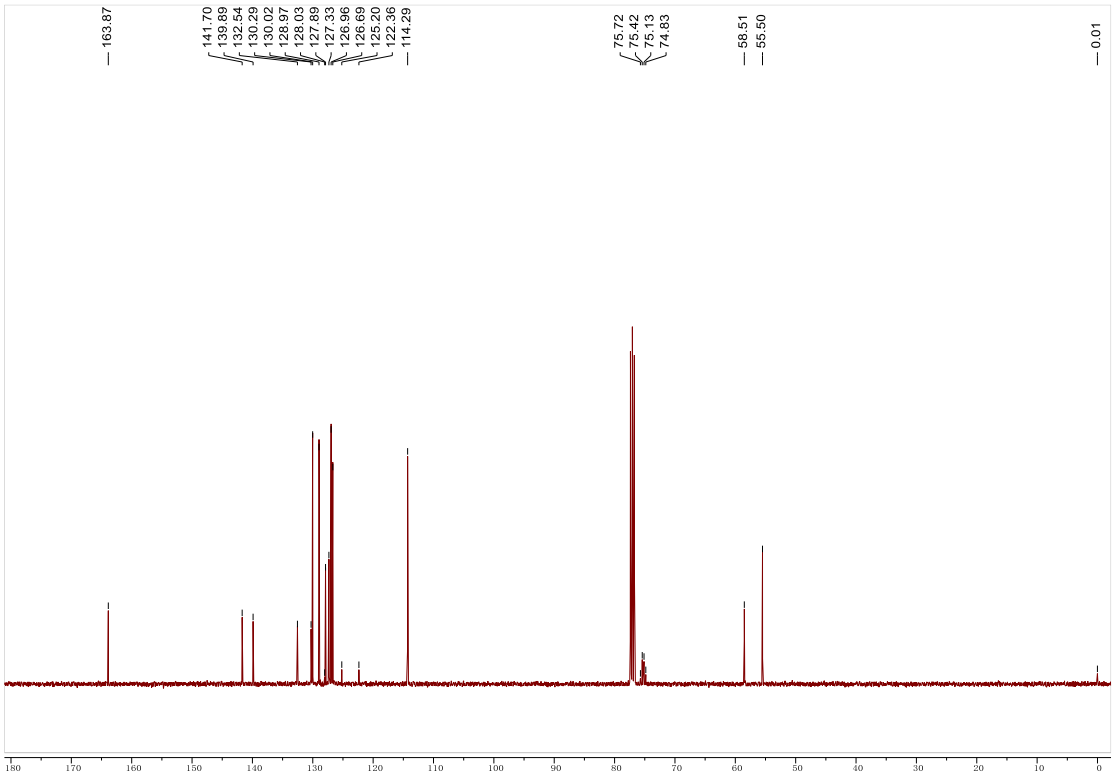


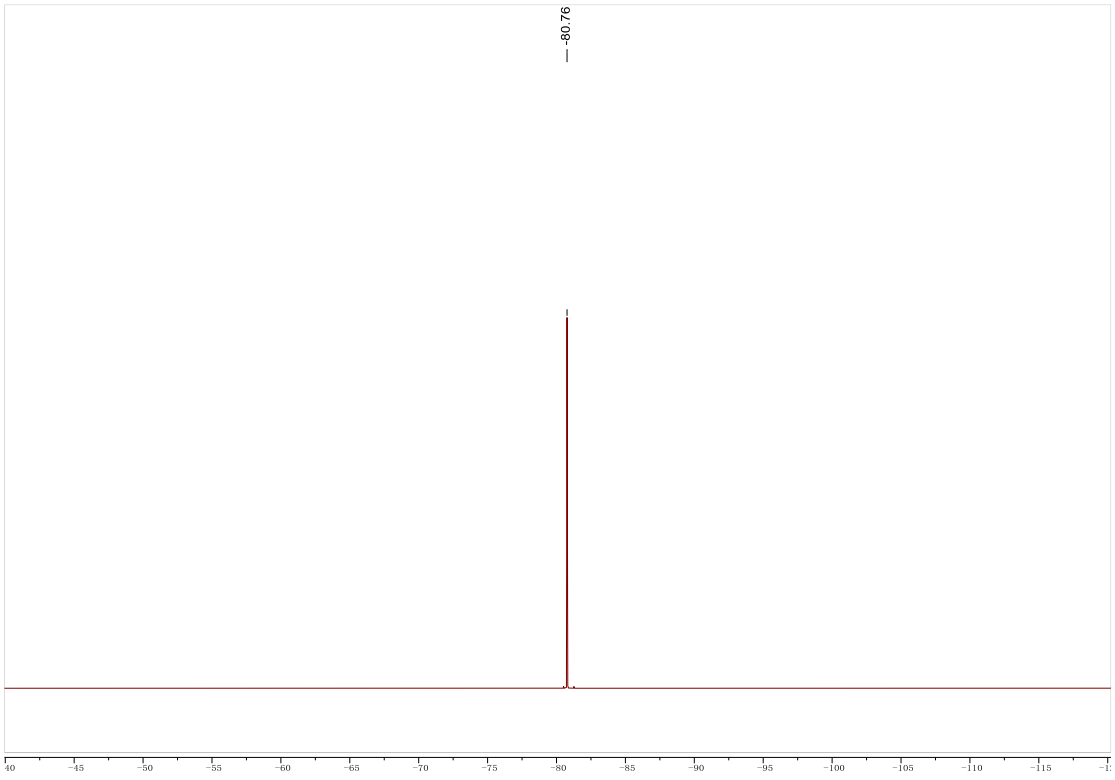



-80.65
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115

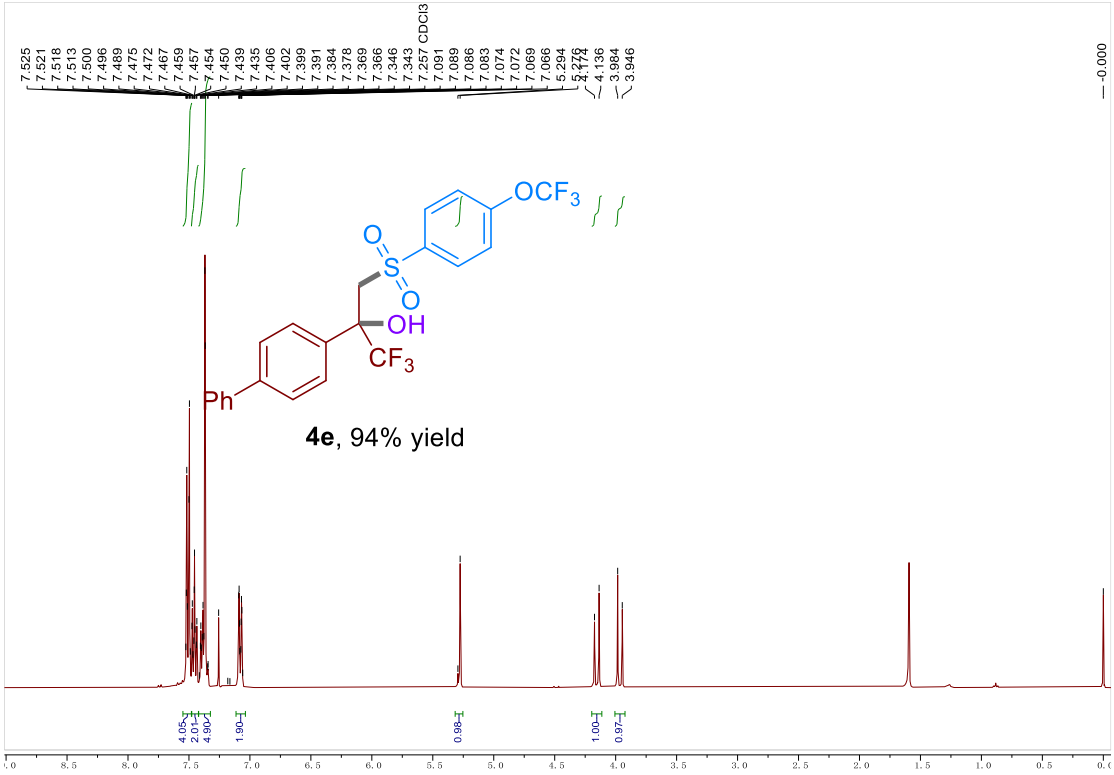
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4d

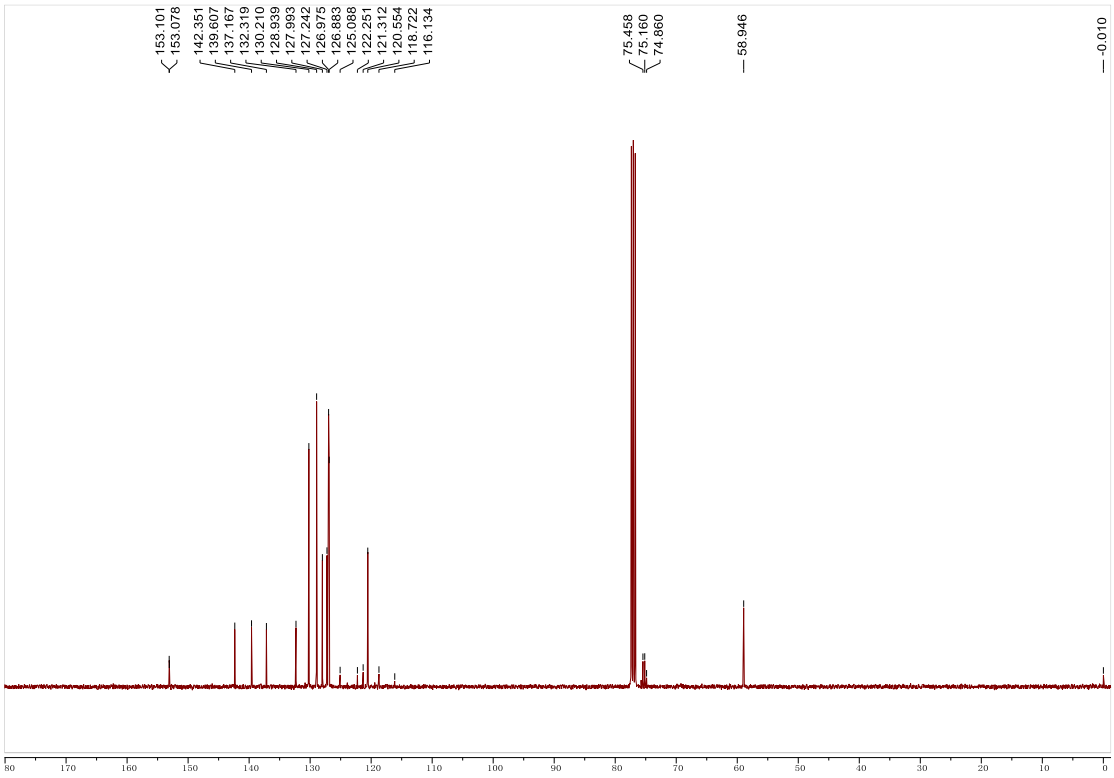


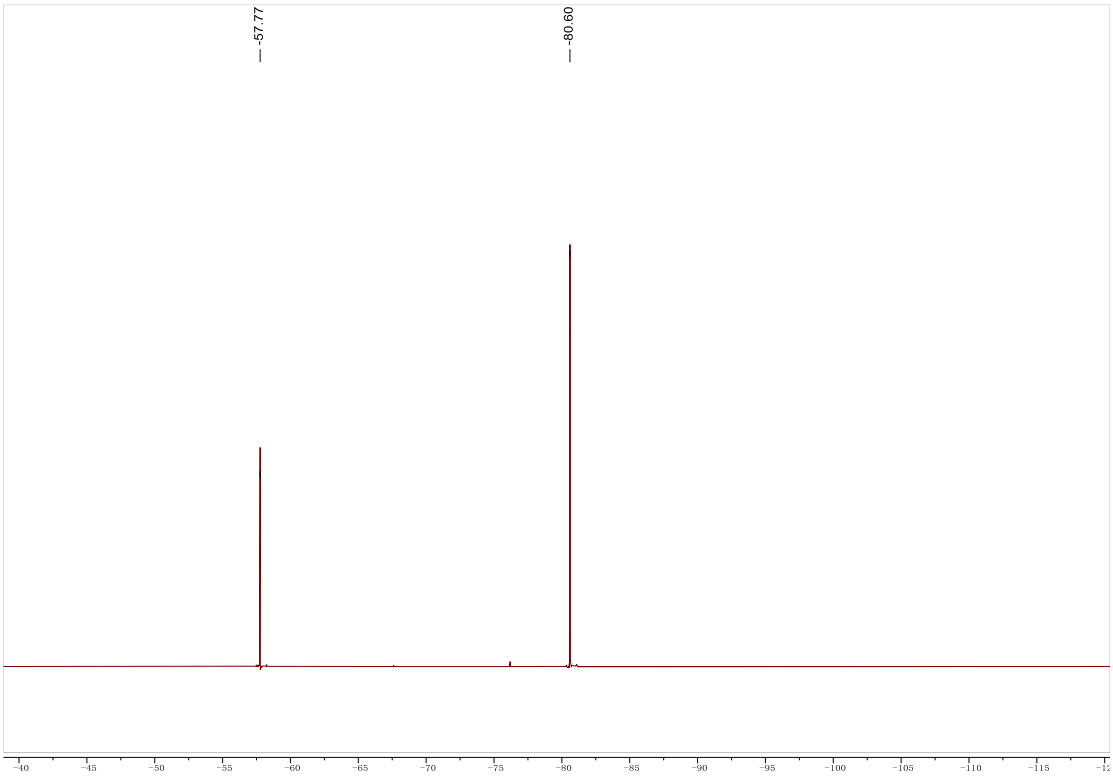



-80.76
40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115

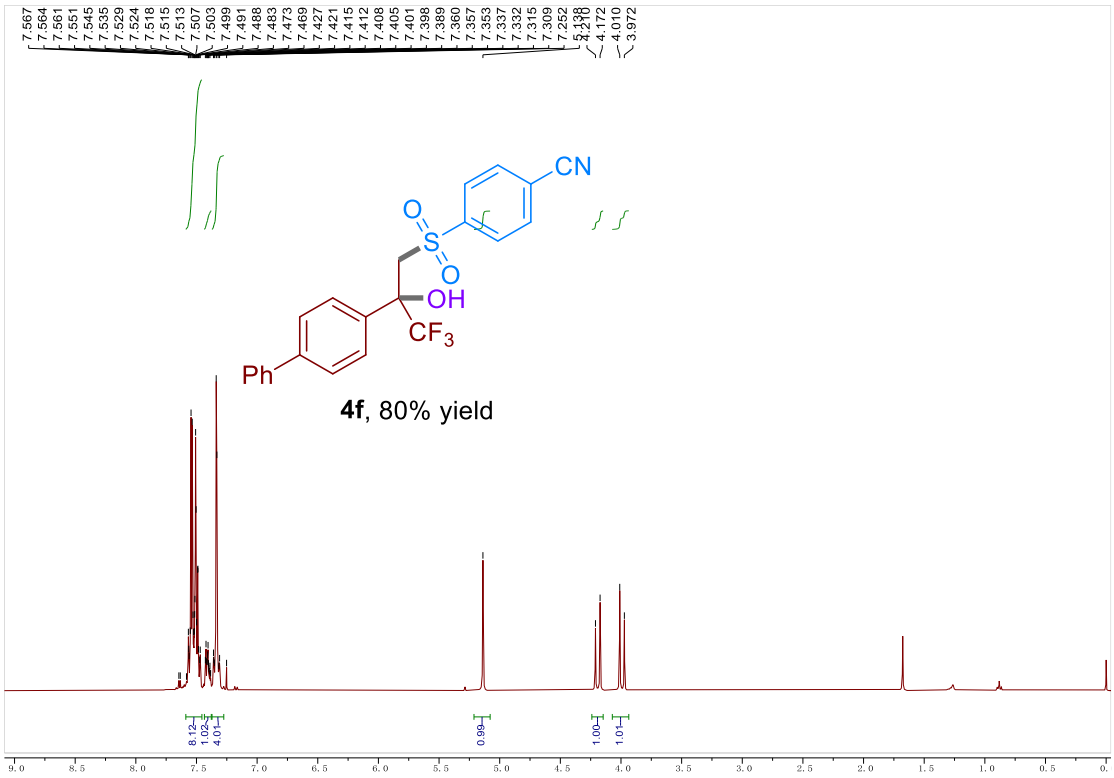
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4e

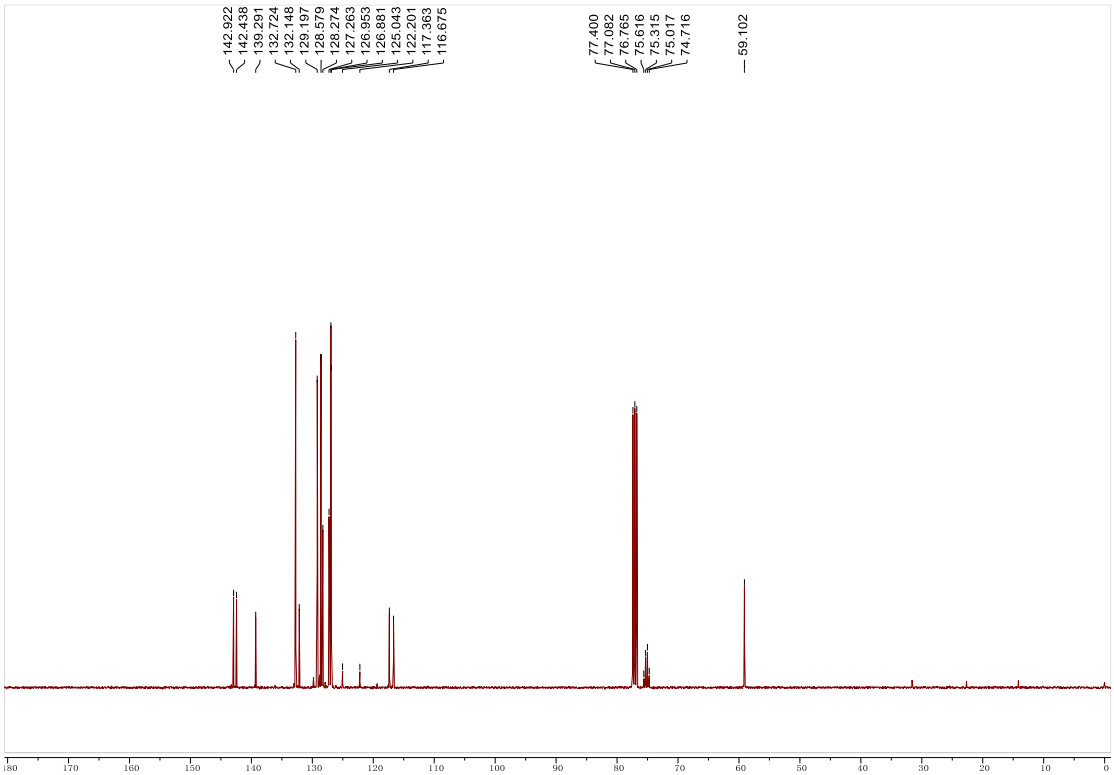


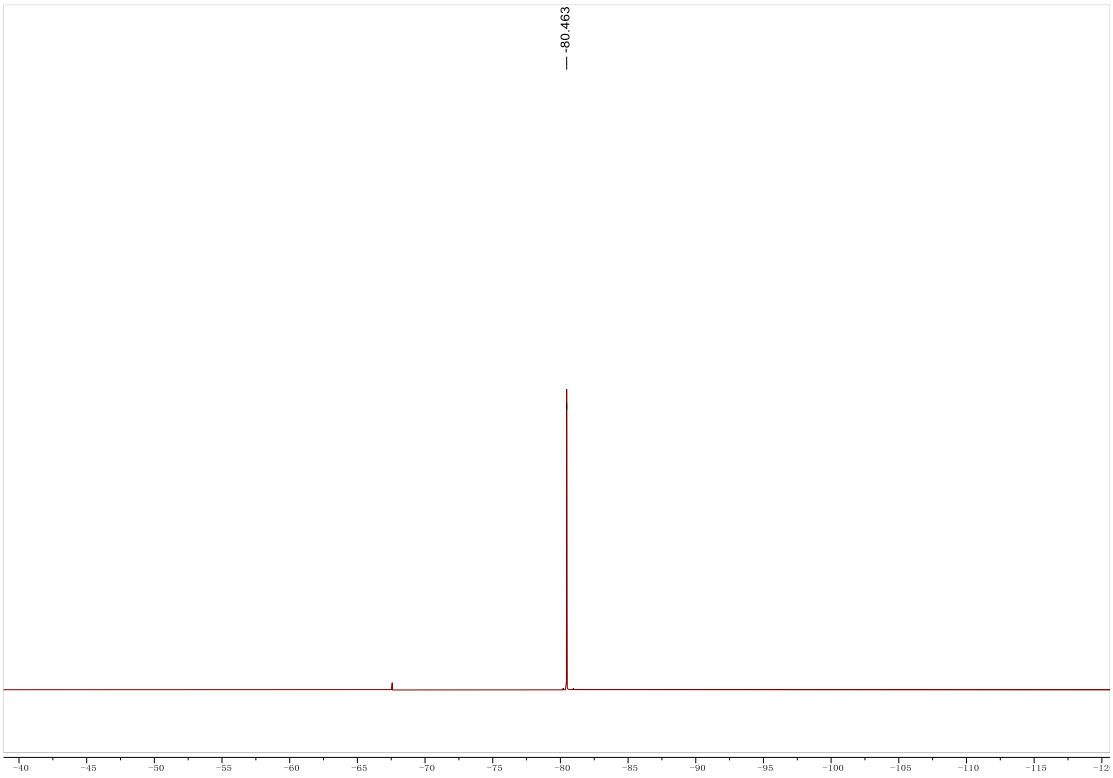



-57.77
-80.60
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115

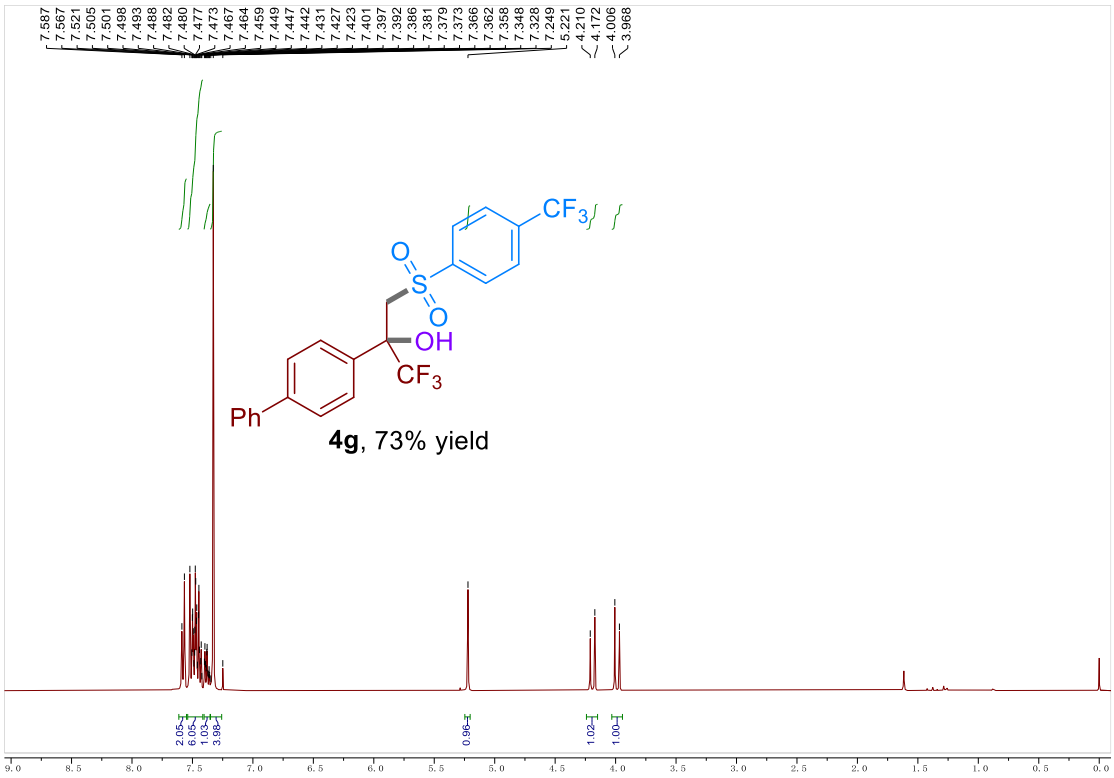
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4f

