Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Visible-light-induced radical hydrodifluoromethylation of alkenes

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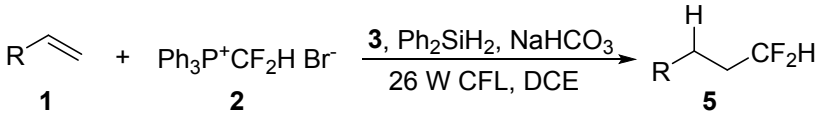
1. General information

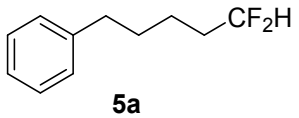
^{1}H, ^{13}C and ^{19}F NMR spectra were detected on a 500 MHz, 400 MHz or 300 MHz NMR spectrometer. Data for ^{1}H NMR, ^{13}C NMR and ^{19}F NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, coupling constants in 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



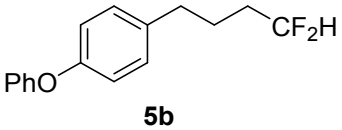
1 **2** **5**

Into a 25mL Schlenk tube were added substrate **1a** (0.5 mmol, 66.1 mg, 1.0 equiv.), phosphonium salt [$Ph_3P^+CF_2H$ 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**.



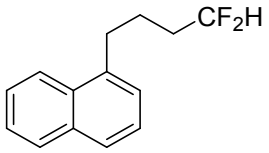
5a

(5,5-difluoropentyl)benzene[1]: 71%; ^{1}H 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).



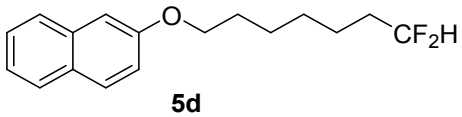
5b

1-(4,4-difluorobutyl)-4-phenoxybenzene: 53%; Slightly yellow liquid; ^{1}H 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) ν = 2929, 1590, 1507, 1489, 1239, 1122, 1072, 1015, 871, 692 cm^{-1}; HRMS (EI) Calcd for $C_{16}H_{16}OF_2$ $[M]^+$: 262.1169, Found: 262.1173.



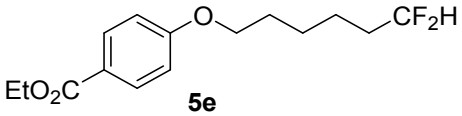
5c

1-(4,4-difluorobutyl)naphthalene[2]: 54%; ^{1}H 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).



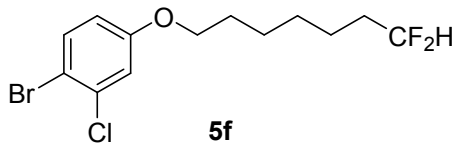
5d

2-((7,7-difluoroheptyl)oxy)naphthalene[1]: 60%; ^{1}H 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).



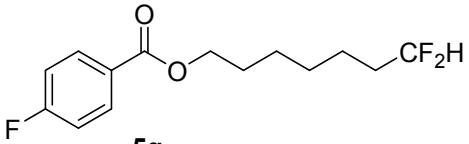
5e

ethyl 4-((6,6-difluorohexyl)oxy)benzoate[1]: 65%; ^{1}H 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).



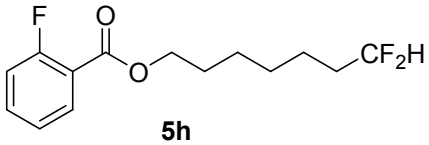
5f

1-bromo-2-chloro-4-((7,7-difluoroheptyl)oxy)benzene[1]: 65%; ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.81 (dt, *J* = 57.1, 17.8 Hz, 2F).



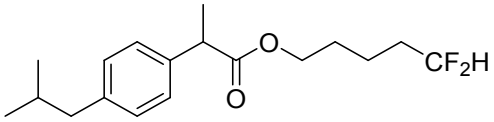
5g

7,7-difluoroheptyl 4-fluorobenzoate: 61%; Colourless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.91 – -106.02 (m, 1F), -115.89 (dt, *J* = 56.9, 17.6 Hz, 2F); ^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{14}H_{17}O_2F_3$ $[M]^+$: 274.1181, Found: 274.1187.



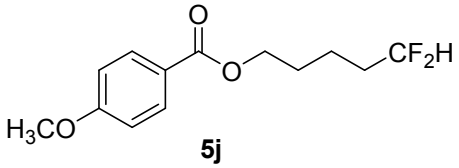
5h

7,7-difluoroheptyl 2-fluorobenzoate: 65%; Colourless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.48 – -109.76 (m, 1F), -115.87 (dt, *J* = 57.0, 17.6 Hz, 2F); ^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{14}H_{17}O_2F_3$ $[M]^+$: 274.1181, Found: 274.1184.



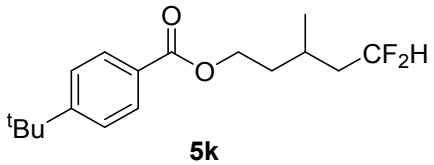
5i

5,5-difluoropentyl 2-(4-isobutylphenyl)propanoate: 63%; Colourless liquid; ^{1}H 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) ν = 2957, 2870, 1734, 1383, 1167, 1125, 1095, 911. 734 cm^{-1}; HRMS (EI) Calcd for $C_{18}H_{26}O_2F_2$ $[M]^+$: 312.1901, Found: 312.1899.



5j

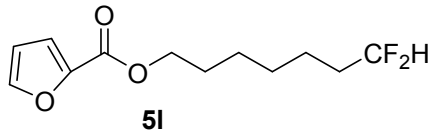
6,6-difluorohexyl 4-methoxybenzoate: 60%; Ligth yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.9 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 5.78 (tt, *J* = 56.9, 4.5 Hz, 1H), 4.27 (t, *J* = 6.5 Hz, 2H), 3.83 (s, 3H), 1.92 – 1.67 (m, 4H), 1.58 – 1.39 (m, 4H); ^{19}F NMR (376 MHz, $CDCl_3$) 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) ν = 2956, 1712, 1607, 1277, 1258, 1168, 1103, 1031, 771 cm^{-1}; HRMS (EI) Calcd for $C_{14}H_{18}O_3F_2$ $[M]^+$: 272.1224, Found: 272.1222.



5k

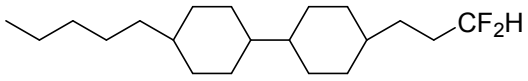
5,5-difluoro-3-methylpentyl 4-(*tert*-butyl)benzoate: 65%; Colourless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 5.90 (tt, *J* = 56.8, 4.7 Hz, 1H), 4.36 (td, *J* = 6.7, 1.9 Hz, 2H), 2.04 – 1.60 (m, 5H), 1.34 (s, 9H), 1.07 (d, *J* = 6.6 Hz, 3H); ^{19}F 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) ν = 2964, 1719, 1610, 1314, 1276, 1118, 1037, 775, 708 cm^{-1}; HRMS (EI) Calcd for $C_{17}H_{24}O_2F_2$ $[M]^+$: 298.1744, Found: 298.1752.



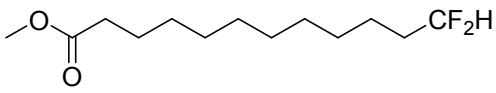
5l

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) ν = 2961, 1724, 1474, 1296, 1115, 1077, 1015, 959, 799, 764 cm^{-1}; HRMS (EI) Calcd for $C_{12}H_{16}O_3F_2$ $[M]^+$: 246.1068, Found: 246.1066.



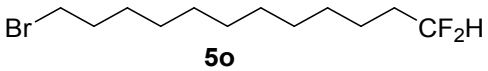
5m

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) ν = 2915, 2848, 1446, 1402, 1217, 1121, 1049, 916, 939, 741 cm^{-1}; HRMS (EI) Calcd for $C_{20}H_{36}F_2$ $[M]^+$: 314.2785, Found: 314.2789.



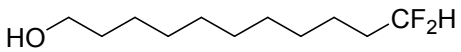
5n

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).



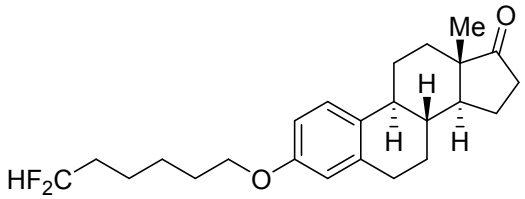
5o

12-bromo-1,1-difluorododecane[1]: 49%; ^{1}H NMR (400 MHz, $CDCl_3$) 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).^{19}F NMR (376 MHz, $CDCl_3$) δ -115.81 (dt, *J* = 57.0, 17.7 Hz, 2F).



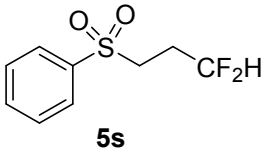
5p

11,11-difluoroundecan-1-ol[1]: 77%; ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.81 (dt, *J* = 57.0, 17.7 Hz, 2F).



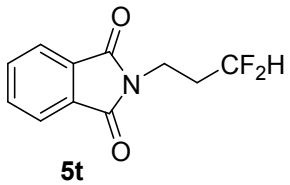
5q

(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; ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.84 (dt, *J* = 56.9, 17.6 Hz, 2F); ^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{24}H_{32}O_2F_2$ $[M]^+$: 390.2370, Found: 390.2373.



5s

((3,3-difluoropropyl)sulfonyl)benzene[1]: 81%; ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.41 (dt, *J* = 56.0, 17.4 Hz, 2F).

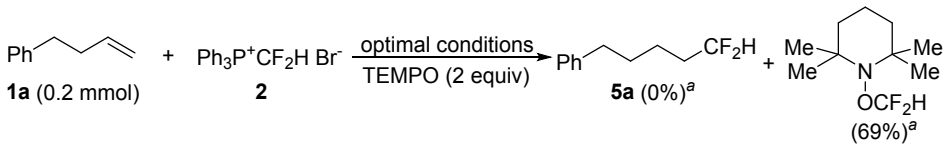


5t

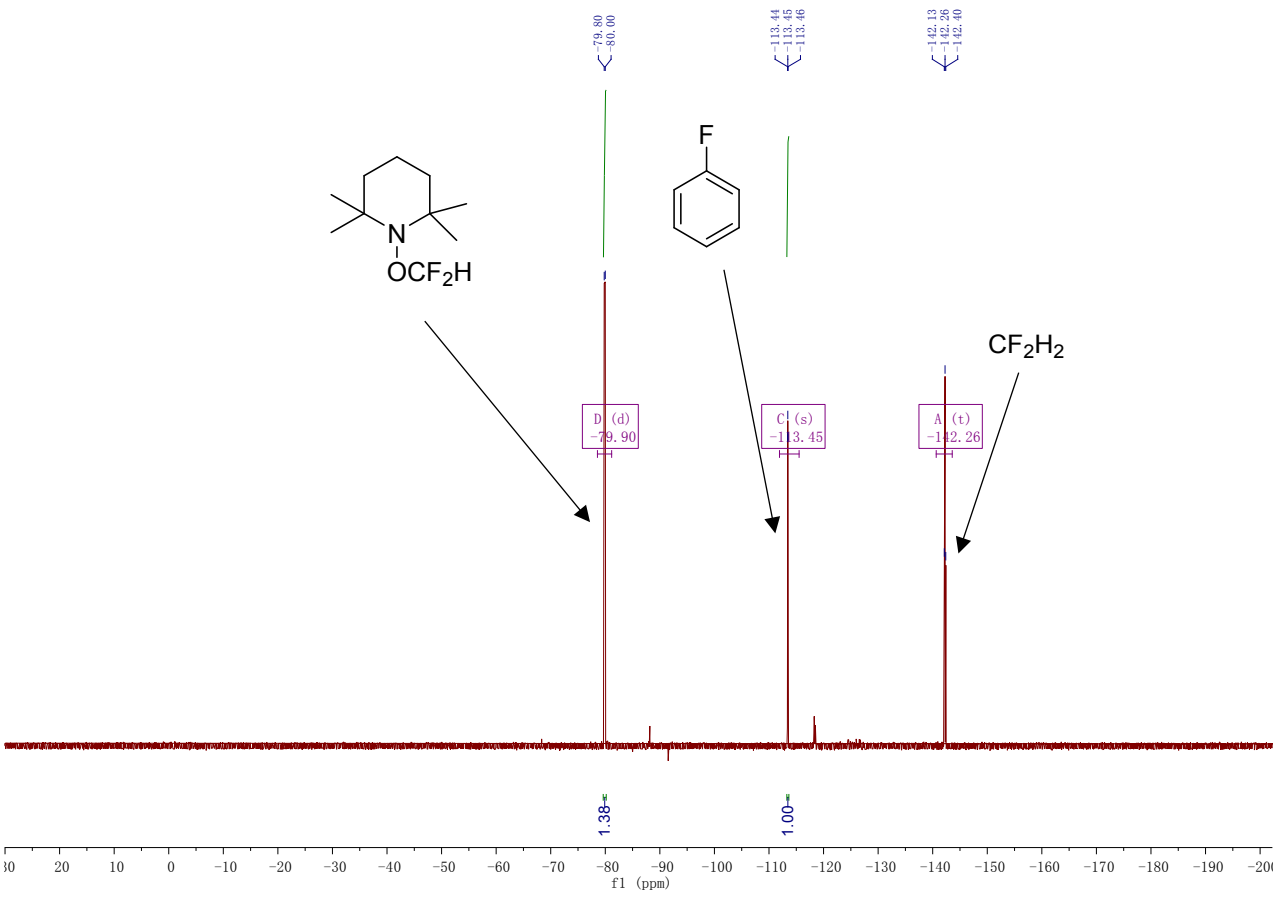
2-(3,3-difluoropropyl)isoindoline-1,3-dione[3]: 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.78 (m, 2H), 7.78 – 7.67 (m, 2H), 5.94 (tt, *J* = 55.9, 4.4 Hz, 1H), 3.89 (t, *J* = 6.9 Hz, 2H), 2.38 – 2.13 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.37 (tt, *J* = 55.9, 17.0 Hz, 2F).

3. Mechanistic investigations

3.1 The formation of TEMPO-CF_2H

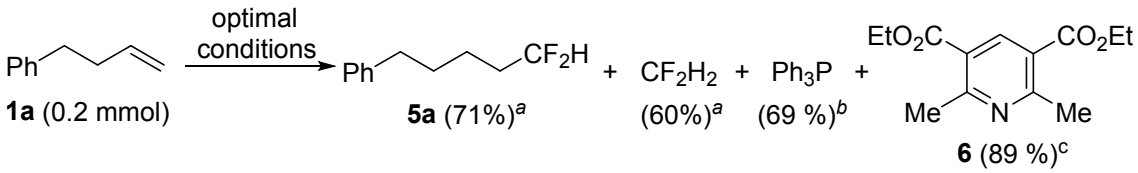


Into a 25mL Schlenk tube were added substrate **1a** (0.2 mmol, 26.4 mg, 1.0 equiv.), phosphonium salt [$Ph_3P^+CF_2H$ Br^-] (0.8 mmol, 314.5 mg, 4 equiv.), Hantzsch ester **3** (0.4 mmol, 101.3 mg, 2 equiv.), Ph_2SiH_2 (0.4 mmol, 73.8 mg, 2 equiv.), $NaHCO_3$ (0.8 mmol, 67.2 mg, 4 equiv.) and TEMPO (0.4 mmol, 62.4 mg, 2 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. After the reaction was finished, fluorobenzene (0.2 mmol, 19.2 mg, 1.0 equiv.) was added as an internal standard. TEMPO-CF_2H was confirmed by ^{19}F NMR and GC-MS spectroscopy. Its yield was determined by ^{19}F NMR spectroscopy. ^{19}F NMR spectrum is shown as follows. 1-(difluoromethoxy)-2,2,6,6-tetramethylpiperidine[4]: 69%; ^{19}F NMR (376 MHz) δ -79.90 (d, *J* = 73.5 Hz, 2F); GC-MS (EI): 207.0 (M^+).



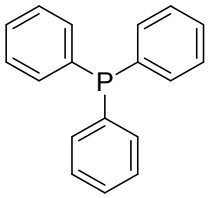
^{19}F NMR spectrum of the reaction mixture

3.2 The isolation of Ph_3P and compound 6

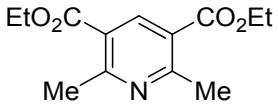


1a (0.2 mmol) **5a** (71%)[a] (60%)[a] (69 %)[b] **6** (89 %)[c]

Into a 25mL Schlenk tube were added substrate **1a** (0.2 mmol, 26.4 mg, 1.0 equiv.), phosphonium salt [$Ph_3P^+CF_2H$ 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%; ^{1}H 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).



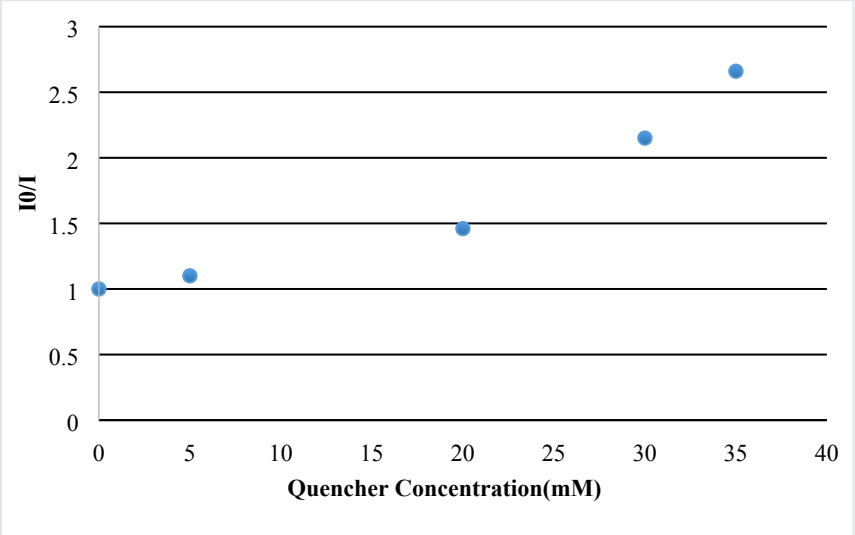
diethyl 2,6-dimethylpyridine-3,5-dicarboxylate[5]: 89%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 4.41 (q, J = 7.1 Hz, 4H), 2.87 (s, 6H), 1.43 (t, J = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.86 (s), 162.15 (s), 141.07 (s), 123.18 (s), 61.45 (s), 24.82 (s), 14.27 (s).

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 [$Ph_3P^+CF_2H$ Br^-] (9.8 mg, 0.025 mmol) under a N_2 atmosphere. 3 mL of the resulting solution (the concentration of the phosphonium salt [$Ph_3P^+CF_2H$ 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 [$Ph_3P^+CF_2H$ 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 [$Ph_3P^+CF_2H$ Br^-] could quench the photoexcited Hantzsch ester.



Hantzsch ester emission quenching with $Ph_3P^+CF_2H\ Br^-$

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.

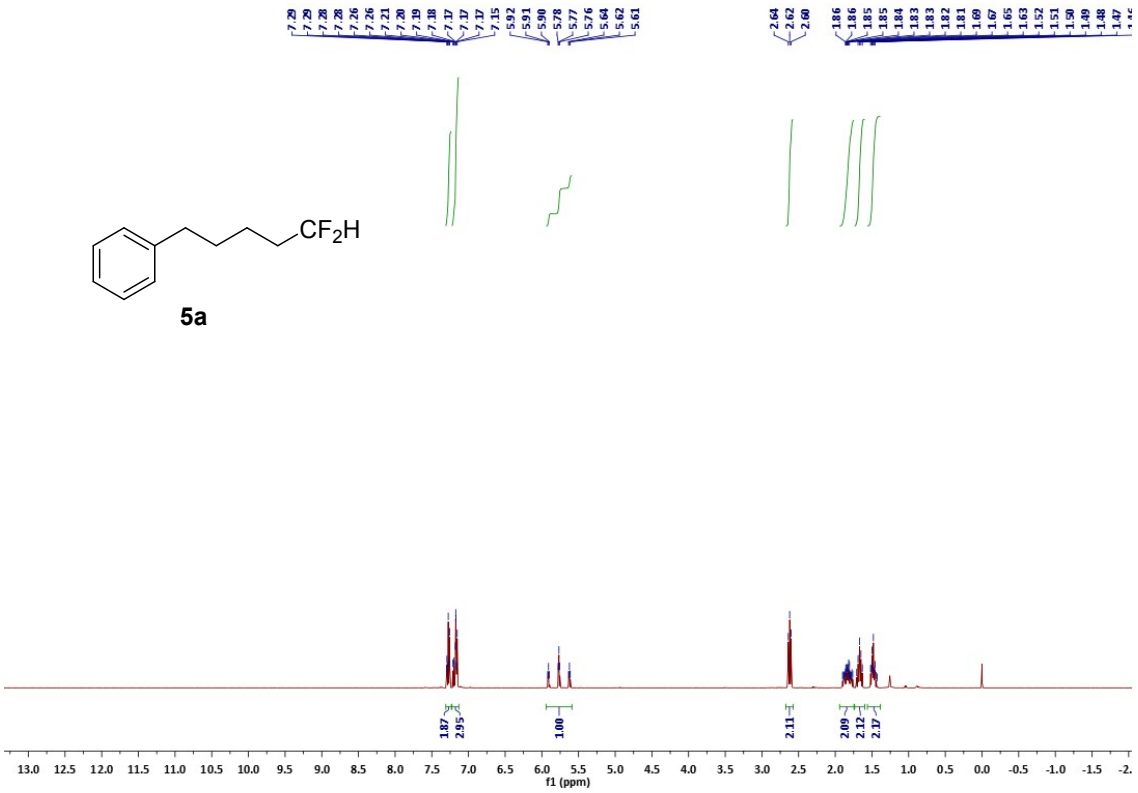
[3] F. Liu, A. Martin-Mingot, M. P. Jouannetaud, C. Bachmann, G. Frapper, F. Zunino, S. Thibaudeau, *J. Org. Chem.* **2011**, *76*, 1460-1463.

