Supporting Information

Electrochemical Heterodifunctionalization of α-CF_3 Alkenes to Access α-Trifluoromethyl-β-sulfonyl Tertiary Alcohols

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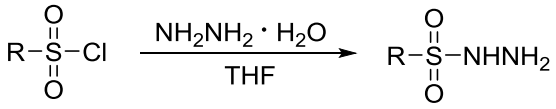
1. General Experimental Informations

Unless otherwise noted, all the reagents were purchased from commercial suppliers and used without further purification. ^{1}H NMR spectra were recorded at 400 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 MHz with complete proton decoupling. ^{19}F NMR data were collected at 376 MHz with complete proton decoupling. Infrared spectra (IR) were measured by FT-IR apparatus. 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. The instrument for electrolysis is DC power supply (Hong Sheng DPS-305CF, made in China). Melting point of all compounds were measured by micro melting point apparatus (WRX-4). Cyclic Voltammetry (CV) experiments were recorded on a CHI650D electrochemical workstation. Column chromatography was carried out on silica gel (200-300 mesh).

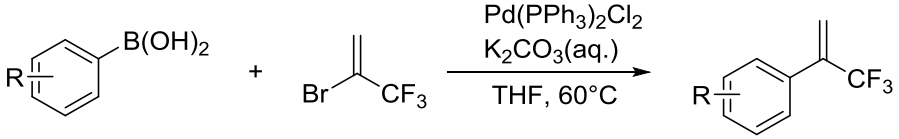
2. Preparation of Sulfonyl Hydrazines and Trifluoromethyl Alkenes

2.1 General procedure for the preparation of sulfonyl hydrazines 2a-2p



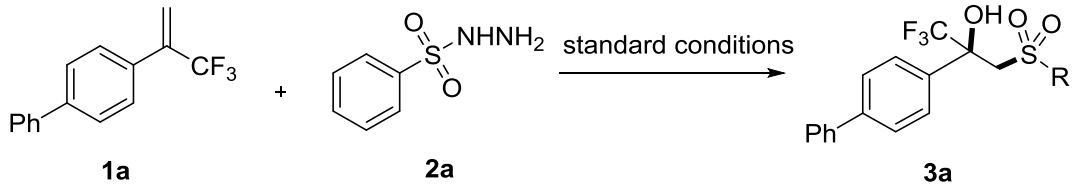
Sulfonyl hydrazides **2** were prepared according to reported synthetic procedures.[1] The hydrazine monohydrate (60.0 mmol) was added dropwise into the solution of sulfonyl chloride (20.0 mmol) in THF (100 mL) under argonatmosphere at 0 ℃. Subsequently, the mixture was further stirred at 0 ℃ for 30 minutes. After the completion of the reaction, the solvent was removed by evaporation, and the residue was extracted with dichloromethane (3 x 20 mL), and the combined organic layer was dried over Na_2SO_4. Concentration in vacuum followed by silica gel column purification with petroleum ether/ethyl acetate eluent gave the desired product.

2.2 General procedure for the preparation of trifluoromethyl alkenes 1a-1o



Trifluoromethyl alkenes **1** were prepared according to reported synthetic procedures.[2] To a two-necked flask 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 into aqueous K_2CO_3 (2.0 M, 20 mL) and THF (30.0 mL). The vessel was evacuated and filled with argon atmosphere (three times). Then, 2-bromo-3,3,3-trifluoropropene (2.0 equiv., 20.0 mmol, 2.1 mL) was added and the solution was stirred at 60 ℃ for 12 hours. The reaction mixture was extracted with dichloromethane and the combined organic layer was dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography to afford the corresponding trifluoromethyl alkenes (PE/EA=100:1).

2.3 General procedure for the synthesis of compound 3a-3p and 3aa-3an



(Using the synthesis of 3a as an example). An undivided cell was equipped with a graphite rod (d: 6 mm) and a platinum plate (1 × 1 cm) and connected to a DC regulated power supply. To the cell was added trifluoromethyl alkene **1a** (0.3 mmol), sulfonyl hydrazides **2a** (3.6 mmol), KI (1.2mmol) and 5.0 mL solvent (CH_3CN:H_2O=6:1). The mixture was electrolyzed using constant voltage conditions (4.0V) at room temperature under magnetic stirring. When TLC analysis indicated that the electrolysis was complete (witnessed by the disappearance of the **2a**), the solvent was removed under reduced pressure. The residue was purified by column

chromatography on silica gel using a mixture of petroleum ether/EtOAc (v:v = 24:1) as eluent to afford the desired pure product **3a**. The pictures of reaction set-up were shown in Figure S1.

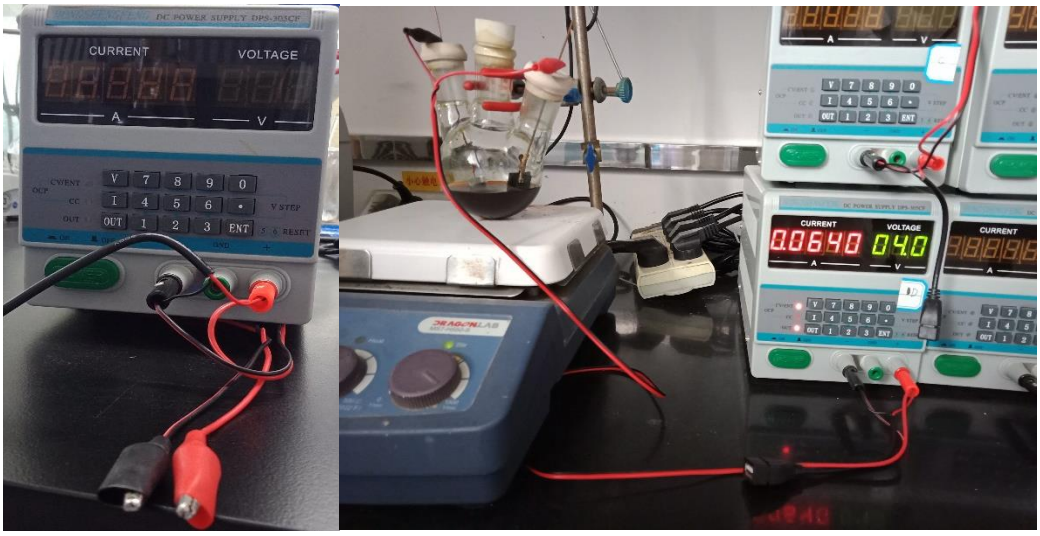


Figure S1. Instrument for electrolysis

2.4 Scale-up reaction

An undivided cell was equipped with a graphite plate (2 × 2 cm) and a platinum plate (2 × 2 cm) and connected to a DC regulated power supply. To the cell was added trifluoromethyl alkene **1a** (3.0 mmol), sulfonyl hydrazides **2a** (36.0 mmol), KI (12.0 mmol) and 50.0 mL solvent (CH_3CN:H_2O = 6:1) were added. The mixture was electrolyzed using constant voltage conditions 4.0V (I = 40 ~ 60 mA) at room temperature under magnetic stirring. When TLC analysis indicated that the electrolysis was complete (witnessed by the disappearance of the **2a**), the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether/EtOAc (v:v = 24:1) as eluent to afford the desired pure product **3a** in 63% yield.

3. Detailed Optimization of Reaction Conditions

3.1 Solvent screening[a]

Entry	Solvent	Yield **3a**[b] (%)	Entry	Solvent	Yield **3a**[b] (%)
1	CH_3CN/H_2O(9:1)	90%	9	1,4-dioxane/H_2O(6:1)	40%
2[c]	CH_3CN/H_2O(9:1)	73%	10	DCM/H_2O(6:1)	ND
3	CH_3CN/H_2O(6:1)	94%	11	MeOH/H_2O(6:1)	25%
4	CH_3CN/H_2O(4:1)	83%	12	THF/H_2O(6:1)	trace
5	CH_3CN/H_2O(2:1)	89%	13	$PhCH_3/H_2O$(6:1)	NR
6	CH_3CN/H_2O(1:1)	78%	14	DMF/H_2O(6:1)	trace
7	H_2O	0%	15	DMSO/H_2O(6:1)	trace
8	CH_3CN	59%			

[a]Reaction conditions: C anode (d: 6 mm), Pt cathode (10 mm×10 mm×0. 2 mm), constant potential = 4.0 V (*I* = 20 ~ 30 mA), **1a** (0.3 mmol, 1.0 equiv), **2a** (3.6 mmol, 12.0 equiv), KI (1.2 mmol, 4.0 equiv), solvent 5.0 mL, room temperature, 36 h. [b] Isolated yields. [c]**2a** (1.8 mmol, 6.0 equiv),

3.2 Electrodes screening and control experiments[a]

Entry	+/-	Yield **3a**[b] (%)	Entry	+/-	Yield **3a**[b](%)
1	C-Ni	60%	7[e]	C-Pt	86%
2	C-Fe	72%	8[f]	C-Pt	85%
3	Pt-Pt	39%	9[g]	C-Pt	54%
4	C-C	81%	10[h]	C-Pt	30%
5[c]	C-Pt	70%	11[i]	C-Pt	0%
6[d]	C-Pt	87%	-	-	-

[a]Reaction conditions: C anode (d: 6 mm), Pt cathode (10 mm×10 mm×0. 2 mm), constant potential = 4.0 V (*I* = 20 ~ 30 mA), **1a** (0.3 mmol, 1.0 equiv), **2a** (3.6 mmol, 12.0 equiv), KI (1.2 mmol, 4.0 equiv), solvent 5.0 mL (CH_3CN:H_2O = 6:1), room temperature, 36 h. [b] Isolated yields. [c]Under argon atmosphere. [d]Under oxygen atmosphere. [e] potential = 2.0 v. [f] potential = 6.0 v. [g]0.15 mmol of **1a** was used. [h]0.6 mmol

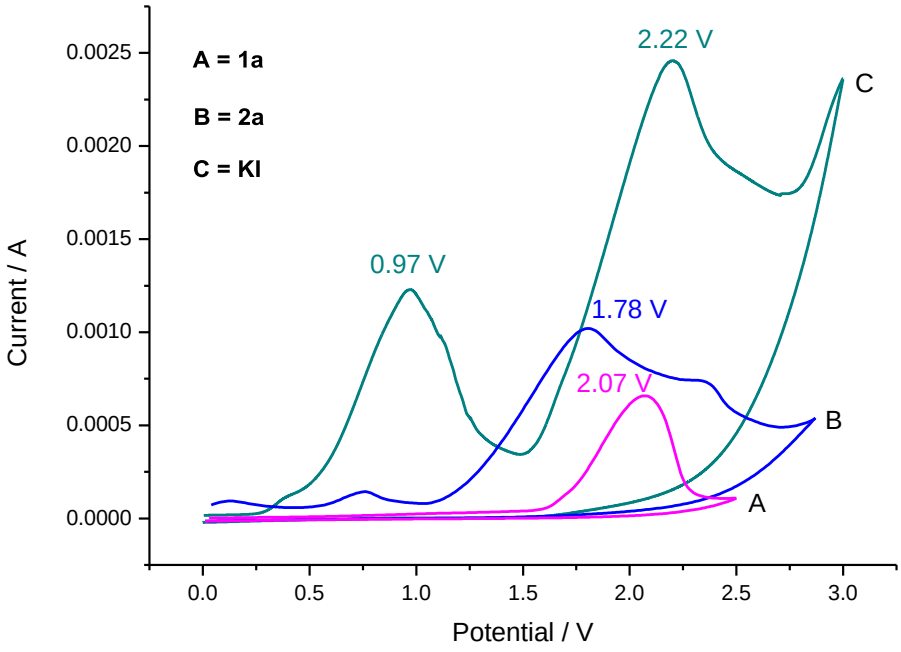
of **1a** was used. [i] without current.

3.3 Electrolyte screening

Entry	Electrolyte	Yield **3a**[b] (%)
1	NaBr	65%
2	$LiClO_4$	38%
3	nBu_4BF_4	62%
4	nBu_4NPF_6	58%
5	NaI	67%
6	-	68%
7[c]	KI	91%
8[d]	KI	90%
9[e]	KI	68%
10[f]	KI	85%
11[g]	KI	72%
12[h]	KI	73%
13[i]	KI	65%
14[j]	KI	68%
15[k]	KI	70%

[a]Reaction conditions: C anode (d: 6 mm), Pt cathode (10 mm×10 mm×0. 2 mm), constant potential = 4.0 V (I = 20 ~ 30 mA), **1a** (0.3 mmol, 1.0 equiv), **2a** (3.6 mmol, 12.0 equiv), electrolyte (1.2 mmol, 4.0 equiv), solvent 5.0 mL (CH_3CN:H_2O = 6:1), room temperature, 36 h. [b] Isolated yields. [c] 2.0 equiv of KI was used. [d] 8.0 equiv of KI was used.[e] controlled current = 10 mA, [f] controlled current = 25 mA, [g] controlled current = 50 mA. [h] catalyst (Cp_2Fe 5 mol%), [i] catalyst (NHPI-OH 5 mol%), [j] 50 °C, [k] 80 °C

4. Cyclic Voltammetry Studies[3]



FigureS2. Cyclic voltammograms in an electrolyte solution of nBu$_4$NBP$_6$ (0.1 M) in MeCN/H$_2$O (6:1) using a glassy carbon disk working electrode (diameter, 3 mm), Pt disk and Ag/AgCl as counter and reference electrode at 100 mV/s scan rate: (A) **1a** (10 mM); (B) **2a** (120 mM); (C) KI (40 mM);

5. Trapping Experiment

An undivided cell was equipped with a graphite rod (d: 6 mm) and a platinum plate (1×1 cm) and connected to a DC regulated power supply. To the cell was added trifluoromethyl alkene **1a** (0.3 mmol), sulfonyl hydrazides **2a** (3.6 mmol), KI (1.2 mmol), TEMPO (12.0 equiv) and 5.0 mL solvent (CH_3CN:H_2O = 6:1) were added. The mixture was electrolyzed using constant voltage conditions (4.0 V) at room temperature under magnetic stirring.In order to ensure whether the involved radicals were trapped by TEMPO, ESI-MS analysis of the crude reaction mixture was performed (Figure S3). The resulting mass spectrum clearly shows a peak corresponding to the coupled product between TEMPO radical and the corresponding radical derived from 1a (HRMS (ESI): $C_{15}H_{23}NNaO_3S^+$ $[M+Na]^+$ Calcd 320.1291, Found 320.1278).

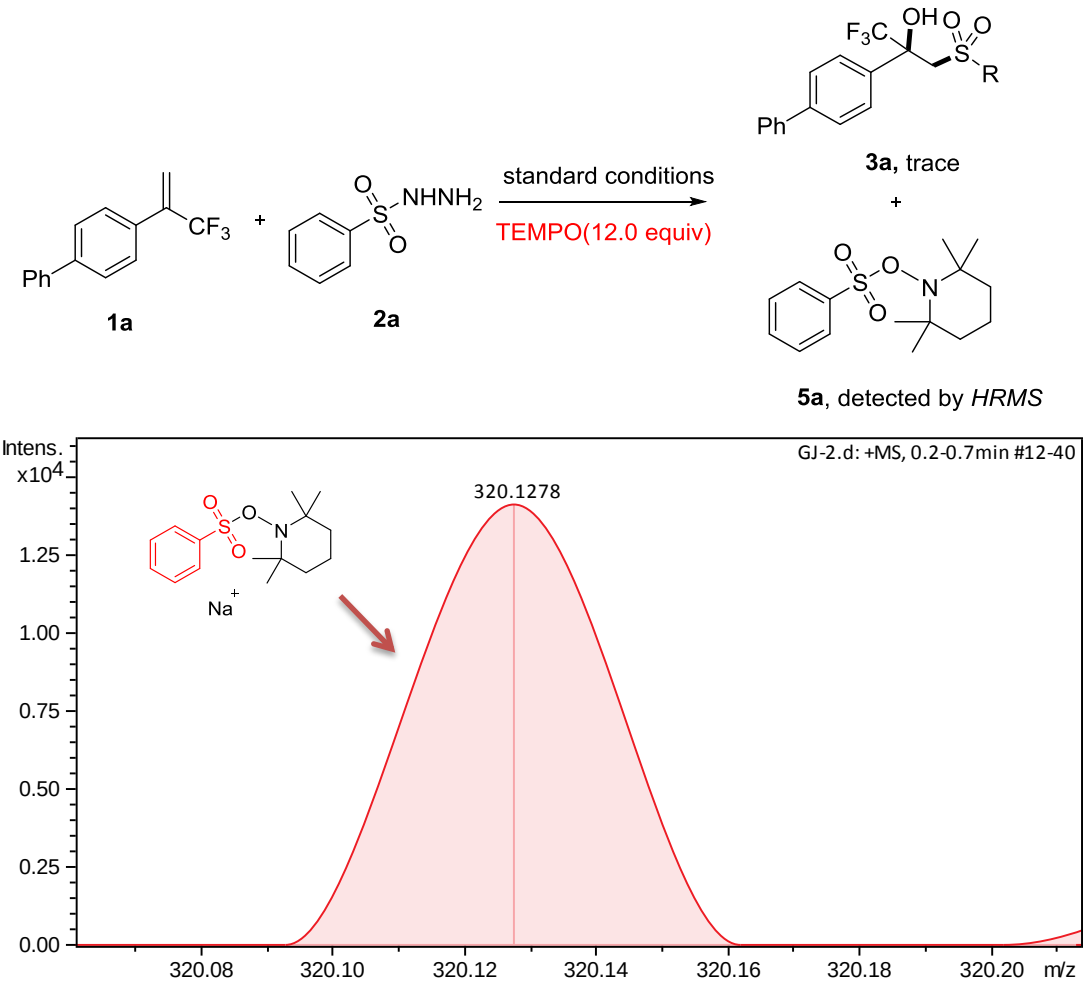


Figure S3. Crude ESI-MS of the TEMPO-trapping experiment described above.

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

An undivided cell was equipped with a graphite rod (d: 6 mm) and a platinum plate (1 ×1 cm) and connected to a DC regulated power supply. To the cell was added trifluoromethyl alkene **1a** (0.3 mmol), sulfonyl hydrazides **2a** (3.6 mmol), KI (1.2 mmol) and 5.0 mL solvent (CH_3CN:$H_2{}^{18}O$ = 6:1) or (CH_3CN:D_2O = 6:1) were added. The mixture was electrolyzed using constant voltage conditions (4.0 V) at room temperature under magnetic stirring.ESI-MS analysis of the crude reaction mixture was performed (Figure S4). The resulting mass spectrum clearly shows two peaks corresponding to the product **3a** (HRMS (ESI): $C_{21}H_{17}F_3NaO_3S^+$ $[M+Na]^+$ Calcd 429.0743, Found 429.0727)and ^{18}O-labelled product (HRMS (ESI): $C_{21}H_{17}F_3NaO_2{}^{18}OS^+$ $[M+Na]^+$ Calcd 431.0785, Found 431.0756).

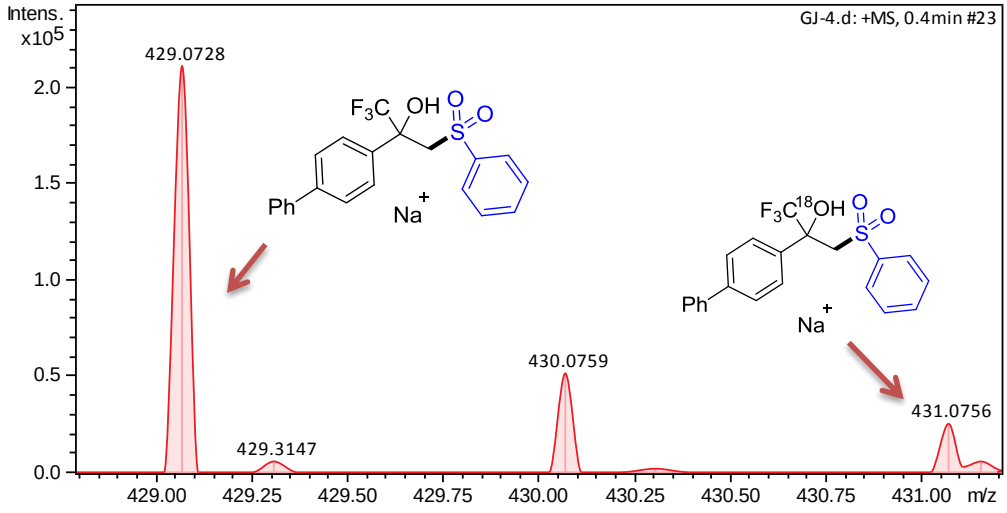


Figure S4. Crude HRMS of the $H_2{}^{18}O$-labellingexperiment described above.

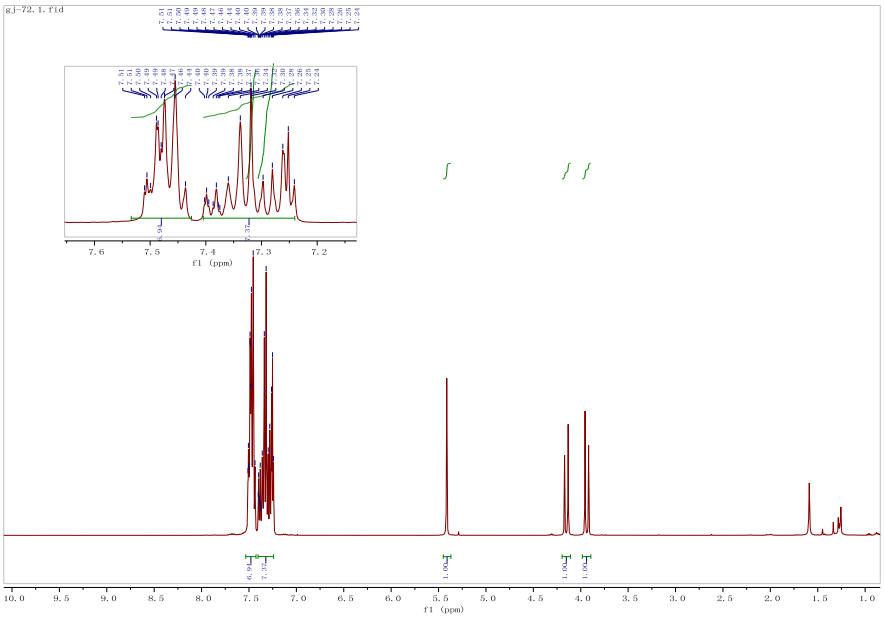


Figure S5. ^1H NMR of the D_2O-labellingexperiment described above.

7. Analyzing the reaction mixture by HRMS

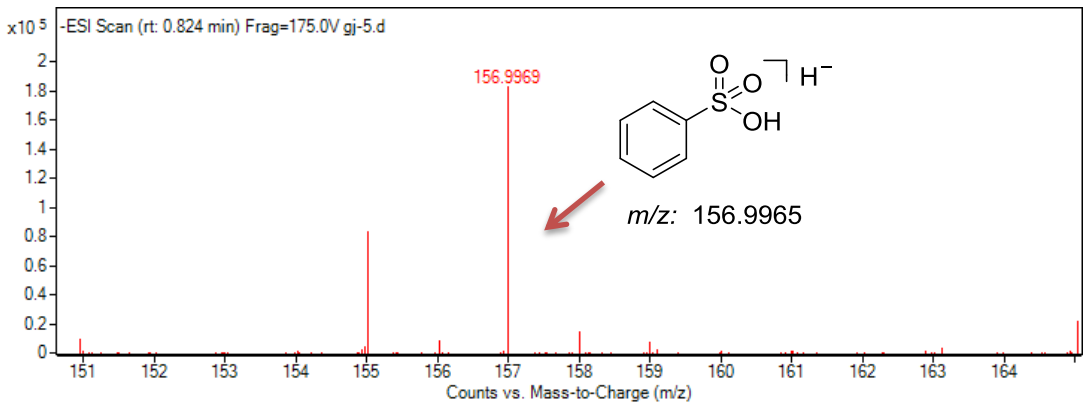


Figure S6. Crude HRMS of the reaction mixture at the end of the reaction

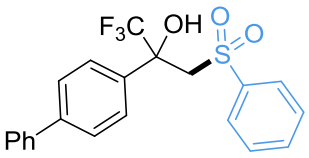
Reference

1.X. Q. Kong, *et al.,* Asian J. Org. Chem., 2020, **9,** 1760-1764.

2.P. J. Xia, *et al., Angew. Chem. Int. Ed.*, 2020, **59**, 6706-6710.

3. Z. Y. Mo, *et al., Adv. Synth. Catal.*,2020, **362**, 2160-2167.

8. Characterization data of compounds 3a-3p, 3aa-3an.



3a, 114.5 mg, (Petroleum ether/EtOAc = 24:1 – 12:1), yellow solid, yield 94%;

m.p. 152 – 153℃;

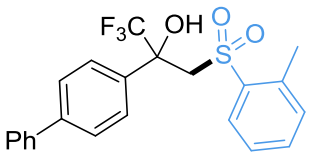
IR (neat) *v* 3445, 2930, 1324, 1309, 1252, 1178, 833, 785 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.41 (m, 7H), 7.40 – 7.32 (m, 3H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 5.43 (s, 1H), 4.16 (d, *J* = 15.0 Hz, 1H), 3.94 (d, *J* = 15.0 Hz, 1H) ppm;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.57 ppm;

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.9, 140.0, 139.1, 133.7, 132.5, 129.2, 129.0, 127.9, 127.8, 127.2, 127.0, 126.9,123.8 (q, $^{1}J_{C\text{-}F}$ = 285.5 Hz), 75.4 (q, $^{2}J_{C\text{-}F}$ = 29.9 Hz), 58.7 ppm;

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{17}F_3NaO_3S^+$ 429.0743; Found 429.0727.



3b, 88.2 mg, (Petroleum ether/EtOAc = 24:1 – 12:1), yellow solid, yield 70%;

m.p. 140 – 142 ℃;

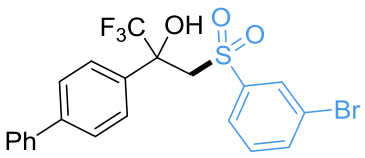
IR (neat) *v* 3465, 2929, 1324, 1285, 1250, 1148, 832, 788 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 4H), 7.38 – 7.32 (m, 4H), 7.32 – 7.25 (m, 3H), 7.19 (d, *J* = 7.5 Hz, 1H), 6.93 (t, *J* = 7.8 Hz, 1H), 5.45 (s, 1H), 4.19 (d, *J* = 15.0 Hz, 1H), 3.91 (d, *J* = 15.0 Hz, 1H), 2.66 (s, 3H) ppm;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.48 ppm;

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.9, 140.0, 137.3, 137.2, 133.8, 132.5, 129.9, 128.9, 127.8, 127.0, 126.9, 126.8, 126.7, 123.8 (q, $^{3}J_{C\text{-}F}$ = 285.4 Hz), 75.6 (q, $^{2}J_{C\text{-}F}$ = 29.8 Hz), 57.5, 20.3 ppm;

HRMS (ESI) m/z: $[M+K]^+$ Calcd for$C_{22}H_{19}F_3KO_3S^+$459.0639; Found 459.0655.



3c, 74.1 mg, (Petroleum ether/EtOAc = 24:1 – 12:1), yellow solid, yield 51%;

m.p. 117 – 119 ℃;

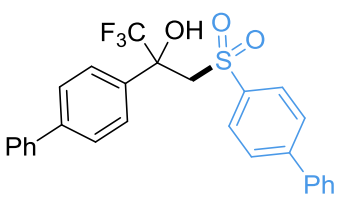
IR (neat) *v* 3471, 2930, 1326, 1288, 1251, 1184, 834, 762 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.51(m, 4H), 7.49 – 7.41 (m, 4H), 7.40 –7 .33 (m, 4H), 7.14 (t, *J* = 7.8 Hz, 1H), 5.24 (s, 1H), 4.17 (d, *J* = 15.1 Hz, 1H), 3.95 (d, *J* = 15.1 Hz, 1H) ppm;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.65 ppm; .

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.1, 140.7, 139.8, 136.8, 132.1, 131.1, 130.6, 128.9, 127.9, 127.2, 127.1, 126.9, 126.3, 123.7 (q, $^{1}J_{C\text{-}F}$ = 285.6 Hz), 123.1, 75.2 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz), 58.7 ppm;

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for$C_{21}H_{16}BrF_3NaO_3S^+$506.9848; Found 506.9861.



3d, 114.2 mg, (Petroleum ether/EtOAc = 24:1 – 12:1), white solid, yield 79%;

m.p. 193 – 194 ℃;

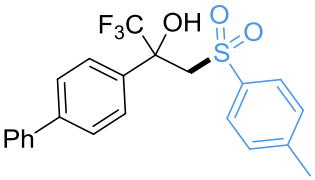
IR (neat) *v* 3466, 2928, 1324, 1247, 1149, 1109, 834, 720 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H), 7.40 – 7.35 (m, 5H), 7.35 – 7.25 (m, 11H), 5.44 (s, 1H), 4.20 (d, J = 15.1 Hz, 1H), 3.96 (d, J = 15.1 Hz, 1H) ppm;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.75 ppm;

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 146.8, 141.9, 139.7, 138.6, 137.3, 132.4, 129.1, 128.9, 128.8, 128.2, 127.8, 127.6, 127.3, 127.3, 127.1, 126.7, 123.8 (q, $^{1}J_{C\text{-}F}$ = 285.5 Hz), 75.3 (q, $^{2}J_{C\text{-}F}$ = 29.9 Hz) , 58.7 ppm;

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for$C_{27}H_{21}F_3NaO_3S^+$505.1056; Found 505.1078.



3e, 94.5 mg, (Petroleum ether/EtOAc = 24:1 – 12:1), white solid, yield 75%;

m.p. 153 – 155 ℃;

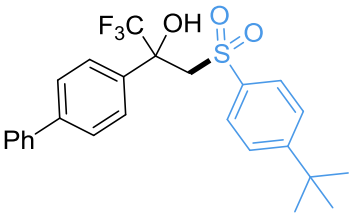
IR (neat) *v* 3383, 2924, 1313, 1301, 1253, 1148, 832, 735 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.41 (m, 4H), 7.41 – 7.28 (m, 7H), 7.02 (d, J = 8.0 Hz, 2H), 5.47 (s, 1H), 4.12 (d, J = 15.0 Hz, 1H), 3.90 (d, J = 15.0 Hz, 1H), 2.23 (s, 3H) ppm;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.62 ppm;

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.1, 141.8, 139.9, 136.1, 132.5, 129.7, 128.9, 127.9, 127.8, 127.3, 127.0, 126.7, 123.8 (q, $^{3}J_{C\text{-}F}$ = 285.5 Hz), 75.3 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz), 58.5, 21.5 ppm;

HRMS (ESI) m/z: $[M+K]^+$ Calcd for$C_{22}H_{19}F_3KO_3S^+$459.0639; Found 459.0667.



3f, 99.2 mg, (Petroleum ether/EtOAc = 24:1 – 12:1), yellow solid, yield 72%;

m.p. 174 – 175 ℃;

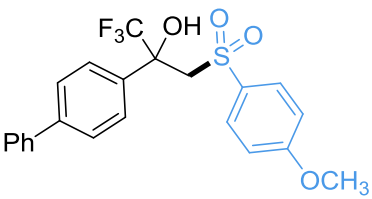
IR (neat) *v* 3466, 2930, 1323, 1251, 1152, 1106, 827, 735 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.39 – 7.29 (m, 7H), 7.25 – 7.20 (m, 2H), 5.48 (s, 1H), 4.14 (d, J = 15.0 Hz, 1H), 3.92 (d, J = 15.0 Hz, 1H), 1.08 (s, 9H) ppm;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.62 ppm;

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.2, 141.8, 139.8, 136.1, 132.6, 128.9, 127.9, 127.5, 127.3, 127.0, 126.6, 126.1, 123.8 (q, $^{1}J_{C\text{-}F}$ = 285.4 Hz), 75.4 (q, $^{2}J_{C\text{-}F}$ = 29.9 Hz), 58.6, 35.0, 30.7 ppm;

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for$C_{25}H_{25}F_3NaO_3S^+$485.1369; Found 485.1378.



3g, 119.0 mg, (Petroleum ether/EtOAc = 24:1 – 12:1), yellow solid, yield 91%;

m.p. 112 – 113 ℃;

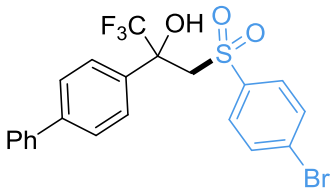
IR (neat) *v* 3458, 2932, 1325, 1264, 1249, 1163, 862, 734 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.50(m, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.40 – 7.28 (m, 7H), 6.63 (d, J = 8.9 Hz, 2H), 5.48 (s, 1H), 4.11 (d, J = 15.0 Hz, 1H), 3.90 (d, J = 15.0 Hz, 1H), 3.56 (s, 3H) ppm;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.70 ppm;.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.9, 141.7, 139.9, 132.6, 130.3, 130.0, 129.0, 127.9, 127.3, 126.9, 126.7, 123.8 (q, $^{1}J_{C\text{-}F}$ = 285.4 Hz), 114.3, 75.3 (q, $^{2}J_{C\text{-}F}$ = 29.8 Hz), 58.5, 55.5 ppm;

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{19}F_3NaO_4S^+$ 459.0848; Found 459.0856.



3h, 116.2 mg, (Petroleum ether/EtOAc = 24:1 – 12:1), white solid, yield: 80%;

m.p. 151 – 152 ℃;

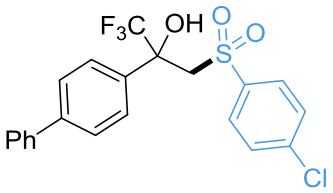
IR (neat) v 3470, 2924, 1322, 1289, 1250, 1153, 829, 738 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.53 (m, 2H), 7.48 – 7.44 (m, 2H), 7.41 – 7.32 (m, 7H), 7.29 – 7.25 (m, 2H), 5.30 (s, 1H), 4.15 (d, J = 15.1 Hz, 1H), 3.94 (d, J = 15.1 Hz, 1H) ppm;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.61 ppm;

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.3, 139.7, 138.0, 132.4, 132.2, 129.4, 129.3, 129.0, 128.0, 127.2, 127.2, 126.9, 123.7 (q, $^{1}J_{C\text{-}F}$ = 285.6 Hz), 75.2 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz), 58.8 ppm;

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{16}BrF_3NaO_3S^+$ 506.9848; Found 506.9859.



3i, 110.9 mg, (Petroleum ether/EtOAc = 24:1 – 12:1), pale yellow solid, yield 84%;

m.p. 156 – 157 ℃;

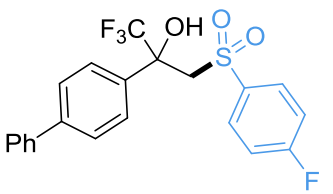
IR (neat) v 3457, 2924, 1324, 1250, 1223, 1149, 831, 824 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 2H), 7.49 – 7.41 (m, 2H), 7.41 – 7.24 (m, 7H), 7.24 – 7.15 (m, 2H), 4.74 (s, 1H), 4.15 (d, J = 15.1 Hz, 1H), 3.94 (d, J = 15.1 Hz, 1H) ppm;.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.61 ppm;

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.3, 140.7, 139.7, 137.4, 132.2, 129.4, 129.3, 129.0, 128.0, 127.2, 127.1, 126.9, 123.7 (q, $^{1}J_{C\text{-}F}$ = 285.5 Hz), 75.2 (q, $^{2}J_{C\text{-}F}$ = 30.1 Hz), 58.8 ppm;

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{16}ClF_3NaO_3S^+$ 463.0353; Found 463.0345.