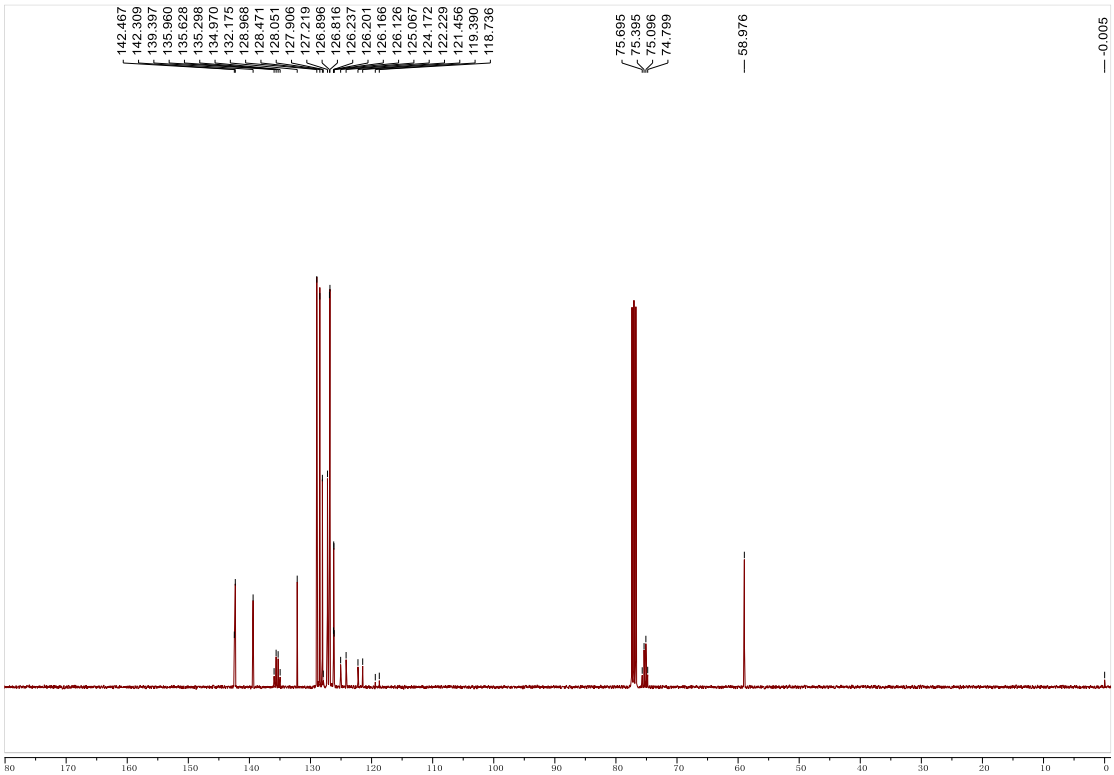


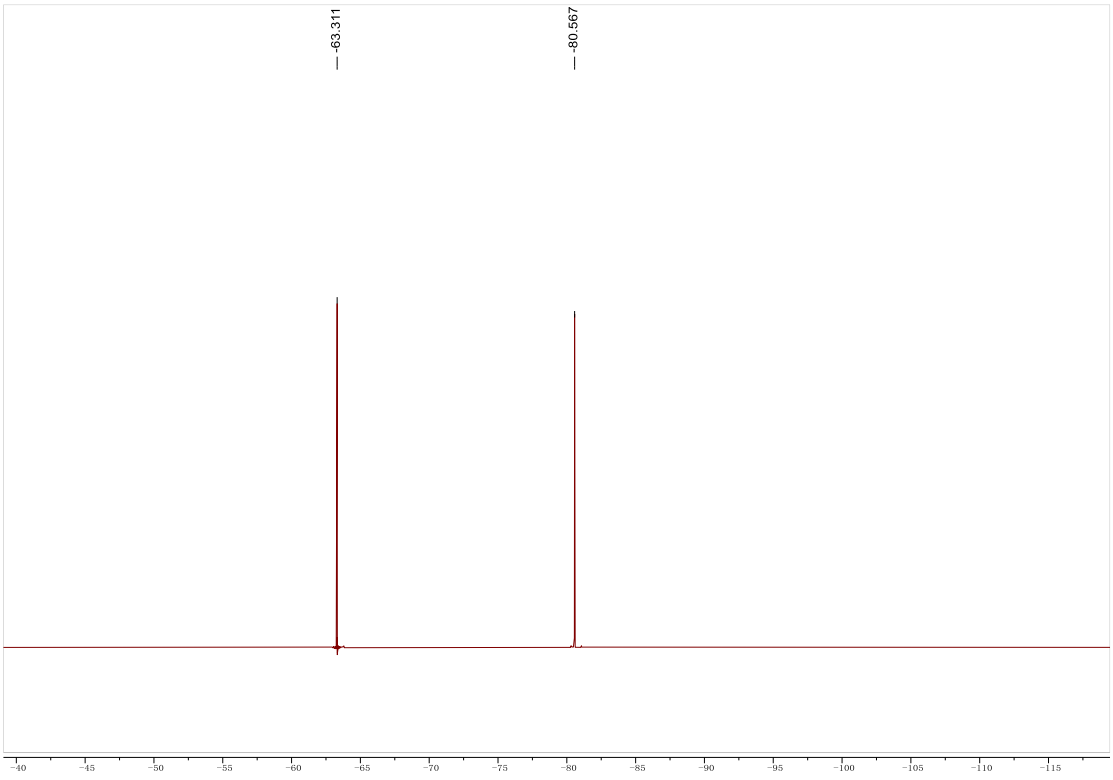



-80.463
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-12

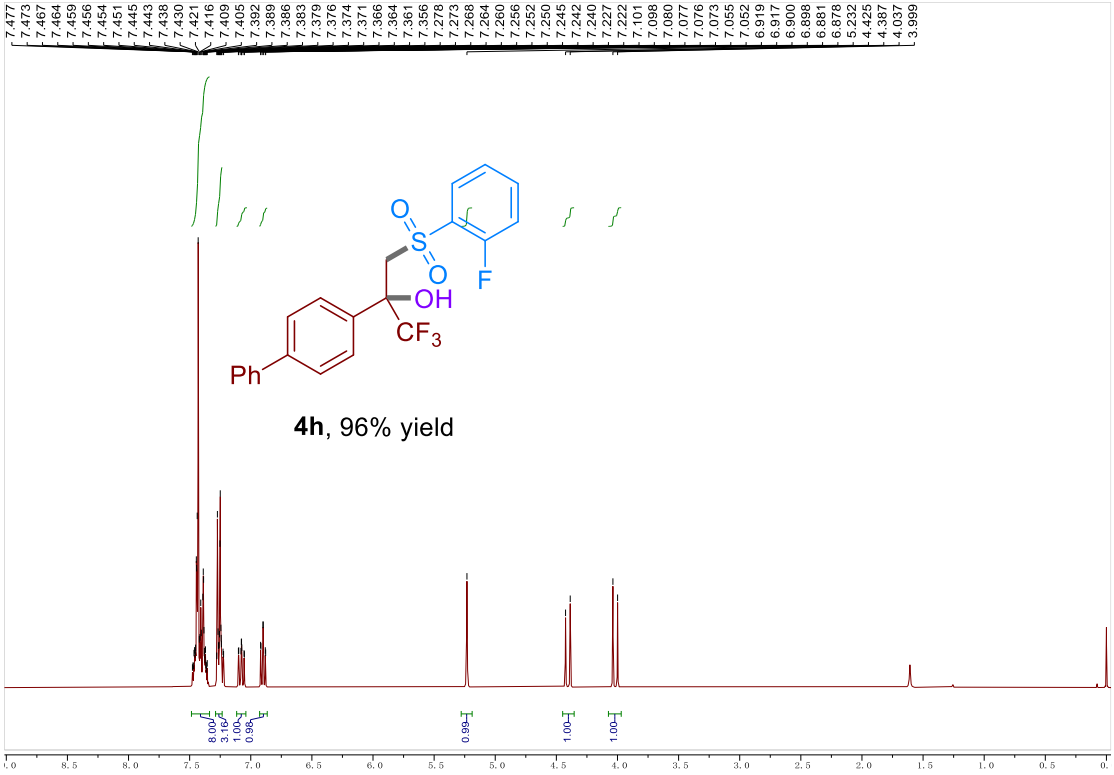
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4g

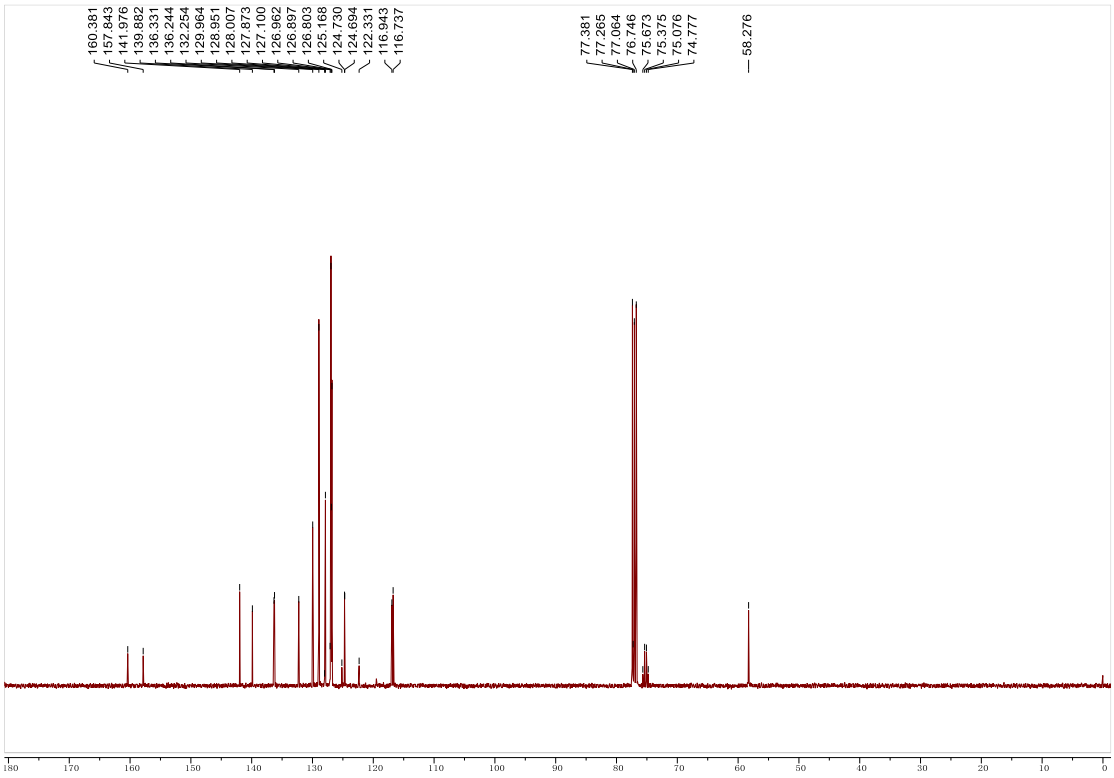


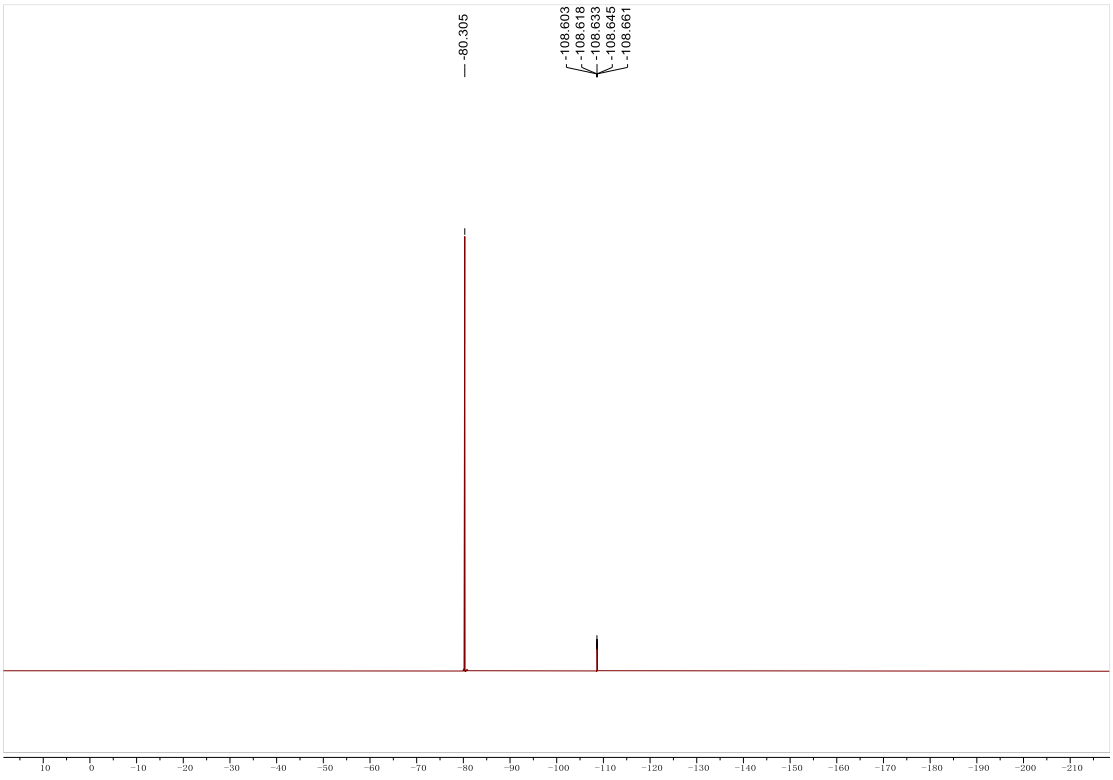



-63.311
-80.567
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115

^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4h






-80.305
-108.603
-108.618
-108.633
-108.645
-108.661
10
0
-10
-20
-30
-40
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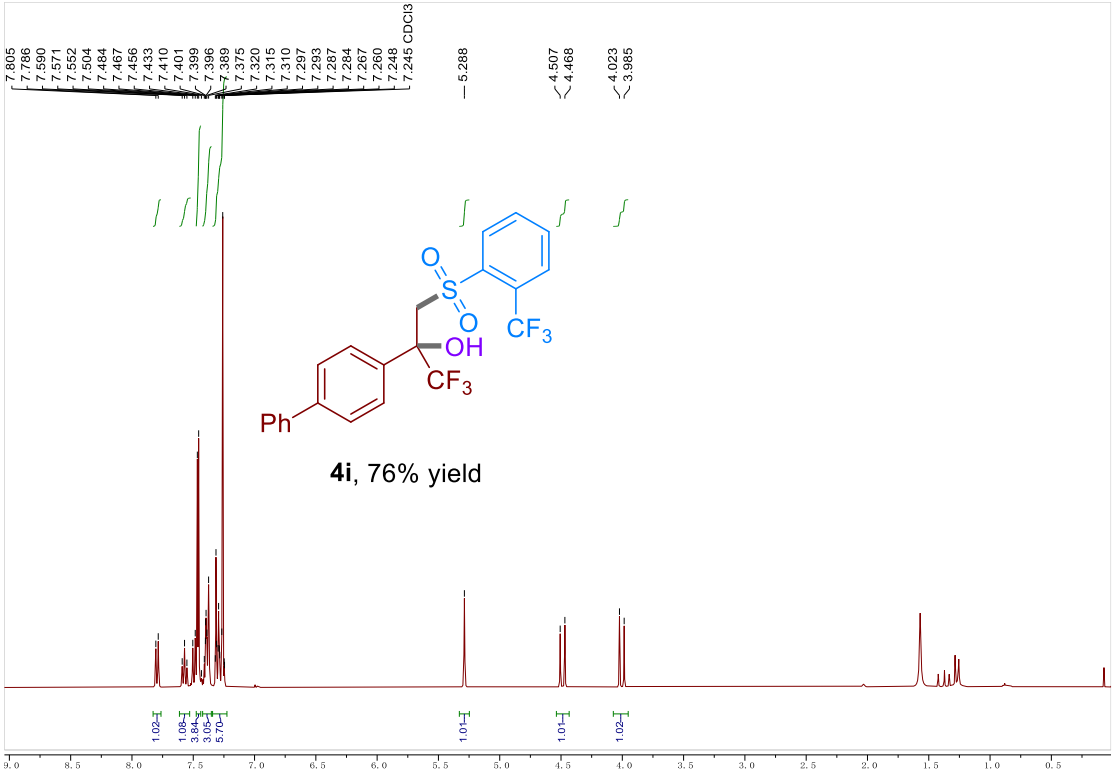
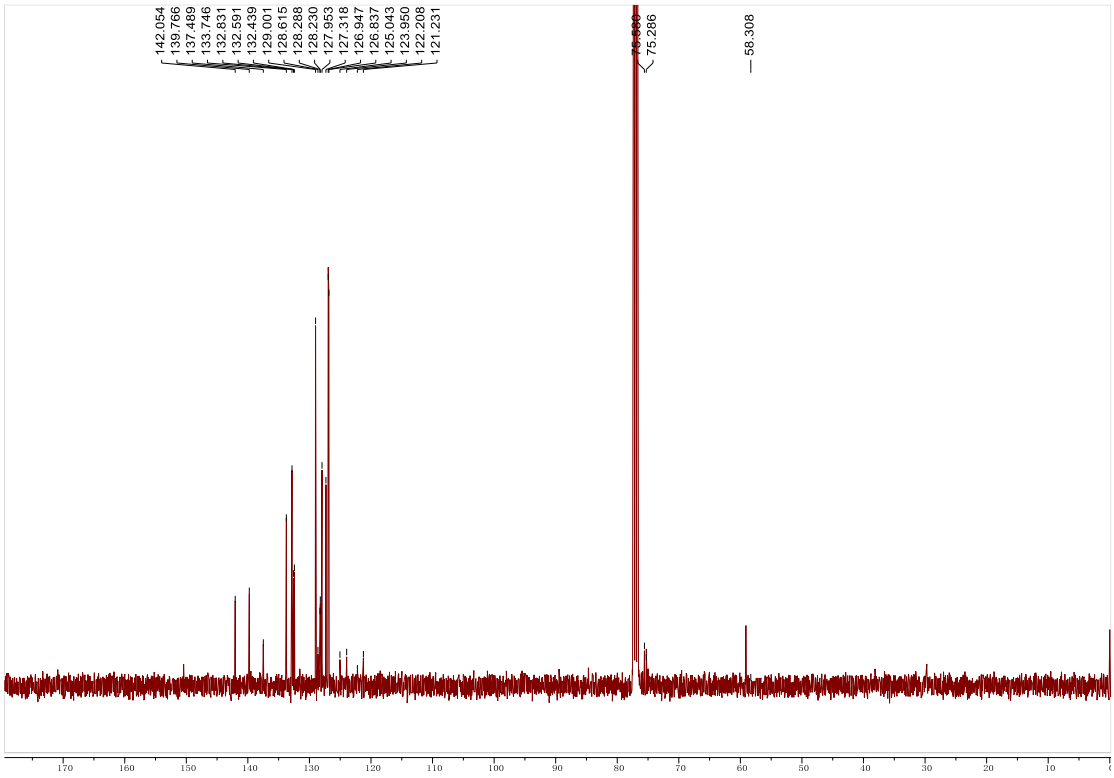
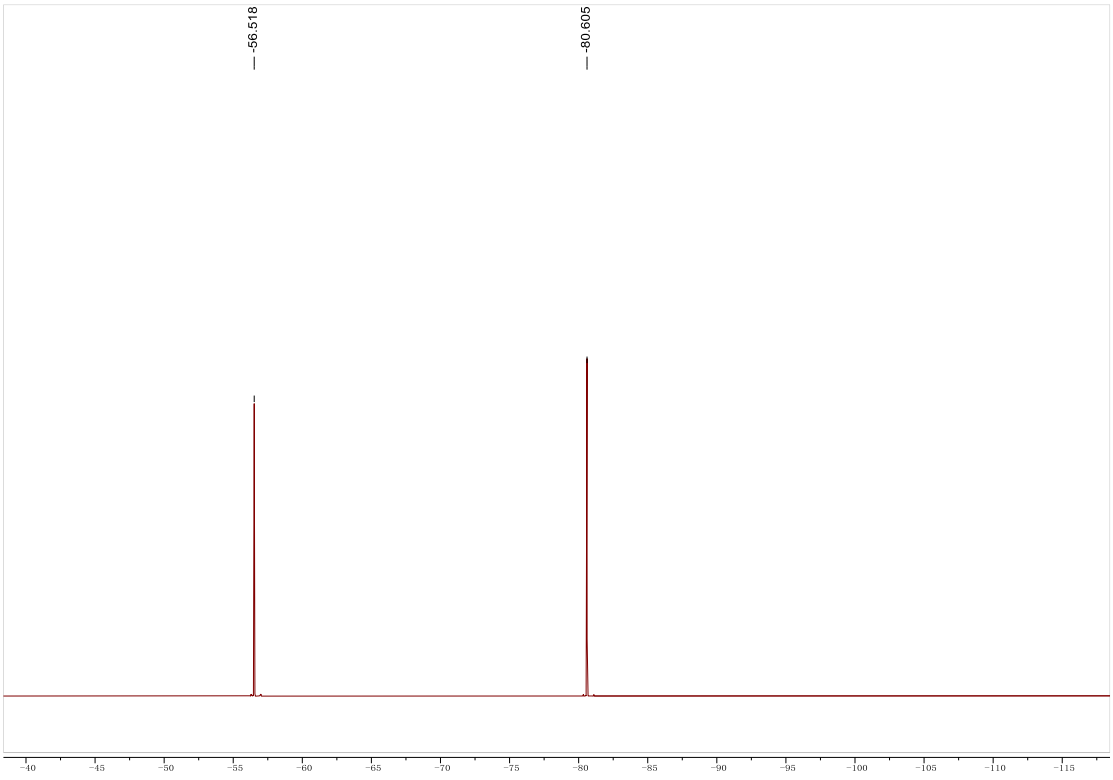
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210