[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 ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra of products

^{1}H NMR:



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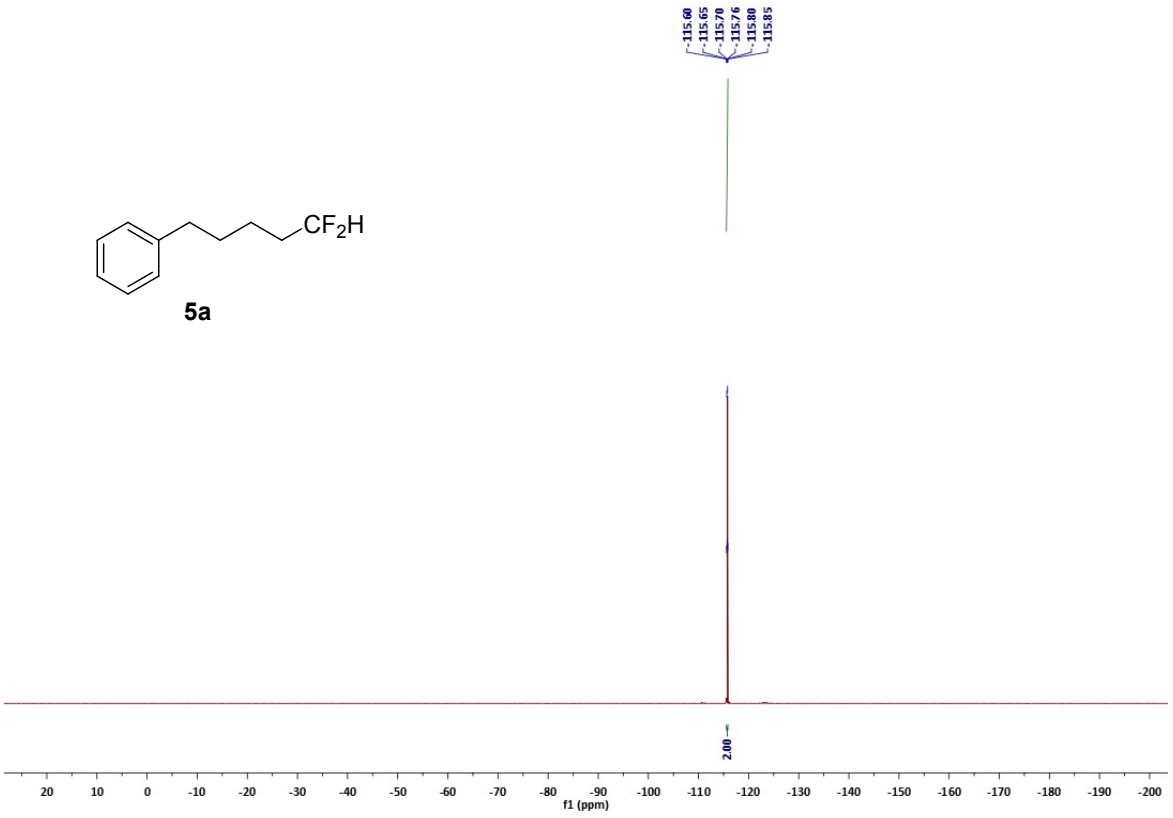

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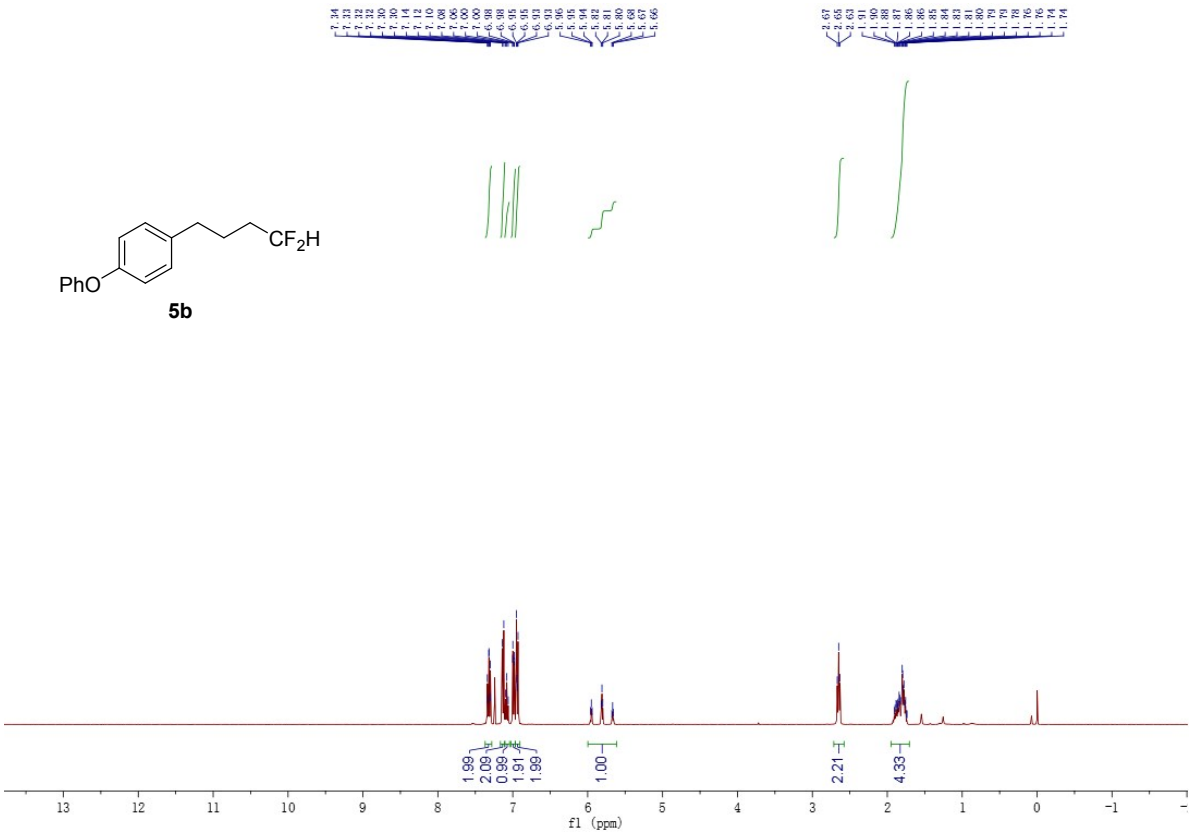

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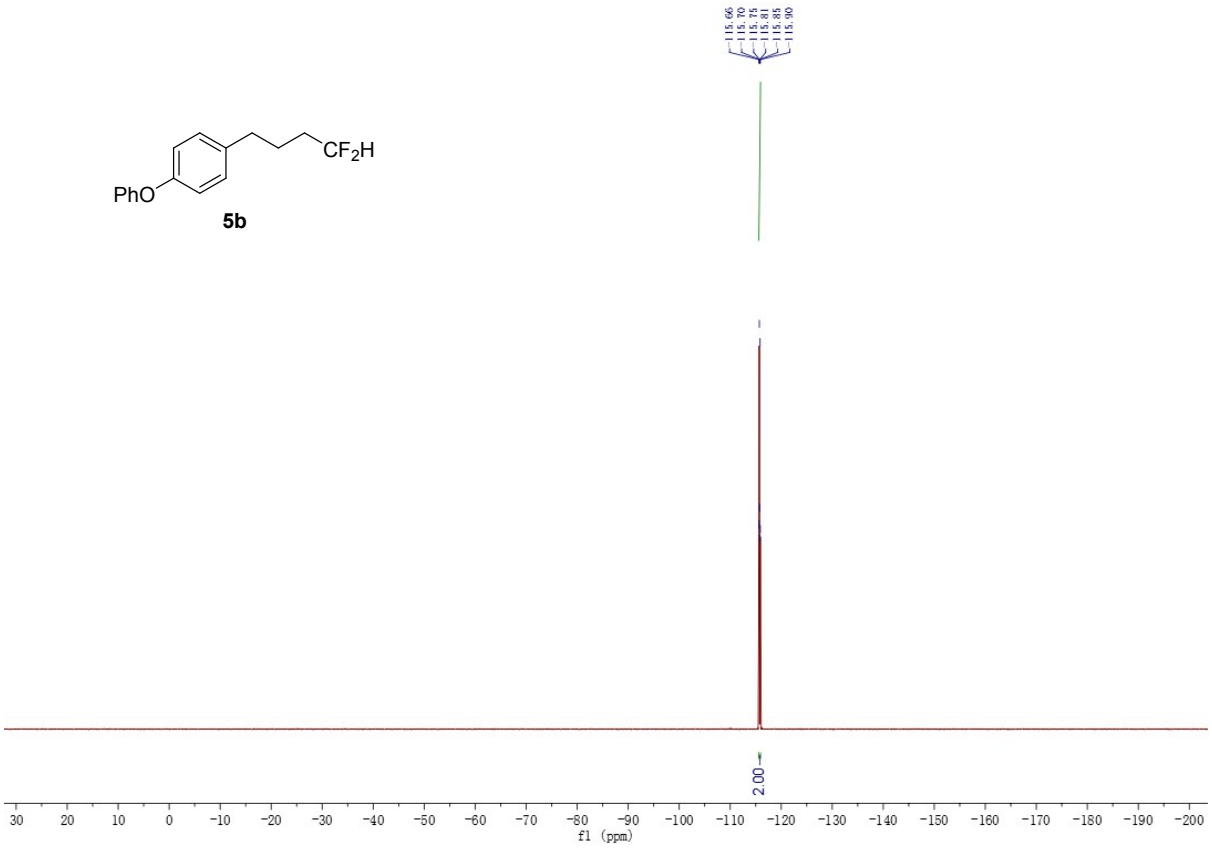

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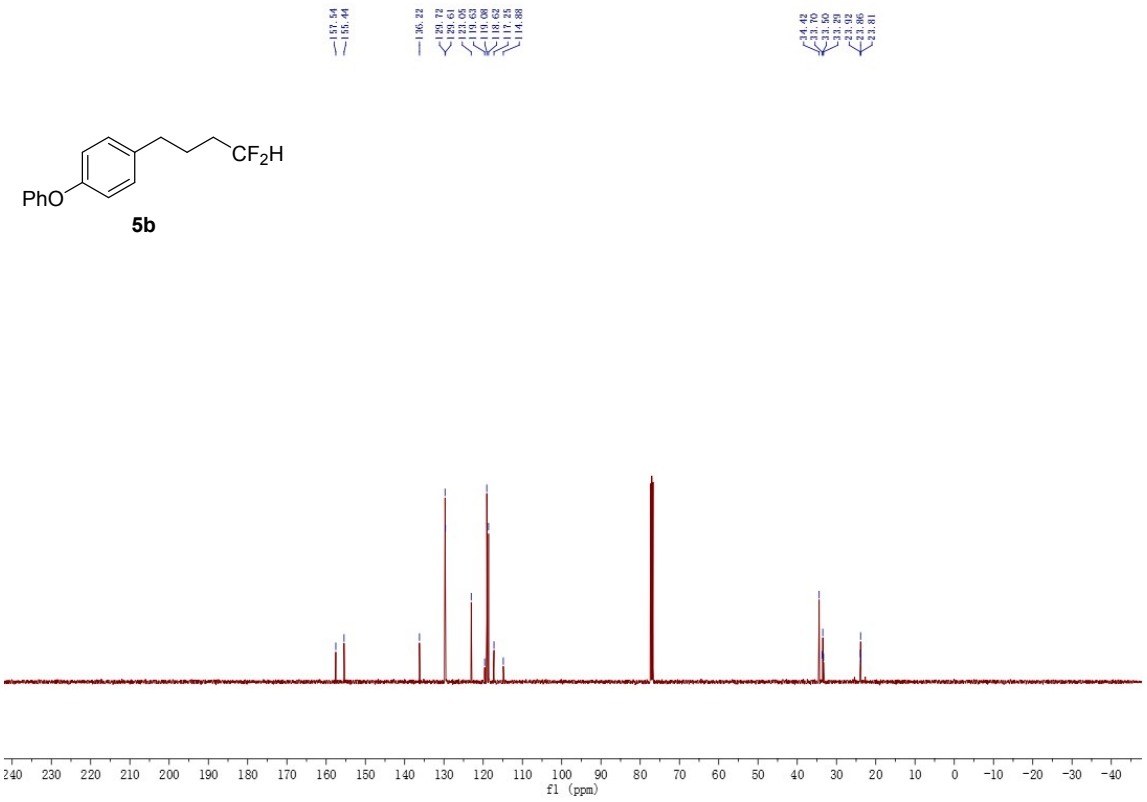

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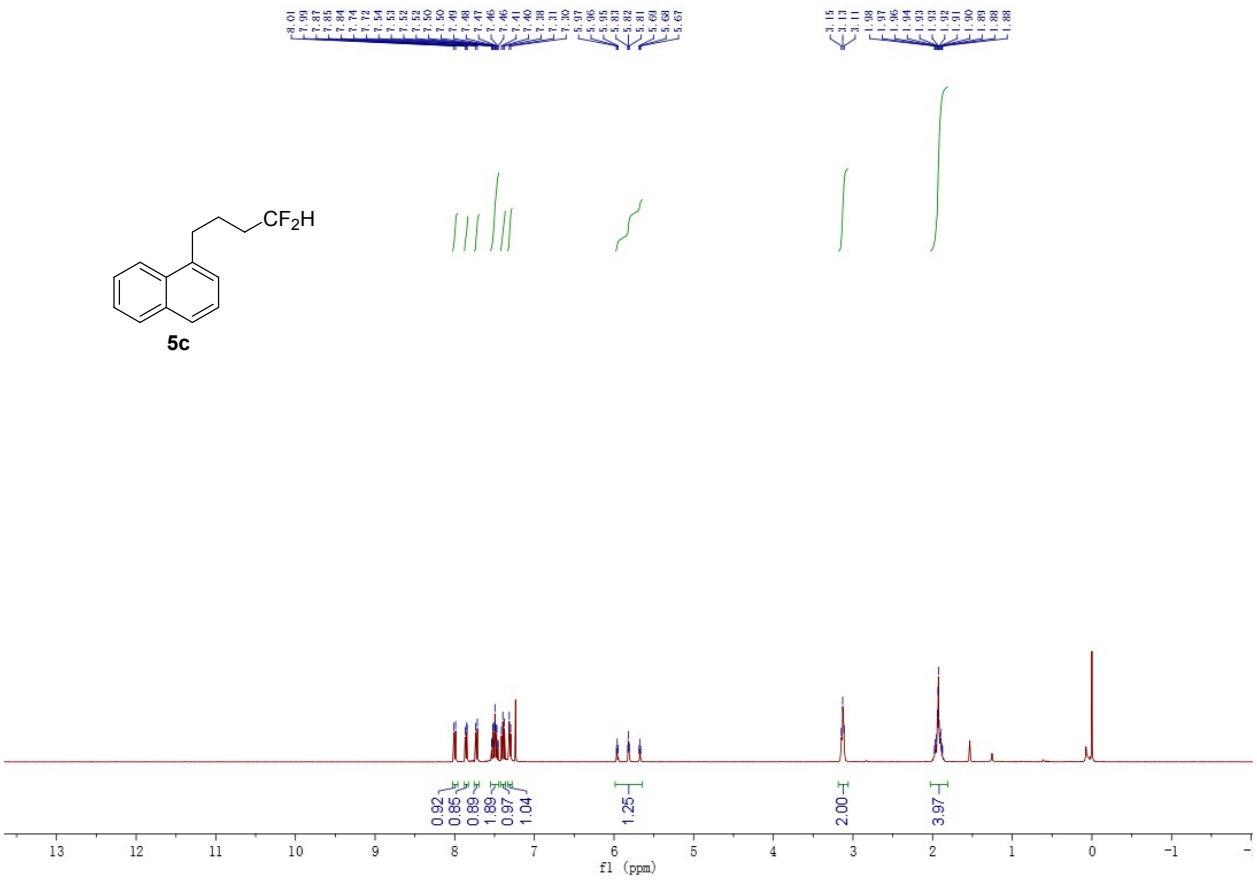

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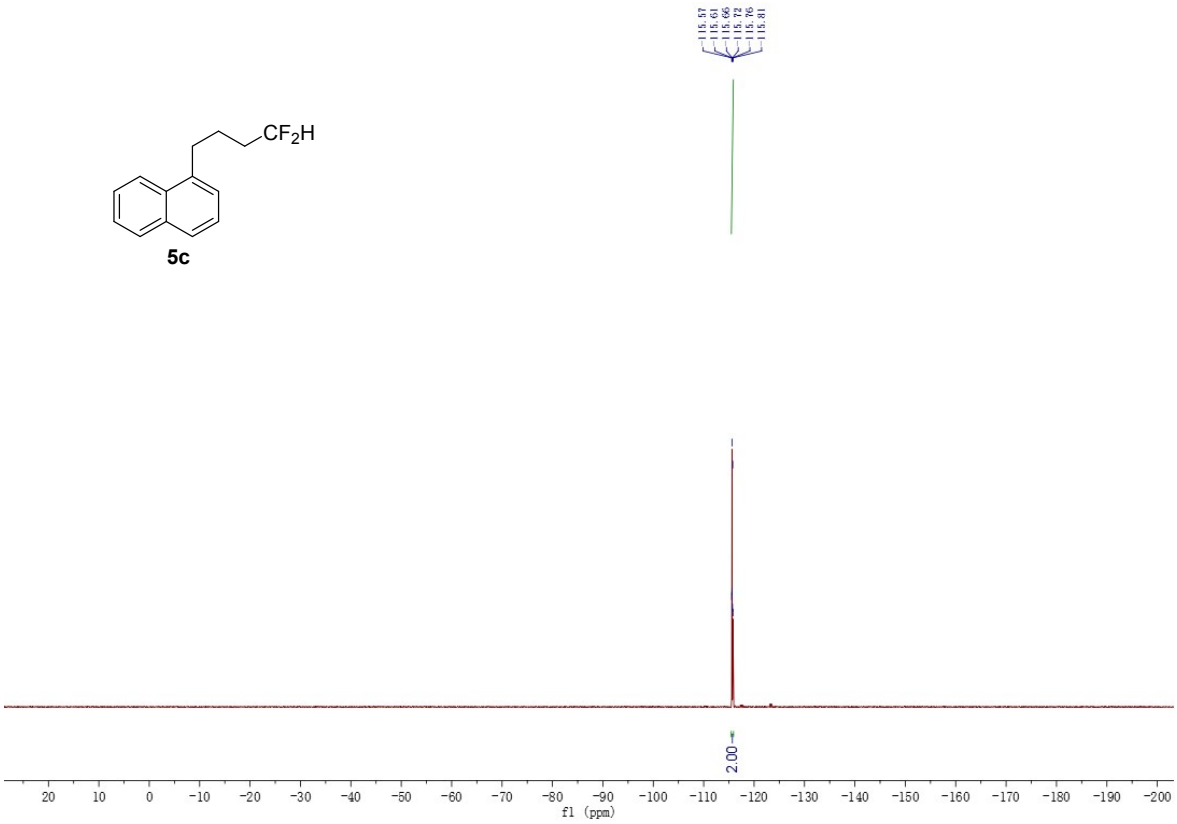

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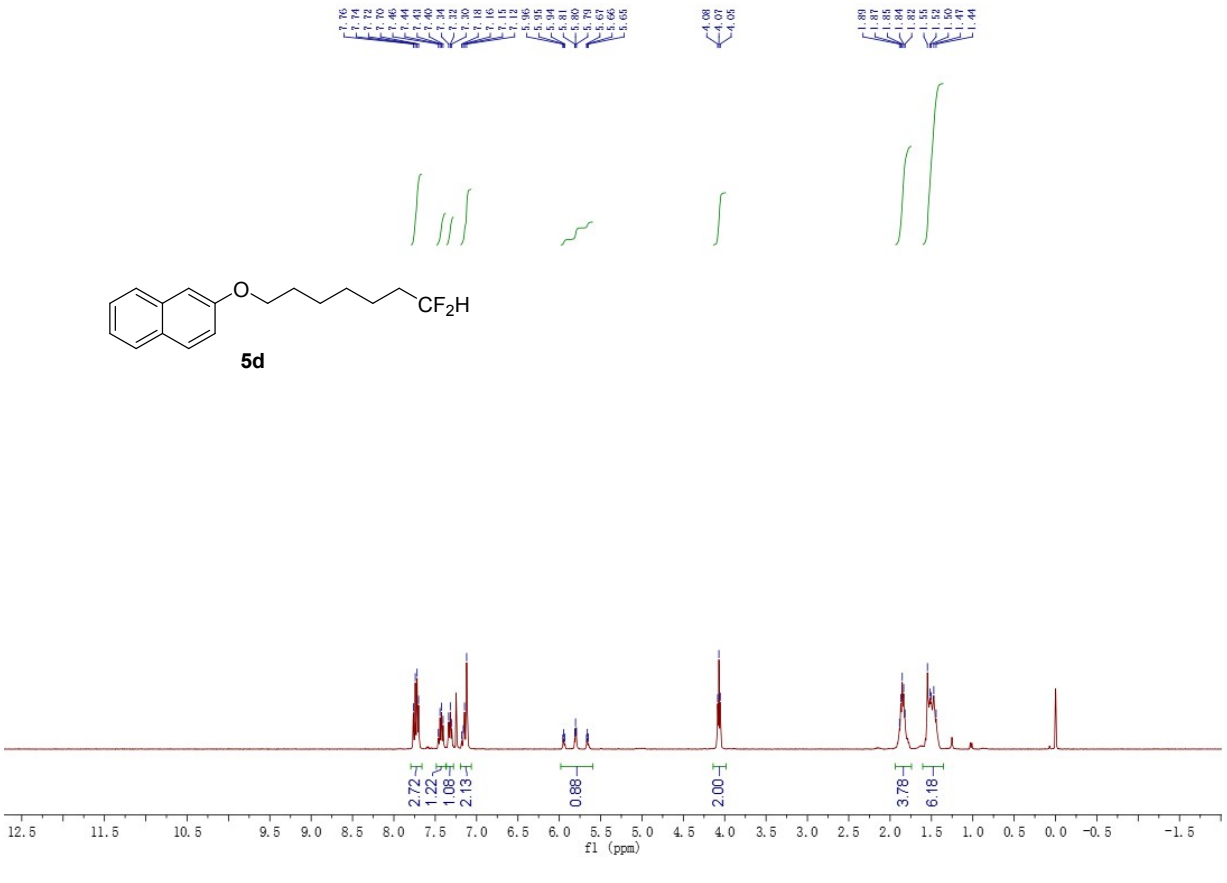

