Supporting Information

Facile difluoromethylation of aliphatic alcohols by *S*-(difluoro-methyl)sulfonium salt: reaction, scope and mechanistic study

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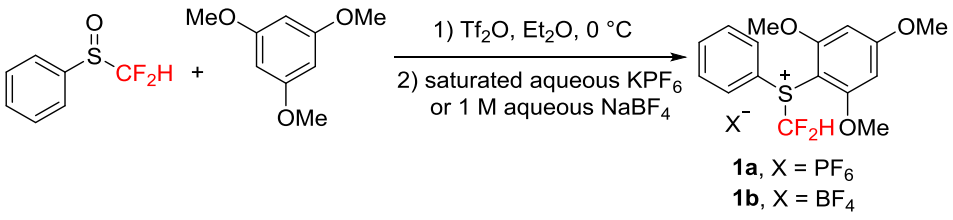
1. General Experimental Information

^{1}H NMR spectra were recorded on either a Bruker Ascend^{TM} 400MHz (400 MHz) spectrometer, or a Bruker Ascend^{TM} 500MHz (500 MHz) spectrometer at ambient temperature unless otherwise indicated. Data were reported as follows: chemical shifts in ppm from tetramethylsilane as an internal standard in $CDCl_3$, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet-doublet, m = multiplet, br = broad), coupling constants (Hz), and assignment. ^{13}C NMR spectra were recorded on either a Bruker Ascend^{TM} 500MHz (126 MHz) spectrometer or a Bruker Ascend^{TM} 400MHz (101 MHz) spectrometer at ambient temperature and were proton decoupled. Chemical shifts are reported in ppm from tetramethylsilane on the scale with the solvent resonance employed as the internal standard. ^{19}F NMR spectra were recorded on a Bruker Ascend^{TM} 400MHz (376 MHz) spectrometer at ambient temperature. Chemical shifts are reported in ppm from $CFCl_3$ as the internal standard. ESI-MS analyses were performed in positive ionization mode on an Agilent 1260-Infinity LC/MSD or a Q-Exactive high resolution mass spectrometer. EI-MS analyses were performed on an Agilent Technologies 7820A-GC/5977E-MSD System or a ThermoFinnigan MAT 95XL. Commercially available reagents were used as received. Reactions were monitored by TLC: Detection with UV light followed by staining potassium permanganate ($KMnO_4$). Flash chromatography: silica gel (300-400 mesh).

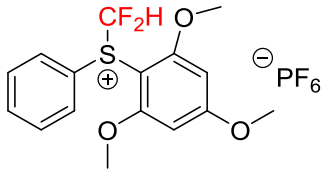
2. General Procedure for the Preparation of *S*-Difluoromethyl-*S*-phenyl-2,4,6 -trimethoxyphenylsulfonium salts (1)

S-Difluoromethyl-*S*-phenyl-2,4,6-trimethoxyphenylsulfonium salts (**1a** and **1b**) were prepared according to the procedure reported by us[1]: Trifluoromethanesulfonic acid anhydride (Tf_2O, 10 mmol) was added dropwise slowly into the stirring solution of (Difluoromethyl)phenylsulfoxide (10 mmol) and 1,3,5-trimethoxybenzene (11 mmol) in dry Et_2O (20 mL) at 0 ^{o}C under N_2 atmosphere. After the reaction was finished, stopped stirring and the upper layer was removed, another dry Et_2O (10 mL) was added and the mixture was stirred again, after stirring for 5 min, the upper Et_2O layer was removed. This procedure aforementioned was repeated three times and the product was precipitated, filtered and washed with dry Et_2O, to give *S*-difluoromethyl-*S*-phenyl-2,4,6-trimethoxyphenylsulfonium trifluoromethanesulfonate. The solid was dissolved in dichloromethane and extracted with saturated aqueous KPF_6 (50 mL ×4) or $NaBF_4$ aqueous solution (1 M, 50 mL ×4). The organic layer was dried over Na_2SO_4, filtered and evaporated in vacuum at 30 ^{o}C. Recrystallization from dichloromethane and hexane afforded **1a** or **1b**.



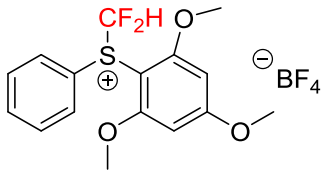
1a, X = PF_6
1b, X = BF_4

***S*-Difluoromethyl-*S*-phenyl-2,4,6-trimethoxyphenylsulfonium Hexafluorophosphate(V) (1a)**:



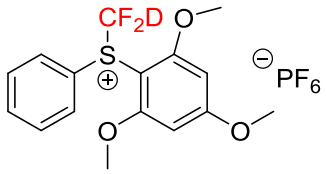
82% yield as white crystalline powder; M.p. 104-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 56.2, 54.1 Hz, 1H), 7.72-7.66 (m, 5H), 6.35 (s, 2H), 3.97 (s, 6H) , 3.95 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 163.0, 134.8, 131.6, 126.6, 120.7, 119.2 (t, *J* = 296.5 Hz), 93.1, 80.6, 57.4, 56.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.6 (d, *J* = 711.1 Hz, 6F), -97.0 (dd, *J* = 233.5, 53.9 Hz, 1F), -98.0 (dd, *J* = 233.5, 53.9 Hz, 1F); MS (ESI): *m/z* 327 ($C_{16}H_{17}O_3F_2S^+$); HRMS (ESI): calcd. for $C_{16}H_{17}O_3F_2S^+$: 327.0861; Found: 327.0851.

***S*-Difluoromethyl-*S*-phenyl-2,4,6-trimethoxyphenylsulfonium Tetrafluoroborate (1b):**



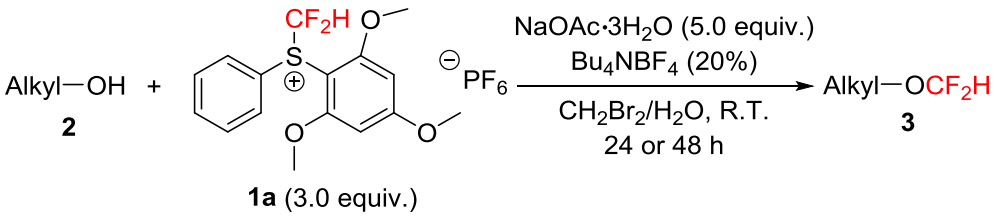
86% yield as white crystalline powder; M.p. 95.5-96.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (t, *J* = 54.6 Hz, 1H), 7.72-7.64 (m, 5H), 6.37 (s, 2H), 3.99 (s, 6H), 3.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 163.0, 134.7, 131.5, 129.9, 120.9, 119.3 (t, *J* = 298.0 Hz), 93.1, 81.2, 57.5, 56.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -97.7 (dd, *J* = 233.6, 54.2 Hz, 1F), -98.4 (dd, *J* = 235.0, 56.2 Hz, 1F), -153.8 (s, 1F), -153.9 (s, 3F); MS (ESI): *m/z* 327 ($C_{16}H_{17}O_3F_2S^+$). HRMS (ESI): calcd. for $C_{16}H_{17}O_3F_2S^+$: 327.0861; Found: 327.0849.

[D]-1a:



81% yield (D/H > 95:5) as white crystalline powder; M.p. 97-98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.62 (m, 5H), 7.34 (s, 2H), 3.96 (s, 6H), 3.94 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 163.0, 134.8, 131.6, 129.6, 120.7, 93.1, 80.7, 57.4, 56.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.6 (d, *J* = 711.1 Hz), -97.9 (d, *J* = 233.9 Hz), -98.8 (d, *J* = 233.9 Hz). MS (ESI): *m/z* 328 ($C_{16}H_{16}{}^{2}HO_3F_2S^+$:); HRMS (ESI): calcd. for $C_{16}H_{16}{}^{2}HO_3F_2S^+$: 328.0924; Found: 328.0917.

3. General Procedure for Electrophilic Difluoromethylation of Alcohols with Reagent 1a

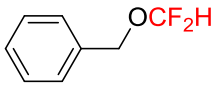


In a small vial (2.0 mL), a magnetic stir bar, alcohol **2** (0.2 mmol, 1.0 equiv.), 1**a** (0.6 mmol, 3.0 equiv.), NaOAc $3H_2O$ (1.0 mmol, 5.0 equiv.), Bu_4NBF_4 (0.04 mmol, 20%), CH_2Br_2 (0.2 mL) and H_2O (0.2 mL) were successively added. After stirring vigorously for 24 or 48 hours at room temperature, benzotrifluoride (0.1 mmol, 0.5 equiv.) and $CDCl_3$ (0.5 mL) were added for the determination of ^{19}F-NMR Yield. Then the mixture was diluted by dichloromethane, dried over

anhydrous Na_2SO_4, filtered, and evaporated. The residue was purified by silica gel column chromatography to give product **3**.

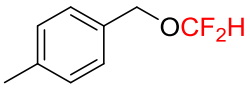
The characterization data of known compounds **3a-e, 3g, 3j-k, 3m-v, 3x, 3aa, 3ab, 3ad, 3ae, 3af and 3ah** are consistent with the previous report.[2]

((Difluoromethoxy)methyl)benzene (3a):



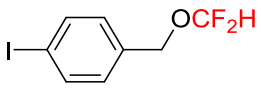
The product was purified by silica gel column chromatography (Hexane) in 65% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.34 (m, 5H), 6.31 (t, *J* = 74.4 Hz, 1H), 4.90 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.8 (d, *J* = 74.3 Hz, 2F); MS (EI): *m/z* 158 (M^+).

1-((Difluoromethoxy)methyl)-4-methylbenzene (3b):



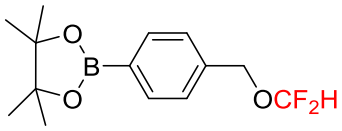
The product was purified by silica gel column chromatography (Hexane) in 78% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 6.29 (t, *J* = 74.6 Hz, 1H), 4.87 (s, 2H), 2.37 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.6 (d, *J* = 74.6 Hz, 2F); MS (EI): *m/z* 172 (M^+).

1-((Difluoromethoxy)methyl)-4-iodobenzene (3c):



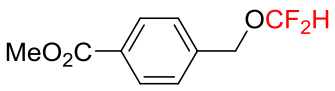
The product was purified by silica gel column chromatography (Hexane) in 70% yield as semisolid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 6.30 (t, *J* = 74.0 Hz, 1H), 4.83 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.9 (d, *J* = 73.9 Hz, 2F); MS (EI): *m/z* 284 (M^+).

2-(4-((Difluoromethoxy)methyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d):



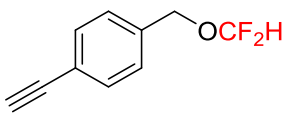
The product was purified by silica gel column chromatography (Hexane) in 57% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.9 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 6.31 (t, *J* = 74.4 Hz, 1H), 4.91 (s, 2H), 1.35 (s, 12H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.8 (d, *J* = 74.3 Hz, 2F); MS (EI): *m/z* 284 (M^+).

Methyl 4-((difluoromethoxy)methyl)benzoate (3e):



The product was purified by silica gel column chromatography (Hexane/Ethyl acetate = 100:1) in 63% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 6.34 (t, *J* = 74.0 Hz, 1H), 4.95 (s, 2H), 3.92 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.0 (d, *J* = 73.8 Hz, 2F); MS (EI): *m/z* 216 (M^+).

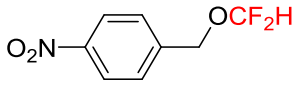
1-((Difluoromethoxy)methyl)-4-ethynylbenzene (3f):



The product was purified by silica gel column chromatography (Hexane) in 60% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 6.31 (t, *J* = 74.0 Hz, 1H), 4.89 (s, 2H), 3.10 (s, 1H); ^{13}C NMR (101 MHz, CDCl3) δ 136.2, 132.5, 127.8, 122.3, 113.3 (t, *J* = 262.7 Hz), 83.3, 77.8, 64.8 (t, *J* = 6.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.9 (d, *J* = 74.0

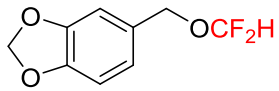
Hz, 2F); MS (EI): *m/z* 182 (M^+); HRMS (APCI): calcd. for $C_{11}H_{13}F_2O_2^+$ ($[M+H+CH_3OH]^+$): 215.0878; found: 215.0879.

1-((Difluoromethoxy)methyl)-4-nitrobenzene (3g):



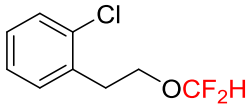
The product was purified by silica gel column chromatography (Hexane/Ethyl acetate = 50:1) in 50% yield as white solid; M.p. 38-39 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.6 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 6.38 (t, *J* = 73.4 Hz, 1H), 5.00 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.3 (d, *J* = 73.3 Hz, 2F); MS (EI): *m/z* 203 (M^+).

5-((Difluoromethoxy)methyl)benzo[*d*][1,3]dioxole (3h):



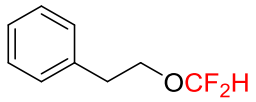
The product was purified by silica gel column chromatography (Hexane) in 84% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86-6.79 (m, 3H), 6.27 (t, *J* = 74.5 Hz, 1H), 5.97 (s, 2H), 4.79 (s, 2H); ^{13}C NMR (101 MHz, CDCl3) δ 148.0, 147.8, 129.0, 122.0, 115.9 (t, *J* = 261.6 Hz), 108.8, 108.3, 101.2, 65.5 (t, *J* = 6.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.6 (d, *J* = 74.4 Hz, 2F); MS (EI): *m/z* 202 (M^+); HRMS (ESI): calcd. for $C_9H_9F_2O_3^+$: 203.0514; found: 203.0515.

1-Chloro-2-(2-(difluoromethoxy)ethyl)benzene (3i):



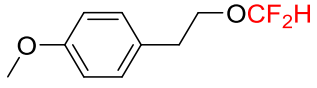
The product was purified by silica gel column chromatography (Hexane) in 90% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.17 (m, 4H), 6.18 (t, *J* = 74.7 Hz, 1H), 4.08 (t, *J* = 7.0 Hz, 2H), 3.10 (t, *J* = 7.0 Hz, 2H); ^{13}C NMR (101 MHz, CDCl3) δ 135.2, 134.3, 131.4, 129.7, 128.4, 127.0, 116.2 (t, *J* = 258.3 Hz), 62.4 (t, *J* = 5.5 Hz), 33.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.6 (d, *J* = 74.6 Hz, 2F); MS (EI): *m/z* 206 (M^+); HRMS (APCI): calcd. for $C_8H_8Cl^+$ ($[M-HCF_2O]^+$): 139.0309; found: 139.0309.

(2-(Difluoromethoxy)ethyl)benzene (3j):



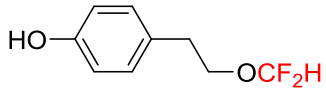
The product was purified by silica gel column chromatography (Hexane) in 78% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.31 (m, 2H), 7.27-7.23 (m, 3H), 6.19 (t, *J* = 74.7 Hz, 1H), 4.07 (t, *J* = 7.1 Hz, 2H), 2.97 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (101 MHz, CDCl3) δ 137.6, 129.0, 128.7, 126.8, 116.1 (t, *J* = 261.4 Hz), 64.1 (t, *J* = 5.4 Hz), 35.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.7 (d, *J* = 74.6 Hz, 2F); MS (EI): *m/z* 172 (M^+).

1-(2-(Difluoromethoxy)ethyl)-4-methoxybenzene (3k):



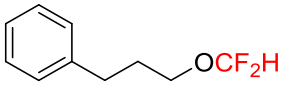
The product was purified by silica gel column chromatography (Hexane) in 91% yield (93% isolated yield in 2.0 mmol scale) as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.19 (t, *J* = 74.9 Hz, 1H), 4.02 (t, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 2.90 (t, *J* = 7.1 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.6 (d, *J* = 74.8 Hz, 2F); MS (EI): *m/z* 202 (M^+).

4-(2-(Difluoromethoxy)ethyl)phenol (3l):



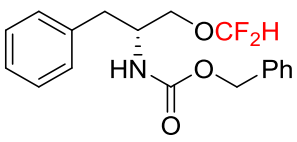
The product was purified by silica gel column chromatography (Hexane/Ethyl acetate = 20:1) in 62% yield as semisolid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 6.18 (t, *J* = 74.9 Hz, 1H), 4.01 (t, *J* = 7.1 Hz, 2H), 2.89 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (101 MHz, CDCl3) δ 154.5, 130.2, 129.7, 116.2 (t, *J* = 261.2 Hz), 115.6, 64.5 (t, *J* = 5.3 Hz), 34.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.5 (d, *J* = 74.9 Hz, 2F); MS (EI): *m/z* 120 ($[M\text{-}HCF_2OH]^+$); HRMS (APCI): calcd. for $C_8H_9O^+$ ($[M\text{-}HCF_2O]^+$): 121.0648; found: 121.0649.

(3-(Difluoromethoxy)propyl)benzene (3m):



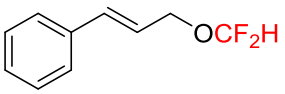
The product was purified by silica gel column chromatography (Hexane) in 78% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.28 (m, 2H), 7.23-7.19 (m, 3H), 6.22 (t, *J* = 75.1 Hz, 1H), 3.86 (t, *J* = 6.4 Hz, 2H), 2.73 (t, *J* = 7.5 Hz, 2H), 1.98 (quint, *J* = 7.0 Hz, 2H); ^{13}C NMR (101 MHz, CDCl3) δ 141.2, 128.6, 126.2, 116.3 (t, *J* = 260.7 Hz), 62.9 (t, *J* = 5.3 Hz), 32.0, 30.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -83.8 (d, *J* = 75.0 Hz, 2F); MS (EI): *m/z* 186 (M^+).

Benzyl (*R*)-(1-(difluoromethoxy)-3-phenylpropan-2-yl)carbamate (3n):



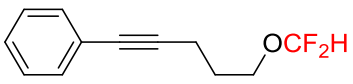
The product was purified by silica gel column chromatography (Hexane/Ethyl acetate = 10:1) in 61% yield as white solid; M.p. 68-69 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 7.39-7.22 (m, 10H), 6.38 (t, *J* = 75.7 Hz, 1H), 5.77 (d, *J* = 8.4 Hz, 1H), 5.02 (d, *J* = 12.7 Hz, 1H), 4.98 (d, *J* = 12.7 Hz, 1H), 4.09-4.00 (m, 1H), 3.89 (dd, *J* = 10.1, 4.6 Hz, 1H), 3.82 (dd, *J* = 10.1, 4.6 Hz, 1H), 2.90 (dd, *J* = 13.8, 5.6 Hz, 1H), 2.75 (dd, *J* = 13.8, 9.1 Hz, 1H), 2.23 (s, 1H); ^{13}C NMR (101 MHz, CD_3CN) δ 155.9, 138.1, 129.3, 128.5, 128.4, 127.8, 127.5, 126.5, 117.4, 116.9 (t, *J* = 258.2 Hz), 65.7, 63.9 (t, *J* = 3.4 Hz), 52.0, 36.8; ^{19}F NMR (376 MHz, CD_3CN) δ -84.6 (d, *J* = 74.3 Hz, 2F); MS (ESI): *m/z* 336.1 ($M+H^+$); HRMS (ESI): calcd. for $C_{18}H_{20}F_2NO_3^+$: 336.1406; found: 336.1394.

(*E*)-(3-(difluoromethoxy)prop-1-en-1-yl)benzene (3o):



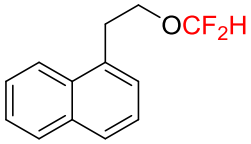
The product was purified by silica gel column chromatography (Hexane) in 73% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 7.1 Hz, 2H), 7.30 (t, *J* = 7.0 Hz, 1H), 6.67 (d, *J* = 15.9 Hz, 1H), 6.29 (t, *J* = 74.6 Hz, 1H), 6.27 (dt, *J* = 15.9, 6.3 Hz, 1H), 4.53 (t, *J* = 6.3 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.5 (d, *J* = 74.6 Hz, 2F); MS (EI): *m/z* 184 (M^+).

(5-(Difluoromethoxy)pent-1-yn-1-yl)benzene (3p):



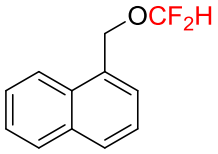
The product was purified by silica gel column chromatography (Hexane) in 80% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.39 (m, 2H), 7.31-7.28 (m, 3H), 6.23 (t, *J* = 75.0 Hz, 1H), 4.02 (t, *J* = 6.2 Hz, 2H), 2.55 (t, *J* = 7.0 Hz, 2H), 1.95 (quint, *J* = 6.5 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.4 (d, *J* = 74.9 Hz, 2F); MS (EI): *m/z* 210 (M^+).

1-(2-(Difluoromethoxy)ethyl)naphthalene (3q):



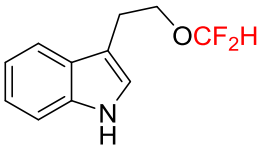
The product was purified by silica gel column chromatography (Hexane) in 92% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.58-7.49 (m, 2H), 7.45-7.39 (m, 2H), 6.23 (t, *J* = 74.7 Hz, 1H), 4.20 (t, *J* = 7.4 Hz, 2H), 3.45 (t, *J* = 7.4 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.5 (d, *J* = 74.6 Hz, 2F); MS (EI): *m/z* 222 (M^+).

1-((Difluoromethoxy)methyl)naphthalene (3r):



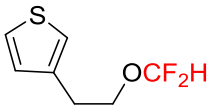
The product was purified by silica gel column chromatography (Hexane) in 85% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.93 (t, *J* = 7.9 Hz, 2H), 7.64-7.55 (m, 3H), 7.52-7.48 (m, 1H), 6.40 (t, *J* = 74.4 Hz, 1H), 5.40 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.7 (d, *J* = 74.4 Hz, 2F); MS (EI): *m/z* 208 (M^+).

3-(2-(Difluoromethoxy)ethyl)-1*H*-indole (3s):



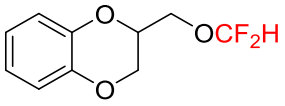
The product was purified by silica gel column chromatography (Hexane/Ethyl acetate = 20:1) in 88% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (br, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.22 (t, *J* = 7.1 Hz, 1H), 7.15 (t, *J* = 7.8 Hz, 1H), 7.08 (s, 1H), 6.23 (t, *J* = 75.1 Hz, 1H), 4.14 (t, *J* = 7.1 Hz, 2H), 3.14 (t, *J* = 7.1 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.2 (d, *J* = 75.0 Hz, 2F); MS (EI): *m/z* 211 (M^+).

3-(2-(Difluoromethoxy)ethyl)thiophene (3t):



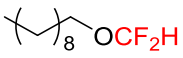
The product was purified by silica gel column chromatography (Hexane) in 81% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 4.8, 3.0 Hz, 1H), 7.03 (d, *J* = 3.0 Hz, 1H), 6.99 (d, *J* = 4.8 Hz, 1H), 6.18 (t, *J* = 74.7 Hz, 1H), 4.04 (t, *J* = 6.9 Hz, 2H), 2.97 (t, *J* = 6.9 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.7 (d, *J* = 74.5, 2.0 Hz, 2F); MS (EI): *m/z* 178 (M^+).

2-((Difluoromethoxy)methyl)-2,3-dihydrobenzo[*b*][1,4]dioxine (3u):



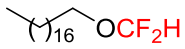
The product was purified by silica gel column chromatography (Hexane/Ethyl acetate = 200:1) in 60% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92-6.85 (m, 4H), 6.29 (t, *J* = 73.7 Hz, 1H), 4.42-4.37 (m, 1H), 4.40 (dd, *J* = 11.5, 2.2 Hz, 1H), 4.14-4.03 (m, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.5 (d, *J* = 73.6 Hz, 2F); MS (EI): *m/z* 216 (M^+).

1-(Difluoromethoxy)decane (3v):



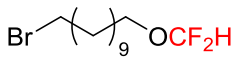
The product was purified by silica gel column chromatography (Hexane) in 91% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.18 (t, *J* = 75.3 Hz, 1H), 3.83 (t, *J* = 6.6 Hz, 2H), 1.63 (quint, *J* = 7.0 Hz, 2H), 1.38-1.27 (m, 14H), 0.88 (t, *J* = 6.5 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.2 (d, *J* = 75.2 Hz, 2F); MS (EI): *m/z* 140 ($[M\text{-}HCF_2OH]^+$).

1-(Difluoromethoxy)octadecane (3w):



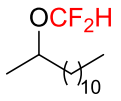
The product was purified by silica gel column chromatography (Hexane) in 95% yield as semisolid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.18 (t, *J* = 75.3 Hz, 1H), 3.83 (t, *J* = 6.6 Hz, 2H), 1.63 (quint, *J* = 6.6 Hz, 2H), 1.36-1.25 (m, 30H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 116.3 (t, *J* = 260.4 Hz), 63.9 (t, *J* = 5.3 Hz), 32.1, 29.9, 29.83, 29.81, 29.73, 29.68, 29.5, 29.4, 29.3, 25.9, 22.9, 14.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.3 (d, *J* = 75.3 Hz, 2F); MS (EI): *m/z* 252 ([M-HCF_2OH]$^+$); HRMS (EI): calcd. for $C_{18}H_{36}^+$ ([M-HCF_2OH]$^+$): 252.2812; found: 252.2811.

1-Bromo-11-(difluoromethoxy)undecane (3x):



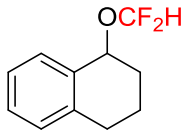
The product was purified by silica gel column chromatography (Hexane) in 98% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.18 (t, *J* = 75.3 Hz, 1H), 3.82 (t, *J* = 6.6 Hz, 2H), 3.40 (t, *J* = 6.9 Hz, 2H), 1.85 (quint, *J* = 7.2 Hz, 2H), 1.63 (quint, *J* = 7.0 Hz, 2H), 1.43-1.28 (m, 14H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.2 (d, *J* = 75.2 Hz, 2F); MS (EI): *m/z* 232 ([M-HCF_2OH]$^+$).

2-(Difluoromethoxy)tridecane (3aa):



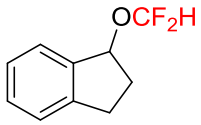
The product was purified by silica gel column chromatography (Hexane) in 75% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20 (t, *J* = 75.8 Hz, 1H), 4.24-4.17 (m, 1H), 1.62-1.55 (m, 1H), 1.50-1.41 (m, 1H), 1.33-1.25 (m, 21H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 116.6 (t, *J* = 258.5 Hz), 72.9 (t, *J* = 3.5 Hz), 37.0, 32.1, 29.81, 29.78, 29.74, 29.70, 29.59, 29.52, 25.4, 22.9, 21.3, 14.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.5 (dd, *J* = 161.3, 75.9 Hz, 1F), -81.1 (dd, *J* = 161.3, 75.9 Hz, 1F); MS (EI): *m/z* 182 ([M-HCF_2OH]$^+$).

1-(Difluoromethoxy)-1,2,3,4-tetrahydronaphthalene (3ab):



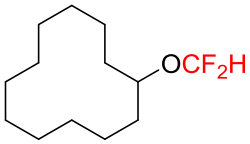
The product was purified by silica gel column chromatography (Hexane) in 70% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.36 (m, 1H), 7.26-7.21 (m, 2H), 7.15-7.12 (m, 1H), 6.37 (dd, *J* = 75.4, 74.4 Hz, 1H), 5.32-5.30 (m, 1H), 2.88 (dt, *J* = 16.7, 5.2 Hz, 1H), 2.79-2.71 (m, 1H), 2.17-2.10 (m, 1H), 2.08-1.97 (m, 2H), 1.86-1.78 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.1 (dd, *J* = 160.0, 75.5 Hz, 1F), -81.5 (dd, *J* = 160.0, 75.5 Hz, 1F); MS (EI): *m/z* 198 (M^+).

1-(Difluoromethoxy)-2,3-dihydro-1*H*-indene (3ac):



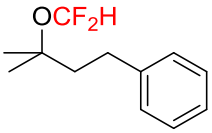
The product was purified by silica gel column chromatography (Hexane) in 77% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (t, *J* = 7.2 Hz, 1H), 7.34-7.24 (m, 3H), 6.35 (t, *J* = 74.6 Hz, 1H), 5.69 (dd, *J* = 6.9, 4.7 Hz, 1H), 3.12 (ddd, *J* = 16.0, 8.5, 5.4 Hz, 1H), 2.87 (ddd, *J* = 16.1, 8.3, 6.0 Hz, 1H), 2.49 (ddd, *J* = 20.8, 7.6, 6.3 Hz, 1H), 2.26-2.17 (m, 1H); ^{13}C NMR (101 MHz, CDCl3) δ 144.0, 140.7, 129.2, 126.9, 125.4, 125.0, 116.2 (t, *J* = 261.1 Hz), 78.7 (t, *J* = 4.9 Hz), 33.5, 30.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.9 (dd, *J* = 160.0, 74.9 Hz, 1F), -81.5 (dd, *J* = 160.0, 74.9 Hz, 1F); MS (EI): *m/z* 184 (M^+); HRMS (ESI): calcd. for $C_{10}H_{11}F_2O^+$: 185.0773; found: 185.0775.

(Difluoromethoxy)cyclododecane (3ad):



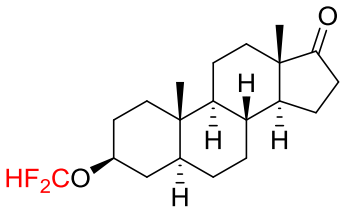
The product was purified by silica gel column chromatography (Hexane) in 93% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.21 (t, *J* = 75.9 Hz, 1H), 4.27 (tt, *J* = 7.2, 4.5 Hz, 1H), 1.78-1.69 (m, 2H), 1.59-1.51 (m, 2H), 1.48-1.33 (m, 18H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.5 (d, *J* = 75.8 Hz, 2F); MS (EI): *m/z* 166 ([M-HCF_2OH]$^+$).

(3-(Difluoromethoxy)-3-methylbutyl)benzene (3ae):



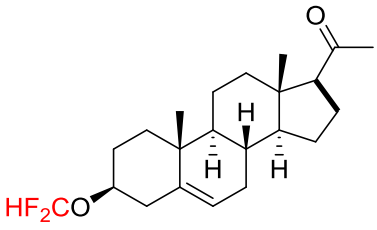
The product was purified by silica gel column chromatography (Hexane) in 38% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.27 (m, 2H), 7.22-7.17 (m, 3H), 6.33 (t, *J* = 76.8 Hz, 1H), 2.57-2.71 (m, 2H), 1.94-1.85 (m, 2H), 1.42 (s, 6H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.8 (d, *J* = 76.7 Hz, 2F); MS (EI): *m/z* 214 (M^+), 146 ([M-OCF_2H_2]$^+$).

(3*S*,5*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-3-(difluoromethoxy)-10,13-dimethylhexadecahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (3af):



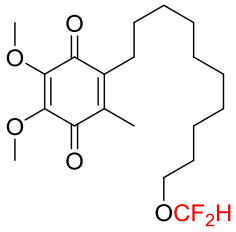
The product was purified by silica gel column chromatography (Hexane/Ethyl acetate = 6:1) in 71% yield as white solid; M.p. 91-92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.21 (t, *J* = 75.8 Hz, 1H), 4.07-3.98 (m, 1H), 2.42 (dd, *J* = 19.2, 8.8 Hz, 1H), 2.10-2.00 (m, 1H), 1.95-1.72 (m, 6H), 1.66-1.42 (m, 6H), 1.36-1.22 (m, 4H), 1.19-1.10 (m, 1H), 1.03-0.96 (m, 2H), 0.85 (s, 3H), 0.84 (s, 3H), 0.69 (td, *J* = 11.3, 3.6 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.3 (dd, *J* = 161.2, 75.7 Hz, 1F), -80.8 (dd, *J* = 161.2, 75.7 Hz, 1F); ^{13}C NMR (101 MHz, CDCl3) δ 116.4 (t, *J* = 258.7 Hz), 75.1 (t, *J* = 3.6 Hz), 54.4, 51.5, 47.9, 44.8, 36.8, 35.9, 35.6, 35.4, 35.1, 31.6, 30.9, 28.8, 28.4, 21.8, 20.5, 13.9, 12.3; MS (ESI): *m/z* 341.4 ($M+H^+$); HRMS (ESI): calcd. for $C_{20}H_{31}F_2O_2^+$: 341.2287; found: 341.2284.

1-((3*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-3-(difluoromethoxy)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)ethan-1-one (3ag)



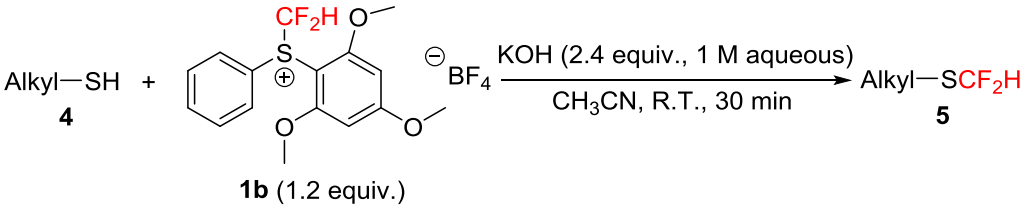
The product was purified by silica gel column chromatography (Hexane/Ethyl acetate = 30:1) in 60% yield as white solid; M.p. 127-128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.21 (t, *J* = 75.6 Hz, 1H), 5.37 (d, *J* = 5.0 Hz, 1H), 3.99-3.91(m, 1H), 2.52 (m, 1H), 2.42-2.33 (m, 2H), 2.20-2.15 (m, 1H), 2.11 (s, 3H), 2.05-1.97 (m, 2H), 1.90-1.84 (m, 2H), 1.71-1.56 (m, 5H), 1.52-1.39 (m, 4H), 1.27-0.94 (m, 3H), 1.00 (s, 3H), 0.62 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.7 (d, *J* = 75.6 Hz, 2F); ^{13}C NMR (101 MHz, CDCl3) δ 209.6, 139.8, 122.5, 116.3 (t, *J* = 259.2 Hz), 75.3 (t, *J* = 3.6 Hz), 63.8, 57.0, 50.0, 44.1, 39.6, 38.9, 37.1, 36.6, 31.9, 31.9, 31.6, 29.1, 24.6, 22.9, 21.1, 19.4, 13.3; MS (ESI): *m/z* 367.2 ($M+H^+$); HRMS (ESI): calcd. for $C_{22}H_{33}F_2O_2^+$: 367.2443; found: 367.2432.

2-(10-(Difluoromethoxy)decyl)-5,6-dimethoxy-3-methylcyclohexa-2,5-diene-1,4-dione (3ah):



The product was purified by silica gel column chromatography (Hexane/Ethyl acetate = 10:1) in 62% yield as dark yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.15 (t, *J* = 75.4 Hz, 1H), 3.96 (s, 6H), 3.79 (t, *J* = 6.6 Hz, 2H), 2.42 (t, *J* = 6.8 Hz, 2H), 1.98 (s, 3H), 1.60 (quint, *J* = 6.7 Hz, 2H), 1.35-1.25 (m, 14H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.2 (d, *J* = 75.3 Hz, 2F); MS (EI): *m/z* 388 (M^+).

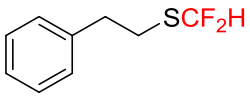
4. General Procedure for Electrophilic Difluoromethylation of Thioalcohols with Reagent 1b



To a solution of **4** (0.2 mmol, 1.0 equiv.) in acetonitrile (0.2 mL), KOH (0.48 mmol, 2.4 equiv., 1 M aqueous) was added. After stirring for 30 min at room temperature, **1b** (0.24 mmol, 1.2 equiv.) was added in one portion. The reaction mixture was stirred for another 30 min, then benzotrifluoride (0.1 mmol, 0.5 equiv.) and $CDCl_3$ (0.5 mL) were added for the determination of ^{19}F-NMR Yield. Followed quenching with saturated aqueous solution of NH_4Cl, and extracted with EtOAc (10 mL ×3). The combined extracts was dried over anhydrous Na_2SO_4, filtered, and evaporated. The residue was purified by silica gel column chromatography to give product **5**.

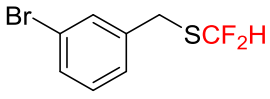
The characterization data of known compounds **5a** and **5c** are consistent with the previous report.[3]

(Difluoromethyl)(phenethyl)sulfane (5a):



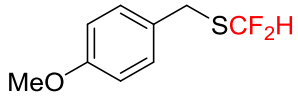
The product was purified by silica gel column chromatography (Hexane) in 50% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.32 (m, 2H), 7.28-7.22 (m, 3H), 6.78 (t, *J* = 56.3 Hz, 1H), 3.09-3.05 (m, 2H), 3.01-2.97 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -92.7 (d, *J* = 56.2 Hz, 2F); MS (EI): *m/z* 188 (M^+).

(3-Bromobenzyl)(difluoromethyl)sulfane (5b):



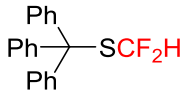
The product was purified by silica gel column chromatography (Hexane) in 50% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (t, *J* = 2.0 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.75 (t, *J* = 56.2 Hz, 1H), 3.98 (s, 2H); ^{13}C NMR (101 MHz, CDCl3) δ 138.9, 132.0, 130.9, 130.4, 127.6, 122.8, 120.1 (t, *J* = 274.8 Hz), 31.1 (t, *J* = 3.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.7 (d, *J* = 56.1 Hz, 2F); MS (EI): *m/z* 252 (M^+), 254 (M^+); HRMS (EI): calcd. for $C_8H_7{}^{79}BrF_2S^+$: 251.9414; found: 251.9415.

(Difluoromethyl)(4-methoxybenzyl)sulfane (5c):



The product was purified by silica gel column chromatography (Hexane) in 57% yield as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.73 (t, *J* = 56.6 Hz, 1H), 3.99 (s, 2H), 3.81 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -95.0 (d, *J* = 56.6 Hz, 2F); MS (EI): *m/z* 204 (M^+).

(Difluoromethyl)(trityl)sulfane (5d):



The product was purified by silica gel column chromatography (Hexane) in 46% yield as white solid; M.p. 96-97 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.26 (m, 15H), 6.05 (t, *J* = 55.8 Hz, 1H); ^{13}C NMR (126 MHz, CDCl3) δ 143.7, 129.7, 128.3, 127.6, 123.3 (t, *J* = 269.0 Hz), 68.7 (t, *J* = 2.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.1 (d, *J* = 55.8 Hz, 2F); MS (EI): *m/z* 243 (M^+); HRMS (APCI): calcd. for $C_{19}H_{15}^+$ ($[M\text{-}SCF_2H]^+$): 243.1168; found: 243.1168.

5. Control Experiments of Mechanistic Study

Control experiments were done as the procedure for electrophilic difluoromethylation of alcohols described above, and the results were determined by ^{19}F NMR spectroscopy analysis.

