SUPPORTING INFORMATION

Mn-Catalysed Photoredox Hydroxytrifluoromethylation of Aliphatic Alkenes Using CF_3SO_2Na

Wenhao Long, Pengcheng Lian, Jingjing Li, Xiaobing Wan*

Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China

Email: *wanxb@suda.edu.cn*

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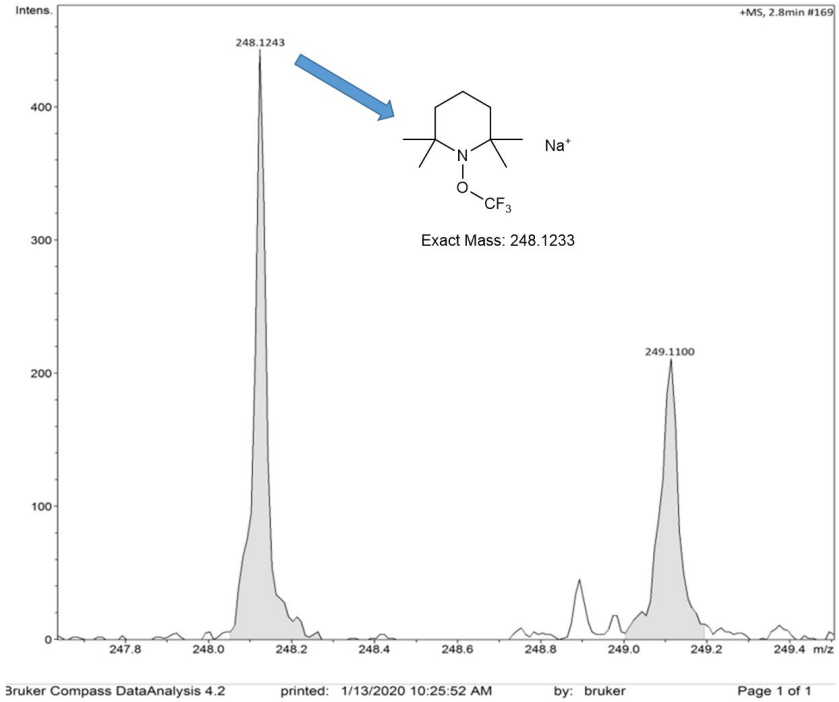
General information

All manipulations were carried out under air atmosphere. All solvents should be dried by activated molecular sieves. White LED model E27 was purchased from Philips. Green and blue LED models were also model E27 and purchased from Shanghai Hongye Optoelectronics Technology Co., Ltd.. Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions. The ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), ^{19}F NMR (376 MHz) data were recorded using $CDCl_3$ as solvent at room temperature. The chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. ^{1}H NMR spectra was recorded with tetramethylsilane (δ = 0.00 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (δ = 77.00 ppm) as internal reference. IR and HRMS, were performed by the State-authorized Analytical Center in Soochow University.

General procedures for synthesis of 3

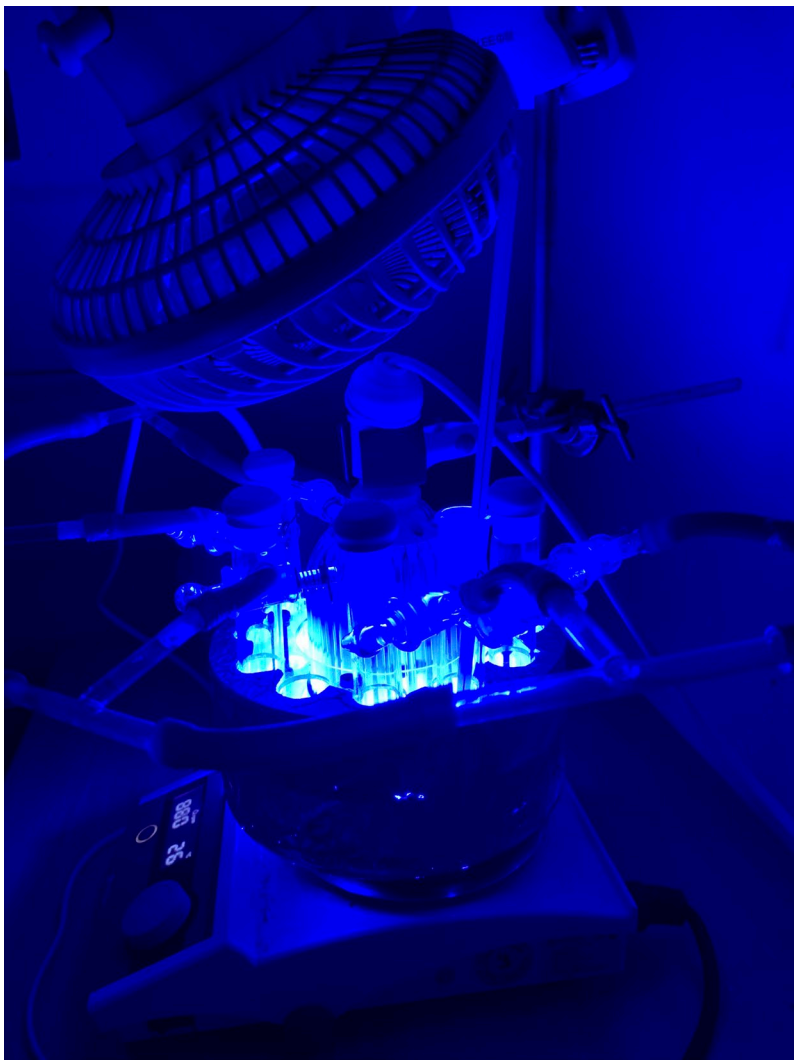
To a 25 mL dry Schlenk tube equipped with a magnetic stirring bar was charged with sodium trifluoromethanesulfinate (0.8 mmol) and $Mn(acac)_3$ (0.02 mmol). Then anhydrous 1,4-dioxane (3 mL) and acetone (1 mL) were added and alkene 1 (0.2 mmol) were added via syringe. The mixture was stirred under an air atmosphere by irradiation of 40 W blue LED for 24 h. After the reaction was complete, the organic layer concentrated under vacuum. The residue was purified with silica gel column chromatography to provide the desired product.

Trapping of trifluoromethyl radical



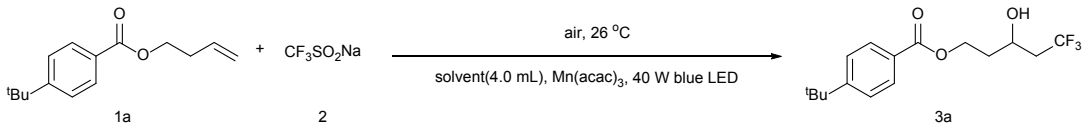
The details for the photoreaction apparatus

The reaction equipment includes a magnetic stirrer, a cooling device-fan, a reaction tank, a light source and temperature measuring device-thermometer. We use air bags as a source of air for reaction.



Optimization of the reaction conditions

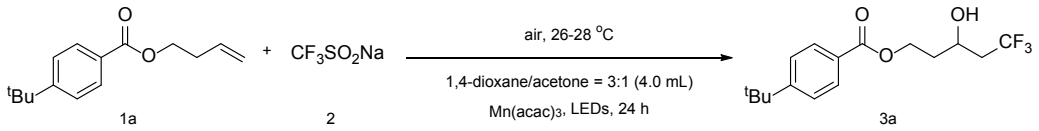
Table S1. Optimization of the reaction solvents



enty	solvent / mL	yield[b]
1	1,4-Dioxane(4.0)	62%
2	acetone(4.0)	< 5
3	DCE(4.0)	< 5
4	DMSO(4.0)	< 5
5	Isopropyl alcohol(4.0)	< 5
6	HFIP(4.0)	< 5
7	EA(4.0)	60%
8	CH_3NO_2(4.0)	56%
9	Toluene(4.0)	< 5
10	1,4-Dioxane/Toluene(2.0/2.0)	< 5
11	1,4-Dioxane/DCE(2.0/2.0)	66%
12	1,4-Dioxane/Isopropyl alcohol(2.0/2.0)	< 5
13	1,4-Dioxane/EA(2.0/2.0)	67%
14	1,4-Dioxane/CH_3NO_2(2.0/2.0)	64%
15	1,4-Dioxane/HFIP(2.0/2.0)	< 5
16	1,4-Dioxane/acetone(2.0/2.0)	71%
17	1,4-Dioxane/acetone(3.0/1.0)	80%
18	1,4-Dioxane/acetone(1.0/3.0)	39%

[a]Reaction conditions: 1a (0.2 mmol), 2 (0.8 mmol), $Mn(acac)_3$ (0.02 mmol, 10 mol%), solvent (4.0 mL), in air at 26 °C for 24 h with 40 W blue LED.
[b]Isolated yields.

Table S2. Optimization of the light sources

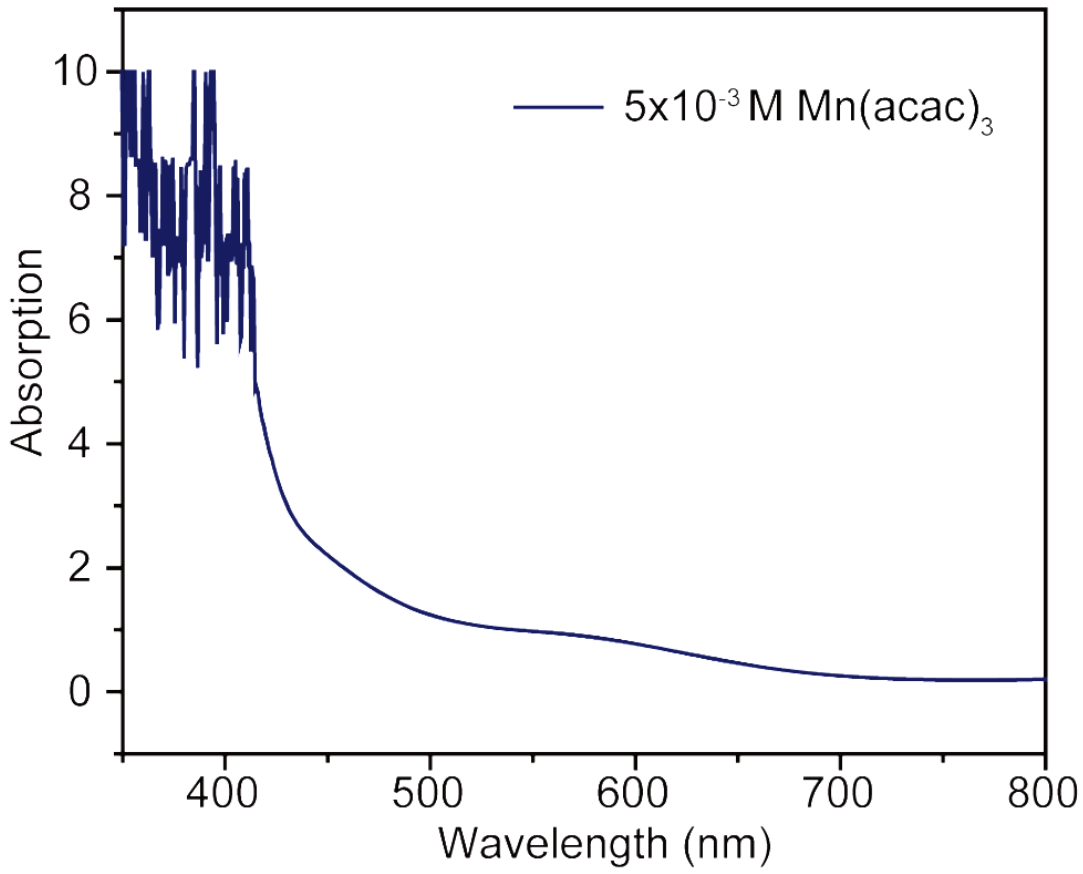


enty	light source	yield[b]
1	40 W blue LED	80%
2	38 W white LED	57%
3	40 W green LED	< 5

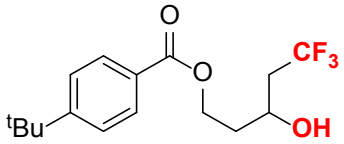
[a]Reaction conditions: 1a (0.2 mmol), 2 (0.8 mmol), $Mn(acac)_3$ (0.02 mmol, 10 mol%), 1,4-dioxane (3.0 mL), acetone (1.0 mL), in air at 26-28 °C for 24 h with different color LEDs. [b]Isolated yields.

UV-visible absorption spectrum

0.02 mmol of $Mn(acac)_3$ in 3 mL 1,4-dioxane and 1 mL acetone was tested the UV-visible absorption spectrum. The result was as follows.

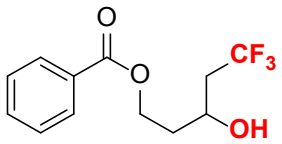


Compound characterizations



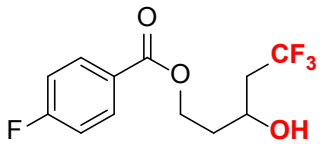
5,5,5-trifluoro-3-hydroxypentyl 4-(tert-butyl)benzoate (3a)

petroleum ether/ ethylacetate = 5:1, colorless oil, 80% yield (51.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.94 (m, 2H), 7.47-7.45 (m, 2H), 4.65-4.59 (m, 1H), 4.42-4.37 (m, 1H), 4.20-4.14 (m, 1H), 2.99 (s, 1H), 2.52-2.19 (m, 2H), 2.08-1.97 (m, 1H), 1.93-1.85 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 157.0, 129.5, 126.9, 126.1, (q, J = 276 Hz), 124.8, 63.0 (q, J = 3 Hz), 61.0, 41.1 (q, J = 27 Hz), 36.3, 35.1, 31.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -63.44 (s, 3F). HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{21}F_3O_3$+Na^+: 341.1335, Found: 341.1346. IR (neat, cm^{-1}): υ 3446, 2966, 1701, 1609, 1458, 1275, 1190, 1121, 1018.



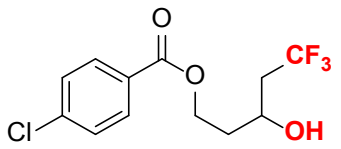
5,5,5-trifluoro-3-hydroxypentyl benzoate (3b)

petroleum ether/ ethylacetate = 5:1, colorless oil, 75% yield (39.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-8.02 (m, 2H), 7.60-7.56 (m, 1H), 7.47-7.43 (m, 2H), 4.68-4.62 (m, 1H), 4.44-4.39 (m, 1H), 4.21-4.16 (m, 1H), 2.70 (s, 1H), 2.47-2.23 (m, 2H), 2.07-1.99 (m, 1H), 1.95-1.87 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 133.2, 129.8, 129.6, 128.5, 126.1 (q, J = 276 Hz), 63.0 (q, J = 3 Hz), 61.2, 41.2 (q, J = 27 Hz), 36.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -63.45 (s, 3F). HRMS (ESI-TOF): Anal. Calcd. For $C_{12}H_{13}F_3O_3$+Na^+: 285.0709, Found: 285.0701. IR (neat, cm^{-1}): υ 3463, 2963, 1716, 1602, 1453, 1387, 1272, 1146, 1070.



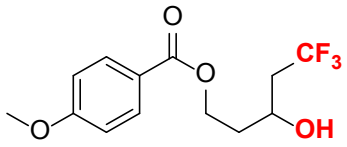
5,5,5-trifluoro-3-hydroxypentyl 4-fluorobenzoate (3c)

petroleum ether/ ethylacetate = 5:1, colorless oil, 76% yield (42.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.03 (m, 2H), 7.14-7.10 (m, 2H), 4.66-4.60 (m, 1H), 4.44-4.38 (m, 1H), 4.20-4.15 (m, 1H), 2.65 (s, 1H), 2.49-2.23 (m, 2H), 2.06-1.98 (m, 1H), 1.95-1.86 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 165.3 (d, J = 137 Hz) , 132.2 (d, J = 9 Hz), 126.1 (q, J = 276 Hz), 126.0 (d, J = 3 Hz), 115.6 (d, J = 22 Hz), 63.0 (q, J = 3 Hz), 61.3, 41.2 (q, J = 26 Hz), 36.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -63.47 (s, 3F), -105.10 (s, 1F). HRMS (ESI-TOF): Anal. Calcd. For $C_{12}H_{12}F_4O_3$+Na^+: 303.0615, Found: 303.0619. IR (neat, cm^{-1}): υ 3481, 2963, 1715, 1603, 1508, 1270, 1115.



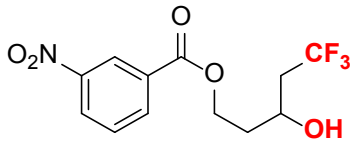
5,5,5-trifluoro-3-hydroxypentyl 4-chlorobenzoate (3d)

petroleum ether/ ethylacetate = 5:1, colorless oil, 71% yield (42.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 4.66-4.60 (m, 1H), 4.44-4.39 (m, 1H), 4.20–4.15 (m, 1H), 2.63 (s, 1H), 2.47-2.23 (m, 2H), 2.06-1.98 (m, 1H), 1.95-1.87 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 139.7, 130.9, 128.8, 128.8, 126.1 (q, *J* = 276 Hz), 63.0 (q, *J* = 3 Hz), 61.5, 41.2 (q, *J* = 27 Hz), 36.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -63.46 (s, 3F). HRMS (ESI-TOF): Anal. Calcd. For $C_{12}H_{12}{}^{35}ClF_3O_3$+$Na^+$: 319.0319, Found: 319.0325; Anal. Calcd. For $C_{12}H_{12}{}^{37}ClF_3O_3$+$Na^+$: 321.0290, Found: 321.0301. IR (neat, cm^{-1}): υ 3463, 2961, 1716, 1595, 1489, 1401, 1270, 1117, 1091, 1014.



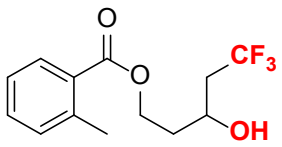
5,5,5-trifluoro-3-hydroxypentyl 4-methoxybenzoate (3e)

petroleum ether/ ethylacetate = 5:1, colorless oil, 82% yield (48.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 4.65-4.59 (m, 1H), 4.39-4.34 (m, 1H), 4.16 (s, 1H), 3.86 (s, 3H), 2.88 (s, 1H), 2.40-2.22 (m, 2H), 2.05-1.97 (m, 1H), 1.92-1.84 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 163.6, 131.7, 126.2 (q, *J* = 275 Hz), 120.8, 113.7, 63.0 (q, *J* = 3 Hz), 60.9, 55.4, 41.1 (q, *J* = 26 Hz), 36.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -63.45 (s, 3F). HRMS (ESI-TOF): Anal. Calcd. For $C_{13}H_{15}F_3O_4$+Na^+: 315.0815, Found: 315.0809. IR (neat, cm^{-1}): υ 3467, 2922, 1708, 1605, 1512, 1250, 1102, 1025.



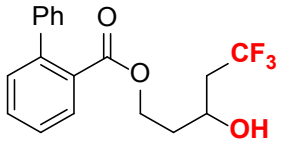
5,5,5-trifluoro-3-hydroxypentyl 3-nitrobenzoate (3f)

petroleum ether/ ethylacetate = 3:1, yellow oil, 77% yield (47.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85-8.84 (m, 1H), 8.45-8.35 (m, 2H), 7.70-7.66 (m, 1H), 4.72-4.65 (m, 1H), 4.54-4.49 (m, 1H), 4.23-4.18 (m, 1H), 2.56 (s, 1H), 2.47-2.26 (m, 2H), 2.12-2.04 (m, 1H), 2.01-1.92 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 148.3, 135.3, 131.6, 129.7, 127.6, 126.1 (q, *J* = 275 Hz), 124.6, 62.9 (q, *J* = 3 Hz), 62.2, 41.3 (q, *J* = 27 Hz), 36.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -63.44 (s, 3F). HRMS (ESI-TOF): Anal. Calcd. For $C_{12}H_{12}F_3NO_5$+Na^+: 330.0560, Found: 330.0558. IR (neat, cm^{-1}): υ 3343, 2963, 1720, 1528, 1345, 1244, 1129, 1065.



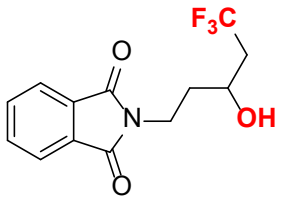
5,5,5-trifluoro-3-hydroxypentyl 2-methylbenzoate (3g)

petroleum ether/ ethylacetate = 5:1, colorless oil, 81% yield (44.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.88 (m, 1H), 7.43-7.40 (m, 1H), 7.27-7.23 (m, 2H), 4.65-4.59 (m, 1H), 4.41-4.36 (m, 1H), 4.20-4.15 (m, 1H), 2.68 (s, 1H), 2.59 (s, 3H), 2.47-2.22 (m, 2H), 2.06-1.97 (m, 1H), 1.94-1.86 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 140.3, 132.2, 131.8, 130.5, 129.2, 126.2 (q, J = 275 Hz), 125.8, 63.1 (q, J = 3 Hz), 61.0, 41.2 (q, J = 27 Hz), 36.3, 21.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -63.47 (s, 3F). HRMS (ESI-TOF): Anal. Calcd. For $C_{13}H_{15}F_3O_3$+Na^+: 299.0866, Found: 299.0874. IR (neat, cm^{-1}): υ 3511, 2960, 1700, 1451, 1245, 1131, 1065.



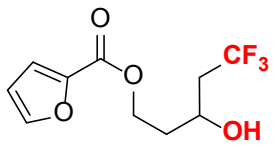
5,5,5-trifluoro-3-hydroxypentyl [1,1'-biphenyl]-2-carboxylate (3h)

petroleum ether/ ethylacetate = 5:1, colorless oil, 80% yield (54.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.81 (m, 1H), 7.56-7.52 (m, 1H), 7.42-7.32 (m, 7H), 4.23-4.11 (m, 2H), 3.59-3.51 (m, 1H), 2.19-1.95 (m, 3H), 1.50-1.46 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 142.1, 141.7, 131.4, 130.9, 130.6, 129.9, 128.4, 128.2, 127.3, 127.1, 126.1 (q, J = 276 Hz), 62.5 (q, J = 3 Hz), 61.0, 41.0 (q, J = 27 Hz), 35.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -63.33 (s, 3F). HRMS (ESI-TOF): Anal. Calcd. For $C_{18}H_{17}F_3O_3$+Na^+: 361.1022, Found: 361.1023. IR (neat, cm^{-1}): υ 3482, 2962, 1714, 1385, 1249, 1123.



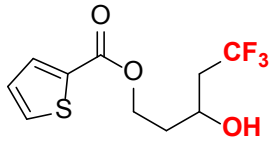
2-(5,5,5-trifluoro-3-hydroxypentyl)isoindoline-1,3-dione (3i)

petroleum ether/ ethylacetate = 5:1, white solid, 80% yield (46.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.86 (m, 2H), 7.76-7.74 (m, 2H), 4.02-3.85 (m, 3H), 3.29 (d, J = 4.5 Hz, 1H), 2.46-2.32 (m, 1H), 2.21-2.14 (m, 1H), 1.92-1.74 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 134.2, 131.8, 126.0 (q, J = 275 Hz), 123.5, 62.9 (q, J = 3 Hz), 40.8 (q, J = 27 Hz), 36.0, 34.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -63.48 (s, 3F). HRMS (ESI-TOF): Anal. Calcd. For $C_{13}H_{12}F_3NO_3$+Na^+: 310.0661, Found: 310.0667. IR (neat, cm^{-1}): υ 3462, 2943, 1681, 1375, 1261, 1140, 1008.



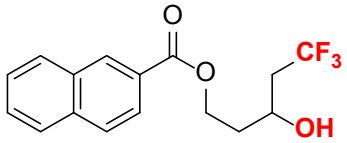
5,5,5-trifluoro-3-hydroxypentyl furan-2-carboxylate (3j)

petroleum ether/ ethylacetate = 5:1, colorless oil, 63% yield (31.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 0.8 Hz, 1H), 7.20 (d, *J* = 3.5 Hz, 1H), 6.53-6.52 (m, 1H), 4.65–4.59 (m, 1H), 4.43–4.37 (m, 1H), 4.20–4.15 (m, 1H), 2.69 (d, *J* = 4.5 Hz, 1H), 2.44–2.25 (m, 2H), 2.07-1.97 (m, 1H), 1.95-1.1.85 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 146.6, 144.2, 126.1 (q, *J* = 277 Hz), 118.4, 112.0, 63.1 (q, *J* = 3 Hz), 61.3, 41.1 (q, *J* = 27 Hz), 36.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -63.48 (s, 3F). HRMS (ESI-TOF): Anal. Calcd. For $C_{10}H_{11}F_3O_4$+Na^+: 275.0502, Found: 275.0499. IR (neat, cm^{-1}): υ 3446, 2928, 1717, 1474, 1298, 1148.



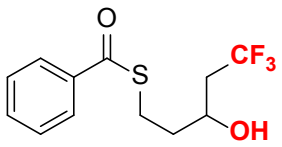
5,5,5-trifluoro-3-hydroxypentyl thiophene-2-carboxylate (3k)

petroleum ether/ ethylacetate = 5:1, colorless oil, 79% yield (42.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.80 (m, 1H), 7.59-7.57 (m, 1H), 7.12-7.10 (m, 1H), 4.63-4.56 (m, 1H), 4.42-4.36 (m, 1H), 4.20-4.16 (m, 1H), 2.79(s, 1H), 2.44-2.26 (m, 2H), 2.04-1.97 (m, 1H), 1.93-1.85 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 133.8, 133.2, 132.8, 127.9, 126.2 (q, *J* = 275 Hz), 63.0 (q, *J* = 3 Hz), 61.4, 41.2 (q, *J* = 27 Hz), 36.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -63.46 (s, 3F). HRMS (ESI-TOF): Anal. Calcd. For $C_{10}H_{11}F_3O_3S$+Na^+: 291.0273, Found: 291.0269. IR (neat, cm^{-1}): υ 3446, 1707, 1419, 1264, 1150, 1098.



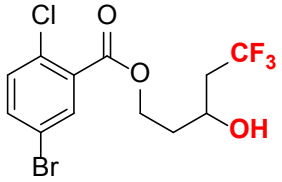
5,5,5-trifluoro-3-hydroxypentyl 2-naphthoate (3l)

petroleum ether/ ethylacetate = 4:1, colorless oil, 52% yield (32.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.04-7.86 (m, 4H), 7.59-7.52 (m, 2H), 4.73-4.67 (m, 1H), 4.50−4.44 (m, 1H), 4.25-4.20 (m, 1H), 2.80 (d, *J* = 4.3 Hz, 1H), 2.47-2.28 (m, 2H), 2.11-2.03 (m, 1H), 1.99-1.90 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 135.6, 132.4, 131.2, 129.3, 128.4, 128.3, 127.8, 127.0, 126.7, 126.2 (q, *J* = 275 Hz), 125.1, 63.1 (q, *J* = 3 Hz), 61.4, 41.2 (q, *J* = 26 Hz), 36.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -63.40 (s, 3F). HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{15}F_3O_3$+Na^+: 335.0866, Found: 335.0862. IR (neat, cm^{-1}): υ 3463, 2925, 1713, 1468, 1278, 1128, 1098.



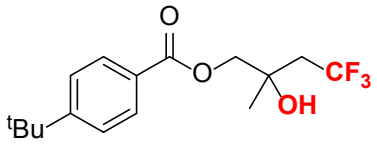
S-(5,5,5-trifluoro-3-hydroxypentyl) benzothioate (3m)

petroleum ether/ ethylacetate = 5:1, pure yellow oil, 63% yield (35.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.96 (m, 2H), 7.61-7.57 (m, 1H), 7.48-7.44 (m, 1H), 4.11-4.06 (m, 1H), 3.36-3.29 (m, 1H), 3.19-3.12 (m, 1H), 3.03 (d, *J* = 4.3 Hz, 1H), 2.42-2.21 (m, 2H), 1.97-1.78 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 136.6, 133.7, 128.7, 127.3, 126.2 (q, *J* = 276 Hz), 64.0 (q, *J* = 3 Hz), 40.9 (q, *J* = 27 Hz), 37.2, 24.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -63.41 (s, 3F). HRMS (ESI-TOF): Anal. Calcd. For $C_{12}H_{13}F_3O_2S$+Na^+: 301.0481, Found: 301.0479. IR (neat, cm^{-1}): υ 3446, 2926, 1660, 1448, 1206, 1109.



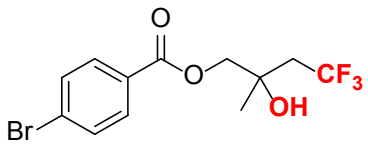
5,5,5-trifluoro-3-hydroxypentyl 5-bromo-2-chlorobenzoate (3n)

petroleum ether/ ethylacetate = 4:1, pure yellow solid, 81% yield (60.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 2.4 Hz, 1H), 7.56-7.53 (m, 1H), 7.32 (d, *J* = 8.6 Hz, 1H), 4.64-4.58 (m, 1H), 4.49-4.44 (m, 1H), 4.25-4.20 (m, 1H), 2.59 (s, 1H), 2.38-2.23 (m, 2H), 2.04-1.99 (m, 1H), 1.96-1.88 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 135.6, 134.1, 132.5, 132.5, 131.3, 126.1 (q, *J* = 275 Hz), 120.2, 64.0 (q, *J* = 3 Hz), 62.3, 41.2 (q, *J* = 27 Hz), 35.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -63.44 (s, 3F). HRMS (ESI-TOF): Anal. Calcd. For $C_{12}H_{11}{}^{79}Br^{35}Cl\ F_3O_3$+$Na^+$:396.9424, Found: 396.9432; Anal. Calcd. For $C_{12}H_{11}{}^{81}Br^{35}ClF_3O_3$+$Na^+$: 398.9404, Found: 398.9422; Anal. Calcd. For $C_{12}H_{11}{}^{79}Br^{37}ClF_3O_3$+$Na^+$: 398.9395, Found: 398.9422; Anal. Calcd. For $C_{12}H_{11}{}^{81}Br^{37}Cl\ F_3O_3$+$Na^+$: 400.9374, Found: 400.9391. IR (neat, cm^{-1}): υ 3446, 2926, 1660, 1448, 1206, 1109.