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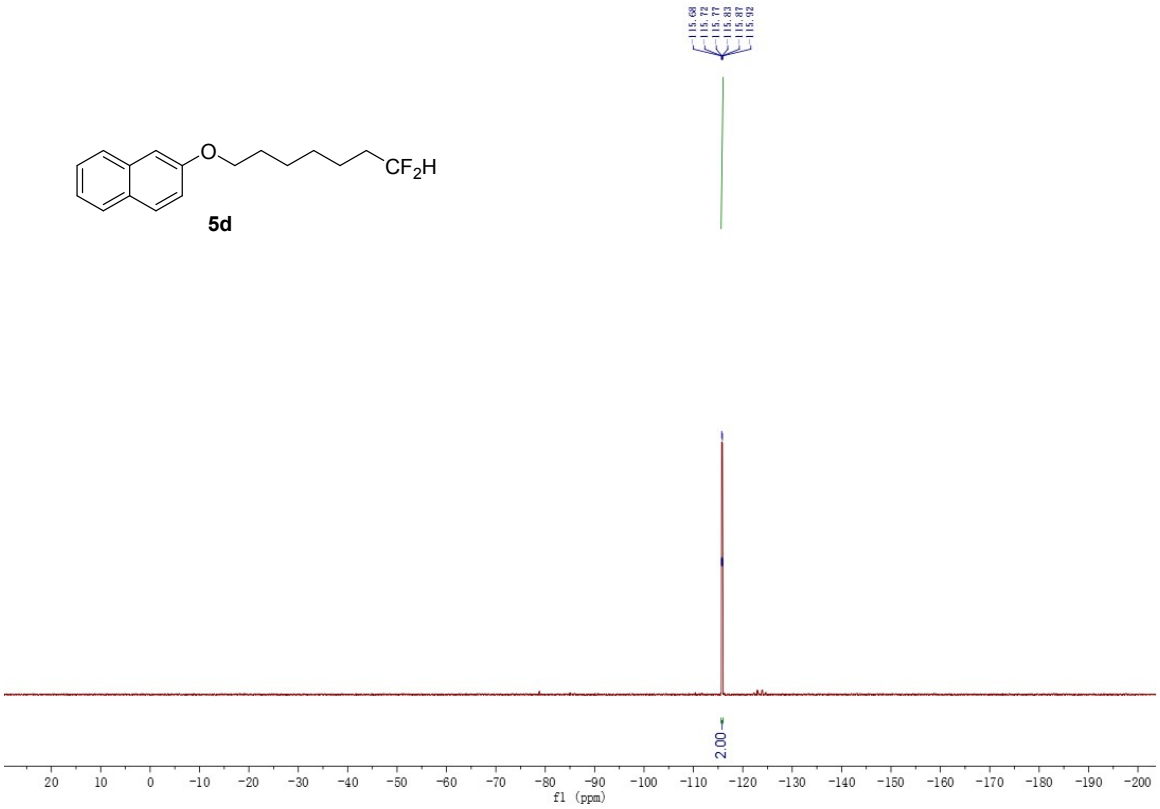

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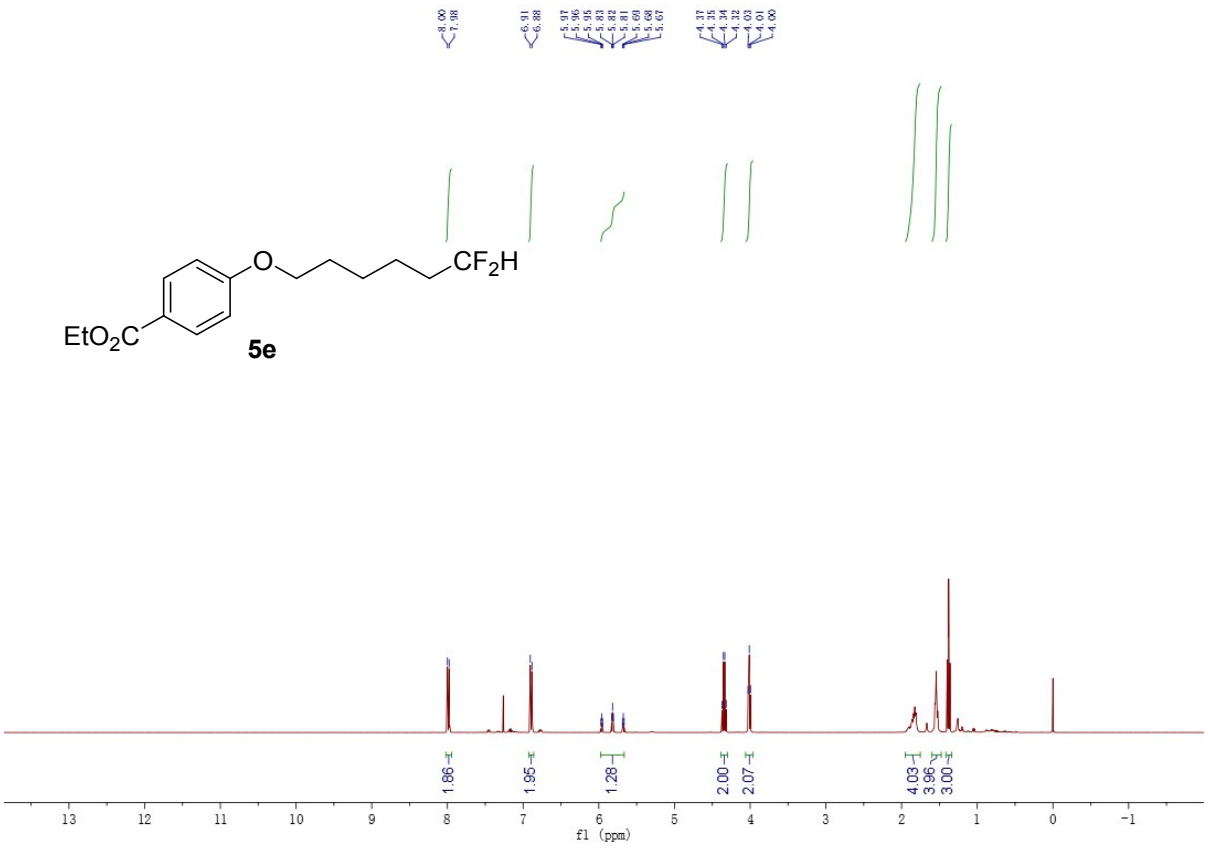

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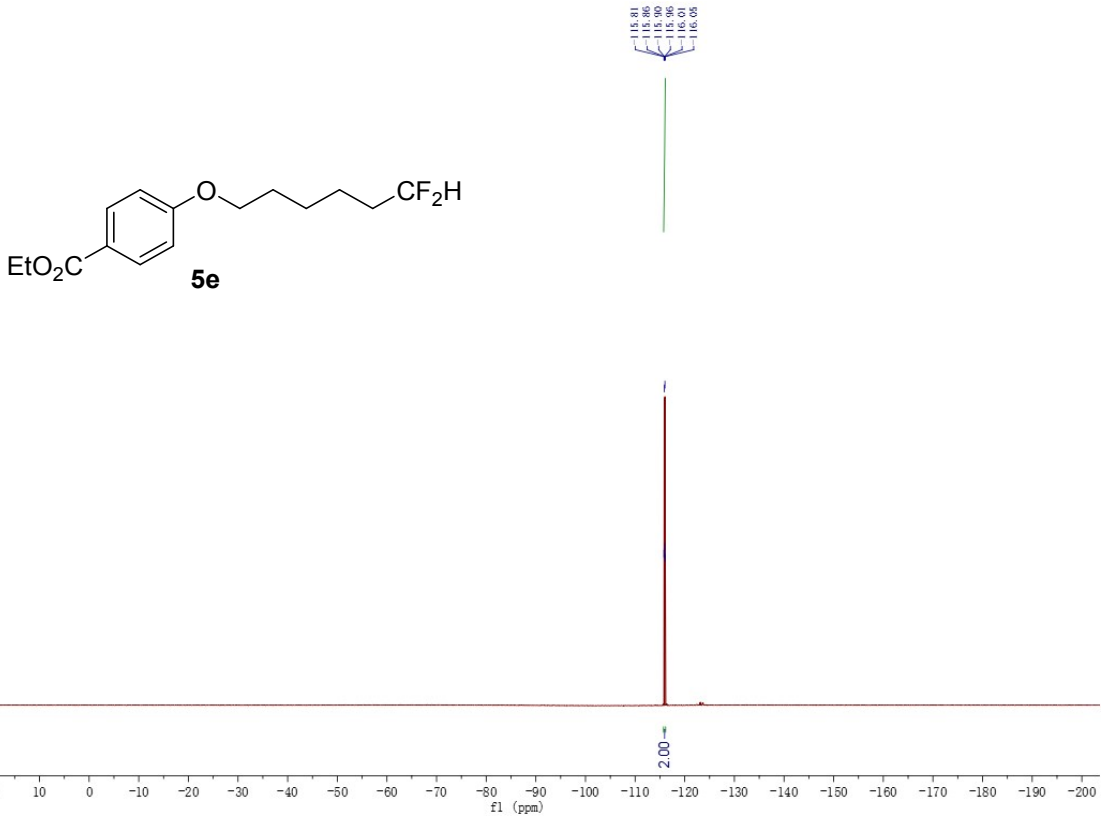

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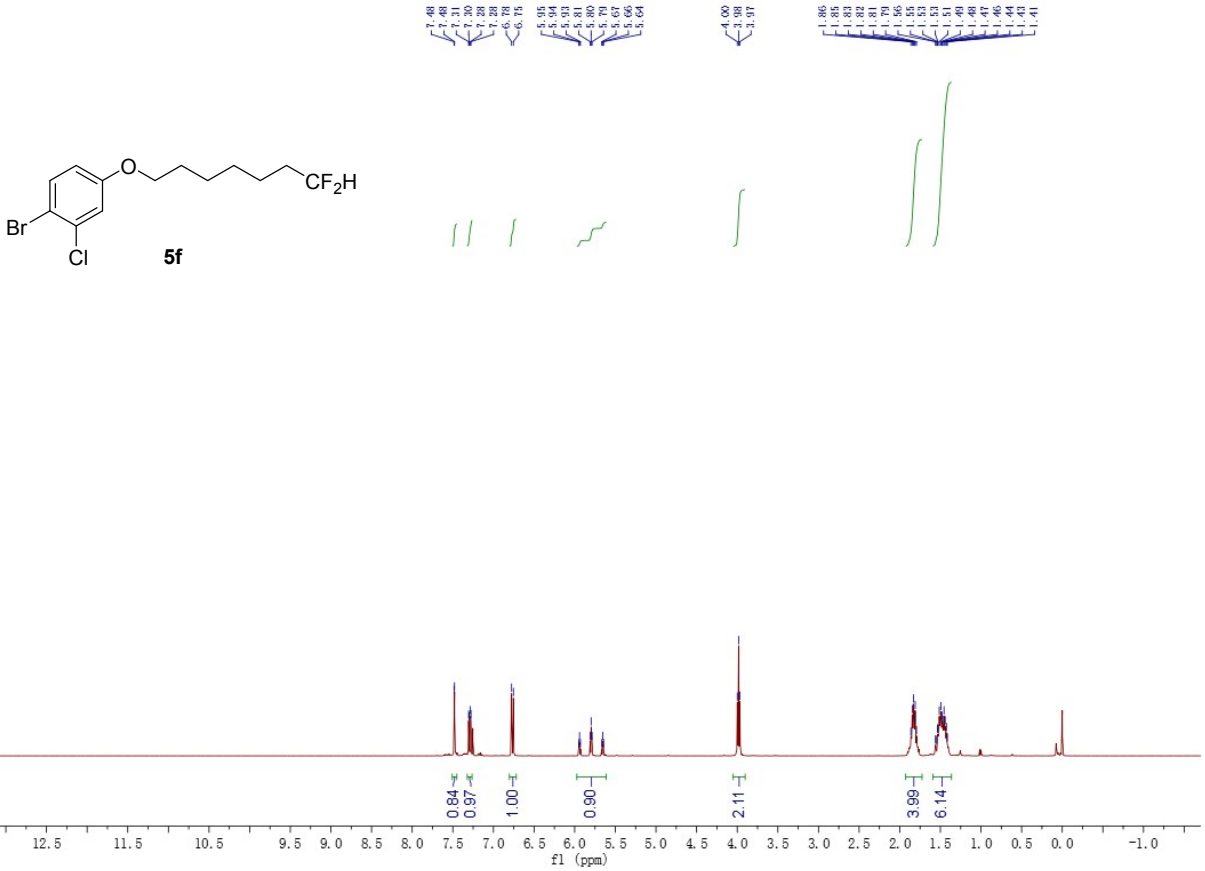

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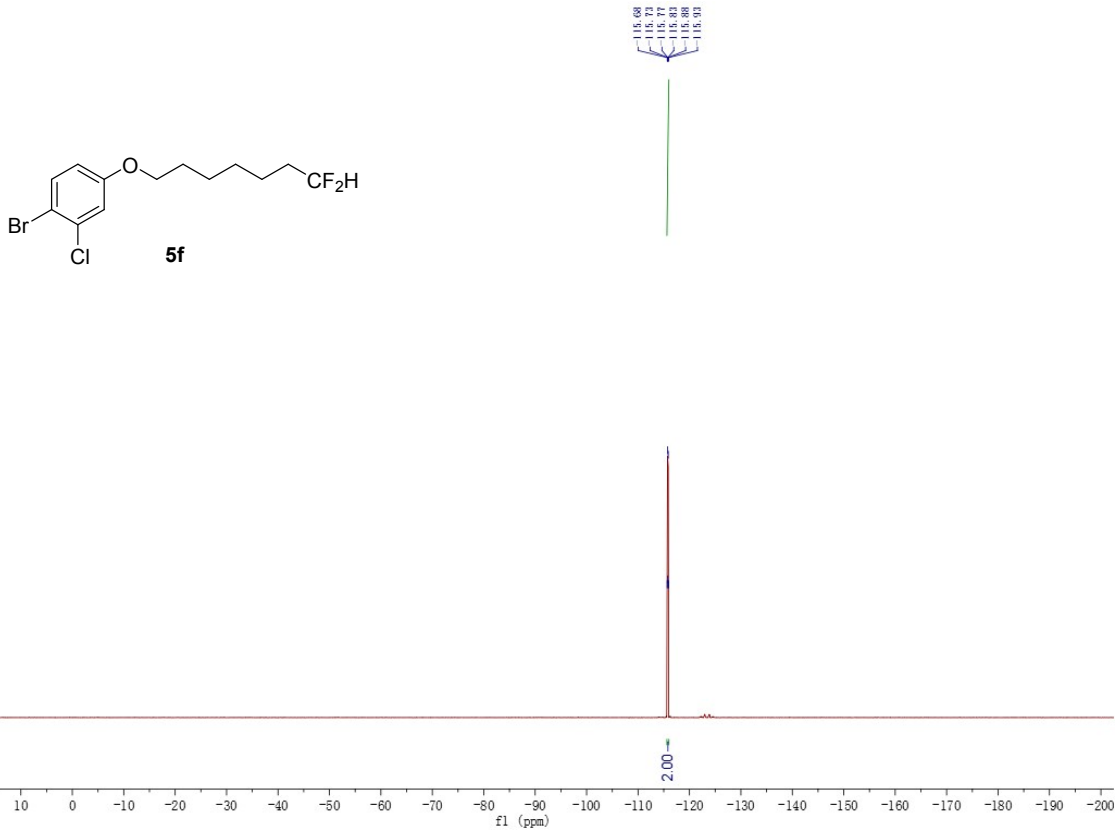

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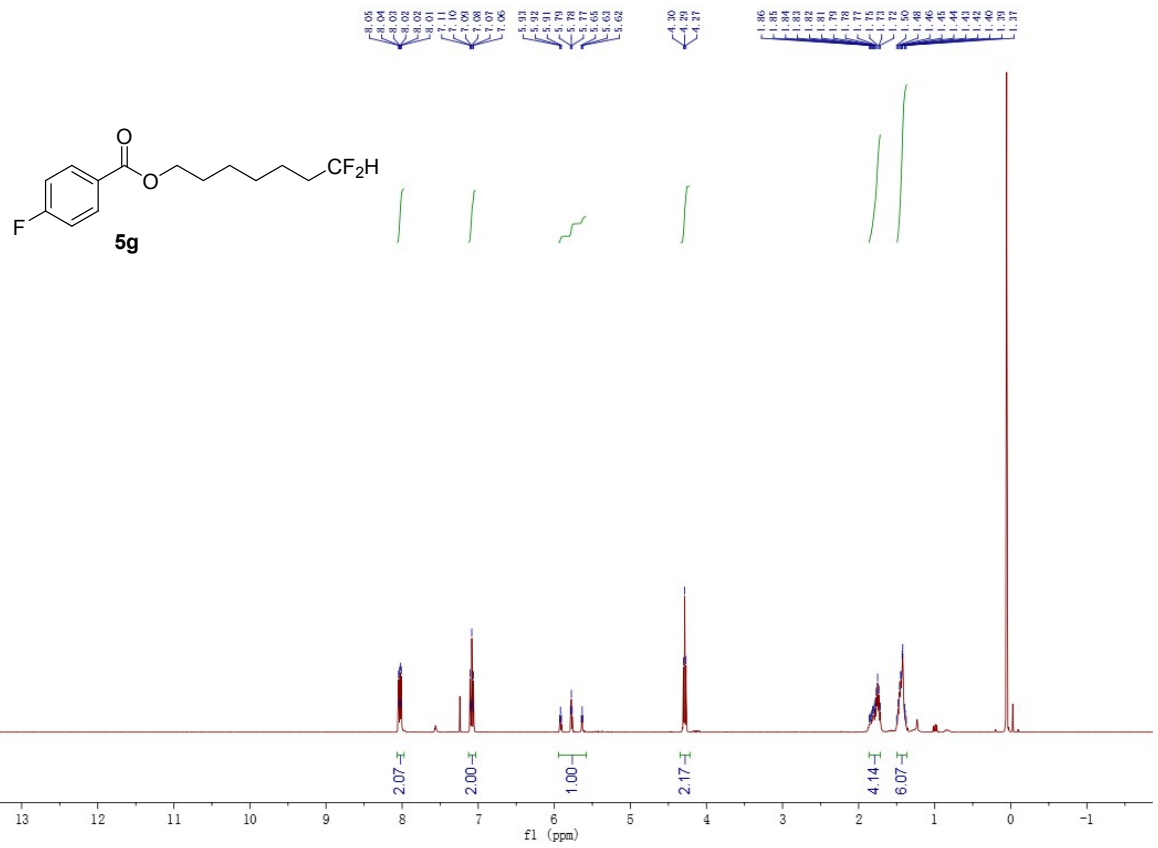

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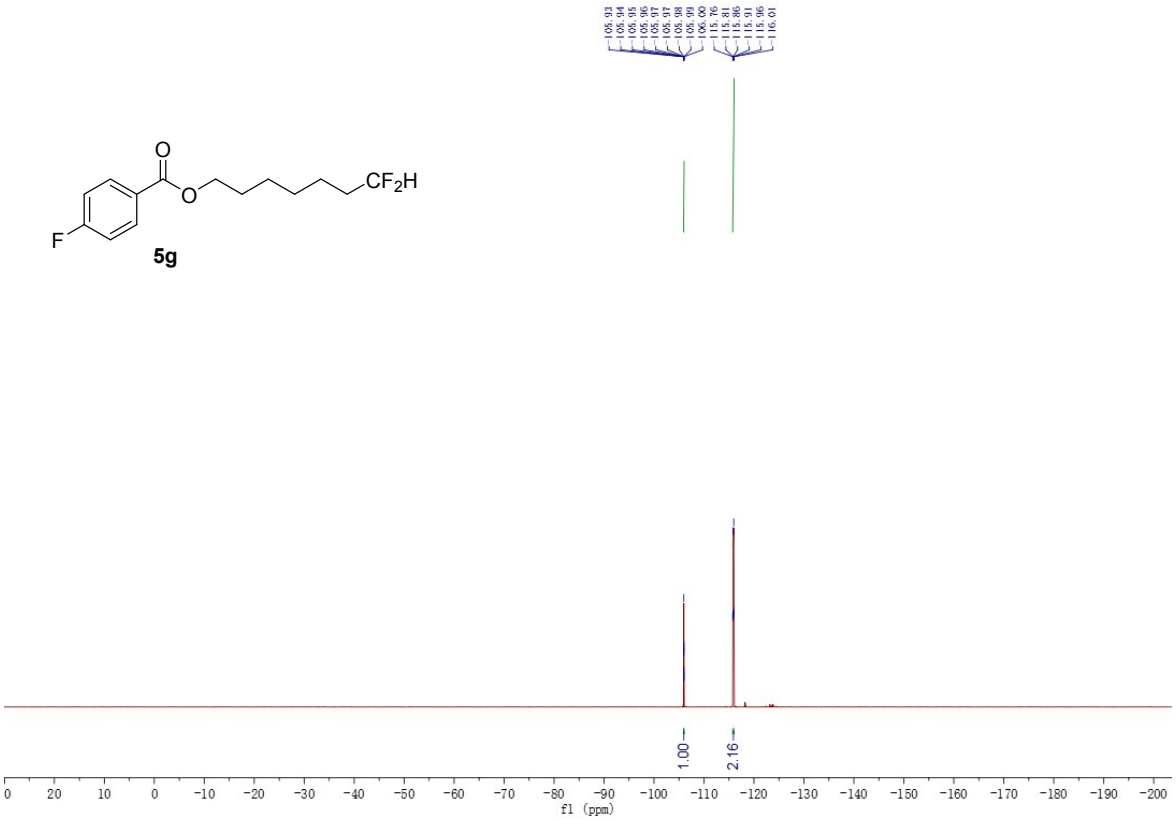