A)

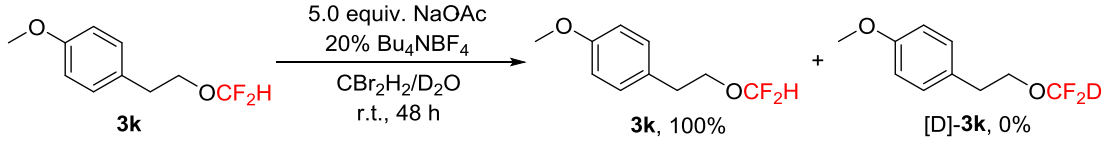
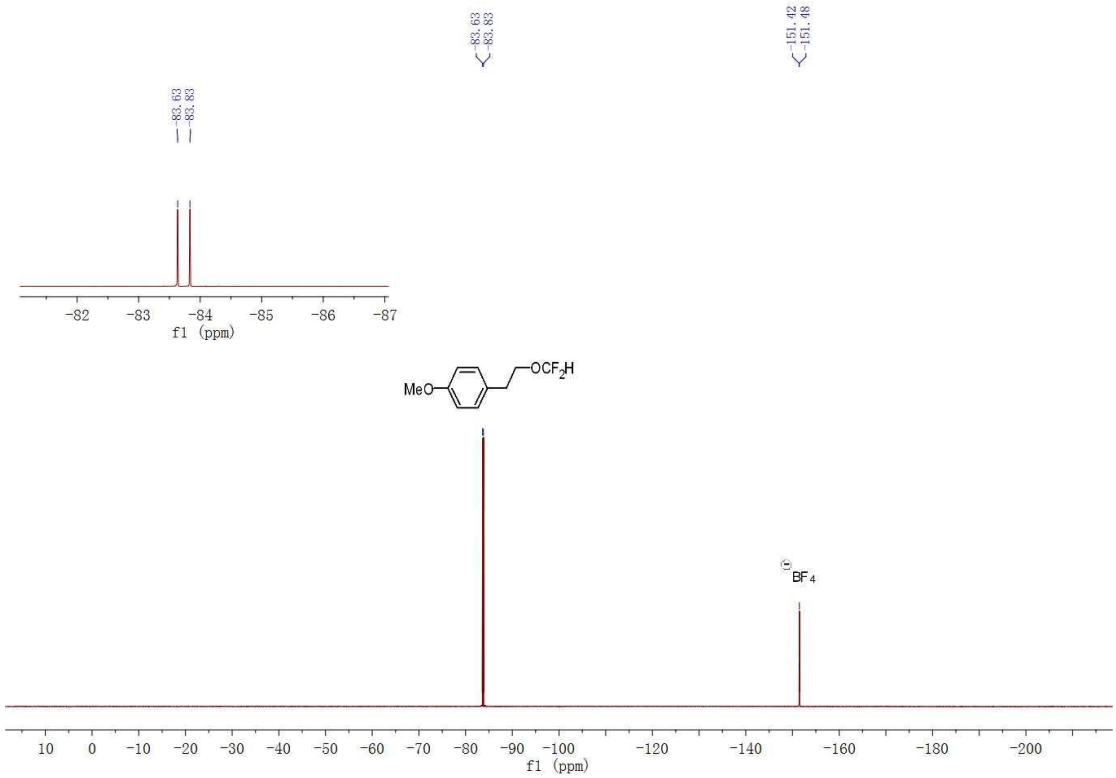


Figure S1. Control Experiment A)



B)

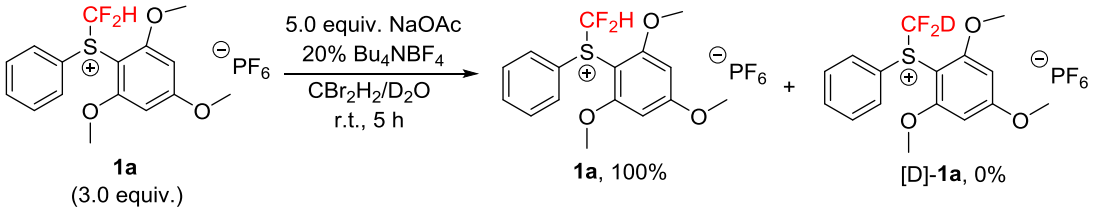
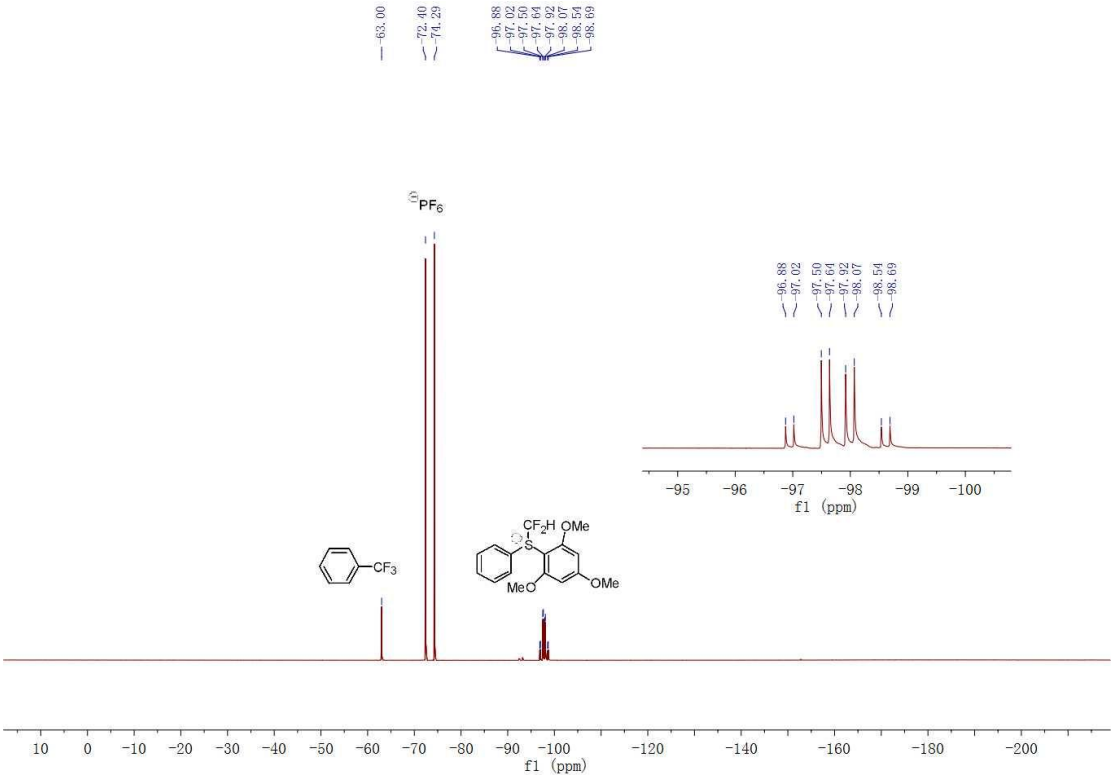


Figure S2. Control Experiment B)



C)

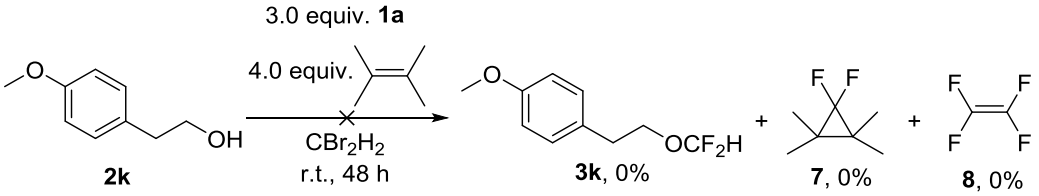
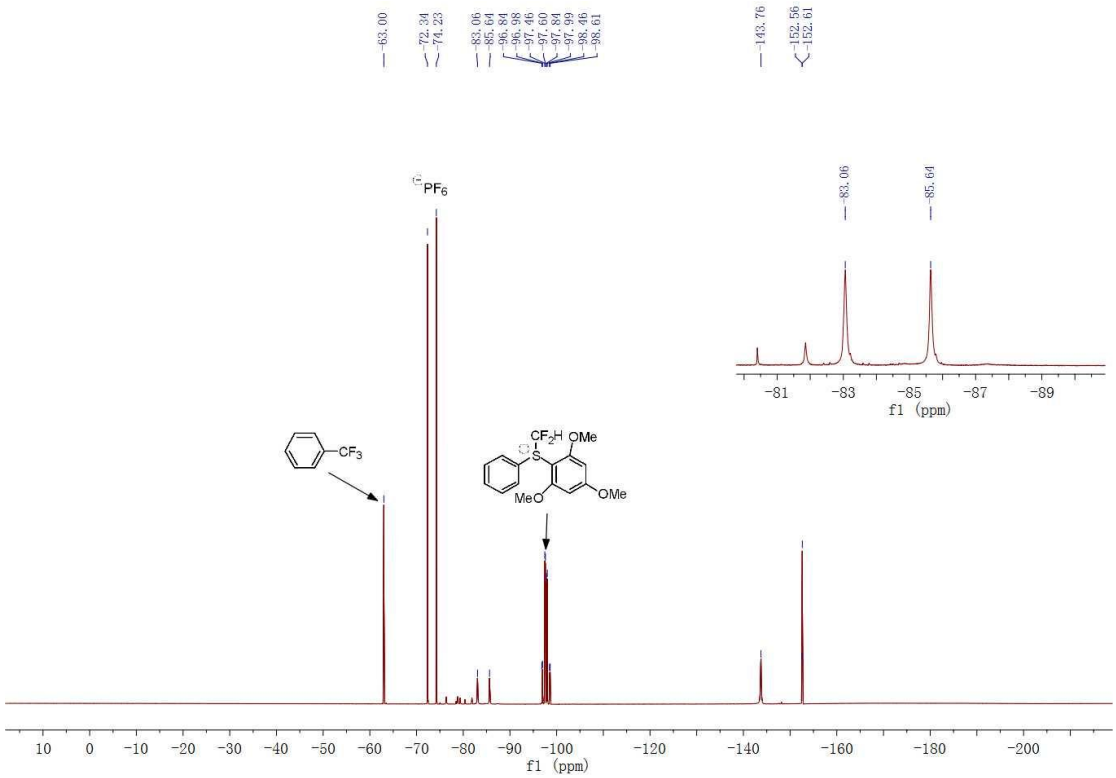


Figure S3. Control Experiment C)



D)

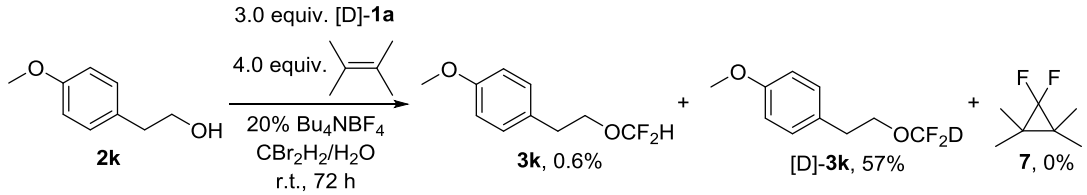
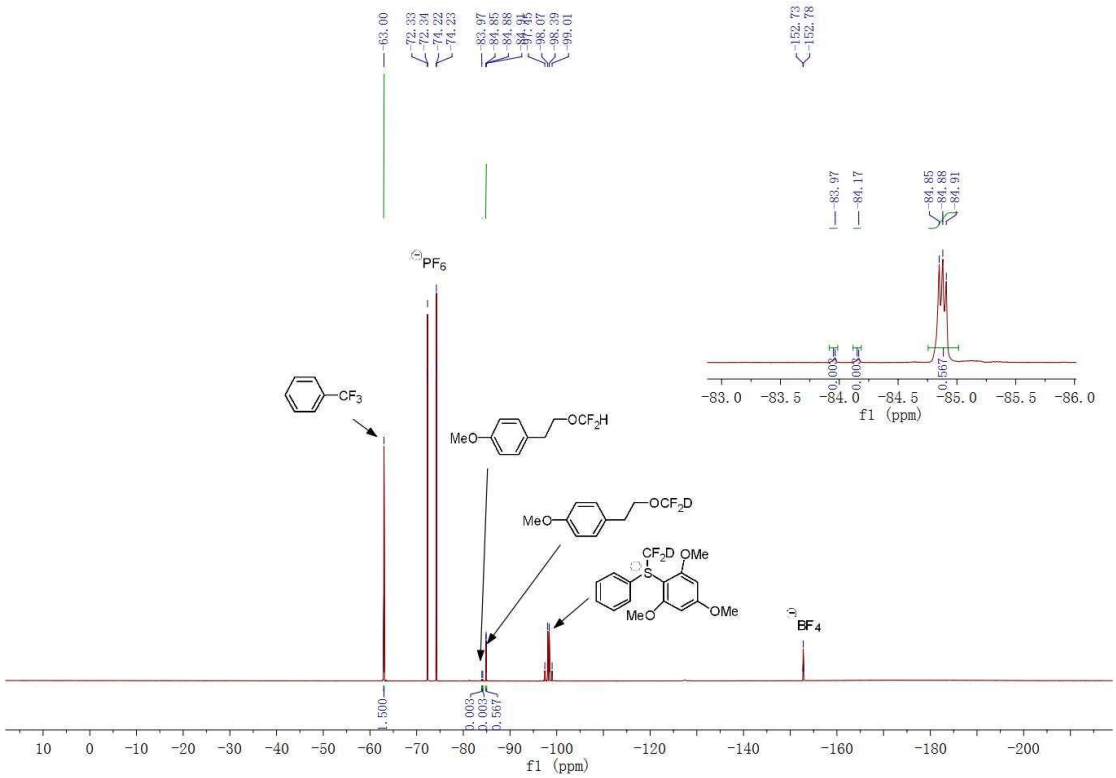


Figure S4. Control Experiment D)



E)

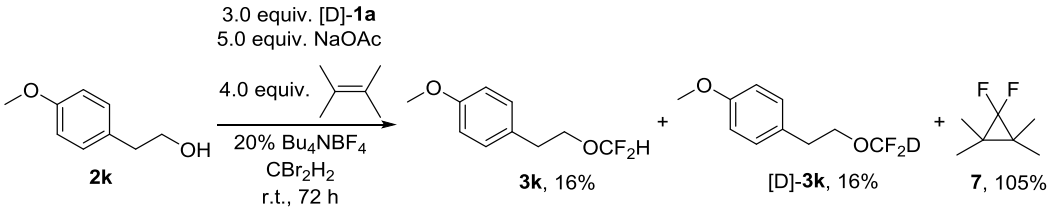
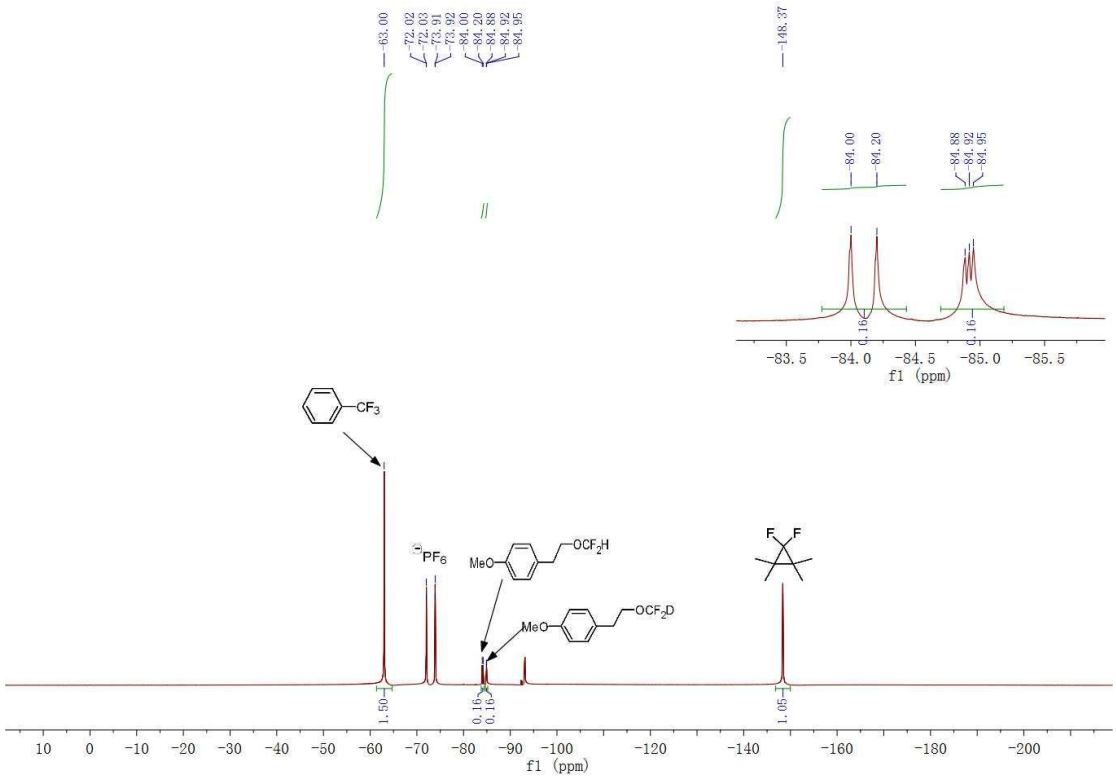


Figure S5. Control Experiment E)



F)

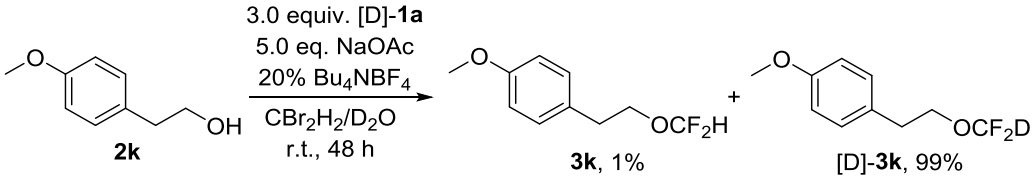
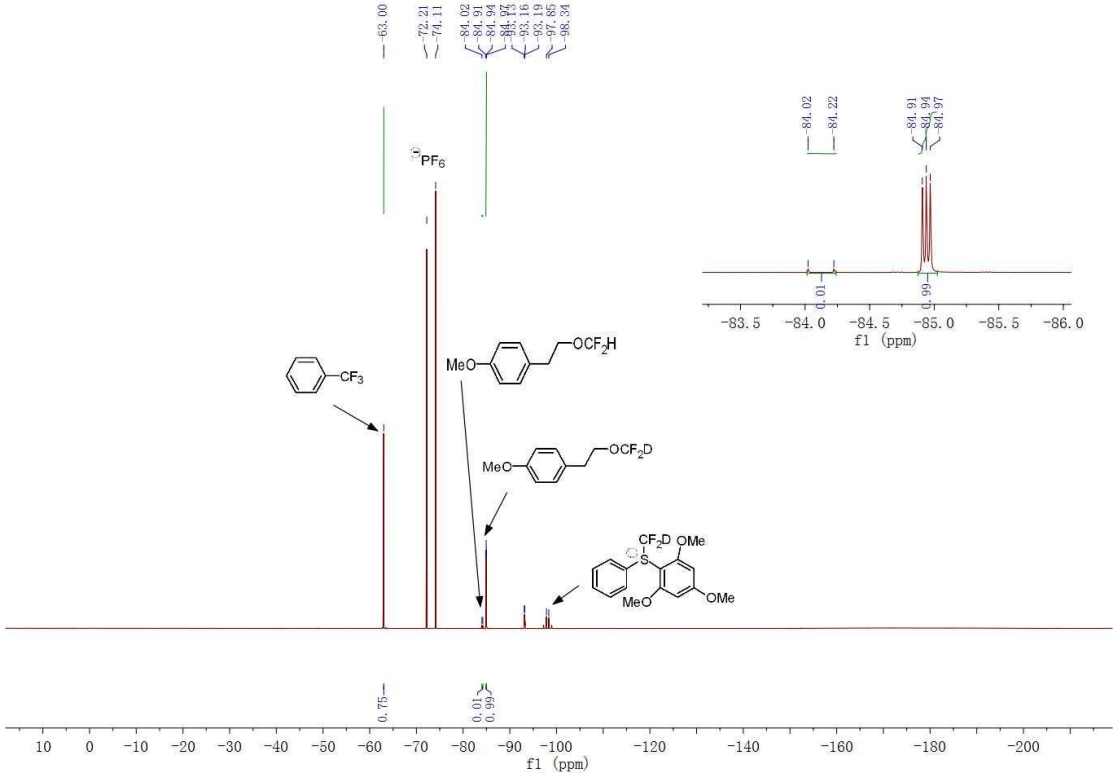


Figure S6. Control Experiment F)



G)

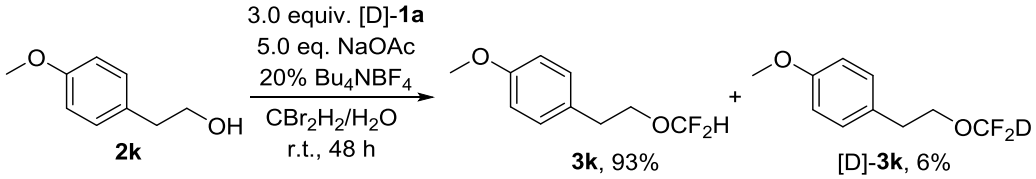


Figure S7. Control Experiment G)

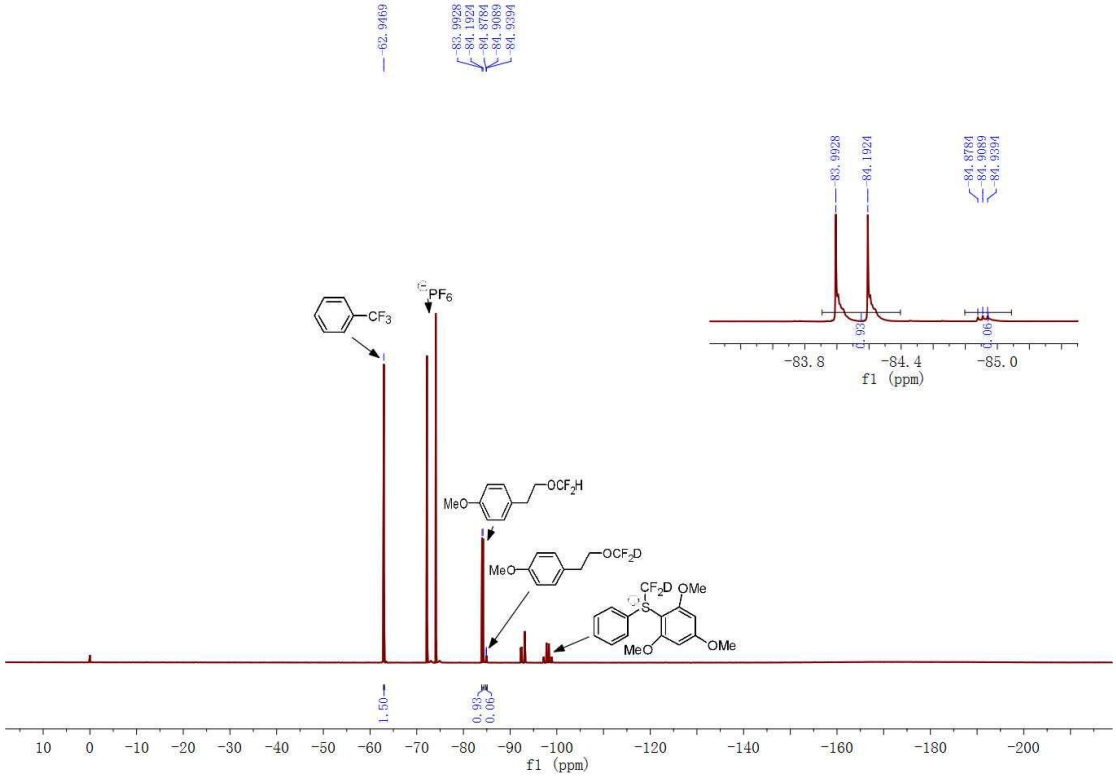
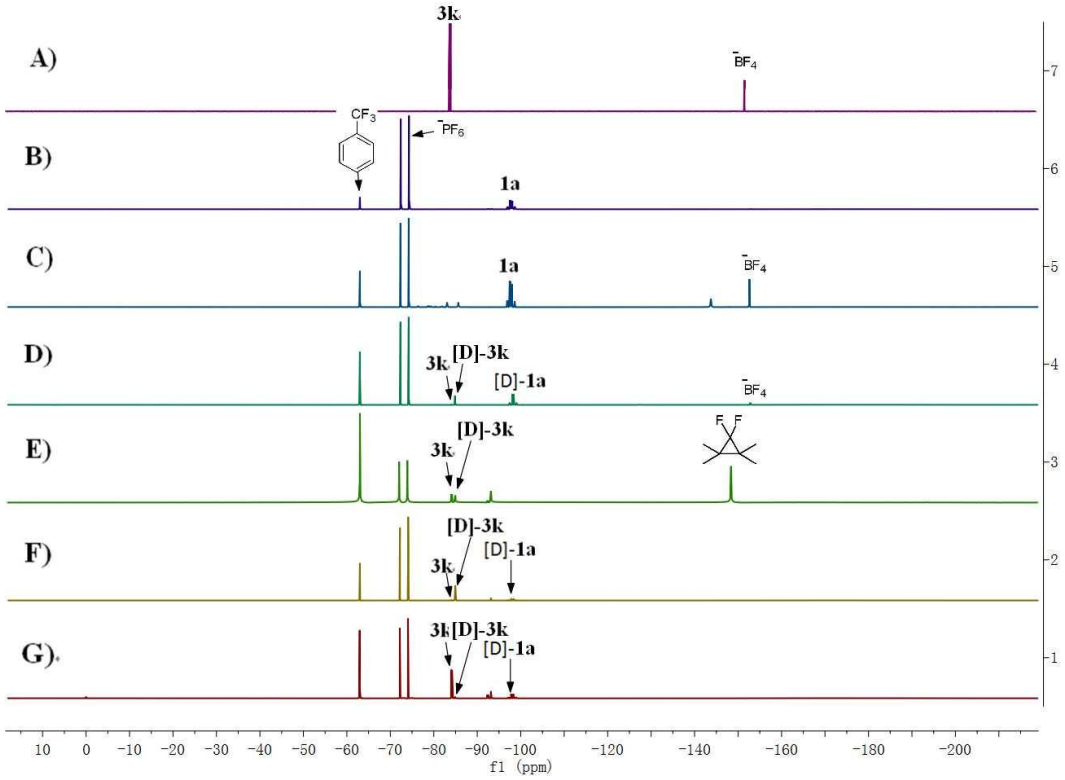


Figure S8. Control Experiments A-G



6. DFT Calculations of Mechanistic Study

All DFT computations were carried out with the Gaussian 09 program package.[4] Geometry optimizations were performed using Truhlar's M06-2X density functional, which performs well for the study of main-group thermochemistry and kinetics.[5] The 6-31G(d) basis set was adopted for all atoms.[6] Solvent effects were taken into account during geometry optimizations *via* SMD in dibromomethane.[7] Frequency analyses were performed at the same level to obtain thermal corrections at 298.15K, and to confirm the stationary points with zero imaginary frequency and transition states with only one imaginary frequency. SMD(dibromomethane)-M06-2X/6-311++G(d,p) single-point energies were computed on the SMD(dibromomethane)-M06-2X/6-31G(d)-optimized structures.[8] The ultrafine integration grid was used in all DFT calculations.[9] All structures shown here in figures were generated with the CYLview program.[10]

Calculated Enthalpy and Gibbs Free Energy

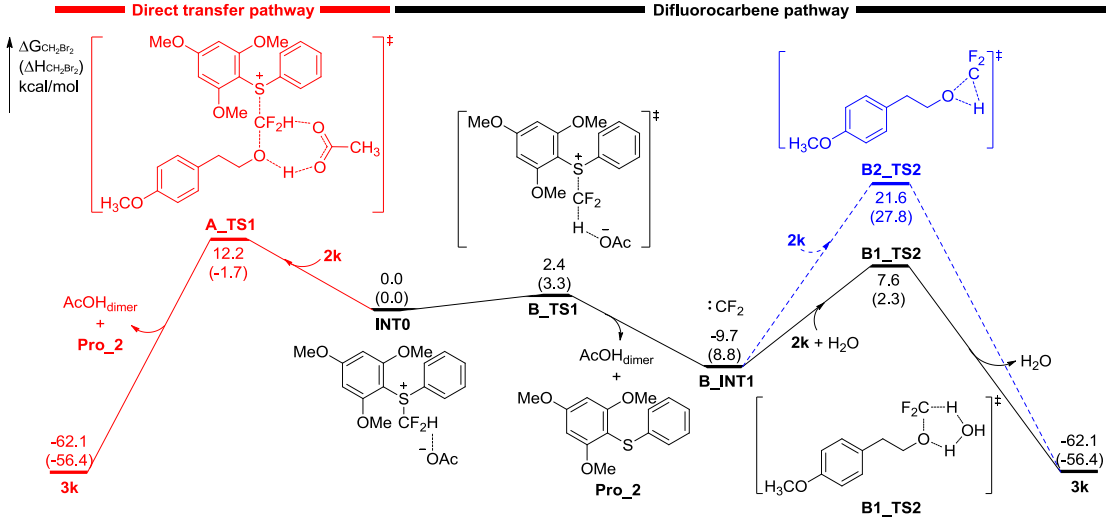


Figure S9. The free energy profile for the difluoromethylation of alcohol. Free energies and enthalpies (in parenthesis) are given in kcal/mol

Table S1. Energies of structures on reaction between **1** and **2k** (units of H and G are Hartree, ΔH and ΔG are kcal/mol).

	H	G	ΔH	ΔG
H_2O	-76.40332	-76.424765	/	/
$AcOH_{dimer}$	-458.027291	-458.073912	/	/
2k	-500.34433	-500.393691	/	/
Pro_2	-1204.647829	-1204.714754	/	/
INT0	-1671.353579	-1671.441543	0.0	0.0
A_TS1	-2171.700633	-2171.815809	-1.7	12.2
B_TS1	-1671.348316	-1671.437689	3.3	2.4
B_INT1	-237.678038	-237.705349	8.8	-9.7
B1_TS2	-814.436054	-814.496153	2.3	7.6
B2_TS2	-737.992064	-738.049063	27.8	21.6
3k	-738.126262	-738.182488	-56.4	-62.1

Cartesian Coordinates

H_2O

O	0.00000000	0.00000000	0.11950600
H	0.00000000	0.76212300	-0.47802200
H	0.00000000	-0.76212300	-0.47802200

$AcOH_{dimer}$

C	1.93256900	-0.05556200	0.00001300
C	3.43038200	-0.08311500	-0.00012800
H	3.80305300	0.44448700	0.88220200
H	3.78492300	-1.11264300	0.00053300
H	3.80283200	0.44325000	-0.88329500
O	1.43089400	1.16268700	-0.00076200
H	0.43252800	1.11486400	-0.00032800
O	1.24143400	-1.06728900	0.00078900
C	-1.93253800	0.05551300	0.00015000
C	-3.43034200	0.08361100	-0.00030800
H	-3.80342600	-0.44417100	0.88173400
H	-3.78448900	1.11327400	0.00062700
H	-3.80276000	-0.44228800	-0.88376700
O	-1.43128000	-1.16290600	-0.00055500
H	-0.43298400	-1.11546500	-0.00019300
O	-1.24106100	1.06701000	0.00104300

2k

C	1.09953000	1.53550700	-0.00146700
C	-0.27001200	1.44382300	0.19650000
C	-0.87765200	0.22503900	0.52624800
C	-0.06024300	-0.89737200	0.64569700
C	1.32006400	-0.82817400	0.44949300
C	1.90482000	0.39678700	0.12276100
H	1.57129300	2.48042800	-0.25268000
H	-0.88339900	2.33651600	0.09706600
H	-0.50649500	-1.85529600	0.90338800
H	1.92044400	-1.72410300	0.55736600
O	3.23393200	0.58116000	-0.08851300
C	4.06865800	-0.55866700	-0.01002400
H	3.77778000	-1.31699600	-0.74627700
H	5.07868800	-0.21164900	-0.23032200
H	4.04923600	-0.99968100	0.99338800
C	-2.37329300	0.11865000	0.68777600
H	-2.62640700	-0.66472800	1.41074500
H	-2.78802300	1.06082800	1.06310100
C	-3.05292400	-0.21260500	-0.63507100

H	-2.81953500	0.56963100	-1.37293600
H	-2.65484900	-1.16225100	-1.02345900
O	-4.44585300	-0.29800800	-0.39862700
H	-4.87959700	-0.49995900	-1.24155600

Pro_2

C	4.74938000	0.27296200	0.33942000
C	3.72120100	0.66123500	-0.51408500
C	2.38697200	0.47298900	-0.13761600
C	2.09435800	-0.10911000	1.09694200
C	3.13074700	-0.50150800	1.94132400
C	4.46039800	-0.31307400	1.57062800
H	5.78075500	0.42464800	0.03526800
H	3.95551100	1.10783300	-1.47704600
H	1.06207200	-0.25456400	1.40038200
H	2.89183400	-0.95607800	2.89837900
H	5.26315100	-0.62077200	2.23309100
S	1.14800700	1.04005600	-1.28768400
C	-0.34918600	0.33374400	-0.66982100
C	-1.39710000	1.15758300	-0.22972600
C	-0.53816400	-1.06546800	-0.65443700
C	-2.60796600	0.61233500	0.21769000
C	-1.72794700	-1.62079900	-0.19660500
C	-2.75579500	-0.77355000	0.22958000
H	-3.40812900	1.25727700	0.55010100
H	-1.89470800	-2.68963400	-0.16626700
O	0.50522900	-1.80357100	-1.08260600
O	-1.17500100	2.48839200	-0.27111500
O	-3.87972700	-1.40055600	0.64520000
C	-2.19368500	3.35583700	0.19573200
H	-2.42420500	3.16725100	1.25008300
H	-1.79573000	4.36499100	0.08813500
H	-3.10557500	3.25985000	-0.40378000
C	0.39353300	-3.21503400	-1.01653700
H	0.22861400	-3.54998300	0.01343900
H	-0.41658300	-3.58040900	-1.65698500
H	1.34494900	-3.60584800	-1.37728500
C	-4.97462400	-0.60122000	1.05771500
H	-5.76871600	-1.29728900	1.32864100
H	-4.71598700	0.01046200	1.92921300
H	-5.32210400	0.04572300	0.24450800

INT0

C	-2.99910000	2.95953400	-0.93842300

C	-2.31390100	2.24217200	0.03860400
C	-0.97557000	1.93047200	-0.18680600
C	-0.30371800	2.32184600	-1.33901800
C	-1.00546400	3.04331600	-2.30102400
C	-2.34807900	3.35936300	-2.10309000
H	-4.04557600	3.19999300	-0.78455100
H	-2.82308100	1.93122700	0.94632800
H	0.74047000	2.06513500	-1.48882800
H	-0.49840700	3.35293300	-3.20890000
H	-2.88925600	3.91736700	-2.86018900
S	-0.09876100	1.05888200	1.11861500
C	1.21635700	0.21110600	0.34487700
C	2.53173700	0.50161500	0.74853200
C	0.96997800	-0.76797800	-0.64538200
C	3.60188400	-0.18338600	0.17288900
C	2.02908000	-1.45353700	-1.21584000
C	3.33507100	-1.15499700	-0.79830300
H	4.61498000	0.03204600	0.47911500
H	1.88073800	-2.21569200	-1.96978500
C	-1.39654400	-0.31996100	1.49766800
H	-2.05674000	-0.47391500	0.62867900
F	-2.03141900	0.15841500	2.57306300
F	-0.67291700	-1.37525200	1.84824500
O	-0.31717800	-0.94614900	-0.95261500
O	2.66843000	1.45376300	1.68361500
O	4.29679500	-1.86884900	-1.40341300
C	3.98102600	1.80274500	2.11031500
H	4.57521100	2.17778300	1.27145400
H	3.84918000	2.59295100	2.84831600
H	4.48060900	0.94643300	2.57340600
C	-0.67395200	-1.96684100	-1.88235400
H	-0.22775800	-1.76457600	-2.86123400
H	-0.34690600	-2.94524200	-1.51573000
H	-1.76108800	-1.92087800	-1.92989400
C	5.65144500	-1.62469600	-1.04829100
H	6.24486500	-2.30517900	-1.65812600
H	5.93566200	-0.59162600	-1.27352800
H	5.82562300	-1.83777600	0.01143000
C	-4.63336400	-3.08288400	-0.41786400
H	-5.15324300	-3.66438300	0.34692900
H	-4.02012900	-3.76917000	-1.01451200
H	-5.35906800	-2.62240100	-1.09397600
C	-3.72242800	-2.01862700	0.20975200
O	-3.34745800	-1.08585000	-0.56024800

O	-3.38979300	-2.16431200	1.40597700

A_TS1

C	-2.60198200	-4.67995100	-1.40550900
C	-2.62142400	-3.72220000	-0.39607300
C	-2.80251800	-2.37771000	-0.72864500
C	-2.96318100	-1.98634000	-2.05564400
C	-2.94389000	-2.95532500	-3.05593700
C	-2.76282400	-4.29947900	-2.73646400
H	-2.45988600	-5.72470500	-1.14784600
H	-2.49484400	-4.02009700	0.64210800
H	-3.10466200	-0.93969600	-2.30615200
H	-3.07032900	-2.65354400	-4.09103100
H	-2.74720700	-5.04832600	-3.52186100
S	-2.83157200	-1.22898600	0.63799800
C	-2.77401400	0.36839600	-0.09268200
C	-3.85393400	1.24905200	0.08465400
C	-1.62540800	0.80837200	-0.78231600
C	-3.79513000	2.55445300	-0.41128300
C	-1.56164200	2.09810200	-1.29059900
C	-2.64556400	2.96073800	-1.09321400
H	-4.62364300	3.23221300	-0.26528000
H	-0.69259600	2.46904500	-1.81770400
C	-0.59301300	-1.61656300	1.52696800
H	-0.39360200	-0.52321600	1.51435500
F	-0.18355800	-2.40860900	0.59782900
F	-1.03512300	-2.25093600	2.56255900
O	-0.64976500	-0.10630900	-0.92448500
O	-4.91814200	0.76149400	0.75060400
O	-2.49092100	4.19608300	-1.61194100
C	-6.01430700	1.62771800	1.00080600
H	-6.46785900	1.97300700	0.06580600
H	-6.73900700	1.03306700	1.55643000
H	-5.70763900	2.48739300	1.60569300
C	0.59084800	0.33319700	-1.45862000
H	0.47154300	0.67719700	-2.49159500
H	1.00729300	1.12953500	-0.83458900
H	1.24741400	-0.53722700	-1.44586400
C	-3.53013700	5.14241000	-1.42025900
H	-3.19057200	6.05969400	-1.90115300
H	-4.46133800	4.80920900	-1.89113800
H	-3.70164700	5.33162400	-0.35504500
C	5.32755700	1.16888200	-0.75592000
C	4.51012700	0.77609900	0.30431300

C	4.62453400	-0.48242500	0.89579100
C	5.58892700	-1.35909000	0.38461400
C	6.41373400	-0.98794900	-0.66781200
C	6.28821800	0.28061100	-1.24527500
H	5.21086600	2.15826700	-1.18266300
H	3.76620600	1.47503300	0.68370100
H	5.69786400	-2.34773500	0.82408000
H	7.16651000	-1.66471800	-1.05993800
O	7.13962000	0.55667400	-2.26746200
C	7.04419600	1.83332200	-2.86999300
H	7.24113700	2.63348200	-2.14697900
H	7.80666700	1.85727600	-3.64928000
H	6.05824200	1.98865600	-3.32387200
C	3.68445800	-0.89470700	2.00008200
H	4.09451700	-1.73842800	2.56510700
H	3.52752600	-0.06573200	2.69954700
C	2.32076700	-1.28512300	1.42529400
H	1.95121200	-0.46357300	0.79473300
H	2.41782900	-2.17928700	0.79936300
O	1.37855300	-1.56821900	2.44483000
H	1.27628200	-0.68655200	2.95497900
C	0.94719900	3.02614000	2.72002800
H	2.01931800	3.24755300	2.70568300
H	0.44726300	3.58538100	1.92761200
H	0.56535400	3.34570800	3.69428700
C	0.73408000	1.52790200	2.55498100
O	0.08629900	1.12951200	1.55362700
O	1.23448100	0.78676200	3.44974300

B_TS1

C	-3.07156200	2.85632900	-0.87569500
C	-2.33254000	2.17263000	0.08667100
C	-0.99232600	1.89130700	-0.17051300
C	-0.37765900	2.28115600	-1.35618700
C	-1.13063100	2.96379600	-2.30765700
C	-2.47376600	3.25123100	-2.07013500
H	-4.11778500	3.07436200	-0.68804800
H	-2.79880100	1.85955500	1.01701600
H	0.66778100	2.05070900	-1.53802700
H	-0.66304200	3.26929300	-3.23819000
H	-3.05456300	3.78211400	-2.81752000
S	-0.07882300	1.06880500	1.12998500
C	1.24499300	0.24339200	0.33205000
C	2.56103600	0.52147600	0.73825400

