Supporting Information

Difluorocarbene-based Cyanodifluoromethylation of Alkenes Induced by a Dual-Functional Cu-catalyst

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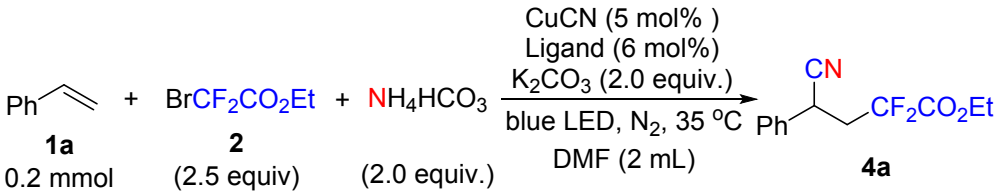
1. General Information

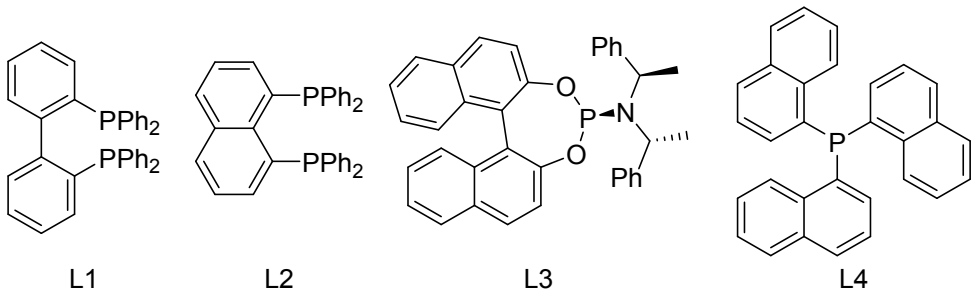
^{1}H, ^{13}C and ^{19}F NMR spectra were detected on a 500 MHz, 400 MHz or 300 MHz NMR spectrometer. Data for ^{1}H NMR, ^{13}C NMR and ^{19}F NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, coupling constant (s)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

2. Screening of Ligand



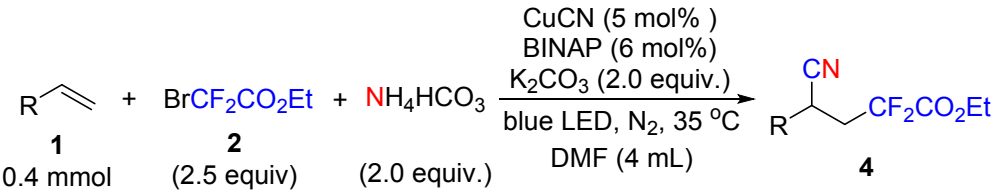
Entry	Ligand	Yield (%)[b]
1	BINAP	85
2	L1	25
3	L2	60
4	L3	25
5	L4	0
6[c]	(*S*)-BINAP	65[d]

[a]Reaction conditions: Substrate **1a** (0.2 mmol), $BrCF_2CO_2Et$ (2.5 equiv), NH_4HCO_3 (2 equiv), CuCN (5 mmol%), BINAP (6 mmol%), K_3PO_4 (2 equiv)，DG (2.5 equiv) and H_2O (3 equivl) in DMF (2 mL) irradiated with blue LEDs at 35 °C under a N_2 atmosphere for 12 h; [b]The yields were determined by ^{19}F NMR spectroscopy with 1-fluoronaphthalene as the internal standard; [c](*S*)-BINAP and CuCN were stirred in 1mL DMF under N_2 atmosphere for 30 min, then add other reagent; [d]No enantioselectivity.



L1 L2 L3 L4

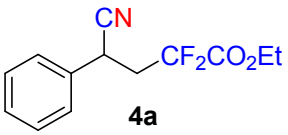
3. General Procedures for Cyanodifluoromethylation of Alkenes



1 0.4 mmol | **2** (2.5 equiv) | (2.0 equiv.) | **4**

Into a 15 mL Schlenk tube were added CuCN (1.8 mg, 0.02 mmol, 5 mol %), BINAP (14.9 mg, 0.024 mmol, 6 mol %), NH_4HCO_3 (63.2 mg, 0.8 mmol, 2 equiv.), K_3PO_4 (169.8 mg, 0.8 mmol, 2 equiv.) and DMF (4 mL) under a N_2 atmosphere. Then substrate **1** (0.4 mmol, 1.0 equiv.), $BrCF_2CO_2Et$ (203.0 mg, 1.0 mmol, 2.5 equiv.), DG (134.2 mg, 1.0 mmol, 2.5 equiv.) and H_2O (21.6 mg, 1.2 mmol, 3 equiv.) were added. The resulting mixture was stirred at 35 °C under the irradiation of 11.5 W blue LEDs for 12 h under a N_2 atmosphere. When the reaction was completed, as monitored by ^{19}F NMR spectroscopy, the crude reaction mixture was diluted with EA (20 mL). The solution was washed with water (3×20 mL) and brine (20 mL), and then dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was subjected to flash column chromatography to give the final product **4**.

Ethyl 4-cyano-2,2-difluoro-4-phenylbutanoate (4a)

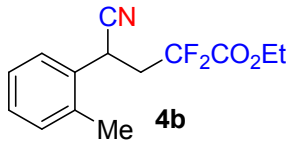


4a

80.3 mg, 79% yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.32 (m, 5H), 4.34 – 4.19 (m, 2H), 4.12 (dd, *J* = 9.3, 5.0 Hz, 1H), 2.84 (ddd, *J* = 30.7, 15.3, 9.4 Hz, 1H), 2.59 (ddd, *J* = 31.0, 15.2, 5.0 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.89 (dt, *J* = 268.5, 15.5 Hz, 1F), -105.62 (dt, *J* = 268.5, 15.4 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.0 (t, *J* = 31.8 Hz), 134.2 (s), 129.6 (s),

128.9 (s), 127.5 (s), 119.3 (s), 114.0 (t, J = 252.9 Hz), 63.6 (s), 40.3 (t, J = 23.9 Hz), 30.8 (t, J = 4.8 Hz), 13.9 (s); **HRMS (EI)**: Calcd. For $C_{13}H_{13}F_2NO_2$ ($[M]^+$): 253.0909; Found: 253.0907; **IR (KBr)**: 2954, 2924, 2852, 2360, 2246, 1738, 1456, 1376, 1216, 1092, 748, 697 cm^{-1}.

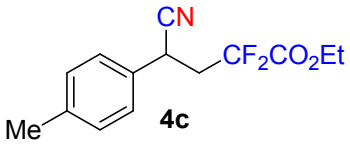
Ethyl 4-cyano-2,2-difluoro-4-(o-tolyl)butanoate (4b)



4b

43.3 mg, 40 % yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 1H), 7.28 – 7.22 (s, 2H), 7.22 – 7.17 (m, 1H), 4.31 – 4.21 (m, 3H), 2.80 (ddd, J = 30.5, 15.1, 10.0 Hz, 1H), 2.48 (ddd, J = 31.3, 15.0, 4.5 Hz, 1H), 2.36 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -105.19 (dt, J = 267.3, 15.5 Hz, 1F), -105.96 (dt, J = 267.7, 15.4 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.0 (t, J = 31.8 Hz), 135.2 (s), 132.6 (s), 131.5 (s), 129.0 (s), 127.7 (s), 127.3 (s), 119.5 (s), 114.0 (t, J = 252.7 Hz), 63.7 (s), 39.1 (t, J = 24.0 Hz), 27.6 (t, J = 4.8 Hz), 19.1 (s), 14.0 (s); **HRMS (EI)**: Calcd. For $C_{14}H_{15}F_2NO_2$ ($[M]^+$): 267.1065; Found: 267.1056; **IR (KBr)**: 2985, 2916, 2849, 2357, 2242, 1769, 1490, 1375, 1218, 1194, 1086, 913, 747 cm^{-1}.

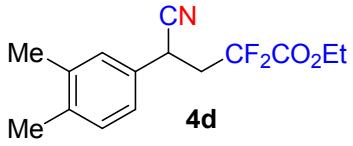
Ethyl 4-cyano-2,2-difluoro-4-(p-tolyl)butanoate (4c) [1]



4c

75.1 mg, 70 % yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, J = 8.2 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H), 4.31 – 4.18 (m, 2H), 4.06 (dd, J = 9.3, 5.1 Hz, 1H), 2.80 (ddd, J = 30.6, 15.3, 9.4 Hz, 1H), 2.55 (ddd, J = 30.7, 15.3, 5.0 Hz, 1H), 2.34 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.92 (dt, J = 268.5, 15.8 Hz, 1F), -105.62 (dt, J = 268.1, 15.4 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.0 (t, J = 31.9 Hz), 138.9 (s), 131.2 (s), 130.2 (s), 127.3 (s), 119.4 (s), 114.0 (t, J = 252.7 Hz), 63.6 (s), 40.3 (t, J = 23.8 Hz), 30.5 (t, J = 4.8 Hz), 21.2 (s), 13.9 (s); **HRMS (EI)**: Calcd. For $C_{14}H_{15}F_2NO_2$ ($[M]^+$): 267.1065; Found: 267.1059; **IR (KBr)**: 2987, 2942 ,2360, 2246, 1770, 1514, 1434, 1223, 1197, 1092, 816 cm^{-1}.

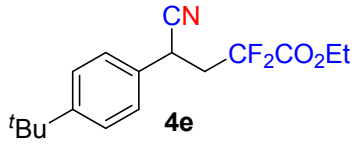
Ethyl 4-cyano-4-(3,4-dimethylphenyl)-2,2-difluorobutanoate (4d)



4d

64.4 mg, 57 % yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 (s, 1H), 7.09 (d, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 4.33 – 4.22 (m, 3H), 2.81 (ddd, *J* = 31.2, 14.9, 9.9 Hz, 1H), 2.47 (dtd, *J* = 17.0, 14.8, 4.3 Hz, 1H), 2.34 (s, 3H), 2.32 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -105.18 (ddd, *J* = 267.0, 16.0, 14.9 Hz, 1F), -106.00 (ddd, *J* = 260.57, 16.7, 14.7 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.1 (t, *J* = 31.9 Hz), 137.0 (s), 132.3 (s), 131.9 (s), 131.4 (s), 129.7 (s), 128.3 (s), 119.7 (s), 114.1 (t, *J* = 252.6 Hz), 63.7 (s), 39.2 (t, *J* = 24.0 Hz), 27.5 (t, *J* = 4.7 Hz), 21.0 (s), 18.6 (s), 14.0 (s); **HRMS (EI)**: Calcd. For $C_{15}H_{17}F_2NO_2$ ($[M]^+$): 281.1222; Found: 281.1215; **IR (KBr)**: 2985, 2928, 2874, 2357, 2245, 1770, 1505, 1376, 1222, 1194,1089, 817 cm^{-1}.

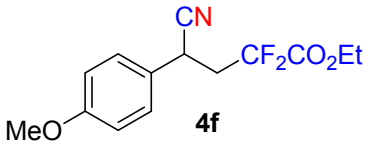
Ethyl 4-(4-(tert-butyl)phenyl)-4-cyano-2,2-difluorobutanoate (4e) [2]



4e

53.8 mg, 43 % yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2 H), 4.31 – 4.17 (m, 2H), 4.09 (dd, *J* = 9.3, 5.1 Hz, 1H), 2.91 – 2.75 (m, 1H), 2.60 (dtd, *J* = 19.9, 14.8, 5.1 Hz, 1H), 1.34 – 1.28 (m, 12H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.82 (ddd, *J* = 267.0**,** 16.5, 14.6 Hz, 1F), -105.69 (dt, *J* = 270.7, 15.0 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.0 (t, *J* = 31.9 Hz), 152.1 (s), 131.1 (s), 127.2 (s), 126.4 (s), 119.4 (s), 114.0 (t, *J* = 252.6 Hz), 63.5 (s), 40.2 (t, *J* = 23.9 Hz), 34.7 (s), 31.3 (s), 30.3 (t, *J* = 4.9 Hz), 13.9 (s); **HRMS (EI)**: Calcd. For $C_{17}H_{21}F_2NO_2$ ($[M]^+$): 309.1535; Found: 309.1528; **IR (KBr)**: 2968, 2871, 2246, 1760, 1513, 1310, 1217, 1092, 834 cm^{-1}.

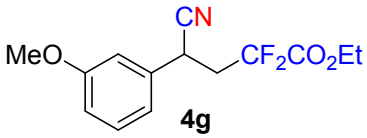
Ethyl 4-cyano-2,2-difluoro-4-(4-methoxyphenyl)butanoate (4f)



4f

78.7 mg, 69 % yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 4.29 – 4.16 (m, 2H), 4.04 (dd, *J* = 9.2, 5.3 Hz, 1H), 3.77 (s, 3H), 2.78 (ddd, *J* = 30.8, 14.9, 9.3 Hz, 1H), 2.54 (dtd, *J* = 20.1, 14.9, 5.3 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.86 (dt, *J* = 267.0, 15.7 Hz, 1F), -105.67 (dt, *J* = 267.0, 15.5 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.9 (t, *J* = 31.9 Hz), 159.9 (s), 128.6 (s), 126.0 (s), 119.5 (s), 114.8 (s), 114.0 (t, *J* = 252.6 Hz), 63.5 (s), 55.4 (s), 40.2 (t, *J* = 23.7 Hz), 30.0 (t, *J* = 4.8 Hz), 13.8 (s); **HRMS (EI)**: Calcd. For $C_{14}H_{15}F_2NO_3$ ($[M]^+$): 283.1015; Found: 283.1009; **IR (KBr)**: 2969, 2841, 2245, 1748, 1514, 1217, 1091, 832 cm^{-1}.

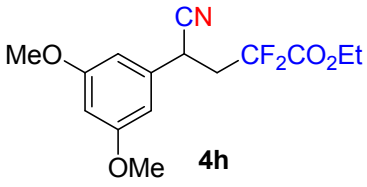
Ethyl 4-cyano-2,2-difluoro-4-(3-methoxyphenyl)butanoate (4g)



4g

50.2 mg, 44 % yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.88 – 6.83 (m, 2H), 4.31 – 4.18 (m, 2H), 4.06 (dd, *J* = 9.4, 4.9 Hz, 1H), 3.79 (s, 3H), 2.80 (ddd, *J* = 30.9, 15.2, 9.5 Hz, 1H), 2.56 (ddd, *J* = 31.1, 15.2, 4.9 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.90 (dt, *J* = 267.0, 15.6 Hz, 1F), -105.64 (dt, *J* = 271.0, 15.5 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.9 (t, *J* = 31.9 Hz), 160.3 (s), 135.6 (s), 130.6 (s), 119.5 (s), 119.2 (s), 114.2 (s), 113.9 (t, *J* = 252.7 Hz), 113.2 (s), 63.6 (s), 55.4 (s), 40.1 (t, *J* = 23.7 Hz), 30.7 (t, *J* = 4.7 Hz), 13.8 (s); **HRMS (EI)**: Calcd. For $C_{14}H_{15}F_2NO_3$ ($[M]^+$): 283.1015; Found: 283.1010; **IR (KBr)**: 2944, 2841, 2357, 2251, 1770, 1470, 1088, 778, 696 cm^{-1}.

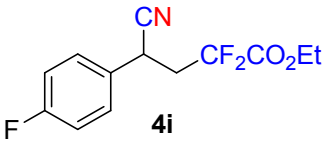
Ethyl 4-cyano-4-(3,5-dimethoxyphenyl)-2,2-difluorobutanoate (4h)



4h

52.7 mg, 42 % yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.48 – 6.46 (m, 1H), 6.43 – 6.40 (m, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 4.02 (dd, *J* = 9.4, 4.6 Hz, 1H), 3.79 (s, 6H), 2.81 (ddd, *J* = 24.5, 15.5, 10.2 Hz, 1H), 2.57 (ddd, *J* = 19.9, 15.6, 4.7 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -105.95 (dt, *J* = 268.5, 15.5 Hz, 1F), -105.68 (dt, *J* = 259.1, 15.5Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.0 (t, *J* = 31.9 Hz), 161.6 (s), 136.3 (s), 119.1 (s), 113.9 (t, *J* = 252.8 Hz), 105.5 (s), 100.5 (s), 63.6 (s), 55.6 (s), 40.2 (t, *J* = 24.0 Hz), 30.9 (t, *J* = 4.8 Hz), 13.9 (s); **HRMS (EI)**: Calcd. For $C_{15}H_{17}F_2NO_4$ ([M]$^+$): 313.1120; Found: 313.1111; **IR (KBr)**: 2943, 2846, 2359, 2247, 1770, 1092, 789, 850 cm^{-1}.

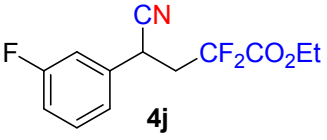
Ethyl 4-cyano-2,2-difluoro-4-(4-fluorophenyl)butanoate (4i)



4i

69.1 mg, 64 % yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.10 (t, *J* = 8.5 Hz, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.12 (dd, *J* = 8.9, 5.3 Hz, 1H), 2.83 (ddd, *J* = 30.7, 15.3, 9.2 Hz, 1H), 2.57 (ddd, *J* = 30.7, 15.3, 5.2 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -105.30 (t, *J* = 15.4 Hz, 2F), -112.34 – -112.47 (m, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.9 (t, *J* = 31.8 Hz), 162.9 (d, *J* = 248.9 Hz), 130.1 (d, *J* = 3.3 Hz), 129.4 (d, *J* = 8.5 Hz), 119.1 (s), 116.6 (d, *J* = 22.0 Hz), 113.9 (t, *J* = 253.1 Hz), 63.7 (s), 40.3 (t, *J* = 23.6 Hz), 30.2 (t, *J* = 4.7 Hz), 14.0 (s); **HRMS (EI)**: Calcd. For $C_{13}H_{12}F_3NO_2$ ([M]$^+$): 271.0815; Found: 271.0824; **IR (KBr)**: 2991, 2970, 2944, 2370, 2247, 1754, 1511, 1375, 1217, 1091, 837 cm^{-1}.

Ethyl 4-cyano-2,2-difluoro-4-(3-fluorophenyl)butanoate (4j)

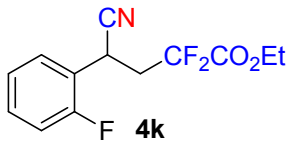


4j

63.7 mg, 59 % yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (td, *J* = 7.9, 6.0 Hz, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.13 – 7.04 (m, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 4.13 (dd, *J* = 9.3, 5.1 Hz, 1H), 2.84 (qd, *J* = 15.4, 9.3 Hz, 1H), 2.59 (qd, *J* = 15.3, 5.0 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -105.26 (t, *J* = 15.6

Hz, 2F), -110.69 (td, J = 8.8, 5.8 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.2 (d, J = 248.7 Hz), 162.9 (t, J = 31.8 Hz), 136.5 (d, J = 7.5 Hz), 131.3 (d, J = 8.3 Hz), 123.2 (d, J = 3.1 Hz), 118.8 (s), 116.1 (d, J = 21.0 Hz), 114.8 (d, J = 23.0 Hz), 113.8 (t, J = 276.0 Hz), 63.8 (s), 40.1 (t, J = 23.9 Hz), 30.6 (td, J = 4.7, 1.9 Hz), 14.0 (s); **HRMS (EI)**: Calcd. For $C_{13}H_{12}F_3NO_2$ ($[M]^+$): 271.0815; Found: 271.0817; **IR (KBr)**: 3002, 2970, 2944, 2370, 2247, 1738, 1435, 1365, 1228, 1092, 744 cm^{-1}.

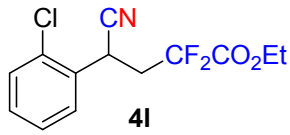
Ethyl 4-cyano-2,2-difluoro-4-(2-fluorophenyl)butanoate (4k)



4k

33.5 mg, 31 % yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (t, J = 7.6 Hz, 1H), 7.38 (dd, J = 14.1, 6.9 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.16 – 7.09 (m, 1H), 4.40 (dd, J = 9.0, 5.1 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 2.85 (ddd, J = 30.7, 15.3, 9.2 Hz, 1H), 2.62 (ddd, J = 30.8, 15.5, 5.0 Hz, 1H), 1.34 (t, J = 7.2 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -105.55 (td, J = 15.5, 3.2 Hz, 2F), -117.25 – -117.33 (m, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.9 (t, J = 31.8 Hz), 159.8 (d, J = 248.8 Hz), 131.1 (d, J = 8.3 Hz), 129.3 (d, J = 2.7 Hz), 125.2 (d, J = 3.7 Hz), 121.4 (d, J = 13.7 Hz), 118.3 (s), 116.3 (d, J = 20.9 Hz), 113.9 (t, J = 253.1 Hz), 63.7 (s), 38.4 (t, J = 24.0 Hz), 25.2 (dd, J = 8.7, 4.9 Hz), 13.9 (s); **HRMS (EI)**: Calcd. For $C_{13}H_{12}F_3NO_2$ ($[M]^+$): 271.0815; Found: 271.0811; **IR (KBr)**: 2987, 2970, 2361, 2248, 1769, 1590, 1494, 1231, 1088, 760 cm^{-1}.

Ethyl 4-(2-chlorophenyl)-4-cyano-2,2-difluorobutanoate (4l)

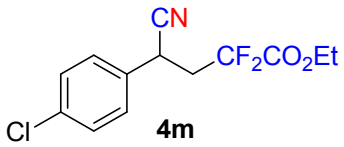


4l

51.9 mg, 45 % yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 1H), 7.44 (dd, J = 7.3, 1.9 Hz, 1H), 7.40 – 7.29 (m, 2H), 4.61 (dd, J = 10.0, 4.0 Hz, 1H), 4.32 (q, J = 7.2 Hz, 2H), 2.87 – 2.70 (m, 1H), 2.68 – 2.53 (m, 1H), 1.36 (t, J = 7.2 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.94 (ddd, J = 267.0, 17.0, 13.3 Hz, 1F), -105.92 (ddd, J = 267.0, 17.6, 13.8 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ

163.0 (t, J = 31.8 Hz), 132.8 (s), 131.9 (s), 130.51 (s), 130.47 (s), 129.3 (s), 128.1 (s), 118.6 (s), 113.9 (t, J = 253.5 Hz), 63.7 (s), 38.3 (t, J = 24.0 Hz), 28.5 (t, J = 4.7 Hz), 14.0 (s); **HRMS (EI)**: Calcd. For $C_{13}H_{12}{}^{35}ClF_2NO_2$ ([M]$^+$): 287.0519; Found: 287.0529; **IR (KBr)**: 2987, 2941, 2874, 2360, 2248, 1760, 1376, 1217, 1092, 756 cm^{-1}.

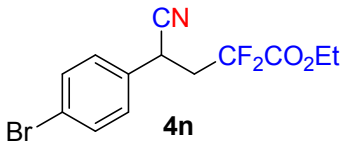
Ethyl 4-(4-chlorophenyl)-4-cyano-2,2-difluorobutanoate (4m)



4m

94.8 mg, 82 % yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.6 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 4.35 – 4.23 (m, 2H), 4.11 (dd, J = 9.1, 5.2 Hz, 1H), 2.82 (qd, J = 15.3, 9.2 Hz, 1H), 2.56 (qd, J = 15.4, 5.2 Hz, 1H), 1.34 (t, J = 7.2 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -105.22 (t, J = 15.4 Hz, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.9 (t, J = 31.8 Hz), 135.1 (s), 132.7 (s), 129.8 (s), 128.9 (s), 118.9 (s), 113.8 (t, J = 253.0 Hz), 63.8 (s), 40.1 (t, J = 23.9 Hz), 30.3 (t, J = 4.7 Hz), 13.9 (s); **HRMS (EI)**: Calcd. For $C_{13}H_{12}{}^{35}ClF_2NO_2$ ([M]$^+$): 287.0519; Found: 287.0516; **IR (KBr)**: 2988, 2942, 2248, 1770, 1494, 1223, 1197, 1095, 829 cm^{-1}.

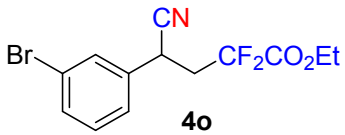
Ethyl 4-(4-bromophenyl)-4-cyano-2,2-difluorobutanoate (4n)



4n

82.9 mg, 62 % yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 6.4 Hz, 2H), 4.27 (q, J = 7.1 Hz, 2H), 4.08 (dd, J = 8.9, 5.3 Hz, 1H), 2.81 (qd, J = 15.4, 9.3 Hz, 1H), 2.54 (ddd, J = 30.7, 15.2, 5.1 Hz, 1H), 1.33 (t, J = 7.1 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -105.22 (t, J = 15.4 Hz, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.9 (t, J = 31.8 Hz), 133.3 (s), 132.8 (s), 129.2 (s), 123.2 (s), 118.8 (s), 113.8 (t, J = 253.1 Hz), 63.8 (s), 40.1 (t, J = 23.8 Hz), 30.4 (t, J = 4.7 Hz), 14.0 (s); **HRMS (EI)**: Calcd. For $C_{13}H_{12}{}^{79}BrF_2NO_2$ ([M]$^+$): 331.0014; Found: 331.0006; **IR (KBr)**: 2928, 2355, 2255, 1766, 1489, 1195, 1086, 822 cm^{-1}.

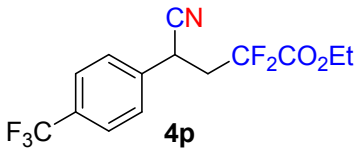
Ethyl 4-(3-bromophenyl)-4-cyano-2,2-difluorobutanoate (4o)



4o

86.6 mg, 65 % yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 2H), 7.35 – 7.27 (m, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 4.10 (dd, *J* = 9.2, 5.2 Hz, 1H), 2.84 (qd, *J* = 15.2, 9.3 Hz, 1H), 2.58 (qd, *J* = 15.4, 5.1 Hz, 1H), 1.36 (t, *J* = 7.2 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -105.23 (t, *J* = 15.4 Hz, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.9 (t, *J* = 31.8 Hz), 136.3 (s), 132.3 (s), 131.1 (s), 130.6 (s), 126.2 (s), 123.5 (s), 118.7 (s), 113.8 (t, *J* = 253.2 Hz), 63.8 (s), 40.1 (t, *J* = 24.0 Hz), 30.5 (t, *J* = 4.8 Hz), 14.0 (s); **HRMS (EI)**: Calcd. For $C_{13}H_{12}{}^{79}BrF_2NO_2$ ([M]$^+$): 331.0014; Found: 331.0024; **IR (KBr)**: 2987, 2925, 2850, 2326, 2247, 1766, 1475, 1195, 1088, 785, 693 cm^{-1}.

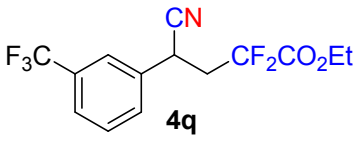
Ethyl 4-cyano-2,2-difluoro-4-(4-(trifluoromethyl)phenyl)butanoate（4p）



4p

87.4 mg, 68 % yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 4.29 (q, *J* = 7.2 Hz, 2H), 4.21 (dd, *J* = 9.1, 5.1 Hz, 1H), 2.86 (ddd, *J* = 30.9, 15.0, 9.2 Hz, 1H), 2.60 (ddd, *J* = 31.1, 15.0, 5.2 Hz, 1H), 1.34 (t, *J* = 7.2 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.92 (s, 3F), -105.20 (td, *J* = 15.4, 5.7 Hz, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.8 (t, *J* = 31.7 Hz), 138.2 (s), 131.4 (q, *J* = 32.9 Hz), 128.1 (s), 126.6 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.3 Hz), 118.6 (s), 113.8 (t, *J* = 253.4 Hz), 63.8 (s), 40.0 (t, *J* = 23.9 Hz), 30.7 (t, *J* = 4.6 Hz), 13.9 (s); **HRMS (EI)**: Calcd. For $C_{14}H_{12}F_5NO_2$ ([M]$^+$): 321.0783; Found: 321.0781; **IR (KBr)**: 2991, 2970, 2945, 2361, 2249, 1766, 1620, 1328, 1092, 842 cm^{-1}.

Ethyl 4-cyano-2,2-difluoro-4-(3-(trifluoromethyl)phenyl)butanoate (4q)

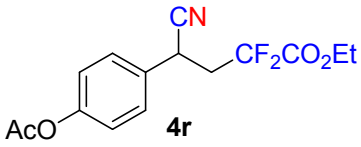


4q

63.1 mg, 49 % yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.54 (m, 4H), 4.30 (q, *J* = 7.1 Hz, 2H), 4.22 (dd, *J* = 9.1, 5.2 Hz, 1H), 2.88 (qd, *J* = 15.3, 9.3

Hz, 1H), 2.61 (qd, *J* = 15.3, 5.1 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.83 (s, 3F), -105.17 (td, *J* = 15.6, 2.1 Hz, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.8 (t, *J* = 31.7 Hz), 135.3 (s), 132.1 (q, *J* = 32.8 Hz), 131.0 (s), 130.3 (s), 126.0 (q, *J* = 3.6 Hz), 124.4 (q, *J* = 3.8 Hz), 123.6 (q, *J* = 272.5 Hz), 118.6 (s), 113.8 (t, *J* = 253.3 Hz), 63.8 (s), 40.0 (t, *J* = 23.9 Hz), 30.7 (t, *J* = 4.7 Hz), 13.9 (s); **HRMS (EI)**: Calcd. For $C_{14}H_{12}F_5NO_2$ ($[M]^+$): 321.0783; Found: 321.0795; **IR (KBr)**: 2990, 2945, 2249, 1770, 1599, 1494, 1330, 1170, 779, 702 cm^{-1}.

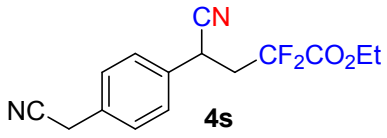
Ethyl 4-(4-acetoxyphenyl)-4-cyano-2,2-difluorobutanoate（4r）



4r

68.0 mg, 55% yield; orange oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.6 Hz, 2H), 7.14 (d, *J* = 8.6 Hz, 2H), 4.34 – 4.21 (m, 2H), 4.13 (dd, *J* = 9.3, 5.1 Hz, 1H), 2.83 (ddd, *J* = 30.8, 14.8, 9.3 Hz, 1H), 2.59 (dtd, *J* = 19.9, 14.8, 5.1 Hz, 1H), 2.31 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$)) δ -104.87 (dt, *J* = 267.0, 15.3 Hz, 1F), -105.68 (dt, *J* = 270.7, 15.3 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.3 (s), 162.9 (t, *J* = 31.8 Hz), 151.1 (s), 131.7 (s), 128.7 (s), 122.8 (s), 119.1 (s), 113.9 (t, *J* = 253.0 Hz), 63.7 (s), 40.3 (t, *J* = 23.9 Hz), 30.4 (t, *J* = 4.9 Hz), 21.2 (s), 14.0 (s); **HRMS (EI)**: Calcd. For $C_{15}H_{15}F_2NO_4$ ($[M]^+$): 311.0964; Found: 311.0956; **IR (KBr)**: 3001, 2970, 2943, 2366, 2247, 1739, 1366, 1217, 1092, 910 cm^{-1}.

Ethyl 4-cyano-4-(4-(cyanomethyl)phenyl)-2,2-difluorobutanoate（4s）

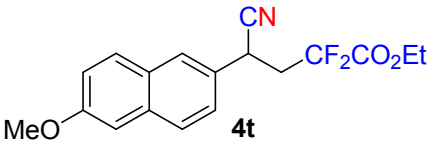


4s

69.2 mg, 59 % yield; white solid; m.p.: 76.6 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 4H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.14 (dd, *J* = 9.2, 5.1 Hz, 1H), 3.77 (s, 2H), 2.83 (ddd, *J* = 30.7, 15.3, 9.3 Hz, 1H), 2.57 (ddd, *J* = 30.9, 15.3, 5.1 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.86 (dt, *J* = 274.5, 15.3 Hz, 1F), -105.59 (dt, *J* = 270.1, 15.5 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.9 (t, *J* = 31.8 Hz), 134.4 (s), 131.0 (s), 129.2 (s), 128.3 (s), 118.9 (s), 117.4 (s), 113.9 (t, *J*

= 253.2 Hz), 63.7 (s), 40.1 (t, *J* = 23.8 Hz), 30.5 (t, J = 4.7 Hz), 23.4 (s), 13.9 (s); **HRMS (EI)**: Calcd. For $C_{15}H_{14}F_2N_2O_2$ ($[M]^+$): 292.1018; Found: 292.1025; **IR (KBr)**: 2995, 2970, 2944, 2366, 2249, 1739, 1365, 1217, 1092, 850 cm^{-1}.

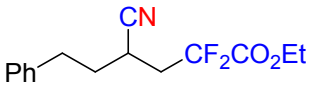
Ethyl 4-cyano-2,2-difluoro-4-(6-methoxynaphthalen-2-yl)butanoate (4t)



4t

56.5 mg, 42 % yield; red solid; m.p.: 58.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.70 (m, 3H), 7.38 (d, *J* = 8.5 Hz, 1H), 7.20 (d, *J* = 8.9 Hz, 1H), 7.13 (s, 1H), 4.29 – 4.13 (m, 3H), 3.93 (s, 3H), 2.90 (ddd, *J* = 30.5, 15.2, 9.3 Hz, 1H), 2.68 (ddd, *J* = 30.5, 15.2, 5.1 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ-104.76 (dt, *J* = 270.7, 15.0 Hz, 1F), -105.60 (dt, *J* = 267.0, 15.4 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.0 (t, *J* = 31.8 Hz), 158.6 (s), 134.5 (s), 129.5 (s), 128.9 (s), 128.8 (s), 128.4 (s), 126.6 (s), 125.1 (s), 120.0 (s), 119.4 (s), 114.0 (t, *J* = 252.7 Hz), 105.8 (s), 63.6 (s), 55.5 (s), 40.3 (t, *J* = 23.9 Hz), 30.9 (t, *J* = 4.8 Hz), 13.9 (s); **HRMS (EI)**: Calcd. For $C_{18}H_{17}F_2NO_3$ ($[M]^+$): 333.1171; Found: 333.1173; **IR (KBr)**: 2986, 2941, 2845, 2246, 1770, 1608, 1485, 1093, 854 cm^{-1}.

Ethyl 4-cyano-2,2-difluoro-6-phenylhexanoate (4u)

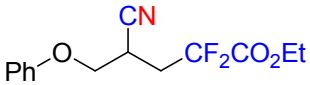


4u

44.7 mg, 40 % yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.3 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.91 (ddd, *J* = 13.3, 9.4, 4.9 Hz, 1H), 2.86 – 2.71 (m, 2H), 2.63 – 2.44 (m, 1H), 2.36 – 2.20 (m, 1H), 2.08 – 1.89 (m, 2H), 1.33 (t, *J* = 7.2 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.18 (ddd, *J* = 267.0, 18.9, 12.1 Hz, 1F), -105.91 (dddd, *J* = 267.0, 16.9, 13.9, 2.5 Hz. 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.1 (t, *J* = 32.0 Hz), 139.4 (s), 128.8 (s), 128.5 (s), 126.7 (s), 120.1 (s), 114.3 (t, *J* = 252.5 Hz), 63.6 (s), 36.8 (t, *J* = 23.9 Hz), 34.3 (s), 32.9 (s), 24.5 (t, *J* = 4.1 Hz), 13.9 (s); **HRMS (EI)**: Calcd. For $C_{15}H_{17}F_2NO_2$ ($[M]^+$): 281.1222; Found: 281.1228; **IR (KBr)**: 2940, 2867, 2366, 2366,

2243, 1767, 1603, 1374, 1098, 913, 744, 700 cm^{-1}.

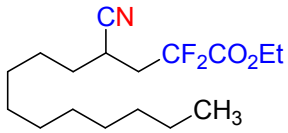
Ethyl 4-cyano-2,2-difluoro-5-phenoxypentanoate (4v)



4v

48.8 mg, 43 % yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.7 Hz, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 8.6 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 4.22 – 4.12 (m, 2H), 3.36 (td, *J* = 10.8, 5.4 Hz, 1H), 2.78 – 2.54 (m, 2H), 1.38 (t, *J* = 7.2 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.65 (ddd, *J* = 267.0, 18.7, 13.1 Hz, 1F), -105.74 (ddd, *J* = 267.0, 18.9, 14.1 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.1 (t, *J* = 31.9 Hz), 157.6 (s), 129.8 (s), 122.3 (s), 118.4 (s), 114.8 (s), 114.3 (t, *J* = 252.5 Hz), 66.8 (s), 63.8 (s), 34.0 (t, *J* = 24.1 Hz), 25.9 (t, *J* = 4.1 Hz), 14.0 (s); **HRMS (EI)**: Calcd. For $C_{14}H_{15}F_2NO_3$ ($[M]^+$): 283.1015; Found: 283.1011; **IR (KBr)**: 2969, 2928, 2850, 2362, 2250, 1752, 1599, 1375, 1217, 1053, 913, 748, 691 cm^{-1}.

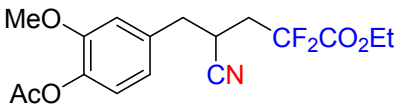
Ethyl 4-cyano-2,2-difluorotetradecanoate (4w)



4w

77.9 mg, 61 % yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.35 (q, *J* = 7.1 Hz, 2H), 2.91 – 2.78 (m, 1H), 2.60 – 2.42 (m, 1H), 2.33 – 2.17 (m, 1H), 1.74 – 1.60 (m, 2H), 1.60 – 1.50 (m, 1H), 1.50 – 1.40 (m, 1H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.33 – 1.17 (m, 14H), 0.87 (t, *J* = 6.7 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.38 (ddd, *J* = 263.2, 18.9, 12.0 Hz, 1F), -106.30 (ddd, *J* = 267.0, 19.4, 14.1 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.2 (t, *J* = 31.9 Hz), 120.5 (s), 114.4 (t, *J* = 252.5 Hz), 63.6 (s), 37.0 (t, *J* = 23.8 Hz), 32.8 (s), 32.0 (s), 29.62 (s), 29.56 (s), 29.4 (s), 29.0 (s), 26.8 (s), 25.0 (t, *J* = 5.0 Hz), 22.8 (s), 14.2 (s), 14.0 (s); **HRMS (EI)**: Calcd. For $C_{17}H_{29}F_2NO_2$ ($[M-H]^+$): 316.2083; Found: 316.2078; **IR (KBr)**: 2927, 2856, 2361, 2244, 1770, 1467, 1377, 1198, 1098 cm^{-1}.

