

Visible-light-induced radical hydrodifluoromethylation of alkenes

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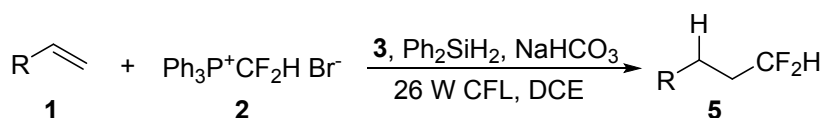
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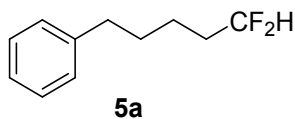
1. General information

^1H , ^{13}C and ^{19}F NMR spectra were detected on a 500 MHz, 400 MHz or 300 MHz NMR spectrometer. Data for ^1H NMR, ^{13}C NMR and ^{19}F NMR were recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, coupling constants in Hz). Mass spectra were obtained on GC-MS. High resolution mass data were recorded on a high resolution mass spectrometer in the EI mode. The mass analyzer type for HRMS-EI is time-of-flight mass spectrometer. Unless otherwise noted, all reagents were obtained commercially and used without further purification.

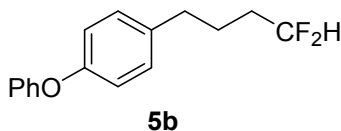
2. Typical procedures for the hydrodifluoromethylation



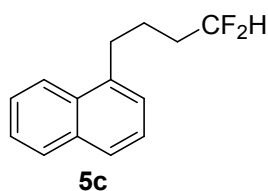
Into a 25mL Schlenk tube were added substrate **1a** (0.5 mmol, 66.1 mg, 1.0 equiv.), phosphonium salt [$\text{Ph}_3\text{P}^+\text{CF}_2\text{H Br}^-$] (2 mmol, 786.4 mg, 4 equiv.), Hantzsch ester **3** (1 mmol, 253.3 mg, 2 equiv.), Ph_2SiH_2 (1 mmol, 184.2 mg, 2 equiv.) and NaHCO_3 (2 mmol, 168.0 mg, 4 equiv.) under a N_2 atmosphere. After the reaction solvent DCE (9 mL) was added, the reaction mixture was stirred at room temperature and irradiated with 26 CFL for 22 h under a N_2 atmosphere. The solvent was removed by concentration, and the residue was subjected to flash column chromatography to afford the pure product **5a**.



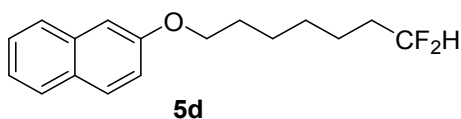
(5,5-difluoropentyl)benzene^[1]: 71%; ^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.22 (m, 2H), 7.22 – 7.13 (m, 3H), 5.77 (tt, $J = 57.0$, 4.5 Hz, 1H), 2.62 (t, $J = 7.5$ Hz, 2H), 1.94 – 1.74 (m, 2H), 1.74 – 1.59 (m, 2H), 1.57 – 1.38 (m, 2H); ^{19}F NMR (376 MHz, CDCl_3) δ -115.73 (dt, $J = 57.0$, 17.6 Hz, 2F).



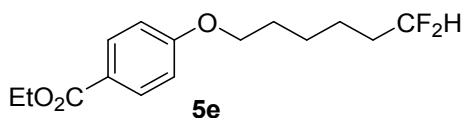
1-(4,4-difluorobutyl)-4-phenoxybenzene: 53%; Slightly yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.27 (m, 2H), 7.13 (d, $J = 8.5$ Hz, 2H), 7.08 (t, $J = 7.4$ Hz, 1H), 7.01 – 6.96 (m, 2H), 6.96 – 6.90 (m, 2H), 5.81 (tt, $J = 56.6, 4.2$ Hz, 1H), 2.65 (t, $J = 7.3$ Hz, 2H), 1.95 – 1.67 (m, 4H).; ^{19}F NMR (376 MHz, CDCl_3) δ -115.78 (dt, $J = 56.6, 17.2$ Hz, 2F); ^{13}C NMR (101 MHz, CDCl_3) δ 157.5 (s), 155.4 (s), 136.2 (s), 129.7 (s), 129.6 (s), 123.0 (s), 119.0 (s), 118.6 (s), 117.2 (t, $J = 238.9$ Hz), 34.4 (s), 33.5 (t, $J = 20.9$ Hz), 23.8 (t, $J = 5.3$ Hz); IR (neat) $\nu = 2929, 1590, 1507, 1489, 1239, 1122, 1072, 1015, 871, 692\text{ cm}^{-1}$; HRMS (EI) Calcd for $\text{C}_{16}\text{H}_{16}\text{OF}_2$ $[\text{M}]^+$: 262.1169, Found: 262.1173.



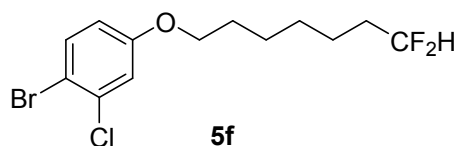
1-(4,4-difluorobutyl)naphthalene^[2]: 54%; ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 8.2$ Hz, 1H), 7.90 – 7.82 (m, 1H), 7.73 (d, $J = 8.2$ Hz, 1H), 7.55 – 7.45 (m, 1H), 7.42 – 7.36 (m, 2H), 7.31 (d, $J = 6.9$ Hz, 1H), 5.82 (tt, $J = 57.1, 4.5$ Hz, 1H), 3.13 (t, $J = 7.2$ Hz, 2H), 2.00 – 1.84 (m, 4H). ^{19}F NMR (376 MHz, CDCl_3) δ -115.69 (dt, $J = 57.1, 17.2$ Hz, 2F).



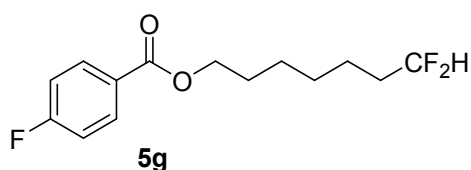
2-((7,7-difluoroheptyl)oxy)naphthalene^[1]: 60%; ^1H NMR (400 MHz, CDCl_3) δ 7.79 – 7.67 (m, 3H), 7.48 – 7.38 (m, 1H), 7.37 – 7.27 (m, 1H), 7.19 – 7.08 (m, 2H), 5.80 (tt, $J = 57.2, 4.5$ Hz, 1H), 4.07 (t, $J = 6.2$ Hz, 2H), 1.95 – 1.71 (m, 4H), 1.65 – 1.35 (m, 6H); ^{19}F NMR (376 MHz, CDCl_3) δ -115.80 (dt, $J = 57.2, 17.6$ Hz, 2F).



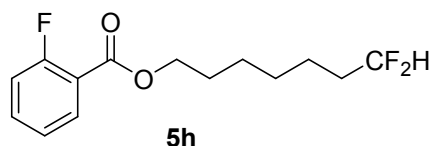
ethyl 4-((6,6-difluorohexyl)oxy)benzoate^[1]: 65%; ^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, $J = 8.9$ Hz, 2H), 6.89 (d, $J = 8.9$ Hz, 2H), 5.82 (tt, $J = 56.9, 4.4$ Hz, 1H), 4.34 (q, $J = 7.1$ Hz, 2H), 4.01 (t, $J = 6.3$ Hz, 2H), 1.95 – 1.76 (m, 4H), 1.60 – 1.49 (m, 4H), 1.38 (t, $J = 7.1$ Hz, 3H); ^{19}F NMR (376 MHz, CDCl_3) δ -115.92 (dt, $J = 57.0, 17.4$ Hz, 2F).



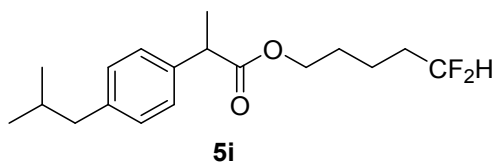
1-bromo-2-chloro-4-((7,7-difluoroheptyl)oxy)benzene^[1]: 65%; ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, *J* = 2.4 Hz, 1H), 7.29 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.77 (d, *J* = 8.8 Hz, 1H), 5.77 (tt, *J* = 57.1, 4.4 Hz, 1H), 3.98 (t, *J* = 6.4 Hz, 2H), 1.93 – 1.72 (m, 4H), 1.60 – 1.35 (m, 6H); ¹⁹F NMR (376 MHz, CDCl₃) δ -115.81 (dt, *J* = 57.1, 17.8 Hz, 2F).



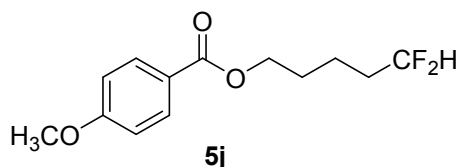
7,7-difluoroheptyl 4-fluorobenzoate: 61%; Colourless liquid; ¹H NMR (400 MHz, CDCl₃) δ 8.16 – 7.85 (m, 2H), 7.17 – 6.94 (m, 2H), 5.78 (tt, *J* = 56.9, 4.5 Hz, 1H), 4.29 (t, *J* = 6.6 Hz, 2H), 1.91 – 1.65 (m, 4H), 1.58 – 1.32 (m, 6H); ¹⁹F NMR (376 MHz, CDCl₃) δ -105.91 – -106.02 (m, 1F), -115.89 (dt, *J* = 56.9, 17.6 Hz, 2F); ¹³C NMR (101 MHz, CDCl₃) δ 165.7 (d, *J* = 253.9 Hz), 165.6 (s), 132.0 (d, *J* = 9.3 Hz), 126.6 (d, *J* = 3.4 Hz), 117.3 (t, *J* = 238.8 Hz), 115.4 (d, *J* = 22.0 Hz), 65.0 (s), 33.9 (t, *J* = 20.8 Hz), 28.7 (s), 28.5 (s), 25.8 (s), 21.9 (t, *J* = 5.5 Hz); IR (neat) ν = 2962, 1719, 1603, 1261, 1152, 1090, 1016, 800, 769 cm⁻¹; HRMS (EI) Calcd for C₁₄H₁₇O₂F₃ [M]⁺: 274.1181, Found: 274.1187.



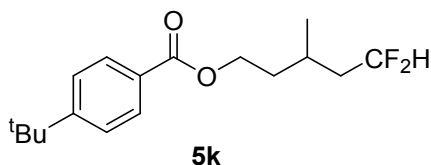
7,7-difluoroheptyl 2-fluorobenzoate: 65%; Colourless liquid; ¹H NMR (400 MHz, CDCl₃) δ 7.90 (td, *J* = 7.6, 1.8 Hz, 1H), 7.54 – 7.42 (m, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.11 (dd, *J* = 10.4, 8.7 Hz, 1H), 5.77 (tt, *J* = 56.9, 4.5 Hz, 1H), 4.31 (t, *J* = 6.5 Hz, 2H), 1.90 – 1.64 (m, 4H), 1.53 – 1.31 (m, 6H); ¹⁹F NMR (376 MHz, CDCl₃) δ -109.48 – -109.76 (m, 1F), -115.87 (dt, *J* = 57.0, 17.6 Hz, 2F); ¹³C NMR (101 MHz, CDCl₃) δ 164.4 (d, *J* = 3.7 Hz), 161.8 (d, *J* = 259.7 Hz), 134.3 (d, *J* = 8.9 Hz), 132.0 (s), 123.8 (d, *J* = 3.9 Hz), 118.9 (d, *J* = 9.9 Hz), 117.3 (t, *J* = 238.7 Hz), 116.9 (d, *J* = 22.5 Hz), 65.1 (s), 33.9 (t, *J* = 20.7 Hz), 28.6 (s), 28.3 (s), 25.7 (s), 21.9 (t, *J* = 5.5 Hz); IR (neat) ν = 2938, 1716, 1613, 1299, 1273, 1251, 1127, 1085, 1034, 790, 758 cm⁻¹; HRMS (EI) Calcd for C₁₄H₁₇O₂F₃ [M]⁺: 274.1181, Found: 274.1184.



5,5-difluoropentyl 2-(4-isobutylphenyl)propanoate: 63%; Colourless liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.19 (d, $J = 8.0$ Hz, 2H), 7.08 (d, $J = 8.0$ Hz, 2H), 5.70 (tt, $J = 56.8, 4.4$ Hz, 1H), 4.17 – 3.96 (m, 2H), 3.68 (q, $J = 7.1$ Hz, 1H), 2.44 (d, $J = 7.2$ Hz, 2H), 1.90 – 1.54 (m, 5H), 1.48 (d, $J = 7.1$ Hz, 3H), 1.44 – 1.33 (m, 2H), 0.89 (d, $J = 6.6$ Hz, 6H); ^{19}F NMR (376 MHz, CDCl_3) δ -116.03 (dt, $J = 56.8, 17.5$ Hz, 2F); ^{13}C NMR (101 MHz, CDCl_3) δ 174.6 (s), 140.5 (s), 137.7 (s), 129.2 (s), 127.0 (s), 117.0 (t, $J = 239.0$ Hz), 63.9 (s), 45.1 (s), 44.9 (s), 33.4 (t, $J = 20.9$ Hz), 30.1 (s), 27.9 (s), 22.3 (s), 18.5 (t, $J = 5.6$ Hz), 18.3 (s); IR (neat) $\nu = 2957, 2870, 1734, 1383, 1167, 1125, 1095, 911.734\text{ cm}^{-1}$; HRMS (EI) Calcd for $\text{C}_{18}\text{H}_{26}\text{O}_2\text{F}_2$ $[\text{M}]^+$: 312.1901, Found: 312.1899.

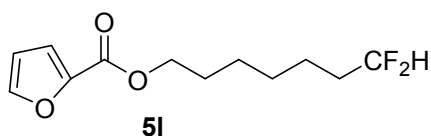


6,6-difluorohexyl 4-methoxybenzoate: 60%; Light yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 8.9$ Hz, 2H), 6.89 (d, $J = 8.9$ Hz, 2H), 5.78 (tt, $J = 56.9, 4.5$ Hz, 1H), 4.27 (t, $J = 6.5$ Hz, 2H), 3.83 (s, 3H), 1.92 – 1.67 (m, 4H), 1.58 – 1.39 (m, 4H); ^{19}F NMR (376 MHz, CDCl_3) δ -115.91 (dt, $J = 56.9, 17.6$ Hz, 2F); ^{13}C NMR (101 MHz, CDCl_3) δ 166.4 (s), 163.3 (s), 131.5 (s), 122.7 (s), 117.2 (t, $J = 238.8$ Hz), 113.6 (s), 64.3 (s), 55.4 (s), 33.9 (t, $J = 20.8$ Hz), 28.5 (s), 25.6 (s), 21.8 (t, $J = 5.5$ Hz); IR (neat) $\nu = 2956, 1712, 1607, 1277, 1258, 1168, 1103, 1031, 771\text{ cm}^{-1}$; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_3\text{F}_2$ $[\text{M}]^+$: 272.1224, Found: 272.1222.

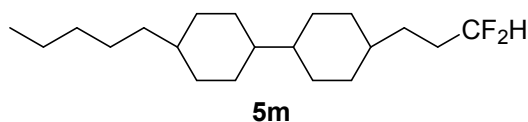


5,5-difluoro-3-methylpentyl 4-(*tert*-butyl)benzoate: 65%; Colourless liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 8.5$ Hz, 2H), 7.46 (d, $J = 8.5$ Hz, 2H), 5.90 (tt, $J = 56.8, 4.7$ Hz, 1H), 4.36 (td, $J = 6.7, 1.9$ Hz, 2H), 2.04 – 1.60 (m, 5H), 1.34 (s, 9H), 1.07 (d, $J = 6.6$ Hz, 3H); ^{19}F NMR (376 MHz, CDCl_3) δ -114.55 – -114.97 (m, 2F); ^{13}C NMR (101 MHz, CDCl_3) δ 166.5 (s), 156.6 (s), 129.4 (s), 127.4 (s), 125.3 (s), 116.8 (t, $J = 238.7$ Hz), 62.4 (s), 40.8 (t, $J = 20.3$ Hz), 35.5 (s), 35.0

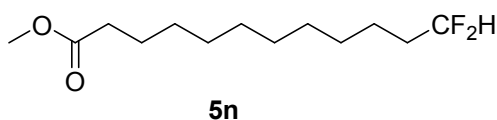
(s), 31.1 (s), 25.2 (t, $J = 5.3$ Hz), 19.5 (s); IR (neat) $\nu = 2964, 1719, 1610, 1314, 1276, 1118, 1037, 775, 708$ cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_2\text{F}_2$ $[\text{M}]^+$: 298.1744, Found: 298.1752.



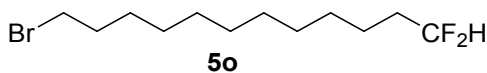
7,7-difluoroheptyl furan-2-carboxylate: 44%; Colourless liquid; ^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, $J = 1.7$ Hz, 1H), 7.14 (d, $J = 3.4$ Hz, 1H), 6.48 (dd, $J = 3.4, 1.7$ Hz, 1H), 5.77 (tt, $J = 56.9, 4.5$ Hz, 1H), 4.27 (t, $J = 6.7$ Hz, 2H), 1.90 – 1.64 (m, 4H), 1.54 – 1.31 (m, 6H); ^{19}F NMR (376 MHz, CDCl_3) δ -115.88 (dt, $J = 56.9, 17.6$ Hz, 2F); ^{13}C NMR (101 MHz, CDCl_3) δ 158.8 (s), 146.2 (s), 144.8 (s), 117.7 (s), 117.3 (t, $J = 238.7$ Hz), 111.8 (s), 64.8 (s), 33.9 (t, $J = 20.6$ Hz), 28.6 (s), 28.4 (s), 25.7 (s), 21.9 (t, $J = 5.4$ Hz); IR (neat) $\nu = 2961, 1724, 1474, 1296, 1115, 1077, 1015, 959, 799, 764$ cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{12}\text{H}_{16}\text{O}_3\text{F}_2$ $[\text{M}]^+$: 246.1068, Found: 246.1066.



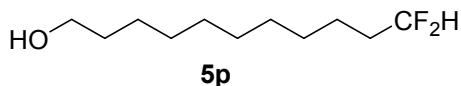
4-(3,3-difluoropropyl)-4'-pentyl-1,1'-bi(cyclohexane): 82%; Colourless liquid; ^1H NMR (400 MHz, CDCl_3) δ 5.77 (tt, $J = 57.1, 4.6$ Hz, 1H), 1.95 – 1.57 (m, 10H), 1.43 – 1.05 (m, 12H), 1.04 – 0.65 (m, 13H); ^{19}F NMR (376 MHz, CDCl_3) δ -115.64 (dt, $J = 57.1, 17.6$ Hz, 2F); ^{13}C NMR (101 MHz, CDCl_3) δ 117.7 (t, $J = 238.8$ Hz), 43.4 (s), 43.3 (s), 37.9 (s), 37.4 (s), 37.3 (s), 33.6 (s), 33.3 (s), 32.2 (s), 31.7 (t, $J = 20.5$ Hz), 30.1 (s), 29.8 (s), 29.4 (t, $J = 5.0$ Hz), 26.6 (s), 22.7 (s), 14.1 (s); IR (neat) $\nu = 2915, 2848, 1446, 1402, 1217, 1121, 1049, 916, 939, 741$ cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{20}\text{H}_{36}\text{F}_2$ $[\text{M}]^+$: 314.2785, Found: 314.2789.



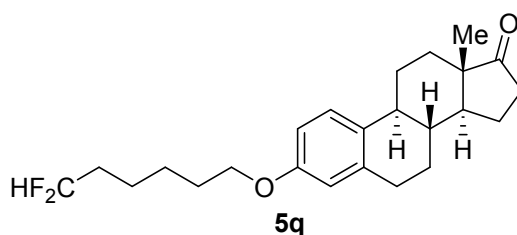
methyl 12,12-difluorododecanoate^[1]: 67%; ^1H NMR (400 MHz, CDCl_3) δ 5.77 (tt, $J = 57.1, 4.6$ Hz, 1H), 3.67 (s, 3H), 2.30 (t, $J = 7.5$ Hz, 2H), 1.92 – 1.68 (m, 2H), 1.68 – 1.51 (m, 2H), 1.53 – 1.38 (m, 2H), 1.38 – 1.18 (m, 12H); ^{19}F NMR (376 MHz, CDCl_3) δ -115.80 (dt, $J = 57.1, 17.7$ Hz, 2F).



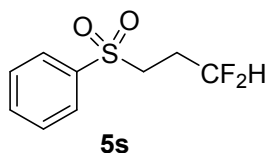
12-bromo-1,1-difluorododecane^[1]: 49%; ¹H NMR (400 MHz, CDCl₃) δ 5.73 (tt, *J* = 57.0, 4.7 Hz, 1H), 3.38 (t, *J* = 6.9 Hz, 2H), 1.97 – 1.67 (m, 4H), 1.49 – 1.13 (m, 16H). ¹⁹F NMR (376 MHz, CDCl₃) δ -115.81 (dt, *J* = 57.0, 17.7 Hz, 2F).



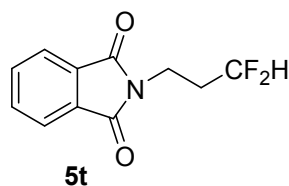
11,11-difluoroundecan-1-ol^[1]: 77%; ¹H NMR (400 MHz, CDCl₃) δ 5.75 (tt, *J* = 57.0, 5.0 Hz, 1H), 3.61 (t, *J* = 6.7 Hz, 2H), 1.95 – 1.73 (m, 2H), 1.66 – 1.50 (m, 2H), 1.51 – 1.40 (m, 2H), 1.38 – 1.19 (m, 12H); ¹⁹F NMR (376 MHz, CDCl₃) δ -115.81 (dt, *J* = 57.0, 17.7 Hz, 2F).