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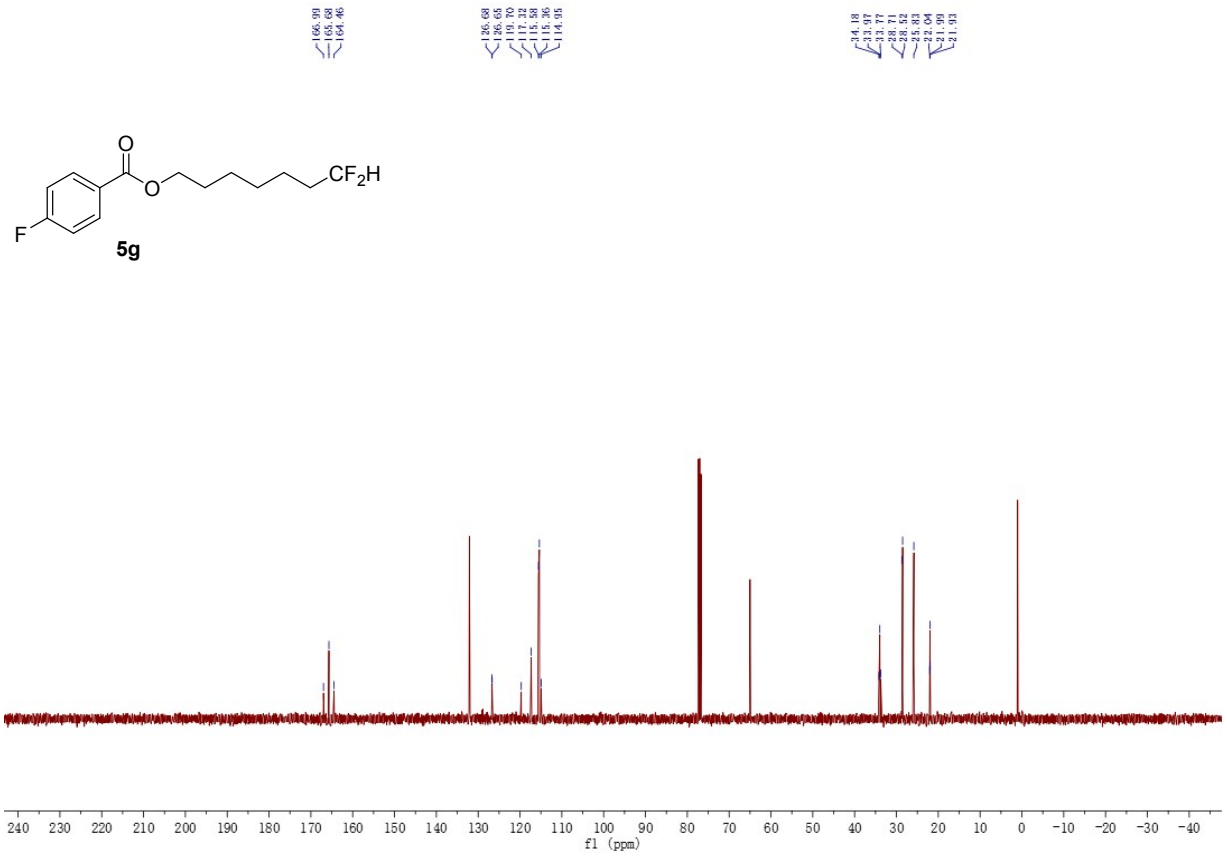

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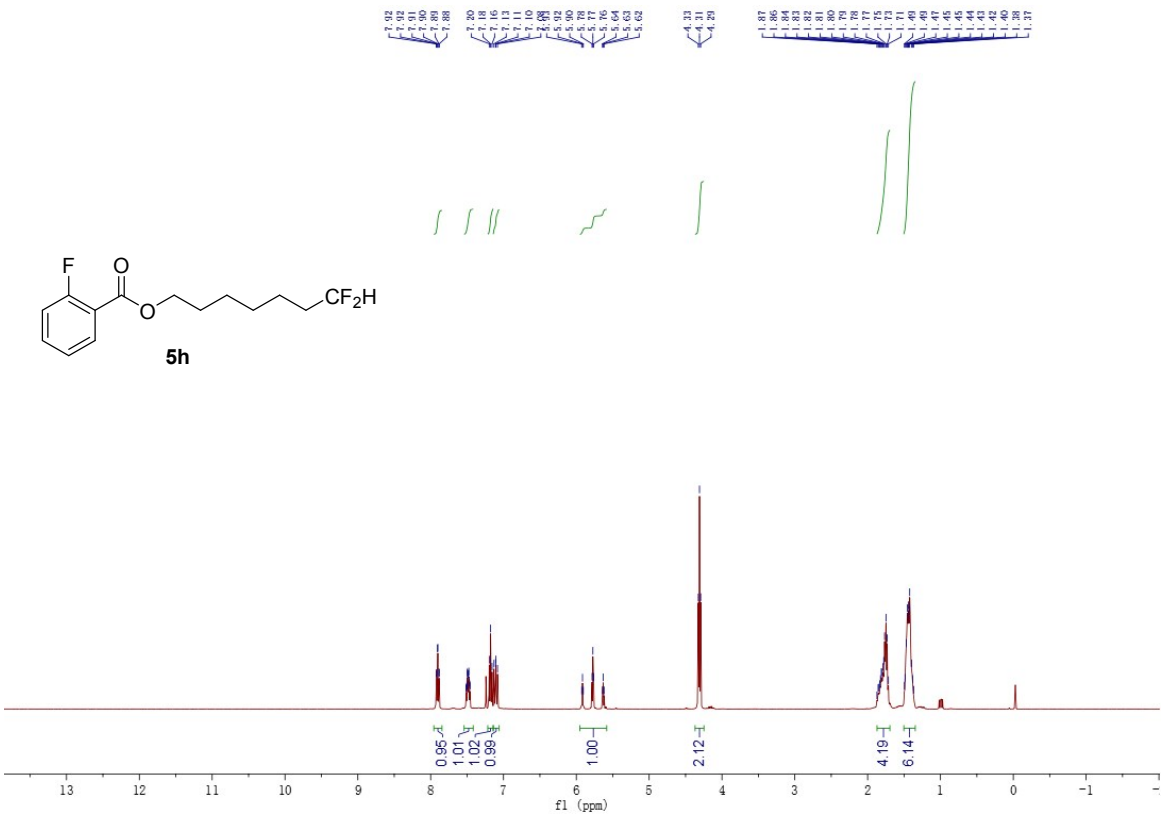

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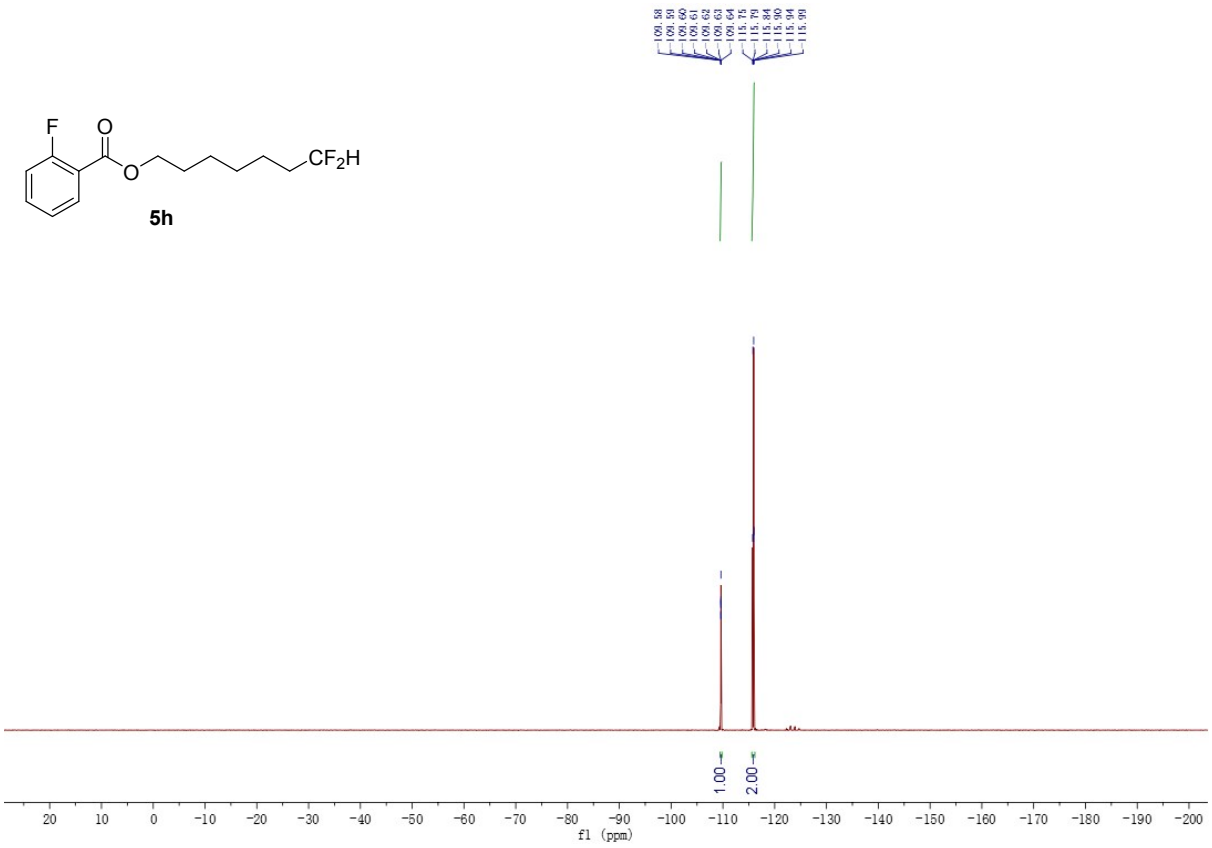

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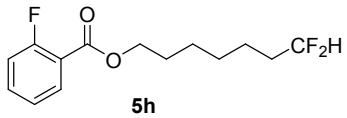

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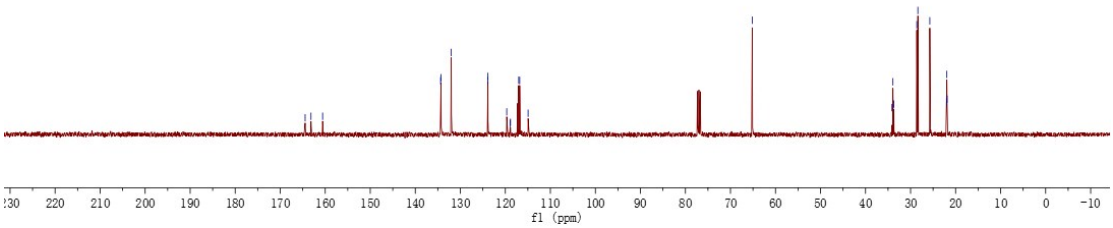

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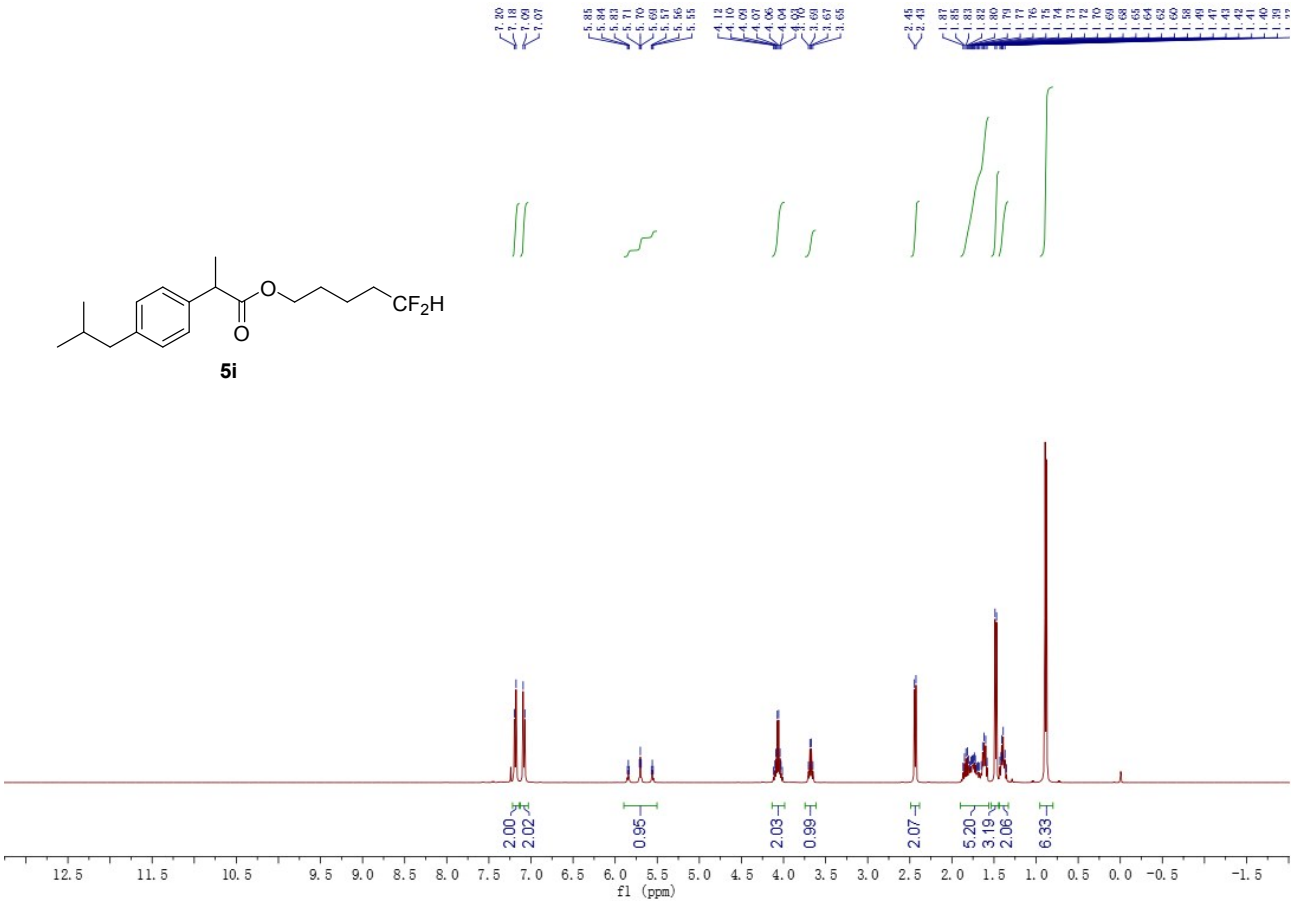

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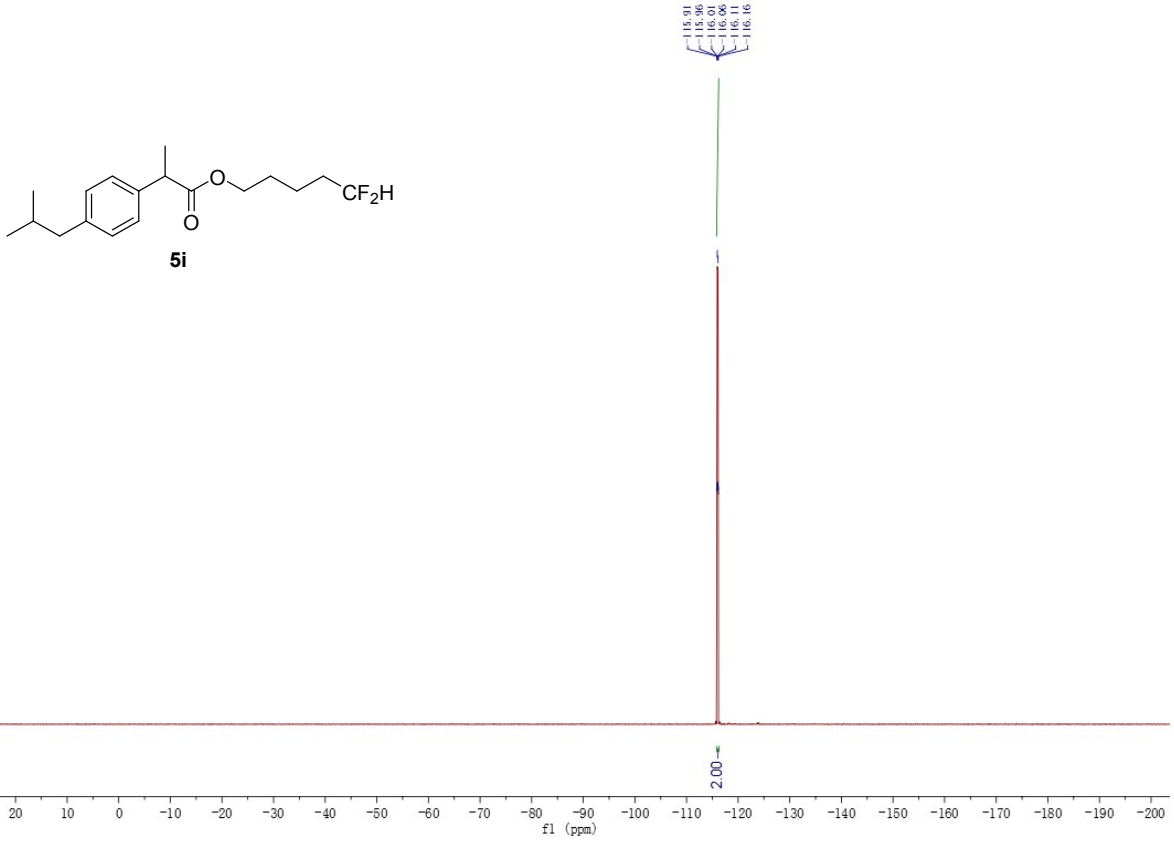

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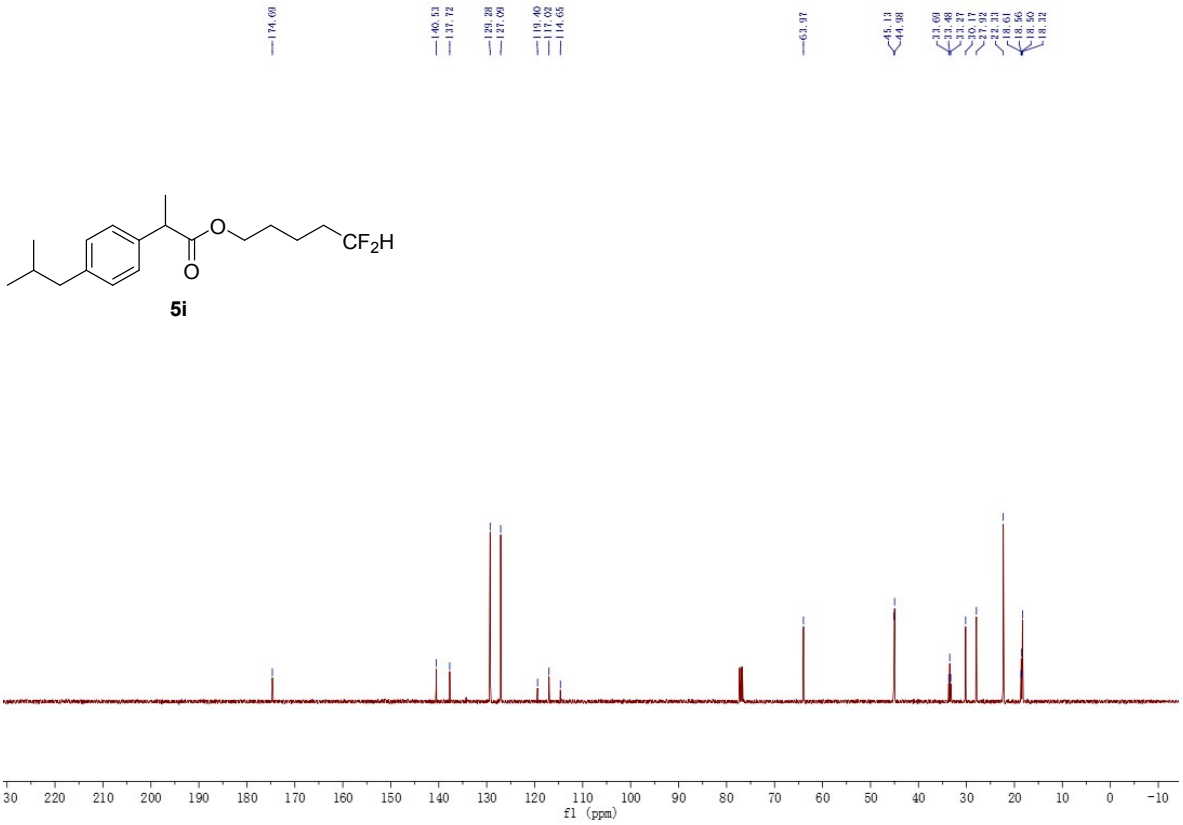