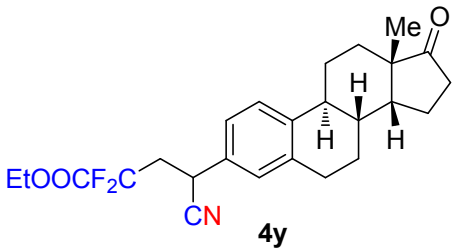
Ethyl 5-(4-acetoxy-3-methoxyphenyl)-4-cyano-2,2-difluoropentanoate (4x)



4x

69.5 mg, 50 % yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 8.0 Hz, 1H), 6.87 (s, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 3.19 – 3.08 (m, 1H), 2.97 (d, *J* = 7.0 Hz, 2H), 2.58 – 2.41 (m, 1H), 2.40 – 2.25 (m, 1H), 2.30 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.13 (ddd, *J* = 266.6, 18.9, 12.0 Hz, 1F), -105.32 -106.22 (m, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.1 (s), 163.1 (t, *J* = 31.8 Hz), 151.4 (s), 139.4 (s), 134.4 (s), 123.2 (s), 121.4 (s), 120.0 (s), 114.4 (t, *J* = 203.0 Hz), 113.3 (s), 63.7 (s), 56.0 (s), 38.3 (s), 36.1 (t, *J* = 23.8 Hz), 26.8 (t, *J* = 3.7 Hz), 20.7 (s), 13.9 (s); **HRMS (EI)**: Calcd. For $C_{17}H_{19}F_2NO_5$ ($[M]^+$): 355.1226; Found: 355.1218; **IR (KBr)**: 2985, 2941, 2245, 1606, 1512, 1467, 1371, 1124, 1095, 852 cm^{-1}.

Ethyl-4-cyano-2,2-difluoro-4-((8R,9S,13S,14R)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)butanoate (4y)



4y

83.7 mg, 49 % yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 7.09 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.04 (dd, *J* = 9.6, 4.7 Hz, 1H), 2.95 – 2.88 (m, 2H), 2.87 – 2.71 (m, 1H), 2.62 – 2.46 (m, 2H), 2.45 – 2.37 (m, 1H), 2.28 (t, *J* = 8.3 Hz, 1H), 2.15 (dd, *J* = 18.4, 9.3 Hz, 1H), 2.11 – 1.99 (m, 2H), 1.95 (dd, *J* = 11.1, 8.9 Hz, 1H), 1.68 – 1.39 (m, 6H), 1.33 (t, *J* = 7.1 Hz, 3H), 0.90 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -105.30 (t, *J* = 15.5 Hz, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 220.7 (s), 162.9 (t, *J* = 32.0 Hz), 140.6 (s), 137.9 (s), 131.6 (s), 127.9 (s), 126.5 (s), 124.7 (s), 119.4 (s), 113.9 (t, *J* = 252.5 Hz), 63.5 (s), 50.4 (s), 47.9 (s), 44.3 (s), 40.2 (t, *J* = 23.8 Hz), 38.0 (s), 35.8 (s), 31.5 (s), 30.34 – 30.10 (m),

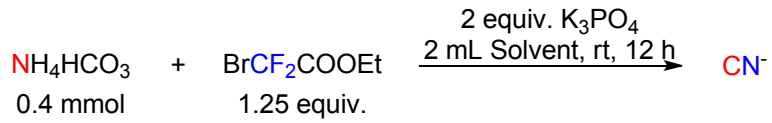
29.35 (s), 29.32 (s), 26.3 (s), 25.7 (s), 21.6 (s), 13.9 (s), 13.8 (s); **HRMS (EI)**: Calcd. For $C_{25}H_{29}F_2NO_3$ ([M]$^+$): 429.2110; Found: 429.2106; **IR (KBr)**: 2933, 2865,2358, 2345, 2244, 1770, 1738, 1500, 1375, 1192, 1088, 851, 732 cm^{-1}.

4. Preliminary Mechanistic Studies

4.1 Cyanide Detection Test with Picric Acid Paper

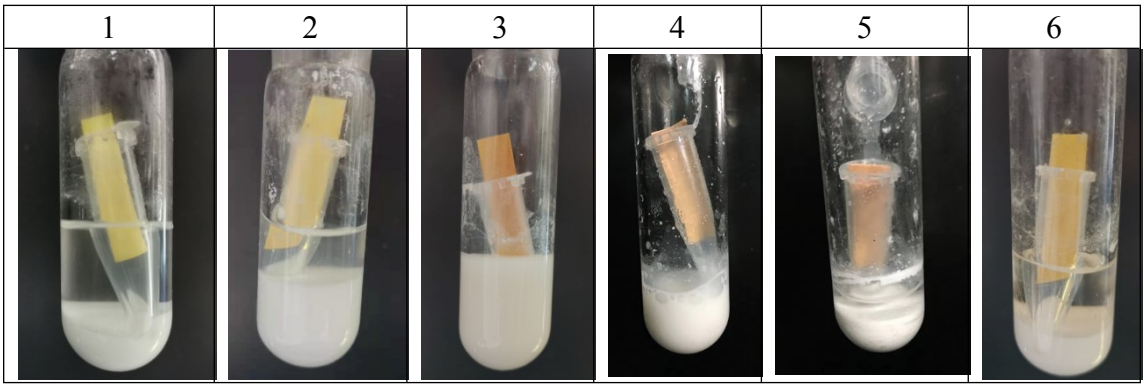
The cyanide detection tests with picric acid paper were performed according to previous procedures.[3] Picrate paper was prepared by wetting filter paper with a solution of sodium bicarbonate (5.0 g) and picric acid (0.5 g) in water (100 mL). After being dried, the paper was cut into strips and the strips were separately inserted into 2 mL vials.

The reaction mixture indicated in Table 2 in the main text was stirred at room temperature for 12 h in a 15 mL Schlenk tube under a N_2 atmosphere. The Schlenk tube was opened, tartrate acid (0.5 g) was added into the reaction mixture, and the vial containing the picric acid paper obtained above was inserted into the Schlenk tube. The vial was kept opened, and the Schlenk tube was sealed. The reaction mixture was stirred at 60 °C for 30 minutes. If CN^- anion was generated from the reaction mixture, the color of the test paper would turn to rose-red. If not, no change in the color would be observed. The Schlenk tubes containing the vials were shown as follows.



Entry	NH_4HCO_3	$BrCF_2COOEt$	Solvent	CN^- produce
1	√	×	DMF	-
2	×	√	DMF	-
3	√	√	DMF	+
4	√	√	DMAc	+
5	√	√	MeCN	+
6	√	√	DG	+

[a] "√" means the reagent was used; "×" means the reagent was not used; "+" means positive result; "–" means negative result.



Rose-red color indicating CN^- generation, no change in color indicating no CN^-.

4.2 The Exclusion of the Path Involving

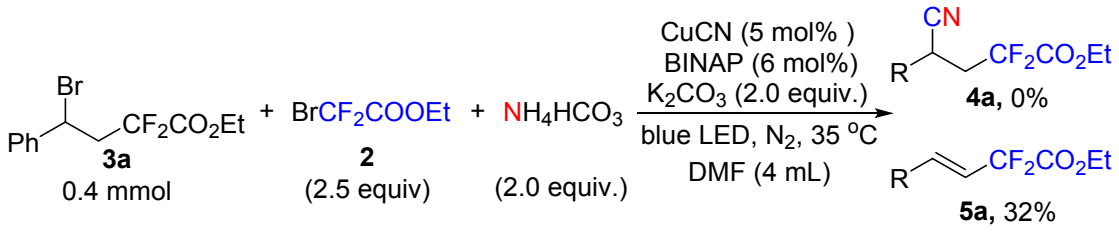
4.2.1 The Preparation of 3a

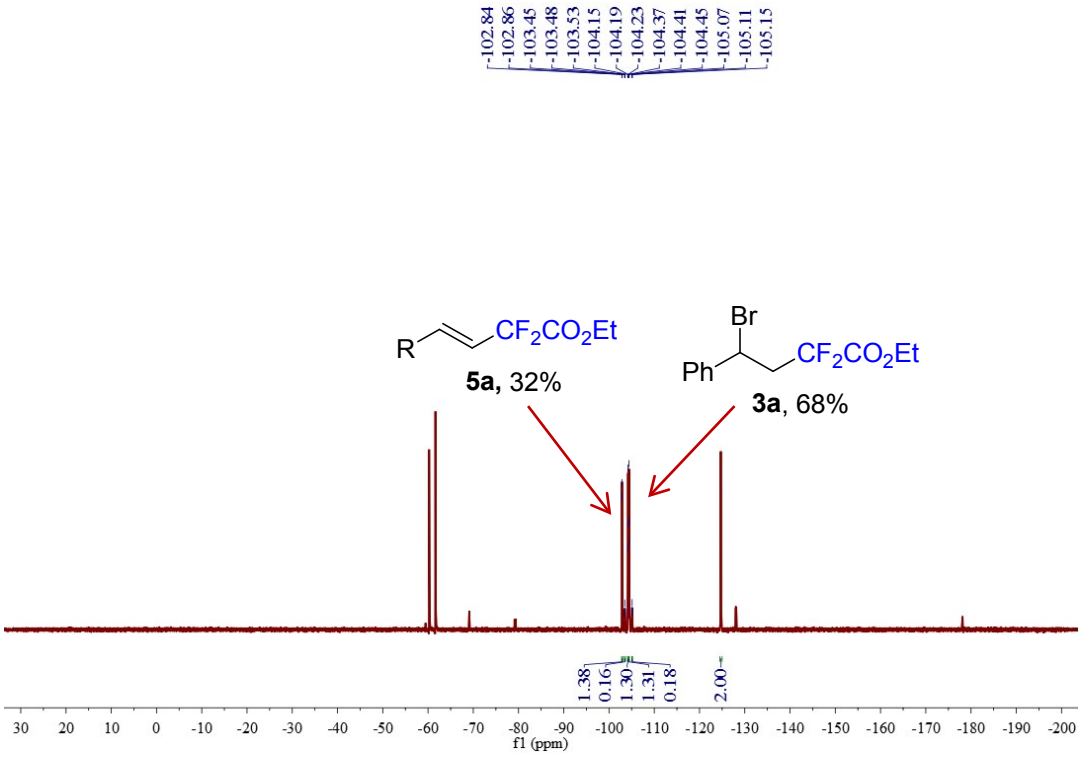
Into a 15 mL Schlenk tube were added CuCN (1.8 mg, 0.02 mmol, 5 mol %), binap (14.9 mg, 0.024 mmol, 6 mol %), NH_4Br (78.3 mg, 0.8 mmol, 2 equiv.) and DMF (4 mL) under a N_2 atmosphere. Then the alkene substrate **1a** (41.6 mg, 0.4 mmol, 1.0 equiv.) and $BrCF_2CO_2Et$ (203.0 mg, 1.0 mmol, 2.5 equiv.) were added. The resulting mixture was stirred at 35 °C and irradiated with blue LEDs for 12 h under a N_2 atmosphere. When the reaction was completed, as monitored by ^{19}F NMR spectroscopy, the crude reaction mixture was diluted with EA (20 mL). The solution was washed with water (3×20 mL) and brine (20 mL), and then dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was subjected to flash column chromatography (1%→2% ethyl acetate/petroleum ether) to give the final product **3a**.

104.1 mg, 85 % yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.39 – 7.28 (m, 3H), 5.18 (t, *J* = 7.3 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.27 – 3.04 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.93 (dt, *J* = 265.8, 14.7 Hz, 1F), -104.67 (dt, *J* = 265.8,14.7 Hz, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.2 (t, *J* = 32.1 Hz), 140.4 (s), 129.1 (s), 128.9 (s), 127.4 (s),

114.3 (t, J = 252.3 Hz), 63.2 (s), 44.57 (t, J = 24.0 Hz), 44.55 (t, J = 5.6 Hz), 13.8 (s); **HRMS (FI)**: Calcd. For $C_{12}H_{13}{}^{79}BrF_2O_2$ ([M]$^+$): 306.0062; Found: 306.0064; **IR (KBr)**: 2964, 1766, 1455, 1433, 1375, 1094, 1024, 798, 696 cm^{-1}.

4.2.2 The Conversion of 3a



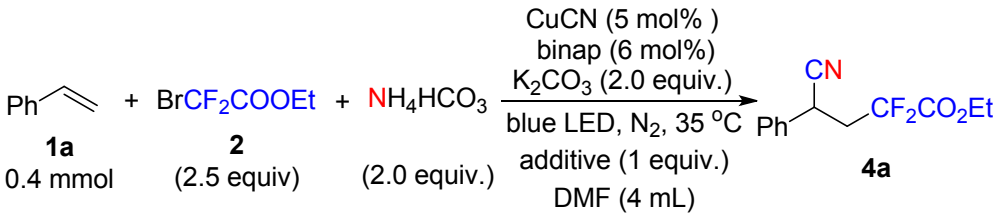


Into a 15 mL Schlenk tube were added CuCN (1.8 mg, 0.02 mmol, 5 mol %), BINAP (14.9 mg, 0.024 mmol, 6 mol %), NH_4HCO_3 (63.2 mg, 0.8 mmol, 2 equiv.), K_3PO_4 (169.8 mg, 0.8 mmol, 2 equiv.) and DMF (4 mL) under a N_2 atmosphere. Then substrate **3a** (0.4 mmol, 1.0 equiv.), $BrCF_2CO_2Et$ (203.0 mg, 1.0 mmol, 2.5 equiv.), DG (134.2 mg, 1.0 mmol, 2.5 equiv.) and H_2O (21.6 mg, 1.2 mmol, 3 equiv.) were added. The resulting mixture was stirred at 35 °C under the irradiation of 11.5 W blue LEDs for 12 h under a N_2 atmosphere. When the reaction was completed, as monitored by ^{19}F NMR spectroscopy, while 32 % of **3a** was converted to **5a**.The ^{19}F

NMR spectrum is shown as follows. Characterization data of 5a[4]: **^{19}F NMR** (376 MHz, DMF) δ -102.85 (dd, *J* = 11.2, 2.4 Hz, 2F); **MS** (**EI**, *m/z*, %): 226 (M^+, 13.0), 153 (100.0), 133 (82.0).

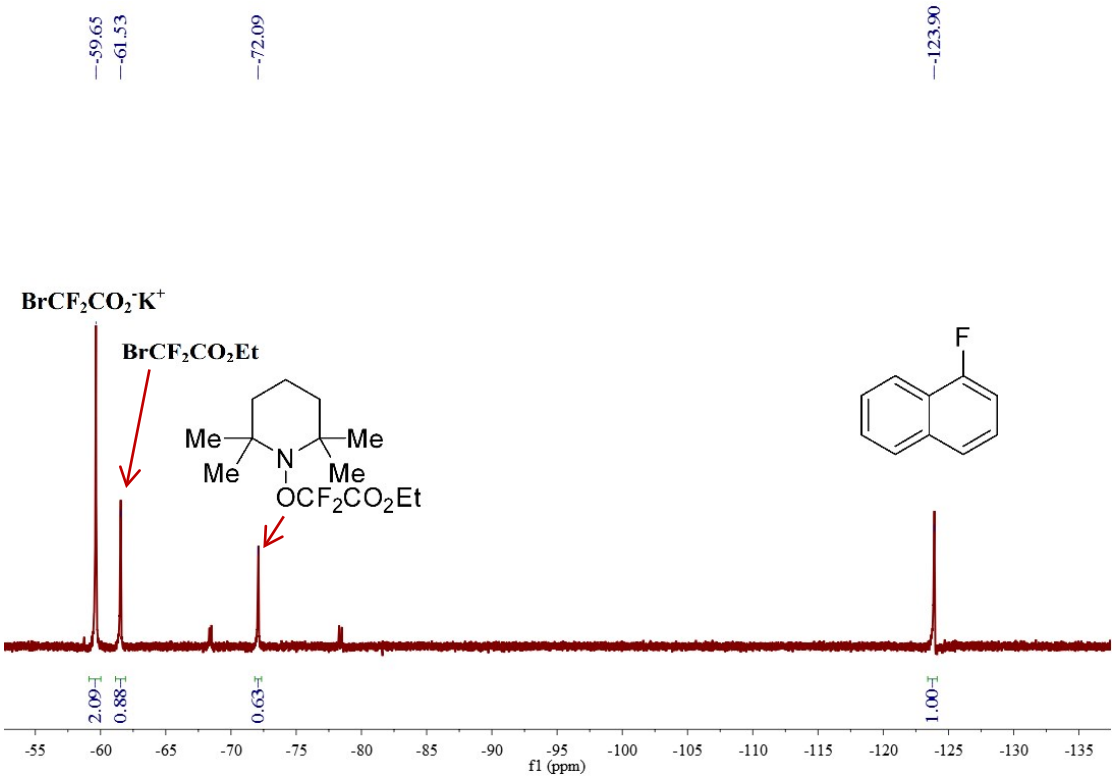
4.3 Radical Trapping Experiments

Into a 15 mL Schlenk tube were added CuCN (1.8 mg, 0.02 mmol, 5 mol %), BINAP (14.9 mg, 0.024 mmol, 6 mol %), NH_4HCO_3 (63.2 mg, 0.8 mmol, 2 equiv.), K_3PO_4 (169.8 mg, 0.8 mmol, 2 equiv.), a radical scavenger (0.4 mmol, 1.0 equiv.) and DMF (4 mL) under a N_2 atmosphere. Then alkene substrate **1a** (41.6 mg, 0.4 mmol, 1.0 equiv.), $BrCF_2CO_2Et$ (203.0 mg, 1.0 mmol, 2.5 equiv.), DG (134.2 mg, 1.0 mmol, 2.5 equiv.) and H_2O (21.6 mg, 1.2 mmol, 3 equiv.) were added. The resulting mixture was stirred at 35 °C and irradiated with blue LEDs for 12 h under a N_2 atmosphere. 1-Fluoronaphthalene (0.2 mmol), an internal standard, was added into the reaction mixture for the calculation of the yield of product **4a**.



Entry	additive	Yield(%)[a]
1	-	85
2	TEMPO	0
3	BHT	44
4	hydroquinone	trace
5	HOBT	22

In the case of TEMPO, ^{19}F NMR and GC-MS analysis of the reaction mixture revealed that TEMPO-CF_2CO_2Et was produced (16% yield determined by ^{19}F NMR spectroscopy). The ^{19}F NMR spectrum is shown as follows. Characterization data of TEMPO-CF_2CO_2Et [5]: **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.0 (s, 2F); **MS** (**EI**, *m/z*, %): 279 (M^+, 1.0), 264 (85.0), 109 (38.0), 69 (50.0), 58 (73.0), 56 (100.0).

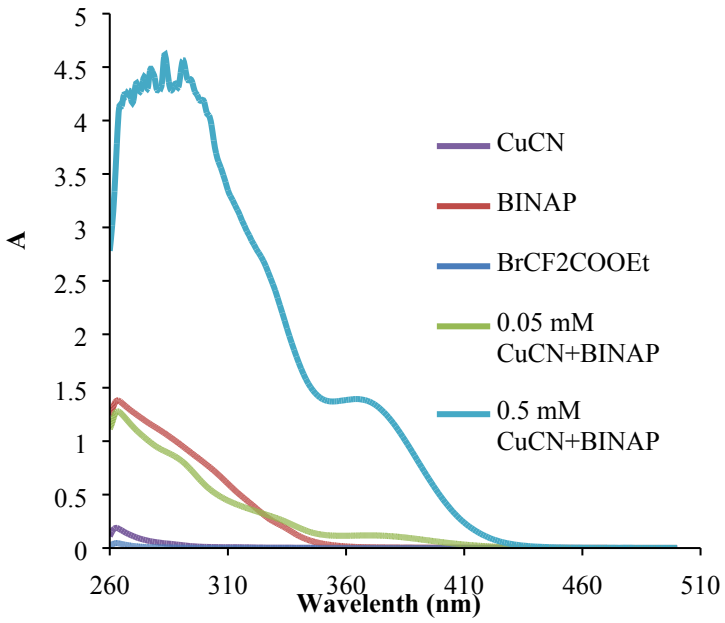


The ^{19}F NMR of TEMPO-CF_2CO_2Et

4.4 UV-Vis absorption experiment

UV-Vis absorption were recorded using UV-3600 UV-VIS-NIR spectrophotometer for all experiments.

Solutions of CuCN in DMF (5×10^{-5} M), BINAP in DMF (5×10^{-5} M), $BrCF_2CO_2Et$ in DMF (5×10^{-5} M), [CuCN and BINAP] in DMF (5×10^{-5} and 5×10^{-4} M, respectively) were prepared. Each above solution (3 mL) was added into a screw top 1.0 cm quartz cuvette for UV-Vis absorption experiment. For CuCN, BINAP and $BrCF_2CO_2Et$, the absorption was less than 300 nm wavelength. Only the in situ generated (BINAP)-CuCN complex has absorptions in the visible-light range.



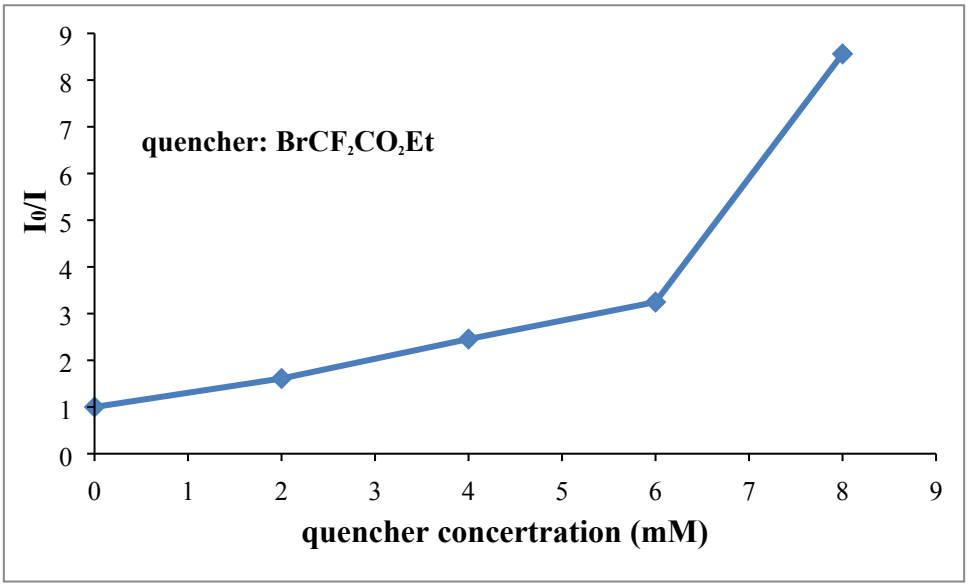
Scheme S1. UV-vis absorption spectra of CuCN (0.05 mM), $BrCF_2CO_2Et$ (0.05 mM), BINAP (0.05 mM), the in-situ-generated (BINAP)-CuCN (0.5 and 0.05 mM, CuCN: BINAP = 1:1) in DMF.

4.5 Stern–Volmer Measurements

Emission intensities were recorded using HITACHI F-2700 fluorescence spectrometer for all experiments. All [CuCN and BINAP] solutions were excited at 370 nm and emission intensity at 516 nm was collected.

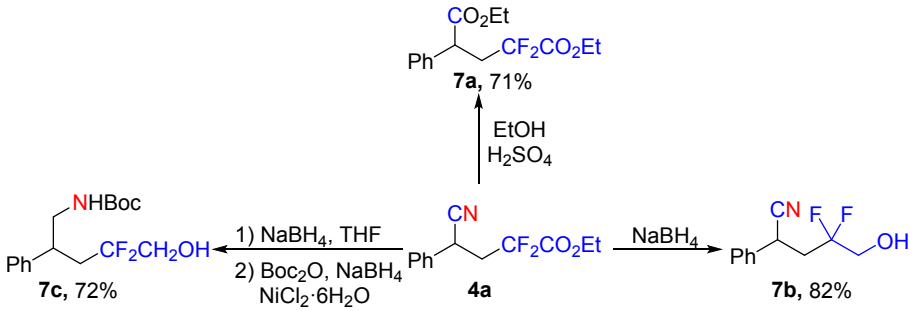
Typical procedure for the preparation of a sample: Into a solution of [CuCN and BINAP] in DMF (5×10^{-5} M, 5 mL) was added $BrCF_2CO_2Et$ (2.0 mg, 0.01 mmol) under a N_2 atmosphere. 3 mL of the resulting solution (the concentration of $BrCF_2CO_2Et$ was 2.0 mM) was added into a screw top 1.0 cm quartz cuvette under a N_2 atmosphere.

The emission spectra of five samples containing varied concentration of $BrCF_2CO_2Et$ (0, 2.0 mM, 4.0 mM, 6.0 mM and 8.0 mM) were collected. I_0 is the luminescence intensity without the quencher and I is the intensity with the quencher. The emission quenching of [CuCN and BINAP] indicated that the photoexcited complex (BINAP)-CuCN could be easily quenched by $BrCF_2CO_2Et$.



Scheme S2. [CuCN and BINAP] emission quenching with $BrCF_2COOEt$

5. The Transformations of 4a



The Procedure for the preparation of 7a: To a stirring solution of **4a** (101.3 mg, 0.4 mmol) in EtOH (0.90 mL) was added sulfuric acid (0.36 mL) at room temperature. The resulting mixture was stirred at 110 °C for 24 h. After being cooled to roomtemperature, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (3 mL) and extracted with CH_2Cl_2. The organic solution was washed with brine, dried over Na_2SO_4, and filtered. After the solvent was removed under reduced pressure, the residue was subjected to flash column chromatography (ethyl acetate/hexanes = 1/100) to afford the desired product as a yellow oil (85.3 mg, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.22 (m, 5H), 4.21–4.10 (m, 3H), 4.10 – 4.00 (m, 1H), 3.89 (dd, J = 8.4, 5.2 Hz, 1H), 3.13 – 2.95 (m, 1H), 2.56 – 2.39 (m, 1H), 1.27 (t, J = 7.2 Hz, 3H), 1.17 (t, J = 7.1 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.61 (ddd, J = 261.7,

17.9, 13.5 Hz), -106.05 (ddd, J = 262.1, 18.0, 16.4 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.4 (s), 163.6 (t, J = 33.8 Hz), 137.6 (s), 128.9 (s), 127.81 (s), 127.80 (s), 115.0 (t, J = 251.0 Hz), 63.0 (s), 61.4 (s), 44.9 (t, J = 4.2 Hz), 37.9 (t, J = 23.5 Hz), 14.0 (s), 13.8 (s); **HRMS (FI)**: Calcd. For $C_{15}H_{18}F_2O_4$ ($[M]^+$): 300.1168; Found: 300.1169; **IR (KBr)**: 3032, 2985, 1759, 1738, 1603, 1497, 1456, 1203, 1099, 1018, 731, 699 cm^{-1}.

The Procedure for the preparation of 7b[6]: To a solution of **4a** (101.3 mg, 0.4 mmol) in dry THF (6 mL) was added $NaBH_4$ (155.3 mg, 4 mmol, 10 equiv) gradually at 0 °C. Then the mixture was stirred under room temperature. After **4a** was consumed completely (detected by TLC), the crude production was diluted with saturated NaCl solution and then extracted with DCM (3 times). The organic layers were combined and concentrated under vacuo. The residue was purified by flash column chromatography (ethyl acetate/hexanes = 1/3) to afford the desired product as a colorless oil (69.3 mg, 82% yield); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.31 (m, 5H), 4.15 (dd, J = 10.0, 4.2 Hz, 1H), 3.86 – 3.67 (m, 2H), 2.81 – 2.59 (m, 2H), 2.41 (ddd, J = 33.7, 15.3, 4.3 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -107.44 – -107.73 (m, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.0 (s), 129.5 (s), 128.7 (s), 127.3 (s), 121.4 (t, J = 244.2 Hz), 120.3 (s), 63.9 (t, J = 32.0 Hz), 39.4 (t, J = 24.1 Hz), 30.7 (t, J = 4.4 Hz); **HRMS (EI)**: Calcd. For $C_{15}H_{20}F_2O_2$ ($[M]^+$): 211.0803; Found: 211.0796; **IR (KBr)**: 3453, 2936, 2248, 1738, 1601, 1497, 1455, 1071, 754, 700 cm^{-1}.

The Procedure for the preparation of 7c[7]: To a solution of **4a** (101.3 mg, 0.4 mmol) in dry THF (6 mL) was added $NaBH_4$ (151.3 mg, 4 mmol, 10 equiv) gradually at 0 °C. Then the mixture was stirred under room temperature. After **4a** was consumed completely (detected by TLC), the crude production was diluted with saturated NaCl solution and then extracted with DCM (3 times). The organic layers were combined and concentrated under vacuo. The residue was used for the next step without purification. The residue was dissolved in MeOH (8 mL). $NiCl_2 \cdot 6H_2O$ (2 equiv.) and Boc_2O (6 equiv.) were then added. Into the resulting mixture was added $NaBH_4$ (16 equiv) gradually at 0 °C. Then the mixture was stirred at room temperature for 24 h.

The solvent was then removed under reduced pressure, leaving a black precipitate. The precipitate was then dissolved in EtOAc (20 mL) and then washed with brine. The organic phases were dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate/hexanes = 1/5) to afford the desired product as colorless oil (113.7 mg, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.3 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 7.3 Hz, 2H), 4.51 (br, 1H), 3.69 – 3.57 (m, 1H), 3.58 – 3.46 (m, 2H), 3.23 – 3.08 (m, 2H), 2.91 (br, 1H), 2.40 – 2.21 (m, 2H), 1.39 (S, 9H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.58 – -106.24 (m, 2F); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.2 (s), 142.1 (s), 128.9 (s), 127.8 (s), 127.2 (s), 123.1 (t, *J* = 195.5 Hz), 79.7 (s), 64.0 (t, *J* = 26.0 Hz), 46.3 (s), 40.0 (s), 36.8 (t, *J* = 20.4 Hz), 28.4 (s); **HRMS (FI)**: Calcd. For $C_{16}H_{23}F_2NO_3$ ($[M]^+$): 315.1641; Found: 315.1638; **IR (KBr)**: 3435, 3367, 2977, 2934, 1694, 1603, 1515, 1367, 1172, 1076, 758, 701 cm^{-1}.

6. References

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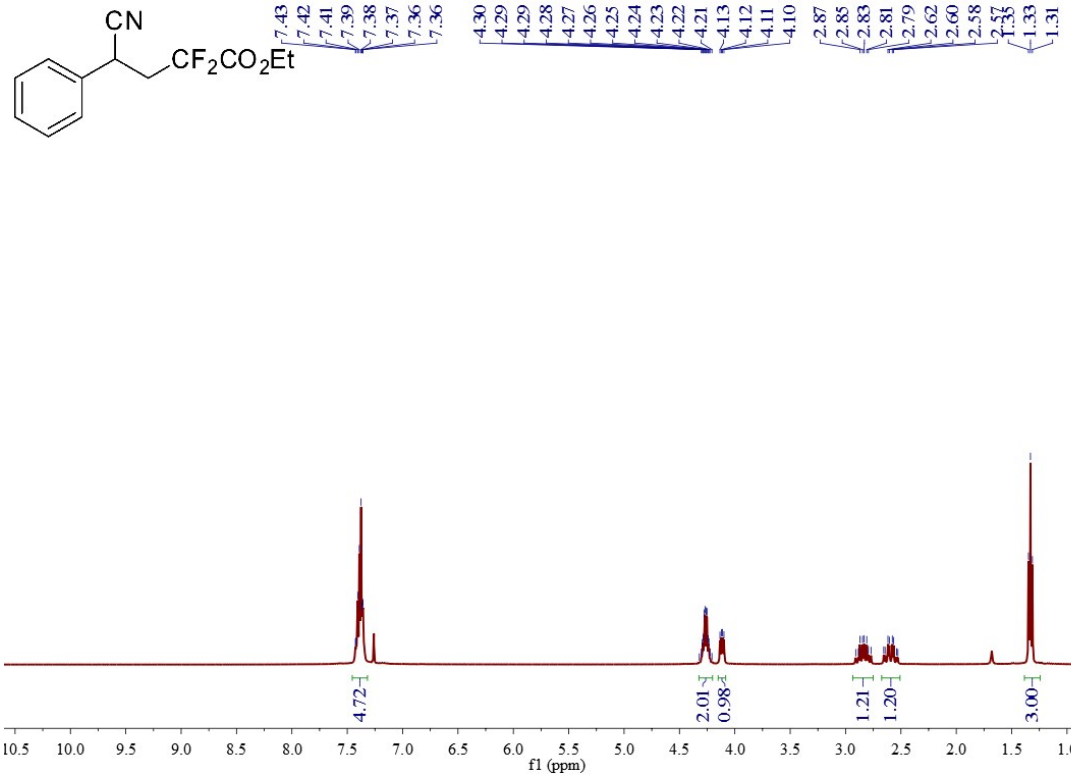
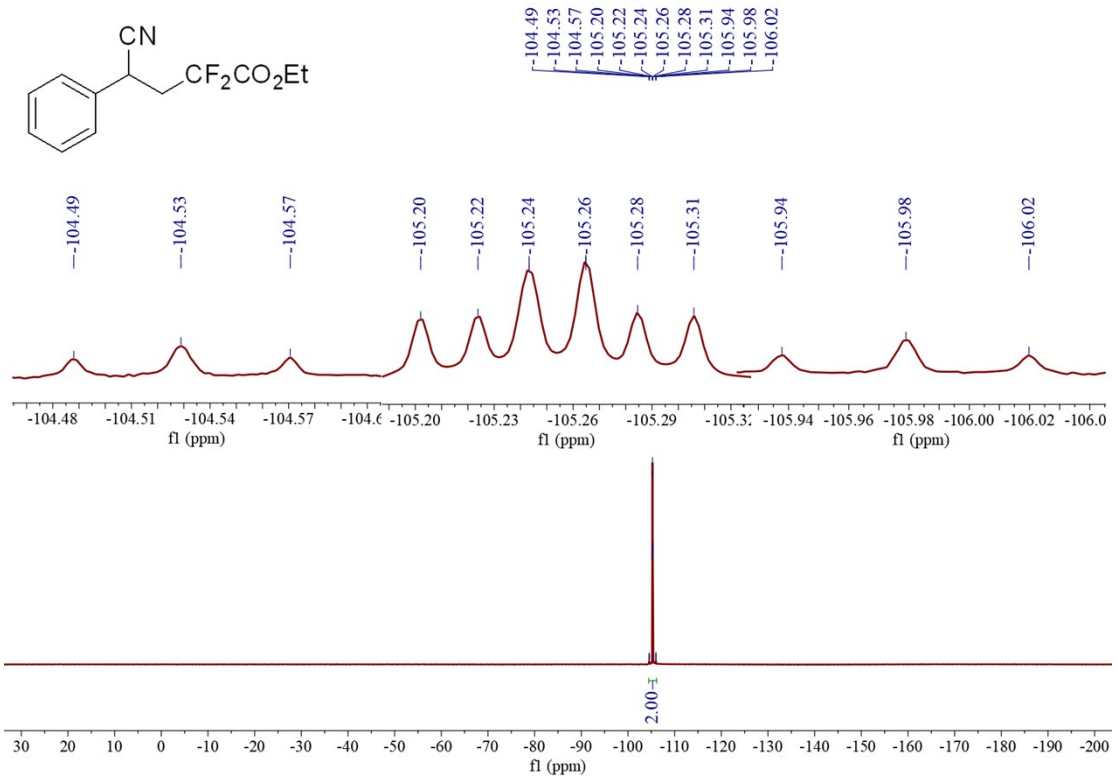
41, 3513-3516.