3j, 108.1 mg, (Petroleum ether/EtOAc = 24:1 – 12:1), yellow solid, yield 85%;

m.p. 156 – 158℃;

IR (neat) v 3508, 2929, 1326, 1289, 1250, 1226, 858, 836 cm^{-1};

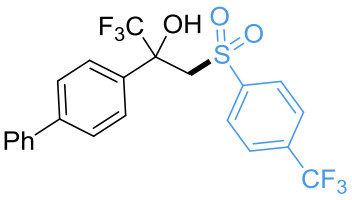
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 6H), 7.41 – 7.32 (m,

5H), 6.93 (t, *J* = 8.5 Hz, 2H), 5.32 (s, 1H), 4.14 (d, *J* = 15.1 Hz, 1H), 3.94 (d, *J* = 15.1 Hz, 1H) ppm;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.65, -101.98 ppm;

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.8 (d, $^{1}J_{C\text{-}F}$ = 257.9 Hz), 142.2, 139.8, 135.1 (d, $^{4}J_{C\text{-}F}$ = 3.3 Hz), 132.3, 130.8 (d, $^{3}J_{C\text{-}F}$ = 9.9 Hz), 129.0, 128.0, 127.2, 127.0, 127.0, 123.7 (q, $^{1}J_{C\text{-}F}$ = 285.7 Hz), 116.5 (d, $^{3}J_{C\text{-}F}$ = 22.9 Hz), 75.3 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz), 58.8 ppm;

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for$C_{21}H_{16}F_4NaO_3S^+$447.0648; Found 447.0635.



3k, 108.1 mg, (Petroleum ether/EtOAc = 24:1 – 12:1), pale yellow solid, yield 76%;

m.p. 139 – 140 ℃;

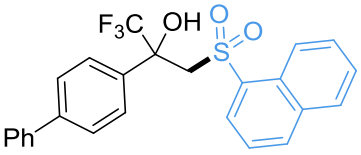
IR (neat) *v* 3496, 2930, 1322, 1250, 1155, 1123, 831, 774 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.53 – 7.44 (m, 6H), 7.43 – 7.38 (m, 1H), 7.33 (s, 4H), 5.24 (s, 1H), 4.19 (d, *J* = 15.2 Hz, 1H), 3.99 (d, *J* = 15.2 Hz, 1H) ppm;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -63.33, -80.44 ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 142.3, 139.4, 135.4 (q, $^{2}J_{C\text{-}F}$ = 33.2 Hz), 132.2, 129.0, 128.5, 128.0, 127.2, 126.9, 126.8, 126.2 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 123.7 (q, $^{1}J_{C\text{-}F}$ = 285.5 Hz), 122.8 (q, $^{1}J_{C\text{-}F}$ = 273.4 Hz), 75.2 (q, $^{2}J_{C\text{-}F}$ = 30.1 Hz), 59.0 ppm;

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for$C_{22}H_{16}F_6NaO_3S^+$497.0617; Found 497.0614.



3l, 104.0 mg, (Petroleum ether/EtOAc = 24:1 – 12:1), yellow solid, yield 76%;

m.p. 151 – 153 ℃;

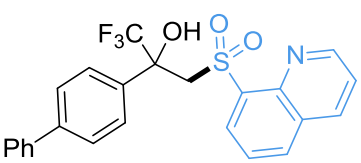
IR (neat) *v* 3490, 3064, 2928, 1315, 1152, 1120, 835, 762 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.6 Hz, 1H), 7.91 – 7.85 (m, 2H), 7.77 (m, 1H), 7.66 – 7.57 (m, 2H), 7.47 – 7.35 (m, 5H), 7.10 – 6.98 (m, 5H), 5.47 (s, 1H), 4.44 (d, *J* = 15.0 Hz, 1H), 4.05 (d, *J* = 15.0 Hz, 1H) ppm;.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.59 ppm;

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.5, 139.9, 135.2, 133.9, 133.4, 132.2, 131.0, 129.6, 129.4, 128.9, 128.1, 127.8, 127.2, 126.9, 126.7, 126.4, 124.3, 123.8 (q, $^{1}J_{C\text{-}F}$ = 285.4 Hz), 123.0, 75.4 (q, $^{2}J_{C\text{-}F}$ = 29.9 Hz), 57.4 ppm;

HRMS (ESI) m/z: $[M+K]^+$ Calcd for$C_{25}H_{19}F_3KO_3S^+$495.0639; Found 495.0640.



3m, 89.1 mg, (Petroleum ether/EtOAc = 24:1 – 12:1), yellow solid, yield 65%;

m.p. 141 – 142 ℃;

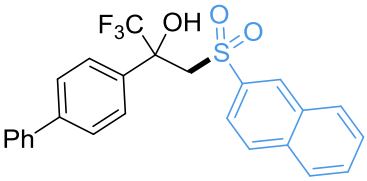
IR (neat) *v* 3478, 2929, 1315, 1248, 1152, 1121, 800, 734 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 8.6 Hz, 1H), 7.92 – 7.83 (m, 2H), 7.79 – 7.74(m, 1H), 7.65 – 7.56 (m, 2H), 7.49 – 7.25 (m, 5H), 7.07 – 6.99 (m, 4H), 4.44 (d, J = 15.0 Hz, 1H), 4.06 (d, J = 15.0 Hz, 1H) ppm;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.59 ppm;

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.5, 139.9, 135.2, 133.9, 133.4, 132.2, 131.0, 129.6, 129.4, 128.9, 127.8, 127.2, 126.9, 126.7, 126.4, 124.3, 123.8 (q, $^{1}J_{C\text{-}F}$ = 285.1 Hz), 123.1, 75.5 (q, $^{2}J_{C\text{-}F}$ = 29.8 Hz), 57.4 ppm;

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for$C_{24}H_{18}F_3NNaO_3S^+$480.0852; Found 480.0877.



3n, 106.7 mg, (Petroleum ether/EtOAc = 24:1 – 12:1), yellow solid, yield 78%;

IR (neat) v 3454, 3057, 2935, 1321, 1289, 1252, 1141, 810 cm^{-1};

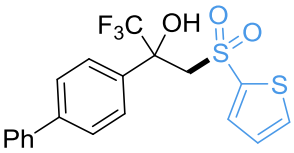
m.p. 110 – 112℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 1.9 Hz, 1H), 7.78 (t, J = 8.7 Hz, 2H), 7.63 (d, J = 8.4 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.39 (m, 1H), 7.32 (m, 5H), 7.13 – 7.02 (m, 4H), 5.49 (s, 1H), 4.24 (d, J = 15.1 Hz, 1H), 3.99 (d, J = 15.1 Hz, 1H) ppm;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.75 ppm;

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.8, 139.4, 135.6, 135.0, 132.2, 131.7, 130.4, 129.6, 129.6, 129.4, 128.5, 127.9, 127.7, 127.7, 127.1, 126.9, 126.5, 123.7 (q, $^{1}J_{C\text{-}F}$ = 285.6 Hz), 121.7, 75.4 (q, $^{2}J_{C\text{-}F}$ = 29.9 Hz), 58.3 ppm;

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for$C_{25}H_{19}F_3NaO_3S^+$479.0899; Found 479.0882.



3o, 80.3 mg, (Petroleum ether/EtOAc = 24:1 – 12:1), yellow solid, yield 65%;

m.p. 135 – 137℃;

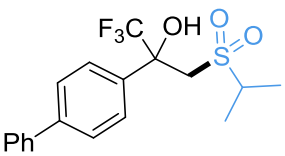
IR (neat) v 3475, 2932, 1326, 1300, 1250, 1147, 852, 732 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 3H), 7.48 – 7.38 (m, 7H), 7.13 (dd, J = 3.8, 1.4 Hz, 1H), 6.80 (dd, J = 4.9, 3.8 Hz, 1H), 5.28 (s, 1H), 4.24 (d, J = 15.0 Hz, 1H), 4.02 (d, J = 15.0 Hz, 1H) ppm;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.54 ppm;

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.0, 140.0, 139.9, 135.2, 135.1, 132.5, 129.0, 127.9, 127.9, 127.1, 127.0, 127.0, 123.7 (q, $^{1}J_{C\text{-}F}$ = 285.6 Hz), 75.5 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz), 59.9 ppm;

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for$C_{19}H_{15}F_3NaO_3S_2^+$435.0307; Found 435.0309.



3p, 51.3 mg, (Petroleum ether/EtOAc = 24:1 – 12:1), white solid, yield 46%;

m.p. 112 – 113 ℃;

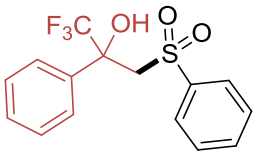
IR (neat) *v* 3465, 2992, 1305, 1251, 1226, 1192, 1125, 764 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.66 (m, 4H), 7.65 – 7.59 (m, 2H), 7.48 – 7.42 (m, 2H), 7.41 – 7.32 (m, 1H), 5.42 (s, 1H), 3.93 (d, *J* = 14.7 Hz, 1H), 3.68 (d, *J* = 14.8 Hz, 1H), 2.72 (p, *J* = 6.8 Hz, 1H), 1.32(d, *J* = 6.8 Hz, 3H),1.29 (d, *J* = 6.8 Hz, 3H) ppm;.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.00 ppm;

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.5, 139.9, 133.9, 128.9, 127.9, 127.3, 127.2, 127.0, 123.9 (q, $^{1}J_{C\text{-}F}$ = 285.7 Hz), 75.5 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz), 55.7, 52.1, 15.4, 14.3 ppm;

HRMS (ESI) m/z: $[M+K]^+$ Calcd for$C_{18}H_{19}F_3KO_3S^+$411.0639; Found 411.0654.



3aa, 61.4 mg, (from **1a**, 51.6 mg), (Petroleum ether/EtOAc = 24:1 – 12:1), yellow solid, yield 62%;

m.p. 104 – 106℃;

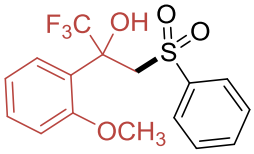
IR (neat) *v* 3448, 2989, 1321, 1274, 1235, 1146, 791, 753 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.46(m, 3H), 7.34 – 7.28 (m, 4H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 2H), 5.36 (s, 1H), 4.10 (d, *J* = 15.0 Hz, 1H), 3.90 (d, *J* = 15.0 Hz, 1H) ppm;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.63 ppm;

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.2, 133.9, 133.6, 129.2, 129.1, 128.3, 127.7, 126.7, 123.7 (q, $^{1}J_{C\text{-}F}$ = 285.5 Hz), 75.5 (q, $^{2}J_{C\text{-}F}$ = 29.9 Hz), 58.5 ppm;

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{13}F_3NaO_3S^+$ 353.0430; Found 353.0460.



3ab, 21.6 mg, (from **1b**, 60.6 mg), (Petroleum ether/EtOAc = 24:1 – 12:1), white solid, yield 20%;

m.p. 97 – 98 ℃;

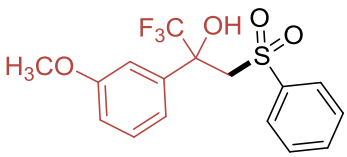
IR (neat) *v* 3467, 2931, 1305, 1288, 1258, 1183, 863, 788 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.9, 1.8Hz, 1H), 7.49 – 7.42 (m, 3H), 7.34 – 7.27 (m, 2H), 7.24 – 7.19 (m, 1H), 7.02 (td, *J* = 7.6, 1.1 Hz, 1H), 6.37 (dd, *J* = 8.3, 1.1 Hz, 1H), 5.64 (s, 1H), 4.97 (d, *J* = 14.7 Hz, 1H), 3.78 (d, *J* = 14.7 Hz, 1H), 3.42 (s, 3H) ppm;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.29 ppm;

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.5, 138.9, 136.6, 133.5, 131.2, 129.9, 129.4, 128.5, 128.1, 127.6, 123.9 (q, $^{1}J_{C\text{-}F}$ = 286.8 Hz), 121.0, 111.2, 75.0 (q, $^{2}J_{C\text{-}F}$ = 30.8 Hz), 56.8, 54.8 ppm; .

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{15}F_3NaO_4S^+$ 383.0535; Found 383.0559.



3ac, 75.6 mg, (from **1c**, 60.6 mg), (Petroleum ether/EtOAc = 24:1 – 12:1), yellow solid, yield 70%;

m.p. 91 – 93 ℃;

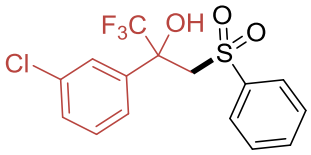
IR (neat) *v* 3398, 2929, 1306, 1256, 1211, 1175, 789, 717 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.44(m, 3H), 7.35 – 7.28 (m, 2H), 7.04 (t, J = 8.0 Hz, 1H), 6.89 – 6.82 (m, 2H), 6.75 (dd, J = 7.8, 3.0 Hz, 1H), 5.38 (s, 1H), 4.08 (d, J = 15.0 Hz, 1H), 3.89 (d, J = 15.0 Hz, 1H), 3.68 (s, 3H) ppm;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.48 ppm;

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.4, 139.1, 135.1, 133.8, 129.3, 129.1, 127.7, 123.7 (q, $^{1}J_{C\text{-}F}$ = 285.5 Hz), 119.0, 114.5, 112.8, 75.4 (q, $^{2}J_{C\text{-}F}$ = 29.9 Hz) , 58.5, 55.1 ppm;

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{15}F_3NaO_4S^+$ 383.0535; Found 383.0565.



3ad, 94.6 mg, (from **1d**, 61.8 mg), (Petroleum ether/EtOAc = 24:1 – 12:1), white solid, yield 41%;

m.p. 128 – 129 ℃;

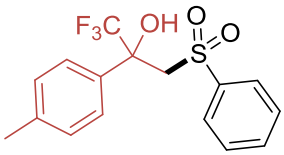
IR (neat) ν 3421, 2941, 1303, 1276, 1251, 1198, 883, 716 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.48 (m, 3H), 7.39 – 7.30(m, 2H), 7.28 (s, 1H), 7.26 – 7.16 (m, 2H), 7.11 (t, J = 7.9 Hz, 1H), 5.41 (s, 1H), 4.04 (d, J = 15.0 Hz, 1H), 3.88 (d, J = 15.0 Hz, 1H) ppm;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.62 ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 135.7, 134.5 , 134.3, 129.5, 129.4, 129.2, 127.7, 127.3, 125.0, 124.0 (q, $^{1}J_{C\text{-}F}$ = 258.1 Hz), 75.1 (q, $^{2}J_{C\text{-}F}$ = 30.1 Hz), 58.0 ppm;

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{12}ClF_3NaO_3S^+$ 387.0040; Found 383.0036.



3ae, 70.2 mg, (from **1e**, 55.8 mg), (Petroleum ether/EtOAc = 24:1 – 12:1), yellow solid, yield 68%;

m.p. 106 – 108 ℃;

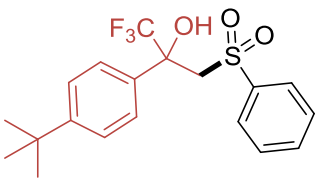
IR (neat) ν 3469, 2981, 1323, 1284, 1177, 1150, 860, 812 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.43 (m, 3H), 7.34 – 7.27 (m, 2H), 7.18 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 8.1 Hz, 2H), 5.30 (s, 1H), 4.09 (d, J = 15.0 Hz, 1H), 3.88 (d, J = 14.9 Hz, 1H), 2.27 (s, 3H) ppm;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.74 ppm;

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.3, 139.0, 133.6, 130.6, 129.0, 128.9, 127.7, 126.6, 123.8 (q, $^{1}J_{C\text{-}F}$ = 285.4 Hz), 75.4 (q, $^{2}J_{C\text{-}F}$ = 29.9 Hz) , 58.7, 21.0 ppm;

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{15}F_3NaO_3S^+$ 367.0586; Found 367.0568.



3af, 90.3 mg, (from **1f**, 68.4 mg), (Petroleum ether/EtOAc = 24:1 – 12:1), yellow solid, yield 78%;

m.p. 109 – 111 ℃;

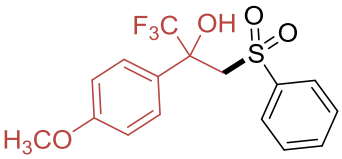
IR (neat) ν 3414, 2930, 1450, 1310, 1254, 1218, 826, 787 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 3H), 7.38 – 7.33 (m, 2H), 7.28 – 7.18 (m, 3H), 7.11 (t, J = 7.9 Hz, 1H), 5.44 (s, 1H), 4.05 (d, J = 15.0 Hz, 1H), 3.88 (d, J = 15.0 Hz, 1H) ppm;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.80 ppm;.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.9, 139.2, 133.7, 130.4, 129.0, 127.8, 126.4, 125.2, 121.1 (q, $^{1}J_{C\text{-}F}$ = 249.4 Hz), 75.3 (q, $^{2}J_{C\text{-}F}$ = 29.8 Hz), 58.4, 34.5, 31.2 ppm;

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{21}F_3NaO_3S^+$ 409.1056; Found 409.1082.



3ag, 89.6 mg, (from **1g**, 60.6 mg), (Petroleum ether/EtOAc = 24:1 – 12:1), white solid, yield 83%;

m.p. 79 – 81 ℃;

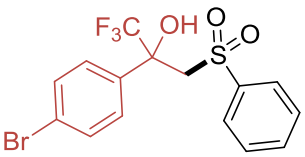
IR (neat) ν 3471, 2982, 1324, 1253, 1150, 1083, 825, 745 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 3H), 7.38 – 7.29 (m, 2H), 7.21 (d, J = 8.6 Hz, 2H), 6.64 (d, J = 8.9 Hz, 2H), 5.31 (s, 1H), 4.08 (d, J = 15.0 Hz, 1H), 3.87 (d, J = 15.0 Hz, 1H), 3.76 (s, 3H) ppm;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -81.01 ppm;

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.1, 139.4, 133.8, 129.1, 128.1, 127.7, 125.4, 123.7 (q, $^{1}J_{C\text{-}F}$ = 285.3 Hz), 113.6, 75.3 (q, $^{2}J_{C\text{-}F}$ = 29.9 Hz), 58.6, 55.3 ppm;

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{15}F_3NaO_4S^+$ 383.0535; Found 383.0506.



3ah, 46.5 mg, (from **1h**, 75.0 mg), (Petroleum ether/EtOAc = 24:1 – 12:1), white solid, yield 38%;

m.p. 113 – 115℃;

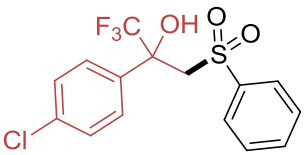
IR (neat) ν 3454, 2919, 1322, 1292, 1251, 1150, 819, 745 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 1H), 7.50 – 7.46 (m, 2H), 7.39 – 7.34 (m, 2H), 7.27 – 7.23 (m, 2H), 7.18 (d, J = 8.5 Hz, 2H), 4.05 (d, J = 15.0 Hz, 1H), 3.87 (d, J = 15.0 Hz, 1H) ppm;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.76 ppm;

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 134.0, 132.8, 131.4, 129.3, 128.5, 127.7, 123.8, 123.4 (q, $^{1}J_{C\text{-}F}$ = 285.4 Hz), 75.2 (q, $^{2}J_{C\text{-}F}$ = 30.1 Hz), 58.3 ppm;

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{12}BrF_3NaO_3S^+$ 430.9535; Found 430.9512.



3ai, 56.8 mg, (from **1i**, 61.8 mg), (Petroleum ether/EtOAc = 24:1 – 12:1), white solid, yield 52%;

m.p. 79 – 81℃

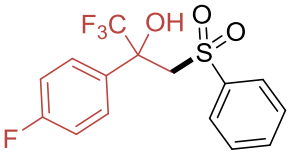
IR (neat) ν 3458, 2921, 1251, 1195, 1123, 827, 820 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.45(m, 3H), 7.40 – 7.31 (m, 2H), 7.30 – 7.17(m, 2H), 7.10 (t, J = 7.9 Hz, 2H), 5.37 (s, 1H), 4.05 (d, J = 15.0 Hz, 1H), 3.88 (d, J = 15.0 Hz, 1H) ppm;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.78 ppm;

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.0, 135.5, 134.0, 132.2, 129.3, 128.4, 128.3, 127.7, 123.5 (q, $^{1}J_{C\text{-}F}$ = 285.5 Hz), 75.2 (q, $^{2}J_{C\text{-}F}$ = 30.1 Hz) , 58.4 ppm;

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{12}ClF_3NaO_3S^+$ 387.0040; Found 387.0066.



3aj, 15.7 mg, (from **1j**, 57.0 mg), (Petroleum ether/EtOAc = 24:1 – 12:1), yellow solid, yield 15%;

m.p. 109 – 111℃**;**

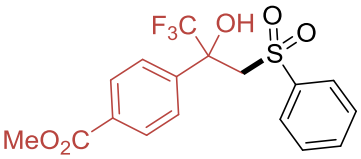
IR (neat) *v* 3482, 2921, 1321, 1311, 1255, 1148, 829, 817 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 1H), 7.53 – 7.46 (m, 2H), 7.40 – 7.34 (m, 2H), 7.31 (dd, *J* = 8.7, 5.2 Hz, 2H), 6.99 – 6.51 (m, 2H), 5.38 (s, 1H), 4.07 (d, *J* = 15.0 Hz, 1H), 3.88 (d, *J* = 15.0 Hz, 1H) ppm;.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.94 , -112.52 ppm;

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.1 (d, $^{1}J_{C\text{-}F}$ = 249.5 Hz), 139.2, 134.1, 129.2, 128.8 (d, $^{3}J_{C\text{-}F}$ = 9.5 Hz), 127.7, 123.6 (q, $^{1}J_{C\text{-}F}$ = 285.7 Hz), 115.2 (d, $^{3}J_{C\text{-}F}$ = 21.8 Hz), 75.2 (q, $^{2}J_{C\text{-}F}$ = 30.1 Hz), 58.4 ppm;.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{12}F_4NaO_3S^+$ 371.0335; Found 371.0346.



3ak, 55.9 mg, (from **1k**, 69.0 mg), (Petroleum ether/EtOAc = 24:1 – 12:1), pale yellow solid, yield 48%;

m.p. 161 – 162 ℃;

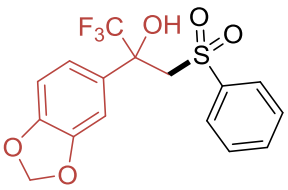
IR (neat) *v* 3408, 2985, 1317, 1282, 1260, 866, 831 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.65 – 7.36 (m, 5H), 7.31 (t, *J* = 7.7 Hz, 2H), 5.44 (s, 1H), 4.11 (d, *J* = 15.0 Hz, 1H), 3.93 (d, *J* = 3.3 Hz, 4H) ppm;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.38 ppm;.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.2, 138.9, 138.5, 134.2, 130.9, 129.3, 129.2, 127.7, 126.9, 123.5 (q, $^{1}J_{C\text{-}F}$ = 285.7 Hz), 75.5 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz), 58.2, 52.3 ppm;

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{15}F_3NaO_5S^+$ 411.0484; Found 411.0472.



3al, 95.4 mg, (from **1l**, 64.8 mg), (Petroleum ether/EtOAc = 24:1 – 12:1), yellow solid, yield 85%;

m.p. 109 – 111℃;

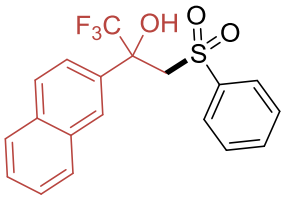
IR (neat) *v* 3465, 2940, 1320, 1251, 1167, 1142, 888, 864 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.50 (m, 3H), 7.44 – 7.33 (m, 2H), 6.85 (dd, *J* = 8.2, 2.0 Hz,1H), 6.69 (dd, *J* = 2.2, 1.1 Hz, 1H), 6.57 (d, *J* = 8.2 Hz, 1H), 5.92(d, *J* = 1.4 Hz, 1H), 5.87 (d, *J* = 1.4 Hz, 1H), 4.04 (d, *J* = 15.0 Hz, 1H), 3.85 (d, *J* = 15.0 Hz, 1H) ppm;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.87 ppm;.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.3, 147.6, 139.2, 133.9, 129.1, 127.8, 127.2, 123.6 (q, $^{1}J_{C\text{-}F}$ = 285.5 Hz), 120.9, 107.8, 107.4, 101.5, 75.3 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz), 58.5 ppm;

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{13}F_3NaO_5S^+$ 397.0328; Found 397.0354.



3am,94.6 mg, (from **1m**, 66.6 mg), (Petroleum ether/EtOAc = 24:1 – 12:1), yellow solid, yield 83%;

m.p. 154 – 156 ℃;

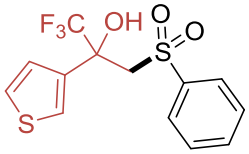
IR (neat) *v* 3406, 2932, 1302, 1225, 1188, 1148, 890, 860 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.74(d, J = 7.8Hz, 1H),7.69 (d, J = 7.8 Hz, 1H),7.54 – 7.44 (m, 3H), 7.37 – 7.33 (m, 2H), 7.28 (d, J = 9.1 Hz, 1H), 7.23 – 7.17 (m, 1H), 6.99 (t, J = 7.9 Hz, 2H), 5.49 (s, 1H), 4.22 (d, J = 15.0 Hz, 1H), 3.97 (d, J = 15.0 Hz, 1H) ppm;.

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -81.28 ppm;

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.9, 133.7, 133.2, 132.5, 130.8, 128.8, 128.5, 128.0, 127.6, 127.3, 127.2, 127.1, 126.5, 123.8 (q, $^{1}J_{C\text{-}F}$ = 285.6 Hz), 123.3, 75.6 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz) , 58.6 ppm;

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{15}F_3NaO_3S^+$ 403.0586; Found 403.0557.



3an, 78.6 mg, (from **1n**, 53.4 mg), (Petroleum ether/EtOAc = 24:1 – 12:1), yellow solid, yield 78%;

m.p. 109 – 111℃;

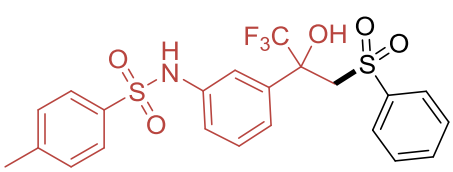
IR (neat) *v* 3465, 2927, 1310, 1251, 1145, 1081, 894, 870 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 3H), 7.42 – 7.35 (m, 3H), 7.00 (dd, J = 5.1, 3.1 Hz, 1H), 6.66 – 6.64(m, 1H), 5.45 (s, 1H), 3.96 (d, J = 14.9 Hz, 1H), 3.85 (d, J = 14.9 Hz, 1H) ppm;

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -81.29 ppm;

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.2, 135.7, 133.9, 129.2, 127.6, 126.4, 125.4, 125.4, 123.4 (q, $^{1}J_{C\text{-}F}$ = 285.2 Hz), 74.5 (q, $^{2}J_{C\text{-}F}$ = 30.8 Hz), 58.8 ppm;

HRMS (ESI) m/z: $[M+K]^+$ Calcd for $C_{13}H_{11}F_3KO_3S_2^+$ 374.9733; Found 374.9751.



3ao, 112.6 mg, (Petroleum ether/EtOAc = 17:3 – 12:1), yellow oil, yield 75%;

IR (neat) *v* 3258, 1596, 1309, 1243, 1147, 1090, 924, 719 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.63 (m, 2H), 7.50 – 7.37 (m, 4H), 7.27 – 7.20 (m, 4H), 7.14 (d, J = 2.0 Hz, 1H), 7.05 – 6.95 (m, 3H), 5.34 (s, 1H), 4.09 (d, J = 15.0 Hz, 1H), 3.84 (d, J = 15.0 Hz, 1H), 2.33 (s, 3H) ppm;

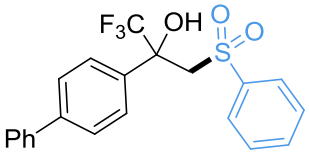
^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.64 ppm;

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.3, 138.8, 137.0, 135.6, 135.0, 134.2, 129.7, 129.2, 127.7, 127.3, 123.5 (q, $^{1}J_{C\text{-}F}$ = 285.8 Hz), 123.3, 121.7, 119.6, 75.2 (q, $^{2}J_{C\text{-}F}$ = 29.9 Hz), 58.1, 21.5 ppm;

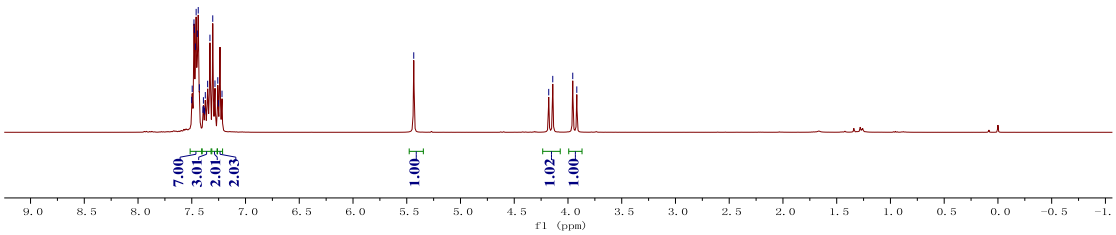
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{18}F_3NNaO_5S_2^+$ 508.0471; Found 508.0464.

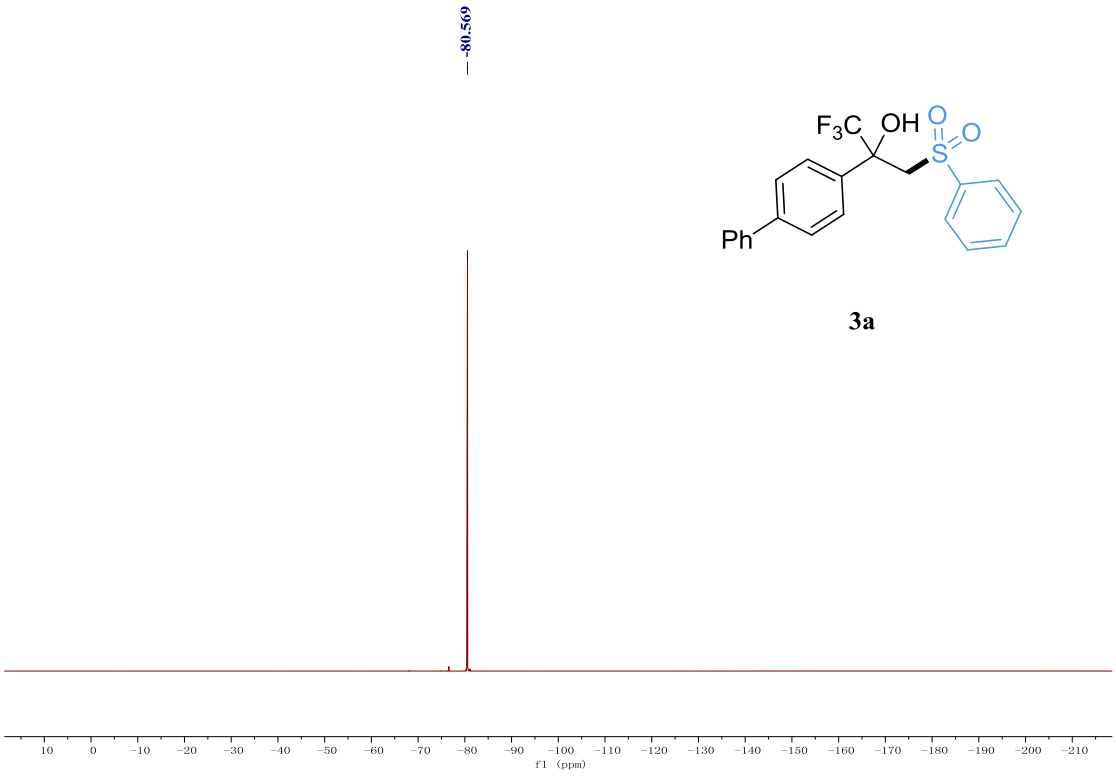
9. Copies of NMR Spectra

^{1}H NMR (400 MHz, $CDCl_3$), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of product **3a**

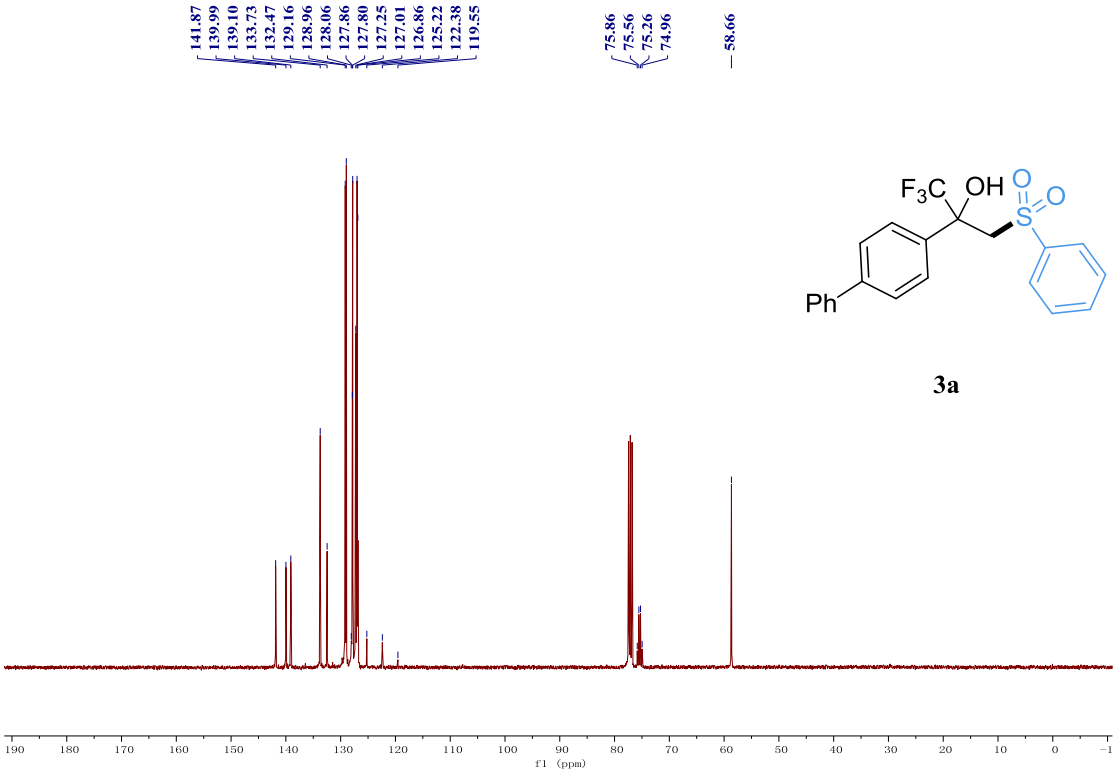


3a



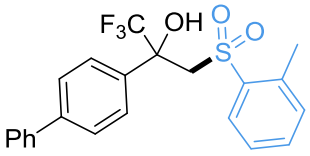


3a

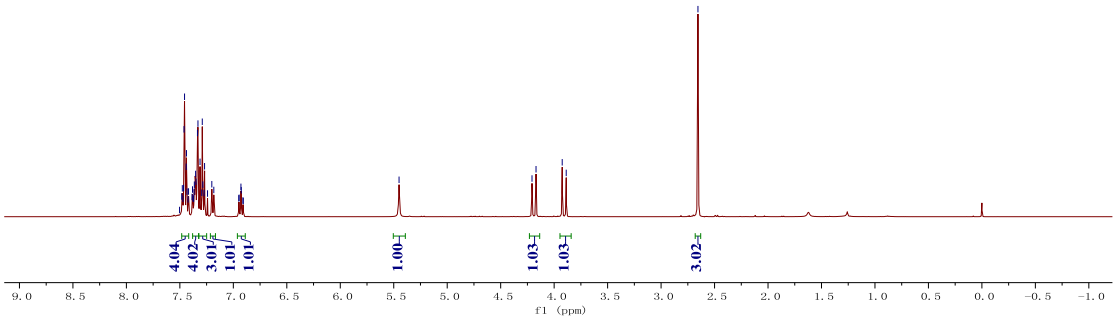

141.87
139.99
139.10
133.73
132.47
129.16
128.96
128.06
127.86
127.80
127.25
127.01
126.86
125.22
122.38
119.55
75.86
75.56
75.26
74.96
58.66
F3C
OH
O
S
O
Ph
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)