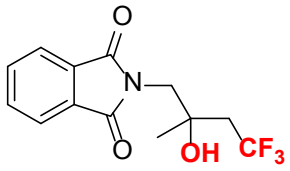
4,4,4-trifluoro-2-hydroxy-2-methylbutyl 4-(tert-butyl)benzoate (3o)

petroleum ether/ ethylacetate = 5:1, colorless oil, 79% yield (50.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.97 (m, 2H), 7.50-7.47 (m, 2H), 4.33-4.26 (m, 2H), 2.57-2.46 (m, 2H), 1.46 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 157.3, 129.6, 126.6, 125.8, (q, *J* = 276 Hz), 125.5, 70.6, 69.8 (q, *J* = 2 Hz), 41.9 (q, *J* = 27 Hz), 35.1, 31.0, 24.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -60.40 (s, 3F). HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{21}F_3O_3$+Na^+: 341.1335, Found: 341.1330. IR (neat, cm^{-1}): υ 3446, 2944, 1701, 1620, 1458, 1275, 1190, 1127.



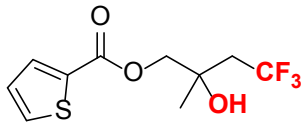
4,4,4-trifluoro-2-hydroxy-2-methylbutyl 4-bromobenzoate (3p)

petroleum ether/ ethylacetate = 5:1, colorless oil, 80% yield (54.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.6 Hz, 2H), 7.60 (d, J = 8.6 Hz, 2H), 4.44–4.18 (m, 2H), 2.64-2.34 (m, 3H), 1.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 131.9, 131.1, 128.7, 128.3, 125.7 (q, J = 276 Hz), 70.8, 69.7 (q, J = 2 Hz), 42.00 (q, J = 27 Hz), 24.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -60.38 (s, 3F). HRMS (ESI-TOF): Anal. Calcd. For $C_{12}H_{12}{}^{79}Br\ F_3O_3$+$Na^+$: 362.9814, Found: 362.9818; Anal. Calcd. For $C_{12}H_{12}{}^{81}Br\ F_3O_3$+$Na^+$: 364.9794, Found: 364.9816. IR (neat, cm^{-1}): υ 3473, 2926, 1719, 1283, 1241, 1144, 1121, 731.



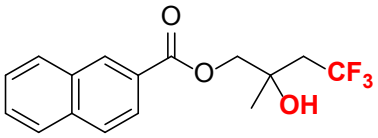
2-(4,4,4-trifluoro-2-hydroxy-2-methylbutyl)isoindoline-1,3-dione (3q)

petroleum ether/ ethylacetate = 4:1, white solid, 73% yield (42.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.88 (m, 2H), 7.78-7.76 (m, 2H), 3.87 (s, 2H), 3.16 (s, 1H), 2.43 (q, J = 11.2 Hz, 2H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 134.5, 131.7, 125.8 (q, J = 276 Hz), 123.7, 71.0 (q, J = 2 Hz), 48.1, 43.3 (q, J = 27 Hz), 25.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -59.91 (s, 3F). HRMS (ESI-TOF): Anal. Calcd. For $C_{13}H_{12}F_3NO_3$+Na^+: 310.0661, Found: 310.0669. IR (neat, cm^{-1}): υ 3464, 2966, 1703, 1315, 1262, 1100, 993, 732.



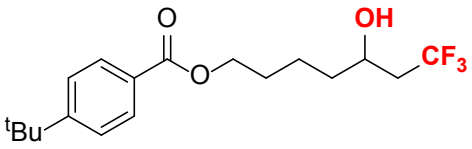
4,4,4-trifluoro-2-hydroxy-2-methylbutyl thiophene-2-carboxylate (3r)

petroleum ether/ ethylacetate = 5:1, colorless oil, 80% yield (43.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.84 (m, 1H), 7.61-7.60 (m, 1H), 7.14-7.12 (m, 1H), 4.31-4.24 (m, 2H), 2.49 (q, J = 11.3 Hz, 3H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 134.0, 133.0, 132.7, 128.0, 125.7 (q, J = 276 Hz), 70.7, 69.7 (q, J = 2 Hz), 41.9 (q, J = 27 Hz), 24.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -60.39 (s, 3F). HRMS (ESI-TOF): Anal. Calcd. For $C_{10}H_{11}F_3O_3S$+Na^+: 291.0273, Found: 291.0279. IR (neat, cm^{-1}): υ 3479, 2984, 1710, 1591, 1258, 1099, 1012, 755, 731.



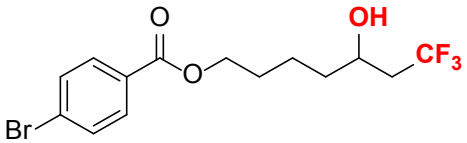
4,4,4-trifluoro-2-hydroxy-2-methylbutyl 2-naphthoate (3s)

petroleum ether/ ethylacetate = 5:1, colorless oil, 61% yield (38.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.05-8.02 (m, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.90-7.87 (m, 2H), 7.63-7.53 (m, 2H), 4.41-4.34 (m, 2H), 2.59-2.51 (m, 3H), 1.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 135.6, 132.4, 131.3, 129.3, 128.5, 128.3, 127.7, 126.8, 126.6, 126.1 (q, *J* = 276 Hz), 125.0, 70.9, 69.8 (q, *J* = 2 Hz), 42.0 (q, *J* = 27 Hz), 24.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -60.28 (s, 3F). HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{15}F_3O_3$+Na^+: 335.0866, Found: 335.0876. IR (neat, cm^{-1}): υ 3466, 2984, 1704, 1631, 1370, 1260, 1094.



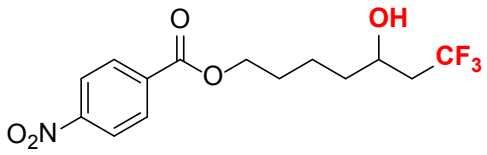
7,7,7-trifluoro-5-hydroxyheptyl 4-(tert-butyl)benzoate (3t)

petroleum ether/ ethylacetate = 5:1, colorless oil, 66% yield (45.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 4.33 (t, *J* = 6.5 Hz, 2H), 4.08-3.99 (m, 1H), 2.35-2.20 (m, 2H), 2.08 (s, 1H), 1.86-1.73 (m, 2H), 1.69-1.48 (m, 4H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 156.6, 129.4, 126.4 (q, *J* = 216 Hz), 125.3, 62.9 (q, *J* = 3 Hz), 64.4, 41.2 (q, *J* = 26 Hz), 36.7, 35.0, 31.1, 28.5, 21.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -63.47 (s, 3F). HRMS (ESI-TOF): Anal. Calcd. For $C_{18}H_{25}F_3O_3$+Na^+: 369.1648, Found: 369.1655. IR (neat, cm^{-1}): υ 3447, 2958, 1716, 1271, 1118, 1016.



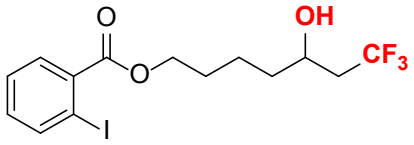
7,7,7-trifluoro-5-hydroxyheptyl 4-bromobenzoate (3u)

petroleum ether/ ethylacetate = 4:1, colorless oil, 65% yield (48.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 4.33 (t, *J* = 6.5 Hz, 2H), 4.07-4.02 (m, 1H), 2.35 -2.21 (m, 2H), 2.00 (d, *J* = 4.2 Hz, 1H), 1.84-1.77 (m, 2H), 1.69-1.49 (m, 4H).^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 131.7, 131.0, 129.2, 128., 126.4 (q, *J* = 276 Hz), 65.9 (q, *J* = 3 Hz), 64.9, 41.2 (q, *J* = 26 Hz), 36.6, 28.4, 21.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -60.48 (s, 3F). HRMS (ESI-TOF): Anal. Calcd. For $C_{14}H_{16}{}^{79}Br$ F_3O_3+Na^+: 391.0127, Found: 391.0128; Anal. Calcd. For $C_{14}H_{16}{}^{81}Br$ F_3O_3+Na^+: 393.0107, Found: 393.0111. IR (neat, cm^{-1}): υ 3460, 2943, 1700, 1473, 1245, 1113.



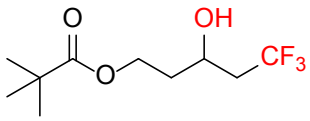
7,7,7-trifluoro-5-hydroxyheptyl 4-nitrobenzoate (3v)

petroleum ether/ ethylacetate = 3:1, yellow oil, 71% yield (47.7 mg). ^{1}H NMR (400 MHz, CDCl3) δ 8.31-8.28 (m, 2H), 8.22-8.19 (m, 2H), 4.40 (t, *J* = 6.6 Hz, 2H), 4.11-4.01 (m, 1H), 2.35-2.22 (m, 2H), 1.98 (s, 1H), 1.91-1.79 (m, 2H), 1.72-1.49 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 150.5, 135.6, 130.6, 126.4 (q, *J* = 275 Hz), 123.5, 65.9 (q, *J* = 3 Hz), 65.6, 41.3 (q, *J* = 26 Hz), 36.5, 28.4, 21.8. ^{19}F NMR (376 MHz, CDCl3) δ = -63.48 (s, 3F). HRMS (ESI-TOF): Anal. Calcd. For $C_{14}H_{16}F_3NO_5$+Na^+: 358.0873, Found: 358.0880. IR (neat, cm^{-1}): υ 3345, 2965, 1723, 1524, 1341, 1240, 1122, 1061.



7,7,7-trifluoro-5-hydroxyheptyl 2-iodobenzoate (3w)

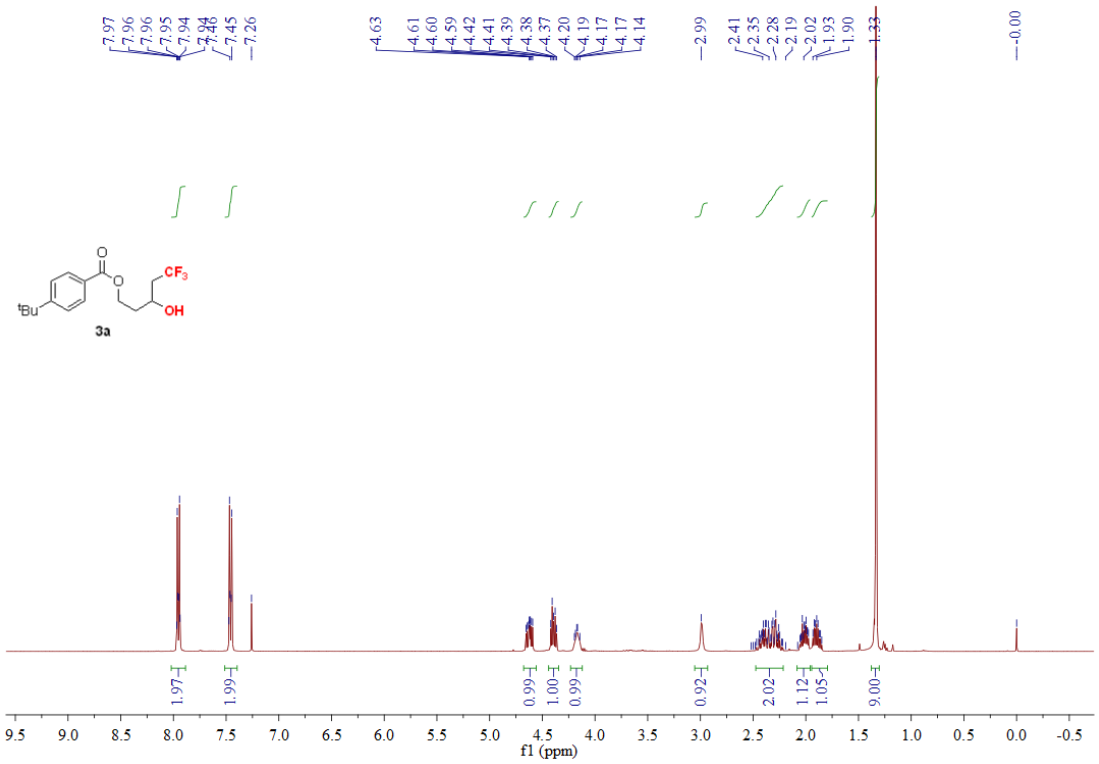
petroleum ether/ ethylacetate = 5:1, colorless oil, 60% yield (50.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.98 (m, 1H), 7.79-7.76 (m, 1H), 7.43-7.39 (m, 1H), 7.17-7.13 (m, 1H), 4.36 (t, *J* = 6.5 Hz, 2H), 4.04 (s, 1H), 2.35-2.21 (m, 2H), 1.97 (s, 1H), 1.87-1.79 (m, 2H), 1.68-1.56 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7,141.2, 135.4, 132.6, 130.8, 127.9, 126.4 (q, *J* = 275 Hz), 93.9, 65.9 (q, *J* = 3 Hz), 65.4, 41.2 (q, *J* = 26 Hz), 36.6, 28.3, 21.8. ^{19}F NMR (376 MHz, CDCl3) δ = -60.38 (s, 3F).HRMS (ESI-TOF): Anal. Calcd. For $C_{14}H_{16}F_3IO_3$+Na^+: 438.9988, Found: 438.9978. IR (neat, cm^{-1}): υ 3464, 2948, 1713, 1269, 1103, 1085, 757, 729.



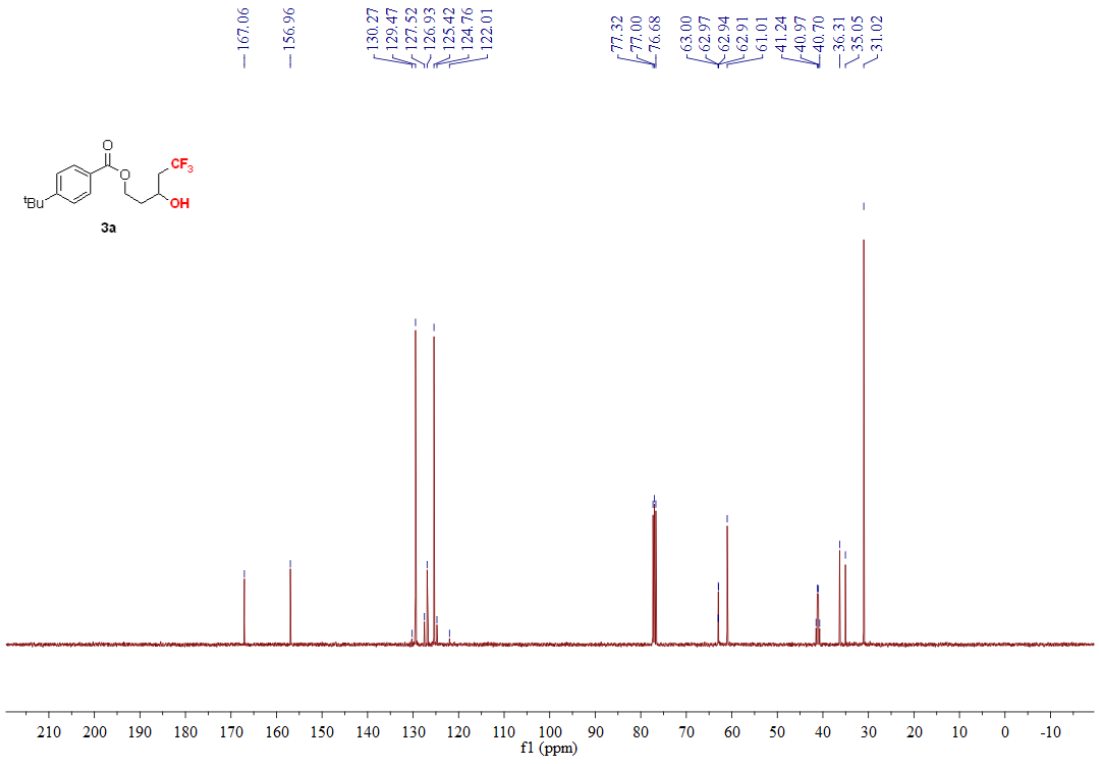
5,5,5-trifluoro-3-hydroxypentyl pivalate (3x)

petroleum ether/ ethylacetate = 5:1, colorless oil, 15% yield (7.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.34-4.28 (m, 1H), 4.15-4.10 (m, 1H), 4.05-3.99 (m, 1H), 3.07 (s, 1H), 2.38-2.13 (m, 2H), 1.89-1.71 (m, 2H), 1.17 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 126.1 (q, *J* = 275 Hz), 62.9 (q, *J* = 3 Hz), 60.7, 41.0 (q, *J* = 26 Hz), 38.7, 36.1, 27.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -63.69 (s, 3F). HRMS (ESI-TOF): Anal. Calcd. For $C_{10}H_{17}F_3O_3$+H^+: 243.1203, Found: 243.1206. IR (neat, cm^{-1}): υ 2975, 1709, 1282, 1252, 1145, 864, 669.