C	1.00735700	-0.72784700	-0.66659000
C	3.63616200	-0.15393200	0.15553000
C	2.07015800	-1.39946000	-1.25200800
C	3.37481200	-1.10830900	-0.83095400
H	4.64783700	0.05684100	0.46935600
H	1.92477000	-2.14954900	-2.01846200
C	-1.42614200	-0.43946400	1.55003300
H	-2.30260800	-0.68933800	0.50293100
F	-1.94016500	0.01847000	2.70833600
F	-0.59613100	-1.43398700	1.88781700
O	-0.27851700	-0.91706700	-0.98804600
O	2.70455100	1.45506200	1.69488000
O	4.34023800	-1.81363000	-1.44794200
C	4.01822800	1.79030500	2.12192300
H	4.61247800	2.18161700	1.29007000
H	3.89368700	2.56527600	2.87758000
H	4.51954100	0.92426200	2.56553900
C	-0.59850600	-1.88211400	-1.98136100
H	-0.13785100	-1.61844000	-2.93901300
H	-0.27055700	-2.87952400	-1.67080600
H	-1.68363800	-1.85426300	-2.06097000
C	5.69166100	-1.56826300	-1.08722800
H	6.29096400	-2.23528700	-1.70654200
H	5.97195100	-0.53005700	-1.29449200
H	5.86706400	-1.79679200	-0.03063600
C	-4.86155300	-2.62078600	-0.64125500
H	-5.40015400	-3.40849200	-0.11297500
H	-4.41542000	-3.03103300	-1.55289400
H	-5.55850100	-1.83434500	-0.94518600
C	-3.77600600	-2.03230100	0.23980300
O	-3.12594400	-1.04643400	-0.30745000
O	-3.55128200	-2.46955800	1.36581600

B_INT1

C	0.00000000	0.00000000	0.59735400
F	0.00000000	1.02635300	-0.19911800
F	0.00000000	-1.02635300	-0.19911800

B1_TS2

C	-2.60247900	-1.20588900	-0.64805200
C	-1.26168400	-1.15827700	-0.30001500
C	-0.75324300	-0.11616700	0.48697500
C	-1.63499500	0.87685600	0.90736300
C	-2.98918200	0.84640600	0.56986500

C	-3.47665200	-0.20133400	-0.21379400
H	-3.00039000	-2.01567400	-1.25143100
H	-0.59326700	-1.94704500	-0.63784200
H	-1.26402800	1.69512100	1.52021500
H	-3.64514800	1.63378700	0.92225900
O	-4.77099700	-0.33246100	-0.60002100
C	-5.68859300	0.64443600	-0.14483600
H	-5.42726600	1.64191800	-0.51683400
H	-6.66154800	0.35495100	-0.54294900
H	-5.73708500	0.66587400	0.95006600
C	0.71784300	-0.05091400	0.81802900
H	0.88369000	0.50540200	1.74604600
H	1.12347800	-1.05725400	0.95232300
C	1.46851800	0.64210100	-0.31038600
H	1.36988600	0.09811000	-1.25303700
H	1.11722800	1.66721400	-0.44637200
O	2.87452500	0.76346700	0.02256500
H	3.56592500	1.36755400	-0.64189600
C	3.76024800	-0.46678600	0.12730500
F	3.59395800	-0.84959000	1.42127500
F	3.07746400	-1.41758300	-0.58236900
O	4.80901900	1.46204600	-1.10022800
H	4.84089200	1.30863800	-2.06143400
H	4.84577500	0.47894500	-0.62252300

B2_TS2

C	2.14053300	1.37810200	0.06808800
C	0.80679500	1.07880500	0.29874800
C	0.37917200	-0.24391300	0.47581800
C	1.33555500	-1.25460900	0.40182700
C	2.68340700	-0.97530500	0.16966200
C	3.08932600	0.35005300	0.00249600
H	2.47492800	2.40237700	-0.06341100
H	0.07857500	1.88534000	0.34765800
H	1.02870900	-2.28957300	0.53479200
H	3.39799800	-1.78905200	0.12578400
O	4.37093900	0.73770100	-0.22178700
C	5.35085300	-0.27871900	-0.31770300
H	5.13927600	-0.95897400	-1.15092100
H	6.29877200	0.22899000	-0.49869900
H	5.42198300	-0.85436800	0.61258100
C	-1.08258200	-0.56266800	0.66799900
H	-1.20389800	-1.48364700	1.24823900
H	-1.58314000	0.24354800	1.21440200

C	-1.77725300	-0.74328100	-0.67781600
H	-1.68651400	0.17047300	-1.28083900
H	-1.31996100	-1.56330200	-1.24187000
O	-3.15309700	-1.07406500	-0.47871700
H	-3.84927300	-0.58739200	-1.31241600
C	-4.22567000	0.33839800	-0.49392400
F	-3.44916700	1.34801500	-0.13846500
F	-5.01094500	0.07035300	0.52708300

3k

C	-2.46251200	-1.00236800	0.11068000
C	-1.08544500	-0.93350600	0.32765600
C	-0.41970200	0.28568200	0.43609000
C	-1.17635800	1.45917500	0.31810400
C	-2.54537500	1.41304200	0.10501100
C	-3.19843300	0.17858000	-0.00249000
H	-2.94330600	-1.97068500	0.03660700
H	-0.52184400	-1.85940400	0.41867300
H	-0.68183100	2.42425400	0.40065800
H	-3.13367600	2.32119700	0.01880400
O	-4.53841400	0.23053400	-0.21288800
C	-5.22138600	-0.99969400	-0.36816700
H	-5.15245600	-1.61158600	0.53865300
H	-6.26576200	-0.74588800	-0.55233500
H	-4.83097600	-1.56638100	-1.22150000
C	1.07768500	0.34107800	0.61202800
H	1.37080600	1.22760600	1.18476500
H	1.42511500	-0.53838400	1.16372900
C	1.76321100	0.39844600	-0.75223800
H	1.55355100	-0.51213700	-1.32954800
H	1.40057200	1.25582300	-1.32306000
O	3.17886600	0.58815500	-0.66089700
C	3.86764900	-0.48048700	-0.20604800
H	3.45868500	-1.44454900	-0.52507700
F	5.13912300	-0.35736000	-0.63531200
F	3.92770900	-0.47475800	1.15710800

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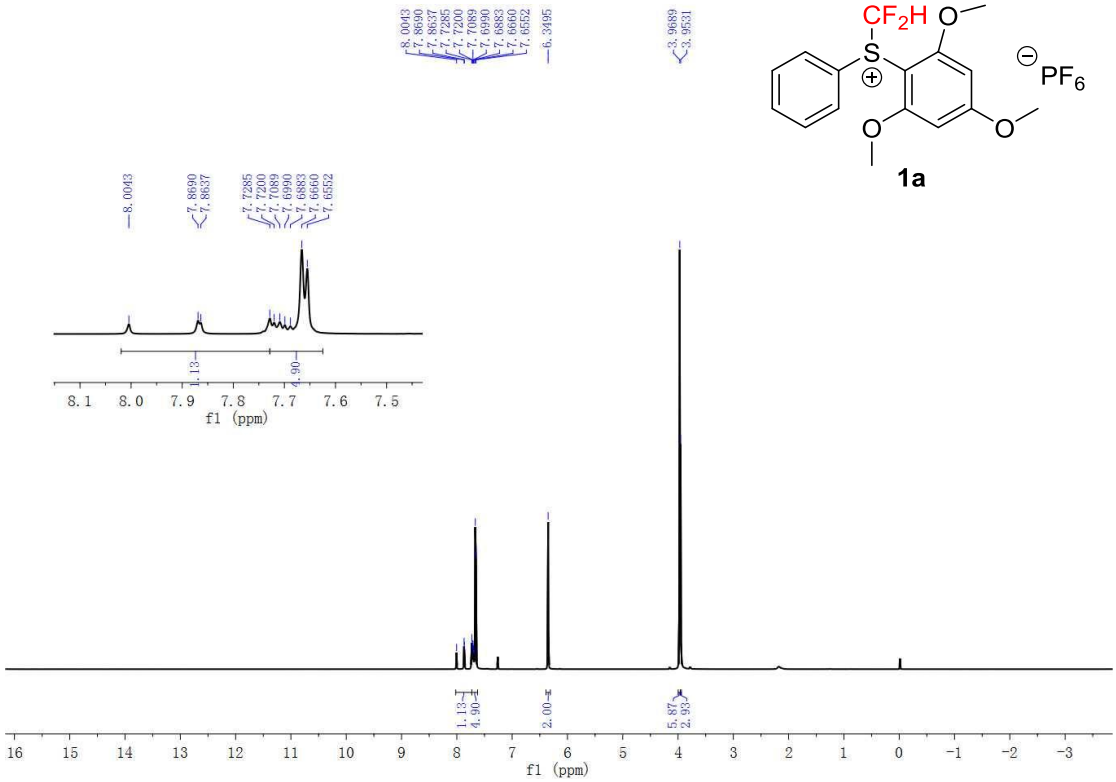
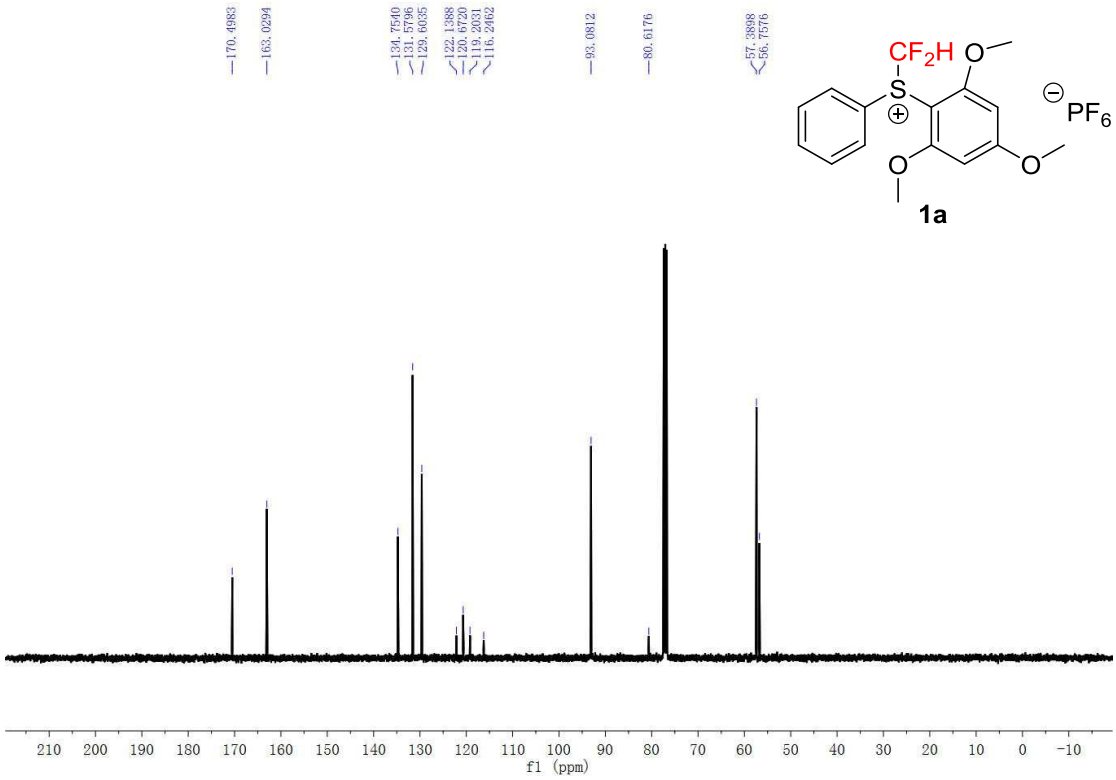
8. Copies of ^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR Spectra of Compounds