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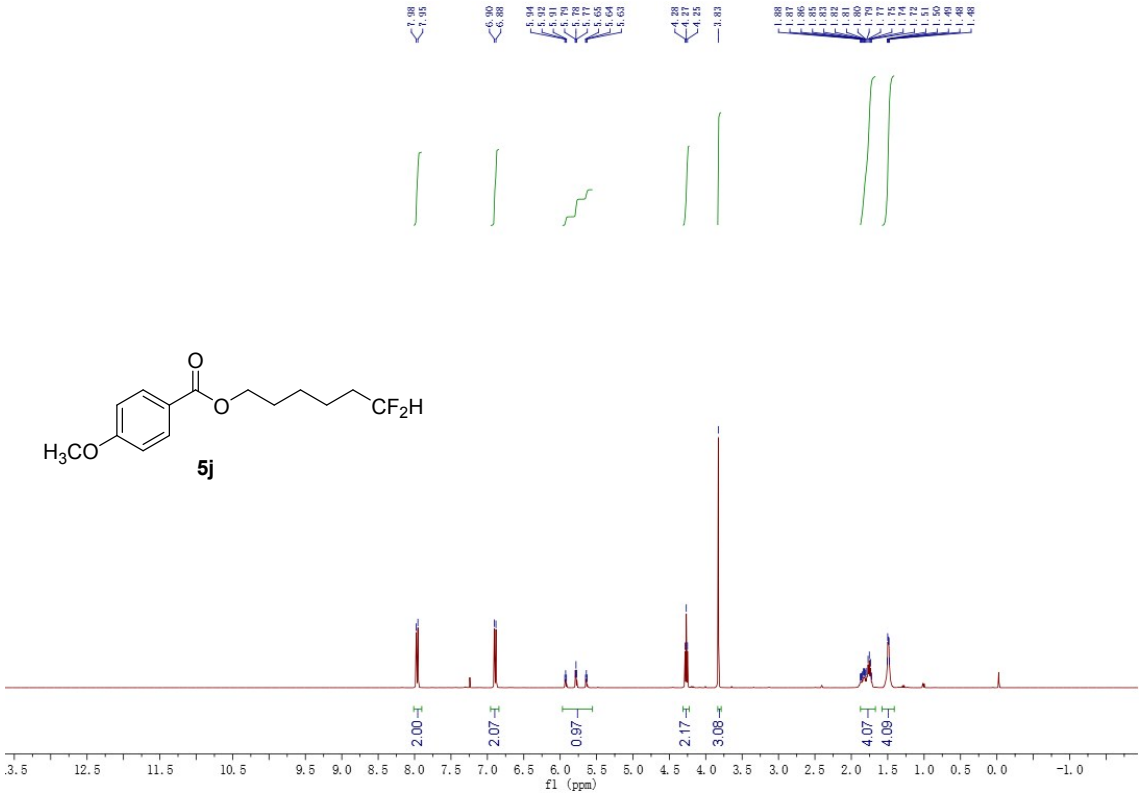

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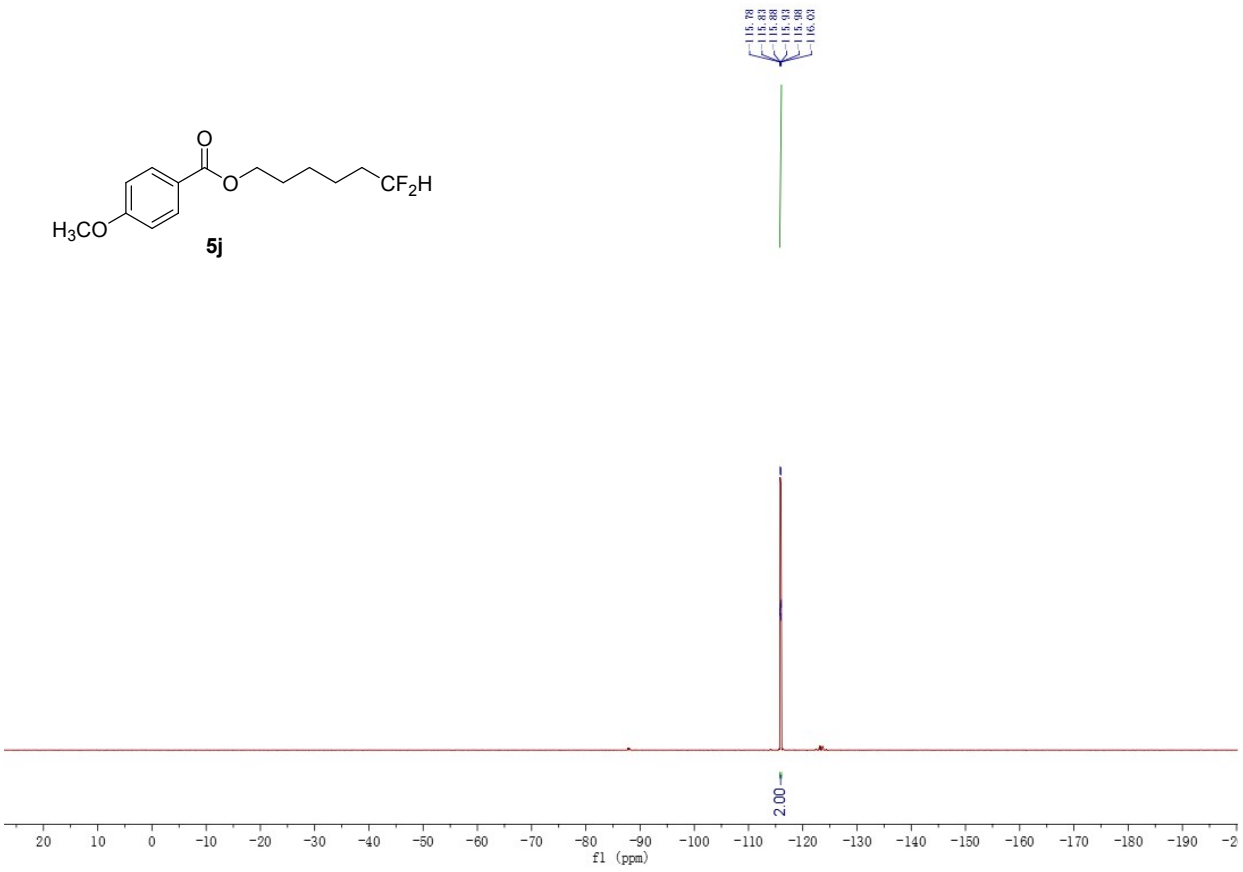

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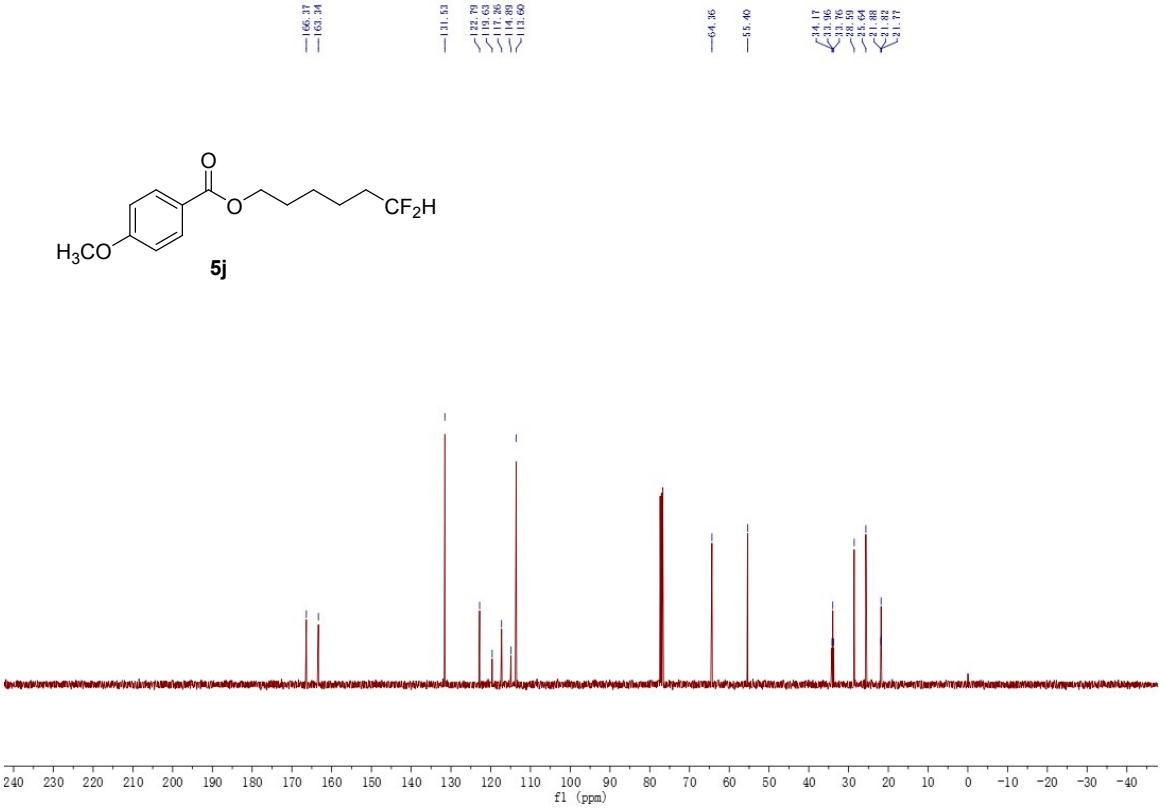

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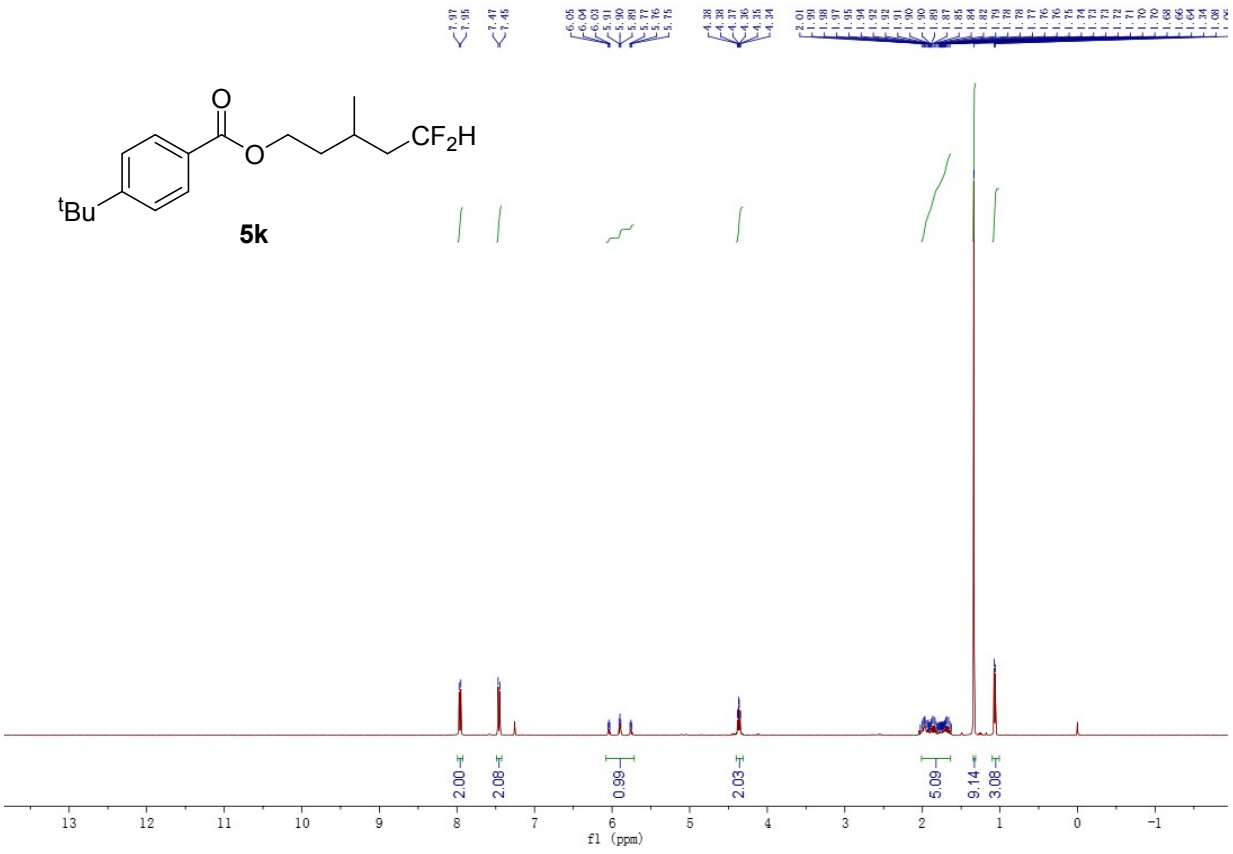

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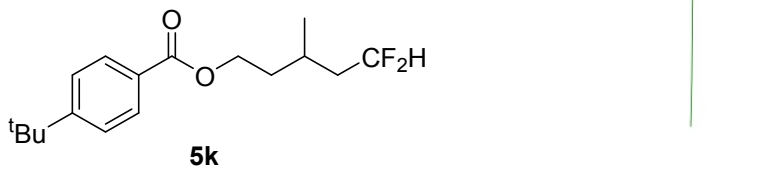

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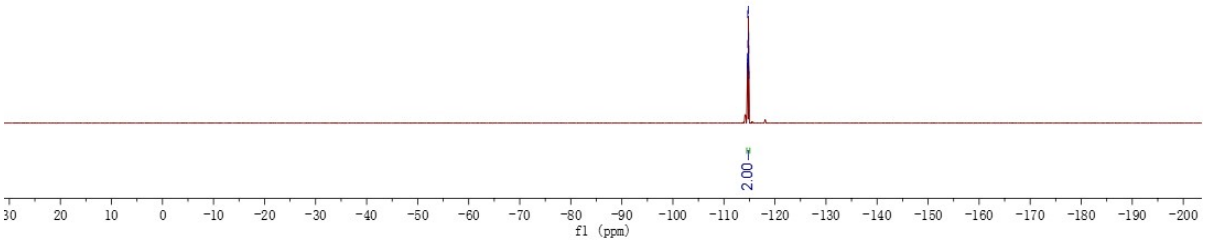

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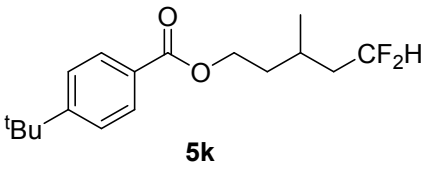

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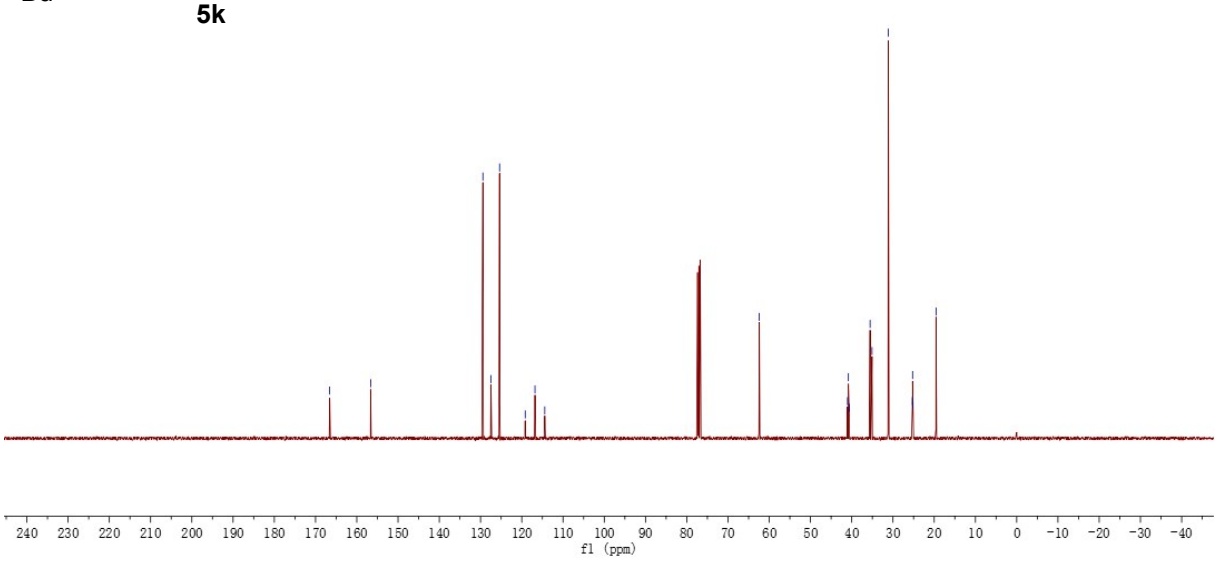

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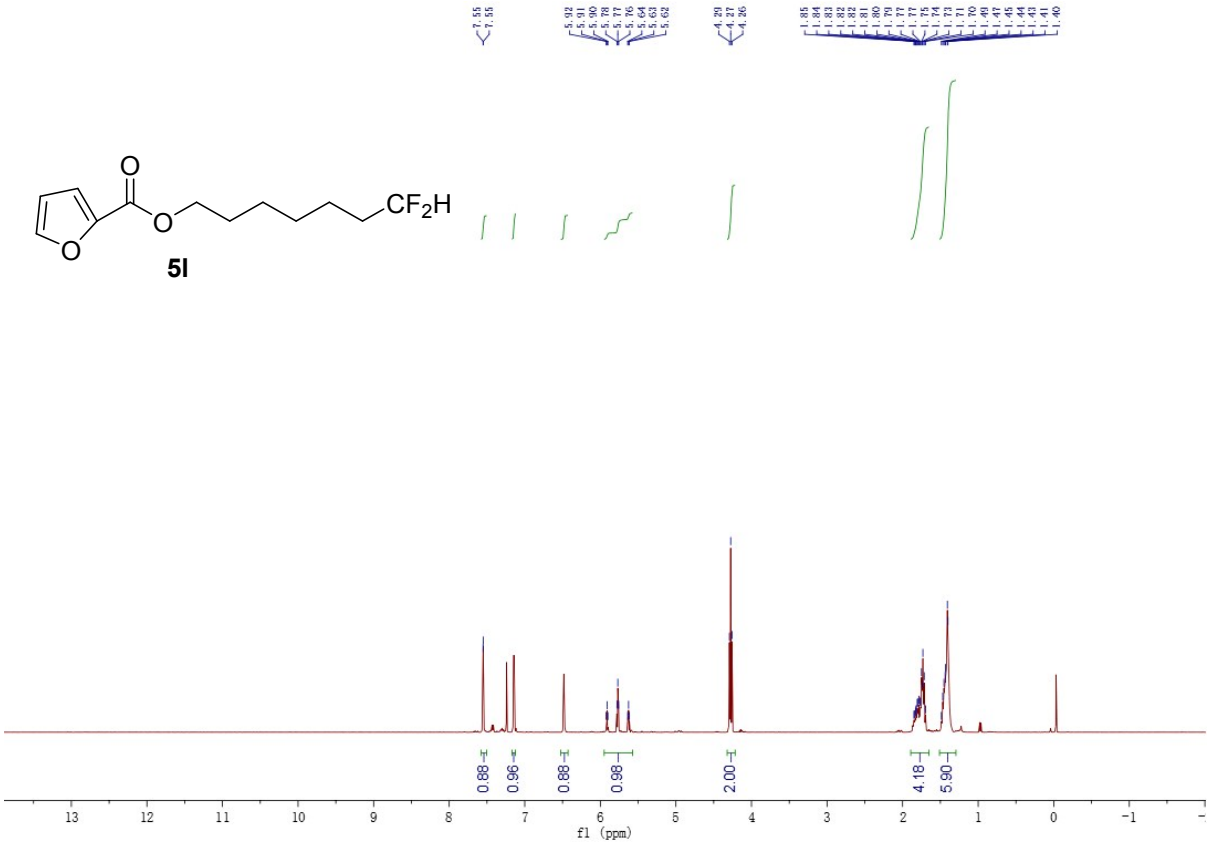
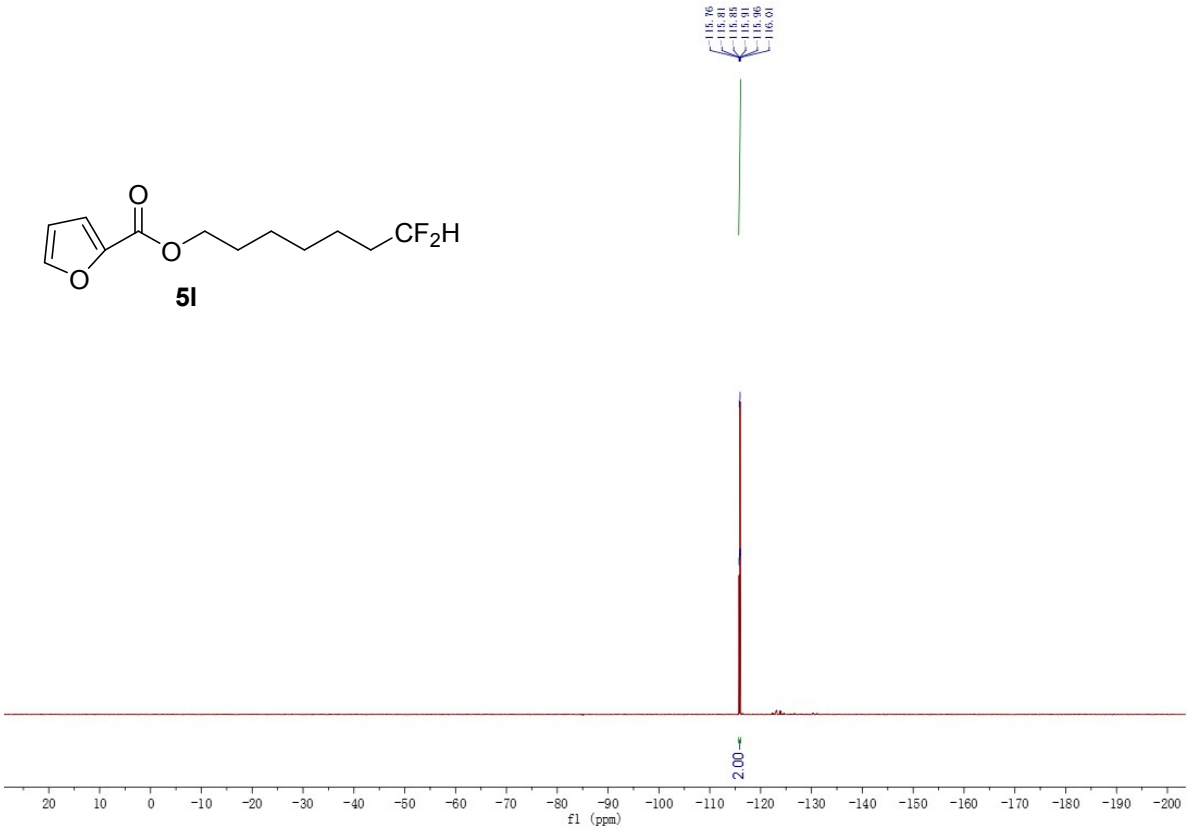