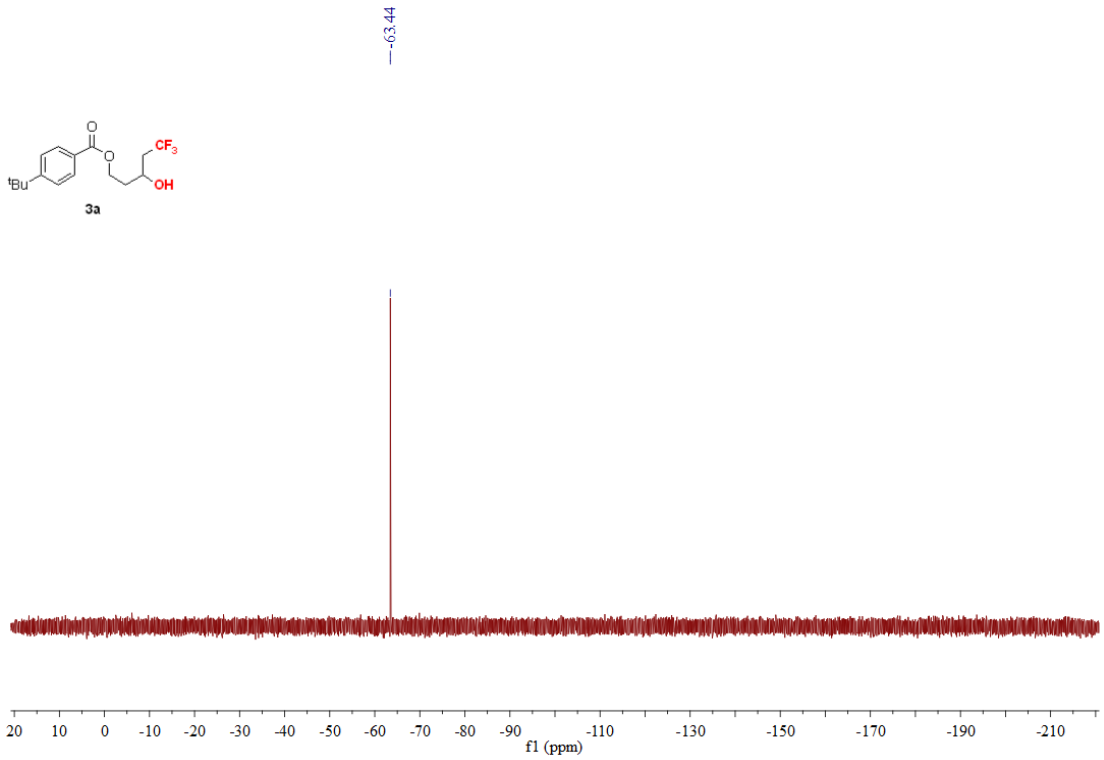
Spectroscopic data for products



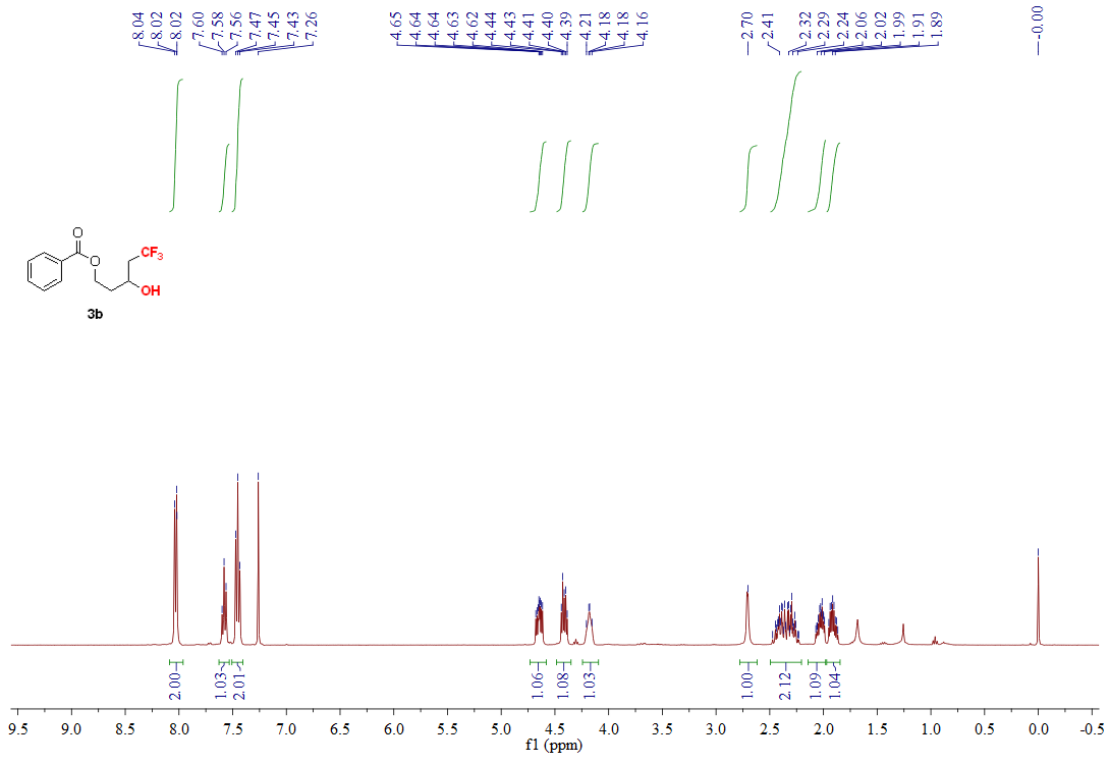
^{1}H NMR Spectrum of Compound **3a**



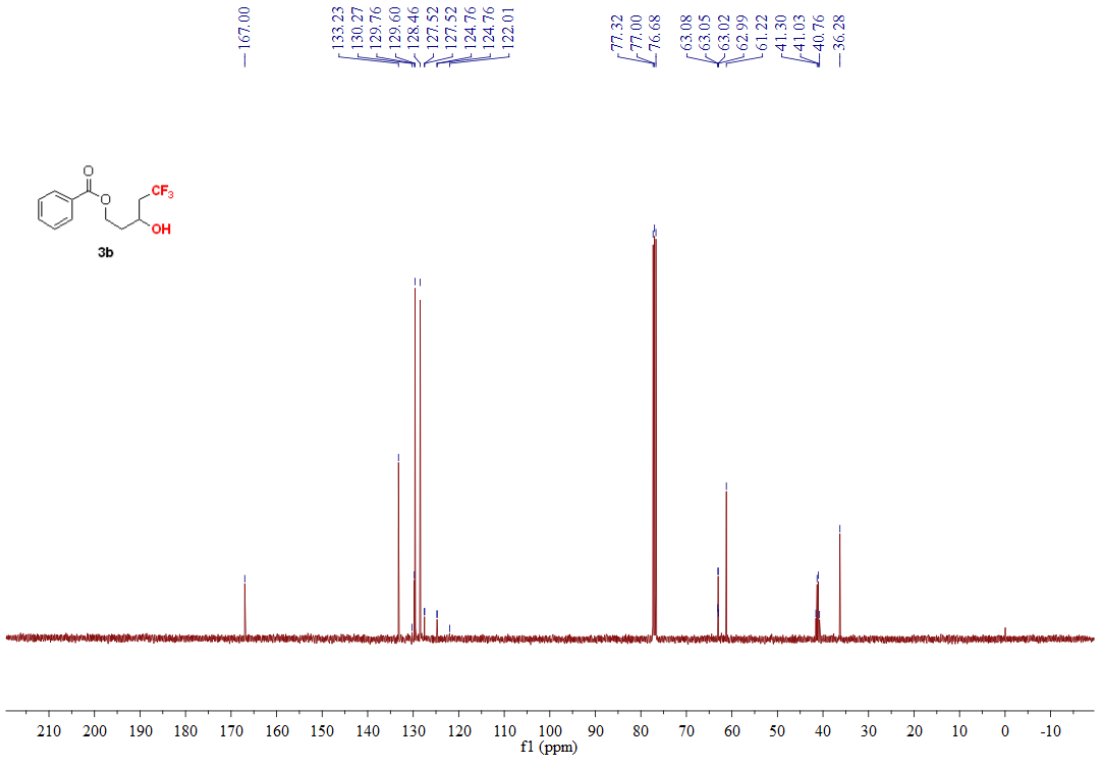
^{13}C NMR Spectrum of Compound **3a**



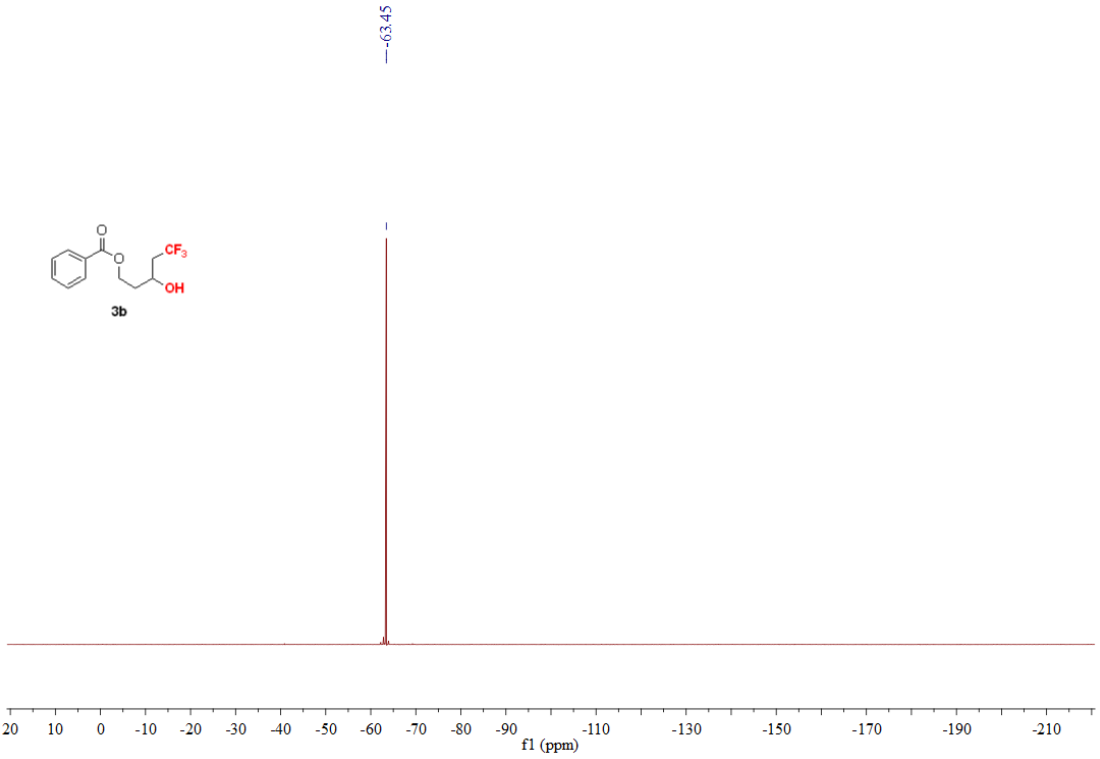
^{19}F NMR Spectrum of Compound **3a**



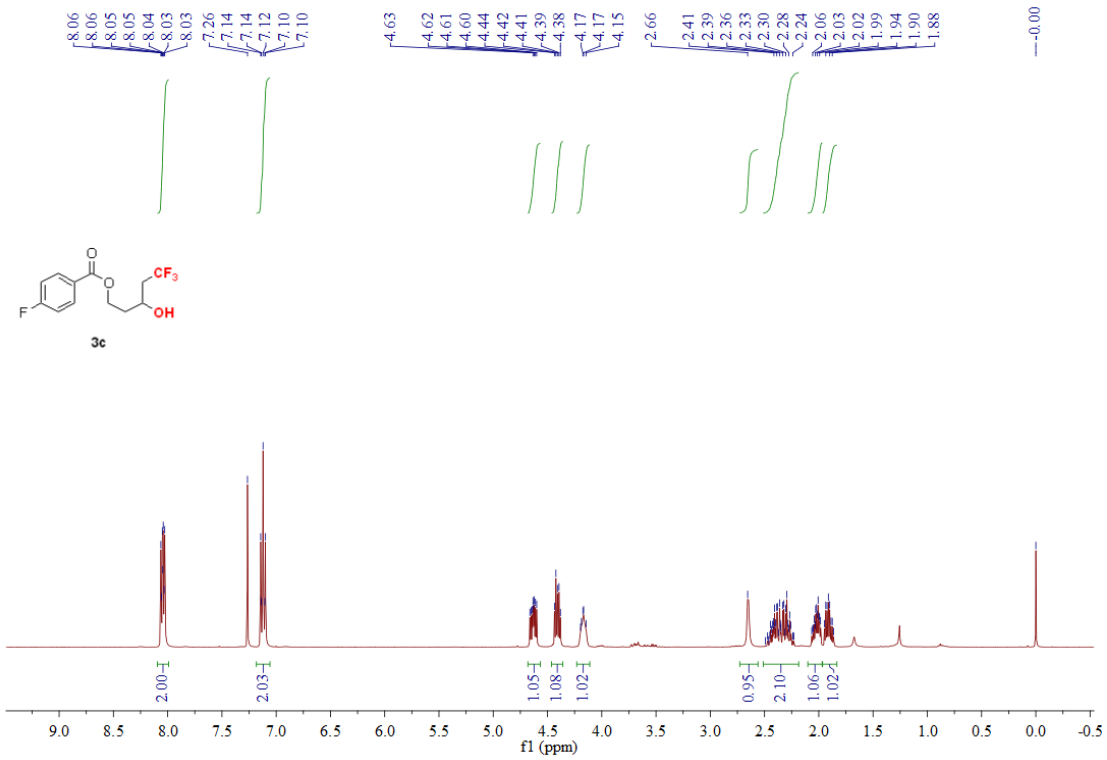
^{1}H NMR Spectrum of Compound **3b**



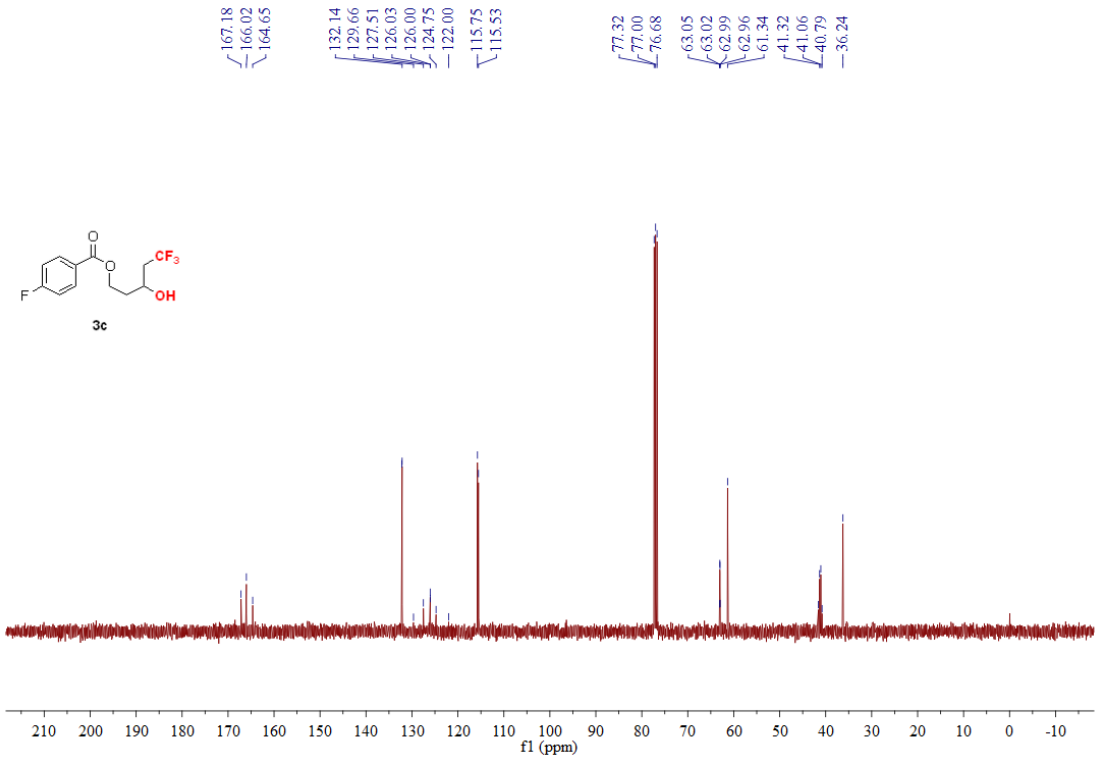
^{13}C NMR Spectrum of Compound **3b**



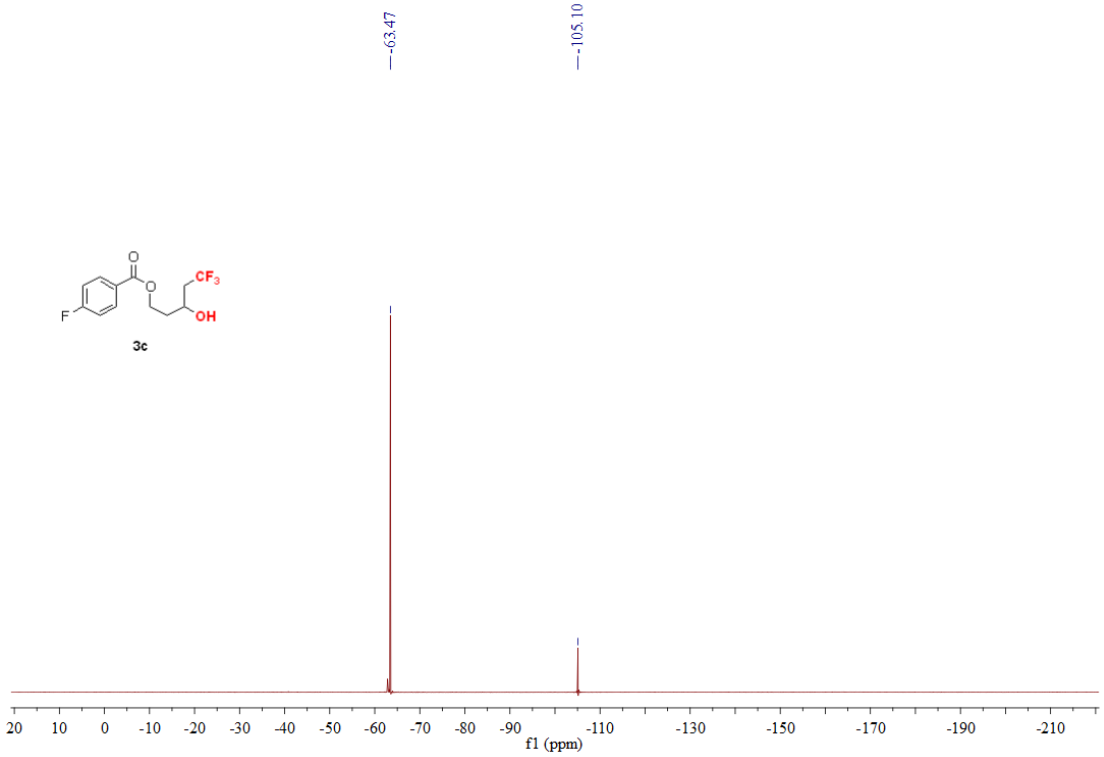
^{19}F NMR Spectrum of Compound **3b**



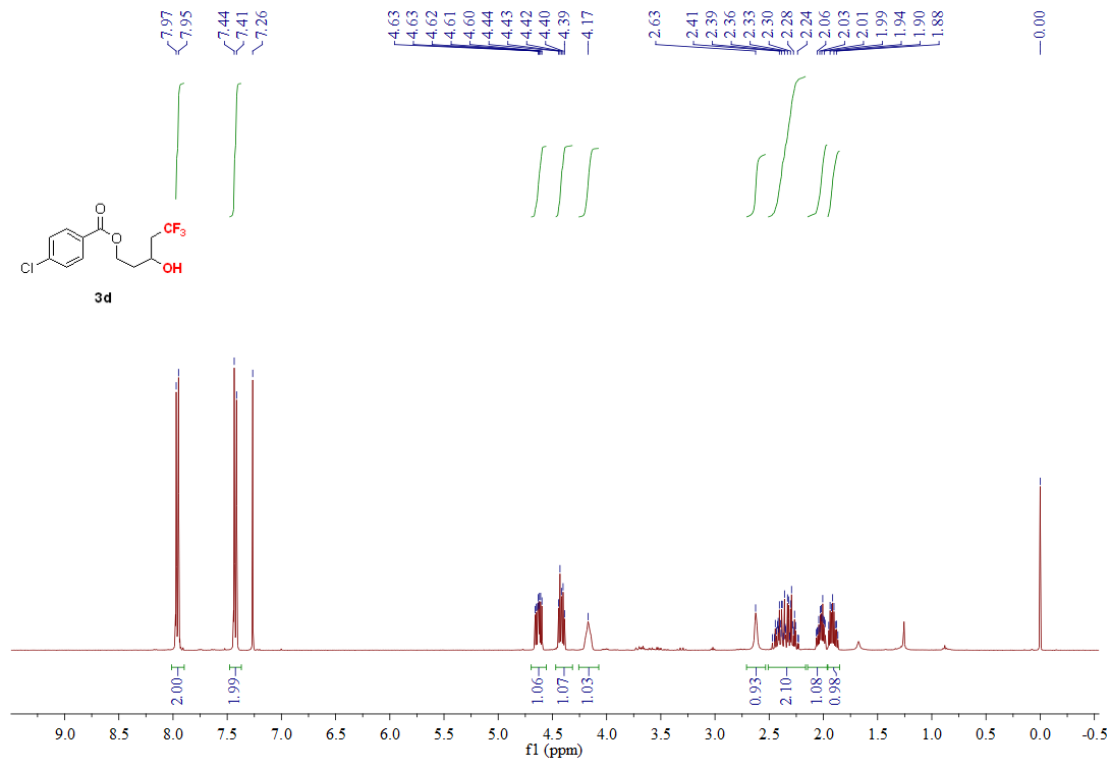
^{1}H NMR Spectrum of Compound **3c**



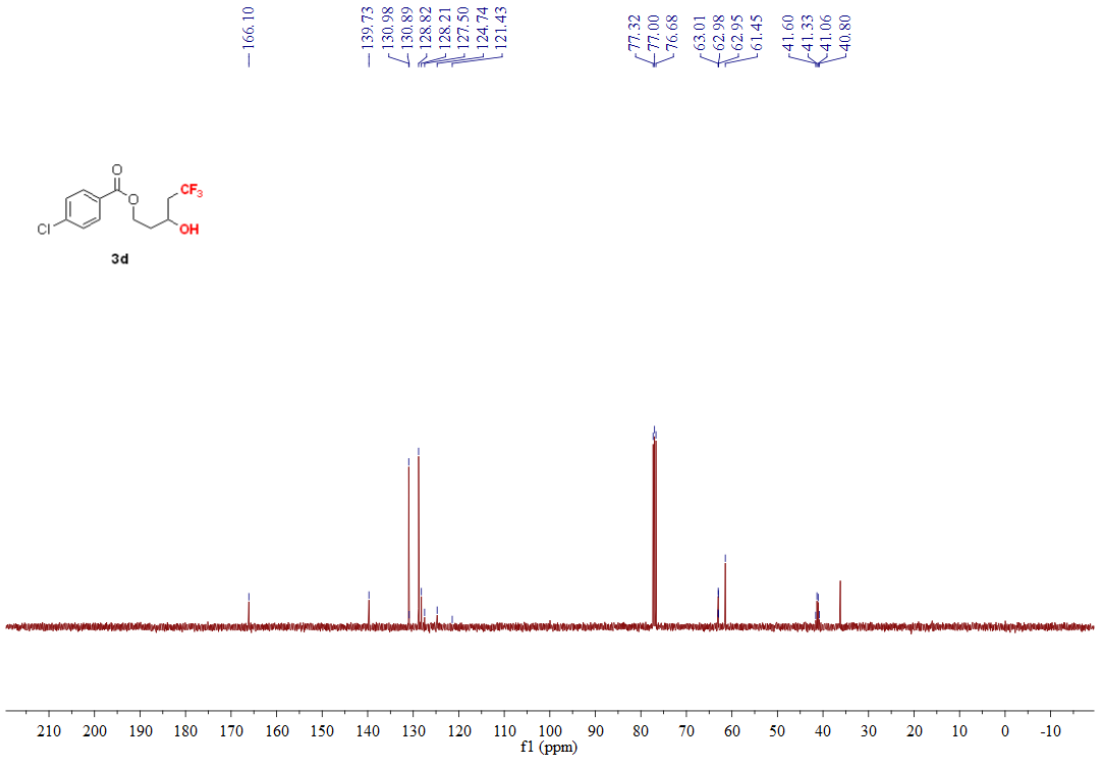
^{13}C NMR Spectrum of Compound **3c**



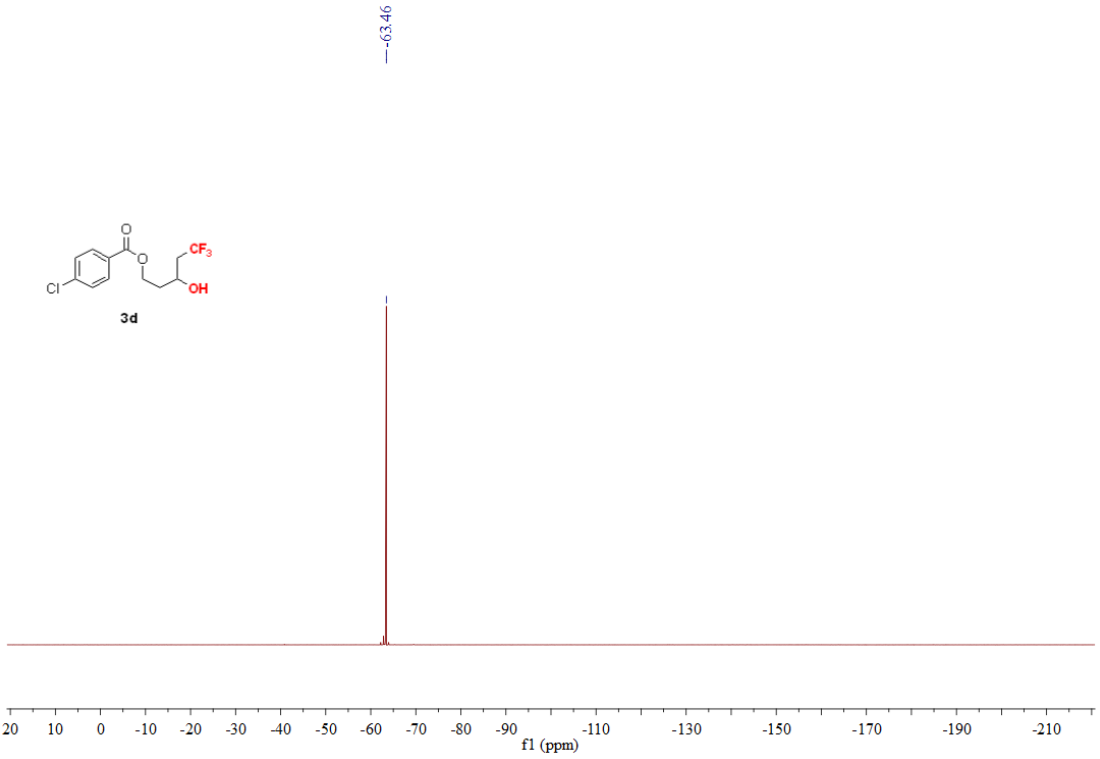
^{19}F NMR Spectrum of Compound **3c**



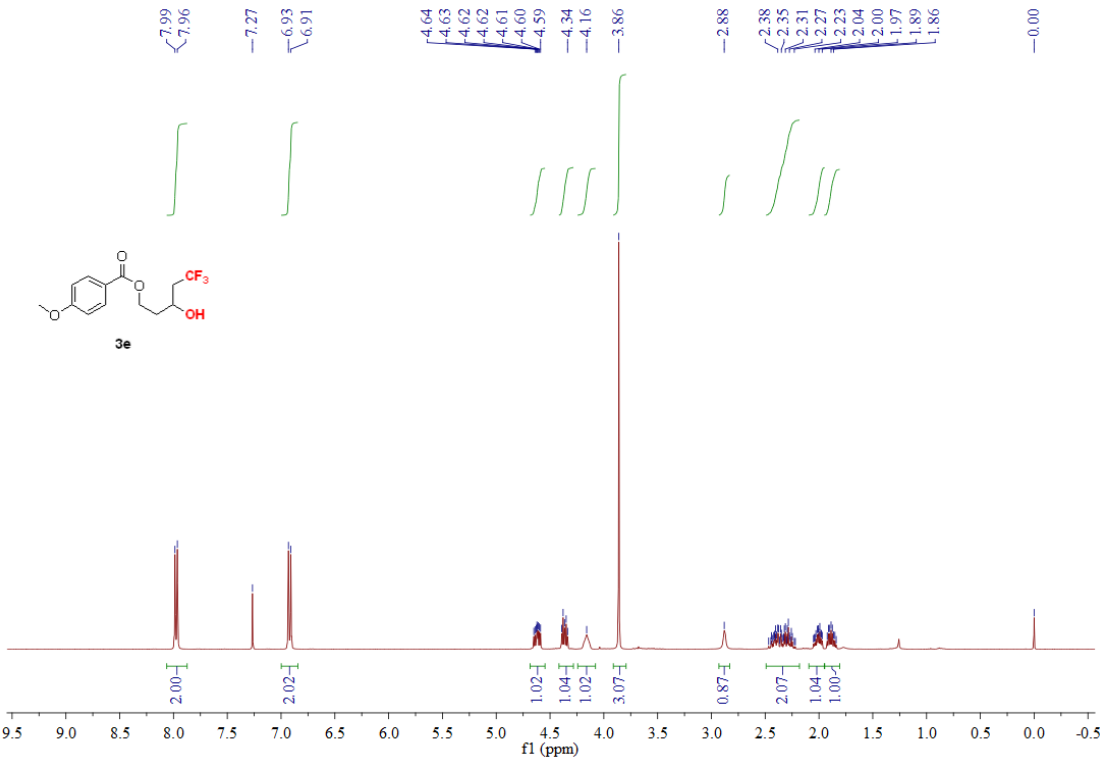
^{1}H NMR Spectrum of Compound **3d**



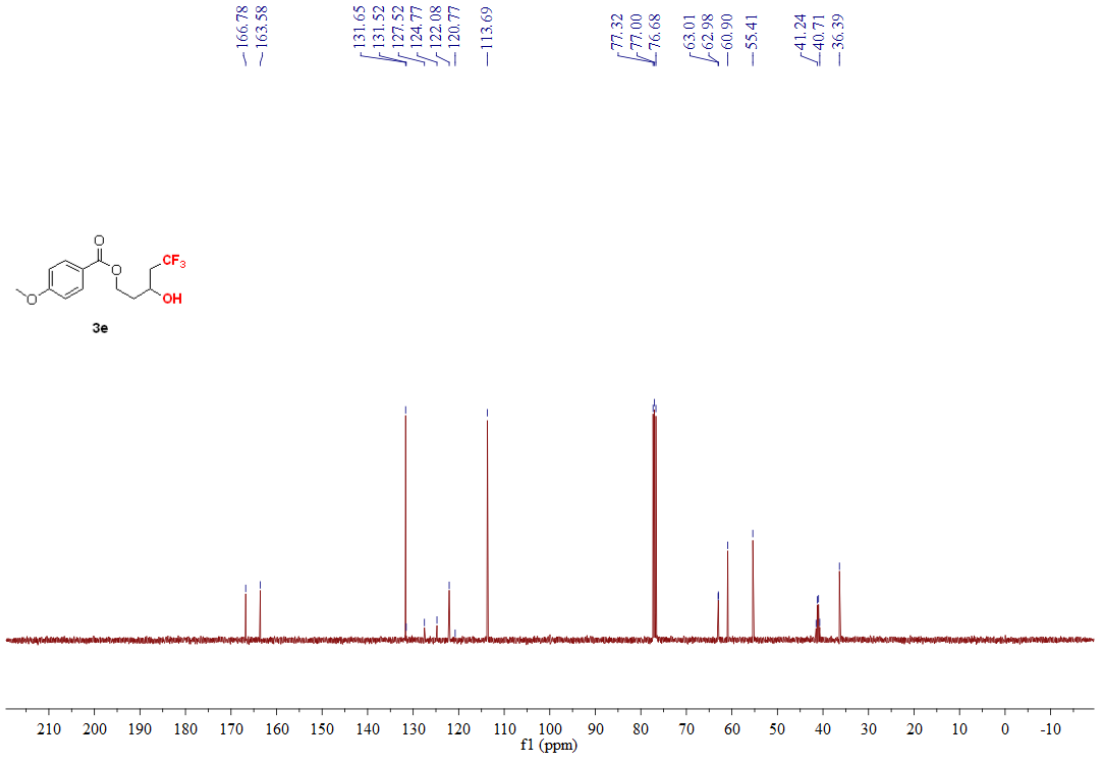
^{13}C NMR Spectrum of Compound **3d**



