Construction of β-Quaternary α,α-Difluoroketones via Catalytic Nucleophilic Substitution of Tertiary Alcohols with Difluoroenoxysilanes

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Supporting information

1. General information

Reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the progress of reaction. Purification of reaction products was carried out by flash chromatography on 300−400 mesh silica gel. Chemical yields referred to pure isolated substances. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker DPX-400 or DPX-500 spectrometer. The HRMS spectra were measured on Waters Synapt TOF G2-S mass spectrometer or Bruker maXis impact spectrometer using electron spray ionization (ESI) method. Chemical shifts (δ) are expressed in parts per million (ppm) units using $(CH_3)_4Si$ as the internal standard. HPLC analysis was performed on a Shimadzu LC-20AD instrument using Daicel Chiral columns at 30 °C and a mixture of HPLC-grade hexanes and isopropanol as eluent. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets. Coupling constants (*J*) are reported in Hertz.

Unless mentioned, all reactions were carried out under an atmosphere of N_2. Anhydrous CH_2Cl_2, DCE, and CH_3CN were prepared by first distillation over P_2O_5 and then from CaH_2. Anhydrous toluene and THF were prepared by distillation over sodium-benzophenone ketyl prior to use. The 3-substituted 3-hydroxyoxindoles **2** were prepared from the corresponding isatins and Grignard reagents according to the reported procedure.[1] Difluoroenoxysilanes[2a,b] and monofluorinated silyl enol ethers[2c] were prepared by using the literature methods.

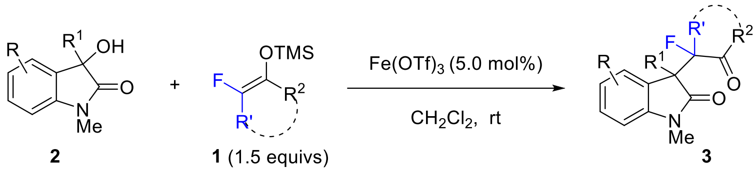
List of abbreviation:

Entry	Chemical name	Abbreviation
1	Dichloromethane	CH_2Cl_2
2	1,2-Dichloroethane	DCE
3	Tetrahydrofuran	THF
4	Petroleum ether	PE
5	Ethyl acetate	EtOAc
6	Hexafluoroisopropyl alcohol	HFIP

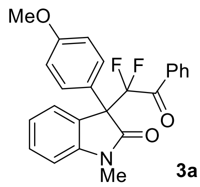
1 (a) Hamashima, Y.; Suzuki, T.; Takano, H.; Shimura, Y.; Sodeoka, M. *J. Am. Chem. Soc.* **2005**, *127*, 10164; (b) Wu, H.-X.; Xue, F.; Xiao, X.; Qin, Y. *J. Am. Chem. Soc.* **2010**, *132*, 14052.
2 (a) Amii, H.; Kobayashi, T.; Hatamoto, Y.; Uneyama, K. *Chem. Commun.* **1999**, 1323; (b) Prakash, G. K. S.; Hu, J.; Olah, G. A. *J. Fluorine Chem.* **2001**, *112*, 357; (c) Bélanger, É.; Cantin, K.; Messe, O.; Tremblay, M.; Paquin, J. F. *J. Am. Chem. Soc.* **2007**, *129*, 1034.

2. General procedure for the substitution reaction

2.1 The reaction of 3-hydroxyoxindoles 2 with fluorinated enol silyl ethers 1

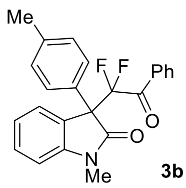


Under an atmosphere of N_2, to a 25 mL flame-dried Schleck tube were added 3-hydroxyoxindoles **2** (0.25 mmol, 1.0 equiv) and $Fe(OTf)_3$ (0.0125 mmol, 6.3 mg, 5.0 mol%), followed by the addition of anhydrous CH_2Cl_2 (2.5 mL). After being stirred at room temperature for about 5 min, fluorinated enol silyl ethers **1** (0.375 mmol, 1.5 equivs) was then added. The resulting mixture was stirred at room temperature until full conversion of **2** by TLC analysis. The reaction mixture was then concentrated under reduced pressure to give the residue, which was purified by silica gel column chromatography to afford the products **3**, using PE/EtOAc as eluent.



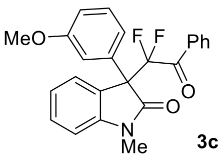
3a

Column chromatography with PE/EtOAc (10/1, v/v) afforded product **3a** in 91% yield (92.6 mg) as white solid, m.p. 148-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 7.4 Hz, 2H), 7.78 (dd, J = 8.9, 1.1 Hz, 2H), 7.59-7.53 (m, 2H), 7.42-7.35 (m, 3H), 7.07 (td, J = 7.6 Hz, 0.9 Hz, 1H), 6.91-6.88 (m, 3H), 3.80 (s, 3H), 3.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.6 (t, J = 31.7 Hz, 1C), 173.4 (d, J = 10.6 Hz, 1C), 159.7, 144.4, 134.4, 131.8 (t, J = 3.3 Hz, 1C), 130.8 (d, J = 1.9 Hz, 1C), 130.1 (t, J = 2.9 Hz, 1C), 129.3, 128.5, 126.5 (d, J = 5.7 Hz, 1C), 126.2 (d, J = 4.2 Hz, 1C), 123.2, 122.1, 117.5 (dd, J = 268.5, 261.9 Hz, 1C), 113.6, 108.8, 57.9 (t, J = 20.5 Hz, 1C), 55.2 (d, J = 2.7 Hz, 1C), 26.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ -97.45 (d, J = 310.7 Hz, 1F), -99.35 (d, J = 310.6 Hz, 1F); IR (ATR): 2976, 2885, 1720, 1510, 1253, 1082, 941, 675 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{24}H_{19}F_2NO_3Na$ 430.1231; Found 430.1201.



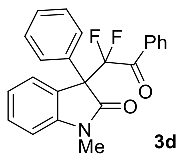
3b

Column chromatography with PE/EtOAc (10/1, v/v) afforded product **3b** in 90% yield (88.0 mg) as white solid (m.p. 148-150 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 7.5 Hz, 2H), 7.76 (d, J = 7.4 Hz, 2H), 7.59-7.56 (m, 2H), 7.43-7.35 (m, 3H), 7.20 (d, J = 8.3 Hz, 2H), 7.08 (td, J = 7.5, 0.9 Hz, 1H), 6.91 (d, J = 7.8 Hz, 1H), 3.27 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.5 (t, J = 31.6 Hz, 1C), 173.2 (d, J = 10.5 Hz, 1C), 144.3, 138.4, 134.3, 131.7 (t, J = 3.3 Hz, 1C), 130.1 (t, J = 2.8 Hz, 1C), 129.4, 129.4, 129.3, 129.0, 128.5, 126.5 (d, J = 5.4 Hz, 1C), 126.2 (d, J = 3.9 Hz, 1C), 122.1, 117.5 (dd, J = 268.9, 262.3 Hz, 1C), 108.8, 58.2 (t, J = 21.0 Hz, 1C), 26.7, 20.9 (d, J = 2.8 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ -97.26 (d, J = 310.8 Hz, 1F), -99.08 (d, J = 310.8 Hz, 1F); IR (ATR): 2976, 1710, 1263, 1072, 1049, 939, 881, 659 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{24}H_{19}F_2NO_2Na$ 414.1282; Found 414.1281.



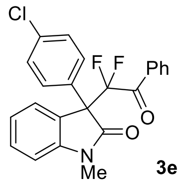
3c

Column chromatography with PE/EtOAc (10/1, v/v) afforded product **3c** in 60% yield (61.5 mg) as white solid (m.p. 97-99 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 7.4 Hz, 2H), 7.59-7.53 (m, 2H), 7.47-7.46 (m, 1H), 7.42-7.35 (m, 4H), 7.28 (t, J = 8.0 Hz, 1H), 7.06 (td, J = 7.6 Hz, 0.9 Hz, 1H), 6.92-6.89 (m, 2H), 3.81 (s, 3H), 3.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.5 (t, J = 32.3 Hz, 1C), 173.0 (d, J = 10.6 Hz, 1C), 159.3, 144.4, 134.4, 133.1, 131.8 (t, J = 3.3 Hz, 1C), 130.1 (t, J = 2.9 Hz, 1C), 129.4, 129.1, 128.5, 126.3 (t, J = 4.1 Hz, 1C), 122.2, 121.9, 117.5 (dd, J = 267.7, 261.2 Hz, 1C), 115.8 (d, J = 1.8 Hz, 1C), 113.8, 108.8, 58.5 (dd, J = 22.6, 20.6 Hz, 1C), 55.2 (d, J = 4.9 Hz, 1C), 26.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ -97.21 (d, J = 310.0 Hz, 1F), -98.98 (d, J = 310.4 Hz, 1F); IR (ATR): 2976, 1714, 1695, 1492, 1259, 1047, 779, 756 cm^{-1}; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{24}H_{19}F_2NO_3Na$ 430.1225; Found 430.1226.



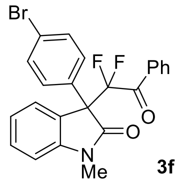
3d

Column chromatography with PE/EtOAc (10/1, v/v) afforded product **3d** in 76% yield (71.6 mg) as white solid (m.p. 150-152 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 7.4 Hz, 2H), 7.88-7.86 (m, 2H), 7.59-7.56 (m, 2H), 7.43-7.36 (m, 6H), 7.08 (td, J = 7.6 Hz, 0.7 Hz, 1H), 6.91 (d, J = 7.8 Hz, 1H), 3.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.4 (t, J = 21.6 Hz, 1C), 173.1 (d, J = 10.6 Hz, 1C), 144.4, 134.4, 131.7 (t, J = 3.2 Hz, 1C), 131.6, 130.2 (t, J = 2.8 Hz, 1C), 129.5, 129.5, 129.4, 128.51, 128.48, 128.2, 126.4 (d, J = 4.3 Hz, 1C), 122.2, 117.5 (t, J = 269.3 Hz, 262.6 Hz, 1C), 108.8, 58.5 (t, J = 20.2 Hz, 1C), 26.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ -97.18 (d, J = 310.7 Hz, 1F), -98.94 (d, J = 310.7 Hz, 1F); IR (ATR): 2976, 1708, 1319, 1261, 1087, 1051, 881 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{23}H_{17}F_2NO_2Na$ 400.1125; Found 400.1110.



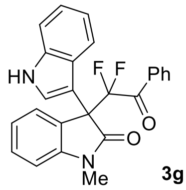
3e

Column chromatography with PE/EtOAc (10/1, v/v) afforded product **3e** in 63% yield (64.7 mg) as white solid (m.p. 146-148 ºC). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 7.4 Hz, 2H), 7.80 (dd, J = 8.6, 1.1 Hz, 2H), 7.60-7.56 (m, 1H), 7.52 (dd, J = 7.2, 2.0 Hz, 1H), 7.43-7.33 (m, 5H), 7.09 (td, J = 7.6 Hz, 0.8 Hz, 1H), 6.92 (d, J = 7.8 Hz, 1H), 3.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.2 (t, J = 31.5 Hz, 1C), 172.8 (d, J = 10.2 Hz, 1C), 144.4, 134.9, 134.5, 131.6 (t, J = 3.3 Hz, 1C), 130.9 (d, J = 2.0 Hz, 1C), 130.1 (t, J = 2.9 Hz, 1C), 129.7, 128.5, 128.4, 126.3 (d, J = 4.1 Hz, 1C), 125.9 (td, J = 5.6 Hz, 1C), 122.4, 117.4 (dd, J = 269.4, 263.2 Hz, 1C), 109.0, 58.1 (t, J = 22.4 Hz, 1C), 26.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ -97.24 (d, J = 310.6 Hz, 1F), -98.97 (d, J = 310.6 Hz, 1F); IR (ATR): 2976, 1701, 1608, 1259, 1101, 1053, 881 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{23}H_{17}{}^{35}ClF_2NO_2$ 412.0916; Found 412.0917.



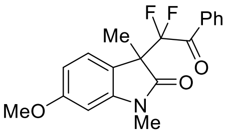
3f

Column chromatography with PE/EtOAc (10/1, v/v) afforded product **3f** in 54% yield (61.6 mg) as white solid (m.p. 141-143 ºC). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93-7.90 (m, 2H), 7.73 (dd, J = 8.7 Hz, 1.2, 2H), 7.58-7.56 (m, 1H), 7.51-7.48 (m, 3H), 7.43-7.38 (m, 3H), 7.08 (td, J = 7.6 Hz, 1.0 Hz, 1H), 6.92 (d, J = 7.8 Hz, 1H), 3.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 182.2 (t, J = 31.8 Hz, 1C), 172.7 (d, J = 10.4 Hz, 1C), 144.4, 134.5, 131.6 (t, J = 3.4 Hz, 1C), 131.4, 131.3 (d, J = 2.4 Hz, 1C), 130.7, 130.2 (t, J = 3.2 Hz, 1C), 129.7, 128.5, 126.3 (d, J = 4.2 Hz, 1C), 125.8 (d, J = 5.5 Hz, 1C), 123.2, 122.4, 117.3 (dd, J = 269.7, 262.9 Hz, 1C), 109.1, 58.1 (t, J = 20.4 Hz, 1C), 26.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ -97.25 (d, J = 310.2 Hz, 1F), -98.96 (d, J = 310.6 Hz, 1F); IR (ATR): 2978, 2360, 1710, 1608, 1265, 1101, 1078, 742 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{23}H_{17}{}^{79}BrF_2NO_2$ 456.0411; Found 456.0427.



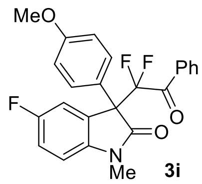
3g

Column chromatography with PE/EtOAc (5/1, v/v) afforded product **3g** in 37% yield (38.5 mg) as white solid (m.p. 174-176ºC). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, br, 1H), 7.96 (d, J = 7.2 Hz, 2H), 7.89 (dd, J = 8.1, 2.8 Hz, 1H), 7.59-7.55 (m, 1H), 7.50 (dd, J = 7.3, 2.7 Hz, 1H), 7.42-7.38 (m, 3H), 7.32-7.30 (m, 1H), 7.18-7.16 (m, 2H), 7.10-7.03 (m, 2H), 6.92 (d, J = 7.8 Hz, 1H), 3.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.8 (t, J = 32.9 Hz, 1C), 173.2 (d, J = 9.7 Hz, 1C), 144.4, 136.8, 134.3, 132.1 (t, J = 3.5 Hz, 1C), 130.1 (t, J = 3.0 Hz, 1C), 129.4, 128.5, 127.1 (d, J = 6.3 Hz, 1C), 126.2, 126.1, 125.7 (d, J = 4.1 Hz, 1C), 122.4 (d, J = 6.2 Hz, 1C), 122.2 (d, J = 5.6 Hz, 1C), 120.1, 118.6 (dd, J = 267.4, 260.7 Hz, 1C), 111.3, 108.6, 107.7, 56.5 (t, J = 22.1 Hz, 1C), 26.6; ^{19}F NMR (376 MHz, $CDCl_3$): -96.63 (d, J = 305.7 Hz, 1F), -99.40 (d, J = 306.6 Hz, 1F); IR (ATR): 2974, 2358, 1610, 1288, 1257, 1047 cm^{-1}; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{25}H_{18}F_2N_2O_2Na$ 439.1229; Found 439.1225.



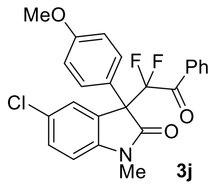
3h

Column chromatography with PE/EtOAc (5/1, v/v) afforded product **3h** in 57% yield (49.2 mg) as white solid (m.p. 89-91 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96-7.94 (m, 2H), 7.59-7.55 (m, 1H), 7.44-7.39 (m, 2H), 7.17 (dd, J = 8.5, 1.1 Hz, 1H), 6.49-6.46 (m, 2H), 3.81 (s, 3H), 3.24 (s, 3H), 1.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.5 (t, J = 31.6 Hz, 1C), 175.5 (d, J = 8.6 Hz, 1C), 160.9, 145.1, 134.2, 132.0 (t, J = 3.2 Hz, 1C), 130.1 (t, J = 3.2 Hz, 1C), 128.4, 124.7 (d, J = 2.6 Hz, 1C), 120.6 (d, J = 4.7 Hz, 1C), 118.3 (dd, J = 265.1, 260.6 Hz, 1C), 106.3, 96.4, 55.4 (t, J = 2.8 Hz, 1C), 51.2 (d, J = 22.3 Hz, 1C), 26.5, 18.3 (t, J = 5.1 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ -102.12 (d, J = 306.9 Hz, 1F), -103.17 (d, J = 306.6 Hz, 1F); IR (ATR): 2885, 2360, 1724, 1510, 1186, 1051, 883, 763 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{19}H_{18}F_2NO_3$ 346.1255; Found 346.1281.



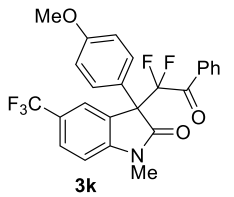
3i

Column chromatography with PE/EtOAc (10/1, v/v) afforded product **3i** in 92% yield (97.8 mg) as yellow solid (m.p. 168-170 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (dd, J = 7.4, 4.0 Hz, 2H), 7.76 (dd, J = 8.9, 1.1 Hz, 2H), 7.61-7.58 (m, 1H), 7.42 (t, J = 7.9 Hz, 2H), 7.32 (dt, J = 8.1 Hz, 2.3 Hz, 1H), 7.08 (td, J = 8.8, 2.6 Hz, 1H), 6.93-6.91 (m, 2H), 6.84 (dd, J = 8.6, 4.3 Hz, 1H), 3.80 (s, 3H), 3.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.3 (t, J = 32.2 Hz, 1C), 173.2 (d, J = 10.4 Hz, 1C), 159.8, 158.6 (d, J = 240.5 Hz, 1C), 140.4, 134.6, 131.4 (t, J = 3.4 Hz, 1C), 130.6 (d, J = 1.5 Hz, 1C), 130.2 (t, J = 3.0 Hz, 1C), 128.6, 128.1 (dd, J = 8.4, 5.5 Hz, 1C), 122.6, 117.4 (dd, J = 267.7, 260.0 Hz, 1C), 115.5 (d, J = 23.1 Hz, 1C), 114.4 (dd, J = 25.8, 2.9 Hz, 1C), 113.7, 109.2 (d, J = 8.2 Hz, 1C), 58.2 (t, J = 21.7 Hz, 1C), 55.2 (d, J = 5.2 Hz, 1C), 26.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ -97.36 (d, J = 314.7 Hz, 1F), -99.32 (d, J = 314.8 Hz, 1F), -120.41 (s, 1F); IR (ATR): 2976, 1714, 1697, 1512, 1259, 1078, 1051, 812 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{24}H_{18}F_3NO_3Na$ 448.1136; Found 448.1148.



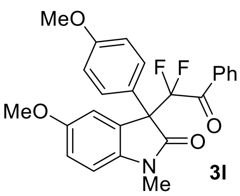
3j

Column chromatography with PE/EtOAc (10/1, v/v) afforded product **3j** in 85% yield (93.7 mg) as white solid (m.p. 185-187 ºC). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.4 Hz, 2H), 7.74 (dd, *J* = 8.9, 1.1 Hz, 2H), 7.62-7.58 (m, 1H), 7.53 (t, *J* = 1.9 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 2H), 7.35 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.94-6.91 (m, 2H), 6.84 (d, *J* = 8.4 Hz, 1H), 3.81 (s, 3H), 3.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.3 (t, *J* = 32.7 Hz, 1C), 173.1 (d, *J* = 10.7 Hz, 1C), 159.9, 143.0, 134.7, 131.4 (t, *J* = 3.4 Hz, 1C), 130.7 (d, *J* = 1.7 Hz, 1C), 130.3 (t, *J* = 2.9 Hz, 1C), 129.2, 128.6, 128.4 (d, *J* = 5.4 Hz, 1C), 127.4, 126.4 (d, *J* = 4.6 Hz, 1C), 122.4, 117.4 (dd, *J* = 269.3, 261.9 Hz, 1C), 113.7, 109.7, 58.1 (t, *J* = 20.8 Hz, 1C), 55.3 (d, *J* = 4.8 Hz, 1C), 26.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ -97.19 (d, *J* = 315.2 Hz, 1F), -99.15 (d, *J* = 315.9 Hz, 1F); IR (ATR): 2976, 1701, 1608, 1257, 1099 1051, 881, 734 cm^{-1}; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{24}H_{18}{}^{35}ClF_2NO_3Na$ 464.0835; Found 464.0840.



3k

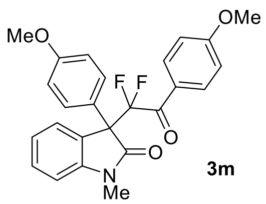
Column chromatography with PE/EtOAc (10/1, v/v) afforded product **3k** in 59% yield (70.1 mg) as white solid (m.p. 172-174 ºC). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.4 Hz, 2H), 7.76 (s, 1H), 7.70 (dd, *J* = 8.9, 1.2 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.62-7.58 (m, 1H), 7.43 (t, *J* = 7.9 Hz, 2H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.94-6.90 (m, 2H), 3.80 (s, 3H), 3.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.4 (t, *J* = 32.4 Hz, 1C), 173.4 (d, *J* = 10.8 Hz, 1C), 160.0, 147.3, 134.8, 131.3 (t, *J* = 3.5 Hz, 1C), 130.7 (d, *J* = 1.8 Hz, 1C), 130.3 (t, *J* = 3.1 Hz, 1C), 128.6, 127.4 (d, *J* = 5.5 Hz, 1C), 127.1 (q, *J* = 3.8 Hz, 1C), 125.6, 124.4 (q, *J* = 32.8 Hz, 1C), 122.9 (t, *J* = 3.9 Hz, 1C), 122.1, 117.4 (dd, *J* = 269.6, 262.0 Hz, 1C), 113.9, 108.6, 57.8 (t, *J* = 22.8 Hz, 1C), 55.3 (d, *J* = 3.4 Hz, 1C), 26.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ -61.28 (s, 3F), -97.07 (d, *J* = 316.0 Hz, 1F), -99.29 (d, *J* = 315.3 Hz, 1F); IR (ATR): 2978, 1691, 1608, 1328, 1259, 1101, 740, 700 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{25}H_{19}F_5NO_3$ 476.1285; Found 476.1266.



3l

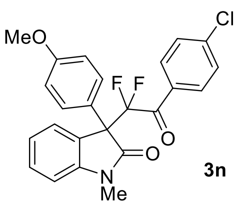
Column chromatography with PE/EtOAc (15/1, v/v) afforded product **3l** in 73% yield (79.8 mg) as yellow solid (m.p. 167-169 ºC). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.4 Hz, 2H), 7.78 (dd, *J* = 9.0, 1.2 Hz, 2H), 7.60-7.55 (m, 1H), 7.43-7.39 (m, 2H), 7.15 (t, *J* = 2.4 Hz, 1H), 6.92-6.87 (m, 3H), 6.81 (d, *J* = 8.5 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.4 (t, *J* = 32.4

Hz, 1C), 173.1 (t, J = 10.5 Hz, 1C), 159.7, 155.4, 137.9, 134.4, 131.8 (t, J = 3.3 Hz, 1C), 130.7 (d, J = 3.0 Hz, 1C), 130.2 (t, J = 32.4 Hz, 1C), 128.5, 127.8 (d, J = 5.4 Hz, 1C), 123.2, 117.5 (dd, J = 268.9, 261.9 Hz, 1C), 114.3 (d, J = 3.7 Hz, 1C), 113.6, 113.0, 109.0, 58.3 (t, J = 20.6 Hz, 1C), 55.8 (d, J = 3.5 Hz, 1C), 55.2 (d, J = 3.7 Hz, 1C), 26.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ -97.44 (d, J = 311.8 Hz, 1F), -99.51 (d, J = 311.9 Hz, 1F); IR (ATR): 2978, 1701, 1608, 1510, 1099, 1049, 805, 700 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M+Na]$^+$ Calcd for $C_{25}H_{21}F_2NO_4Na$ 460.1336; Found 460.1351.



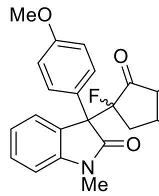
3m

Column chromatography with PE/EtOAc (4/1, v/v) afforded product **3m** in 88% yield (96.1 mg) as yellow solid (m.p. 131-133 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 8.9 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 7.1 Hz, 1H), 7.36 (td, J = 7.8 Hz, 0.9 Hz, 1H), 7.07 (td, J = 7.6 Hz, 0.6 Hz, 1H), 6.93-6.86 (m, 5H), 3.84 (s, 3H), 3.79 (s, 3H), 3.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.7 (t, J = 32.1 Hz, 1C), 173.5 (t, J = 10.7 Hz, 1C), 164.5, 159.6, 144.3, 132.8 (t, J = 3.3 Hz, 1C), 130.8 (d, J = 1.2 Hz, 1C), 129.2, 126.8 (d, J = 5.5 Hz, 1C), 126.1 (d, J = 4.1 Hz, 1C), 124.5 (t, J = 3.4 Hz, 1C), 123.3, 122.0, 117.8 (dd, J = 268.7, 262.1 Hz, 1C), 113.8, 113.5, 108.7, 57.9 (t, J = 20.6 Hz, 1C), 55.5 (d, J = 3.2 Hz, 1C), 55.2 (d, J = 3.2 Hz, 1C), 26.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ -96.60 (d, J = 310.3 Hz, 1F), -98.43 (d, J = 310.5 Hz, 1F); IR (ATR): 2976, 2360, 1512, 1444, 1257, 1087 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M+Na]$^+$ Calcd for $C_{25}H_{21}F_2NO_4Na$ 460.1336; Found 460.1351.

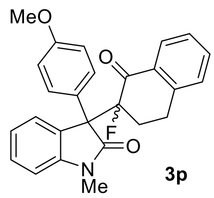


3n

Column chromatography with PE/EtOAc (15/1, v/v) afforded product **3n** in 79% yield (87.1 mg) as white solid (m.p. 119-121 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 8.6 Hz, 2H), 7.77 (d, J = 7.6, 2H), 7.57-7.50 (m, 1H), 7.42-7.33 (m, 3H), 7.08 (td, J = 7.6 Hz, 1.1 Hz, 1H), 6.93-6.86 (m, 3H), 3.79 (s, 3H), 3.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 186.5 (t, J = 32.3 Hz, 1C), 173.2 (d, J = 10.8 Hz, 1C), 159.8, 144.3, 141.1, 131.5 (t, J = 2.8 Hz, 1C), 130.8 (d, J = 2.3 Hz, 1C), 130.1 (t, J = 3.5 Hz, 1C), 129.4, 128.9, 126.4 (d, J = 5.8 Hz, 1C), 126.2 (d, J = 4.1 Hz, 1C), 123.0, 122.2, 117.4 (dd, J = 266.5, 260.0 Hz, 1C), 113.6, 108.9, 57.8 (t, J = 20.2 Hz, 1C), 55.2, 26.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ -97.45 (d, J = 311.4 Hz, 1F), -99.46 (d, J = 310.7 Hz, 1F); IR (ATR): 1708, 1512, 1259, 1089, 1051, 881, 694 cm^{-1}; HRMS (ESI) *m/z*: [M+Na]$^+$ Calcd for $C_{24}H_{18}{}^{35}ClF_2NO_3Na$ 464.0835; Found 464.0831.

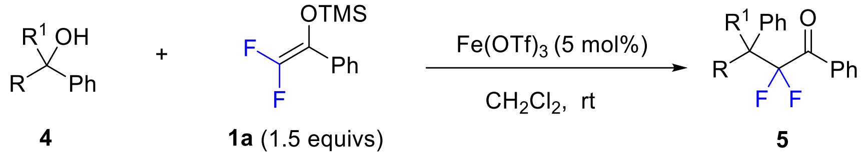

3o

Column chromatography with PE/EtOAc (6/1, v/v) afforded product **3o** in 57% yield (57.1 mg) as white solid (m.p. 181-183 °C). ^{1}H and ^{19}F NMR analysis of the crude mixture revealed that the dr was >20:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.63 (m, 2H), 7.58-7.54 (m, 2H), 7.32-7.30 (m, 2H), 7.28-7.24 (m, 2H), 6.88-6.82 (m, 4H), 3.78 (s, 3H), 3.59-3.50 (m, 1H), 3.36-3.30 (m, 1H), 3.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2 (d, *J* = 19.0 Hz, 1C), 173.6 (d, *J* = 4.2 Hz, 1C), 159.3, 149.8 (d, *J* = 2.9 Hz, 1C), 144.4, 136.0, 134.9, 130.0, 129.9, 129.3, 128.1, 126.8, 126.2, 125.9, 124.7, 122.0, 113.7, 108.7, 98.9 (d, *J* = 201.6 Hz, 1C), 55.2 (d, *J* = 3.1 Hz, 1C), 38.3 (d, *J* = 24.7 Hz, 1C), 26.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ -157.71 (s, 1F); IR (ATR): 2976, 2358, 1444, 1259, 1089, 1052, 852, 605 cm^{-1}; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{25}H_{20}FNO_3Na$ 424.1319; Found 424.1325.

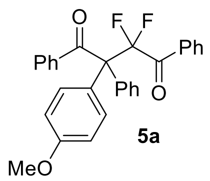

3p

Column chromatography with PE/EtOAc (5/1, v/v) afforded product **3p** in 47% yield (48.8 mg) as white solid (m.p. 174-176 °C). ^{1}H and ^{19}F NMR analysis of the crude mixture revealed that the dr was >20:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.46-7.42 (m, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.26-7.17 (m, 2H), 7.00 (t, *J* = 7.9 Hz, 1H), 6.91-6.85 (m, 3H), 3.78 (s, 3H), 3.27 (s, 3H), 3.22-3.14 (m, 1H), 2.75 (dt, *J* = 4.0, 16.8 Hz, 1H), 2.58-2.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.8 (d, *J* = 21.2 Hz, 1C), 175.4 (d, *J* = 2.2 Hz, 1C), 159.3, 145.0, 143.2, 133.8, 131.6, 130.7 (d, *J* = 3.5 Hz, 1C), 129.0, 128.5, 128.2, 127.2 (d, *J* = 6.0 Hz, 1C), 126.9, 126.4, 126.3, 121.4, 113.5, 108.8, 97.1 (d, *J* = 192.3 Hz, 1C), 58.3 (d, *J* = 19.8 Hz, 1C), 55.2, 31.3 (d, *J* = 6.9 Hz, 1C), 26.6, 24.7 (d, *J* = 7.0 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ -166.54 (s, 1F); IR (ATR): 2974, 2358, 1597, 1276, 1257, 1093, 758, 659 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{26}H_{22}FNO_3Na$ 438.1476; Found 438.1467.

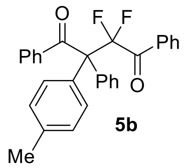
2.2 The reaction of acyclic tertiary alcohols 4 with difluoroenoxysilane 1a



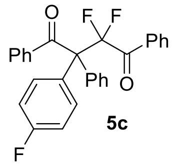
Under an atmosphere of N_2, to a 25 mL flame-dried Schleck tube were added acyclic tertiary alcohols **4** (0.25 mmol, 1.0 equiv) and $Fe(OTf)_3$ (0.0125 mmol, 6.3 mg, 5.0 mol%), followed by the addition of anhydrous CH_2Cl_2 (2.5 mL). After being stirred at room temperature for about 5 min, difluoroenoxysilane **1a** (0.375 mmol, 1.5 equivs) was then added. The resulting mixture was stirred at room temperature until full conversion of **4** by TLC analysis. The reaction mixture was then concentrated under reduced pressure to give the residue, which was purified by silica gel column chromatography to afford the products **5**, using the indicated eluent.



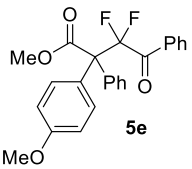
Column chromatography with PE/EtOAc (16/1, v/v) afforded product **5a** in 62% yield (70.7 mg) as white solid (m.p. 52-54 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92-7.89 (m, 2H), 7.56-7.48 (m, 3H), 7.48-7.44 (m, 4H), 7.42-7.38 (m, 2H), 7.36-7.31 (m, 4H), 7.20-7.16 (m, 2H), 6.89-6.87 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9 (t, J = 2.5 Hz, 1C), 189.7 (t, J = 32.1 Hz, 1C), 159.1, 138.2, 136.2, 133.7 (t, J = 2.4 Hz, 1C), 133.4, 132.6 (t, J = 2.2 Hz, 1C), 131.4, 131.3 (t, J = 2.2 Hz, 1C), 130.2, 129.9 (t, J = 3.4 Hz, 1C), 128.2, 128.0, 127.9, 127.7 (t, J = 1.8 Hz, 1C), 127.5, 118.5 (t, J = 266.2 Hz, 1C), 113.4, 70.4 (t, J = 18.9 Hz, 1C), 55.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -94.29 (s, 2F); IR (ATR): 2927, 2360, 1598, 1512, 1448, 1255, 1018, 812 cm^{-1}; HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for $C_{29}H_{22}F_2O_3Na$ 479.1435; Found 479.1423.



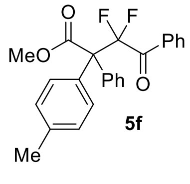
Column chromatography with PE/EtOAc (20/1, v/v) afforded product **5b** in 59% yield (64.9 mg) as white solid (m.p. 143-145 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 7.7 Hz, 2H), 7.55-7.52 (m, 3H), 7.44-7.37 (m, 6H), 7.33-7.31 (m, 4H), 7.17-7.13 (m, 4H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 189.6(t, J = 32.1 Hz, 1C), 138.1, 137.8, 136.1, 133.6 (t, J = 2.7 Hz, 1C), 133.4, 132.8, 131.6, 131.4, 131.2, 130.2, 129.9 (t, J = 3.4 Hz, 1C), 128.8, 128.2, 128.0, 127.9, 127.5, 118.4 (t, J = 266.4 Hz, 1C), 70.6 (t, J = 18.8 Hz, 1C), 21.0 (d, J = 1.9 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ -94.40 (s, 2F); IR (ATR): 2974, 2927, 2358, 1587, 1276, 1257, 1093, 758 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{29}H_{22}F_2O_2Na$ 463.1486; Found 463.1472.


5c

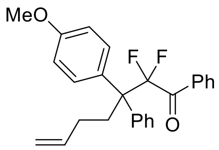
Column chromatography with PE/EtOAc (20/1, v/v) afforded product **5c** in 41% yield (45.5 mg) as white solid (m.p. 101-103 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 7.6 Hz, 2H), 7.57-7.52 (m, 3H), 7.48-7.44 (m, 2H), 7.42-7.31 (m, 8H), 7.18 (t, *J* = 7.8 Hz, 2H), 7.01 (t, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 189.4 (t, *J* = 31.9 Hz, 1C), 162.2 (d, *J* = 247.0 Hz, 1C), 138.1, 135.8, 133.7, 133.4 (d, *J* = 7.5 Hz, 1C), 131.9, 131.6, 131.1, 130.1, 129.9 (t, *J* = 3.1 Hz, 1C), 128.3 (d, *J* = 7.1 Hz, 1C), 128.2, 127.6, 118.4 (t, *J* = 267.2 Hz, 1C), 114.9 (d, *J* = 21.2 Hz, 1C), 70.4 (t, *J* = 18.8 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ -93.42 (d, *J* = 294.8 Hz, 1F), -94.41 (d, *J* = 295.8 Hz, 1F), -113.93 (s, 1F); IR (ATR): 2885, 2360, 1724, 1510, 1271, 1089, 1051, 881 cm^{-1}; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{28}H_{20}F_3O_2$ 467.1229; Found 467.1228.


5e

Column chromatography with PE/EtOAc (15/1, v/v) afforded product **5e** in 54% yield (55.4 mg) as white solid (m.p. 90-92 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.33-7.30 (m, 2H), 7.30-7.28 (m, 3H), 7.24-7.22 (m, 2H), 6.83-6.79 (m, 2H), 3.78 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.6 (t, *J* = 32.7 Hz, 1C), 170.5, 158.8, 137.7, 134.2, 132.4 (t, *J* = 3.2 Hz, 1C), 131.9, 130.4, 130.2 (t, *J* = 3.3 Hz, 1C), 129.4, 128.5, 127.7, 127.6, 118.4 (t, *J* = 265.7 Hz, 1C), 113.0, 65.3 (t, *J* = 20.4 Hz, 1C), 55.1 (d, *J* = 3.1 Hz, 1C), 52.7 (d, *J* = 3.3 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ -92.40 (d, *J* = 309.3 Hz, 1F), -93.35 (d, *J* = 308.1 Hz, 1F); IR (ATR): 2976, 1720, 1510, 1253, 1082, 941, 808, 675 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{24}H_{20}F_2O_4Na$ 433.1227; Found 433.1241.

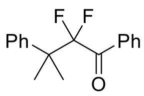

5f

Column chromatography with PE/EtOAc (15/1, v/v) afforded product **5f** in 47% yield (46.3 mg) as white solid (m.p. 94-96 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 7.7 Hz, 2H), 7.61-7.44 (m, 1H), 7.48-7.44 (m, 2H), 7.35-7.29 (m, 5H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 3.80 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.6 (t, *J* = 32.5 Hz, 1C), 170.5 (t, *J* = 4.0 Hz, 1C), 137.6, 137.4, 134.5, 134.2, 132.4 (t, *J* = 3.3 Hz, 1C), 130.6, 130.5, 130.3 (t, *J* = 3.3 Hz, 1C), 128.5, 128.5, 127.7, 127.6, 118.5 (t, *J* = 263.7 Hz, 1C), 65.6 (t, J = 20.0 Hz, 1C), 52.8, 20.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ -92.79 (s, 2F); IR (ATR): 2974, 2358, 1707, 1514, 1288, 1257, 758, 727 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{20}F_2O_3Na$ 417.1278; Found 417.1284.



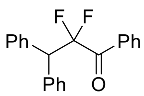
5h

Column chromatography with PE/EtOAc (30/1, v/v) afforded product **5h** in 48% yield (43.0 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 7.8 Hz, 2H), 7.38-7.35 (m, 3H), 7.24-7.16 (m, 7H), 6.74-6.72 (m, 2H), 5.79-5.70 (m, 1H), 4.98-4.90 (m, 2H), 3.74 (s, 3H), 2.57-2.53 (m, 2H), 1.87-1.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.5 (t, J = 30.1 Hz, 1C), 158.5, 140.2, 138.4, 134.5, 132.9, 131.6, 131.4, 130.1, 129.5 (t, J = 4.1 Hz, 1C), 127.8, 127.7, 127.1, 121.2 (t, J = 267.1 Hz, 1C), 114.5, 113.1, 57.5 (t, J = 19.6 Hz, 1C), 55.2, 34.7, 28.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ -97.42 (d, J = 256.4 Hz, 1F), -99.14 (d, J = 256.8 Hz, 1F); IR (ATR): 2922, 2358, 1691, 1598, 1512, 1253, 908, 823 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{24}F_2O_2Na$ 429.1637; Found 429.1639.



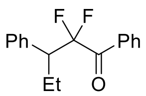
5i

Column chromatography with PE/CH_2Cl_2 (20/1, v/v) afforded product **5i** in 74% yield (50.7 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61-7.58 (m, 2H), 7.45-7.41 (m, 3H), 7.26-7.17 (m, 5H), 1.63 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.1 (t, J = 30.5 Hz, 1C), 140.9 (t, J = 2.4 Hz, 1C), 134.2 (t, J = 2.0 Hz, 1C), 133.3, 129.8 (t, J = 4.0 Hz, 1C), 128.0 (t, J = 2.0 Hz, 1C), 127.3, 120.6 (t, J = 261.1 Hz, 1C), 44.5 (t, J = 21.0 Hz, 1C), 22.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ -105.39 (s, 2F); IR (ATR): 1693, 1597, 1448, 1278, 1055, 908, 698, 608 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}F_2O$ 275.1247; Found 275.1240.



5k

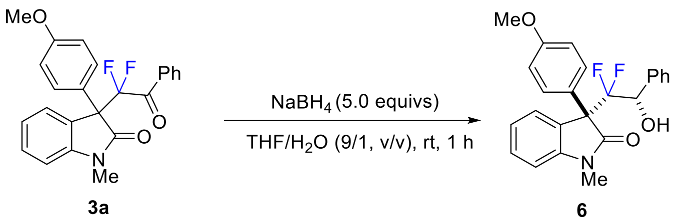
Column chromatography with PE/CH_2Cl_2 (20/1, v/v) afforded product **5k** in 98% yield (78.9 mg) as white solid (m.p. 46-48 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 7.8 Hz, 2H), 7.44 (t, J = 7.4 Hz, 1H), 7.31-7.27 (m, 6H), 7.20-7.10 (m, 6H), 4.93 (t, J = 18.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.9 (t, J = 30.1 Hz, 1C), 136.3 (t, J = 2.3 Hz, 1C), 133.9, 132.9 (t, J = 2.2 Hz, 1C), 129.8 (t, J = 3.4 Hz, 1C), 129.6 (t, J = 2.0 Hz, 1C), 128.5, 127.5, 118.9 (t, J = 259.2 Hz, 1C), 54.9 (t, J = 21.0 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ -99.90 (s, 2F); IR (ATR): 1701, 1598, 1496, 1450, 1170, 1118, 929, 698 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{17}F_2O$ 323.1247; Found 323.1265.



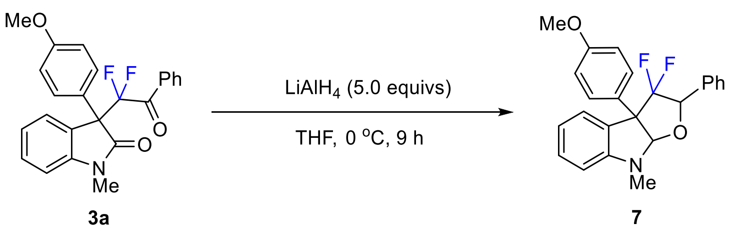
5l

Column chromatography with PE/CH_2Cl_2 (20/1, v/v) afforded product **5l** in 47% yield (32.2 mg) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 7.2 Hz, 2H), 7.51-7.46 (m, 1H), 7.35-7.32 (m, 2H), 7.22-7.14 (m, 5H), 3.42-3.30 (m, 1H), 2.02-1.93 (m, 1H), 1.88-1.76 (m, 1H), 0.73 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 190.4 (t, J = 30.2 Hz, 1C), 135.2 (d, J = 4.5 Hz, 1C), 133.9, 133.0 (t, J = 2.5 Hz, 1C), 129.82 (t, J = 3.5 Hz, 1C), 129.8, 128.5, 128.4, 127.7, 119.5 (t, J = 257.5 Hz, 1C), 51.7 (t, J = 21.4 Hz, 1C), 21.3 (t, J = 4.1 Hz, 1C), 11.71; ^{19}F NMR (376 MHz, $CDCl_3$): δ -103.42 (d, J = 272.8 Hz), -105.08 (d, J = 272.8 Hz); IR (ATR): 1705, 1450 1184, 912, 700, 688 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{17}F_2O$ 275.1247; Found 275.1240.

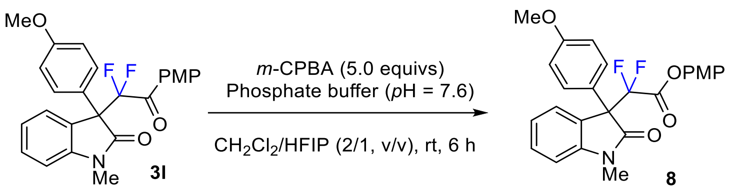
3. Transformation of products



To a stirred solution of **3a** (61.1 mg, 0.15 mmol) in the mixed solvent of THF and H_2O (1.5 mL, 9:1, v/v) was added $NaBH_4$ (28.4 mg, 0.75 mmol). The resulting mixture was stirred at room temperature until full consumption of **3a** by TLC analysis (about 1 h), and then quenched by saturated NH_4Cl (aq.). The mixture was extracted with EtOAc (6 mL × 3), the combined organic layer was washed with brine, and dried over Na_2SO_4, filtered, and concentrated under vacuo. The obtained crude residue was purified by column chromatography (PE/EtOAc = 5/1, v/v) to give the corresponding alcohol **6** in 78% yield (47.8 mg) as white solid (m.p. 149-151 °C). ^{1}H and ^{19}F NMR analysis of the crude mixture revealed that the dr value was 5.6:1. The related configuration of the major isomer of product **6** was determined by its X-ray crystallographic structure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.7 Hz, 2H), 7.67 (d, J = 7.2 Hz, 1H), 7.35 (td, J = 7.8, 1.2 Hz, 1H), 7.29 (s, 5H), 7.13 (t, J = 7.6 Hz, 1H), 6.95-6.91 (m, 2H), 6.86 (d, J = 7.8 Hz, 1H), 5.57 (s, 1H), 4.99 (ddd, J = 19.9, 3.6, 2.0 Hz, 1H), 3.81 (s, 3H), 3.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.8 (dd, J = 8.4, 2.5 Hz, 1C), 159.6, 143.2, 136.4, 129.4 (d, J = 1.7 Hz, 1C), 129.2, 128.5, 127.8, 127.7 (d, J = 3.0 Hz, 1C), 127.2 (d, J = 4.8 Hz, 1C), 125.3 (d, J = 6.2 Hz, 1C), 123.4, 120.2 (dd, J = 260.0 Hz, 256.6 Hz, 1C), 114.2, 108.9, 73.9 (dd, J = 30.5, 23.1 Hz, 1C), 62.9 (dd, J = 27.8, 23.9 Hz, 1C), 55.3 (d, J = 3.1 Hz, 1C), 26.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ -101.42 (d, J = 265.5 Hz, 1F), -114.51 (d, J = 265.5 Hz, 1F); HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{24}H_{21}F_2NO_3Na$ 432.1387; Found 432.1395.



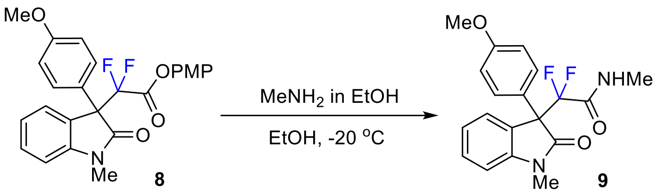
To a stirred solution of **3a** (41.1 mg, 0.10 mmol) in THF (2.5 mL) was added $LiAlH_4$ (20.0 mg, 0.5 mmol) at 0 ºC. The resulting mixture was stirred at the same temperature until full consumption of **3a** by TLC analysis (about 9 h), and then quenched by saturated NaCl (aq.). The mixture was extracted with EtOAc (6 mL × 3), the combined organic layers were washed with brine, and dried over Na_2SO_4, filtered, and concentrated under vacuo. The obtained crude residue was purified by column chromatography (PE/EtOAc = 30/1, v/v) to give tricyclic product **7** in 89% yield (35.2 mg) as colorless oil. ^{1}H and ^{19}F NMR analysis of the crude mixture revealed that the dr value was 16:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, J = 8.9, 1.4 Hz, 1H), 7.26-7.15 (m, 5H), 7.03-7.01 (m, 2H), 6.90-6.87 (m, 2H), 6.71 (td, J = 7.5, 1.0 Hz, 1H), 6.62 (d, J = 7.8 Hz, 1H), 5.83 (s, 1H), 5.27 (dd, J = 16.8, 6.8 Hz, 1H), 3.78 (s, 3H), 3.16 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1, 149.7, 134.6 (d, J = 4.2 Hz, 1C), 129.3, 128.5, 128.1, 127.83, 127.76 (d, J = 1.9 Hz, 1C), 127.6 (d, J = 3.4 Hz, 1C), 127.5 (t, J = 2.3 Hz, 1C), 127.0 (dd, J = 210.2, 200.8 Hz, 1C), 126.8, 119.0, 113.9, 107.9, 102.1 (d, J = 6.9 Hz, 1C), 83.9 (dd, J = 26.8, 20.5 Hz, 1C), 62.9 (dd, J = 19.1, 17.4 Hz, 1C), 55.3, 31.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ -89.40 (d, J = 232.0 Hz, 1F), -107.52 (d, J = 232.0 Hz, 1F); IR (ATR): 2974, 2358, 1710, 1253, 1047, 823 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{24}H_{21}F_2NO_2Na$ 416.1433; Found 416.1422.



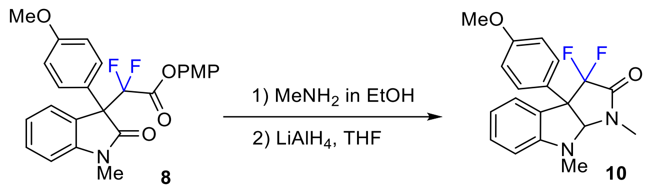
To a solution of compound **3l** (66.3 mg, 0.15 mmol, 1.0 equiv) in the mixed solvent of CH_2Cl_2 and HFIP (3 mL, 2:1, v/v) was added *m*-chloroperoxybenzoic acid (*m*-CPBA, 154.5 mg, 0.75 mmol, 85 wt%, 5.0 equivs) and phosphate buffer (0.15 mL, pH = 7.6) subsequently.[3] The resulting mixture was stirred at room temperature until full consumption of **3l** by TLC analysis (about 6 h), then saturated $NaHCO_3$ (aq.) was added to quench the reaction. After extracting with CH_2Cl_2 (6 mL × 3), the combined organic layer was washed with brine, then dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by column chromatography (PE/EtOAc = 4/1, v/v) to give the desired ester **8** in 73% yield (49.6 mg) as yellow solid (m.p. 134-136 ºC). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.9 Hz, 2H), 7.68 (d, J = 7.5 Hz, 1H), 7.47 (td,

3 Kobayashi, S.; Tanaka, H.; Amii, H.; Uneyama, K. *Tetrahedron*. **2003**, *59*, 1547

J = 7.8 Hz, 1.1 Hz, 1H), 7.23 (td, J = 7.7 Hz, 0.8 Hz, 1H), 6.92-6.89 (m, 3H), 6.79-6.75 (m, 2H), 6.58-6.54 (m, 2H), 3.79 (s, 3H), 3.74 (s, 3H), 3.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7 (d, J = 6.4 Hz, 1C), 161.0 (t, J = 33.8 Hz, 1C), 159.9, 157.8, 144.5, 142.8, 130.3 (d, J = 2.8 Hz, 1C), 127.4, 124.4 (d, J = 4.2 Hz, 1C), 123.1 (d, J = 1.7 Hz, 1C), 122.7, 121.3, 114.5, 114.1 (t, J = 263.0 Hz, 1C), 113.8, 108.9, 58.3 (t, J = 23.1 Hz, 1C), 55.5 (d, J = 3.2 Hz, 1C), 55.2 (d, J = 3.4 Hz, 1C), 26.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ -106.13 (d, J = 265.3 Hz, 1F), -106.95 (d, J = 265.4 Hz, 1F); IR (ATR): 2360, 1722, 1608, 1500, 1257, 1087, 1051, 881, 678 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{25}H_{22}F_2NO_5$ 454.1466; Found 454.1481.