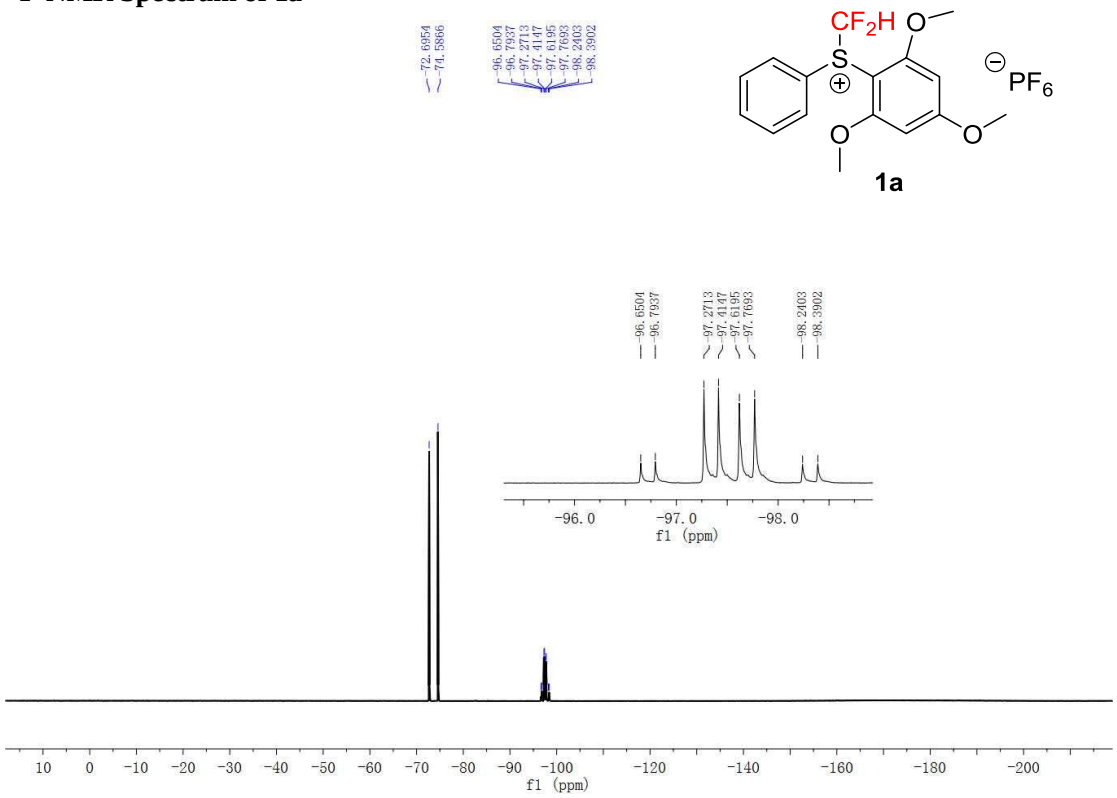
^{1}H-NMR Spectrum of 1a



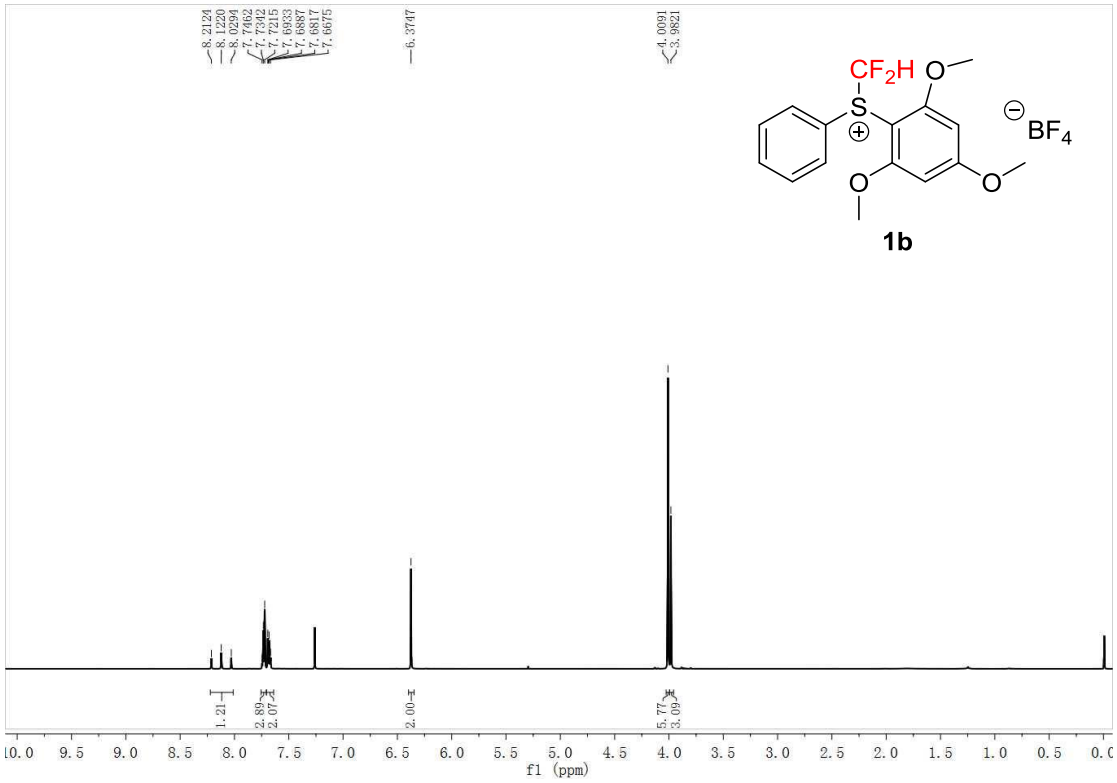
^{13}C-NMR Spectrum of 1a



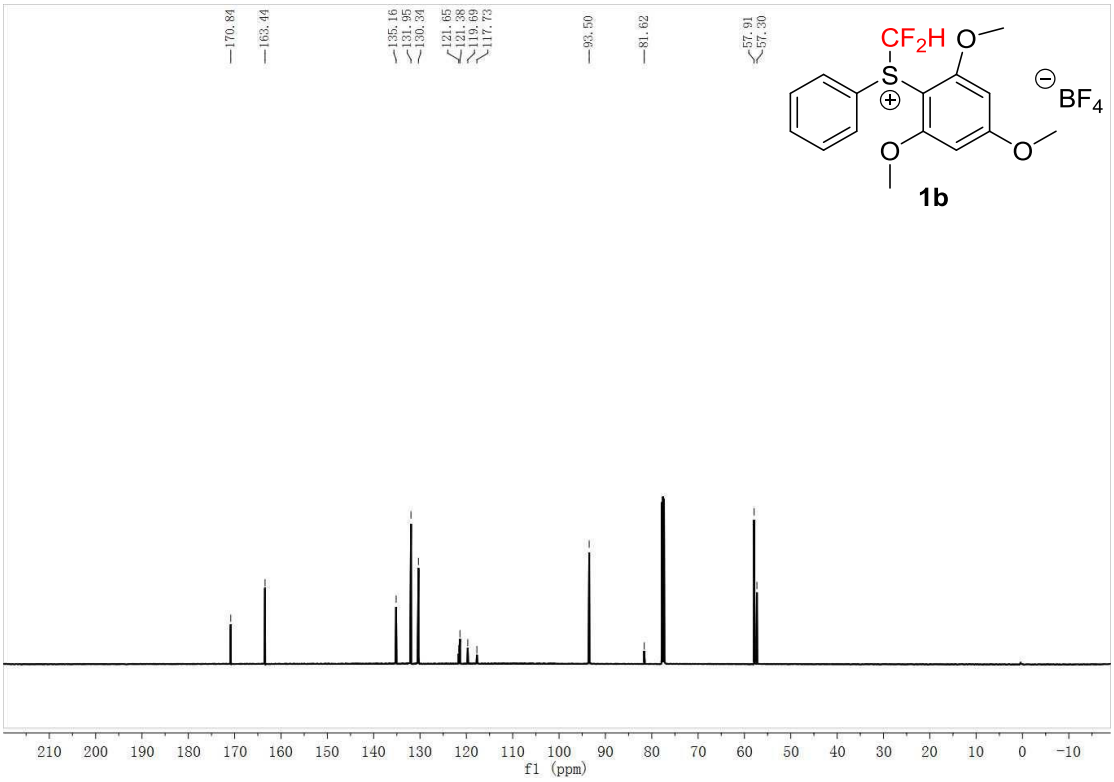
^{19}F-NMR Spectrum of 1a



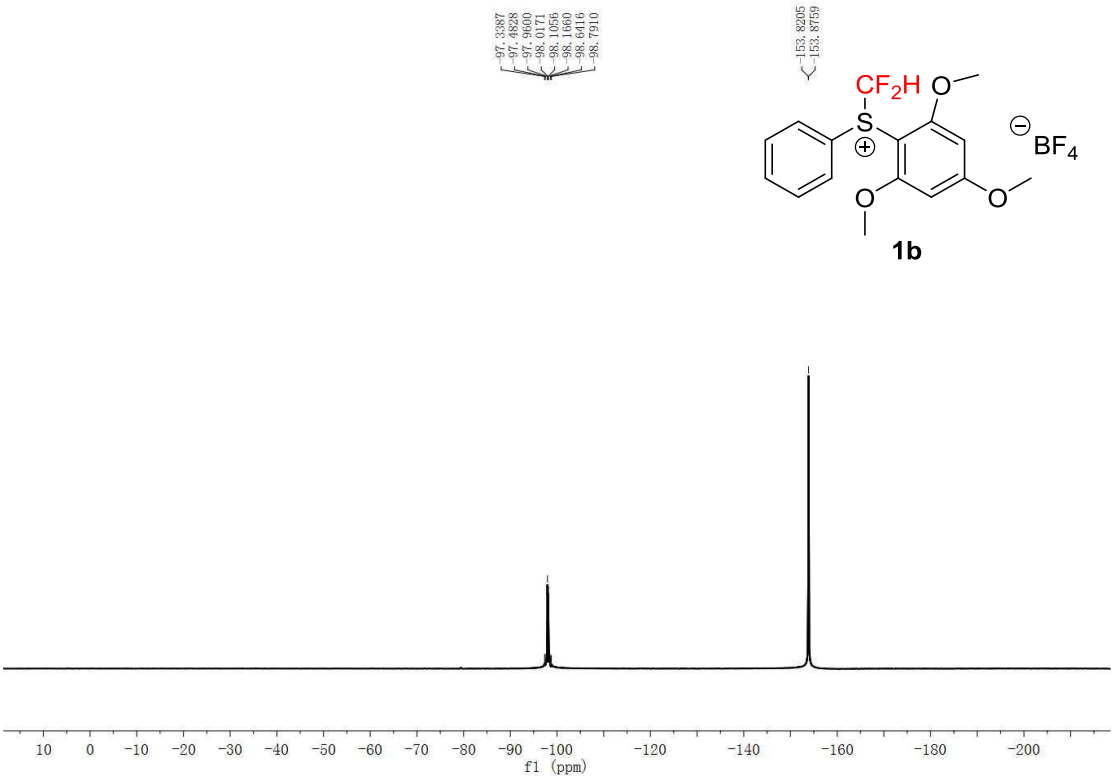
^{1}H-NMR Spectrum of 1b



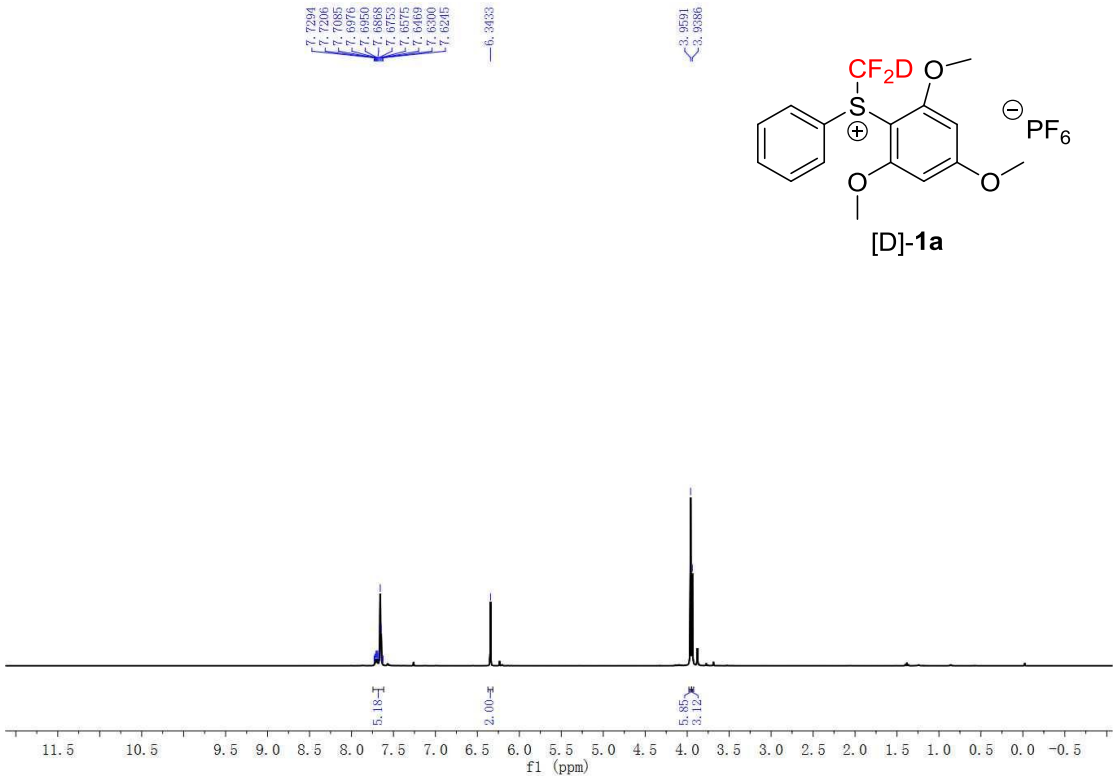
^{13}C-NMR Spectrum of 1b



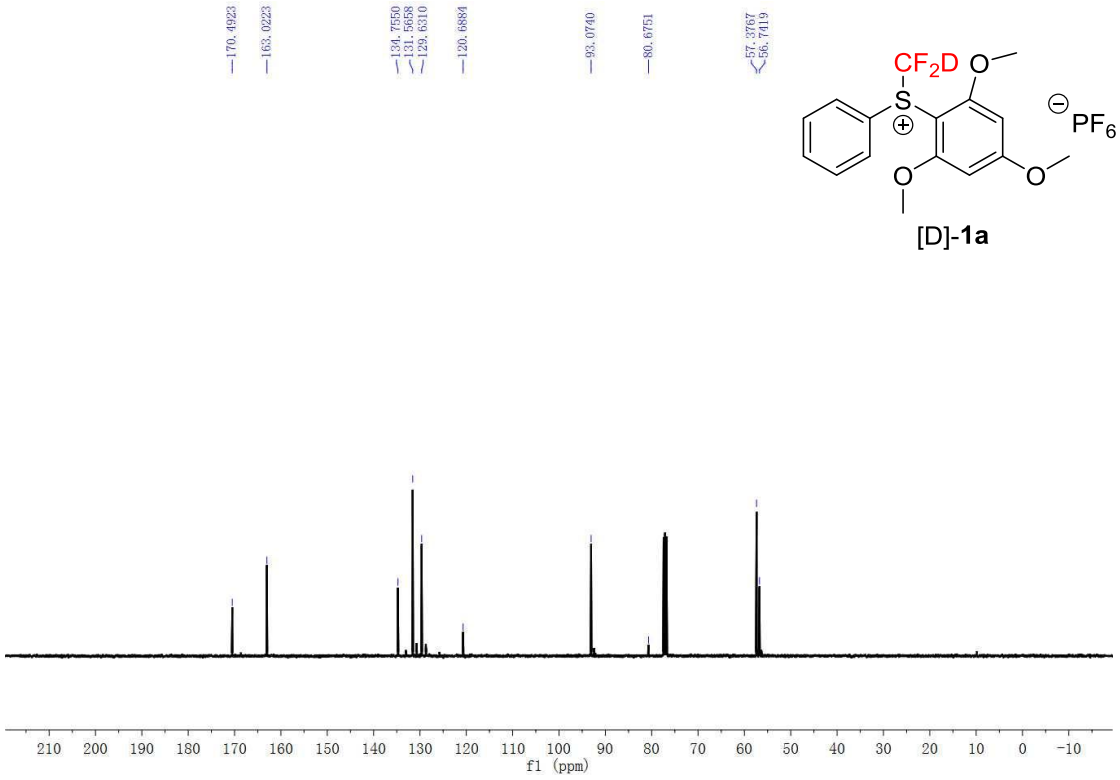
^{19}F-NMR Spectrum of 1b



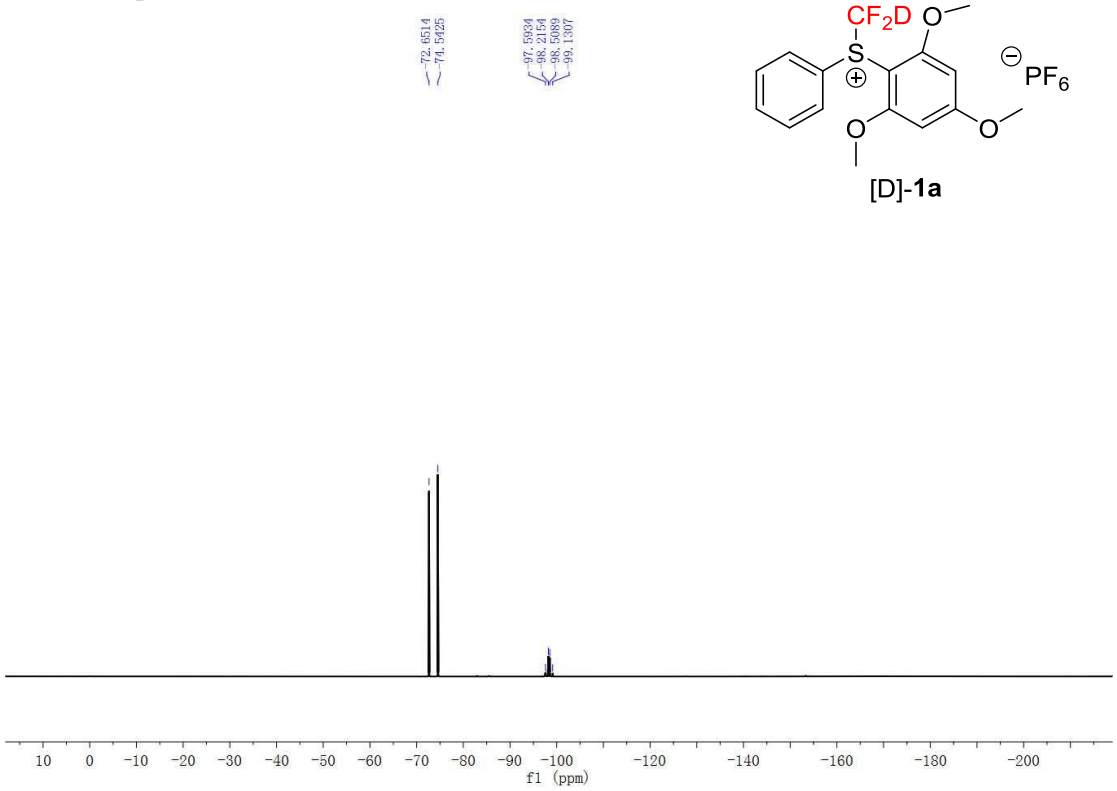
^{1}H-NMR Spectrum of [D]-1a



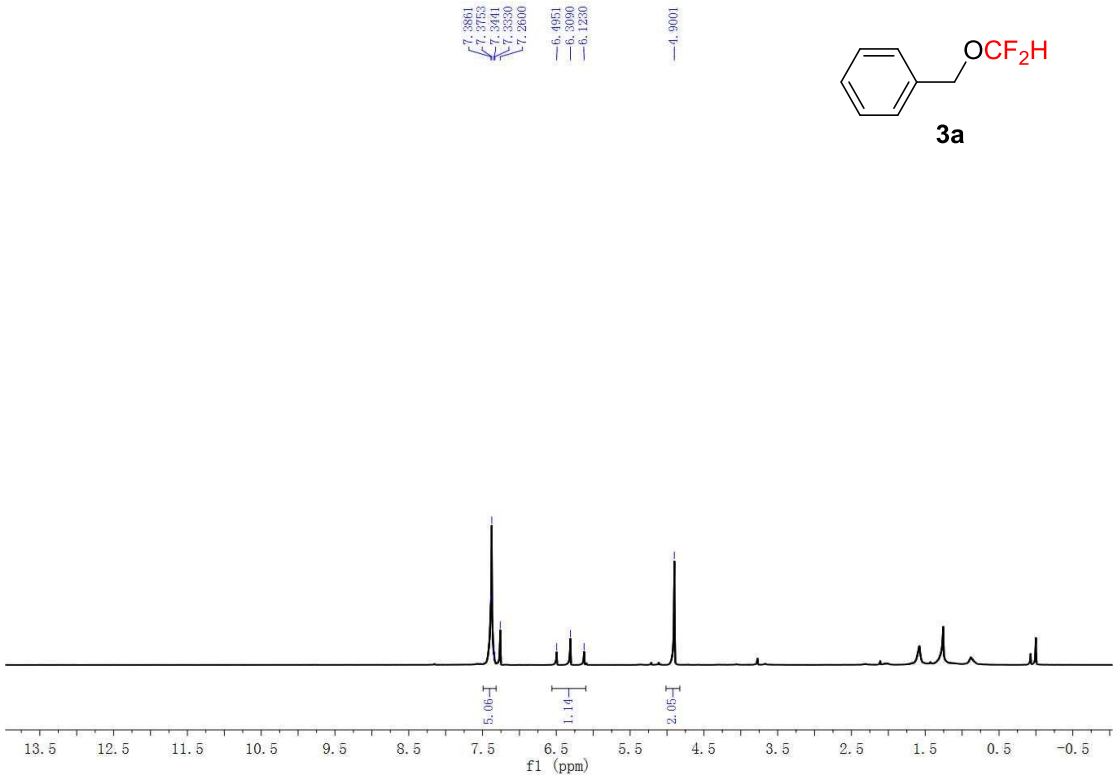
^{13}C-NMR Spectrum of [D]-1a



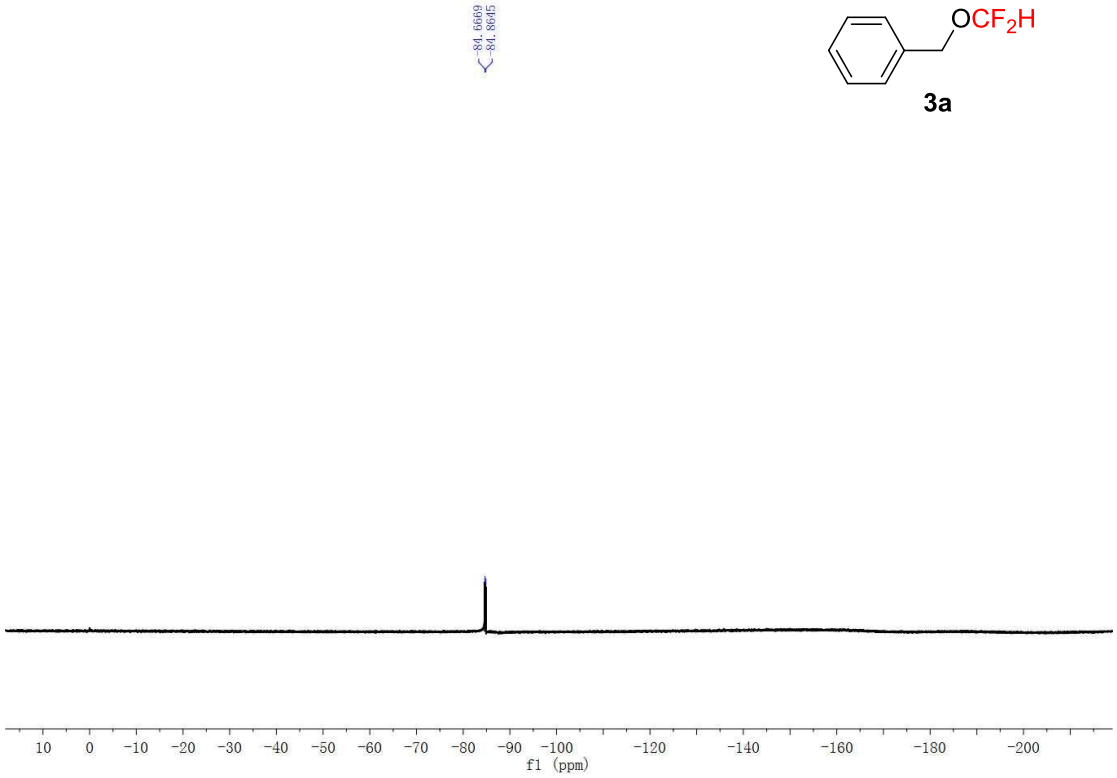
^{19}F-NMR Spectrum of [D]-1a



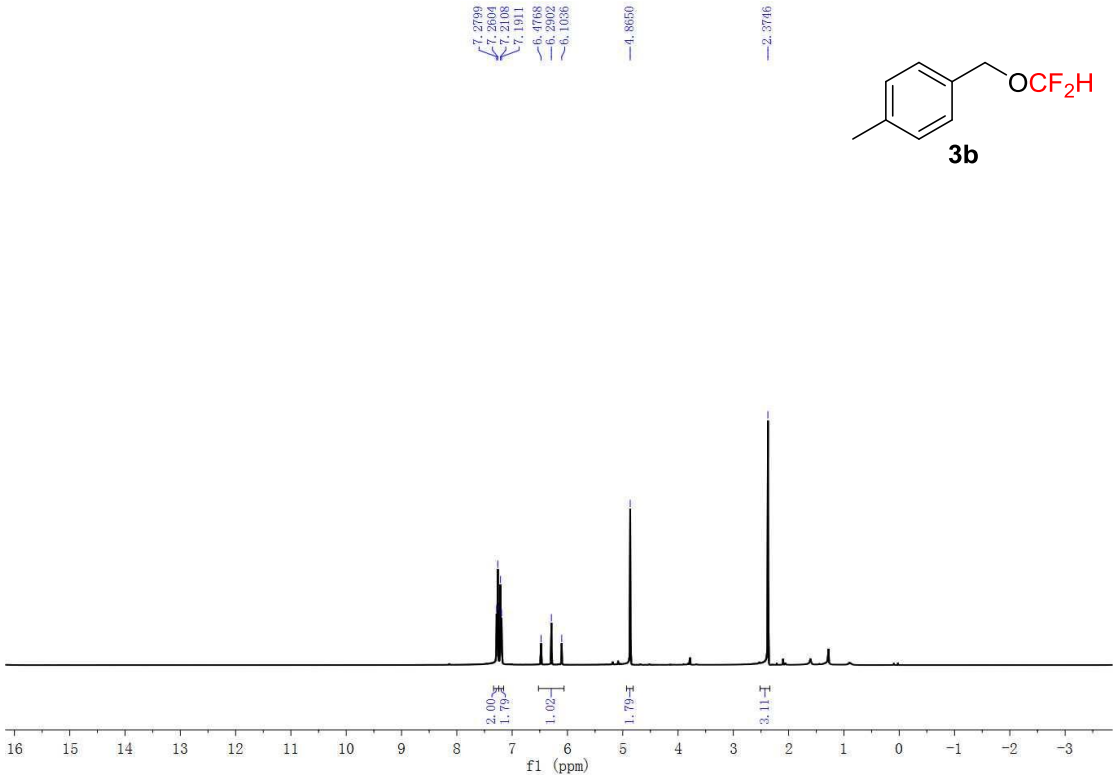
^{1}H-NMR Spectrum of 3a



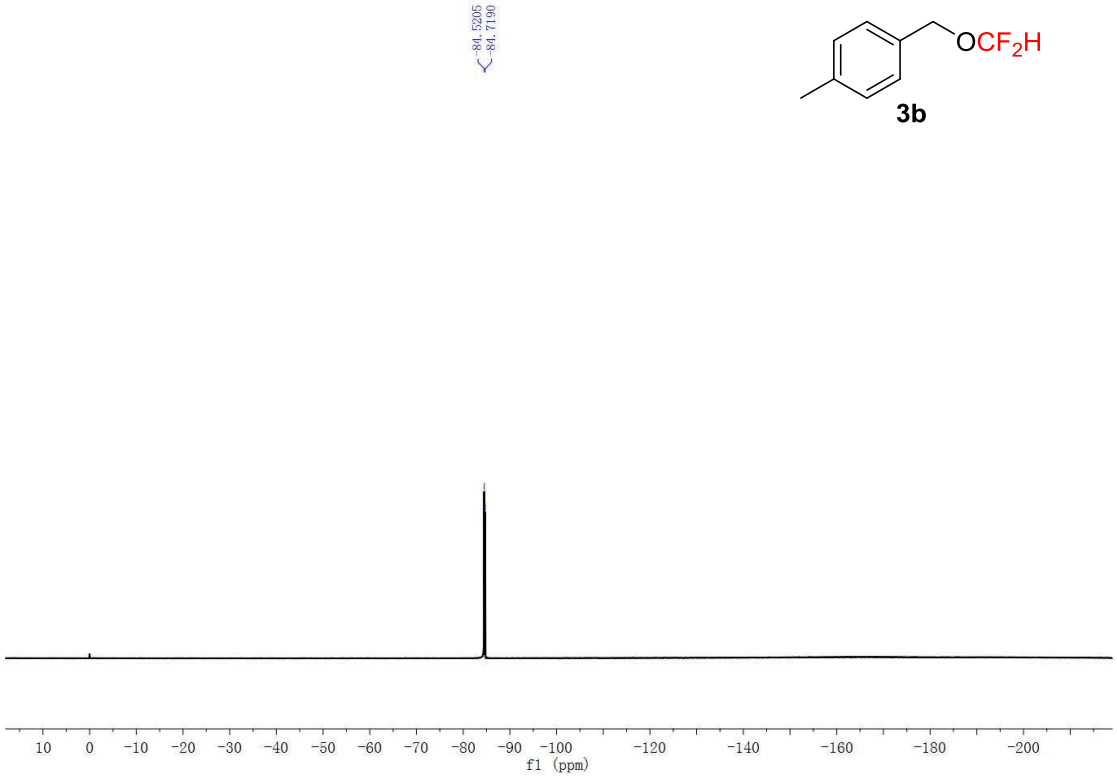
^{19}F-NMR Spectrum of 3a



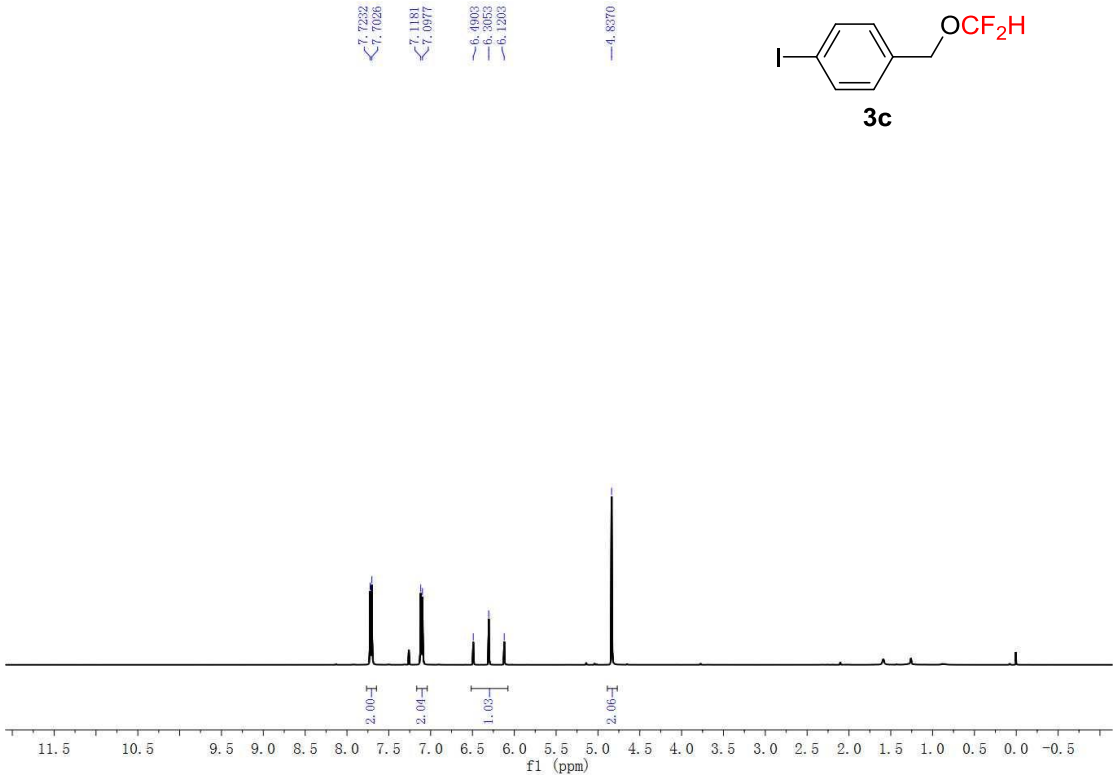
^{1}H-NMR Spectrum of 3b



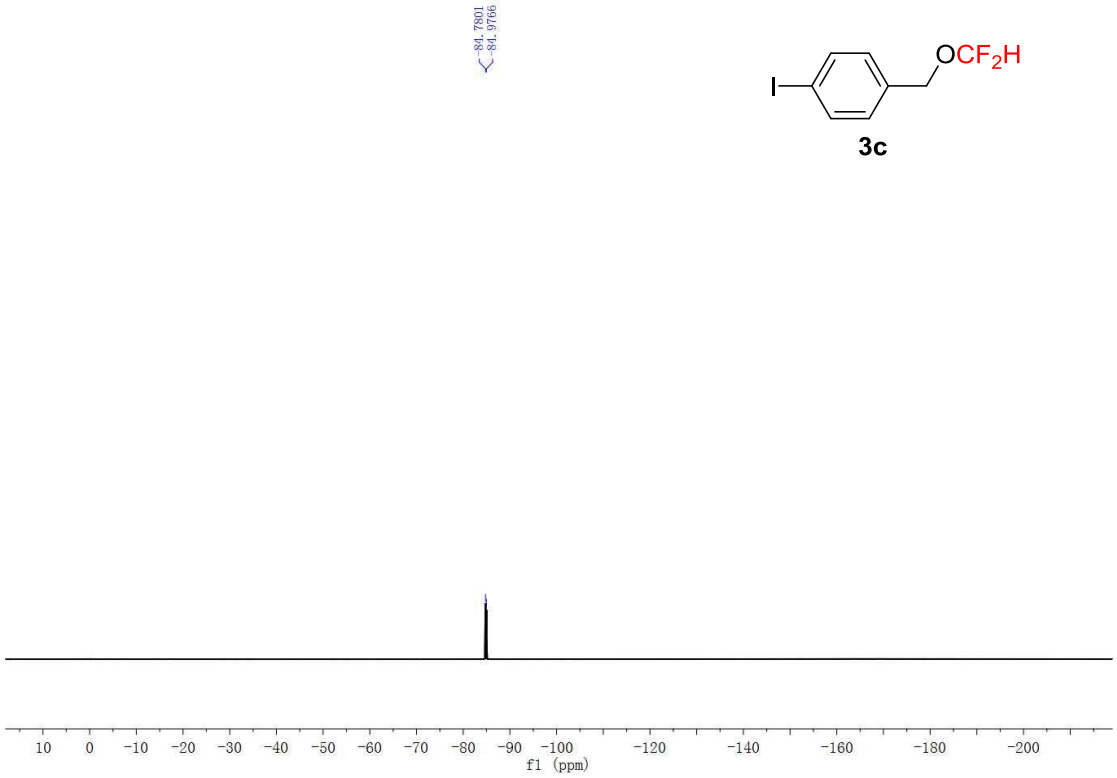
^{19}F-NMR Spectrum of 3b



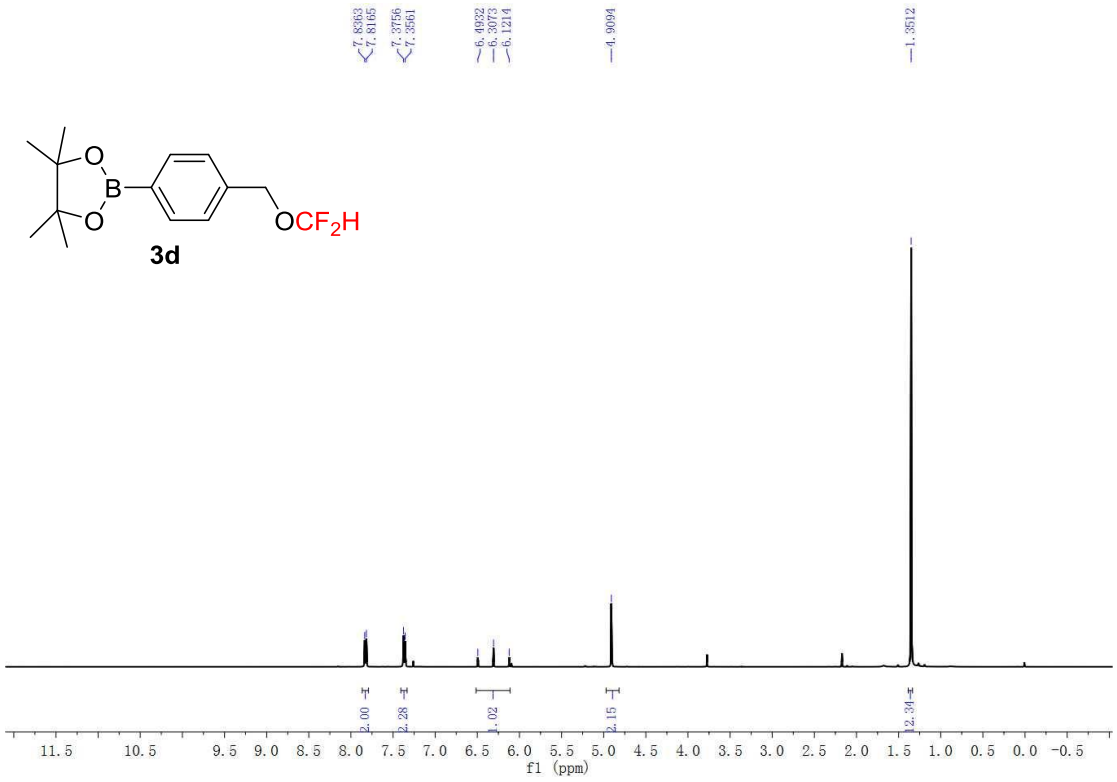
^{1}H-NMR Spectrum of 3c



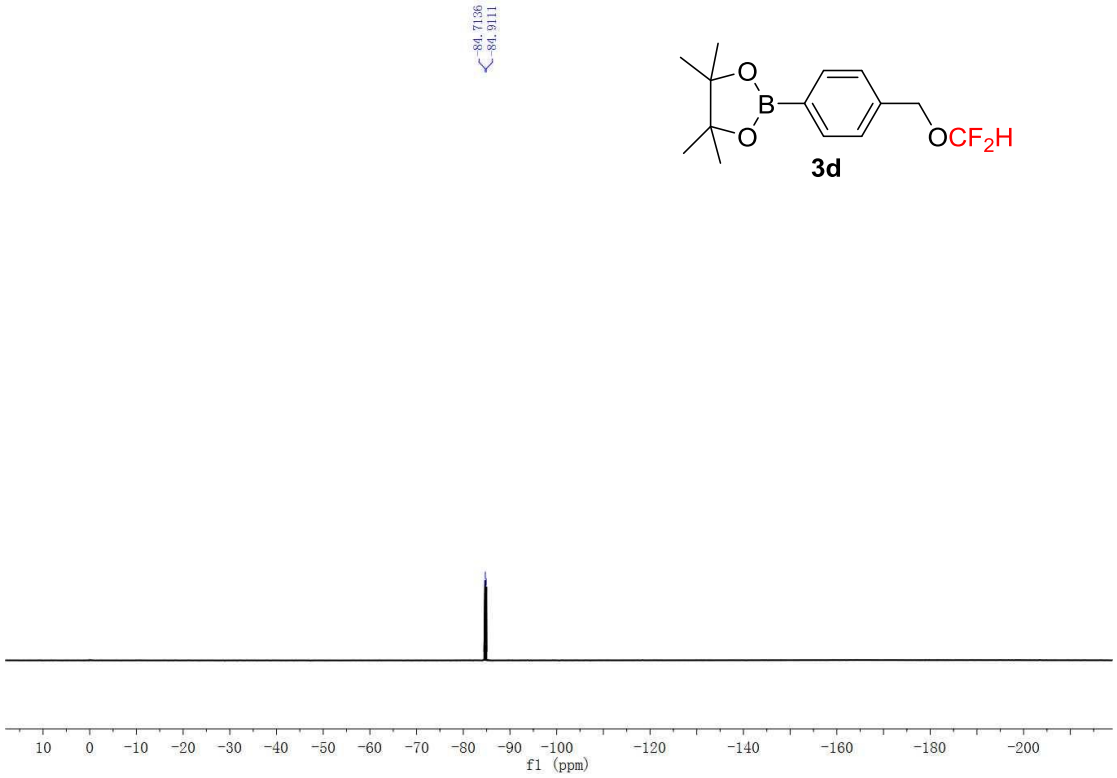
^{19}F-NMR Spectrum of 3c



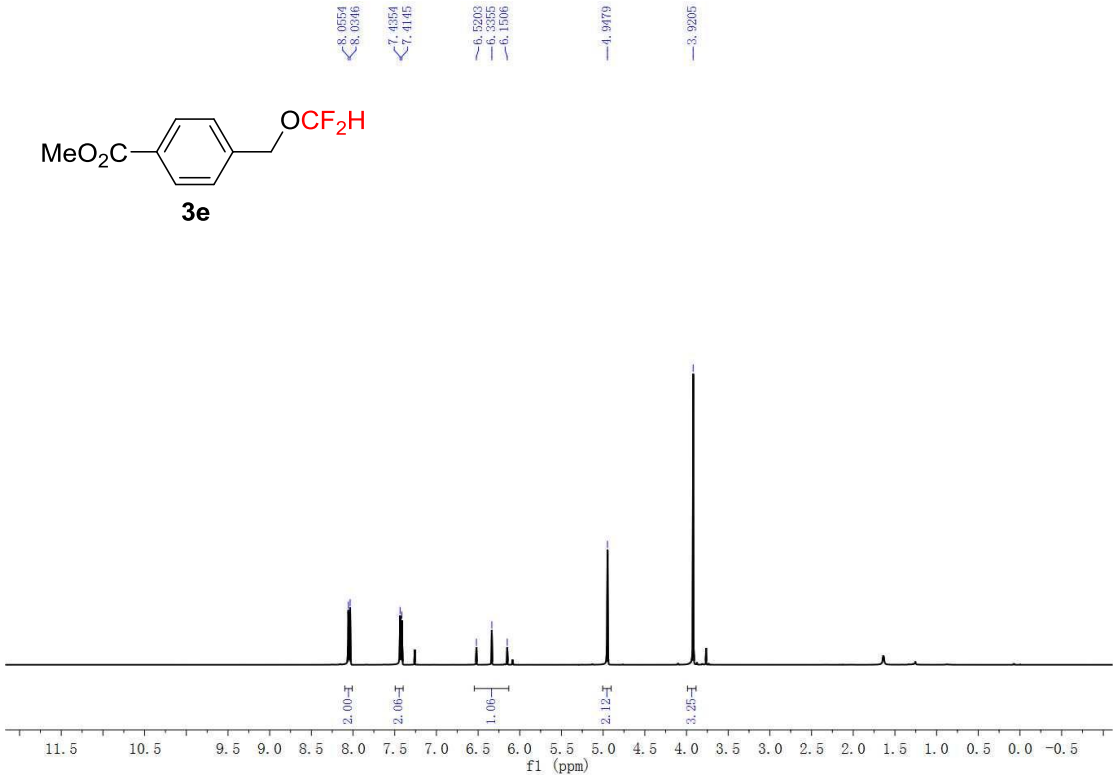
^{1}H-NMR Spectrum of 3d



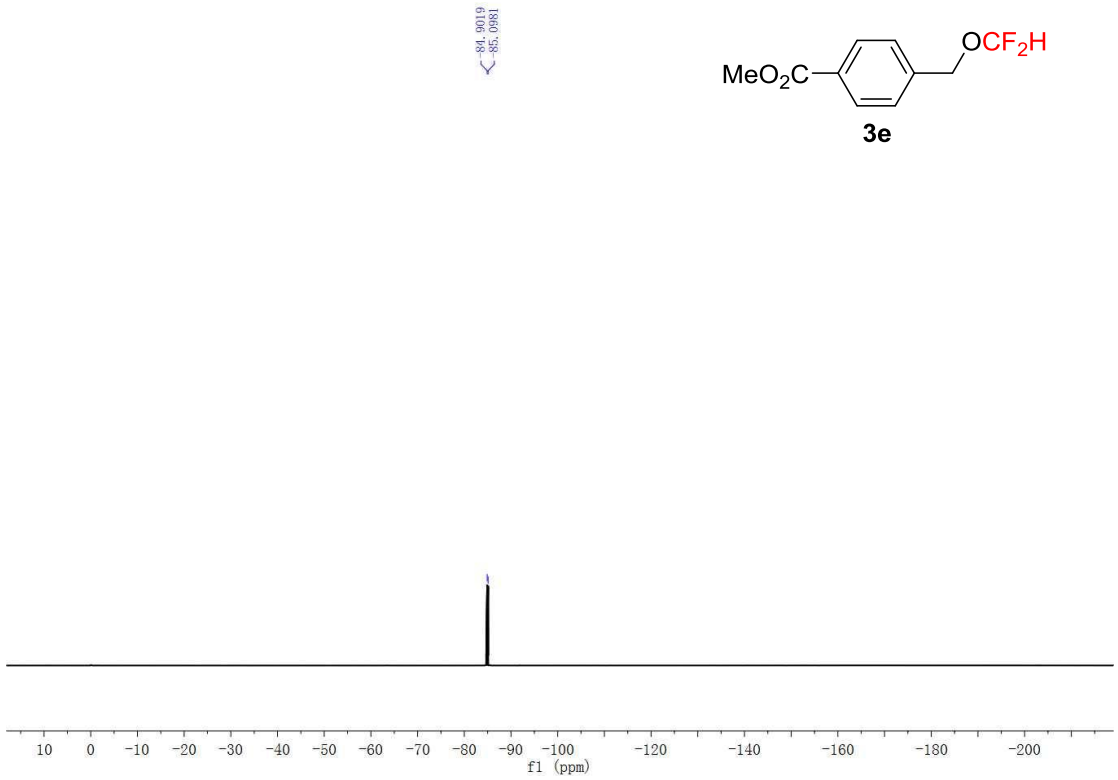
^{19}F-NMR Spectrum of 3d



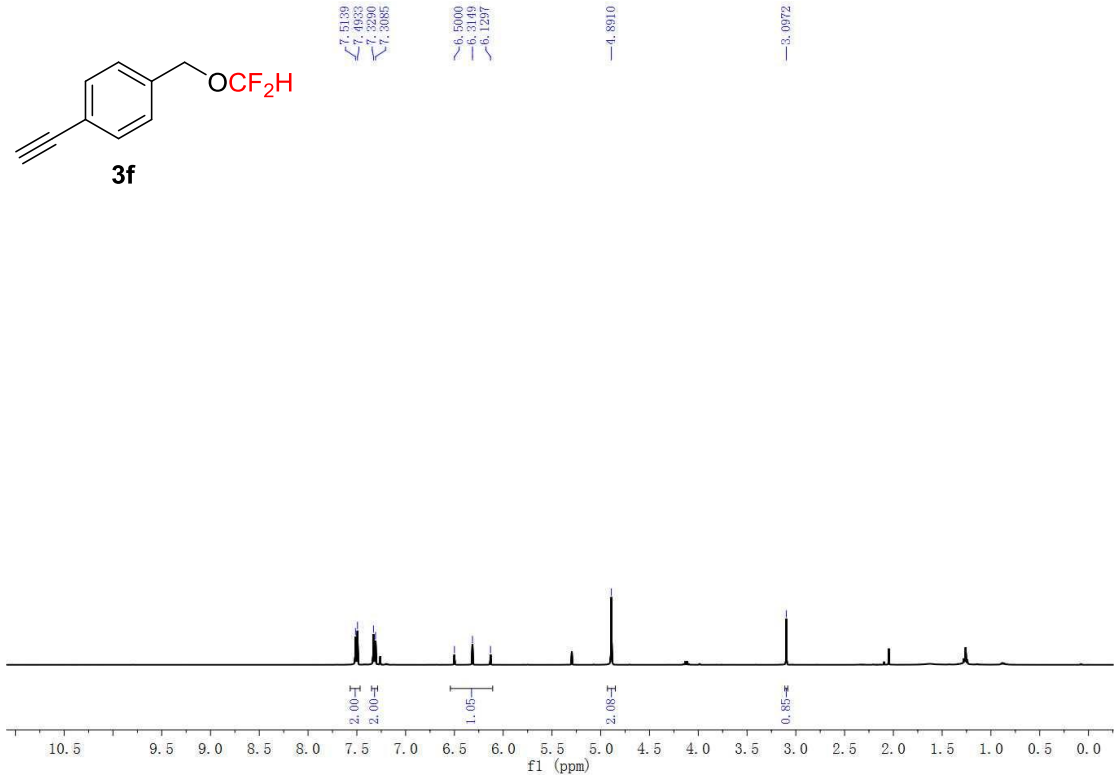
^{1}H-NMR Spectrum of 3e



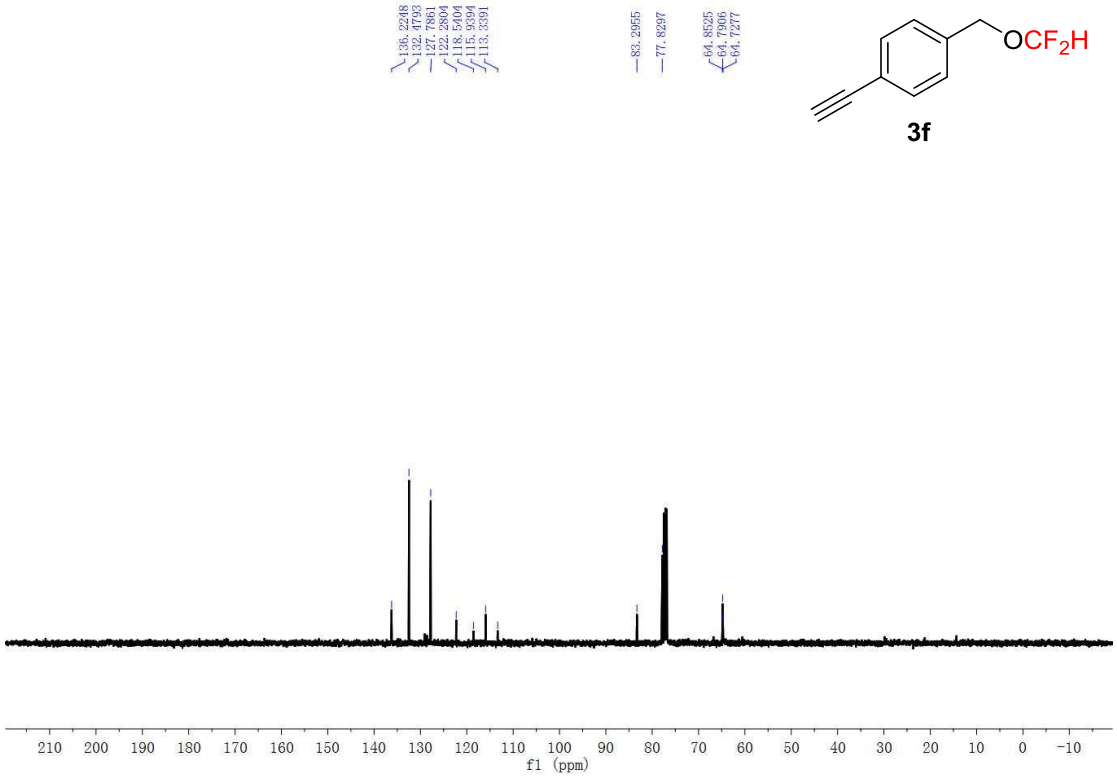
^{19}F-NMR Spectrum of 3e



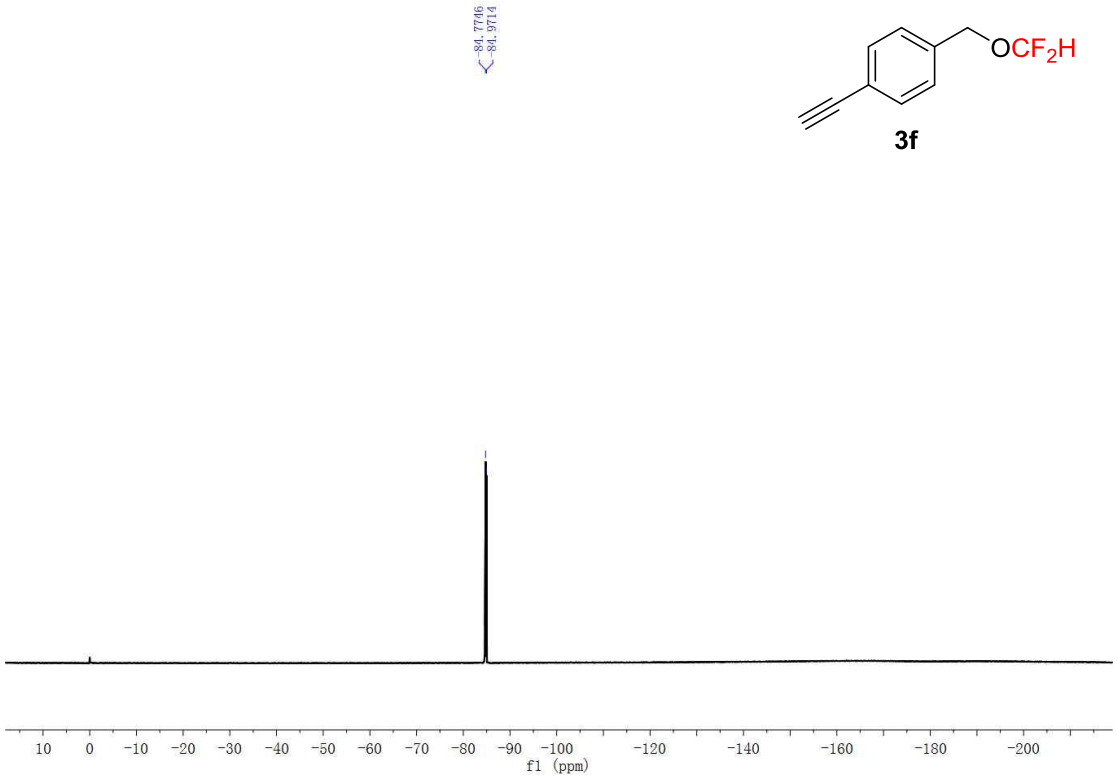
^{1}H-NMR Spectrum of 3f