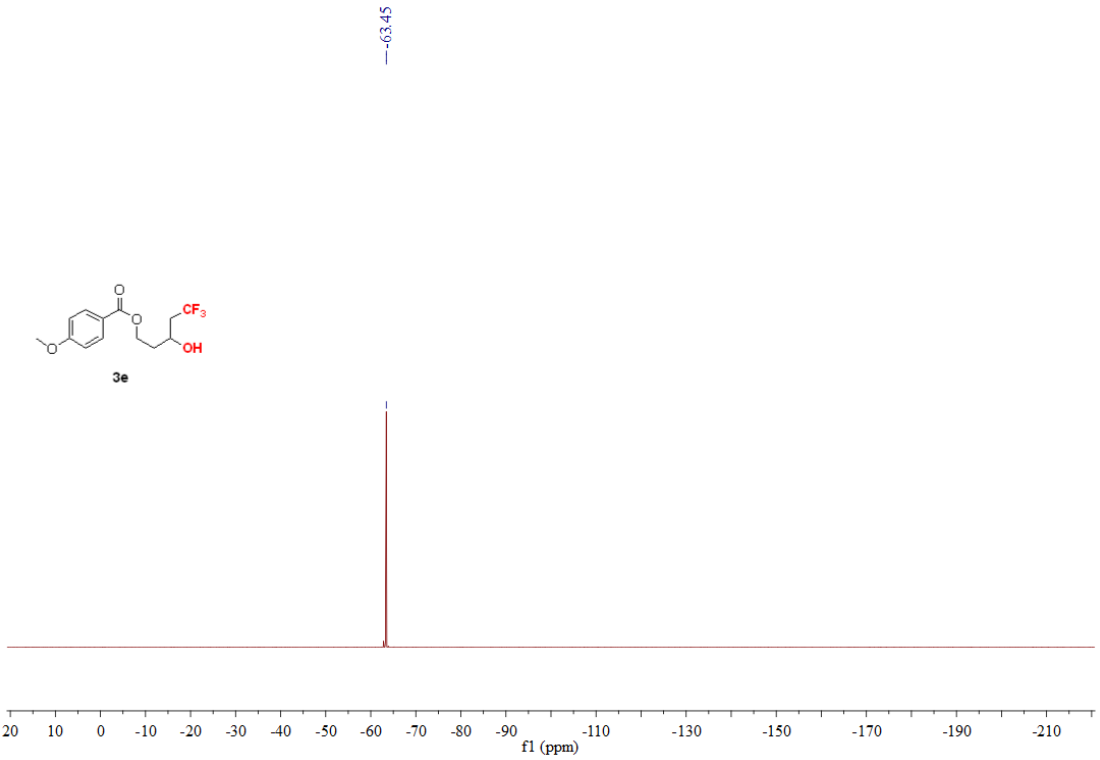
^{19}F NMR Spectrum of Compound **3d**



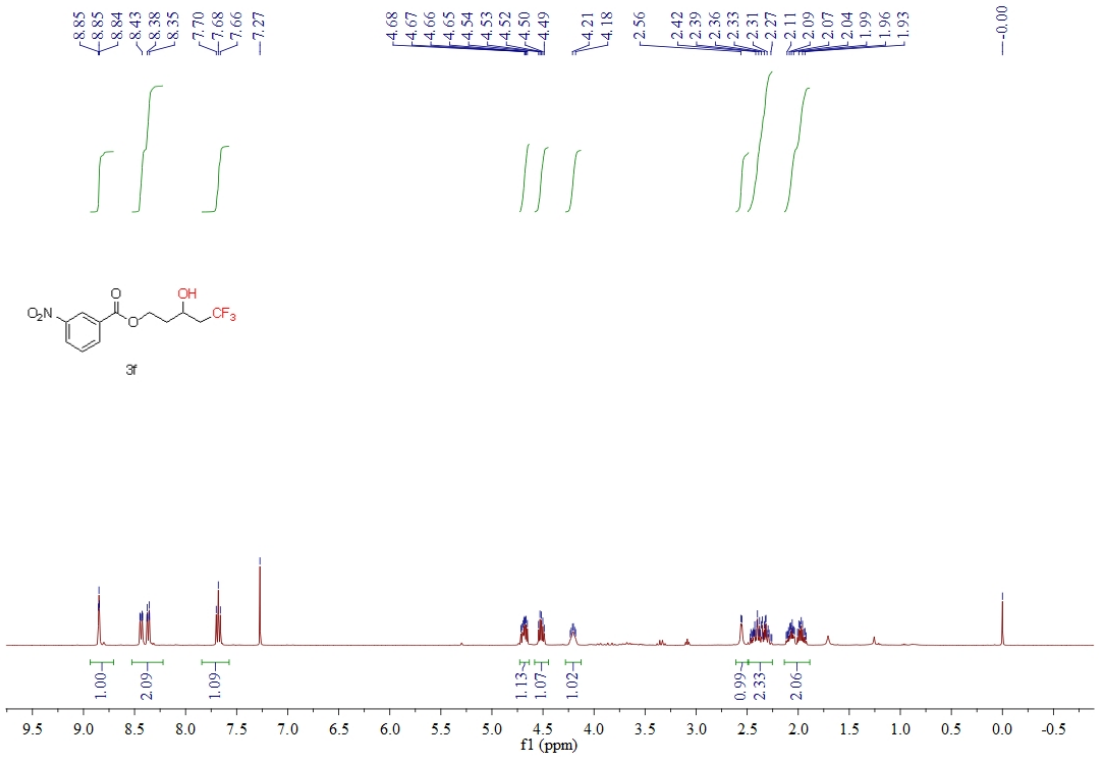
^{1}H NMR Spectrum of Compound **3e**



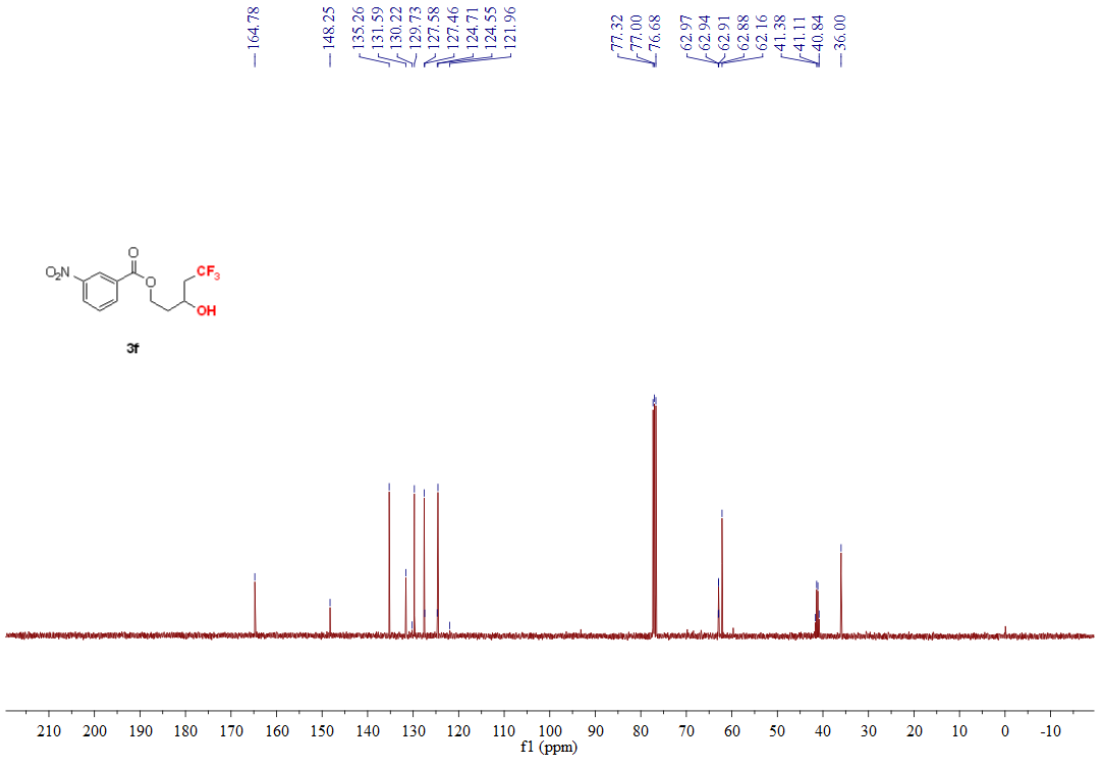
^{13}C NMR Spectrum of Compound **3e**



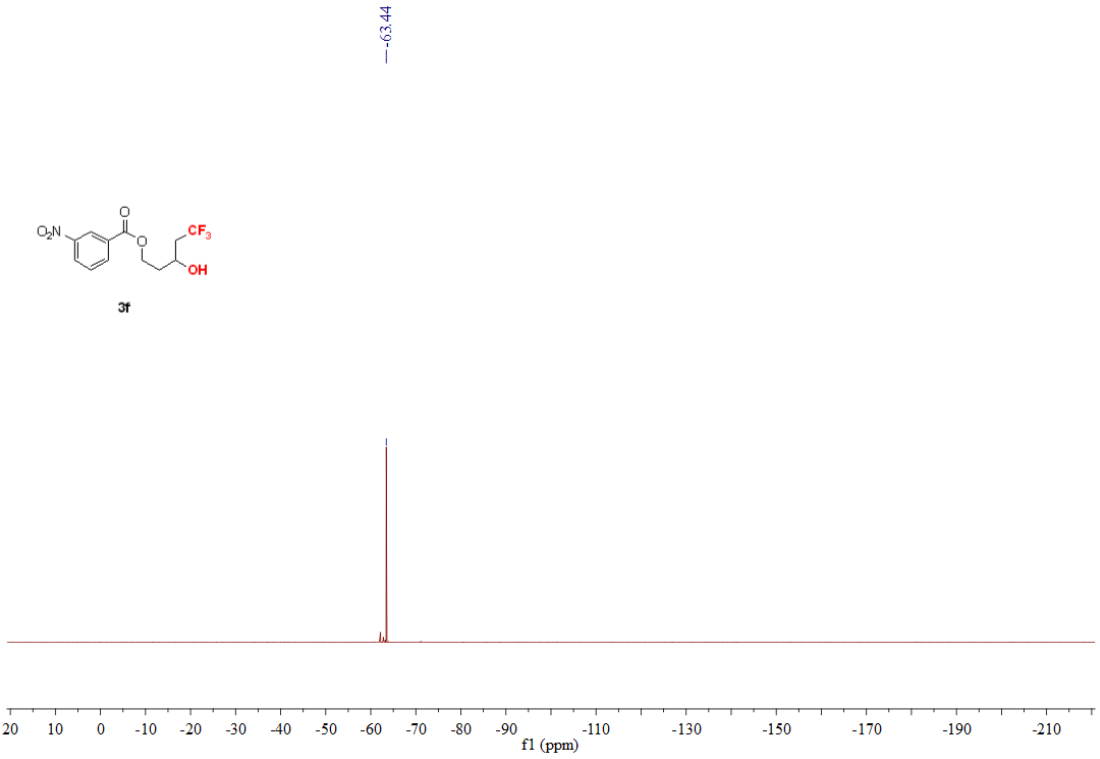
^{19}F NMR Spectrum of Compound **3e**



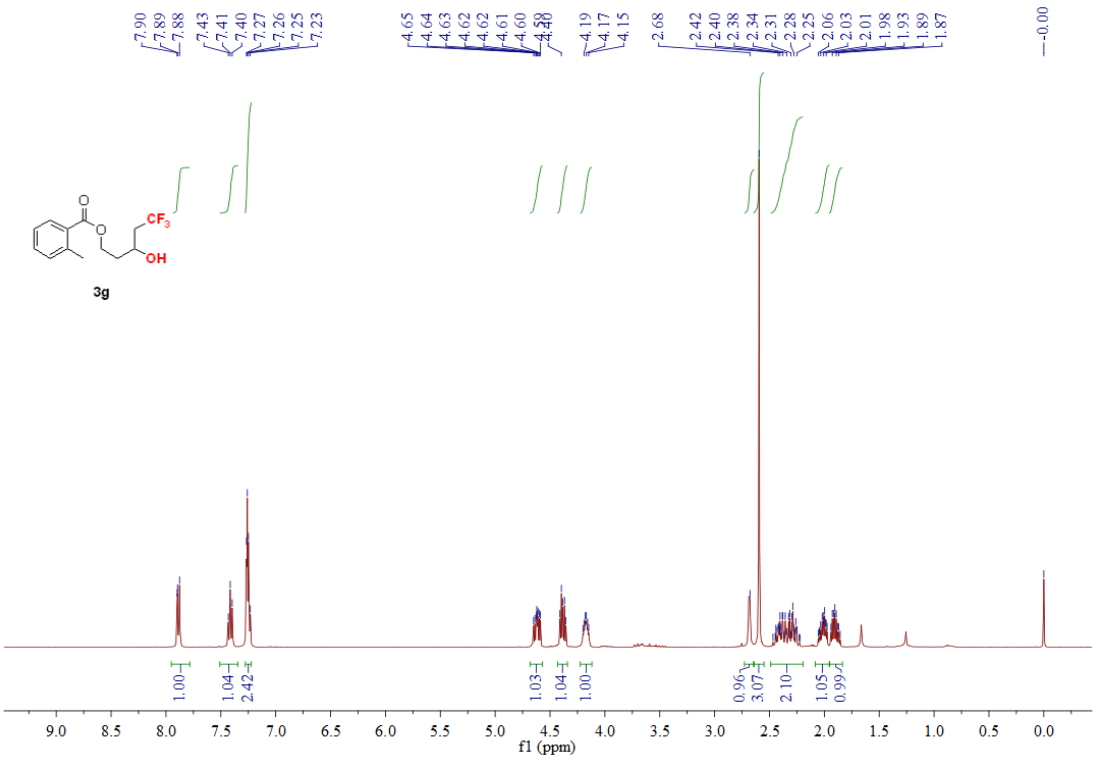
^{1}H NMR Spectrum of Compound **3f**



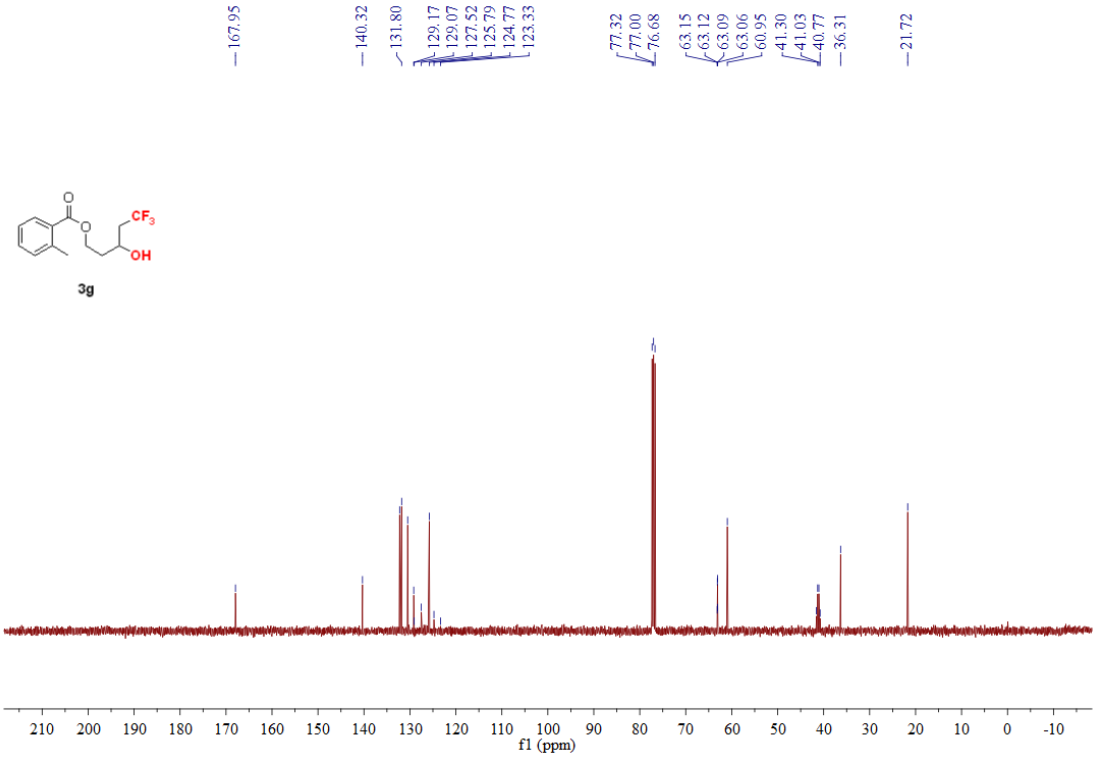
^{13}C NMR Spectrum of Compound **3f**



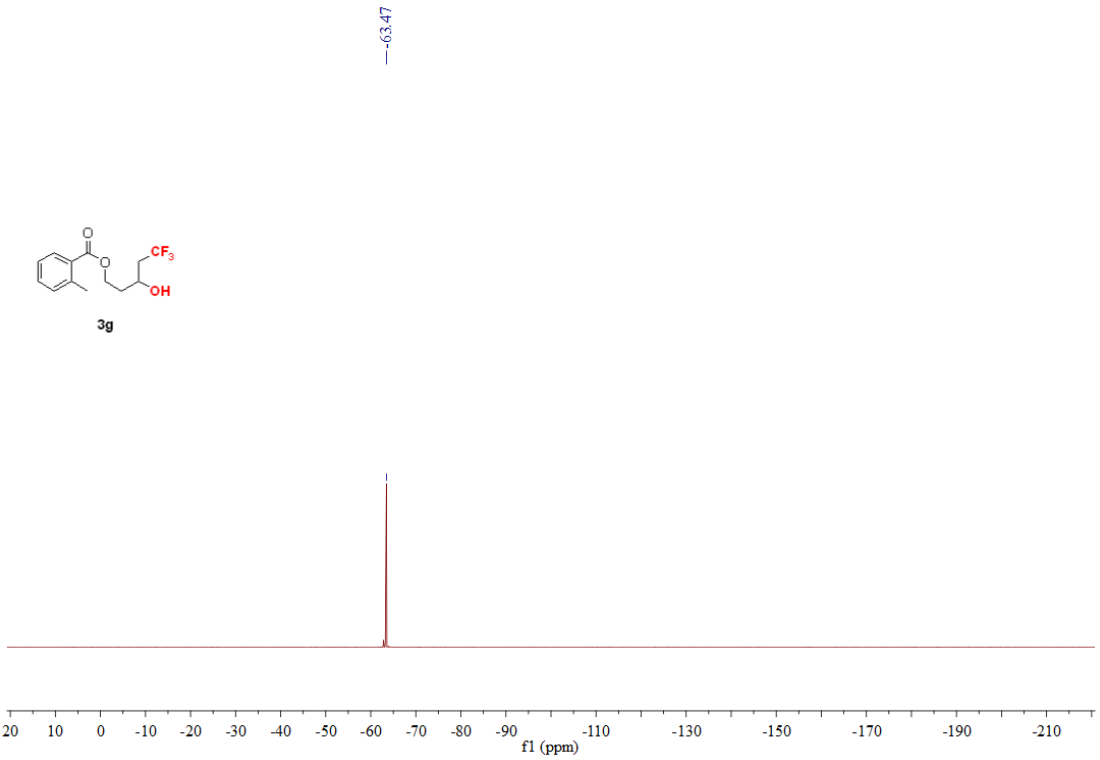
^{19}F NMR Spectrum of Compound **3f**



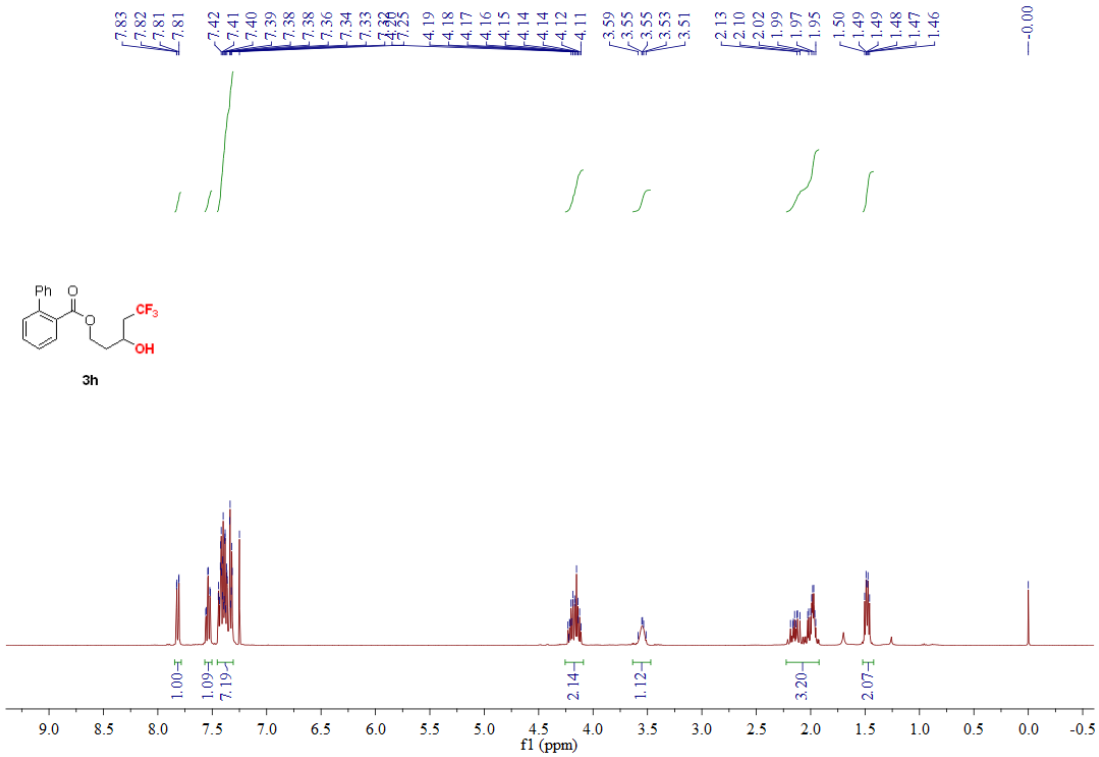
^{1}H NMR Spectrum of Compound **3g**



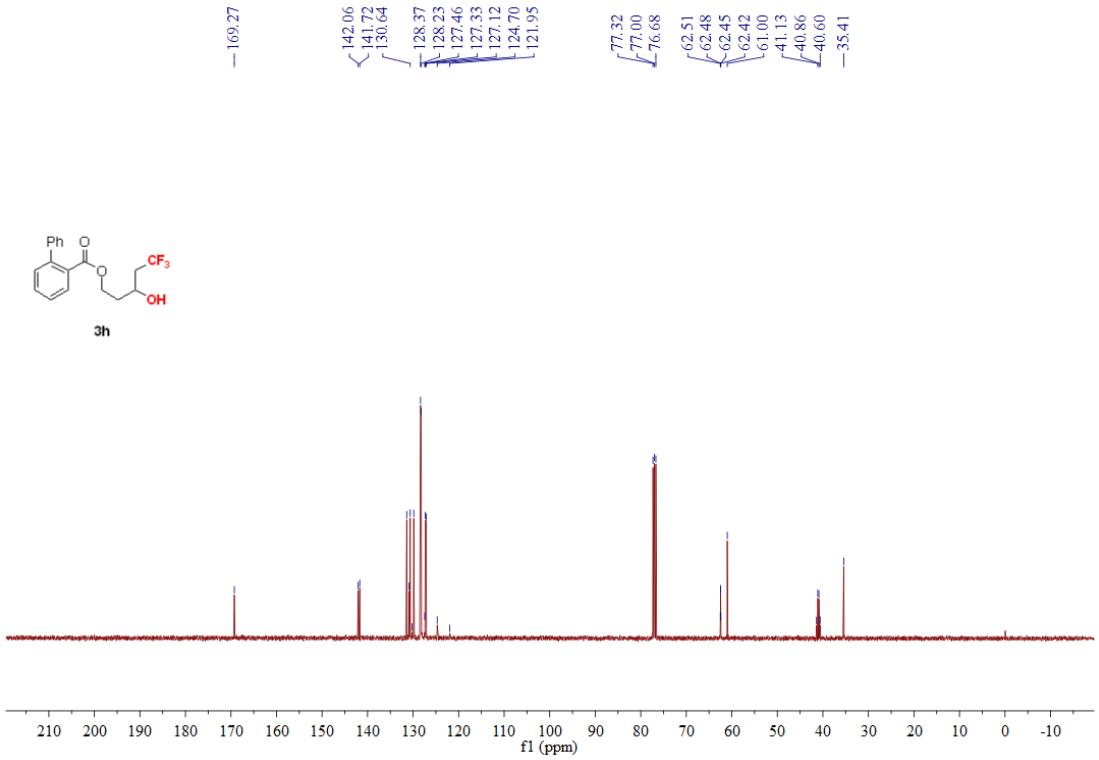
^{13}C NMR Spectrum of Compound **3g**



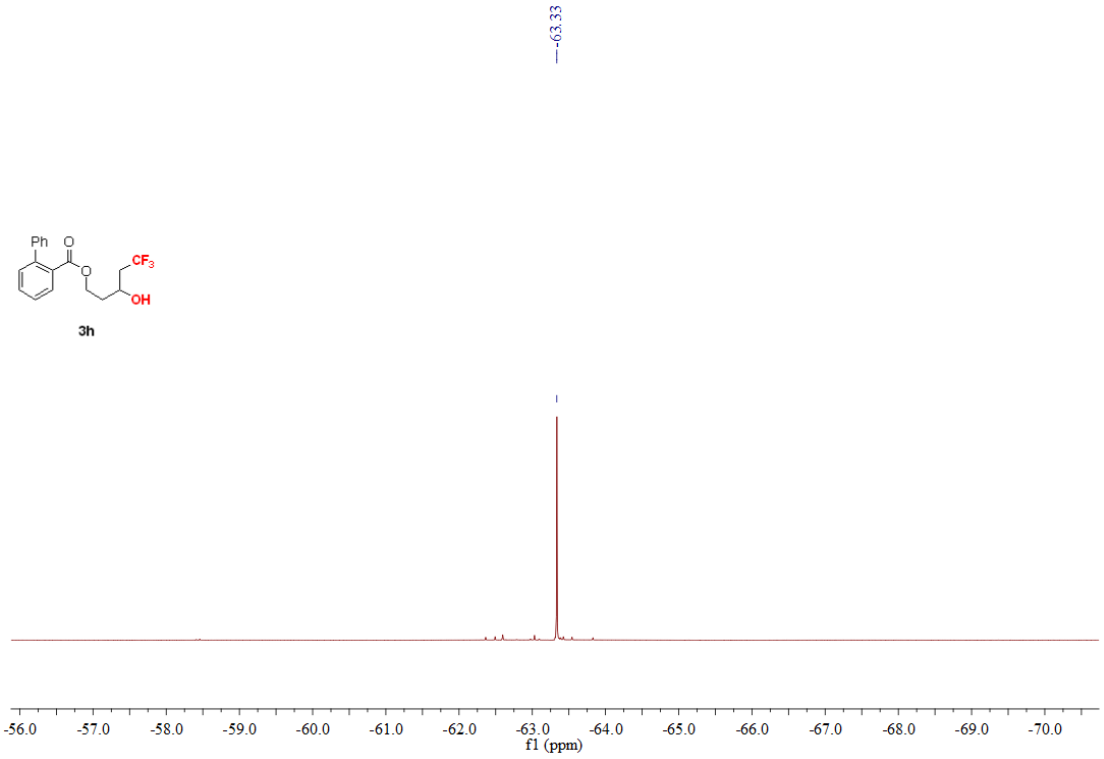
^{19}F NMR Spectrum of Compound **3g**



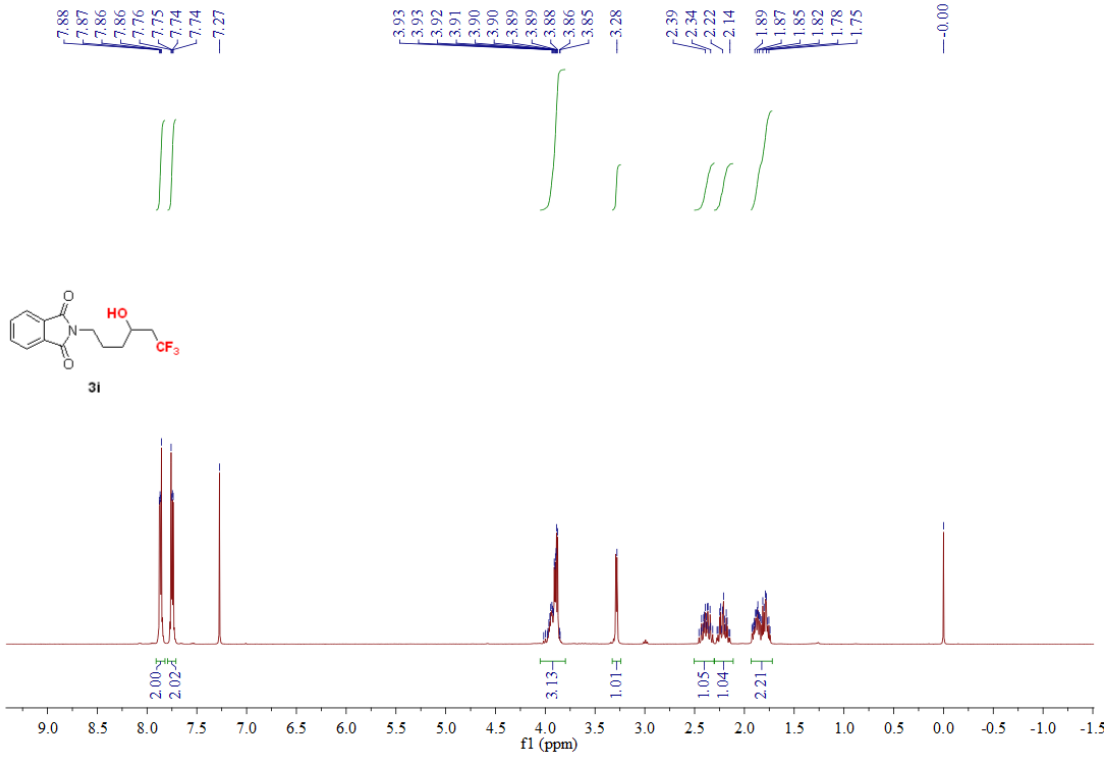
^{1}H NMR Spectrum of Compound **3h**



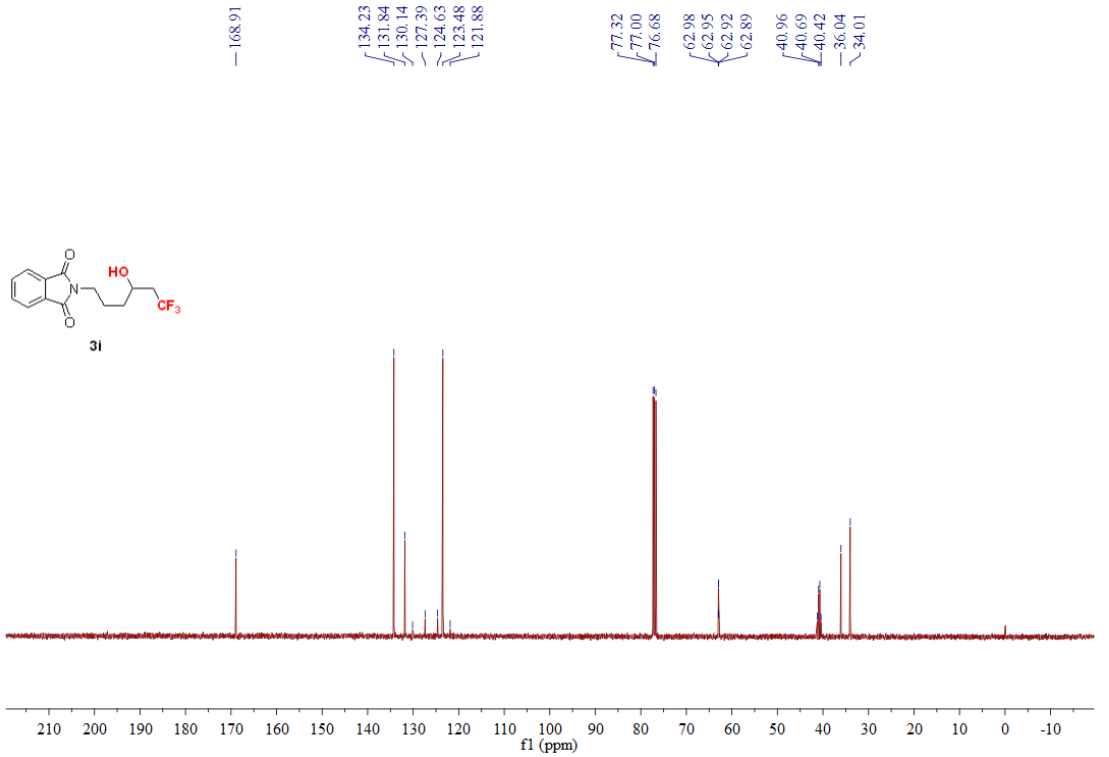
^{13}C NMR Spectrum of Compound **3h**