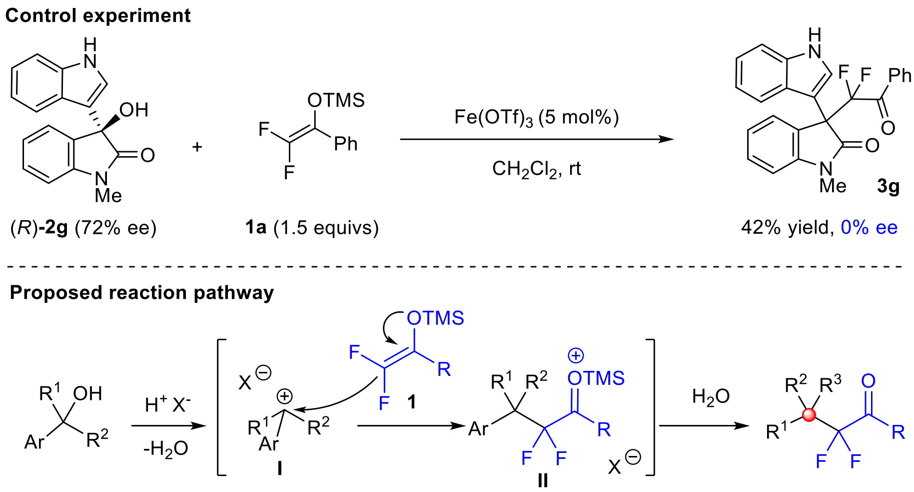
To a stirred solution of **8** (46.0 mg, 0.1 mmol) in EtOH (1.0 mL) was added $MeNH_2$ (150.7 mg, 2.0 mmol, 37% in EtOH) at 0 °C. The resulting mixture was stirred at room temperature until full consumption of **8** by TLC analysis. The reaction mixture was concentrated under vacuo, and then purified by column chromatography (PE/EtOAc = 5/1, v/v) to give the fluorinated amide **9** in 99% yield (35.7 mg) as white solid (m.p. 133-135 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 7.2 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.13 (t, J = 7.6 Hz, 1H), 6.88-6.85 (m, 3H), 6.71 (s, 1H), 3.77 (s, 3H), 3.23 (s, 3H), 2.65 (d, J = 4.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.8 (d, J = 8.2 Hz, 1C), 162.7 (t, J = 28.8 Hz, 1C), 159.7, 144.2, 130.0 (d, J = 2.3 Hz), 129.7, 126.8, 125.8 (d, J = 5.1 Hz, 1C), 124.0 (d, J = 3.1 Hz, 1C), 122.5, 115.4 (dd, J = 339.0, 209.8 Hz, 1C), 113.8, 108.9, 58.8 (t, J = 21.6 Hz), 55.2, 26.7, 26.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ -104.14 (d, J = 264.0 Hz, 1F), -105.98 (d, J = 264.0 Hz, 1F); IR (ATR):2974, 2358, 1608, 1290, 1257, 1091, 756 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{19}H_{18}F_2N_2O_3Na$ 383.1178; Found 383.1187.



To a stirred solution of **8** (46.0 mg, 0.1 mmol) in EtOH (1.0 mL) was added $MeNH_2$ (151.2 mg, 2.0 mmol, 37% in EtOH) at 0 °C. The resulting mixture was stirred at room temperature until full consumption of **8** by TLC analysis. The reaction solution was concentrated under vacuo, and used directly for the next step without purification. To a stirred solution of above crude residue in THF (2.5 mL) was added $LiAlH_4$ (50.0 mg, 1.3 mmol). The resulting mixture was stirred at 0 °C until full consumption of intermediate by TLC analysis (about 2 h), and then quenched by saturated NaCl (aq.). The mixture was extracted with EtOAc (6 mL × 3), the combined organic layer was washed with brine, then dried over Na_2SO_4, filtered, and concentrated under vacuo. The crude residue was then purified by column chromatography (PE/EtOAc = 5/1, v/v) to give the tricyclic pyrroloindoline **10** in 77% yield (26.4 mg) as white solid (m.p. 148-150 °C). ^{1}H and ^{19}F NMR analysis of the crude mixture revealed that the dr value was above 20:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (dd, J = 7.6, 3.2 Hz, 1H), 7.32 (dd, J = 8.8, 1.2 Hz, 2H), 7.23 (t, J = 7.6 Hz, 1H), 6.88-6.81 (m, 3H), 6.53 (d, J = 8.0 Hz, 1H), 5.30 (s, 1H), 3.77 (s, 3H), 3.19 (s, 3H), 3.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6 (t, J = 28.6 Hz, 1C), 159.4, 147.7, 130.2, 128.2 (d, J = 1.5 Hz, 1C), 128.0 (d, J = 5.7 Hz, 1C), 126.8, 126.5 (d, J = 3.8 Hz, 1C), 119.4, 116.7 (dd, J = 246.3, 257.2 Hz, 1C), 114.1, 108.4, 85.5 (d, J = 7.8 Hz, 1C), 59.9 (dd, J = 18.1, 5.2 Hz, 1C), 55.2, 34.7, 28.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ -97.30 (d, J = 266.6 Hz, 1F), -116.71 (d, J = 266.2 Hz, 1F); IR (ATR): 2974, 2358, 1714, 1604, 1514, 1259, 839 cm^{-1}; HRMS (ESI-TOF) *m/z*: [M+Na]$^+$ Calcd for $C_{19}H_{18}F_2N_2O_2Na$ 367.1229; Found 367.1219.

4. Control experiment and a proposed reaction pathway

To gain some insight into the reaction mechanism, the enantioenriched 3-hydroxyoxindole (*R*)-**2g** was chosen to react with **1a** under the standard conditions, which afforded the desired product **3g** in racemic form. Based on this result, and control experiments shown in Table 1 of main text, together with previous reports,[4] we temporarily proposed that the reaction was initiated by the dehydration of tertiary alcohols, under the action of *in-situ* generated HOTf from the hydrolysis of $Fe(OTf)_3$, to produce a reactive carbocation intermediate which subsequently reacted with difluoroenoxysilanes **1** to give the targets.



General procedure: The 3-hydroxyoxindole (*R*)-**2g** (72% ee) was synthesized according to the reported method.[5] Under an atmosphere of N_2, to a 25 mL flame-dried Schleck tube were added (*R*)**-2g** (69.5 mg, 0.25 mmol, 72% ee) and $Fe(OTf)_3$ (0.0125 mmol, 6.3 mg, 5.0 mol%), followed by the addition of anhydrous CH_2Cl_2 (2.5 mL). After being stirred at room temperature for about 5 min, difluoroenoxysilane **1a** (0.375 mmol, 1.5 equivs) was added. The resulting mixture was stirred at room temperature until full conversion of (*R*)**-2g** by TLC analysis. The reaction mixture was then concentrated under reduced pressure to give the residue, which was purified by silica gel column chromatography to afford the products **3g** with 42% yield (44.0 mg) as white solid, using PE/EtOAc (5/1, v/v) as eluent. HPLC analysis [Chiralpak AS-H, iPrOH/hexane = 20/80, 1.0 mL/min, 230 nm; t_r = 11.68 min, t_r = 14.73 min] indicated the enantioselectivity of product **3g** was 0%.

4 Zhu, F.; Zhou, F.; Cao, Z.-Y.; Wang, C.; Zhang, Y.-X.; Wang, C.-H.; J. Zhou, *Synthesis*, **2012**, *44*, 3129.
5 Chauhan, P.; Chimni, S. S. *Chem. Eur. J.* **2010**, *16*, 7709.

5. X-ray crystallographic data of 6 (CCDC 1939141)

Data intensity of **6** was collected using a Bruker SMART APEX-II (Mo radiation) at 293 K in a nitrogen stream. The X-ray condition of was 50 kV × 30 mA. Data collection and reduction were done by using the Bruker ApexII software package. The structures were solved by direct methods and refined by fullmatrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. Crystal data for major isomer of **6**: $C_{24}H_{21}F_2NO_3$, T = 100(10) K, monoclinic, space group $P2_1/c$, a = 18.4223(2) Å, b = 6.41470(10) Å, c = 16.93010(10) Å, α = 90 deg, β = 102.9240(10) deg, γ = 90 deg, V = 1950.01(4) Å^3. Z = 4, dcalc = 1.395 mg/m^3. Total number of reflections 42980 (R_{int} = 0.0441), R_1 = 0.0355, wR_2 = 0.0824 (all data), GOF = 1.043, and 274 parameters.

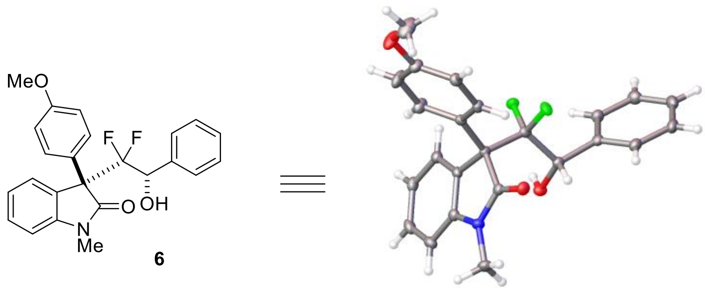


Table S1. Crystal data and structure refinement for **6**.

Identification code	**6**
Empirical formula	$C_{24}H_{21}F_2NO_3$
Formula weight	409.42
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	18.4223(2)
b/Å	6.41470(10)
c/Å	16.93010(10)
α/°	90
β/°	102.9240(10)
γ/°	90
Volume/Å^3	1950.01(4)
Z	4
ρ_{calc}g/cm^3	1.395

μ/mm^{-1}	0.872
F(000)	856.0
Crystal size/mm^3	0.36 × 0.28 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.722 to 149.014
Index ranges	$-23 \leq h \leq 22$, $-7 \leq k \leq 7$, $-20 \leq l \leq 21$
Reflections collected	42980
Independent reflections	3948 [R_{int} = 0.0441, R_{sigma} = 0.0208]
Data/restraints/parameters	3948/0/274
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0334, wR_2 = 0.0810
Final R indexes [all data]	R_1 = 0.0355, wR_2 = 0.0824
Largest diff. peak/hole / e Å^{-3}	0.29/-0.23

Table S2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **6**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ}tensor.

Atom	*x*	*y*	*z*	U(eq)
F1	2188.3(4)	2934.1(11)	2664.6(4)	19.12(16)
F2	2591.1(3)	5954.0(11)	3166.1(4)	17.83(15)
O1	1336.3(4)	5985.2(13)	3986.8(5)	17.25(18)
O2	5352.6(5)	-767.9(16)	3681.7(6)	31.3(2)
O3	1901.4(4)	-14.4(13)	3963.5(5)	18.64(18)
N1	2133.0(5)	1903.1(15)	5139.5(6)	16.4(2)
C1	4098.9(7)	2874(2)	4330.0(8)	22.7(3)
C2	4737.7(7)	1881(2)	4224.8(9)	28.1(3)
C3	4690.8(6)	117(2)	3738.9(7)	21.0(3)
C4	3995.8(6)	-629.9(19)	3353.6(7)	18.1(2)
C5	3358.1(6)	389.7(18)	3460.9(7)	17.0(2)
C6	3392.8(6)	2147.0(18)	3950.5(6)	14.8(2)
C7	2674.8(6)	3170.5(17)	4096.0(6)	14.2(2)
C8	2811.8(6)	4644.7(18)	4817.3(6)	14.8(2)
C9	3172.0(6)	6541.6(19)	4954.1(7)	16.9(2)
C10	3214.6(6)	7549.6(19)	5696.5(7)	19.5(2)
C11	2893.3(7)	6659(2)	6282.9(7)	21.3(3)
C12	2523.0(7)	4756(2)	6151.4(7)	19.7(2)
C13	2490.6(6)	3786.0(18)	5416.1(7)	15.8(2)
C14	2188.8(6)	1465.8(18)	4372.4(6)	14.7(2)
C15	5327.8(8)	-2645(2)	3228.1(10)	37.2(4)
C16	1681.4(7)	705(2)	5580.5(7)	22.1(3)

C17	2209.5(6)	4216.2(17)	3318.4(6)	14.5(2)
C18	1394.1(6)	4754.0(18)	3312.5(6)	15.0(2)
C19	982.8(6)	5643.8(18)	2502.2(7)	16.0(2)
C20	434.0(6)	4435(2)	2009.0(7)	19.0(2)
C21	24.8(6)	5213(2)	1276.6(7)	22.9(3)
C22	161.4(7)	7207(2)	1032.2(7)	24.1(3)
C23	707.7(7)	8424(2)	1518.7(7)	22.5(3)
C24	1117.5(6)	7652.7(19)	2250.9(7)	18.5(2)

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **6** The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	22.2(3)	21.4(4)	12.8(3)	-3.9(3)	2.0(2)	4.2(3)
F2	16.9(3)	17.8(4)	19.3(3)	4.0(3)	5.2(2)	-2.6(3)
O1	19.4(4)	16.3(4)	17.2(4)	-2.3(3)	6.5(3)	-1.3(3)
O2	16.7(4)	30.1(5)	47.6(6)	-17.6(4)	8.1(4)	1.1(4)
O3	18.4(4)	16.0(4)	20.9(4)	-1.3(3)	3.2(3)	-3.2(3)
N1	17.5(5)	16.6(5)	16.0(4)	1.8(4)	5.6(4)	-0.4(4)
C1	18.7(6)	21.6(6)	27.5(6)	-10.0(5)	4.4(5)	-1.6(5)
C2	14.8(6)	29.6(7)	38.7(7)	-14.3(6)	3.3(5)	-2.6(5)
C3	17.1(6)	20.8(6)	26.2(6)	-2.7(5)	7.2(5)	1.5(5)
C4	20.0(6)	15.6(6)	18.6(5)	-2.2(4)	4.3(4)	0.1(4)
C5	16.3(5)	16.4(6)	17.5(5)	-1.0(4)	2.0(4)	-1.6(4)
C6	15.9(5)	15.0(6)	14.0(5)	1.3(4)	4.2(4)	-0.1(4)
C7	14.4(5)	13.7(6)	14.3(5)	-0.4(4)	3.0(4)	-0.7(4)
C8	13.4(5)	17.3(6)	13.4(5)	-0.2(4)	2.1(4)	2.2(4)
C9	14.5(5)	18.5(6)	17.3(5)	-1.0(4)	2.6(4)	0.2(4)
C10	16.7(5)	17.6(6)	21.8(6)	-4.1(5)	-0.6(4)	0.9(4)
C11	22.5(6)	25.2(7)	14.5(5)	-4.4(5)	0.2(4)	6.0(5)
C12	22.3(6)	23.1(6)	14.1(5)	2.0(4)	4.8(4)	5.2(5)
C13	14.4(5)	16.7(6)	15.8(5)	1.9(4)	2.0(4)	2.4(4)
C14	12.6(5)	14.5(6)	16.5(5)	2.3(4)	2.4(4)	2.1(4)
C15	24.5(7)	31.4(8)	56.2(9)	-19.9(7)	10.0(6)	4.4(6)
C16	21.8(6)	23.9(7)	23.0(6)	5.5(5)	10.0(5)	-1.4(5)
C17	17.2(5)	13.1(5)	13.7(5)	-1.9(4)	4.5(4)	-2.4(4)
C18	15.2(5)	14.1(6)	15.8(5)	-1.0(4)	3.8(4)	-1.3(4)
C19	13.5(5)	18.4(6)	16.4(5)	-1.4(4)	4.2(4)	1.7(4)
C20	15.3(5)	20.4(6)	21.7(6)	-2.3(5)	5.1(4)	-0.8(4)
C21	14.7(5)	31.7(7)	20.9(6)	-4.9(5)	0.9(4)	-0.8(5)
C22	18.5(6)	34.6(7)	18.3(5)	2.3(5)	2.2(4)	6.3(5)

C23	22.3(6)	22.6(7)	23.0(6)	4.3(5)	6.1(5)	3.3(5)
C24	17.5(5)	18.7(6)	18.8(5)	-0.6(4)	3.1(4)	-0.8(4)

Table S4. Bond Lengths for **6**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	C17	1.3725(12)	C7	C14	1.5504(15)
F2	C17	1.3727(13)	C7	C17	1.5535(15)
O1	C18	1.4116(13)	C8	C9	1.3805(16)
O2	C3	1.3677(14)	C8	C13	1.3963(15)
O2	C15	1.4233(16)	C9	C10	1.4000(16)
O3	C14	1.2236(14)	C10	C11	1.3877(17)
N1	C13	1.4050(15)	C11	C12	1.3916(18)
N1	C14	1.3549(14)	C12	C13	1.3811(16)
N1	C16	1.4552(14)	C17	C18	1.5392(15)
C1	C2	1.3842(17)	C18	C19	1.5222(15)
C1	C6	1.3960(16)	C19	C20	1.3940(16)
C2	C3	1.3902(18)	C19	C24	1.3966(17)
C3	C4	1.3859(17)	C20	C21	1.3916(17)
C4	C5	1.3916(16)	C21	C22	1.3843(19)
C5	C6	1.3922(16)	C22	C23	1.3895(18)
C6	C7	1.5449(15)	C23	C24	1.3902(16)
C7	C8	1.5203(15)			

Table S5. Bond Angles for **6**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	O2	C15	117.89(10)	C10	C11	C12	121.27(11)
C13	N1	C16	124.21(10)	C13	C12	C11	117.39(11)
C14	N1	C13	111.52(9)	C8	C13	N1	109.91(10)
C14	N1	C16	123.86(10)	C12	C13	N1	127.60(10)
C2	C1	C6	121.23(11)	C12	C13	C8	122.47(11)
C1	C2	C3	120.58(11)	O3	C14	N1	125.94(10)
O2	C3	C2	116.19(11)	O3	C14	C7	125.64(10)
O2	C3	C4	124.58(11)	N1	C14	C7	108.42(9)
C4	C3	C2	119.24(11)	F1	C17	F2	104.99(8)
C3	C4	C5	119.61(11)	F1	C17	C7	109.61(9)
C4	C5	C6	122.05(10)	F1	C17	C18	106.11(8)
C1	C6	C7	121.84(10)	F2	C17	C7	107.53(8)
C5	C6	C1	117.29(10)	F2	C17	C18	110.90(9)

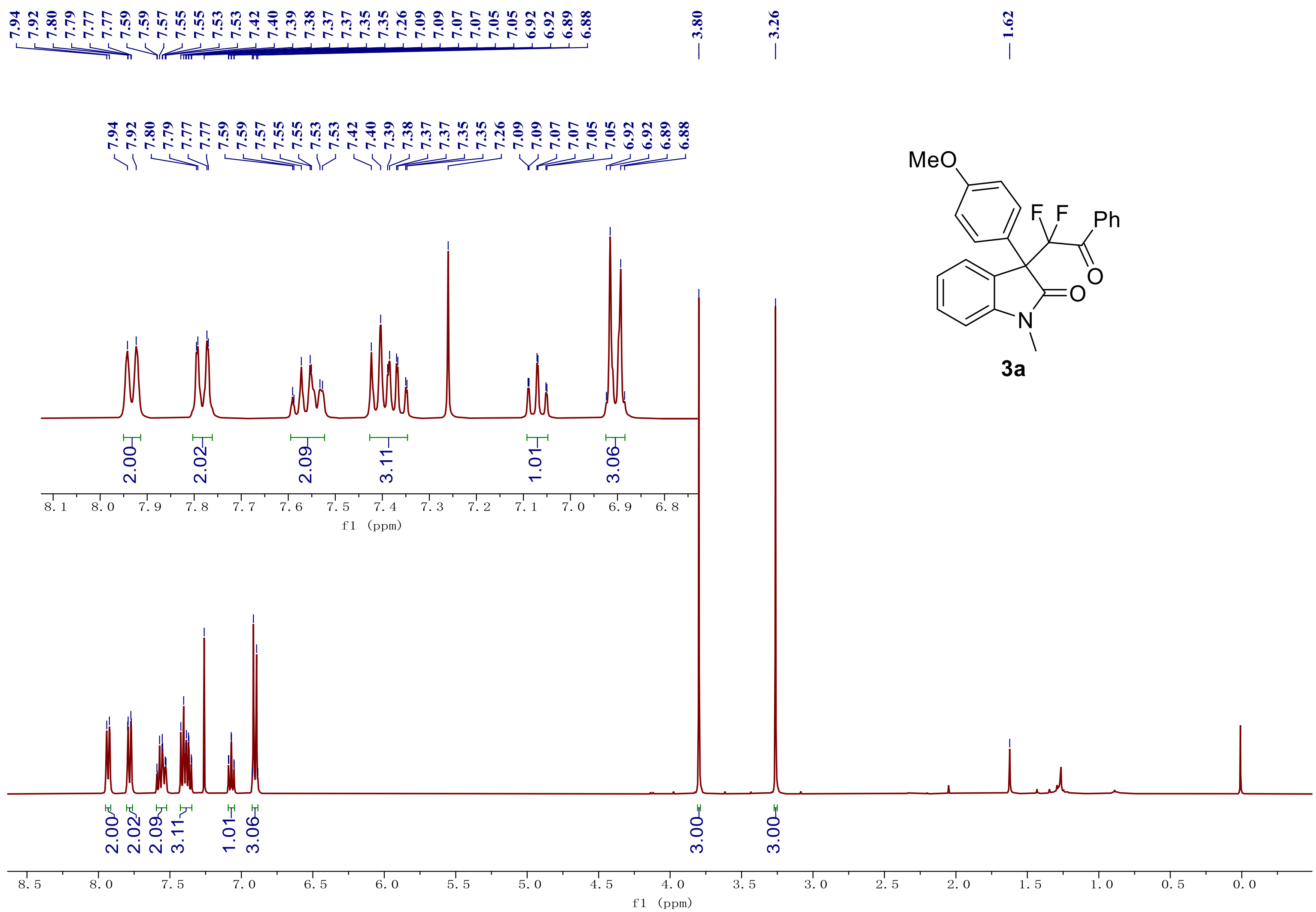
C5	C6	C7	120.81(10)	C18	C17	C7	117.06(9)
C6	C7	C14	108.73(9)	O1	C18	C17	111.73(9)
C6	C7	C17	112.22(9)	O1	C18	C19	114.00(9)
C8	C7	C6	113.47(9)	C19	C18	C17	112.22(9)
C8	C7	C14	101.52(8)	C20	C19	C18	118.65(10)
C8	C7	C17	111.91(9)	C20	C19	C24	119.03(10)
C14	C7	C17	108.29(8)	C24	C19	C18	122.28(10)
C9	C8	C7	132.08(10)	C21	C20	C19	120.66(12)
C9	C8	C13	119.46(10)	C22	C21	C20	119.95(11)
C13	C8	C7	108.46(10)	C21	C22	C23	119.87(11)
C8	C9	C10	119.08(11)	C22	C23	C24	120.35(12)
C11	C10	C9	120.32(11)	C23	C24	C19	120.14(11)

Table S6. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **6**.

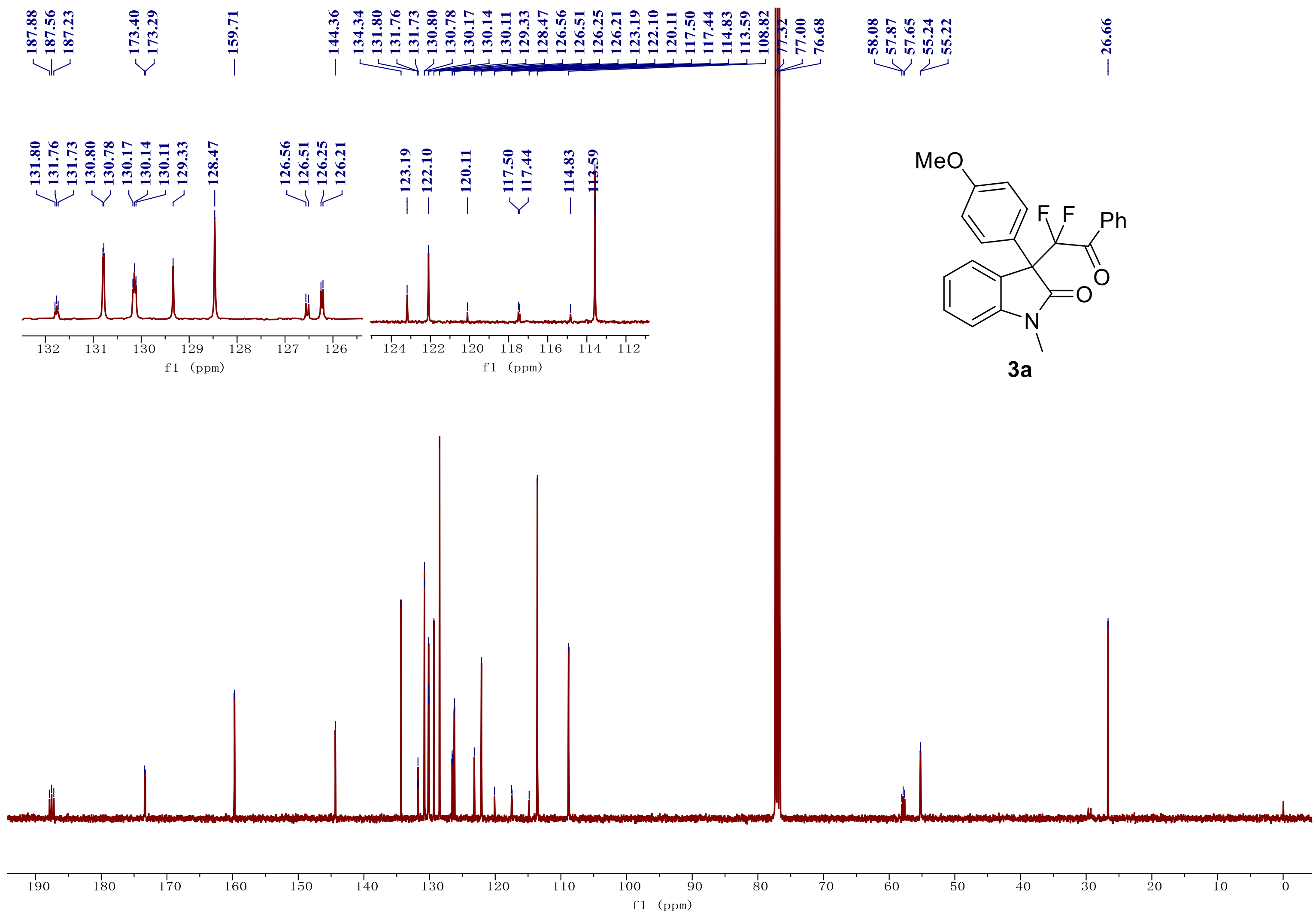
Atom	*x*	*y*	*z*	U(eq)
H1	1515.45	7139.97	3946.38	26
H1A	4141.02	4047.89	4659.57	27
H2	5202.23	2397.88	4481.44	34
H4	3955.88	-1805.69	3025.3	22
H5	2894.3	-118.47	3197.25	20
H9	3383.47	7141.56	4558.52	20
H10	3459.46	8822.57	5797.15	23
H11	2926.08	7346.14	6773.23	26
H12	2305.9	4160.87	6543.43	24
H15A	5078.01	-2391.34	2675.22	56
H15B	5062.66	-3691.69	3455.32	56
H15C	5825.96	-3117.33	3247.76	56
H16A	1959.85	460.14	6123.37	33
H16B	1549.46	-604.75	5312.73	33
H16C	1237.06	1470.49	5596.41	33
H18	1149.61	3427.63	3376.51	18
H20	340.38	3094.89	2170.9	23
H21	-340.14	4394.7	951.66	28
H22	-112	7729.96	543.35	29
H23	799.76	9762.63	1353.7	27
H24	1482.11	8476.03	2573.96	22

6. ^{1}H, ^{13}C and ^{19}F NMR spectra and HPLC spectra

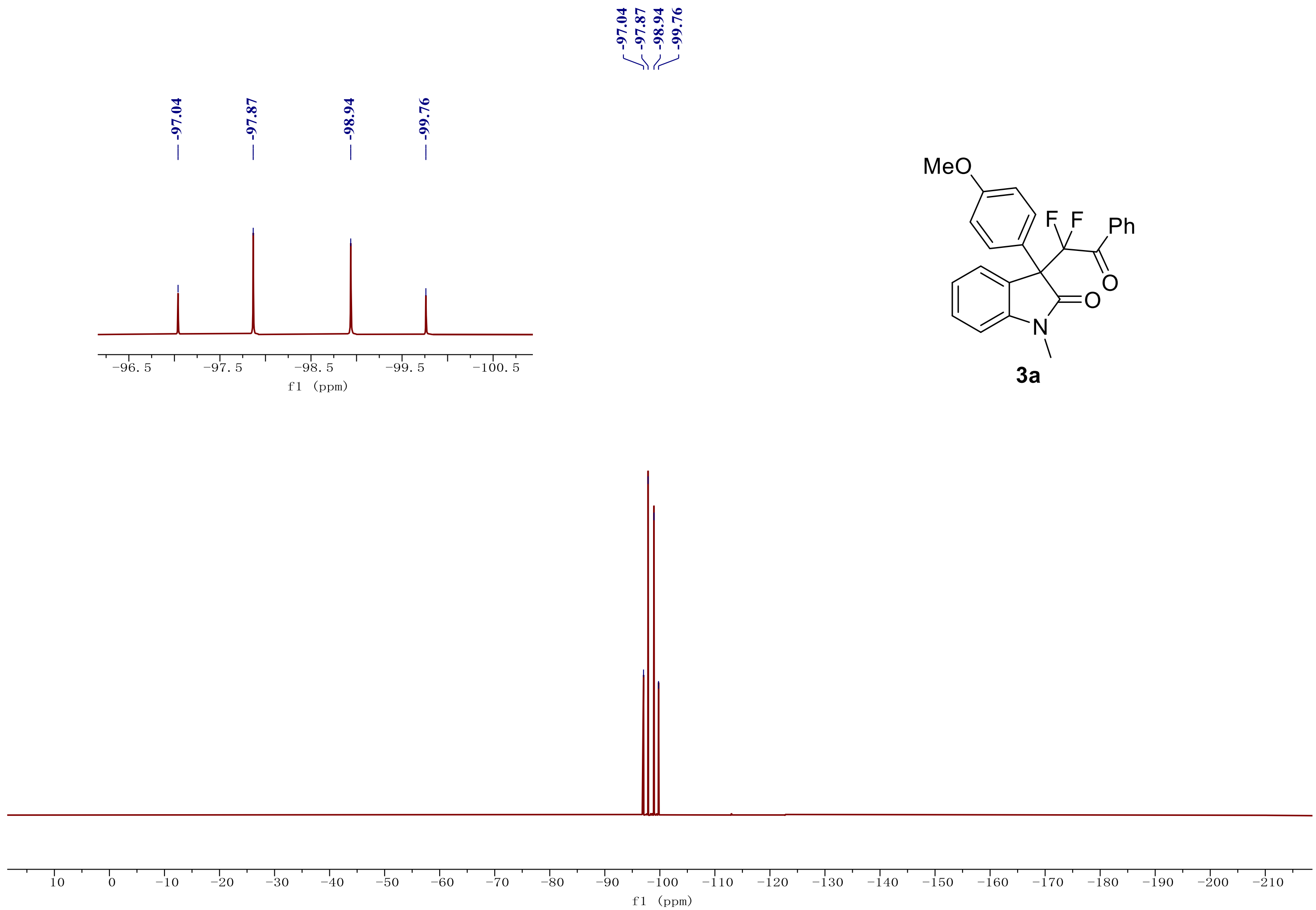
^{1}H NMR of Compound 3a (400 MHz, $CDCl_3$)



^{13}C NMR of Compound 3a (100 MHz, $CDCl_3$)

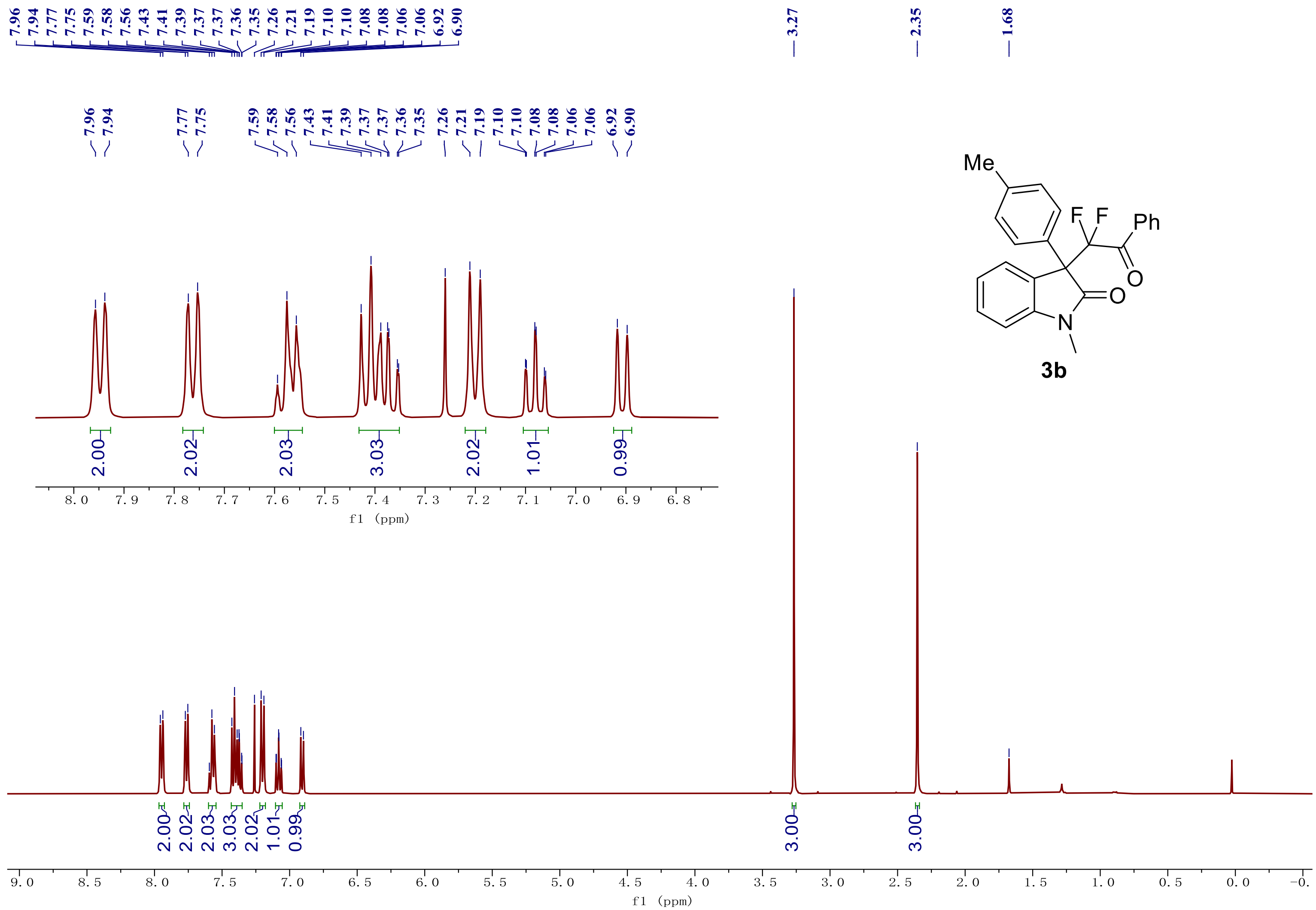


[19]F NMR of Compound 3a (376 MHz, $CDCl_3$)

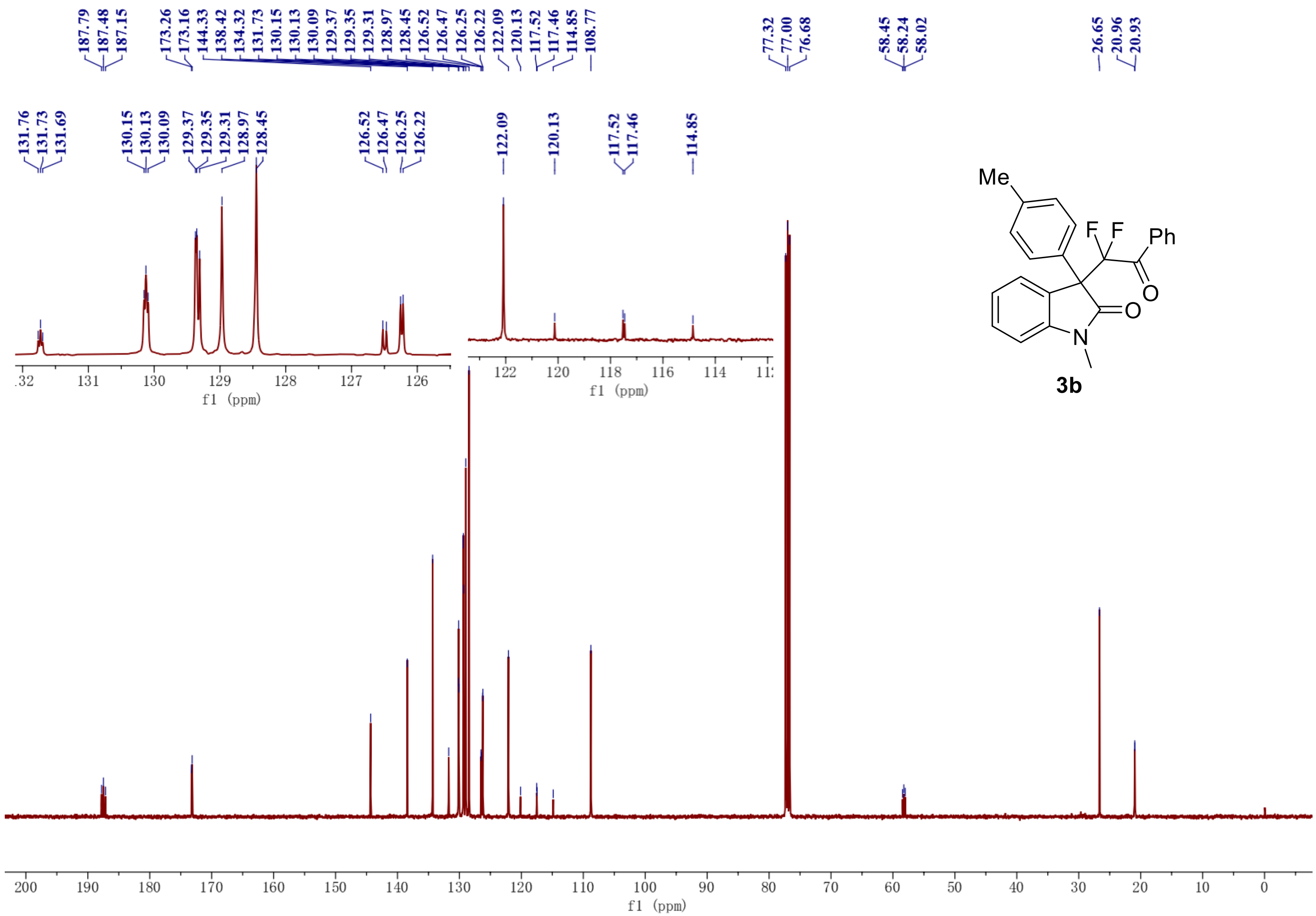


3a

^{1}H NMR of Compound 3b (400 MHz, $CDCl_3$)

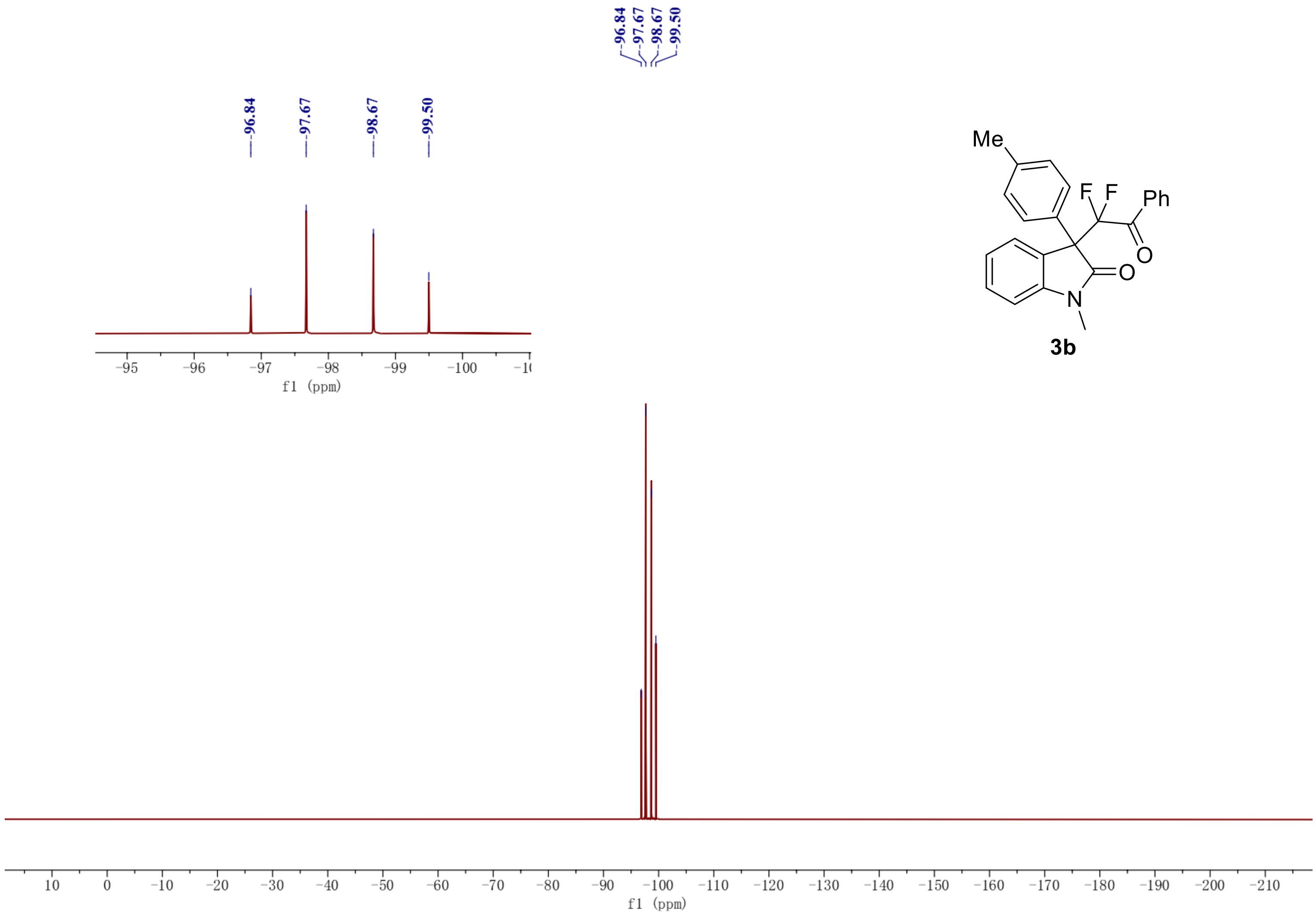


^{13}C NMR of Compound 3b (100 MHz, $CDCl_3$)



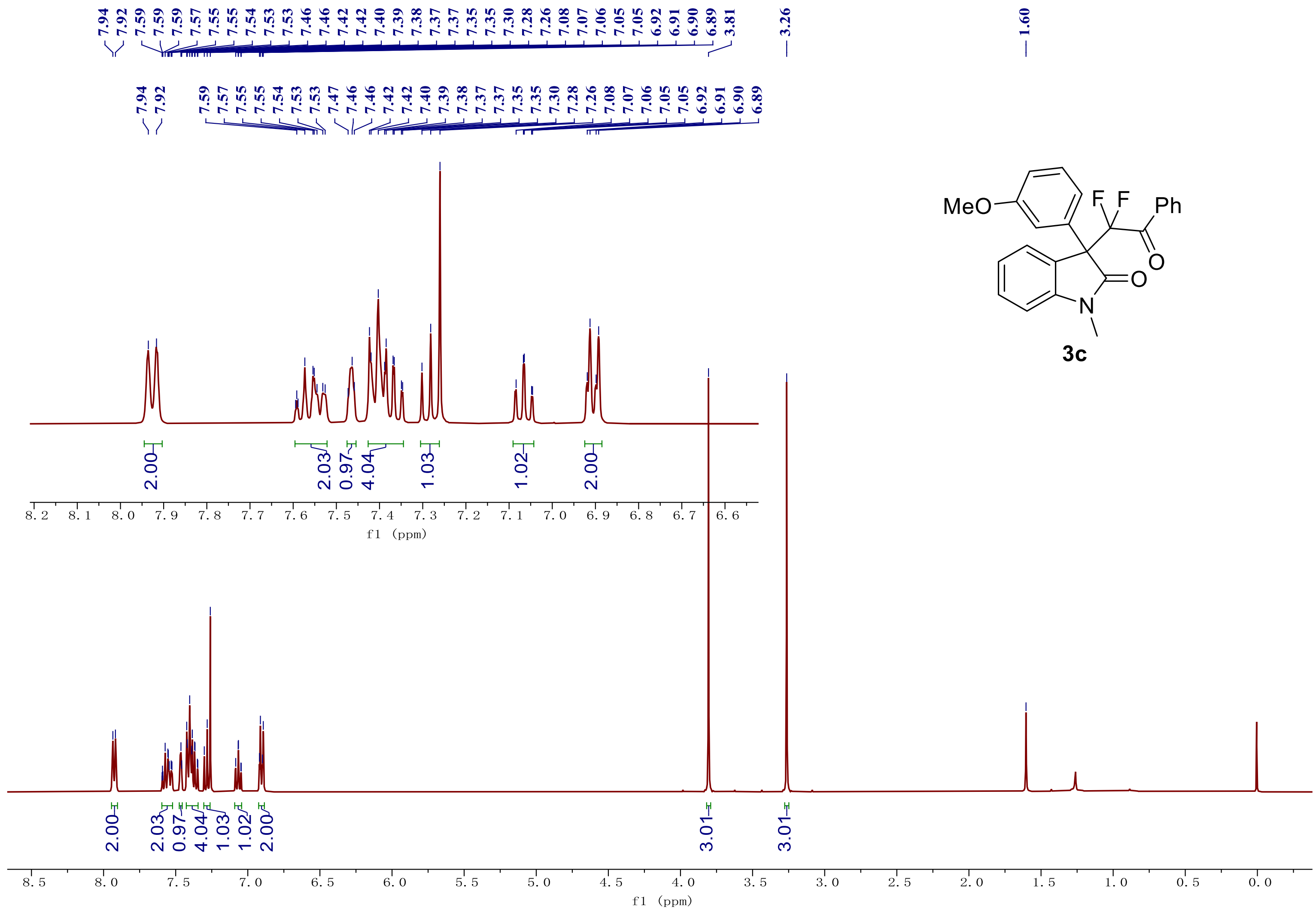
3b

^{19}F NMR of Compound 3b (376 MHz, $CDCl_3$)

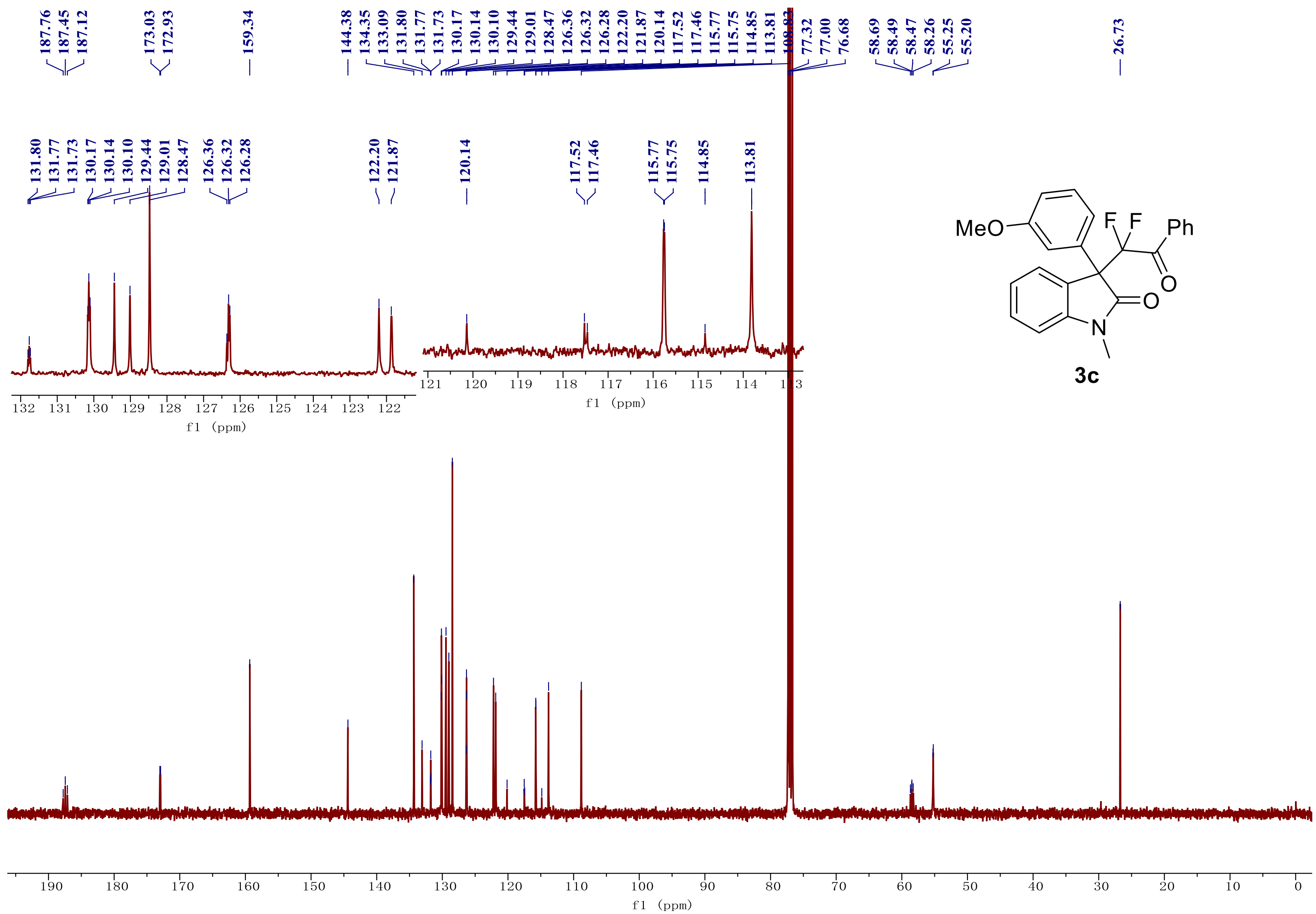


3b

[1]H NMR of Compound 3c (400 MHz, $CDCl_3$)

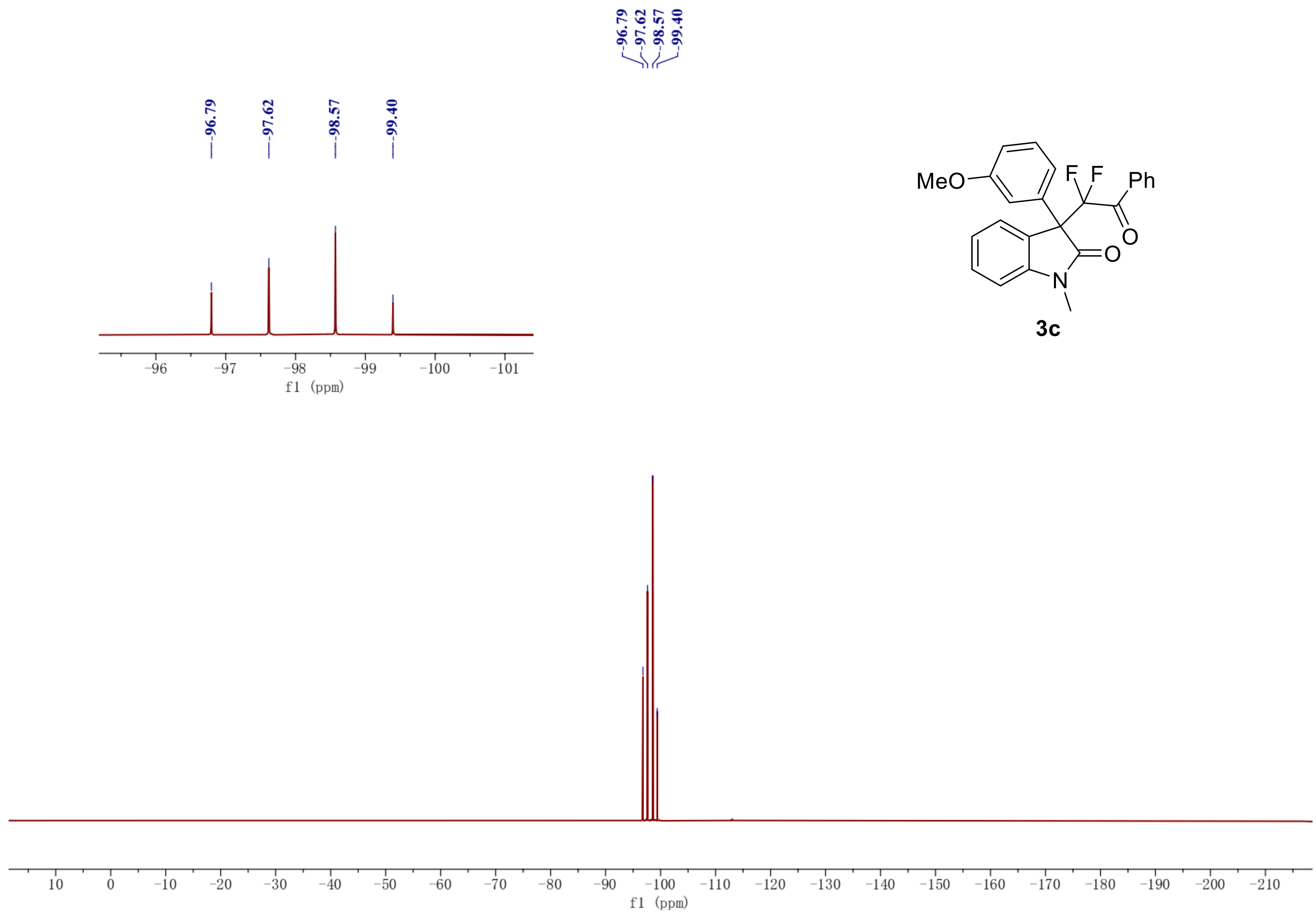


^{13}C NMR of Compound 3c (100 MHz, $CDCl_3$)