^{19}F NMR:



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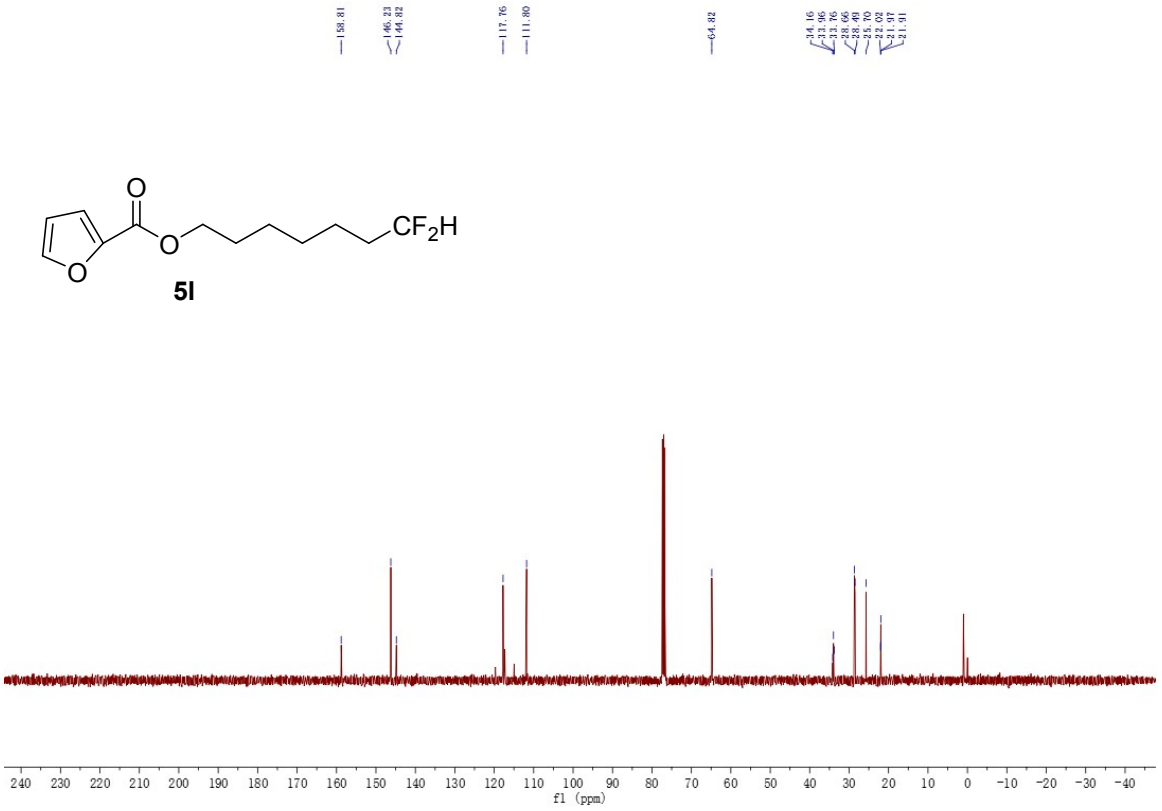

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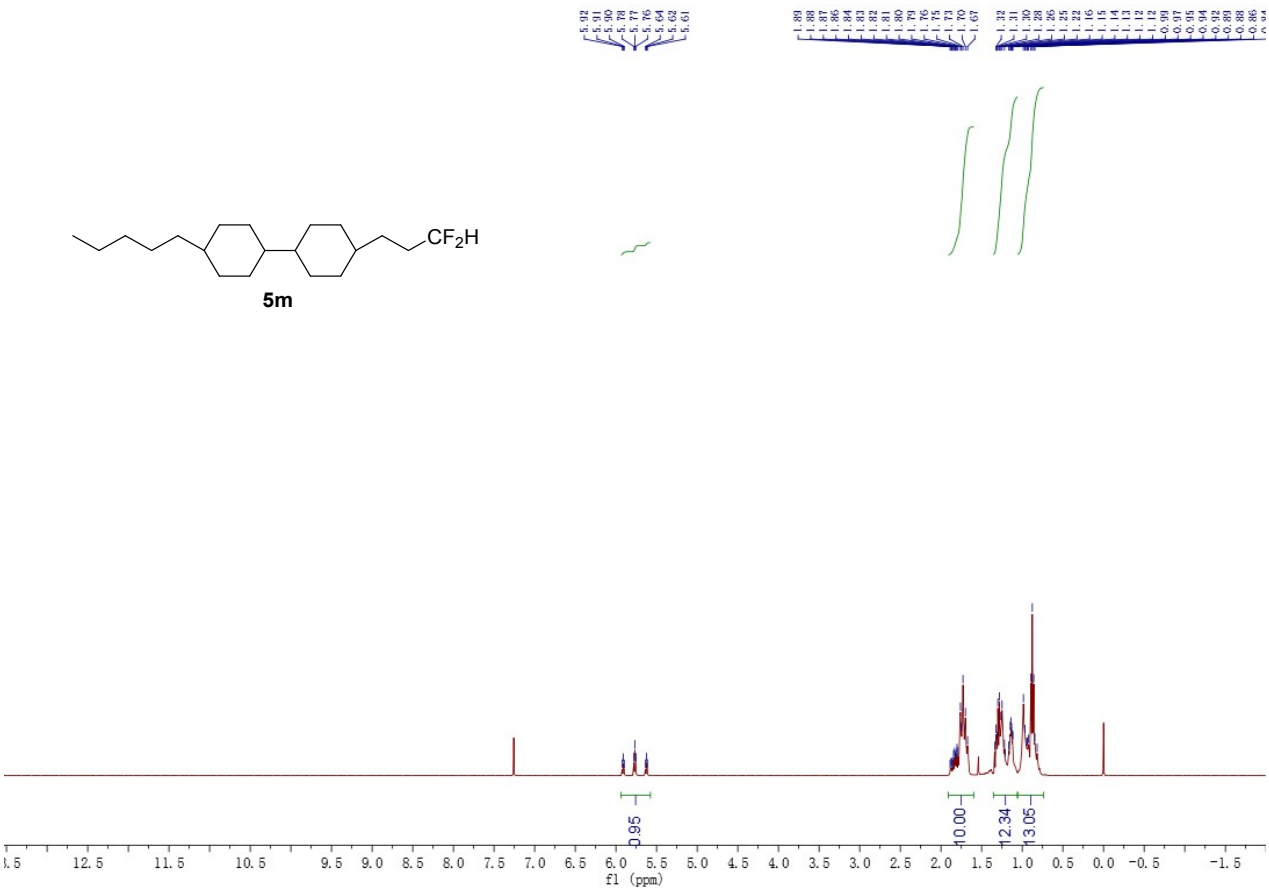

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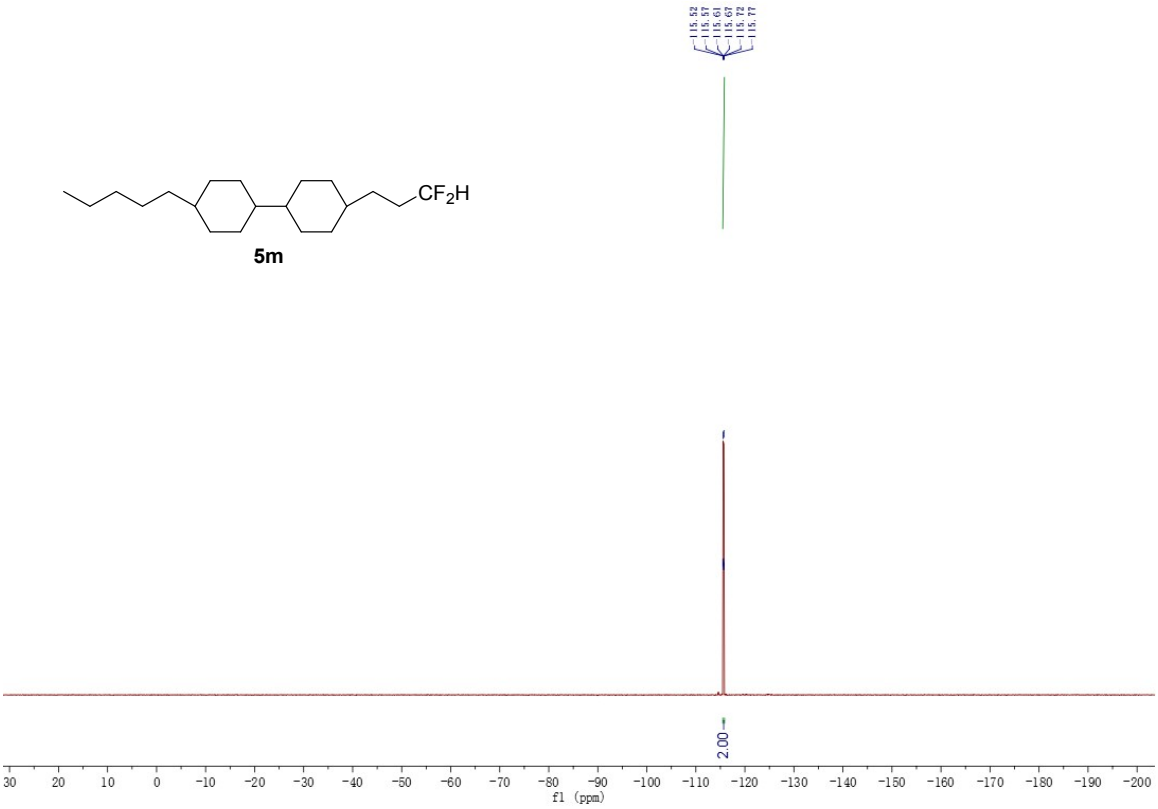

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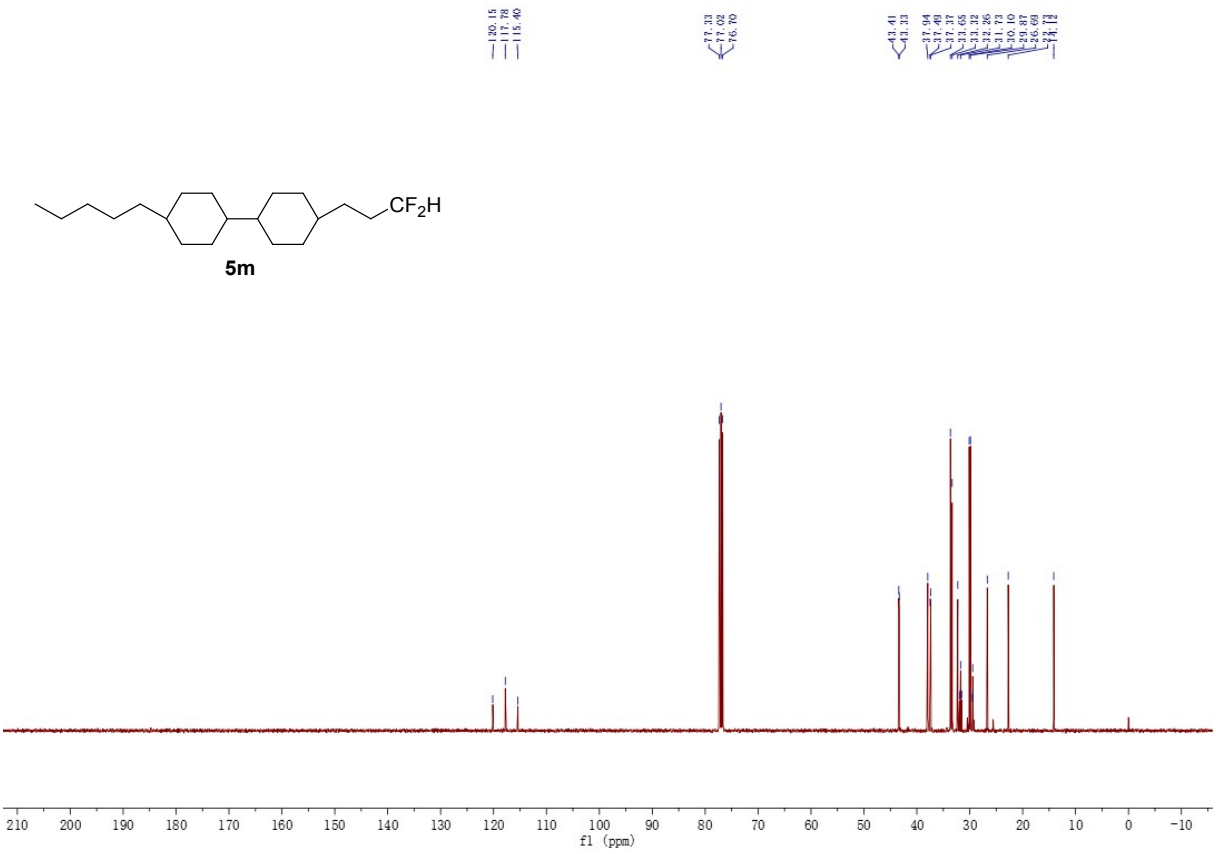

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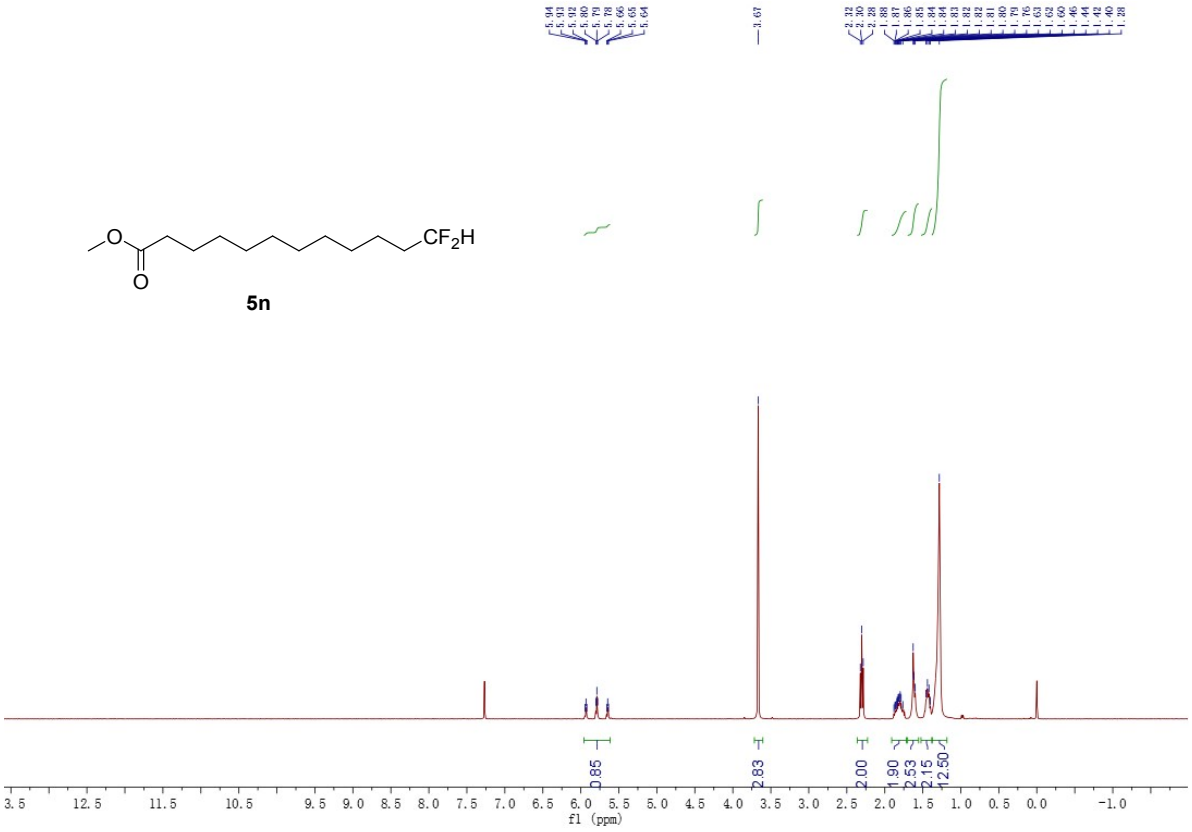

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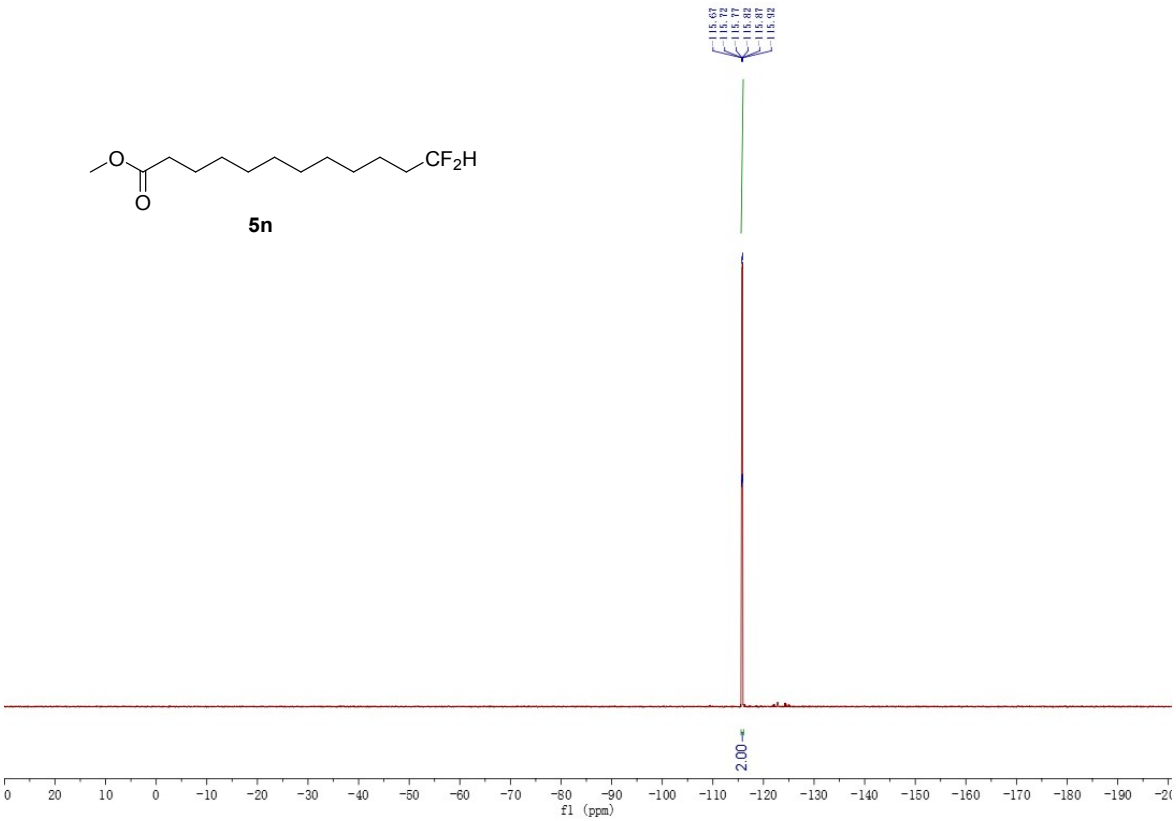