(8*R*,9*S*,13*S*,14*S*)-3-((6,6-difluorohexyl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one: 64%; White solid. M.P. 78.8-80.3 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.19 (d, *J* = 8.6 Hz, 1H), 6.70 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.64 (d, *J* = 2.5 Hz, 1H), 5.81 (tt, *J* = 56.9, 4.5 Hz, 1H), 3.93 (t, *J* = 6.3 Hz, 2H), 2.97 – 2.80 (m, 2H), 2.57 – 2.44 (m, 1H), 2.43 – 2.34 (m, 1H), 2.30 – 1.70 (m, 9H), 1.70 – 1.32 (m, 10H), 0.90 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ -115.84 (dt, *J* = 56.9, 17.6 Hz, 2F); ¹³C NMR (101 MHz, CDCl₃) δ 220.9 (s), 157.0 (s), 137.7 (s), 132.0 (s), 126.3 (s), 117.3 (t, *J* = 238.8 Hz), 114.5 (s), 112.1 (s), 67.4 (s), 50.4 (s), 48.0 (s), 44.0 (s), 38.4 (s), 35.8 (s), 34.0 (t, *J* = 20.7 Hz), 31.6 (s), 29.6 (s), 29.1 (s), 26.5 (s), 25.9 (s), 25.6 (s), 21.9 (t, *J* = 5.5 Hz), 21.6 (s), 13.8 (s); IR (neat) ν = 2931, 2872, 1734, 1498, 1470, 1403, 1372, 1280, 1256, 1186, 1118, 1082, 1055, 1034, 1005, 946, 921 cm⁻¹; HRMS (EI) Calcd for C₂₄H₃₂O₂F₂ [M]⁺: 390.2370, Found: 390.2373.



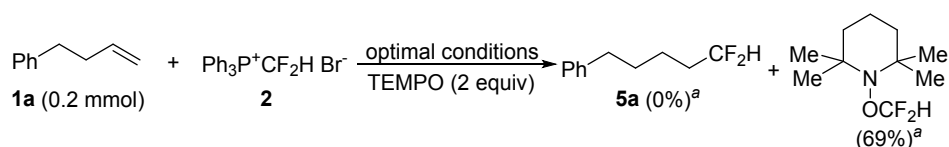
((3,3-difluoropropyl)sulfonyl)benzene^[1]: 81%; ¹H NMR (400 MHz, CDCl₃) δ 7.96 – 7.86 (m, 2H), 7.74 – 7.66 (m, 1H), 7.64 – 7.55 (m, 2H), 5.99 (tt, *J* = 56.0, 3.9 Hz, 1H), 3.25 (t, *J* = 7.9 Hz, 2H), 2.37 – 2.20 (m, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -117.41 (dt, *J* = 56.0, 17.4 Hz, 2F).



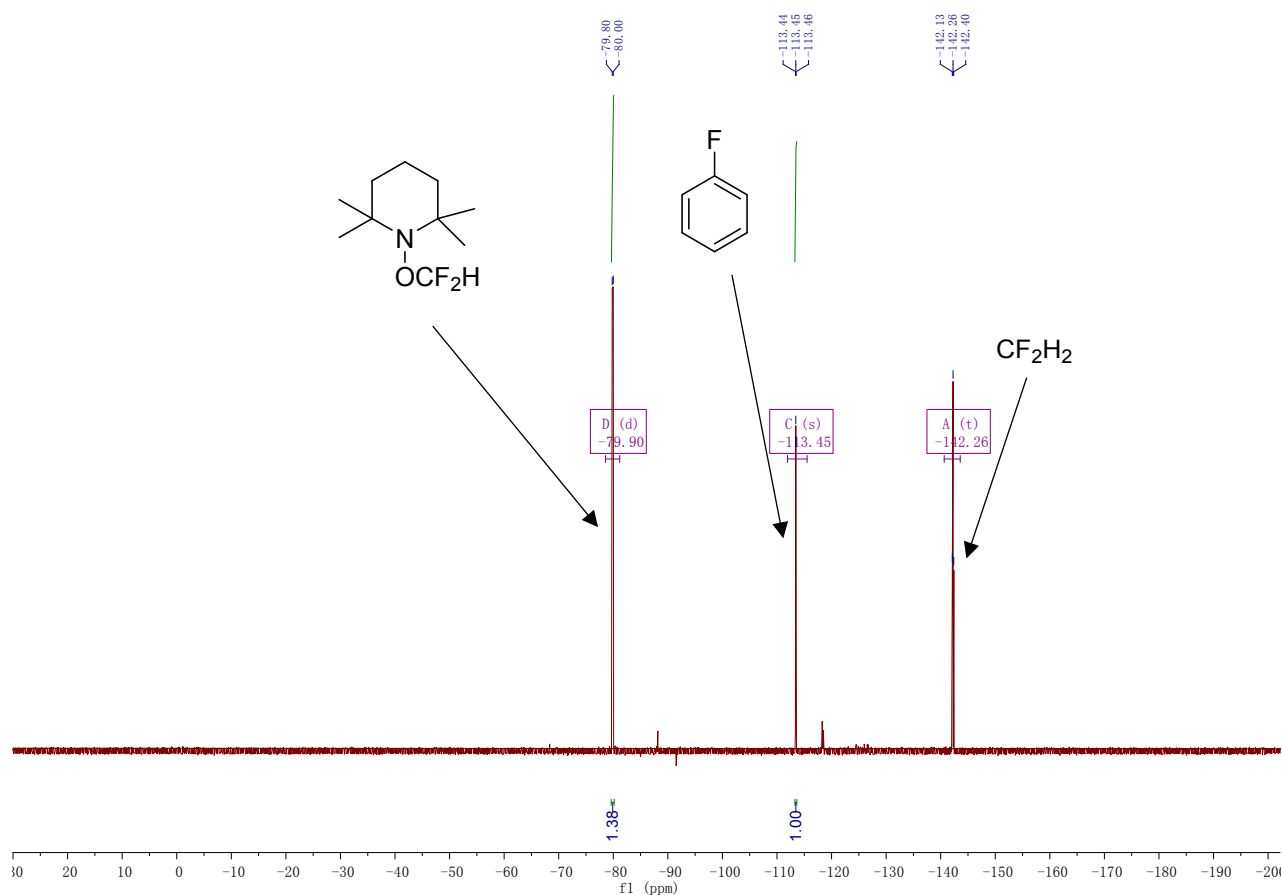
2-(3,3-difluoropropyl)isoindoline-1,3-dione^[3]: 60%; ¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.78 (m, 2H), 7.78 – 7.67 (m, 2H), 5.94 (tt, *J* = 55.9, 4.4 Hz, 1H), 3.89 (t, *J* = 6.9 Hz, 2H), 2.38 – 2.13 (m, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -116.37 (tt, *J* = 55.9, 17.0 Hz, 2F).

3. Mechanistic investigations

3.1 The formation of TEMPO-CF₂H

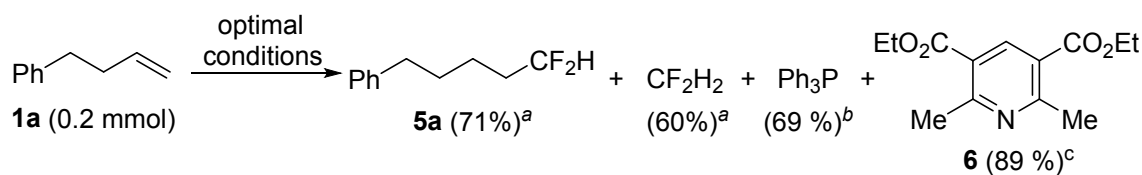


Into a 25mL Schlenk tube were added substrate **1a** (0.2 mmol, 26.4 mg, 1.0 equiv.), phosphonium salt [Ph₃P⁺CF₂H Br⁻] (0.8 mmol, 314.5 mg, 4 equiv.), Hantzsch ester **3** (0.4 mmol, 101.3 mg, 2 equiv.), Ph₂SiH₂ (0.4 mmol, 73.8 mg, 2 equiv.), NaHCO₃ (0.8 mmol, 67.2 mg, 4 equiv.) and TEMPO (0.4 mmol, 62.4 mg, 2 equiv.) under a N₂ atmosphere. After the reaction solvent DCE (3.5 mL) was added, the reaction mixture was stirred at room temperature and irradiated with 26 CFL for 22 h under a N₂ atmosphere. After the reaction was finished, fluorobenzene (0.2 mmol, 19.2 mg, 1.0 equiv.) was added as an internal standard. TEMPO-CF₂H was confirmed by ¹⁹F NMR and GC-MS spectroscopy. Its yield was determined by ¹⁹F NMR spectroscopy. ¹⁹F NMR spectrum is shown as follows. 1-(difluoromethoxy)-2,2,6,6-tetramethylpiperidine^[4]: 69%; ¹⁹F NMR (376 MHz) δ -79.90 (d, *J* = 73.5 Hz, 2F); GC-MS (EI): 207.0 (M⁺).

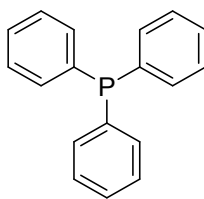


^{19}F NMR spectrum of the reaction mixture

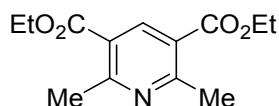
3.2 The isolation of Ph_3P and compound **6**



Into a 25mL Schlenk tube were added substrate **1a** (0.2 mmol, 26.4 mg, 1.0 equiv.), phosphonium salt $[\text{Ph}_3\text{P}^+\text{CF}_2\text{H Br}^-]$ (0.8 mmol, 314.5 mg, 4 equiv.), Hantzsch ester **3** (0.4 mmol, 101.3 mg, 2 equiv.), Ph_2SiH_2 (0.4 mmol, 73.8 mg, 2 equiv.) and NaHCO_3 (0.8 mmol, 67.2 mg, 4 equiv.) under a N_2 atmosphere. After the reaction solvent DCE (3.5 mL) was added, the reaction mixture was stirred at room temperature and irradiated with 26 CFL for 22 h under a N_2 atmosphere. The yields of **5a** and CF_2H_2 were determined by ^{19}F NMR spectroscopy by using fluorobenzene as an internal standard. Ph_3P and compound **6** were isolated by flash column chromatography.



triphenylphosphane: 69%; ^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.27 (m, 15H); ^{13}C NMR (101 MHz, CDCl_3) δ 136.9 (d, $J = 9.7$ Hz), 133.7 (d, $J = 19.4$ Hz), 128.7 (s), 128.5 (d, $J = 7.0$ Hz).



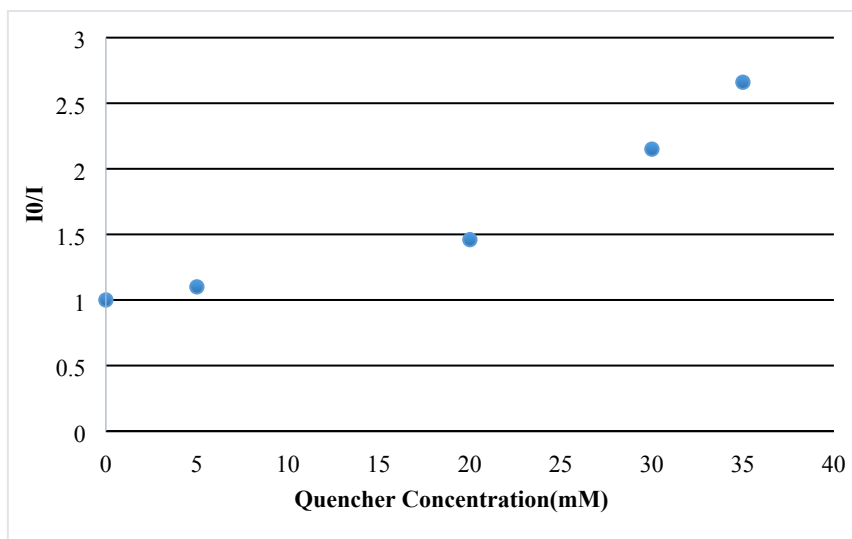
diethyl 2,6-dimethylpyridine-3,5-dicarboxylate^[5]: 89%; ^1H NMR (400 MHz, CDCl_3) δ 8.70 (s, 1H), 4.41 (q, $J = 7.1$ Hz, 4H), 2.87 (s, 6H), 1.43 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 165.86 (s), 162.15 (s), 141.07 (s), 123.18 (s), 61.45 (s), 24.82 (s), 14.27 (s).

3.3 Stern–Volmer Measurements

Emission intensities were recorded using HITACHI U-3900 fluorescence spectrometer for all experiments. All Hantzsch ester solutions were excited at 378 nm and emission intensity at 444 nm was collected.

Typical procedure for the preparation of a sample: A solution of Hantzsch ester (126.6 mg, 0.5 mmol) in DCE (100 mL) was first prepared. Into a 5 mL solution of Hantzsch ester (5×10^{-3} M) was added phosphonium salt [$\text{Ph}_3\text{P}^+\text{CF}_2\text{H Br}^-$] (9.8 mg, 0.025 mmol) under a N_2 atmosphere. 3 mL of the resulting solution (the concentration of the phosphonium salt [$\text{Ph}_3\text{P}^+\text{CF}_2\text{H Br}^-$] was 5.0 mM) was added into a screw top 1.0 cm quartz cuvette under a N_2 atmosphere.

The emission spectra of five samples containing varied concentration of the phosphonium salt [$\text{Ph}_3\text{P}^+\text{CF}_2\text{H Br}^-$] (0, 5.0 mM, 20 mM, 30 mM and 35 mM) were collected. I_0 is the luminescence intensity without the quencher and I is the intensity with the quencher. The emission quenching of the Hantzsch ester (See the figure shown as follows) indicated that the phosphonium salt [$\text{Ph}_3\text{P}^+\text{CF}_2\text{H Br}^-$] could quench the photoexcited Hantzsch ester.



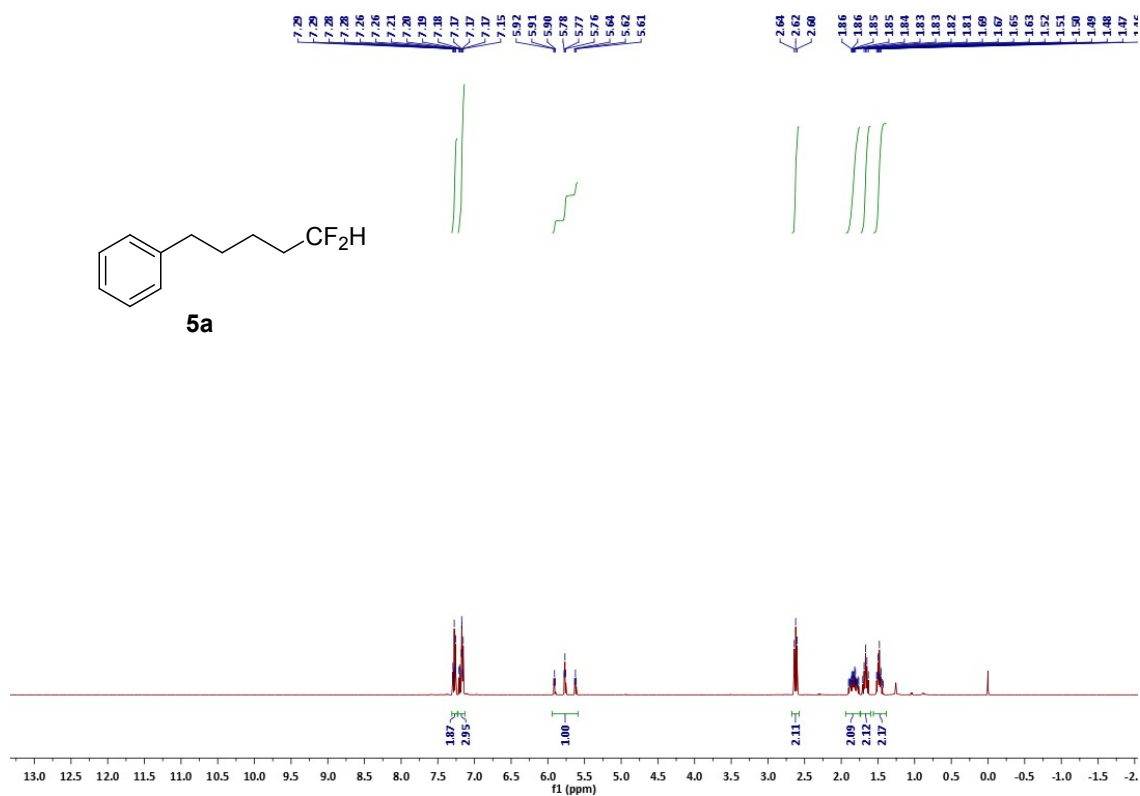
Hantzsch ester emission quenching with $\text{Ph}_3\text{P}^+\text{CF}_2\text{H Br}^-$

4. References

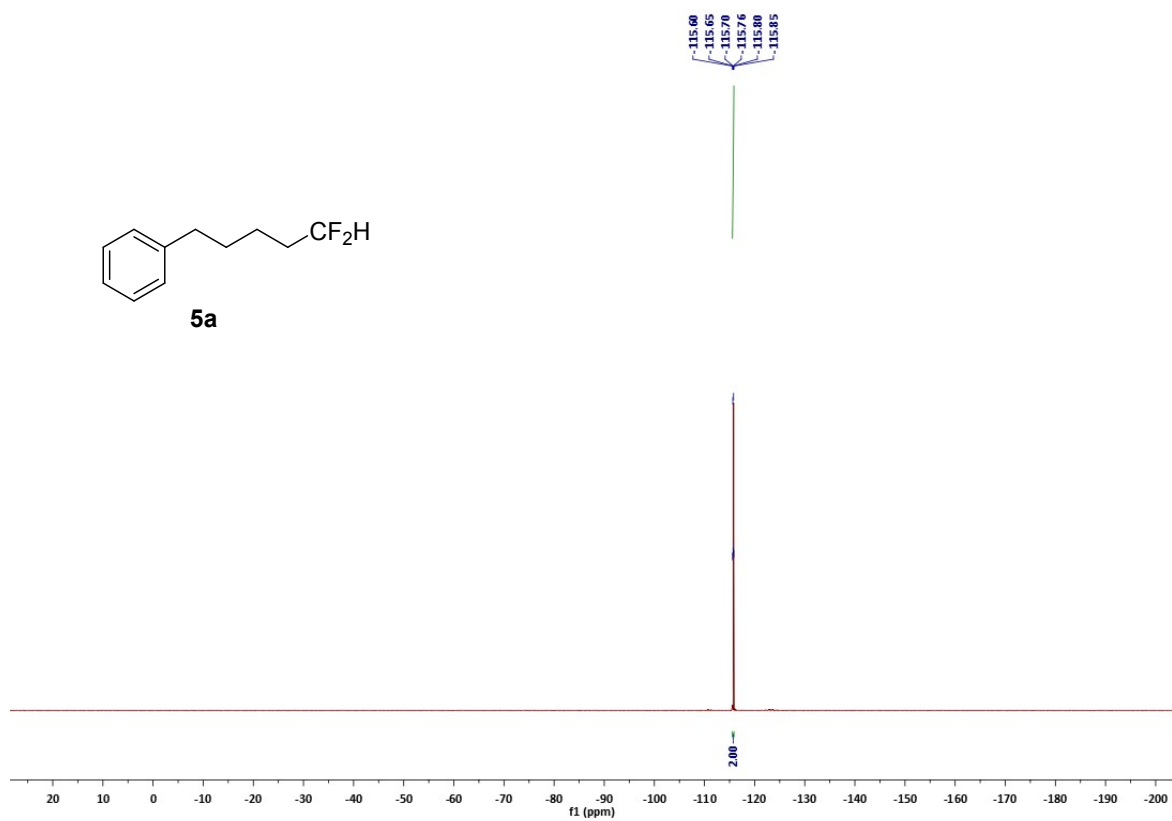
- [1] Q. Y. Lin, X. H. Xu, K. Zhang, F. L. Qing, *Angew. Chem. Int. Ed.* **2016**, 55, 1479-1483.
- [2] K. Funabiki, Y. Murase, Y. Furuno, Y. Kubota, M. Ebihara, M. Matsui, *Tetrahedron* **2010**, 66, 3283-3289.
- [3] F. Liu, A. Martin-Mingot, M. P. Jouannetaud, C. Bachmann, G. Frapper, F. Zunino, S. Thibaudeau, *J. Org. Chem.* **2011**, 76, 1460-1463.
- [4] J. Rong, L. Deng, P. Tan, C. Ni, Y. Gu, J. Hu, *Angew. Chem. Int. Ed.* **2016**, 55, 2743-2747.
- [5] K. Mullick, S. Biswas, A. M. Angeles-Boza, S. L. Suib, *Chem. Commun.* **2017**, 53, 2256-2259.