7. Copies of ^{1}H NMR, ^{19}F NMR and ^{13}C NMR Spectra of Products

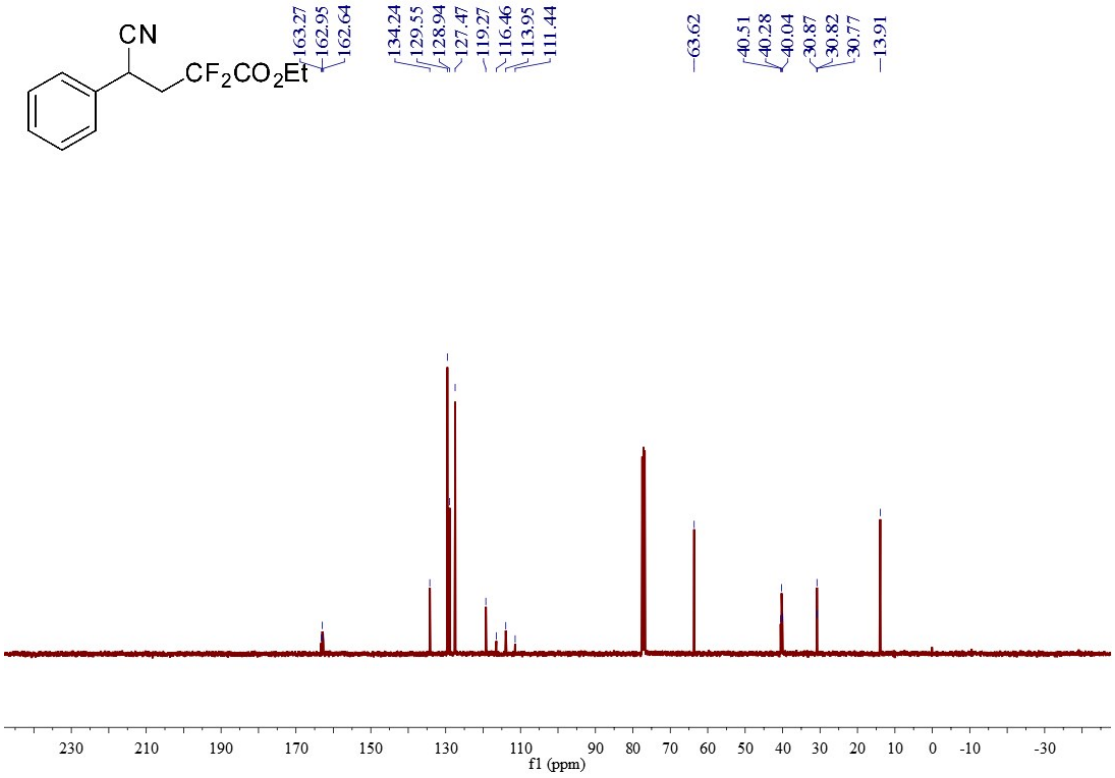
^{1}H NMR Spectrum of **4a**



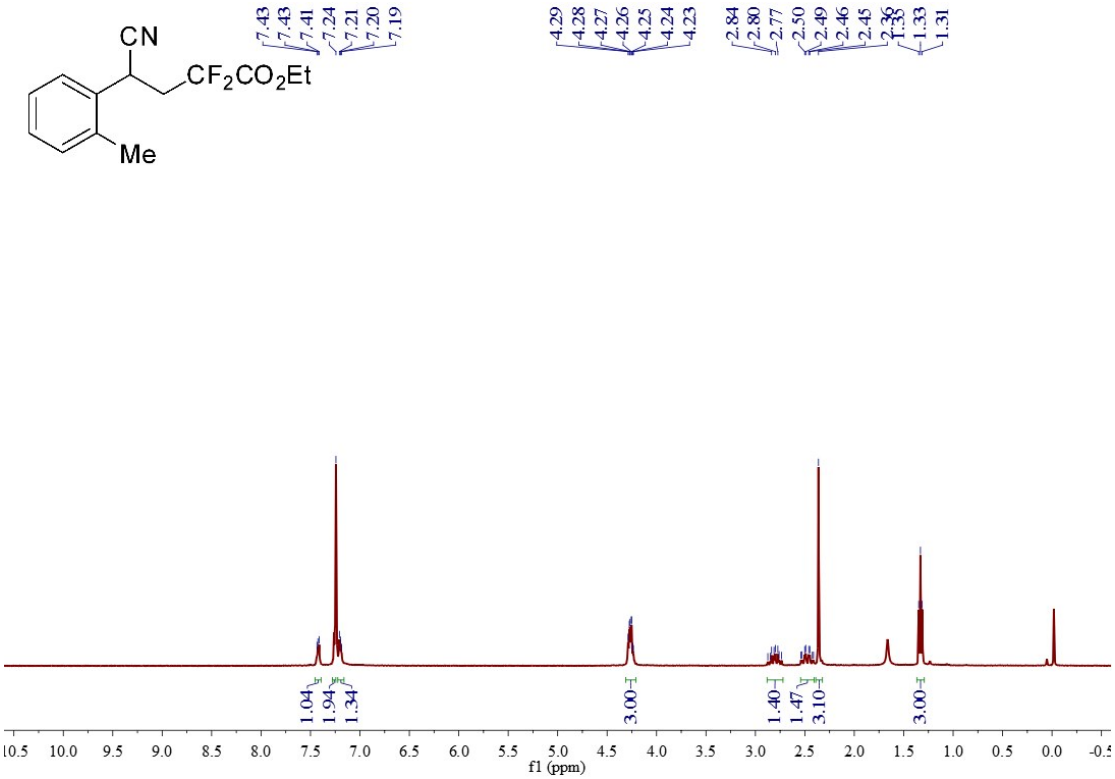
^{19}F NMR Spectrum of **4a**



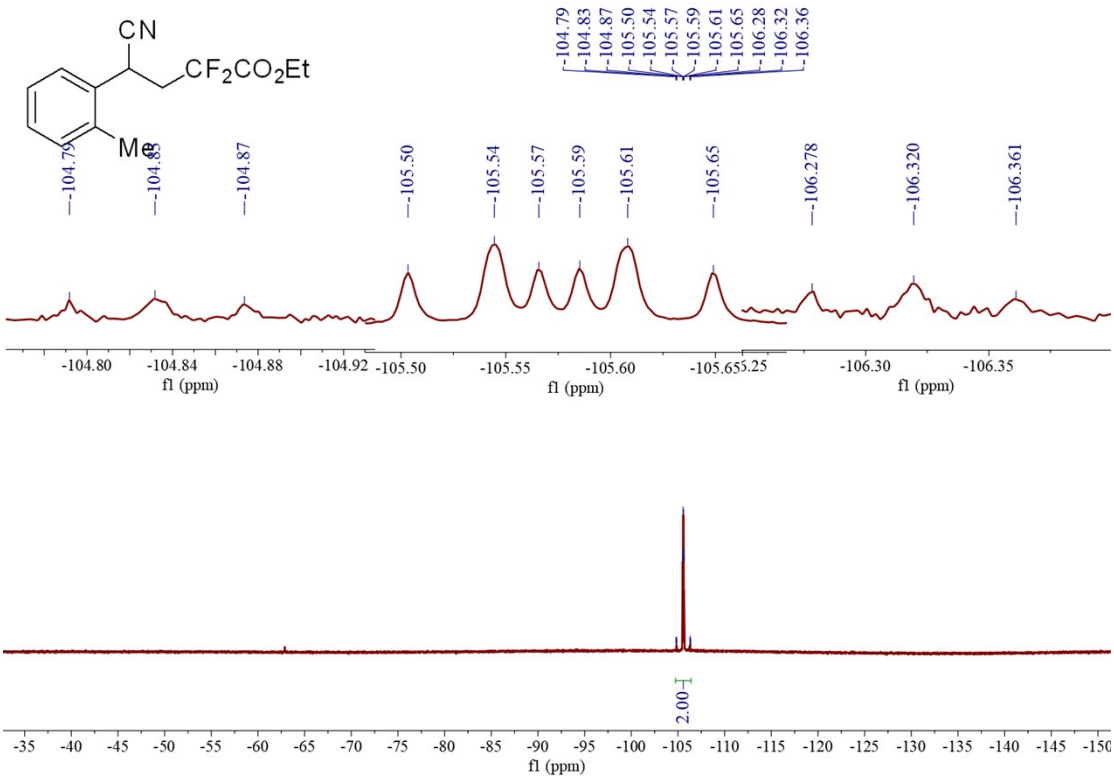
^{13}C NMR Spectrum of **4a**



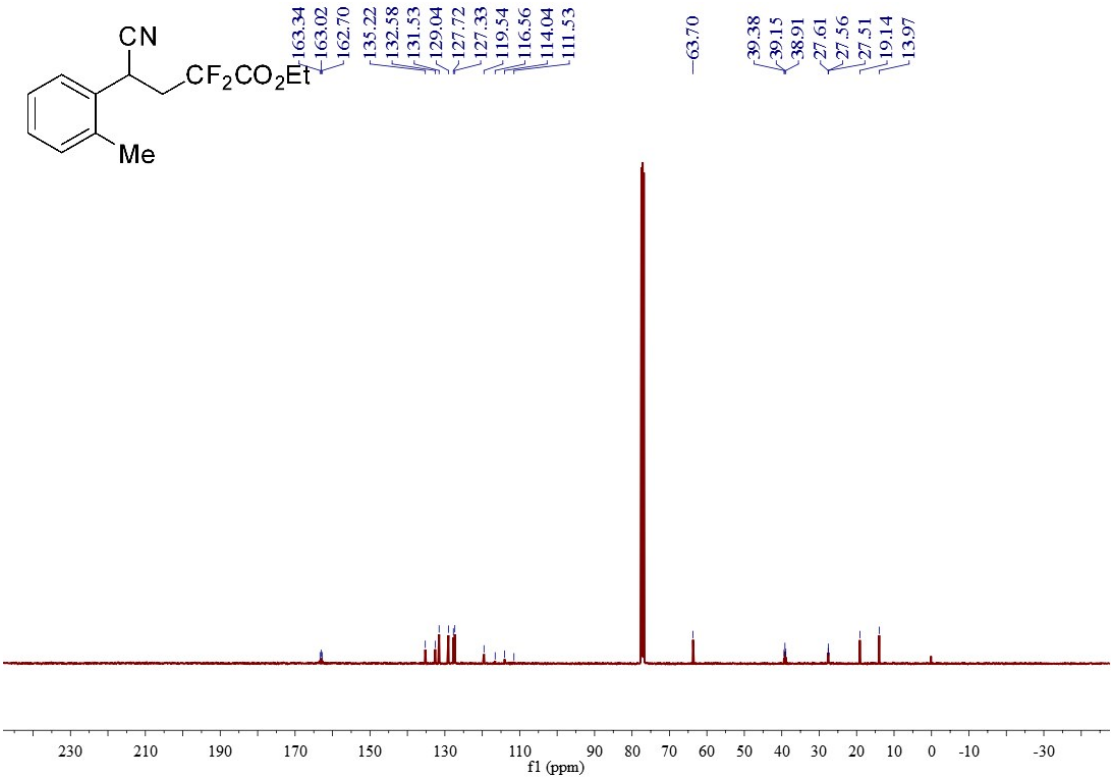
^{1}H NMR Spectrum of **4b**



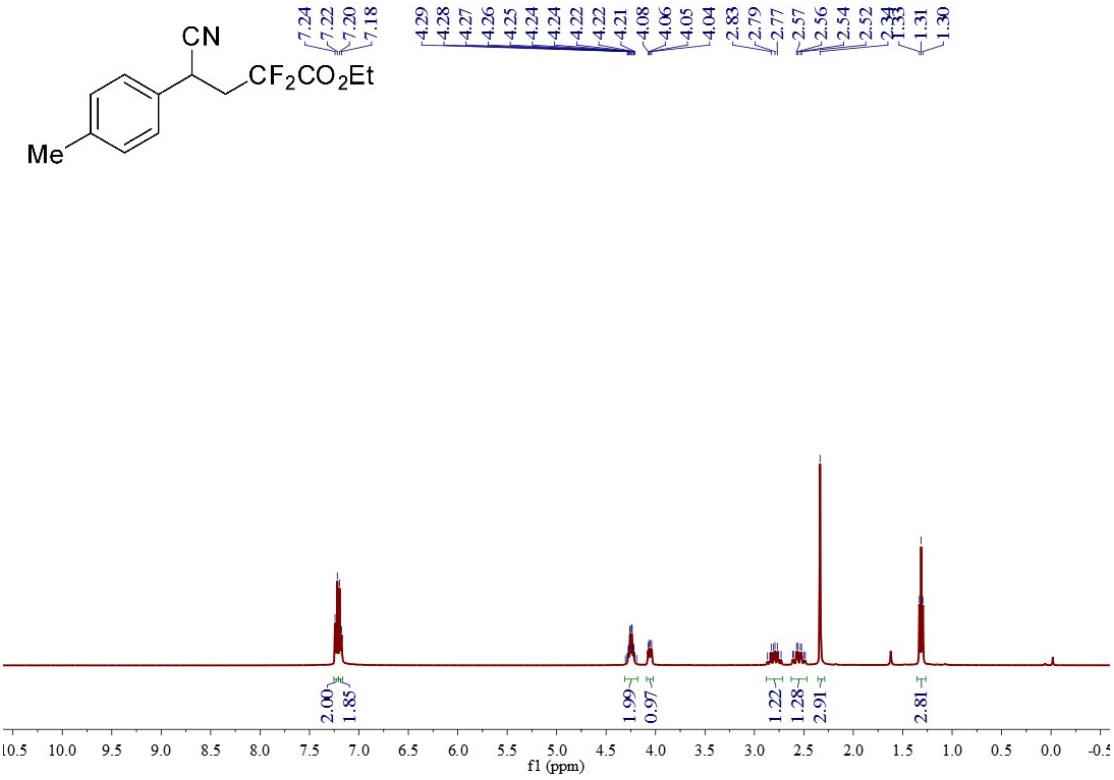
^{19}F NMR Spectrum of **4b**



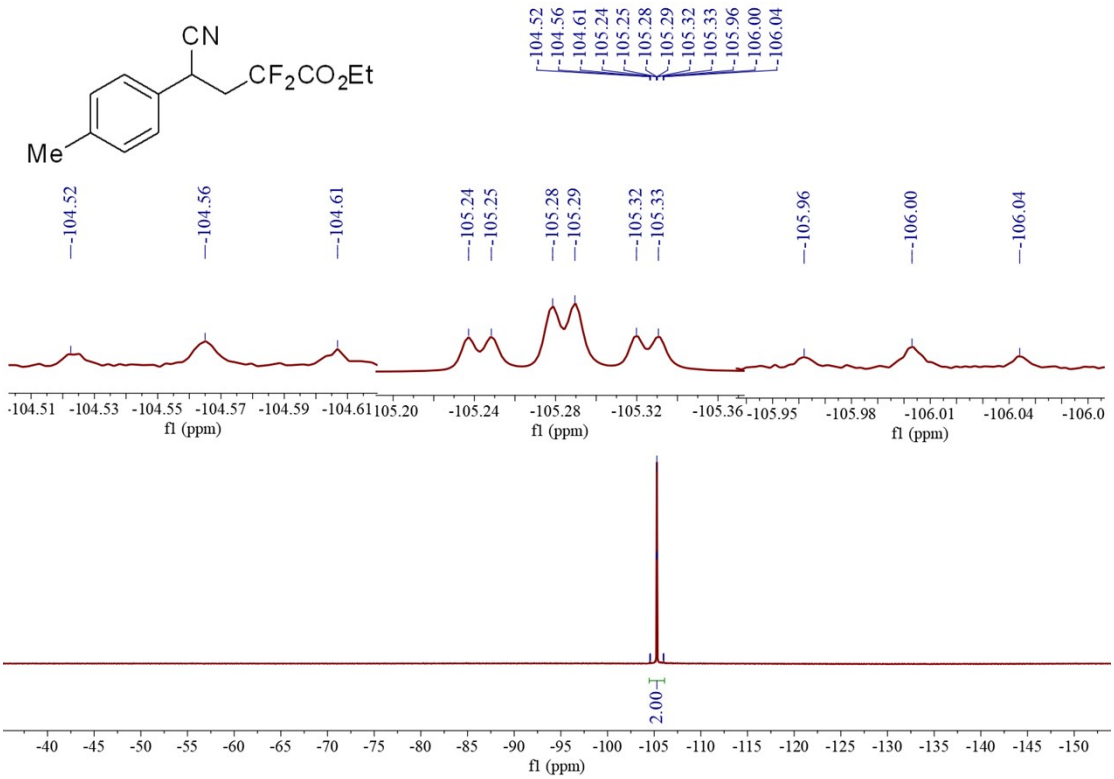
^{13}C NMR Spectrum of **4b**



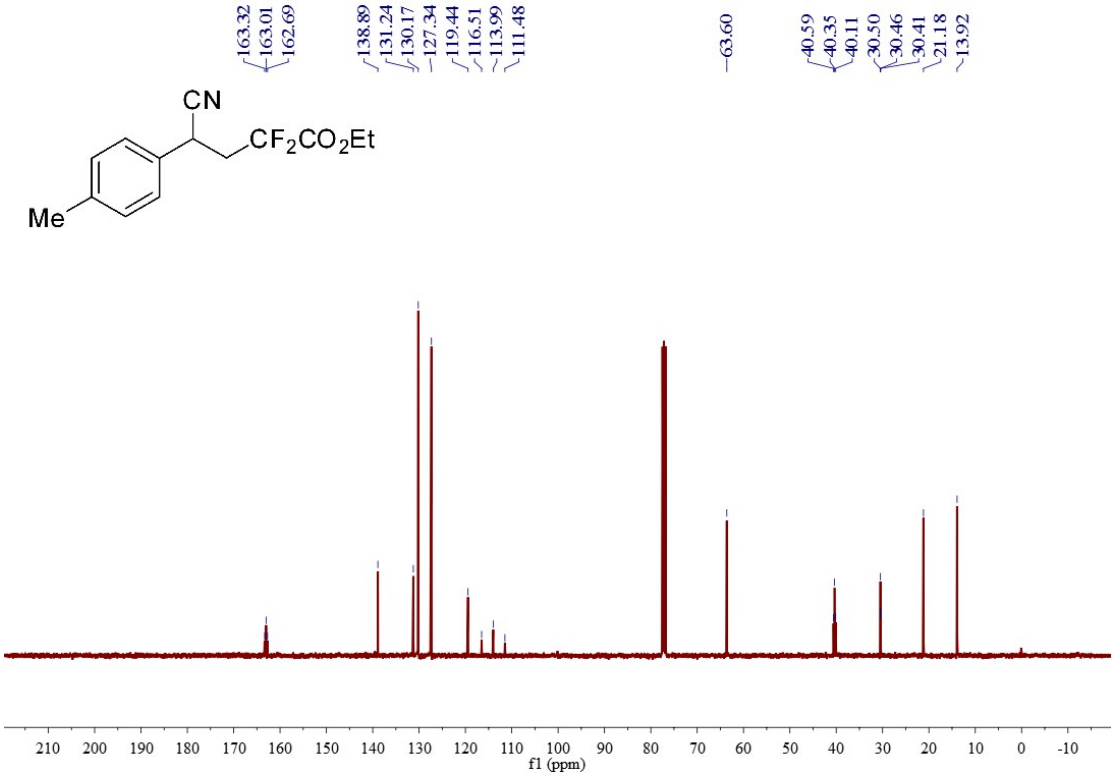
^{1}H NMR Spectrum of **4c**



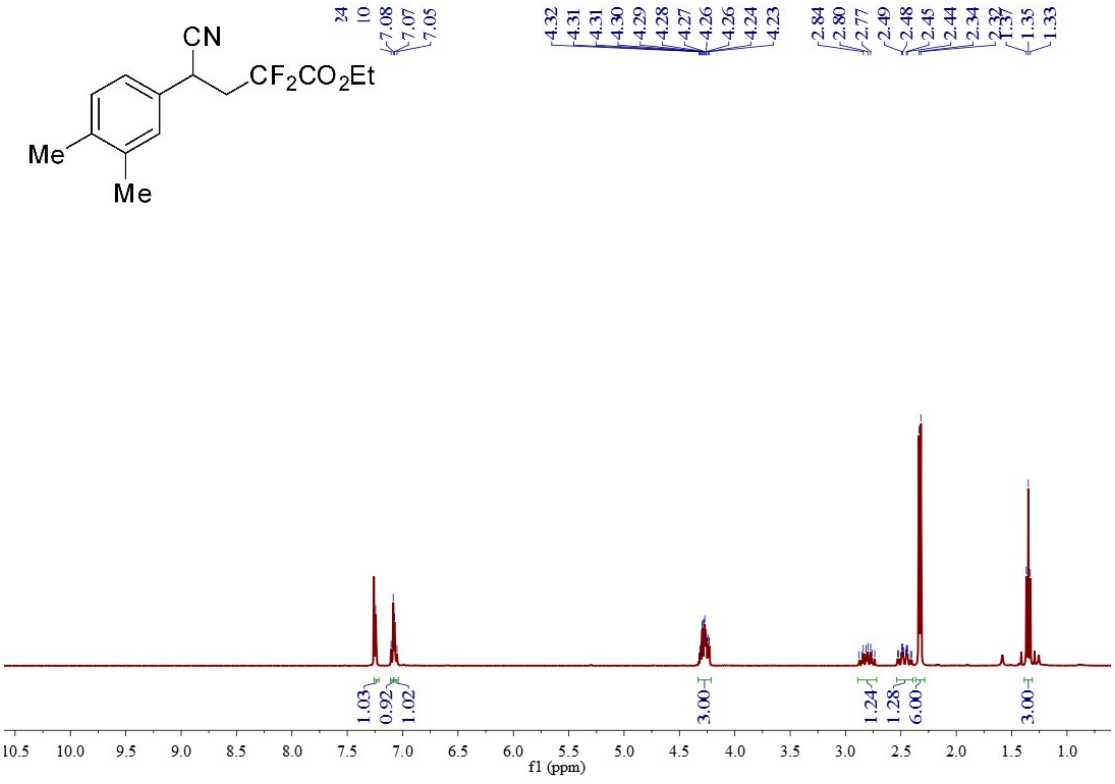
^{19}F NMR Spectrum a of **4c**



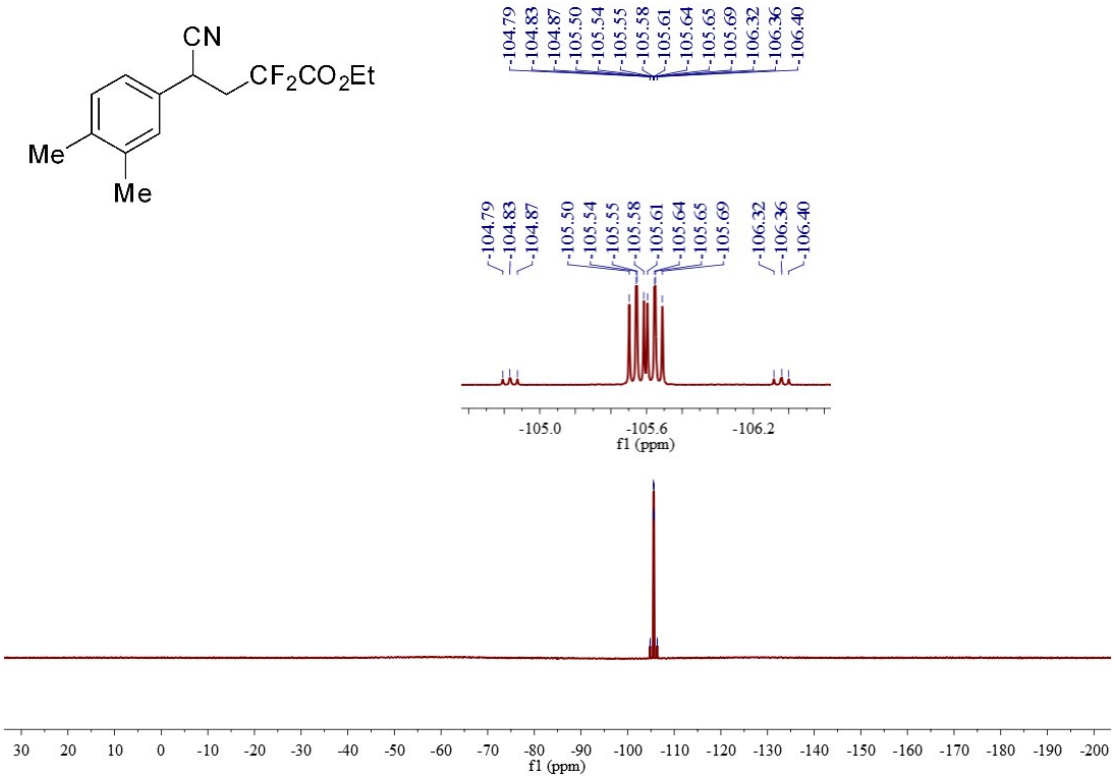
^{13}C NMR Spectrum of **4c**



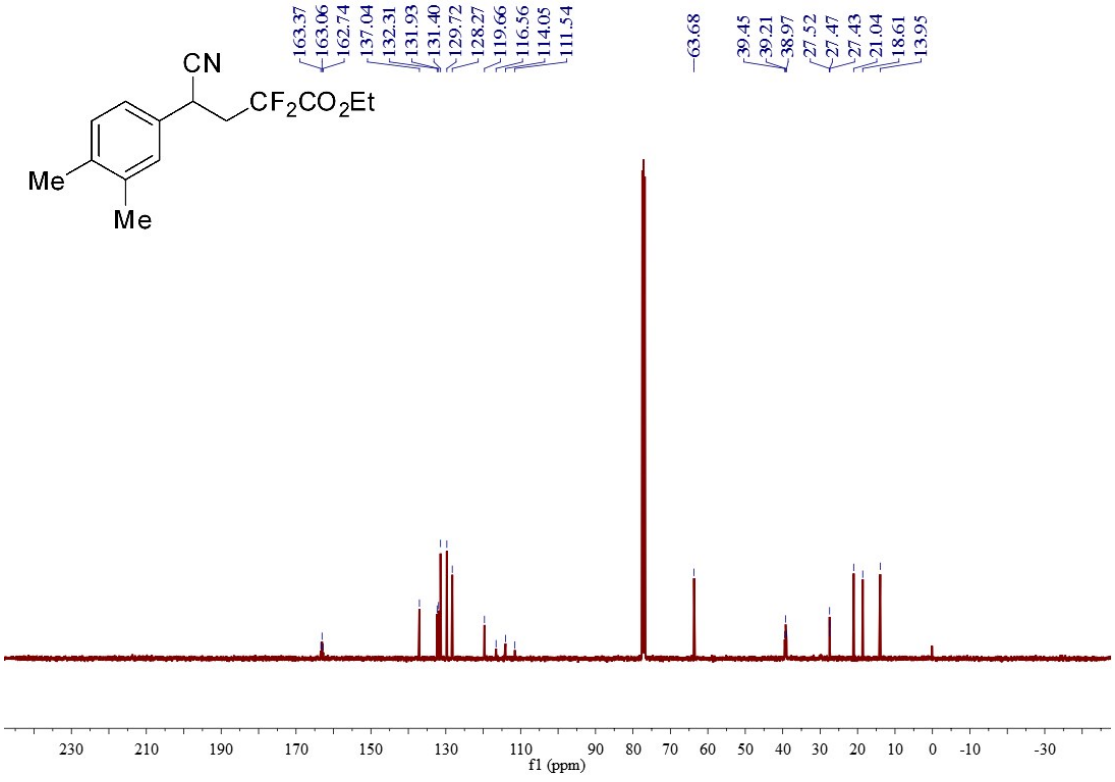
^{1}H NMR Spectrum of **4d**



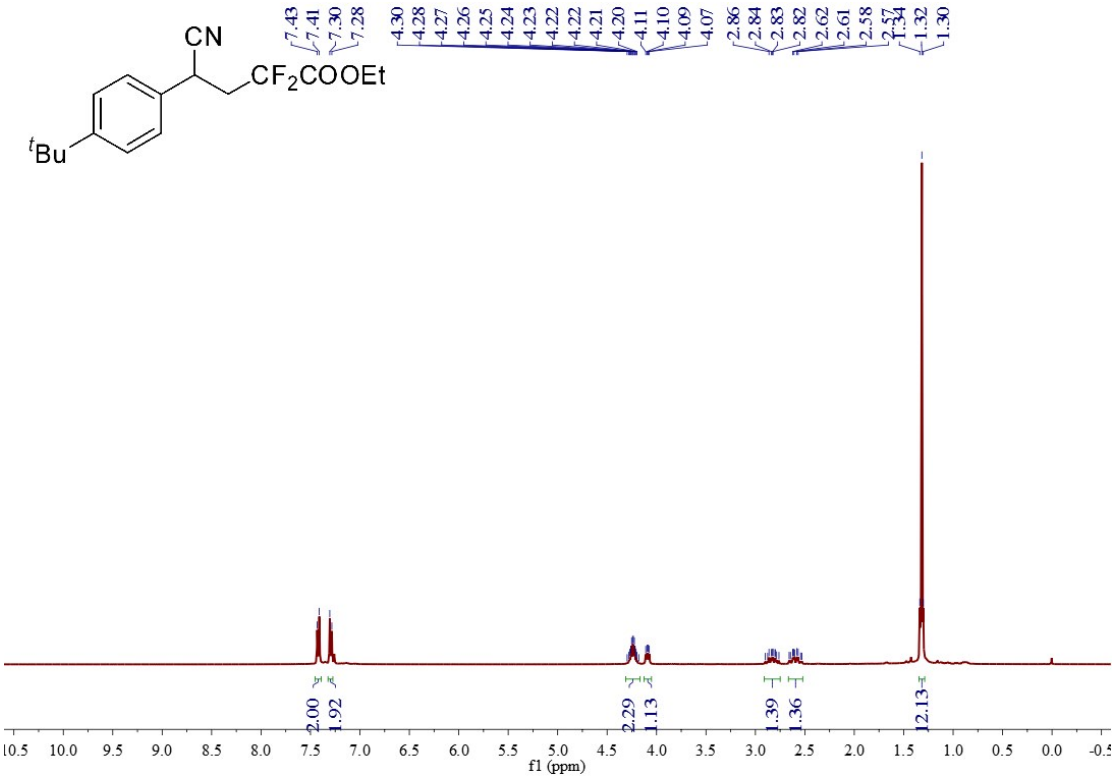
^{19}F NMR Spectrum of **4d**



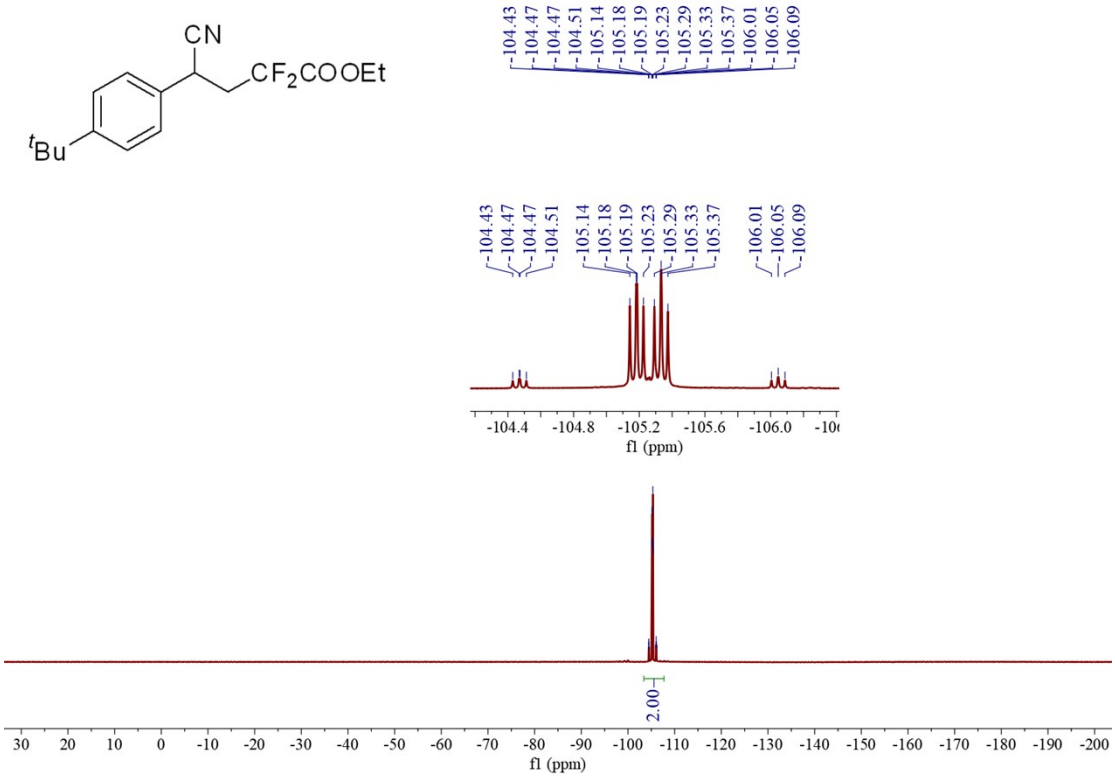
^{13}C NMR Spectrum of **4d**



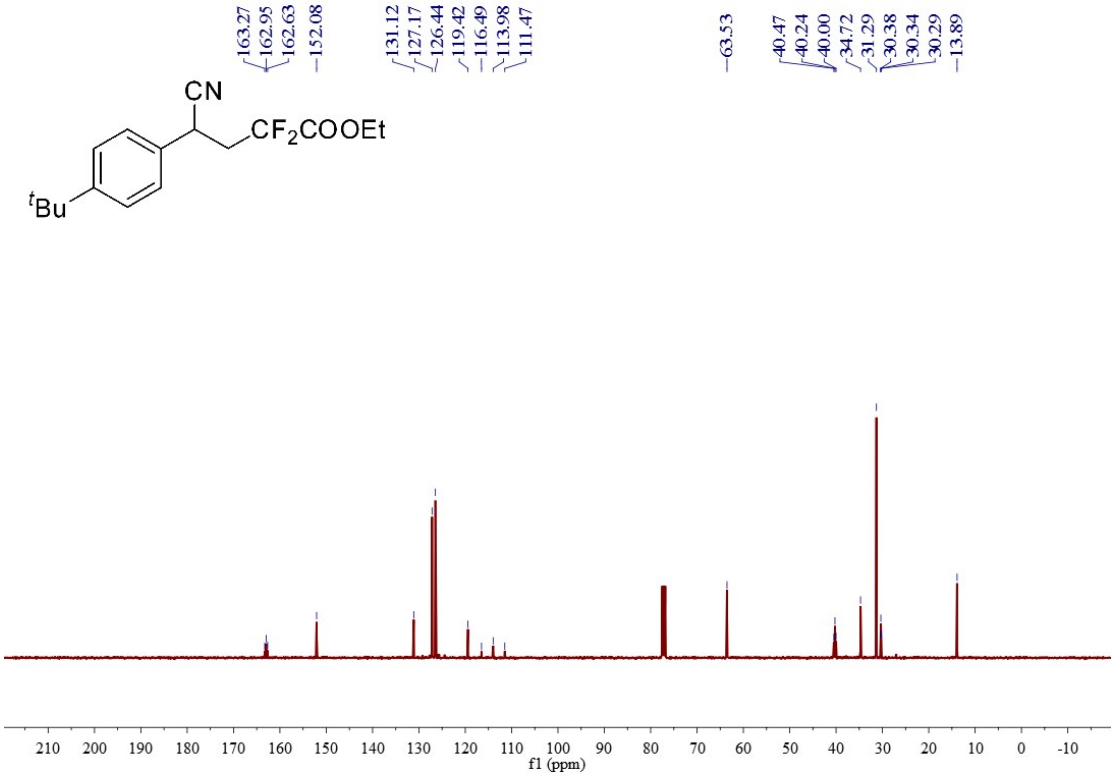
^{1}H NMR Spectrum of **4e**



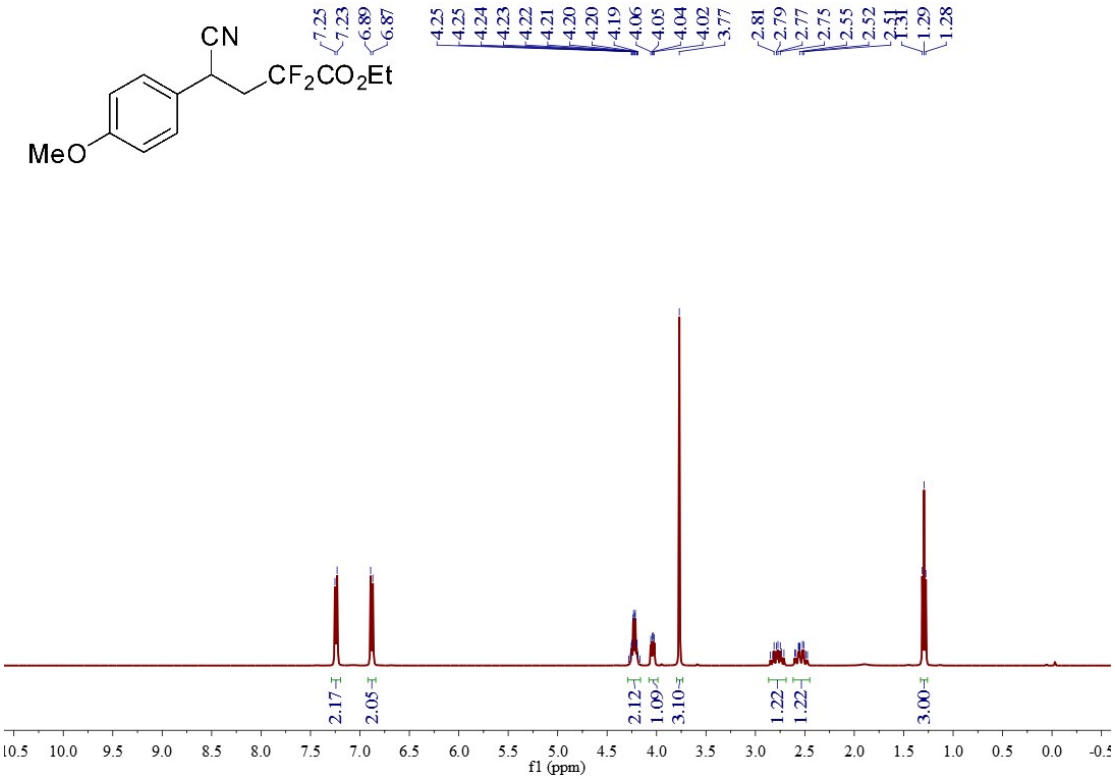