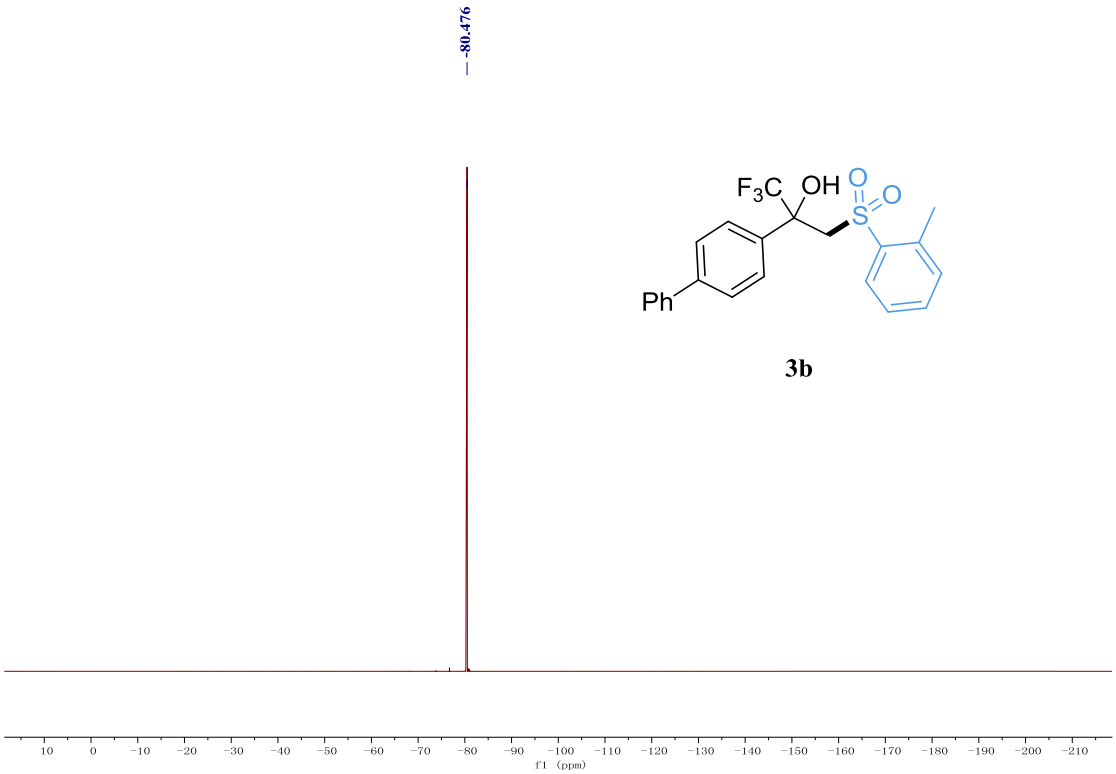
3a

^{1}H NMR (400 MHz, $CDCl_3$), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)spectrum of product **3b**

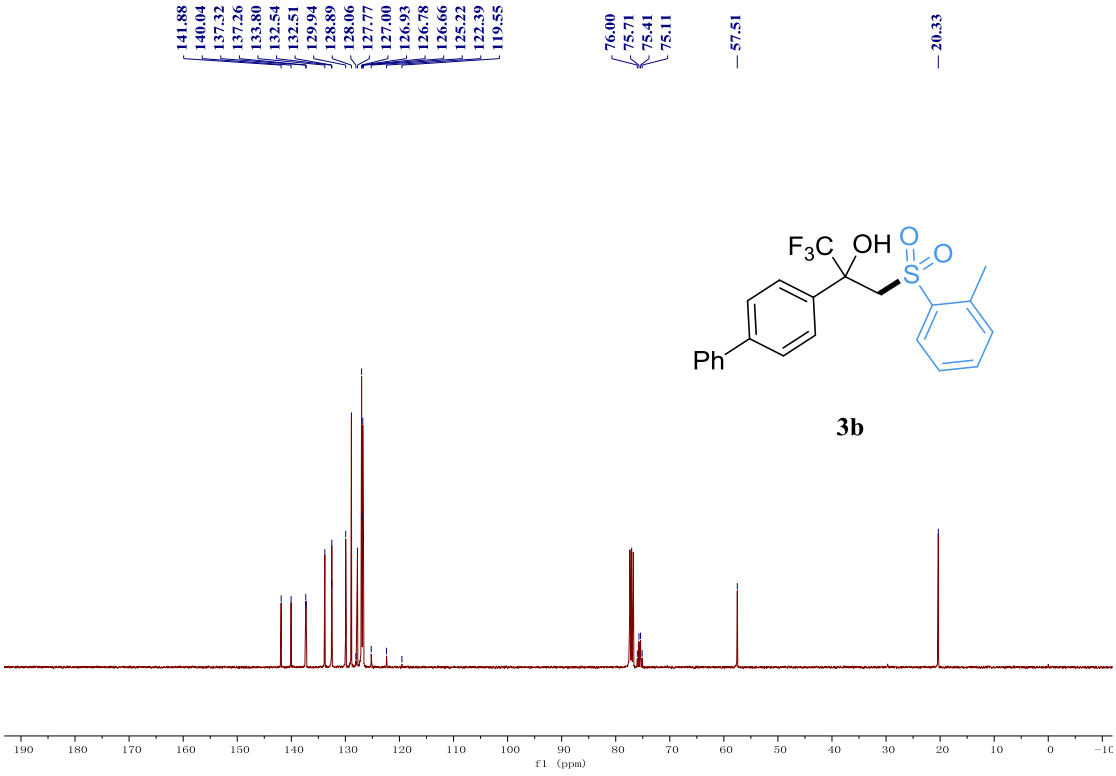


3b



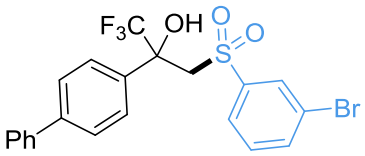


3b

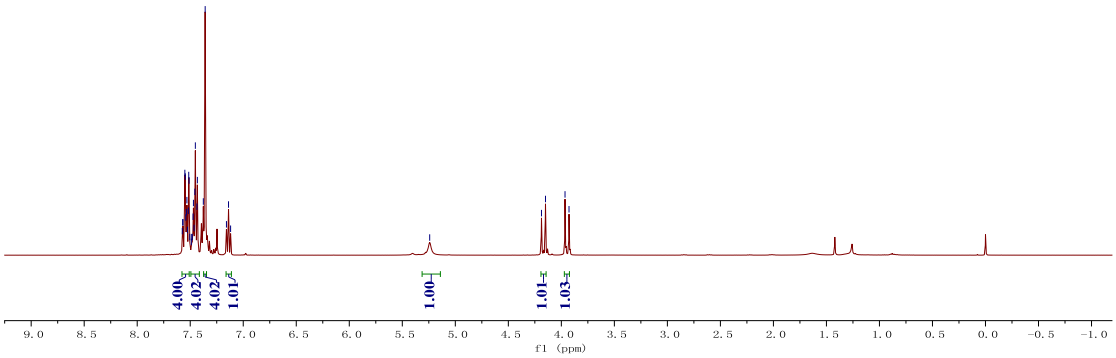

141.88
140.04
137.32
137.26
133.80
132.54
132.51
129.94
128.89
128.06
127.77
127.00
126.93
126.78
126.66
125.22
122.39
119.55
76.00
75.71
75.41
75.11
57.51
20.33
F3C
OH
O
S
O
Ph
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

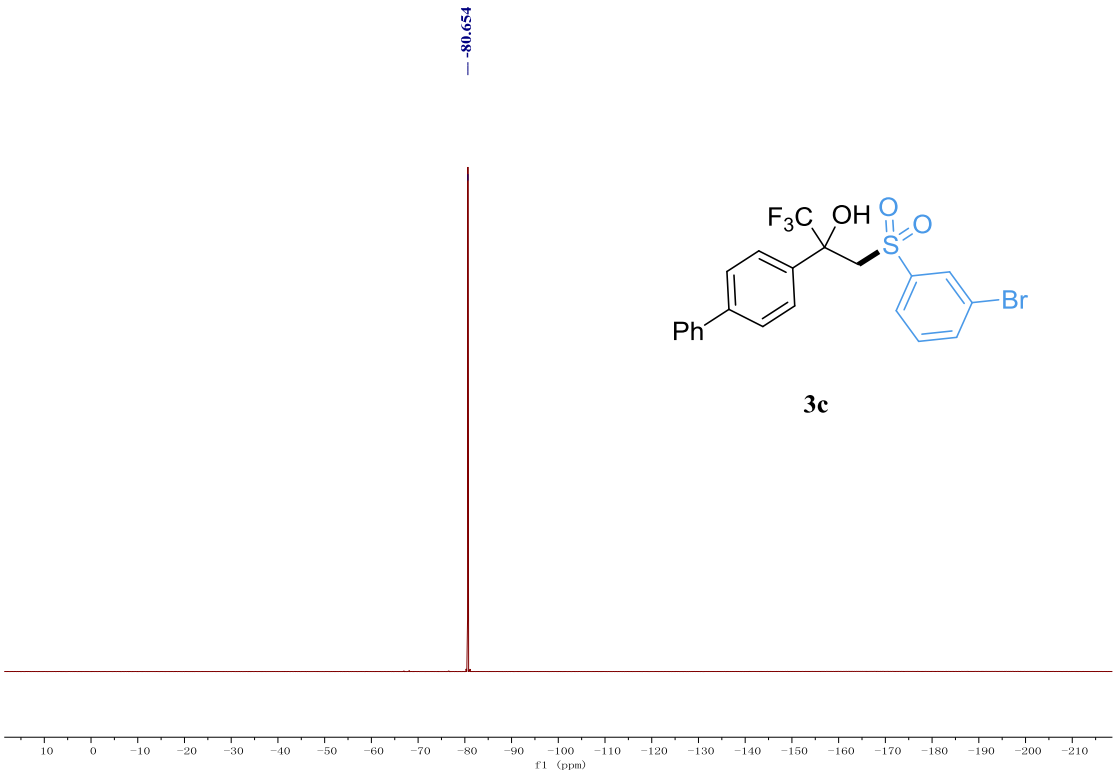
3b

^{1}H NMR (400 MHz, $CDCl_3$), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)spectrum of product **3c**



3c



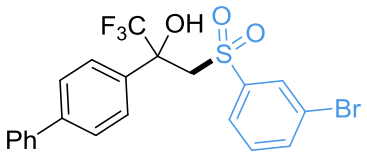


3c

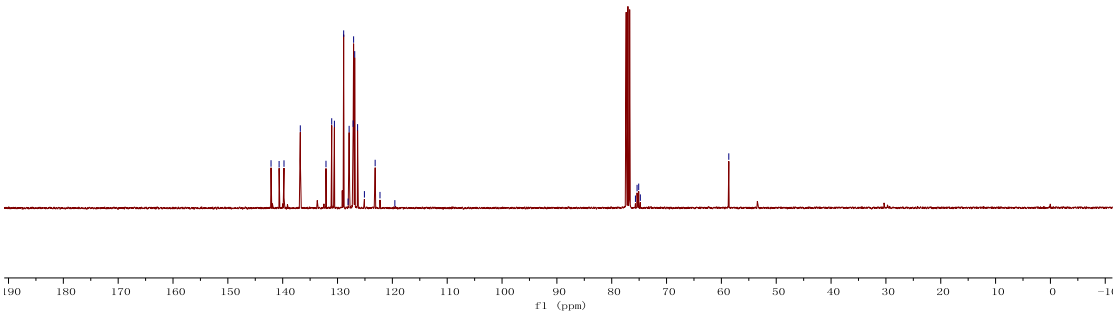
142.13
140.65
139.76
136.79
132.11
131.06
130.57
128.88
128.07
127.89
127.15
127.07
126.87
126.34
125.10
123.14
122.26
119.55

75.68
75.38
75.08
74.78

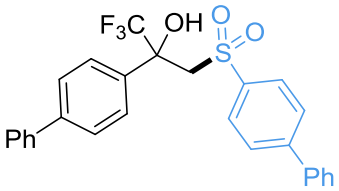
58.65



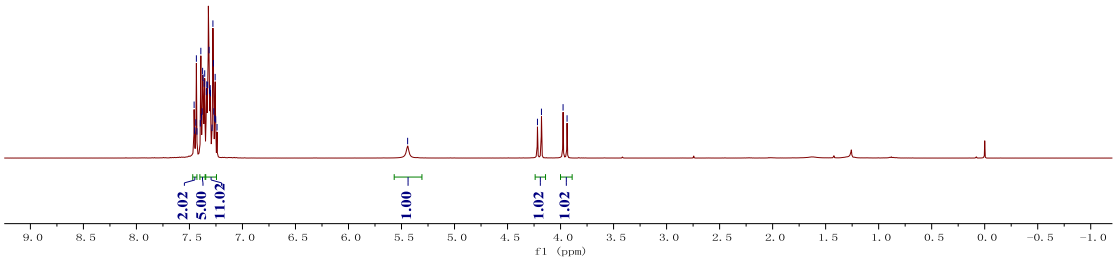
3c

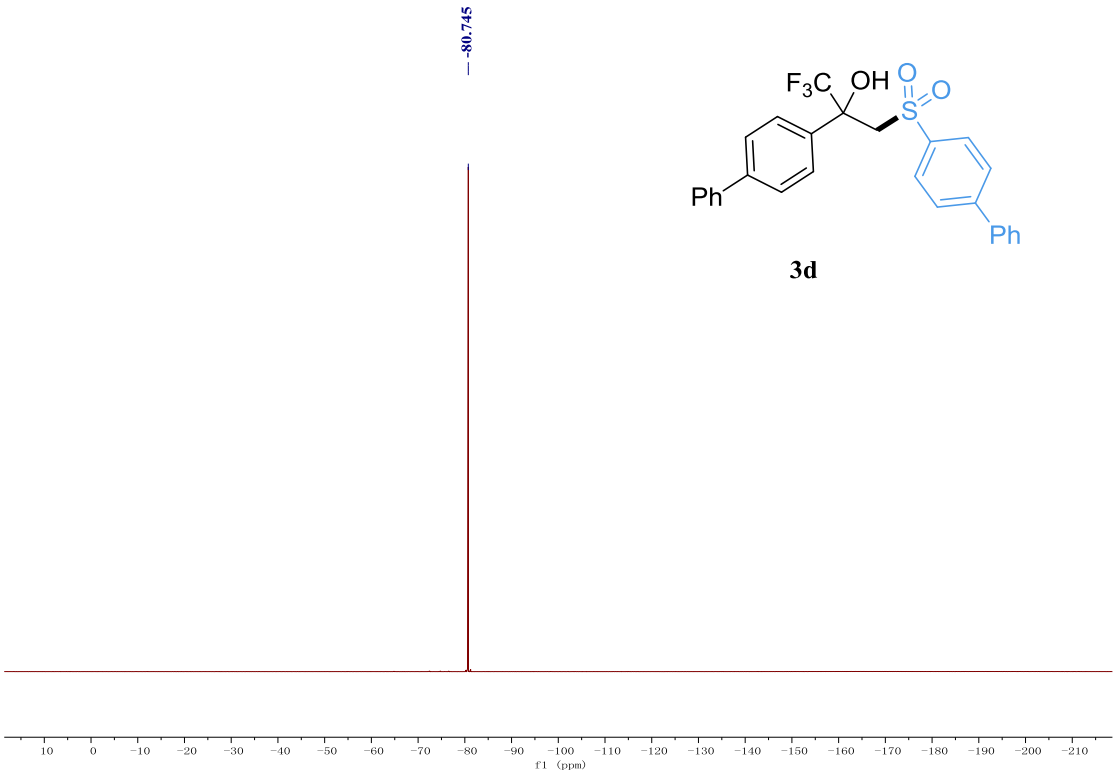


^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) and ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)spectrum of product **3d**

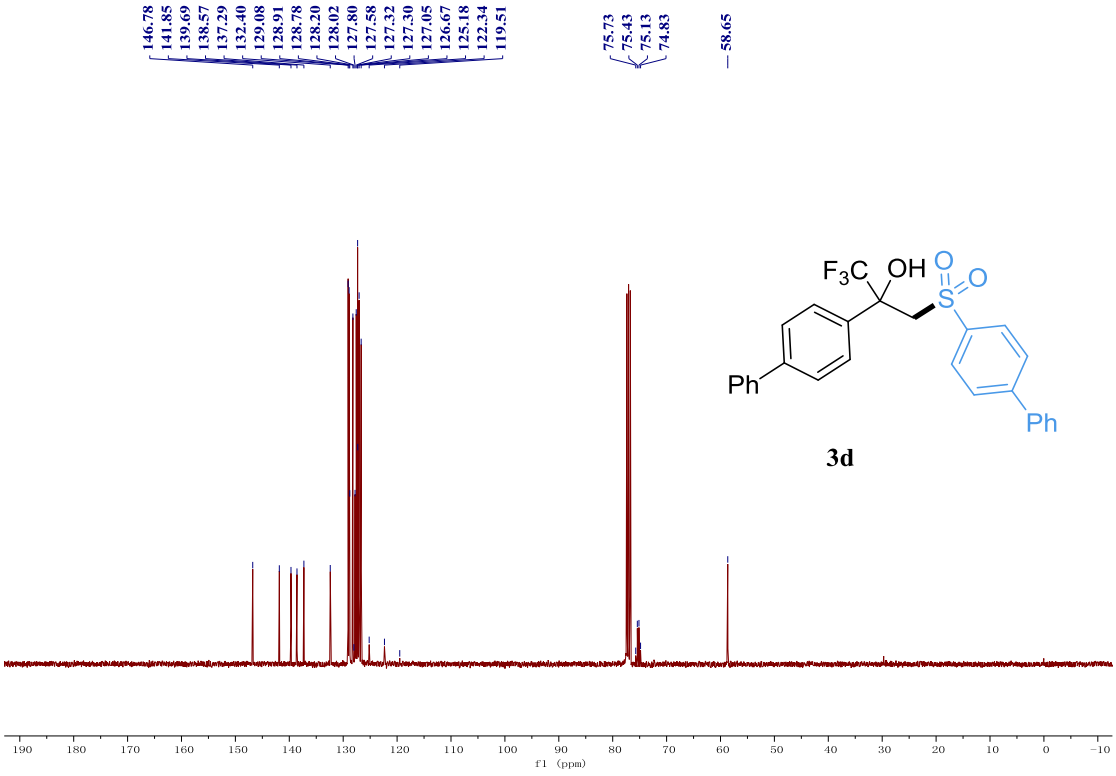


3d



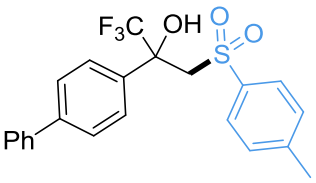


3d

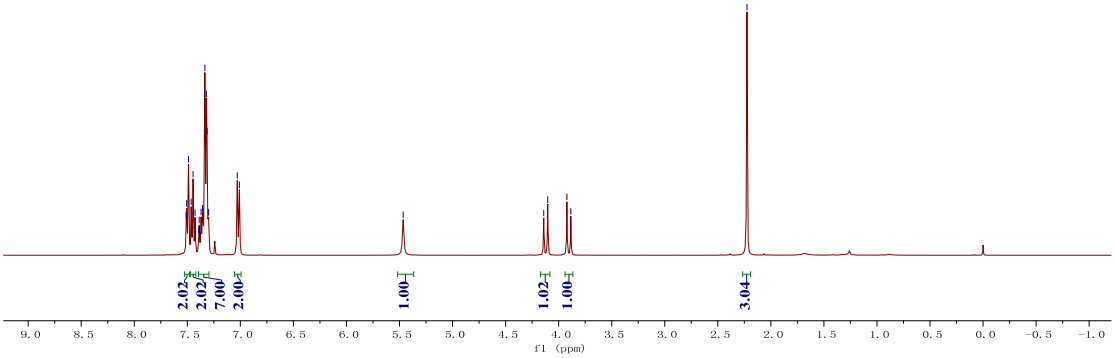

146.78
141.85
139.69
138.57
137.29
132.40
129.08
128.91
128.78
128.20
128.02
127.80
127.58
127.32
127.30
127.05
126.67
125.18
122.34
119.51
75.73
75.43
75.13
74.83
58.65
F3C
OH
O
S
O
Ph
Ph
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

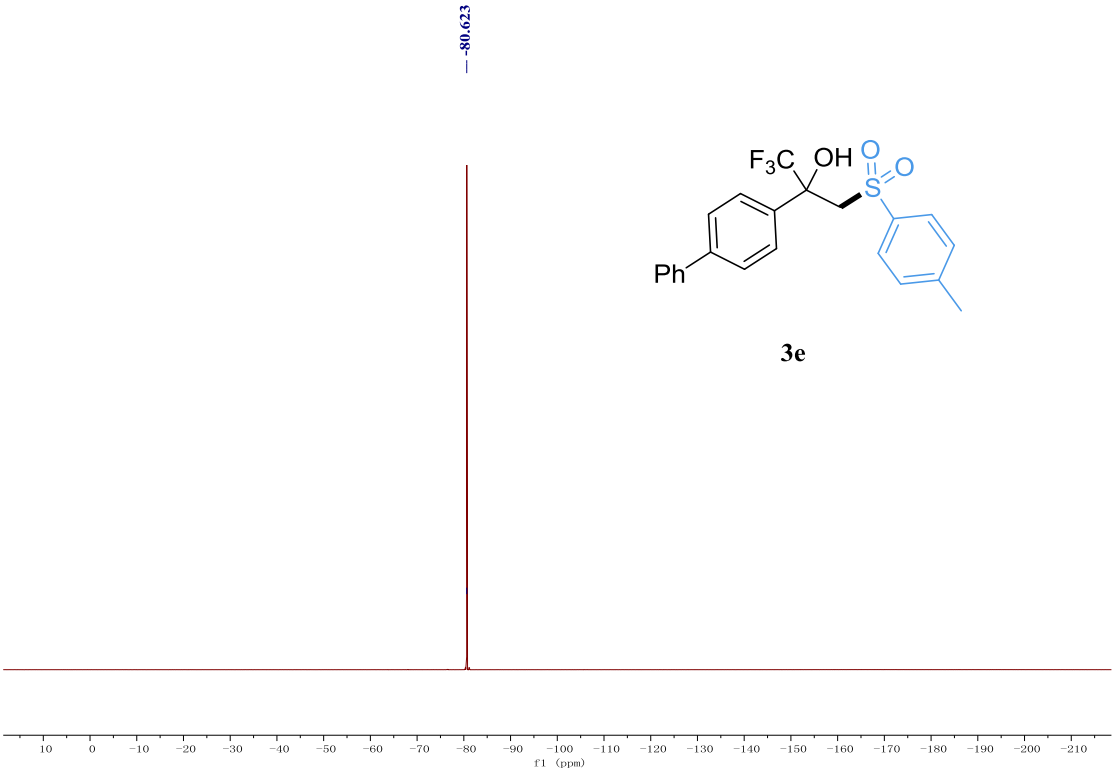
3d

^{1}H NMR (400 MHz, $CDCl_3$), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)spectrum of product **3e**

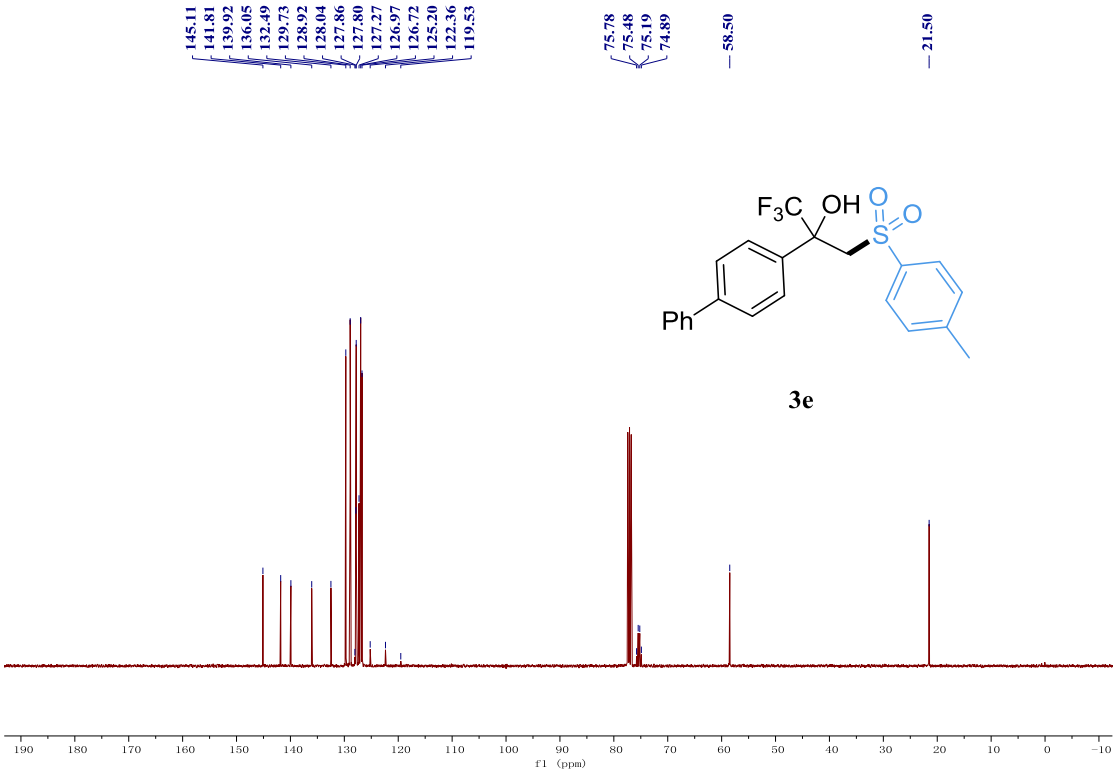


3e



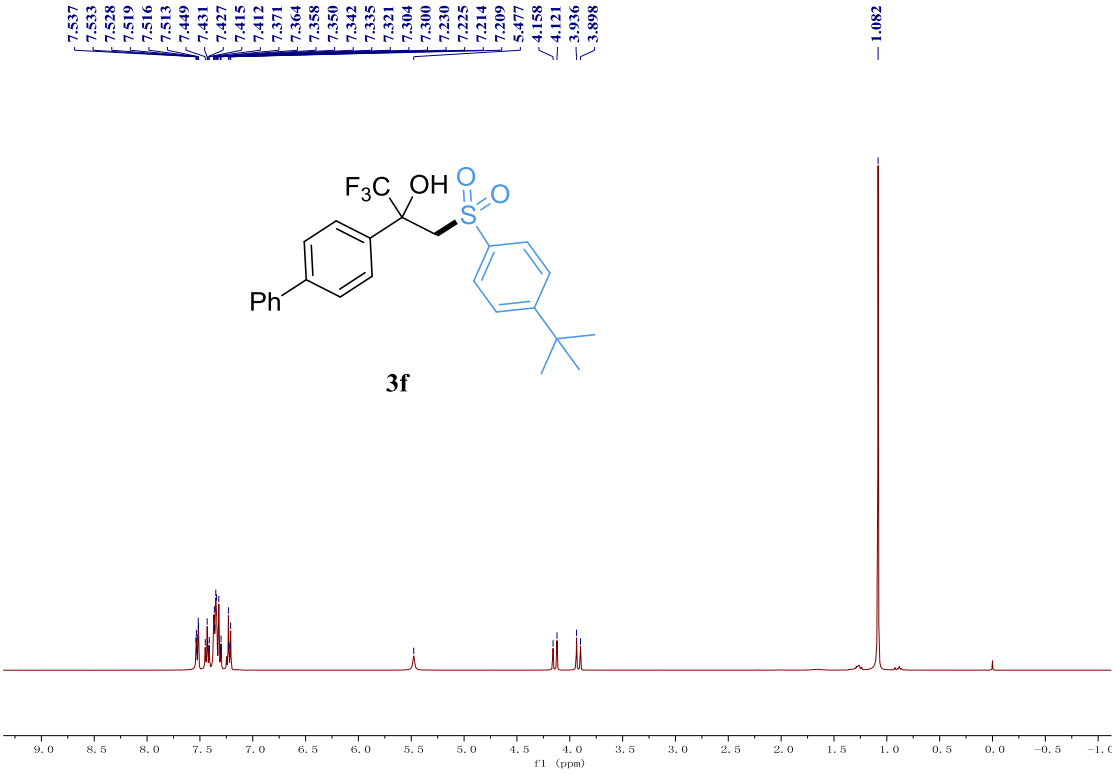


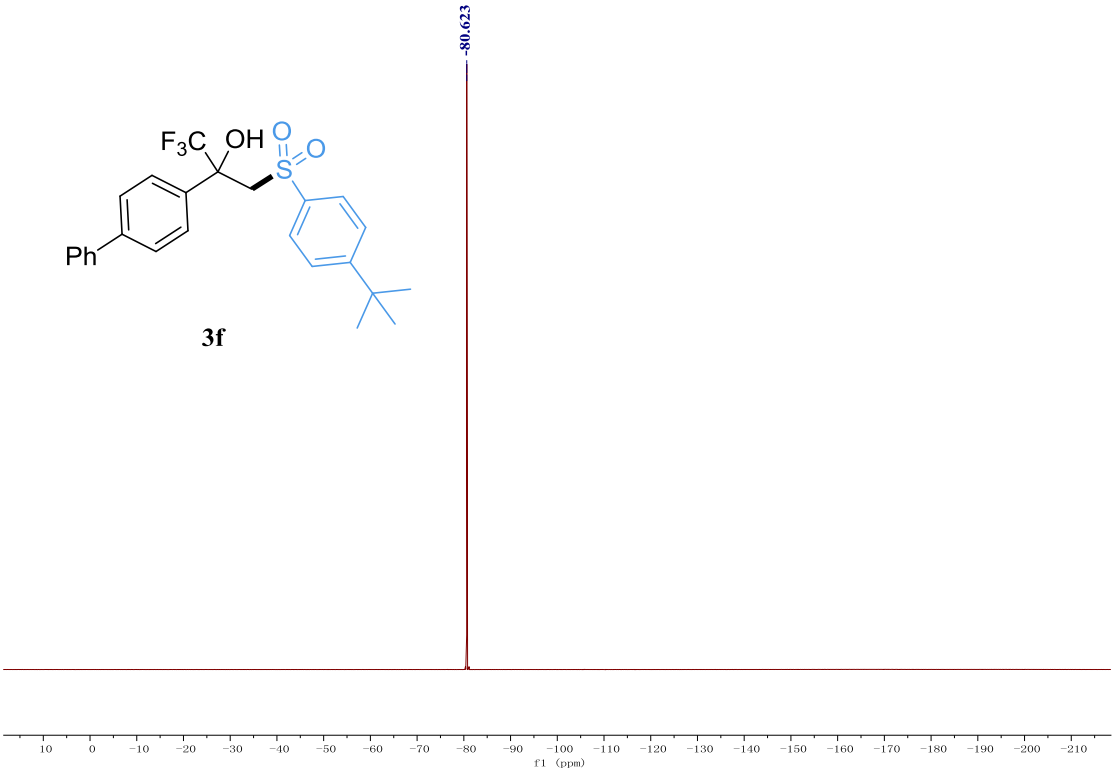
3e

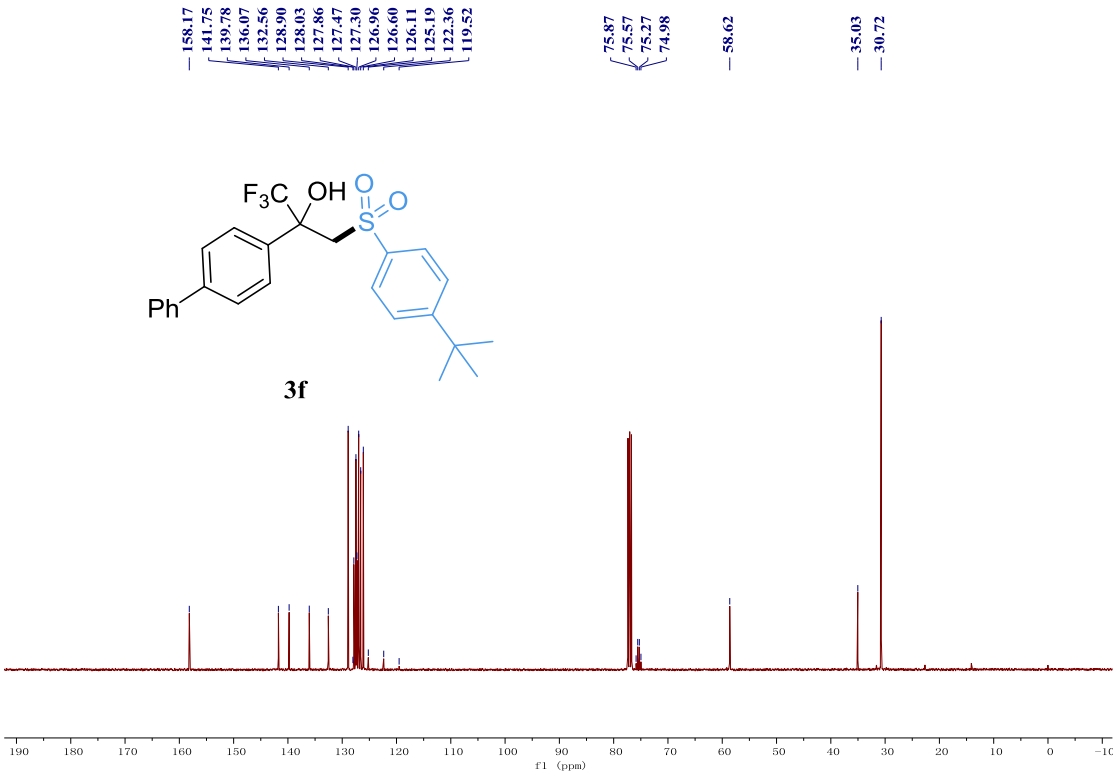

145.11
141.81
139.92
136.05
132.49
129.73
128.92
128.04
127.86
127.80
127.27
126.97
126.72
125.20
122.36
119.53
75.78
75.48
75.19
74.89
58.50
21.50
F3C
OH
O
S
O
Ph
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3e