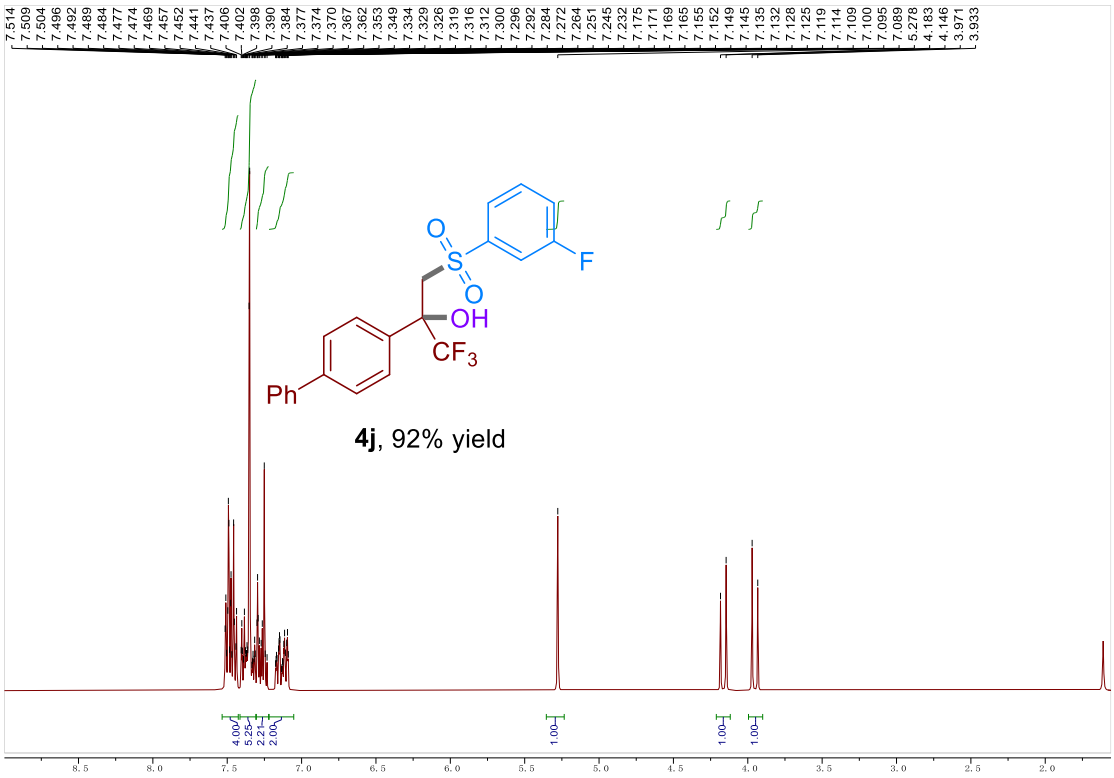
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4i

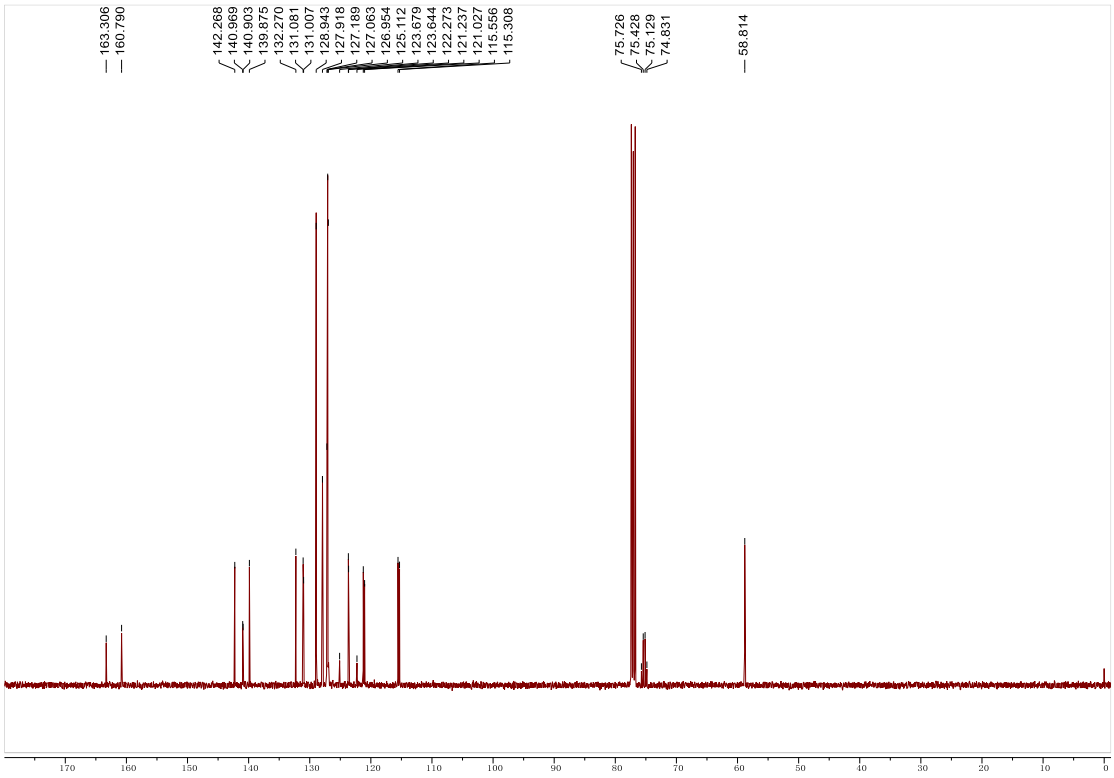


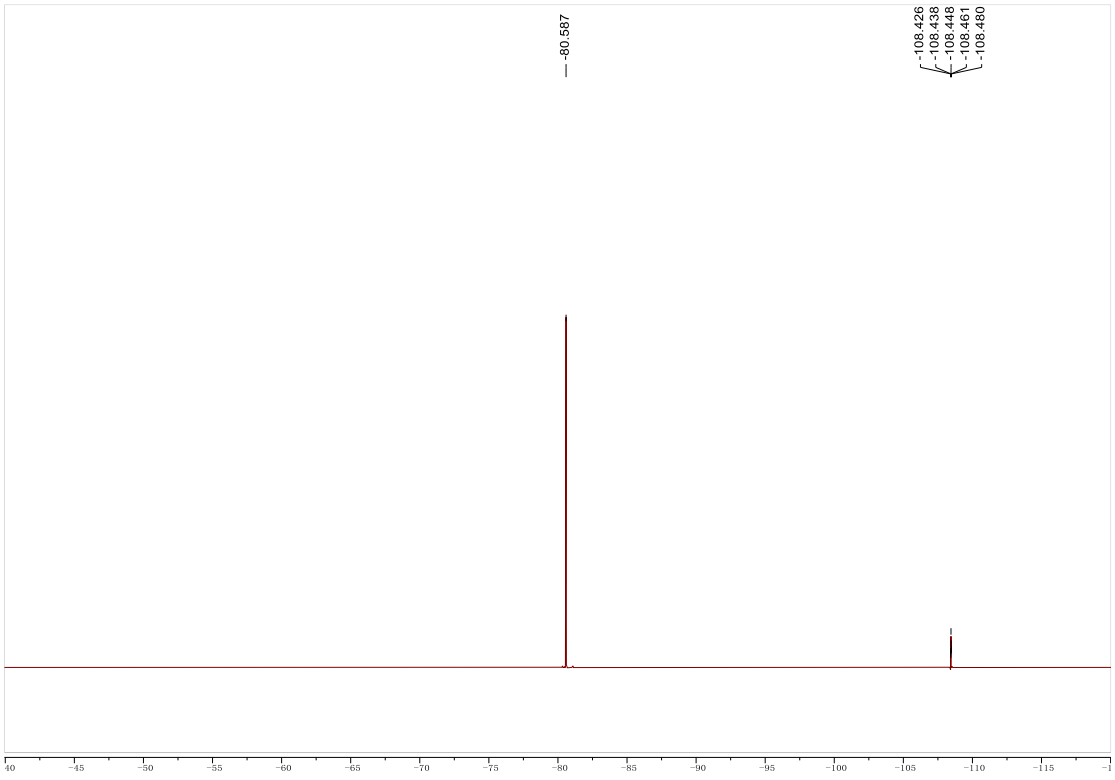



-56.518
-80.605
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115

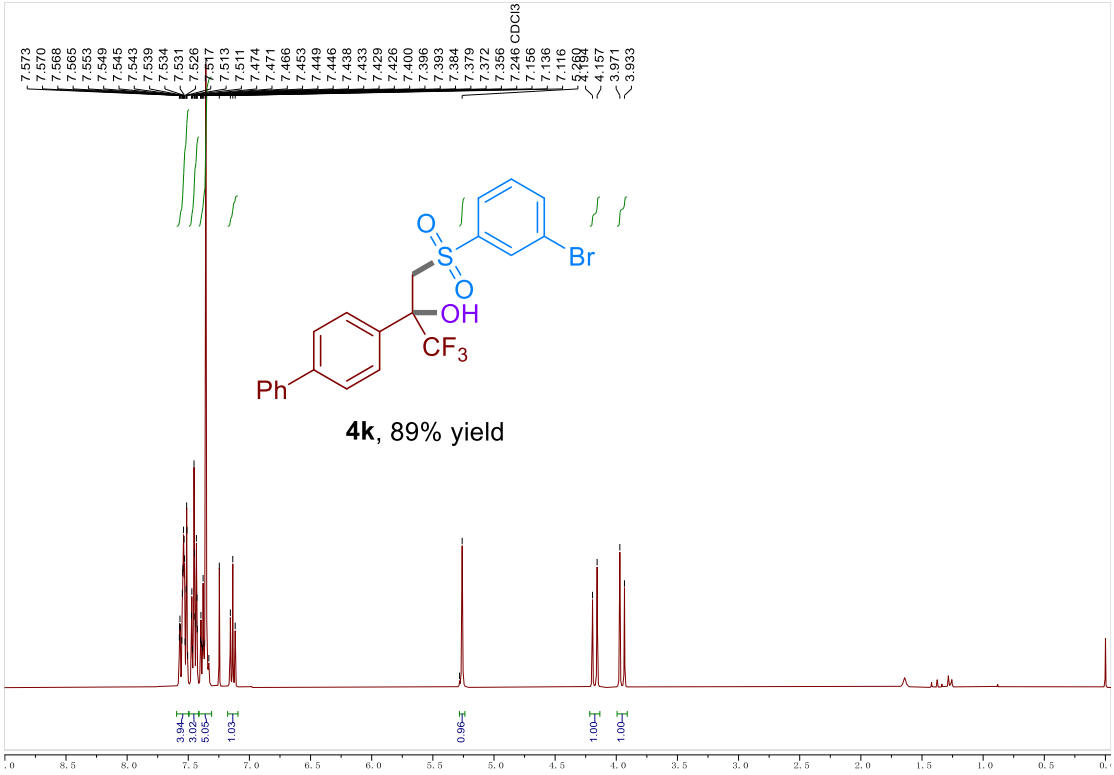
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4j

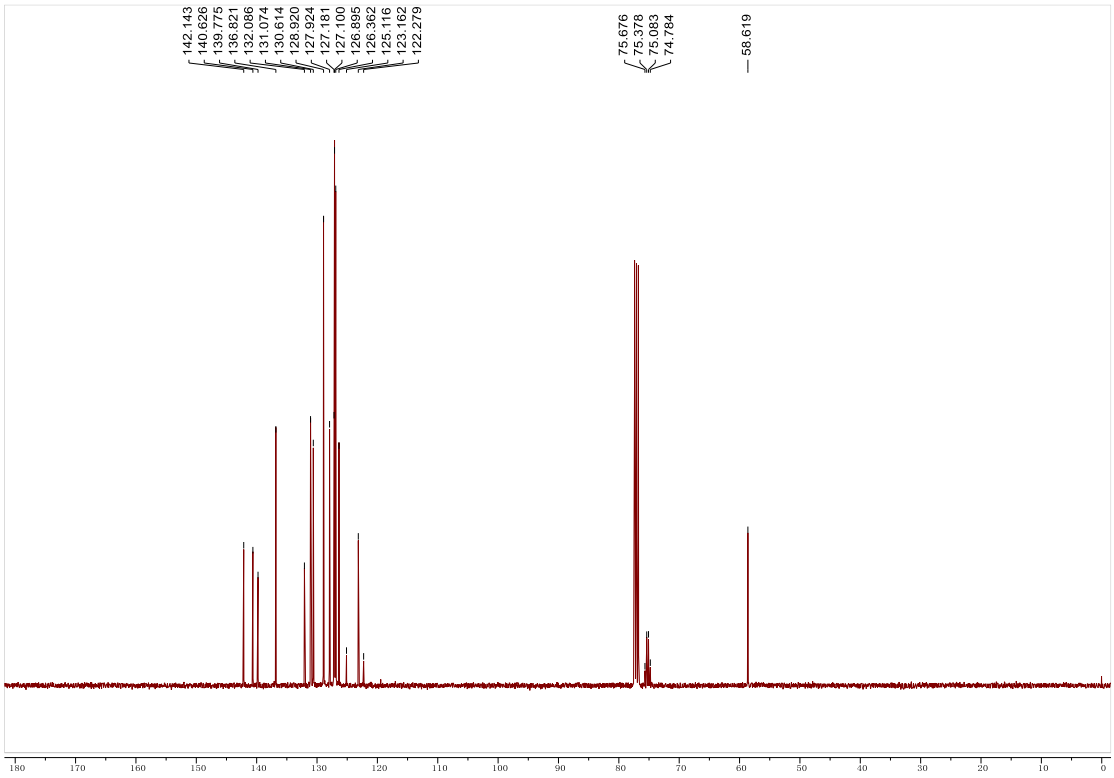


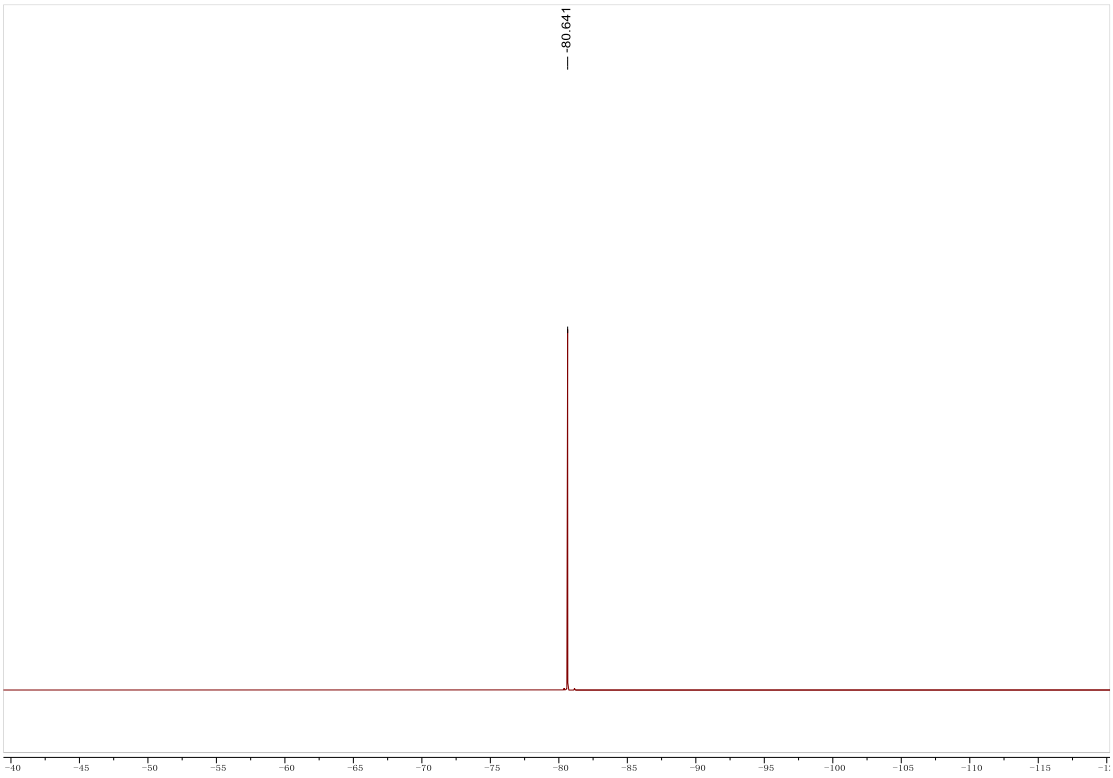



-80.587
-108.426
-108.438
-108.448
-108.461
-108.480
40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-1

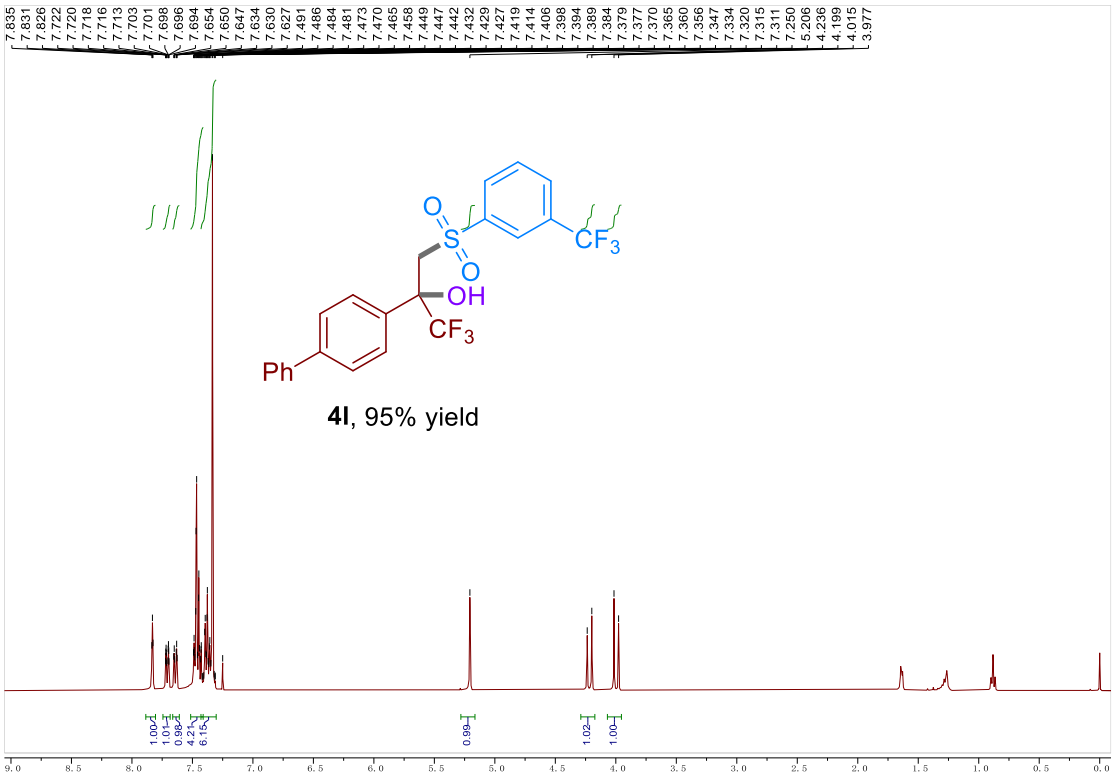
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4k