^{19}F NMR Spectrum of **4e**



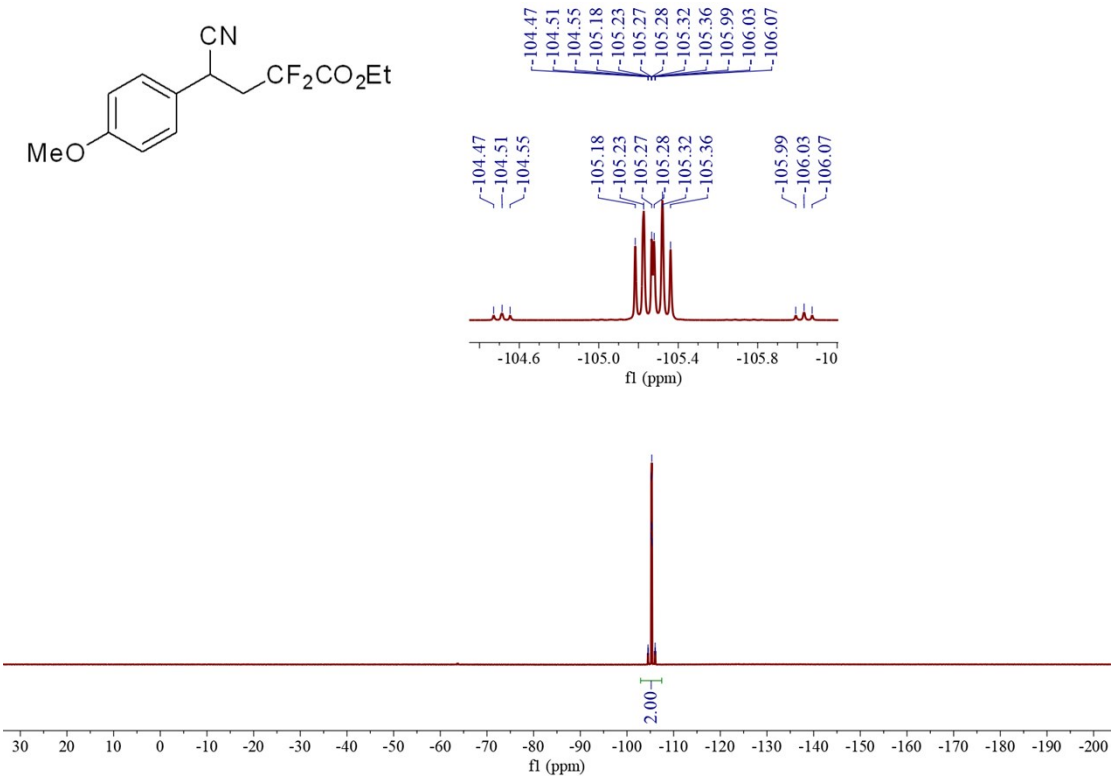
^{13}C NMR Spectrum of **4e**



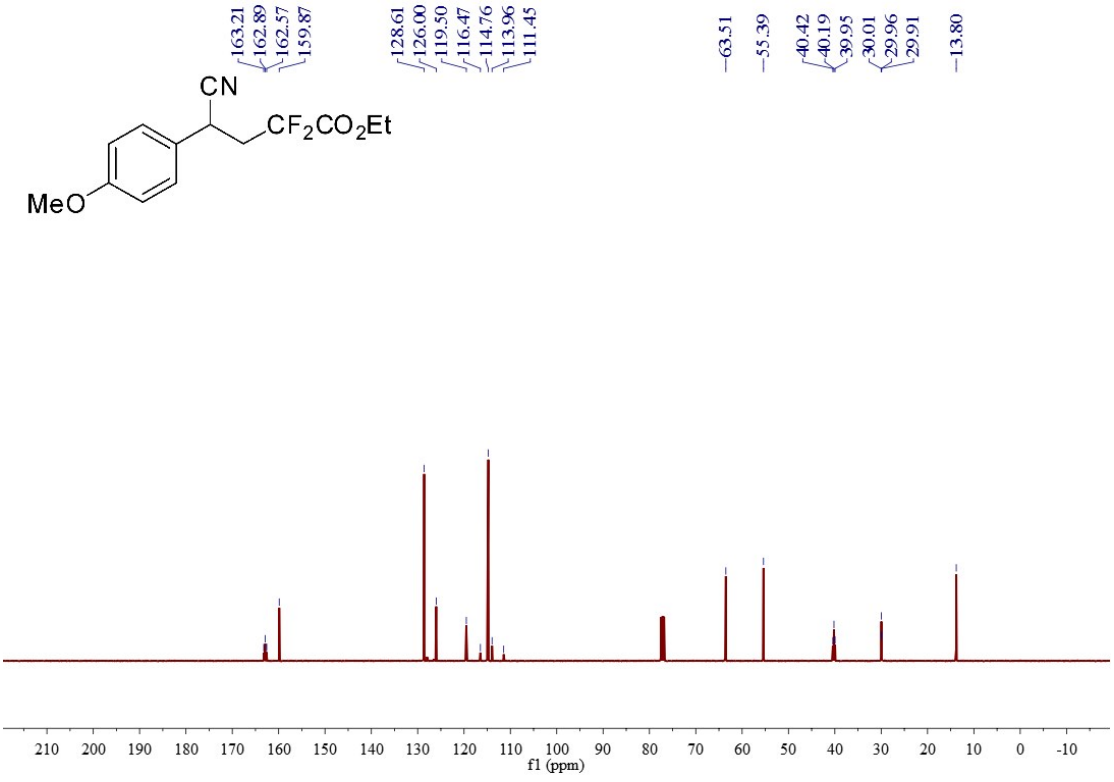
^{1}H NMR Spectrum of **4f**



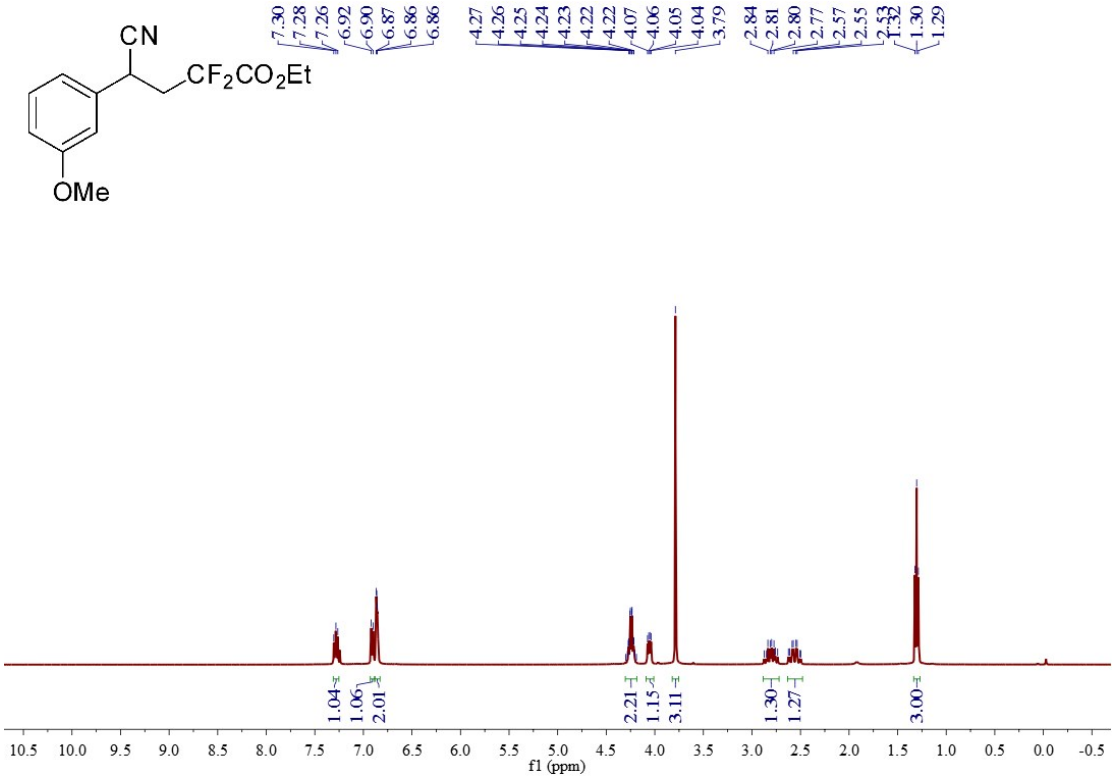
^{19}F NMR Spectrum of **4f**



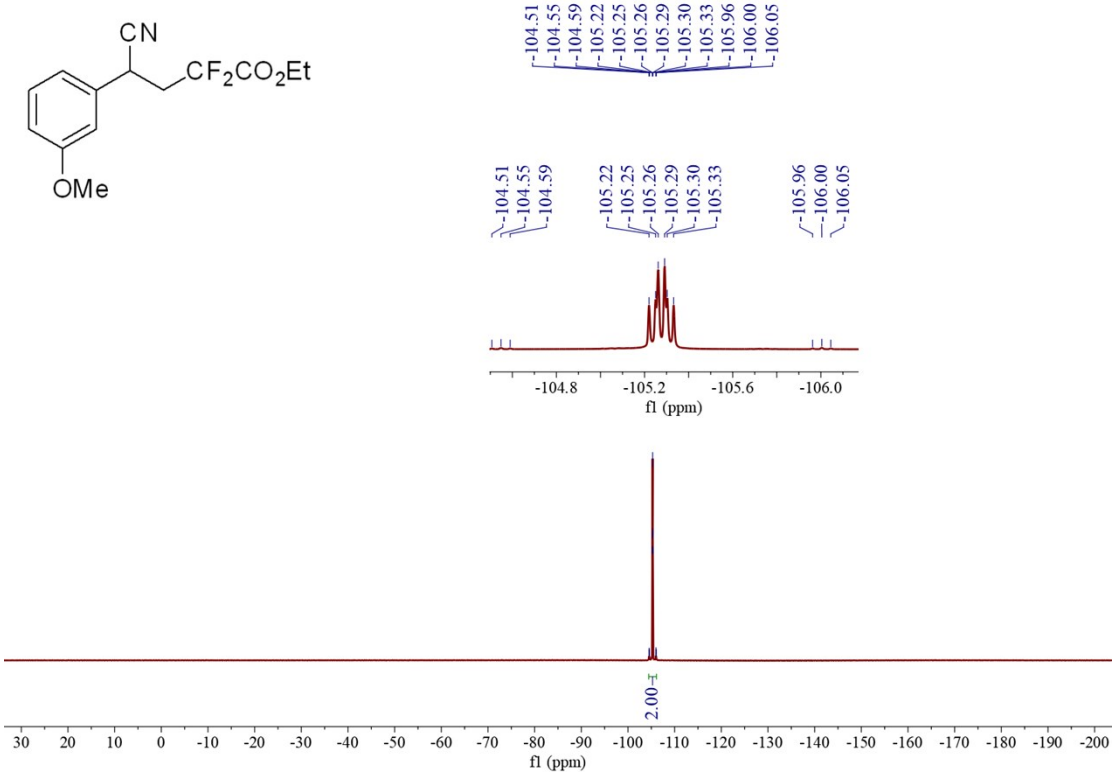
^{13}C NMR Spectrum of **4f**



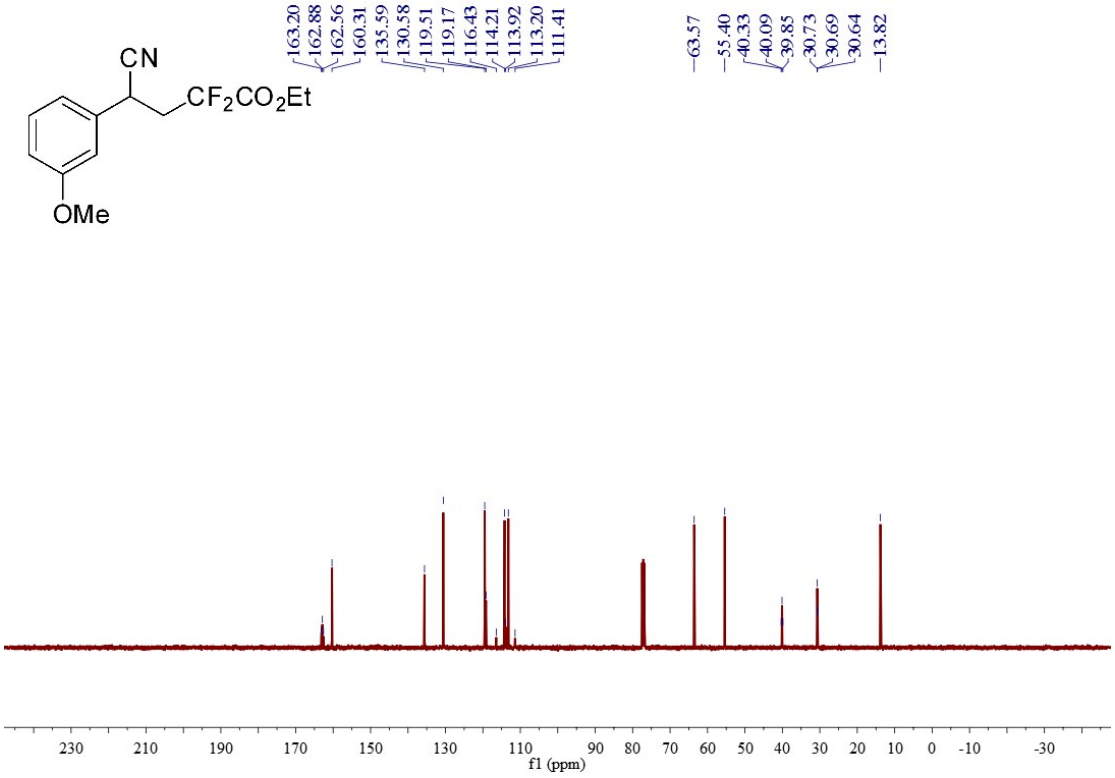
^{1}H NMR Spectrum of **4g**



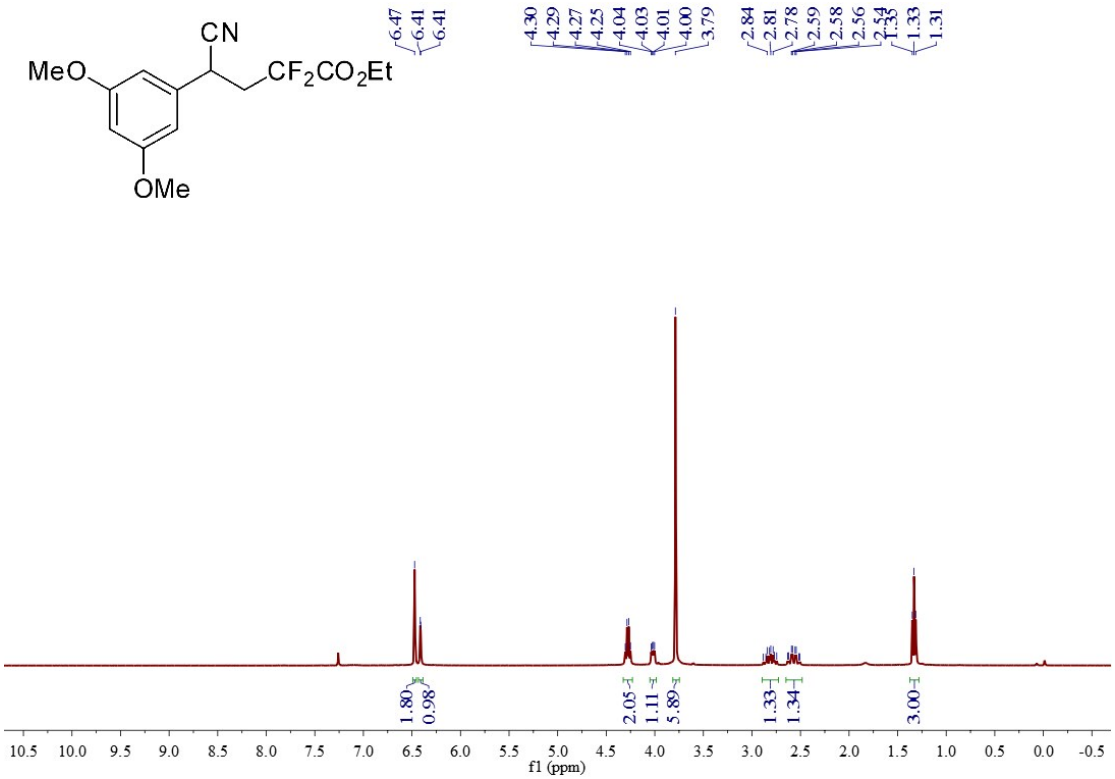
^{19}F NMR Spectrum of **4g**



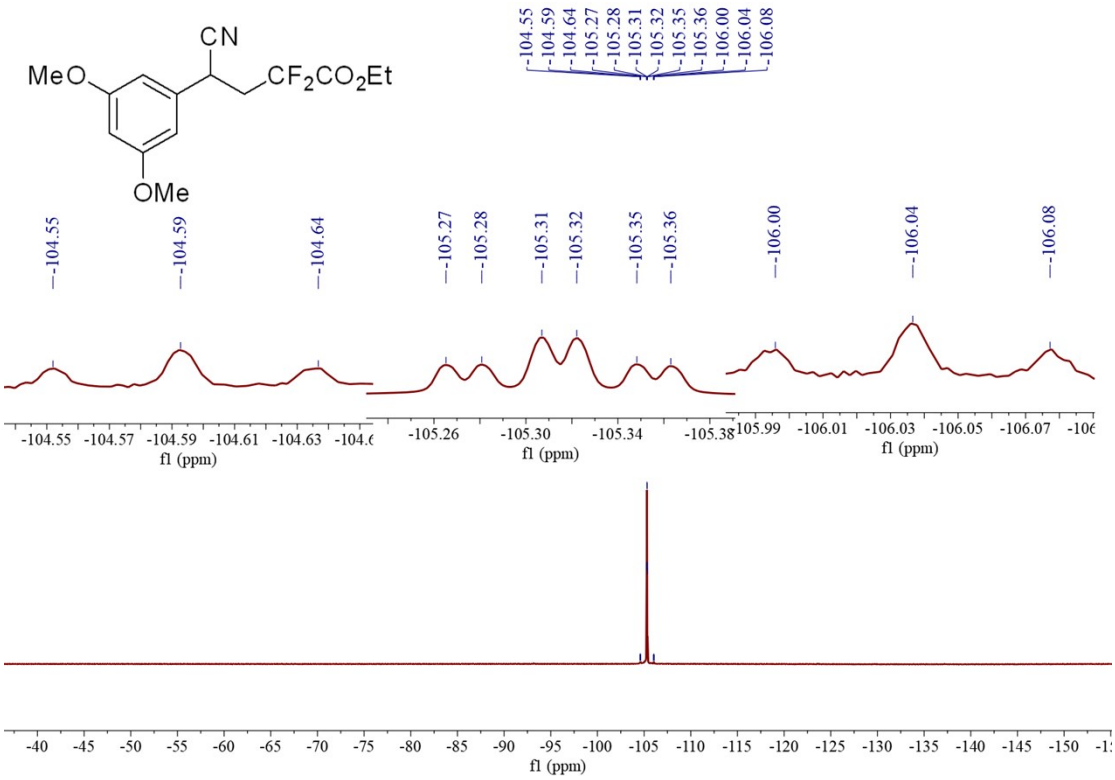
^{13}C NMR Spectrum of **4g**



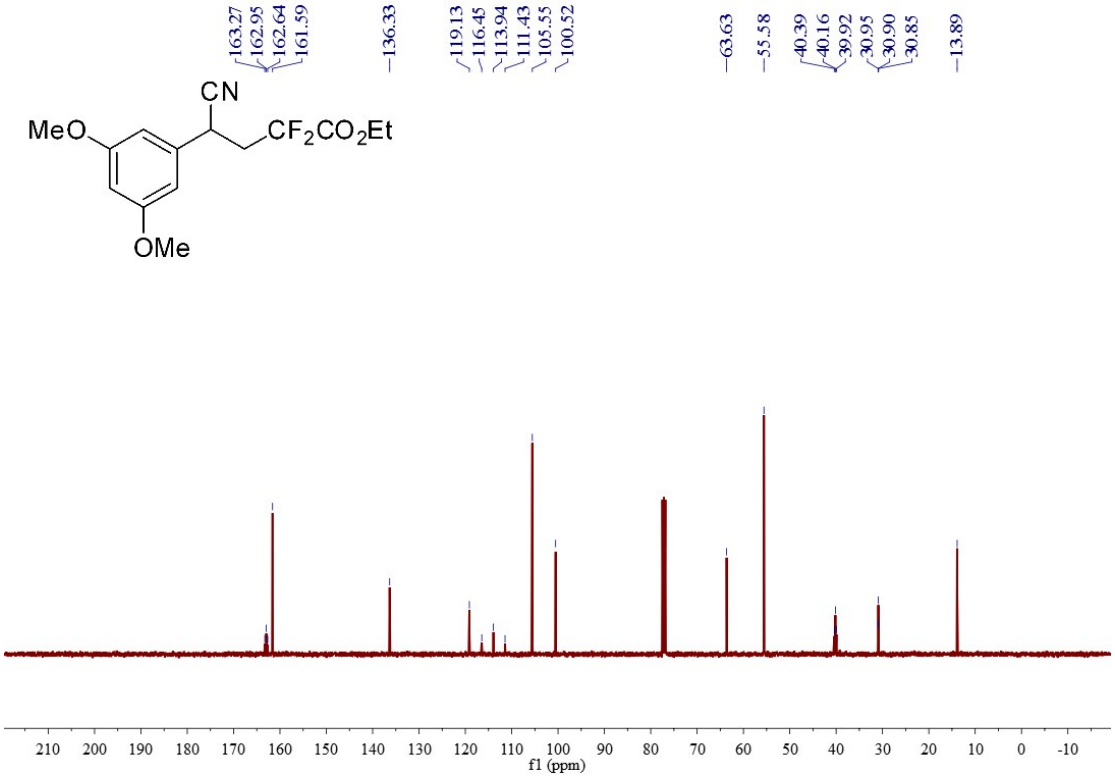
^{1}H NMR Spectrum of **4h**



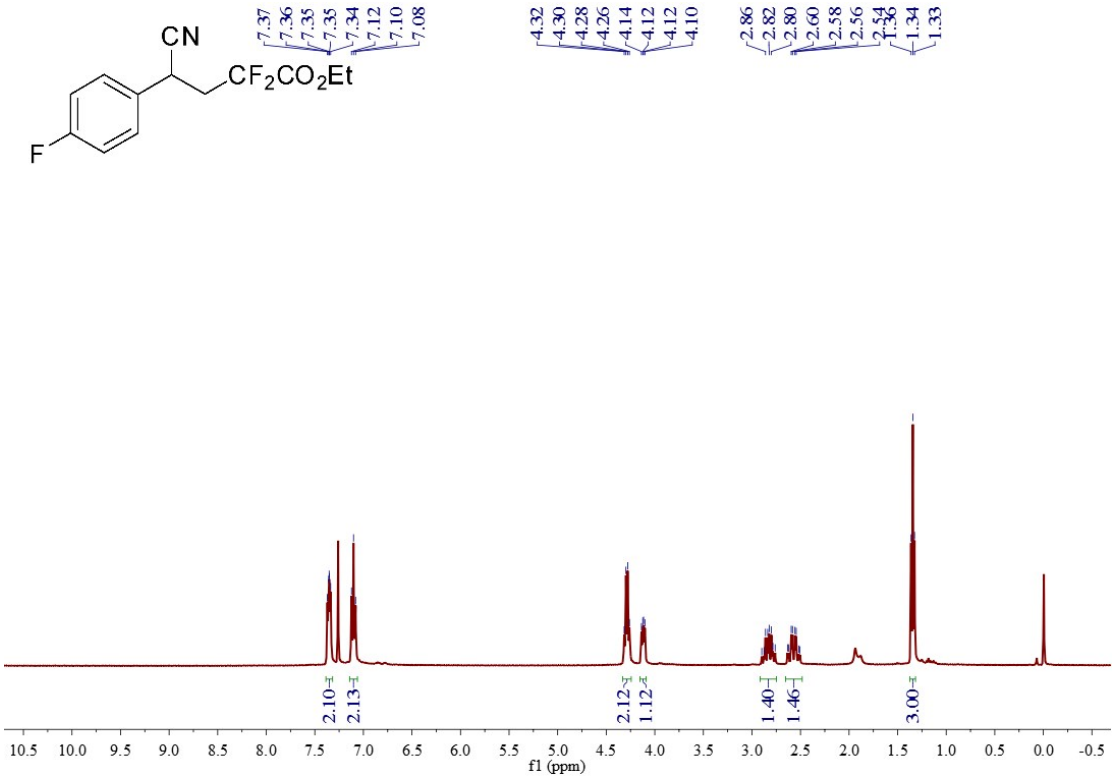
^{19}F NMR Spectrum of **4h**



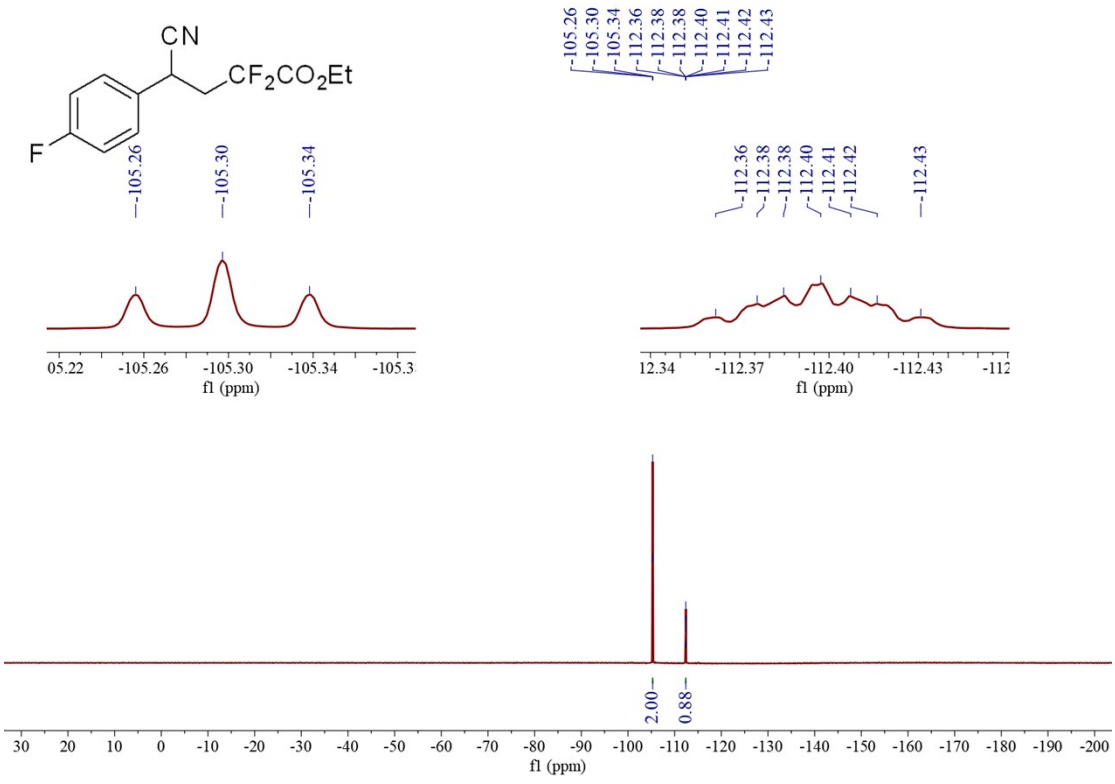
^{13}C NMR Spectrum of **4h**



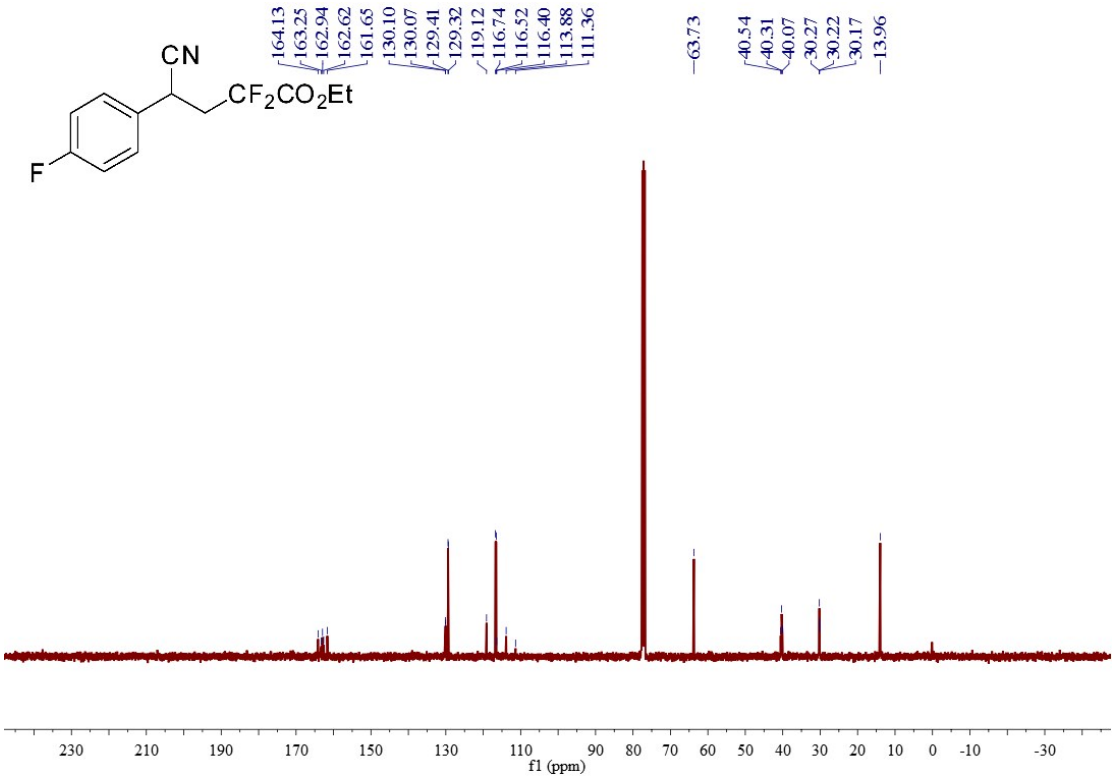
^{1}H NMR Spectrum of **4i**



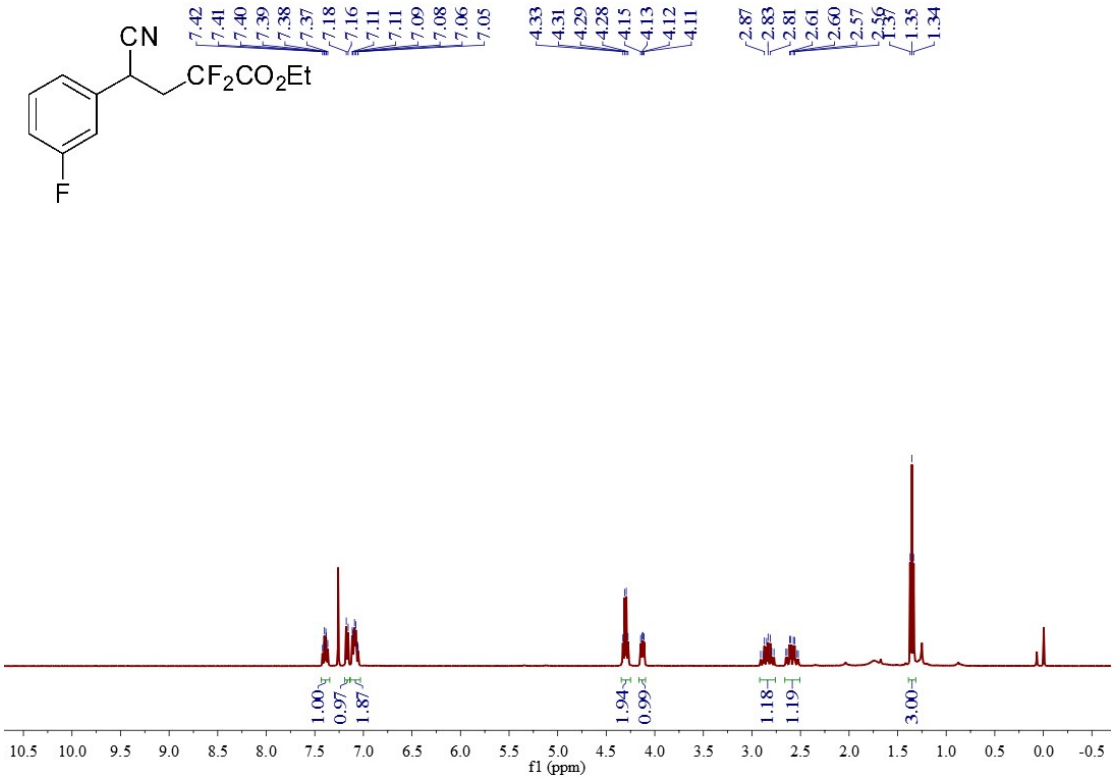
^{19}F NMR Spectrum of **4i**



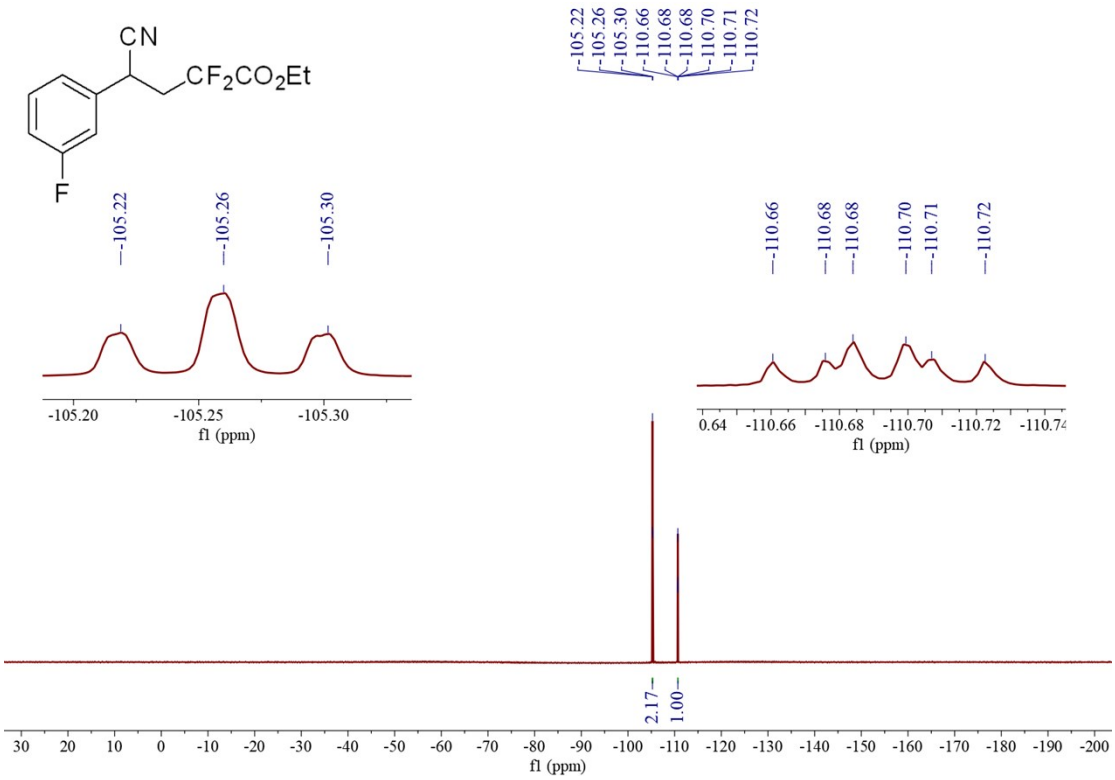
^{13}C NMR Spectrum of **4i**



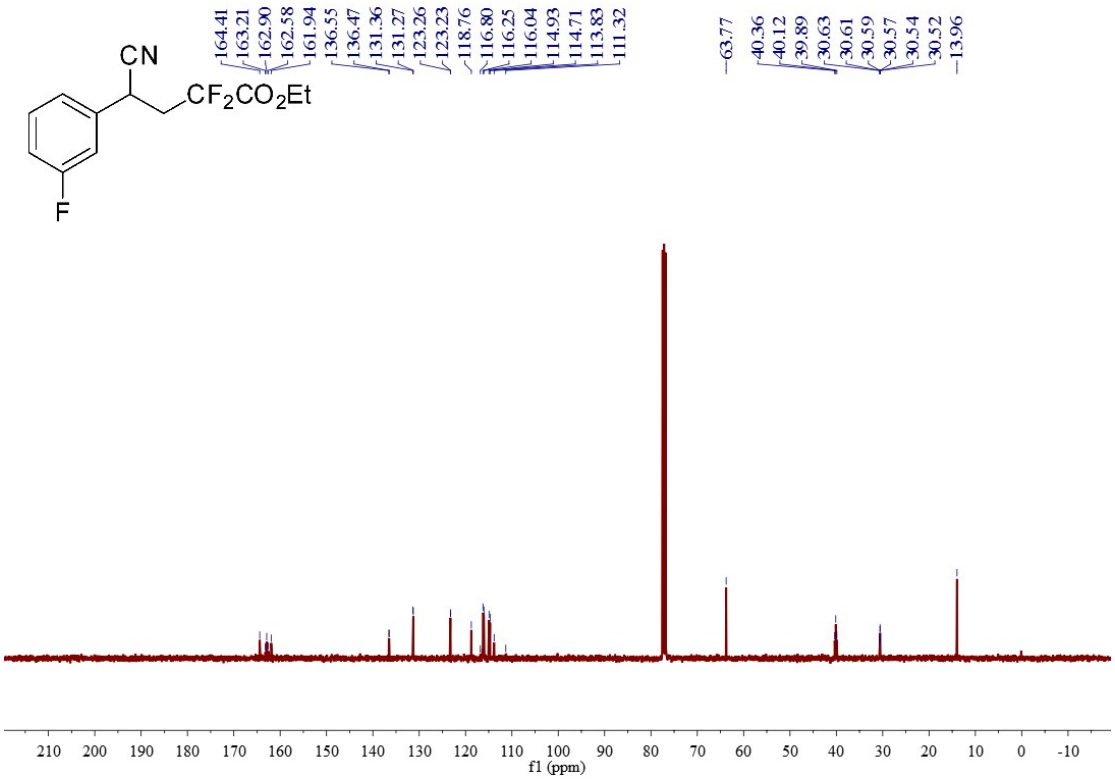