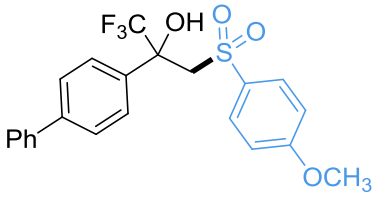
^{1}H NMR (400 MHz, $CDCl_3$), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)spectrum of product **3f**



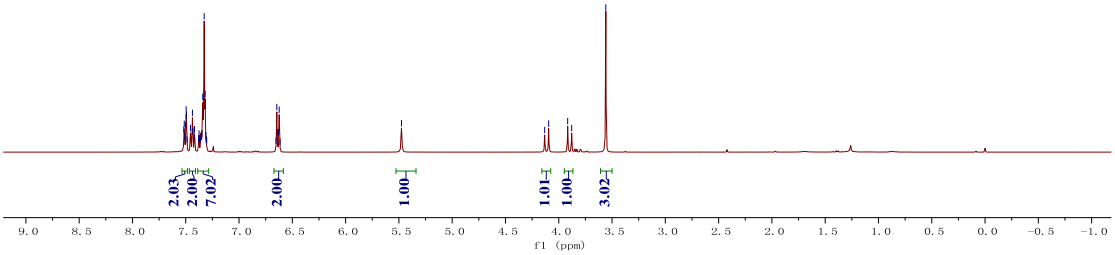


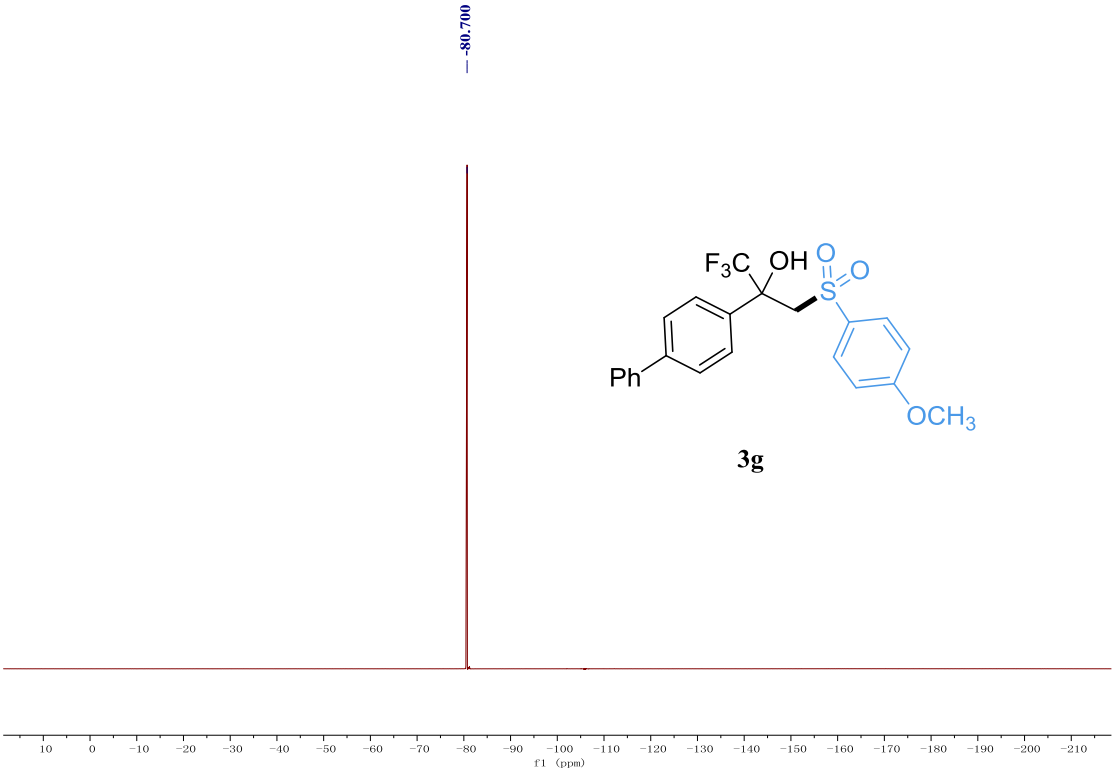

158.17
141.75
139.78
136.07
132.56
128.90
128.03
127.86
127.47
127.30
126.96
126.60
126.11
125.19
122.36
119.52
75.87
75.57
75.27
74.98
58.62
35.03
30.72
F3C
OH
O
S
O
Ph
3f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)spectrum of product **3g**

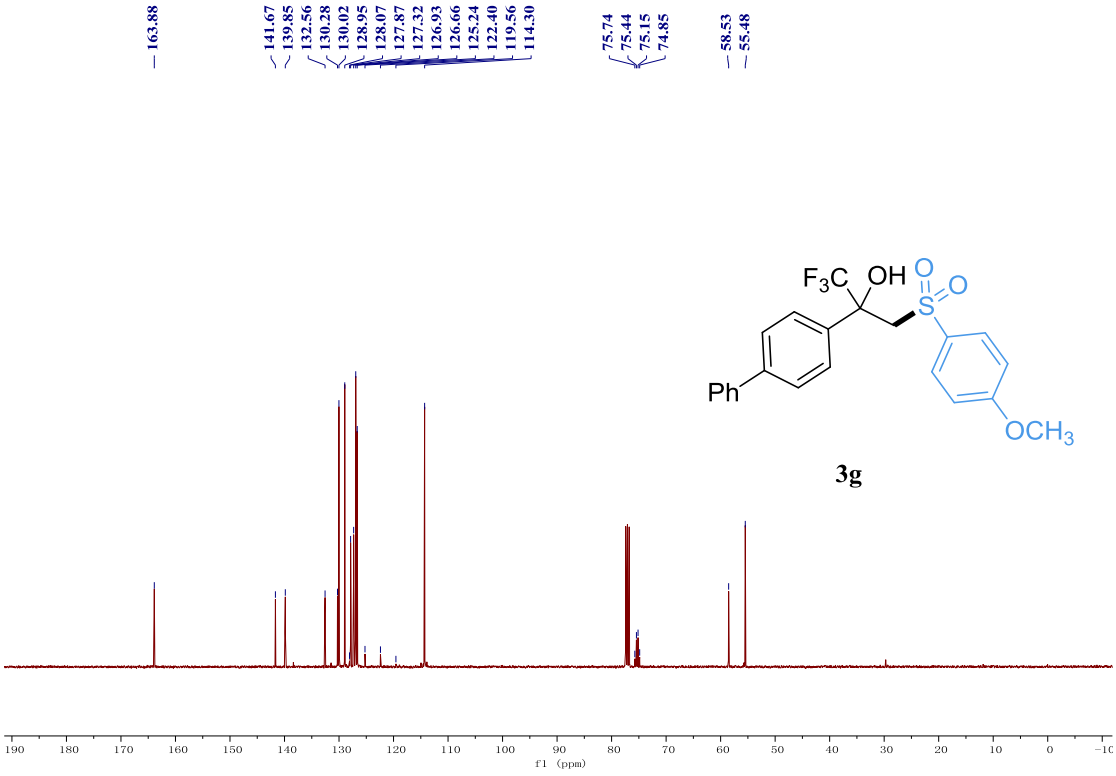


3g



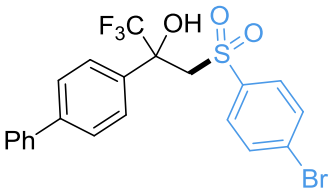


3g

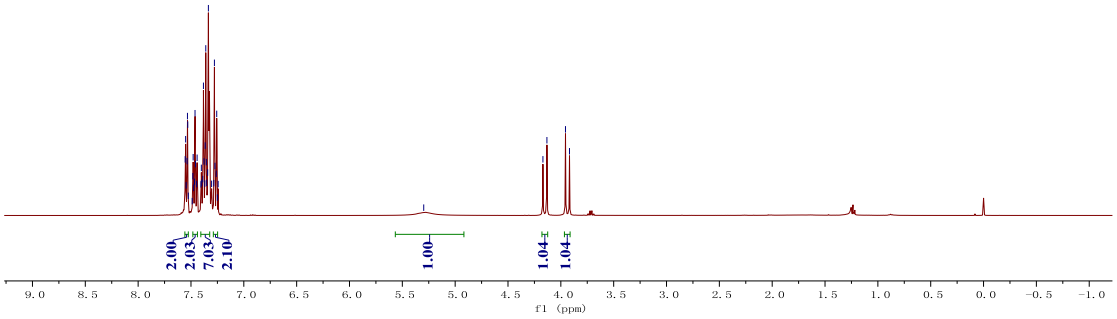

163.88
141.67
139.85
132.56
130.28
130.02
128.95
128.07
127.87
127.32
126.93
126.66
125.24
122.40
119.56
114.30
75.74
75.44
75.15
74.85
58.53
55.48
F3C
OH
O
O
S
Ph
OCH3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

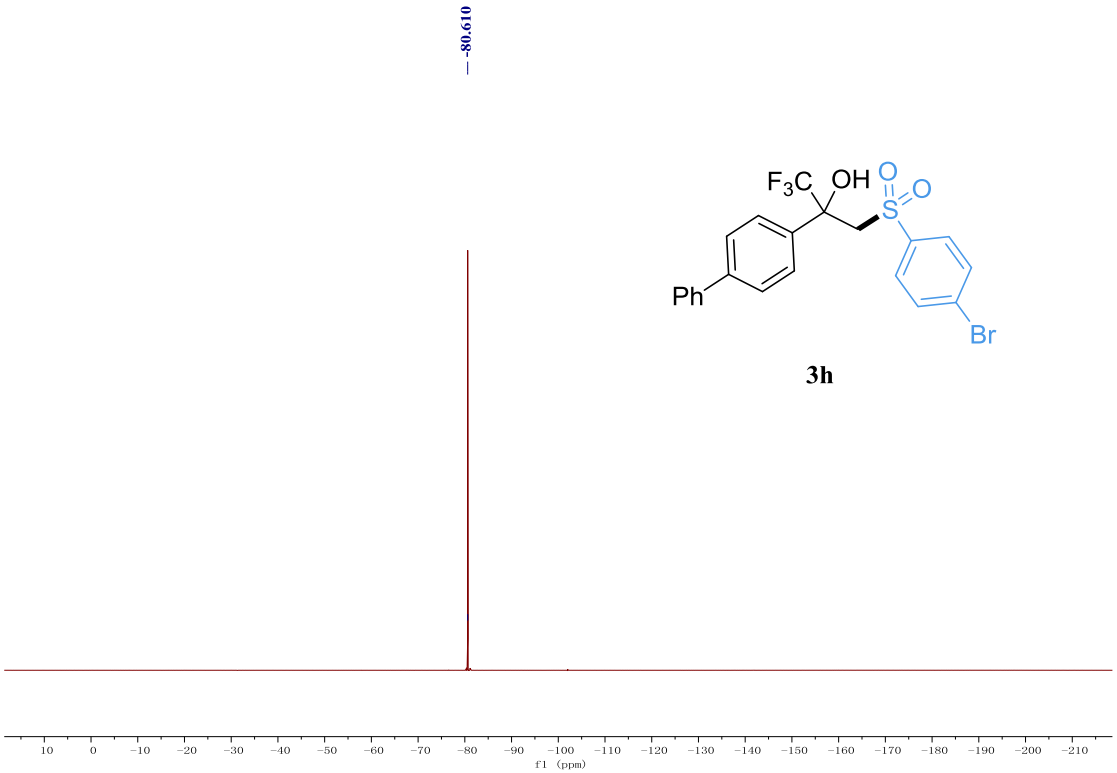
3g

^{1}H NMR (400 MHz, $CDCl_3$), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)spectrum of product **3h**

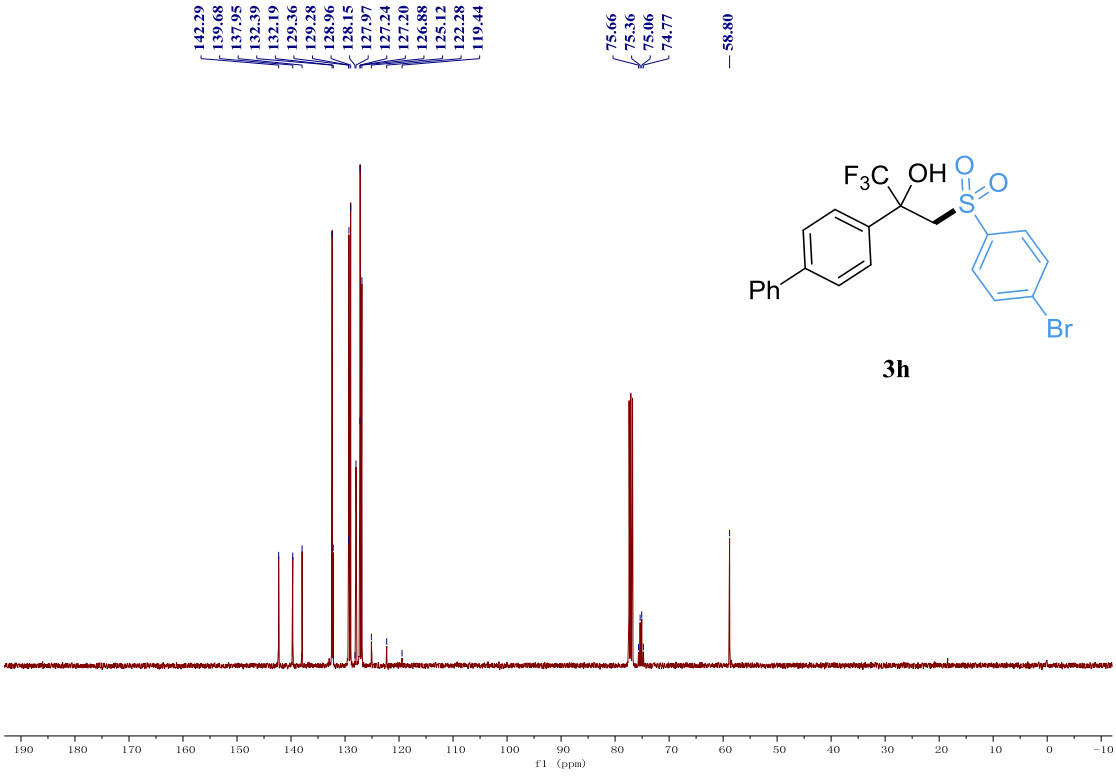


3h



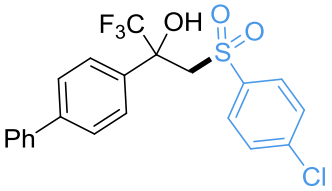


3h

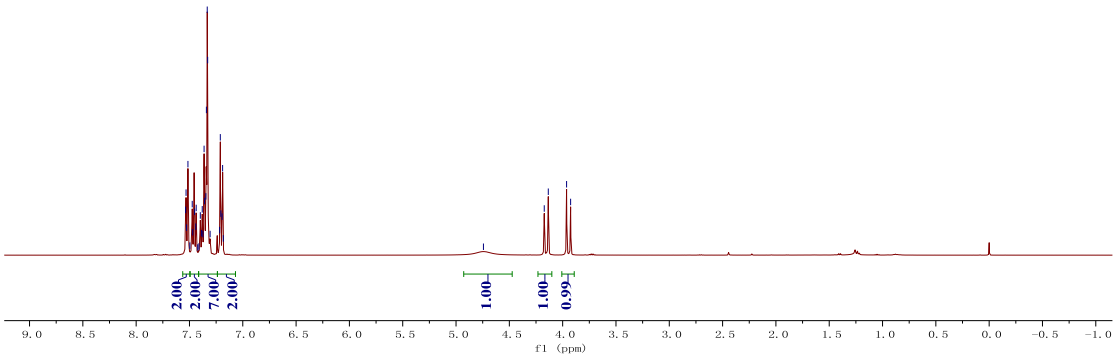

142.29
139.68
137.95
132.39
132.19
129.36
129.28
128.96
128.15
127.97
127.24
127.20
126.88
125.12
122.28
119.44
75.66
75.36
75.06
74.77
58.80
F3C
OH
O
O
S
Ph
Br
f1 (ppm)

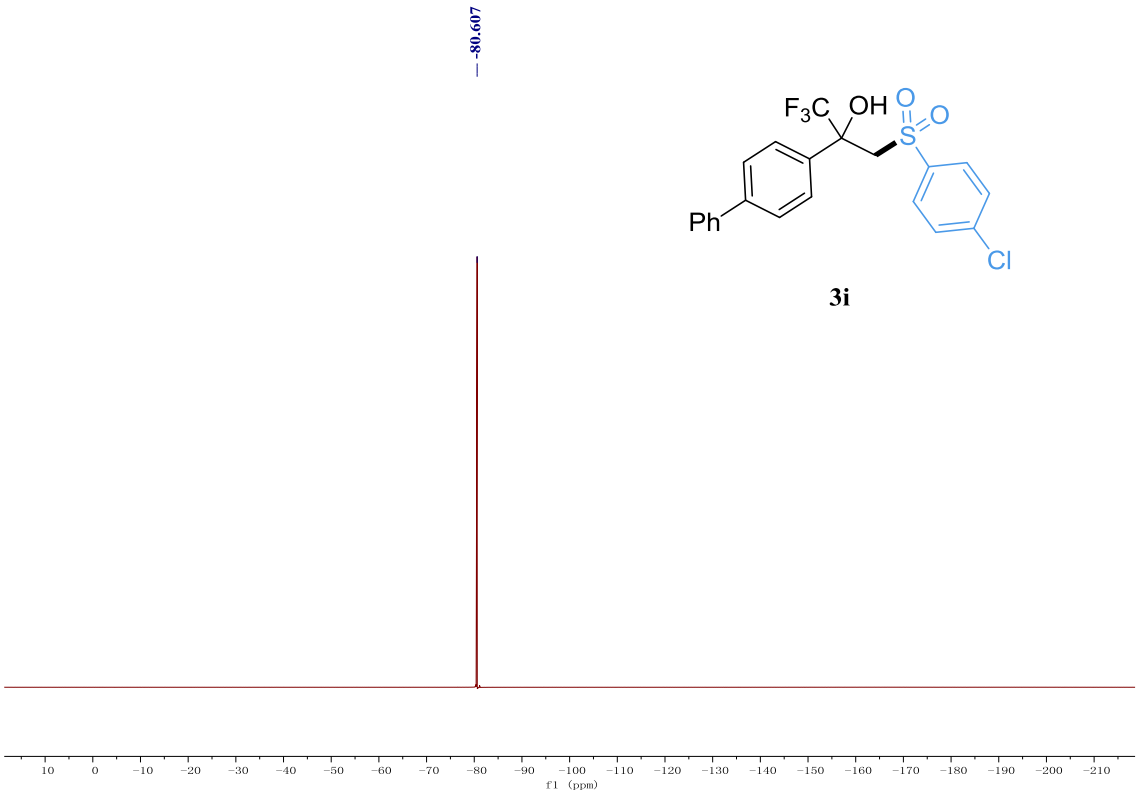
3h

^{1}H NMR (400 MHz, $CDCl_3$), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)spectrum of product **3i**

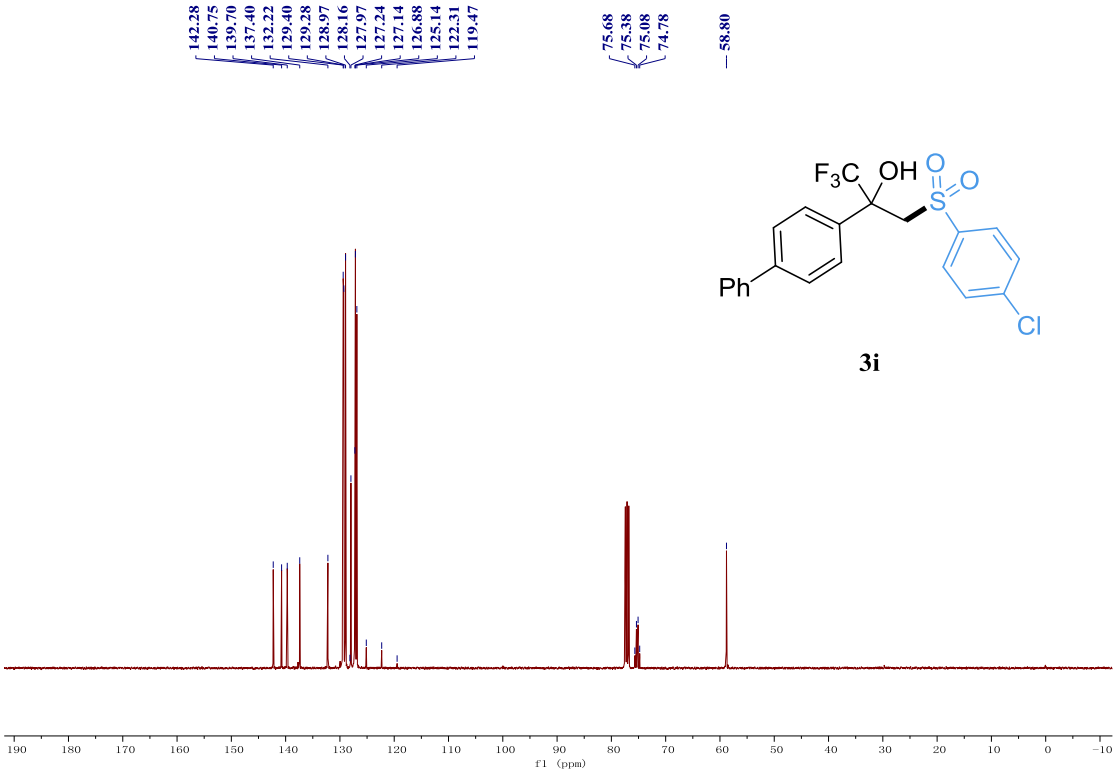


3i



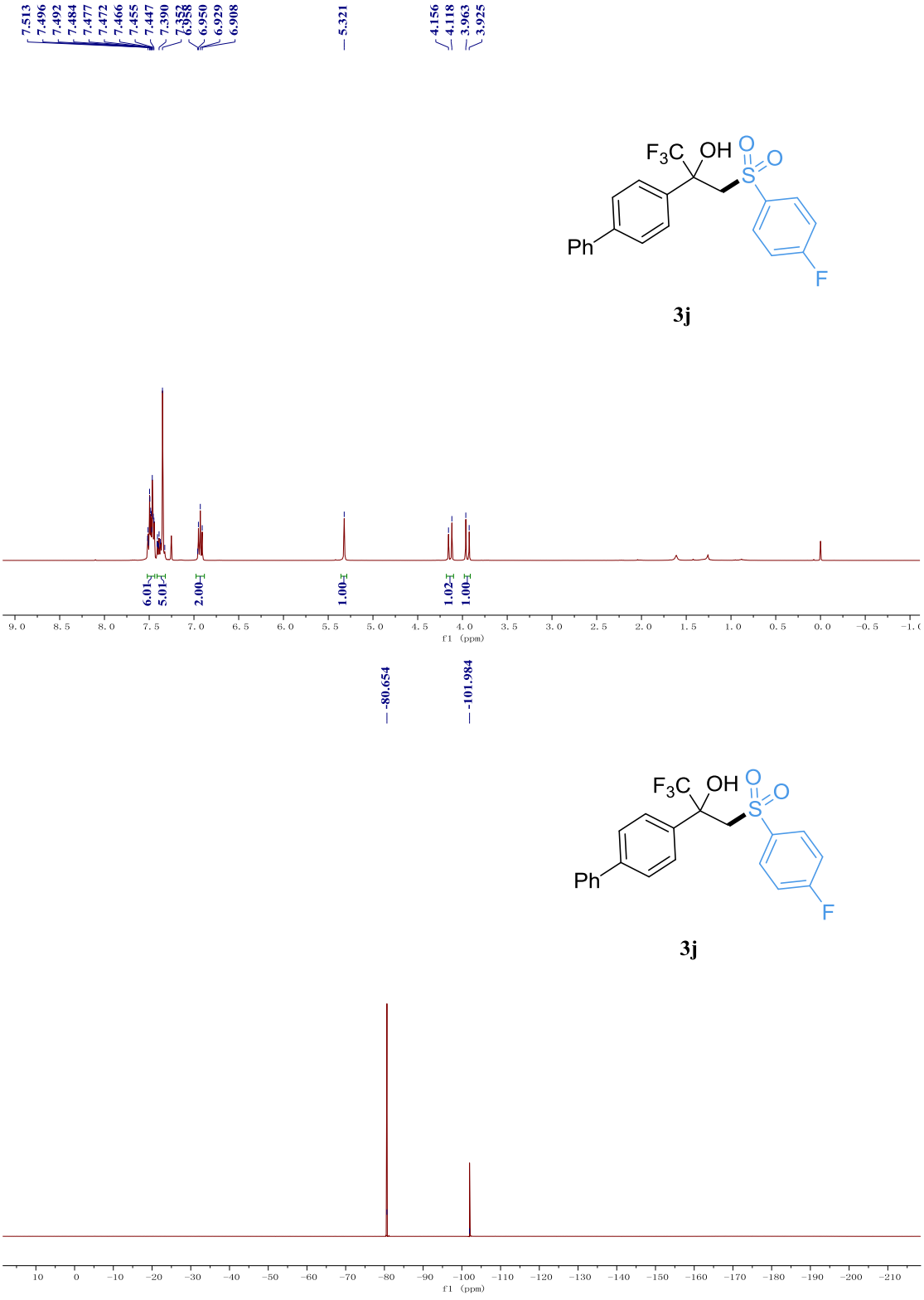


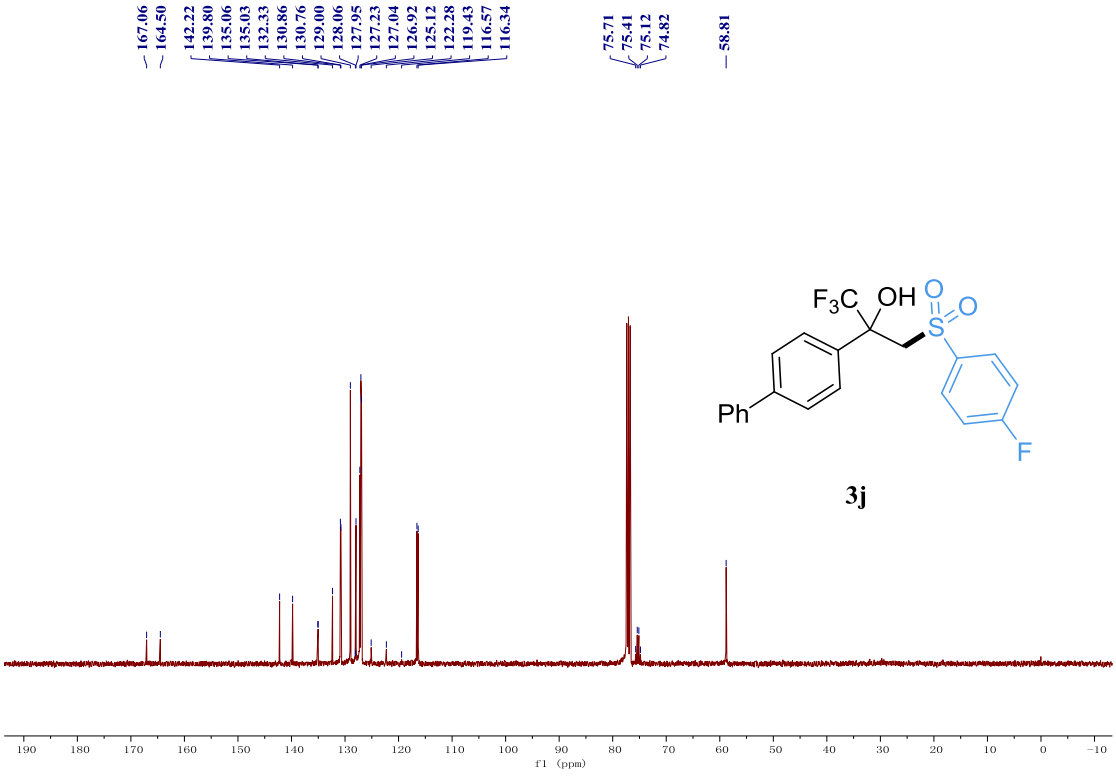
3i


142.28
140.75
139.70
137.40
132.22
129.40
129.28
128.97
128.16
127.97
127.24
127.14
126.88
125.14
122.31
119.47
75.68
75.38
75.08
74.78
58.80
F3C
OH
O
O
S
Ph
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

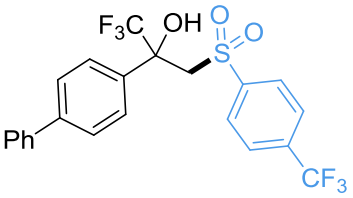
3i

^{1}H NMR (400 MHz, $CDCl_3$), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)spectrum of product **3j**

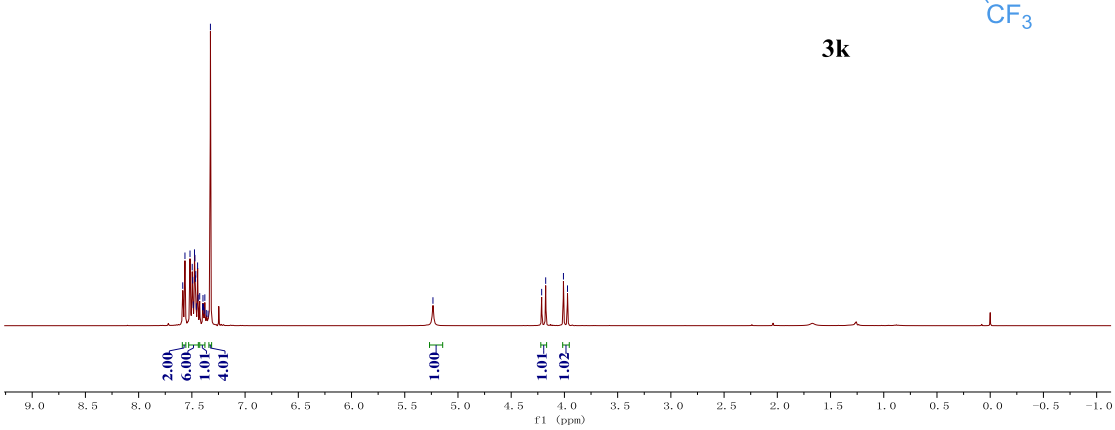


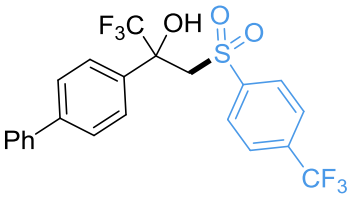

167.06
164.50
142.22
139.80
135.06
135.03
132.33
130.86
130.76
129.00
128.06
127.95
127.23
127.04
126.92
125.12
122.28
119.43
116.57
116.34
75.71
75.41
75.12
74.82
58.81
F3C
OH
O
S
O
Ph
F
3j
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)spectrum of product **3k**

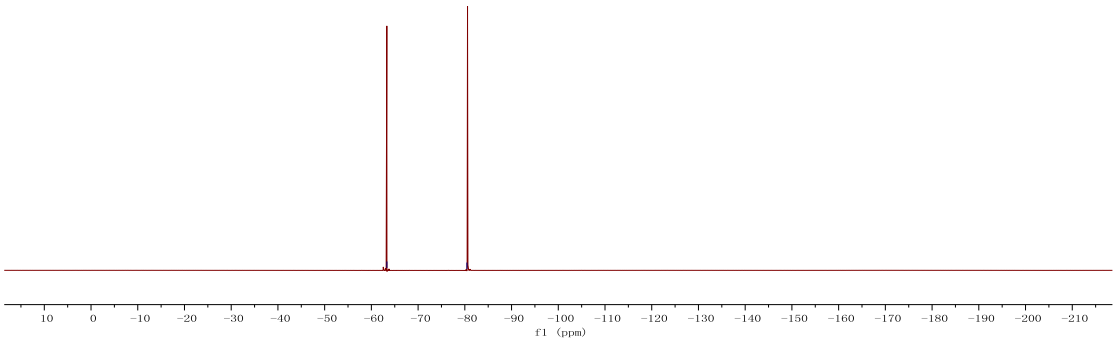


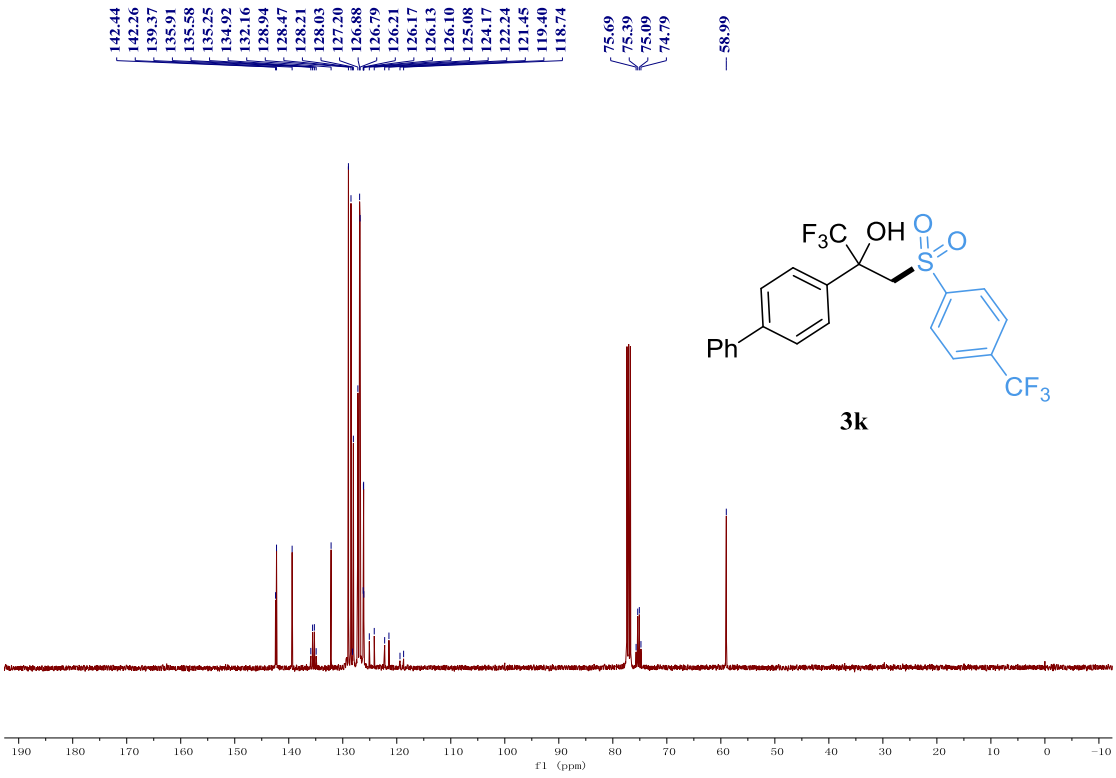
3k





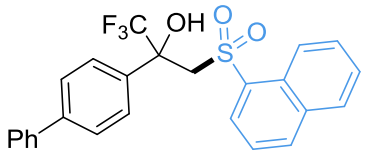
3k



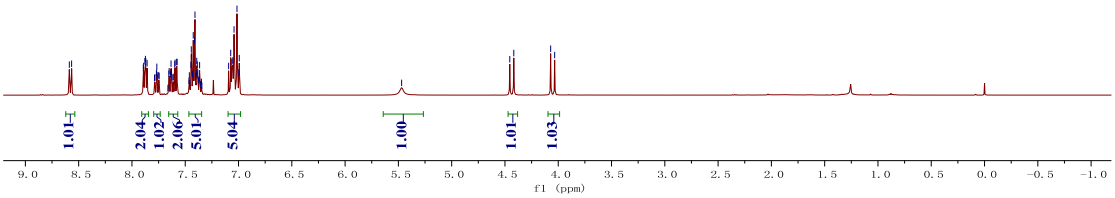

142.44
142.26
139.37
135.91
135.58
135.25
134.92
132.16
128.94
128.47
128.21
128.03
127.20
126.88
126.79
126.21
126.17
126.13
126.10
125.08
124.17
122.24
121.45
119.40
118.74
75.69
75.39
75.09
74.79
58.99
F3C
OH
O
O
S
Ph
CF3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