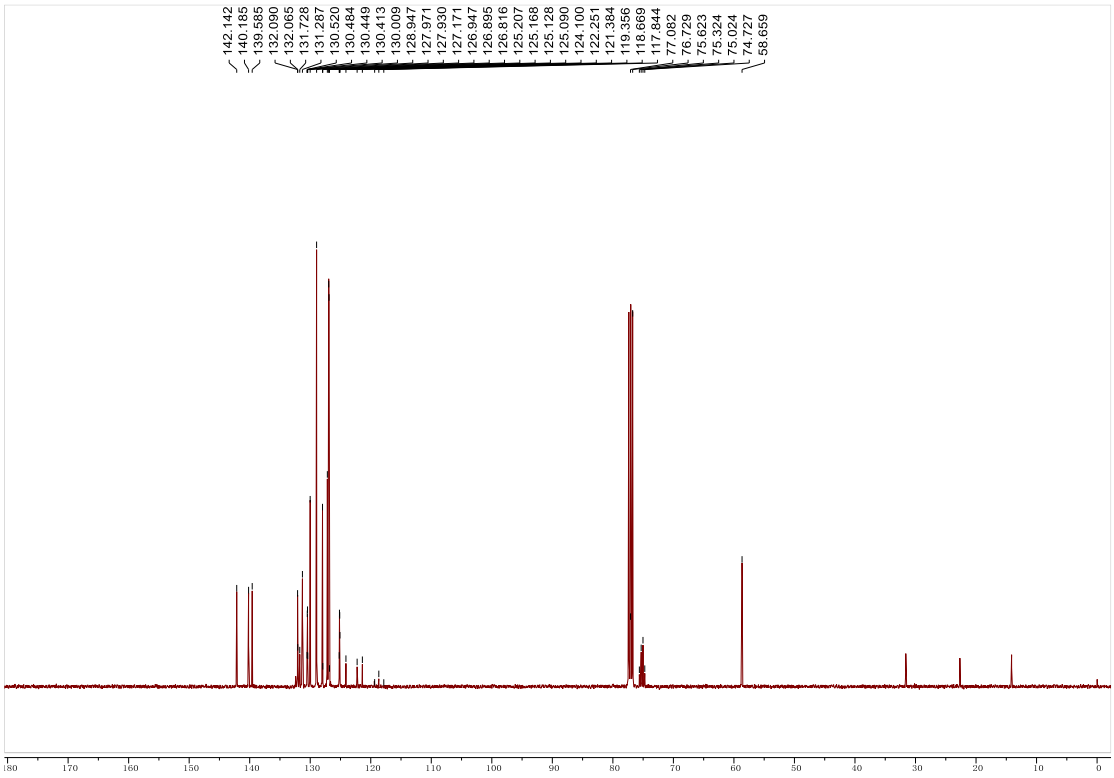


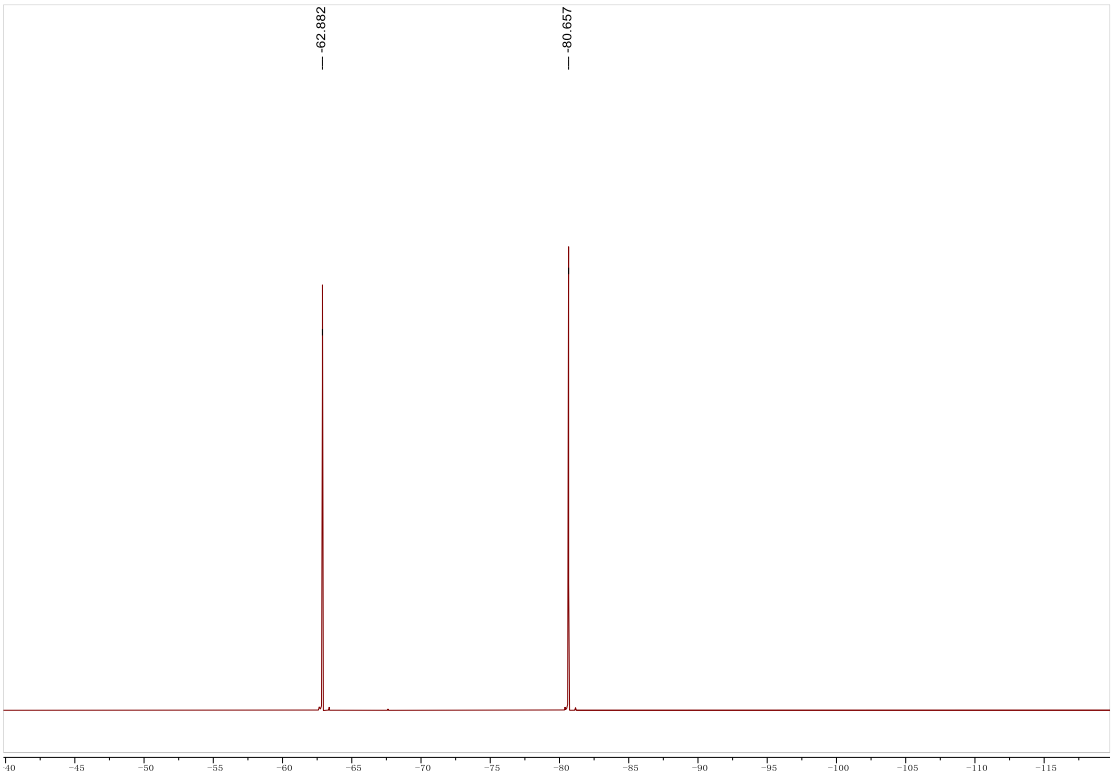



-80.641
−40
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115

^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4l



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-40
-45
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-60
-65
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-75
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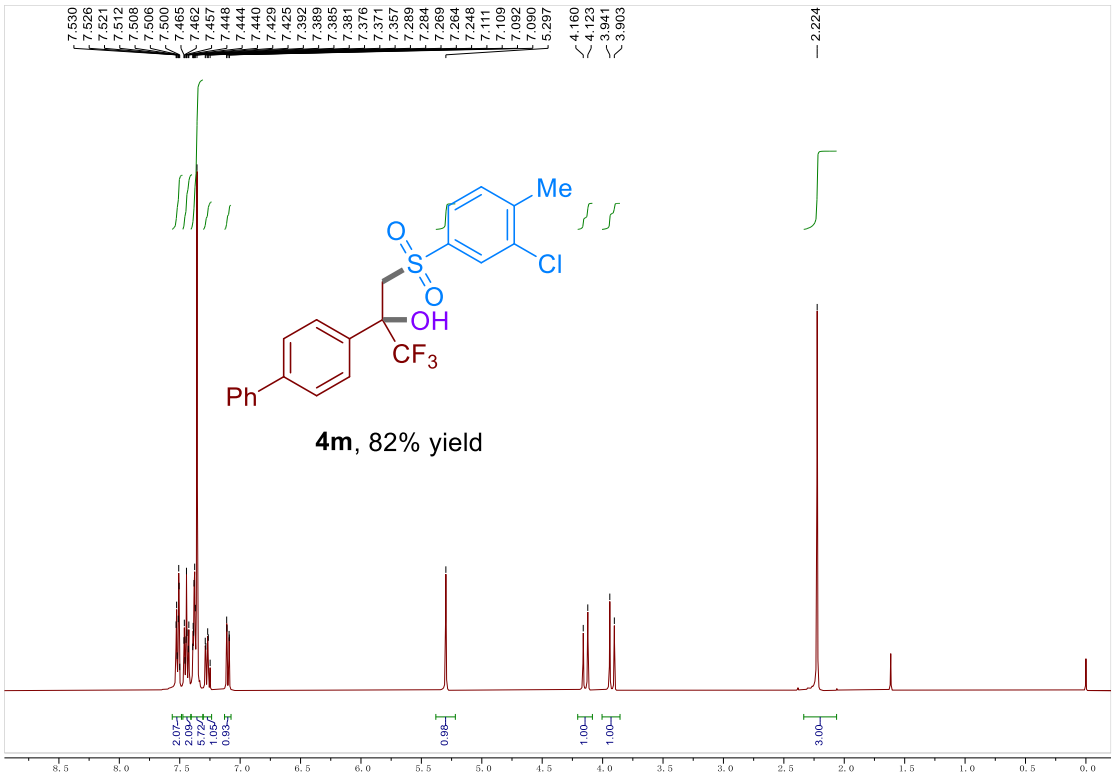
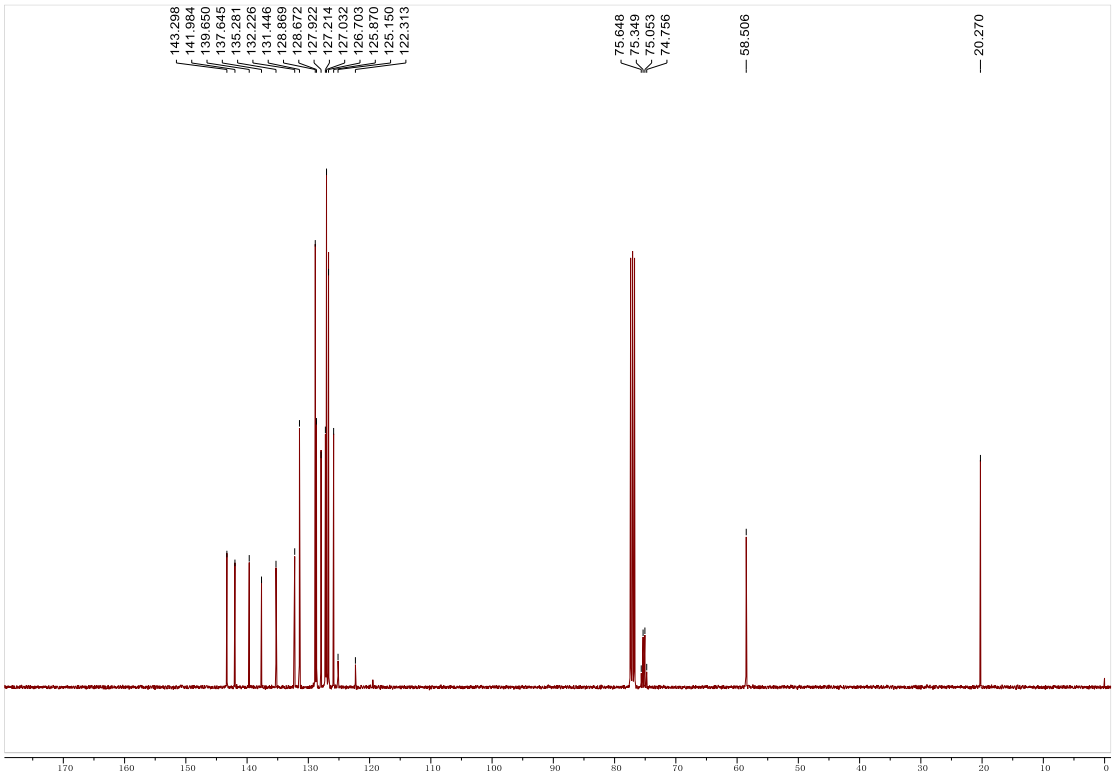
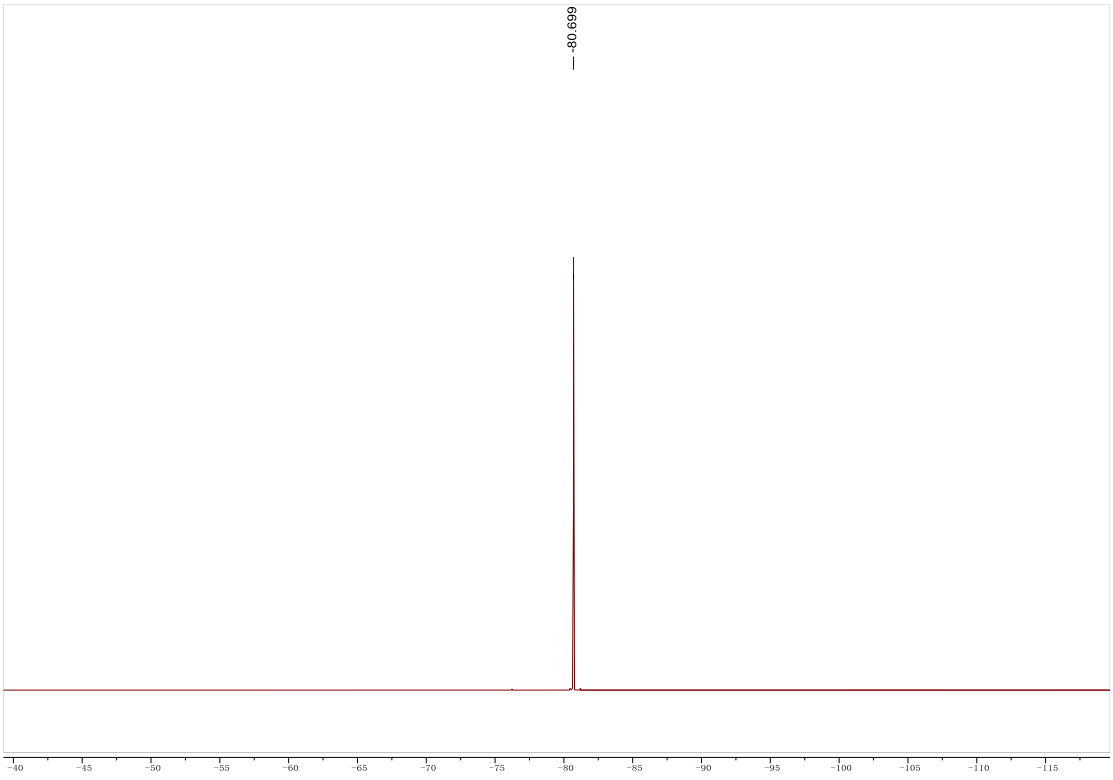
-85
-90
-95
-100
-105
-110
-115

^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4m



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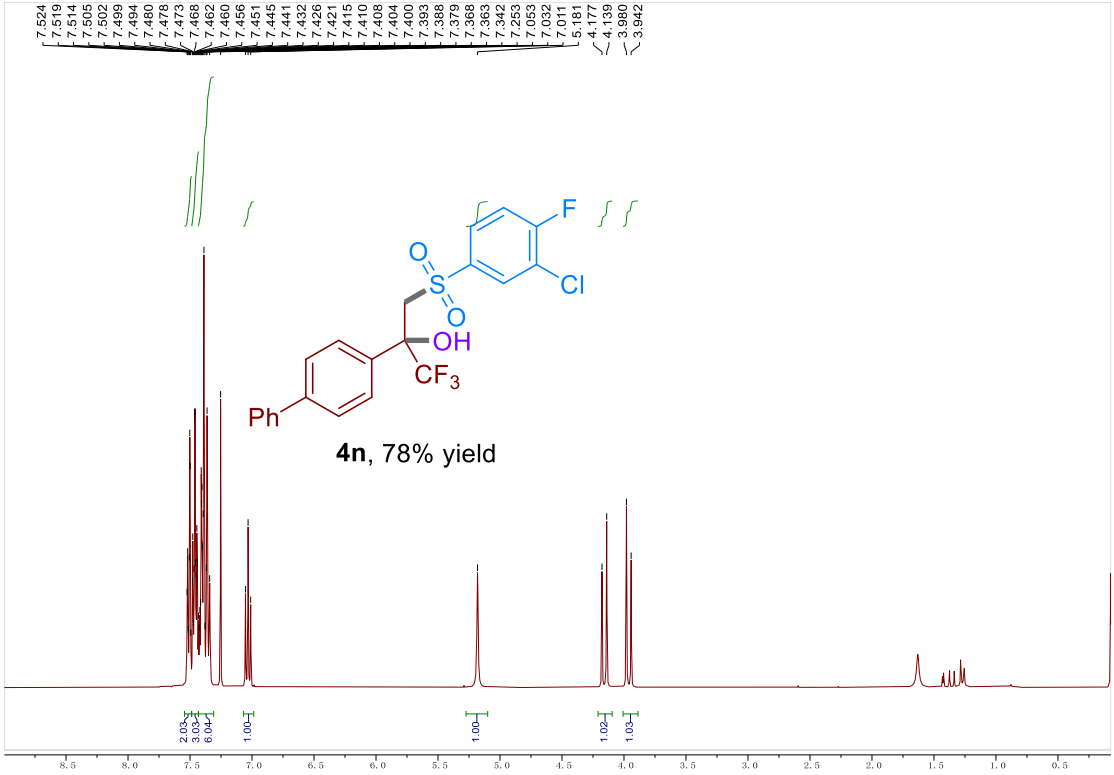
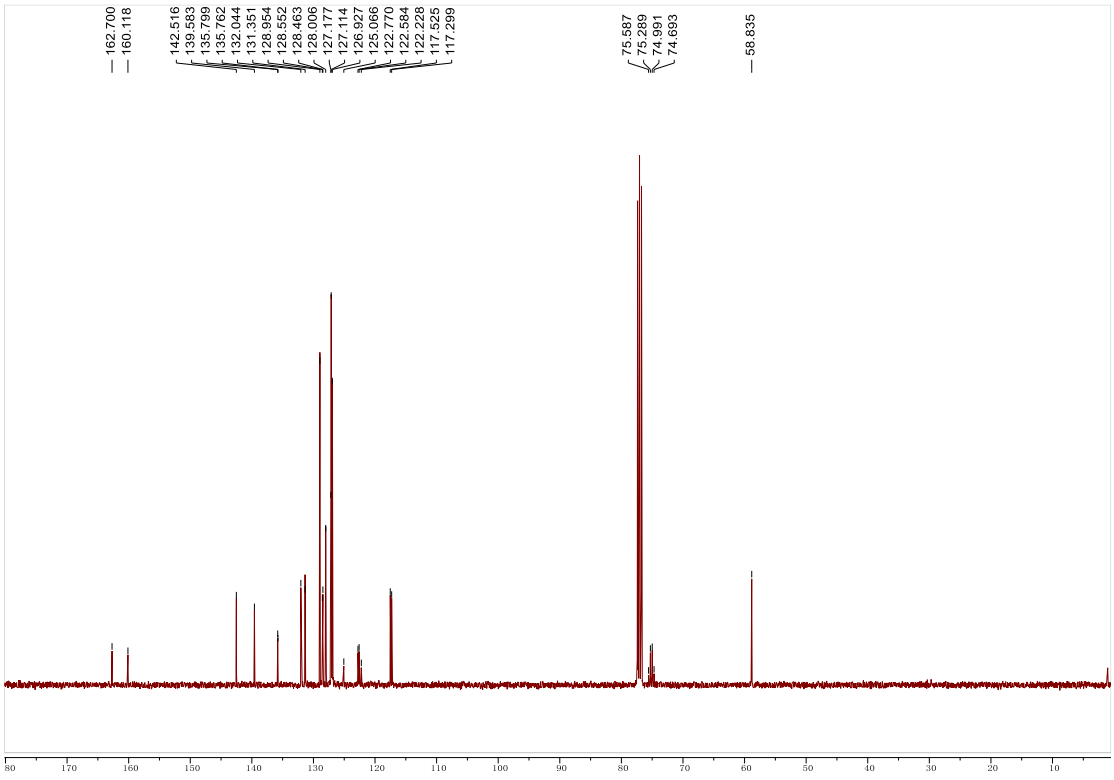
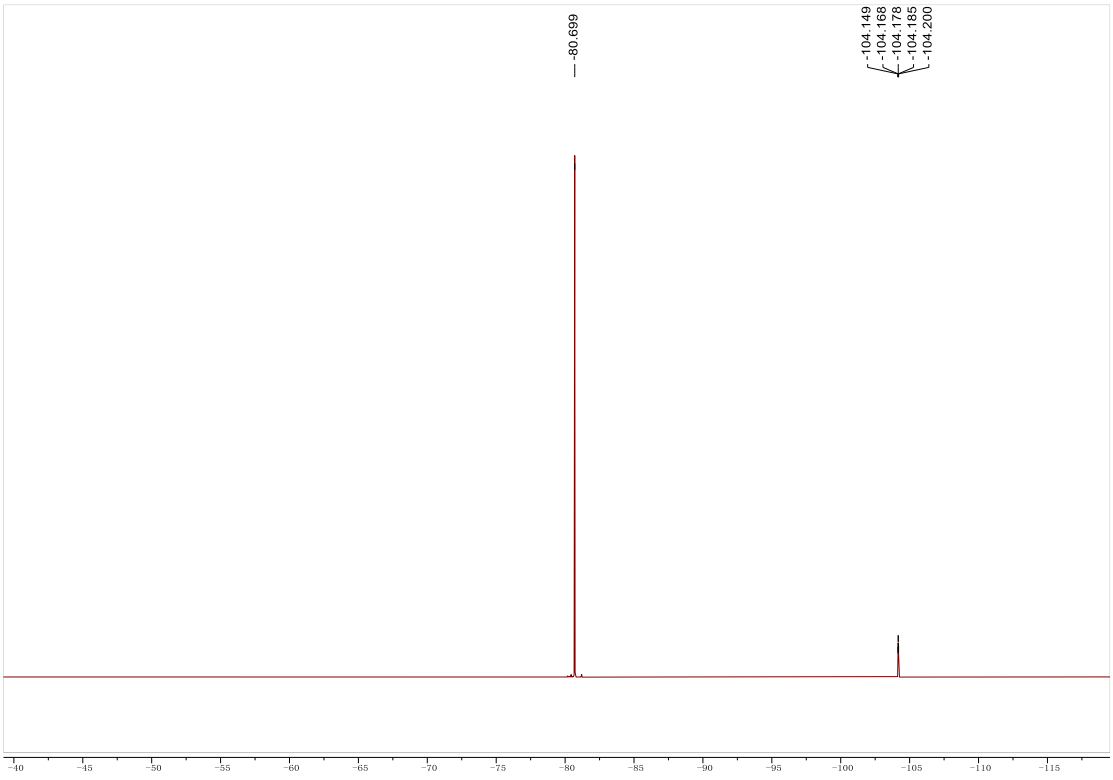
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115