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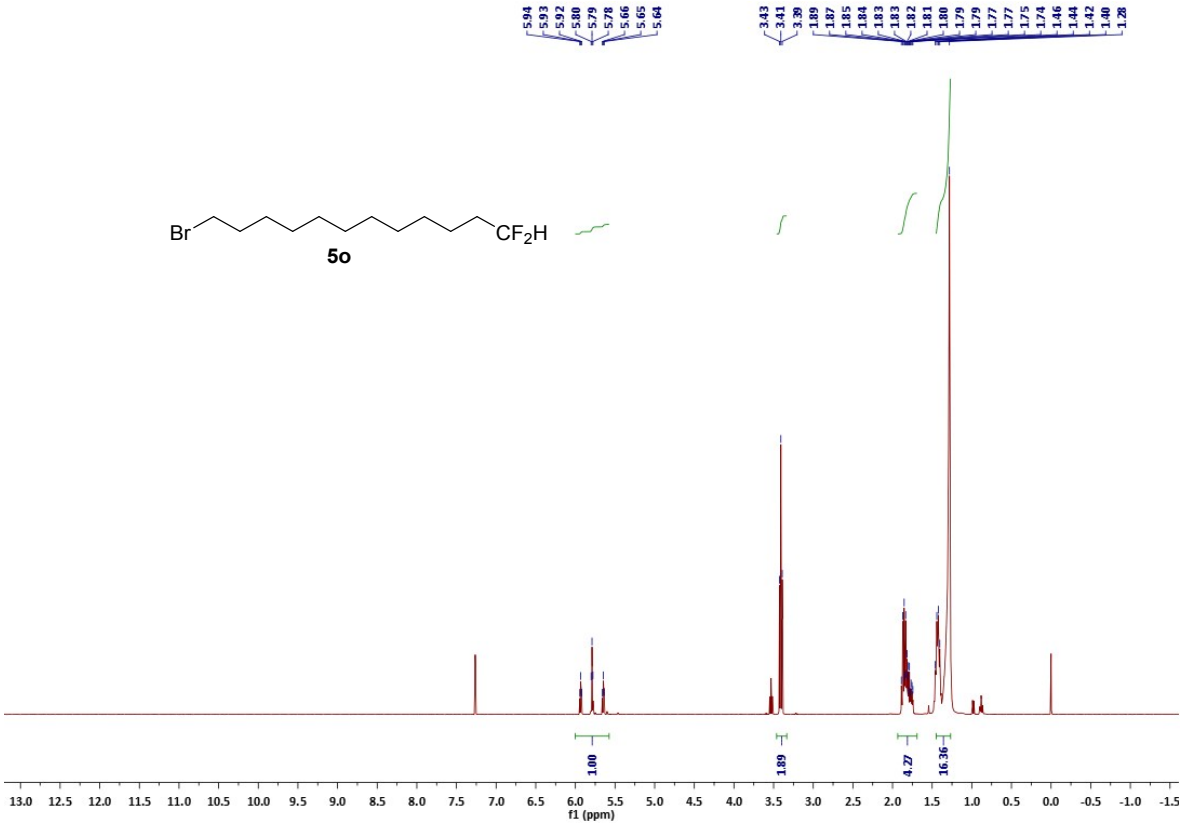

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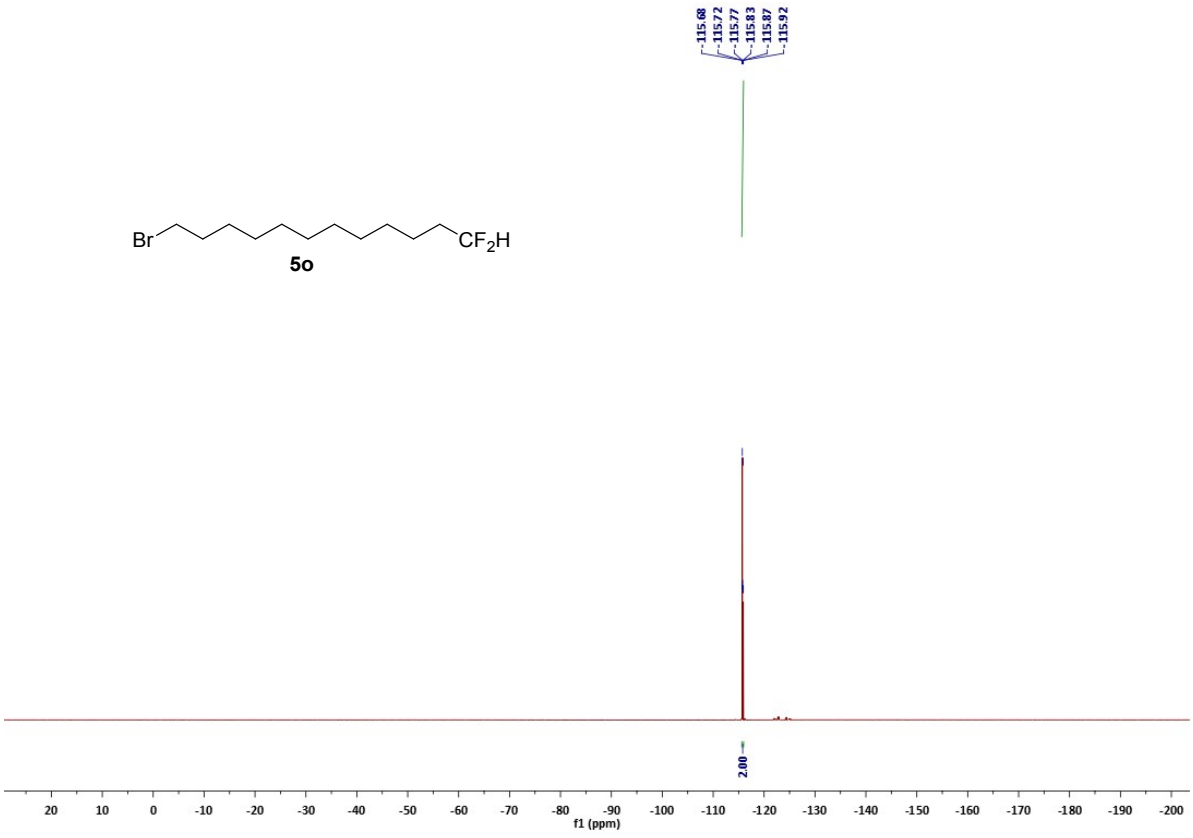

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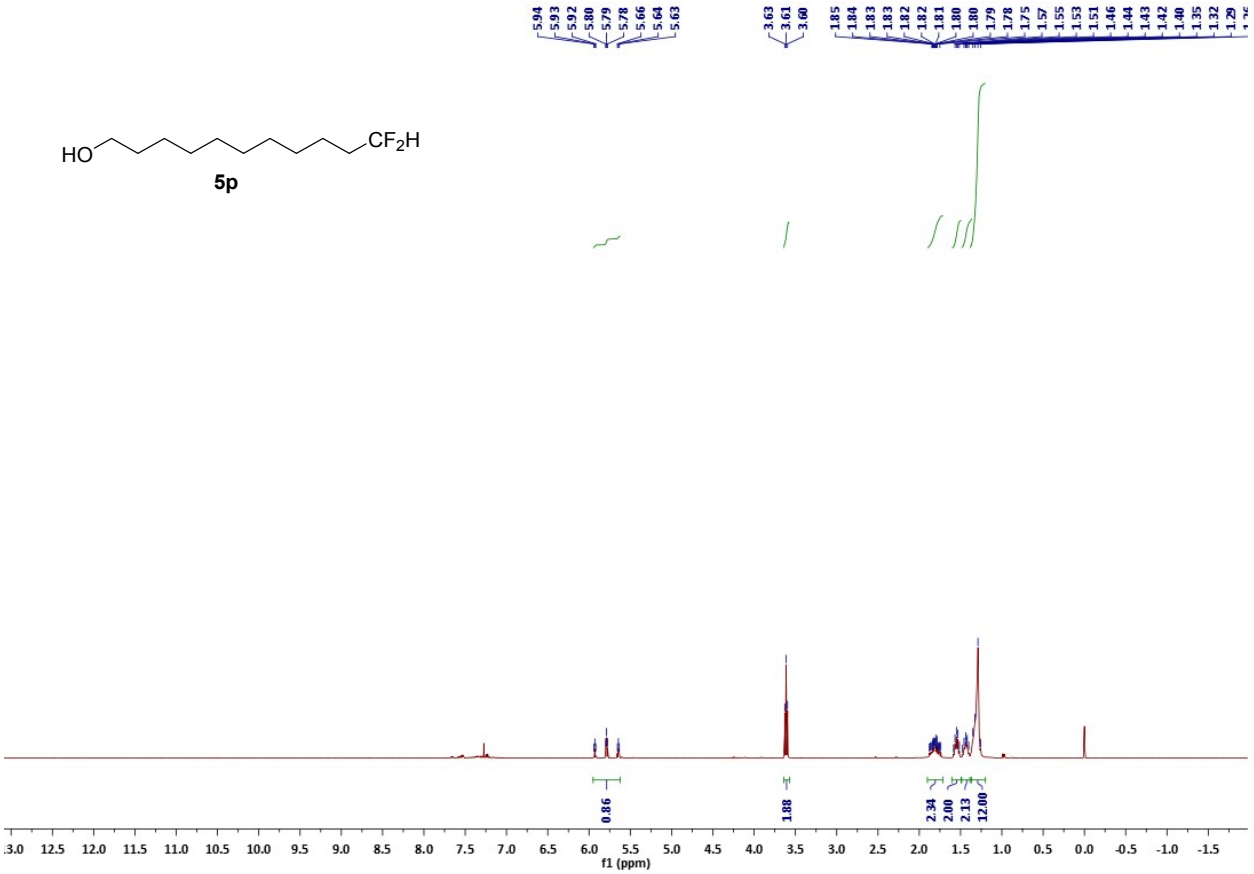

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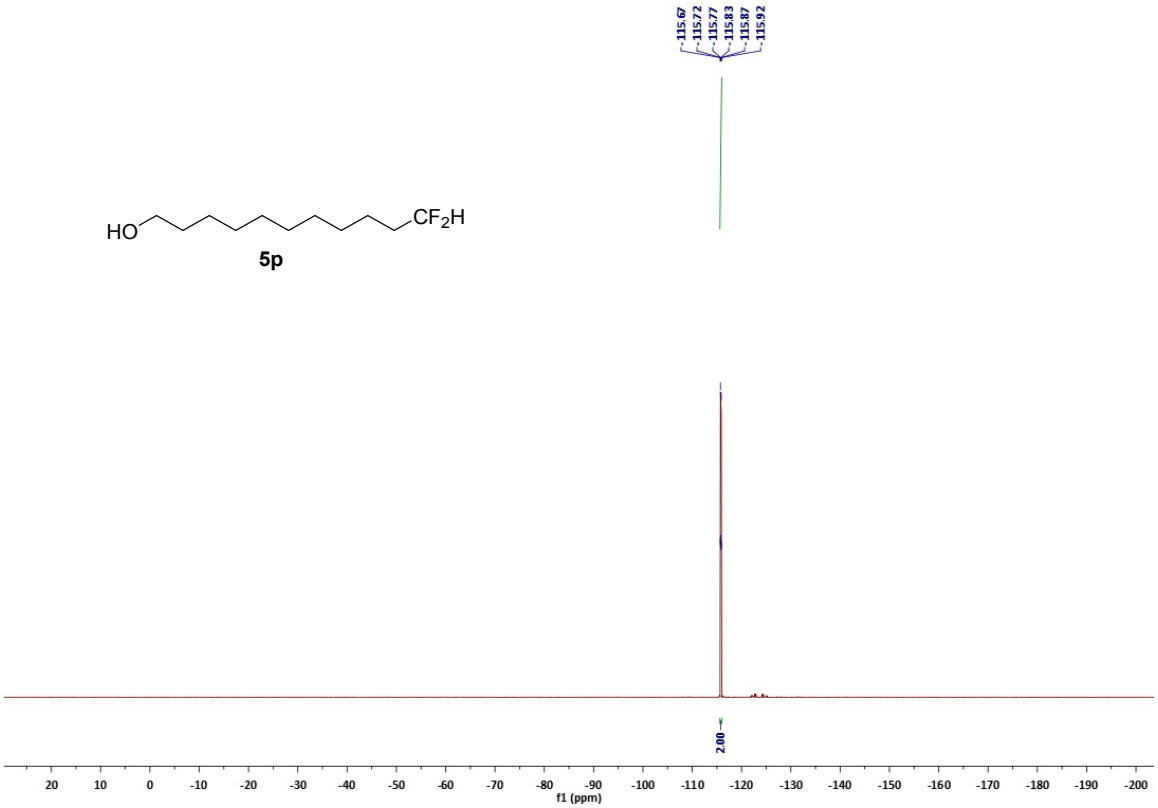

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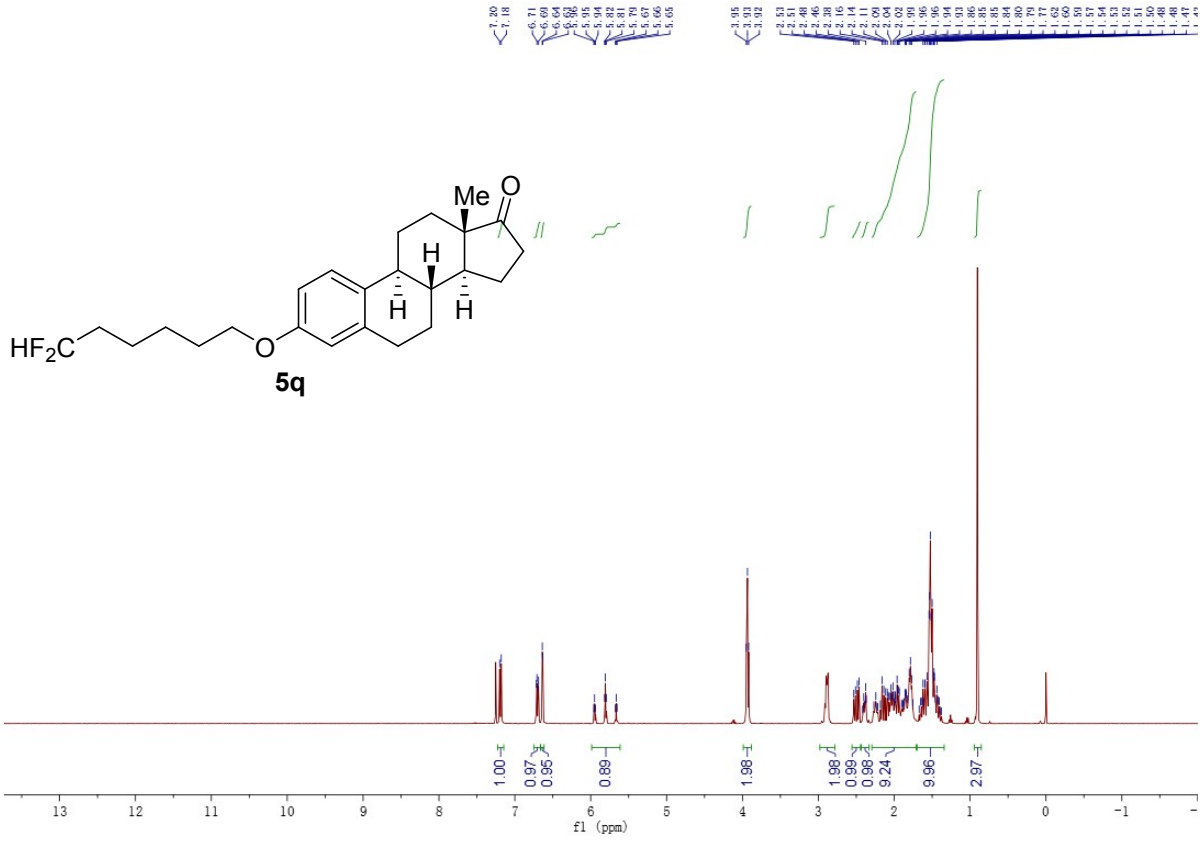

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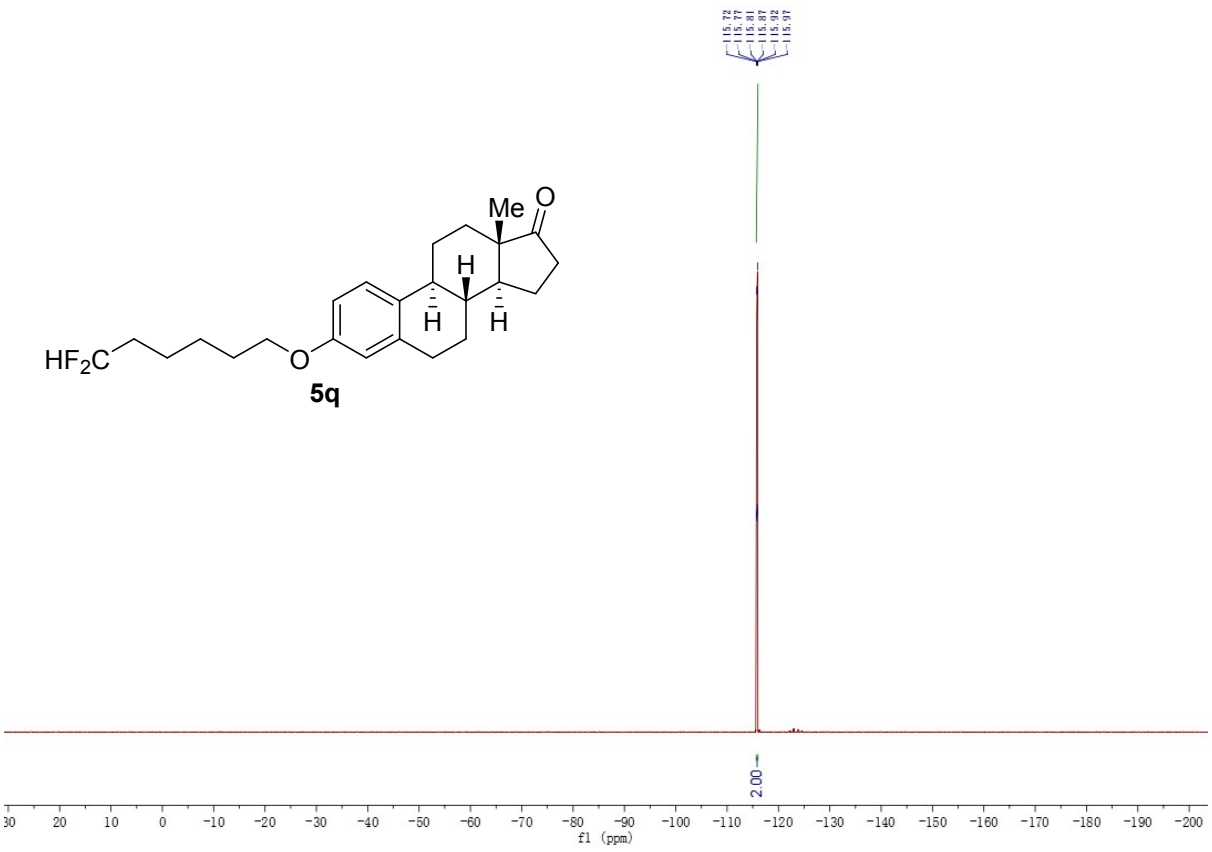

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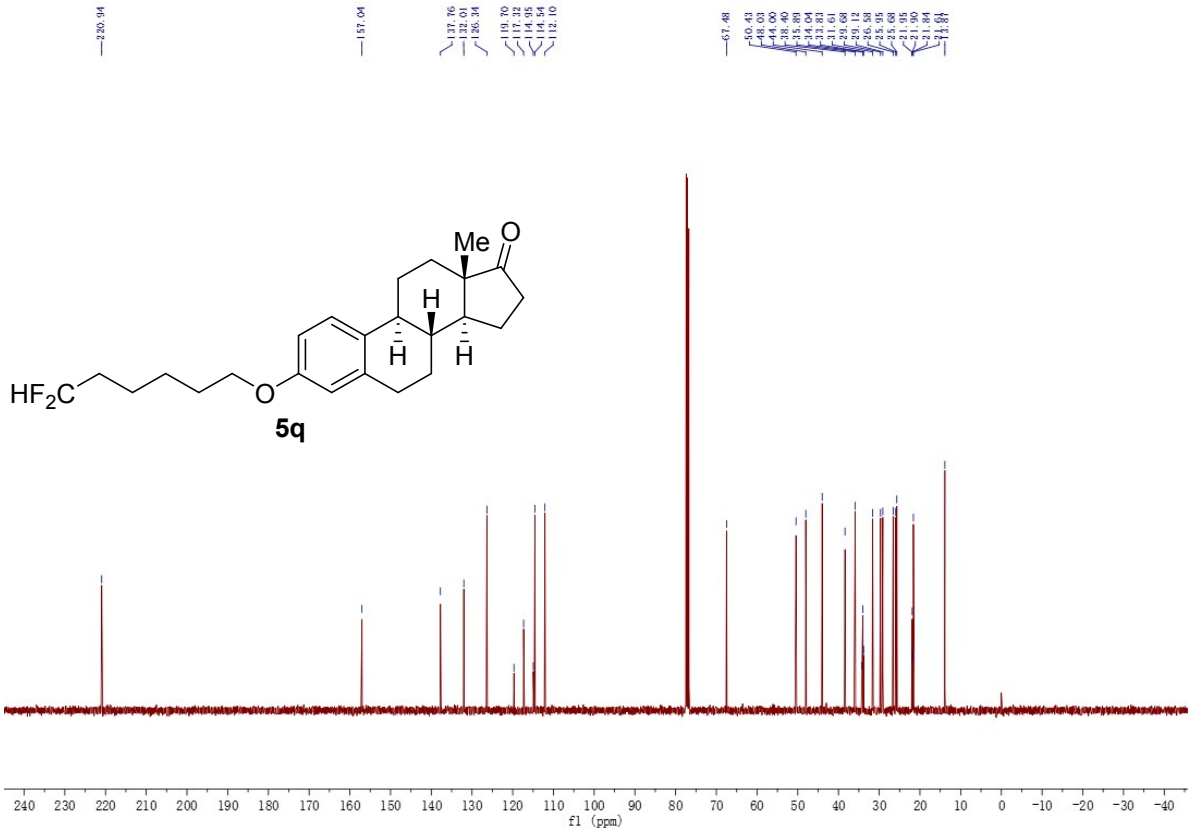