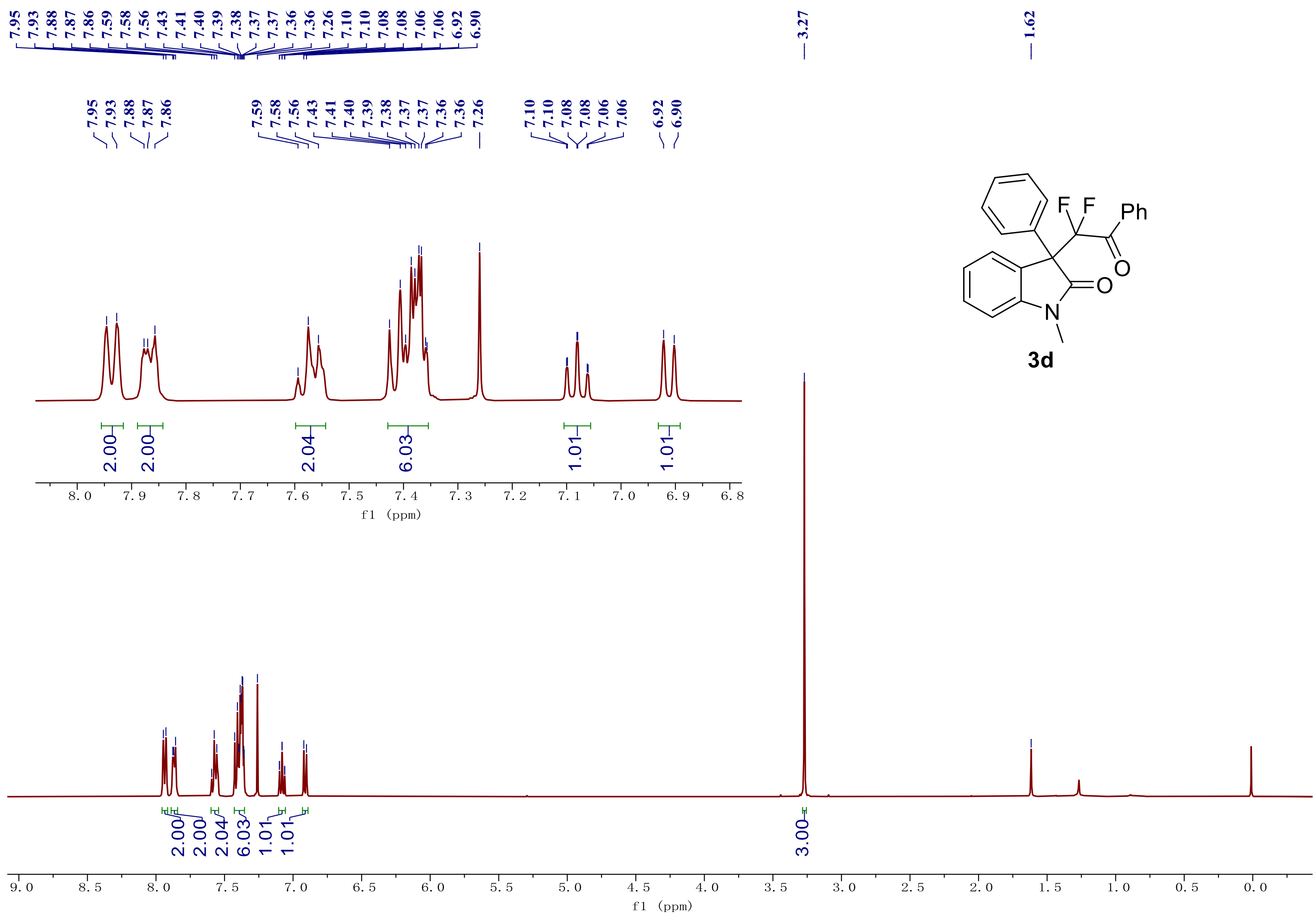


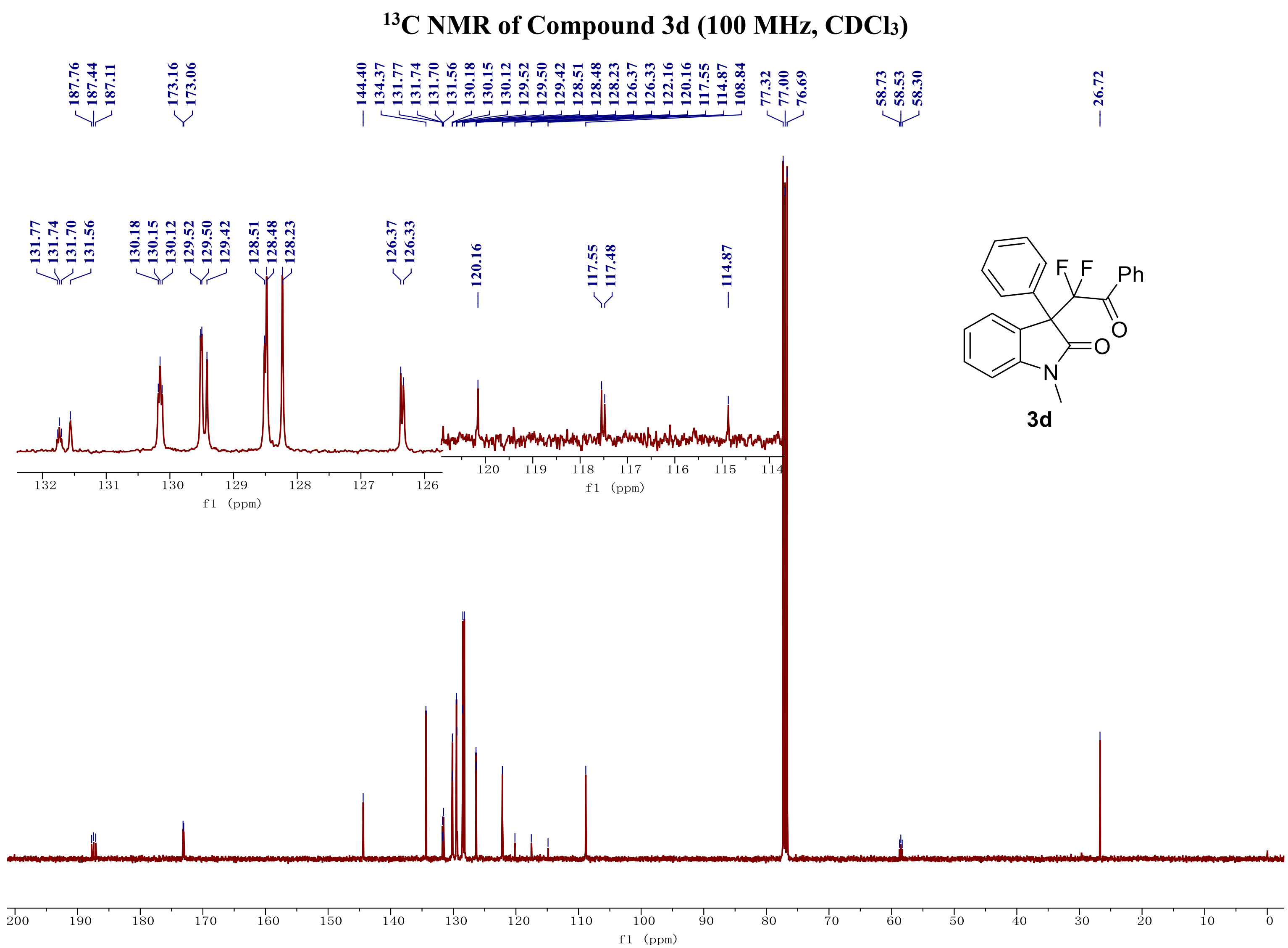
3c

^{19}F NMR of Compound 3c (376 MHz, $CDCl_3$)



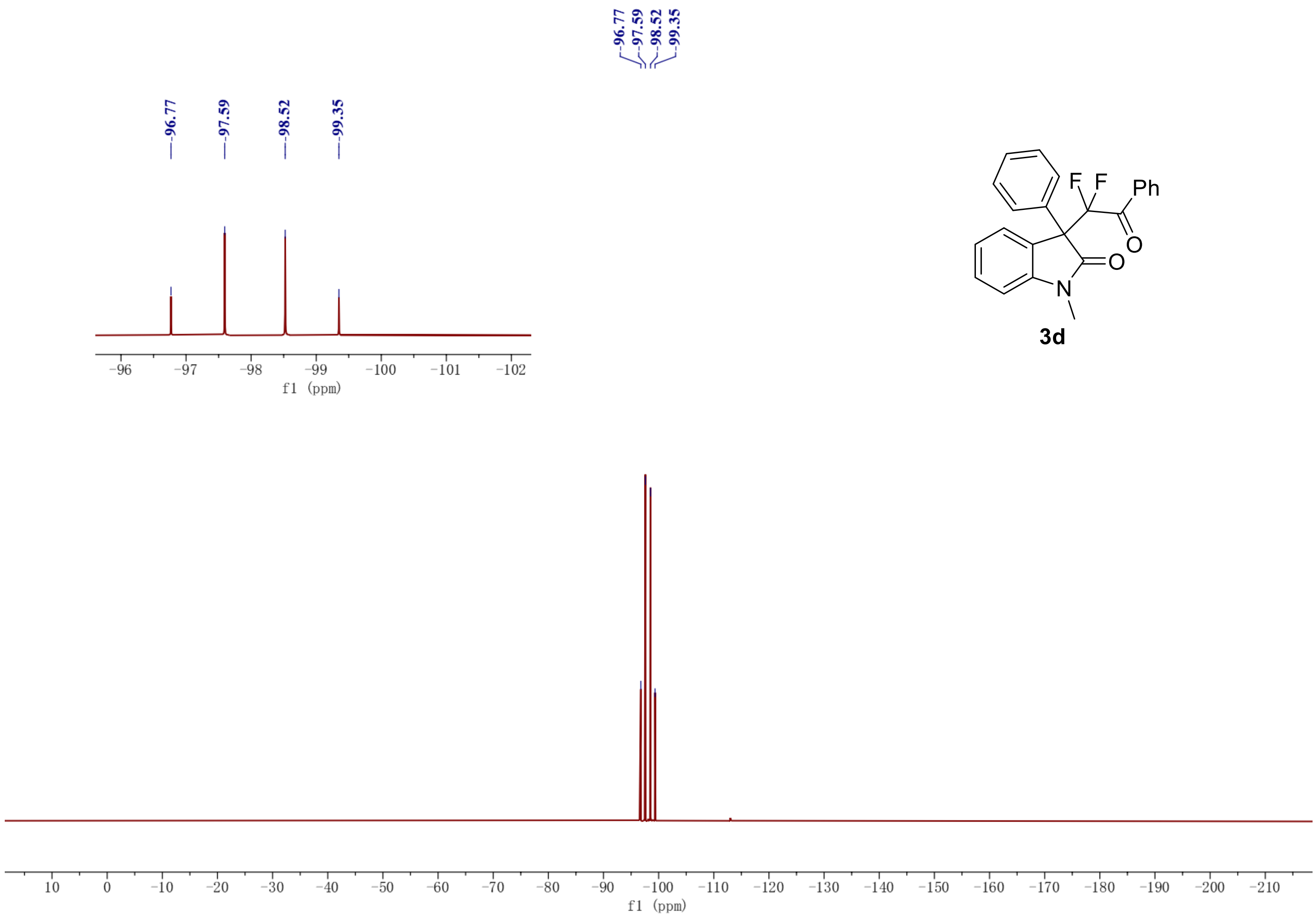
^{1}H NMR of Compound 3d (400 MHz, $CDCl_3$)





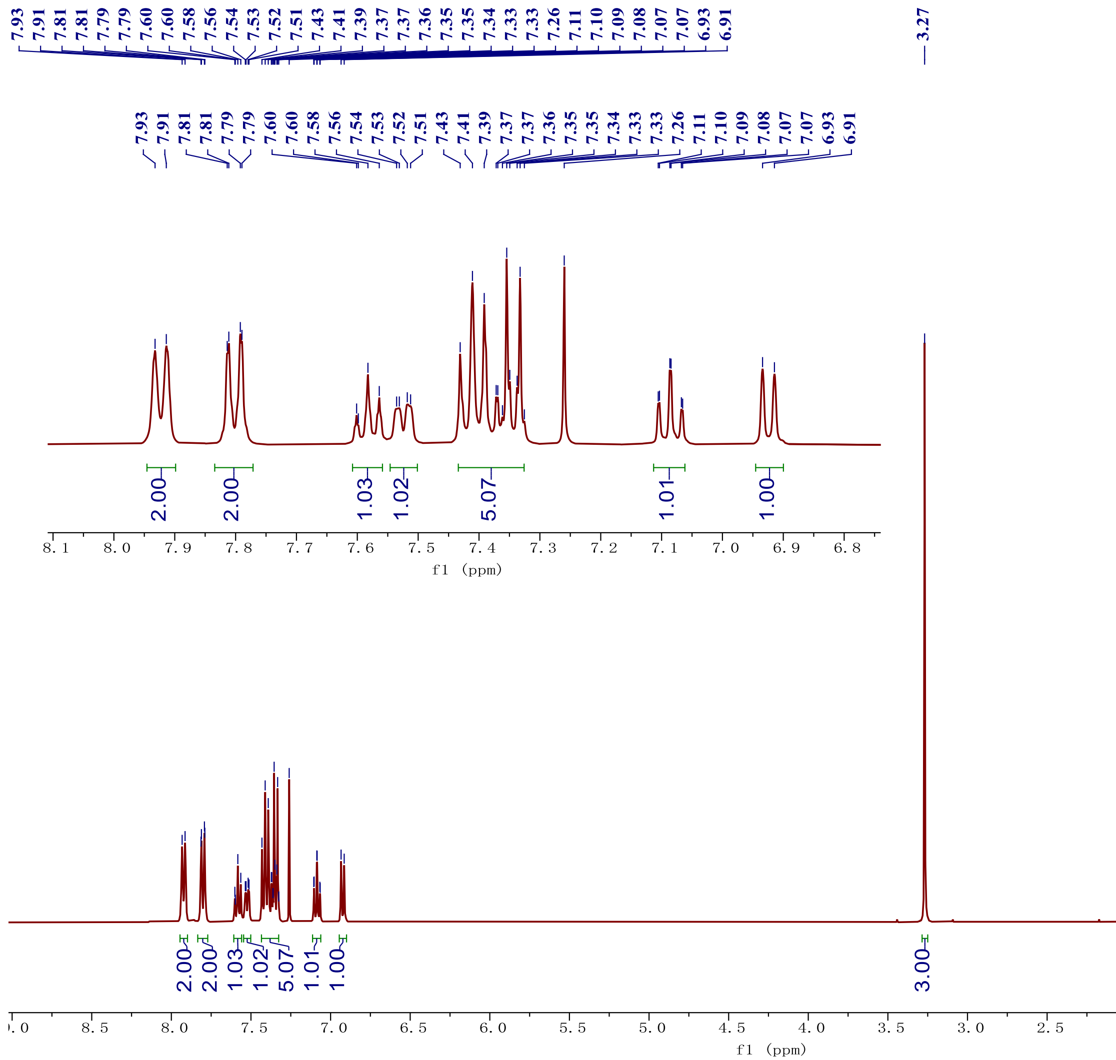
^{13}C NMR of Compound 3d (100 MHz, CDCl$_3$)
187.76
187.44
187.11
173.16
173.06
144.40
134.37
131.77
131.74
131.70
131.56
130.18
130.15
130.12
129.52
129.50
129.42
128.51
128.48
128.23
126.37
126.33
122.16
120.16
117.55
114.87
108.84
77.32
77.00
76.69
58.73
58.53
58.30
26.72
117.48
F
F
Ph
O
O
N
3d
f1 (ppm)

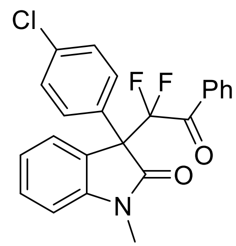
^{19}F NMR of Compound 3d (376 MHz, $CDCl_3$)



3d

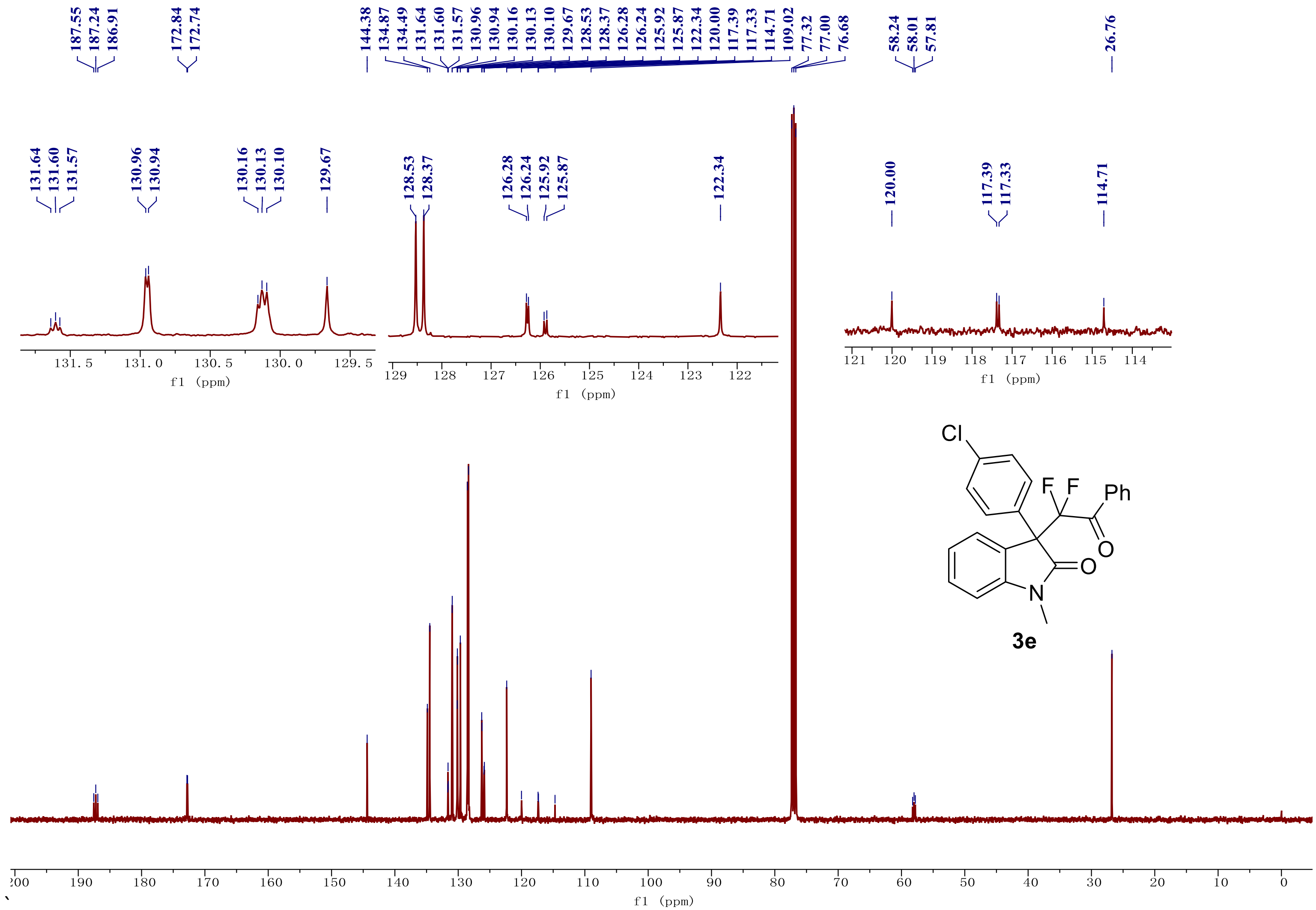
^{1}H NMR of Compound 3e (400 MHz, $CDCl_3$)



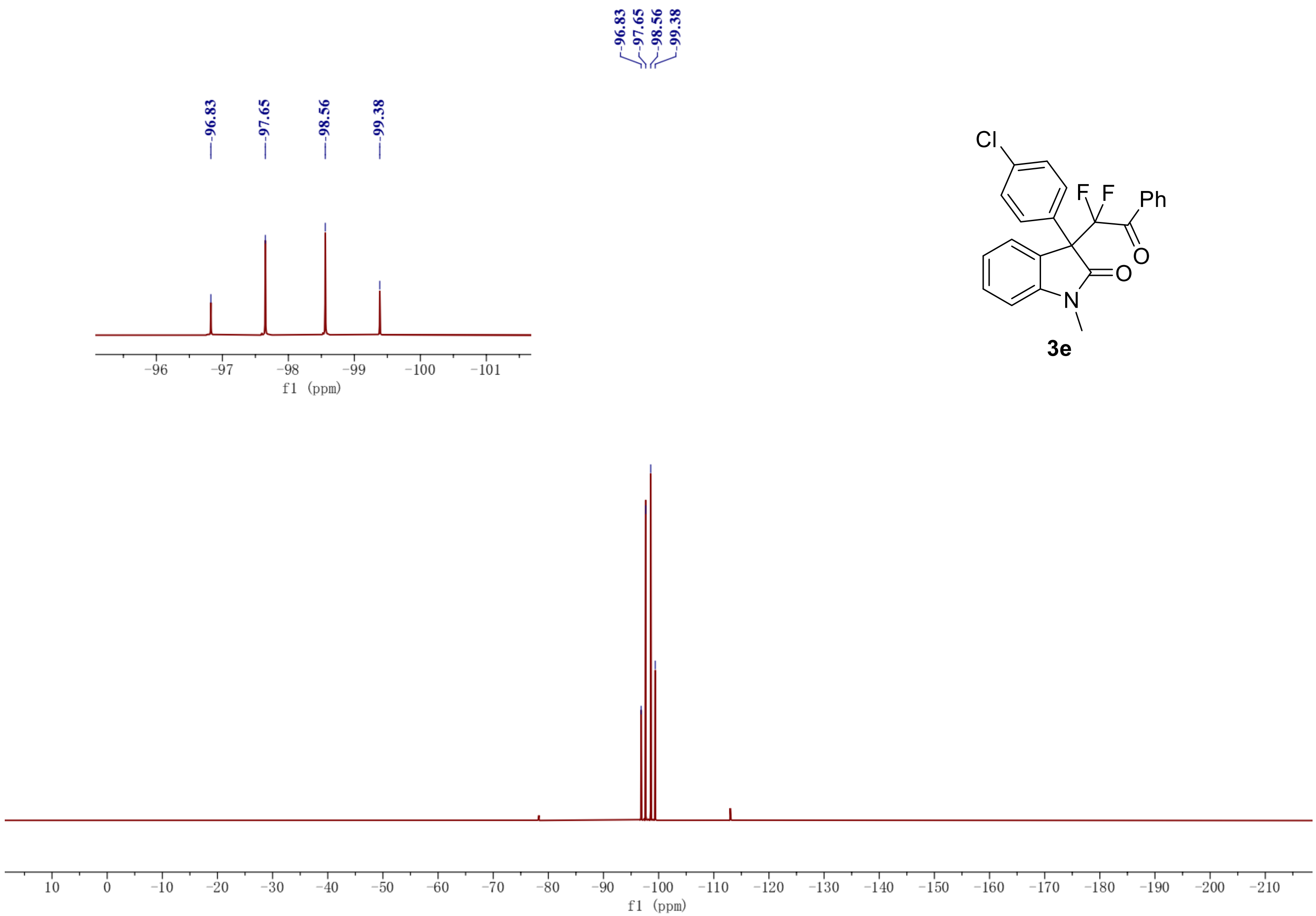


3e

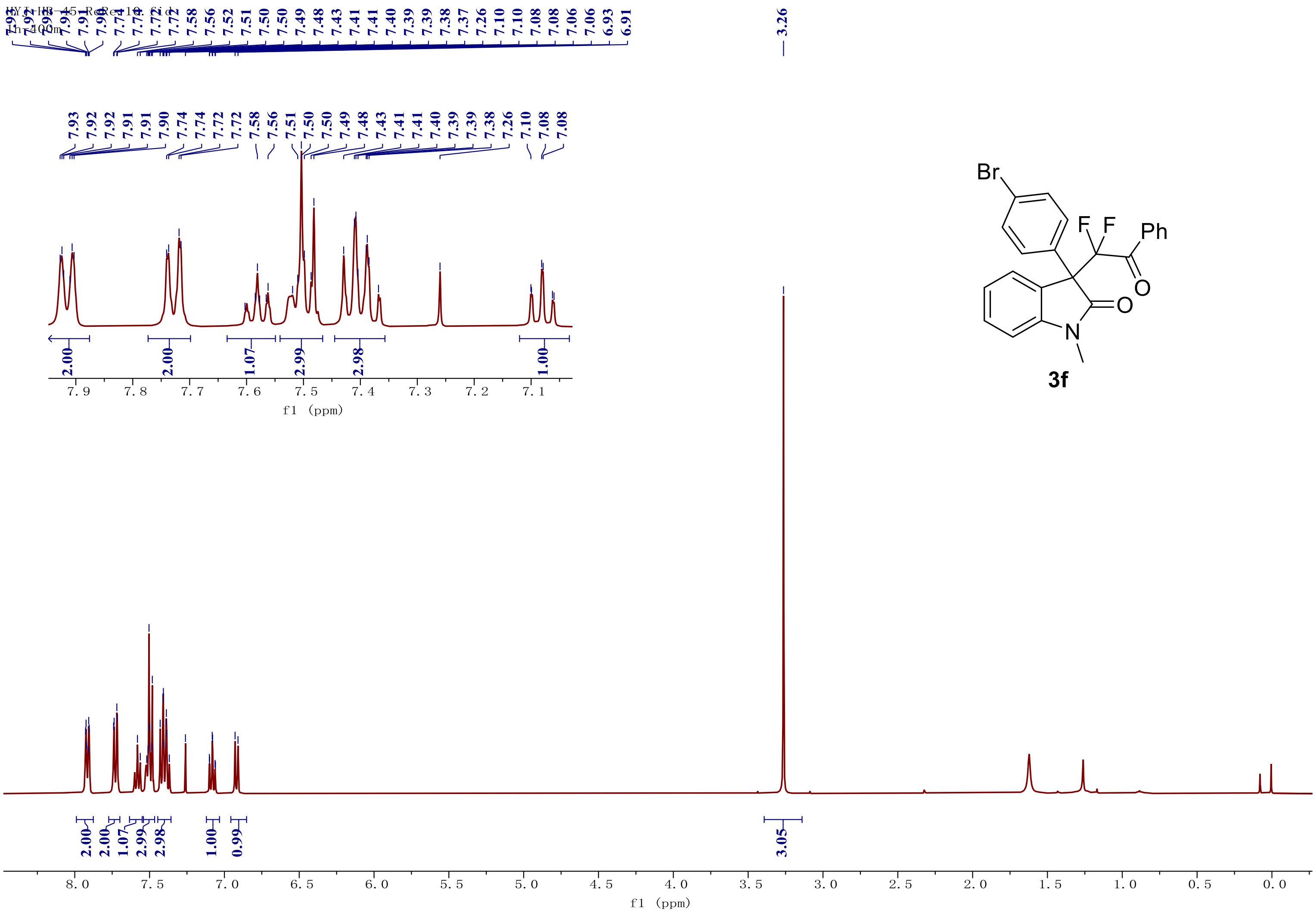
^{13}C NMR of Compound 3e (100 MHz, CDCl$_3$)



^{19}F NMR of Compound 3e (376 MHz, $CDCl_3$)

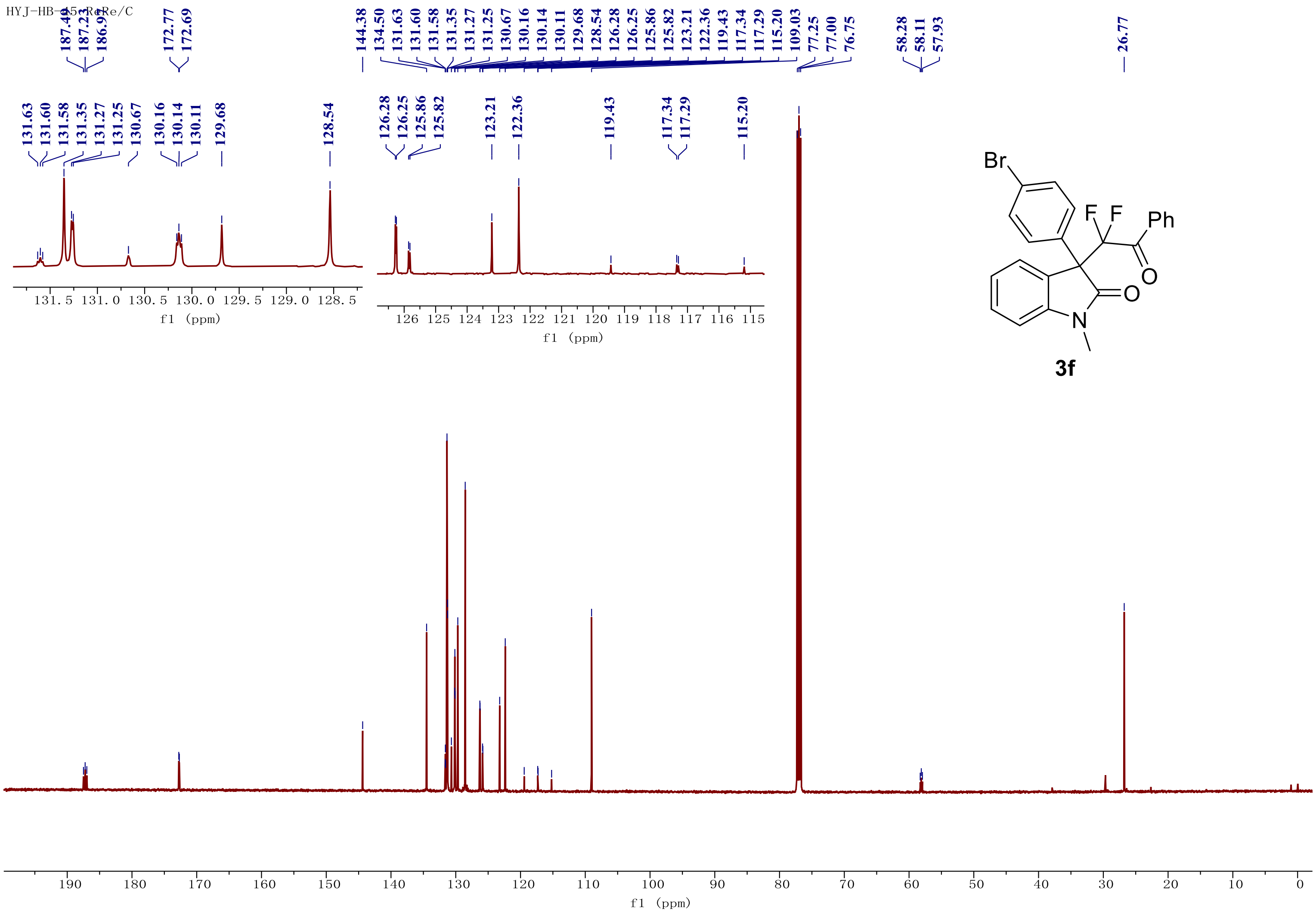


^{1}H NMR of Compound 3f (400 MHz, $CDCl_3$)

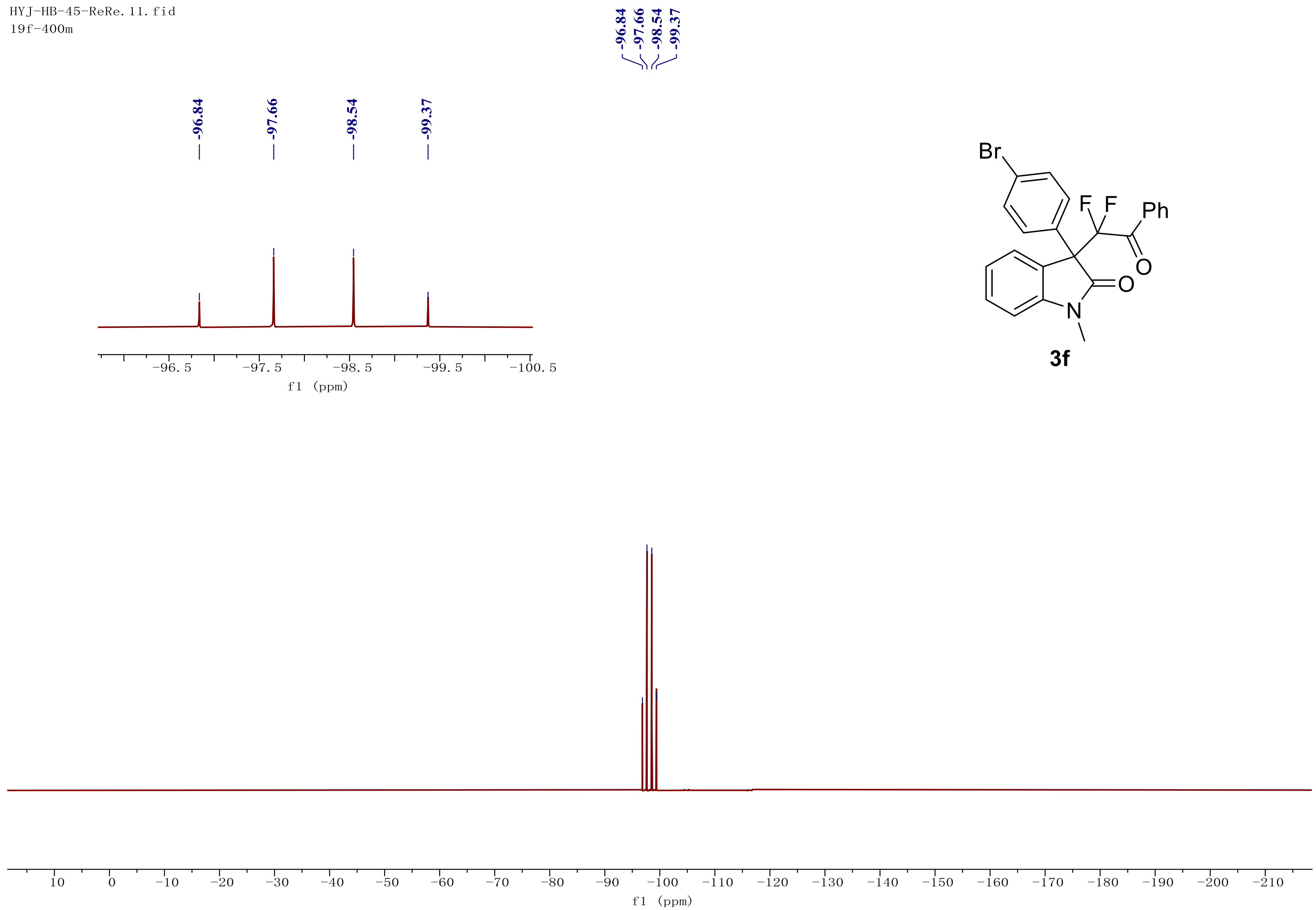


3f

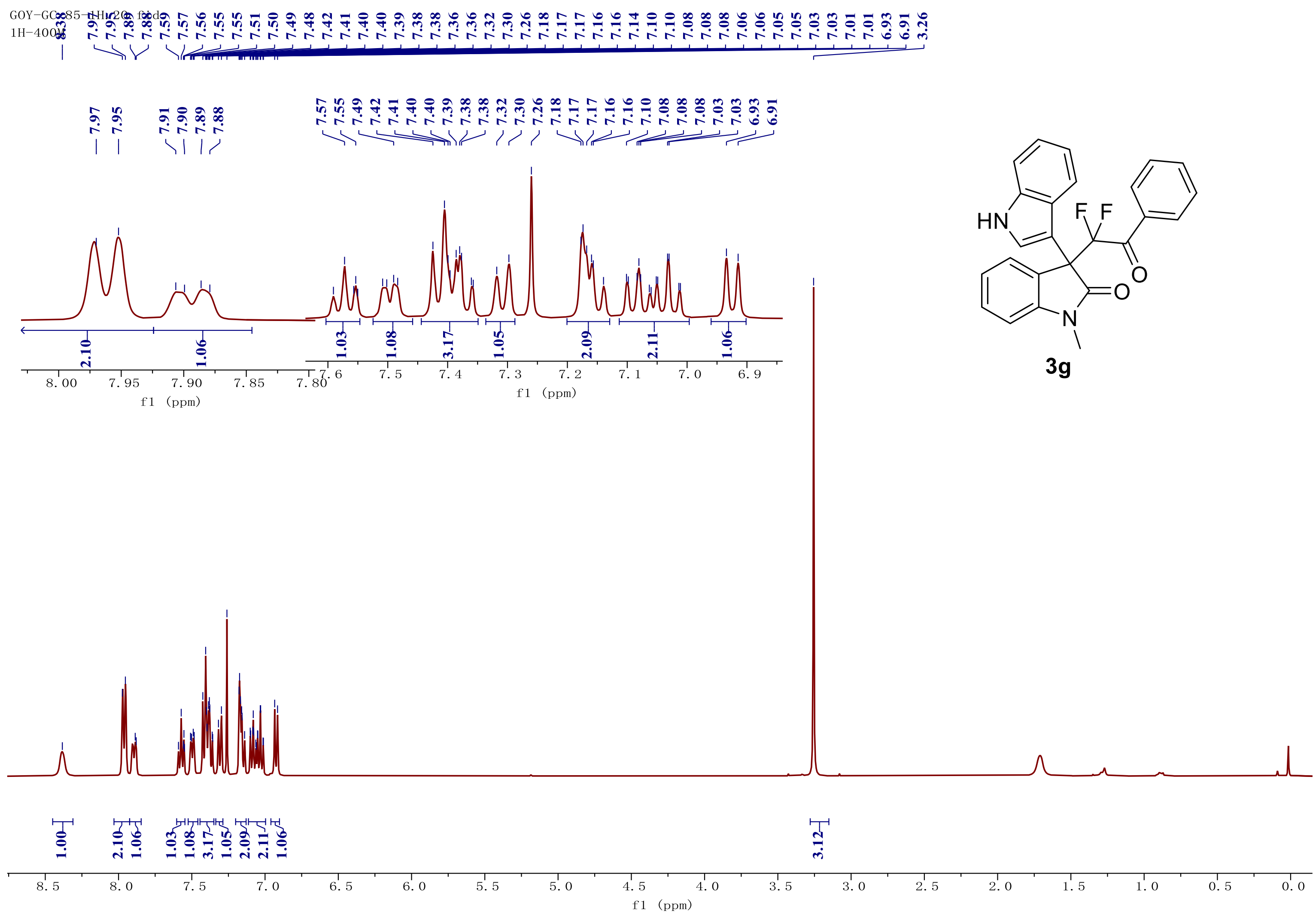
[13]C NMR of Compound 3f (500 MHz, $CDCl_3$)



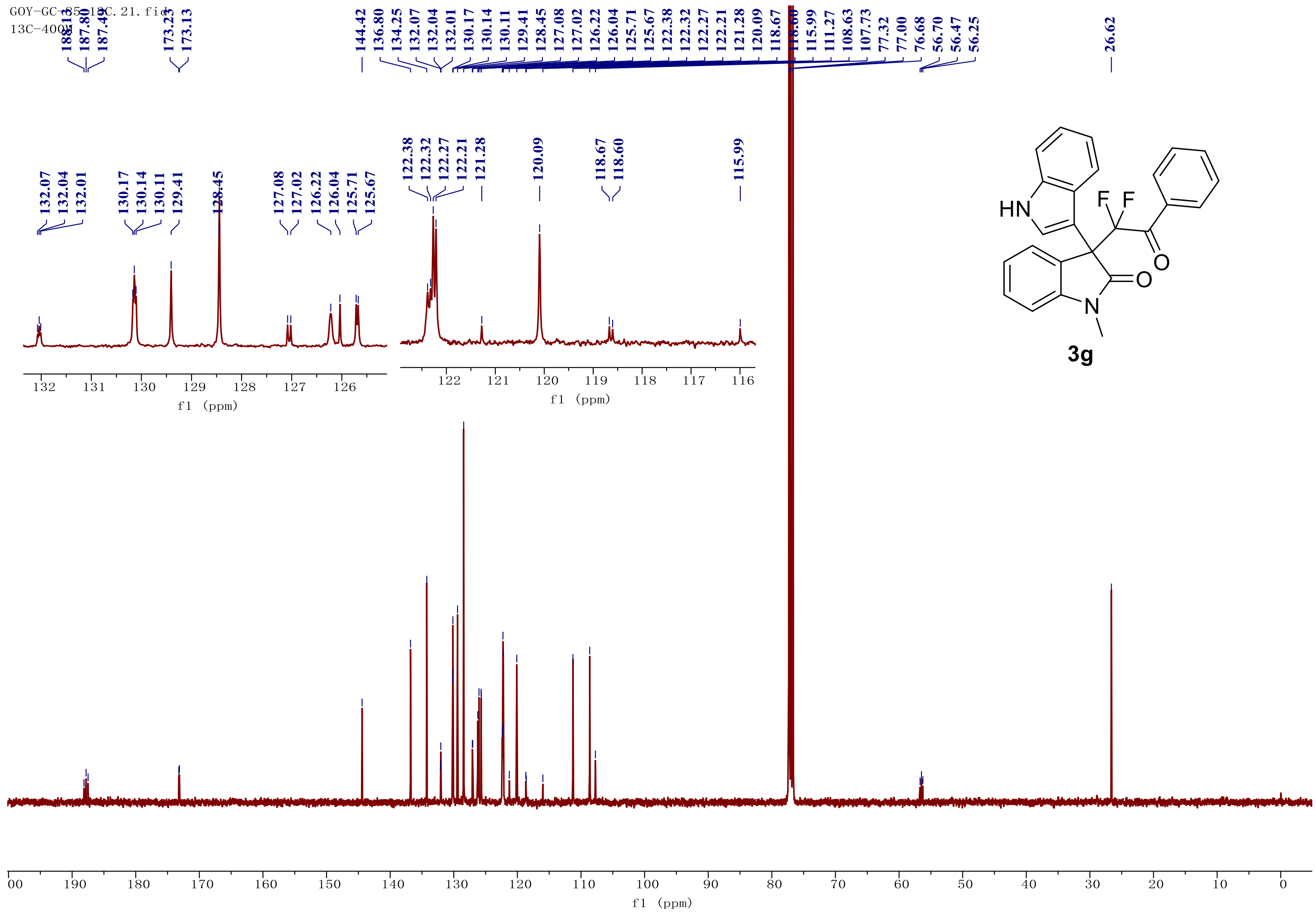
^{19}F NMR of Compound 3f (376 MHz, $CDCl_3$)



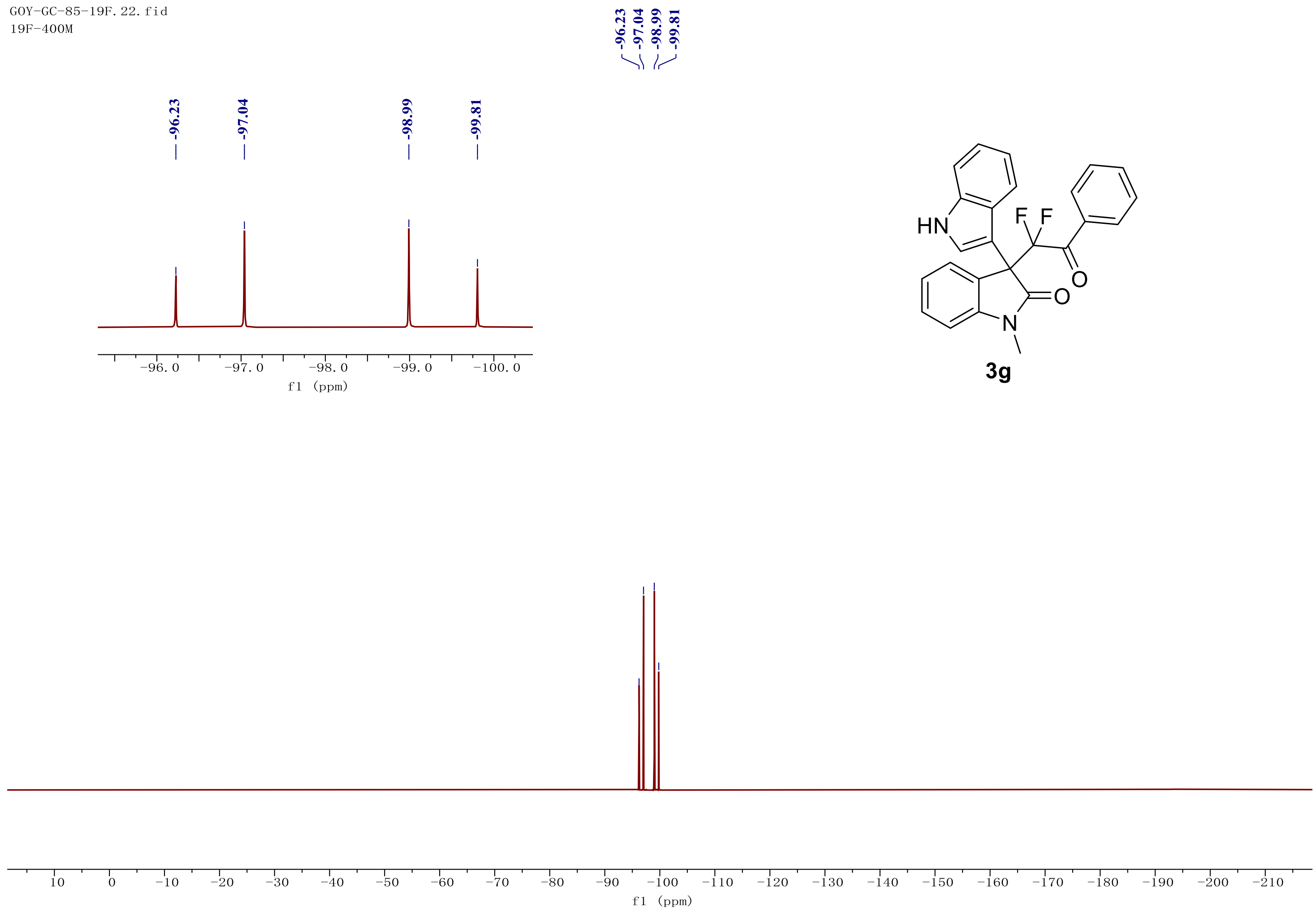
[1]H NMR of Compound 3g (400 MHz, CDCl₃)



^{13}C NMR of Compound 3g (100 MHz, $CDCl_3$)

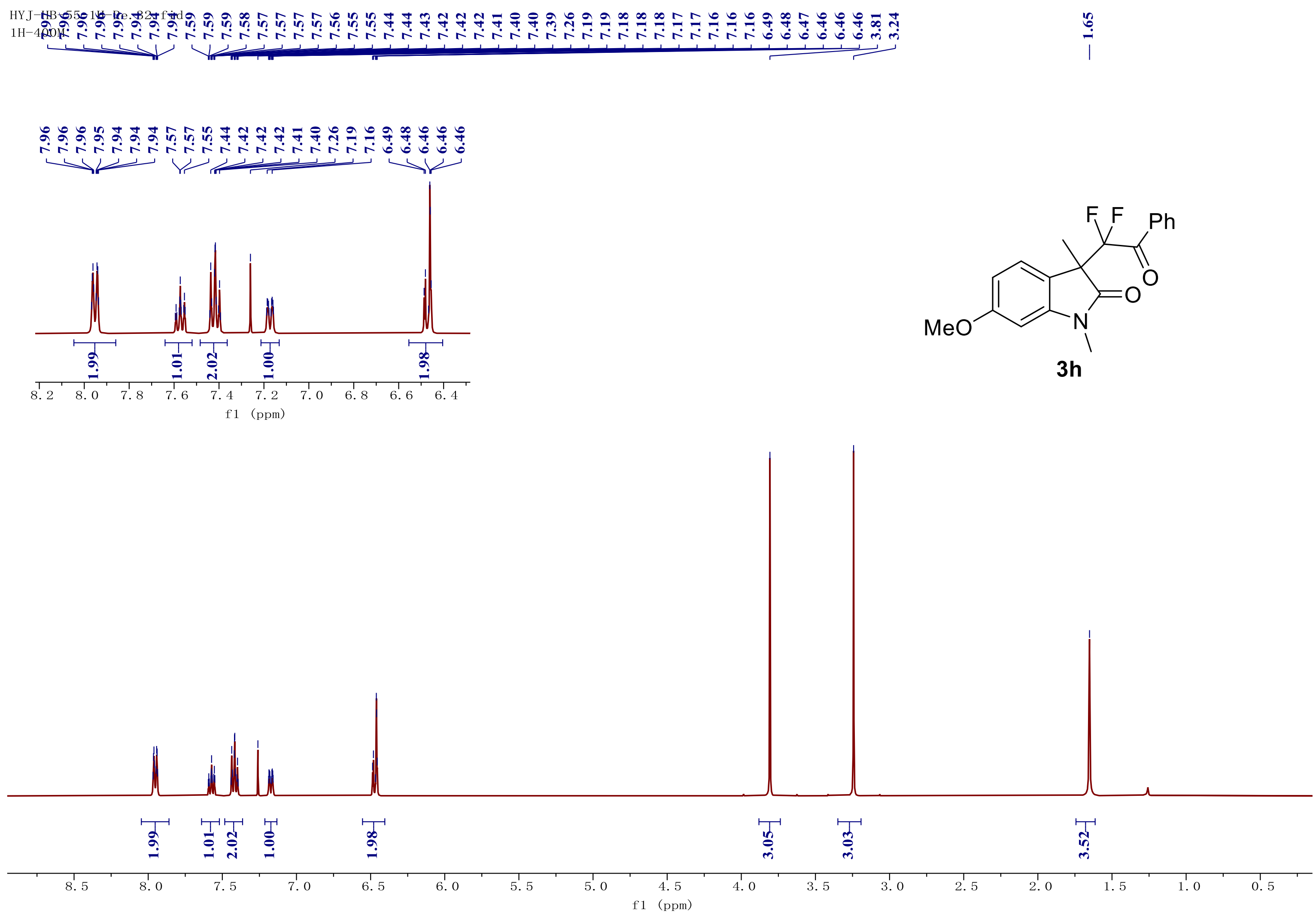


^{19}F NMR of Compound 3g (376 MHz, $CDCl_3$)