^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4n



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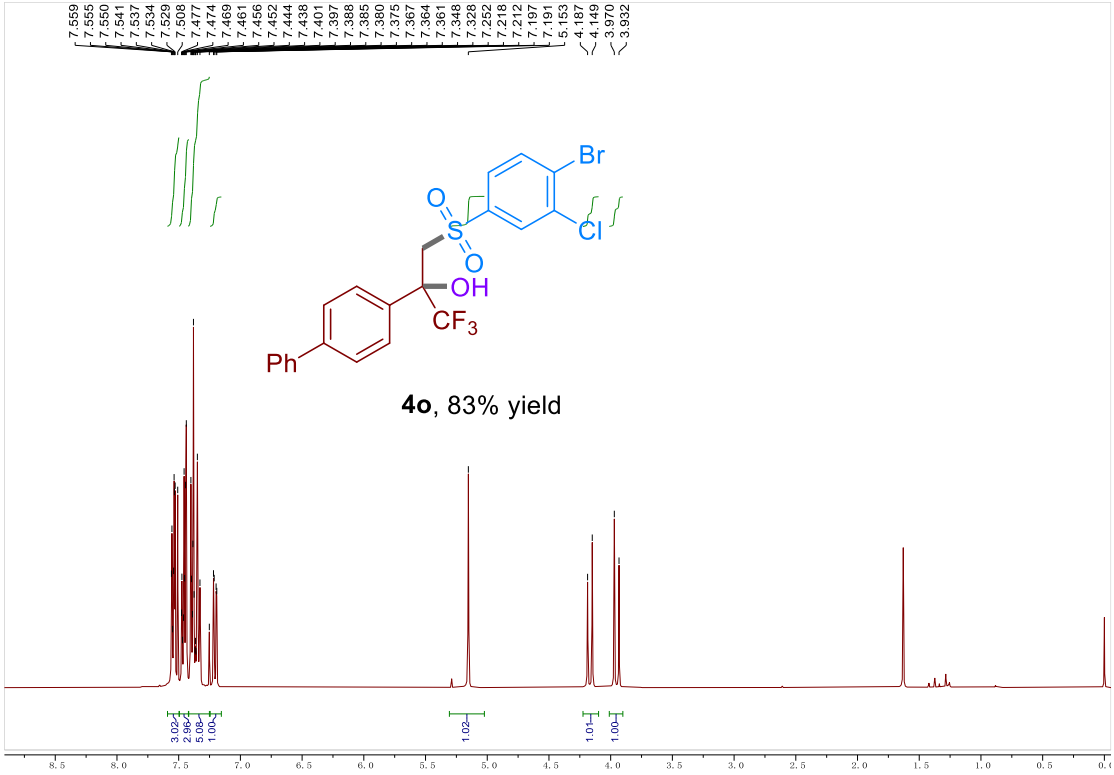
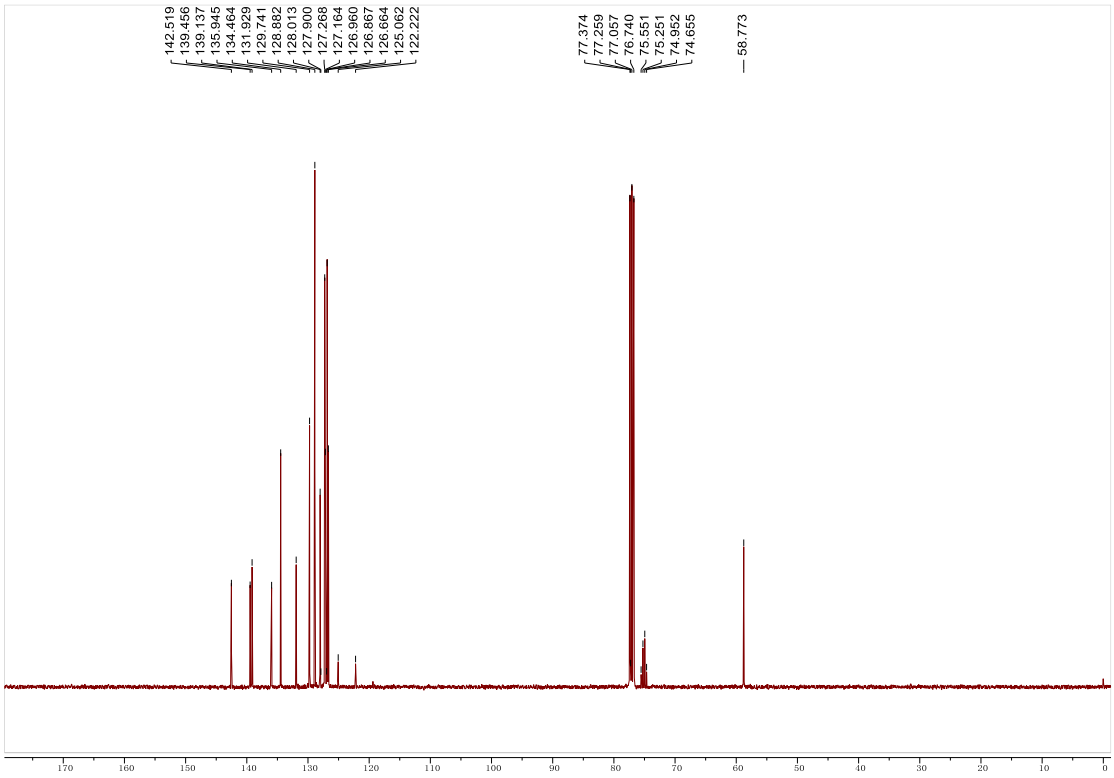
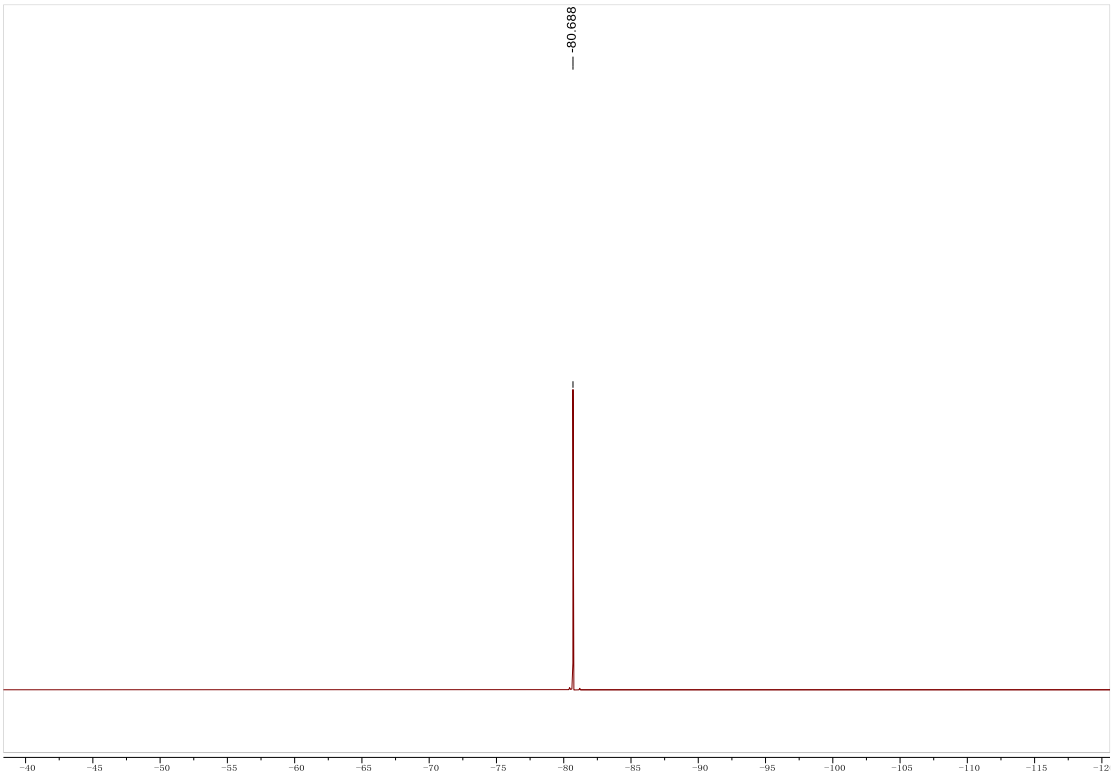
-104.149
-104.168
-104.178
-104.185
-104.200
−40
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115

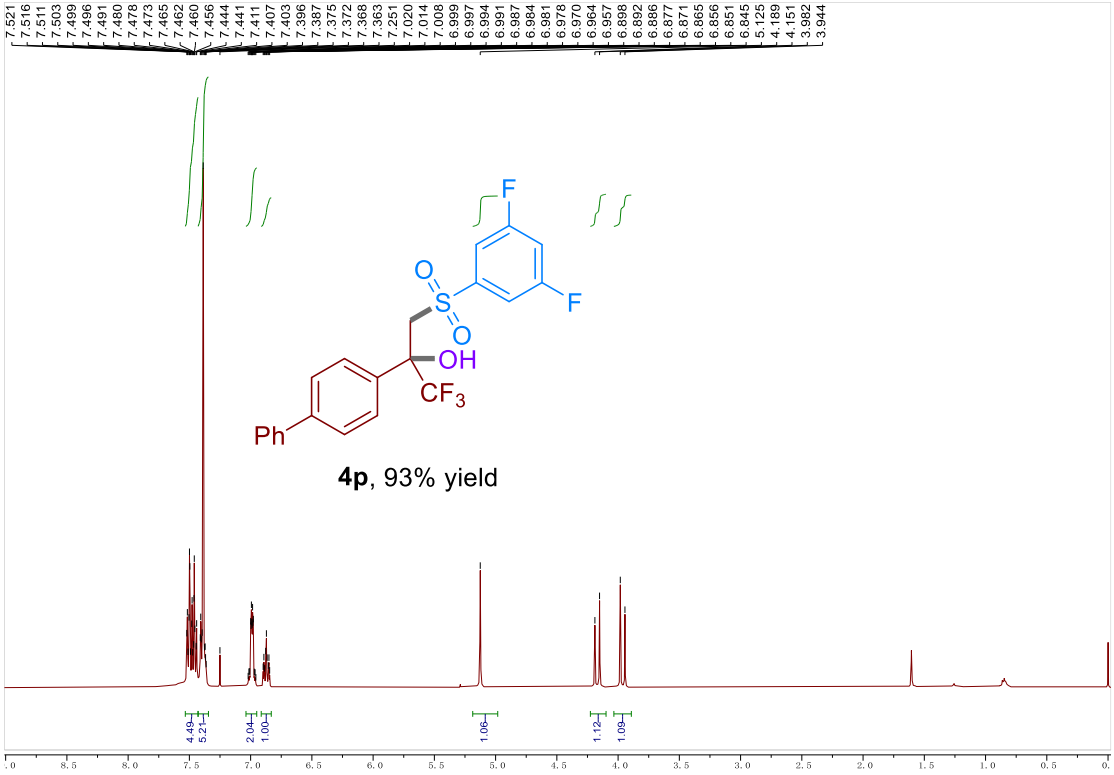
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4o

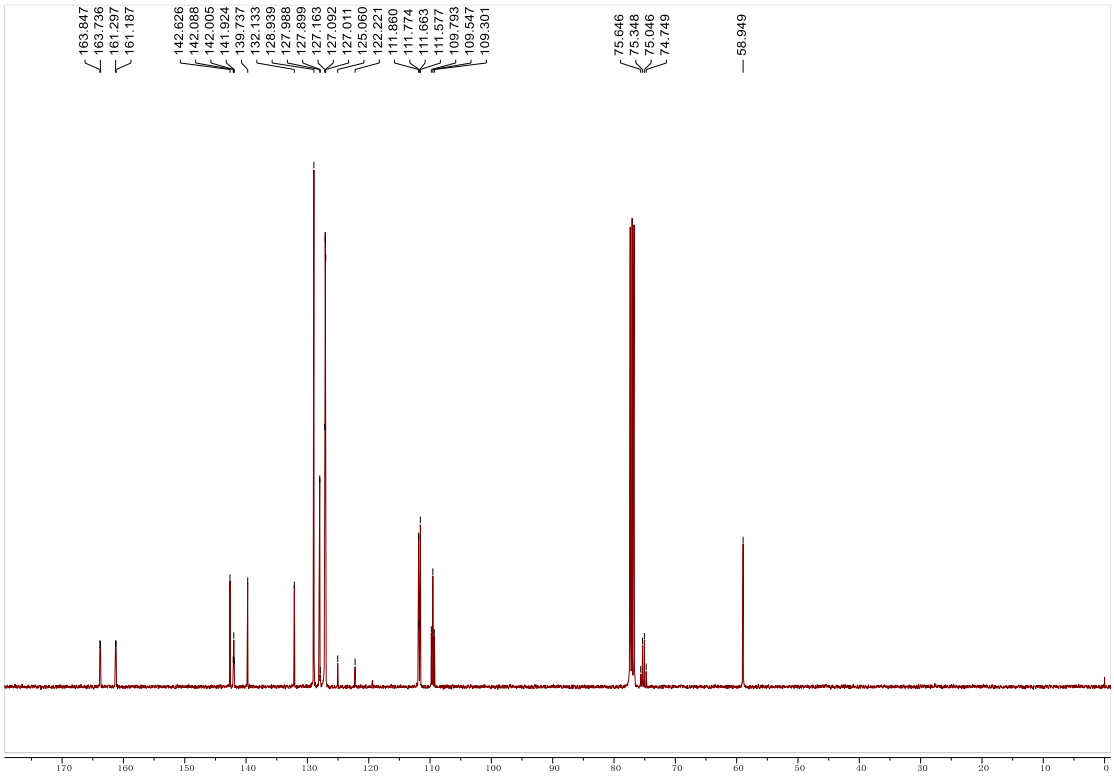


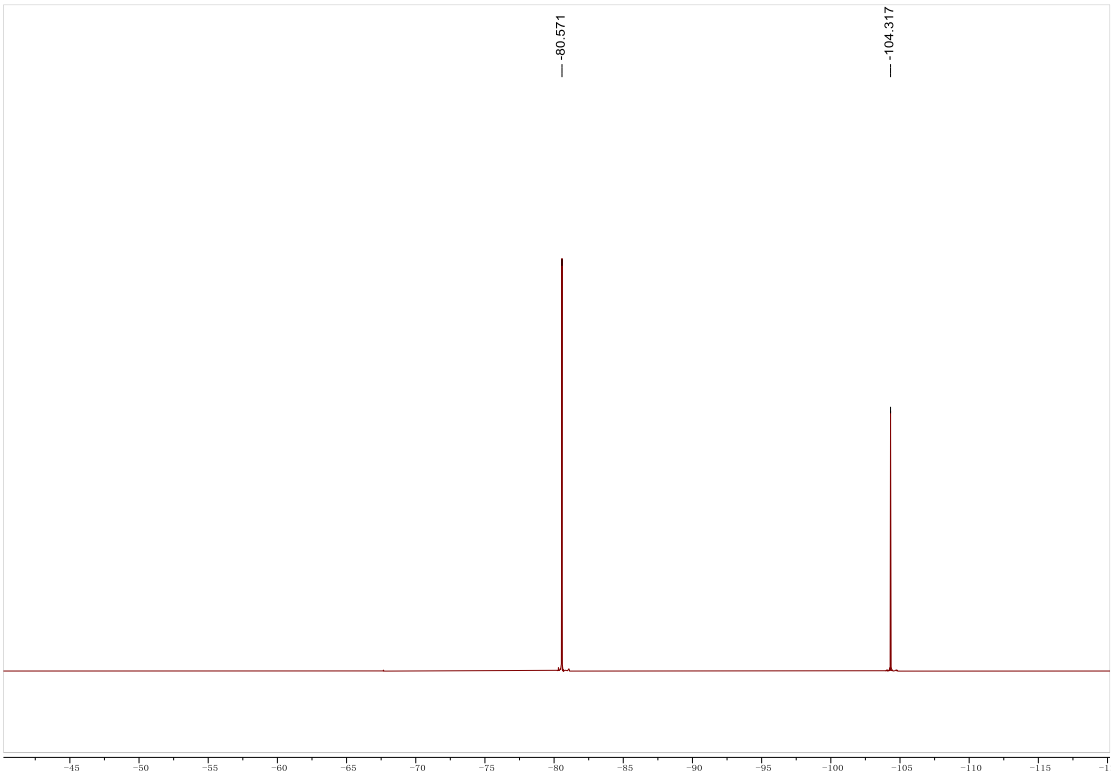



−80.688
−40
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115
−12

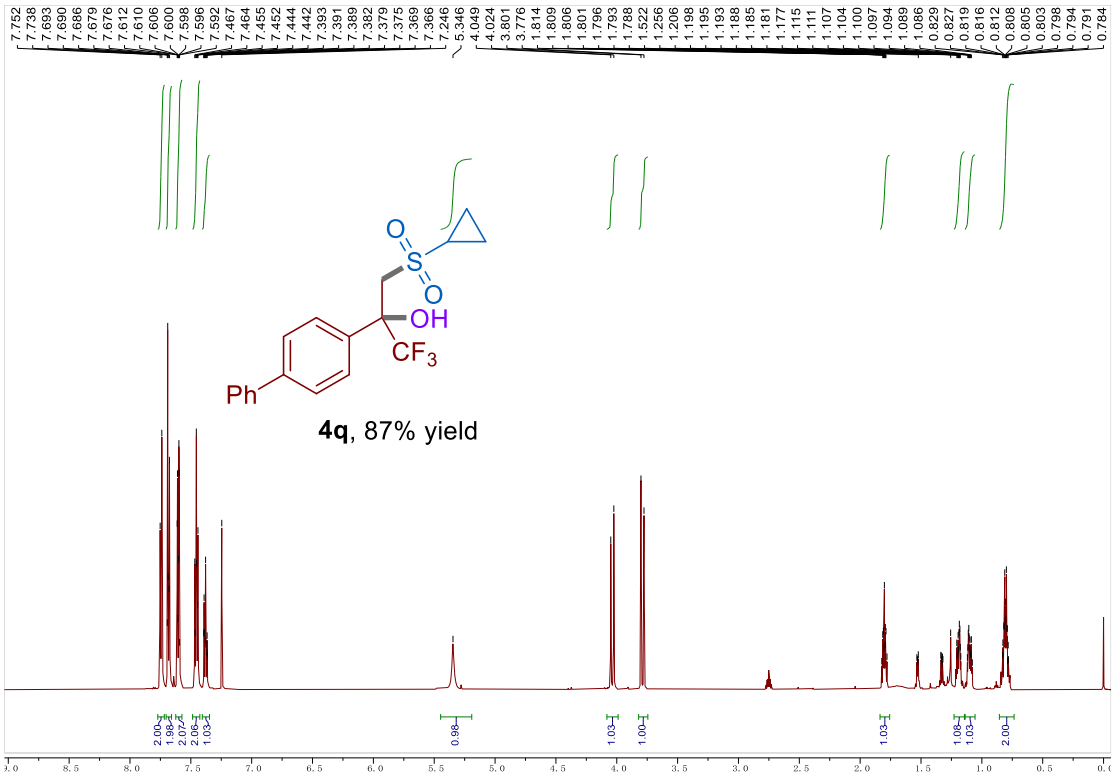
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4p