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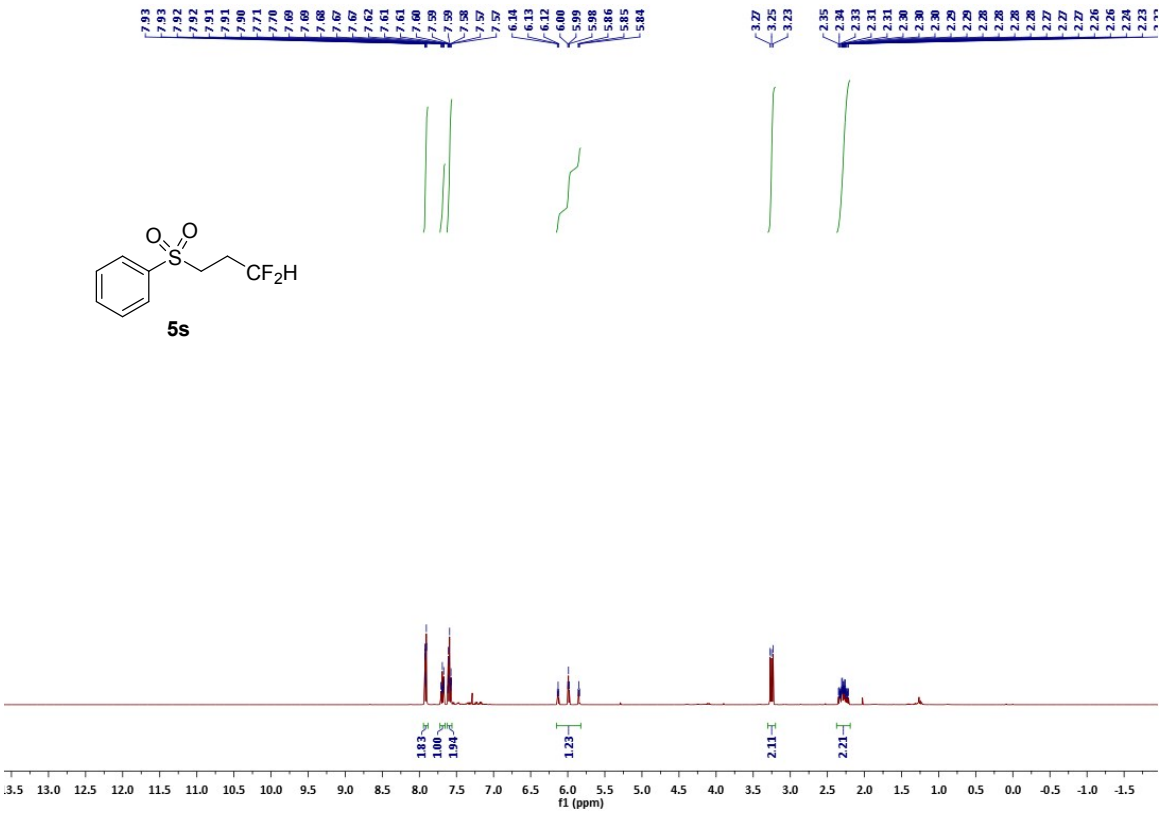

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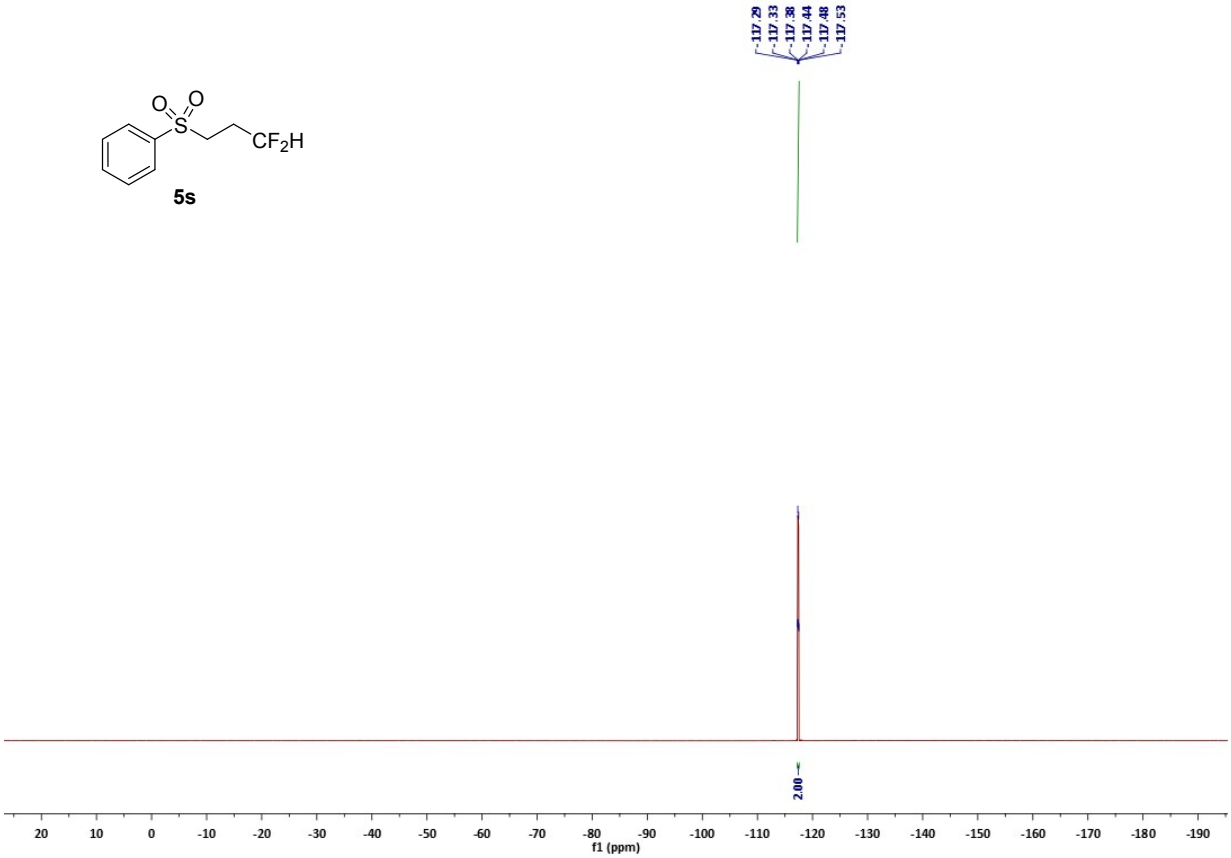

5s

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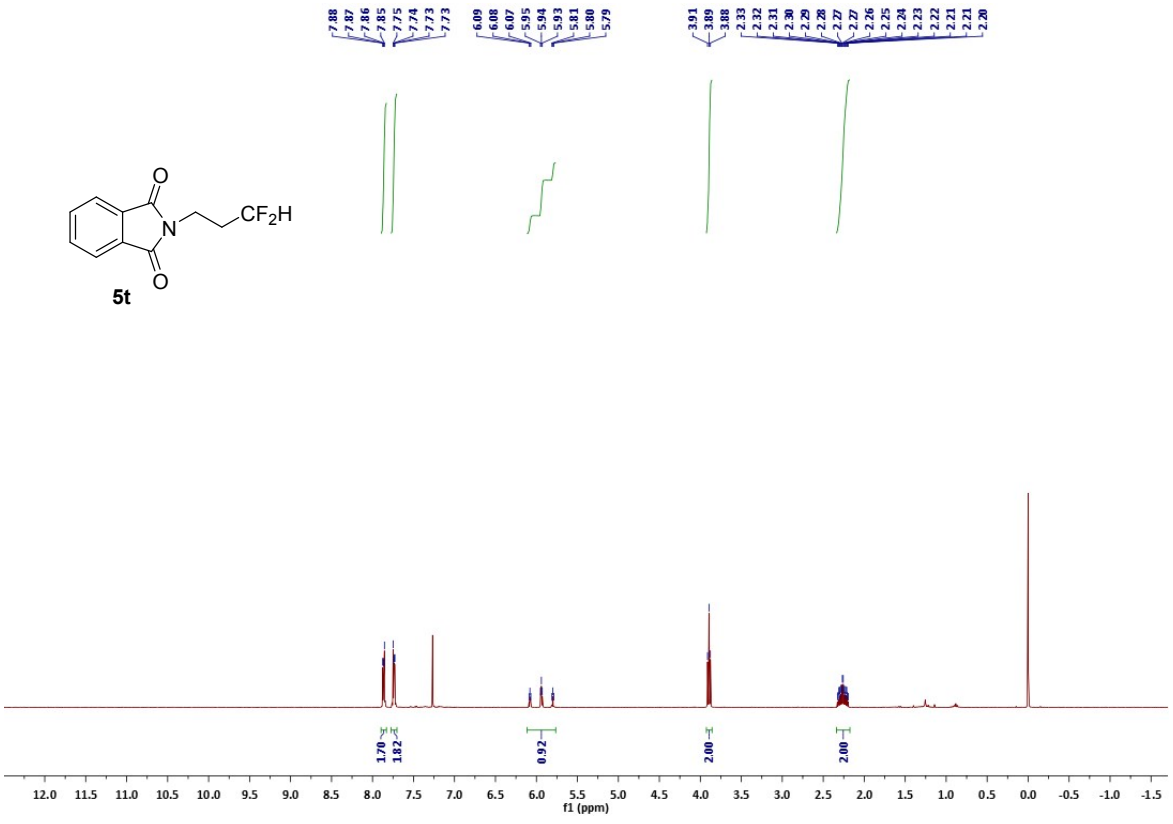

5t

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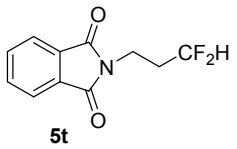

5t

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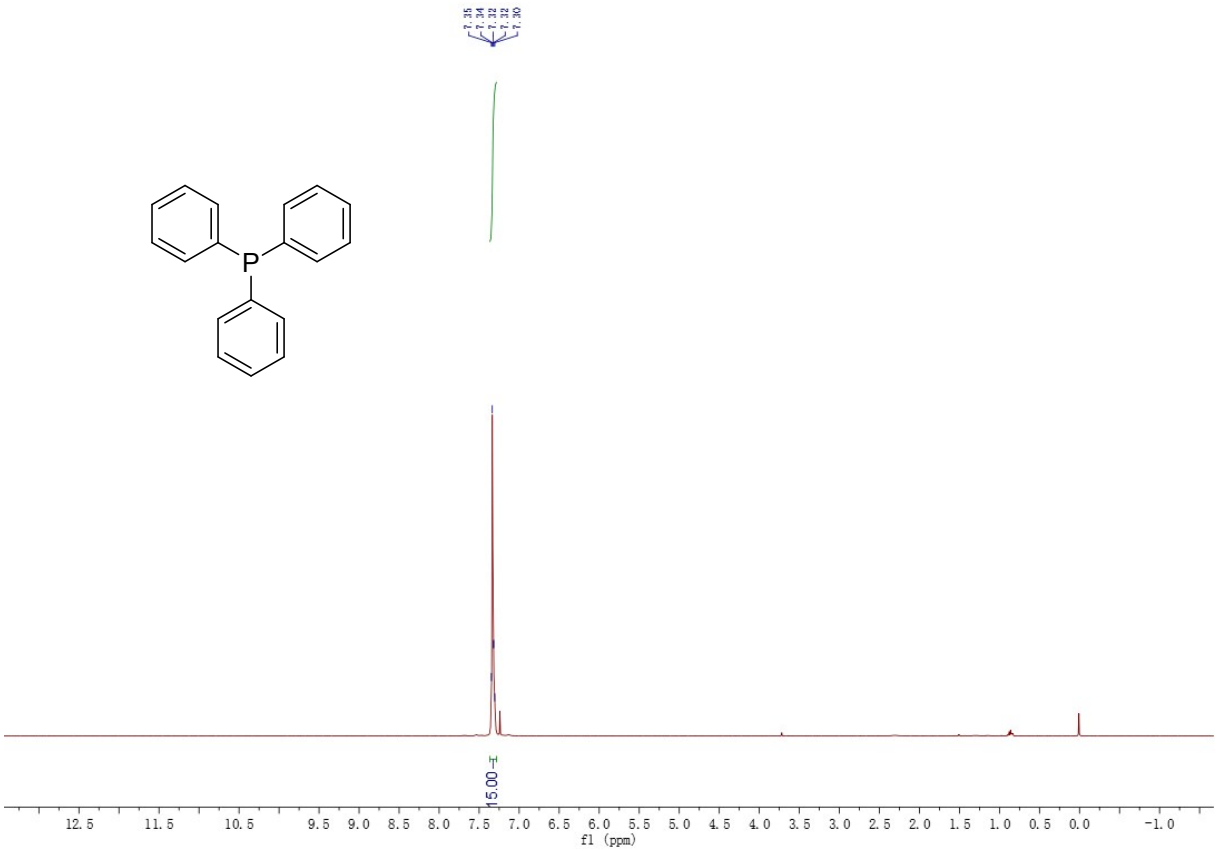

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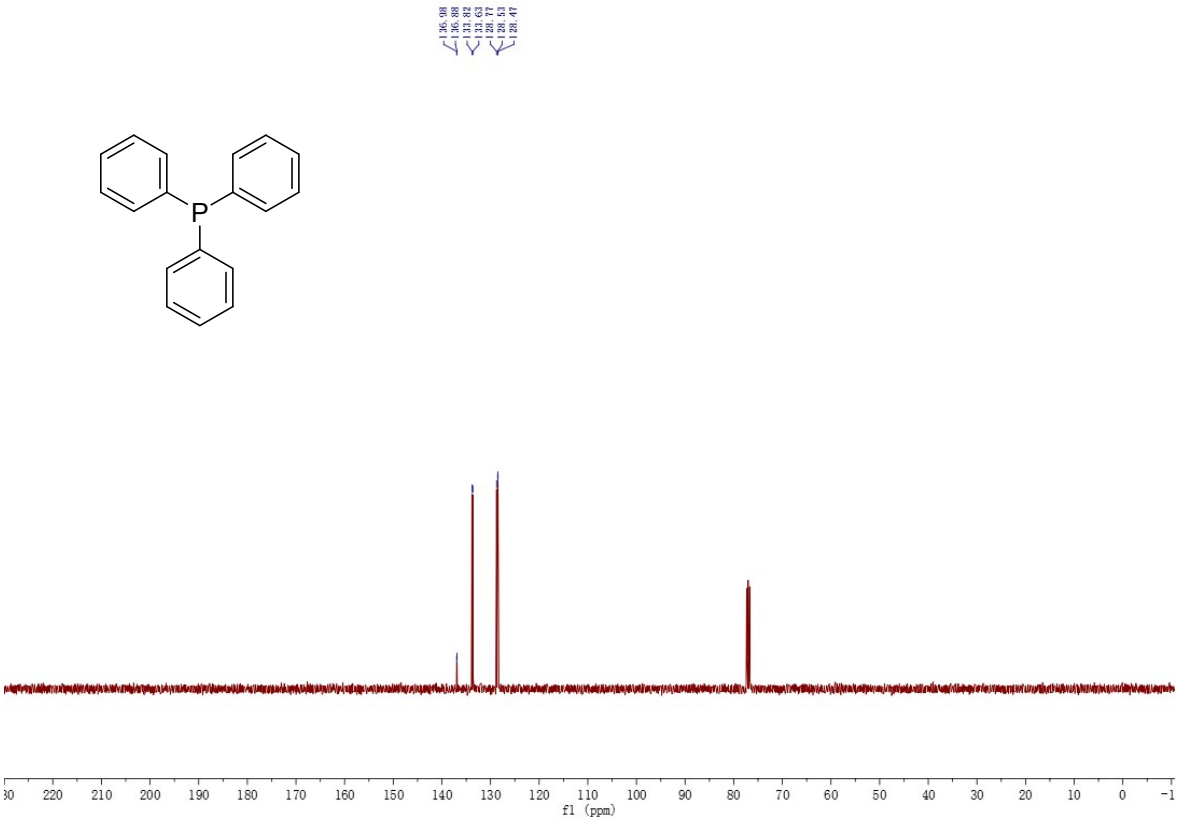

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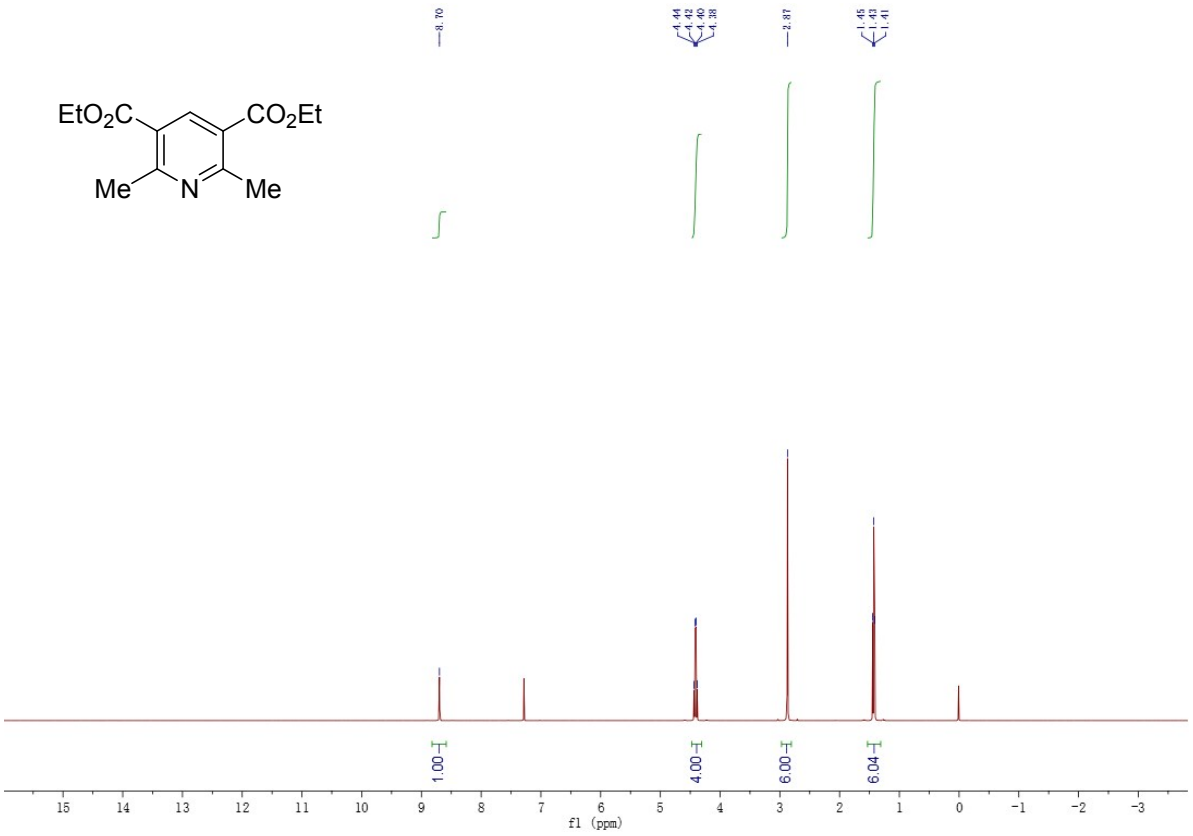

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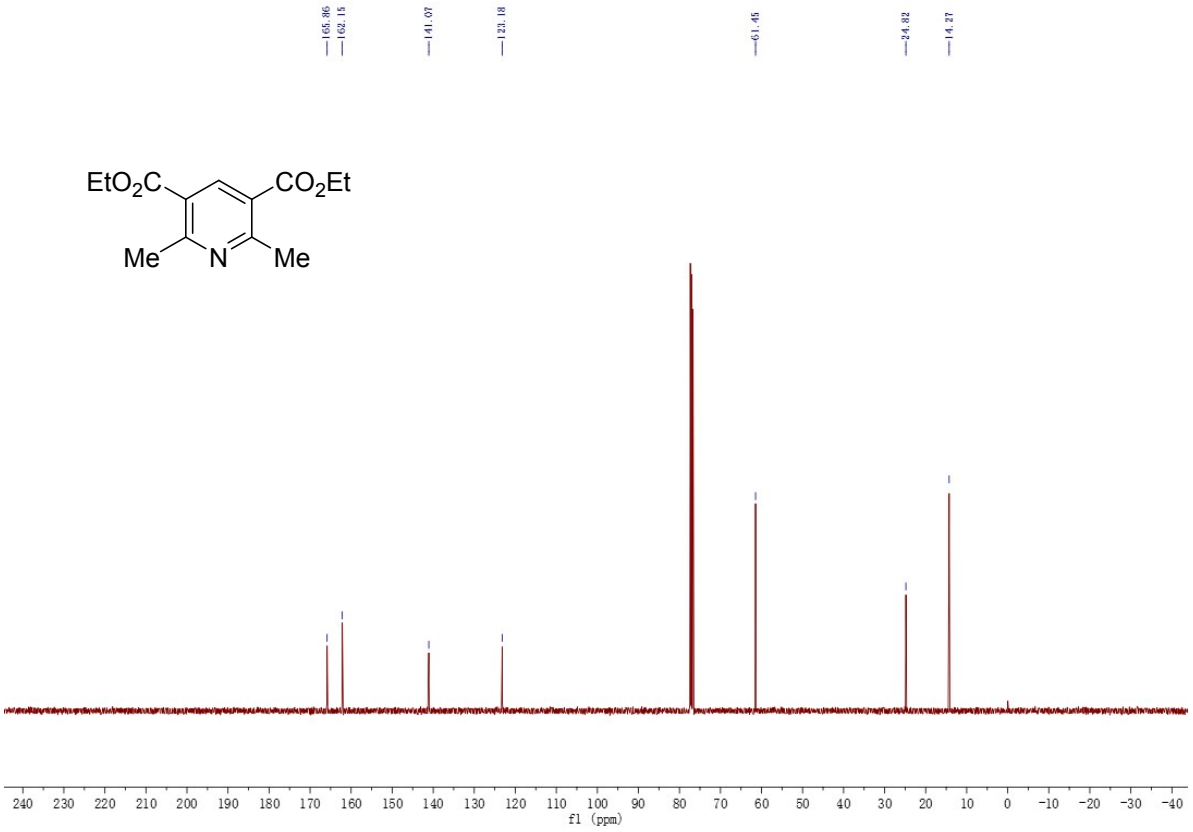
165.86
162.15
141.07
123.18
61.45
24.82
14.27
EtO2C
CO2Et
Me
N
Me
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)