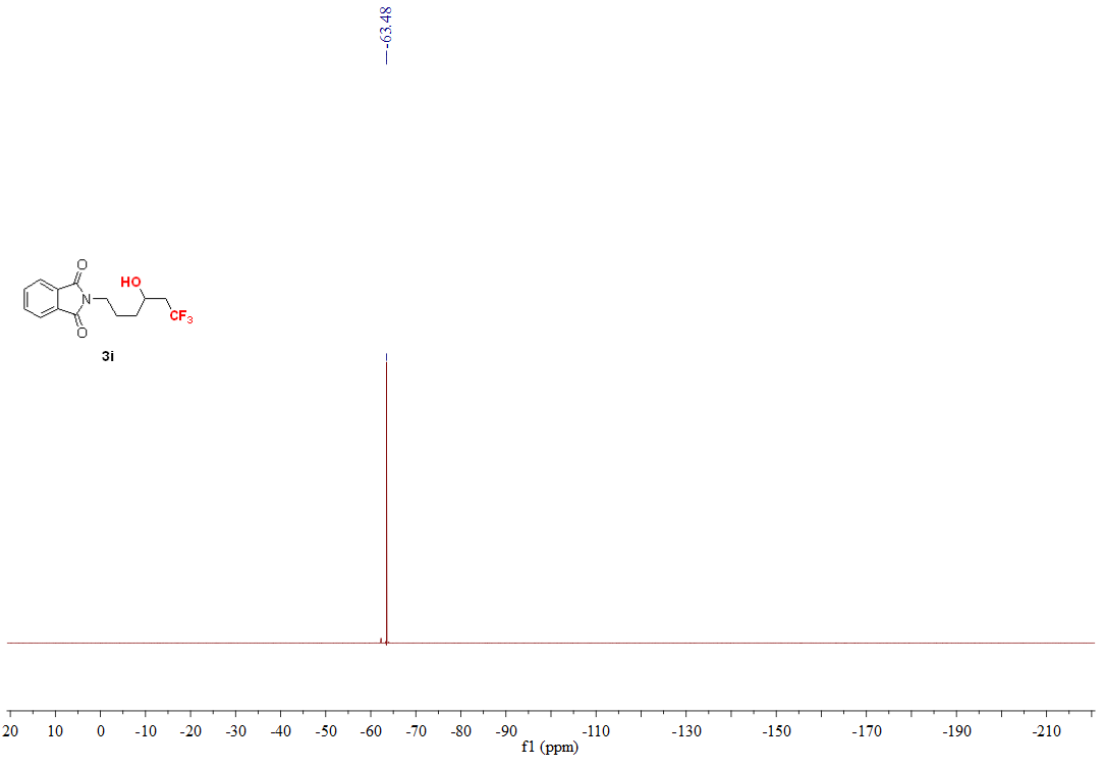
^{19}F NMR Spectrum of Compound **3h**



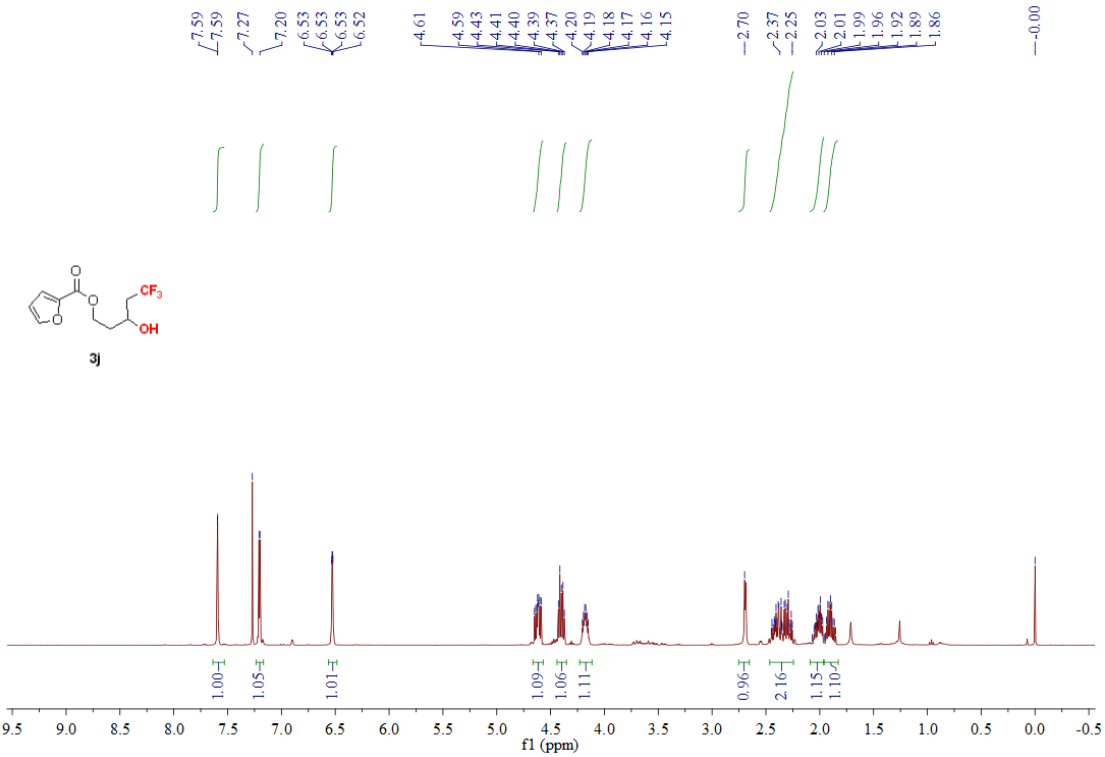
^{1}H NMR Spectrum of Compound **3i**



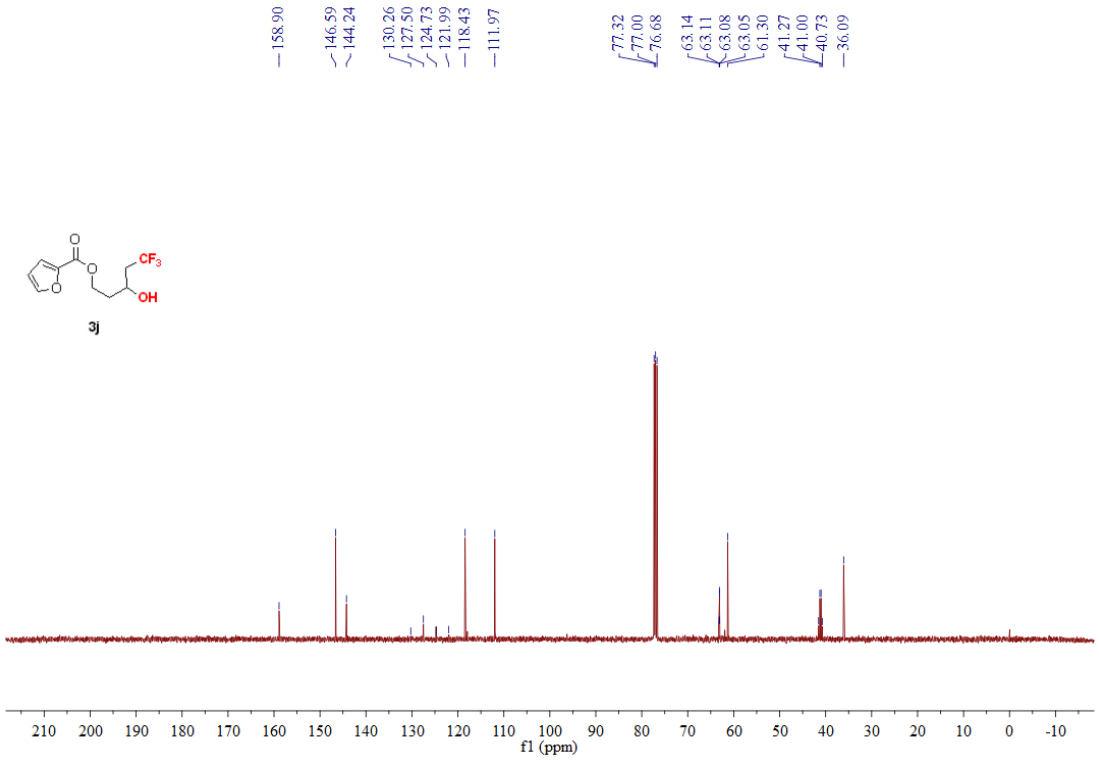
^{13}C NMR Spectrum of Compound **3i**



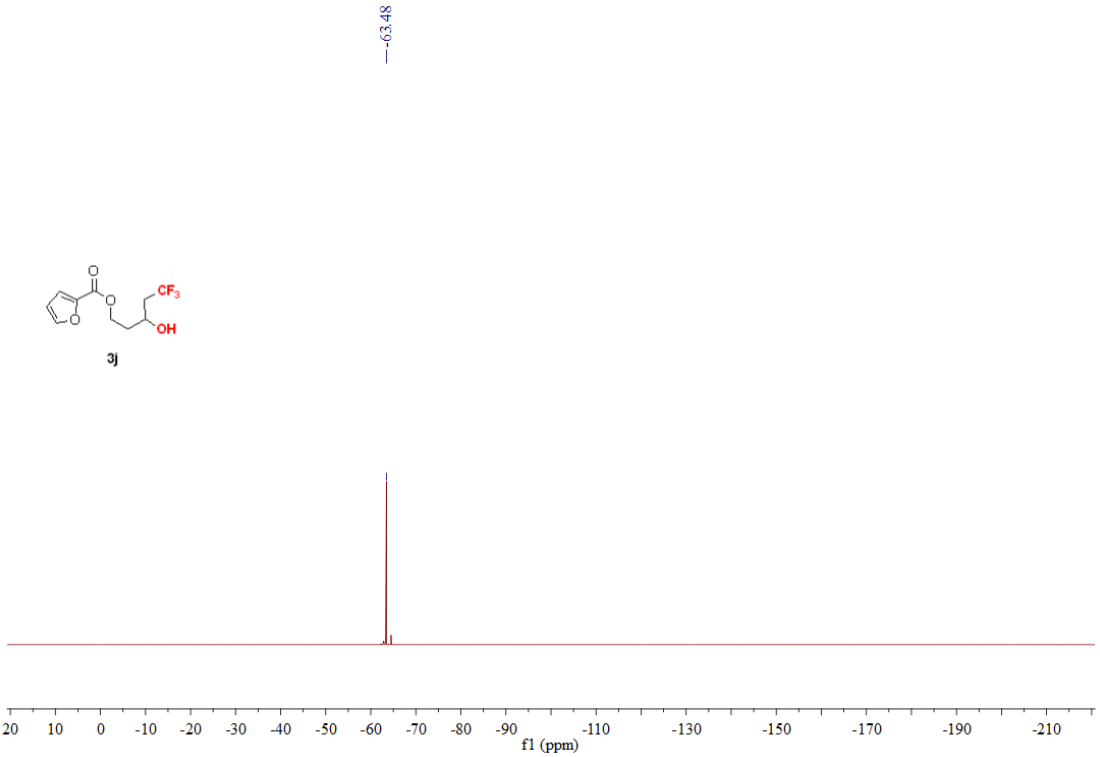
^{19}F NMR Spectrum of Compound **3i**



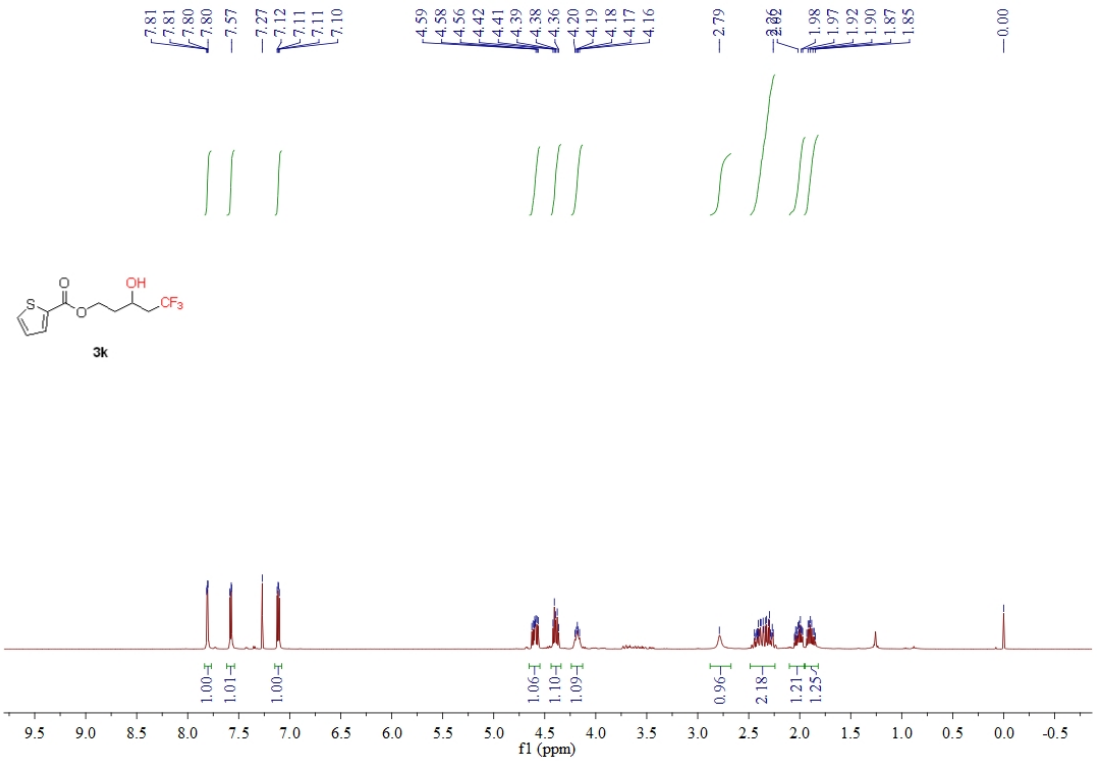
^{1}H NMR Spectrum of Compound **3j**



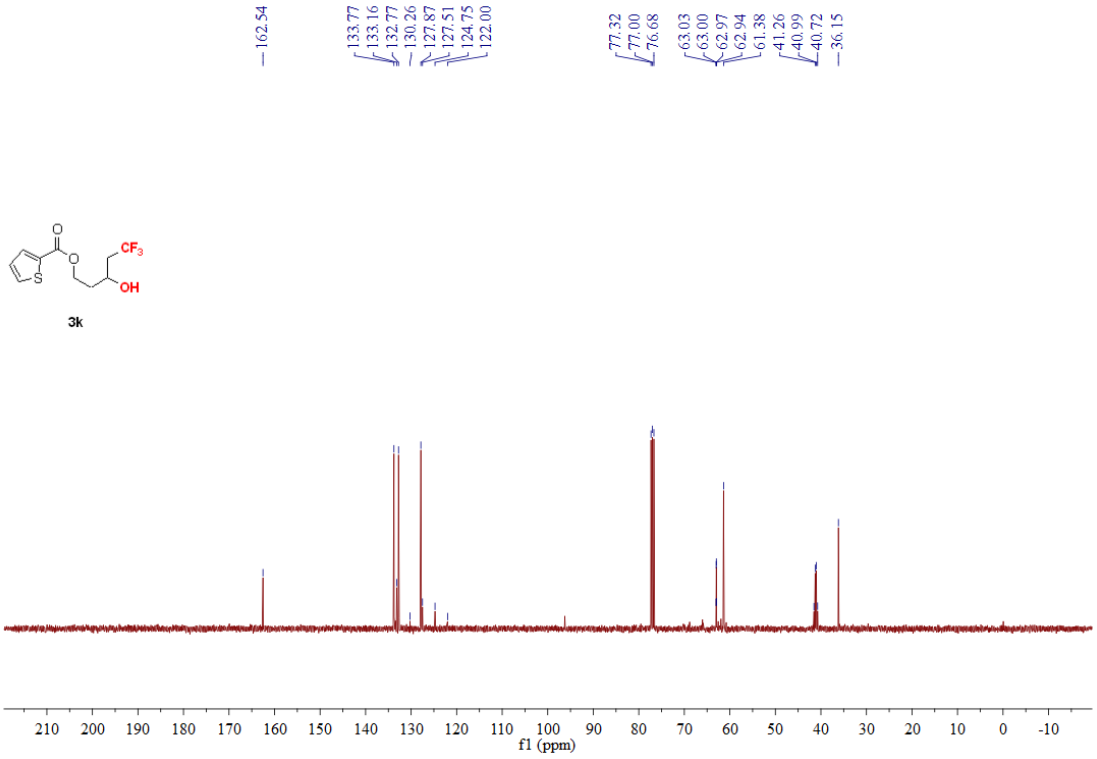
^{13}C NMR Spectrum of Compound **3j**



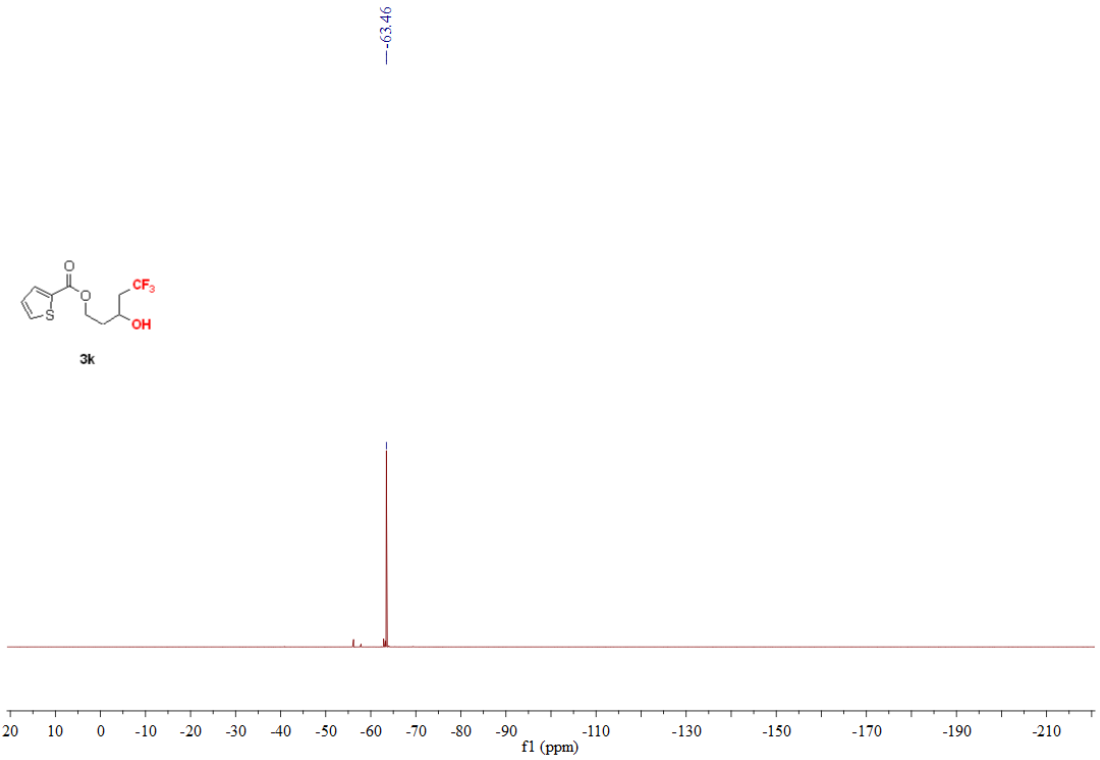
^{19}F NMR Spectrum of Compound **3j**



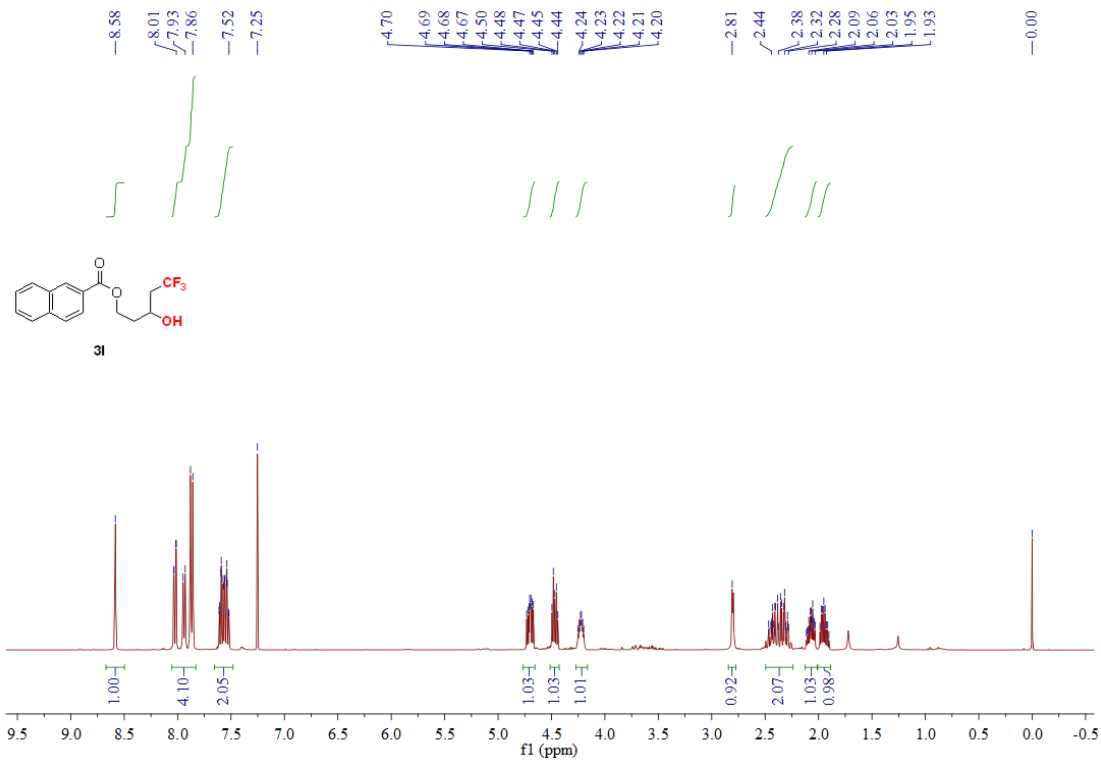
^{1}H NMR Spectrum of Compound **3k**



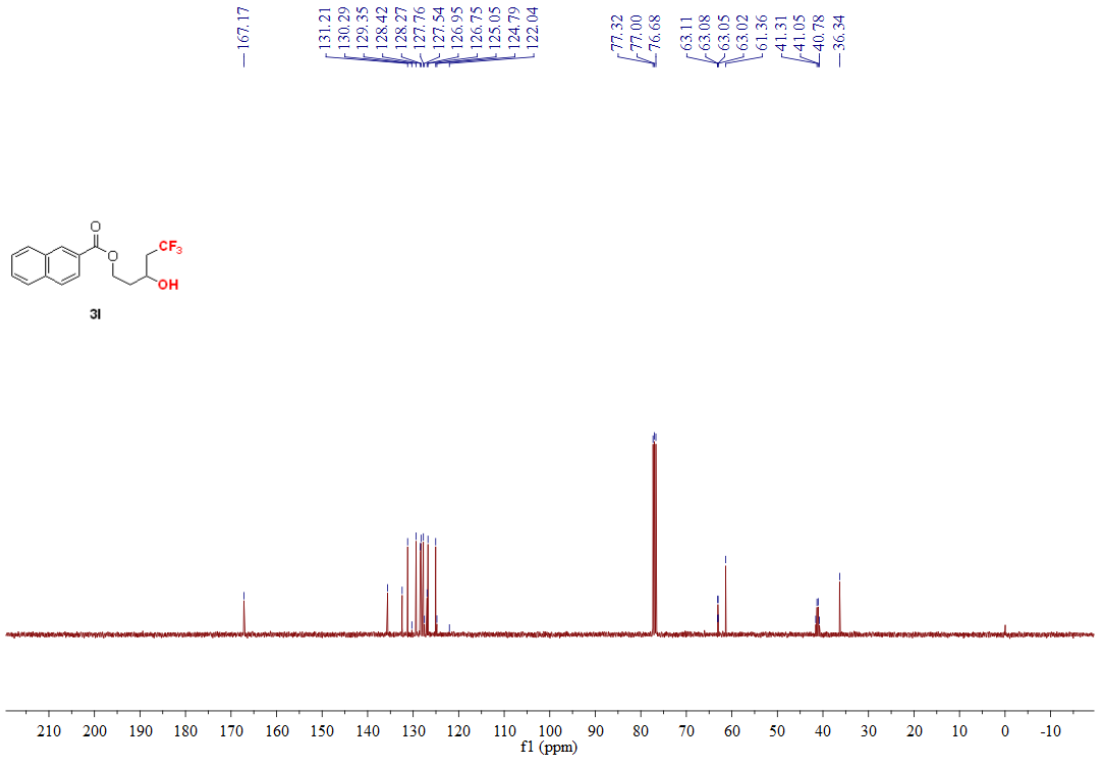
^{13}C NMR Spectrum of Compound **3k**



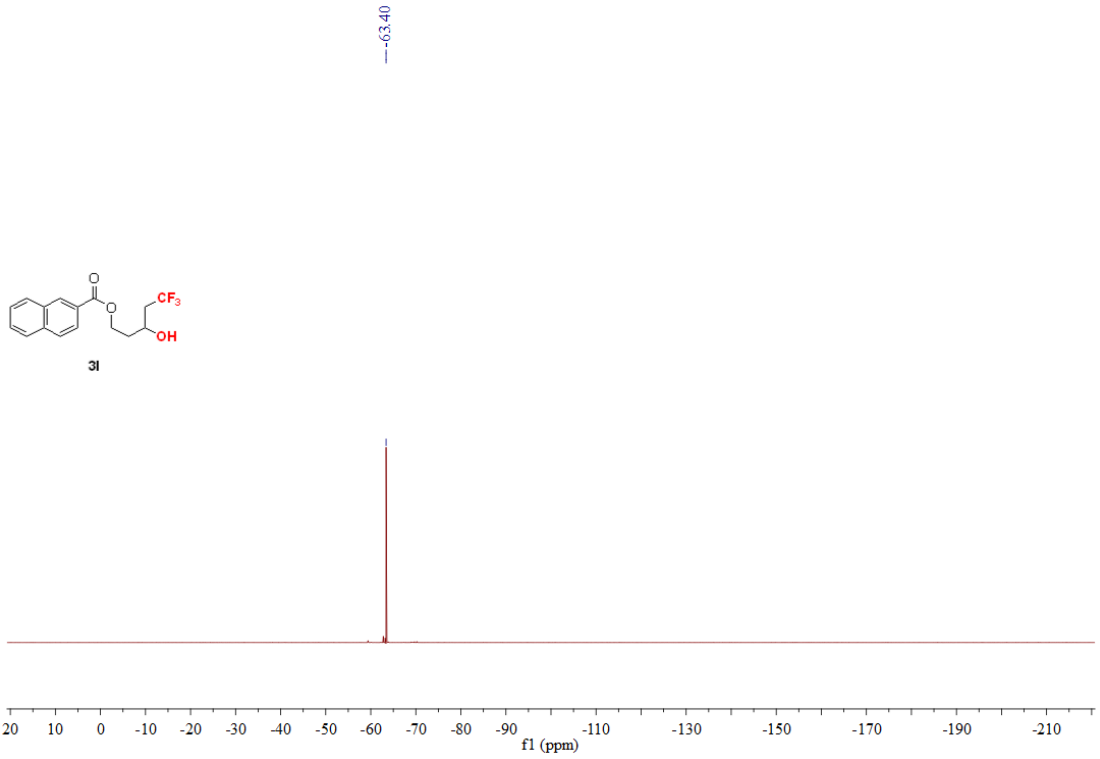
^{19}F NMR Spectrum of Compound **3k**



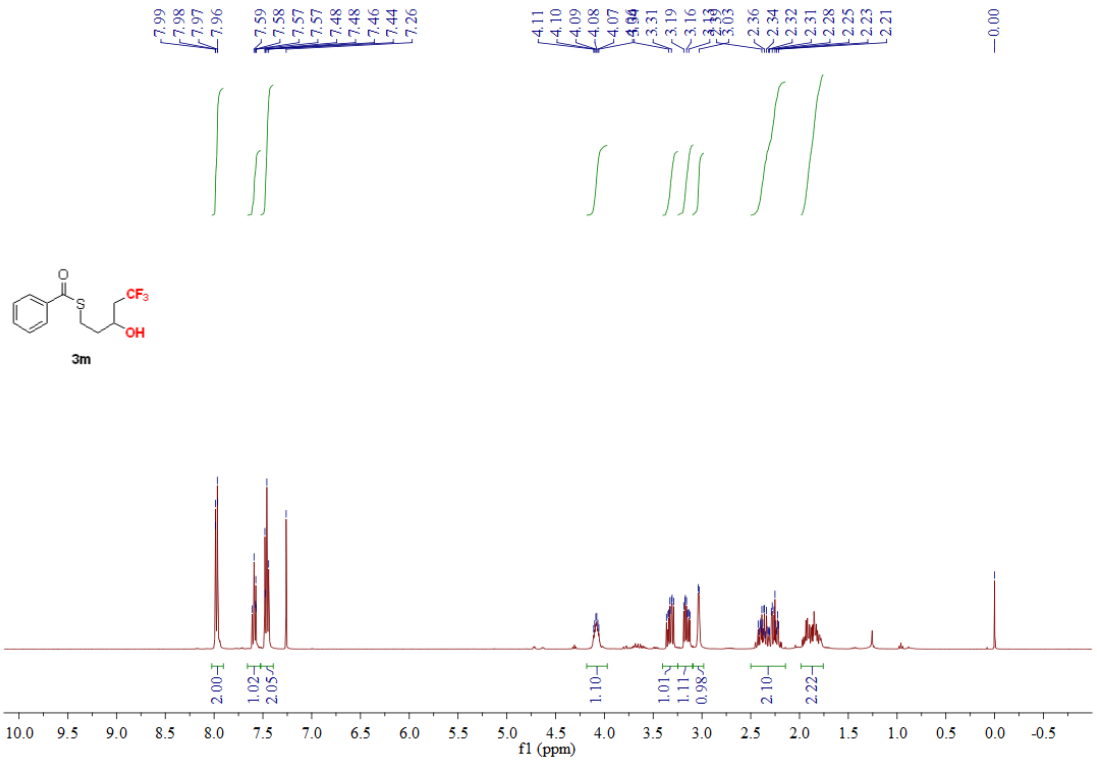
^{1}H NMR Spectrum of Compound **3l**



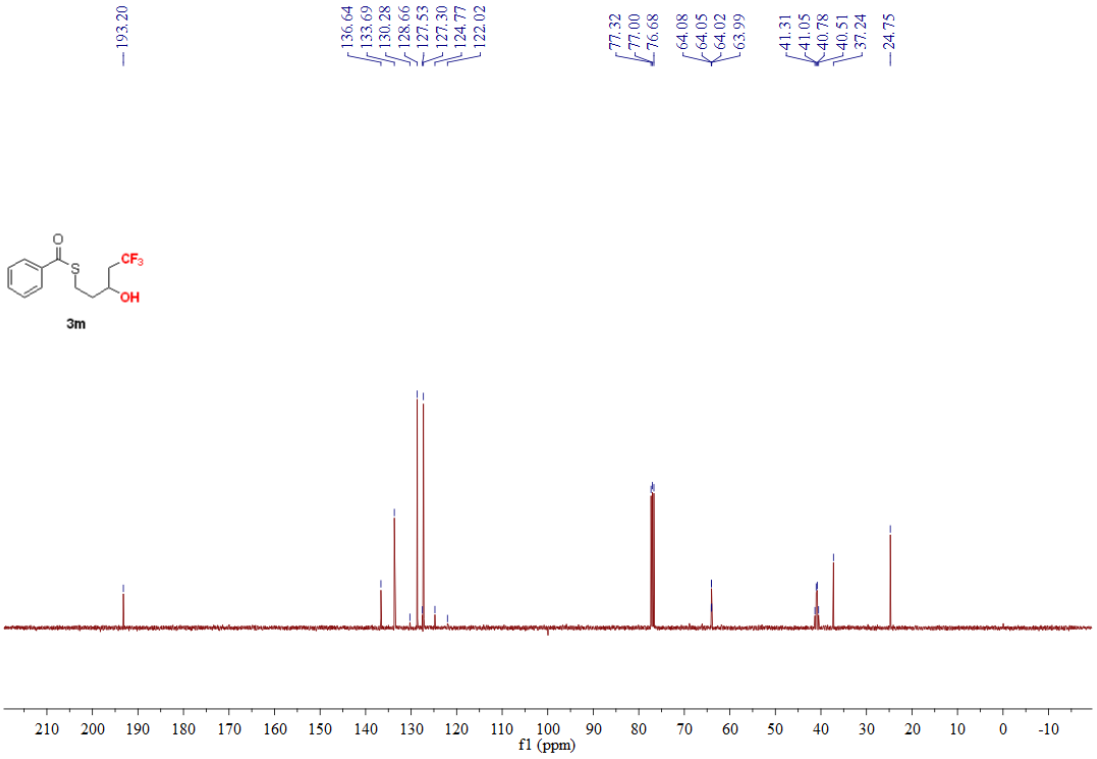
^{13}C NMR Spectrum of Compound **3l**