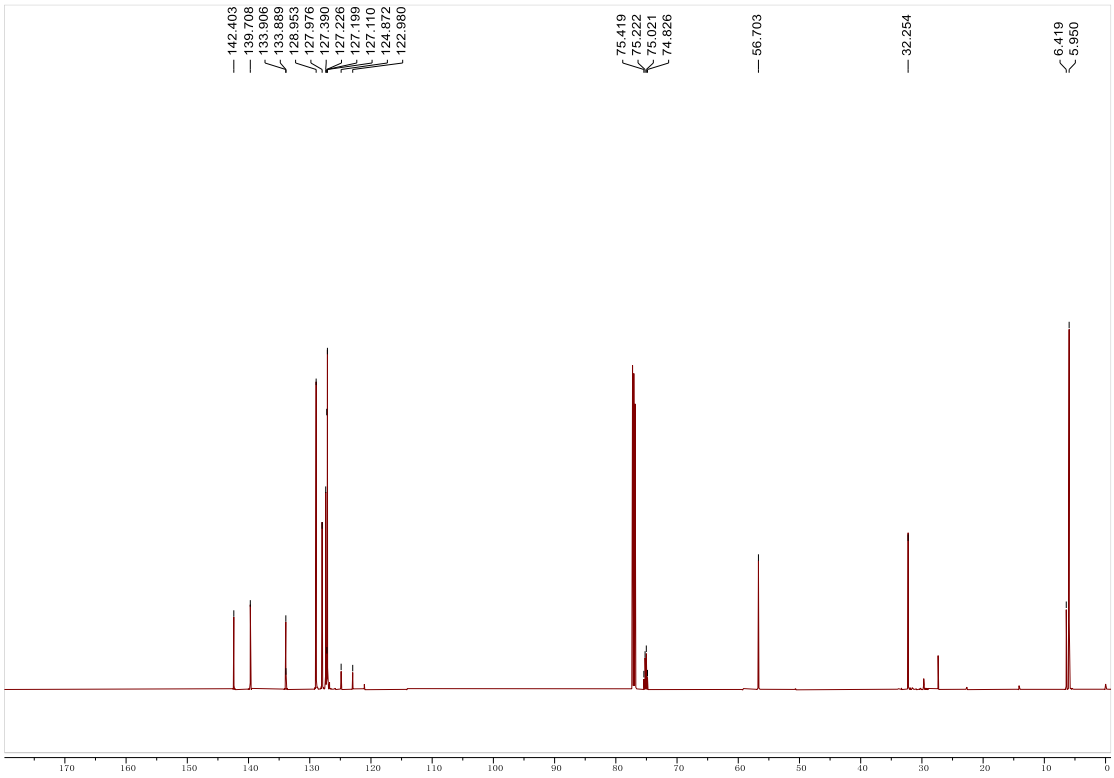


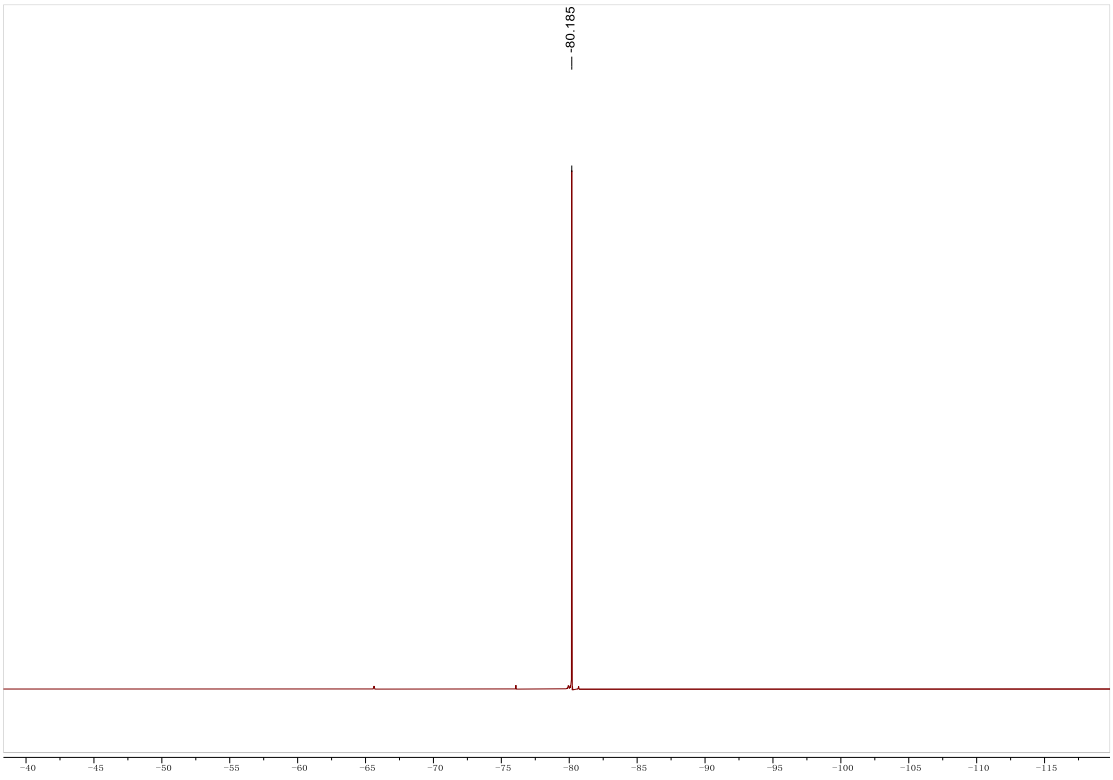



-80.571
-104.317
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115

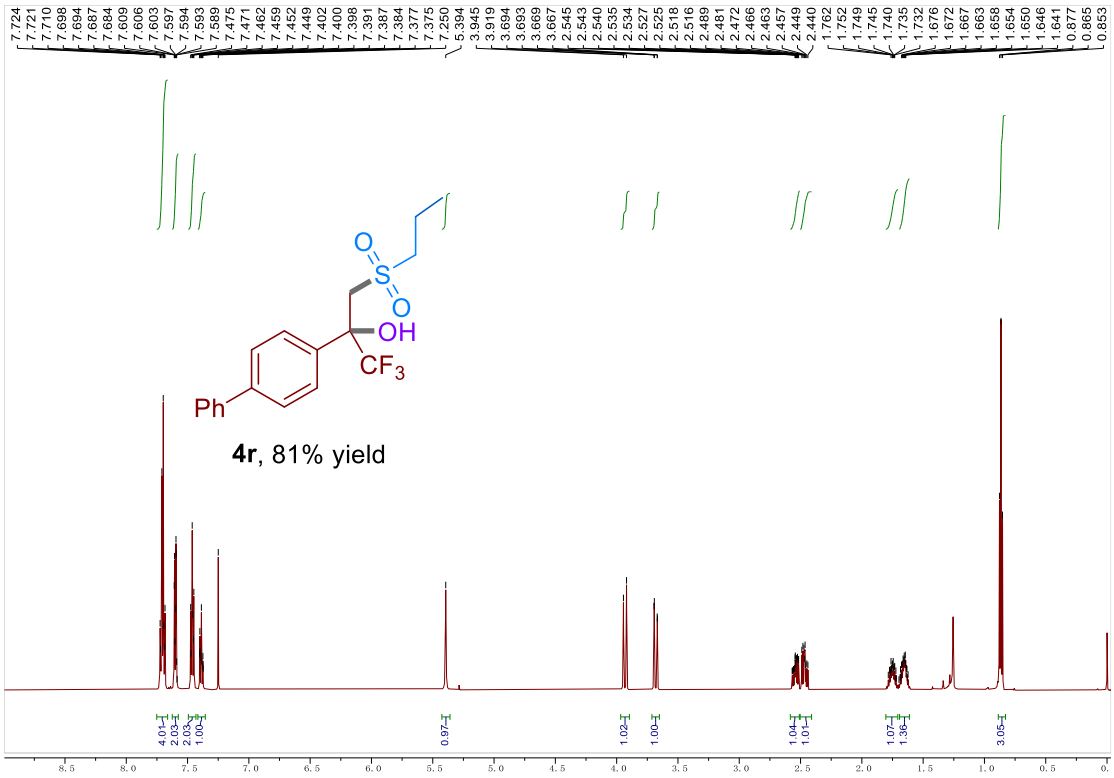
^{1}H NMR (600 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of product 4q

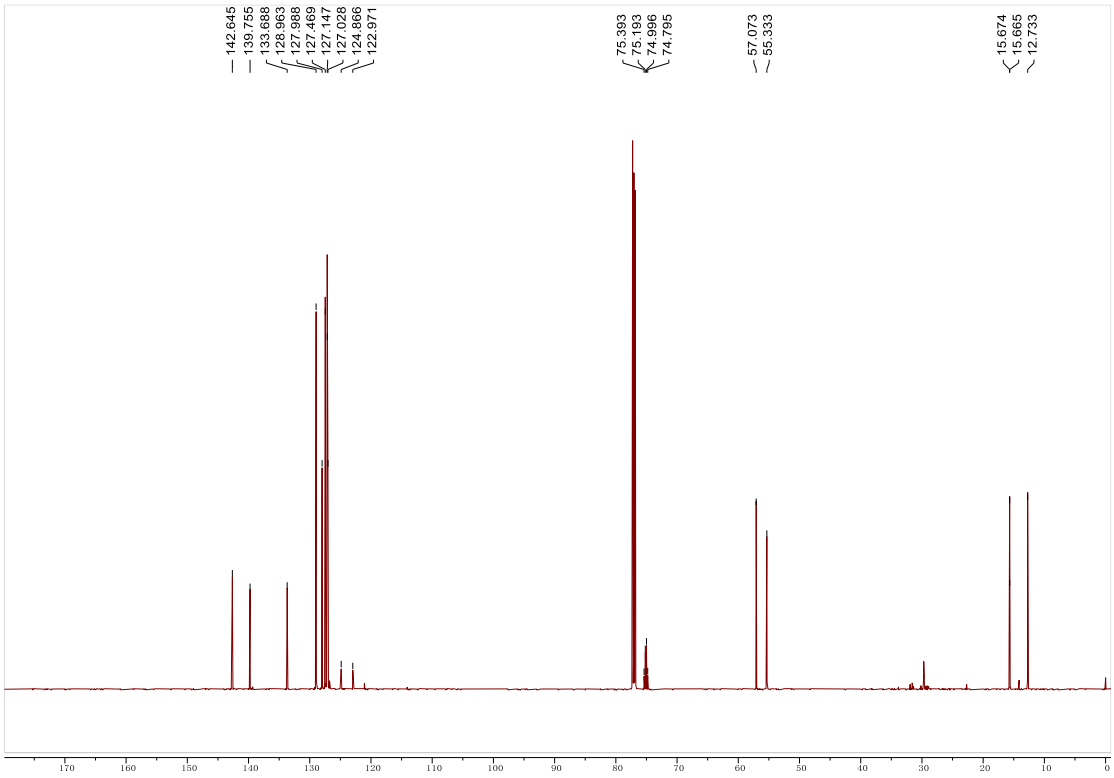


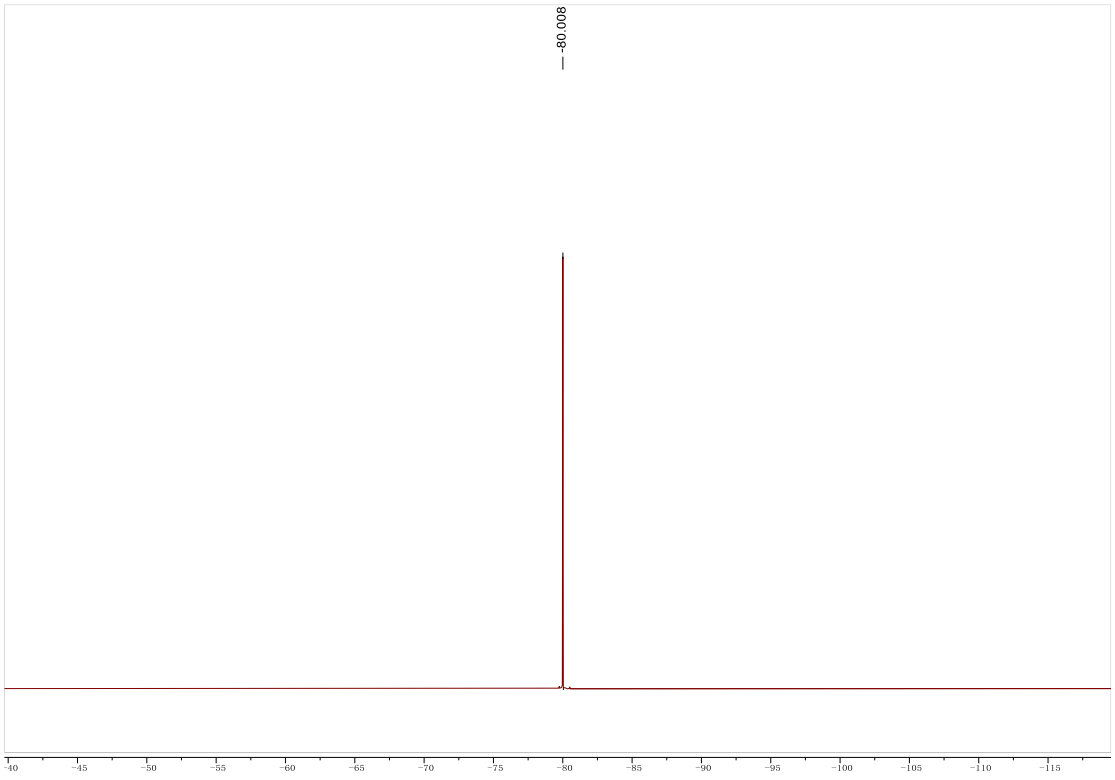



-80.185
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115

^{1}H NMR (600 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of product 4r






-80.008
-40
-45
-50
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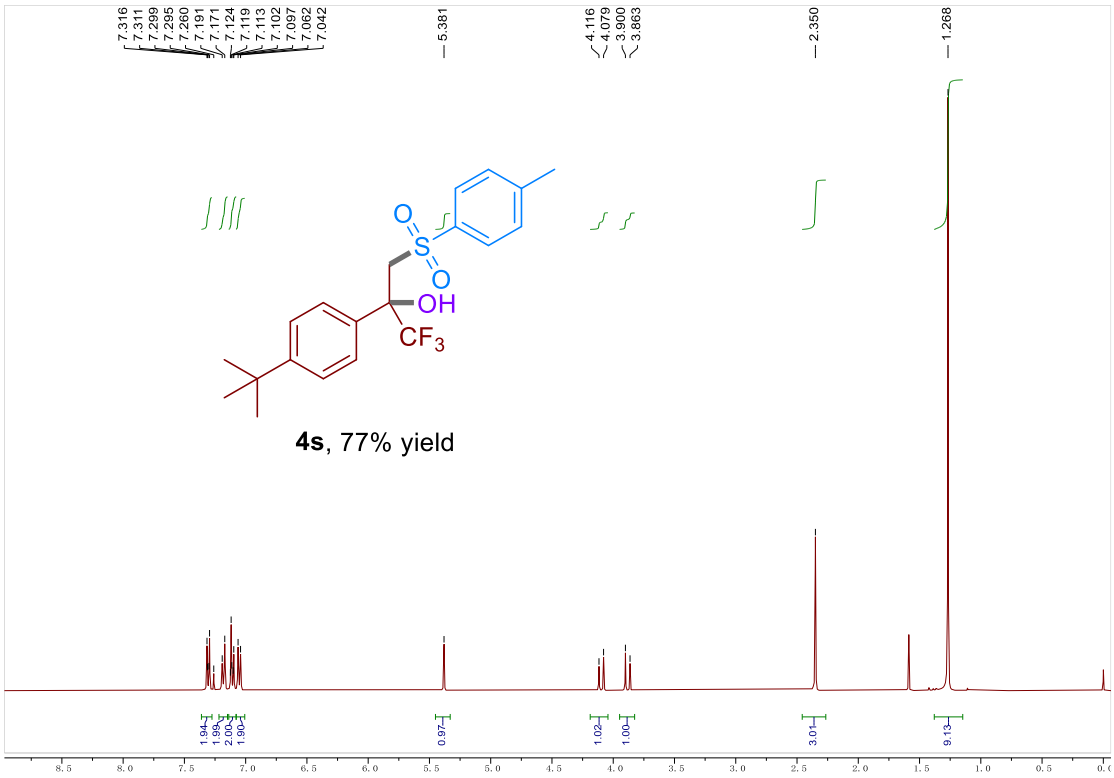
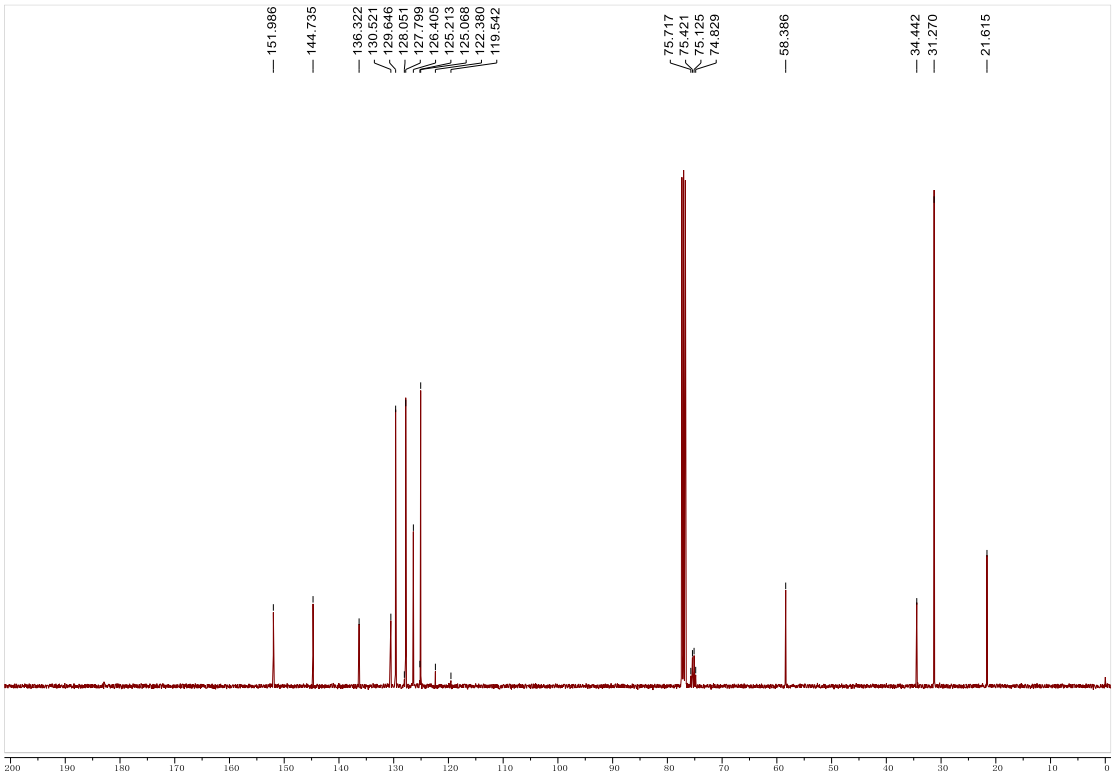
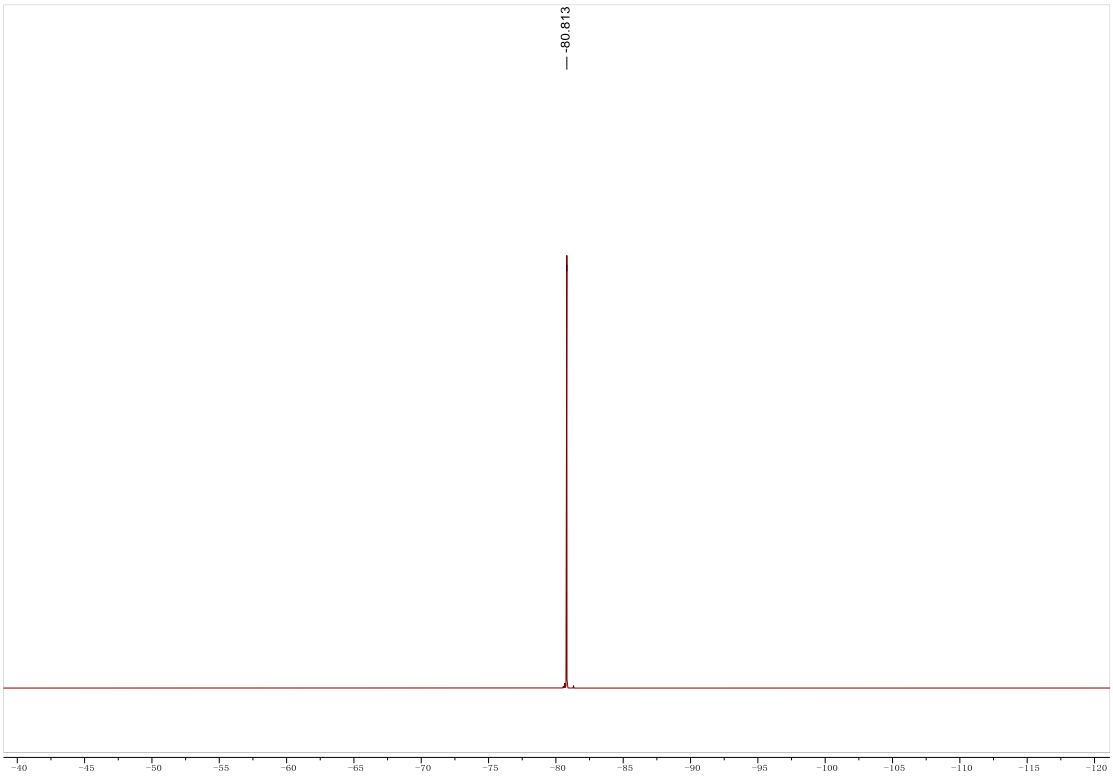
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115

^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4s



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-45
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-55
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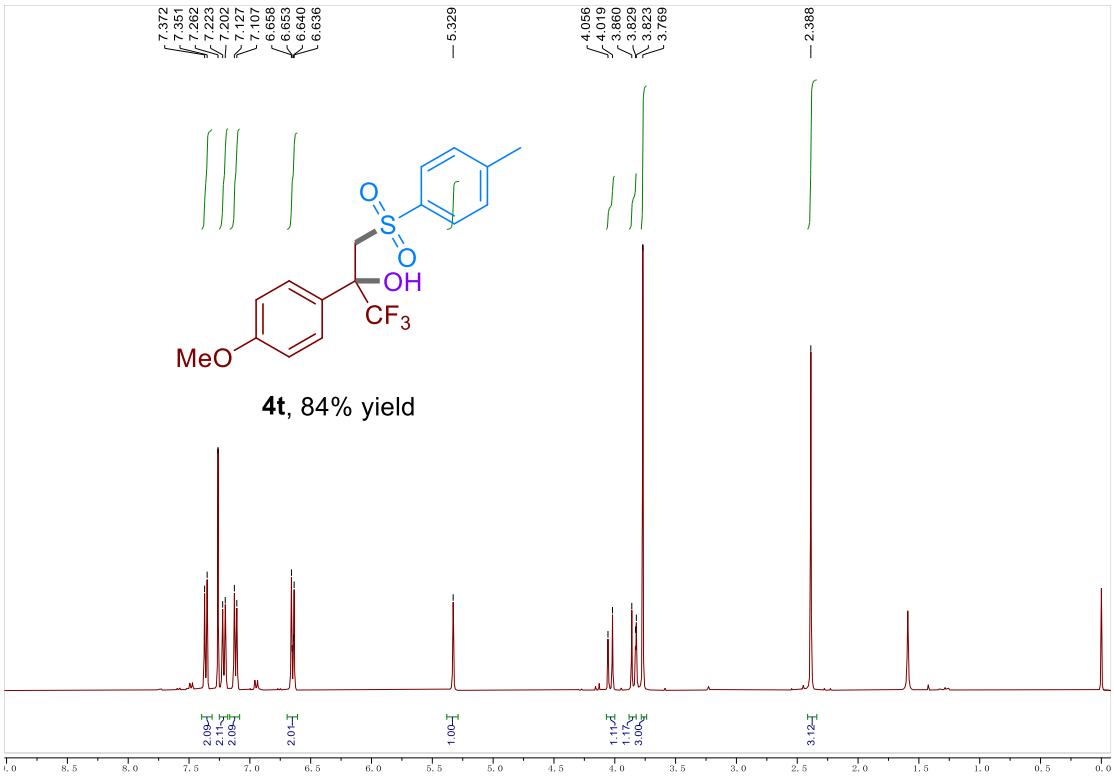
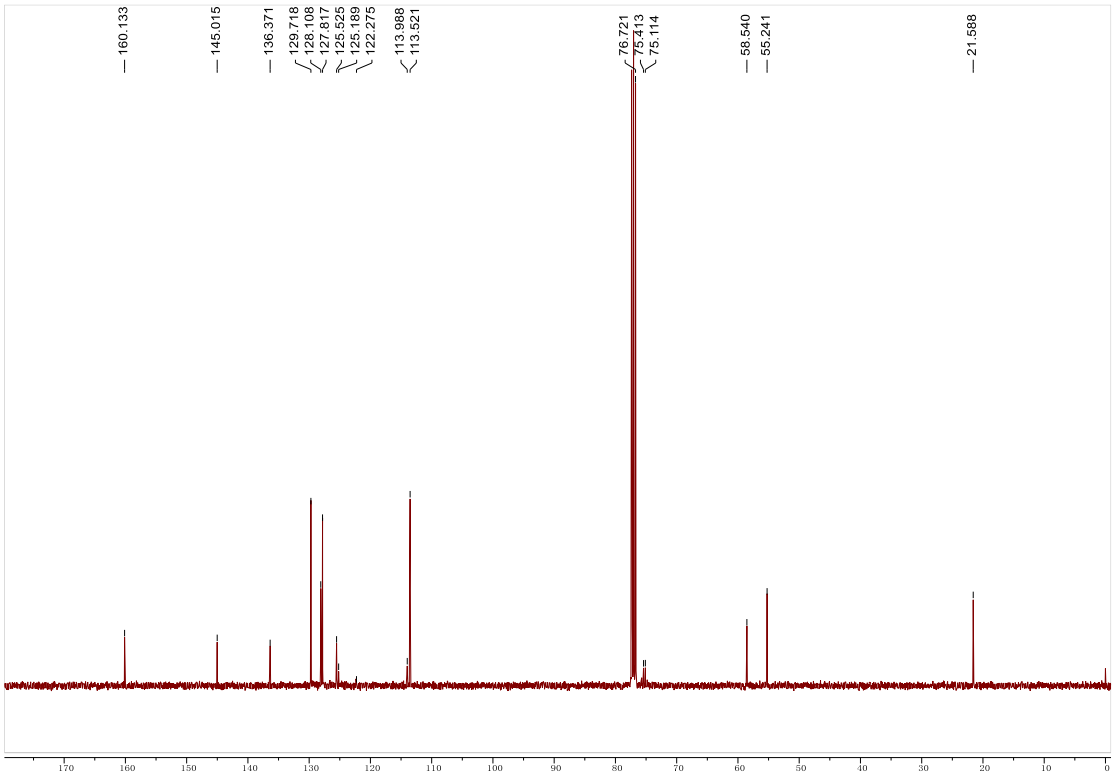
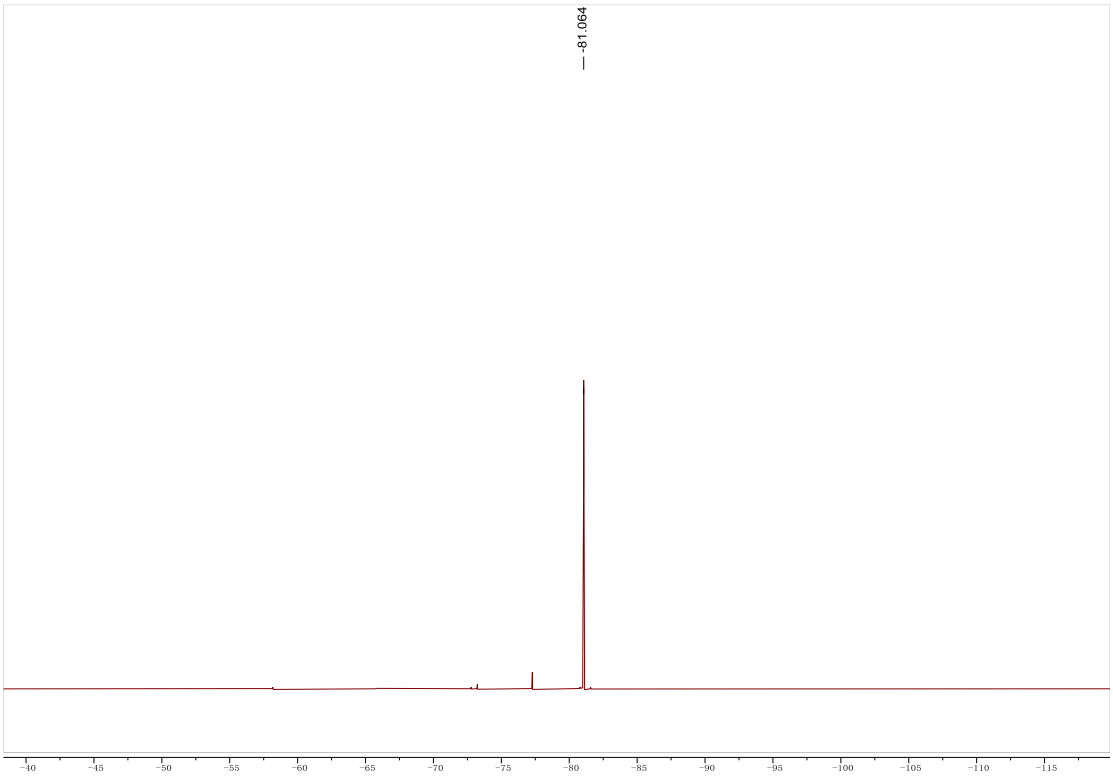
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120