^{1}H NMR Spectrum of **4j**



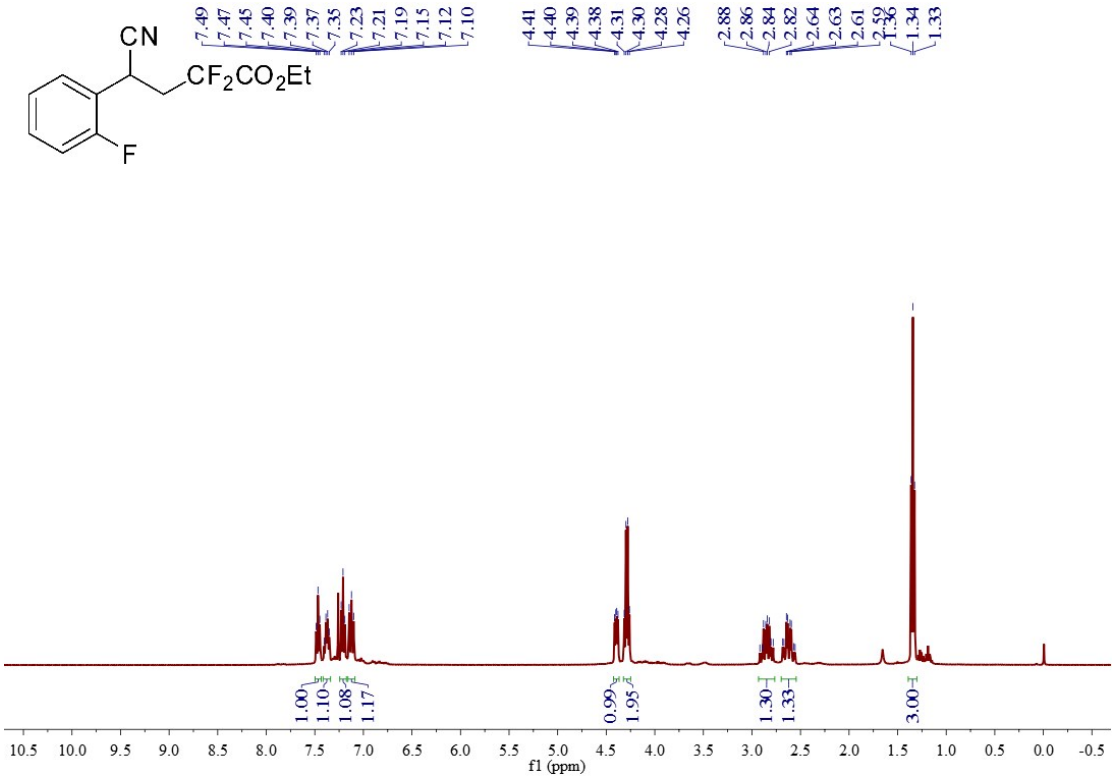
^{19}F NMR Spectrum of **4j**



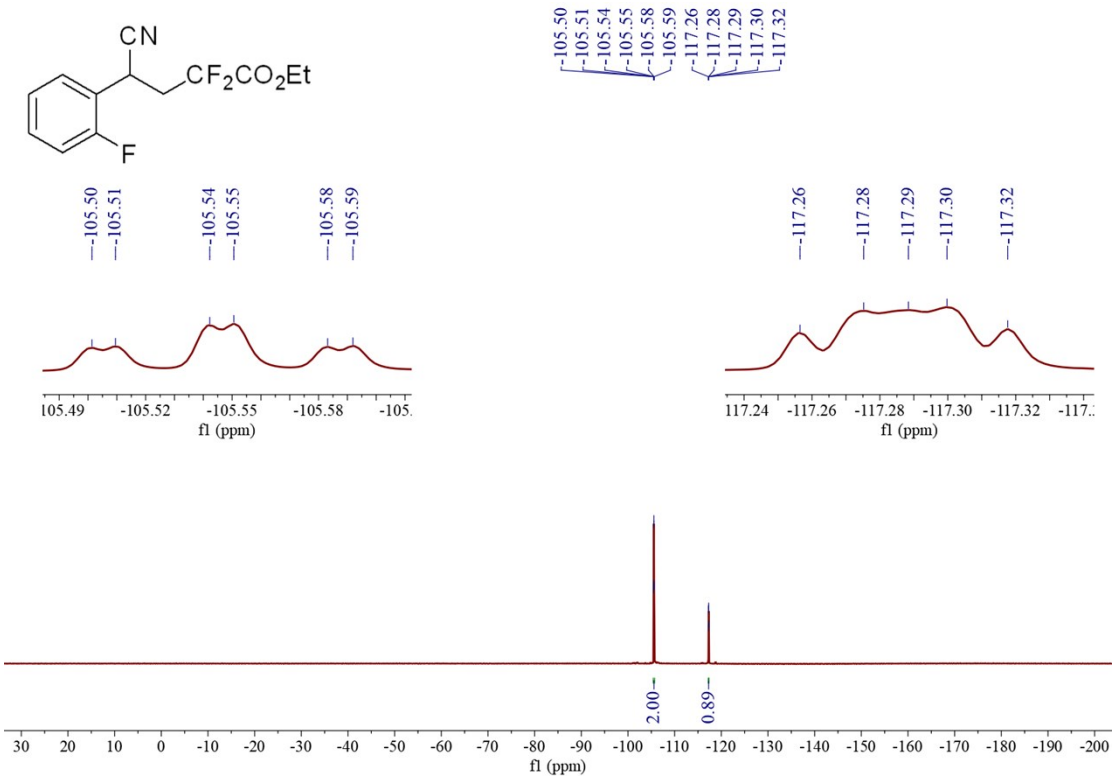
^{13}C NMR Spectrum of **4j**



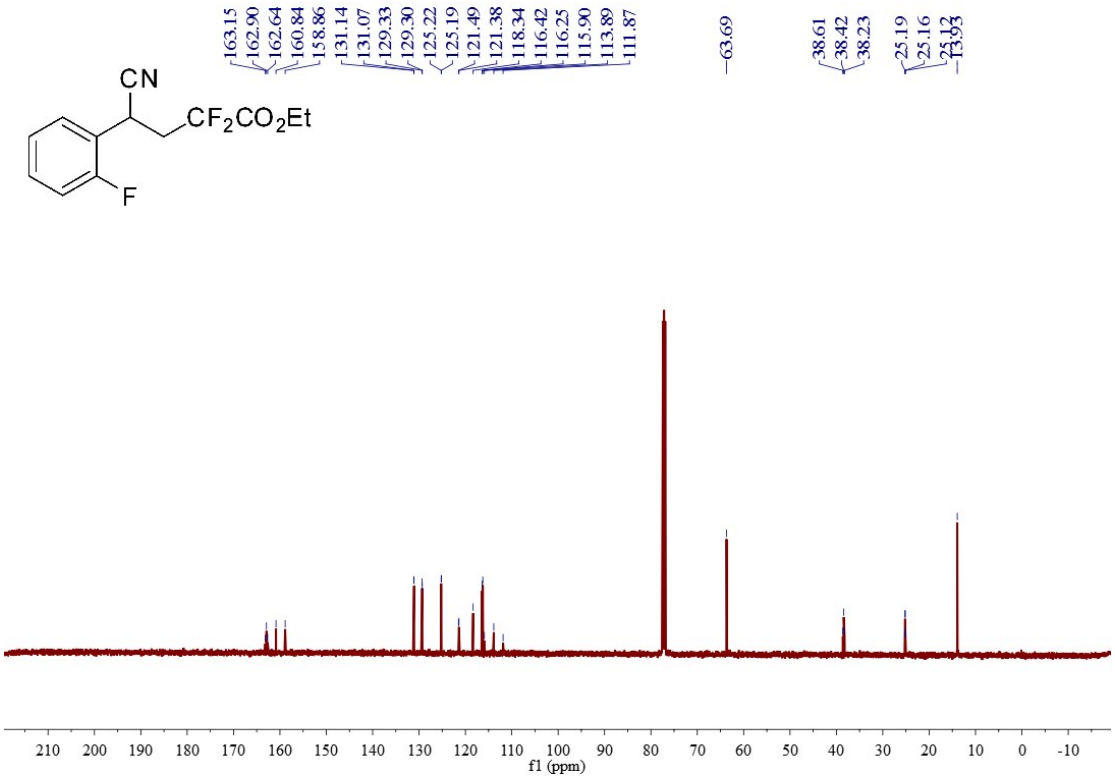
[1]H NMR Spectrum of **4k**



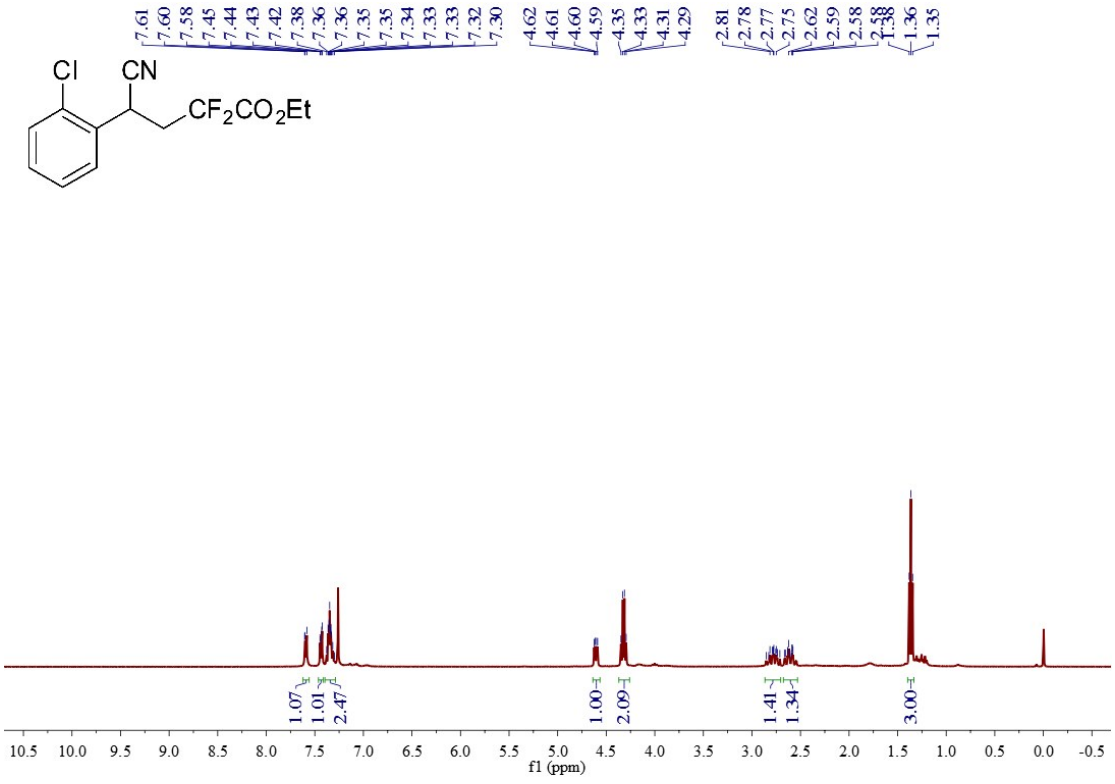
[19]F NMR Spectrum of **4k**



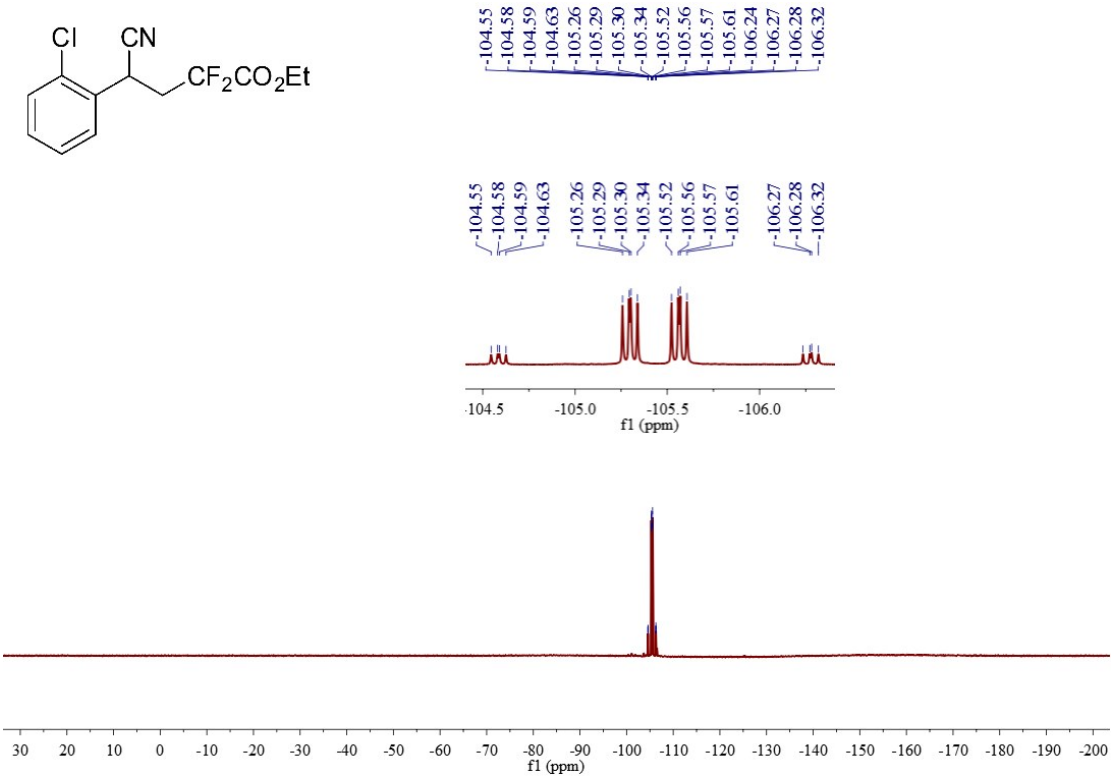
^{13}C NMR Spectrum of **4k**



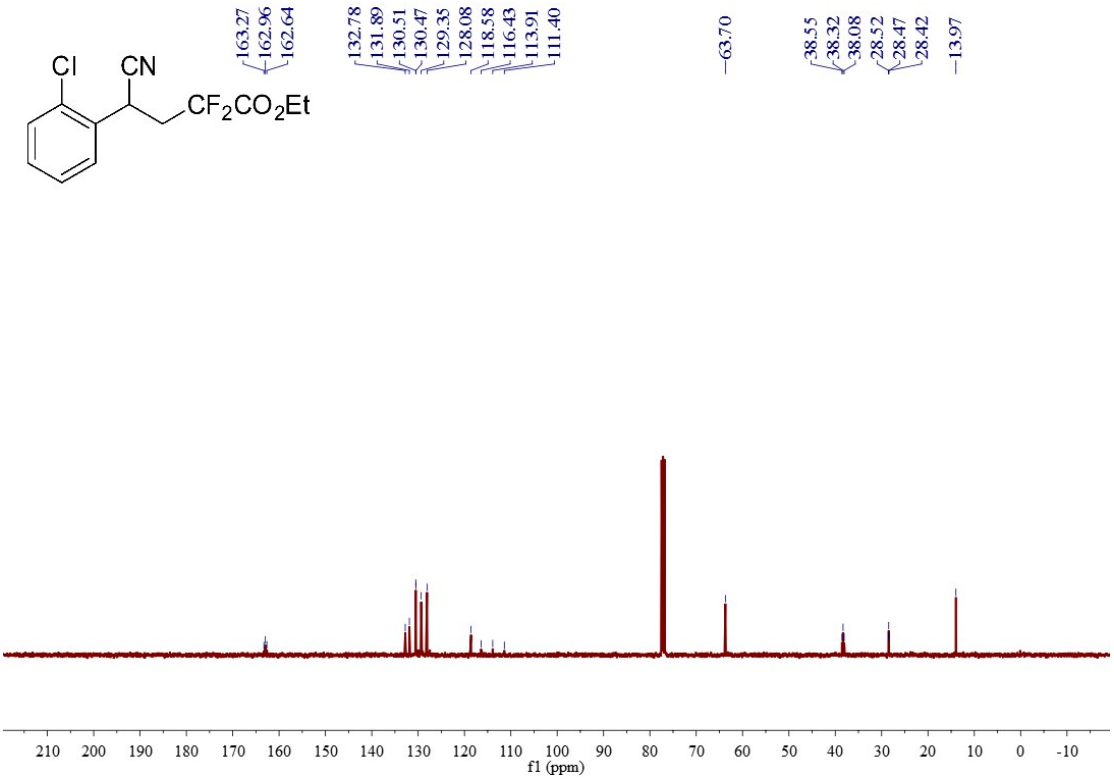
^{1}H NMR Spectrum of **4l**



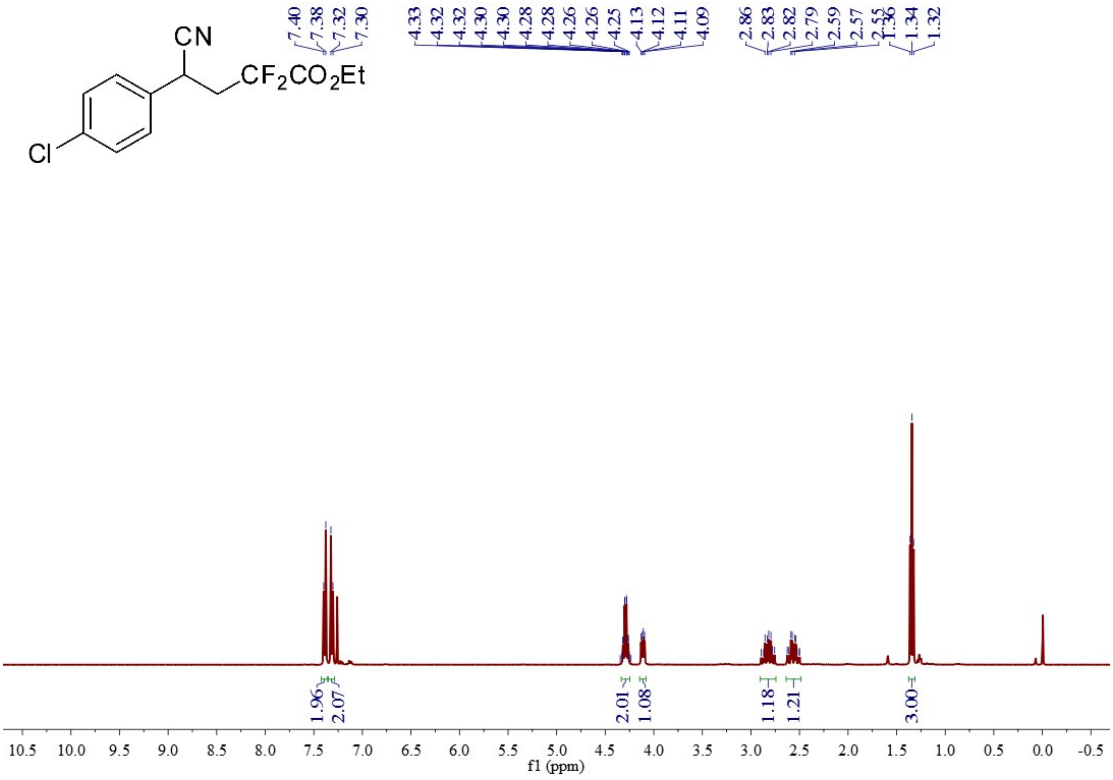
^{19}F NMR Spectrum of **4l**



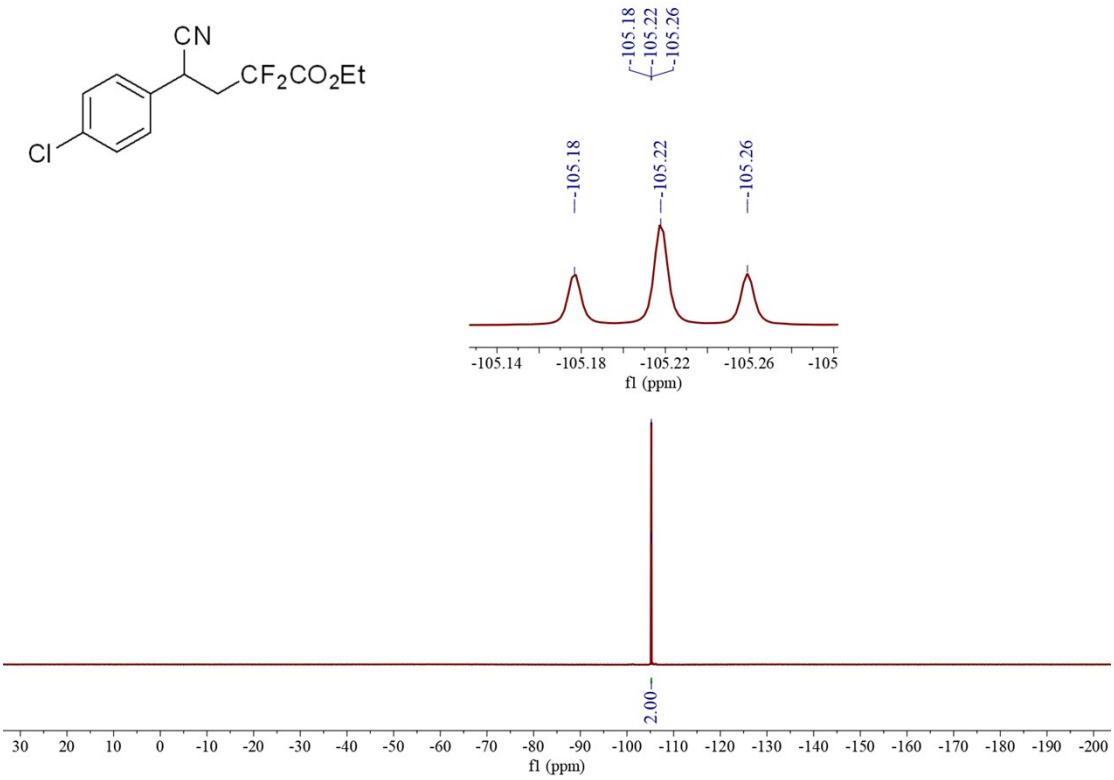
^{13}C NMR Spectrum of **4l**



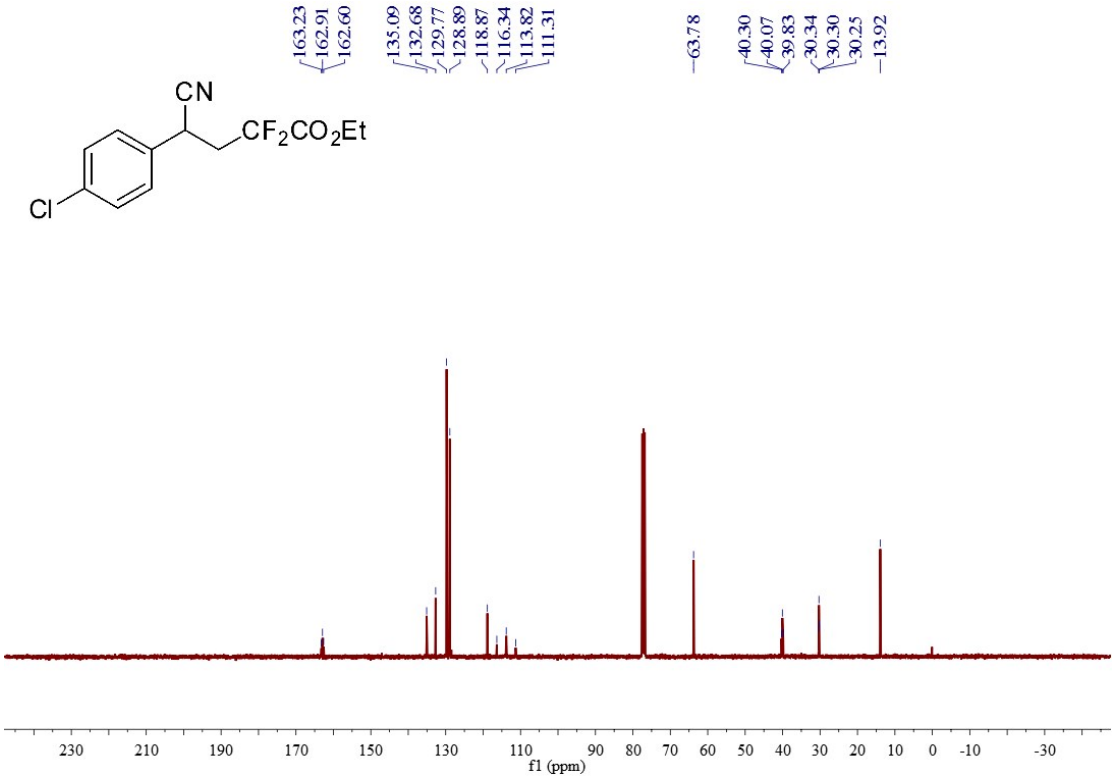
^{1}H NMR Spectrum of **4m**



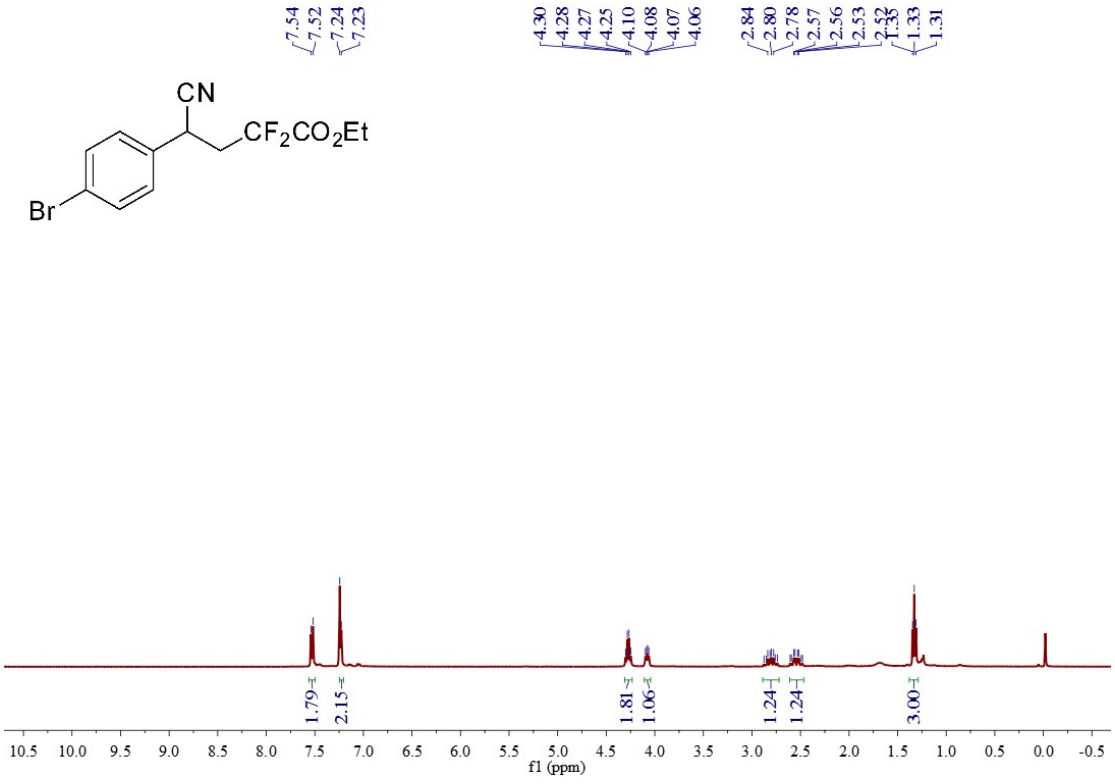
^{19}F NMR Spectrum of **4m**



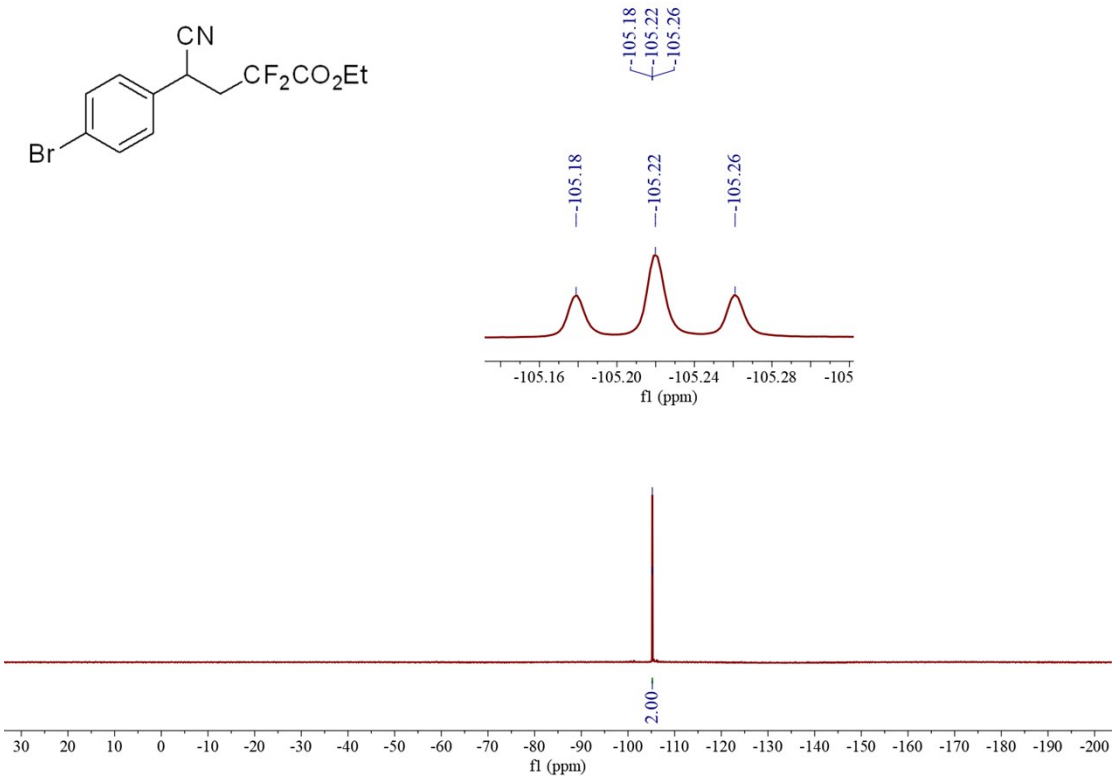
^{13}C NMR Spectrum of **4m**



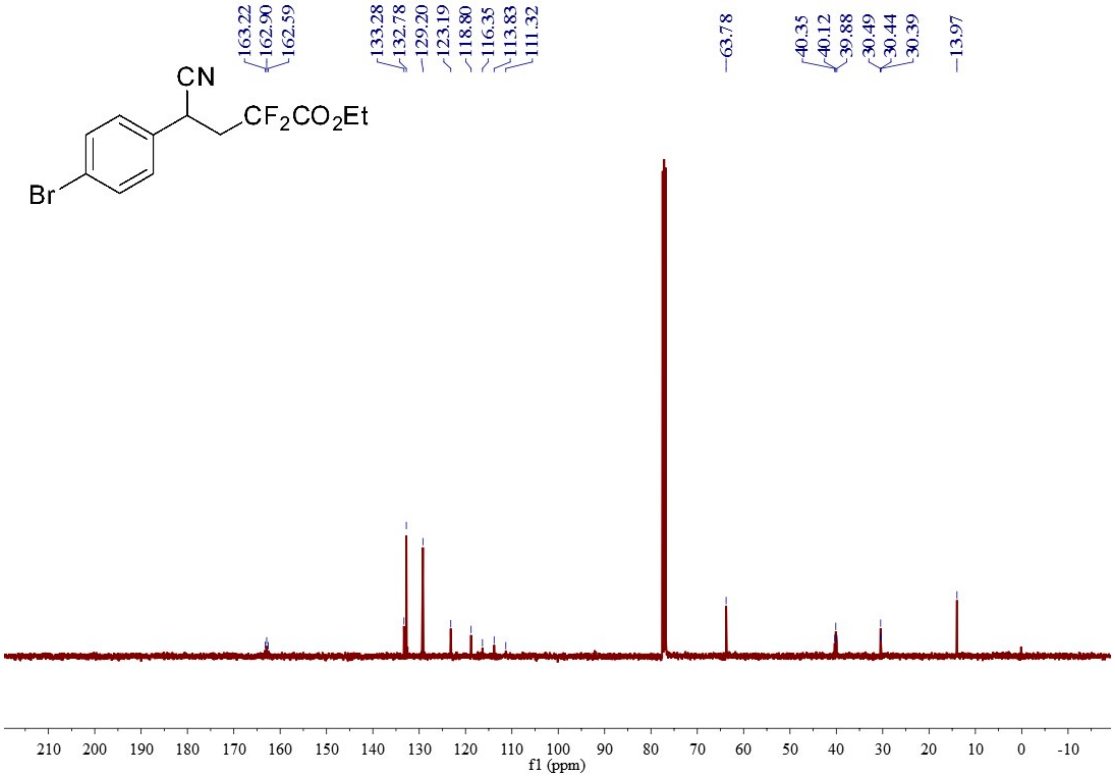
^{1}H NMR Spectrum of **4n**



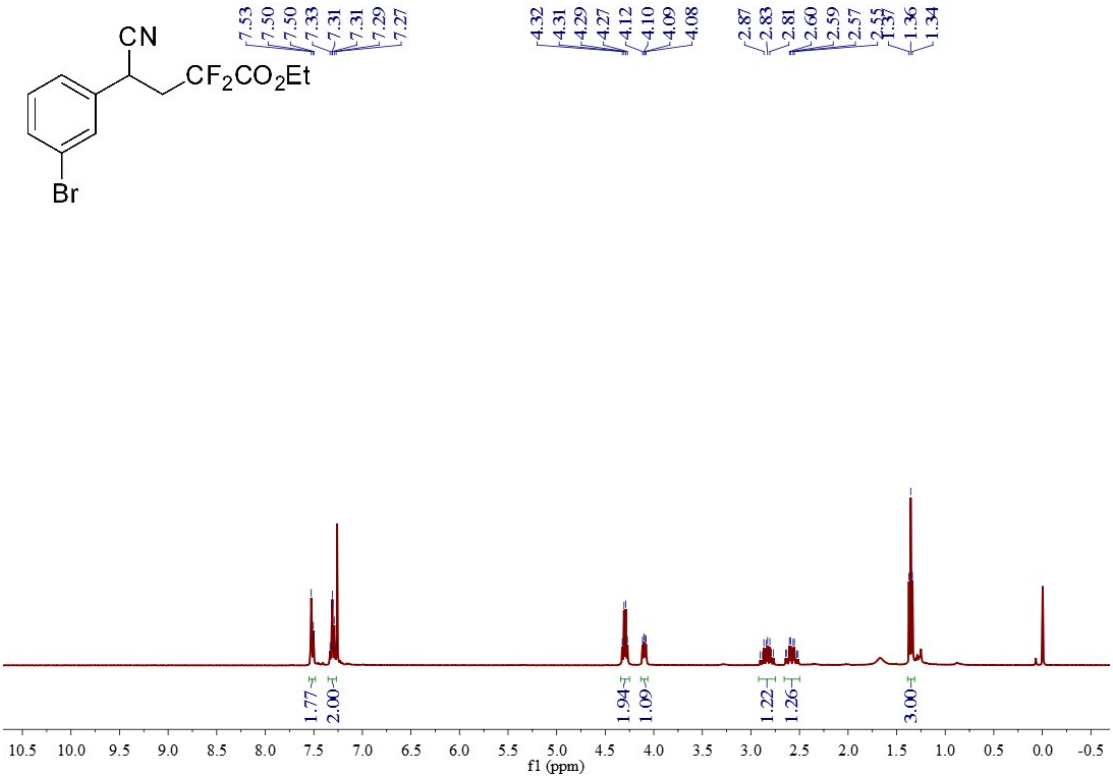
^{19}F NMR Spectrum of **4n**



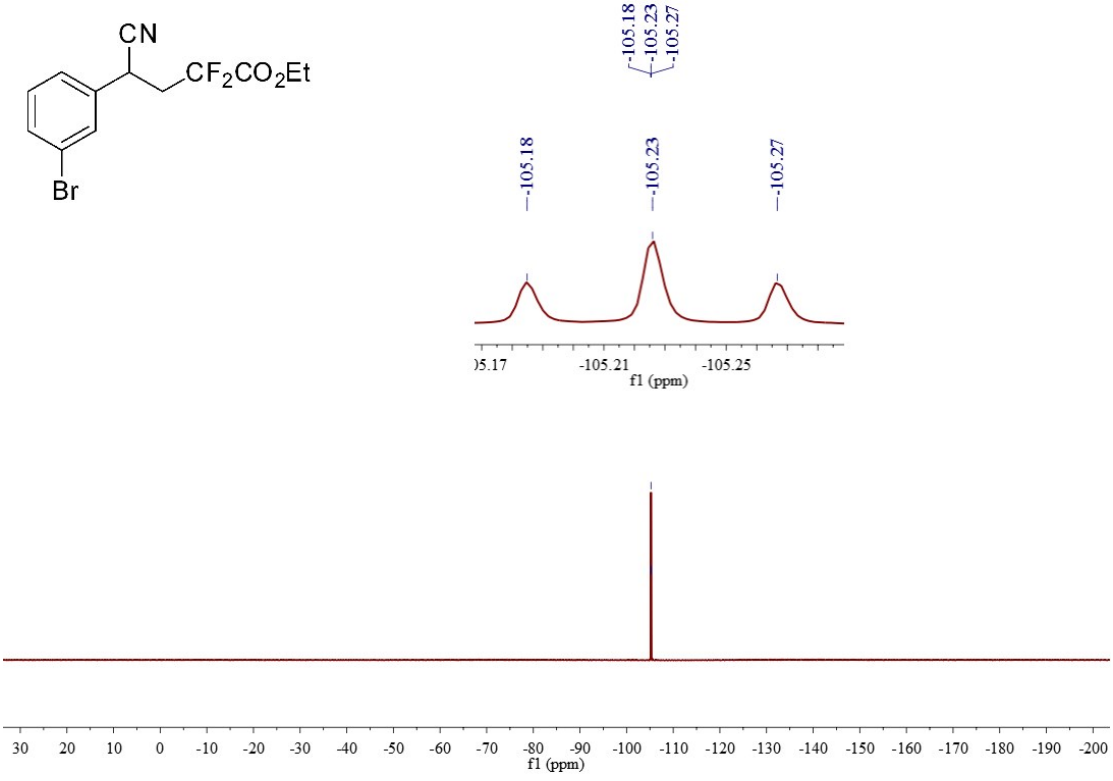
^{13}C NMR Spectrum of **4n**