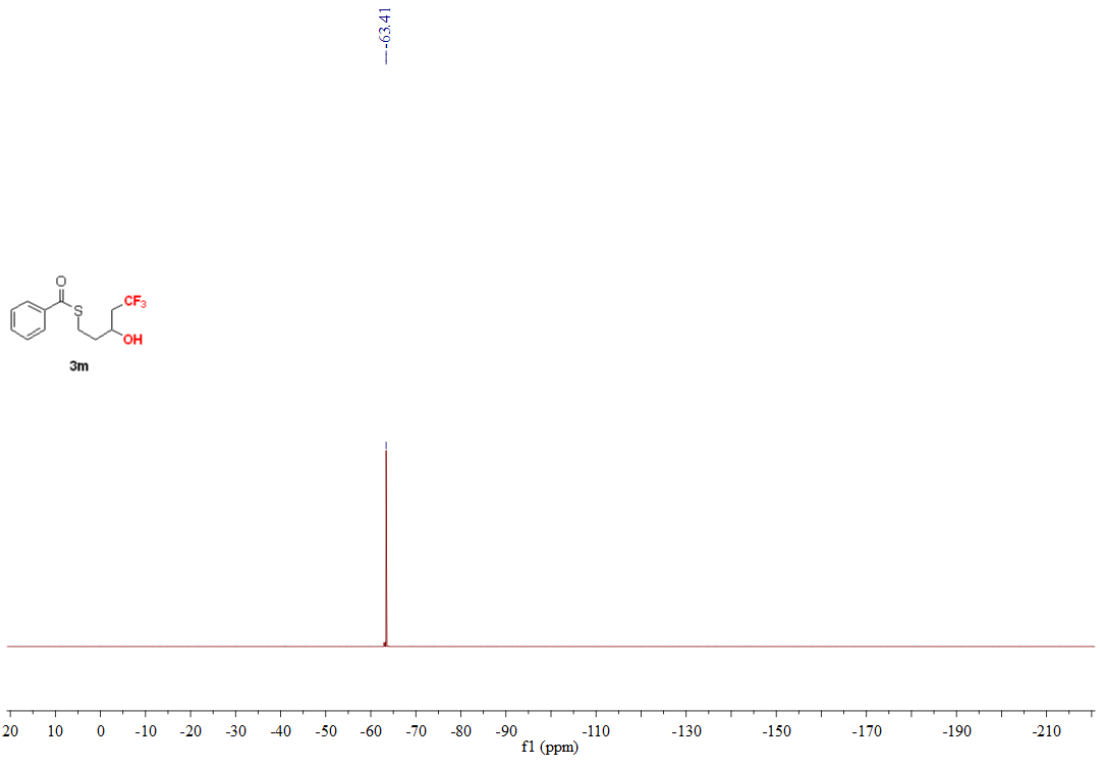
^{19}F NMR Spectrum of Compound **3l**



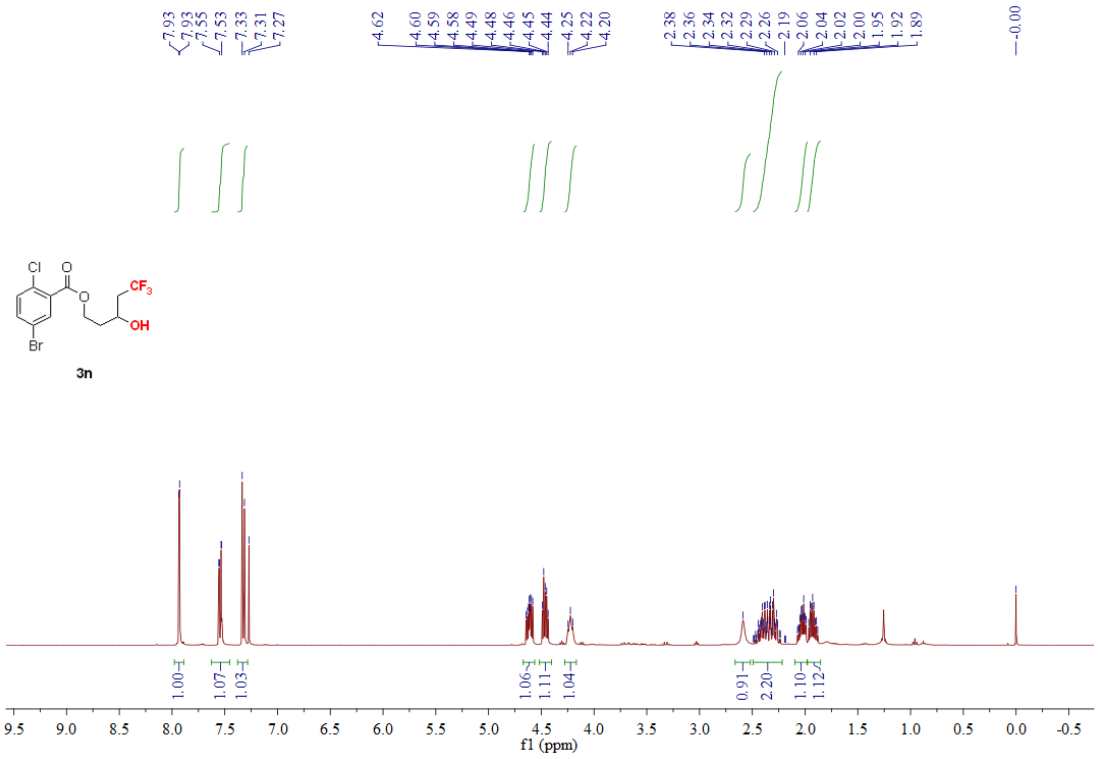
^{1}H NMR Spectrum of Compound **3m**



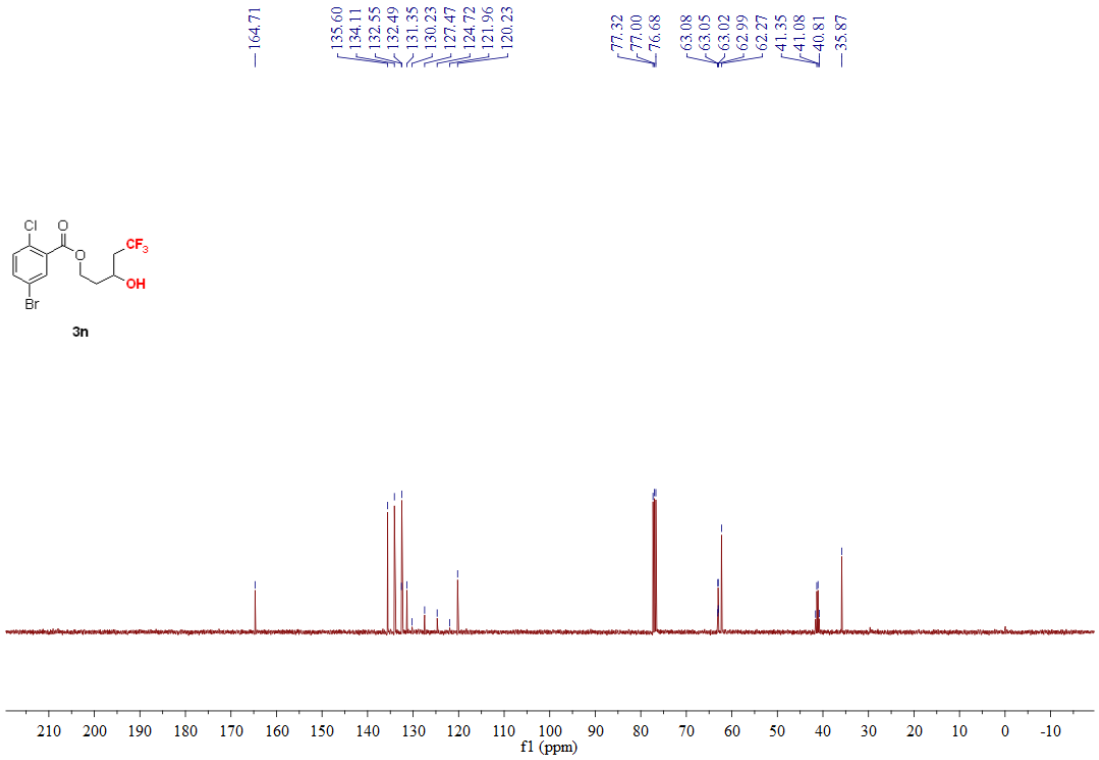
^{13}C NMR Spectrum of Compound **3m**



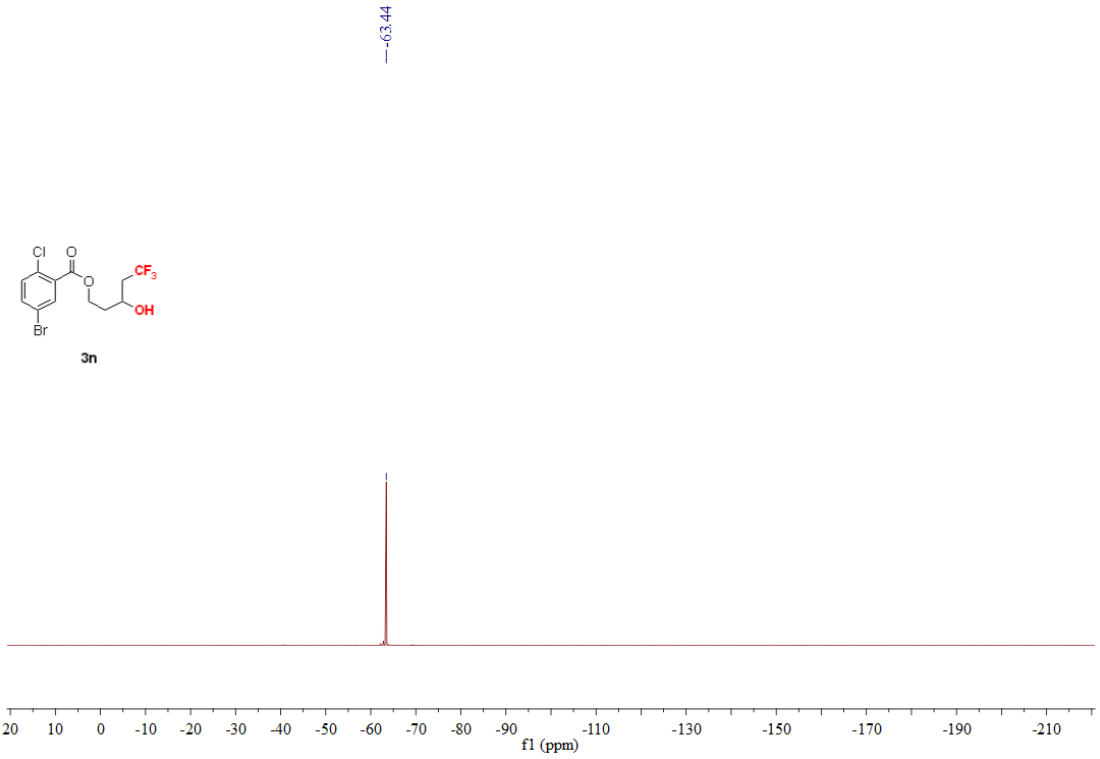
^{19}F NMR Spectrum of Compound **3m**



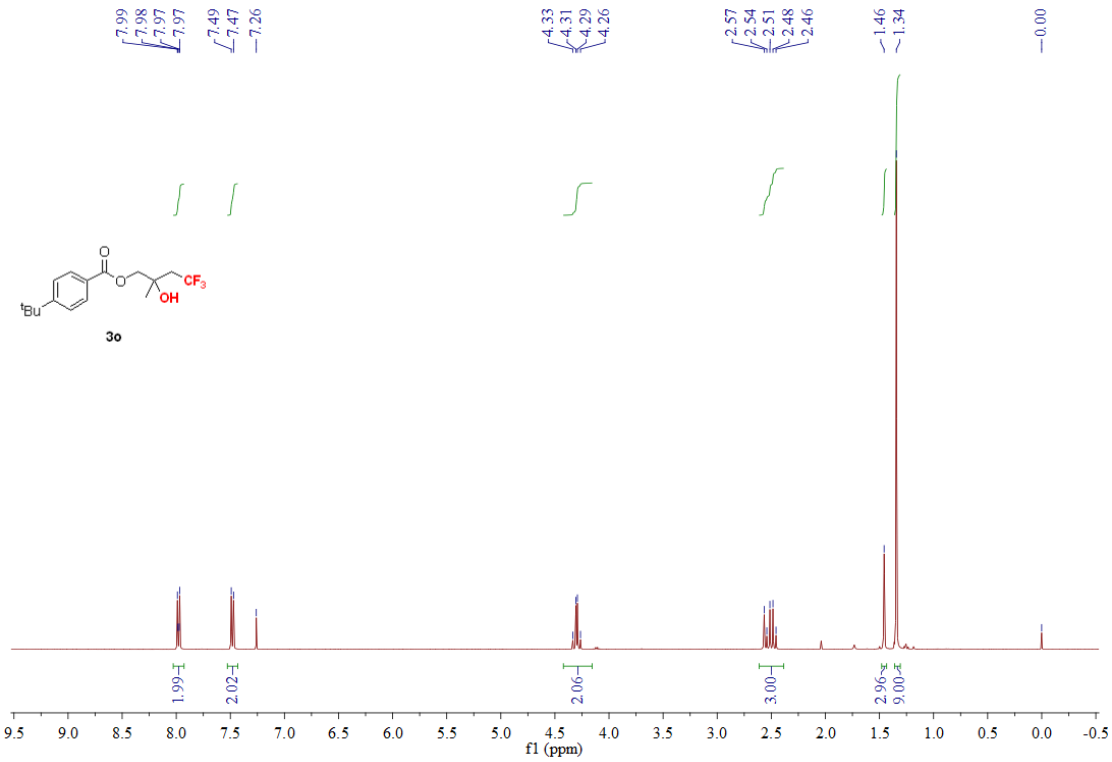
^{1}H NMR Spectrum of Compound **3n**



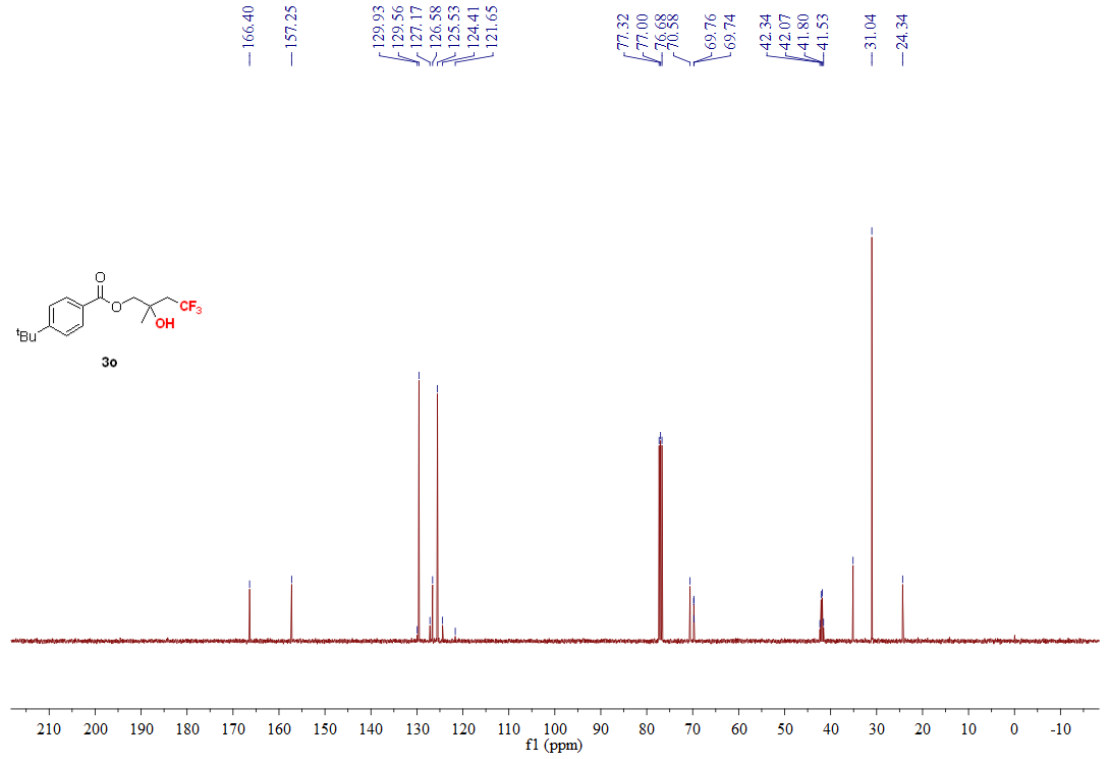
^{13}C NMR Spectrum of Compound **3n**



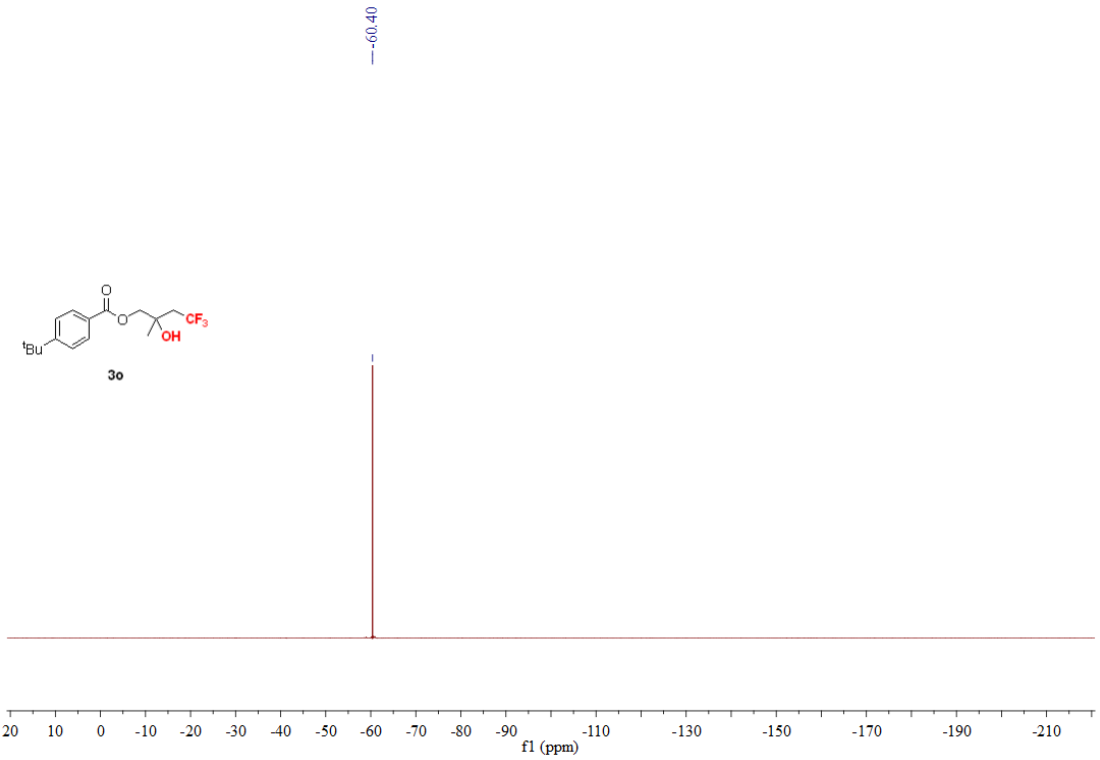
^{19}F NMR Spectrum of Compound **3n**



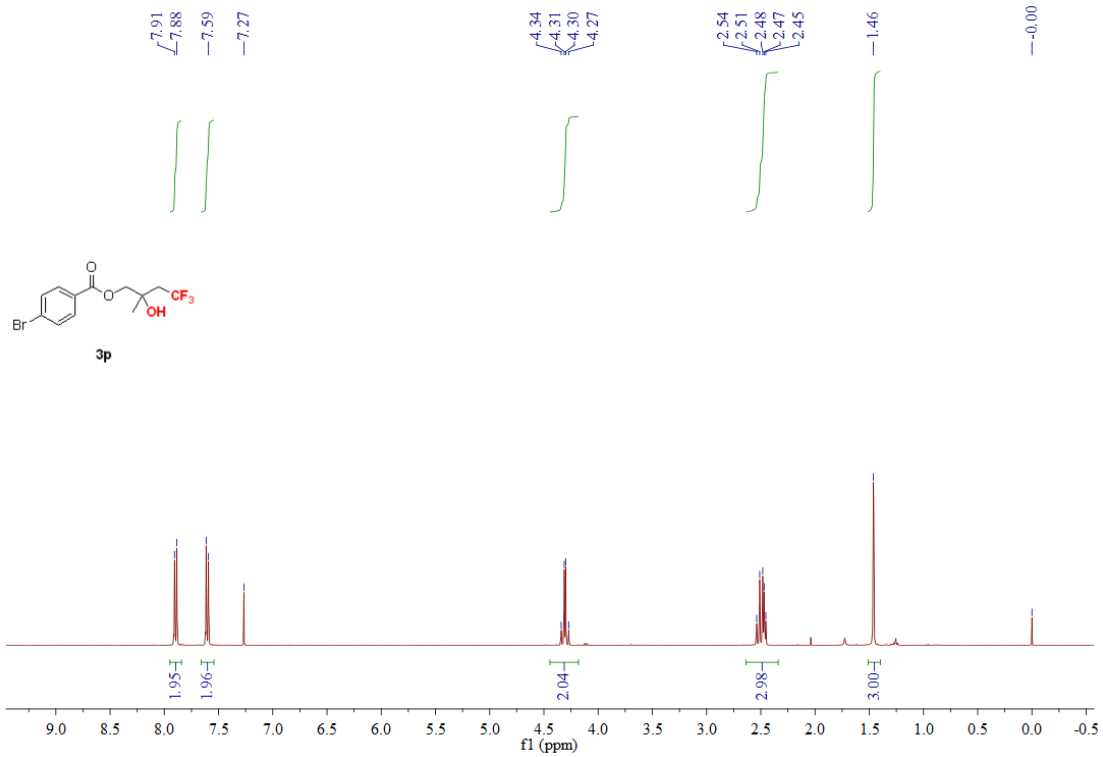
^{1}H NMR Spectrum of Compound **3o**



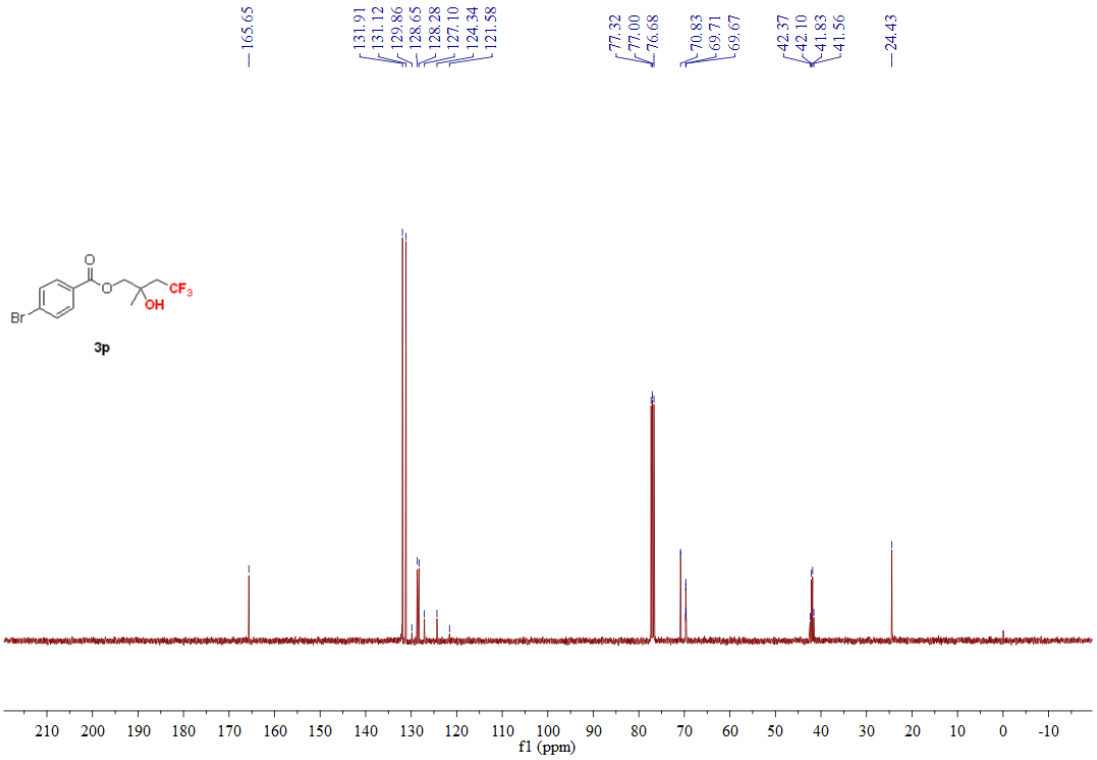
^{13}C NMR Spectrum of Compound **3o**



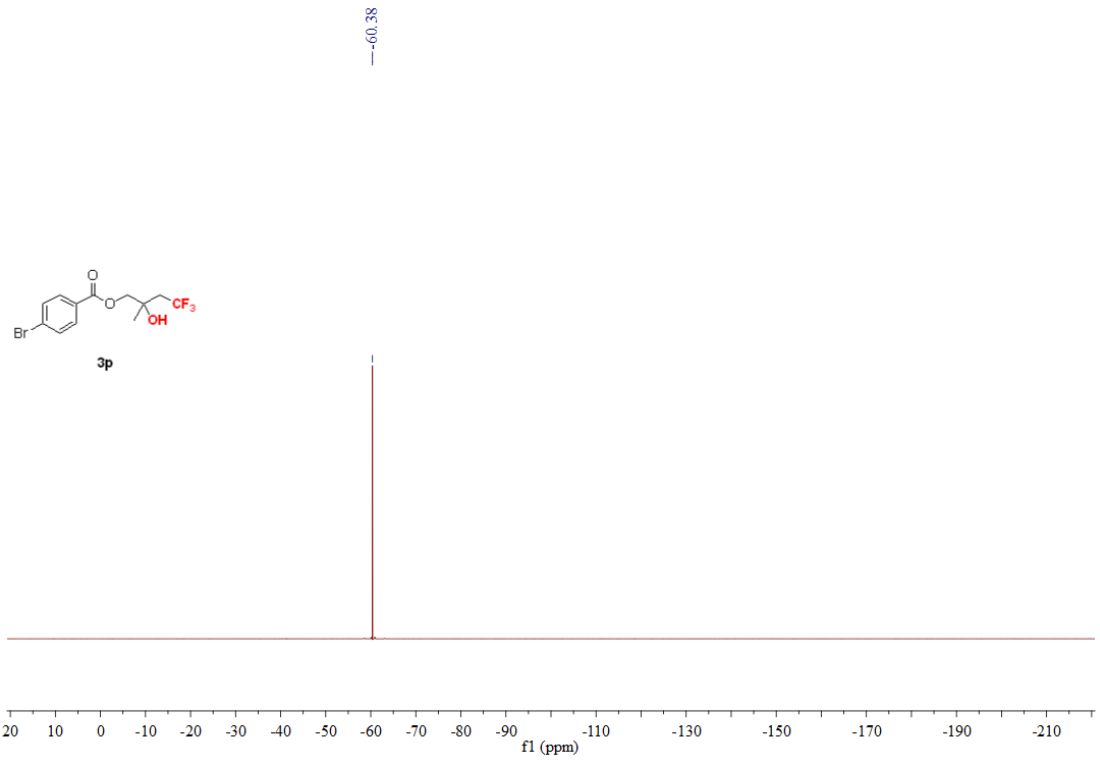
^{19}F NMR Spectrum of Compound **3o**



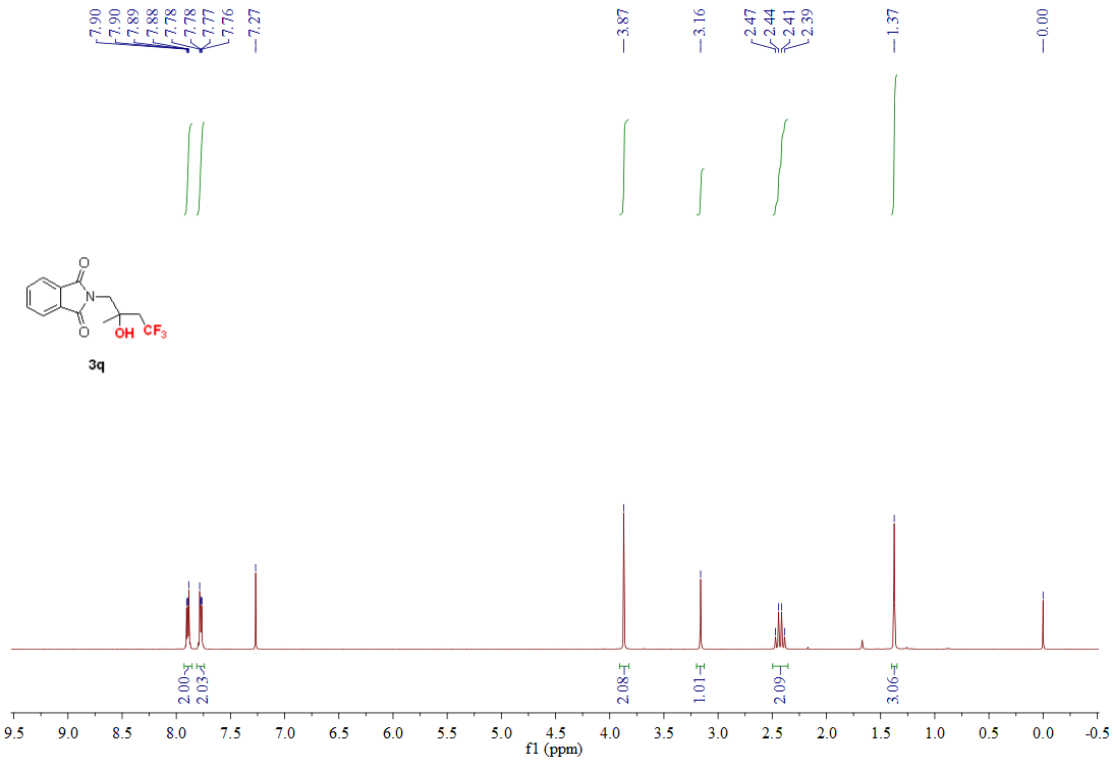
^{1}H NMR Spectrum of Compound **3p**



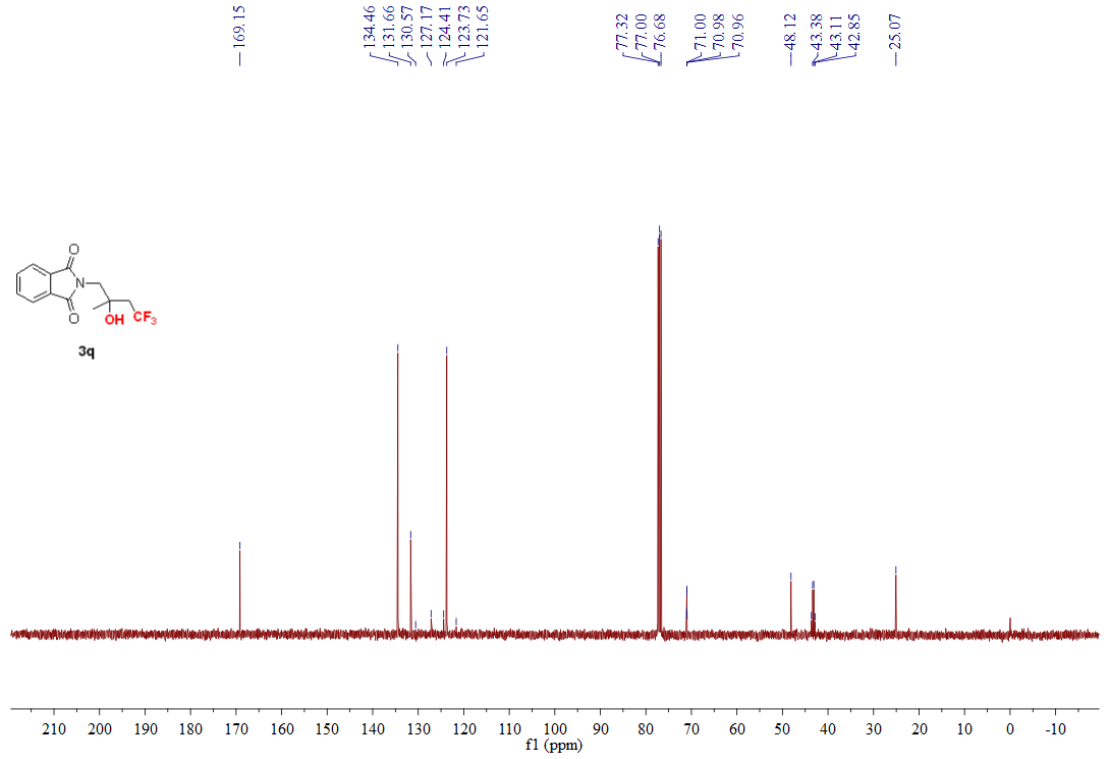