^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4t



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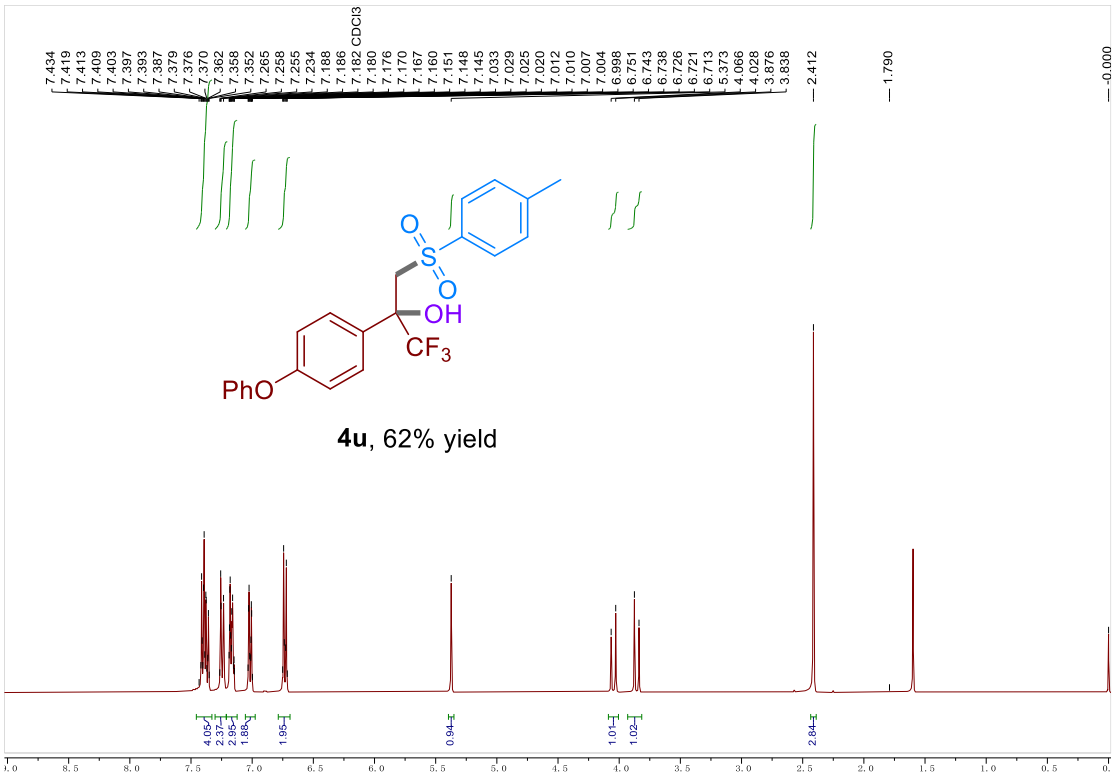
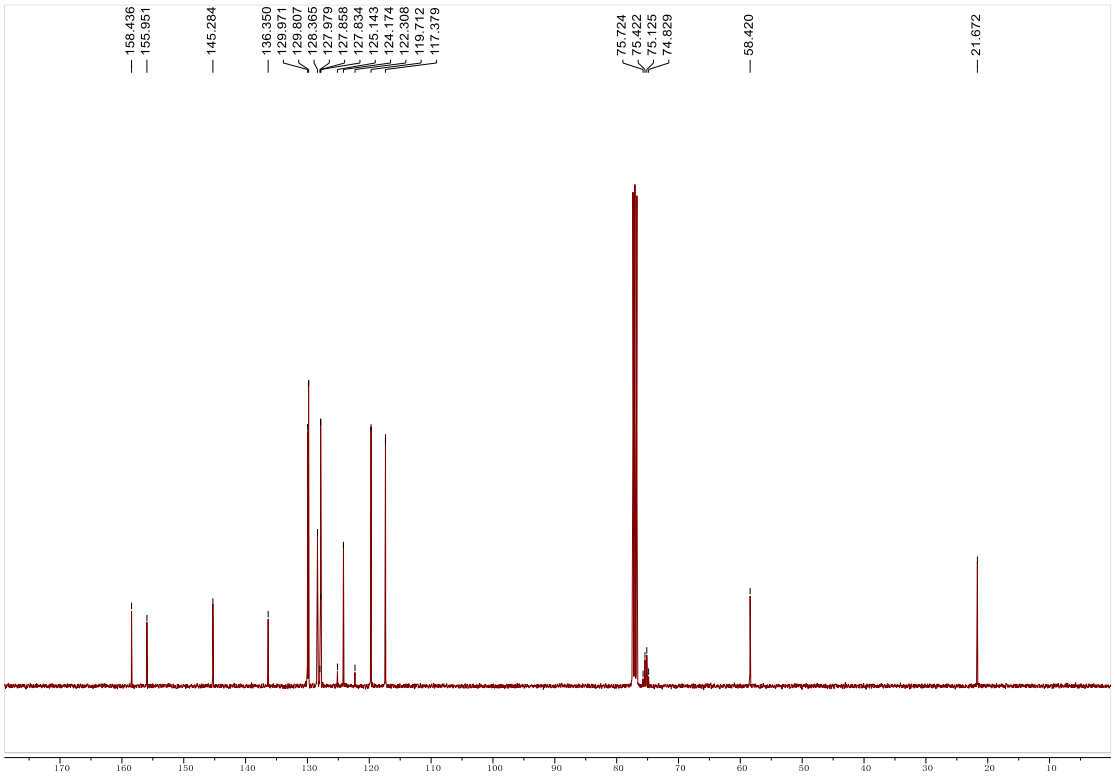
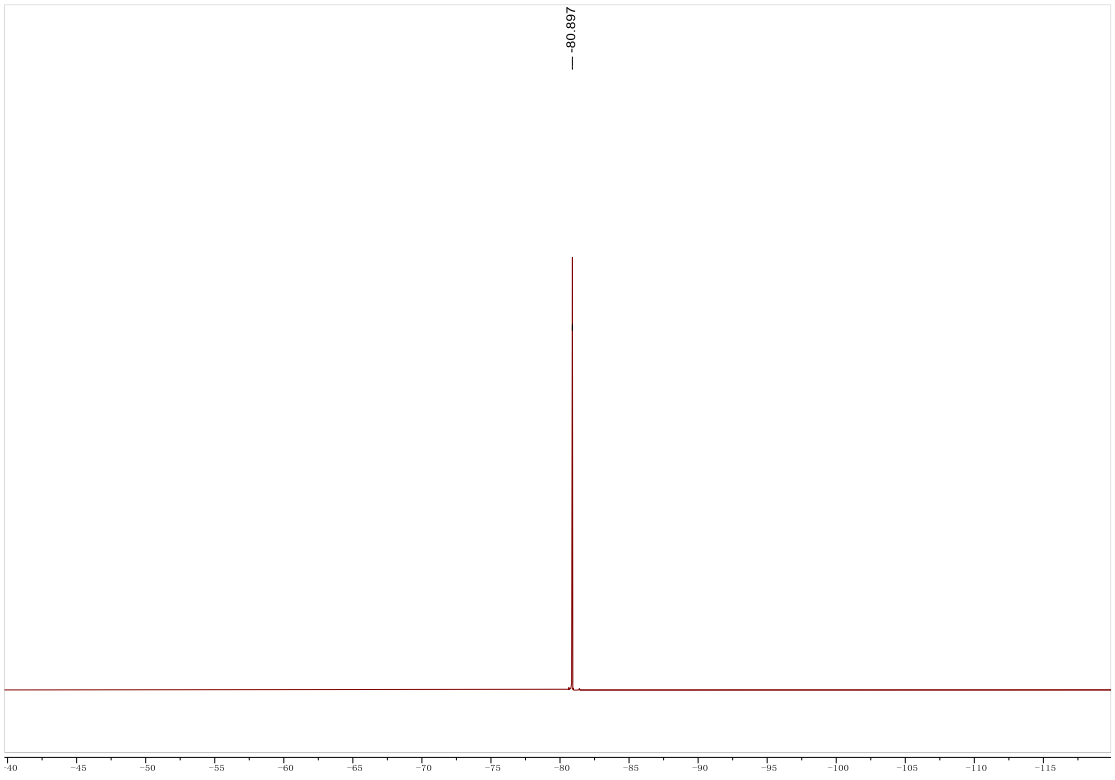
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115

^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4u



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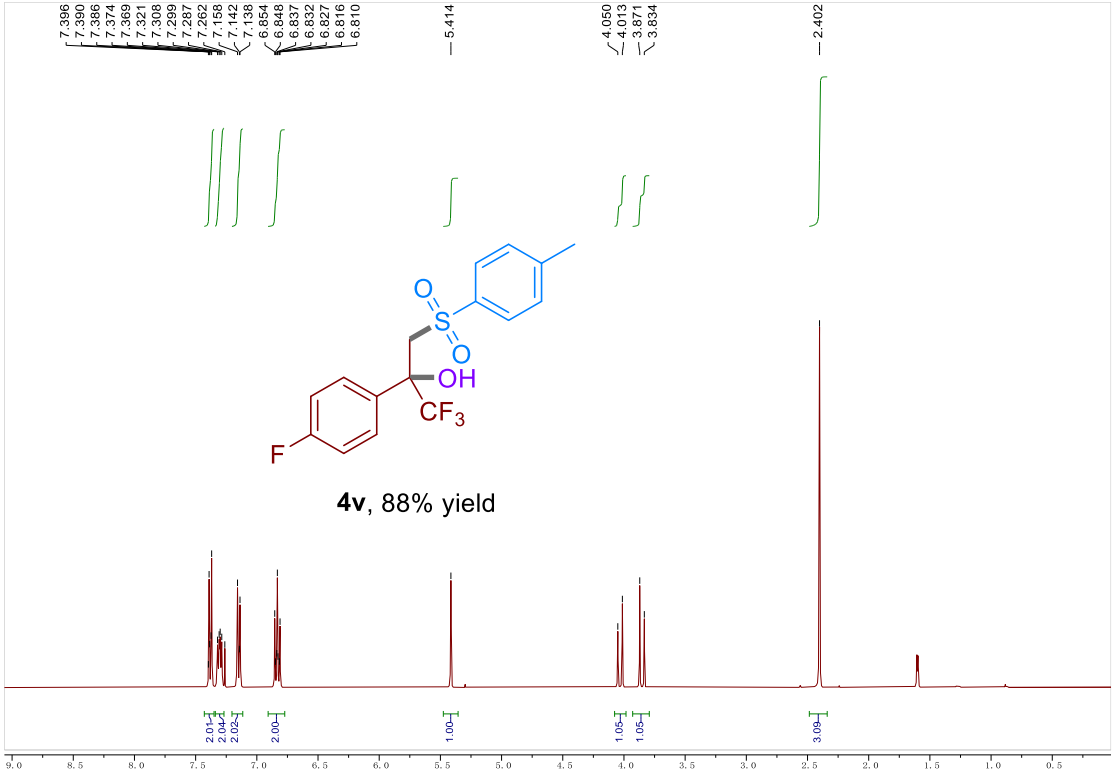
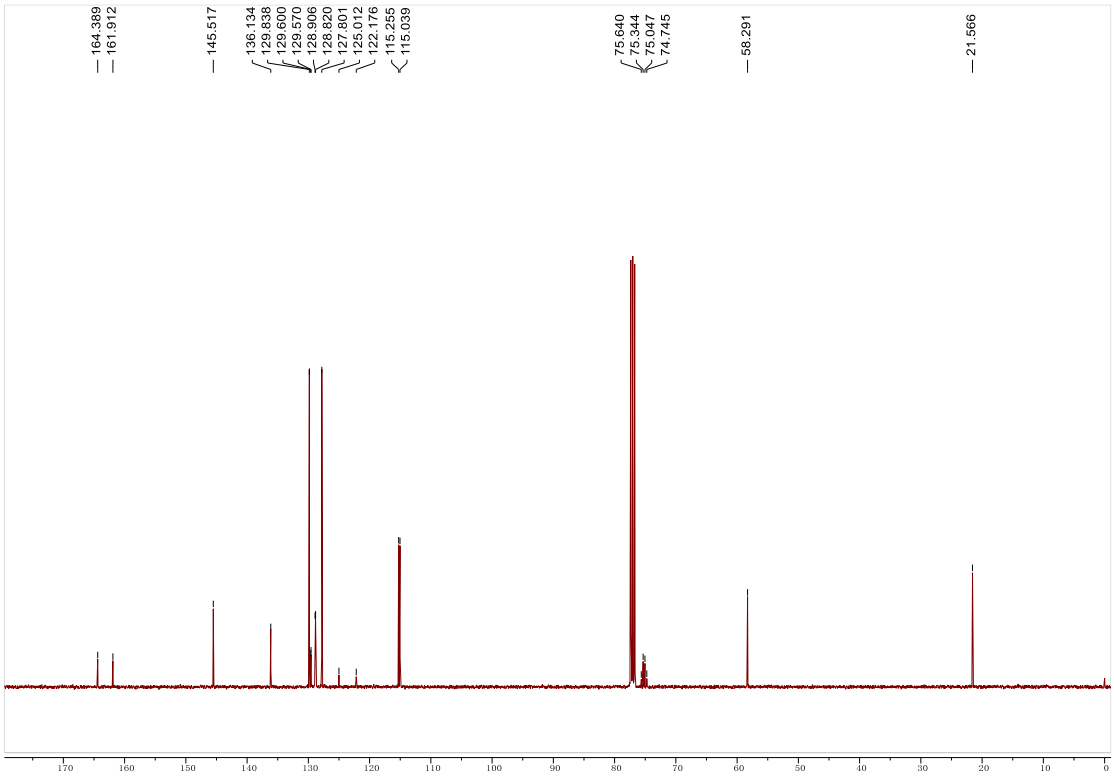
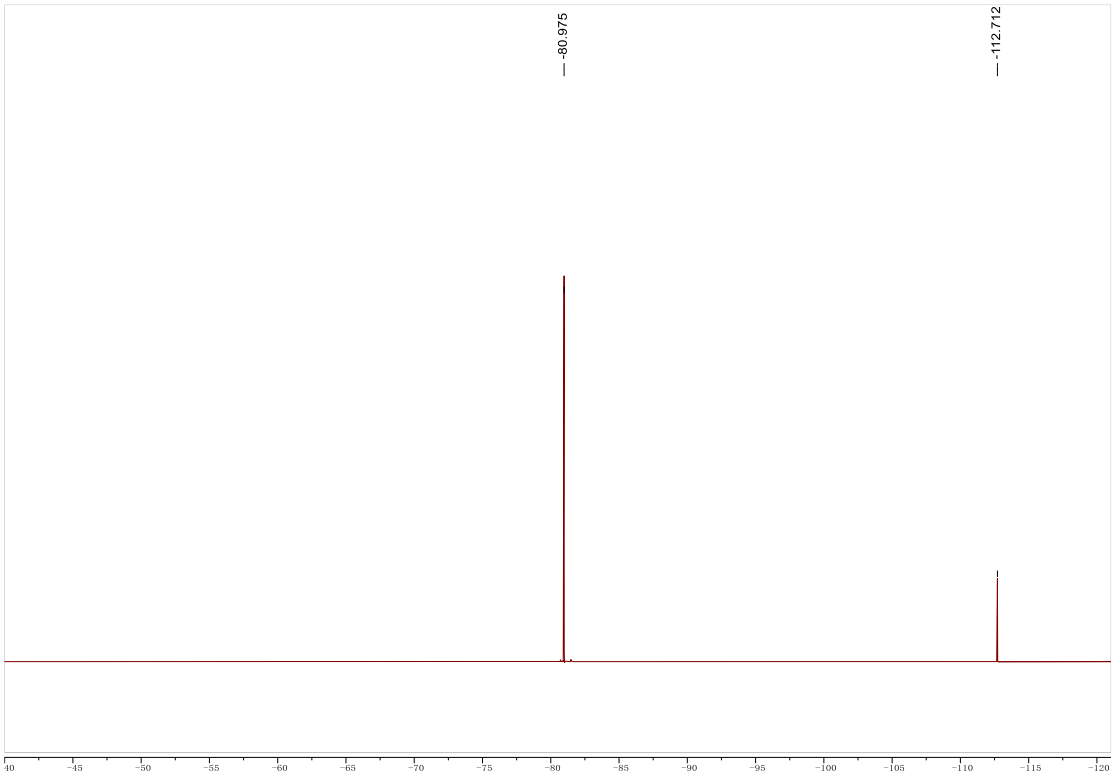
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115