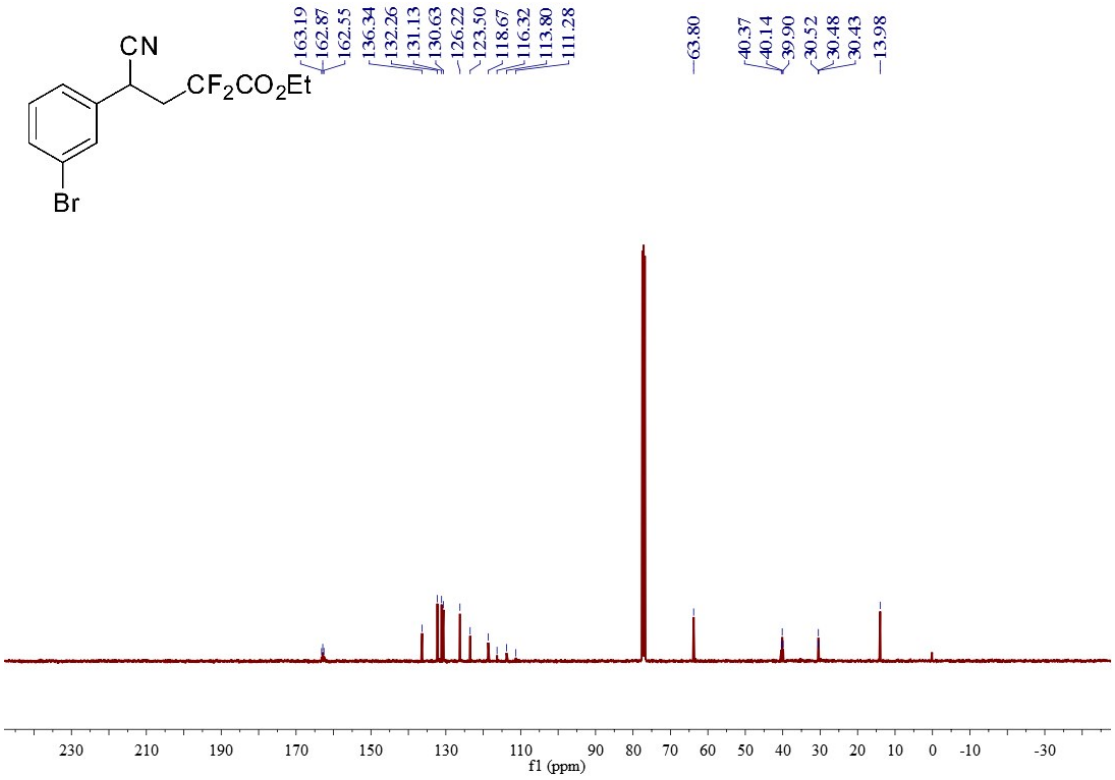
^{1}H NMR Spectrum of **4o**



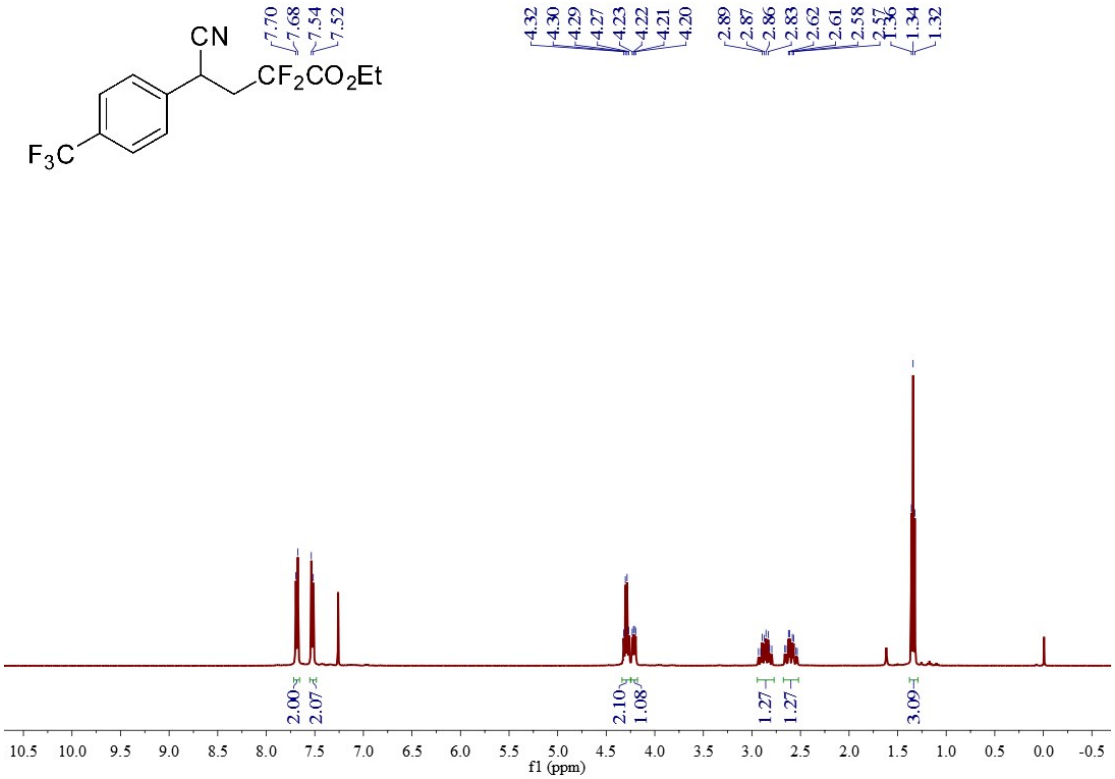
^{19}F NMR Spectrum of **4o**



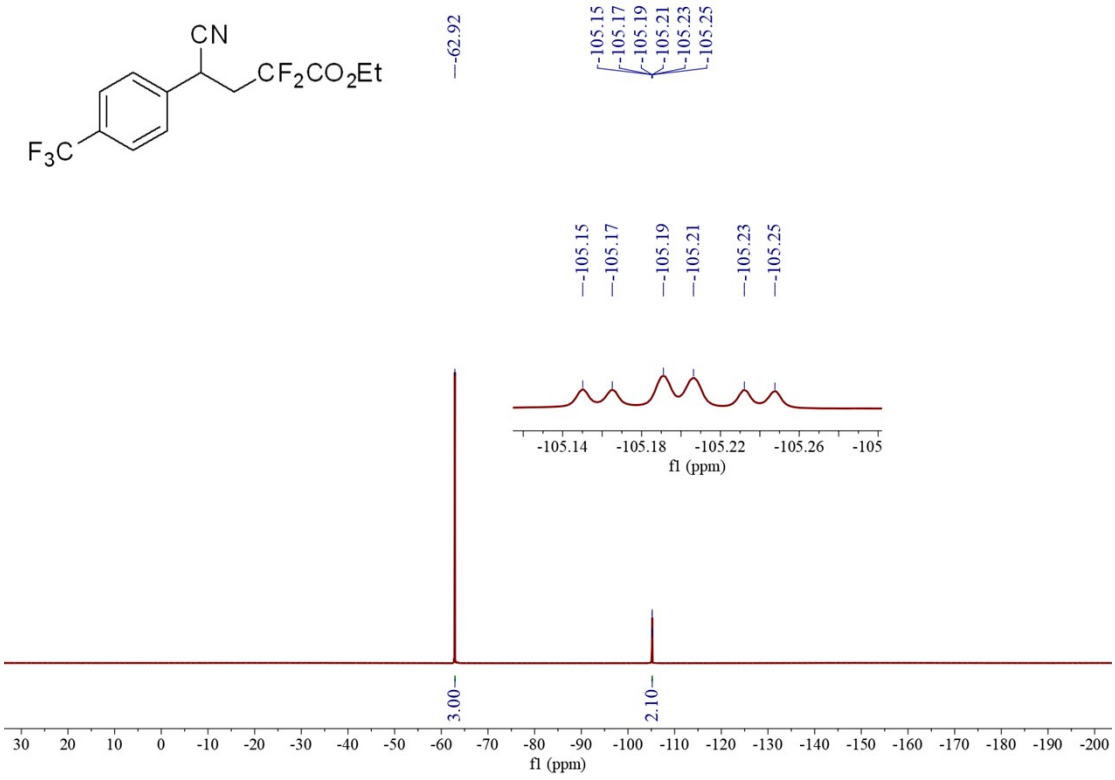
^{13}C NMR Spectrum of **4o**



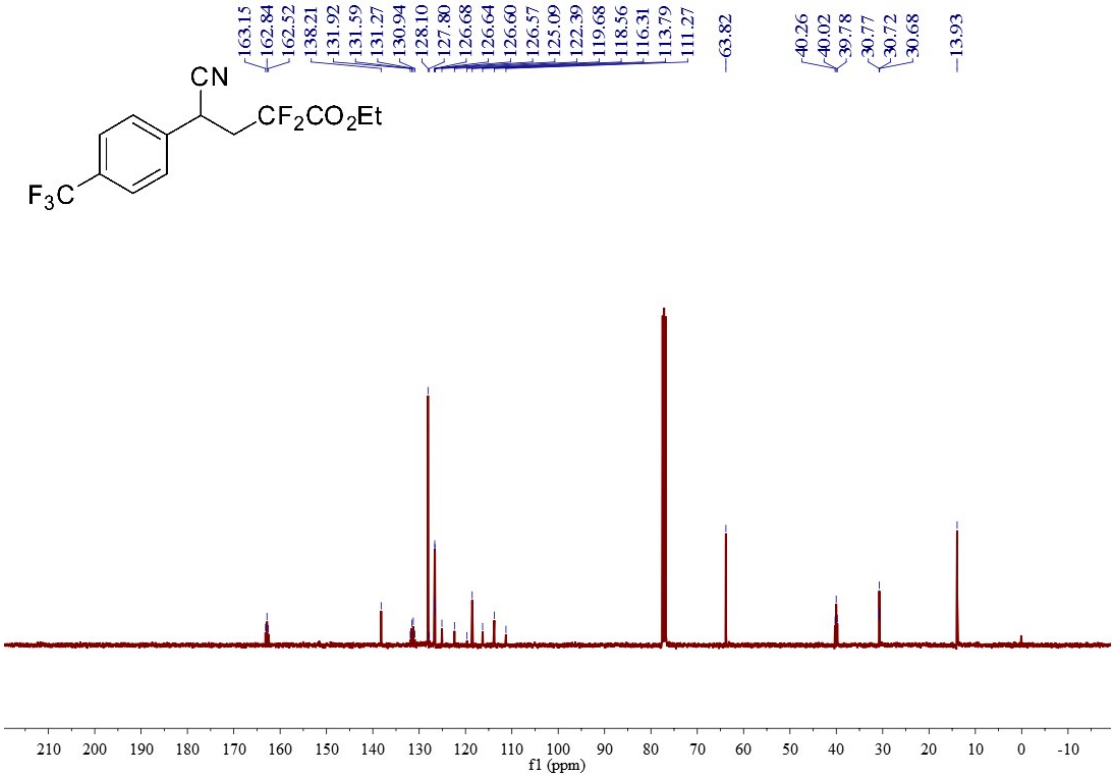
^{1}H NMR Spectrum of **4p**



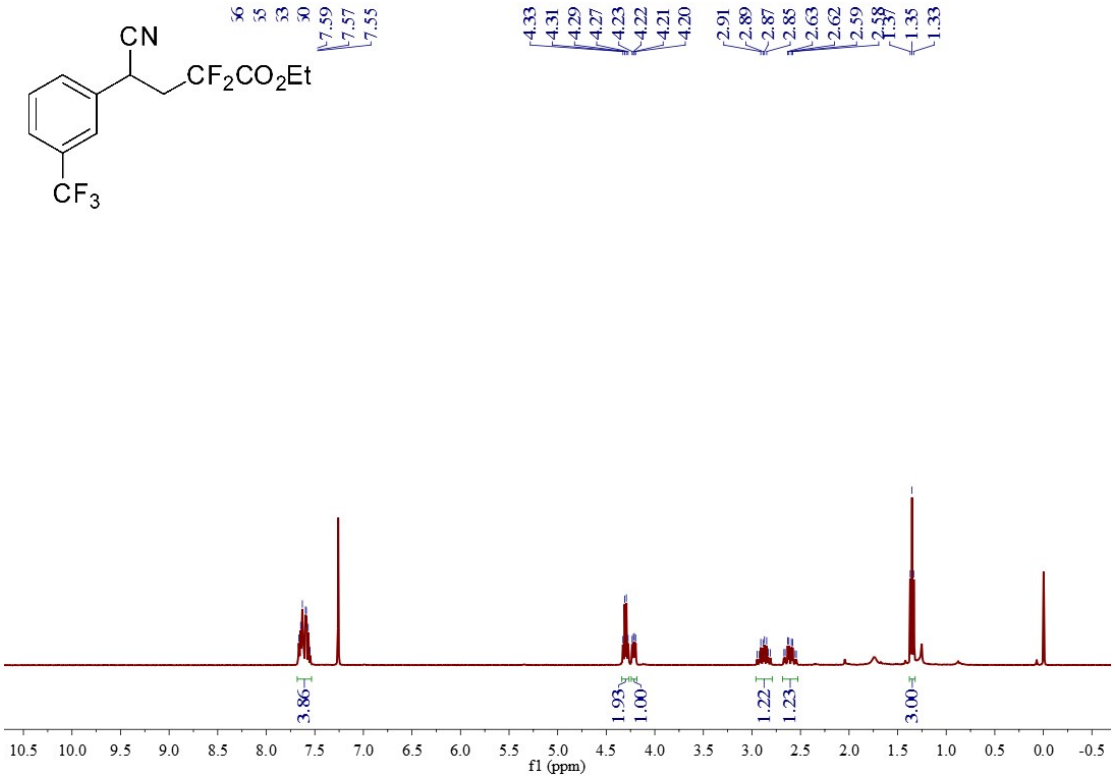
^{19}F NMR Spectrum of **4p**



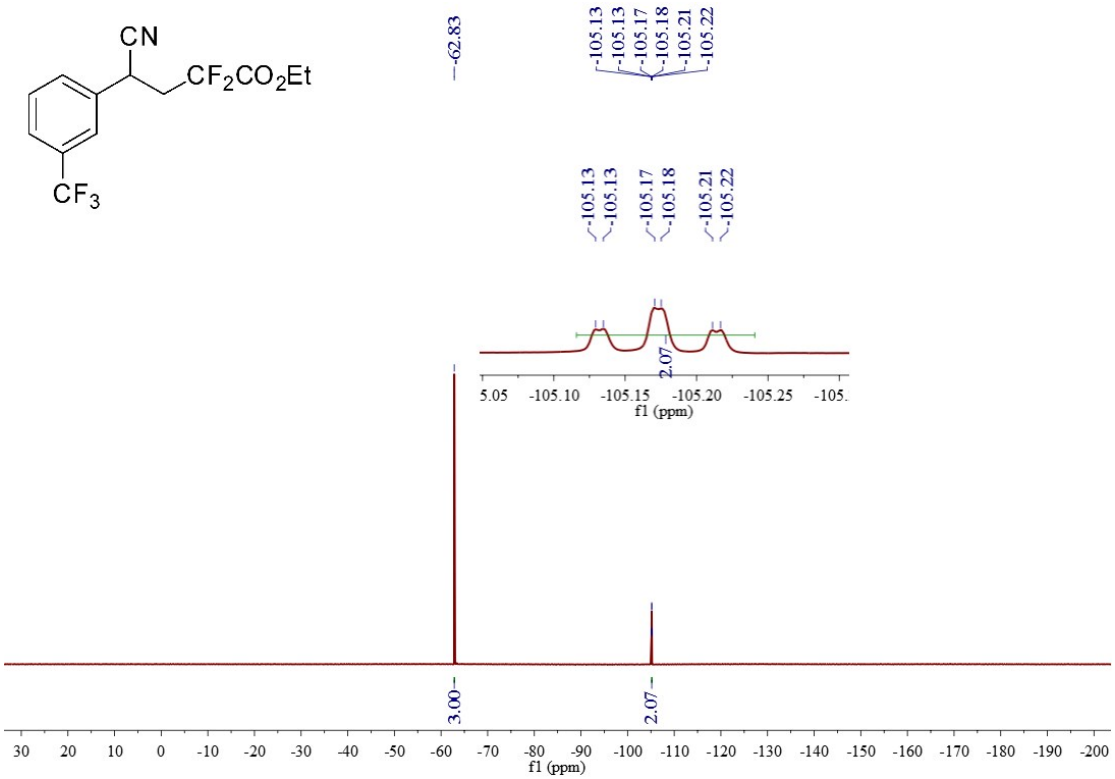
^{13}C NMR Spectrum of **4p**



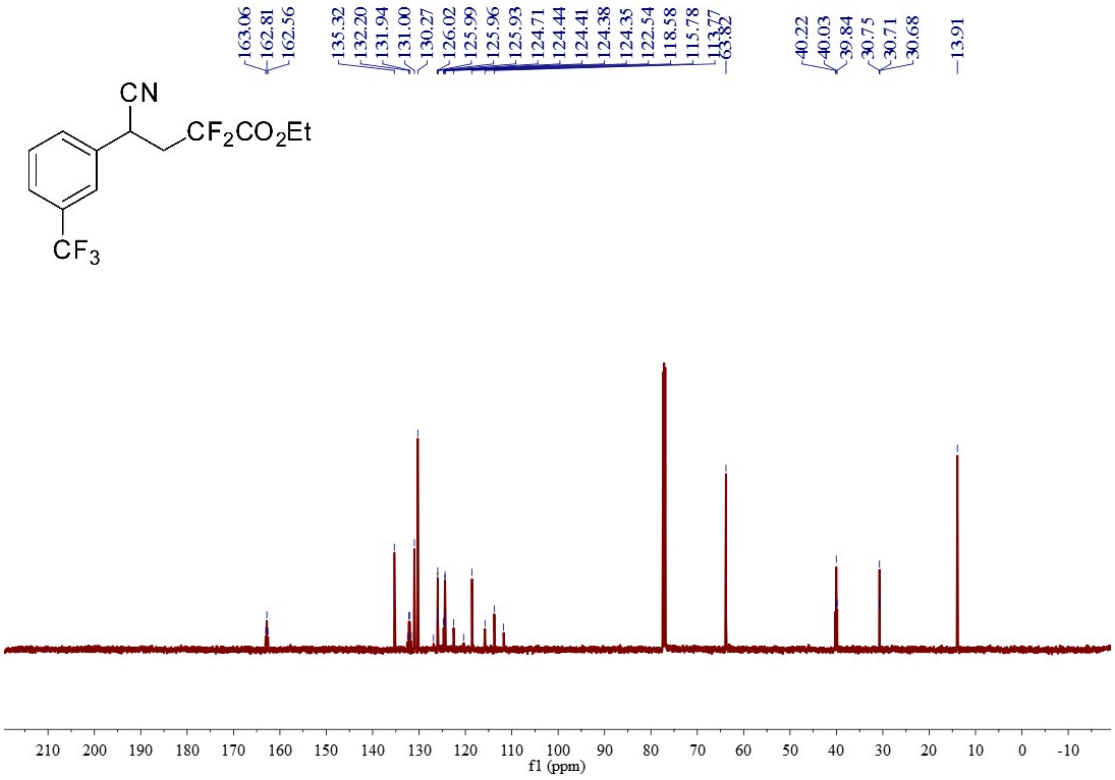
^{1}H NMR Spectrum of **4q**



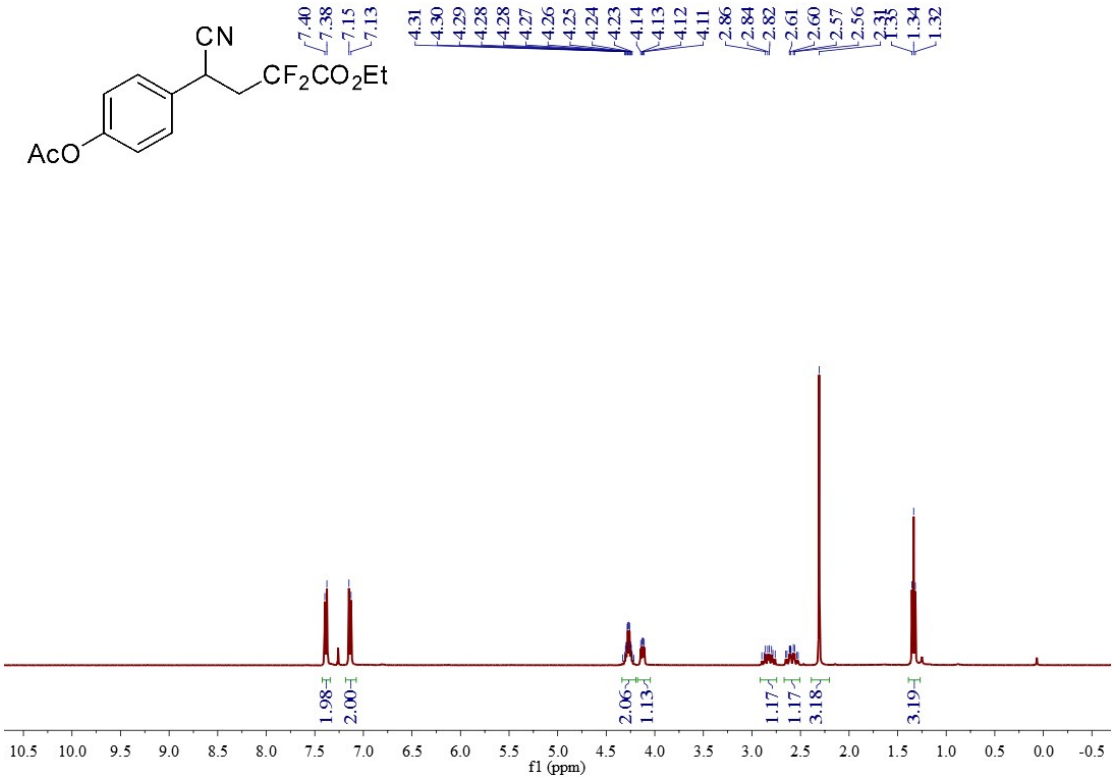
^{19}F NMR Spectrum of **4q**



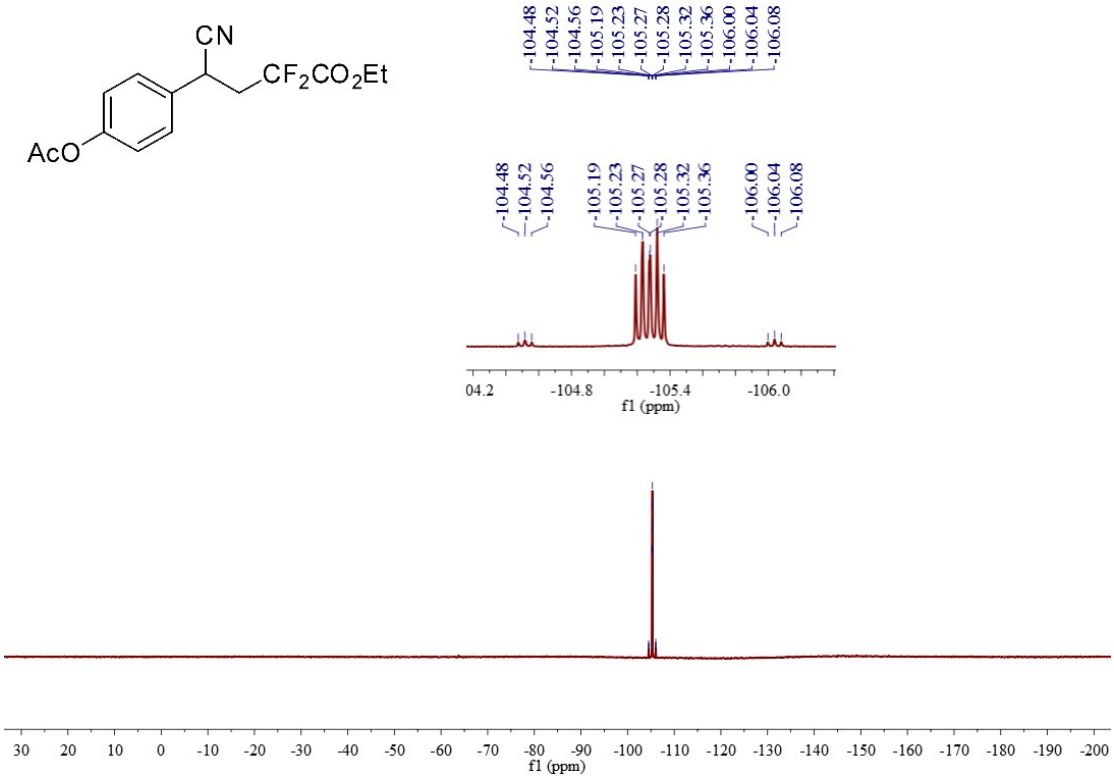
^{13}C NMR Spectrum of **4q**



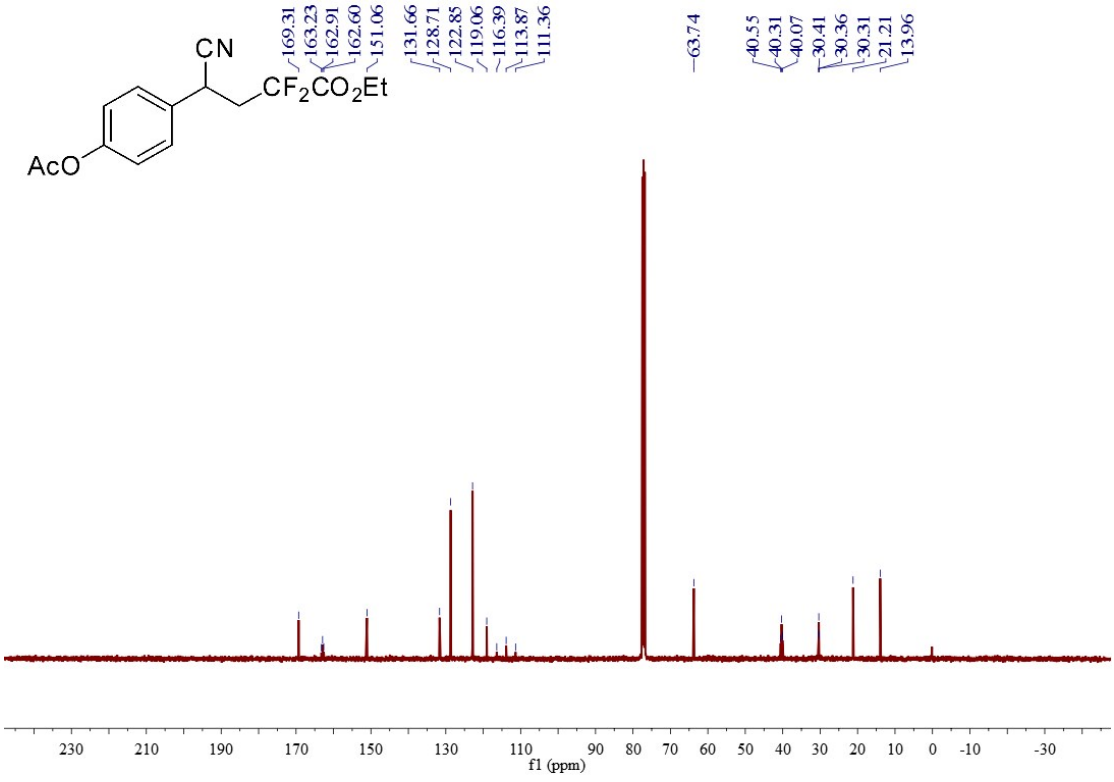
^{1}H NMR Spectrum of **4r**



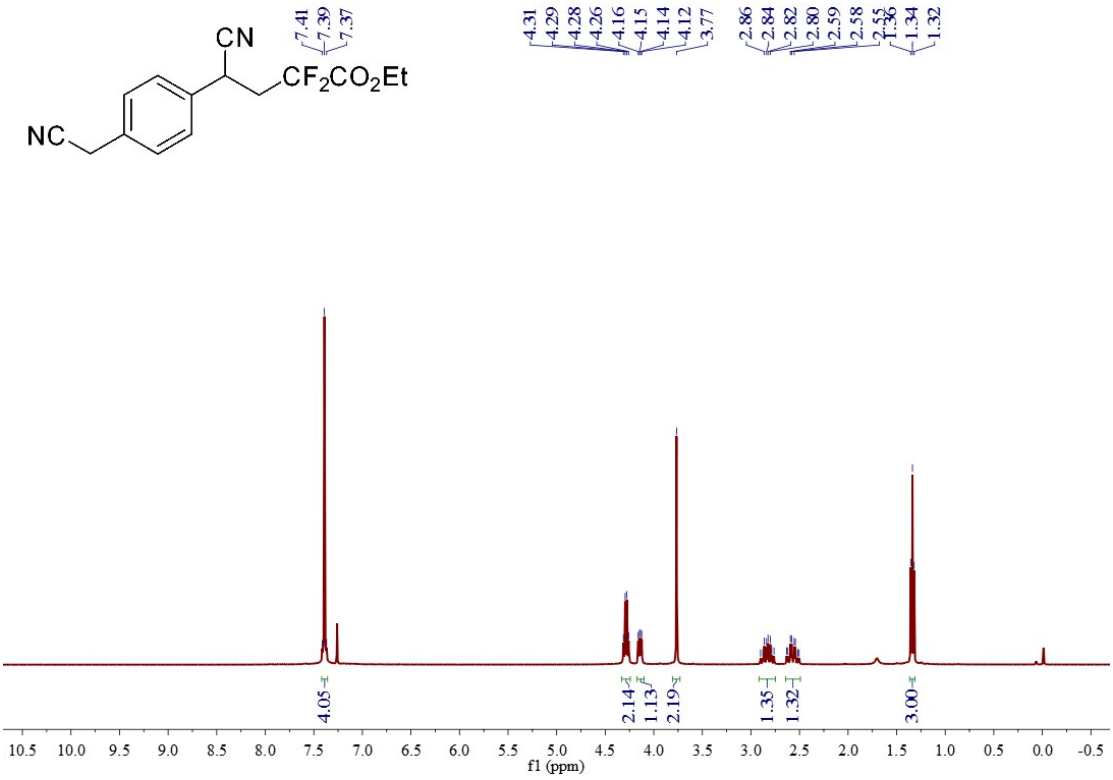
^{19}F NMR Spectrum of **4r**



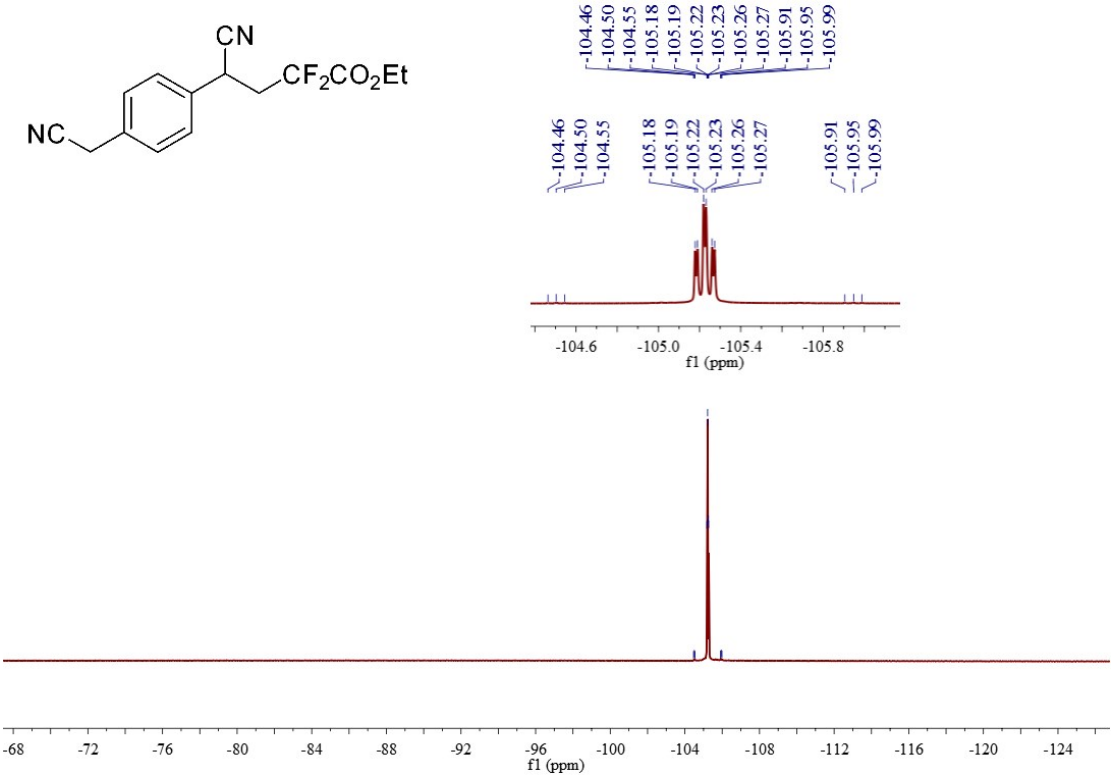
^{13}C NMR Spectrum of **4r**



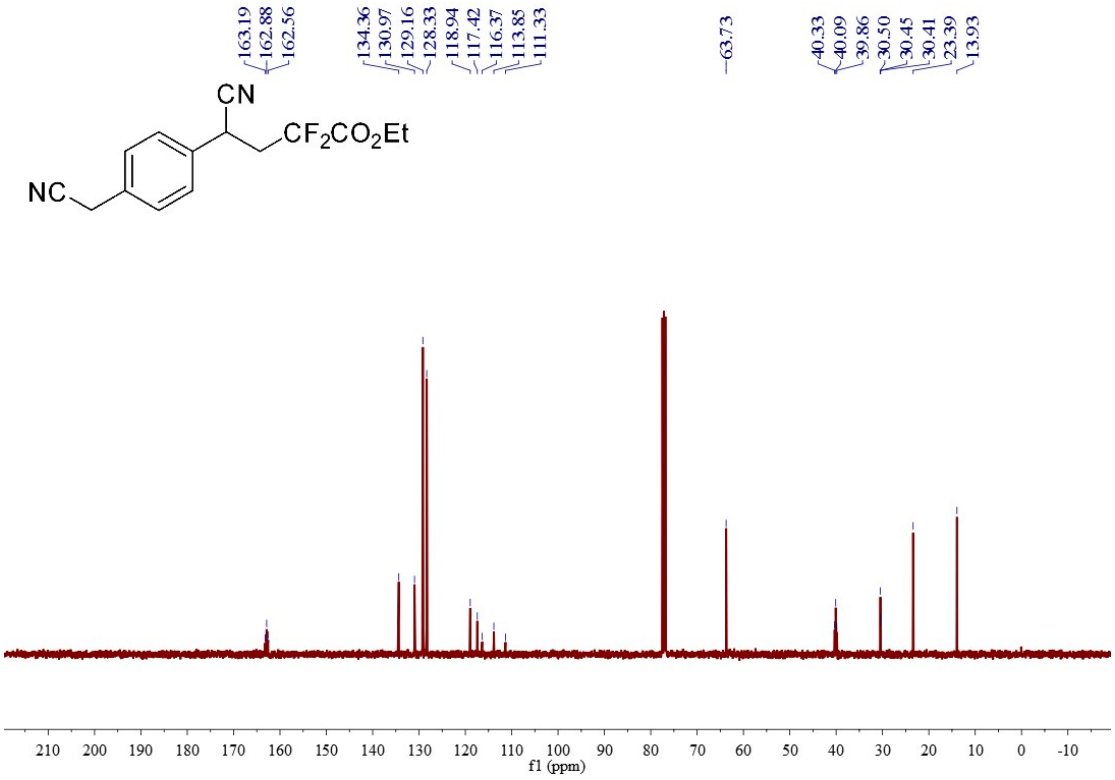
^{1}H NMR Spectrum of **4s**



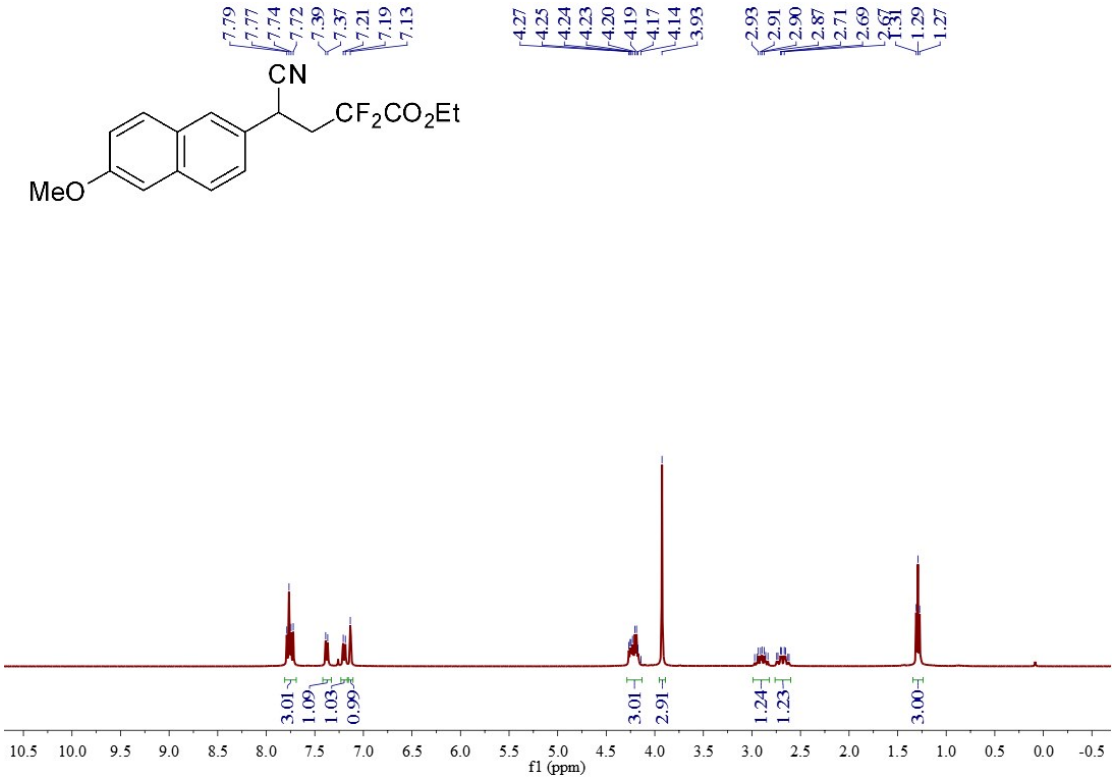
^{19}F NMR Spectrum of **4s**



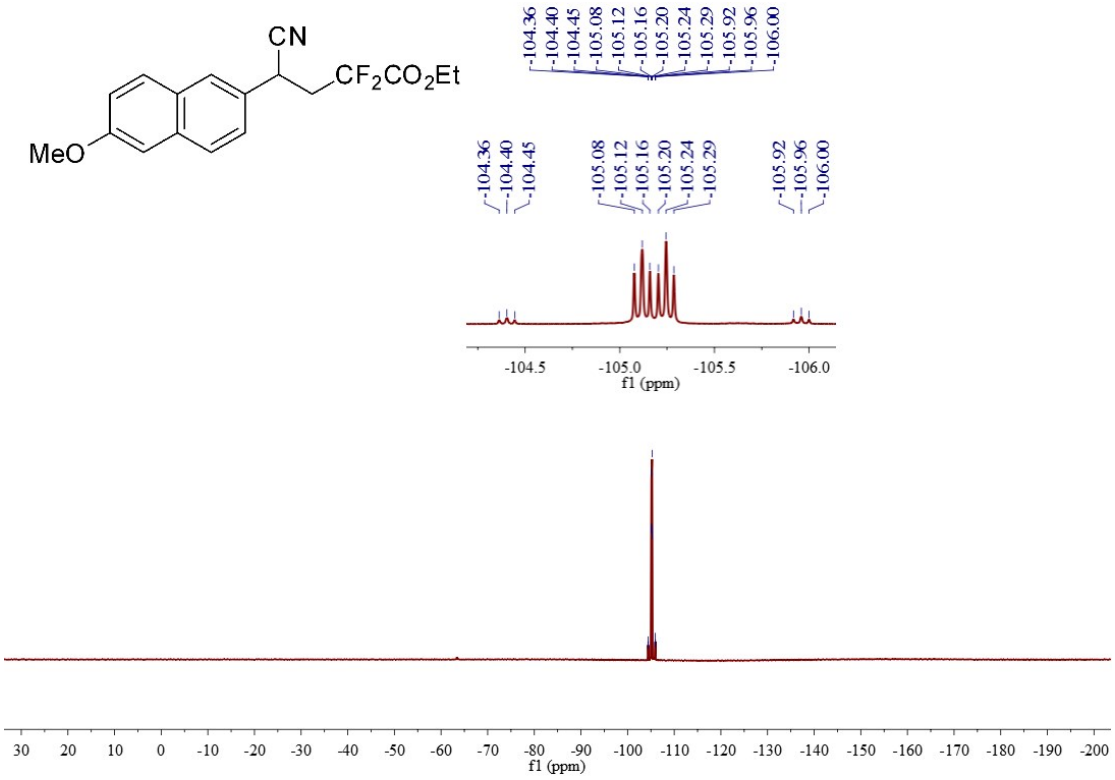