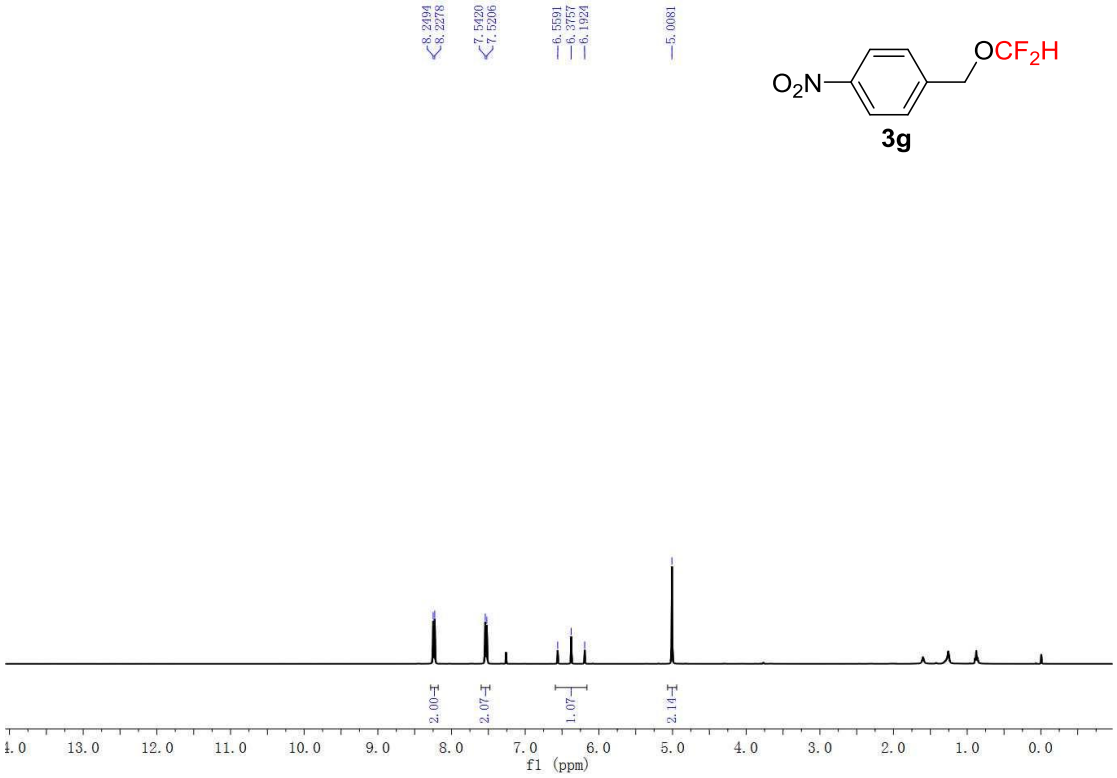
^{13}C-NMR Spectrum of 3f



^{19}F-NMR Spectrum of 3f

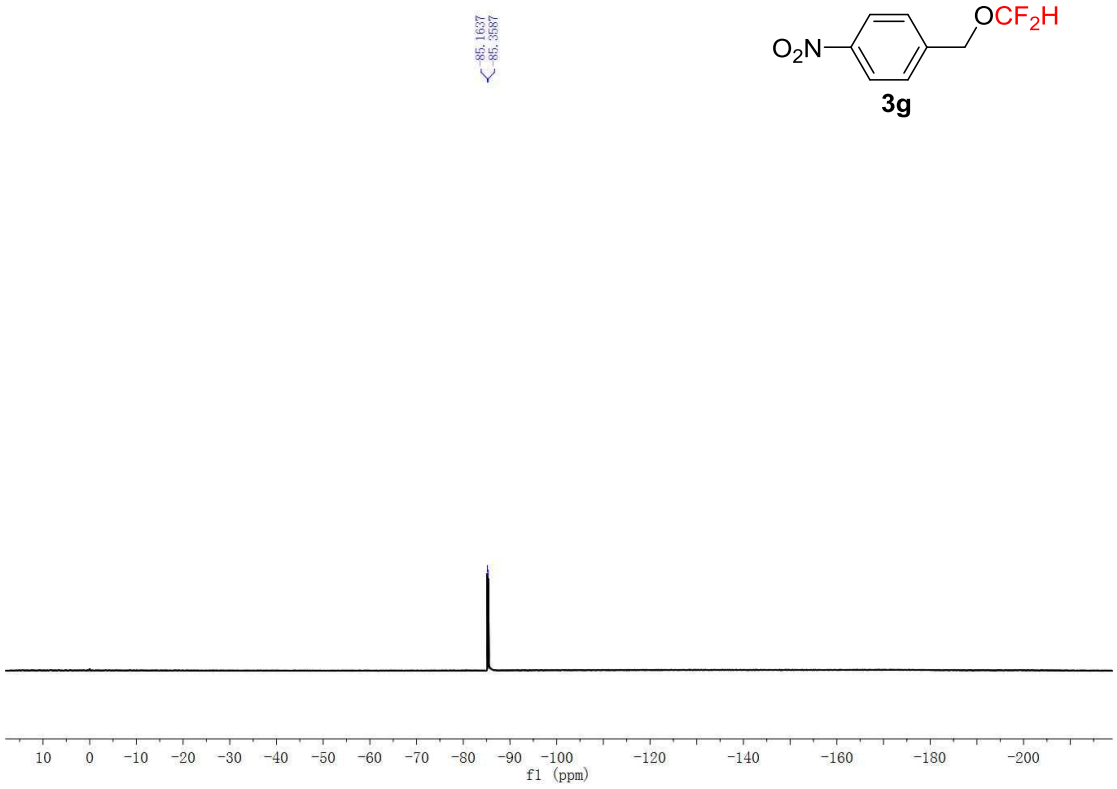


^{1}H-NMR Spectrum of 3g



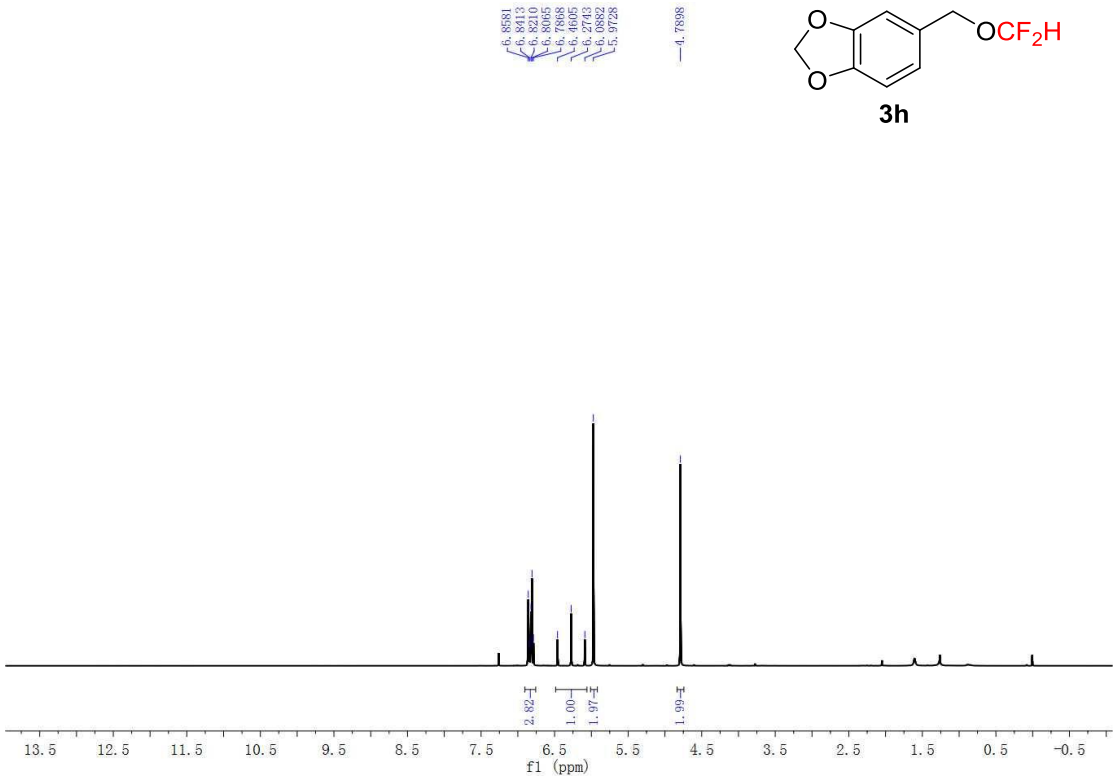
3g

^{19}F-NMR Spectrum of 3g

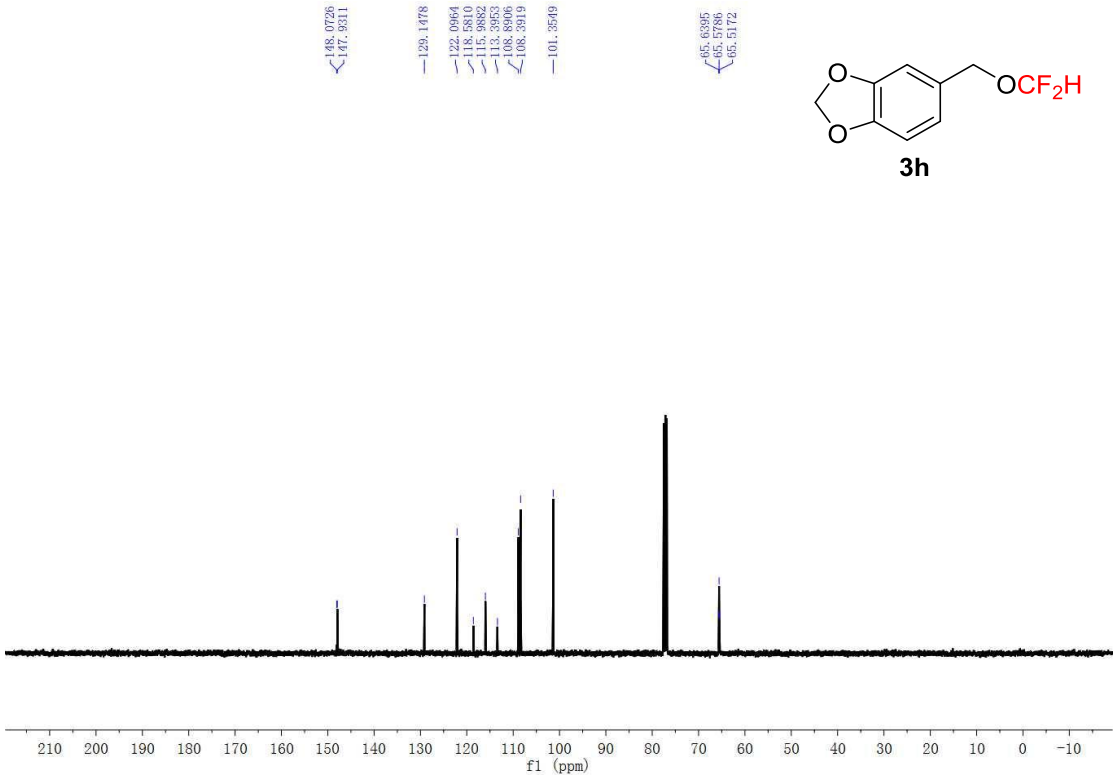


3g

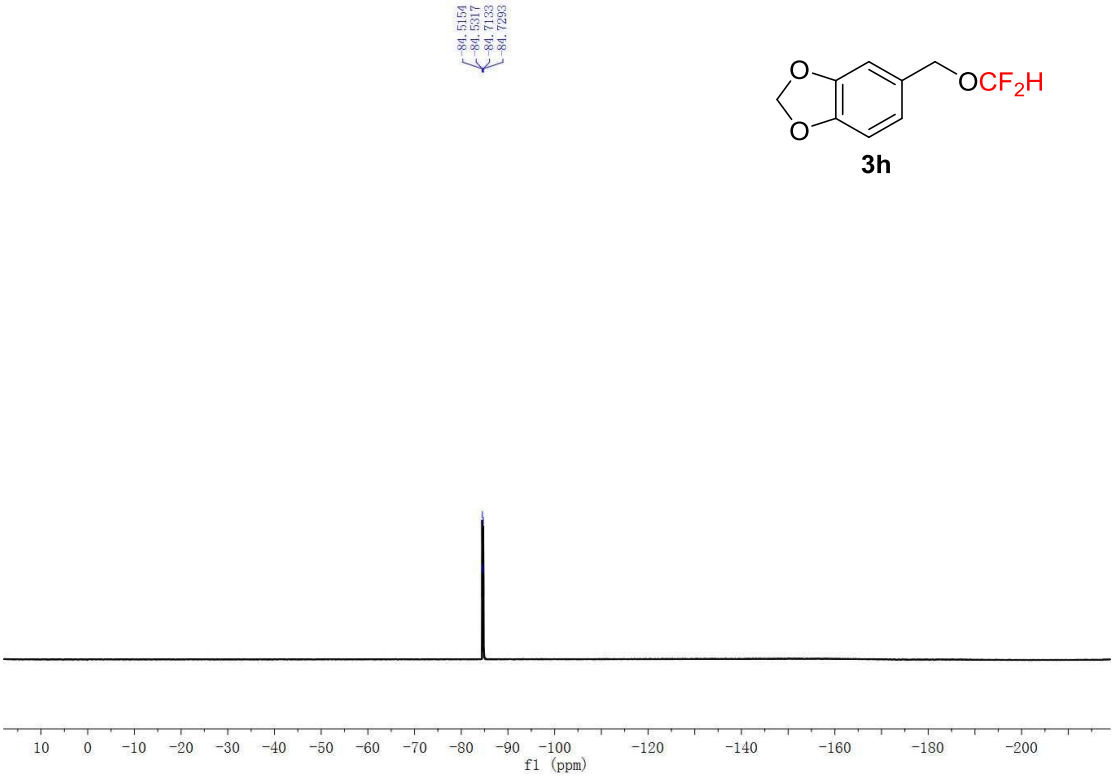
^{1}H-NMR Spectrum of 3h



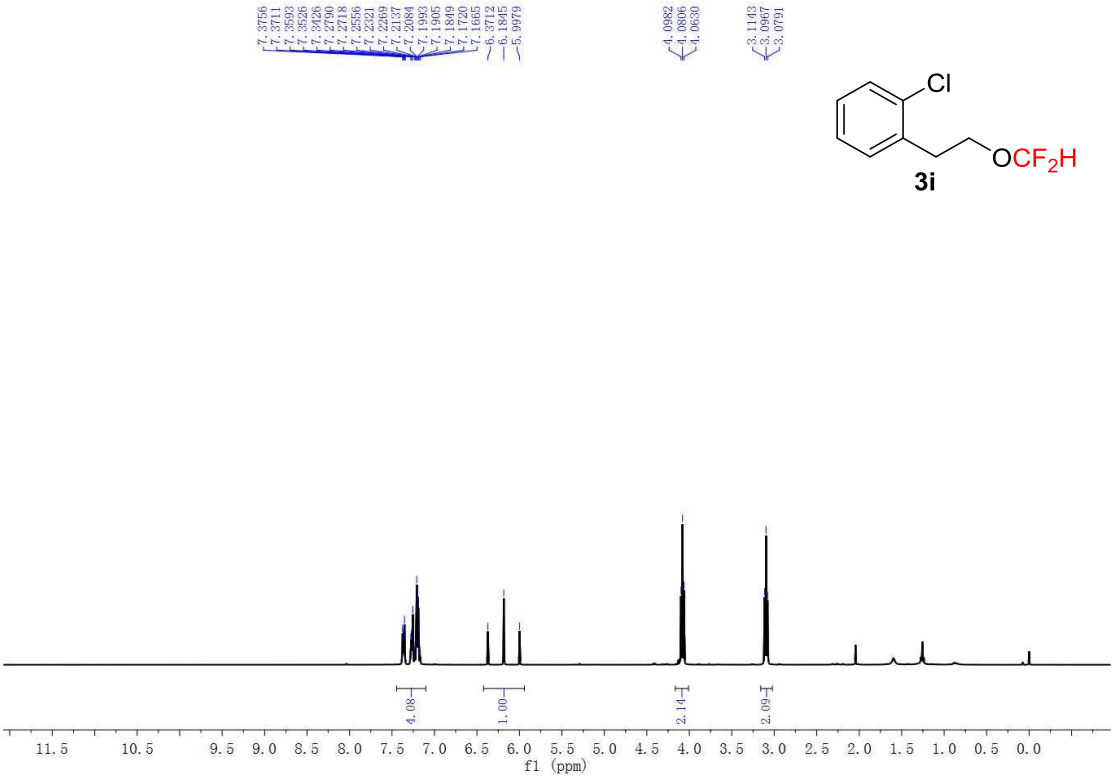
^{13}C-NMR Spectrum of 3h



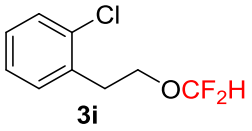
^{19}F-NMR Spectrum of 3h



^{1}H-NMR Spectrum of 3i

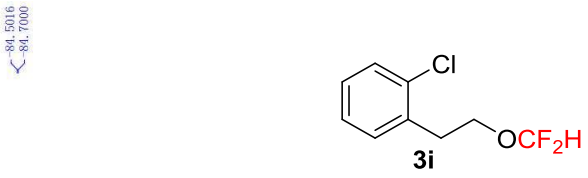


^{13}C-NMR Spectrum of 3i

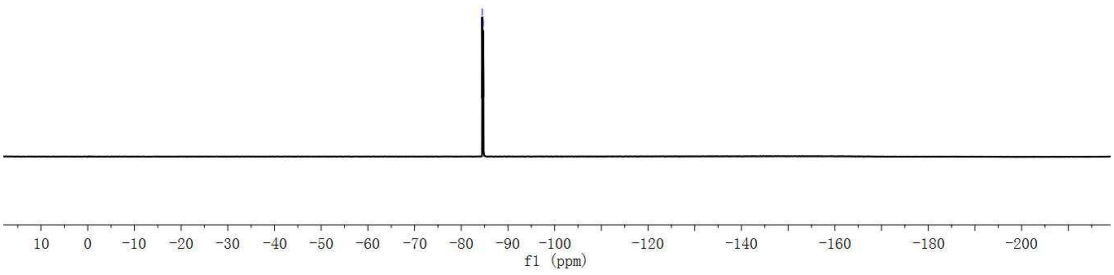


3i

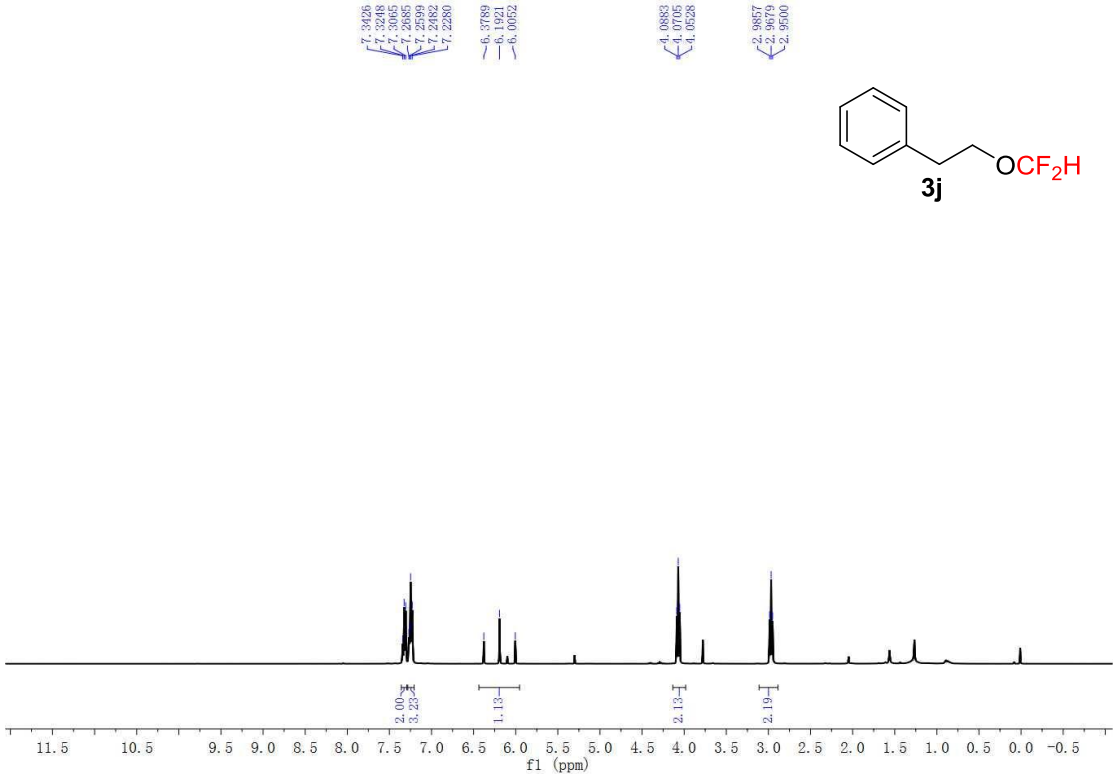
^{19}F-NMR Spectrum of 3i



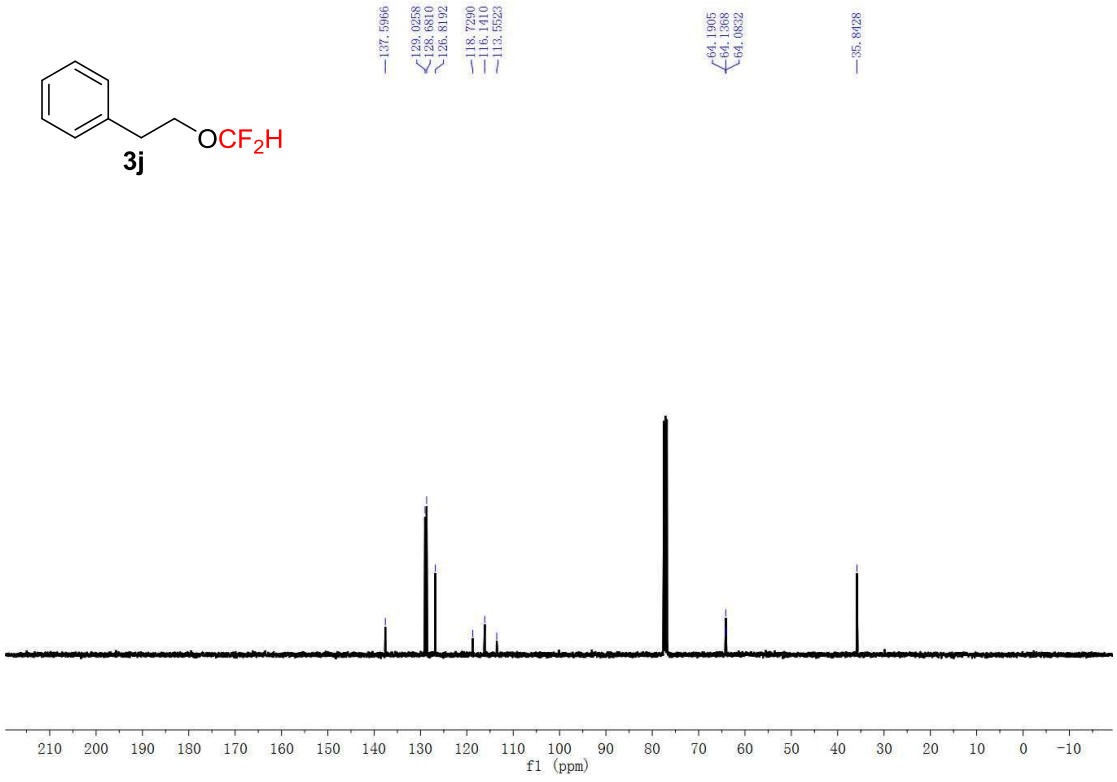
3i



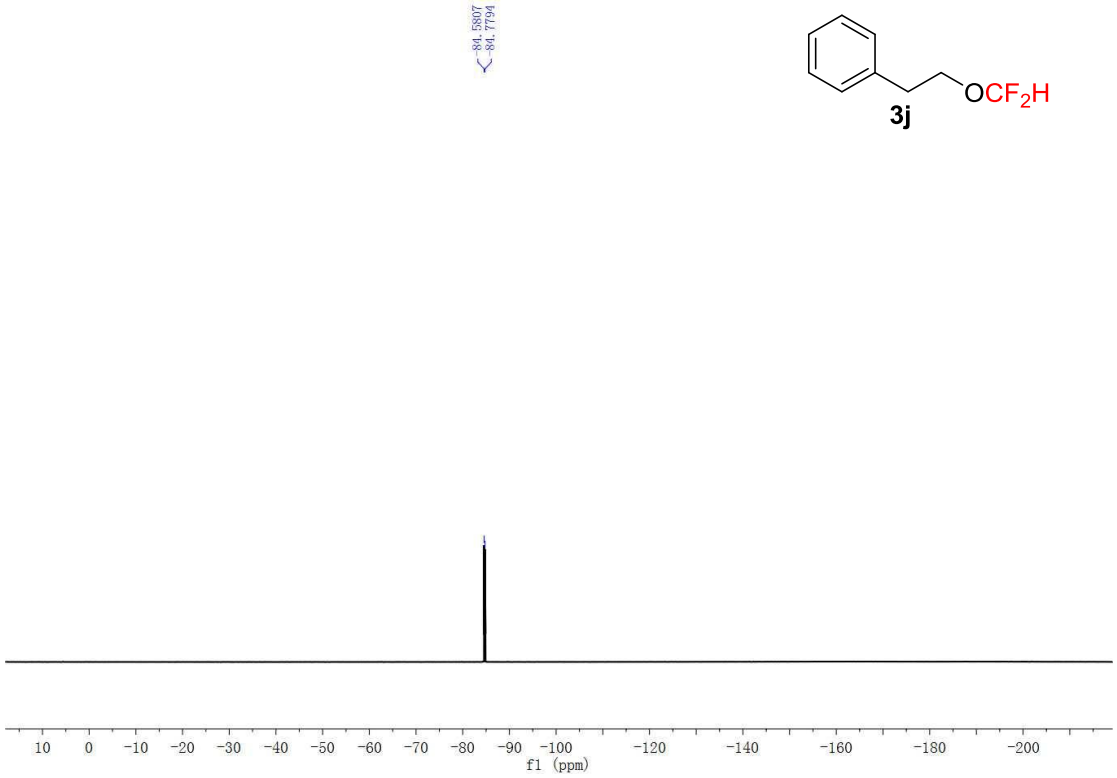
[1]H-NMR Spectrum of 3j



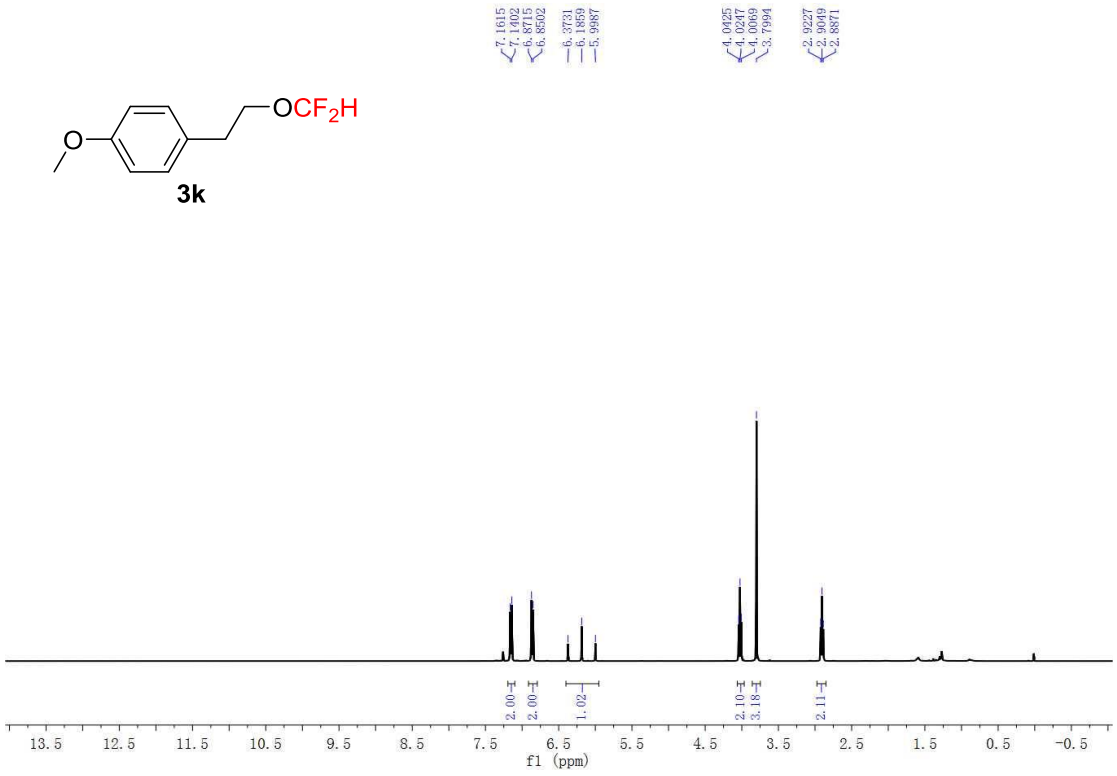
[13]C-NMR Spectrum of 3j



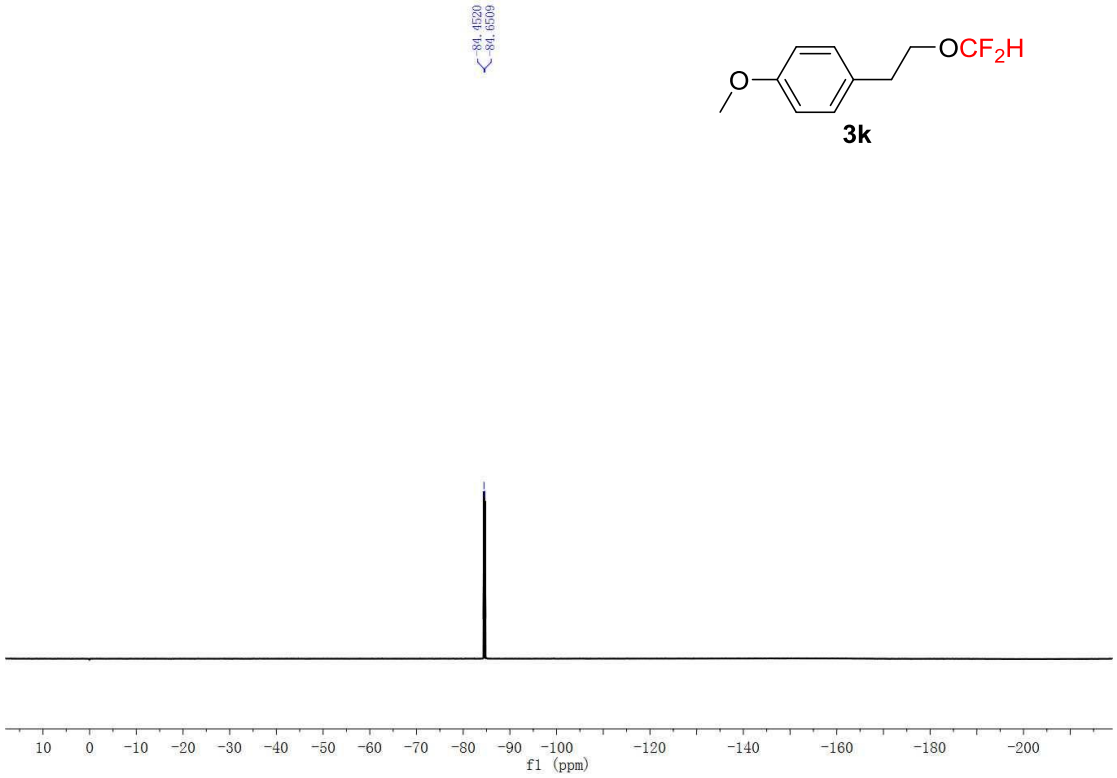
^{19}F-NMR Spectrum of 3j



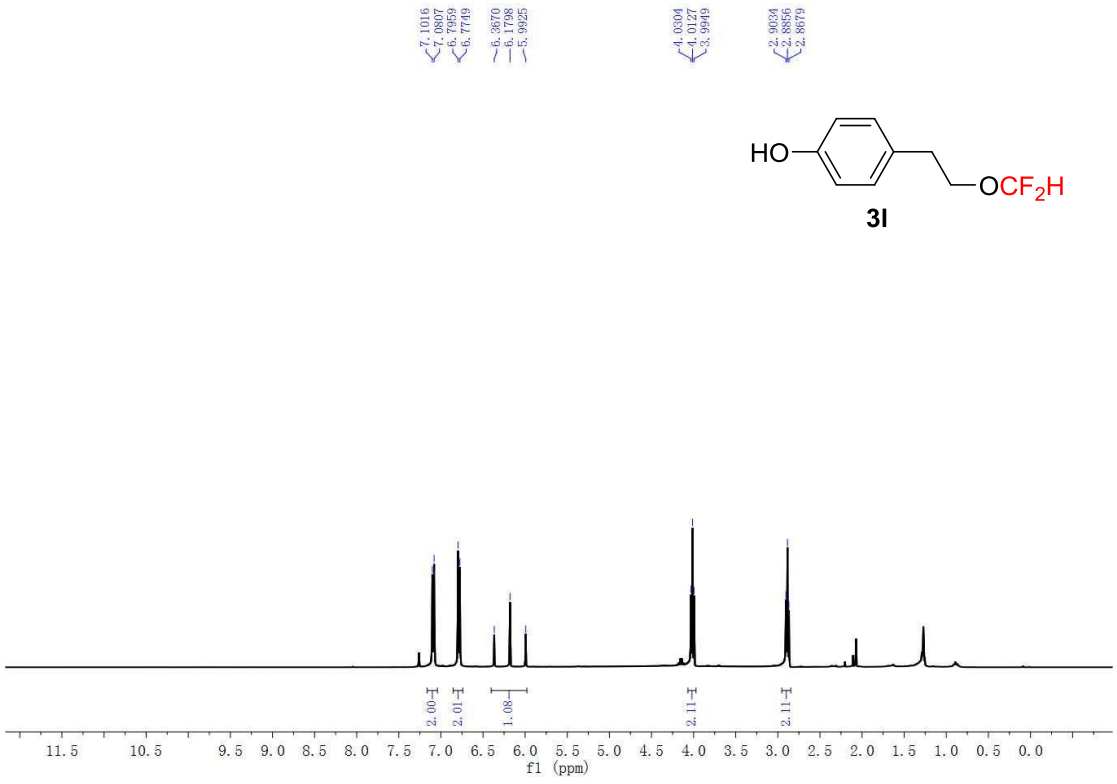
^{1}H-NMR Spectrum of 3k



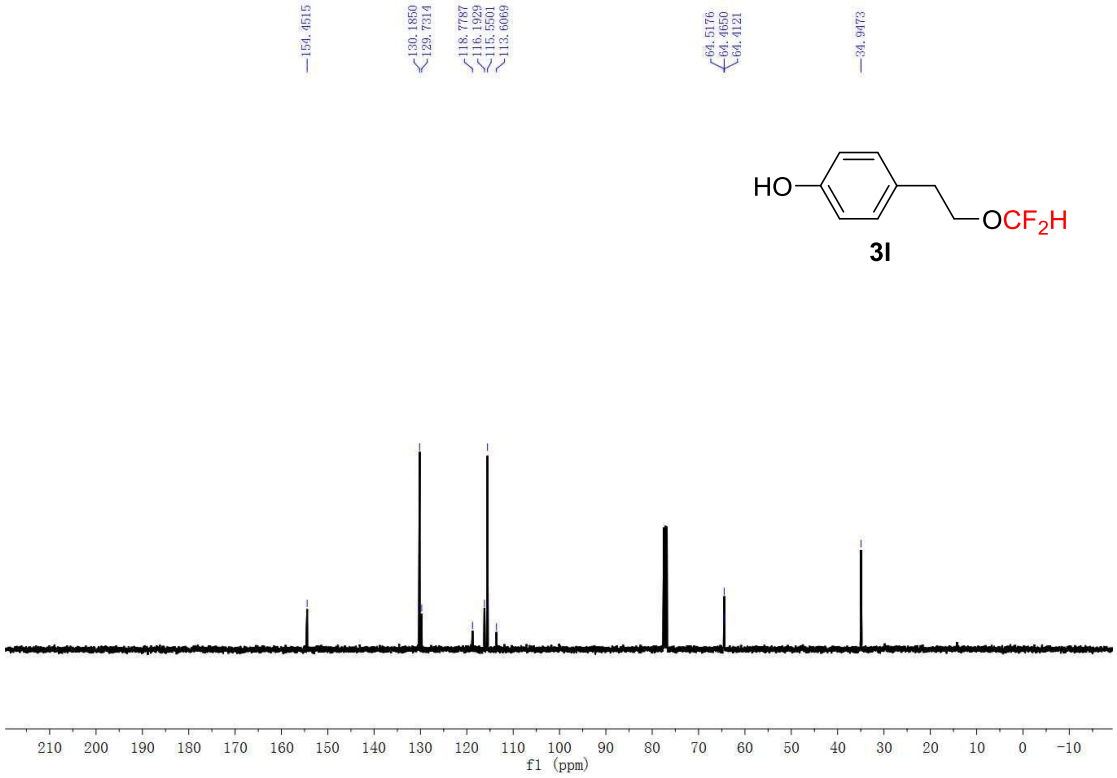
^{19}F-NMR Spectrum of 3k



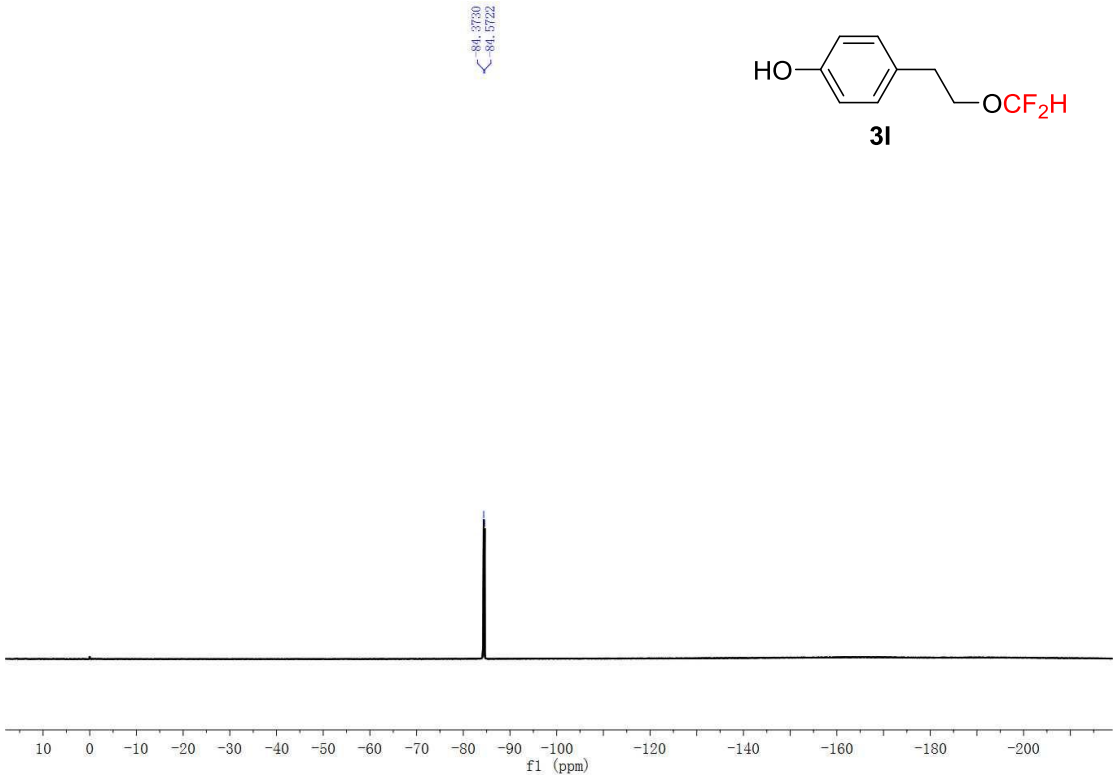
^{1}H-NMR Spectrum of 3l



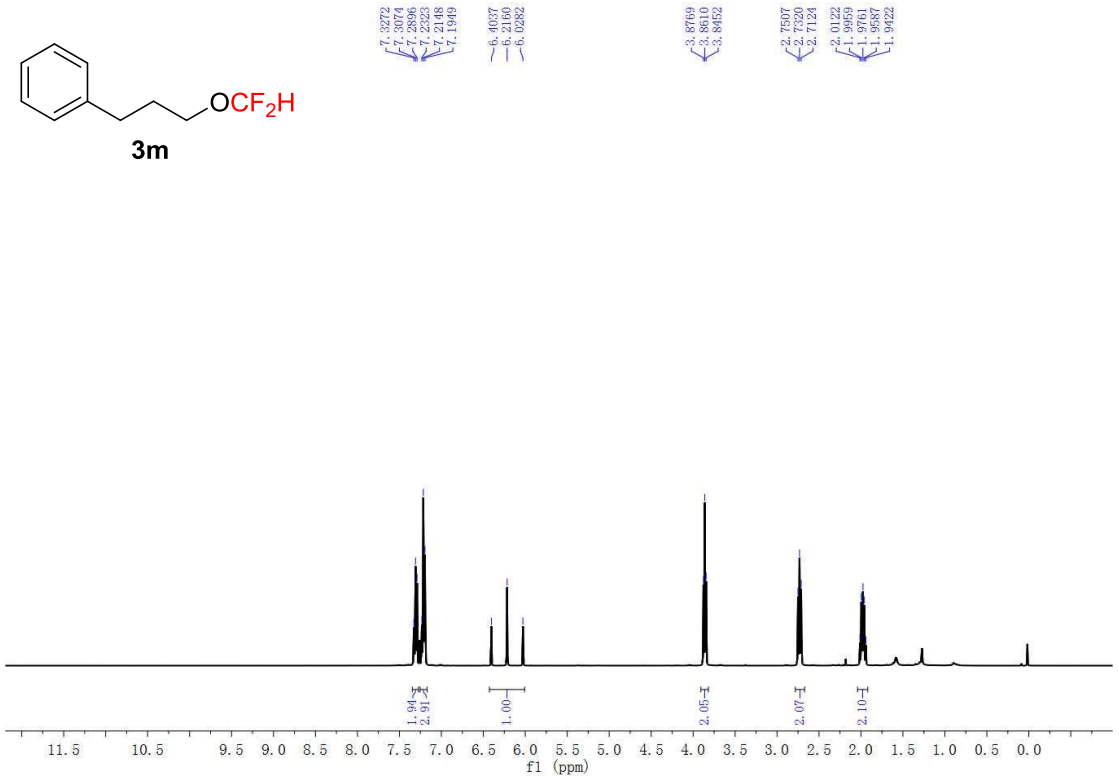
^{13}C-NMR Spectrum of 3l



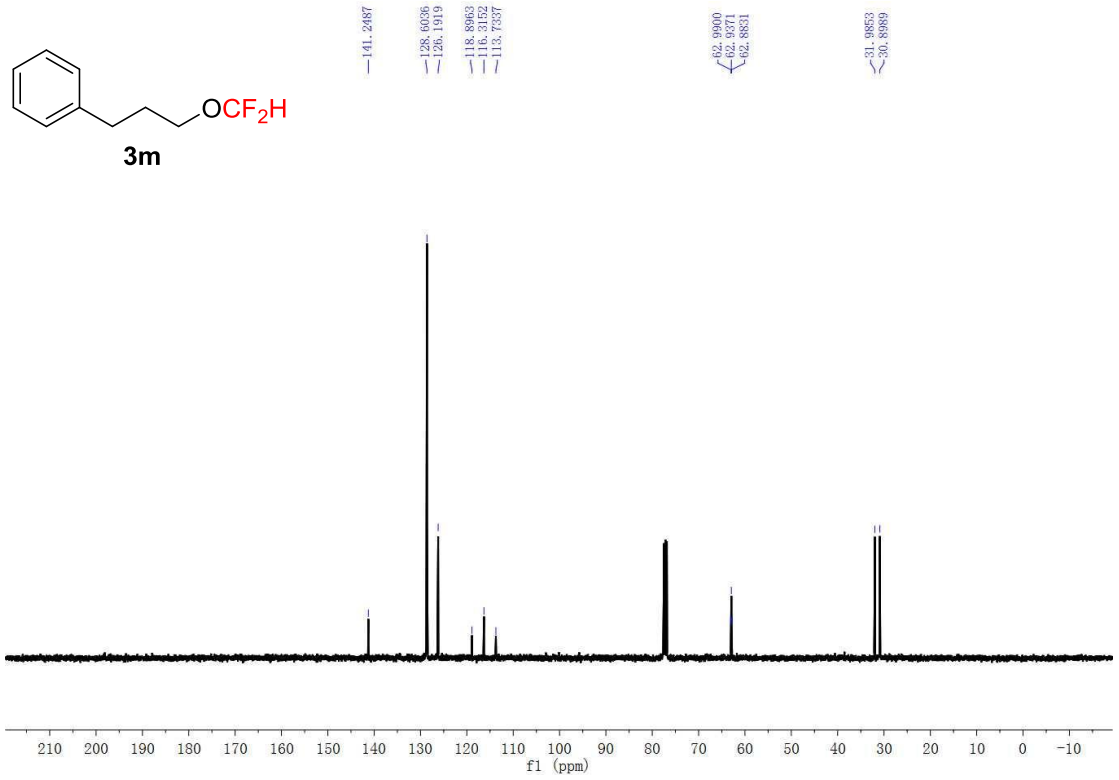
^{19}F-NMR Spectrum of 3l



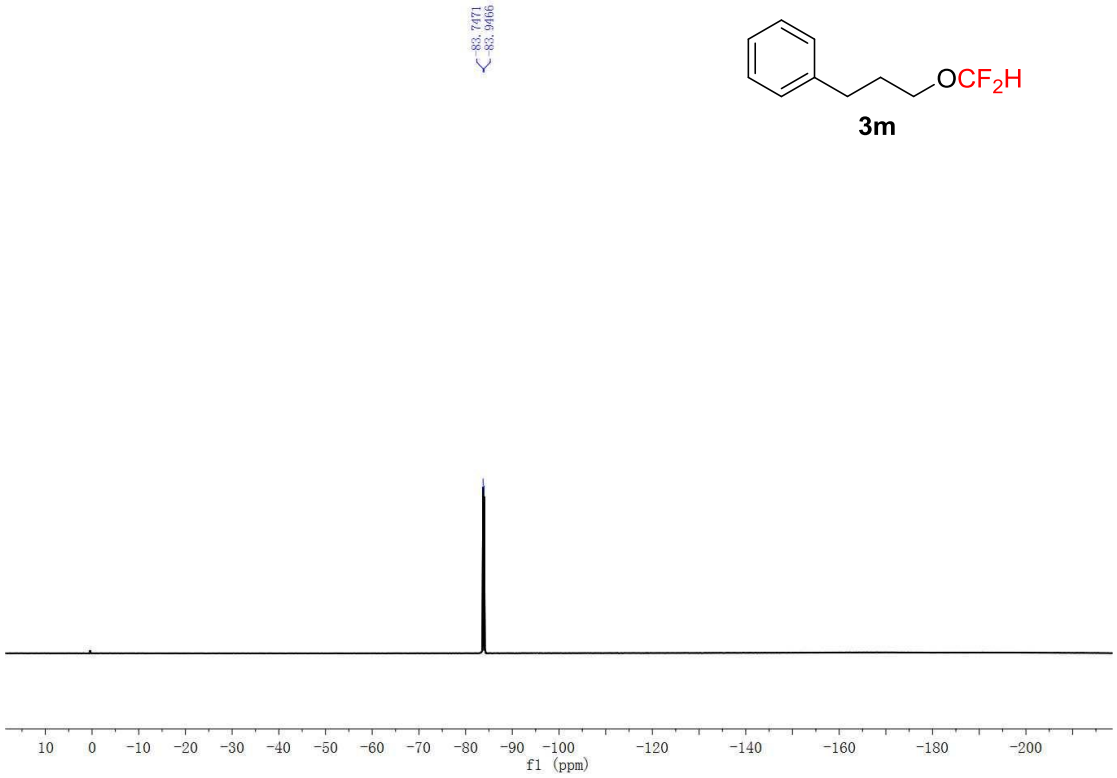
[1]H-NMR Spectrum of 3m