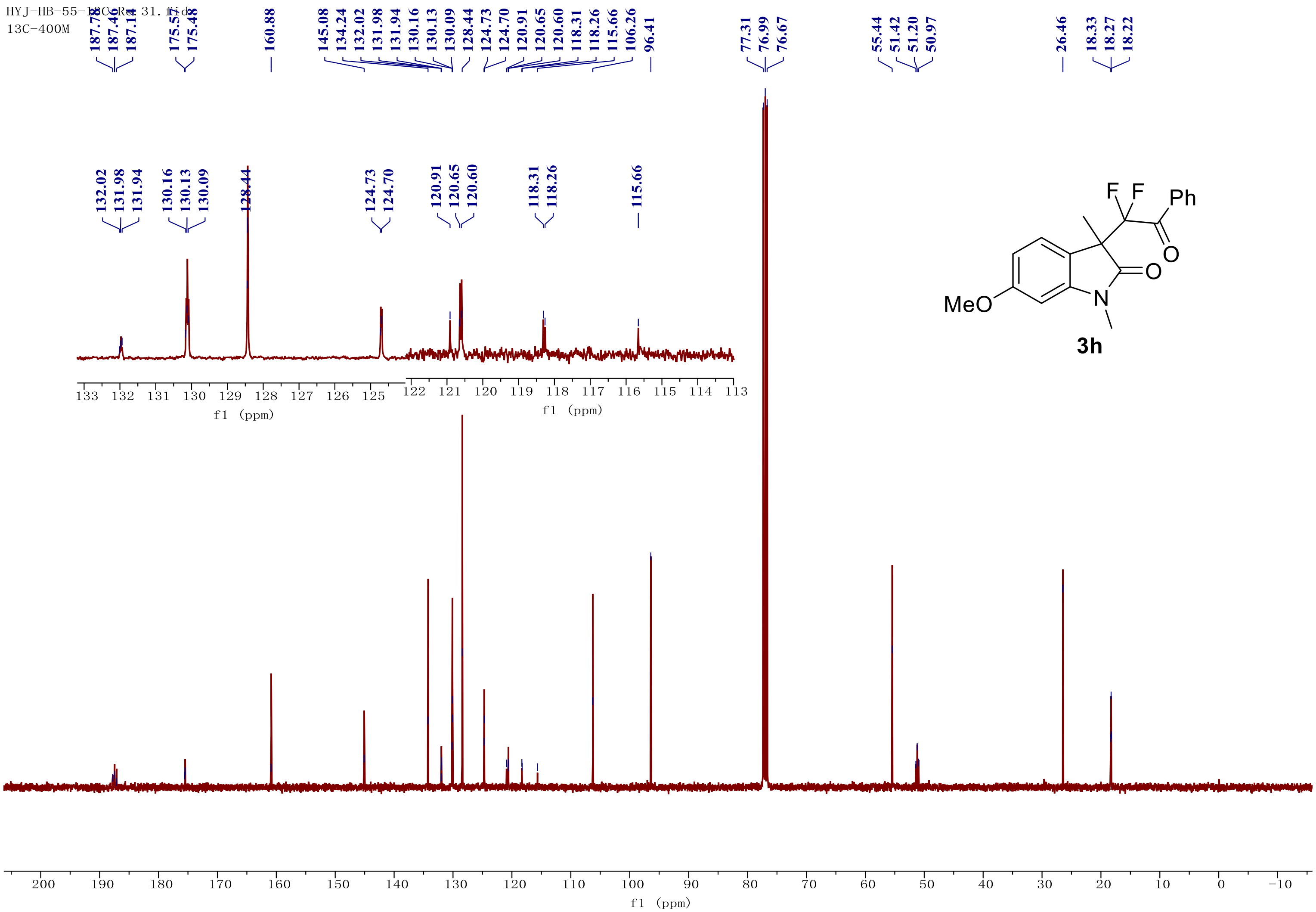


3g

^{1}H NMR of Compound 3h (400 MHz, $CDCl_3$)

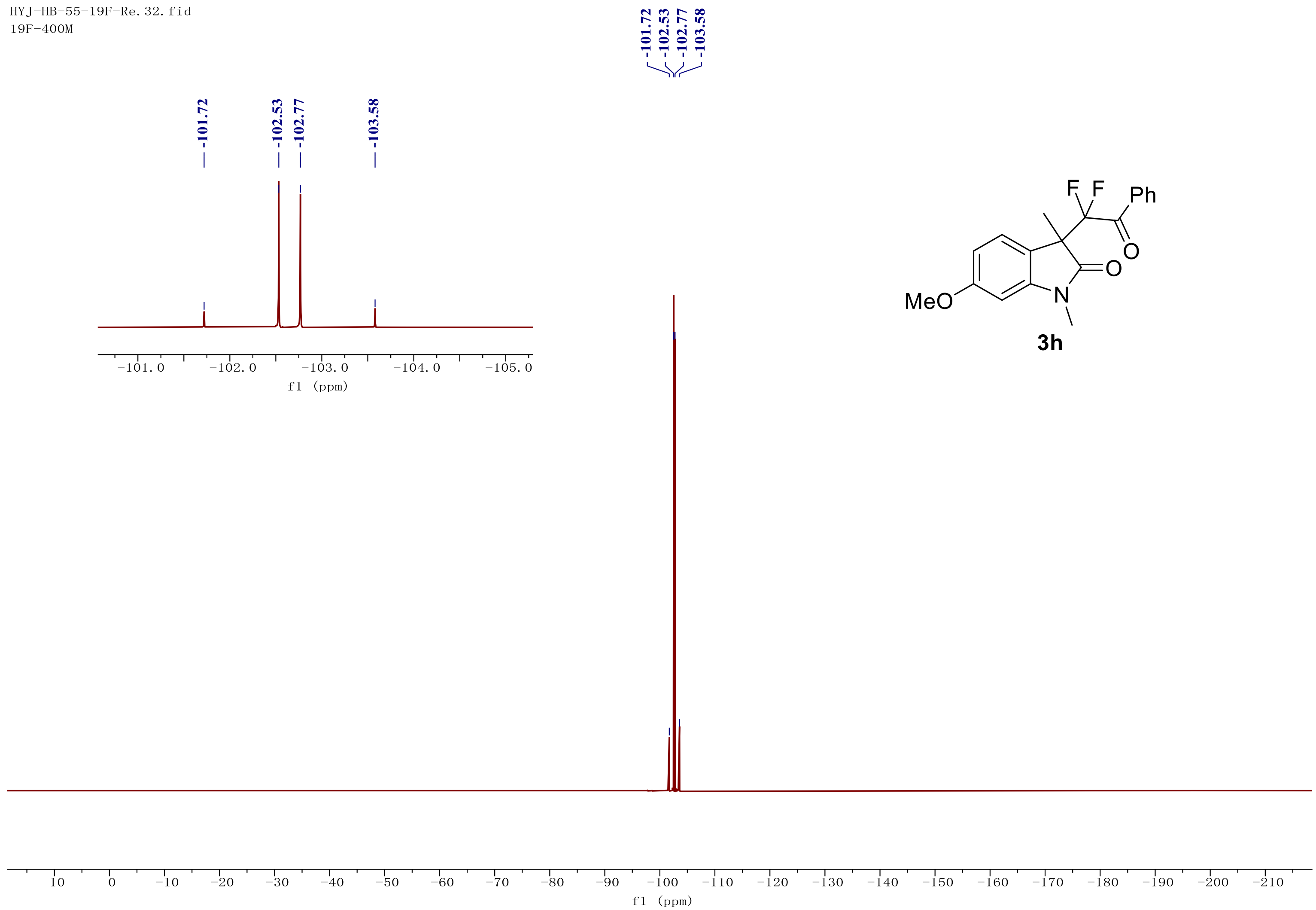


^{13}C NMR of Compound 3h (100 MHz, $CDCl_3$)



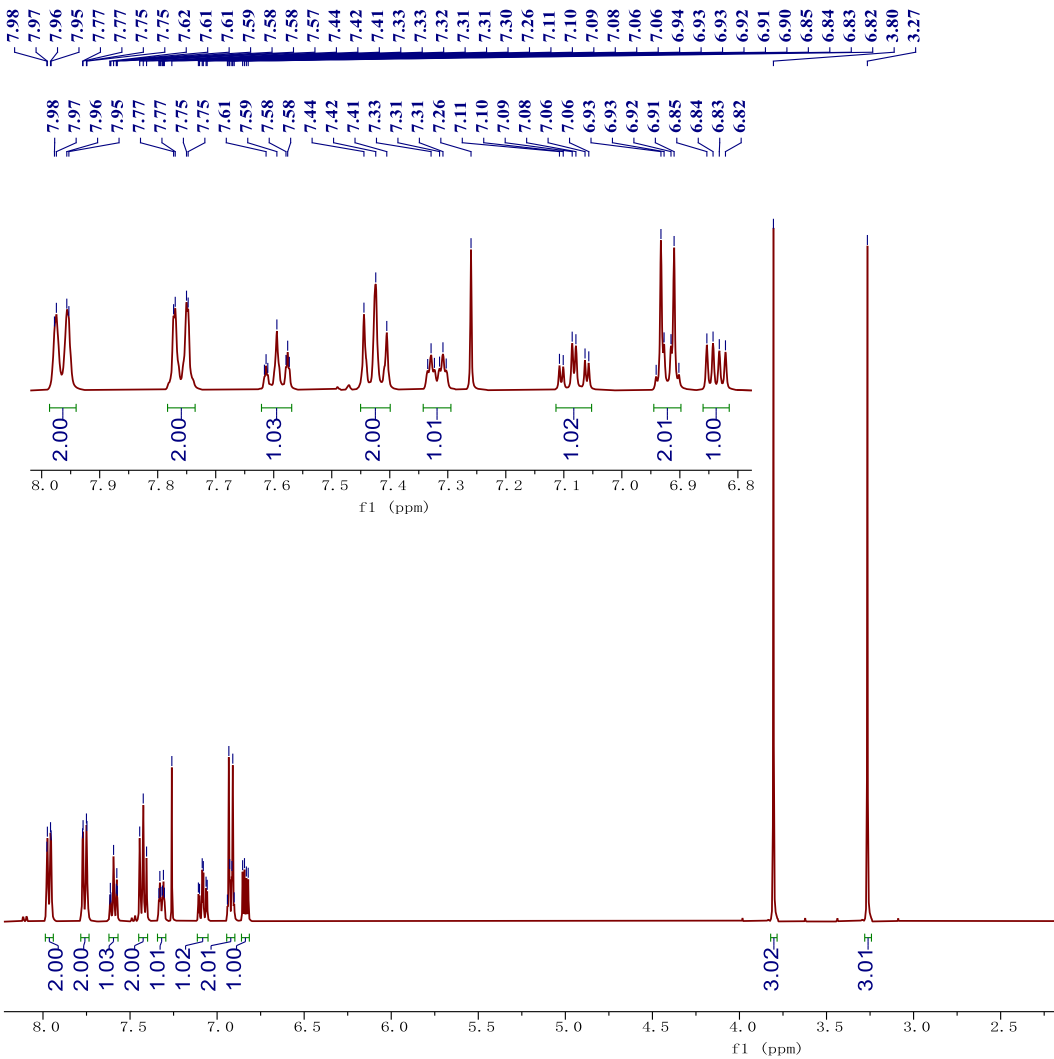
3h

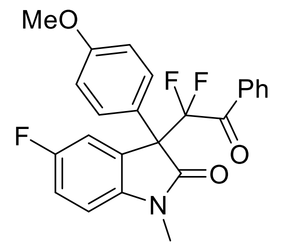
^{19}F NMR of Compound 3h (376 MHz, $CDCl_3$)



3h

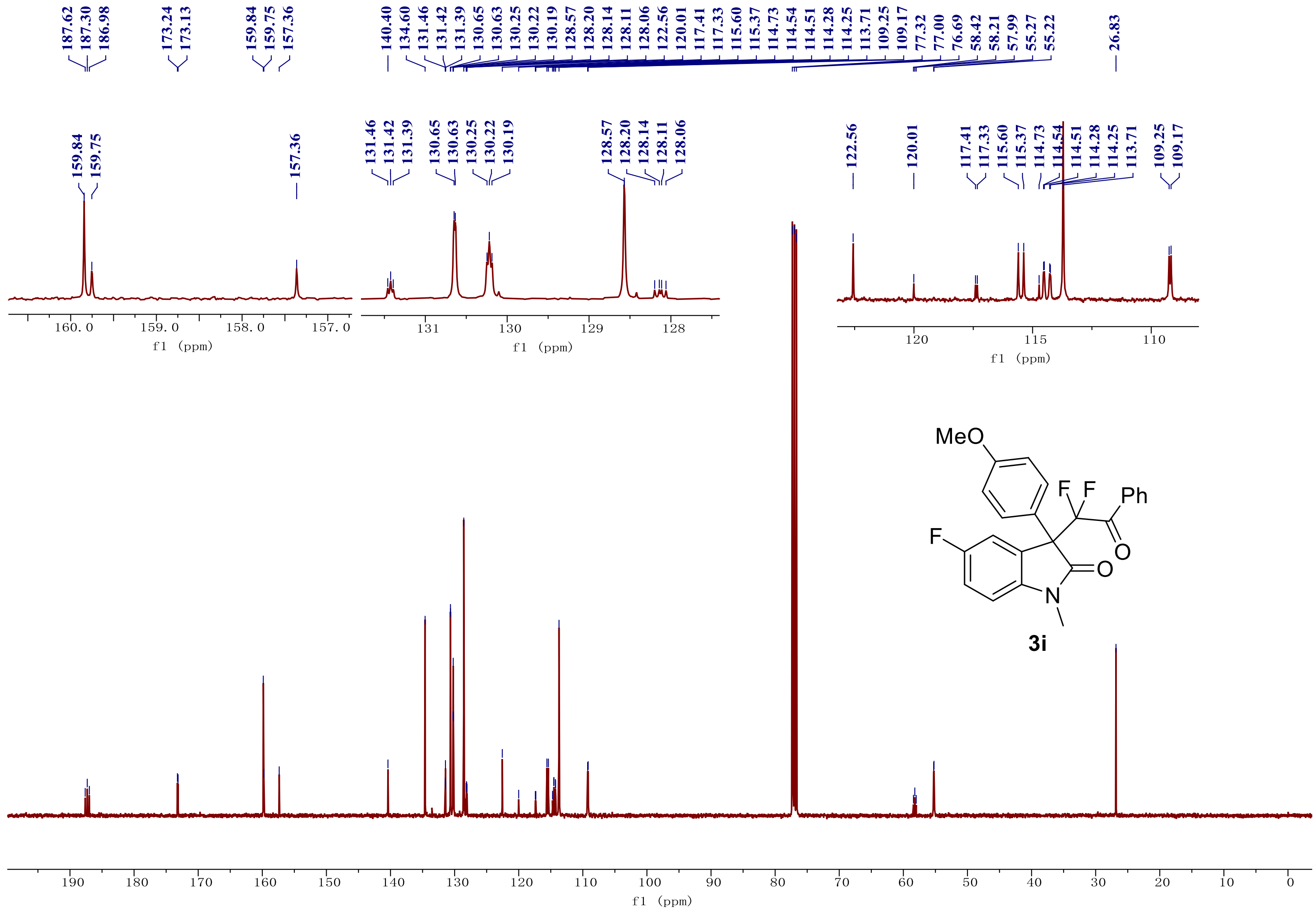
^{1}H NMR of Compound 3i (400 MHz, CDCl$_3$)



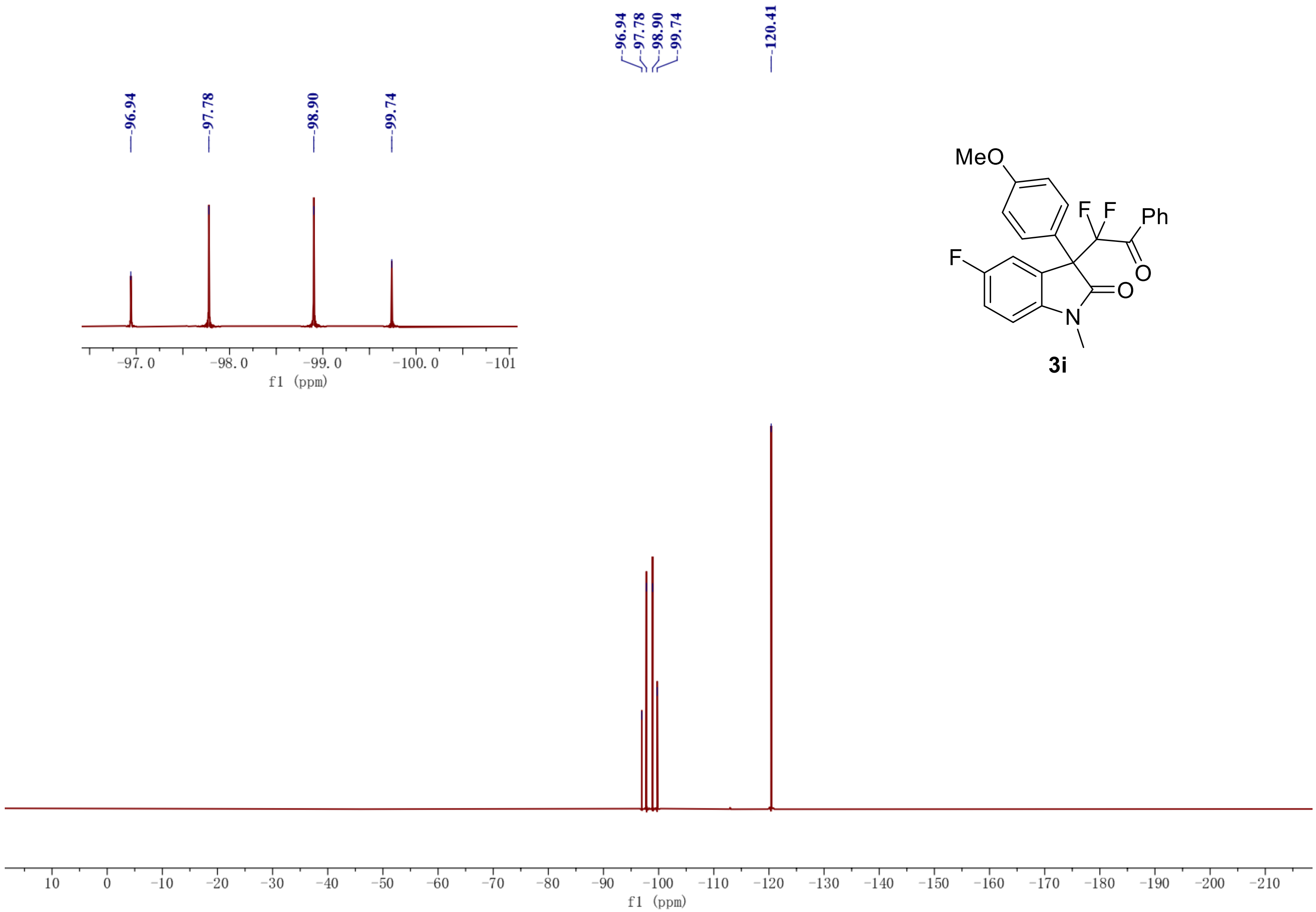


3i

^{13}C NMR of Compound 3i (100 MHz, $CDCl_3$)

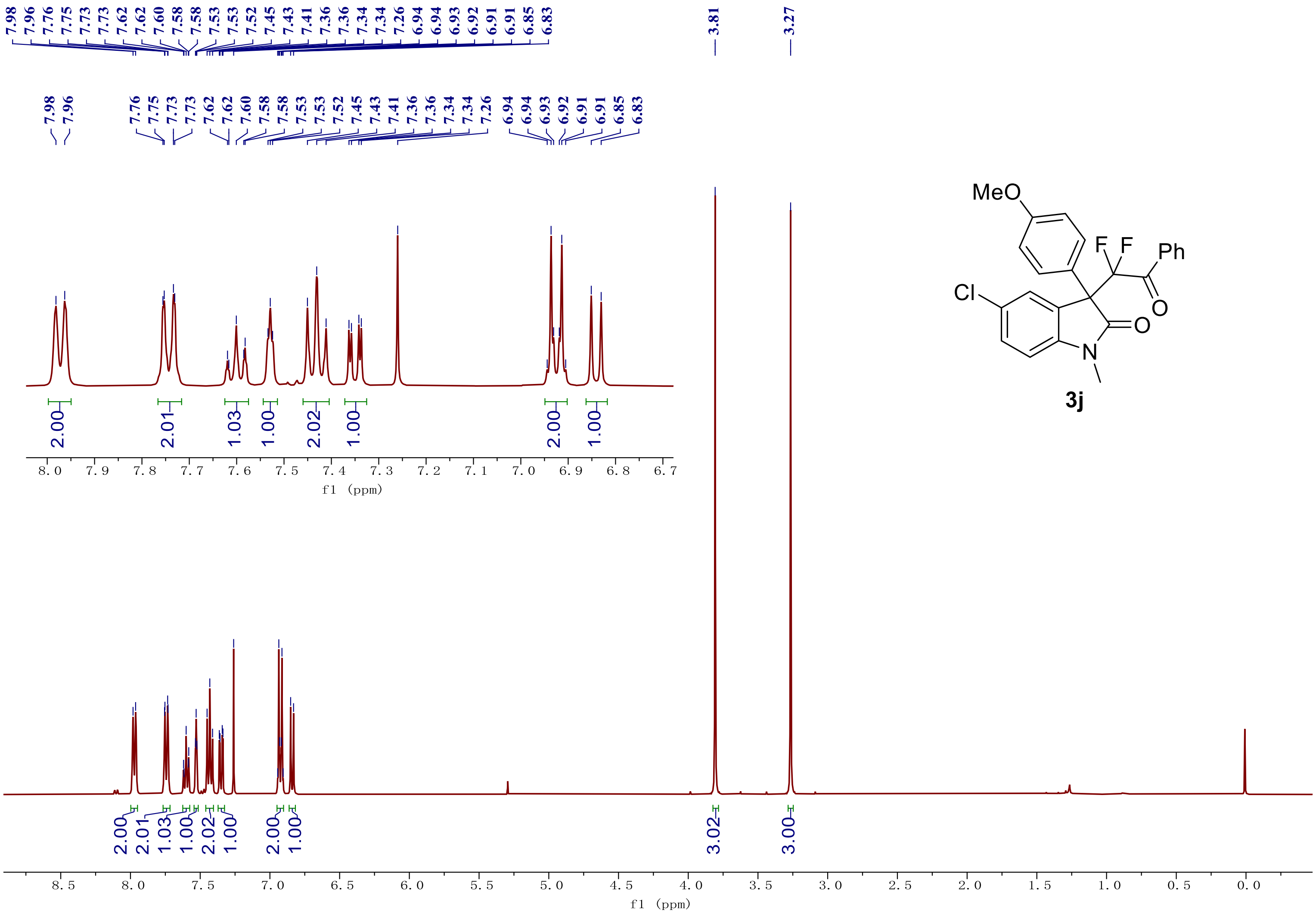


^{19}F NMR of Compound 3i (376 MHz, $CDCl_3$)



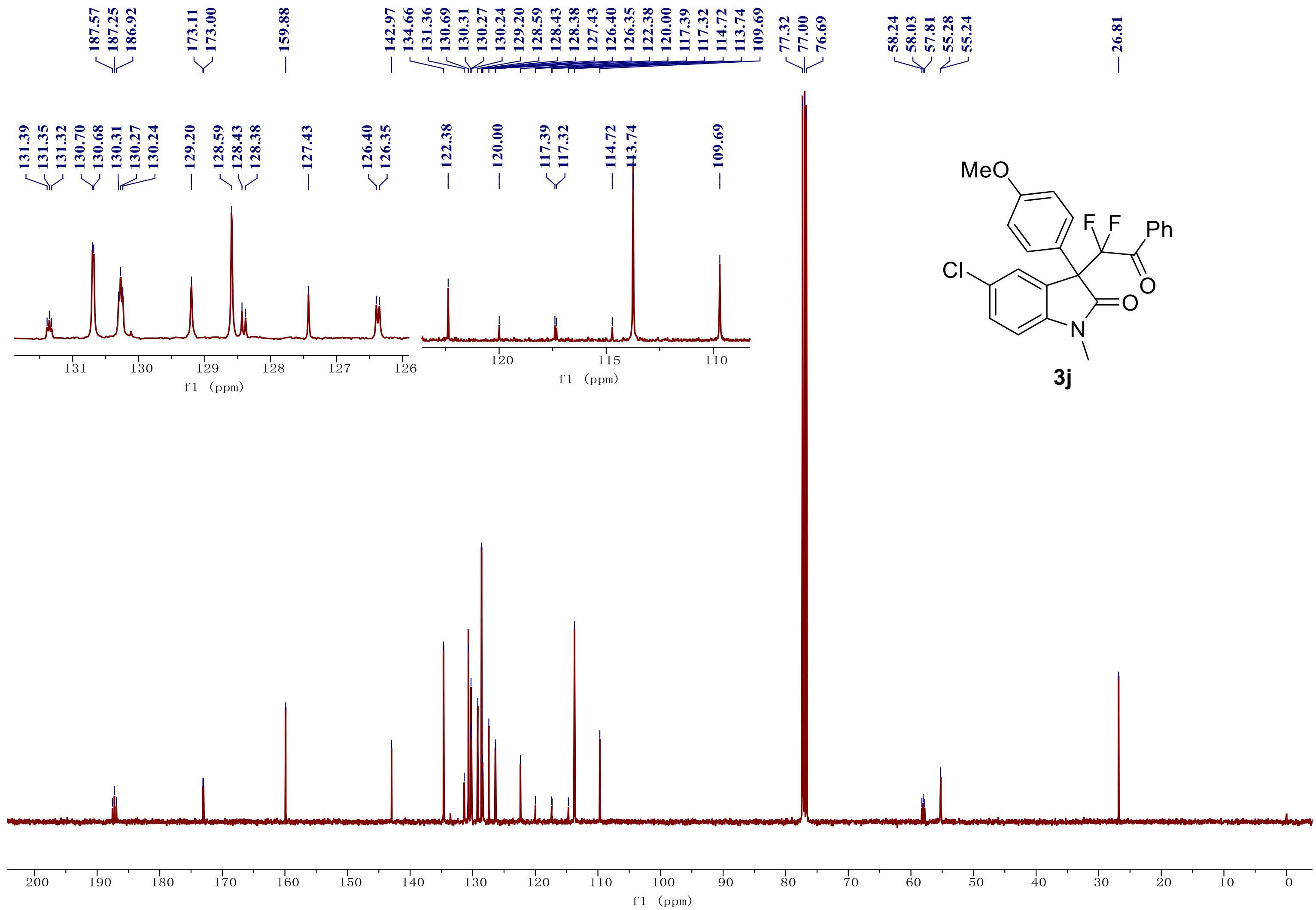
3i

^{1}H NMR of Compound 3j (400 MHz, $CDCl_3$)



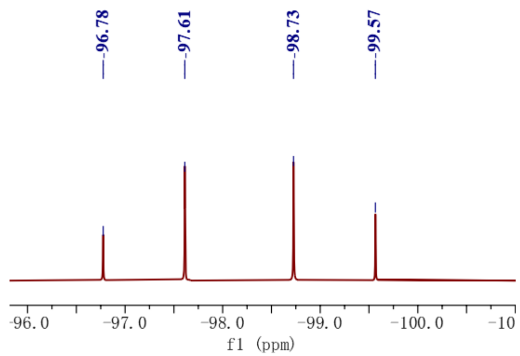
3j

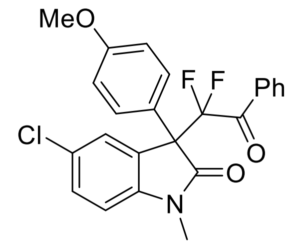
^{13}C NMR of Compound 3j (100 MHz, $CDCl_3$)



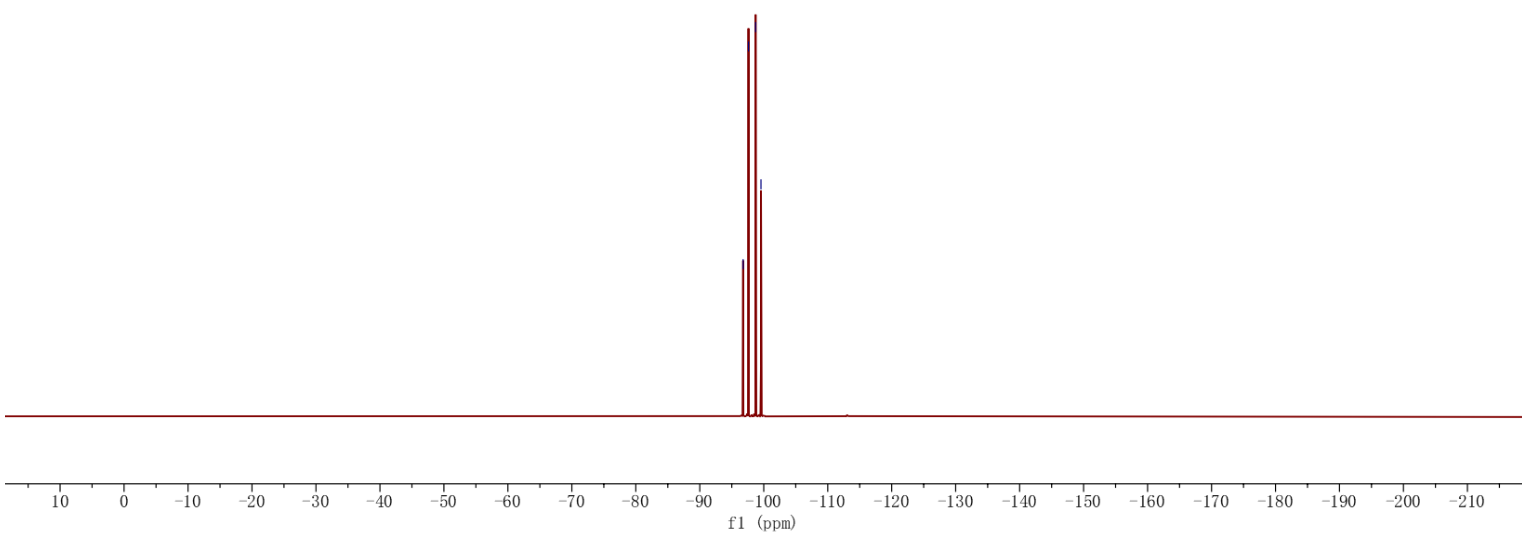
3j

^{19}F NMR of Compound 3j (376 MHz, $CDCl_3$)

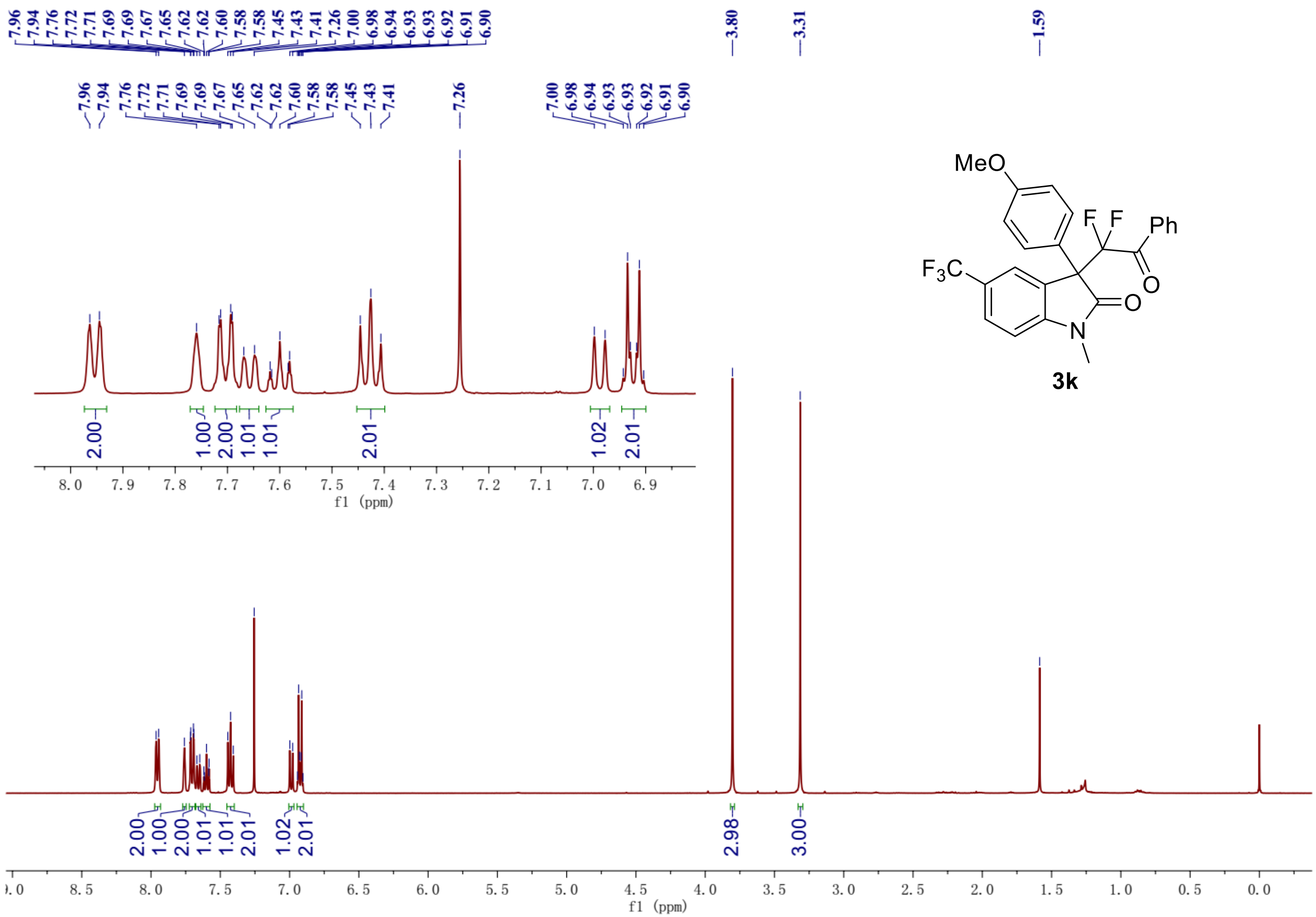




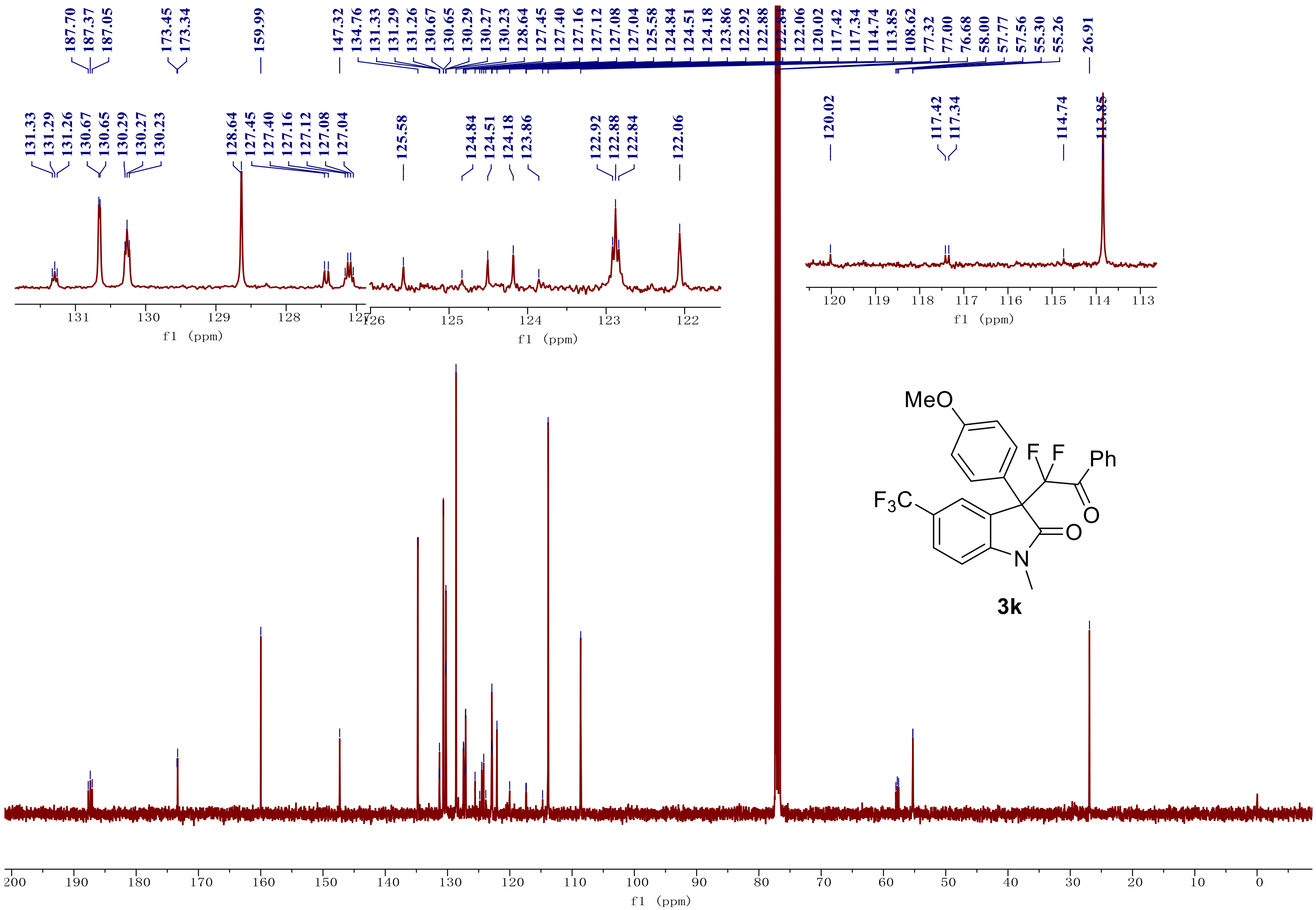
3j



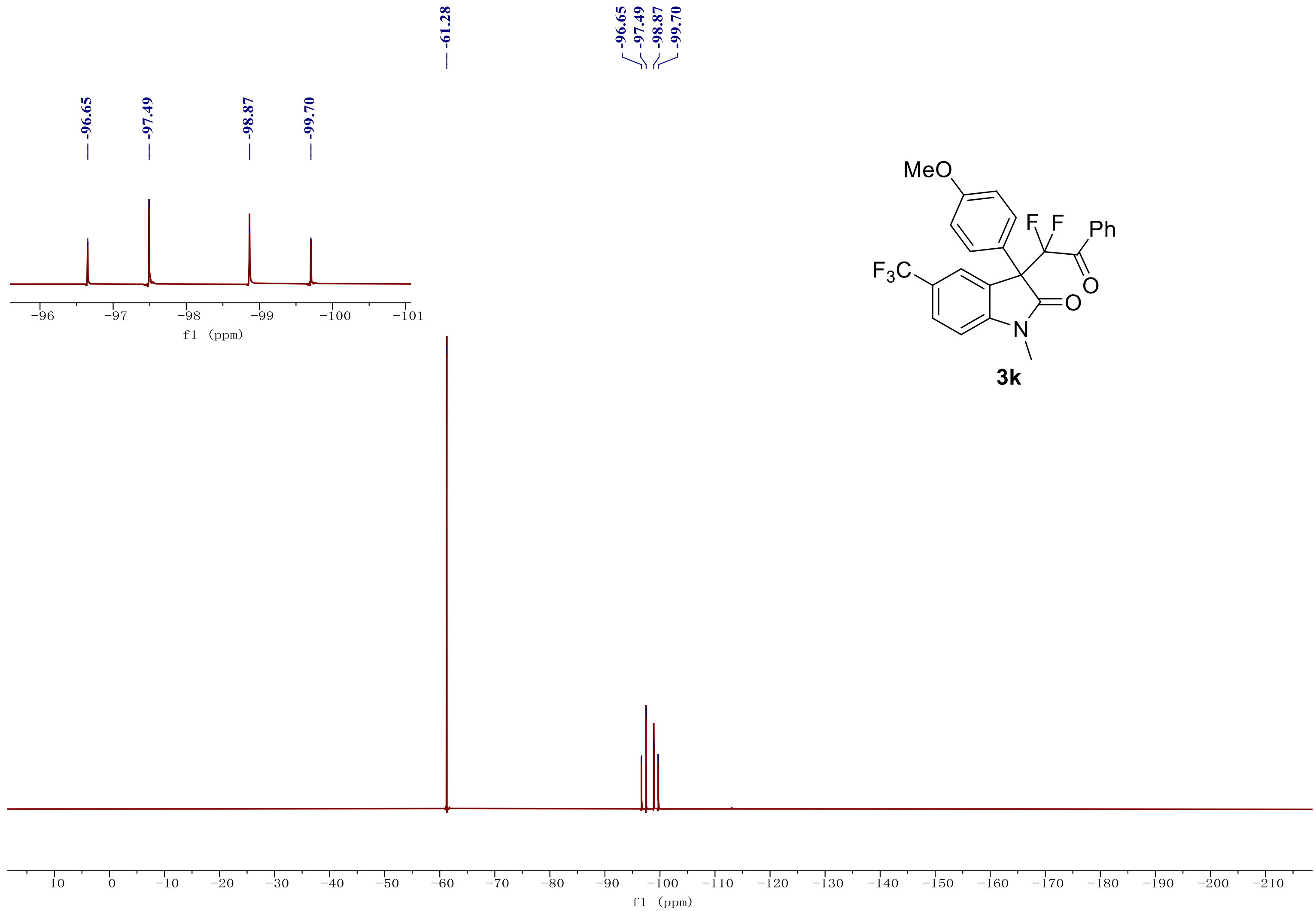
[1]H NMR of Compound 3k (400 MHz, $CDCl_3$)



^{13}C NMR of Compound 3k (100 MHz, $CDCl_3$)

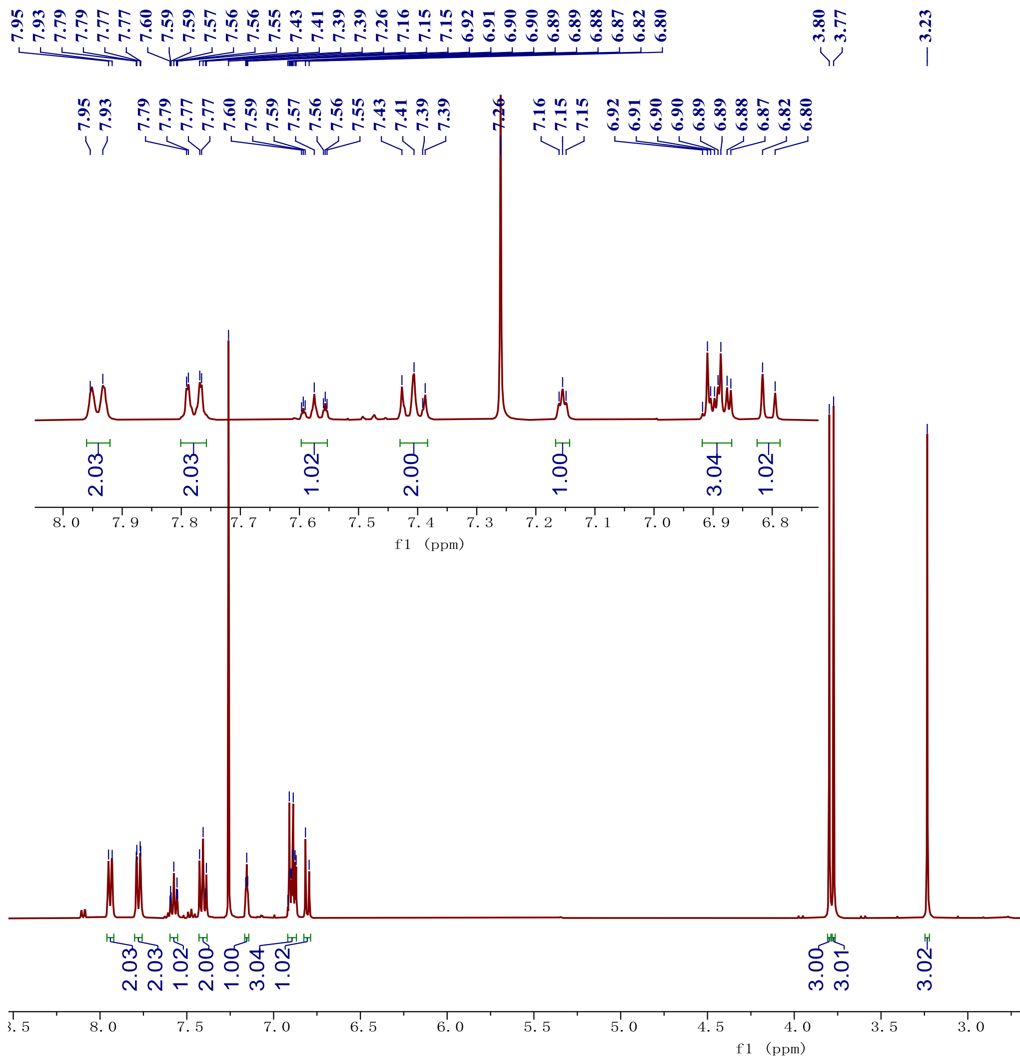


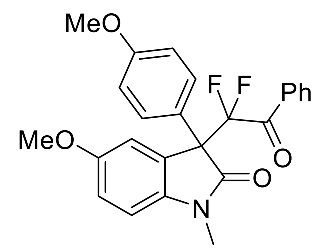
^{19}F NMR of Compound 3k (376 MHz, $CDCl_3$)



3k

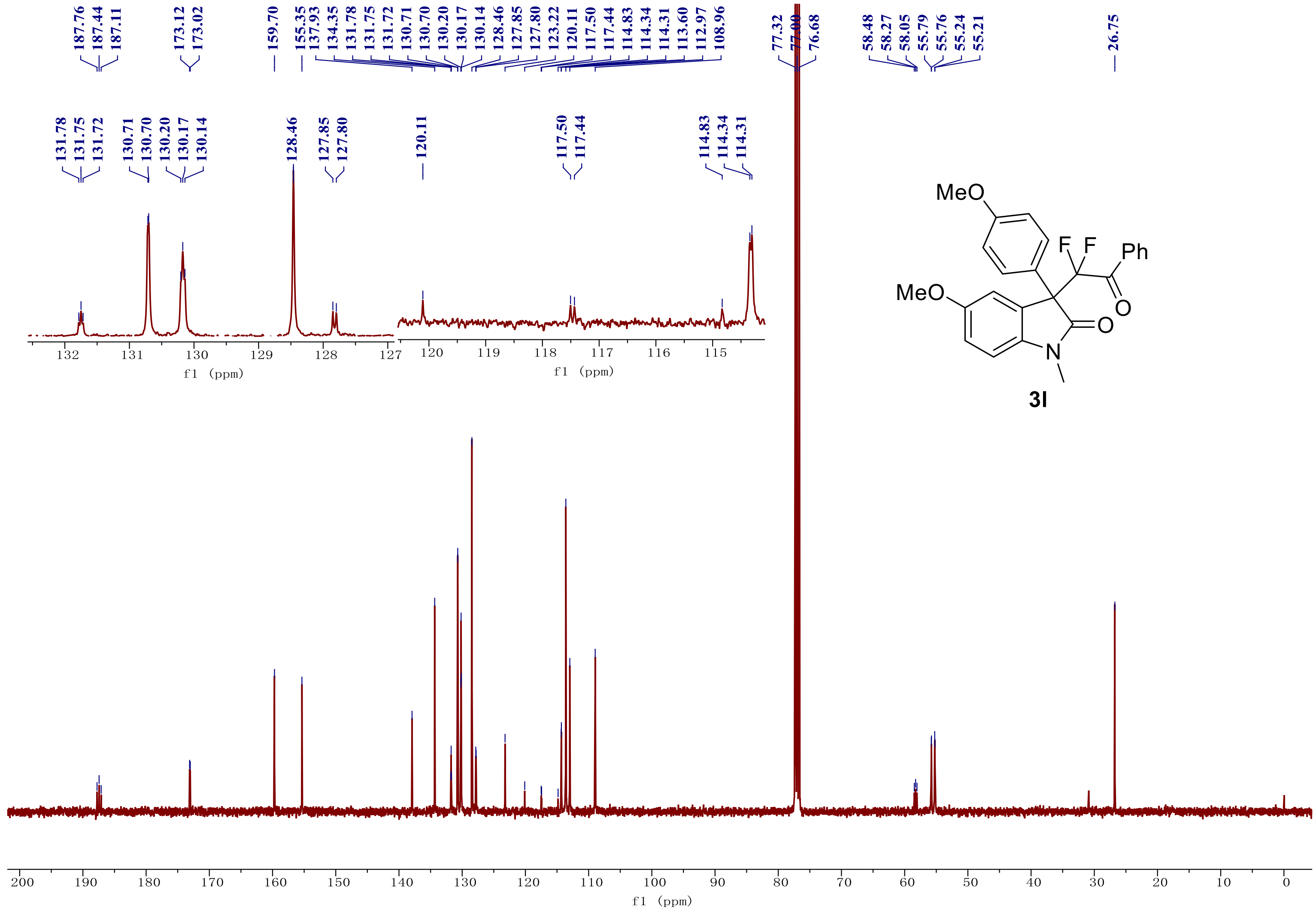
^{1}H NMR of Compound 3l (400 MHz, $CDCl_3$)



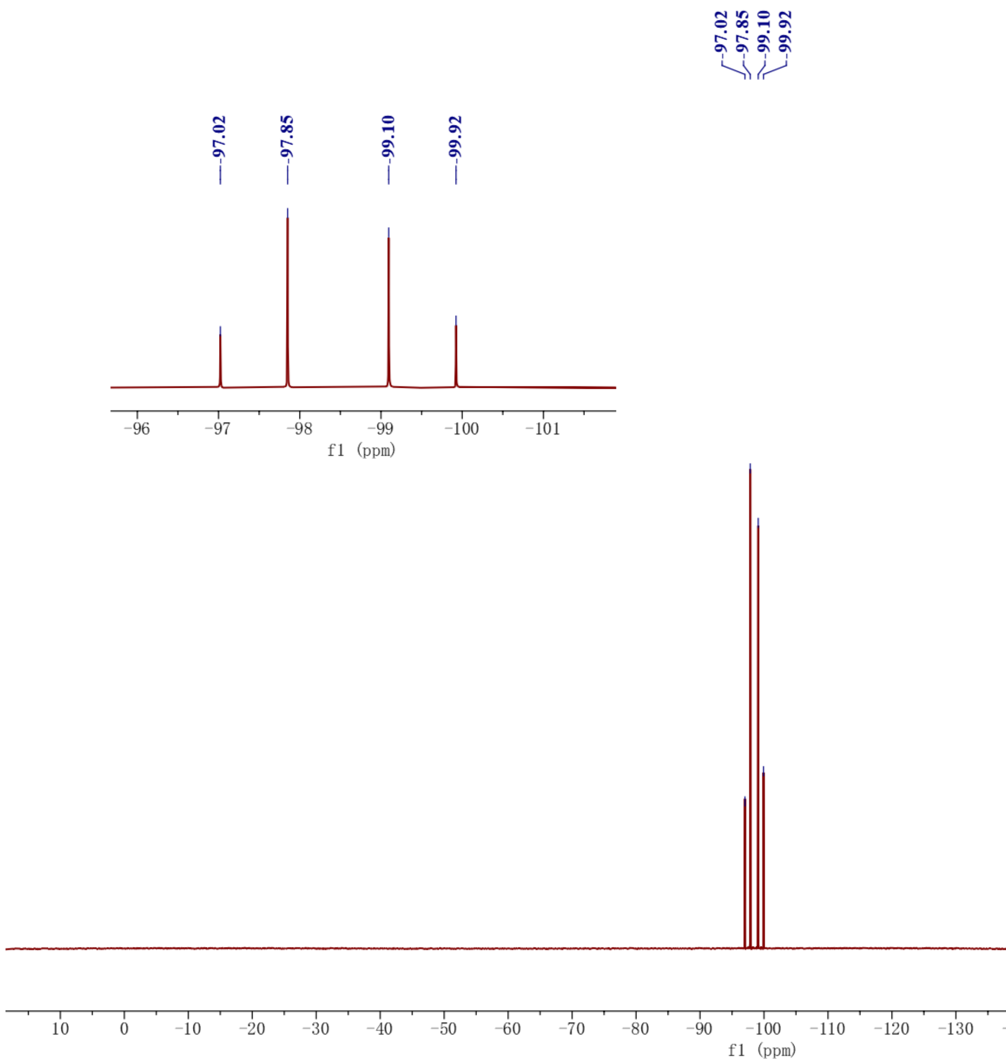


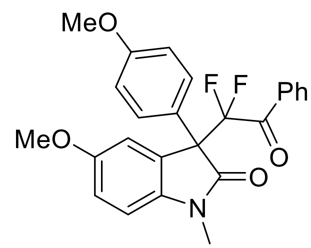
3l

^{13}C NMR of Compound 3l (100 MHz, $CDCl_3$)