^{13}C NMR Spectrum of **4s**



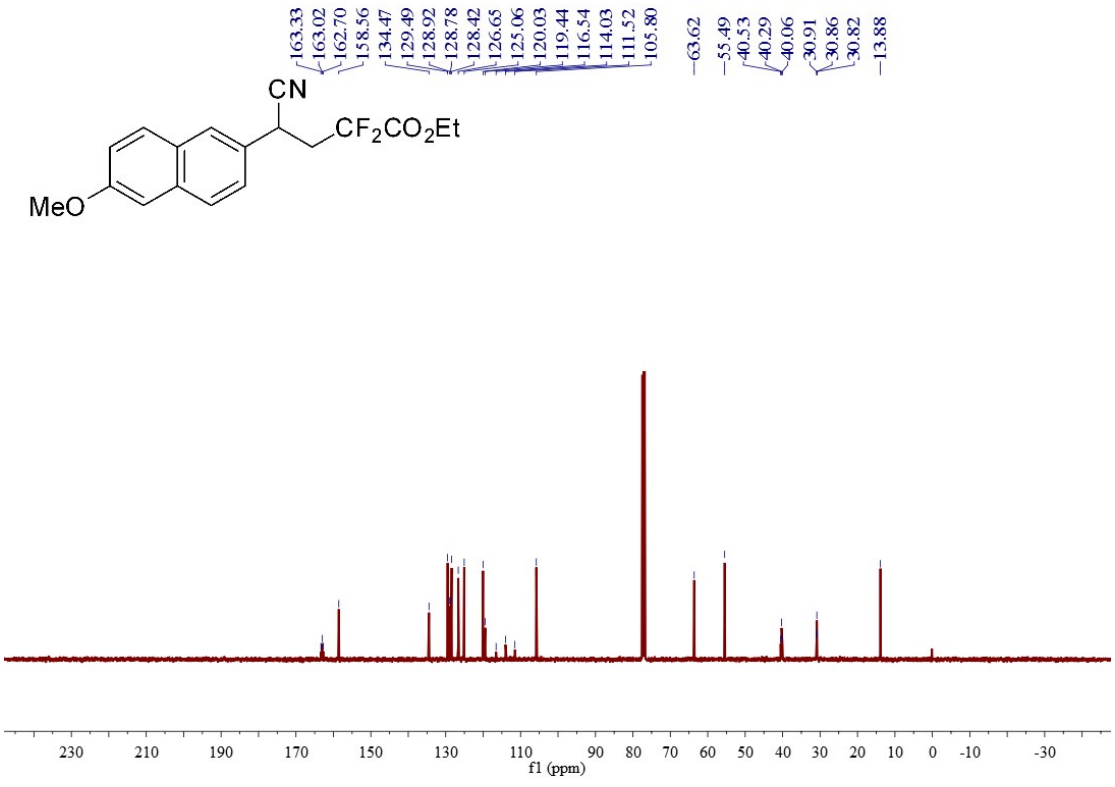
^{1}H NMR Spectrum of **4t**



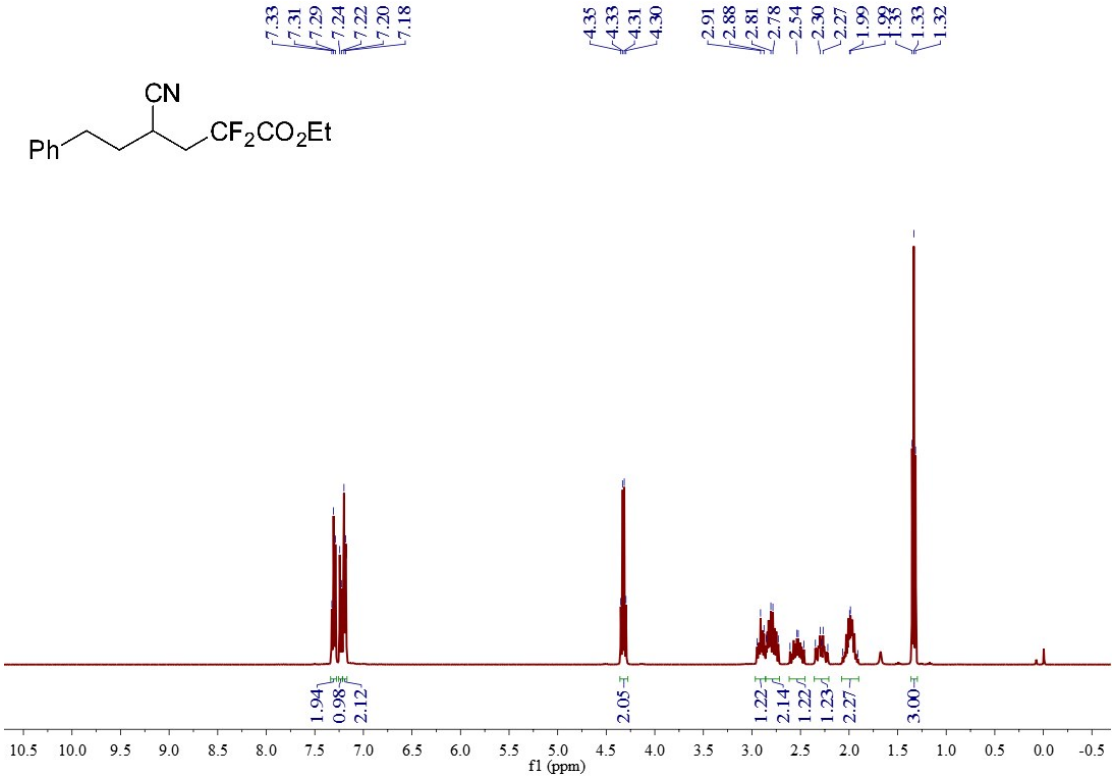
^{19}F NMR Spectrum of **4t**



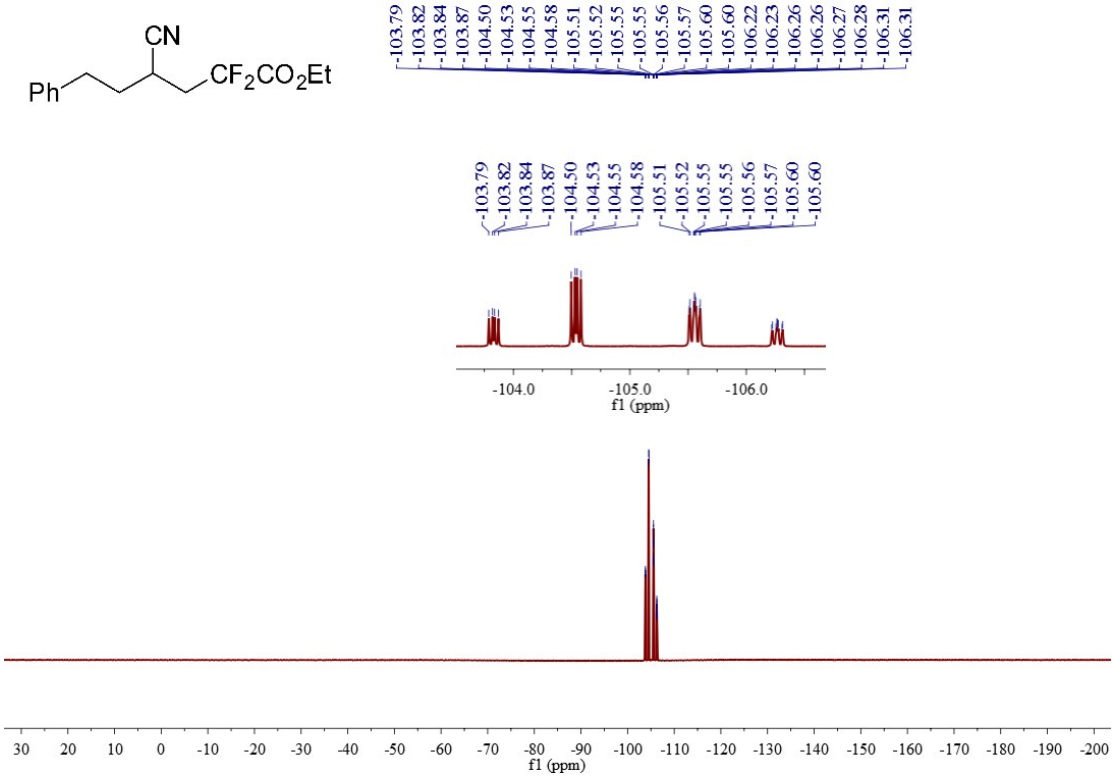
^{13}C NMR Spectrum of **4t**



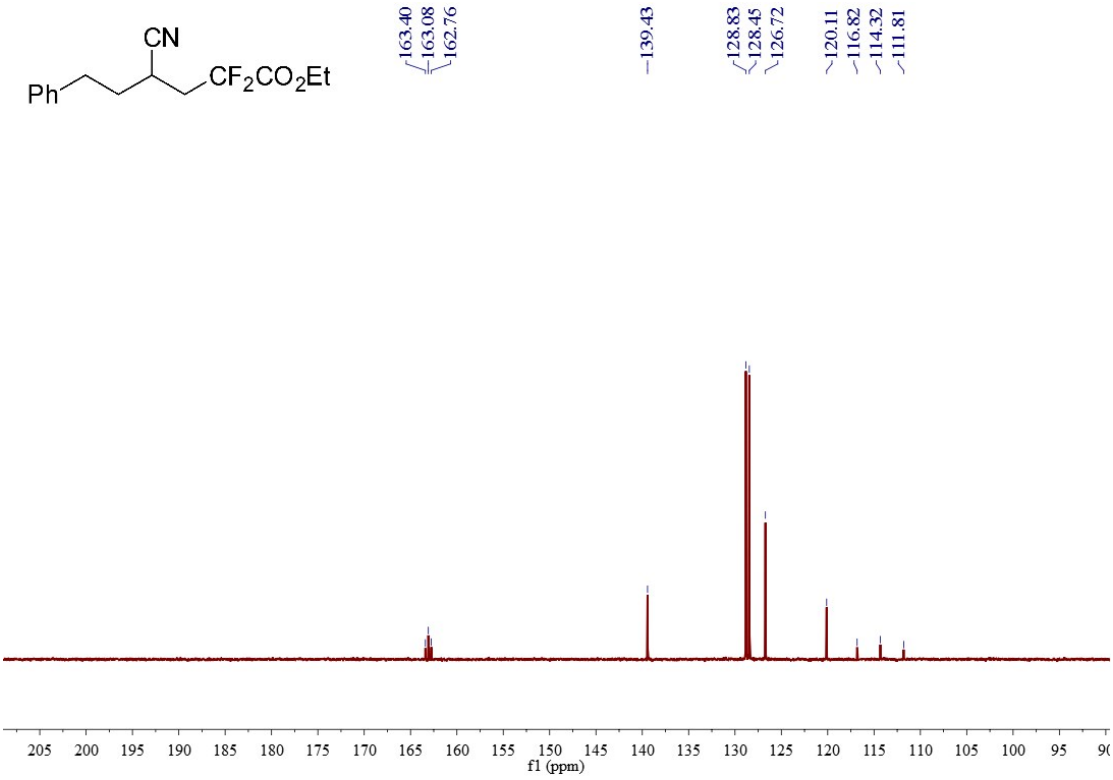
^{1}H NMR Spectrum of **4u**



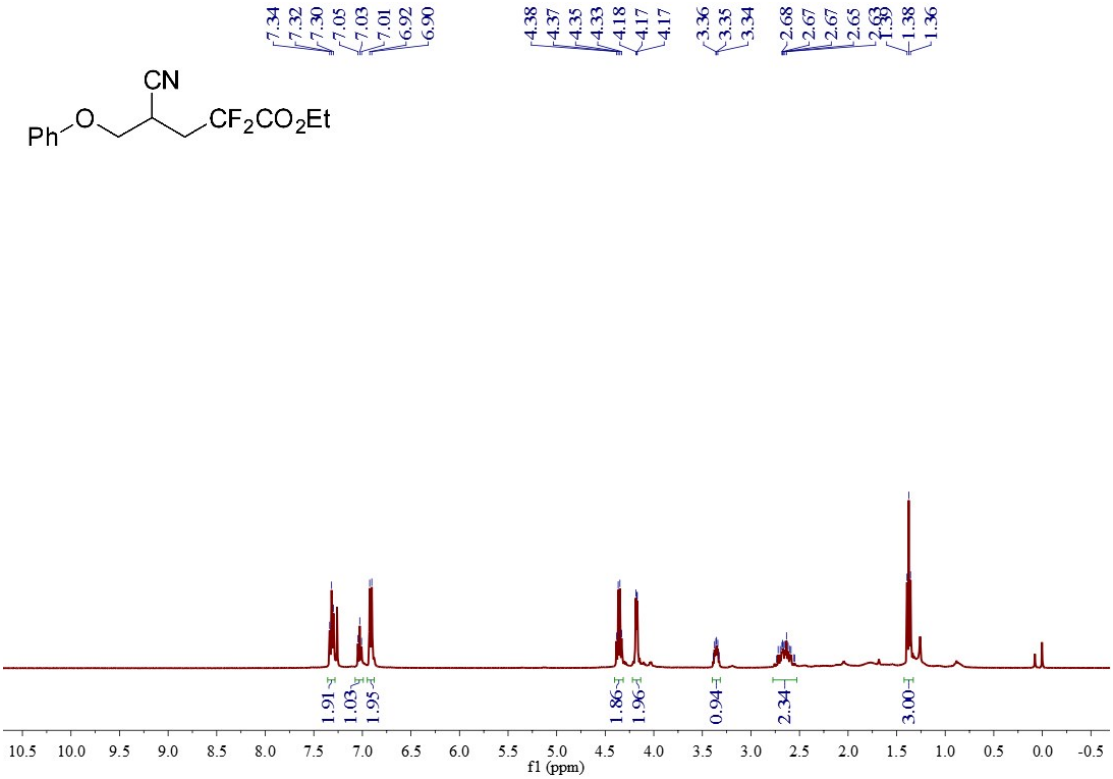
^{19}F NMR Spectrum of **4u**



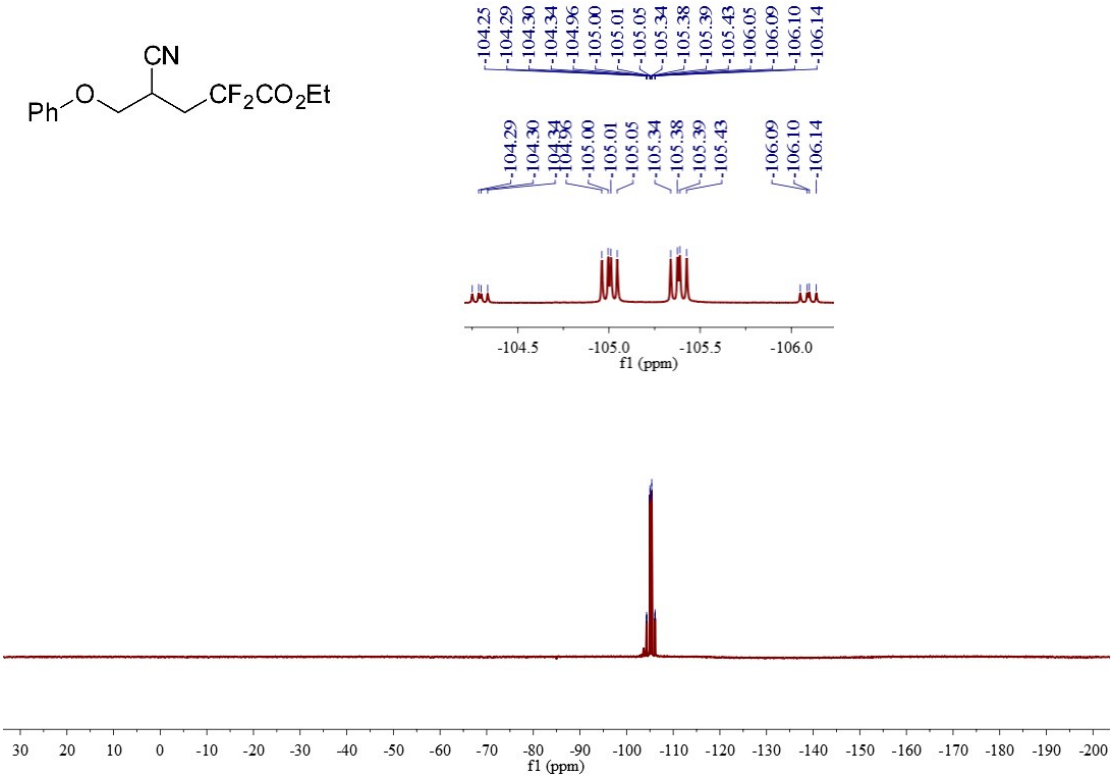
^{13}C NMR Spectrum of **4u**



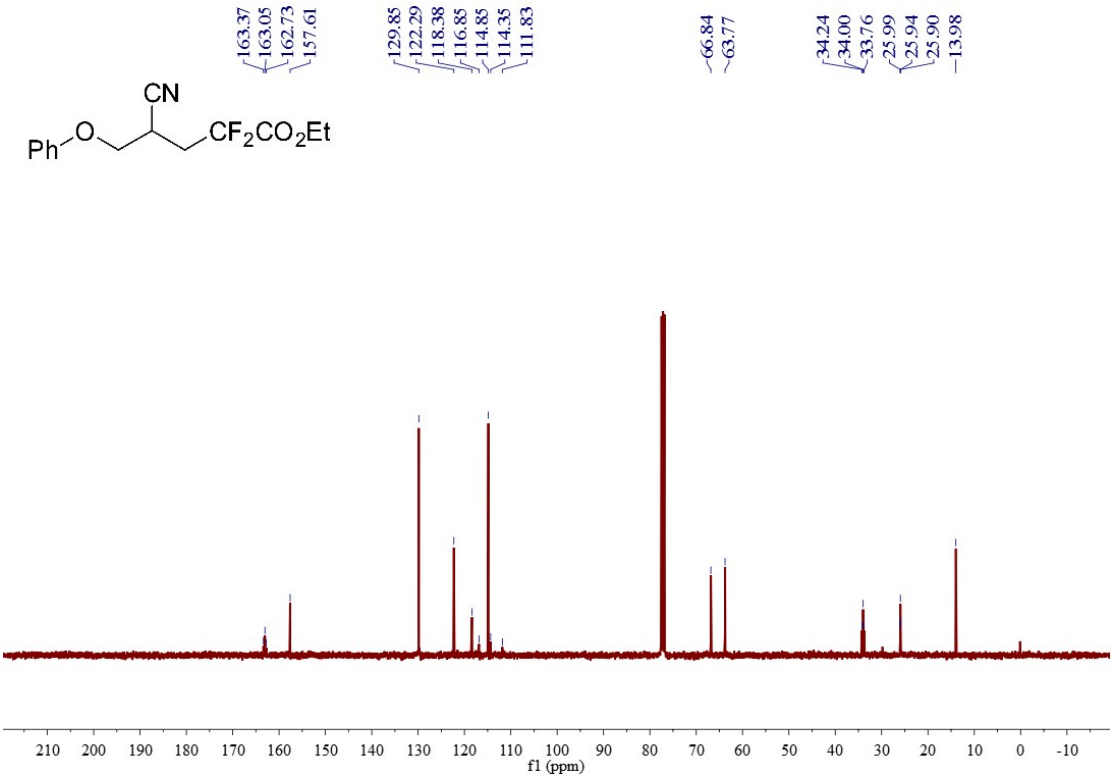
^{1}H NMR Spectrum of **4v**



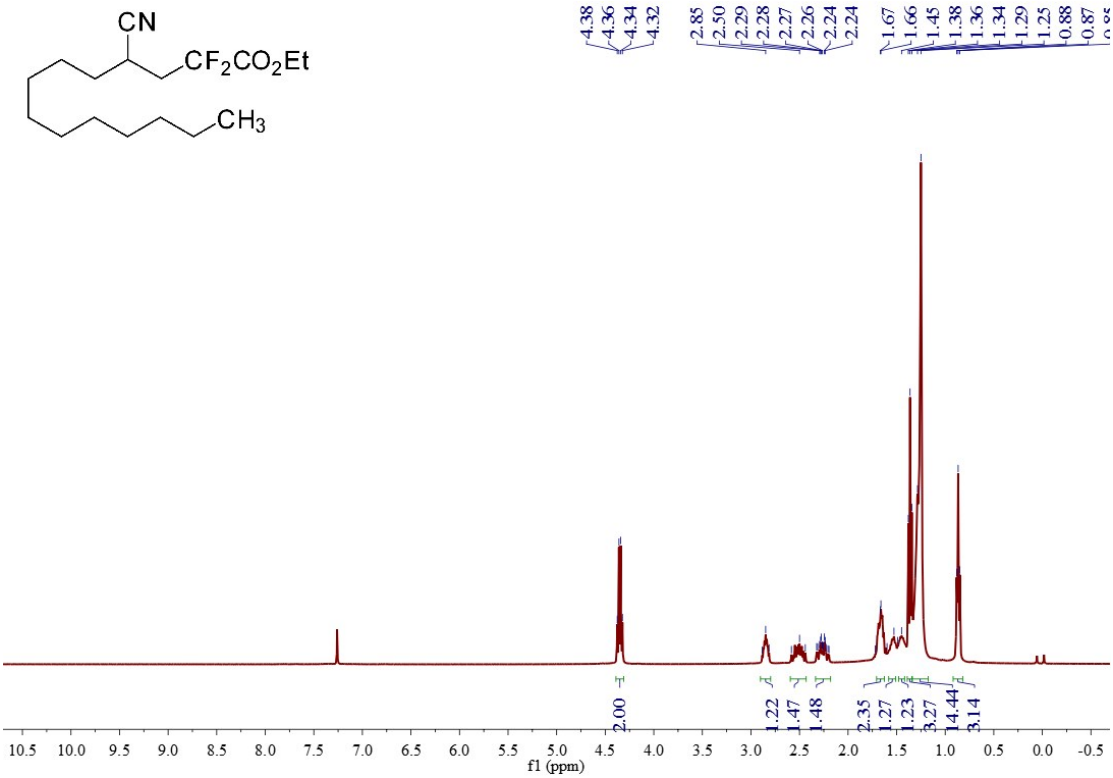
^{19}F NMR Spectrum of **4v**



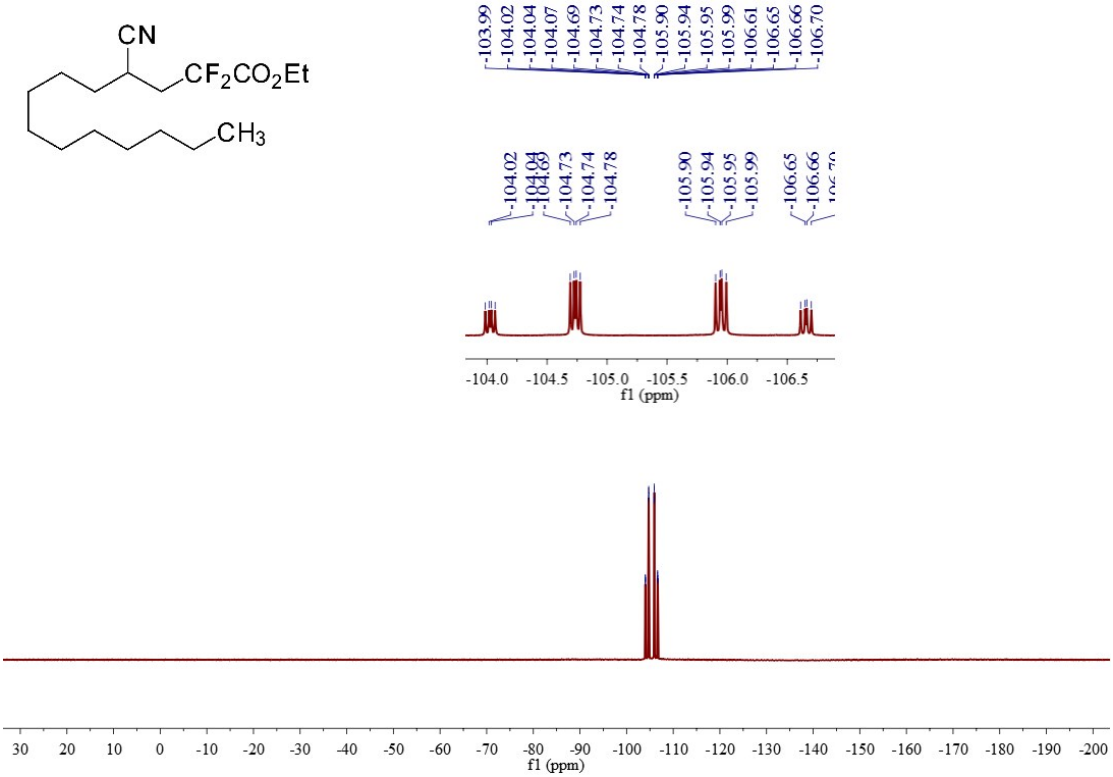
^{13}C NMR Spectrum of **4v**



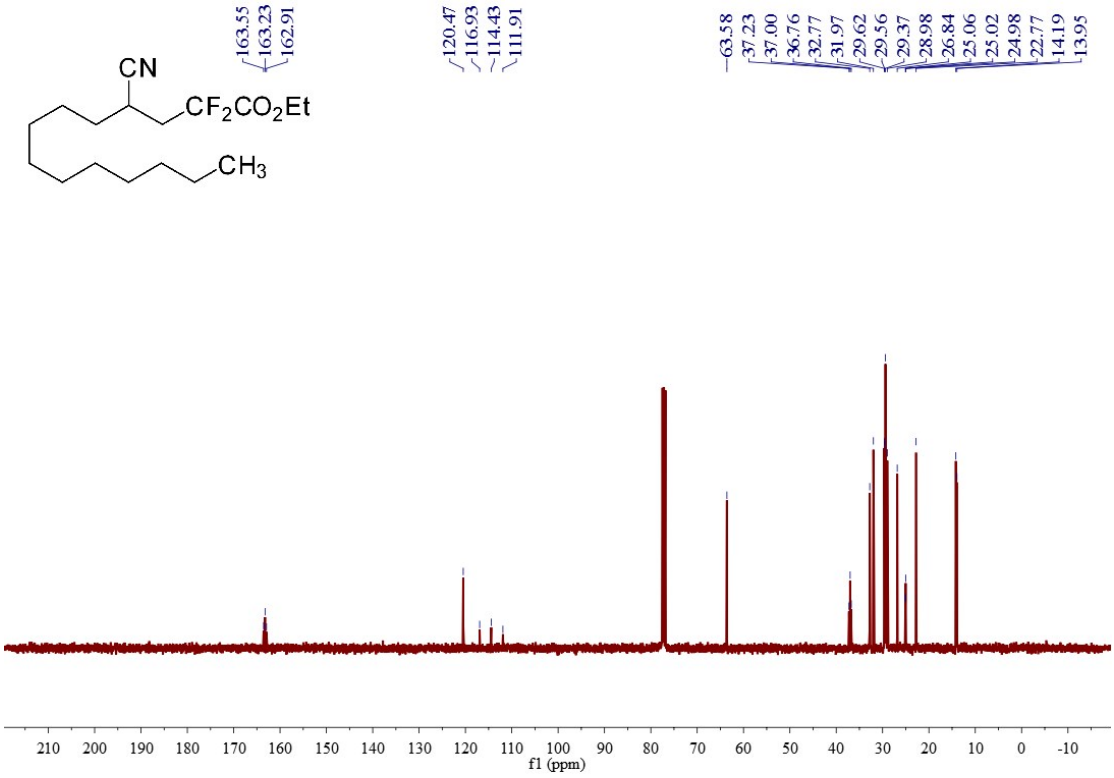
^{1}H NMR Spectrum of **4w**



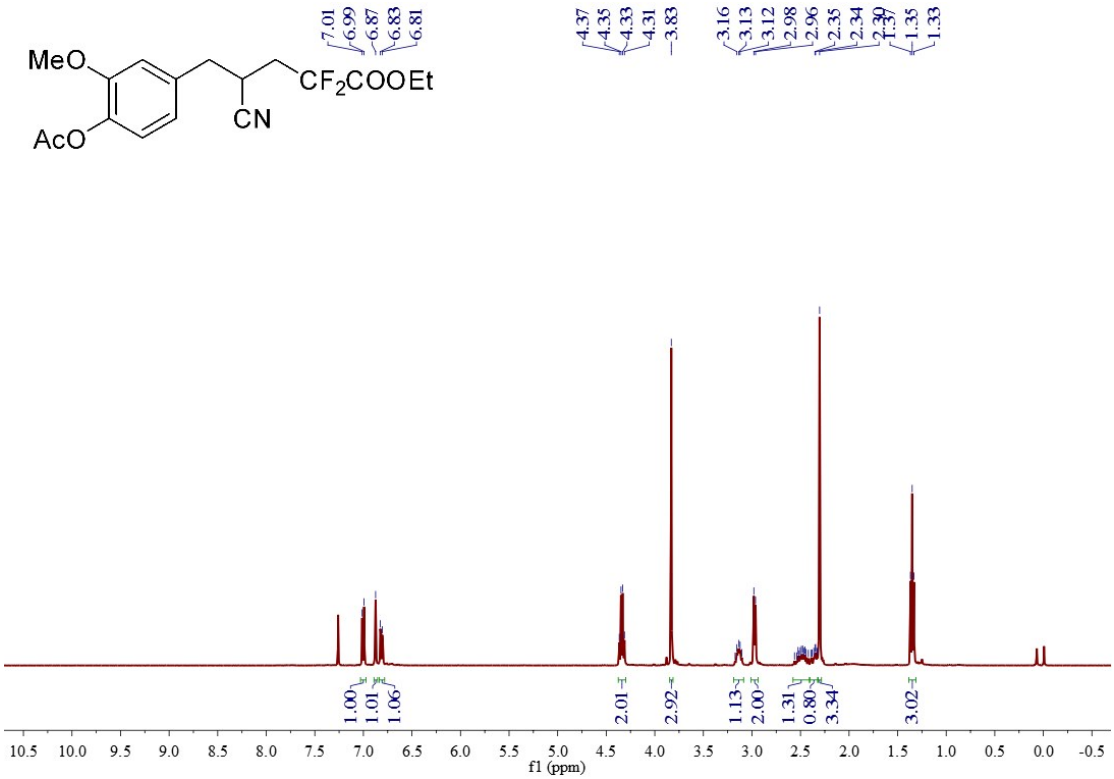
^{19}F NMR Spectrum of **4w**



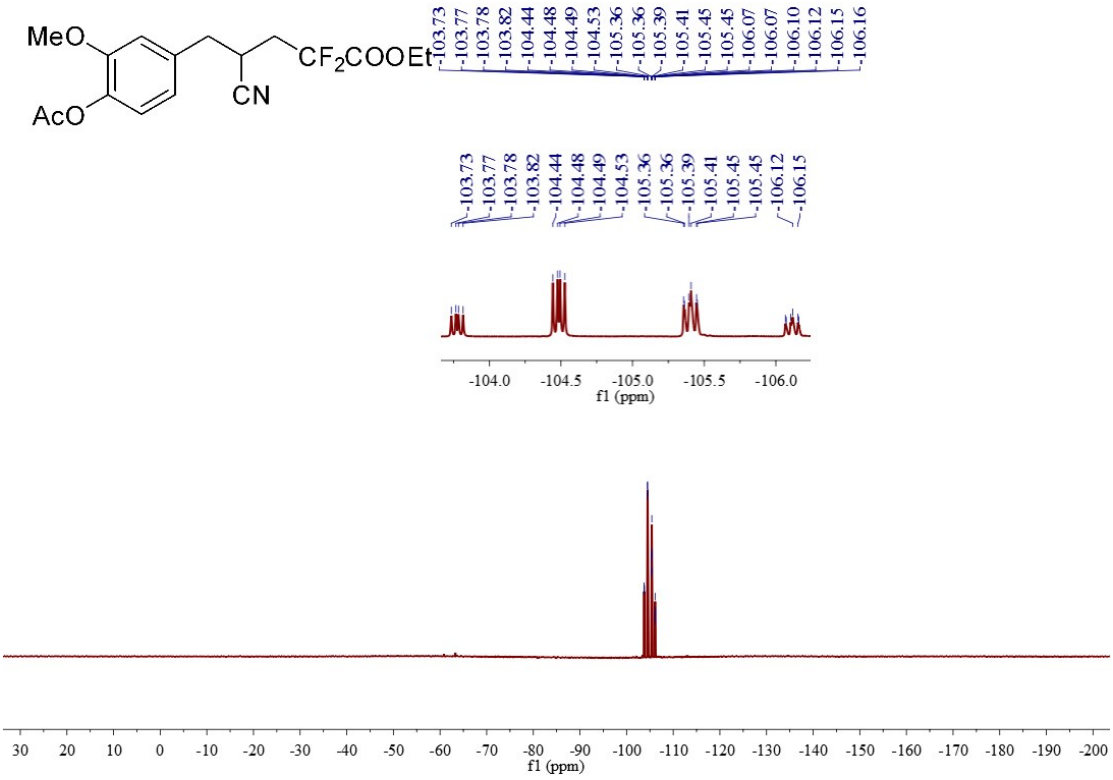
^{13}C NMR Spectrum of **4w**



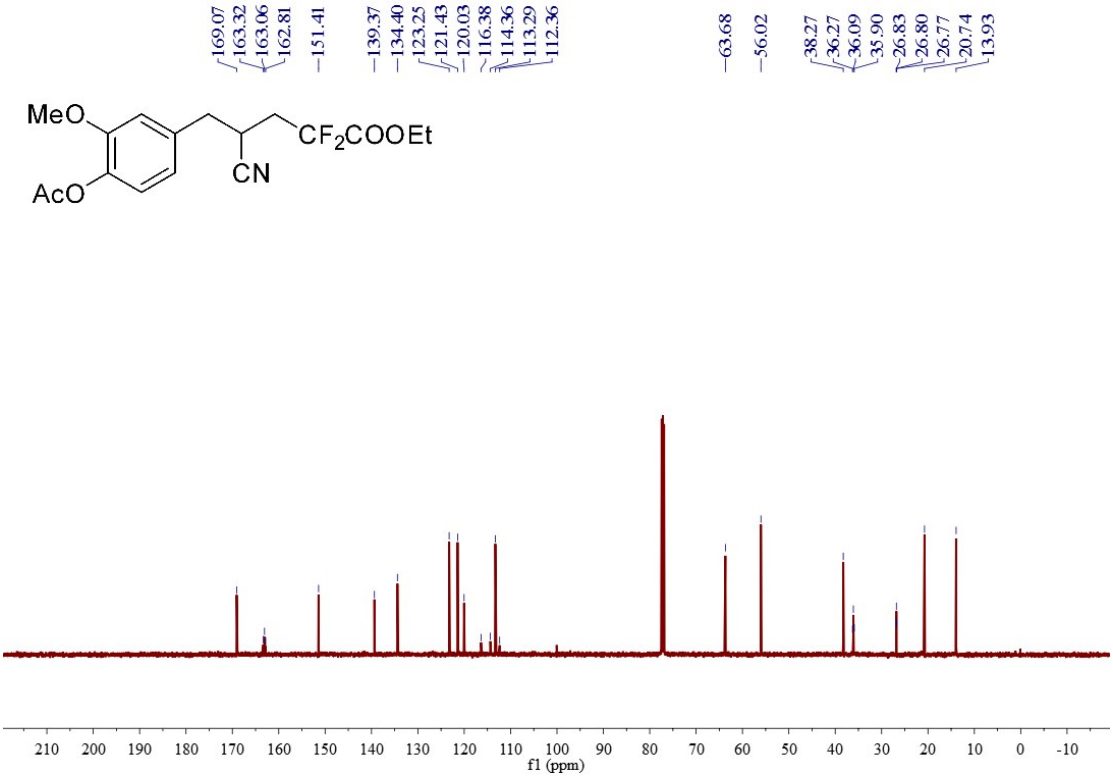
^{1}H NMR Spectrum of **4x**



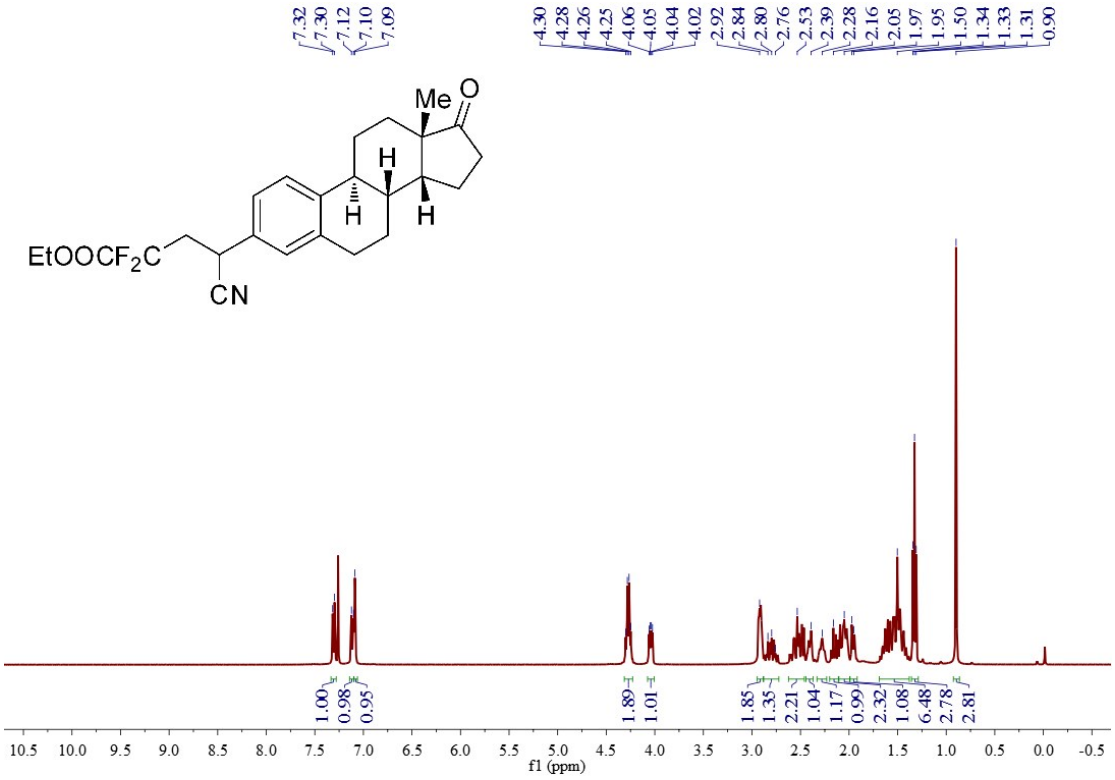
^{19}F NMR Spectrum of **4x**