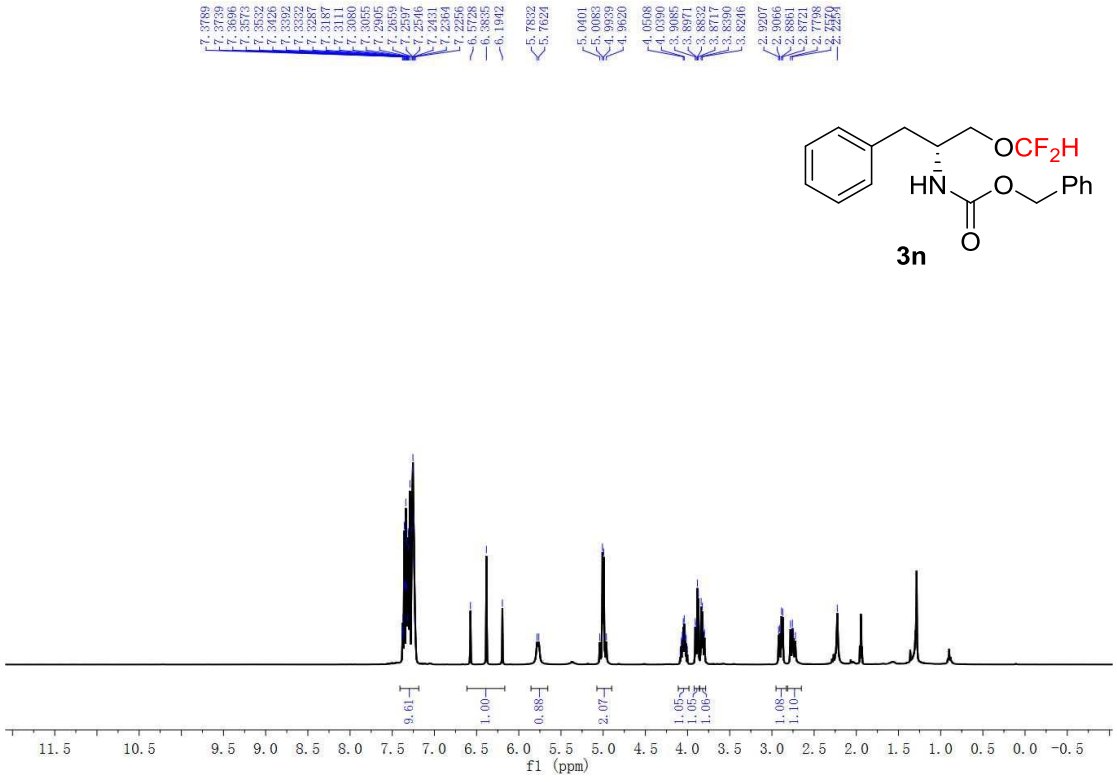
[13]C-NMR Spectrum of 3m



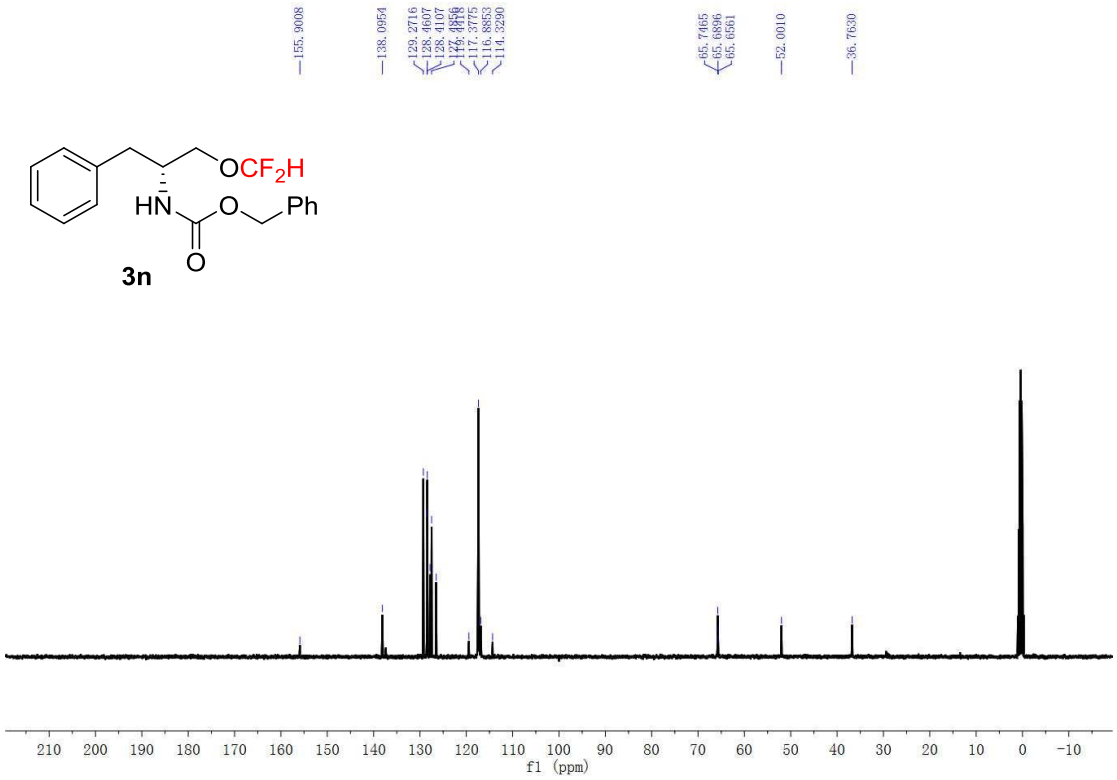
^{19}F-NMR Spectrum of 3m



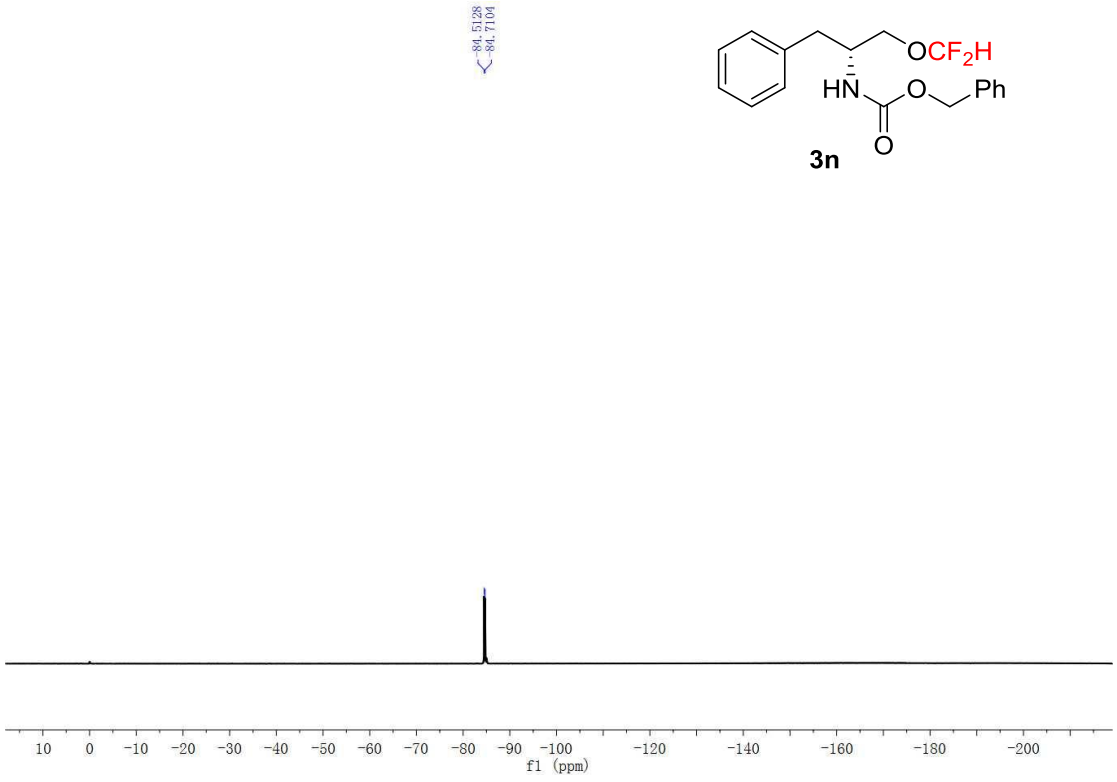
^{1}H-NMR Spectrum of 3n



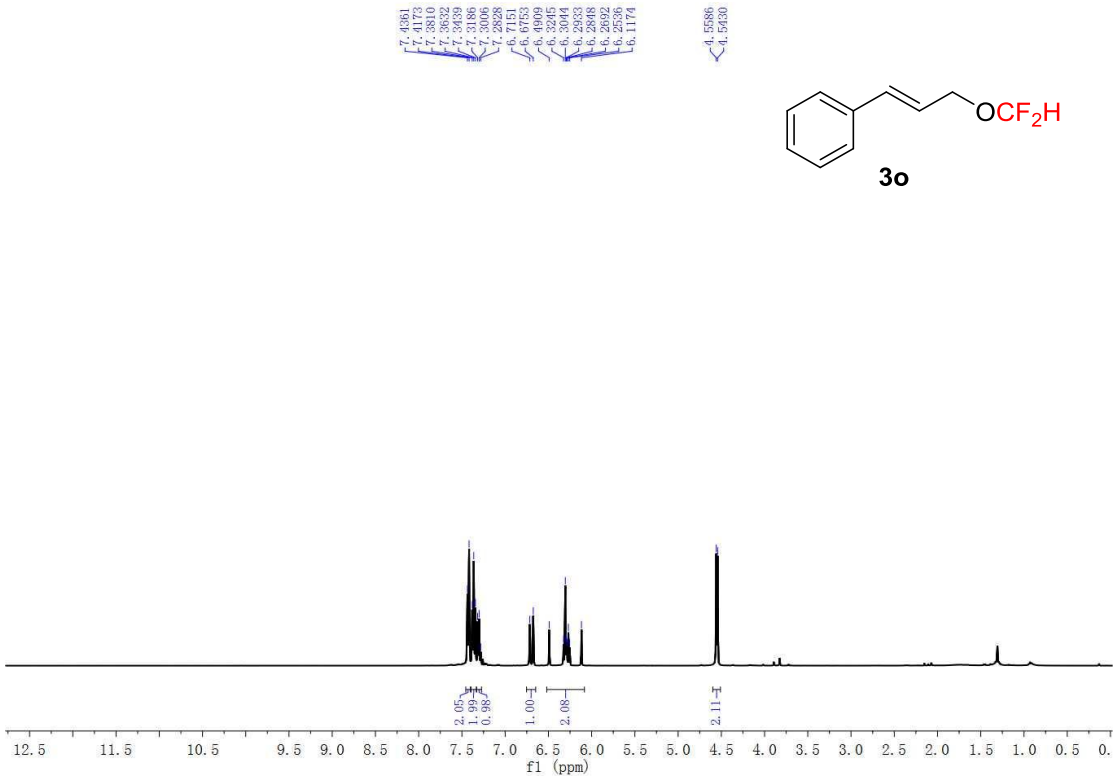
^{13}C-NMR Spectrum of 3n



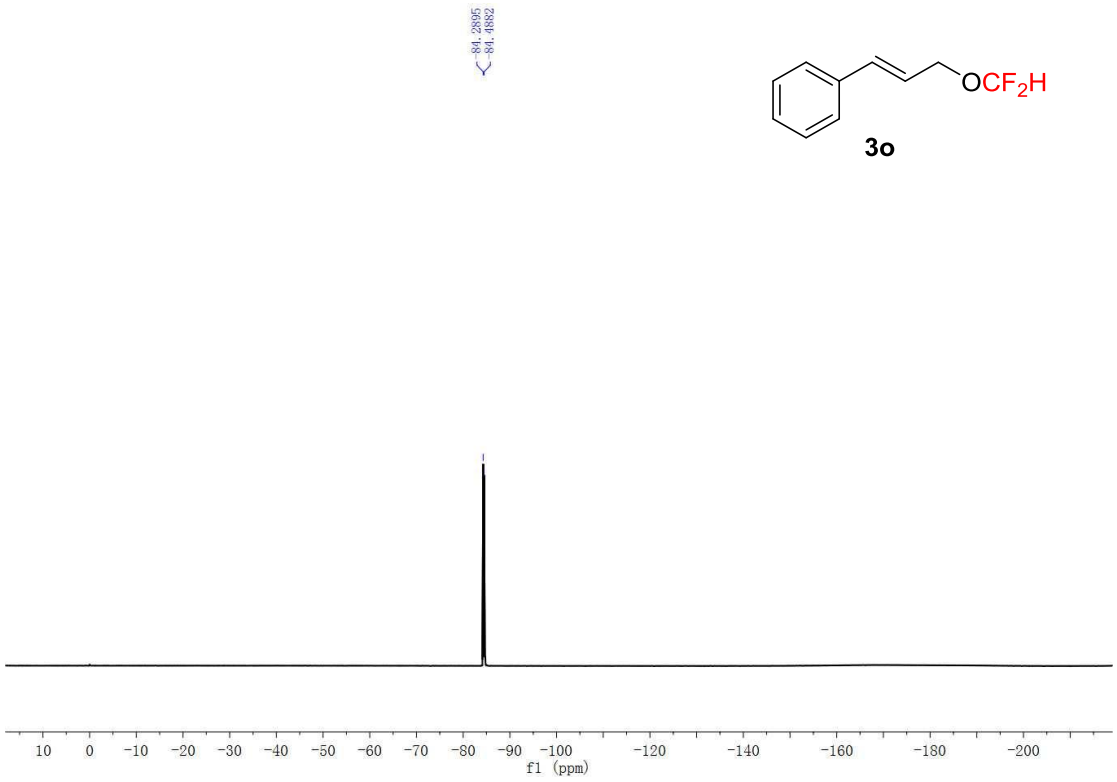
^{19}F-NMR Spectrum of 3n



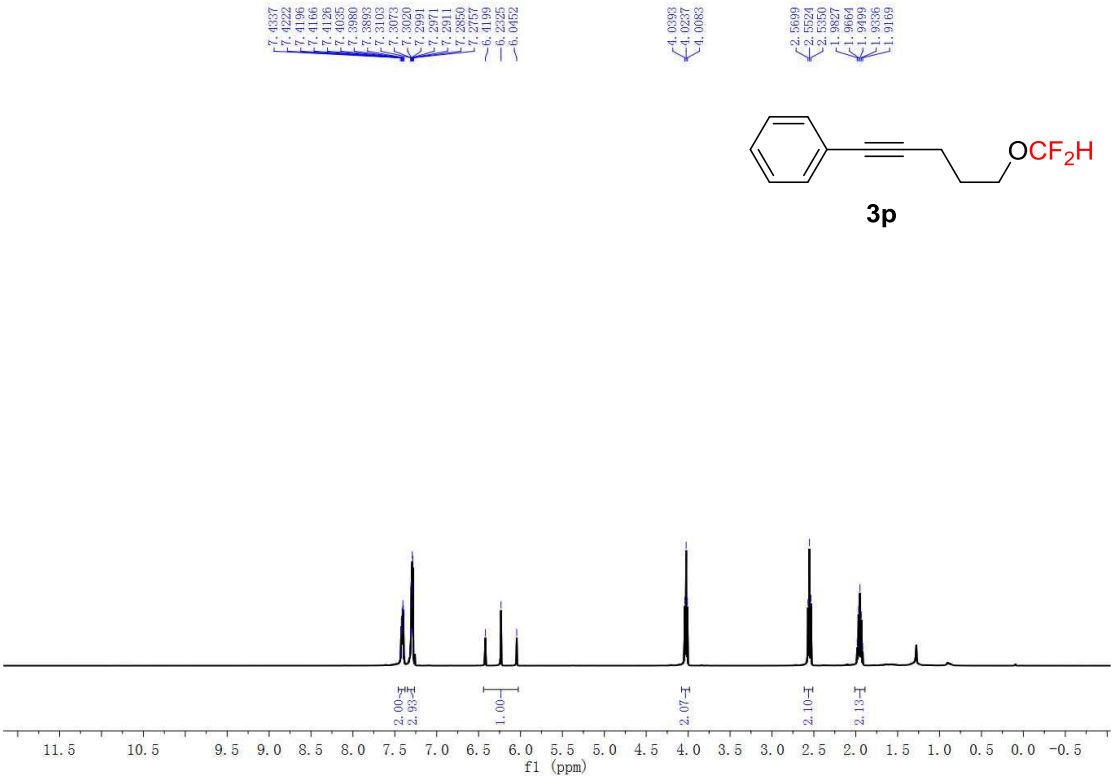
^{1}H-NMR Spectrum of 3o



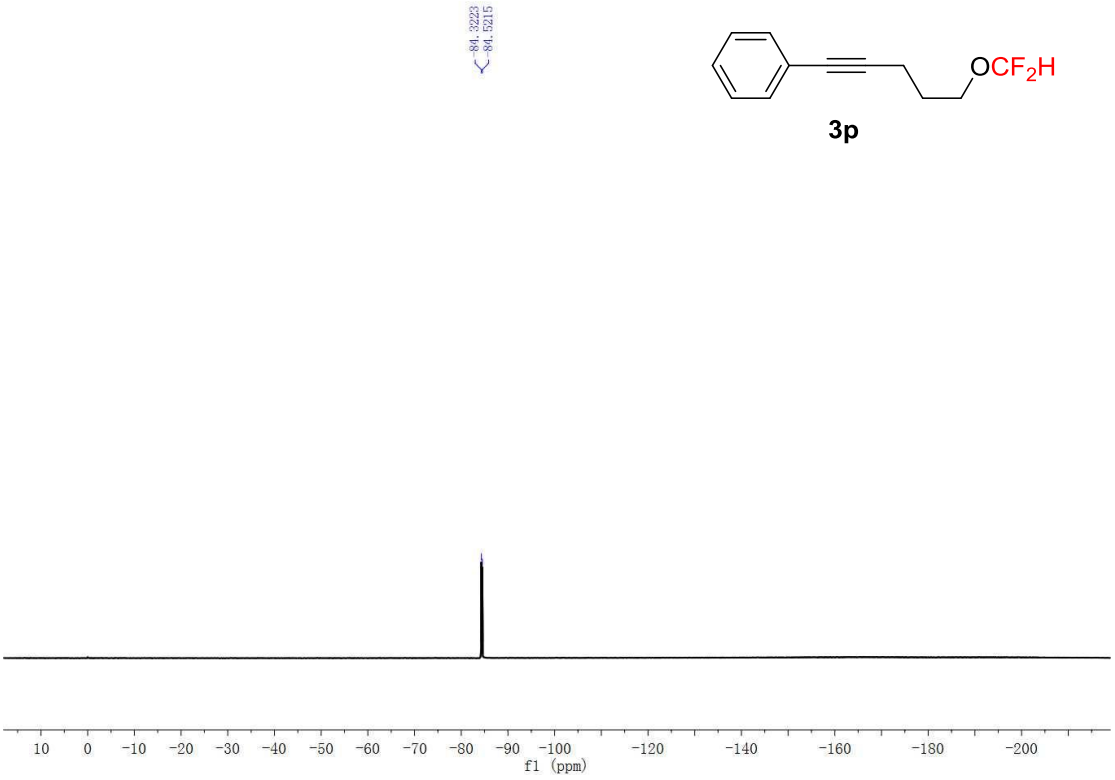
^{19}F-NMR Spectrum of 3o



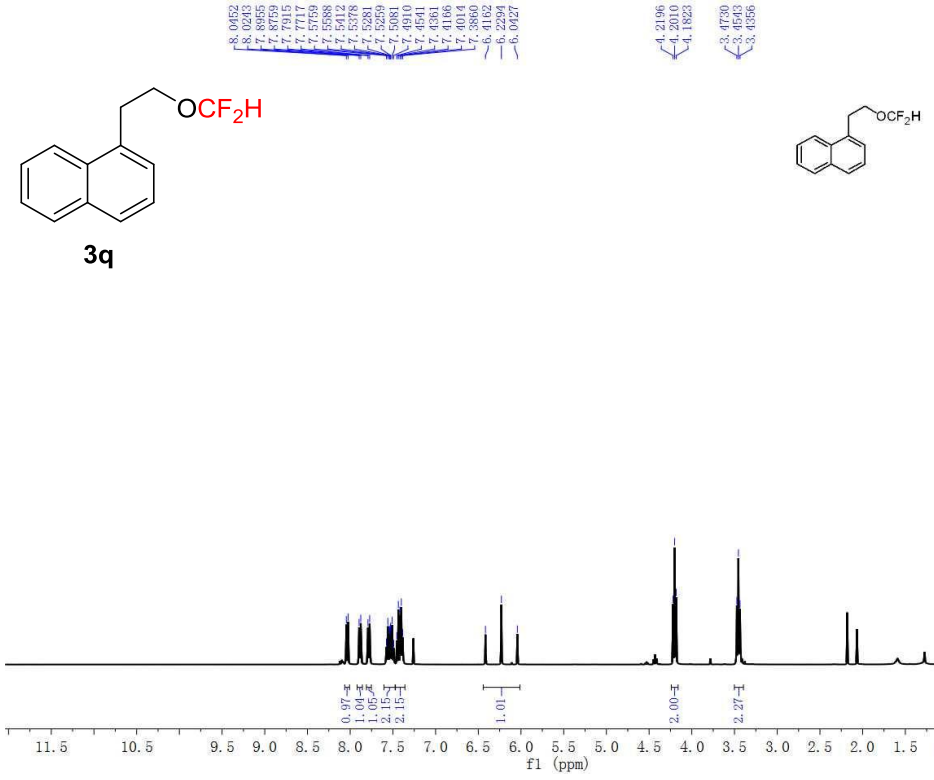
[1]H-NMR Spectrum of 3p



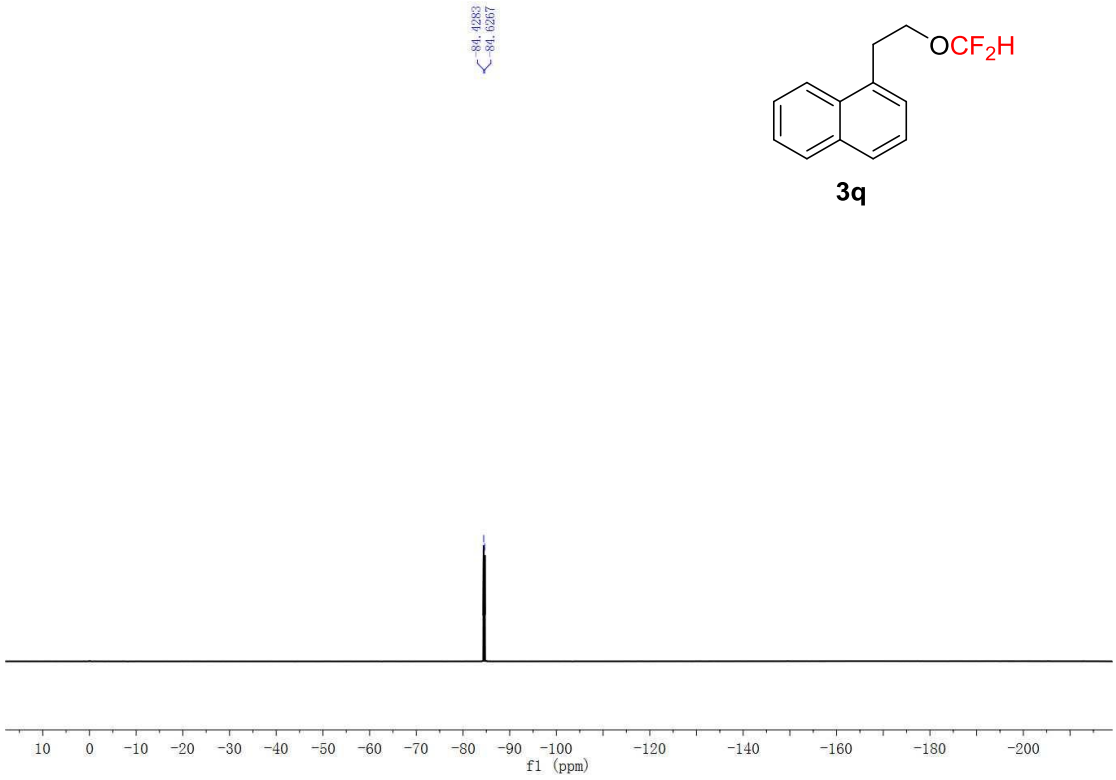
[19]F-NMR Spectrum of 3p



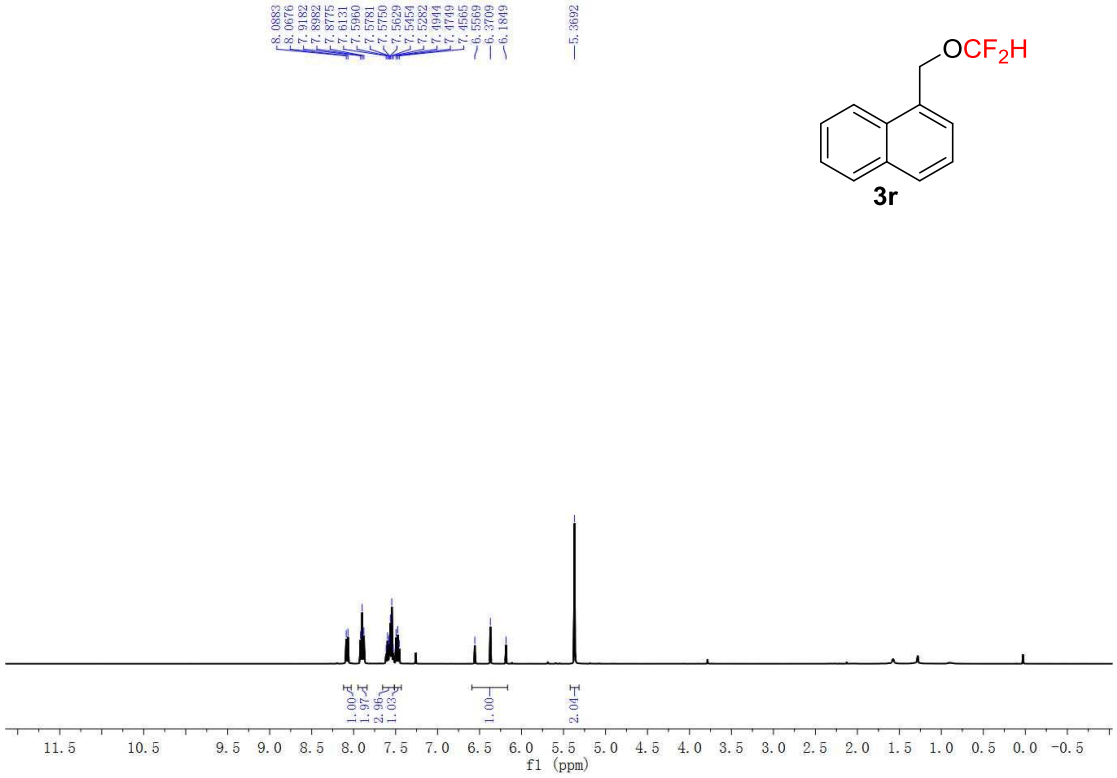
^{1}H-NMR Spectrum of 3q



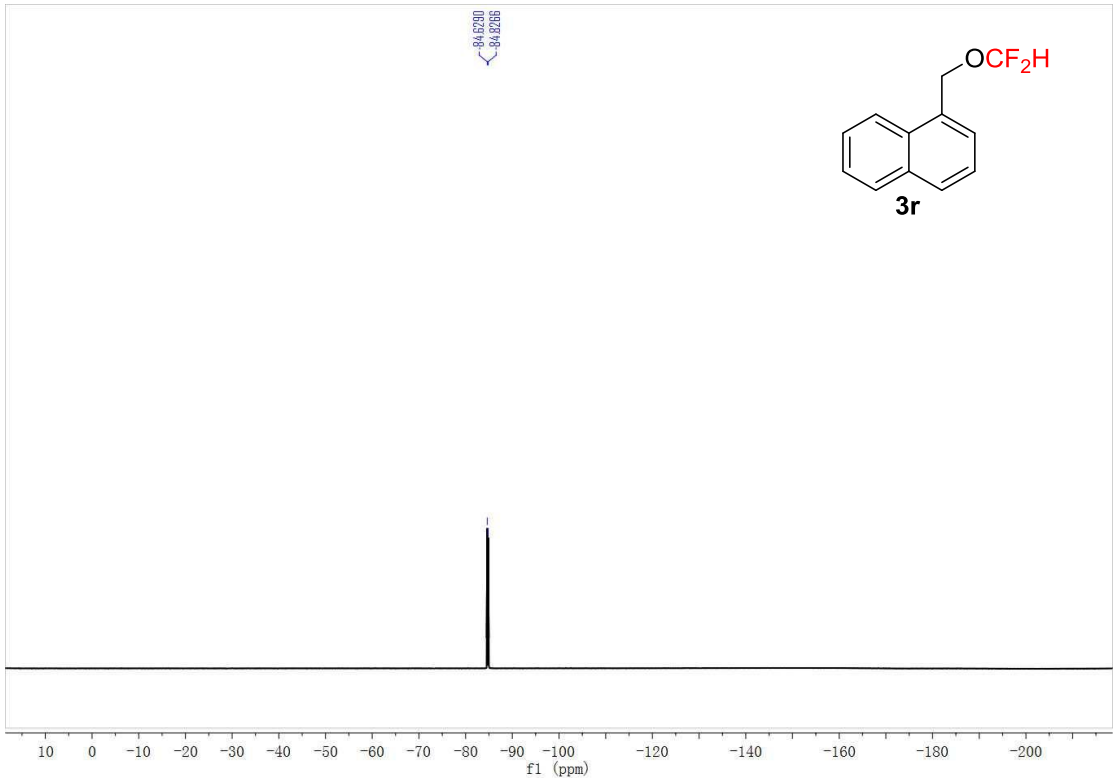
^{19}F-NMR Spectrum of 3q



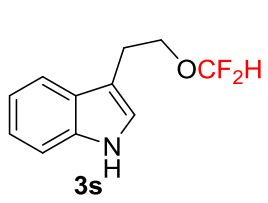
^{1}H-NMR Spectrum of 3r



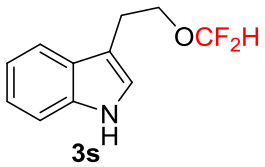
^{19}F-NMR Spectrum of 3r

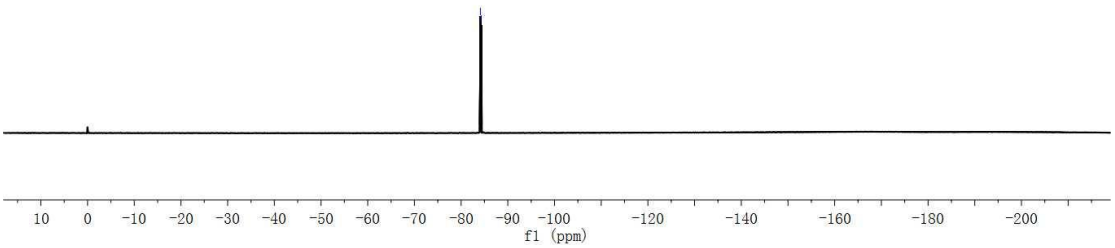


[1]H-NMR Spectrum of 3s

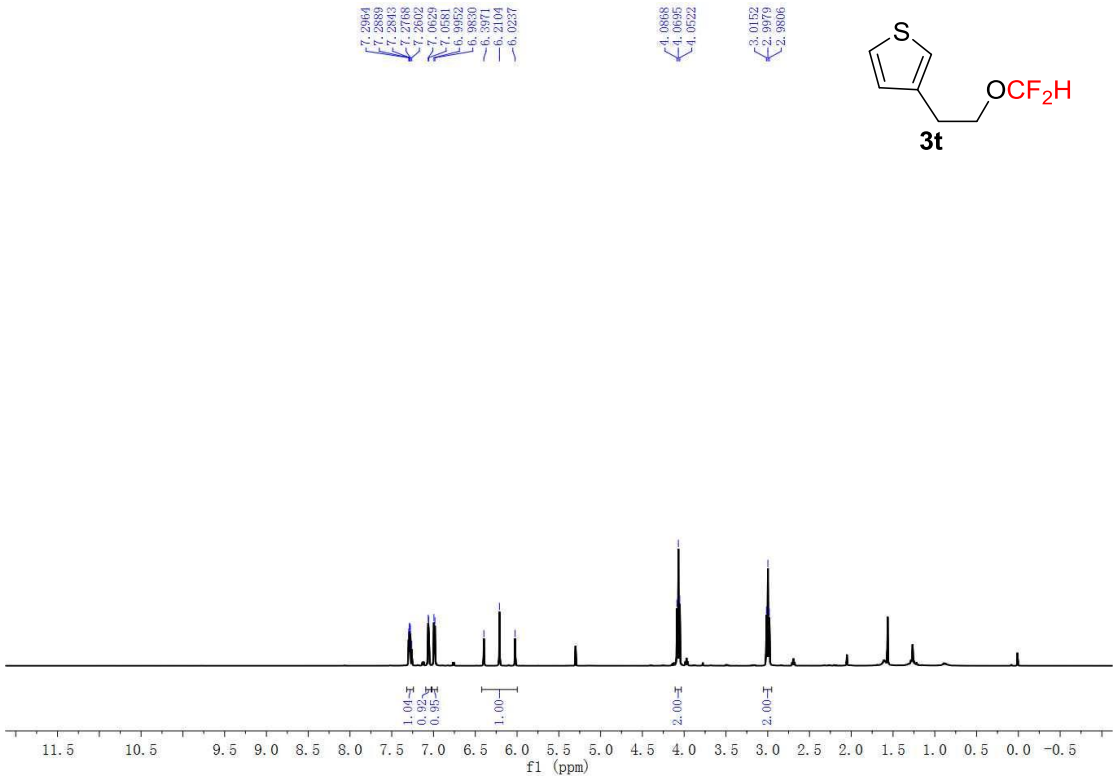


[19]F-NMR Spectrum of 3s

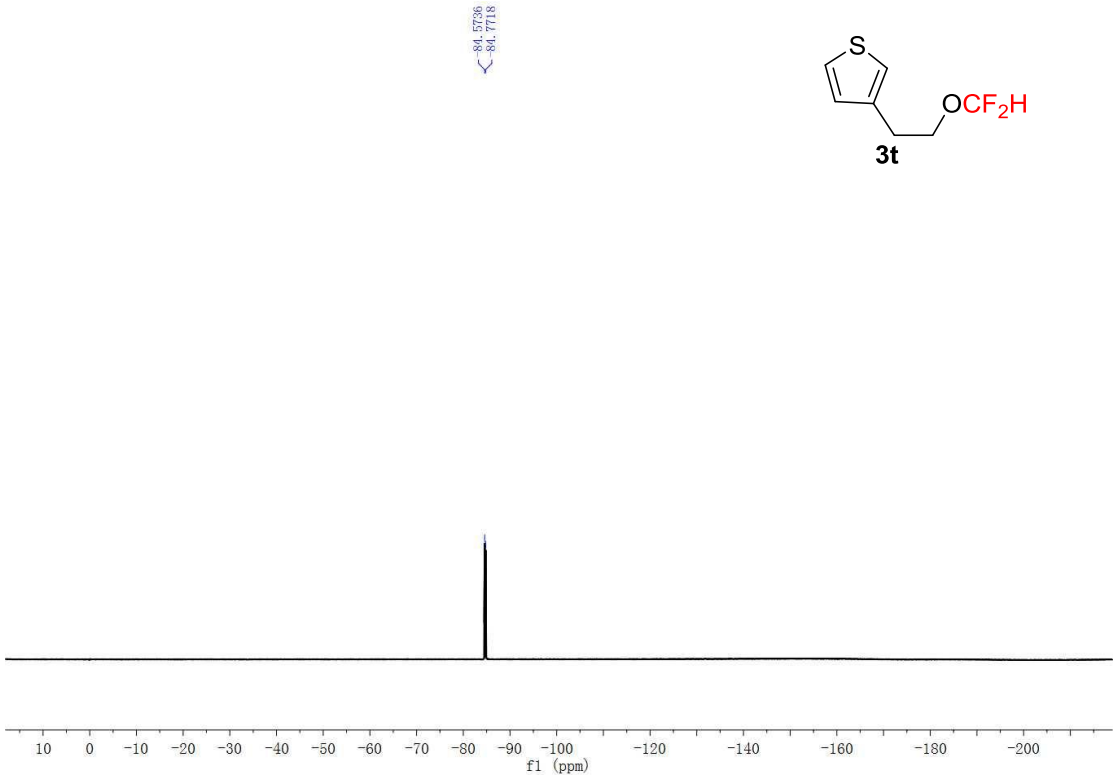




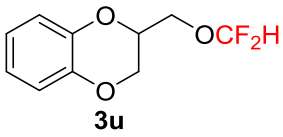
[1]H-NMR Spectrum of 3t



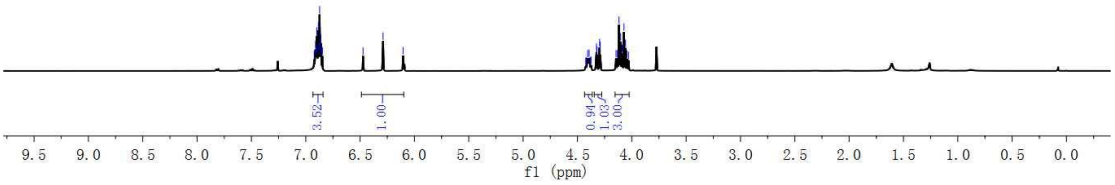
[19]F-NMR Spectrum of 3t



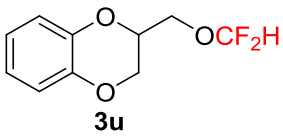
[1]H-NMR Spectrum of 3u



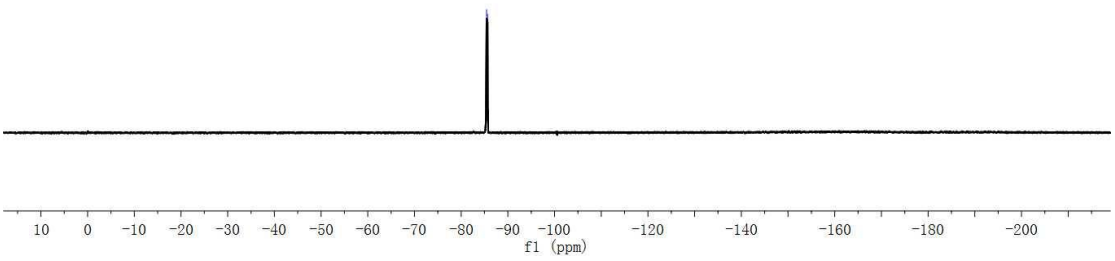
3u



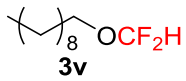
[19]F-NMR Spectrum of 3u