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

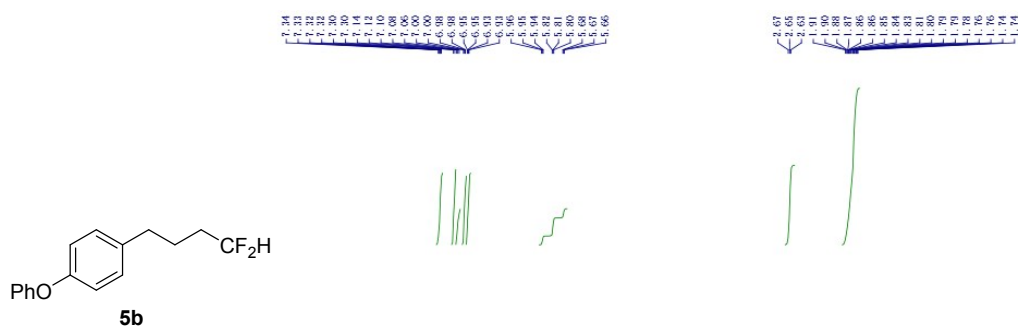
^1H NMR:



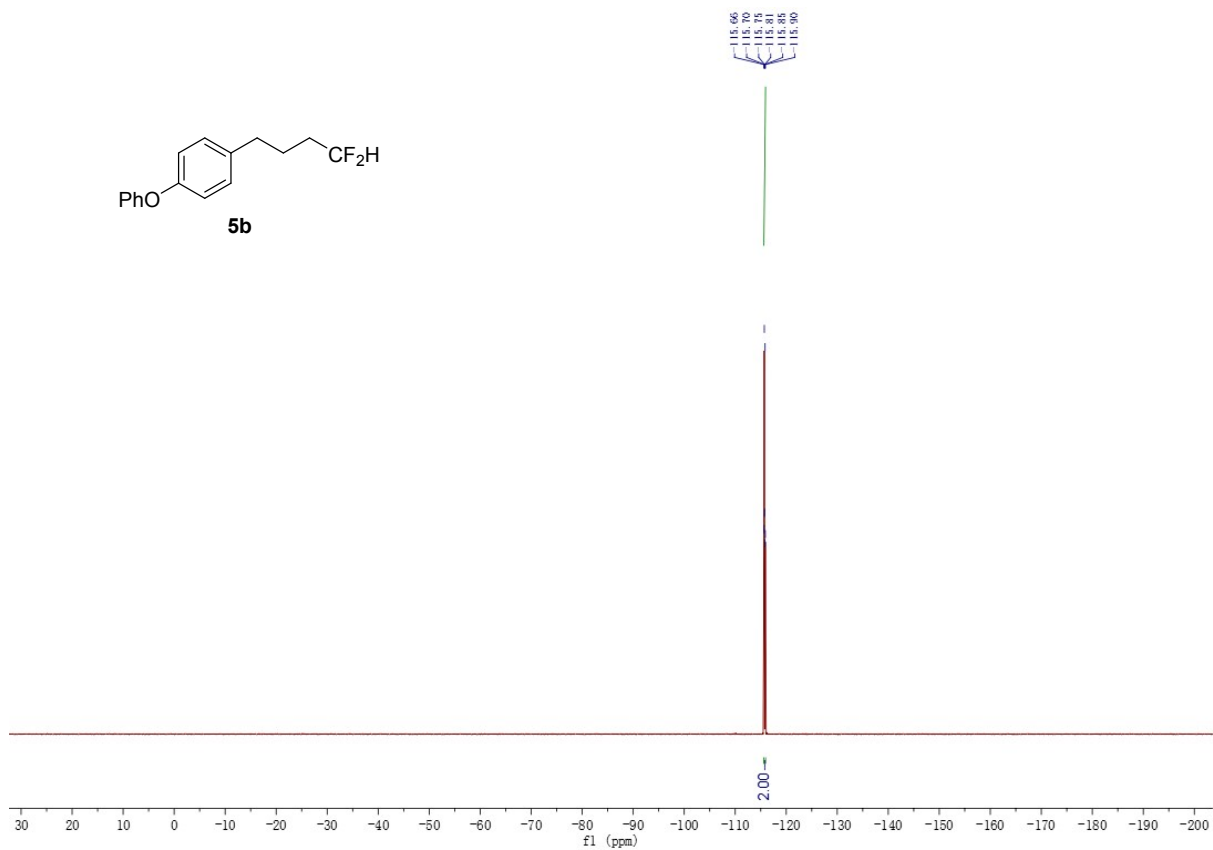
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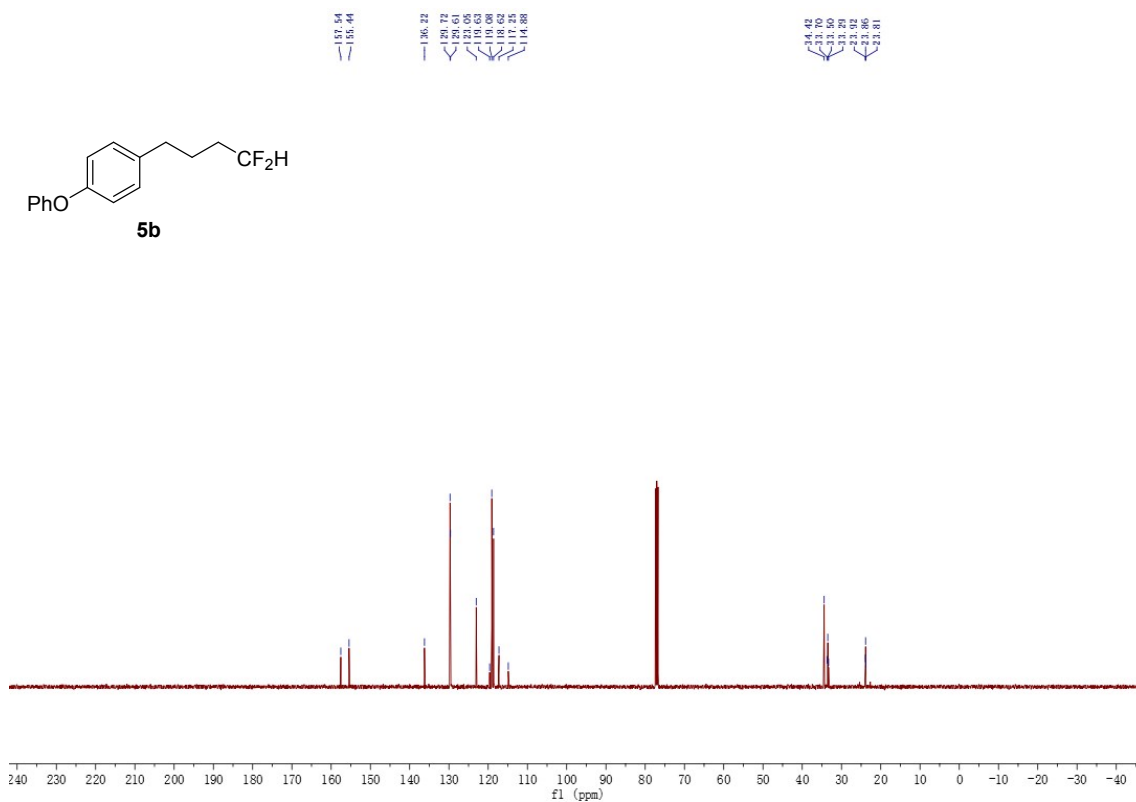
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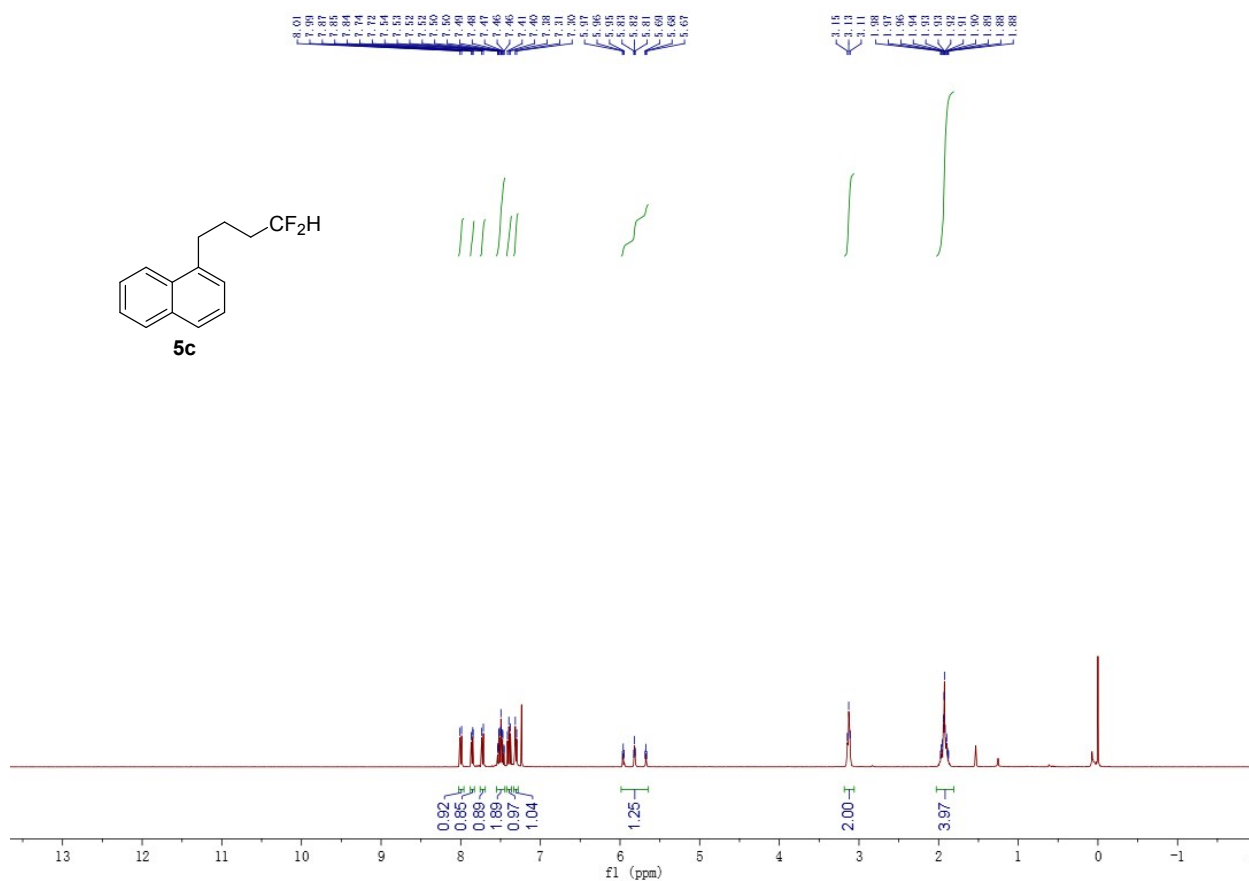
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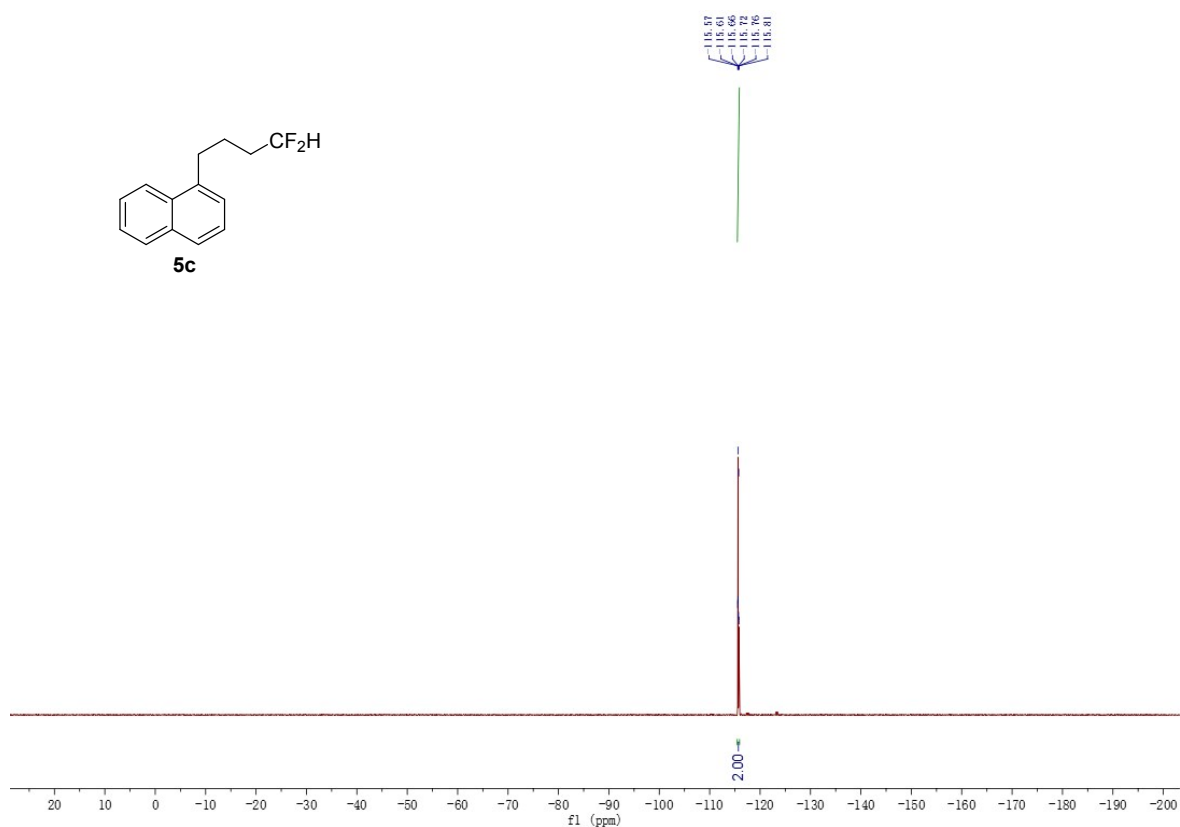
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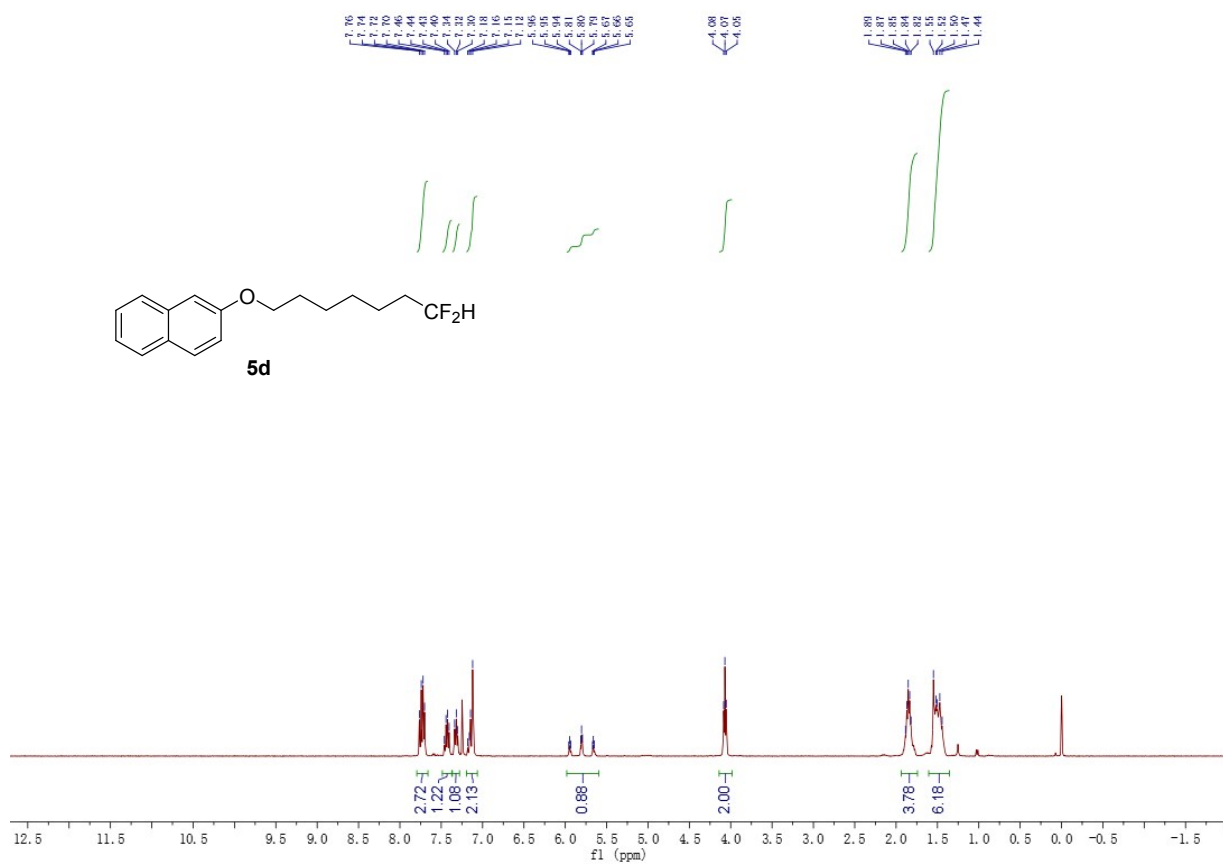
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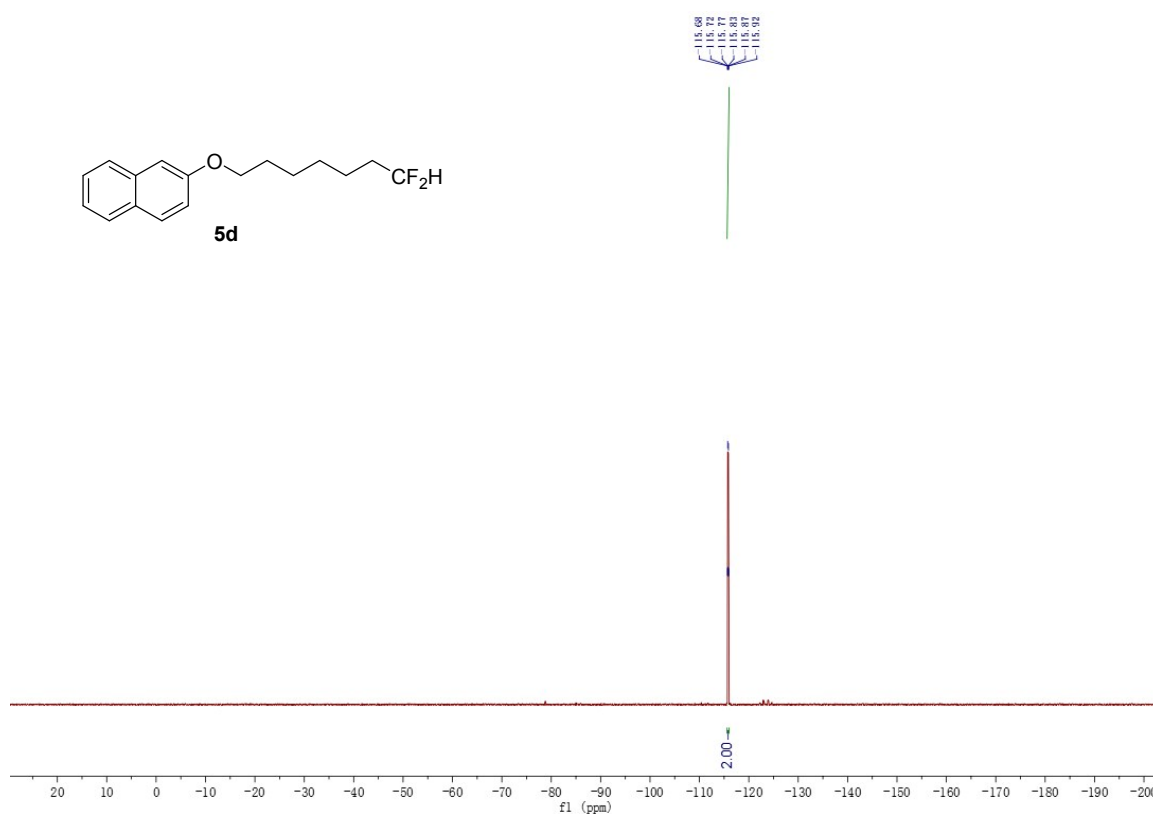
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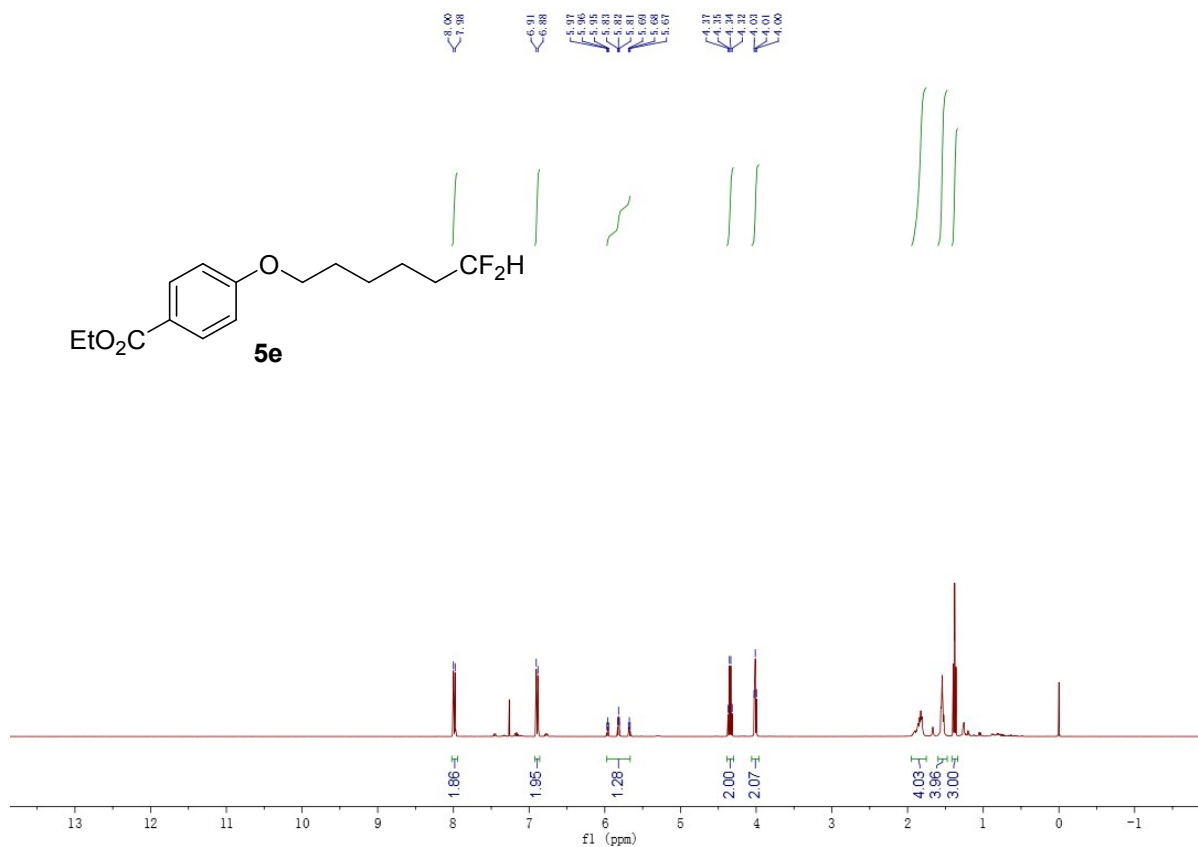
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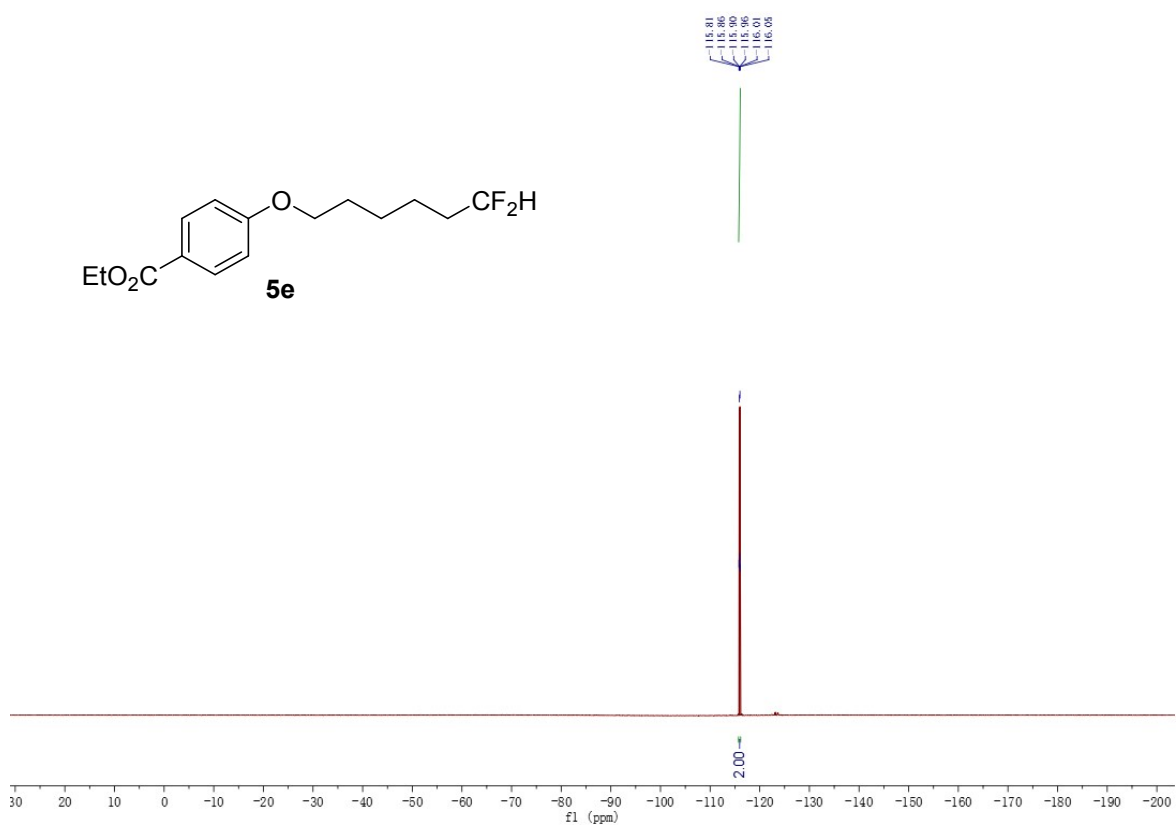
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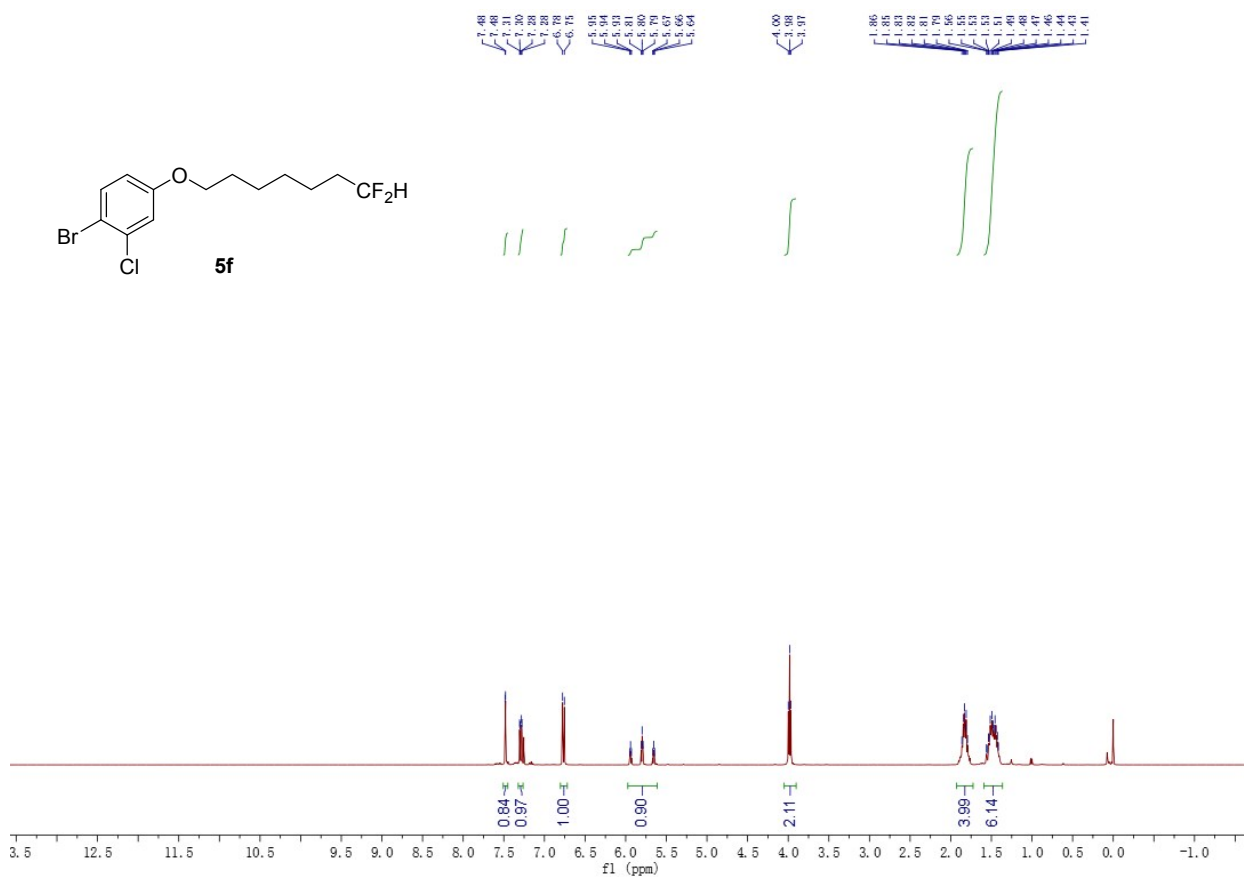
^1H NMR:



^{19}F NMR:



^1H NMR:



Chemical structure of compound **5f** is shown above the spectrum. The structure is 1-(2-bromo-3-chlorophenyl) 6-(difluoromethyl) hexan-1-ol. The spectrum displays a multiplet in the aromatic region (115.5-115.9 ppm) and a sharp peak at approximately 118.8 ppm, both integrated to 2.00. The x-axis represents the chemical shift in ppm, ranging from 20 to -200.

5g

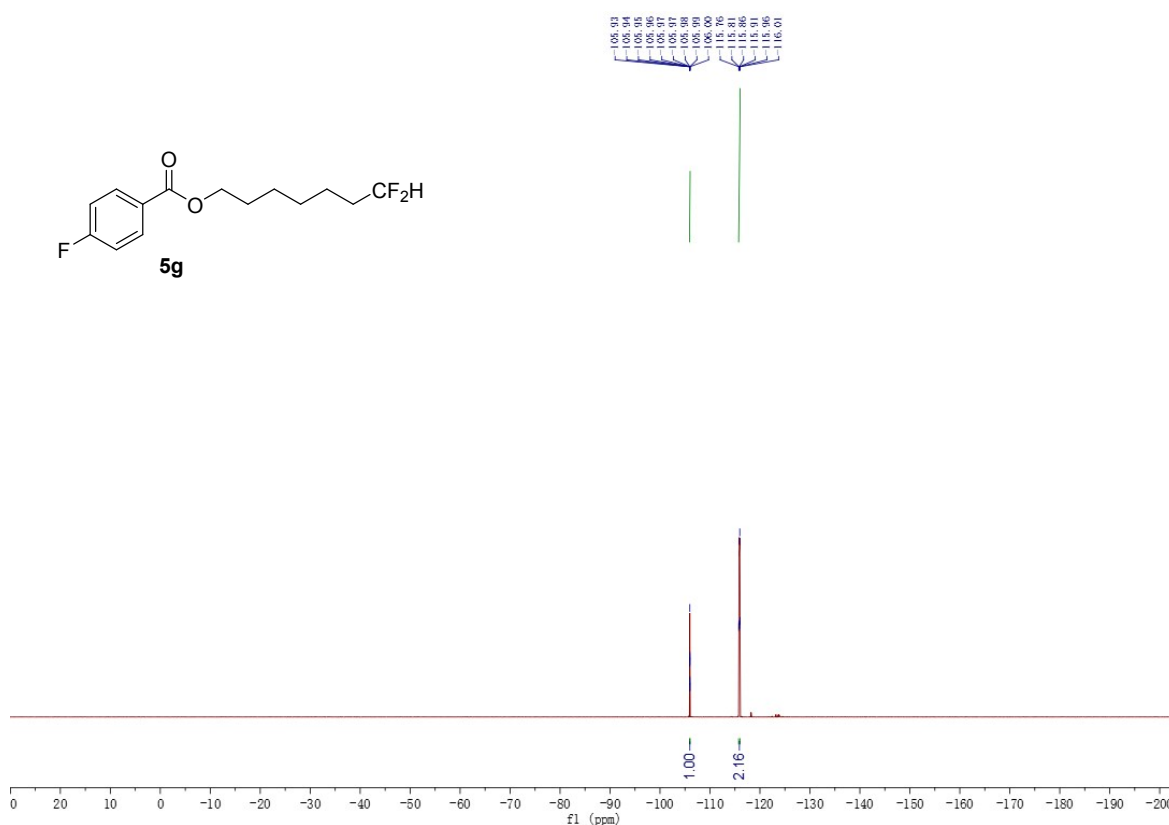
Chemical structure of **5g**: CCCCCCCC(=O)c1ccc(F)cc1

¹H NMR spectrum (CDCl₃) of **5g**. The x-axis represents the chemical shift in ppm, ranging from 0 to 13. The spectrum shows several peaks corresponding to the protons in the molecule. Integration values are provided below the peaks: 2.07, 2.00, 1.00, 2.17, 4.14, 6.07.

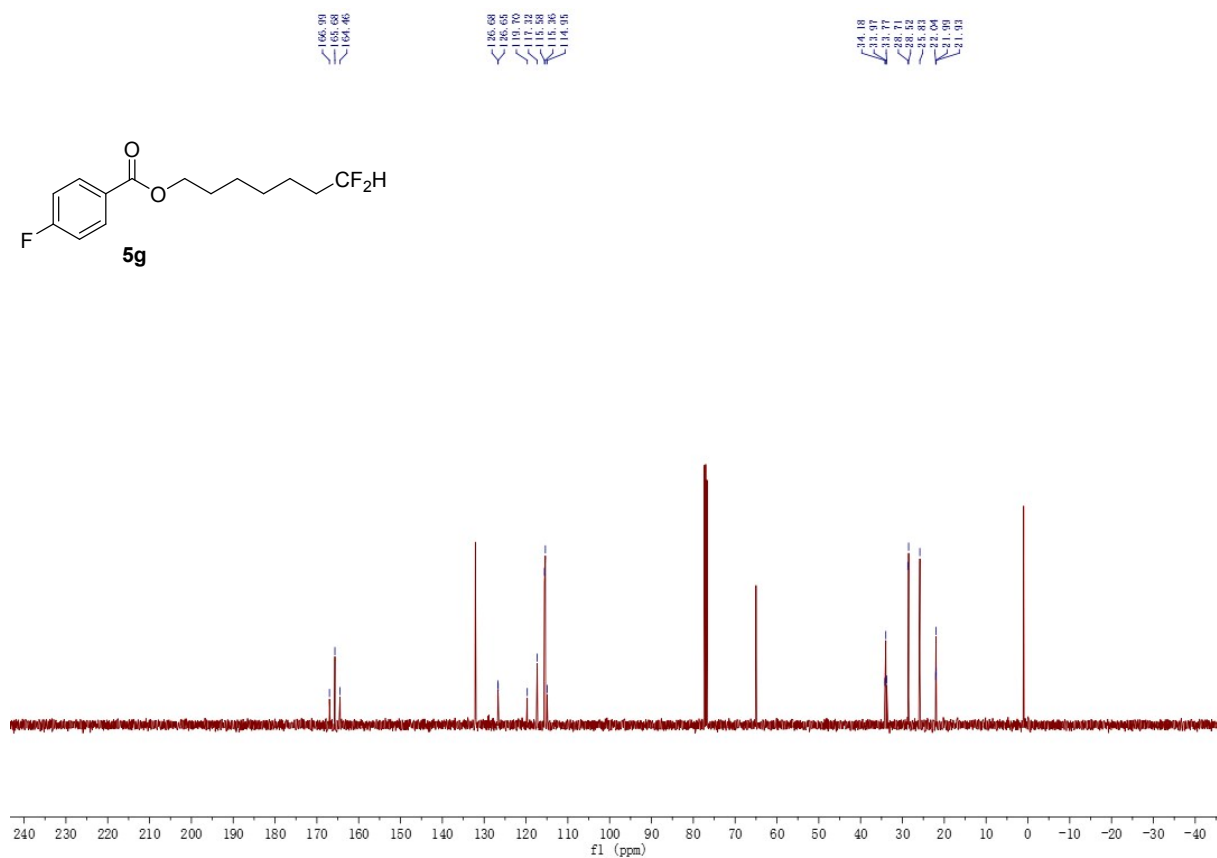
Peak list (ppm):

- 7.85, 7.83, 7.82, 7.81, 7.80, 7.79, 7.78, 7.77, 7.76, 7.75, 7.74, 7.73, 7.72, 7.71, 7.70, 7.69, 7.68, 7.67, 7.66, 7.65, 7.64, 7.63, 7.62, 7.61, 7.60, 7.59, 7.58, 7.57, 7.56, 7.55, 7.54, 7.53, 7.52, 7.51, 7.50, 7.49, 7.48, 7.47, 7.46, 7.45, 7.44, 7.43, 7.42, 7.41, 7.40, 7.39, 7.38, 7.37, 7.36, 7.35, 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22, 7.21, 7.20, 7.19, 7.18, 7.17, 7.16, 7.15, 7.14, 7.13, 7.12, 7.11, 7.10, 7.09, 7.08, 7.07, 7.06, 7.05, 7.04, 7.03, 7.02, 7.01, 7.00, 6.99, 6.98, 6.97, 6.96, 6.95, 6.94, 6.93, 6.92, 6.91, 6.90, 6.89, 6.88, 6.87, 6.86, 6.85, 6.84, 6.83, 6.82, 6.81, 6.80, 6.79, 6.78, 6.77, 6.76, 6.75, 6.74, 6.73, 6.72, 6.71, 6.70, 6.69, 6.68, 6.67, 6.66, 6.65, 6.64, 6.63, 6.62, 6.61, 6.60, 6.59, 6.58, 6.57, 6.56, 6.55, 6.54, 6.53, 6.52, 6.51, 6.50, 6.49, 6.48, 6.47, 6.46, 6.45, 6.44, 6.43, 6.42, 6.41, 6.40, 6.39, 6.38, 6.37, 6.36, 6.35, 6.34, 6.33, 6.32, 6.31, 6.30, 6.29, 6.28, 6.27, 6.26, 6.25, 6.24, 6.23, 6.22, 6.21, 6.20, 6.19, 6.18, 6.17, 6.16, 6.15, 6.14, 6.13, 6.12, 6.11, 6.10, 6.09, 6.08, 6.07, 6.06, 6.05, 6.04, 6.03, 6.02, 6.01, 6.00, 5.99, 5.98, 5.97, 5.96, 5.95, 5.94, 5.93, 5.92, 5.91, 5.90, 5.89, 5.88, 5.87, 5.86, 5.85, 5.84, 5.83, 5.82, 5.81, 5.80, 5.79, 5.78, 5.77, 5.76, 5.75, 5.74, 5.73, 5.72, 5.71, 5.70, 5.69, 5.68, 5.67, 5.66, 5.65, 5.64, 5.63, 5.62, 5.61, 5.60, 5.59, 5.58, 5.57, 5.56, 5.55, 5.54, 5.53, 5.52, 5.51, 5.50, 5.49, 5.48, 5.47, 5.46, 5.45, 5.44, 5.43, 5.42, 5.41, 5.40, 5.39, 5.38, 5.37, 5.36, 5.35, 5.34, 5.33, 5.32, 5.31, 5.30, 5.29, 5.28, 5.27, 5.26, 5.25, 5.24, 5.23, 5.22, 5.21, 5.20, 5.19, 5.18, 5.17, 5.16, 5.15, 5.14, 5.13, 5.12, 5.11, 5.10, 5.09, 5.08, 5.07, 5.06, 5.05, 5.04, 5.03, 5.02, 5.01, 5.00, 4.99, 4.98, 4.97, 4.96, 4.95, 4.94, 4.93, 4.92, 4.91, 4.90, 4.89, 4.88, 4.87, 4.86, 4.85, 4.84, 4.83, 4.82, 4.81, 4.80, 4.79, 4.78, 4.77, 4.76, 4.75, 4.74, 4.73, 4.72, 4.71, 4.70, 4.69, 4.68, 4.67, 4.66, 4.65, 4.64, 4.63, 4.62, 4.61, 4.60, 4.59, 4.58, 4.57, 4.56, 4.55, 4.54, 4.53, 4.52, 4.51, 4.50, 4.49, 4.48, 4.47, 4.46, 4.45, 4.44, 4.43, 4.42, 4.41, 4.40, 4.39, 4.38, 4.37, 4.36, 4.35, 4.34, 4.33, 4.32, 4.31, 4.30, 4.29, 4.28, 4.27, 4.26, 4.25, 4.24, 4.23, 4.22, 4.21, 4.20, 4.19, 4.18, 4.17, 4.16, 4.15, 4.14, 4.13, 4.12, 4.11, 4.10, 4.09, 4.08, 4.07, 4.06, 4.05, 4.04, 4.03, 4.02, 4.01, 4.00, 3.99, 3.98, 3.97, 3.96, 3.95, 3.94, 3.93, 3.92, 3.91, 3.90, 3.89, 3.88, 3.87, 3.86, 3.85, 3.84, 3.83, 3.82, 3.81, 3.80, 3.79, 3.78, 3.77, 3.76, 3.75, 3.74, 3.73, 3.72, 3.71, 3.70, 3.69, 3.68, 3.67, 3.66, 3.65, 3.64, 3.63, 3.62, 3.61, 3.60, 3.59, 3.58, 3.57, 3.56, 3.55, 3.54, 3.53, 3.52, 3.51, 3.50, 3.49, 3.48, 3.47, 3.46, 3.45, 3.44, 3.43, 3.42, 3.41, 3.40, 3.39, 3.38, 3.37, 3.36, 3.35, 3.34, 3.33, 3.32, 3.31, 3.30, 3.29, 3.28, 3.27, 3.26, 3.25, 3.24, 3.23, 3.22, 3.21, 3.20, 3.19, 3.18, 3.17, 3.16, 3.15, 3.14, 3.13, 3.12, 3.11, 3.10, 3.09, 3.08, 3.07, 3.06, 3.05, 3.04, 3.03, 3.02, 3.01, 3.00, 2.99, 2.98, 2.97, 2.96, 2.95, 2.94, 2.93, 2.92, 2.91, 2.90, 2.89, 2.88, 2.87, 2.86, 2.85, 2.84, 2.83, 2.82, 2.81, 2.80, 2.79, 2.78, 2.77, 2.76, 2.75, 2.74, 2.73, 2.72, 2.71, 2.70, 2.69, 2.68, 2.67, 2.66, 2.65, 2.64, 2.63, 2.62, 2.61, 2.60, 2.59, 2.58, 2.57, 2.56, 2.55, 2.54, 2.53, 2.52, 2.51, 2.50, 2.49, 2.48, 2.47, 2.46, 2.45, 2.44, 2.43, 2.42, 2.41, 2.40, 2.39, 2.38, 2.37, 2.36, 2.35, 2.34, 2.33, 2.32, 2.31, 2.30, 2.29, 2.28, 2.27, 2.26, 2.25, 2.24, 2.23, 2.22, 2.21, 2.20, 2.19, 2.18, 2.17, 2.16, 2.15, 2.14, 2.13, 2.12, 2.11, 2.10, 2.09, 2.08, 2.07, 2.06, 2.05, 2.04, 2.03, 2.02, 2.01, 2.00, 1.99, 1.98, 1.97, 1.96, 1.95, 1.94, 1.93, 1.92, 1.91, 1.90, 1.89, 1.88, 1.87, 1.86, 1.85, 1.84, 1.83, 1.82, 1.81, 1.80, 1.79, 1.78, 1.77, 1.76, 1.75, 1.74, 1.73, 1.72, 1.71, 1.70, 1.69, 1.68, 1.67, 1.66, 1.65, 1.64, 1.63, 1.62, 1.61, 1.6

^{19}F NMR:



^{13}C NMR:



5h

CCCCCCCCC(=O)c1ccccc1F

¹H NMR spectrum (CDCl₃) of compound 5h. The spectrum shows peaks in the aromatic region (7.2-7.8 ppm), a methylene region (1.2-1.8 ppm), and a terminal CF₂H group (4.5-4.8 ppm). Integration values are provided below the peaks.