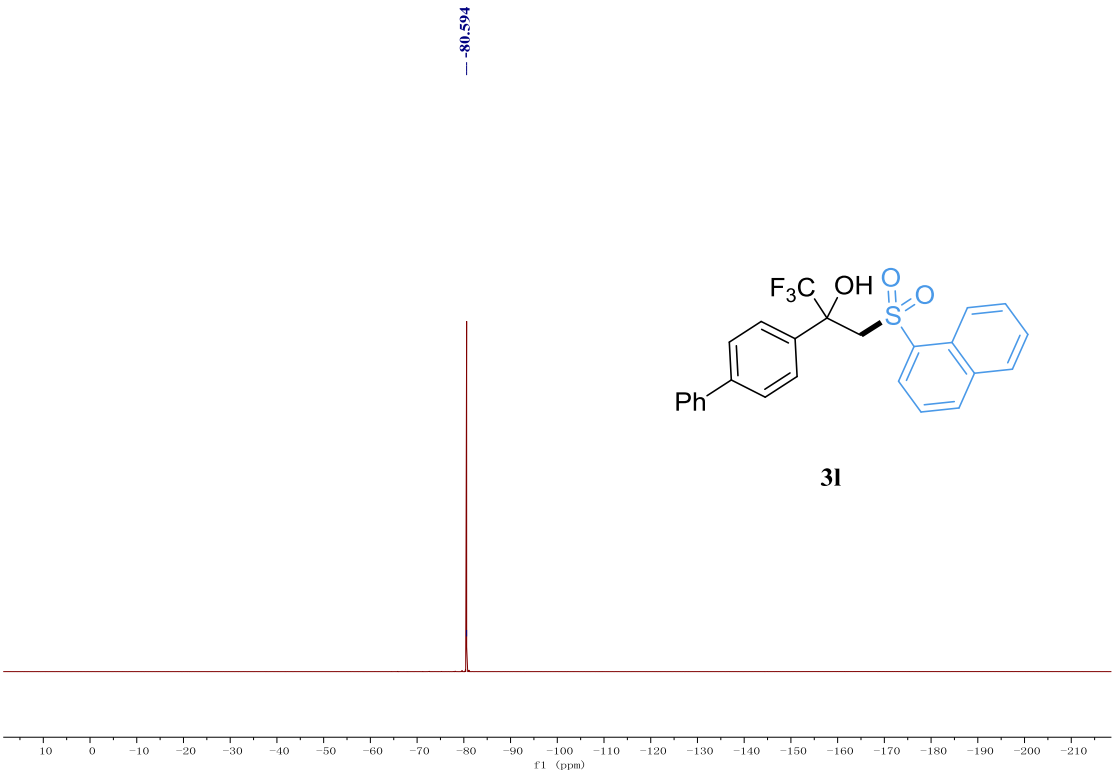
3k

^{1}H NMR (400 MHz, $CDCl_3$), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)spectrum of product **3l**

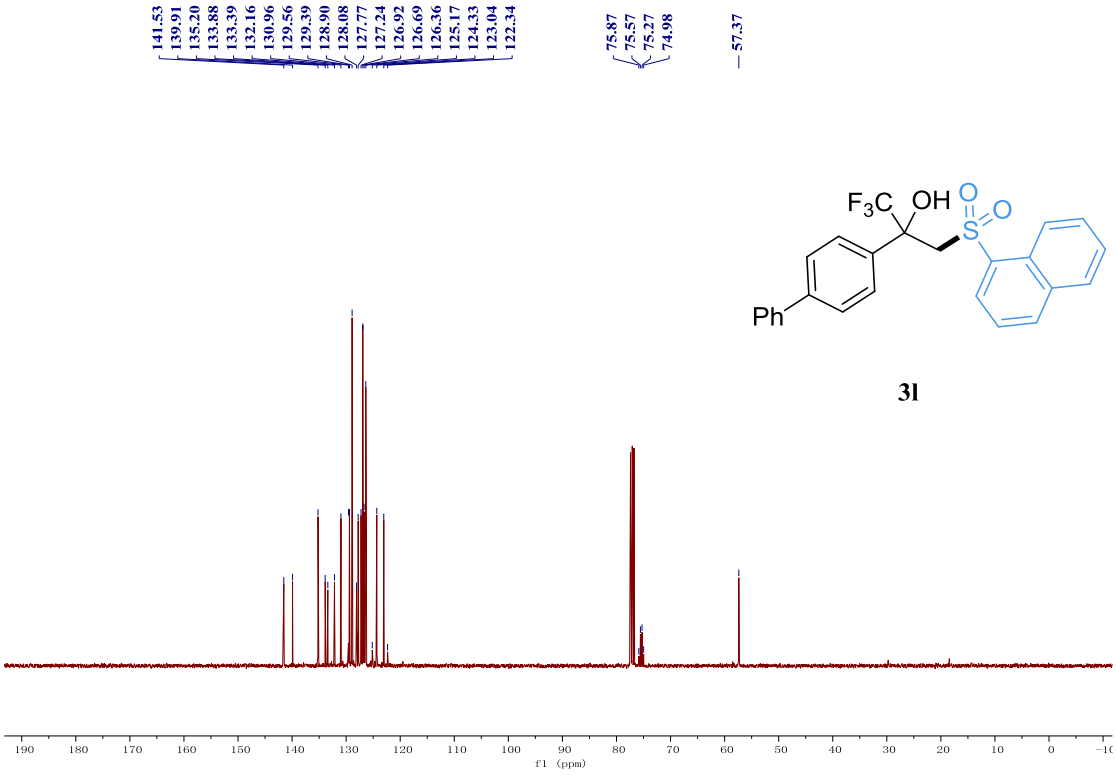


3l



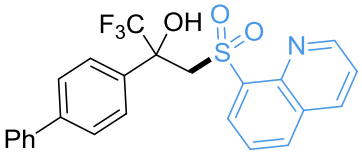


3l

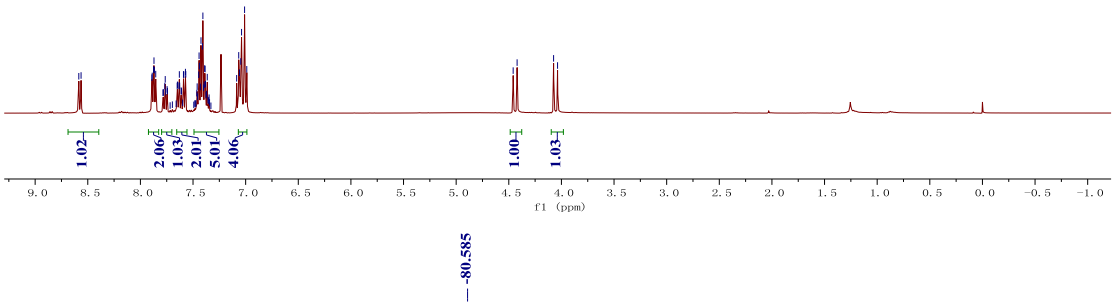

141.53
139.91
135.20
133.88
133.39
132.16
130.96
129.56
129.39
128.90
128.08
127.77
127.24
126.92
126.69
126.36
125.17
124.33
123.04
122.34
75.87
75.57
75.27
74.98
57.37
F3C
OH
O
O
S
Ph
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

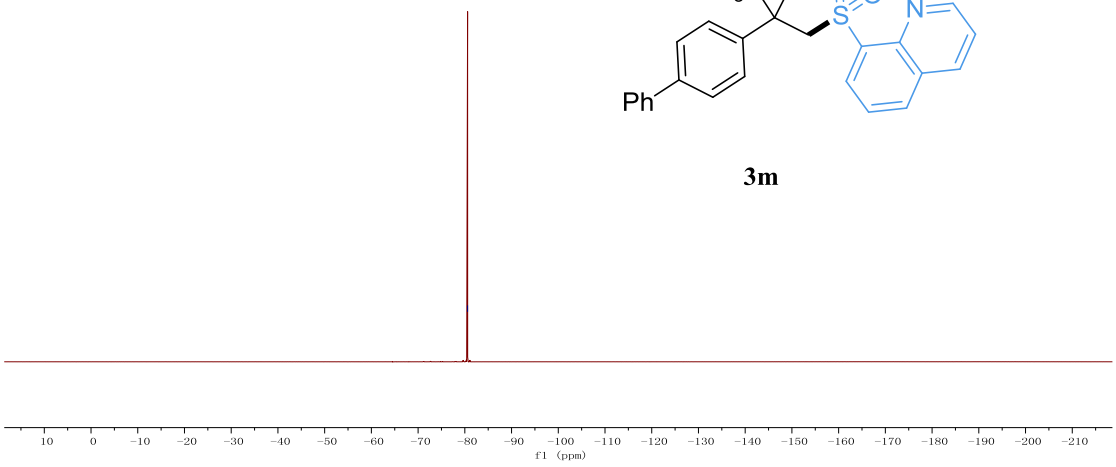
3l

^{1}H NMR (400 MHz, $CDCl_3$), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)spectrum of product **3m**

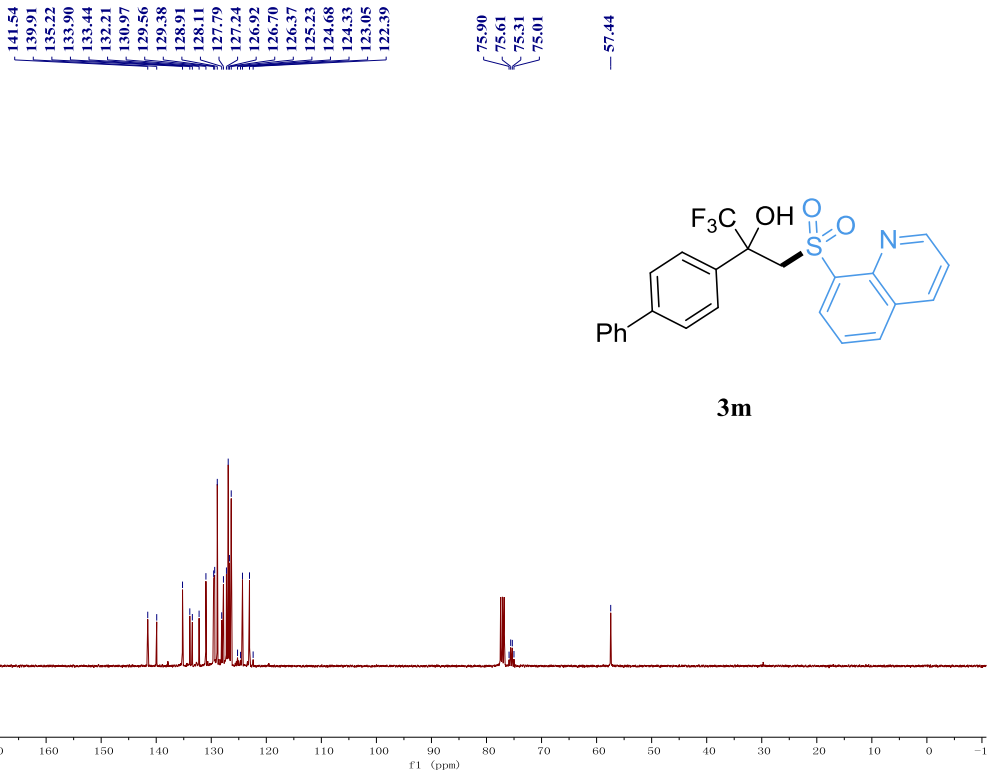


3m



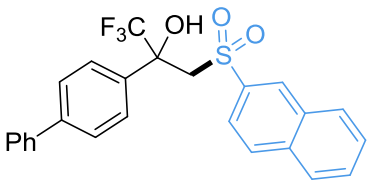


3m

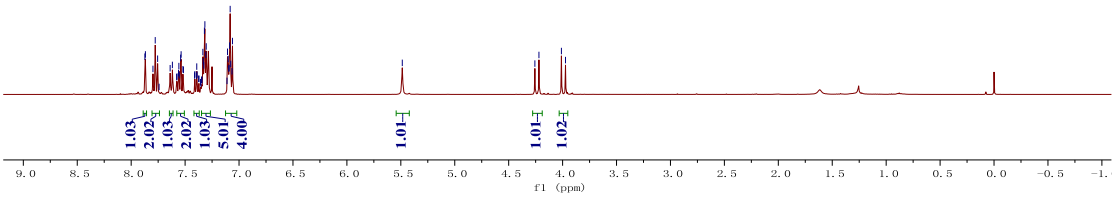

141.54
139.91
135.22
133.90
133.44
132.21
130.97
129.56
129.38
128.91
128.11
127.79
127.24
126.92
126.70
126.37
125.23
124.68
124.33
123.05
122.39
75.90
75.61
75.31
75.01
57.44
F3C
OH
O
O
S
N
Ph
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)

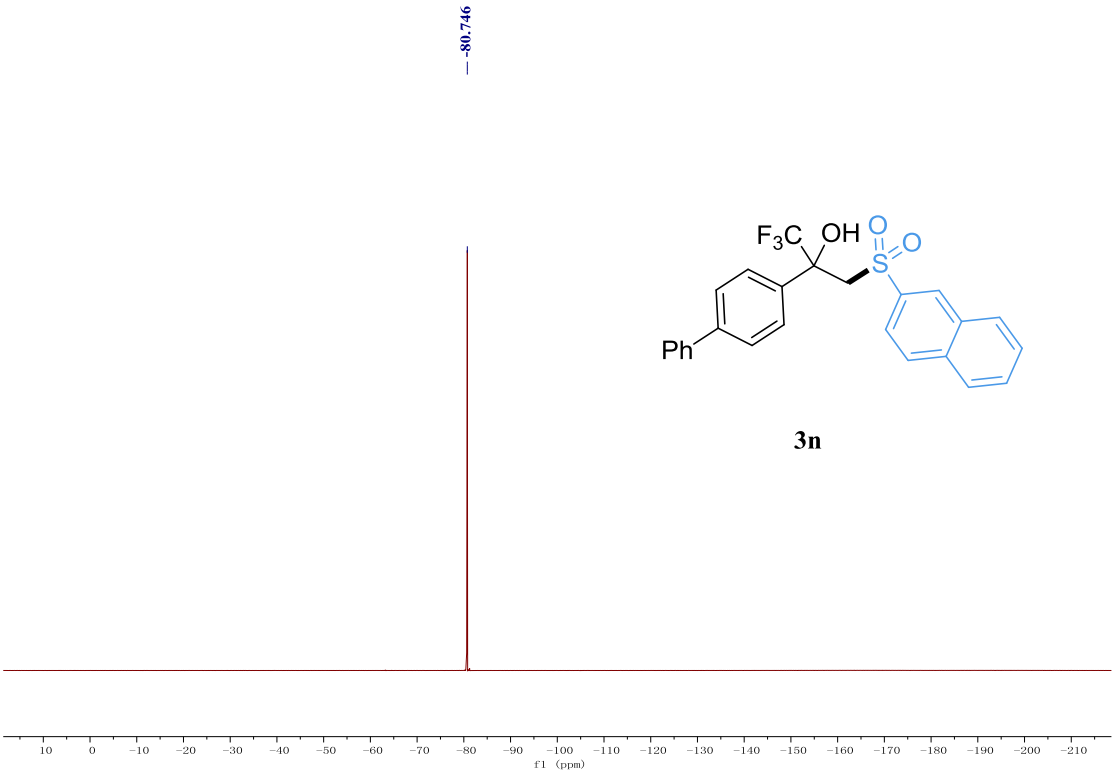
3m

^{1}H NMR (400 MHz, $CDCl_3$), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)spectrum of product **3n**

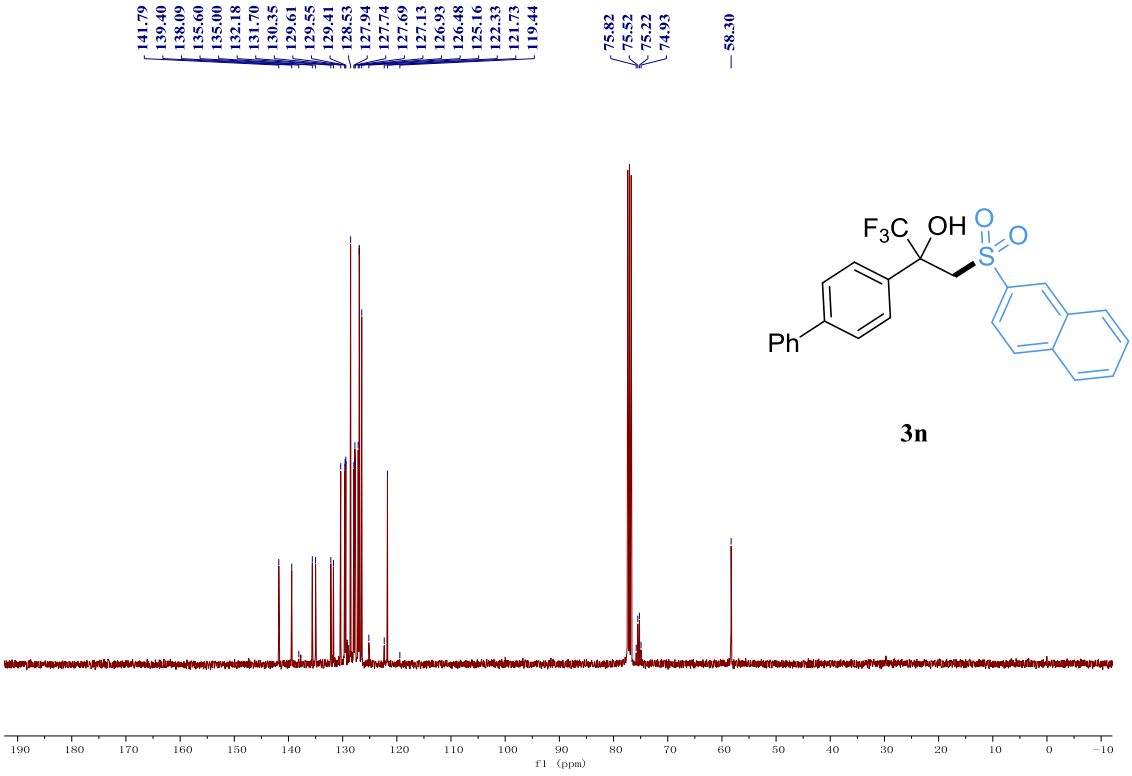


3n



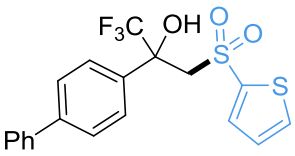


3n

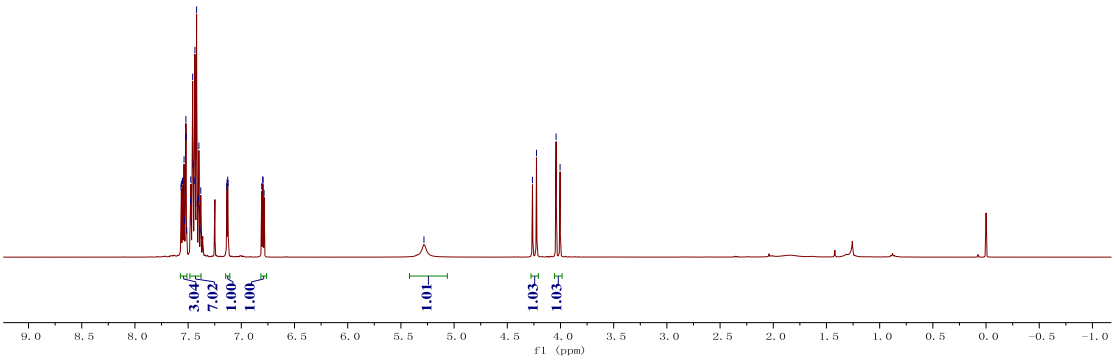

141.79
139.40
138.09
135.60
135.00
132.18
131.70
130.35
129.61
129.55
129.41
128.53
127.94
127.74
127.69
127.13
126.93
126.48
125.16
122.33
121.73
119.44
75.82
75.52
75.22
74.93
58.30
F3C
OH
O
S
O
Ph
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

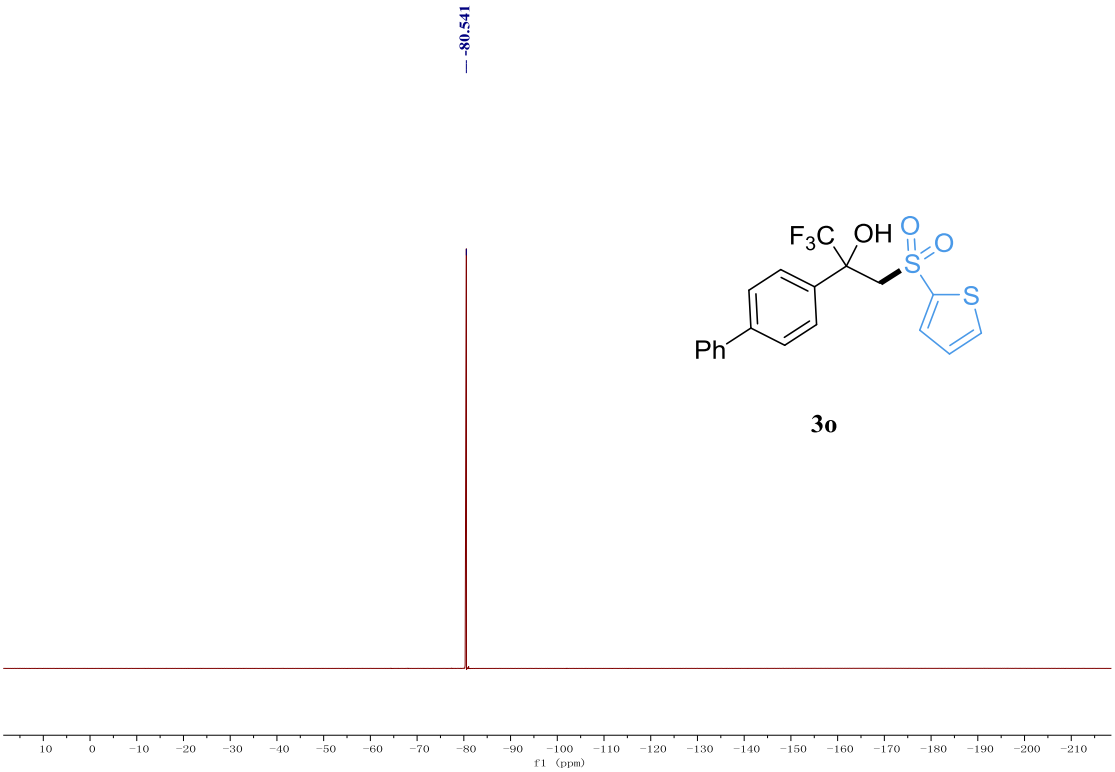
3n

^{1}H NMR (400 MHz, $CDCl_3$), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)spectrum of product **3o**

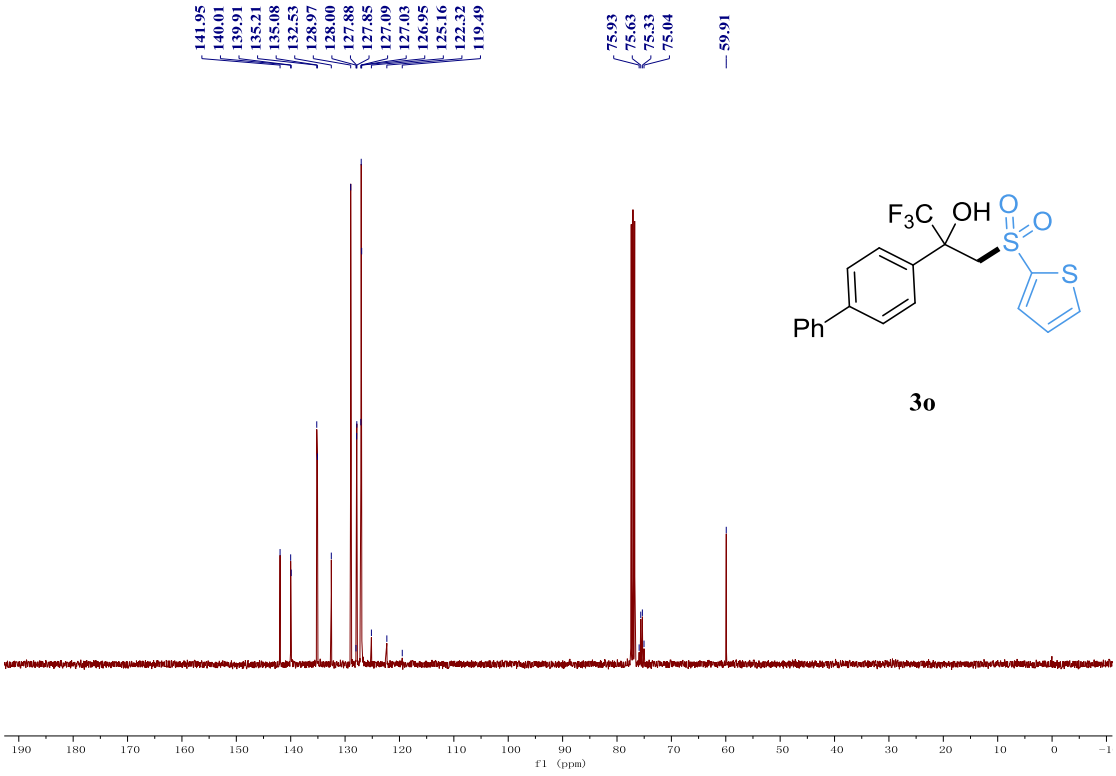


3o



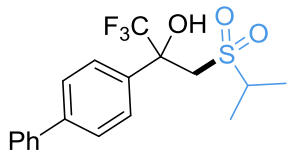


3o

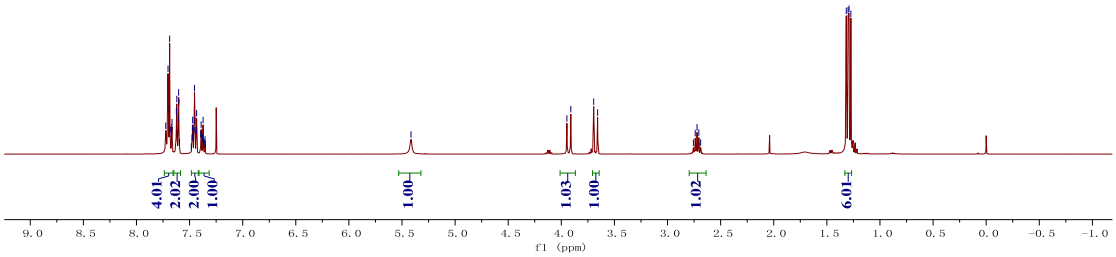

141.95
140.01
139.91
135.21
135.08
132.53
128.97
128.00
127.88
127.85
127.09
127.03
126.95
125.16
122.32
119.49
75.93
75.63
75.33
75.04
59.91
F3C
OH
O
O
S
S
Ph
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)

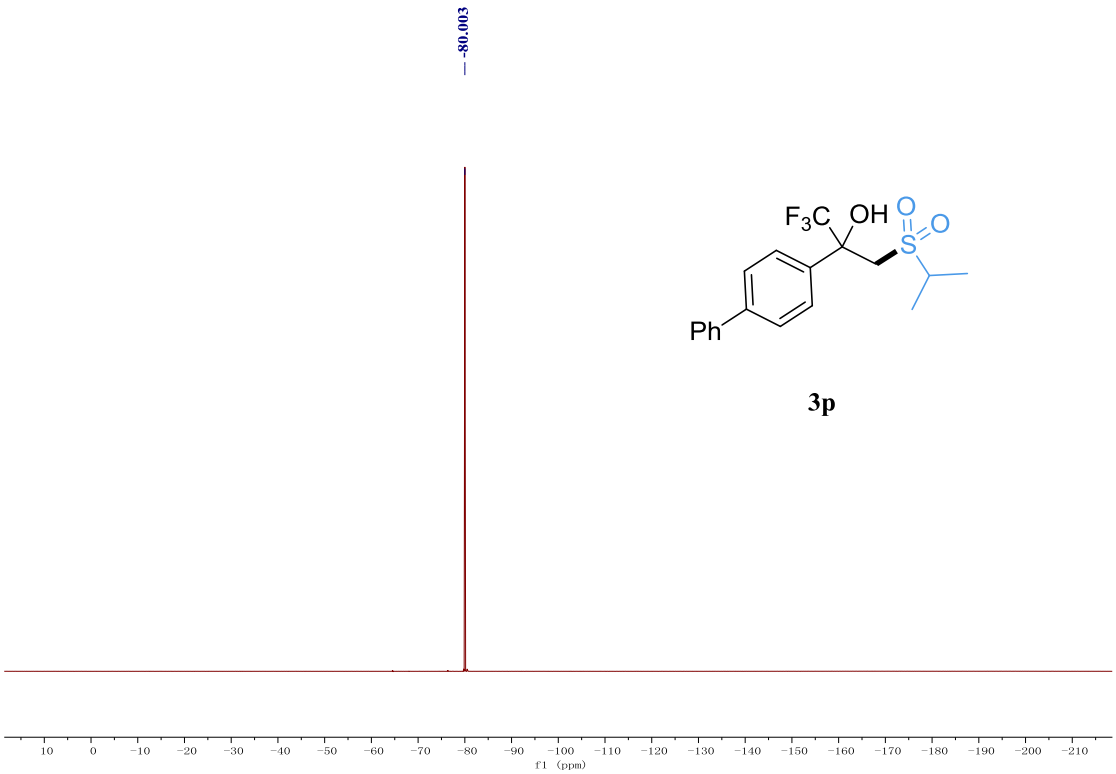
3o

^{1}H NMR (400 MHz, $CDCl_3$), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)spectrum of product **3p**

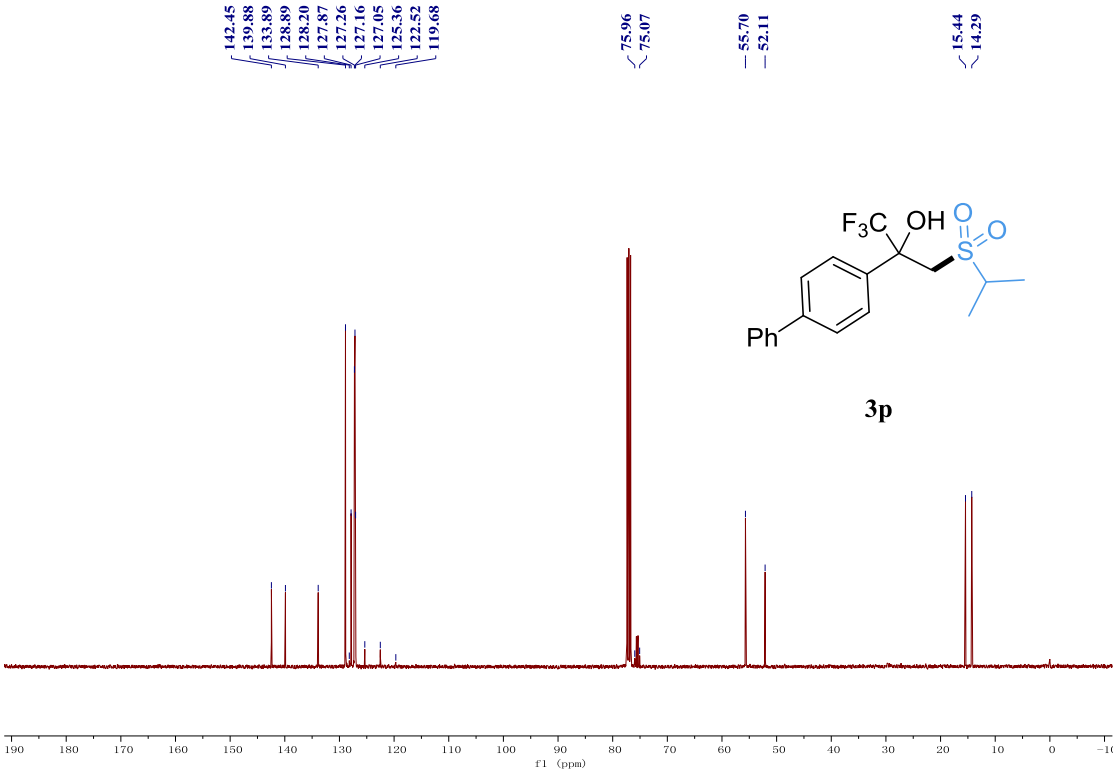


3p

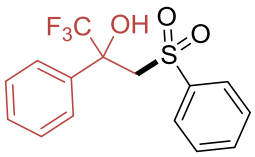




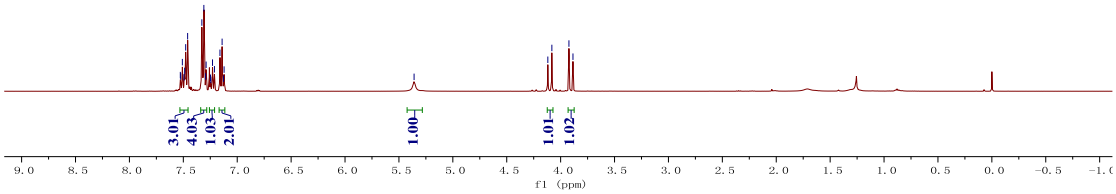
3p

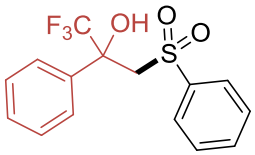

142.45
139.88
133.89
128.89
128.20
127.87
127.26
127.16
127.05
125.36
122.52
119.68
75.96
75.07
55.70
52.11
15.44
14.29
F3C
OH
O
S
O
Ph
3p
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)spectrum of product **3aa**