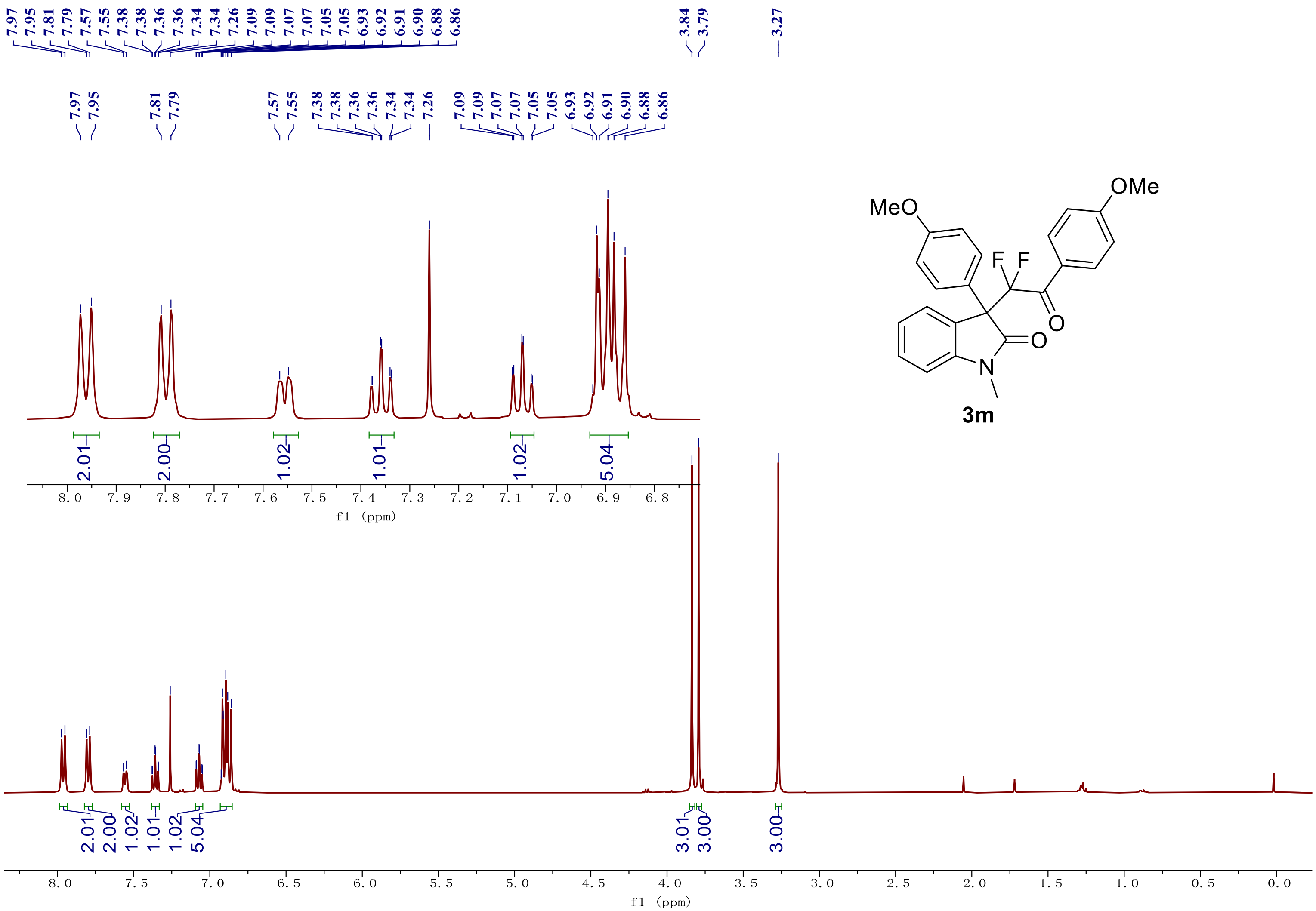
^{19}F NMR of Compound 3l (376 MHz, $CDCl_3$)





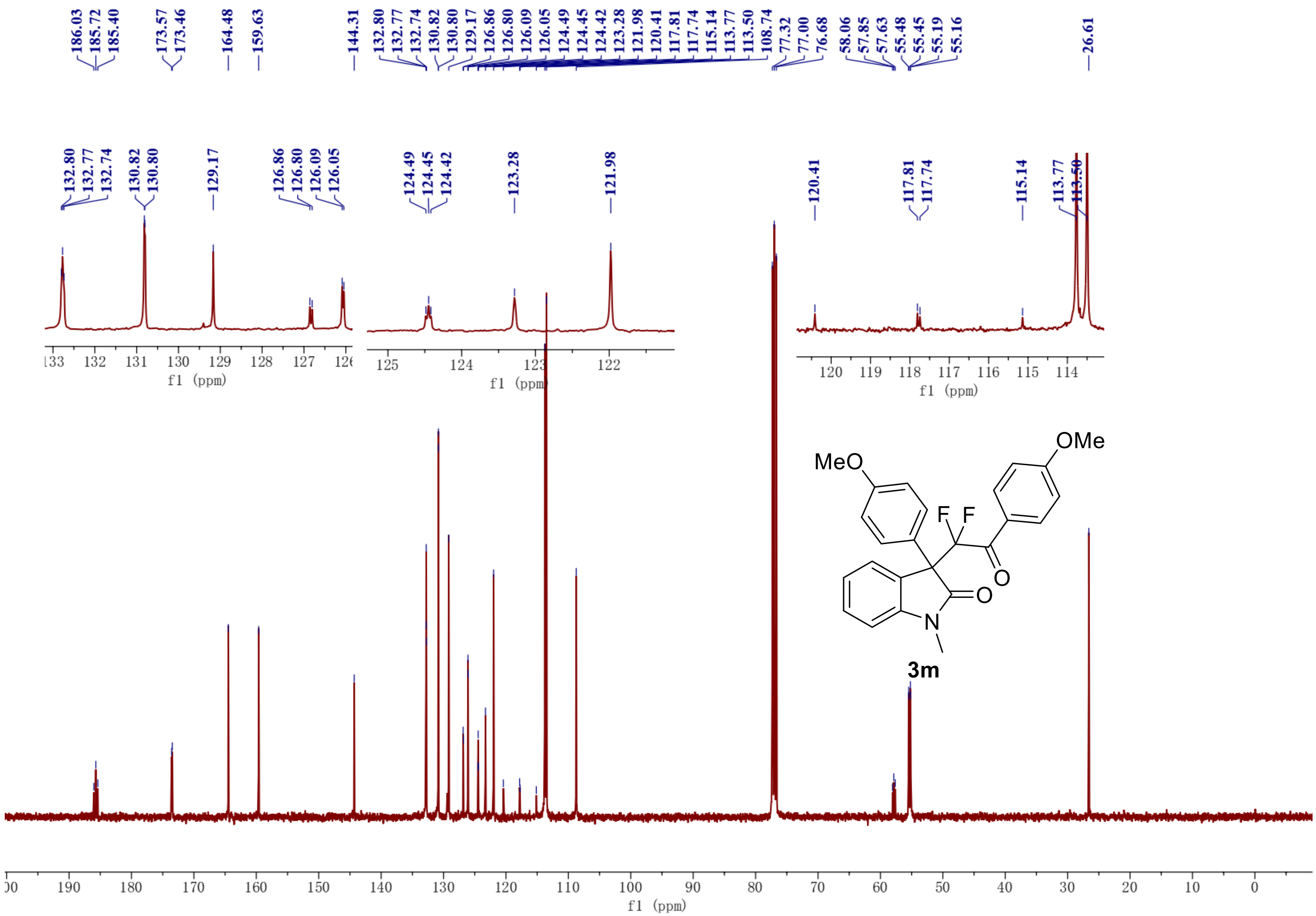
3l

^{1}H NMR of Compound 3m (400 MHz, $CDCl_3$)

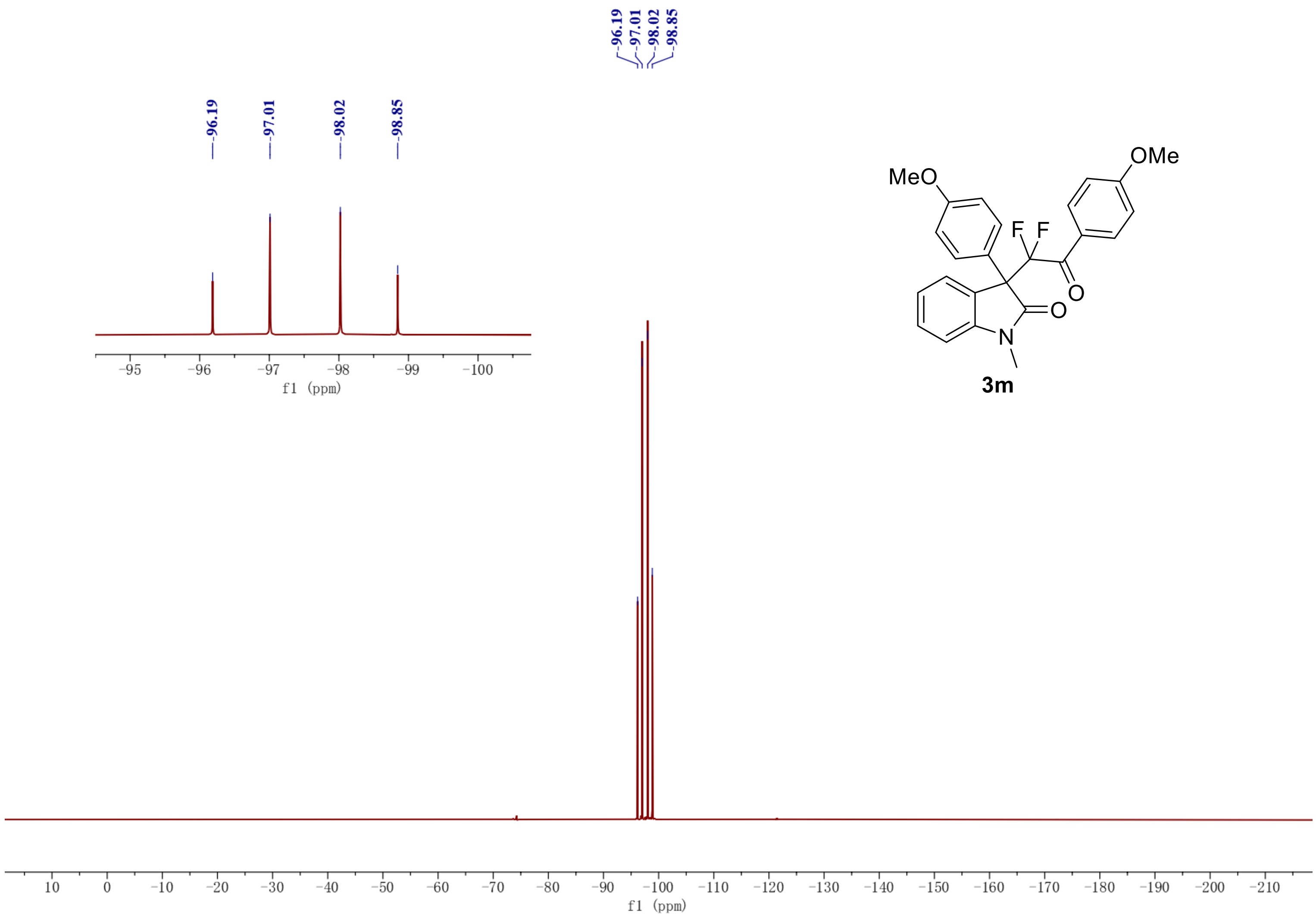


3m

^{13}C NMR of Compound 3m (100 MHz, $CDCl_3$)

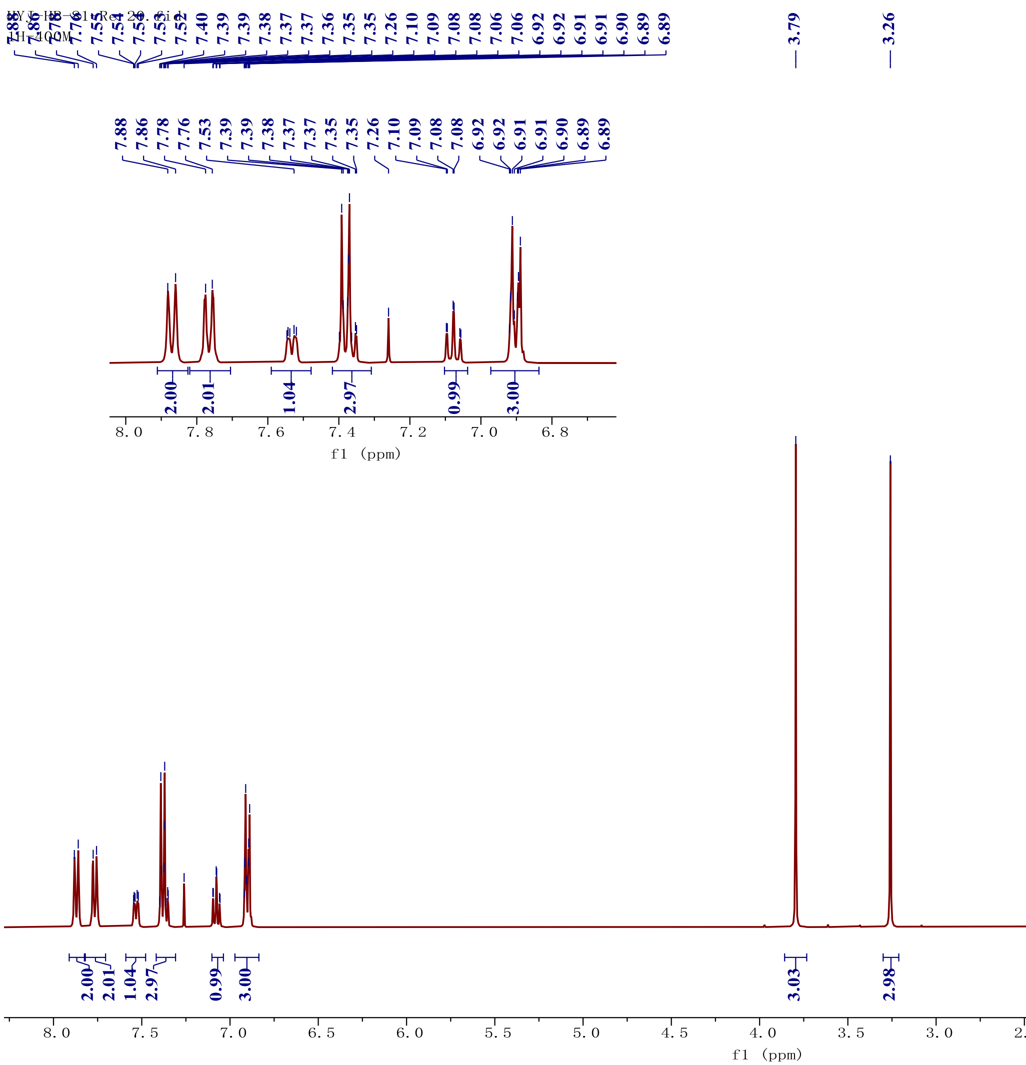


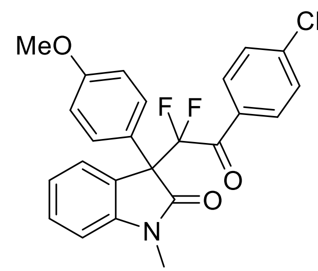
^{19}F NMR of Compound 3m (376 MHz, $CDCl_3$)



3m

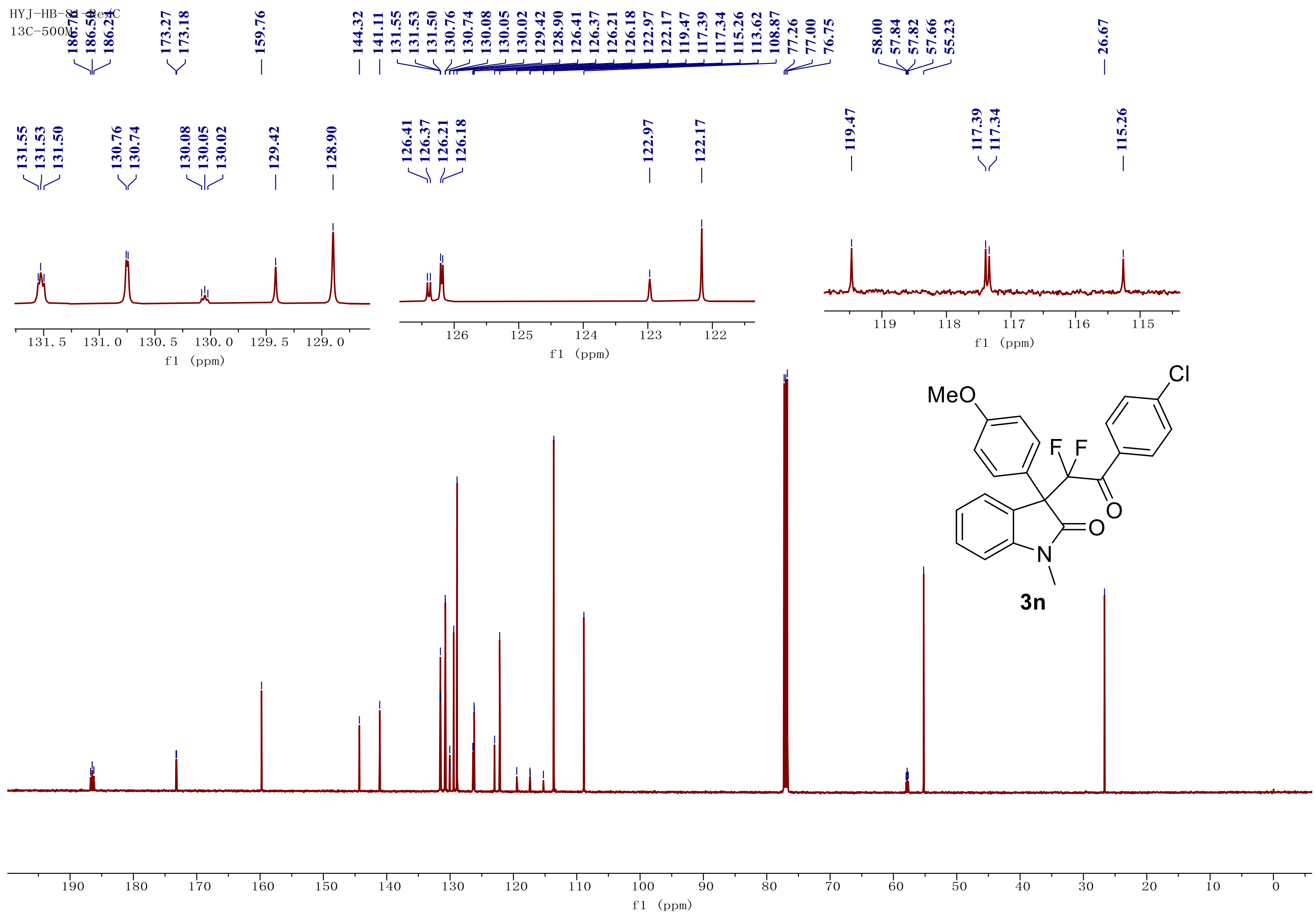
[1]H NMR of Compound 3n (400 MHz, $CDCl_3$)



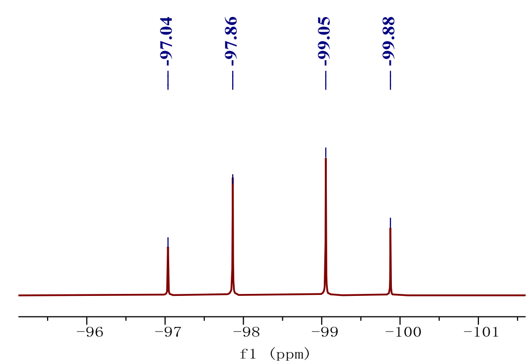


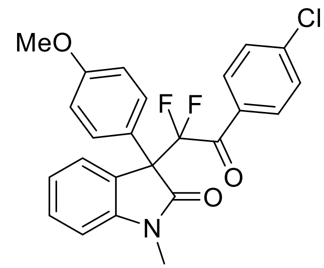
3n

^{13}C NMR of Compound 3n (125 MHz, $CDCl_3$)

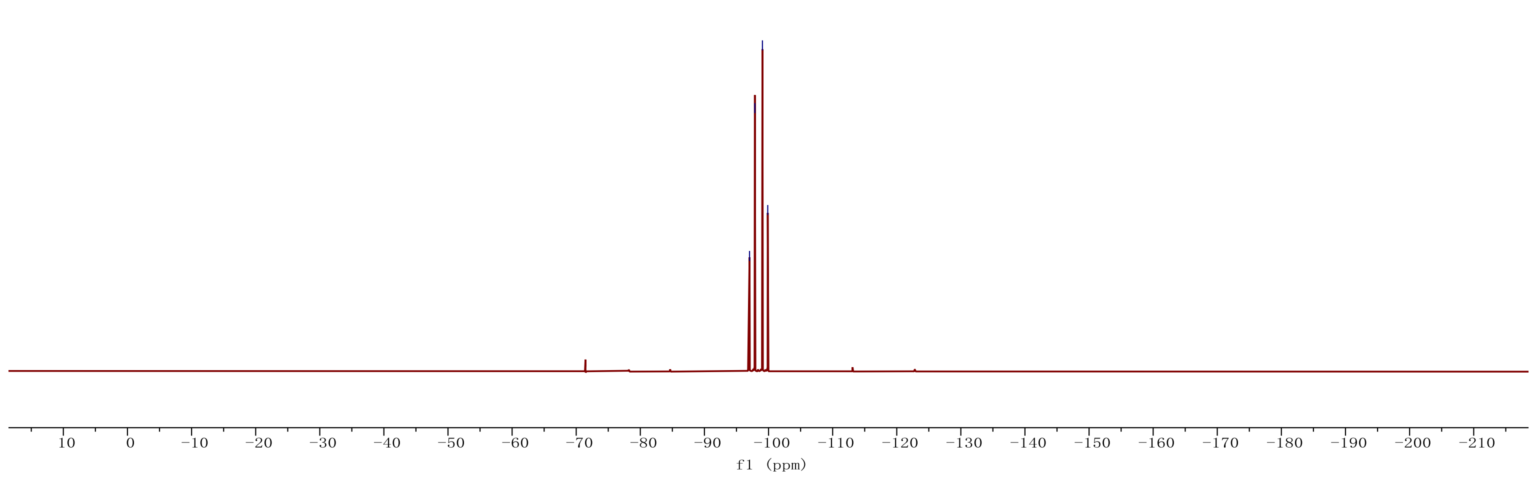


^{19}F NMR of Compound 3n (376 MHz, $CDCl_3$)

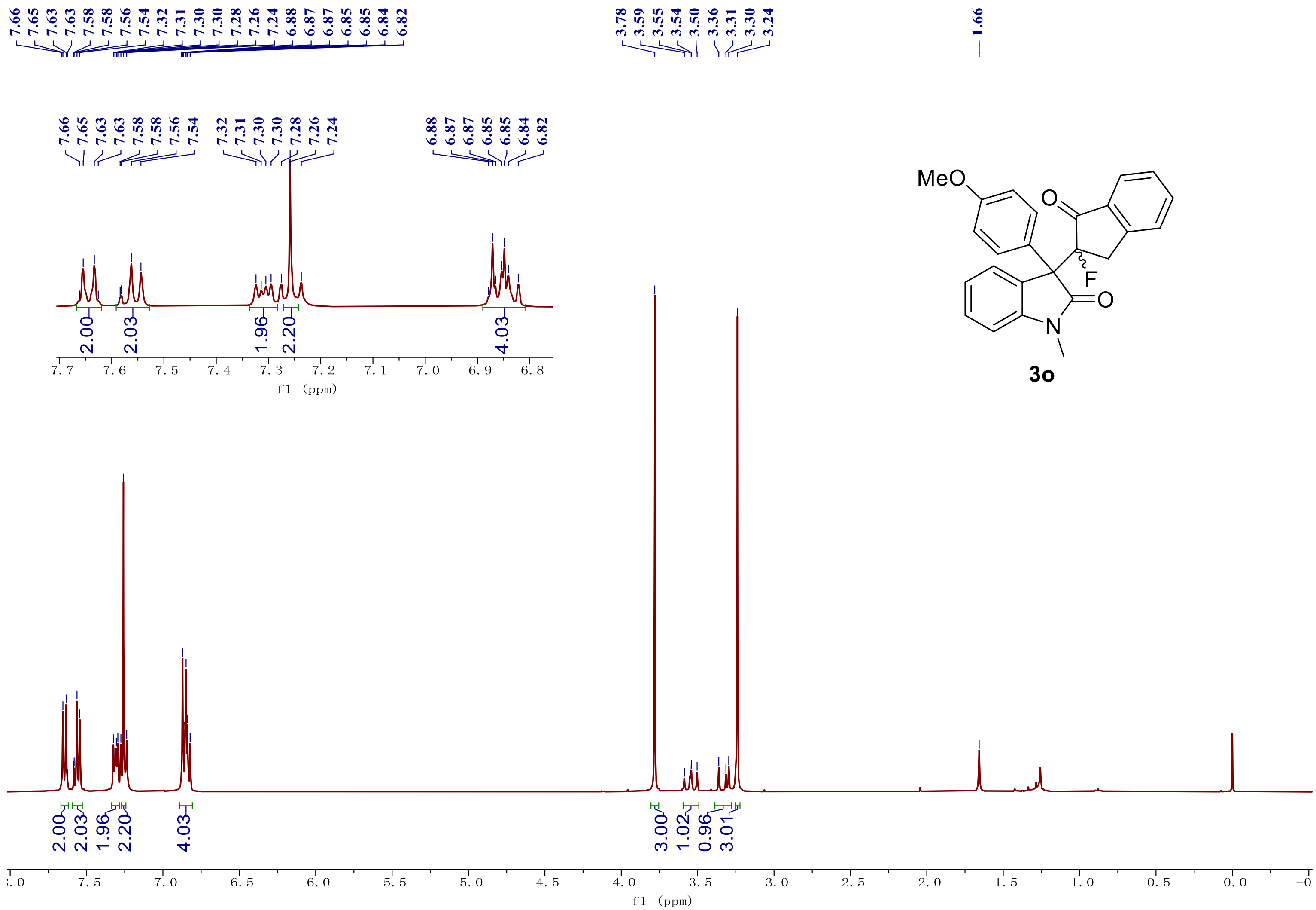




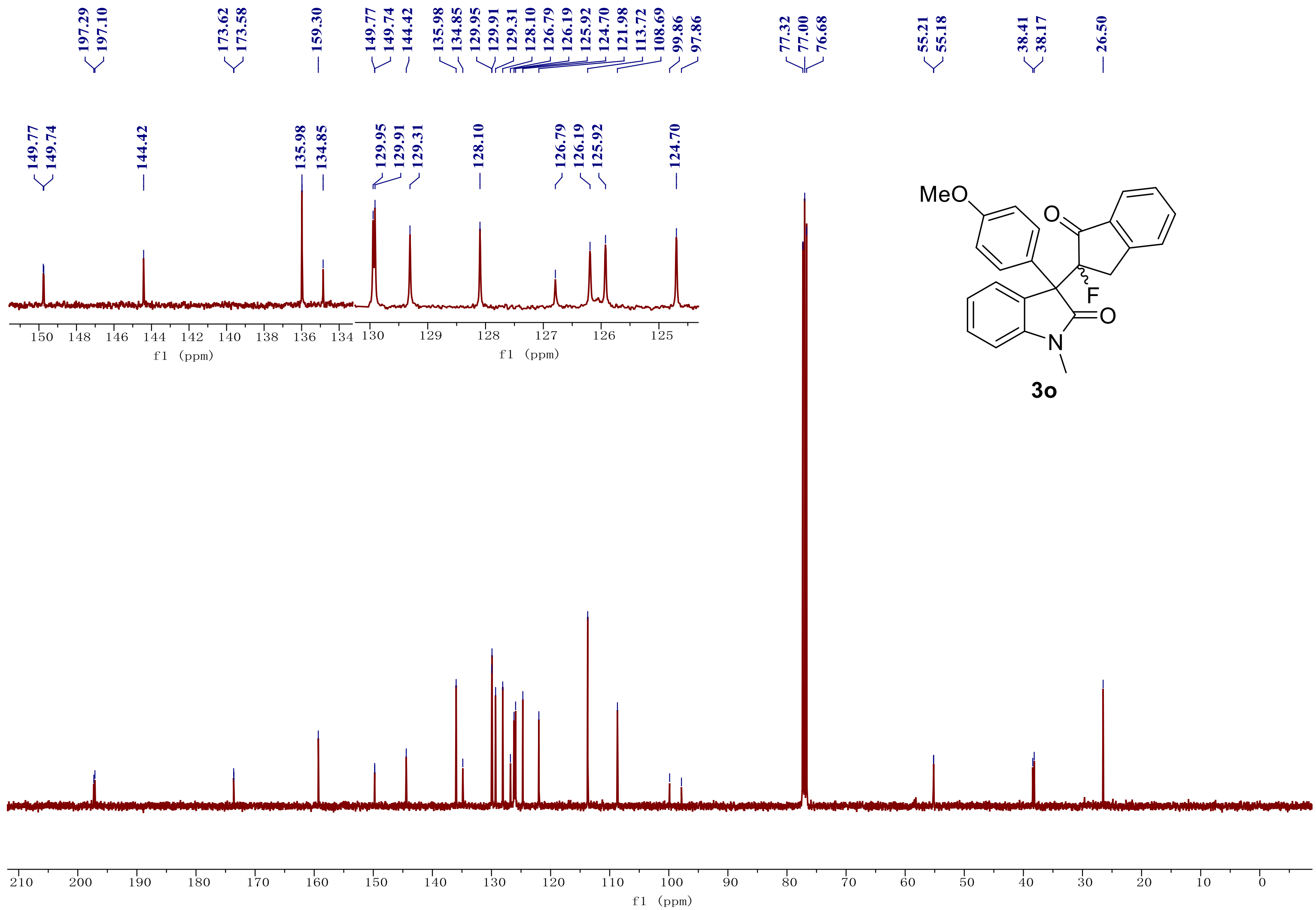
3n



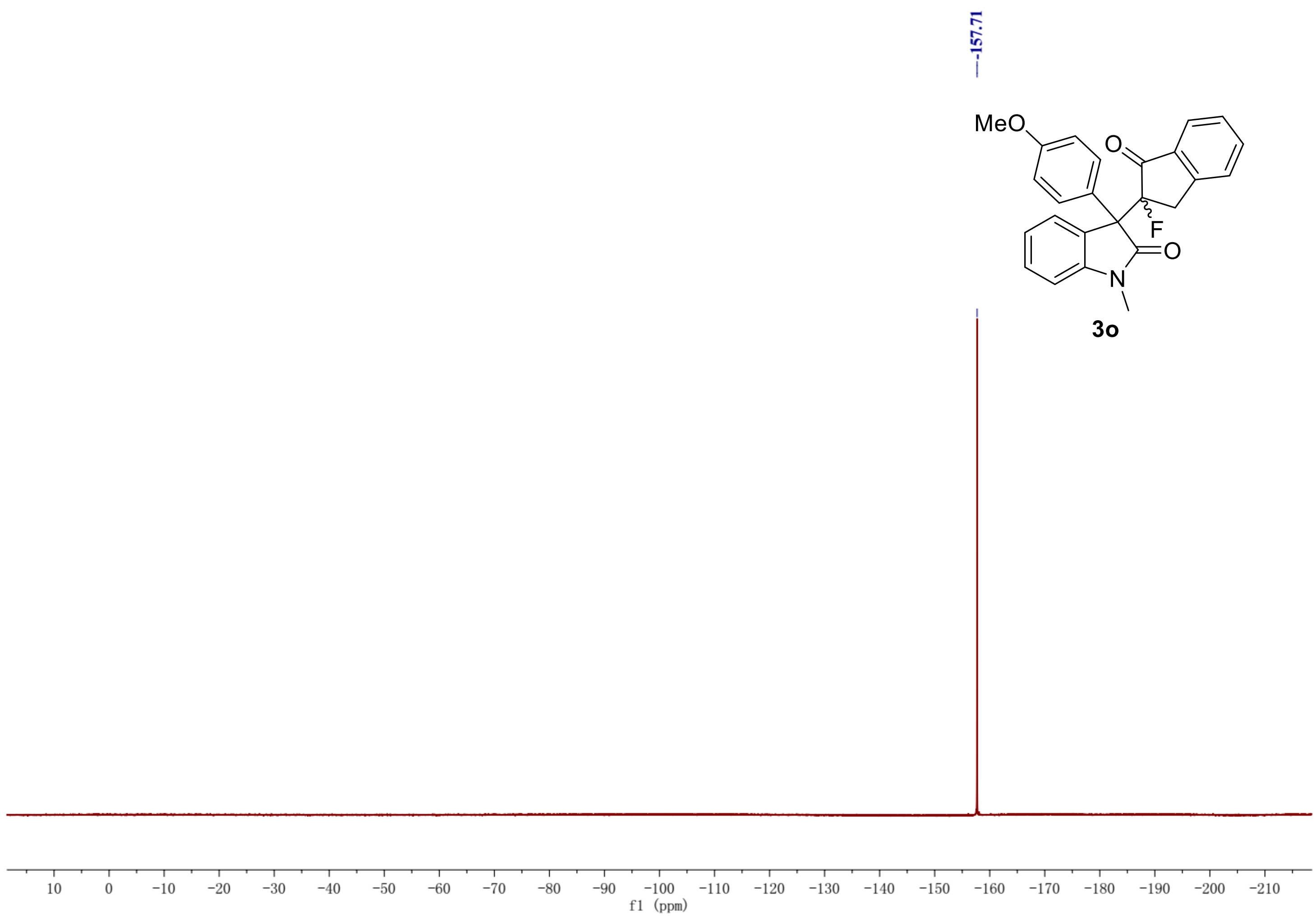
^{1}H NMR of Compound 3o (400 MHz, $CDCl_3$)



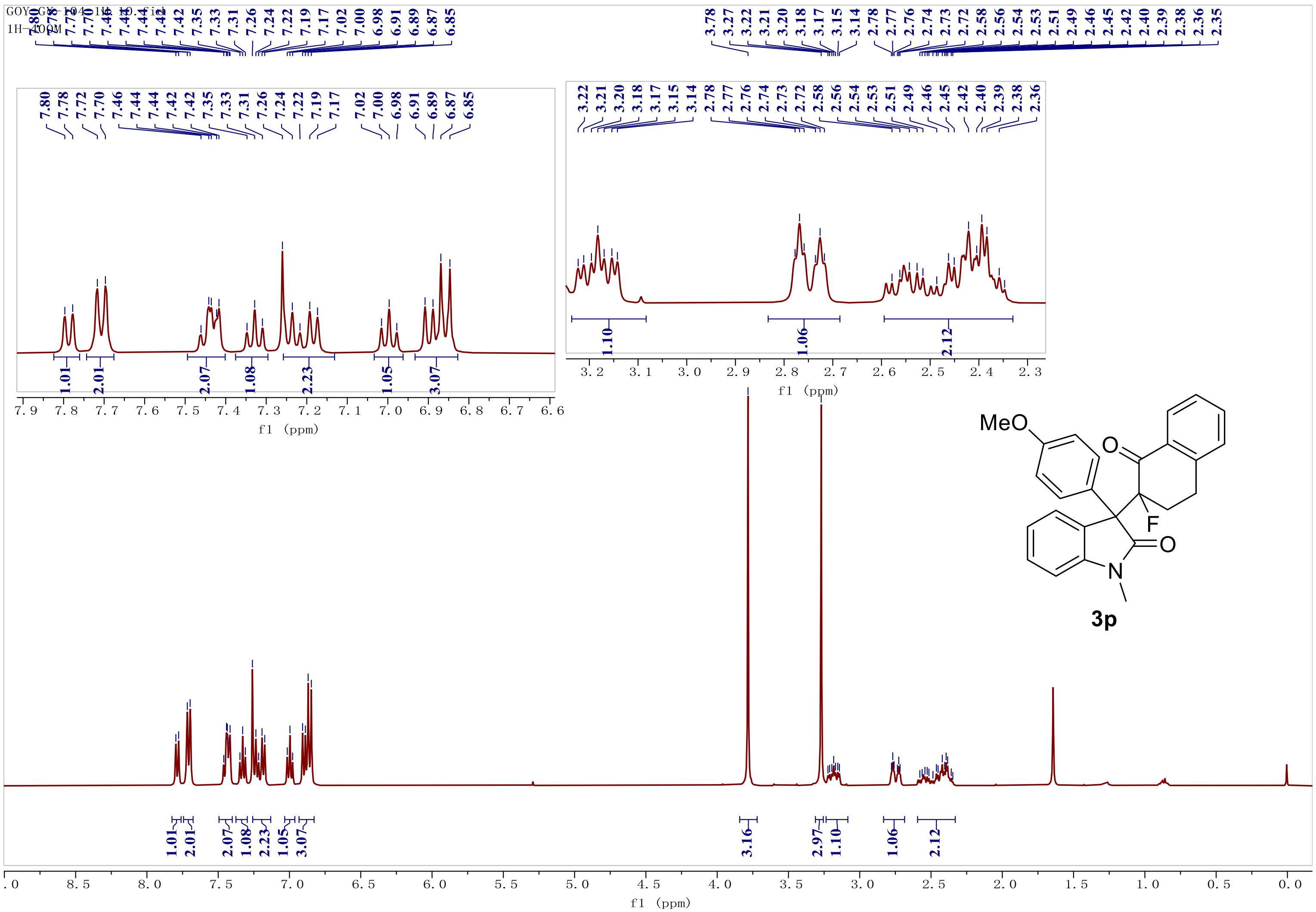
^{13}C NMR of Compound 3o (100 MHz, CDCl$_3$)



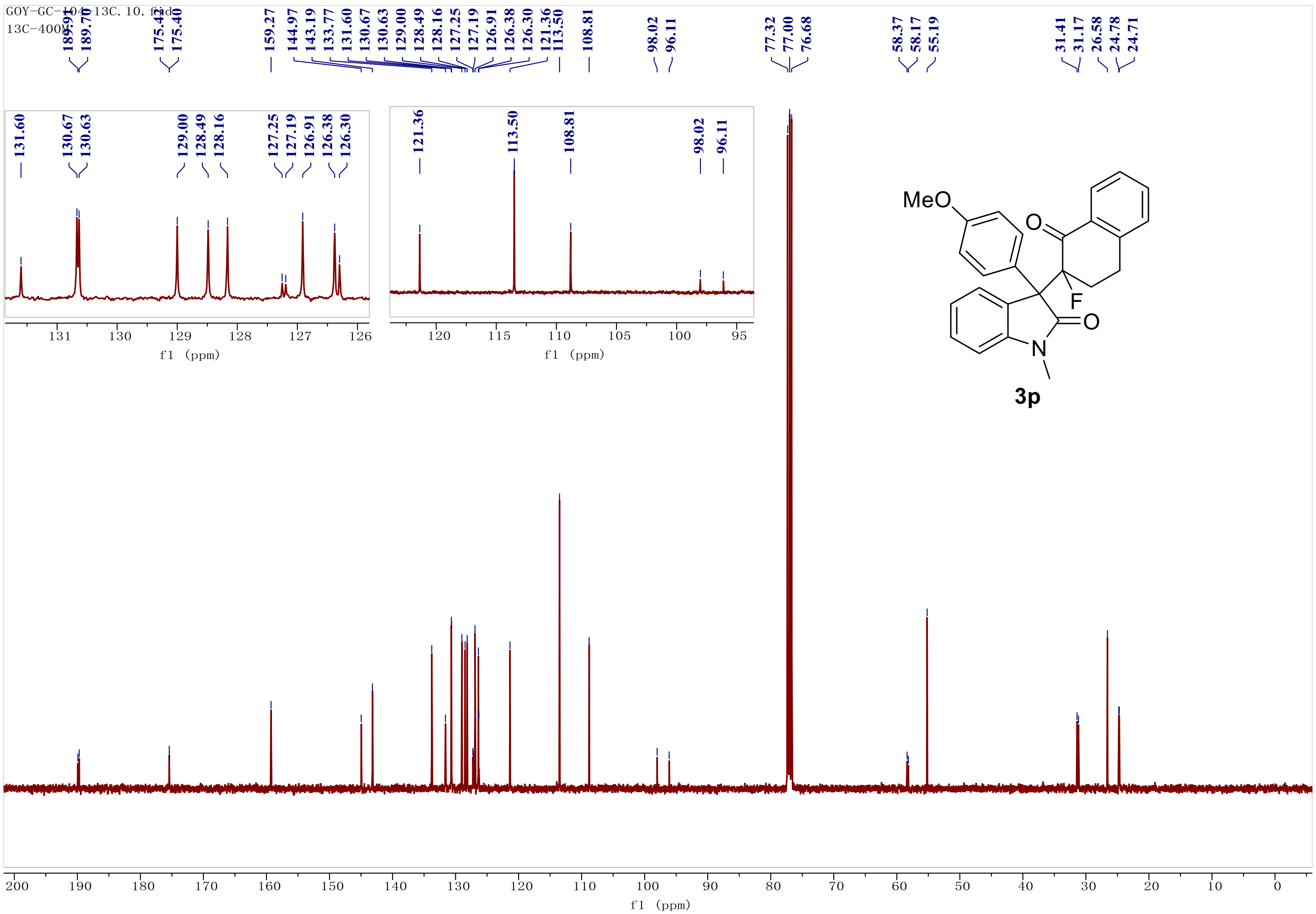
^{19}F NMR of Compound 3o (376 MHz, $CDCl_3$)



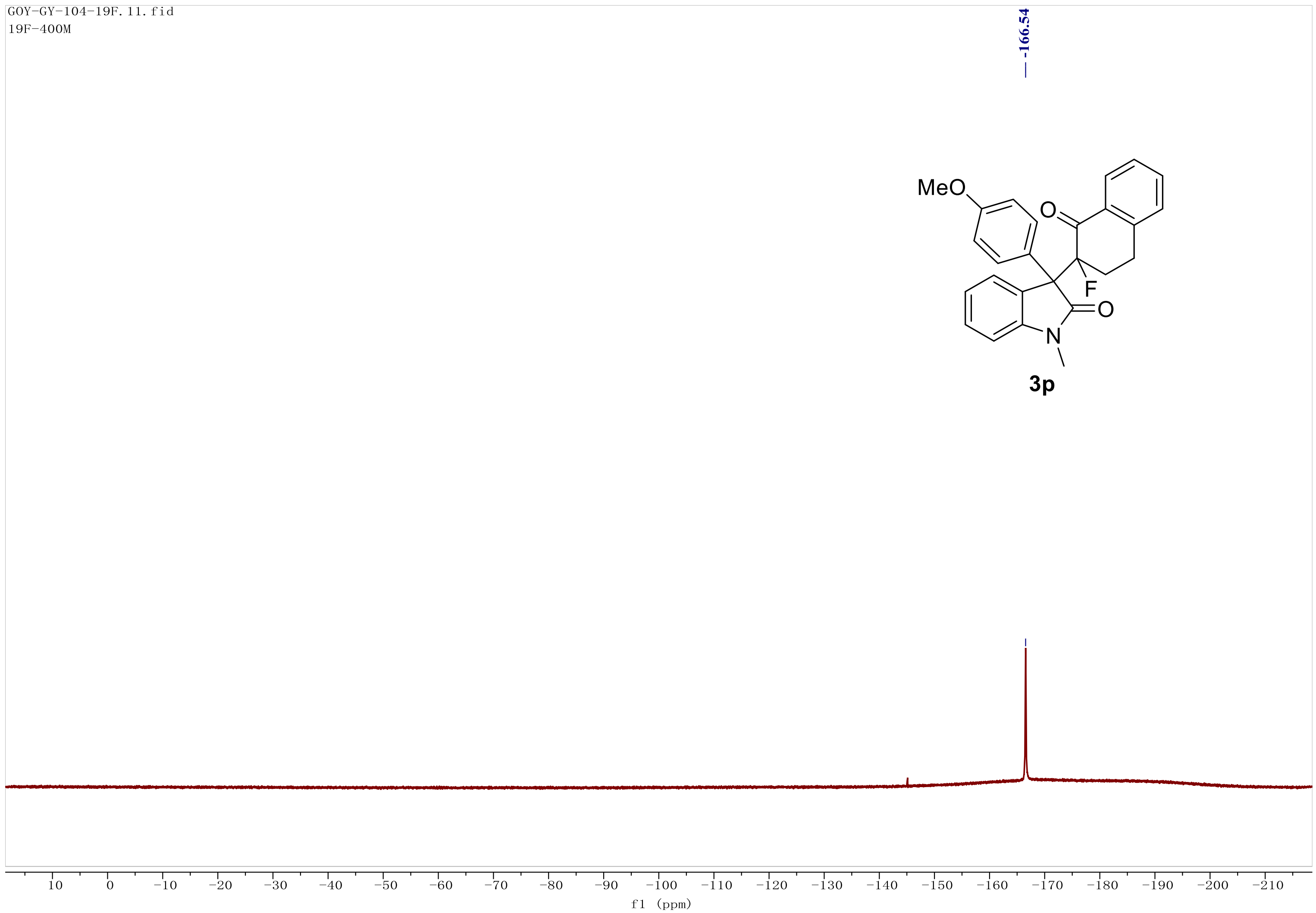
^{1}H NMR of Compound 3p (400 MHz, CDCl$_3$)



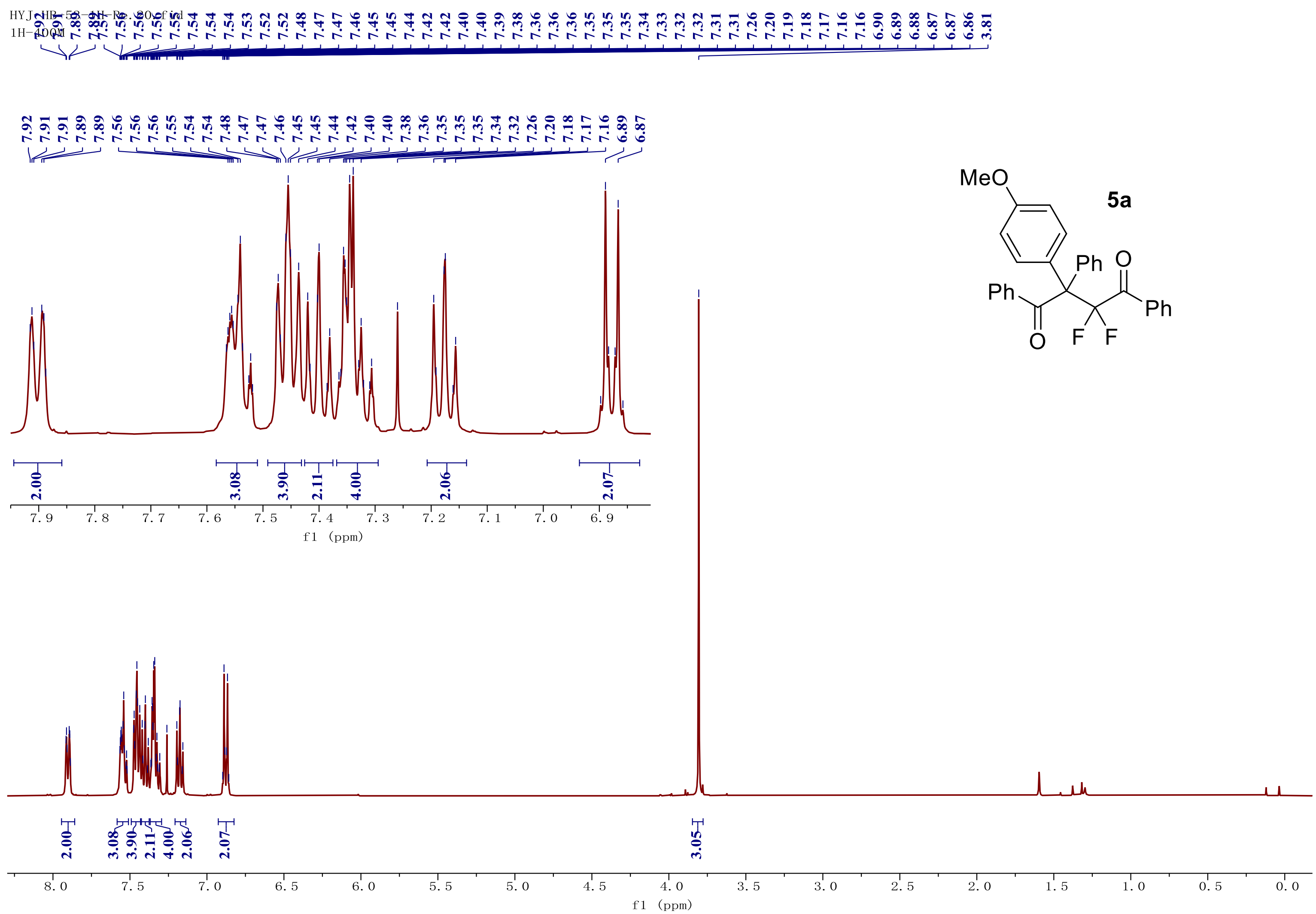
^{13}C NMR of Compound 3p (100 MHz, $CDCl_3$)



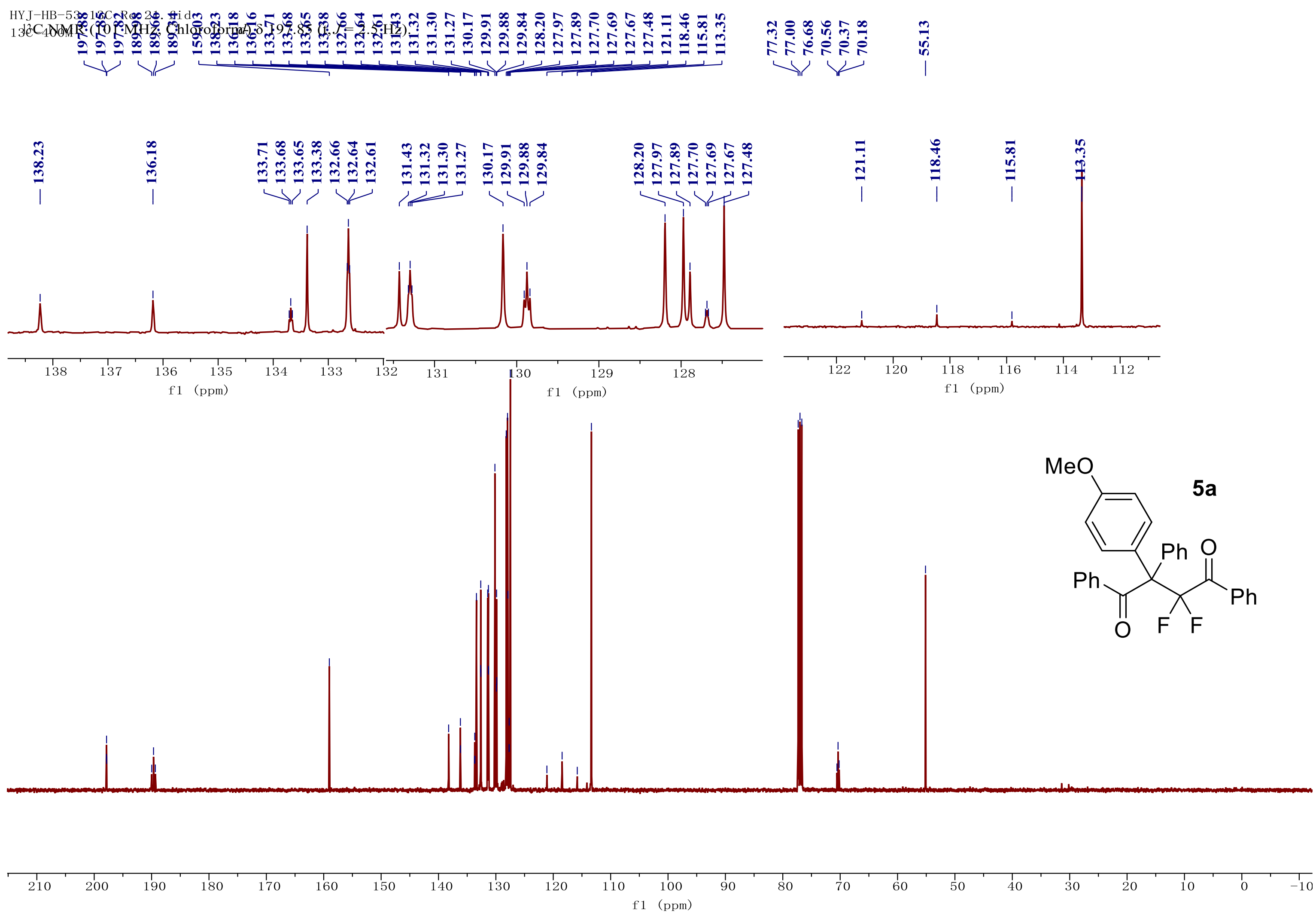
^{19}F NMR of Compound 3p (376 MHz, $CDCl_3$)