Chemical Shift (ppm)	Integration
7.2-7.8	0.95, 1.01, 1.02, 0.99
5.8-6.0	1.00
4.5-4.8	2.12
1.2-1.8	4.19, 6.14

5h

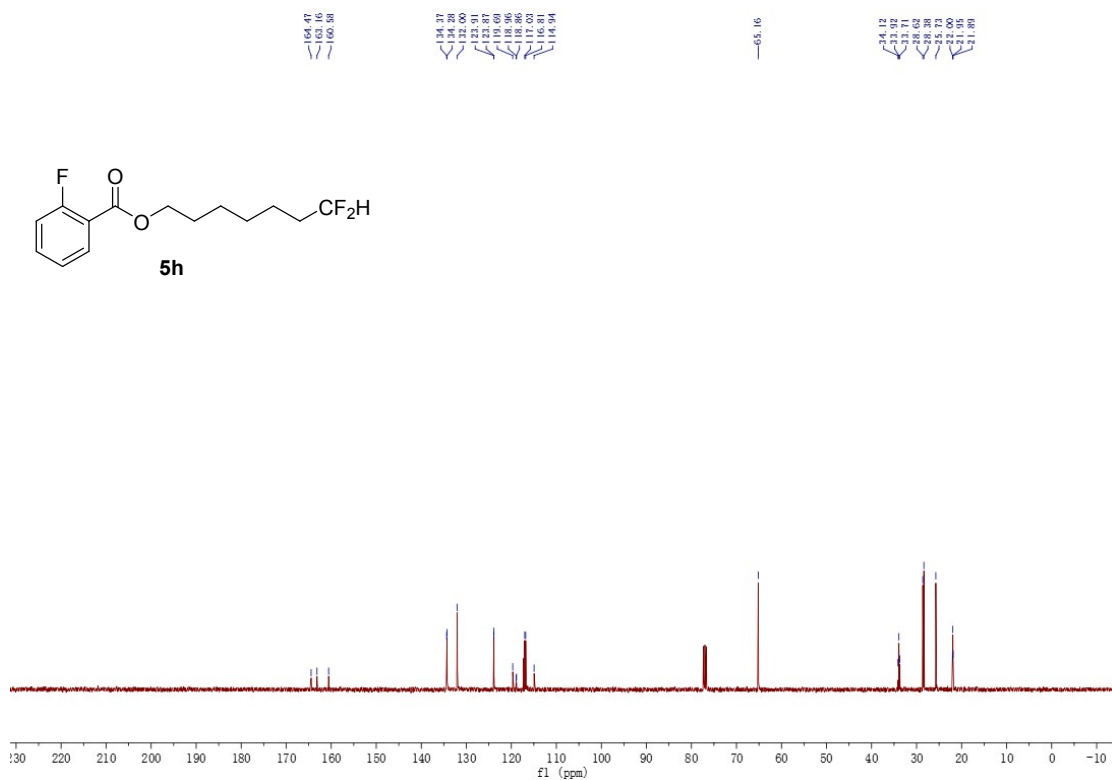
FC(F)(F)CCCCCOC(=O)c1ccccc1F

100.58
100.50
100.46
100.61
100.62
100.63
100.64
115.74
115.79
115.84
115.89
115.90
115.99

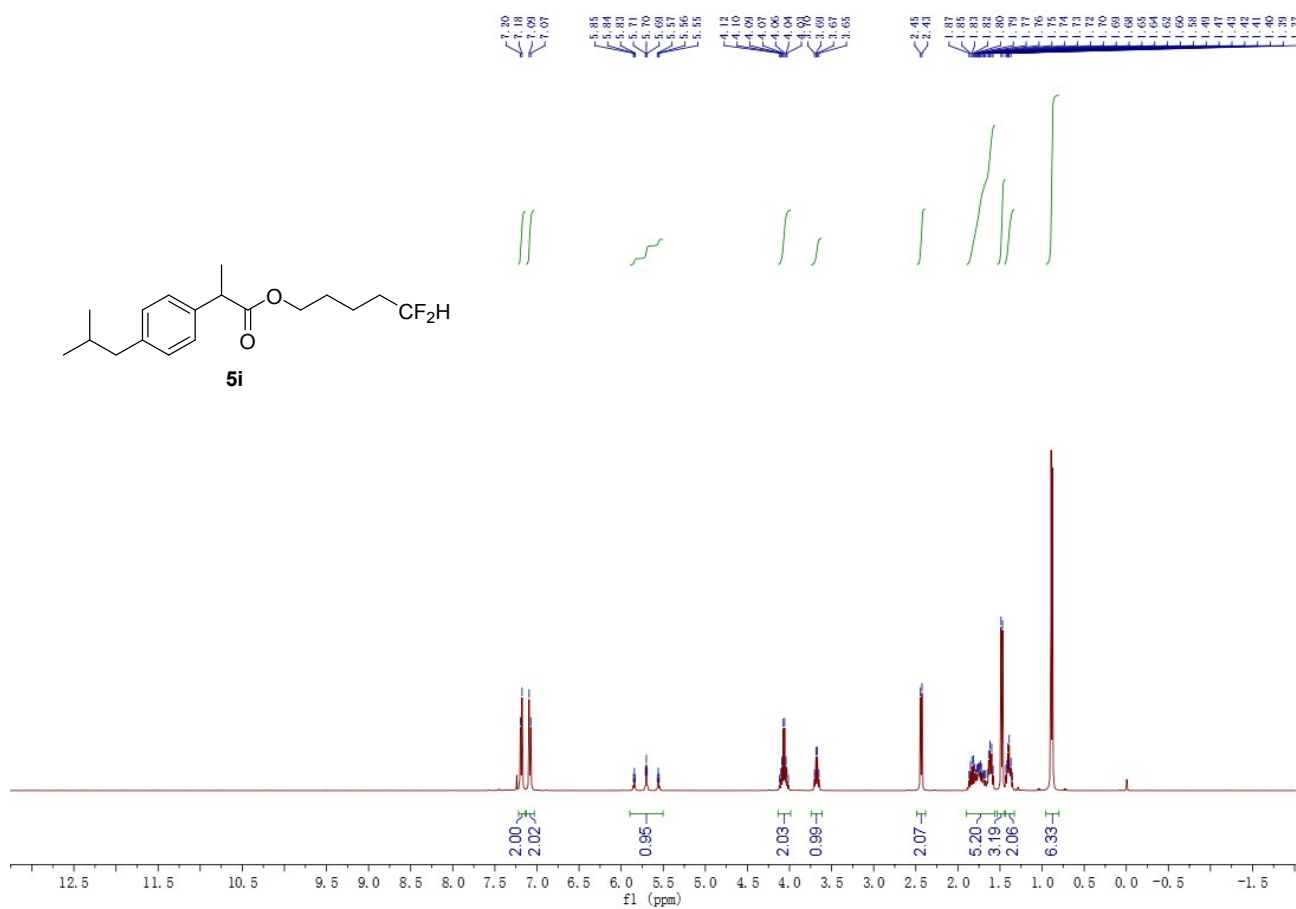
1.00
2.00

f1 (ppm)

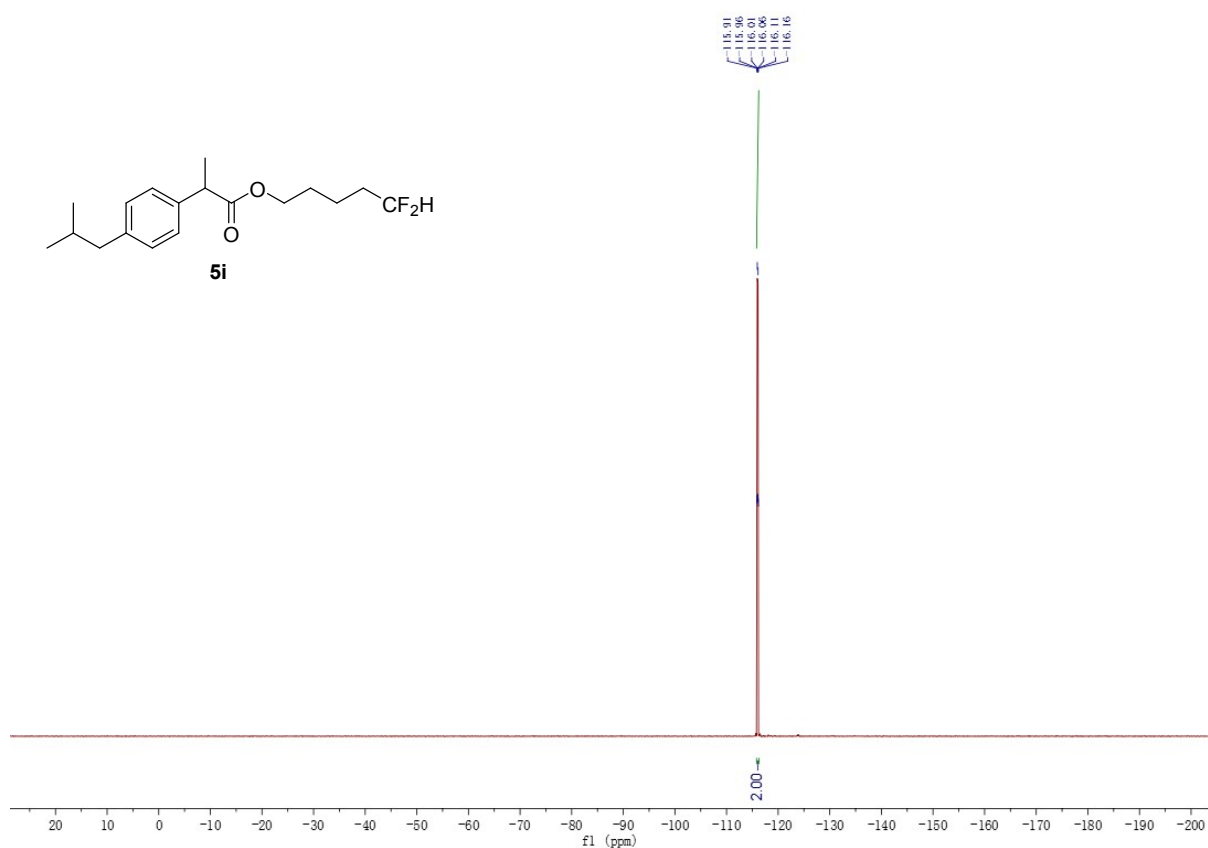
^{13}C NMR:



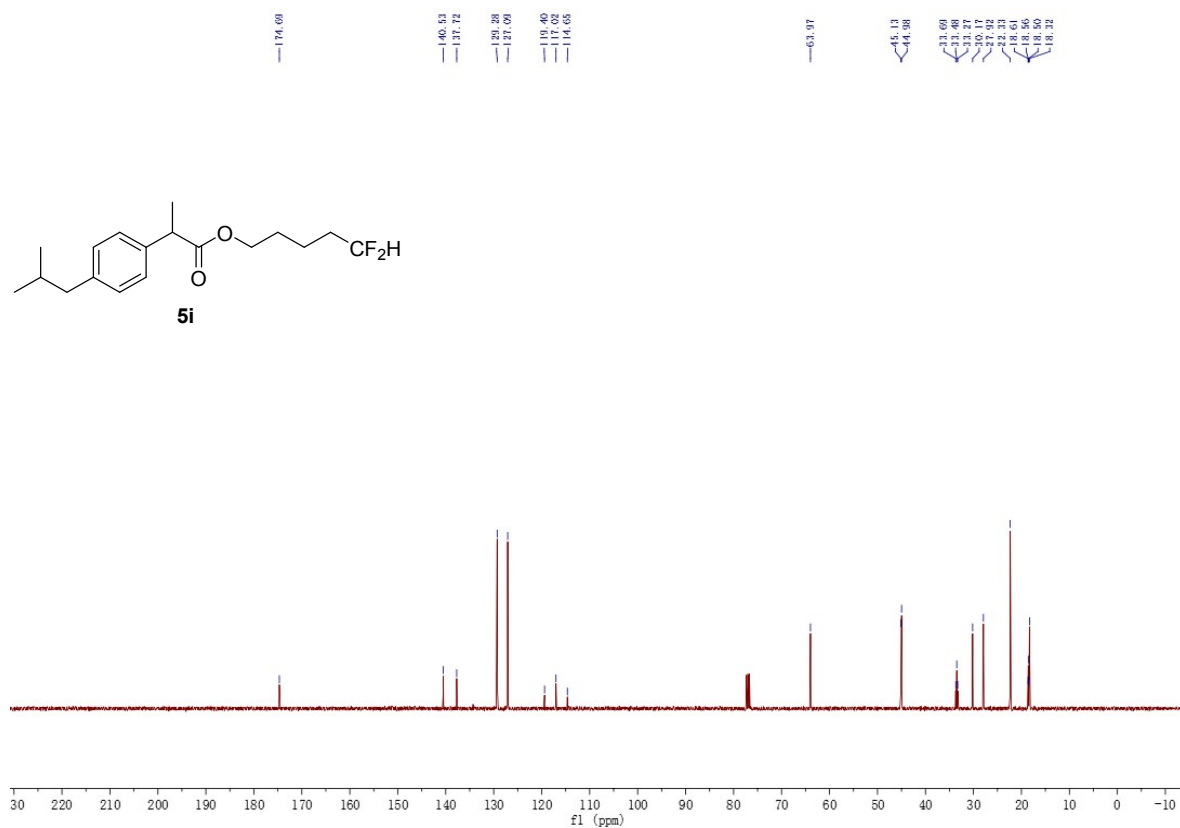
^1H NMR:



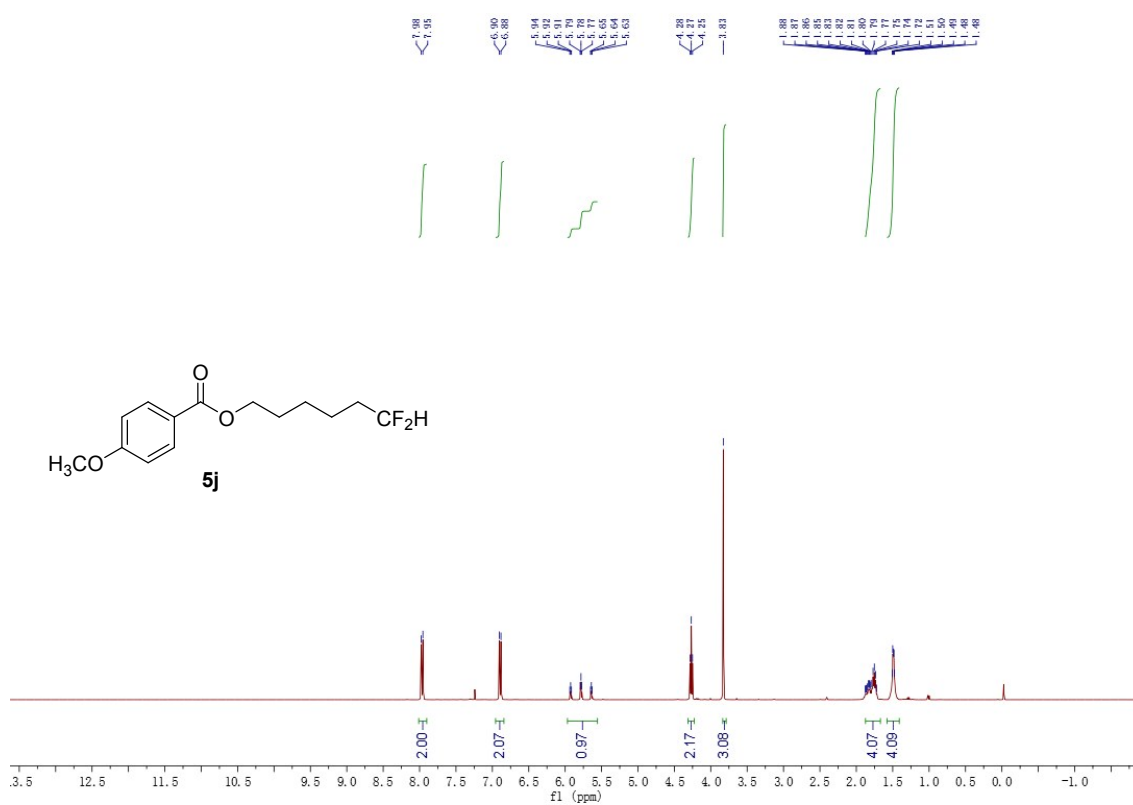
^{19}F NMR:



^{13}C NMR:



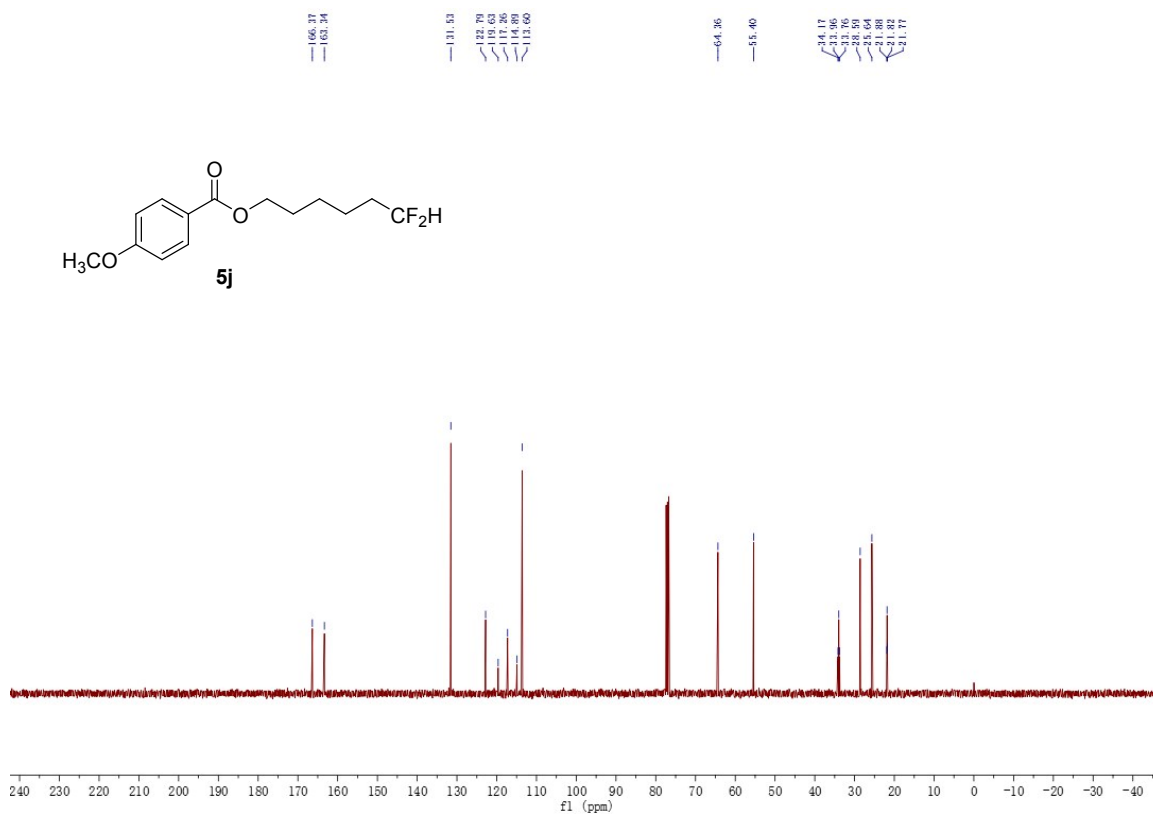
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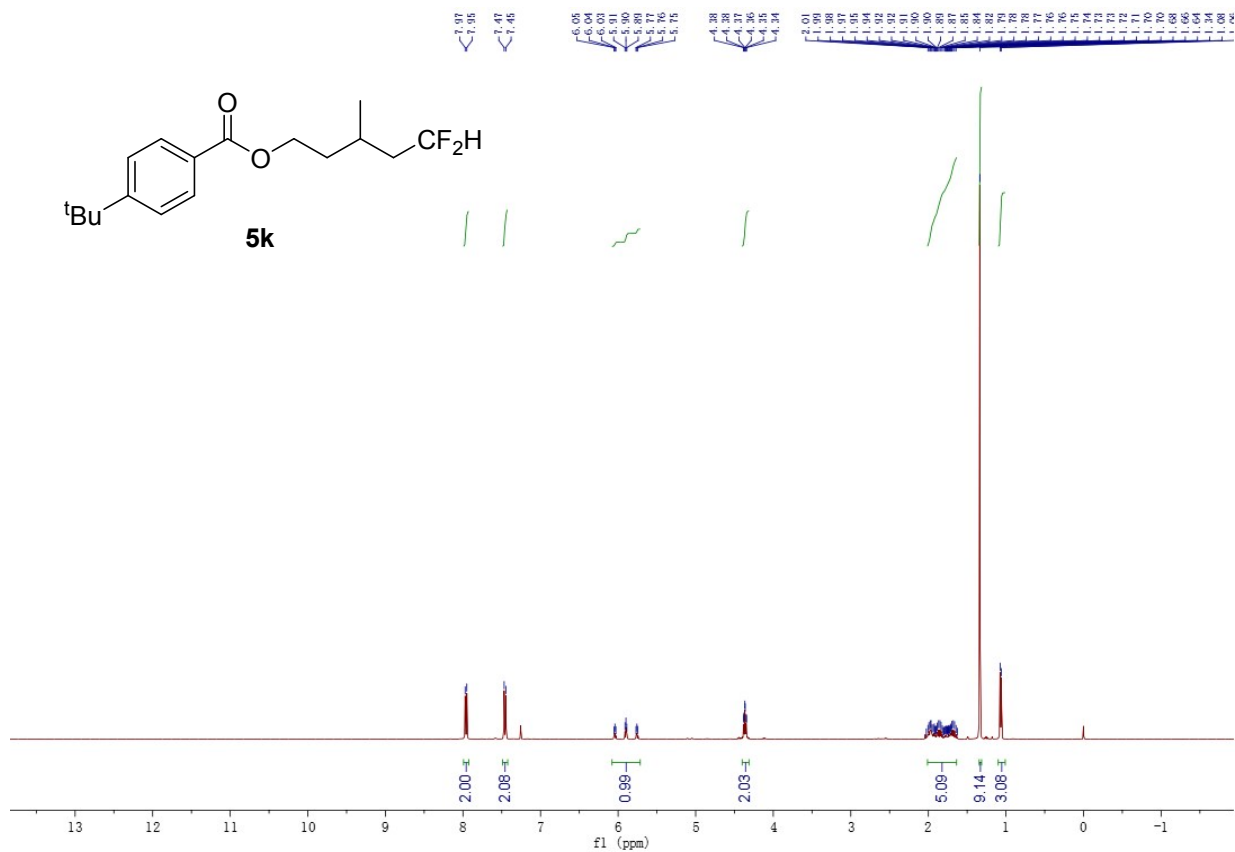
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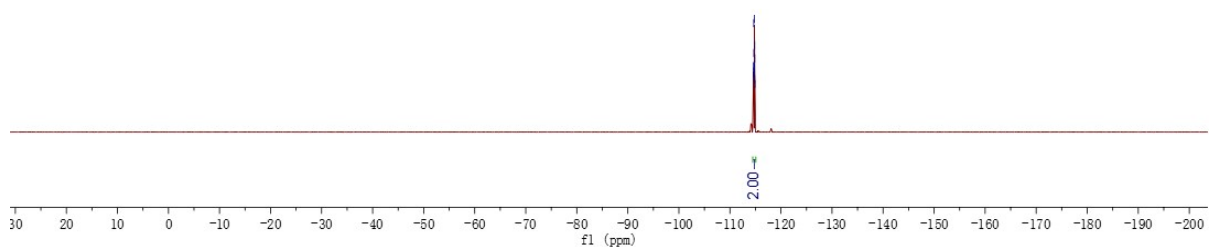
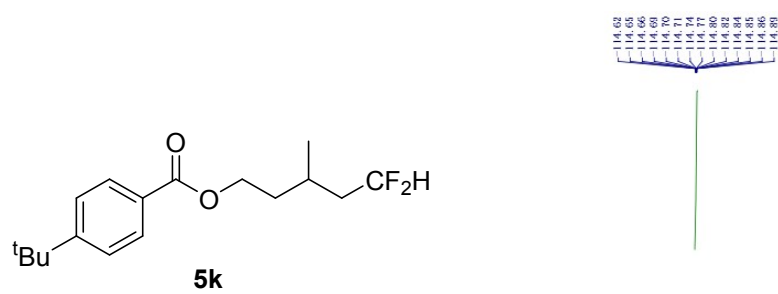
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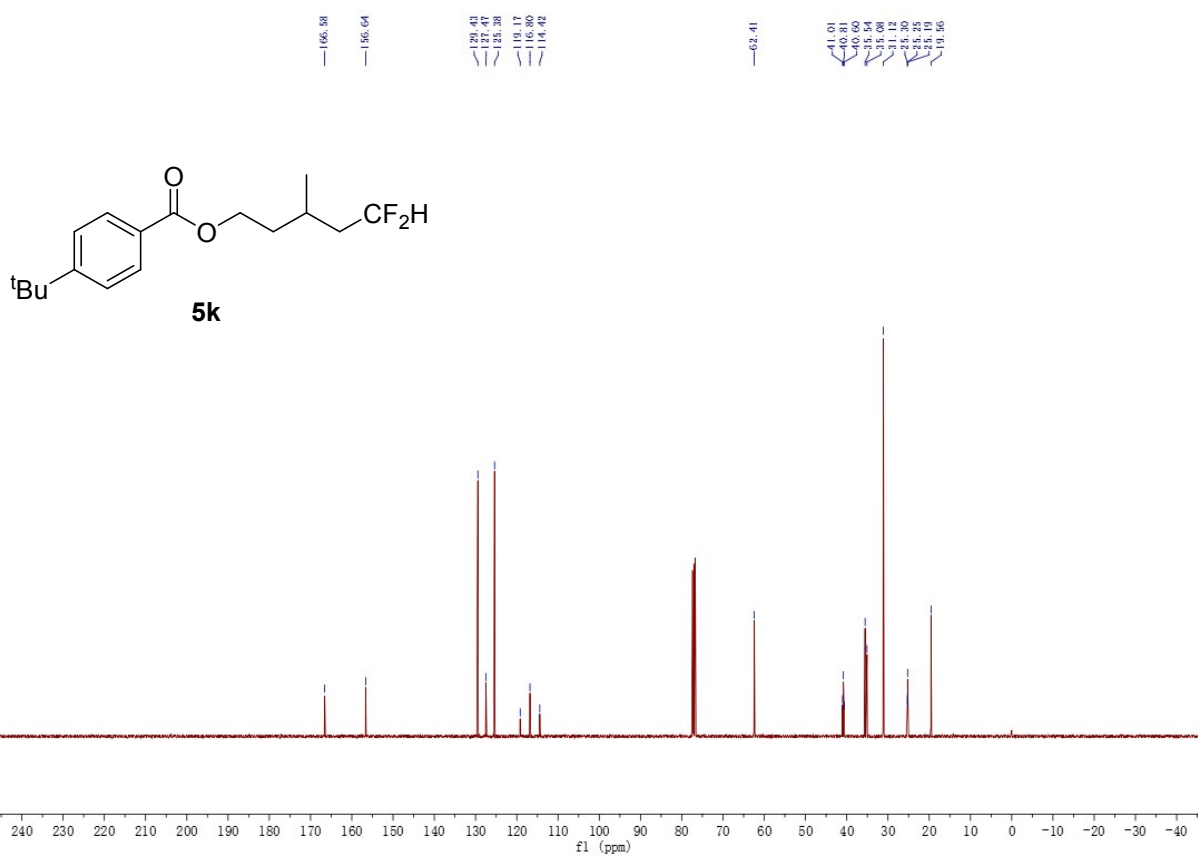
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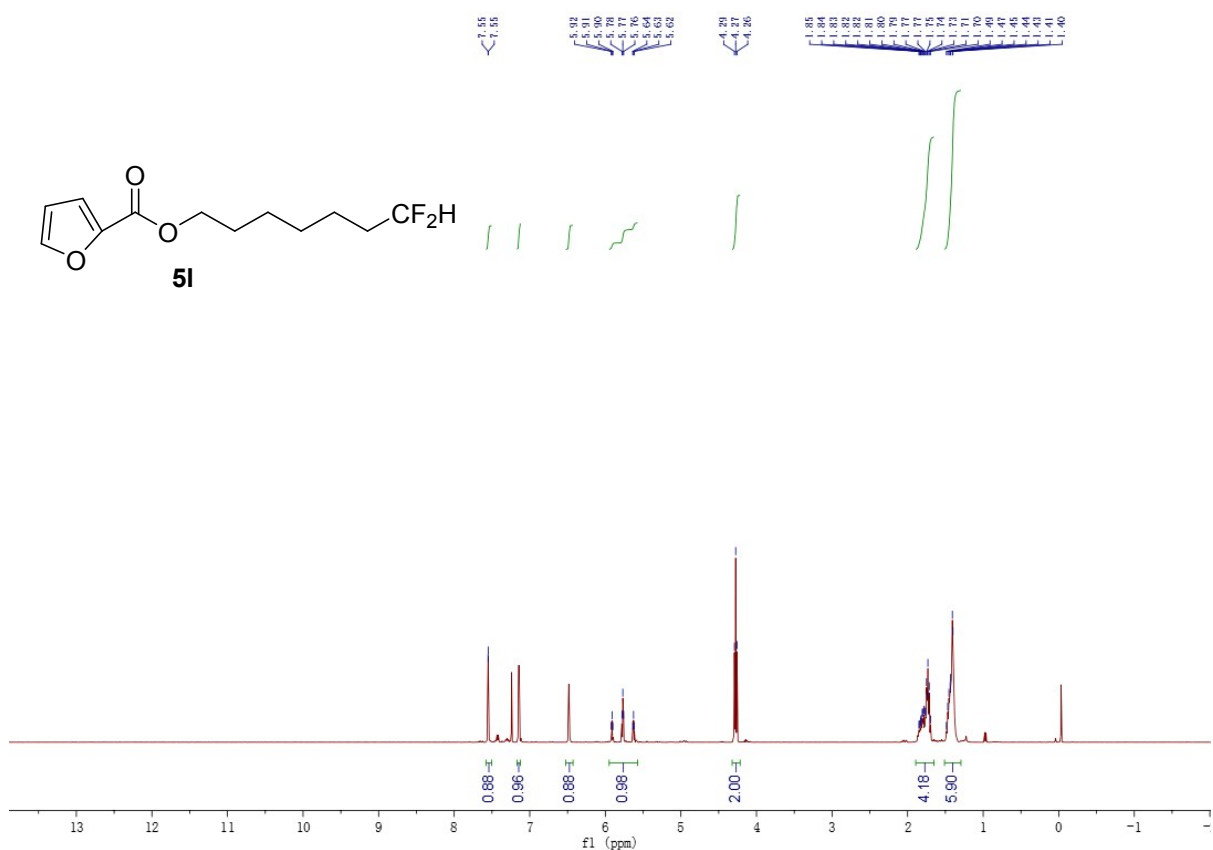
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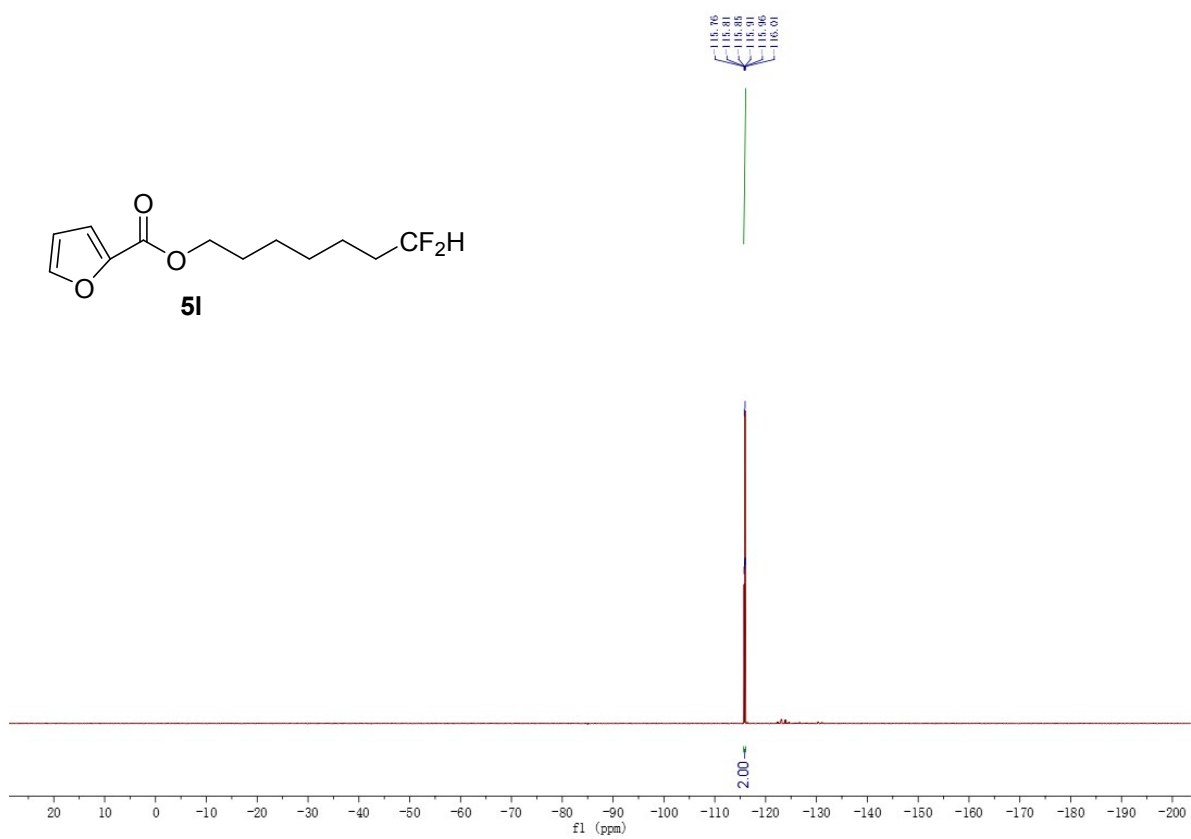
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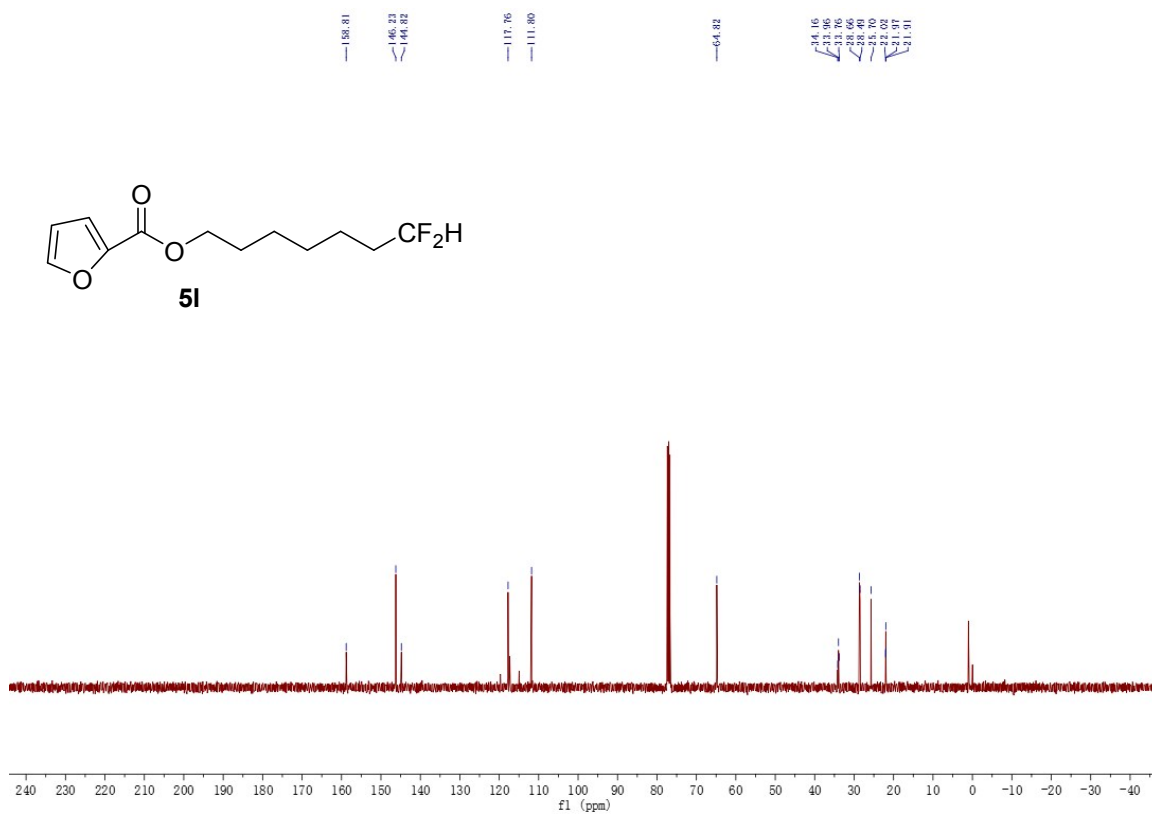
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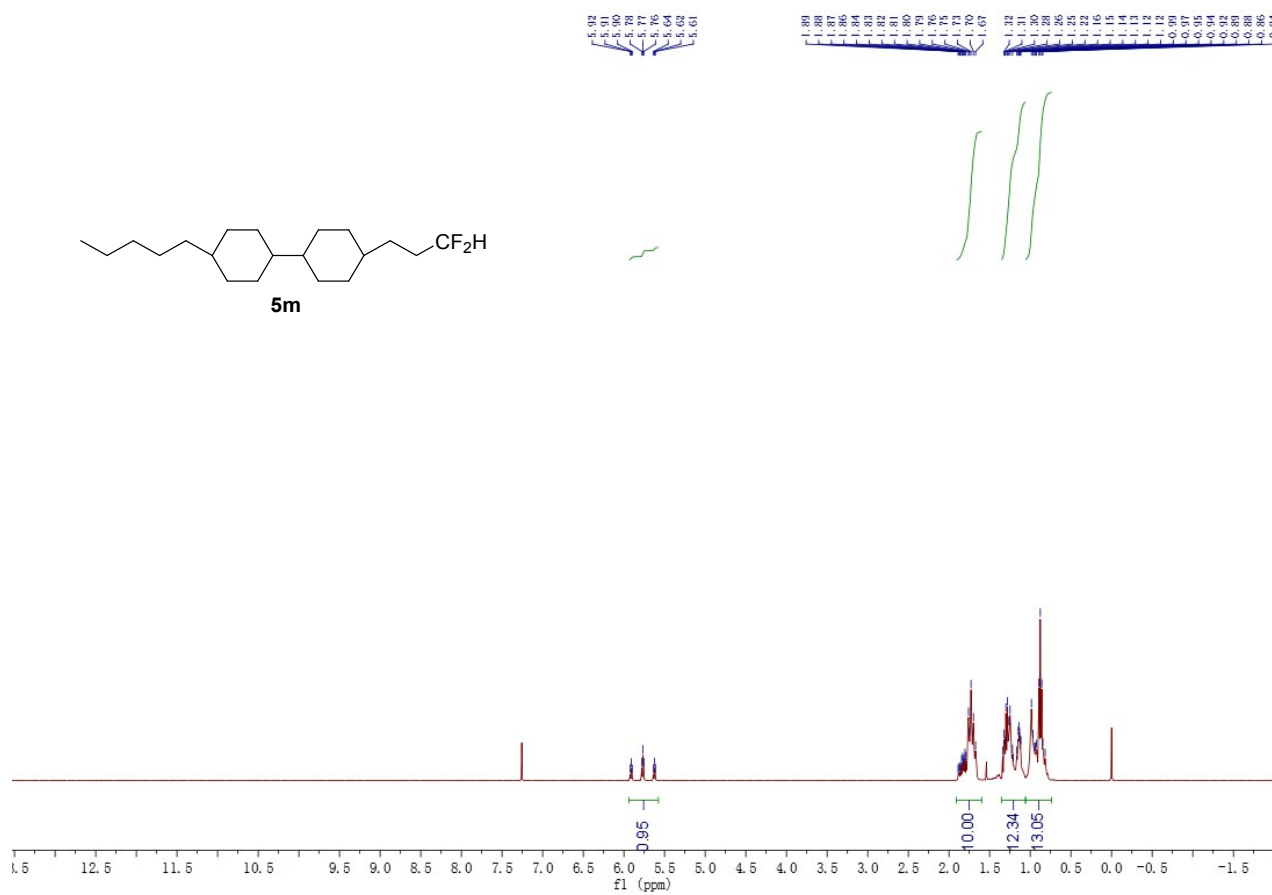
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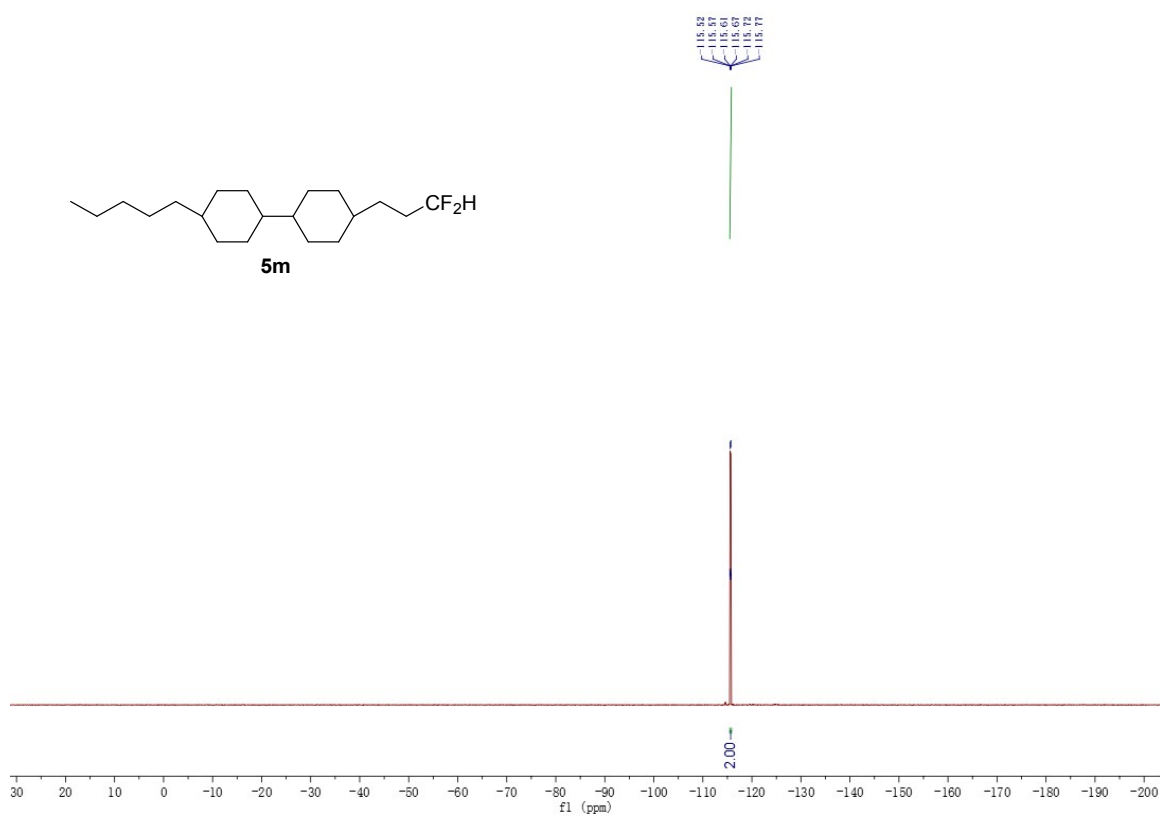
^{13}C NMR:



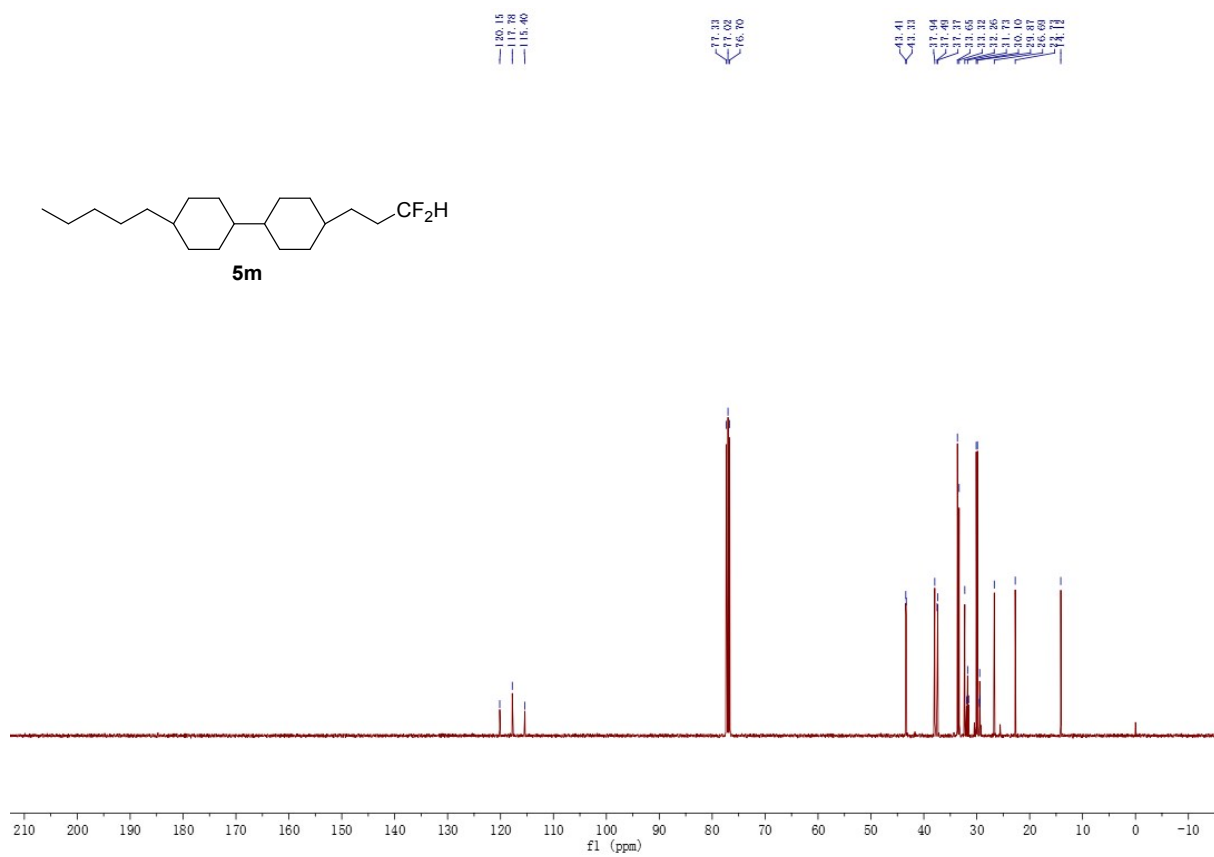
^1H NMR:



^{19}F NMR:



^{13}C NMR:



CCCCCCCCCCCCCCCC(=O)OC

5n

¹H NMR spectrum (CDCl₃) of compound **5n**. The spectrum shows a triplet at ~7.2 ppm (TMS), a multiplet between 5.5-6.0 ppm (CH₂ groups), a singlet at ~3.7 ppm (OCH₃), and a large multiplet between 1.0-2.0 ppm (alkyl chain). Integration values are shown below the peaks: 0.85, 2.83, 2.00, 1.90, 2.53, 2.15, 12.50. A chemical structure of **5n** is shown in the top left.