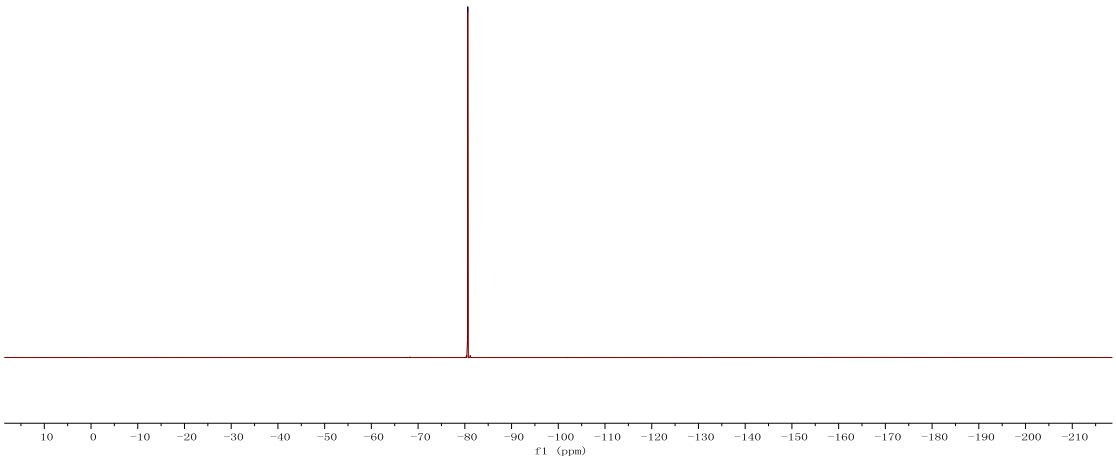


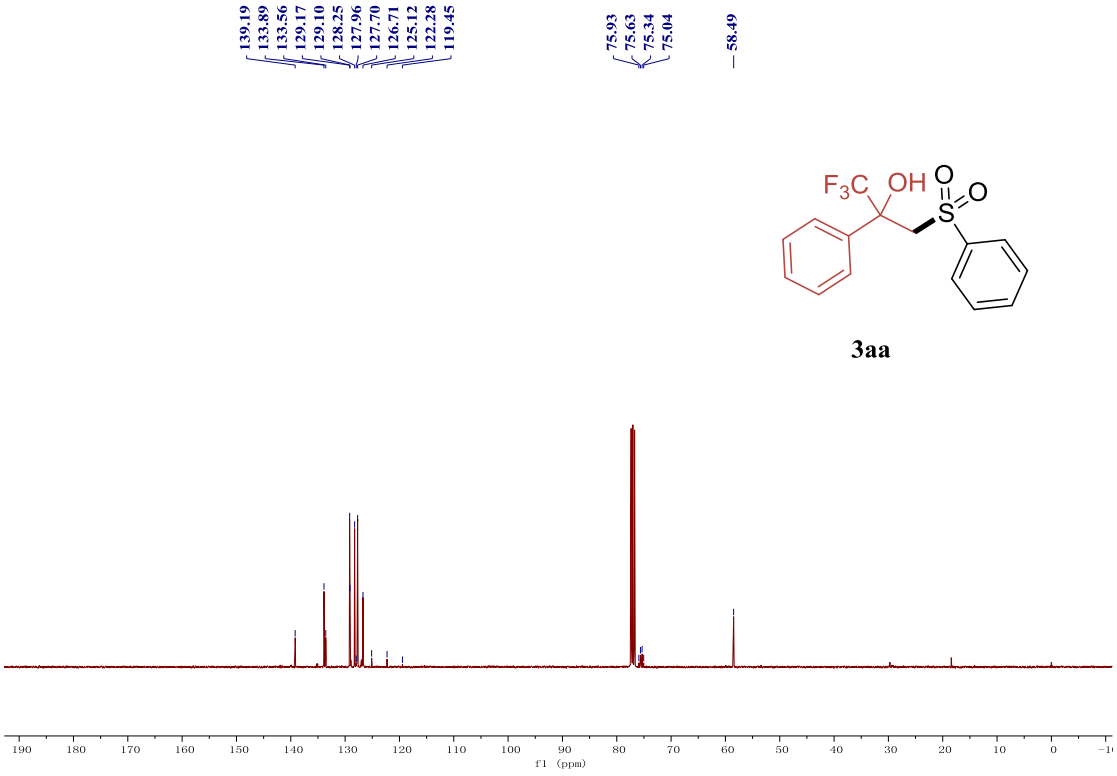
3aa





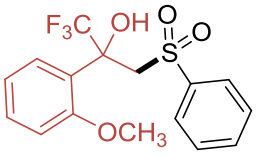
3aa



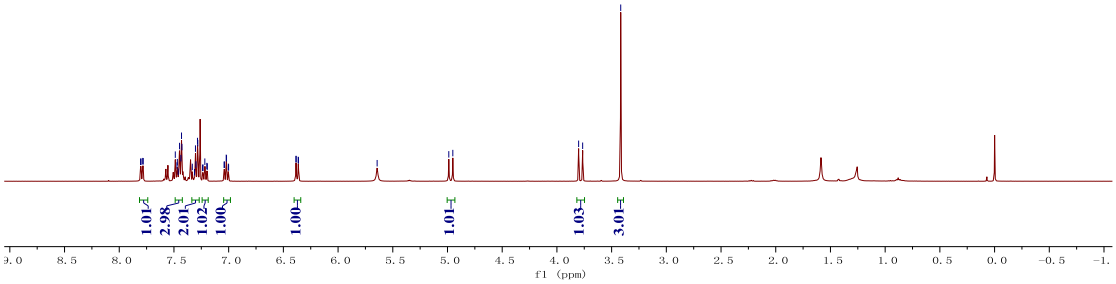

139.19
133.89
133.56
129.17
129.10
128.25
127.96
127.70
126.71
125.12
122.28
119.45
75.93
75.63
75.34
75.04
58.49
F3C
OH
O
O
S
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

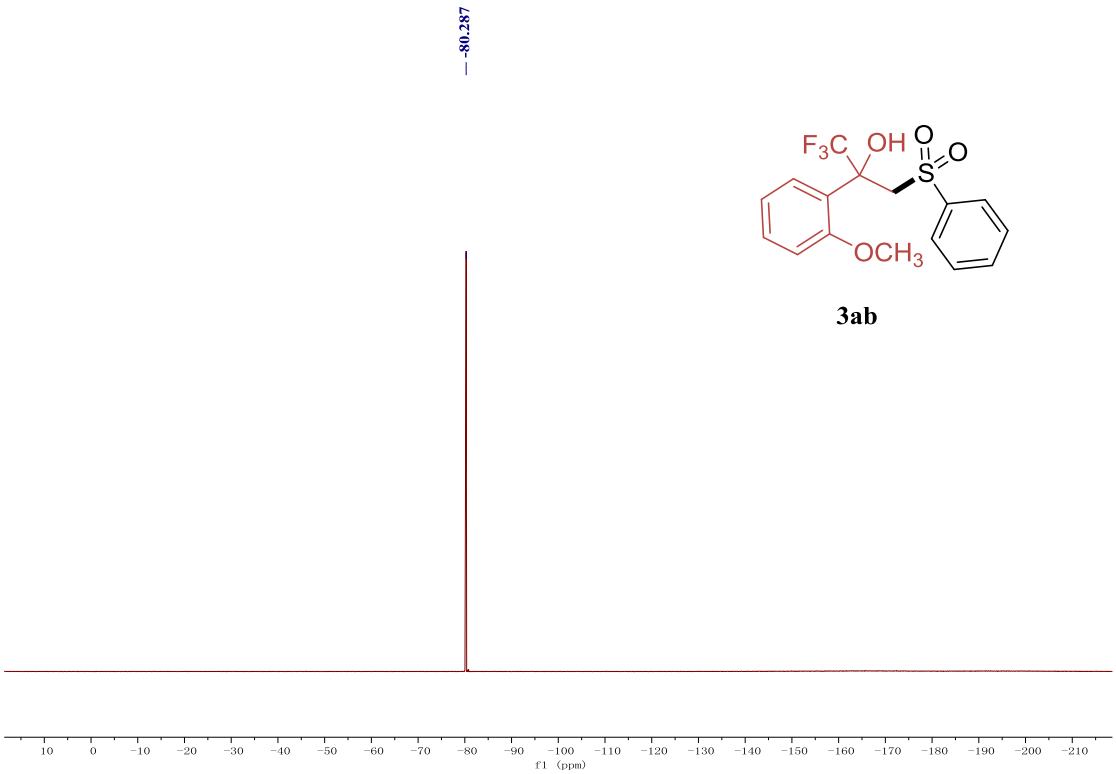
3aa

^{1}H NMR (400 MHz, $CDCl_3$), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)spectrum of product **3ab**

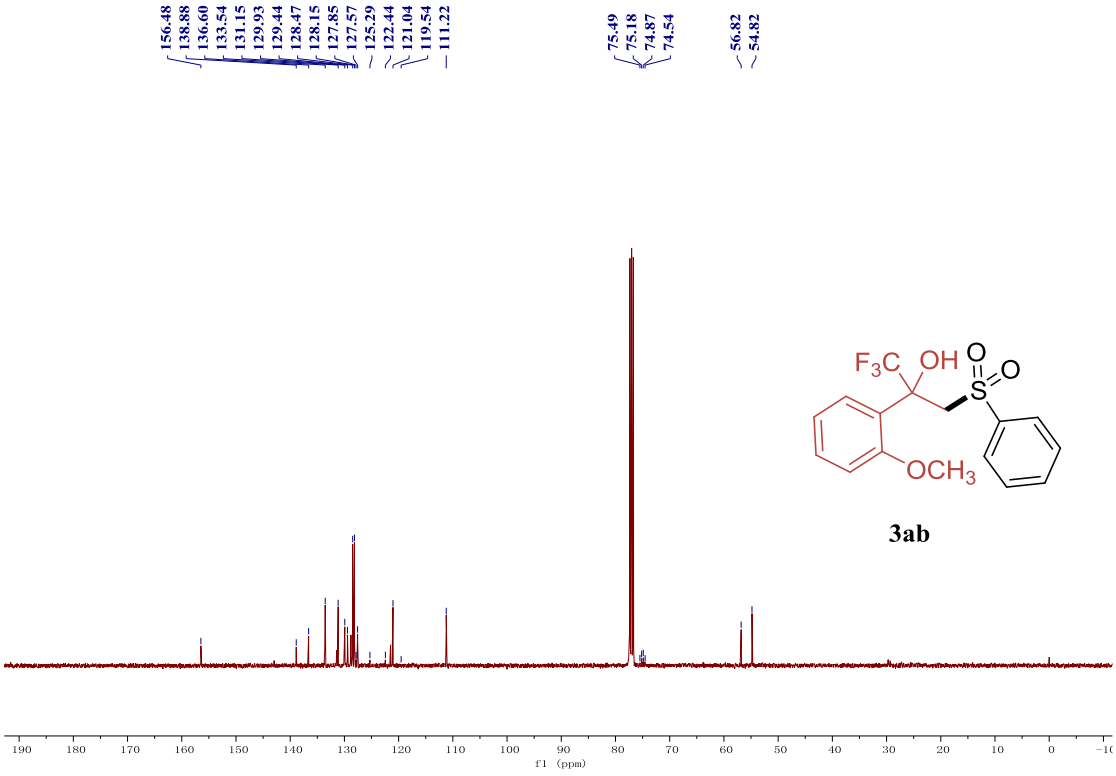


3ab



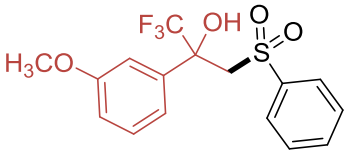


3ab

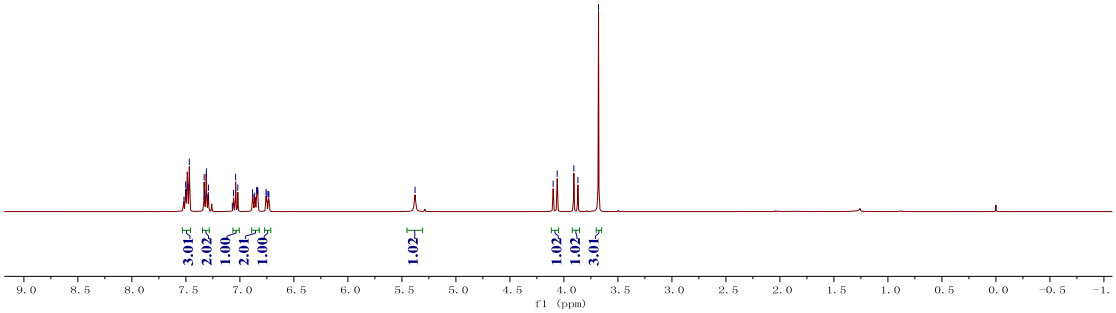

156.48
138.88
136.60
133.54
131.15
129.93
129.44
128.47
128.15
127.85
127.57
125.29
122.44
121.04
119.54
111.22
75.49
75.18
74.87
74.54
56.82
54.82
F3C
OH
O
O
S
OCH3
f1 (ppm)

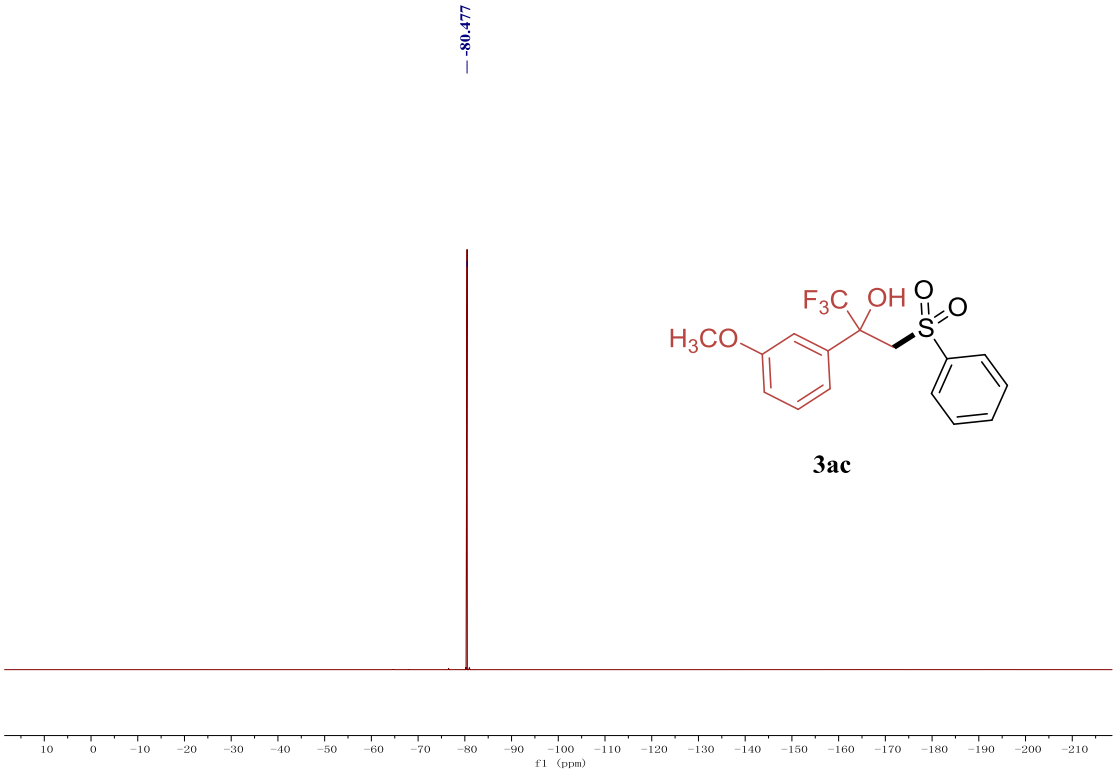
3ab

^{1}H NMR (400 MHz, $CDCl_3$), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)spectrum of product **3ac**

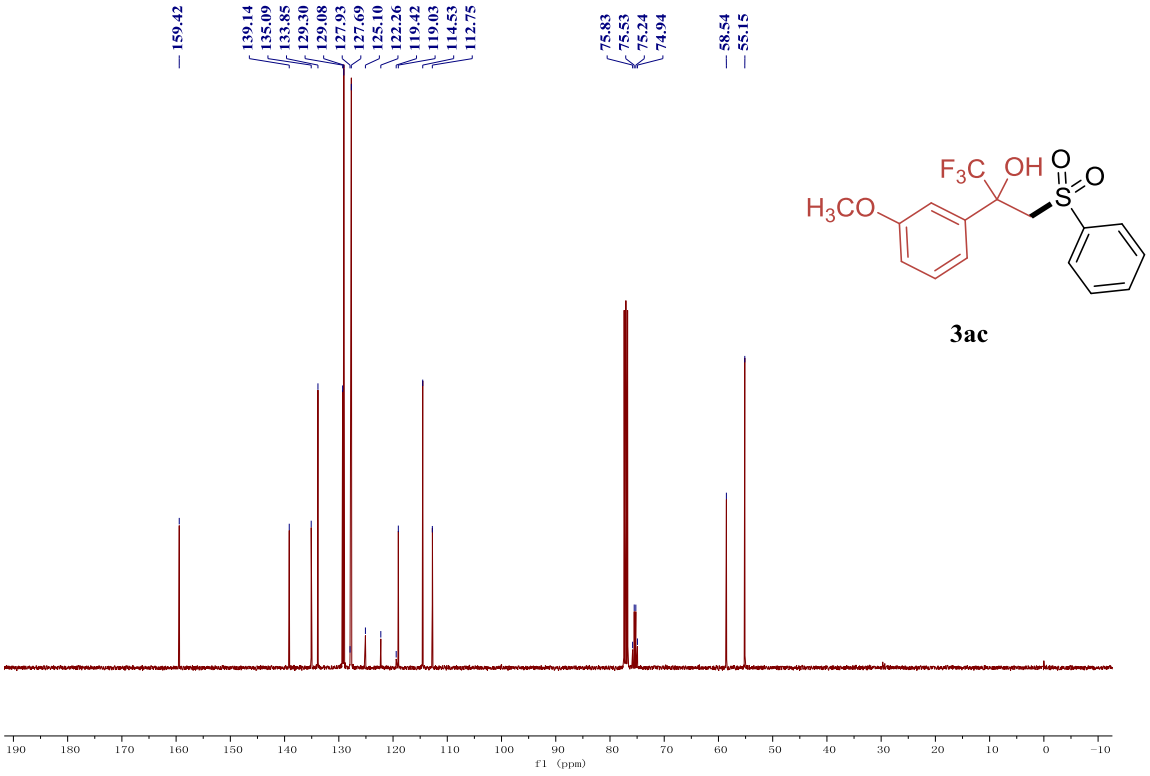


3ac



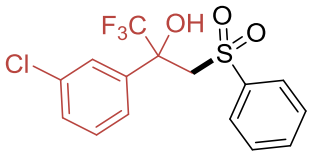


3ac

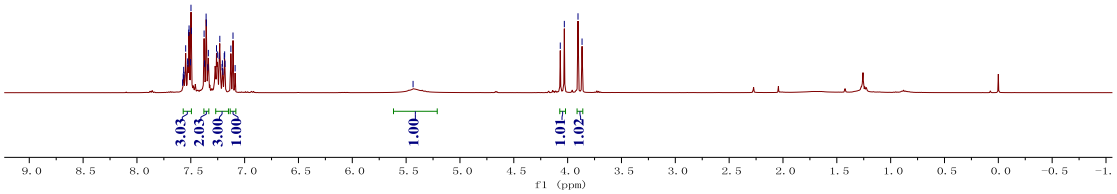

159.42
139.14
135.09
133.85
129.30
129.08
127.93
127.69
125.10
122.26
119.42
119.03
114.53
112.75
75.83
75.53
75.24
74.94
58.54
55.15
F3C
OH
O
O
S
H3CO
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

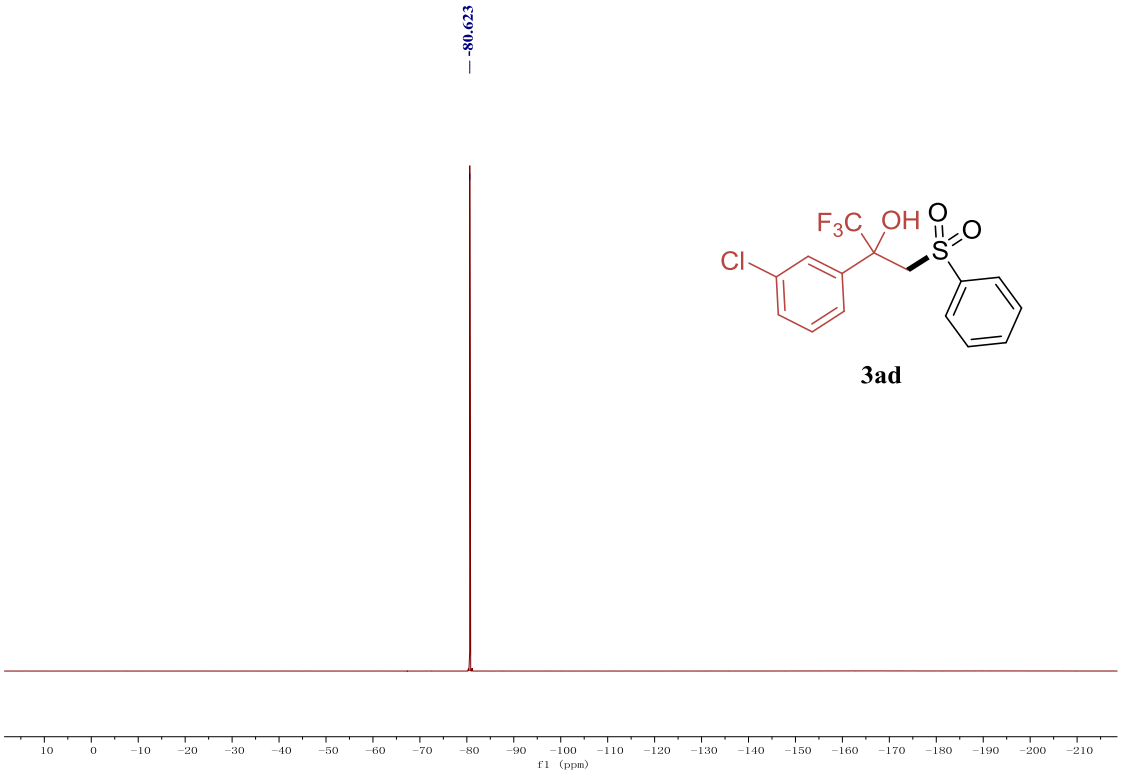
3ac

^{1}H NMR (400 MHz, $CDCl_3$), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)spectrum of product **3ad**

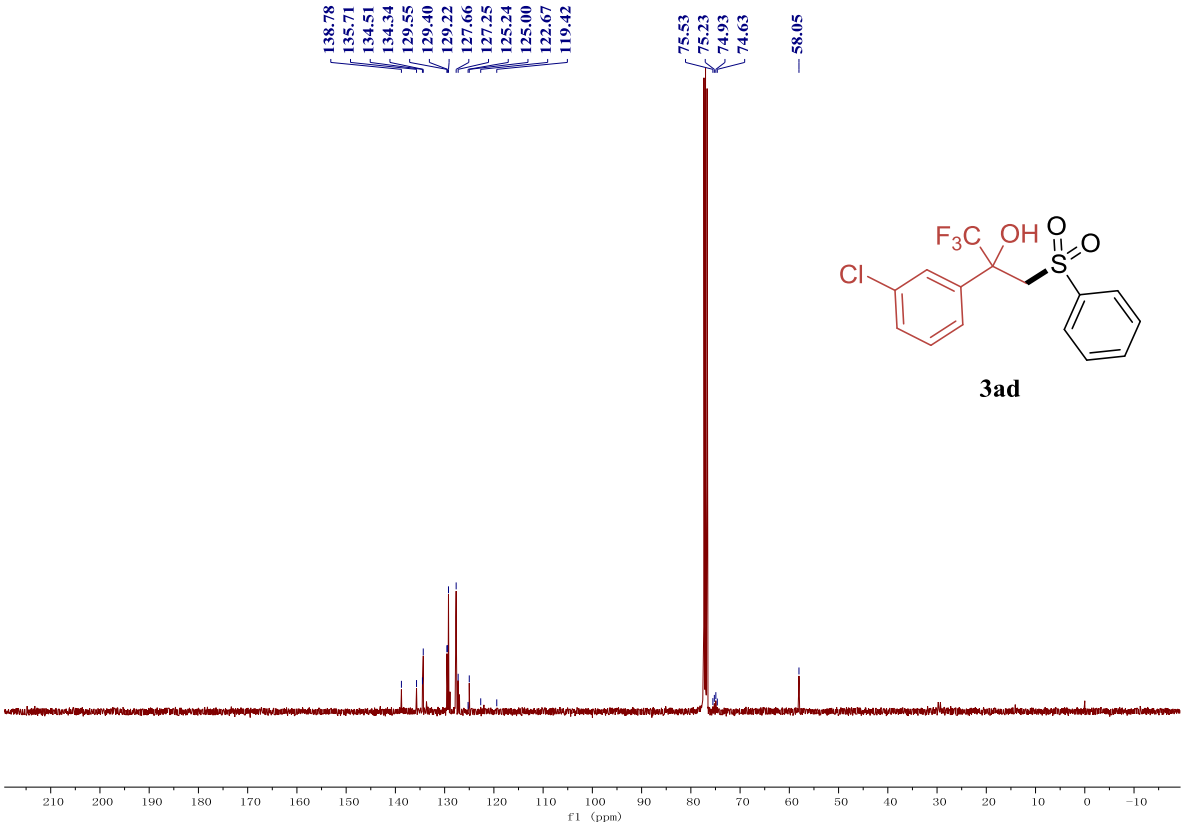


3ad



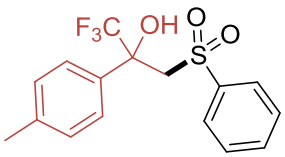


3ad

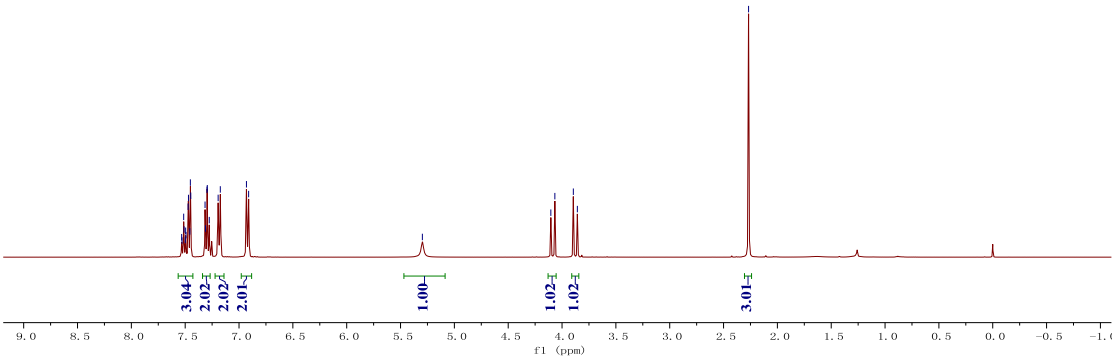

138.78
135.71
134.51
134.34
129.55
129.40
129.22
127.66
127.25
125.24
125.00
122.67
119.42
75.53
75.23
74.93
74.63
58.05
F3C
OH
O
O
S
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

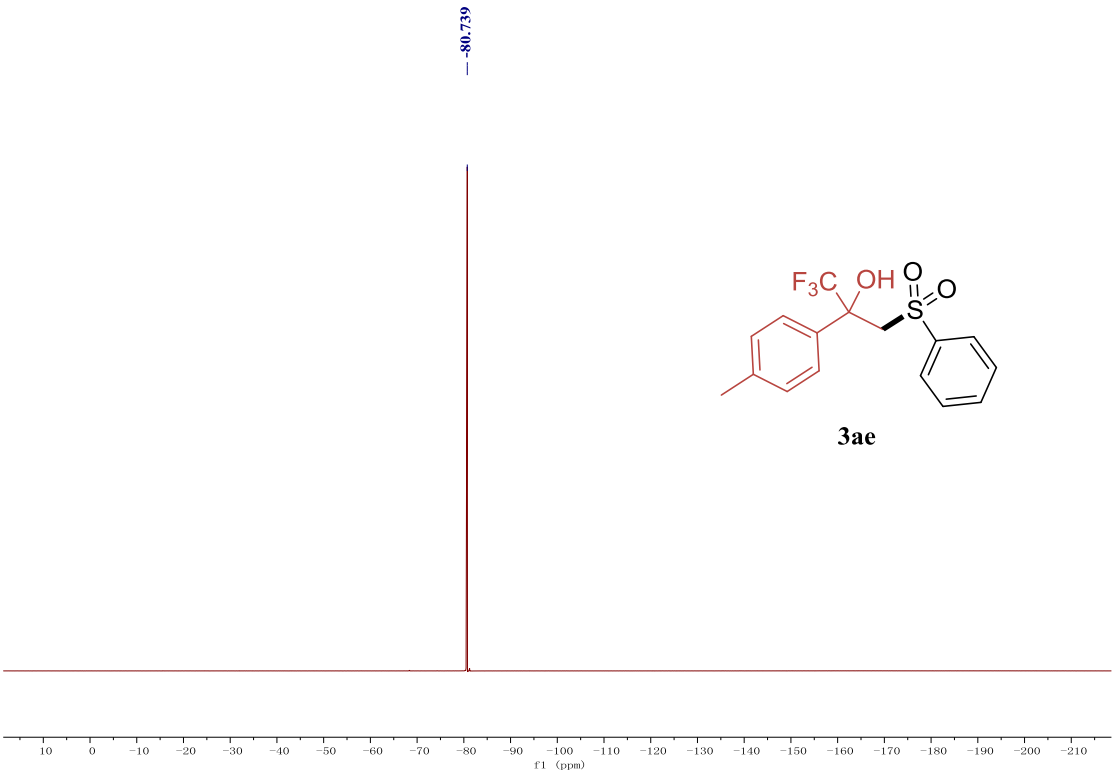
3ad

^{1}H NMR (400 MHz, $CDCl_3$), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)spectrum of product **3ae**

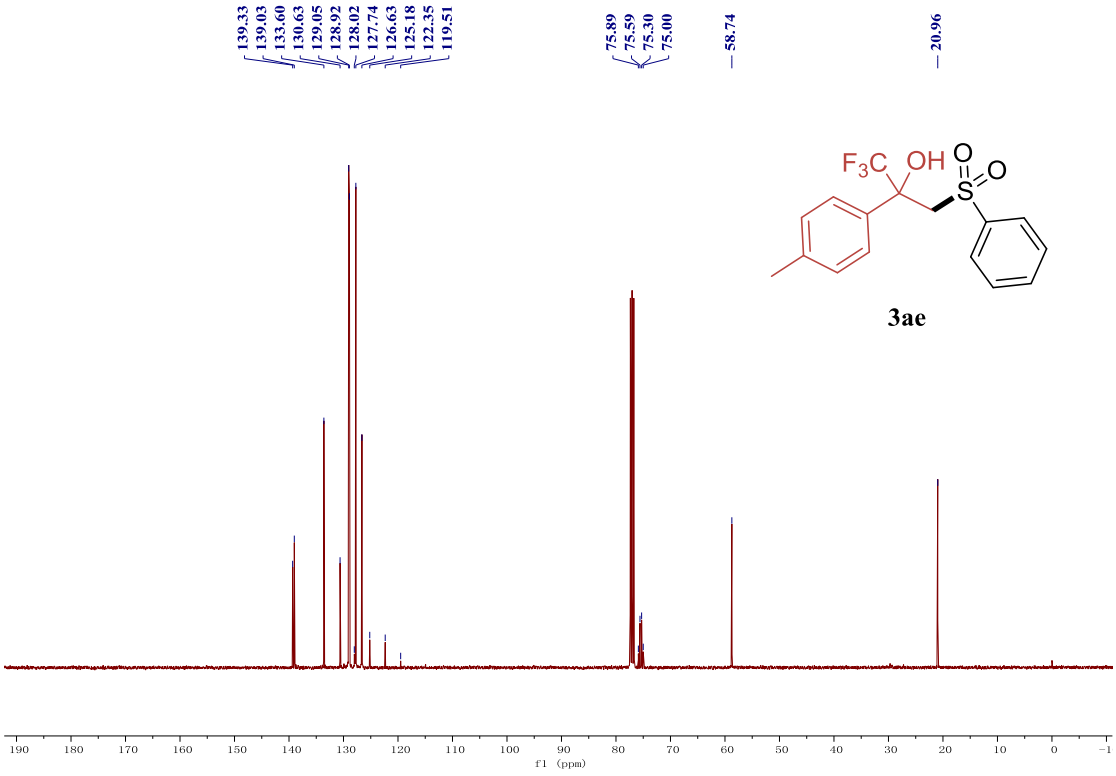


3ae

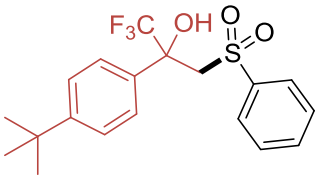




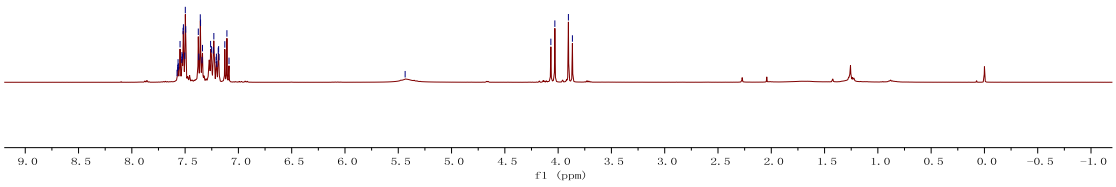
3ae

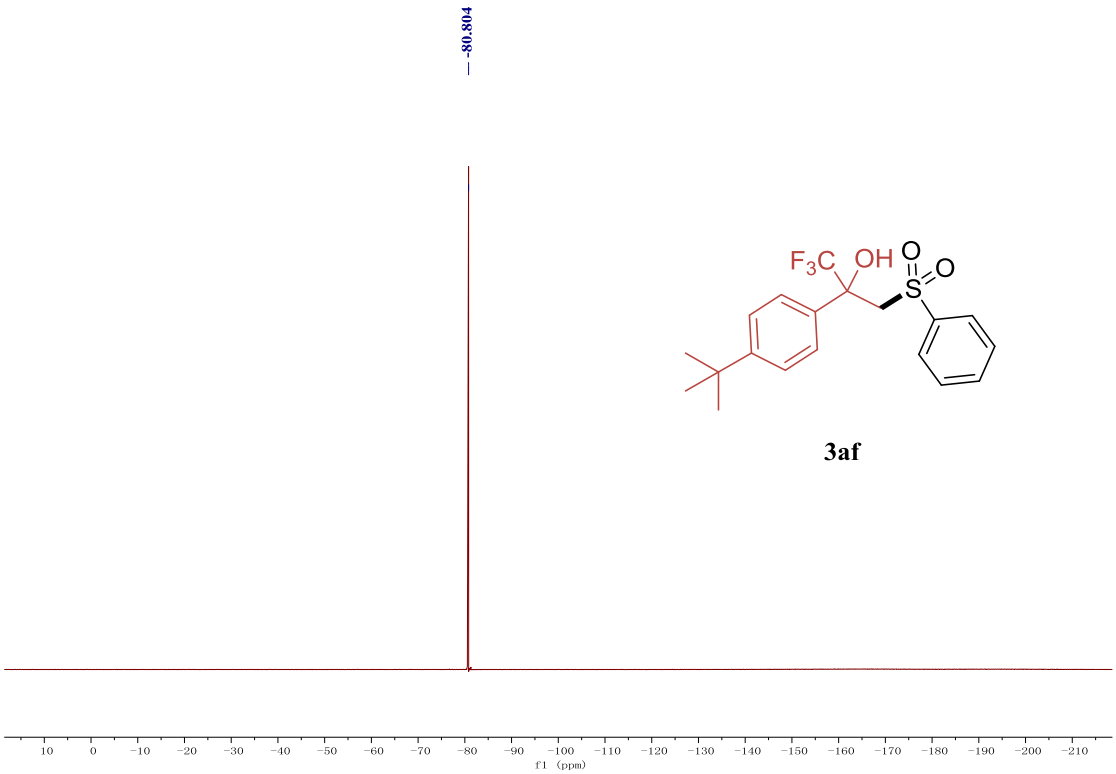

139.33
139.03
133.60
130.63
129.05
128.92
128.02
127.74
126.63
125.18
122.35
119.51
75.89
75.59
75.30
75.00
58.74
20.96
F3C
OH
O
S
O
3ae
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)spectrum of product **3af**