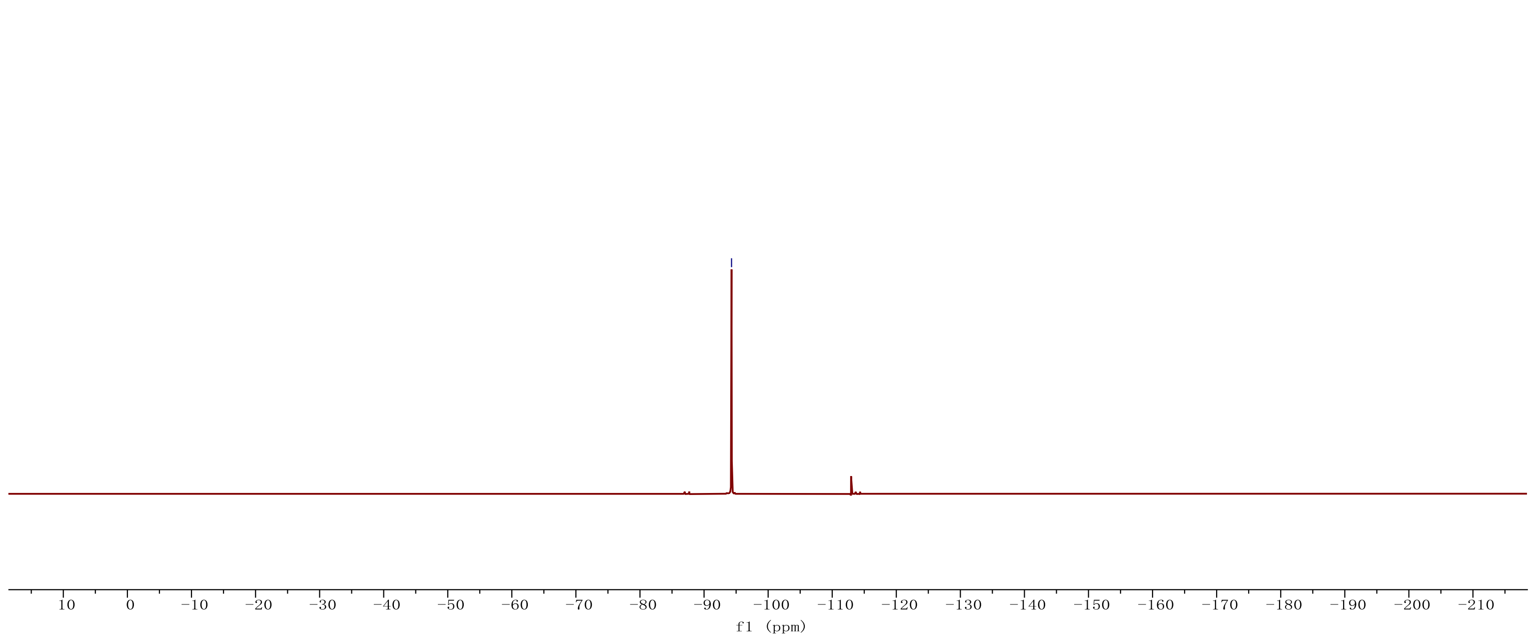
[1]H NMR of Compound 5a (400 MHz, CDCl₃)

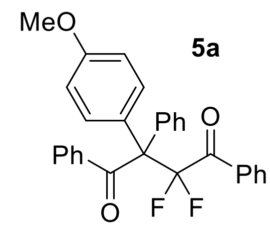


^{13}C NMR of Compound 5a (100 MHz, $CDCl_3$)



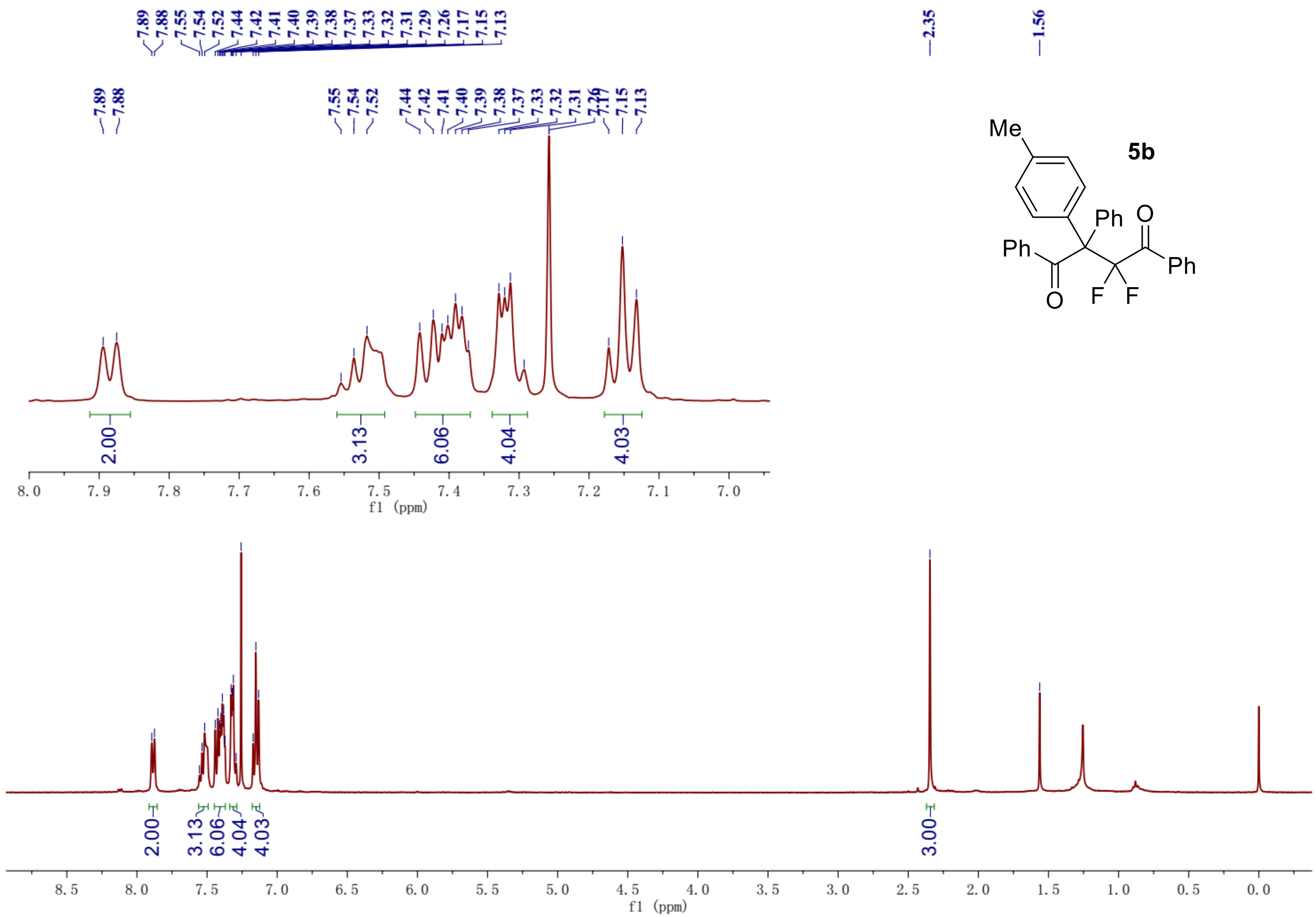
^{19}F NMR of Compound 5a (376 MHz, $CDCl_3$)





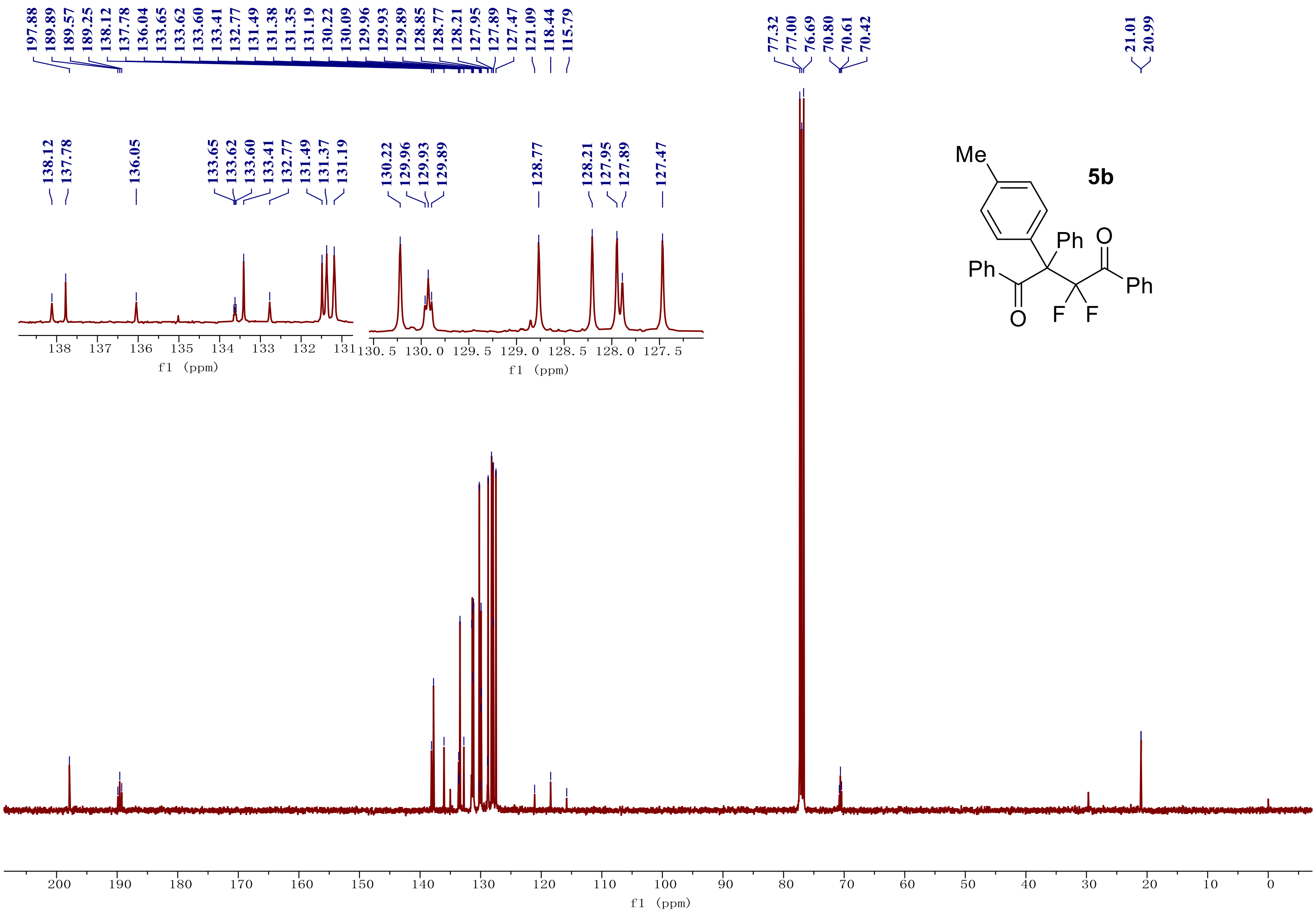
5a

^{1}H NMR of Compound 5b (400 MHz, $CDCl_3$)



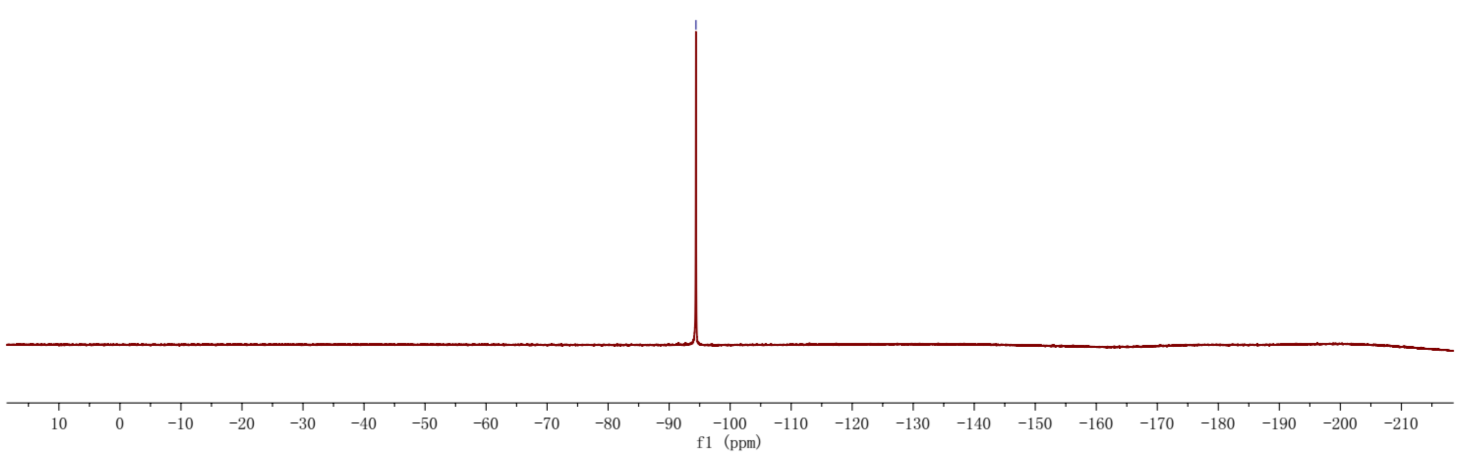
5b

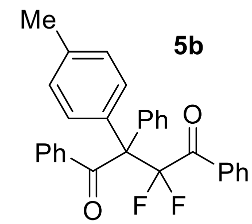
^{13}C NMR of Compound 5b (100 MHz, $CDCl_3$)



^{19}F NMR of Compound 5b (376 MHz, $CDCl_3$)

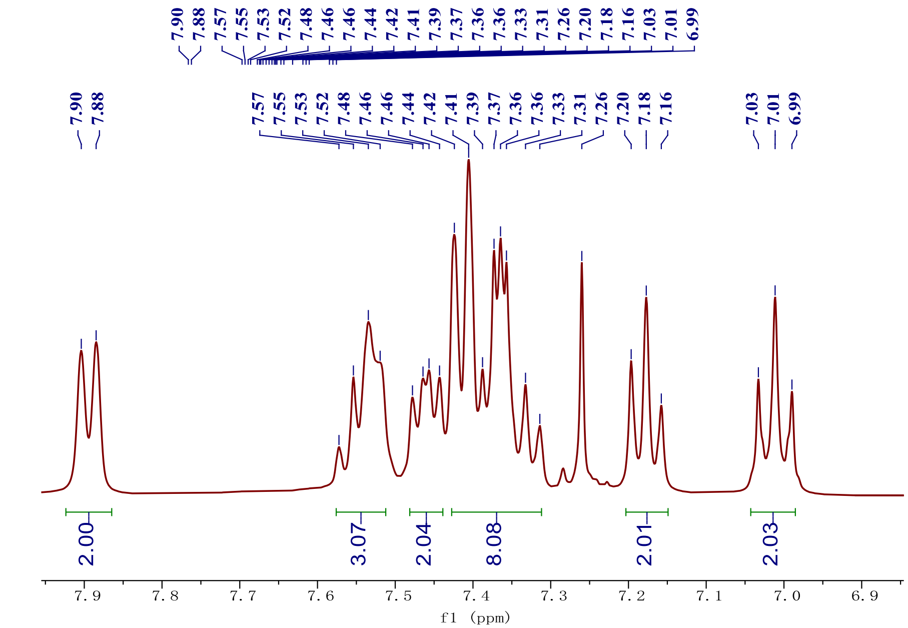
-94.40

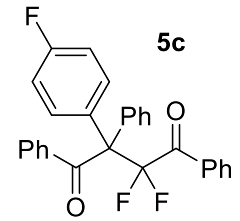




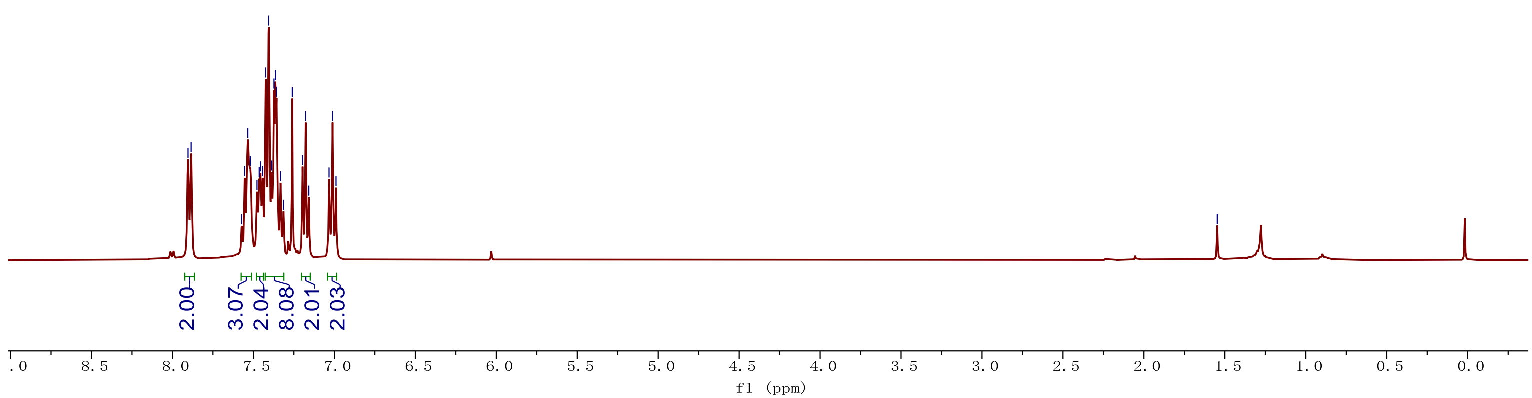
5b

^{1}H NMR of Compound 5c (400 MHz, CDCl$_3$)

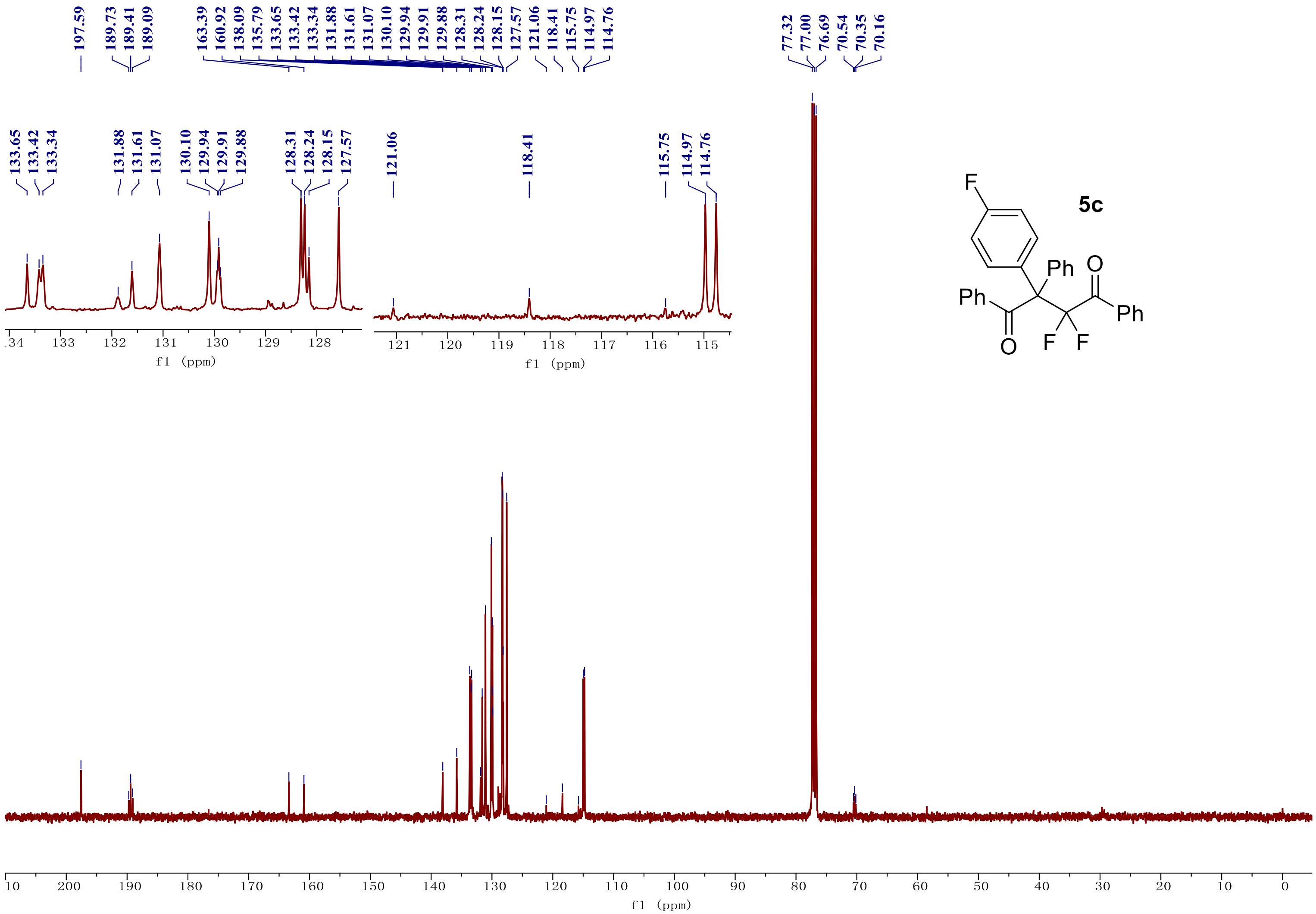




5c

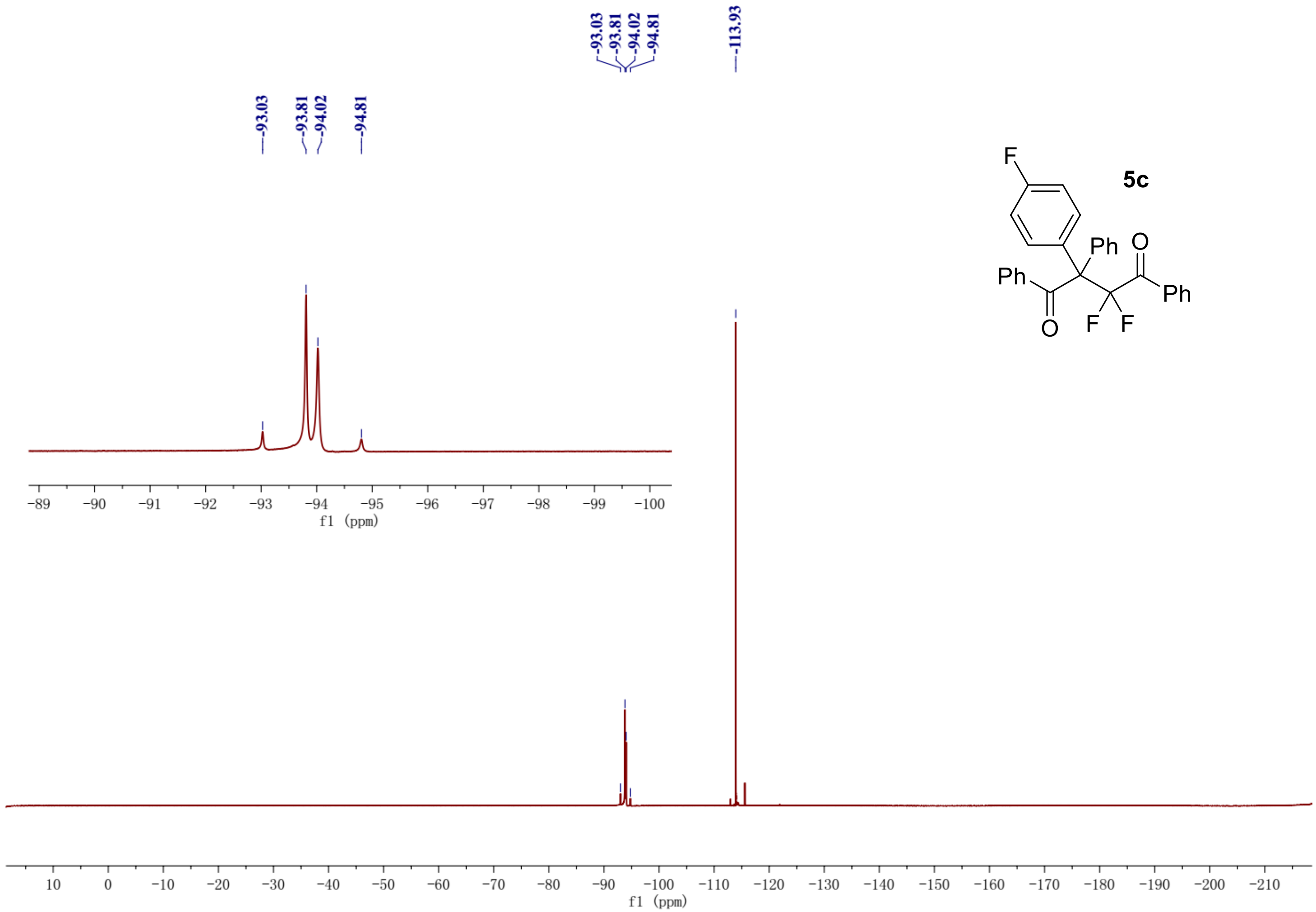


^{13}C NMR of Compound 5c (100 MHz, $CDCl_3$)

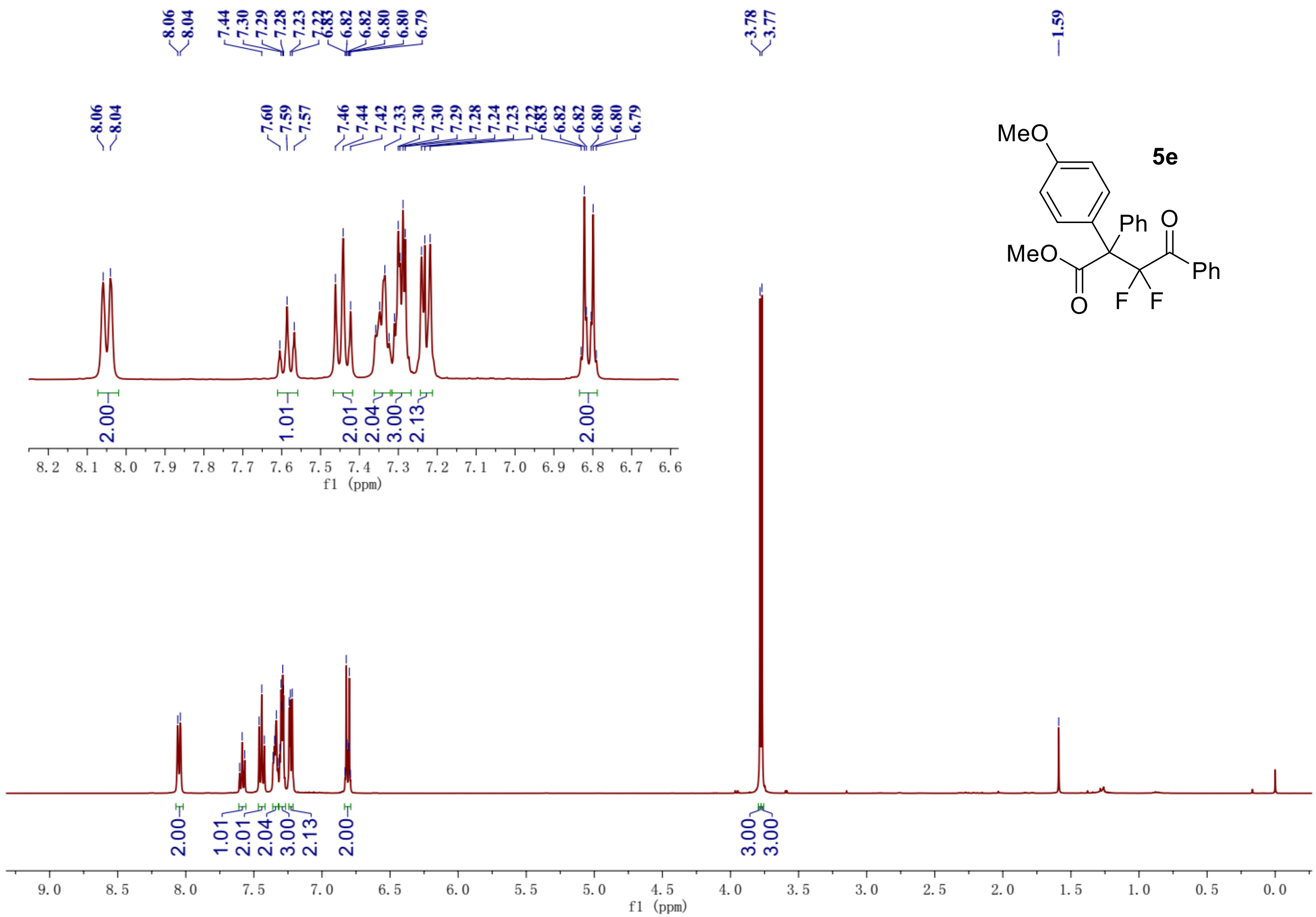


5c

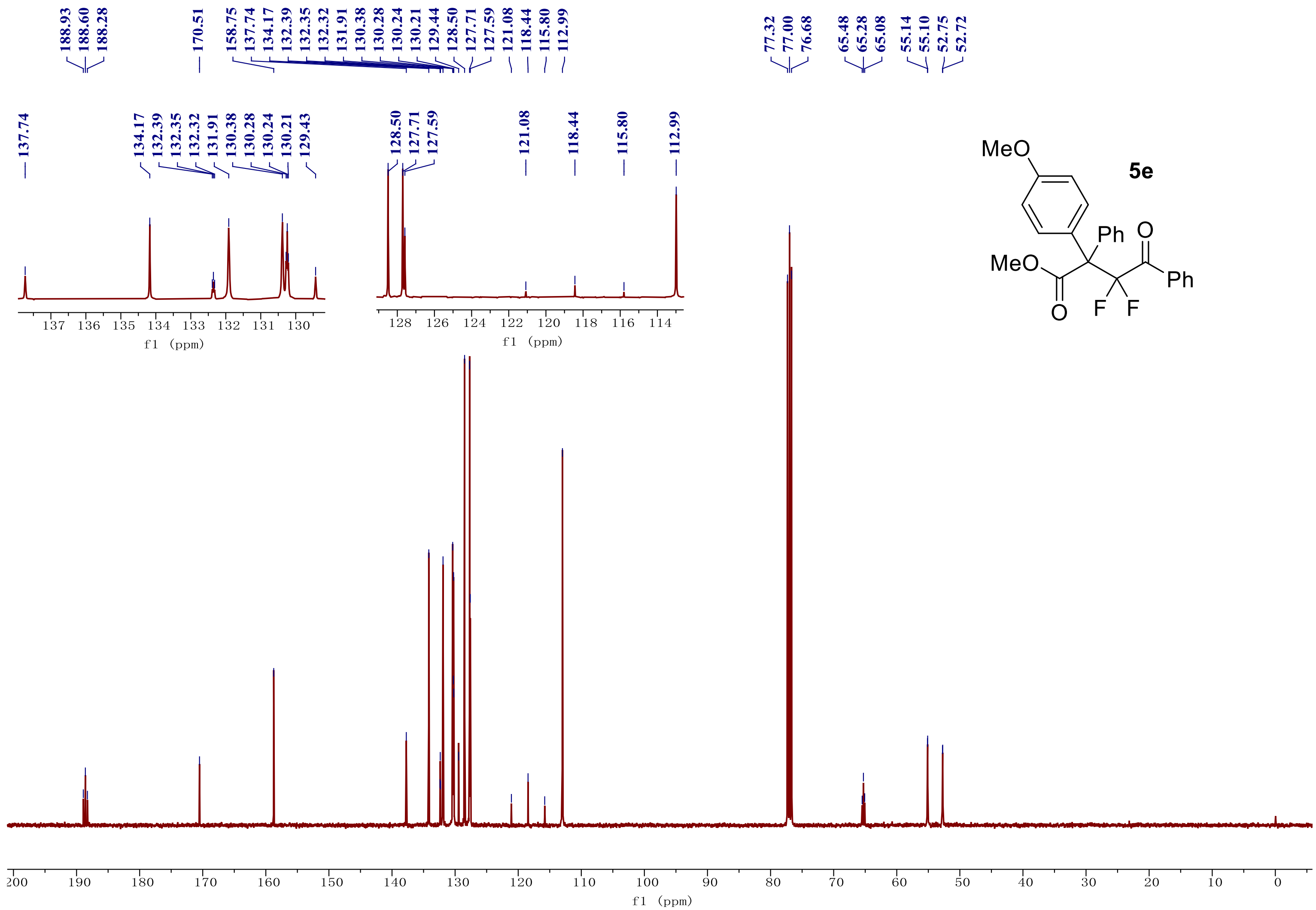
^{19}F NMR of Compound 5c (376 MHz, $CDCl_3$)



^{1}H NMR of Compound 5e (400 MHz, $CDCl_3$)

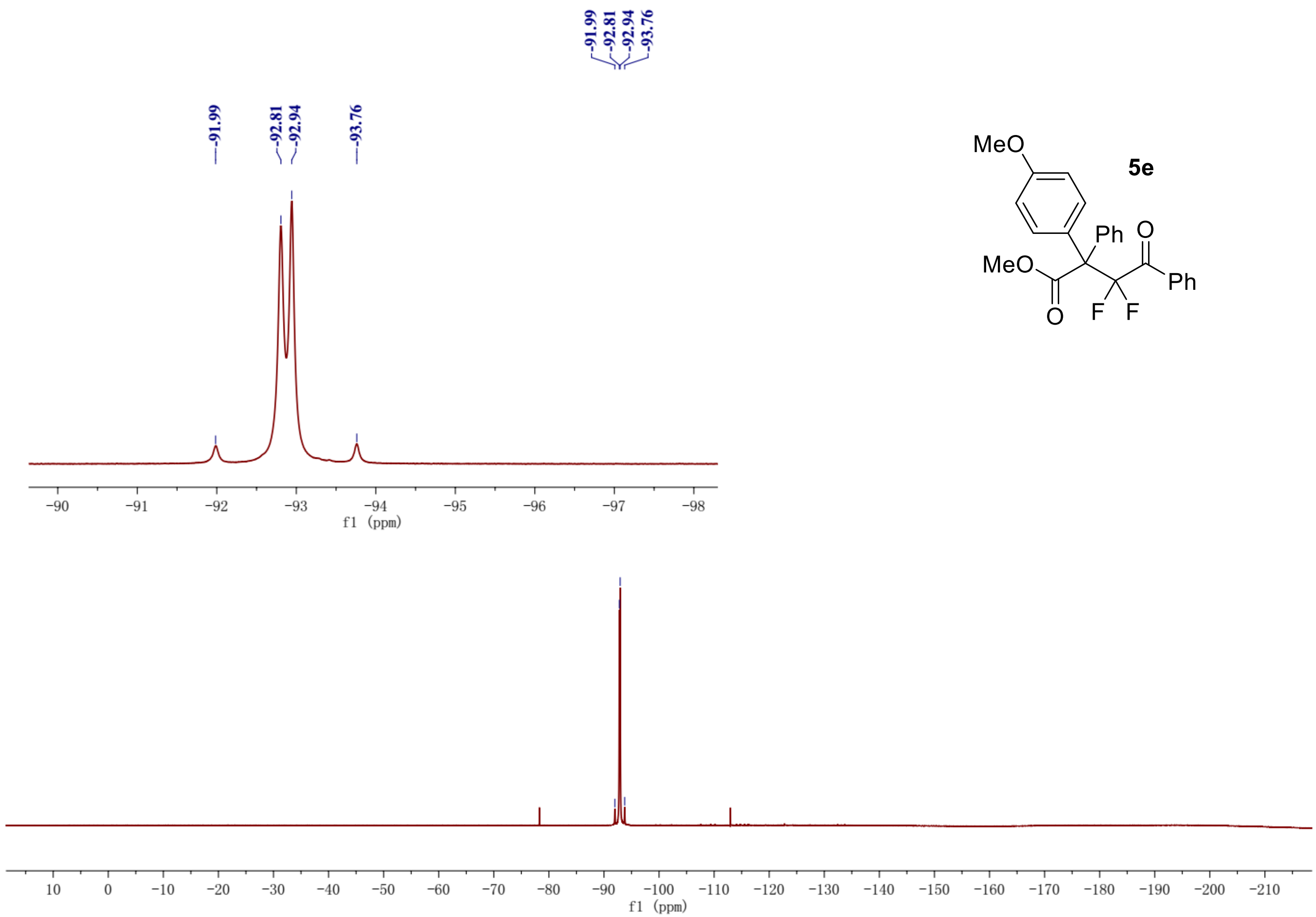


^{13}C NMR of Compound 5e (100 MHz, CDCl$_3$)

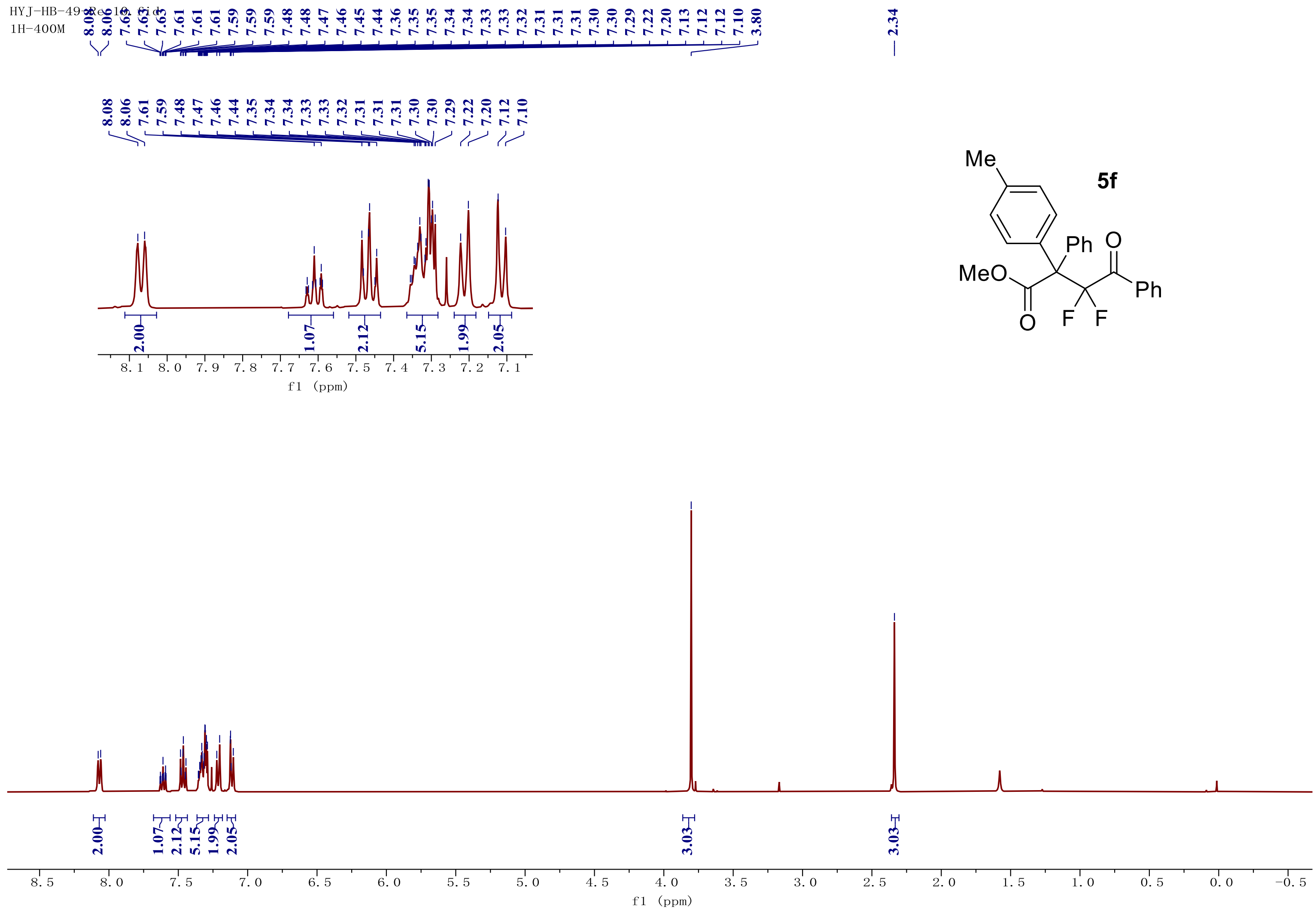


5e

^{19}F NMR of Compound 5e (376 MHz, CDCl$_3$)

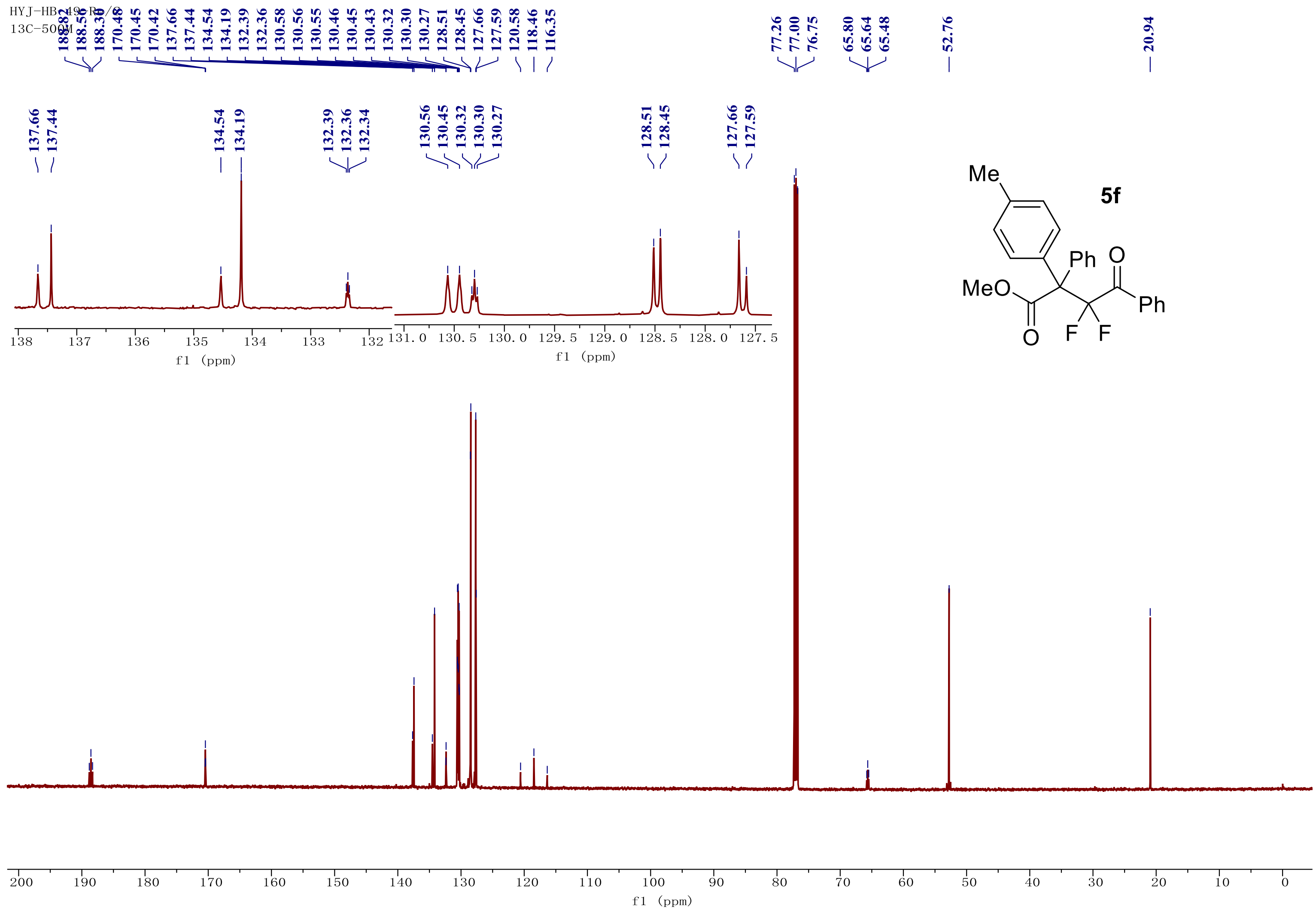


^{1}H NMR of Compound 5f (400 MHz, $CDCl_3$)

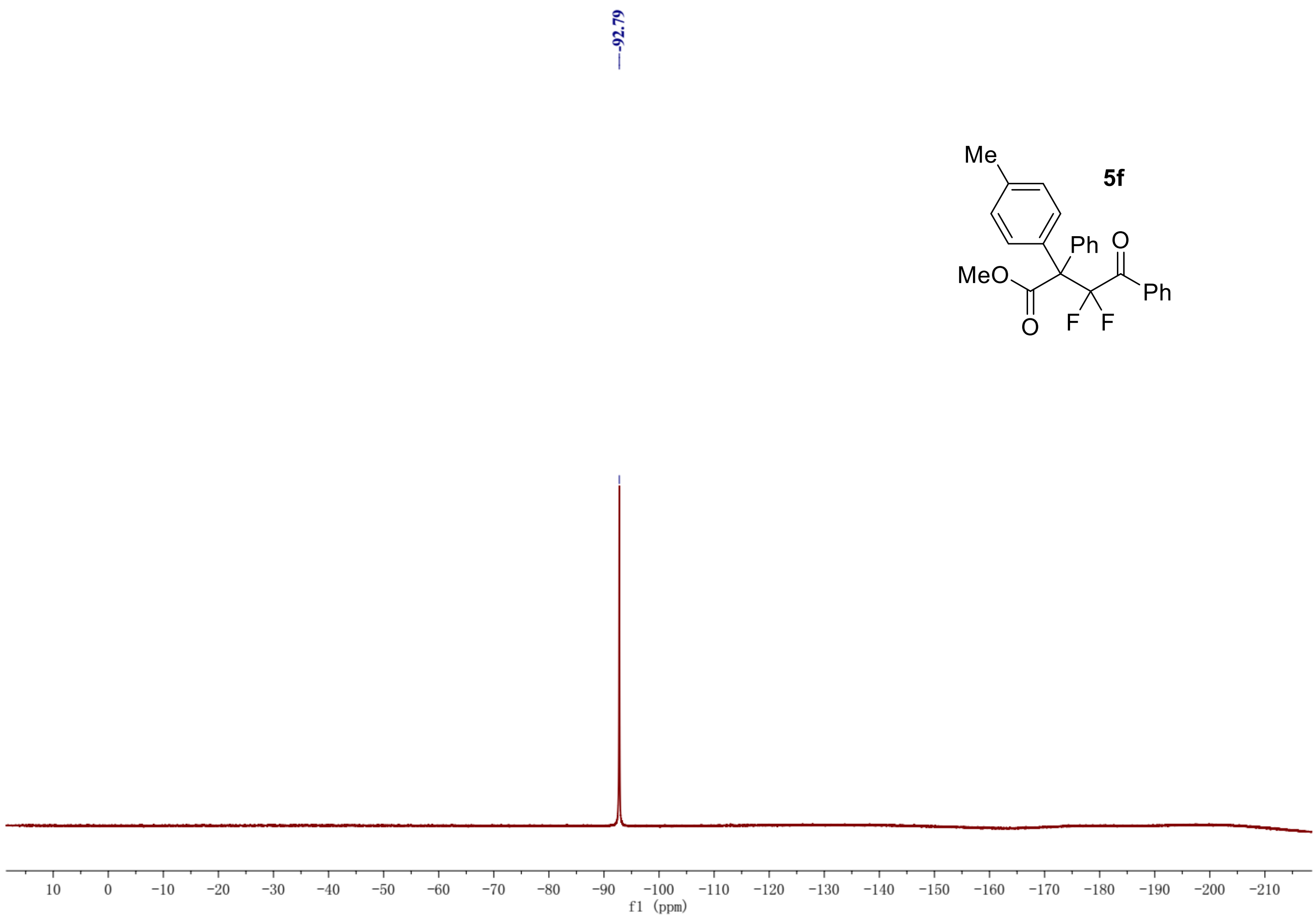


5f

^{13}C NMR of Compound 5f (125 MHz, $CDCl_3$)

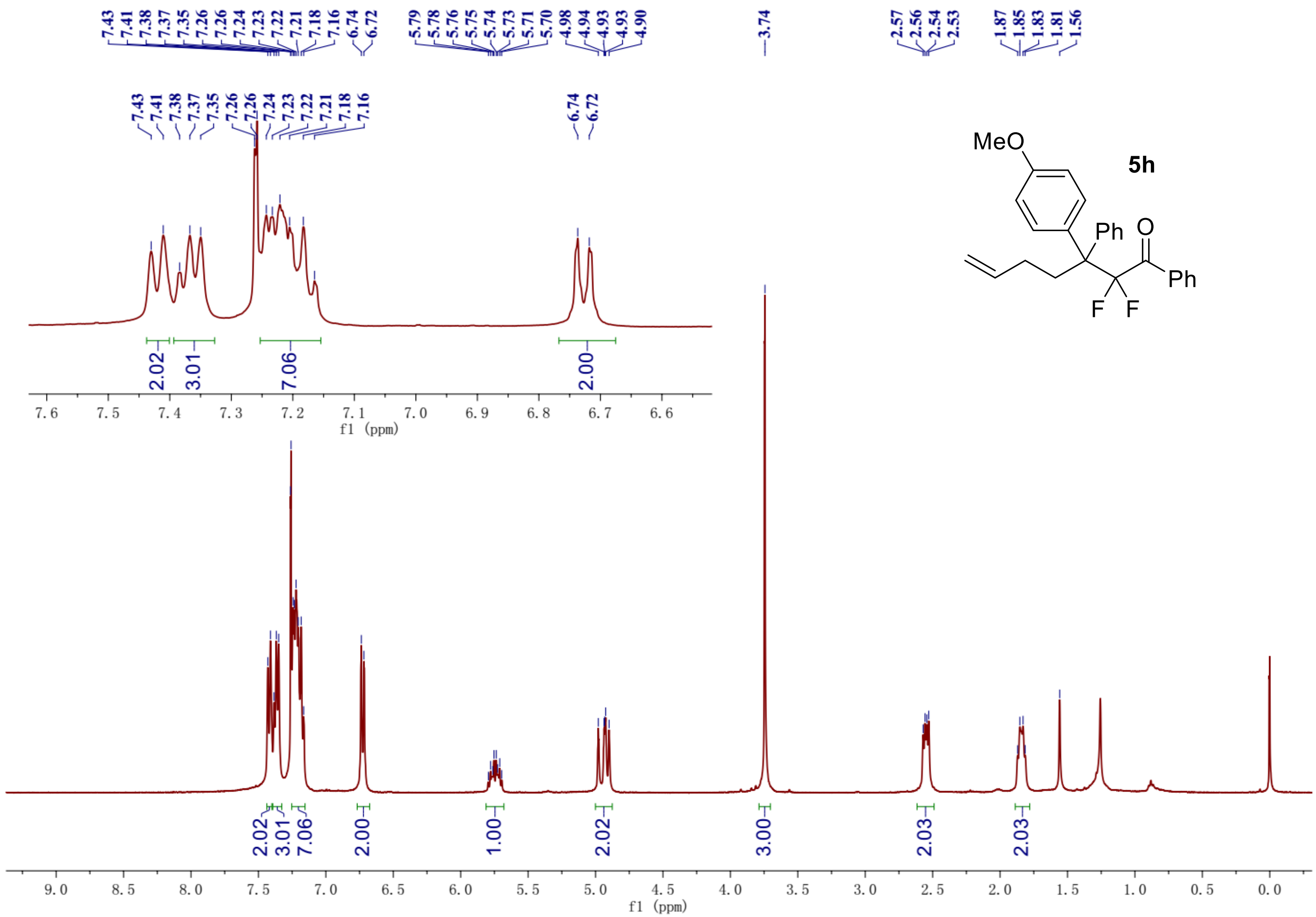


^{19}F NMR of Compound 5f (376 MHz, $CDCl_3$)

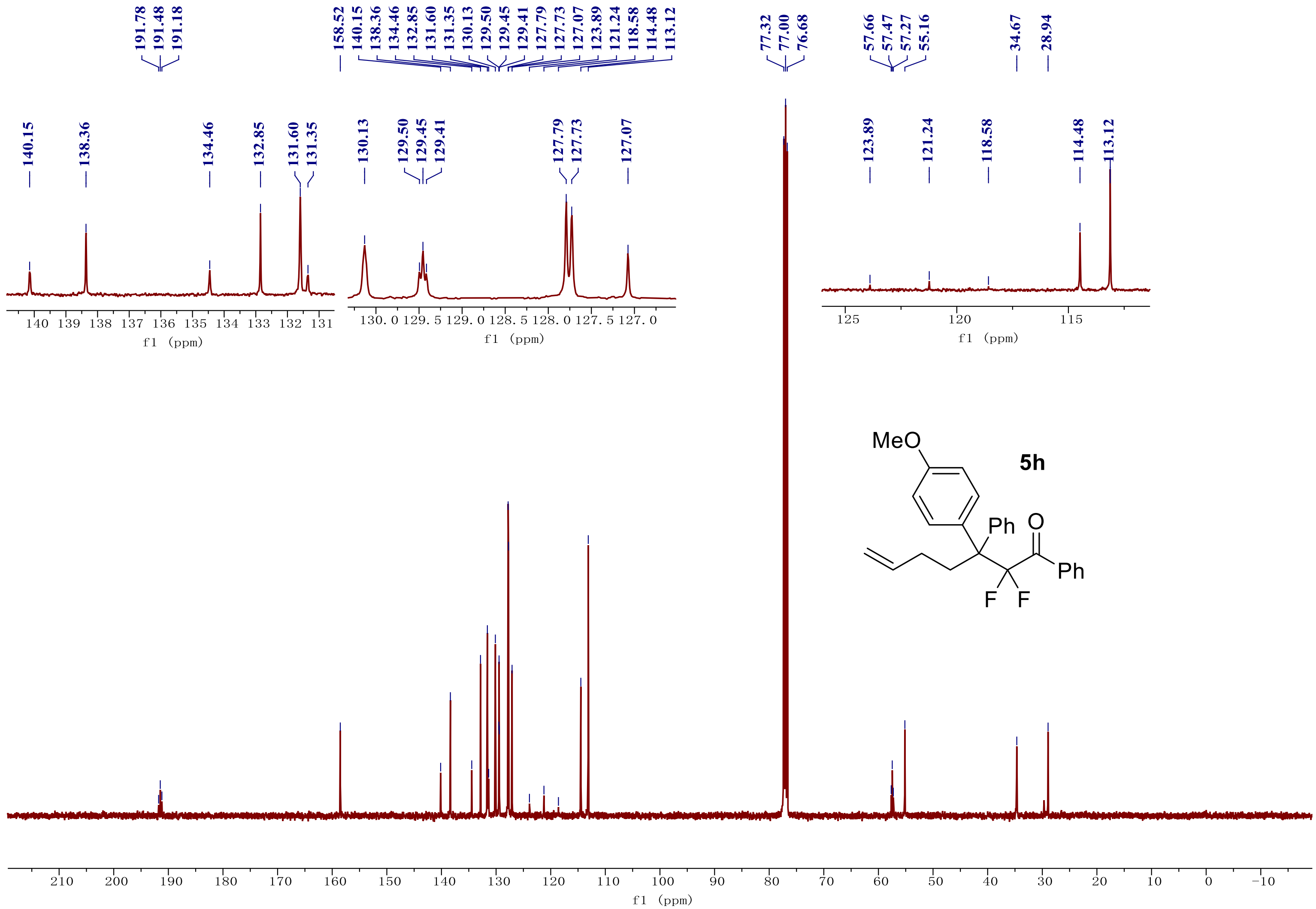


5f

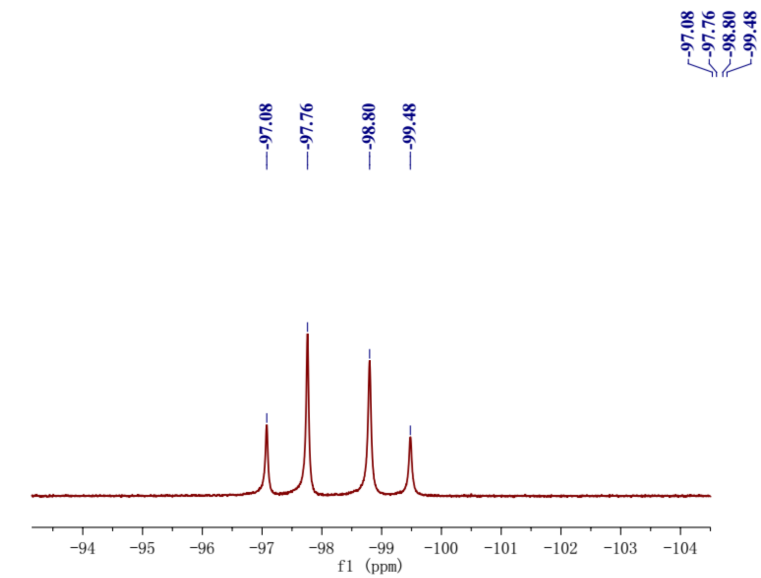
[1]H NMR of Compound 5h (400 MHz, $CDCl_3$)

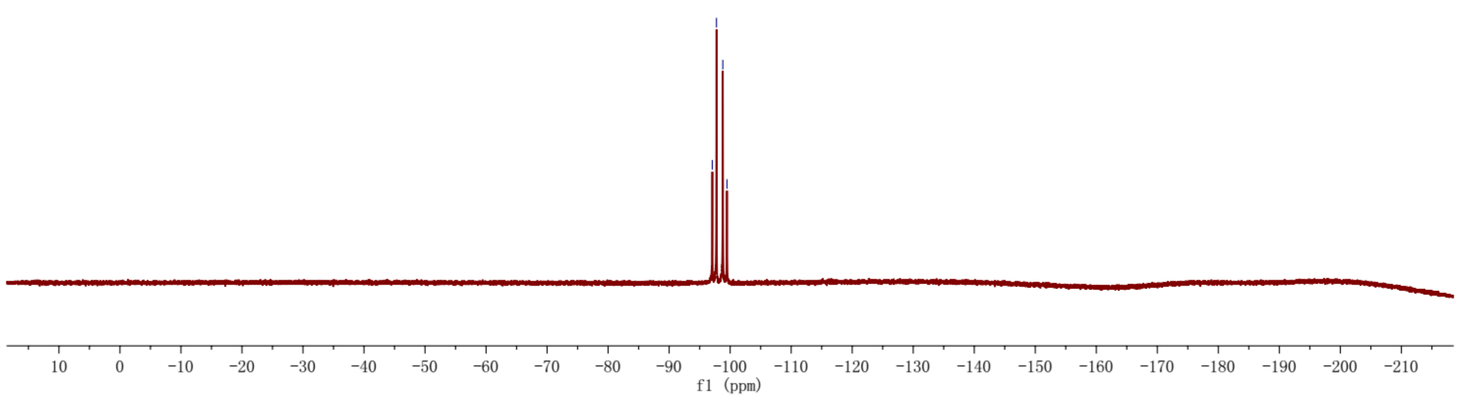


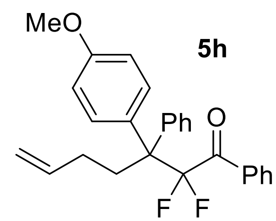
^{13}C NMR of Compound 5h (100 MHz, CDCl$_3$)



^{19}F NMR of Compound 5h (376 MHz, $CDCl_3$)

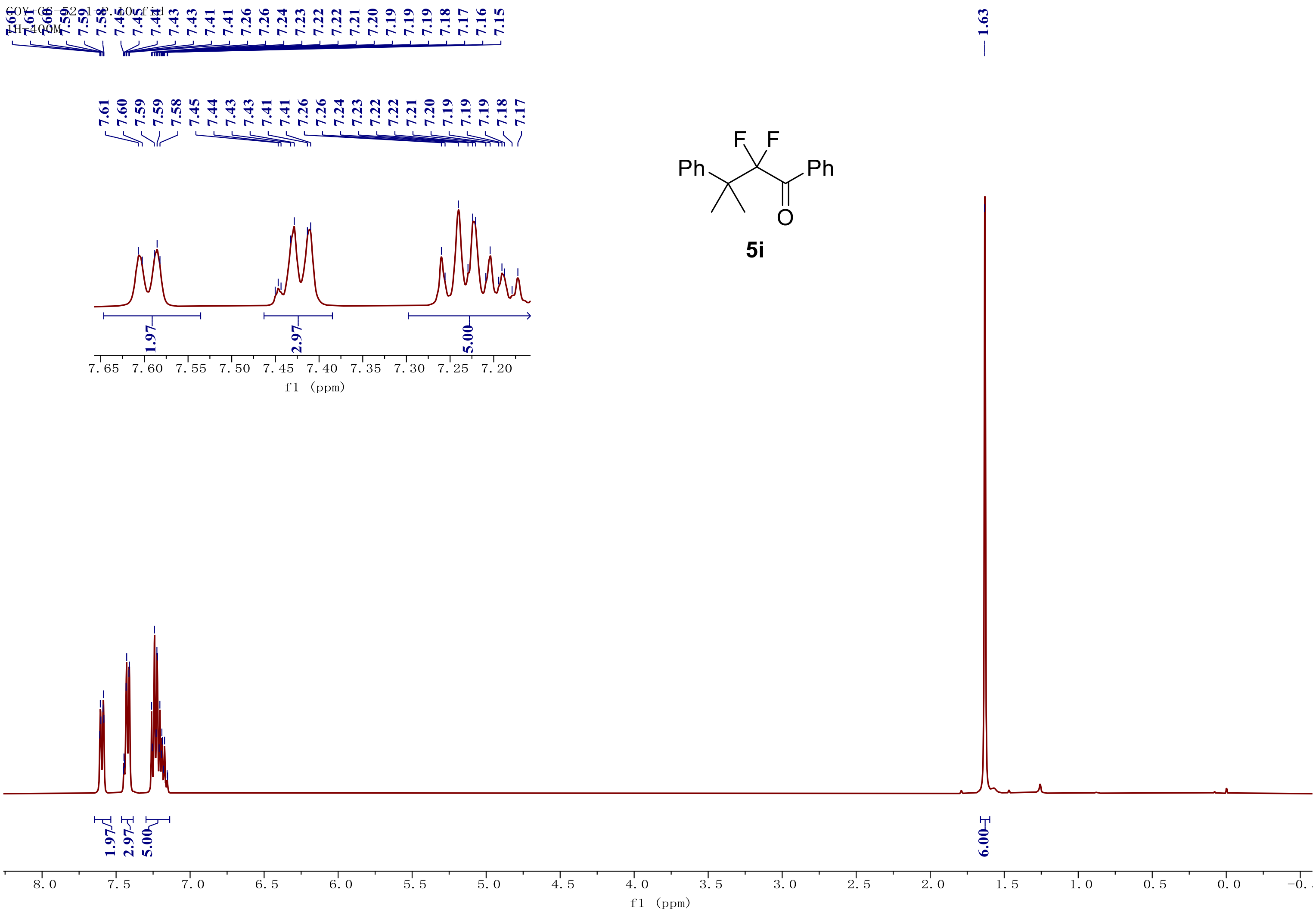






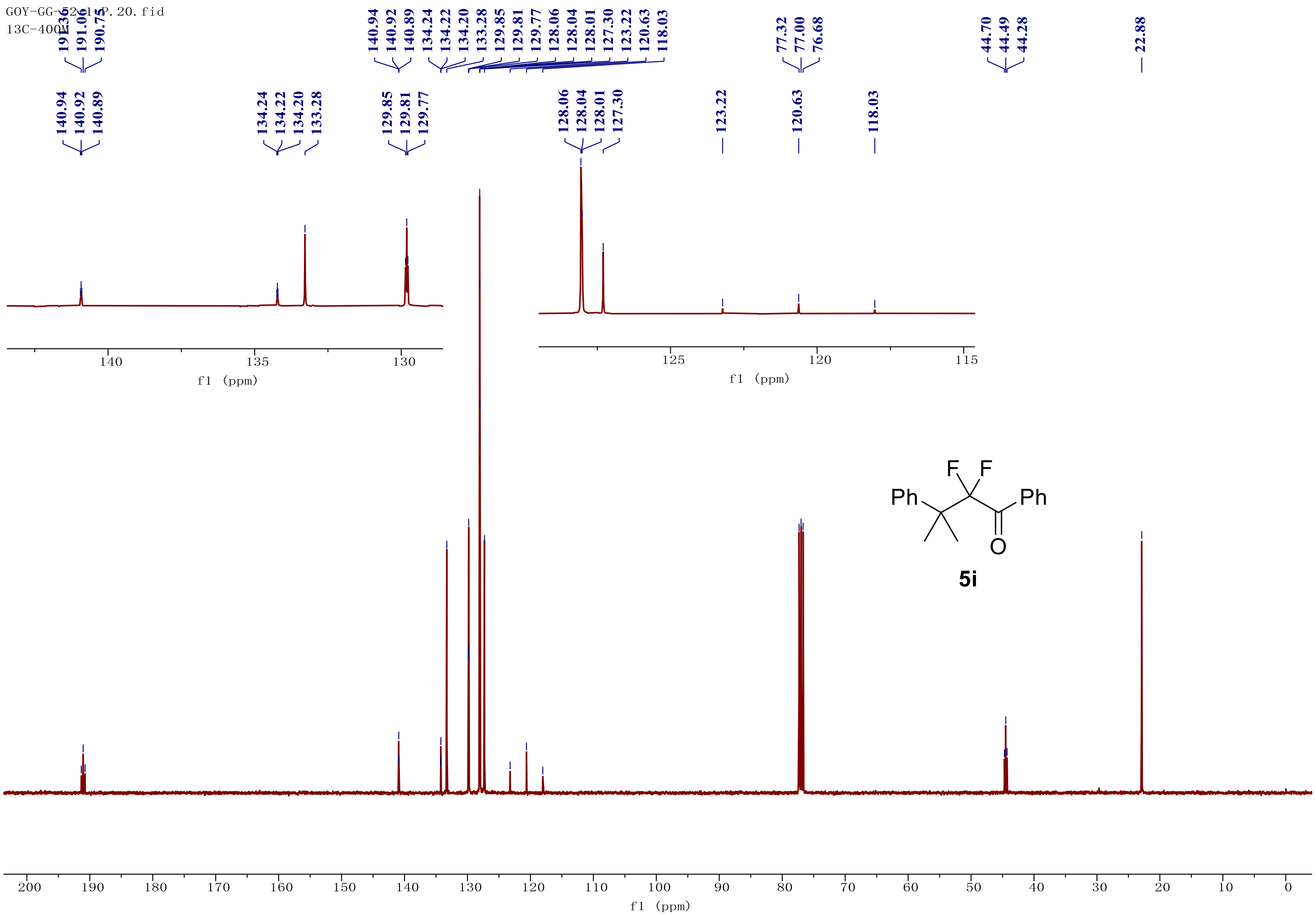
5h

[1]H NMR of Compound 5i (400 MHz, CDCl3)

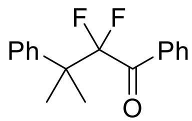


5i

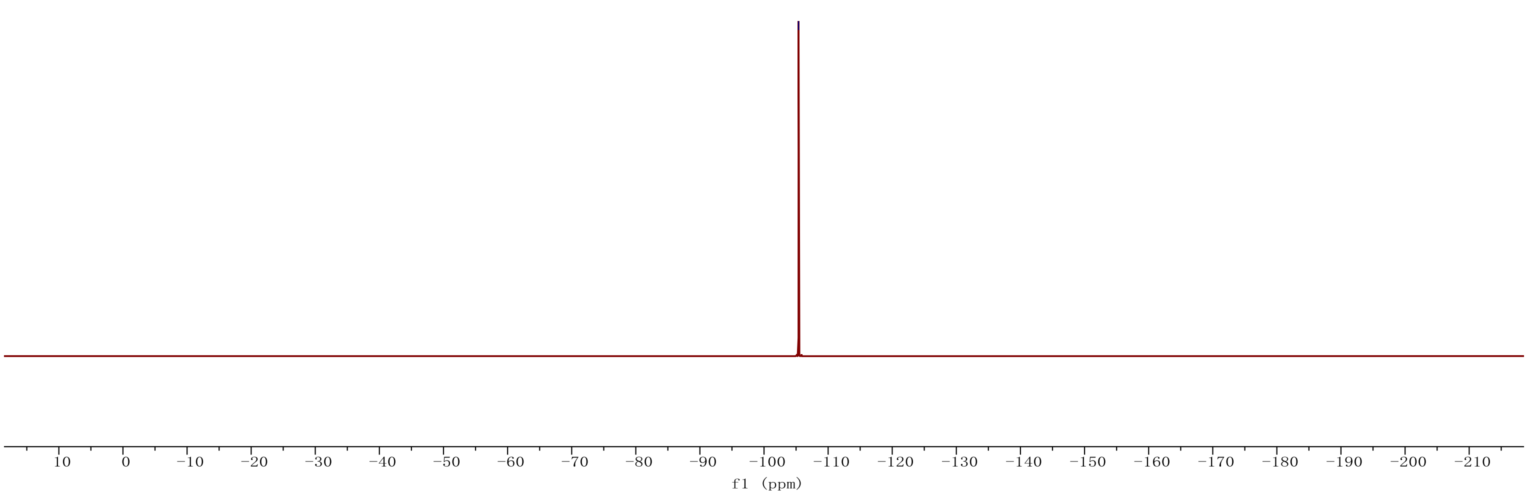
^{13}C NMR of Compound 5i (100 MHz, $CDCl_3$)



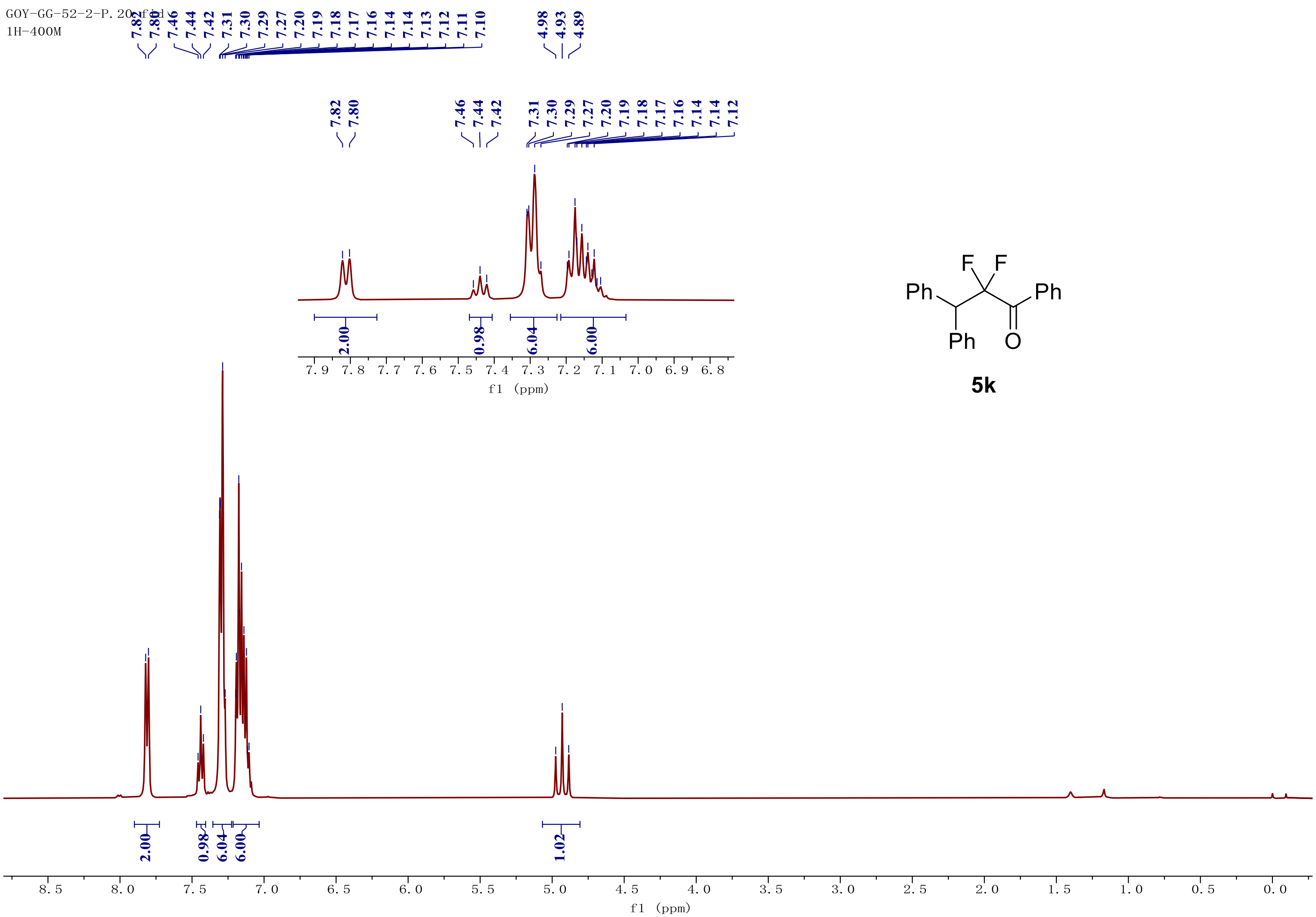
^{19}F NMR of Compound 5i (376 MHz, CDCl$_3$)



5i

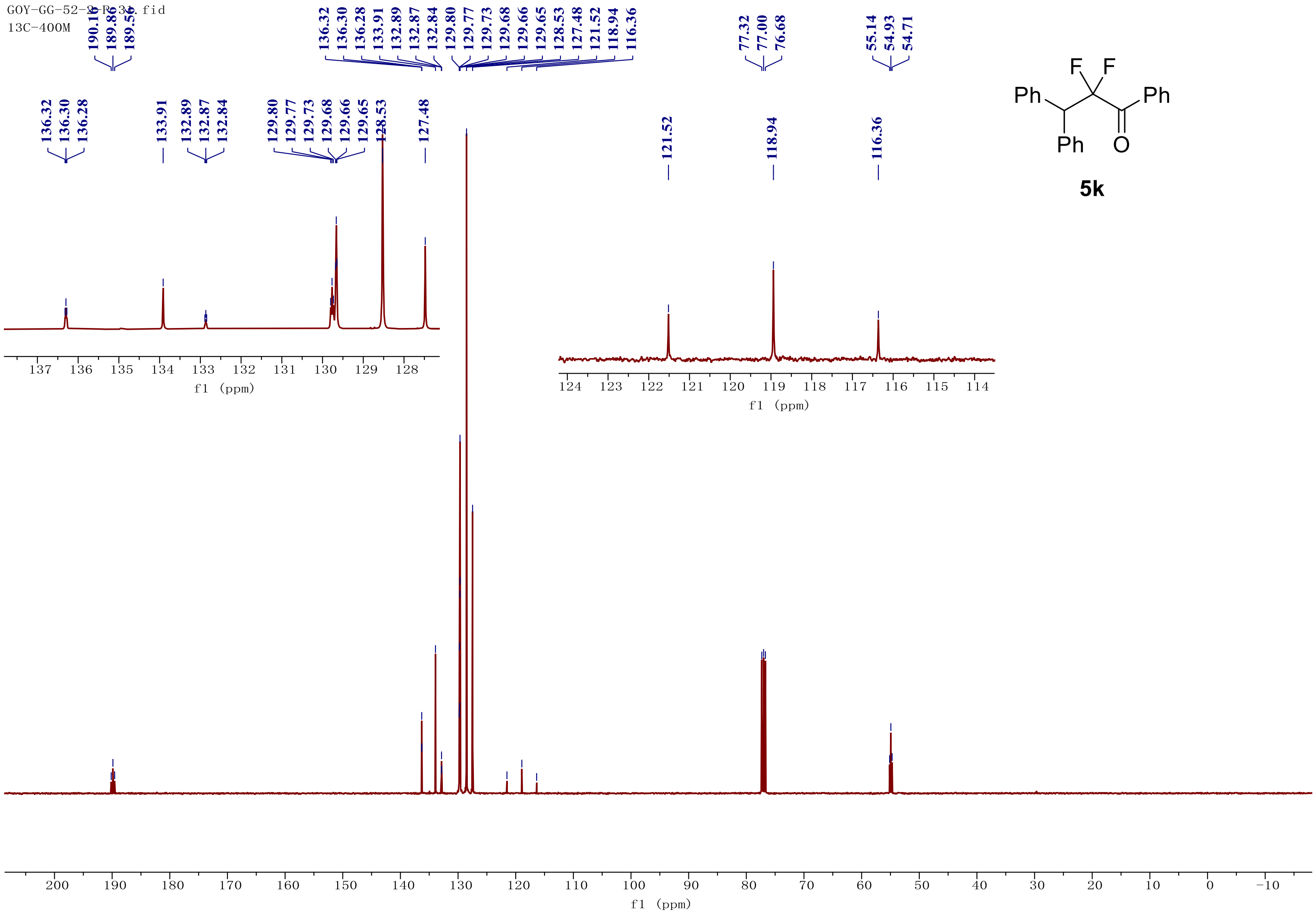


[1]H NMR of Compound 5k (400 MHz, CDCl3)



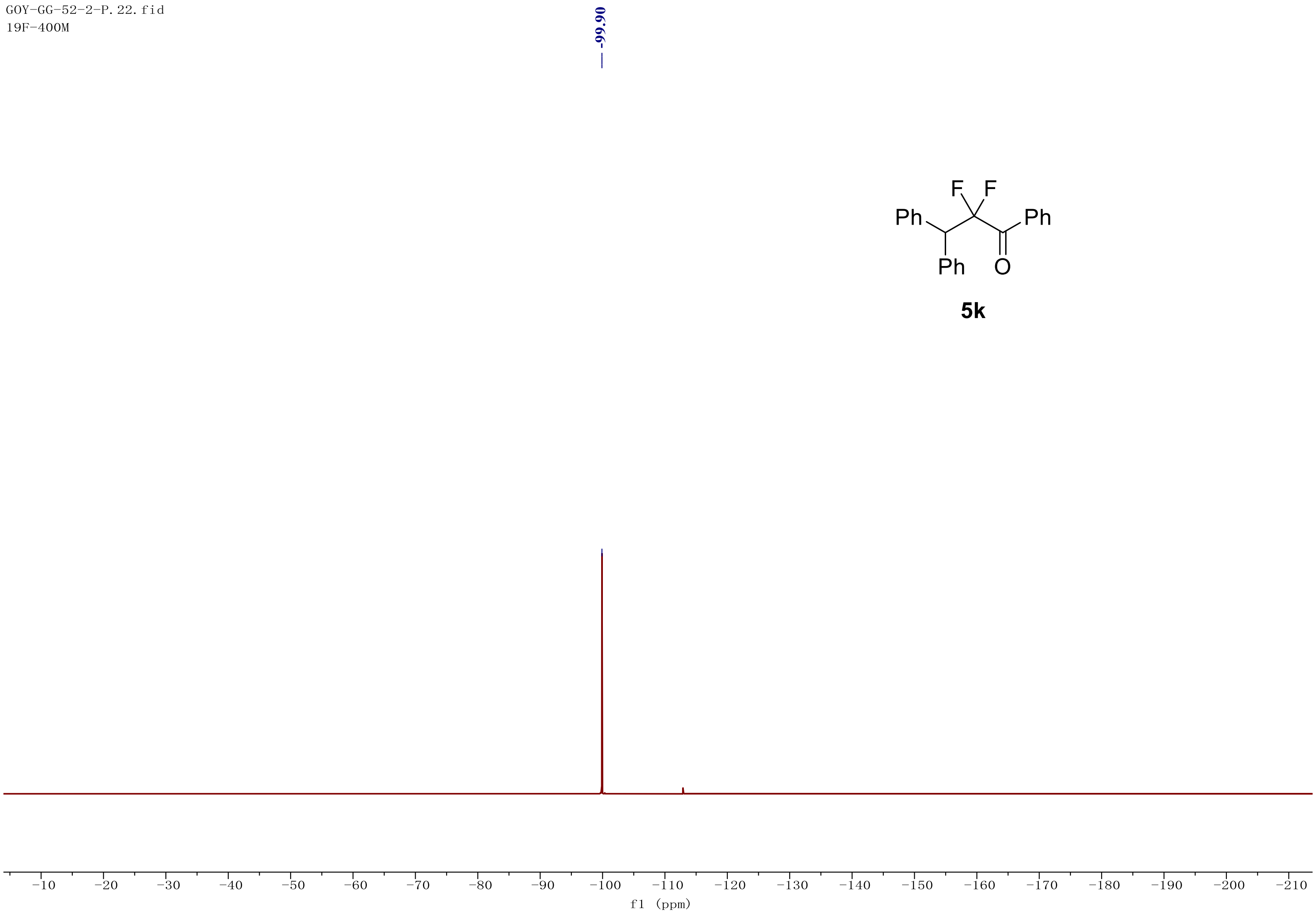
5k

^{13}C NMR of Compound 5k (100 MHz, $CDCl_3$)



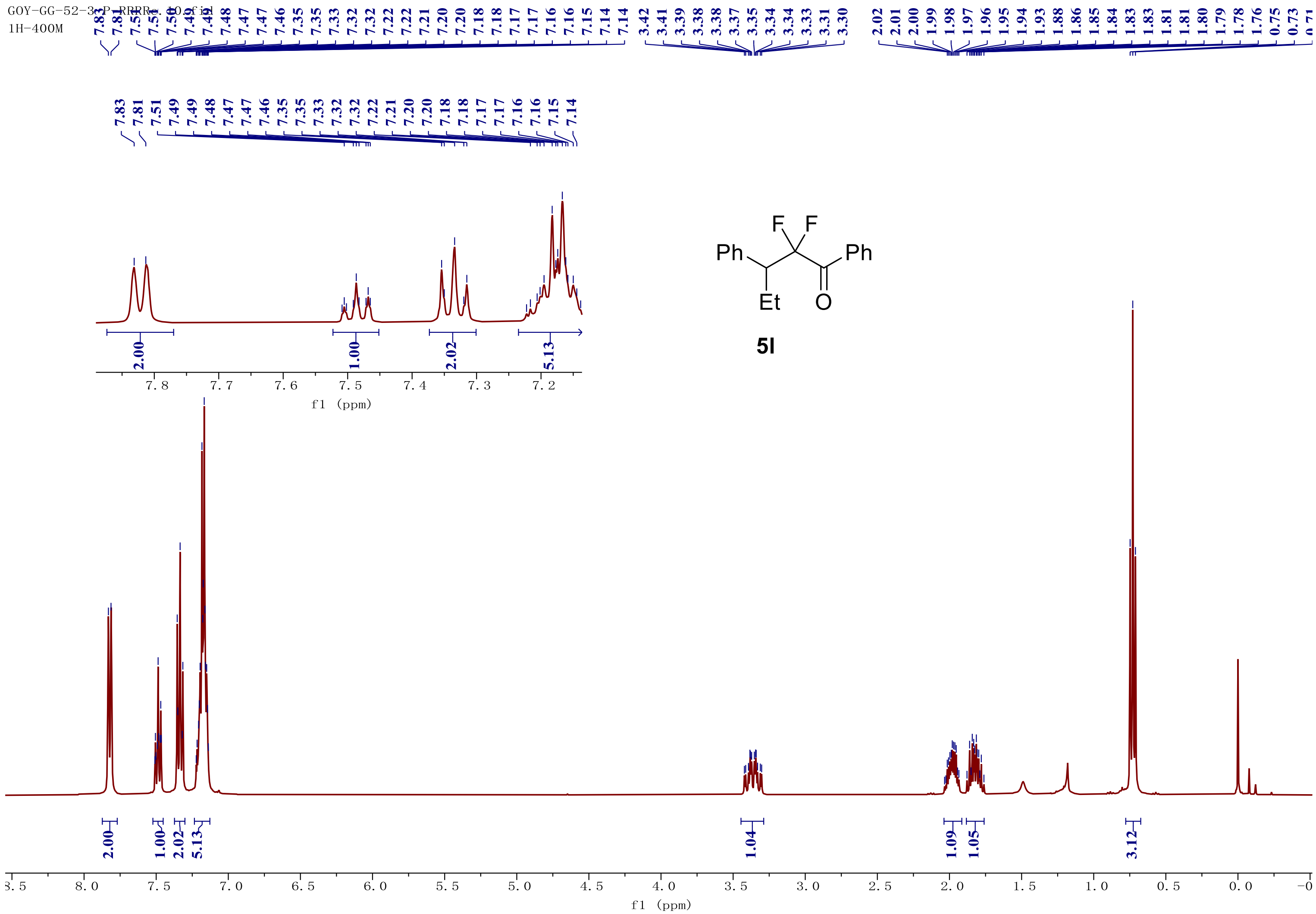
5k

^{19}F NMR of Compound 5k (376 MHz, $CDCl_3$)

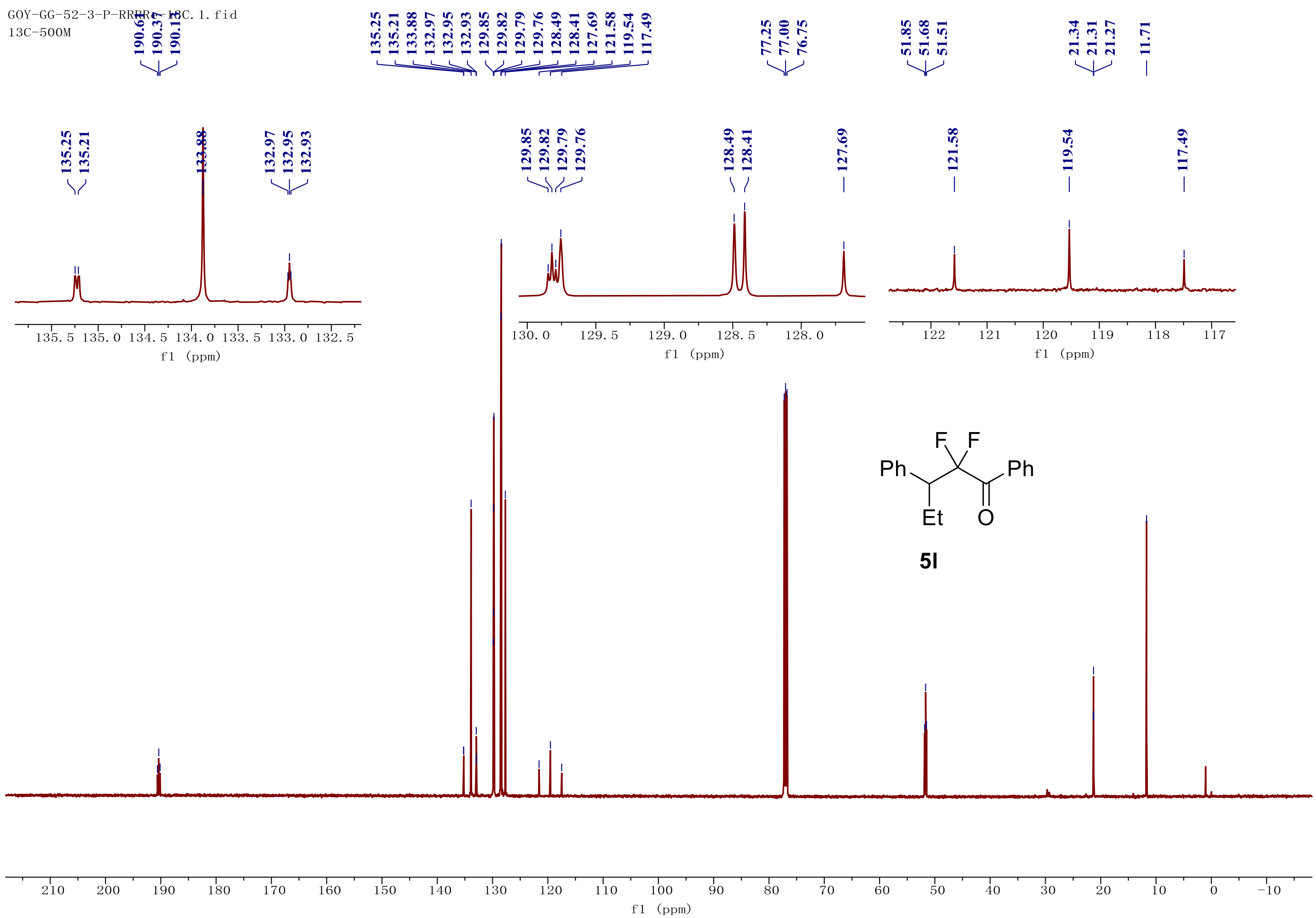


5k

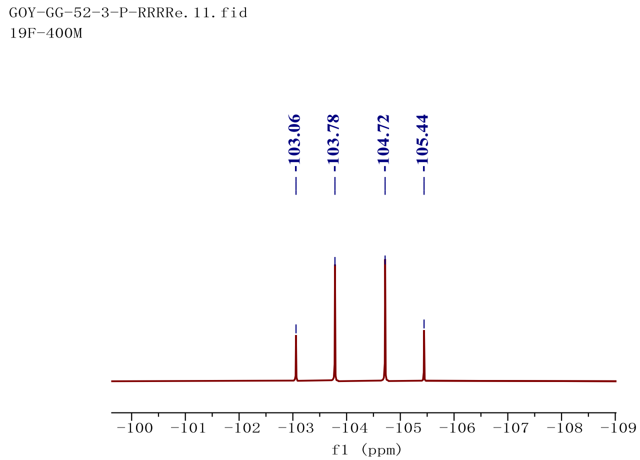
^{1}H NMR of Compound 5l (400 MHz, $CDCl_3$)

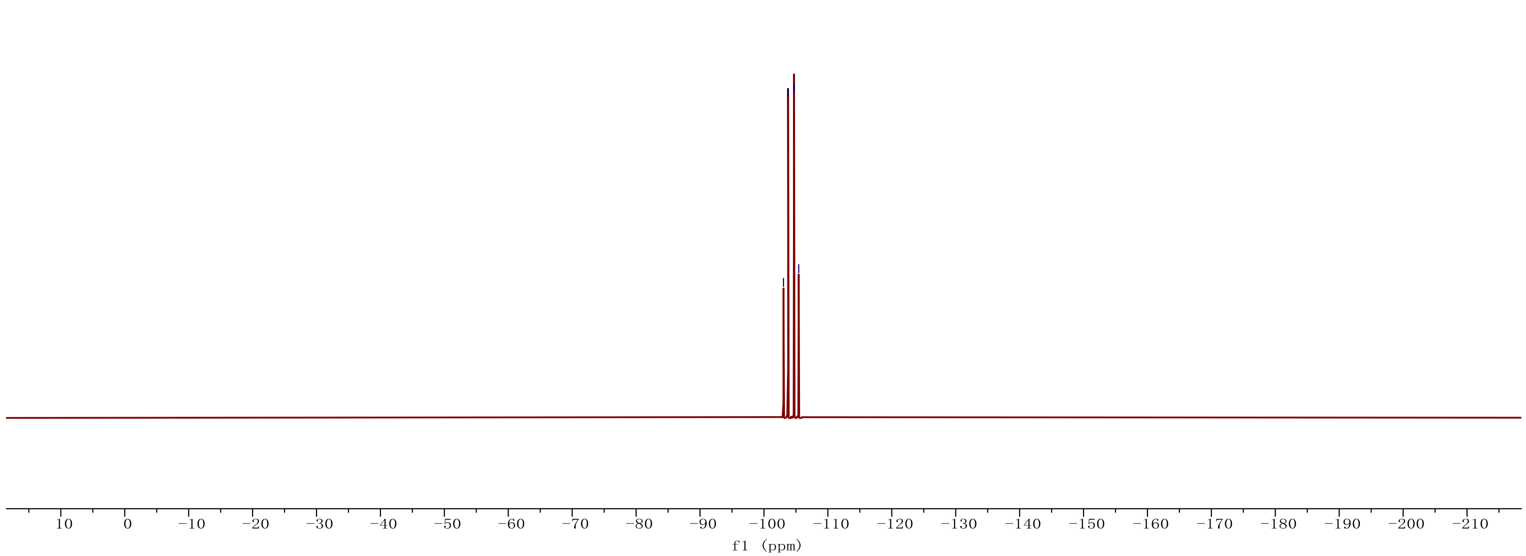


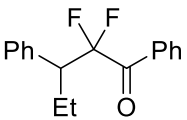
^{13}C NMR of Compound 5l (125 MHz, $CDCl_3$)



^{19}F NMR of Compound 5l (376 MHz, $CDCl_3$)

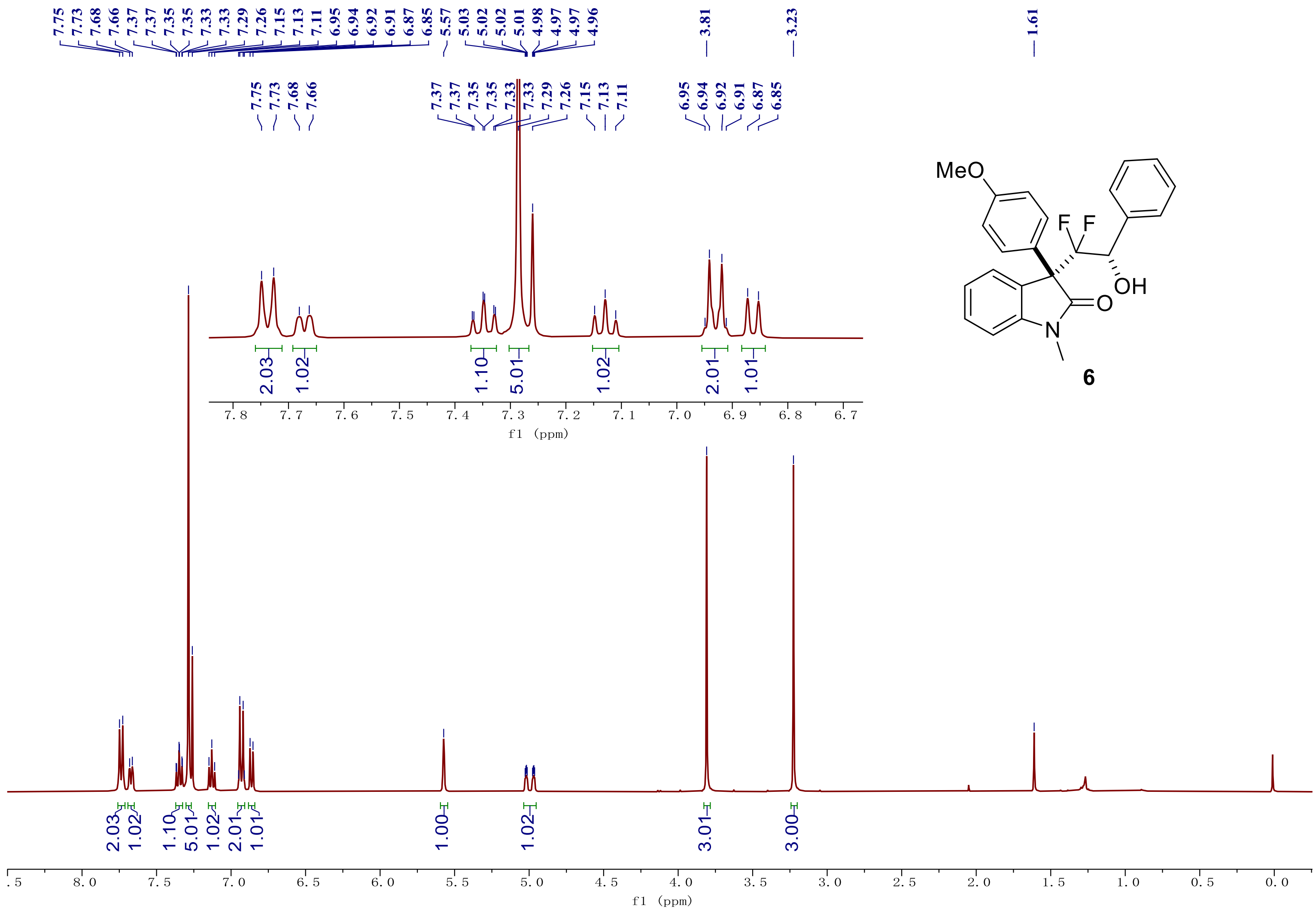






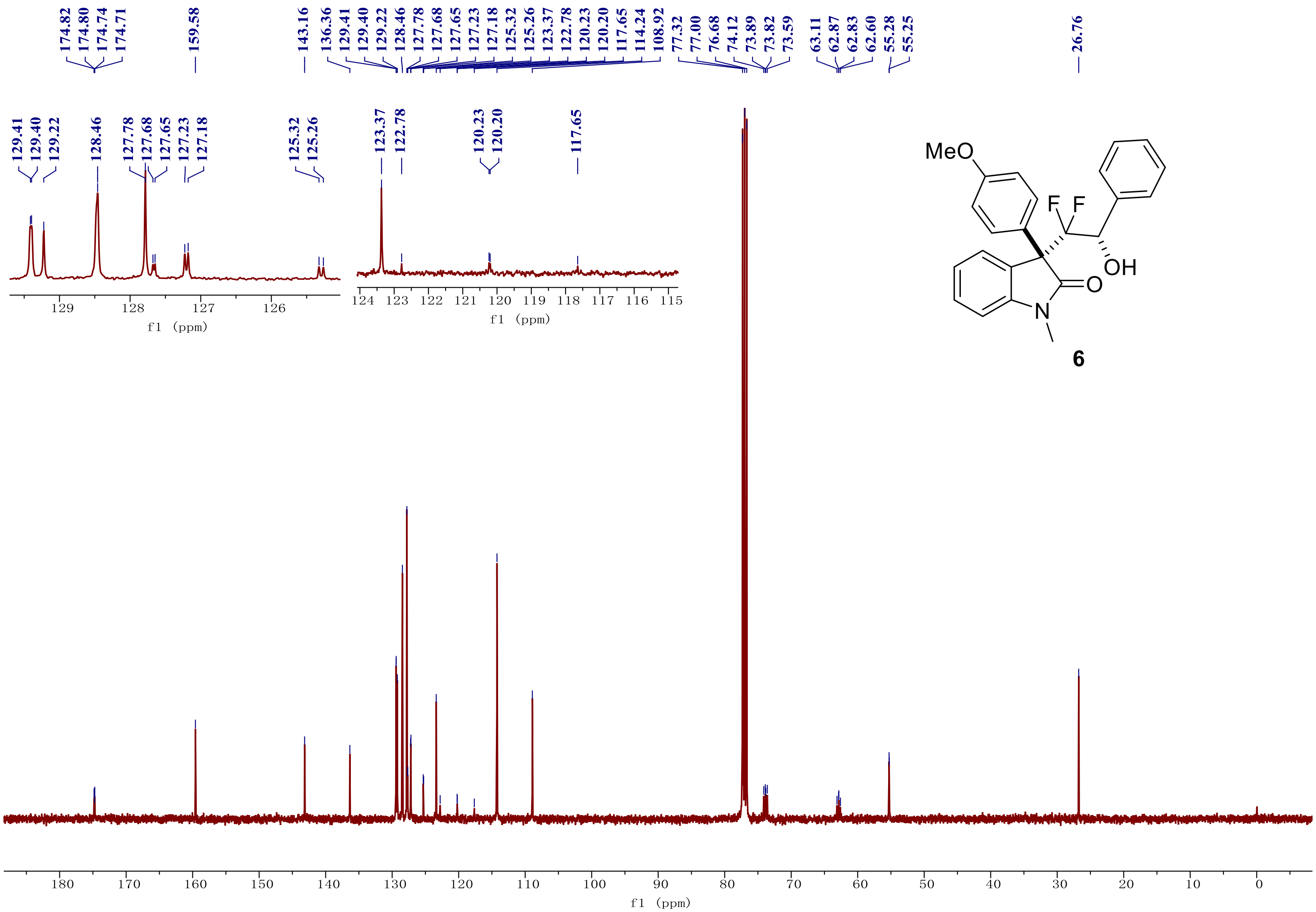
5l

^{1}H NMR of Compound 6 (400 MHz, $CDCl_3$)

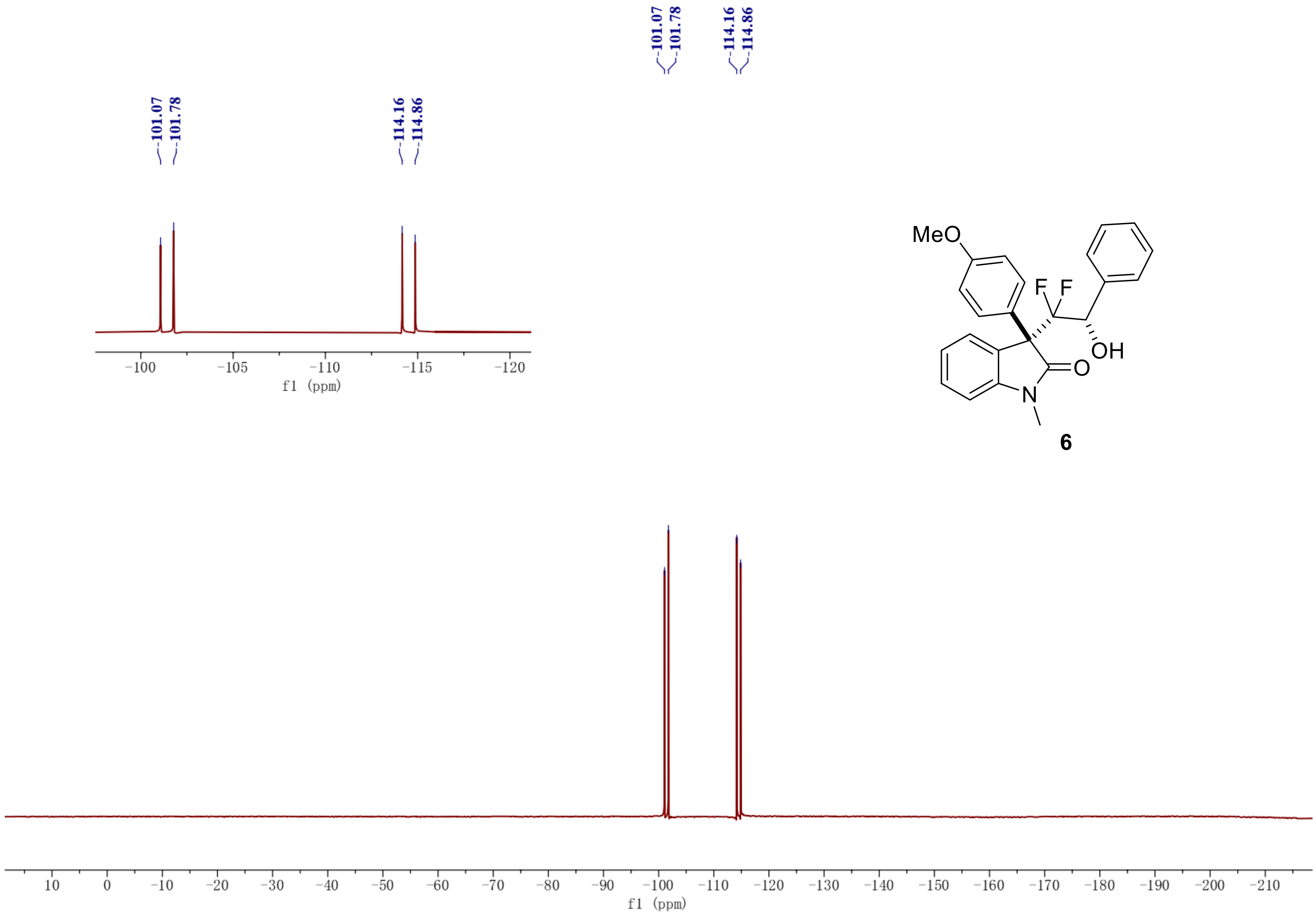


6

^{13}C NMR of Compound 6 (100 MHz, $CDCl_3$)