3u

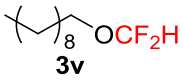


^{1}H-NMR Spectrum of 3v

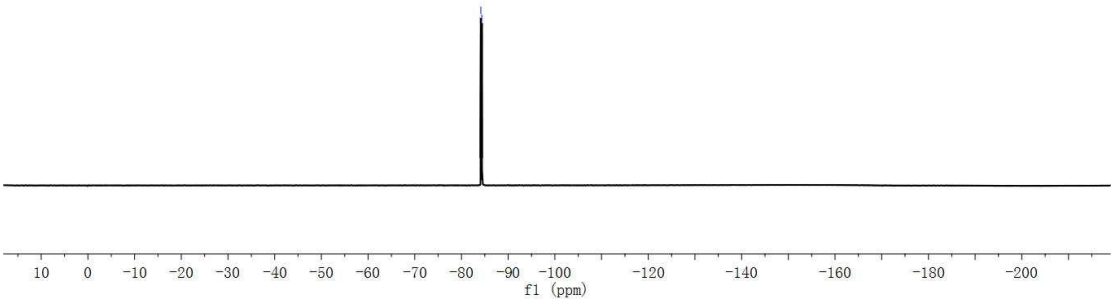


3v

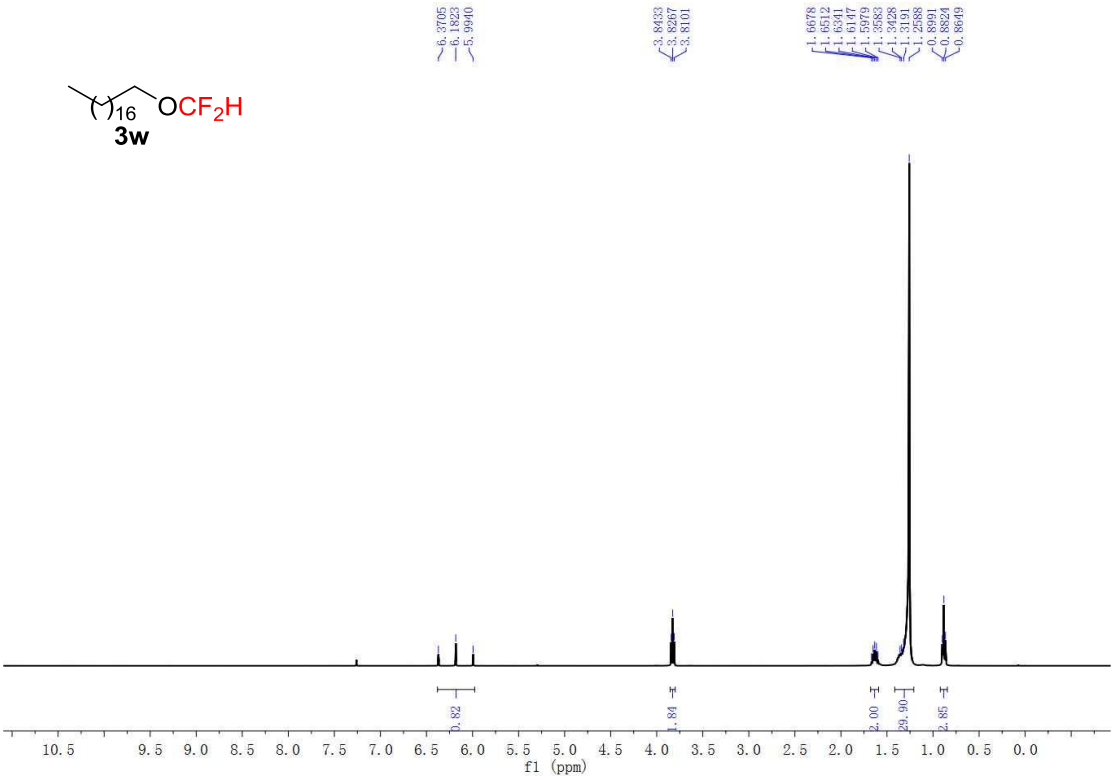
^{19}F-NMR Spectrum of 3v



3v



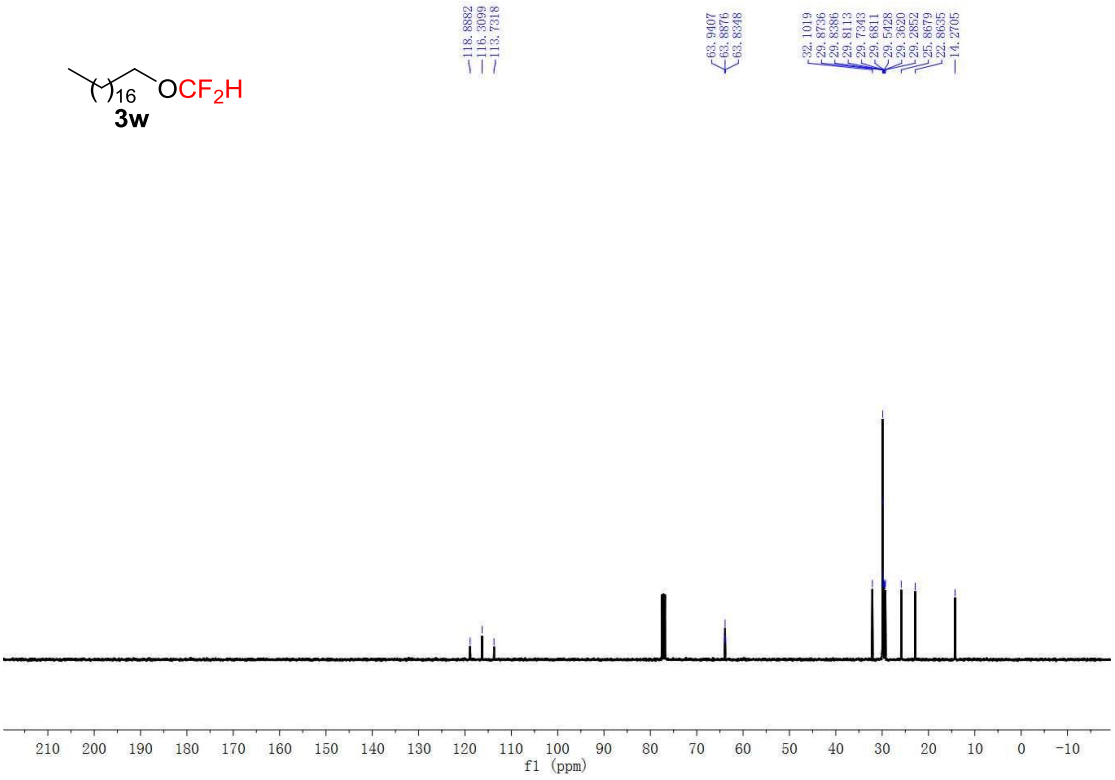
^{1}H-NMR Spectrum of 3w



16 OCF_2H

3w

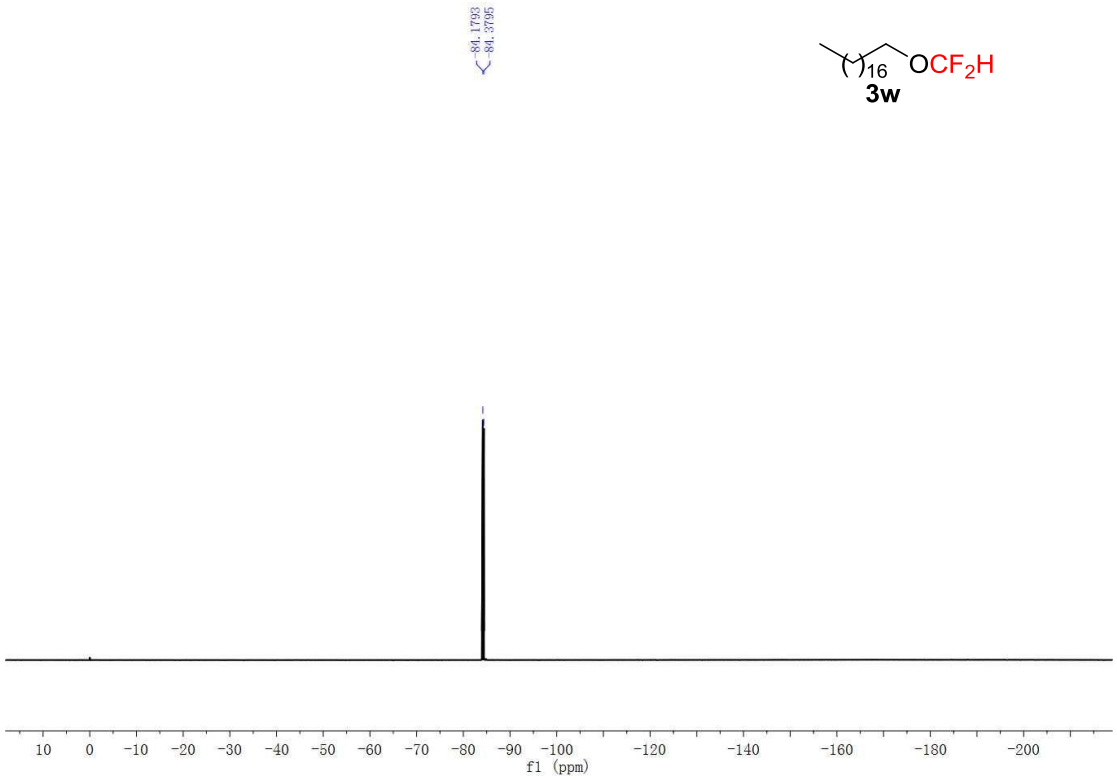
^{13}C-NMR Spectrum of 3w



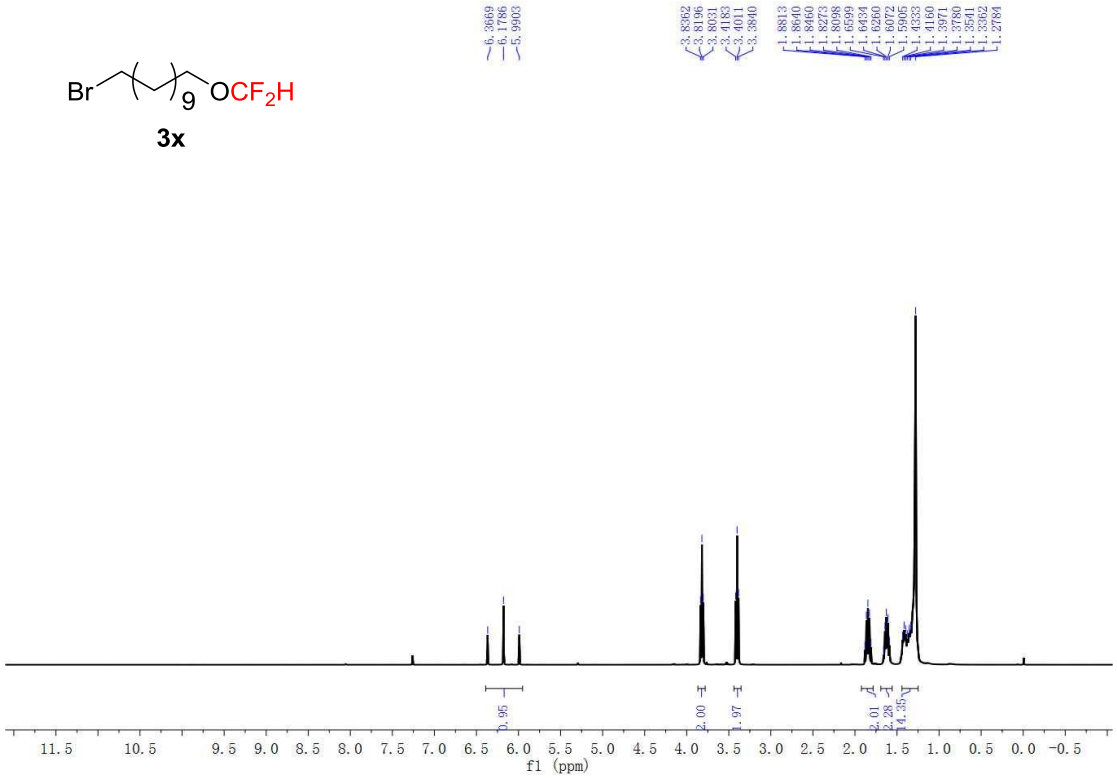
16 OCF_2H

3w

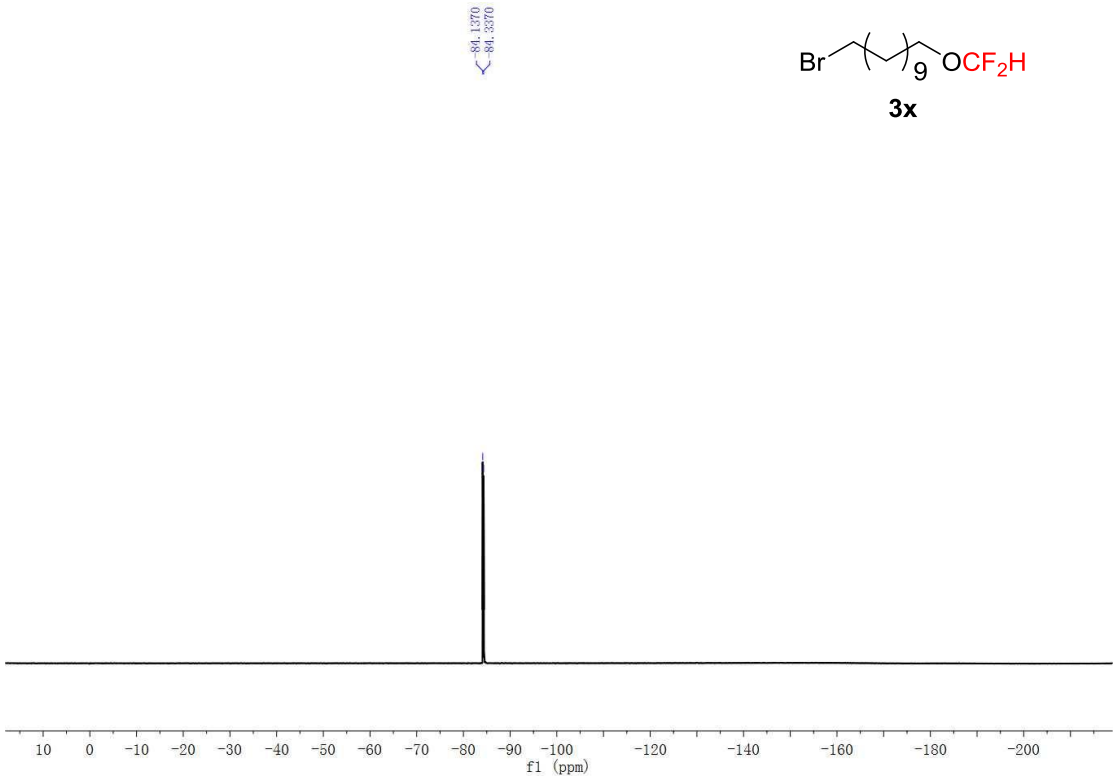
^{19}F-NMR Spectrum of 3w



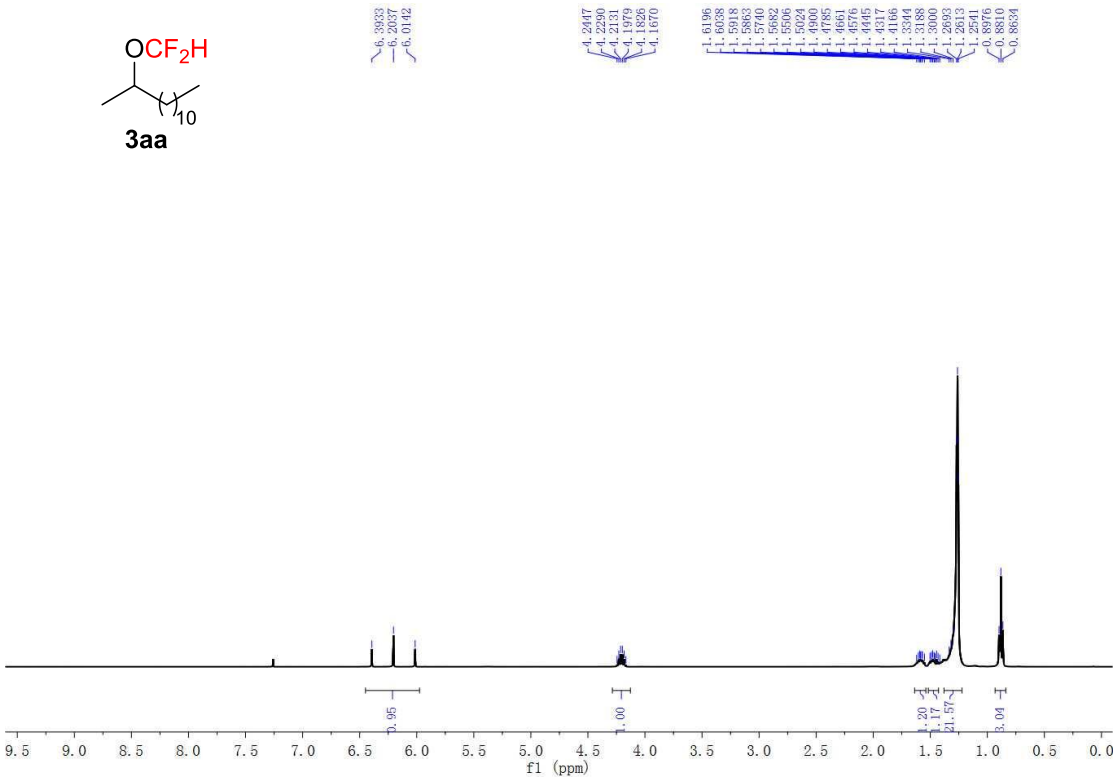
^{1}H-NMR Spectrum of 3x



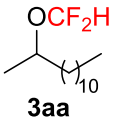
^{19}F-NMR Spectrum of 3x



^{1}H-NMR Spectrum of 3aa

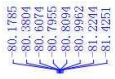


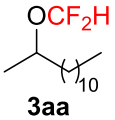
^{13}C-NMR Spectrum of 3aa



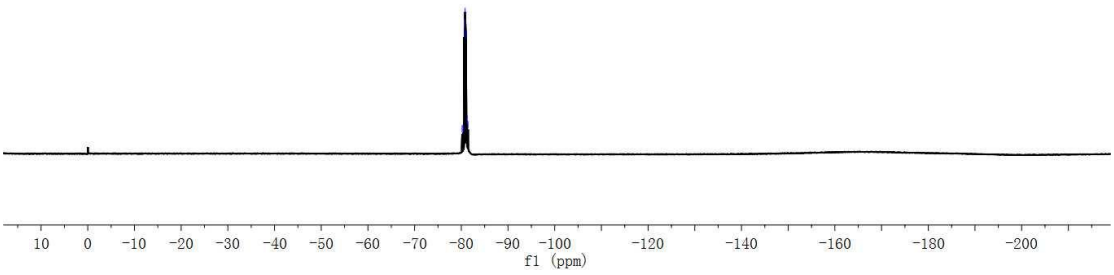
3aa

^{19}F-NMR Spectrum of 3aa

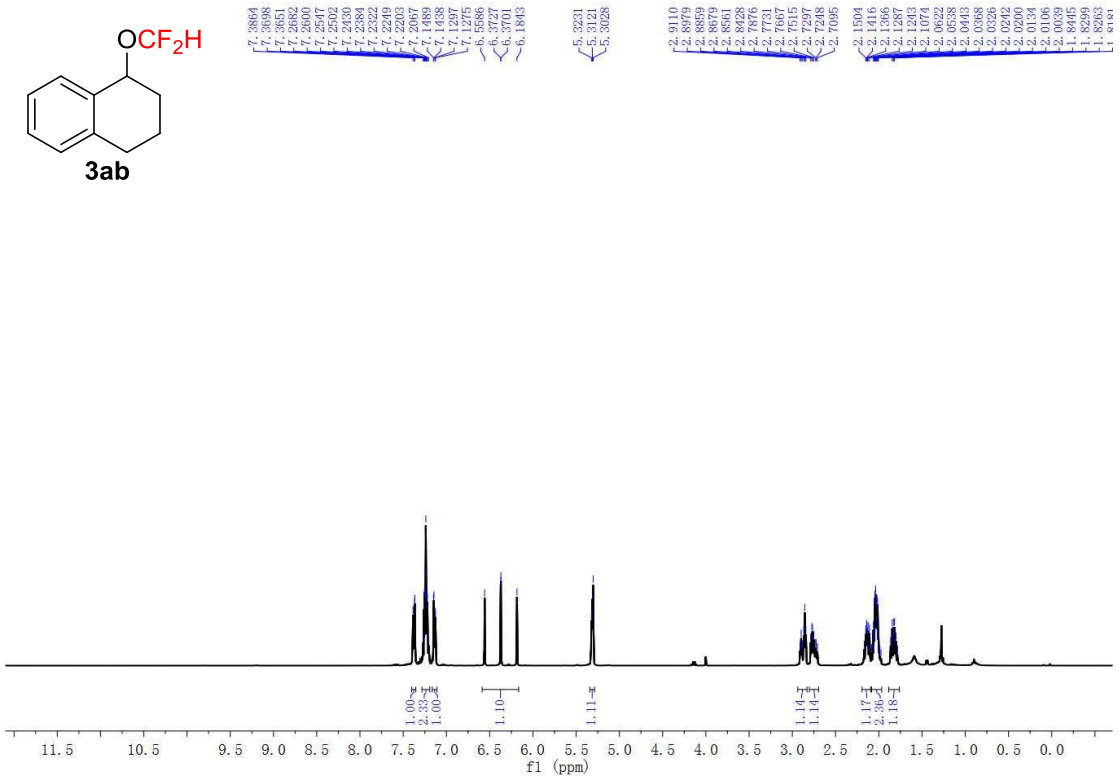




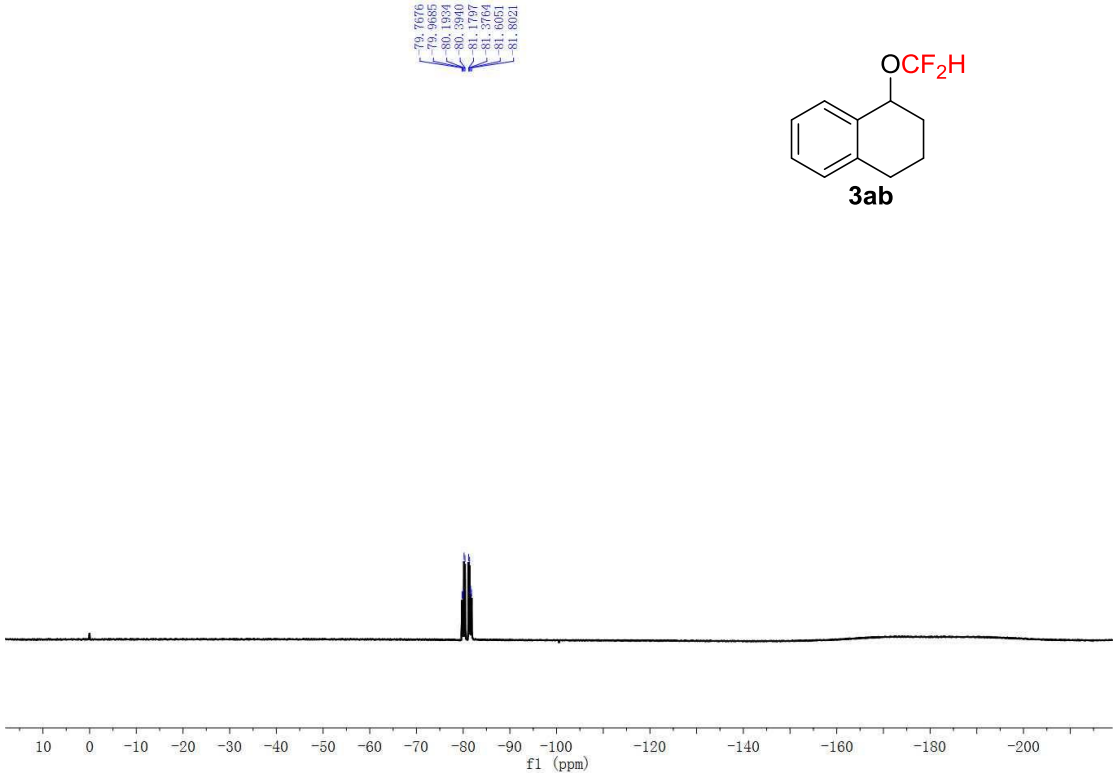
3aa



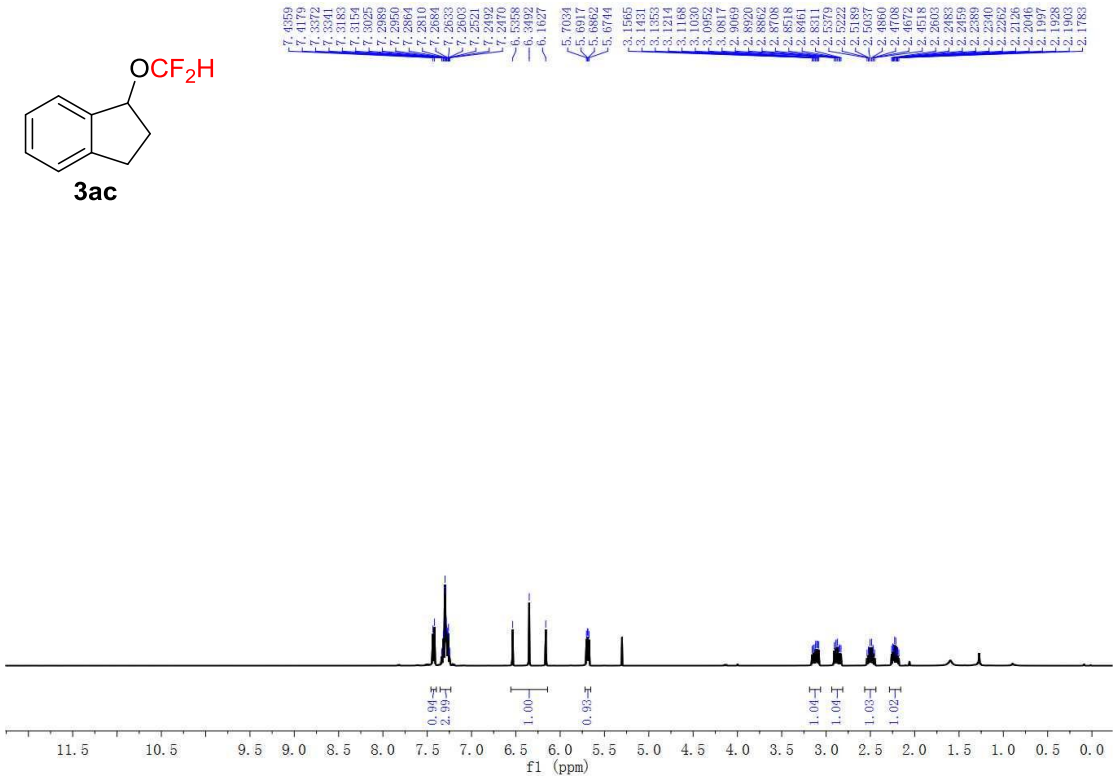
^{1}H-NMR Spectrum of 3ab



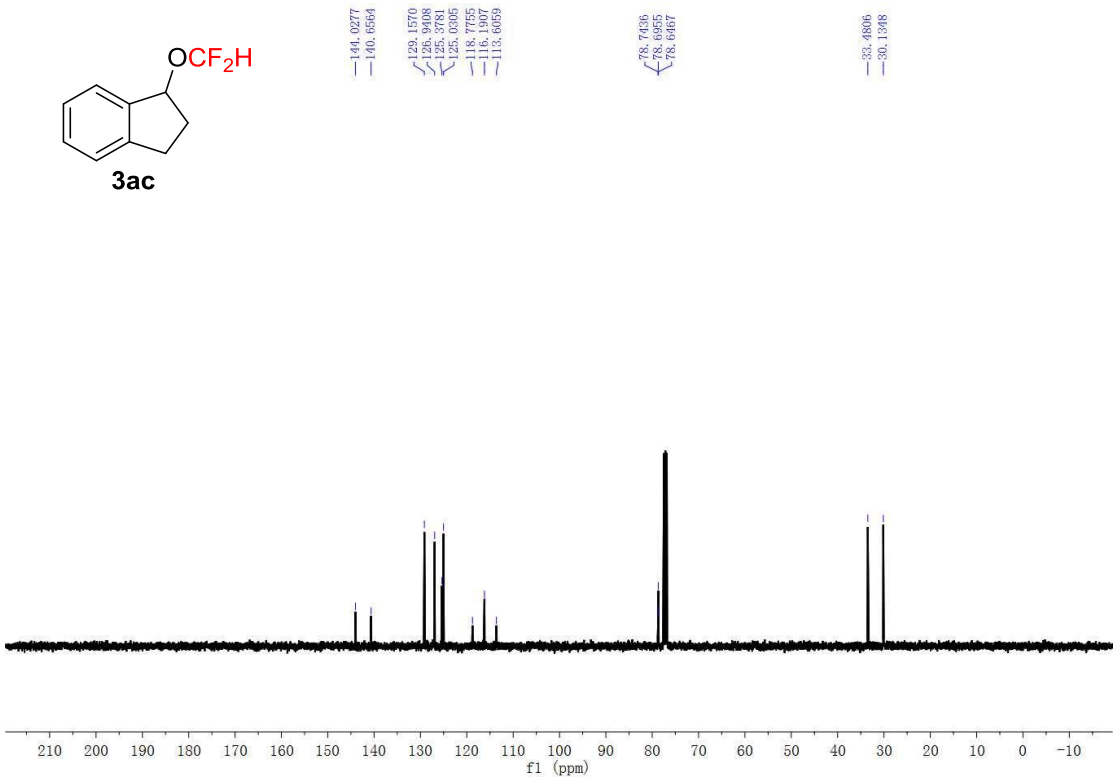
^{19}F-NMR Spectrum of 3ab



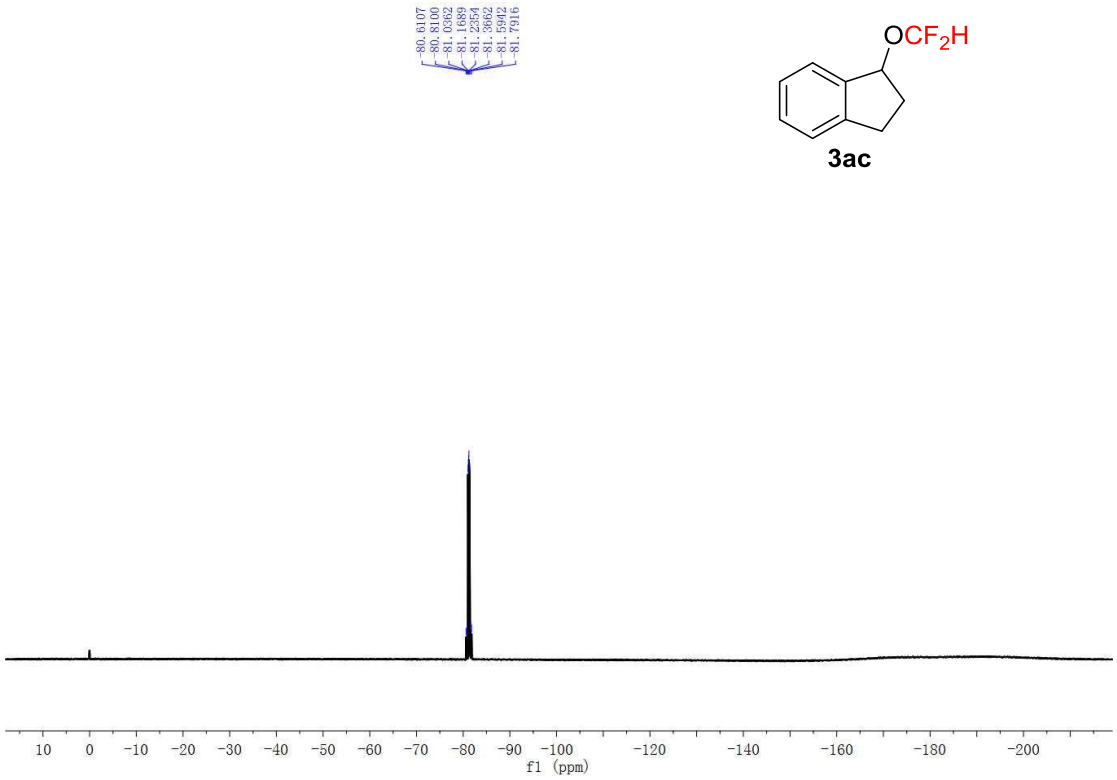
^{1}H-NMR Spectrum of 3ac



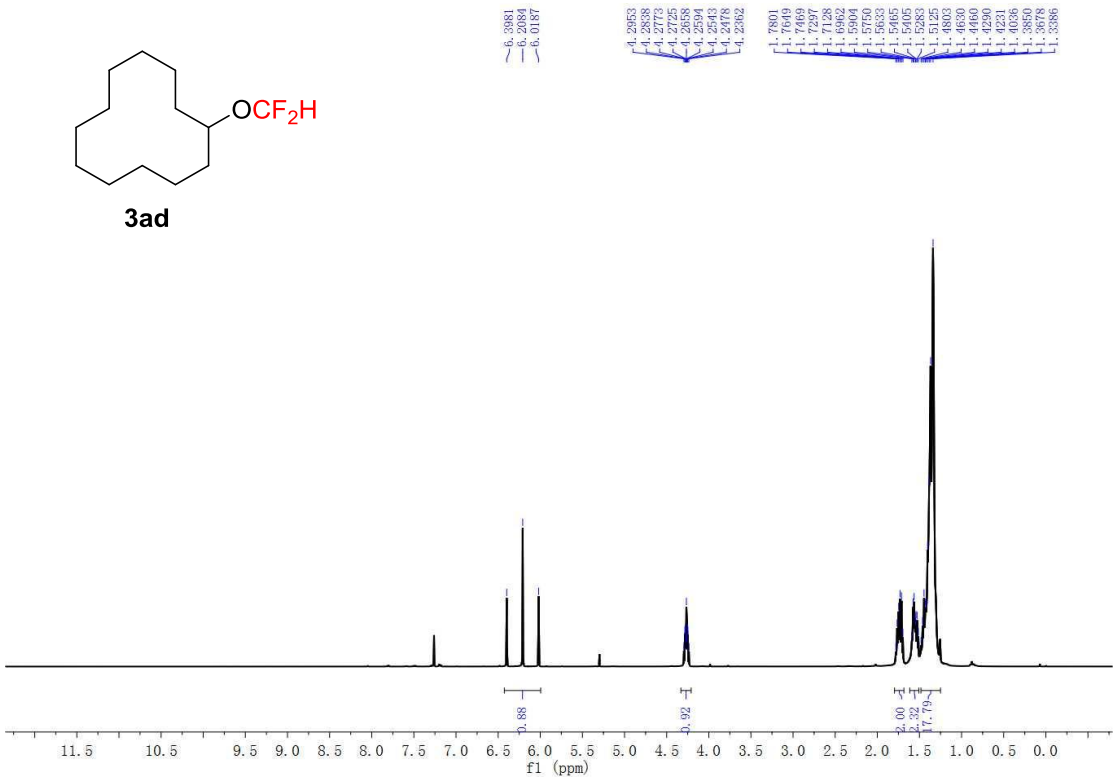
^{13}C-NMR Spectrum of 3ac



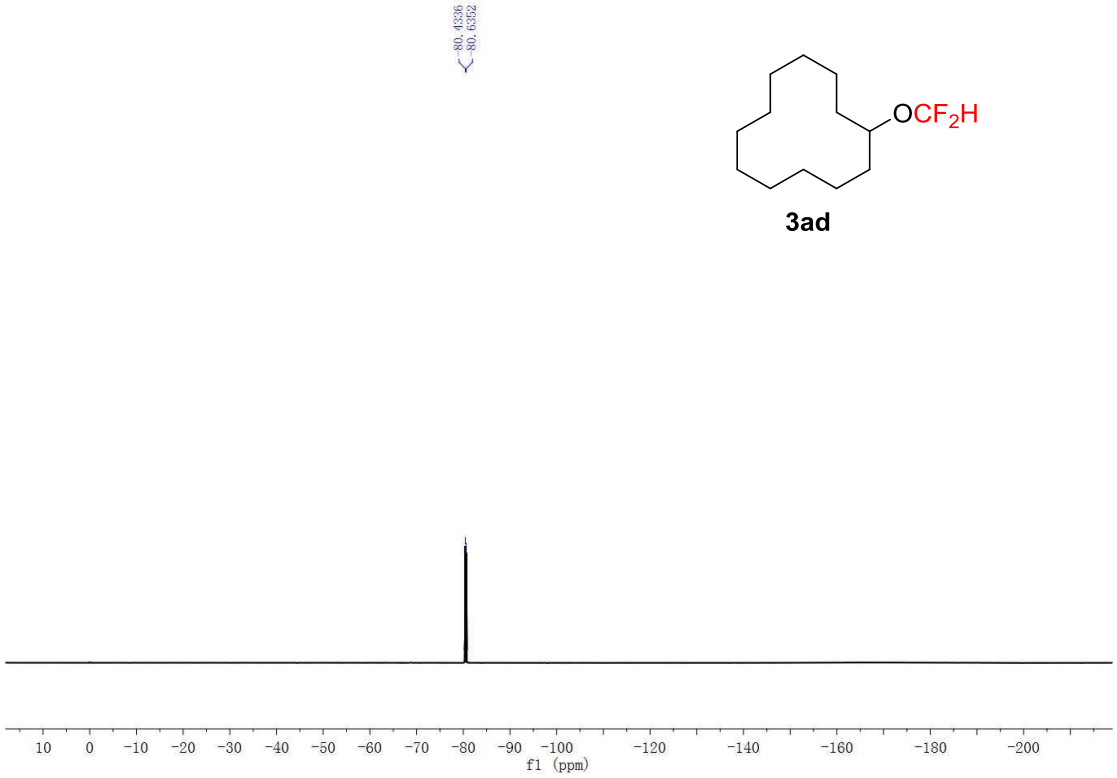
^{19}F-NMR Spectrum of 3ac



^{1}H-NMR Spectrum of 3ad

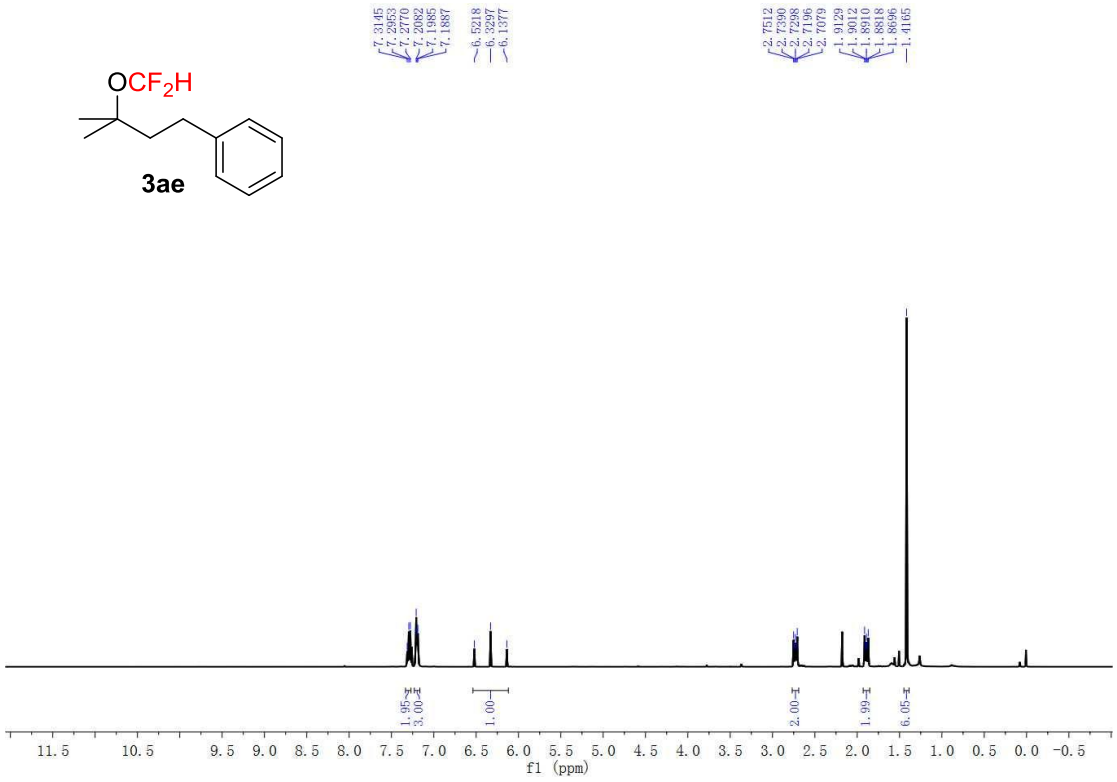


^{19}F-NMR Spectrum of 3ad



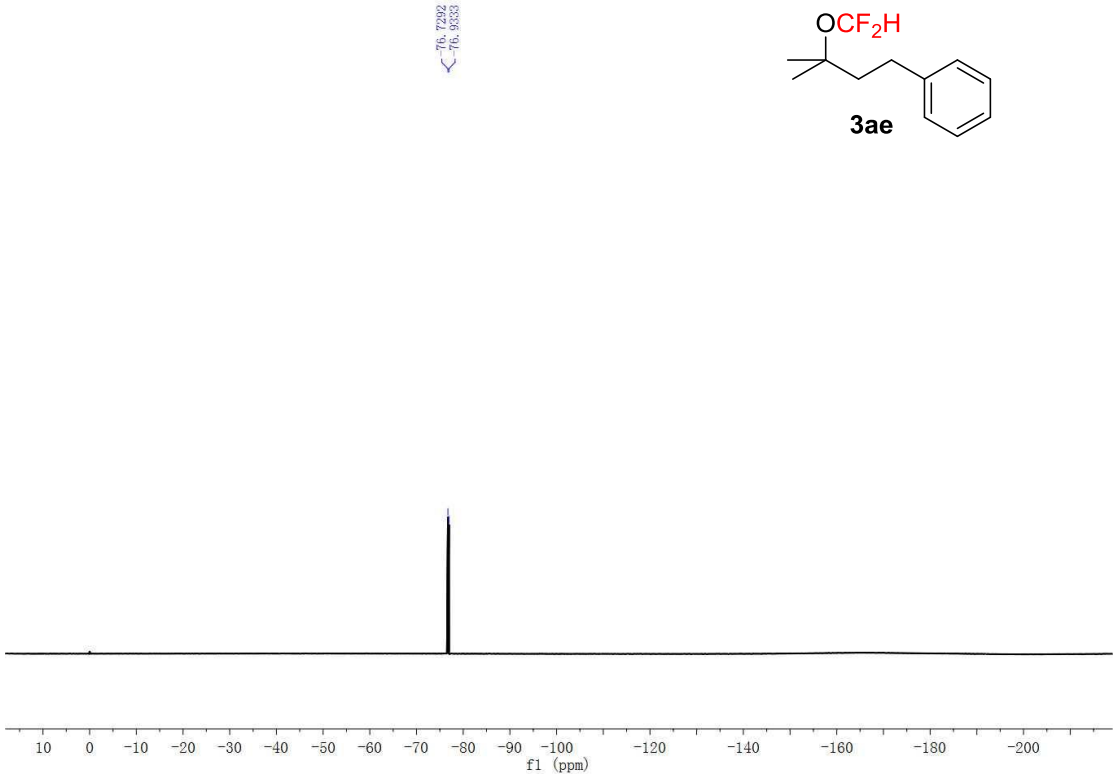