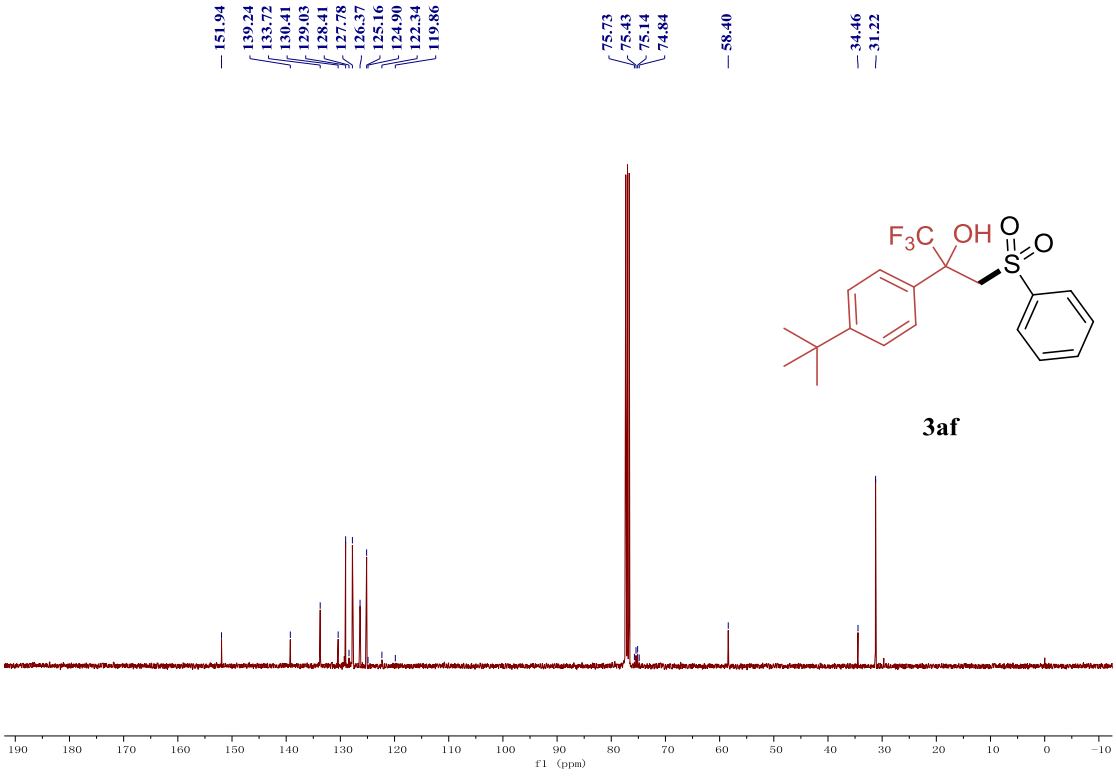


3af

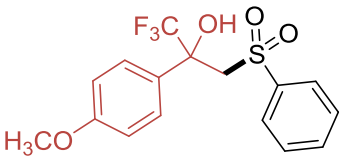




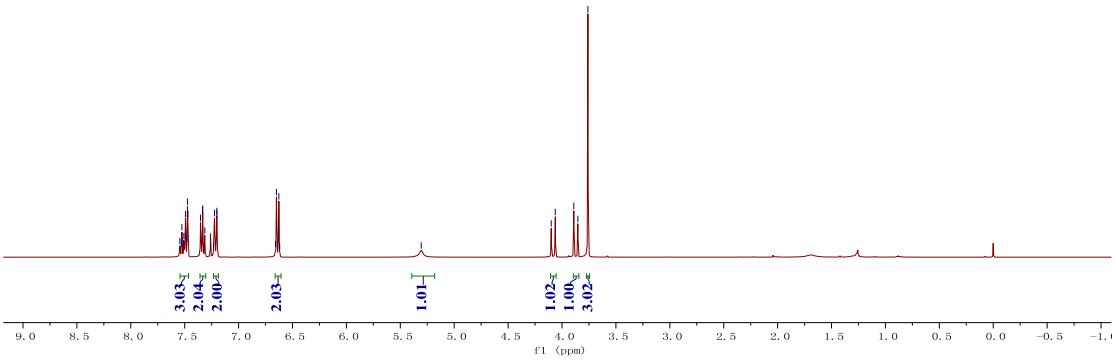
3af

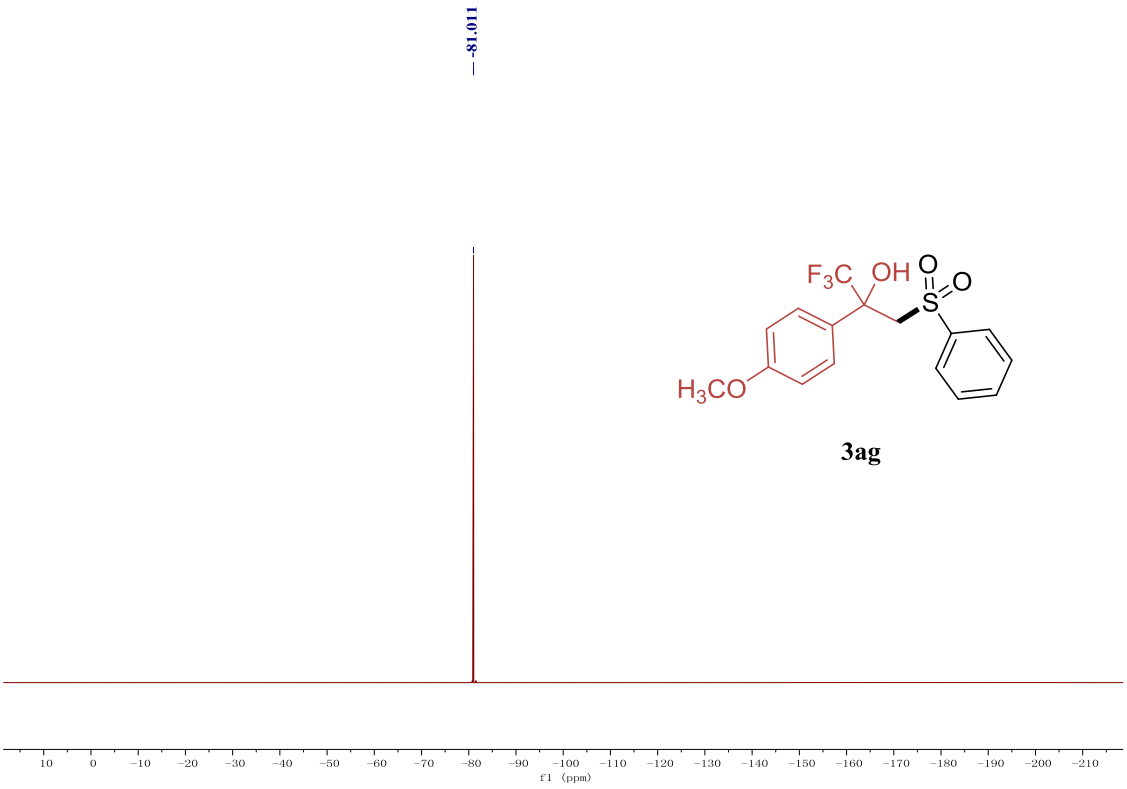

151.94
139.24
133.72
130.41
129.03
128.41
127.78
126.37
125.16
124.90
122.34
119.86
75.73
75.43
75.14
74.84
58.40
34.46
31.22
F3C
OH
O
S
O
3af
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)spectrum of product **3ag**

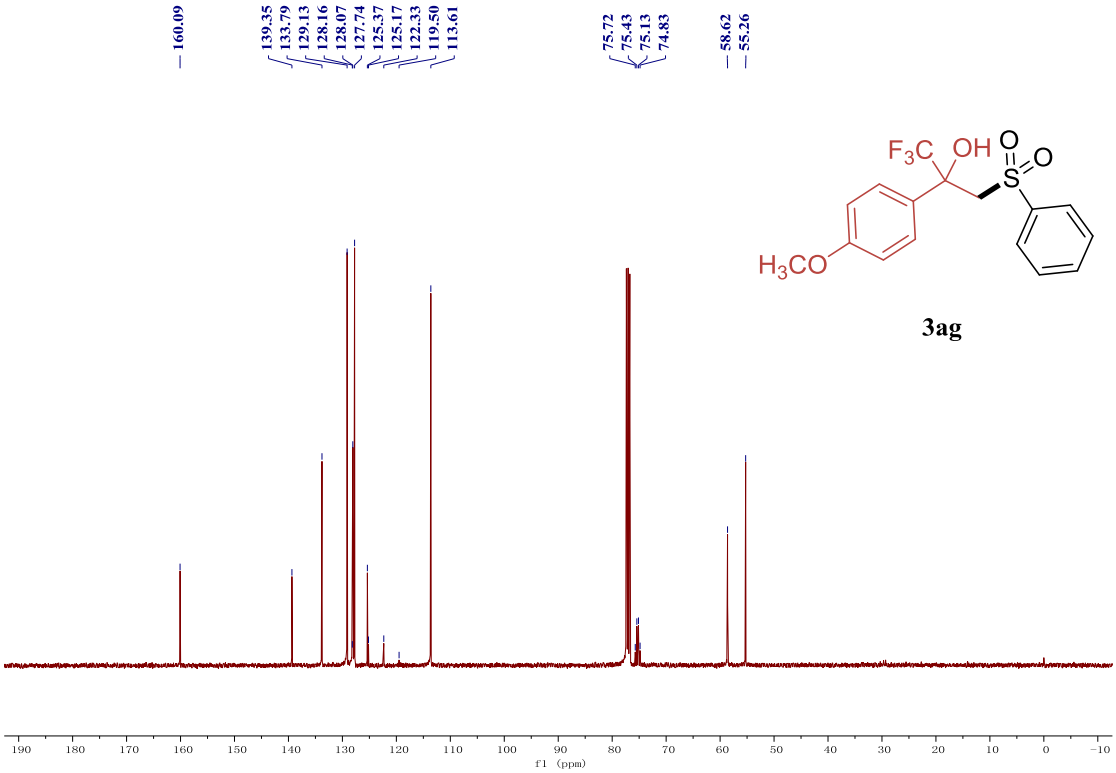


3ag



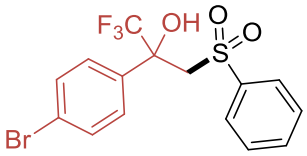


3ag

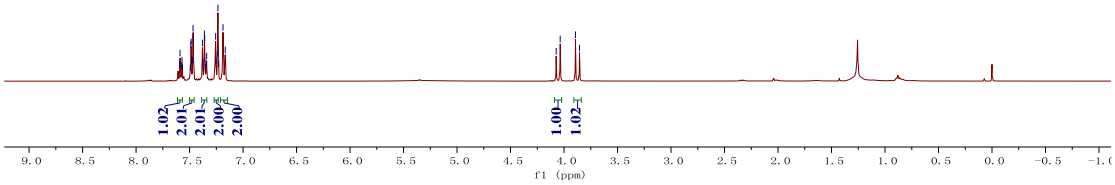

160.09
139.35
133.79
129.13
128.16
128.07
127.74
125.37
125.17
122.33
119.50
113.61
75.72
75.43
75.13
74.83
58.62
55.26
F3C
OH
O
O
S
H3CO
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

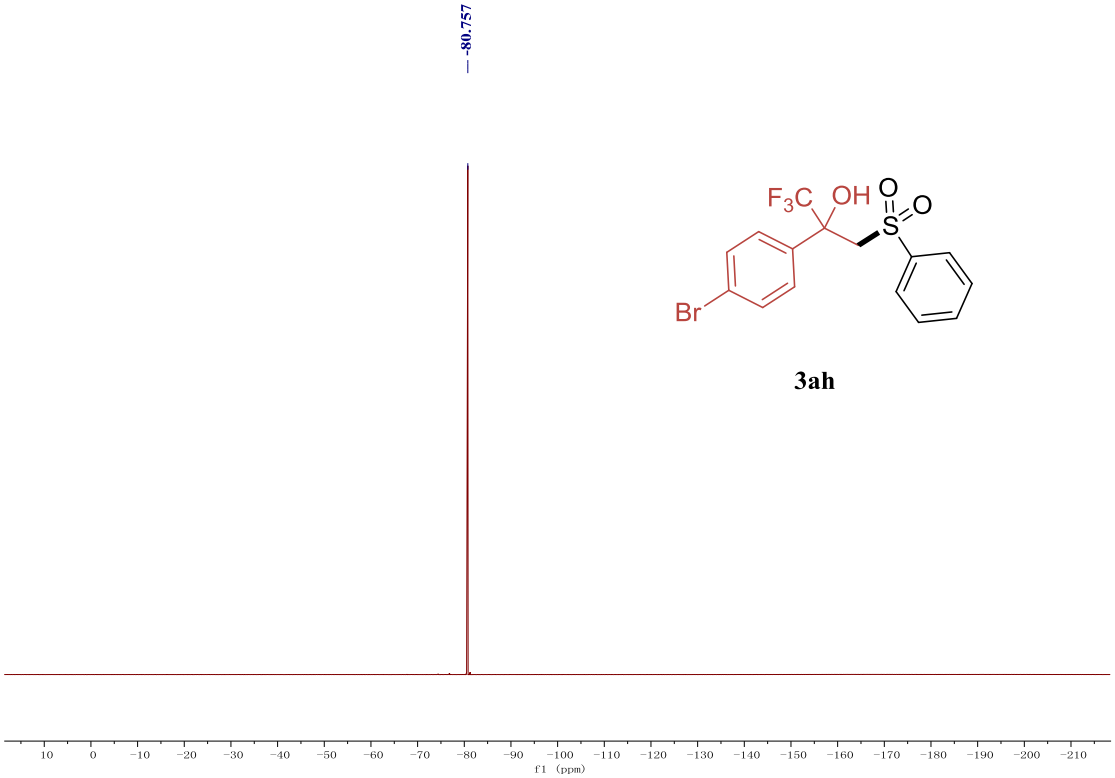
3ag

^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) and ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)spectrum of product **3ah**

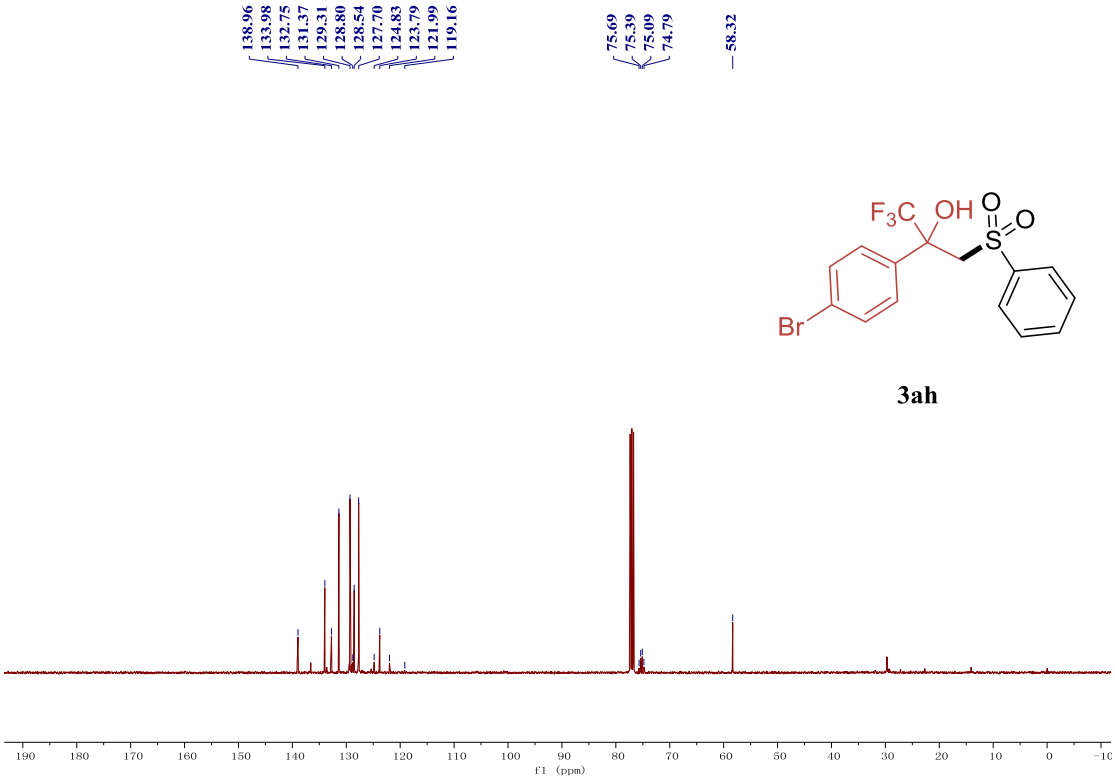


3ah



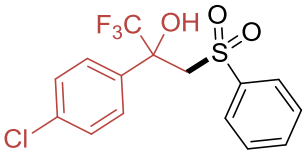


3ah

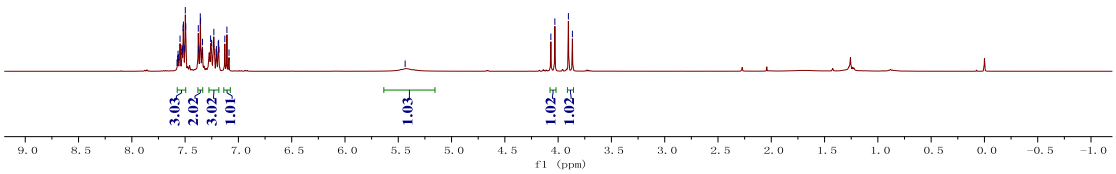

138.96
133.98
132.75
131.37
129.31
128.80
128.54
127.70
124.83
123.79
121.99
119.16
75.69
75.39
75.09
74.79
58.32
F3C
OH
O
S
O
Br
f1 (ppm)

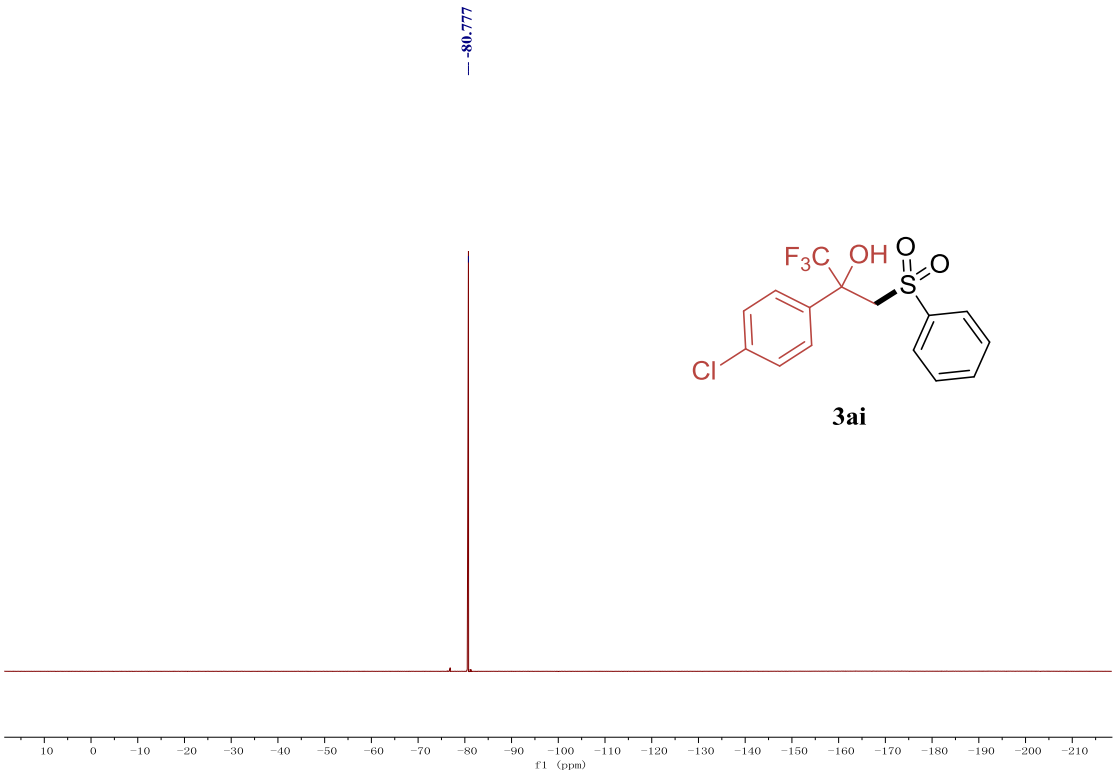
3ah

^{1}H NMR (400 MHz, $CDCl_3$), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)spectrum of product **3ai**

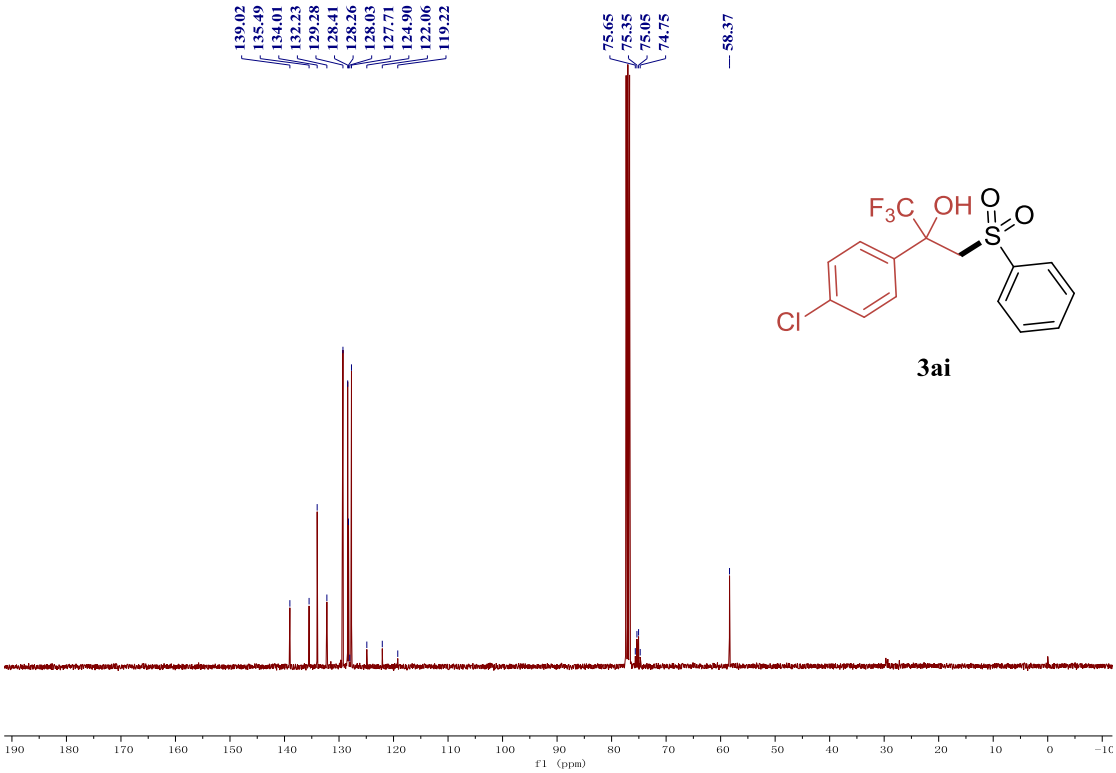


3ai



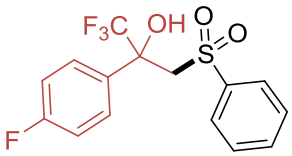


3ai

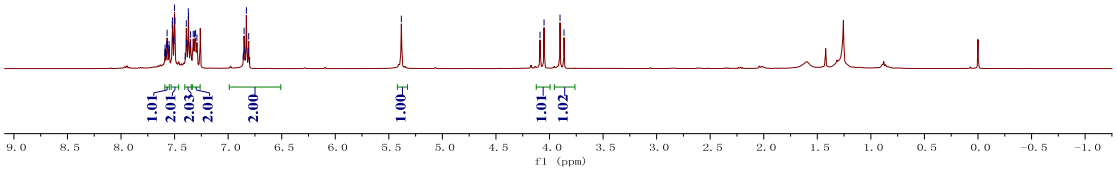

139.02
135.49
134.01
132.23
129.28
128.41
128.26
128.03
127.71
124.90
122.06
119.22
75.65
75.35
75.05
74.75
58.37
F3C
OH
O
S
O
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

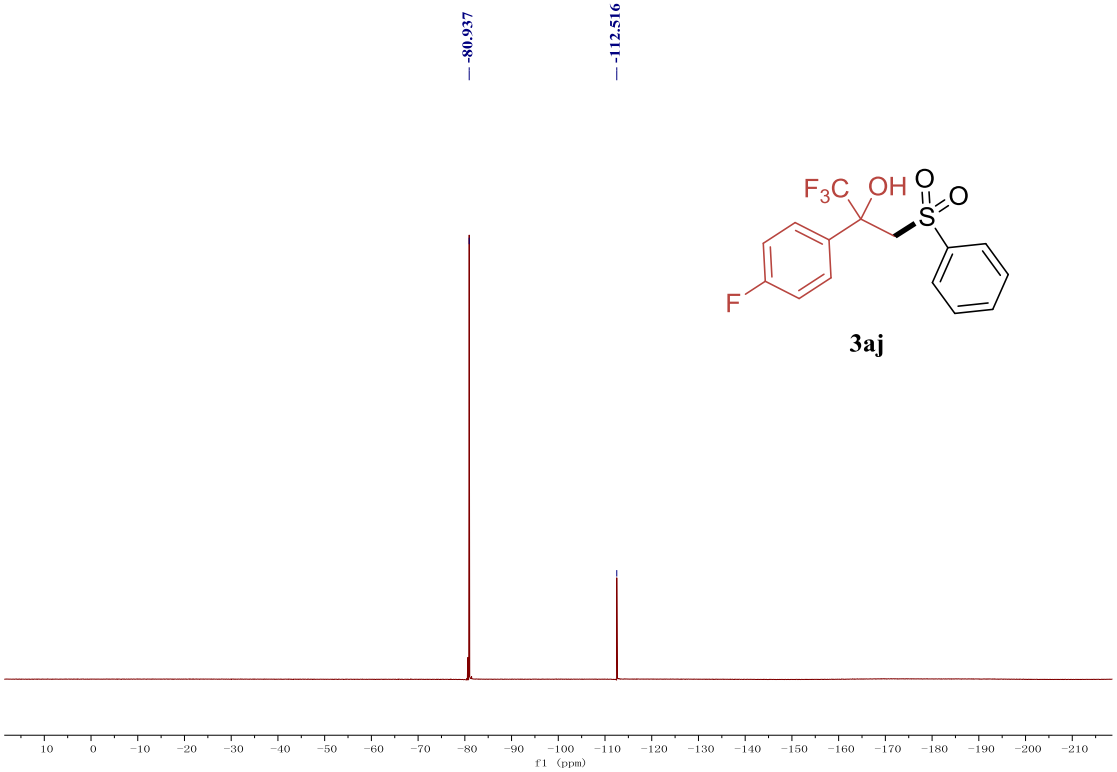
3ai

^{1}H NMR (400 MHz, $CDCl_3$), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)spectrum of product **3aj**

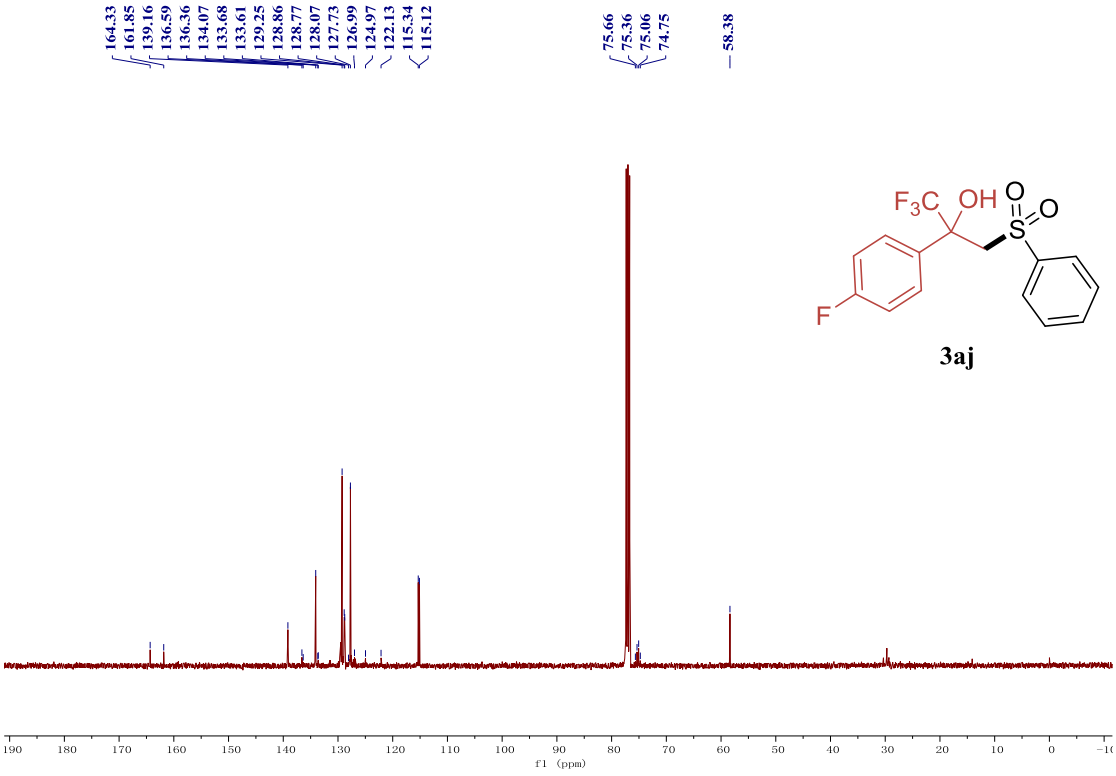


3aj



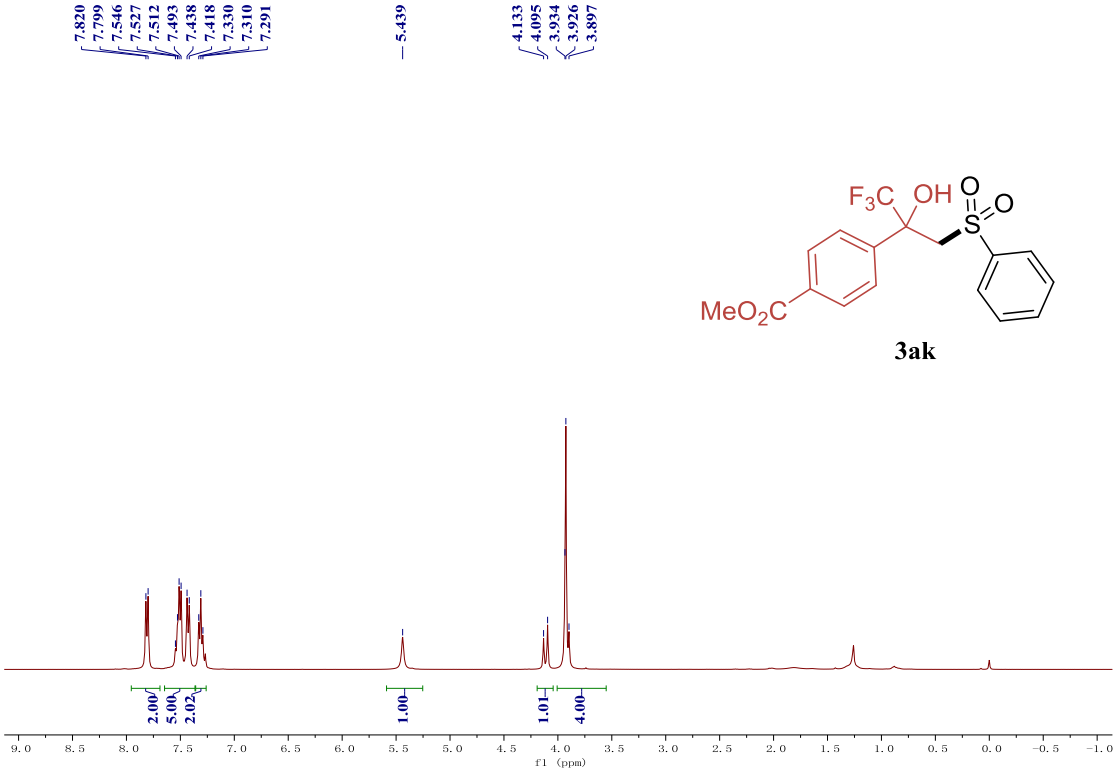


3aj

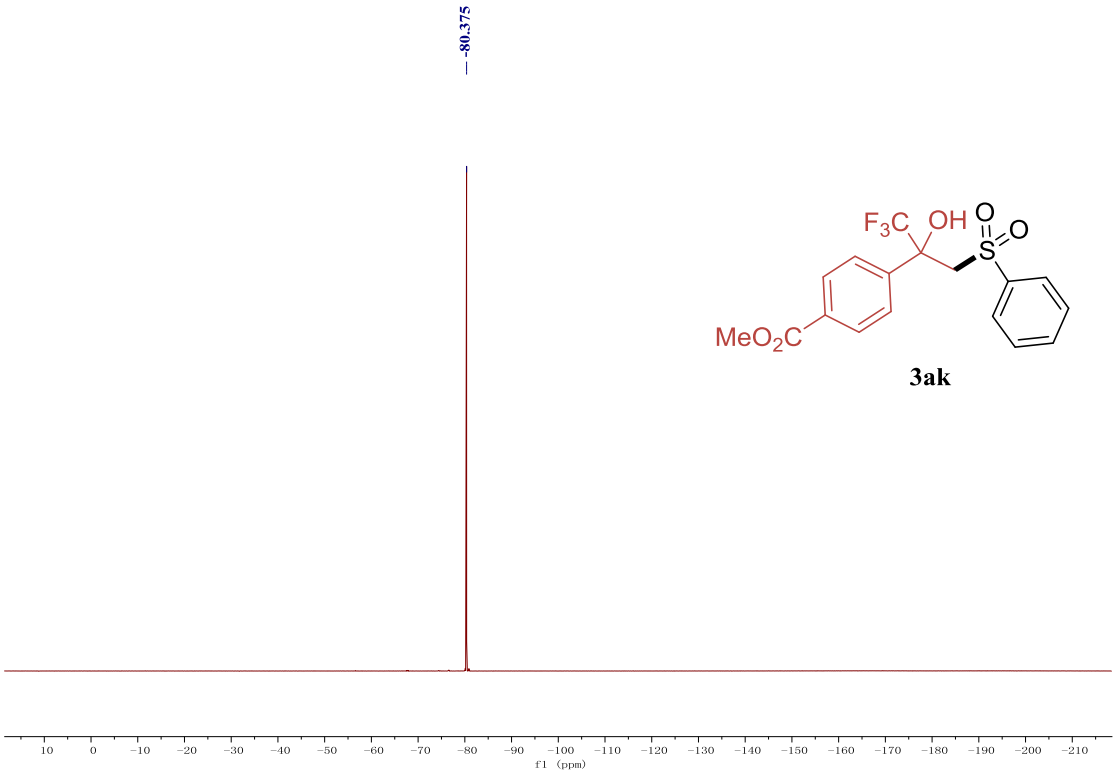

164.33
161.85
139.16
136.59
136.36
134.07
133.68
133.61
129.25
128.86
128.77
128.07
127.73
126.99
124.97
122.13
115.34
115.12
75.66
75.36
75.06
74.75
58.38
F3C
OH
O
O
S
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3aj