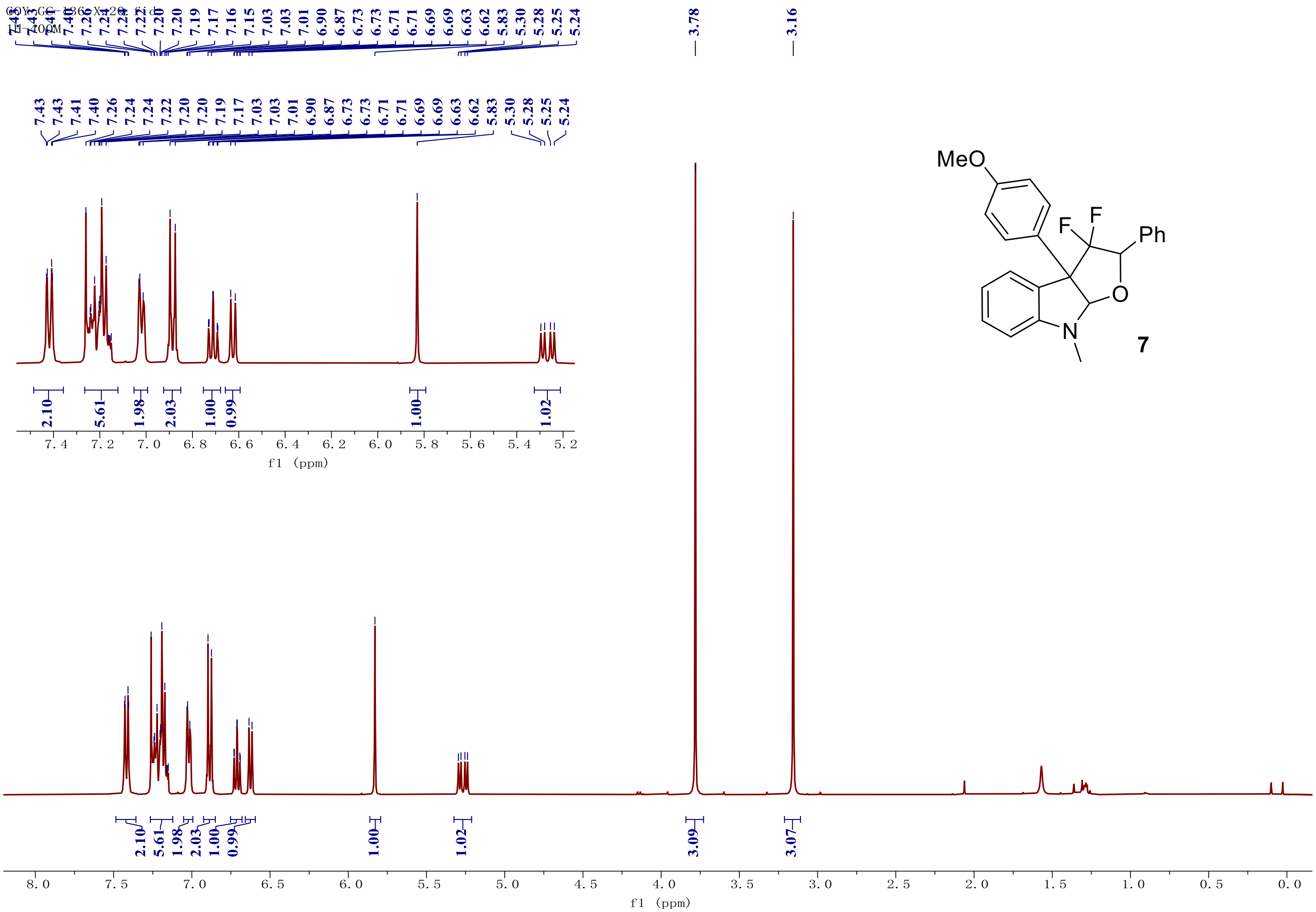


^{19}F NMR of Compound 6 (376 MHz, $CDCl_3$)



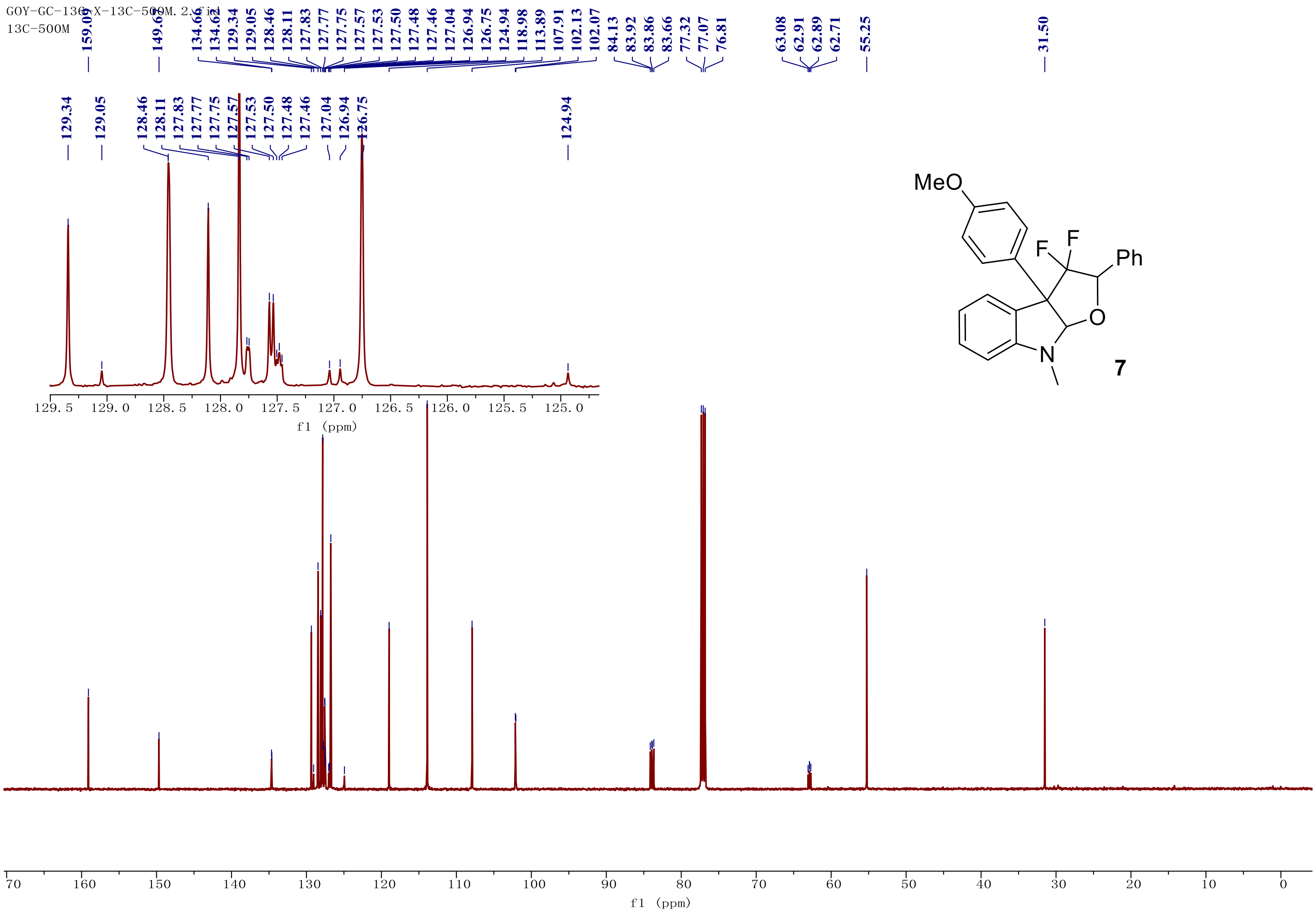
6

^1H NMR of Compound 7 (400 MHz, $CDCl_3$)



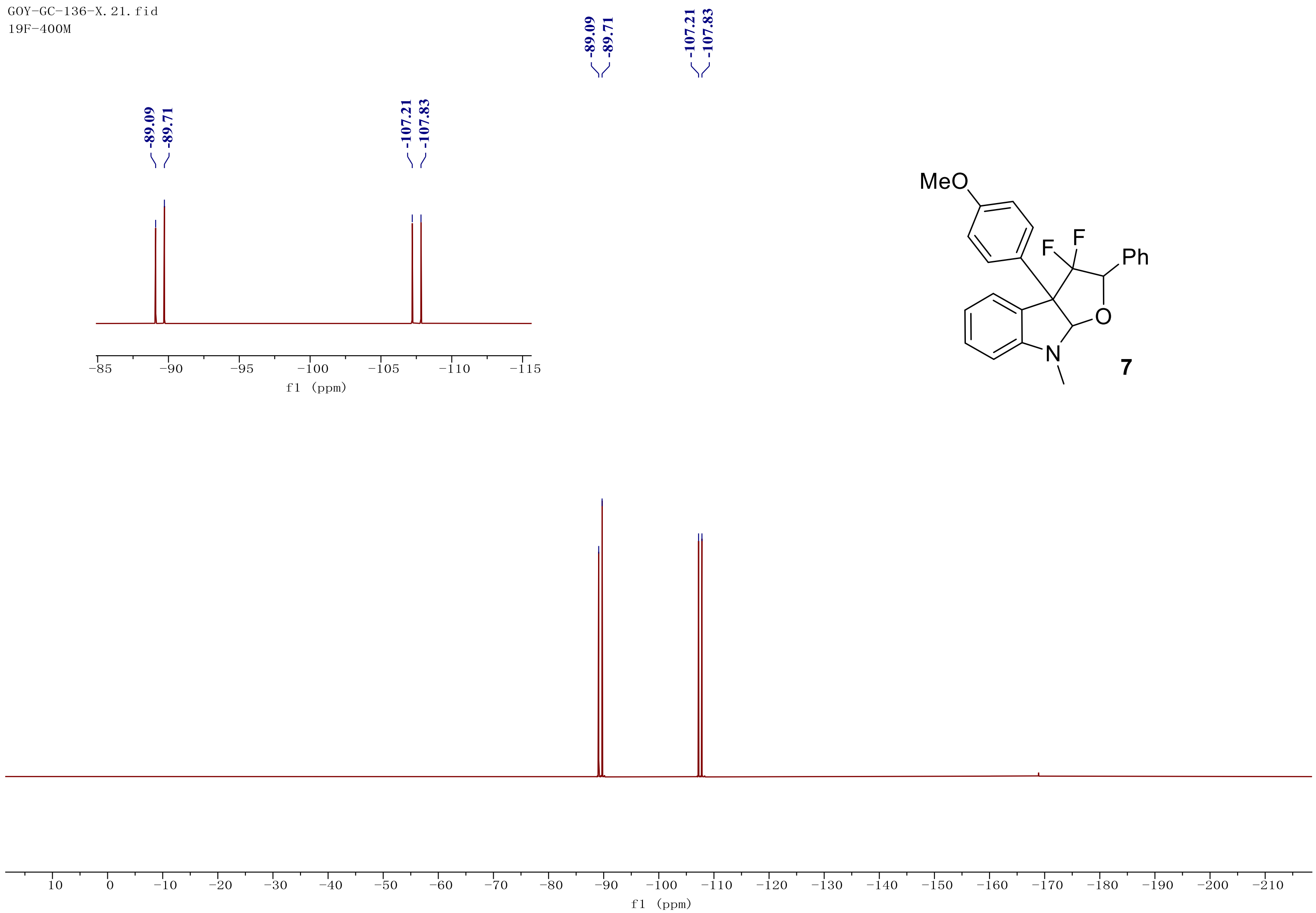
7

^{13}C NMR of Compound 7 (125 MHz, $CDCl_3$)



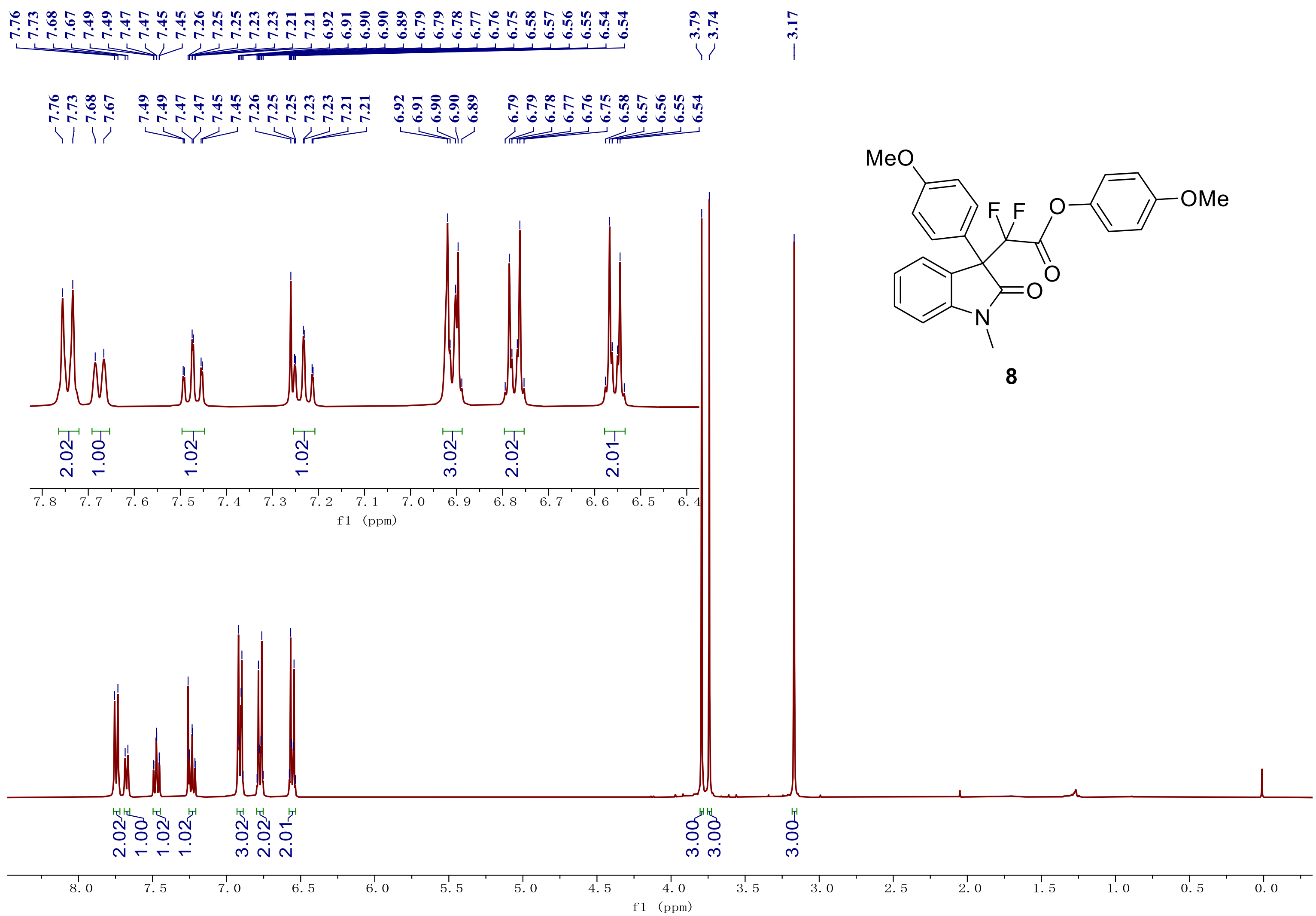
7

^{19}F NMR of Compound 7 (376 MHz, $CDCl_3$)



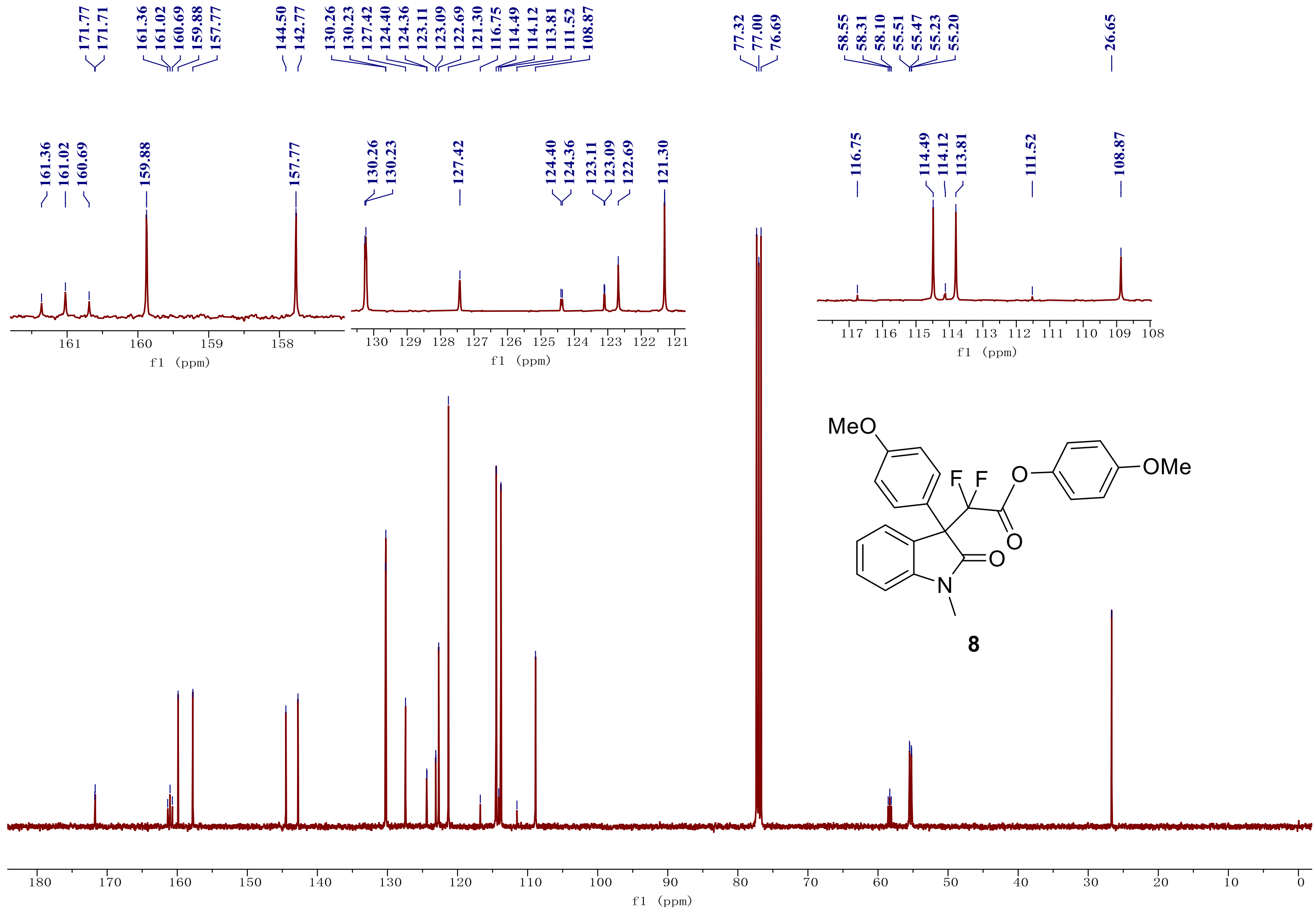
7

^{1}H NMR of Compound 8 (400 MHz, $CDCl_3$)

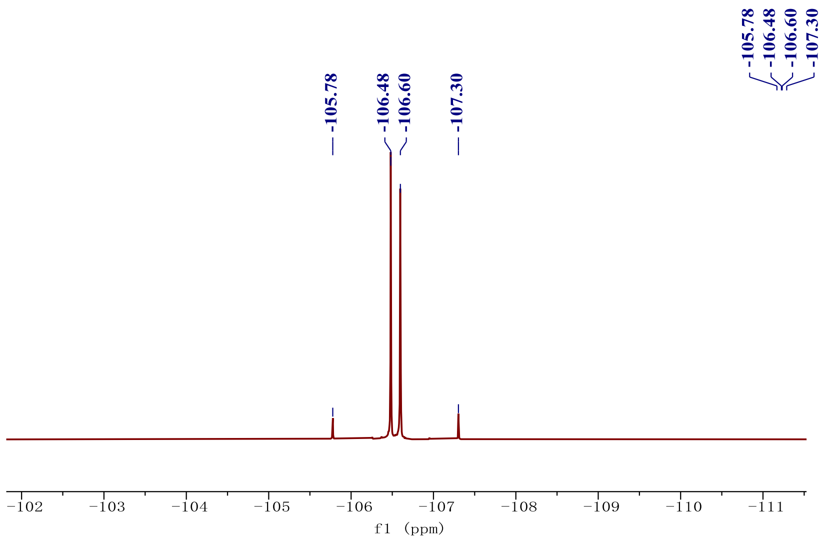


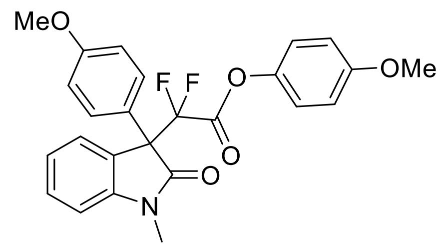
8

^{13}C NMR of Compound 8 (100 MHz, $CDCl_3$)

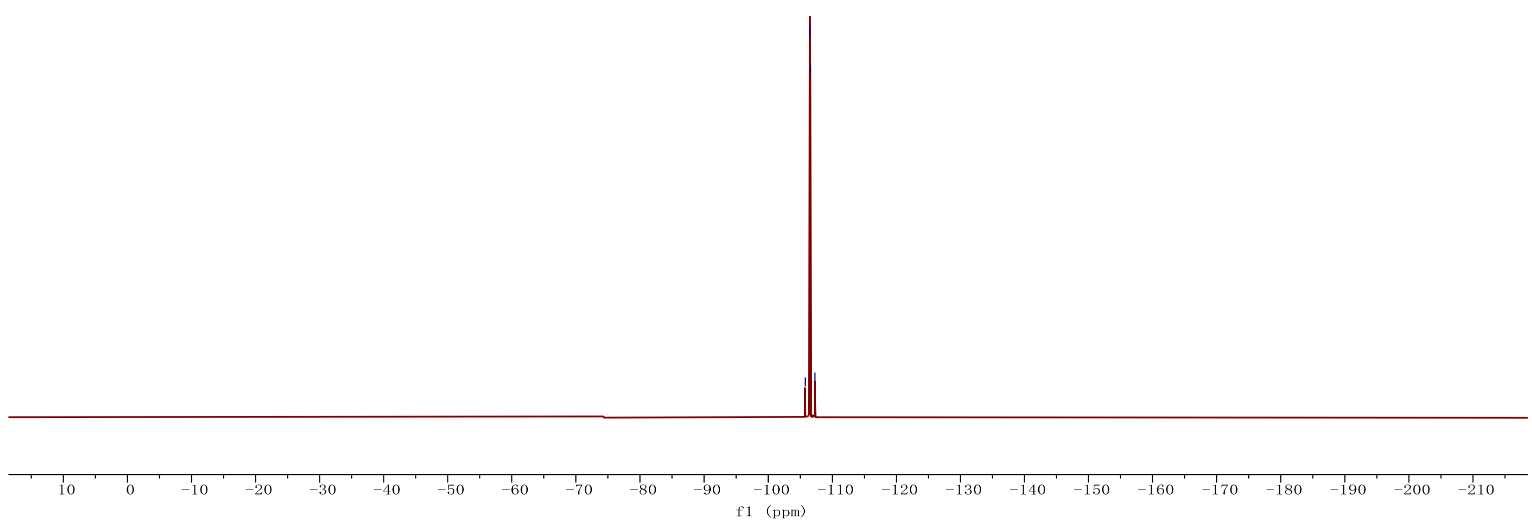


^{19}F NMR of Compound 8 (376 MHz, CDCl$_3$)

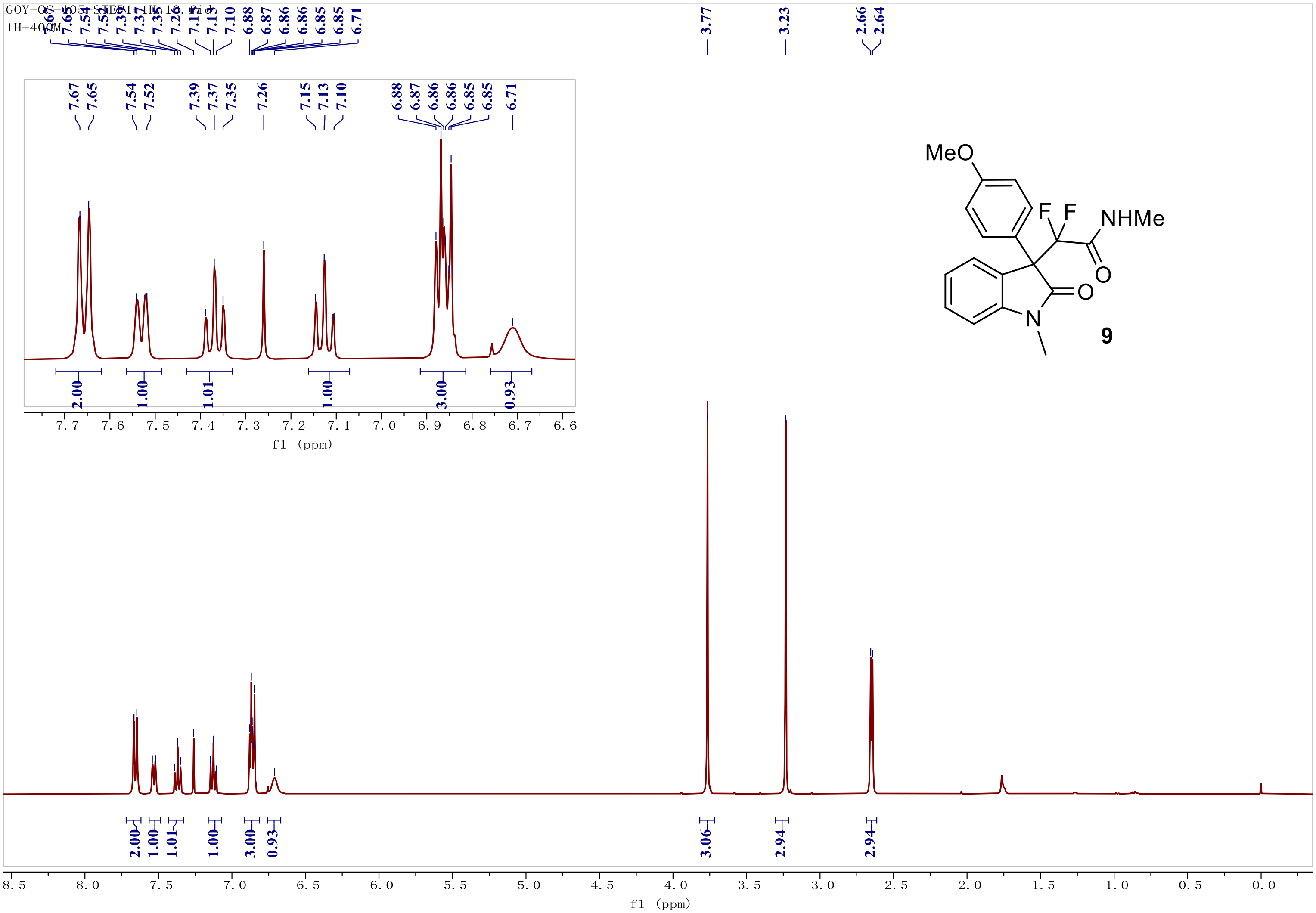




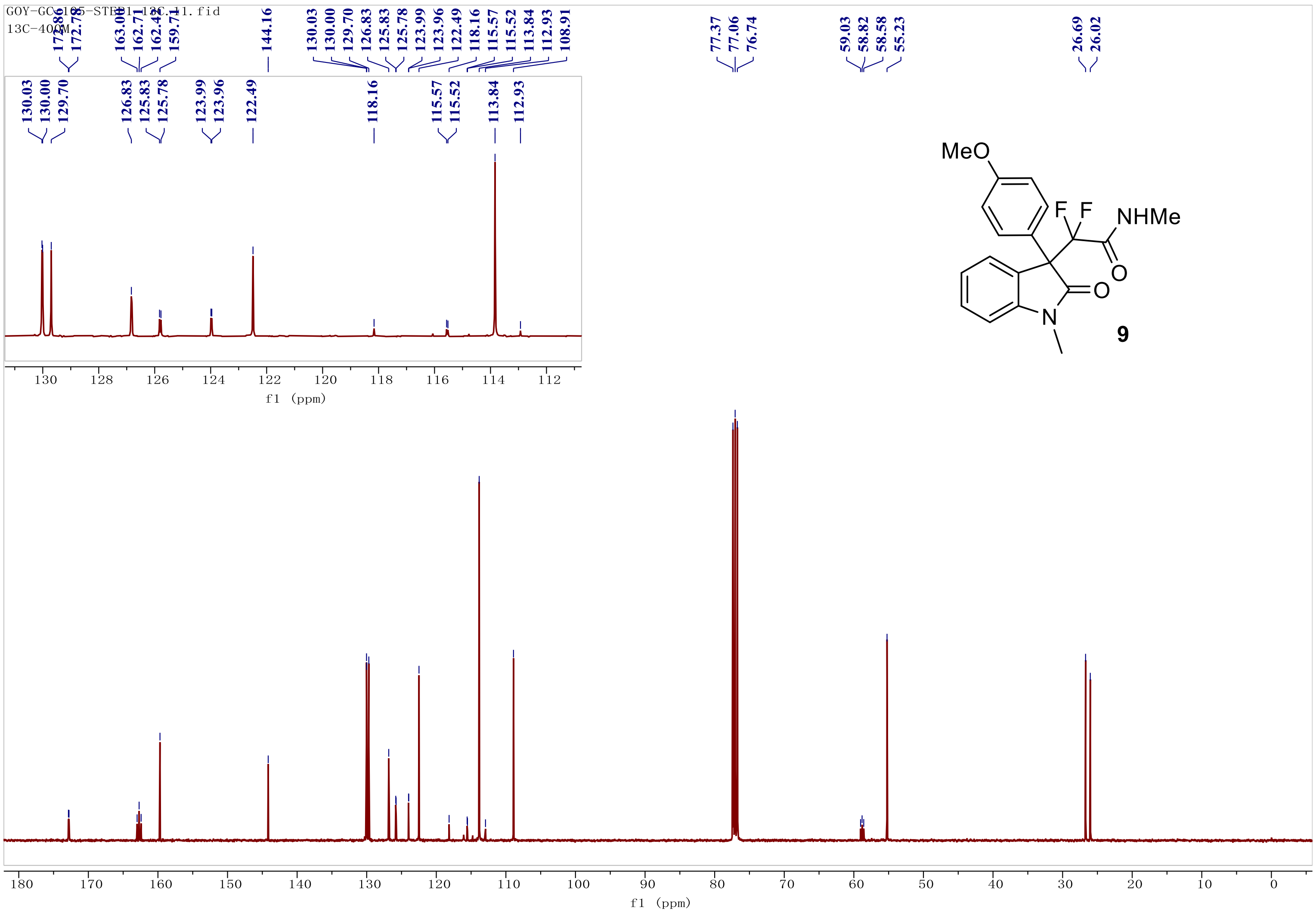
8



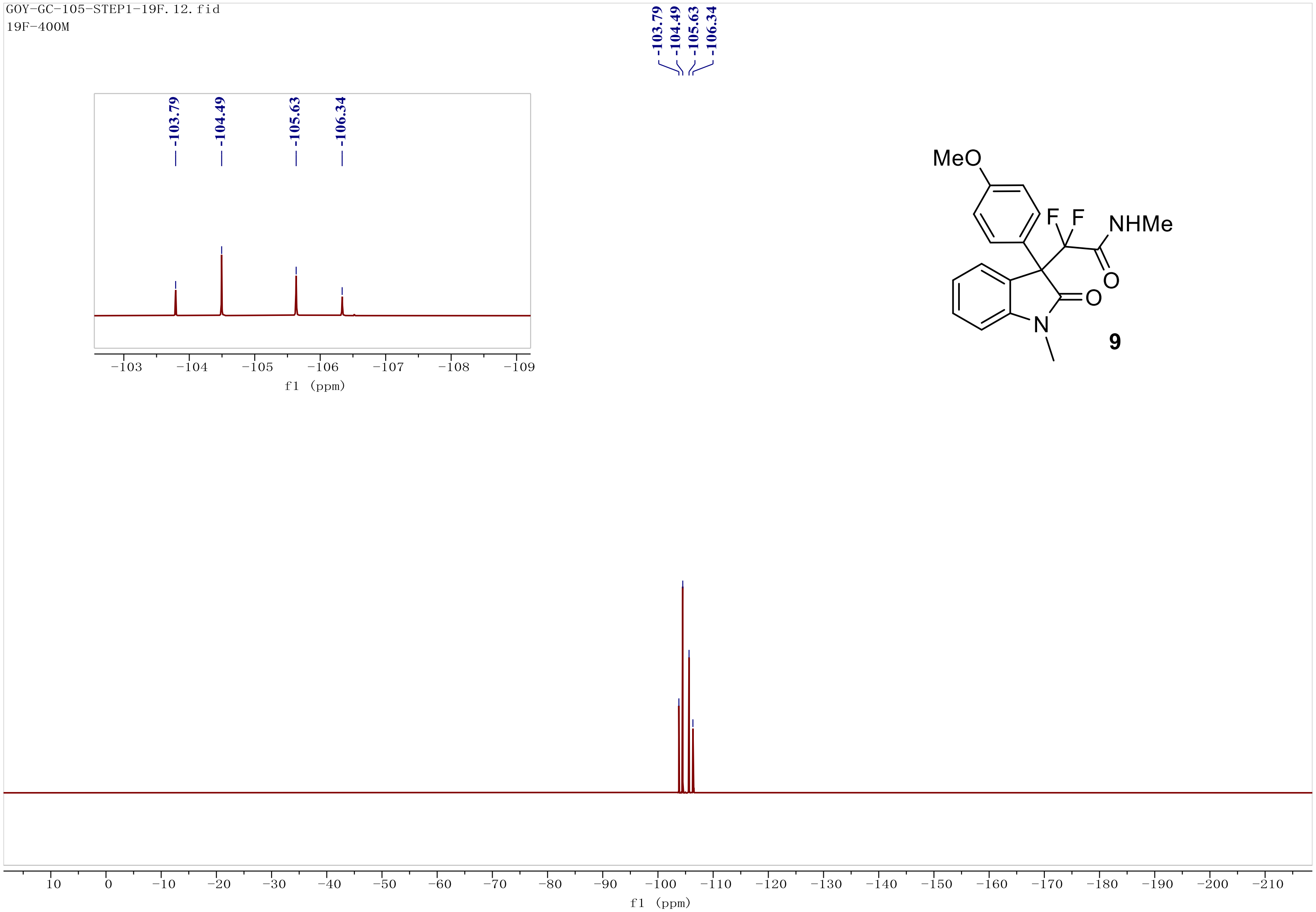
[1]H NMR of Compound 9 (400 MHz, CDCl3)



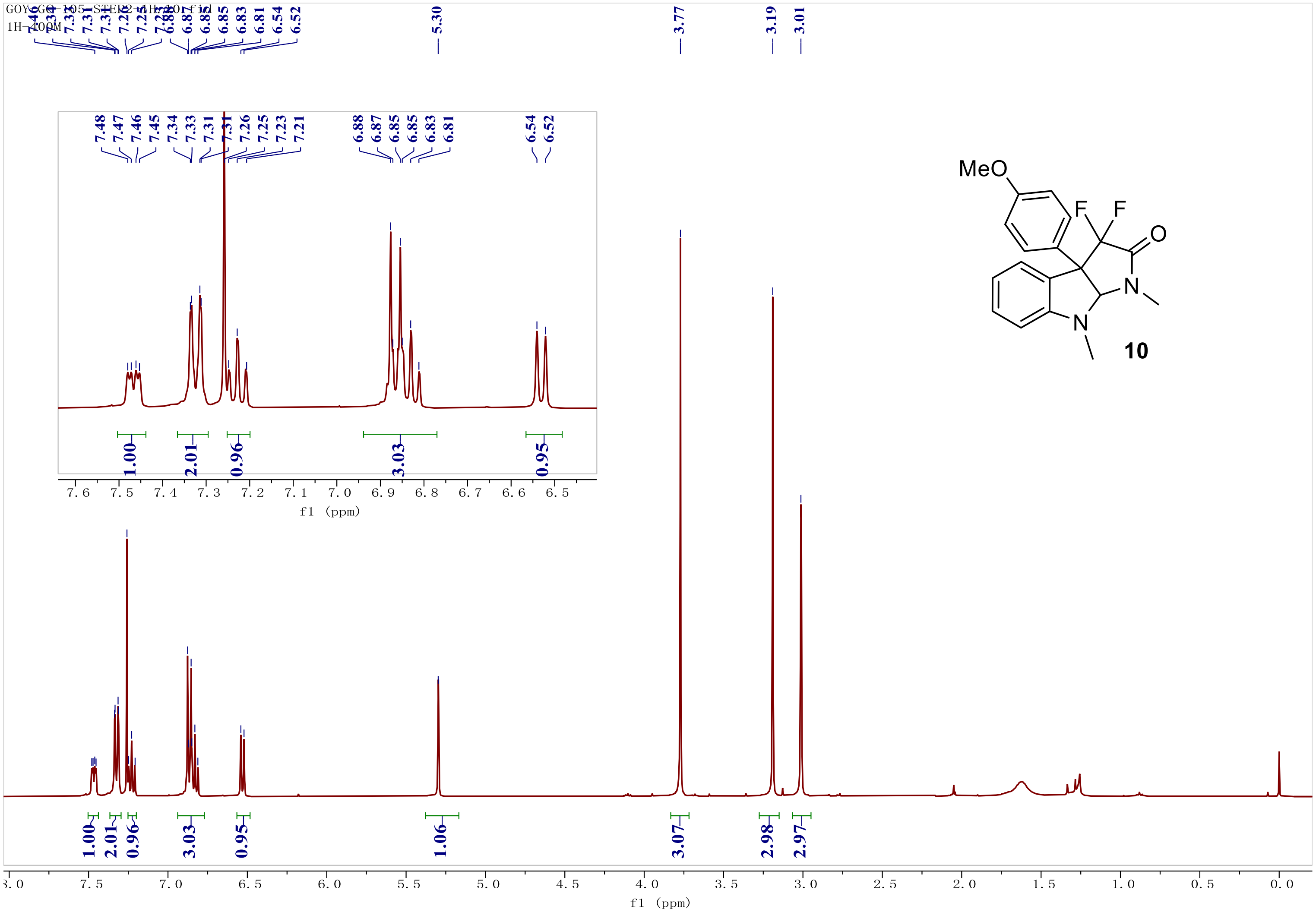
^{13}C NMR of Compound 9 (100 MHz, $CDCl_3$)



^{19}F NMR of Compound 9 (376 MHz, $CDCl_3$)

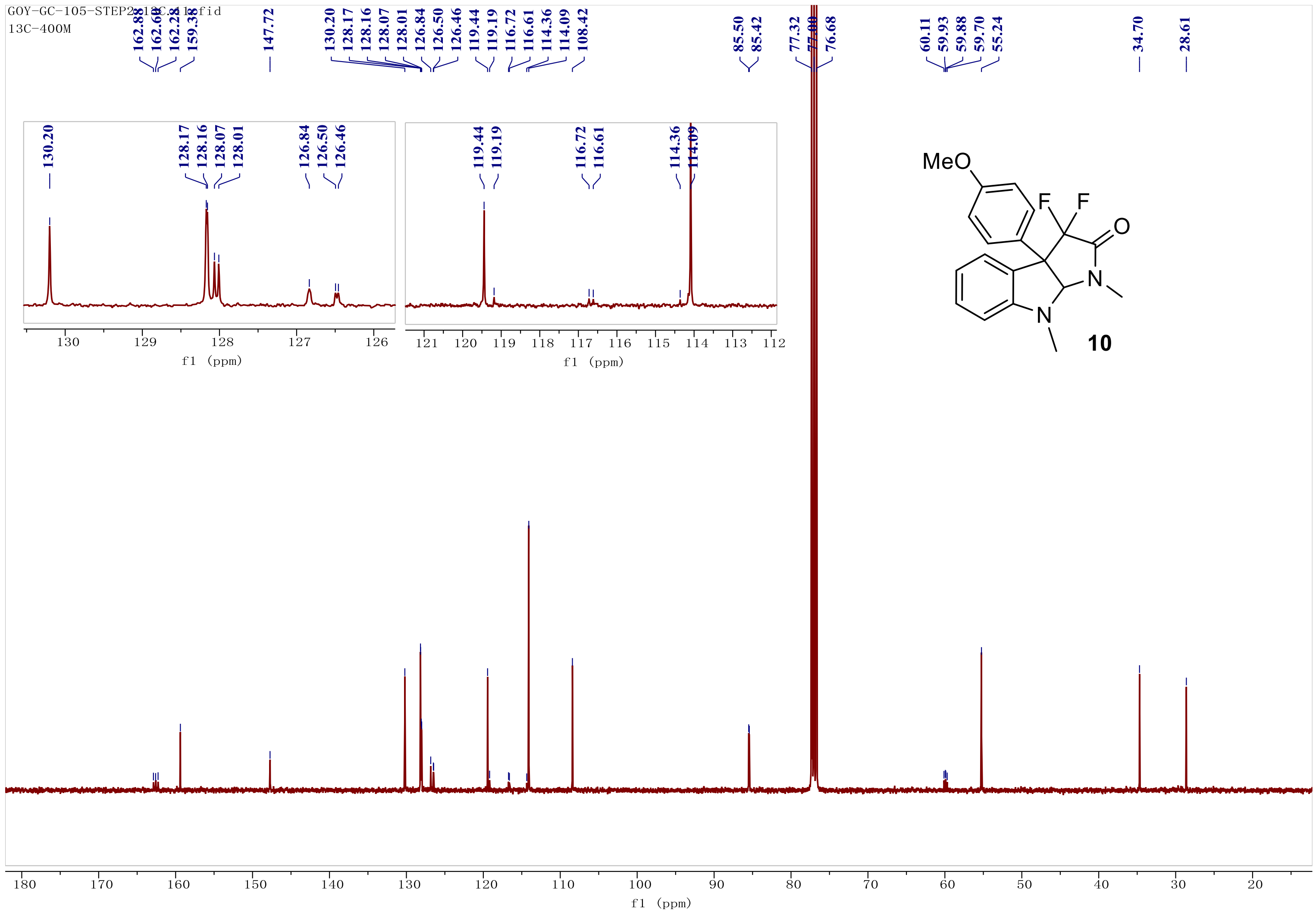


^{1}H NMR of Compound 10 (400 MHz, $CDCl_3$)

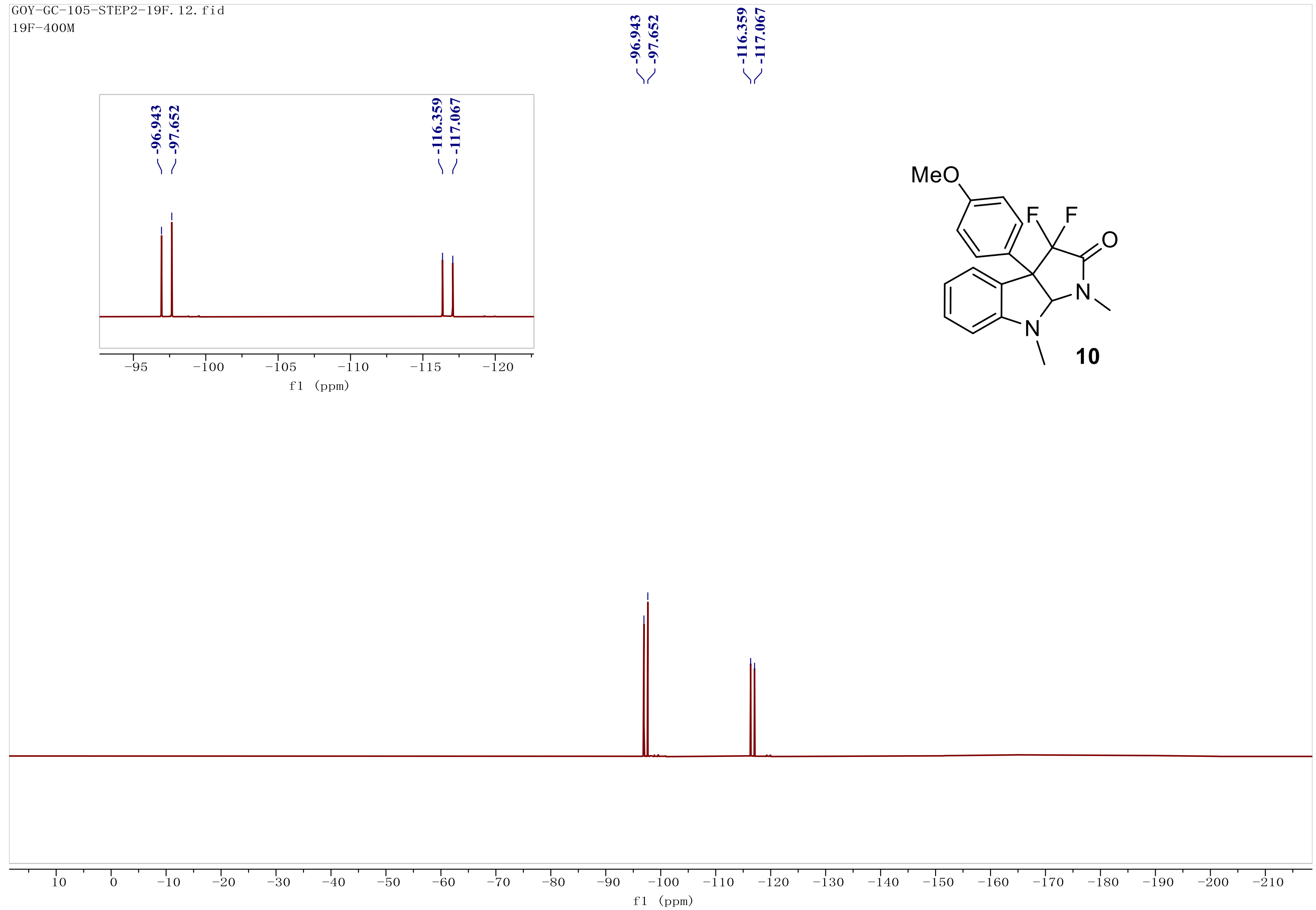


10

^{13}C NMR of Compound 10 (100 MHz, $CDCl_3$)



^{19}F NMR of Compound 10 (376 MHz, $CDCl_3$)



The HPLC spectra of *rac*-**3g** (synthesized from *rac*-**2g**)

<Sample Information>

Sample Name : GOY-GC-90-RAC-ASH-8020-1.0-230
Sample ID :
Data Filename : GOY-GC-90-RAC-ASH-8020-1.0-231.lcd
Method Filename : GY-1.0.lcm
Batch Filename :
Vial # : 1-1 Sample Type : Unknown
Injection Volume : 20 uL
Date Acquired : 6/6/2019 2:34:02 PM Acquired by : System Administrator
Date Processed : 9/29/2020 9:21:33 AM Processed by : System Administrator

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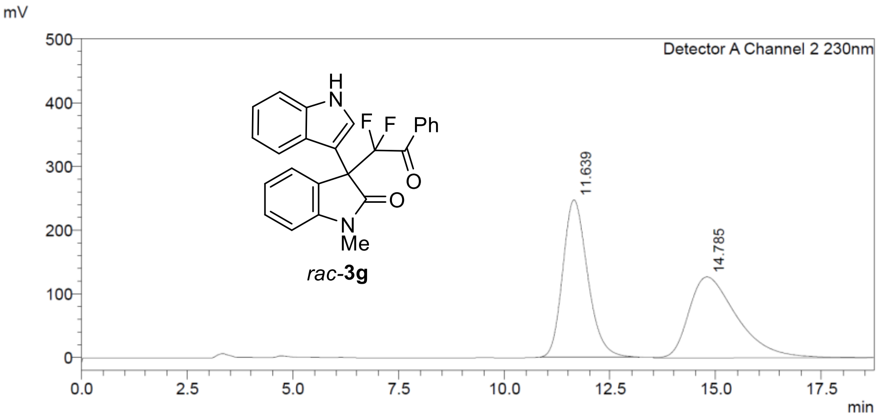


<Peak Table>

Detector A Channel 2 230nm

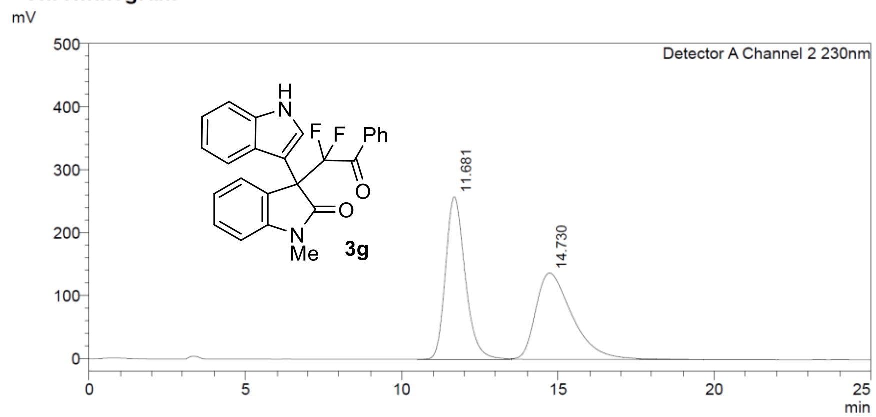
Peak#	Ret. Time	Area	Height	Conc.
1	11.639	10074719	246846	49.984
2	14.785	10081332	127147	50.016
Total		20156051	373994	

The HPLC spectra of **3g** (synthesized from (*R*)-**2g** (72% ee))

<Sample Information>

Sample Name : GOY-GC-90-workup-ASY-ASH-8020-1.0-230
Sample ID :
Data Filename : GOY-GC-90-workup-ASY-ASH-8020-1.0-230.lcd
Method Filename : GY-1.0.lcm
Batch Filename :
Vial # : 1-1 Sample Type : Unknown
Injection Volume : 20 uL
Date Acquired : 6/6/2019 9:09:42 PM Acquired by : System Administrator
Date Processed : 9/29/2020 9:24:51 AM Processed by : System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.
1	11.681	11291092	258311	50.272
2	14.730	11169028	137259	49.728
Total		22460119	395570	