^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4v



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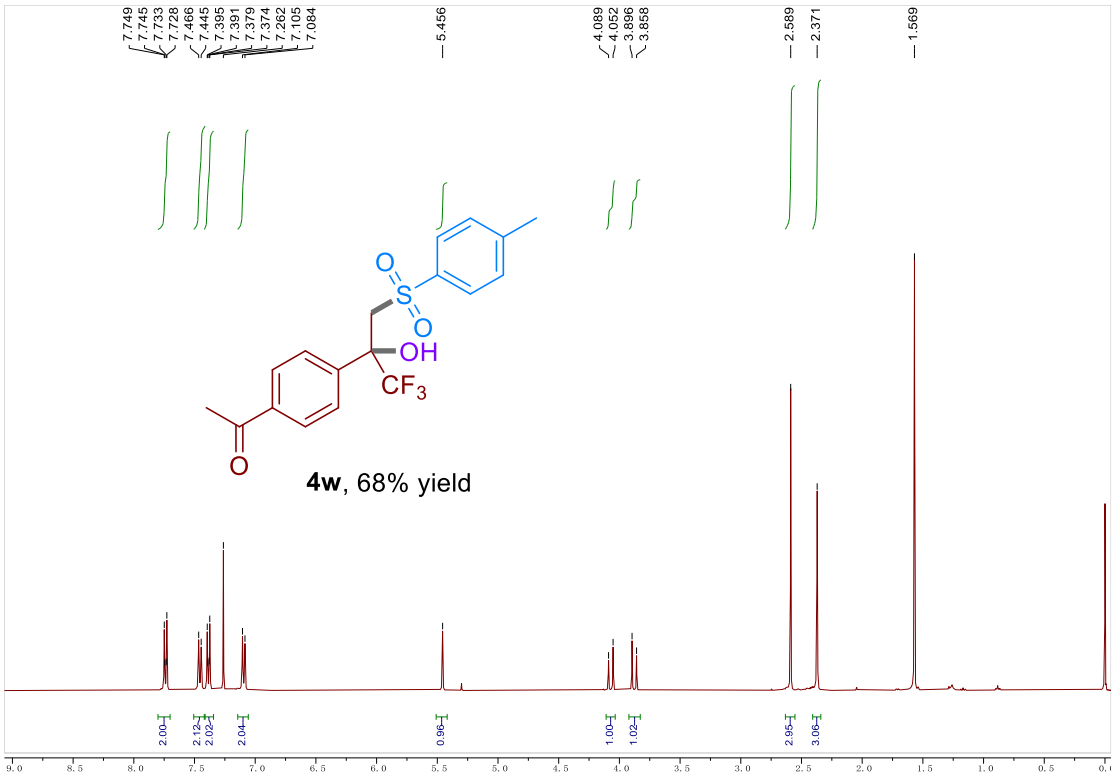
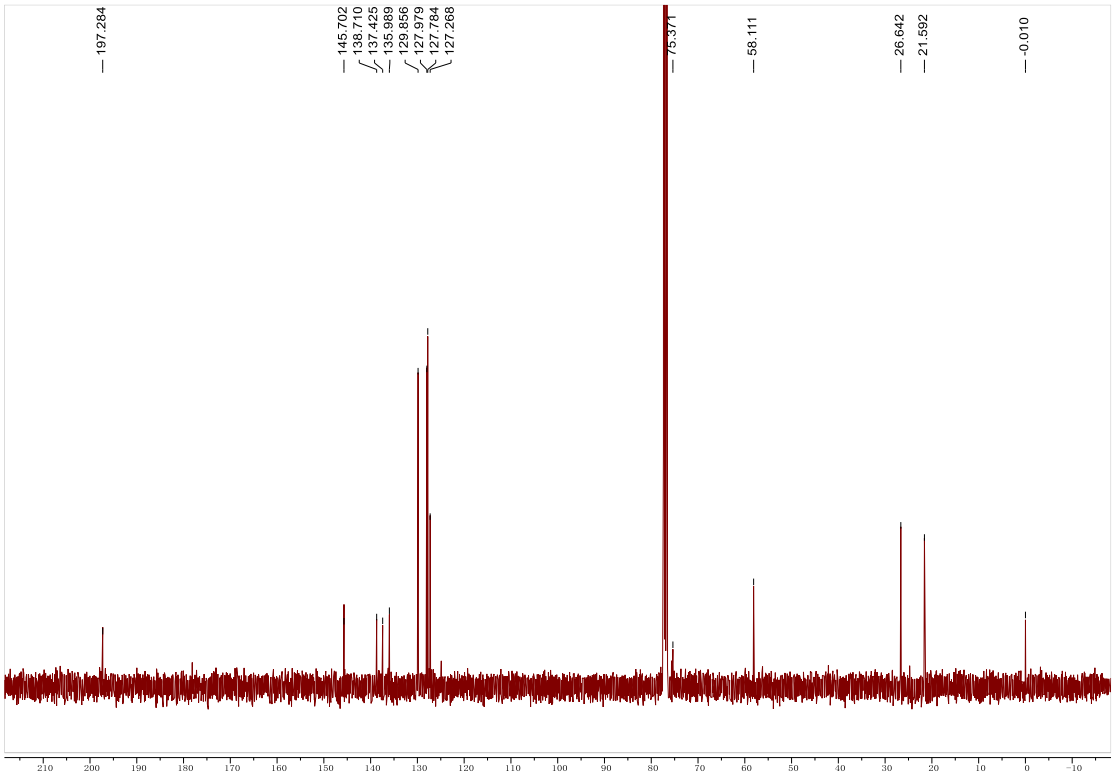
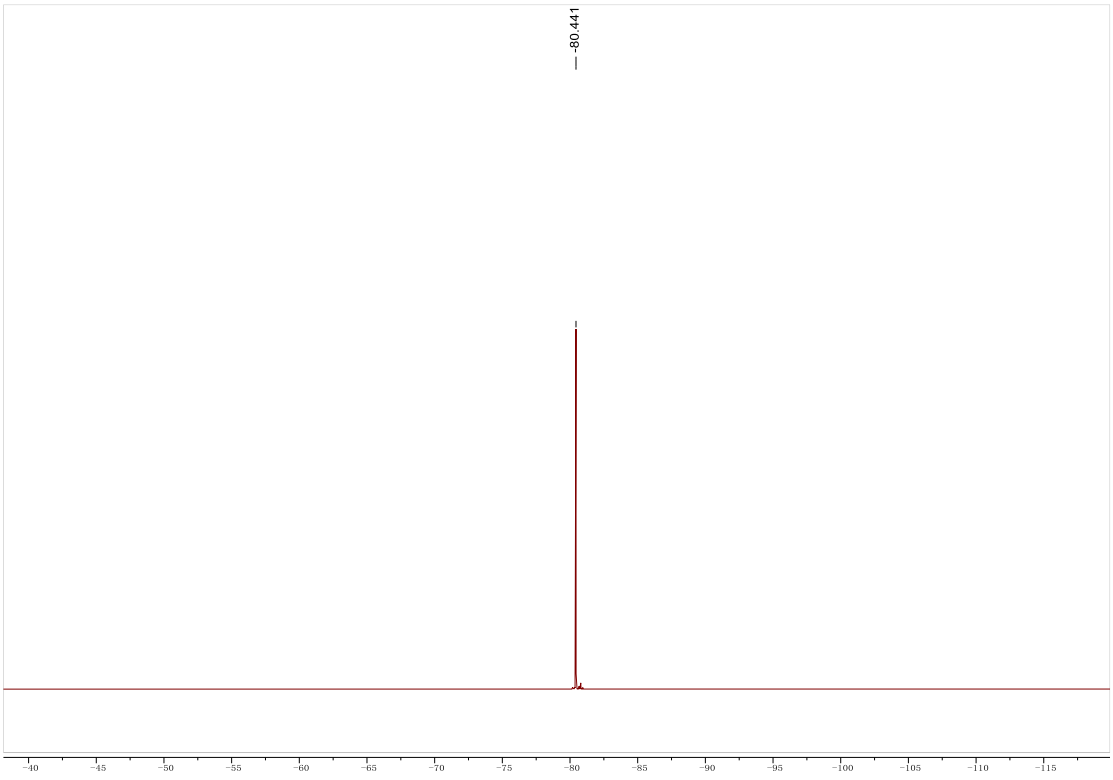
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120

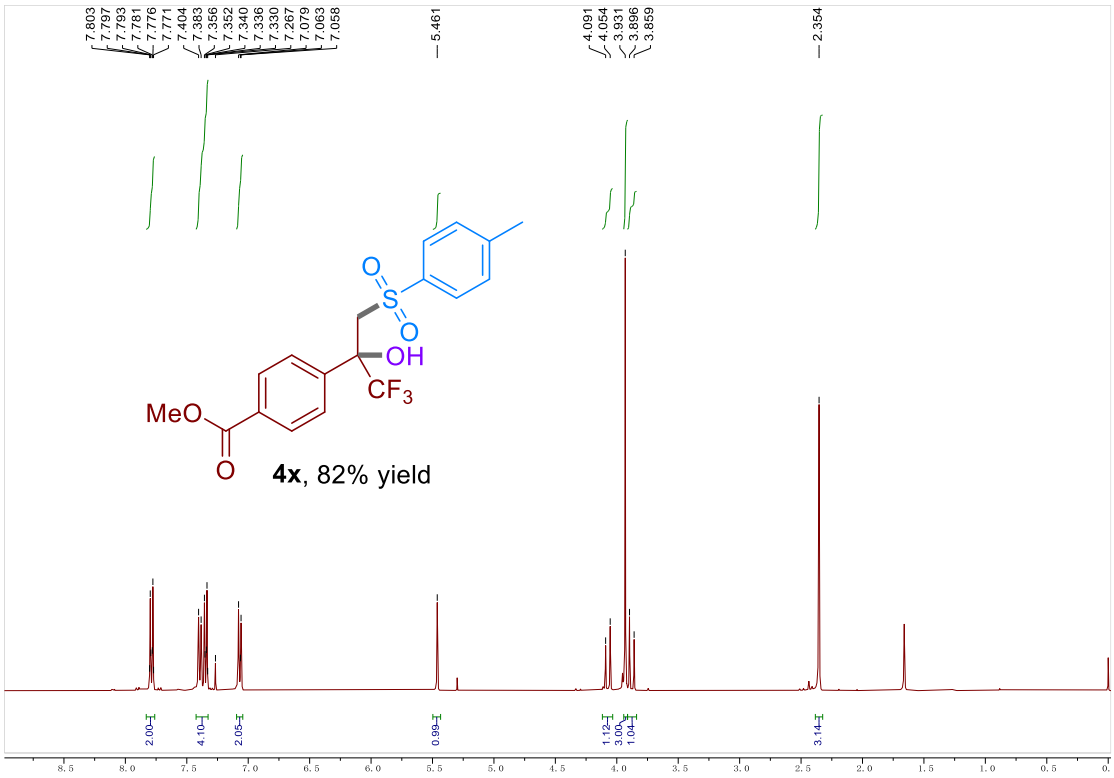
^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4w

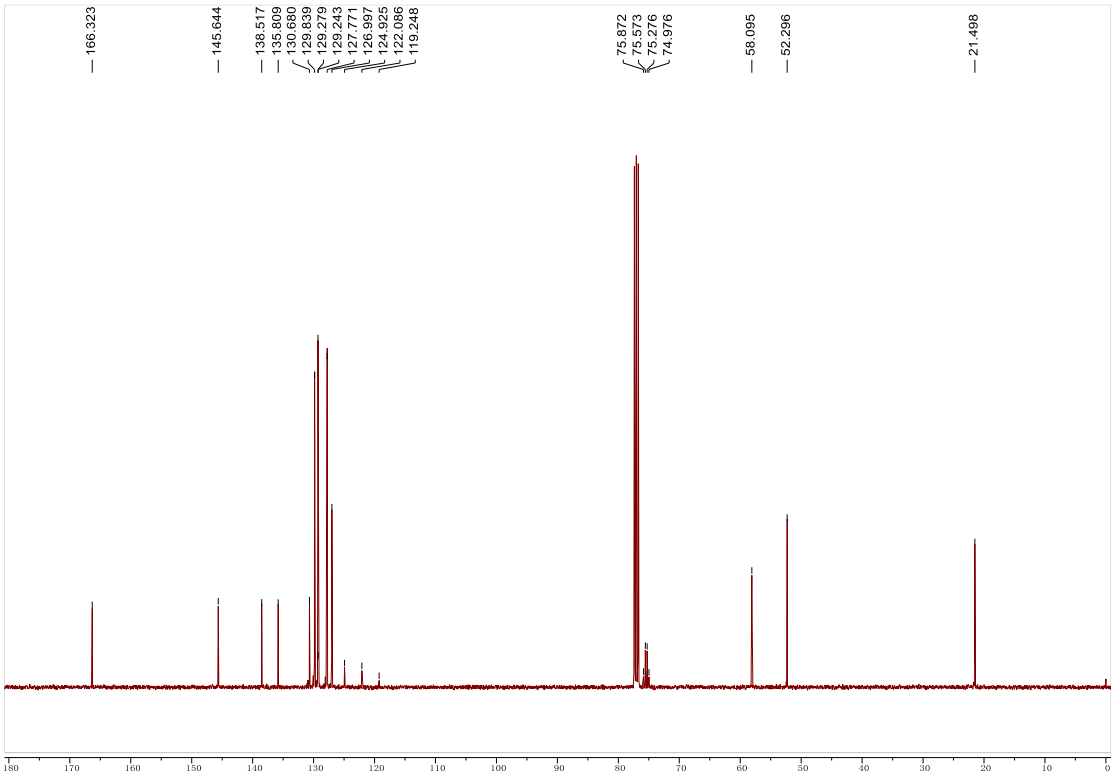


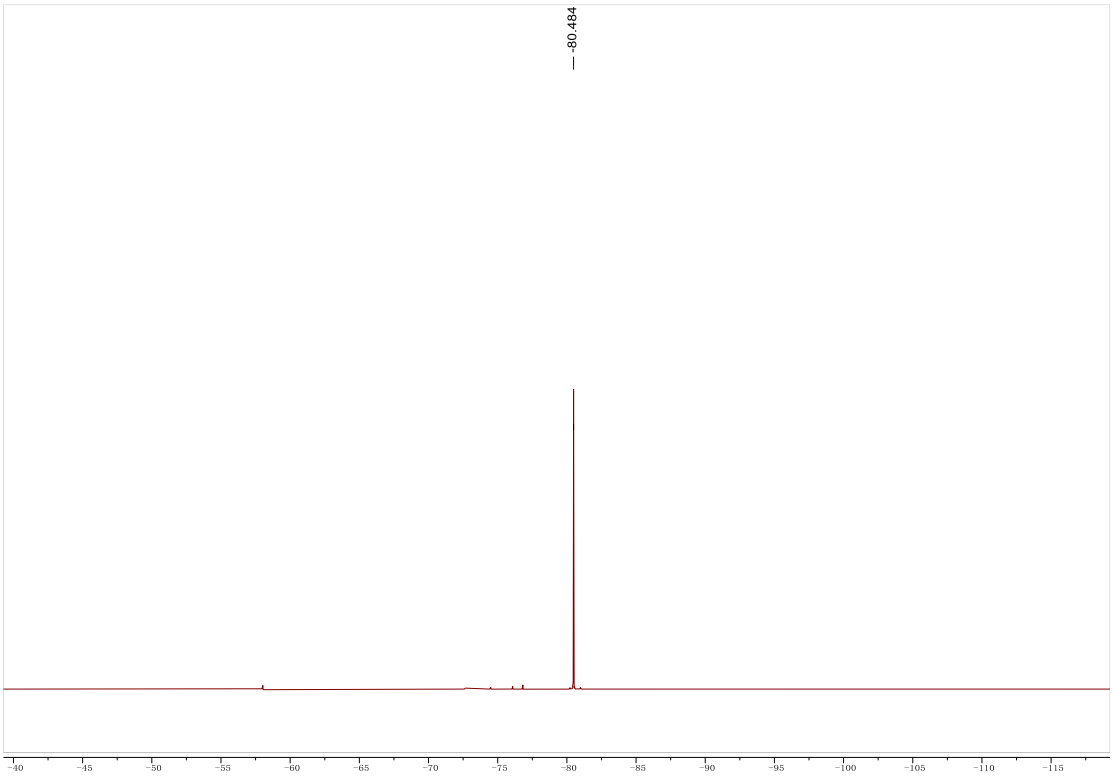



-80.441
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115

^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4x



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−40
−45
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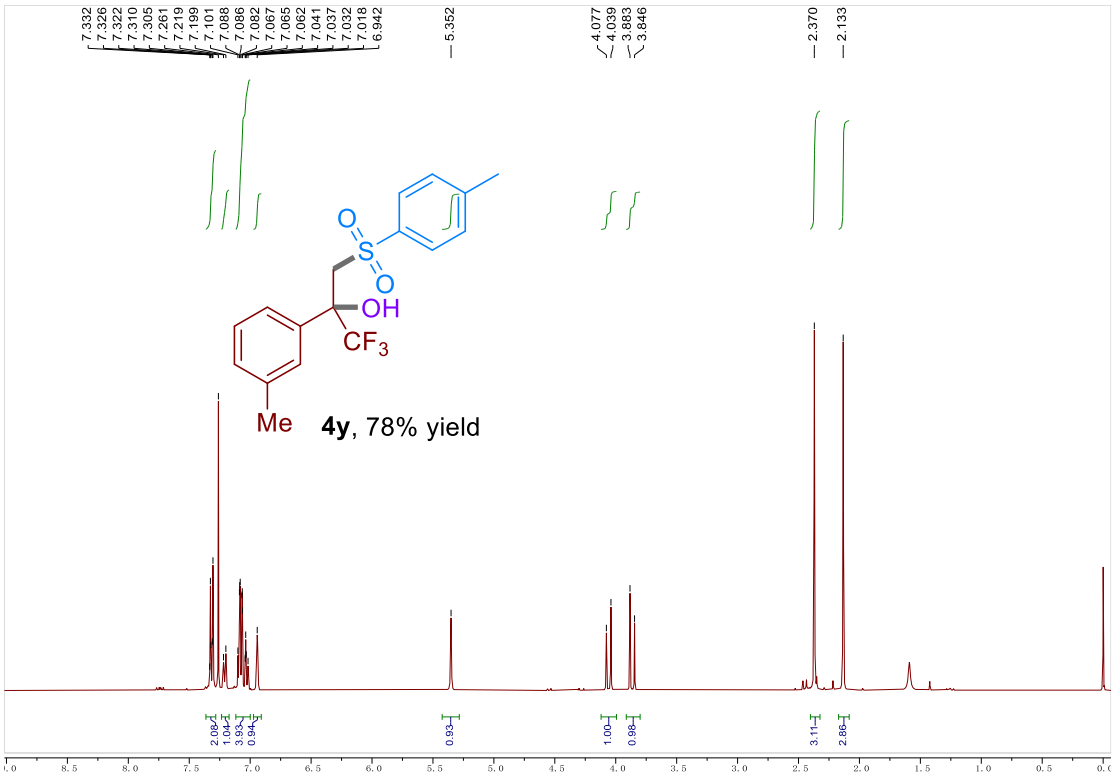
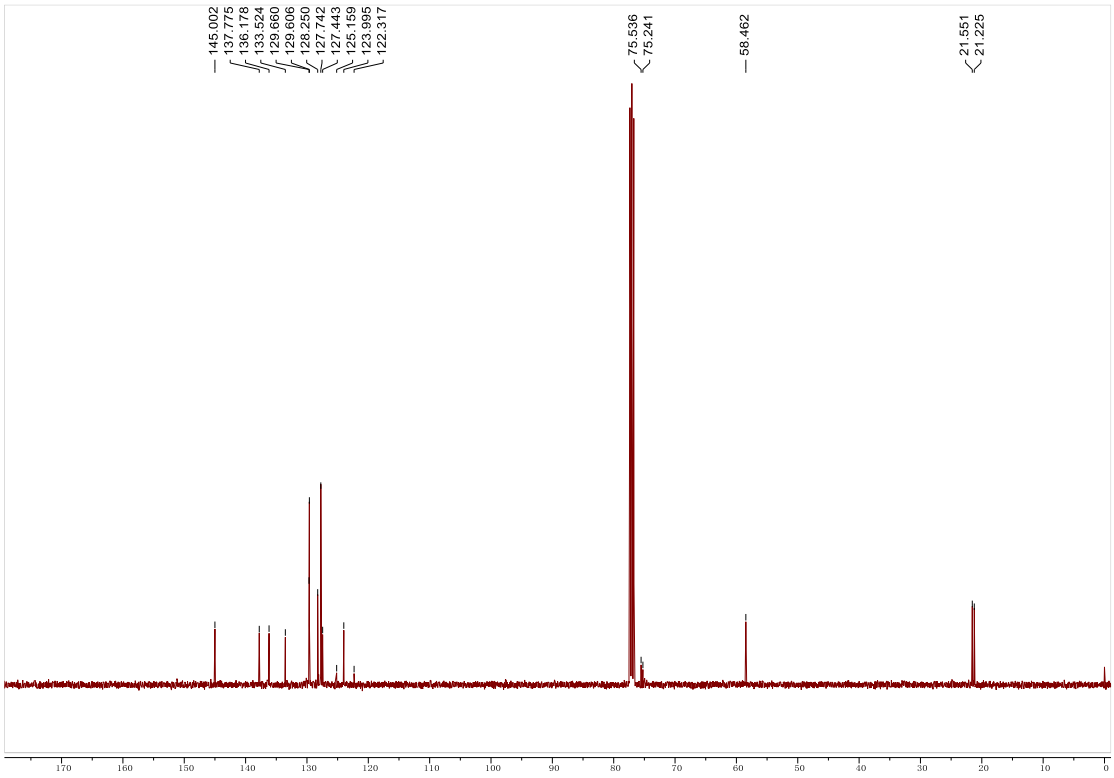
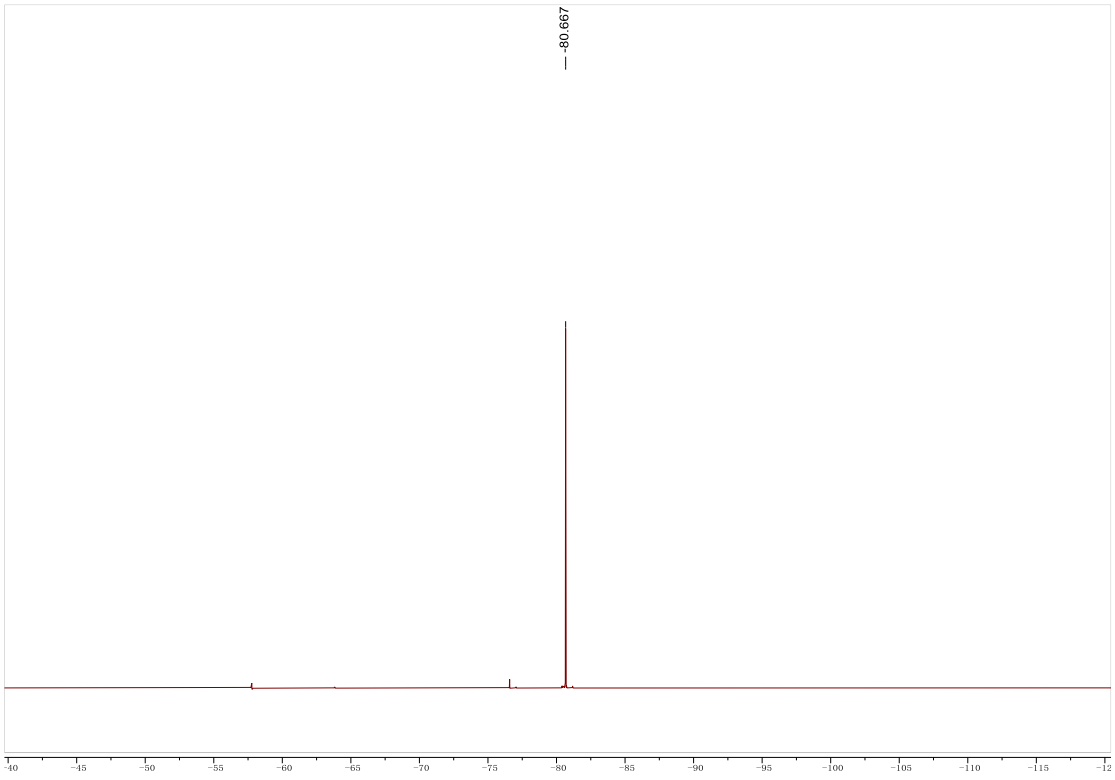
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115

^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 4y






−80.667
−40
−45
−50
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115
−12

^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F NMR (375 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of product 3aa