^{13}C NMR Spectrum of Compound **3p**



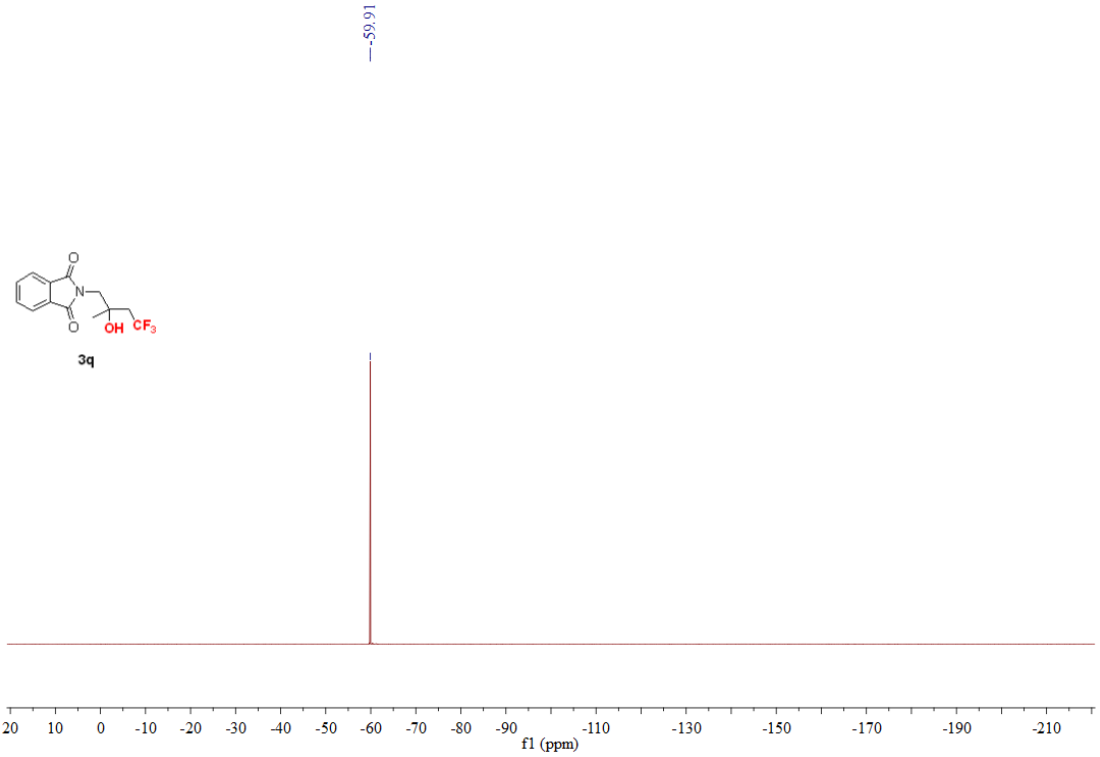
^{19}F NMR Spectrum of Compound **3p**



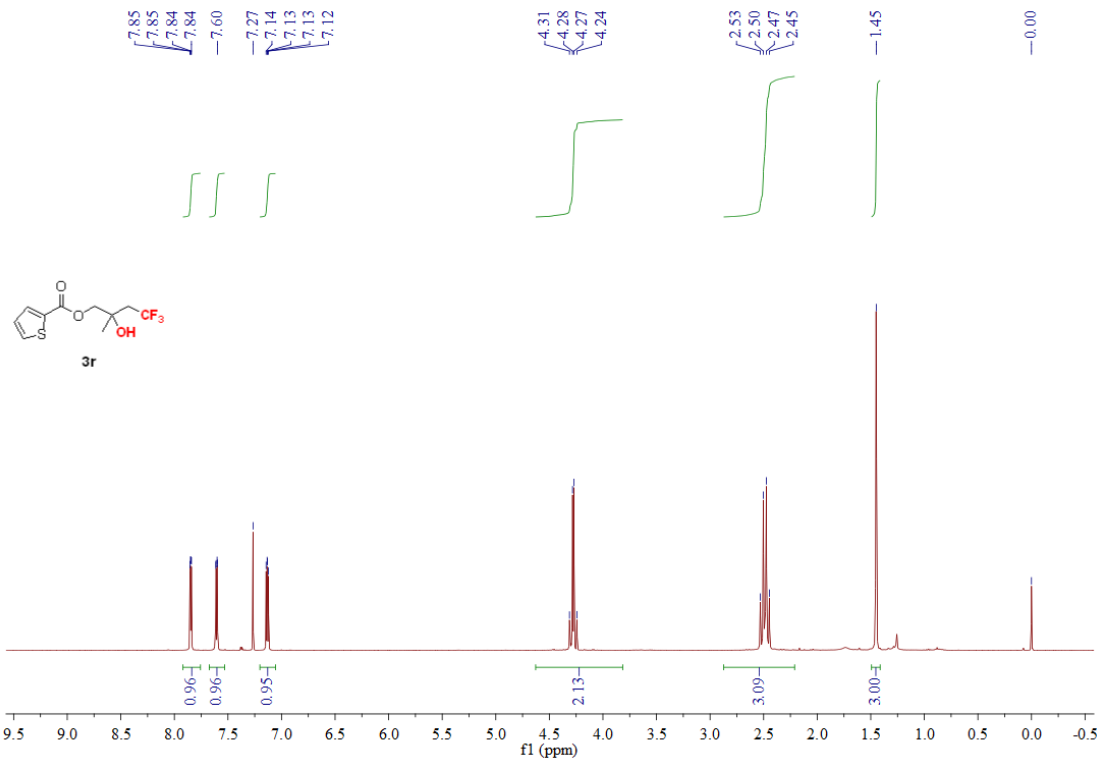
^{1}H NMR Spectrum of Compound **3q**



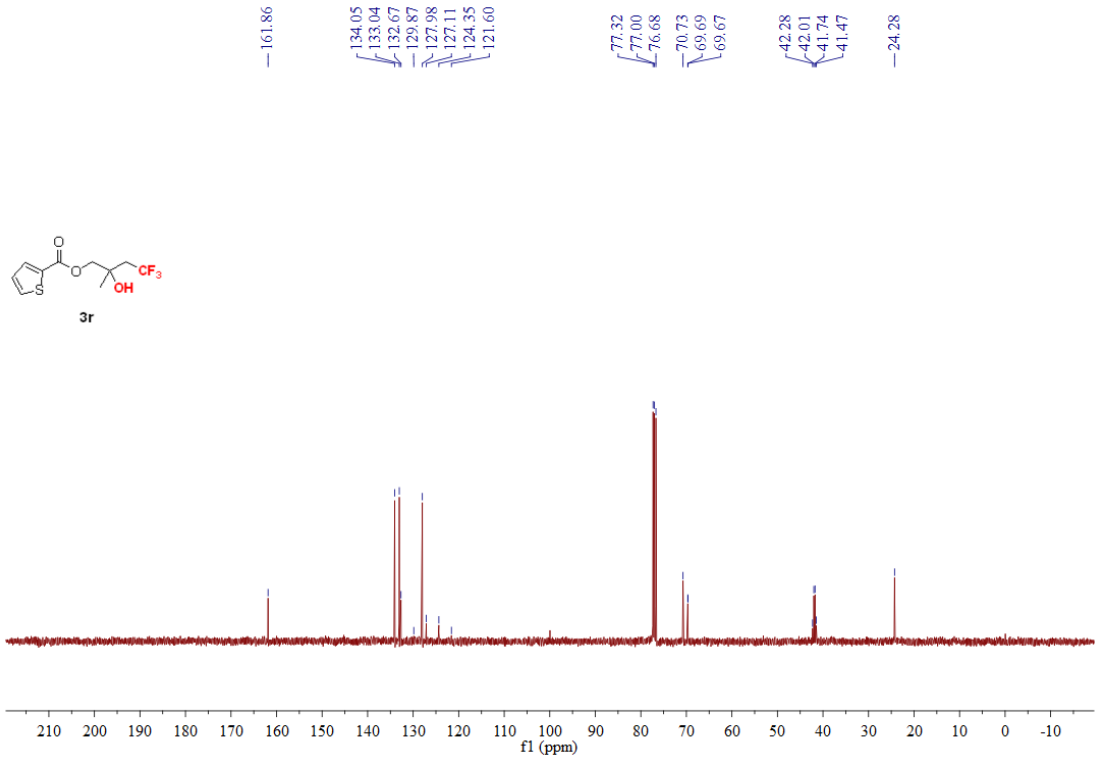
^{13}C NMR Spectrum of Compound **3q**



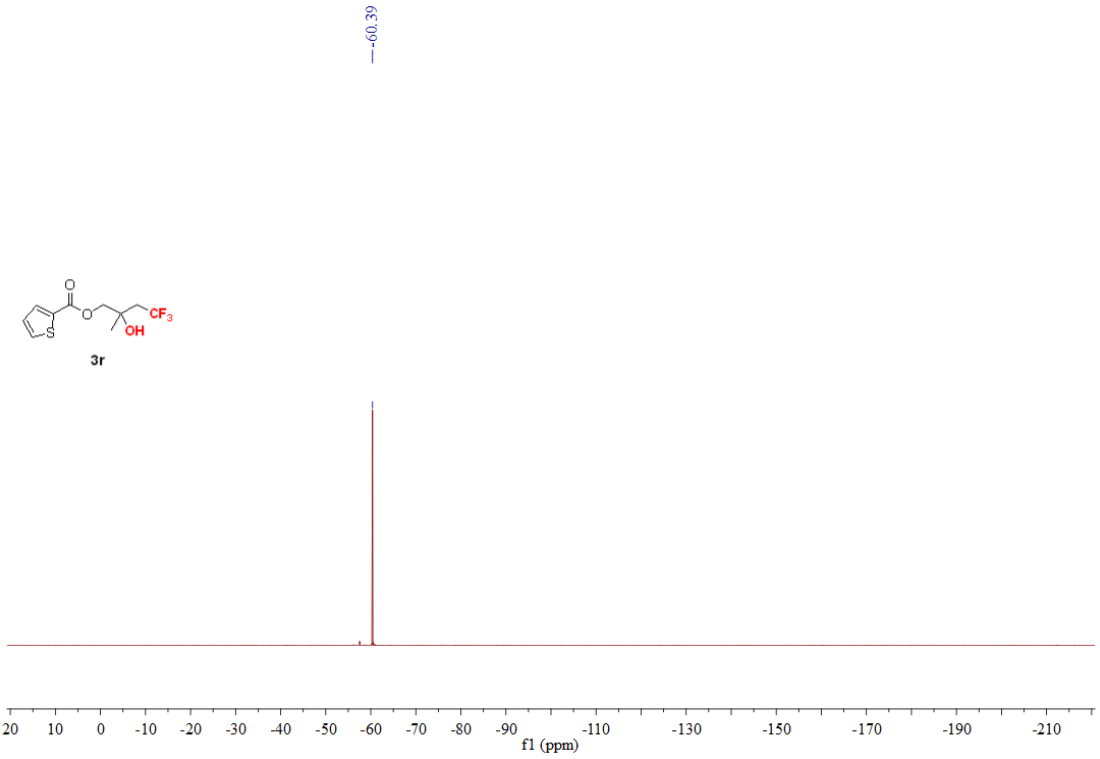
^{19}F NMR Spectrum of Compound **3q**



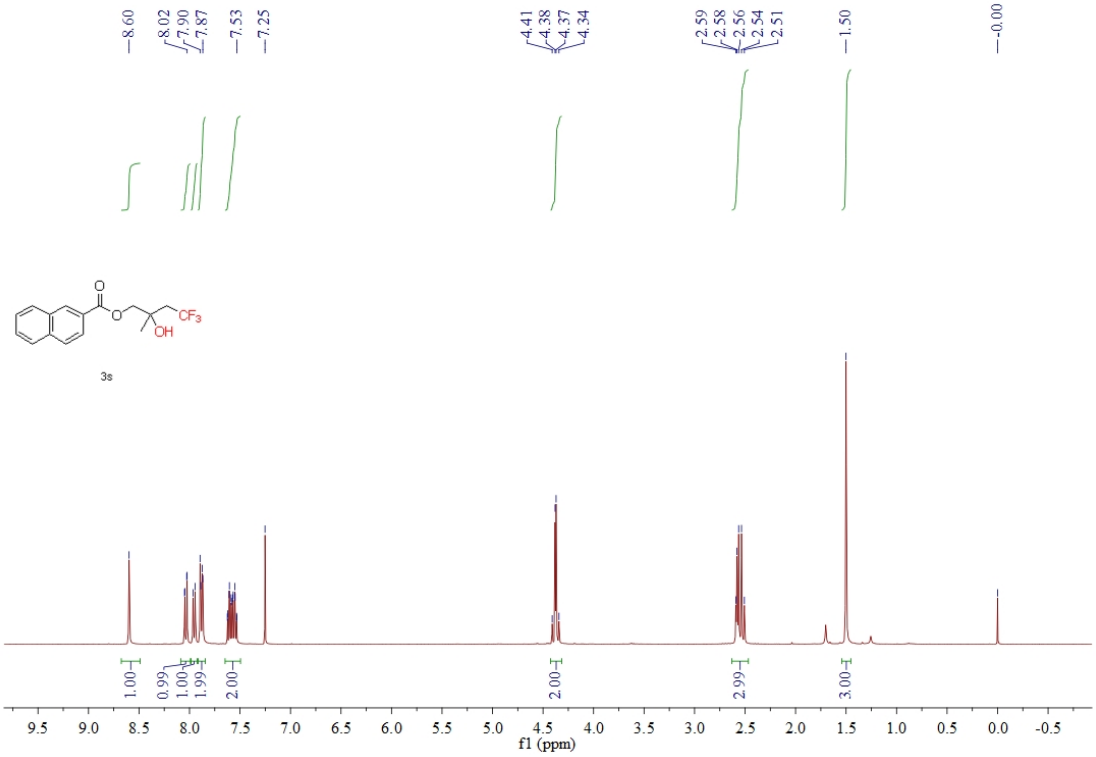
^{1}H NMR Spectrum of Compound **3r**



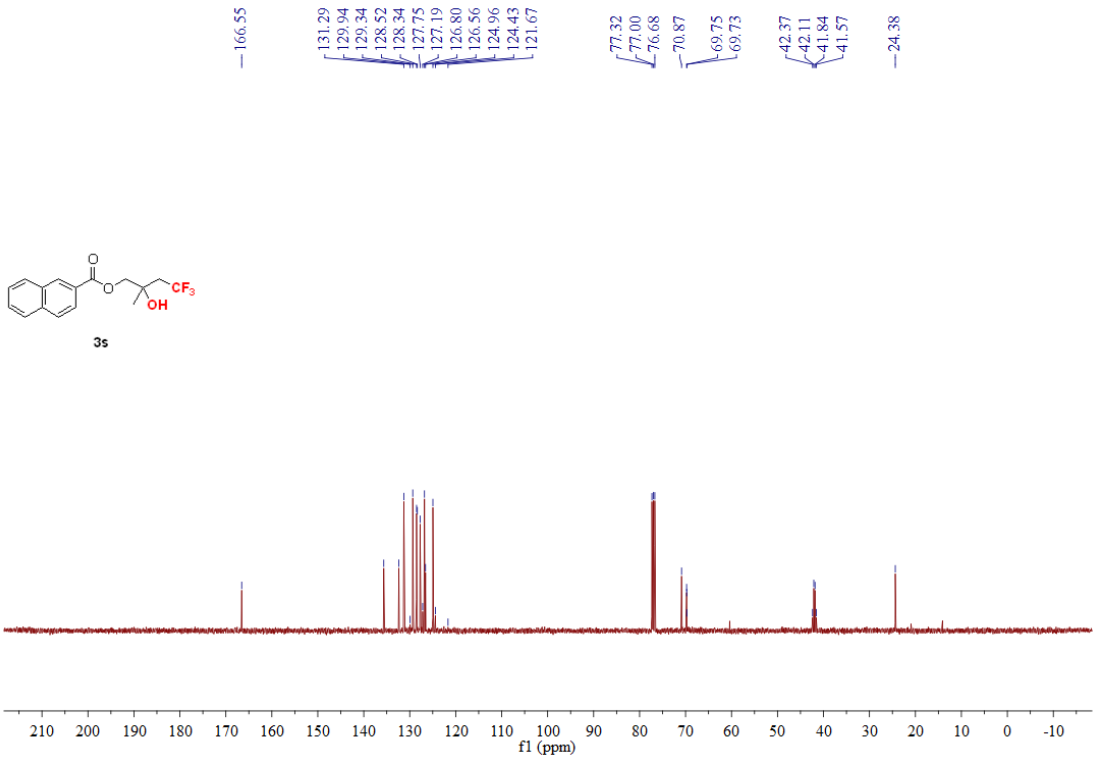
^{13}C NMR Spectrum of Compound **3r**



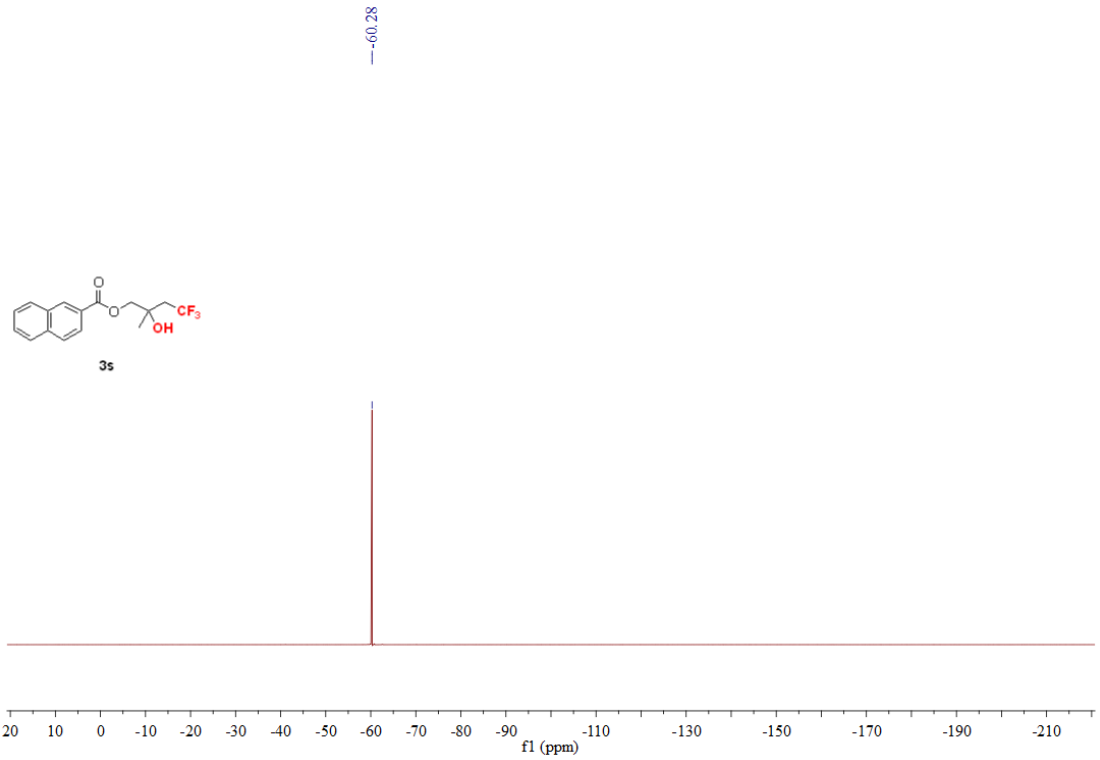
^{19}F NMR Spectrum of Compound **3r**



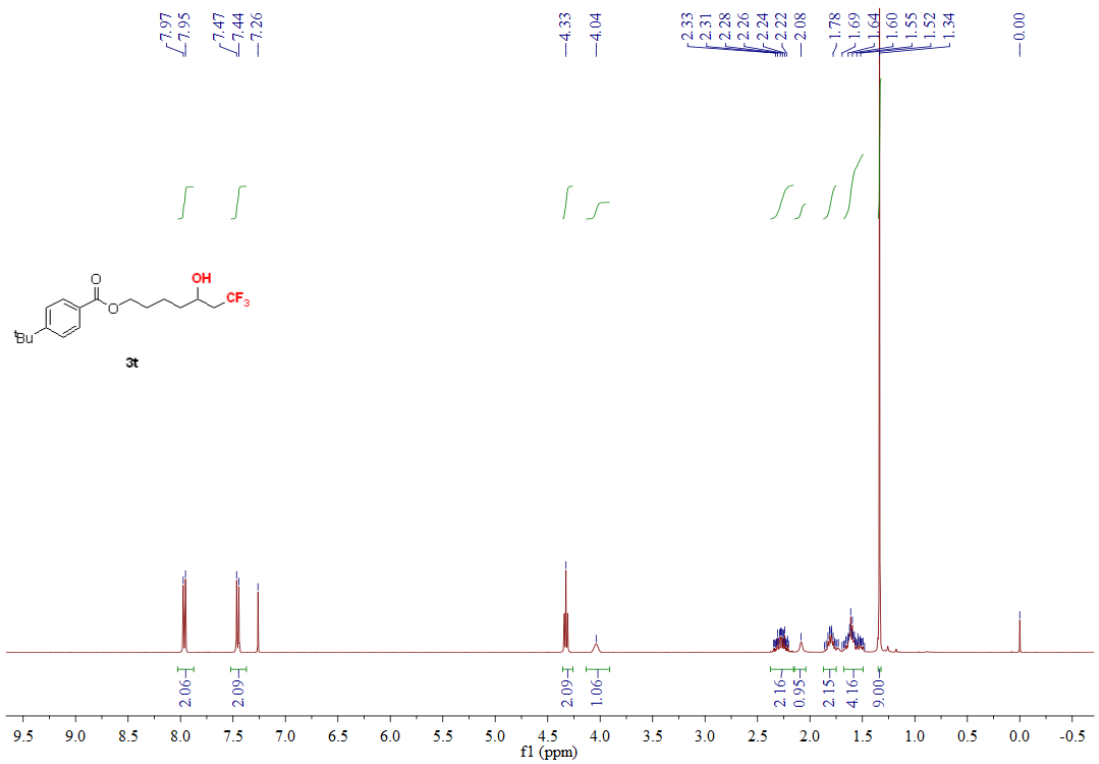
^{1}H NMR Spectrum of Compound **3s**



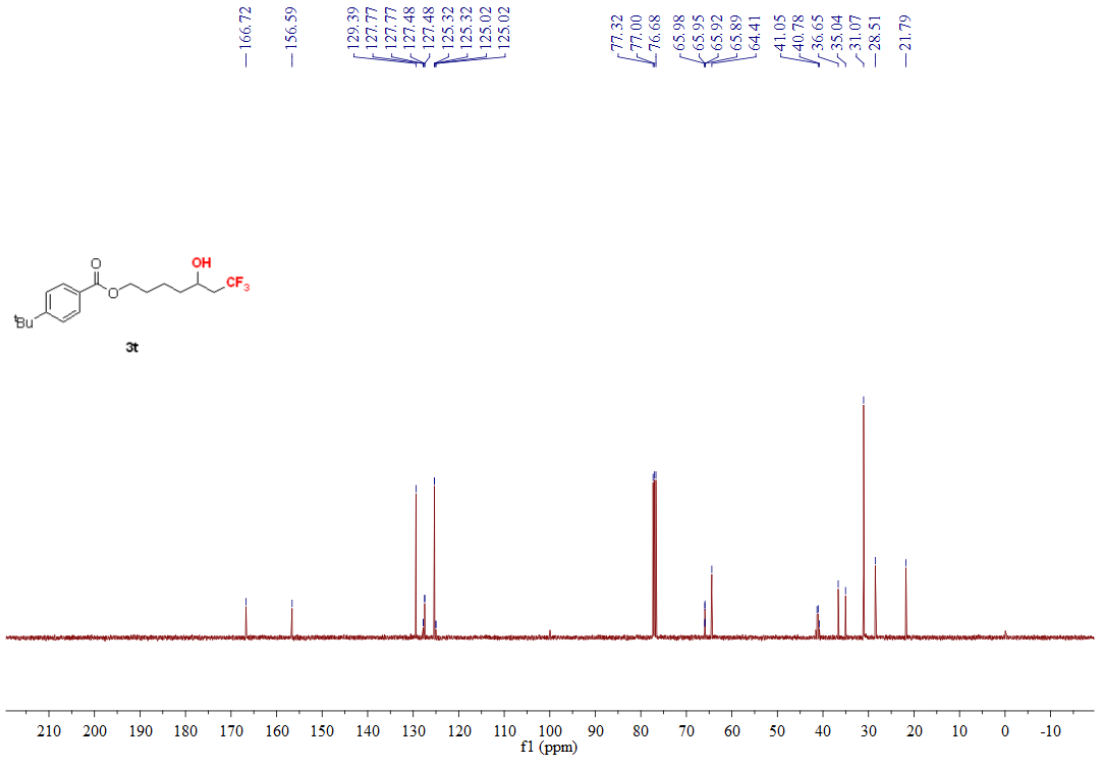
^{13}C NMR Spectrum of Compound **3s**



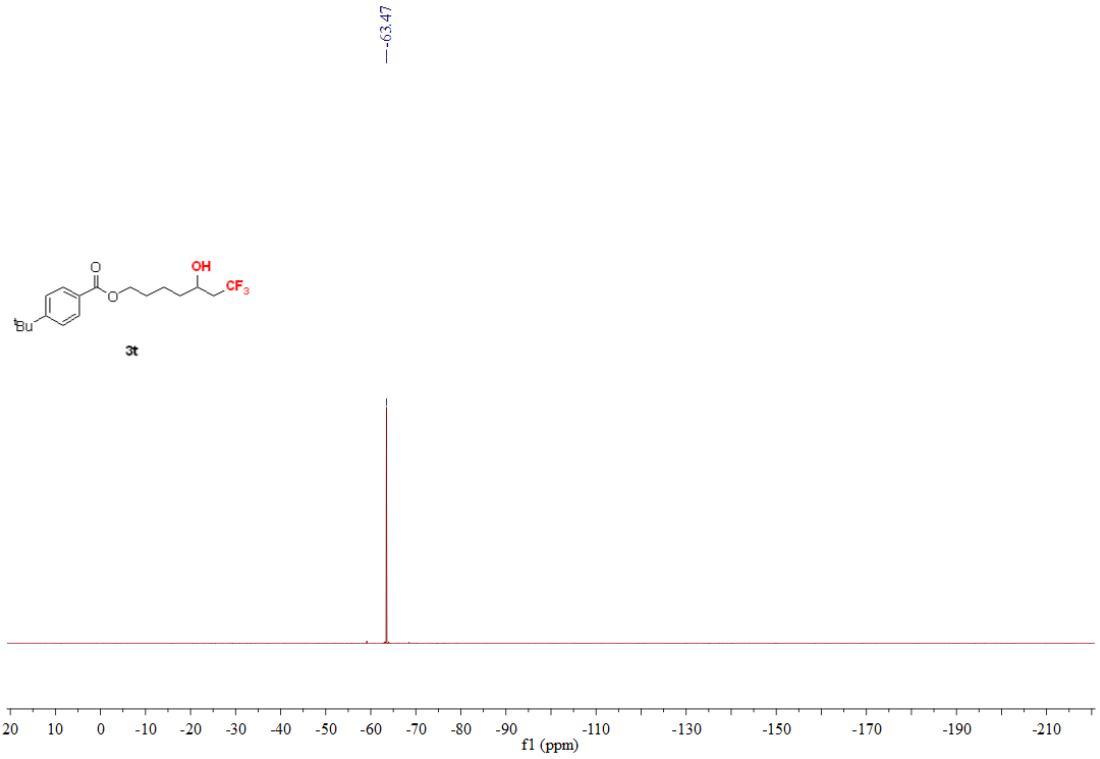
^{19}F NMR Spectrum of Compound **3s**



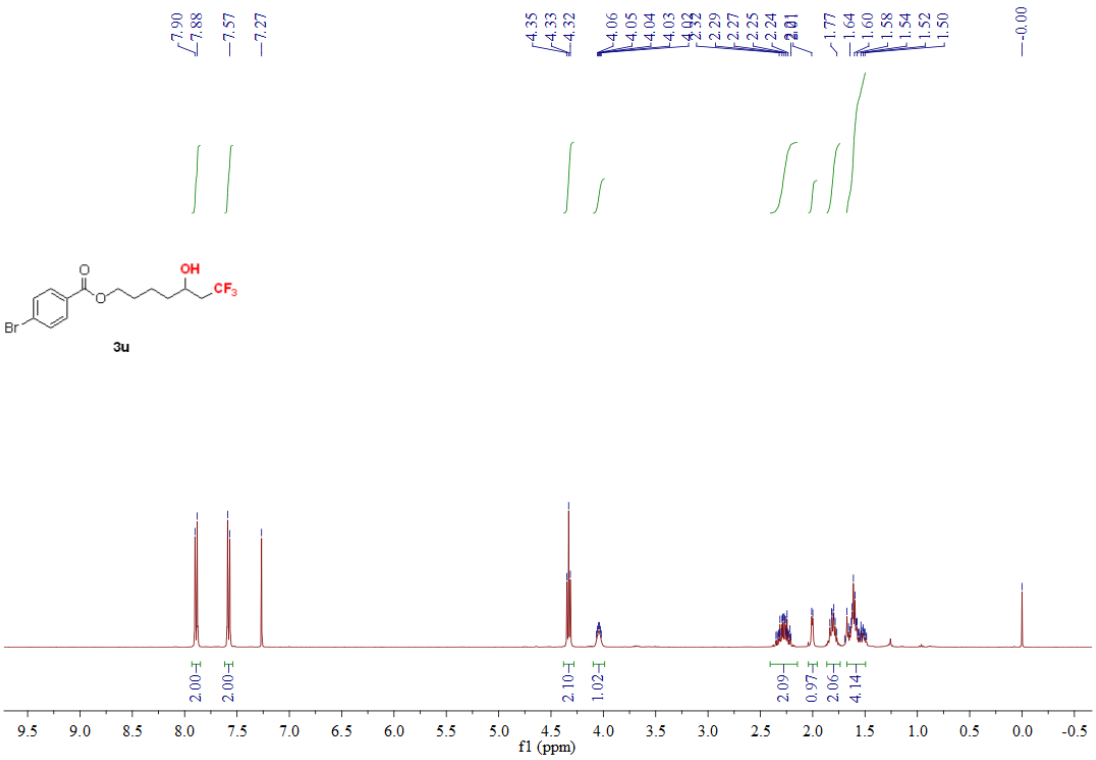
^{1}H NMR Spectrum of Compound **3t**



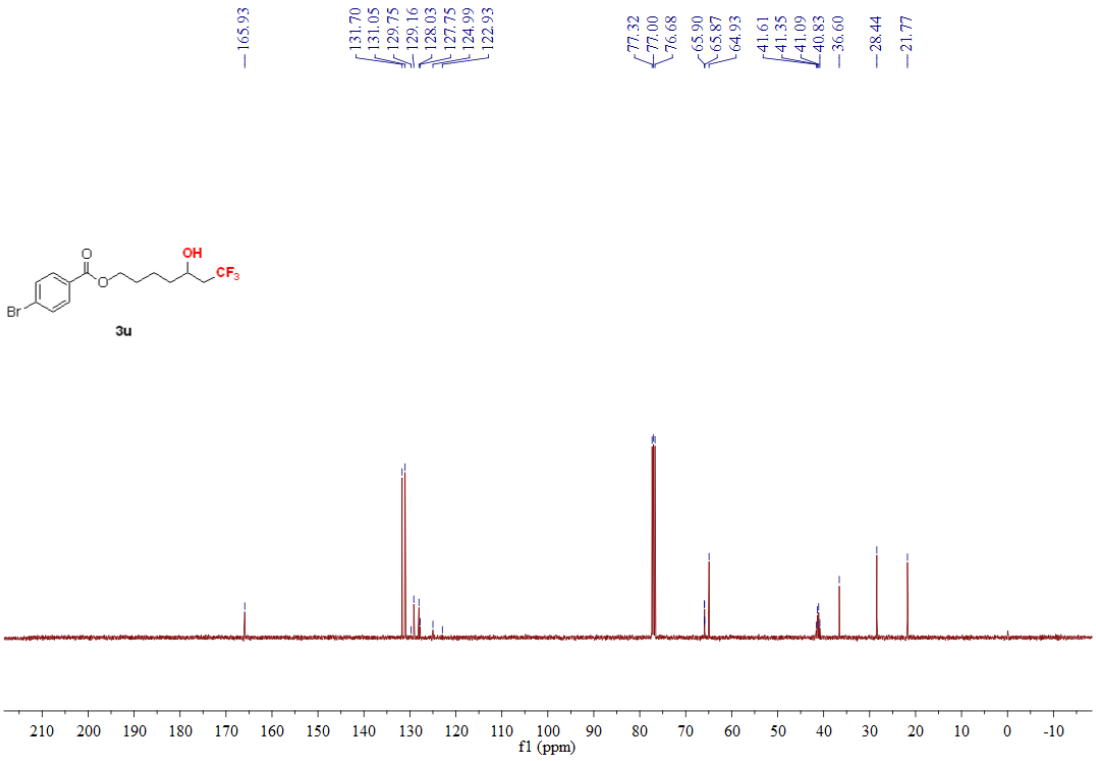