3ad

^{1}H-NMR Spectrum of 3ae

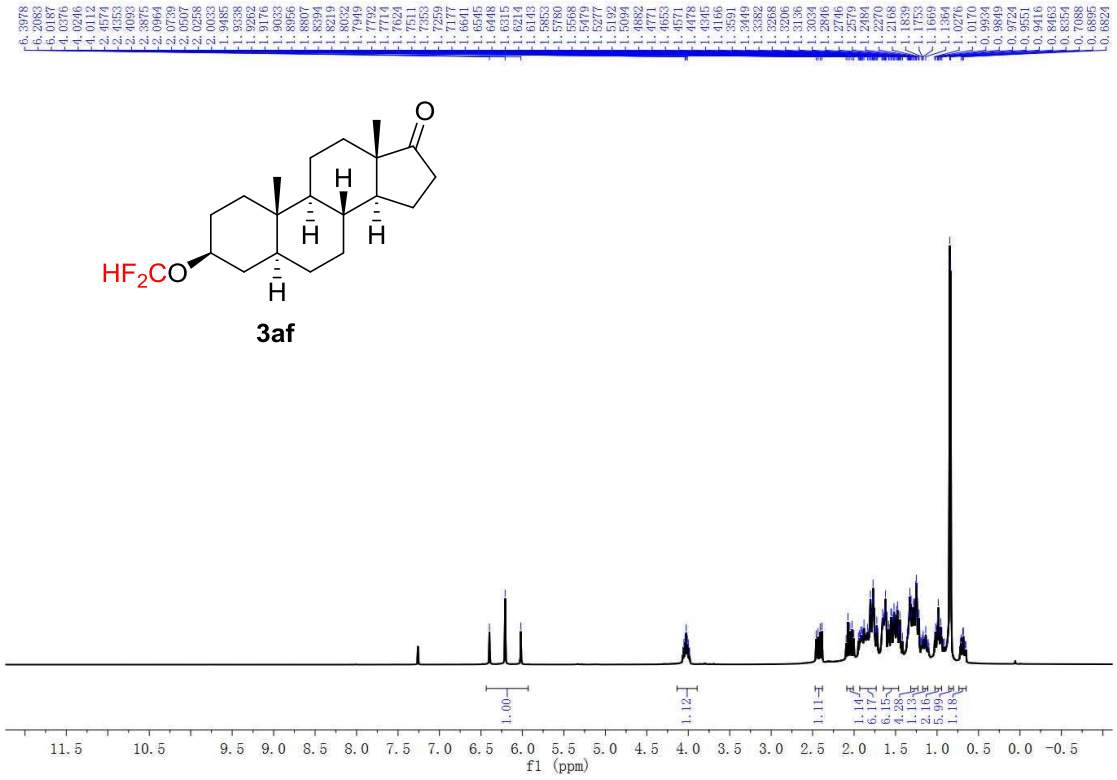


3ae

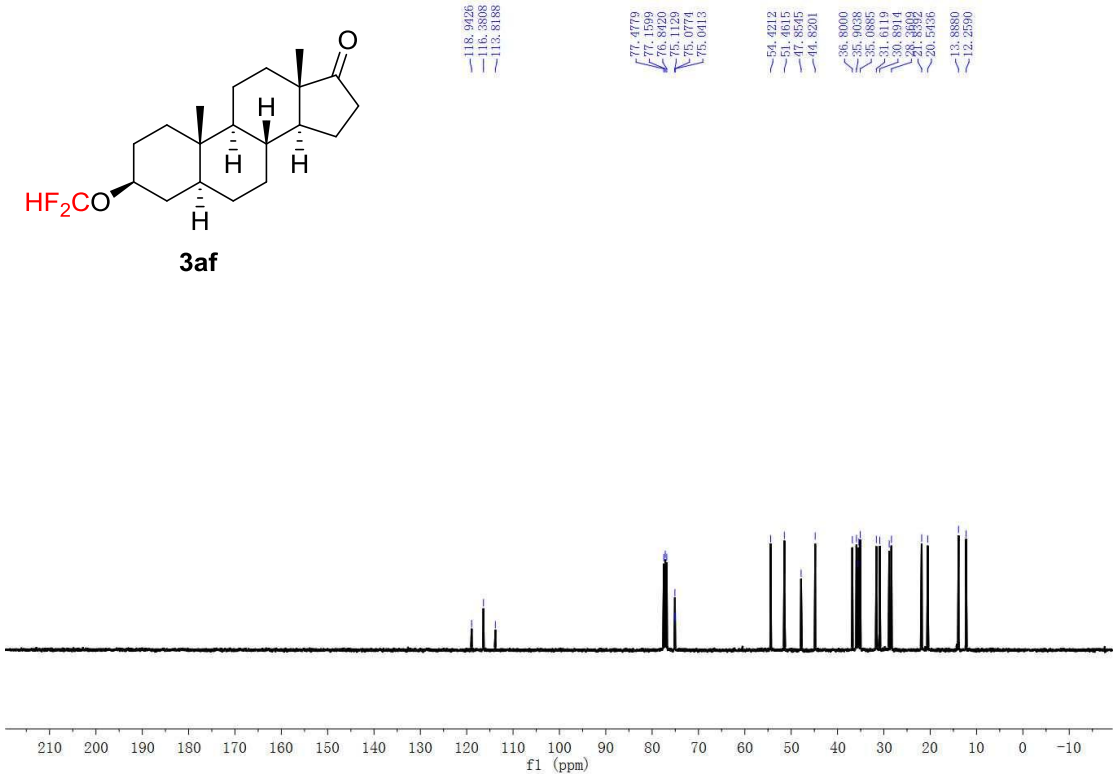
^{19}F-NMR Spectrum of 3ae



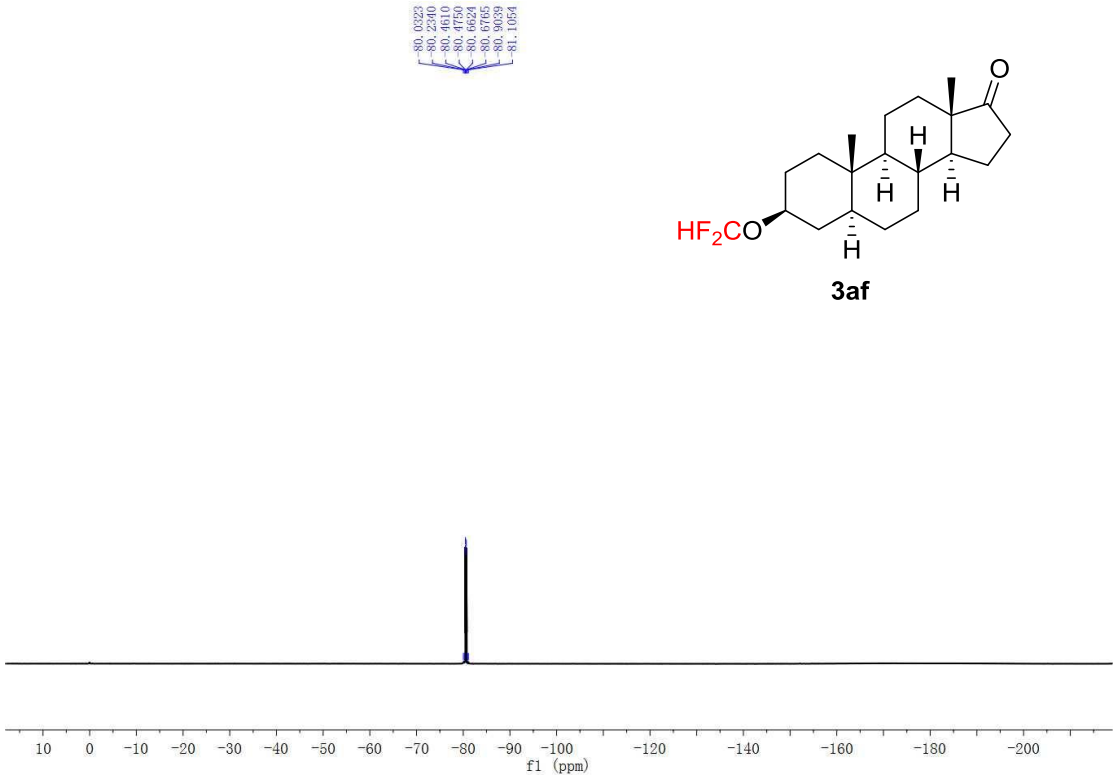
^{1}H-NMR Spectrum of 3af



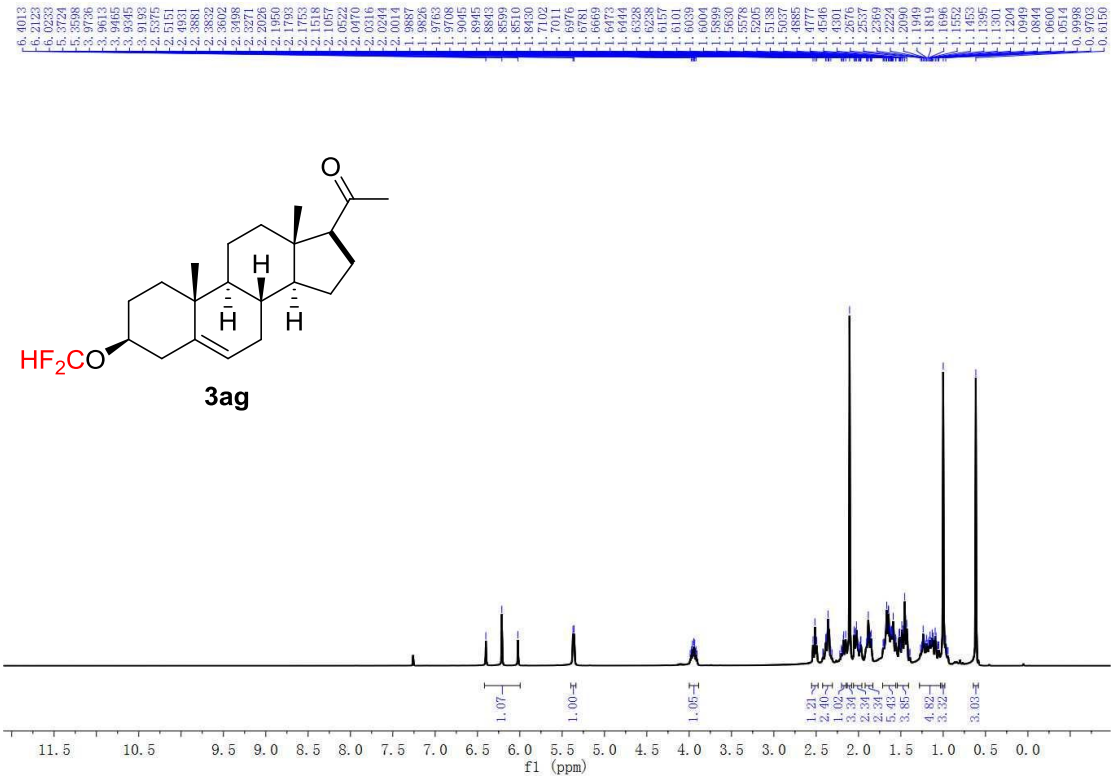
^{13}C-NMR Spectrum of 3af



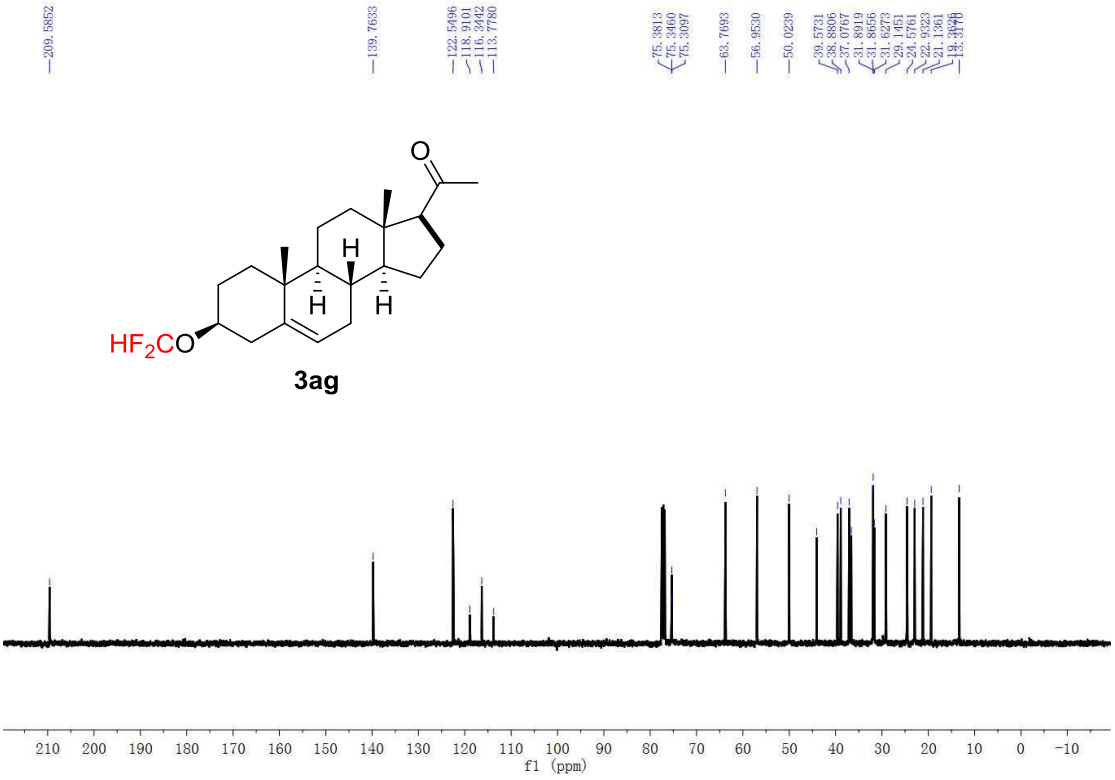
^{19}F-NMR Spectrum of 3af



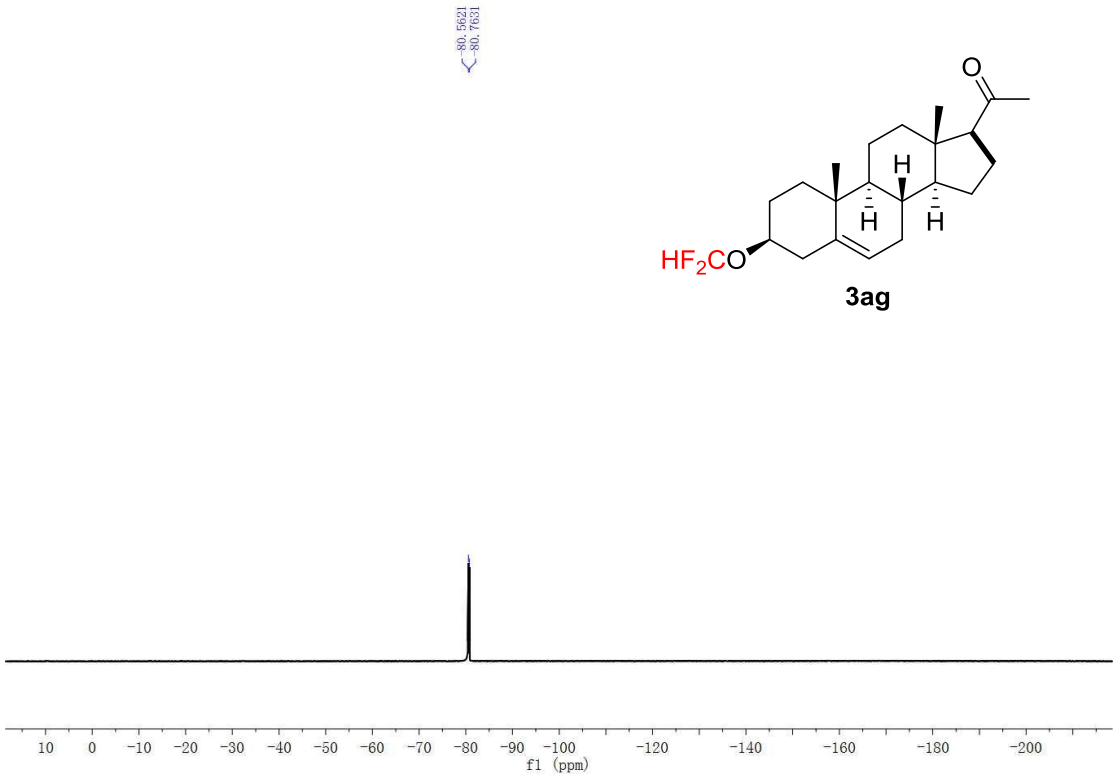
[1]H-NMR Spectrum of 3ag



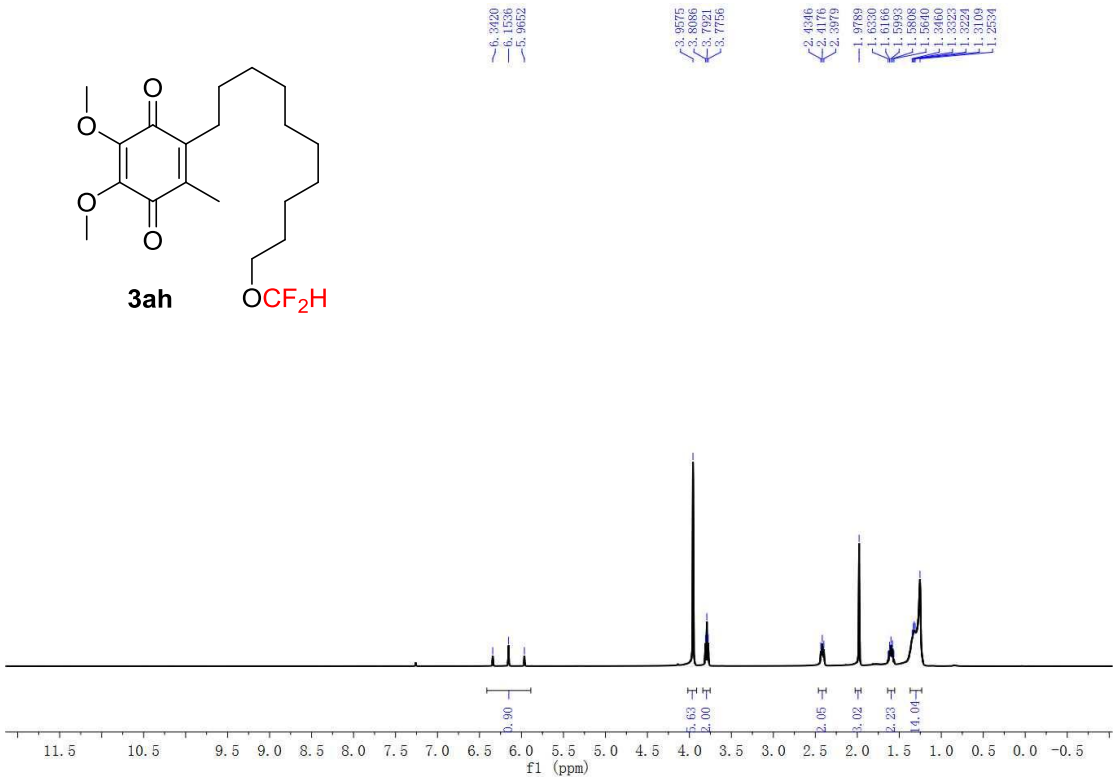
[13]C-NMR Spectrum of 3ag



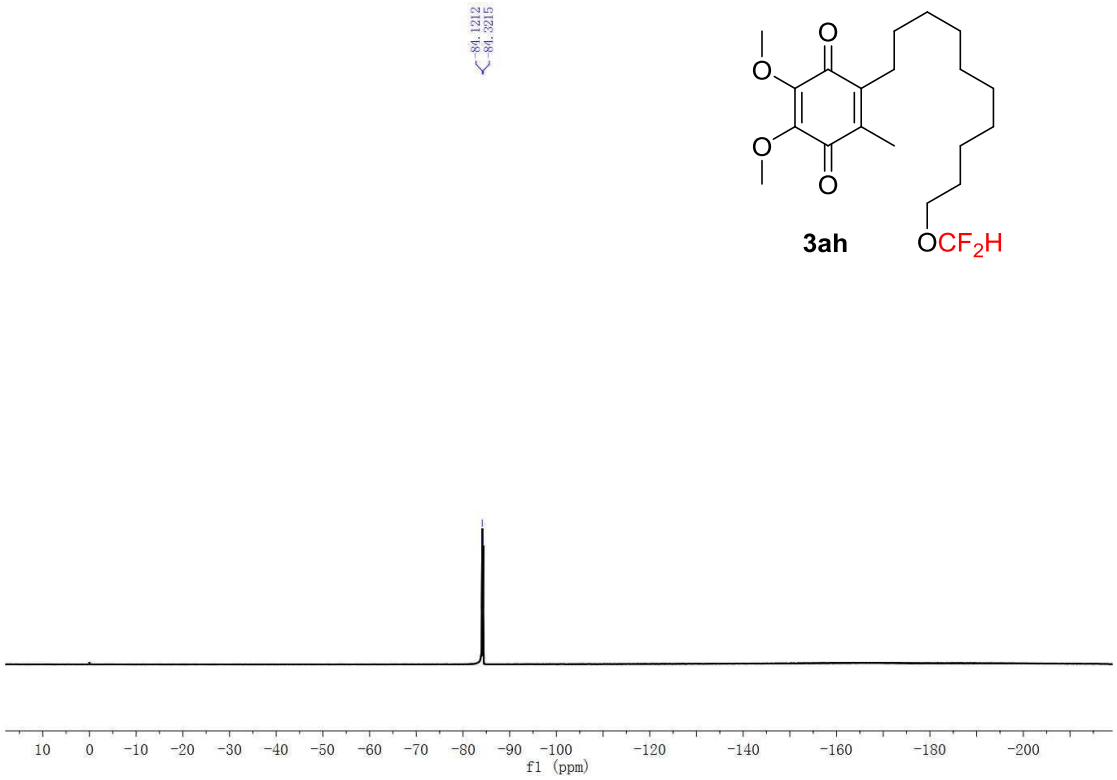
^{19}F-NMR Spectrum of 3ag



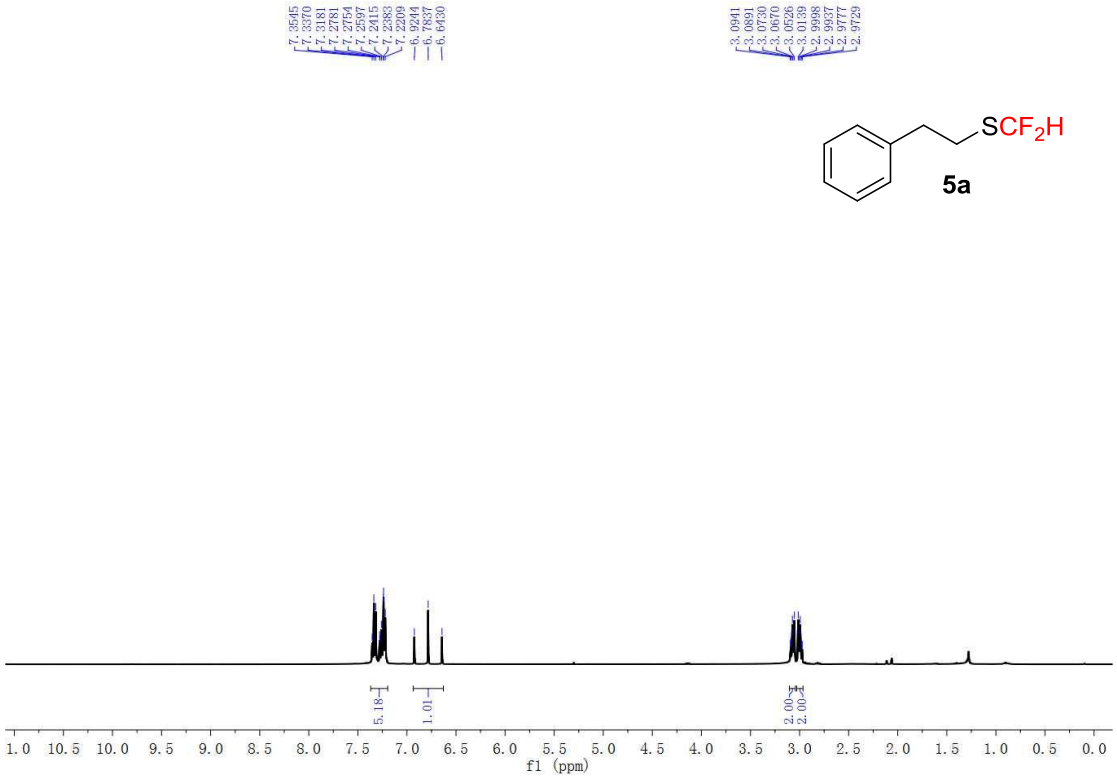
^{1}H-NMR Spectrum of 3ah



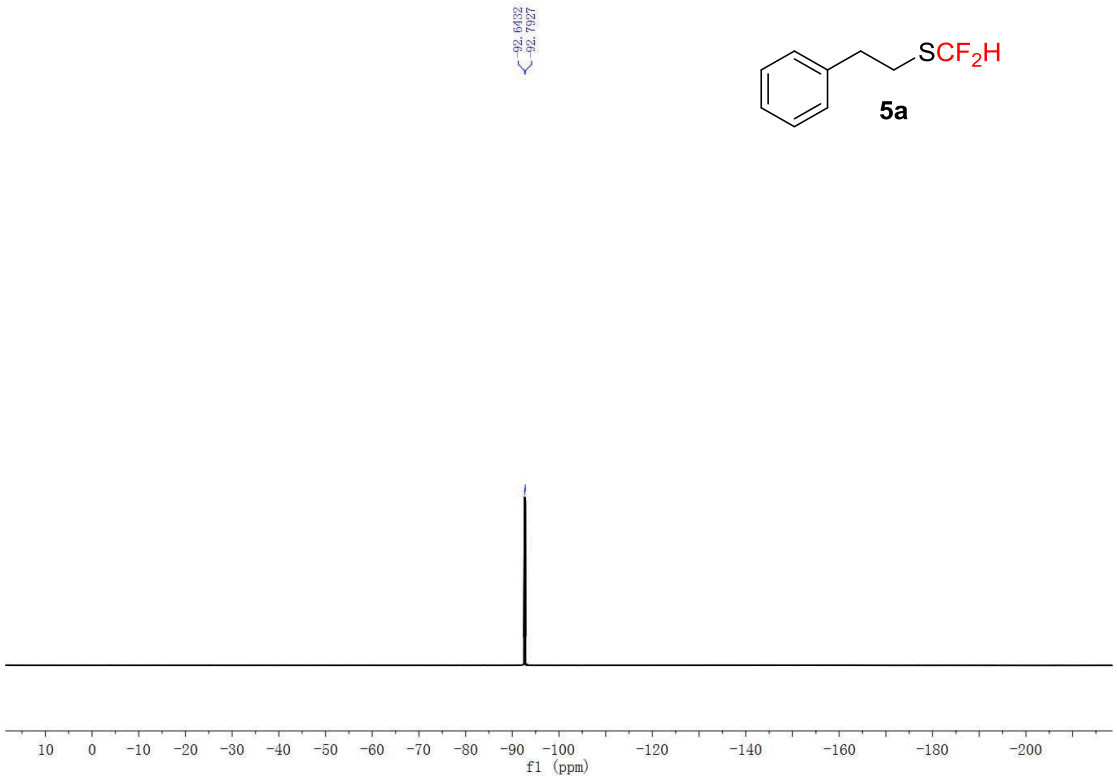
^{19}F-NMR Spectrum of 3ah



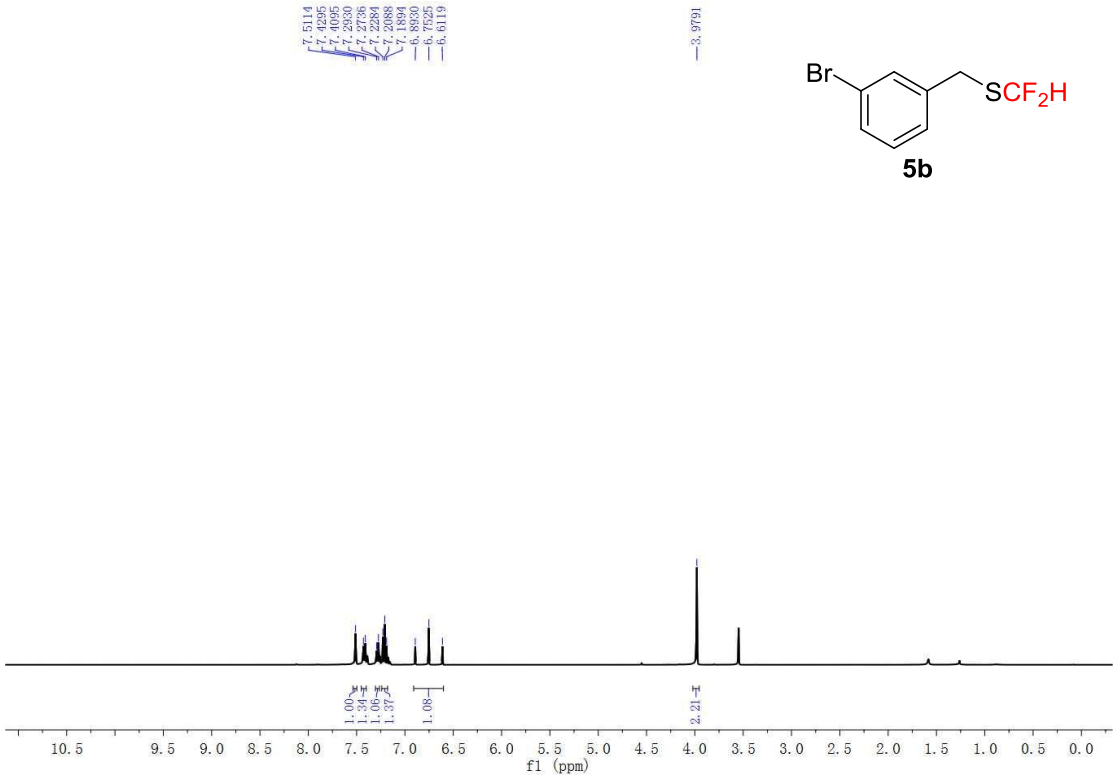
^{1}H-NMR Spectrum of 5a



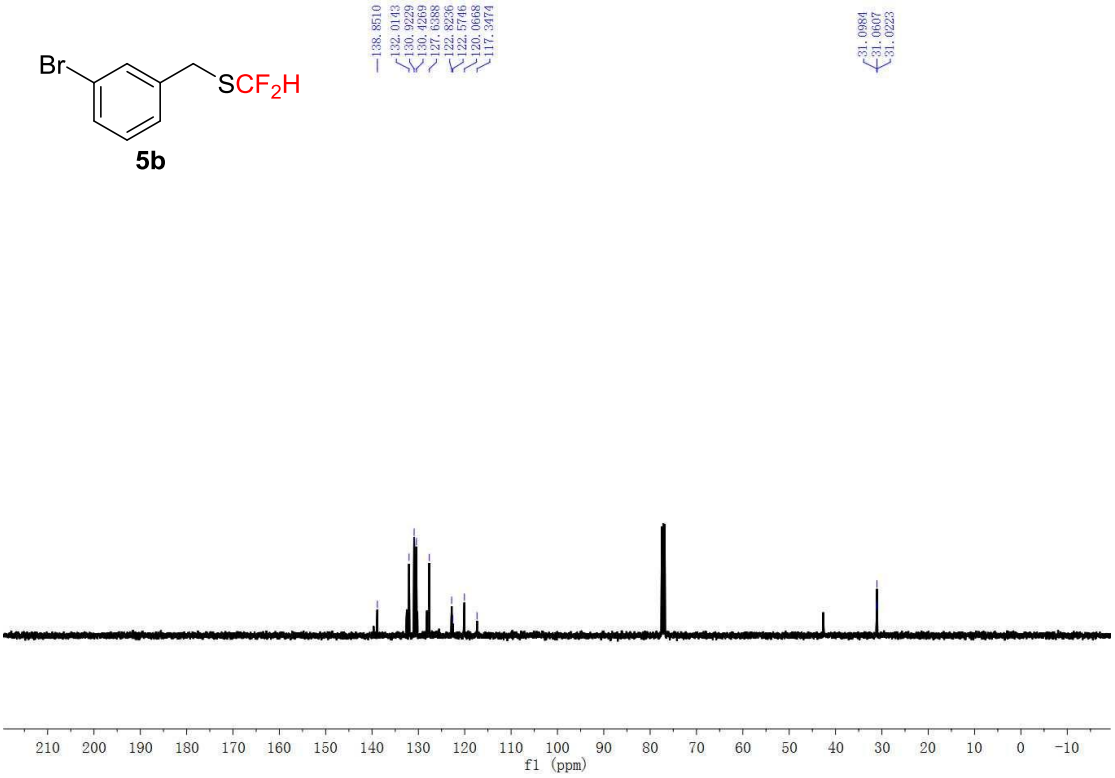
^{19}F-NMR Spectrum of 5a



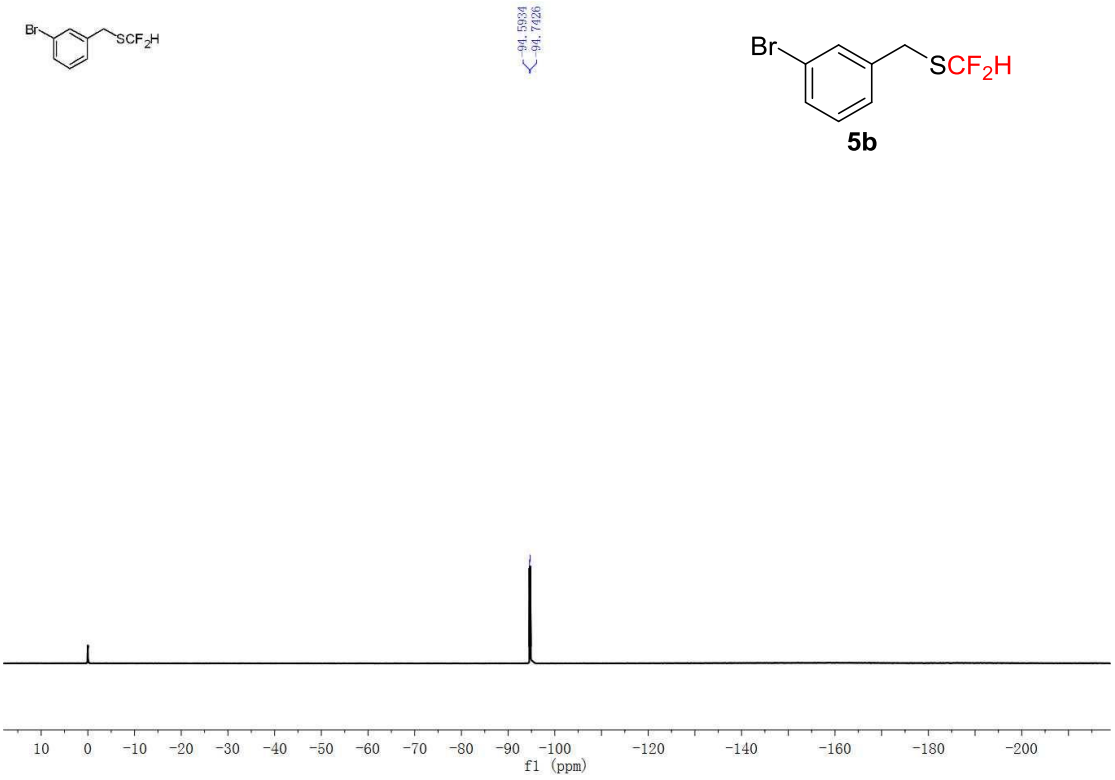
^{1}H-NMR Spectrum of 5b



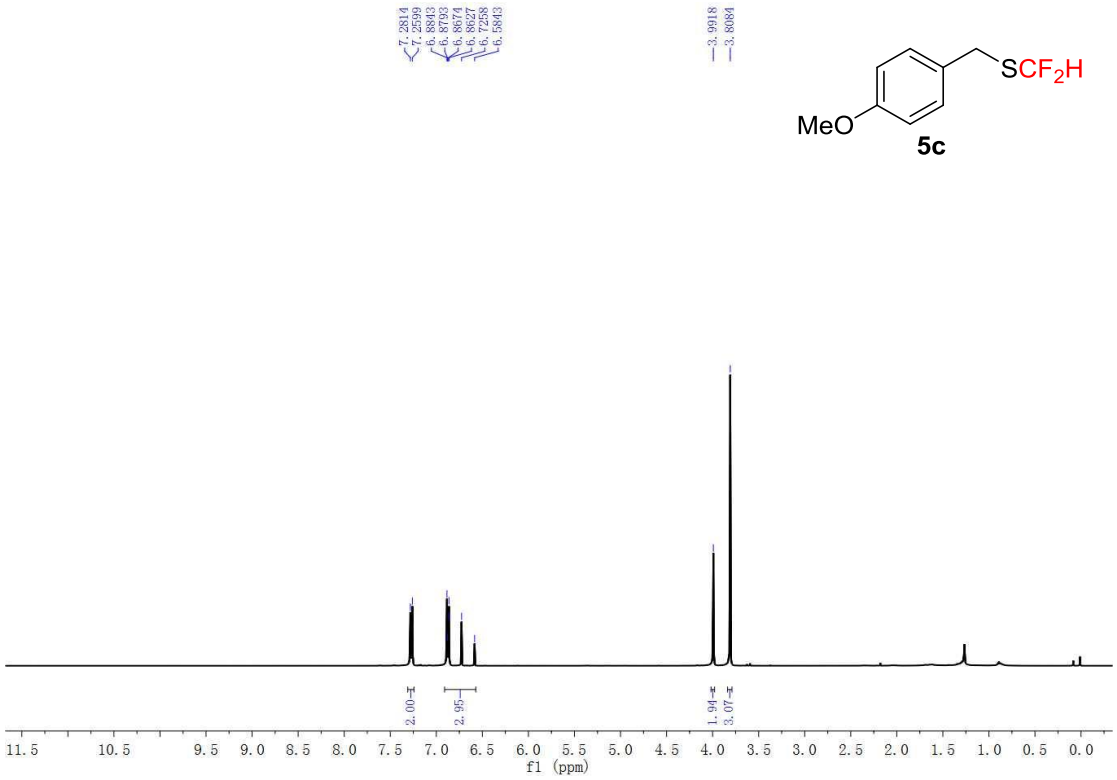
^{13}C-NMR Spectrum of 5b



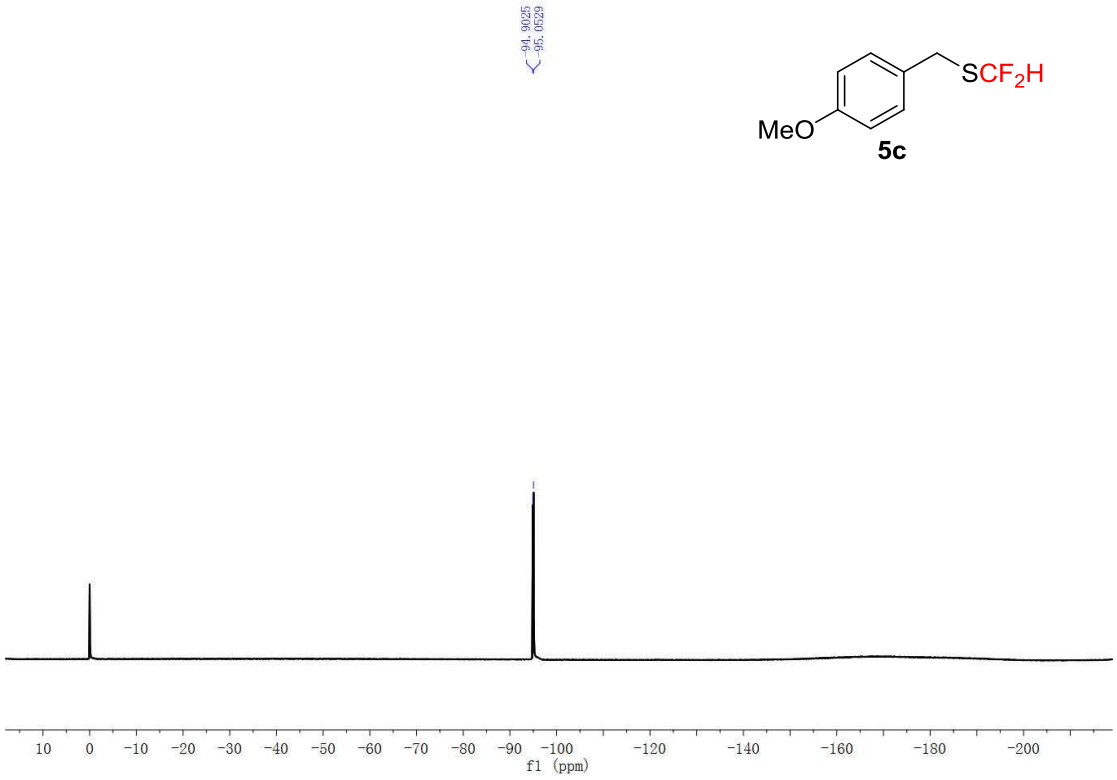
^{19}F-NMR Spectrum of 5b



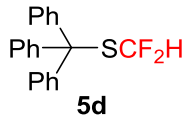
[1]H-NMR Spectrum of 5c



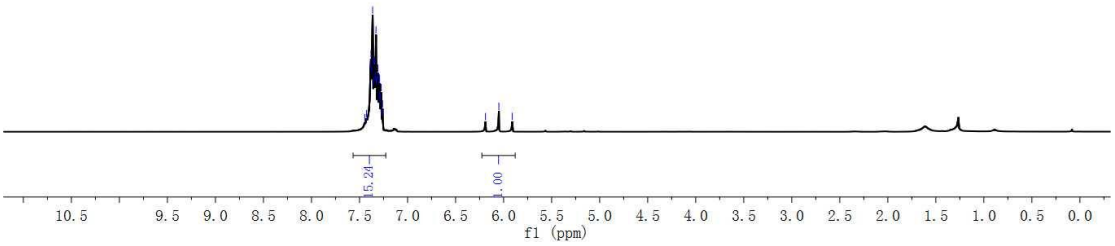
[19]F-NMR Spectrum of 5c



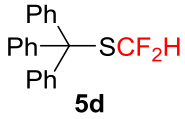
^{1}H-NMR Spectrum of 5d



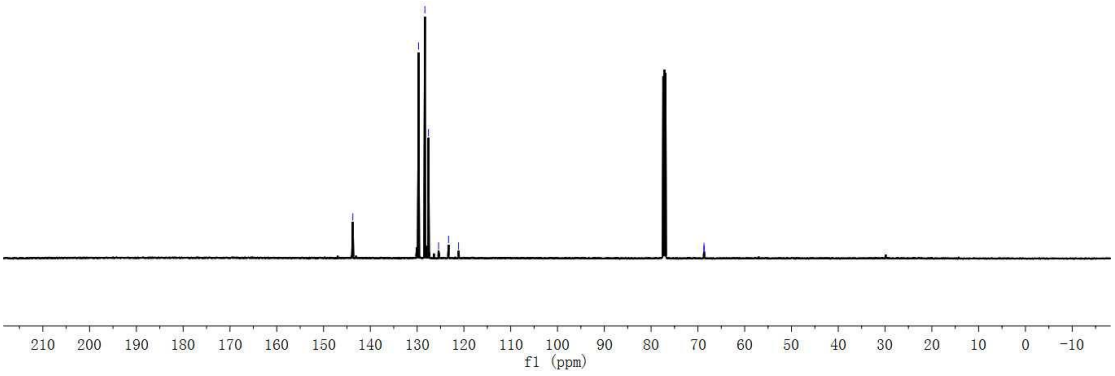
5d



^{13}C-NMR Spectrum of 5d



5d



^{19}F-NMR Spectrum of 5d