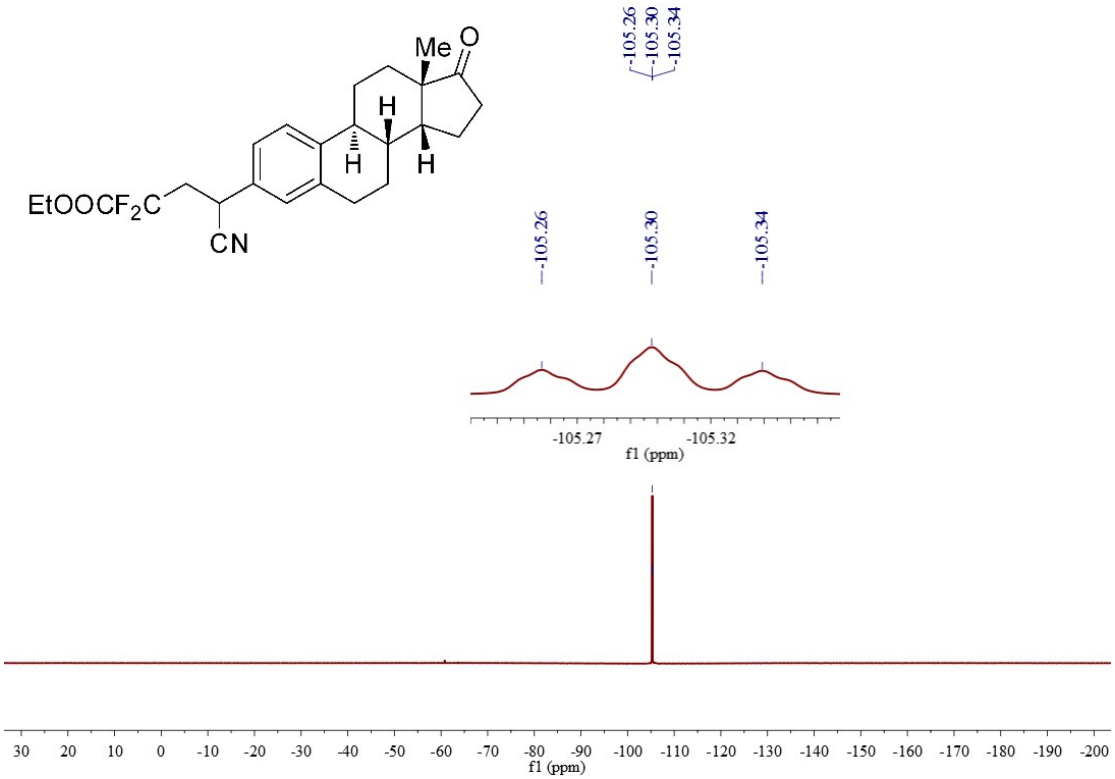
^{13}C NMR Spectrum of **4x**



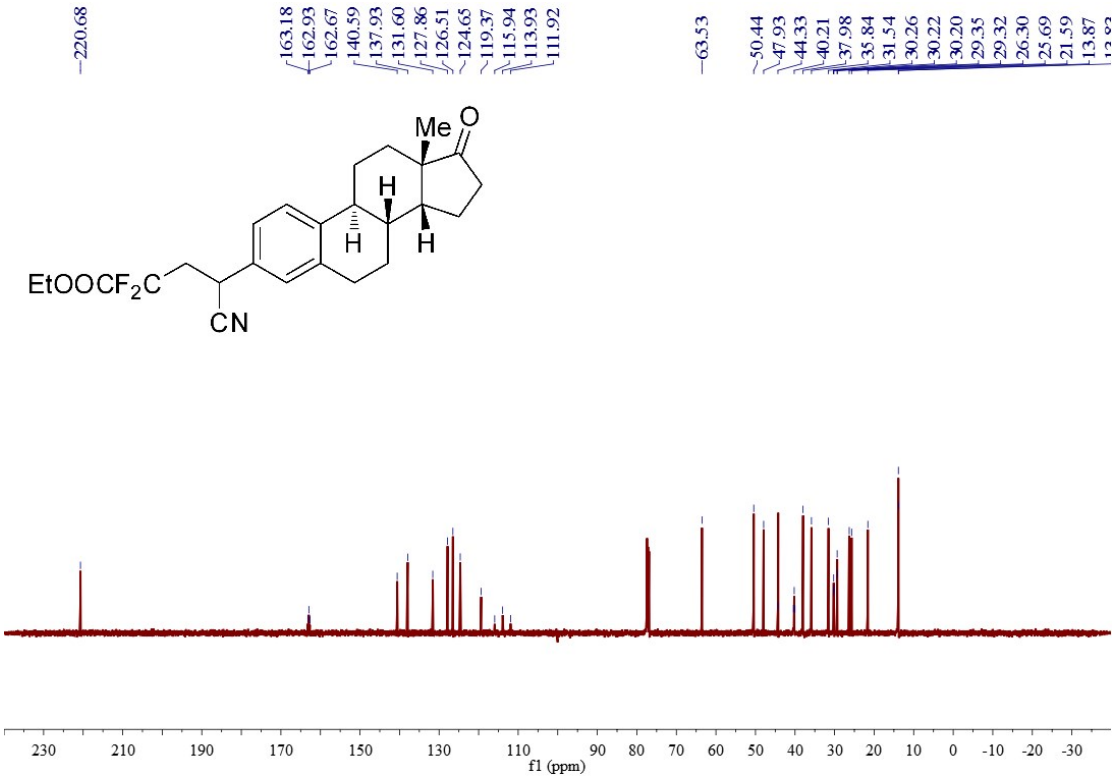
^{1}H NMR Spectrum of **4y**



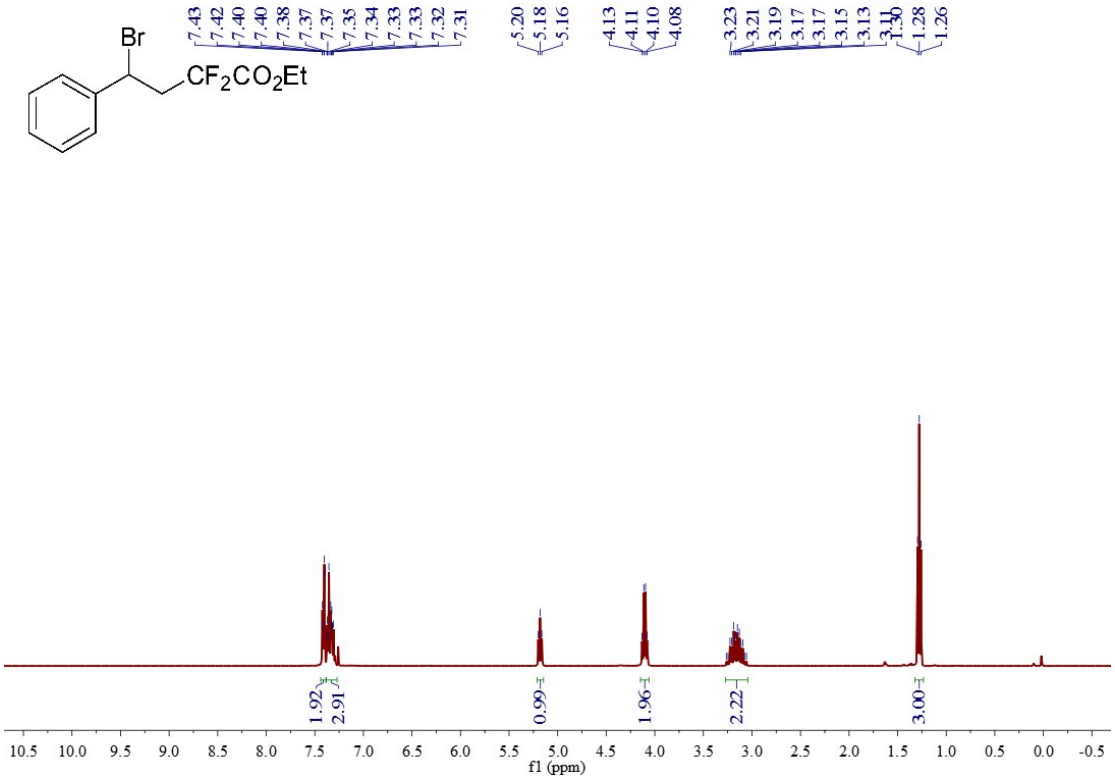
^{19}F NMR Spectrum of **4y**



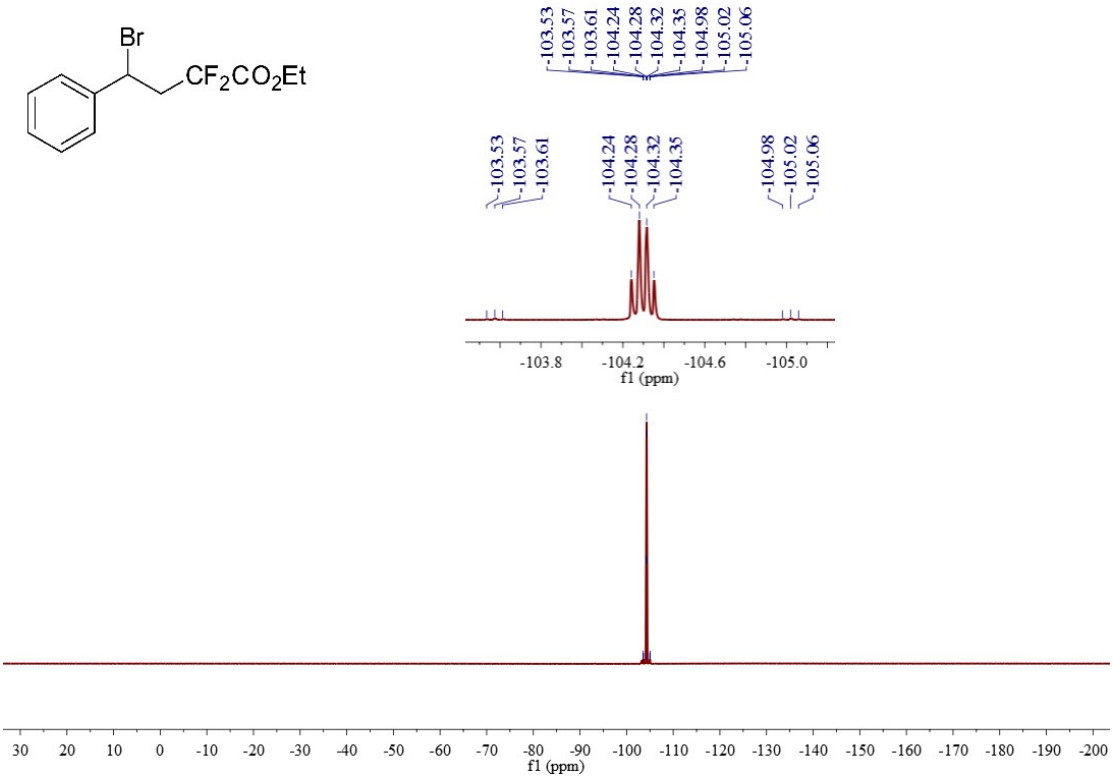
^{13}C NMR Spectrum of **4y**



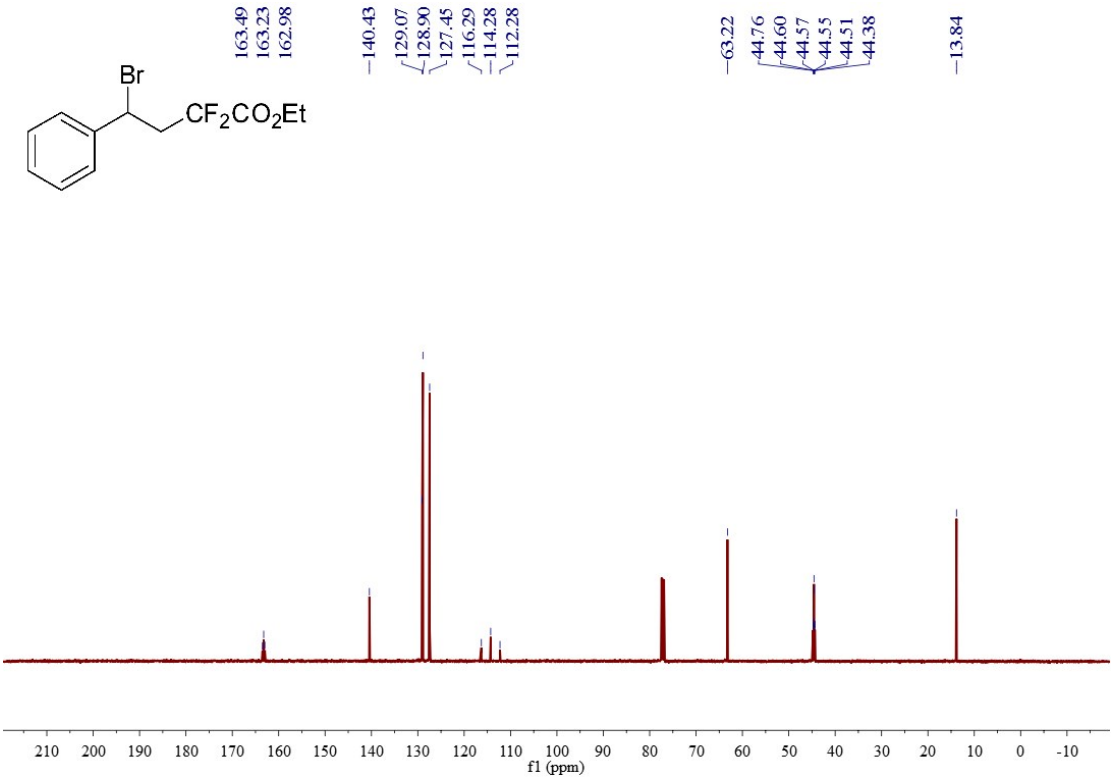
^{1}H NMR Spectrum of **3a**



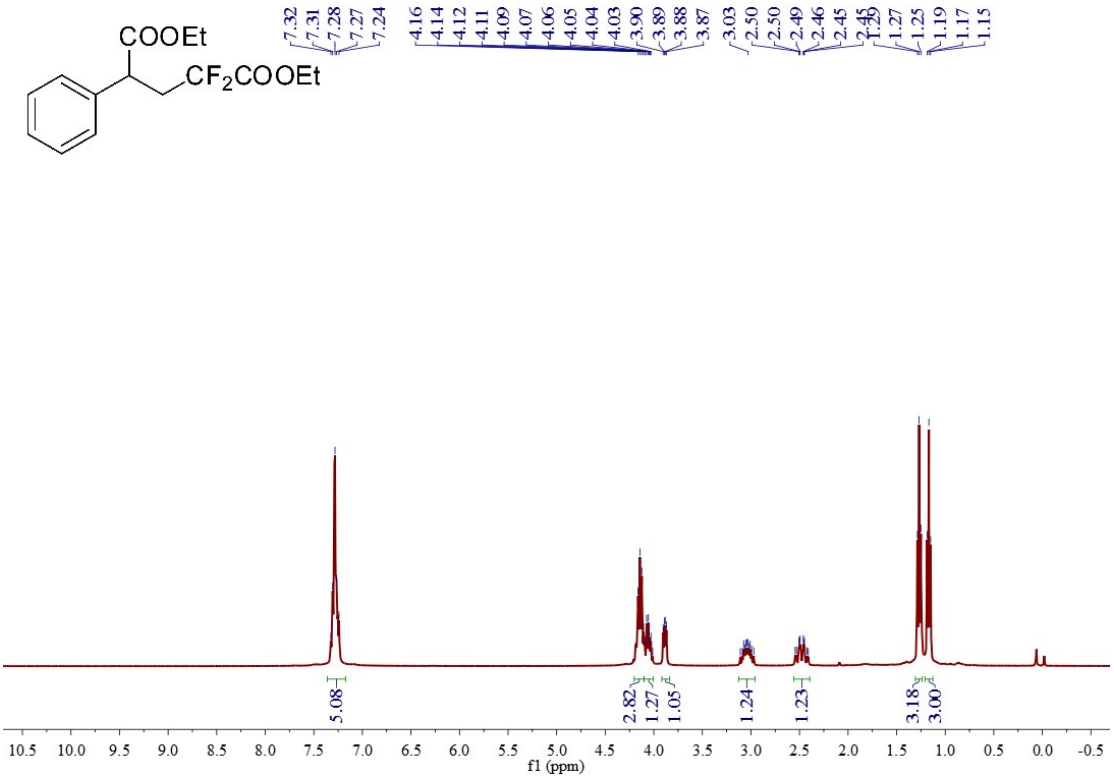
^{19}F NMR Spectrum of **3a**



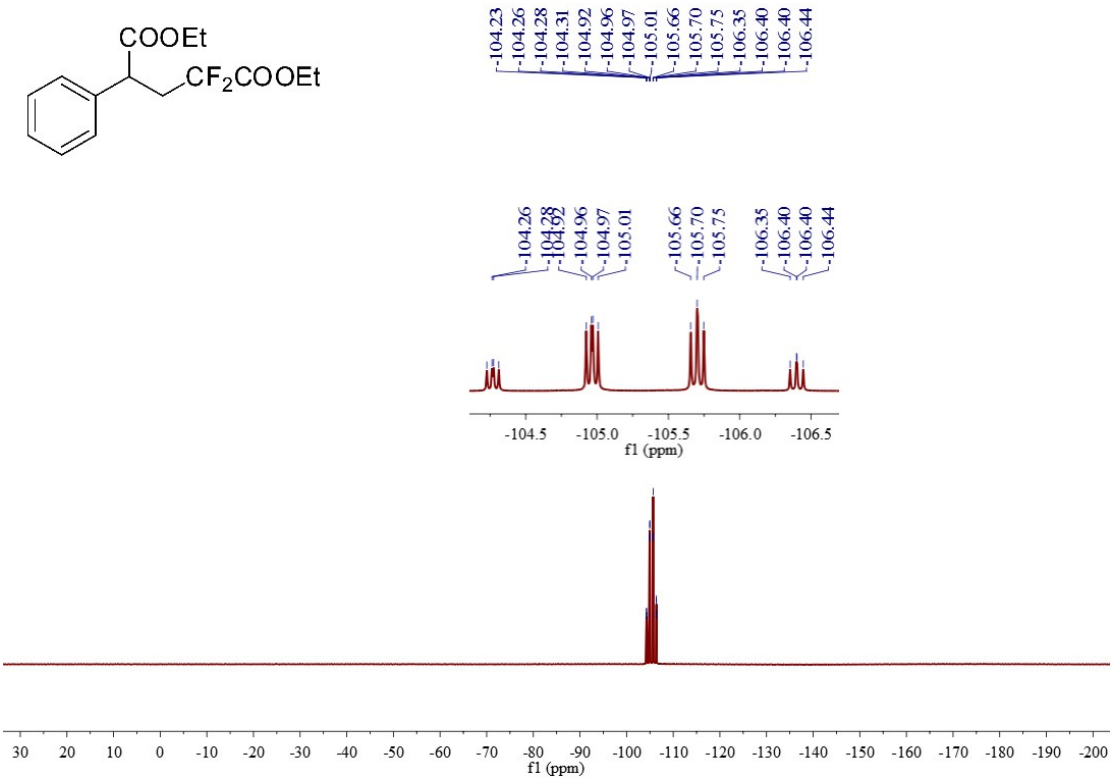
^{13}C NMR Spectrum of **7a**



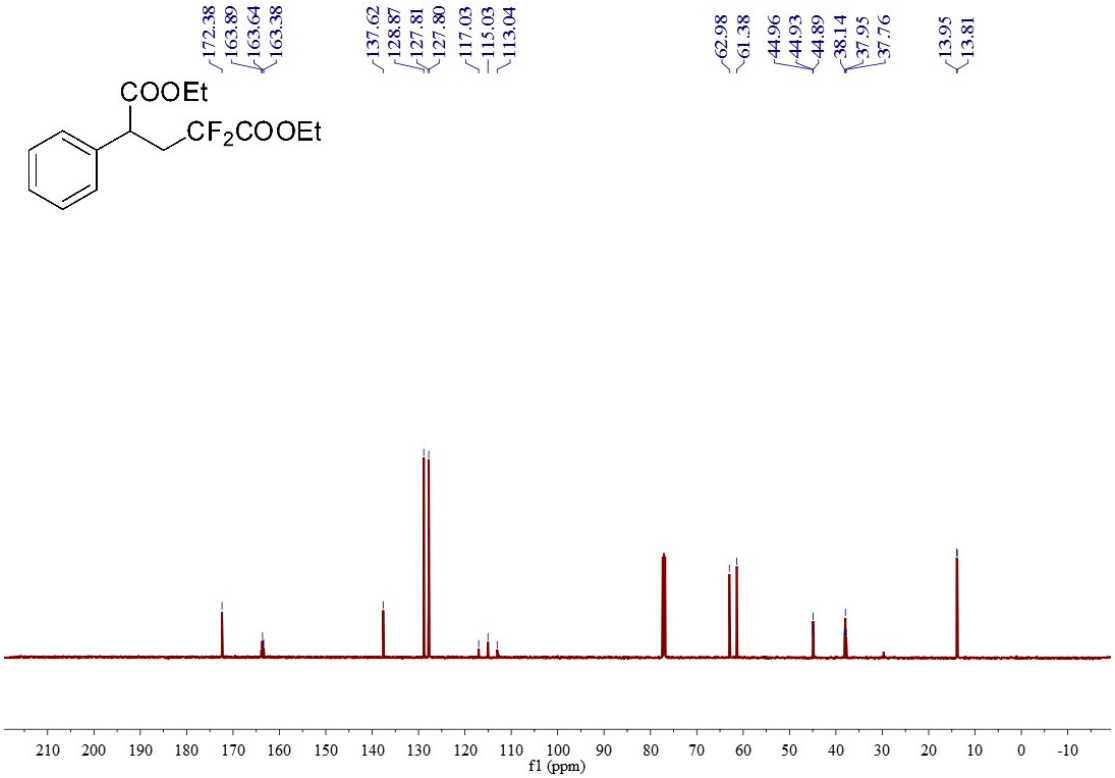
[1]H NMR Spectrum of **7a**



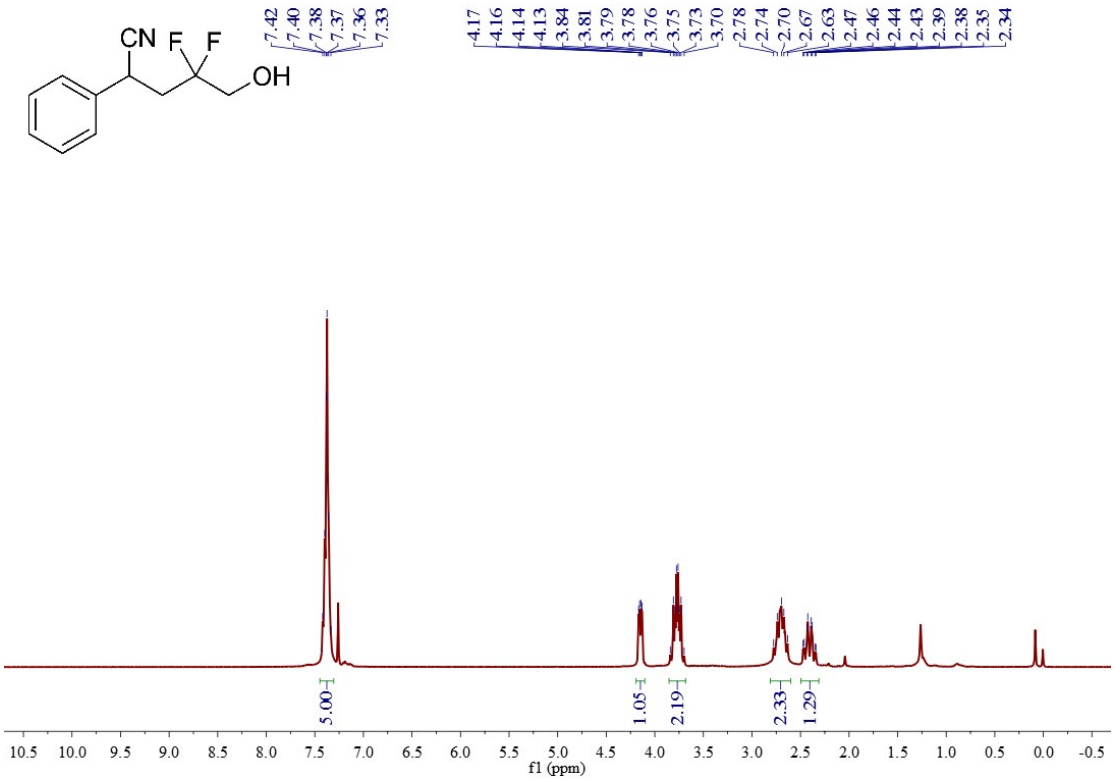
[19]F NMR Spectrum of **7a**



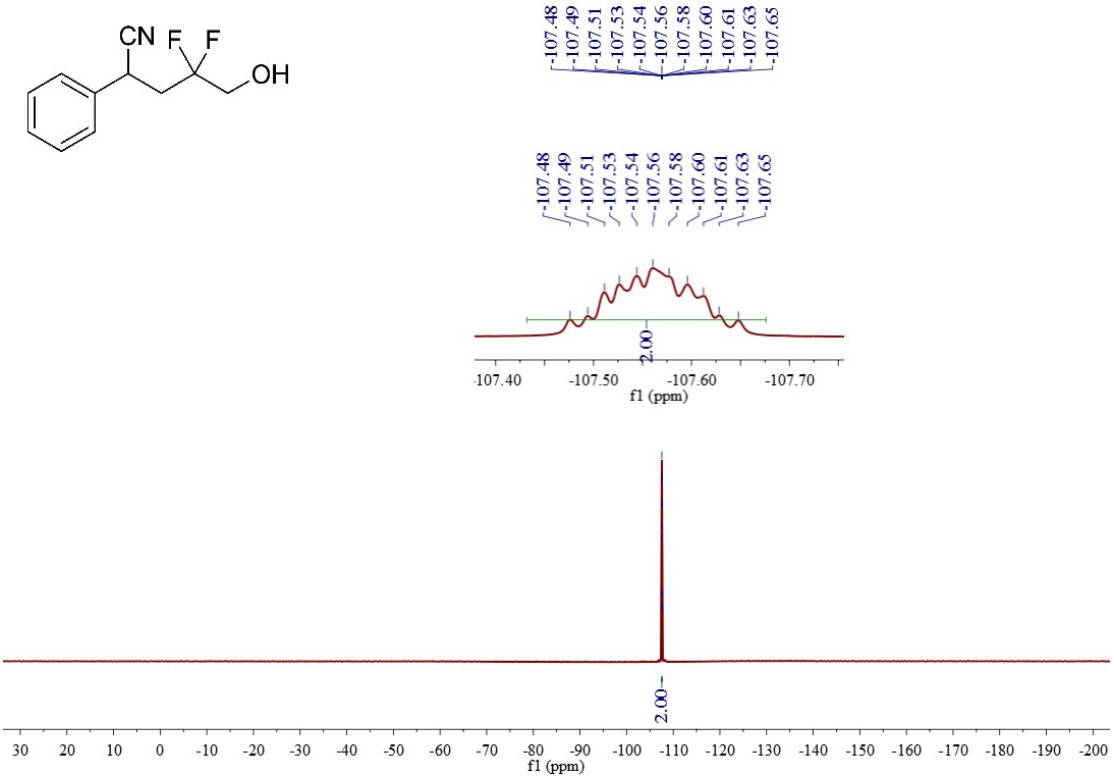
^{13}C NMR Spectrum of **7a**



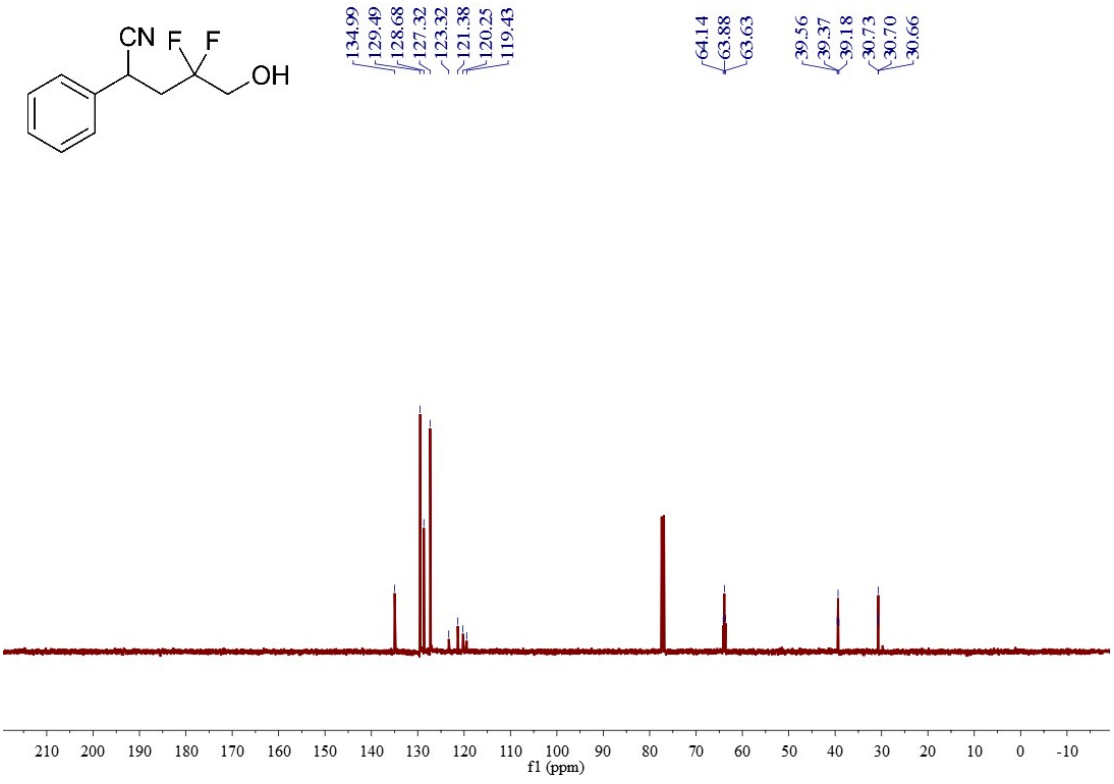
^{1}H NMR Spectrum of **7b**



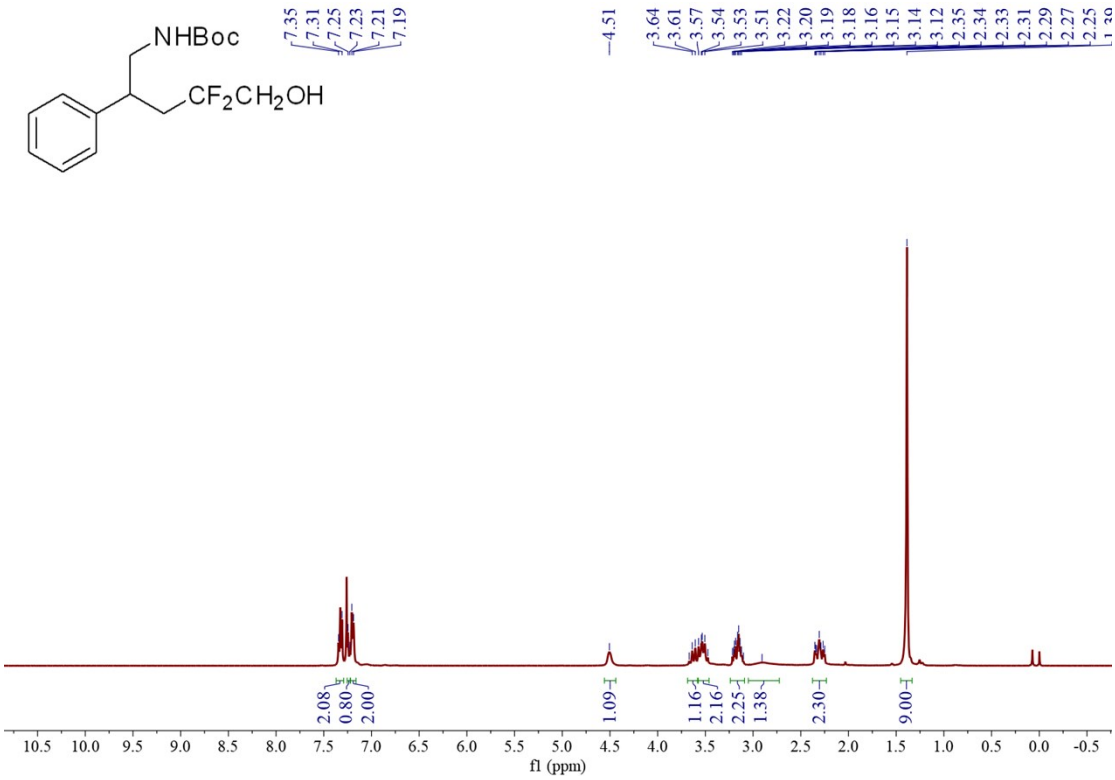
^{19}F NMR Spectrum of **7b**



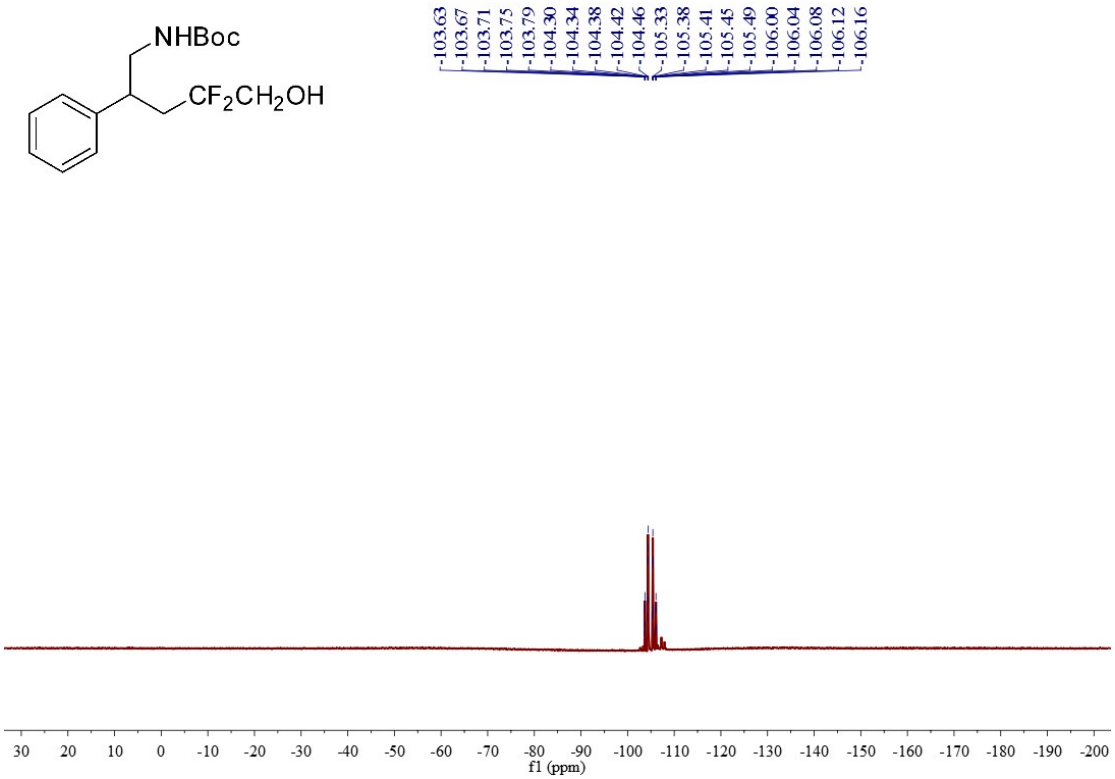
^{13}C NMR Spectrum of **7b**



^{1}H NMR Spectrum of **7c**



^{19}F NMR Spectrum of **7c**



^{13}C NMR Spectrum of **7c**