^{13}C NMR Spectrum of Compound **3t**



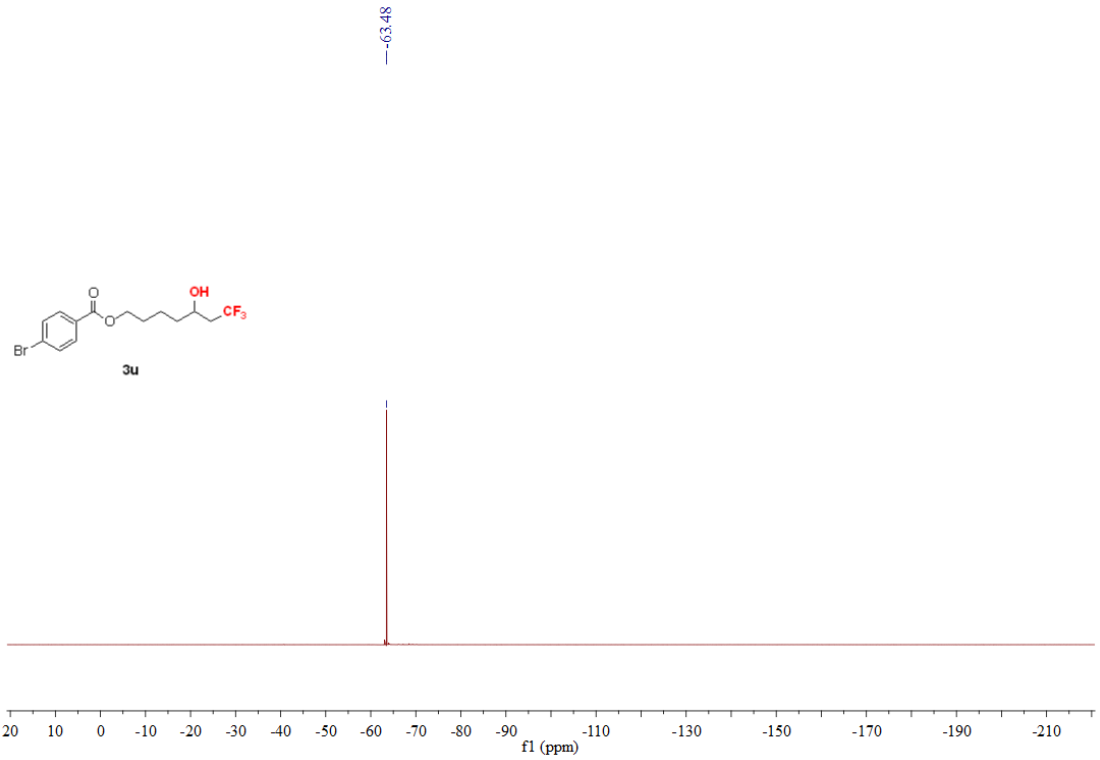
^{19}F NMR Spectrum of Compound **3t**



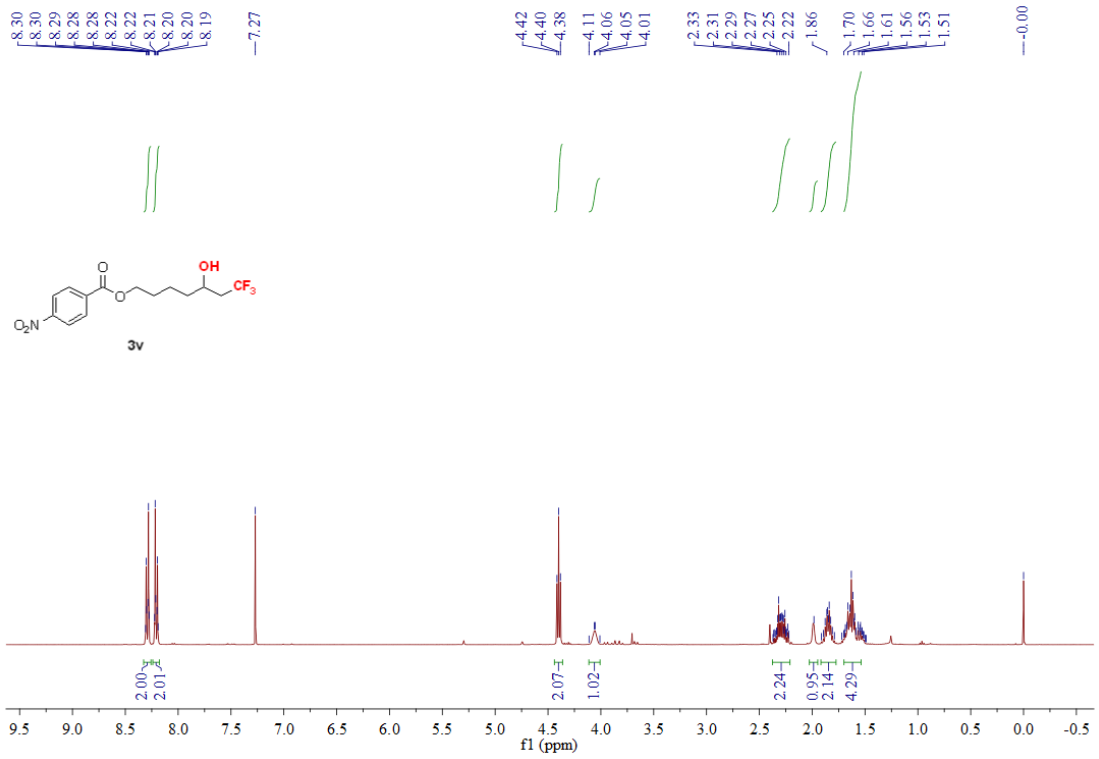
^{1}H NMR Spectrum of Compound **3u**



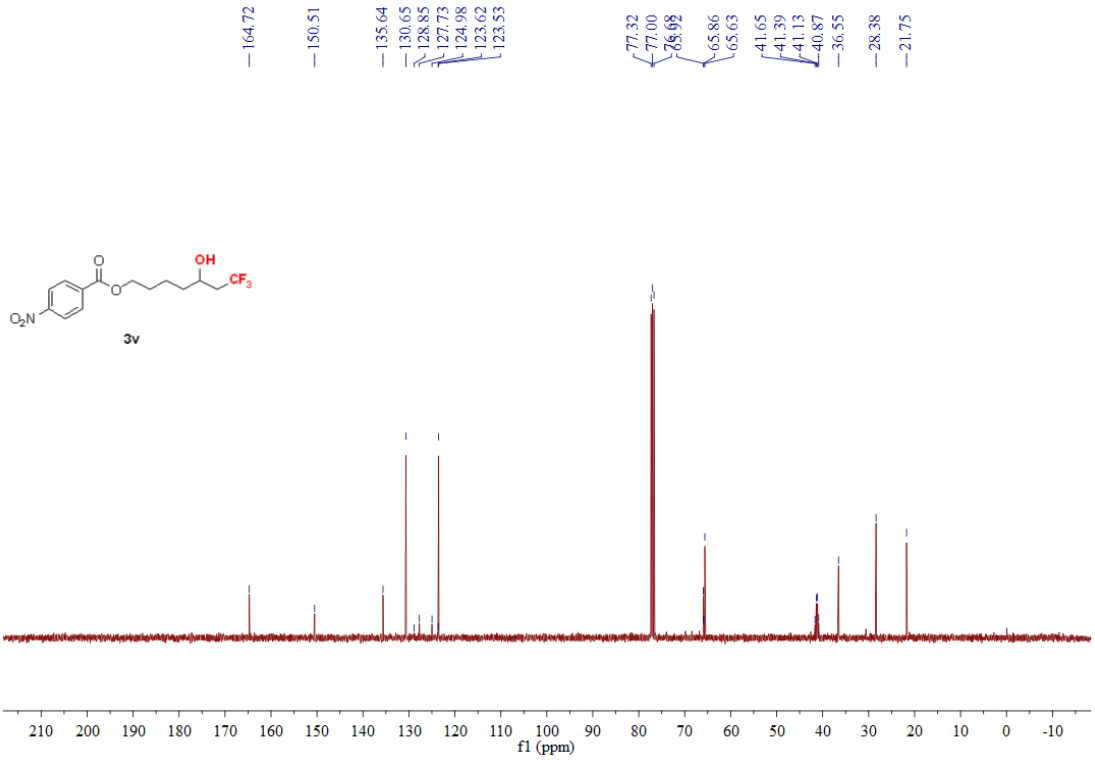
^{13}C NMR Spectrum of Compound **3u**



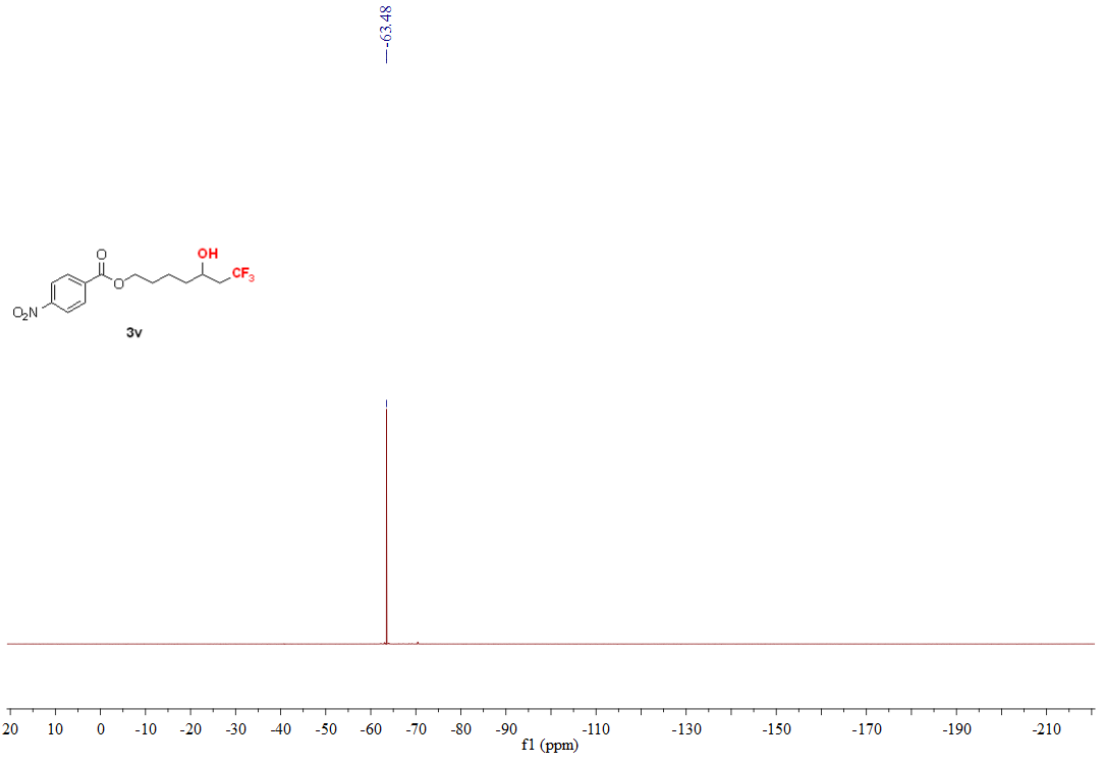
^{19}F NMR Spectrum of Compound **3u**



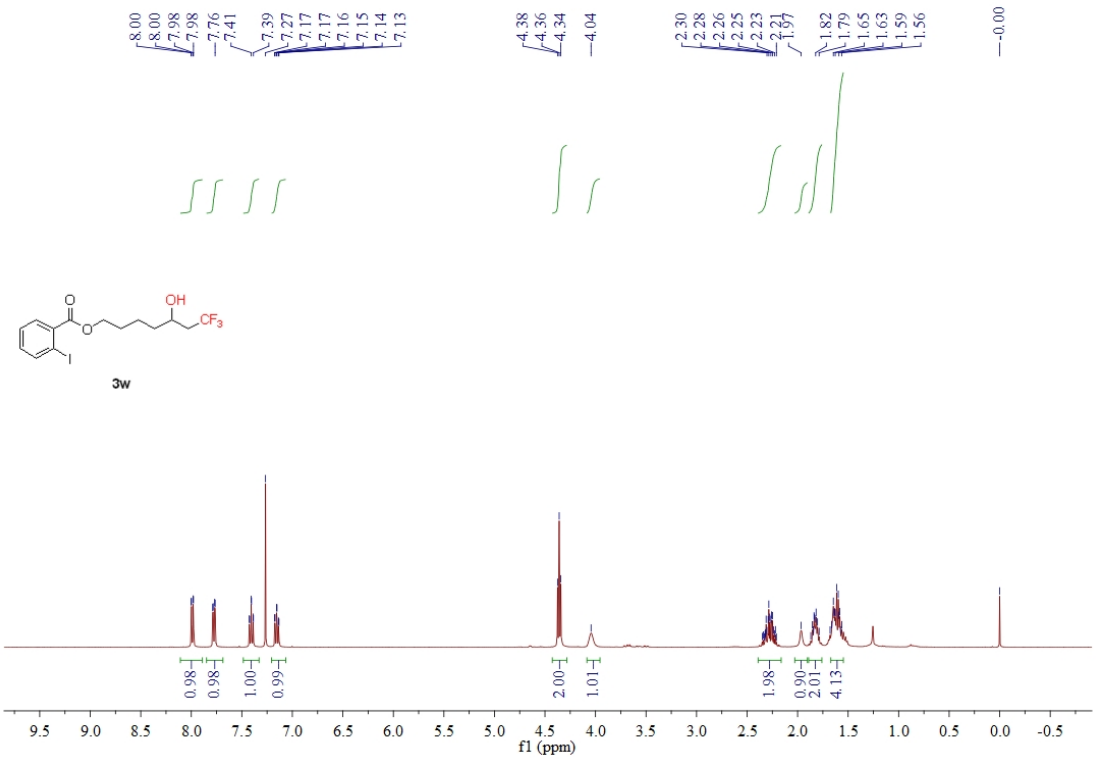
^{1}H NMR Spectrum of Compound **3v**



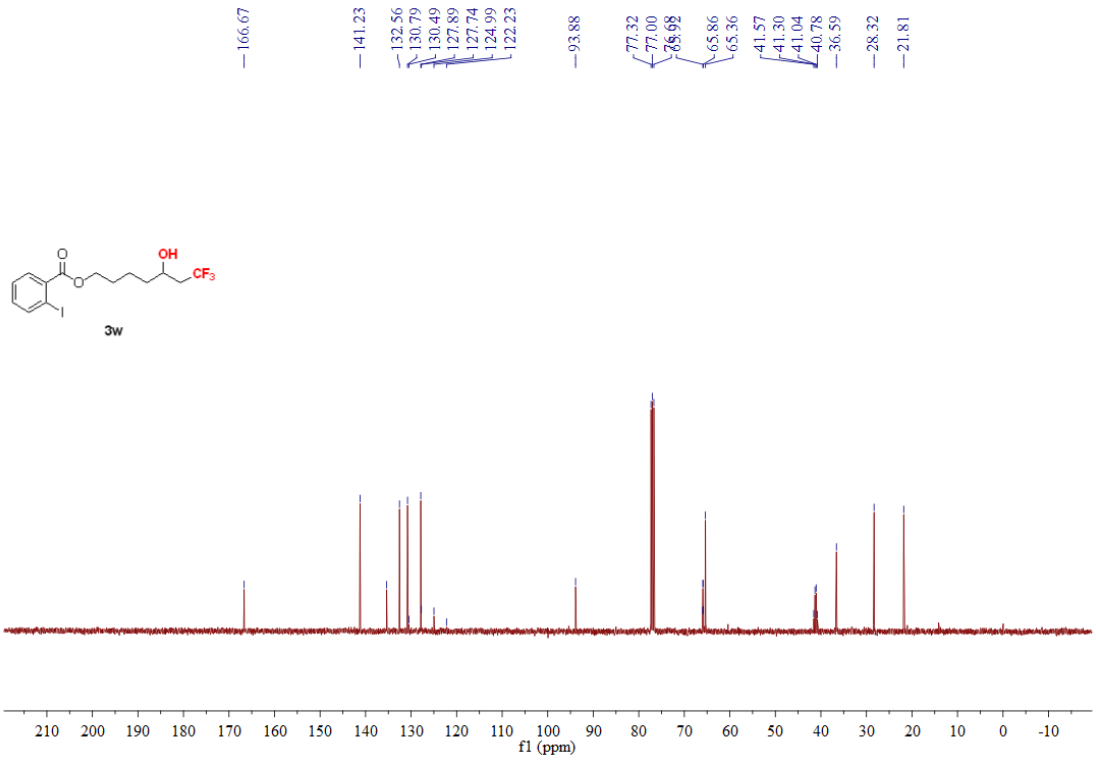
^{13}C NMR Spectrum of Compound **3v**



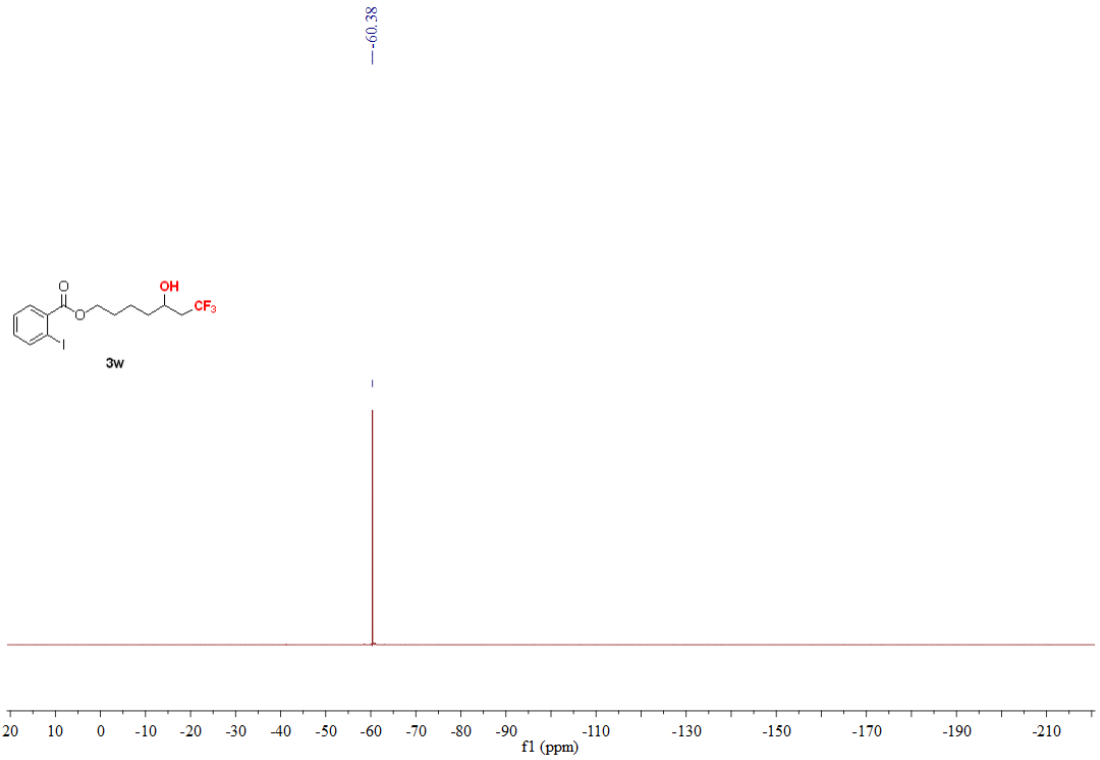
^{19}F NMR Spectrum of Compound **3v**



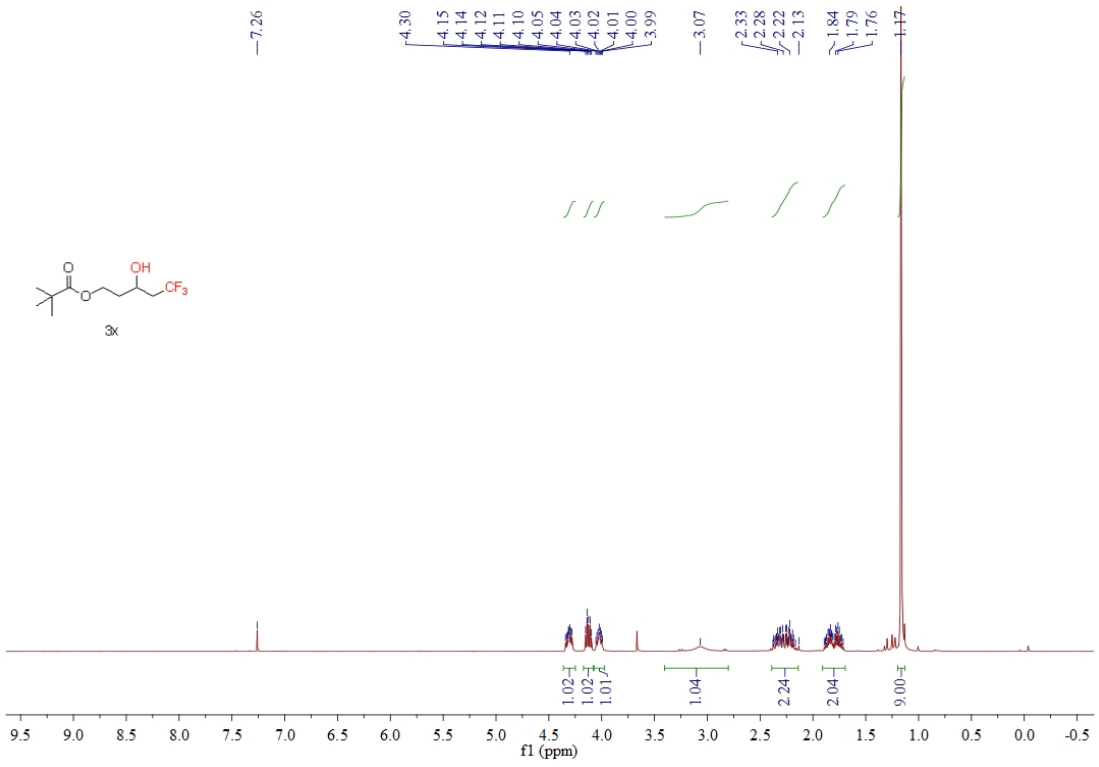
^{1}H NMR Spectrum of Compound **3w**



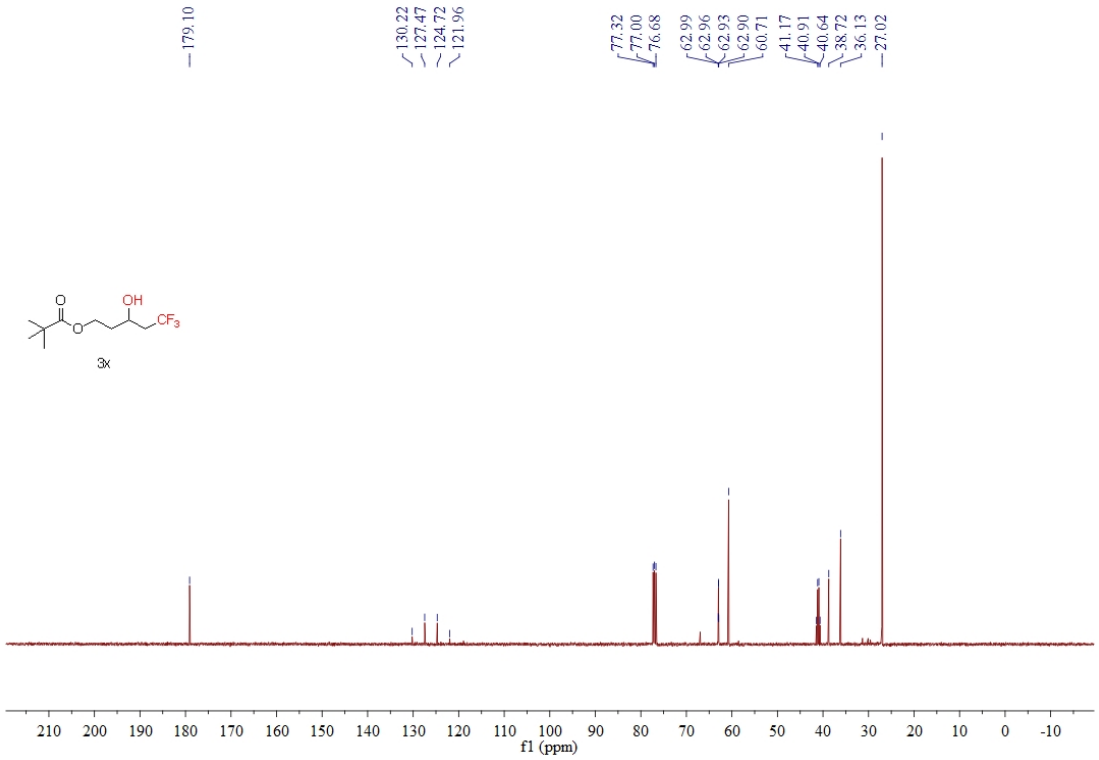
^{13}C NMR Spectrum of Compound **3w**



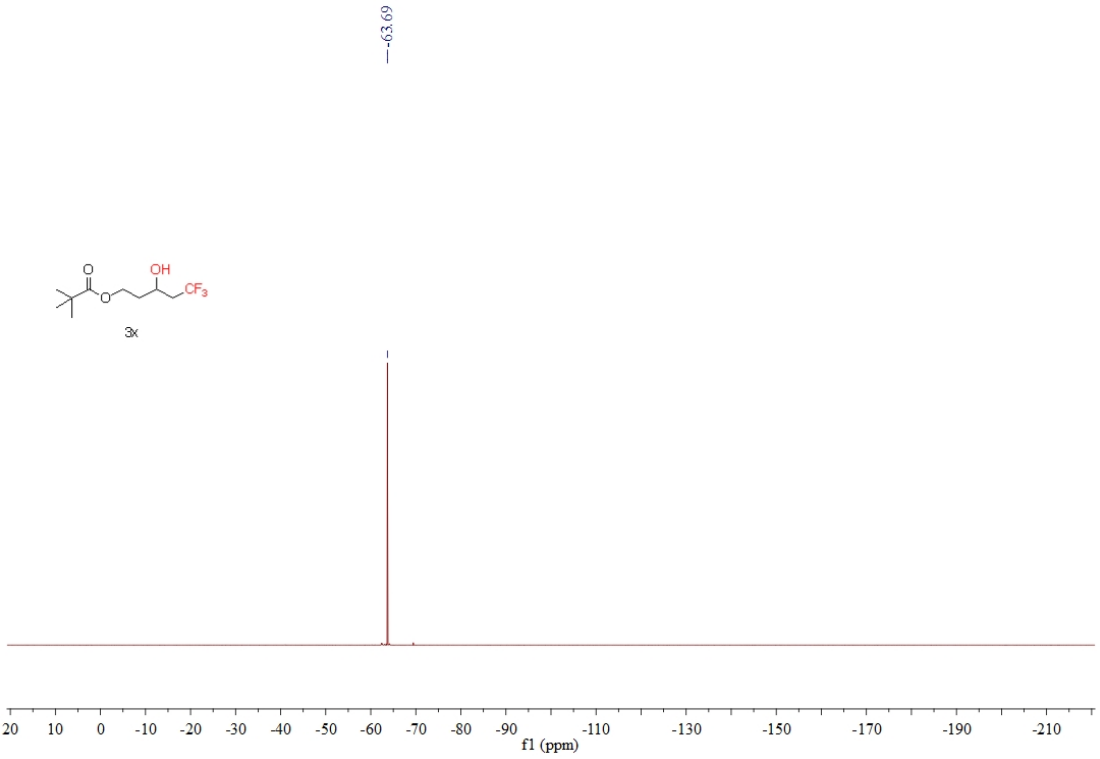
^{19}F NMR Spectrum of Compound **3w**



^{1}H NMR Spectrum of Compound **3x**



^{13}C NMR Spectrum of Compound **3x**



^{19}F NMR Spectrum of Compound **3x**