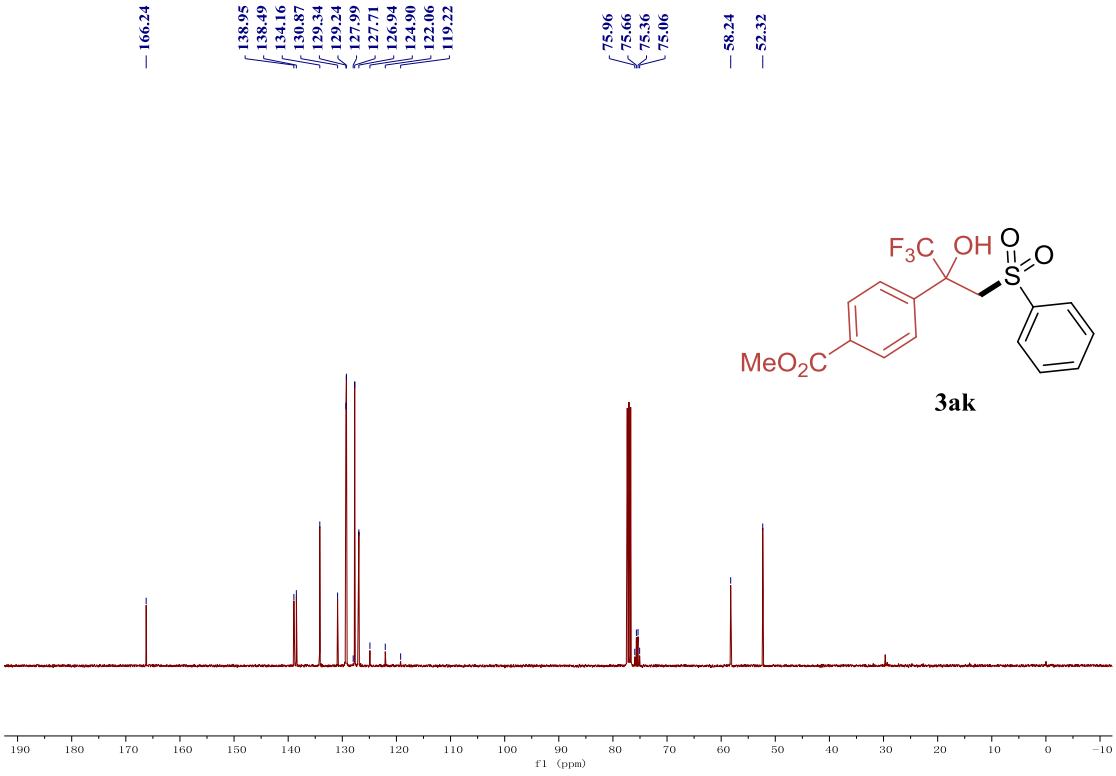
^{1}H NMR (400 MHz, $CDCl_3$), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)spectrum of product **3ak**



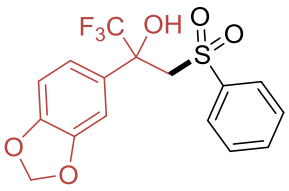
3ak



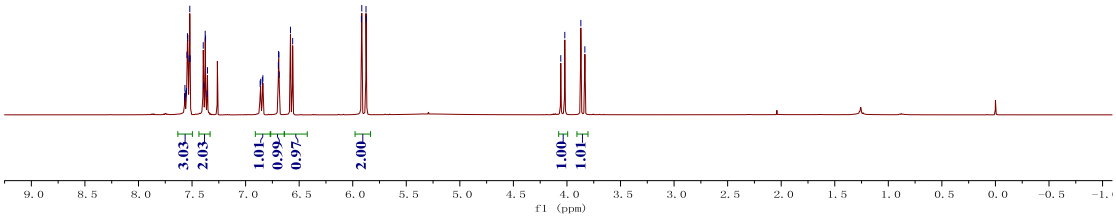
3ak

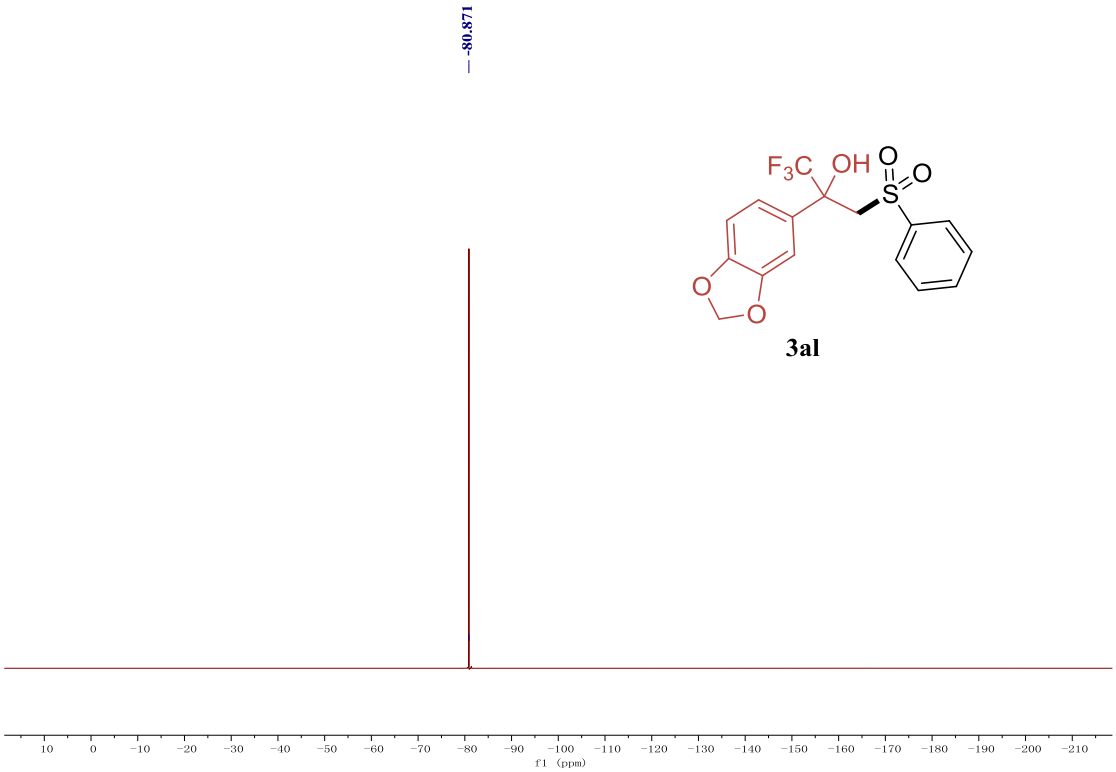

166.24
138.95
138.49
134.16
130.87
129.34
129.24
127.99
127.71
126.94
124.90
122.06
119.22
75.96
75.66
75.36
75.06
58.24
52.32
F3C
OH
O
O
S
MeO2C
3ak
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) and ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)spectrum of product **3al**

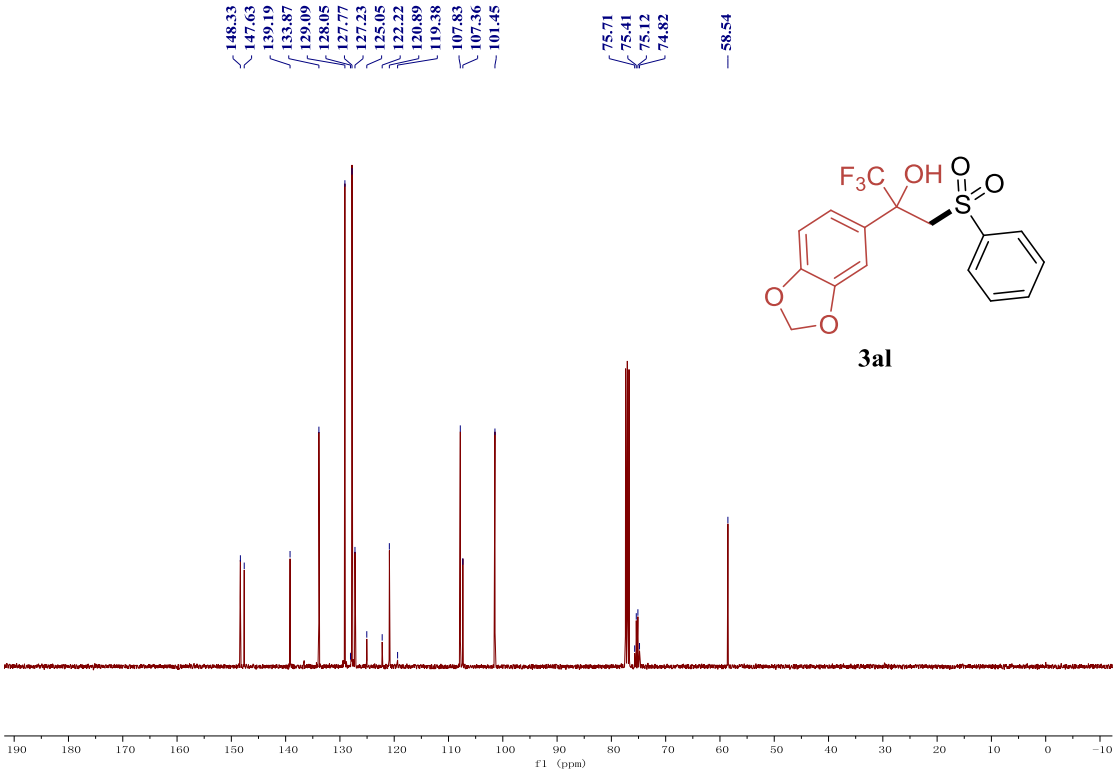


3al

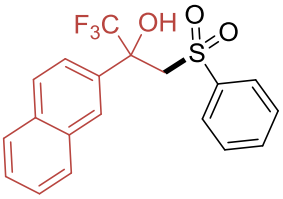




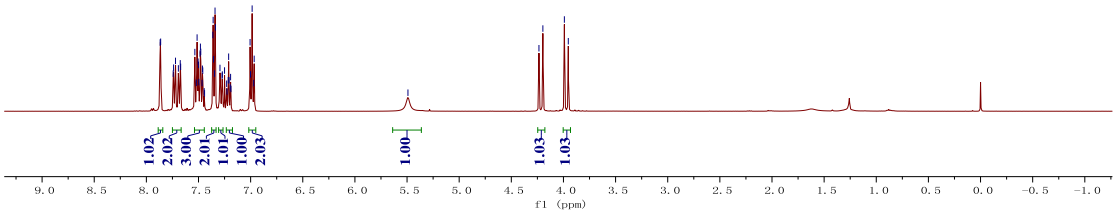
3al

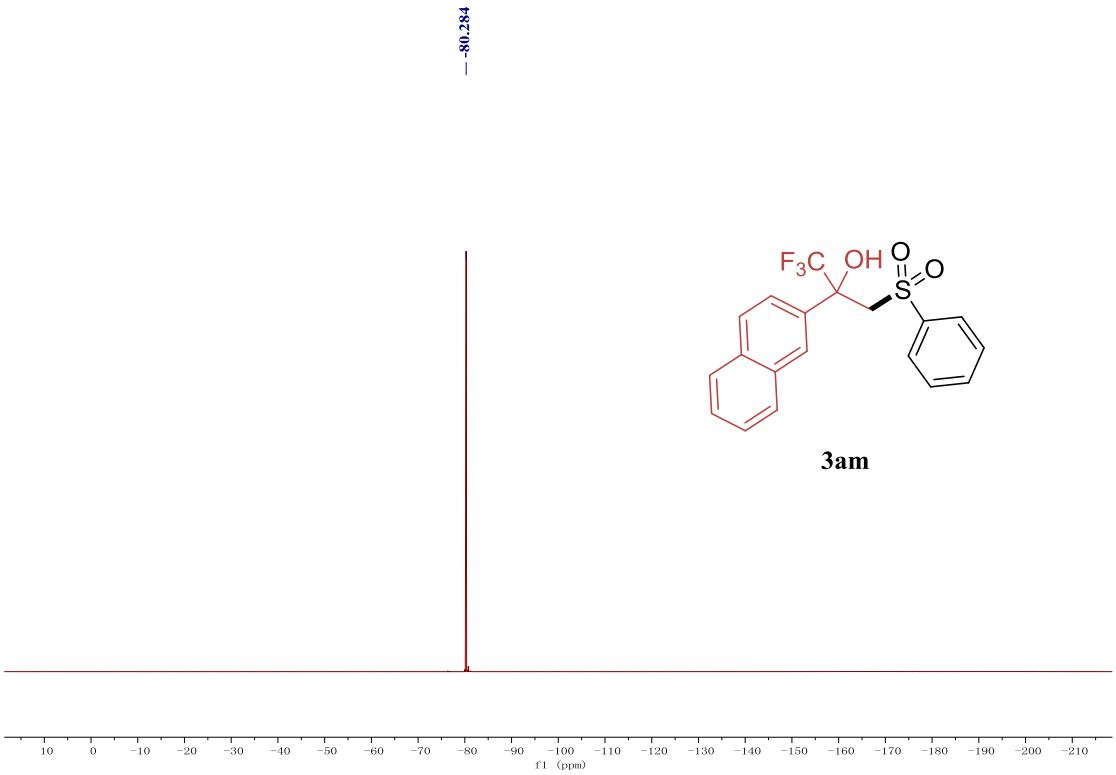

148.33
147.63
139.19
133.87
129.09
128.05
127.77
127.23
125.05
122.22
120.89
119.38
107.83
107.36
101.45
75.71
75.41
75.12
74.82
58.54
F3C
OH
O
O
S
O
O
3al
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) and $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)spectrum of product **3am**

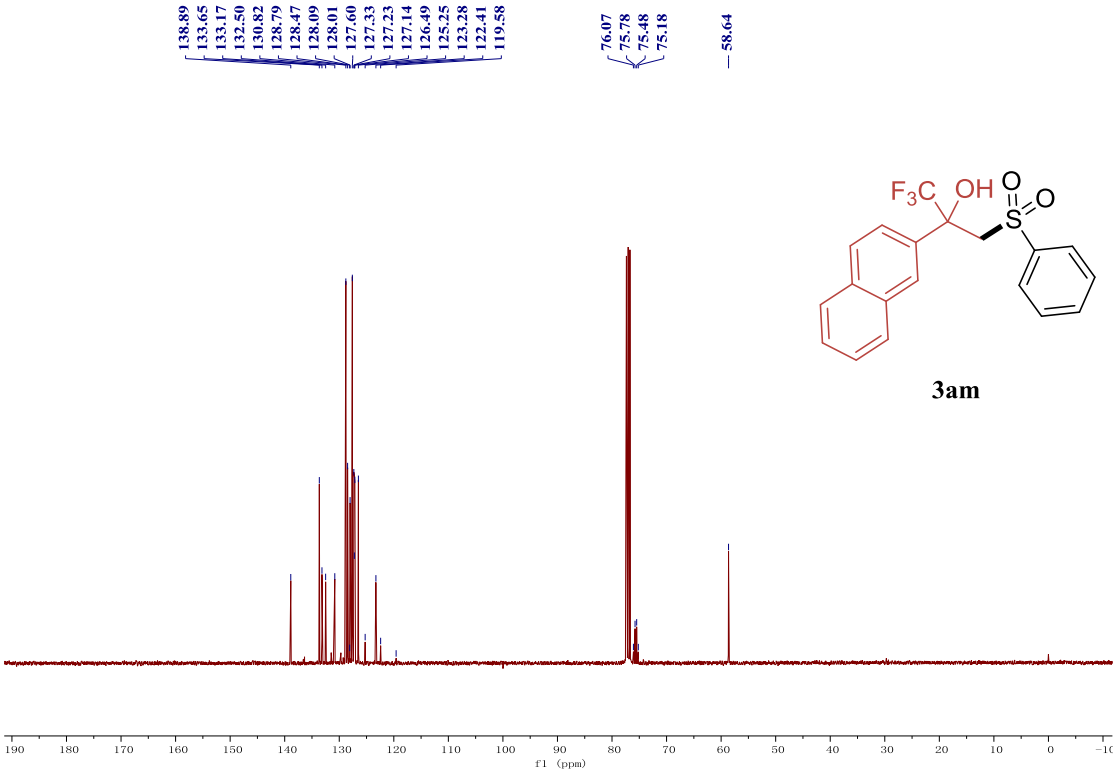


3am



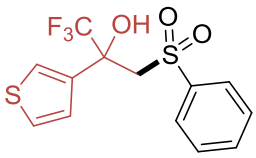


3am

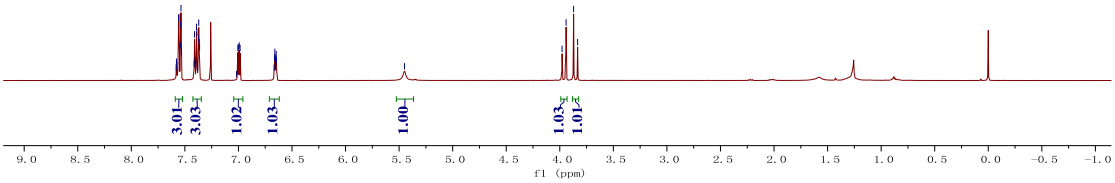

138.89
133.65
133.17
132.50
130.82
128.79
128.47
128.09
128.01
127.60
127.33
127.23
127.14
126.49
125.25
123.28
122.41
119.58
76.07
75.78
75.48
75.18
58.64
F3C
OH
O
O
S
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

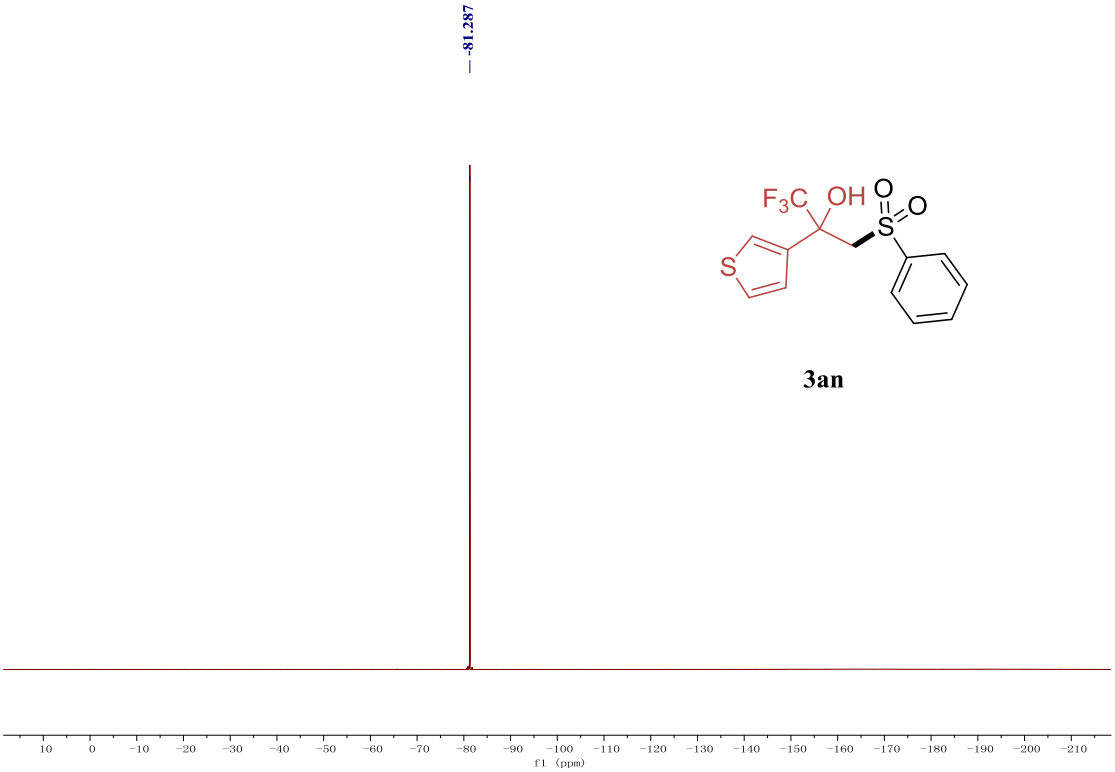
3am

^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) and ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)spectrum of product **3an**

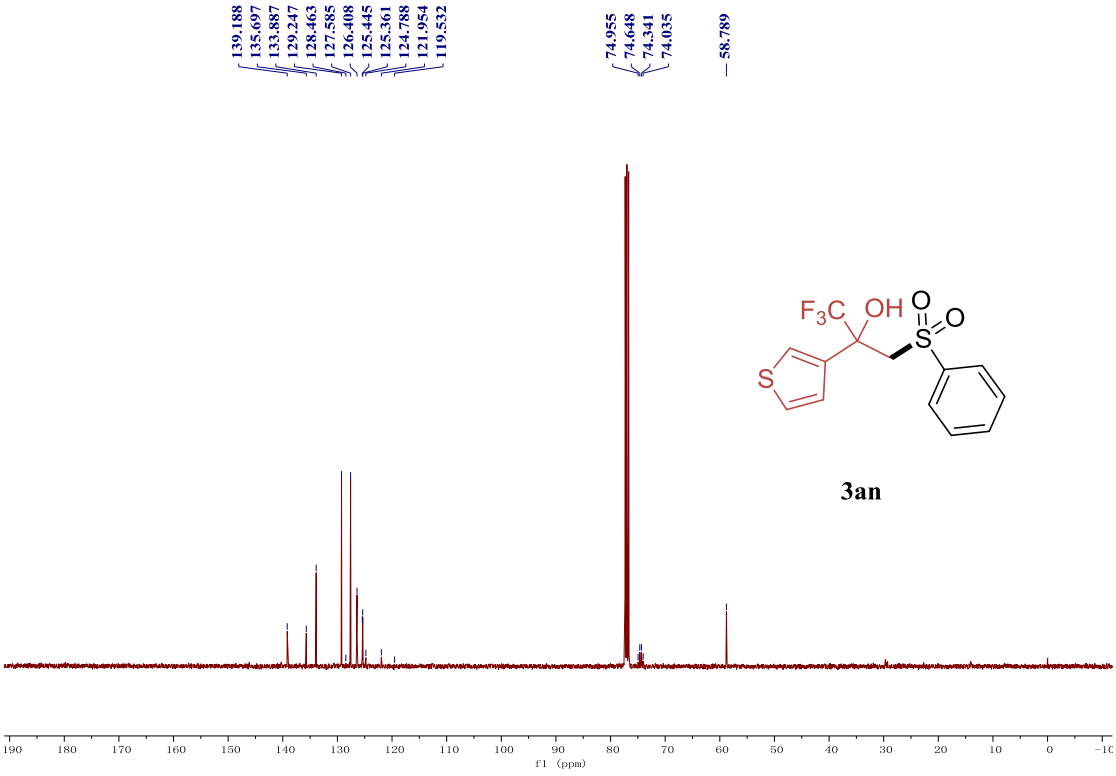


3an

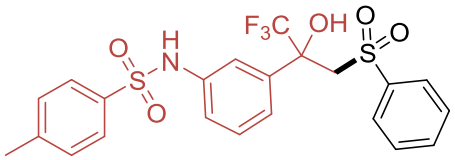


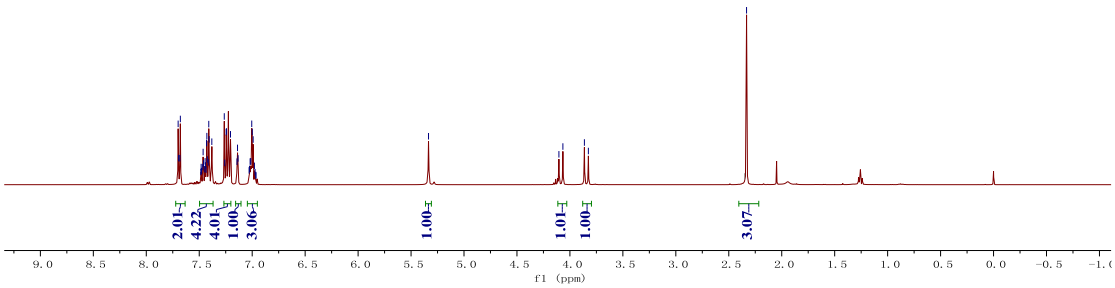


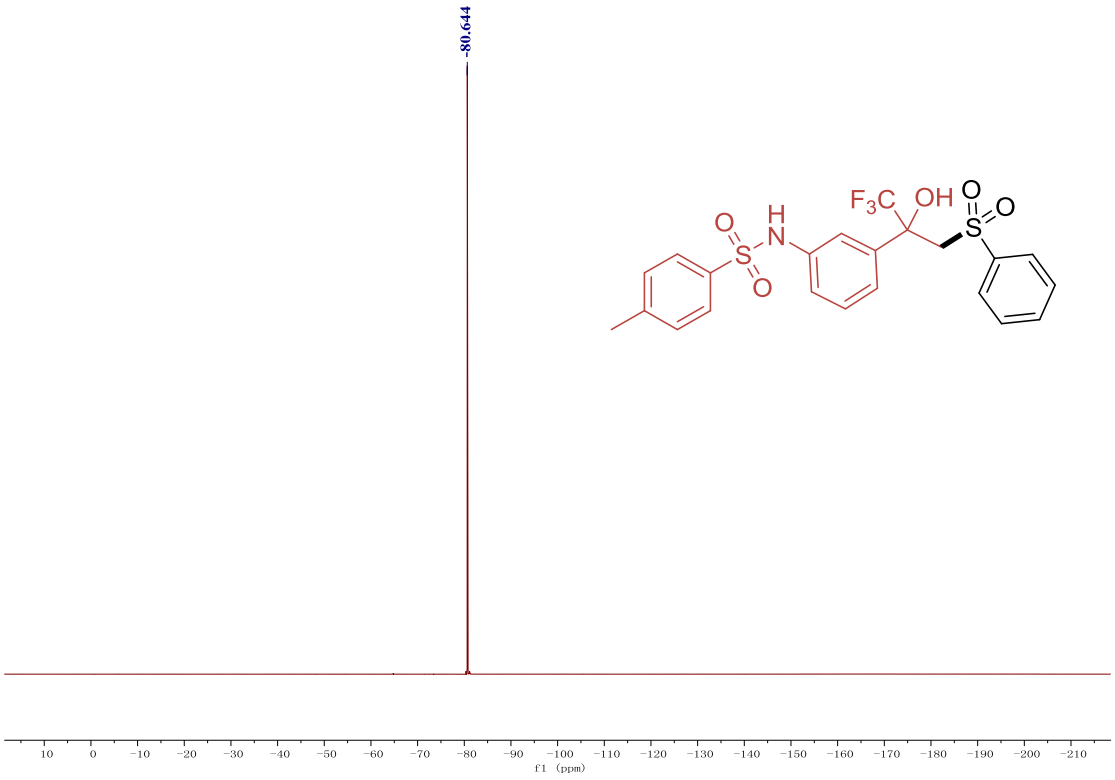
3an

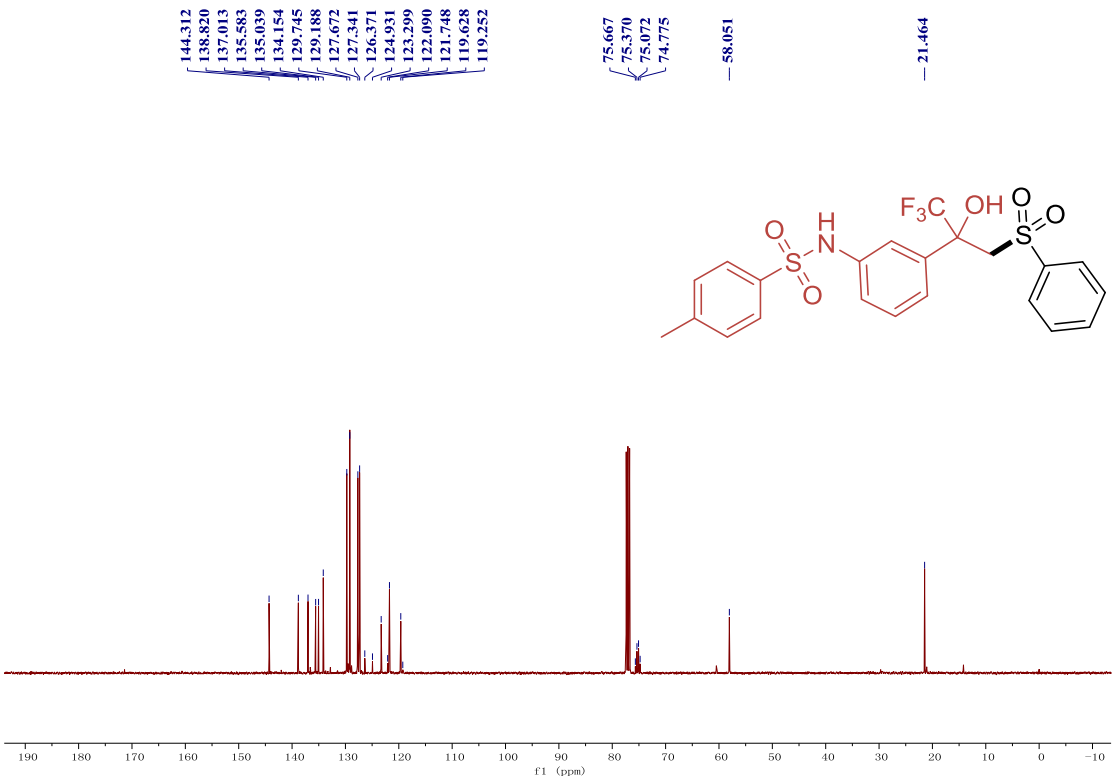

139.188
135.697
133.887
129.247
128.463
127.585
126.408
125.445
125.361
124.788
121.954
119.532
74.955
74.648
74.341
74.035
58.789
F3C
OH
O
O
S
S
3an
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$), ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) and ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)spectrum of product **3ao**



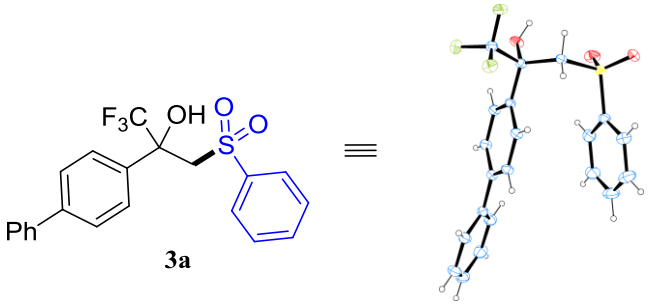





144.312
138.820
137.013
135.583
135.039
134.154
129.745
129.188
127.672
127.341
126.371
124.931
123.299
122.090
121.748
119.628
119.252
75.667
75.370
75.072
74.775
58.051
21.464
F3C
OH
H
N
O
S
O
O
S
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

10. X-ray crystallographic data of compound 3a

X-Ray crystallographic analysis of 2-([1,1'-biphenyl]-4-yl)-1-trifluoromethyl-3-(phenylsulfonyl)-pro-pan-2-ol 3**a** (CCDC 2090639) showing the thermal ellipsoids at 30% probability level.



3a

Crystal of compound **3a** was prepared in a solvent mixture of DCM and *n*-hexane (~v/v = 1/1).Yellow solid of **3a** (~70 mg) was dissolved in DCM (~1 mL) until all material was dissolved in vial, then adding *n*-hexane dropwise (~1 mL). The vial not fully screwed down and the sample was carefully setting in room temperature. The crystal was obtained about 48h.

All the measurements were obtained on a BRUKER Single Crystal X-Ray Diffractometer, Germany (model of the instrument –AXS D8 Quest System).

Specification: D8 QUEST, Photon 100 CMOS Detector, Horizontal Goniometer, Fixed Chi stage, Goniometer head manual, Ceramic Tube KFF Mo-2K-90c, two pinhole collimator (0.3/17 mrad, 0.6/17 mrad), Head turned by 90^0 , APEX2 w. SHELXTL S/W, Video microscope SCD, Cryostream-700plus extended range low Temperature.

```
Bond precision:  C-C = 0.0030 A          Wavelength=0.71073

Cell:         a=5.9954(2)         b=10.0675(4)      c=16.2734(7)
              alpha=100.6367(19)  beta=95.0698(19)  gamma=103.2609(19)
Temperature: 296 K

                 Calculated                Reported
Volume           930.81(6)                 930.81(6)
Space group      P -1                      P -1
Hall group       -P 1                      -P 1
Moiety formula   C21 H17 F3 O3 S           2(C21 H17 F3 O3 S)
Sum formula      C21 H17 F3 O3 S           C42 H34 F6 O6 S2
Mr               406.41                    812.81
Dx,g cm-3        1.450                     1.450
Z                2                         1
Mu (mm-1)        0.223                     0.223
F000             420.0                     420.0
F000'            420.51
h,k,lmax         7,13,21                   7,13,21
Nref             4355                      4236
Tmin,Tmax        0.948,0.956
Tmin'            0.935

Correction method= Not given

Data completeness= 0.973          Theta(max)= 27.680

R(reflections)= 0.0431( 3689)     wR2(reflections)= 0.1215( 4236)

S = 1.047                 Npar= 254
```