5n

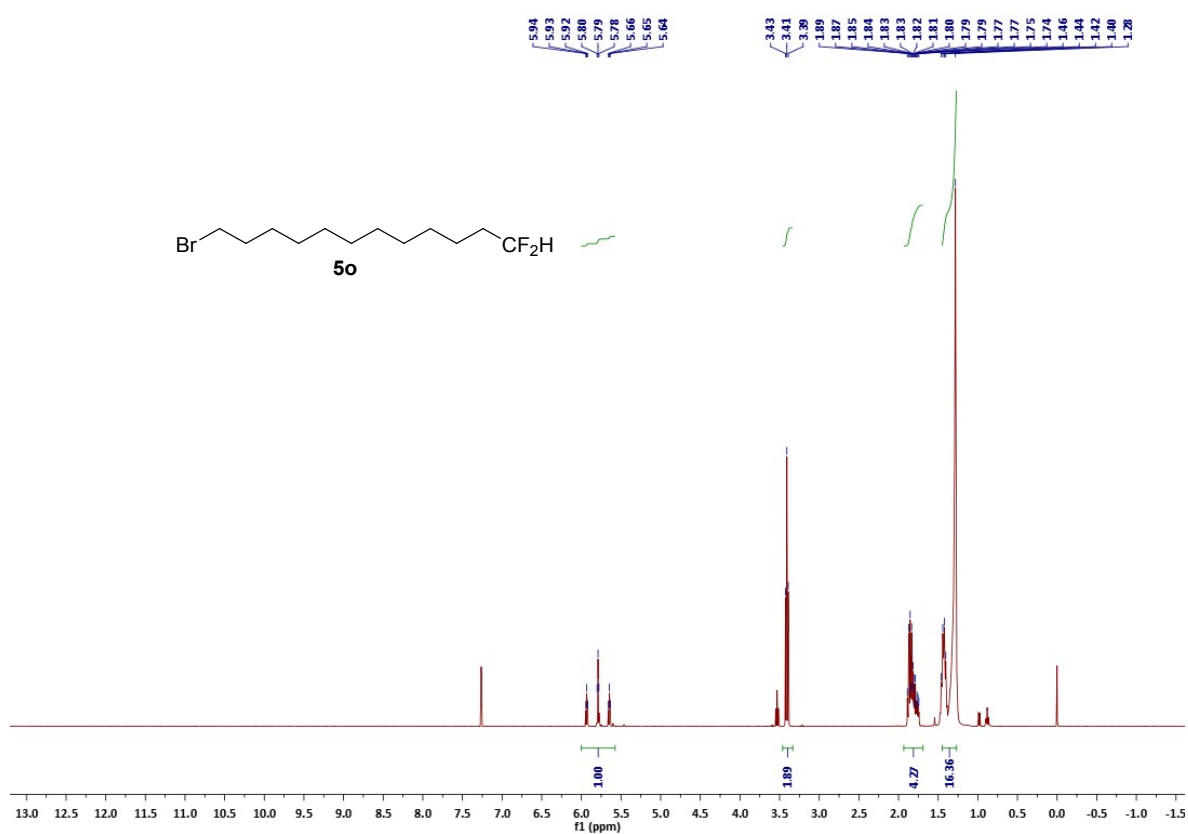
115.67
115.72
115.77
115.82
115.87
115.92

2.00

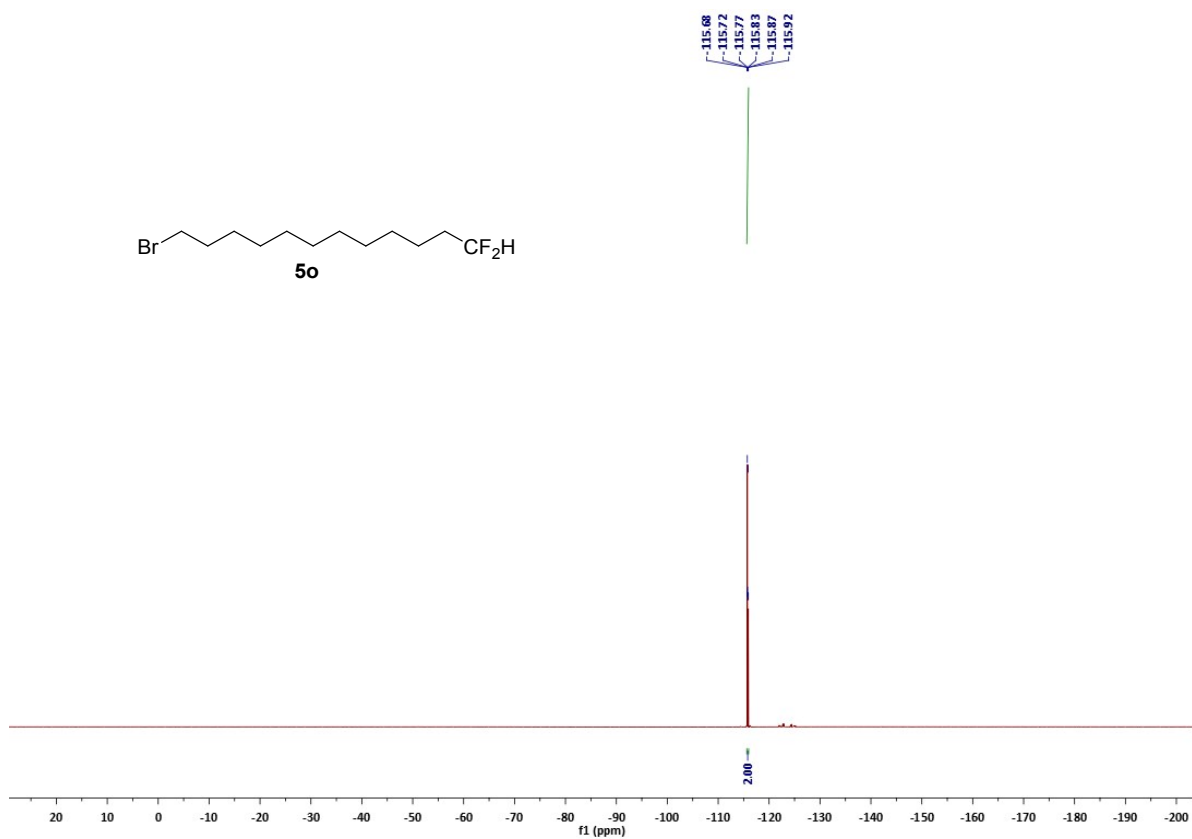
121.5

f1 (ppm)

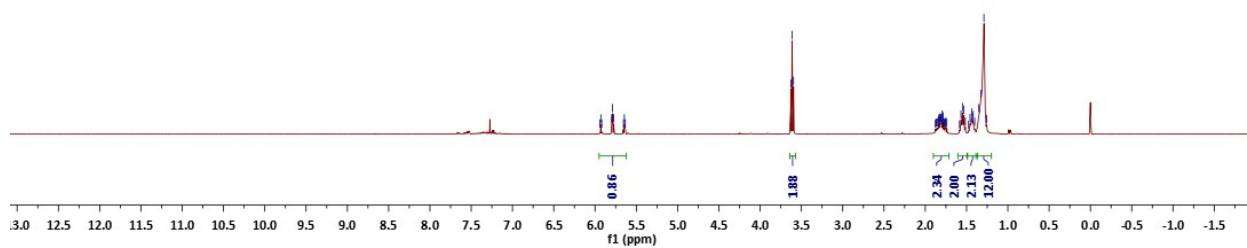
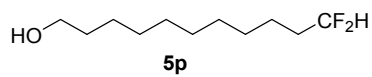
^1H NMR:



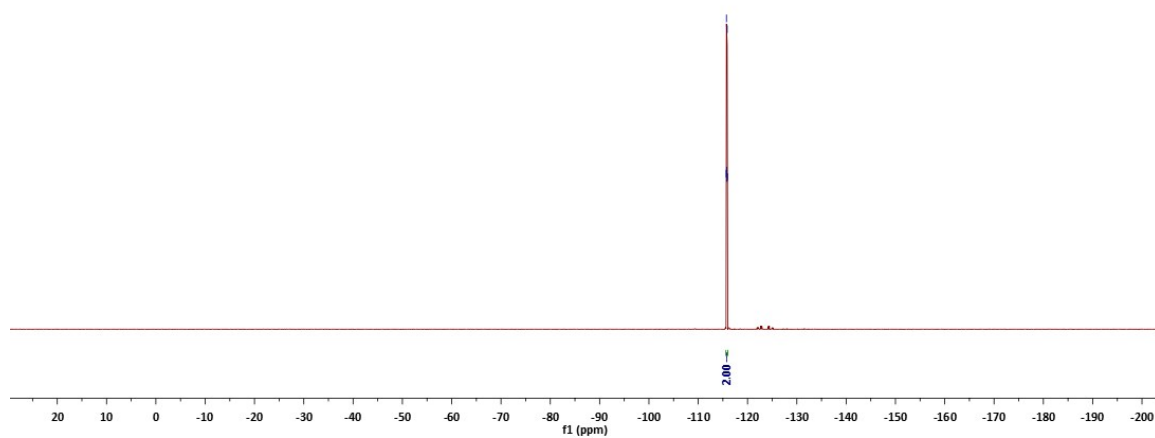
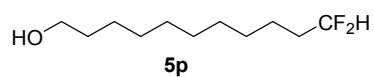
^{19}F NMR:



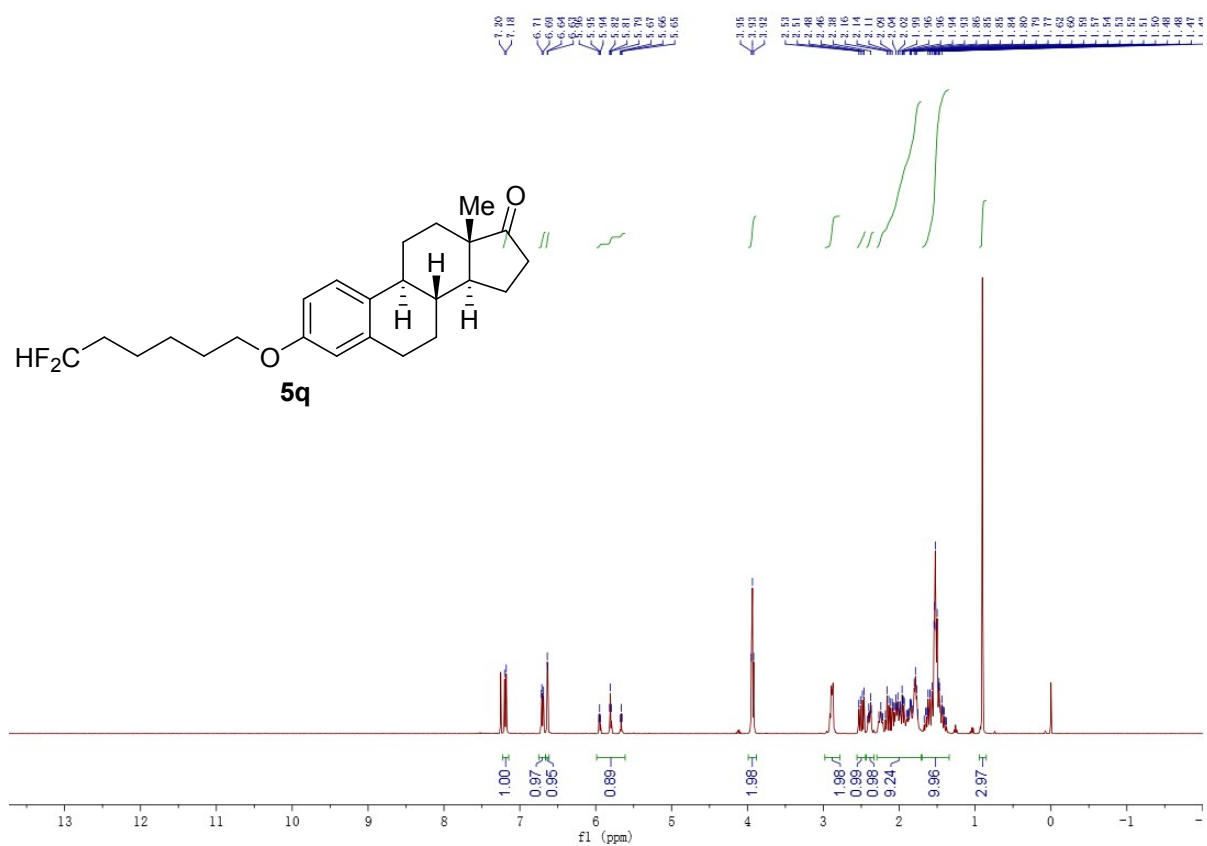
^1H NMR:



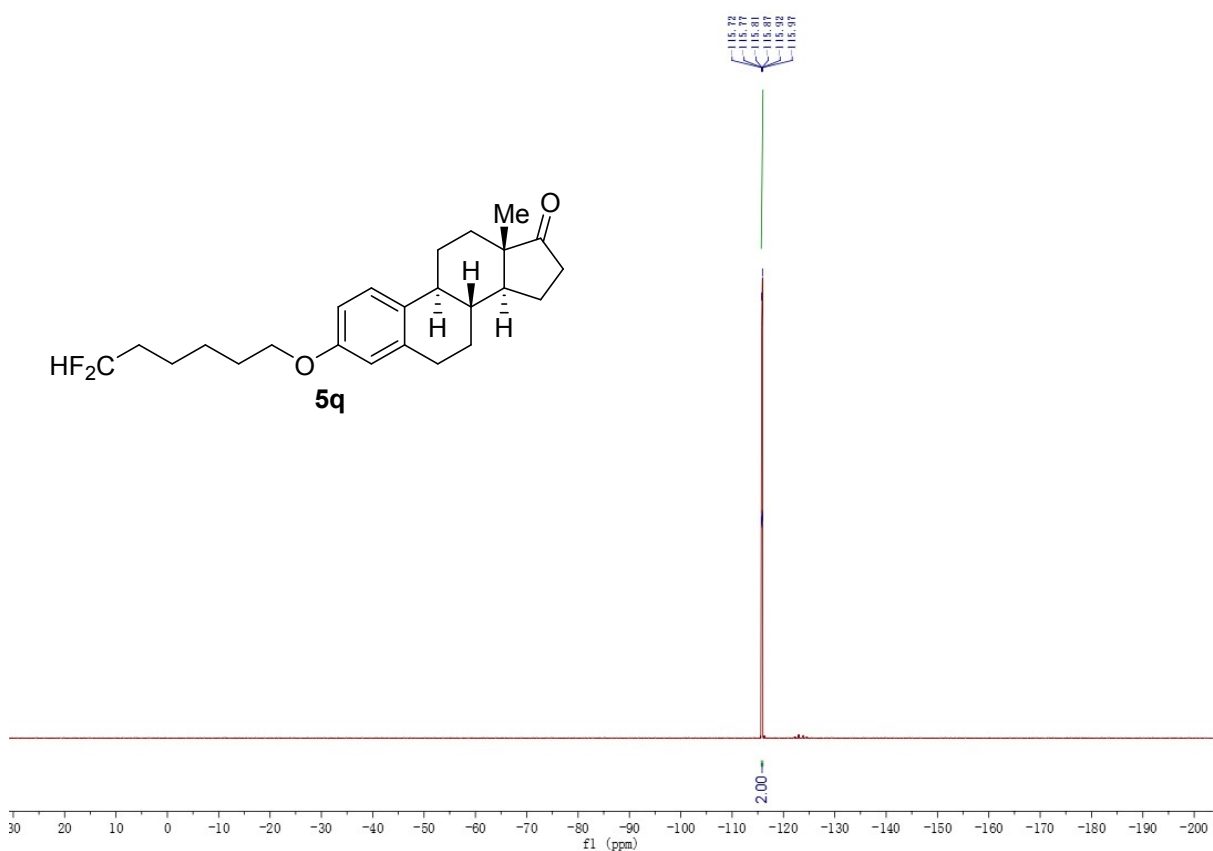
^{19}F NMR:



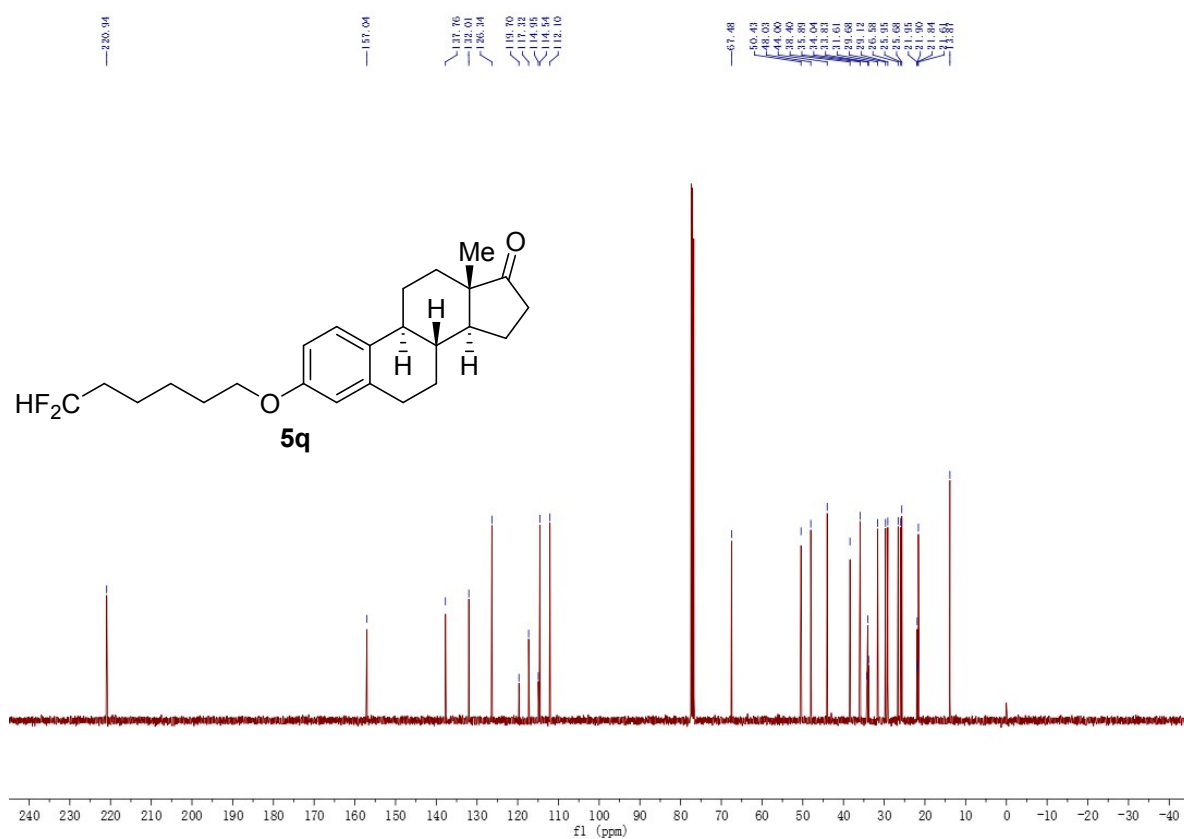
^1H NMR:



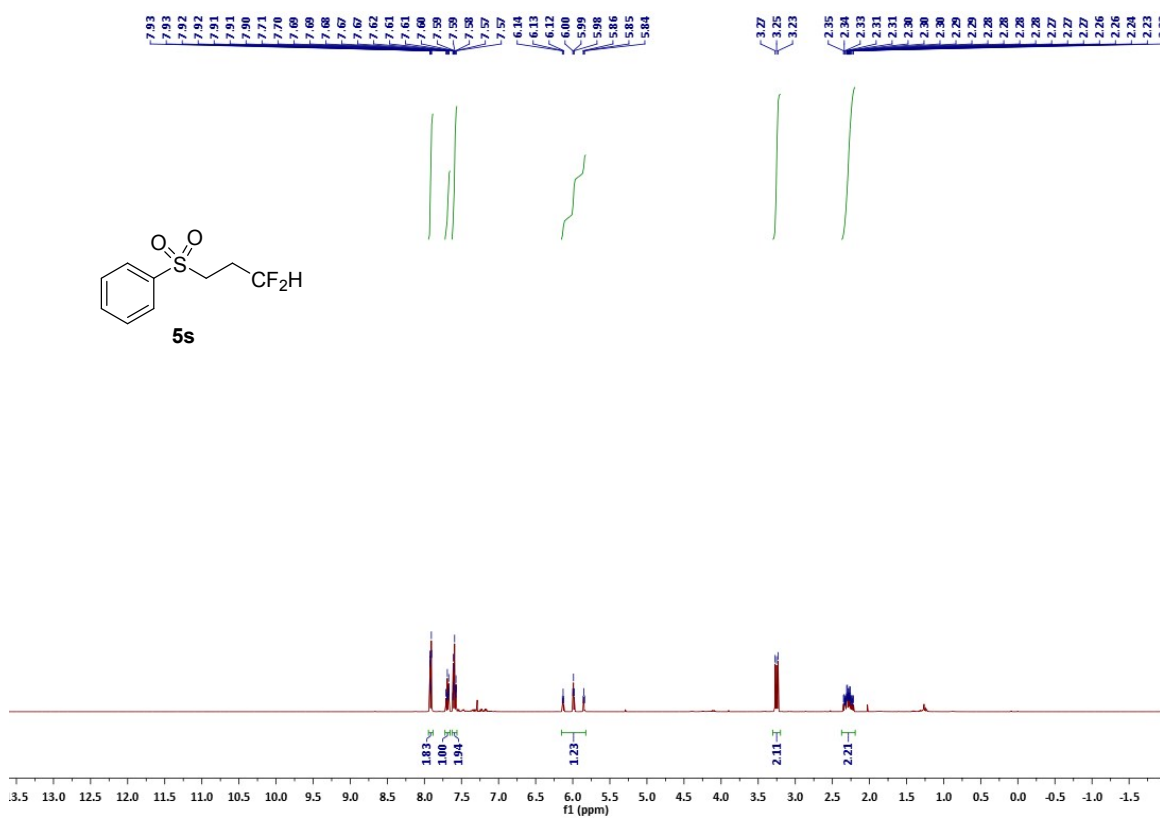
^{19}F NMR:



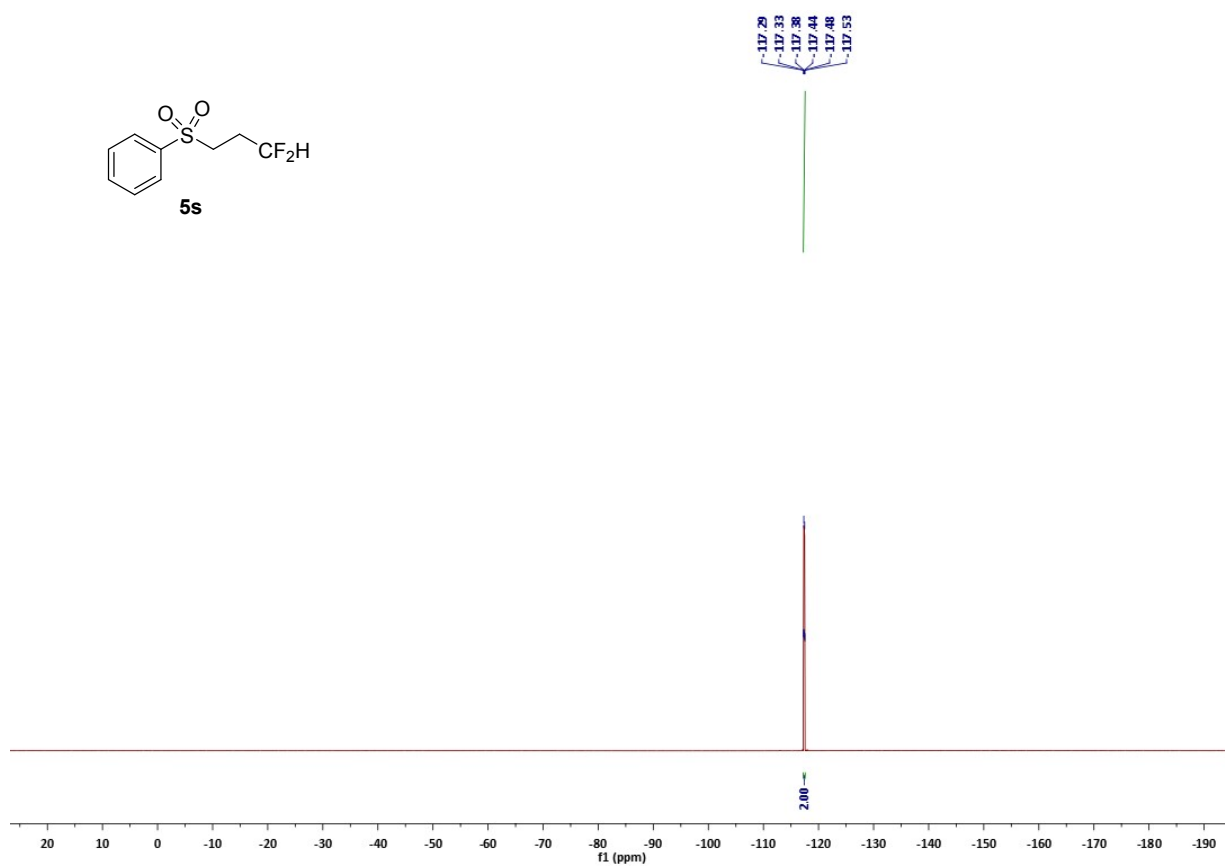
^{13}C NMR:



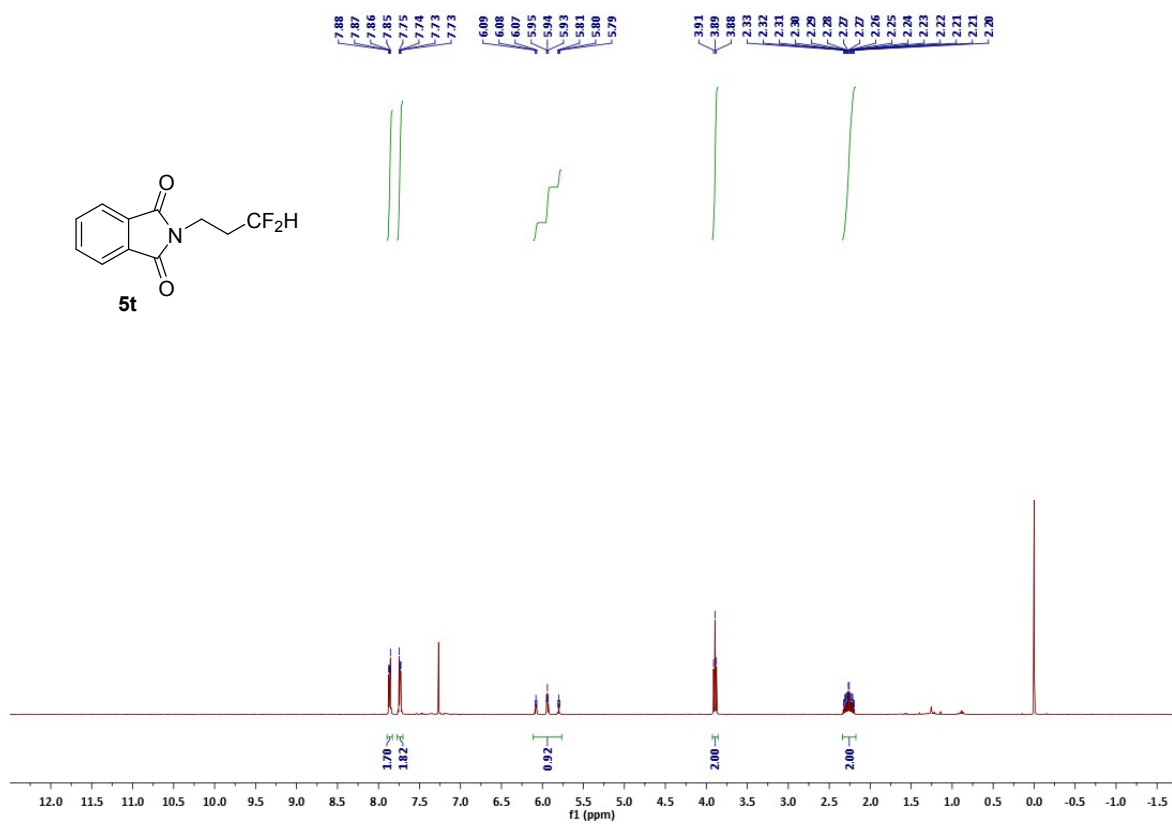
^1H NMR:



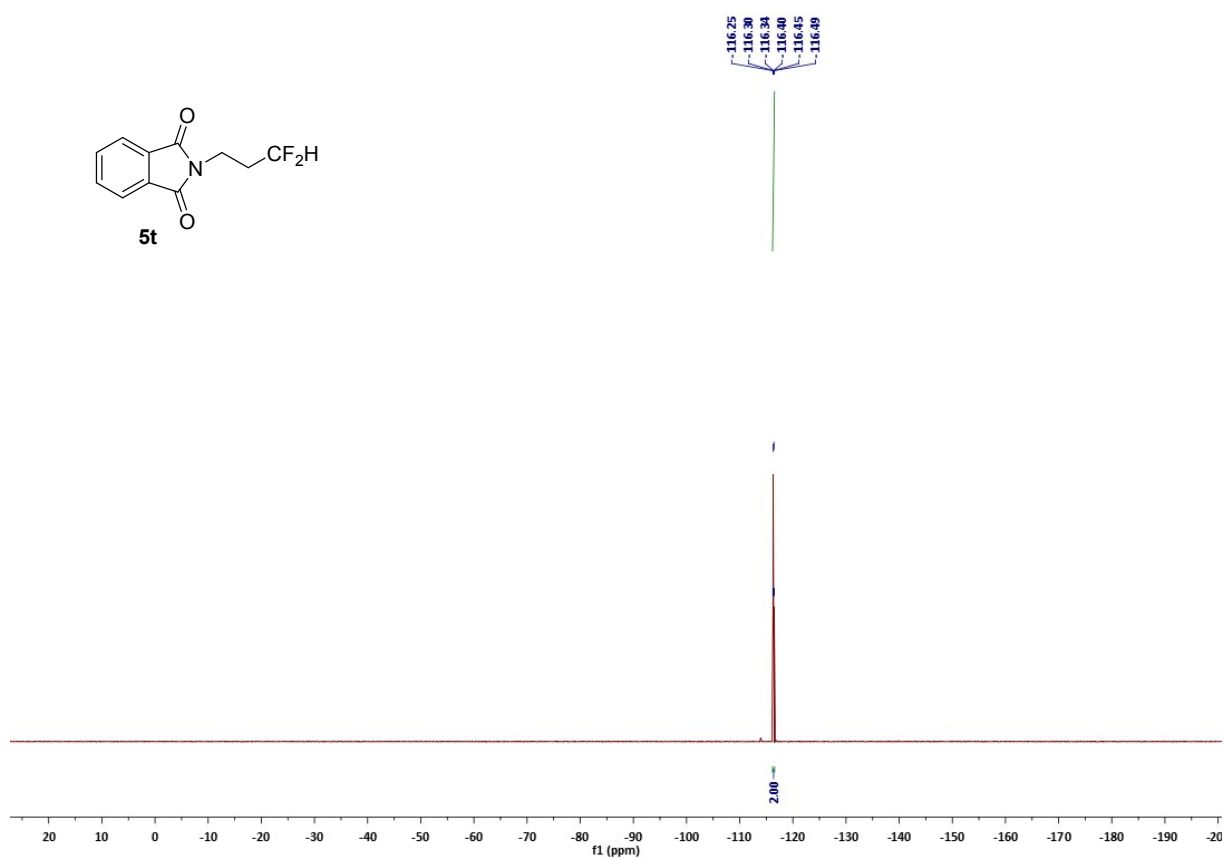
^{19}F NMR:



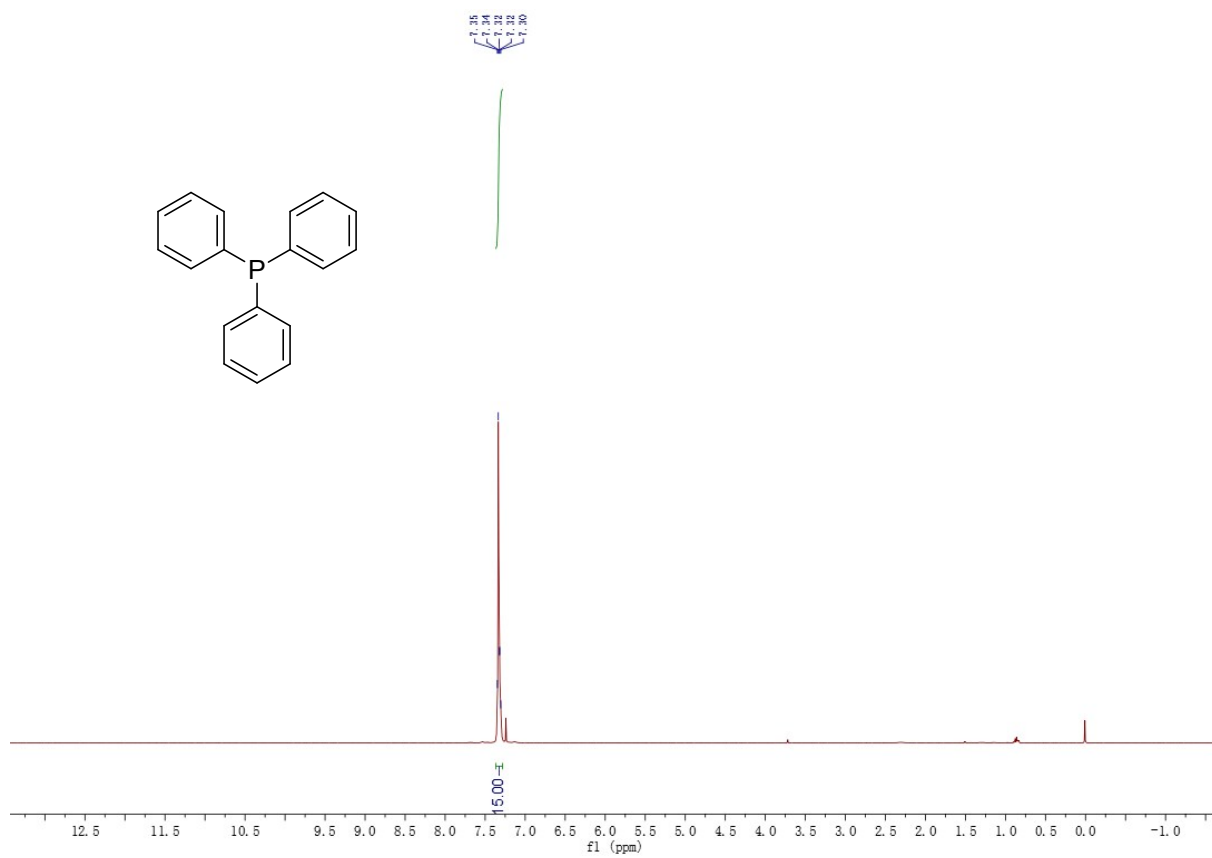
^1H NMR:



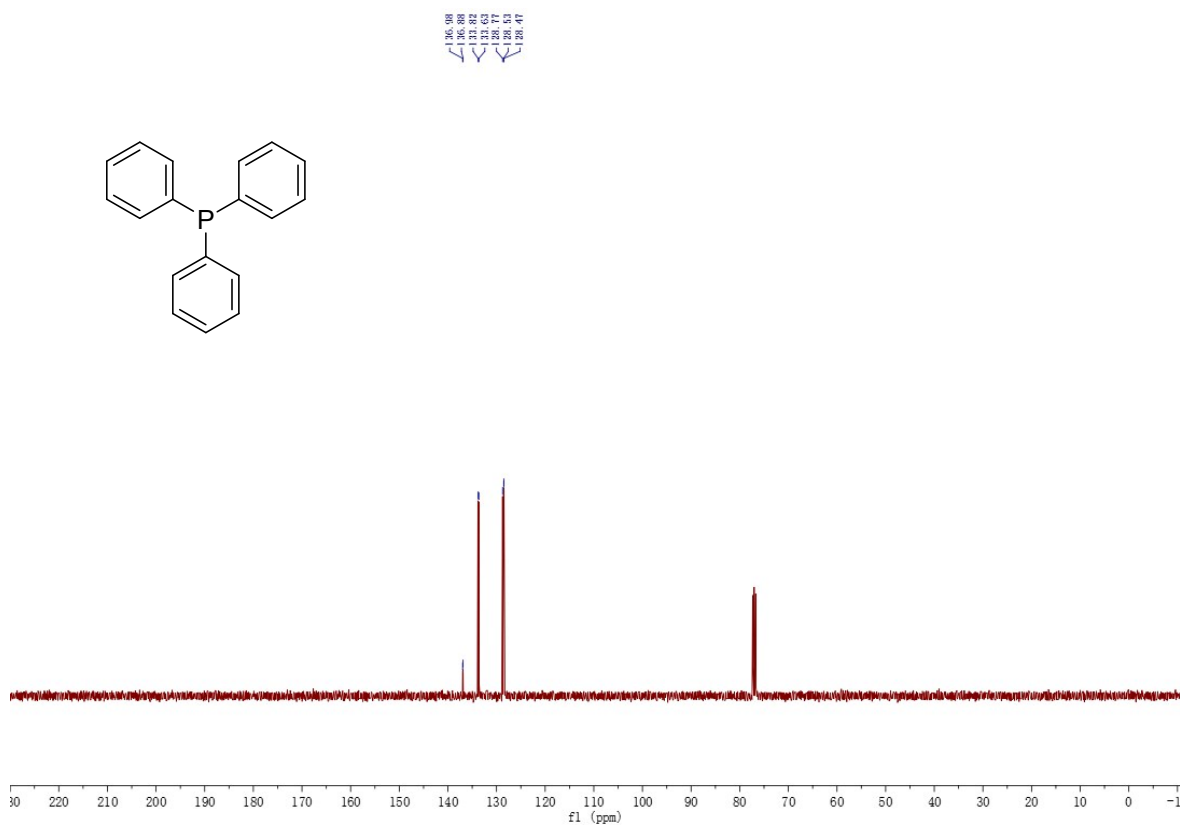
^{19}F NMR:



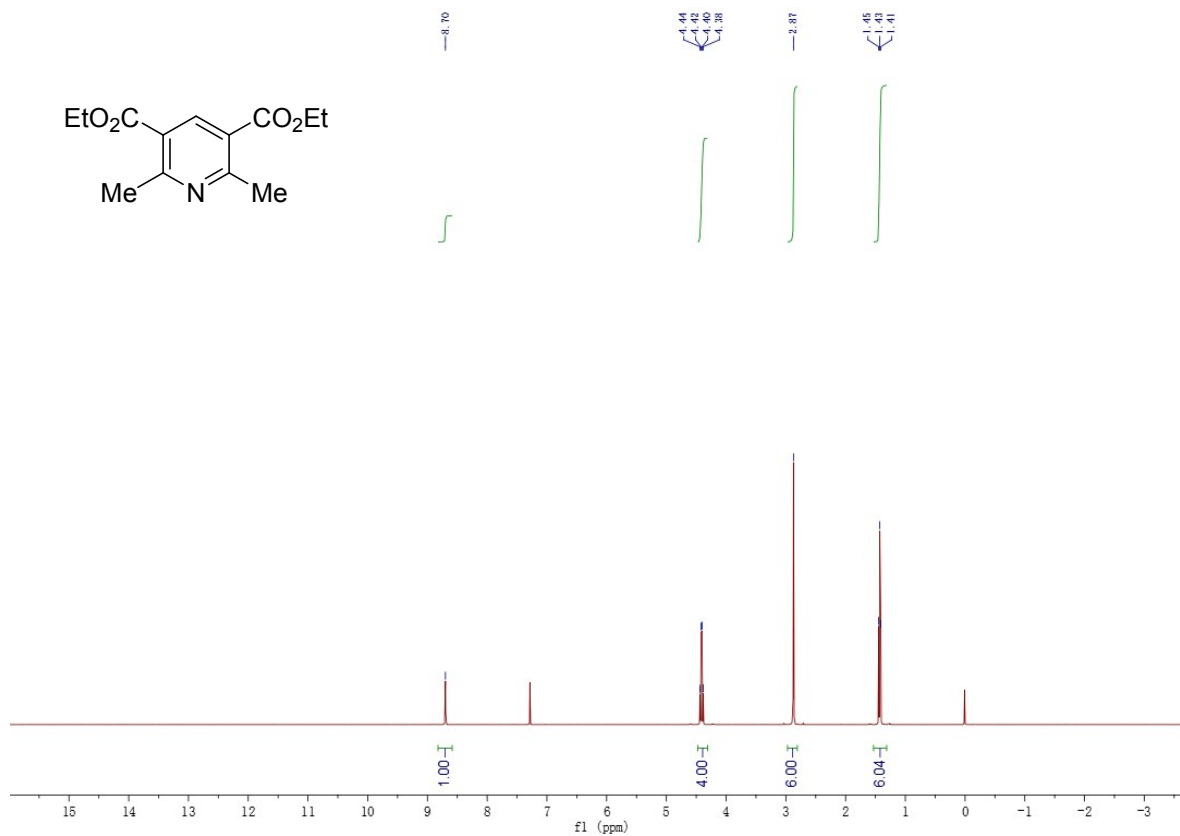
^1H NMR:



^{13}C NMR:



^1H NMR:



^{13}C NMR:

